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SITE CHARACTERIZATION WORK PLAN

2283 Second Avenue –Site #231126
2283 Second Avenue
New York, New York 10035

Prepared For:

Contract# D009808, Work Assignment No. 38
New York State Department of Environmental Conservation
Division of Environmental Remediation
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1.0 INTRODUCTION

On November 23, 2022, HRP Associates, Inc. (HRP) was authorized to complete this New York State Department of Environmental Conservation (NYSDEC) Work Assignment (WA) No. 38 (D009808-38) for Site Characterization (SC) for 2283 Second Avenue Site (Site No. 231126), which is located at 2283 Second Avenue, New York, NY (the Site). The focus of this SC is to characterize potential impacts to soil, groundwater, and soil vapor on the Site associated with its historic use as a dry cleaner. The scope of work for the SC, discussed herein, was developed based on HRP's review of a previous investigation conducted by the New York City Office of Environmental Remediation (NYC OER) at the neighboring 249 East 117th Street (Voluntary Cleanup Program [VCP] Project Nos. 18EH-N080M/18CVCP022M) in 2017 as well as discussions and planning with NYSDEC staff.

1.1 Purpose and Objectives

This site-specific SC Work Plan (Work Plan) describes the details of the scope of work, including all proposed field activities, laboratory analyses, and data QA/QC evaluation that will be associated with the SC at the Site. This document is intended to supplement information provided in the NYSDEC-approved *Generic Field Activities Plan for Work Assignments*, completed by HRP on August 8, 2019.

The purpose of the SC is to determine whether the Site poses little or no threat to public health and the environment or if it poses a threat and whether the threat requires further investigation. In accordance with DER-10 *Technical Guidance for Site Investigation and Remediation (May 2010),* the primary objectives of the SC scope of work are to:

- Investigate the identified areas of concern (AOCs) associated with the Site, determine if they have resulted in surface or subsurface contamination and evaluate the extent of the contamination.

- Obtain geologic and hydrogeologic data from the Site. The specific information that should be collected and/or verified includes soil types (or fill), depth to groundwater, groundwater flow direction, subsurface geology, bedrock characteristics, etc.

- Determine if applicable standards, criteria, and guidance contained in NYSDEC DER-10 and set forth for the Site are contravened.

- Preliminarily delineate the vertical and horizontal extent of contaminated soil, groundwater, and soil vapor if any.

- Establish a baseline for any remedial work that will be necessary to address impacted media.

- Determine if the Site represents a threat to public health or the environment.

1.2 Site Description and Background Information

The 2283 Second Avenue Site (#231126), located at 2283 Second Avenue, New York, NY (**Figure 1**), is the focus of this investigation. The property is identified on the NYC Department of Finance (DOF) tax map as Manhattan block 1667, lot 21. The 0.0420-acre Site currently consists of two four-story buildings with a two-story slab-on-grade connecting structure on the west of the southern building and a rear yard located west of the northern building. The Site buildings are mixed-use with a connected first floor commercial space (occupied by a credit union) and residential apartments on upper floors. Based on a site visit performed by the NYSDEC, each building includes a separate unfinished basement. Each basement includes a boiler room in the eastern portion of the basement and each boiler room contains a sump. During NYSDEC's visit to the Site, it was noted that the concrete slab of the basement floor was in good condition and did not appear to be the original slab. Floor drains were also observed in the building basements during NYSDEC's visit to the Site. The Site is depicted on **Figure 2**.

The property is zoned R9A (high density contextual residential) with a C2-5 commercial overlay on the NYC Zoning Tax Lot Database. Properties surrounding the Site consist of residential apartments, mixed-use commercial/residential buildings, and commercial buildings. At present the areas surrounding the property include:

North: Mixed use multi-story commercial/residential buildings including a catering service, hair/nail salons, and an HVAC shop, followed by E 118th Street (190 ft).

South: East 117th Street (0 ft) followed by multi-story mixed use commercial/residential buildings including community organizations, retail stores, and restaurants followed by East 116th Street (285 ft).

East: Second Avenue and the MTA Second Avenue Subway line (0 ft), a mixed use commercial/residential building with retail space on the ground floor (100 ft), PS – 155: The William Paca School (205 ft), followed by other mixed-use buildings and First Avenue.

West: 247 East 117th Street : NYC OER Site Nos. 18EH-N080M/18CVCP022M, which is currently a vacant lot (0 ft), multi-story mixed-use commercial/residential properties including a computer repair store, an automotive service facility (100 ft), restaurants and retail space, followed by Third Avenue (600 ft).

History of the Site and surrounding area described here is based on available information obtained by Environmental Data Resources, (EDR), which includes a repository of Sanborn Fire Insurance maps, historic topographic maps and aerial photos, city directory listings, and environmental documentation of surrounding properties including, but not limited to, the NYSDEC spill database and Resource Conservation and Recovery Act (RCRA) registered sites. According to Sanborn Fire Insurance Maps, the Site has been developed since at least 1896. On the 1896 Sanborn map, the Site is depicted as being improved with two multi-story buildings with a basement. Beginning on the 1911 Sanborn map, the Site labeled as "stores/dwellings" indicating mixed commercial and residential use. The Site continues to be depicted as two mixed-use commercial/residential buildings on successive Sanborn maps up through the final available map dated 2005.

According to city directories obtained from EDR, historic uses of the Site include a shoe cleaning business operating under the name Soranello J Shoe Cleaning (1927), a food distributor/grocery store operating under the name Conczoniri Frank Fruit & Falcone Emilio Josephine Meats (1934), an automotive repair or automotive parts shop operating under the name of Eppy's Automotive Accessories (1947-1950), a dry cleaning facility operating under the name of Twins Cleaners (1968-1999), and an emergency towing service operating under the name of 24 Hour 7 Day Emergency Towing (2006). Currently, a credit union operates out of the Site building with apartments above. In 1992 Twins Cleaners was registered as a RCRA "Large Quantity Generator" of D001 undefined hazardous waste and F002 spent halogenated solvents. Twins Cleaners was listed as "not a generator, verified" in 1999, 2006, and 2007 according to RCRA records.

Several properties of interest have been identified surrounding the Site based on historic uses and regulatory records obtained through EDR. Notably, nearby properties 2287-2289 Second Avenue, 2291 Second Avenue, and 245 East 117th Street have been identified as historic dry cleaners.

Regulatory records include "E designations" which are issued by the NYC OER due to potential presence of hazardous materials, noise impacts, or air quality impacts associated with a property. The "E designation" restricts development and use changes on the given tax lot and requires testing, remediation, or ongoing site management for hazardous materials to be completed before the removal of an "E designation."

Properties of interest identified based on historic use or environmental database entries located within 500 feet of the Site are presented on **Table 1**. Current and historical property use is depicted on **Figure 3**.

1.3 Site Geology and Hydrogeology

The Site lies at an elevation of approximately 18 ft above mean sea level (amsl). Topography of the Site and surrounding area slopes east towards the Harlem River.

The New York State "Geologic Map of New York – Lower Hudson Sheet" indicates the bedrock underlying the Site is part of the Inwood Marble, a dolomite marble, calc-schist, granulite, and quartzite overlain by calcite marble (Fisher D.W. et al, 1970). Surficial geology is mapped as till, deposited by glacial ice with a variable texture consisting of poorly sorted mixtures of clay, sand, silt, and gravel (Caldwell et. al., 1986). According to the United States Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS) Web Soil Survey, the Site and surrounding area are mapped as Urban Land.

Based on documents reviewed by HRP, no previous subsurface investigations have been performed on-site. A remedial investigation on the immediately adjacent 247-249 East 117th Street property conducted by Hillmann Consulting, LLC (Hillmann) in 2017 described subsurface soils as sand overlain by a discontinuous layer of fill material with a maximum thickness of 5 feet below grade (ft bg). Bedrock was encountered at 8-12 ft bg at the 247-249 East 117th Street Site.

According to the Hillmann 2017 Remedial Investigation, on the 247-249 East 117th Street Site, approximate depth to groundwater was reported to be 10 ft bg. Groundwater flow direction has not

been determined by any previous investigations but is inferred to flow east/southeast towards the Harlem River.

1.4 Previous Investigations and Remedial Actions

Based on HRP's review, no previous environmental investigations have been conducted on-site. In preparation of this work plan HRP reviewed the following previous investigation reports and documents prepared for the neighboring 247-249 East 117th Street Site:

- Remedial Investigation Report (RIR), prepared by Hillmann and dated September 2017.
- Remedial Action Work Plan, prepared by Hillmann and dated October 2017.

In September 2017, Hillmann conducted a RI on the 247-249 East 117th Street property – a vacant lot immediately adjacent to 2283 Second Avenue to the northwest – which characterized impacts to soil, groundwater, and soil vapor on the 247-249 East 117th Street property related to a #2 fuel oil spill registered in the NYSDEC database (Spill No. 9601565; closed April 30, 1996) and potential contamination from surrounding properties which were used as dry cleaning facilities either historically or at the time of the investigation (**Table 1**). According to the RI and review of available documents obtained through EDR, historic uses of the 247-249 East 117th Street property include residential uses, a doctor's office, a recreation center, and a dry nursery (1911-2005). The RI included the installation of five soil borings to refusal depths of 8-12 ft bg, three temporary monitoring wells installed in the overburden, and four exterior soil vapor points. Findings from the RI are summarized below:

- Chlorinated volatile organic compounds (CVOCs) including tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and vinyl chloride were detected in groundwater and soil vapor on the 247-249 East 117th Street property. The source of CVOC contamination was attributed to historic and contemporary surrounding property use as dry cleaning facilities (including the 2283 Second Avenue Site).
- Laboratory analysis of 10 soil samples collected from 5 soil borings indicated pesticides and metals were detected at concentrations exceeding Unrestricted Use Soil Cleanup Objectives (UUSCOs) including 4'4-DDE, dieldrin, 4'4-DDD, 4'4-DDT, copper, lead, mercury, and zinc. Concentrations of metals including barium and manganese exceeded UUSCOs. VOCs, semivolatile organic compounds (SVOCs), and polychlorinated biphenyls (PCBs) were not detected at concentrations exceeding UUSCOs in any soil samples.
- Laboratory analysis of 3 grab groundwater samples from 3 temporary monitoring wells indicated CVOCs were detected at concentrations exceeding Technical and Operational Guidance Series (TOGS) 1.1.1 Class GA criteria. The pesticides dieldrin, 4'4-DDT, and chlordane and metals manganese (dissolved), aluminum, barium, beryllium, and iron, were also detected in concentrations exceeding TOGS 1.1.1 Class GA criteria in grab groundwater samples collected from the property. PCE and TCE were detected at maximum concentrations of 1,660 micrograms per liter (µg/L) and 120 µg/L in a grab groundwater sample GW-1, located on the southeastern portion of the 247-249 East 117th Street property, bordering

the 2283 Second Avenue Site. Grab groundwater results from the 2017 RI conducted at 247-249 East 117th Street property are depicted on **Figure 2**.

- Laboratory analysis of samples from 4 soil vapor points indicated elevated concentrations of CVOCs were present in soil vapor beneath the property. PCE and TCE were detected at maximum concentrations of 1,600 micrograms per cubic meter (µg/m³) and 120 µg/m³, respectively in soil vapor sample SV-4 located on the southwestern portion of the 247-249 East 117th Street property. Soil vapor results from the 2017 RI conducted at 247-249 East 117th Street property are depicted on **Figure 2**.

Based on the findings of the RI, a Track 4 remedy was proposed for the 247-249 East 117th Street property consisting of excavation and off-site disposal of approximately 900 tons of soil/fill exceeding Track 4 Restricted Residential SCOs, the installation of a composite cover system, a soil vapor barrier system, and an active sub-slab depressurization system (SSDS); and the implementation of institutional controls through a site management plan. The NYC OER memorialized this remedy selection in a Notice to Proceed dated October 1, 2018. Aerial imagery from January 2023 indicates the 247-249 East 117th Street property remains undeveloped.

Based on available information, CVOC contamination in groundwater and soil vapor on the adjacent 247-249 East 117th Street property may be attributable to historic property use on the 2283 Second Avenue Site.

1.5 Areas of Concern

Based on review of the RI conducted on the adjacent 247-249 East 117th Street property, environmental database records obtained from EDR, and discussions with NYSDEC, HRP has identified CVOCs including PCE, TCE, cis-1,2-DCE and vinyl chloride as Site contaminants of concern. Chlorinated solvents may have historically been used at the Site while operating as a dry cleaner and auto parts store. Additionally, the Site was listed as a "Large Quantity Generator" of waste code F002 – spent halogenated solvents in 1992. Given the time period which the Site reportedly operated as a dry cleaner (1968-1999) and auto parts store (1947-1950), which supersede RCRA and other environmental regulations, improper disposal of PCE and other chlorinated solvents may have occurred on-site. Based on HRP's review of photographs from the NYSDEC's visit to the Site, and discussions with NYSDEC, the following AOCs have been identified:

- Sumps and floor drains within the basements of the Site buildings which may have historically received discharges of PCE or other chemicals. It should be noted that NYSDEC's observations of the Site indicate the slab has been replaced. Although the current sumps and floor drains may not have been present during dry cleaning operations, it is possible that the original slab included similar features in the same location, therefore these features will be investigated as AOCs.
- The rear yard on the western portion of the Site which may be a historic dumping area for PCE and other chemicals.
- Off-site properties which may have used chlorinated solvents, including those identified below. A list of properties of interest within 500 feet of the Site are presented on **Table 1** and **Figure 3**.

- 2287-2289 Second Avenue (Property 1 on **Figure 3**): Historic use as a mattress manufacturer, refrigerator repair, and automotive repair. The tax lot containing 2287-2289 Second Avenue has been issued an "E designation" for potential hazardous materials from NYC OER.
- 247-249 E 117th Street (Property 2 on **Figure 3**): Registration in the NYC OER Voluntary Cleanup Program (VCP) as project number 18EH-N080M/18CVCP022M. The tax lot containing 247-249 E 117th Street has been issued an "E designation" for potential hazardous materials from NYC OER.
- 245 E 117th Street (Property 3 on **Figure 3**): Historic use as an automotive repair shop (1980-2005) and a dry-cleaning facility (2005-2021).
- 2291 Second Avenue (Property 4 on **Figure 3**): Historic use as a dry-cleaning facility (2001-2012).
- 2293 Second Avenue (Property 5 on **Figure 3**): Historic use as a coal yard (1927-1942) and an automotive repair center (1958-2017). The tax lot containing 2293 Second avenue has been issued an "E designation" for potential hazardous materials from NYC OER.

Additional AOCs warranting further characterization may be identified during Site walkthroughs and initial phases of investigation.

Based on the findings of previous investigations and discussions with NYSDEC, HRP has developed the following scope of work to investigate impacts to Site soil, groundwater, and soil vapor related to historic Site operations and surrounding property use through the installation of soil borings, monitoring wells, and soil vapor points on the Site. A Site plan with proposed investigation locations is depicted on **Figure 2**.

2.0 SITE CHARACTERIZATION SCOPE OF WORK

This scope of work has been designed to gather data to evaluate each project objective listed in **Section 1.1**. The following sections provide specifics regarding the scope of work developed under this NYSDEC-approved Work Assignment (D009808-38) in support of the 2283 Second Avenue Site SC (#231126).

2.1 Preliminary Activities

As part of the scope of work, the following documents have been prepared under this Work Assignment:

- Project-specific Work Plan (this document) to accompany the generic Field Activities Plan (FAP),
- Site-specific Health and Safety Plan (HASP) (included as **Appendix A** of this Work Plan),
- Generic Quality Assurance Project Plan (QAPP).

These NYSDEC-approved generic FAP, HASP, and QAPP are on file with the NYSDEC. The site-specific elements are provided below.

2.1.1 Work Plan

This Work Plan has been prepared for use in performing the SC and will serve as the "site-specific FAP". This Work Plan identifies the components of the SC and a description of the tasks to be performed including the specific methods or procedures that will be used to conduct the field sampling. A proposed project schedule is included in **Section 4.1** of this Work Plan.

2.1.2 Health and Safety Plan

A site-specific HASP is provided in **Appendix A**. The site-specific HASP provides guidance to maximize health and safety of on-site workers during SC - specific tasks including media sampling, installation of wells, surveying and other field related activities.

2.1.3 Community Air Monitoring Plan

A Community Air Monitoring Plan (CAMP) that details procedures for air monitoring during intrusive activities is included in **Appendix B**.

2.1.4 Quality Assurance Project Plan

A site-specific QAPP has been prepared and is included in **Section 4** of this Work Plan. The site-specific QAPP was prepared as a supplement to the Generic QAPP with necessary site-specific information. Deviations from the protocols specified in the QAPP will be subject to the NYSDEC approval.

The Generic QAPP provides general information related to QA/QC procedures associated with the collection and analysis of samples of environmental media and includes specific representative standard operating procedures (SOPs) applicable to sample handling and field instrumentation use. Information provided in the Generic QAPP includes definitions and generic goals for data quality and required types and quantities of QA/QC samples. The procedures address field documentation; sample handling, custody, and shipping; instrument calibration and maintenance; auditing; data reduction, validation, and reporting; corrective action requirements; and QA/QC reporting specific to the analyses performed by the laboratories that are used for analysis of environmental media collected under Standby Contract No. D009808.

All laboratory analytical work will be performed by a NYSDOH Environmental Laboratory Approval Program (ELAP) approved laboratory certified in all categories of Contract Laboratory Protocol (CLP) and Solid and Hazardous Waste analytical testing. A Data Usability Summary Report (DUSR) will be included in a SC Report (described in **Section 2.3** of this Work Plan) for each round of analytical work. Category B deliverables will be retained in the project files and available for full data validation by a qualified, independent third party.

2.2 Investigation, Environmental Sampling, and Implementation

The SC will include investigation activities performed on-site as well as in the right-of-way (sidewalks on Second Avenue and East 117th Street). Due to the presence of subway tunnels under Second Avenue, permits from the Metropolitan Transit Authority (MTA) will be required to drill in the right-of-way. Therefore, HRP proposes to complete on-site investigation activities (in the basements and rear yard of the Site buildings) in the initial phases of investigation, concurrently with permit application and review. A site walkthrough, utility clearance and ground penetrating radar (GPR) survey, and sub-slab soil vapor intrusion (SVI) sampling will be conducted as the first stage of the SC in order to be completed within the current heating season. A Site survey will be conducted during the sub-slab SVI mobilization. The survey will be used to prepare a basemap of the site, survey utilities, and SVI locations. The survey will support the MTA permitting process. Sub-slab SVI will be followed by collection of water and sediment samples from each of the basement sumps, collection of sub-slab soil samples from the Site basements, and installation of soil borings and monitoring wells in the Site basements and rear yard. Installation and sampling of soil borings, monitoring wells, and exterior soil vapor points in the right-of-way will be performed upon receipt of necessary permits, following completion of on-site activities. Following completion of all Site sampling, a final survey will be conducted to locate all investigation sampling points. The number and types of samples to be collected are discussed below and summarized on **Table 2**. The field investigation tasks for the Site are listed below in the order that they are expected to be completed:

1. Permit Acquisition
2. Underground Utility Identification and Clearance using Ground-Penetrating Radar (GPR)
3. Sub-Slab SVI Investigation (Site walkthrough and collection of sub-slab soil vapor and indoor air samples)
4. Site Survey (base map survey of site, survey of utilities and SVI investigation locations)

5. Basement/Rear Yard Sampling (collection of water and sediment samples from basement sumps, installation of soil borings and monitoring wells in basement and rear yard)
6. Right-of-Way Sampling (installation of soil borings, monitoring wells, and soil vapor points on sidewalks surrounding the Site)
7. Characterization and Disposal of Investigation Derived Waste
8. Analytical Data Quality Evaluation
9. Final Survey (survey of final investigation locations)

The following sections describe procedures for investigation activities, generally organized by media to be investigated (i.e. soil, groundwater, and soil vapor).

2.2.1 Permit Acquisition

Prior to commencement of intrusive work to be conducted in the right-of-way (sidewalks), all necessary permits will be obtained by the drilling contractor or HRP. This will include New York City Department of Transportation (NYCDOT) "street opening" permits. In accordance with New York City building code section 3304.3.5, approval and applicable permits from the New York City Transit Authority (NYCTA), MTA, and/or the Port Authority of New York and New Jersey (Port Authority) will be obtained for any intrusive work to be conducted within 200 feet of subways and tunnels and other property of these agencies (e.g. elevated rail lines). This will include preparation of scaled site plans and cross-sections showing boring locations in relation to NYCTA/MTA/Port Authority infrastructure. It is anticipated that an MTA permit will be required for the installation of monitoring wells and soil vapor points on Second Avenue and East 117th Street sidewalks.

2.2.2 Underground Utility Clearance and Ground Penetrating Radar (GPR)

Prior to implementing any intrusive activities, a utility clearance will be conducted. HRP will rely upon multiple lines of evidence to ensure to the maximum extent practicable that subsurface features are identified prior to commencement of intrusive work.

HRP will mark sampling locations prior to installation and contact public utility clearance services to mark out the utilities prior to the survey. The drilling contractor will request utility mark outs through NYS Code Rule 753/Dig Safe System. The dig safe system is limited to public right-of ways and will only identify utilities entering private property rather than utilities within property boundaries.

HRP requests that a knowledgeable party (property owner) provide all available utility information prior to the survey or drilling activities and that, if possible, that person clear each boring location prior to drilling.

HRP will utilize a qualified subcontractor to conduct a GPR survey to attempt to locate any privately installed underground structures or utilities to ensure boring areas are clear of obstructions and identify any other potential AOCs. The GPR survey and underground utility markout will be conducted across all accessible areas of the Site exterior, including Second Avenue and East 117th Street sidewalks bordering Site buildings, the rear yard, and Site basements.

GPR is a non-destructive and non-intrusive geophysical exploration technique that uses radar waves to detect subsurface objects, such as tanks, drums and piping. The GPR is also capable of detecting discontinuities in the subsurface materials indicative of excavated and backfilled areas, such as those associated with possible UST graves. The objective of performing this survey is not only to make subsurface investigation as safe as possible for the field staff while protecting utilities, but also to identify possible sources and migration pathways (utility corridors, etc.). All anomalies identified during the GPR survey will be marked out in the field.

If necessary, the upper five feet of each soil boring location will be cleared of any underground utilities by non-mechanical means, such as a hand-digging methods.

2.2.3 Soil Characterization

In order to assess subsurface soils, the unconsolidated soils at the Site will be evaluated at representative locations. It is anticipated that any of the soil cuttings not used to backfill boreholes will be containerized and labelled in 55-gallon drum(s) for proper disposal during the investigation. Further discussion of investigation derived waste is included in **Section 2.2.9.** These proposed testing locations are provided on **Figure 2**; final locations may vary based on the results from the GPR survey and identification of AOCs during field work.

2.2.3.1. Soil Boring Installation

Up to 14 soil borings will be installed to collect continuous soil samples and characterize subsurface conditions from surface grade to approximately 20 ft bg or refusal using a direct push drill rig. Due to accessibility, soil borings installed in Site basements and the rear yard will be installed with a limited-access drill rig (Geoprobe 420M or similar). Soil borings installed in the right-of-way will be installed with a standard direct push drill rig. The rear yard soil boring will be installed to assess contamination to soils associated with a potential dumping area behind the buildings and to assess conditions upgradient of the Site buildings. Soil borings installed on sidewalks along East 117th Street and Second Avenue will evaluate soil conditions upgradient and downgradient of the Site. Soil borings installed in Site basements will assess the presence of contamination beneath the buildings associated with the potential release of contaminants through spills on the basement slab or discharges to sumps and floor drains. Proposed soil boring locations are depicted on **Figure 2**. Final locations will be determined based on results from the sub-slab SVI investigation, field observations, and the GPR survey.

All soil samples will be screened for volatile organic vapors using a photoionization detector (PID), and any evidence of impacts will be noted and used for the selection of soil samples for laboratory analysis. Up to 3 soil samples per boing are to be collected and submitted for laboratory analysis, biased to evidence of contamination such as elevated PID readings, staining, or odors. If evidence of contamination is not observed, soil samples will be collected from ground surface or near surface (beneath concrete sidewalk/slabs), at the groundwater table interface, and at the bedrock surface (refusal), if encountered. Up to 48 soil samples (42 site samples, 2 duplicate, 2 matrix spike (MS) and 2 matrix spike duplicate (MSD) will be analyzed by an ELAP approved laboratory selected from the NYSDEC call-out contract for Target Compound List (TCL) VOCs +10 by EPA Method 8260.

Up to 10 soil samples (7 site samples, 1 duplicate, 1 MS, 1 MSD) will be analyzed for the following expanded list of characterization parameters:

- TCL SVOCs +20 by EPA Method 8270
- Target Analyte List (TAL) metals by EPA Method 6010B
- TCL PCBs by EPA Method 8082
- TCL chlorinated pesticides by EPA Method 8081
- TCL chlorinated herbicides by EPA Method 8151
- Per-and polyfluoroalkyl substances (PFAS) by Draft EPA Method 1633

Soil sample totals are presented by sample type and lab analysis on **Table 2.** Analytical details are summarized in **Table 3**.

2.2.4 Sump Sampling

Sediment and water samples will be collected from each of the basement sumps in order to evaluate these AOCs as potential contaminant release areas, and evaluate impacts to Site groundwater. The sump locations are depicted on **Figure 2**. Up to 5 sediment samples (2 site samples, 1 duplicate, 1 MS, 1 MSD) and 5 water samples (2 site samples, 1 duplicate, 1 MS, 1 MSD) will be collected from the sumps located within the basement of each building. Sediment samples and water samples will be submitted to the ELAP accredited laboratory and analyzed for TCL VOCs via EPA Method 8260.

2.2.5 Groundwater Characterization

To evaluate Site groundwater quality and obtain groundwater flow information, 8 permanent overburden groundwater monitoring wells are proposed for installation throughout the Site. The proposed locations were selected based on elevated CVOC concentrations in groundwater samples collected from the neighboring 247-249 E 177th Street Site adjacent to the western Site boundary, identified AOCs in the rear yard (potential dumping area) and Site basements (sumps and floor drains) and the inferred groundwater flow direction to the east-southeast as inferred by previous investigations. The proposed monitoring well locations are depicted on **Figure 2**.

2.2.5.1. Monitoring Well Installation

Up to 8 monitoring wells will be installed to a maximum depth of 20 ft bg or bedrock refusal. In locations accessible to a standard track mounted drill rig (monitoring wells proposed in the right of way), wells will be installed using the hollow stem auger method. It is anticipated the Site basements and rear yard will not be accessible to a full size drill rig, therefore these wells will be installed with a limited-access drilling rig and the direct push method. Each monitoring well will be screened to intercept the shallow overburden groundwater table. Proposed monitoring well locations are depicted on **Figure 2**. Final locations will be determined based on results from the sub-slab SVI investigation, field observations, and the GPR survey.

The monitoring wells are to be constructed of Schedule 40 PVC solid well pipe riser and a 10-foot PVC 10-slot screen that will be positioned to intercept the water table. Due to accessibility,

monitoring wells installed in Site basements and the rear yard will be installed with a limited-access drill rig (Geoprobe 420M or similar) and the direct push method. These monitoring wells will be installed using 1-inch PVC with pre-pack sand packs and bentonite seals. Monitoring wells installed in the right-of-way will be installed using a hollow-stem auger drilling rig. These wells will be installed using 2-inch PVC with appropriately sized sand packs and bentonite seals. The wells will be finished with either a stick-up protective casing or a flush mounted protective cover. All equipment will be appropriately decontaminated between sampling locations, as described in **Section 2.2.8**. Any soil cuttings generated by the monitoring well installation will be containerized as discussed in **Section 2.2.9**.

2.2.5.2. Monitoring Well Development

The newly installed monitoring wells will be developed a minimum of 24 hours after completion by pumping and surging for two hours or until the field parameters stabilize for a minimum of three consecutive readings of 10 percent variability of less. The field parameters include: temperature, pH and specific conductance. In addition, the turbidity of the groundwater must achieve a reading of 50 Nephelometric Turbidity Units (NTUs) or less during the field parameter readings.

All purge water obtained during well development will be containerized in appropriately labeled 55-gallon drums and disposed of in accordance with NYSDEC DER-10. If impacts are observed, the contaminated groundwater will be segregated and handled as described in **Section 2.2.7**. All sampling equipment will be appropriately decontaminated between sampling locations or disposed of after a one-time use.

2.2.5.3. Monitoring Well Sampling

Depth to groundwater measurements will be collected from the newly installed monitoring wells to the nearest 0.01 foot from the surveyed points (the survey is discussed in **Section 2.2.11**) prior to sampling activities and the data will be used to construct a groundwater contour map to determine the direction of groundwater flow and the hydraulic gradient on the Site.

Groundwater samples will be collected from the newly installed wells a minimum of 7 days after well development has been completed. Groundwater samples will be collected in accordance with EPA low-flow groundwater sampling procedures and will be submitted to a NYSDOH ELAP and NYSDEC approved laboratory for analysis. Up to 13 groundwater samples (8 site samples, 1 duplicate, 1 MS, 1 MSD, 1 trip blank, and 1 field blank) will be collected for VOC analysis. Duplicate, MS, MSD samples (one of each) will be analyzed at a frequency of one per 20 samples. VOC and PFAS field blanks and VOC trip blanks will be analyzed at a frequency of 1 per 20 samples. Up to 6 groundwater samples (3 site samples, 1 duplicate, 1 MS, 1 MSD) of the following:

- TCL SVOCs +20 by EPA Method 8270
- 1,4-dioxane by EPA Method 8270 SIM
- TAL metals by EPA Method 6010B
- TCL PCBs by EPA Method 8082
- TCL chlorinated pesticides by EPA Method 8081
- TCL chlorinated herbicides by EPA Method 8151

- PFAS by Draft EPA Method 1633

Sample locations and totals are summarized on **Table 2** and laboratory QA/QC details are summarized on **Table 3**.

2.2.6 Soil Vapor Intrusion (SVI) Investigation

In an effort to assess the migration of gaseous vadose zone contamination and verify previous data, HRP proposes the following SVI investigation activities:

- Conduct a sub-slab SVI investigation within the Site buildings.
- To further delineate soil vapor impacts downgradient of the Site, install up to five permanent soil vapor points in the right-of-way (city sidewalks) for the collection of 2-hour soil vapor samples.

SVI investigation locations are depicted on **Figure 2**.

2.2.6.1. Sub-Slab SVI Investigations

Up to 6 sub-slab soil vapor points will be installed in the basements of the two Site buildings to evaluate SVI in the buildings. Indoor air samples will be collected in the Site basements (separate samples in boiler rooms and main basements), and on the first floor of each building. One outdoor air sample will be collected outside of the building. Proposed sub-slab, indoor air, and outdoor air sampling locations of are depicted on **Figure 2**. Final sampling locations are to be determined in the field. The SVI investigation will include the completion of a NYSDOH Indoor Air Quality Questionnaire and Building Inventory.

Sub-slab soil vapor points will be installed and sampled in accordance with NYSDOH's *Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October 2006* and HRP's Generic FAP, on file with the NYSDEC. Prior to sampling a leak test will be performed using a tracer gas and a minimum of three tubing volumes of air will be purged from the vapor point. Indoor and outdoor air samples will be collected simultaneous to sub-slab samples and will be placed at a height corresponding to the average breathing level (i.e., approximately five feet above the ground surface). All SVI air and sub-slab soil vapor samples will be collected using 6-liter summa canisters fitted with 24-hour regulators and analyzed for VOCs via EPA Method TO-15.

TO-15 samples will be collected with a minimum of 0.5 inches of mercury vacuum at the end of the sampling period. To ensure the cannisters are collected with minimum vacuum, regulators will be checked 2 hours after the sampling period commences and a minimum of 2 hours before the 24-hour sampling period is concluded.

Up to 14 air samples (6 indoor air, 6 sub-slab soil vapor, 1 duplicate sub-slab soil vapor, and 1 outdoor air sample) will be submitted to the ELAP accredited laboratory and analyzed for VOCs via EPA Method TO-15. Laboratory reporting limits will be required to meet the lower limits of the soil vapor and indoor air guidance values included in the 2017 NYSDOH Soil Vapor/Indoor Air Decision Matrices. Duplicate sub-slab soil vapor samples will be collected at a frequency of 1 per 20 air

samples. Locations of sub-slab samples, indoor air, and outdoor air samples for the SVI investigation will be determined in the field. Sample locations and totals are summarized on **Table 2** and laboratory QA/QC details are summarized on **Table 3**.

2.2.6.2. Permanent Soil Vapor Points

Up to 5 permanent soil vapor points will be installed in the right-of-way (city sidewalks) around the Site co-located with the five soil borings and monitoring wells. Proposed locations for the permanent soil vapor points are depicted on **Figure 2**; exact locations may vary based on the GPR survey and field observations.

Prior to installation of each soil vapor point, soils will be sampled continuously, characterized by HRP's on-site geologist, and screened using a calibrated PID.

Permanent soil vapor points will be installed by advancing a 6-inch stainless steel screen and tubing (nylon, Teflon, or Teflon-lined) to a depth of 10 feet below the sidewalk slab into the vadose zone, or no deeper than 1 foot above the groundwater table interface. The annular space around the tubing will be backfilled with a #0 filter sand pack. A minimum 6-inch-thick time releasing bentonite (TR-30) seal will be installed to ground surface above the sand pack. Bentonite will be hydrated with potable or distilled water during placement. Each soil vapor point will be finished with a locking road box.

Soil vapor sampling will occur a minimum of 24 hours after installation of the exterior soil vapor points. All soil vapor sampling will be conducted in accordance with NYSDOH's *Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October 2006* and HRP's Generic FAP, on file with the NYSDEC. Prior to sampling a leak test will be performed using a tracer gas with a minimum of 3 tubing volumes of air purged from the vapor point. Following purging, soil vapor will be screened for VOCs using a calibrated PID. One soil vapor sample will be collected from each point using a 6-liter summa canister fitted with 2-hour regulator and analyzed for VOCs via EPA Method TO-15.

Up to 7 air samples (5 soil vapor, 1 outdoor ambient air, 1 duplicate soil vapor), will be submitted to the ELAP accredited laboratory and analyzed for VOCs via EPA Method TO-15. Up to 1 outdoor air sample will be collected per day of sampling. Duplicate soil vapor samples will be collected at a frequency of 1 per 20 soil vapor samples. Sample locations and totals are summarized on **Table 2** and laboratory QA/QC details are summarized on **Table 3**.

2.2.7 Sample Handling Procedures

Nitrile gloves will be worn at all times by personnel collecting and handling the samples. All non-disposable equipment and tooling used for sampling will be properly decontaminated between sampling locations and intervals. Decontamination procedures are described in **Section 2.2.8**.

2.2.8 Decontamination Procedures

Non-dedicated sampling equipment (i.e., submersible pumps, water level indicators, etc.) will be subject to decontamination procedures prior to each sample collected to reduce the potential for cross-contamination, as described in the Generic FAP on file with NYSDEC. The decontamination procedures will include the use of a scrub wash with a solution consisting of Alconox® detergent and potable water followed by a rinse with DI water. The decontaminated equipment will be stored in clean environments (i.e., the manufacturer's storage case). Decontamination fluids will be properly labeled and securely stored in a designated waste-container staging area.

2.2.9 Disposal of Investigation Derived Waste

Investigation derived waste (IDW) that is generated from the monitoring well installation and the development of monitoring wells shall be handled in accordance with NYSDEC DER-10. HRP will be responsible for supplying the equipment and materials necessary for the proper handling and storage of the IDW, such as DOT-approved 55-gallon drums, roll-off containers and/or holding tanks. All containers will be labeled and stored in accordance with applicable NYSDEC regulations.

Soil shall be handled and disposed of in accordance with DER-10. If off-site disposal of IDW is required, it will be disposed of or treated according to applicable local, state, and federal regulations. Soils from the investigation may be disposed within the monitoring well borehole as backfill over the bentonite seal provided the cuttings do not exhibit staining, odors, or elevated PID readings.

It is anticipated that purge water generated during the development and sampling of the monitoring wells will require off-site disposal based on the previous off-site data. Decontamination fluids will be containerized separately from other IDW, and any decontamination fluids that do not exhibit evidence of contamination will be containerized separately from those exhibiting evidence of contamination.

2.2.10 Analytical Data Quality Evaluation

This Work Plan and the associated site-specific QAPP Section detail the data quality objectives and analytical requirements needed for this WA. All quality assurance protocols will be provided in the Generic QAPP.

During the final Work Plan review period, the site-specific QAPP Section and Work Plan will be reviewed and modified according to NYSDEC requirements and comments. Once the plans are finalized, deviations, if required, from protocols specified in the plans will be approved in advance by NYSDEC. As required, the selected analytical laboratory will maintain NYSDOH ELAP certification in all categories of USEPA Contract Laboratory Program (CLP) and Solid and Hazardous Waste analytical testing for the duration of the project.

The ELAP certified laboratory will supply all required data deliverables (USEPA CLP and NYSDEC ASP deliverable format) to enable the data to be validated. All environmental data will be submitted electronically in a specified format named 'NYSDEC' in accordance with the data submission procedures outlined on the NYSDEC's web site (http://www.dec.ny.gov/chemical/62440.html).

Upon receipt of the sample data, the validation contractor will quantitatively and qualitatively validate the laboratory data. The validation of the analytical data will be performed according to the protocols and QC requirements of the analytical methods, the CLP National Functional Guidelines for Organic and Inorganic Data Review (January 2017), the USEPA Region II CLP Data Review SOP, and the reviewer's professional judgment.

2.2.11 Base Map Development and Site Survey

The subject property will be surveyed by a New York State licensed land surveyor. The field survey will include establishing project horizontal control and the collection of planimetric features for the development of 2D mapping. Subsequently, a base map of the Site will be developed using Computer Aided-Design (CAD) software that will be utilized to place all sampling locations from previous on-site and off-site investigations. The sample locations will be placed on the base map by geo-referencing previous figures into the local CAD coordinate system and will include all monitoring wells and soil borings.

Upon completion of the investigation fieldwork, a survey will be conducted to properly locate all sampling points such as monitoring wells, soil borings, soil vapor points, sub-slab soil and soil vapor locations, and any other sample locations. The elevations of all monitoring well casings will be established to within an accuracy of plus or minus 0.01 feet based on an arbitrary local vertical benchmark. A notch will be etched in all interior casings, or a permanent black mark, to provide a reference point for all future groundwater elevation measurements.

2.3 Site Characterization Report

2.3.1 Electronic Data Delivery

In addition to appropriate data summary tables and boring logs included in the report, all environmental data will be submitted electronically in a specified Electronic Data Deliverable (EDD) format named in accordance with the data submission procedures outlined on the NYSDEC's web site (http://www.dec.ny.gov/chemical/62440.html).

2.3.2 Site Characterization Report

The Site Characterization Report (SCR) will provide a description of the field activities, present data collected during field characterization, present a physical description of the Site including geology and hydrogeology, and provide an analysis and interpretation of the available data in the context of existing Site conditions. The SCR will include tabulated laboratory analytical results, Site maps and a discussion of contaminant concentrations, including a comparison to NYSDEC Standards, Criteria and Guidelines as described in Section 3.13 of DER-10.

The SCR prepared as part of this assignment will also provide a summary of the general nature of contamination on the Site to the extent investigated by the SC including, without limitation, the numbers of areas of concern requiring further investigation and/or remediation and any significant events or seasonal variation which may have influenced sampling procedures or analytical results. A

description of each area of concern identified, including dimensions, suspected and actual contamination and suspected source of discharge or disposal recommendations for either additional investigation in the SC, remediation or no further action for each area of concern. The submitted report will include the report text, appropriate tables, figures, photographs, data summary tables, and boring logs in a PDF format on a compact disc. The electronic file will contain 'bookmarks'. In addition, one hard copy of the report will be sent.

3.0 GREEN AND SUSTAINABLE REMEDIATION BEST MANAGEMENT PRACTICES (BMPS)

Through the course of the SC investigation, HRP will implement Green and Sustainable Best Management Practices (BMPs) to reduce negative impacts to air, water, solid waste, etc. (presented in Section 17.0 and Appendix C of the NYSDEC-approved Revised FAP, dated February 2, 2022). **Table 2**, Site Investigation Green and Sustainable Remediation Calculation Sheet, summarizes BMPs to be implemented as part of the 2283 Second Avenue SC and will be used to assess and track environmental impact reductions versus traditional field activity approaches.

In consultation with NYSDEC, quantifiable impact reductions achieved by green and sustainable remediation BMPs implemented during the SC investigation (e.g. tons of carbon reduced, gallons of fuel saved, pounds of waste reduced) may be included in Site fact sheets to promote public awareness of NYSDEC green and sustainable BMPs.

Green and Sustainable Remediation BMPs to be implemented as part of this project are summarized below, organized by BMPs implemented in project planning and field work phases of work.

Project Planning BMPs

BMP 1) A well-conceived dynamic sampling plan has been developed for the Site to assure that the data collected at project on-set adequately addresses Site data gaps, consequently reducing remobilization of field crews and equipment. A conceptual site model (CSM) has been developed for the Site, incorporating the Site sampling data, Site history, and current and historical land use to identify data gaps and allows for refinement as additional data becomes available. Data visualization techniques such as concentration "heat maps" for contaminants of concern will be utilized to refine the CSM and project SOW. Results from each phase of work will be used to refine the SOW for each successive phase. For instance, results from the on-site SVI investigation will be used to select soil boring and monitoring well locations. No alterations will be made to the SOW without NYSDEC approval. Refinement of the CSM and SOW will be performed with the primary goal of achieving the purposes and objectives of the SC as described in **Section 1.1**. Green and sustainable impact reductions will be a secondary goal of CSM/SOW refinement and care will be taken to ensure SOW changes do not impact the efficacy of the SC.

BMP 2) Efforts will be made to schedule Site visits and field work to reduce energy consumption and air emissions associated with mobilizations to and from the Site. The following BMPs will be implemented related to HRP mobilization:

- BMP 2a) Field work schedules will be consolidated by coordinating with contractors. Specifically, the Site walkthrough, GPR work, Site survey, and sub-slab SVI will be completed within the same mobilization.
- BMP 2b) When two or more HRP personnel are involved in a trip to and from the Site which requires a passenger vehicle (i.e., cannot be completed by mass-transit), personnel will "car-pool" by sharing a vehicle, reducing energy consumption and emissions associated with taking multiple vehicles to the Site.

Field Work BMPs

BMP 3) All soil borings (except those converted to permanent monitoring wells) and soil vapor points will be installed with direct push drilling methods instead of hollow stem auger methods to reduce the generation of waste drill cuttings and reduce drill rig operation time.

BMP 4) Monitoring wells and exterior soil vapor points will be installed as permanent points with protective road boxes so they may be utilized for potential future sampling events. This will reduce energy usage, air emissions, and mobilizations associated with installing new soil vapor points if re-sampling is required during a future investigation.

BMP 5) When not in use, vehicles, trucks, drill rigs, and other equipment will be shut off to reduce energy consumption and emissions related to engine idling.

BMP 6) Dedicated plastic tubing will be installed to collect groundwater samples from permanent monitoring wells, reducing waste generated by using new tubing if monitoring wells are sampled during future events.

BMP 7) Waste cardboard generated from labware (sample jars, bottle ware, and summa cannisters) will be reused or recycled to reduce waste.

BMP 8) Soil samples collected for VOC analysis will be collected in soil jars, reducing material and waste associated with terrorcore kits (additional glassware and plastic sample plungers).

4.0 SITE-SPECIFIC QUALITY ASSURANCE PROJECT PLAN

The Site specific QAPP has been prepared and is included below. Deviations from the protocols specified in the QAPP will be subject to approval by the NYSDEC.

The Generic QAPP (on file with the NYSDEC) provides general information related to QA/QC procedures associated with the collection and analysis of samples of environmental media and includes specific representative SOPs applicable to sample handling and field instrumentation use. Information provided in the Generic QAPP includes definitions and generic goals for data quality and required types and quantities of QA/QC samples. The procedures address field documentation; sample handling, custody, and shipping; instrument calibration and maintenance; auditing; data reduction, validation, and reporting; corrective action requirements; and QA/QC reporting specific to the analyses performed by the laboratories that are used for analysis of environmental media collected under Standby Contract No. D009808.

Laboratory analytical work will be performed by a NYSDOH ELAP approved laboratory certified in CLP and solid and hazardous waste analytical testing. A DUSR will be included in the RIR for each round of analytical work. Category B deliverables will be retained in the project files and available for full data validation by a qualified, independent third party.

4.1 Site-specific Sampling

Soil, groundwater and air samples will be collected during this Site Characterization Investigation. Detailed sampling procedures are detailed in Section 4.0 of the Generic QAPP. Matrix types, number of samples (including QA/QC) and analytical details are summarized in **Table 3**. Proposed sample locations are depicted on **Figure 2.**

4.1.1 PFAS Sampling

Sampling for PFAS will occur at the Site during the planned activities covered in this SCWP. Specific requirements for field sampling procedures including precautions to be taken, pump and equipment types, decontamination procedures, and a list of approved materials to be used during sampling for PFAS compounds are included in Section 14.1 of HRP's Generic FAP (on file with the NYSDEC). Only regular ice will be used in the transport of samples being analyzed for PFAS.

The PFAS compounds will be analyzed by methods based on EPA Method 1633. Specific PFAS compounds to be analyzed include:

Group	Chemical Name	Abbreviation	CAS Number
Perfluoroalkyl sulfonic acids	Perfluorobutanesulfonic acid	PFBS	375-73-5
	Perfluoropentanesulfonic acid	PFPeS	2706-91-4
	Perfluorohexanesulfonic acid	PFHxS	355-46-4
	Perfluoroheptanesulfonic acid	PFHpS	375-92-8
	Perfluorooctanesulfonic acid	PFOS	1763-23-1
	Perfluorononanesulfonic acid	PFNS	68259-12-1
	Perfluorodecanesulfonic acid	PFDS	335-77-3
	Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Perfluoroalkyl carboxylic acids	Perfluorobutanoic acid	PFBA	375-22-4
	Perfluoropentanoic acid	PFPeA	2706-90-3
	Perfluorohexanoic acid	PFHxA	307-24-4
	Perfluoroheptanoic acid	PFHpA	375-85-9
	Perfluorooctanoic acid	PFOA	335-67-1
	Perfluorononanoic acid	PFNA	375-95-1
	Perfluorodecanoic acid	PFDA	335-76-2
	Perfluoroundecanoic acid	PFUnA	2058-94-8
	Perfluorododecanoic acid	PFDoA	307-55-1
	Perfluorotridecanoic acid	PFTrDA	72629-94-8
	Perfluorotetradecanoic acid	PFTeDA	376-06-7
Per- and Polyfluoro-ether carboxylic acids	Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
	4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
	Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1
	Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
	Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Fluorotelomer sulfonic acids	4:2 Fluorotelomer sulfonic acid	4:2-FTS	757124-72-4
	6:2 Fluorotelomer sulfonic acid	6:2-FTS	27619-97-2
	8:2 Fluorotelomer sulfonic acid	8:2-FTS	39108-34-4
Fluorotelomer carboxylic acids	3:3 Fluorotelomer carboxylic acid	3:3 FCTA	356-02-5
	5:3 Fluorotelomer carboxylic acid	5:3 FCTA	914637-49-3
	7:3 Fluorotelomer carboxylic acid	7:3 FCTA	812-70-4
Perfluorooctane-sulfonamides	Perfluroroctane sulfonamide	PFOSA	754-91-6
	N-methylperfluorooctane sulfonamide	NMeFOSA	31506-32-8
	N-ethylperfluorooctane sulfonamide	NEtFOSA	4151-50-2

Group	Chemical Name	Abbreviation	CAS Number
Perfluorooctane-sulfonamidoacetic acids	N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9
	N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6
Perfluorooctane sulfonamide ethanols	N-methylperfluorooctane sulfonamidoethanol	MeFOSE	24448-09-7
	N-ethylperfluorooctane sulfonamidoethanol	EtFOSE	1691-99-2
Ether sulfonic acids	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (F-53B Major)	9Cl-PF3ONS	756426-58-1
	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (F-53B Minor)	11Cl-PF3OUdS	763051-92-9
	Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7

The laboratory SOP for PFAS analysis is attached (included as **Appendix C** of this RIWP)**.**

4.1.2 1,4-Dioxane Sampling

Sampling for 1,4-dioxane will occur at the Site during the planned activities covered in this RIWP. Specific requirements for field sampling procedures include precautions to be taken, pump and equipment types, detailed decontamination procedures, a prohibition on using Liquinox, and approved materials only to be used for 1,4-dioxane are included in Section 14.2 of HRP's Generic FAP.

The minimum method achievable Reporting Limits for 1,4-dioxane will be less than or equal to 0.2 µg/L (ppb) for aqueous samples.

Laboratory provided specifics for 1,4-dioxane sampling MDL and RL is as follows:

Method	Analyte	Matrix	RL
8270D SIM	1,4-Dioxane	Water	0.2 µg/L

4.2 Data Quality Assessment and Usability

Data quality objectives for the 2283 Second Avenue Site SC are focused on the characterization of releases of hazardous substances impacting environmental media at the Site and surrounding properties.

To achieve these objectives, QA/QC measures will be implemented throughout the Off-Site Investigation to provide input as to the validity and usability of data generated through soil, groundwater, soil vapor and indoor air sampling. The procedures for data QA/QC management

includes field documentation; sample handling, custody, and shipping; instrument calibration and maintenance; auditing; data reduction, validation, and reporting; corrective action requirements; and QA reporting specific to the analyses performed by the laboratory under subcontract to HRP. **Table 3** lists the sample containers, preservation, and holding time requirements for the parameters specific to this Site. This table will be referenced by field personnel.

For all data generated during the SC Investigation, a Category B Data package and Data Usability Summary Report (DUSR) will be prepared to provide a thorough evaluation of analytical data utilizing third-party data validation. Environmental Data Services, Inc. WBE (EDS) will be the third-party data validator for this project. EDS's qualifications are attached (included in **Appendix D** of this RIWP).

5.0 PROJECT MANAGEMENT

HRP has the responsibility of the overall management of this project and will respond to any NYSDEC requests. A proposed project schedule, key milestones, key project personnel, and project-specific subcontractors follow.

5.1 Project Schedule and Key Milestones

The proposed project schedule for this work assignment is outlined below. Key milestones are identified to monitor work progress. Efforts will be made to consolidate field tasks into as few mobilizations as possible, however the sub-slab SVI investigations will be prioritized to be completed during the heating season. Basement and rear yard sampling separately from drilling if the necessary permits are still in process. The following milestones will be applicable for this project:

CATEGORY	TASK	START	END
Task 1 – Preliminary Activities	Work Plan, QAPP, HASP (Includes Department Review and Approval)	11/30/2022	03/24/2023
Task 2 – Investigation, Environmental Sampling, and Implementation	Sub-slab SVI Investigation and Site Walkthrough	03/27/2023	03/31/2023
	Off-site Property Access and NYCDOT Permit Acquisition	03/27/2023	05/31/2023
	Basement/Rear Yard Soil and Groundwater Sampling	4/17/2023	4/21/2023
	Right-of-Way Soil and Groundwater Sampling	5/15/2023	5/19/2023
Task 3 – Site Characterization Report (SCR)	Report Preparation and Submittal	06/01/2023	08/31/2023

5.2 Key Project Personnel

A list of the project personnel of the prime consultant and subcontractors responsible for performance of the investigation has been submitted to the NYSDEC for approval. Primary project staffs are listed in the table below.

Personnel	Company	Title for this Work Assignment	Responsibility
Patrick Montuori, PG (Project Manager)	HRP Associates, Inc. (Prime Consultant)	Project Manager	Overall management of the WA
Bryan Sherman, ASP (Project Manager)	HRP Associates, Inc.	Office Health and Safety Manager	Approval of HASP and responsible for overall health and safety issues with the WA
Michael Varni (Senior Project Geologist)	HRP Associates, Inc.	Corporate QA/QC Officer	Responsible for QA/QC on the WA
Elliott Jackson (Project Consultant)	HRP Associates, Inc.	Field Manager and Site Health & Safety Officer	Responsible for the on-site sampling and investigative tasks

Subcontractors for this project will include:

- GPR – American Geophysics
- Drilling – Island Pump & Tank
- Laboratory – ELAP certified laboratory selected through NYSDEC call-out contract
- Data Validation – Environmental Data Services, Inc. WBE
- IDW Disposal - Island Pump & Tank

6.0 REFERENCES

Caldwell, D.H., et.al., 1986, Surficial Geologic Map of New York, New York State Museum – Geological Survey, Map and Chart series No. 40.

Fisher, D.W., et. al., 1970, Geologic Map of New York, New York State Museum and Science Service, Map and Chart Series No. 15.

Hillmann Consulting, LLC., September 2017, Remedial Investigation Report, NYC OER Project No. 18TMP0068M

Hillmann Consulting, LLC., October 2017, Remedial Action Work Plan, NYC OER Project No. 18TMP0068M

New York State Department of Environmental Conservation, Division of Environmental Remediation, DER-10 Technical Guidance for Site Investigation and Remediation, May 2010.

New York State Department of Environmental Conservation, Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances (PFAS) Under NYSDEC's Part 375 Remedial Programs DRAFT, June 2022.

New York State Department of Health, Center for Environmental Health, Bureau of Environmental Exposure Investigation, Final Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October 2006, Updated May 2017.

United States Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, National Functional Guidelines for Inorganic Data Review, January 2017.

