PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN SOIL BY MULTIPLE REACTION MONITORING (MRM) LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS)

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1.0 SCOPE AND APPLICATION

This method is used for the extraction and analysis of selected per- and poly-fluoroalkyl substances (PFAS) in soil by solvent extraction followed by analysis using liquid chromatography/tandem mass spectrometry (LC/MS/MS). The analytes are extracted with methanol: water (1:1) under basic conditions (pH ~ 9-10 adjusted with ammonium hydroxide), filtered, acidified with acetic acid (pH ~3-4) and analyzed by LC/MS/MS.

The following PFAS analytes have been determined by this method and are provided below. The analyte list, method detection limits (MDLs) and reporting ranges for these compounds are listed in Table 1 (Section 17.0). This standard operating procedure (SOP) has been tested on Ottawa sand and four (ASTM) soils: sand, silt, fat clay, and lean clay.

Analyte	CAS RN
PFAS sulfonic acids	
Perfluorobutyl sulfonic acid (PFBS)	29420-49-3
Perfluorohexyl sulfonic acid (PFHxS)	3871-99-6
Perfluorooctyl sulfonic acid (PFOS)	1763-23-1
1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS)	757124-72-4
1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	27619-97-2
1H, 1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	39108-34-4

Analyte	CAS RN
Perfluoro-1-pentanesulfonic acid (L-PFPeS)	706-91-4
Perfluoro-1-heptanesulfonic acid (L-PFHpS)	375-92-8
Perfluoro-1-nonanesulfonic acid (L-PFNS)	68259-12-1
Perfluoro-1-decanesulfonic acid (L-PFDS)	2806-15-7
PFAS carboxylic acids	
Perfluorobutanoic acid (PFBA)	375-22-4
Perfluoropentanoic acid (PFPeA)	2706-90-3
Perfluorohexanoic acid (PFHxA)	307-24-4
Perfluoroheptanoic acid (PFHpA)	375-85-9
Perfluorooctanoic acid (PFOA)	335-67-1
Perfluorononanoic acid (PFNA)	375-95-1
Perfluorodecanoic acid (PFDA)	335-76-2
Perfluoroundecanoic acid (PFUdA)	2058-94-8
Perfluorododecanoic acid (PFDoA)	307-55-1
Perfluorotridecanoic acid (PFTrDA)	72629-94-8
Perfluorotetradecanoic acid (PFTeDA)	376-06-7
PFAS sulfonamides and sulfonamidoacetic acids	
N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)	2355-31-9
Perfluoro-1-octanesulfonamide (FOSA)	754-91-6

1.1 The information contained in this method is provided by the U.S. Environmental Protection Agency (EPA) as guidance to be used by the analyst in making judgments necessary to generate results that meet the data quality objectives (DQOs) or the intended application.

1.2 This method is restricted to use by, or under supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A soil sample (~ 2 g) is weighed in a polypropylene tube, spiked with surrogates (all samples) and then extracted with 10 mL of methanol: water (1:1) at a pH of 9-10 (adjusted by adding ammonium hydroxide). The sample is then tumbled on a rotator for 1 hour and filtered through an Acrodisc GxF/0.2 micron GHP membrane syringe-driven filter unit. Acetic

acid (~ 50 µL) is added to all the samples to adjust the pH (~ 3-4) and is then analyzed by LC/MS/MS.

2.2 The target compounds are identified by comparing the single reaction monitoring (SRM) transitions ratio in the sample to the SRM transitions ratio in the standards (Appendix – Table 3). Certain PFAS analytes only have a primary SRM transition that is used for identification and quantitation. The retention time (RT) for the analytes of interest must also agree with the RT of the mid-level standard by ±5% (0.05). The target compounds are quantitated by external calibration. As an additional QC measure, isotopically-labeled PFAS surrogate (listed in Sections 7.3.10) recoveries are monitored; the percent recovery of each should fall within the control limits of the method (Section 17.0, Table 2). Compounds from this SOP are reported to the quantitation limit (QL) in nanograms per kilogram (ng/kg) dry weight.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure. See Glossary (Section 17.0, Appendix THREE) for relevant terms and acronyms.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, LC vials/caps, disposable pipettes, and other apparatus that lead to discrete artifacts or elevated baselines in the selected ion current profiles. All materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Careful selection of reagents and consumables is necessary to ensure they are PFAS free. Refer to each method to be used for specific guidance on QC procedures and to Chapter Four for general guidance on glassware cleaning.

4.2. Refer to Methods 3500 and 8000 for discussions of interferences. Matrix interferences may be caused by contaminants from the sample, sampling devices, or storage containers. The extent of matrix interferences will vary considerably from sample source to sample source, depending upon variations of the sample matrix.

4.3 Procedures employed to prevent or minimize problems are as follows:

4.3.1 All reagents and solvents should be of pesticide-residue purity or higher to minimize interference problems, preferably LC/MS Grade.

4.3.2 PFAS have been found in reagents, glassware, tubing, polytetrafluoroethylene (PTFE) LC vial caps, glass disposable pipettes, filters, degassers, and other apparatus. All the supplies should be checked to determine if any target analytes of interest could potentially be contaminants by analyzing laboratory

method blanks under the same conditions as the samples. If found, measures should be taken to remove the contamination or data should be qualified.

4.3.3 The LC system used should have components replaced when possible with materials known to not contain fluorinated target analytes of interest.

4.3.4 Polyethylene LC autosampler vial caps or target analyte-free vial caps should be used. PTFE-lined caps may not be used.

4.3.5 Polyethylene disposable pipettes or target analyte-free pipettes should be used. All disposable pipettes should be checked for release of target analytes of interest.

4.3.6 Degassers are important to continuous LC operation and most commonly are made of fluorinated polymers. To enable use, an isolator column should be placed after the degasser and prior to the sample injection valve to prevent contamination.

4.3.7 The procedure described in the glassware cleaning section (Section 6.4) should be followed to be sure that glassware is free from interferences. Solvents, reagents, gases, other samples, and the environment in which the analysis is performed may yield PFAS artifacts and/or interferences for target analytes. The sample preparation and analysis process must be demonstrated to be free from observable interferences by the analysis of method blanks. All solvents should be of pesticide residue purity or higher to minimize interference problems, preferably LC/MS grade.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of U.S. Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs) must be available to all personnel involved in these analyses.

5.2 Users of this method should operate a formal safety program.

5.3 The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound is treated as a health hazard. Exposure to these chemicals should be reduced to the lowest possible level and the appropriate personal protective equipment (PPE) should be utilized. Review SDSs for specific physical and health hazards including appropriate PPE to be used. SDSs may be accessed at multiple locations (e.g., www.sigmaaldrich.com, www.well-labs.com, and www.isotope.com).

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in this method represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented. This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Equipment

6.1.1 Liquid chromatograph (LC) system: A Waters Acquity H-Class UPLC® (ultraperformance liquid chromatograph) with stainless steel flow through needle design was used to generate data during method development (PEEK needles may not puncture polyethylene caps; pre-slitting of caps is not allowed). Other systems may be used, provided that method performance is appropriate for the application.

6.1.2 Analytical column: A Waters Acquity UPLC® CSHTM Phenyl-Hexyl, 2.1×100 mm and 1.7 µm particle size (Waters part no. 186005407) was used to generate data during method development. Other columns may be used, provided that method performance can be achieved.

6.1.3 Isolator column: XBridge BEH C18, 2.1×50 mm, 3.5 µm particle size (Waters part no. 186003021) was used to generate data during method development. Other columns may be used, provided that method performance can be achieved.

6.1.4 Mass spectrometer (MS) system: An MS capable of multiple reaction monitoring (MRM) analysis with fast enough cycle time to obtain at least ten scans over a peak is needed with adequate sensitivity. A Waters Xevo TQ-S triple quadrupole MS was used to generate data during method development. Other systems may be used provided that method performance can be achieved.

6.1.5. Data Backup Device - A data archival unit to store data. All lab generated data are stored on the primary lab server. In addition, the laboratory should have the capability to store and retrieve data using other devices such as the networked secure server, external drives, and CD or DVD writers.

6.1.6. Data System - MassLynx™ interfaced to the LC/MS/MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. QuanLynx™ or TargetLynx™ is used in conjunction for data quantitation. Other equivalent data systems may be used.

6.2 Support equipment

6.2.1 Adjustable volume pipettes, 10-µL, 20-µL, 100-µL, 200-µL, and 1000-µL, 5-mL, and 10-mL

6.2.2 Analytical balance, accurate to ± 0.1% of sample mass.

6.3 Glassware and miscellaneous supplies

6.3.1 Autosampler vials, 2 mL (Waters, Part no. 186000847C or equivalent)

6.3.2 Polyethylene autosampler vial caps (Waters, Part no. 186004169 or equivalent)

6.3.3 Filter-adaptable glass syringe with luer lock, 10-to 25 mL (polypropylene syringes with rubber tipped plungers are not to be used).

6.3.4 Polypropylene tubes, 50-mL (BD Falcon, Catalog # 352098, shown to be

PFAS free)

6.3.5 Polypropylene tubes, 15-mL pre-weighed for collection of field samples and QC (BD Falcon, Catalog # 352097, shown to be PFAS free)

6.3.6 Ultrapure argon and nitrogen gases

6.3.7 Volumetric glassware, Class A

6.3.8 Polypropylene pipette tips free of release agents or low retention coating of various sizes (Eppendorf, catalogue nos. 022491997, 022492080, 022491954, 022491946, and 022491512 or equivalent)

6.3.9 Acrodisc GxF/0.2µm GHP membrane syringe-driven filter unit (Source - PALL Life Sciences, Part # AP-4307T). The Acrodisc filters are washed with at least 10 mL acetonitrile followed by 20 mL methanol prior to use.

6.3.10 Polyethylene disposable pipettes (SEDI-PETTM PIPET, Source - Samco Scientific, part no. 252 or equivalent)

6.4 Glassware cleaning instructions – If glassware is used, wash in hot water and rinse with reagent water. The glassware is then dried in an oven at 300 ºC up to 1 hour (except volumetric glassware, which is air dried). All glassware is subsequently rinsed with an organic solvent such as methanol, and/or acetonitrile.

It is highly recommended to soak the syringe and plunger in **hot tap water** in a PFAS-free container and then rinse thoroughly with PFAS-free reagent water, and then two times with 10 mL of acetonitrile methanol (1:1). Attach the Acrodisc filters to the syringe and wash the assembly two times with 10 mL of acetonitrile and twice with 10 mL of methanol prior to use. Repeat this process for subsequent batches. Air dry to ensure that solvent residues do not remain in the assembly.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade or pesticide grade chemicals, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where specifications are available. Other grades may be used, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent leaching of contaminants from plastic containers. All reagents must be tested to ensure that they are PFAS-free prior to use.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Items shown are for informational purpose only; equivalent reagents and standards may be used. All reagents and solvents should be of pesticide residue purity or higher to minimize interference problems, preferably LC/MS grade or equivalent.

7.3.1 Acetonitrile, (CAS # 75-05-8, Source: Fisher Scientific, Catalog # A955-4)

7.3.2 Water, HPLC mass spectrometry pesticide quality, in-house ASTM Type I water of specification D1193.

7.3.3 Methanol, (CAS # 67-56-1, Source: Fisher Scientific, Catalog # A456-4)

7.3.4 Isopropyl alcohol, (CAS # 67-63-0, Source: OmniSolv, Catalog # PX1834-1)

7.3.5 Ammonium hydroxide, (CAS # 1336-21-6, Catalog # 221228-1L-A, Source: Sigma Aldrich)

7.3.6 Ammonium acetate, (CAS # 631-61-8, Catalog # 372331-100g, Source: SigmaAldrich)

7.3.7 Acetic acid, (CAS # 64-19-7, Source: Fisher Scientific, Catalog # A38-500)

7.3.8 Reagent Sand, (CAS # 14808-60-7, Source: Sigma-Aldrich, Catalog # 274739)

7.3.9 Native Per-and Poly-fluoroalkyl Substance Stock Solution, containing eleven native linear perfluoroalkylcarboxylic acids, seven native perfluoroalkylsulfonates, three native telomere sulfonates, two native perfluorooctanesulfonamidoacetic acids and one perfluoro -1 octanesulfomide, 2000 ng/ml Methanol/Isopropanol (4%)/Water (<1%), (Wellington Labs, Product code PFAC-24PAR).

