Memo

SUBJECT
2025 Groundwater PFAS Sampling Plan
RACER Trust – Buick City, Flint, Michigan

TO
Evin Maguire – EGLE
Jeremy Pepin – EGLE
Shaun Shields – EGLE

DATE
Original Submittal: October 1, 2025
Revised: March 5, 2026

OUR REF
30275629

COPIES TO
Brendan Mullen – RACER Trust
Dave Favero – RACER Trust

NAME
Patrick Curry – Arcadis
patrick.curry@arcadis.com

On behalf of Revitalizing Auto Communities Environmental Response (RACER) Trust, Arcadis of Michigan, LLC (Arcadis) has prepared this work plan for sampling groundwater at select monitoring wells for per- and polyfluoroalkyl substances (PFAS) analysis at RACER Buick City (Site) in Flint, Michigan. Please note this work plan has been revised to address comments from EGLE provided in the December 1, 2025 *Conditional Approval: 2025 Groundwater PFAS Sampling Plan* letter included as **Attachment 1** to this document. This work plan was revised to incorporate the changes requested by EGLE, all of which were carried out during the field activities.

Groundwater samples will be collected from 62 existing monitoring wells, which includes the following monitoring wells EGLE requested to be added to the sampling plan: SB-04-34 (4-9); SB-04-100 (9-14); SB-04-64 (19-24); SB-16-23 (7-12); MW-09-86 (15-20); MW-84-77 (6-16); RFI-84-11S (3-13); and RFI-84-10S (7-12). The purpose of the sampling is to assess trends in plume concentrations for the three primary PFAS plumes identified in the southern portion of the RACER site. The three plumes are associated with the source areas located north of Hamilton Ave in the Building 44 area (Plume 1), at the north end of Building 40 (Plume 2), and at Building 16 (Plume 3). The source area locations for the three plumes are depicted on **Figure 1**, along with PFAS groundwater analytical results compared to Michigan Part 201 Groundwater-Surface Water Interface Criteria.

Wells were selected for sampling to support evaluation of:

- Source area hotspot concentrations (Plumes 1, 2, and 3)
- Plume 2 centerline concentrations
- Concentrations proximal to the proposed IM strategy groundwater collection trench (Plume 1)
- Concentrations downgradient of the Plume 1 source area to evaluate potential plume migration
- Concentrations along the Flint River to assess the groundwater-surface water interface (GSI) pathway
- Concentrations along Industrial Avenue to evaluate sewer infiltration
- Sampling wells installed within the deeper alluvial sand (well RFI-84-04I)

Sampling will be conducted in accordance with the Arcadis technical guidance instruction (TGI): *TGI – Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide,* and *TGI – Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells* included as **Attachment 2**. Sampling will be completed using low-flow groundwater purging and sampling procedures in accordance with the TGI guidance.

Equipment decontamination will be performed in accordance with *TGI – Groundwater and Soil Sampling Equipment Decontamination*, including a water level meter, multiparameter meter, and if needed the submersible pump. Note a submersible pump will only be used if the well is too deep for a peristaltic pump. Two equipment blanks will be collected with decontaminated sampling equipment in accordance with *TGI - Equipment and Reagent Blank Sample Collection for PFAS Analysis*. Duplicate samples will be collected at a frequency of 1

duplicate sample for every 10 samples (6 total) and matrix spike/matrix spike duplicate (MS/MSD) samples will be collected at a frequency of 1 MS/MSD sample for every 20 samples (3 total). The equipment decontamination and sample blank collection TGIs are included in **Attachment 2**.

Groundwater samples will be analyzed by ALS Environmental Laboratories by modified method ASTM D7979 (**Attachment 3**). The reported analytes will include the 34 compounds listed in **Table 2**.

Results of the sampling will be compared to EGLE Part 201 groundwater-surface water interface (GSI) criteria and provided to EGLE electronically within sixty (60) days of completion of the sampling event (R 299.9611 Environmental Monitoring, Rule 611(6)) and later as a summary report. Analytical results will be managed using the EQuIS database.

Enc.

Figures

Figure 1 – Area Wide PFAS Results

Figure 2 – Proposed Shallow Monitoring Well Network

Figure 3 – Proposed Deep Monitoring Well Network

Tables

Table 1 – Proposed Monitoring Well Network and Rationale

Table 2 – PFAS Analyte List

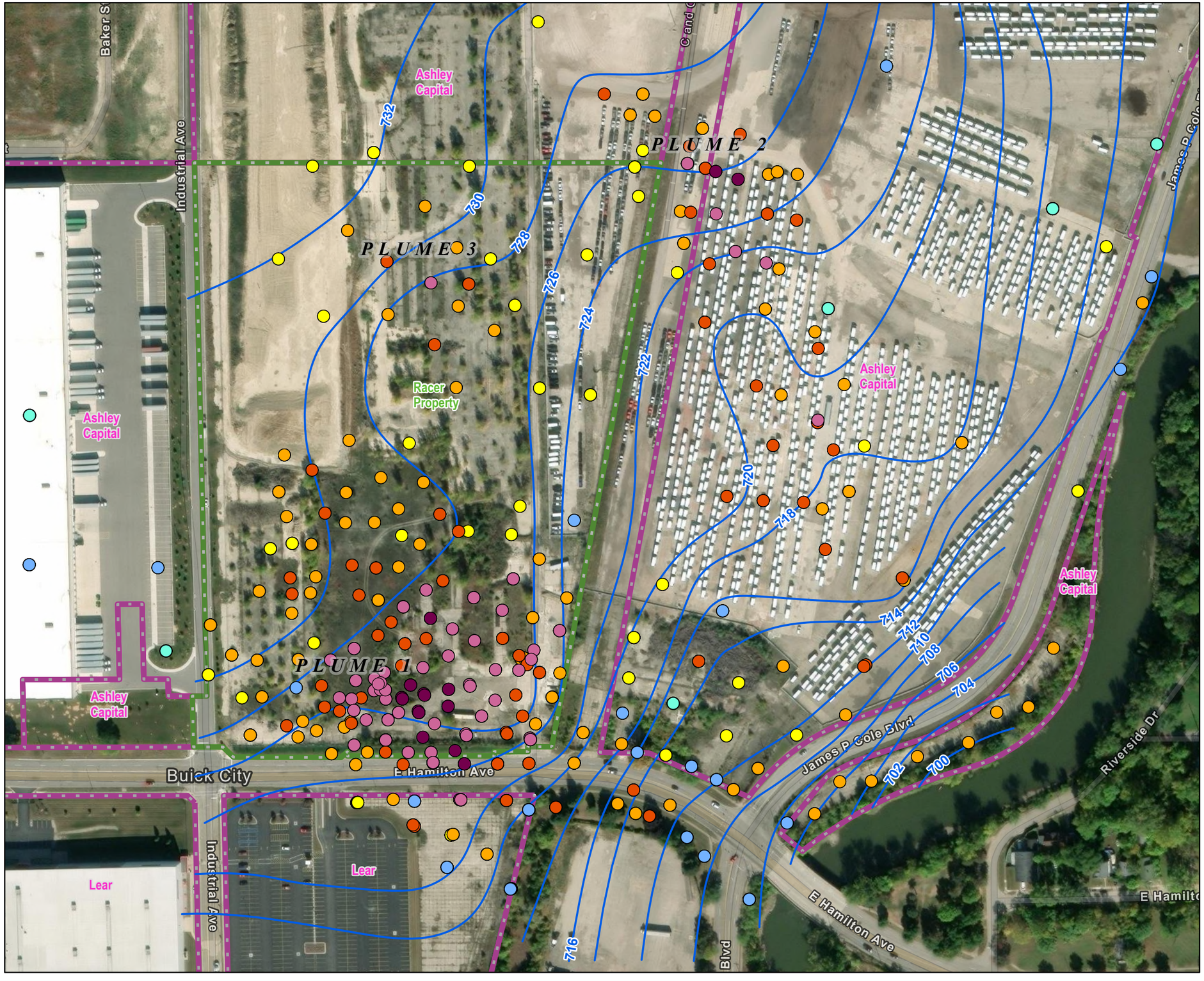
Attachments

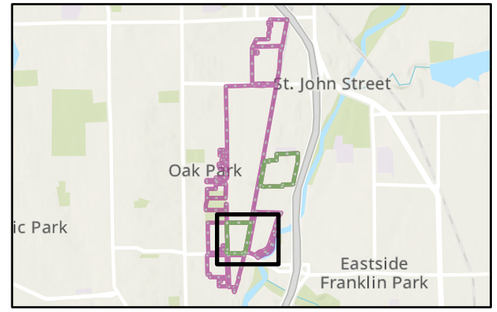
Attachment 1 – December 1, 2025 EGLE *Conditional Approval: 2025 Groundwater PFAS Sampling Plan*

Attachment 2 –Technical Guidance Instructions

Attachment 3 – Laboratory Standard Operating Procedure for ASTM D7979

Figures





LEGEND

Maximum PFAS Exceedance in Groundwater Sample

- >10,000x to 100,000x the SL
- >1,000x to 10,000x the SL
- >100x to 1,000x the SL
- >10x to 100x the SL
- ≥SL to 10x the SL
- Detection < SL
- Non-detect (RL > SL)
- Non-detect (RL ≤ SL)
- Current Racer-owned Properties
- Former Racer-owned Properties
- Potentiometric Surface Contour, October 2022 (ft. amsl)

Notes:
1. Symbol color represents the maximum SL exceedance for PFAS from samples at the location (as represented by the centroid of the symbol).
2. SL = screening level, based on Michigan Part 201 Groundwater-Surface Water Interface Criteria:
   Perfluorobutane sulfonic acid = 670,000 ng/L
   Perfluorohexane sulfonic acid = 210 ng/L
   Perfluorononanoic acid = 30 ng/L
   Perfluorooctanoic acid = 170 ng/L
   Perfluorooctane sulfonic acid = 12 ng/L

Acronyms:
PFAS = Per- and Polyfluoroalkyl Substances
RL = Reporting Limit
ft. amsl = feet above mean sea level
ng/L = nanograms per liter
x = times
> = greater than
< = less than
≥ = greater than or equal to
≤ = less than or equal to

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RACER TRUST
BUICK CITY
FLINT, MI

AREA-WIDE PFAS RESULTS

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FIGURE
1

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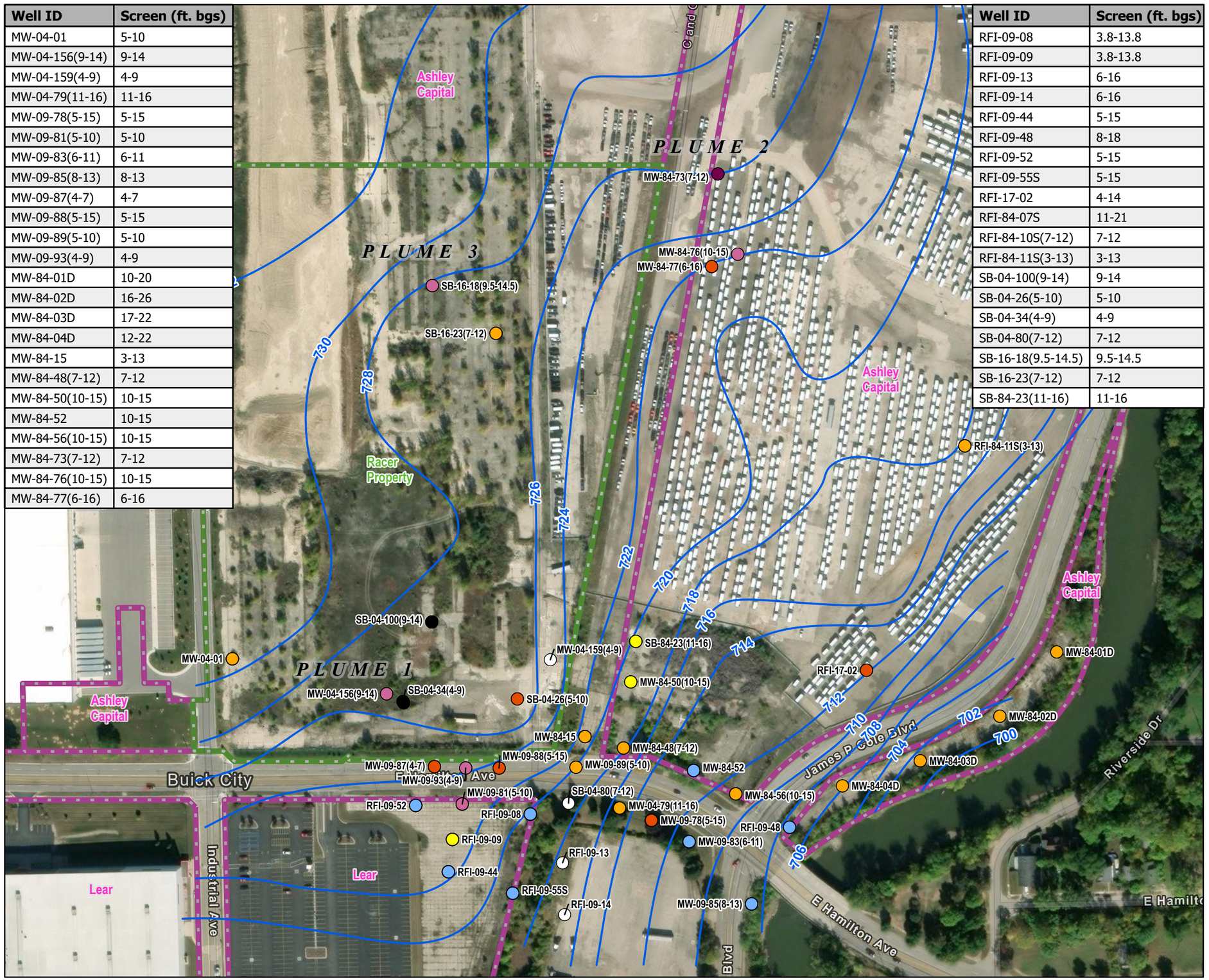
Well ID	Screen (ft. bgs)
MW-04-01	5-10
MW-04-156(9-14)	9-14
MW-04-159(4-9)	4-9
MW-04-79(11-16)	11-16
MW-09-78(5-15)	5-15
MW-09-81(5-10)	5-10
MW-09-83(6-11)	6-11
MW-09-85(8-13)	8-13
MW-09-87(4-7)	4-7
MW-09-88(5-15)	5-15
MW-09-89(5-10)	5-10
MW-09-93(4-9)	4-9
MW-84-01D	10-20
MW-84-02D	16-26
MW-84-03D	17-22
MW-84-04D	12-22
MW-84-15	3-13
MW-84-48(7-12)	7-12
MW-84-50(10-15)	10-15
MW-84-52	10-15
MW-84-56(10-15)	10-15
MW-84-73(7-12)	7-12
MW-84-76(10-15)	10-15
MW-84-77(6-16)	6-16

Well ID	Screen (ft. bgs)
RFI-09-08	3.8-13.8
RFI-09-09	3.8-13.8
RFI-09-13	6-16
RFI-09-14	6-16
RFI-09-44	5-15
RFI-09-48	8-18
RFI-09-52	5-15
RFI-09-55S	5-15
RFI-17-02	4-14
RFI-84-07S	11-21
RFI-84-10S(7-12)	7-12
RFI-84-11S(3-13)	3-13
SB-04-100(9-14)	9-14
SB-04-26(5-10)	5-10
SB-04-34(4-9)	4-9
SB-04-80(7-12)	7-12
SB-16-18(9.5-14.5)	9.5-14.5
SB-16-23(7-12)	7-12
SB-84-23(11-16)	11-16



LEGEND

Maximum PFAS Exceedance in Groundwater Sample

- Greater than 100,000x SL
- Between 10000x SL and 100000x SL
- >1,000x to 10,000x the SL
- >100x to 1,000x the SL
- >10x to 100x the SL
- ≥SL to 10x the SL
- Detection < SL
- Non-detect (RL > SL)
- Non-detect (RL ≤ SL)
- PFAS Data Not Available
- Current Racer-owned Properties
- Former Racer-owned Properties
- Potentiometric Surface Contour, October 2022 (ft. amsl)

Notes:
1. Symbol color represents the maximum SL exceedance for PFAS from samples at the location (as represented by the centroid of the symbol).
2. SL = screening level, based on Michigan Part 201 Groundwater-Surface Water Interface Criteria:
   Perfluorobutane sulfonic acid = 670,000 ng/L
   Perfluorohexane sulfonic acid = 210 ng/L
   Perfluorononanoic acid = 30 ng/L
   Perfluorooctanoic acid = 170 ng/L
   Perfluorooctane sulfonic acid = 12 ng/L

Acronyms:
PFAS = Per- and Polyfluoroalkyl Substances
RL = Reporting Limit
ft. amsl = feet above mean sea level
ft. bgs = feet below ground surface
ng/L = nanograms per liter
x = times
> = greater than
< = less than
≥ = greater than or equal to
≤ = less than or equal to

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FLINT, MI

PROPOSED SHALLOW MONITORING WELL NETWORK

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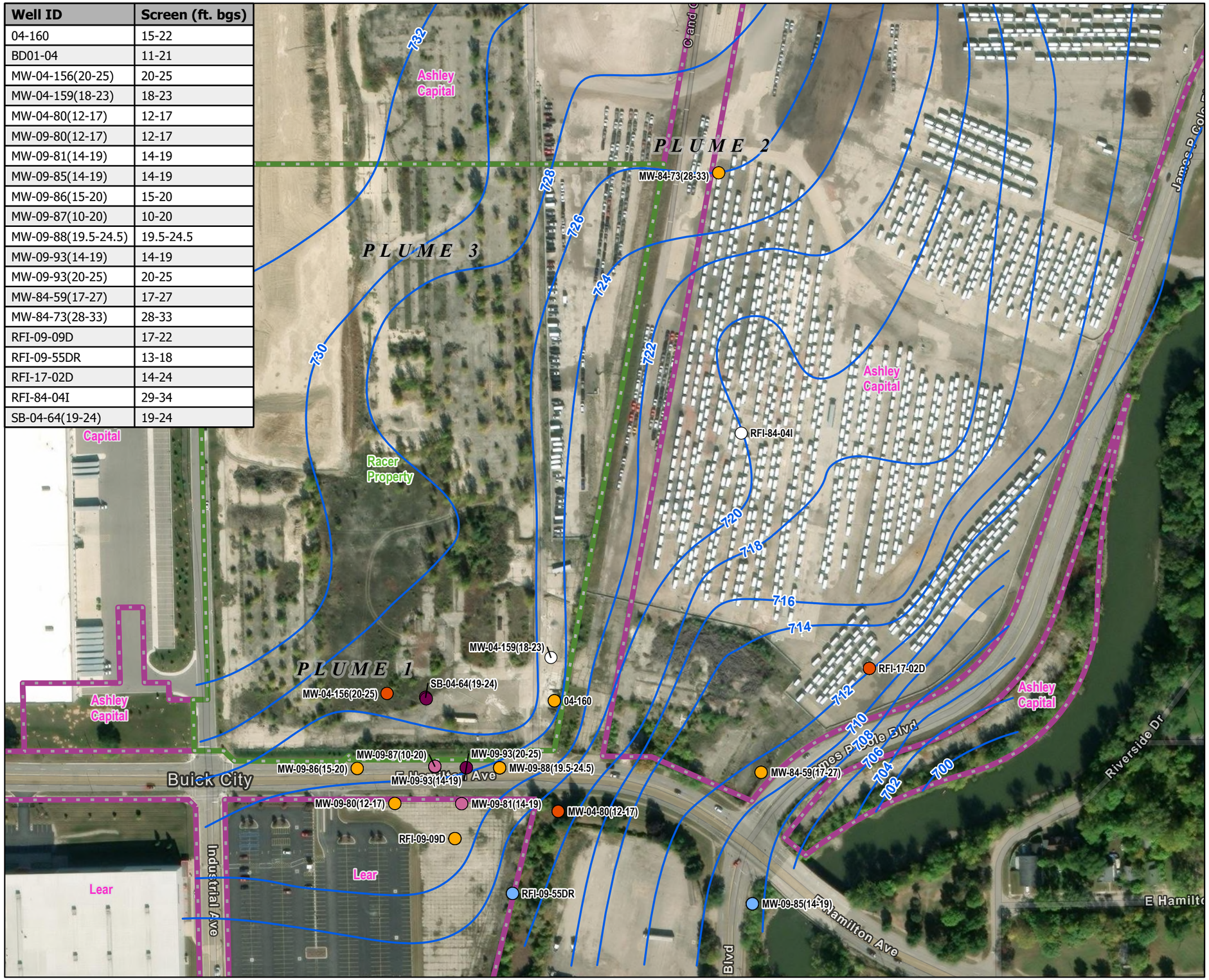
FIGURE
2

Path: T:_ENV\RACER_BuickCity_Prof\Figures\Reference_figures.aprx\Proposed Shallow Monitoring Well Network Last Saved By: jchen 2/27/2026

Well ID	Screen (ft. bgs)
04-160	15-22
BD01-04	11-21
MW-04-156(20-25)	20-25
MW-04-159(18-23)	18-23
MW-04-80(12-17)	12-17
MW-09-80(12-17)	12-17
MW-09-81(14-19)	14-19
MW-09-85(14-19)	14-19
MW-09-86(15-20)	15-20
MW-09-87(10-20)	10-20
MW-09-88(19.5-24.5)	19.5-24.5
MW-09-93(14-19)	14-19
MW-09-93(20-25)	20-25
MW-84-59(17-27)	17-27
MW-84-73(28-33)	28-33
RFI-09-09D	17-22
RFI-09-55DR	13-18
RFI-17-02D	14-24
RFI-84-04I	29-34
SB-04-64(19-24)	19-24



LEGEND

Maximum PFAS Exceedance in Groundwater Sample

- Between 10000x SL and 100000x SL
- >1,000x to 10,000x the SL
- >100x to 1,000x the SL
- >10x to 100x the SL
- ≥SL to 10x the SL
- Detection < SL
- Non-detect (RL > SL)
- Non-detect (RL ≤ SL)
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- Current Racer-owned Properties
- Former Racer-owned Properties
- Potentiometric Surface Contour, October 2022 (ft. amsl)

Notes:
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   Perfluorobutane sulfonic acid = 670,000 ng/L
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   Perfluorononanoic acid = 30 ng/L
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x = times
> = greater than
< = less than
≥ = greater than or equal to
≤ = less than or equal to

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GRAPHIC SCALE IN FEET

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BUICK CITY
FLINT, MI

PROPOSED DEEP MONITORING WELL NETWORK

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FIGURE
3

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Tables

Table 1
Proposed Monitoring Well Network and Rationale
RACER Trust Buick City
Flint, Michigan

Well ID	Screen Depth (ft bgs)	Zone	Rationale*
MW-04-01	5-10	shallow	6
MW-04-156(9-14)	9-14	shallow	1
MW-04-159(4-9)	4-9	shallow	3 & 4
MW-04-79(11-16)	11-16	shallow	4
MW-09-78(5-15)	5-15	shallow	4
MW-09-81(5-10)	5-10	shallow	4
MW-09-83(6-11)	6-11	shallow	4
MW-09-85(8-13)	8-13	shallow	5
MW-09-87(4-7)	4-7	shallow	3 & 4
MW-09-88(5-15)	5-15	shallow	3 & 4
MW-09-89(5-10)	5-10	shallow	3 & 4
MW-09-93(4-9)	4-9	shallow	3 & 4
MW-84-01D	10-20	shallow	5
MW-84-02D	16-26	shallow	5
MW-84-03D	17-22	shallow	5
MW-84-04D	12-22	shallow	5
MW-84-15	3-13	shallow	3 & 4
MW-84-48(7-12)	7-12	shallow	4
MW-84-50(10-15)	10-15	shallow	4
MW-84-52	10-15	shallow	4
MW-84-56(10-15)	10-15	shallow	4
MW-84-73(7-12)	7-12	shallow	1
RFI-09-08	3.8-13.8	shallow	4
RFI-09-09	3.8-13.8	shallow	4
RFI-09-13	6-16	shallow	4
RFI-09-14	6-16	shallow	4
RFI-09-44	5-15	shallow	4
RFI-09-48	8-18	shallow	5
RFI-09-52	5-15	shallow	4
RFI-09-55S	5-15	shallow	4
RFI-17-02	4-14	shallow	2
RFI-84-07S	11-21	shallow	2
SB-04-26(5-10)	5-10	shallow	3 & 4
SB-04-80(7-12)	7-12	shallow	4
SB-16-18(9.5-14.5)	9.5-14.5	shallow	4
SB-84-23(11-16)	11-16	shallow	4

Well ID	Screen Depth (ft bgs)	Zone	Rationale*
04-160	15-22	deep	4
BD01-04	11-21	deep	6
MW-04-156(20-25)	20-25	deep	1
MW-04-159(18-23)	18-23	deep	4
MW-04-80(12-17)	12-17	deep	
MW-09-80(12-17)	12-17	deep	4
MW-09-81(14-19)	14-19	deep	4
MW-09-85(14-19)	14-19	deep	5
MW-09-87(10-20)	10-20	deep	3 & 4
MW-09-88(19.5-24.5)	19.5-24.5	deep	3 & 4
MW-09-93(14-19)	14-19	deep	3 & 4
MW-09-93(20-25)	20-25	deep	3 & 4
MW-84-59(17-27)	17-27	deep	4
MW-84-73(28-33)	28-33	deep	1
RFI-09-09D	17-22	deep	4
RFI-09-55DR	13-18	deep	4
RFI-17-02D	14-24	deep	2
RFI-84-04I	29-34	deep	7

Notes:

ft bgs = feet below ground surface

*Rationale:

1. Source area hotspot concentrations (Plumes 1, 2, and 3);
2. Plume 2 centerline concentrations;
3. Concentrations proximal to the proposed interceptor trench (Plume 1);
4. Concentrations downgradient of the Plume 1 source area for plume migration analysis;
5. Concentrations along the Flint River for GSI assessment;
6. Concentrations along Industrial Avenue for sewer infiltration assessment; and
7. Deep sand zone for vertical delineation assessment (well RFI-84-04I).

Table 2
PFAS Analyte List
RACER Trust Buick City
Flint, Michigan

Analyte
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)
Fluorotelomer sulfonic acid 4:2 (4:2 FTS)
Fluorotelomer sulfonic acid 6:2 (6:2FTS)
Fluorotelomer sulfonic acid 8:2 (8:2FTS)
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)
4,8-dioxa-3H-perfluorononanoic acid (ADONA)
2H,2H,3H,3H-Perfluorodecanoic acid (FHpPA)(7:3 FTCA)
2H,2H,3H,3H-Perfluorooctanoic acid (FPePA) (5:3 FTCA)
2H,2H,3H,3H-Perfluorohexanoic acid (FPrPA) (3:3 FTCA)
Hexafluoropropylene oxide dimer acid (HFPO-DA)
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)
Perfluorobutanesulfonic acid (PFBS)
Perfluorobutanoic acid (PFBA)
Perfluorodecanesulfonic acid (PFDS)
Perfluorodecanoic acid (PFDA)
Perfluorododecanoic acid (PFDoA)
Perfluoroheptanesulfonic Acid (PFHpS)
Perfluoroheptanoic acid (PFHpA)
Perfluorohexanesulfonic acid (PFHxS)
Perfluorohexanoic acid (PFHxA)
Perfluorononanesulfonic acid (PFNS)
Perfluorononanoic acid (PFNA)
Perfluorooctane Sulfonamide (FOSA)
Perfluorooctane sulfonic acid (PFOS)
Perfluorooctanoic acid (PFOA)
Perfluoropentanesulfonic acid (PFPeS)
Perfluoropentanoic acid (PFPeA)
Perfluorotetradecanoic acid (PFTeA)
Perfluorotridecanoic Acid (PFTriA)
Perfluoroundecanoic acid (PFUnA)
Perfluorobutylsulfonamide (PFBSA)
Perfluoro-4-ethylcyclohexanesulfonic Acid (PFECHS)
Perfluorohexanesulfonamide (PFHxSA)

Attachment 1

December 1, 2025 EGLE Conditional Approval:

2025 Groundwater PFAS Sampling Plan

STATE OF MICHIGAN
DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY
MATERIALS MANAGEMENT DIVISION

GRETCHEN WHITMER
GOVERNOR

PHILLIP D. ROOS
DIRECTOR

December 1, 2025

VIA EMAIL

Brendan Mullen, Cleanup Manager – Michigan
RACER Trust
1505 Woodward Avenue, Suite 200
Detroit, Michigan 48226

Dear Brendan Mullen:

SUBJECT: Conditional Approval: *2025 Groundwater PFAS Sampling Plan*; RACER Buick City; MID 005 356 712; Waste Data System Number 393423

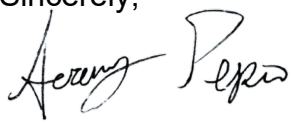
The Department of Environment, Great Lakes, and Energy (EGLE), Materials Management Division (MMD), reviewed the *2025 Groundwater PFAS Sampling Plan* (PFAS Sampling Plan), dated October 1, 2025, and prepared by Arcadis U.S., Inc. on behalf of the Revitalizing Auto Communities Environmental Response (RACER) Trust, for the Buick City facility located at 902 East Leith Street, Flint, Michigan. The PFAS Sampling Plan was evaluated for acceptable actions necessary to protect public health, safety, welfare, and the environment, pursuant to the August 5, 2020, Corrective Action Consent Order, MMD-111-02-2020.