FIGURES

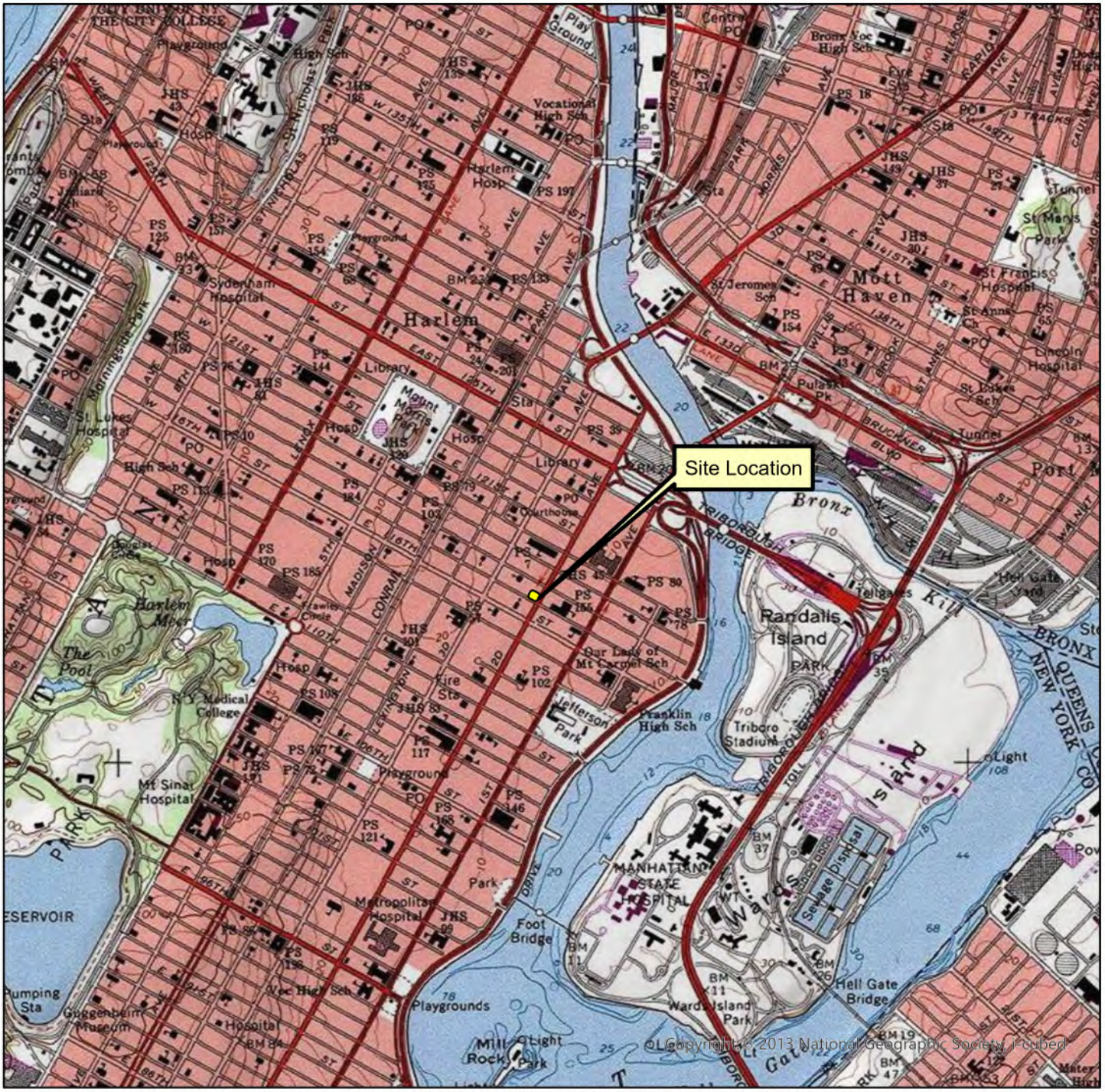

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Figure 1
Site Location
2283 Second Avenue
Site #231126
2283 Second Avenue
New York, New York 10035
HRP # DEC1038.P2
Scale 1" = 2,000'

USGS Quadrangle Information
Quad ID: X24K7974
Name: Central Park, NY, NJ
Date Rev: 2019
Date Pub: 2019

HRP
MOVE YOUR ENVIRONMENT FORWARD
ONE FAIRCHILD SQUARE
SUITE 110
CLIFTON PARK, NY 12065
(518) 877-7101
HRPASSOCIATES.COM

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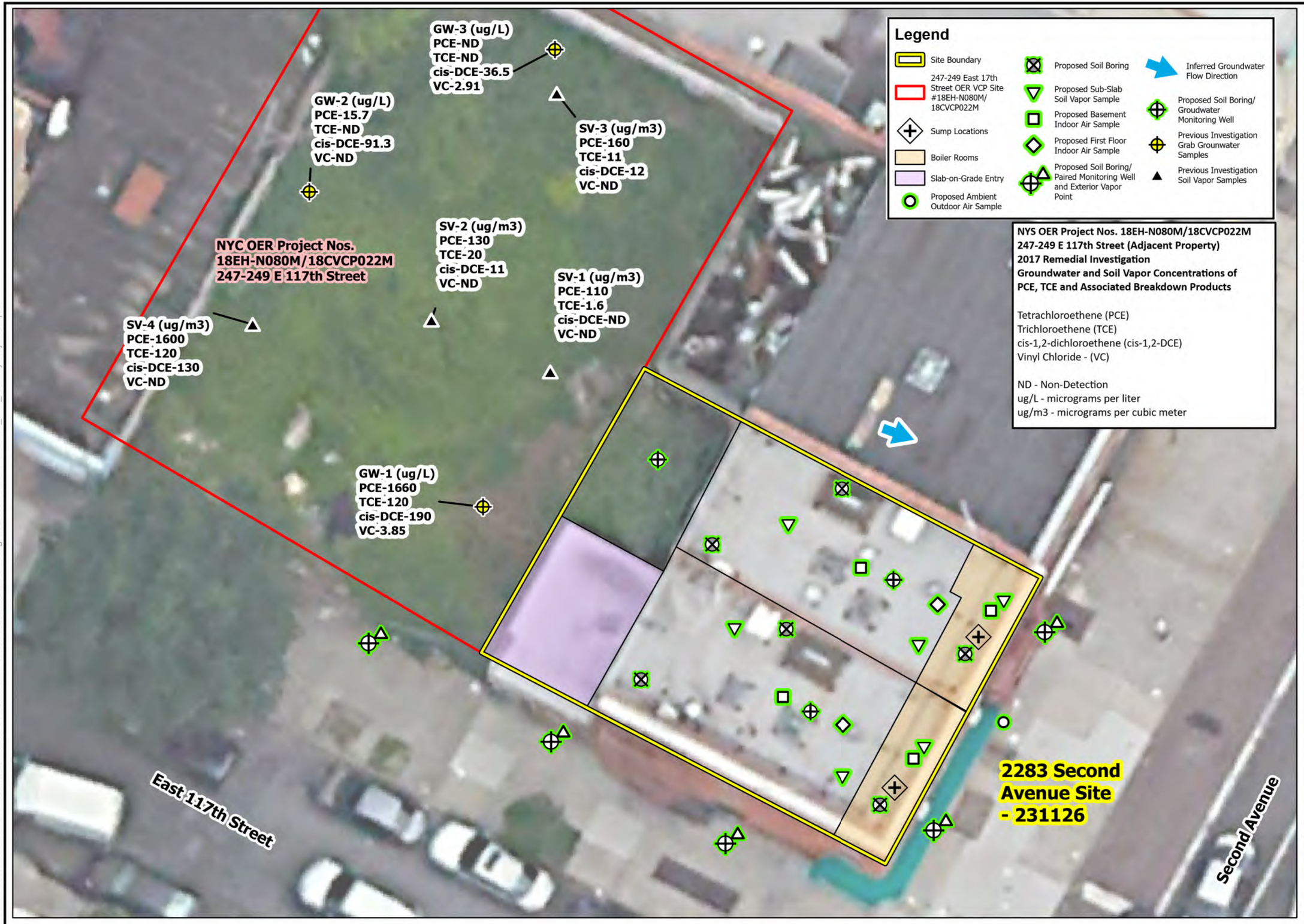

Legend

- Site Boundary
- 247-249 East 17th Street OER VCP Site #18EH-N080M/ 18CVCP022M
- Sump Locations
- Boiler Rooms
- Slab-on-Grade Entry
- Proposed Ambient Outdoor Air Sample
- Proposed Soil Boring
- Proposed Sub-Slab Soil Vapor Sample
- Proposed Basement Indoor Air Sample
- Proposed First Floor Indoor Air Sample
- Proposed Soil Boring/ Paired Monitoring Well and Exterior Vapor Point
- Inferred Groundwater Flow Direction
- Proposed Soil Boring/ Groudwater Monitoring Well
- Previous Investigation Grab Grounwater Samples
- Previous Investigation Soil Vapor Samples

NYS OER Project Nos. 18EH-N080M/18CVCP022M
247-249 E 117th Street (Adjacent Property)
2017 Remedial Investigation
Groundwater and Soil Vapor Concentrations of PCE, TCE and Associated Breakdown Products

Tetrachloroethene (PCE)
Trichloroethene (TCE)
cis-1,2-dichloroethene (cis-1,2-DCE)
Vinyl Chloride - (VC)

ND - Non-Detection
ug/L - micrograms per liter
ug/m3 - micrograms per cubic meter

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(518) 877-7101
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North

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Revisions					
No.					
Date					

Designed By: EWJ	Drawn By: CMS	Reviewed By: PWM
Issue Date: 03/24/2023	Project No: DEC1038.P2	Sheet Size: 11x17

Site Plan - Proposed Investigation Locations and Previous Investigation of Adjacent Property

2283 Second Avenue
NYSDEC Site # 231126
2283 Second Avenue
New York, NY 11035

Figure No.
2

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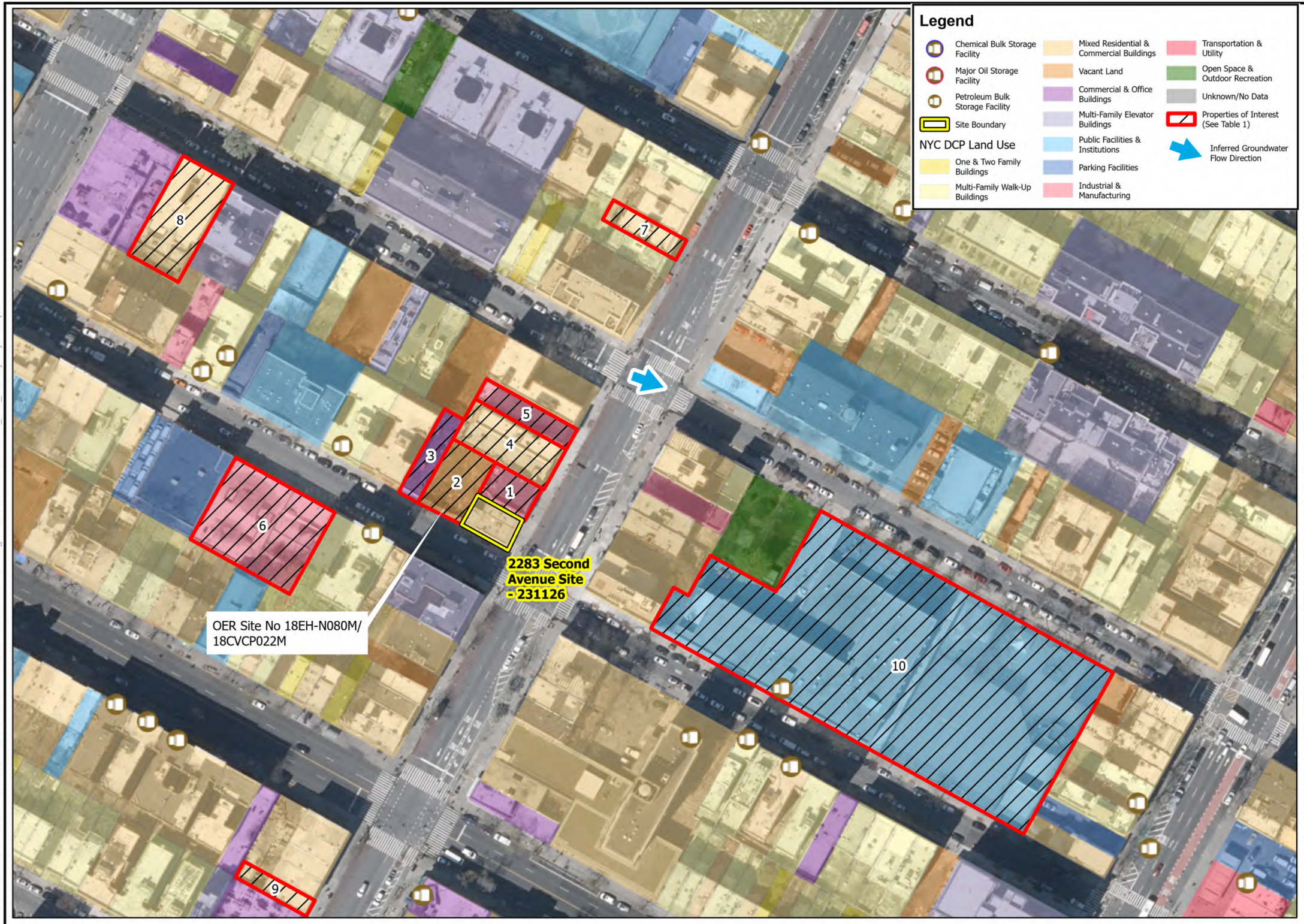

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No.					
Date					

Designed By: EWJ	Drawn By: EWJ	Reviewed By: PWM
Issue Date: 02/21/2023	Project No: DEC1038.P2	Sheet Size: 11x17

Surrounding Property Use

2283 Second Avenue
NYSDEC Site # 231126
2283 Second Avenue
New York, NY 11035

Figure No.

3

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TABLES

Table 1
Historic Property Use and Relevant Regulatory Findings

2883 Second Avenue Site
NYSDEC Site # 231126
2883 Second Avenue
New York, NY

Map ID	Distance from Site Boundary (ft)	Address	Historic Use	Years Listed	Relevant Regulatory Findings
On-Site					
-	N/A	2883 Second Avenue	Shoe Cleaning	1927	NYSDEC Site No. 231126 Historic LQG (1992) of D000, F002 Non-Generator 1999-Present
			Auto Parts Store	1947-1950	
			Dry Cleaner	1968-1999	
			Towing Service	2006	
Off-Site (within 500 ft)					
1	0	2287-2289 Second Avenue	Mattress Manufacturing	1927-1956	E-Designation: E-422 -Hazardous Materials
			Refrigerator Repair	1978	
			Automotive Repair	1980-2005	
2	0	247-249 E 117th Street	Dry Nursery	1911-2005	NYSDEC Spill No. 9601565 - #2 Fuel Oil - Closed 06/27/1996 NYCOER VCP Project No. 18EH-N080M/18CVCP022M E-Designation: E-422 -Hazardous Materials
3	60	245 E 117th Street	Automotive Repair	1980-2005	-
			Dry Cleaner	2005-2021	
4	65	2291 Second Avenue	Dry Cleaner	2001-2012	-
5	85	2293 Second Avenue	Coal Yard	1927-1942	E-Designation: E-422 -Hazardous Materials
			Automotive Repair/Sales	1958-2017	
6	160	228 E 117th Street	Auto Garage and Servicing	1969-2005	Historic LQG (2016) of D008 PBS Nos. 2-001090 & 2-070963 - Diesel USTs NYSDEC Spill No. 0806548 - Petroleum Closed 10/03/2008
			Unknown	-	
7	325	2311 Second Avenue	Job Printer	1911	-
			Dry Cleaner	2000-2008	
8	350	212 E 118th Street	Dry Cleaner	1923	-
9	450	2251 Second Avenue	Dry Cleaner	1991-1997	-
10	460	319 E 117th Street	Slate Works	1939	SQG (2013) of D000, D001, D002, D003, D008
			Public School	1968-Present	

UST= Underground Storage Tank
LQG = Large Quantity Generator
SQG = Small Quantity Generator
PBS= Petroleum Bulk Storage

D000= Not Defined
D001 = Ignitable Waste
D002= Corrosive Waste
D003= Reactive Waste
D008= Lead
F002= Spent Halogenated Solvents

Table 2
Sampling Summary
Site Characterization

2283 Second Avenue Site
NYSDEC Site # 231126
2283 Second Avenue
New York, NY

Activity/ Matrix	Number of Sample Locations	Proposed Sample Locations	Number of Samples to be Collected	Analyses
Soil/Sediment	8	Up to 14 soil borings installed in Site basements, rear yard and Second Avenue/ E 117th Street sidewalks Up to 3 soil samples per boring	48 (42 site samples, 6 QA/QC)	TCL VOCs+10 by EPA Method 8260 QA/QC: 2 duplicate, 2 MS, 2 MSD
			10 (7 site samples, 3 QA/QC)	TCL SVOCs +20 by EPA Method 8270 TAL metals by EPA Method 6010B TCL PCBs by EPA Method 8082 TCL chlorinated pesticides by EPA Method 8081 TCL chlorinated herbicides by EPA Method 8151 PFAS by Draft EPA Method 1633 QA/QC: 1 duplicate, 1 MS, 1 MSD
	2	Up to 2 sediment samples collected from basement sumps	5 (2 site samples, 3 QA/QC)	TCL VOCs+10 by EPA Method 8260 QA/QC: 1 duplicate, 1 MS, 1 MSD
Groundwater	5	Up to 8 proposed permanent monitoring wells (low flow groundwater samples)	13 (8 site samples, 5 QA/QC)	TCL VOCs+10 by EPA Method 8260 QA/QC: 1 duplicate, 1 MS, 1 MSD, 1 field blank, 1 trip blank per 20 samples
			6 (3 site sample, 3 QA/QC)	TCL SVOCs +20 by EPA Method 8270 1,4-dioxane by EPA Method 8270 SIM TAL metals by EPA Method 6010B TCL PCBs by EPA Method 8082 TCL chlorinated pesticides by EPA Method 8081 TCL chlorinated herbicides by EPA Method 8151 PFAS by Draft EPA Method 1633 QA/QC: 1 duplicate, 1 MS, 1 MSD, 1 PFAS field blank
	2	Up to 2 grab water samples collected from basement sumps	7 (2 site samples, 5 QA/QC)	TCL VOCs+10 by EPA Method 8260 QA/QC: 1 duplicate, 1 MS, 1 MSD, 1 field blank, 1 trip blank per 20 samples
Soil Vapor	6	SVI investigations in up to 2 structures with 5 samples collected per structure, including: 1 first floor indoor air sample, 2 basement indoor air samples, and 3 sub-slab soil vapor samples per structure; 1 outdoor air sample per day of sampling	14 (6 sub-slab soil vapor, 6 indoor air; 1 outdoor air, 1 duplicate)	VOCs by EPA Method TO-15 QA/QC: 1 duplicate soil vapor sample per 20 samples
	5	Up to 5 proposed permanent vapor point locations; 1 soil vapor grab sample per location; 1 outdoor ambient air sample per day of sampling	7 (5 soil vapor, 1 outdoor ambient air, 1 duplicate)	VOCs by EPA Method TO-15 QA/QC: 1 duplicate soil vapor sample per 20 samples

Acronym List:
MS/MSD: Matrix spike/matrix spike duplicate
PCBs: polychlorinated biphenyls
SVI: Soil vapor intrusion
TAL: Target analyte list
TCL: Total compound list
VOCs: Volatile organic compounds

Table 3
Analytical Methods/Quality Assurance Summary
Site Characterization

2283 Second Avenue Site
NYSDEC Site # 231126
2283 Second Avenue
New York, NY

					Containers per Sample			Preservation Requirements			
Parameter	**Matrix**	**Number of Samples (including Field QC)**	**Preparation Method**	**Analytical Method**	**No.**	**Size**	**Type**	**Temp.**	**Light Sensitive**	**Chemical**	**Maximum Holding Time**
SOIL											
VOCs by EPA 8260, with TICs	Soil	53	8260	EPA 8260	1	4 oz	glass jar	2-6° C	No	HCL	14 days
SVOCs by GC/MS, with TICs	Soil/Sediment	10	3546	SW-846 Method 8270C	1	4 oz	amber glass jar	2-6º C	Yes	NA	14 days
TAL Metals by ICP	Soil/Sediment	10	3050B	SW-846 Method 6010B	1	2 oz	clear glass jar	NA	No	NA	6 months
Chlrorinated Pesticides by GC	Soil/Sediment	10	3546	SW-846 Method 8081A	1	8 oz	clear glass jar	2-6º C	No	NA	14 days
Chlorinated Herbicides by GC	Soil/Sediment	10	3546	SW-846 Method 8151	1	8 oz	clear glass jar	2-6º C	No	NA	14 days
PCBs by GC	Soil/Sediment	10	3546	SW-846 Method 8082	1	8 oz	clear glass jar	2-6º C	No	NA	14 days
PFAS	Soil/Sediment	10	NA	Draft Method 1633	2	8 oz	polypropylene	2-6º C	No	NA	
GROUNDWATER											
VOCs by GC/MS, with TICs	Aqueous	20	5035	SW-846 Method 8260B	3	40 ml	glass vial	2-6º C	No	HCL	14 days
SVOCs by GC/MS, with TICs	Aqueous	6	3510C	SW-846 Method 8270C	2	Liter	amber bottle	2-6º C	Yes	NA	7 days
1,4-Dioxane	Aqueous	6	3510C	SW-846 Method 8270 SIM	2	Liter	amber bottle	2-6º C	Yes	NA	7 days
TAL Metals by ICP	Aqueous	6	3005A	SW-846 Method 6010B	1	500 ml	plastic bottle	2-6º C	No	Nitric Acid	6 months
Chlorinated Pesticides by GC	Aqueous	6	3510C	SW-846 Method 8081	2	Liter	clear glass bottle	2-6º C	No	NA	14/28 days
Chlorinated Herbicides by GC	Aqueous	6	3546	SW-846 Method 8151	2	Liter	clear glass bottle	2-6º C	No	NA	14/28 days
PFAS	Aqueous	6	NA	Draft Method 1633	3	250 ml	polypropylene	2-6º C	No	NA	14/28 days
SOIL VAPOR/AMBIENT AIR											
VOCs	Soil Vapor, Air	14	NA	EPA TO-15	1	6-Liter	summa canister, 2-hour regulator	NA	No	NA	30 days (summa canister)
VOCs	Soil Vapor, Air	7	NA	EPA TO-15	1	6-Liter	summa canister, 24-hour regulator	NA	No	NA	30 days (summa canister)

Table 4
Site Investigation Green and Sustainable Remediation Calculation Sheet
2283 Second Avenue
Site # 231126
2283 Second Avenue
Brooklyn, New York

BMP No.	Activity	Negative Impact	Green Remediation Option/ Best Management Practice (BMP)	Comments and Assumptions	Impact Reduction						
					Material & Waste	Water	Energy	Air	Sustainable Transportation	Species & Habitat Protection	Educational Programing and Outreach
PROJECT PLANNING BMPs											
1	Various Investigation Activities	* Drill cuttings (soil) IDW generated during soil boring installation * PVC pipe used in permanent monitoring well samples * Groundwater IDW produced by monitoring well development *Combustion emissions associated with site mobilizations and drill rig operation	Reduce sampling locations by using data visualization techniques to refine CSM/SOW	TBD							BMPs and impact reductions to be included on fact sheet †
2a	HRP Mobilization to and from Site	Fuel consumption and combustion emissions associated with HRP travel	* Reduce mobilizations by consolidating schedules by conducting the Site walkthrough, GPR work, Site survey, and sub-slab SVI will be completed within the same mobilization.	* 350 miles per round trip from HRP office in Clifton Park, NY to Site. * Light duty truck, 22.9 miles/gallon[1] * 8,774 grams (19.34 lbs.) CO2 emitted per gallon, light duty truck[3]							BMPs and impact reductions to be included on fact sheet †
2b	HRP Mobilization to and from Site	Fuel consumption and combustion emissions associated with HRP travel	Car-pool using a single vehicle whenever two or more HRP personnel are required for a site visit.	* 350 miles per round trip from HRP office in Clifton Park, NY to Site. * Crew of two HRP personnel will car-pool for SVI sampling/drilling mobilization, saving one round trip. * Light duty vehicle, 22.9 miles/gallon[1] * 8,774 grams (19.34 lbs.) CO2 emitted per gallon, light duty truck[3]							BMPs and impact reductions to be included on fact sheet †

Table 4
Site Investigation Green and Sustainable Remediation Calculation Sheet
2283 Second Avenue
Site # 231126
2283 Second Avenue
Brooklyn, New York

BMP No.	Activity	Negative Impact	Green Remediation Option/ Best Management Practice (BMP)	Comments and Assumptions	Impact Reduction						
					Material & Waste	Water	Energy	Air	Sustainable Transportation	Species & Habitat Protection	Educational Programing and Outreach
FIELD WORK BMPs											
3	Drilling (Soil Borings/Soil Vapor Point Installation)	Drill cuttings (soil) IDW generated during soil boring installation	Reduce drill cutting generation by installing soil borings, monitoring wells, and soil vapor points using the direct push method instead of hollow stem auger method	*Soil borings and soil vapor points will be installed using direct push/2-inch macrocores instead of 4-inch hollow stem auger. * Soil from all borings will be removed as IDW. * One well volume is 10 ft of water (3.7 gal). * Monitoring well development requires purging 5 well volumes, 18.5 gallons per well. * Low-flow sampling requires purging 1 well volume, 3.7 gal per well. * Soil weighs 1.5 tons per cu yd.							BMPs and impact reductions to be included on fact sheet †
4	Drilling (Soil Boring/Monitoring Well/Soil Vapor Point Installation)	Fuel consumption and combustion emissions associated with drill rig operation IDW generated during soil boring installation and monitoring well development. PVC pipe used in permanent monitoring well samples	Install permanent soil vapor points with protective road boxes which allow for re-sampling, reducing drill rig operation time and mobilizations associated with re-installing points.	* Geoprobe 7822 DT, Kubota 03 Series 4-cylinder engine, 0.5 gallons of diesel/hour operating at 15% engine output (when idling)2. * 10,217 grams (22.53 lbs.) CO2 emitted per gallon, construction equipment3 * Soil weighs 1.5 tons per cu yd. * PVC pipe weighs 3.65 lbs./ft.							BMPs and impact reductions to be included on fact sheet †
5	Drilling (Soil Boring/Monitoring Well/Soil Vapor Point Installation)	Fuel consumption and combustion emissions associated with drill rig operation	Shut off drill rig when not in use.	* Geoprobe 7822 DT, Kubota 03 Series 4-cylinder engine, 0.5 gallons of diesel/hour operating at 15% engine output (when idling)[2]. * 10,217 grams (22.53 lbs.) CO2 emitted per gallon, construction equipment[3]							BMPs and impact reductions to be included on fact sheet †
6	Groundwater Sampling	Waste plastic associated with tubing used for monitoring well sampling	Dedicated plastic tubing will be left in monitoring wells for future sampling events.	TBD							BMPs and impact reductions to be included on fact sheet †

Table 4
Site Investigation Green and Sustainable Remediation Calculation Sheet
2283 Second Avenue
Site # 231126
2283 Second Avenue
Brooklyn, New York

BMP No.	Activity	Negative Impact	Green Remediation Option/ Best Management Practice (BMP)	Comments and Assumptions	Impact Reduction						
					Material & Waste	Water	Energy	Air	Sustainable Transportation	Species & Habitat Protection	Educational Programing and Outreach
7	Soil/Groundwater /Air Sampling	Waste cardboard generated from delivery of sample-ware	Re-use or recycle cardboard generated by sample-ware delivery	* 1 cardboard box generated from groundwater sample containers. * 1 cardboard boxes used per summa cannister. * Each box is equivalent to 0.0067 cu ft of cardboard. * 1 cu ft cardboard weighs 43 lbs.							BMPs and impact reductions to be included on fact sheet †
8	Soil Sampling	Waste plastic and glass associated with terrorcore kits	Use soil jars instead of terrorcore kits for VOC sample collection	* 2-ounce glass soil jars will be used in place of terrorcore kits. * Each terrorcore kit consists of 2.8 oz glass, 0.8 oz plastic, 0.2 oz Styrofoam.							BMPs and impact reductions to be included on fact sheet †
Totals											**BMPs and impact reductions to be included on fact sheet †**

Notes:

Activity – Describe the field activity including duration, amount material consumed.
Negative Impact- describe and quantify the negative impact on material and waste, water, energy air emissions (i.e. 300 ft of plastic tubing consumed, amount of fuel used on-site and to mobilize to the site, etc.)
Green and Sustainable Remediation Option/ Best Management Practice (BMP) – see partial list included in Appendix C of Field Activity Plan
Impact Reduction- quantify the reduction of material, air emissions, energy consumption etc.
Comment and Assumptions- list basis of calculations.
1 - Bureau of Transportation Statistics, Average Fuel Efficiency of Light Duty Vehicles, Light Duty Vehicle, Short Wheel Base
2- Kubota Corporation, Kubota 03 Series (4 -Cylinder) V2403-M-DIE3B Specification Sheet
3 - United States Environmental Protection Agency, Office of Transportation and Air Quality, U.S. Transportation Sector Greenhouse Gas Emissions 1990-2020, May 2022
4 - U.S. Energy Information Administration Heavy-Duty Trucks Fuel Economy, Annual 2020
† - Quantifiable impact reductions achieved by green and sustainable remediation BMPs may be included in site fact sheets to promote public awareness of NYSDEC green and sustainable BMPs.

APPENDIX A
Site-Specific Health and Safety Plan

MOVE YOUR ENVIRONMENT FORWARD

SITE-SPECIFIC HEALTH AND SAFETY PLAN (HASP)

2283 Second Avenue –Site # 231126
2283 Second Avenue
New York, New York 10035

Prepared For:

New York State Department of Environmental Conservation
625 Broadway
Albany, New York 12233
Contract #D009808

Prepared By:

HRP Associates, Inc.
1 Fairchild Square, Suite 110
Clifton Park, NY 12065

HRP #: DEC1038.P2

Issued On: March 24, 2023

Addendum Number	Date Issued	Reason For Modification

Disclaimer

HRP Associates does not guarantee the health or safety of any person entering this site. Due to the potential hazards of this site and the activity occurring thereon, it is not possible to discover, evaluate, and provide protection for all possible hazards which may be encountered. Strict adherence to the health and safety guidelines set forth herein will reduce, but not eliminate, the potential for injury at this site. The health and safety guidelines in this plan were prepared specifically for this site for use and should not be used on any other site.

CERTIFICATION

This Addendum to HRP's Generic Health and Safety Plan has been prepared under the supervision of, and has been reviewed by, an Associate Safety Professional (ASP) certified by the Board of Certified Safety Professionals.

Bryan Sherman, ASP
ASP # 31838

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Figures

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Appendices

1.0 EMERGENCY CONTACTS/PLANNING

The Health and Safety Officer will coordinate the entry and exit of response personnel in the event of an emergency. The following information, including directions to the nearest hospital shall be posted at the Site. When contacting the local authorities, be sure to provide: your name, facility name, full address, telephone number, and the nature of the emergency.

Emergency Phone Numbers 2283 Second Avenue, New York, NY	
Emergency Contact	**Phone Number**
Fire, Ambulance, Police Emergency:	911
NYCPD 25th Precinct Police Department (routine calls):	212-860-6511
FDNY Engine 58/Ladder 26 - Fire Department (routine calls):	212-504-4115
NYC Health + Hospitals/Metropolitan	212-423-6262
Poison Control Center:	1-800-222-1222
DEC spills hotline:	1-800-457-7362
National Response Center:	800-424-8802
Project Manager: Patrick Montuori	845-531-9490
Site Safety Officer: Elliott Jackson	716-489-0415
NYSDEC Project Manager: Dan McNally	518-402-9143

Map and directions to the following medical facilities are provided in **Figure 3**:

- **NYC Health and Hospitals/Metropolitan-** located at 1901 First Avenue, New York, NY 10029
  (approximately 0.9 miles from the work site)

First Aid, Fire Protection, Emergency Response Equipment Storage Locations	
First Aid Kit:	In Vehicle
Fire Extinguisher:	In Vehicle
Eye Wash (Bottle):	In Vehicle

A Safety and Logistics Planning call will be held prior to conducting any intrusive activities at the site. Representatives from HRP and each subcontractor will attend the call to discuss logistical and safety challenges general to the scope of work and specific to the Site. This call is documented on the Safety and Logistics Planning Call Log in **Appendix A.**

2.0 INTRODUCTION

2.1 Purpose and Scope

This Health and Safety Plan (HASP) addresses the health and safety practices that will be employed by HRP Associates, Inc. personnel and our subcontractors participating in the Site Characterization (SC) that will be performed at the site. The SC will be comprised of several tasks to evaluate the environmental condition of the Site and the surrounding area, including installation of soil vapor points and monitoring wells to collect air and groundwater samples.

This HASP has been developed in accordance with HRP's Generic Safety and Health Program as required under OSHA's Hazardous Waste Operations Standard (29 CFR 1910.120). This Plan has been developed to establish minimum standards necessary for onsite investigation activities to protect the health and safety of HRP personnel. HRP site personnel have received the required level of training and field experience as required under subpart (e) of the Standard and have received medical examinations in accordance with HRP's medical surveillance program as required under subpart (f) of the Standard. No other personnel will be permitted in the Exclusion Zone unless they have received training and medical surveillance under the Standard.

HRP personnel and associated contractors shall be familiar with this HASP prior to conducting proposed site work. This plan must be present on site and be available for reference/inspection when the subject site work is being conducted.

2.2 Site Information and Areas of Environmental Concern

2.2.1 Site Information and Description

Site Name: 2283 Second Avenue

Site Address: 2283 Second Avenue, New York, NY

Site Contact: Dan McNally, NYSDEC

Phone Number: (518) 402-9143

2.3 Background and Project Description

The 2283 Second Avenue Site (#231126), located at 2283 Second Avenue, New York, NY (**Figure 1**), is the focus of this investigation. The property is identified on the NYC Department of Finance (DOF) tax map as Manhattan block 1667, lot 21. The 0.0420-acre Site currently consists of two four-story buildings with a two-story slab-on-grade connecting structure on the west of the southern building and a rear yard located west of the northern building. The Site buildings are mixed-use with a connected first floor commercial space (occupied by a credit union) and residential apartments on upper floors. Based on a site visit performed by the NYSDEC, each building includes a separate unfinished basement. Each basement includes a boiler room in the eastern portion of the basement and each boiler room contains a sump. During NYSDEC's visit to the Site, it was noted that the concrete slab of the basement floor was in good condition and did

not appear to be the original slab. Floor drains were also observed in the building basements during NYSDEC's visit to the Site. The Site is depicted on **Figure 2**. Based on documents reviewed, no previous subsurface investigations have been performed on-site. Historic uses of the Site include a shoe cleaning business operating under the name Soranello J Shoe Cleaning (1927), a food distributor operating under the name Conczoniri Frank Fruit & Falcone Emilio Josephine Meats (1934), an automotive repair shop under the name of Eppy's Auto Accessories (1947-1950), a dry cleaning facility operating under the name of Twins Cleaners (1968-1999), and an emergency towing service operating under the name of 24 Hour 7 Day Emergency Towing. Currently, a credit union operates out of the Site building with apartments above. Twins Cleaners was registered as a RCRA "Large Quantity Generator" in 1992 of D001 undefined hazardous waste and F002 spent halogenated solvents. Twins Cleaners was listed as "not a generator, verified" in 1999 through 2007 on the same registry.

Identified areas of concern (AOCs) include:

- Sumps and floor drains within the basements of the Site buildings which may have historically received discharges of tetrachloroethylene (PCE) or other chemicals. It should be noted that NYSDEC's observations of the Site indicate the slab has been replaced, therefore the current sumps and floor drains may not have been present during dry cleaning operations.

- The rear yard on the western portion of the Site which may be a historic dumping area for PCE and other chemicals.

- Off-site properties which may have used chlorinated solvents, including those identified below. A list of properties of interest within 500 feet of the Site are presented on **Table 1** and **Figure 3**.

    - 2287-2289 Second Avenue (Property 1 on **Figure 3**): Historic use as a mattress manufacturer, refrigerator repair, and automotive repair. The tax lot containing 2287-2289 Second Avenue has been issued an "E designation" for potential hazardous materials from NYC OER.
    - 247-249 E 117th Street (Property 2 on **Figure 3**): Registration in the NYC OER Voluntary Cleanup Program (VCP) as project number 18EH-N080M/18CVCP022M. The tax lot containing 247-249 E 117th Street has been issued an "E designation" for potential hazardous materials from NYC OER.
    - 245 E 117th Street (Property 3 on **Figure 3**): Historic use as an automotive repair shop (1980-2005) and a dry-cleaning facility (2005-2021).
    - 2291 Second Avenue (Property 4 on **Figure 3**): Historic use as a dry-cleaning facility (2001-2012).
    - 2293 Second Avenue (Property 5 on **Figure 3**): Historic use as a coal yard (1927-1942) and an automotive repair center (1958-2017). The tax lot containing 2293 Second avenue has been issued an "E designation" for potential hazardous materials from NYC OER.

The Site lies at an elevation of approximately 18 ft above mean sea level (amsl). Topography of the Site and surrounding area slopes east towards the Harlem River.

The purpose of the SC is to determine soil, groundwater and soil gas/vapor quality in this area to determine whether the Site conditions pose a risk to public health and the environment. In accordance with DER-10 *Technical Guidance for Site Investigation and Remediation (May 2010),* the primary objectives of the SC scope of work are to:

- Investigate the identified areas of concern (AOCs) associated with the Site and determine if they have resulted in surface or subsurface contamination and evaluate the extent of the contamination, if any;

- Obtain geologic and hydrogeologic data from the Site. The specific information that should be collected and/or verified includes: soil types (or fill), depth to groundwater, groundwater flow direction, subsurface geology, bedrock characteristics, etc. Determine if applicable standards, criteria, and guidance contained in NYSDEC DER-10 and set forth for the Site are contravened;

- Preliminarily delineate the vertical and horizontal extent of contaminated groundwater, if any; and

- Determine if the site represents a threat to public health or the environment.

2.3.1 Personnel Designations

The following personnel are designated to perform the stated project activities and to ensure that the requirements of this HASP are met. The same person may fill more than one role, and/or serve as an alternate in the absence of the designated team member.

The following personnel are designated to perform the stated project activities and to ensure that the requirements of this HASP are met. The same person may fill more than one role, and/or serve as an alternate in the absence of the designated team member. All subcontractors must have received the required level of training and field experience as required under subpart (e) of OSHA 29 CFR 1910.120 and OSHA 29 CFR 1926.65 for Hazardous Waste Operations and Emergency Response (HAZWOPER).

Project Team Member	Responsibilities and Tasks
Elliott Jackson (or Qualified Alternate Safety Officer)	HSO – HRP Associates, Inc. - Ensuring all site work is being performed in accordance with HRP Associates, Inc. Safety Program, as well as in accordance with local, state and federal regulations. - Directing and implementing HRP's HASP. - Conduct a job orientation meeting and routine safety meetings for HRP Associates, Inc. employees and subcontractors, as applicable. - Provide copies of these inspections, recordkeeping/personnel logs to the engineer/contractor as required. - Ensuring all project personnel have been adequately trained in the recognition and avoidance of unsafe conditions. - Authorizing Stop Work Orders that shall be executed upon the determination of an imminent health and safety concern, and will notify the appropriate contacts upon issuance of this order. - Authorizing work to resume, upon approval from the Contractor. - Directing activities, as defined in the HRP's written HASP, during emergency situations. - Providing personnel monitoring where applicable. - Ensuring that adequate personal protective equipment and first aid supplies are available. - Ensure site security, to the extent practicable. - Ensure accident victims are promptly cared for, and the incident is investigated and properly reported.
Patrick Montuori (Site Supervisor/ Project Manager) **Jessica Kruczek (Alternate Site Supervisor)**	Site Supervisor/Project Manager – HRP Associates, Inc. - Monitor and assist the site Health and Safety officer. - Maintain appropriate rules, regulations and codes at the job site. - Provide advance safety planning for all activities through the use of scheduling and administrative controls. - Obtain site-specific health and safety information and communicate that information with the appropriate personnel (i.e. contractors, client, etc.) - Report all injuries, illnesses and other incidents to the Director of Safety. - Ensure all HRP personnel are trained and qualified to perform site work.
Site Workers (Subcontractors)	**Site Workers** - Read and work in accordance with this HASP. - Report all unsafe work practices to the HSO. - Report all incidents, including near-misses to the HSO. - Work in a safe manner. - Provide Designated Competent Person
A complete list of HRP employee and subcontractor responsibilities (as applicable) can be found in the HRP Generic Health and Safety Plan. 1 A list of site workers will be maintained in the Personnel Log (**Appendix B**) 2 Supervisors Investigation Report included as (**Appendix C**)	

3.0 AREAS OF ENVIRONMENTAL CONCERN

3.1 Scope of Work

In general, the work to be performed by HRP and HRP's subcontractors consists of investigative methods to evaluate the environmental condition of the Site. The SC investigation fieldwork for this task includes the following subtasks:

1. Permit Acquisition
2. Underground Utility Identification and Clearance using Ground-Penetrating Radar (GPR)
3. Sub-Slab SVI Investigation (Site walkthrough and collection of sub-slab soil vapor and indoor air samples)
4. Site Survey (base map survey of site, survey of utilities and SVI investigation locations)
5. Basement/Rear Yard Sampling (collection of water and sediment samples from basement sumps, installation of soil borings and monitoring wells in basement and rear yard)
6. Right-of-Way Sampling (installation of soil borings, monitoring wells, and soil vapor points on sidewalks surrounding the Site)
7. Characterization and Disposal of Investigation Derived Waste
8. Analytical Data Quality Evaluation
9. Final Survey (survey of final investigation locations)

Permit Acquisition

Prior to commencement of intrusive work to be conducted in the right-of-way (sidewalks), all necessary permits will be obtained by the drilling contractor or HRP. This will include New York City Department of Transportation (NYCDOT) "street opening" permits. In accordance with New York City building code section 3304.3.5, approval and applicable permits from the New York City Transit Authority (NYCTA), MTA, and/or the Port Authority of New York and New Jersey (Port Authority) will be obtained for any intrusive work to be conducted within 200 feet of subways and tunnels and other property of these agencies (e.g. elevated rail lines). This will include preparation of scaled site plans and cross-sections showing boring locations in relation to NYCTA/MTA/Port Authority infrastructure. It is anticipated that an MTA permit will be required for the installation of monitoring wells and soil vapor points on Second Avenue and East 117th Street sidewalks.

Underground Utility Clearance and Ground Penetrating Radar (GPR)

Prior to implementing any intrusive activities, a utility clearance will be conducted. HRP will rely upon multiple lines of evidence to ensure to the maximum extent practicable that subsurface features are identified prior to commencement of intrusive work.

HRP will mark sampling locations prior to installation and contact public utility clearance services to mark out the utilities prior to the survey. The drilling contractor will request utility mark outs

through NYS Code Rule 753/Dig Safe System. The dig safe system is limited to public right-of ways and will only identify utilities entering private property rather than utilities within property boundaries.

HRP requests that a knowledgeable party (property owner) provide all available utility information prior to the survey or drilling activities and that, if possible, that person clear each boring location prior to drilling.

HRP will utilize a qualified subcontractor to conduct a GPR survey to attempt to locate any privately installed underground structures or utilities to ensure boring areas are clear of obstructions and identify any other potential AOCs. The GPR survey and underground utility markout will be conducted across all accessible areas of the Site exterior, including Second Avenue and East 117th Street sidewalks bordering Site buildings, the rear yard, and Site basements.

GPR is a non-destructive and non-intrusive geophysical exploration technique that uses radar waves to detect subsurface objects, such as tanks, drums and piping. The GPR is also capable of detecting discontinuities in the subsurface materials indicative of excavated and backfilled areas, such as those associated with possible UST graves. The objective of performing this survey is not only to make subsurface investigation as safe as possible for the field staff while protecting utilities, but also to identify possible sources and migration pathways (utility corridors, etc.). All anomalies identified during the GPR survey will be marked out in the field.

If necessary, the upper five feet of each soil boring location will be cleared of any underground utilities by non-mechanical means, such as a hand-digging methods.

Soil Characterization

In order to assess subsurface soils, the unconsolidated soils at the Site will be evaluated at representative locations. It is anticipated that any of the soil cuttings not used to backfill boreholes will be containerized and labelled in 55-gallon drum(s) for proper disposal during the investigation.

Up to 14 soil borings will be installed to collect continuous soil samples and characterize subsurface conditions from surface grade to approximately 20 ft bg or refusal using a direct push drill rig. Due to accessibility, soil borings installed in Site basements and the rear yard will be installed with a limited-access drill rig (Geoprobe 420M or similar). Soil borings installed in the right-of-way will be installed with a standard direct push drill rig. The rear yard soil boring will be installed to assess contamination to soils associated with a potential dumping area behind the buildings and to assess conditions upgradient of the Site buildings. Soil borings installed on sidewalks along East 117th Street and Second Avenue will evaluate soil conditions upgradient and downgradient of the Site. Soil borings installed in Site basements will assess the presence of contamination beneath the buildings associated with the potential release of contaminants through spills on the basement slab or discharges to sumps and floor drains. Proposed soil boring locations are depicted on **Figure 2**. Final locations will be determined based on results from the sub-slab SVI investigation, field observations, and the GPR survey.

All soil samples will be screened for volatile organic vapors using a photoionization detector (PID), and any evidence of impacts will be noted and used for the selection of soil samples for laboratory analysis. Up to 3 soil samples per boing are to be collected and submitted for laboratory analysis,

biased to evidence of contamination such as elevated PID readings, staining, or odors. If evidence of contamination is not observed, soil samples will be collected from ground surface or near surface (beneath concrete sidewalk/slabs), at the groundwater table interface, and at the bedrock surface (refusal), if encountered. Up to 48 soil samples (42 site samples, 2 duplicate, 2 matrix spike (MS) and 2 matrix spike duplicate (MSD) will be analyzed by an ELAP approved laboratory selected from the NYSDEC call-out contract for Target Compound List (TCL) VOCs +10 by EPA Method 8260.

Sump Sampling

Sediment and water samples will be collected from each of the basement sumps in order to evaluate these AOCs as potential contaminant release areas, and evaluate impacts to Site groundwater. The sump locations are depicted on **Figure 2**. Up to 5 sediment samples (2 site samples, 1 duplicate, 1 MS, 1 MSD) and 5 water samples (2 site samples, 1 duplicate, 1 MS, 1 MSD) will be collected from the sumps located within the basement of each building. Sediment samples and water samples will be submitted to the ELAP accredited laboratory and analyzed for TCL VOCs via EPA Method 8260.

Groundwater Characterization

To evaluate Site groundwater quality and obtain groundwater flow information, 8 permanent overburden groundwater monitoring wells are proposed for installation throughout the Site. The proposed locations were selected based on elevated CVOC concentrations in groundwater samples collected from the neighboring 247-249 E 177th Street Site adjacent to the western Site boundary, identified AOCs in the rear yard (potential dumping area) and Site basements (sumps and floor drains) and the inferred groundwater flow direction to the east-southeast as inferred by previous investigations. The proposed monitoring well locations are depicted on **Figure 2**.

The monitoring wells are to be constructed of Schedule 40 PVC solid well pipe riser and a 10-foot PVC 10-slot screen that will be positioned to intercept the water table. Due to accessibility, monitoring wells installed in Site basements and the rear yard will be installed with a limited-access drill rig (Geoprobe 420M or similar) and the direct push method. These monitoring wells will be installed using 1-inch PVC with pre-pack sand packs and bentonite seals. Monitoring wells installed in the right-of-way will be installed using a standard drill rig and the hollow stem auger method. These wells will be installed using 2-inch PVC with appropriately sized sand packs and bentonite seals. The wells will be finished with either a stick-up protective casing or a flush mounted protective cover.

The newly installed monitoring wells will be developed a minimum of 24 hours after completion by pumping and surging for two hours or until the field parameters stabilize for a minimum of three consecutive readings of 10 percent variability of less. The field parameters include: temperature, pH and specific conductance. In addition, the turbidity of the groundwater must achieve a reading of 50 Nephelometric Turbidity Units (NTUs) or less during the field parameter readings.

All purge water obtained during well development will be containerized in appropriately labeled 55-gallon drums and disposed of in accordance with NYSDEC DER-10. If impacts are observed, the contaminated groundwater will be segregated and handled as described in **Section 2.2.7**.

All sampling equipment will be appropriately decontaminated between sampling locations or disposed of after a one-time use.

Depth to groundwater measurements will be collected from the newly installed monitoring wells to the nearest 0.01 foot from the surveyed points (the survey is discussed in **Section 2.2.11**) prior to sampling activities and the data will be used to construct a groundwater contour map to determine the direction of groundwater flow and the hydraulic gradient on the Site.

Groundwater samples will be collected from the newly installed wells a minimum of 7 days after well development has been completed. Groundwater samples will be collected in accordance with EPA low-flow groundwater sampling procedures and will be submitted to a NYSDOH ELAP and NYSDEC approved laboratory for analysis. Up to 13 groundwater samples (8 site samples, 1 duplicate, 1 MS, 1 MSD, 1 trip blank, and 1 field blank) will be collected for VOC analysis. Duplicate, MS, MSD samples (one of each) will be analyzed at a frequency of one per 20 samples. VOC and PFAS field blanks and VOC trip blanks will be analyzed at a frequency of 1 per 20 samples.

Soil Vapor Intrusion (SVI) Investigation

In an effort to assess the migration of gaseous vadose zone contamination and verify previous data, HRP proposes the following SVI investigation activities:

- Conduct a sub-slab SVI investigation within the Site buildings.
- To further delineate soil vapor impacts downgradient of the Site, install up to five permanent soil vapor points in the right-of-way (city sidewalks) for the collection of 2-hour soil vapor samples.

SVI investigation locations are depicted on **Figure 2**.

Up to 6 sub-slab soil vapor points will be installed in the basements of the two Site buildings to evaluate SVI in the buildings. Indoor air samples will be collected in the Site basements (separate samples in boiler rooms and main basements), and on the first floor of each building. One outdoor air sample will be collected outside of the building. Proposed sub-slab, indoor air, and outdoor air sampling locations of are depicted on **Figure 2**. Final sampling locations are to be determined in the field. The SVI investigation will include the completion of a NYSDOH Indoor Air Quality Questionnaire and Building Inventory.

Sub-slab soil vapor points will be installed and sampled in accordance with NYSDOH's *Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October 2006* and HRP's Generic FAP, on file with the NYSDEC. Prior to sampling a leak test will be performed using a tracer gas and a minimum of three tubing volumes of air will be purged from the vapor point. Indoor and outdoor air samples will be collected simultaneous to sub-slab samples and will be placed at a height corresponding to the average breathing level (i.e., approximately five feet above the ground surface). All SVI air and sub-slab soil vapor samples will be collected using 6-liter summa canisters fitted with 24-hour regulators and analyzed for VOCs via EPA Method TO-15.

Up to 14 air samples (6 indoor air, 6 sub-slab soil vapor, 1 duplicate sub-slab soil vapor, and 1 outdoor air sample) will be submitted to the ELAP accredited laboratory and analyzed for VOCs

via EPA Method TO-15. Laboratory reporting limits will be required to meet the lower limits of the soil vapor and indoor air guidance values included in the 2017 NYSDOH Soil Vapor/Indoor Air Decision Matrices. Duplicate sub-slab soil vapor samples will be collected at a frequency of 1 per 20 air samples. Locations of sub-slab samples, indoor air, and outdoor air samples for the SVI investigation will be determined in the field.

Up to 5 permanent soil vapor points will be installed in the right-of-way (city sidewalks) around the Site co-located with the five soil borings and monitoring wells. Proposed locations for the permanent soil vapor points are depicted on **Figure 2**; exact locations may vary based on the GPR survey and field observations.

Prior to installation of each soil vapor point, soils will be sampled continuously, characterized by HRP's on-site geologist, and screened using a calibrated PID.

Permanent soil vapor points will be installed by advancing a 6-inch stainless steel screen and tubing (nylon, Teflon, or Teflon-lined) to a depth of 10 feet below the sidewalk slab into the vadose zone, or no deeper than 1 foot above the groundwater table interface. The annular space around the tubing will be backfilled with a #0 filter sand pack. A minimum 6-inch-thick time releasing bentonite (TR-30) seal will be installed to ground surface above the sand pack. Bentonite will be hydrated with potable or distilled water during placement. Each soil vapor point will be finished with a locking road box.

Soil vapor sampling will occur a minimum of 24 hours after installation of the exterior soil vapor points. All soil vapor sampling will be conducted in accordance with NYSDOH's *Guidance for Evaluating Soil Vapor Intrusion in the State of New York, October 2006* and HRP's Generic FAP, on file with the NYSDEC. Prior to sampling a leak test will be performed using a tracer gas with a minimum of 3 tubing volumes of air purged from the vapor point. Following purging, soil vapor will be screened for VOCs using a calibrated PID. One soil vapor sample will be collected from each point using a 6-liter summa canister fitted with 2-hour regulator and analyzed for VOCs via EPA Method TO-15.

Up to 7 air samples (5 soil vapor, 1 outdoor ambient air, 1 duplicate soil vapor), will be submitted to the ELAP accredited laboratory and analyzed for VOCs via EPA Method TO-15. Up to 1 outdoor air sample will be collected per day of sampling. Duplicate soil vapor samples will be collected at a frequency of 1 per 20 soil vapor samples.

Additional information is provided in the Site-Specific Work Plan prepared for this Site under separate cover.

4.0 HAZARD ANALYSIS

The project hazard analysis below identifies the hazards that are anticipated to be encountered by the project team.

Physical Hazards Present	☐ Electricity ☒ Trips/Falls/Floor openings ☒ Holes/Pits ☐ Inclement weather ☐ Heat ☐ Cold ☐ Vibration ☐ Flying particles	☐ Ionizing radiation ☐ Non-Ionizing radiation ☐ Lasers ☒ Overhead hazards ☒ Noise ☒ Visible dust ☐ Falling objects ☐ Other _____
Health/Chemical Hazards Present [1]	☒ Dust/Fumes/Particulates ☐ Flammable/Combustible ☐ Compressed gas ☐ Explosive ☐ Water reactive ☐ Unstable ☒ Contact with contaminated media	☐ Oxidizer ☐ Corrosive ☐ Toxic ☐ Highly Toxic ☐ Irritant ☐ Sensitizer ☐ Carcinogen/Mutagen ☐ Other _____
Environmental/Equipment Hazards Present	☒ Heavy machinery ☒ Drilling ☐ Water operations ☒ Mobile equipment ☒ Road work ☐ Railroad work ☐ Forklifts ☐ Power tools ☐ Welding ☐ Gas cylinders ☒ Overhead/underground utilities	☐ Trenching/excavation ☐ Elevated heights/man lifts ☐ Scaffolding ☐ Ladders ☐ Confined spaces ☐ Energized equipment ☐ Overhead hazards ☒ Drums/container handling ☒ Insects/rodents/snakes ☐ Biological hazards ☐ Other _____
Personal Safety Considerations	☐ Security Issues ☐ Remote setting ☐ Employees working alone ☐ Limited lighting	☐ Off hour shifts ☐ Dangerous wildlife/animals ☐ Limited cell phone service ☐ Other _____
[1] **Table 1** (following the text of this HASP) provides a list of chemical substances for reference, along with odor threshold, permissible exposure limit (PEL), threshold limit value (TLV), OSHA ceiling, IDLH concentration, route of exposure and symptoms of acute exposure, if any.		

Details of specific hazards associated with individual tasks will be discussed in the Daily Job Brief Record (**Appendix D**).

4.1 Hazard Analysis Summary/Minimization

HRP's Corporate Health & Safety Plan (in conjunction with this HASP) will be cross-referenced in order to obtain the safe work practice procedures for mitigating and preventing project site hazards identified in the table above. Job site hazard prevention and minimization information can be found in Section 3 of HRP's Generic Health & Safety Plan.

Confined Spaces

Only properly trained HRP personnel are authorized to enter confined spaces. Confined space entry may be performed by subcontractors who have the proper training and experience to conduct this work. Confined space entry is not anticipated during the SC.

Excavations

It is HRP's policy to ensure that for excavation projects the subcontracted environmental contractor will provide a competent person to perform daily and as needed inspections of excavation sites. This policy will be conveyed through the subcontract agreement with the environmental contractor. At a minimum HRP will provide our employees involved with construction projects with awareness level training regarding excavation hazards and notify the subcontracted firm if any obvious excavation safety hazard exists during on-site activities.

Chemical Hazards

Hazardous chemicals known or suspected to be onsite are listed in **Table 1a** (follows text). **Table 1a** includes Chemical name, odor threshold OSHA PEL, ACGIH TLV, OSHA STEL, IDLH Concentrations, routes of exposure and symptoms of acute exposure. Chemicals likely to be encountered during site work are highlighted.