7.3.9.1 Perfluorobutyl sulfonic acid (PFBS), $C_4F_9SO_3$- (CAS RN 29420-49-3)

7.3.9.2 Perfluorohexyl sulfonic acid (PFHxS), $C_6F_{13}SO_3$- (CAS RN 3871-99-6)

7.3.9.3 Perfluorooctyl sulfonic acid (PFOS), $C_8F_{17}SO_3$- (CAS RN 1763-23-1)

7.3.9.4 1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS), $C_6H_4F_9SO_3$- (CAS RN 757124-72-4)

7.3.9.5 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS), $C_8H_4F_{13}SO_3$- (CAS RN 27619-97-2)

7.3.9.6 1H, 1H, 2H, 2H-perfluordecane sulfonic acid (8:2 FTS), $C_{10}H_4F_{17}SO_3$- (CAS RN 39108-34-4)

7.3.9.7 Perfluoro-1-pentanesulfonic acid (PFPeS, $C_5F_{11}SO_3$-, CAS RN 2706-91-4)

7.3.9.8 Perfluoro-1-heptanesulfonic acid (PFHpS), $C_7F_{15}SO_3$- (CAS RN 375-92-8)

7.3.9.9 Perfluoro-1-nonanesulfonic acid (PFNS), $C_9F_{19}SO_3$- (CAS RN 68259-12-1)

7.3.9.10 Perfluoro-1-decanesulfonic acid (PFDS) $C_{10}F_{21}SO_3$- (CAS RN 2806-15-7)

7.3.9.11 Perfluorobutanoic acid (PFBA), $C_4F_7O_2$- (CAS RN 375-22-4)

7.3.9.12 Perfluoropentanoic acid (PFPeA), $C_5F_9O_2$- (CAS RN 2706-90-3)

7.3.9.13 Perfluorohexanoic acid (PFHxA), $C_6F_{11}O_2$- (CAS RN 307-24-4)

7.3.9.14 Perfluoroheptanoic acid (PFHpA), $C_7F_{13}O_2$- (CAS RN 375-85-9)

7.3.9.15 Perfluorooctanoic acid (PFOA), $C_8F_{15}O_2$ (CAS RN 335-67-1)

7.3.9.16 Perfluorononanoic acid (PFNA), $C_9F_{17}O_2$- (CAS RN 375-95-1)

7.3.9.17 Perfluorodecanoic acid (PFDA), $C_{10}F_{19}O_2$- (CAS RN 335-76-2)

7.3.9.18 Perfluoroundecanoic acid (PFUdA), $C_{11}F_{21}O_2$- (CAS RN 2058-94-8)

7.3.9.19 Perfluorododecanoic acid (PFDoA), $C_{12}F_{23}O_2$- (CAS RN 307-55-1)

7.3.9.20 Perfluorotridecanoic acid (PFTrDA), $C_{13}F_{25}O_2$- (CAS RN 72629-94-8)

7.3.9.21 Perfluorotetradecanoic acid (PFTeDA), $C_{14}F_{27}O_2$- (CAS RN 376-06-7)

7.3.9.22 N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA), $C_{12}H_8F_{17}NO_4S$ (CAS RN 2991-50-6, Wellington Labs, Part No. N-EtFOSAA)

7.3.9.23 N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA), $C_{11}H_6F_{17}NO_4S$ (CAS RN 2355-31-9)

7.3.9.24 Perfluoro-1-octanesulfonamide (FOSA), $C_8H_2F_{17}NO_2S$ (CAS RN 754-91-6)

7.3.10 PFAS Stock Surrogates Mix, 1000 ng/mL in Methanol/Isopropanol (2%)/Water (<1%), (Wellington Labs, Product code MPFAC-24ES)

7.3.10.1 Perfluoro-1-[2,3,4-$^{13}C_3$]butyl sulfonic acid (M3PFBS) [sodium salt form]

7.3.10.2 Perfluoro-1-[1,2,3-$^{13}C_3$]hexyl sulfonic acid (M3PFHxS) [sodium salt form]

7.3.10.3 Perfluoro-1-[$^{13}C_8$]octyl sulfonic acid (M8PFOS) [sodium salt form]

7.3.10.4 Perfluoro-n-[$^{13}C_4$]butanoic acid (M4PFBA)

7.3.10.5 Perfluoro-n-[$^{13}C_5$]pentanoic acid (M5PFPeA)

7.3.10.6 Perfluoro-n-[1,2,3,4,6-$^{13}C_5$hexanoic acid (M5PFHxA)

7.3.10.7 Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid (M4PFHpA)

7.3.10.8 Perfluoro-n-[$^{13}C_8$]octanoic acid (M8PFOA)

7.3.10.9 Perfluoro-n-[$^{13}C_9$]nonanoic acid (M9PFNA)

7.3.10.10 Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$]decanoic acid (M6PFDA)

7.3.10.11 Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$]undecanoic acid (M7PFUnA)

7.3.10.12 Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid (MPFDoA)

7.3.10.13 Perfluoro-n-[1,2-$^{13}C_2$]tetradecanoic acid (M2PFTeDA)

7.3.10.14 1H, 1H, 2H, 2H-perfluoro-(1,2-$^{13}C_2$) hexyl sulfonic acid (M2-4:2 FTS) [sodium salt form]

7.3.10.15 1H, 1H, 2H, 2H-perfluoro-1(1,2-$^{13}C_2$) octyl sulfonic acid (M2-6:2 FTS), Wellington Labs, Part No. M2-6:2FTS, sold as the sodium salt)

7.3.10.16 1H, 1H, 2H, 2H-perfluoro-1(1,2-$^{13}C_2$) decyl sulfonic acid (M2-8:2 FTS) [sodium salt form]

7.3.10.17 N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)

7.3.10.18 N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA), (Wellington Labs, Part No. d5-N-EtFOSAA)

7.3.10.19 Perfluoro-1-[$^{13}C_8$]octanesulfonamide (M8FOSA)

NOTE: Alternatively neat standards may be purchased and prepared for the target and surrogate spike solutions. This gives the lab the option of using a mixed standard solution from which they would prepare their calibration and spike solutions or weigh out each individual PFAS compound, adjust for purity and dilute accordingly. When standard compound purity is assayed to be 98% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Expiration time is one year from the time prepared. The spiking standards and surrogates can be used for more than one year if they fall within ± 20% of the expected concentration from a calibration standard that is less than 1 year old.

7.3.11 Second source standard

7.3.11.1 The second source must be different than the one shown here. Another Wellington Standard, PFAC-24PAR (Different Lot number) may be available as a second source that contains all twenty-four target analytes. If a

second source is available, an initial calibration verification (ICV) sample should be prepared at or near the mid-level calibration standard.

7.4 Standard solutions - All standards must be kept away from PFAS-containing packaging and materials used in preparation and storage. In order to prevent standard solutions from degrading, all standard solutions are stored at ≤6º C in the refrigerator. Instruction procedures for the preparation of QC batch samples and calibration standards are found in Sec. 7.4.1-7.4.4. The instructions for the preparation of Calibration standards, spiking solutions, and QC batch samples are listed below.

7.4.1 A surrogate spiking solution containing the nineteen isotopically-labeled PFAS is added to all environmental and QC samples. Add 1000 µL of a 1.0 µg/mL PFAS surrogate mix purchased from Wellington (Section 7.3.10) to 50 mL with 95:5 acetonitrile and water, producing a spiking solution at 20 µg/L. Add 40 µL of this intermediate solution to a 2-g sample to achieve a final concentration of 400 ng/kg.

7.4.2 A PFAS Spiking Solution is prepared from a commercially available 2 µg/mL standard from Wellington Labs, Product code PFAC-24PAR (Section 7.3.9). Add 500 µL of this standard to a 50-mL volumetric flask and dilute up to volume using 95:5 acetonitrile/water (v/v) to produce a 20 µg/L intermediate spiking solution. Dilute to prepare the highest-level calibration standard (LV9). Use calibrated automatic pipettes with polypropylene tips to prepare solutions without transferring from any other container or glassware.

The calibration levels (prepared from the LV9 calibration standard), laboratory control samples, matrix spike samples, and duplicates are prepared for each batch of samples. A continuing calibration verification (CCV) check standard is also prepared for each batch of samples. Should field and/or batch QC samples require re-analysis, calibration standard levels, a second source calibration check (if available), a CCC, and a reagent blank shall be freshly prepared.

7.4.3 Matrix spike/matrix spike duplicate (MS/MSD) and laboratory control sample (LCS) spiking solution - Each MS/MSD and LCS sample are spiked with the PFAS 20 µg/mL intermediate spiking solution to achieve a nominal concentration of 400 ng/kg for in a 2-g soil sample. Add 40 µL of the PFAS intermediate spiking solution to each MS/MSD and LCS.

7.4.4 Lower Limit of Quantitation (LLOQ) spiking solution

The LLOQ spiking solution is prepared in 95:5 acetonitrile and water from the 2 µg/mL standard from Wellington Labs (Product code PFAC-24PAR). Add 50 µL of a 2 µg/mL standard into a 50 mL volumetric flask and dilute to with 95:5 acetonitrile/water (v/v) resulting in a 2 µg/L concentration for all analytes. The LLOQ sample is prepared by spiking 2-g reagent sand with the 25 µL of the PFAS LLOQ spiking solution to achieve a nominal concentration of 25 ng/kg for the 24 PFAS analytes (Sections 7.3.9).

7.4.5 Calibration standards

Add 500 µL of the surrogate spiking solution and 500 µL of the PFAS Spiking Solution into a 50-mL volumetric flask and dilute to volume with a 1:1 methanol and water solution containing 0.1% acetic acid. This LV9 standard (Section 17.0, Table 4), containing 200 ng/L of all PFAS analytes, is diluted to prepare Levels 1 through 8 as

shown in Tables 4 and 5 (Section 17.0). All calibration standards should contain 1:1 methanol and water with 0.1% acetic acid.

CAUTION: The continuing calibration check analyzed at the end of the sequence must be prepared in a separate LC vial near the mid-point of the calibration. All prepared calibration level standards should only be injected once since some of the analytes or solvent may evaporate after the vial cap is pierced; the polypropylene caps are not self-sealing.

7.4.6. Second source calibration check solution

A second source calibration check solution should be prepared and analyzed (if a second source is available) at a concentration at or near the mid-point of the calibration curve and at the same composition of the calibration solvent.

NOTE: The second source standard may contain PFOS and PFHxS as linear compounds as opposed to branched. PFOS and PFHxS are calibrated as branched compounds as that's how they are likely to appear in nature.

NOTE: The availability of commercial PFAS standards is quite limited. Currently, only one vendor has been identified by the Chicago Regional Laboratory that provides all the PFAS standards necessary to perform this SOP that are of adequate purity and accompanied by certificates of analysis.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation, and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation, and storage requirements.

8.1 Sample collection criteria - Grab samples are collected in 50-mL polypropylene containers or PFAS-free containers such as high-density polyethylene (HDPE) bottles. PTFE containers and contact surfaces with PTFE must be avoided. Field blanks are needed to follow conventional sampling practices.

Conventional laboratory practices involving chain of custody, field sampling, lab custody beginning with receipt and transfer custody, and sampling protocols should be followed. Extra samples must be collected in order to analyze duplicate and matrix spike samples for quality control purposes.

8.2 Sample preservation and storage - All samples are iced or refrigerated at ≤6 °C (protect from freezing) from the time of collection until sample analysis. Once extracted, filtered samples are stored in the refrigerator at ≤6°C (protect from freezing). Holding times have not yet been established for these analytes in various matrices. Based on an EPA preliminary holding time study, a 28-day limit for analysis may be used for analyses used as a guide until a more formal study is completed.

9.0 QUALITY CONTROL

9.1 General guidance - Refer to Chapter One for guidance on quality assurance (QA) and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and Chapter One criteria; technique-specific QC criteria take precedence over Chapter One criteria. Any effort involving collection of analytical data should include development of a structured and systematic planning document, such as a quality assurance project plan (QAPP) or a sampling and analysis plan (SAP), which translates project objectives and specifications into directions for those implementing the project and assess the results.

Each laboratory should maintain a formal QA program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged, as described in Sec. 9.9.1.3. Use of instrument specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and QC data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation and cleanup techniques. Any more specific QC procedures provided in this method will supersede those noted in Methods 3500 or 8000.

9.3 QC procedures necessary to evaluate the LC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification, and chromatographic analysis of samples.

9.4 Initial demonstration of proficiency (IDP) - The initial demonstration of method proficiency must be performed by the laboratory prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure, and change in analyst). Refer to Method 8000 Sec. 9.0 for additional information regarding instrument, procedure, and analyst IDPs. An IDP must consist of replicate reference samples from each sample preparation and determinative method combination it utilizes by generating data of acceptable precision and bias for target analytes in a clean reference matrix taken through the entire preparation and analysis. If an autosampler is used to perform sample dilutions, prior to use, the laboratory should demonstrate that those dilutions are equivalent to that achieved by an experienced analyst performing manual dilutions.

For an IDP study, at least 4 samples containing all the PFAS and surrogates at or near the midpoint (e.g. LV 6 concentration in Sec. 17.0, Table 4) must be analyzed as replicates. These samples are then analyzed according to the method described in Method 8000 Sec. 9.0. Preliminary precision and bias (P&B) acceptance criteria are 30% (RSD) and 70-130% (recovery). Each analyst must have an approved IDP prior to reporting data.

The concentration of an analyte is calculated using Equation 1.

$$\mathrm{Cs\ (ng\ /\ kg)} = \frac{[\mathrm{Ci\ (ng\ /\ L)}] \times [\mathrm{Vs\ (L)}]}{[\mathrm{Wd\ (kg)}]}$$

Where:

C_s = Concentration of target analyte in sample
C_i = Concentration of target analyte in sample from instrument
V_s = Volume of sample
W_d = Dry weight of sample

Example calculation of sample dilution

The analysis of PFAS may require dilution per sample. An example calculation is given in Equation 2.

$$\frac{V_f}{V_i}(C_u) = C_f$$

V_f = final volume (total volume of sample and methanol)
V_i = initial volume (amount of sample from difference weight)
C_u = uncorrected concentration
C_f = final concentration (corrected for dilution)

9.5 Blanks

9.5.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank (MB) and instrument or reagent blank that equipment and reagents are free from contaminants and interferences. If a peak is found in the blank that would prevent the identification or bias the measurement of an analyte, the analyst should determine the source of the contaminant peak and eliminate it, if possible. As a continuing check, each time a batch of samples is prepared and analyzed, and when there is a change in reagents, a MB must be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. MBs and field blanks must be carried through all stages of sample preparation and analysis. At least one MB or instrument blank must be analyzed on every instrument after calibration standard(s) and prior to the analysis of any samples.

