Quality Assurance Project Plan/Field Sampling Plan for Emerging Contaminants in Soil

HPS Parcel F
Block 6, Lot 30
Hunter's Point South Project Area,
Queens, New York
BCP Site #C241225

April 10, 2019

Prepared for:

GO HPS LLC
c/o Gotham Organization, LLC
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Prepared by:

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1. Introduction

Roux Environmental Engineering and Geology, D.P.C. (Roux), on behalf of GO HPS LLC, has prepared this Quality Assurance Project Plan/Field Sampling Plan (QAPP/FSP) to describe the measures that will be taken to ensure that the data generated during sampling of emerging contaminants (ECs) in soil during the Remedial Investigation (RI) for HPS Parcel F (Site), located at the southern tip of the Hunter's Point South Project Area (HPSPA) in the Hunter's Point South neighborhood of Queens are of quality sufficient to meet project-specific data quality objectives (DQOs). The Site is comprised of Block 6 Lot 30 of the New York City Tax Map and is located on Center Boulevard between 56th and 57th Avenues. This QAPP/FSP also includes field sampling procedures.

GO HPS LLC is a Volunteer in the Brownfield Cleanup Program (BCP). RI activities will be conducted under the New York State Department of Environmental Conservation (NYSDEC) BCP (Site #C241225). This QAPP/FSP was prepared in accordance with the guidance provided in NYSDEC Technical Guidance DER-10 Technical Guidance for Site Investigation and Remediation (DER-10), the NYSDEC BCP Guide, and the United States Environmental Protection Agency's (USEPA's) Guidance for the Data Quality Objectives Process (EPA QA/G-4).

1.1 Purpose

The QAPP/FSP describes in detail the field sampling and quality assurance/quality control (QA/QC) methods to be used during EC soil sampling tasks performed during the RI.

This QAPP/FSP provides guidelines and procedures to be followed by field personnel during performance of sampling during the RI. Information contained in this QAPP/FSP relates to:

- sampling objectives (Section 2);
- project organization (Section 3);
- sample media, sampling locations, analytical suites, sampling frequencies and analytical laboratory (Section 4);
- field sampling procedures (Section 5);
- sample handling, sample analysis, and quality assurance/quality control (Section 6); and
- site control procedures and decontamination (Section 7).

2. Sampling Objectives

The objective of the proposed sampling is to meet the emerging contaminant sampling requirements of NYSDEC to obtain a current representation of the environmental conditions at the Site. The sampling of other media and analyses is addressed by the March 25, 2019 Remedial Investigation QAPP/FSP.

Sampling procedures are discussed in Section 5 of this QAPP/FSP. A discussion of the DQOs and quality assurance/quality control is provided in Section 6.

3. Project Organization

A general summary of the overall management structure and responsibilities of project team members are presented below. Professional profiles for the team are provided in Attachment 1.

Project Principal

Joseph Duminuco, P.G. of Roux will serve as Project Principal. The Project Principal is responsible for defining project objectives and bears ultimate responsibility for the successful completion of the investigation.

Remedial Engineer

The Remedial Engineer for this project will be Charles McGuckin, P.E. The Remedial Engineer is a registered professional engineer licensed by the State of New York. The Remedial Engineer will have primary direct responsibility for implementation of the RI and future remedial program for the Site. The Remedial Engineer will certify in the Remedial Investigation Report (RIR) that the investigation activities were observed by qualified environmental professionals under her supervision as well as any other relevant provisions of ECL 27-1419 have been achieved in full conformance with the RI.

Project Manager

Jessica Taylor, P.G. of Roux will serve as Project Manager. The Project Manager is responsible for defining project objectives and bears ultimate responsibility for the successful completion of the work. This individual will provide overall management for the implementation of the scope of work and will coordinate all field activities. The Project Manager is also responsible for data review/interpretation and report preparation.

Field Team Leader

The Field Team Leader will be Lauren D'Orsa. The Field Team Leader bears the responsibility for the successful execution of the field program. The Field Team Leader will direct the activities of the technical staff in the field, as well as all subcontractors. The Field Team Leader will also assist in the interpretation of data and in report preparation. The Field Team Leader reports to the Project Manager.

Laboratory Project Manager

Laboratory analysis will be completed by TestAmerica Laboratories of Edison, New Jersey and Sacramento, California, New York State Department of Health (NYSDOH) Environmental Laboratory Accreditation Program (ELAP)-certified laboratories (11452 and 11666, respectively). The Laboratory Project Manager is Melissa Haas. The Laboratory Project Manager is responsible for sample container preparation, sample custody in the laboratory, and completion of the required analysis through oversight of the laboratory staff. The Laboratory Project Manager will ensure that quality assurance procedures are followed and that an acceptable laboratory report is prepared and submitted. The Laboratory Project Manager reports to the Project Principal and Project Manager.

Quality Assurance Officer

Levi Curnutte of Roux will serve as the Quality Assurance Officer (QAO) for this project. The QAO is responsible for conducting reviews, inspections, and audits to ensure that the data collection is conducted in accordance with the FSP and QAPP. The QAO's responsibilities range from ensuring effective field equipment decontamination procedures and proper sample collection to the review of all laboratory analytical data for completeness and usefulness. The QAO reports to the Project Manager and makes independent recommendations to the Field Team Leader.

4. Sample Media, Locations, Analytical Suites, and Frequency

This QAPP/FSP is specifically designed for the collection of soil samples for ECs 1,4-dioxane and Per- and Polyfluoroalkyl Substances (PFAS), which include the 21 compounds listed in the NYSDEC March 2019 Groundwater Sampling for Emerging Contaminants Guidance (NYSDEC March 2019 Guidance). These compounds and their associated laboratory reporting limits for soil are listed in the table below.

Analyte	Laboratory Reporting Limit	Units
Perfluorobutanoic acid (PFBA)	0.200	µg/kg
Perfluoropentanoic acid (PFPeA)	0.200	µg/kg
Perfluorohexanoic acid (PFHxA)	0.200	µg/kg
Perfluoroheptanoic acid (PFHpA)	0.200	µg/kg
Perfluorooctanoic acid (PFOA)	0.200	µg/kg
Perfluorononanoic acid (PFNA)	0.200	µg/kg
Perfluorodecanoic acid (PFDA)	0.200	µg/kg
Perfluoroundecanoic acid (PFUnA)	0.200	µg/kg
Perfluorododecanoic acid (PFDoA)	0.200	µg/kg
Perfluorotridecanoic acid (PFTriA)	0.200	µg/kg
Perfluorotetradecanoic acid (PFTeA)	0.200	µg/kg
Perfluorobutanesulfonic acid (PFBS)	0.200	µg/kg
Perfluorohexanesulfonic acid (PFHxS)	0.200	µg/kg
Perfluoroheptanesulfonic Acid (PFHpS)	0.200	µg/kg
Perfluorooctanesulfonic acid (PFOS)	0.500	µg/kg
Perfluorodecanesulfonic acid (PFDS)	0.200	µg/kg
Perfluorooctanesulfonamide (FOSA)	0.200	µg/kg
N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2.00	µg/kg
N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2.00	µg/kg
6:2 FTS	2.00	µg/kg
8:2 FTS	2.00	µg/kg
1,4-Dioxane	0.100	mg/kg

A discussion of the sampling schedule is provided below, while the assumed number of field samples to be collected, including quality control (QC) samples, is shown in Tables 1 and 2. Specifics regarding the collection of samples at each location and for each task are provided in Section 5 of this QAPP/FSP. All elevations discussed in these sections are in reference to the North American Vertical Datum of 1988 (NAVD88).

Soil samples from two soil borings are proposed to be collected at the locations shown in Figure 3 of the Remedial Investigation Work Plan (RIWP).

The summary table below provides details for soil sampling locations (including depth intervals represented as feet below land surface [ft bls] and elevation) that are proposed to be used to characterize the EC conditions in soil at the Site:

Locations	**Depth Intervals (Elevation)**	**Analyses** (see notes below)	**Rationale**
RMW-F1 RMW-F3	11-13 ft bls (+4 to +2 ft) 0-2 ft bls (+19 to +21 ft)	ECs	To evaluate soil quality.

For aqueous Field Blanks, PFAS will be analyzed by USEPA Method 537 Modified and 1,4-Dioxane will be analyzed by USEPA Method 8270D SIM. The TestAmerica Standard Operating Procedures (SOPs) for completing ECs analysis, list of all EC compounds to be analyzed, and reporting limits/minimum detection limits for EC compounds are included in Attachment 2.

5. Field Sampling Procedures

This section provides a detailed discussion of the field procedures to be used during sampling soil for ECs. As discussed, the sample locations are shown on Figure 3 of the RIWP. Additional details regarding sampling procedures and protocols are described in Roux's relevant Standard Operating Procedures (SOPs), which are provided in Attachment 3.

Soil borings will be advanced using a GeoProbe® Direct-Push drill rig. Should the sampling location need to be located at a distance greater than ten feet from the original proposed location due to access constraints, Roux will contact the NYSDEC case manager to confirm. Samples of the soil profile will be collected continuously from land surfance to a maximum depth of approximately 13 ft bls for EC soil sample collection.

The soil from each five foot interval will be observed for lithology and evidence of contamination (e.g., staining, odors, and/or visible free product) and placed immediately thereafter into large Zip-loc™ bags for ecording headspace using a PID. After a minimum of 15 minutes for equilibration with the headspace in the Zip-loc™ bag, each sample will be screened for organic vapors using a PID equipped with a 10.6 eV lamp. Samples for possible VOC analysis will be placed in a laboratory-supplied jar or encore sampler prior to screening, due to the potential for loss of VOCs through volatilization. Soil samples will be collected according to Section 3.2.2 of the RIWP. These samples will be placed in the laboratory-supplied containers and shipped to the laboratory under chain of custody procedures in accordance with Roux's SOPs in Attachment 3.

Soil samples collected from borings RMW-F1 and RMW-F3 will be analyzed for the NYSDEC-required ECs, in addition to the TCL + 30/TAL list. Additional necessary precautions will be taken when sampling for ECs in the field, incuding but not limited to:

- Using the proper field clothing or personal protective equipment (i.e. no materials will contain Gore-Tex or Tyvek);
- Avoid using Grundfos and bladder pumps and sampling equipment components/containers making contact with aluminum foil, low density polyethylene (LDPE), glass, or polytetrafluoroethylene materials;
- Following PFAS field sampling guidelines (i.e. using sampling materials made from high density polyethylene [HDPE], silicon, or stainless steel and avoid using equipment containing Teflon and using sharpies, permanent markers, adhesives, and waterproof/plastic clipboards and notebooks); and
- Utilizing regular ice cubes for sample presevation and only Alconox or Liquinox for decontamination.

All samples will be collected and placed in the laboratory-supplied containers and shipped to the laboratory on ice under chain of custody procedures in accordance with Roux's field sampling SOPs included as Attachment 3.

Following sample collection, boreholes will be converted into monitoring wellsas indicated on Figure 3 of the RIWP. Contaminated soil cuttings, if encountered, will be placed in sealed and labeled U.S. Department of Transportation (DOT) approved 55-gallon drums pending characterization and off-site disposal at a permitted facility.

6. Sample Handling and Analysis

To ensure quality data acquisition and collection of representative samples, there are selective procedures to minimize sample degradation or contamination. These include procedures for preservation of the samples, as well as sample packaging, shipping procedures, and QA/QC.

6.1 Field Sample Handling

A discussion of the proposed number and types of samples to be collected during each task, as well as the analyses to be performed, can be found in Section 4.0 of this QAPP/FSP. The types of containers, volumes, and preservation techniques for the aforementioned testing parameters are presented in Table 3.

6.2 Sample Custody Documentation

The purpose of documenting sample custody is to ensure that the integrity and handling of the samples is not subject to question. Sample custody will be maintained from the point of sampling through the analysis (and return of unused sample portion, if applicable).

Each individual collecting samples is personally responsible for the care and custody of the samples. All sample labels should be pre printed or filled out using waterproof ink. The technical staff will review all field activities with the Field Team Leader to determine whether proper custody procedures were followed during the field work and to decide if additional samples are required.

All samples being shipped offsite for analysis must be accompanied by a properly completed chain of custody form. The sample numbers will be listed on the chain of custody form. When transferring the possession of samples, individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to/from a secure storage area, and to the laboratory.

Samples will be packaged for shipment and dispatched to the appropriate laboratory for analysis with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be locked and/or secured with strapping tape in at least two locations for shipment to the laboratory.

6.3 Sample Shipment

Laboratory analysis will be completed by TestAmerica Laboratories of Edison, New Jersey and Sacramento, California. Sample packaging and shipping procedures are based upon USEPA specifications, as well as DOT regulations. The procedures vary according to potential sample analytes, concentration, and matrix and are designed to provide optimum protection for the samples and the public. Sample packaging and shipment must be performed using the general outline described below.

All samples will be shipped within 24 hours of collection and will be preserved appropriately from the time of sample collection. A description of the sample packing and shipping procedures is presented below:

1. Prepare cooler(s) for shipment:
   - tape drain(s) of cooler shut;
   - affix “This Side Up” arrow labels and “Fragile” labels on each cooler; and
   - place mailing label with laboratory address on top of cooler(s).

2. Arrange sample containers in groups by sample number.
3. Ensure that all bottle labels are completed correctly. Place clear tape over bottle labels to prevent moisture accumulation from causing the label to peel off.
4. Arrange containers in front of assigned coolers.
5. Place packaging material approximately at the bottom of the cooler to act as a cushion for the sample containers.
6. Arrange containers in the cooler so that they are not in contact with the cooler or other samples.
7. Fill remaining spaces with packaging material.
8. Ensure all containers are firmly packed in packaging material.
9. If needed, loose ice cubes should be repackaged in Zip-lock™ bags and placed on top of the packaging material. Blue ice or freezer packs will not be used when shipping sampling to be analyzed for PFAS.
10. Sign chain of custody form (or obtain signature) and indicate the time and date it was relinquished to courier as appropriate.
11. Separate chain of custody forms. Seal proper copies within a large Zip-loc™ bag and tape to inside cover of cooler. Retain copies of all forms.
12. Close lid and latch.
13. Secure each cooler using custody seals.
14. Tape cooler shut on both ends.
15. Relinquish to overnight delivery service as appropriate. Retain air bill receipt for project records. (Note: All samples requiring overnight delivery will be shipped for “NEXT A.M.” delivery).

6.4 Quality Assurance/Quality Control

Judy Harry of Data Validation Services will review the analytical data for quality assurance and quality control in accordance with NYSDEC standards. The professional profile for Judy Harry is provided in Attachment 1.

The primary intended use for the RI data is to characterize Site conditions and determine if remediation needs to be undertaken at the Site. The primary DQO of the soil, groundwater, and soil vapor programs, therefore, is that data be accurate and precise, and hence representative of the actual Site conditions. Accuracy refers to the ability of the laboratory to obtain a true value (i.e., compared to a standard) and is assessed through the use of laboratory quality control (QC) samples, including laboratory control samples and matrix spike samples, as well as through the use of surrogates, which are compounds not typically found in the environment that are injected into the samples prior to analysis. Precision refers to the ability to replicate a value and is assessed through both field and laboratory duplicate samples.

Sensitivity is also a critical issue in generating representative data. Laboratory equipment must be of sufficient sensitivity to detect target compounds and analytes at levels below NYSDEC standards and guidelines whenever possible. Equipment sensitivity can be decreased by field or laboratory contamination of samples, and by sample matrix effects. Assessment of instrument sensitivity is performed through the analysis of reagent blanks, near-detection-limit standards, and response factors. Potential field and/or laboratory contamination is assessed through use of trip blanks, method blanks, and equipment rinse blanks (also called “field blanks”).

Table 1 lists the requirements for field and laboratory QC samples that will be analyzed to assess data accuracy and precision, as well as to determine if equipment sensitivity has been compromised. Table 2 lists the number/type of field and QA/QC samples that will be collected during the RI. Table 3 lists the preservation, holding times and sample container information.

All analyses will be performed in accordance with the NYSDEC Analytical Services Protocol (ASP), using USEPA SW-846 methods.

All laboratory data are to be reported in NYSDEC ASP Category B deliverables and will be delivered to NYSDEC in electronic data deliverable (EDD) format as described on NYSDEC's website (http://www.dec.ny.gov/chemical/62440.html). A Data Usability Summary Report (DUSR) will be prepared meeting the requirements in Section 2.2(a)1.ii and Appendix 2B of DER-10 for all data packages generated for the RI.

7. Site Control Procedures

Site control procedures, including decontamination and waste handling and disposal, are discussed below. Site control procedures have been developed to minimize both the risk of exposure to contamination and the spread of contamination during field activities at the Site. All personnel who come into designated work areas, including contractors and observers, will be required to adhere strictly to the conditions imposed herein and to the provisions of a Site-Specific Health and Safety Plan (HASP). The HASP is included as Appendix C to the RIWP.

7.1 Decontamination

In an attempt to avoid the spread of contamination, all drilling and sampling equipment must be decontaminated at a reasonable frequency in a properly designed and located decontamination area. Detailed procedures for the decontamination of field and sampling equipment are included in Roux's SOPs for the Decontamination of Field Equipment located in Attachment 3. The location of the decontamination area will be determined prior to the start of field operations. The decontamination area will be constructed to ensure that all wash water generated during decontamination can be collected and containerized for proper disposal. As mentioned above, only Alconox or Liquinox will be used during decontamination procedures when groundwater sampling is underway.

7.2 Waste Handling and Disposal

All waste materials (drill cuttings, decontamination water, etc.) generated during the RI will be consolidated, and stored in appropriate labeled bulk containers (drums, etc.), and temporarily staged at an investigation derived waste storage area onsite. Roux will then coordinate waste characterization and disposal by appropriate means.

TABLES

Table 1. Field and Laboratory QC Summary

QC Check Type	Minimum Frequency	Use
Field QC		
Duplicate	1 per matrix per 20 samples or SDG*	Precision
Trip Blank	1 per VOC cooler	Sensitivity
Field Blank	1 per matrix per 20 samples	Sensitivity
Laboratory QC		
Laboratory Control Sample	1 per matrix per SDG	Accuracy
Matrix Spike/Matrix Spike Duplicate/Matrix Duplicate**	1 per matrix per SDG	Accuracy/Precision
Surrogate Spike	All organics samples	Accuracy
Laboratory Duplicate	1 per matrix per SDG	Precision
Method Blank	1 per matrix per SDG	Sensitivity

Notes:
QC - Quality Control
* SDG - Sample Delivery Group - Assumes a single extraction or preparation
** Provided to lab by field sampling personnel

Table 2. Remedial Investigation Sampling Summary

Sample Matrix	Target Analytes	Field Samples	Replicates[1]	Trip Blanks[2]	Field Blanks[1]	Matrix Spikes[1]	Spike Duplicates[1]	Total No. of Samples
Soil	PFAS	2	1	-	1	1	1	6
	1,4-Dioxane	2	1	-	1	1	1	6

Totals are estimated based on scope of work as written, actual sample quantities may vary based on field conditions. QA/QC sample quantities will be adjusted accordingly.

[1] Based on 1 per 20 samples or 1 per Sample Delivery Group (3 days max)

[2] Based on 1 cooler per day

TCL - USEPA Contract Laboratory Program Target Compound List

USEPA - United States Environmental Protection Agency

PFAS - Per- and Polyfluoroalkyl Substances

Table 3. Preservation, Holding Times, and Sample Containers

Analysis	Matrix	Bottle Type	Preservation[a]	Holding Time[b]
PFAA vis USEPA 537(M)-Isotope Dilution	Soil	250 mL HDPE	Cool to 4°C	14 days to extract, 28 days to analysis
	Water	Three 250 mL plastic bottles	Trizma	14 days
1,4-Dioxane via 8270SIM	Soil	4 oz wide mouth glass	Cool to 4°C	14 days to extract, 40 days to analysis
	Water	500 mL amber glass	Cool to 4°C	7 days to extract, 40 days to analysis

[a] All soil and groundwater samples to be preserved in ice during collection and transport

[b] Days from date of sample collection.

PFAA - Perfluorinated Alkyl Acids

HDPE - High Density polyethylene

ATTACHMENTS

1. Professional Profiles
2. Laboratory's Standard Operating Procedures
3. Roux's Standard Operating Procedures

ATTACHMENT 1

Professional Profiles

ROUX

PROFESSIONAL PROFILE

Joseph Duminuco, P.G.

Executive Vice President/Principal Hydrogeologist

TECHNICAL SPECIALTIES

Providing environmental consulting services and strategic planning to the real estate industry focused on Brownfield Redevelopment projects. Investigation and remediation of soil, groundwater, and soil vapor at commercial and industrial sites, focusing on the use of innovative solutions.

EXPERIENCE SUMMARY

Thirty-two years of experience: Executive Vice President, Vice President, Practice Area Leader, Office Manager, Principal, Senior, and Project Hydrogeologist at Roux; Staff Hydrogeologist at Geraghty & Miller; and Geologist at Mueser Rutledge Consulting Engineers.

CREDENTIALS

M.S. in Geology, Wright State University, 1990
B.S. in Geology, Hofstra University, 1983
Licensed Professional Geologist, NY (License No. 000119)

EXPERIENCE OVERVIEW

- Principal-in-Charge of multiple dry cleaner remediation project takeovers:
  - Brooklyn, New York – NYSDEC BCP
  - Long Island, New York – NYSDEC BCP
  - Long Island, New York – NYSDEC Inactive Hazardous Waste Site
  - Bernardsville, New Jersey – LSRP Program
  - Enfield, Connecticut – LEP Program

  Sites included a mixed use multifamily affordable housing neighborhood retail complex, a healthcare facility, and retail shopping centers. Impacts included soil, groundwater, vapor, indoor air, and building material contamination from chlorinated VOCs from the former dry cleaner operations. Activities included historical research, re-delineation of contaminant source areas, negotiations with regulatory agencies and remediation including hot spot soil removal, SVE, in situ groundwater treatment, and negative pressure approaches (SSDS) for vapor mitigation in the existing buildings.

- Principal in Charge of multiple NYSDEC BCP/VCP Site Redevelopments:
  - Brooklyn – Former railroad freight yard and dry cleaner solvent distribution plant into mixed use multifamily housing and retail.
  - Brooklyn – Former manufactured gas plant into big box retail.
  - Brooklyn – Mixed use multifamily affordable housing with neighborhood retail complex.
  - Long Island – Former NYSDEC Inactive Hazardous Waste Site into mixed use multifamily housing, retail, hotel, office and community space.
  - Long Island – Former defense contractor manufacturing facility into multifamily waterfront housing.
  - Long Island – Former dry cleaner and auto repair into a healthcare facility.
  - Staten Island – Former gas station into a fast food restaurant.
  - Queens – Former paint and varnish factory into waterfront mixed use multifamily housing, retail and community space.
  - Westchester – Multi-block former auto sales and service, dry cleaner and gas station into mixed use multifamily housing and retail.

  Activities included Pre-Application scoping meetings, agency negotiations, Phase I ESAs, investigation, remedial design and oversight, in-situ waste characterization, CAMP and preparation of: BCP Application; CPP; RIWP; RIR; RAWP; SMP; and FER.

- Principal in Charge of multiple NYCOER/NYCDEP/HPD Site Redevelopments:
  - Bronx – Expansion and renovation of retail center built on former illegal landfill.
  - Bronx – Multi-block redevelopment of former industrial/manufacturing area into mixed use multifamily affordable housing, retail, and community services.
  - Bronx – Redevelopment of an abandoned recreational property into supportive housing.
  - Bronx – Redevelopment of residential and commercial parcels into supportive housing.
  - Brooklyn – Redevelopment of a vacant residential and wooded lot into supportive housing.
  - Manhattan – A full city block redevelopment of former commercial and tenement housing into a mixed use multifamily affordable housing, retail and community services.
  - Manhattan – Expansion and renovation of former auto sales and service center into high-end US auto dealer flagship facility.
  - Manhattan – Former parking lot into mixed use NYC Public School and multifamily luxury tower.
  - Manhattan – The redevelopment of a former garage and auto repair operation and a manufacturing facility on two adjacent lots into a multi-story single-family residence.
  - Queens – Redevelopment of former industrial use parcels on land previously underwater into multifamily affordable housing.

  Activities included Pre-Application scoping meetings, agency negotiations, Phase I ESAs, investigation, remedial design and oversight, in situ waste characterization, CAMP and preparation of: VCP Application; RIWP; RIR; RAP; CHASP: SMP; and Completion Reports.

KEY PROJECTS

- Principal-in-Charge of the 45-acre development of a state of the art sports arena and commercial/retail complex at

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an existing sports venue on Long Island, NY. Responsibilities include: Phase I and Phase II ESAs, EIS support, and Waste Characterization sampling design and implementation.

- Principal-in-Charge of the redevelopment of an entire city block into a mix of public and private open space with community gardens, 655 mixed-income residential units, and community services containing three multi-use buildings in Harlem, NY. The buildings will be certified to Passive House standards. Responsibilities include: Phase I and II ESAs, Remedial Action Plans, waste characterization sampling design, and implementation and reporting to the NYCDEP.
- Principal-in-Charge of the redevelopment of a waterfront Site that will include two high-rise affordable residential towers in Queens, NY. Additionally, the development includes public spaces, including two piers extending into the East River. The Site is being entered into the NYSDEC BCP and is immediately adjacent to the Newtown Creek Federal Superfund Site.
- Principal-in-Charge of the redevelopment of a former garage and auto repair operation and a manufacturing facility on two adjacent lots into a multi-story single-family residence in lower Manhattan, NY. The Site contains an E-Designation and as such is going through the NYCOER VCP. Roux completed a Phase I ESA, an RI, a RAWP, a waste characterization plan, and is providing oversight of waste management, UST removals, and CAMP.
- Principal-in-Charge of a NYSDEC BCP redevelopment of a property adjacent to a dry-cleaning solvent distribution facility in Brooklyn, New York. The Site was a former freight railyard, and offloading spillage on-site and migration from the off-site solvent facility resulted in significant soil, groundwater, and vapor contamination with chlorinated VOCs. The Site was developed into multifamily units with first floor retail use and the remedy consisted of soil hot spot removal, a physical barrier to limit on-site migration, a permeable reactive wall to eliminate off-site migration, hot-spot in situ injections, and a sub-slab depressurization system. The Site contained an E-Designation which was satisfied through the NYCOER simultaneously with the BCP process. Roux was awarded the Big Apple Brownfield Award for Innovation based on our successful cleanup approach.
- Principal-in-Charge of a NYSDEC BCP redevelopment project that also required a RCRA-compliant facility closure. The Site is a former paint factory located in Queens, NY. Historical site operations adversely impacted the subsurface including a LNAPL plume, in addition to petroleum hydrocarbon impacts to the soil and groundwater. Roux completed a RI at the Site which characterized the nature and extent of the impacts. The remedial action included a large excavation that required SOE and was completed under a tent due to odor concerns, multiple ISCO injections, UST removal/abandonment, installation of a LNAPL recovery system, and installation of an SSDS. Additionally, Roux provided oversight of RCRA closure activities at the Site, which included emptying, cleaning, and scrapping 65 ASTs/vessels; decontaminating the ceilings, walls, and floors of the Paint Factory Building; and collection of compliance samples.
- Principal-in-Charge of a NYSDEC VCP redevelopment of a former MGP site into a Big Box retail site in Brooklyn, NY. The project consisted of negotiations with the NYSDEC and Roux limited remediation to former gasholders filled with coal tar, soil hot spots with mobile coal tar, and perimeter containment of coal tar. All the remaining soil at the Site was impacted with MGP waste and most of the Site was underlain by liquid coal tar. Roux negotiated use of institutional/engineering controls to allow significant contamination to remain in place. A sub-slab depressurization system and vapor barrier was installed to address the mobile coal tar left below the retail building.
- Principal-in-Charge for a NYSDEC BCP redevelopment project at a site in White Plains, NY, which consists of 16 separate parcels spanning 4.5 acres and had a variety of former uses including automotive service/repair and multiple dry cleaners. The Site has both chlorinated and petroleum hydrocarbon impacts to the soil and groundwater. The remedy will consist of a site cover system, soil hot spot removals, in situ chemical oxidation for groundwater contamination, and installation of a sub-slab depressurization system.
- Principal-in-Charge for ongoing large and complex mixed use redevelopment of a 92-acre site located in Long Island, NY. The Site was accepted into the NYSDEC BCP. The Site has an extensive environmental history, including former use as a wire and conduit manufacturer (former NYS Inactive Hazardous Waste Site), former landfill (currently a Federal Superfund Site), and town DPW facility. Activities completed included compiling, reviewing, extracting, and summarizing numerous historical environmental reports prepared for the Site; interacting with the NYSDEC, USEPA, and NCDOH; completing a supplemental soil investigation (including extensive use of XRF Technology as metals are the compound of concern); and a groundwater investigation (water is over 100 feet deep). The remedy will likely consist of hot spot removals, a site cover system and a sub-slab depressurization system.
- Principal-in-Charge for a NYSDEC BCP redevelopment in Staten Island, NY of a former retail service station site. There is soil, groundwater, and vapor contamination from petroleum-related constituents in the vicinity of the former gasoline piping and pump island (the petroleum source area), as well as historic fill across the entire Site. The remedy, described in the Remedial Action Work Plan prepared by Roux, will consist of a sheet pile containment wall around the petroleum source area, a Site Cover System across the entire Site comprised of

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Executive Vice President/Principal Hydrogeologist

concrete building slab/walkways, asphalt parking areas and limited landscaped areas, and site-wide a sub-slab depressurization system to prevent vapor intrusion into the proposed retail building and off-site migration of impacted soil vapor.

- Principal-in-Charge of a mixed-use (public school and residential) Brownfield redevelopment in lower Manhattan, NY. Project consisted of a Phase I and a Phase II ESA to satisfy NYCDEP requirements. Due to the presence of contaminated historic fill, Roux performed in situ waste characterization to assist in the development of NYCDEP-required plans. In addition, Roux provided oversight of the waste removal, completion of waste manifests, and full-time CAMP during all soil moving activities. Roux provided support to the excavation contractor when two previously unknown USTs were discovered during excavation activities.
- Principal-in-Charge of a multi-phased NYSDEC VCP redevelopment of a former Defense Site to water front, upscale housing in Long Island, NY. This investigation included determining the nature and extent of chlorinated VOCs in soil, groundwater, and vapor- phase contamination on-site and off-site. Utilized a risk assessment to argue the level of residual contamination allowed to remain on-site with an intended residential future use. Remedial alternatives were selected in accordance with future development plans and institutional/engineering controls were proposed to limit cleanup costs. Successfully argued the technical impracticability of remediation of the heavily contaminated deeper aquifer beneath the site and off-site.
- Principal-in-Charge of a retail/commercial redevelopment in the Bronx, NY. The Site contained a NYCDEP E-Designation due to a previous on-site service station UST release. In addition, a previous Phase I and Phase II ESA identified a former dry cleaner with a chlorinated VOC release. Roux performed a focused Phase II ESA at the dry cleaner and determined the chlorinated solvent release was not a hazard. Roux obtained closure under the NYSDEC Spills group and the Site was redeveloped with a restaurant, a pharmacy, and reuse of a former supermarket.
- Principal-in-Charge of the redevelopment and expansion of an automobile dealer/service center in New York, NY into the US Flagship dealer for a major European luxury car manufacturer. Supported the client and legal team during lease negotiations. Worked closely with the NYCOER to address NYCDEP "E" designation. Coordination with the NYCOER to implement remedial investigation and develop a Site Materials Management Plan as part of the expansion. Also, worked closely with the NYSDEC to address an on-site spill, as well as coordinate efforts to evaluate whether a 19,000-gallon dielectric fluid release by others impacted the Site.
- Principal-in-Charge for the completion of Phase I and Phase II Environmental Site Assessment activities associated with a proposed mixed use redevelopment located in Westchester, NY waterfront. Work included management of subsurface investigation activities to characterize soil conditions, and working closely with the client's architects and construction contractors to integrate the proposed site remediation into the project development plan (including evaluating multiple potential disposal scenarios). Site contaminants included hydrocarbons (including free-product plume from former USTs) and historic fill constituents.
- Principal-in-Charge of an 80-acre redevelopment in Yonkers, NY. Work included Phase I and Phase II investigations, asbestos surveys and abatement support, and response to a free product impact form an adjacent landowner. Coordinated with the NYSDEC and responsible party to address contamination issue and not impact the client's construction schedule.
- Principal-in-Charge for the redevelopment of a property in Brooklyn, NY into supportive housing. Worked closely with the NYCOER to address the NYCDEP "E" designation. Coordination with the NYCOER to implement remedial investigation and develop RAP/CHASP as part of the NYC VCP.
- Principal-in-Charge for the redevelopment of a property in the Bronx, New York into supportive housing. Worked closely with NYCDEP to address "E" designation. Coordination with NYCDEP to implement remedial investigation and develop RAP/CHASP as part of the redevelopment. Also performed an ASTM VEC to address vapor concerns.
- Principal-in-Charge of a Brownfield Redevelopment for a large vacant parcel (460 acres) on Long Island, NY. The project involved an extensive investigation, UST, and PCB remediation; removal and proper disposal of numerous tanks, drums, abandoned vehicles and transformers; and participation in contentious public meetings. The Site was redeveloped into a golf course and a senior care facility.
- Project Manager of an RI/FS at a former electronics manufacturing facility in an industrial area of Long Island, NY. Metals and solvents (plating wastes) were detected in on-site leach pools and in soil and groundwater. Responsibilities included reviewing and revising the work plan and providing technical oversight of the project, including Geoprobe® drilling, soil sampling; soil-gas surveys, leach pool sediment sampling, monitoring well installation, groundwater sampling, geophysical mapping, report preparation, and negotiations with the NYSDEC. Convinced the NYSDEC that groundwater remediation was inappropriate in an industrialized area. Focused remediation to a few soil hot spots only.

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ROUX

PROFESSIONAL PROFILE

Charles J. McGuckin, P.E.

Principal Engineer

TECHNICAL SPECIALTIES

Engineering design of soil and groundwater remediation systems. brownfields cleanup plans, stormwater studies and engineered natural treatment systems.

EXPERIENCE SUMMARY

Thirty years of experience: Principal, Senior and Project Engineer with Roux Associates; President of Remedial Engineering, P.C.; and Design Engineer at Dvirka and Bartilucci Consulting Engineers.

CREDENTIALS

B.C.E., Civil Engineering, University of Delaware, 1987
M.B.A., Management, Adelphi University, 1992
Professional Engineer: New York, New Jersey, Pennsylvania, Rhode Island, Connecticut, Vermont, Virginia, North Carolina, Ohio, Michigan and Montana

PROFESSIONAL AFFILIATIONS

National Society of Professional Engineers
American Society of Civil Engineers
WEF Hazardous Waste Committee, 1996 – 1998

PUBLICATIONS

Assessment and Remediation of Off-Spec Asphalt Disposal Areas - Co-authored, Contaminated Soils, Volume 3, Amherst Scientist Publishers, 1998

Use of a Subsurface Flow Constructed Wetlands for Collection and Removal of Water Containing BTEX, Co-authored, Proceedings of the 2000 Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, National Ground Water Association

KEY PROJECTS

- Principal Engineer for environmental consulting support services for a large landfill O&M contract under review by the New York City Department of Investigation. The work entailed reviewing the scope of routine vs. non-routine work performed over a one-year period for compliance with contract requirements. The O&M Work included routine cover maintenance, groundwater and gas monitoring, landfill gas extraction, major system repairs and waste handling. Memos of findings were prepared assessing acceptability of work, compliance with permit regulations and providing recommendations for improvements.
- Principal Engineer for the independent engineering review of change orders for the New York MTA Office of the Inspector General associated with electric utility substations reconstruction damaged during the 2012 Superstorm Sandy. The cost review focused on contracting procedures, waste classification of impacted structures and soils, proper waste management and disposal. Findings were compiled in a report to determine if costs were legitimate and justifiable and providing recommendations for improved specifications for bidding and of management waste handling contracts.
- Principal Engineer providing program management of interior building materials surveys for 22 residential buildings along the south shore of long island under an Army Corps of Engineers contract for dune reconstruction. Building materials surveys included testing and analysis of suspect contaminants and reporting in support of building abatement and demolition planning. Testing was completed using multiple teams on a tight timeline to meet project schedule requirements.
- Principal Engineer for remedial action plan implementation oversight and certification for the CornellTech campus development on Roosevelt Island, New York. The first phase of the campus development included lead paint and ACM abatement and demolition of the former Goldwater Hospital, construction of six main campus buildings, new utilities, roadways and lawn/landscaped areas. Responsibilities include oversight of soil/subsurface structures excavation handling, disposal and reuse; community air monitoring; dewatering permit compliance; and SWPPP inspections.
- Principal Engineer for the preparation of an expert report for a former valve manufacturing facility in Coxsackie, New York. The report was prepared on behalf of counsel for a Contractor who performed remedial construction work for this State "Superfund" site. The actions were against the holder of the construction contract, NYSDEC, and their engineering consultant. The remedial action included building demolition, remediation of soils impacted by chlorinated VOCs, removal of DNAPL source areas, treatment of excavated soils using low temperature thermal desorption, and consolidation and capping of metals impacted soils. The expert project work involved a detailed review of the RI/FS, remedial action plans and construction progress documentation to formulate opinions as to the industry acceptable accuracy of the Contract Documents.
- Senior Engineer for the decommissioning and decontamination of a pharmaceutical facility covering seven city blocks as a part of a NYSDEC Voluntary Cleanup Agreement in Brooklyn, New York. The former office and laboratory complex would be decontaminated for reuse as a school and small business space. Multiple other buildings were demolished. Responsibilities included preparation of interior abatement plans to address mercury, lead and PCBs in building materials and review of Interim Remedial Measure (IRM) work plans for lead, benzene and mercury-contaminated soil excavation and disposal. Groundwater remediation design included air sparge/soil vapor extraction, in situ oxidation and a reactive barrier wall using colloidal carbon and ZVI.
- Principal Engineer for the performance of a Brownfields Demonstration Pilot Program in the Hamlet of New Cassel for the Town of North Hempstead, New York. Under an EPA grant, Roux Associates created an inventory of 50 potential commercial/industrial properties within New Cassel and evaluated these properties based on perceived contamination and potential for redevelopment/reuse. Eight sites exhibiting the greatest potential for redevelopment were selected to perform Phase I

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Environmental Site Assessments. Of these eight sites, four sites were selected for Brownfield Site investigations to identify the nature and extent of contamination in soil and groundwater and provide potential remedial alternatives and cleanup costs to revitalize these properties. The Brownfields Demonstration Pilot Program also included community outreach activities to promote a unified approach to the redevelopment of Brownfields in new Cassel.

- Principal Engineer responsible for engineering certification of all remediation activities related to the seven-city-block Barclay's Arena and Atlantic Yards redevelopment in Brooklyn, New York. This multi-billion-dollar redevelopment includes the Arena, which will be focal point of the largest redevelopment project in Brooklyn, consisting of an urban complex of housing, commercial and retail space, as well as several acres of landscaped public open space. The existing properties being redeveloped are residential, commercial, and industrial properties, including a large railroad yard. Engineering certification included multiple RAWPs under NYSDEC Spills Program, UST removals, soil excavation, in situ groundwater treatment and remedy oversight services. The project also includes ACM abatement, building demolition, soil pre-waste-classification, coordination (with the receiving facilities), and oversight of the removal of 1,000,000 cubic yards of soil (~550,000 yards removed to date), representing one of the largest excavation and soil removal projects performed in New York City.
- Principal engineer for the preparation of the feasibility study, IRM plans, and remedial design/remedial action plans for a 40-acre former manufacturing facility in Rensselaer, New York. IRM Soil remediation included excavation of over 10,000 cubic yards of CVOC and metals source material for disposal at multiple facilities based on waste characteristics. Basement cleaning was performed in three large buildings to remove accumulated process sludges. Lagoon closure plans included sediment removal, dewatering, soil washing, and soil capping. The final remedy for the site includes a groundwater perimeter containment trench and 40 gpm treatment system for metals and VOCs and a 9-acre vegetated cap for a former landfill.
- Principal Engineer responsible for the preparation of the remediation completion report at Captain's Cove former municipal landfill State Superfund Site located in Glen Cove, New York. This work has been performed in accordance with Title 3 of the NYS Environmental Quality Bond Act under contract to the City of Glen Cove. Design elements included excavation plans, radiological waste monitoring, demo debris and waste separation and screening, dewatering water management, waste disposal, and site restoration. Additional work included the delisting of a six acre "clean" portion of the site to allow the development of a ferry terminal and esplanade and development of alternative cleanup standards consistent with future site uses. Site remediation will accommodate site redevelopment as a commercial waterfront and operating ferry service and seaport area.
- Principal Engineer for the feasibility studies and remedial action work plans for multiple operable units of a large railyard located in Sunnyside, Queens, New York under the NYSDEC Inactive hazardous waste program. For the former engine house and maintenance area unit, pre-design studies included product plume thickness data collection and modeling, ex situ biopiles treatment, *in situ* enhanced bioremediation, and *in situ* chemical oxidation. The final design consisted of decontamination and removal of structures, excavation of hot spot soils for PCBs and lead, UST closures, a dual phase high vacuum extraction system and *in situ* bioremediation.
- Principal Engineer for the remediation of a former Manufactured Gas Plant (MGP) facility in Brooklyn, NY, including oversight of the excavation of both the former gasholders, and adjacent contaminated hotspots requiring offsite thermal desorption of over 30,000 tons of coal tar impacted soil. Directed the Community Air Monitoring Program (CAMP) specific to the MGP impacted soil removal, as required by both New York State Department of Environmental Conservation (NYSDEC) and New York State Department of Health (NYSDOH). Remedial activity met all substantive requirements of the NYSDEC approved Remedial Action Work Plan for the Site. The remedy included design of a passive subsurface vapor monitoring/recovery system for a 500,000 sq. ft. retail structure in Brooklyn, NY. The system design integrated a perforated piping system complemented by a protective vapor barrier below the structural floor slab to monitor and mitigate volatile organic compound vapors. Multiple vapor barrier options were evaluated to determine the optimum design based on the site conditions.
- Principal Engineer providing expert settlement support services to a county municipality in New York State. The case involved an EPA Order for underground storage tank (UST) compliance for over 50 county operated facilities with over 125 USTs. The project involved the field inventory of the USTs at each facility and development of both Interim and final compliance plans to comply with EPA, NYSDEC and local UST regulations. Detailed cost estimates were prepared for multiple scenarios for upgrading USTs including tightness testing, manway repairs, leak detection and overfill protection monitoring systems, UST removal and replacement, and new piping. The upgrade evaluation and negotiations included incorporation of Supplemental Environmental Project (SEPs) in accordance with EPA requirements. SEPs included centralized monitoring systems for leak detection and inventory control.
- Principal Engineer for preparation of a site management plan for redevelopment of a former watch case factory in Sag Harbor, New York. The primary engineering controls for the former factory conversion to a residential building consisted of a vapor barrier and an active subslab depressurization

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system (SSDS) to address chlorinated VOCs. The SSDS system was complicated due to the existing 100-year-old structure. A unique raised floor approach was designed to allow for the SSDS installation. The system design, approved by NYSDEC and NYSDOH includes multiple legs, dual blowers, low vacuum alarms and monitoring points.