4.2 Changes in Conditions or Scope

Should conditions or the scope of work described herein change significantly; a HASP Addendum will be completed.

4.3 Monitoring Procedures

Air monitoring will be used to determine the concentrations of various chemicals while working in the exclusion zone to evaluate worker exposure to contaminated media. In order to determine potential health hazards and to determine the level of personal protection needed during sampling activities within the areas of concern, a Photoionization Detector (PID) will be periodically operated to monitor air quality for the purpose of ensuring minimal exposure to volatile organic compounds. Monitoring of atmospheres adjacent to on-going excavations and around the treatment area shall also be conducted with a PID.

The following environmental monitoring instruments/procedures shall be used on-site at the specified intervals.

Instrument/Procedure	**Sampling Interval**
Photoionization Detector (PID) in the breathing zone	Periodically as deemed by HSO

Background ambient air levels will be established outside the exclusion zone prior to commencement of site work. Ambient air sampling will occur in the breathing zone of site workers for comparison to the action levels (described below). Additionally, air sampling will be conducted in the vicinity of any intrusive exploration (i.e., near excavations, trenches, etc.) to determine if any contaminants are present.

The following *Action Levels* will be used:

Instrument	Action Level	Level of Protection or Action Required
PID	No reading above background	▪ No action required. ▪ Continue PID monitoring. ▪ (Modified) Level D protection.
PID	Up to 5 ppm above background	▪ Evacuate exclusion zone. ▪ Recheck levels after 15 minutes. ▪ If levels are sustained, reassess. ▪ Use engineering controls to lower breathing zone vapors. ▪ Level C protection (at the HSO direction).
PID	>5 ppm above background	▪ Evacuate exclusion zone. ▪ Recheck levels after 15 minutes. ▪ Use engineering controls to lower breathing zone vapors. ▪ If levels are sustained, contact Safety Manager, and re-evaluate HASP.

When an action level is equaled or exceeded, the work area should be evacuated, and the area re-tested with the sampling device. If the appropriate action level continues to be exceeded, the HSO will have to assess the use of engineering controls to lower vapor levels or availability of required increased personal protection equipment before authorizing re-entry.

Calibration of all instruments will occur at least once per day, when in use. An equipment calibration log is included in **Appendix E.**

For the indoor drilling work in enclosed air spaces and inadequate air flow, air monitoring will be conducted while drilling equipment is being used. The on-site air monitoring will include using direct reading air monitoring equipment such as the Systems 5-gas detector includes a PID with a 10.6 eV lamp or approved equal for the detection of volatile organic vapors and dedicated sensors for the detection of combustible gas, oxygen, hydrogen sulfide and carbon monoxide.

Action Level	Action to be Taken
>10% LEL scale	Halt work, evacuate area and allow ventilating to below 10% LEL prior to resuming work. Notify Project Management Personnel.

Action Level	Action to be Taken
<20.5%	Continuous monitoring. Consider engineering controls.
< 19.5%	Evacuate work area. Institute ventilation and engineering controls. Maintain site condition for at least 10 min. before proceeding. Notify Project Management Personnel.
>22%	Continuous monitoring. Identify combustion sources.
>23.5%	Evacuate. Institute engineering controls as necessary before proceeding. Explosive condition may be present. Notify Project Management Personnel.
<1 ppm	Continue monitoring.
>10 ppm	Halt work, evacuate area and allow area to ventilate below 10 ppm. Contact the Project Management Personnel.
<25ppm	Continue monitoring.
>35ppm	Halt work, evacuate area and allow area to ventilate below 10 ppm. Contact the Project Management Personnel.

When an action level is equaled or exceeded, the work area should be evacuated, and the area re-tested with the sampling device. If the appropriate action level continues to be exceeded, the HSO will have to assess the use of engineering controls to lower vapor levels or availability of required increased personal protection equipment before authorizing re-entry.

Calibration of all instruments will occur at least once per day, when in use.

Community Air Monitoring

To ensure the protection of receptors surrounding the site HRP has developed and will implement a Community Air Monitoring Program (CAMP), which requires real time monitoring of volatile organics and dust during the remedial investigation.

Particulate concentrations will be monitored continuously at the upwind and downwind perimeters of the exclusion zone at temporary particulate monitoring stations. The particulate monitoring will be performed using real-time monitoring equipment capable of measuring particulate matter less than 10 micrometers in size (PM-10) and capable of integrating over a period of 15 minutes (or less) for comparison to the airborne particulate action level. The equipment will be equipped with an audible alarm to indicate exceedance of the action level. In addition, fugitive dust migration will be visually assessed during all work activities.

If the downwind PM-10 particulate level is 100 micrograms per cubic meter (mcg/m3) greater than the background (upwind perimeter) for the 15-minute period or if airborne dust is observed

leaving the work area, then dust suppression techniques will be employed. Work may continue with dust suppression techniques provided that no visible dust is migrating from the work area.

If, after implementation of dust suppression techniques, downwind PM-10 particulate levels are greater than 150 mcg/m3 above the upwind level, work will be stopped, and a re-evaluation of activities initiated. Work can resume provided that dust suppression measures and other controls are successful in reducing the downwind PM-10 particulate concentration to within 150 mcg/m3 of the upwind level and in preventing visible dust migration.

5.0 ENGINEERING CONTROL MEASURES/GENERAL SAFETY

5.1 Air Monitoring

In order to determine potential health hazards and to determine the level of personal protection needed during drilling, excavation and sampling activities within the areas of concern, a PID will be periodically operated to monitor air quality for the purpose of ensuring minimal exposure to volatile organic compounds. Please refer to Section 4.3 of this plan for specific air monitoring procedures/action levels.

5.2 Protective Zones

Prior to commencement of work in area of suspected contamination, protective zones specific for each phase of the Plan will be established by the HSO if necessary, prior to the start of field work. The purpose of the protective zones is to prevent potential cross-contamination of adjacent areas as well as to protect project personnel from exposure to contaminated areas.

Protective zones shall be delineated as follows:

- Exclusion Zone: This is the contaminated area in which intrusive activities are performed. The "Area of Environmental Concern" (AOEC) is located within this area. A single access point for entrance and exit should be established and maintained, if possible. This zone should be delineated from the Contaminant Reduction Zone via perimeter cones or caution tape, or other applicable method. The Exclusion Zone delineation and any necessary modifications will be based on site conditions.

- Contaminant Reduction Zone: This zone is a transition zone located between the Exclusion Zone and the Support Zone and is utilized to decontaminate personnel and equipment.

- Support Zone: This zone will be utilized by equipment and vehicle storage and will be kept free of contaminated material. The HSO will determine the location of this zone. In the event of a site evacuation, the rally point will be on the sidewalk entrance to the Site building at 2283 Second Avenue (**Figure 2**). The designated rally point may be relocated by the HSO based on project or site conditions. All site workers will be notified of any relocation prior to implementation.

6.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

6.1 Level of Protection

As identified in Section 4.0, the overall health and safety risk associated with chemical hazards for HRP and associated contractors is considered significant. This is primarily due to the moderate concentrations of chemical contaminants expected based on minimal contact personnel will have with any potentially contaminated media. Therefore, the minimal level of protection for HRP personnel during the conduct of all the environmental work performed at the site will be Level D PPE, and will generally consist of the PPE listed below:

- Steel toe/shank work boots
- Hard hat, as necessary
- Safety vest, as necessary
- Coveralls/tyvek, as necessary
- Safety glasses/goggles/face shield, as necessary
- Hearing protection, as necessary

If site conditions warrant, an upgrade to Level C PPE may be required (refer to Section 4.3 for the appropriate *Action Levels*) then the contractors will make Level C personal protective equipment (PPE) readily available. Level C PPE generally includes:

- Full face, air purifying respirator with organic vapor cartridges
- Same as Level D, but also includes tyvek taped pant/boot and glove/shirt

If it is determined protection beyond Level C is required, HRP will re-evaluate the HASP as well as the site conditions, and will revise the HASP as required. The following table provides a summary of the minimum level of PPE required on site:

Description	Level of Protection [1]	
	D	C
Body		
Work Clothes	R	R
Chemical Protective Suit (Tyvek)	O	R
Visibility Vest	O [2]	O [2]
Apron	O	O
Fall Protection	O [2]	O [2]
Head		
Hard Hat	R	R
Head Warmer	O	O
Eyes & Face		
Safety Glasses	R	R
Goggles (based on hazard)	O	R
Face Shield	O	O
Ears		
Plugs or Muffs	R [2]	R [2]
Hands & Arms		
Work Gloves	R	O [2]
Chemical Resistant Gloves (Nitrile)	O	R

Description	Level of Protection [1]	
	D	C
Insulated Gloves	O	O
Foot		
Work Boots/Steel Toe Boots	R	R
Chemical Resistant Boots	O	O
Disposable Boot Covers	O	O
Respiratory Protection [3]		
½ Mask Air Purifying Respirator (APR) or Full face APR	NA	R
Dust Protection	O	NA
Powered APR	NA	NA
SCBA/Supplied Air Respirator	NA	NA

R = Required, **O** = Optional, **NA** = Not Applicable

[1] The level of protection identified here does not include the necessary equipment for entering confined spaces. Refer to Moran Environmental Recovery's Safety Manual Confined Space Program for atmospheric sampling protocols and breathing and rescue equipment necessary for those operations.

[2] The use of this PPE may or may not be required depending on site conditions/location and will be addressed at the time of task assignment by the HSO.

[3] Respiratory protection necessary to protect against VOC, dusts/particulates and not oxygen deficient atmospheres.

The following table provides a general description of potential field activity tasks to be performed and associated (recommended) PPE. The use of this PPE may or may not vary depending on site conditions and will be addressed at the time of task assignment by the HSO.

Task Description	Invasive (Y/N)	Protection Level
Site Mobilization - Surveying, fence and barrier installation, hay bale installation, decon and work zone set up, soil staging areas preparation	N	Level D
Soil and Water Sampling - Drilling, sampling, soil moving as needed.	Y	Modified Level D or Level C – Respirator as needed based on monitoring. Eye protection required during collection of any liquid sample
Decontamination - Truck dry sweeping, decon pressure wash of equipment, PPE change out	Y	Modified Level D – or Upgrade to Level C dependent on monitoring
Waste Management - Soil load-out for off-site disposal, water removal for disposal, PPE disposal	Y	Modified Level D – or Upgrade to Level C dependent on monitoring
Site Control (Exclusion, Decontamination, Support Zones)	N	Modified Level D – or Upgrade to Level C dependent on monitoring
Communications - Use of hand signals, backup alarms, and voice	N	NA
Site Restoration	Y	Level D

7.0 DECONTAMINATION

7.1 Decontamination Procedures

All personnel and equipment leaving the exclusion zone must be properly cleaned and decontaminated. When there is evidence of chemical contamination during the site operations, all personnel will be decontaminated under the direction of the HSO. Clean-up and/or decontamination of personnel shall consist of washing off excessively soiled PPE with a disinfectant detergent scrub and water. At the very least, all personnel should wash their hands and face before leaving the exclusion zone. After washing, all disposable clothing (tyvek, gloves, etc.) will be removed and placed in a double lined plastic bag.

Sampling tools and any other non-disposable items will be decontaminated between sampling points, and at the direction of HRP personnel, to prevent cross-contamination of work areas or environmental samples, as applicable.

7.2 Emergency Decontamination

If immediate medical attention is required in an emergency, decontamination will be performed after the victim has been stabilized. If a worker has been exposed to an extremely toxic or corrosive material, then emergency decontamination will consist of flushing with copious amounts of water. If the victim cannot be decontaminated because it will interfere with emergency medical aid being administered, then the victim should be wrapped with plastic or other available items (i.e. an uncontaminated coverall) to reduce potential contamination of other personnel or medical equipment.

If a site worker has been overcome by heat related illness, then any protective clothing should be removed immediately. In the case of non-medical emergency evacuation, decontamination should be performed as quickly as possible, unless instant evacuation is necessary to save life or prevent injury.

7.3 Personal Hygiene

All employees will be required to wash hands and face prior to eating, smoking, drinking and going to the bathroom. Workers will be required to remove contaminated PPE and clothing prior to leaving the Contaminant Reduction Zone. All field personnel should avoid contact with potentially contaminated substances such as puddles, pools, mud, etc.

Additional personal hygiene requirements, intended to prevent the spread of the novel corona virus to site workers will be in effect during site activities. These procedures include mobile handwashing stations and the requirement for site workers to wear face coverings. Additional details are included in **Appendix H**.

8.0 EMERGENCY ACTION PLAN/SPILL RESPONSE

In the event of a worker injury, fire, explosion, spill, flood, or other emergency that threatens the safety and health of site workers, the following procedure will be followed:

1. If the emergency originates within the work area covered by this Plan, the HRP HSO shall act as the Emergency Coordinator. The emergency evacuation signal is an air horn or a loud yell. All emergency situations (including worker injuries, no matter how small) will be reported to the HSO, who will determine the appropriate emergency response, up to and including evacuation. Only the HSO may initiate evacuation of the work area. The HSO will be responsible for reporting any emergency situation to the appropriate authorities, using a telephone or other appropriate method.

2. In the case of an evacuation, site workers will exit the site along the safest route(s) and assemble with team members at a safe rally point. Those workers in the Exclusion Zone will follow the emergency decontamination procedures outlined in Section 7.2. Accounting of all site personnel will be conducted by the HSO using the personnel log at a location determined by the HSO.

3. HRP personnel are not permitted to participate in handling the emergency. Fire and medical emergencies will be handled by the local fire department and ambulance service. In the case of a spill of hazardous materials the NYSDEC will be contacted.

   In addition, the HSO/Project Manager must advise the site contact that the New York Spill Hotline should be contacted and, if the spill quantity is greater than the Reportable Quantity (RQ) under CERCLA and/or SARA, the National Response Center (NRC) and Local Emergency Planning Committee should also be contacted. If the spill begins to flow overland and threatens to contaminate a storm drain or surface water, HRP personnel may attempt to contain and isolate the spill using any available resources, but only if, in the judgment of the HSO, such action will not expose the workers to dangerous levels of hazardous substances and is necessary to preserve life or property. In the event that a spill of material of any amount threatens to reach navigable waters, the NRC shall be contacted.

4. Once initial emergency procedures to protect worker safety and health have been addressed, and control of emergency has been completed, the HSO will complete an Investigation Report and submit this form to the appropriate personnel (HRP and/or client contact).

5. All site workers will be familiarized with the above procedures during the pre-entry briefing to be conducted before site work begins.

9.0 TRAINING/MEDICAL SURVEILLANCE

9.1 Training Requirements

All HRP and HRP subcontractor personnel who enter the work zone and/or Exclusion Zone must have successfully completed the 40-hour or 24-hour training requirement outlined in 29 CFR 1910(e). If the 40-hour or 24-hour training of any person occurred more than 12 months prior to commencement of work, then that person must have attended an 8-hour refresher course within the 12 months prior to commencement of work. If respirators are in use in the Exclusion Zone, then all personnel must have undergone respirator training and a fit test within the last 12 months. Training certificates and records for HRP employee(s) are on file at HRP. All other contractors will be required to supply written proof of training before being allowed into the Exclusion Zone.

9.2 Pre-Entry Briefing

Prior to commencement of work in an area of suspected contamination, HRP's Health and Safety Officer will conduct a pre-entry briefing with on-site contractors, which will include the following:

- Name of the HSO and person responsible for the visitor log.
- Description of the parcel as well as location of emergency telephones and the location/boundaries of the Exclusion Zone, Contamination Reduction Zone, and Support Zone, if established.
- Review of hospital locations and directions.
- Review of tasks to be conducted within the parcel by the site workers.
- Review of the Emergency Action Plan and rally point, including the nearest emergency communications and telephone numbers.
- The nature, level, and degree of anticipated hazards (physical and chemical) involved in the site work.
- Required personal protective equipment.
- Decontamination procedures.

The HSO should also, at this time, ensure that all on-site HRP and HRP subcontractor personnel have read the HASP and signed the last page of the original (Section 11.0). If additional information on the site becomes available, the HSO will call additional briefings as necessary.

9.3 Morning Safety (Tailgate) Meeting

The HRP HSO will conduct a safety overview meeting at the beginning of each workday on the site. The meeting will be given in addition to any tailgate meetings that the subcontractor conducts. A summary of the meeting topics signed by the personnel attending the meeting is included in **Appendix D**.

9.4 Medical Surveillance

All HRP and HRP subcontractor personnel entering the Exclusion Zone must have had a physical within the 12 months prior to commencement of site work. A physician's written opinion regarding fitness for work for each employee including work limitations, if any, is on file at HRP, as applicable. A written opinion for all other site personnel must be supplied prior to commencement of site work to the HRP HSO. Any work limitations for site personnel, or relevant medical information (i.e. allergic reactions to medication) should be included in this Plan.

10.0 AUTHORIZATIONS

Personnel authorized to enter the Exclusion Zone include the personnel listed in Section 2.4. Persons not listed in Section 2.4 may enter the Exclusion Zone only if the appropriate training and medical fitness certifications have been supplied to either the HRP Project Manager or Health and Safety Manager and the HSO or his/her designee on site has approved site entry. All personnel entering or leaving the Exclusion Zone must sign in and sign out with the recordkeeper.

11.0 FIELD TEAM REVIEW

All HRP personnel shall sign below after reading this HASP and shall agree with the following statement:

"I have read and understand this site specific Health and Safety Plan.
I will comply with the provisions set forth therein."

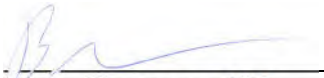
Printed Name	Signature	Date

12.0 APPROVALS

This plan meets the minimum requirements of 29 CFR 1910.120 and 29 CFR 1929.65 and has been written for specified site conditions, dates, and personnel, and must be amended if conditions change. By their signature, the undersigned certify that this HASP is approved and will be utilized during activities at the project.

3/24/2023
Elliott Jackson — Date
On-Site Health and Safety Officer

3/24/2023
Patrick Montuori, PG — Date
Project Manager



3/24/2023
Bryan Sherman, ASP — Date
Office Health and Safety Manager

Subcontractor:

I have been provided a copy of this HASP for review.

Name — Date

Representing _____

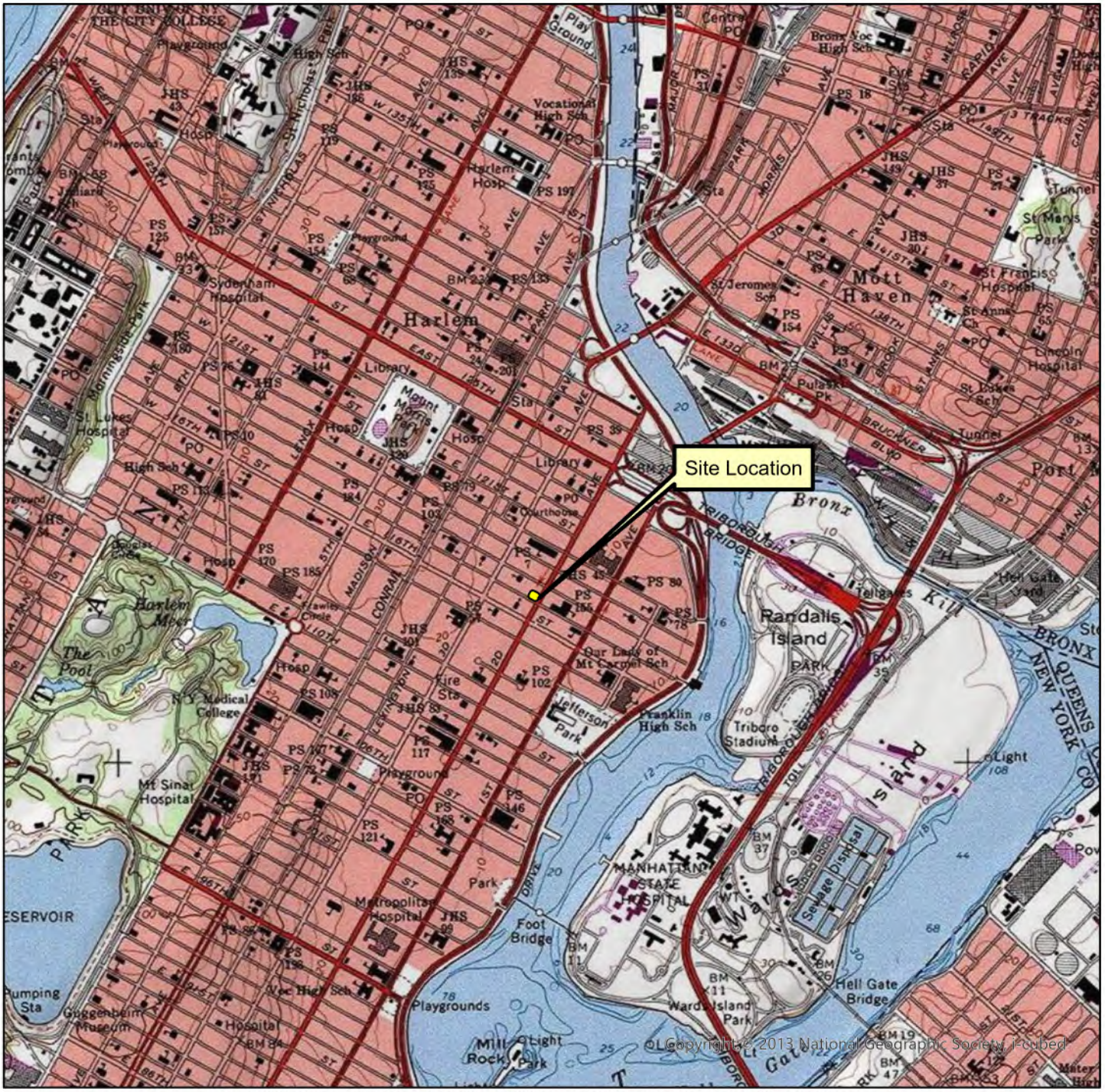
The Designated Competent person representing [subcontractor] at the site will be

_____.

Any alternate Competent Person will be noted in the Daily Job Brief Record (**Appendix D**).

ADDITIONAL APPROVALS (or Re-Approvals)	
Name:	**Date:**

FIGURES



0 500 1,000 2,000 3,000 4,000 5,000 6,000 7,000 8,000

Feet

1:24,000

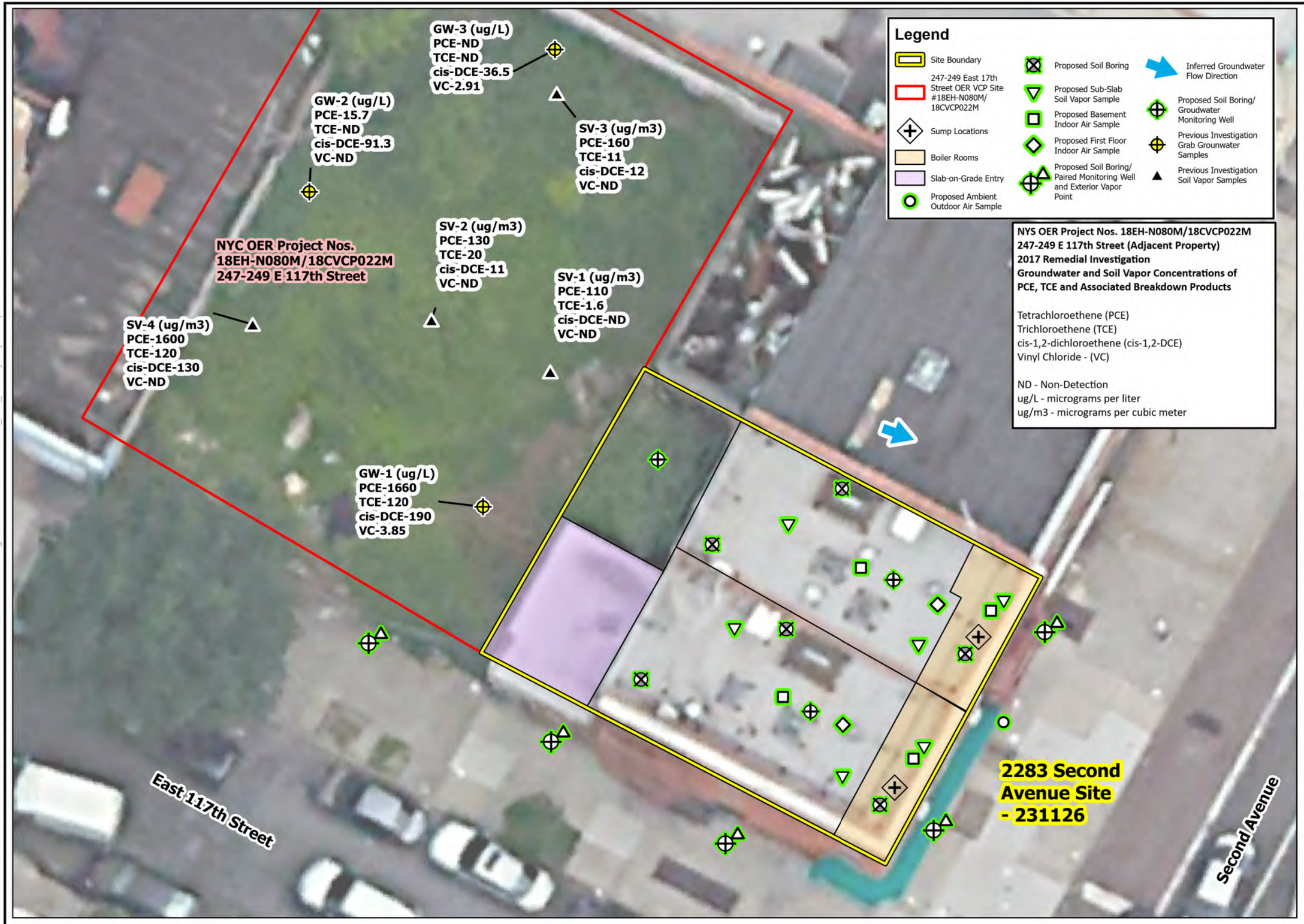
N

Figure 1
Site Location
2283 Second Avenue
Site #231126
2283 Second Avenue
New York, New York 10035
HRP # DEC1038.P2
Scale 1" = 2,000'

USGS Quadrangle Information
Quad ID: X24K7974
Name: Central Park, NY, NJ
Date Rev: 2019
Date Pub: 2019

HRP
MOVE YOUR ENVIRONMENT FORWARD
ONE FAIRCHILD SQUARE
SUITE 110
CLIFTON PARK, NY 12065
(518) 877-7101
HRPASSOCIATES.COM

Path: S:\Data\N\NYDEC - NYSDEC\NEW YORK\VARIOUS NYC\DEC1038P2 - Region 2 NYC Sites\GIS\2283_2nd_Ave\MyProject1.aprx



Legend

- Site Boundary
- 247-249 East 17th Street OER VCP Site #18EH-N080M/ 18CVCP022M
- Sump Locations
- Boiler Rooms
- Slab-on-Grade Entry
- Proposed Ambient Outdoor Air Sample
- Proposed Soil Boring
- Proposed Sub-Slab Soil Vapor Sample
- Proposed Basement Indoor Air Sample
- Proposed First Floor Indoor Air Sample
- Proposed Soil Boring/ Paired Monitoring Well and Exterior Vapor Point
- Inferred Groundwater Flow Direction
- Proposed Soil Boring/ Groudwater Monitoring Well
- Previous Investigation Grab Grounwater Samples
- Previous Investigation Soil Vapor Samples

NYS OER Project Nos. 18EH-N080M/18CVCP022M
247-249 E 117th Street (Adjacent Property)
2017 Remedial Investigation
Groundwater and Soil Vapor Concentrations of PCE, TCE and Associated Breakdown Products

Tetrachloroethene (PCE)
Trichloroethene (TCE)
cis-1,2-dichloroethene (cis-1,2-DCE)
Vinyl Chloride - (VC)

ND - Non-Detection
ug/L - micrograms per liter
ug/m3 - micrograms per cubic meter

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SUITE 110
CLIFTON PARK, NY 12065
(518) 877-7101
HRPASSOCIATES.COM

North

0 5 10 Feet

Revisions					
No.					
Date					

Designed By: EWJ	Drawn By: CMS	Reviewed By: PWM
Issue Date: 03/24/2023	Project No: DEC1038.P2	Sheet Size: 11x17

Site Plan - Proposed Investigation Locations and Previous Investigation of Adjacent Property

2283 Second Avenue
NYSDEC Site # 231126
2283 Second Avenue
New York, NY 11035

Figure No.
2

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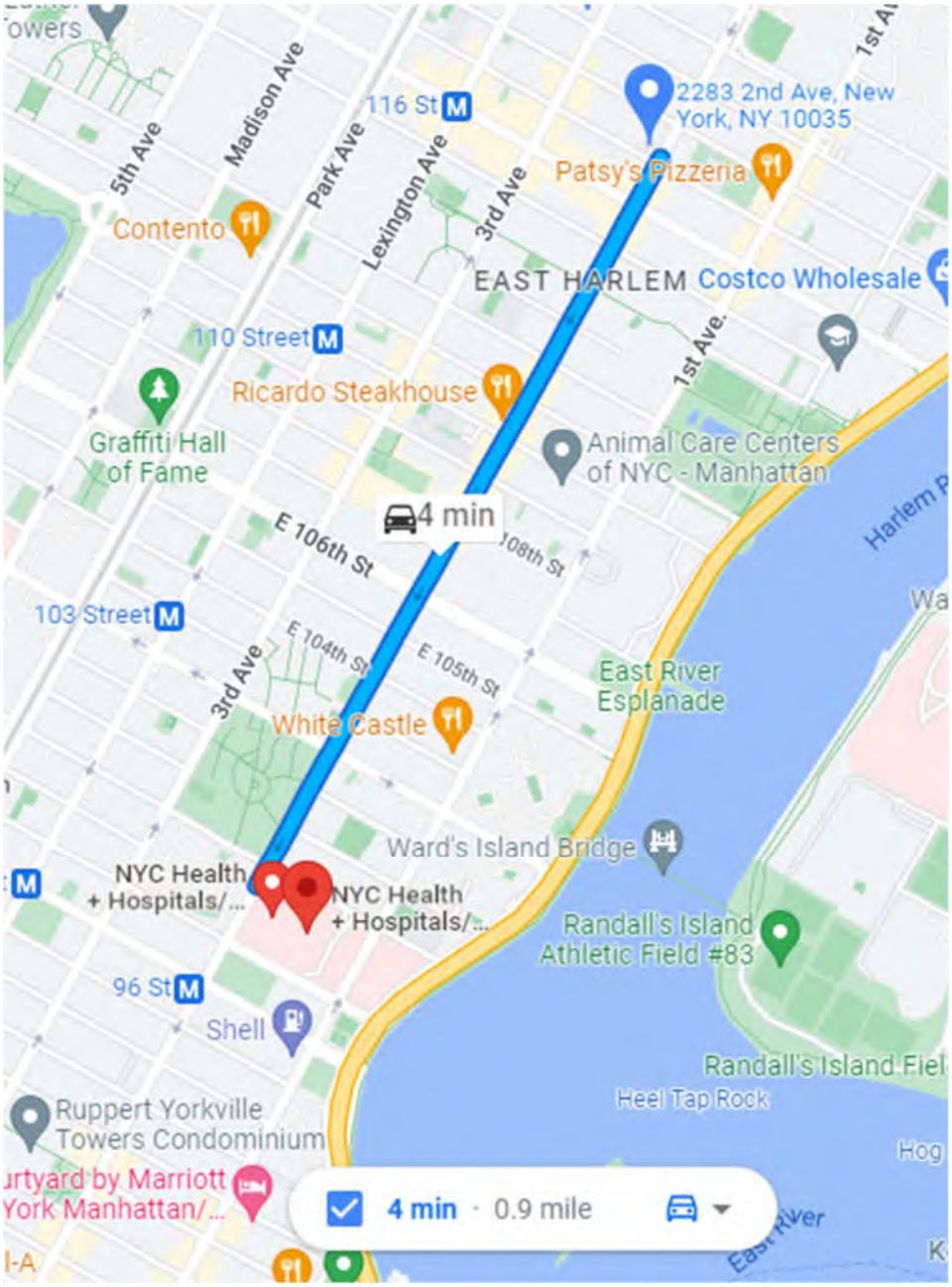
Figure 3: Route and Map to Nearest Hospital and Medical Center

Directions to NYC Health and Hospitals/Metropolitan Hospital

Total Estimated Time: 4 minutes
Total Estimated Distance: 0.9 miles

Begin at 2283 2nd Avenue, New York, NY
End at to NYC Health and Hospitals/Metropolitan
New York, NY 10035



TABLES

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
1,1,1 Trichloroethane	44 ppm	350 ppm	350 ppm	---	700 ppm	Inh, Ing, Con	Head, Lass, CNS, Derm
1,1,2-Trichloroethane	---	10 ppm	10 ppm	----	[100 ppm]	Inh, Ing, Abs, Con	Eyes, Nose Irrit, Resp Irrit, CNS, Liver, Kidney Damage, Derm, [Carc]
1,2,4 Trimethylbenzene 1,3,5 Trimethylbenzene		25 mg/m^3	25 ppm	25 mg/m^3	ND	Inh, Ing, Con	Irrit Eyes, Skin, Nose, Throat, Resp Sys, Bron, Hyprochronic Anemia, Head, Drow, Ftg, Dizz, Nau, Inco, Vomit, Conf, Chemical Pneu (aspir lig)
1,1' Biphenyl	0.0062 mg/m^3	0.2 ppm	0.2 ppm	---	100 mg/m^3	Inh	
1,1-Dichloroethane	120 ppm	100 ppm	100 ppm	---	3,000 ppm	Inh, Ing, Con	CNS Depres, Skin Irrit, Liver, Lung and Kidney Damage
1,1-Dichloroethylene***	500 ppm	---	5 ppm	---	---	Inh, Con	CNS depress, Resp, [Carc]
1,2-Dichlorobenzene	50 ppm	50 ppm	25 ppm		200 ppm	Inh, Ing, Abs, Con	Irrit, Resp
1,2-Dichloroethylene	26-87 ppm	200 ppm	200 ppm	---	1,000 ppm	Inh, Ing, Con	Vomit, Irrit Eyes, Resp Sys; CNS Depres
1,2-Dichloropropane	130-190 ppm	75 ppm	75 ppm	---	[400 ppm]	Inh, Con, Ing	Eye irritation, Drow, light-headedness; irritated skin, [Carc]
1,3-Dichlorobenzene	---	----	---	----	---	----	----
1,4-Dichlorobenzene	20 ppm	75 ppm	10 ppm	----	[150 ppm]	Inh, Ing	[Carc], Eye Irrit, swelling around eye, headache, nausea, vomiting
1-Methylnaphthalene	0.02 ppm	---	---	---	---	---	---
2,4-Dichlorophenol	1.4007 mg/m^3	---	---	---	---	---	---
2,4-Dimethylphenol	0.001 mg/m^3	---	---	---	---	---	---
2-Methylnaphthalene	0.01 ppm	---	---	---	---	---	---
2-Methylphenol (o-cresol) [skin]	1.4 mg/L	5 ppm	5 ppm	---	250 ppm	Inh, Abs, Ing, Con	Confusion, depression, Resp Fail; difficulty breathing, irregular rapid respiration, weak pulse; skin, eye burns; dermatitis

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
3, 3'-Dichlorobenzidine	---	None	**---**	---	---	Inh, Abs, Ing, Con	Sens, Derm, Head, Dizz, Burns, GI Upset, [Carc]
4-Isopropyltoluene	---	---	---	---	---	Con, Inh, Ing	Defat, Eryt
Acenephthene	0.5048 mg/m^3	---	---	---	---	---	---
Acenaphthylene	---	---	---	---	---	---	---
Acetone	47.5 mg/m^3	1,000 ppm	500 ppm		2,500 ppm	Ing, Inh, Con	Head, Dizz; Irrit Eyes, Nose, Throat; Derm, CNS, Depress, Derm
Acetonitrile	70 mg/m^3	40 ppm	20 ppm	---	500 ppm	Inh, Ing, Abs, Con	Asphy; Nau, Vomit; Chest Pain; Weak, Stupor, Convuls; Eye Irrit
Aldrin	---	0.25 mg/m^3	0.25 mg/m^3	---	25 mg/m^3	Inh, Abs, Ing, Con	Head, Dizz, Nau, Vomit, Mal, Myo, [Carc]
Anthracene (Coal Tar Pitch)	---	0.2 mg/m^3			[80 mg/m^3]	Inh, Con	Derm, bron, [carc]
Antifreeze		50 ppm	100 mg/m^3 (aerosol)	---	ND	Inh, Ing, Con	Irrit Eyes, Skin, Nose, Throat, Nau, Vomit, Abdom Pain, Lass, Dizz, Stup, Conv, CNS, Depres, Skin Sen
Arsenic	----	0.010 mg/m^3	0.01 mg/m^3	----	[5 mg/m^3]	Abs, Inh, Con, Ing	Derm; GI; Resp Irrit; ulceration of nasal septum; Resp, Irrit, Hyper Pig of Skin, [Carc]
Barium (elemental)	---	0.5 mg/m^3	0.5 mg/m^3		50 mg/m^3 (barium components)	Inh, Ing, Con	Resp. Irrit, GI, Muscle Spasm, Eye Irrit, Slow Pulse; skin burns
Benzene*	4.7 ppm	1 ppm	0.5 ppm	5 ppm	[500 ppm]	Inh, Ing, Abs, Con	Irrit Eyes, Nose, Throat; Head, Nau, Derm, Ftg, Anor, Lass, [Carc]
Benzo(a)anthracene (coal tar pitch)	---	0.2 mg/m^3			[80 mg/m^3]	Inh, Con	[Carc], Derm, Bron
Benzo(a)pyrene (coal tar pitch)	---	0.2 mg/m^3	---		[80 mg/m^3]	Inh, Con	[Carc], Derm, Bron
Benzo(b)fluoranthene (coal tar pitch)	---	0.2 mg/m^3	---		[80 mg/m^3]	Inh, Con	[Carc], Derm, Bron

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
Benzo(g,h,i)perylene (coal tar pitch)	---	0.2 mg/m^3			[80 mg/m^3]	Inh, Con	[Carc], Derm, Bron
Benzo(k)fluoranthene (coal tar pitch)	---	0.2 mg/m^3			[80 mg/m^3]	Inh, Con	[Carc], Derm, Bron
Bis (2-ethylhexyl) Phthalate**	N/A	5 mg/m^3	5 mg/m^3	10 mg/m^3	[5,000 mg/m^3]	Inh, Ing, Con	[Carc], Irrit Eyes
Cadmium (dust)	---	0.005 mg/m^3	Lowest concentration feasible 0.01 mg/m^3	---	[9 mg/m^3]	Inh, Ing	CNS, Resp, Irrit, Vomit, Cough, Head, Chills, Nau, Diarr, Pulm Edema, Dysp, Chest Tight, [Carc]
Carbazole	---	---	---	---	---	Inh	---
Carbon disulfide	0.1-0.2 ppm	20 ppm	1 ppm	30 ppm	500 ppm	Inh, Abs, Ing, Con	Diz, Head,Ftg, Ner, anorexia, trembling hands, loss of fine motor coord, gastritis, eye, skin burns, Derm
Carbon Tetrachloride***	21.4 ppm	10 ppm	5 ppm	25 ppm	[200 ppm]	Inh, Abs, Con, Ing	CNS Depres, Nau, Vomit, Irrit, Irrit Eyes, Skin, Drow, Dizz, [Carc]
Chlorobenzene***	0.98 mg/m^3	75 ppm	10 ppm	---	1,000 ppm	Inh, Ing, Con	Irrit, Drow, CNS, Depres, Eyes, Skin, Nose, Inco.
Chloroform***	85 ppm	50 ppm	10 ppm	50 ppm	[500 ppm]	Inh, Ing. Con, Abs	Dizz, Dullness, Nau, Head, Ftg, Irrit Eyes, Skin, Conf, [Carc]
Chromium	---	1 mg/m^3	0.5 mg/m^3	---	250 mg/m^3	Inh, Ing, Con	Irrit Eyes, Sens Derm
Chrysene (coal tar pitch)		0.2 mg/m^3	---		[80 mg/m^3]	Inh, Con	Derm, Bron, [Carc]
Cis-1-2-Dichloroethylene	---	200 ppm	200 ppm	----	1000 ppm	Inh, Con, Ing	Irrit Eyes, Resp, CNS Depress
Copper (dusts and mists) (fumes)		1 mg/m^3 0.1 mg/m^3	1 mg/m^3 0.2 mg/m^3	----	100 mg/m^3	Inh, Ing, Con	Vomit, Derm, CNS, Irrit, Derm, Nau, Taste (metallic)
Cyanide	0.9 mg/m^3	5 mg/m^3	5 mg/m^3 (10 min)	5 mg/m^3	25 mg/m^3	Inh, Ing, Abs, Con	Weak, Head, Nau, Conf, Cyan
Dibenzo(a,h)anthracene						Inh, Ing	

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
Dichloromethane	540 mg/m^3	25 ppm	50 ppm	125 ppm	[2,300 ppm]	Inh, Abs, Ing, Con	Irrit Eyes, Skin, lass, drow, dizz, Numb, tingl, Nau, [Carc]
Diethylphthalate**	---	None	5 mg/m^3	---	N.D.	Inh, Ing, Con	Irrit Eyes, Skin, Nose, Throat, Head, Dizz, Nau, Lac, Possible Polyneur, Vestibular Dysfunc, Pain, Numb, lass, Spasms in Arms and Legs
Di-n-octylphthalate	---	---	---	---	---	Inh, Ing, Con	---
Dimethylpthalate	---	5 mg/m^3	5 mg/m^3	---	2,000 mg/m^3	Inh, Ing, Con	Irrit, Resp, Abdom
Ethyl Benzene*	8.7 mg/m^3	100 ppm	100 ppm	125 ppm	700 ppm	Inh, Abs, Con	Head. Irrit, Derm, Narc., Irrit Eyes, Skin; Coma
Fluoranthene		0.2 mg/m^3	0.2 mg/m^3			Ing, Inh	[Carc]
Fluorine*	6 mg/m^3	0.1 ppm	1 ppm	2 ppm	25 ppm	Inh, Con	
Fuel Oil/#2	----	----	300 ppm	----		Inh, Abs, Ins, Con	Irrit Eyes, Skin, Derm, Head, Ftg, Blurred Vision, Dizz, Conf
Ideno(1,2,3-cd)pyrene		0.2 mg/m^3				Ing, Inh	
Lead (inorganic forms and dust as Pb)****		0.05 mg/m^3	0.05 mg/m^3		100 mg/m^3	Inh, Ing, Con	Irrit, Cns, Vomit, Narco, Weak, Pall, Insom, Lass, Abdom, Constip
Mercury (organic alkyl compounds) [skin]		0.01 mg/m^3	0.01 mg/m^3	0.03 mg/m^3	2 mg/m^3	Inh, Abs, Ing, Con	Irrit Eyes, Skin; Cough & Chest Pain, Bron Pneu, Tremor, Insom, Irrty, Indecision, Head, Ftg, Weak, Stomatitis, Salv, GI Dist, Anor, Low-wgt, Ataxia
Mercury (compounds)	----	0.1 mg/m^3	0.025 mg/m^3	0.1 mg/m^3	10 mg/m^3	Inh, Abs, Ing, Con	Irrit Eyes, Skin; Cough & Chest Pain, Bron Pneu, Tremor, Insom, Irrty, Indecision, Head, Ftg, Weak, Stomatitis, Salv, GI Dist, Anor, Low-wgt, Ataxia

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
Methanol	13.1150 mg/m^3	200 ppm	200 ppm	---	6,000 ppm	Inh, Abs, Ing, Con	Irrit Eyes, Skin, Resp, Head, drow, dizz, Nau, Vomit, vis dist, Optic, derm
Methyl Ether	----	----	---	----	---	Inh	Poison
Methyl Ethyl Ketone (2-Butanone)***	0.7375 mg/m^3	200 ppm	200 ppm	300 ppm	3,000 ppm	Inh, Con, Ing	Irrit Eyes, Skin, Nose, Throat, Head, Dizz, Vomit, Derm
Methylene Chloride	540 mg/m^3	25 ppm	50 ppm	125 ppm	[2,300 ppm]	Inh, Ing, Con, Abs	Ftg, Weak, dizz, drow, Numb, Tingle [carc], Irrit Eyes, Skin, Nau
Mineral Spirit	20 ppm	500 ppm	100 ppm	---	20,000 mg/m^3	Inh, Ing, Con	Irrit Eyes, Nose, Throat, Dizz, Derm, Chemical pneu
Methyl tert butyl ether (MTBE)	---	---	50 ppm	---		Inh, Abs	
Naphtha	0.86 ppm	100 ppm	400 ppm	---	1,000 ppm	Inh, Con, Ing	Light Head, Drow, Irrit, Derm, Irrit Eyes, Skin, Nose
Naphthalene*	0.084 ppm	10 ppm	10 ppm	15 ppm	250 ppm	Inh, Abs, Ing, Con	Eye irritation; headache; confusion, excitement, malaise (vague feeling of ill-being); nausea, vomiting, abdominal pain; irritated bladder; profuse sweating; renal shutdown; dermatitis
Nickel (metal)	---	1 mg/m^3	1.5 mg/m^3	---	[10 mg/m^3]	Inh, Ing, Con	Head, Verti, Nau, Vomit, Pain, Cough, Weak, Convuls, Delirium, Pneu, ,[Carc]
Nitrobenzene	0.0235 mg/m^3	1 ppm	1 ppm	---	200 ppm	Inh, Abs, Ing, Con	Irrit Eyes, Skin, Anoxia, Derm, Anem, Methem
n-Butylbenzene	---	---	---	---	---	---	---
n-Propylbenzene	---	---	---	---	---	---	---

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
PCBs 42% chlorine (Aroclor 1242)	---	1 mg/m^3 (skin)	1 mg/m^3 (skin)	---	[5 mg/m^3]	Inh, Abs, Ing, Con	Irrit Eyes, Chloracne, Liver Damage [carc]
PCBs 54% chlorine (Aroclor 1254)	---	0.5 mg/m^3 (skin)	0.5 mg/m^3 (skin)	---	[5 mg/m^3]	Inh, Abs, Ing, Con	Irrit Eyes; Chloracne, Liver Damage [carc]
Petroleum Distillates	---	500 ppm	100 ppm		[1,100 ppm]	Inh, Ing, Con	Dizz, Drow, Head, Dry Skin, Nau, Irrit Eyes, Nose, Throat, [Carc]
Phenanthrene (Coal Tar Pitch)		0.2 mg/m^3	0.2 mg/m^3		[80 mg/m^3]	Inh, Con	Derm, bron, (carc)
Phenol**	0.1786 mg/m^3	5 ppm	5 ppm	---	250 ppm	Inh, Abs, Ing, Con	Irrit Eyes, Nose, Throat, Anor, Low Wgt, Weak Musc Ache, Pain, Dark Urine, Cyan, Liver, Kidney Damage, Skin, Burns, Derm, Ochronosis, Tremor, Convuls, Twitch
Pyrene		0.2 mg/m^3			[80 mg/m^3]	Inh, Con	[Carc]
Sec-Butylbenzene	---	---	---	---	---	---	---
Selenium	N/A	0.2 mg/m^3	0.2 mg/m^3	Unknown	1 mg/m^3	Inh, Ing, Con	Irrit, Head, Fever, Chills, Skin/Eye Burns, Metallic Taste, GI, Dysp, Bron
Silver (metal and soluble compounds as Ag)	----	0.01 mg/m^3	Metal = 0.1 mg/m^3 Soluble 0.01 mg/m^3		10 mg/m^3	Inh, Ing, Con	Blue-gray Eyes, Nasal Septum, Throat, Skin; Irrit, Ulcer, Skin, GI Dist
Tetrachloroethylene (a.k.a. perchloroethylene)***	4.68 ppm	100 ppm	25 ppm	200 ppm	[150 ppm]	Inh, Ing, Con, Abs	Irrit Eyes, Skin, Nose, throat, Resp. Nau, flush face, Neck, dizz, inco, head, drow, eryth, [Carc]
Toluene*	2.14 ppm	200 ppm	50 ppm	300 ppm	500 ppm	Inh, Abs, Ins, Con	Resp, Irrit, Ftg, Conf, Dizz, Head, Derm, Euph, Head, Dilated Pupils, Lac, Ner, Musc FTg, Insom, Pares, Derm, lass

TABLE 1a CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE							
CONTAMINANT	**ODOR THRESHOLD**	**OSHA PEL[1]**	**TLV (ACGIH)**	**OSHA CEILING[2] /STEL**	**IDLH CONC.**	**ROUTES OF EXPOSURE**	**SYMPTOMS OF ACUTE EXPOSURE[3]**
Petroleum Distillates (naphtha)	10 ppm	100 ppm	400 ppm	---	1,000 ppm	Con, Inh, Ing	---
Trans 1,2-Dichloroethylene	0.3357 mg/m^3	200 ppm	200 ppm	---	1,000 ppm	Inh, Con	Irrit, Resp, CNS depress
Trichloroethylene***	21.4 ppm	100 ppm	50 ppm	200 ppm	[1,000 ppm]	Inh, Con, Abs, Ing	Head, Vert, Nau, Vomit, Derm, Vis Dist, Tremors, Som, Nau, Irrit Eyes, Skin, Card Acc., Ftg, [Carc]
Trichlorofluoromethane	28 mg/m^3	1,000 ppm	1,000 ppm		2,000 ppm	Inh, Con, Ing	Inco, trem, derm, card, asph, frost
Trichlorotrifluoroethane	45 ppm	1,000 ppm	1,000 ppm	1,250 ppm	2,000 ppm	Inh, Con, Ing	Irrit Skin, throat, Drow, Derm, CSN, Depress
Vinyl Chloride***	10-20 ppm	1 ppm	1 ppm	5 ppm	ND	Inh, Con	Lass, Abdom, Gi Bleeding; Hepatomegaly; Pallor or Cyan of Extremities; Liq: Frostbite; [Carc]
VM&P Naphtha (petroleum naphtha)	---	---	300 ppm	---	ND	Con, Ing, Inh	Irrit Eyes, Nose, Throat, Dizz, drow, head, nau, dry skin, chem. Pneumonitis
Xylene*	4.5 mg/m^3	100 ppm	100 ppm	150 ppm	900 ppm	Inh, Ing, Abs, Con	Dizz, Drow, Irrit, Excite, Nau, Vomit, Eyes, Skin, Nose, Throat
Zinc (oxide)	---	5 mg/m^3	2 mg/m^3	---	500 mg/m^3	Inh	Dry Throat, Cough, Chills, Tight Chest, Blurred Vision
4,4' DDD	---	---	---	---	---	Ing, Inh, Con	---
4,4' DDE	---	---	---	---	---	Ing, Inh, Con	---
4,4' DDT	5.0725 mg/m^3	1 mg/m^3	1 mg/m^3	---	[500 mg/m^3]	Inh, Abs, Ing, Con	Irrit Eyes, Skin, Pares, Tongue, Lips, Face, Trem, Anxi, Dizz, Conf, Mal, Head, Lass, Conv, Paresi Hands, Vomit, [Carc]
Aldrin		0.25 mg/m^3	0.25 mg/m^3	---	[25 mg/m^3]	Inh, Abs, Ing, Con	Head, Dizz, Nau, Vomit, Mal, Myo [Carc]

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]
Chlordane [skin]	0.0084 mg/m^3	0.5 mg/m^3	0.5 mg/m^3		[100 mg/m^3]	Inh, Abs, Ing, Con	Blurred vision, confusion, delirium, cough; abdominal pian, nausea, vomiting diarrhea; irritability, tremor, convulsions [Carc]
EDB	76.8 mg/m^3	20 ppm		30 ppm	[100 ppm]	Inh, Abs	Resp. Irr, Eye Irr. [Carc]
Endosulfan I Endosulfan II	---	0.1 mg/m^3	0.1 mg/m^3	---	N.D.	Inh, Abs, Ing, Con	Irrit, Skin, Nau, Conf, Agit, Flush, Dry, Trem, Conv, Head
Endosulfan Sulfate		---	0.1 mg/m^3	---	---	Ing, Con	---
Endrin	1.8 x 10^{-2} ppm	0.1 mg/m^3	0.1 mg/m^{-3}	---	2 mg/m^3	Inh, Abs, Ing, Con	Epil Conv, Stup, Head, Dizz, Abdom, Nau, Vomit, Insom, Agress, Conf, Drow, Lass, Anor
Endrin Aldehyde	1.8 x 10^{-2} ppm	---	---	---	---	Inh, Con	---
Endrin Ketone	---	---	---	---	---	---	---
Heptachlor	0.02 ppm	0.5 mg/m^3	0.05 mg/m^3	---	[35 mg/m^3]	Inh, Abs, Ing, Con	In animals, Trem, Conv, [Carc]
Heptachlor epoxide	0.02 ppm	---	0.05 mg/m^3	---	---	Ing, Inh	Trem, Conv, [Carc]
Hydrogen Cyanide(Hydrocyanic Acid)	0.9 mg/m^3	10 ppm (11 mg/m^3)	4.7 ppm	4.7 ppm	50 ppm	Con, Inh, Ing, Abs	Asphy & death at high levels; Weak, Head, Conf, Nau, Vomit, Incr. Rate and Depth of Respiration or Respiration Slow and Gasping

TABLE 1a
CHEMICAL HAZARDS KNOWN OR SUSPECTED ON-SITE

CONTAMINANT	ODOR THRESHOLD	OSHA PEL[1]	TLV (ACGIH)	OSHA CEILING[2] /STEL	IDLH CONC.	ROUTES OF EXPOSURE	SYMPTOMS OF ACUTE EXPOSURE[3]

NOTES

* = Constituent found in ETPH
**=Constituent found in Acid/Base/Neutral Extractable Compounds
***=Constituent found in Volatile Organic Compounds
****=Constituent found in Leaching Lead

[1]PEL = Permissible Exposure Limit. If no PEL is available, then the NIOSH Threshold Limit Value (TLV) should be used, if available.
[2]Ceiling limit or Short Term Exposure Limit (STEL), if available. Again, the NIOSH TLV may be used if no OSHA standard exists.
[3]Abbreviations are contained on the next page

[ ] = Potential Occupational Carcinogen
ND = Not Been Determined

ABBREVIATIONS

abdom = Abdominal
abs = Absorption
aggress = Aggressiveness
agit = Agitation
anor = Anorexia
anos = Anosmia (loss of the sense of smell)
Anxi = anxiety
anem – Anemia
aspir = Aspiration
asph – asphyxia
bron = Bronchitis
bron pneu = Bronchitis pneumonitis
[carc] = Potential occupational carcinogen
Card = Cardiac arrhythmias
CNS = Central nervous system
conf = Confusion
constip = Constipation
con = Skin and/or eye contact
conv = Convulsions
corn = Corneal
cyan = Cyanosis
defat = Defatting
depres = Depressant/Depression
derm = Dermatitis
diarr = Diarrhea
dist = Disturbance
dizz = Dizziness
drow = Drowsiness
dry = Dry mouth
dysp = Dyspnea (breathing difficulty)
emphy = Emphysema
epil-conv = Epileptiform convulsions
eryth = Erythema
euph = Euphoria
fib = Fibrosis
frost = frostbite
ftg = Fatigue
flush = Flushing
GI = Gastrointestinal
head = Headache
hyperpig = Hyperpigmentation
inco = Incoordination
ing = Ingestion
inh = Inhalation
inj = Injury
insom = Insomnia
irrit = Irritation
irrty = Irritability
lac = Lacrimination (discharge of tears)
lass = Lassitude (weakness, exhaustion)
li-head = Lightheadedness
liq = Liquid
low-wgt = Weight loss
mal = Malaise (vague feeling of discomfort)
malnut = Malnutrition
methem = Methemoglobinemia
myo = Myochonic (jerks of limbs)
mg/m = milligrams/cubic meter
muc memb = Mucous membrane
mus ftg = Muscle fatigue
narco = Narcosis
nau = Nausea
ner = Nervousness
numb = Numbness
optic = Optic nerve damage (blindness)
pall = Facial pallor
parap = Paralysis
ppm = Parts per million
pares = Paresthesia
paresi = Paresis
peri neur = Peripheral neuropathy
pneu = Pneumonitis
prot = Proteinuria
pulm = Pulmonary
peri neur = Peripheral neuropathy
pneu = Pneumonia
prot = Proteinuria
pulm = Pulmonary
repro = Reproductive
resp = Respiratory
skin sen = skin sensitization
salv = Salvation
som = Somnolence (sleepiness unnatural drowsiness)
subs = Substernal (occurring beneath the sternum)
stup = Stupor
sys = System
tingle = tingle limbs
trem – Tremors
verti = Vertigo
vis dist = Visual disturbance
vomit = Vomiting
weak = Weakness

TABLE 1b: Physical Hazards Known or Suspected On-Site

TABLE 1b PHYSICAL HAZARDS KNOWN OR SUSPECTED ON-SITE			
Description of Hazard	**Methods to Identify and Minimize**	**Potential for Occurrence**	**Potentially Affected Tasks**
1. Operating Heavy Equipment	• Utilizing proper equipment operation methods • Maintain safe clearance distances • Wear appropriate eye/ear protection according to manufacturer's recommendations	Moderate	Drilling/Sampling
2. Inclement weather	• Determine probable weather conditions prior to arrival at site • Avoid working during hurricanes, blizzards, persistent heavy rain or snow, close thunderstorms	Moderate	Drilling/Sampling
3. Heat/cold Stress	• Determine probable weather conditions prior to arrival at site • Wear proper clothing • Monitoring of yourself and team mates • Drink plenty of fluids • Utilize work breaks as often as necessary • Avoid working in extreme cold conditions	Moderate	Drilling/Sampling
4. Slip, trip, and fall hazards caused by irregular and loose rocky topography	• Wear appropriate footwear to increase traction when possible • Be aware of surroundings	Low	Drilling/Sampling

TABLE 1b PHYSICAL HAZARDS KNOWN OR SUSPECTED ON-SITE			
Description of Hazard	**Methods to Identify and Minimize**	**Potential for Occurrence**	**Potentially Affected Tasks**
5. Utilities	• Complete a Call Before You Dig markout prior to the work start date • Obtain buried private lines information from and clear sampling locations with Site Contact • Avoid using heavy equipment or drill rig in close proximity to overhead utilities • Inspect sampling areas for Call Before You Dig markings; inspect catch basins and manholes to determine buried pipeline directions prior to sampling • Avoid sampling within area of pavement cuts that may be indicative of buried lines	Moderate	Drilling/Sampling
6. Vehicle Traffic	• Wear appropriate high visibility clothing • Block off the work area to prevent vehicles from entering	Moderate	High Traffic areas
7. Use of heavy machinery in indoor spaces	• Monitor the indoor air for appropriate gases with a 4-gas meter • Ensure proper ventilation of interior spaces while using gas powered machines • Use appropriate respirator protection and adequate wetting of the area if cutting or drilling through concrete creates silica dust	Low	Drilling in indoor spaces

TABLE 1b PHYSICAL HAZARDS KNOWN OR SUSPECTED ON-SITE			
Description of Hazard	**Methods to Identify and Minimize**	**Potential for Occurrence**	**Potentially Affected Tasks**
8. Inhalation of Volatiles	• Implement and adhere to action levels stipulated in air monitoring program for volatile organics • Wear appropriate protective equipment • Report potential exposure symptoms immediately • Utilize engineering controls such as fans	Low	Drilling/Sampling
9. Skin contact with volatile organic compounds, semi volatile organic compounds, metals, TPHs, PCBs, pesticides, cyanide	• Wear appropriate protective clothing • Follow proper decontamination procedures • Report potential exposure symptoms immediately	Low	Drilling/Sampling

APPENDIX A

Safety and Logistics Planning Call Log

Safety and Logistics Call Log
DEC009808

Date of Call _____

Work Assignment Number / Task _____

DEC Site Name and Number _____

Names of Attendees (and phone #s):

HRP

- HRP PM _____
- HRP SSO _____
- HRP Other _____
- HRP Other _____
- HRP Other _____

Subcontractors

- Driller Contact _____
- Utility Survey _____
- Surveyor _____
- Construction _____
- Other _____

DEC

- DEC PM _____
- DEC Other _____

Other _____

Brief Description Scope of Work (Task Specific): Use additional forms for additional tasks.