9.5.2 Blanks are generally considered to be acceptable if target analyte concentrations are less than one half the LLOQ or are less than project-specific requirements. Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e., targets are not present in samples or sample concentrations/responses are ≥10X the blank). Other criteria may be used depending on the needs of the project.

9.5.3 If an analyte of interest is found in a sample in the batch near a concentration confirmed in the blank (refer to Sec. 9.5.2), the presence and/or concentration of that analyte should be considered suspect and may require qualification. Samples may require re-extraction and/or re-analysis if the blanks do not meet laboratory-established or project-specific criteria. Re-extraction and/or re-analysis is *not* necessary if the analyte concentration falls well below the action or regulatory limit or if the analyte is deemed not important for the project.

9.5.4 When new reagents or chemicals are received, the laboratory should monitor the blanks associated with samples for any signs of contamination. It may be necessary to test every new batch of reagents or chemicals prior to sample preparation as PFAS contamination is common. If reagents are changed during a preparation batch, separate blanks should be prepared for each set of reagents.

9.5.5 The laboratory should not subtract the results of the MB from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the MB results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the MB results, and a discussion of the corrective actions undertaken by the laboratory.

9.5.6 For every 20 field samples, at least two method blanks will be prepared in sand to investigate for contamination throughout sample preparation, extraction, and analysis. A reagent blank is prepared each day with a 1:1 methanol and water solution containing 0.1% acetic acid for every 20 samples (or a batch) to investigate for system/laboratory contamination. Data qualification based on interference evident in the method blank follows the guidelines provided in Sec. 9.5.2.

9.5.7 The concentration of target analytes in either/both blank(s) must be less than half the LLOQ, or the associated data must be qualified “K” for high bias due to blank contamination. Alternatively, the LLOQ in the associated sample(s) must be raised to three times the blank contamination concentration. Since a quadratic fit is often used, the concentrations below the LLOQ have greater bias. The response of the blank should be less than half the response in the LLOQ calibration standard, or the data are qualified “J” for a possible blank contamination issue or the LLOQ is raised to three times above the estimated blank contamination concentration.

9.5.8 A reagent blank is prepared each day with a 1:1 methanol and water solution containing 0.1% acetic acid to investigate for system/laboratory contamination. The concentration of target analytes in the reagent blank must be less than half the LLOQ, or the associated data must be qualified “K” for high bias due to blank contamination if analyte present. Alternatively, the LLOQ in the associated sample(s) must be raised to three times the blank contamination concentration. PFAS contamination at low levels is common in laboratory supplies and equipment. The 1:1 methanol and water solution containing 0.1% acetic acid is checked to ensure undetectable or negligible PFAS presence that will not affect the quantitation at the LLOQ.

9.6 Sample QC for preparation and analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch. The addition of surrogates to each field sample and QC sample is also required. Any method blanks, matrix spike samples, and duplicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.6.1 Matrix Spikes/Duplicates - Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an

unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.6.1.1 When required or available, a matrix spike and matrix spike duplicate (Sec. 11.1.5) is prepared for each matrix at a frequency of at least one MS/MSD pair for every 20 field samples to investigate for matrix interferences. If the laboratory has not received MS/MSD samples for site-specific matrix evaluation, this QC check is excluded.

9.6.1.2 As part of a QC program, spike accuracy for each matrix is monitored. The preliminary acceptance criteria are 70-130%. Bias is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate (if performed) and LCS according to the following

$$Recovery = \%R = \frac{(C_s - C_u)}{C_n} \; x \; 100$$

where:

C_s = Measured concentration of spiked sample aliquot

C_u = Measured concentration of unspiked sample aliquot (use 0 for LCS)

C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot (for LCS).

Matrix spike/matrix spike duplicate recoveries may not be meaningful if the amount of analyte in the sample is large relative to the amount spiked.

9.6.1.3 Criteria for flagging sample data based on MS/MSD recoveries are shown in Table 2: If one is high or low and one acceptable, no qualifier is required. If one is high and one is low, flag “J”, If both are high, flag “K” if the analyte is present in the unspiked field sample; otherwise, no data qualifier is required. If both MS and MSD recoveries are low and the analyte is present, flag “L”; and if the analyte is not present flag “UJ”. These criteria pertain only to the source sample used to prepare the MS/MSD.

9.6.2 Laboratory Control Sample (LCS) - A LCS must be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.6.2.1 As part of the requirements of a QC program, spike accuracy in a clean matrix is monitored with each batch. At least one LCS for every 20 samples is prepared and analyzed. The preliminary acceptance criteria are 70-130%.

9.6.3 A duplicate sample or matrix spike duplicate is analyzed with every batch of 20 field samples, where available. The relative percent difference between the duplicates should be less than 30%. If not, the source sample is qualified estimated, "J".

Calculate the relative percent difference (RPD) between the duplicates using the following equation:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \quad X \quad 100$$

where:
C1 =Measured concentration of first sample aliquot
C2 =Measured concentration of second sample aliquot.

9.7 Initial Calibration Acceptance Criteria - There must be an ICAL of the LC/MS/MS system as described in Sec. 11. Prior to analyzing samples, verify the ICAL standards using a second source ICV standard, if readily available (See Sec. 7.4.5).

Note: No ICV standards were provided for the inter laboratory comparison study.

9.8 Continuing calibration verification (CCV) and/or end calibration check - The LC/MS/MS system must meet the CCV acceptance criteria in Sec. 11.4

See Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.9 Lower limit of quantitation (LLOQ)

General guidance for LLOQ is provided in this section and in Method 8000. The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence. The LLOQ shall be analyzed at the concentration equal to the lowest point in the calibration curve. The laboratory shall establish the LLOQ at concentrations where both quantitative and qualitative requirements can consistently be met (see Sec. 11.6 and 11.7). The laboratory shall verify the LLOQ at least annually, and whenever significant changes are made to the preparation and/or analytical procedure, to demonstrate quantitation capability at lower analyte concentration levels. Additional LLOQ verifications may be useful on a project-specific basis if a matrix is expected to contain significant interferences at the LLOQ. The verification may be accomplished with either clean control material (e.g. reagent water) or a representative sample matrix, free of target compounds. Optimally, the LLOQ should be less than the desired decision level or regulatory action level based on the stated DQOs.

NOTE: LLOQs should be established at concentrations where both quantitative and qualitative requirements can be consistently and reliably met. Target analyte peaks in the calibration standard at the LLOQ should be visually inspected to ensure that peak signal is adequately distinguishable from background and where the signal/noise ratio for all quantitative peaks is ≥3.

9.9.1 LLOQ Verification

9.9.1.1 The verification of LLOQs using spiked clean control material represents a best-case scenario because it does not evaluate the potential matrix

effects of real-world samples. For the application of LLOQs on a project-specific basis, with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.9.1.2 The LLOQ verification is prepared by spiking a clean control material with the analyte(s) of interest at the concentration level of the low standard. Alternatively, a representative sample matrix free of targets may be spiked with the analytes of interest at 0.5 - 2 times the LLOQ concentration levels. The LLOQ check is carried through the same preparation and analytical procedures as environmental samples and other QC samples.

9.9.1.3 Recovery of target analytes in the LLOQ verification should be within established in-house limits or within other such project-specific acceptance limits to demonstrate acceptable method performance at the LLOQ. Preliminary acceptance criteria for the LLOQ verification are 50-150%. This practice acknowledges the potential for greater uncertainty at the low end of the calibration curve. Practical, historically based LLOQ acceptance criteria should be determined once sufficient data points have been acquired.

9.9.1.4 Analyze the LLOQ verification in every batch of samples within a 24-hr analysis window. If the analytes are not present or biased low in the LLOQ verification, the data for all non-detects are qualified “UJ” and “J” if detected up to a passing LCS concentration level. If the recovery is biased high, non-detects in site samples are not qualified but detects are qualified “J” to the level of a passing LCS concentration. The QC failure is explained in the narrative accompanying the data.

9.9.1.5 Reporting concentrations below LLOQ – Concentrations that are below the established LLOQ may still be reported; however, these analytes must be qualified as estimated. The procedure for reporting analytes below the LLOQ should be documented in the laboratory's SOP or in a project-specific plan. Analytes below the LLOQ that are reported should meet most or all of the qualitative identification criteria in Sec. 11.6.

9.10 Surrogate recoveries - Surrogates must be added to every blank, field sample, laboratory QC, and field QC. The laboratory recovery acceptance criteria should be developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate recovery acceptance criteria. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in the laboratory's SOP or in an approved project plan.

9.10.1 As part of a QC program, all samples are spiked with a surrogate standard spiking solution as described in Sec. 11. The preliminary acceptance criteria are 70-130%.

9.10.2 There are 19 surrogates recommended for this analysis. The isotopically-labeled surrogates represent the unlabeled native analytes.

9.10.3 If the surrogate recovery is low and the native analyte is present, the data are qualified “L”; if not present, the data are qualified “UJ”. If the surrogate recovery is high and the native analyte is present, the analyte is qualified “K”; if not present, no qualifier is required.

9.11 It is recommended that the laboratory adopt additional QA practices for use with this method. Specific practices that are most productive depend upon the needs of the laboratory, the nature of the samples, and project-specific requirements. Field duplicates may be analyzed to assess precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.5 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation - Each batch of samples (up to 20 samples) must contain at least two method blanks, a reagent blank, laboratory control sample, matrix spike and matrix spike duplicate (if available), and an LLOQ verification sample.

11.1.1 MB - Prepare two MBs by weighing 2 g of reagent sand into each of two 15-mL polypropylene tube. Spike with 40 µL of the surrogate spiking solution (Sec. 7.4.1). Take the MBs through sample extraction (Sec. 11.2).

11.1.2 LCS – Weigh approximately 2 g of reagent sand in a 15-mL polypropylene centrifuge tubes. Spike with 40 µL of the surrogate spiking solution (Sec. 7.4.1). Spike the sample with 40 µL of PFAS spiking solution (Sec. 7.4.2), and then take the samples through sample extraction (Sec. 11.2).

11.1.3 LLOQ Verification Sample - Weigh approximately 2 g of reagent sand in a 15-mL polypropylene centrifuge tube. Spike with 40 µL of the surrogate spiking solution (Sec. 7.4.1) and 25 µL of the LLOQ spiking solution (Sec. 7.4.4). Extract the sample as in Section 11.2. Prepare LLOQ verification samples at higher concentration as needed (Sec. 7.4.4).

11.1.4 Sample - Weigh approximately 2 g of sample in a 15-mL polypropylene centrifuge tube. Allow the sample to come to room temperature and then weigh. Spike with 40 µL of the surrogate spiking solution (Sec. 7.4.1) and extract as in Sec. 11.2.

11.1.5 MS/MSD - Weigh approximately 2 g of sample in each of two 15-mL polypropylene centrifuge tubes for the matrix spike and/or matrix spike duplicate. Spike with 40 µL of the surrogate spiking solution (Sec. 7.4.1). Spike each aliquot with 40 µL of PFAS spiking solution (Sec. 7.4.3), and then follow the take the samples through sample extraction procedures (Sec. 11.2).

11.1.6 CCV – The CCV standard is prepared as a mid-level calibration standard (See Section 7.4.5 and Table 5). The suggested concentration is 80 ng/L (calibration level 6).

11.2 Sample Extraction

11.2.1 To all samples, add 10 mL of methanol: water (1:1) and hand shake/vortex for ~ 1 minute. After vortexing, the pH of the sample is adjusted to pH ~ 9-

10 with ammonium hydroxide (~20 µL) and hand shaken/vortexed again for ~ 1 minute. The sample tubes are tumbled on a rotator for 1 hour and centrifuged at 1900 rpm for 10 minutes.

11.2.2. The liquid phase of the sample is filtered through an Acrodisc GxF/0.2µm GHP membrane syringe-driven filter unit (refer to Section 11.2.2.1 before use) to remove particulates in the sample, leaving the solids behind. Acetic acid (50 µL) is added to all samples to adjust the pH to ~ 3-4 after filtration. Approximately a 1-mL aliquot of that solution is transferred to an amber LC autosampler vial. The final volume of the solution is assumed to be 10 mL for quantitation purposes since 10 mL of methanol/water was added.

CAUTION: Use only polyethylene caps to seal the LC autosampler vials. All prepared LC autosampler vials should only be injected once since some of the analytes or solvent may evaporate after the vial cap is pierced; the polypropylene caps are not self-sealing.

11.2.2.1. The Acrodisc filters are washed with at least 10 mL of acetonitrile followed by 20 mL of methanol prior to use. The syringes must be rinsed with ASTM Type I water followed by acetonitrile and then methanol between all samples.

11.2.3. A moisture determination should be conducted for all soil samples since the concentration of analyte in the sample is reported in ng/kg dry weight of soil, unless otherwise requested.

11.3 Analytical procedure –

11.3.1 Calibrate the mass spectrometer monthly according to manufacturer's specifications or when mass shifts of more than 0.2 dalton (Da) are noticed by the analyst.