- Principal Engineer for the Remedial Action Work Plan (RAWP) for redevelopment of a shopping center in the Bronx, New York. The RAWP elements included soil and groundwater management plans, stormwater management, air monitoring and vapor mitigation systems. To address vapor intrusion, active subslab depressurization systems were designed for two pad buildings. One system for a new retail building construction and one retro-fit system for an existing building to be used as a restaurant. Closure reports were prepared and certified documenting all remediation work and approved by NYC Mayor's Office of Environmental Remediation (OER).
- Principal Engineer for the preparation of a preliminary remedial design for the remediation and restoration of a pond and surface water tributaries to Canaan Lake that have been impacted from leachate generated from an upgradient former municipal landfill located in Holtsville, New York. Completed a preliminary remedial design for the construction of a compost-based permeable reactive barrier for the removal and treatment of leachate prior to discharge to the surface water, followed by restoration of the surface water body and surrounding wetlands. The project included development of a long term remedial strategy to reduce rainfall infiltration into the landfill and minimize leachate generation. Current plans to reduce rainfall infiltration include the planting of 3,250 hybrid poplars, regrading and lining of drainage swales, and the resurfacing of low lying areas consistent with recreational facilities.
- Principal Engineer for final capping elements and wetlands restoration work and completion of the Final Engineering Report for an inactive hazardous waste site in Syracuse, New York. The project included onsite consolidation of lead impacted waste; 7-acre landfill cap with vegetated layer, cover soil, and geomembrane; stormwater runoff controls; reconstruction of waste water ponds; and an 8-acre wetland restoration. An O &M Plan was prepared and implemented consisting of groundwater, surface water and landfill gas monitoring, and annual cap and wetland inspections.
- Principal Engineer for the preparation of the remedial action work plan for an 11-acre former Department of Defense owned Site that manufactured airplane parts along Hempstead Harbor in Manorhaven, New York. The project is regulated under the NYSDEC Voluntary Cleanup Program. The remedial design consisted of both soil vapor extraction/air sparging and *in situ* enhanced bioremediation systems for Site groundwater impacted by chlorinated VOCs. The final remedial design and site management plan are expected to include soil capping, vapor barriers and passive ventilation systems to be incorporated into a residential redevelopment with waterfront access.
- Project Engineer for the design and construction management of a 600 gpm groundwater extraction and treatment system to prevent offsite migration at a petroleum storage and pipeline transfer facility in Providence, Rhode Island. The treatment system was designed to remove iron, BTEX, and naphthalene from the groundwater to below surface water discharge standards for the Providence River. The system processes consisted of equalization, aeration, de-aeration, flocculation, clarification, air stripping, dual media filtration, granular activated carbon adsorption (liquid and vapor phase), and sludge thickening and dewatering. The system included an outfall diffuser designed in accordance with the CORMIX computer model.
- Senior Engineer responsible for the design, construction management, and O&M of a 60,000-gpd constructed wetlands treatment system for a former manufacturing facility in Virginia. The 16-acre treatment system was designed within an existing phragmites wetland to remove zinc and iron from landfill leachate prior to discharge to an adjacent creek. The treatment system consisted of alkalinity producing cells, oxic ponds, compost and limestone berms, anaerobic cells and aerobic cells. The design included a 400-foot reinforced earthen dike together with hydraulic control structures and piping to maintain cell water levels and flow rates. The system also includes a pump station and force main for both effluent discharge and irrigation purposes. Joint wetlands and local permit approvals were obtained for the project.
- Senior Engineer for the performance of a stormwater runoff evaluation for a manufacturing facility in Watertown, New York. Roux Associates was retained as third party to evaluate the drainage design and construction elements for an industrial landfill cap. The evaluation was performed for the facility owner in support of potential litigation arising from onsite building flooding incidents following a severe snow and rain storm event. The scope of work included an evaluation of the existing onsite storm sewer system capacity, calculation of runoff flow rates for the 300-acre contributing area, review of landfill cap surface drainage design, review of erosion control measures implemented during construction, and analysis of specific flooding incident causes. The runoff analyses were performed using the TR 55 Method for three conditions: pre-capped, capping under construction prior to establishment of vegetation, and final vegetated cap design. Recommendations were made to improve the site drainage including design of surface drainage swales, temporary berms and sediment traps during construction and modification of snow handling practices.
- Senior Engineer for the performance of a feasibility study and remedial design for the closure of a concrete oil/water separator filled with refinery sludge and demolition materials impacted with lead at a former

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refinery in Providence, Rhode Island. Remedial alternatives were developed and evaluated including capping and containment using a perimeter slurry wall, sheet piling or concrete wall sealing; excavation and disposal; and *in situ* solidification. The capping and containment using a slurry wall alternative was selected for implementation of the remedial design. The design consisted of removal and replacement of existing monitoring wells, sealing of separator wall openings, a 2-acre multi-layer cap, a 1200-foot long by 30-foot deep soil-bentonite slurry wall, and a perimeter drainage swale. The multi-layer cap included a 40-mil HDPE geomembrane and a geosynthetic clay liner. The slurry wall was keyed into the existing clay confining layer beneath the separator. The design incorporated disposal of an additional 10,000 cubic yards of petroleum impacted soil under the cap.

- Principal Engineer for the preparation of field implementation plans, construction monitoring, and Engineers Certification Report for a former manufactured gas Plant (MGP) site in Manhattan, New York. The site was one of the first projects completed under the NYS Brownfields Cleanup Program. The remedy included soil excavation and offsite thermal treatment, a sheet pile barrier wall, a vapor barrier and basement ventilation system. A comprehensive air monitoring program was conducted due to the concerns over coal tar residue emissions and odors on the surrounding community. The remedy was incorporated into the design and construction of the headquarters office building of an international media company.
- Principal Engineer for the management of a soil and ground-water remediation system for a nationwide overnight delivery distribution center in Brooklyn, New York as part of the NYSDEC Voluntary Cleanup Program. A risk-based remedial approach that called for the remediation of "hot spot" source area soils, and mass-reduction of VOCs was successfully utilized for the Site. As a result, the focus of remediation was on reducing the mass of VOCs in on-site groundwater to a level where natural attenuation would be effective in remediation of VOCs. To address the contamination in the source area, a soil vapor extraction (SVE) and air sparge (AS) system consisting of 8 SVE wells and 17 AS wells was designed, constructed, operated and maintained for a period of approximately 3 years. Permanent shutdown of the system was approved by the NYSDEC.
- Senior Engineer for the design and construction management of a soil remediation and stormwater management project at a 16-acre former pesticide warehouse facility in Dayton, New Jersey. The Site was redeveloped for storage and trailer parking. The project consisted of consolidation of pesticide contaminated soils; asphalt capping of the 3.5-acre contaminated soils area; stormwater collection, conveyance and detention; and site regrading. The evaluation included TR-55 runoff modeling for pre and post capping and development conditions. The storm sewer system consisted of multiple catch basins, over 2,000 linear feet of reinforced concrete pipe ranging in size from 15 to 30 inches, and a recharge basin. A Soil Erosion and Sedimentation Control Plan and a NJPDES General Permit were prepared for the project.
- Project Principal for the performance of LNAPL remediation studies at the New Jersey Transit former Lake Street Bus Garage in Newark, New Jersey. The studies involved evaluating remedial alternatives for free product recovery, performance of an LNAPL recovery pilot test and cost estimating. A RAWP and engineering design plans were prepared for both the bus garage and the adjacent park properties. The remedy included excavation of the source area, horizontal recovery wells, a vertical recovery trench, *in situ* oxidation injections and product recovery using vacuum extraction.
- Senior Engineer for the performance of a stormwater management analysis for a 28-acre industrial landfill in Virginia. The principal objective of the study was to identify engineering controls to minimize stormwater runoff to a metals-contaminated sediment impoundment. The study included TR-55 runoff modeling and storage analyses for multiple detention ponds. Three engineering control alternatives were identified including landfill cap regrading, diversion using berms and swales, and diking and weir raising.
- Senior Engineer for the investigation, design, and construction management of the closure of a 2-acre fire-water supply pond and modification of the stormwater conveyance system at a former manufacturing facility in Williamsburg, Virginia. The investigation phase of the project was focused on determining the sources and loading of metals influent to the pond. Field activities included examination of the existing stormwater drainage system, subwatershed delineation, groundwater monitoring, and installation of automatic stormwater sampling devices. The final design included 400 feet of open concrete channels, 250 feet of culvert replacement, sliplining of 370 feet of 36-inch RCP culvert, reconstruction of five catch basins, placement of 10,000 cubic yards of clay fill within the pond and regrading of existing drainage ditches. Erosion control measures and slope stabilization were also included as well as the design of a special outlet structure for minimizing erosion at the outfall.
- Project Principal for the investigation and closure of five USTs at the New Jersey Transit Broad Street Station site in Summit, New Jersey. Tank sizes ranged from 20,000 to 30,000-gallon capacity. UST closure program completed in accordance with the NJDEP Technical Requirements for Site Remediation. Closure report prepared and submitted to the NJDEP and subsequent issuance of a No Further Action letter from the NJDEP.
- Project Engineer of the underground storage tank (UST) program for a major retail chain store in the New York, New Jersey and Pennsylvania region. Responsibilities included preparation of a UST management plan based on federal, state, and local regulations and costs to prioritize UST maintenance.

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Principal Engineer

The tank designs included plans and specifications for the removal and replacement, or upgrading, of USTs to meet regulatory requirements. The engineering design involved fuel requirements for dual heating and back-up generator usage, mechanical pumping equipment and fire wall design.

- Project Engineer for the design and construction management of a 1,000 sq. ft. hazardous and flammable materials storage facility in Syosset, New York. The facility included concrete secondary containment dikes, access ramps, sprinkler system modifications, and lighting. The separate flammable materials area included 2-hour fire rated concrete block walls and doors, ventilation equipment and a fire alarm system. Permitting services were performed for the Nassau County Department of Health, the Nassau County Fire Marshall, and the Building Department.
- Project Engineer for the design of a 2,000 sq. ft. hazardous waste storage facility in Astoria, New York. Prior to construction, demolition of an existing building was required and included removal of asbestos and lead paint. The project included driving treated timber piles and excavation and removal of contaminated soil and groundwater. The structure consisted of a steel frame with a metal standing seam roof system, decorative masonry block walls, and a roll-up door. Temporary and permanent fencing were required along with concrete sidewalk replacement.
- Senior Engineer for the decommissioning of a pharmaceutical facility covering two entire city blocks as a part of a NYSDEC Voluntary Cleanup Agreement in Brooklyn, New York. Responsibilities include technical review of Interim Remedial Measure (IRM) work plans for lead and mercury-contaminated soil excavation and disposal, implementation of these work plans (excavation and offsite disposal), preparation of biddable plans and specifications, review of IRM Closure Reports, and obtaining closure documentation from regulators on a fast track basis to allow redevelopment for a large-scale shopping complex and public schools.
- Senior Engineer providing construction management services in support of the BNYCP Cogeneration Facility construction and Brooklyn Navy Yard facility decommissioning. Work included preparation of construction management plans, supervision of soil, concrete, and sediment disposal activities, asbestos surveys, and PCB sampling and analysis work. A NYCDEP wastewater discharge permit was prepared for the million gallon per day stream condensate and wastewater backwash flow rate.
- Project Principal for performing remedial alternative cost estimating for a New Jersey Transit site in Montclair, New Jersey, which is to be redeveloped as a firehouse. A cost estimate prepared by another consultant was reviewed as part of the scope of work. The proposed remedial alternative for the site consisted of excavation and disposal of PAH-impacted fill material and capping. The alternative remedy proposed by Roux Associates was a more risk-based approach, resulting in a cost savings of approximately $100,000 for New Jersey Transit.
- Project Engineer for the design and construction management of cap repair and drainage improvement measures for an industrial hazardous waste landfill in Tennessee. Components of the design included replacement of the primary clay cover material, temporary and permanent erosion and sedimentation control measures, and a lined drainage channel to minimize the generation of landfill leachate. The project included the performance of a focused feasibility study to characterize the flow, quality, and treatability of the leachate. A feasibility study was also performed in order to evaluate constructed wetlands remedial technology as a method of effective and economical treatment of leachate.
- Senior Engineer for the remedial design and construction management of a 7-acre off-spec asphalt waste pond at a former refinery in New England. The asphalt material exhibited a low load bearing capacity combined with a viscous, tacky surface. An *in situ* solidification mix design was developed consisting of liquification using hot water and a 2-stage lime kiln dust reagent injection and mixing step. Gravel was added to the mix when the existing subgrade material was of insufficient bearing capacity. Solidified material was tested for unconfined compressive strength, durability, and TCLP. The final cover material consisted of a 6-inch vegetated layer.
- Principal Engineer for the performance of LNAPL remediation studies for a former bus maintenance facility and a segment of a Metropolitan Subway System in Newark, New Jersey. The studies involved evaluating groundwater and soil monitoring data, performance of LNAPL recovery pilot tests, evaluation of remedial alternatives and cost estimating. Recommendations included the use of mobile high vacuum extraction methods to collect LNAPL while minimizing capital expenditures and permanent low vacuum extraction methods to minimize odors to subway cars and surrounding communities.

Litigation Support Experience

- Project Engineer for the evaluation of remedial investigations and remedial cost estimates for a 30-acre former book publishing facility in Poughkeepsie, New York. The evaluation included the review of Phase I and Phase II investigation reports, remedial investigation (RI) and feasibility study (FS) reports, and the remedial investigation work plan. The findings included the presence of chlorinated volatile organic compounds in the soil and groundwater as well as identification of underground storage tanks. Deficiencies were identified in both the RI and FS reports by comparing with the NYSDEC's required criteria and recommendations were proposed for the RI work plan to further delineate source areas. Based on the remedial investigation review, revised costing assumptions were made and remedial cost estimates were prepared totaling $3.6 million.

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Principal Engineer

- Project Engineer for the evaluation of expected remedial costs for nine hazardous waste sites, two of which are federal superfund sites. The evaluation of both single and multiple PRP sites was performed to identify costs for an insurance claim. The expected remedial costs for nine sites, which include landfills or facility surface impoundments, totaled approximately $65 million. Remedial plans evaluated for multiple site operable units included groundwater pump and treat, alternative water supply systems, soil/sludge *in situ* solidification and treatment, and wetlands restoration. Additional work included evaluating invoices for site work previously performed and allocating expenses into their appropriate operable unit and work type, i.e., defense or indemnity.

Water Treatment Experience

- Senior Engineer for the engineering design of a 10 gpm groundwater recovery and treatment system at a former tank farm in Rhode Island. The recovery system included a 200-foot slotted HDPE horizontal well, a 400-foot coated concrete swale and curbing, and a series of seepage collection points manifolded to a common receiving structure. The entire system was designed for passive recovery and gravity flow transmission targeting free-product seepage areas. The treatment system consisted of a collection sump retrofitted within an existing separator, a coalescing plate oil/water separator, a surge tank, a bag filter, and carbon adsorption units. The project included a permit modification for discharge to the Providence River.
- Design Engineer for the design and start-up operation of a 2 mgd packed tower aeration system for potable water in Williston Park, New York. The primary contaminants were trichloroethane and tetrachloroethene which were stripped below drinking water standards. The design process included full scale pilot testing to assure proper removal levels.
- Design Engineer for the design, construction and start-up operation of a 5 mgd industrial cooling water treatment system utilizing mechanical surface aeration. The system consisted of two lined aeration basins operating in series with floating mechanical aerators to remove volatile organic contaminants to levels suitable for recharge into the Long Island groundwater aquifer. The primary contaminants were 1,1-dichloroethene, trichloroethane, tetrachloroethene and vinyl chloride.
- Design Engineer for the design and construction of a 4 mgd granular activated carbon system for potable water in Hempstead, New York. The primary contaminants consisted of more than 8 volatile and semivolatile organic compounds. Responsibilities included site inspection for the installation of the six vessels containing 20,000 lbs. of carbon in each. The system was designed for 99.9% removal efficiency with two units operating in series.

Constructed Wetlands Experience

- Senior engineer for the conceptual design of a constructed wetlands stormwater treatment system for a coal handling freight railroad facility in Norfolk, Virginia. The design consists of treatment of contaminated stormwater runoff generated from maintenance and fuel handling areas onsite. The design treatment performance objective is the reduction of total suspended solids, oil and grease, and selected metals to levels below the SPDES permit discharge standards established for two of the site's outfalls discharging to the Elizabeth River. The 3-acre system consists of a passively operated 200,000-gpd subsurface-type constructed wetlands with a low visual impact and specialized structural design to meet the needs of a busy railyard facility. Additional design components include stormwater bypass structures, jacking beneath tracks, a grit chamber, a lift station, and outfall modifications. A joint wetlands permit will be prepared for the project.
- Senior Engineer for the feasibility study, conceptual design and construction of four constructed wetlands units and sedimentation basin for a stormwater treatment system along Cedar Swamp Creek for the City of Glen Cove, New York. The project consisted of review of stormwater studies of the 12 square mile contributing watershed, compilation of USGS water quality and flow data, evaluation of stormwater treatment methods and best management practices and optimum site selection along the creek. The constructed wetlands design included a forebay, high and low marsh cells, a micropool, and stormwater bypass structures for removal of sediment, nitrogen, phosphorus, and trace metals during first flush events. Final design for the first 1.8 acre constructed wetlands unit was completed and performance of construction management is ongoing. Design activities include structural and hydraulic design tasks with specific emphasis on storm water bypass. The design has been integrated into an into an intermodal transportation project with the addition of bicycle and walking paths. NYSDEC and Army Corps permits were obtained for the project.
- Project Engineer for the design of a 7,000 gpd subsurface flow-type constructed wetlands treatment system for a refinery site in Rhode Island. The system was designed to treat a surface-water stream impacted by petroleum hydrocarbons. The system's high aesthetic, low visual impact appeal was ideal for its golf course setting. Both phragmites SPP and Typha SPP wetland species were incorporated in the design in order to assess the biodegradation/biotransformation processes effectiveness. A growth and maturation plan and a treatment evaluation plan were developed in order to evaluate the system performance.
- Lead Engineer responsible for technical review of a design for modifications to a constructed wetlands system in Nicholas County, West Virginia. The system was designed to treat the leachate from a solid waste landfill at a maximum capacity of 30 gpm. The complete water tight treatment system consisted of a sedimentation basin, stabilization basin, a series of three wetland cells and a finishing ditch. The wetland cells consisted of a double liner system with leachate collection piping overlaid with stone fill and a matrix of plant life. The technology combines physical,

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Principal Engineer

geochemical and biological removal mechanisms operating simultaneously.

Permitting/Compliance Plans

- Project Engineer for the preparation of a Spill Prevention Control and Countermeasure (SPCC) Plan and a Storm Water Pollution Prevention Plan (SWPPP) for an 850-acre petroleum storage terminal in New England. The SPCC Plan involved the inventory of 50 bulk storage tanks and miscellaneous storage vessels and an assessment of barge loading areas, truck loading racks, additive loading areas, pumping stations, and a network of aboveground pipelines. The SWPPP encompassed an inventory and surveying of the existing storm sewer system, an evaluation of oil/water separator performance and identification of storm water management controls and practices.
- Project Engineer for the design of modifications to multiple discharge facilities along the Providence and Runnins Rivers in Rhode Island. Permitting activities were performed with the following agencies: Rhode Island Department of Environmental Management (RIDEM) Pollutant Discharge Elimination System (RPDES), RIDEM Division of Freshwater Wetlands, Coastal Resources Management Council (CRMC), and the Army Corps of Engineers.

Sanitary Experience

- Design Engineer for the evaluation of a municipal sanitary sewer system consisting of approximately 70 miles of piping ranging in size from 8 inches to 16 inches, in Garden City, New York. The sewer system was evaluated for existing and proposed flow capacity, surcharging, infiltration of groundwater, inflow of storm water, root encroachment, and sewer breaks. Evaluation methods consisted of hydraulic profile analysis, television inspection of piping, field inspection of manholes, and flow measurement. Sewer upgrading methods were evaluated including direct replacement, manhole restoration and pipe slip lining, and a rehabilitation program was implemented.
- Design Engineer for the City of Glen Cove's industrial wastewater pretreatment program which was established to monitor significant industrial users discharging to the city's wastewater treatment plant to minimize upsets to the biological treatment mechanisms. The program work included annual facility inspections, wastewater discharge sampling, review and evaluation of quarterly self-monitoring results, calculation of discharge penalty fees, preparation of annual monitoring reports for each facility and development of wastewater discharge permits to comply with City regulations.
- Design Engineer for a heavy metals study for the municipal sanitary sewer system in the City of Glen Cove, New York. The heavy metals study consisted of the development and performance of a city-wide sewer sampling program to identify the sources of heavy metals loadings on the wastewater treatment plant. The evaluation included industrial sources, scavengers, non-industrial sources, the plant operation itself, and review of existing heavy metal studies. Recommendations were provided for minimization of loadings and pretreatment to protect the plant operations.

Stormwater Experience

- Design Engineer for the evaluation and conceptual design of a water management plan for a 200-acre proposed office complex in Bethpage, New York. The design included inlets, piping and recharge basin sizing for peak storm water runoff flows as well as a system of architectural ponds and level control structures. For dry periods, the design included flow controls connected to an existing cooling water system to maintain pond levels and for utilization as a water supply for an irrigation sprinkler system during the growing season.
- Design Engineer for the design of a municipal storm drainage system for a 200-acre contributing area in Garden City, New York. The purpose of the drainage system was to alleviate severe flooding problems for eight homes located in a local low point of a residential neighborhood. The system included over 4,800 linear feet of reinforced concrete piping ranging in size from 12 to 60 inches. Design considerations included hydraulic gradient analysis, inlet capacity, utility crossings, minimization of removals of established trees, a county road crossing, utilization of existing structures and piping, and a headwall discharge to a recharge basin. Additional design items included pavement restoration, service line relocations, curbs and sidewalks, and maintenance and protection of traffic.

Site Assessment Experience

- Senior Engineer for coordination and review of Phase I environmental site assessments for five large research and development complexes located throughout the eastern United States for a major chemical company. The site assessments were performed for due diligence prior to engaging in long-term property lease agreements. The site assessments evaluated chemical storage and handling areas and previous site usage.
- Senior Engineer for coordination and review of Phase I environmental site assessments for 12 properties associated with tennis centers acquisition on Long Island, New York. The properties were either active tennis center facilities or vacant parcels available for new construction. All site assessments were conducted in accordance with ASTM standards for commercial real estate transactions. Primary concerns identified were USTs, drum storage areas, and unauthorized dumping.
- Project Manager representing a group of banks investing in a 20-acre commercial property in Westchester, New York. The onsite soil was contaminated with several volatile and semivolatile organics. Performed an evaluation of the remediation plan which included onsite biological treatment of soils and aeration and oil water separation of groundwater.

Water Main Experience

- Project Engineer for the design of over 6,000 feet of ductile iron water main in sizes from 4 to 16 inches for Town of Hempstead, New York Department of Water

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Principal Engineer

and the Nassau County, New York Department of Public Works. The designs included wet and dry connections to existing mains, fittings, valves, copper services and fire hydrants. Restoration work included replacement of asphalt pavement, concrete sidewalk and curbs, and grass areas.

- Design Engineer for the design and construction management of over 10,000 feet of ductile iron water main in sizes from 6 to 12 inches for the Town of Wallkill, New York. The designs included booster pump station upgrades, a stream crossing, a wetlands crossing, jacking of 36-inch casing beneath a state highway, air release chambers, copper service re-connections, fire hydrants, valves and appurtenances. Restoration work included wetlands restoration, backfilling and regrading within a NYSDOT right-of-way and grass and pavement replacement.
- Design Engineer for the design and construction management of upgrades to a 3.7 mgd potable water booster pump station for the Town of Wallkill, New York. The design featured the replacement of a hydropneumatic tank and pump system with three larger capacity centrifugal pumps. The upgrades were performed while maintaining the pump station service. The pump station revisions included piping, pump pads, shut-off valves, silent check valves, pressure relief valves, gauges, ventilation equipment and a motor control center.

Feasibility Study Experience

- Senior Engineer for the performance of a feasibility study and remedial design of a free product containment and recovery system at a former refinery in New England. The areal extent of the free-product plume was approximately 10 acres with a measured thickness of up to eight feet. Pilot testing activities consisted of pump tests, baildown tests, and funnel and gate systems with and without sheeting. The selected remedial alternative consisted of re-routing and repair of active storm sewer piping, closure-in place of a former 72-inch storm drain using clay fill material to form a barrier wall, and installation of multiple recovery trenches totaling 450 linear feet. The recovery trenches were installed to a depth of 14 feet using a deep trenching machine and were completed with gravel, horizontal perforated piping, recovery wells, and monitoring wells to accommodate both passive and active product recovery pumping equipment. Product recovery enhancement pilot testing was also performed by using non-ionic surfactants, mechanical re-working of soil and vacuum extraction methods.
- Project Engineer for the performance of a feasibility study for the containment of a free-product plume beneath a refinery site in Rhode Island. The feasibility study included analysis of groundwater modeling, bench and pilot scale treatability studies, groundwater quality characterization, identification and screening of discharge alternatives, and treatment process evaluations. The work also included the evaluation of the discharge of treatment system effluent to several receptors including groundwater, wetlands, sanitary sewers, and storm sewers. Discharge requirements were evaluated for process water, off-gas air and residual wastes. Several treatment processes were also evaluated including metals precipitation and sludge dewatering, VOC and SVOC removal, and off-gas treatment. Preferred alternatives for each process were selected for remedial design development.
- Project Engineer for the performance of a feasibility study for a hazardous waste landfill located at a Superfund site in Tennessee. The feasibility study focused on the characterization and quantification of landfill leachate consisting of chlorinated organic compounds as well as proprietary pesticide compounds. The remedial technologies which were evaluated included leachate collection alternatives, onsite treatment alternatives and offsite disposal methods. An analysis was performed for onsite treatment technologies which included constructed wetlands, biological fluidized bed reactor, and granular activated carbon adsorption. The technologies were assembled into four feasible remedial alternatives and treatability studies were recommended to confirm the suitability of selected processes.

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ROUX

PROFESSIONAL PROFILE

Jessica L. Taylor, P.G.
Principal Hydrogeologist

TECHNICAL SPECIALTIES

Project Management and Field Management for large-scale soil excavation and remediation projects, including site assessment, remediation implementation, and construction activities. Coordination and management of large-scale demolition and renovation support. Performance of sampling and direction of field sampling teams for the following media: soil, groundwater, surface water, soil vapor, sludge, and sediment. Excavation sampling and oversight and waste tracking.

EXPERIENCE SUMMARY

Fourteen years of experience: Senior, Project and Staff Hydrogeologist, Roux Environmental Engineering and Geology, D.P.C., Islandia, New York; Staff Hydrogeologist and Intern at GSC|Kleinfelder.

CREDENTIALS

B.S. Geology, Binghamton University, 2005
Professional Geologist, New York, 2017
OSHA 40-Hour HAZWOPER Training, 2005
OSHA 10-Hour Construction Safety Training, 2008
NJDEP UST Subsurface Evaluator Certification, 2009

KEY PROJECTS

- Senior Project Manager for a large ongoing redevelopment project in Brooklyn, New York. Project includes coordination and oversight of *in situ* waste characterization sampling, excavation, and proper disposal of soil. Coordination of pre-demolition asbestos and hazardous materials surveys. Construction management and support for excavation of 600,000 tons of soil; environmental support for demolition and relocating of an active nine-acre 100-year old rail yard. Responsible for implementing and managing remediation work at several NYSDEC spill sites within the project footprint, including *in situ* chemical oxidation, UST removal, and soil excavation. Agency support for NYSDEC, NYCDEP, NYCOER, MTA (LIRR/NYCT), and ESDC. The project will encompass 336,000 square feet of office space, 6.4 million square feet of residential space, an 18,000 seat sports and entertainment venue – the Barclays Center (home of the Nets professional basketball team) – 247,000 square feet of retail space, a 165,000 square-foot hotel, and over 8 acres of intricately designed publicly accessible open space.
- Senior Project Manager for two parcels in Queens as part of NYSDEC Brownfield Cleanup Program. This project included due-diligence environmental assessment and investigation, development of NYSDEC-approved Remedial Investigation Work Plans, and future remediation during construction of two mixed-use, affordable housing developments. Also required coordination with NYCHPD and NYCDEP to meet regulatory requirements for funding.
- Senior Project Manager for the environmental management of asbestos remediation during the renovation of Nassau Coliseum. Responsible for coordinating inspections and delineation of ACM, preparing budgetary estimates, and bid support for full abatement. Also includes management of decommissioning and replacement of existing emergency generator UST.
- Project Manager for redevelopment of four properties in Brooklyn, with NYCOER to address NYCDEP "E" designations. Coordination with NYCOER to implement remedial investigation and develop RAP as part of the NYC VCP.
- Project Manager for commercial redevelopment site in the Bronx, including *in situ* waste characterization, management and coordination of excavation, community air monitoring, and development of NYCDEP-approved RAP.
- Project Manager for petroleum spill closure at active retail gasoline service station in Brooklyn, NY. Included remedial investigation and coordination with NYSDEC for spill closure.
- Project Manager for design, implementation, and reporting of *in situ* waste characterization for the largest retail developer in the world as part of new construction at a premier shopping center on Long Island.
- Client liaison and full-time onsite construction manager at redevelopment site in Rego Park, New York. Collection of 500 *in situ* waste characterization soil samples, oversight of 250,000 cubic yards of soil excavation and remediation, development of post-remediation sampling plan, organization of waste manifests and hazardous waste documents to ensure proper disposal. Coordination of daily site activities with multiple construction contractors and other involved parties on behalf of client. Oversight and confirmatory soil sampling for on-site treatment of 75,000 cubic yards of hazardous lead contaminated soil.
- Field Manager for *in situ* soil characterization as part of RAP implementation for a one-acre brownfield site containing chlorinated solvents, heavy metals and petroleum compounds in soil, soil vapor and groundwater over one city block in Manhattan, New York. This project is part of the NYSDEC BCP.
- Project and Field Manager for multiple Phase I and Phase II ESAs of retail gasoline stations in New York and New Jersey. This includes drilling and sampling oversight and health and safety management, as well as writing Phase II ESA reports for over 40 sites.

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ROUX

Professional Profile

Levi Curnutte
Project Scientist

Technical Specialties:
Project Management and Field Management of Phase II environmental site assessments/investigations, remedial implementations, and soil excavation/redevelopment projects. New York State Brownfields Cleanup Program (BCP); New York City Office of Environmental Remediation (NYCOER) E-Designation and Voluntary Cleanup Programs; New York State Spills Program. Additional technical skills include waterproofing, vapor barrier, sub-slab depressurization system (SSDS) installation inspections along with soil, groundwater, and soil vapor sampling.

Experience Summary:
Four years' experience; Project and Staff Scientist at Roux Environmental Engineering and Geology, D.P.C., Islandia, NY.

Credentials:
B.S. Marine Science, Coastal Carolina University, 2011
M.S. Environmental Studies, College of Charleston, 2013
OSHA 40-hour HAZWOPER Training
OSHA 10-hour Construction Safety Training
NYCOER Gold Certified Professional
ExxonMobil Loss Prevention System-certified
MTA LIRR Roadway Worker Protection Training

Publications:
Climate Change and Bemisia tabaci (Hemiptera: Aleyrodidae): Impacts of Temperature and Carbon Dioxide on Life History. Curnutte, L., Simmons, A. M., and S. Abd-Rabou. Ann. Ent. Soc. Amer. 107(5): 933-943. 2014.

Key Projects:

- Project Manager providing support for all soil and groundwater disturbances during development of Cornell NYCTech campus located on Roosevelt Island, NY, NY. Management tasks include Agency support for NYCDEP and NYSDEC, community action monitoring plan (CAMP), soil characterization for reuse and disposal, SWPPP implementation, UST removal following NYSDEC regulations, asbestos abatement coordination, and preparation of a NYCDEP Remedial Closure Report.
- Project Manager for former Manufactured Gas Plant (MGP) site in Brooklyn, New York. Under NYSDEC regulation, responsibilities include coordination of monitoring of recovery wells known to be former and current producers of coal tar (DNAPL) and DNAPL recovery and disposal.
- Project Manager for an 85-acre commercial site, Staten Island Mall, within the NYCOER Voluntary Cleanup Program (VCP) undergoing a 500K sq. ft. mall expansion. Project involved the construction an adjacent building to the existing mall and a new above grade parking structure. Manager for remedial action work plan implementation and production of multiple Remedial Action Reports leading to one NYCOER Notice of Satisfaction for the client to date.
- Field Investigation Manager for previously abandoned oil-water separator delineating residual contamination at a NYSDEC-regulated 175-acre former petroleum refinery and terminal in Brooklyn, New York. Responsibilities included the oversight of all field tasks, site management, property owner and tenant coordination, and investigation report.
- Project Manager and Field Manager for the largest ongoing redevelopment project in New York City, including the relocation of a nine-acre 100-year old active rail yard. Project includes management of sites with NYCDEP "E" designation and the implementation of *in situ* soil characterization sampling, soil disposal, and NYSDEC spill remediation at multiple sites within project footprint. Achieved an NYCOER Notice of Satisfaction for one property within the OER VCP. The project will encompass 336,000 sq. ft. of office space, 6.4 million sq. ft. of residential space, an 18,000 seat sports and entertainment venue - the Barclays Center (home of the Nets professional basketball team) - 247,000 sq. ft. of retail space, a 165,000 square-foot hotel, and over 8 acres of intricately designed publicly accessible open space.
- Field Manager at 149 Kent Avenue, a NYSDEC BCP Site, implementing a RAWP requiring extensive remediation of chlorinated VOC-impacted soil and groundwater to accommodate development of a mix-used building and underground parking garage. Primary contaminants of concern were PCE and TCE. Project responsibilities include a 12-month oversight period involving zero-valent iron injections (ZVI) for a permeable reactive barrier (PRB), installation of sub-slab depressurization system (SSDS), Grace® waterproofing inspections, groundwater monitoring/sampling, CAMP, coordination and tracking of hazardous and non-hazardous waste, and providing contractor work zone health and safety recommendations/oversight in accordance with OSHA guidance. Involved in submissions of the Periodic, Annual, and Final Engineering Reports submitted to NYSDEC leading to Certificate of Completion. Project received the NYC Brownfield Partnership's 2017 Big Apple Brownfield Award for Innovation.
- Field Manager of subset of field operations for a large scale, high profile investigation of 500 residential and sensitive-use properties located throughout Los Angeles County. As a result of lengthy aerial depositions of emissions originating from a former battery recycling facility in Vernon, CA, soil was analyzed *in-situ* for lead contamination on a real-time basis through the use of X-ray fluorescence (XRF) instruments. Helped coordinate and perform the rapid assessment of soils by multiple teams while under heavy scrutiny by the press, regulators, and home owners.

ROUX

PROFESSIONAL PROFILE

Lauren D'Orsa

Staff Assistant Scientist

TECHNICAL SPECIALTIES

Remedial construction and soil excavation oversight; management of waste characterization and removal; environmental site assessments focusing on soil, groundwater, and soil vapor investigations using multiple sampling techniques; implementation of Community Air Monitoring Programs (CAMP).

EXPERIENCE SUMMARY

9 months of experience: Staff Assistant Scientist, Roux Environmental Engineering and Geology, D.P.C., Islandia, NY

CREDENTIALS

B.A. Sustainability, Hofstra University, 2016
M.A. Sustainability, Hofstra University, 2018
OSHA 40-Hour HAZWOPER Training, 2018
OSHA 10-hour Construction Safety Training, 2018
OSHA 30-hour Construction Safety Training, 2019
LIRR Roadway Worker Protection Training, 2019

KEY PROJECTS

- Field scientist responsible for soil boring investigation at a former oil refinery in Brooklyn, NY. Responsibilities included subcontractor oversight of pre-clearance and drilling, soil boring advancement for 40 locations, classification of soil lithology, the collection and screening of approximately 100 soil samples, and installation of temporary monitoring wells.
- Field manager responsible for subcontractor oversight of soil boring advancement and monitoring well installation at a demolition location in Bronx, NY.
- Field manager responsible for annual groundwater sampling and monitoring program at a former petroleum refinery and terminal in Brooklyn, New York. This work was done to monitor the largest subsurface free-product plume in North America. Field work responsibilities included the sampling of over fifty wells for petroleum contaminated groundwater using multiple sampling methods.
- Implemented CAMP during excavation and disposal activities at various locations in Brooklyn, Manhattan, and the Bronx, New York. Responsible for monitoring airborne dust and VOCs during remedial action work activities, reviewing the collected data for exceedances of the New York State Department of Health (NYSDOH) guidelines, and for signing manifests for the shipment of soil to approved facilities.
- Field manager responsible for conducting a bi-annual soil vapor sampling and monitoring program at a former petroleum refinery and terminal in Brooklyn, New York. Field work responsibilities included the sampling of over 30 vapor points using multiple sampling methods. Soil vapor samples were analyzed for VOCs and methane.
- Field manager responsible for soil excavation and waste removal oversight for a housing development in Bronx, New York. Responsibilities included oversight of excavation, organization and proper handling of waste manifests, and ensuring compliance with the Site Remedial Action Plan.
- Field manager responsible for oversight of remediation of a 1.43-acre New York State Brownfield site containing chlorinated solvents, heavy metals, and petroleum compounds in soil, soil vapor, and groundwater over one city block in Manhattan, New York. This project includes the implementation of a Remedial Investigation and completion of a Track 1 Unrestricted Use remediation through the New York State Department of Environmental Conservation (NYSDEC) Brownfields Cleanup Program (BCP). Responsibilities included implementation of CAMP, oversight of soil excavation, and manifesting of soils, including hazardous waste.
- Site Safety Officer for various investigations and construction sites. Responsibilities include preparation of health and safety plans (HASPs), job safety analysis (JSA) documents development and review, onsite safety meeting management, safety document preparation (Lessons Learned, Near Loss, Field Audits, etc.), and planning/execution of corrective actions.

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JUDY V. HARRY
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120 Cobble Creek Rd.
North Creek, NY 12853

Occupation: Data Validator/Environmental Technical Consultant

Years Experience: 41

Education: B.S., Chemistry, Magna cum laude, 1976, Phi Beta Kappa

Certifications: New York State Woman-Owned Business Enterprise (WBE)

Relevant Work History:

Data Validation Services: September 1989 - present

Sole proprietor of Data Validation Services, a woman-owned small business registered with SAM, providing consultation/validation services to regulatory and commercial clients.

These services include the review of analytical laboratory data for compliance with respect to specific protocols, accuracy and defensibility of data, verification of reported values, and evaluation of quality parameters for analytical usability of results. Approved by USEPA, NYSDEC, NJDEP, NYSERDA, and NYCDEP as a data validator for projects, including USEPA Superfund, Brownfield, and lead sites, and those contracted through the NYSDEC Division of Hazardous Waste Remediation, Division of Solid Waste, and Division of Water Quality.

Performed validation for compliance with laboratory analytical protocols including USEPA OLM, USEPA OLC, USEPA ILM, USEPA DFLM, USEPA SOW3/90, USEPA SOW 7/87 CLP, USEPA SOW 2/88 CLP, USEPA SW846, RCRA, AFCEE, NYS 6 NYCRR Part 360, 40 CFR, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, including TO-15, 1989/1991/1995/2000/2005 NYSDEC ASPs, and 1987 NYSDEC CLP.

Performed validation according to the USEPA National and Regional SOPs and Functional Guidelines, AFCEE requirements, NYSDEC Validation Scope of Work, NYS DUSR, and NJDEP Division of Hazardous Site Mitigation/Publicly Funded Site Remediation SOPs.