Based on this review, the PFAS Sampling Plan is approved with the condition that the following wells are added:

- SB-04-34 (4-9)
- SB-04-100 (9-14)
- SB-04-64 (19-24)
- SB-16-23 (7-12)
- MW-09-86 (15-20)
- MW-84-77 (6-16)
- RFI-84-11S (3-13)
- RFI-84-10S (7-12)

Please contact me if you have any questions at 517-219-2288; PepinJ2@Michigan.gov; or EGLE-MMD-HWS@Michigan.gov.

Sincerely,



Jeremy Pepin, Environmental Engineer
Corrective Action Unit
Hazardous Waste Section
Materials Management Division
517-219-2288

Cc: Dave Favero, RACER Trust, Deputy Cleanup Manager – Michigan
Patrick Curry, Arcadis, Vice President
Tiffany Linder, Arcadis, Project Manager
Kimberly Tyson, EGLE
Elizabeth Garver, EGLE
Steve Busch, EGLE
Brian Zuber, EGLE
Evin Maguire, EGLE
Shaun Shields, EGLE
Plan Approval – CA – PFAS

Attachment 2

Technical Guidance Instructions

TGI - Equipment and Reagent Blank Sample Collection for PFAS Analysis

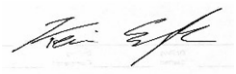
Rev: 2.1

Rev Date: March 20, 2025

Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
--	0	October 2, 2018	All	TGI – Equipment and Reagent Blank Sample Collect for PFAS Analysis	Erika Houtz
Outdated template	1	December 10, 2021	All	Updated to current TGI format. Also updated sections to match the most recent TGI for PFAS Field Sampling Guidance (Arcadis 2021)	Kevin Engle
Template Updates	2	February 21, 2022	All	Additional template updates	Kevin Engle, Johnsie Lang
Annual Review	2.1	March 20, 2025		Editorial changes only	Kevin Engle, Johnsie Lang

Approval Signatures

Prepared by:		3/20/2025
	Kevin Engle (Preparer)	Date
Reviewed by:		3/20/2025
	Johnsie Lang, PhD (Subject Matter Expert)	Date

1 Introduction

This document is intended to provide guidance to field staff collected equipment blanks for Per- and Polyfluoroalkyl Substances (PFAS). The content in this document describes the intended use, scope and application, personnel qualifications, equipment, cautions, health and safety considerations, procedures, waste management, data recording and management, and quality assurance of PFAS sampling.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

Equipment and reagent blanks will be collected in the field during sampling activities and submitted for laboratory analysis. These samples are primarily intended to verify that sampling and decontamination practices are effectively preventing cross-contamination caused by reusable sample equipment or (PFAS)-containing materials.

The intent of this Technical Guidance Instruction (TGI) is to provide instructions for collection of equipment and reagent blanks. More detailed instructions related to general PFAS sampling considerations is provided in the TGI Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance.

4 Personnel Qualifications

Equipment and reagent samples will be collected by persons who have been trained in proper sampling procedures under the guidance of an experienced field geologist, engineer, or technician. Blank sampling should be completed with a two-person sampling team.

5 Equipment List

The following equipment and materials must be available for equipment and reagent blank sampling:

- Site plan which specifies frequency/quantity of blank sampling;
- Relevant work plan (e.g., PQAPP);
- Site Safety and Health Plan (SSHP);
- Appropriate health and safety equipment, as specified in the SSHP;
- Laboratory-provided “PFAS-free” water;
- Nitrile gloves;
- Dedicated plastic sheeting (preferably low-density polyethylene) or other clean surface to prevent sample contact with the ground;
- Pail or bucket with closable lid for excess rinse water;
- Garbage bags;
- Appropriate sample containers and labels:
    - Labeled high density polypropylene (HDPE) sample bottles: see the Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance (Arcadis 2021) for PFAS-specific considerations;
    - Ziploc®-style bags to hold ice and samples;
    - Packing and shipping materials;
    - Chain-of-Custody (COC) Forms; see the Sample Chain of Custody Standard Operating Procedure (SOP) for reference (Arcadis 2017a); and
    - Appropriate transport containers (coolers) with ice and appropriate labeling; no blue ice is to be used.
- Decontamination:
    - Equipment cleaning materials: see the Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance (Arcadis 2021) or the Groundwater and Soil Sampling Equipment Decontamination TGI (Arcadis 2017b) as applicable;
    - An organic solvent such as isopropanol, methanol, or acetone should be used to decontaminate reusable equipment if it can be brought to the site safely. While strongly recommended, the use of solvents may be excluded for project-specific health and safety concerns. Refer to Section 7.1.1 for more details; and
    - Drum labels as required for investigation-derived waste handling: see the Investigation-Derived Waste Handling and Storage TGI for details.

- Field Notes:
    - Pens, pencils, and/or fine point Sharpies® for writing;
    - Appropriate field forms; and
    - Clipboards, field binders, field notebook, and field note pages that are not waterproof.

6 Cautions

In general, sampling techniques used for PFAS sample collection are consistent with conventional sampling techniques used in the environmental industry, but special consideration is made regarding PFAS-containing materials and cross-contamination potential. The most important consideration during PFAS-related sampling is to prevent contact between sample media and suspect PFAS sources. During collection of equipment and reagent blanks, the sampled media (i.e., PFAS-free water) should not contact anything but the sample container. New nitrile gloves should be donned after handling of any non-dedicated sampling equipment; contact with contaminated surfaces; and whenever judged necessary by field personnel. When in doubt change your gloves. More detailed instructions related to general PFAS sampling considerations is provided in the TGI - Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance.

7 Health and Safety Considerations

Field activities associated with equipment and reagent blank sampling will be performed in accordance with the SSHP, a copy of which will be present on site during such activities. Additional health and safety considerations can be found in TGI for PFAS Field Sampling Guidance.

8 Procedure

The specific procedure for equipment and reagent blank sampling was developed after careful review and consideration of project data quality objectives. Procedures for equipment blank sampling and reagent blank sampling are further described in this section. Note: the laboratory has to analyze the entire sample bottle for aqueous solutions of PFASs. When collecting each blank, fill two sample bottles and instruct the lab to hold one of them in reserve. If an unacceptable detection occurs in a blank, the second bottle of sample may be analyzed.

For additional sampling considerations, reference the TGI for PFAS Field Sampling Guidance.

8.1 Blank Sampling

8.1.1 Decontamination

Prior to collecting blank samples, the applicable piece of equipment should be properly decontaminated following these steps:

- Hand Tools and Sampling Devices (including hand augers and bladder pumps)
    1. Don new pair of nitrile gloves prior to decontamination.
    2. Remove O-rings and bladder (applies only to bladder pump).

3. Scrub using a plastic brush and a non-phosphate soap free of volatile organic compounds (VOCs) (e.g., Liquinox, Alconox);
4. Double-rinse in deionized or distilled water;
5. Rinse once with the site-approved organic rinsing solvent (e.g., isopropanol, methanol, acetone);
6. Rinse once with PFAS-free water;
7. Collect all rinsate in a sealed pail for disposal;
8. Allowed time to air dry prior to re-use; and
9. Insert new o-rings and bladder (applies only to bladder pump);

While strongly recommended, the use of solvents may be excluded for project-specific health and safety concerns. If solvents are prohibited, then additional procedures should be evaluated by the project team. Contingencies could include the use of dedicated sampling equipment at each sampling location or amending laboratory procedures to mitigate the increased risk of cross-contamination.

The following decontamination procedure could be utilized when organic solvent use is not possible:

1. Don new pair of nitrile gloves prior to decontamination.
2. Remove o-rings and bladder (applies only to bladder pump);
3. Scrub using a plastic brush and a non-phosphate soap free of VOCs (e.g., Liquinox, Alconox);
4. Single-rinse in deionized or distilled water;
5. Scrub using a plastic brush and a non-phosphate soap free of VOCs (e.g., Liquinox, Alconox);
6. Rinse twice with deionized water and once with PFAS-free water;
7. Collect all rinsate in a sealed pail for disposal;
8. Allowed time to air dry prior to re-use.
9. Insert new o-rings and bladder (applies only to bladder pump)

- Drilling Rods
    - Drive casings and other drilling equipment will be steam cleaned or replaced with new equipment between boreholes.
    - The drilling equipment will be cleaned in an area designated by the supervising engineer or geologist that is located outside of the work zone.

After verifying the piece of equipment is properly decontaminated, and after determining an equipment blank is warranted per the sampling quality assurance and quality control (QA and QC) plan, follow the specific procedures for the relevant type of equipment found in the following sections.

8.1.2 Drilling Equipment (Hand Auger or Cutting Shoe/Drill Rod)

Two field personnel should participate in the collection of the equipment blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should pour the rinse water.

The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep bottle lid on until immediately prior to sample collection.
2. Lay down dedicated plastic sheeting or other clean surface to prevent sample contact with the ground.
3. Place the sealable bucket or pail on top of plastic sheeting.
4. Don a new pair of nitrile gloves prior to blank collection (Field Personnel #1 and #2). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
5. Open the sample container and position the piece of clean, decontaminated sample equipment (i.e., hand auger or drilling rod/cutting shoe) above the container (Field Personnel #1). Keep the sample cap in the hand of the sampler (Field Personnel #1) until it is replaced on the bottle.
    a. The bucket of the hand auger can be removed from the rods/handle and held manually.
    b. The drillers should assist the field staff with removing the cutting shoe from the drill string and positioning it for sampling.
6. Slowly pour laboratory-provided “PFAS-free” water over any surface of the decontaminated sampling device that previously contacted sampled material (Field Personnel #2).
    a. Pour water through the inside of the hand auger bucket while manually rotating the bucket so that “PFAS-free” water contacts all sides of the sampling device. Collect runoff in the sample container (Field Personnel #1), making sure that any excess “PFAS-free” water is contained in the sealable bucket or pail.
    b. Pour water through the inside of cutting shoe while drilling contractor holds and manually rotates the shoe so that “PFAS-free” water contacts all sides of the shoe (Field Personnel #2). Collect runoff in the sample container, making sure that any excess “PFAS-free” water is contained in the sealable bucket or pail.
7. After collecting the necessary sample volume, place cap back on the sample bottle (Field Personnel #1). The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
8. Collect the second bottle with the same procedure (Steps 5 to 7), if collecting a backup.
9. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
10. Add sample to the laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
11. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
12. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.3 Reusable Sediment Sampling Equipment (Stainless-Steel Hand Tools, Petite Ponar Grab Sampler)

Two field personnel should participate in the collection of the equipment blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should pour the rinse water.

The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep bottle lid on until immediately prior to sample collection.
2. Lay down dedicated plastic sheeting or other clean surface to prevent sample contact with the ground.
3. Place sealable bucket or pail on top of plastic sheeting.
4. Don new pair of nitrile gloves prior to blank collection (both field personnel). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
5. Open sample container and position the clean, decontaminated piece of sample equipment (i.e., hand tool, grab sampler) above the container (Field Personnel #1). Keep the sample cap in the hand of the sampler (Field Personnel #1) until it is replaced on the bottle.
6. Slowly pour the laboratory-provided “PFAS-free” water over any surface of the sampling device that contacted sampled material (Field Personnel #2).
    a. Pour water over front and back of all decontaminated hand tools such as spoons, spatulas, and trowels so that “PFAS-free” water touches all sides of the sampling device. Collect runoff in the sample container, making sure that any excess “PFAS-free” water is contained in the sealable bucket or pail (Field Personnel #1).
    b. Pour water through inside of the decontaminated Petite Ponar Grab Sampler while rotating the sampler (or the “PFAS-free” water container) so that “PFAS-free” water contacts all interior sides of the sampler (Field Personnel #2). Collect runoff in the sample container, making sure that any excess “PFAS-free” water is contained in the sealable bucket or pail.
7. After collecting the necessary sample volume, place cap back on the sample bottle (Field Personnel #1). The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
8. Collect the second bottle with the same procedure (Steps 5 to 7), if collecting a backup.
9. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
10. Add the sample to the laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
11. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
12. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.4 Disposable Sediment Sampling Equipment (Lexan TM Liner Sleeve)

Two field personnel should participate in the collection of the equipment blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should pour the rinse water.

The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep the bottle lid on until immediately prior to sample collection.
2. Lay down dedicated plastic sheeting or other clean surface to prevent sample contact with the ground.
3. Place sealable bucket or pail on top of plastic sheeting.
4. Don new pair of nitrile gloves prior to blank collection (both field personnel). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
5. Open sample container and position a clean, new, and unused section of Lexan™ liner above the container (Field Personnel #1). Keep the sample cap in the hand of the sampler (Field Personnel #1) until it is replaced on the bottle.
6. Slowly pour laboratory-provided "PFAS-free" water over any surface of the sampling device that contacted sampled material (Field Personnel #2).
    a. Pour water through inside of Lexan™ liner while rotating the liner so that "PFAS-free" water contacts all interior sides of the liner. Collect runoff in the sample container, making sure that any excess "PFAS-free" water is contained in the sealable bucket or pail.
7. After collecting the necessary sample volume, place cap back on the sample bottle (Field Personnel #1). The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
8. Collect the second bottle with the same procedure (Steps 5 to 7), if collecting a backup.
9. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
10. Add sample to the laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
11. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
12. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.5 Reusable Water Sampling Equipment (Peristaltic Pump, Bladder Pump, Stainless-Steel Bailer)

8.1.5.1 Peristaltic Pump

Two field personnel should participate in the collection of the equipment blank. One person ("Field Personnel #1") should hold the sampling bottle and collect the sample, and the second person ("Field Personnel #2") should set up the pump and pour/ transfer the blank water.

The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep bottle lid on until immediately prior to sample collection.

2. Lay down dedicated plastic sheeting other clean surface to prevent sample contact with the ground.
3. Don new pair of nitrile gloved prior to blank collection (both field personnel). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
4. Pour laboratory-supplied “PFAS-free” water into a clean HDPE sample bottle (Field Personnel #2).
5. Insert new HDPE tubing into the HDPE bottle containing “PFAS-free” water and connect tubing to peristaltic pump (with new silicone tubing) (Field Personnel #2).
6. Open sample container, keeping the sample cap in the hand of the sampler until it is replaced on the bottle (Field Personnel #1).
7. Turn the peristaltic pump on and slowly pump the “PFAS-free” water into the labeled sample container (Field Personnel #2).
8. After collecting the necessary sample volume, place cap back on the sample bottle (Field Personnel #1). The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
9. Collect the second bottle with the same procedure (Steps 6 to 8), if collecting a backup.
10. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
11. Add the sample to the laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
12. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
13. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.5.2 Bladder Pump

1. Two field personnel should participate in the collection of the equipment blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should set up the pump and pour/ transfer the blank water.
2. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.
3. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep the bottle lid on until immediately prior to sample collection.
4. Lay down dedicated plastic sheeting or other clean surface to prevent sample contact with the ground.
5. Don new pair of nitrile gloved prior to blank collection (both field personnel). Do not use gloved hands to handle papers, pens, clothes, equipment, etc., before collecting samples.
6. Pour laboratory-supplied “PFAS-free” water into an approved container (to avoid PFAS cross-contamination) large enough to submerge the bladder pump.
7. After properly decontaminating the bladder pump and replacing the bladder, attach a new section of HDPE tubing to the bladder pump, long enough to hold and direct flow into the labeled sample container. Submerge the bladder pump into the approved container of “PFAS-free” water (Field Personnel #2).

8. Open sample container, keeping the sample cap in the hand of the sampler until it is replaced on the bottle (Field Personnel #1).
9. Turn the bladder pump on and slowly pump the “PFAS-free” water into the labeled sample container (Field Personnel #2).
10. After collecting the necessary sample volume, place cap back on the sample bottle. The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
11. Collect the second bottle with the same procedure (Steps 6 to 8), if collecting a backup.
12. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
13. Add sample to laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
14. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
15. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.5.3 Stainless-Steel Bailer

Two field personnel should participate in the collection of the equipment blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should pour the rinse water.

The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFASs, after the sampling equipment has been appropriately decontaminated.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep bottle lid on until immediately prior to sample collection.
2. Lay down dedicated plastic sheeting or other clean surface to prevent sample contact with the ground.
3. Place sealable bucket or pail on top of plastic sheeting.
4. Don new pair of nitrile gloves prior to blank collection (both field personnel). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
5. Open sample container (Field Personnel #1) and position the bailer above the container (Field Personnel #2). Keep the sample cap in the hand of the sampler (Field Personnel #1) until it is replaced on the bottle.
6. Fill the stainless-steel bailer with enough laboratory-provided “PFAS-free” water to collect the necessary sample volume (Field Personnel #2).
7. Slowly pour laboratory-provided “PFAS-free” water from the stainless-steel bailer into the sample container (Field Personnel #2).
8. After collecting the necessary sample volume, place cap back on the sample bottle. The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
9. Collect the second bottle with the same procedure (Steps 5 to 8), if collecting a backup.

10. Place filled sample bottles in sealed Ziploc® bags, record any label information that was not pre-filled out, if necessary (e.g., sample time). Record the label information and time of sampling in the field notes and sampling forms.
11. Fill out the laboratory COC and check against the labels on the Equipment Blank sample bottle(s) progressively after each Equipment Blank is collected. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
12. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in a separate cooler from any other types of samples.
13. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

8.1.6 Field Reagent Blank Sampling

Two field personnel should participate in the collection of the reagent blank. One person (“Field Personnel #1”) should hold the sampling bottle and collect the sample, and the second person (“Field Personnel #2”) should pour the blank water.

This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

1. Label the laboratory-provided HDPE bottles with applicable information (e.g., sample ID, date, time, analysis required). Keep the bottle lid on until immediately prior to sample collection.
2. Don new pair of nitrile gloves prior to blank collection (both field personnel). Do not use gloved hands to handle other objects (e.g., papers, pens, clothes, equipment) before collecting samples.
3. Open sample container, keeping the sample cap in the hand of the sampler (Field Personnel #1) until it is replaced on the bottle (Field Personnel #1).
4. Slowly pour laboratory-provided “PFAS-free” water from the laboratory-provided container into the sample container (“Field Personnel #2”).
5. After collecting the necessary sample volume, place cap back on the sample bottle. The bottle should be filled approximately full, but some headspace in the bottle is acceptable.
6. Collect the second bottle with the same procedure (Steps 3 to 5) if collecting a backup.
7. Record any label information that was not pre-filled out, if necessary (e.g., sample time), and place filled sample bottles in sealed Ziploc® bags. Record the label information and time of sampling in the field notes.
8. Add sample to the laboratory COC. Double check that the sample labels and COC agree. Note on the COC that one bottle should be held in reserve, if a backup bottle is collected.
9. Place sealed Ziploc® bag into the sample cooler. Store PFAS samples in separate cooler from any other types of samples.
10. Place dedicated plastic sheeting and nitrile gloves in plastic bags. These bags will be transferred into appropriately labeled waste containers for appropriate disposal.

9 Waste Management

Excess water generated during equipment and reagent blank collection procedures will be collected and contained on site in appropriate containers, (see TGI for Investigation-Derived Waste Handling and Storage, for details). All investigation-derived waste (IDW) generated will be placed in Department of Transportation approved containers, sealed, and labeled. Containerized IDW will be stored on site until it is profiled and subsequently transported to an approved facility for disposal or recycling. Waste manifests for all IDW suspected to have come into contact with PFAS should clearly note the presence of PFAS. Additional IDW sampling and management details will be provided in the site-specific Work Plan (Quality Assurance Project Plan, QAPP addendum) and will be consistent with applicable client policies and requirements. Disposable personal protective equipment (e.g., gloves, disposable clothing, disposable equipment) will be placed in plastic bags. These bags will be transferred into appropriately labeled containers for appropriate disposal.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

If digital data collection isn't possible, waterproof field books should be avoided for field notes. Instead, field notes on loose paper on Masonite, plastic, or aluminum clip boards is preferred. Please note that newer Rite in the Rain® notebooks are approved for PFAS sampling. Other requirements for field notes include:

- Pens, pencils, and fine point Sharpies® may be used.
- Keep field notes and writing implements away from samples and sampling materials.
- Do not write on sampling bottle labels unless the sample bottle covers are tightly closed.
- Complete sampling logs in their entirety.
- Make sure COC forms are properly completed. Verify that the analysis method requested is US EPA Method 537.1 for potable water and includes the appropriate analytes desired for analysis.

11 Quality Assurance

Refer to quality control requirements for the project to ensure that appropriate QA and QC samples are collected. When collecting QA and QC samples, the same guidelines apply as when collecting regular samples – specifically:

- **Duplicate samples of each equipment blank and reagent blank should be collected and submitted to the laboratory with instructions to hold for analysis. The purpose of this sample is to provide analytical back-up in case there are any issues with the original blank sample.**

- Samples should be collected in laboratory-supplied HDPE bottles.
- Bottle caps must remain in the hand of the sampler until replaced on the bottle;
- Labels must be completed after the caps have been placed back on each bottle.

Samples must be stored in appropriate transport containers (coolers) with ice (Ziploc®-type bags for use as ice containers) with appropriate labeling. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

12 References

Arcadis TGI – TGI for Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide.pdf

Arcadis SOP – TGI for Sample Chain of Custody.pdf

Arcadis TGI – TGI for Groundwater and Soil Sampling Equipment Decontamination.pdf

Arcadis TGI – TGI for Investigation-Derived Waste Handling and Storage.pdf

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TGI – Groundwater and Soil Sampling Equipment Decontamination

Rev: 3

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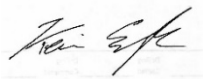
Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	February 23, 2017	All	Conversion from SOP to TGI	Cassandra McCloud / Pete Frederick
	1	May 8, 2020	4, 5	Added note regarding use of Liquinox and 1,4-Dioxane	Marc Killingstad
	2	June 14, 2022	All	Conversion to new TGI format and minor edits.	Kevin Engle / Marc Killingstad
	3	August 30, 2023	All	Annual review completed by SME. Updated Rev 1.	Marc Killingstad

Approval Signatures

Prepared by: 8/30/2023



Name (Preparer) Date

Reviewed by: 8/30/2023

Marc Killingstad (Subject Matter Expert) Date

1 Introduction

This document is intended to provide guidance to staff performing decontamination procedures at project sites. The content in this document describes the intended use, scope and application, personnel qualifications, equipment, cautions, health and safety considerations, procedures, waste management, data recording and management, and quality assurance of decontamination procedures.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

Decontamination is performed on sampling equipment prior to sample collection to ensure that the sampling equipment that contacts a sample, or monitoring equipment that is brought into contact with environmental media to be sampled, is free from analytes of interest and/or constituents that could interfere with laboratory analysis for analytes of interest. Sampling equipment must be appropriately cleaned prior to use for sampling or coming into contact with environmental media to be sampled and following completion of the sampling event prior to shipment or storage. The effectiveness of the decontamination procedure should be verified by collecting and analyzing equipment blank samples.

The sampling equipment cleaning procedures described herein includes pre-field, in the field, and post- field cleaning of sampling equipment which may be conducted at an established equipment decontamination area (EDA) on site, as appropriate and necessary. Sampling equipment that may require decontamination at a given site include soil sampling tools; groundwater, sediment, and surface-water sampling devices; water testing instruments; down-hole instruments; and other activity-specific sampling equipment. Non-disposable equipment will be cleaned before collecting each sample, between each sample collected, and prior to placing sampling equipment in protective cases, or containers for transport. Cleaning procedures for sampling equipment should be monitored by collecting equipment blank samples as required in project work plans, field sampling plans, quality assurance project plans (QAPP), or other pertinent project documents. Dedicated and/or single-use (i.e., not to be re-used) sampling equipment will not require decontamination.

4 Personnel Qualifications

Arcadis field sampling personnel will have completed or are in the process of completing site-specific training as well as having current health and safety training as required by Arcadis, client, or regulations, such as 40-hour hazardous waste operations and emergency response (HAZWOPER) training and/or Occupational Safety and Health Administration (OSHA) HAZWOPER site supervisor training. Arcadis personnel will also have current training as specified in the Health and Safety Plan (HASP) which may include first aid, cardiopulmonary resuscitation (CPR), Blood Borne Pathogens (BBP) as needed. In addition, Arcadis field sampling personnel will be knowledgeable in the relevant processes, procedures, and Technical Guidance Instructions (TGIs) and possess the demonstrated required skills and experience necessary to successfully complete the desired field work. The project HASP and other documents will identify other training requirements or access control requirements.

5 Equipment List

The equipment required for equipment decontamination is presented below. Note that certain contaminants may require specific materials be used that are not captured in this list. Always review project and contaminant specific TGIs or work plans to ensure proper equipment is utilized. Note for per- and polyfluoroalkyl substances (PFAS) see *TGI – Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide*.

- Health and safety equipment, including appropriate personal protective equipment (PPE), as required in the site HASP
- Deionized water that meets the analytical criteria for deionized water with no detectable constituents above the reporting limits for the methods to be used and analytes being analyzed for. Deionized water is used for inorganics, and organic-free water for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides, etc.
- Non-phosphate detergent such as Alconox® or, if sampling for phosphorus or phosphorus- containing compounds, Liquinox (or equivalent). NOTE: Liquinox has shown to provide false positives for 1,4-Dioxane and should not be used at sites where that may be a constituent of concern (COC).
- Tap water
- Rinsate collection plastic containers

- Department of Transportation (DOT)-approved waste shipping container(s), as specified in the work plan, field sampling plan, or regulatory requirements if decontamination waste is to be shipped for disposal
- Brushes
- Large heavy-duty garbage bags
- Spray bottles
- (Optional) – Isopropyl alcohol (free of ketones) or methanol. These can be wipes or diluted with water (usually 1part isopropyl/methanol to 10 parts water) if a spray is needed.
- Airtight, sealable plastic baggies, such as Ziploc®-type
- Plastic sheeting

6 Cautions

Rinse equipment thoroughly and allow the equipment to dry before re-use or storage to prevent introducing solvent into sample medium. If manual drying of equipment is required, use clean lint-free material to wipe the equipment dry. Ensure all rinse materials do not adversely affect sample collection efficiency or analytical results.

Store decontaminated equipment in a clean, dry environment. Do not store near combustion engine exhausts. Properly containerize equipment to ensure cross-contamination doesn't happen from other uncontaminated surfaces or equipment.

If equipment is damaged to the extent that decontamination is uncertain due to cracks, gouges, crevices, or dents, the equipment should not be used and should be discarded or submitted for repair prior to use for sample collection.

A proper shipping determination regarding hazardous materials will be performed by a DOT-trained individual for cleaning materials shipped by Arcadis.

Caution should be exercised to avoid contact with the pump casing and water in the container while the pump is running (do not use metal drums or garbage cans) to avoid electric shock.

7 Health and Safety Considerations

Review the safety data sheets (SDS) for the cleaning agents and materials used in decontamination. If solvent is used during decontamination, use appropriate PPE and work in a well-ventilated area and stand upwind while applying solvent to equipment. Apply solvent in a manner that minimizes potential for exposure to workers and bystanders. Follow health and safety procedures outlined in the HASP.

8 Procedure

A designated area will be established to clean sampling equipment in the field prior to and following sample collection. Equipment cleaning areas will be set up within or adjacent to the specific work area, but not at a location that expose equipment to contamination (i.e., exposed to combustion engine exhaust). Detergent solutions will be prepared in clean containers for use in equipment decontamination. Decontaminated equipment

will be handled by workers wearing clean gloves, properly changed to prevent cross-contamination. The procedures detailed in this section provide an overview of common decontamination techniques. Additional steps may be required based on the type of contaminant present or client/site requirements.

Cleaning Sampling Equipment

1. Wash the equipment/pump with potable water.
2. Wash with detergent solution (Alconox®, Liquinox® or equivalent) to remove all visible particulate matter and any residual oils or grease. NOTE: Liquinox® has shown to provide false positives for 1,4-Dioxane and will not be used at sites where that may be a COC.
3. If equipment is very dirty, precleaning gross debris with a brush and tap water may be necessary.
4. If non-aqueous phase liquids are present, the use of isopropyl alcohol (free of ketones) or methanol is recommended. Cloth wipes or diluted solution can be used to remove the non-aqueous phase liquids that are hard to remove with detergent solution in step 2. Consult with project manager if non-aqueous phase liquids are present onsite and design an appropriate decontamination procedure that includes step 4.
5. Rinse with deionized water.