11.3.2 Initial Calibration - Inject standards using suitable instrument conditions; LC conditions used in method development are listed in Table 6, and MS conditions used in method development are listed in Appendix TWO. Identify the target compounds by comparing the single reaction monitoring (SRM) transitions ratio in the sample to the SRM transitions ratio in the standards. A qualifier transition ratio is available for most of the analytes (Table 3). The laboratory must optimize instrument settings to obtain acceptable responses for each parent to product ion transition for every target analyte and surrogate (e.g., cone voltage, collision energy). The retention time (RT) for the analytes of interest must also agree with the RT of the mid-level standard by ±5%. Quantitate using the MRM transitions of the target and surrogate compounds with external calibration.

Study note: If quantifier/qualifier MRM transitions are used other than those listed in Table 3, please include this information in the narrative associated with the data submission.

11.3.3 Refer to Table 3 for the MRM transitions and retention times. Set the quantitation method using the peak areas with concentration units in parts per trillion (ng/L).

11.3.4 Use either linear or quadratic regression fits that exclude the point of origin (X=0, Y=0) and are weighted by 1/x. The coefficient of determination, r^2, should be

>0.99 for each analyte. Upon inspection of the calibration curves, if one of the calibration standard injections, other than the high or low, skews the curve such that the r^2 is unacceptable, reinject and replace this point in all the analyte calibration curves, or as an alternative, the data may be reported estimated "J" and explained in the narrative. If the low and/or high points are excluded, a six-point curve is acceptable for quadratic fit and five-point for a linear fit, but the calibration range and LLOQs must be modified to reflect this change The calculated calibration level concentrations used to generate the curve should have less than 30% deviation from the true concentration of the points used to generate the curve; if this is exceeded, a new calibration curve must be generated or the data reported must be qualified as estimated "J" with an explanation in the narrative accompanying the data.

NOTE: The signal/noise ratio for all quantifier transitions must be ≥3, if not this must be noted in the case narrative and the data qualified "J" and/or the LLOQ must be raised to meet this criterion.

11.3.5 The mass spectrometer must be calibrated adequately, i.e. within 0.2 Da of target analyte mass-to-charge ratio (m/z) settings compared to a previous day's analysis or compared to a calibration solution, on each day of analysis. When infusing a calibration solution, it is important to set the resolution settings across the calibration range of the instrument to obtain a width of about 0.75 Da at half height for each peak. This can be done with low mass and high mass resolution settings for each quadrupole. Set the ion energies in order to obtain adequate movement or sensitivity without affecting peak shape or increasing baseline. In order to obtain optimal results, optimize all tunable tune page settings for the calibration solution at the infusion flow rate chosen by the analyst, usually a low flow rate < 20 µL/min.

11.4 CCV acceptance criteria – Verify the initial calibration by analysis of a mid-level calibration standard after every 10 field samples, and at the end of the analysis sequence. All analytes should be within ±30% of their expected values. If not, a separately prepared CCV may be analyzed. If the second CCV fails the criteria, the data may be reported qualified as estimated "J". If sample and time is available, samples can be re-analyzed with a new ICAL and ending CCV. If any data are reported with any failing QC, it must be explained in the case narrative and properly qualified.

Study note: Follow normal CCV failure procedures. If the CCV passes, continue with analysis using original calibration curve. If the CCV fails, perform corrective action and reanalyze the CCV or recalibrate the system.

11.5 One of the method blanks must be analyzed directly after the initial calibration and after the reagent blank prior to the analysis of any samples and the second method blank analyzed after the CCV to ensure the total system is free of contamination.

11.6 Sample analysis procedure

11.6.1 Auto sampler schedule/analytical sequence - Prepare a sequence that includes all QC samples and field samples. Analyze a reagent blank first, the initial calibration standards, reagent blank and then analyze the samples in the following recommended order: MB, LLOQ check, LCS, any diluted samples, samples, duplicates,

Matrix spike/matrix spike duplicate, with a CCV every 10 field samples and a CCV at the end.

11.6.2 Inject samples using the same LC and MS conditions as used to generate the ICAL. Evaluate the instrument response for each analyte' s quantifier and qualifier transitions. LC conditions used to generate data for the single laboratory study are given in Table 5.

11.6.3 As an additional QC measure, monitor 19 isotopically-labeled surrogate (listed in Sec. 7.3.10) recoveries; the percent recovery of each should fall within the preliminary acceptance criteria of 70-130%.

NOTE: The MRM analysis provides qualitative identification by isolating the precursor ion and fragmenting it into the product ions, which are then used to calculate ion ratios that can be compared between samples and standards to confirm the identification of the analyte. The retention times of the analytes are also monitored between samples and standards to further confirm the identification.

11.6.4 Target Identification - Identify the target compounds by comparing the quantifier SRM transition ratio and its qualifier SRM transition ratio in the sample to the SRM transitions ratio in the standard. Qualifier transitions ratios are available for most of the analytes (Table 3). The quantifier/qualifier SRM ion ratio must be within ±30% of the average of the quantifier/qualifier SRM ion ratios calculated from the calibration levels on the day of analysis or ±30% of the ion ratios calculated from a midlevel ICAL point or from the CCV). This ratio will vary depending on the instrument acquisition parameters. Due to sensitivity issues, some ion ratios may not meet the ±30% ion ratio at the lower concentrations in this case, the data should be qualified "I" and explained in the case narrative

NOTE: Depending on sensitivity and matrix interference issues, a qualifier SRM transition ratio might be used as a quantifier SRM transition ratio for quantitation during the analysis. This must be explained in the case narrative if these changes are made.

11.6.5 The qualifier ion ratios in "weathered samples" may not match the ion ratios in the calibration standards for the target analytes that may contain isomeric mixtures. Figures 1 - 4 (Sec. 17.0) are examples of this for PFHxS and PFOS. These differences in isomer mixtures may be observed with analytes that have the possibility of containing isomeric mixtures. The complete isomer grouping must be quantitated consistently for all samples. These differences for PFHxS and PFOS were found in groundwater samples and may either be due to different compositions used, weathering or degradation, or the affinity of the branched isomers to be more soluble than the linear in water and to leach into the water from the soil at a higher rate than the linear. If the ion ratios do not meet the specified criteria (Sec. 11.6.4), document in the case narrative. Use analyst judgment to determine if data should be qualified ("J").

11.6.6 The retention time window of the MRM transitions must be within 5% of the retention time of the analyte in a mid-level calibration standard. If this is not true, examine the ICAL to see if there was a shift in retention time during the analysis and the sample needs to be re-injected.

11.6.7 If there is no qualifier transition for the analyte (Table 3) and the presence of the analyte in the sample cannot be confirmed with a quantifier transition

and retention time, list the analyte as a non-detect or as having a matrix interference present. Use analyst judgment to determine if data should be qualified (“UJ”/”J”).

11.7 Analyte quantitation - Once a target compound has been identified, the quantitation of that compound will be based on the integrated abundance of the quantifier transition. It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations than an analyst will manually. However, manual integrations may be necessary when the software does not produce proper integrations because baseline selection is improper; the correct peak is missed; a co-elution is integrated; the peak is partially integrated; etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.7.1 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g., RT updates, integration parameter files, etc.). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating RTs, and configuring peak integration parameters.

11.8 If the absolute amount of a target compound in a sample exceeds the working calibration range, the sample must be diluted and re-analyzed. This should be done by diluting the sample with 1:1 methanol and water solution containing 0.1% acetic acid.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations and documentation - Computer programs used for method development and analysis of data included MassLynx™ with QuanLynx™ or TargetLynx™ software.

12.2 Document the use of professional judgment in the data reduction and verification process. Since some PFAS consist of complicated isomeric mixtures, the chromatograms are often manually integrated. Document all manual integrations. In general, report analytical results to two significant figures.

12.3 All data packages are verified by a qualified analyst.

12.4 Report all QA/QC data and final results to the customer.

12.5 Electronic data storage reference: Archive all data according to the lab’s quality management program (QMP).

12.6 Reporting result procedure - Refer to Sec. 9.4 for the calculation of target analyte concentrations in the sample.

13.0 METHOD PERFORMANCE

Tables 9 - 12 (Sec. 17.0) show the performance data for the target analytes and surrogates in various matrices.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult Less is Better: Laboratory Chemical Management for Waste Reduction, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety,

http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

15.1 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society at the address listed in Sec. 14.2.

15.2 Place a tag identifying the contents of the carboy as organics-containing liquid waste on the waste container. Label and date all waste containers before using the container.

15.3 Report all major spills according to the Chemical Hygiene Officer.

15.4 Place all used vials containing unused sample or standard in a separate labeled carboy for vial disposal.

16.0 REFERENCES

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2. U.S. Department of Health, Education, and Welfare, Centers for Disease Control, National Institute for Occupational Safety and Health, “Carcinogens - Working with Carcinogens,” Publication No. 77-206, August 1977.

3. U.S. Environmental Protection Agency, Region 5 Laboratory, “Standard Operating Procedure for the Analysis of Polyfluorinated Compounds of Interest to OSRTI in Soil by Multiple Reaction Monitoring Liquid Chromatography/Mass Spectrometry (LC/MS/MS),” 61 pp., 2017.

4. Occupational Safety and Health Administration, OSHA Safety and Health Standards, General Industry, 29 CFR 1910, OSHA 2206 (Revised, January 1976).

5. Standard Practices for Sampling Water, American Society for Testing and Materials, Philadelphia. ASTM Annual Book Standards, Part 31, D3370-76.

6. J.W. Eichelberger, L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," *Analytical Chemistry* 47, 995, 1075.

7. N.M. McNair and E.J. Bonelli, Basic Chromatography, Consolidated Printing: Berkeley, CA, p. 52, 1969.

8. P. Olynyk, W.L. Budde, and J.W. Eichelberger, "Method Detection Limit for Methods 624 and 625," Unpublished report, October 1980.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables, figures, and appendix referenced by this method.

APPENDIX ONE - QUALIFIERS USED IN THIS METHOD

Qualifier	Text Description	Criterion	Section(s)
J	Estimated value / target present	Outside acceptance limits / generic	Many
ICV	2nd source calibration check	Not within 70-130%	9.8, 11.4
K	Blank: potential high bias	Target @ > ½ LLOQ in blank	9.5.8, 9.6.1.3
L	Low bias	Low surrogate recovery Suggests low bias	9.6.1.3
I	Ion ratios	Sample ion ratio not within 30% of ical ratio	11.6.4
None-listed	Aliquot used for sample	aliquot used, not entire container as specified, strong low bias expected	8.1
UJ	Estimated value / target not present	Outside acceptance limits / generic	9.6.1.3

APPENDIX TWO – INSTRUMENT CONDITIONS USED IN METHOD DEVELOPMENT

Instrument: Waters Xevo TQ-S
Capillary voltage: 0.75 kV
Cone: Variable depending on analyte (see Table 8, Appendix)
Source temperature: 150 °C
Desolvation gas temperature: 450°C
Desolvation gas flow: 800 L/hr
Cone gas flow: 200 L/hr
Collision gas flow: 0.15 mL/min
Low mass resolution 1: 2.6
High mass resolution 1: 14
Ion energy 1: 1
Entrance energy: 1
Collision energy: Variable (see Table 8, Appendix)
Exit energy: 1
Low mass resolution 2: 2.5
High mass resolution 2: 14
Ion energy 2: 3
Gain: 1.0
Multiplier: 511.1
Inter-scan delay: 0.004 seconds

TABLE 1. METHOD PARAMETERS

Analyte	MDL* (ng/Kg)	Reporting Range* (ng/Kg)
PFTreA	6.8	25 - 1000
PFTriA	5.3	25 - 1000
PFDoA	3.6	25 - 1000
PFUnA	2.5	25 - 1000
PFDA	5.5	25 - 1000
PFDS*	3.0	25 - 1000
PFOS*	9.6	25 - 1000
PFNA	2.8	25 - 1000
PFNS*	2.9	25 - 1000
PFOA	6.2	25 - 1000
PFHpS*	3.4	25 - 1000
PFHxS	7.8	25 - 1000
PFHpA	5.8	25 - 1000
PFHxA	15.4	25 - 1000
PFBS	6.5	25 - 1000
PFPeS*	2.0	25 - 1000
PFPeA	20.9	125 - 1000
PFBA	22.0	125 - 1000
FOSA*	4.5	25 - 1000
4:2 FTS*	3.1	25 - 1000
6:2 FTS*	3.5	25 - 1000
8:2 FTS*	7.4	25 - 1000
NEtFOSAA*	7.3	25 - 1000
NMeFOSAA*	4.2	25 - 1000

MDLs and RLs were determined from the IDOC performed on LC/MS/MS #2 analyzed in May 2014 (LIMS work order #1406012), unless otherwise noted. This SOP is for use with LC/MS/MS #2 and #3.
*MDLs and RLs for these analytes were determined from the IDOC performed on LC/MS/MS #3 analyzed in September 2016 (LIMS work order #1702009, Qualtrax workflow ID #9754).