Performed validation for USEPA Superfund Sites including Salem Acres, York Oil, Port Washington L-4 Landfill, Bridgeport Rental and Oil Services, GE-MRFA, MMR/ OTIS AFB, LCP, and Peter Cooper site; and for USEPA lead sites including SJ&J Piconne, Maska, Bowe System, Jones Sanitation, and Syossett Landfill, involving CLP, RAS, and SAS protocols.

Contracted for NYSDEC Superfund Standby Contracts with LMS Engineers, HDR, CDM Smith, Malcolm-Pirnie/ARCADIS, Ecology & Environment, Shaw Environmental, CG&I, O'Brien & Gere Engineers, and EC Jordan, involving samples collected at NYS Superfund Sites and analyzed under the NYSDEC ASP.

Performed validation services for NYSDEC Phase II remedial investigations, RI/FS projects, Brownfield sites, and PRP over-site projects for hazardous waste sites.

Performed validation services for clients conducting RI/FS activities involving samples of many matrices, including waste, air, sludges, leachates, solids/sediments, aqueous, and biota.

Clients have included AECOM, ARCADIS, Barton & Loguidice, Benchmark Engineering, Bergmann Associates, Blasland, Bouck & Lee, Brown and Caldwell, CDM Smith, CB&I Shaw Environmental, C&S Consulting Engineers, Chazen Companies, Clough Harbour & Associates, Columbia Analytical Services, C.T. Male, Dames & Moore, Day Engineering, EA Engineering, EcolSciences, Ecology & Environment, Ecosystems, EC Jordan, Environmental Chemical Corporation, EHRT, ENSR Consulting, ELM, ERM-Northeast, Fagan Engineers, Fanning Phillips & Molnar, FluorDaniel GTI, Frontier, Foster Wheeler Environmental Corp, Frontier Technical, Galson Consultants, GE&R, Geomatrix Consultants, GZA Environmental, Handex of N, H2M Group, HDR, HRP, IT Corp, Jacques Whitford, JTM Associates, Labella Associates, Langan Engineers, Leader Environmental, Lockwood, Kessler & Bartlett, LMS Engineers, Malcolm-Pirnie, Metcalf & Eddy, NWEC&C, O'Brien & Gere Engineers, Pace, Parsons Engineering-Science, Plumley Engineering, Prescott Environmental, P. W. Grosser, Rizzo Associates, Roux Associates, Sear Brown Group, SECOR, Shaw Environmental, Stantec, ThermoRemediation Inc., TRC Environmental, Turnkey Environmental Restoration, TVGA Engineering, URS Consultants, Wehran Emcon, Weston, YEC, and private firms.

Provided consultation services to laboratories regarding analytical procedures and protocol interpretation, and to law firms for litigation support.

Provided services to firms involving audits of environmental analytical laboratories to determine analytical capability, particularly for compliance with NYSDEC ASP and AFCEE requirements.

Guest speaker on a panel discussing Data Review/Compliance and Usability, for an analysis workshop for the New York Association of Approved Environmental Laboratories, 1993.

Adirondack Environmental Services: June 1987 - August 1989

Senior mass spectroscopist for AES. Responsible for GC/MS analyses of environmental samples by USEPA and NYSDEC protocols, development of the GC/MS laboratory, initiating the instrumental and computer operations from the point of installation, and for implementing the procedures and methodologies for Contract Laboratory Protocol.

CompuChem Laboratories: May 1982 - January 1987

Managed a GC/MS production laboratory; developed, implemented, and supervised QA/QC criteria at three different levels of review; and was responsible for the development and production of the analysis of environmental and clinical samples. Directed a staff of 23 technical and clerical personnel, and managed the extraction and GC/MS labs and data review operations.

Research Triangle Institute: December 1979 - May 1982

Worked as an analytical research chemist responsible for development of analytical methods for the EPA Federal Register at RTI. This involved analysis of biological and environmental samples for priority pollutants, primarily relating to wastewaters and to human sampling studies. Method development included modification and interfacing of the initially developed Tekmar volatile purge apparatus to GC/MS, development and refinement of methods for entrapment and concentration of the air medium for subsequent volatile analysis, and the analysis and resolution/ identification of individual PCB congeners within Aroclor mixtures by capillary column and mass spectra.

Guardsman Chemical Company: February 1977 - November 1979

Performed all quality control functions for the manufacturing plant. Performed research and development on coatings and dyes.

Almay Cosmetics: May 1976 - December 1976

Product evaluation chemist. Responsible for analytical QC of manufactured products.

Publication

Pellizzzari, E.D., Moseley, M.A., Cooper, S.D., Harry, J.V., Demian, B., & Mullin, M. D. (1985). Recent Advances in the Analysis of Polychlorinated Biphenyls in Environmental and Biological Media. *Journal of Chromatography*, 334(3) 277-314.

ATTACHMENT 2

Laboratory's Standard Operating Procedures

Emerging Contaminants - PFAS and 1,4-Dioxane

Analysis Group	Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	LOD	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
Groundwater - PFAS (Sacramento Lab)	Fluorinated Alkyl Substances	PFC_IDA	3535_PFC	Perfluorobutanoic acid (PFBA)	375-22-4	2.00	0.350	1.50	ng/L	70	130	30	70	130	30		
				Perfluoropentanoic acid (PFPeA)	2706-90-3	2.00	0.490	1.50	ng/L	66	126	30	66	126	30		
				Perfluorohexanoic acid (PFHxA)	307-24-4	2.00	0.580	1.50	ng/L	66	126	30	66	126	30		
				Perfluoroheptanoic acid (PFHpA)	375-85-9	2.00	0.250	1.50	ng/L	66	126	30	66	126	30		
				Perfluorooctanoic acid (PFOA)	335-67-1	2.00	0.850	1.50	ng/L	64	124	30	64	124	30		
				Perfluorononanoic acid (PFNA)	375-95-1	2.00	0.270	1.50	ng/L	68	128	30	68	128	30		
				Perfluorodecanoic acid (PFDA)	335-76-2	2.00	0.310	1.50	ng/L	69	129	30	69	129	30		
				Perfluoroundecanoic acid (PFUnA)	2058-94-8	2.00	1.10	1.50	ng/L	60	120	30	60	120	30		
				Perfluorododecanoic acid (PFDoA)	307-55-1	2.00	0.550	1.50	ng/L	71	131	30	71	131	30		
				Perfluorotridecanoic acid (PFTriA)	72629-94-8	2.00	1.30	1.50	ng/L	72	132	30	72	132	30		
				Perfluorotetradecanoic acid (PFTeA)	376-06-7	2.00	0.290	1.50	ng/L	68	128	30	68	128	30		
				Perfluorobutanesulfonic acid (PFBS)	375-73-5	2.00	0.200	1.50	ng/L	73	133	30	73	133	30		
				Perfluorohexanesulfonic acid (PFHxS)	355-46-4	2.00	0.170	1.50	ng/L	63	123	30	63	123	30		
				Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	2.00	0.190	1.50	ng/L	68	128	30	68	128	30		
				Perfluorooctanesulfonic acid (PFOS)	1763-23-1	2.00	0.540	1.50	ng/L	67	127	30	67	127	30		
				Perfluorodecanesulfonic acid (PFDS)	335-77-3	2.00	0.320	1.50	ng/L	68	128	30	68	128	30		
				Perfluorooctanesulfonamide (FOSA)	754-91-6	2.00	0.350	1.50	ng/L	70	130	30	70	130	30		
				N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	20.0	3.10	10.0	ng/L	67	127	30	67	127	30		
				N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	20.0	1.90	10.0	ng/L	65	125	30	65	125	30		
				6:2 FTS	27619-97-2	20.0	2.00	10.0	ng/L	66	126	30	66	126	30		
				8:2 FTS	39108-34-4	20.0	2.00	10.0	ng/L	67	127	30	67	127	30		
Groundwater - PFAS (Burlington Lab)	Fluorinated Alkyl Substances	PFC_IDA	3535_IVWT	Perfluorobutanoic acid (PFBA)	375-22-4	2.00	1.00	1.20	ng/L	50	150	30	40	160	30		
				Perfluoropentanoic acid (PFPeA)	2706-90-3	2.00	0.630	1.20	ng/L	50	150	30	40	160	30		
				Perfluorohexanoic acid (PFHxA)	307-24-4	2.00	0.760	1.20	ng/L	70	130	20	40	160	20		
				Perfluoroheptanoic acid (PFHpA)	375-85-9	2.00	0.910	1.20	ng/L	70	130	20	40	160	20		
				Perfluorooctanoic acid (PFOA)	335-67-1	2.00	0.630	1.20	ng/L	70	130	20	40	160	20		
				Perfluorononanoic acid (PFNA)	375-95-1	2.00	0.270	1.20	ng/L	70	130	20	40	160	20		
				Perfluorodecanoic acid (PFDA)	335-76-2	2.00	0.770	1.20	ng/L	70	130	20	40	160	20		
				Perfluoroundecanoic acid (PFUnA)	2058-94-8	2.00	0.530	1.20	ng/L	70	130	20	40	160	20		
				Perfluorododecanoic acid (PFDoA)	307-55-1	2.00	0.590	1.20	ng/L	70	130	20	40	160	20		
				Perfluorotridecanoic acid (PFTriA)	72629-94-8	2.00	0.600	1.20	ng/L	70	130	20	40	160	20		
				Perfluorotetradecanoic acid (PFTeA)	376-06-7	2.00	0.920	1.20	ng/L	70	130	20	40	160	20		
				Perfluorobutanesulfonic acid (PFBS)	375-73-5	2.00	0.490	1.06	ng/L	70	130	20	40	160	20		
				Perfluorohexanesulfonic acid (PFHxS)	355-46-4	2.00	0.800	1.09	ng/L	70	130	20	40	160	20		
				Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	2.00	0.950	1.14	ng/L	50	150	30	40	160	30		
				Perfluorooctanesulfonic acid (PFOS)	1763-23-1	2.00	0.610	1.11	ng/L	70	130	20	40	160	20		
				Perfluorodecanesulfonic acid (PFDS)	335-77-3	2.00	0.900	1.16	ng/L	50	150	30	40	160	30		
				Perfluorooctanesulfonamide (FOSA)	754-91-6	2.00	0.640	1.20	ng/L	50	150	30	40	160	30		
				N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	20.0	1.70	6.40	ng/L	70	130	20	40	160	20		
				N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	20.0	1.50	6.40	ng/L	70	130	20	40	160	20		
				6:2 FTS	27619-97-2	20.0	4.60	6.07	ng/L	50	150	30	40	160	30		
				8:2 FTS	39108-34-4	20.0	2.90	6.13	ng/L	50	150	30	40	160	30		
Groundwater - 1,4-Dioxane (Edison Lab)	Semivolatile Organic Compounds (GC/MS SIM / Isotope Dilution)	8270D_SIM_MS_ID	3510C_LVI	1,4-Dioxane	123-91-1	0.350	0.0160		ug/L	10	200	50	70	130	20		
				1,4-Dichlorobenzene-d4	3855-82-1	0.400	0.00100		ug/L								
				1,4-Dioxane-d8	17647-74-4	0.400			ug/L	10	200	50	10	200	20	10	150

Emerging Contaminants in Soil - TestAmerica

Analysis Group	Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	LOD	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %
Solid - PFAS (Sacramento)	Fluorinated Alkyl Substances	PFC_IDA	Shake_Bath_14D	Perfluorobutanoic acid (PFBA)	375-22-4	0.200	0.0280	0.150	ug/Kg	81	133	30	81	133	30
				Perfluoropentanoic acid (PFPeA)	2706-90-3	0.200	0.0770	0.150	ug/Kg	79	120	30	79	120	30
				Perfluorohexanoic acid (PFHxA)	307-24-4	0.200	0.0420	0.150	ug/Kg	75	125	30	75	125	30
				Perfluoroheptanoic acid (PFHpA)	375-85-9	0.200	0.0290	0.150	ug/Kg	76	124	30	76	124	30
				Perfluorooctanoic acid (PFOA)	335-67-1	0.200	0.0860	0.150	ug/Kg	76	121	30	76	121	30
				Perfluorononanoic acid (PFNA)	375-95-1	0.200	0.0360	0.150	ug/Kg	74	126	30	74	126	30
				Perfluorodecanoic acid (PFDA)	335-76-2	0.200	0.0220	0.150	ug/Kg	74	124	30	74	124	30
				Perfluoroundecanoic acid (PFUnA)	2058-94-8	0.200	0.0360	0.150	ug/Kg	74	114	30	74	114	30
				Perfluorododecanoic acid (PFDoA)	307-55-1	0.200	0.0670	0.150	ug/Kg	75	123	30	75	123	30
				Perfluorotridecanoic acid (PFTriA)	72629-94-8	0.200	0.0510	0.150	ug/Kg	43	116	30	43	116	30
				Perfluorotetradecanoic acid (PFTeA)	376-06-7	0.200	0.0540	0.150	ug/Kg	22	129	30	22	129	30
				Perfluorobutanesulfonic acid (PFBS)	375-73-5	0.200	0.0250	0.150	ug/Kg	73	142	30	73	142	30
				Perfluorohexanesulfonic acid (PFHxS)	355-46-4	0.200	0.0310	0.150	ug/Kg	75	121	30	75	121	30
				Perfluoroheptanesulfonic Acid (PFHpS)	375-92-8	0.200	0.0350	0.150	ug/Kg	78	146	30	78	146	30
				Perfluorooctanesulfonic acid (PFOS)	1763-23-1	0.500	0.200	0.200	ug/Kg	69	131	30	69	131	30
				Perfluorodecanesulfonic acid (PFDS)	335-77-3	0.200	0.0390	0.150	ug/Kg	54	113	30	54	113	30
				Perfluorooctanesulfonamide (FOSA)	754-91-6	0.200	0.0820	0.150	ug/Kg	62	135	30	62	135	30
				N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	2.00	0.390	1.50	ug/Kg	65	135	30	65	135	30
				N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	2.00	0.370	1.50	ug/Kg	65	135	30	65	135	30
				6:2 FTS	27619-97-2	2.00	0.150	1.50	ug/Kg	65	135	30	65	135	30
				8:2 FTS	39108-34-4	2.00	0.250	1.50	ug/Kg	65	135	30	65	135	30
Solid - 1,4-Dioxane 8270D	Semivolatile Organic Compounds (GC/MS)	8270D	3546												
				1,4-Dioxane	123-91-1	0.100	0.00912		mg/Kg	27	70	30	27	70	30

Title: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometery (GC/MS), SW846 Method 8270D

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Approvals (Signature/Date):

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1.0 Scope and Application

1.1 Analytes, Matrix(s), and Reporting Limits

USEPA Method 8270D is an analytical method which employs the use of GC/MS to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, and water samples. TestAmerica Edison has the capability to analyze and report the compounds listed in Table 1 via Method 8270D.

Table 1

Compound	CAS No.	Compound	CAS No.
1,1'-Biphenyl	92-52-4	Anthracene **(1)**	120-12-7
1,2,4,5-Tetrachlorobenzene	95-94-3	Atrazine	1912-24-9
1,2,4-Trichlorobenzene	120-82-1	Benzaldehyde	100-52-7
1,2-Dichlorobenzene	95-50-1	Benzidine	92-87-5
1,2-Diphenylhydrazine	122-66-7	Benzo[a]anthracene **(1)**	56-55-3
1,3-Dichlorobenzene	541-73-1	Benzo[a]pyrene **(1)**	50-32-8
1,3-Dimethylnaphthalene	575-41-7	Benzo[b]fluoranthene **(1)**	205-99-2
1,4-Dichlorobenzene	106-46-7	Benzo[g,h,i]perylene **(1)**	191-24-2
1,4-Dichlorobenzene-d4 **(ISTD)**	3855-82-1	Benzo[k]fluoranthene **(1)**	207-08-9
1,4-Dioxane **(1) (2)**	123-91-1	Benzoic acid	65-85-0
1-Methylnaphthalene	90-12-0	Benzyl alcohol	100-51-6
1-Naphthylamine	134-32-7	Bis(2-chloroethoxy)methane	111-91-1
2,2'-oxybis[1-chloropropane]	108-60-1	Bis(2-chloroethyl)ether **(1)**	111-44-4
2,3,4,6-Tetrachlorophenol	58-90-2	Bis(2-ethylhexyl) phthalate	117-81-7
2,3,7,8-TCDD	1746-01-6	Bisphenol-A	80-05-7
2,3-Dihydroindene	496-11-7	Butyl benzyl phthalate	85-68-7
2,3-Dimethylaniline	87-59-2	Caprolactam	105-60-2
2,4,5-Trichlorophenol	95-95-4	Carbamazepine	298-46-4
2,4,5-Trimethylaniline	137-17-7	Carbazole	86-74-8
2,4,6-Tribromophenol **(Surrogate)**	118-79-6	Chrysene **(1)**	218-01-9
2,4,6-Trichlorophenol	88-06-2	Chrysene-d12 **(ISTD)**	1719-03-5
2,4-Dichlorophenol	120-83-2	Coumarin	91-64-5
2,4-Dimethylphenol	105-67-9	Dibenz(a,h)anthracene **(1)**	53-70-3
2,4-Dinitrophenol	51-28-5	Dibenzofuran	132-64-9
2,4-Dinitrotoluene	121-14-2	Diethyl phthalate	84-66-2
2,4-Xylidine	95-68-1	Dimethyl phthalate	131-11-3
2,6-Dinitrotoluene	606-20-2	Di-n-butyl phthalate	84-74-2
2-Chloronaphthalene	91-58-7	Di-n-octyl phthalate	117-84-0
2-Chlorophenol	95-57-8	Fluoranthene **(1)**	206-44-0
2-Ethylaniline	578-54-1	Fluorene **(1)**	86-73-7
2-Fluorobiphenyl **(Surrogate)**	321-60-8	Hexachlorobenzene **(1)**	118-74-1
2-Fluorophenol **(Surrogate)**	367-12-4	Hexachlorobutadiene	87-68-3
2-Methylnaphthalene	91-57-6	Hexachlorocyclopentadiene	77-47-4
2-Methylphenol	95-48-7	Hexachloroethane	67-72-1
2-Naphthylamine	91-59-8	Indeno[1,2,3-cd]pyrene **(1)**	193-39-5
2-Nitroaniline	88-74-4	Isophorone	78-59-1
2-Nitrophenol	88-75-5	n,n'-Dimethylaniline	121-69-7
2-tertbutyl-4-methylphenol	2409-55-4	Naphthalene **(1)**	91-20-3
2-Toluidine	95-53-4	Naphthalene-d8 **(ISTD)**	1146-65-2
3 & 4 Methylphenol	15831-10-4	n-Decane	124-18-5

Table 1

Compound	CAS No.	Compound	CAS No.
3,3'-Dichlorobenzidine	91-94-1	Nitrobenzene	98-95-3
3,4-Dimethylaniline	95-64-7	Nitrobenzene-d5 **(Surrogate)**	4165-60-0
3,5-di-tert-butyl-4-hydroxytol	128-37-0	N-Nitrosodimethylamine **(1)**	62-75-9
3-Nitroaniline	99-09-2	N-Nitrosodi-n-propylamine	621-64-7
4,6-Dinitro-2-methylphenol **(1)**	534-52-1	N-Nitrosodiphenylamine	86-30-6
4-Bromophenyl phenyl ether	101-55-3	n-Octadecane	593-45-3
4-chloro-2-methylaniline	95-69-2	o-Toluidine-d9 **(Surrogate)**	194423-47-7
4-Chloro-3-methylphenol	59-50-7	Pentachloronitrobenzene	82-68-8
4-Chloroaniline	106-47-8	Pentachlorophenol **(1)**	87-86-5
4-Chloroaniline–d4 **(Surrogate)**	191656-33-4	Perylene-d12 **(ISTD)**	1520-96-3
4-Chlorophenyl phenyl ether	7005-72-3	Phenanthrene **(1)**	85-01-8
4-Methylphenol	106-44-5	Phenanthrene-d10 **(ISTD**)	1517-22-2
4-Nitroaniline	100-01-6	Phenol	108-95-2
4-Nitrophenol	100-02-7	Phenol-d5 **(Surrogate)**	4165-62-2
Acenaphthene **(1)**	83-32-9	Phenyl ether	101-84-8
Acenaphthene-d10 **(ISTD)**	15067-26-2	Pyrene **(1)**	129-00-0
Acenaphthylene **(1)**	208-96-8	Pyridine	110-86-1
Acetophenone	98-86-2	Terphenyl-d14 **(Surrogate)**	1718-51-0
Aniline	62-53-3	Total Cresols	STL00160
Aniline-d5 **(Surrogate)**	4165-61-1		

(1) Compound can be analyzed by full scan or Selected Ion Monitoring (SIM).
(2) Compound can also be analyzed by Isotope Dilution/SIM.

1.2 For a listing of method detection limits (MDLs) and Reporting Limits (RLs) please refer to the currently active Method 8270D Method Limit Groups in TALS (TestAmerica LIMS).

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 7 (*Review of Work)*, and Section 19 (*Test Methods and Method Validation)* in TestAmerica Edison's Quality Assurance Manual (TestAmerica Edison Document No. ED-QA-LQM).

2.0 Summary of Method

2.1 This method is used for the analysis of aqueous and solid matrices for semi-volatile base, neutral and acid organic compounds that are extracted from the sample matrix with an organic solvent.

2.2 An aliquot of sample containing surrogate spiking compounds is extracted with an organic solvent. The extract is concentrated on a steam bath to a suitable volume. Internal standards are added to the extract.

2.3 Sample extraction techniques are specified for each matrix in the following TestAmerica Edison SOPs:

- ED-ORP-002 (*Extraction of Semivolatile Organic Compounds in Water by Separatory Funnel, SW846 Method 3510C*);

- ED-ORP-043 (*SW846 Method 3580A - Waste Dilution Prep for Analysis of BNAs by SW846 Method 8270)*
- ED-ORP-0044 (*Microwave Extraction for Solids, SW846 Method 3546*);
- ED-ORP-006 (*Extraction of Semivolatile Compounds in Soil Using Medium Level Extraction Techniques, SW846 Method 3550B)*.

2.4 A small aliquot of the extract is injected into a gas chromatograph (GC) equipped with a capillary column. The GC is temperature programmed to separate the compounds which were recovered during the extraction step by boiling point. The effluent of the gas chromatograph is interfaced to a mass spectrometer (MS) which is used to detect the compounds eluting from the GC. The detected compounds are fragmented with an electron beam to produce a mass spectrum which is characteristic of the compound introduced into the MS. Identification of target analytes is accomplished by comparing their mass spectra with the electron ionization spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion (quantitation ion) relative to an internal standard established through a five-point calibration (six points for second order regression). Specific calibration and quality control steps are included in the method that must be performed and must meet the specifications of SW846 Method 8270D.

2.5 Standard procedure involves preparation of aqueous samples using a Reduced Volume Extraction (RVE) followed by analysis using a Large Volume Injection (LVI). Optionally, a full volume (1000 ml nominal) may be employed. The details of the extractions are outlined in the applicable prep SOPs while the analytical details for 8270D are presented in this SOP.

2.6 This method is also applicable to the analysis of samples by Selected Ion Monitoring (SIM) for the purpose of obtaining lower reporting limits for the following compounds:

Table 2 – SIM Analytes

SIM Analytes	CAS #
1,4-Dioxane	123-91-1
4,6-Dinitro-2-methylphenol	534-52-1
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benzo[a]anthracene	56-55-3
Benzo[a]pyrene	50-32-8
Benzo[b]fluoranthene	205-99-2
Benzo[g,h,i]perylene	191-24-2
Benzo[k]fluoranthene	207-08-9
Bis(2-chloroethyl)ether	111-44-4
Chrysene	218-01-9

Table 2 – SIM Analytes	
SIM Analytes	**CAS #**
Dibenz(a,h)anthracene	53-70-3
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
Indeno[1,2,3-cd]pyrene	193-39-5
Naphthalene	91-20-3
N-Nitrosodimethylamine	62-75-9
Pentachlorophenol	87-86-5
Phenanthrene	85-01-8
Pyrene	129-00-0

2.7 An isotope dilution selected ion monitoring (SIM) technique for the analysis of 1,4-dioxane in water at a reporting level of 0.4 ug/l is also described in this SOP. Using this technique 1,4-dioxane-d8 is added prior to sample extraction and is used as an internal standard to calculate the concentration of 1,4-dioxane present. Additionally, 1,4-dichorobenzene-d4 is added to the extract prior to analysis to monitor the recovery of 1,4-dioxane-d8.

3.0 Definitions

For a complete list of definitions refer to Appendix 2 in the most current revision of the Quality Assurance Manual (ED-QA-LQM).

4.0 Interferences

4.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Analysts must take steps to determine the source of the interference and take corrective action to eliminate the problem.

4.1.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe is automatically rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a solvent blank to check for cross-contamination. Alternately, verify that the sample analyzed after the high concentration sample does not show any carryover through inspection of chromatogram and target results.

4.1.2 Contaminants from the extraction process, detected in the method blank should be evaluated to determine the impact on the analysis. Interferences from any target analyte must not be present in the method blank above the reporting limit for that

compound. If these types of interferences occur, corrective action is required. The source should be identified and corrective action initiated to eliminate the interference from the extraction process. Affected samples must be re-extracted and re-analyzed.

4.1.3 The analyst must take precautions to make sure that contaminants do not enter the analytical system. These precautions include systematic procedures designed to eliminate interferences.

4.2 Some compounds analyzed by this method are unstable or sensitive. Benzidine, for example, is easily oxidized during extraction. Hexachlorocyclopentadiene breaks down photochemically and can decompose from high temperatures, particularly in the injection port of the GC. 1,2-Diphenylhydrazine is unstable even at room temperature and readily converts to azobenzene. Phenols are sensitive to active sites and can give a low response or exhibit poor chromatography by tailing. Therefore, it is important the GC is maintained in the best possible condition. See Section 10.1 for proper daily maintenance.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section.

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Dimethyl-dichloro-silane	Flammable	none	Can be corrosive to the respiratory tract causing severe irritation and tissue damage. Harmful if absorbed through the skin. May cause severe irritation and systemic damage. Severely irritating to the skin and eyes. Harmful if swallowed. Can cause abdominal discomfort, nausea, vomiting, diarrhea, and irritation to the mouth, throat and stomach.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Gas chromatograph/mass spectrometer system

6.1.1 Gas chromatograph: An Agilent/HP 5890/6890/7890 (or equivalent) houses the capillary column. The GC provides a splitless injection port and allows the column to be directly coupled to the mass spectrometer. The oven is temperature programmable to meet the requirements of the method. An HP 7673/7683 autosampler (or

equivalent) with a 10 ul syringe provides automatic injection of sample extracts while the instrument is unattended.

6.1.2 Analytical Column: 30m x 0.25mm ID, 0.25 um film thickness, Restek Rxi-5Sil MS, Catalog #13623 Zebron ZB-Semivolatiles, Catalog # 7HG-G027-11.

6.1.3 Mass spectrometer: Agilent (HP) 5972, 5973, 5975 or 5977A Mass Selective Detector (MSD) Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts electron energy in the electron ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 50 ng of decafluorotriphenylphosphine (DFTPP) which meets the criteria in Section 9.2.1 when 2 ul of the 25 ug/ml GC/MS tuning standard is injected through the GC.

6.1.4 GC/MS interface: Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria.

6.1.5 Data system: The data system is interfaced to the mass spectrometer and accommodates continuous acquisition and storage of GC/MS data throughout the duration of the chromatographic program. The data system consists of a Hewlett-Packard Chemstation equipped with Mustang software used for instrument control and data acquisition. This, in turn, is interfaced to TestAmerica's Chrom software for data processing. Data from sample extract analysis can be accessed in real-time, while sample data reports and library searches can be performed on data files from previously run samples. The software is also capable of searching any GC/MS data file for ions of a specific mass whose abundances can be plotted versus time or scan number which allows integration of abundances for any extracted ion between specified times or scan-number limits. Library searches utilize a NIST 02.1 Mass Spectral Library.

6.2 Bottles, glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

6.3 Injection port liners, splitless

6.4 Injection port septa

6.5 Injection port graphite seals

6.6 Pre-silanized glass wool (Supelco 2-0411 or equivalent)

6.7 Syringes, Assorted sizes 10ul - 1000ul; gas-tight

6.8 Bottles, 10 and 5ml amber screw cap with Teflon liner

6.9 Vials, 2ml amber screw cap with Teflon liner

6.10 Wheaton microvials 100ul (or equivalent)

6.11 Volumetric Flasks, Class A with ground glass stoppers (2ml - 100ml)

6.12 Analytical balance, ASP Model SP-180 (or equivalent), capable of accurately weighing to 0.0001 gr.

7.0 Reagents and Standards

7.1. Reagents:

7.1.1. Methylene Chloride: J.T.Baker Resi-Analyzed, used for Organic Residue Analysis (P/N 9266-V8 or equivalent).

7.1.2. Methanol: J.T.Baker Purge and Trap Grade (P/N 9077-02 or equivalent).

7.1.3. Toluene: J.T.Baker Resi-Analyzed, for Organic Residue Analysis (P/N 9460-03 or equivalent).

7.1.4. Sylon-CT: Supelco (P/N 33065-U or equivalent). Sylon-CT is a highly reactive silanizing reagent consisting of 95% Toluene and 5% Dimethyldichlorosilane (DMDCS).

7.1.5. Each lot of solvent is screened for contaminants before being used for analysis as detailed in TestAmerica Corporate Quality SOP No. CA-Q-S-001 (*Solvent & Acid Lot Testing & Approval*) and TestAmerica Edison SOP No. ED-GEN-023 (*Bulk Solvent Testing and Approval*).

7.2. Standards:

7.2.1. **Calibration Standards (Full Scan Analysis)**: Stock analytical standard solutions are purchased mainly from Restek Corporation. Other standards are prepared in the laboratory as needed using neat compounds or prepared solutions purchased from SPEX CertiPrep, Chem Service, Accustandard, Supelco or other suppliers. Standards prep instructions are detailed for the following full scan analyte list options:

- Full Volume Aqueous Prep and Soils – Long Analyte List
- Full Volume Aqueous Prep and Soils – Short Analyte List
- Full Volume Aqueous Prep and Soils – Aromatic Amines
- Reduced Volume Aqueous Prep and Soils – Long Analyte List
- Reduced Volume Aqueous Prep and Soils – Short Analyte List
- Reduced Volume Aqueous Prep and Soils – Aromatic Amines

Secondary dilutions are either made from purchased stock solutions as listed below or from prepared solutions as listed in the following table:

NOTE: Second sources (from certified separate lots) are used for ICV standards.

Table 3 – Full Scan Stock Standards			
Target Analyte Standard Name	**Conc. (PPM)**	**Vendor**	**Catalog #**
1,2,3,4-TCDD	50	SPEX	SVO-TANJ-12
SPEX Super Mix (contains compounds listed in table below)	2000 *	SPEX	SVO-TANJ-16
8270 List 1/ Std #1 Megamix	Varied	Restek	567672
8270 List 1/ Std #7 N-Diphenylamine	2000	Restek	567676
8270 List 1/ Std #8	2000	Restek	568724
8270 Surrogate Standard	5000*	Restek	567685
8270 Internal Standard	2000	Restek	567684
8270 List 1/ Std#2 Amines	2000	Restek	567673
Custom Aromatic Amine Mix (see Table 5 below)	2000	Supelco	21892423
Custom Aromatic Amine Surrogate Standard (see Table 17A)	2000	Restek	569641
Bisphenol-A	1000	SPEX	S-509-MC

*SPEX Super Mix and 8270 Surrogate standard are diluted to 100ppm prior to the preparation of the 1.0ppm and 0.5ppm standards.

Table 4	
SPEX Super Mix SPEX Catalog No. SVO-TANJ-16	
Analyte	**Concentration (PPM)**
Pentachloronitrobenzene	2000
2 -tert-butyl-4-Methylphenol	2000
2,6-Di-tert-butyl-4-Methylphenol	2000
Coumarin	2000
Phenyl ether	2000
N,N'-Dimethylaniline	2000
N-Methylaniline	2000
Carbamazepine	2000
Benzonitrile	2000
1,3-Dimethylnaphthalene	2000

Table 5 Supelco Custom Aromatic Amine Mix Catalog No. 2168334	
Analyte	**Concentration (PPM)**
Aniline	2000
o-Toluidine	2000
2-Ethylaniline	2000
2,4-Dimethylaniline	2000
3,4-Dimethylaniline	2000
2,3-Dimethylaniline	2000
2,4,5-Trimethylaniline	2000
4-Chloro-o-Toluidine	2000
4-Chloroaniline	2000
2-Naphthylamine	2000

7.2.1.1. Individual calibration standards for full scan analysis are prepared in one of several ways depending upon the technique (full volume aqueous prep, soils prep, reduced volume prep with LVI) as well as the target analyte list (long list, short list, aromatic amines). The following tables detail the preparation of calibration standard solutions for each of these techniques and analyte lists. Prepare by combining the indicated volumes of each stock solution using volumetric flask. Dilute to the volume marker with methylene chloride.

Table 6 Full Volume Aqueous Prep and Soils – Long Analyte List Working Standards Preparation								
Solution Name	**120 PPM**	**80 PPM**	**50 PPM**	**20 PPM**	**10 PPM**	**5 PPM**	**1 PPM**	**0.5 PPM**
8270 List 1/ Std #1 Megamix	1200ul	800ul	500ul	200ul	100ul	50ul	10ul	5ul
8270 List 1/ Std #7	600ul	400ul	250ul	100ul	50ul	25ul	-	-
8270 List 1/ Std #8	600ul	400ul	250ul	100ul	50ul	25ul	-	-
SPEX Super Mix	600ul	400ul	250ul	100ul	50ul	25ul	100ul*	50ul*
1,2,3,4-TCDD	-	-	100ul	-	-	-	-	-
8270 Surrogate Standard	240ul	160ul	100ul	40ul	20ul	10ul	100ul*	50ul*
8270 Internal Standard	200ul	200ul	200ul	200ul	200ul	200ul	200ul	200ul
Bisphenol-A	600ul	400ul	250ul	100ul	50ul	25ul		
Final Volume (ml)	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**

Note: The 1.0ppm and 0.5pmm standards (above) are prepared using the 100ug/ml standard for Spex Super Mix and 8270 Surrogate Standard.

Table 7 Full Volume Aqueous Prep and Soils – Short Analyte List Working Standards Preparation						
Solution Name	**120 PPM**	**80 PPM**	**50 PPM**	**20 PPM**	**10 PPM**	**5 PPM**
8270 Internal Standard	200ul	200ul	200ul	200ul	200ul	200ul
8270 List 1/ Std#8	600ul	400ul	250ul	100ul	50ul	25ul
Final Volume (ml)	**10**	**10**	**10**	**10**	**10**	**10**

Table 8 Full Volume Aqueous Prep and Soils - Aromatic Amines Working Standards Preparation						
Solution Name	**120 PPM**	**80 PPM**	**50 PPM**	**20 PPM**	**10 PPM**	**0.5 PPM**
8270 Internal Standard	200ul	200ul	200ul	200ul	200ul	200ul
Custom Aromatic Amine Mix	600ul	400ul	250ul	100ul	50ul	2.5ul
Custom Aromatic Amine Surrogate Std	600ul	400ul	250ul	100ul	50ul	2.5ul
Final Volume (ml)	**10**	**10**	**10**	**10**	**10**	**10**

Table 9 Reduced Volume Extraction/LVI – Long Analyte List Working Standards Preparation								
Solution Name	**24 PPM**	**16 PPM**	**10 PPM**	**4 PPM**	**2 PPM**	**1 PPM**	**0.2 PPM**	**0.1 PPM**
120 ppm Long Cal Std (see Table 6)	1.0 mL							
80 ppm Long Cal Std (see Table 6)		1.0 mL						
50 ppm Long Cal Std (see Table 6)			1.0 mL					
20 ppm Long Cal Std (see Table 6)				1.0 mL				
10 ppm Long Cal Std (see Table 6)					1.0 mL			
5.0 ppm Long Cal Std (see Table 6)						1.0 mL		
1.0 ppm Long Cal Std (see Table 6)							1.0 mL	
0.5 ppm Long Cal Std (see Table 6)								1.0 mL
Final Volume (ml)	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Table 10 Reduced Volume Extraction/LVI – Short Analyte List Working Standards Preparation						
Solution Name	**24 PPM**	**16 PPM**	**10 PPM**	**4 PPM**	**2 PPM**	**1 PPM**
120 ppm Short Cal Std (see Table 7)	1.0 ml					
80 ppm Short Cal Std (see Table 7)		1.0 ml				
50 ppm Short Cal Std (see Table 7)			1.0 ml			
20 ppm Short Cal Std (see Table 7)				1.0 ml		

Table 10 Reduced Volume Extraction/LVI – Short Analyte List Working Standards Preparation						
Solution Name	**24 PPM**	**16 PPM**	**10 PPM**	**4 PPM**	**2 PPM**	**1 PPM**
10 ppm Short Cal Std (see Table 7)					1.0 ml	
5.0 ppm Short Cal Std (see Table 7)						1.0 ml
Final Volume (ml)	**5**	**5**	**5**	**5**	**5**	**5**

Table 11 Reduced Volume Extraction/LVI -Aromatic Amine Working Standards Preparation						
Solution Name	**24 PPM**	**16 PPM**	**10 PPM**	**4 PPM**	**2 PPM**	**0.1 PPM**
120 ppm Aromatic Amines Cal Std (see Table 8)	1.0 ml					
80 ppm Aromatic Amines Cal Std (see Table 8)		1.0 ml				
50 ppm Aromatic Amines Cal Std (see Table 8)			1.0 ml			
20 ppm Aromatic Amines Cal Std (see Table 8)				1.0 ml		
10 ppm Aromatic Amines Cal Std (see Table 8)					1.0 ml	
0.5 ppm Aromatic Amines Cal Std (see Table 8)						1.0 ml
Final Volume (ml)	**5**	**5**	**5**	**5**	**5**	**5**

7.2.1.2. **Initial Calibration Verification (full scan**): Second source ICVs for full scan analysis are prepared in one of several ways depending upon the technique (full volume aqueous prep, soils prep, reduced volume prep with LVI) as well as the target analyte list (long list, short list, aromatic amines). The following tables detail the preparation of ICVs for each of these techniques and analyte lists. Prepare by combining the indicated volumes of each stock solution using volumetric flask. Dilute to the volume marker with methylene chloride.

Table 12 8270/625 ICV -Long List Working Standards Preparation	
Solution Name	**25 PPM**
8270 List 1/ Std #1 Megamix (2nd Lot)	250ul
8270 List 1/ Std #7 (2nd Lot)	125ul
8270 List 1/ Std #8 (2nd Lot)	125ul
SPEX Super Mix (2nd Lot)	125ul
8270 Internal Standard	200ul
Bisphenol-A (2nd Lot)	125ul
Final Volume (ml)	**10**

Table 13 8270/625 ICV - Short List Working Standards Preparation	
Solution Name	**25 PPM**
8270 Internal Standard (2nd Lot)	200ul
8270 List 1/ Std#2 Amines (2nd Lot)	125ul
Final Volume (ml)	**10**

Table 14 Aromatic Amines ICV Working Standards Preparation	
Solution Name	**25 PPM**
8270 Internal Standard	200ul
Supelco Aromatic Amines 2nd Lot (Cat. No. 21467482)	125ul
Final Volume (ml)	**10**

Table 15 8270/625 ICV LVI - Long List Working Standards Preparation	
Solution Name	**5 PPM**
25PPM 8270/625 ICV (Long List) (see Table 12)	1.0 mL
Final Volume (ml)	**5**

Table 16 8270/625 ICV LVI -Short List Working Standards Preparation	
Solution Name	**5 PPM**
25PPM 8270/625 ICV (Short List) (see Table 13)	1.0 mL
Final Volume (ml)	**5**

7.2.1.3. **Surrogate Standards (Full Scan Analysis):** A 5000ppm Surrogate Standard is purchased from Restek for use in spiking blanks, samples and associated QC prior to extraction (reference the applicable sample prep SOPs for spiking instructions).

Table 17 Full Scan Surrogate Standards Solution Restek Catalog No. 567685	
Surrogate Standard Compounds	**Concentration (PPM)**
Nitrobenzene-d5	5000
p-Terphenyl-d14	5000
2,4,6-Tribromophenol	5000
Phenol-d5	5000
2-Fluorobiphenyl	5000
2-Fluorophenol	5000

7.2.1.3.1 Surrogate Standards (Aromatic Amine Analysis): A 2000 ppm Surrogate Standard is purchased from Restek (Cat. # 569641) for use in spiking blanks, samples and associated QC prior to extraction and analysis of samples for Aromatic Amines (reference the applicable prep SOPs for spiking instructions).

Table 17a Aromatic Amine Surrogate Standards Solutions Restek Catalog Nos. 569641	
Surrogate Standard Compounds	**Concentration (PPM)**
Aniline-d5	5000
o-Toluidine-d9	5000
4-Chloroaniline-d4	5000

7.2.1.4. Internal Standards (**Full Scan Analysis**): The Internal Standards Solution at 2000ppm is purchased from Restek (Catalog # 567684). The Internal Standard solution is stored in 10ml amber screw cap bottles with Teflon liners in the dark at 4°C. The Internal standard solution is used in preparing all analytical standards. Inject 20ul of this solution (2000ppm) per ml of sample extract prior to analysis resulting in a concentration of 40ppm (ug/ml) in the extract.