_____

_____

_____

_____

_____

_____

_____

_____

_____

Logisitics:

Date of Work: _____

Time to Meet: _____

Site Contact (phone): _____

Notification of Site Contact made by: _____

Describe any unusal site-specific conditions/logistics here (if any): _____

_____

Notes below as needed:

Water Needed? Source Confirmed?	Y / N	_____
Electricity Needed? Source Confirmed?	Y / N	_____
Water Storage Needed?	Y / N	_____
Water Discharges? Permits Needed/Attained?	Y / N	_____
Air Monitoring - CAMP?	Y / N	_____

Will there be intrusive work? Y / N _____

Locations marked in the field? Y / N _____

NYS Code Rule 753/Dig Safe System: Ticket Number: _____

Confirmed that mark-out complete? Y / N

Anticipated Subsurface Conditions (Geology, Utilites, etc.): _____

Anticipated Depth to Groundwater: _____

Will NAPL/Product be Present: Y / N Describe: _____

_____

Safety and Logistics Call Log
DEC009808

Will there be any other parties entering the work zones? Describe control measures:

Lab and Equipment:

Equipment: Y / N PID IP Water Level Indicator CAMP Pumps controllers Survey Eq. GPS
Other: _____

Lab Analytical Required: Y / N VOCs SVOCs Metals PFAS 1,4D PCBs Pest/Herb
Other: _____

Media Tested: Soil Sediment Groundwater Surface Water Sub-slab[soil] Vapor Indoor Air
Notes of sample collection methods: _____

Bottle Order Received/ Checked? Y / N
How will samples be conveyed to lab? _____
Sample TAT? Standard 24 hr TAT 48 hr TAT Other: _____

Review Site - Specific Hazards (per Site-Specific HASP to be provided prior to all parties):

Site Constituents of Concern: (circle)
VOCs HVOCs AVOCs SVOCs PFAS 1,4-Dioxane
metals pesticides herbicides
Asbestos PCBs
Lead Other:_____
Biologicals

Site Setting: Urban Suburban Unoccupied
Traffic Bystanders Crime Plants Animals Vectors
Overhead Utilities Underground Utilities Large Equipment
High Voltage Flood/Tidal Limited Access
Confined Spaces

Task-Specific Chemicals and Hazards (describe): _____
PPE Level (circle): D C B A Modifications: _____
Glove types: _____ Face covering needed? Y/ N
Other specialty PPE: _____

Safe to Work Alone: Y / N
Other Precautions: Y / N Describe: _____

COVID 19 Protocols to be Observed: Y / N

Waste Containment:

How/ where will materials be contained, labelled, stored, or disposed? _____

Miscellaneous:

APPENDIX B
Personnel Log

PERSONNEL LOG

Name	Representing	Date	Time In	Time Out

APPENDIX C

Supervisor's Investigation Report

INCIDENT REPORT

Section 1.0: Complete By Employee and Project Manager

(provide to Human Resources Manager) Incident Case No. _____

Employee Name: Employee Title/Position:	Age: Sex: □ Female □ Male	Time employee began work: Date of Incident: Time of Incident:	Weather Conditions: Date of Report: Time Report Completed:
Department: Office Location: Supervisor:			
Employee Address: Street: City/Town: Zip Code: Phone Number:	Location of Incident: Address: City/Town: State:		

Type of Incident:
□ Motor Vehicle Accident or □ Near Miss or □ Injury occurred during routine work

□ Company or □ Personal Vehicle?

First-Aid performed on-site? Yes / No
Other Medical Attention Provided? Yes / No

Time lost from work? Yes / No Number of Hours: or Number of Days:

If injuries occurred, list names and describe nature, degree, and body part injured: Number of injured:_____

1.

2.

3.

4.

Complete Section 3.0

WITNESS STATEMENT: WHAT HAPPENED AND WHAT WAS THE EMPLOYEE DOING BEFORE THE INCIDENT OCCURRED? WHAT WAS THE EMPLOYEE DOING WHEN THE INCIDENT OCCURRED? WHAT WAS THE EMPLOYEE DOING AFTER THE INCIDENT OCCURRED?	Describe what took place? Who was at fault for vehicle accidents, citation? Was power equipment involved, if so, describe?

WHAT WAS THE NATURE OF THE INJURY OR ILLNESS?	Tell us the body part that was affected and how it was affected – be specific Examples: strained lower back; chemical burn on hand
WHAT WAS THE ROOT CAUSE OF THE INCIDENT? List other individual involved in Section 3. COULD INCIDENT HAVE BEEN AVOIDED? HOW?	Get all the facts by studying the Job and situation involved. Question by use of WHY - WHAT – WHERE – WHEN – WHO – HOW Were there other factors (e.g., noise, ventilation, illumination, fatigue, age, medical conditions) that contributed to the accident?
WAS TRAINING FOR THE WORK ACTIVITY PROVIDED: TYPE: DATES:	WERE WARNING SIGNS OR LABELS POSTED:
WHAT SHOULD BE DONE? HOW CAN INCIDENT BE AVOIDED IN THE FUTURE?	WAS PERSONAL PROTECTIVE EQUIPMENT USED? NEEDED: AVAILABLE: CONTRIBUTED TO INJURY:
WHAT HAVE YOU DONE THUS FAR?	Take or recommend action, depending upon your authority. Follow up – was action effective?
HOW WILL THIS IMPROVE OPERATIONS?	OBJECTIVE Eliminate job hindrances

Completed by:	Reviewed by:	Date

Section 2.0: Complete By Supervisor or Human Resources Manager

Name: Role (witness, observer, injured, participant, etc.):	Address: Phone Number
Name: Role:	Address: Phone Number
Name: Role:	Address: Phone Number
Name: Role:	Address: Phone Number
Name: Role:	Address: Phone Number
Name: Role:	Address: Phone Number

Section 3.0: Corrective Actions (To be Completed by OHSM and CHSO)

Are corrective actions warranted? □ Yes □ No If so, proceed with corrective action list

Corrective Actions. List long term actions to be taken as a result of incident (use additional sheets if needed)	How was the corrective action implemented?	Target date of completion

OHSM Name:	CHSO Name:
OHSM Signature:	CHSO Signature:

End of incident report. Section 4.0 is to be completed and maintained by the Human Resources Department.

Section 4.0: Complete By Human Resources Manager

Incident Report Case No. _____

The information on this page is considered CONFIDENTIAL and must be treated as such. This page will only be available to Human Resources Department or the employee's supervisor.

Insured Name:	Employee Hire Dates: Start at Company: Current Position:
Policy Number:	Is employee a company: Owner, Officer, Neither.
Employee Soc. Sec. No.:	Marital Status: Spouse Name:
Was Employee Pay Interrupted, or paid in full for time:	Employee Pay Period: Weekly, Bi-Weekly, Monthly, Other (specify)
Employee Compensated by hourly or salary? Wage Information: (tips, bonuses, commission)	Typical No. of hours worked per day____, hours per week____. Typical Start of day time_____, end of day time_____.
Date of Stop Work: Date Returned to Work:	How often has employee visited doctor/hospital?
Doctor: Authorized by Co.: Y / N Street: City/Town: Zip Code: Phone Number: Authorized by Co.: Y / N	Hospital: Street: City/Town: Zip Code: Phone Number: Authorized by Co.: Y /N
Was the employee treated in an emergency room? □ Yes □ No	Was employee hospitalized overnight as an in-patient? □ Yes □ No If so, for how many days? _____

APPENDIX D
Daily Job Brief Record

JOB BRIEF RECORD

Person Conducting	2283 Second Avenue, New York, NY Site Name/Address	DEC1038.P2 HRP Client Name/Job #
Dan McNally (518) 402-9143 Client Contact/Phone	HRP H&S Rep.	Patrick Montuori (845) 531-9490 HRP Supervisor
Date/Time	Number Attending	Weather

Designated Competent Person: _____

Description of Work: _____

Attendees (use additional sheets as needed):

Name	Company	Signature

Emergency Telephone Numbers

FIRE / POLICE / AMBULANCE: 911

Hospital Name & Location: **NYC Health and Hospitals/Metropolitan: 1901 1st Ave, New York, NY 10029**

NYSDEC Spill Line: 1-518-457-7362 National Response Center: 800-424-8802 CBYD: 800-922-4455

Health & Safety Manager: Jake Smith: 864-289-0311 ext 1508

HAZARDS

☐ Toxic	☐ Extreme Cold/Heat	☐ Soil Excavation	☐ Vehicle Traffic	☐ Powerwashing
☐ Corrosive	☐ Drains/Sumps	☐ Tank Excavation	☐ Hot Work	☐ Elevated Work Area
☐ Flammable	☐ Sharp Objects	☐ Trenching	☐ Vac Truck	☐ Live Electrical Circuits
☐ Combustible	☐ Drilling in Soil	☐ Floor Holes	☐ Ladders	☐ Pneumatic Tools
☐ Reactive	☐ Lighting	☐ Working on/near Water	☐ Noise	☐ Drum Handling
☐ Path Waste	☒ Slips/Trips/Falls	☒ Underground/Overhead Utilities	☐ Lifting	☐ Abrasive Blasting
☐ Asbestos	☐ Lead			

PERSONAL SAFETY

☐ Supplied Air Respirator	☐ SAR w/Egress Bottle	☐ SCBA	☐ Air Purifying Respirator Cartridge: _____	
☐ Fully Encapsulating Suit	☐ Flash Suit	☐ NOMEX (flam resistant)	☐ Protected Coveralls, Type: _____	
☐ Overboots	☐ Lifebelt/Lanyard	☒ Hardhats	☐ Outer Gloves, Type: _____	
☐ Safety Glasses	☐ Chemical Goggles	☐ Face Shield	☐ Inner Gloves, Type: _____	
☒ Reflective Vests	☐ Eye Wash	☐ Safety Shower	☐ First Aid Kit	☐ PFD's
☐ Hearing Protection	☐ Evacuation Plan	☐ Communications	☐ Properly Sloped Excavation/ Trench	☐ Ventilation

FIRE SAFETY

- ☐ Fire Extinguishers
- ☐ Hot Work Permit
- ☐ Fire Blanket
- ☐ Explosion-Proof Equipment
- ☐ Equipment Grounded & Bonded
- ☐ Non-Sparking Tools
- ☐ Eliminate Ignition Sources
- ☐ Area Kept Wet
- ☐ Smoking Area Designated Location: _____
- ☐ Alarm Box in Area, Location: _____
- ☐ Fire Hose Laid Out

ISOLATE EQUIPMENT

- ☐ Establish Exclusion Zone/Traffic Cones
- ☐ Work Signs
- ☐ Stop Transfers
- ☐ Caution Tape Area
- ☐ GFCIS
- ☐ Temporary Fencing

ELECTRICAL EQUIPMENT

- ☐ LockOut/TagOut
- ☐ Non-Conductive Tools
- ☐ Equipment Grounded
- ☐ FR Suits/Coveralls

AIR MONITORING Type of Meter: _____ Date last calibrated: _____

SUBSTANCE	LEVEL B MAX.	ACTION LEVEL/LEVEL C MAX.	LEVEL D MAX.

Health & Safety Comments / Topics & Safety Rules Reviewed / Questions / Concerns:

_____

_____

_____

_____

_____

_____

_____

Contaminants of Concern: _____

HEALTH & SAFETY SIGNATURE: _____ Date: _____

Is there a Site-Specific or Generic Health & Safety Plan available on-site? Yes ☐ No ☐

☐ HAZARD ZONES NOT APPLICABLE, GENERAL WORK AREA

Level D ☐ Modified Level D ☐ Level C ☐

Anything above Level C, foreman should use a Confined Space Permit/Form.

Note: HOT WORK requires a hot work permit and minimum 20# fire extinguisher. Foreman or HSM must record at least one contaminant of concern above. Toxic plants may be considered a COC if no chemical hazards are expected.

LEVEL C
Respirator Type: _____

Name	Zone	Time In	Time Out	Decon Type

Before performing Level C work, ALL employees must review HRP's Respiratory Protection Program - a copy of which must be on-site along with a HASP.

APPENDIX E
Equipment Calibration Log

EQUIPMENT CALIBRATION LOG		
Instrument	**Calibration Date**	**Calibrated By**

APPENDIX F
HRP Safe Work Permit

General Information:		
Project Number: DEC1038.P2	**Project Location*:** 2283 Second Avenue, New York, New York, 10035	
Client: NYSDEC	Dan McNally, NYSDEC PM	518-402-9143
	Contact Name	**Contact Phone**
Contractor (*If applicable*):		
	Contractor Name	**Contractor Phone**

Site Characterization:
Investigate Site for groundwater and soil vapor.

Purpose and Scope of Work:
HRP to perform: Monitoring well installation and sampling; Soil vapor point installation and sampling.

Client or Contractor Required Training or other Site Specific Requirements:			
Created By:	Patrick Montuori	**Approved by:**	Bryan Sherman, CSP

Reviewed with affected HRP employees:			
Employee Name	**Signature**	**Date**	**Contact Number**

***If the Site is located outside the United States, check the US State Department page for any travel warnings or restrictions**

HRP Standard Operating Procedures (SOPs) to be used during Site Work.	
SOP Number and Revision	**SOP Title**

Project Hazard Assessment				
Check if Project Involves:	**Yes**	**No**	**Initial to Verify Completion**	**Criteria**
Alone work/alone travel	☒	×		Touch base with HRP manager or HRP admin prior to alone work/travel. Communicate when expected back. Communicate once work complete and back home/office.
Hot Work *(Welding, Grinding, etc.)*	☐	×		Hot Work Permit Issued – Fire Watch Required
Electrical Work	×	☒		LOTO, confirm zero energy
Rigging or Heavy Lifting	☐	×		Load Ratings, Employee Certification
Scaffolds	☐	×		Competent Person Inspection Required
Confined Space Entry	☐	×		Permit or Reclassification Form Required
Hazardous Chemicals	×	☒		Chemical Names and SDS review with Employees
Ladders and/or Stairways	×	☐		Proper Rating, No Metal Ladders, Current Inspection
Work at Heights	☒	×		Training (verified), PPE, Approved Anchor Points or Fall Protection
Lockout Tagout	☐	×		Training (verified), site first lock on
Excavation/Ground Penetration	×	☒		Line Locate performed *(verify UI has performed mark-outs)*
Roof Work	☐	×		Fall protection within 6 feet of edge
Walking/Working Surface Hazards	☒	×		Special gear/footwear to avoid falls on sloped and/or slick areas & marking fixed stumble-hazards in pathways
Portable Electrical Tools, cords	×	☒		GFCI used, No damaged cords, Inspected
Fire System Impairment	☐	×		External notifications made
Blocked Exits, Locked Gates	☐	×		Post signs and alternate exits, secure access arrangement
Demolition/Construction Site	☐	×		Training (verified), PPE
Hazardous Materials Abatement/Inspection	☐	×		Training (verified), PPE
Roadway Traffic	☒	×		Training (verified), PPE
Ergonomic Concerns	☒	×		Repetitive motion, uneven or cluttered work surface
Other (list):	☐	☒		

Required Permits		PPE Required for Job or Required by Client	
☐ None	☐ Subsurface Work	× Safety Glasses	× Hearing Protection
☐ Confined Space	☐ Scaffold Inspection	× Safety Toe Shoes	☒ Class 2 Safety Vest
☐ Hot Work	☐ Working At Heights	☐ Metatarsal Guards	☐ Class 3 Safety Vest
☐ Excavation Checklist:	☐ Other Permits:	☒ Cut Resistant Gloves/Sleeves	☐ Chemical Resistant Gloves
		☐ Protective Clothing: ☐ Tyvek, ☐ Chemical, ☐ Biological, ☐ Radiological ☐ Other:	☐ Respirator: ☐ Face Mask ☐ Dust Mask ☐ N95 Respirator** ☐ Air purifying Respirator**
		☒ Hard hat ☒ Other PPE Not Listed:	

Special Considerations				
☐ Chemical	× Tight/Crowded Area	☐ Laceration/Abrasion	☐ Struck By	☐ Press
☐ Explosion	☐ Fire/heat	☐ Temperature Extremes (hot/cold)	☐ Struck Against	☐ Allergies
☐ Slip/Trip/Fall	☐High Pressure	× Noise	☐ Automated Equip.	☐ Animal Feces
☐ Exposed Movement	☐ Lighting/Visibility	☐ Caught in/on	☐ Conveyors	☐ Mold
☐ Ergonomics ☐ Repetitive Motion ☐ Vibration ☐ Other	☐ Dust/Silica ☐ Working Near Water	☐ Lead ☐ PCB ☐ Asbestos	☐ Insects/pests ☐ Toxic Plants ☐ Dangerous Wildlife	☐ Electricity ☐ Radiation ☐ Poor Cell Reception

** Please consult with Office Health and Safety Manager prior to using respiratory protection.

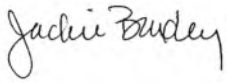
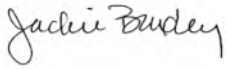
Emergency Phone Numbers	
Emergency Contact	**Phone Number**
Project Manager: Patrick Montuori	845-531-9490
Site Safety Officer: Elliott Jackson	716-489-0415
NYCPD 25th Precinct Police Department (routine calls):	911
FDNY Engine 58/Ladder 26 - Fire Department (routine calls):	212-860-6511
NYC Health + Hospitals/Metropolitan	212-504-4115
Poison Control Center:	212-423-6262
DEC spills hotline:	1-800-222-1222
National Response Center:	1-800-457-7362
State/Local Oil and Chemical Spill Reporting	800-424-8802

*Map and directions to the following medical facility are provided in an attachment to this permit.

REVISION APPROVAL LOG (Project Team)

REV. #	PREPARED BY	REVIEWED BY	APPROVED BY
00	Date: Name: Sign:	Date: Name: Sign:	Date: Name: Sign:
01	Date: Name: Sign:	Date: Name: Sign:	Date: Name: Sign:
02	Date: Name: Sign:	Date: Name: Sign:	Date: Name: Sign:

REVISION APPROVAL LOG			
REV. #	**PREPARED BY**	**REVIEWED BY**	**APPROVED BY**

00	Date: 1/18/2021 Name: Scot Frost Sign: 	Date: 1/20/2021 Name: Jackie Baxley Sign: 	Date: 1/20/2021 Name: Tad Goetcheus Sign: 
01	Date: 12/15/2022 Name: Scot Frost Sign: 	Date: 12/15/2022 Name: Jackie Baxley Sign: 	Date: 12/15/2022 Name: Tad Goetcheus Sign: 
02	Date: Name: Sign:	Date: Name: Sign:	Date: Name: Sign:

CHANGE / REVIEW RECORDS			
REVISION DATE	**REVISION LEVEL**	**REASON / REVISION DESCRIPTION**	**APPROVED BY**
1/20/2021	00	Original Release. Document developed to provide a new hazard assessment "checklist" process for Non-Hazwoper project sites. Replaces the use of former Site HASP document.	Tad Goetcheus
12/15/2022	01	Revision added: new hazard checks with associated criteria to improve the hazard assessment and other project planning details to the form e.g., project number, emergency contact table, worker review for signoff, and SOPs to be referenced.	Tad Goetcheus

APPENDIX G

COVID-19 Health and Safety Guidelines

COVID19
SITE SPECIFIC HASP ADDENDUM

This addendum will remain in effect until what time the CDC, NIAID, and/or Surgeon General guidance is provided that removes the heightened awareness of social distancing, hand washing, and other protocols in response to COVID-19.

NECESSARY ADDITIONAL SUPPLIES

- Hand sanitizer (minimum 60% alcohol)
- Squeeze bottles of water (if no running water at job site)
- Soap
- Disinfectant (for tools, vehicles, common areas, etc.)
- Caution tape, cones or similar to set up social distancing boundaries as needed

EMPLOYEE HEALTH PROTECTION – ZERO TOLERANCE

The following applies to both HRP employees and contracted staff working on behalf of the HRP or the client.

- ZERO TOLERANCE FOR SICK WORKERS REPORTING TO WORK. IF YOU ARE SICK, STAY HOME! IF YOU FEEL SICK, GO HOME! IF YOU SEE SOMEONE SICK, SEND THEM HOME!
- If you are exhibiting any of the symptoms below, you are to report this to your supervisor (via phone, text or email) right away, and head home from the job site or stay home if already there.
  If you notice a co-worker showing signs or complaining about such symptoms, he or she should be directed to their supervisor (via phone, text or email) and asked to leave the project site immediately.
  COVID-19 Typical Symptoms:
    - Fever
    - Cough
    - Shortness of Breath
    - Sore Throat
    - Loss of taste or smell
- Prior to starting a shift, each employee will verbally self-certify to their supervisor that they:
    - Have no signs of a fever or a measured temperature above 100.3 degrees or greater, a cough or trouble breathing within the past 24 hours.
    - Have not had “close contact” with an individual diagnosed with COVID-19. “Close contact” means living in the same household as a person who has tested positive for COVID-19, caring for a person who has tested positive for COVID-19, being within 6 feet of a person who has tested positive for COVID-19 for about 15 minutes, or coming in direct contact with secretions (e.g., sharing utensils, being coughed on) from a person who has tested positive for COVID-19, while that person was symptomatic.
    - Have not been asked to self-isolate or quarantine by their doctor or a public health official.
    - These self-certifications may be documented at the request of the site owner
- Workers that are working in a confined space or inside a closed building envelope will have to be temperature screened by a Medical Professional or designated individual. Such screening shall be performed out of public view to respect privacy and results are kept private.
- Employees exhibiting symptoms or unable to self-certify should be directed to leave the work

site and seek medical attention and applicable testing by their health care provider. They are not to return to the work site until cleared by a medical professional.

GENERAL ON-THE-JOB GUIDANCE TO PREVENT EXPOSURE & LIMIT THE TRANSMISSION OF THE VIRUS

All Job Sites

- No touching or direct contact with other individuals, including handshaking.
- Wash hands often with soap and water for at least 20 seconds or alternatively when soap and water are not available, use an alcohol-based hand sanitizer with at least 60% ethanol or 70% isopropanol
- A "No Congregation" policy is in effect, individuals must implement social distancing by maintaining a minimum distance of 6-feet from all other individuals
- Avoid face to face meetings – critical situations requiring in-person discussion must follow social distancing
- Conduct all meetings via conference calls, if possible. Do not convene meetings of more than 10 people. Recommend use of cell phones, texting, web meeting sites and conference calls for project discussion
- Be sure to use your own water bottle, and do not share
- To avoid external contamination, bring food from home
- Maintain Social Distancing separation during breaks and lunch.
- To avoid sharing germs, please clean up after yourself. DO NOT make others responsible for moving, unpacking and packing up your personal belongings
- If you or a family member is feeling ill, stay home!

Multi-person job sites (i.e. HRP and subcontractors, etc.)

- Contractor and Field Offices are to be locked down to all but authorized personnel
- Each jobsite should develop cleaning and decontamination procedures that are posted and shared (if multi-person job site). These Procedures must cover all areas including trailers, gates, equipment, vehicles, etc. and shall be posted at all entry points to the sites, and throughout the project site.
- All individual work crew meetings/tailgate talks should be held outside and follow social distancing
- Please keep all crews a minimum of 6' apart at all times to eliminate the potential of cross contamination
- At each job briefing/tool box talk, employees are asked if they are experiencing any symptoms, and are sent home if they are
- Each jobsite should have laminated COVID-19 safety guidelines and handwashing instructions (last page of this addendum)
- All restroom facilities/porta-potties should be cleaned and handwashing stations must be provided with soap, hand sanitizer and paper towels
- All surfaces should be cleaned at least twice a day, including desk, work stations, door handles, laptops, etc.
- All common areas and meeting areas are to be regularly cleaned and disinfected at least once a day but preferably twice a day

- Single person job sites (just one HRP employee, no subs, vendors, etc.)
  - It is that person's responsibility to clean and disinfect all tools and reusable supplies upon return to the office

- Cover coughing or sneezing with a tissue, then throw the tissue in the trash and wash hands, if no tissue is available then cough into your elbow
- Avoid touching eyes, nose, and mouth with your hands

WORK SITE RISK PREVENTION PRACTICES

- At the start of each shift, confirm with all employees that they are healthy.
- All employees will be required to wear gloves (either latex or cut resistant depending on the task at hand)
- Use of eye protection is required (Safety glasses or googles at a minimum with or without face shields).
- In work conditions where required social distancing is impossible to achieve, affected employees shall be supplied PPE including as appropriate a standard face covering, gloves, and eye protection.
- All employees shall drive to work site/parking area in a single occupant vehicle. No one should ride together in the same vehicle
- When entering a machine or vehicle which you are not sure you were the last person to enter, make sure that you wipe down the interior and door handles with disinfectant prior to entry
- In instances where it is possible, workers should maintain separation of 6' from each other per CDC guidelines.
- Multi person activities will be limited where feasible (two person lifting activities)
- Large gathering places on the site such as shacks and break areas will be eliminated and instead small break areas will be used with seating limited to ensure social distancing.
- Contact the cleaning person for your office trailer or office space and ensure they have proper COVID- 19 sanitation processes. Increase their cleaning visits to daily
- Clean all high contact surfaces a minimum of twice a day in order to minimize the spread of germs in areas that people touch frequently. This includes but is not limited to desks, laptops and vehicles

Wash Stations: All sites without ready access to an indoor bathroom or running water MUST install Wash Stations or provide other means for handwashing

- Install hand wash stations with hot water, if possible, and soap at fire hydrants or other water sources to be used for frequent handwashing for all onsite employees.
- All onsite workers must help to maintain and keep stations clean
- If a worker notices soap or towels are running low or out, immediately notify supervisors
- Garbage barrels will be placed next to the hand wash station for disposal of tissues/towels
- If no other alternative exists, bring squeeze bottles with water and soap (only authorized for single employee job sites)

Please Note: This document is not intended to replace any formalized procedures currently in place within the site specific HASP or any job related contracts.

Where this guidance does not meet or exceed the standards put forth by the state, municipality, site owner, contractor or subcontractor, everyone shall abide by the most stringent procedure.

A site-specific COVID-19 Officer (also known as the Health and Safety Officer) shall be designated for every site.

Print and post at each job site

COVID-19/ Health and Safety Officer Name: _____

Phone Number: _____

Any issue of non-compliance with these guidelines shall be a basis for pausing the work. The Health and Safety Officer will address corrective actions with the subcontractor. Any additional issues of non-conformance may be subject to action against the subcontractor's prequalification and certification status.

Safety Data Sheet

according to 1907/2006/EC (REACH), 1272/2008/EC (CLP), 29CFR1910/1200 and GHS Rev. 3

Effective date: 12.08.2015 **Revision** : 12.10.2015

Trade Name: Alconox

1 Identification of the substance/mixture and of the supplier

1.1 Product identifier

Trade Name: Alconox
Synonyms:
Product number: Alconox

1.2 Application of the substance / the mixture : Cleaning material/Detergent

1.3 Details of the supplier of the Safety Data Sheet

Manufacturer	**Supplier**
Alconox, Inc. 30 Glenn Street White Plains, NY 10603 1-914-948-4040	Not Applicable

Emergency telephone number:
ChemTel Inc
North America: 1-800-255-3924
International: 01-813-248-0585

2 Hazards identification

2.1 Classification of the substance or mixture:

In compliance with EC regulation No. 1272/2008, 29CFR1910/1200 and GHS Rev. 3 and amendments.

Hazard-determining components of labeling:
Tetrasodium Pyrophosphate
Sodium tripolyphosphate
Sodium Alkylbenzene Sulfonate

2.2 Label elements:

Skin irritation, category 2.
Eye irritation, category 2A.

Hazard pictograms:

Signal word: Warning

Hazard statements:
H315 Causes skin irritation.
H319 Causes serious eye irritation.

Precautionary statements:
P264 Wash skin thoroughly after handling.
P280 Wear protective gloves/protective clothing/eye protection/face protection.
P302+P352 If on skin: Wash with soap and water.
P305+P351+P338 If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
P321 Specific treatment (see supplemental first aid instructions on this label).
P332+P313 If skin irritation occurs: Get medical advice/attention.
P362 Take off contaminated clothing and wash before reuse.
P501 Dispose of contents and container as instructed in Section 13.

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Trade Name: Alconox

Additional information: None.

Hazard description

Hazards Not Otherwise Classified (HNOC): None

Information concerning particular hazards for humans and environment:

The product has to be labelled due to the calculation procedure of the "General Classification guideline for preparations of the EU" in the latest valid version.

Classification system:

The classification is according to EC regulation No. 1272/2008, 29CFR1910/1200 and GHS Rev. 3 and amendments, and extended by company and literature data. The classification is in accordance with the latest editions of international substances lists, and is supplemented by information from technical literature and by information provided by the company.

3 Composition/information on ingredients

3.1 Chemical characterization : None

3.2 Description : None

3.3 Hazardous components (percentages by weight)

Identification	Chemical Name	Classification	Wt. %
CAS number: 7758-29-4	Sodium tripolyphosphate	Skin Irrit. 2 ; H315 Eye Irrit. 2; H319	12-28
CAS number: 68081-81-2	Sodium Alkylbenzene Sulfonate	Acute Tox. 4; H303 Skin Irrit. 2 ; H315 Eye Irrit. 2; H319	8-22
CAS number: 7722-88-5	Tetrasodium Pyrophosphate	Skin Irrit. 2 ; H315 Eye Irrit. 2; H319	2-16

3.4 Additional Information : None.

4 First aid measures

4.1 Description of first aid measures

General information: None.

After inhalation:

Maintain an unobstructed airway.

Loosen clothing as necessary and position individual in a comfortable position.

After skin contact:

Wash affected area with soap and water.

Seek medical attention if symptoms develop or persist.

After eye contact:

Rinse/flush exposed eye(s) gently using water for 15-20 minutes.

Remove contact lens(es) if able to do so during rinsing.

Seek medical attention if irritation persists or if concerned.

After swallowing:

Rinse mouth thoroughly.

Seek medical attention if irritation, discomfort, or vomiting persists.

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4.2 Most important symptoms and effects, both acute and delayed

None

4.3 Indication of any immediate medical attention and special treatment needed:

No additional information.

5 Firefighting measures

5.1 Extinguishing media

Suitable extinguishing agents:

Use appropriate fire suppression agents for adjacent combustible materials or sources of ignition.

For safety reasons unsuitable extinguishing agents : None

5.2 Special hazards arising from the substance or mixture :

Thermal decomposition can lead to release of irritating gases and vapors.

5.3 Advice for firefighters

Protective equipment:

Wear protective eye wear, gloves and clothing.
Refer to Section 8.

5.4 Additional information :

Avoid inhaling gases, fumes, dust, mist, vapor and aerosols.
Avoid contact with skin, eyes and clothing.

6 Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures :

Ensure adequate ventilation.
Ensure air handling systems are operational.

6.2 Environmental precautions :

Should not be released into the environment.
Prevent from reaching drains, sewer or waterway.

6.3 Methods and material for containment and cleaning up :

Wear protective eye wear, gloves and clothing.

6.4 Reference to other sections : None

7 Handling and storage

7.1 Precautions for safe handling :

Avoid breathing mist or vapor.
Do not eat, drink, smoke or use personal products when handling chemical substances.

7.2 Conditions for safe storage, including any incompatibilities :

Store in a cool, well-ventilated area.

7.3 Specific end use(s):

No additional information.

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8 Exposure controls/personal protection

8.1 Control parameters :

7722-88-5, Tetrasodium Pyrophosphate, OSHA TWA 5 mg/m3.

8.2 Exposure controls

Appropriate engineering controls:

Emergency eye wash fountains and safety showers should be available in the immediate vicinity of use or handling.

Respiratory protection:

Not needed under normal conditions.

Protection of skin:

Select glove material impermeable and resistant to the substance.

Eye protection:

Safety goggles or glasses, or appropriate eye protection.

General hygienic measures:

Wash hands before breaks and at the end of work.
Avoid contact with skin, eyes and clothing.

9 Physical and chemical properties

Appearance (physical state, color):	White and cream colored flakes - powder	**Explosion limit lower:** **Explosion limit upper:**	Not determined or not available. Not determined or not available.
Odor:	Not determined or not available.	**Vapor pressure at 20°C:**	Not determined or not available.
Odor threshold:	Not determined or not available.	**Vapor density:**	Not determined or not available.
pH-value:	9.5 (aqueous solution)	**Relative density:**	Not determined or not available.
Melting/Freezing point:	Not determined or not available.	**Solubilities:**	Not determined or not available.
Boiling point/Boiling range:	Not determined or not available.	**Partition coefficient (n-octanol/water):**	Not determined or not available.
Flash point (closed cup):	Not determined or not available.	**Auto/Self-ignition temperature:**	Not determined or not available.
Evaporation rate:	Not determined or not available.	**Decomposition temperature:**	Not determined or not available.

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Flammability (solid, gaseous):	Not determined or not available.	**Viscosity**:	a. Kinematic: Not determined or not available. b. Dynamic: Not determined or not available.
Density at 20°C:	Not determined or not available.		

10 Stability and reactivity

10.1 Reactivity : None

10.2 Chemical stability : None

10.3 Possibility hazardous reactions : None

10.4 Conditions to avoid : None

10.5 Incompatible materials : None

10.6 Hazardous decomposition products : None

11 Toxicological information

11.1 Information on toxicological effects :

Acute Toxicity:

Oral:

: LD50 > 5000 mg/kg oral rat - Product .

Chronic Toxicity: No additional information.

Skin corrosion/irritation:

Sodium Alkylbenzene Sulfonate: Causes skin irritation. .

Serious eye damage/irritation:

Sodium Alkylbenzene Sulfonate: Causes serious eye irritation .

Tetrasodium Pyrophosphate: Rabbit - Risk of serious damage to eyes .

Respiratory or skin sensitization: No additional information.

Carcinogenicity: No additional information.

IARC (International Agency for Research on Cancer): None of the ingredients are listed.

NTP (National Toxicology Program): None of the ingredients are listed.

Germ cell mutagenicity: No additional information.

Reproductive toxicity: No additional information.

STOT-single and repeated exposure: No additional information.

Additional toxicological information: No additional information.

12 Ecological information

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12.1 Toxicity:

Sodium Alkylbenzene Sulfonate: Fish, LC50 1.67 mg/l, 96 hours.
Sodium Alkylbenzene Sulfonate: Aquatic invertebrates, EC50 Daphnia 2.4 mg/l, 48 hours.
Sodium Alkylbenzene Sulfonate: Aquatic Plants, EC50 Algae 29 mg/l, 96 hours.
Tetrasodium Pyrophosphate: Fish, LC50 - other fish - 1,380 mg/l - 96 h.
Tetrasodium Pyrophosphate: Aquatic invertebrates, EC50 - Daphnia magna (Water flea) - 391 mg/l - 48 h.

12.2 Persistence and degradability: No additional information.

12.3 Bioaccumulative potential: No additional information.

12.4 Mobility in soil: No additional information.

General notes: No additional information.

12.5 Results of PBT and vPvB assessment:

PBT: No additional information.

vPvB: No additional information.

12.6 Other adverse effects: No additional information.

13 Disposal considerations

13.1 Waste treatment methods (consult local, regional and national authorities for proper disposal)

Relevant Information:

It is the responsibility of the waste generator to properly characterize all waste materials according to applicable regulatory entities. (US 40CFR262.11).

14 Transport information

14.1	**UN Number:** ADR, ADN, DOT, IMDG, IATA	None
14.2	**UN Proper shipping name:** ADR, ADN, DOT, IMDG, IATA	None
14.3	**Transport hazard classes:** ADR, ADN, DOT, IMDG, IATA	**Class:** None **Label:** None **LTD. QTY:** None

US DOT

Limited Quantity Exception: None

Bulk:	**Non Bulk:**
RQ (if applicable): None	**RQ (if applicable):** None
Proper shipping Name: None	**Proper shipping Name:** None
Hazard Class: None	**Hazard Class:** None
Packing Group: None	**Packing Group:** None
Marine Pollutant (if applicable): No additional information.	**Marine Pollutant (if applicable):** No additional information.

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Effective date: 12.08.2015 **Revision** : 12.10.2015

Trade Name: Alconox

	Comments: None	**Comments:** None
14.4	**Packing group:** ADR, ADN, DOT, IMDG, IATA	None
14.5	**Environmental hazards** :	None
14.6	**Special precautions for user:**	None
	Danger code (Kemler):	None
	EMS number:	None
	Segregation groups:	None
14.7	**Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code:** Not applicable.	
14.8	**Transport/Additional information:**	
	Transport category:	None
	Tunnel restriction code:	None
	UN "Model Regulation":	None

15 Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture.

North American

SARA

Section 313 (specific toxic chemical listings): None of the ingredients are listed.
Section 302 (extremely hazardous substances): None of the ingredients are listed.

CERCLA (Comprehensive Environmental Response, Clean up and Liability Act) Reportable

Spill Quantity: None of the ingredients are listed.

TSCA (Toxic Substances Control Act):

Inventory: All ingredients are listed.
Rules and Orders: Not applicable.

Proposition 65 (California):

Chemicals known to cause cancer: None of the ingredients are listed.

Chemicals known to cause reproductive toxicity for females: None of the ingredients are listed.

Chemicals known to cause reproductive toxicity for males: None of the ingredients are listed.

Chemicals known to cause developmental toxicity: None of the ingredients are listed.

Canadian

Canadian Domestic Substances List (DSL):
All ingredients are listed.

EU

REACH Article 57 (SVHC): None of the ingredients are listed.

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Germany MAK: Not classified.

Asia Pacific

Australia

Australian Inventory of Chemical Substances (AICS): All ingredients are listed.

China

Inventory of Existing Chemical Substances in China (IECSC): All ingredients are listed.

Japan

Inventory of Existing and New Chemical Substances (ENCS): All ingredients are listed.

Korea

Existing Chemicals List (ECL): All ingredients are listed.

New Zealand

New Zealand Inventory of Chemicals (NZOIC): All ingredients are listed.

Philippines

Philippine Inventory of Chemicals and Chemical Substances (PICCS): All ingredients are listed.

Taiwan

Taiwan Chemical Substance Inventory (TSCI): All ingredients are listed.

16 Other information

Abbreviations and Acronyms: None

Summary of Phrases

Hazard statements:

H315 Causes skin irritation.
H319 Causes serious eye irritation.

Precautionary statements:

P264 Wash skin thoroughly after handling.
P280 Wear protective gloves/protective clothing/eye protection/face protection.
P302+P352 If on skin: Wash with soap and water.
P305+P351+P338 If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
P321 Specific treatment (see supplemental first aid instructions on this label).
P332+P313 If skin irritation occurs: Get medical advice/attention.
P362 Take off contaminated clothing and wash before reuse.
P501 Dispose of contents and container as instructed in Section 13.

Manufacturer Statement:

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

NFPA: 1-0-0

Safety Data Sheet

according to 1907/2006/EC (REACH), 1272/2008/EC (CLP), 29CFR1910/1200 and GHS Rev. 3

Effective date: 12.08.2015 **Revision** : 12.10.2015

Trade Name: Alconox

HMIS: 1-0-0

SAFETY DATA SHEET

Version 5.2
Revision Date 02/24/2014
Print Date 11/13/2016

1. PRODUCT AND COMPANY IDENTIFICATION

1.1 Product identifiers

Product name : Distilled water

Product Number : 07-6061
Brand : Katayama OEM Partner
REACH No. : A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.
CAS-No. : 7732-18-5

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA

Telephone : +1 800-325-5832
Fax : +1 800-325-5052

1.4 Emergency telephone number

Emergency Phone # : +1-703-527-3887 (CHEMTREC)

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Not a hazardous substance or mixture.

2.2 GHS Label elements, including precautionary statements

Not a hazardous substance or mixture.

2.3 Hazards not otherwise classified (HNOC) or not covered by GHS - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Formula : H2O H_2O
Molecular Weight : 18.02 g/mol
CAS-No. : 7732-18-5
EC-No. : 231-791-2

No ingredients are hazardous according to OSHA criteria.
No components need to be disclosed according to the applicable regulations.

4. FIRST AID MEASURES

4.1 Description of first aid measures

If inhaled
If not breathing give artificial respiration

4.2 Most important symptoms and effects, both acute and delayed
The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed
no data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

5.2 Special hazards arising from the substance or mixture
no data available

5.3 Advice for firefighters
no data available

5.4 Further information
The product itself does not burn.

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures
For personal protection see section 8.

6.2 Environmental precautions
no data available

6.3 Methods and materials for containment and cleaning up
Wipe up with absorbent material (e.g. cloth, fleece).

6.4 Reference to other sections
For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling
For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities
No special storage conditions required.

7.3 Specific end use(s)
Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters
Contains no substances with occupational exposure limit values.

8.2 Exposure controls

Appropriate engineering controls
Handle in accordance with good industrial hygiene and safety practice.

Personal protective equipment

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact
Material: Nitrile rubber
Minimum layer thickness: 0.11 mm
Break through time: 480 min

Material tested:Dermatril® (KCL 740 / Aldrich Z677272, Size M)

Splash contact
Material: Nitrile rubber
Minimum layer thickness: 0.11 mm
Break through time: 480 min
Material tested:Dermatril® (KCL 740 / Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Respiratory protection
No special protective equipment required.

Control of environmental exposure
Prevent product from entering drains.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: liquid Colour: colourless
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	6.0 - 8.0 at 25 °C (77 °F)
e)	Melting point/freezing point	0.0 °C (32.0 °F)
f)	Initial boiling point and boiling range	100 °C (212 °F) - lit.
g)	Flash point	not applicable
h)	Evapouration rate	no data available
i)	Flammability (solid, gas)	no data available
j)	Upper/lower flammability or explosive limits	no data available
k)	Vapour pressure	no data available
l)	Vapour density	no data available
m)	Relative density	1.000 g/cm3 at 3.98 °C (39.16 °F)
n)	Water solubility	completely miscible
o)	Partition coefficient: n-octanol/water	no data available
p)	Auto-ignition temperature	no data available
q)	Decomposition temperature	no data available
r)	Viscosity	no data available
s)	Explosive properties	no data available
t)	Oxidizing properties	no data available

9.2 Other safety information
no data available

10. STABILITY AND REACTIVITY

10.1 Reactivity
no data available

10.2 Chemical stability
Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions
no data available

10.4 Conditions to avoid
no data available

10.5 Incompatible materials
no data available

10.6 Hazardous decomposition products
In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
no data available

Inhalation: no data available

Dermal: no data available

no data available

Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitisation
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

ACGIH: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

OSHA: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
no data available

no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Additional Information
RTECS: ZC0110000

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

12. ECOLOGICAL INFORMATION

12.1 Toxicity
no data available

12.2 Persistence and degradability
not applicable

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Taking into account local regulations the product may be disposed of as waste water after neutralisation.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

REACH No. : A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
No SARA Hazards

Massachusetts Right To Know Components
No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Water	7732-18-5	

New Jersey Right To Know Components

	CAS-No.	Revision Date
Water	7732-18-5	

California Prop. 65 Components

This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

HMIS Rating

Health hazard:	0
Chronic Health Hazard:	
Flammability:	0
Physical Hazard	0

NFPA Rating

Health hazard:	0
Fire Hazard:	0
Reactivity Hazard:	0

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 5.2 Revision Date: 02/24/2014 Print Date: 11/13/2016

APPENDIX H

Safety Data Sheets
(for chemicals brought to the site)

Hydrochloric Acid,ACS

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : **Hydrochloric Acid,ACS**

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: **S25358**

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:

Corrosive
Serious eye damage, category 1
Corrosive to metals, category 1
Skin corrosion, category 1B

Irritant
Specific target organ toxicity following single exposure, category 3

Corr. Metals 1
Corr. Skin 1B
Eye Damage 1
STOT. SE 3

Signal word :Danger

Hazard statements:
May be corrosive to metals
Causes severe skin burns and eye damage
May cause respiratory irritation

Precautionary statements:
If medical advice is needed, have product container or label at hand
Keep out of reach of children
Read label before use
Use only outdoors or in a well-ventilated area
Wear protective gloves/protective clothing/eye protection/face protection
Keep only in original container
Do not get in eyes, on skin, or on clothing
Wash skin thoroughly after handling
IF SWALLOWED: Rinse mouth. Do NOT induce vomiting

IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing
Immediately call a POISON CENTER or doctor/physician
Specific treatment (see supplemental first aid instructions on this label)
Wash contaminated clothing before reuse
Absorb spillage to prevent material damage
Store in a well ventilated place. Keep container tightly closed
Store locked up
Store in corrosive resistant stainless steel container with a resistant inner liner
Dispose of contents and container to an approved waste disposal plant

Other Non-GHS Classification:

WHMIS

D1A 

E 

NFPA/HMIS

NFPA SCALE (0-4)

HMIS RATINGS (0-4)

SECTION 3 : Composition/information on ingredients

Ingredients:		
CAS 7647-01-0	Hydrochloric Acid, ACS	30-50 %
CAS 7732-18-5	Water	50-70 %
		Percentages are by weight

SECTION 4 : First aid measures

Description of first aid measures

After inhalation: Move exposed individual to fresh air. Loosen clothing as necessary and position individual in a comfortable position.Seek medical attention if irritation or coughing persists.

After skin contact: Wash affected area with soap and water. Immediately remove contaminated clothing and shoes.Rinse thoroughly with plenty of water for at least 15 minutes.Immediately seek medical attention.

After eye contact: Protect unexposed eye. Flush thoroughly with plenty of water for at least 15

minutes.Remove contact lenses while rinsing.Continue rinsing eyes during transport to hospital.

After swallowing: Rinse mouth thoroughly. Do not induce vomiting. Have exposed individual drink sips of water. Immediately seek medical attention.

Most important symptoms and effects, both acute and delayed:

Inhalation may cause irritation to nose and upper respiratory tract, ulceration, coughing, chest tightness and shortness of breath. Higher concentrations cause tachypnoea, pulmonary oedema and suffocation . Ingestion may cause corrosion of lips, mouth, oesophagus and stomach, dysphagia and vomiting.Pain, eye ulceration, conjunctival irritation, cataracts and glaucoma may occur following eye exposure.Erythema and skin irritation, as well as chemical burns to skin and mucous membranes may arise following skin exposure.;Potential sequelae following ingestion of hydrochloric acid include perforation, scarring of the oesophagus or stomach and stricture formation causing dysphagia or gastric outlet obstruction. In some cases, RADS may develop. Respiratory symptoms may take up to 36 hours to develop.Symptoms of burning sensation, cough, wheezing, laryngitis, shortness of breath, spasm, inflammation, edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema. Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin.

Indication of any immediate medical attention and special treatment needed:

Provide SDS to Physician.Physician should treat symptomatically.

SECTION 5 : Firefighting measures

Extinguishing media

Suitable extinguishing agents: Use water, dry chemical, chemical foam, carbon dioxide, or alcohol-resistant foam.

For safety reasons unsuitable extinguishing agents:

Special hazards arising from the substance or mixture:

Combustion products may include carbon oxides or other toxic vapors.If in contact with metals toxic fumes may be released.

Advice for firefighters:

Protective equipment: Wear protective eyeware, gloves, and clothing. Refer to Section 8. Wear respiratory protection.

Additional information (precautions): Thermal decomposition can produce poisoning chlorine. Hydrochloric acid reacts also with many organic materials with liberation of heat.Avoid inhaling gases, fumes, dust, mist, vapor, and aerosols. Avoid contact with skin, eyes, and clothing.

SECTION 6 : Accidental release measures

Personal precautions, protective equipment and emergency procedures:

Ensure adequate ventilation. Ensure that air-handling systems are operational.

Environmental precautions:

Should not be released into environment. Prevent from reaching drains, sewer, or waterway.

Methods and material for containment and cleaning up:

Always obey local regulations. If necessary use trained response staff or contractor. Evacuate personnel to safe areas. Containerize for disposal. Refer to Section 13. Keep in suitable closed containers for disposal. Soak up with inert absorbent material and dispose of as hazardous waste. Cover spill with soda ash or calcium carbonate. Mix and add water to form slurry.Wear protective eyeware, gloves, and clothing. Refer to Section 8.

Reference to other sections:

SECTION 7 : Handling and storage

Precautions for safe handling:

Prevent formation of aerosols. Never use hot water and never add water to the acid.Do not allow contact between hydrochloric acid, metal, and organics.Follow good hygiene procedures when handling chemical materials. Refer to Section 8. Prevent contact with skin, eyes, and clothing. Follow proper disposal methods. Refer to Section 13. Do not eat, drink, smoke, or use personal products when handling chemical substances. Use only in well ventilated areas.Avoid splashes or spray in enclosed areas.

Conditions for safe storage, including any incompatibilities:

Store in a cool location. Keep away from food and beverages. Protect from freezing and physical damage. Store away from incompatible materials. Provide ventilation for containers. Keep container tightly sealed.Containers for hydrochloric acid must be made from corrosion resistant materials: glass, polyethylene, polypropylene, polyvinyl chloride, carbon steel lined with rubber or ebonite.

SECTION 8 : Exposure controls/personal protection




Control Parameters:	7647-01-0, Hydrochloric Acid, ACGIH: 2 ppm Ceiling 7647-01-0, Hydrochloric Acid, NIOSH: 5 ppm Ceiling; 7 mg/m3 Ceiling
Appropriate Engineering controls:	Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapor and mists below the applicable workplace exposure limits (Occupational Exposure Limits-OELs) indicated above. Emergency eye wash fountains and safety showers should be available in the immediate vicinity of handling.
Respiratory protection:	Not required under normal conditions of use. Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. When necessary use NIOSH approved breathing equipment.
Protection of skin:	Select glove material impermeable and resistant to the substance. Select glove material based on rates of diffusion and degradation. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Use proper glove removal technique without touching outer surface. Avoid skin contact with used gloves. Wear protective clothing.
Eye protection:	Faceshield (8-inch minimum).Tightly fitting safety goggles.
General hygienic measures:	Perform routine housekeeping. Wash hands before breaks and immediately after handling the product. Avoid contact with skin, eyes, and clothing. Before rewearing wash contaminated clothing.