TABLE 2. STATISTICAL PERFORMANCE DATA

Analyte	Average Recovery (%)	Standard Deviation (%)	# of Replicates (n)	Lower Control Limit (LCL) %	Upper Control Limit (UCL) %
PFTreA	108.5	9.2	6	70.0	130
PFTriA	97.7	3.6	6	70.0	130
PFDoA	88.9	1.8	6	70.0	130
PFUnA	88.4	2.3	6	70.0	130
PFDA	89.1	2.3	6	70.0	130
PFDS	94.2	3.1	6	70.0	130
PFOS	93.1	3.6	6	70.0	130
PFNA	88.0	2.4	6	70.0	130
PFNS	93.4	1.5	6	70.0	130
PFOA	89.7	1.7	6	70.0	130
PFHpS	91.7	2.9	6	70.0	130
PFHxS	89.3	2.3	6	70.0	130
PFHpA	87.5	1.5	6	70.0	130
PFHxA	88.9	3.9	6	70.0	130
PFPeS	89.7	1.5	6	70.0	130
PFBS	93.5	4.9	6	70.0	130
PFPeA	87.7	0.8	6	70.0	130
PFBA	78.2	0.9	6	70.0	130
FOSA	99.4	2.1	6	70.0	130
4:2 FTS	91.9	1.6	6	70.0	130
6:2 FTS	92.9	2.6	6	70.0	130
8:2 FTS	99.6	4.1	6	70.0	130
NEtFOSAA	96.3	5.1	6	70.0	130
NMeFOSAA	90.7	2.8	6	70.0	130
MPFBA	79.5	1.6	8	70.0	130
MPFHxA	91.1	1.5	8	70.0	130
MPFHxS	93.4	2.8	8	70.0	130
MPFOA	90.6	2.7	8	70.0	130
MPFNA	90.4	2.8	8	70.0	130
MPFOS	94.2	3.4	8	70.0	130
MPFDA	89.5	1.8	8	70.0	130
MPFDoA	92.3	3.3	8	70.0	130
M4:2 FTS	91.8	4.4	8	70.0	130

Analyte	Average Recovery (%)	Standard Deviation (%)	# of Replicates (n)	Lower Control Limit (LCL) %	Upper Control Limit (UCL) %
MPFUnA	90.9	3.2	8	70.0	130
MPFDoA	92.3	3.3	8	70.0	130
M4:2 FTS	91.8	4.4	8	70.0	130
M6:2 FTS	95.1	5.5	8	70.0	130
M8:2 FTS	97.9	7.0	8	70.0	130
MNEtFOSAA	99.8	3.9	8	70.0	130
MNMeFOSAA	91.7	4.2	8	70.0	130

Laboratory control sample recovery statistics were calculated in March 2017 from LCS QC samples analyzed in September 2016 as part of the IDOC performed on LC/MS/MS #3 (LIMS work order #1702009, Qualtrax workflow ID # 9754). This SOP is for use with LC/MS/MS #2 and #3

TABLE 3. RETENTION TIME (RT) AND MRM IONS

Analyte	Primary/Confirmatory	MRM Transition	Retention Time (Minutes)	Primary/ Confirmatory SRM Area Ratio
PFTreA	Primary	712.9⟶ 668.9	10.63	7.4
	Confirmatory	712.9⟶ 169		
PFTriA	Primary	662.9⟶ 618.9	10.17	7.4
	Confirmatory	662.9⟶ 169		
PFDoA	Primary	612.9⟶568.9	9.61	8.2
	Confirmatory	612.9⟶169		
PFUnA	Primary	562.9⟶519	9.05	7.2
	Confirmatory	562.9⟶269		
PFDA	Primary	512.9⟶468.9	8.45	6.5
	Confirmatory	512.9⟶219		
PFDS	Primary	598.9⟶79.9	9.8	1.2
	Confirmatory	598.9⟶98.9		
PFOS	Primary	498.9⟶80.1	8.78	1.3
	Confirmatory	498.9⟶99.1		
PFNA	Primary	462.9⟶418.9	7.78	4.9
	Confirmatory	462.9⟶219		
PFNS	Primary	548.9⟶79.9	9.2	1.2
	Confirmatory	548.9⟶98.9		
PFOA	Primary	412.9⟶369	7.11	3.6
	Confirmatory	412.9⟶169		
PFHpS	Primary	448.9⟶79.9	7.95	1.3
	Confirmatory	448.9⟶98.9		
PFHxS	Primary	398.9⟶80.1	7.39	1
	Confirmatory	398.9⟶99.1		
PFHpA	Primary	362.9⟶319	6.35	4.1
	Confirmatory	362.9⟶169		
PFHxA	Primary	312.9⟶ 269	5.54	24.1
	Confirmatory	312.9⟶119.1		
PFBS	Primary	298.9⟶80.1	5.66	1.6
	Confirmatory	298.9⟶99.1		
PFPeA	Primary	263⟶219	4.68	NA

Analyte	Primary/Confirmatory	MRM Transition	Retention Time (Minutes)	Primary/ Confirmatory SRM Area Ratio
PFPeS	Primary	348.9⟶79.9	6.4	1.4
	Confirmatory	348.9⟶98.9		
PFBA	Primary	212.9⟶169	3.67	NA
4:2 FTS	Primary	327⟶307	5.2	3.5
	Confirmatory	327⟶80.9		
6:2 FTS	Primary	427⟶406.9	6.7	4.3
	Confirmatory	427⟶80.9		
8:2 FTS	Primary	526.9⟶506.9	8	4.5
	Confirmatory	526.9⟶ 80.9		
N-MeFOSAA	Primary	569.9⟶419	8.4	1.8
	Confirmatory	569.9⟶482.9		
N-EtFOSAA	Primary	583.9⟶419	8.7	1.7
	Confirmatory	583.9⟶482.9		
FOSA	Primary	497.9⟶77.9	9.8	NA
M4PFBA	Primary	217→172	3.7	NA
M5PFHxA	Primary	318→273	5.5	NA
M3PFHxS	Primary	403→84	7.4	NA
M8PFOA	Primary	421→376	7.1	NA
M9PFNA	Primary	472→427	7.8	NA
M8PFOS	Primary	507→80	8.8	NA
M6PFDA	Primary	519→474	8.4	NA
M7PFUnA	Primary	565→520	9.0	NA
M2PFDoA	Primary	615→570	9.6	NA
M2-4:2 FTS	Primary	329→309	5.2	NA
M2-6:2 FTS	Primary	429→409	6.7	NA
M2-8:2 FTS	Primary	529→509	8.0	NA
d3-NMeFOSAA	Primary	573→419	8.4	NA
d5-NEtFOSAA	Primary	589→419	8.7	NA
M3PFBS	Primary	302→80	5.7	NA
M5PFPeA	Primary	268→223	4.7	NA

Analyte	Primary/Confirmatory	MRM Transition	Retention Time (Minutes)	Primary/ Confirmatory SRM Area Ratio
M4PFHpA	Primary	367→322	6.3	NA
M2PFTreA	Primary	715→670	10.6	NA
M8FOSA	Primary	506→78	9.8	NA

TABLE 4. CONCENTRATIONS OF CALIBRATION STANDARDS

Analyte (Concentrations in ppt)	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8	LV9
All PFAS	5	10	20	40	60	80	100	150	200

***** These values are the concentrations in the calibration standards. The concentration obtained from the instrument is then corrected for the volume of methanol/water (1:1) added during the sample preparation process and the dry weight of the sample, producing the reporting ranges in Table 1.

TABLE 5. PREPARATION OF CALIBRATION STANDARDS

Solution	LV1	LV2	LV3	LV4	LV5	LV6	LV7	LV8	LV9
A	25 µL	50 µL	100 µL	200 µL	300 µL	400 µL	500 µL	750 µL	1000 µL
B	975 µL	950 µL	900 µL	800 µL	700 µL	600 µL	500 µL	250 µL	0 µL

Solution A: Level 9 calibration stock solution prepared according to Section 7.3.4 and at Table 5 concentrations, once prepared
Solution B: 1:1 methanol and water with 0.1% acetic acid

TABLE 6. GRADIENT CONDITIONS FOR LIQUID CHROMATOGRAPHY

Time (min)	Flow (mL/min)	% Solvent Line A 95% water: 5% acetonitrile	% Solvent Line B Acetonitrile	% Solvent Line C 400mM ammonium acetate (95% water: 5% acetonitrile)
0	0.3	95	0	5
1	0.3	75	20	5
6	0.3	50	45	5
13	0.3	15	80	5
14	0.4	0	95	5
17	0.4	0	95	5
18	0.4	95	0	5
21	0.4	95	0	5

TABLE 7. DETECTION LIMIT STUDY*

Analyte	Spike Conc. (ng/Kg)	Mean Recovery (ng/Kg)	Mean Recovery (%)	RSD (%)	Standard Deviation	MDL (ng/Kg)
PFTreA	15	23.2	155	10.1	2.33	6.8
PFTriA	15	18.5	124	9.80	1.82	5.3
PFDoA	15	16.6	111	7.38	1.23	3.6
PFUnA	15	17.9	119	4.72	0.85	2.5
PFDA	15	15.9	106	12.0	1.91	5.5
PFDS	15	16.9	113	6.17	1.04	3.0
PFOS	15	21.2	141	15.7	3.33	9.6
PFNA	15	17.6	117	5.54	0.97	2.8
PFNS	15	16.8	112	5.92	1.00	2.9
PFOA	15	16.3	108	13.3	2.16	6.2
PFHpS	15	13.0	86.4	8.99	1.16	3.4
PFHxS	15	16.1	107	16.7	2.68	7.8
PFHpA	15	18.4	122	10.9	2.00	5.8
PFHxA	15	19.2	128	27.7	5.33	15.4
PFBS	15	14.0	93.4	16.0	2.24	6.5
PFPeS	15	12.4	82.6	5.48	0.68	2.0
PFPeA	75	65.7	87.6	11.0	7.23	20.9
PFBA	75	41.4	55.3	18.3	7.60	22.0
FOSA	15	15.9	106	9.84	1.57	4.5
4:2 FTS	15	16.2	108	6.66	1.08	3.1
6:2 FTS	15	13.8	91.7	8.75	1.20	3.5
8:2 FTS	15	12.2	81.6	20.9	2.56	7.4
NEtFOSAA	15	13.9	92.4	18.3	2.53	7.3
NMeFOSAA	15	15.8	105	9.21	1.46	4.2

* MDL values are reported below the LLOQ and lowest point of the calibration curve. They are estimated concentrations because they are not bracketed by calibration points

TABLE 8. VARIABLE MASS SPECTROMETER PARAMETERS DEPENDING ON ANALYTE

Analyte	Primary/Confirmatory	MRM Transition	Cone (V)	Collision Energy (eV)
PFTreA	Primary	712.9⟶ 668.9	20	13
	Confirmatory	712.9⟶ 169	20	30
PFTriA	Primary	662.9⟶ 618.9	25	12
	Confirmatory	662.9⟶ 169	25	28
PFDoA	Primary	612.9⟶568.9	10	12
	Confirmatory	612.9⟶169	10	25
PFUnA	Primary	562.9⟶519	15	10
	Confirmatory	562.9⟶269	15	18
PFDA	Primary	512.9⟶468.9	20	10
	Confirmatory	512.9⟶219	20	16
PFDS	Primary	598.9⟶79.9	15	45
	Confirmatory	598.9⟶98.9	15	45
PFOS	Primary	498.9⟶80.1	10	42
	Confirmatory	498.9⟶99.1	10	40
PFNA	Primary	462.9⟶418.9	20	10
	Confirmatory	462.9⟶219	20	16
PFNS	Primary	548.9⟶79.9	15	42
	Confirmatory	548.9⟶98.9	15	42
PFOA	Primary	412.9⟶369	20	10
	Confirmatory	412.9⟶169	20	16
PFHpS	Primary	448.9⟶79.9	15	38
	Confirmatory	448.9⟶98.9	15	36
PFHxS	Primary	398.9⟶80.1	15	32
	Confirmatory	398.9⟶99.1	15	32
PFHpA	Primary	362.9⟶319	15	10
	Confirmatory	362.9⟶169	15	15
PFHxA	Primary	312.9⟶ 269	15	8
	Confirmatory	312.9⟶119.1	15	18
PFBS	Primary	298.9⟶80.1	10	30
	Confirmatory	298.9⟶99.1	10	25
PFPeA	Primary	263⟶219	10	8

Analyte	Primary/Confirmatory	MRM Transition	Cone (V)	Collision Energy (eV)
PFPeS	Primary	348.9⟶79.9	15	34
	Confirmatory	348.9⟶98.9	15	30
PFBA	Primary	212.9⟶169	10	8
4:2 FTS	Primary	327⟶307	10	20
	Confirmatory	327⟶80.9	10	24
6:2 FTS	Primary	427⟶406.9	10	22
	Confirmatory	427⟶80.9	10	30
8:2 FTS	Primary	526.9⟶506.9	10	26
	Confirmatory	526.9⟶ 80.9	10	34
N-MeFOSAA	Primary	569.9⟶419	15	20
	Confirmatory	569.9⟶482.9	15	16
N-EtFOSAA	Primary	583.9⟶419	15	20
	Confirmatory	583.9⟶482.9	15	16
FOSA	Primary	497.9⟶77.9	15	28
M4PFBA	Primary	217→172	10	7
M5PFHxA	Primary	318→273	15	8
M3PFHxS	Primary	402→80	15	34
M8PFOA	Primary	421→376	15	10
M9PFNA	Primary	472→427	15	9
M8PFOS	Primary	507→80	15	40
M6PFDA	Primary	519→474	15	10
M7PFUnA	Primary	570→525	15	10
M2PFDoA	Primary	615→570	15	12
M2-4:2 FTS	Primary	329→309	20	10
M2-6:2 FTS	Primary	429→409	10	22
M2-8:2 FTS	Primary	529→509	10	26
d3-NMeFOSAA	Primary	573→419	15	20
d5-NEtFOSAA	Primary	589→419	15	20
M3PFBS	Primary	302→80	10	29
M5PFPeA	Primary	268→223	15	9
M4PFHpA	Primary	367→322	10	10
M2PFTreA	Primary	715→670	20	15
M8FOSA	Primary	506→78	15	30