Decontaminating Submersible Pumps

Submersible pumps may be used during well development, groundwater sampling, or other investigative activities. The pumps must be cleaned and flushed before and between uses. This cleaning process will consist of an external detergent solution wash and tap water rinse, a flush of detergent solution through the pump, followed by a flush of potable water through the pump. Flushing will be accomplished by using an appropriate container filled with detergent solution and another container filled with potable water. The pump will be be flushed with deionized water as the last step prior to use. The pump will run long enough to effectively flush the pump housing and hose (unless new, disposable hose is used). Disconnect the pump from the power source before handling. The pump and hose will be placed on or in clean polyethylene sheeting to avoid contact with the ground surface.

9 Waste Management

Equipment decontamination rinsate will be managed in conjunction with all other waste produced during the field sampling effort. Waste management procedures are outlined in the work plan or Waste Management Plan (WMP).

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff

are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

Equipment cleaning and decontamination will be noted during project documentation. Information will include the type of equipment cleaned, the decontamination location, specific procedures utilized, solvents and/or cleaning agents used, source of water, and deviations or omissions from this TGI.

Unusual field conditions should be noted if there is potential to impact the efficacy of the decontamination or subsequent sample collection.

An inventory of the solvents brought on site and used and removed from the site will be maintained in the project documentation. Records will be maintained for solvents used in decontamination, including lot number and expiration date.

Containers with decontamination fluids will be labeled.

11 Quality Assurance

Equipment blanks should be collected to verify that the decontamination procedures are effective in minimizing potential for cross contamination. The equipment blank is prepared by pouring deionized water (or organic-free water, for organic analyses) over the clean and dry tools and collecting the water into appropriate sample containers. Equipment blanks should be analyzed for the same set of parameters that are performed on the field samples collected with the equipment that was cleaned as specified in the sampling and analysis plan. Equipment blanks are collected per equipment set, which represents all the tools needed to collect a specific sample.

12 References

USEPA Region 9 - Field Sampling Guidance #1230, Sampling Equipment Decontamination.

USEPA Region 1 - Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells.

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TGI – Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells

Rev: 3

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Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	October 12, 2018	All	Updated and re-written as TGI with new branding and content	Marc Killingstad
	1	May 8, 2020	Pages 5, 10-11	Added clarification/details for equipment requirements and procedure steps based on USEPA guidance	Marc Killingstad
	2	April 5, 2022	All	Updated to new branding template and minor edits	Marc Killingstad
	3	April 5, 2023	All	Annual review completed by SME. Document version number and document date updated.	Marc Killingstad

Approval Signatures

Prepared by:	Xuan Xu	4/5/2023
	Xuan Xu (Preparer)	Date
Reviewed by:		4/5/2023
	Marc Killingstad (Subject Matter Expert)	Date

1 Introduction

Groundwater samples are collected from monitoring wells to evaluate groundwater quality. The protocol presented in this Technical Guidance Instruction (TGI) describes the procedures to purge monitoring wells and collect groundwater samples using the low flow purging/sampling methodology. This protocol has been developed in accordance with the United States Environmental Protection Agency (USEPA) Region I *Low Stress (Low Flow) Purging and Sampling Procedures for the Collection of Groundwater Samples from Monitoring Wells* (EQASOP-GW4; September 19, 2017).

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

Both filtered and unfiltered groundwater samples may be collected using this low-flow sampling method. Filtered samples will be obtained using a 0.45-micron disposable filter. Project teams will evaluate the last time the monitoring wells were developed and determine if additional development might be necessary. Water samples will not be taken immediately following well development. Sufficient time will be allowed for the groundwater flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well

construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

4 Personnel Qualifications

Arcadis field sampling personnel will have completed or are in the process of completing site-specific training as well as having current health and safety training as required by Arcadis, client, or regulations,such as 40-hour HAZWOPER training and/or OSHA HAZWOPER site supervisor training. Arcadis personnel will also have current training as identified in the site-specific Health and Safety Plan (HASP) which may include first aid, cardiopulmonary resuscitation (CPR), Blood Borne Pathogens (BBP) as needed. The HASP will also identify any access control requirements.

Prior to mobilizing to the field, the groundwater sampling team will review and be thoroughly familiar withrelevant site-specific documents including but not limited to the task-specific work plan or field implementation plan (FIP)/field sampling plan, Quality Assurance Project Plan (QAPP), HASP, historical information, and other relevant site documents.

Arcadis field sampling personnel will be knowledgeable in the relevant processes, procedures, and TGIs and possess the demonstrated required skills and experience necessary to successfully complete the desired field work. Additionally, the groundwater sampling team will review and be thoroughly familiar with documentation provided by equipment manufacturers and become familiar with the operation of (i.e., hands-on experience) all equipment that will be used in the field prior to mobilization.

5 Equipment List

Specific to this activity, the following materials (or equivalent) will be used:

- Site-specific HASP and health and safety documents identified in the HASP
- Field Implementation Plan (FIP) that includes site map, well construction records, sampling plan (sample analyses, sample volume required, and sample holding time), and prior groundwater sampling records (if available)
- Field notebook and/or smart device (phone or tablet)
- Low-flow sampling field forms (**Attachment A**)
- Appropriate personal protective equipment (PPE) (e.g., latex or nitrile gloves, safety glasses, etc.)as specified in the HASP
- Well keys and other tools to remove manhole covers (manual torque wrench with 9/16” socket and flat head screwdriver typical)
- Photoionization detector (PID) or Flame ionization detector (FID) (as appropriate, depending onsite-specific constituents of concern)
- Electronic water-level indicator (e.g., Solinist Model 101) or oil/water interface probe with 0.01- foot accuracy (oil/water as appropriate, note that sampling will not be performed when sheen orlight non-aqueous phase liquid [LNAPL] is present)
- Down-hole multi-parameter water-quality sonde (temperature/pH/specific conductivity/oxidationreduction [ORP]/turbidity/dissolved oxygen) meter coupled with flow-through-cell for measurements, for example:

  - YSI 6-Series Multi-Parameter Instrument
  - Horiba U-22 Multi-Parameter Instrument.
  - Hydrolab Series 3 or Series 4a Multiprobe and Display.

  NOTE: *Transparent, small volume flow-through-cells (e.g., 250 milliliters or less) are preferred as they allow for easy detection of air bubbles and sediment buildup in the cell, which can interfere with the monitoring instrument probes. A small volume cell also allows for quick turnover of water in the cell between measurements of the indicator field parameters. It is recommended to use a flow-through-cell and monitoring probes from the same manufacturer and model to avoid incompatibility between the probes and flow-through-cell.*

- Plastic sheeting (e.g., Weatherall Visqueen) to protect all down-hole sampling equipment from contact with potential sources of contamination.
- Decontamination equipment
  - Non-phosphate laboratory soap (Alconox or equivalent), brushes, and clean buckets, and/or clean wash tubs—new buckets or tubs will be purchased if it cannot be determined if the present items are clean
  - Distilled or de-ionized water for equipment decontamination
- Indelible ink pen
- 150-foot measuring tape (or sufficient length for the maximum site depth requirement)
- Sampling pump, which may consist of one or more of the following:
  - Submersible pump (e.g., Grundfos Redi-Flo 2)
  - Peristaltic pump (e.g., ISCO Model 150)
  - Bladder pump (e.g., Marschalk System 1, QED Micropurge, Geotech)
- Appropriate controller and power source for pump:
  - Submersible and peristaltic pumps require electric power from either a generator or a deep cell battery
  - Submersible pumps such as Grundfos require a pump controller to run the pump
  - Bladder pumps require a pump controller and a gas source (e.g., air compressor or compressed N_2 or CO_2 gas cylinders)
- Teflon® tubing or Teflon®-lined polyethylene tubing of an appropriate size for the pump being used
  - For peristaltic pumps, dedicated Tygon® tubing (or other type as specified by the manufacturer) will be used through the pump apparatus
  - Teflon® will not be used when sampling for per- and polyfluoroalkyl substances (PFAS)
- Graduated cylinder and stopwatch or other device to measure time to determine pumping rate
- Appropriate water sample containers (supplied by the laboratory)
- Appropriate blanks (trip blank supplied by the laboratory)
- Sample labels and Chain-of-Custody forms (COC)
- 0.45-micron disposable filters (if field filtering is required)

- A supplemental turbidity meter (e.g., Horiba U-10, Hach 2100P, LaMotte 2020) may be required for specific projects and will be specified in the project FIP/ work plan and the kick-off notes.
    - If used, in-line 'T' and valve allows for collection of water for turbidity measurements before the pump discharge enters the flow-through cell

NOTE: *The maintenance requirements for the above equipment generally involve decontamination or periodic cleaning, battery charging, and proper storage, as specified by the manufacturer. For operational difficulties, the equipment will be serviced by a qualified technician.*

6 Cautions

Different USEPA regions and/or state regulatory agencies may stipulate deviations from this document. Itis the responsibility of the Project Team (Project Manager and Technical Lead) to be fully aware of the requirements from the applicable regulatory framework.

Weather

- If heavy precipitation occurs, and no cover over the sampling area and monitoring well can be erected, sampling may be discontinued until adequate cover is provided. Rainwater could compromise groundwater samples.
- Avoid extreme weather situations. Be aware that thermal currents and vertical mixing of cold and warm water inside the well casing could create a convection cell within the well and compromise data collection (e.g., biological mechanisms).
    - Direct sunlight and hot ambient temperatures may cause the groundwater in the tubing orflow-through-cell to heat up and de-gas. This may result in the loss of volatile organic compounds (VOCs) and dissolved gases. Shade the equipment from direct sunlight, keep the tubing as short as possible and avoid the hottest times of the day.
    - Sampling during freezing conditions may adversely impact the data quality objectives. USEPA recommends low-flow sampling be conducted at air temperatures above 32°F (0°C) or taking special precautions to prevent groundwater from freezing in the equipment.

Cross-Contamination

- To mitigate potential cross-contamination, groundwater samples are to be collected in a pre- determined order from least impacted to impacted based on previous analytical data. If no analytical data are available, collect samples in order of up-gradient, then furthest down-gradient tosource area locations.
- Note that permanent markers could introduce volatile constituents into the samples*; therefore, indelible ink is recommended* to be used for labels on sample containers or sample coolers.
- When using a gasoline generator, this power source will be set-up at least 30 feet downwind from the well to avoid exhaust fumes to contaminate samples.

Pumps

- Preferred methods of extracting groundwater are adjustable rate, submersible pumps - such as centrifugal pumps or bladder pumps – constructed of stainless steel or polytetrafluoroethylene (PTFE, i.e., Teflon®). However, *PTFE will not be used when sampling for per- and polyfluoroalkyl substances (PFAS). PTFE could contain PFAS*.

- When using a bladder pump for collecting VOCs and dissolved gases, “best practice” is to set-up the pump to deliver sufficient water to fill a 40 mL VOC vial.
- The use of peristaltic pumps will be based on the type of data to be collected. *Because the use a peristaltic pump can result in de-gassing of VOC and / or dissolved gases from groundwater, a different type of pump will be considered if these compounds are of concern.*
- *Manual or motor driven inertial pumping devices are not recommended because they cause greater disturbance during purging and pumping than regular pumps and are less easily controlled. This could cause a higher degree of data variability.*

Tubing

- When sampling for VOCs, SVOCs, pesticides, PCBs and inorganics, use of PTFE (Teflon®) or PTFE-lined tubing is preferred. However, PTFE tubing will not be used when sampling for PFAS.
- PVC, polypropylene or polyethelene tubing may be used when sampling for metals or other inorganics.
- Tubing with inside diameters of 1/4 or 3/8 inch is recommended because this will help ensure tubing remains water filled when operating at very low pumping rates.

General Precautions

- Store and/or stage empty and full sample containers and coolers out of direct sunlight.
- It may be necessary to field filter the groundwater for some parameters (e.g., metals) during collection, depending on preservation, analytical method, and project quality objectives. The task-kick-off notes and the FIP/work plan will list the samples that require field filtering.
- Be careful not to overtighten lids with Teflon® liners or septa (e.g., 40 mL vials). Over-tightening can cause the glass to shatter or impair the integrity of the Teflon® seal.

7 Health and Safety Considerations

The HASP will be followed, as appropriate, to ensure the safety of field personnel.

Appropriate personal protective equipment (PPE) will be always worn in line with the task and the site-specific HASP.

Review all site-specific and procedural hazards as they are provided in the HASP, and review Job Safety Analysis (JSA) documents in the field each day prior to beginning work.

Access to wells may expose field personnel to hazardous materials such as contaminated groundwater or non-aqueous phase liquid (NAPL) (e.g., oil). Other potential hazards include pressurized wells, stinging insects that may inhabit well heads, other biologic hazards (e.g. ticks in long grass/weeds around well head), and potentially the use of sharp cutting tools (scissors, knife)—open well caps slowly and keep face and body away to allow to vent any built-up pressure; only use non-toxic peppermint oil spray for stinging insect nests; review client-specific health and safety requirements, which may preclude the use of fixed/folding-blade knives, and use appropriate hand protection.

Generators and cord and plug equipment will employ an overcurrent protection device such as an integrated ground fault circuit interrupter (GFCI) cord. Grundfos pump controllers will not run properly with a GFCI, so the power source will be equipped with other overcurrent protection means.

Overtightening of lids with Teflon® liners can cause the glass to shatter and create a risk for hand injuries.

8 Procedure

Field personnel will set up and perform low-flow sampling in accordance with the following procedures.

1. Review FIP and groundwater sampling records from previous sampling events (if available) prior to mobilization to estimate the optimum pumping rate and anticipated drawdown for each well to perform sampling as efficiently as possible (i.e., reach a stabilized pumping condition).
2. Calibrate field instruments according to manufacturer procedures for calibration and record calibration procedure and results in field log.
3. All equipment will either be new or decontaminated in accordance with appropriate guidance document *(TGI – Groundwater and Soil Sampling Equipment Decontamination)* prior to use.
4. Visually inspect the well to ensure that it is undamaged, properly labeled and secured
   a. Damage or other conditions that may affect the integrity of the well will be recorded in the Field Activity Daily Log and brought to the attention of the designated Field Manager and/or Project Manager
   b. Record well construction and conditions on the Low-Flow Sampling Field Form **(Attachment A)**.
5. Place clean plastic sheeting on the ground near the well to keep monitoring and sampling equipment off the surface unless the equipment is elevated above the ground (e.g., on a table).
6. Open the well cover while standing upwind of the well. Remove the well cap and place it on the plastic sheeting. If appropriate or required for site-specific conditions, insert the photoionization detector (PID) probe approximately 4 to 6 inches into the casing or the well headspace and cover it with a gloved hand. Record the PID reading in the field log. Perform air monitoring in the breathing zone according to the HASP and/or JSA.
7. Measure and record the initial depth to groundwater prior to placing the pumps.
8. Prepare and install the pump in the well.

   NOTE: *Groundwater will be purged from the wells using an appropriate pump. If the depth to water is below the sampling range of a peristaltic pump (approximately 25 feet below ground surface), a submersible or bladder pump will be used, provided that the well is constructed with a casing diameter of at least two (2) inches (the minimum well diameter capable of accommodating such pumps). For smaller diameter wells, where the depth to water is below the sampling range of a peristaltic pump, alternative sampling methods (i.e., bailing or small diameter bladder pumps) will be used to purge and sample the groundwater. Bladder pumps are preferred over peristaltic and submersible pumps to prevent volatilization if sampling of VOCs and/or dissolved gasses is required. Purge water will be collected and containerized according to the direction of the project team.*

   a. For submersible and non-dedicated bladder pumps, decontaminate the pump according to site decontamination procedures. Non-dedicated bladder pumps will require a new bladder and attachment of an air-line, sample discharge line, and safety cable prior to placement in the well. Attach the air-line tubing to the air-port on the top of the bladder pump. Attach the sample discharge tubing to the water port on the top of the bladder pump. Take care not to reverse the air and discharge tubing lines during bladder pump setup, as this could result in bladder failure or rupture. Attach and secure a safety cable to the eyebolt on the top of pump (if present, depending on pump model used). Slowly lower the pump, safety cable, tubing, and electrical lines into the well to a depth corresponding to the approximate center of the saturated screen section of the well. Avoid twisting

and tangling of safety cable, tubing, and electrical lines while lowering the pump into the well; twisted and tangled lines could result in the pump becoming stuck in the well casing. Also, make sure to keep tubing and lines from touching the ground or other surfaces while introducing them into the well, as this could lead to unintended contamination.

b. If using a bladder pump, connect the air-line to the pump controller output port. The pump controller will be connected to a supply line from an air compressor or compressed gas cylinder using an appropriate regulator and air hose. Tighten the regulator connector onto the gas cylinder (if used) to prevent leaks. Teflon® tape may be used on the threads of the cylinder to provide a tighter seal. Once the air compressor or gas cylinder is connected to the pump controller, turn on the compressor or open the valve on the cylinder to begin the gas flow. Turn on the pump controller power (if an on/off switch is present) and verify that all batteries are charged and fully functioning before starting the pump.

c. If a peristaltic pump is being used, slowly lower the sampling tubing into the well to a depth corresponding to the approximate center of the saturated screen section of the well. The pump intake or sampling tube must be kept at least two (2) feet above the bottom of the well to prevent mobilization of any sediment present in the bottom of the well.

d. If using an in-line 'T' and valve, install between pump discharge water line and the bottom inlet port of the flow-through cell. Attach a short piece of tubing to the outlet. This set-up will be used to collect samples for turbidity readings.

9. Connect the pump discharge water line to the bottom inlet port on the flow-through cell connected to the multi-parameter water-quality sonde and make sure to record equipment/instrument identification (manufacturer and model number).

10. Before starting the pump, ensure that the water level inside the well has stabilized (i.e., measure the water level multiple times after deploying the pump in the well).

11. Start pumping the well at 200 to 500 milliliters (mL) per minute (or at lower site-specific rate if specified) and adjust the pumping rate to cause little or no water level drawdown in the well (less than 0.3 feet below the initial static depth to water measurement): the water level should stabilize, however, this is not always possible.

12. If the well diameter is of sufficient size, measure the water level every 3 to 5 minutes (or as appropriate, lower flow rates may require longer time between readings) during pumping.

13. Maintain a steady flow rate to the extent practicable and do not break pump suction or cause entrainment of air in the sample.

14. Record pumping rate adjustments and depths to water.

    If necessary, reduce pumping rates to the minimum capabilities of the pump to avoid pumping the well dry and/or to stabilize indicator parameters; if the recharge rate of the well is very low, use alternative purging techniques, which will vary based on the well construction and screen position.

    For wells screened across the water table, the well may be pumped dry, and sampling can commence as soon as the volume in the well has recovered sufficiently to permit collection of samples.

    For wells screened entirely below the water table, the well can be pumped until a stabilized level (which may be greater than the maximum displacement goal of 0.3 feet) is maintained and monitoring for stabilization of field indicator parameters can commence; if a lower stabilization level cannot be

maintained, the well may be pumped until the drawdown is at a level slightly higher than top of the well screen.

15. After water levels have stabilized and a sufficient volume has been purged (see note below), continue pumping and begin monitoring field indicator parameters using a multi-parameter water-quality sonde coupled with a flow-through-cell.

    NOTE: *The final purge volume must be greater than the stabilized drawdown volume plus the pump's tubing volume. If the drawdown has exceeded 0.3 feet and stabilizes, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are collected.*

16. Use the flow to measure all indicator field parameters, except for turbidity, every 3 to 5 minutes (or after each volume of the flow-through cell has been purged or other appropriate interval); turbidity samples will be collected before the flow-through-cell using the T-valve and a clean container such as a glass beaker.

17. Record field indicator parameters on the groundwater sampling log.

18. The well is considered stabilized and ready for sample collection when three consecutive readings are within the following limits:

    - **Turbidity** within ± 10% for values greater than 5 nephelometric turbidity units [NTUs] or if three turbidity values are less than 5 NTUs, consider the values stabilized
    - **Dissolved Oxygen (DO)** within ± 10% for values greater than 0.5 mg/L or if three DO values are less than 0.5 mg/L, consider the values stabilized
    - **Specific Conductance** within ± 3%
    - **Temperature** within ± 3%
    - **pH** within ± 0.1 unit
    - **Oxidation/Reduction Potential (ORP)** within ±10 millivolts (mV)

    NOTE: *Alternate stabilization goals may exist in different geographic regions, consult the site- specific FIP/work plan for stabilization criteria).*

    NOTE: *While achieving turbidity levels less than 5 NTU and a stable drawdown of less than 0.3 feet is desirable, sample collection may still take place provided the indicator field parameter criteria in this procedure are met.*

19. If the parameters have stabilized but turbidity remains relatively high (e.g., greater than 50 NTUs), the pump flow rate may be decreased to a minimum rate of 100 mL/min to reduce turbidity levels as low as possible. If groundwater turbidity has been minimized (i.e., consecutive readings within ± 10%) and the values for all other parameters have stabilized, the well may be sampled; however, consult specifications in the FIP/work plan and/or the project technical lead prior to sampling.

20. If after one (1) hour of purging indicator field parameters have not stabilized, consult specifications in the FIP/work plan and/or the project technical lead prior to sampling.

    In general, three potential options are available if stabilization criteria are not met:

    a. Continue purging until stabilization is achieved.

    b. Discontinue purging, do not collect any samples, and record in field logbook/on the sampling form that stabilization could not be achieved (documentation must describe attempts to achieve stabilization).

c. Discontinue purging, collect samples, and provide full explanation of attempts to achieve stabilization. There is a risk that the analytical data obtained under these conditions, particularly metals and hydrophobic organic analytes, may reflect a sampling bias and, as a result, the data may not meet the data quality objectives of the sampling event.

NOTE: *DO is extremely susceptible to various external influences (including temperature or the presence of bubbles on the DO meter); therefore, great care will be taken to minimize the agitation or other disturbance of water within the flow-through cell while collecting these measurements. If air bubbles are present on the DO probe or in the discharge tubing, remove them before taking a measurement. If DO values are not within acceptable range for the temperature of groundwater, again check for and remove air bubbles on the probe before re-measuring. The table below may be used as a general guide for DO values under various temperatures; however, understand that the table corresponds to freshwater solubility and groundwater contaminants may affect oxygen solubility. If DO value is 0.00 or less, then the meter will be serviced and re-calibrated. If DO values are above possible results, then the meter will be serviced and re-calibrated.*

NOTE: *During extreme weather conditions, stabilization of field indicator parameters may be difficult to attain. Modifications to the sampling procedures to alleviate these conditions (e.g., measuring the water temperature in the well adjacent to the pump intake) will be documented in the field logbook/on the sampling form.*

NOTE: *If other field conditions are suspected of preventing stabilization of certain parameters, detailed observations will be documented in the field logbook/on the sampling form.*

Oxygen Solubility in Fresh Water

Temperature (degrees C)	Dissolved Oxygen (mg/L)
0	14.6
1	14.19
2	13.81
3	13.44
4	13.09
5	12.75
6	12.43
7	12.12
8	11.83
9	11.55
10	11.27
11	11.01
12	10.76
13	10.52
14	10.29
15	10.07
16	9.85
17	9.65
18	9.45
19	9.26
20	9.07
21	8.9
22	8.72
23	8.56
24	8.4
25	8.24
26	8.09
27	7.95
28	7.81
29	7.67
30	7.54
31	7.41
32	7.28
33	7.16
34	7.05
35	6.93

Reference: Vesilind, P.A., Introduction to Environmental Engineering, PWS Publishing Company, Boston, 468 pages (1996)

21. Complete the sample label(s) and cover the label(s) with clear packing tape to secure the label onto the container.
22. After the indicator parameters have stabilized, collect groundwater samples by diverting flow out of the unfiltered discharge tubing into the appropriate labeled sample container.
    a. If a flow-through analytical cell is being used to measure field parameters, the flow-through cell will be disconnected after stabilization of the field indicator parameters and prior to groundwater sample collection.
    b. Under no circumstances will analytical samples be collected from the discharge of the flow- through cell.
    c. If an in-line ‘T’ and valve are used, the valve needs to be removed as well.

d. Samples will be collected in the following order: VOCs, total organic carbon (TOC), semi- volatile organic compounds (SVOCs), metals and cyanide, and others (or other order as defined in the site-specific FIP/work plan).
e. When the container is full, tightly screw on the cap.

23. If sampling for total and filtered metals and/or polychlorinated biphenyls (PCBs), a filtered and unfiltered sample will be collected.
    a. Install an in-line, disposable 0.45-micron particle filter on the discharge tubing after the appropriate unfiltered groundwater sample has been collected.
    b. Continue to run the pump until an initial volume of "flush" water has been run through the filter in accordance with the manufacturer's directions (generally 100 to 300 mL).
    c. Collect the filtered groundwater sample by diverting flow out of the filter into the appropriately labeled sample container.
    d. When the container is full, tightly screw on the cap.
24. Secure with packing material and store the samples on ice in an insulated transport container provided by the laboratory and include a temperature blank in each container to be shipped.
25. Record on the Low-Flow Sampling Field Form (and bound field logbook) the time at which sampling procedures were completed, any pertinent observations of the sample (e.g., physical appearance and the presence or lack of odors or sheens), and the values of the stabilized field indicator parameters as measured during the final reading during purging **(see Attachment A)**.
26. Turn off the pump and air compressor or close the gas cylinder valve if using a bladder pump setup.
27. Slowly remove the pump, tubing, lines, and safety cable from the well.
    a. If using dedicated tubing, do not allow the tubing or lines to touch the ground or any other surfaces which could contaminate them.
    b. If using dedicated tubing, it will be folded - without pinching it - to a length that will allow the well to be capped and also facilitate retrieval of the tubing during later sampling events.
    c. Use a length of rope or string to tie the tubing to the well cap.
    d. Alternatively, if tubing and safety line are to be saved and reused for sampling the well at a later date, coil the tubing neatly and placed in a clean plastic bag that is clearly labeled with the well ID ensuring the bag is tightly sealed before placing it in storage.
28. Secure the well and properly dispose of personal protective equipment (PPE) and disposable equipment.
29. Complete the procedures for packaging, shipping, and handling with the associated Chain-of- Custody.
30. Complete decontamination for flow-through analytical cell and submersible or bladder pump, as appropriate *(TGI – Groundwater and Soil Sampling Equipment Decontamination).*
31. At the end of each day of the sampling event, perform calibration check of field instruments and record procedure and results in field log.

9 Waste Management

Materials generated during groundwater sampling activities, including disposable equipment and excess purge water, will be stored on site in appropriately labeled containers and disposed of properly. Waste will be managed in accordance with the *TGI – Investigation-Derived Waste Handling and Storage*, the procedures identified in the

FIP or QAPP as well as state-, federal- or client-specific requirements. Be certain that waste containers are properly labeled and documented in the field logbook.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

Management of the original documents from the field will be completed in accordance with the site- specific QAPP.

In general, forms (e.g., Low-Flow Sampling Field Forms), logs/notes (including daily field and calibration logs), digital records, and Chain-of-Custody records will be maintained by the field team lead.

Field logs and Chain-of-Custody records will be transmitted to the Arcadis Project Manager and/or Task Manager, as appropriate, at the end of each day unless otherwise directed. Electronic data files will be sent to the project team and uploaded to the electronic project folder daily.

Records generated as a result of this TGI will be controlled and maintained in the project record files in accordance with project requirements.

11 Quality Assurance

Quality assurance procedures shall be conducted in accordance with the Arcadis Quality Management System or the site-specific QAPP.

Unless described otherwise in the project-specific FIP/work plan, QAPP, or Sampling and Analysis Plan, quality assurance/quality control samples will be collected as follows:

- One duplicate for every 10 samples
- One laboratory matrix/matrix spike sample for every 20 samples
- In addition to the quality control samples to be collected in accordance with this TGI, the following quality control procedures will be observed in the field:
- Collect samples from monitoring wells, in order of increasing concentration, to the extent known based on review of historical site information if available
- Equipment blanks will include the pump and tubing (if using disposable tubing) or the pump only (if using tubing dedicated to each well)
- Collect equipment blanks after wells with higher concentrations (if known) have been sampled

- Operate all monitoring instrumentation in accordance with manufacturer's instructions and calibration procedures—calibrate instruments at the beginning of each day, verify the calibration at the end of each day, and record all calibration activities in the field notebook
- Clean all groundwater sampling equipment prior to use in the first well and after each subsequent well following the procedure for equipment decontamination

12 References

USEPA. 1986. *RCRA Groundwater Monitoring Technical Enforcement Guidance Document* (September 1986).