SECTION 9 : Physical and chemical properties

Appearance (physical state,color):	Clear, colorless liquid.	**Explosion limit lower**: **Explosion limit upper**:	Non Explosive Non Explosive
Odor:	Pungent odor	**Vapor pressure**:	5.7mmHg @ 0C
Odor threshold:	0.3 – 14.9 mg/m3	**Vapor density**:	1.27 (Air=1)
pH-value:	< 1	**Relative density**:	1.0 - 1.2

Melting/Freezing point:	- 74 C	**Solubilities**:	Miscible
Boiling point/Boiling range:	81.5 - 110 C	**Partition coefficient (n-octanol/water)**:	Not Determined
Flash point (closed cup):	Not Applicable	**Auto/Self-ignition temperature**:	Not Determined
Evaporation rate:	>1.00	**Decomposition temperature**:	Not Determined
Flammability (solid,gaseous):	non combustible	**Viscosity**:	a. Kinematic:Not Determined b. Dynamic: Not Determined
Density: Not Determined **Hydrochloric Acid:**MW is36.46			

SECTION 10 : Stability and reactivity

Reactivity: Reacts violently with bases and is corrosive.
Chemical stability: No decomposition if used and stored according to specifications.
Possible hazardous reactions: Attacks many metals in the presence of water forming flammable explosive gas (hydrogen).Reacts violently with oxidants forming toxic gas (chlorine).
Conditions to avoid: Incompatible materials.
Incompatible materials: Bases, Amines, Alkali metals, Metals, permanganates (potassium permanganate), Fluorine, Metal acetylides, Hexalithium disilicide.
Hazardous decomposition products: Hydrogen chloride gas.Carbon oxides.

SECTION 11 : Toxicological information

Acute Toxicity:		
Inhalation:	7647-01-0	LD50 Rat 3124 ppm/hour
Oral:	7647-01-0	LD50 Rat 238 - 277 mg/kg
Dermal:	7647-01-0	LD50 Rabbit >5010 mg/kg
Chronic Toxicity: No additional information.		
Corrosion Irritation:		
Dermal:	7647-01-0	Skin - rabbit Result: Causes burns.
Ocular:	7647-01-0	Eyes - rabbit Result: Corrosive to eyes
Sensitization:		No additional information.
Single Target Organ (STOT):		7647-01-0: The substance or mixture is classified as specific target organ toxicant, single exposure, category 3 with respiratory tract irritation.
Numerical Measures:		No additional information.
Carcinogenicity:		No additional information.
Mutagenicity:		No additional information.

Reproductive Toxicity:	No additional information.

SECTION 12 : Ecological information

Ecotoxicity

7647-01-0: Toxicity to fish LC50 - Gambusia affinis (Mosquito fish) - 282 mg/l - 96 h (Hydrochloric acid)

Persistence and degradability:
Bioaccumulative potential:
Mobility in soil:
Other adverse effects:

SECTION 13 : Disposal considerations

Waste disposal recommendations:

Do not allow product to reach sewage system or open water.It is the responsibility of the waste generator to properly characterize all waste materials according to applicable regulatory entities (US 40CFR262.11). Contact a licensed professional waste disposal service to dispose of this material. Dispose of empty containers as unused product. Product or containers must not be disposed together with household garbage. Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations. Ensure complete and accurate classification.

SECTION 14 : Transport information

UN-Number

1789

UN proper shipping name

HYDROCHLORIC ACID

Transport hazard class(es)

Class:
8 Corrosive substances

Packing group:II
Environmental hazard:
Transport in bulk:
Special precautions for user:

SECTION 15 : Regulatory information

United States (USA)

SARA Section 311/312 (Specific toxic chemical listings):

Acute

SARA Section 313 (Specific toxic chemical listings):

7647-01-0 Hydrochloric Acid

RCRA (hazardous waste code):

None of the ingredients is listed

TSCA (Toxic Substances Control Act):

All ingredients are listed.

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act):

7647-01-0 Hydrochloric Acid 5000 lbs

Proposition 65 (California):

Chemicals known to cause cancer:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for females:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for males:

None of the ingredients is listed

Chemicals known to cause developmental toxicity:

None of the ingredients is listed

Canada

Canadian Domestic Substances List (DSL):

All ingredients are listed.

Canadian NPRI Ingredient Disclosure list (limit 0.1%):

None of the ingredients is listed

Canadian NPRI Ingredient Disclosure list (limit 1%):

7647-01-0 Hydrochloric Acid

SECTION 16 : Other information

This product has been classified in accordance with hazard criteria of the Controlled Products Regulations and the SDS contains all the information required by the Controlled Products Regulations.Note:. The responsibility to provide a safe workplace remains with the user.The user should consider the health hazards and safety information contained herein as a guide and should take those precautions required in an individual operation to instruct employees and develop work practice procedures for a safe work environment.The information contained herein is, to the best of our knowledge and belief, accurate.However, since the conditions of handling and use are beyond our control, we make no guarantee of results, and assume no liability for damages incurred by the use of this material.It is the responsibility of the user to comply with all applicable laws and regulations applicable to this material.

GHS Full Text Phrases:

Abbreviations and acronyms:

IMDG: International Maritime Code for Dangerous Goods
PNEC: Predicted No-Effect Concentration (REACH)
CFR: Code of Federal Regulations (USA)
SARA: Superfund Amendments and Reauthorization Act (USA)
RCRA: Resource Conservation and Recovery Act (USA)
TSCA: Toxic Substances Control Act (USA)
NPRI: National Pollutant Release Inventory (Canada)
DOT: US Department of Transportation
IATA: International Air Transport Association
GHS: Globally Harmonized System of Classification and Labelling of Chemicals
ACGIH: American Conference of Governmental Industrial Hygienists
CAS: Chemical Abstracts Service (division of the American Chemical Society)
NFPA: National Fire Protection Association (USA)

HMIS: Hazardous Materials Identification System (USA)
WHMIS: Workplace Hazardous Materials Information System (Canada)
DNEL: Derived No-Effect Level (REACH)

Effective date : 01.08.2015
Last updated : 03.20.2015

APPENDIX B
Community Air Monitoring Plan (CAMP)

Community Air Monitoring Plan

This Community Air Monitoring Plan (CAMP) requires real-time monitoring for volatile organic compounds (VOCs) and particulates (i.e., dust) at the downwind perimeter of each designated work area when certain activities are in progress during remedial activities at the site. The CAMP is not intended for use in establishing action levels for workers respiratory protection. Rather, its intent is to provide a measure of protection for the downwind community (i.e., off-site receptors including residences and businesses and on-site workers not directly involved with the subject work activities) from potential airborne contaminant releases as a direct result of investigative and remedial work activities. The action levels specified herein require increased monitoring, corrective actions to abate emissions, and/or work shutdown. Additionally, the CAMP helps to confirm that work activities did not spread contamination off-site through the air. The CAMP was developed in accordance with Appendices 1A & 1B of DER-10, included at the end of this CAMP.

Reliance on the CAMP should not preclude simple, common-sense measures to keep VOCs, dust, and odors at a minimum around the work areas.

Depending on the nature of known or potential contaminants at the site, real-time air monitoring for VOCs and/or particulate levels at the perimeter of the exclusion zone or work area will be necessary.

Continuous monitoring will be required for all ground intrusive activities. Ground intrusive activities include, but are not limited to, soil/waste excavation and handling, test pitting or trenching.

Periodic monitoring for VOCs will be required during non-intrusive activities such as the collection of soil and groundwater samples. "Periodic" monitoring during sample collection might reasonably consist of taking a reading upon arrival at a sample location, monitoring while opening a well cap or overturning soil, monitoring during well baling/purging, and taking a reading prior to leaving a sample location. In some instances, depending upon the proximity of potentially exposed individuals, continuing monitoring may be required during sampling activities.

Particulate Monitoring, Response Levels, and Actions

Particulate concentrations will be monitored continuously at the upwind and downwind perimeters of the exclusion zone at temporary particulate monitoring stations. The particulate monitoring will be performed using real-time monitoring equipment capable of measuring particulate matter less than 10 micrometers in size (PM-10) and capable of integrating over a period of 15 minutes (or less) for comparison to the airborne particulate action level. The equipment will be equipped with an audible alarm to indicate exceedance of the action level. In addition, fugitive dust migration will be visually assessed during all work activities.

- If the downwind PM-10 particulate level is 100 micrograms per cubic meter (mcg/m^3) greater than the background (upwind perimeter) for the 15-minute period or if airborne dust is observed leaving the work area, then dust suppression techniques will be employed. Work may continue with dust suppression techniques provided that no visible dust is migrating from the work area.

- If, after implementation of dust suppression techniques, downwind PM-10 particulate levels are greater than 150 mcg/m^3 above the upwind level, work will be stopped and a re- evaluation of activities initiated. Work can resume provided that dust suppression measures

and other controls are successful in reducing the downwind PM-10 particulate concentration to within 150 mcg/m^3 of the upwind level and in preventing visible dust migration.

- All readings will be recorded and be available for State (DEC and DOH) personnel to review.

VOC Monitoring, Response Levels, and Actions

VOCs will be monitored at the downwind perimeter of the immediate work area (i.e., the exclusion zone) on a continuous basis or as otherwise specified. Upwind concentrations will be measured at the start of each workday and periodically thereafter to establish background conditions. The monitoring work will be performed using a photo ionization detector (PID) equipped with a 10.2 eV bulb. The PID will be calibrated at least daily for the contaminant(s) of concern or for an appropriate surrogate. The equipment will be capable of calculating 15-minute running average concentrations, which will be compared to the levels specified below.

- If the ambient air concentration of total organic vapors at the downwind perimeter of the work area or exclusion zone exceeds 5 parts per million (ppm) above background for the 15- minute average, work activities must be temporarily halted and monitoring continued. If the total organic vapor level readily decreases (per instantaneous readings) below 5 ppm over background, work activities can resume with continued monitoring.

- If total organic vapor levels at the downwind perimeter of the work area or exclusion zone persist at levels in excess of 5 ppm over background but less than 25 ppm, work activities will be halted, the source of the vapors identified, corrective actions taken to abate emissions, and monitoring continued. After these steps, work activities can resume provided that the total organic vapor level 200 feet downwind of the exclusion zone or half the distance to the nearest potential receptor or residential/commercial structure, whichever is less- but in no case less than 20 feet, is below 5 ppm over background for the 15-minute average.

- If the organic vapor level is above 25 ppm at the perimeter of the work area, activities will be shutdown.

- All 15-minute readings will be recorded and be available for State (DEC and DOH) personnel to review. Instantaneous readings, if any, used for decision purposes will also be recorded.

Special Requirements for Work Within 20 Feet of Potentially Exposed Individuals or Structures

When work areas are within 20 feet of potentially exposed populations or occupied structures, the continuous monitoring locations for VOCs and particulates must reflect the nearest potentially exposed individuals and the location of ventilation system intakes for nearby structures. The use of engineering controls such as vapor/dust barriers, temporary negative-pressure enclosures, or special ventilation devices should be considered to prevent exposures related to the work activities and to control dust and odors. Consideration should be given to implementing the planned activities when potentially exposed populations are at a minimum, such as during weekends or evening hours in non-residential settings.

- If total VOC concentrations opposite the walls of occupied structures or next to intake vents exceed 1 ppm, monitoring should occur within the occupied structure(s). Depending upon the nature of contamination, chemical-specific colorimetric tubes of sufficient sensitivity may be necessary for comparing the exposure point concentrations with appropriate pre-determined response levels (response actions should also be predetermined). Background readings in the occupied spaces must be taken prior to commencement of the planned work. Any unusual background readings should be discussed with NYSDOH prior to commencement of the work.

- If total particulate concentrations opposite the walls of occupied structures or next to intake vents exceed 150 mcg/m3, work activities should be suspended until controls are implemented and are successful in reducing the total particulate concentration to 150 mcg/m3 or less at the monitoring point.

- Depending upon the nature of contamination and remedial activities, other parameters (e.g., explosivity, oxygen, hydrogen sulfide, carbon monoxide) may also need to be monitored. Response levels and actions should be pre-determined, as necessary, for each site.

Special Requirements for Indoor Work with Co-Located Residences or Facilities

Unless a self-contained, negative-pressure enclosure with proper emission controls will encompass the work area, all individuals not directly involved with the planned work must be absent from the room in which the work will occur. Monitoring requirements shall be as stated above under "Special Requirements for Work Within 20 Feet of Potentially Exposed Individuals or Structures" except that in this instance "nearby/occupied structures" would be adjacent occupied rooms. Additionally, the location of all exhaust vents in the room and their discharge points, as well as potential vapor pathways (openings, conduits, etc.) relative to adjoining rooms, should be understood and the monitoring locations established accordingly. In these situations, it is strongly recommended that exhaust fans or other engineering controls be used to create negative air pressure within the work area during remedial activities. Additionally, it is strongly recommended that the planned work be implemented during hours (e.g. weekends or evenings) when building occupancy is at a minimum.

Appendix 1A
New York State Department of Health
Generic Community Air Monitoring Plan

Overview

A Community Air Monitoring Plan (CAMP) requires real-time monitoring for volatile organic compounds (VOCs) and particulates (i.e., dust) at the downwind perimeter of each designated work area when certain activities are in progress at contaminated sites. The CAMP is not intended for use in establishing action levels for worker respiratory protection. Rather, its intent is to provide a measure of protection for the downwind community (i.e., off-site receptors including residences and businesses and on-site workers not directly involved with the subject work activities) from potential airborne contaminant releases as a direct result of investigative and remedial work activities. The action levels specified herein require increased monitoring, corrective actions to abate emissions, and/or work shutdown. Additionally, the CAMP helps to confirm that work activities did not spread contamination off-site through the air.

The generic CAMP presented below will be sufficient to cover many, if not most, sites. Specific requirements should be reviewed for each situation in consultation with NYSDOH to ensure proper applicability. In some cases, a separate site-specific CAMP or supplement may be required. Depending upon the nature of contamination, chemical- specific monitoring with appropriately-sensitive methods may be required. Depending upon the proximity of potentially exposed individuals, more stringent monitoring or response levels than those presented below may be required. Special requirements will be necessary for work within 20 feet of potentially exposed individuals or structures and for indoor work with co-located residences or facilities. These requirements should be determined in consultation with NYSDOH.

Reliance on the CAMP should not preclude simple, common-sense measures to keep VOCs, dust, and odors at a minimum around the work areas.

Community Air Monitoring Plan

Depending upon the nature of known or potential contaminants at each site, real-time air monitoring for VOCs and/or particulate levels at the perimeter of the exclusion zone or work area will be necessary. Most sites will involve VOC and particulate monitoring; sites known to be contaminated with heavy metals alone may only require particulate monitoring. If radiological contamination is a concern, additional monitoring requirements may be necessary per consultation with appropriate DEC/NYSDOH staff.

Continuous monitoring will be required for all ground intrusive activities and during the demolition of contaminated or potentially contaminated structures. Ground intrusive activities include, but are not limited to, soil/waste excavation and handling, test pitting or trenching, and the installation of soil borings or monitoring wells.

Periodic monitoring for VOCs will be required during non-intrusive activities such as the collection of soil and sediment samples or the collection of groundwater samples from existing monitoring wells. “Periodic” monitoring during sample collection might reasonably consist of taking a reading upon arrival at a sample location, monitoring while opening a well cap or

overturning soil, monitoring during well baling/purging, and taking a reading prior to leaving a sample location. In some instances, depending upon the proximity of potentially exposed individuals, continuous monitoring may be required during sampling activities. Examples of such situations include groundwater sampling at wells on the curb of a busy urban street, in the midst of a public park, or adjacent to a school or residence.

VOC Monitoring, Response Levels, and Actions

Volatile organic compounds (VOCs) must be monitored at the downwind perimeter of the immediate work area (i.e., the exclusion zone) on a continuous basis or as otherwise specified. Upwind concentrations should be measured at the start of each workday and periodically thereafter to establish background conditions, particularly if wind direction changes. The monitoring work should be performed using equipment appropriate to measure the types of contaminants known or suspected to be present. The equipment should be calibrated at least daily for the contaminant(s) of concern or for an appropriate surrogate. The equipment should be capable of calculating 15-minute running average concentrations, which will be compared to the levels specified below.

1. If the ambient air concentration of total organic vapors at the downwind perimeter of the work area or exclusion zone exceeds 5 parts per million (ppm) above background for the 15-minute average, work activities must be temporarily halted and monitoring continued. If the total organic vapor level readily decreases (per instantaneous readings) below 5 ppm over background, work activities can resume with continued monitoring.

2. If total organic vapor levels at the downwind perimeter of the work area or exclusion zone persist at levels in excess of 5 ppm over background but less than 25 ppm, work activities must be halted, the source of vapors identified, corrective actions taken to abate emissions, and monitoring continued. After these steps, work activities can resume provided that the total organic vapor level 200 feet downwind of the exclusion zone or half the distance to the nearest potential receptor or residential/commercial structure, whichever is less - but in no case less than 20 feet, is below 5 ppm over background for the 15-minute average.

3. If the organic vapor level is above 25 ppm at the perimeter of the work area, activities must be shutdown.

4. All 15-minute readings must be recorded and be available for State (DEC and NYSDOH) personnel to review. Instantaneous readings, if any, used for decision purposes should also be recorded.

Particulate Monitoring, Response Levels, and Actions

Particulate concentrations should be monitored continuously at the upwind and downwind perimeters of the exclusion zone at temporary particulate monitoring stations. The particulate monitoring should be performed using real-time monitoring equipment capable of measuring particulate matter less than 10 micrometers in size (PM-10) and capable of integrating over a period of 15 minutes (or less) for comparison to the airborne particulate action level. The equipment must be equipped with an audible alarm to indicate exceedance of the action level. In addition, fugitive dust migration should be visually assessed during all work activities.

1. If the downwind PM-10 particulate level is 100 micrograms per cubic meter (mcg/m^3) greater than background (upwind perimeter) for the 15-minute period or if airborne dust is observed leaving the work area, then dust suppression techniques must be employed. Work may continue with dust suppression techniques provided that downwind PM-10 particulate levels do not exceed 150 mcg/m^3 above the upwind level and provided that no visible dust is migrating from the work area.

2. If, after implementation of dust suppression techniques, downwind PM-10 particulate levels are greater than 150 mcg/m^3 above the upwind level, work must be stopped and a re-evaluation of activities initiated. Work can resume provided that dust suppression measures and other controls are successful in reducing the downwind PM-10 particulate concentration to within 150 mcg/m^3 of the upwind level and in preventing visible dust migration.

3. All readings must be recorded and be available for State (DEC and NYSDOH) and County Health personnel to review.

December 2009

Appendix 1B
Fugitive Dust and Particulate Monitoring

A program for suppressing fugitive dust and particulate matter monitoring at hazardous waste sites is a responsibility on the remedial party performing the work. These procedures must be incorporated into appropriate intrusive work plans. The following fugitive dust suppression and particulate monitoring program should be employed at sites during construction and other intrusive activities which warrant its use:

1. Reasonable fugitive dust suppression techniques must be employed during all site activities which may generate fugitive dust.

2. Particulate monitoring must be employed during the handling of waste or contaminated soil or when activities on site may generate fugitive dust from exposed waste or contaminated soil. Remedial activities may also include the excavation, grading, or placement of clean fill. These control measures should not be considered necessary for these activities.

3. Particulate monitoring must be performed using real-time particulate monitors and shall monitor particulate matter less than ten microns (PM10) with the following minimum performance standards:

(a) Objects to be measured: Dust, mists or aerosols;
(b) Measurement Ranges: 0.001 to 400 mg/m3 (1 to 400,000 :ug/m3);
(c) Precision (2-sigma) at constant temperature: +/- 10 :g/m3 for one second averaging; and +/- 1.5 g/m3 for sixty second averaging;
(d) Accuracy: +/- 5% of reading +/- precision (Referred to gravimetric calibration with SAE fine test dust (mmd= 2 to 3 :m, g= 2.5, as aerosolized);
(e) Resolution: 0.1% of reading or 1g/m3, whichever is larger;
(f) Particle Size Range of Maximum Response: 0.1-10;
(g) Total Number of Data Points in Memory: 10,000;
(h) Logged Data: Each data point with average concentration, time/date and data point number
(i) Run Summary: overall average, maximum concentrations, time/date of maximum, total number of logged points, start time/date, total elapsed time (run duration), STEL concentration and time/date occurrence, averaging (logging) period, calibration factor, and tag number;
(j) Alarm Averaging Time (user selectable): real-time (1-60 seconds) or STEL (15 minutes), alarms required;
(k) Operating Time: 48 hours (fully charged NiCd battery); continuously with charger;
(l) Operating Temperature: -10 to 50^{o} C (14 to 122^{o} F);
(m) Particulate levels will be monitored upwind and immediately downwind at the working site and integrated over a period not to exceed 15 minutes.

4. In order to ensure the validity of the fugitive dust measurements performed, there must be appropriate Quality Assurance/Quality Control (QA/QC). It is the responsibility of the remedial party to adequately supplement QA/QC Plans to include the following critical features: periodic instrument calibration, operator training, daily instrument performance (span) checks, and a record keeping plan.

5. The action level will be established at 150 ug/m3 (15 minutes average). While conservative,

this short-term interval will provide a real-time assessment of on-site air quality to assure both health and safety. If particulate levels are detected in excess of 150 ug/m3, the upwind background level must be confirmed immediately. If the working site particulate measurement is greater than 100 ug/m3 above the background level, additional dust suppression techniques must be implemented to reduce the generation of fugitive dust and corrective action taken to protect site personnel and reduce the potential for contaminant migration. Corrective measures may include increasing the level of personal protection for on-site personnel and implementing additional dust suppression techniques (see paragraph 7). Should the action level of 150 ug/m3 continue to be exceeded work must stop and DER must be notified as provided in the site design or remedial work plan. The notification shall include a description of the control measures implemented to prevent further exceedances.

6. It must be recognized that the generation of dust from waste or contaminated soil that migrates off-site, has the potential for transporting contaminants off-site. There may be situations when dust is being generated and leaving the site and the monitoring equipment does not measure PM10 at or above the action level. Since this situation has the potential to allow for the migration of contaminants off-site, it is unacceptable. While it is not practical to quantify total suspended particulates on a real-time basis, it is appropriate to rely on visual observation. If dust is observed leaving the working site, additional dust suppression techniques must be employed. Activities that have a high dusting potential--such as solidification and treatment involving materials like kiln dust and lime--will require the need for special measures to be considered.

7. The following techniques have been shown to be effective for the controlling of the generation and migration of dust during construction activities:

(a) Applying water on haul roads;
(b) Wetting equipment and excavation faces;
(c) Spraying water on buckets during excavation and dumping;
(d) Hauling materials in properly tarped or watertight containers;
(e) Restricting vehicle speeds to 10 mph;
(f) Covering excavated areas and material after excavation activity ceases; and
(g) Reducing the excavation size and/or number of excavations.

Experience has shown that the chance of exceeding the 150ug/m3 action level is remote when the above-mentioned techniques are used. When techniques involving water application are used, care must be taken not to use excess water, which can result in unacceptably wet conditions. Using atomizing sprays will prevent overly wet conditions, conserve water, and provide an effective means of suppressing the fugitive dust.

8. The evaluation of weather conditions is necessary for proper fugitive dust control. When extreme wind conditions make dust control ineffective, as a last resort remedial actions may need to be suspended. There may be situations that require fugitive dust suppression and particulate monitoring requirements with action levels more stringent than those provided above. Under some circumstances, the contaminant concentration and/or toxicity may require additional monitoring to protect site personnel and the public. Additional integrated sampling and chemical analysis of the dust may also be in order. This must be evaluated when a health and safety plan is developed and when appropriate suppression and monitoring requirements are established for protection of health and the environment.

APPENDIX C
PFAS Laboratory Analytical SOP

Pace ANALYTICAL SERVICES	**ENV-SOP-BTRO-0149 v02_Draft Method 1633 SOP**	
	Effective Date: 06/07/2022	COPYRIGHT© 2019, 2021, 2022 Pace®

Management Approval:
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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure for the determination of the per- and polyfluoroalkyl substances (PFAS) in Table 1 in aqueous (all non-potable water and leachate), solid (soil, biosolids, sediment) and tissue samples by liquid chromatography/mass spectrometry (LC-MS/MS).

The method calibrates and quantifies PFAS analytes using isotopically labeled standards. Where linear and branched isomers are present in the sample and either qualitative or quantitative standards containing branched and linear isomers are commercially available, the PFAS analyte is reported as a single analyte consisting of the sum of the linear and branched isomer concentrations.

The instrumental portion of this method is for use only by analysts experienced with LC-MS/MS or under the close supervision of such qualified persons. The laboratory must demonstrate the ability to generate acceptable results using the procedure in Sections 11.3.1 and 11.4.

By their very nature, many components of PFAS present analytical challenges unique to this class of analytes. For example, PFAS analytes readily adhere to the walls of the sample containers and may also stratify in the container.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes and the normal LODs and LOQs that can be achieved with this procedure are provided in Table 1, Appendix A.

LOQs are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A. LOQ is equivalent to Minimum Level of Quantitation (ML).

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

2.0 SUMMARY OF METHOD

Environmental samples are prepared and extracted using method-specific procedures. Sample extracts are subjected to cleanup procedures designed to remove interferences. Analyses of the sample extracts are conducted by LC-MS/MS in the multiple reaction monitoring (MRM) mode. Sample concentrations are determined by isotope dilution or extracted internal standard quantification (see Section 9.2.1) using isotopically labeled compounds added to the samples before extraction.

Individual PFAS analytes are identified through peak analysis of the quantification and confirmation ions, where applicable.

Quantitative determination of target analyte concentrations is made with respect to an isotopically labeled PFAS standard; the concentrations are then used to convert raw peak areas in sample chromatograms to final concentrations.

Results for target analytes are recovery corrected by the method of quantification (i.e., either isotope dilution or extracted internal standard quantification, see Section 9.2.1). Isotopically labeled compound recoveries are determined by comparison to the responses of one of seven non-extracted internal standards (a.k.a., the “recovery” standards) and are used as general indicators of overall analytical quality.

The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and LC-MS/MS systems.

2.1 Extraction

2.1.1 **Aqueous samples** are spiked with isotopically labeled standards (EIS), extracted using solid-phase extraction (SPE) cartridges and undergo cleanup using carbon before analysis.

2.1.2 **Solid samples** are spiked with EIS, extracted into basic methanol, and cleaned up by carbon and SPE cartridges before analysis.

2.1.3 **Tissue samples** are spiked with EIS, extracted in methanol with potassium hydroxide and acetonitrile, and cleaned up by carbon and SPE cartridges before analysis.

3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and solvents is required.

Clean all equipment prior to, and after each use to avoid PFAS cross-contamination. Typical cleaning solvents used include water, methanol, and methanolic ammonium hydroxide. The residual PFAS content of disposable plasticware and filters must be verified by batch/lot number and may be used without cleaning if PFAS levels are **less than half the LOQ**.

Prior to use, glassware must be solvent rinsed and then air dried. A solvent rinse procedure using methanolic ammonium hydroxide (1%) and methanol is recommended.

All parts of the SPE manifold must be cleaned between samples by rinsing with methanolic ammonium hydroxide (1%) and air drying prior to use. Smaller parts, like the needles, adapters, reservoirs, and stopcocks associated with the manifold should be rinsed with tap water prior to rinsing with methanolic ammonium hydroxide (1%) and air drying. After loading the samples but prior to elution procedures, the chamber should be rinsed with methanolic ammonium hydroxide (1%).

All equipment used in the filleting, dissecting, shucking, compositing, and homogenization of tissue must be cleaned with detergent and hot water, then rinsed with ultra-pure water followed by a series of solvent rinses. A typical solvent rinse procedure would be acetone, followed by toluene, and then dichloromethane.

All materials used in the analysis must be demonstrated to be free from interferences by running method blanks (Section 11.1.1) at the beginning and with each extraction batch (samples started through the extraction process on a given analytical batch to a maximum of 20 field samples).

Reagent water (Section 8.1) can be used to simulate water samples and Ottawa sand and/or reagent-grade sand (Section 7.2) can be used to simulate soils. For tissue, fish fillets, chicken breast or other

similar animal tissue (see Section 7.2) may be used as the reference matrix. The laboratory must verify that the source product used does not contain PFAS in detectable amounts.

Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the native PFAS. Because low levels of PFAS are measured by this method, elimination of interferences is essential. The cleanup steps given in Section 9.3 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PFAS at the levels shown in Table 1. The most frequently encountered interferences are fluoropolymers; however, when analyzing whole fish samples, bile salts (e.g., Taurodeoxycholic Acid [TDCA]) can interfere in the chromatography. For this reason, analysis of a standard containing TDCA is required as part of establishing the initial chromatographic conditions (see Sections 8.2.7 and 9.2.3).

4.0 DEFINITIONS

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

Extracted Internal Standard (EIS) quantification – The response of the target compound is compared to the response of the isotopically labeled analog of another compound with chemical and retention time similarities.

Isotope dilution (ID) quantitation – A means of determining a naturally occurring (native) compound by reference to the same compound in which one or more atoms has been isotopically enriched. The labeled PFAS are spiked into each sample and allow identification and correction of the concentration of the native compounds in the analytical process.

Isotopically labeled compound – An analog of a target analyte in the method which has been synthesized with one or more atoms in the structure replaced by a stable (non-radioactive) isotope of that atom. Common stable isotopes used are 13C (Carbon-13) or Deuterium (D or 2H). These labeled compounds do not occur in nature, so they can be used for isotope dilution quantitation or other method-specific purposes.

Minimum Level of quantitation (ML) – The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. It may be equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

5.0 HEALTH AND SAFETY

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

PFOA has been described as likely to be carcinogenic to humans. Pure standards should be handled by trained personnel, with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and

environmental (HSE) policies and procedures specified in this SOP and in the Pace Chemical Hygiene / Safety Manual.

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

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

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

6.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIME, AND STORAGE

Samples should be collected in accordance with a sampling plan and procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project. Many states have state-specific sampling instructions for PFAS, which should be followed by the client where required. Collect samples in HDPE containers following conventional sampling practices (Reference 5). All sample containers must have linerless HDPE or polypropylene caps. Other sample collection techniques, or sample volumes, may be used if documented.

The laboratory does not perform sample collection or field measurements for this test method. To assure sample collection and field checks and treatment are performed in accordance with applicable regulations, Pace project managers will inform the client of these requirements at the time of request for analytical services when the request for testing is received prior to sample collection. If samples were already collected, the laboratory will record any nonconformance to these requirements in the laboratory's sample receipt record when sufficient information about sample collection is provided with the samples.

The nature of the tissues of interest may vary by project. Field sampling plans and protocols should explicitly state the samples to be collected and if any processing will be conducted in the field (e.g., filleting of whole fish or removal of organs). All field procedures must involve materials and equipment that have been shown to be free of PFAS. Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis. If whole fish are collected, wrap the fish in aluminum foil or food-grade polyethylene wrap, and maintain at 0 - 6 ºC from the time of collection until receipt at the laboratory, to a maximum time of 24 hours. If a longer transport time is necessary, freeze the sample before shipping. Ideally, fish should be frozen upon collection and shipped to the laboratory as soon as possible.

The laboratory will provide containers for the collection of samples upon client request for analytical services.

Requirements for container type, preservation, and field quality control (QC) for the common list of test methods offered by Pace are included in the laboratory's quality manual.

General Requirements

Matrix	Routine Container[1]	Sample Amount[2]	Preservation	Holding Time Collection to Prep/ Prep to Analysis
Aqueous (non-potable water) containing <100 mg/L SS	2 x 500 mL linerless HDPE 1 x 125 mL linerless HDPE[3]	500 mL	Thermal: 0-6°C OR ≤ -20°C	28/28[4] OR 90/28
Aqueous (leachate)	2 x 125 mL linerless HDPE	100 mL	Thermal: 0-6°C OR ≤ -20°C	28/28 OR 90/28
Solid (soil and sediment)	3 oz/ 90 mL linerless polypropylene straight sided	5 g	Thermal: 0-6°C OR ≤ -20°C	90/28[5]
Solid (biosolid)	3 oz/ 90 mL linerless polypropylene straight sided	0.5 g	Thermal: 0-6°C OR ≤ -20°C	90/28
Tissue[6]	3 oz/ 90 mL linerless polypropylene straight sided	2 g	Thermal: ≤ -20°C	90/28

[1]Aqueous sample containers should be filled only to the appropriate gradation marked on the container, or to the shoulder of the container if no gradations are provided. To allow room for expansion during freezing (if necessary), aqueous sample containers should not be overfilled.

[2]Miniumum amount needed for each discrete analysis. Solid and biosolid sample amounts reflect the dry sample weight.

[3]Needed for percent suspended solids and screening analyses.

[4]In the single lab validation, issues were observed with certain perfluorooctane sulfonamidoethanols and perfluorooctane sulfonamidoacetic acids after 7 days.

[5]Samples may need to be extracted as soon as possible if NFDHA is an important analyte. The onus is on the client to indicate if NFDHA is an important analyte, prior to shipment. If no such designation is given, follow stated hold time.

[6]Container listed here will be used for tissue homogenate; samples may be received at the laboratory as whole fish or filets wrapped in aluminum foil or food grade polyethylene wrap. Ideally fish should be frozen upon collection and shipped to the laboratory as soon as possible.

Note: Project-specific requirements dictate which storage condition applies. The storage condition to be used for each project must be formally documented in written form (QAPP or otherwise) before samples are received. Without any prior indication from the client, the lab will store all aqueous and solid samples at 0-6°C until extraction, with a 28-day preparation holding time.

Thermal preservation is checked and recorded on receipt in the laboratory.

Prepared sample extracts of all matrices are stored at 0-6°C until sample analysis.

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

7.0 EQUIPMENT AND SUPPLIES

7.1 Equipment

Due to the possibility of adsorption of analytes onto glass, HDPE containers are used for all standard, sample, and extraction preparations. Any time a new lot of SPE cartridges, solvents, cryovials, or autosampler vials are used, it must be demonstrated that a MB is reasonably free of contamination and that the criteria in Section 11.1.1 are met.

Sample Preparation

- Oven – Capable of maintaining a temperature of 105 ± 5 ºC
- Analytical balance – Capable of weighing 0.0001 g
- Top loading balance – Capable of weighing 0.01 g
- Calibrated mechanical variable volume pipettes with disposable HDPE or polypropylene tips (10 µL to 5 mL) – used for preparation of calibration standards and spiked samples
- Point of Use water preparation system – Millipore Synergy UV
- Ultrasonic mixer (sonicator) – Fisher Scientific Ultrasonic Cleaner FS60
- pH Paper, range 0-14 - (Whatman® PanpehaTM or equivalent), 0.5-unit readability
- Analog or digital vortex mixer, single or multi-tube (Fisher Scientific 02-215-452, or equivalent)
- Volumetric flasks, Class A
- 15 and 50-mL conical polypropylene tubes with polypropylene screw caps for preparing and storing extract solutions and for collection of eluents (Fisher Scientific 05-527-90 and 14-432-22, or equivalent)
- Variable speed mixing table (VWR Model 3500 Orbital Shaker, or equivalent)

Filtration

- Silanized glass wool (Pyrex 3950 or equivalent)
- Disposable syringe filter, 25 mm, 0.2 µm Nylon membrane, Phenomenex AF0-1207-52 or equivalent
- Glass fiber filter, 47 mm, 1 µm, PALL 61631 or equivalent
- Centrifuge (Thermo Scientific ST-40 or equivalent), capable of reaching at least 3000 rpm
- Syringe (BD 309646 or equivalent), polypropylene/HDPE, 5 mL
- Disposable glass and plastic pipets

Solid-Phase Extraction

- Solid Phase Extraction (SPE) cartridges (Phenomenex 8B-S038-SCH, 150 mg WAX, or equivalent)
- SPE reservoirs – 60 mL, Phenomenex part# AH0-7189, or equivalent
- SPE adapter caps – Phenomenex Part# AH0-7191 (Adapter cap for 1, 3, 6 mL SPE tubes)
- Vacuum manifold for SPE Cartridges – Sigma-Aldrich Cat# 57265: Visiprep SPE Vacuum manifold, or equivalent
- Disposable liners for Visiprep Manifold – Millipore-Sigma part# 57059 / Restek part# 28310-VM, or equivalent
- Vacuum tubing – 1/4” ID, 5/8” OD, 3/16” wall; Fisher Scientific part# 14-176-6B or equivalent

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

Evaporation

- Automatic or manual solvent evaporation system – TurboVap® LV or equivalent
- Evaporation/concentrator tubes, 60 mL clear glass, 30 x 125 mm, without caps – Fisher cat# 02-993-275; Caps: Qorpak item # CAP-00178; Tubes with Caps: Qorpak item# GLC-07878; or equivalent

Instrument

- High-performance liquid chromatograph (HPLC) equipped with tandem quadrupole mass spectrometer – Agilent 6495C or equivalent; LC/MS Data Acquisition for 6400 Series Triple Quadrupole Version 10.1, Build 10.1.67; Quantitative Analysis Version 10.1, Build 10.1.733.0
- Agilent Zorbax RRHD Eclipse Plus C18, 2.1 x 50 mm analytical column (Agilent Part # 959757-902), or equivalent
- Guard cartridge/column – ZORBAX RRHD Eclipse Plus C18, 2.1mm, 1.8 µm, 1200 bar pressure, UHPLC guard (Agilent Part # 821725-901), or equivalent
- Trap/delay column – Agilent Zorbax Eclipse Plus C18, 2.1 mm, 1.8 µm (Agilent Part# 821725-901), or equivalent

7.2 Supplies

Due to the possibility of adsorption of analytes onto glass, HDPE containers are used for all standard, sample, and extraction preparations. Any time a new lot of SPE cartridges/tubes, solvents, cryovials, or autosampler vials are used, it must be demonstrated that a MB is reasonably free of contamination and that the criteria in Section 11.1.1 are met.

- Reference matrix: Aqueous – reagent water
- Reference matrix: Solid – Ottawa sand
- Reference matrix: Tissue – fish fillets, chicken breast or similar animal tissue
- Bottles – HDPE or glass, with linerless HDPE or polypropylene caps. Various sizes. QEC item # 6212-Q016/BC-150-PACE (500 mL), 6212-Q008/BC-280-PACE (250 mL), 6213-U004/BC-500-PACE (125 mL), 6213-U002/BC-400-PACE (60 mL)
- Screw top vials, 250 µL PP, and Cap, 9mm, clear, thin PP/silicone septa – used in sample analysis and pre-screening (Agilent Cat # 5190-2243 and 5191-8151), or equivalent
- Polypropylene vials – for storage (Wheaton W985872: 2 mL cryovials), or equivalent
- Single step filter vials – Restek Thomson SINGLE StEP® Standard Filter Vials, 0.2 µm Nylon membrane, with Black Preslit caps Cat # 25891 or equivalent; used in sample pre-screening
- Extract/Standard storage containers – 15 mL, 8 mL, or 4 mL narrow-mouth HDPE container - Thermo Scientific item# 2002-9050, 2002-9025, 2002-9125; 2.0 mL screw-top polypropylene cryogenic vials – Grainger item# 6EMV1;1.5 mL snap-cap polypropylene microcentrifuge tubes - Fisher item# 05-408-129; or equivalent

8.0 REAGENTS AND STANDARDS

8.1 Reagents

Reagents prepared by the laboratory may be stored in either glass or HDPE containers. Proper cleaning procedures (Section 3) must be followed prior to using the containers.

- Acetic acid – ACS grade or equivalent, store at room temperature; Fisher cat# A38C-212 or equivalent
    - Acetic acid (0.1%) - dissolve acetic acid (1 mL) in reagent water (1 L), store at room temperature, replace after 3 months
- Acetonitrile – UPLC grade or equivalent, verified before use, store at room temperature; Fisher A996-4 or equivalent
- Ammonium acetate – LC/MS grade or equivalent, store at 2-8° C, replace 2 years after opening date; Fisher A637-500 or equivalent
- Ammonium hydroxide – certified ACS+ grade or equivalent, 30% in water, store at room temperature; Fisher A470-250 or equivalent
    - Aqueous ammonium hydroxide (3%) – add ammonium hydroxide (10 mL, 30%) to reagent water (90 mL), store at room temperature, replace after 3 months
    - Methanolic ammonium hydroxide (0.3%) – add ammonium hydroxide (1 mL, 30%) to methanol (99 mL), store at room temperature, replace after 1 month
    - Methanolic ammonium hydroxide (1%) – add ammonium hydroxide (3.3 mL, 30%) to methanol (97 mL), store at room temperature, replace after 1 month
    - Methanolic ammonium hydroxide (2%) – add ammonium hydroxide (6.6 mL, 30%) to methanol (93.4 mL), store at room temperature, replace after 1 month
- Carbon – EnviCarb® 1-M-USP or equivalent, verified by lot number before use, store at room temperature. Sigma 57210-U
- Eluent A – Acetonitrile, Ultra LCMS grade or equivalent; Fisher A996-4 or equivalent
- Eluent B – 2 mM ammonium acetate in 95:5 water/acetonitrile. Dissolve 0.154 g of ammonium acetate in 950 mL of water and 50 mL of acetonitrile. Store at room temperature, shelf life 2 months
- Formic acid – greater than 96% purity or equivalent, store at room temperature; Acros 14793-0010 or equivalent
    - Formic acid (aqueous, 0.1 M) – dissolve formic acid (4.6 g) in reagent water (1 L), store at room temperature, replace after 2 years
    - Formic acid (aqueous, 0.3 M) – dissolve formic acid (13.8 g) in reagent water (1 L), store at room temperature, replace after 2 years
    - Formic acid (aqueous, 5% v/v) – mix 5 mL formic acid with 95 mL reagent water, store at room temperature, replace after 2 years

- Formic acid (aqueous, 50% v/v) – mix 50 mL formic acid with 50 mL reagent water, store at room temperature, replace after 2 years
- Formic acid (methanolic 1:1, 0.1 M formic acid/methanol) – mix equal volumes of methanol and 0.1 M formic acid, store at room temperature, replace after 2 years.

- Methanol with 4% water, 1% ammonium hydroxide and 0.625% acetic acid – add ammonium hydroxide (3.3 mL, 30%), reagent water (1.7 mL) and acetic acid (0.625 mL) to methanol (92 mL), store at room temperature, replace after 1 month. This solution is used to prepare the instrument blank (Section 11.2.1) and sample extract dilutions.
- Methanol – HPLC grade or better, 99.9% purity, store at room temperature; Fisher A452-4 or equivalent
- Potassium hydroxide – certified ACS or equivalent, store at room temperature, replace after 2 years; Fisher P250-500 or equivalent
  - Methanolic potassium hydroxide (0.05 M) – add 3.3 g of potassium hydroxide to 1 L of methanol, store at room temperature, replace after 3 months.
- Reagent water – Laboratory reagent water, test by lot/batch number for residual PFAS content.

8.2 Standards

Prepare standard solutions from materials of known purity and composition or purchase as solutions or mixtures with certification to their purity, concentration, and authenticity. Observe the safety precautions in Section 5.

Purchase of commercial standard solutions or mixtures is highly recommended for this method; however, when these are not available, preparation of stock solutions from neat materials may be necessary. If the chemical purity is 98% or greater, the weight may be used without correction to calculate the concentration of the standard.

When not being used, store standard solutions in the dark at 4 °C, unless the vendor recommends otherwise, in tightly sealed screw-capped vials. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be detected. Replace the solution if solvent loss has occurred.

Note: ^{18}O-mass labeled perfluoroalkyl sulfonates may undergo isotopic exchange with water under certain conditions, which lowers the isotopic purity of the standards over time.

The laboratory must maintain records of the certificates for all standards for traceability purposes. Copies of the certificates should be provided as part of the data packages in order to check that proper calculations were performed.

8.2.1 Extracted Internal Standard (EIS) – (isotopically labeled compound) Prepare the EIS solution containing the isotopically labeled compounds listed in Table 2 as extracted internal standards in methanol from stock standards. An aliquot of EIS solution is added to each sample prior to extraction. The list of isotopically labeled compounds in Table 2 represents the compounds that were available at the time this method was validated. Other isotopically labeled compounds may be used as they become available. Prepare the EIS Standard according to the table below:

Component	Aliquot for 2.2 mL Prep	Aliquot for 6.6 mL Prep
MPFAC-HIF-ES	1.1 mL	3.3 mL

Component	Aliquot for 2.2 mL Prep	Aliquot for 6.6 mL Prep
Methanol	1.1 mL	3.3 mL

8.2.2 Non-Extracted Internal Standard (NIS) – Prepare the NIS solution containing the isotopically labeled compounds listed in Table 2 as non-extracted internal standards in methanol from stock standards. An aliquot of NIS solution is added to each sample prior to instrumental analysis. Prepare the NIS Standard according to the table below:

Component	Aliquot for 2.2 mL Prep	Aliquot for 6.6 mL Prep
MPFAC-HIF-IS	1.1 mL	3.3 mL
Methanol	1.1 mL	3.3 mL

8.2.3 Native Standards Solutions – Prepare spiking solutions containing the method analytes listed in Table 3 in methanol from stock standards. The solution(s) is used to prepare the calibration standards and to spike the known reference QC samples that are analyzed with every batch. Quantitative standards containing a mixture of branched and linear isomers must be used for method analytes if they are commercially available. Currently, these include PFOS, PFHxS, NMeFOSAA, and NEtFOSAA. Prepare the Primary Dilution Standards (PDS) according to the table below. A set of 10X-dilute PDS solutions (10X PDS A, 10X PDS B, 10X PDS C, 10X PDS D) is then created from the original PDS solutions, as noted below the table. Finally, a separate set of PDS solutions is prepared according to the table below and used for Initial Calibration Verification purposes. This set of ICV PDS solutions (PDS 2A, PDS 2B, PDS 2C, PDS 2D) is prepared either from a separate, second source or separate manufacturer lot than that used for the original PDS/10XPDS solutions. If a second source or lot is unavailable, a separate preparation using the same stocks is acceptable.

All values in mL	PDS A	PDS B	PDS C	PDS D
PFAC-MXH	1.1			
PFAC-MXI	1.1			
PFAC-MXJ		1.1		
PFAC-MXF			1.1	
PFAC-MXG				1.1
MeOH	0.55	1.1	0.275	1.65
Final Volume	2.75	2.2	1.375	2.75

Note: 10X PDS Mixes are prepared by diluting 200 µL of PDS A, B, C, or D with 1.8 mL of MeOH for a final volume of 2 mL. Alternately, 200 µL each of PDS A, B, C, and D may be diluted with 1.2 mL of MeOH for a final volume of 2 mL. If the latter preparation is used, MeOH volumes used to prep ICAL L1-L4 must be adjusted.

ICV PDS Preparation:

All values in µL	PDS 2A	PDS 2B	PDS 2C	PDS 2D
PFAC-MXH	40			
PFAC-MXI	40			
PFAC-MXJ		50		
PFAC-MXF			80	
PFAC-MXG				40
MeOH	920	950	920	960

All values in µL	PDS 2A	PDS 2B	PDS 2C	PDS 2D
Final Volume	1000	1000	1000	1000

Note: PDS 2A/2B/2C/2D concentrations are equivalent to 10X PDS A/B/C/D

8.2.4 Calibration standard solutions – A series of calibration solutions containing the target analytes and the EIS and NIS is used to establish the initial calibration of the analytical instrument. The concentration of the method analytes in the solutions varies to encompass the working range of the instrument, while the concentrations of the EIS and NIS remain constant. The calibration solutions are prepared using methanolic ammonium hydroxide (1%), water, acetic acid and the method analyte and isotopically labeled compound standard solutions. After dilution, the final solution will match the solvent mix of sample extracts, which contain methanol with 4% water, 1% ammonium hydroxide and 0.625% acetic acid (Section 8.1). Calibration standard solutions do not undergo solid phase extraction/cleanup. Prepare the calibration standard solutions according to the table below:

Component[1]	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
10X PDS A/B/C/D	25	25	62.5	156.25						
PDS A/B/C/D					62.5	62.5	156.25	312.5	625	781.25
EIS	100	50	50	50	100	50	50	50	50	50
NIS	100	50	50	50	100	50	50	50	50	50
Water	400	200	200	200	400	200	200	200	200	200
Acetic Acid	62.5	31.25	31.25	31.25	62.5	31.25	31.25	31.25	31.25	31.25
Methanol[2]	9237.5	4568.75	4418.75	4043.75	9087.5	4418.75	4043.75	3418.75	2168.75	1543.75
Final Volume	10000	5000	5000	5000	10000	5000	5000	5000	5000	5000

[1]All values listed are µL

[2]Methanolic Ammonium Hydroxide (1%)

Prepare the ICV Standard according to the table below:

Component	Aliquot for ICV STD (µL)
PDS 2A/2B/2C/2D	62.5
EIS	20
NIS	20
Water	80
Acetic Acid	12.5
Methanol[1]	1617.5
Final Volume	2000

[1] Methanolic Ammonium Hydroxide (1%)

Concentrations for calibration solutions are presented in Table 3. A minimum of six contiguous calibration standards are required for a valid analysis when using a linear calibration model, with at least five of the six calibration standards being within the quantitation range (e.g., from the LOQ to the highest calibration standard). If a second-order calibration model is used, then a minimum of seven calibration standards are required, with at least six of the seven calibration standards within the quantitation range. The lowest level calibration standard must meet a signal-to-noise ratio of 3:1 and be at a concentration less than or equal to the Limit of Quantitation (LOQ). All initial calibration requirements listed in Section 9.2 must be met.

Note: Additional calibration standards, at levels lower than the lowest calibration standard listed in the method, may be added to accommodate a lower limit of quantitation if the instrument sensitivity allows. Calibration standards at the high end of the calibration may be eliminated if the linearity of the instrument is exceeded or at the low end if those calibration standards do not meet the S/N ratio criterion of 3:1, so long as the required number of calibration points is met. All analytes with commercially available stable isotope analogues must be quantified using isotope dilution.

8.2.5 Qualitative Standards – Standards that contain mixtures of the branched and linear isomers of the method analytes and that are used for comparison against suspected branched isomer peaks in field samples. These qualitative standards are not required for those analytes where the quantitative standards in Section 8.2.4 already contain the branched and linear isomers. Qualitative standards that are currently commercially available include PFOA, PFNA, PFOSA, NEtFOSE, and NMeFOSE. Create intermediate standards of each individual qualitative standard at a concentration of approximately 1 µg/mL and use those to prepare the check standard according to the table below.

Component	Aliquot for Isomer Check STD (µL)
Intermediate STD (each of 7)	100
EIS STD	100
NIS STD	100
Water	400
Acetic Acid	62.5
Methanol[1]	8637.5
Final Volume	10000

[1] *Methanolic Ammonium Hydroxide (1%)*

8.2.6 Instrument Blank – A solvent blank is analyzed at the beginning of each analytical sequence, to demonstrate clean instrumental background, and after samples containing high levels of target compounds (e.g., calibration, CCV) to monitor carryover from the previous injection. The instrument blank consists of clean reagent fortified with the EIS and NIS for quantitation purposes.

8.2.7 Bile Salts Check Standard containing Taurodeoxycholic Acid (TDCA) –TDCA is used to evaluate the chromatographic program relative to the risk of an interference from bile salts in samples. A solution is prepared at a concentration of 10 ng/mL in the same solvent as the calibration standards and is analyzed at the beginning of each analytical sequence**.** Using Cayman Chemical item# 15935 (or equivalent), create a stock standard and then an intermediate standard with a concentration of 1 µg/mL. Use the intermediate standard to prepare the Bile Salts Check Standard according to the table below.

Component	Aliquot for Bile Salts Check STD (µL)
Intermediate TDCA Standard	100
EIS STD	100
NIS STD	100
Water	400
Acetic Acid	62.5
Methanol[1]	9237.5
Final Volume	10000

[1] *Methanolic Ammonium Hydroxide (1%)*

9.0 PROCEDURE

9.1 Equipment Preparation

9.1.1 Support Equipment – Refer to lab-specific SOP(s) for additional information on calibration and verification requirements for support equipment that may be used in this procedure.

9.1.2 Instrument – All maintenance activities are listed in daily maintenance logs that are assigned to each instrument.

Mass Calibration – The mass spectrometer must undergo mass calibration to ensure accurate assignments by the instrument. This mass calibration must be performed at least annually to maintain instrument sensitivity and stability. Mass calibration must be repeated on an as-needed basis (e.g., QC failures, ion masses fall outside of the instrument required mass window, major instrument maintenance, or if the instrument is moved). Mass calibration must be performed using the calibration compounds and procedures prescribed by the manufacturer. The procedures used for mass calibration and mass calibration verification must evaluate an ion range that encompasses the ion range (Q1 and Q2 m/z) of the analytes of interest of this method.

Mass Calibration Verification – A mass calibration verification must be performed following mass calibration, prior to standard and sample analyses. Mass verification checks must also be performed after any subsequent mass calibrations. The laboratory must follow the instructions for the individual instrument software to confirm the mass calibration, mass resolution and peak relative response. Mass calibration verification must be performed using standards whose mass range brackets the masses of interest (quantitative and qualitative ions). Check the instrument mass resolution to ensure that it is at least unit resolution. Unit resolution is demonstrated when the value of the peak width at half-height is within 0.5 ± 0.1 amu or Da.

Multiple Reaction Monitoring (MRM) is required to achieve better sensitivity with the mass spectrometer than full-scan analysis. The ions to be monitored (quantitation and confirmation transitions, also referred to as precursor and product ions) for each native compound, EIS, and NIS are given in Table 2.

The chromatographic conditions should be optimized for compound separation and sensitivity. The same optimized operating conditions must be used for the analysis of all standards, blanks, IDOCs, MDL and LCS standards, and samples. Different instruments may require slightly different operating conditions. Modification of the solvent composition of the standard or extract by increasing the aqueous content to prevent poor peak shape is not permitted. The peak shape of early eluting compounds may be improved by increasing the volume of the injection loop or increasing the aqueous content of the initial mobile phase composition.

Retention Time (RT) calibration – After RT windows have been empirically confirmed for each analyte, once per ICAL and at the beginning of the analytical sequence, the position of each method target analyte, EIS analyte, and NIS analyte peak shall be set using the midpoint standard of the ICAL curve when ICAL is performed. When ICAL is not performed, the initial CCV retention times or the midpoint standard of the ICAL curve can be used to establish the RT window position.

Native target analyte, EIS analyte, and NIS analyte RTs must fall within 0.4 minutes (24 sec) of the predicted retention times from the midpoint standard of the ICAL or initial daily CCV, whichever was used to establish the RT window position for the analytical batch. All branched isomer peaks identified in either the calibration standard or the qualitative standard must fall within in the retention time window for that analyte.

For all target analytes with exact corresponding isotopically labeled analogs, target analyte peaks must elute within ±0.1 minutes (±6 sec) of the associated EIS.

When establishing the chromatographic conditions, it is important to consider the potential interference of bile salts during analyses of samples. Inject the Bile Salt Check standard (Sections 8.2.7, 9.2.3) during the retention time calibration process and adjust the conditions to ensure that TDCA does not coelute with any of the target analytes, EIS, or NIS standards. Analytical conditions must be set to allow a separation of at least 1 minute between TDCA and PFOS.