Table 18 Full Scan Internal Standards Solution Restek Catalog No. 567684	
Internal Standard Compounds	**Concentration (PPM)**
1,4-Dichlorobenzene-d4	2000
Phenanthrene-d10	2000
Naphthalene-d8	2000
Chrysene-d12	2000
Acenaphthene-d10	2000

Table 18 Full Scan Internal Standards Solution Restek Catalog No. 567684	
Internal Standard Compounds	**Concentration (PPM)**
Perylene-d12	2000

7.2.2. Calibration Standards (SIM analysis): The Edison lab currently analyzes only a select list of compounds by 8270D SIM (see Sections 1.0 and 2.0). Stock analytical SIM standard solutions are purchased mainly from Accustandard and Spex. Working standards are prepared from these solutions as listed in the tables in Section 7.2.2.1:

Table 19- Stock SIM Standards			
Standard Name	**Concentration**	**Vendor**	**Catalog #**
Pentachlorophenol	100ppm	Accustandard	App-9-176
n-Nitrosodimethylamine	100ppm	Accustandard	APP-9-149
Hexachlorobenzene	100ppm*	Accustandard	APP-9-112
PAH Mix	100ppm	Accustandard	M-610
Bis(2-chloroethyl)ether	100ppm*	Accustandard	App-9-027
4,6-Dinitro-2-methylphenol	100ppm	Accustandard	P-3845
1,4-Dioxane	1000ppm**	Accustandard	APP-9-096

*Hexachlorobenzene and Bis(2-chloroethyl)ether are diluted to 10ppm prior to SIM Standards prep

** 1,4-Dioxane is diluted (10x) to 100ppm prior to SIM Standards prep

NOTE: Second sources (from separate lots are used for ICV standards).

7.2.2.1 Individual calibration standards for SIM analysis are prepared in one of two ways depending upon the technique (full volume aqueous prep or reduced volume prep with LVI) as well as the target analyte list (long list, short list, aromatic amines). The following tables detail the preparation of calibration standard solutions for each of these techniques and analyte lists. Prepare by combining the indicated volumes of each stock solution using volumetric flask. Dilute to the volume marker with methylene chloride.

Table 20 Full Volume Aqueous Prep – SIM Working Standards Preparation						
	0.025 PPM	**0.05 PPM**	**0.1 PPM**	**0.5 PPM**	**1.0 PPM**	**5.0 PPM**
Pentachlorophenol	10uL	25uL	50uL	50uL	100uL	250uL
n-Nitrosodimethylamine	10uL	25uL	50uL	50uL	100uL	250uL
PAH mix	2.5uL	5uL	100uL	25uL	50uL	100uL

Table 20 Full Volume Aqueous Prep – SIM Working Standards Preparation						
	0.025 PPM	**0.05 PPM**	**0.1 PPM**	**0.5 PPM**	**1.0 PPM**	**5.0 PPM**
Hexachlorobenzene	10uL	25uL	100uL	500uL	1000uL	2500uL
Bis(2-chloroethyl)ether	10uL	25uL	100uL	500uL	1000uL	250uL*
4,6-dinitro-2-methylphenol	50ul	100ul	200ul	200ul	250ul	500ul
1,4-Dioxane	20ul	50ul	100ul	100ul	200ul	500ul
ISTD	200uL	200uL	200uL	100uL	100uL	100uL
Final Volume (ml)	**10**	**10**	**10**	**5**	**5**	**5**

*For Bis(2-chloroethyl)ether the 5.0 ppm level is prepared using the 100ppm standard.

Table 21 Reduced Volume Extraction/LVI – SIM Working Standards Preparation						
	0.005 PPM	**0.01 PPM**	**0.02 PPM**	**0.10 PPM**	**0.20 PPM**	**1.0 PPM**
0.025 PPM Std (see Table 20)	1.0 mL					
0.05 PPM Std (see Table 20)		1.0 mL				
0.1 PPM Std (see Table 20)			1.0 mL			
0.5 PPM Std (see Table 20)				1.0 mL		
1.0 PPM Std (see Table 20)					1.0 mL	
5.0 PPM Std (see Table 20)						1.0 mL
Final Volume (ml)	**5**	**5**	**5**	**5**	**5**	**5**

7.2.2.2 Initial Calibration Verification (SIM): A 0.1 ppm separate lot SIM ICV is prepared as detailed in Table 6 using the stock standards detailed in Section 7.2.1.4 (above)

Table 22 0.1ppm SIM ICV preparation	
Pentachlorophenol	25uL
n-Nitrosodimethylamine	25uL
PAH mix	5uL
Hexachlorobenzene	5uL
1,4-Dioxane	5ul
4,6-Dinitro-2-methylphenol	100ul
ISTD	**100uL**
Final Volume	**5 ml**

7.2.2.3 Internal Standard solution (SIM): A 50 ppm Internal Standard solution for SIM analysis is prepared by adding 125ul of the 2000ppm stock ISTD (see Section 7.2.1.4) and bringing to volume with Methylene Chloride in a 5ml volumetric flask.

7.2.2.3.1 For SIM analysis inject 20ul of this solution (50ppm) per ml of sample extract prior to analysis resulting in a concentration of 1ppm (ug/ml) in the extract.

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7.2.3. Calibration Standards (Isotope Dilution SIM – 1,4-Dioxane): The Edison lab currently analyzes only for 1,4-dioxane by 8270D isotope dilution SIM (see Sections 1.0 and 2.0). Stock analytical isotope dilution SIM standard solutions are purchased mainly from Accustandard and Restek. Working standards are prepared from these solutions as listed in the tables below.

Table 23 -
Stock 1,4-Dioxane Isotope Dilution SIM Standards

Standard Name	Concentration	Vendor	Catalog #
1,4-Dioxane	1000ppm*	Accustandard	APP-9-096

* 1,4-Dioxane is diluted (10x) to 100ppm prior to SIM Standards prep

Table 24 -
Stock Labeled 1,4-Dioxane SIM Surrogate/Internal Standard (added at prep)

Standard Name	Concentration	Vendor	Catalog #
1,4-Dioxane-d8	2000ppm	Restek	A0120108

Table 25 -
Stock 1,4-Dioxane Isotope Dilution SIM Internal Standard (added to extract)

Standard Name	Concentration	Vendor	Catalog #
1,4-Dichlorobenzene-d4	2000ppm	Restek	A0121898

Table 26 -
Stock 1,4-Dioxane Isotope Dilution SIM Separate Source ICV

Standard Name	Concentration	Vendor	Catalog #
1,4-Dioxane	1000ppm	Absolute	70373

7.2.3.1 Individual calibration standards for 1,4-dioxane isotope dilution SIM analysis are prepared at the concentrations detailed in the following tables. Prepare by combining the appropriate volumes of each stock solution using volumetric flask. Dilute to the volume marker with methylene chloride.

Table 27 Reduced Volume Extraction/LVI – 1,4-Dioxane Isotope Dilution SIM ICAL Standard Concentrations (ug/ml)							
	Lev 1	**Lev 2**	**Lev 3**	**Lev 4**	**Lev 4**	**Lev 6**	**ICV***
1,4-Dioxane	10	2	0.8	0.4	0.1	0.04	0.2
1,4-Dioxane-d8	4	4	4	4	4	4	4
1,4-Dichlorobenzene-d4	0.2	0.2	0.2	0.2	0.2	0.2	0.2

***:** The ICV is prepared from the second source stock in Table 26.

7.2.4. GC/MS Instrument Performance Check (DFTPP): The DFTPP standard is prepared by is prepared at 25 ppm by adding 2.5ml of EPA 8270 GC/MS Tuning Solution II (Supelco Catalog # 47548-U) to a 100ml volumetric flask and bringing to volume with Methylene Chloride.

7.2.5. Information on prepared standard solutions must be recorded in a standards logbook or in the TALS Reagent Module. Information such as standard supplier, lot number, original concentration, a description of how the standard was made, are required along with the laboratory lot number, analyst's initials, date prepared, expiration date and verification signature. Standards must be remade every 6 months, or sooner, if the standards expire or begin to show signs of unacceptable degradation. Class "A" volumetric must be used at all times and syringes, preferably gas-tight syringes when available, should be checked for accuracy using an analytical balance. Class "A" pipettes should also be used if volumes permit.

7.2.6. Please refer to TestAmerica Edison SOP No. ED-GEN-008, Standard Operating Procedure for Preparation, Purity and storage of Reagents and Standards.

- Shelf Life of Standard: 6 months
- Storage Requirements: Stock standards are stored at 4°C and Working Standards stored at -10°C to -20°C.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 All samples must be stored at 4ºC (± 2ºC) upon receipt.

8.2 Sample Extract Storage. Samples extracts must be protected from light and refrigerated at 4ºC (± 2ºC) from time of extraction until analysis.

8.3 Sample Extract Holding Time. All sample extracts must be analyzed within 40 days of extraction.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Amber glass, 1L	1000 ml or 250 ml (1)	Cool 4 ± 2°C	7 days to extraction; Analyze within 40 days of extraction	EPA Method SW846 8270D
Solids	Wide mouth glass, 8 or 16 oz.	50g	Cool 4 ± 2°C	14 days to extraction; Analyze within 40 days of extraction	EPA Method SW846 8270D

(1) : Reduced volume extaction (RVE) LVI option

9.0 Quality Control

9.1. **Sample QC** - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples	Statistical Limits [4]
Matrix Spike (MS)[2]	1 in 20 or fewer samples	Statistical Limits [4]
MS Duplicate (MSD)[2]	1 in 20 or fewer samples	Statistical Limits [4]
Surrogates	every sample[3]	Statistical Limits [4]
Internal Standards	Every sample	Response within -50% to +100% of CCV

[1] LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD are randomly selected, unless specifically requested by a client….predetermined by the extraction lab.
[3] Analytical and QC samples (MB, LCS, MS/MSD, Method Blank)
[4] Statistical control limits are updated annually and are updated into lab reporting software.

9.1.1. **Method blanks** are extracted with every sample batch on each day that samples are extracted. To be considered acceptable, the method blank must contain less than the reporting limit of all target compounds except for phthalates, which can be present at up to 5x the MDL. .

If method blanks are unacceptably contaminated with target compounds that are also present in field samples, all affected samples must be re-extracted and re-analyzed. Corrective action must be taken to identify and eliminate the contamination source. Demonstrate that acceptable blanks can be obtained before continuing with sample extraction and analysis. Method blanks must be analyzed on each instrument on which the associated samples are analyzed.

9.1.1.1. Surrogate recoveries for the method blank are compared to laboratory generated limits. If two or more surrogates for any one fraction (base-neutral or acid) are outside of recovery limits or if any one surrogate recovers at <10%, the sample must be re-extracted and re-analyzed to confirm matrix interference.. If any surrogate is still outside limits, all samples and QC samples associated with that method blank must be re-extracted (volume permitting).

9.1.2. Matrix Spike (MS)/Matrix Spike Duplicate (MSD): A matrix spike/matrix spike duplicate (MS/MSD) pair is extracted and analyzed with every 20 environmental samples of a specific matrix (defined as a sample batch). Full compound list spiking is employed for MS/MSDs and LCSs. These spikes are prepared and extracted concurrent with sample preparation. MS and MSD recoveries are calculated and compared to lab generated acceptance criteria. See the current active TALS 8270D Method Limit Group for QC limits. The MS/MSD spiking solution should the same as used for the calibration standards.

9.1.2.1 A Laboratory Control Sample Duplicate (LCSD) is extracted and analyzed only when insufficient client sample is available for preparation of an MS/MSD pair. The LCS/LSCD is evaluated in the same manner as the MS/MSD (see Section 9.1.2)

9.1.2.2 An LCS/LCSD may be substituted for the MS/MSD if insufficient sample volume is available.

9.1.3. Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD): A Laboratory Control Sample (LCS) (aka blank spike) must be extracted and analyzed with each batch of 20 environmental samples. The LCS data is used to assess method performance if the MS/MSD recoveries fall outside of the lab generated limits (See the current active TALS 8270D Method Limit Group for QC limits). If the LCS recovery is within the current lab generated limits, the MS/MSD recoveries are attributed to matrix interference.

9.1.3.1 A Laboratory Control Sample Duplicate (LCSD) is extracted and analyzed only when insufficient client sample is available for preparation of an MS/MSD pair. The LCS/LSCD is evaluated in the same manner as the MS/MSD (see Section 9.1.2)

9.1.3.2 Spike recovery limits are lab generated and are updated annually. Certain state regulatory programs have defined recovery limits which, where applicable, are used for spike recovery evaluations. The TALS Method Limit Groups detail these regulatory program criteria.

9.1.4. Surrogate Standards: All full scan samples, blanks and QC samples are spiked with a six (6) component surrogate standard mix (see Section 7.2.1.3). The percent recovery of the surrogate standards is calculated and compared to lab generated limits (See the current active TALS 8270D Method Limit Group for QC limits). **Note:** Three (3) surrogates are used when analyzing for Aromatic Amines (see Section 7.2.1.3.1).

If any two or more surrogates for any one fraction (base-neutral or acid) are outside of recovery limits or if any one surrogate recovers at <10%, the sample must be re-extracted and re-analyzed to confirm matrix interference. If a surrogate is diluted to a concentration below that of the lowest calibration standard, no corrective action is necessary.

9.1.4.1 Surrogate recovery limits are lab generated and are updated annually. Certain state regulatory programs have defined recovery limits which, where applicable, are used for spike recovery evaluations. The TALS Method Limit Groups detail these regulatory program criteria.

9.1.5. Internal Standards: The response (area count) of each internal standard in the sample must be within -50 +100% of its corresponding internal standard in the CCV or, the ICAL midpoint for samples analyzed under the initial calibration range. Failure to meet these criteria is indicative of sample matrix effects. All samples failing these criteria must be reanalyzed to confirm matrix effects.

9.2. Instrument QC

9.2.1 GC/MS Instrument Performance Check (DFTPP): (**Note**: the DFTPP performance check applies only to full scan analyses and is not evaluated for SIM analysis). The GC/MS system is tuned using Perfluortributylamine (PFTBA) such that an injection of 50ng of Decafluorotriphenylphosphine (DFTPP) meet the abundance criteria listed in the table below. Prior to the analysis of any calibration standards or samples, the GC/MS system must meet all DFTPP key ion abundance criteria. This analysis will verify proper tuning of the system for a period of 12 hours post-injection. After 12 hours, the instrument performance must again be verified prior to the analysis of standards, QC or samples.

DFTPP Key Ions and Abundance Criteria	
Mass	**Ion Abundance Criteria**
51	30-60% of mass 198
68	<2% of mass 69
69	reference only
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base Peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198

DFTPP Key Ions and Abundance Criteria	
365	>1% of mass 198
441	present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

9.2.1.1. Evaluate DFTPP using three scan averaging and background subtraction techniques. Select the scan at the peak apex, add +1 scan from the apex and -1 scans from the apex.

9.2.1.2. The mass spectrum of DFTPP may be background subtracted to eliminate column bleed or instrument background ions. Background subtract DFTPP by selecting a scan for subtraction ≤20 scans before the apex scan of DFTPP.

9.2.1.3. Check column performance using pentachlorophenol and the benzidine peaks (these compounds are included in the DFTPP solution). Benzidine & Pentachlorophenol should respond normally without significant peak tailing (Tailing Factor should be <2 measured at 10% peak height). If responses are poor and excessive peak tailing is present, corrective action for the GC/MS instrument may be required. Corrective actions may include:

9.2.1.3.1 Retune the GC/MS;
9.2.1.3.2 Clip the injector end of the GC column;
9.2.1.3.3 Replace the septum and injection port liner;
9.2.1.3.4 Change the injection port seal;
9.2.1.3.5 Replace the GC column;
9.2.1.3.6 Clean the injection port with MeCl2
9.2.1.3.7 Clean the MS ion source;
9.2.1.3.8 Place a service call.

9.2.1.4. The breakdown of 4, 4-DDT into 4,4-DDD and 4,4'DDE may also be used to assess GC column performance and injection port inertness. If so evaluated the breakdown must be <20%.

9.2.1.5. DFTPP parameter settings are stored in a tune file, which will be used in all subsequent analysis of standards and sample extracts.

9.2.2 Initial Calibration Range and Initial Calibration Verification

9.2.2.1. **Initial Calibration:** The initial calibration range consists of a minimum of five concentration levels of analytical standards (six for second order regression) prepared as described in Section

7.2. and analyzed once the DFTPP instrument performance check has met the criteria in Section 9.2.1. .

9.2.2.2. Initial Calibration Verification (ICV): An Initial Calibration Verification (ICV) standard is analyzed immediately after the Initial Calibration Range and before any samples are analyzed. The ICV is prepared as detailed in Section 7.2. The ICV must be from a source (or lot) separate from the standards used in the Initial Calibration Range.

9.2.3 Continuing Calibration Verification (CCV) and Low Level Continuing Calibration Verification (LLCCV): A mid-point Continuing Calibration Verification (CCV) must be analyzed every 12 hours after the DFTPP instrument performance check (when applicable).. The CCV is prepared as detailed in Section 7.2. (typically, 50 ug/ml for full volume aqueous and soils, 10 ug/ml for LV, 0.02 ug/ml for LVI SIM) and 0.2 for isotope dilution SIM). Additionally a Low Level Continuing Calibration Verification (LLCCV) is analyzed after the CCV for full scan analysis. The LLCCV is the same as the lowest calibration level analyzed with the initial calibration range (See Section 7.2).

9.2.4 Calibration Acceptance Summary

9.2.4.1. Retention Time Windows: Retention time windows must be established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. Obtain the retention time for all compounds from the analysis of the midpoint standard for the calibration curve. Establish the center of the retention time window by using the absolute retention time for each analyte, internal standard and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. For qualitative identification to be acceptable the retention time of the relative retention time (automatically calculated in Chrom) must be within 0.8 - 1.2 RRT units of its assigned internal standard. The relative retention times of each compound in the five calibration standards must agree within .06 relative retention time units.

9.2.4.2. Initial Calibration Range: Internal standard calibration is employed for this method. After the initial calibration range has been analyzed the relative response factor (RRF) for each target/surrogate compound at each concentration level is determined using the following equation.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:
A_x = Area characteristic ion (see Table 31) for the compound
Ais = Area characteristic ion (see Table 31) of associated internal standard
Cis = Concentration of internal standard
Cx = Concentration of compound in standard

9.2.4.2.1. Determine the mean RRF for each compound. Minimum response factors must be met for each of the compounds listed in Table 28 (below). Any compound that fails the minimum response factor must be reported as estimated for detects and must have a demonstration of sensitivity in the analytical batch to report non-detects. To demonstrate adequate sensitivity for out of criterion compounds analyze the low level point of the calibration (LLCCV) in the analytical sequence. The criterion for the LLCCV is detection only but the standard qualitative identification criteria in the method must be met.

Table 28:
Minimum Response Factors

Compound	Minimum Response Factor
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl) ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200

Table 28: Minimum Response Factors	
Compound	**Minimum Response Factor**
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalene	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroanailine	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalene	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010
Pentachloronitrobenzene	0.050

9.2.4.2.2. Calculate the Standard Deviation (SD) and Percent Relative Standard Deviation (% RSD) of the response factors for each compound:

$$\% \text{ RSD} = \frac{\text{Standard Deviation of RRFs}}{\text{Mean RRF}}$$

9.2.4.2.3. The % RSD of the RRF's must be ≤20% for each target analyte listed in Table 28. The % RSD of each target analytes must be ≤20% in order for the calibration range to be acceptable. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit or do not meet the minimum correlation coefficient (0.99) for alternate fits (see below) then appropriate corrective maintenance action must be performed. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit **AND** do not meet the minimum correlation coefficient (0.99) then recalibration is necessary.

9.2.4.2.4. If the above listed criteria is met, the system can be assumed to be linear and sample analysis may begin and the average RF from the initial calibration range is used to quantitate all samples.

9.2.4.2.4.1 Certain state regulatory programs have defined calibration acceptance limits which, where applicable, are used for calibration evaluations. The TALS ICAL Limit Groups detail these regulatory program criteria.

9.2.4.2.5. An alternative calibration technique may be employed for those any compounds exceeding the 20% RSD criteria:

9.2.4.2.5.1 Calculate the first order linear regression for any compound which did not meet the 20% criteria. First order linear regression calibration may be employed if alternative average response calibration procedures were not applicable. The r value (Correlation Coefficient) of the equation must be ≥0.99 for the calibration to be employed.

9.2.4.2.5.2 Second order regression calibration can be used for any compound that has an established history as a non-linear performer.

9.2.4.2.5.3 If second order regression calibration is used a minimum of six (6) calibration levels must be analyzed.

9.2.4.2.5.4 If second order regression calibration is used, the r^2 (Correlation Coefficient) value must be $\geq$ 0.99

9.2.4.2.5.5 Any compound that fails to meet the 20% RSD or or 0.99 correlation coefficient criteria must be flagged as estimated for detects (or must be noted in the narrative). If there are non-detects the compounds may be reported if there is adequate sensitivity to detect at the quantitation limit. To demonstrate adequate sensitivity analyze the low level point of the initial calibration in each analytical batch (LLCCV) The criteria for demonstrating adequate sensitivity is detection in the LLCCV using the standard qualitative identification criteria.

9.2.4.2.5.6. When calculating the calibration curve using the linear calibration model a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration back into the curve. The recalculated concentration of the low calibration point should be within ±30% of the standard's concentration. This evaluation can be checked using the Initial Calibration %Drift Report in Chrom. Any detects for analytes calibrated using the linear model and failing this readback criterion must be flagged as estimated or detailed in the narrative.

9.2.4.3. Initial Calibration Verification (ICV):.Once the initial calibration has been analyzed and has met the above criteria, a second source Initial Calibration Verification (ICV) (as prepared in Section 7.2) must be analyzed and evaluated. The ICV must meet the criteria of 70-130% recovery for all compounds with the exception of the poor performing compounds listed in Attachment 1 which are allowed to be within 50-150% : An NCM must be initiated to denote any ICV non-conformances.

9.2.4.4. The ICV must meet the criteria of 70-130% recovery for all compounds however up to 10% of the compounds are allowed to exceed these criteria as long as their recoveries are within 65-135%. For the poor performers (see Attachment 1) the range is 50-150%. If the criterion is not met, a second ICV may be analyzed after corrective measures are taken. If a second ICV analysis fails to meet criteria proceed with corrective action and the analysis of a new initial calibration range. Flagging: If the ICV limits are outside of criteria (high) for an analyte and that analyte is undetected in the sample, no flagging or narration is

required. If the ICV limits are outside of criteria (low) for an analyte and that analyte is undetected in a sample, narrate the non-conformance in an NCM. When that out of spec analyte is detected in a sample, describe the issue in the narrative, or flag as estimated.

9.2.4.5. Continuing Calibration Verification (CCV): A CCV consisting of a standard at or near the midpoint of the Initial Calibration Range is analyzed every 12 hours of instrument operation or at the beginning of an analytical sequence to verify the initial calibration. The calibration verification consists of a DFTPP instrument performance check, and analysis of a calibration verification standard. **Note:** Certain state regulatory programs have defined calibration acceptance limits which, where applicable, are used for calibration evaluations. The TALS ICAL Limit Groups detail these regulatory program criteria.

9.2.4.5.1 Tune Verification: Follow the procedure for verifying the instrument tune described in section 9.2.1 using a 50 ng injection of DFTPP. If the tune cannot be verified, analysis must be stopped, corrective action taken and a return to "control" demonstrated before continuing with the calibration verification process.

9.2.4.5.2 Calibration Verification: Analyze the calibration verification standard immediately after a DFTPP that meets criteria. Use the mid point calibration standard (approximately 50ug/l). NOTE: The calibration standard contains internal standards; Dichlorobenzene d_4, Naphthalene d_8, Acenaphthene d_{10}, Phenanthrene d_{10}, Chrysene d_{12}, and Perylene d_{12} at 40ug/l (0.1ug/L for SIM). The calibration check standard must also include all the target analytes from the original calibration.

9.2.4.5.3 The RFs must meet the criteria for the compounds in Table 28. Any compound that fails the minimum response factor must be reported as estimated for detects and must have a demonstration of sensitivity to report non-detects. To demonstrate adequate sensitivity for out of criterion compounds analyze the low level point of the calibration (LLCCV) in the analytical sequence. The criterion for the LLCCV is detection only but the standard qualitative identification criteria in the method must be met

9.2.4.5.4 The percent difference (when using average response factor) or percent drift (when using linear regression) of

the compounds in Table 28 must be ≤20% for at least 80% of the total analyte list. If more than 20% of the compound list fail to 20% difference or drift criterion then appropriate corrective action must be taken prior to the analysis of the samples. Any individual compound that fails must be reported as estimated for detects and must have a demonstration of sensitivity to report non-detects. To demonstrate adequate sensitivity for out of criterion compounds analyze the low level point of the calibration (LLCCV) in the analytical sequence. The criterion for the LLCCV is detection only (%D criteria are not applied) but the standard qualitative identification criteria in the method must be met.

9.2.4.5.5 **CCV Poor Performers**: Refer to Attachment 1 for the identification of poor and/or erratic performing analytes. These analytes are allowed a %D >20% but must be <50 %D to be acceptable. If there are poor performers that exceed 50%D, the data may be reported provided results are noted as estimated. An NCM must be initiated to denote this situation.

9.2.4.5.6 The retention times of the internal standards from the calibration check must be within ±30 seconds of the internal standards from the mid point standard of the original calibration. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system is inspected for malfunctions, and corrections made as required. If corrective action does not result in the retention time criteria being achieved, the system must be re-calibrated using four additional standards.

9.2.4.5.7 The response (area count) of each internal standard in the calibration verification standard must be within 50 - 100% of its corresponding internal standard in the mid-level calibration standard of the active calibration curve. If the EICP area for any internal standard changes by more than a factor of two (-50% +100%), the mass spectrometer system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

9.2.4.5.8 The relative retention times of each compound in the calibration verification standard must agree within .06 relative retention time units of its value in the initial calibration.

9.2.4.5.9 Use the average response factors from the original five-point calibration for quantitative analysis of target analytes identified in field samples.

9.2.4.5.10 Prepare a calibration summary or list indicating which compounds did not meet the 20% average percent difference criteria. Record this information in that run log.

9.2.4.6. Low Level Continuing Calibration Verification (LLCCV): An LLCCV consisting of the low level standard from the initial calibration range is analyzed every 12 hours of instrument operation after the CCV. The purpose and evaluation of the LLCCV is described in Section 9.2.4.4.4.

10.0 Procedure

10.1. Gas Chromatograph/Mass Spectrometer Operation

10.1.1. The sequence of events for GC/MS analysis involves many steps. First the injection system and column performance and calibration must be verified. Maintenance operations are performed as needed.

10.1.2. Preparation of the Injection Port Liner and Installation Procedure: Prior to the start of initial calibration and each daily analysis of sample extracts, a new liner for the injection port must be prepared. Once a liner has been used it is no longer inert and will cause serious chromatography problems with phenols and other compounds. When preparing the liner, proper laboratory protection must be worn and the liner must be prepared in a well-ventilated hood. When the procedure is completed all traces of toluene, Sylon-Ct and methanol will be removed immediately so that extraction solvents and preparation of sample extracts will not come into contact with these solvents and become contaminated.

10.1.2.1 Remove one liner from a 40ml VOA bottle containing other liners immersed in Sylon-Ct solution. Rinse off the liner with Toluene and wipe dry. Insert 1cm of pre-silanized glass wool partially into one end of the liner and trim neatly. Push the glass wool into the center of the liner so that it is 1 1/4" from the bottom. Do not use glass wool or solvents that are dirty (i.e. suspended particles) or use liners which are chipped on the ends, deformed or fractured. Inspect the glass wool for cleanliness after it has been inserted.

10.1.2.2 Using a Pasteur pipette flush out the interior of the liner containing the glass wool with Sylon-Ct. Rest the liner horizontally on a small beaker and allow the Sylon-Ct to re-deactivate the interior surfaces and the glass wool. There should be no air bubbles caught in the glass wool. After several minutes flush out the Sylon-Ct with toluene and finally with

methanol. Dry the outer surface of the liner and rest it on the injection port housing until the remaining methanol is boiled off

10.1.2.3 Insert the liner with the newly silanized glass wool plug into the injection port. Verify that the column extends up into the injection port and is perpendicular. Inspect the graphite seal and replace it if the edges are knife-shaped.

10.1.2.4 The septum is always replaced daily. Bake out the column at 300^{O}C for 15 minutes after the vacuum in the analyzer has returned to normal.

10.1.2.5 Performance may enhanced by clipping a small portion of the column at the injection port end. Document this activity in the maintenance record.

10.1.3. Prior to calibration or sample analysis always verify that the analyzer is under sufficient vacuum and that the column has proper carrier gas flow.

10.1.4. Establish the following GC/MS operating conditions:

10.1.4.1 Full Scan Operating Mode

Full Scan Mode – Standard Injection Volume
Mass Range: 35 to 500amu
Scan Time: 1 sec/scan
Transfer Line Temperature: 300^{O}C
Source Temperature: Preset by H.P. at 280^{O}C
Scan start time: 1.0 minutes
Initial Column Temperature and Hold Time: 45^{O}C for 0.5 minutes
Column Temperature Program: 20°C /min to 100°C 25°C/min to 270°C 10° C/min to 310°C
Final Column Temperature Hold: 310^{O}C for 5 minutes
Carrier Gas: Ultra High Purity Grade Helium at 1.3ml/min
Injector Temperature: 275^{O}C
Injector: Grob-type, pulse, splitless
Injection Volume: 1ul
Splitless Valve Time: 0.3 minutes

Full Scan Mode – Large Volume Injection (LVI)
Mass Range: 35 to 500amu
Scan Time: 1 sec/scan
Transfer Line Temperature: 300^{O}C
Source Temperature: Preset by H.P. at 280^{O}C
Scan start time: 1.0 minutes
Initial Column Temperature and Hold Time: 45^{O}C for 0.5 minutes
Column Temperature Program: 20°C /min to 100°C 25°C/min to 270°C 10° C/min to 310°C
Final Column Temperature Hold: 310^{O}C for 5 minutes
Carrier Gas: Ultra High Purity Grade Helium at 1.3ml/min
Injector Temperature: 275^{O}C
Injector: Grob-type, pulse, splitless
Injection Volume: 5ul
Splitless Valve Time: 0.3 minutes

10.1.4.2 SIM Operating Mode

SIM Mode
Mass Range: 35 to 500amu
Scan Time: 1 sec/scan
Transfer Line Temperature: 300^{O}C
Source Temperature: Preset by H.P. at 280^{O}C
Scan start time: 1.5 minutes
Initial Column Temperature and Hold Time: 40^{O}C for 0.5 minutes
Column Temperature Program: 20°C /min to 100°C 25°C/min to 270°C 10° C/min to 310°C
Final Column Temperature Hold: 310^{O}C for 3 minutes
Carrier Gas: Ultra High Purity Grade Helium at 1.3ml/min
Injector Temperature: 275^{O}C
Injector: Grob-type, pulse splitless
Injection Volume: 1ul
Splitless Valve Time: 0.3 minutes

10.1.4.3 Isotope Dilution Selected Ion Monitoring Mode :

SIM Parameters

Group 1
Plot 1 Ion: 74.0

Ions/Dwell in Group	(Mass	Dwell)	(Mass	Dwell)	(Mass	Dwell)
	42.0	50	43. 0	50	68.0	50
	74.0	50	128.0	50	129.0	50
	136.0	50	150.0	50	152.0	50
	93.0	50	66.0	50		
	58.0	50				
	88.0	50				

Group 2
Group Start Time: 6.00
Plot 1 Ion: 152.0

Ions/Dwell in Group	(Mass	Dwell)	(Mass	Dwell)	(Mass	Dwell)
	151.0	50	152.0	50	153.0	50
	154.0	50	162.0	50	164.0	50
	165.0	50	166.0	50		

Group 3
Group Start Time: 7.80
Plot 1 Ion: 188.0

Ions/Dwell in Group	(Mass	Dwell)	(Mass	Dwell)	(Mass	Dwell)
	94.0	50	101.0	50	142.0	50
	178.0	50	179.0	50	188.0	50
	202.0	50	264.0	50	266.0	50
	284.0	50				

Group 4
Group Start Time: 10.50
Plot 1 Ion: 228

Ions/Dwell in Group	(Mass	Dwell)	(Mass	Dwell)	(Mass	Dwell)
	120.0	50	228.0	50	229.0	50
	240.0	50				

Group 5
Group Start Time: 12.00
Plot 1 Ion: 252.0

Ions/Dwell in Group	(Mass	Dwell)	(Mass	Dwell)	(Mass	Dwell)
	138.0	50	139.0	50	252.0	50
	253.0	50	260.0	50	264.0	50
	267.0	50	276.0	50	278.0	50

Table 29: Target Compound - Primary and Monitoring Ions

Compound	1	2	3
1,4-Dioxane-d8	96	64	62
1,4-Dioxane	88	58	57
1,4-Dichlorobenzene-d4	152	150	

10.1.5. The above listed instrument conditions are used for all analytical standards for calibration and for all sample extracts analyzed by this method.

10.1.5.1 The column conditions, scan start time, and splitless valve time for analysis of DFTPP only are as follows are as follows:

Initial Column Temperature and Hold Time: 140^{o}C for 0.5 minutes
Column Temperature Program: 140^{o} to 320^{o}C at 22^{o}C/minute
Final Column Temperature Hold: 320C for 0.5 minutes
Scan Start Time: approx. 5 minutes
Splitless Valve Time: 0.3 minutes
Injection Volume: 2 ul

10.2. Analytical Sequence

10.2.1. Screening: All samples extracts must be screened by GC/FID using the identical chromatographic conditions described in section 9.2. Screening is used to determine the dilution factor of the sample (if any) prior to GC/MS analysis (for additional details see TestAmerica Edison SOP No. ED-GCS-001, *Preparation and Screening of Semivolatile Organic Extracts for GC/MS Analysis*, current revision).

10.2.1.1. Aqueous samples: Prior to extract screening, the extract is diluted to 2ml and split into two 1-ml aliquots:

- One 1-ml aliquot is internal standardized with 20ul of the 2000 ng/ul internal standard solution for full scan analysis and is analyzed by GC/FID for screening.
- The other aliquot is archived for SIM analysis which is internal standardized with 20ul of 50ppm SIM Internal Standard

10.2.1.2. Soil samples: Final volume is 1ml and extracts are internal standardized with 20ul of the 2000 ng/ul internal standard solution and analyzed by GC/FID for screening.

10.2.1.3. After screening analysis, the chromatogram is evaluated for high concentrations of organics. Determine dilutions by comparing the peak heights of compounds in the sample with the internal standard. The ratio of naturally present compounds to internal standards must be <5:1.

10.2.1.4. Dilutions are made based on the screening analysis and prior to GC/MS analysis. Dilutions are made in 1-ml vials using microsyringes. Calculate the dilution factor using the equation below:

$$DF = Ph / 5 \times Is$$

Where:

DF = Dilution Factor
Ph = Sample Peak Height
Is = Internal Standard Peak Height

When DF >1 but <2, combine 500ul of sample extract with 500ul methylene chloride in a 1 ml amber vial, add20 ul internal standard and crimp seal

Use **Table 30** to determine dilution and internal standard amount.

Table 30
Dilution Factor Calculations

DF Value	Volume of Sample (ul)	Volume of Methylene Chloride (ul)	Volume of ISTD (ul)
<1	1,000	None	None
>1, <2	500	500	10
>4, <5	200	800	16
>10, <20	100	900	36
>20	500*	500	10

*Prepare this dilution by serially diluting the >10, <20 dilution

10.2.2. Instrument Performance and Calibration Sequence

10.2.2.1. Once the GC/MS instrument has been setup and maintained as detailed in Section 10.1, the first operations to be performed are the performance checks and calibration standards.

10.2.2.2. Analyze the Instrument Performance Check Standard (DFTPP) as discussed in Section 9.2.1.

10.2.2.3. Initially and as required, analyze the Initial Calibration Range (minimum 5 points, six points for second order regression) as detailed in Sections 7.2.1 and 9.2.4.2. Evaluate the acceptability of the Initial Calibration Range as detailed in Section 9.2.4.2.

10.2.2.4. Immediately after the Initial Calibration Range only, analyze the Initial Calibration Verification (ICV) as detailed in Sections 7.2. and 9.2.4.3. Evaluate the acceptability of the ICV as detailed in Section 9.2.4.3.

10.2.2.5. Every 12 hours, reanalyze and evaluate the Instrument Performance Check Standard (DFTPP) followed by the Continuing Calibration Verification (CCV) and Low Level Continuing Calibration Verification (LLCCV) as detailed in Section 9.2.3, 9.2.4.4 and 9.2.4.5. Evaluate the acceptability of the CCV and LLCCV as detailed in Section 9.2.4.4

10.2.2.6. Client samples and QC samples are analyzed (as detailed in Section 10.2.3) after acceptable Instrument Performance and Calibration Checks and until the 12 hour clock expires. Repeat the sequence as required. The automation of GC/MS runs is accomplished via the “SEQUENCE” macro of the ChemStation.

10.2.3. Sample Analysis Sequence

10.2.3.1. Sample extracts are normally prepared on the same day as analysis. The GC/MS operator will prepare the extracts that will be run on his or her instrument. Volume adjustments to the extracts will be made at the discretion of the supervisor.

10.2.3.2. Prior to the start of sample analysis the GC/MS operator will generate a sequence program containing the list of the sample extracts to be analyzed, the position on the autosampler tray, and the proper acquisition and tune methods that are to be used. This sequence program contains all the necessary information on the samples to be analyzed and how the GC/MS system is to analyze them. The sample extracts are loaded onto the autosampler (ALS) tray. Their position is verified by checking them against the ALS number on the sequence. This batch analysis will be performed automatically over the 12-hour period.

10.2.3.3. The analytical run log is printed as a record of samples analyzed. The analyst will annotate the run log with any required information regarding anomalies or unusual events. The run log must be signed by the analyst and a reviewed and signed by a trained peer or manager

10.3. Data Processing

10.3.1. Prior to processing any standards or samples, target compound lists and sublists must be assembled. Chrom's auto-processing system queries TALS (LIMS) for each sample's processing parameters (including target compounds lists) and downloads the required processing methods from LIMS to analyze data. These lists are required for processing of all data files including calibration files. The data includes compound names, retention time data, quantitation ions, qualitative identification ions, and the assigned internal standard for qualitative and quantitative identification.

10.3.2. Key data is manually entered the first time a compound list is used for data processing. Processing data using a compound list automatically generates response factor data and updates retention information.

10.3.3. The characteristic ions for target compounds, surrogate compounds, and internal standards which can be determined using SW8270D are listed in Table 31.

10.4. Interpretation and Qualitative Identification: Qualitative identification of target compounds is based on retention time and mass spectral comparison with characteristic ions in the target compound list. The reference mass spectrum is taken from a standard of the target compound analyzed by this method. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

10.4.1 Target Analytes: Qualitative identification of target compounds is based on retention time and mass spectral comparison with characteristic ions in the target compound list. The reference mass spectrum is taken from a standard of the target compound analyzed by this method. The characteristic ions are the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

10.4.1.1. Once the GC/MS instrument has been setup and maintained as detailed in Section 10.1, the first operations to be performed are the performance checks and calibration standards.

10.4.1.2. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.

10.4.1.3. The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

10.4.1.4. The most abundant ion in the standard target spectrum that equals 100% MUST also be present in the sample target spectrum.

10.4.1.5. All other ions that are greater than 10% in the standard target spectra should also be present in the sample.

10.4.1.6. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

10.4.1.7. If the compound does not meet all of the criteria listed above, but is deemed a match in the technical judgment of the mass spectral interpretation specialist, the compound will be positively identified and reported with documentation of the identification noted in the raw data record.

10.4.2 Non-Target Analytes: Upon client request a library search to identify non-target Tentatively Identified Compounds (TIC) is performed. The NIST/EPA/NIH mass spectral library is used to identify non-target compounds (not including internal standard and surrogate compounds) of greatest apparent concentration by a forward search of the library. The following guidelines are used by the analyst when making TIC identifications:

10.4.2.1. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

10.4.2.2. The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

10.4.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

10.4.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

10.4.2.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.4.2.6. If, in the technical judgement of the mass spectral interpretation specialist, no tentative identification can be

made, the compound will be reported as 'Unknown'. If the compound can be further classified the analyst may do so (i.e, 'Unknown hydrocarbon', 'Unknown acid' , etc.).

10.5. Data Reporting

10.5.1. Final Report. The Chom data system automatically produces a data report consisting of hardcopy reports corresponding to specific data reporting requirements, which is uploaded to the TALS LIMS System for the report production group.

10.5.1.1. Total Ion Chromatogram. Full length chromatogram depicting the full length of the GC/MS acquisition.

10.5.1.2. Spectra of all detected target compounds. A page for each detected target compound spectra with a standard reference spectrum for comparison.

10.5.1.3. The calculations of the concentrations of each target compound in the sample, reported in units of ppb, ug/kg or ug/l.

10.5.1.4. Data summaries for each method blank indicating which samples were extracted with the indicated blank.

10.5.1.5. A copy of the initial calibration range together with the calibration verification report, and tune report.

10.5.1.6. Quality Control (QC) data report for each batch including surrogate recoveries, internal standard area summaries, LCS, MS/MSD and RPD summaries.

10.6. The low-level calibration standard establishes the reporting limit. All reported data must be at a concentration at or above the low concentration standard. Any quantitative values below the report limit must be qualified as estimated.