USEPA. 1991. *Handbook Groundwater, Volume II Methodology*, Office of Research and Development, Washington, DC. USEPN62S, /6-90/016b (July 1991).

USEPA Region I. 2017. *Low Stress (Low Flow) Purging and Sampling Procedures for the Collection of Groundwater Samples from Monitoring Wells (*EQASOP-GW4; September 19, 2017).

U.S. Geological Survey (USGS). 1977. *National Handbook of Recommended Methods for Water-Data Acquisition: USGS Office of Water Data Coordination*. Reston, Virginia.

13 Attachments

Attachment A – Low Flow Sampling Field Form

Attachment A

Low-Flow Sampling Field Form

GROUNDWATER SAMPLING FORM

Project No. _____ Well ID _____ Date _____

Project Name/Location _____ Weather _____

Measuring Pt. Description _____ Screen Setting (ft-bmp) _____ Casing Diameter (in.) _____ Well Material ____ PVC ____ SS

Static Water Level (ft-bmp) _____ Total Depth (ft-bmp) _____ Water Column (ft) _____ Gallons in Well _____

MP Elevation _____ Pump Intake (ft-bmp) _____ Purge Method: _____ Sample Method _____

Pump On/Off _____ Centrifugal _____ Submersible _____ Other _____

Sample Time: _____ Volume Purged _____

Purge Start _____ Gallons Purged _____ Sample ID _____ Sampled by _____

Purge End _____ Replicate/Code No. _____

Time	Minutes Elapsed	Rate (gpm)/(mL/min) 200mL/min +	Depth to Water (ft) -0.3	Gallons Purged	pH ± 0.1	Cond. (µMhos)/(mS/cm) ± 3%	Turbidity (NTU) ± 10%	DO (mg/L) ± 10%	Temp. (°C)/(°F) ± 3%	Redox (mV) ± 10mV	Appearance	
											Color	Odor
Stabilization Calculations (±)												
Stabilization Criteria					**± 0.1 s.u.**	**±3%**	**± 10% or within 1 NTU (1)**	**± 10%**	**±3%**	**±10 mV**		

(1) **Turbidity** < 50 NTU and ±10% or within 1 NTU of a previous reading when <10 NTU

Constituents Sampled	Container	Number	Preservative

Comments _____

Well Casing Volumes

Gallons/Foot					
	1" = 0.04	*1.5" = 0.09*	*2.5" = 0.26*	*3.5" = 0.50*	*6" = 1.47*
	1.25" = 0.06	*2" = 0.16*	*3" = 0.37*	*4" = 0.65*	

Well Information

Well Location: _____ Well Locked at Arrival: Yes / No

Condition of Well: _____ Well Locked at Departure: Yes / No

Well Completion: Flush Mount / Stick Up Key Number To Well: _____

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TGI – Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide

Rev: 13

Rev Date: April 24, 2025

Version Control

Revision No.	Date Issued	Page No.	Description	Reviewed By
0	April 27, 2017	All	Initial Release	Erica Kalve Erika Houtz Sue Tauro
1	June 19, 2018	1 through 4 and 17	Updated Information on Sampling Materials	Erica Kalve Erika Houtz
2	October 15, 2018	6 to 16	Minor updates on laboratory elements, updates to decontamination procedures, and clarification on equipment and reagent blank collection	Erika Houtz Erica Kalve
3	December 17, 2018	4, 6, 17	Removed Sharpies from acceptable field writing implements; Changed language in Section 3.2 and Section 10.5 to provide stricter guidance for DoD projects.	Erika Houtz, Erica Kalve
4	March 26, 2019	4,5	Removed Citranox from acceptable Decon solutions in Table 1a, added all fluoropolymer containing materials to prohibited items in Table 1b. Made a correction that Liquinox contains trace levels of 1,4 Dioxane, not Alconox.	Erika Houtz
5	October 16, 2020	14	Added Air Force preference to sample surface water at surface for Air Force investigations.	Erika Houtz
6	March 23, 2021	4, 5, 7, 12, 13, 14, 15, 16, 17	Made clarifications that fine/ultra-fine point Sharpies are allowed. Referenced 2018 MDEQ sampling guidance. Made updates to ‘After Sample Collection’ in Section 7.	Kevin Engle

7	April 18, 2021	All	Changed title from Poly- and Perfluoroalkyl Substances to **"Per- and Polyfluoroalkyl Substances"** and changed PFASs to PFAS.	Rosario Varrella, Erika Houtz
8	May 4, 2021	12, 13, 15, 16	Clarified that sample containers should have an HDPE lined screw cap and that LDPE plastic sheeting should be used.	Kevin Engle, Erika Houtz
9	October 20, 2021	Note that numbers have shifted one page forward relative to prior versions. 5, 7, 9-12, 15, 16, 18-25.	Specific acceptable sunscreen and insect repellent brands were added to Table 1. Clarified language regarding footwear and H&S trainings. Laboratories section and Section 10.5 was updated to reflect new laboratory names and an updated version of the QSM. Sections 5 and 6 were updated to provide clearer language on health and safety protocols for sunscreen, insect repellent, and rain events. Added language to specify decontamination of reusable equipment prior to initial use in Section 7.1. Section 8 on Waste Management was updated to state that waste storage and disposal should be determined in the site specific workplan. Section 9 was updated to include Rite in the Rain® notebooks as approved for PFAS sampling. Changed the term "sample port" to "sample location" when describing where to place plastic sheeting. Section 10.1 was updated to indicate an equipment blank can be collected for unvetted hazard controls that contact a sample. References were updated to include the newer version of the DoD QSM, MDEQ Sampling Guidance, and	Kevin Engle, Erika Houtz

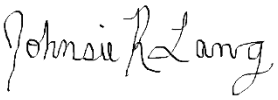
			California State Water Board PFAS Sampling Guidance.	
10	January 26, 2022	Various, Section 7	TGI formatted to comply with new QMS TGI template and Arcadis brand compliance. Indicated to avoid use of anti-fog spray on safety glasses due to possible presence of PFAS.	Rosario Varrella, Kevin Engle
11	January 13, 2023	Various	TGI updated to include specific information found in the June 2022 ITRC Guidance document. Updates reflecting current state of the practice analytical procedures. Table 1a and Table 1b updates	Kevin Engle, Joey Matzke, Lauren March
12	September 20, 2023	Various	Decontamination procedure in Section 8.1 has been updated to remove solvent rinse. Procedure is now: Scrub with alconox, rinse with DI/distilled water, rinse with “PFAS-free” water, repeat. Updated “Shipping” section 8.4, allowing for Saturday delivery with laboratory approval. Made various minor corrections and clarifications related to specific brand names	Alexander Hamilton, Johnsie Lang
13	April 24, 2025	Various	General template updates, insect repellant and watch band updates added by Dana Schmidt	Lydia Cox, Johnsie Lang

Approval Signatures

Prepared by: 4/24/2025

Lydia Cox, Staff Geologist — Date

Reviewed by: 4/24/2025



Johnsie Lang, PhD (Subject Matter Expert) — Date

1 Introduction

This document is intended to provide guidance to field staff sampling for Per- and Polyfluoroalkyl Substances (PFAS). The content in this document describes the intended use, scope and application, personnel qualifications, equipment, cautions, health and safety considerations, procedures, waste management, data recording and management, and quality assurance of PFAS sampling.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

The purpose of this Technical Guidance Instructions (TGI) is to provide guidance on field sampling to be used for **Per- and Polyfluoroalkyl Substances** (PFAS). This protocol was adapted from various sources including Arcadis Australia, Transport Canada, and the U.S Army Corp of Engineers (USACE) Omaha. In general, sampling techniques used for PFAS site characterization are consistent with conventional sampling techniques used in the environmental industry, but special consideration is made regarding PFAS-containing materials and cross-contamination potential. **Table 1a** provides a summary of materials that have been approved for site investigation; this list is expected to grow longer as industry experience increases. **Table 1b** provides a summary of field equipment and materials that have available testing information and/or industry knowledge regarding

PFAS cross-contamination potential, and it is recommended that these materials be prohibited for sample collection; for materials that are suspected of containing PFAS and/or to retain PFAS, these recommendations are considered preliminary and subject to change. Further discussion of approved and prohibited materials is found throughout this document. In general, prohibited materials include but are not limited to peolytetrafluoroethylene (PFTE), waterproof coatings containing PFAS, fluorinated ethylene-propylene (FEP), ethylene tetrafluoroethylene (ETFE), low density polyethylene (LDPE), polyvinylidene fluoride (PVDF) [ITRC 2022].

Table 1a: Summary of Acceptable Sampling Equipment and Materials for PFAS Site Investigations

Sampling Materials	Additional Considerations	References
Water Sampling Materials		
High density polyethylene (HDPE) or silicone tubing materials	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
HDPE HydraSleeves™	LDPE HydraSleeves™ are not recommended	USACE 2016; MassDEP 2017
Drilling and Soil Sampling Materials		
PFAS-free drilling fluids	--	DER 2016
PFAS-free makeup water	Confirm PFAS-free water source via laboratory analysis prior to investigation	--
Acetate liners	For use in soil sampling	USACE 2016
Sample Containers and Storage		
HDPE sample containers with HDPE lined lids for soil and water samples	Laboratory should provide; whole bottle analysis of aqueous samples combined with a solvent rinse of bottle is recommended	DER 2016, MassDEP 2017
Ice contained in plastic (polyethylene) bags (double bagged)	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation		
Ball point pens	--	MassDEP 2017
Standard paper and paper labels	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Fine/Ultra-Fine point Sharpies®	Larger point Sharpies® should be avoided.	MDEQ 2018
Decontamination		

Sampling Materials	Additional Considerations	References
Water-only decontamination	Confirm PFAS-free water source via laboratory analysis prior to investigation	DER 2016
Alconox® or Liquinox® followed by deionized water or PFAS-free water rinse	Liquinox® known to contain trace levels of 1,4-dioxane	NHDES 2016; USACE 2016; MassDEP 2017
Sun and Biological Protection		
OFF® Deep Woods Insect Repellent	Apply >10 m away from sampling area. Topical spray. Generally observed to be more effective against mosquitos than permethrin. Topical spray. Replace nitriles following application.	MDEQ 2018
Sawyer® Do-It-Yourself Permethrin Treatment for Clothing; Insect Shield® Permethrin Spray	Apply >10 m away from sampling area, ideally, prior to conducting field activities. Do not allow contact with skin. Manufacturer application instructions may vary, including how to apply, how often reapplication should occur, how long to allow the clothing/fabric to dry prior to wearing/using the item, etc. Replace nitriles if they contact treated clothing/items during fieldwork. Generally observed to be more effective against ticks than OFF® Deep Woods (DEET).	Bartlett 2018; MDEQ 2018
Insect Shield® Permethrin-Treated Clothing	Generally observed to be more effective against ticks than OFF® Deep Woods (DEET). Replace nitriles if they contact treated clothing/items during fieldwork.	Bartlett 2018
Banana Boat, Coppertone, Neutrogena, Meijer, and L'Oreal Sunscreens	Apply >10 m away from sampling area	MDEQ 2018

Note: This list is considered preliminary and additional materials may be added as additional information becomes available. Project teams are expected to follow a methodical evaluation process of materials to be used and confirm acceptance prior to implementation of field activities.

Table 1b: Summary of Sampling Equipment and Materials Not Recommended for PFAS Site Investigations.

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFAS	References
Water Sampling Materials				

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFAS	References
Teflon®, PTFE-containing or other fluoropolymer coated or containing field equipment (e.g., tubing, bailers, liners, tape, plumbing paste, pump parts)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Passive diffusion bags			x	MassDEP 2017
LDPE HydraSleeves ™			x	USACE 2016; MassDEP 2017
Water particle filters			x	MassDEP 2017
Drilling and Soil Sampling Materials				
Aluminium foil			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Drilling fluid containing PFAS	x	x		DER 2016
Coated bentonite		x		Radford et al 2023
Pipe thread compounds and tape			x	ITRC 2022
Sample Containers and Storage				
Glass sample containers with lined lids			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
LDPE containers and lined lids			x	USACE 2016
Teflon® or PTFE- lined lids on containers (e.g., sample containers, rinsate water storage containers)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Reusable chemical or gel ice packs (e.g., BlueIce®)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation				
Self-sticking notes and similar office products (e.g., 3M Post-it-notes)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Waterproof paper, notebooks, and labels	x			DER 2016, MassDEP 2017
Markers		x		NHDES 2016

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFAS	References
Decontamination				
[Some] detergents and decontamination solutions (e.g., Decon 90® Decontamination Solution)	x	x		DER 2016; NHDES 2016; MassDEP 2017

Note: For materials that are suspected of containing PFAS, or have the potential to retain PFAS, project specific considerations may provide adequate justification for use during the field event. For example, further evaluation may be conducted in the form of pre-field equipment blank sample analysis.

Given the extremely low detection limits associated with PFAS analysis and the many potential sources of trace levels of PFAS, field personnel are advised to err on the side of caution by strictly following these protocols, frequently replacing nitrile gloves, and rinsing field equipment to help mitigate the potential for false detections of PFAS. A summary of other specific items related to field sampling for PFAS are discussed in the sections below.

This TGI applies to all Arcadis and subcontractor personnel involved in field sampling for PFAS.

4 Personnel Qualifications

4.1 Sampling Personnel

Field personnel must have current health and safety training, including 40-hour HAZWOPER training, up to date 8-hour refresher, site supervisor training, and site-specific training, as needed. In addition, field personnel will be versed in the other relevant SOPs (e.g., low flow sampling) and will possess the skills and experience necessary to successfully complete the desired field work. The site Health and Safety Plan (HASP) and other documents will identify any other training requirements such as site-specific safety training or access control requirements.

4.2 Laboratories

These laboratories are example laboratories that could be used to analyze environmental media for PFAS, pending project approval:

- United States: Pace, SGS, Vista, ALS, and Eurofins
- Canada: AXYS-SGS and Bureau Veritas

Other laboratories may be used if they are appropriately accredited for PFAS analysis according to any project requirements. It is recommended that a laboratory is Environmental Laboratory Accreditation Program (ELAP)-accredited for PFAS analysis in accordance with the Department of Defense (DoD) Quality Systems Manual (QSM) 5.3 Table B-15 or any subsequent updates. **For all data collection efforts at DoD sites, PFAS data must be obtained using a method that is DoD ELAP-accredited under QSM 5.3 or later.**

5 Equipment List

The following equipment and materials must be available for sampling:

- Site plan of sampling locations, relevant work plan (or equivalent), and this TGI;
- Appropriate health and safety equipment, as specified in the site HASP;
- Dedicated plastic sheeting (preferably high-density polyethylene [HDPE]) or other clean surface to prevent sample contact with the ground;
- Conductivity/temperature/pH meter;
- Dissolved oxygen meter, oxidation reduction potential meter, and turbidity meter;
- Depth to water meter;
- If using low-flow groundwater sampling techniques, peristaltic pump (groundwater sampling)/bladder pump (with PFAS free bladder/ HDPE bladder), flow through cell, and accompanying HDPE and silicone tubing;
- Hydrasleeves™, if using Hydrasleeves™ for groundwater sampling;
- Metal trowel for soil samples; specialized soil/sediment sampling equipment as required;
- Brushes for scrubbing sampling equipment;
- Pens, pencils, and/or fine/ultra-fine point Sharpies® for writing;
- Clipboards, field binders, and field note pages that are not waterproof;
- Labeled sample bottles:
    - There are various laboratory and analytical methods in place at the time of this TGI revision (Revision 11). Only use certified PFAS free materials provided by the laboratory for sample collection.
- If high concentrations of PFAS related to class B firefighting foams are expected, bring additional small vials to conduct field-based shaker tests for foaming;
- Ziploc® bags to hold ice and samples;
- Bottles containing “PFAS-free” water used for reagent blanks;
- Labeled, thoroughly decontaminated coolers for samples with ice; Blue ice is not permitted;
- Deionized or distilled water for initial decontamination rinsing;
- “PFAS-free” water provided by the laboratory for final decontamination rinsing;
- Alconox or Liquinox®;
- Packing and shipping materials;
- Groundwater and/or Sampling Log; and
- Chain-of-Custody (COC) Forms.

6 Cautions

6.1 Food Packaging

Some food packaging may be treated with PFAS-containing chemicals to prevent permeation of oil and water in the food outside of the packaging. To avoid potential food packaging-related PFAS contact:

- Do not bring any food outside of the field vehicles onsite and eat snacks and meals offsite.
- Wash hands after eating.
- Remove any field garments or outer layers prior to eating. Do not put them back on until done eating and hands are washed.

6.2 Field Gear

6.2.1 Clothing

Many types of clothing are treated with PFAS for stain and water resistance, in particular outdoor performance wear. Certain clothing or accessories may be manufactured with PFAS for durability (e.g., certain “sport” smartwatch bands which are made of high-quality fluoroelastomers). To avoid potential clothing-related PFAS contact:

- Do not wear any outdoor performance wear that is water or stain resistant, or appears to be. Err on the side of caution.
- Wear pre-laundered (multiple washings, i.e., 6+) clothing that is not stain resistant or waterproof (unless made from the materials listed in Section 5.3.1).
- Natural fabrics such as cotton are preferred. Synthetic fabrics may also be acceptable if there is no indication on the label that the fabric is water and stain resistant.
- Remove smartwatches or watches that are made of high-quality elastomeric materials, or replace smartwatch bands with those made of metal or silicone.
- Change nitrile gloves frequently, as described in **Section 6.2.2**.
- Most importantly, avoid contacting your clothing with sampling equipment, bottles, and samples.
    - Consider specifying roles during field work; one field team member could document sampling (e.g., entering data into Fulcrum, taking photos, and timing groundwater sampling) while another contacts sampling materials more directly

6.2.2 Personal Protective Equipment

Safety Footwear

Some safety footwear has been treated to provide a degree of waterproofing and increased durability and may represent a source of trace PFAS. If at all possible, safety footwear without waterproofing should be worn;

footwear that provides adequate safety from physical hazards is required and takes precedence over potential PFAS concerns. To avoid any PFAS cross contamination to samples from footwear:

- Do not contact your footwear with equipment, bottles, or samples in any way.
- Do not allow gloves used for sampling to come in contact with safety footwear.

Nitrile Gloves

Wear disposable nitrile gloves at all times. Assume that everything you touch contains PFAS, and replace nitriles between subtasks. Don a new pair of nitrile gloves **before** the following activities at each sample location:

- Decontamination of re-usable sampling equipment;
- Contact with sample bottles or "PFAS-free" water bottles;
- Handling personal items (e.g., watches, phones, etc.);
- Recording notes or capturing photos;
- Insertion of anything into the sample ports (e.g., HDPE tubing); and
- Handling of any quality assurance/quality control (QA/QC) samples including field blanks and equipment blanks.

Don a new pair of nitrile gloves **after** the following activities:

- Handling of any non-dedicated sampling equipment;
- Contact with contaminated surfaces; or
- When judged necessary by field personnel.

6.3 Personal Hygiene

- Shower at night.
- Do not use personal care products after showering such as lotions, makeup, and perfumes, UNLESS medically necessary.
- Use sunscreen and insect repellent as necessary for health and safety, i.e., if sampling is to occur outdoors in direct sunlight and/or if insect hazards may be present. Specific products that are acceptable for PFAS sampling are listed in Table 1 and in Section 6.1. Apply sunscreen and insect repellant prior to initiating field sampling. If sunscreen and/or repellant need to be reapplied, ensure a safe distance away from the sampling locations and equipment (i.e., more than 10 meters (m) away). Wash hands after application and don new gloves following hand washing.

6.4 Visitors

Visitors to the site are asked to remain at least 10 meters from sampling areas.

7 Health and Safety Considerations

7.1 Biological and Environmental Hazard Controls

7.1.1 Sunscreens and Insect Repellents

When site conditions warrant, insect repellent and sunscreen should be applied. Some insect repellents and sunscreen have been approved for PFAS sampling by individual states. According to Michigan Department of Environmental Quality (MDEQ; now known as Michigan Department of Environment, Great Lakes, and Energy [EGLE]), the products below are allowable (MDEQ 2018). Note that California State Water Quality Control Board's PFAS sampling guidance refers to MDEQ/EGLE's allowable list of sunscreens and insect repellents (California State Water Quality Control Board 2020).

Insect Repellents

- Topical spray:
  - OFF® Deep Woods Insect Repellent (DEET)
- Treatment sprays for workwear:
  - Sawyer® Do-It-Yourself Permethrin Treatment for Clothing
  - Insect Shield® Permethrin Spray
- Treated workwear:
  - Insect Shield® brand

Sunscreen

- Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Meijer Sunscreen Lotion Broad Spectrum SPF 30
- Neutrogena Ultra-Sheer Dry-Touch Sunscreen Broad Spectrum SPF 30
- Banana Boat for Men Triple Defense Continuous Spray Sunscreen SPF 30
- Banana Boat Sport Performance Coolzone Broad Spectrum SPF 30
- Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Banana Boat Sport Performance Sunscreen Stick SPF 50
- Coppertone Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
- Coppertone Sport High-Performance AccuSpray Sunscreen SPF 30
- Coppertone Sunscreen Stick Kids SPF 55
- L'Oréal Silky Sheer Face Lotion 50+
- Meijer Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
- Meijer Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
- Neutrogena Beach Defense Water + Sun Barrier Lotion SPF 70
- Neutrogena Beach Defense Water + Sun Barrier Spray Broad Spectrum SPF 30
- Neutrogena Pure & Free Baby Sunscreen Broad Spectrum SPF 60+

Please plan for sampling events and purchase these products ahead of time. For any sunscreens and bug sprays, including those listed above, always follow these instructions for application:

- Topical insect repellent and sunscreen should be applied away from the work area prior to initiating sampling.
- Workwear treated with insect repellent sprays should be treated according to manufacturers instructions and prior to conducting fieldwork.
- When re-applying, stay at least 10 m away from the sampling locations and equipment.
- Wash hands after application/contact with treated materials and don new nitrile gloves.

7.1.2 Rain Event

Special care should be taken when rain is falling at the project site:

- Field sampling during extreme rainfall should be avoided if possible. If sampling needs to take place during a rain event (or other extreme weather condition), ensure the rain gear or other safety clothing is appropriate. For example, rain gear made from the following materials is allowable: polyurethane, PVC, wax coated fabrics, rubber/neoprene, uncoated Tyvek® (MDEQ 2018).
- If project timelines are tight, consider the use of a gazebo tent that can be erected over the top of the monitoring well to provide shelter from the rain. The canopy material is possibly a PFAS-treated surface and should be managed as such; therefore, wear gloves when moving the tent, change them immediately after moving the tent, and avoid further contact with the tent until all sampling activities have been finished and the team is ready to move on to the next site.

7.1.3 Other H&S Considerations

- ***If an unapproved or potentially suspect hazard control is needed for health and safety, apply or keep that control away from the samples, document its use in field notes, and, if it does contact a sample, take an equipment blank with that material.***
- The ability to safely access the surface water sampling locations must be verified before sampling.
- Field activities must be performed in accordance with the site HASP, a copy of which will be present onsite during such activities.
- Safety hazards associated with sampling surface water include fast-moving water, deep water, and steep slopes close to sampling sites. Use extreme caution when approaching sampling sites
- If thunder or lighting is present, discontinue sampling and take cover until 30 minutes have passed after the last occurrence of thunder or lighting.
- Use caution when removing well caps as well may be under pressure, cap can dislodge forcefully and cause injury.
- Avoid the use of anti-fog sprays on glasses, which may contain PFAS. It's recommended to instead purchase pre-treated anti-fog safety glasses.

8 Procedure

8.1 Field Equipment Cleaning

Reusable field sampling equipment will require cleaning before initial use and between uses. For groundwater sampling, between uses, decontaminate the flow-through cell and any non-dedicated equipment (i.e., interface probe of depth to water meter) that comes into contact with well water. Trowels and other materials used to sample soil samples will also require decontamination, although dedicated, single use equipment such as liners should be used where possible.

After donning a new pair of nitrile gloves:

- Rinse sampling equipment with Alconox or Liquinox® cleaning solution; Scrub equipment with a plastic brush if needed;
- Rinse with distilled water or deionized water;
- Rinse with “PFAS-free” water
- Repeat this entire process, scrubbing equipment a second time, rinsing with distilled or deionized water, then rinsing again with “PFAS-free” water (i.e., two scrubbings and four water rinsings total).
- Collect all rinsate in a sealed pail for disposal. Do not reuse decontamination solutions between sampling locations.

8.2 Borehole/Monitoring Well Development

If a drill rig is being used to drill for soil cores or to install monitoring wells, wear clean nitrile gloves before collecting each continuous soil sample. Additional requirements include the following:

- Verify in writing with the manufacturer that single-use liners used to collect each sample are made of a material that does not contain PFAS;
- Collect soil samples in laboratory-supplied HDPE bottles.
- Store the sample bottles in coolers and keep at a temperature of 0 to 6ºC until transported to the laboratory.

8.2.1 Well Condition Survey/ Water Level Monitoring

Using equipment that has been thoroughly decontaminated according to the procedures in Section 7.1, conduct the well condition surveys and water level monitoring:

- Conduct monitoring well inspections and record water levels.
- Use an interface probe to evaluate the presence/absence of non-aqueous phase liquid (NAPL).
- Measure the depth to water from the top of the polyvinyl chloride (PVC) riser and the total depth of the well.
- Record information in the field notes.

8.2.2 Monitoring Well Development and Purging

Follow these requirements for monitoring well development and purging:

- Do not use Teflon™ tubing for purging or sample collection. HDPE tubing is acceptable.
- Do not re-use materials between wells. Upon completion of use, remove all disposable materials (such as HDPE and/or silicone tubing) and place in heavy duty garbage bags for disposal.
- During development of the well, create sufficient energy to agitate the water column and create flow reversals in the well screen, filter pack and formation to loosen fine-grained materials and draw them into the well. The pumping or bailing action should then draw all drilling fluids and fine-grained material out of the borehole and adjacent formation and then out of the well. Review the Arcadis Monitoring Well Development guidance (Arcadis 2010) for more detailed information.
- Follow the low-flow purge and sampling techniques per the U.S. Protection Agency's (EPA's) guidance document titled *Low Stress (Low Flow) purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells* (2010) and ASTM's standard titled *Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations* (2002). Also available for review is the Arcadis Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells (Arcadis 2011).
- To purge the well, if using HDPE tubing and a peristaltic pump, insert the end of the tubing to the approximate depth of the midpoint of the screened section of the monitoring wells. Measure the length of HDPE tubing to be inserted into each monitoring well and pre-cut it to approximate lengths (such as the previously measured arm span of a field technician) to avoid contact with any materials other than the monitoring well and peristaltic pump. Flow rates should be as low as can be reasonably achieved. Collect and appropriately dispose of purge water.
- Silicone tubing should direct the purge water through a flow-through cell for field parameter measurements of pH, conductivity, temperature, dissolved oxygen, and turbidity. Calibrate the instrument in the field prior to use.
- Record field parameters in intervals (generally of 3-minute duration) to ensure purge water has cycled through the flow-through cell. Sample the wells after field parameter measurements indicate stabilization, which allows collection of representative formation water (generally acceptable standards are three consecutive pH readings to within ±0.1 units, and three consecutive conductivity, temperature and dissolved oxygen measurements to within 3%). Turbidity must be monitored but does not need to be used as a stabilization indicator of purge completion. Record field parameter measurements at each well. Drawdown should be monitored throughout the purge. Prior to collecting sample, disconnect tubing from flow-through cell and collect sample directly from tubing coming out of the monitoring well.
- If wells are suspected to be dewatering throughout the purge (i.e., reduced flow rate/difficulty pumping water or bubbles begin to come through the flow through cell), turn off the pump and allow the water level to recover for ½ hour, followed by sample collection. Document these activities in the field notes.

8.3 Sample Collection

Different laboratories may supply sample collection bottles of varying sizes depending on the type of media to be sampled. This section focuses on the collection of only soil, groundwater, surface water, and sediment. Different media may not follow these procedures. For example, AFFF concentrate should be sampled in accordance with DoD AFFF01 (DoD 2021).

8.3.1 Sample Containers

- Collect samples in HDPE bottles fitted with a HDPE lined (no Teflon™) screw cap.
- Complete bottle labels after the caps have been placed back on each bottle.
- Do not use glass bottles due to potential loss of analyte through adsorption. This is particularly important for aqueous samples.
- Review with analytical lab the sample size, sample container, etc. depending upon the type of PFAS analysis that is being requested.