9.2 Initial Calibration

9.2.1 Calibration Design

Prior to the analysis of samples, and after the mass calibration check has met all criteria in Section 9.1.2, each LC-MS/MS system must be calibrated at a minimum of 6 standard concentrations (Section 8.2.4 and Table 3). This method procedure calibrates and quantifies 40 PFAS target analytes, using the isotopically labeled compounds added to the sample prior to extraction, by one of two approaches:

- Isotope Dilution quantification (ID), whereby the response of the target compound is compared to the response of its isotopically labeled analog; twenty-four target compounds are quantified in this way.
- Extracted Internal Standard quantification (EIS), whereby the response of the target compound is compared to the response of the isotopically labeled analog of another compound with chemical and retention time similarities; sixteen target compounds are quantified in this way.

Initial calibration is performed using a series of at least six solutions, with the concentrations of at least five of the six calibration standards being within the quantification range. If a second-order calibration model is used, one additional concentration is required. The initial calibration solutions contain the entire suite of EIS, NIS, and target compounds. Calibration is verified at least once every ten field samples with a calibration verification (CV/CCV) standard, performed by analysis of a mid-level calibration solution. Calibration verification uses the mean RRs or RFs determined from the initial calibration to calculate the analyte concentrations in the verification standard.

Note: Six is the minimum number of calibration standards that must be used in the initial calibration; however, the laboratory may use more standards, as long as the criteria in Section 9.2.3 can be met.

Each LC-MS/MS system must be calibrated whenever the laboratory takes corrective action that might change or affect the initial calibration criteria, or if either the CCV or ISC acceptance criteria have not been met.

9.2.2 Calibration Sequence

Calibration standards must be analyzed in sequence from lowest to highest concentration to minimize the chance that carryover from a higher concentration standard will boost the area of a lower concentration standard. A typical sequence for days when calibration is required is shown below.

Description[1]	Comment
ICAL L1	
ICAL L2	
ICAL L3	
ICAL L4	
ICAL L5	
ICAL L6	
ICAL L7	
ICAL L8	
ICAL L9	
ICAL L10	
IBLK	Must be <1/2 LOQ
ICV	%R must be 70 – 130%
ISOMER CHECK	
BILE SALTS CHECK	TDCA must be resolved by ≥1 min from PFOS
CCV (ISC)	%R must be 70-130%; begins and ends Analytical Sequence

[1]*See Table 3 for calibration concentrations.*

9.2.3 ICAL Evaluation

If the criteria for initial calibration are not met, inspect the system for problems and take corrective actions to achieve the criteria. This may require the preparation and analysis of fresh calibration standards. All initial calibration criteria must be met before any samples or required blanks are analyzed.

Instrument Sensitivity – Sufficient instrument sensitivity is established if a signal-to-noise ratio ≥ 3:1 can be achieved when analyzing the lowest concentration standard within the quantitation range that the laboratory includes in its assessment of calibration linearity (see Table 3).

Curve Fit – One of the following two approaches must be used to evaluate the linearity of the instrument calibration. Weighting (typically 1/x or $1/x^2$) is allowed for linear and non-linear regressions.

Option 1: Calculate the relative standard deviation (RSD) of the RR or RF values of the initial calibration standards for each native compound and isotopically labeled compound. The RSD must be ≤ 20% to establish instrument linearity.

Option 2: Calculate the relative standard error (RSE) of the initial calibration standards for each native compound and isotopically labeled compound. The RSE for all method analytes must be ≤ 20% to establish instrument linearity.

If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action is taken to reanalyze the ICAL standards, restrict the range of calibration, or select an alternate method of calibration.

If more than the minimum number of standards are analyzed and levels are excluded from the calibration, only the lowest or highest standards may be excluded, except as noted

here. The removal of calibration levels from the interior of the curve is allowed only when there is sound technical reason for doing so and when the level is removed for all analytes; for example, when it can be proven that the wrong standard was analyzed for the calibration level or there is obvious evidence that the instrument malfunctioned during injection of the standard. The removal of any calibration level from the interior of the curve must be approved by the department supervisor/manager. Management approval and the rationale for the level removal must be documented and kept with the technical record.

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

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

Qualitative Isomer Check – Calibration standards for PFOS, PFHxS, NMeFOSAA and NEtFOSAA contain both branched and linear isomers. For target compounds which have multiple chromatographic peaks due to branched and linear isomers, but for which quantitative standards are not available, a qualitative isomer check is analyzed with each calibration event and at the beginning of each analysis sequence to demonstrate the peak shape and retention time of the branched isomers. See Section 10.1 for integration information.

Bile Salts Check – The laboratory must analyze a Bile Salts Check standard (Section 8.2.7) after the initial calibration, and prior to the analysis of samples, to check for interferences caused by bile salts. If an interference is present, the chromatographic conditions must be modified to eliminate the interference from TDCA (e.g., changing the retention time of TDCA such that it is resolved from PFOS by at least one minute), and the initial calibration repeated.

9.2.4 Continuing Calibration Verification (CCV or CV) – After a passing MS resolution and a successful initial calibration is achieved and prior to the analysis of any samples, the calibration is verified by injecting an aliquot of the appropriate concentration ICAL standard, analyzed with the same conditions used during the ICAL. CCV is performed at the beginning of each analytical sequence, after every ten samples, and at the end of the analytical sequence. In this context, a “sample” is defined as a field sample. MBs, CCVs, LCSs, MSs, FDs, TBs and MSDs are not counted as samples. All CCV analyses are

performed using the mid-level ICAL standard, except for the daily Instrument Sensitivity Check, as noted below.

Calculate concentration for each native and EIS compound in the CCV using the equation in Section 10.3. The recovery of native and EIS compounds for the CCVs must be within 70 – 130%. If the CCV criteria are not met, recalibrate the LC-MS/MS according to Section 9.2. Alternately, the analyst may immediately analyze two CCVs for confirmation. If both confirmation CCV analyses meet the recovery criteria, analysis may proceed; however, the analyst must rerun any samples that were analyzed after the failing CCV and before the 2 passing CCVs. If either of the 2 confirmation CCV analyses fails to meet the acceptance criteria, recalibrate the LC-MS/MS according to Section 9.2.

If an individual target compound recovery in a CCV is above the upper control limit and all associated samples are ND for that compound, the data for those samples may be reported. In such cases, a narrative statement must be included in the report indicating the specific compound result that was biased high in the CCV, and that samples were ND for that compound and thus reportable.

Instrument Sensitivity Check (ISC) – An ISC at the concentration of the lowest calibration standard within the quantitation range is required to be analyzed at the beginning of the analytical run (Section 9.4). The signal-to-noise ratio (Section 10.1.1) of the ISC must be greater than or equal to 3:1. Recovery of the native and EIS compounds for the ISC must be within 70-130%. If the requirements cannot be met, the problem must be corrected before analyses can proceed.

9.3 Sample Preparation

This section describes the sample preparation procedures for aqueous samples with <100 mg/L Suspended Solids (Section 9.3.3), solid samples (soil, sediment or biosolid; Section 9.3.4) and tissue samples (Section 9.3.5). For solid samples and aqueous samples that contain particles, percent solids are determined using the procedures in Section 9.3.2. This section also describes the solid phase extraction (SPE, Section 9.3.6) and extract cleanup protocols for all matrices (Sections 9.3.7 – 9.3.9).

Note: The laboratory may choose to pre-screen some samples prior to performing the analysis, following the protocol described in Appendix C. For aqueous samples, use the secondary container provided for suspended solids to perform the pre-screening. If high levels of PFAS are present in the sample, a lower volume is required for analysis.

Do not use any fluoropolymer articles or task wipes in these extraction procedures. Use only HDPE or polypropylene wash bottles and centrifuge tubes. Reagents and solvents for cleaning syringes may be kept in glass containers.

9.3.1 Subsampling – The laboratory may subsample the aqueous samples as described in Appendix D; however, subsampling must meet project-specific requirements. The laboratory must notify the client that subsampling has occurred. Subsampling is acceptable for samples which exceed the 100 mg/L SS method application limit, samples which require greater than a 10X dilution for over-range detections or are known/expected to be highly contaminated, and samples which fail the acceptance criteria for EIS compounds (see Section 9.4.2). Any time subsampling is required, no less than 2% of the typical extracted volume (or mass) may be subsampled. In cases where less than 2% of an aqueous sample

is required for subsample (i.e., less than 10 mL, or less than 2 mL for leachates), serial dilution must be employed.

9.3.2 Determination of Percent Solids

Percent solids analysis must be performed on all aqueous, solid, and multi-phase samples prior to preparation and analysis.

Suspended Solids (SS) in aqueous liquids and multi-phase samples consisting of mainly an aqueous phase – All aqueous samples will be logged in for both DM1633 and TSS analysis. The TSS analysis will follow the Method SM2540D protocol, with the analyst filtering ≥50 mL of aqueous sample, and the LOQ being adjusted accordingly. This should provide an LOQ of ≤100 mg/L. Any aqueous sample returning a SS content of >100 mg/L shall be diluted following the prescriptions in Section 9.4.2. Samples containing 100-499 mg/L SS will be subsampled and prepared at a 5X dilution; samples containing 500-999 mg/L SS will be subsampled and prepared at a 10X dilution; samples containing 1000-1999 mg/L will be subsampled and prepared at a 20X dilution.

Percent Solids in solid samples (excluding tissues) – All solid samples will be logged in for both DM1633 and percent solids analysis. The percent solids analysis will follow the Method SM2540G protocol.

9.3.3 Aqueous Sample Processing

This method is applicable to aqueous samples containing up to 100 mg/L SS per sample. Therefore, aqueous sample preparation cannot begin until the TSS analysis is completed on each sample. The procedure requires the preparation of the entire sample. Smaller sample volumes may be analyzed for samples containing SS greater than specified for this method, or when unavoidable due to high level of PFAS. Typical sample size is 500 mL; however, sample size may vary, depending on project requirements, applicable regulations, and sample characteristics. The sample is to be analyzed in its entirety and should not be filtered. Leachate samples are analyzed using a 100 mL sample volume. Therefore, they must not be included in the same sample preparation batch as aqueous samples analyzed using 500 mL sample volumes.

Homogenize the sample by inverting the sample 3 – 4 times. Do not filter the sample. The standard procedure is to analyze the entire sample, plus a basic methanol rinse of the container.

The volume of the aqueous sample analyzed is determined by weighing the full sample bottle and then the empty sample bottle. Weigh each sample bottle (with the lid) to the nearest 0.1 g.

Prepare a method blank and two LCSs using PFAS-free water in HDPE bottles. Select a volume of water that is typical of the samples in the batch. Spike one LCS sample with native standard solution at 2x the LOQ. This aliquot (LLLCS) will serve to verify the LOQ. Spike the other LCS sample at a concentration near the mid-level calibration point. This aliquot will serve as the traditional LCS.

Note: If matrix spikes are required for a specific project, spike the field sample bottles designated for use as MS/MSD samples with native standard solution (Section 8.2.3) at a concentration equivalent to the mid-level calibration point.

Spike an aliquot of EIS solution (Section 8.2.1) directly into the sample in the original bottle (or subsampled bottle) as well as to the bottles prepared for the QC samples. Mix by swirling or inverting the sample container.

Check that the pH is 6.5 ± 0.5. If necessary, adjust pH with 50% formic acid (Section 8.1) or ammonium hydroxide (or with 5% formic acid [Section 8.1] and 3% aqueous ammonium hydroxide [Section 8.1]). The sample is now ready for solid-phase extraction (SPE) and cleanup (Sections 9.3.6 and 9.3.7).

9.3.4 Solid Sample (excluding tissues) Processing

Mix the sample in its original jar. If it is impractical to mix the sample within its container transfer the sample to a larger container. Mix the sample thoroughly, stirring from the bottom to the top and in a circular motion along the sides of the jar, breaking particles up by pressing against the side of the container. The homogenized sample should be even in color and have no separate layers. Store the homogenized material in its original container or in multiple smaller containers. Determine the percent solids as per Section 9.3.2.

Note: The target sample weight for sediment or soil is 5 g dry weight. The target sample weight for biosolids is 0.5 g dry weight. Small amounts of reagent free water used for method blanks (10% of sample weight or less) can be added to unusually dry samples. This is an option, not a requirement.

Check the LIMS system for the percent solids data associated with the samples to be prepared. Using the percent solids data and the calculation below, weigh out an aliquot of each solid sample, not dried, into a 50 mL polypropylene centrifuge tube. Sample mass should be within ±0.2 g of target mass for soil and sediment samples, and within ±0.02 g of target mass for biosolids samples. Sample aliquot should provide 5 g dry weight (Wi_{Dry} below) for soil and sediment or 0.5 g dry weight for biosolids. Because biosolid samples are analyzed with a 0.5 g sample mass, they must not be included in the same sample preparation batch as solid samples analyzed with 5 g sample masses.

$$Solid\ Sample\ Target\ Mass\ (g) = \frac{Wi_{Dry}\ (g)}{\%\ solids\ (decimal)}$$

Prepare batch QC samples using 5 g of reference solid (Section 7.2) wetted with 2.5 g of reagent water for the method blank and two LCSs (use 0.5 g of reference solid with 0.25 g of reagent water for biosolid extraction batches). The addition of reagent water to the sand provides a matrix closer in composition to real-world samples. Spike one LCS sample with native standard solution at 2x the LOQ. This aliquot (LLLCS) will serve to verify the LOQ. Spike the other LCS sample at a concentration near the mid-level calibration point. This aliquot will serve as the traditional LCS.

Note: If matrix spikes are required for a specific project, spike the field sample bottles designated for use as MS/MSD samples with native standard solution (Section 8.2.3) at a concentration equivalent to the mid-level calibration point.

Spike an aliquot of EIS solution (Section 8.2.1) directly into each centrifuge tube containing the aliquoted field and QC samples. Vortex or shake the sample to disperse the standard and allow to equilibrate for approximately 30 minutes.

Add 10 mL of 0.3% methanolic ammonium hydroxide (Section 8.1) to each centrifuge tube. Vortex to disperse, then shake for 30 minutes on a variable speed mixing table. Centrifuge

at 2800 rpm for 10 minutes and transfer the supernatant to a clean 50 mL polypropylene centrifuge tube.

Add 15 mL of 0.3% methanolic ammonium hydroxide (Section 8.1) to the remaining solid sample in each centrifuge tube. Vortex to disperse, then shake for 30 minutes on a variable speed mixing table. Centrifuge at 2800 rpm for 10 minutes and decant the supernatant from the second extraction into the centrifuge tube with the supernatant from the first extraction.

Add another 5 mL of 0.3% methanolic ammonium hydroxide (Section 8.1) to the remaining sample in each centrifuge tube. Shake by hand to disperse, centrifuge at 2800 rpm for 10 minutes and decant the supernatant from the third extraction into the centrifuge tube with supernatant from the first and second extractions.

Using a 10 mg scoop, add 10 mg of carbon (Section 8.1) to the combined extract, mix by occasional hand shaking for no more than five minutes and then centrifuge at 2800 rpm for 10 minutes. Immediately decant the extract into a 60 mL glass or plastic evaporation or concentrator tube.

Dilute to approximately 35 mL with reagent water. A separate concentrator tube marked at the 35 mL level may be kept for a visual reference to get the approximate volume, but a close accounting of all water present in the sample should be maintained by the analyst regardless. Samples containing more than 50% water may yield extracts that are greater than 35 mL in volume; therefore, do not add water to these. Adding water to the sample extract is recommended for dry solid samples. Determine the water content in the sample as follows (percent moisture is determined from the % solids):

$$Water\ Content\ in\ Sample = \frac{Sample\ Weight\ (g)\ x\ Moisture\ (\%)}{100} + water\ added\ earlier$$

Or, if the Target Solid Sample Mass equation was used and the target sample mass was aliquoted for extraction as calculated, determine the water content in the sample as follows (use 0.5 instead of 5 for biosolid samples):

$$Water\ Content\ in\ Sample\ (g)\ =\ Recorded\ Solid\ Sample\ Mass\ (g) - 5$$

Concentrate each extract at approximately 55 ºC with a N2 flow of approximately 1.2 L/min to a final volume that is based on the water content of the sample (see table below). Allow extracts to concentrate for 25 minutes, then mix (by vortex if the volume is < 20 mL or using a glass pipette if the volume is > 20 mL). Continue concentrating and mixing every 10 minutes until the extract has been reduced to the required volume as specified in the table below. If the extract volume appears to stop dropping, the concentration must be stopped and the volume at which it was stopped recorded. The concentrated extract must still contain some methanol, about 5-10 mL. The pre-cleanup extract in 11.3.10 should contain no more than 20% methanol. The laboratory has flexibility to modify the volumes used to achieve this goal. Some laboratories may prefer not to add water in Section 11.3.8. The following table provides guidance to help determine the final extract volume, based on the water content of the original solid sample. A good rule of thumb is to make the "Concentrated Final Volume" 7-10 mL above the "Water Content in Sample" value.

Water Content in Sample[1]	Concentrated Final Volume
< 5 g	12 mL

5 – 8 g	12-15 mL
8 – 9 g	15-18 mL
9 – 10 g	16-19 mL

[1]*Determined from the % solids results determined in Section 9.3.2, and includes any water added to the sample or extract in the steps above.*

Note: Slowly concentrating extracts, in 1 mL increments, is necessary to prevent excessive concentration and the loss of neutral compounds (methyl and ethyl FOSEs and FOSAs) and other highly volatile compounds. The extract must be concentrated to remove the methanol as excess methanol during SPE clean-up results in poor recovery of C13 and C14 carboxylic acids and C10 and C12 sulfonates. If all the methanol is evaporated, the neutral compounds are likely to have poor recovery; if too much methanol is in the final concentrated extract, then the longer-chain compounds are likely to have poor recovery.

Add 40 - 50 mL of reagent water to the extract and vortex. Check that the pH is 6.5 ± 0.5. If necessary, adjust pH with 50% formic acid (Section 8.1) or ammonium hydroxide (or with 5% formic acid [Section 8.1] and 3% aqueous ammonium hydroxide [Section 8.1]). The extract is now ready for solid-phase extraction (SPE) and cleanup (Sections 9.3.6 and 9.3.8).

9.3.5 Tissue Sample Processing

Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish with the skin on, whole fish with the skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the samples must be prepared and homogenized.

Pace utilizes the Green Bay location for tissue homogenization, following ENV-SOP-GBAY-0129 (Sample Homogenization, Compositing, and Subsampling; specifically, Section 9.4).

For each sample, weigh a 2 g aliquot of homogenized tissue into a 15 mL polypropylene centrifuge tube. Reseal the container with the remaining homogenized portion of the sample and return it to frozen storage in case it needs to be used for reanalysis.

Note: The default sample weight for tissue is 2 g wet weight; however, a 1 g sample may be used. Higher sample weights are not recommended for this method.

Prepare the batch QC samples using 2 g of reference tissue matrix (Section 7.2) for the method blank and two LCSs. Spike one LCS sample with native standard solutions at 2x the LOQ. This aliquot (LLLCS) will serve to verify the LOQ. Spike the other LCS sample at a concentration near the mid-level calibration point. This aliquot will serve as the traditional LCS.

Note: If matrix spikes are required for a specific project, spike the field sample bottles designated for use as MS/MSD samples with native standard solution (Section 8.2.3) at a concentration equivalent to the mid-level calibration point.

Spike an aliquot of EIS solution (Section 8.2.1) directly into each field and QC sample.

Vortex and allow to equilibrate for approximately 30 minutes.

Add 10 mL of 0.05M KOH in methanol (Section 8.1) to each sample. Vortex to disperse the tissue then place tubes on a variable speed mixing table to shake for at least 16 hours. Centrifuge at 2800 rpm for 10 minutes and collect the supernatant in a 50-mL polypropylene centrifuge tube.

Add 10 mL of acetonitrile to remaining tissue in the 15 mL centrifuge tube, vortex to mix and disperse the tissue. Sonicate for 30 minutes. Centrifuge at 2800 rpm for 10 minutes and collect the supernatant, adding it to the 50 mL centrifuge tube containing the initial extract.

Add 5 mL of 0.05M KOH in methanol to the remaining sample in each centrifuge tube. Vortex to disperse the tissue and hand mix briefly. Centrifuge at 2800 rpm for 10 minutes and collect the supernatant, adding it to the 50-mL centrifuge tube containing the first two extracts.

Using a 10 mg scoop, add 10 mg of carbon (Section 8.1) to the combined extract, mix by occasional hand shaking over a period of no more than five minutes and then centrifuge at 2800 rpm for 10 minutes. Immediately decant the extract into a 60 mL glass evaporation or concentrator tube.

Add 1 mL of reagent water to each evaporation/concentrator tube, set the evaporator/concentrator to 55 ºC with a N_2 flow of 1.2 L/min and concentrate the extract to 2.5 mL (only ~1 mL of the methanol should remain).

Add reagent water to each evaporation/concentrator tube to dilute the extracts to 50 mL.

Check that the pH is 6.5 ± 0.5. If necessary, adjust pH with 50% formic acid or ammonium hydroxide (or with 5% formic acid and 3% aqueous ammonium hydroxide). The extract is now ready for solid-phase extraction (SPE) and cleanup (Sections 9.3.6 and 9.3.9).

9.3.6 Solid Phase Extraction

All matrices (including batch QC) must undergo SPE and carbon cleanup to remove interferences (Section 9.3.7). The SPE cartridge conditioning and sample loading process described below is for use with all matrices; SPE cartridge elution and any additional extract treatment is matrix specific and may be found in Sections 9.3.7 through 9.3.9.

Note: Carbon cleanup is required. Carbon cleanup may remove analytes if the sample has a very low organic carbon content (this is unusual for non-drinking water environmental samples). This will be apparent if the isotope dilution standard recoveries are significantly higher on the reanalysis. If the laboratory can demonstrate that the carbon cleanup is detrimental to the sample analysis (by comparing results when skipping the carbon cleanup during reanalysis), then the carbon cleanup may be skipped for that specific sample. Carbon cleanup is performed prior to the SPE process for solid and tissue samples.

Pack clean salinized glass wool to half the height of the WAX SPE cartridge barrel (Section 7.1).

Set up the vacuum manifold with one WAX SPE cartridge plus a reservoir and reservoir adaptor for each cartridge for each sample and QC aliquot.

Pre-condition the cartridges by washing them with 15 mL of 1% methanolic ammonium hydroxide (Section 8.1) followed by 5 mL of 0.3M formic acid (Section 8.1). Do not allow the WAX SPE to go dry. Discard the wash solvents.

Pour the sample into the reservoir (do not use a pipette), taking care to avoid splashing while loading. Adjust the vacuum and pass the sample through the cartridge at 10-15 mL/min. Retain the empty sample bottle for later rinsing (Section 9.3.7). Discard eluate.

Note: For aqueous samples, in the event the SPE cartridge clogs during sample loading, first attempt to rinse and dry the clogged cartridge, following protocol in the following paragraph. The cartridge is then ready for elution. Place a second cartridge in the appropriate manifold location and pre-condition as above. Continue loading the remaining sample aliquot on the second cartridge, using the same reservoir. Proceed to next step.

Rinse the walls of the reservoir with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1M formic acid/methanol (Section 8.1) and pass those rinses through the cartridge using vacuum. Dry the cartridge by pulling air through. Discard the rinse solution. Continue to the elution and concentration steps based on the matrix.

9.3.7 Elution, Cleanup, and Filtration of Aqueous Sample Extracts

Note: If two cartridges were used, each cartridge must separately be submitted to the elution steps described below. Elute both cartridges into the same collection tube, using 5 mL of elution solvent for each. One of the elution aliquots must be used to perform the sample bottle rinse prior to eluting the cartridge. Using a gentle stream of Nitrogen and 55 ºC water bath to concentrate the ~10 mL of combined eluate to ~5 mL, then follow the carbon cleanup and filtration steps below. This concentration step is only applicable to situations where two SPE cartridges were eluted, each with 5 mL of elution solvent.

Place clean collection tubes inside the manifold, ensuring that the extract delivery needles do not touch the walls of the tubes. Resume vacuum and ensure a proper seal is achieved. DO NOT add NIS to these collection tubes.

Add 5 mL of 1% methanolic ammonium hydroxide (Section 8.1) to the sample bottle. Cap the bottle and rotate to ensure all internal surfaces of each bottle are rinsed; avoid vigorous shaking when rinsing the 500 mL aqueous sample bottles with only 5 mL of methanol – any evaporation/vaporization will contribute to loss of extract here. After rinsing the inside of the sample bottle, use a plastic transfer pipette to transfer the rinse to the SPE reservoir, using it to wash the walls of the reservoir. Allow the elution solvent to soak the SPE sorbent for 2 minutes, then use vacuum to pull the elution solvent through the cartridge and into the collection tubes in a slow, dropwise manner.

Note: Air dry the empty sample bottle after the rinse is transferred. Weigh the empty bottle with the cap on and subtract that from the weight of the bottle with sample, determined in Section 9.3.3.

Add 25 µL of concentrated acetic acid to each sample eluted in the collection tubes and vortex to mix. Add 10 mg of carbon (Section 8.1) to each sample and batch QC extract, using a 10 mg scoop. Hand shake occasionally for no more than 5 minutes. It is important to minimize the time the sample extract is in contact with the carbon. Immediately vortex (30 seconds) and centrifuge at 2800 rpm for 10 minutes.

Remove the plunger from a 5 mL polypropylene syringe and place a syringe filter (25 mm filter, 0.2 µm nylon membrane) onto the syringe; repeat to prepare one syringe for each

sample in the prep batch. Add NIS solution (Section 8.2.2) to a clean collection tube for each sample prepared. Carefully decant the sample supernatant into the syringe barrel. Replace the plunger and filter the entire extract into the new collection tube containing the NIS. Repeat for all samples in the prep batch. Vortex to mix and transfer a portion of each extract into an autosampler vial for LC-MS/MS analysis. Cap the collection tubes containing the remaining extracts and store at 0 - 6 °C.

Note: Avoid attaching the filter to the syringe before removing the plunger from the syringe barrel, as the syringe disk filters can be compromised by the sudden vacuum created when the plunger is removed.

9.3.8 Elution and Filtration of Solid Sample Extracts

Place a clean collection tube in the manifold rack for each sample and QC aliquot, ensuring the extract delivery needles are not touching the walls of the tubes. Resume vacuum and ensure a proper seal is achieved.

Rinse the inside of the evaporation/concentrator tube using 5 mL of 1% methanolic ammonium hydroxide (Section 8.1). Then, using a plastic transfer pipette, transfer the rinse to the SPE reservoir, washing the walls of the reservoir. Allow the elution solvent to soak the SPE sorbent for 2 minutes, then use vacuum to pull the elution solvent through the cartridge and into the collection tubes in a slow, dropwise manner.

Add 25 µL of concentrated acetic acid to each sample extract in its collection tube and swirl to mix. Remove the plunger from a 5-mL polypropylene syringe and place a syringe filter (25 mm filter, 0.2 µm nylon membrane) onto the syringe; repeat to prepare one syringe for each sample in the prep batch. Add NIS solution (Section 8.2.2) to a clean collection tube for each sample prepared. Carefully decant the sample supernatant into the syringe barrel. Replace the plunger and filter the entire extract into the new collection tube containing the NIS. Repeat for all samples in the prep batch. Vortex to mix and transfer a portion of each extract into an autosampler vial for LC-MS/MS analysis. Cap the collection tubes containing the remaining extracts and store at 0 - 6 °C.

Note: Avoid attaching the filter to the syringe before removing the plunger from the syringe barrel, as the syringe disk filters can be compromised by the sudden vacuum created when the plunger is removed.

9.3.9 Elution and Filtration of Tissue Sample Extracts

Place a clean collection tube in the manifold rack for each sample and QC aliquot, ensuring the extract delivery needles are not touching the walls of the tubes. Resume vacuum and ensure a proper seal is achieved.

Rinse the inside of the evaporation/concentrator tube using 5 mL of 1% methanolic ammonium hydroxide (Section 8.1). Then, using a plastic transfer pipette, transfer the rinse to the SPE reservoir, washing the walls of the reservoir. Allow the elution solvent to soak the SPE sorbent for 2 minutes, then use vacuum to pull the elution solvent through the cartridge and into the collection tubes in a slow, dropwise manner.

Add 25 µL of concentrated acetic acid to each sample extract in its collection tube and swirl to mix. Remove the plunger from a 5 mL polypropylene syringe and place a syringe filter (25 mm filter, 0.2 µm nylon membrane) onto the syringe; repeat to prepare one syringe for each sample in the prep batch. Add NIS solution (Section 8.2.2) to a clean collection tube

for each sample prepared. Carefully decant the sample supernatant into the syringe barrel. Replace the plunger and filter the entire extract into the new collection tube containing the NIS. Repeat for all samples in the prep batch. Vortex to mix and transfer a portion of each extract into an autosampler vial for LC-MS/MS analysis. Cap the collection tubes containing the remaining extracts and store at 0 - 6 °C.

Note: Avoid attaching the filter to the syringe before removing the plunger from the syringe barrel, as the syringe disk filters can be compromised by the sudden vacuum created when the plunger is removed.

9.4 Analysis

Analysis of sample extracts for PFAS by LC-MS/MS is performed running manufacturer's data acquisition software. The mass spectrometer is run with unit mass resolution in the multiple reaction monitoring (MRM) mode.

Perform mass calibration, establish the operating conditions (Section 9.1.2), and perform an initial calibration (Section 9.2) prior to analyzing samples.

Only after all performance criteria are met may blanks, MDLs, IPRs/LCSs, and samples be analyzed.

9.4.1 Example Analytical Sequence

After a successful initial calibration has been completed, an example analytical sequence for a batch of samples analyzed during the same analysis period is as follows. The volume injected for samples and QCs must be identical to the volume used for calibration (Section 9.2). Standards and sample extracts must be brought to room temperature and vortexed prior to aliquoting into an instrument vial to ensure homogeneity of the extract.

- Instrument Blank
- Instrument Sensitivity Check
- Calibration Verification Standard (CCV)
- Isomer Check Standard
- Bile Salts Check Standard
- Instrument Blank
- Method Blank
- Low-level LCS (LLLCS)
- LCS
- Samples (10 or fewer)
- CCV
- Instrument Blank
- Samples (10 or fewer)
- CCV
- Instrument Blank

If the results are acceptable, the closing calibration verification solution may be used as the opening solution for the next analytical sequence.

If the response exceeds the calibration range for any sample, extracts are diluted as per Section 9.4.2 to bring all target responses within the calibration range.

Note: If the analytes that exceed the calibration range in the original analysis are known to not be of concern for the specific project (e.g., are not listed in a discharge permit), then the laboratory may consult with the client regarding the possibility of reporting that sample from the undiluted analysis.

9.4.2 Sample Dilutions

If the measured concentration for any compound exceeds the calibration range of the system, dilute a subsample of the sample extract with the methanolic ammonium hydroxide and acetic acid solution in Section 8.1 by a factor no greater than 10x and analyze the diluted extract. If the responses for each applicable EIS in the diluted extract meet the S/N and retention time requirements in Sections 10.1.1 and 10.1.2, and the EIS recoveries from the analysis of the diluted extract are greater than 5% (uncorrected for the dilution), then the compounds associated with those EISs may be quantified using isotope dilution. Use the EIS recoveries from the original analysis to select the dilution factor, with the objective of keeping the un-adjusted EIS recoveries in the dilution above that 5% lower limit (i.e., if the EIS recovery of the affected analyte in the undiluted analysis is 50%, then the sample should not be diluted more than 10:1). To account for the dilution, adjust the EIS and NIS recoveries as well as reported compound concentrations, detection limits, and LOQs.

If the EIS responses in the diluted extract do not meet the S/N and retention time requirements listed in Sections 10.1.1 and 10.1.2, then the compound cannot be measured reliably by isotope dilution in the diluted extract. In such cases, the lab must subsample a smaller aliquot of any affected aqueous sample and dilute it to 500 mL with reagent water or prepare a smaller aliquot of soil, biosolid, sediment, or tissue sample. The reduced sample volume (or mass) chosen for the re-extraction should match the dilution applied to the original extract (i.e., if the original aqueous sample extract was analyzed at a 10X dilution, 50 mL should be subsampled for the re-extraction). To account for the dilution, adjust the reported compound concentrations, detection limits, and LOQs.

If the recovery of any isotopically labeled compound is outside of the acceptance limits (Appendix B) in the original, undiluted analysis, a diluted aqueous sample or smaller aliquot (for solids and tissue) must be analyzed.

10.0 Data Analysis And Calculations

10.1 Qualitative Identification

A native or EIS/NIS compound is positively identified in a standard, blank, sample, or QC sample when all criteria in Sections 10.1.1 through 10.1.3 are met.

10.1.1 Signal-to-noise Ratio (S/N) – Peak responses must be at least three times the background noise level (S/N 3:1). If the S/N ratio is not met due to high background noise, the laboratory must correct the issue (e.g., perform instrument troubleshooting to check and if needed, replace, the transfer line, column, detector, liner, filament, etc.). If the S/N ratio is not met but the background is low, then the analyte is to be considered a non-detect.

10.1.2 RT Criteria – Target analyte, EIS analyte, and NIS analyte RTs must fall within ± 0.4 minutes of the predicted retention times from the midpoint standard of the ICAL or initial daily CCV, whichever was used to establish the RT window position for the analytical batch. The retention time window used must be of sufficient width to detect earlier-eluting

branched isomers. For all method analytes with exact corresponding isotopically labeled analogs, method analytes must elute within ± 0.1 minutes of the associated EIS.

10.1.3 Branched Isomer Integration – For concentrations at or above the method LOQ, the total (branched and linear isomer) quantification ion response to the total (branched and linear isomer) confirmation ion response ratio (ion ratio) must fall within ± 50% of the ratio observed in the mid-point initial calibration standard. If project-specific requirements involve reporting sample concentrations below the LOQ, the ion ratio must also fall within ± 50% of the ratio observed in the initial daily CCV**.**

The response of all isomers in the quantitative standards should be used to define ion ratios. In samples, the total response should include the branched isomer peaks that have been identified in either the quantitative or qualitative standard. If standards (either quantitative or qualitative) are not available for purchase, only the linear isomer can be identified and quantitated in samples. The ratio requirement does not apply for PFBA, NMeFOSE, NEtFOSE, PFMPA, and PFMBA because suitable secondary transitions are unavailable (not detectable or inadequate S/N).

10.1.4 Qualification – If the field sample result does not meet all criteria stated in Sections 10.1.1 through 10.1.3, and all sample preparation avenues (e.g., extract cleanup, sample dilution, etc.) have been exhausted, the result may only be reported with a data qualifier alerting the data user that the result could not be confirmed because it did not meet the method-required criteria and therefore should be considered an estimated value. If the criteria listed above are not met for the standards, the laboratory must stop analysis of samples and correct the issue.

10.1.5 Manual Integration

Sample integration is performed automatically by quantitation software and reviewed by the analyst for any incorrect analyte identification or poor integration. Manual changes to automated integration are called manual integrations. Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are performed consistently and are ethically justified, all manual integrations must be performed, reviewed, and recorded in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration.*

10.2 Quantitative Identification

Concentrations of the target analytes are determined with respect to the extracted internal standard (EIS) which is added to the sample prior to extraction. The EIS is quantitated with respect to a NIS, as shown in Table 2, using the response ratios or response factors from the most recent multi-level initial calibration (Section 9.2). Other equations may be used if the laboratory demonstrates that those equations produce the same numerical result as produced by the equations below.

All results for aqueous samples will be reported in ng/L. All results for solid samples will be reported in ng/g, on a dry-weight basis, and the percent solids for each sample will be reported separately. All results for tissue samples will be reported in ng/g, on a wet-weight basis. All QC data will be reported with the sample results.

Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the LOQ (Section

11.3.1) established by the laboratory through calibration of the instrument. EPA considers the terms “reporting limit,” “quantitation limit,” “limit of quantitation,” and “minimum level” to be synonymous.

Results for each analyte found in each field sample or QC standard at or above the LOQ will be reported to 3 significant figures. Results for each analyte found in each field sample or QC standard below the LOQ will be reported as “<LOQ,” where LOQ is the concentration of the analyte at the LOQ, or as required by the regulatory/control authority or permit.

Results for each analyte found in a blank at or above the MDL will be reported to 2 significant figures. Results for each analyte found in a blank below the MDL will be reported as “<MDL,” where MDL is the concentration of the analyte at the MDL, or as required by the regulatory/control authority or permit.

Results for any analyte found in a sample or extract that has been diluted will be reported at the least dilute level for which the measured concentration is within the calibration range (e.g., above the LOQ for the analyte and below the highest calibration standard) and in which isotopically labeled compound recoveries are within their respective QC acceptance criteria. This may require reporting results for some analytes from different analyses.

Recoveries of all associated EIS compounds will be reported for all field samples and QC standards.

10.3 Calculations

See the ENV-SOP-BTRO-0142, *Laboratory Calculations*, for equations for common calculations.

For the native analytes:

$$\boldsymbol{Concentration}\left(\boldsymbol{ng/Lor ng/g}\right) = \frac{\boldsymbol{Area_N M_{EIS}}}{\boldsymbol{Area_{EIS}(\overline{RR}\ or\ \overline{RF})}}\ \boldsymbol{x}\ \frac{\boldsymbol{1}}{\boldsymbol{W_S}}$$

Where:

$Area_N$ = The measured area of the Q1 m/z for the native (unlabeled) PFAS

$Area_{EIS}$ = The measured area at the Q1 m/z for the EIS. See note below.

M_{EIS} = The mass of the EIS added (ng)

$\boldsymbol{\overline{RR}}$ = Average response ratio used to quantify target compounds by the isotope dilution method

$\boldsymbol{\overline{RF}}$ = Average response ratio used to quantify target compounds by the extracted internal standard method

W_S = Sample volume (L) or dry weight (g)

And for the EIS analytes:

$$\boldsymbol{Concentration}\left(\boldsymbol{ng/L\ or\ ng/g}\right) = \frac{\boldsymbol{Area_{EIS} M_{NIS}}}{\boldsymbol{Area_{NIS}\overline{RF}_S}}\ \boldsymbol{x}\ \frac{\boldsymbol{1}}{\boldsymbol{W_S}}$$

Where:

$Area_{EIS}$ = The measured area at the Q1 m/z for the EIS

$Area_{NIS}$ = The measured area of the Q1 m/z for the non-extracted internal standard (NIS)

M_{NIS} = The mass of the added non-extracted internal standard (NIS) compound (ng)

W_S = Sample volume (L) or dry weight (g)

$\overline{RF_S}$ = Average response factor used to quantify the isotopically labeled compound by the non-extracted internal standard method

Results for native compounds are recovery corrected by the method of quantification. Extracted internal standard (EIS) recoveries are determined similarly against the non-extracted internal standard (NIS) and are used as general indicators of overall analytical quality.

11.0 Quality Control and Method Performance

11.1 Quality Control

The following QC samples are prepared and analyzed with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Method Blank (MB)	1 per batch of 20 or fewer samples.
Laboratory Control Sample (LCS) / Ongoing Recovery and Precision Standard (OPR)	1 per batch of 20 or fewer samples.
Low-Level Laboratory Control Sample (LLLCS) / Low-Level Ongoing Recovery and Precision Standard (LLOPR)	1 per batch of 20 or fewer samples.
Matrix Spike (MS)	1 pair per batch of 20 or fewer samples.
Matrix Spike Duplicate (MSD)	
Sample Duplicate	1 per AFFF sample.
Extracted Internal Standard (EIS) Analytes	All CAL standards, batch QC and field samples.
Non-extracted Internal Standards (NIS)	All CAL standards, batch QC and field samples.

The minimum quality control requirements of this method consist of an initial demonstration of laboratory capability, analysis of samples spiked with isotopically labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to a sample matrix other than water (e.g., soils, biosolids, tissue), the appropriate alternative reference matrix (Section 7.2) is substituted for the reagent water matrix in all performance tests.

The laboratory must make an initial demonstration of the ability to generate acceptable precision and recovery with this method. This demonstration is given in Section 11.4.

Analyses of method blanks (MBs) are required on an on-going basis to demonstrate the extent of background contamination in any reagents or equipment used to prepare and analyze field samples. The procedures and criteria for analyses of a MBs are described in Section 11.1.1.

The laboratory must spike all samples with isotopically labeled compounds to monitor method performance. This procedure is described in Section 11.3. When results of these spikes indicate

atypical method performance for samples, the samples are diluted to evaluate whether the performance issue is caused by the sample matrix. Procedures for dilution are given in Section 9.4.2.

The laboratory must, on an ongoing basis, demonstrate that the analytical system is in control through calibration verification and the analysis of ongoing precision and recovery standards (LCS), spiked at low (LLLCS) and mid-level, and blanks. These procedures are given in Sections 11.1.2 and 11.2.1.

11.1.1 Method Blanks (MB) – A method blank is analyzed with each extraction batch to demonstrate freedom from contamination. The matrix for the method blank must be similar to the sample matrix for the batch (e.g., reagent water blank, solids matrix blank, or tissue blank [Section 7.2]).

Analyze the cleaned extract (Sections 9.3.7, 9.3.8, 9.3.9) of the method blank aliquot before the analysis of the LCSs (Section 11.1.2).

If any PFAS is found in the MB 1) at a concentration greater than the LOQ for the analyte, 2) at a concentration greater than one-third the regulatory compliance limit, or 3) at a concentration greater than one-tenth the concentration in a sample in the extraction batch, whichever is greatest, analysis of samples must be halted, and the problem corrected. Other project-specific requirements may apply; therefore, the laboratory may adopt more stringent acceptance limits for the method blank at their discretion. If the contamination is traceable to the extraction batch, samples affected by the blank must be re-extracted and analyzed, provided enough sample volume is available and the samples are still within holding time.

Note: For DoD (B-24) compliance, MBs must not show any analytes detected >½ LOQ, > 1/10th the amount measured in any associated sample, or 1/10th the regulatory limit, whichever is greatest.

If continued re-testing results in repeated blank contamination, the laboratory must document and report the failures (e.g., as qualifiers on results), unless the failures are not required to be reported as determined by the regulatory/control authority.

11.1.2 Laboratory Control Sample (LCS)/Ongoing Precision and Recovery (OPR) – Analyze the extract of the LCS/OPR to ensure the analytical process is under control.

Compute the percent recovery of the native compounds by the appropriate quantification method depending on the compound (Sections 9.2.1, 10.2, 10.3). Compute the percent recovery of each isotopically labeled compound by the non-extracted internal standard quantitation method and the equation below:

$$Recovery\ \% = \frac{Concentration\ Found\ (^{ng}/_{mL})}{Concentration\ Spiked\ (^{ng}/_{mL})}\ x\ 100$$

For the native compounds and isotopically labeled compounds, compare the recovery to the LCS limits. Analyte recoveries must be within in-house limits if project limits are not provided; otherwise, project limits must be met. Preliminary in-house acceptance criteria of 40-150% must be used for LCS analyses until in-house limits are generated in accordance with Section 14.5.4 of EPA Draft Method 1633. The lower in-house acceptance criteria for LCS recovery cannot be <40%.

If all compounds meet the acceptance criteria, system performance is acceptable, and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the given range, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the extraction batch and repeat the ongoing precision and recovery test.

11.1.3 **Matrix Spike (MS) –** Analysis of an MS may be required in each extraction batch. Assessment of method precision can be accomplished by preparation and analysis of a matrix spike duplicate (MSD). See Appendix E for MS/MSD, MS/FD sample selection guidance.

Note: For DoD (B-24) compliance, one MS/MSD pair is required per preparatory batch. For all other regulatory programs, follow project- or client-specific requirements.

Within each extraction batch, a minimum of one pair of sample bottles is spiked as MS/MSD for every 20 samples analyzed. MS/MSD samples are spiked in the same manner as the mid-level LCS.

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

If the recovery for any analyte is outside the acceptance criteria for the matrix spike and the LCS, the laboratory is out of control and corrective action will be taken. Corrective action may include repreparation and reanalysis of the batch. A narrative statement will be added to document the corrective action taken.

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

11.2 Instrument QC

The following Instrument QC checks are performed. Refer to Appendix B for acceptance criteria and required corrective action.

QC Item	Frequency
Mass Calibration	Annually and on as-needed basis
Mass Calibration Verification	After mass calibration
Initial Calibration (ICAL)	Prior to analysis, and on as-needed basis
Initial Calibration Verification (ICV)	Following each ICAL
Instrument Blank (IBLK)	Daily prior to analysis and after high standards
Qualitative Isomer Check	Daily prior to analysis
Bile Salts Check	Daily prior to analysis
Instrument Sensitivity Check (ISC)	Daily prior to analysis
Continuing Calibration Verification (CCV)	At the beginning and every 10 samples
Continuing Calibration Blank (IBLK)	After each CCV

RT Window	After ICAL and at the beginning of analytical sequence

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

11.2.2 Qualitative Isomer Check – A qualitative identification standard (Section 8.2.7) containing all available isomers (branched and linear) is analyzed once daily at the beginning of the analytical sequence, to confirm the retention time of each linear and known branched isomer or isomer group. All required branched isomer peaks must be present and visibly resolved from their corresponding linear peak.

11.3 Method Performance

Routine method performance is validated through analysis of matrix-specific reference samples, including spikes and PTs. Ongoing method performance is monitored through QC samples analyzed alongside samples. The parameters monitored include percent recovery of EIS compounds, blank concentrations, and native compound recoveries.

The specifications contained in this method can be met if the apparatus used is calibrated and maintained properly. The standards used for initial calibration (Section 8.2.4), calibration verification (Sections 9.2.4), and for initial (Section 11.4) and ongoing (Section 11.1.2) precision and recovery may be prepared from the same source; however, the use of a secondary source for calibration verification is highly recommended whenever available. If standards from a different vendor are not available, a different lot number from the same vendor can be considered a secondary source. A LC-MS/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for determination of PFAS by this method.

To assess method performance on the sample matrix, the laboratory must spike all samples with the EIS solution (Section 8.2.1) and all sample extracts with the NIS spiking solution (Section 8.2.2). Analyze each sample according to the procedures in this SOP. Compute the percent recovery of the EIS compound concentration using the NIS quantitation method and the equation in Section 11.1.2. The recovery of each EIS and NIS compound must be assessed and be within the control limits; the lab must maintain records of these assessments. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample. If the recovery cannot be brought within the normal range, water samples are diluted, and smaller amounts of soils, biosolids, sediments, and other matrices are prepared and analyzed, per Section 9.4.2.

NIS areas must be greater than 30% of the average area of the calibration standards in undiluted sample extracts and extracts that required additional NIS to be added. NIS areas corrected for the dilution factor must be greater than 30% of the average area of the calibration standards in diluted samples when additional NIS was not added during dilution of the extract.

EIS Preliminary inhouse acceptance criteria of 20-150% must be used until inhouse limits are generated as described below; the inhouse lower acceptance limit cannot be <20% for any EIS compound.

After the analysis of 30 samples of a given matrix type (water, soil, biosolids, tissues, etc.) for which the isotopically labeled compounds pass the tests in Section 9.3, compute the R and the standard deviation of the percent recovery (SR) for the isotopically labeled compounds only. Express the assessment as a percent recovery interval from R - 2SR to R + 2SR for each matrix. For example, if R = 90% and SR = 10% for five analyses of soil, the recovery interval is expressed as 70 to 110%. Update the accuracy assessment for each isotopically labeled compound in each matrix on a regular basis (e.g., after each five to ten new measurements).

11.3.1 Method Validation

Detection limits (DL) and limits of quantitation (LOQ) are established at initial method setup and verified on an on-going basis thereafter. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 (Method Validation and Instrument Verification) and to the laboratory's relevant SOP for these procedures. DLs must be established for all the analytes using the MDL procedure at 40 CFR Part 136, Appendix B. An MDL determination must be performed for all compounds.

11.4 Analyst Qualifications and Training

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

IDOC - To establish the ability to generate acceptable precision and recovery, the laboratory must perform the following operations for each sample matrix type to which the method will be applied by that laboratory.

Extract, concentrate, and analyze four aliquots of the matrix type to be tested (Section 7.2), prepared in the same way as the mid-level LCS/OPR. At least one method blank, matching the matrix being analyzed, must be prepared with the IDOC batch. If more than one MB was prepared and analyzed with the IDOC batch, all blank results must be reported. All sample processing steps that are to be used for processing samples, including preparation and extraction, cleanup, and concentration (Sections 9.3.3 through 9.3.9), must be included in this test.

Using results of the set of four analyses, compute the average percent recovery (R) of the extracts and the relative standard deviation (RSD) of the concentration for each target and EIS compound.

For each native and isotopically labeled compound, compare RSD and R with the corresponding limits for initial precision and recovery. If RSD and R for all compounds meet the acceptance criteria, system performance is acceptable, and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual R falls outside the range for recovery, system performance is unacceptable for that compound. Correct the problem and repeat the test.

12.0 Data Review And Corrective Action

12.1 Data Review

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

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

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

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

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

Refer to laboratory SOP for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

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

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

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

Refer to Appendix B for a summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

13.0 Pollution Prevention And Waste Management

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

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

14.0 MODIFICATIONS

A modification is a change to a reference test method made by the laboratory. For example, changes in stoichiometry, technology, quantitation ions, reagent or solvent volumes, reducing digestion or extraction times, instrument runtimes, etc. are all examples of modifications. Refer to Pace ENV corporate SOP ENV-SOP-CORQ-0011 (Method Validation and Instrument Verification) for the conditions under which the procedures in test method SOPs may be modified and for the procedure and document requirements.

In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options to improve separations or lower the costs of measurements. These options include alternative extraction, concentration, and cleanup procedures, and changes in sample volumes, columns, and detectors. Alternative determinative techniques and other changes are not allowed without prior review and approval.

Each time a modification is made to this method, the laboratory is required to repeat the procedure in Sections 11.3.1 and 11.4. If calibration will be affected by the change, the instrument must be recalibrated per Section 9.2. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method as written, that modification may be used routinely thereafter, so long as the other requirements in this method are met (e.g., isotopically labeled compound recovery).

If a column or column system other than those specified in this method is used, that column or column system must meet all the requirements of this method.

The laboratory is required to maintain records of any modifications made to this method. These records include the following, at a minimum:

a) The names, titles, business addresses, and telephone numbers of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

b) A listing of pollutant(s) measured, by name and CAS Registry number.

c) A narrative stating reason(s) for the modifications.

d) Results from all quality control (QC) tests comparing the modified method to this method, including:

i. Calibration (ICAL)

ii. Calibration verification (CCV)

iii. Initial Demonstration of Capability (IDOC)

iv. Isotopically labeled compound recovery (EIS/NIS)

v. Analysis of blanks (IBLK, MB)

vi. Accuracy assessment (Section 11.3)

e) Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

i. Sample numbers and other identifiers

ii. Extraction dates

iii. Analysis dates and times

iv. Analysis sequence/run chronology

v. Sample weight or volume

vi. Extract volume prior to each cleanup step

vii. Extract volume after each cleanup step

viii. Final extract volume prior to injection

ix. Injection volume

x. Dilution data, differentiating between dilution of a sample or extract

xi. Instrument Identification

xii. Column (dimensions, liquid phase, solid support, film thickness, etc.)

xiii. Operating conditions (temperatures, temperature program, flow rates)

xiv. Detector (type, operating conditions, etc.)

xv. Chromatograms, printer tapes, and other recordings of raw data

xvi. Quantitation reports, data system outputs, and other data to link the raw data to the results reported

15.0 RESPONSIBILITIES

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

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

16.0 ATTACHMENTS

Not applicable.

17.0 REFERENCES

1. "Working with Carcinogens," Department of Health, Education, & Welfare, Public Health Service, Centers for Disease Control, NIOSH, Publication 77-206, August 1977, NTIS PB-

277256.

2. "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 CFR 1910.

3. "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety, 1979.

4. “Standard Methods for the Examination of Water and Wastewater,” 18th edition and later revisions, American Public Health Association, 1015 15th St, NW, Washington, DC 20005, 1-35: Section 1090 (Safety), 1992.

5. “Standard Practice for Sampling Water,” ASTM Annual Book of Standards, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.

6. “Handbook of Analytical Quality Control in Water and Wastewater Laboratories,” USEPA EMSL, Cincinnati, OH 45268, EPA 600/4-79-019, April 1979.

7. “Less is Better: Laboratory Chemical Management for Waste Reduction,” American Chemical Society, 1993. Available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

8. “Environmental Management Guide for Small Laboratories,” USEPA, Small Business Division, Washington DC, EPA 233-B-00-001, May 2000.

9. “The Waste Management Manual for Laboratory Personnel,” American Chemical Society, 1990. Available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

10. SERDP. Single-Laboratory Validation Study of PFAS by Isotope Dilution LC-MS/MS. ER19-1409. January 26, 2022.

11. DoD QSM (US Department of Defense Quality Systems Manual for Environmental Laboratories, Version 5.4, 2021)

12. Woudneh, Million B., Bharat Chandramouli, Coreen Hamilton, Richard Grace, 2019, “Effects of Sample Storage on the Quantitative Determination of 29 PFAS: Observation of Analyte Interconversions during Storage”, Environmental Science and Technology 53(21): 12576-12585.

13. EPA. Draft Method 1633, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. August 2021.

14. Standard Methods for the Examination of Water and Wastewater, 23rd Edition, 2017 – Total, Fixed, and Volatile Solids in Solid and Semisolid Samples, Method 2540.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Stephen Somerville	PFAS Technical Director	5/5/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
6.0	Thermal preservation changed for “0-6°C” to “0-6°C or ≤ -20°C”

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
ENV-SOP-BTRO-0149 v01	Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in	05/09/2022

	Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS	

Appendix A: Target Analyte Limits, Analytical Parameters, and Calibration

Table 1: Routine Analyte List Limits of Detection (LOD) and Limits of Quantitation (LOQ)[1]

Analyte	Aqueous (ng/L)		Leachate (ng/L)		Solid (ng/g)		Biosolid (ng/g)		Tissue (ng/g)	
	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
PFBA	2	4	10	20	0.4	0.8	4	8		2.0
PFPeA	1	2	5	10	0.2	0.4	2	4		1.0
PFHxA	0.5	1	2.5	5	0.16	0.2	1.6	2		0.5
PFHpA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFOA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFNA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFDA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFUnA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFDoA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFTrDA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFTeDA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFBS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFPeS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFHxS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFHpS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFOS	0.75	1	3.75	5	0.15	0.2	1.5	2		0.5
PFNS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFDS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
PFDoS	0.5	1	2.5	5	0.1	0.2	1	2		0.5
4:2 FTS	2	4	10	20	0.4	0.8	4	8		2.0
6:2 FTS	2	4	10	20	0.4	0.8	4	8		2.0
8:2 FTS	2	4	10	20	0.4	0.8	4	8		2.0
PFOSA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
NMeFOSA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
NEtFOSA	0.5	1	2.5	5	0.15	0.2	1.5	2		0.5
NMeFOSAA	0.5	1	2.5	5	0.1	0.2	1	2		0.5
NEtFOSAA	0.75	1	3.75	5	0.1	0.2	1	2		0.5
NMeFOSE	5	10	25	50	1	2.0	10	20		5.0
NEtFOSE	5	10	25	50	1	2.0	10	20		5.0
HFPO-DA	2	4	10	20	0.4	0.8	4	8		2.0
ADONA	2	4	10	20	0.4	0.8	4	8		2.0
PFEESA	1	2	5	10	0.2	0.4	2	4		1.0
PFMPA	1	2	5	10	0.2	0.4	2	4		1.0
PFMBA	1	2	5	10	0.2	0.4	2	4		1.0
NFDHA	1	2	5	10	0.2	0.4	2	4		1.0
9Cl-PF3ONS	2	4	10	20	0.4	0.8	4	8		2.0
11Cl-PF3OUdS	2	4	10	20	0.4	0.8	4	8		2.0
3:3 FTCA	3	5	15	25	0.5	1.0	5	10		2.5
5:3 FTCA	6	25	30	125	2.5	5.0	25	50		12.5
7:3 FTCA	10	25	50	125	2.5	5.0	25	50		12.5

[1] Values in place as of effective date of this SOP. LOD/LOQ are subject to change. For the most up to date LOD/LOQ, refer to the LIMS or contact the laboratory.