TABLE 9A-C. P&A STUDY IN ASTM CH-1 SOIL

TABLE 9A. PRECISION AND ACCURACY STUDY FOR PFASS IN ASTM CH-1 SOIL

Sample	Fat Clay ASTM CH-1										
	Measured ng/Kg from 400 ng/Kg spike for all PFASAs except 2000 ng/Kg (PFBA and PFPeA)										
	PFTreA	**PFTriA**	**PFDoA**	**PFUnA**	**PFDA**	**PFNA**	**PFOA**	**PFHpA**	**PFHxA**	**PFPeA**	**PFBA**
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	83.6	<RL	70.2	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	81	<RL	73.5	<RL	<RL
Spiked 1	361.85	350.45	339.45	345	344.45	338.5	338.65	348.7	340.4	1634.5	1579.8
Spiked 2	369.75	370	350.45	353.4	359.1	349.4	359.75	379.15	354	1805.5	1736.4
Spiked 3	372.35	369.9	358.8	356.5	342.05	348.2	350.65	358.8	346.25	1734.65	1560.15
Spiked 4	367	374.15	353.65	343.2	354.2	349.6	347.9	365.95	368.55	1684.35	1639.4
Spiked 5	379.95	384.4	364.25	367.2	364.15	361.5	362.65	356.85	362.55	1786.8	1613.05
Spiked 6	371.1	361.15	349.7	341.7	348.6	338.95	352.15	352.75	350.15	1757.75	1638.6
Average Recovery (ng/Kg)	370.33	368.34	352.72	351.17	352.09	347.69	351.96	360.37	353.65	1733.93	1627.90
% Average Recovery	92.58	92.09	88.18	87.79	88.02	86.92	87.99	90.09	88.41	86.70	81.40
Standard Deviation	6.01	11.56	8.50	9.81	8.61	8.47	8.61	10.89	10.43	64.54	61.88
RSD (%)	1.62	3.14	2.41	2.79	2.44	2.44	2.45	3.02	2.95	3.72	3.80

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 9B. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM CH-1 SOIL

Sample	Fat Clay ASTM CH-1 Measured ng/Kg from 400 ng/Kg spike												
	PFBS	**PFHxS**	**PFOS**	**PFDS**	**PFNS**	**PFHpS**	**PFPeS**	**FOSA**	**4:2 FTS**	**6:2 FTS**	**8:2 FTS**	**N-ETFOSAA**	**N-MeFOSAA**
Unspiked 1	<RL	54.25	146.05	<RL	<RL	<RL	<RL	68.6	<RL	<RL	<RL	<RL	<RL
Unspiked 2	<RL	56.75	141.6	<RL	<RL	<RL	<RL	64.55	<RL	<RL	<RL	<RL	<RL
Spiked 1	360.15	342.9	348.5	365.05	365.45	358.2	351.15	327.4	374.25	371	371.25	370	348
Spiked 2	373.65	366.9	369.95	368.7	361.15	361.35	358.35	339.85	393.2	376.6	381.65	374.55	352.5
Spiked 3	362.55	357.75	361.7	367.05	368.1	367.9	352.55	346.55	380.2	372.55	359.3	390.4	343.3
Spiked 4	367.25	365.5	380.7	370.1	366.45	357.7	349.95	346.35	390.05	377.9	383.65	382.05	344.85
Spiked 5	382.25	364.7	387.35	374.25	375.7	376	369.5	370.65	396.35	391.9	396.2	378.75	357.85
Spiked 6	369.35	361.85	367.55	365.35	361.7	364.85	344.6	342.85	377.9	382.65	363.5	387.55	341.7
Average Recovery (ng/Kg)	369.20	359.93	369.29	368.42	366.43	364.33	354.35	345.61	385.33	378.77	375.93	380.55	348.03
% Average Recovery	92.30	89.98	92.32	92.10	91.61	91.08	88.59	86.40	96.33	94.69	93.98	95.14	87.01
Standard Deviation	8.00	8.95	13.78	3.45	5.29	6.92	8.64	14.15	9.05	7.64	13.83	7.73	6.15
RSD (%)	2.17	2.49	3.73	0.94	1.44	1.90	2.44	4.09	2.35	2.02	3.68	2.03	1.77

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 9C. PRECISION AND ACCURACY STUDY FOR SURROGATES IN ASTM CH-1 SOIL

Sample	Surrogates- (Fat Clay ASTM CH -1– 400 ng/Kg spike)													
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	**M4:2 FTS**	**M6:2 FTS**	**M8:2 FTS**	**MN-ETFOSAA**	**MN-MeFOSAA**
Unspiked 1	332.9	353.7	363.35	336.8	345.9	361.95	354.8	352.85	351.9	354.15	339.95	372.2	370.15	354.7
Unspiked 2	342.1	358.45	362.2	348	347.9	379.45	354.25	358.4	352.5	382.55	366.7	375.85	363.55	356.95
Spiked 1	323.35	344	352.8	345.25	329.4	370.6	347.2	344.55	344.8	380.95	361.1	375.15	351.7	343
Spiked 2	347.05	357.35	360.1	357.75	355.7	372.9	355.9	354	357.4	406.5	374.85	380	372.5	367.85
Spiked 3	322.9	355.8	364.95	347.45	356.6	371.4	355.1	359.25	354.25	386.45	380.85	401.5	370.5	357.3
Spiked 4	335.1	358.65	368.45	346.7	351.65	369.9	358.75	351.35	359	395.7	375.65	374.45	359.2	354.45
Spiked 5	343.75	359.35	371.5	364.55	350.95	379.65	364.6	364.3	359.25	398.95	397.75	402.7	377.75	365.1
Spiked 6	325.3	349.7	356.75	336.65	344.85	351.65	339.95	350.45	349.6	385.2	369.2	381.1	355.3	344.9
Average Recovery (ng/Kg)	334.06	354.63	362.51	347.89	347.87	369.69	353.82	354.39	353.59	386.31	370.76	382.87	365.08	355.53
% Average Recovery	83.51	88.66	90.63	86.97	86.97	92.42	88.45	88.60	88.40	96.58	92.69	95.72	91.27	88.88
Standard Deviation	9.60	5.34	6.05	9.51	8.58	9.21	7.40	6.12	4.98	15.74	16.61	12.22	9.12	8.62
RSD (%)	2.88	1.51	1.67	2.73	2.47	2.49	2.09	1.73	1.41	4.07	4.48	3.19	2.50	2.43

10A-C. P&A STUDY IN ASTM SP-1 SOIL

TABLE 10A. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM SP-1 SOIL

Sample	Frederick Sand ASTM SP-1										
	Measured ng/Kg from 400 ng/Kg spike for all PFASAs except 2000 ng/Kg (PFBA and PFPeA)										
	PFTreA	**PFTriA**	**PFDoA**	**PFUnA**	**PFDA**	**PFNA**	**PFOA**	**PFHpA**	**PFHxA**	**PFPeA**	**PFBA**
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	65.35	<RL	28.6	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	73.4	<RL	35.8	<RL	<RL
Spiked 1	383.25	376	358.3	348.25	366.45	361.85	329.9	357.25	342.35	1759.3	1558.45
Spiked 2	378.45	365.3	350.4	349.15	353.4	351.55	334.7	357.75	334.4	1740.5	1530.7
Spiked 3	365.4	359.15	342.65	347.9	350.3	351.55	337.35	348.65	322	1749.05	1507.55
Spiked 4	374.55	357.4	352.55	341.1	355.45	350	333.65	361.1	338.05	1735.25	1496.9
Spiked 5	354.05	352.3	336.15	339.2	345.7	344.85	326.3	354.15	330.9	1682.4	1469
Spiked 6	336.15	338.7	333.85	333.05	349.25	340.35	321.95	350.4	325.6	1655.2	1456.6
Average Recovery (ng/Kg)	365.31	358.14	345.65	343.11	353.43	350.03	330.64	354.88	332.22	1720.28	1503.20
% Average Recovery	91.33	89.54	86.41	85.78	88.36	87.51	82.66	88.72	83.05	86.01	75.16
Standard Deviation	17.65	12.52	9.68	6.42	7.22	7.28	5.75	4.73	7.63	41.60	37.97
RSD (%)	4.83	3.50	2.80	1.87	2.04	2.08	1.74	1.33	2.30	2.42	2.53

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 10B. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM SP-1 SOIL

Sample	Frederick Sand ASTM SP-1												
	Measured ng/Kg from 400 ng/Kg spike												
	PFBS	**PFHxS**	**PFOS**	**PFDS**	**PFNS**	**PFHpS**	**PFPeS**	**FOSA**	**4:2 FTS**	**6:2 FTS**	**8:2 FTS**	**N-ETFOSAA**	**N-MeFOSAA**
Unspiked 1	29.55	26.6	624.9	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Unspiked 2	18.35	35.25	825.7	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Spiked 1	343.65	360.6	317.25	378.35	383.25	380.65	362.1	406.45	348.1	363.65	368.85	388.8	368.3
Spiked 2	332.35	342.8	214.75	352.9	362.6	361.55	345.3	391.95	351.8	356.25	363.6	370.25	361.55
Spiked 3	339.2	355.25	298.55	359.65	354.5	360.8	353.6	387.2	351.9	350.4	372.85	365.45	364.9
Spiked 4	345	347.15	270.35	375.25	359.95	363.2	363.55	398.75	355.25	360.7	395.75	353.05	368.7
Spiked 5	339.65	338.45	213.35	370	380.25	376.15	365.15	400.6	368.75	375.8	386.4	350.45	380.4
Spiked 6	330.35	349.95	299.25	359.85	349.7	359.2	361.9	378.25	343.65	351.15	380.6	347.85	355.25
Average Recovery (ng/Kg)	338.37	349.03	268.92	366.00	365.04	366.93	358.60	393.87	353.24	359.66	378.01	362.64	366.52
% Average Recovery	84.59	87.26	67.23	91.50	91.26	91.73	89.65	98.47	88.31	89.91	94.50	90.66	91.63
Standard Deviation	5.91	8.10	45.07	10.04	13.72	9.09	7.65	10.19	8.57	9.46	11.92	15.55	8.43
RSD (%)	1.75	2.32	16.76	2.74	3.76	2.48	2.13	2.59	2.42	2.63	3.15	4.29	2.30

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥RL.

TABLE 10C. PRECISION AND ACCURACY STUDY FOR SURROGATES IN ASTM SP-1 SOIL

Sample	Surrogates- (Frederick Sand ASTM SP -1– 400 ng/Kg spike)													
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	**M4:2 FTS**	**M6:2 FTS**	**M8:2 FTS**	**MN-ETFOSAA**	**MN-MeFOSAA**
Unspiked 1	315.5	360.85	372.4	349.3	351.2	358.7	347	348.9	358.9	354.55	368.5	353.15	384	357.55
Unspiked 2	322.35	352	364.95	355.2	349.95	367.9	338.85	340.95	346.6	350.75	353.15	368.95	375.8	359.3
Spiked 1	300.8	347	374.05	354.45	346.1	379.2	341.4	346.55	356.8	365.95	383.95	389.05	384.1	352.75
Spiked 2	298.6	349.05	365.55	346.5	336.3	353.25	342.1	339.2	344.35	357.15	362.45	385.65	383.3	354.9
Spiked 3	290.5	334.4	357.6	340.4	331.4	359.4	331.3	328.35	334.95	355.55	350.1	376.75	379.5	345.35
Spiked 4	292	336.85	357.65	342.35	336.95	359.85	338.35	335.3	335.3	365.1	369.45	388.2	373.6	363.5
Spiked 5	278.9	334.75	346.6	333.9	324.7	349.15	327.7	321.3	326.75	350.25	369.8	350.2	357.35	342.65
Spiked 6	280.1	317	325.2	327.35	315.95	355.5	317.65	312.6	318	345.2	353.6	364.3	353.2	339.35
Average Recovery (ng/Kg)	297.34	341.49	358.00	343.68	336.57	360.37	335.54	334.14	340.21	355.56	363.88	372.03	373.86	351.92
% Average Recovery	74.34	85.37	89.50	85.92	84.14	90.09	83.89	83.54	85.05	88.89	90.97	93.01	93.46	87.98
Standard Deviation	15.50	13.57	15.93	9.73	12.40	9.38	9.46	12.58	14.19	7.18	11.36	15.40	12.14	8.59
RSD (%)	5.21	3.97	4.45	2.83	3.69	2.60	2.82	3.76	4.17	2.02	3.12	4.14	3.25	2.44