8.3.2 Soil Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Trowels or drilling equipment that will come into contact with a sample should be decontaminated prior to sample collection, preferably with methanol/isopropanol/acetone;
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Collect soil samples using a clean stainless-steel trowel or with single-use PFAS-free liners;
- Place soil samples in HDPE bottles supplied by the laboratory.
- Note the time on the sample label.
- Collect any necessary duplicates/co-located samples and matrix spikes – verify with laboratory whether they need to be collected in separate sample bottles.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.

- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place soil sample bottles in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. Do not use blue ice.

8.3.3 Groundwater Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPEbottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.
- Measure depth to water and field parameters. Turbidity and the physical appearance of the purged water should be noted on the Groundwater Sampling Log.

During Sample Collection

- Start groundwater sample collection upon stabilization of field parameters.
- If low-flow groundwater sampling techniques are being used, disconnect the silicone tubing from the flow-through cell, enabling collection of groundwater samples without passing through the cell.
- Hydrasleeves are also considered acceptable for sampling of PFAS in groundwater – consult the project manager to determine which technique should be used. In general, low flow sampling is preferable.
- Collect groundwater samples (to the neck of the bottle, some headspace is acceptable) from the dedicated sampling ports at the center of the well screen. While collecting the sample, make sure the bottle cap remains in the other hand of the sampler, until replaced on the bottle.
- To mitigate cross contamination, collect groundwater samples in a pre-determined order from least impacted to greater impacted based on previous analytical data or knowledge about past activities at the site. If no analytical data are available, samples are to be collected in the following order:
    1. First sample the upgradient well(s).
    2. Next, sample the well located furthest downgradient of the interpreted or known source.
    3. The remaining wells should be progressively sampled in order from downgradient to upgradient, such that the wells closest to the interpreted or known source are sampled last.

- NOTE: If high concentrations of PFAS related to class B firefighting foams are expected in a groundwater sample, conduct a Shaker test by collecting and shaking a small portion of the sample (~10 to 25 mL) on site in a small disposable vial. If foaming is noted within the sample, document the foaming when samples are submitted for analysis; the 'shaker test' vial can then be disposed. This shaker test provides information about how each of the samples should be handled analytically.
- After collecting the sample, tightly screw on the polypropylene cap (snug, but not too tight). This will minimize leaking or cross contamination of the sample.
- Note the time on the sample label.
- Collect any necessary duplicates and matrix spikes. As the laboratory should be analyzing the entire aqueous sample rather than sub-sampling, separate bottles will be required for these samples.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.
- Do not rinse PFAS sample bottles during sampling. Do not filter samples.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes and COC. Note ‘shake test’ results if appropriate.
- Place groundwater samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

  Treat all disposable sampling materials as single use and dispose of them appropriately after sampling at each monitoring well.

8.3.4 Surface Water Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Avoid sampling the surface, in general.
- However, for Air Force investigations, collect samples from the water surface.
- Where surface water samples and sediment samples are collected at the same location, collect surface water samples first to minimize siltation.
- Collect surface water samples directly into laboratory-supplied bottles; wide-mouth bottles may be preferable to narrow mouth bottles for ease of surface water collection.
- Make sure bottle caps remain in the gloved hand of the sampler until sampling is complete and caps are replaced on the bottle.
- Note the time on the sample bottle.
- Collect any necessary duplicates and matrix spikes. As the laboratory should be analyzing the entire aqueous sample rather than sub-sampling, separate bottles will be required for these samples.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**
- Measure surface water pH, conductivity, temperature, and TDS at each location **after** both surface water and sediment sampling.

8.3.5 Sediment Sampling

Before Sample Collection

- Place LDPE plastic sheeting adjacent to the sample location for use as a clean work area, if conditions allow. Otherwise, prevent sampling equipment from contacting the ground or other surface that could compromise sample integrity.
- Don a new set of nitrile gloves. Do not use gloved hands to subsequently handle papers, pens, clothes, etc., before collecting samples.
- Use the HDPE bottles that are supplied by the laboratory. Make sure that the caps remain on the bottle until immediately prior to sample collection.

During Sample Collection

- Where surface water samples and sediment samples are collected at the same location, collect surface water samples first to minimize siltation.
- Collect sediment samples either manually using a stainless-steel trowel or using a petite ponar grab sampler, depending on field conditions at each sampling location during sampling program.
- Collect sediment samples from the upper 10 cm of sediment.
- For a sample to be acceptable overlying, low turbidity water must be present.
- Decant the overlying water and use a stainless-steel trowel to collect only the upper 5 centimeters (cm) of sediment.
- Collect sediment samples directly into laboratory-supplied bottles that are suitable in both material and size.
- Do not overfill the sample bottle.
- Make sure that the sample does not contain vegetation, that the sediment is undisturbed, and that the sampler shows no signs of winnowing or leaking.
- Make sure bottle caps remain in the gloved hand of the sampler until sampling is complete and caps are replaced on the bottle.
- Note the time on the sample label.
- Collect any necessary duplicates and matrix spikes.
- Collect any necessary equipment blanks. The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated.
- Collect any necessary field reagent blanks. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel.

After Sample Collection

- Place each sample bottle in two sealed Ziploc® bags. Another brand of LDPE bag is acceptable.
- Record the label information and time of sampling in the field notes.
- Place samples in coolers that are durable in transportation and keep the temperature between 0 and 6ºC until transported to the laboratory. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**
- Measure surface water pH, conductivity, temperature, and total dissolved solids (TDS) at each location **after** both surface water and sediment sampling is completed.

8.4 Shipping

- If samples cannot be shipped the same day as collected, arrange an appropriate means of keeping the samples cool overnight and maintain the temperature between 0 and 10°C for the first 48 hours after collection, and then between 0 and 6°C thereafter.

- Store samples in appropriate transport bottles (coolers) with ice (Ziploc© bags for use as ice containers) with appropriate labeling. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**
- Complete the appropriate procedures for COC, handling, packing, and shipping.
- Fill out and check COC Forms against the labels on the sample bottles progressively after each sample is collected.
- Place all disposable sampling materials (such as plastic sheeting, and health and safety equipment) in appropriate containers.
- Ship samples via courier service with priority overnight delivery. Tracking numbers for all shipments should be provided and recorded after they have been sent out to ensure their timely delivery.
- Confirm with the laboratory before shipping samples via Fed Ex for Saturday delivery.

9 Waste Management

All rinsate should be collected in a sealed pail for disposal. Drill cuttings and purge water will be managed as specified in the Field Sampling Plan (FSP) or Work Plan, and according to state and/or federal requirements. PPE and decontaminated fluids will be contained separately and staged at the sampling location. Containers must be labeled at the time of collection. Labels will include date, location(s), site name, city, state, and description of matrix contained (e.g., soil, groundwater, PPE). General guidelines for investigation derived waste (IDW) handling and storage are set forth in a separate IDW guidance document (Arcadis 2009).

Typical waste characterization procedures include collection of a composite sample of the drill cutting material and a composite sample of the purge water for laboratory analysis. Samples are typically analyzed for disposal toxicity characteristic leaching procedure (TCLP) analysis for metals and VOCs. For PFAS, a simple leach test with neutral pH water may be more indicative of actual risk. Additionally, generators of waste are required to include analysis of other constituents that are reasonably believed to be present including (in this case) PFAS.

Waste storage and final waste disposition should be determined in the site specific workplan.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

If digital data collection isn't possible, waterproof field books should be avoided for field notes. Instead, field notes on loose paper on Masonite, plastic, or aluminum clip boards is preferred. Please note that newer Rite in the Rain® notebooks are approved for PFAS sampling. Other requirements for field notes include:

- Pens, pencils, and fine/ultra-fine point Sharpies® may be used.
- Keep field notes and writing implements away from samples and sampling materials.
- One person should conduct sampling while another records field notes.
- Do not write on sampling bottles unless they are closed.

10.1 Other Project Documentation

- Complete groundwater and/or soil sampling logs.
- Make sure COC Forms are properly completed. Verify which PFAS analytes and methods (e.g., just PFOS/PFOA, some or all of the /1633 lists, etc.) are required for analysis and note on the COC.

11 Quality Assurance

Refer to quality control requirements for the project to ensure that appropriate quality assurance and quality control (QA/QC) samples are collected. When collecting QA/QC samples, the same guidelines apply as when collecting regular samples – specifically that:

- Samples should be collected in laboratory-supplied HDPE bottles;
- Bottle caps must remain in the hand of the sampler until replaced on the bottle;
- Labels must be completed after the caps have been placed back on each bottle; and
- Samples must be stored in appropriate transport bottles (coolers) with ice (Ziploc© bags for use as ice containers) with appropriate labeling. **Do not use blue ice. Store PFAS samples in a separate cooler from other types of samples.**

11.1 Equipment Blanks (if relevant)

QA/QC sampling typically includes daily collection of equipment blanks using the laboratory-supplied “PFAS-free” water. For peristaltic pump tubing, laboratory supplied “PFAS-free” water should be poured into a clean HDPE sample bottle and then pumped through new HDPE tubing using the peristaltic pump (with new silicone tubing). The best timing to collect equipment blanks is immediately after the collection of a sample likely to contain high concentrations of PFAS, after the sampling equipment has been appropriately decontaminated. Note that an equipment blank can also be collected if an unapproved or potentially suspect hazard control is needed for health and safety and it contacts a sample, i.e., that material would be exposed to PFAS free water then the water would be collected in a separate sample container.

11.2 Field Duplicates

QA/QC sampling typically includes the collection of one field duplicate for every 10 or 20 samples collected. Each duplicate sample will be collected immediately after the initial sample of which it is a duplicate into a separate laboratory-provided sample bottle. Do not indicate to the laboratory which sample the duplicate replicates, i.e., it should be given a blind reference on the COC and sample name such as “Duplicate-01”.

11.3 Field Reagent Blanks

QA/QC sampling for PFAS typically includes the submission of one laboratory supplied field reagent blank per day. The field reagent blank sample is brought to the site in a laboratory-supplied sample bottle. Field staff transfer the laboratory-supplied reagent blank to an empty sample bottle. This sample should be collected after field staff return from an offsite break (e.g., lunch) to capture any potential cross-contamination from field personnel and should be placed in the same cooler as the other PFAS samples.

11.4 Matrix Spikes (optional in some cases)

QA/QC sampling includes submitting samples to be used as a matrix spike and matrix spike duplicate (MS/MSD) if the project requires it. If separate sample bottles are required, additional samples will be collected immediately after the initial sample of which it is a duplicate into separate laboratory-supplied sample bottles.

11.5 Laboratory Analytical QA/QC

- Arcadis recommends that any request for PFAS analysis in groundwater or soil should be conducted by an ELAP-accredited method compliant with QSM 5.3 Table B-15. Requirements laid out in Table B-15 strictly govern acceptable laboratory data quality for PFAS analysis in environmental samples. **For all data collection efforts at DoD sites, PFAS data must be obtained using a method that is DoD ELAP-accredited under QSM 5.3 or later.**
- Laboratory QA/QC should consist of one laboratory blank and one laboratory control sample (or blank spike) per batch of samples, and additional QA/QCs as indicated by the laboratory QA/QC procedures.
- Isotope dilution must be used for quantification with isotope-labeled spiked standards (extracted internal standards EIS), as available, according to the guidelines of QSM 5.3 Table B-15. See EPA method 1633 and DoD QSM 5.4 Table B-24 for quantification requirements by isotope dilution with EIS standards. The USEPA has two drinking water methods (USEPA Method 537.1 and USEPA Method 533).
- For drinking water, groundwater, and surface water samples, laboratories must extract the entire sample and include a solvent rinse of the bottle for analysis. Aqueous samples should generally not be sub-sampled prior to analysis, unless they are high concentration and require serial dilution (US DoD 2017).
- Soil samples should be analyzed in their entirety or thoroughly homogenized before extraction and analysis.
- As part of the internal QA/QC of laboratory results, relative percent difference (RPD) should be calculated between samples and corresponding field or laboratory duplicates. The laboratory quality assurance portion of the laboratory certificates should be reviewed to verify that all calculations/recoveries were within acceptable limits as established by the laboratory method and guidelines in Table B-15 of QSM 5.3 or later (USDoD 2019).

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Attachment 3

Laboratory Standard Operating Procedure for ASTM D7979

SOP DEPARTURE REQUEST

Requested by: Emily Smith Date Requested: 1/10/2025

SOP Number: HN-LCMS-002-R04
SOP Title: PFAS by HPLC/MS/MS
SOP Section Title: Standards - Intermediate Qualitative Identification Standard (QIS)
SOP Section Number: 8.2.5

Detailed Description of Requested SOP Modification (add additional pages as needed)

Qualitative branched/linear isomer mix of PFOA added to QIS (Qualitative Identification Standard) along with the existing isomers for PFNA and PFNS present in the standard.

Current Table 8.2.5 –

Table 8.2.5 – Intermediate Qualitative Identification Standard @ 50 ug/L (50 ppb)			
Wellington Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Added (uL)**	**Final Concentration (ppb)**
ip-PFNA (branched)	50	1	50
PFNA (linear)	50	1	50
ip-PFNS (branched)	50	1	50
L-PFNS (linear)	50	1	50
Diluted in 996 uL Methanol (Total Volume of 1 mL)			

Instructions for preparation of intermediate QIS:

- Add 996 uL of methanol to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 1 uL of each standard listed in Table 8.2.5 using an appropriate gastight micro-syringe.
- Seal with PP/silicone cap and vortex vial.

New Table 8.2.5 –

Table 8.2.5 – Intermediate Qualitative Identification Standard @ 50 ug/L (50 ppb)			
Wellington Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Added (uL)**	**Final Concentration (ppb)**
ip-PFNA (branched)	50	1	50
PFNA (linear)	50	1	50
ip-PFNS (branched)	50	1	50
L-PFNS (linear)	50	1	50
T-PFOA (branched and linear)	50	1	50
Diluted in 995 uL Methanol (Total Volume of 1 mL)			

Instructions for preparation of intermediate QIS:

- Add 995 uL of methanol to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 1 uL of each standard listed in Table 8.2.5 using an appropriate gastight micro-syringe.
- Seal with PP/silicone cap and vortex vial.

Approved by:

Dept Supervisor: ES QA Manager: _____ Lab Director: _____

QA Control Number: HN-QMS-002-R04.1

Per- and Polyfluoroalkyl Substances (PFAS) by High performance Liquid Chromatography/Tandem Mass Spectrometry (HPLC/MS/MS)

DOCUMENT ID: HN-LCMS-002, REV 4.0

METHODS: ASTM D7979-2017, ASTM D7968-2017A, EPA 8327

Prepared By: Emily Smith Date: 11/19/24
Professional Scientist, Emily Smith

Approved By: Date: 11/21/24
Technical Director, Angela Karst

Approved By: Date: 11/21/2024
Quality Manager, Michael Oshinski

Biennial Review:

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

Reviewed By: _____ Date: _____

1) Scope & Applicability

1.1 This Standard Operating Procedure (SOP) describes the method used for trace analysis of Per- and Polyfluoroalkyl Substances (PFAS) by high performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS). A list of analyte acronyms is given in Table 1. This method describes both the extraction and chromatographic procedures used to determine the target analytes.

1.2 This procedure is used to determine the analytes of interest in water, solid, and tissue matrices. The procedure may be applied to other miscellaneous sample matrices providing that the analyst demonstrates the ability of the procedure to give data of acceptable quality in that matrix.

1.3 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPPs supersede method specific requirements.

1.4 This SOP is based upon ASTM D7979-17, ASTM D7968-17a, and EPA 8327. The analytical test codes based on this SOP include LCMS_D7968_S, LCMS_D7979_W, LCMS_8327_W, and LCMS_8327_S. The test code EPA 8327_S is a modification of D7968 for solids/soils as EPA 8327 method is only applicable to aqueous matrices. The preparation test codes include LCMSPR_D7968_S, LCMSPR_D7979_W, and LCMSPR_3512_W. Each ASTM method has its own corresponding prep test code. EPA 8327 test codes LCMS_8327_S and LCMS_8327_W each correspond to LCMSPR_D7968_S and LCMSPR_3512_W, respectively.

2) Summary of Procedure

2.1 This group of compounds will provide a broad view of common per- and polyfluorinated compounds (PFAS) found in the environment. This procedure provides low ng/L (ppt) determination for these analytes in water, and low ng/kg (ppt) in solid samples.

2.2 Branched and linear PFAS can potentially be found in the environment. This results in more than one chromatographic peak being observed in samples. When quantitative or qualitative standards for linear and branched isomers are utilized, all peaks in the standard and corresponding peaks in any sample must be integrated and the areas summed. Currently, PFOA, PFOSA, PFOS, PFHxS, NEtFOSAA and MEtFOSAA branched and linear isomers are present in the calibration standard. A qualitative standard of linear and branched isomers of PFNA and PFNS is also utilized.

3) Definitions

3.1 Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc...) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Atmospheric Pressure Chemical Ionization (APCI) – A vapor phase ionization mode for HPLC/MS/MS in which the mobile phase is desolvated by high temperatures prior

to ions being formed. A corona discharge needle produces reagent ion plasma primarily made up of charged mobile phase vapor. The sample vapor is ionized by ion-molecular reactions with the reagent ions in the plasma. This ionization may be used in either the positive (producing $[M+H]^+$ ions) or negative (producing [M-H]-) mode.

3.3 Electrospray Ionization (ESI) – A liquid phase ionization mode for HPLC/MS/MS in which the ions are formed in solution before the mobile phase is desolvated. A proton donor such as acetic or formic acid, or a proton acceptor such as ammonium hydroxide are commonly added to the mobile phase. A potential is applied to the electrospray needle to assist in ionization of the solution prior to desolvation. This ionization may be used in either the positive (producing $[M+H]^+$ ions) or negative (producing [M-H]-) mode.

3.4 Independent Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration. The ICV standards are prepared from materials obtained from a source different from that used to prepare calibration standards or are prepared by a second analyst.

3.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample extraction and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Duplicate aliquots of the same field sample are spiked and analyzed as Matrix Spike and Matrix Spike Duplicate. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the samples is calculated from the raw values and used to assess analytical precision. The concentration of the spike should be at 5 to 10 times the MRL or at levels specified by a project analysis plan. If sufficient sample volume is present, the matrix spike duplicate (MSD) is prepared alongside the matrix spike (MS) instead of a sample duplicate (DUP).

3.6 Duplicate (DUP) – An additional aliquot of a field sample that is prepared and analyzed in addition to the field sample. The relative percent difference (RPD) between the field sample and its duplicate is calculated from the raw values and used to assess analytical precision. A duplicate (DUP) is used in the absence of a matrix spike duplicate (MSD) due to insufficient sample volume.

3.7 Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte. Other calibration models may be used as described in the calibration section of this SOP. The appropriate criteria for assessing the validity of the calibration curve must be followed prior to quantitation of target analytes in actual sample analyses.

3.8 Multiple Reaction Monitoring (MRM) – An HPLC/MS/MS technique where most background noise/interfering compounds are filtered out by the tandem mass spectrometer. MRM mode allows multiple parent ions (generally the $[M+H]^+$ ions in positive mode and the $[M-H]^-$ ions in negative mode) through the first quadrupole. In the collision cell, the parent ions are fragmented. In the third quadrupole (Q3) all ions except the quantitation fragments (product ions) are filtered out. The only ions that are allowed through the instrument are ions that have the same parent mass producing the same product mass during a particular segment of analysis time. MRM mode analyzes multiple mass transitions during sequential time segments. Each

analysis segment is specified for a particular retention time range that corresponds to the retention time of a certified standard.

3.9 Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are added to all blanks, standards, samples and spiked samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.10 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water and/or sand and is designed to monitor the introduction of artifacts into the preparation and analytical process. The method blank is carried through the entire preparation and analytical procedure.

3.11 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS and LCSD) – An LCS is an aliquot of analyte free water to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control. A duplicate LCS (LCSD) can be prepared with an extraction batch in place of matrix spikes (MS/MSD/DUP) to monitor precision and repeatability. The LCSD is prepared, spiked, extracted, and analyzed in exactly the same manner as the LCS.

3.12 Prep Batch Reporting Limit Verification Sample (PB-RLVS) – Each preparation batch requires a reporting limit verification sample. This sample is prepared in the same manner as an LCS but is spiked at or near the reporting limit. The RLVS is used to check whether analytes found at reporting limits would be detected at the time of preparation. Since spike mixes are used to generate the RLVS's, multiple RLVS's may be prepared to address the varying reporting limits of the analytes.

3.13 Analytical Batch Reporting Limit Verification Sample (AB-RLVS) –The AB-RLVS is prepared in the same manner as a calibration point. The AB-RLVS is used to check whether analytes found at reporting limits would be detected at time of analysis in the case that the midpoint verification standard fails. Since spike mixes are used to generate the RLVS's, multiple RLVS's may be prepared to address the varying reporting limits of the analytes.

3.14 Continuing Calibration Verification Standard (CCV) - A standard spiked at the midpoint of the curve or lower, injected into the instrument at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.15 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a clean volume of the diluent spiked with surrogates that is used to prepare the calibration that runs before and after a calibration and prior to an analytical batch. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly regarding instrument cleanliness and the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.16 PFAS – Per- and Polyfluoroalkyl substances – A group of man-made fluorinated compounds that are hydrophobic and lipophobic, manufactured and used in a variety of industries globally. These compounds are persistent in the environment as well as in the human body.

3.17 LC – Liquid chromatograph or liquid chromatography

3.18 MS – Mass spectrometer or mass spectrometry

3.19 Precursor Ion – For the purpose of this method, the precursor ion is the deprotonated molecule ([M-H]-) of the method analyte. In MS/MS, the precursor ion is mass selected and fragmented by collision activated dissociation to produce distinctive product ions of smaller m/z.

3.20 Qualitative Identification Standards (QIS) – A standard that contains mixtures of the branched and linear isomers of the target analytes. This allows for the proper integration of suspected branched isomer peaks in field samples. The QIS mix is analyzed once daily, at the beginning of the analytical sequence, and confirms the linear and known branched isomer or isomer group retention times. Also known as branched isomer mix.

3.21 Reverse Osmosis (RO) water – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

3.22 Relative standard deviation (RSD) – The standard deviation multiplied by 100 and divided by the mean. Also termed "coefficient of variation."

3.23 RT – Retention time; the time it takes for an analyte or labeled compound to elute off the HPLC/UPLC column.

3.24 Practical Quantitation Limit (PQL) – The PQL is defined as the lowest concentration that can be reliably quantitated during routine laboratory operating conditions. The PQL is also known as the limit of quantitation (LOQ) or method reporting limit (MRL). The PQL is generally ten thirds (3.33) times the calculated MDL for the target analyte.

3.25 Minimum Reporting Limit/Level (MRL) – 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.

3.26 Minimum Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than the method blank. This is a statistical determination of precision, and accurate quantitation is not expected at this level. It is also known as method detection limit.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

4.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the *ALS-Holland Training*

Procedure (HN-QS-013), is also the responsibility of the department supervisor/manager.

5) Interferences

5.1 The reporting limits for these analytes are in the low ng/L level. PFAS are organic compounds used in the manufacture of PTFE as well as a wide variety of common products in household use; therefore, contamination is a concern when conducting this method. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences. Aluminum foil is known to be a source of PFOA contamination and should not be used in any part of the process.

5.2 The compounds listed in Table 1 have been chromatographically resolved adequately for quantitation purposes.

5.3 Raw LC/MS/MS data from all blanks, samples, and spikes must be evaluated for interferences. The source of interference should be identified and corrective action should be taken to eliminate it.

5.4 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample injection syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination. In addition, an instrument blank is analyzed after the calibration point with the highest concentration to ensure that there is no carryover at that level. The concentration of analytes in the instrument blank should be less than the analyte reporting limit.

6) Safety

6.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as, safety glasses, lab coat and the correct gloves.

6.2 Chemicals, reagents, and standards must be handled as described in the ALS safety policies, approved methods and in SDSs where available. Refer to the ALS Chemical Hygiene Plan and the appropriate SDSs prior to beginning this method.

6.3 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Sample Collection - Containers for sample collection must be entirely free of any PTFE or PFAS. 5 mL of water sample should be collected into a pre-tared 15 mL polypropylene centrifuge tube. Soils should be collected in HDPE or polypropylene bottles (125 mL or 250 mL).

7.2 Sample Preservation and Storage - Samples must be iced or refrigerated at 0-6 ºC from time of collection until extraction.

7.3 Methods ASTM D7979 and D7968-17a require that samples must be prepared and analyzed within 28 days of collection. Method 8327 requires that water samples must be prepared within 14 days of collection and must be analyzed within 30 days of preparation. As of the date of publication method 8327 has no guidelines for preparation or analysis solids; a holding time of 28 days from collection for preparation and analysis of solids has been assigned.

8) Standards, Reagents, and Consumable Materials

8.1 Reagents

8.1.1 Reagent grade chemicals or better shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. All solvents must be verified by lot number and stored in accordance with manufacturer specifications or safety guidelines.

8.1.2 Reverse Osmosis (RO) Water – Resistivity ≥10mΩ (obtained from in-house RO system, or equivalent)

8.1.3 Methanol, CH_3OH – LCMS grade (Honeywell Cat. No. LC230-4 or equivalent).

8.1.4 Acetic Acid (Glacial), ACS reagent grade, >99.7% (Sigma-Aldrich Cat. No. 695092 – 100mL or equivalent).

8.1.5 Ammonium Acetate – Mass spectrometry grade >99% (Thermo Scientific Catalog # 60-020-13, or equivalent).

8.1.6 Ammonium Hydroxide LC/MS grade, ≥ 25% (Sigma Aldrich Catalog # 221228-100ML-A, or equivalent).

8.1.7 Acetonitrile, CH_3CN – LCMS grade (Birch Cat. No. 1930-5 or equivalent).

8.1.8 Mobile Phases A and B

8.1.8.1 Mobile Phase A – 5.0 mM Ammonium Acetate in Water

Using a 1 or 2 L graduated cylinder, add the appropriate volume of RO water (Section 8.1.2) shown in Table 8.1.8.1 to the appropriately sized glass reagent bottle. The appropriate amount

of Ammonium Acetate (Section 8.1.5) shown in Table 8.4.8 is weighed on a top loading balance and added to the bottle. The ammonium acetate is dissolved by shaking the bottle thoroughly. The mobile phase must be replaced after 14 days or when degradation is noticed, whichever comes first; the expiration date may not exceed the manufacturer's expiration date.

Table 8.1.8.1 – Mobile Phase A – 5 mM Ammonium Acetate in Water

Mass of Ammonium Acetate (Section 8.1.5)	Volume of RO Water (Section 8.1.2)	Concentration of Ammonium Acetate (Section 8.1.5)	Final Volume
0.77 g	2 L	5.0 mM	2 L
1.925 g	5 L	5.0 mM	5 L

8.1.8.2 Mobile Phase B – 5.0 mM ammonium acetate in Methanol

Using a 1 or 2 L graduated cylinder, add the appropriate volume of methanol (Section 8.1.3) shown in Table 8.1.8.2 to the appropriately sized glass reagent bottle. The appropriate amount of Ammonium Acetate (Section 8.1.5) shown in Table 8.1.8.2 is weighed on a top loading balance and added to the bottle. The ammonium acetate is dissolved by shaking the bottle thoroughly. The mobile phase must be replaced monthly or when degradation is noticed, whichever comes first; the expiration date may not exceed the manufacturer's expiration date.

Table 8.1.8.2 – Mobile Phase B – 5 mM Ammonium Acetate in Methanol

Mass of Ammonium Acetate (Section 8.1.5)	Volume of Methanol (Section 8.1.3)	Concentration of Ammonium Acetate (Section 8.1.5)	Final Volume
0.77 g	2 L	5.0 mM	2 L
1.925 g	5 L	5.0 mM	5 L

Note: Ammonium Acetate is hygroscopic. The solid should be stored in a desiccator, the bottle should be open for a minimum amount of time, and the solid should be weighed quickly so moisture is not absorbed by the ammonium acetate.

8.1.9 50:50 Methanol:Water 0.1% Acetic Acid Diluent - 15 mL of methanol (Section 8.1.3) and 15 mL of RO water (Section 8.1.2) measured with a graduated cylinder are added to a beaker. 30 uL of glacial acetic acid (Section 8.1.4) is added to the mixture from an appropriate variable volume pipette and the mixture is vortexed. The mixture is made fresh with each batch and calibration.

8.1.10 Isopropyl Alcohol, IPA – LCMS grade. (Fisher CAT#A461-1 or equivalent)

8.1.11 Matrix Sand – silica sand (Fisher Scientific, Catalog # S2350 or equivalent). Sand must be demonstrated to be free of PFAS above the Method Detection Limit (MDL).

8.1.12 96:4 Methanol:Water Solution – 40 mL of water and 960 mL of methanol are measured using 1 L graduated cylinders and combined in a 1 L glass reagent bottle. The solution is homogenized by shaking the bottle thoroughly and is replaced every three months or if degradation is noticed, whichever comes first. Expiration date cannot exceed that of the stock standards/solvents.