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11.0. Calculations/Data Reduction

11.1. Target Compounds: are quantitated using the internal standard method (see the formula in Section 11.3).

11.1.1. Identified target compounds are quantitated using the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of the analyte).

11.1.2. The average response factor (RRF) from the initial calibration is used to calculate the target analyte concentration in client samples using the formula found in Section 11.3. See Section 9.2.4 for discussion of RRF.

11.1.3. Secondary ion quantitation is utilized only when there are sample interferences preventing use of the primary characteristic ion. If secondary ion quantitation is used an average relative response factor (RRF) must be calculated using that secondary ion.

11.2. Non-Target Compounds (Tentatively Identified Compounds): An estimated concentration for non-target (tentatively identified compounds) is calculated using the internal standard method (see formula in Section 11.3). For quantiation, the nearest eluting internal standard free of interferences is used. The procedure used for calculating the concentration of non-target compounds is the same as that used for target compounds (see Section 11.1) with the following revisions:

11.2.1. The total area count of the non-target compound is used for As (instead of the area of a characteristic ion).

11.2.2. The total area count of the chosen internal standard is used as Ais (instead of the area of a characteristic ion).

11.2.3. A RF on 1.0 is assumed.

11.2.4. The resulting concentration is qualified as estimated ('J') indicating the quantitative uncertainties of the reported concentration.

11.3. Internal Standard Calculation:

11.3.1. Aqueous Samples

$$\text{Concentration } (\mu g/L) = \frac{(As)(Cis)(D)}{(Ais)(RF)(Vs)\ (Vi)\ (1000)}$$

Where:

As	=	Area of the characteristic ion for the target analyte in the sample
Cis	=	Concentration of the internal standard (ug/L)
D	=	Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution is performed, D = 1.
Vi	=	Volume of the extract injected (ul)
Ais	=	Area of the characteristic for the associated internal standard
RF	=	Average response factor from the initial calibration.
Vs	=	Volume of sample extracted (ml)

The 1000 in the denominator represents the number of ul in 1 ml.

11.3.2. Solid Samples

$$\text{Concentration (µg/KG)} = \frac{(As)(Cis)(D)(Vt)}{(Ais)(RF)(Ws)\ (Vi)\ (1000)}$$

Where:

As	=	Area of the characteristic ion for the target analyte in the sample
Cis	=	Concentration of the internal standard (ug/L)
D	=	Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution is performed, D = 1.
Vi	=	Volume of the extract injected (ul)
Ais	=	Area of the characteristic for the associated internal standard
RF	=	Average response factor from the initial calibration.
Vt	=	Volume of concentrated extract (ul)
Ws	=	Weight of sample (g)

The 1000 in the denominator represents the number of ul in 1 ml.

11.4. Relative Response Factors

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area characteristic ion for the compound (see Table 31)
Ais = Area characteristic ion of associated internal std (See Table 31)
Cis = Concentration of internal standard
Cx = Concentration of compound in standard

11.5. Percent Relative Standard Deviation (% RSD) : as discussed in Section 9.2.4.4 (Initial calibration):

$$\%\ RSD = \frac{\text{Standard Deviation of RRFs}}{\text{Mean RRF}}$$

11.6. Percent Difference (% D):as discussed in Section 9.2.4.4 (Continuing calibration):

$$\%\ D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

Where: RRFc = RRF from continuing calibration

$\overline{RRF_i}$ = Mean RRF from current initial calibration

11.7. Percent Recovery (% R): Surrogates and Spikes

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

11.8. Dry Weight Correction: All solid samples must be corrected for dry weight using the following formula for dry weight determination.

$$DW = \frac{Gd}{Gw} \times 100$$

Where:

DW	=	Percent % Dry Weight
Gd	=	Dry weight of selected sample aliquot
Gw	=	Wet weight of selected sample aliquot

Multiply the DW value times the wet weight of the sample extracted. NOTE: This calculation can also be performed automatically by the target system provided the DW value is available and entered into the system.

12.0. Method Performance

12.1. Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in Section 19 (Test Methods and Method Validation) of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2. Demonstration of Capabilities

For DOC procedure refer to Section 19 in the most current revision of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM).

12.3. Training Requirements

Refer to TestAmerica SOP No. ED-GEN-022, (*Training*), for the laboratory's training program.

13.0. Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0. Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to TestAmerica Edison SOPs Nos. ED-SPM-007 (*Disposal of Samples and Associated Laboratory Waste, current revision)* and ED-SPM-008 (*Laboratory Waste Disposal Procedures, current revision).* The following waste streams are produced when this method is carried out:

- Auto sampler vials and expired standards: These vials are collected in satellite accumulation within the instrument laboratory. The vials are then placed into a 55 steel open top drum in the waste room. When the drums are full, the drum will be collected by the waste vendor for disposal. This waste is treated for incineration.

  Teris Profile Number: 50016652
  Onyx Profile WIP Number: 282493

- Mixed Solvent Waste: Mixed solvent waste is collected in a small beaker inside the bench top hood. This waste is then transferred into the satellite accumulation container in the Organic Prep. Lab. on a daily basis. This material is transferred into 5 gallon solvent cans as satellite accumulation. These cans are emptied every 24 hours into a steel drum in the waste room. This drum is kept in the walk in hood until it is full. The full drum is then removed from the hood and placed on secondary containment in the waste room.

  Teris Profile Number: 50016624
  Onyx Profile WIP Number: 545240

14.1. Pollution Prevention

14.2.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention 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.

14.2.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.0. References / Cross-References

15.1. United States Environmental Protection Agency, "Method SW8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry", Test Methods for Evaluating Solid Wastes, SW846 Third Edition, Volume 1B: Laboratory Manual, Physical/Chemical Methods, Revision 4, February 2007.

15.2. United States Environmental Protection Agency, "Method SW8000C: Determinative Chromatographic Separations", Test Methods for Evaluating Solid Wastes, SW846, Laboratory Manual, Physical/Chemical Methods, Revision 3, March 2003.

15.3. TestAmerica Edison Document No. ED-QA-LQM, *Laboratory Quality Manual*, current revision.

15.4. TestAmerica Edison SOP No. ED-ORP-002, *SW846 Method 3510C-Extraction of Semi-Volatile Organic Compounds in Water by Separatory Funnel,* current revision.

15.5. TestAmerica Edison SOP No. ED-ORP-043, *SW846 Method 3580A - Waste Dilution Prep for Analysis of BNAs by SW846 Method 8270,* current revision.

15.6. TestAmerica Edison SOP No. ED-ORP-044, *Procedure for the Microwave Extraction of Solids, SW3546, current revision.*

15.7. TestAmerica Edison SOP No. ED-ORP-006, SW846 *Method 3550B- Extraction of Semi-Volatile Organic Compounds in Soil Using Medium--level Extraction Technique,* current revision.

15.8. TestAmerica Document No. CW-E-M-001, Corporate Environmental Health and *Safety Manual,* current revision.

15.9. TestAmerica Corporate Quality SOP No. CA-Q-S-001, *Solvent & Acid Lot Testing & Approval*, current revision.

15.10. TestAmerica Edison SOP No. ED-GEN-023 (*Bulk Solvent Testing and Approval*), current revision.

15.11. TestAmerica Edison SOP No. ED-GCS-001, *Preparation and Screening of Semivolatile Organic Extracts for GC/MS Analysis*, current revision.

15.12. TestAmerica Edison Work Instruction Document No. EDS-WI-012, *Client Complaint/Corrective Action Form,* current revision.

15.13. TestAmerica Edison SOP No. ED-GEN-003, *Standard Operating Procedure for Control of Non-Conformances and Corrective Action,* current revision.

15.14. TestAmerica Edison SOP No. ED-ORP-001, *Extraction of Semivolatile Organic Compounds in Water, EPA Method 625,* current revision.

15.15. TestAmerica Edison SOP No. ED-GEN-022, *Training,* current revision.

15.16. TestAmerica Corporate Quality Memorandum, CA-Q-QM-002, *GC/MS Tuning Policy*, current revision.

16.0. Method Modifications:

N/A

17.0. Attachments

Attachment 1 Poor Performing Analytes

18.0. Revision History

- Revision 7, date 06/08/2018
    - Section 2.3: revised to clarify that RVE/LVI is lab standard procedure.
    - Section 9.1.3: removed statement regarding allowance for up to five analytes to recover outside of lab acceptance limits in LCS/LCSD.
    - Section 9.2.4.3: Replace table 'ICV Poor Performers (50-150% Recovery) with expanded list of 'Poor Performing Analytes' in Attachment 1.
    - Added Section 9.2.4.4.5: CCV Poor Performers
    - Corrected number in section 9.2.4.5
    - Added Attachment 1 – Poor Performing Analytes
- Revision 6, date 01/12/2018:
    - Section 7.2.5 included to specify reagent and standard storage conditions.
    - Revised Section 9.1.3 to clarify requirements for specific LCS/LCSD evaluation criteria regarding the # of out of criteria analytes.
    - Revised Section 9.2.4.3 to add 2,4-Dimethylphenol as a poor performing analyte, increased the range for the poor performers to 50-150 and also expanded the guidelines for flagging the ICV outliers.
- Revision 5, dated 09/29/2017:
    - Revised Section 9.1.1 to clarify requirements for surrogate recovery in method blanks.

- Revision 4, dated 08/21/2017:
    - Updated throughout to add a procedure for the analysis of 1,4-dioxane by isotope dilution selected ion monitoring (SIM)
    - Added tables for isotope dilution SIM standards. Renumbered all tables as necessary.
    - Section 7.2.1: added a list of full scan calibration list options.
    - Table 3: Renamed 'Full Scan Stock Standards'.
    - Section 9.2.1: noted that DFTTP applies only to full scan analysis.
    - Section 9.2.3: updated CCV concentrations
    - Added reference to GC/MS Tuning Policy in Section 15.16.

- Revision 3, dated 01/07/2016:
    - Tables 1 and 2: added SIM as option for 1,4-Dioxane.
    - Section 2.3: removed SW3541 (Soxtherm) as option for soils prep (lab has discontinued use of this method). Also removed SW3541 SOP reference from Section 15.0.
    - Tables 19 and 20: added source and prep instructions for 1,4-Dioxane SIM standard. Updated source and prep instructions for 4,6-Dinitro-2-methylphenol.
    - Table 22: added prep instructions for 1,4-Dioxane and 4,6-Dinitro-2-methylphenol SIM ICV standard.
    - Corrected the information in the 'DFTPP Key Ions and Abundance Criteria' table in Section 9.2.1 to match the info found in SW846 8270C.
    - Section 10.1.4.2: updated "SIM Parameters" to included ion masses/dwell times for 1,4-Dioxane.

- Revision 2, dated 01/28/2015:
    - Extensively reformatted the SOP. Placed tables that had been in rear of document into the body of the text. Renumbered tables as applicable and fixed text references to tables.
    - Section 1.1, Table 1: Revised table to include all current analytes. Also footnoted those compounds which are currently analyzed by SIM.
    - Section 2.3: added options for extraction of solids by SW846 3456 (Microwave Extraction) and by SW3580A (Waste Dilution) and added SOP references. Deleted reference to SOP ED-ORP-005 (SW3550B – Low Level); Updated Section 15 (References).
    - Section 2.5: added text detailing the RVE/LVI options.
    - Section 2.6: added table which includes all analytes routinely analyzed by SIM.
    - Section 6: updated to include newer GC, MS and autosampler models currently in use.
    - Section 6.1.3: added Zebron ZB column as an option.
    - Section 7.2: extensively revised standards information to reflect switch to Restek standards.
    - Table 3:Added Custom Aromatic Amine Surrogate Standard and revised Table 8 to include initial calibration prep instructions for the Aromatic Amine surrogates.
    - Throughout document: removed references to Target and replaced with Chrom.
    - Section 7.2.1: Added reference to section 10.2.1.2 for LVI.
    - Added Section 7.2.1.3.1 and Table 17A both of which discuss use of Aromatic Amine surrogates.
    - Section 7.2.1.2: Added reference to Tables 9,10 and 11 (ICV Preparation)
    - Section 8.0: Added Sample container and minimum sample size (250 ml) for

Reduced volume extraction.
- Sections 9.1.2, 9.1.3, 9.1.4 and 9.2.4: added statement that certain state regulatory programs have defined recovery limits which, where applicable, are used for spike and calibration evaluations.
- Section 9.1.2: Deleted sentence "A minimum of 16 spiked analytes are reported to in client reports (the full list is reported at least once during each 2 year period because we employ full spiking list.
- Section 9.1.4: Added note regarding use of Aromatic Amine Surrogates.
- Section 9.2.2.2: Added reference to ICV Preparation tables in Section 7.2.
- Section 9.2.3: added more specific info as to the concentration of the CCVs for all techniques.
- Section 9.2.4.2.1: Changed to reflect that each analyte should meet minimum RF's, not the average across the calibration. Added LLCCV requirement.
- Section 10.3.1: added explanation of Chrom's interaction with TALS. Removed references to Target.
- Section 9.2.4.2.5.5: Added: (or can be noted in the narrative)
- Section 9.2.4.2.5.6: Revised last sentence to read: "This evaluation can be checked using the Initial Calibration %Drift Report in Chrom."
- Section 9.2.4.3: Removed 65-135% criteria and added "poor performing" analyte list and associated criteria of 60-140%.
- Section 9.2.4.4.3: Added LLCCV criterion for RFs
- Section 9.2.4.4.4: Added LLCCV criterion for %D
- Section 10.1.4: Updated GC/MS operating conditions for full scan, SIM and DFTPP.
- Section 10.1.4.1: added a table detailing operating conditions for LVI option.
- Table 2: Added 2-ethylaniline, 2,4-dimethylaniline, 3,4-dimethylaniline, 2,3-dimethylaniline, 2,4,5-trimethylaniline and 4-chloro-o-toluidine to Working Standards preparation information.
- Table 25: updated to include all current analytis/surrogates/internal standards and associated ions.
- Throughout document: updated LQM section references as appropriate as some have changed with the latest LQM revision.

- Revision 1, dated 11/07/2011

  - Section 1.1, Table 1: Added Pentachloronitrobenzene and associated CAS# to the analyte list.
  - Section 7.2.1: Added Pentachloronitrobenzene standard information.
  - Table 2: Added Pentachloronitrobenzene to Working Standards preparation information.
  - Table 4: Added Pentachloronitrobenzene and associated minimum RF.
  - Table 8: Added Pentachloronitrobenzene and associated ions.

- Revision 0, dated 02/22/2011: NEW

Table 31 Characteristic Ions Of Semi-Volatile Organic Compounds		
Compound	**Primary Ion**	**Secondary Ion(s)**
1,1'-Biphenyl	154	153,76
1,2,4,5-Tetrachlorobenzene	216	214, 179
1,2,4-Trichlorobenzene	180	182, 145
1,2-Dichlorobenzene	146	148, 111
1,2-Diphenylhydrazine	77	105, 182
1,3-Dichlorobenzene	146	148, 111
1,3-Dimethylnaphthalene	156	141, 115
1,4-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene d4 **(ISTD)**	152	150, 115
1,4-Dioxane	88	58, 43
1-Methylnaphthalene	142	141, 115
1-Naphthylamine	143	115, 116
2,2'-oxybis[1-chloropropane]	45	77, 121
2,3,4,6-Tetrachlorophenol	232	131, 230
2,3,7,8-TCDD (screen)	320	322, 324
2,3-Dihydroindene		
2,3-Dimethylaniline	106	129
2,4,5-Trichlorophenol	196	198, 200
2,4,5-Trimethylaniline	102	55, 56
2,4,6-Tribromophenol **(Surrogate)**	330	132, 141
2,4,6-Trichlorophenol	196	198, 200
2,4-Dichlorophenol	162	164, 98
2,4-Xylidine	121	120, 106
2,4-Dimethylphenol	122	107, 121
2,4-Dinitrophenol	184	63, 154
2,4-Dinitrotoluene	165	63, 89
2,6-Dinitrotoluene	165	63, 89
2-Chloronaphthalene	162	127, 164
2-Chlorophenol	128	64, 130
2-Ethylaniline	106	122,104
2-Fluorobiphenyl **(Surrogate)**	172	171
2-Fluorophenol **(Surrogate)**	112	64
2-Methylnaphthalene	142	141
2-Methylphenol	108	107
2-Naphthylamine	143	115, 116
2-Nitroaniline	65	108, 138
2-Nitrophenol	139	109, 65
2-tert-butyl-4-Methylphenol	149	121, 91
2-Toluidine	107	106, 77
3,3'-Dichlorobenzidine	252	254, 126
3,4-Dimethylaniline	106	129, 127
3,5-Di-tert-butyl-4-Hydroxytol	205	220, 145
3-Nitroaniline	138	108, 65
4,6-Dinitro-2-methylphenol	198	51, 105
4-Bromophenyl phenyl ether	248	250, 141
4-chloro-2-methylaniline	106	144, 142

Table 31 Characteristic Ions Of Semi-Volatile Organic Compounds		
Compound	**Primary Ion**	**Secondary Ion(s)**
4-Chloro-3-methylphenol	107	144, 142
4-Chloroaniline	127	129
4-Chloroaniline-d4 **(Surrogate)**	131	133
4-Chlorophenyl phenyl ether	204	206, 141
4-Methylphenol	108	107
4-Nitroaniline	138	108, 65
4-Nitrophenol	139	109, 65
Acenaphthene	154	153, 152
Acenaphthene d10 **(ISTD)**	164	162, 160
Acenaphthylene	152	151, 153
Acetophenone	105	77, 51
Aniline	93	66
Aniline-d5 **(Surrogate**)	98	71,42
Anthracene	178	176, 179
Atrazine	200	173,215
Benzaldehyde	77	105,106
Benzidine	184	92, 185
Benzo(a)anthracene	228	229, 226
Benzo(a)pyrene	252	253, 125
Benzo(b)fluoranthene	252	253, 125
Benzo(g,h,i)perylene	276	138, 277
Benzo(k)fluoranthene	252	253, 125
Benzoic Acid	122	105, 77
Benzyl Alcohol	108	79, 77
Bis(2-chloroethoxy)methane	93	95, 123
Bis(2-chloroethyl)ether	93	63, 95
Bis(2-ethylhexyl)phthalate	149	167, 279
Bisphenol-A	213	228, 119
Butyl benzyl phthalate	149	91, 206
Caprolactam	113	55,56
Carbamazepine	193	236, 135
Carbazole	167	166, 139
Chrysene	228	226, 229
Chrysene d12 **(ISTD)**	240	120, 136
Coumarin	146	118, 63
Dibenz(a,h)anthracene	278	139, 279
Dibenzofuran	168	139
Diethylphthalate	149	177, 150
Dimethylphthalate	163	194, 164
Di-n-butylphthalate	149	150, 104
Di-n-octylphthalate	149	167, 43
Fluoranthene	202	101, 203
Fluorene	166	165, 167
Hexachlorobenzene	284	142, 249
Hexachlorobutadiene	225	223, 227
Hexachlorocyclopentadiene	237	235, 272

Table 31 Characteristic Ions Of Semi-Volatile Organic Compounds		
Compound	**Primary Ion**	**Secondary Ion(s)**
Hexachloroethane	117	201, 199
Indeno(1,2,3-cd)pyrene	276	138, 227
Isophorone	82	95,138
Kepone	272	237, 355
N,N-Dimethylaniline	120	122, 104
Naphthalene	128	129, 127
Naphthalene d8 **(ISTD)**	136	68
n-decane	43	57
Nitrobenzene	77	123, 65
Nitrobenzene-d5 **(Surrogate)**	82	128, 54
N-Nitrosodimethylamine	42	74, 44
N-Nitroso-di-n-propylamine	170	42,101,130
N-Nitrosodiphenylamine	169	168, 167
n-Octadecane	57	43, 85
o-Toluidine-d9 **(Surrogate)**	114	112, 42
Pentachloronitrobenzene	237	214,295
Pentachlorophenol	266	264, 268
Perylene d12 **(ISTD)**	264	260, 265
Phenanthrene	178	179, 176
Phenanthrene d10 **(ISTD)**	188	94, 80
Phenol	94	65, 66
Phenol-d5 **(Surrogate)**	99	42, 71
Phenyl ether	170	77, 115
Pyrene	202	200, 203
Pyridine	79	52, 51
Terphenyl-d14 **(Surrogate)**	244	122, 212

Attachment 1
Poor Performing Compounds

1,2,4,5-Tetrachlorobenzene
1,4-Dioxane
1-Naphthylamine
2,3,4,6-Tetrachlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2-Chloroaniline
2-Naphthylamine
3&4-Methylphenol
3'3-Dichlorobenzidine
4,6-Dinitro-2-methyl- phenol
4-Chloroaniline
4-Nitrophenol
Aniline
Atrazine
Benzaldehyde
Benzidine
Benzoic Acid
Benzyl Alcohol
Biphenyl
Caprolactam
Diphenylamine
Hexachlorocyclopentadiene
Hexachloroethane
n-Decane
n-Nitrosodimethylamine
o,o,o-Triethylphosphorothioate
o-Toluidine
Pentachloronitrobenzene
Pentachlorophenol
Phenol
Pyridine

These analytes are exempt from the ICV and CCV criteria as detailed in this SOP

Title: Per- and Poly-fluorinated Substances (PFAS) in Drinking Water and Non-Potable Water

[Method 537 (Modified)]

Approval Signatures:

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1.0 Scope and Application

This SOP describes the laboratory procedure for the preparation and analysis of per- and polyfluorinated substances using liquid chromatography/tandem mass spectrometry (LC/MS/MS).

Program specific requirements are not included in this SOP. The details of program specific requirements are specified in other laboratory work instructions relevant to the program.

1.1 Analytes, Matrices, and Reporting Limits

This procedure may be used for *drinking water and non-potable water.
***Matrices not certified for under Primary Accreditation Body (NJDEP). These matrices are project specific, therefore method modifications have been included throughout this SOP.**

The list of target compounds that may be determined from this procedure is provided below. Table 1 presents the compounds along with their associated reporting limits (RL).

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA (PFUnA)	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA (PFTA)	376-06-7
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-4
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3
***Perfluorinated sulfonamides (FOSA)**		
*Perfluoro-1-octanesulfonamide	FOSA	754-91-6
***Perfluorinated sulfonamidoacetic acids (FOSAA)**		
*N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
*N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
***Fluorotelomer sulfonates (FTS)**		
*1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*	4:2 FTS	757124-72-4
*1H,1H,2H,2H-perfluorooctane sulfonate *(6:2)*	6:2 FTS	27619-97-2
*1H,1H,2H,2H-perfluorodecane sulfonate *(8:2)*	8:2 FTS	39108-34-4

***Analytes are not certified under Primary Accreditation Body (NJDEP)**
Abbreviations in parenthesis are the abbreviations listed in Method 537, where they differ from the abbreviation used by the laboratory's LIMS.

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

Matrix	Nominal Sample Size	Working Range
*Drinking Water (DW)	250 mL	2.0 ng/L - 400 µg/L
*Non-potable Water (NPW)	250 mL	2.0 ng/L - 400 µg/L

***Laboratory not certified for all analytes by PAB**

2.0 Summary of Method

Water Samples: Water samples are extracted using a solid phase extraction (SPE) cartridge. PFAS are eluted from the cartridge with an ammonium hydroxide/methanol solution.

The final 80:20 methanol:water extracts are analyzed by LC/MS/MS operated in electrospray (ESI) negative ion mode. PFAS are separated from other components on a C18 column with a solvent gradient program using 5mM ammonium acetate (aq) and methanol.

Most analytes employ the isotope dilution technique, where each analyte response is compared to the response of its isotopically labeled version. The isotope dilution analytes (IDA) consists of carbon-13 labeled analogs, oxygen-18 labeled analogs or deuterated analogs of the compounds of interest. This technique allows for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. The isotopically labeled compounds are chemically similar to the compounds of concern and are therefore affected by sample-related interferences to the same extent as the compounds of concern. Compounds that do not have a labeled analog are quantitated by the IDA method using a closely related labeled analog.

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

This SOP is based on the following reference methods:

- US EPA, "Method 537 - Determination of Selected Perfluorinated alkyl acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometery (LC/MS/MS)", Version 1.1, September 2009.
- Method ISO 25101, "Water quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry", First Edition, 2009-03-01, International Organization for Standardization, Technical Committee ISO/TC 147, Water Quality, Subcommittee SC 2, Physical, chemical and biochemical methods.

If the laboratory's SOP is modified from the reference method, a list of method modifications along with technical justification may be found in Section 16. Modifications to this SOP may be applied on a project specific basis to meet project data quality objectives. Project specific modifications are documented in the project record.

3.0 Definitions

Definitions of terms used in this SOP may be found in Appendix A.

4.0 Interferences

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

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

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

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

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

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

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

Both branched and linear isomers of PFOS, PFOA, PFHxS, PFBS, EtFOSAA and MeFOSAA can potentially be found in the environment, based upon scientific literature. If multiple isomers are present for one of these PFAS, these adjacent peaks are either completely resolved or not resolved but with a profound deflection that can be resolved during peak integration. The later of the peaks matches the retention time of the single labeled PFAS peak. In general, earlier peaks are branched isomers and are not a result of peak splitting, and all the chromatographic peaks observed in the standard and/or sample must be integrated and the areas included. When reference standards of technical mixtures of specific PFAS area available, they should be used to ensure that all appropriate peaks are included during peak integration (at this time, only PFOS, PFOA, PFHxS, EtFOSAA and MeFOSAA are available as technical mixtures). Refer to Section 7, Reagents, for the available technical mixtures utilized by this SOP.

In an attempt to reduce PFOS bias, it is required that m/z 449>80 transition be used as the quantitation transition.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

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

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

The HPLC and MS/MS have areas of high voltage. Depending on the type of work involved, the instrument should be turned off or disconnected from its source of power prior to extensive maintenance.

5.2 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- 15 mL polypropylene test tubes with screw caps, Fisherbrand 05-539-5 or equivalent.
- 250-mL HDPE wide-mouth bottles with screw caps (ESS 0250-1901-).
- Analytical balance capable of weighing to the nearest 0.01g, and checked for accuracy each day it is used in accordance with BR-GT-008.
- SPE Vacuum manifold, 24-port, Restek # 26080 or equivalent.
- Polypropylene SPE Reservoir, 150mL, UCT # RFV00150P, or equivalent.
- 1/8” OD Poly siphon lines, 30” long for sample loading.
- SPE Adaptor Caps for 1, 3, and 6 mL SPE Tubes, Polyethylene, Phenomenex # AH0-7191, or equivalent.
- SPE Stopcocks, Polyethylene and Polypropylene, Restek # 26083, or equivalent.
- Stainless steel solvent guide needles, Supelco # 57036, or equivalent.

- Heavy-Wall filter flask, Fisherbrand 4000mL, #FB-300-4000, or equivalent.
- Glass-Col ZipVap 24-port extract concentrator.
- Polypropylene Syringe, 10 mL with luer-lok or luer slip tips, Norm-Ject AB10LL or equivalent.
- Volumetric Syringes, Class "A" (25µL, 50µL 100µL, and 500µL), Hamilton or equivalent.
- Automatic Pipettor, Finnpette, 1-5mL.
- Polypropylene autosampler vials, 300µL, 700µL and 2mL with polyethylene screw caps.
- Vacuum manifold for Solid Phase Extraction (SPE).
- Waters Oasis WAX 500 mg/6mL, (PN 186004647) or equivalent.
- 250mL Poly bottles containing 1.25g of Trizma Pre-Set Crystals, used for batch QC for samples received with Trizma preservation.

6.2 Analytical System

- HPLC: Waters Alliance/2795 with binary pumping capability, chilled sample compartment and heated column oven. All PTFE solvent lines have been replaced with PEEK to reduce the amount of contamination coming from the system.
- MSMS: Waters Quattro Premier tandem mass spectrometer.
- Instrument Software: MassLynx 4.1: Instrument control and data acquisition.
- Data Processing - Chrom Peak Review (Version 2.1 or later), Integrated with TALS (TestAmerica LIMS).
- Isolator Column: Restek Ultra C18 5µm, 10 x 2.1mm, two aligned in series. These are plumbed between the HPLC pump and autosampler valve to resolve system-based PFAS from sample-based PFAS.
- Analytical Column: Restek Raptor C18 5µm, 100 x 2.1mm, Cat No 9304512 or equivalent.

7.0 Reagents and Standards

7.1 Reagents

All reagents must follow traceability guidelines found in SOP BR-QA-002.

- Ammonium acetate Stock Solution, 100mM in 90/10 reagent water/MeOH. Prepare by adding 7.7g of ammonium acetate to 1L of 90/10 water/MeOH. The methanol is added to retard bacterial growth.
- Ammonium acetate Eluent, (5mM in water). Prepare by diluting the 100mM 20-fold in reagent water (Ex. add 25mL of ammonium acetate stock to 475mL of reagent water).
- Ammonium hydroxide (NH_4OH) (0.3% in methanol). Prepare by adding 3 mL of NH_4OH to 1 L of Methanol. Volume prepared may be adjusted based on usage/need.
- Reagent Water, house reverse-osmosis reagent water ("PFAS-Free" via in-house testing).
- Hexane
- Methanol, Ultra-Resi Analyzed. JT Baker or equivalent.
- Sodium hydroxide (NaOH), 0.1N, in water. Prepare by adding 4g of NaOH to 1 L water.

7.2 Standards

Purchase high purity, technical grade solids (96% or greater) or certified solutions from commercial vendors. Standard materials are verified compared to a second source material at the time of initial calibration. The solid stock material is stored at room temperature or as specified by the manufacturer or vendor. If solid material is used for preparing a standard, stock standard solutions are prepared from the solids and are stored at 4 ± 2℃. Stock standard solutions should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of preparation. PFBS, PFHxS, PFOS and many other PFAS are not available in the acid form, but rather as their corresponding salts, such as sodium or potassium. The standards are prepared and corrected for their salt content according to the equation below.

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

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

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

For example, the molecular weight of PFOS is 500.1295 and the molecular weight of NaPFOS is 523.1193. Therefore, the amount of NaPFOS used must be multiplied by a factor of 0.956 to account for the amount of PFOS in the final solution.

Prepare calibration and working standards by diluting a known volume of stock standard in an appropriate solvent to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix B along with the recommended source materials, expiration dates and storage conditions.

A technical (qualitative) grade PFOA standard is analyzed initially, then after initial calibration when a new column is installed or when significant changes are made to the HPLC parameters. This solution is used as a reference for the PFOA isomers (branched and linear) retention times.

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

Extraction Spiking Solutions

PFAS Low Level LCS Solution, 20/200 ng/mL

The PFAS spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 20 ng/mL in methanol (except 4:2FTS, 6:2FTS, 8:2FTS, MeFOSAA and EtFOSAA, which are at 200 ng/mL).

PFAS LCS/Matrix Spike Solution, 400 ng/mL

The PFAS spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 400 ng/mL in methanol.

PFAS High Level LCS Solution, 1000 ng/mL

The PFAS spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 1000 ng/mL in methanol.

PFAS Isotope Dilution Analyte Solution, 1000 ng/mL

The PFAS-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each compound at a concentration of 1000 ng/mL in methanol.

Internal Standard Solution, $^{13}C_2$-PFOA, 5000 ng/mL

The internal standard solution is prepared by diluting the stock 50 µg/mL $^{13}C_2$-PFOA 10-fold in methanol.

See Appendix B for analyte lists and concentrations.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP, sampling requirements may be found in the published reference method. Water samples are collected in pre-cleaned 250 mL HDPE containers. Soil samples are collected in pre-cleaned 8 oz. HDPE containers. Other containers may also be suitable. Samples are chilled to 0-6℃ for shipment to the laboratory.

Listed below are recommended sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
DW	250 mL HDPE Bottle	250 mL	0-6℃ & Trizma (5g/L)	Extraction:14 days from collection Analysis: 28 days from extraction	Method 537
NPW	250 mL HDPE Bottle	250 mL	0-6℃ Trizma (5g/L) (if from a known chlorinated source)	14 days from collection	Method 537
Extract	700 µL Polypropylene (PP) Vial with HDPE Screw cap	NA	0-6℃	28 days from extraction	NJDEP guidance

Extraction holding time is calculated from date of collection. Analytical holding time is determined from date of extraction.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

When samples contain the preservative Trizma, all associated QC must be treated with the same preservative.

Initial Demonstration of Capability (IDOC) and Method Detection Limit (MDL) studies described in Section 12 must be acceptable before analysis of samples may begin.

Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence.

The laboratory prepares the following sample QC for each extraction batch (an extraction batch is limited to a maximum of 20 field samples of the same matrix processed using the same procedure and reagents within the same time period):

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 per extraction batch	See Table 3
Laboratory Control Sample (LCS)	1 per extraction batch (Spiking Level rotates between Low, Medium and High on a batch-by-batch basis)	See Table 3
LCS Duplicate (LCSD)	1 per extraction batch whenever insufficient sample is available for an MS/MSD/DU	See Table 3
*Matrix Spike (MS/MSD)	1 per extraction batch (if sufficient sample is available)	See Table 3
*Sample Duplicate (SD)	DW-1 per extraction batch (if sufficient sample is available); Non-DW matrices- client request if sufficient sample is available	See Table 3
Field Reagent Blank, FRB	Per client set of samples	See Table 3

*An NCM must be applied if there is insufficient volume for a duplicate

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initially, when CCV fails and after major instrument maintenance	See Table 3
Initial Calibration Blank (ICB)	Immediately after ICAL	See Table 3
Second Source Verification (ICV)	Immediately after ICB	See Table 3
Continuing Calibration Verification (CCV)	Beginning, end and after every 10 field samples. Alternate between ICAL Levels 4, 3 and 5 (in order) throughout sequence	See Table 3

Continuing Calibration Verification Low (CCVL)	Immediately following Level 4 CCV at beginning of every non-ICAL analytical sequence	See Table 3
Isotope Dilution Analytes (IDA)	Added to Every injection (Standards, QC and Field Samples) at the same concentration	See Table 3

10.0 Procedure

One-time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo (NCM). The NCM process is described in more detail in SOP BR-QA-0016. The NCM shall be filed in the project file and addressed in the case narrative.

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

10.1 Water Sample Preparation

Visually inspect samples for the presence of settled and/or suspended sediment. If the amount of sediment is so great that the SPE cartridge will clog before the majority of the sample has eluted, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent). Gravity or vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

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

Due to the high surface activity of the analytes, filtration should be regarded as a last resort. All samples will be spiked with IDA and LCS/MS (where appropriate) prior to filtration; this will allow any losses caused by filtration to be monitored and corrected for.

NOTE: for samples which full volume extraction is not possible, care MUST be taken to ensure the actual sample volume that is extracted and documented in the sample worksheet notes.

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

Rotate the LCS concentration with each batch.

-Low Level LCS (50-150 %R), spike with 0.025mL of PFAS Low Level LCS Spike solution. This will result in sample concentrations at the method Reporting Limit.

-Medium Level LCS (70-130 %R), spike with 0.025 mL (25 µL) of the PFAS LCS/Matrix Spike solution (Section 7.2). This will result in a sample concentration of 40 ng/L.

-High level LCS (70-130 %R), spike at 0.05mL (50uL) of the PFAS High Level LCS Spike solution (Section 7.2). This will result in a sample concentration of 200 ng/L.

Spike the MS/MSD (if available volume) with 0.025 mL (25 µL) of the PFAS LCS/Matrix Spike solution (Section 7.2). This will result in a sample concentration of 40 ng/L. NCM if there is insufficient volume to perform the MS/MSD.

Add 0.025 mL (25 µL) of the PFAS-IDA solution (Section 7.2) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

Due to the surface active nature of the PFAS analytes, it is necessary to extract the entire sample as well as the container walls to maximize recovery. It is therefore ideal to receive full 250 mL HDPE bottles for each sample (and MS/MSD if sufficient volume is received) so the entire sample can be processed from that container.

Weigh each container to determine its pre-extraction mass (Gross Weight). Spike each container in the batch with PFAS-IDA solution. Spike the LCS and LCSD (or MS/MSD, if available volume) with PFAS LCS/Matrix solution. Shake to mix the contents. After the extraction has been completed, allow the container to completely dry (uncapped). Replace the cap and reweigh the container to determine the container mass (Tare Weight). The sample volume extracted can be determined by subtracting the Tare Weight from the Gross Weight. These calculations are captured in the PFAS water sample prep module (TALS Method 3535_IVWT and 25101_2009_SPE).

Solid Phase Extraction (SPE) of Aqueous Samples

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

> ***NOTE:*** *The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*
>
> **WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.**

Wash with 5.0 mL of 0.3% NH_4OH/methanol.

Wash with 5.0 mL of 0.1N NaOH/water. Close valve when ~ 1 mL remains on top to keep column wet. After this step, the columns cannot go dry until the completion of loading and rinsing samples.

Appropriately label the SPE cartridges.

Either add a reservoir or a poly siphon line to an adapter which has been firmly inserted into the SPE cartridge. If reservoirs are to be used, carefully pour the spiked samples into their respective reservoirs. If poly siphon lines are employed, place the other end of the line into the corresponding sample container.

Turn on the vacuum and pull the entire sample volume (minimum of 250 mL) through the cartridge at rate of approximately 2 to 5 drops per second (6-15 mL/minute).

Stop the sample elution when ~0.1 mL remains. Add ~5 mL of water to the SPE column and restart the elution to complete the loading process. The added water volume ensures there are no small sample droplets remaining that may be clinging to the wall of the SPE cartridge.

After the sample and water rinse has passed through the cartridge, allow the cartridge to completely dry with vacuum (this could take up to 90 minutes). The cartridge should return to a uniform color. NOTE: Remove and replace each cartridge during the drying process to ensure any water droplets that may be in the flow path are eliminated.

SPE Column Wash of Aqueous Samples with Hexane

Add 5 mL of hexane to each SPE column and allow to soak for five minutes, then elute to waste.

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

Allow the column to dry with vacuum for 5 to 10 minutes. Columns must be dried thoroughly before continuing. The cartridge should return to a uniform color. Wipe any remaining water droplets from the bottom of the stainless steel guide needles using a fresh Kimwipe for each needle prior to proceeding to the next step.

SPE Elution of Aqueous Samples

Place labeled 15 mL polypropylene test tubes as receiving tubes in the SPE manifold. Add 100 µL of reagent water to each test tube as a "keeper".

Rinse the dried sample bottles with 5 mL of 0.3% NH_4OH/methanol and transfer to the corresponding SPE cartridge using a disposable glass pipet (NOTE: the sample container has molded ridges in the neck that can trap up to 0.5mL of the solvent rinsate; make sure to tip the container slightly to draw the rinsate out of the ridges). Allow the solution to soak the cartridge for 5 minutes and then elute into the 15 mL collection tube.

Repeat sample bottle to cartridge elution process with a second 5 mL aliquot of 0.3% NH_4OH/methanol (without the soaking period) The total collection should be approximately 10 mL.

Extract Concentration for Aqueous Samples

Using the ZipVap, concentrate each extract under a gentle stream of nitrogen using a warmed block heater (mild heat ~15-20°C below solvent boiling point; ZipVap set point is 53) until the volume is below 500µL. The concentration should take more than 1 hour to complete. If the concentration proceeds faster than 1 hour, adjust the block temperature and/or nitrogen flow rate to increase the concentration time.

Add methanol dropwise to each extract until the volume is 0.5mL as determined by comparing the volume to a reference vial prepared daily containing 400µL methanol and 100µL water, then vortex to mix well.

Add 5µL of 5000 ng/mL to each 0.5 mL extract and vortex to mix well.

Transfer a portion of the extract to a 300µL polypropylene autosampler vial (6 drops or approximately 60µL is sufficient). Archive the rest of the extracts in a 700µL PP autosampler vial for re-injection and dilution.

Seal the vials with polyethylene screw caps. Note: Teflon lined caps may not be used due to detection of low level concentration of PFAS.

10.2 Other types of Sample Cleanup

Freezing technique to remove lipids

If samples contain lipids, freeze the methanol extract and QC extracts at -20°C for at least 1 hour. Collect the solvent layer.

Cleanup with graphitized carbon which may also be used to remove organic interferences.

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

Shake vigorously and then let sit for 10 minutes.

Centrifuge each sample for 2 minutes at 1000 rpm.

Decant the solvent layer.

Concentrate each sample under a gentle stream of nitrogen to approximately 0.5 mL.

Add 200µL of Millipore water to each sample.

Bring the final volume to 1.0mL with methanol (80% methanol/20% water).

Filter through a 0.45 µm syringe filter as necessary or centrifuge the extracts to obtain a clear supernatant. *Note: Syringe filter should be checked for PFAS background before using.*

WARNING: Application of excessive pressure has caused disc filters to rupture and burst. Exercise discretion when filtering.