Table 2: Identification and Quantification Information for Target Analytes, Extracted Internal Standards and Non-extracted Internal Standards

Compound Name	CAS Number	Compound Abbreviation	Parent Ion Mass	Quantification Ion Mass	Confirmation Ion Mass	Quantification Reference Compound
Perfluorobutanoic acid	375-22-4	PFBA	213	169	NA	13C4-PFBA
Perfluoropentanoic acid	2706-90-3	PFPeA	263	218.9	69	13C5-PFPeA
Perfluorohexanoic acid	307-24-4	PFHxA	313	268.9	118.9	13C5-PFHxA
Perfluoroheptanoic acid	375-85-9	PFHpA	362.9	319	169	13C4-PFHpA
Perfluorooctanoic acid	335-67-1	PFOA	413	369	169	13C8-PFOA
Perfluorononanoic acid	375-95-1	PFNA	463	419	219	13C9-PFNA
Perfluorodecanoic acid	335-76-2	PFDA	513	469	219	13C6-PFDA
Perfluoroundecanoic acid	2058-94-8	PFUnA	563	518.9	269.1	13C7-PFUnA
Perfluorododecanoic acid	307-55-1	PFDoA	613	569	319	13C2-PFDoA
Perfluorotridecanoic acid	72629-94-8	PFTrDA	663.0	618.9	168.9	13C2-PFDoA
Perfluorotetradecanoic acid	376-06-7	PFTeDA	713	668.9	168.9	13C2-PFTeDA
Perfluorobutanesulfonic acid	375-73-5	PFBS	298.9	80	98.8	13C3-PFBS
Perfluoropentansulfonic acid	2706-91-4	PFPeS	349	80	98.9	13C3-PFHxS
Perfluorohexanesulfonic acid	355-46-4	PFHxS	398.9	80	99	13C3-PFHxS
Perfluoroheptanesulfonic acid	375-92-8	PFHpS	449	80	98.8	13C8-PFOS
Perfluorooctanesulfonic acid	1763-23-1	PFOS	499	80	99	13C8-PFOS
Perfluorononanesulfonic acid	68259-12-1	PFNS	549	80	98.8	13C8-PFOS
Perfluorodecanesulfonic acid	335-77-3	PFDS	599	80	98.8	13C8-PFOS
Perfluorododecanesulfonic acid	79780-39-5	PFDoS	698.9	80	99	13C8-PFOS
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	757124-72-4	4:2FTS	327	306.9	80.9	13C2-4:2FTS
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	27619-97-2	6:2FTS	427	406.9	80.9	13C2-6:2FTS
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	39108-34-4	8:2FTS	527	506.9	81	13C2-8:2FTS
Perfluorooctanesulfonamide	754-91-6	PFOSA	497.9	78	478	13C8-PFOSA
N-methyl perfluorooctanesulfonamide	31506-32-8	NMeFOSA	512	219	169	D3-NMeFOSA
N-ethyl perfluorooctanesulfonamide	4151-50-2	NEtFOSA	526	219	169	D5-NEtFOSA
N-methyl perfluorooctanesulfonamidoacetic acid	2355-31-9	NMeFOSAA	570	418.9	483	D3-NMeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6	NEtFOSAA	584	418.9	526	D5-NEtFOSAA
N-methyl perfluorooctanesulfonamidoethanol	24448-09-7	NMeFOSE	616	59.1	NA	D7-NMeFOSE
N-ethyl perfluorooctanesulfonamidoethanol	1691-99-2	NEtFOSE	630	59.1	NA	D9-NEtFOSE
Hexafluoropropylene oxide dimer acid (GenX)	13252-13-6	HFPO-DA	285	169	184.9	13C3-HFPODA

Compound Name	CAS Number	Compound Abbreviation	Parent Ion Mass	Quantification Ion Mass	Confirmation Ion Mass	Quantification Reference Compound
4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	ADONA	377	251	85.1	13C3-HFPODA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	9Cl-PF3ONS	530.9	350.9	533→353	13C3-HFPODA
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	11Cl-PF3OUdS	630.9	450.9	633→453	13C3-HFPODA
3-Perfluoropropyl propanoic acid (FPrPA)	356-02-5	3:3FTCA	241	177	117	13C5-PFPeA
2H,2H,3H,3H-Perfluorooctanoic acid (FPePA)	914637-49-3	5:3FTCA	341	237.1	217	13C5-PFHxA
3-Perfluoroheptyl propanoic acid (FHpPA)	812-70-4	7:3FTCA	441	317	337	13C5-PFHxA
Perfluoro(2-ethoxyethane)sulfonic acid	113507-82-7	PFEESA	315	135	83	13C5-PFHxA
Perfluoro-3-methoxypropanoic acid	377-73-1	PFMPA	229	85	NA	13C5-PFPeA
Perfluoro-4-methoxybutanoic acid	863090-89-5	PFMBA	279	85	NA	13C5-PFPeA
Nonafluoro-3,6-dioxaheptanoic acid	151772-58-6	NFDHA	295	201	85	13C5-PFHxA
Extracted Internal Standard (EIS) Compounds						
Perfluoro-n-[13C4] butanoic acid	N/A	13C4-PFBA	217	172	NA	13C3-PFBA
Perfluoro-n-[13C5] pentanoic acid	N/A	13C5-PFPeA	268	223	NA	13C2-PFHxA
Perfluoro-n-[1,2,3,4,6-13C5] hexanoic acid	N/A	13C5-PFHxA	318	273	NA	13C2-PFHxA
Perfluoro-n-[1,2,3,4-13C4] heptanoic acid	N/A	13C4-PFHpA	366.9	322	NA	13C2-PFHxA
Perfluoro-n-[13C8] octanoic acid	N/A	13C8-PFOA	421	376	NA	13C4-PFOA
Perfluoro-n-[13C9] nonanoic acid	N/A	13C9-PFNA	472	427	NA	13C5-PFNA
Perfluoro-n-[1,2,3,4,5,6-13C6] decanoic acid	N/A	13C6-PFDA	519	474	NA	13C2-PFDA
Perfluoro-n-[1,2,3,4,5,6,7-13C7] undecanoic acid	N/A	13C7-PFUnA	570	525	NA	13C2-PFDA
Perfluoro-n-[1,2-13C2] dodecanoic acid	N/A	13C2-PFDoA	615	570	NA	13C2-PFDA
Perfluoro-n-[13C2] tetradecanoic acid	N/A	13C2-PFTeDA	715	669.9	NA	13C2-PFDA
Perfluoro-1-[13C3] butanesulfonic acid	N/A	13C3-PFBS	301.9	80	NA	18O2-PFHxS
Perfluoro-1-[1,2,3-13C3] hexanesulfonic acid	N/A	13C3-PFHxS	402	80	NA	18O2-PFHxS
Perfluoro-1-[13C8] octanesulfonic acid	N/A	13C8-PFOS	507	79.9	NA	13C4-PFOS
1H,1H,2H,2H-Perfluoro-1-[1,2-13C2] hexanesulfonic acid	N/A	13C2-4:2FTS	329	81	NA	18O2-PFHxS
1H,1H,2H,2H-Perfluoro-1-[1,2-13C2] octanesulfonic acid	N/A	13C2-6:2FTS	429	81	NA	18O2-PFHxS

Compound Name	CAS Number	Compound Abbreviation	Parent Ion Mass	Quantification Ion Mass	Confirmation Ion Mass	Quantification Reference Compound
1H,1H,2H,2H-Perfluoro-1-[1,2-13C2] decanesulfonic acid	N/A	13C2-8:2FTS	529	81	NA	18O2-PFHxS
Perfluoro-1-[13C8] octanesulfonamide	N/A	13C8-PFOSA	505.9	78	NA	13C4-PFOS
N-methyl-d3-perfluoro-1-octanesulfonamide	N/A	D3-NMeFOSA	515	219	NA	13C4-PFOS
N-ethyl-d5-perfluoro-1-octanesulfonamide	N/A	D5-NEtFOSA	531	219	NA	13C4-PFOS
N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid	N/A	D3-NMeFOSAA	573	419	NA	13C4-PFOS
N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid	N/A	D5-NEtFOSAA	589	418.9	NA	13C4-PFOS
N-methyl-d7-perfluorooctanesulfonamidoethanol	N/A	D7-NMeFOSE	623	59	NA	13C4-PFOS
N-ethyl-d9 -perfluorooctanesulfonamidoethanol	N/A	D9-NEtFOSE	639	59	NA	13C4-PFOS
Tetrafluoro-2-heptafluoropropoxy-13C3 -propanoic acid	N/A	13C3-HFPO-DA	287	169	NA	13C2-PFHxA
Non-Extracted Internal Standard (NIS) Compounds						
Perfluoro-n-[2,3,4-13C3] butanoic acid	N/A	13C3-PFBA	216	172	NA	NA
Perfluoro-n-[1,2-13C2] hexanoic acid	N/A	13C2-PFHxA	315	270	NA	NA
Perfluoro-n-[1,2,3,4-13C4] octanoic acid	N/A	13C4-PFOA	417	172	NA	NA
Perfluoro-n-[1,2,3,4,5-13C5] nonanoic acid	N/A	13C5-PFNA	468	423	NA	NA
Perfluoro-n-[1,2-13C2] decanoic acid	N/A	13C2-PFDA	515	470	NA	NA
Perfluoro-1-hexane[18O2] sulfonic acid	N/A	18O2-PFHxS	403	84	NA	NA
Perfluoro-n-[1,2,3,4-13C4] octanesulfonic acid	N/A	13C4-PFOS	503	80	NA	NA

Table 3: Calibration Standard Concentrations (ng/mL)

Compound	L1 (ISC)	L2	L3	L4	L5 (CCV)[1]	L6	L7	L8	L9	L10
Perfluoroalkyl carboxylic acids										
PFBA	0.4	0.8	2	5	10	20	50	100	200	250
PFPeA	0.2	0.4	1	2.5	5	10	25	50	100	125
PFHxA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFHpA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFOA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5

Compound	L1 (ISC)	L2	L3	L4	L5 (CCV)[1]	L6	L7	L8	L9	L10
PFNA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFDA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFUnA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFDoA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFTrDA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
PFTeDA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
Perfluoroalkyl sulfonic acids										
PFBS	0.0887	0.1774	0.4435	1.109	2.218	4.435	11.088	22.175	44.35	55.438
PFPeS	0.0941	0.1882	0.4705	1.176	2.353	4.705	11.763	23.525	47.050	58.813
PFHxS	0.0914	0.1828	0.457	1.143	2.285	457	11.425	22.850	45.7	57.125
PFHpS	0.0953	0.1906	0.4765	1.191	2.383	4.765	11.913	23.825	47.65	59.563
PFOS	0.0928	0.1856	0.464	1.16	2.32	4.64	11.6	23.2	46.4	58.0
PFNS	0.0962	0.1924	0.481	1.203	2.405	4.81	12.025	24.050	48.1	60.125
PFDS	0.0965	0.193	0.4825	1.206	2.413	4.825	12.063	24.125	48.25	60.313
PFDoS	0.097	0.194	0.485	1.213	2.425	4.85	12.125	24.25	48.5	60.625
Fluorotelomer sulfonic acids										
4:2FTS	0.375	0.75	1.875	4.688	9.375	18.75	46.875	93.75	187.5	NA
6:2FTS	0.38	0.76	1.9	4.75	9.5	19	47.5	95	190	NA
8:2FTS	0.384	0.768	1.92	4.8	9.6	19.2	48	96	192	NA
Perfluorooctane sulfonamides										
PFOSA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
NMeFOSA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
NEtFOSA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
Perfluorooctane sulfonamidoacetic acids										
NMeFOSAA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
NEtFOSAA	0.1	0.2	0.5	1.25	2.5	5	12.5	25	50	62.5
Perfluorooctane sulfonamide ethanols										
NMeFOSE	1	2	5	12.5	25	50	125	250	500	625
NEtFOSE	1	2	5	12.5	25	50	125	250	500	625
Per- and polyfluoroether carboxylic acids										
HFPO-DA	0.4	0.8	2	5	10	20	50	100	200	250
ADONA	0.378	0.756	1.89	4.725	9.45	18.9	47.25	94.5	189	236.25
PFMPA	0.2	0.4	1	2.5	5	10	25	50	100	125
PFMBA	0.2	0.4	1	2.5	5	10	25	50	100	125
NFDHA	0.2	0.4	1	2.5	5	10	25	50	100	125
Ether sulfonic acids										
9Cl-PF3ONS	0.374	0.748	1.87	4.675	9.35	18.7	46.75	93.5	187	233.75
11Cl-PF3OUdS	0.378	0.756	1.89	4.725	9.45	18.9	47.25	94.5	189	236.25
PFEESA	0.178	0.356	0.89	2.225	4.45	8.9	22.25	44.5	89	111.25
Fluorotelomer Carboxylic Acids										

Compound	L1 (ISC)	L2	L3	L4	L5 (CCV)[1]	L6	L7	L8	L9	L10
3:3FTCA	0.5	1	2.5	6.25	12.5	25	62.5	125	250	312.5
5:3FTCA	2.5	5	12.5	31.25	62.5	125	312.5	625	1250	1560
7:3FTCA	2.5	5	12.5	31.25	62.5	125	312.5	625	1250	1560
Extracted Internal Standard (EIS) Compounds										
13C4-PFBA	10	10	10	10	10	10	10	10	10	10
13C5-PFPeA	5	5	5	5	5	5	5	5	5	5
13C5-PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFHpA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C8-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C9-PFNA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C6-PFDA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C7-PFUnA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C2-PFDoA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C2-PFTeDA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C3-PFBS	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C3-PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C8-PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C2-4:2FTS	5	5	5	5	5	5	5	5	5	5
13C2-6:2FTS	5	5	5	5	5	5	5	5	5	5
13C2-8:2FTS	5	5	5	5	5	5	5	5	5	5
13C8-PFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
D3-NMeFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
D5-NEtFOSA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
D3-NMeFOSAA	5	5	5	5	5	5	5	5	5	5
D5-NEtFOSAA	5	5	5	5	5	5	5	5	5	5
D7-NMeFOSE	25	25	25	25	25	25	25	25	25	25
D9-NEtFOSE	25	25	25	25	25	25	25	25	25	25
13C3-HFPODA	10	10	10	10	10	10	10	10	10	10
Non-Extracted Internal Standard (NIS) Compounds										
13C3-PFBA	5	5	5	5	5	5	5	5	5	5
13C2-PFHxA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFOA	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C5-PFNA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
13C2-PFDA	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
18O2-PFHxS	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
13C4-PFOS	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

[1] *This calibration point is used as the calibration verification (CCV)*

Appendix B: QC Summary

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
Mass Calibration	Annually and on as-needed basis.	Must meet manufacturer's acceptance criteria.	Identify and correct source of problem, repeat.	None. Do not proceed with analysis.
Mass Calibration Verification	After each Mass Calibration performed.	Must meet manufacturer's acceptance criteria.	Identify and correct source of problem, repeat Mass Calibration.	None. Do not proceed with analysis.
ICAL	At instrument set up, after CCV failure and/or major maintenance.	Must meet one of the curve fit options presented in Section 9.2.3.	Identify and correct source of problem, repeat.	None. Do not proceed with analysis.
ICV	After Each ICAL.	All analytes must be within ± 30% of their true values. (%R)	Identify and correct source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
RT Window Position	Once per ICAL and at the beginning of the analytical window.	Position is set using the mid-point of the ICAL on the day ICAL is performed; otherwise, mid-level CCV is used.	NA	NA
RT Window Study	At method set-up and after major instrument maintenance	RT Window is ± 30 secs from RT position.	NA	NA

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ISC	Daily before sample analysis.	All native compounds within ± 30% recovery.	Identify and correct source of problem and reanalyze ISC. If problem persists, repeat ICAL.	No samples shall be analyzed until ISC has met acceptance criteria. See Section 9.2.4 for exceptions.
Qualitative Isomer Check	Once per ICAL and daily before sample analysis.	All required branched isomer peaks present and visibly resolved from linear peaks.	Identify and correct source of problem and reanalyze Isomer Check.	No samples shall be analyzed until Isomer Check has met acceptance criteria.
Bile Salts Check	Once per ICAL and daily before sample analysis.	Bile Salt peak detected >1 min outside RT window for PFOS.	Identify and correct source of problem and reanalyze Bile Salts Check.	No samples shall be analyzed until Bile Salts Check has met acceptance criteria.
CCV	Daily before sample analysis, after every 10 samples, and at end of analytical sequence.	All native and isotopically labelled compounds within ± 30% recovery.	See Section 9.2.4 for required corrective actions based on circumstance.	Qualify analytes with CCV out of criteria.
Instrument Blank (IBLK) / CCB	Daily prior to analysis and after high standards, including CCV.	Must meet criteria specified in Section 11.2.1: all detections ≤1/2 LOQ.	Identify and correct source of contamination or performance issue. Reanalyze IBLK.	No samples shall be analyzed until IBLK has met acceptance criteria.
Extracted Internal Standards (EIS)	Every field sample, standard and QC sample.	Must meet criteria specified in Section 11.3. Preliminary acceptance range: 20-150% REC (based on calculated concentration).	If batch QC is acceptable, reanalyze to confirm. If confirmed, reprepare and reanalyze samples. If reprep is within acceptance, report reprep data. If failure is confirmed by reprep, qualify as matrix impacted.	Qualify outages and explain in case narrative.

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
Non-extracted Internal Standards (NIS)	Every field sample, standard and QC sample.	Must meet criteria specified in Section 11.3. Preliminary acceptance criteria: >30% REC (based on response).	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Method Blank (MB)	1 per batch of 20 or fewer samples.	Must meet criteria specified in Section 11.1.1.	If IBLK is acceptable, reanalyze MB to confirm. If confirmed, reprepare and reanalyze associated impacted samples (if sufficient sample remains). If insufficient sample remains for reprep, narrate and report data associated to unacceptable MB.	Qualify outages and explain in case narrative.
LCS/LLLCS	1 pair per batch of 20 or fewer samples.	DoD: 40-150% until in-house limits generated; must meet criteria specified in Section 11.1.2.	If most recent ISC/CCV is acceptable, reanalyze LCS to confirm. If low-failure results are confirmed, reprepare and reanalyze associated samples (if sufficient sample remains). If insufficient sample remains for reprep, narrate and report data associated to low-failure LCS. If high-failure results are confirmed and sample(s) is ND for failing compound, narrate and report sample data.	Qualify outages and explain in case narrative.
MS/MSD	1 pair per batch of 20 or fewer samples.	DoD: RSD <30% between MS/MSD	If possible, reprep to confirm.	Qualify outages and explain in case narrative.
Sample Duplicate	1 per AFFF sample.	DoD: RSD <30% between parent/DUP	If possible, reprep to confirm.	Qualify outages and explain in case narrative.

Appendix C: Sample Pre-screening Instructions

Samples that are known or suspected to contain high levels of analytes may be pre-screened using the following procedure. These are example procedures using smaller sample aliquots spiked with EIS and NIS and no clean up procedures. Other pre-screening procedures may be used.

Aqueous Samples

1. Weight out 10 (±0.1) g of sample into a 50 mL centrifuge tube.

2. Add 100 µL of EIS to the sample and vortex to mix.

3. Filter 1 mL of the sample through 0.2 µm membrane filter into a microvial. Sample is ready for instrumental analysis.

Solid and Tissue Samples

1. Weigh 1.0 (±0.1) g sample into 50 mL polypropylene centrifuge tubes.

2. Add 10 mL of 0.3% methanolic ammonium hydroxide to the sample. Vortex and mix on a shaker table (or equivalent) for 10 min. Allow to settle and/or centrifuge to produce a clear extract.

3. Filter using a filter vial:

   a. Add ~400 µL of clear extract from step 2 (e.g., by adding extract until it reaches the fill line).

   b. Use filter/plunger part and filter.

4. Transfer 200 µL of filtrate to a 1 mL polypropylene autosampler vial and dilute with 10 µL of EIS and 790 µL of 0.3% methanolic ammonium hydroxide to a final volume of 1 mL. The extract is now approximately 50X dilute, relative to a solid sample prepared by the protocols in Section 9. Sample is ready for instrumental analysis.

Calculate results using the equivalent sample weight computed as follows:

$$Equivalent\ Weight = Sample\ weight\ (g) x \frac{0.2\ mL}{10\ mL}$$

Appendix D: Aqueous Sample Subsampling Instructions

Note: Because some target analytes may be stratified within the sample (e.g., AFFF- contaminated media, surfactants), or adhere to the walls of the sample container, subsampling may only be done on a project-specific basis. Subsampling has been shown to increase uncertainty in PFAS analysis, especially on foaming samples.

If a reduced sample size is required, transfer a weighed subsample using the following subsampling procedure to a 60 mL HDPE bottle and dilute to approximately 60 mL using reagent water. This container is now considered the “sample bottle.”

1. Gently invert sample 3-4 times being careful to avoid foam formation and subsample immediately (do not let stand).

2. If foam forms and more than 5 mL is required – pour sample, avoiding any foam.

3. If foaming forms and a volume less than 5 mL is required – pipette from ½ cm below the foam.

4. If no foam forms – pour or pipette based on volume required.

APPENDIX E: MS/MSD, MS/FD SAMPLE SELECTION PROTOCOL

Background: DOD QSM 5.4, Table B-24 requires that a matrix spike (MS) sample and a matrix spike duplicate (MSD) or field duplicate (FD) be prepped with every prep batch. Therefore, all aqueous prep batches must include an MS/MSD or MS/FD pair, if possible. Prep analysts will select samples to be used for this purpose following a hierarchy of preference, as defined below:

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

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

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

3. Lacking any samples received with 3 or more bottles, the prep analyst must use two different samples to fulfill the MS/FD pair requirement. Find two samples out of the set of samples selected for prep which were received with 2 bottles and pull both bottles for each sample. Pick one sample (pair of bottles) to be used for parent/MS prep and the other sample (pair of bottles) to be used for parent/FD. The sample selected for parent/MS will have one bottle spiked with targets and one prepped as normal, with no added spiking. The bottle which is spiked should be identified in the LIMS as MS. The sample selected for parent/FD will have both bottles prepared following normal procedures but one of the two should be identified in the LIMS as DUP.

4. If all samples in a particular prep batch were all received in just one bottle, analysis of an MS/MSD or MS/FD pair will not be possible. This should be an uncommon occurrence, as prep analysts will attempt to adjust batching to ensure that every prep batch contains an MS/MSD or MS/FD.

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedures used by Contest, A Pace Analytical Laboratory (ELON) for the determination of selected Per- and Polyfluorinated Alkyl Substances (PFAS) by Solid Phase Extraction & Isotope Dilution by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) in a water sample.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided in Table 1, Appendix A.

2.0 SUMMARY OF METHOD

A water sample of approximately 250mLs (preserved with Trizma if chlorinated source) is fortified with spikes and surrogates and extracted via Solid Phase Extraction (SPE). The sample is then concentrated to near dryness and subsequently brought up to a final volume of 1mL. All samples are analyzed using a Triple Quad LC/MS 6470 or 6495 (LC/MS/MS) system. Target analytes are identified by comparing mass spectra and retention times to reference spectra and retention times of calibration standards. Analytes are quantitated using the isotope dilution technique explained in the initial calibration section.

3.0 INTERFERENCES

- Standards and samples should not come into contact with glass other than standards purchased in glass ampules. PFAS commonly adsorb to the surface and could result in recovery discrepancies.
- Matrix interferences may be caused by co-extracted contaminants present in the sample.
- Method interferences may be caused by contaminants in solvents, reagents, and other sample processing hardware.
- Other common lab supplies that are associated with PFAAs and should be avoided where possible: aluminum foil, permanent marker, and PTFE.
- To eliminate any residual PTFE from the Agilent LC, an inline filter column has been installed to reduce any background contamination prior to sample introduction into the system. See Equipment and Supplies Section 7.0.
- Organic contaminants can pose a threat of interference due to the high quantities of de-chlorinating agent added to samples.
- Contamination levels should be monitored, and all blanks should be free from interferences (less than 1/2 the MRL) in all Laboratory Reagent Blanks (LRB).
- Blank subtraction is not permitted in this method.
- There is a possibility of matrix effects due to co-extracted organic material. When high levels of TOC are present, this can affect the ionization of 4:2 FTS considerably

4.0 DEFINITIONS

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

5.0 HEALTH AND SAFETY

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

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides containers for the collection of samples upon client request. Samples are to be collected in lab-provided plastic containers. Guidance for sampling is obtained through Pace corporate website or preferably local project authorities/municipalities.

The laboratory does not perform sample collection or field measurements for this test method. Samples should be collected in accordance with a sampling plan and sampling procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Water	Wide mouth 250-mL polypropylene bottle fitted with a	250mL	Thermal: Samples cannot exceed 10°C during the first 48 hours following sample collection.	Collection to Prep: 28 days Prep To Analysis: 28 days stored at room temperature.

	polypropylene screw cap		Samples must be received at or below 10°C OR have ice remaining in the cooler. -Prior to extraction, samples must be stored at or below 6°C and cannot be frozen.	

[1] *Amount of sample required for each discrete test.*

Thermal preservation is checked and recorded on receipt in accordance with laboratory ELON SOP Log-in.

After receipt, samples are stored at or below 6°C until sample preparation. Prepared samples (extracts, digestates, distillates, other) are stored at room temperature until sample analysis.

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

- Triple Quad LC/MS System
- SPE System
- Supelco Visiprep manifold or equivalent
- Vacuum pump capable of reaching up to 20” Hg
- N-Evap concentrator system
- Balance: Analytical, capable of accurately weighing 0.0001g
- Vortexer

7.2 Supplies

- Inline Delay column**:** Agilent Zorbax Eclipse Plus C18 3.0x50mm 1.8-micron P.N. PFCDELAY or equivalent
- Analytical Column**:** Agilent Zorbax Eclipse Plus C18 3.0x50mm 1.8-micron P.N. 959757-02 or equivalent
- Auto-pipettors: 0-10uL, 10-100uL, 100-1000uL
- Polypropylene pipet tip: 0-10uL, 10-100uL, 100-1000uL
- Polypropylene transfer pipets
- Polypropylene graduated cylinder: 10mL, 50mL, 100mL, 1000mL
- Vials: 2ml polypropylene vials
- Caps: 11mm polypropylene snap caps
- Sample containers: 250ml wide mouth polypropylene containers
- Polypropylene centrifuge tubes

- Non-PTFE SPE Reservoirs and/or sample transfer tubing with adapters
- Phenomenex Pre-Stacked WAX/GCB Cartridge or equivalent - Each lot should be checked to be free of contamination prior to usage for any field samples or batch QC. This can be done in the form of an additional LRB prior to usage for extraction.
- 13L Safety coated Pyrex waste collection container
- Polypropylene tubing for vacuum pump and manifold
- Polypropylene inserts

8.0 REAGENTS & STANDARDS

8.1 Reagents

- Reagent Water: interferent free
- Methanol: LC/MS Grade
- Nitrogen: Ultra high purity
- Ammonium Acetate: LC/MS Grade
- 5 mM Ammonium Acetate reagent water: Prepared by adding 1 mL of 5 M ammonium acetate to a final volume of 1000mLs DI water.
- 1 g/L Ammonium Acetate reagent water.
- 96:4 Methanol: Water- Made fresh every 2 days.
- Ammonium hydroxide (56.6% w/w)
- 0.1 M Sodium Phosphate Monobasic
- 0.1 M Sodium Phosphate Dibasic
- 0.1 M Phosphate Buffer: Prepared by mixing 500 mL of dibasic sodium phosphate with 275 mL of monobasic sodium phosphate. Verify solution pH of about 7.0.
- Ammonium Hydroxide
- Acetic acid, glacial
- Elution Solvent: 1% ammonium hydroxide in methanol (made fresh daily)

8.2 Standards

All standards must be documented in Element and have Certificate of Analysis forms attached electronically. All information should be documented, and each standard should be given an Element Standard ID#.

Standards may be received in purchased glass ampoules, but any transfer or dilution must be stored in polypropylene vials with non-PTFE caps

All standards purchased from Wellington come pre-treated with sodium hydroxide for compound stability. If making standards from solid, standards must be stored under basic condition to prevent esterification of fluorinated carboxylic acids. See calculation 1 in section 10.2.

- Stock Standard Solutions: Purchased as either certified solutions or neat standards - All purchased PFAA spike standard stock standards are to be stored until expiration date provided by manufacturer at 4°C.
- Prepared and in use PFAA stock standard solutions should be stored at room temperature and vortexed prior to usage. These standards will expire 2 months after preparation date or manufacturer's expiration date, whichever comes first.

8.2.1 Analyte Standards:

Compound	Vendor	Concentration of Standard (ng/ mL)
PFAC-30PAR	Wellington	1000*
PFAC-24PAR	Wellington	2000*
PFEESA	Wellington	50000*
NFDHA	Wellington	50000
PFMPA	Wellington	50000
PFMBA	Wellington	50000
HPFO-DA	Wellington	50000
NaDONA	Wellington	50000*
9ClPF3ONS	Wellington	50000*
11ClPF3OUdS	Wellington	50000*
FBSA	Wellington	50000
FHxSA	Wellington	50000

*Individual analyte concentration may vary due to amount of anion present in solution. All calculations must use the anion concentration, not the salt concentration. See Calculation 2 in section 10.2.

- PFEESA, NFDHA, PFMPA, PFMBA, HPFO-DA, NaDONA, 9ClPF3ONS, 11ClPF3OUdS, FBSA, and FHxSA are not included in the 24PAR mixture and are mixed into a separate "supplemental" 1000 ng/ mL stock. See below table for mixture.
- The Supplemental Stock is used to make a 500ppb spike dilution with 24PAR so that a different lot is used for spiking. The calibration stock is made using 30PAR and directly adding PFEESA, NFDHA, PFMPA, and PFMBA, which are missing from that mixture. See below table for prep instructions:

8.2.2 Stock Dilution Prep Table:

	Volume of Compound/Standard Mixtures (µL)	Volume of Methanol (µL)	Final Volume (µL)	Final Concentration (ng/mL)
Supplemental Stock	100µL – HPFO-DA 100µL – NaDONA 100µL – 9ClPF3ONS 100µL – 11ClPF3OUdS 100µL – PFEESA 100µL – PFMBA 100µL – PFMPA 100µL – NFDHA 100µL – FBSA 100µL – FHxSA	4000µL	5000µL	1000
500 ng/ mL **Spike**	1250µL – PFAC24PAR 2500µL – Supplemental Stock	1250µL	5000µL	500
100 ng/ mL **Spike**	250µL – PFAC24PAR 500µL – Supplemental Stock	4250µL	5000µL	100
100 ng/ mL **Cal Stock**	500µL – PFAC30PAR 10µL – PFEESA 10µL – PFMBA 10µL – PFMPA 10µL – NFDHA	4460µL	5000µL	100

8.2.3 Calibration Table**: The calibration is prepared as follows using the stock dilutions prepared above.**

Volume 100ppb Stock Standard (µL)	Volume 30PAR Stock Standard (µL)	Volume Supplemental Stock Standard (µL)	Volume of Surrogate Stock (µL)	Volume of M3HFPODA Surrogate Stock	Volume of 96:4 Methanol: Water (µL)	Final Volume (µL)	Final Concentration (ng/mL)
12.5	0	0	25	25	4937.5	5000	0.25*
25	0	0	25	25	4925	5000	0.5*
50	0	0	25	25	4900	5000	1.0*
125	0	0	25	25	4825	5000	2.5*
250	0	0	25	25	4700	5000	5.0*
0	50	50	25	25	4850	5000	10.0*
0	125	125	25	25	4700	5000	25.0*

- Individual analyte concentration may vary due to amount of anion present in solution. All calculations must use the anion concentration, not the salt concentration. See Calculation 2 in section 10.2.
- Continuing calibration verification (CCVs) standards are made at the mid-level, identically to the 4th calibration level above. The ICV/QCS is made similarly, just like the 5th calibration level above, except instead of calibration stock 100 ppb Spike is used as shown in the table below.

8.2.4 QCS/ICV Preparation Table:

Standard Name	Volume Standards	Volume of 96:4 Methanol: Water (µL)	Final Volume (µL)	Final Concentration (ng/mL)
QCS/ICV	25µL- PFAC-24ES 25µL-M3HPFO-DA Surrogate Dilution 250µL- 100ppb Spike	4700µL	5000µL	5.0

8.2.5 Surrogate, Internal Standard, and ESI-L Low concentration tuning mix:

Purchased as certified solutions - All purchased surrogate stock standards are to be stored until expiration date provided by manufacturer at 4°C.

Ordered as MPFAC-24ES from Wellington Labs:

Compound	Abbreviation	PDS, ng/mL
Perfluoro-n-[1,2,3,4-13C4]butanoic acid	MPFBA	1000
Perfluoro-n-[1,2,3,4,5-13C5]pentanoic acid	M5PFPeA	1000
Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate	M3PFBS	929
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]hexane sulfonate	M2-4:2FTS	935
Perfluoro-n-[1,2,3,4,6-13C5]hexanoic acid	M5PFHxA	1000
Perfluoro-n-[1,2,3,4-13C4]heptanoic acid	M4PFHpA	1000
Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate	M3PFHxS	946
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]-octane sulfonate	M2-6:2FTS	949
Perfluoro-n-[13C8]octanoic acid	M8PFOA	1000
Perfluoro-n-[13C9]nonanoic acid	M9PFNA	1000
Sodium perfluoro-[13C8]octanesulfonate	M8PFOS	957
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]-decane sulfonate	M2-8:2FTS	958
Perfluoro-n-[1,2,3,4,5,6-13C6]decanoic acid	M6PFDA	1000
Perfluoro-n-[1,2,3,4,5,6,7-13C7]undecanoic acid	M7PFUnA	1000
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-	M3HFPO-DA	1000

heptafluoropropoxy-13C3-propanoic acid		
Perfluoro-n-[1,2-13C2]dodecanoic acid	**M2PFDoA**	**1000**
Perfluoro-n-[12-13C2]tetradecanoic acid	**M2PFTA**	**1000**
Perfluoro-1-[13C8]octanesulfonamidoacetic acid	**M8FOSA**	**1000**
N-methyl-d3-perfluoro-1-octansulfonamidoacetic acid	**d3-N-MeFOSAA**	**1000**
N-ethyl-d5-perfluoro-1-octansulfonamidoacetic acid	**d5-N-EtFOSAA**	**1000**

Ordered as M3HFPO-DA from Wellington Labs:

2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-13C3-propanoic acid	**M3HFPO-DA**	**1000**

- Agilent ESI-L Low Concentration Tuning Mix

9.0 PROCEDURE

9.1 Calibration

All analytes must first be product ion optimized with the LC/MS/MS system using the MassHunter Optimizer program to determine optimal fragmentor and collision cell energy for applicable ions. This optimization should be done using a high-level standard for each analyte and using all of the LC parameters used in the analytical method. A level 4 standard must then be run to identify all retention time windows for all compounds of interest (See Section 9.3). A minimum of 10 spectra scans are acquired across each chromatographic peak. See Appendix A for further analyte MS/MS conditions.

- Prior to initial calibrations, and when the instrument is having difficulty passing regular calibrations, a mass calibration will be performed using Agilent ESI-L Low Concentration Tuning Mix. The MassHunter program has an autotune feature that performs the mass calibration using this mix and verifies it in a report.
- A calibration is to be run when continuing calibration checks or surrogates do not pass QC criteria. A calibration should also be performed when any hardware is changed, or major instrument maintenance is performed.
- The initial calibration must contain a minimum of five points with the lowest point being at or below the MRL. A minimum of six points is required for a quadratic calibration. The total of the branched and linear isomers must be used for calibration for the following target analytes: PFOS, PFHxS, NEtFOSAA, NMeFOSAA.

- The LC/MS/MS system is to be calibrated using the isotope dilution technique. Therefore, isotope dilution analogues are added at a constant concentration in all standards prior to injection. Either linear or quadratic regression can be used, but it must always be forced through zero and can be concentration weighted. Forcing through zero allows for more sensitivity to detect background contamination within the system. The calibration shall be done using the same LC conditions as the samples (See Section 7.7.2). Because the isotope dilution analogues are added in equal concentrations, calibrate for them using an average response factor. Not all analytes have an exact mass-labeled analogue, in which case the closest analogue is used (either by chemical properties or retention time). See Appendix A for the list of isotope analogues and corresponding target analytes.
- The isotope dilution technique utilizes extracted compounds to serve as a traditional internal standard. In this case, the extracted analogues must pass criteria listed in section 8.2.6. The analogue is then used as the internal standard compound for associated target analytes.
- Calibration levels for linear or non-linear analyte targets must have a r2 ≥ 0.99 for each analyte and the recovery for each analyte must be within 70-130% of the true value. Surrogate and internal standards must have an RSD of the RFs for all analytes of ≤20%.
- A quality control standard (QCS) will serve as an initial calibration verification (ICV) and be run following initial calibration and all subsequent calibrations. The ICV shall be prepared from a separate dilution of a different stock standard. This sample must be run following a calibration or quarterly, whichever comes first. The accepted values for the ICV are 70-130% of the true value for each analyte.
- If any instrumentation or analytical setpoints are changed to the instrument calibration, an initial demonstration of capability (IDOC) for the procedure and instrumentation shall be performed.

9.1.1 Continuing Calibration

- An instrument blank (IBL) and a low-level instrument sensitivity check (ISC) must be run at the MRL before any other injections and once every 12 hours. The results must be between 70-130% of the true value for all analytes. The IBL should have no hits greater than ½ the MRL. The ISC can serve as your initial CCV for the day.
- Prior to samples analysis, a low-level continuing calibration verification (CCV) must be run. After every ten field samples a subsequent CCV must be at Level 4 (same as calibration point 4 above). A closing CCV must also be run at the end of each analysis. The requirements for the CCVs are 70-130% of the true value for method analytes.
- An instrument blank is required to be run following analysis of the highest-level standard analyzed (after a calibration in this case). One is also required daily prior to sample analysis. All analytes must be at >½ the MRL in order to pass.
- All isotope dilution analogues (surrogates) must have a recovery between 50-150%
- In the case of CCV failure, two consecutive CCVs should be immediately run. If these pass, analysis can continue. Otherwise, a calibration or tuning and re-analysis of affected samples is required.
- A checktune will be run as needed to verify MS operating criteria. This is run through the MassHunter program using Agilent ESI-L Low Concentration Tuning Mix. If criteria are out of spec, the parameters set forth in the Agilent 6400 Series Triple Quadrupole LC/MS System

Quick Start Guide must be followed to adjust values. If re-run of checktune does not pass, an autotune must be run and the instrument must be recalibrated.

9.2 Sample Extraction Preparation

- For each required lab QC sample, fill a clean sample bottle with 250 mL DI water. Verify pH is 7.0 ± 2.0 pH units with pH paper. If sample pH is not 7.0 ± 2.0 pH units, note on bench sheet and adjust using either ammonium hydroxide or acetic acid.
- For every 20 field samples, a blank and a blank spike must be extracted. (Field blanks are considered field samples in this consideration as they are treated as such) Ideally, if adequate sample volume is available, a matrix spike and matrix spike duplicate should be included on every batch.
- All polypropylene equipment including graduated cylinders and sample transfer lines/reservoirs should be washed prior to using with extraction solvent (96:4 Methanol: water), followed by a DI water rinse.
- Add 5uL of surrogate to each sample and 25ul of 100ppb spike to all BS and MS samples included on the extraction batch. Cap and invert to mix well.
- Take initial weight (in grams) of each bottle and sample with the Sartorius Top Loading Balance. Observe if any samples have heavy sediment or are very cloudy and decide if it seems like the cartridge will clog. These samples can be extracted following a special protocol using a centrifuge outlined in Appendix C.
- After SPE system is set up, condition the cartridges first with 5mL methanol, followed by 5mL of 0.1M Sodium Phosphate Buffer.

  *Note: The sample cartridges must not be allowed to run dry at any point during conditioning. If they become dry, the conditioning must be started over.
- Next add 2 mL of 0.1M Sodium Phosphate Buffer and attach either sample transfer tube or reservoir to the cartridge and begin transferring sample. The samples should be passed through the cartridge at approximately 5mL/min. This equates to a drop wise fashion eluting from the cartridge.
- Rinse sample bottle with 7.5mL of reagent water and pass-through tubing or reservoir and cartridge. Repeat once more.
- Add 0.5mL of acetonitrile to each cartridge. Remove sample transfer tubes/reservoirs and allow air to pass through the cartridges for a minimum of 5 minutes at approximately 10-15” Hg.
- Turn off vacuum and add tray of labeled collection vials to manifold.
- Using a pipette, rinse each respective reservoir into the sample container taking care to rinse the sides with 6mL of 1% NH4OH methanol. Pour solvent from sample bottles directly into cartridge. Then, allow to elute through the cartridge at a low vacuum elute with an additional 5-6mL of solvent so the final eluent is ~12mL.

- Samples can then be concentrated to ~850uL at room temperature
- Add 96:4 methanol: water, taking care to rinse the side of the container until the final volume reaches 1mL.
- Determine initial volume by taking the weight (in grams) of the empty container following extraction. Subtract this from the weight taken in step 7.5.5 to determine the volume by weight of the sample (it is assumed that 1 gram is equal to 1 mL).

9.3 Instrumentation Procedure

- Before any QC or samples can be run, the HPLC must be allowed to purge for at least thirty minutes. This purge can be done using any combination of the mobile phases, but prior to samples running, the initial mobile phase conditions used in the method must be allowed to run for 15 minutes or until pressure has stabilized.
- The instrument must be stable in all parameters before a run is started. The following are the HPLC and ESI-MS Method Conditions. Also, See Appendix C for additional MS/MS Method Conditions.

Time (min)	% 5 mM Ammonium Acetate in water	% Methanol	Flow Rate (mL/minute)
0.00	95	5	1.0
0.10	65	35	1.0
2.00	50	50	1.0
3.00	25	75	1.0
4.50	1	99	1.0
4.51	1	99	1.0
5.00	1	99	1.0
5.10	95	5	1.0
6.50	95	5	1.0

Injection Volume 6470	10uL
Injection Volume 6495	5uL
Column Compartment Temperature	40 °C
Autosampler Compartment Temperature	10 °C
Polarity	Negative
Gas Temperature	250 °C
Gas Flow	11 L/min
Nebulizer	50 psi

Sheath Gas Temperature	300 °C
Sheath Gas Flow	12 L/min
Capillary Needle Voltage (Negative mode)	-3000 V
Cell Accelerator Voltage	5 V

- An instrument sequence will be made. It will open with a blank and a low level CCV. After the CCV, the batch can start running. Every 10 field samples (excluding QC and FRBs) a subsequent CCV must be run at level 4. The sequence must end with a CCV.
- The run can end with a script to put the instrument into standby mode.

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Qualitative Identification

- The analyst cannot extrapolate beyond the range of the calibration. However, by isotope dilution analysis, the extract cannot be diluted. If an analyte is outside of the determined range, the sample must be re-extracted at an appropriate dilution level.
- There is extrapolation allowed only to determine if there is blank contamination. Since there is no blank subtraction, any contamination present must be below 1/2 of the MRL for specific analyte.
- If a sample exceeds the calibration range the sample must be re-extracted. This would involve diluting the sample with reagent water to be within the calibration range and adding ammonium acetate to be at a final concentration of 1 g/L.
- Additionally, if a sample exceeds the calibration range, one or more LRB must be run until the system meets acceptable criteria. If this occurs during an automated sequence, the samples subsequently must be evaluated. If the over-range analytes are present in the subsequent samples at or above the RL, the samples are considered invalid and must be re-run. If the analyte in question does not exceed the RL, the samples can be reported.
- For samples that are over range a dilution will be performed and the percentage of the EIS will be calculated to reflect the dilution. If the sample has remaining volume and it is deemed to be best to re-extract at a dilution the analyst will perform a dilution prior to extraction. If the sample is still over range or if no additional sample is available, then a refortification dilution will be performed. Narration will be included on refortification dilutions to indicate this procedure was utilized.
- Compounds that have both branched and linear isomers will be reported as total. These compounds include PFOS, PFHxS, N-Et-FOSAA, N-Me-FOSAA and PFOA. PFOS, PFHxS, N-Et-FOSAA, and N-Me-FOSAA have the branched and linear compounds available for quantitation. PFOA is a special case outlined below:
- PFOA will be quantitated by using a qualitative/semi-quantitative approach per EPA guidance. Since there is no standard available, the calibration will be done using the linear isomer only. A technical grade standard will be run to identify the retention time of the branched isomer. All samples will be quantitated using the area of both the linear and branched isomers of PFOA that may be present within the sample. A branched isomer check for PFOA will be run with every calibration curve to verify the retention times of the branched isomers for PFOA.

- All analytes and surrogates will be calculated based off the initial calibration criteria.
- All results for analytes shall be reported as the neutral acid.
- Retention time windows are established once per ICAL and at the beginning of each sequence. On days when an ICAL is not run, the initial CCV is used to set the times. All retention times of analytes and EIS analytes must fall within 0.4 minutes of the established time. Analytes must also elute within 0.1 minutes of their respective EIS.
- In addition to retention time identification criteria, most ions are identified by two ion transitions. (The following ions are exceptions: PFBA, PFPeA, FBSA, FHxSA, PFMPA, PFMBA, 9Cl-PF3ONS, 11Cl-PF3OUdS, ADONA). The secondary, or qualifier ion, must have a signal to noise of 3:1. The ratio between the qualifier and the quantifier ion must be averaged from the calibration. For samples to be valid, the ratio of qualifier to quantifier must be +/-50% from the average ratio from the applicable calibration.

10.2 Calculations

10.2.1 Calculation 1: Adding 4 mole equivalents to standards to prevent esterification

$$\frac{Total\ PFAS\ mass\ (g) \times 160(\frac{g}{mol})}{250\ (\frac{g}{mol})} = Mass\ of\ NaOH\ Required\ (g)$$

10.2.2 Calculation 2: Mass of the anion

Massacid= Measured Masssalt * (Molecular Weightacid/Molecular Weightsalt)

10.2.3 Calculation 3: Percent Recovery

$$\%R = \frac{(A - B)}{C} \times 100$$

10.2.4 Calculation 4: Relative percent deviation calculation

$$RPD = \frac{|LFSMD - LFSM|}{(LFSMD + LFSM)/2} \times 100$$

10.3 Manual Integration

Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are justified and proper all manual integrations must be performed, documented, reviewed, and approved in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration and local ELON Manual Integration*

SOP. Refer to these SOP's for guidance on manual integration techniques and required procedures.

11.0 QUALITY CONTROL & METHOD PERFORMANCE

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Section 11.3 and Appendix B for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	As Required.
Matrix Spike	MS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples
Matrix Spike Duplicate	MSD	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples when enough aliquot is provided.

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Section 11.3 and Appendix B for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Initial Calibration Verification	ICV	After each new calibration
Initial Calibration Blank	ICB	After each new calibration
Continuing Calibration Verification	CCV	After every 10 samples and end

11.3 Method Performance - Quality Control Measures & Acceptance Criteri

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

11.3.2 Method Blank

The method blank is matrix specific and extracted with every batch or every 20 samples (whichever is more frequent). The target compounds and ranges must be ≤1/2 the MRL, or <1/10th the amount measured in any sample, or <1/10th the regulatory limit. If any analytes are present above this level, the detected analytes are considered invalid for all samples extracted in that batch.

11.3.3 Field Reagent Blank

It is highly recommended to collect a Field Reagent Blank per every sampling event. If provided, Field reagent blanks only need to be run and reported if there are analytes at or above the MRL in any associated field samples. Any analyte peaks present in field reagent blanks must be below 1/3 of the MRL of that analyte. If any analytes are present above this level, all samples collected with said FRB are invalid and must be recollected and reanalyzed. Data will be reported to client as suspect, noting the field blank contamination.

11.3.4 Laboratory Control Sample/Duplicate (LCS)

A matrix specific LCS is extracted every 20 samples or per batch. The concentration must be ≥ LOQ and ≤ mid-range of calibration. All analytes' recoveries must be within limits specified in Appendix F. If analyte is not listed in table, acceptance criteria is to remain 50-150% until in-house limits can be determined. Samples should be re-extracted if criteria are not met, even if outside of hold. If samples cannot be re-extracted, then the failures must be notated in the narrative.

11.3.5 Matrix Spikes

A matrix-specific MS is extracted every 20 samples or per batch. MS spike concentrations will be at the mid-level of the calibration curve. If historical data is available, the sample will be spike at a level similar to expected contaminant levels. All analytes' recoveries must be within limits specified in Appendix F. If analyte is not listed in table, acceptance criteria is to remain 50-150% until in-house limits can be determined. See Section 10.2 calculation 3.

*Note: Matrix spike samples may display matrix bias. If the CCC and LFB samples are passing, but the MS recoveries are outside the designated range, the recovery is deemed to be matrix biased. A note on the unfortified sample will indicate the possibility of matrix effects being suspect.

11.3.6 Matrix spike duplicates

Extract a spiked sample duplicate every 20 samples (when enough aliquot is provided). Matrix Spike Duplicate samples should be calculated to have an RPD ≤30%. See section 10.2 calculation 4.

11.3.7 Quality Control Samples

A quality control sample must be run from a second source at least quarterly, or after an initial calibration as an ICV. If a second source is not commercially available, a different lot number from the same vendor is acceptable. The recoveries must be within 70-130% of the true value.

11.3.8 Isotope Dilution Analogue

Isotope dilution analogues are added to all blanks, standards, samples, and spikes. Analogue compounds must have an area of 50-150% of the associated compound in level 4 of the calibration on days when a calibration is run. On days when a calibration is not run, analogue compounds must have an area of 50-150% of the associated compound in the opening instrument sensitivity check/CCV.

If the surrogate is outside these limits, the extract should be re-analyzed. If the re-analysis passes, report re-analyzed sample. If this fails, the associated isotope performance standard should be evaluated. The system may need recalibration or maintenance. If the CCV has surrogate out of range, the instrument needs to be recalibrated.

If the re-analysis fails, re-extract the sample to confirm failure. If the re-extract also fails the criteria or if there is insufficient volume for re-extraction, the original results will be reported with narration. If the re-extraction is within criteria, the re-extraction will be reported if within holding time. If the re-extract was not within holding time but is passing, then both results will be reported.

11.3.9 Calibration Curve

A minimum of a 5-point calibration curve (for linear regression) or a 6-point calibration curve (for quadratic) is used to calibrate the system.

The curve must be verified with an independent standard (QCS) prior to sample analysis, (10 ng/L). The curve will be forced through zero and may or may not be concentration weighted.

If a peak is not properly integrated by the data system, manual integration may be necessary. Manual integrations must comply with the Pace SOP on Chromatographic Integration Procedures. The integration of the peaks for the samples and quality control samples must be as consistent as possible with the integration used with the initial calibration.

11.3.10 Continuing Calibration Verification Checks (CCVs)

The results must be between 70-130% of the true value for all analytes for the initial low level CCV. After every ten field samples, a subsequent CCV must be at level 4. The requirements for the CCVs are 70-130% of the true value. All analogue compound areas must fall within 50-150% of the appropriate calibration point or CCV.

The ending CCV acquisition time must fall within 24 hours of the acquisition starting time of the opening CCV with the associated analysis batch.

11.3.11 Initial Demonstration of Capability (IDOC)

An Initial demonstration of capability (IDOC) must be made prior to performing any test method, and at any time there is a significant change in instrument type, personnel, or test method.

In general, this demonstration does not test the performance of the method in real world samples, but in applicable and available clean matrix (a sample of a matrix in which no target analytes or interferences are present at concentrations that impact the results of a specific test method). Before any results are reported by a new analyst they need to perform and IDOC. See Appendix E.

All demonstrations shall be documented using the IDOC form, which also lists SOP, method associated with the test, certification statement, and authorized signatures.

11.3.12 Continuing Demonstration of Capability (CDOC)

An on-going demonstration of capability must be performed on an annual basis to document the quality of the data produced. On-going data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method.

In general, this demonstration does not test the performance of the method in real world samples, but in applicable and available clean matrix (a sample of a matrix in which no target analytes or interferences are present at concentrations that impact the results of a specific test method). Extract and analyze 4 replicate laboratory fortified blanks at level 4 of the calibration with acceptable recoveries between 70-130%.

All demonstrations shall be documented using the CDOC form, which also lists SOP, method associated with the test, certification statement, and authorized signatures.

12.0 Data Review & Corrective Action

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP Data Review for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

If corrective action is not taken or was not successful, the decision/outcome must be documented in the analytical record. The primary analyst has primary responsibility for taking

corrective action when QA/QC criteria are not met. Secondary data reviewers must verify that appropriate action was taken and/or that results reported with QC failure are properly qualified.

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

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

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have not been modified from the reference test method(s) cited.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.
- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in

corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.

- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: Routine Analyte List and LOQ
- Appendix B: QC Summary & Corrective Action Table
- Appendix C: 6470 and 6495 Transitions and MS Conditions
- Appendix D: Analyte/Acronym/Isotope Dilution Analogue
- Appendix E: Requirement/Specification/acceptance Criteria
- Appendix F: Method PFAS by LCMSMS Compliant with QSM Table B-15 Aqueous Matrix
- Appendix G: PFAS Aqueous sample centrifugation protocol (for DoD work in GW/SW/NPW

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- ELON QA Manual Doc#610
- Pace Analytical Corrective Action SOP.
- Pace Analytical Controlled Document SOP.
- Agilent 1260 Infinity Binary LC Operators manual
- Agilent MassHunter Study Manager
- Agilent MassHunter Optimizer
- MassHunter Personal Compound Database and Library Manager
- Agilent 6400 Series Triple Quadrupole LC/MS System Quick Start Guide
- MassHunter Data Acquisition Compliance Software Quick Start Guide
- MassHunter Quantitative Analysis Compliance Software Quick Start Guide

- Agilent 6000 Series LC/MS System Maintenance Guide
- EPA Method 533, "Determination of Selected Per- and Polyfluoralkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)", November 2019, EPA Document #815-B-19-020.
- Method ISO 25101:2009, "Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry", April 30, 2009.
- EPA Technical Advisory-Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) using EPA Method 537 Rev. 1.1 EPA 815-B-16-021 September 2016
- Agilent Application note by Peter JW Stone, Linda Cote, Jennifer Gushue, Robert J.Letcher and Shaogang Chu. A Low Femtogram Target Screen Method for Perfluorinated Compounds in Food Matrices and Potable Water Using the Agilent 6460 Triple Quadrupole LC/MS System Equipped with Agilent Jet Stream Technology.
- TNI Standard, The NELAC Institute, EL-V1-2009-ISO, 2009.
- Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories Based on ISO/IEC 17025:2005(E) ISO/IEC 17025:2017(E) and The NELAC Institute (TNI) Standards, Volume 1, (September 2009).