8.1.13 Acetonitrile (ACN), CH3CN – HPLC grade (Fisher Part# A9984 or equivalent).

8.2 Standards

The following standards are used to prepare calibrations and spike samples:

8.2.1 Stock Standard Target Mix @ 1 mg/L (2 ppm)

A stock standard solution containing a mixture of the native PFAS analytes included in Table 1 is purchased from Absolute Standards (CAT# 64533) at a concentration of 2 mg/L (2 ppm) in methanol, or equivalent. See Appendix Table 2 for analyte concentrations adjusted for salt compounds. Primary and secondary source suppliers can be interchanged as more inclusive (additional linear/branched isomer analytes) standard mixes become commercially available.

8.2.2 Intermediate Target Spike Standard @ 100 ug/L (100 ppb)

The intermediate target spike @ 100 ug/L (100 ppb) is made from Absolute Standard CAT# 64533 standard (Section 8.2.1, 2.0 mg/L). The spike amounts and concentrations are listed in Table 8.2.2.

Table 8.2.2 – Intermediate Target Spike Standard @ 100 ug/L (100 ppb)				
Supplier Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Standard Added (uL)**	**Volume Solvent Added (uL)**	**Final Concentration (ppb)**
64533	2	50	950	100
Final Volume: 1 mL (in 96:4 methanol:water)				

Instructions for preparation of intermediate standard:

- Add 950 uL of 96:4 methanol:water solution (Section 8.1.12) to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 50 uL of Absolute Standard 64533 using an appropriate single channel variable volume pipette.
- Seal with PP/silicone cap and vortex vial.

NOTE: Some target analytes are not available as acids but rather as their corresponding salts, such as K+ or Na+. The concentrations must be corrected for the salt content accordingly. This can be done in the solution makeup or in the instrument calibration software.

The intermediate target spike standard is stored in a 2mL polypropylene vial between 0-6° C and may be used for up to one year from the date of preparation, or until degradation is observed. The intermediate standard expiration date may not exceed the manufacturer's expiration date.

8.2.3 Intermediate Surrogate Spike Standard @ 100 ug/L (100 ppb)

An intermediate surrogate spike standard solution is made up from diluting a purchased mix (Wellington Laboratories CAT# MPFAC-MXA, 2.0 ppm) and neat standards at 50 ppm (currently from Wellington Laboratories), or equivalent supplier/standards. See Appendix Table 3 for analytes and concentrations. The standard is stored in polypropylene vials between 0-6° C and may be used for up to one year from the date of preparation, or until degradation is observed. The intermediate standard expiration date may not exceed the manufacturer's expiration date.

NOTE: Some surrogate analytes are not available as acids but rather as their corresponding salts, such as K+ or Na+. The concentrations must be corrected for the salt content accordingly. This can be done in the solution makeup or in the instrument calibration software.

Table 8.2.3 – Intermediate Surrogate Spike Standard @ 100 ug/L (100 ppb)

Wellington Catalog Number	Stock Standard Concentration (ppm)	Volume Added (uL)	Final Concentration (ppb)
MPFAC-MXA	2.0	500	**100**
d3-N-MeFOSAA	50.0	20	**100**
d5-N-EtFOSAA	50.0	20	**100**
M3PFBS	46.5	20	**93.0**
M2PFTeDA	50.0	20	**100**
M4PFHpA	50.0	20	**100**
M5PFPeA	50.0	20	**100**
M8FOSA-I	50.0	20	**100**
M2-4:2FTS	46.7	20	**93.5**
M2-6:2FTS	47.5	20	**95**
M2-8:2FTS	47.9	20	**96**
M3HFPO-DA	50.0	20	**100**
Final Volume: 10 mL (in 96:4 methanol:water)			

Instructions for preparation of intermediate standard:

- Add approximately 5 mL of 96:4 methanol:water solution (Section 8.1.12) to a Class A 10.00 mL volumetric flask.
- Add the volume of each standard in Table 8.2.3 using an appropriate single channel variable volume pipette.
- Bring to a final volume with methanol and mix, inverting the flask a minimum of 5 times.
- Transfer to appropriately labelled 2 mL polypropylene vials. Seal with PP/silicone caps and vortex.

8.2.4 Working Surrogate Spike Standard @ 20 ug/L (20 ppb)

A working surrogate spike standard is used in sample extraction and is made from diluting the intermediate surrogate spike standard at 100 ppb (Section 8.2.3). The standard is stored in polypropylene vials between 0-6° C and may be used for up to one year from the date of preparation, or until degradation is observed. The intermediate standard expiration date may not exceed the manufacturer's expiration date.

Table 8.2.4 – Working Surrogate Spike Standard @ 20 ug/L (20 ppb)				
Stock Standard	**Stock Standard Concentration (ppb)**	**Volume Standard Added (uL)**	**Volume Solvent Added (uL)**	**Final Concentration (ppb)**
Intermediate Surrogate Spike Standard @ 100 ug/L (100 ppb) (Section 8.2.3)	100	200	800	20
Final Volume: 1 mL (in 96:4 methanol:water)				

Instructions for preparation of working standard:

- Add 950 uL of 96:4 methanol:water solution (Section 8.1.12) to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 50 uL of Intermediate Surrogate Spike Standard @ 100 ug/L (100 ppb) (Section 8.2.3) using an appropriate single channel variable volume pipette.
- Seal with PP/silicone cap and vortex vial.

8.2.5 Intermediate Qualitative Identification Standard (QIS)

The analytes listed in 8.2.5 are available as a mixture of branched and linear isomers. This mixture is used to qualitatively identify the retention times branched isomers for applicable analytes. One intermediate qualitative identification standard (QIS) is prepared for all lab methods and may contain additional analytes not included in this method. Positive detections at the retention time of the branched isomer should be integrated in addition to the linear isomer (if present) in all field samples, blanks, and MS/MSD's. Ion ratio criteria may not always be met due to the difference in ion transition ratios between linear and branched isomers. In this case the data should be qualified.

Table 8.2.5 – Intermediate Qualitative Identification Standard @ 50 ug/L (50 ppb)			
Wellington Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Added (uL)**	**Final Concentration (ppb)**
ip-PFNA (branched)	50	1	50
PFNA (linear)	50	1	50
ip-PFNS (branched)	50	1	50
L-PFNS (linear)	50	1	50

Table 8.2.5 – Intermediate Qualitative Identification Standard @ 50 ug/L (50 ppb)			
Wellington Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Added (uL)**	**Final Concentration (ppb)**
Diluted in 996 uL Methanol (Total Volume of 1 mL)			

Instructions for preparation of intermediate QIS:

- Add 996 uL of methanol to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 1 uL of each standard listed in Table 8.2.5 using an appropriate gastight micro-syringe.
- Seal with PP/silicone cap and vortex vial.

The above standard is stored in a 2mL polypropylene vial and between 0-6˚ C. The standard may be used for up to 1 year from preparation or whenever degradation is noticed, whichever comes first. The date of expiration may not exceed the manufacturer's expiration.

8.2.6 Initial Calibration Verification (ICV) Standard @ 1 mg/L (1 ppm)

A stock standard solution containing a mixture of the native PFAS analytes included in Appendix Table 1 is purchased from a vendor independent from the primary source to verify the calibration curve. If a source from a secondary vendor is not available, a standard from the primary vendor of a separate lot number may be used. If this is not available, a second analyst/prep technician must prepare an initial calibration verification from the stock standard and surrogate mixes. Primary and secondary source suppliers can be interchanged as more inclusive (additional linear/branched isomer analytes) standard mixes become commercially available.

The ICV is currently made up of a target mix from Wellington Laboratories (CAT# PFAC30PAR) that is purchased at a concentration of 1 mg/L (1 ppm) in methanol. See Appendix Table 2 for analytes and concentrations.

8.2.7 Initial Calibration Verification (ICV) Intermediate Standard @ 100 ug/L (100 ppb)

Wellington CAT# PFAC30PAR (Section 8.2.6, 1.0 mg/L) is diluted in 96:4 methanol:water (Section 8.1.12) to make the ICV intermediate standard @ 100 ug/L (100 ppb). The intermediate target spike standard is stored in a 2mL polypropylene vial between 0-6° C and may be used for up to one year from the date of preparation, or until degradation is observed. The intermediate standard expiration date may not exceed the manufacturer's expiration date.

Table 8.2.7 – Intermediate ICV Standard @ 100 ug/L (100 ppb)			
Supplier Catalog Number	**Stock Standard Concentration (ppm)**	**Volume Added (uL)**	**Final Concentration (ppb)**
PFAC30PAR	1	100	100
96:4 Methanol:Water (Section 8.1.12)	-	900	-
Final Volume: 1 mL			

Instructions for preparation of intermediate standard:

- Add 900 uL of 96:4 methanol:water solution (Section 8.1.12) to a polypropylene 2 mL autosampler vial using an appropriate single channel variable volume pipette.
- Add 100 uL of PFAC30PAR @ 1 ppm (Section 8.2.6) using an appropriate single channel variable volume pipette.
- Seal with PP/silicone cap and vortex vial.

NOTE: Some target analytes are not available as acids but rather as their corresponding salts, such as K+ or Na+. The concentrations must be corrected for the salt content accordingly. This can be done in the solution makeup or in the instrument calibration software.

8.2.8 Working ICV Standard @ 500 ng/L (500 ppt)

The working ICV standard is prepared by adding 990 uL of 50:50 methanol: water 0.1% acetic acid diluent (Section 8.1.9) to a 2 mL polypropylene vial using an appropriate single channel variable volume pipette. 5 uL of intermediate surrogate spike solution @ 100 ppb (Section 8.2.3) and 5 uL of the intermediate ICV standard @ 100 ppb (Section 8.2.7) are added from a 10 uL gastight micro-syringe to the vial. This vial is then mixed by vortex. This results in a 500 ng/L (500 ppt) mix.

The standard is stored in a 2mL polypropylene vial between 0-6° C and may be used for up to one year from the date of preparation. The standard expiration date may not exceed the manufacturer's expiration date.

Table 8.2.8 – Working ICV Standard @ 500 ppt

Intermediate Standard/Solvent	Intermediate Standard Concentration (ppb)	Volume Added (uL)	Final Concentration (ppt)
Intermediate ICV Standard (Section 8.2.7)	100	5	500
Intermediate Surrogate Spike Standard (Section 8.2.3)	100	5	500
50:50 methanol:water 0.1% acetic acid (Section 8.1.9)	--	990	--
Final Volume: 1 mL			

8.2.9 Calibration Standards

Calibration standards containing the target analytes and surrogates listed in Table 1 are prepared at 9 concentration levels in a 50:50 methanol:water 0.1% acetic acid diluent (Section 8.1.9) from the intermediate target [100 ppb] and surrogate [100 ppb] standards (Sections 8.2.2 and 8.2.3) .

8.2.9.1 Working Stock Calibration Standard @ 1000 ppt

Table 8.2.9.1 – Working Stock Calibration Standard @ 1000 ppt

Intermediate Standard	Intermediate Standard Concentration (ppb)	Volume Added (uL)	Final Concentration (ppt)
Intermediate Target Spike Standard (Section 8.2.3)	100	50	**1000**
Intermediate Surrogate Spike Standard (Section 8.2.2)	100	50	**1000**
Final Volume in 50:50 methanol:water 0.1% acetic acid (Section 8.1.9): 5 mL			

Instructions for preparation of Working Stock Calibration Standard:

- Add approximately 2 mL of 50:50 methanol: water 0.1% acetic acid diluent (Section 8.1.9) to a Class A 5.00 mL volumetric flask.
- Add the volume of each intermediate in Table 8.2.9.1 using an appropriate single channel variable volume pipette.
- Bring to a final volume with diluent and mix, inverting the flask a minimum of 5 times.
- Transfer to appropriately labelled 2 mL polypropylene vials. Seal with PP/silicone caps and vortex. This results in a 1000 ng/L (1000 ppt) mix.

The standard is stored in a 2mL polypropylene vial between 0-6° C and may be used for up to one year from the date of preparation, or until degradation is observed. The standard expiration date may not exceed the manufacturer's expiration date.

8.2.9.2 Initial Calibration Standards

The initial calibration standards are comprised of the working stock calibration standard (8.2.9.1) and 50:50 methanol:water 0.1% acetic acid diluent (Section 8.1.9). Target analyte and surrogate calibration concentrations are listed in Table 8.2.9.2. The levels of both labeled and target standards are slightly different for the corresponding salts and are accounted for in the software. Calibration standards include a mixture of linear and branched isomers for target analytes when such mixtures are commercially available at a suitably high grade for quantitative use. Currently, PFOA, PFOSA, PFHxS, PFOS, MeFOSAA, and EtFOSAA are included in the calibration standards as mixes of linear and branched isomers. More will be added as they become commercially available. The solvent blank contains 50:50 methanol:water 0.1% acetic acid diluent and is used in conditioning the system. Level 0 (Instrument Blank/Continuing Calibration Blank) contains spiked surrogates in diluent and is used to evaluate the background and potential carryover in the system. The calibration standards are stored in 2mL polypropylene vials and are stored between 0-6˚ C. They may be used for six months or whenever degradation is noticed, whichever comes first. The date of expiration may not exceed the manufacturer's expiration date.

Table 8.2.9.2 – Initial Calibration Standards

Calibration Level	Volume of Working Stock Standard (Section 8.2.9.1) Added (uL)	Volume of Diluent (Section 8.1.9) Added (uL)	Concentration of Target/Surrogate Analytes (ppt)
Solvent Blank	--	1000	**--**
Level 0 (IB/CCB)	5*	995	**500 (Surrogates Only)**
Level 1 (ABRLVS1)	5	995	**5**
Level 2	10	990	**10**
Level 3 (ABRLVS2)	25	975	**25**
Level 4	50	950	**50**
Level 5	100	900	**100**
Level 6	250	750	**250**
Level 7 (CCV)	500	500	**500**
Level 8	750	250	**750**
Level 9	1000	0	**1000**
Final Volume: 1 mL			
***Level 0 (IB/CCB) is spiked with Intermediate Surrogate Spike Standard @ 100 ug/L (100 ppb) (Section 8.2.3)**			

8.2.10 Continuing Calibration Verification Standard (CCV) (500 ppt)

The Continuing Calibration Verification (CCV) standard must be spiked at the midpoint or below. It is typically spiked at the same concentration as the Level 7 calibration standard (Section 8.2.9.2) and is prepared in the same way.

8.2.11 Analytical Batch Reporting Limit Verification Sample (ABRLVS)

The analytical batch reporting limit verification sample (ABRLVS) must be spiked at the reporting limit listed in LIMS for each analyte. Since reporting limits are different for each analyte, multiple levels may be needed. They are prepared in the same way as the calibration standards listed in Section 8.2.9.2. Typically, two levels are prepared at the same concentrations as the calibration Levels 1 and 3 calibration standards (Section 8.2.9.2) and are prepared in the same way.

8.2.12 Working Qualitative Identification Standard (QIS) @ 1000 ppt

The working qualitative identification standard is prepared by spiking 20 uL of the intermediate qualitative identification standard (Section 8.2.5) in 980 uL of 50:50 methanol:water 0.1% acetic acid diluent (Section 8.1.9) using appropriate single channel variable volume pipettes. The standard is stored

in a 2 mL polypropylene vial and are stored between 0-6° C. They may be used for up to one year from the date of preparation. The standard expiration date may not exceed the manufacturer's expiration date.

Table 8.2.12 – Working Qualitative Identification Standard @ 1000 ppt

Intermediate Standard	Intermediate Standard Concentration (ppb)	Volume of Standard Added (uL)	Volume of Diluent Added (uL)	Final Concentration (ppt)
Intermediate Qualitative Identification Standard (Section 8.2.5)	50	20	980	**1000**
Final Volume in 50:50 Methanol:Water 0.1% acetic acid (Section 8.1.9): 1 mL				

9) Apparatus and Equipment

9.1 High Performance Liquid Chromatograph (HPLC) system

9.1.1 Analytical system - Shimadzu Nexera X2 UHPLC with Shimadzu 8060 MS/MS detector, or equivalent.

9.1.2 Analytical column - Phenomenex Kinetex 2.6 µm EVO C18, 100x4.6mm, P/N: 00D-4725-EO, or equivalent.

9.1.3 A delay column (Restek PFAS Delay Phase 50 x 2.1mm, Restek Catalog # 27854, or equivalent) is installed between the mobile phase mixer and the injector. This isolator column delays elution of PFAS contaminants from the instrument pumps to allow resolution from the target PFAS compounds native to the injected extracts and standards. The isolator column will significantly increase pump backpressure, but the pressure should remain within system tolerances.

9.1.4 Pre-column Filters – Fisher MAC-MOD Analytical UltraShield Pre-Column Filter 0.5 µm porosity, SS Filter, Parker port, Parker male, (5/pk) (Fisher Catalog # 50-900-03755), or equivalent.

9.1.5 Windows based computer system, including monitor and printer, with acquisition analysis software.

9.2 Balance capable of measurements of ±0.0001 g.

9.3 Disposable nylon cartridge filters – 0.45 um pore size, 25mm diameter (Filtrous P/N SFN-AR-2025 or equivalent).

9.4 Disposable glass serological (Kimble Catalog # 72120-10110, or equivalent) and Pasteur pipettes (Labcraft Catalog # 183-624, or equivalent), appropriate sizes.

9.5 Autosampler Vial, 2 mL polypropylene (Agilent Catalog # 5191-8150, or equivalent) screw top vials with polypropylene (non-Teflon) lined caps (Agilent Catalog # 5191-8151, or equivalent).

9.6 Glass micro syringes, appropriate sizes (SGE Catalog # 002030, or equivalent)

9.7 Disposable Luer lock syringes – 10 mL (Labtek Catalog # S3953, or equivalent) and 2 mL (Labtek Catalog # S3951, or equivalent)

9.8 Centrifuge – capable of reaching 3000rpm (Fisher Sorvall ST4 Plus Centrifuge Series CAT#75009511, or equivalent), 750mL bucket rotor (Fisher CAT#75003180, or equivalent), and 15mL (Fisher CAT#75003639, or equivalent) and 50mL adaptors (Fisher CAT#75003638, or equivalent)

9.9 Single channel variable volume pipettes with disposable HDPE or polypropylene tips in 1-200uL (Labtek Catalog # L2133, or equivalent) and 100-1000uL (Gilson Catalog # F167104, or equivalent)

9.10 Centrifuge tubes in polypropylene or HDPE 15mL (Environmental Express Catalog # SC0162, or equivalent) and 50mL (SSE Catalog # 220-3550-080, or equivalent) sizes with caps (SSE Catalog # 300-3541-020, or equivalent).

9.11 pH Paper – range from 2.0-9.0 with 0.5 increments (Fisher P/N 88-841, or equivalent)

9.12 Bottles, HDPE or glass, with linerless HDPE or polypropylene lids. Various sizes, used to store prepared standards and reagents.

9.13 TCLP Rotor Tumbler (Environmental Express Cat No. LE1002 or equivalent) – capable of 30 RPM

9.14 Vortex Mixer (Fisher Digital Vortex Mixer Cat #02-215-418, or equivalent)

9.15 Glassware. All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by reagent water and a final rinse with solvents may be needed. In place of a solvent rinse, non-volumetric glassware can be heated in a muffle furnace at 400 ºC for 2 hours. Volumetric glassware should not be heated above 120 ºC.

9.16 Graduated Cylinders, polypropylene or glass. Various sizes, used to prepare standards and reagents.

10) Preventative Maintenance

10.1 All maintenance activities are recorded in a logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. Maintenance entries should include date, symptom/problem, description of maintenance or corrective action(s), date, and name. The log must contain a reference to return to analytical control.

10.2 HPLC System

10.2.1 Mobile phase solvents are vacuum degassed inline.

10.2.2 The analytical column is back-flushed when necessary, typically due to a dirty column. The main indicators of dirty columns are excessive system pressure and changes to chromatography (poor peak shape and/or retention time shift).

10.2.3 The entire system is flushed with water and isopropyl alcohol when necessary, usually when backpressure becomes out of control. Remove the analytical and delay columns before flushing and connect tubing with unions. Pump RO water (Section 8.1.2) through both Pumps A and B at equal concentrations and a total flow rate of 2 mL/min for 1.5 hours and then isopropyl alcohol (Section 8.1.10) at the same conditions for 1 hour. Then re-equilibrate the instrument with the normal operating conditions for 30 minutes prior to starting analysis. Other mobile phases, times, and flow rates may be used as necessary.

10.2.4 The system may be flushed with water and isopropyl alcohol at a low flow rate to help clean out the system and extend the life of the column. Valve R status should be set to the MS instead of waste (check instrument settings to confirm the correct status setting). MS and oven should be turned on at normal method conditions. With columns left in line, pump RO water (Section 8.1.2) through pumps A and B at equal concentrations for a total flow rate of 0.4 mL/min for several hours (5-8). Pumps can then be switched to pump LCMS grade IPA (Section 8.1.10) and the system flushed overnight under the same conditions. After flushing overnight, replace method specific mobile phase and allow to equilibrate under method conditions for at least 30 minutes prior to beginning a sequence. Other mobile phases, times, and flow rates may be used as necessary.

10.2.5 Over time, the column will exhibit poorer overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. This is especially true when evident in conjunction with calibration difficulties.

10.3 MS/MS system

10.3.1 The ionization chamber and associated parts (heater block, sampling cone, and orifice) should be cleaned with methanol following analysis of extracts with high levels of matrix interferences, suspended solids, and/or color; if residues are observed on chamber surfaces; and/or if a loss of sensitivity is observed. If high level of discoloration is observed, then a very dilute mix of Bar Keeper's Friend in RO water may be used to clean the surfaces. Rinse all parts thoroughly with water then methanol to ensure no residue is left. Other solvents may be used to assist with cleaning the instrumentation as needed.

10.3.2 The desolvation line (DL) should be removed and replaced following the manufacturer's instructions if poor chromatography or loss of sensitivity is observed.

10.3.3 The electrospray needle should be cleaned or replaced if the spray appears irregular or if a loss of sensitivity is observed.

10.3.4 The skimmer, Q-Array, multipoles, and lenses can be cleaned per manufacturer instruction if a loss of sensitivity is observed. This level of cleaning requires breaking vacuum to the MS/MS and is typically only performed after exhausting other maintenance options.

10.4 The instrument should be recalibrated following major maintenance events such as installation of a new column.

11) Procedure

11.1 Sample Preparation – Water/Aqueous/Sludge

11.1.1 The maximum preparation batch size for ASTM methods D7979 and 7968 is 30 field samples plus QC. The maximum preparation batch size for EPA method 8327 (prep test code EPA 3512) is 20 field samples plus QC. 5 mL of sample is collected in a pre-tared 15 mL polypropylene centrifuge tube in the field. When the sample arrives to the lab, the weight of the sample will be recorded in the batch sheet in eLIMS. It is assumed that the density of the sample is 1.0 g/mL unless it is otherwise specified. If more than 6 mL of sample is received, it should be vortexed, and the excess should be poured off to reach an approximate volume of 5 mL. QC's including method blanks, RLVS's, and LCS/LCSD are prepared as approximately 5 mL of RO water using a graduated serological pipette.

11.1.1.1 MS/MSD Samples: A sample is selected from a batch to provide for a matrix spike and duplicate matrix spike. This spike is at calibration level 7 (500 ppt). This is achieved by spiking 25 µL of target spike mix (Section 8.2.2) using an appropriate single channel variable volume pipette into the sample. The sample is then carried through the remainder of the extraction process detailed in this SOP (Section 11).

11.1.1.2 RLVS and LCS: 2 RLVS QCs and 1 LCS are prepared. RLVS1 is spiked with 0.5 µL of target spike mix (Section 8.2.2) with an appropriate gastight micro-syringe resulting in a concentration of 10 ppt of target analytes. RLVS2 is spiked with 2.5 µL of target spike mix (Section 8.2.2) with an appropriate gastight micro-syringe resulting in a concentration of 50 ppt of target analytes. The LCS is spiked with 25 µL of target spike mix (Section 8.2.2) with an appropriate single channel variable volume pipette resulting in a concentration of 500 ppt of target analytes.

11.1.1.3 Using an appropriate single channel variable volume pipette, 40 µL of working surrogate spiking solution [20 ppb] (Section 8.2.4) is added to each sample and QC. With a graduated serological pipette, 5 mL of methanol (Section 8.1.3) is added to each sample

and the QC. This results in a concentration of ~160 ppt of surrogate per 5 mL of sample. The laboratory control, reporting limit check samples, and matrix spikes are spiked with the same amount of surrogate spike solution and methanol as the samples.

11.1.1.4 The sample is then hand shaken or vortexed for 2 minutes.

11.1.1.5 The pH is adjusted to ~9 by adding ~20 µL of ammonium hydroxide (Section 8.1.6) using an appropriate single channel variable volume pipette to the samples and QC. The pH should be recorded in the prep batch sheet in eLIMS.

11.1.1.6 The sample is then hand shaken or vortexed for an additional 2 minutes.

11.1.1.7 Prior to touching any samples, the sample filter is washed with 10 mL of acetonitrile (Section 8.1.13), then 10 mL of methanol (Section 8.1.3) to ensure removal of any PFAS compounds.

11.1.1.8 The sample is poured into the polypropylene syringe and filtered through the pre-washed nylon filter and collected in a clean 15 mL polypropylene centrifuge tube.

11.1.1.9 Using an appropriate single channel variable volume pipette, ~50 µL of acetic acid (Section 8.1.4) is added to adjust the pH to ~3-4; more may be required in order to bring the pH to 3-4 and should be documented in the prep batch notes. The pH must be recorded in the prep batch sheet in eLIMS. The sample is vortexed after the addition of the acid.

11.1.1.10 Using an appropriate single channel variable volume pipette, an 800 µL aliquot of the sample is transferred to a polypropylene 2mL autosampler vial and sealed with a PP/silicone cap. Each vial is then vortexed.

11.1.2 Sample Preparation – Soil

11.1.2.1 The maximum preparation batch size for ASTM methods D7979 and 7968 is 30 field samples plus QC. The maximum preparation batch size for EPA method 8327 (prep test code EPA 3512) is 20 field samples plus QC. ~2 g sample (measured to the hundredth of a gram) is placed in a 15-mL polypropylene centrifuge tube. The mass is recorded in the prep batch sheet in eLIMS. QC's including method blanks, RLVS's, and LCS/LCSD are prepared as approximately 2.0 ± 0.1 g of PFAS free matrix sand weighed out.

11.1.2.2 MS/MSD Samples: A sample is selected from a batch for a matrix spike and duplicate matrix spike. This spike is at calibration level 7 (500 ppt). This is achieved by spiking 10 µL of target spike mix

(Section 8.2.2) with an appropriate gastight micro-syringe into the sample. The sample is then carried through the remainder of the extraction process detailed in this SOP (Section 11).

11.1.2.3 RLVS and LCS: 2 RLVS QCs and 1 LCS are prepared. RLVS1 is spiked with 0.5 µL of target spike mix (Section 8.2.2) with an appropriate gastight micro-syringe resulting in a concentration of 25 ppt of target analytes. RLVS2 is spiked with 2.5 µL of target spike mix (Section 8.2.2) with an appropriate gastight micro-syringe resulting in a concentration of 125 ppt of target analytes. The LCS is spiked with 10 µL of target spike mix (Section 8.2.2) with an appropriate gastight micro-syringe resulting in a concentration of 500 ppt of target analytes.

11.1.2.4 Samples are spiked with 40 µL of surrogate spiking solution (Section 11.1.2.14) using an appropriate single channel variable volume pipette, which results in a concentration of ~400 ppt of surrogate per 2 g of sample. The laboratory control, reporting limit check samples, and matrix spikes are spiked with the same amount of surrogate spike solution as the samples.

11.1.2.5 Using a graduated serological pipette, 10 mL of methanol:water (50:50, Section 8.1.9) is added to each sample and QC. Each sample and QC is then shaken/vortexed for ~1 minute.

11.1.2.6 The pH of samples and QC are adjusted to ~9-10 with ammonium hydroxide (~20 µL, Section 8.1.6) using an appropriate single channel variable volume pipette, and vortexed for another ~1 minute. The pH is recorded in the prep batch sheet in eLIMS.

11.1.2.7 The samples are tumbled in a TCLP rotator for 1 hour, then centrifuged at 1900 rpm for 10 minutes.

11.1.2.8 Prior to touching any samples, each polypropylene sample syringe and nylon filter is washed with 10 mL of acetonitrile (Section 8.1.13), then 10 mL of methanol (Section 8.1.3) to ensure removal of any PFAS compounds.