10.3 Instrument Operating Conditions

Suggested operating conditions are listed below for the Waters LCMS system:

Recommended Instrument Operating Conditions					
HPLC Conditions (Waters Alliance/2795 HPLC)					
Column (Column temp = 40°C)	Restek Raptor C18 5µm, 2.1 x 100 mm				
Mobile Phase Composition	A = 5 mM Ammonium Acetate (Aq) B = Methanol				
Gradient Program	**Time**	**%A**	**%B**	**Curve**	**Flow Rate mL/min.**
	0.00	90	10	6	0.55
	0.10	45	55	6	0.55
	10.00	5	95	6	0.55
	11.00	5	95	6	0.55
	11.01	90	10	6	0.55
	14.75	90	10	6	0.55
	Maximum pressure limit = 5,000 psi				
Injection Size	20 µL (fixed amount throughout the sequence)				
Run Time	16 minutes (includes autosampler load and inject times)				
Mass Spectrometer Interface Settings (Quattro Premier)					
MS Interface Mode	ESI Negative Ion				
Capillary (kV)	2.3				
Cone (V)	Varies from 12 to 60				
Extractor (V)	3				
Source Temp	125ºC				
Desolvation Temp	350ºC				
Cone Gas (nitrogen) Flow	35 L/hour				
Desolvation Gas (nitrogen) Flow	1000 L/hour				
Low Mass Resolution 1	12.0				
High Mass Resolution 1	15.0				
Ion Energy 1	1.5				
Low Mass Resolution 2	10.0				

High Mass Resolution 2	13.0
Ion Energy 2	3.0
Collision Cell Pressure/Flow	1.33e-002/0.5 mL/min

Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function #
PFBA	Native analyte	212.9 > 168.9	0.10	14	9	1
13C4 PFBA	IDA	216.9 > 171.5	0.02	16	10	1
PFPeA	Native analyte	262.9 > 218.8	0.05	16	9	2
13C5 PFPeA	IDA	267.7 > 222.6	0.02	15	9	2
PFBS	Native analyte	298.9 > 80	0.05	50	30	2
PFBS_2	Native analyte	298.9 > 98.9	0.05	50	25	2
13C3 PFBS	IDA	302 > 79.8	0.02	50	30	2
PFHxA	Native analyte	312.8 > 268.6	0.10	14	10	3
PFHxA_2	Native analyte	312.9 > 118.9	0.10	14	20	3
13C2 PFHxA	IDA	314.8 > 269.6	0.02	14	10	3
4:2FTS	Native analyte	327 > 306.7	0.10	40	20	3
PFPeS	Native analyte	348.9 > 80	0.08	55	30	3
PFPeS_2	Native analyte	348.9 > 98.9	0.08	55	30	3
PFHpA	Native analyte	362.9 > 318.8	0.05	15	11	4
PFHpA_2	Native analyte	362.9 > 168.9	0.05	15	16	4
13C4 PFHpA	IDA	366.9 > 321.8	0.02	13	9	4
PFHxS	Native analyte	398.9 > 80	0.05	50	40	4
PFHxS_2	Native analyte	398.9 > 98.9	0.05	50	32	4
18O2 PFHxS	IDA	402.9 > 83.8	0.02	50	40	4
PFOA	Native analyte	412.9 > 368.8	0.05	17	10	5
PFOA_2	Native analyte	412.9 > 168.9	0.05	17	16	5
13C2 PFOA	Internal Standard	414.9 > 369.8	0.02	17	10	5
13C4 PFOA	IDA	416.9 > 371.8	0.02	17	10	5
6:2FTS	Native analyte	426.6 > 406.6	0.05	40	25	5
M2-6:2FTS	IDA	428.6 > 408.6	0.05	40	24	5
PFHpS	Native analyte	448.9 > 80	0.05	55	40	5
PFHpS_2	Native analyte	448.9 > 98.9	0.05	55	35	5
PFNA	Native analyte	462.9 > 418.7	0.05	17	11	6
PFNA_2	Native analyte	462.9 > 168.9	0.05	17	19	6
13C5 PFNA	IDA	467.8 > 422.8	0.02	17	11	6
PFOS	Native analyte	498.8 > 80	0.08	55	45	6
PFOS_2	Native analyte	498.8 > 98.9	0.08	55	38	6
13C4 PFOS	IDA	502.9 > 80	0.02	55	45	6
PFDA	Native analyte	512.9 > 468.5	0.05	20	11	7

PFDA_2	Native analyte	512.9 > 168.9	0.05	20	19	7
13C2 PFDA	IDA	514.9 > 469.5	0.02	20	12	7
8:2FTS	Native analyte	526.8 > 506.5	0.05	54	28	7
M2-8:2FTS	IDA	528.8 > 508.8	0.02	55	28	7
PFNS	Native analyte	548.9 > 80	0.05	70	50	7
PFNS_2	Native analyte	548.9 > 98.9	0.05	70	40	7
MeFOSAA	Native analyte	569.9 > 418.7	0.05	35	20	7
d3-MeFOSAA	IDA	572.9 > 418.7	0.05	35	20	7
FOSA	Native analyte	497.9 > 78.1	0.05	55	30	8
13C8 FOSA	IDA	505.9 > 78	0.02	55	30	8
PFUdA	Native analyte	562.9 > 518.5	0.05	19	12	8
PFUdA_2	Native analyte	562.9 > 168.9	0.05	19	23	8
13C2 PFUdA	IDA	564.8 > 519.8	0.02	20	12	8
EtFOSAA	Native analyte	583.9 > 418.7	0.10	36	20	8
d5-EtFOSAA	IDA	588.9 > 418.7	0.05	36	20	8
PFDS	Native analyte	598.9 > 80	0.05	75	50	8
PFDS_2	Native analyte	598.9 > 98.9	0.05	75	42	8
PFDoA	Native analyte	612.9 > 568.5	0.05	20	13	9
PFDoA_2	Native analyte	612.9 > 168.9	0.05	20	25	9
13C2 PFDoA	IDA	614.9 > 569.5	0.02	20	13	9
PFTrDA	Native analyte	662.9 > 618.5	0.05	23	14	9
PFTrDA_2	Native analyte	662.9 > 168.9	0.05	23	25	9
PFTeDA	Native analyte	712.9 > 668.5	0.05	20	14	10
PFTeDA_2	Native analyte	712.9 > 168.9	0.05	20	25	10
13C2 PFTeDA	IDA	714.8 > 669.6	0.02	20	14	10

Recommended Instrument Operating Conditions

Retention Times & Quantitation (Quattro Premier)

Native Compounds	Typical Native RT (minutes)	IS analog	Typical IDA RT (minutes)	Quantitation Method
PFBA	2.33	13C4 PFBA	2.33	Isotope Dilution
PFPeA	2.77	13C5 PFPeA	2.77	Isotope Dilution
PFBS	2.83	13C3 PFBS	2.83	Isotope Dilution
4:2FTS	3.15	13C3 PFBS	2.83	Internal Standard
PFHxA	3.21	13C2 PFHxA	3.21	Isotope Dilution
PFPeS	3.24	13C3 PFBS	2.83	Internal Standard
PFHpA	3.73	13C4 PFHpA	3.73	Isotope Dilution
PFHxS	3.77	18O2 PFHxS	3.77	Isotope Dilution
6:2FTS	4.33	M2-6:2FTS	4.33	Isotope Dilution
PFOA	4.39	13C4 PFOA	4.39	Isotope Dilution
PFHpS	4.45	13C4 PFOS	5.16	Internal Standard
PFNA	5.14	13C5 PFNA	5.14	Isotope Dilution
PFOS	5.16	13C4 PFOS	5.16	Isotope Dilution
8:2FTS	5.91	M2-8:2FTS	5.91	Isotope Dilution
PFDA	5.91	13C2 PFDA	5.91	Isotope Dilution
PFNS	5.94	13C4 PFOS	5.16	Internal Standard
MeFOSAA	6.27	d3-MeFOSAA	6.27	Isotope Dilution

EtFOSAA	6.64	d5-EtFOSAA	6.64	Isotope Dilution
PFDS	6.64	13C4 PFOS	5.16	Internal Standard
PFUdA	6.67	13C2 PFUdA	6.67	Isotope Dilution
FOSA	6.97	13C8 FOSA	6.97	Isotope Dilution
PFDoA	7.35	13C2 PFDoA	7.35	Isotope Dilution
PFTrDA	7.96	13C2 PFTeDA	8.51	Internal Standard
PFTeDA	8.51	13C2 PFTeDA	8.51	Isotope Dilution

10.4 Instrument Tuning

Instrument tuning is done initially when the method is first developed and thereafter as needed to maintain the sensitivity and selectivity of the method. Tuning is done by infusing each individual compound (native and IDA) into the MS/MS electrospray probe. The responses for the parent and daughter ions for each compound are observed and optimized for sensitivity and resolution. Mass assignments are reviewed and calibrated if necessary. The mass assignments must be within ± 0.5 amu of the values shown in the table above.

10.5 Instrument Calibration

Perform initial calibration with a minimum of five calibration standards before any sample analysis (initial method set-up), whenever a new column is installed, when significant instrument maintenance has been performed, and when the CCV does not meet acceptance criteria. Significant instrument maintenance includes installing a new column, changing the proportioning valve, or changing components of the MS/MS system. A new calibration is not required following minor maintenance.

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

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

For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated by isotope dilution must be < 35% for the curve to be valid.

For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated by internal standard (i.e. those compounds that do not have corresponding isotopically labeled analogs) must be < 50% for the curve to be valid.

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

Evaluation of Calibration Curves

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

-Response must increase with increasing concentration.

-The absolute value of the intercept of a regression line (linear or non-linear) at zero response must be less than the reporting limit.

-There should be no carryover at or above 1/2 MRL after a high CAL standard.

-The low cal. point must recover to within 50-150%, and all others must recover to within 70-130%.

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

Weighting of Calibration Points

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

10.5.1 Initial Calibration

Prepare the working calibration standards using the recommended formulations given in Appendix B ensuring the lowest calibration standard for each analyte is equal to or below the established RL. Unless otherwise specified on a project basis, use calibration levels 1 to 6 to establish the calibration curve for each analyte.

Prime the instrument by analyzing a minimum of 4 “primer” solutions consisting of 80/20 methanol/water. In general, an HPLC contains components made from PTFE, which enable the pumps to work with many types of organic solvents. Despite efforts to remove as much PTFE as possible, certain components cannot be replaced and contribute PFAS. The longer the system remains idle, the more PFAS that is yielded. Therefore these primers serve to reduce and stabilize the amount of PFAS that are contributed. Immediately following the primers is a Blank, the ICAL sequence (run in ascending order of Level 1 to Level 6), the ICB, the ICV and the first analytical window of extracts (up to 10 field samples). The data is acquired using MassLynx 4.1.

The Chrom Review data system generates calibration data by generating relative response factors (RRFs) based on the response of the target analyte and its corresponding Isotope Dilution Analyte (or Internal Standard) as well as their injection concentrations to ultimately generate Mean Response Factors. All analytes calibrated using IDA must have RSD values < 35%, all analytes calibrated using ISTD must have RSD values < 50%. The IDA compounds are also calibrated using an external RF model using response and concentration. The IDA RSD must be < 50%. Alternatively, a linear regression curve of concentration vs. peak area for each analyte relative to their corresponding IDA/ISTD and their concentrations calculates the correlation coefficient with 1/concentration weighting. The calibration must have a correlation coefficient (r) ≥ 0.995 (r^2 ≥ 0.990). If criteria are not met, correct the problem and repeat calibration. Further analysis may not proceed without valid calibration.

10.5.2 Initial Calibration Blank (ICB)

Immediately following the ICAL, a calibration blank is analyzed that consists of an injection of 80:20 methanol:water blank fortified with IDA solution at 50 ng/mL

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

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

10.5.3 Second Source Calibration Verification (ICV)

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

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

The native analyte must be within or equal to 70-130% for all native analytes quantitated by isotope dilution.

The native analyte must be within or equal to 70-130% for all native analytes quantitated by internal standard (i.e. those compounds that do not have corresponding isotopically labeled analogs).

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

See Table 3 for corrective actions in the event that the ICV does not meet the criteria above.

10.5.4 Continuing Calibration Verification (CCV)

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

The recovery for the CCV standards must be equal to or within 70-130% (50-150% for low level standards) for all natives quantitated by isotope dilution and for all natives quantitated by internal standard. The recovery for the IDA must be within or equal to 70-130% of the true value.

If this is not achieved, the instrument has drifted outside the calibration limits. If the CCV fails again following minor maintenance, the instrument must be recalibrated.

10.5.5 Isotope Dilution Analytes (IDA)

The IDA solution is added to each field and QC sample at the time of extraction, as described in Section 10.1. As described in Section 7, this solution consists of isotopically labeled analogs of the analytes of interest.

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

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

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

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

10.6 Troubleshooting:

Check the following items in case of calibration failures:

Evaluate the failure to determine whether it affects all of the compounds in the ICAL equally. If one ICAL point appears low or high, reprep the curve and rerun, as the error was most likely prep-based. If only a subset of the analytes are affected, check the integration and chromatography to see if there are anomalies; if justifiable, correct the integration so it is consistent with the other ICAL levels.

If there are no peaks for all compounds or no peaks after a specific retention time, ensure that the HPLC pump is pumping properly; it may have shut down due to overpressure or has a leak. If the pump has shut down, confirm it is primed and replace the in-line filter. If the pressure climbs above expected levels, changing the guard column and even analytical column may be necessary. It's best to chase high pressure sources from the pump forward (ie the post-pump in-line filter, isolator column, post-autosampler in-line filter, guard column, analytical column and MSMS inlet. If the pump is still pumping, check the system pressure. If it is lower than expected, check for leaks. Start with all connections, then move on to pump seals, especially if there are wide variations in pressure when pumping the same solvents at the same flow rates. If the pump is still pumping and the pressure is normal, check to make sure the MSMS is still functioning properly. Most issues with the MSMS system will be noted by the MassLynx software.

If there are peaks for all analytes, evaluate the peak shapes by comparing them to the ICAL chromatography. If the peaks have changed (shorter and wider), a new guard column may improve peak shape and bring the system back into compliance. If a new column is necessary, a new ICAL will be needed.

Preventive and routine maintenance is described in the table below

HPLC/MS/MS Preventative Maintenance
As Needed: Change pump seals. Change in-line filters in autosampler (HPLC). Check/replace in-line frit if excessive pressure or poor performance. Replace column if no change following in-line frit change. Replace fused silica tube in ESI interface. Clean lenses. Clean skimmer. Ballast rough pump 30 minutes.
Daily (When in use) Check solvent reservoirs for sufficient level of solvent. Verify that pump is primed, operating pulse free. Check needle wash reservoir for sufficient solvent. Verify capillary heater temperature functioning. Verify vaporizer heater temperature. Verify rough pump oil levels. Verify turbo-pump functioning. Verify nitrogen pressure for auxiliary and sheath gasses.

HPLC/MS/MS Preventative Maintenance
Verify that multiplier is functioning.

10.7 Sample Analysis

Place the field and QC samples in a sequence that begins with the calibration standards followed by the analysis of QC samples, field samples and continuing calibration verification standards (CCVs).

An example analytical sequence that includes initial calibration (ICAL) is provided below.

Injection Number	Lab Description
1	Primer 1
2	Primer 2
3	Primer 3
4	Primer 4
5	Blank
6	Calibration Level 1
7	Calibration Level 2
8	Calibration Level 3
9	Calibration Level 4
10	Calibration Level 5 (ICIS)
11	Calibration Level 6
12	Calibration Level 7
13	Calibration Level 8
14	Calibration Level 9
15	ICB
16	ICV
17	MB
18	LCS
19-28	(up to) 10 Field samples
29	CCV L7
30-39	(up to) 10 Field samples
40	MS
41	MSD
42	CCV L3
43	MB
44	LCS
45-54	(up to) 10 Field samples
55	CCV L5
56-65	(up to) 10 Field samples
66	MS
67	MSD
68	CCV L7

An example analytical sequence without ICAL:

Injection Number	Lab Description
1	Primer 1
2	Primer 2
3	Primer 3
4	Primer 4
5	CCV L5 (20 ng/mL)
6	CCV L1 (1.0 ng/mL)
7	CCV L4 (10 ng/mL)
8	MB
9	LCS
10-19	(up to) 10 Field samples
20	CCV L7
21-30	(up to) 10 Field samples
31	MS
32	MSD
33	CCV L3
34	MB
35	LCS
36-45	(up to) 10 Field samples
46	CCV L5
47-56	(up to) 10 Field samples
57	MS
58	MSD
59	CCV L7

Enter the sample ID's into the data acquisition program in the order the samples were placed in the autosampler and initiate the analytical sequence.

11.0 Calculations / Data Reduction

11.1 Qualitative Identification

The data processing system identifies the target analytes by comparing the retention time of the peaks to the retention times of the initial calibration standards. The retention times of PFAS with labeled standards must be the same as that of the labeled IDA's to within 0.05 min. For PFAS with no labeled standards, the RT must be within ± 0.3 minutes of the ICV and CCV standards. *Note: The IS RT and native RT may be offset by 0.02 to 0.04 minutes.*

11.2 Quantitative Identification

The ICAL established in Section 10.7 is used to calculate concentrations for the extracts. The data processing system determines on-column concentration. Final results are calculated by the laboratory's LIMS information system (TALS).

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

Check the results of samples analyzed immediately after high concentration samples (those with results above calibration range) for signs of carry-over. Reanalyze all samples suspected of carry -over.

11.3 Calculations

See Appendix C.

11.4 Data Review

Refer to laboratory SOP BR-QA-019 for additional instruction on the requirements for data review. The following sections summarize the general procedure as described in the data review SOP.

11.4.1 Primary Review

Review the chromatography and quantitation in the data processing system to confirm quantitative and qualitative identification of each target analyte. Perform and document manual integrations only if needed per the instructions in corporate policy CA-Q-S-002, Acceptable Manual Integration Practices.

Upload the data files to TALS and process the batch. Enter job information into the batch editor and add the standards and reagent additions to the worksheet, if necessary. Review the results against acceptance criteria. If acceptance criteria are not met, perform corrective action or make arrangements for corrective action with another analyst.

Set results to primary, secondary, acceptable or rejected. Set results to be reported to a status of primary and secondary. Set results that meet criteria but will not be reported to acceptable. Set results that do not meet criteria to rejected, to prevent inadvertent reporting of data.

Verify that all appropriate QC were performed and acceptable. If insufficient volume is received (MS, MSD, FRB, etc…) document in an NCM. Record all instances where acceptance criteria are not met in a nonconformance memo (NCM).

Verify that all project requirements or program specific requirements were followed. If not, immediately notify the project manager to determine an appropriate course of action. Record decisions made in the data review checklist.

Set the batch to 1st level review. Complete the data review checklist and make arrangements for secondary review by a peer analyst.

11.4.2 Secondary Data Review (Performed by Peer Analyst)

Record review using the data review checklist.

Verify that all project requirements or program specific requirements were followed. If not, consult with the primary analyst to determine cause. Any decisions made should be recorded on the data review checklist and retained as part of the analytical record.

Review the TALS batch editor to verify ancillary information for the work performed is filled in.

Verify that that the procedures in this SOP were followed. If discrepancy between the SOP and the analytical record is found, consult with the primary analyst to determine the source of the discrepancy. Resolve the discrepancy and verify any modifications to the SOP are properly documented and were approved by laboratory management. Record all SOP deviations in an NCM.

Spot-check ~15% of samples in the batch to verify quantitative and qualitative identification.

If manual integrations were performed:

- Review each manual integration to verify that the integration is consistent and compliant with the requirements specified in SOP CA-Q-S-002.

- Check to ensure an appropriate technical reason code is provided for each manual integration. Acceptable technical reason codes are provided in SOP CA-Q-S-002.

- If an error is suspected, the reviewer must consult with the analyst that performed the integration to determine if a correction is necessary. Input from the Technical Manager (TM), Department Manager (DM), or QA Manager (QAM) may be sought as necessary. **The reviewer may not reintegrate except in those circumstances approved by laboratory management**, such as when the analyst that performed the integration is on vacation. If re-integration is performed by the reviewer, the reviewer is now considered the “primary analyst” and the re-integration is subject to the same review and documentation requirements as the original integration.

Verify acceptance criteria were met. If not, verify that corrective actions were performed and the nonconformance was documented with an NCM. Review the NCM to verify the form is filled out and the requisite information has been included in the internal comments tab. If corrective action was not performed and the failure not documented, consult with the primary analyst to determine cause. Consult with the primary analyst and department management to determine what actions should be taken, then follow-through with the decision made.

Run the QC checker and fix any problems found. Run and review the deliverable for gross error such as missing data. Fix any problems found.

When review is complete set the method chain to lab complete. Complete the data review checklist and forward associated paperwork to report/project management.

11.4.3 Data Reporting & Record Retention

The specifications for data reporting are set by the project manager and are performed by TALS using the formatter selected by the PM. The type of deliverable is also set by the PM based on various deliverable options in the TALS system. The formatters and deliverables are programmed into TALS by corporate IT staff and cannot be modified locally.

The following sections describe the default reporting scheme set for this method in TALS:

Data is retained, managed and archived as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ)

See SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP for employee training.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts must also have documentation of initial demonstration of initial proficiency (IDOC) for the test method prior to independent work. On-going proficiency (ODOC) must be demonstrated annually thereafter.

Initial Demonstration of Capability:
Analyze four mid level LCS replicates. These replicates must include all preservatives used in sample collection. The RSD between replicates must be within +/-20%. The average recovery of the replicates must be within +/-30% of the true value. Peak asymmetry factors must be calculated from the first two peaks in the CCV using the formula in Appendix C and must meet in the range 0.8-1.5. If any of these criteria are not met, the issue must be investigated, and the IDOC must be re-prepared and re-analyzed.

13.0 Pollution Control

It is Test America's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed,

preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when this method is carried out.

- Vials containing sample extracts: Satellite Container: 30 gallon poly barrel located under GC-Semi prep hood.
- Solvent Waste: Satellite Container: 5 gallon poly carboy located under LCMSMS.

15.0 References / Cross References

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- U.S. EPA, "Residue Chemistry Test Guidelines, OPPTS 860.1340, Residue Analytical Method", EPA 712-C-95-174, August 1995.
- STL Denver White Paper DEN-W-LC-002, "Method Validation Study for Analysis of Ammonium Perfluorooctanoate in Soil Matrices by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS/MS)", Mark Dymerski, September 5, 2003.
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- Method ISO 25101, "Water quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry", First Edition, 2009-03-01, International Organization for Standardization, Technical Committee ISO/TC 147, Water Quality, Subcommittee SC 2, Physical, chemical and biochemical methods.
- US EPA, "Method 537 - Determination of Selected Perfluorinated alkyl acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometery (LC/MS/MS)", Version 1.1, September 2009, J.A. Shoemaker, P.E. Grimmett, B.K. Boutin, EPA Document #: EPA/600/R-08/092.
- Laboratory SOP BR-QA-005 *Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).*
- Laboratory SOP BR-QA-011 *Employee Training*
- Laboratory SOP BR-EH-001 *Hazardous Waste*

- Laboratory SOP BR-QA-014 *Laboratory Records*
- Laboratory SOP BR-QA-006 *Procedures & Documentation Requirements for Manual Integration*
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

Modification Number	Method Reference	Modification & Technical Justification
1	Section 7.2	Method 25101 specifies that the values reported for PFOA and PFOS shall be the linear isomer only. In keeping with the dictates of USEPA 537 and other US conventions, the laboratory reports both the branched (when present) and linear isomers as a single value for these compounds.
2	Section 10.1	A different SPE cartridge, Waters OASIS WAX, is used for the extraction process. As a result, solvents and elution procedures are different.
3	Section 10.1	The samples are fortified with a greater number of labeled analytes (most analytes have labeled versions) prior to extraction.
4	Section 10.5	The HPLC Column, Eluents and gradient conditions have changed.
5	Section 10.5	For non-drinking water matrices, the analyte list has expanded. The number of labeled analytes has also expanded to improve quantitation.
6	Table 1	The reporting limits have changed to a consistent value.
7	Appendix B	Calibration levels have been changed so all levels have the same analyte concentration.

17.0 Attachments

- Table 1: Routine Compound List and LOQ
- Table 2: Primary Materials Used
- Table 3: QC Summary & Recommended Corrective Action
- Table 4: Control Limits
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History (all revision history must be retained in this SOP)

Revision 3.0

- Updated cover page dates and signatories
- Section 10.1: added note for handling incomplete volume extraction process
- Section 18: added previous revision history back into SOP
- Throughout: updated QC criteria from EPA 537 r1.1 that was missed in previous revision
- Throughout: removed solid extraction/analysis verbiage missed in previous revision.
- Throughout: updated calibration to include criteria from EPA 537 r1.1 and to include the 9 calibration points currently in use.
- Throughout: minor formatting updates

Rev 2.1:

- Updated cover page dates and signatories
- Section 8: added preservation requirements for DW samples.
- Throughout: updated QC criteria to match EPA537 rev1.1
- Throughout: removed references to solid and tissue extraction/analysis.

Rev 2.0

- Updated cover page and signatories
- Section 8: added preservation requirements for DW samples.
- Throughout: included verbiage that Non-drinking water matrices are not certified under PAB.
- Throughout: separated DW and non-DW limits and QC requirements.
- Throughout: minor formatting and typographical corrections.
- Tables 3 & 4: updated limit to meet EPA 537 criteria.
- Appendix A: updated terms and definitions from body of SOP

Rev 1.0

- Extended analyte list to 21 native compounds and 18 IDAs.
- Altered concentration step in extract preparation by employing a reagent water keeper instead of concentrating to dryness.
- Incorporated use of internal standard for IDA recovery calculation.

Revision 0.0: 05/19/2017

- New SOP based on USEPA method 537

Previous revisions are retained by the QA department.

Table 1: Routine Compound List & Limit of Quantitation (LOQ)

Compound Name	Abbreviation	CAS #	Water (ng/L)
Perfluoroalkylcarboxylic acids (PFCAs)			
Perfluoro-n-butanoic acid	PFBA	375-22-4	2.0
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	2.0
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	2.0
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	2.0
Perfluoro-n-octanoic acid	PFOA	335-67-1	2.0
Perfluoro-n-nonanoic acid	PFNA	375-95-1	2.0
Perfluoro-n-decanoic acid	PFDA	335-76-2	2.0
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8	2.0
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	2.0
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	2.0
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	2.0
Perfluorinated sulfonic acids (PFSAs)			
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5	2.0
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-4	
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4	2.0
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8	2.0
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1	2.0
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1	
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3	2.0
Perfluorinated sulfonamides (FOSA)			
Perfluoro-1-octanesulfonamide	FOSA	754-91-6	2.0
Perfluorinated sulfonamidoacetic acids (FOSAA)			
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	20.0
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	20.0
Fluorotelomer sulfonates (FTS)			
1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*	4:2 FTS	757124-72-4	20.0
1H,1H,2H,2H-perfluorooctane sulfonate *(6:2)*	6:2 FTS	27619-97-2	20.0
1H,1H,2H,2H-perfluorodecane sulfonate *(8:2)*	8:2 FTS	39108-34-4	20.0

NOTE: The LOQ values for waters and soils may vary. The Water LOQ is based on a 250mL nominal sample volume. The Soil LOQs represent those that can be achieved in a blank matrix with zero percent moisture. Actual LOQ values will vary with sample matrix, co-extracted interferences and percent moisture in sample. The Soil LOQ is applicable to 5 g sample extraction weight.

Table 2: Primary Materials Used

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

[1] Always add acid to water to prevent violent reactions.
[2] Exposure limit refers to the OSHA regulatory exposure limit.

Table 3: QC Summary, Acceptance Criteria and Recommended Corrective Action (EPA537)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
9-Point Calibration (5 point minimum for CF and Linear Regression) (ICAL)	Before sample analysis, when CCVs indicate calibration is no longer valid; after major instrument maintenance	CF = RSD $\leq$ 35% (compounds calibrated via IDA) CF = RSD $\leq$ 50% (compounds calibrated using "near-IDA" compounds) CF = RSD $\leq$ 50% (IDA standards using ISTD) Each cal pt. = +/-30%Rec. (+/-50%Rec for cal low pt.) Linear Regression: $r^2 \geq 0.990$	Correct problem and repeat initial calibration.
IDA Response	Every injection contains the IDA analytes	DW: 70-130% recovery Non-DW matrices: Standards: 50-150% recovery Field samples: 50-150% recovery (reportable if >10x S/N ratio and >10% ICAL RF)	Standard failures must be investigated to determine the cause of the failure. Recalibration may be required. Samples with recoveries outside acceptance limits must be evaluated for data usability. Re-extraction may be necessary if data quality has been adversely affected.
IS Response	Every injection contains the IS analyte	ICAL Standards: Area of individual points must not deviate by more than 50% of ICAL mean area response Samples following ICAL: 50-150% of ICAL mean response Ongoing CCV: 70-130% (50-150% for non-DW) of ICAL mean response Post-CCV Samples: Area must be within 50-150% of most recent CCV	Standard failures must be investigated to determine the cause of the failure. Recalibration may be required. Sample failures may be matrix related and should be evaluated to determine if the data quality has been adversely affected.
Initial Calibration Blank (ICB)	Immediately following the ICAL	DW: < 1/3 RL for all target analytes Non-DW: < RL for all target analytes	Determine source of interference/contamination, eliminate it and recalibrate.
Second Source Standard Verification (ICV)	Prior to the analysis of samples. Generally immediately after the ICB.	+/-30 for analytes, IS, and SUR.	Correct problem and verify second source standard. If that fails, repeat calibration.
Continuing Calibration Verification (CCV)	Beginning of each analytical sequence, every ten field samples and at the end of each analytical sequence. Alternate between levels 3, 4 and 5.	+/-30%	Rerun any samples analyzed before and after the failing CCV. Take corrective action; if subsequent CCV analyses fail, recalibrate instrument.
Continuing Calibration Verification-Low (CCVL)	Beginning of each analytical sequence that is not preceded by an ICAL to show LOQ is still valid.	Non-DW: CF = 50-150% (IDA targets) CF = 50-150% (ISTD targets) IDA 50-150%	Stop sample acquisition. Take corrective action; if subsequent CCV analyses fail, recalibrate instrument.
Method Blank	One per extraction batch of 20 or fewer samples	DW: < 1/3 RL for all target analytes Non-DW: < RL for all target analytes	Reprocess MB and associated samples if any target analyte in the MB is at or above the RL, greater than 1/10 the amount detected in any sample or 1/10 the regulatory limit, whichever is greater. If the target is not greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with appropriate qualifiers. If insufficient sample is available to reprocess, report data with appropriate qualifiers.
Laboratory Control Sample	One per extraction batch of 20 or fewer samples (rotate between Low, Med, High)	%R within control limits. See Table 4	Reprep and reanalyze samples for failed analytes. If reanalysis is not possible due to insufficient sample volume, report data with appropriate data qualifiers.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Matrix Spike / Matrix Spike Duplicate	One set per extraction batch when sufficient sample volume is provided	%R within control limits. See Table 4	Evaluate to determine if there is a matrix effect or analytical error. If analytical error, reanalyze or reprocess as appropriate.
Sample Duplicate	One per extraction batch of 20 or fewer samples	RPD within control limits. See Table 4	Evaluate data to determine source for error. If analytical error is suspected, reanalyze or reprocess as appropriate.
Field Reagent Blank	Per client sample set	DW: < 1/3 RL for all target analytes Non-DW: < RL for all target analytes	Analysis only required if samples contain target analytes at or above the RL. If analytes are present in the FRB at >1/3 RL, all samples must be recollected and re-analyzed.

Table 4: LCS and MS/MSD Control Limits*

Analyte	Water (Low Level) %R	Water (Med-High Level) %R	RPD
Perfluorobutanoic acid (PFBA)	50-150	70-130	20
Perfluoropentanoic acid (PFPeA)	50-150	70-130	20
Perfluorobutanesulfonic acid (PFBS)	50-150	70-130	20
Perfluorohexanoic acid (PFHxA)	50-150	70-130	20
Perfluoropentanesulfonic acid (PFPeS)	50-150	70-130	20
Perfluoroheptanoic acid (PFHpA)	50-150	70-130	20
Perfluorohexanesulfonic acid (PFHxS)	50-150	70-130	20
Perfluorooctanoic acid (PFOA)	50-150	70-130	20
Perfluoroheptanesulfonic acid (PFHpS)	50-150	70-130	20
Perfluorononanoic acid (PFNA)	50-150	70-130	20
Perfluorooctanesulfonic acid (PFOS)	50-150	70-130	20
Perfluorodecanoic acid (PFDA)	50-150	70-130	20
Perfluorononanesulfonic acid (PFNS)	50-150	70-130	20
Perfluoroundecanoic acid (PFUdA)	50-150	70-130	20
Perfluorodecanesulfonic acid (PFDS)	50-150	70-130	20
Perfluorooctanesulfonamide (FOSA)	50-150	70-130	20
Perfluorododecanoic acid (PFDoA)	50-150	70-130	20
Perfluorotridecanoic acid (PFTrDA)	50-150	70-130	20
Perfluorotetradecanoic acid (PFTeDA)	50-150	70-130	20
1H,1H,2H,2H Perfluorohexanesulfonate (4:2FTS)	50-150	70-130	20
1H,1H,2H,2H Perfluorooctanesulfonate (6:2FTS)	50-150	70-130	20
1H,1H,2H,2H Perfluorodecanesulfonate (8:2FTS)	50-150	70-130	20
N-Methyl Perfluorooctane sulfonamidoacetic acid (N-MeFOSAA)	50-150	70-130	20
N-Ethyl Perfluorooctane sulfonamidoacetic acid (N-EtFOSAA)	50-150	70-130	20

**The limits in this table are those in effect as of the published date of this SOP. The %R limits are specified by EPA 537r1.1 in sections 9.33, 9.36, and 9.37. The RPD the lab uses is more strict than those referenced in EPA 537 r1.1. If the lab makes changes to any of these limits, the updated limits will be no less strict than those specified in EPA537.*

Appendix A: Terms and Definitions

PFCAs: Perfluorocarboxylic acids
PFSAs: Perfluorinated sulfonates
FOSA: Perfluorinated sulfonamide
PFOA: Perfluorooctanoic acid
APFO: Ammonium perfluorooctanoate
PFOS: Perfluorooctane sulfonate
MPFOA: Perfluoro-n-[1,2,3,4-13C4]octanoic acid. Carbon-13 labeled PFOA
MPFOS: Perfluoro-1-[1,2,3,4-13C4]octanesulfonate. Carbon-13 labeled PFOS
PTFE: Polytetrafluoroethylene (e.g., Teflon®)
SPE: Solid phase extraction**.**
PP: Polypropylene
PE: Polyethylene
HDPE: High density polyethylene
IDA: Isotope dilution analytes
Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.
Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.
Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).
Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.
Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.
Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.
Calibration Standard: A substance or reference used to calibrate an instrument.
Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.
Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.
Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)
Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.
Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.
Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.
Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.
Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.
Matrix Spike Duplicate (MSD): a second replicate matrix spike
Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).
Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are only produced in this range and qualified with the proper data reporting flag when a project requires this type of data reporting.
Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.
Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.
Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.
Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.
Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.
Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.
Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

Appendix B: Standard Preparation Tables

The standard formulations contained in this appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in methanol using Class A volumetric glassware and Hamilton syringes and assign an expiration date of 1 year from date of preparation unless the parent standard expires sooner; then use the earlier date. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance. For stock standards solutions made from neat material, assign an expiration date of 2 years from the date of formulation.

Stock Standard Solutions

PFAS LCS/Matrix Spike Solution 1000 ng/mL

Parent Standard	Vendor	Component	Stock Standard Conc (µg/mL)	Volume Added (µL)	Final Volume (mL)	Final Conc (ng/mL)
PFBA	Wellington Laboratories Code: PFBA	Perfluorobutanoic acid	50	200	10	1000
PFPeA	Wellington Laboratories Code: PFPeA	Perfluoropentanoic acid	50	200		1000
PFBS	Wellington Laboratories Code: L-PFBS	Perfluorobutanesulfonic acid	44.2	200		884
PFHxA	Wellington Laboratories Code: PFHxA	Perfluorohexanoic acid	50	200		1000
PFPeS	Wellington Laboratories Code: L-PFPeS	Perfluoropentanesulfonic acid	46.9	200		938
PFHpA	Wellington Laboratories Code: PFHpA	Perfluoroheptanoic acid	50	200		1000
PFHxSK	Wellington Laboratories Code: br-PFHxSK	Perfluorohexanesulfonic acid	45.5	200		910
PFOA	Wellington Laboratories Code: PFOA	Perfluorooctanoic acid	50	200		1000
PFHpS	Wellington Laboratories Code: L-PFHpS	Perfluoroheptanesulfonic acid	47.6	200		952
PFNA	Wellington Laboratories Code: PFNA	Perfluorononanoic acid	50	200		1000
PFOS	Wellington Laboratories Code: br-PFOSK	Perfluorooctanesulfonic acid	46.4	200		928
PFDA	Wellington Laboratories Code: PFDA	Perfluorodecanoic acid	50	200		1000
PFNS	Wellington Laboratories Code: L-PFNS	Perfluorononanesulfonic acid	48.0	200		960
PFUdA	Wellington Laboratories Code: PFUdA	Perfluoroundecanoic acid	50	200		1000
PFDS	Wellington Laboratories Code: L-PFDS	Perfluorodecanesulfonic acid	48.2	200		964
FOSA	Wellington Laboratories Code: FOSA-I	Perfluorooctane sulfonamide	50	200		1000
PFDoA	Wellington Laboratories Code: PFDoA	Perfluorododecanoic acid	50	200		1000
PFTrDA	Wellington Laboratories Code: PFTrDA	Perfluorotridecanoic acid	50	200		1000
PFTeDA	Wellington Laboratories Code: PFTeDA	Perfluorotetradecanoic acid	50	200		1000
4:2FTS	Wellington Laboratories Code: 4:2FTS	1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	46.7	200		934
6:2FTS	Wellington Laboratories Code: 6:2FTS	1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	47.4	200		948
8:2FTS	Wellington Laboratories Code: 8:2FTS	1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	47.9	200		958
NMeFOSAA	Wellington Laboratories Code: br-NMeFOSAA	N-methyl Perfluorooctane sulfonamidoacetic acid	50	200		1000
NEtFOSAA	Wellington Laboratories Code: br-NEtFOSAA	N-ethyl Perfluorooctane sulfonamidoacetic acid	50	200		1000

Solvent: Methanol

PFAS-IDA Solution (Surrogate) 1000 ng/mL

Parent Standard	Vendor	Component	Stock Standard Conc (µg/mL)	Volume Added (µL)	Final Volume (mL)	Final Conc (ng/mL)
13C4 PFBA	Wellington Laboratories Code: MPFBA	$^{13}C_4$-Perfluorobutanoic acid	50	200	10	1000
13C5-PFPeA	Wellington Laboratories Code: MPFPeA	$^{13}C_5$-Perfluoropentanoic acid	50	200		1000
13C3-PFBS	Wellington Laboratories Code: M3PFBS	$^{13}C_3$-Perfluorobutanesulfonic acid	46.5	200		930
13C2 PFHxA	Wellington Laboratories Code: MPFHxA	$^{13}C_2$-Perfluorohexanoic acid	50	200		1000
13C4 PFHpA	Wellington Laboratories Code: M4PFHpA	$^{13}C_4$-Perfluoroheptanoic acid	50	200		1000
18O2 PFHxS	Wellington Laboratories Code: MPFHxS	$^{18}O_2$-Perfluorohexanesulfonic acid	47.3	200		946
13C4 PFOA	Wellington Laboratories Code: MPFOA	$^{13}C_4$-Perfluorooctanoic acid	50.0	200		1000
13C5 PFNA	Wellington Laboratories Code: MPFNA	$^{13}C_5$-Perfluorononanoic acid	50.0	200		1000
13C4 PFOS	Wellington Laboratories Code: MPFOS	$^{13}C_4$-Perfluorooctanesulfonic acid	47.8	200		956
13C2 PFDA	Wellington Laboratories Code: MPFDA	$^{13}C_2$-Perfluorodecanoic acid	50.0	200		1000
13C8 FOSA	Wellington Laboratories Code: M8FOSA-I	$^{13}C_8$-Perfluorooctane sulfonamide	50.0	200		1000
13C2 PFUdA	Wellington Laboratories Code: MPFUdA	$^{13}C_2$-Perfluoroundecanoic acid	50.0	200		1000
13C2 PFDoA	Wellington Laboratories Code: MPFDoA	$^{13}C_2$-Perfluorododecanoic acid	50.0	200		1000
13C2 PFTeDA	Wellington Laboratories Code: MPFTeDA	$^{13}C_2$-Perfluorotetradecanoic acid	50.0	200		1000
M2-6:2FTS	Wellington Laboratories Code: M2-6:FTS	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octane sulfonate (6:2)	47.5	200		950
M2-8:2FTS	Wellington Laboratories Code: M2-8:FTS	Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate (8:2)	47.9	200		958
d3-NMeFOSAA	Wellington Laboratories Code: d3-M-MeFOSAA	N-methyl-d_3-perfluoro-1-octane sulfonamidoacetic acid	50.0	200		1000
d5-NEtFOSAA	Wellington Laboratories Code: d5-M-EtFOSAA	N-ethyl-d_5-perfluoro-1-octane sulfonamidoacetic acid	50.0	200		1000

Solvent: Methanol

PFAS Internal Standard Solution 5000 ng/mL

Parent Standard	Vendor	Component	Stock Standard Conc (µg/mL)	Volume Added (µL)	Final Volume (mL)	Final Conc (ng/mL)
13C2 PFOA	Wellington Laboratories Code: M2PFOA	$^{13}C_2$-Perfluorooctanoic acid	50.0	400	4	5000

Solvent: Methanol

PFAS-IDA-IS Routine Calibration Standards Level 1-Level 9

ICAL Level	Vol of PFAS LCS/Matrix Spike (µL)	Nominal Conc of PFAS (ng/mL)	Vol of PFAS-IDA Solution (µL)	Conc of IDA (ng/mL)	Vol of PFAS-IS Solution (µL)	Conc of IS (ng/mL)	Vol of Water (µL)	Vol of 80/20 MeOH/H2O (µL)	Final Vol (mL)
1	4	1.0	200	50	40	50	51	3745	4.0
2	2	2.0	50	50	10	50	13	935	1.0
3	16	5.0	160	50	32	50	44	2980	3.2
4	20	10.0	100	50	20	50	30	1850	2.0
5	72	20.0	180	50	36	50	63	3285	3.6

6	30	30.0	50	50	10	50	20	900	1.0
7	160	50.0	160	50	32	50	80	2800	3.2
8	120	100	60	50	12	50	45	975	1.2
9	240	200	60	50	12	50	75	825	1.2

The solvent is 80/20 Methanol/Water.