TABLE 11A. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM CL-1 SOIL

Sample	Lean Clay ASTM CL-1										
	Measured ng/Kg from 400 ng/Kg spike for all PFASAs except 2000 ng/Kg (PFBA and PFPeA)										
	PFTreA	**PFTriA**	**PFDoA**	**PFUnA**	**PFDA**	**PFNA**	**PFOA**	**PFHpA**	**PFHxA**	**PFPeA**	**PFBA**
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	MI	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	MI	<RL
Spiked 1	304.4	343.15	339	341.9	337.1	331.65	346.95	333.7	341.05	MI	1695.7
Spiked 2	290.95	328.35	336.65	343.5	350.9	340.1	361.1	334.3	345.6	MI	1677.35
Spiked 3	300.6	327.4	337.15	343.6	346.4	335.65	359.05	328.7	351.2	MI	1666.2
Spiked 4	289.45	319.9	333.4	333.9	326.85	323.8	337.1	327.8	349.1	MI	1655.9
Spiked 5	265.05	364.7	331.5	333	329	330.7	344.55	331.8	348.75	MI	1555.3
Spiked 6	310.55	384.3	347.6	346.4	341.35	334.3	358	333.9	352.9	MI	1645.85
Average Recovery (ng/Kg)	293.50	344.63	337.55	340.38	338.60	332.70	351.13	331.70	348.10		1649.38
% Average Recovery	73.38	86.16	84.39	85.10	84.65	83.18	87.78	82.93	87.03		82.47
Standard Deviation	16.08	25.11	5.62	5.57	9.51	5.48	9.66	2.82	4.24		49.23
RSD (%)	5.48	7.29	1.66	1.64	2.81	1.65	2.75	0.85	1.22		2.98

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 11B. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM CL-1 SOIL

Sample	Lean Clay ASTM CL-1 Measured ng/Kg from 400 ng/Kg spike												
	PFBS	**PFHxS**	**PFOS**	**PFDS**	**PFNS**	**PFHpS**	**PFPeS**	**FOSA**	**4:2 FTS**	**6:2 FTS**	**8:2 FTS**	**N-ETFOSAA**	**N-MeFOSAA**
Unspiked 1	<RL	<RL	29.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	36.55	<RL
Unspiked 2	<RL	<RL	24.1	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	24	<RL
Spiked 1	336.5	342.75	332.85	336.55	346.75	361.7	347.85	243.7	383.35	383.2	384.25	313.9	298.6
Spiked 2	357.5	360.85	358.7	319.45	342.4	357.7	347.5	224.45	391.7	374.15	398.35	334.6	311.45
Spiked 3	359.55	361.85	348.85	311.15	340.25	355.4	341.6	227.9	363.6	376.05	369.1	286.8	275.35
Spiked 4	358.25	350.15	357.25	330.95	335.95	334.2	335.8	231	382.4	365.55	378.1	283.75	277.45
Spiked 5	353.9	346.95	350.15	332.5	347.75	357.15	362.05	233.55	393.85	398.65	545.45	238.85	230.4
Spiked 6	355.1	350.95	349.05	335.6	350.7	345.8	337.6	228.05	378.65	373.65	511.7	303.85	285.2
Average Recovery (ng/Kg)	353.47	352.25	349.48	327.70	343.97	351.99	345.40	231.44	382.26	378.54	431.16	293.63	279.74
% Average Recovery	88.37	88.06	87.37	81.93	85.99	88.00	86.35	57.86	95.56	94.64	107.79	73.41	69.94
Standard Deviation	8.57	7.62	9.20	10.16	5.44	10.20	9.54	6.75	10.82	11.35	76.80	32.68	27.75
RSD (%)	2.42	2.16	2.63	3.10	1.58	2.90	2.76	2.92	2.83	3.00	17.81	11.13	9.92

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 11C. PRECISION AND ACCURACY STUDY FOR SURROGATES IN ASTM CL-1 SOIL

Sample	Surrogates- (Lean Clay ASTM CL-1– 400 ng/Kg spike)													
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	**M4:2 FTS**	**M6:2 FTS**	**M8:2 FTS**	**MN-ETFOSAA**	**MN-MeFOSAA**
Unspiked 1	309.05	353.15	370.7	359.15	350.2	391.65	358.65	362.3	351.4	389.6	382.4	374.95	333.95	328.95
Unspiked 2	310.5	351.05	364.4	344.2	335.2	368.55	356	353.8	344.3	386.1	385.15	378.95	363.1	345.55
Spiked 1	305	348.6	352.8	339	341.6	351.2	337.4	350.15	338.9	387.9	387.95	382.2	316.95	296.75
Spiked 2	307.6	342.2	365.8	350.15	328.05	367.9	337.7	344	339.55	391.4	403	396.95	333.15	320.05
Spiked 3	302.25	337.2	352.3	338.4	332.65	355.2	339.4	328.9	331.45	378.75	364.4	376.1	310.85	290.1
Spiked 4	303.8	343.1	358.85	331.6	340.65	361.3	343.3	333.65	333.7	375.4	374.25	387.5	297.45	283.8
Spiked 5	300.8	346.4	358.3	339.75	335.75	365.05	338.7	338.7	336.95	397.6	399.1	554.7	265.45	230.15
Spiked 6	296.9	336.6	350.7	338.65	335.75	357.45	354.7	344.95	350.1	395.6	404.55	497.4	299	281.85
Average Recovery (ng/Kg)	304.49	344.79	359.23	342.61	337.48	364.79	345.73	344.56	340.79	387.79	387.60	418.59	314.99	297.15
% Average Recovery	76.12	86.20	89.81	85.65	84.37	91.20	86.43	86.14	85.20	96.95	96.90	104.65	78.75	74.29
Standard Deviation	4.53	6.10	7.22	8.53	6.68	12.47	9.12	10.89	7.26	7.67	14.17	68.43	29.38	35.52
RSD (%)	1.49	1.77	2.01	2.49	1.98	3.42	2.64	3.16	2.13	1.98	3.66	16.35	9.33	11.95

12A-C. P&A STUDY IN ASTM ML-1 SOIL

TABLE 12A. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM ML-1 SOIL

Sample	Silt ASTM ML-1										
	Measured ng/Kg from 400 ng/Kg spike for all PFASAs except 2000 ng/Kg (PFBA and PFPeA)										
	PFTreA	**PFTriA**	**PFDoA**	**PFUnA**	**PFDA**	**PFNA**	**PFOA**	**PFHpA**	**PFHxA**	**PFPeA**	**PFBA**
Unspiked 1	<RL	<RL	<RL	<RL	<RL	<RL	123.4	<RL	103.2	<RL	<RL
Unspiked 2	<RL	<RL	<RL	<RL	<RL	<RL	125.9	<RL	102.45	<RL	<RL
Spiked 1	406.35	397.4	384.4	353.95	381.6	376.7	388.25	388.55	383.35	1748.15	1667.4
Spiked 2	407.35	393.25	378	354.65	378.9	367.25	381.3	383.85	371.1	1756.1	1698.7
Spiked 3	406.65	397.95	381.85	356	373.25	369.45	363.4	380.1	358.25	1703.1	1657.95
Spiked 4	407.95	393.4	375.7	354.15	377.4	362.7	369.2	375.65	357.95	1656.55	1666.9
Spiked 5	398.15	390.85	371.55	348.55	369.15	358.65	377	375.3	374.7	1695.7	1587.45
Spiked 6	396.55	387.8	364.7	348.3	378.8	378.15	395.7	392.15	377.9	1742.15	1646.5
Average Recovery (ng/Kg)	403.83	393.44	376.03	352.60	376.52	368.82	379.14	382.60	370.54	1716.96	1654.15
% Average Recovery	100.96	98.36	94.01	88.15	94.13	92.20	94.79	95.65	92.64	85.85	82.71
Standard Deviation	5.08	3.86	7.16	3.31	4.53	7.65	11.94	6.87	10.44	38.56	37.00
RSD (%)	1.26	0.98	1.90	0.94	1.20	2.08	3.15	1.80	2.82	2.25	2.24

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL. *Slightly below Reporting Limit

TABLE 12B. PRECISION AND ACCURACY STUDY FOR PFAS IN ASTM ML-1 SOIL

Sample	Silt ASTM ML-1 Measured ng/Kg from 400 ng/Kg spike												
	PFBS	**PFHxS**	**PFOS**	**PFDS**	**PFNS**	**PFHpS**	**PFPeS**	**FOSA**	**4:2 FTS**	**6:2 FTS**	**8:2 FTS**	**N-ETFOSAA**	**N-MeFOSAA**
Unspiked 1	27.75	96.2	201.35	<RL	<RL	<RL	<RL	125.15	<RL	<RL	<RL	101.25	<RL
Unspiked 2	24.55	98.05	202.2	<RL	<RL	<RL	<RL	123.5	<RL	<RL	<RL	99.6	<RL
Spiked 1	365.5	386.45	386.15	379.65	382.9	367.55	361.9	372.55	386.5	384.05	392.5	379.65	386.6
Spiked 2	369.2	381.8	381	373.4	378.4	382.4	366.95	379.7	377.7	379.15	380.35	383.75	379
Spiked 3	367.4	365.1	362.8	385.6	370.8	369.1	361.6	363.25	387	386.95	390.85	372.1	373.2
Spiked 4	369.15	360.95	404.4	391.9	379.9	389.25	369.35	368.2	386.1	384.85	400.95	385.65	390.3
Spiked 5	424.05	369.9	416.8	383.35	375.7	369.8	360.6	374.5	371.85	383.5	399.45	390.55	384.15
Spiked 6	407.55	389.25	402.25	376.3	358.75	367.15	378.25	340.8	385.9	382.55	387.25	350.8	377.35
Average Recovery (ng/Kg)	383.81	375.58	392.23	381.70	374.41	374.21	366.44	366.50	382.51	383.51	391.89	377.08	381.77
% Average Recovery	95.95	93.89	98.06	95.43	93.60	93.55	91.61	91.63	95.63	95.88	97.97	94.27	95.44
Standard Deviation	25.36	11.83	19.40	6.70	8.70	9.31	6.73	13.78	6.28	2.60	7.69	14.29	6.36
RSD (%)	6.61	3.15	4.95	1.75	2.32	2.49	1.84	3.76	1.64	0.68	1.96	3.79	1.67

NOTE: P&A concentration for each analyte are values after subtracting average of the Unspiked samples if ≥ RL.

TABLE 12C. PRECISION AND ACCURACY STUDY FOR SURROGATES IN ASTM ML-1 SOIL

Sample	Surrogates- (Silt ASTM ML1 – 400 ng/Kg spike)													
	MPFBA	MPFHxA	MPFHxS	MPFOA	MPFNA	MPFOS	MPFDA	MPFUnA	MPFDoA	**M4:2 FTS**	**M6:2 FTS**	**M8:2 FTS**	**MN-ETFOSAA**	**MN-MeFOSAA**
Unspiked 1	346.85	382.45	375.25	368.25	372.8	394.05	383	353.85	384.7	370.05	371.7	389.15	399.9	390.7
Unspiked 2	335.8	384.15	356.55	370.45	362.35	383.1	372	354.05	369.85	379.6	361.5	379.6	388.9	375.5
Spiked 1	347.75	391.85	385.45	385.4	386.85	400.8	384.9	371.3	384.55	407	394.9	419.9	393.4	393.2
Spiked 2	349.7	383.45	382.3	370.5	368.95	396.9	372.7	354.7	374.45	394.7	397.35	416.85	388.2	398.5
Spiked 3	343.65	392.85	383.7	370.35	378.35	391.9	367.45	363.6	387.1	398.5	377.35	413.3	408	385.05
Spiked 4	324	377.6	376.45	373.75	367.9	367	383.35	361.4	379.85	386.05	386.75	429.85	399.05	375.85
Spiked 5	327.05	362.75	368.55	366.45	370.25	391	359.65	349.7	367	378.45	387.4	430.15	389.65	373.1
Spiked 6	344.8	373.4	371.5	365.5	360.6	385.65	367.7	342.4	361.05	392.15	379.65	392.45	375.15	380.1
Average Recovery (ng/Kg)	339.95	381.06	374.97	371.33	371.01	388.80	373.84	356.38	376.07	388.31	382.08	408.91	392.78	384.00
% Average Recovery	84.99	95.27	93.74	92.83	92.75	97.20	93.46	89.09	94.02	97.08	95.52	102.23	98.20	96.00
Standard Deviation	9.85	9.85	9.52	6.25	8.50	10.48	9.11	8.90	9.50	12.07	12.00	19.32	9.85	9.36
RSD (%)	2.90	2.58	2.54	1.68	2.29	2.70	2.44	2.50	2.53	3.11	3.14	4.73	2.51	2.44

TABLE 13. DIFFERENT/ADDITIONAL ACCEPTABLE ISOTOPES

Different Isotopes	Analyte	Abbreviation	Transition	SRM	Cone	Collision
1	Perfluoro-n-(1,2,3,4,6-$^{13}C_5$)hexanoic acid	M5PFHxA	Primary	317.9>272.9	10	10
2	Perfluoro-n-($^{13}C_8$)octanoic acid	M8PFOA	Primary	420.9>375.9	15	10
3	Perfluoro-n-($^{13}C_9$)nonanoic acid	M9PFNA	Primary	471.9>426.9	15	10
4	Perfluoro-n-(1,2,3,4,5,6,7-$^{13}C_7$)undecanoic acid	M7PFUnA	Primary	569.9>525	15	12
5	Perfluoro-1-(1,2,3-$^{13}C_3$)hexanesulfonate	M3PFHxS	Primary	401.9>79.8	15	32
6	Perfluoro-n-(1,2,3,4,5,6-$^{13}C_6$)decanoic acid	M6PFDA	Primary	518.9>473.9	15	12
7	Perfluoro-1-($^{13}C_8$)octanesulfonate	M8PFOS	Primary	507>79.8	15	40
Additional Isotopes						
1	Perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	M3PFBS	Primary	301.8>79.8	10	29
2	Perfluoro-n-($^{13}C_5$)pentanoic acid	M5PFPeA	Primary	267.8>222.9	15	9
3	Perfluoro-n-(1,2,3,4-$^{13}C_4$)heptanoic acid	M4PFHpA	Primary	366.9>321.9	10	10
4	Perfluoro-n-(1,2-$^{13}C_2$)tetradecanoic acid	M2PFTreA	Primary	714.9>669.9	20	15
5	Perfluoro-1-($^{13}C_8$)octanesulfonate	M8FOSA	Primary	505.9>77.8	15	30