11.1.2.9 The sample is poured into the polypropylene syringe and filtered through the pre-washed nylon filter and collected in a clean 15 mL polypropylene centrifuge tube.

11.1.2.10 Prior to placing the sample into an autosampler vial, the pH is adjusted to ~3-4 with ~80 uL acetic acid (Section 8.1.4) using an appropriate single channel variable volume pipette. The pH is recorded in the prep batch sheet in eLIMS.

11.1.2.11 The final volume of the solution is estimated to be 10 mL for quantitation purposes since 10 mL of MeOH/water was added.

11.1.2.12 Using an appropriate single channel variable volume pipette, an 800 µL aliquot of the sample is transferred to a polypropylene 2mL autosampler vial and sealed with a PP/silicone cap. Each vial is then vortexed.

11.2 Document all sample preparation steps using the current batch sheets and forms. This includes the matrix, amount extracted, final volume, and any additional sample description necessary. Record the applicable start/stop times, lot numbers of reagents, filters, etc., the analyst, and dates. Refer to the appropriate batch sheet for all documentation items. These items document that the steps listed above were completed. Include comments for any additional steps taken during the preparation. The batch sheet is included with the analytical data.

11.3 HPLC/MS/MS Analysis

11.3.1 The mass detector should be tuned in accordance with manufacturer recommendations with respect to frequency and standards used to tune. The mass detector should also be tuned after any major maintenance events. A tune verification must be performed prior to calibration. The manufacture tuning solution will be infused with criteria of ±0.5 amu of the true value.

11.3.2 ESI negative analysis: Establish the operating parameters on the instrument by loading the appropriate method into the LabSolutions software. The recommended chromatographic conditions are shown below:

Time (mins)	5mM Ammonium Acetate in Methanol (MPB, Section 8.1.8)	5mM Ammonium Acetate in H2O (MPA, Section 8.1.8)	Flow Rate (mL/min)
0	2%	98%	1.0
0.4	2%	98%	1.0
5.5	75%	25%	1.0
8.0	90%	10%	1.0
11.0	90%	10%	1.0
11.2	2%	98%	1.0
12.5	2%	98%	1.0

Analytical Column:	Kinetix EVO C18, 100 x 4.6 (or equivalent)
Column temperature:	35ºC
Total LC Time:	13 minutes
Injection Volume:	25 µl

11.3.3 The autosampler is programmed to wash the needle with methanol after every injection to minimize carryover.

11.3.4 All analytes shall have a minimum 10 scans across each chromatographic

peak.

11.3.5 Calibration

NOTE: The default calibration procedure is listed below, and the analyst should also refer to *Calibration of Instruments for Organics Chromatographic Analyses* (HN-QS-019). The calibration procedure(s) and options chosen must follow the ALS protocols.

11.3.5.1 The system must be calibrated prior to conducting sample analyses. The calibration is started with the standard of lowest concentration. Each calibration standard is analyzed, and a calibration curve is generated based on the peak area of each MRM transition against the spiked concentration of each compound.

11.3.5.2 ASTM D7979 and D7968 methods require calibrations to be linear or quadratic curves with 1/x weighting. Linear calibration curves require a minimum of five calibration points and quadratic calibrations require a minimum of six calibration points. Forcing the calibration curve through zero is not permitted. Linear calibrations must have an $r^2 \geq 0.98$. Quadratic calibrations must have an $r^2 \geq 0.99$.

Each standard used in the calibration must be re-quantitated against the initial calibration. The % deviation (%D) of the lowest point of the calibration curve must fall within 50-150% of its expected value. The remaining calibration points must fall between 70-130% of their expected values.

11.3.5.3 Method 8327 allows for the use of average response factor, linear, or quadratic calibrations. Weighting is optional. Average response factor and linear calibration curves must use a minimum of five calibration points and quadratic calibrations must use a minimum of six calibration points. Average response factor calibrations must have a %RSD ≤ 20%. Linear and quadratic calibrations must have an $r^2 \geq 0.99$. Forcing the calibration curve through zero is not permitted.

Each standard used in the calibration must be requantitated against the initial calibration. The % deviation (%D) of the lowest point of the calibration curve must fall within 50-150% of its expected value. The remaining calibration points must fall between 70-130% of their expected values.

11.3.5.4 Immediately following the highest standard analyzed, an instrument blank must be evaluated to determine the level of carry-over observed from the calibration standard. Detections in the instrument blank must be lower than the MRL.

11.3.5.5 Following initial calibration, an ICV is analyzed. The ICV must contain all of the target analytes and surrogates in the calibration and is quantitated against the initial calibration. The percent difference (%D) of the ICV should be within ±30% of the expected concentration.

11.3.5.6 Analytes that do not have suitable ion transition ratio (>20%) are not evaluated by the ion ratio criteria in Appendix Table 6 due to unreliable or unstable secondary transitions. This includes (but is

not limited to) PFBA, PFPeA, PFOSA, etc.

For method EPA 8327 samples, product ions used for quantitation should have signal to noise (S/N) ≥10, and any product ions used to support qualitative identification should have S/N ≥3.

Similar signal-to-noise and ion transition ratio criteria are outlined in EPA 1633 Section 15.1.

11.3.6 Continuing Calibration Verification

11.3.6.1 The working calibration curve or calibration factor must be verified on each analytical sequence by the analysis of one or more mid-level calibration standards (CCV). ASTM methods D7979 and D7968 require a mid-level standard (CCV) to be injected at the end of the batch of 30 samples or every 24 hours, whichever comes first. EPA Method 8327 requires a mid-level standard (CCV) to be injected prior to field samples (on non-ICAL days only) as well as after every 20 samples and at the end of the analytical sequence. It is recommended that CCV's are analyzed more frequently.

The percent difference in the CCV must be within ± 30% of the expected value, as compared to the initial calibration. Refer to the ALS protocols for organics analyses calibration for CCV evaluation protocols. The product ion must be within ± 35% of the calibration for ASTM D7968/D7979 and must be within ± 50% of either the mid-point or the average of the calibration for EPA 8327.

11.3.7 Qualitative Identification Standard (QIS)

11.3.7.1 After each calibration and prior to the analysis of samples, a qualitative identification standard that includes both linear and branched isomers is analyzed. This standard is used as a retention time marker indicating the beginning and ending retention times for the integration of branched isomers in samples for branched isomer analytes not included in the calibration standards. Currently, PFNA and PFNS (linear and branched) retention times are evaluated in this standard.

11.3.8 Sample Analysis

11.3.8.1 Analyze the samples using the chromatographic conditions determined for the acquisition method in MRM mode. The specific parent, fragment, and product ions monitored during this analysis are specified in Table 3.

11.3.8.2 Evaluate the sample data and chromatograms. Determine if the analysis was acceptable from a chromatographic standpoint,

based on typical responses, chromatographic resolution, baseline, and background.

11.3.8.3 Identify a sample component by comparison of its retention time to the retention time of the CCV standard chromatogram and retention time window. Identification of an analyte occurs when a product ion peak from a sample extract falls within the daily retention time window for the product ion peak of the certified standard.

11.3.8.4 The retention time window of the MRM transitions shall be within 5 % of the retention time of the analyte in a midpoint calibration standard. If this is not the case, the calibration must be re-analyzed to determine if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, the analyte is referred to as an unknown.

11.3.8.5 ASTM Methods D7979/D7968

11.3.8.5.1 For target analytes that produce a reliable secondary ion transition, ion transition ratios are to be calculated and recoveries should fall within ±35% of expected ratio from the average of all ICAL standards. When the ion ratio fails, the result will be reported and qualified as failing the ion ratio.

11.3.8.5.2 For target analyte identification in samples, the retention time of the identified peak in the sample must be within ±5% of the retention time of the analyte peak in the midpoint ICAL standard to be considered a valid positive result.

11.3.8.6 EPA 8327

11.3.8.6.1 For target analytes that produce a reliable secondary ion transition, ion transition ratios are to be calculated and recoveries should fall within ±50% of expected ratio from any of the following: the midpoint ICAL standard, the average of all ICAL standards, or the preceding CCV. When the ion ratio fails, the result will be reported and qualified as failing the ion ratio.

11.3.8.6.2 For target analyte identification in samples, the retention time of the identified peak in the sample must be within ±0.1 minutes of the isotopically-labeled analog of the target analyte (if available) to be considered a valid positive result. Otherwise, the retention time must be within ±0.2 minutes of the target analyte retention time in any of the following: the midpoint ICAL

standard, the average of all ICAL standards, or the preceding CCV.

12) QA/QC Requirements

12.1 Initial Precision and Recovery Validation

The precision of the extraction procedure and the HPLC/MS/MS procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four liquid and solid matrix samples are spiked with the appropriate matrix spike solution, extracted, and analyzed according to this SOP.

12.2 Method Detection Limits and Limit of Detection

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the procedure outlined in SOP HN-QS-006. Follow the extraction and analysis procedures in this SOP to analyze the samples.

12.2.2 Calculate the average concentration found (x) in ng/L, and the standard deviation of the concentrations (s) in ng/L for each analyte. Calculate the MDL for each analyte. The MDL study is used to establish the Limit of Detection (LOD). The LOD is equivalent to the MDL, unless otherwise defined by project or program. The LOD must be evaluated annually (or MDL repeated) and verified quarterly.

12.3 Limits of Quantification (LOQ)

12.3.1 The laboratory establishes a LOQ (or PQL) for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 35-150% of the true values to verify the data reporting limit. Refer to *SOP HN-QS-006*.

12.4 Ongoing QC Samples required are described in the Quality Assurance Manual and in the SOP for Batch QC Evaluation (HN-QS-020). Additional QC Samples may be required in project specific quality assurance plans (QAPP). The routine QC Samples are as follows:

12.4.1 Method Blank

A method blank is a sample of RO water or matrix sand extracted with every batch of samples to demonstrate that there are no method interferences. Each ASTM D7979/7968 batch must have at least two method blanks per 30 or less field samples. Each EPA 8327/3512 batch must have at least one method blank per 20 or less field samples. If either of the method blanks show any positive detections above ½ the reporting limit (or above 10% of the sample concentration for EPA 8327 only), corrective action must be taken.

Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction of the associated extraction batch and reanalysis. For some project specific needs, exceptions may be noted and method blank results above the MRL may be reported for common lab contaminants (PFBA and PFHxA).

12.4.2 Lab Control (Duplicate) Sample (LCS/LCSD)

12.4.2.1 The laboratory control sample (LCS) is composed of analyte-free water or sand into which all target analytes are spiked. The LCS is designed to monitor the extraction efficiency of the method, since it can be safely presumed that no matrix interferences are present in the sample as prepared. The concentration of the spike in the LCS matrix should be at the midpoint of the calibration or below at levels specified by a project analysis plan.

12.4.2.2 A lab control sample (LCS) must be extracted and analyzed with every batch of samples. An additional LCSD prepared in the same manner as the LCS can be extracted in place of a MS/MSD/DUP if there is insufficient sample volume. The LCS and LCSD recovery and relative percent difference (RPD) requirements may be found in eLIMS. The percent recovery (%R) is calculated as follows:

$$\%R = \frac{X}{TV} x\ 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

12.4.2.3 If the lab control sample (LCS) or lab control duplicate sample (LCSD) fail acceptance limits for any of the compounds, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction of the associated extraction batch and reanalysis. If the corrective action cannot be taken, the samples associated with the failing LCS/LCSD must be narrated. High bias without positive detections in the samples is permitted.

12.4.3 Reporting Limit Verification Samples (RLVS1 and RLVS2)

12.4.3.1 The reporting limit check sample is composed of analyte-free RO water or matrix sand into which all target analytes are spiked at the reporting limit and is taken through the entire extraction method. The RLVS is designed to monitor efficiency of the method at the reporting limit. It can be safely presumed that no matrix interferences are present in the sample as prepared. The concentration of the spike in the RLVS matrix should be at the reporting limit or at levels specified by a project analysis plan.

12.4.3.2 For ASTM methods D7979/7968, at least one RLVS must be extracted and analyzed with every batch of samples or within the

24-hour analysis window of the batch. For EPA 8327, at least one RLVS must be extracted and analyzed annually, but is recommended to be extracted and analyzed with every batch of samples. The RLVS recovery should be between 35-150% for ASTM methods D7979/7968 and between 50-150% for EPA method 8327. The percent recovery (%R) is calculated as follows:

$$\%R = \frac{X}{TV} \, x \, 100$$

Where: X = Concentration of the analyte recovered
TV = True value of amount spiked

12.4.3.3 The RLVS should run after the extraction blank preceding the LCS and samples.

12.4.3.4 If the RLVS fails acceptance limits for any of the compounds of similar concentration, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction of the associated extraction batch and reanalysis. If the corrective action cannot be taken, then the samples associated with the failing RLVS must be narrated. High bias without positive detections in the samples is permitted.

12.4.4 Matrix Spike/Matrix Spike Duplicate

12.4.4.1 A matrix spike (MS) and matrix spike duplicate (MSD) must be extracted and analyzed with every batch of samples. If insufficient sample volume, a matrix duplicate (DUP) or lab control duplicate sample (LCSD) can be prepared instead. The MS/MSD is prepared by adding a known volume of the matrix spike solution to the sample and determining the spiked sample concentration. Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \, x \, 100$$

Where: X = Concentration of the analyte recovered
X1 = Concentration of the unspiked analyte
TV = True value of amount spiked

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \, x \, 100$$

Where: R1= Higher result
R2= Lower result

12.4.4.2 The default acceptance criteria for the percent recovery (%R) can be found in eLIMS.

12.4.4.3 The default acceptance criteria for the relative percent recovery difference (% RPD) can be found in eLIMS.

12.4.4.4 If the MS/MSD recovery is out of acceptance limits for reasons other than matrix effects, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction of the parent field sample and reanalysis. If for any reason the re-extraction and reanalysis cannot be completed, then the project must be narrated. Any compound exceeding the upper reporting limit in the matrix spike and matrix spike duplicate should be diluted to get the concentrations within the reporting limit.

12.4.5 Surrogate

12.4.5.1 The analyst should monitor the performance of the extraction and the analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with the appropriate surrogate mix. Surrogate spike is added to every sample, blank and spike prior to extraction. Calculate surrogate percent recovery (%R) as:

$$\%R = S/V \times 100$$

Where: S = the concentration of surrogate recovered
V = the concentration spiked

12.4.5.2 The acceptance criteria can be found in eLIMS. If surrogate recoveries are outside of acceptance limits for reasons other than matrix effects, corrective action must be taken. Corrective action includes recalculation, reanalysis, or re-extraction of the sample and reanalysis. There may be high bias in surrogate recoveries if there are no positive detections in the samples.

12.5 Prior to preparation of stock solutions, methanol, and water/sand blanks should be run to determine possible interferences with analyte peaks. If the methanol or water/sand blanks show contamination, a different batch should be used.

12.6 Control charts should be maintained for results of matrix spike analyses. The charts should be reviewed periodically for trends in results.

13) Data Reduction and Reporting

13.1 Calibration Factor (CF) and calibration RSD calculations:

13.1.1 Calibration Factor and Mean Calibration Factor:

13.1.1.1 $$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

13.1.1.2 $$\text{Mean} \quad CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where: n is the number of standards analyzed.

13.1.2 Standard Deviation (SD) and RSD:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \times 100$$

13.2 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{\left(\sum X^2 - \frac{(\sum X)^2}{n}\right)\left(\sum Y^2 - \frac{(\sum Y)^2}{n}\right)}}$$

Where:

X = individual values for independent variable
Y = individual values for dependent variable
n = number of pairs of data.

13.3 Calculation of % difference (using the calibration factors):

$$\% \text{ Difference} = \frac{[(CF - \text{mean } CF) \times 100]}{\text{mean } CF}$$

Where:

CF = the calibration factor from the CCV and
Mean CF = the mean calibration factor from the initial calibration

13.4 Calculation of % drift (linear and non-linear regression) uses the following formula:

$$\% \text{ Drift} = \frac{[(\text{Calculated Conc.} - \text{Theoretical Conc.}) \times 100]}{\text{Theoretical Conc.}}$$

13.5 Sample Quantitation using External calibration, aqueous samples:

$$\text{Concentration (ng/L)} = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

Where:

A_x = for the analyte in the sample.
V_t = Total volume of the concentrated extract (ml).
D = Dilution factor (if sample/extract was diluted prior to analysis)
CF = Mean calibration factor from the initial calibration (area/ng).
V_i = Volume of the extract injected (ml).
V_s = Volume of the aqueous sample extracted in L.

13.6 Sample concentrations are reported when all QC criteria for the analysis has been met. Reported results not meeting QC criteria must be qualified in the sample narrative.

13.7 Data Review

13.7.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the SOP for *Data Reduction, Review, and Evaluation* (HN-QS-009) for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Manager to inclusion in the report narrative.

13.8 Reporting

13.8.1 Reports are generated in the ALS LIMS by compiling the login, sample prep database, instrument data, and client-specified report requirements (when specified). The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs. Labcoat is used to generate level 4 reports.

13.8.2 Procedures for applying data qualifiers are described in the SOP for *Report Formatting* (HN-ADM-005) or in project-specific requirements.

13.8.3 When clients request that various sulfonic acids be reported as sulfonates, the results must be converted by using the proper conversion applicable for each compound.

14) Contingencies for Handling Our-of-Control or Unacceptable Data

14.1 Refer to the SOP for *Non Conformance and Corrective Action* (HN-QS-003) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2 Handling out-of-control or unacceptable data

14.2.1 On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, run logs, for example.

14.2.2 Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision.
- Method blanks with target analytes above acceptable levels.
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements.
- Laboratory analysis errors impacting sample or QC results.
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc).
- Sample preservation or handling discrepancies due to laboratory or operations error.

14.3 Table 5 summarizes the quality control criteria and applicable corrective action.

15) Method Performance

15.1 This method was validated through single laboratory studies of accuracy and precision. Refer to ASTM Methods 7979 and 7968 and SW-846 method 8327 for additional method performance data available.

15.2 The method detection limit (MDL) is established using the procedure described in the SOP *HN-QS-006*. Method Reporting Limits are established for this method based on the low calibration point and the MDL study results.

16) Pollution Prevention and Waste Management

16.1 It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the ALS Chemical Hygiene Plan and Lab Waste Management Plan.

16.3 This method uses non-halogenated solvents. Waste solvents generated through the lab ware cleaning, sample prep, and LC mobile phase usage are collected in containers near the point of creation. They are then stored at a satellite storage center in the lab which is transferred as needed to the main facility waste management area. The waste solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

17) Training

17.1 Training outline

17.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3 Perform initial demonstration of capability (IDC) as described above for water and soil samples. Summaries of the IDCs are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2 Training is documented following *SOP HN-QS-013*.

17.3 When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18) Method Modifications

18.1 This section is not applicable.

19) References

19.1 ASTM D7979-17, Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), Revised 2017.

19.2 ASTM D7968-17a, Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS), Revised 2017.

19.3 EPA 8327, Per- and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), June 2019.

20) Changes Since the Last Revision

Revision Number	Document Editor	Description of Changes
0.0	S. Krzyzanowski	New SOP
1.0	S. Krzyzanowski	Added 4 "Next Gen" analytes to comply with the new Michigan Minimum 28 Analyte list. Revised expiration of prepared standard mixes to one year, unless discarded due to quality control failures, per the ASTM D7979 method. Added soil prep procedure, details, and reporting limits for soil analysis, per the ASTM D7968 method.
2.0	S. Krzyzanowski	Procedural steps revised to include documentation of pH verification after modification of sample pH.
3.0	M. McClendon / E. Smith / A. Karst	Addition of base to water sample preparation, Addition of SW-846 requirements, Correction of r 2 requirements for calibration curves, Additional information for standard, reagent, and calibration curve preparation, Addition of branched isomer standard.
4.0	E. Smith / M.	Removed Appendix Table 3 – Analyte RL's, Updated standards section 8.2 with

	McClendon	new primary and secondary target sources, Updated Appendix Table 2, Additional information for standard and sample preparation sections 8.2 and 11.1, respectively, Added CAS# to Appendix Table 1. Updated initial calibration Table 8.2.9.2 and added 8327 vs ASTM7979/7968 Appendix Table 6. Updated CAS# for NEtFOSAA and NMeFOSAA in Appendix Table 1. Updated injection volume in section 11.3.2. Incorporated SOP departures 1-4.

21) Attachments, Tables, and Appendices

21.1 Table 1 – Analyte Acronyms

21.2 Table 2 – Target Standard Composition and Concentrations

21.3 Table 3 – Surrogate Standard Composition and Concentrations

21.4 Table 4 – Target Analyte and Surrogate Ion Transitions

21.5 Table 5 – Summary of Corrective Actions.

21.6 Table 6 – Method Criteria Comparison of ASTM 7979, 7968, and EPA 8327

21.7 Appendix A – Additional Prep Information for Perfluorinated Compounds.

21.8 Appendix B – Analytical Batch Summary

Table 1 – PFAS Acronyms		
Analytes		**CAS#**
PFBA	Perfluorobutanoic acid	375-22-4
PFPeA	Perfluoropentanoic acid	2706-90-3
PFHxA	Perfluorohexanoic acid	307-24-4
PFHpA	Perfluoroheptanoic acid	375-85-9
PFOA	Perfluorooctanoic acid	335-67-1
PFNA	Perfluorononanoic acid	375-95-1
PFDA	Perfluorodecanoic acid	335-76-2
PFUnA	Perfluoroundecanoic acid	2058-94-8
PFDoA	Perfluorododecanoic acid	307-55-1
PFTrDA	Perfluorotridecanoic Acid	72629-94-8
PFTeDA	Perfluorotetradecanoic Acid	376-06-7
PFBS	Perfluorobutane sulfonate	375-73-5
PFPeS	Perfluoropentane sulfonic acid	2706-91-4
PFHxS	Perfluorohexane sulfonic acid	355-46-4
PFHpS	Perfluoroheptane sulfonic acid	375-92-8
PFOS	Perfluorooctane sulfonic acid	1763-23-1
PFNS	Perfluorononane sulfonic acid	68259-12-1
PFDS	Perfluorodecane sulfonic acid	335-77-3
PFOSA	Perfluorooctanesulfonamide	754-91-6
4:2-FTS	4:2 Fluorotelomer sulfonic acid	757124-72-4
6:2 FTS	6:2 Fluorotelomer sulfonic acid	27619-97-2
8:2 FTS	8:2 Fluorotelomer sulfonic acid	39108-34-4
N-EtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6
N-MeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	13252-13-6
DONA	Dodecafluoro-3H-4,8-dioxanonanoate	919005-14-4
11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	763051-92-9
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	756426-58-1
PFBSA*	Perfluoro-1-butanesulfonamide*	30334-69-1
PFHxSA*	Perfluoro-1-hexanesulfonamide*	41997-13-1

Table 1 – PFAS Acronyms		
Surrogates		
13C4-PFBA	Perfluoro-n-($^{13}C_4$)butanoic acid	N/A
13C2-PFHxA	Perfluoro-n-(1,2-^{13}C2)hexanoic acid	N/A
13C4-PFOA	Perfluoro-n-(1,2,3,4-$^{13}C_4$)octanoic acid	N/A
13C5-PFNA	Perfluoro-n-(1,2,3,4,5-$^{13}C_5$)nonanoic acid	N/A
13C2-PFDA	Perfluoro-n-(1,2-$^{13}C_2$)decanoic acid	N/A
13C2-PFUnA	Perfluoro-n-(1,2-$^{13}C_2$)undecanoic acid	N/A
13C2-PFDoA	Perfluoro-n-(1,2-$^{13}C_2$)dodecanoic acid	N/A
18O2-PFHxS	Sodium perfluoro-1-hexane($^{18}O_2$)sulfonate	N/A
13C4-PFOS	Sodium perfluoro-1-(1,2,3,4-$^{13}C_4$)octanesulfonate	N/A
d3-N-MeFOSAA	N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	N/A
d5-N-EtFOSAA	N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	N/A
13C3-PFBS	Sodium perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	N/A
13C2-PFTeA	Perfluoro-n-(1,2-$^{13}C_2$)tetradecanoic acid	N/A
13C4-PFHpA	Perfluoro-n-(1,2,3,4-$^{13}C_4$)heptanoic acid	N/A
13C5-PFPeA	Perfluoro-n-($^{13}C_5$)pentanoic acid	N/A
13C8-FOSA	Perfluoro-1-($^{13}C_8$)octanesulfonamide	N/A
13C2-FtS 4:2	Sodium 1H,1H,2H,2H-perfluoro(1,2-$^{13}C_2$)hexanesulfonate	N/A
13C2-FtS 6:2	Sodium 1H,1H,2H,2H-perfluoro(1,2-$^{13}C_2$)octanesulfonate	N/A
13C2-FtS 8:2	Sodium 1H,1H,2H,2H-perfluoro (1,2-$^{13}C_2$)decanesulfonate	N/A
13C3-HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)($^{13}C_3$)propanoic acid	N/A

***Analyte not available for this method**

Table 2 – Target Standard Composition and Concentrations

Supplier Catalog Number	Analyte Name	Concentration (ng/mL)
Secondary Source Target Analytes (Wellington Laboratories Inc)		
PFAC30PAR	PFBA - Perfluorobutanoic acid	1000
PFAC30PAR	PFPeA - Perfluoropentanoic acid	1000
PFAC30PAR	PFHxA - Perfluorohexanoic acid	1000
PFAC30PAR	PFHpA - Perfluoroheptanoic acid	1000
PFAC30PAR	PFOA - Perfluorooctanoic acid	1000
PFAC30PAR	PFNA - Perfluorononanoic acid	1000
PFAC30PAR	PFDA - Perfluorodecanoic acid	1000
PFAC30PAR	PFUnDA - Perfluoroundecanoic acid	1000
PFAC30PAR	PFDoA - Perfluorododecanoic acid	1000
PFAC30PAR	PFTrDA - Perfluorotridecanoic acid	1000
PFAC30PAR	PFTeDA - Perfluorotetradecanoic acid	1000
PFAC30PAR	PFBS - Perfluorobutane sulfonic acid	887
PFAC30PAR	PFPeS - Perfluoropentane sulfonic acid	941
PFAC30PAR	PFHxS - Perfluorohexane sulfonic acid (linear/branched)	914
PFAC30PAR	PFHpS - Perfluoroheptane sulfonic acid	953
PFAC30PAR	PFOS - Perfluorooctane sulfonic acid (linear/branched)	928
PFAC30PAR	PFNS - Perfluorononane sulfonic acid	962
PFAC30PAR	PFDS - Perfluorodecane sulfonic acid	965
PFAC30PAR	4:2 FTS - 4:2 Fluorotelomer sulfonic acid	937
PFAC30PAR	6:2 FTS - 6:2 Fluorotelomer sulfonic acid	951
PFAC30PAR	8:2 FTS - 8:2 Fluorotelomer sulfonic acid	960
PFAC30PAR	PFOSA - Perfluorooctane sulfonamide	1000
PFAC30PAR	MeFOSAA - N-Methyl perfluorooctane sulfonamidoacetic acid (linear/branched)	1000
PFAC30PAR	EtFOSAA - N-Ethylperfluorooctane sulfonamidoacetic acid (linear/branched)	1000
PFAC30PAR	HFPO-DA - Hexafluoropropylene oxide dimer acid	1000
PFAC30PAR	ADONA - 4,8-Dioxa-3H-perfluorononanoic acid	945
PFAC30PAR	9Cl-PF3ONS - 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	933
PFAC30PAR	11Cl-PF3OUnDS - 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	943
PFAC30PAR	PFBSA – Perfluorobutylsulfonamide**	1000
PFAC30PAR	PFHxSA – Perfluorohexanesulfonamide**	1000

***NOTE**: Some analytes are not available as acids but rather as their corresponding salts, such as K+ or Na+. The concentrations must be corrected for the salt content accordingly. This can be done in the solution makeup or in the instrument calibration software.