Appendix C: Equations

Initial Calibration Curve Evaluation:

The linear curve uses the following function:

Equation 1 $$y = bx + c$$

Where:

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

x = concentration
b = slope
c = intercept

The quadratic curve uses the following function:

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

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

The external standard method uses the following equation:

Equation 3 $$Response\ Factor = \frac{Peak\ \ Area}{Concentration\ of\ \ Solution\ (ng/mL)}$$

Equation 4 $$\text{Concentration, ng/mL} = \frac{y - c}{b}$$

Equation 5 $$\text{Concentration, ng/mL} = \frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$$

Where:

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

x = concentration
a = curvature
b = slope
c = intercept

Water Sample Result Calculation:

Equation 6 $$\text{Concentration, ng/L} = \frac{C_{ex} V_t}{V_o}$$

Where:

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

IDA Recovery Calculation:

Equation 8

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

Where ng/g = µg/kg and:

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

Calibration Factor (CF_x) = $\frac{\text{Peak area or height}_{(x)}}{\text{Standard concentration}_{(\mu g/L)}}$

Mean Calibration Factor ($\overline{CF}$) = $\frac{\sum_{i=1}^{n} CF_i}{n}$

where: n = number of calibration levels

Standard Deviation of the Calibration Factor (SD) = $\sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)2}{n-1}}$

where: n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Calibration Factor = $\frac{SD}{\overline{CF}} \times 100\%$

Percent Difference (%D) = $\frac{CF_v - \overline{CF}}{\overline{CF}} \times 100\%$

where: CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Drift = $\frac{\text{Calculated Concentration – Theoretical Concentration}}{\text{Theoretical Concentration}}$ x 100%

Percent Recovery (%R) = $\frac{C_s}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD = $\frac{C_s - C_u}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD) = $\frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$

where: C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration

Extract

$C_{extract}$ (µg/L) = $\frac{\text{Peak Area (or Height)}}{\overline{CF}}$

Note: The concentrations of the 3-5 peaks chosen for quantificaton is calculated and the average is then taken for final calculation.

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

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

Approvals (Signature/Date):

11/27/2018	11/27/2018
Robert Hrabak Date	Joe Schairer Date
Technical Manager	Health & Safety Manager / Coordinator
11/30/2018	11/27/2018
Lisa Stafford Date	Chris Williams Date
Quality Assurance Manager	Laboratory Manager

Facility Distribution No. Uncontrolled **Distributed To:** Sacramento Bids Folder

1. SCOPE AND APPLICATION

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

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA (PFUnA)	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA (PFTA)	376-06-7
Perfluoro-n-hexadecanoic acid (non-routine analyte)	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid (non-routine analyte)	PFODA	16517-11-6
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-1
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1
Perfluoro-nonanesulfonic acid	PFNS	8789-57-2
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3
Perfluoro-1-dodecansulfonic acid	PFDoS	79780-39-5
Perfluorinated sulfonamides (FOSA)		
Perfluoro-1-octanesulfonamide	FOSA	754-91-6
Perfluorinated sulfonamidoacetic acids (FOSAA)		
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
Fluorotelomer sulfonates (FTS)		
1H,1H,2H,2H-perfluorohexane sulfonate *(4:2)*	4:2 FTS	757124-72-4
1H,1H,2H,2H-perfluorooctane sulfonate *(6:2)*	6:2 FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate *(8:2)*	8:2 FTS	39108-34-4
1H,1H,2H,2H-perfluorododecane sulfonate *(10:2)*	10:2 FTS	120226-60-0

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

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

Compound Name	Abbreviation	CAS #
Fluorinated Replacement Chemicals		
Dona (Donic acid)	Dona	919005-14-4
Perfluoro(2-propoxypropanoic) acid	HFPO-DA or GenX	13252-13-6
F53B (reported as the summation of the following)	F53B	NA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	F53B major	73606-19-6
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	F5B minor	83329-89-9

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

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

1.4. The procedure for the analysis of water samples via in line solid phase extraction (SPE) for a subset of the list in Section 1.1 using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500 is described in Attachment 1 of this SOP.

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

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

2. SUMMARY OF METHOD

2.1. Water samples are extracted using a solid phase extraction (SPE) cartridge. PFAS are eluted from the cartridge with an ammonium hydroxide/methanol solution.

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

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

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

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

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

3. DEFINITIONS

3.1. PFCAs: Perfluorocarboxylic acids

3.2. PFSAs: Perfluorinated sulfonic acids

3.3. FOSA: Perfluorinated sulfonamide

3.4. PFOA: Perfluorooctanoic acid

3.5. PFOS: Perfluorooctane sulfonic acid

3.6. MPFOA: Perfluoro-n-[1,2,3,4-13C4]octanoic acid. Carbon-13 labeled PFOA

3.7. MPFOS: Perfluoro-1-[1,2,3,4-13C4]octanesulfonic acid. Carbon-13 labeled PFOS

3.8. PTFE: Polytetrafluoroethylene (e.g., Teflon®)

3.9. SPE: Solid phase extraction

3.10. PP: Polypropylene

3.11. PE: Polyethylene

3.12. HDPE: High density polyethylene

3.13. AFFF: Aqueous Film Forming Foam

3.14. IDA: Isotope dilution analyte

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

4. INTERFERENCES

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

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

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

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

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

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

4.4. Volumetric glassware and syringes are difficult to clean after being used for solutions containing high levels of PFOA. These items should be labeled for use only with

similarly concentrated solutions or verified clean prior to re-use. To the extent possible, disposable labware is used.

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

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

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

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

5. SAFETY

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

5.1. Specific Safety Concerns

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

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

5.1.3. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best

position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

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

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

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

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

5.2. Primary Materials Used

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

Material[1]	Hazards	Exposure Limit[2]	Signs and Symptoms of Exposure
Acetic Acid (3-2-1)	Corrosive Poison Flammable	10 ppm-TWA 15 ppm-STEL	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.

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

(1) Always add acid to water to prevent violent reactions.
(2) Exposure limit refers to the OSHA regulatory exposure limit.

6. EQUIPMENT AND SUPPLIES

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

6.2. 50 mL graduated plastic centrifuge tubes.

6.3. 125 mL HDPE bottles with HDPE screw caps.

6.4. 250 mL HDPE bottles with HDPE screw caps.

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

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

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

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

6.9. SPE columns

6.9.1. Phenomenex Strata SPE C18, 6 mL, 500 mg, part number 8B-S002-HCH, Waters SepPak C18, 1 to 10g, or equivalent.

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

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

6.9.4. Phenomenex Gemini 3 µm C18 110Å, 50 X 2 mm, Part No. 00B-4439-B0.

6.9.5. Phenomenex Luna 5 µm C18(2) 100Å, 30 X 3 mm, Part No. 00A-4252-Y0.

6.9.6. Penomenex Gemini 3 µm C18 110A, 50 X 3mm, Part No. 00B-4439-Y0.

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

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

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

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

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

6.15. pH indicator paper, wide range.

6.16. Bottle rotating apparatus for soil extractions.

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

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

6.18.1. SCIEX LC/MS/MS

This system consists of a Shimadzu HPLC interfaced with a SCIEX 5500 Triple Quad MS. The instrument control and data acquisition software is SCIEX Analyst, version 1.6.3 or equivalent.

6.18.1.1. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.

6.18.1.2. Phenomenex Gemini C_{18} 3 um, 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.

6.18.1.3. PFAS Isolator column, Phenomenex Luna C_{18} 5 um, 50 mm x 4.6 mm, part no. 00B-4252-E0 or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

6.18.2. Waters LC/MS/MS

This consists of a Waters Acquity UPLC system interfaced with a Waters Quattro Premier tandem mass spectrometer. The instrument control and data acquisition software is MassLynx version 4.1, or equivalent.

6.18.2.1. Analytical column: Waters Acquity UPLC BEH C18 1.7 um, 3.0 mm x 150 mm, Part No. 186004690

6.18.2.2. PFAS Isolator column, Waters Acquity UPLC BEH Shield RP-18, 1.7 um, 2.1 mm x 50 mm, PN 186004476, or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

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

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

7. REAGENTS AND STANDARDS

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

7.1.1. Acetic acid, glacial

7.1.2. Ammonium acetate (20 mM in water): Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.

7.1.3. Ammonium hydroxide (NH4OH), 0.3% in methanol: Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.

7.1.4. Hexane

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

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

7.1.7. Methanol

7.1.8. Potassium hydroxide (KOH), 0.4% in methanol: Prepared by weighing 16g of potassium hydroxide and dissolving in 4L of methanol.

7.1.9. Potassium persulfate, reagent grade

7.1.10. Ottawa Sand

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

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

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

7.2. Standards

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

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

7.2.2. If solid material is used for preparing a standard, stock standard solutions are prepared from the solids and are stored at 4 ± 2°C. Stock standard solutions should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of preparation.

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

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

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

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

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

7.3. Calibration Standards

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

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

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluoroalkylcarboxylic acids (PFCAs)							
PFBA	0.5	1.0	5.0	20	50	200	400
PFPeA	0.5	1.0	5.0	20	50	200	400
PFHxA	0.5	1.0	5.0	20	50	200	400
PFHpA	0.5	1.0	5.0	20	50	200	400
PFOA	0.5	1.0	5.0	20	50	200	400
PFNA	0.5	1.0	5.0	20	50	200	400
PFDA	0.5	1.0	5.0	20	50	200	400
PFUdA	0.5	1.0	5.0	20	50	200	400
PFDoA	0.5	1.0	5.0	20	50	200	400
PFTrDA	0.5	1.0	5.0	20	50	200	400
PFTeDA	0.5	1.0	5.0	20	50	200	400
PFHxDA	0.5	1.0	5.0	20	50	200	400
PFODA	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonic acids (PFSAs)							
PFBS	0.5	1.0	5.0	20	50	200	400
PFPeS	0.5	1.0	5.0	20	50	200	400
PFHxS *	0.5	1.0	5.0	20	50	200	400
PFHpS	0.5	1.0	5.0	20	50	200	400
PFOS *	0.5	1.0	5.0	20	50	200	400
PFNS	0.5	1.0	5.0	20	50	200	400
PFDS	0.5	1.0	5.0	20	50	200	400
PFDoS	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonamides (FOSA)							

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
FOSA	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonamidoacetic acids (FOSAA)							
EtFOSAA	0.5	1.0	5.0	20	50	200	400
MeFOSAA	0.5	1.0	5.0	20	50	200	400
Fluorotelomer sulfonates (FTS)							
4:2 FTS	0.5	1.0	2.0	20	50	200	400
6:2 FTS	0.5	1.0	5.0	20	50	200	400
8:2 FTS	0.5	1.0	5.0	20	50	200	400
10:2 FTS	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes (IDA)							
13C4-PFBA	50	50	50	50	50	50	50
13C5-PFPeA	50	50	50	50	50	50	50
13C2-PFHxA	50	50	50	50	50	50	50
13C4-PFHpA	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50
13C2-PFDA	50	50	50	50	50	50	50
13C2-PFUdA	50	50	50	50	50	50	50
13C2-PFDoA	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50
13C3-PFBS	50	50	50	50	50	50	50
13C2-PFTeDA	50	50	50	50	50	50	50
13C2-PFHxDA	50	50	50	50	50	50	50
13C8-FOSA	50	50	50	50	50	50	50
d5-EtFOSAA	50	50	50	50	50	50	50
d3-MeFOSAA	50	50	50	50	50	50	50
M2-4:2FTS ǂ	50	50	50	50	50	50	50
M2-6:2FTS	50	50	50	50	50	50	50
M2-8:2FTS	50	50	50	50	50	50	50
Internal Standard (IS)							
13C2-PFOA	50	50	50	50	50	50	50

* Both branched and linear isomers are used.

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

Note: Sample extracts are in 80% MeOH/H_2O.

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
HFPO-DA	0.5	1.0	5.0	20	50	200	400
9Cl-PF3ONS	0.5	1.0	5.0	20	50	200	400

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
(F53B major)							
11Cl-PF3OUdS (F53B minor)	0.5	1.0	5.0	20	50	200	400
Dona	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes							
13C3-HFPO-DA	0.5	1.0	5.0	20	50	200	400

Note: Sample extracts are in 80% MeOH/H_2O.

***Note**: The above calibration limits are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program. The concentration of the calibration solutions for non-concentrated extracts is 1/20th the levels indicated above.*

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

7.5. Initial Calibration Verification Standard (ICV)

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

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

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

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

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

7.8. Reverse Surrogate Solution, 1000 ng/mL

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

7.9. Internal Standard Solution, 250 ng/mL

The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 250 ng/mL in methanol. This is added to all extracts prior to analysis. The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

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

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6°C. Water samples must be extracted within 14 days of collection. Soil samples must also be extracted within 14 days of collection. Tissue samples must be extracted within 1 year of collection if stored at -20°C. Extracts must be refrigerated at 0 - 6°C, and analyzed within 40 days from extraction.

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

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability (IDOC)

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

9.2. Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to

analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC program document (WS-PQA-003) for further details of the batch definition.

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

9.3. One method blank (MB, laboratory reagent blank) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. For aqueous samples, the method blank is an aliquot of laboratory reagent water. For solid samples, the method blank is an aliquot of Ottawa sand. The method blank is processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, and then implemented when target analytes are detected in the method blank above the reporting limit or when IDA recoveries are outside of the control limits. Re-extraction of the blank, other batch QC and the affected samples are required when the method blank is deemed unacceptable. See policy WS-PQA-003 for specific acceptance criteria.

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

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

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

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

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

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

9.4. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water for aqueous samples and Ottawa sand for solids) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside of the control limits. Re-extraction of the blank, other batch QC, and all associated samples are required if the LCS is deemed unacceptable. See WS-PQA-0003 for specific acceptance criteria. The control limits for the LCS are stored in TALS.

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

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

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

Corrective actions for the ICV include:

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

- Rerun the initial calibration.

9.8. Isotope Dilution Analytes

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

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

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

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

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

9.8.2.3. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for IDA recoveries which are 50-150%. If QC or field samples do not meet these criteria then re-extraction is required.

9.9. Internal Standard

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

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

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

10. CALIBRATION

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

10.2. Routine instrument operating conditions are listed in the table in Section 11.18.

10.3. Instrument Tuning

Instrument tuning is done initially when the method is first developed and thereafter as needed to maintain the sensitivity and selectivity of the method. Tuning is done by infusing each individual compound (native and IDA) into the mobile phase using a tee fitting at a point just before the entrance to the electrospray probe. The responses for the parent and daughter ions for each compound are observed and optimized for sensitivity and resolution. Mass assignments are reviewed and calibrated if necessary. The mass assignments must be within ± 0.5 amu of the values shown in the table in Section 11.18.

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

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

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

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

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

10.8. Initial Calibration

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

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

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

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

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

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

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

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

10.8.2.5. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for initial calibration: The %RSD of the RFS for all analytes must be <20%. Linear or non-linear calibrations must have r^2>0.99 for each analyte. Analytes must be within 70-130% of their true value for each calibration standard.

10.9. Calibration Curve Fits

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

10.9.2. The linear curve uses the following function:

Equation 1

$$y = bx + c$$

Where:

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

x = concentration
b = slope
c = intercept

10.9.3. The quadratic curve uses the following function:

Equation 2

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

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

10.9.4. Evaluation of Calibration Curves

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

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

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

10.9.5. Weighting of Calibration Points

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

10.10. Initial Calibration Blank (ICB)

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

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

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

10.10.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for instrument blanks. One is required immediately following the highest standard analyzed and *daily prior to sample analysis*. The instrument blank must be < ½ the LOQ.

10.11. Initial Calibration Verification (ICV)

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

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

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

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

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

10.11.3. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for the ICV. Analyte concentrations must be within ±30% of their true values for all analytes, IDA and target.

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

10.12. Continuing Calibration Verification (CCV)

Analyze a CCV at the beginning of a run, the end of a run, and after every 10 samples to determine if the calibration is still valid. The exception is after an acceptable curve and ICV are run 10 samples can be analyzed before a CCV is required. The CCVs are

usually at the mid-level range of the curve and should vary throughout the run from low level (LOQ/RL) to mid level. The curve and ICV do not need to be run every day. To start an analytical run a CCV can be analyzed and if it meets acceptance criteria a run can be started. In addition, the low standard in the curve must be analyzed and must be within ± 50% of the expected value.

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

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

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

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

10.12.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for CCV. All analyte concentrations must be within ± 30% of their true value. Additionally, prior to analysis and at least once every 12 hours an instrument sensitivity check (ISC/CCVL) must be analyzed. The analyte concentrations must be at LOQ and the concentrations must be within ± 30% of their true value. This can be used as a CCV.

11. PROCEDURE

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

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

11.2. Water Sample Preparation

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

Decanting or filtering of the sample can lead to a low bias.

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

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

11.2.3. Weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume. Unless otherwise directed by client, use the entire sample volume.

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

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

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

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

11.3. Solid Phase Extraction (SPE) of Aqueous Samples

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

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

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

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

11.3.2. Wash with 5.0 mL of 0.3% NH_4OH/methanol.

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

dry until the completion of loading and rinsing samples.

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

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

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

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

11.4. SPE Column Wash of Aqueous Samples with Hexane

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

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

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

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

11.5.1. Rinse sample bottles with 5 mL of 0.3% NH_4OH/methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.5.2. Repeat sample bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH_4OH/methanol. The total collection should be approximately 10 mL.

11.5.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol.**

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

11.6. Extract Concentration for Aqueous Extracts (Note, if the extract will not be concentrated, proceed to Section 11.7.)

11.6.1. Prior to concentrating each sample, add 100 uL of water.

11.6.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.

11.6.2.1. This blow down must take a minimum of 3.5 hours.

11.6.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.

11.6.3. Add 300 uL of methanol and mix the contents well using a vortex mixer.

11.6.4. Add 100 uL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

11.6.5. This will create an extract with a final solvent composition of 80:20 methanol:water.

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

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

11.7. Final volume for non-concentrated extract

11.7.1. If the extract does not undergo concentration add 0.5 mL of IS 50 ng/mL concentration and 2 mL of water to the extract. This will create an extract with a final solvent composition of 80:20 methanol:water.

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

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

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

11.8. Soil, Sediment and Tissue Sample Preparation and Extraction

11.8.1. Visually inspect soil samples for homogeneity.

11.8.1.1. Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria (see SOP WS-QA-0018).

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

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

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

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

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

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

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

11.8.7. Add 20 mL of 0.4% KOH/methanol to each sample.

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

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

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

11.8.11. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.

11.8.12. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.8.13. Combine the rinsate to the first corresponding tubes.

11.8.14. To the final KOH/methanol extract, add 2 mL of water to each.

11.8.15. Concentrate the KOH/methanol/water extract under nitrogen to less than 2 mL, and dilute with water to 15 mL final volume.

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

11.8.17. Centrifuge at 3500 rpm for 15 minutes.

11.9. Solid Extract Cleanup by SPE

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

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

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

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

11.9.2. Wash with 5.0 mL of 0.3% NH_4OH/methanol.

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

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

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

11.9.6. Dry the columns with vacuum for 15 minutes.

11.10. SPE Column Wash of Solid Extracts with Hexane

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

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

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

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

11.11.1. Rinse extraction bottles with 5 mL of 0.3% NH_4OH/methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.11.2. Repeat extract bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH_4OH/methanol. The total collection should be approximately 10 mL.

11.11.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol.**

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

11.12. Extract Concentration for Solid Samples (Note, if the extract will not be concentrated, proceed to Section 11.7)

11.12.1. Prior to concentrating each sample, add 200 uL of water.

11.12.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 200 uL of water remains.

11.12.2.1. This blow down must take a minimum of 3.5 hours.

11.12.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.

11.12.2.3. Add 600 uL of methanol and mix the contents well using a vortex mixer.

11.12.2.4. Add 200 uL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

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

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

11.13. Product/Dispersion Samples

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

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

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

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

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

11.13.2. Take 100 uL of the 10 mL solution and dilute it to 10 mL in MeOH.

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

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

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

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

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

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

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

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

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

11.14.6. Add 2g of potassium persulfate and 1.9 mL of 10 M NaOH to each “Post” sample container.

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

11.14.8. Set aside all "Pre" sample containers.

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

11.14.10. Add 2 g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container.

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

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

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

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

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

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

11.14.15.2. Establish a sample loading flow rate of 1 mL/minute for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.14.15.3. Wash/condition the SPE column with 5 mL of 0.3% NH_4OH/Methanol, then 5 mL water.

11.14.15.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 1 mL/minute.

11.14.15.5. Add 5 mL rinse water

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

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

11.14.15.8. Allow the column to dry well using vacuum with a flow rate of 1 mL/minute for 5 minutes. Columns must be dry before continuing.

11.14.15.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH_4OH/methanol, and add to the SPE cartridge as eluent.

11.14.15.10. Repeat with another 5 mL of 0.3% NH_4OH/methanol.

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

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

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

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

11.15.3. Add 20 mL of 0.4% KOH/methanol to each sample.

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

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

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

11.15.7. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.

11.15.8. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.

11.15.9. Combine the rinsate to the first corresponding tubes.

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

11.15.11. To the final KOH/methanol extract, add 0.5 mL of water to each.

11.15.12. Concentrate the KOH/methanol/water extract under nitrogen to less than 0.25 mL.

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

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

11.15.15. Spike the "Pre" and "Post" MB 125 mL containers with 25 uL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).

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

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

11.15.18. Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container.

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

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

11.15.21. Set aside all "Pre" sample containers.

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

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

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

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

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

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

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

11.15.27.2. Establish a sample loading flow rate of 1 mL/minute for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.

11.15.27.3. Wash/condition the SPE column with 5 mL of 0.3% NH_4OH/Methanol, then 5 mL water.

11.15.27.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 1 mL/minute.

11.15.27.5. Add 5 mL rinse water

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

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

11.15.27.8. Allow the column to dry well using vacuum with a flow rate of 1 mL/minute for 5 minutes. Columns must be dry before continuing.

11.15.27.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH_4OH/methanol, and add to the SPE cartridge as eluent.

11.15.27.10. Repeat with another 5 mL of 0.3% NH_4OH/methanol.

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

Note: *If the extracts will not be concentrated elute extract with a total of 8 mL (2 4 mL rinses) of 0.3% NH_4OH/methanol.*

11.16. Other Types of Sample Cleanup

11.16.1. Freezing technique to remove lipids.

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

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

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

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

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

11.16.2.4. Decant the solvent layer.

11.16.2.5. Proceed to Section 11.6, 11.7 or 11.12 as applicable.

11.17. AFFF Sample Preparation

11.17.1. QC for AFFF samples consists of a method blank, a laboratory control sample and a sample or matrix duplicate only. No matrix spike or matrix spike duplicate is needed.

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

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

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

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

11.18. Instrument Analysis

Suggested operating conditions are listed in Tables 1-7 for the Waters and SCIEX LCMS systems:

Table 1 - Recommended Instrument Operating Conditions

HPLC Conditions (Shimadzu HPLC)				
Column (Column temp = 45°C)	Phenomenex Gemini 3 µm C18 110Å, 50 X 2 mm			
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol			
Gradient Program	**Time**	**%A**	**%B**	**Flow Rate - mL/min**
	0	90	10	0.60
	0.1	45	55	0.60
	4.5	1	99	0.60
	4.95	1	99	0.60
	5	90	10	0.60
	Maximum pressure limit = 5,000 psi			
Injection Size	2 µL (fixed amount throughout the sequence). If non-concentrated extract then use 20 uL.			
Run Time	~6.6 minutes			
Mass Spectrometer Interface Settings (SCIEX 5500)				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.			
Ion Spray Voltage (kV)	4.5			

Table 1 - Recommended Instrument Operating Conditions	
HPLC Conditions (Shimadzu HPLC)	
Entrance Potential (V)	5
Declustering Potential (V)	25
Desolvation Temp	600ºC
Curtain Gas	35 psi
Collision Gas	8 psi

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
PFBA	Native analyte	212.9 > 169	0.011	-5	-12	-25	-31	1.74
13C4-PFBA	IDA	217 > 172	0.011	-5	-12	-25	-31	1.74
PFBS	Native analyte	298.9 > 80	0.011	-6	-58	-55	-37	1.76
PFBS_2	Native analyte	298.9 > 99	0.011	-5	-40	-55	-12	1.76
13C3-PFBS	IDA	301.9 > 83	0.011	-5	-40	-55	-12	1.76
PFPeA	Native analyte	262.9 > 219	0.011	-7	-12	-20	-34	1.99
13C5-PFPeA	IDA	267.9 > 223	0.011	-7	-12	-20	-35	1.99
4:2 FTS	Native analyte	327 > 307	0.011	-7	-32	-50	-10	2.06
M2-4:2FTS	IDA or Reverse Surrogate for TOP	329 > 81	0.011	-7	-32	-50	-10	2.06
PFHxA	Native analyte	313 > 269	0.011	-5	-12	-25	-37	2.25
PFHxA_2	Native analyte	313 > 119	0.011	-5	-12	-25	-37	2.25
13C2-PFHxA	IDA	315 > 270	0.011	-5	-12	-25	-38	2.25
PFHpA	Native analyte	363 > 319	0.011	-6	-12	-25	-41	2.57
PFHpA_2	Native analyte	363 > 169	0.011	-6	-12	-25	-41	2.57
13C4-PFHpA	IDA	367 > 322	0.011	-6	-12	-25	-41	2.57
PFPeS	Native analyte	349 > 80	0.011	-9	-66	-57	-40	2.15
PFPeS_2	Native analyte	349 > 99	0.011	-9	-40	-57	-12	2.15
PFHxS	Native analyte	399 > 80	0.011	-12	-74	-60	-43	2.59
PFHxS_2	Native analyte	399 > 99	0.011	-12	-74	-60	-43	2.59
18O2-PFHxS	IDA	403 > 84	0.011	-12	-74	-60	-43	2.59
6:2 FTS	Native analyte	427 > 407	0.011	-7	-32	-50	-10	2.91
M2-6:2FTS	IDA	429 > 81	0.011	-7	-32	-50	-10	2.91
PFOA	Native analyte	413 > 369	0.011	-6	-14	-25	-44	2.93
PFOA_2	Native analyte	413 > 169	0.011	-5	-22	-25	-12	2.93
13C4-PFOA	IDA	417 > 372	0.011	-6	-14	-25	-44	2.93
13C2-PFOA	IS	415 > 370	0.011	-6	-14	-25	-44	2.93
PFHpS	Native analyte	449 > 80	0.011	-11	-88	-65	-46	2.94
PFHpS_2	Native analyte	449 > 99	0.011	-11	-88	-65	-46	2.94
PFNA	Native analyte	463 > 419	0.011	-6	-14	-25	-47	3.29
PFNA_2	Native analyte	463 > 169	0.011	-6	-14	-25	-47	3.29

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
13C5-PFNA	IDA	468 > 423	0.011	-6	-14	-25	-48	3.29
PFOS	Native analyte	499 > 80	0.011	-9	-108	-65	-50	3.29
PFOS_2	Native analyte	499 > 99	0.011	-5	-58	-65	-12	3.29
PFNS	Native analyte	549 > 80	0.011	-10	-113	-75	-52	3.40
PFNS_2	Native analyte	549 > 99	0.011	-8	-71	-75	-12	3.40
PFDoS	Native analyte	699 > 80	0.011	-11	-76	-10	-11	4.48
PFDoS_2	Native analyte	699 >99	0.011	-11	-130	-10	-5	4.48
13C4-PFOS	IDA	503 > 80	0.011	-9	-108	-65	-50	3.29
PFDA	Native analyte	513 > 469	0.011	-6	-16	-25	-51	3.65
PFDA_2	Native analyte	513 > 169	0.011	-6	-16	-25	-51	3.65
13C2-PFDA	IDA	515 > 470	0.011	-6	-16	-25	-51	3.65
8:2 FTS	Native analyte	527 > 507	0.011	-7	-40	-50	-15	3.65
10:2 FTS	Native analyte	627 > 607	0.011	-7	-38	-110	-5	4.25
M2-8:2FTS	IDA	529 > 81	0.011	-7	-40	-50	-15	3.65
PFOSA	Native analyte	498 > 78	0.011	-8	-85	-60	-50	3.7
13C8-PFOSA	IDA	506 > 78	0.011	-8	-85	-60	-50	3.7
N-MeFOSAA	Native analyte	570 > 419	0.011	-7	-36	-40	-15	3.82
d3-MeFOSAA	IDA	573 > 419	0.011	-7	-36	-40	-15	3.82
PFDS	Native analyte	599 > 80	0.011	-11	-118	-85	-54	3.96
PFDS_2	Native analyte	599 > 99	0.011	-11	-118	-85	-54	3.96
PFUdA	Native analyte	563 > 519	0.011	-7	-18	-25	-54	3.97
PFUdA_2	Native analyte	563 > 169	0.011	-7	-18	-25	-54	3.97
13C2-PFUdA	IDA	565 > 520	0.011	-7	-18	-25	-54	3.97
N-EtFOSAA	Native analyte	584 > 419	0.011	-7	-36	-50	-15	3.99
d5-EtFOSAA	IDA	589 > 419	0.011	-7	-36	-50	-15	3.99
PFDoA	Native analyte	613 > 569	0.011	-5	-18	-25	-54	4.3
PFDoA_2	Native analyte	613 > 169	0.011	-5	-18	-25	-54	4.3
13C2-PFDoA	IDA	615 > 570	0.011	-5	-18	-25	-54	4.3
PFTrDA	Native analyte	663 > 619	0.011	-7	-20	-25	-54	4.56
PFTrDA_2	Native analyte	663 > 169	0.011	-7	-20	-25	-54	4.56
PFTeDA	Native analyte	713 > 169	0.011	-2	-22	-25	-10	4.79
PFTeDA_2	Native analyte	713 > 219	0.011	-7	-36	-25	-30	4.79
13C2-PFTeDA	IDA	715 > 670	0.011	-2	-22	-25	-10	4.79
PFHxDA	Native analyte	813 > 769	0.011	-7	-24	-25	-54	5.25
PFHxDA_2	Native analyte	813 > 169	0.011	-7	-24	-25	-54	5.25
13C2-PFHxDA	IDA	815 > 770	0.011	-7	-24	-25	-54	5.25
PFODA	Native analyte	913 > 869	0.011	-7	-26	-25	-54	5.55
PFODA_2	Native analyte	913 > 169	0.011	-7	-26	-25	-54	5.55

Table 3 - Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
HFPO-DA	Native analyte	329.1 > 285	0.011	-10	-6	-48	-17	2.06
13C3-HFPO-DA	IDA	332.1 > 287	0.011	-10	-10	-40	-17	2.06
9Cl-PF3ONS (F53B major)	Native analyte	531 > 351	0.011	-10	-30	-120	-17	3.23
11Cl-PF3OUdS (F53B minor)	Native analyte	631 > 451	0.011	-10	-40	-160	-17	3.84
Dona	Native analyte	377 > 251	0.011	-10	-16	-55	-17	2.33
Dona_2	Native analyte	377 > 85	0.011	-10	-35	-55	-17	2.33

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBA	1.54	13C4-PFBA	1.54	Isotope Dilution
PFPeA	1.56	13C5-PFPeA	1.56	Isotope Dilution
PFBS	1.78	13C3-PFBS	1.78	Isotope Dilution
PFHxA	2.03	13C2-PFHxA	2.03	Isotope Dilution
PFPeS	2.06	13C3-PFBS	1.78	Isotope Dilution
PFHpA	2.36	13C4-PFHpA	2.36	Isotope Dilution
PFHxS	2.37	18O2-PFHxS	2.37	Isotope Dilution
PFOA	2.71	13C4-PFOA	2.71	Isotope Dilution
PFHpS	2.72	13C4-PFOS	3.09	Isotope Dilution
PFNA	3.09	13C5-PFNA	3.09	Isotope Dilution
PFOS	3.09	13C4-PFOS	3.09	Isotope Dilution
PFNS	3.40	13C4-PFOS	3.09	Isotope Dilution
PFDA	3.45	13C2-PFDA	3.45	Isotope Dilution
FOSA	3.43	13C8-FOSA	3.43	Isotope Dilution
PFDS	3.77	13C4-PFOS	3.09	Isotope Dilution
PFUdA	3.78	13C2-PFUdA	3.78	Isotope Dilution
PFDoA	4.07	13C2-PFDoA	4.07	Isotope Dilution
PFTrDA	4.34	13C2-PFDoA	4.07	Isotope Dilution
PFDoS	4.48	13C4-PFOS	3.09	Isotope Dilution
PFTeDA	4.58	13C2-PFTeDA	4.58	Isotope Dilution
PFHxDA	4.99	13C2-PFHxDA	4.99	Isotope Dilution
PFODA	5.34	13C2-PFHxDA	4.99	Isotope Dilution
EtFOSAA	3.78	d5-EtFOSAA	3.78	Isotope Dilution
MeFOSAA	3.61	d3-MeFOSAA	3.60	Isotope Dilution

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
4:2 FTS	1.98	M2-4:2 FTS (If TOP then 13C-PFBS)	1.78	Isotope Dilution
6:2FTS	2.69	M2-6:2FTS	2.69	Isotope Dilution
8:2FTS	3.44	M2-8:2FTS	3.44	Isotope Dilution
HFPO-DA	2.06	13C3-HFPO-DA	2.06	Isotope Dilution
9Cl-PF3ONS (F53B major)	3.23	13C4-PFOS	3.09	Isotope Dilution
11Cl-PF3OUdS (F53B minor)	3.84	13C4-PFOS	3.09	Isotope Dilution
Dona	2.33	13C4-PFOS	3.09	Isotope Dilution
10:2 FTS	4.25	M2-8:2 FTS	3.44	Isotope Dilution

Table 5 - Recommended Instrument Operating Conditions						
HPLC Conditions (Waters Acquity UPLC)						
Column (Column temp = 50°C)	Waters Acquity BEH 1.7µm C18, 3.0 x 150 mm					
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol					
Gradient Program	**Time**	**%A**	**%B**	**Curve**	**Flow Rate - mL/min.**	
	0	98	2	6	0.30	
	1	98	2	6	0.30	
	2	50	50	6	0.30	
	12	10	90	6	0.30	
	12.5	0	100	6	0.30	
	16	0	100	6	0.30	
	16.2	98	2	6	0.30	
	Maximum pressure limit = 15,000 psi					
Injection Size	10 µL (fixed amount throughout the sequence)					
Run Time	~20 minutes					
Mass Spectrometer Interface Settings (Quattro Premier XE)						
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.					
Capillary (kV)	2.8					
Cone (V)	Varies from 8.0 to 65					
Extractor (V)	3					
Source Temp	135ºC					
Desolvation Temp	350ºC					
Cone Gas (nitrogen) Flow	25 L/hour					
Desolvation Gas (nitrogen) Flow	1100 L/hour					

Table 6 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
PFBA	Native analyte	213 > 169	0.02	8	10	1
13C4-PFBA	IDA	217 > 172	0.02	12	10	1
PFPeA	Native analyte	263 > 219	0.02	10	10	2
13C5-PFPeA	IDA	268 > 223	0.02	11	9	2
PFBS	Native analyte	299 > 80	0.02	45	35	2
PFBS_2	Native analyte	299 > 99	0.02	45	35	2
13C3-PFBS	IDA	302 > 83	0.02	45	35	2
PFHxA	Native analyte	313 > 269	0.02	10	10	3
PFHxA_2	Native analyte	313 > 119	0.02	10	10	3
13C2-PFHxA	IDA	315 > 270	0.02	12	9	3
PFHpA	Native analyte	363 > 319	0.02	10	10	4
PFHpA_2	Native analyte	363 > 169	0.02	10	10	4
13C4-PFHpA	IDA	367 > 322	0.02	12	10	4
PFHxS	Native analyte	399 > 80	0.02	55	35	4
PFHxS_2	Native analyte	339 > 99	0.02	55	35	4
18O2-PFHxS	IDA	403 > 84	0.02	50	40	4
PFOA	Native analyte	413 > 369	0.02	12	10	5
PFOA_2	Native analyte	413 > 169	0.02	12	10	5
13C2-PFOA	IS	415 > 370	0.02	12	12	5
13C4-PFOA	IDA	417 > 372	0.02	12	12	5
PFHpS	Native analyte	449 > 80	0.02	60	38	5
PFHpS_2	Native analyte	449 > 99	0.02	60	38	5
PFNA	Native analyte	463 > 419	0.02	16	10	7
PFNA_2	Native analyte	463 > 169	0.02	16	10	7
13C5-PFNA	IDA	468 > 423	0.02	12	12	7
PFOS	Native analyte	499 > 80	0.02	60	40	6
PFOS_2	Native analyte	499 > 99	0.02	60	40	6
PFNS	Native analyte	549 > 80	0.02	60	40	6
PFNS_2	Native analyte	549 > 99	0.02	60	40	6
13C4-PFOS	IDA	503 > 80	0.02	35	48	6
PFDA	Native analyte	513 > 469	0.02	16	12	8
PFDA_2	Native analyte	513 > 169	0.02	16	12	8
13C2-PFDA	IDA	515 > 470	0.02	14	12	8
PFUdA	Native analyte	563 > 519	0.02	15	12	10
PFUdA_2	Native analyte	563 > 169	0.02	15	12	10
13C2-PFUdA	IDA	565 > 520	0.02	14	12	10
PFDS	Native analyte	599 > 80	0.02	74	48	10
PFDS_2	Native analyte	559 > 99	0.02	74	48	10
FOSA	Native analyte	498 > 78	0.02	40	32	9

Table 6 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
13C8-FOSA	IDA	506 > 78	0.02	48	32	9
PFDoA	Native analyte	613 > 569	0.02	15	14	11
PFDoA_2	Native analyte	613 > 169	0.02	15	14	11
13C2-PFDoA	IDA	615 > 570	0.02	16	12	11
PFTrDA	Native analyte	663 > 619	0.02	12	12	11
PFTrDA_2	Native analyte	663 > 169	0.02	12	12	11
PFTeDA	Native analyte	713 > 169	0.02	12	18	11
PFTeDA_2	Native analyte	713 > 219	0.02	12	18	11
13C2-PFTeDA	IDA	715 > 670	0.02	15	15	11
PFHxDA	Native analyte	813 > 769	0.02	18	15	12
PFHxDA_2	Native analyte	813 > 169	0.02	18	15	12
PFODA	Native analyte	913 > 869	0.02	20	16	12
PFODA_2	Native analyte	913 > 169	0.02	20	16	12
13C2-PFHxDA	IDA	815 > 770	0.02	18	15	12
EtFOSAA	Native analyte	584 > 419	0.02	35	20	9
d5-EtFOSAA	IDA	589 > 419	0.02	30	25	9
MeFOSAA	Native analyte	570 > 419	0.02	30	28	9
d3-MeFOSAA	IDA	573 > 419	0.02	30	25	9
4:2FTS	Native analyte	327 > 307	0.02	40	30	5
M2-4:2FTS	IDA or Reverse Surrogate for TOP	329 > 81	0.02	40	30	5
6:2FTS	Native analyte	427 > 407	0.02	40	30	5
M2-6:2FTS	IDA	429 > 81	0.02	40	28	5
8:2FTS	Native analyte	527 > 507	0.02	40	28	8
M2-8:2FTS	IDA	529 > 81	0.02	40	28	8

Table 7 - Recommended Instrument Operating Conditions				
Retention Times & Quantitation (Quattro Premier XE)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBA	4.77	13C4-PFBA	4.79	Isotope Dilution
PFPeA	5.90	13C5-PFPeA	5.92	Isotope Dilution
PFBS	6.01	13C3-PFBS	6.01	Isotope Dilution
PFHxA	7.22	13C2-PFHxA	7.25	Isotope Dilution
PFPeS	7.20	18O2-PFHxS	8.64	Isotope Dilution
PFHpA	8.57	13C4-PFHpA	8.59	Isotope Dilution
PFHxS	8.60	18O2-PFHxS	8.64	Isotope Dilution
PFOA	9.80	13C4-PFOA	9.83	Isotope Dilution
PFHpS	9.80	13C4-PFOS	10.90	Isotope Dilution

Table 7 - Recommended Instrument Operating Conditions				
Retention Times & Quantitation (Quattro Premier XE)				
Native Compounds	**Typical Native RT (minutes)**	**IDA analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFNA	10.88	13C5-PFNA	10.92	Isotope Dilution
PFOS	10.87	13C4-PFOS	10.90	Isotope Dilution
PFNS	11.70	13C4-PFOS	10.90	Isotope Dilution
PFDA	11.82	13C2-PFDA	11.86	Isotope Dilution
FOSA	12.41	13C8-FOSA	12.46	Isotope Dilution
PFDS	12.57	13C4-PFOS	10.90	Isotope Dilution
PFUdA	12.62	13C2-PFUdA	12.66	Isotope Dilution
PFDoA	13.32	13C2-PFDoA	13.34	Isotope Dilution
PFTrDA	13.91	13C2-PFDoA	13.34	Isotope Dilution
PFTeDA	14.39	13C2-PFTeDA	14.39	Isotope Dilution
PFHxDA	15.16	13C2-PFHxDA	15.16	Isotope Dilution
PFODA	15.57	13C2-PFHxDA	15.16	Isotope Dilution
EtFOSAA	12.63	d5-EtFOSAA	12.62	Isotope Dilution
MeFOSAA	12.3	d3-MeFOSAA	12.28	Isotope Dilution
4:2FTS	7.02	M2-4:2 FTS (If TOP then 13C-PFBS)	6.01	Isotope Dilution
6:2FTS	10.08	M2-6:2FTS	10.08	Isotope Dilution
8:2FTS	11.95	M2-8:2FTS	11.95	Isotope Dilution

11.18.1. Post Spike Sample Analysis for AFFF samples

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

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

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

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

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

11.18.3. A typical run sequence is as follows:

- Rinse Blank (RB, not linked to anything)

- Start ICAL with CCVL but called IC in TALS (starts the 12 hour clock or time 0:00)
- Rest of ICAL
- ICB: link to midpoint of ICAL and samples
- ICV: link to midpoint of ICAL and samples (If ICAL good)
- CCB: link to midpoint of ICAL and samples
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- 10 more samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- Etc.
- CCVL (within 12 hours from CCVL in ICAL, can be the ending CCV and starts 12 hours all over again): if this occurs link to the midpoint of the ICAL/toggle it as opening/closing CCV.
- CCV: link to midpoint of ICAL
- 10 samples: link to midpoint of ICAL
- CCV: link to midpoint of ICAL
- If no ICAL run that day
- CCB: link to CCVIS
- CCVL (starts 12 hour clock): link to CCVIS
- CCVIS: link to midpoint of ICAL
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS
- Etc.
- If going over 12 hours in the sequence: CCVL (within 12 hours from CCVL at item 2 above, can be the ending CCV and starts 12 hours all over again): if this occurs link to the CCVIS /toggle as opening and closing CCV.
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS

12. CALCULATIONS

12.1. If the concentration of the analyte ions exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. It may be necessary to dilute samples due to matrix.