FIGURES 1-4. PFOS & PFHXS INTEGRATION EXAMPLES

FIGURE 1. PFOS IN CALIBRATION STANDARD

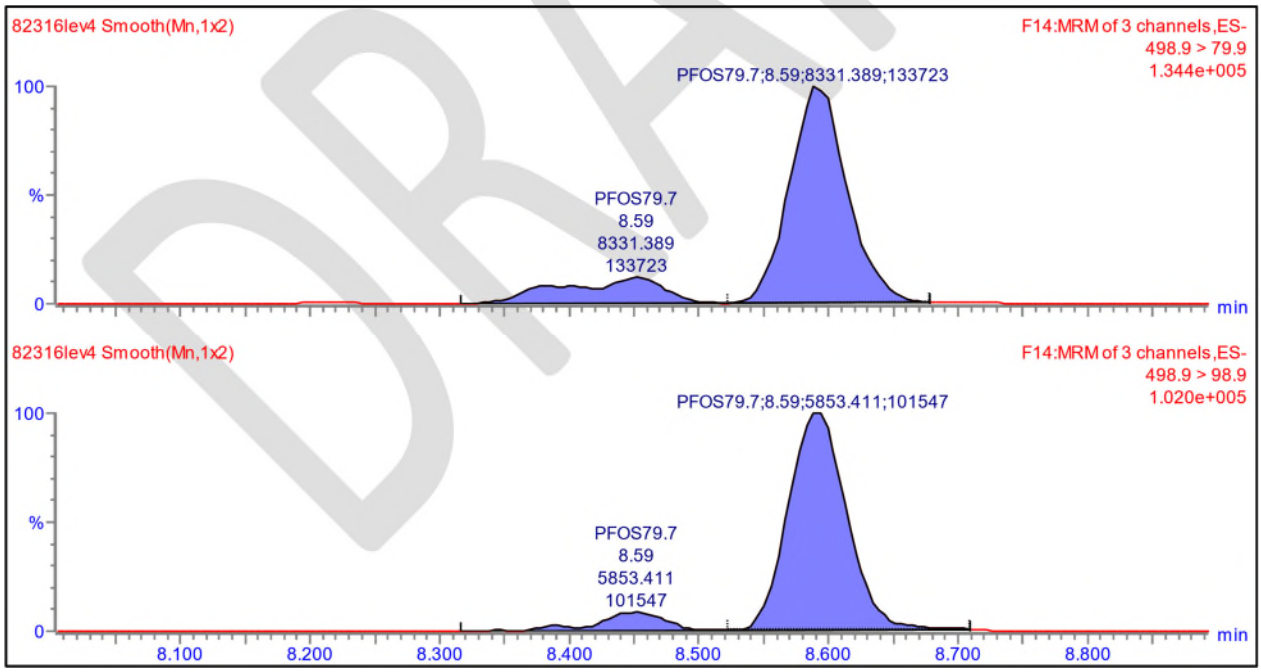
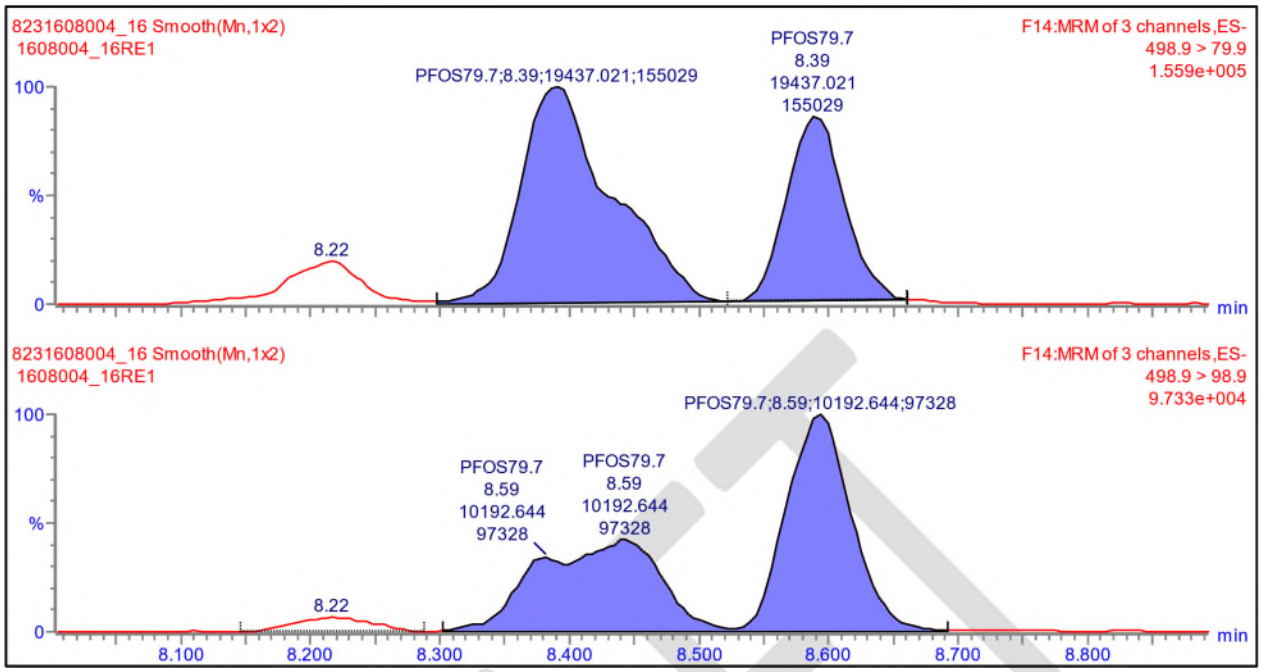


FIGURE 2. PFOS IN GROUNDWATER SAMPLE



The peak at 8.22 minutes is probably another isomer group of PFOS, but it's not included in the quantitation of the calibration standard so it can't be included in the quantitation of the groundwater sample.

FIGURE 3. PFHXS IN CALIBRATION STANDARD

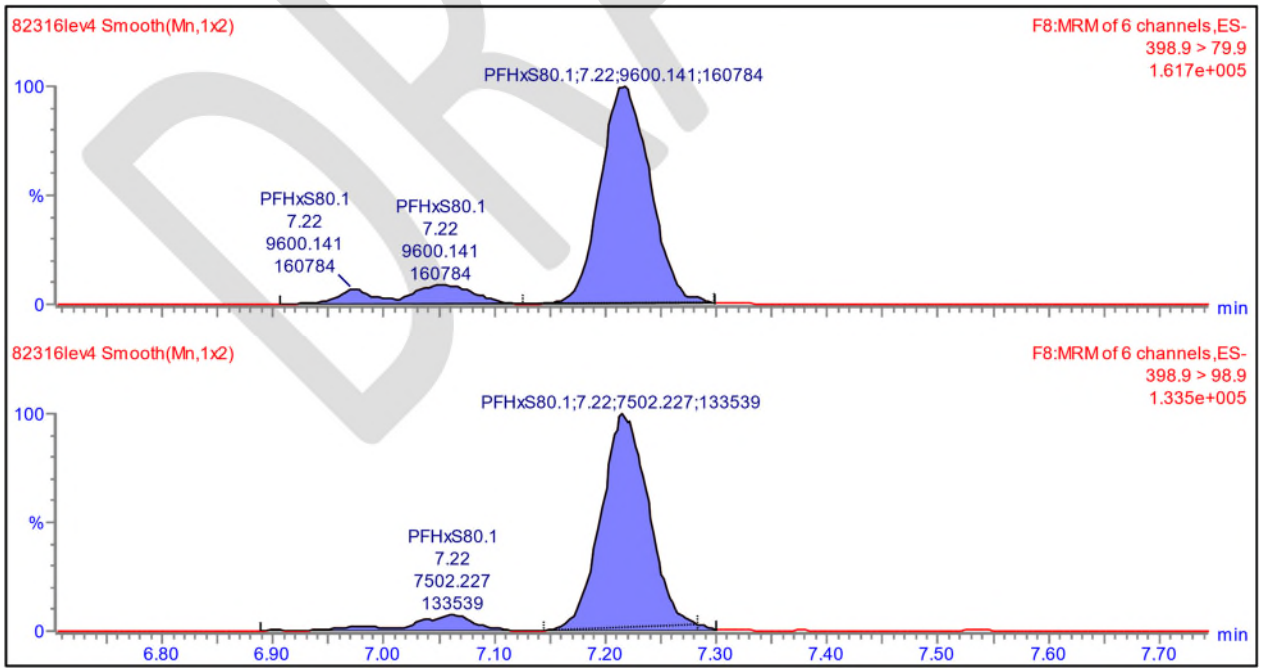
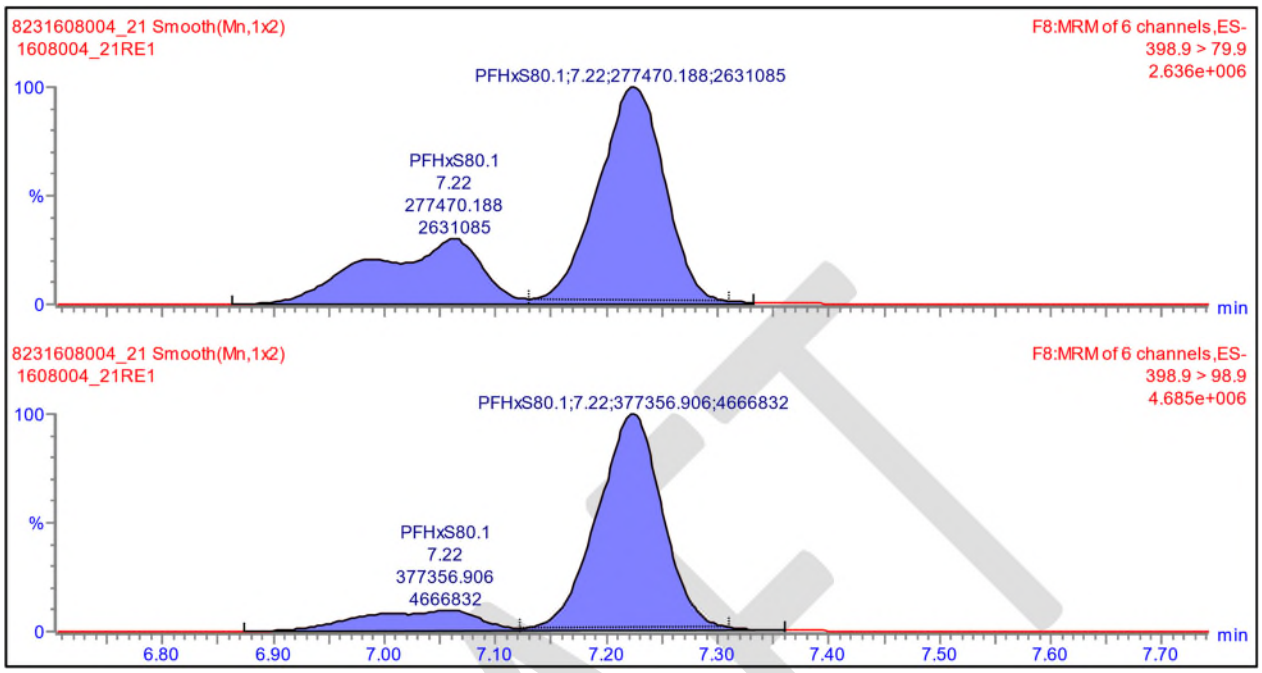


FIGURE 4. PFHXS IN GROUNDWATER SAMPLE



APPENDIX THREE - GLOSSARY

ASTM	ASTM International, formerly American Society for Testing and Materials
CAS RN	Chemical Abstract Service Registry Number®
CCV	continuing calibration verification
CD	compact disc
Da	dalton
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
HDPE	high density polyethylene
ICV	initial calibration verification
IDP	initial demonstration of proficiency
LC	liquid chromatography
LCS	laboratory control sample
LIMS	Laboratory Information Management System
LLOQ	lower limit of quantitation
LV	level
MDL	method detection limit
m/z	mass-to-charge ratio
MB	method blank
MRM	multiple reaction monitoring
MS	mass spectrometer
NA	not available
OSHA	Occupational Health and Safety Administration
PFAS	per- and poly-fluoroalkyl substances
ppt	parts per trillion
PPE	personal protective equipment
P&B	precision and bias
PTFE	polytetrafluoroethylene
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QL	quantitation limit
QMP	quality management program
RPD	relative percent difference
RSD	relative standard deviation
RT	retention time
SAP	sampling and analysis plan
SDS	Safety Data Sheet
SOP	standard operating procedure
SRM	single reaction monitoring
UPLC	ultraperformance liquid chromatograph

Definitions

Method Detection Limit (MDL): The minimum concentration of analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

Quantitation Limit (QL): This is the lowest concentration reported by this SOP, except in the case of a special request.

Batch QC: All the quality control samples and standards included in an analytical procedure. A batch typically consists of 20 field samples.

ASTM Type I Water: Shall conform to ASTM Standard D1193 specifications.

SRM Transition: Single Reaction Monitoring transition.