**Analyte not available by this method

Table 2 – Target Analytes and Concentrations in Purchased Mixes (Continued)

Supplier Catalog Number	Analyte Name	Concentration (ng/mL)
Primary Source Target Analytes (Absolute Standards Inc)		
64533	PFBA - Perfluorobutanoic acid	2000
64533	PFPeA - Perfluoropentanoic acid	2000
64533	PFHxA - Perfluorohexanoic acid	2000
64533	PFHpA - Perfluoroheptanoic acid	2000
64533	PFOA - Perfluorooctanoic acid (linear/branched)	2000
64533	PFNA - Perfluorononanoic acid	2000
64533	PFDA - Perfluorodecanoic acid	2000
64533	PFUnDA - Perfluoroundecanoic acid	2000
64533	PFDoA - Perfluorododecanoic acid	2000
64533	PFTrDA - Perfluorotridecanoic acid	2000
64533	PFTeDA - Perfluorotetradecanoic acid	2000
64533	PFBS - Perfluorobutane sulfonic acid	2000
64533	PFPeS - Perfluoropentane sulfonic acid	2000
64533	PFHxS - Perfluorohexane sulfonic acid (linear/branched)	2000
64533	PFHpS - Perfluoroheptane sulfonic acid	2000
64533	PFOS - Perfluorooctane sulfonic acid (linear/branched)	2000
64533	PFNS - Perfluorononane sulfonic acid	2000
64533	PFDS - Perfluorodecane sulfonic acid	2000
64533	4:2 FTS - 4:2 Fluorotelomer sulfonic acid	2000
64533	6:2 FTS - 6:2 Fluorotelomer sulfonic acid	2000
64533	8:2 FTS - 8:2 Fluorotelomer sulfonic acid	2000
64533	PFOSA - Perfluorooctane sulfonamide (linear/branched)	2000
64533	MeFOSAA - N-Methyl perfluorooctane sulfonamidoacetic acid (linear/branched)	2000
64533	EtFOSAA - N-Ethylperfluorooctane sulfonamidoacetic acid (linear/branched)	2000
64533	HFPO-DA - Hexafluoropropylene oxide dimer acid	2000
64533	ADONA - 4,8-Dioxa-3H-perfluorononanoic acid	2000
64533	9Cl-PF3ONS - 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	2000
64533	11Cl-PF3OUnDS - 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	2000
64533	3:3 FTCA – 2H,2H,3H,3H-Perfluorohexanoic acid**	2000
64533	5:3 FTCA - 2H,2H,3H,3H-Perfluorooctanoic acid**	2000
64533	7:3 FTCA - 2H,2H,3H,3H-Perfluorodecanoic acid**	2000
64533	PFecHS - Perfluoro-4-ethylcyclohexanesulfonic Acid**	2000
64533	PFBSA – Perfluorobutylsulfonamide**	2000
64533	PFHxSA – Perfluorohexanesulfonamide**	2000

***NOTE**: Analytes listed in the mix above are shown in their anion form concentration as indicated by the manufacturer.
**Analyte not available by this method

1. Primary and secondary source suppliers can be interchanged as more inclusive (additional linear/branched isomer analytes) standard mixes become commercially available.

Table 3 – Surrogate Standard Composition and Concentrations				
Surrogate	**Wellington Catalog Number**	**Initial Concentration As Acid Form (mg/L)***	**Volume Added (uL)**	**Final Concentration (ppm)**
13C4-PFBA	MPFAC-MXA	2	100	**20**
13C2-PFHxA		2		**20**
13C4-PFOA		2		**20**
13C5-PFNA		2		**20**
13C2-PFDA		2		**20**
13C2-PFUnA		2		**20**
13C2-PFDoA		2		**20**
18O2-PFHxS		1.89		**18.9**
13C4-PFOS		1.91		**19.1**
d3-N-MeFOSAA	d3-N-MeFOSAA	50	4	**20**
d5-N-EtFOSAA	d5-N-EtFOSAA	50	4	**20**
13C3-PFBS	M3PFBS	46.5	4	**18.6**
13C2-PFTeA	M2PFTeDA	50	4	**20**
13C4-PFHpA	M4PFHpA	50	4	**20**
13C5-PFPeA	M5PFPeA	50	4	**20**
13C8-FOSA	M8FOSA-I	50	4	**20**
13C2-FtS 4:2	M2-4:2FTS	46.7	4	**18.7**
13C2-FtS 6:2	M2-6:2FTS	47.5	4	**19.0**
13C2-FtS 8:2	M2-8:2FTS	47.9	4	**19.2**
13C3-HFPO-DA	M3HFPO-DA	50	4	**20**

Table 4 – Target Analyte and Surrogate Ion Transitions				
	Primary/Quantitation		Secondary/Confirmation	
Analytes	Parent ion (m/z)	Product Ion (m/z)	Parent ion (m/z)	Product Ion (m/z)
PFBA-$^{13}C_4$	217	172		
PFBA	213	169		
PFPeA-$^{13}C_5$	268	223		
PFPeA	263	219		
PFBS	299	80	299	99
PFBS-$^{13}C_3$	302	80		
PFPeS	349	80	349	99
4_2-FTS	327	307	327	81
4_2-FTS-$^{13}C_2$	329	309		
PFHxA-$^{13}C_2$	315	270		
PFHxA	313	269	313	119
PFHxS	399	80	399	99
PFHxS-$^{18}O_2$	403	84		
PFHpA	363	319	363	169
PFHpA-$^{13}C_4$	367	322		
PFHpS	449	80	449	99
6_2-FTS-$^{13}C_2$	429	409		
6_2-FTS	427	407	427	81
PFOA-$^{13}C_4$	417	372		
PFOA	413	369	413	169
PFOS	499	80	499	99
PFOS-$^{13}C_4$	503	80		
PFNA-$^{13}C_5$	468	423		
PFNA	463	419	463	219
PFNS	549	99	549	80
PFDA-$^{13}C_2$	515	470		
PFDA	513	469	513	219
8_2-FTS-$^{13}C_2$	529	509		
8_2-FTS	527	507	527	487

Table 4 – Target Analyte and Surrogate Ion Transitions				
	Primary/Quantitation		Secondary/Confirmation	
Analytes	Parent ion (m/z)	Product Ion (m/z)	Parent ion (m/z)	Product Ion (m/z)
N-MeFOSAA	570	419	570	512
N-MeFOSAA-d_3	573	419		
PFDS	599	80	599	99
PFUnDA	563	519	563	219
PFUnDA-$^{13}C_2$	565	520		
N-EtFOSAA	584	419	584	526
N-EtFOSAA-d_5	589	419		
FOSA-$^{13}C_8$	506	78		
FOSA	498	78	498	64
PFDoA	613	569	613	169
PFDoA-$^{13}C_2$	615	570		
PFTrDA	663	619	663	169
PFTeDA	713	669	713	169
PFTeDA-$^{13}C_2$	715	670		
HFPO-DA	329	169	329	285
HFPO-DA-$^{13}C_3$	332	287		
NaDONA	377	251		
11Cl-PF3OUdS	631	451		
9Cl-PF3ONS	531	351		

1. Exact m/z is dependent on instrument optimization.

TABLE 5
Method Criteria and Summary of Corrective Actions

Summary of Corrective Actions			
Control	**Specification and Frequency**	**Acceptance Criteria**	**Corrective Action**
ICAL	Prior to sample analysis	Five points minimum if linear, six if quadratic. $r^2 \geq 0.98$ if linear and $r^2 \geq 0.99$ if quadratic for D7979/D7968; linear/quadratic $r^2 \geq 0.99$ or mean RF %RSD ≤ 20 for 8327 Points refit to ICAL must be 70-130%, low point may be 50-150%.	Correct problem then repeat ICAL.
ICV	After ICAL	± 30% Diff	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
CCV	After analysis of the batch or every 24 hours, whichever comes first	± 30% Diff	Correct problem then repeat CCV or repeat ICAL.
Method Blank	Include two with each batch (up to 30 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 10x amount in blank.
Laboratory Control Sample	Include with each batch (up to 30 samples)	See eLIMS	If exceeds limits, re-extract and re-analyze.
Prep Batch Reporting Limit Verification Sample	Include with each batch (up to 30 samples) spiked at or below the method reporting limit	Compounds must be within 35-150% of true value.	If exceeds limits, re-extract and re-analyze.
Matrix Spike/Matrix Spike Duplicate	Include with each batch (up to 30 samples)	See eLIMS	Evaluate data to determine if the there is a matrix effect or analytical error.
Duplicate	Include with each	RPD ≤ 30	Re-extract, and reanalyze if result is >

	analysis batch (up to 30 samples)		5 X the MRL.

Table 6 – Method Criteria Comparison of ASTM 7979, 7968, and EPA 8327

	ASTM 7979 (Aqueous)	ASTM 7968 (Soilds)	EPA 8327 (Aqueous)
Maximum Preparation Batch	30 Samples + QC	30 Samples + QC	20 Samples + QC
Frequency of CCV Analysis	After every 30 samples or every 24 hours, Recommended to analyze more frequently	After every 30 samples or every 24 hours, Recommended to analyze more frequently	Non-ICAL days, prior to field samples, After every 20 samples and at the end of the sequence
RLVS (Reporting Limit Verification Sample)	One or more per extraction batch of 30 samples or less (depending on varying analyte reporting limits) Or Within 24 hour analysis window of batch	One or more per extraction batch of 30 samples or less (depending on varying analyte reporting limits) Or Within 24 hour analysis window of batch	Required annually, Recommended one or more per extraction batch of 20 samples or less (depending on varying analyte reporting limits)
RLVS Percent Recovery Acceptance Limits	35-150%	35-150%	50-150%
Ion Abundance Ratio Criteria*	Within ±35% of expected ratio from the average of all ICAL standards	Within ±35% of expected ratio from the average of all ICAL standards	Within ±50% of expected ratio from any of the following: midpoint ICAL standard, average of all ICAL standards, or preceding CCV
Retention Time Criteria for Target Analyte Identification	RT in sample within ±5% of the RT of the analyte in the midpoint ICAL standard	RT in sample within ±5% of the RT of the analyte in the midpoint ICAL standard	RT in sample within ±0.1 min of isotopically-labeled analog of target analyte (if available), otherwise within ±0.2 min of target analyte RT in any of the following: midpoint ICAL standard, average of all ICAL standards, or preceding CCV
Method Blank	Two per extraction batch of 30 samples or less	Two per extraction batch of 30 samples or less	One per extraction batch of 20 samples or less
Method Blank Acceptance Limits	MB < ½ PQL for each target analyte	MB < ½ PQL for each target analyte	MB < ½ PQL for each target analyte or < 10% of sample concentration

Initial Calibration Criteria	Linear (≥5 cal points) Or Quadratic (≥6 cal points) Regression With 1/C weighting Not forced through zero $r^2 \geq 0.98$ (linear) or 0.99 (quadratic) %Error ≤±30% all cal points	Linear (≥5 cal points) Or Quadratic (≥6 cal points) Regression With 1/C weighting Not forced through zero $r^2 \geq 0.98$ (linear) or 0.99 (quadratic) %Error ≤±30% all cal points	Mean RF (response factor): RSD ≤ 20% Or Linear (≥5 cal points) or Quadratic (≥6 cal points) Regression Not forced through zero $r^2 \geq 0.99$ RSE ≤ 20% %Error ≤±50% PQL and ≤±30% all other cal points

*For target analytes that produce a reliable secondary ion transition

Appendix A

ALS Environmental

HPLC-MS/MS Prep: ASTM Method 7979 / 7968	
Batch ID:	
Date:	
Analyst:	
Methanol BPL:	
Acetonitrile BPL:	
Acetic Acid (LCMS Grade) BPL:	
28-30% NH4OH BPL:	
LCS/MS/MSD Target Spike BPL:	
Surrogate Spike BPL:	
Matrix Sand BPL:	
10 mL Polypropylene Syringe Lot:	
Pipette IDs:	
Pipette Tip Lot:	
Nylon Filter Lot:	
15mL Polypropylene Centrifuge Tube Lot	
Vial Lot:	
Vial Cap Lot:	
Pasteur Pipette Lot:	
Serological Pipette Lot:	
pH Strips (2-9):	
Analytical Scale:	
Extraction Start Time:	
Extraction Stop Time:	
Completed Time:	
Storage Location:	
Comments/Observations:	

Aqueous Sample Prep Checklist:

Batch Preparation

- ☐ Remove standard mixes: ASTM Tgt Spike 100 ppb (Section 8.2.2) and ASTM Surrogate Mix 20 ppb (Section 8.2.4) from the fridge and let warm to room temp. Vortex before use.
- ☐ Assemble a batch of 30 samples (or fewer), 1 LCS, 2 MBLKs, 1 RLVS1, 1 RLVS2, 1 MS, and 1 MSD/DUP (or 1 LCSD if necessary)
- ☐ Write MBLK1, MBLK2, LCS, RLVS1, and RLVS2 on polypropylene centrifuge tubes.
- ☐ Weigh samples (5 mL samples) and record in batch sheet.
- ☐ Select a clean beaker and rinse 2 times with RO water (Section 8.1.2).
- ☐ Fill with ~30 mL RO water.
- ☐ Weigh 5 g of RO water into polypropylene centrifuge tubes for the MBLK1, MBLK2, LCS, RLVS1 and RLVS2.
- ☐ Pull the MS, MSD, LCS, RLVS1 and RLVS2 samples to the front.
- ☐ Target spike (ASTM Tgt Spike 100 ppb (Section 8.2.2)):
    - MS, MSD, and LCS
        - Ensure that the P-200 is set to 25 microliters (025)
        - New pipet tip on P-200
        - Wet pipet tip (1st stop)
        - Dispense to the second stop
        - Pull to the 1st stop.
        - Drag the tip across the vial lip to remove drops.
        - Guide the tip below the surface of the water and dispense to the 2nd stop
        - Dispose of tip.
        - Repeat procedure from “New pipet tip…” for MSD and LCS samples
    - RLVS1
        - Use the 3 culture tubes of Honeywell methanol to clean the 10 microliter syringe. Put the syringe needle into the “rough rinse” methanol. Pull the plunger up passed 10 microliters.
        - Dispense syringe in waste.
        - Repeat 3x for rough rinse. 2x for mid-level rinse, 1x for fine level rinse.
        - Pull target to the 4 microliter mark. Dispense to remove air bubbles.
        - Pull target to the 4 microliter mark. Dispense until there are 1.5 microliters of target in the syringe.
        - Use the syringe to transfer 0.5 microliters of target to the RLVS1 by placing the syringe tip into the centrifuge tube and dispensing until there is 1 microliter of target in the syringe.
        - Dispense the remaining target to waste.
    - RLVS2
        - Use the 3 culture tubes of Honeywell methanol to clean the 10 microliter syringe. Put the syringe needle into the “rough rinse” methanol. Pull the plunger up passed 10 microliters.
        - Dispense syringe in waste.
        - Repeat 3x for rough rinse. 2x for mid-level rinse, 1x for fine level rinse.
        - Pull target to the 4 microliter mark. Dispense to remove air bubbles.
        - Pull target to the 4 microliter mark. Dispense until there are 2.5 microliters of target in the syringe.

- Use the syringe to transfer 2.5 microliters of target to the RLVS2 by placing the syringe tip into the centrifuge tube and dispensing.

☐ Select a clean beaker and rinse once with a splash of Honeywell methanol (Section 8.1.3).
☐ Fill to just below the 200 mL mark for a full batch (30 samples + QC's)
☐ Using a graduated serological pipette, transfer 5 mL aliquots of methanol to each sample tube.
☐ Add 40 microliters of ASTM surrogate mix 20 ppb (Section 8.2.4) to all samples using the P-200 pipet.
- Ensure P-200 is set to 40 microliters (040)
- New pipet tip
- Wet pipet tip to the 1st stop
- Dispense to the 2nd stop
- Pull to the 1st stop.
- Drag tip across the vial lip to remove drops.
- Hover the tip over the lip of the centrifuge tube and dispense to 2nd stop.
- Repeat procedure from "Pull to the 1st…" until all samples are spiked with surrogate.

☐ Cap all centrifuge tubes.

Extraction

☐ Vortex all sample tubes and place each tube into Styrofoam holder.
☐ Shake the samples vigorously for 2 minutes.
☐ Return all samples to the test tube rack.
☐ Uncap all samples
☐ Using a P-200 spike 20 microliters of NH_4OH (Section 8.1.6) into each sample
- Ensure P-200 is set to 20 microliters (020)
- New pipet tip
- Wet pipet tip to the 1st stop
- Dispense to the 2nd stop
- Pull to the 1st stop
- Drag tip across vial lip to remove drops
- Hover the tip over the lip of the centrifuge tube and dispense to the 2nd stop.
- Repeat procedure from "Pull to the 1st…" until all samples are spiked with NH_4OH.

☐ Recap all centrifuge tubes. Make sure caps return to the tube they came from.
☐ Vortex samples and check pH (should fall around ~9). Adjust pH with additional NH_4OH if needed.
☐ Place each tube into Styrofoam holder.
☐ Shake all samples vigorously for 2 minutes.

Filtering

☐ Clean filters
- Collect a clean beaker.
- Rinse the beaker with a splash of acetonitrile (Section 8.1.13). Fill the beaker with acetonitrile.
- Collect the methanol beaker from earlier in the procedure. Fill this beaker with Honeywell methanol (Section 8.1.3).
- Attach an RT nylon filter (Filtrous, 0.45 um, 25 mm, SFN-AR-2025) to a 10 mL syringe (10 mL HSW 2-tlg/2-part dispenser)
- Take the plunger out of the syringe. Do not touch the bottom plunger with your gloves, or let it sit on the bench.
- Add ~10 mL of acetonitrile to the syringe. Do not touch the lip of the beaker.
- Replace the plunger. Depress and drain the acetonitrile into the waste.

- Remove the plunger again. Do not touch the bottom plunger with your gloves, or let it sit on the bench.
- Add ~10 mL of Honeywell methanol to the syringe. Do not touch the lip of the beaker.
- Replace the plunger. Depress and drain the methanol into the MeOH rinsate container.
- Remove the plunger once more. Replace the plunger to dispense air through the filter to remove residual solvent.

☐ Collect and label the correct number of clean 15 mL polypropylene centrifuge tubes.

☐ Filter samples

- Keep filters on clean paper towel.
- Work with one sample at a time.
- Remove the plunger
- Uncap sample tube that will be filtered.
- Pour the sample solution into the base of the syringe.
- Place the tip of the filter into the correctly labeled tube.
- Replace the plunger and dispense the extract into the polypropylene centrifuge tube.
- Spike 50 microliters of glacial acetic acid (Section 8.1.4)
  - Ensure the P-200 is set to 50 microliters (050)
  - New pipet tip
  - Wet tip to the 1st stop
  - Dispense to the 2nd stop
  - Draw to the 1st stop
  - Wipe tip on the lip of the vial to remove drops
  - Use free hand to steady the pipet
  - Hover the pipet tip over the lip of the culture tube
  - Dispense to the 2nd stop.
  - You can reuse this pipet tip if it only comes in contact with the acid.
- Cap centrifuge tube.
- Repeat this procedure from "Remove the plunger…" until all samples have been filtered and capped.

☐ Check the pH of each sample (should be ~3). Adjust pH with glacial acetic acid if required.

Prepping Vials

☐ Collect and label the correct number of 2 mL polypropylene autosampler vials.

☐ Using a P-1000 transfer an 800 microliter aliquot of each sample solution into vials

- Ensure the P-1000 is set to 800 microliters (080)
- New pipet tip
- Uncap the sample
- Wet tip to the 1st stop
- Dispense to the 2nd stop
- Draw to the 1st stop
- Wipe tip on the lip of the tube
- Guide the pipet tip into the correctly labeled vial
- Dispense to the 2nd stop.
- Cap vial with white PP/silicone caps.
- Repeat procedure from "New pipet tip…" until all samples have been put into vials.

☐ Vortex each vial and load samples in correct batch order.

Solid Sample Prep Checklist:

Batch Preparation

- ☐ Remove standard mixes: ASTM Tgt Spike 100 ppb (Section 8.2.2) and ASTM Surrogate Mix 20 ppb (Section 8.2.4) from the fridge and let warm to room temp. Vortex before use.
- ☐ Prepare 50:50 MeOH: H2O solvent
  - Make 400 mL for a full batch (make enough for the batch size)
  - Select a clean beaker
  - Rinse with a splash of Honeywell methanol (Section 8.1.3)
  - Clean a 250 mL graduated cylinder with a splash of Honeywell methanol.
  - Fill the graduated cylinder to the 200 mL mark.
  - Pour this portion into the beaker.
  - Rinse the 250 mL graduated cylinder 2x with RO water (Section 8.1.2).
  - Fill the graduated cylinder to the 200 mL mark.
  - Combine this portion with the methanol in the beaker.
  - Swirl to mix. Mix well.
- ☐ Assemble a batch of 30 samples (or fewer), 1 LCS, 2 MBLKs, 1 RLVS1, 1 RLVS2, 1 MS, and 1 MSD/DUP (and 1 LCSD if necessary)
- ☐ Label 15 mL polypropylene centrifuge tubes with correct sample ID's.
- ☐ Write MBLK1, MBLK2, LCS, RLVS1, and RLVS2 on polypropylene centrifuge tubes.
- ☐ Weigh samples (2.00 ± 0.10 g) and record in batch sheet.
- ☐ Weigh 2.00 ± 0.10 g of blank sand (Section 8.1.11) into polypropylene centrifuge tubes for the MBLK1, MBLK2, LCS, RLVS1 and RLVS2.
- ☐ Pull the MS, MSD, LCS, RLVS1 and RLVS2 samples to the front.
- ☐ Target spike (ASTM Tgt Spike 100 ppb (Section 8.2.2)):
  - MS, MSD, and LCS
    - Ensure that the P-20 is set to 10 microliters (100)
    - New pipet tip on P-20
    - Wet pipet tip (1st stop)
    - Dispense to the second stop
    - Pull to the 1st stop.
    - Drag the tip across the vial lip to remove drops.
    - Guide the tip into the matrix and dispense to the 2nd stop
    - Dispose of tip.
    - Use a graduated pipet to transfer a 10 mL aliquot of 50:50 MeOH: H_2O into the sample tube.
    - Do not touch the lip of the beaker or the tip of the pipet.
    - Repeat procedure from "New pipet tip…" for MSD and LCS samples
  - RLVS1
    - Use the 3 culture tubes of Honeywell methanol to clean the 10 microliter syringe. Put the syringe needle into the "rough rinse" methanol. Pull the plunger up passed 10 microliters.
    - Dispense syringe in waste.
    - Repeat 3x for rough rinse. 2x for mid-level rinse, 1x for fine level rinse.
    - Pull target to the 4 microliter mark. Dispense to remove air bubbles.
    - Pull target to the 4 microliter mark. Dispense until there are 1.5 microliters of target in the syringe.

- Use the syringe to transfer 0.5 microliters of target to the RLVS1 by placing the syringe tip into the sand and dispensing until there is 1 microliter of target in the syringe.
- Dispense the remaining target to waste.
- Use a graduated pipet to transfer a 10 mL aliquot of 50:50 MeOH: H_2O into the sample tube.

- RLVS2
  - Use the 3 culture tubes of Honeywell methanol to clean the 10 microliter syringe. Put the syringe needle into the "rough rinse" methanol. Pull the plunger up passed 10 microliters.
  - Dispense syringe in waste.
  - Repeat 3x for rough rinse. 2x for mid-level rinse, 1x for fine level rinse.
  - Pull target to the 4 microliter mark. Dispense to remove air bubbles.
  - Pull target to the 4 microliter mark. Dispense until there are 2.5 microliters of target in the syringe.
  - Use the syringe to transfer 2.5 microliters of target to the RLVS2 by placing the syringe tip into the sand and dispensing.
  - Use a graduated pipet to transfer a 10 mL aliquot of 50:50 MeOH: H_2O into the sample tube.

☐ Add 40 microliters of ASTM surrogate mix 20 ppb (Section 8.2.4) to all samples using the P-200 pipet.
- Ensure P-200 is set to 40 microliters (040)
- New pipet tip
- Wet pipet tip to the 1st stop
- Dispense to the 2nd stop
- Pull to the 1st stop.
- Drag tip across the vial lip to remove drops.
- Hover the tip over the lip of the centrifuge tube and dispense to 2nd stop.
- Repeat procedure from "Pull to the 1st…" until all samples are spiked with surrogate.

☐ Add 20 microliters of NH_4OH (Section 8.1.6) to all samples using the P-200 pipet
- Ensure P-200 is set to 20 microliters (020)
- New pipet tip
- Wet pipet tip to the 1st stop
- Dispense to the 2nd stop
- Pull to the 1st stop.
- Drag tip across the vial lip to remove drops.
- Hover the tip over the lip of the centrifuge tube and dispense to 2nd stop.
- Repeat procedure from "Pull to the 1st…" until all samples are spiked with NH_4OH.

☐ Cap and vortex all centrifuge tubes.

☐ Vortex samples and check pH (should fall around ~9). Adjust pH with additional NH_4OH if needed.

Extraction

☐ Vortex all sample tubes until fully mixed and place each tube into the Styrofoam holder.

☐ Place the tubes and holder inside of a plastic bag.

☐ Place the bag with the tubes inside a compartment of a rotor tumbler.

☐ Pack the samples in securely with foam to stabilize the samples.

☐ Close and latch the tumbler.

☐ Turn on the tumbler. You should not hear the samples moving inside.

☐ Allow the samples to tumble for 1 hour.

- ☐ Transfer samples to the centrifuge
  - **BALANCE THE CENTRIFUGE**
  - Place the centrifuge tubes in the small brown inserts.
  - Place the inserts in the centrifuge.
  - Ensure the centrifuge is balanced and the inserts are fully in place
  - Centrifuge at 1900 rpm for 10 minutes (Setting 1)
- ☐ Pull the inserts from the centrifuge.
- ☐ Collect sample tubes and put them into numeric order.

Filtering

- ☐ Clean filters
  - Collect a clean beaker.
  - Rinse the beaker with a splash of acetonitrile (Section 8.1.13). Fill the beaker with acetonitrile.
  - Collect a second beaker and rinse with a splash of Honeywell methanol (Section 8.1.3). Fill this beaker with Honeywell methanol.
  - Attach an RT nylon filter (Filtrous, 0.45 um, 25 mm, SFN-AR-2025) to a 10 mL syringe (10 mL HSW 2-tlg/2-part dispenser)
  - Take the plunger out of the syringe. Do not touch the bottom plunger with your gloves, or let it sit on the bench.
  - Add ~10 mL of acetonitrile to the syringe. Do not touch the lip of the beaker.
  - Replace the plunger. Depress and drain the acetonitrile into the waste.
  - Remove the plunger again. Do not touch the bottom plunger with your gloves, or let it sit on the bench.
  - Add ~10 mL of Honeywell methanol to the syringe. Do not touch the lip of the beaker.
  - Replace the plunger. Depress and drain the methanol into the MeOH rinsate container.
  - Remove the plunger once more. Replace the plunger to dispense air through the filter to remove residual solvent.
- ☐ Collect and label the correct number of clean 15 mL polypropylene centrifuge tubes.
- ☐ Filter samples
  - Keep filters on clean paper towel.
  - Work with one sample at a time.
  - Remove the plunger
  - Uncap sample tube that will be filtered.
  - Pour the sample solution into the base of the syringe.
  - Place the tip of the filter into the correctly labeled tube.
  - Replace the plunger and dispense the extract into the centrifuge tube
  - Spike 80 microliters of glacial acetic acid (Section 8.1.4)
    - Ensure the P-200 is set to 80 microliters (080)
    - New pipet tip
    - Wet tip to the 1st stop
    - Dispense to the 2nd stop
    - Draw to the 1st stop
    - Wipe tip on the lip of the vial to remove drops
    - Use free hand to steady the pipet
    - Hover the pipet tip over the lip of the tube

- Dispense to the 2nd stop.
- You can reuse this pipet tip if it only comes in contact with the acid.

- Cap tube.
- Repeat this procedure from "Remove the plunger…" until all samples have been filtered and capped.

☐ Check the pH of each sample (should be ~3). Adjust pH with additional glacial acetic acid if required.

Prepping Vials

☐ Collect and label the correct number of 2 mL polypropylene autosampler vials.

☐ Using a P-1000, transfer an 800 microliter aliquot of each sample solution into vials

- Ensure the P-1000 is set to 800 microliters (080)
- New pipet tip
- Uncap the sample
- Wet tip to the 1st stop
- Dispense to the 2nd stop
- Draw to the 1st stop
- Wipe tip on the lip of the tube
- Guide the pipet tip into the correctly labeled vial
- Dispense to the 2nd stop.
- Cap vial with white PP/silicone cap.
- Repeat procedure from "New pipet tip…" until all samples have been put into vials.

☐ Vortex each vial and load samples in correct batch order.

Appendix B: Extraction Batch and Analytical Batch Sequence Summaries:

Extraction Batch Summary:

Each ASTM D7979/D7968 extraction batch of 30 or less samples must contain:
2 method blanks
1 RLVS (typically 2)
1 LCS
(1 LCSD if necessary)
1 MS
1 Duplicate or MSD

Each EPA 8327/3512 extraction batch of 20 or less samples must contain:
1 method blank (or 2)
1 RLVS (typically 2)
1 LCS
(1 LCSD if necessary)
1 MS
1 Duplicate or MSD

Suggested Analytical Batch Sequence:

CCB (not required)
CCV (not required)
Extraction Blank 1
RLVS1
Extraction Blank 2 (if applicable)
RLVS2 (if applicable)
LCS
LCSD (if applicable)
Matrix QC
Samples
CCV