12.2. Qualitative Identification

12.2.1. The retention times of PFAS with labeled standards should be the same as that of the labeled IDA's to within 0.05 min. For PFAS with no labeled standards, the RT must be within ± 0.3 minutes of the ICV and CCV standards. ***Note**: The IDA RT and native RT may be offset by 0.02 to 0.04 minutes.*

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

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

Equation 3

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

Equation 4

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

Where:

y = $\frac{\text{Area (analyte)}}{\text{Area (IS)}} \times \text{Concentration (IS)}$
x = concentration
a = curvature
b = slope
c = intercept

12.5. Water Sample Result Calculation:

Equation 5

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

Where:

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

12.6. Soil Sample Result Calculation:

Equation 6

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

Where ng/g = µg/kg and:

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

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

12.7. IDA Recovery Calculation:

Equation 7

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

Where ng/g = µg/kg and:

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

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

13. METHOD PERFORMANCE

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

13.2. Method Detection Limit

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

13.3. Initial Demonstration of Capability (IDOC)

Each analyst performing this procedure must successfully analyze four LCS QC samples using current laboratory LCS control limits. IDOCs are approved by the

Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

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

14. POLLUTION PREVENTION

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

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

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

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

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

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

15. WASTE MANAGEMENT

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

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

15.2. Extracted soil samples, used sodium sulfate, paper funnel filters, glass wool, thimbles, and extracted solids saturated with solvents. Dump these materials into an orange contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the incineration steel collection

drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

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

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

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

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

16. REFERENCES

16.1. Cheryl Moody, Wai Chi Kwan, Johnathan W. Martin, Derek C. G. Muir, Scott A. Mabury, “Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and 19FNMR,” Analytical Chemistry 2001, 73, 2200-2206.

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

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

16.4. STL Denver White Paper DEN-W-LC-002, “Method Validation Study for Analysis of Ammonium Perfluorooctanate in Soil Matrices by High Performance Liquid

Chromatography/Mass Spectrometry (HPLC/MS/MS)", Mark Dymerski, September 5, 2003.

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

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

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

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

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

17. METHOD MODIFICATIONS

17.1. Modifications from Method 537 are detailed below:

17.1.1. Water sample containers are not preserved with Trizma.

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

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

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

17.1.5. Calibration levels differ from the referenced method.

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

17.1.7. There is no symmetry requirement.

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

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

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

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

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

18. ATTACHMENTS

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

19. REVISION HISTORY

Revisions to Attachment 1 are documented in the attachment.

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

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

19.1.1. Added Section 6.9, “Phenomenex Gemini 3 µm C18 110A, 50 X 3 mm, Part No. 00B-4439-Y0.”

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

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

19.1.4. Editorial changes.

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

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

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

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

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

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

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

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

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

19.2.9. Editorial changes.

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

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

19.3.2. Editorial changes.

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

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

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

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

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

19.4.5. Section 7.1.2 added, “Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.”

19.4.6. Section 7.1.3 added, “Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.”

19.4.7. Section 7.1.8 added, “Prepared by weighing 16g of potassium hydroxide and dissolving in 4L of methanol.”

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

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

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

19.4.11. Added Section 8.1.1, “Water samples collected from a known chlorinated source should be preserved with Trizma.”

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

19.4.13. Added Section 11.14.6, “Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.”

19.4.14. Removed Section 11.14.8, “Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.”

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

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

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

19.4.18. Section 11.8 added Table 6, “Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals”

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

19.4.20. Editorial changes.

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

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

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

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

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

19.5.5. Editorial changes.

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

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

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

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

and 0.015 ug/kg.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

19.6.22. Added Section 11.15.2.5, "Proceed to Section 11.6, 11.7, or 11.12 as applicable."

19.6.23. Removed Sections 11.15.3 through 11.15.6.

19.6.24. Added Section 11.16, "AFFF Sample Preparation".

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

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

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

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

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

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

19.6.31. Editorial changes.

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

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

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

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

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

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

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

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

19.7.8. Section 7.4 table, added:

4:2 FTS	0.5	1.0	2.0	20	50	200	400

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

19.7.10. Section 7.4 table, added:

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

19.7.11. Section 7.4, removed "FOSAA may be added to the mix and are added at the same concentration as FOSA."

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

19.7.13. Section 8.1, changed "250 mL" to "8 oz."

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

19.7.15. Added Section 9.9, "Internal Standard."

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

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

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

19.7.19. Added Section 11.2.3.1, "Alternatively, weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume."

19.7.20. Added Section 11.5.3, "Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH/methanol."

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

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

19.7.23. Added Section 11.7, "Final volume for non-concentrated extract".

19.7.24. Revised Section 11.11, "SPE Elution of Solid Extracts".

19.7.25. Revised Section 11.12, "Extract Concentration for Solid Samples".

19.7.26. Removed Section 12.8, "If results are to be reported as ammonium

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

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

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

19.7.29. Editorial changes.

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

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

19.8.2. Section 11.15, added 13C-PFBS to the Recommended Instrument Operating Conditions table for SCIEX 5500.

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

19.8.4. Editorial changes.

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

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

19.9.2. Revised Section 11.6.2 to read "Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.

11.6.2.1 This blow down must take a minimum of 3.5 hours.

11.6.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.9.3. Revised Section 11.6.3 to read "Add 400 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

19.9.4. Revised Section 11.11.1 to read "Prior to concentrating each sample, add 200 uL of water."

19.9.5. Revised Section 11.11.2 to read "Concentrate each sample under a gentle

stream of nitrogen until the methanol is evaporated and the 200 uL of water remains."

11.11.2.1 This blow down must take a minimum of 3.5 hours.

11.11.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated."

19.9.6. Revised Section 11.11.3 to read "Add 800 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water."

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of water samples via in line solid phase extraction (SPE) for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500.

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1

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

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	1.0 mL	2.0 ng/L	2 to 200 ng/L

2. SUMMARY OF METHOD

2.1. A 1 mL aliquot of sample is diluted to a 40:60 methanol:water extract and analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using 20mM ammonium acetate/water and methanol.

3. DEFINITIONS

Refer to Section 3 of the main body of this SOP for a summary of definitions.

4. INTERFERENCES

Refer to Section 4 of the main body of this SOP for interferences.

5. SAFETY

Refer to Section 5 of the main body of this SOP for safety information.

6. EQUIPMENT AND SUPPLIES

Refer to Section 6 of the main body of this SOP for supplies, other than those listed below specific to the in line SPE analysis.

6.1. 2 mL auto sampler vials, clear glass, Thermo Scientific Nation surestop vial, part no. C5000-1, or equivalent**.**

6.2. Vial caps, Thermo Scientific National AVCS blue cap, pre slit TEF/STL septa, part no. C5000-55B or equivalent.

6.3. Eppendorf 1000 uL epTIPS, part no. 022491954 or equivalent.

6.4. Eppendorf 200 uL epTIPS, part no. 022491938 or equivalent.

6.5. 50 mL graduated plastic centrifuge tubes, SCP Science DigiTUBES part no. 010-500-263 or equivalent

6.6. 1000 uL Pipette: Eppendorf Research Plus

6.7. 100 uL Pipette: Rainin EDP3-Plus

6.8. 250 mL HDPE bottles with PPE screw caps, ESS part no. 0250-1902-QC or equivalent.

6.9. Analytical columns

6.9.1. Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.

6.9.2. PFAS Isolator column, Phenomenex Luna C18 5 um, 50 mm x 4.6 mm, part no. 00B-4252-E 0 or equivalent.

6.10. SCIEX 5500 Triple Quad MS. The system utilizes Chrom Peak Review, version 2.1 or equivalent.

6.11. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.

7. REAGENTS AND STANDARDS

Refer to Section 7 of the main body of this SOP for reagents and standards, other than those listed below specific to the in line SPE analysis.

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

7.1.1. Ammonium acetate, Fisher Optima LCMS grade (20 mM in water), part no. A114-50, or equivalent.

7.1.2. Methanol, Baker HPLC grade, part no. 9093-03.

7.1.3. Water, Nanopure or Millipore or Fisher Optima LCMS grade, part no. W6-4, must be free of interference and target analytes.

7.2. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of the stock solutions (Section 7.2 of the main body of this SOP) in 40:60 methanol:water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.3. Initial Calibration (ICAL) Levels (ng/L)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7	CS-8
Perfluoroalkylcarboxylic acids (PFCAs)								
PFHpA	1.0	2.0	5.0	10	20	50	100	200
PFOA	1.0	2.0	5.0	10	20	50	100	200
PFNA	1.0	2.0	5.0	10	20	50	100	200
Perfluorinated sulfonic acids (PFSAs)								
PFBS	1.0	2.0	5.0	10	20	50	100	200
PFHxS	1.0	2.0	5.0	10	20	50	100	200
PFOS	1.0	2.0	5.0	10	20	50	100	200
Labeled Isotope Dilution Analytes (IDA)								
13C4-PFHpA	50	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50	50

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

7.4. LCS/Matrix PFC Spike Solution, 100 ng/mL.

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at 100 ng/mL in methanol.

7.5. PFC Isotope Dilution Analyte (IDA) Spike Solution, 1 ng/mL.

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each at 1 ng/mL in methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6 °C. Water samples must be analyzed within 28 days of collection.

9. QUALITY CONTROL

Refer to Section 9 of the main body of this SOP for Quality Control information.

9.1. If potable water samples from the state of New York (NY) are analyzed via this method the control limits for LCS and IDA for PFOS and PFOA recoveries are 70-130%. If these limits are not met, refer to Section 9 of the main body of this SOP for corrective action.

9.2. If POST (treatment) samples have positive detections, review the associated PRE and MID (treatment) samples for similar detections. Re-preparation and re-analysis may be needed.

9.3. If PFBS is detected in the method blank greater than the RL, evaluate data for impact. PFBS is a known laboratory artifact. Re-preparation and re-analysis may be needed.

10. CALIBRATION

Refer to Section 10 of the main body of the SOP for calibration information.

11. PROCEDURE

Refer to Section 11 of the main body of this SOP for procedures, other than those listed below specific to the in line SPE analysis.

11.1. Water Sample Preparation

11.1.1. Visually inspect samples for the presence of settled and or suspended sediment/particulate. Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.

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

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

11.1.2. Prepare an LCS and method blank by adding 250 mL of HPLC grade water into a 250 mL HDPE bottle.

11.1.3. If requested, find the client assigned sample for MS/MSD.

11.1.4. Spike directly into the sample bottles for the LCS and MS/MSD (if requested) with 0.050 mL (50 uL) of the LCS/Matrix PFC Spike solution (Section 7.4). This will result in a sample concentration of 20 ng/L. Shake well to disperse spike.

11.1.5. Measure 1 mL of each sample using an Eppendorf pipette and pour into a labeled 2.0 mL injection vial. This includes the LCS and method blank samples as well.

11.1.6. Be sure to "prepare" the pipette by collecting two 1 mL aliquots and disposing of them, and then collect the aliquot for testing.

11.1.7. Add 83 uL of surrogate solution (PFC IDA Spike Solution, Section 7.5) into each vial for each sample and QC sample. This will result in an extract concentration of 50 ng/L for the surrogate.

11.1.8. Add 577 uL of methanol to each sample for a final solvent composition of 40:60 methanol:water.

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

11.1.10. Vortex to mix the mixture well.

11.2. Instrument Analysis

11.2.1. Suggested operation conditions are listed in Tables 1A-1C below:

Table 1A - Routine Instrument Operating Conditions

HPLC Conditions (Shimadzu HPLC)					
Column (Column temp = 35°C)	Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm				
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol				
Gradient Program	**Time (min)**	**%A**	**%B**	**Curve**	**Flow Rate (mL/min)**
	0	90	10	6	0.60
	1	90	10	6	0.60

Table 1A - Routine Instrument Operating Conditions					
HPLC Conditions (Shimadzu HPLC)					
	1.5	35	65	6	0.60
	8	5	95	6	0.60
	8.1	1	99	6	0.60
	12	1	99	6	0.60
	12.5	90	10	6	0.60
	Maximum Pressure limit = 5,000 psi				
Injection Size	950 uL (fixed amount throughout the sequence)				
Run Time	17.1 minutes				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Ion Spray Voltage (kV)	4.5				
Entrance Potential (V)	5				
Declustering Potential (V)	25				
Desolvation Temp	550 ºC				
Curtain Gas (nitrogen) Flow	35 psi				
Collision Gas (nitrogen) Flow	8 psi				

Table 1B - Routine Instrument Operating Conditions						
Mass Spectrometer Scan Settings (SCIEX 5500)						
Compound	**Comments**	**Reaction (MRM)**	**Dwell (sec)**	**Ent. Pot. (V)**	**Col. Energy (V)**	**Declu. Pot. (V)**
PFBS	Perfluorobutanesulfonate	299 > 80	0.02	6	58	55
18O2-PFHxS	IDA	403 > 84	0.02	12	74	60
PFHpA	Perfluoroheptanoic acid	363 > 319	0.02	6	12	25
13C4-PFHpA	IDA	367 > 322	0.02	6	12	25
PFHxS	Perfluorohexanesulfonate	399 > 80	0.02	12	74	60
18O2-PFHxS	IDA	403 > 84	0.02	12	74	60
PFOA	Perfluorooctanoic acid	413 > 369	0.02	6	14	25
13C4PFOA	IDA	417 > 372	0.02	6	14	25
PFNA	Perfluorononanoic acid	463 > 419	0.02	6	14	25
13C5-PFNA	IDA	468 > 423	0.02	6	14	25
PFOS	Perfluorooctanesulfonate	499 > 80	0.02	9	108	65
13C4-PFOS	IDA	503 > 80	0.02	9	108	65

Table 1C				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFBS	6.68	18O2-PFHxS	7.76	Isotope Dilution
PFHpA	7.77	13C4-PFHpA	7.77	Isotope Dilution

Table 1C				
Native Compounds	**Typical Native RT (minutes)**	**IS analog**	**Typical IDA RT (minutes)**	**Quantitation Method**
PFHxS	7.76	18O2-PFHxS	7.76	Isotope Dilution
PFOA	8.44	13C4-PFOA	8.44	Isotope Dilution
PFNA	9.10	13C5-PFNA	9.10	Isotope Dilution
PFOS	9.06	13C4-PFOS	9.06	Isotope Dilution

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

11.2.3. A typical run sequence is as follows:

- Primer (A number of primers are injected for conditioning of the instrument before analysis, especially when the instrument was idled or changed from a different analysis).
- Blank
- Calibration Curve
- ICB
- ICV
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- MB
- LCS
- LCSD (if applicable)
- Sample 1
- Sample 1 MS (if applicable)
- Sample 1 MSD (if applicable)
- Sample 2 (up to sample 10 before next CCV)
- CCV
- Up to 10 samples.
- End sequence with CCV

12. CALCULATIONS

Refer to Section 12 of the main body of this SOP for calculation information.

13. METHOD PERFORMANCE

Refer to Section 13 of the main body of this SOP for method performance information.

14. POLLUTION PREVENTION

Refer to Section 14 of the main body of this SOP for pollution prevention information.

15. WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP for waste management information.

16. REFERENCES

Refer to Section 16 of the main body of this SOP for reference information.

17. METHOD MODIFICATIONS

17.1. Refer to Section 17 of the main body of this SOP for modifications from Method 537, except as detailed below:

17.1.1. Water samples are prepared at 1.0 mL, not 250 mL.

17.1.2. Water sample containers are not preserved with Trizma. Holding time has been changed to 28 days for analysis.

17.1.3. The eluents and HPLC configuration differs. As a result the final extract is in 40:60 methanol:water.

18. ATTACHMENTS

There are no attachments to this Appendix.

19. REVISION HISTORY

Revisions prior to 04/10/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025, Attachment 1, Revision 3.0, Effective 04/13/2018

19.1.1. Updated labeling and formatting of Tables 1A-1C.

19.1.2. Added section 11.2.3, detailing a typical run sequence.

19.2. WS-LC-0025, Attachment 1, Revision 2.9, Effective 11/27/2017

19.2.1. No changes to the attachment with this revision.

19.3. WS-LC-0025, Attachment 1, Revision 2.8, Effective 11/06/2017

19.3.1. Section 11.2.1, Routine Instrument Operating Conditions table (SCIEX 5500), added “Minimum of 10 scans/peak”.

19.4. WS-LC-0025, Attachment 1, Revision 2.7, Effective 09/22/2017

19.4.1. Section 6.5, removed "The 5 items above are to be maintained in the drawer labeled "Segregated Supplies for in line SPE Analysis" in the LC/MS instrument room."

19.4.2. Added Sections 9.1 – 9.3.

19.4.3. Updated Section 11.1.

19.4.4. Editorial changes.

19.5. WS-LC-0025 Attachment 1, Revision 2.6, Effective 08/11/2017

19.5.1. No revisions to this attachment.

19.6. WS-LC-0025 Attachment 1, Revision 2.5, Effective 07/10/2017

19.6.1. No revisions to this attachment.

19.7. WS-LC-0025 Attachment 1, Revision 2.4, Effective 04/25/2017

19.7.1. No revisions to this attachment.

19.8. WS-LC-0025 Attachment 1, Revision 2.3, Effective 04/10/2017

19.8.1. Changed all mentions of "direct aqueous injection (DAI)" to "in line solid phase extraction (SPE)."

19.8.2. Inserted Section 17.1, and changed formatting of the modifications to Method 537 to Section 17.2 and subheadings.

ATTACHMENT 3

Roux's Standard Operating Procedures

Date: May 5, 2000

1.0 PURPOSE

The purpose for this standard operating procedure (SOP) is to establish the guidelines for decontamination of all field equipment potentially exposed to contamination during drilling, and soil and water sampling. The objective of decontamination is to ensure that all drilling, and soil-sampling and water-sampling equipment is decontaminated (free of potential contaminants): 1) prior to being brought onsite to avoid the introduction of potential contaminants to the site; 2) between drilling and sampling events/activities onsite to eliminate the potential for cross-contamination between boreholes and/or wells; and 3) prior to the removal of equipment from the site to prevent the transportation of potentially contaminated equipment offsite.

In considering decontamination procedures, state and federal regulatory agency requirements must be considered because of potential variability between state and federal requirements and because of variability in the requirements of individual states. Decontamination procedures must be in compliance with state and/or federal protocols in order that regulatory agency(ies) scrutiny of the procedures and data collected do not result in non-acceptance (invalidation) of the work undertaken and data collected.

2.0 PROCEDURE FOR DRILLING EQUIPMENT

The following is a minimum decontamination procedure for drilling equipment. Drilling equipment decontamination procedures, especially any variation from the method itemized below, will be documented on an appropriate field form or in the field notebook.

2.1 The rig and all associated equipment should be properly decontaminated by the contractor before arriving at the test site.

2.2 The augers, drilling casings, rods, samplers, tools, rig, and any piece of equipment that can come in contact (directly or indirectly) with the soil, will be steam cleaned onsite prior to set up for drilling to ensure proper decontamination.

2.3 The same steam cleaning procedures will be followed between boreholes (at a fixed on-site location[s], if appropriate) and before leaving the site at the end of the study.

2.4 All on-site steam cleaning (decontamination) activities will be monitored and documented by a member(s) of the staff of Roux Associates, Inc.

2.5 If drilling activities are conducted in the presence of thick, sticky oils (e.g., PCBs) which coat drilling equipment, then special decontamination procedures may have to be utilized before steam cleaning (e.g., hexane scrub and wash).

2.6 Containment of decontamination fluids may be necessary (e.g., rinseate from steam cleaning) or will be required (e.g., hexane), and disposal must be in accordance with state and/or federal procedures.

3.0 PROCEDURE FOR SOIL-SAMPLING EQUIPMENT

The following is a minimum decontamination procedure for soil-sampling equipment (e.g., split spoons, stainless-steel spatulas). Soil-sampling equipment decontamination procedures, especially any variation from the method itemized below, will be documented on an appropriate field form or in the field notebook.

3.1 Wear disposable gloves while cleaning equipment to avoid cross-contamination and change gloves as needed.

3.2 Steam clean the sampler or rinse with potable water. If soil-sampling activities are conducted in the presence of thick, sticky oils (e.g., PCBs) which coat sampling equipment, then special decontamination procedures may have to be utilized before steam cleaning and washing in detergent solution (e.g., hexane scrub and wash).

3.3 Prepare a non-phosphate, laboratory-grade detergent solution and distilled or potable water in a clean bucket.

3.4 Disassemble the sampler, as necessary and immerse all parts and other sampling equipment in the solution.

3.5 Scrub all equipment in the bucket with a brush to remove any adhering particles.

3.6 Rinse all equipment with copious amounts of potable water followed by distilled or deionized water.

3.7 Place clean equipment on a clean plastic sheet (e.g., polyethylene)

3.8 Reassemble the cleaned sampler, as necessary.

3.9 Transfer the sampler to the driller (or helper) making sure that this individual is also wearing clean gloves or wrap the equipment with a suitable material (e.g., plastic bag, aluminum foil.

As part of the decontamination procedure for soil-sampling equipment, state and/or federal protocols must be considered. These may require procedures above those specified as minimum for Roux Associates, Inc., such as the use of nitric acid, acetone, etc. Furthermore, the containment and proper disposal of decontamination fluids must be considered with respect to regulatory agency(ies) requirements.

4.0 PROCEDURE FOR WATER-SAMPLING EQUIPMENT

The following is a decontamination procedure for water-sampling equipment (e.g., bailers, pumps). Water-sampling equipment decontamination procedures, especially any variation from the method itemized below, will be documented on an appropriate field form or in the field notebook.

4.1 Decontamination procedures for bailers follow:

a. Wear disposable gloves while cleaning bailer to avoid cross-contamination and change gloves as needed.

b. Prepare a non-phosphate, laboratory-grade detergent solution and potable water in a bucket.

c. Disassemble bailer (if applicable) and discard cord in an appropriate manner and scrub each part of the bailer with a brush and solution.

d. Rinse with potable water and reassemble bailer.

e. Rinse with copious amounts of distilled or deionized water.

f. Air dry.

g. Wrap equipment with a suitable material (e.g., clean plastic bag, aluminum foil).

h. Rinse bailer at least three times with distilled or deionized water before use.

4.2 Decontamination procedures for pumps follow:

a. Wear disposable gloves while cleaning pump to avoid cross-contamination and change gloves as needed.

b. Prepare a non-phosphate, laboratory-grade detergent solution and potable water in a clean bucket, clean garbage can, or clean 55-gallon drum.

c. Flush the pump and discharge hose (if not disposable) with the detergent solution and discard disposable tubing and/or cord in an appropriate manner.

d. Flush the pump and discharge hose (if not disposable) with potable water.

e. Place the pump on clear plastic sheeting.

f. Wipe any pump-related equipment (e.g., electrical lines, cables, discharge hose) that entered the well with a clean cloth and detergent solution, and rinse or wipe with a clean cloth and potable water.

g. Air dry.

h. Wrap equipment with a suitable material (e.g., clean plastic bag).

As part of the decontamination procedure for water-sampling equipment, state and/or federal protocols must be considered. These may require procedures above those specified as minimum for Roux Associates, Inc., such as the use of nitric acid, acetone, etc. Furthermore, the containment and proper disposal of decontamination fluids must be considered with respect to regulatory agency(ies) requirements.

Date: May 5, 2000

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish guidelines for the collection of soil samples for laboratory analysis. This SOP is applicable to soil samples collected from split-spoon samplers during drilling, hand auger samples, grab samples from stockpiled soils, surface samples, test pit samples, etc.

2.0 CONSIDERATIONS

Soil samples may be collected in either a random or biased manner. Random samples can be based on a grid system or statistical methodology. Biased samples can be collected in areas of visible impact or suspected source areas. Soil samples can be collected at the surface, shallow subsurface, or at depth. When samples are collected at depth the water content should be noted, since generally "soil sampling" is restricted to the unsaturated zone. Equipment selection will be determined by the depth of the sample to be collected. A thorough description of the sampling locations and proposed methods of sample collection should be included in the work plan.

Commonly, surface sampling refers to the collection of samples at a 0 to 6-inch depth interval. Certain regulatory agencies may define the depth interval of a surface sample differently, and this must be defined in the work plan. Collection of surface soil samples is most efficiently accomplished with the use of a stainless-steel trowel or scoop. For samples at greater depths a decontaminated bucket auger or power auger may be needed to advance the hole to the point of sample collection. Another clean bucket auger should then be used to collect the sample. To collect samples at depths of greater than approximately six feet the use of a drill rig and split spoon samples will usually be necessary. In some situations, sample locations are accessed with the use of a backhoe.

3.0 MATERIALS/EQUIPMENT

a. A work plan which outlines soil sampling requirements.

b. Field notebook, field form(s), maps, chain-of-custody forms, and custody seals.

c. Decontamination supplies (including: non-phosphate, laboratory grade detergent, buckets, brushes, potable water, distilled water, regulatory-required reagents, aluminum foil, plastic sheeting, etc.).

d. Sampling device (split-spoon sampler, stainless steel hand auger, stainless steel trowel, etc.).

e. Stainless steel spoons or spatulas.

f. Disposable sampling gloves.

g. Laboratory-supplied sample containers with labels.

h. Cooler with blue or wet ice.

i. Plastic sheeting.

j. Black pen and indelible marker.

k. Zip-lock bags and packing material.

l. Tape measure.

m. Paper towels or clean rags.

n. Masking and packing tape.

o. Overnight (express) mail forms.

4.0 DECONTAMINATION

All reusable sampling equipment will be thoroughly cleaned according to the decontamination SOP. Where possible, thoroughly pre-cleaned and wrapped sampling equipment should be used and dedicated to individual sampling locations. Disposable items such as sampling gloves, aluminum foil, and plastic sheeting will be changed after each use and discarded in an appropriate manner.

5.0 PROCEDURE

5.1 Prior to collecting soil samples, ensure that all sampling equipment has been thoroughly cleaned according to the decontamination SOP. If samples are to be collected at depth, then the boring must be advanced with thoroughly cleaned equipment to the desired sampling horizon and a different thoroughly cleaned sampler must be used to collect the sample.

5.2 Using disposable gloves and a pre-cleaned, stainless steel spatula or spoon, extract the soil sample from the sampler, measure the recovery, and separate the wash from the true sample. Where allowed by regulatory agency(ies), disposable plastic spoons may be used.

5.3 Place the sample in a laboratory-supplied, pre-cleaned sample container. This should be done as quickly as possible and this is especially important when sampling for volatile organic compounds (VOCs). Samples to be analyzed for VOCs must be collected prior to other constituents.

5.4 The sample container will be labeled with appropriate information such as, client name, site location, sample identification (location, depth, etc.), date and time of collection, and sampler's initials.

5.5 Using the remaining portion of soil from the sampler, log the sample in detail and record sediment characteristics (color, odor, moisture, texture, density, consistency, organic content, layering, grain size, etc.).

5.6 If soil samples are to be composited in the field, then equal portions from selected locations will be placed on a clean plastic sheet and homogenized. Alternately, several samples may be submitted to the laboratory for compositing by weight. The method used is dependent upon regulatory requirements. Specific compositing procedures shall be approved by the appropriate regulatory agency and described in the work plan. Samples to be analyzed for VOCs will not be composited unless required by a regulatory agency.

5.7 After the sample has been collected, labeled, and logged in detail, it is placed in a zip-lock bag and stored in a cooler at 4°C.

5.8 A chain-of-custody form is completed for all samples collected. One copy is retained and two are sent with the samples in a zip-lock bag to the laboratory. A custody seal is placed on the cooler prior to shipment.

5.9 Samples collected from Monday to Friday are to be delivered to the laboratory within 24 hours of collection. If Saturday delivery is unavailable, samples collected on Friday must be delivered by Monday morning. Check the work plan to determine if any analytes require a shorter delivery time.

5.10 The field notebook and appropriate forms should include, but not be limited to the following: client name, site location, sample location, sample depth, sample identification, date and time collected, sampler's name, method of sample collection, number and type of containers, geologic description of material, description of decontamination procedures, etc. A site map should be prepared with exact measurements to each sample location in case follow-up sampling is necessary.

5.11 All reusable sampling equipment must be thoroughly cleaned in accordance with the decontamination SOP. Following the final decontamination (after all samples are collected) the sampling equipment is wrapped in aluminum foil. Discard any gloves, foil, plastic, etc. in an appropriate manner that is consistent with site conditions.

END OF PROCEDURE

Date: May 5, 2000

1.0 PURPOSE

The purpose of this standard operating procedure (SOP) is to establish guidelines for sample handling which will allow consistent and accurate results. Valid chemistry data are integral to investigations that characterize media-quality conditions. Thus, this SOP is designed to ensure that once samples are collected, they are preserved, packed and delivered in a manner which will maintain sample integrity to as great an extent as possible. The procedures outlined are applicable to most sampling events and any required modifications must be clearly described in the work plan.

2.0 CONSIDERATIONS

Sample containers, sampling equipment decontamination, quality assurance/quality control (QA/QC), sample preservation, and sample handling are all components of this SOP.

2.1 Sample Containers

Prior to collection of a sample, considerations must be given to the type of container that will be used to store and transport the sample. The type and number of containers selected is usually based on factors such as sample matrix, potential contaminants to be encountered, analytical methods requested, and the laboratory's internal quality assurance requirements. In most cases, the overriding considerations will be the analytical methodology, or the state or federal regulatory requirements because these regulations generally encompass the other factors. The sample container selected is usually based on some combination of the following criteria:

a. Reactivity of Container Material with Sample

Choosing the proper composition of sample containers will help to ensure that the chemical and physical integrity of the sample is maintained. For sampling potentially hazardous material, glass is the recommended container type because it is chemically inert to most substances. Plastic containers are not recommended for most hazardous wastes because the potential exists for contaminants to adsorb to the surface of the plastic or for the plasticizer to leach into the sample.

In some instances, however, the sample characteristics or analytes of interest may dictate that plastic containers be used instead of glass. Because some metals species will adhere to the sides of the glass containers in an aqueous matrix, plastic bottles (e.g., nalgene) must be used for samples collected for metals analysis. A separate, plastic

container should accompany glass containers if metals analysis is to be performed along with other analyses. Likewise, other sample characteristics may dictate that glass cannot be used. For example, in the case of a strong alkali waste or hydrofluoric solution, plastic containers may be more suitable because glass containers may be etched by these compounds and create adsorptive sites on the container's surface.

b. Volume of the Container

The volume of sample to be collected will be dictated by the analysis being performed and the sample matrix. The laboratory must supply bottles of sufficient volume to perform the required analysis. In most cases, the methodology dictates the volume of sample material required to complete the analysis. However, individual laboratories may provide larger volume containers for various analytes to ensure sufficient quantities for duplicates or other QC checks.

To facilitate transfer of the sample from the sampler into the container and to minimize spillage and sample disturbance, wide-mouth containers are recommended. Aqueous volatile organic samples must be placed into 40-milliliter (ml) glass vials with polytetrafluoroethylene (PTFE) (e.g., TeflonTM) septums. Non-aqueous volatile organic samples should be collected in the same type of vials or in 4-ounce (oz) wide-mouth jars provided by the laboratory. These jars should have PTFE-lined screw caps.

c. Color of Container

Whenever possible, amber glass containers should be used to prevent photodegradation of the sample, except when samples are being collected for metals analysis. If amber containers are not available, then containers holding samples should be protected from light (i.e., place in cooler with ice immediately after filling).

d. Container Closures

Container closures must screw on and off the containers and form a leak-proof seal. Container caps must not be removed until the container is ready to be filled with the sample, and the container cap must be replaced (securely) immediately after filling it. Closures should be constructed of a material which is inert with respect to the sampled material, such as PTFE (e.g., TeflonTM). Alternately, the closure may be separated from the sample by a closure liner that is inert to the sample material such as PTFE sheeting. If soil or sediment samples are being collected, the threads of the container must be wiped clean with a dedicated paper towel or cloth, so the cap can be threaded properly.

e. Decontamination of Sample Containers

Sample containers must be laboratory cleaned by the laboratory performing the analysis. The cleaning procedure is dictated by the specific analysis to be performed on the sample. Sample containers must be carefully examined to ensure that all containers appear clean. Do not mistake the preservative as unwanted residue. The bottles should not be field cleaned. If there is any question regarding the integrity of the bottle, then the laboratory must be contacted immediately and the bottle(s) replaced.

f. Sample Bottle Storage and Transport

No matter where the sample bottles are, whether at the laboratory waiting to be packed for shipment or in the field waiting to be filled with sample, care must be taken to avoid contamination. Sample shuttles or coolers, and sample bottles must be stored and transported in clean environments. Sample bottles and clean sampling equipment must never be stored near solvents, gasoline, or other equipment that is a potential source of cross-contamination. When under chain of custody, sample bottles must be secured in locked vehicles, and custody sealed in shuttles or in the presence of authorized personnel. Information which documents that proper storage and transport procedures have been followed must be included in the field notebook and on appropriate field forms.

2.2 Decontamination of Sampling Equipment

Proper decontamination of all re-usable sampling equipment is critical for all sampling episodes. The SOP for Decontamination of Field Equipment and SOPs for method-specific or instrument-specific tasks must also be referred to for guidance for decontamination of various types of equipment.

2.3 Quality Assurance/Quality Control Samples

QA/QC samples are intended to provide control over the proper collection and tracking of environmental measurements, and subsequent review, interpretation and validation of generated analytical data. The SOPs for Collection of Quality Control Samples, for Evaluation and Validation of Data, and for Field Record Keeping and Quality Assurance/Quality Control must be referred to for detailed guidance regarding these respective procedures. SOPs for method-specific or instrument-specific tasks must also be referred to for guidance for QA/QC procedures.

2.4 Sample Preservation Requirements

Certain analytical methodologies for specific analytes require chemical additives in order to stabilize and maintain sample integrity. Generally, this is accomplished under the following two scenarios:

a. Sample bottles are preserved at the laboratory prior to shipment into the field.

b. Preservatives are added in the field immediately after the samples are collected.

Many laboratories provide pre-preserved bottles as a matter of convenience and to help ensure that samples will be preserved immediately upon collection. A problem associated with this method arises if not enough sample could be collected, resulting in too much preservative in the sample. More commonly encountered problems with this method include the possibility of insufficient preservative provided to achieve the desired pH level or the need for additional preservation due to chemical reactions caused by the addition of sample liquids to pre-preserved bottles. The use of pre-preserved bottles is acceptable; however, field sampling teams must always be prepared to add additional preservatives to samples if the aforementioned situations occur. Furthermore, care must be exercised not to overfill sample bottles containing preservatives to prevent the sample and preservative from spilling and therefore diluting the preservative (i.e., not having enough preservative for the volume of sample).

When samples are preserved after collection, special care must be taken. The transportation and handling of concentrated acids in the field requires additional preparation and adherence to appropriate preservation procedures. All preservation acids used in the field should be trace-metal or higher-grade.

2.5 Sample Handling

After the proper sample bottles have been received under chain-of-custody, properly decontaminated equipment has been used to collect the sample, and appropriate preservatives have been added to maintain sample integrity, the final step for the field personnel is checking the sample bottles prior to proper packing and delivery of the samples to the laboratory.

All samples should be organized and the labels checked for accuracy. The caps should be checked for tightness and any 40-ml volatile organic compound (VOC) bottles must be checked for bubbles. Each sample bottle must be placed in an individual Ziploc® bag to protect the label, and placed on ice. The bottles must be carefully packed to prevent breakage during transport. When several bottles have been collected for an individual sample, they should not be placed adjacent to each other in the cooler to prevent possible breakage of all bottles for a given sample. If there are any samples which are known or suspected to be highly

contaminated, these should be placed in an individual cooler under separate chain-of-custody to prevent possible cross contamination. Sufficient ice (wet or blue packs) should be placed in the cooler to maintain the temperature at 4 degrees Celsius (°C) until delivery at the laboratory. Consult the work plan to determine if a particular ice is specified as the preservation for transportation (e.g., the United States Environmental Protection Agency does not like the use of blue packs because they claim that the samples will not hold at 4°C). If additional coolers are required, then they should be purchased. The chain-of-custody form should be properly completed, placed in a "zip-lock" bag, and placed in the cooler. One copy must be maintained for the project files. The cooler should be sealed with packing tape and a custody seal. The custody seal number should be noted in the field book. Samples collected from Monday through Friday will be delivered to the laboratory within 24 hours of collection. If Saturday delivery is not available, samples collected on Friday must be delivered by Monday morning. Check the work plan to determine if certain analytes require a shorter delivery time. If overnight mail is utilized, then the shipping bill must be maintained for the files and the laboratory must be called the following day to confirm receipt.

3.0 EQUIPMENT AND MATERIALS

3.1 General equipment and materials may include, but not necessarily be limited to, the following:

a. Sample bottles of proper size and type with labels.

b. Cooler with ice (wet or blue pack).

c. Field notebook, appropriate field form(s), chain-of-custody form(s), custody seals.

d. Black pen and indelible marker.

e. Packing tape, "bubble wrap," and "zip-lock" bags.

f. Overnight (express) mail forms and laboratory address.

g. Health and safety plan (HASP).

h. Work plan/scope of work.

i. Pertinent SOPs for specified tasks and their respective equipment and materials.

3.2 Preservatives for specific samples/analytes as specified by the laboratory. Preservatives must be stored in secure, spillproof glass containers with their content, concentration, and date of preparation and expiration clearly labeled.

3.3 Miscellaneous equipment and materials including, but not necessarily limited to, the following:

a. Graduated pipettes.

b. Pipette bulbs.

c. Litmus paper.

d. Glass stirring rods.

e. Protective goggles.

f. Disposable gloves.

g. Lab apron.

h. First aid kit.

i. Portable eye wash station.

j. Water supply for immediate flushing of spillage, if appropriate.

k. Shovel and container for immediate containerization of spillage-impacted soils, if appropriate.

4.0 PROCEDURE

4.1 Examine all bottles and verify that they are clean and of the proper type, number, and volume for the sampling to be conducted.

4.2 Label bottles carefully and clearly with project name and number, site location, sample identification, date, time, and the sampler's initials using an indelible marker.

4.3 Collect samples in the proper manner (refer to specific sampling SOPs).

4.4 Conduct preservation activities as required after each sample has been collected. Field preservation must be done immediately and must not be done later than 30 minutes after sample collection.

4.5 Conduct QC sampling, as required.

4.6 Seal each container carefully and place in an individual "zip lock" bag.

4.7 Organize and carefully pack all samples in the cooler immediately after collection (e.g., bubble wrap). Insulate samples so that breakage will not occur.

4.8 Complete and place the chain-of-custody form in the cooler after all samples have been collected. Maintain one copy for the project file. If the cooler is to be transferred several times prior to shipment or delivery to the laboratory, it may be easier to tape the chain-of-custody to the exterior of the sealed cooler. When exceptionally hazardous samples are known or suspected to be present, this should be identified on the chain-of-custody as a courtesy to the laboratory personnel.

4.9 Add additional ice as necessary to ensure that it will last until receipt by the laboratory.

4.10 Seal the cooler with packing tape and a custody seal. Record the number of the custody seal in the field notebook and on the field form. If there are any exceptionally hazardous samples, then shipping regulations should be examined to ensure the sample containers and coolers are in compliance and properly labeled.

4.11 Samples collected from Monday through Friday will be delivered to the laboratory within 24 hours of collection. If Saturday delivery is not available, samples collected on Friday must be delivered by Monday morning. Check the work plan to determine if certain analytes require a shorter delivery time.

4.12 Maintain the shipping bill for the project files if overnight mail is utilized and call the laboratory the following day to confirm receipt.

END OF PROCEDURE