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Brianna Henriquez	PFAS Supervisor	04/28/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
All	Updated to Pace SOP format as well as updates to procedure: Removal of mentioning preservative and referencing Trizma.preservative. Edits to remove reference to Trizma and corrected pH range typo. Updates to procedure: Added current dilution procedure and edited to include reporting changes.
8.1	Updated 5mM Ammonium Acetate, Ammonium Hydroxide, Glacial Acetic Acid
10.1	Updated dilutions over calibration

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
454 Rev7	SOP 454 PFAS Water Isotope Dilution	7/28/2021

Appendix A: Target Analyte List and LOQ

Table 1: Standard Analyte List and LOQ

Analyte	CAS #	LOQ[1] Water (ng/L)
11-chloroeicosafluoro-3-oxanone-1-sulfonic acid (11Cl-PF3OUdS)	763051-92-9	2.0
9-Chlorohexadecafluoro-3-oxapentane-1-sulfonic acid (9Cl-PF3ONS)	756426-58-1	2.0
4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	919005-14-4	2.0
Hexafluoropropylene oxide dimer acid (HFPO-DA)	13252-13-6	2.0
Perfluoro-3,6-dioxaheptanoic acid (NFDHA)	151772-58-6	2.0
Perfluorobutanoic acid (PFBA)	375-22-4	2.0
Perfluorobutanesulfonic acid (PFBS)	375-73-5	2.0
8:2 Fluorotelomer sulfonic acid (8:2FTS)	39108-34-4	2.0
Perfluorodecanoic acid (PFDA)	335-76-2	2.0
Perfluorododecanoic acid (PFDoA)	307-55-1	2.0
Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)	113507-82-7	2.0
Perfluoroheptanesulfonic acid (PFHpS)	375-92-8	2.0
Perfluoroheptanoic acid (PFHpA)	375-85-9	2.0
4:2 Fluorotelomer sulfonic acid (4:2FTS)	757124-72-4	2.0
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	2.0
Perfluorohexanoic acid (PFHxA)	307-24-4	2.0
Perfluoro-3-methoxypropanoic acid (PFMPA)	377-73-1	2.0
Perfluoro-4-methoxybutanoic acid (PFMBA)	863090-89-5	2.0
Perfluorononanoic acid (PFNA)	375-95-1	2.0
6:2 Fluorotelomer sulfonic acid (6:2FTS)	27619-97-2	2.0
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	2.0
Perfluorooctanoic acid (PFOA)	335-67-1	2.0
Perfluoropentanoic acid (PFPeA)	2706-90-3	2.0
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	2.0
Perfluoroundecanoic acid (PFUnA)	2058-94-8	2.0
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2991-50-6	2.0
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2355-31-9	2.0
Perfluoro-1-butanesulfonamide (FBSA)	30334-69-1	2.0
Perfluoro-1-hexanesulfonamide (FHxSA)	41997-13-1	2.0
Perfluorotetradecanoic acid (PFTA)	376-06-7	2.0
Perfluorotridecanoic acid (PFTrDA)	72629-94-8	2.0
Perfluorooctanesulfonamide (FOSA)	754-91-6	2.0
Perfluorononanesulfonic acid (PFNS)	68259-12-1	2.0
Perfluorodecanesulfonic acid (PFDS)	335-77-3	2.0

[1] *Values as of effective date of this SOP. LOQ are subject to change, contact quality personnel for most current information.*

Appendix B: QC Summary and Corrective Action Table

Table B-15. Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water						Pace SOP Section
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Aqueous Sample Preparation	Each sample and associated batch QC samples.	Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., Aqueous Film Forming Foam (AFFF) formulations). Inline SPE is acceptable. Entire sample plus bottle rinsate must be extracted using SPE. Known high PFAS concentration samples require serial dilution be performed in duplicate. Documented project approval is needed for samples prepared by serial dilution as opposed to SPE.	NA.	NA.	Samples with > 1% solids may require centrifugation prior to SPE extraction. Pre-screening of separate aliquots of aqueous samples is recommended.	9.0 Procedure & Summary, Scope & Application
Solid Sample Preparation	Each sample and associated batch QC samples.	Entire sample received by the laboratory must be homogenized prior to subsampling.	NA.	NA.	NA.	Soil SOP: 9.2
Biota Sample Preparation	Each sample and associated batch QC samples.	Sample prepared as defined by the project (e.g., whole fish versus filleted	NA.	NA.	NA.	N/A

		fish).				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
AFFF and AFFF Mixture Samples Preparation	Each sample and associated batch QC samples.	Each field sample must be prepared in duplicate (equivalent to matrix duplicate). Serial dilutions must be performed to achieve the lowest LOQ possible for each analyte.	NA.	NA.	Adsorption onto bottle is negligible compared to sample concentration so subsampling is allowed. Multiple dilutions will most likely have to be reported in order to achieve the lowest LOQ possible for each analyte.	N/A
Sample Cleanup Procedure	Each sample and associated batch QC samples. Not applicable to AFFF and AFFF Mixture Samples.	ENVI-Carb™ or equivalent must be used on each sample and batch QC sample.	NA.	Flagging is not appropriate.	Cleanup should reduce bias from matrix interferences.	Soil:9.2
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. Mass calibration is verified after each mass calibration, prior to initial calibration (ICAL).	Calibrate the mass scale of the MS with calibration compounds and procedures described by the manufacturer. Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used for every acquisition in an analytical run. Mass calibration must be verified to be ±0.5 amu of the true value, by acquiring a full scan continuum mass spectrum of a PFAS stock standard.	If the mass calibration fails, then recalibrate. If it fails again, consult manufacturer instructions on corrective maintenance.	Flagging is not appropriate.	Problem must be corrected. No samples may be analyzed under a failing mass calibration. The mass calibration is updated on an as-needed basis (e.g., QC failures, ion masses fall outside of the ±0.5 amu of the true value, major instrument maintenance is performed, or the instrument is moved).	9.1

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments	SOP SECTION
Mass Spectral Acquisition Rate	Each analyte, Extracted Internal Standard (EIS) Analyte.	A minimum of 10 spectra scans are acquired across each chromatographic peak.	NA.	Flagging is not appropriate.	NA.	9.0
Calibration, Calibration Verification, and Spiking Standards	All analytes.	Standards containing both branched and linear isomers must be used when commercially available. PFAS method analytes may consist of both branched and linear isomers, but quantitative standards that contain the linear and branched isomers do not exist for all method analytes. For PFAS that do not have a quantitative branched and linear standard, identify the branched isomers by analyzing a qualitative standard that includes both linear and branched isomers and determine retention times, transitions and transition ion ratios. Quantitate samples by integrating the total response (i.e., accounting for peaks that are identified as	NA.	Flagging is not appropriate.	Standards containing both branched and linear isomers are to be used during method validation and when reestablishing retention times, to ensure the total response is quantitated for that analyte. Technical grade standards cannot be used for quantitative analysis.	10.1

		linear and branched isomers) and relying on the initial calibration that uses the linear isomer quantitative standard.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Sample PFAS Identification	All analytes detected in a sample.	The chemical derivation of the ion transitions must be documented. A minimum of two ion transitions (Precursor → quant ion and precursor → confirmation ion) and the ion transitions ratio per analyte are required for confirmation. Exception is made for analytes where two transitions do not exist (PFBA and PFPeA). Documentation of the primary and confirmation transitions and the ion ratio is required. In-house acceptance criteria for evaluation of ion ratios must be used and must not exceed 50- 150%. Signal to Noise Ratio (S/N) must be ≥ 10 for all ions used for quantification and must be ≥ 3 for all ions used for	NA.	PFAS identified with Ion ratios that fail acceptance criteria must be flagged. Any quantitation ion peak that does not meet the maximization criteria shall be included in the summed integration and the resulting data flagged as “estimated, biased high”.	For example: Ion Ratio = (quant ion abundance/ confirm ion abundance) Calculate the average ratio (A) and standard deviation (SD) using the ICAL standards. An acceptance range of ratio could be within A ±3SD for confirmation of detection.	10.1

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

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments	SOP SECTION
Initial Calibration (ICAL)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	The isotopically labeled analog of an analyte (Extracted Internal Standard Analyte) must be used for quantitation if commercially available (Isotope Dilution Quantitation). Commercial PFAS standards available as salts are acceptable providing the measured mass is corrected to the neutral acid concentration. Results shall be reported as the neutral acid with appropriate CAS number. If a labeled analog is not commercially available, the Extracted Internal Standard Analyte with the closest retention time or chemical similarity to the analyte must be used for quantitation. (Internal Standard Quantitation) Analytes must be within 70-130% of their true value for each calibration standard. *(continued next page)*	Correct problem, then repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ICAL has passed. External Calibration is not allowed for any analyte. Calibration can be linear (minimum of 5 standards) or quadratic (minimum of 6 standards); weighting is allowed.	9.1

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments	SOP SECTION
Initial Calibration (ICAL) *(Continued)*		ICAL must meet one of the two options below: Option 1: The RSD of the RFs for all analytes must be ≤ 20%. Option 2: Linear or non- linear calibrations must r^2 have r ≥ 0.99 for each analyte.				9.1
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and EIS.	10.1
Retention Time (RT) window width	Every field sample, standard, blank, and QC sample.	RT of each analyte and EIS analyte must fall within 0.4 minutes of the predicted retention times from the daily calibration verification or, on days when ICAL is performed, from the midpoint standard of the ICAL. Analytes must elute within 0.1 minutes of the associated EIS. This criterion applies only to analyte and	Correct problem and reanalyze samples.	NA.	Calculated for each analyte and EIS.	10.1

		labeled analog pairs.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Instrument Sensitivity Check (ISC)	Prior to analysis and at least once every 12 hours.	Analyte concentrations must be at LOQ; concentrations must be within ±30% of their true values.	Correct problem, rerun ISC. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until ISC has met acceptance criteria. ISC can serve as the initial daily CCV.	9.1.1
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Analyte concentrations must be within ±30% of their true value.	Correct problem, rerun ICV. If problem persists, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.	9.1
Continuing Calibration Verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analytical sequence.	Concentration of analytes must range from the LOQ to the mid-level calibration concentration. Analyte concentrations must be within ±30% of their true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary;	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without valid CCVs. Instrument Sensitivity Check (ISC) can serve as a bracketing CCV.	9.1.1

			then reanalyze all associated samples since the last acceptable CCV.			
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Instrument Blanks	Immediately following the highest standard analyzed and daily prior to sample analysis.	Concentration of each analyte must be ≤ ½ the LOQ. Instrument Blank must contain EIS to enable quantitation of contamination.	If acceptance criteria are not met after the highest calibration standard, calibration must be performed using a lower concentration for the highest standard until acceptance criteria is met. If sample concentrations exceed the highest allowed standard and the sample(s) following exceed this acceptance criteria (>1/2 LOQ), they must be reanalyzed.	Flagging is only appropriate in cases when the sample cannot be reanalyzed and when there is no more sample left.	No samples shall be analyzed until instrument blank has met acceptance criteria. Note: Successful analysis following the highest standard analyzed determines the highest concentration that carryover does not occur. When the highest standard analyzed is not part of the calibration curve, it cannot be used to extend out the calibration range, it is used only to document a higher concentration at which carryover still does not occur.	9.2
QC Check	**Minimum Frequency**	**Acceptance**	**Corrective**	**Flagging**	**Comments**	**SOP SECTION**

		Criteria	**Action**	**Criteria**		
Extracted Internal Standard (EIS) Analytes	Every field sample, standard, blank, and QC sample.	Added to solid sample prior to extraction. Added to aqueous samples, into the original container, prior to extraction. For aqueous samples prepared by serial dilution instead of SPE, added to final dilution of samples prior to analysis. Extracted Internal Standard Analyte recoveries must be within 50% to 150% of ICAL midpoint standard area or area measured in the initial CCV on days when an ICAL is not performed.	Correct problem. If required, re-extract and reanalyze associated field and QC samples. If recoveries are acceptable for QC samples, but not field samples, the field samples must be re-extracted and analyzed (greater dilution may be needed). Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure.	Apply Q-flag and discuss in the Case Narrative only if reanalysis confirms failures in exactly the same manner.	Failing analytes shall be thoroughly documented in the Case Narrative. EIS should be 96% (or greater) purity. When the impurity consists of the unlabeled analyte, the EIS can result in a background artifact in every sample, standard and blank, if the EIS is fortified at excessive concentrations.	11.3.8
Method Blank (MB)	One per preparatory batch.	No analytes detected >½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit,	Correct problem. If required, re-extract and reanalyze MB and all QC samples	If reanalysis cannot be performed, data must be qualified and explained in the	Results may not be reported without a valid MB. Flagging is only appropriate in cases where the samples cannot	11.3.2

		whichever is greater.	and field samples processed with the contaminated blank. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	Case Narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	be reanalyzed.	
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Laboratory Control Sample (LCS)	One per preparatory batch.	Blank spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not	Correct problem, then re-extract and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient	If reanalysis cannot be performed, data must be qualified and explained in the Case Narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.	11.3.4

		specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	sample material is available. Samples may be re-extracted and analyzed outside of hold times, as necessary for corrective action associated with QC failure. Examine the project-specific requirements. Contact the client as to additional measures to be taken.	batch.		
Matrix Spike (MS)	One per preparatory batch. Not required for aqueous samples prepared by serial dilution instead of SPE.	Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).	11.3.5

		specified.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**	**SOP SECTION**
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	For MSD: One per preparatory batch. For MD: Each aqueous sample prepared by serial dilution instead of SPE.	For MSD: Sample spiked with all analytes at a concentration ≥ LOQ and ≤ the mid-level calibration concentration. A laboratory must use the DoD/DOE QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the Case Narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is ≥ LOQ. The MD is a second aliquot of the field sample that has been prepared by serial dilution.	11.3.6
Post Spike Sample	Only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of < LOQ for analyte(s).	Spike all analytes reported as < LOQ into the dilution that the result for that analyte is reported from. The spike must be at the LOQ concentration to be reported for this sample as < LOQ. When analyte concentrations are calculated as < LOQ, the post spike for that analyte must	When analyte concentrations are calculated as < LOQ, and the spike recovery does not meet the acceptance criteria, the sample, sample duplicate, and post	Flagging is not appropriate.	When analyte concentrations are calculated as < LOQ, results may not be reported without acceptable post spike recoveries.	N/A

		recover within 70-130% of its true value.	spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.			

Appendix C:

6470 Transitions and MS Conditions:

Analyte	Precursor Ion	Product Ion	Collision Energy Voltage (V)	Fragmentor Voltage (V)	Qualifer/Quantifier
11Cl-PF3OUdS	631	451	24	100	N/A
4-2 FTS	327	307	20	120	Quant
4-2 FTS	327	81	30	120	Qual
6-2 FTS	427	406.9	24	135	Quant
6-2 FTS	427	80	40	125	Qual
8-2 FTS	527	507	28	145	Quant
8-2 FTS	527	80	40	170	Qual
9Cl-PF3ONS	531	351	24	100	N/A
ADONA	377	251	12	100	Quant
ADONA	377	85	12	100	Qual
d3-N-MeFOSAA	573.2	419	20	114	N/A
d5-N-EtFOSAA	589.2	419	20	104	N/A
FBSA	297.99	78	28	115	N/A
FHXSA	398	78.1	30	135	N/A
HFPO-DA	285.1	184.9	5	150	Quant
HFPO-DA	285.1	169	5	150	Qual
M2-4-2-FTS	328.99	309.2	20	135	N/A
M2-6-2-FTS	428.99	409.2	24	160	N/A
M2-8-2-FTS	528.99	509	28	170	N/A
M2PFDA	514.9	469.9	5	102	N/A
M2PFHxA	315	270	4	66	N/A
M2PFOA	415	370	4	69	N/A
M2PFTA	715	670	9	100	N/A
M3HFPO-DA	287	169	2	50	N/A
M3PFBA	216	171.8	4	56	N/A
M3PFBS	301.9	80	45	100	N/A
M3PFHxS	401.9	80	49	100	N/A
M4PFHpA	367	322	4	102	N/A
M5PFHxA	318	273	4	68	N/A
M5PFPeA	268	223	8	120	N/A
M6PFDA	519	474	4	81	N/A
M7PFUnA	570	525	5	73	N/A
M8FOSA	506	78	36	125	N/A
M8PFOA	421	376	5	65	N/A
M8PFOS	506.9	80	50	100	N/A
M9PFNA	472	427	4	85	N/A
MPFBA	217	172	8	60	N/A
MPFDoA	615	570	5	79	N/A
MPFOS	502.9	80	60	180	N/A

N-EtFOSAA	584	525.9	20	115	Qual
N-EtFOSAA	584	418.9	20	115	Quant
NFDHA	201	85	14	115	N/A
N-MeFOSAA	570	482.9	16	115	Qual
N-MeFOSAA	570	418.9	20	115	Quant
PFBA	213	169	8	60	N/A
PFBS	298.9	98.9	29	100	Qual
PFBS	298.9	80	45	100	Quant
PFDA	513	469	4	81	Quant
PFDA	513	169	16	100	Qual
PFDoA	613	569	5	79	Quant
PFDoA	613	268.7	20	100	Qual
PFDS	598.9	99	60	100	Qual
PFDS	598.9	80	80	100	Quant
PFEESA	315	135	24	110	N/A
PFHpA	362.9	319	8	72	Quant
PFHpA	362.9	169	20	72	Qual
PFHpS	448.9	98.7	44	44	Qual
PFHpS	448.9	79.7	52	52	Quant
PFHxA	313	268.9	8	8	Quant
PFHxA	313	119	18	18	Qual
PFHxS	398.9	99	45	100	Qual
PFHxS	398.9	80	49	100	Quant
PFMBA	279	85.1	8	55	N/A
PFMPA	229	85.1	12	55	N/A
PFNA	463	419	4	66	Quant
PFNA	463	169	17	66	Qual
PFNS	548.9	98.9	40	165	Qual
PFNS	548.9	79.9	40	165	Quant
PFOA	413	369	4	69	Quant
PFOA	413	169	12	69	Qual
PFOS	498.9	99	50	100	Qual
PFOS	498.9	80	50	100	Quant
PFOSA	497.9	77.9	36	125	Quant
PFOSA	497.9	47.9	80	100	Qual
PFPeA	263	218.9	8	60	N/A
PFPeS	348.9	98.9	40	135	Qual
PFPeS	348.9	79.9	40	135	Quant
PFTA	713	669	9	100	Quant
PFTA	712.9	169	30	100	Qual
PFTrDA	663	619	9	91	Quant
PFTrDA	663	169	30	100	Qual
PFUnA	563	519	5	73	Quant

PFUnA	563	218.7	20	100	Qual

6495 Transitions and MS Conditions:

Analyte	Precursor Ion	Product Ion	Collision Energy Voltage (V)	Fragmentor Voltage (V)	Qualifer/Quantifier
11Cl-PF3OUdS	631	451	24	166	N/A
4-2 FTS	327	307	20	166	Quant
4-2 FTS	327	81	30	166	Qual
6-2 FTS	427	406.9	24	166	Quant
6-2 FTS	427	80	40	166	Qual
8-2 FTS	527	507	28	166	Quant
8-2 FTS	527	80	40	166	Qual
9Cl-PF3ONS	531	351	24	166	N/A
ADONA	377	251	12	166	Quant
ADONA	377	85	12	166	Qual
d3-N-MeFOSAA	573.2	419	20	166	N/A
d5-N-EtFOSAA	589.2	419	20	166	N/A
FBSA	297.99	78	28	166	N/A
FHXSA	398	78.1	30	166	N/A
HFPO-DA	285.1	184.9	5	166	Quant
HFPO-DA	285.1	169	5	166	Qual
M2-4-2-FTS	328.99	309.2	20	166	N/A
M2-6-2-FTS	428.99	409.2	24	166	N/A
M2-8-2-FTS	528.99	509	28	166	N/A
M2PFDA	514.9	469.9	5	166	N/A
M2PFHxA	315	270	4	166	N/A
M2PFOA	415	370	4	166	N/A
M2PFTA	715	670	9	166	N/A
M3HFPO-DA	287	169	2	166	N/A
M3PFBA	216	171.8	4	166	N/A
M3PFBS	301.9	80	45	166	N/A
M3PFHxS	401.9	80	49	166	N/A
M4PFHpA	367	322	4	166	N/A
M5PFHxA	318	273	4	166	N/A
M5PFPeA	268	223	8	166	N/A
M6PFDA	519	474	4	166	N/A
M7PFUnA	570	525	5	166	N/A
M8FOSA	506	78	36	166	N/A
M8PFOA	421	376	5	166	N/A
M8PFOS	506.9	80	50	166	N/A
M9PFNA	472	427	4	166	N/A
MPFBA	217	172	8	166	N/A
MPFDoA	615	570	5	166	N/A

MPFOS	502.9	80	60	166	N/A
N-EtFOSAA	584	525.9	20	166	Qual
N-EtFOSAA	584	418.9	20	166	Quant
NFDHA	201	85	14	166	N/A
N-MeFOSAA	570	482.9	16	166	Qual
N-MeFOSAA	570	418.9	20	166	Quant
PFBA	213	169	8	166	N/A
PFBS	298.9	98.9	29	166	Qual
PFBS	298.9	80	45	166	Quant
PFDA	513	469	4	166	Quant
PFDA	513	169	16	166	Qual
PFDoA	613	569	5	166	Quant
PFDoA	613	268.7	20	166	Qual
PFDS	598.9	99	60	166	Qual
PFDS	598.9	80	80	166	Quant
PFEESA	315	135	24	166	N/A
PFHpA	362.9	319	8	166	Quant
PFHpA	362.9	169	20	166	Qual
PFHpS	448.9	98.7	44	166	Qual
PFHpS	448.9	79.7	52	166	Quant
PFHxA	313	268.9	8	166	Quant
PFHxA	313	119	18	166	Qual
PFHxS	398.9	99	45	166	Qual
PFHxS	398.9	80	49	166	Quant
PFMBA	279	85.1	8	166	N/A
PFMPA	229	85.1	12	166	N/A
PFNA	463	419	4	166	Quant
PFNA	463	169	17	166	Qual
PFNS	548.9	98.9	40	166	Qual
PFNS	548.9	79.9	40	166	Quant
PFOA	413	369	4	166	Quant
PFOA	413	169	12	166	Qual
PFOS	498.9	99	50	166	Qual
PFOS	498.9	80	50	166	Quant
PFOSA	497.9	77.9	36	166	Quant
PFOSA	497.9	47.9	80	166	Qual
PFPeA	263	218.9	8	166	N/A
PFPeS	348.9	98.9	40	166	Qual
PFPeS	348.9	79.9	40	166	Quant
PFTA	713	669	9	166	Quant
PFTA	712.9	169	30	166	Qual
PFTrDA	663	619	9	166	Quant
PFTrDA	663	169	30	166	Qual

PFUnA	563	519	5	166	Quant
PFUnA	563	218.7	20	166	Qual

Appendix D:

Analyte	Acronym	Isotope Dilution Analogue
11- Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	M8PFOS
9- Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	M8PFOS
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	M4PFHpA
Hexafluoropropylene oxide dimer acid	HFPO-DA	M3HFPO-DA
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	M5PFHxA
Perfluorobutanoic acid	PFBA	MPFBA
Perfluorobutanesulfonic acid	PFBS	M3PFBS
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	M2-8:2FTS
Perfluorodecanoic acid	PFDA	M6PFDA
Perfluorododecanoic acid	PFDoA	MPFDoA
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	M3PFBS
Perfluoroheptanesulfonic acid	PFHpS	M8PFOS
Perfluoroheptanoic acid	PFHpA	M4PFHpA
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	M2-4:2FTS
Perfluorohexanesulfonic acid	PFHxS	M3PFHxS
Perfluorohexanoic acid	PFHxA	M5PFHxA
Perfluoro-3-methoxypropanoic acid	PFMPA	MPFBA
Perfluoro-4-methoxybutanoic acid	PFMBA	M5PFPeA
Perfluorononanoic acid	PFNA	M9PFNA
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	M2-6:2FTS
Perfluorooctanesulfonic acid	PFOS	M8PFOS
Perfluorooctanoic acid	PFOA	M8PFOA
Perfluoropentanoic acid	PFPeA	M5PFPeA
Perfluoropentanesulfonic acid	PFPeS	M3PFHxS
Perfluoroundecanoic acid	PFUnA	M7PFUnA
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	d5-N-EtFOSAA

N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	d3-N-MeFOSAA
Perfluoro-1-butanesulfonamide	FBSA	M5PFHxA
Perfluoro-1-hexanesulfonamide	FHxSA	M8PFOA
Perfluorotetradecanoic acid	PFTA	M2PFTA
Perfluorotridecanoic acid	PFTrDA	M2PFTA
Perfluorooctanesulfonamide	FOSA	M8FOSA
Perfluorononanesulfonic acid	PFNS	M8PFOS
Perfluorodecanesulfonic acid	PFDS	M3PFBS

Appendix E:

Requirement	Specification	Acceptance Criteria
Demonstration of precision	Extract and analyze 7 replicate laboratory fortified blanks at the mid-range of the calibration.	Percent relative standard deviation must be </=20%.
Demonstration of accuracy	Calculate mean recovery for replicated used in demonstration of precision.	Mean recovery within 70-130% of the true value.
MDL Confirmation	Extract and analyze 9 blanks, and 9 laboratory fortified blanks at the proposed reporting limit over three days.	Calculated MDL and MDL-b is < Proposed reporting limit. Calculation done using 40CFR.
Calibration Verification	Analyze a mid-level QCS after each initial calibration.	Results must be within 70-130% of the true value.

Appendix F:

Table C-44. Method PFAS by LCMSMS Compliant with QSM Table B-15 Aqueous Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
2991-50-6	2-(N-Ethylperfluorooctanesulfonamido) acetic acid	1210	97.9	12.2	61	135
2355-31-9	2-(N-Methylperfluorooctanesulfonamido) acetic acid	1219	100.9	11.7	65	136
757124-72-4	Fluorotelomer sulphonic acid 4:2	789	103.2	13.2	63	143
27619-97-2	Fluorotelomer sulphonic acid 6:2	1673	102.4	12.5	64	140
39108-34-4	Fluorotelomer sulphonic acid 8:2	1657	102.3	11.6	67	138
31506-32-8	N-methylperfluorooctanesulfonamide	404	104.1	12.0	68	141
375-73-5	Perfluorobutanesulfonic acid	1832	100.8	9.4	72	130
375-22-4	Perfluorobutanoic acid	1270	100.6	9.2	73	129
335-77-3	Perfluorodecanesulfonic acid	1361	97.7	14.8	53	142
335-76-2	Perfluorodecanoic acid	1722	100.4	9.5	71	129
307-55-1	Perfluorododecanoic acid	1714	102.8	10.2	72	134
375-92-8	Perfluoroheptanesulfonic acid	1552	101.9	10.7	69	134
375-85-9	Perfluoroheptanoic acid	1837	101.4	9.5	72	130
355-46-4	Perfluorohexanesulfonic acid	1849	99.7	10.3	68	131
307-24-4	Perfluorohexanoic acid	1797	100.4	9.4	72	129
68259-12-1	Perfluorononanesulfonic acid	780	97.7	9.5	69	127
375-95-1	Perfluorononanoic acid	1846	99.9	10.0	69	130
754-91-6	Perfluorooctanesulfonamide	1453	101.9	11.4	67	137
1763-23-1	Perfluorooctanesulfonic acid	1744	102.7	12.4	65	140
335-67-1	Perfluorooctanoic acid	1962	102.2	10.1	71	133
2706-91-4	Perfluoropentanesulfonic acid	812	99.0	9.2	71	127
2706-90-3	Perfluoropentanoic acid	1695	100.7	9.3	72	129
376-06-7	Perfluorotetradecanoic acid	1714	101.8	10.0	71	132
72629-94-8	Perfluorotridecanoic acid	1696	104.8	13.0	65	144
2058-94-8	Perfluoroundecanoic acid	1746	100.8	10.6	69	133

Appendix G:

PFAS Aqueous sample centrifugation protocol (for DoD work in GW/SW/NPW)

Preliminary considerations:

The DoD QSM5.3, Table B-15, states that "[aqueous] samples with >1% solids may require centrifugation prior to SPE extraction." Samples should only be centrifuged when the suspended solids content appears visually high enough, by chemist inspection, that it would cause the SPE cartridge to clog. It is expected that the solid phase remains in the container when rinsing the container walls with the polar elution solvent. Rinsing the container walls would therefore also include rinsing of the solids. If removing the solvent disrupts the solid phase significantly, the container can be centrifuged again before removing the solvent for use during the elution step of the SPE procedure. When the sample has significant solids, the laboratory should account for the weight or volume displaced by the solids in the initial sample volume determination. One or more rinses of polar solvent can be used for quantitative transfers. Rinse the sample bottle and cap with elution solvent, pour the solvent from each rinse through the SPE cartridge during the elution step, and collect the filtrate for analysis. Bring to a quantitative final volume with the final injection solvent and vortex well. Whether or not an individual sample will require centrifugation for proper preparation will be determined and documented by the preparation analyst.

Procedure:

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

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

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

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

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

6. Transfer capped centrifuge bottles to centrifuge, ensuring that the centrifuge carousel is symmetrically balanced. Close top and centrifuge at 2200 RPM for 20 minutes.

7. Remove centrifuge bottles and decant the centrifuged liquid off of the condensed solids and back into the original sample bottle. Try to avoid transferring any of the condensed solids from the centrifuge bottle back to the original sample bottle, while maximizing the amount of liquid decanted off of the solid portion. Take weight for initial volume of sample without solids in original container.

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

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

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

11. Concentrate samples down to ~0.5 mL and reconstitute as outlined in sample extraction procedure.

12. Add a case narrative onto the work order indicating which samples had to be centrifuged.

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Management Approval:
Katherine Allen Approved on 5/18/2022 1:27:27 PM
Tod Kopyscinski Approved on 5/19/2022 11:33:10 AM

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure used by Contest, A Pace Analytical Laboratory (ELON) for the determination of Volatile Organic Compounds (VOCs) by Purge and Trap Gas Chromatography/Mass Spectrometry (GC/MS) by Method EPA 8260D.

The method is intended for the analysis of volatile compounds in all types of solid waste matrices, soils, sediment, sludges, TCLP extracts, waste solvents, oils, and ground and surface water.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided in Table 1, Appendix A.

LOQ are established in accordance with Pace policy and SOPs for method validation and for the determination of detection limits (DL) and quantitation limits (LOQ). DL and LOQ are routinely verified and updated when needed. The current LOQ for each target analyte that can be determined by this SOP as of the effective date of this SOP is provided in Table 1, Appendix A.

2.0 SUMMARY OF METHOD

Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a 5-ml water sample with helium (nitrogen – VOA7) at ambient temperature. The volatiles are transferred from the aqueous phase to the vapor phase and are swept through a sorbent trap where volatiles are trapped. At the completion of the purge time, the trap is rapidly heated and back flushed with helium (nitrogen – VOA7) to drive out the trapped analytes. The analytes are transferred into the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The mass spectrometer is operated in a repetitive scan mode. Analytes are identified by the GC/MS retention times and by a comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected primary ion relative to an internal standard against a calibration curve. Solid samples are analyzed via procedures outlined in Methods EPA 5030B/C and EPA 5035A. Samples can be handled in a closed loop system according to Method EPA 5035A.

3.0 INTERFERENCES

- Purge gas contamination
- Sample contamination due to septum diffusion
- Cross contamination
- Column contamination: bake
- Trap contamination: bake
- Purge and trap system contamination: wash purging chamber, bake out spargers, extended dry purges

Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the absorbent trap. The use of polytetrafluoroethylene (PTFE, Teflon) as thread sealants, tubing, or in flow controllers is highly recommended since other materials can be sources of contamination which may concentrate in the trap during the purging.

All materials utilized during this analysis and the GC/MS system must be demonstrated to be free from contamination. Running frequent instrument blanks and method blanks along with using purge and trap grade solvents will assist with the monitoring of laboratory contaminants within the analytical system. When potential interfering peaks are noted in laboratory reagent blanks, the analyst must determine the source of contamination and correct the problem before analysis of samples may continue.

A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive action to this condition is rinsing the purging apparatus and sample syringes with two or more portions of organic free water between samples. Analyze one or more blanks to check for cross contamination prior to sample analysis.

Since methylene chloride and acetone are common laboratory solvents, special precautions must be taken. The volatiles analysis and sample storage area should be located as far as possible from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system and maintained under positive pressure to prevent intrusion of contaminants. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

Chloroform is an interference from Chlorinated town water, which the DI system does not completely remove. Purging DI water prior to use eliminates interference.

4.0 DEFINITIONS

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

5.0 HEALTH AND SAFETY

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

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)

- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides containers for the collection of samples upon client request. Refer to laboratory SOP ENV-SOP-ELON-0017_Bottle Prep for procedures related to preparation of bottle kits for the test method(s) associated with this SOP.

The laboratory does not perform sample collection or field measurements for this test method. Samples should be collected in accordance with a sampling plan and sampling procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Aqueous	40mL VOA vials with Teflon-lined septa screw caps	5mL	Thermal: 4 ± 2℃ Chemical: Acidified with 1:1 HCL to pH <2 (3-4 drop), no headspace	14 Days
Soil/Sediment Samples High-Level Analysis (EPA 5035A/5030)	40mL VOA vials with Teflon-lined septa screw caps	5grams/10grams/15grams	Thermal: 4 + 2℃ Chemical: 1mL purge and trap grade methanol for every gram soil/sediment. (5g/5mL, 10g/10mL, or 15g/15mL) -Protect from sunlight	14 Days
Soil/Sediment Samples Low-Level Analysis (EPA 5035A)	40mL VOA vials with Teflon-lined septa screw caps	5grams	Thermal: 4 + 2℃ Chemical: 5grams soil to5 mL sodium bisulfate solution, Teflon-coated magnetic stir bar; protect from light OR freeze sample in vial (containing 5mLs of purged DI water) within 48 hours of collection	14 Days

[1] *Amount of sample required for each discrete test.*

All samples should be collected straight into VOA vials in the field. When this is not done a lab prep will be performed and data will be qualified.

Thermal preservation is checked and recorded on receipt in accordance with laboratory SOP Log-in. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

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

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

- Purge and trap systems:
    - EST Encon concentrator and EST Archon Autosampler
    - EST Encon Evolution concentration and EST Centurion WS Autosampler
- GC/MS systems
    - HP 6890/HP5973 and
    - HP7890/HP5975
    - HP7890/HP5977
- GC/MS data system: Windows NT or 2000 and Windows 7
- Teledyne Tekmar Atomx Autosampler/concentrator
- Analytical balance; capable of accurately weighing 0.0001g

7.2 Supplies

- GC column
    - Restek DB- 624 capillary 20 m, 0.18 mm ID, 1um thickness
    - Restek DB-VRX capillary 20m, 0.18mm ID, 1um thickness
- Analytical Trap: VOCARB3000 or equivalent
- 40-ml vials/cap and Teflon silicone septum
- Micro syringes
- Volumetric glassware
- 2-ml vials/caps and Teflon silicone septum
- 50mL Gastight Syringe
- 5mL Gastight Syringe

8.0 REAGENTS & STANDARDS

8.1 Reagents

- Organic free water: distilled and purged with ultra-high purity nitrogen for 30min

- Methanol: purge and trap grade

  Ultra-high purity helium: carrier and purge gas

8.2 Standards

8.2.1 Internal Standard/Surrogate Stock:

Purchased as certified solutions from Agilent. IS solutions have a 6-month expiration date and should be refrigerated when not in use.

The internal standard stock solution (cat # STM-341N) contains pentafluorobenzene, d4-dichlorobenzene, chlorobenzene-d5, and 1.4-difluorobenzene-d4: all are at a concentration of 2000 ug/mL in methanol.

The surrogate stock solution (cat #STM-260) contains 4-bromofluorobenzene, 1, 2-dichloroethane-d4, and toluene-d8: all are at a concentration of 2500 ug/mL in methanol.

All client samples, blanks, and quality control samples contain the internal standard compounds at a concentration of 30ug/L and the surrogate standards at 25ug/L.

Note: 1.0uL of the working internal standard/surrogate solution is added by the Archon Autosampler directly to all client samples, blanks, and quality control samples before purging is initiated.

Note: 5.0uL of the working internal standard/surrogate solution is added by the Centurion WS Autosampler directly to all client samples, blanks, and quality control samples before purging is initiated.

Note: IS solutions have a 6-month expiration date and should be refrigerated when not in use.

8.2.2 GC/MS Volatile Organic Standards

The GC/MS VOA (8260) Working Stock is prepared from the following stocks:

Stock	Vendor	Stock Conc. (mg/mL)	uL Stock Added into 10 mLs MeOH	Working Stock Conc. (ug/mL)
M-8260-ADD-10X	AccuStandard	2.0	500	100
M-502	AccuStandard	2.0	50	10
M-8015B/5031-03	AccuStandard	10	100	100
S-17412-R2	AccuStandard	2/20	50	10/100
70174	Absolute	1	1000	100
V-028S-20X	AccuStandard	2.0	50	10

Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at 4℃. Methanol solutions prepared from gaseous analytes are not stable for more than one week.

Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer unless the acceptability of the standard can be documented.

The light gases including Dichlorodifluoromethane, Chloroethane, chloromethane, bromomethane and vinyl chloride will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases need to be replaced after six months or as recommended by the standard manufacturer unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

All three xylene isomers will be included at a concentration of 0.5 ppb each in the low concentration initial calibration standard. The RL for each of the xylene isomers will be 0.5 ppb or the lowest standard in the initial calibration.

Note: m+p xylenes reported together (co-elute) (1.0 ppb RL) o-xylene reported separately (0.5 ppb R.L)

8.2.3 Calibration Standards

Standard concentrations are prepped daily from the working solution.

For 8260 Water (Stock = 10ug/mL); 5mL of std. is purged on the autosampler:

Working Stock (uLs)	Final Volume D.I. water (mLs)	Final Conc. (ppb)
4uL	100mL	0.4ppb
5uL	100mL	0.5ppb
10uL	100mL	1.0ppb
20ul	100mL	2.0ppb
50uL	100mL	5.0ppb
100uL	100mL	10ppb
200uL	100mL	20ppb
100uL (50ug/mL)	100mL	50ppb
200uL (50ug/mL)	100mL	100ppb
400uL (50ug/mL)	100mL	200ppb

For 8260 Soil (Stock = 50ug/mL); 5mL of water is added to 5mL of std. before purge by the autosampler:

Working Stock (uLs)	Final Volume D.I. water (mLs)	Final Conc. (ppb)
4uL (10ug/mL)	100mL	0.2ppb (for VOA4 only)
8uL (10ug/mL)	100mL	0.4ppb (for VOA1 and VOA7 only)
2uL (50ug/mL)	100mL	0.5ppb
4uL (50ug/mL)	100mL	1.0ppb
20uL (50ug/mL)	100mL	5.0ppb
40uL (50ug/mL)	100mL	10ppb

80uL (50ug/mL)	100mL	20ppb
10uL (50ug/mL)	5mL	50ppb
16uL (50ug/mL)	5mL	80ppb
20uL (50ug/mL)	5mL	100ppb (for VOA1 and VOA7 only)
40uL (50ug/mL)	5mL	200ppb (for VOA4 only)

Note: After the calibration standards are prepared in 100 mL volumetric flasks, they are transferred to 40-mL vials and placed into the Autosampler.

8.2.4 QC Check/LCS & Matrix Spike Stock

Stock	Vendor*	Cat # *	Stock Conc. ug/mL	uL Stock Added Into 10 mLs MeOH	Final Working Conc. (ug/mL)
VOC Mixture with MTBE	Agilent	DWM-596-1	2000	100	20
Custom Gas Mix	Agilent	CUS-28408	Various concentrations	100	20/200
Vinyl Acetate	RESTEK	30216	2000	1ml	200
Ethanol	RESTEK	30288	2000	1mL	200
Custom Mix	Agilent	CUS-28609, CUS-00002161, or CUS-00004852 or equiv.	2000/20000	100	20/200
1,2,3-Trimethylbenzene	Phenova	ALO-101810	2000	100	20

*Or equivalent

8.2.5 Internal Standards/Surrogates

624/8260 H2O IS/SURR mix VOA 2,3,5,6:

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 50mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Agilent	2.0	750	30
STM-262(SURR)	Agilent	2.5	500	25

8260 Soil IS/SURR mix VOA 1:

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 5mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Agilent	2.0	750	300
STM-262(SURR)	Agilent	2.5	500	250

8260 Soil IS/SURR mix VOA 4 and VOA7:

Stock	Vendor	Stock Conc. (mg/mL)	µL Stock added into 25mLs	Working Stock Conc. (µg/mL)
STM-341N(IS)	Agilent	2.0	750	60
STM-262(SURR)	Agilent	2.5	500	50

9.0 PROCEDURE

9.1 Analysis Sequence

The order of analysis for each 12-hour analysis shift is as follows:

Time 0: BFB Instrument Performance Check
Calibration Verification Standard
LCS/LCSD
Method Blank
Last Reported Sample Runs at 12Hrs: Samples

The last sample in the sequence must be injected within 12 hours of the time that the BFB instrument performance check was injected at the start of the sequence.

Note: For 8260D BFB is only required to pass before ICAL, not every 12 hours.

If more than 20 samples are run during any 12-hour shift, then additional batch QC samples must be analyzed to achieve an overall frequency of 5 percent (1 set of QCs and blank for every 20 samples) during each analysis shift.

The analysis sequence is documented on an analysis run log maintained by the analyst.

9.2 MS Calibration and Tuning

Auto tune with PFTBA with column temperature at 45℃

Tune with 50ng of BFB with column temperature at 125℃ and meet the following criteria:

Mass	m/z abundance criteria
50	15 to 40% of Mass 95
75	30 to 60% of Mass 95
95	Base Peak, 100% relative abundance
96	5 to 9% of Mass 95
173	<2% of Mass 174
174	>50% but <200% of Mass 95
175	5 to 9% of Mass 174
176	>95% but <101% of Mass 174
177	5 to 9% of Mass 176

Note: These limits are tighter than the method required limits. See Table 3 of 8260D.

The mass spectrum of BFB that is evaluated against the acceptance criteria is obtained in the following manner: three scans (the peak apex and the scans immediately preceding and following

the apex) are averaged, and a single scan no more than 20 scans prior to the BFB peak is subtracted. No part of the BFB peak itself may be background-subtracted.

The BFB relative abundance criteria must be met before any standards, site samples, or quality control samples are analyzed.

9.3 Default Archon/Centurion and Encon Instrument Conditions (VOA Instruments #1, 2, 4, 5 and 7)

9.3.1 Encon concentrator:

Flow rate: 40.0 ml/min.
Purge ready temp.: 35℃
Purge time: 11min.
Desorb time: 1.0 min.
Desorb temp: 250℃
Bake time: 8 min.
Bake temp: 260 ℃
Dry Purge: 2 min.
Water Management: Ready – 40°C
Bake – 260°C

9.3.2 Archon Autosampler:

Sample volume: 5 mL
Rinse volume: 5 ml (waters only).
Rinses: 2 (waters only).
Syringe flushes: 1
Preheat temp: 40 (soils only).
Preheat time: 0.5 min (soils only).
Purge time: 11 min.
Desorb time: 0.5-1.0 min.

9.3.3 Gas Chromatogram

Injector temp.: 200℃
Detector temp.: 230℃
Interface temp: 180-230℃ (instrument dependent)
Oven equilibration time: 0.5min.
Column program: 45℃ for 3 min.,
Ramp at 15-28℃/min.,
final temp. 210-220℃for 1-2 min.
Run time: 12-15 min.
Splitless valve time: 0.0
Split flow: 50-90ml/min
Split ratio: 50-60:1

9.3.4 Mass Spec

Mass range: 35 to 300
Number of A/D samples: 16
Peak threshold: 10000
Threshold: 20 counts

Scan start time: 0.5-1.4 min.

The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound, and compounds quantitated by SIM must be noted in the final report

9.4 Default Tekmar Instrument Conditions (VOA Instruments #3 and 6)

9.4.1 Purge

Valve Oven Temp: 140°C
Transfer Line Temp: 140°C
Sample Mount temp: 90°C
Water Heater Temp: 90°C
Sample Vial Temp: 20°C
Sample Equilibrate Time: 0.00 min
Soil Valve Temp: 50°C
Standby Flow: 10mL/min
Purge Ready Temp: 40°C
Condensate Ready Temp: 45°C
Pre-sweep Time: 0.25 min
Prime Sample Fill Volume: 3.0mL
Sample Volume: 5.0mL
Sweep Sample Time: 0.25 min
Sweep Sample Flow: 100mL/min
Sparge Vessel Heater: Off
Sparge Vessel Temp: 20°C
Pre-purge Time: 0.00 min
Pre-purge Flow: 0mL/min
Purge Time: 11.00 min
Purge Flow: 40mL/min
Purge Temp: 20°C
Condensate Purge Temp: 20°C
Dry Purge Time: 0.50 min
Dry Purge Flow: 100mL/min
Dry Purge Temp: 20°C

9.4.2 Desorb

Methanol Needle Rinse: Off
Methanol Needle Rinse Volume: 3.0mL
Water Needle Rinse Volume: 7.0mL
Sweep Needle Time: 0.25 min
Desorb Preheat Temp: 245°C
GC Start Signal: Start of Desorb
Desorb Time: 1.00 min
Drain Flow: 250mL/min
Desorb Temp: 250°C

9.4.3 Bake

Methanol Glass Rinse: Off
Number of Methanol Glass Rinses: 1
Methanol Glass Rinse Volume: 3.0mL
Number of Water Bake Rinses: 1
Water Bake Rinse Volume: 7.0mL
Bake Rinse Sweep Time: 0.25 min
Bake Rinse Sweep Flow: 100mL/min
Bake Rinse Drain Time: 0.40min
Bake Time: 8.00 min
Bake Flow: 200mL/min
Bake Temp: 280°C
Condensate Bake Temp: 200°C

9.5 Sample Preparation and Analysis

9.5.1 Low Level Water Samples

Low level water samples need no preparation. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler. 1.0uL of IS/Surr standard is added by the Archon AS or 5.0uL of IS/Surr standard is added by the Centurion AS.

9.5.2 High Level Water Samples

High level water samples are diluted in a volumetric flask by analyst. The diluted sample is then transferred to a 40 ml VOA vial. 5 mL of the sample is transferred from the 40mL vial and to the concentrator for analysis. Internal standards and surrogates are added by the autosampler. 1.0uL of IS/Surr standard is added by the Archon AS or 5.0uL of IS/Surr standard is added by the Centurion AS.

9.5.3 Low Level Soils

If low level soil samples are not preserved, then lab analyst will weigh samples to nearest 0.1 gram using approximately 5 grams and record in the 8260soil prep excel spreadsheet.

OR

Method 5035A: Low concentration soil method (generally applicable to soils and other solid samples with VOC concentrations in the range of 0.5 to 200 ug/kg).

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screwcap that already contains sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40 degrees C and the volatiles purged into an appropriate trap using an inert gas. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

Method 5035A: Low concentration soil method for frozen soil samples

Samples are taken in the field with DI vials provided by the lab and then vials are frozen within 48 hours. These vials are sampled with approximately 5 grams; same procedure as the above 5035. Frozen samples are to be allowed to warm up to room temperature for ~ 30 minutes prior to analysis.

9.5.4 High Level Soils/Wastes/Oils

High level samples are extracted with methanol in a 40 mL vial. Samples are weighed, between 0.1g and 10g, recorded in the 8260soil prep excel spreadsheet, (to the nearest 0.1g) in a 40 mL vial and 15mls of purge&trap methanol are added. 1mL of surrogate solution is added through the septum, using a 1mL syringe, when requested by client, otherwise surrogate is added through the auto-sampler. The sample is shaken for two minutes and allowed to settle. After settling a portion of the methanol extract, between 5uL and 500uL is added to a final volume of 100mL. (Varied amounts depending on sample matrix) and Transfer 40mL to VOA vial. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler. Note: the amount of sample used, and the amount of extract analyzed may vary depending on the expected concentration of the sample.

OR

Method 5035A: High concentration soil method (generally applicable to soils and other solid samples with VOC concentrations greater than 200 ug/kg).

Samples are preserved in pre-weighed vials containing methanol in the field. Analysis proceeds as above.

The low-level sample introduction technique listed above is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 ug/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system. In such instances, this method describes two collection options and the corresponding sample purging procedures.

The first option is to collect a bulk sample in a vial or other suitable container without the use of preservative solution. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

The second option is to collect an approximately 15-g sample in a pre-weighed vial with a septum-sealed screwcap that contains 15 mL methanol. At the time of analysis, an aliquot of the solvent is removed from the vial, diluted w/ H20, and purged using Method 5030 and analyzed by an appropriate determinative method.

High concentration oily waste method (generally applicable to oily samples with VOC concentrations greater than 200 ug/kg that can be diluted in a water-miscible solvent).

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

9.5.5 TCLP Extracts

The TCLP extract is diluted 10x with zero headspace in a 40 ml VOA vial. 5 mL of the sample is transferred from the 40mL vial and transferred to the concentrator. Internal standards and surrogates are added by the autosampler.

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Water Sample Calculation

Sample concentration, ppb = (direct reading from instrument) X (dilution factor, if any dilutions were required).

10.2 Soil Sample Calculation

$$\frac{\text{(ug/L from instrument) X (0.010 L sparger volume)}}{\text{(g/mL, from sample prep) X (mL of sample used)}} = \text{ug/gram = mg/Kg (ppm)}$$

10.3 Internal Standard Calculation from Response Factor 8260 Method Calculation:

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

Where:
As = Peak area (or height) of the analyte or surrogate.
Ais = Peak area (or height) of the internal standard.
Cs = Concentration of the analyte or surrogate.
Cis = Concentration of the internal standard.

10.4 Data Analysis

A minimum signal-to-noise ratio of 3:1 (based on peak height) must be achieved for any peak used in a calibration standard, client sample, or quality control sample.

To prevent overwriting manual integrations, the analyst should not re-quantitate calibration standard files, unless dictated by certain regulations to validate the calibration.

When preparing to establish a new initial calibration, to prevent carry-over of numbers from previous calibrations, the analyst should “clear all response factors” (which is a function in the software) from old calibration curves prior to processing the new curve.

10.5 Data Processing

10.5.1 GC/MS VOA files

Data files numbered sequentially starting with instrument, date, and file number.

10.5.2 Reporting Package

The reporting package that is delivered to clients will consist of the sample results, the surrogate recovery results and any matrix spikes, blanks, duplicates, and lab fortified blanks that pertain to the clients' samples.

MCP Data Enhancement and Connecticut RCP projects will include required deliverables plus a case narrative and certification form.

10.5.3 Data Filing

Injection logs and bench sheets are filed in File Boxes and all raw data are archived on the A: drive as a pdf.

Data to be saved on CD or DVD.

All data batch files from instruments.

10.6 Tentatively Identified Compounds (TICs)

Initially include all the non-target compounds that have a peak area count of ≥ 10% of the nearest internal standard.

Use the following guidelines for making tentative identification:

The spectral library match must be ≥80% for a tentative identification to be made.

For 8260 MA MCP match must be ≥85%

The 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.

The relative intensities of the major ions should agree within ± 20%.

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

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.

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.

Quantitative analysis:

The nearest internal standard shall be the one that is used to calculate concentration, and the RF for the compound should be assumed to be 1.

The resulting concentration should be reported indicating that the value is an estimate.

10.6.1 Manual Integration

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

approved in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration.* Refer to this SOP for guidance on manual integration techniques and required procedures.

When performing manual integration of any peak in a calibration standard, client sample, or quality control sample, the integration must be performed in conformance with the procedures outlined in the Manual Integration SOP. In summary:

The most appropriate instrument parameters should be used during method development to allow for automatic integration by the data system in most cases.

All data must be integrated consistently for all standards, samples, and QC samples.

In those instances when the automated software does not integrate a peak correctly, manual integration may be used to correct the improper integration performed by the data system. Manual integration should always be performed to create the analyst's best estimate of the actual peak area discerned from the chromatogram.

All manual integrations must be documented by printing before and after, initialing and dating the manual integrations as well as by recording the reasons for the manual integrations.

11.0 Quality Control & Method Performance

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action(s). An analytical batch is defined as up to 20 client samples of a similar matrix for the same analysis. All quality control samples are assigned to and associated with a particular analytical batch, which is designated at the time samples are logged-in or at the time of sample preparation. All quality control samples must be traceable to the associated analytical batch for review and evaluation purposes.

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	As Required.
Matrix Spike	MS	As Requested, or 1 per batch of 20 or fewer samples, if provided sufficient sample. If batch exceeds 20 samples, every 20 samples
Matrix Spike Duplicate	MSD	As Requested, or 1 per batch of 20 or fewer samples, if provided sufficient sample. If batch exceeds 20 samples, every 20 samples
Sample Duplicate	SD	Client requested
Trip Blank	TB	Client requested
Surrogate	SSTD	Added to all blanks, standards, client samples, and quality control samples
Internal Standards	ISTD	Internal standards are monitored in each client sample, blank, quality control sample analysis.

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Appendix B for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Tune (MS Only)		Required before calibration – Lab performs daily
Initial Calibration Verification	ICV	After each new ICAL
Continuing Calibration Verification	CCV	At the start of each 12-hour analysis sequence

11.3 Method Performance

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

11.3.2 Calibration Curve

Initial calibration is performed before any samples are analyzed. Initial calibration must also be performed when major instrument maintenance is performed.

Calibration Criteria for samples run by Method 8260 D protocols:

A minimum (5)-point calibration curve is used to calibrate the system for all target analytes and surrogates. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the low initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates.

The %RSD for all target analytes compounds over the working range must be ≤20% for the average RRF to be used for subsequent calculations.

A minimum response factor for compounds in TABLE 4.0, is for guidance, it is neither expected nor required that these minimum RFs be meet. However, is recommended that if RF is <0.01, that the concentration of said analyte be increase.

If %RSD is >20% for any target analyte, then a linear regression must be established using the calibration data for that compound (see EPA Method 8000D, Section 11.5.2). For the linear regression to be acceptable for quantitative purposes, when using r must be ≥0.995 and when using r^2 must be ≥0.99. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results. When calculating the calibration curves using linear regression, a minimum quantitation check should be performed by re-fitting the response from the low concentration calibration standard back into the curve (SEE Method 8000D). The recalculated concentration of the low calibration point should be within ± 50% of the standards true calculation if it is the lowest point and ± 30% for all others (i.e., above the low standard). Analytes which do not meet the minimum quantitation calibration criteria should be considered “Out of

control" and corrective action such as redefining the lower limit and/or reporting "Out of control" analytes as estimated.

Additional Calibration Criteria for samples run by MA MCP protocols:

A minimum response factor for compounds in TABLE 4.0, must be demonstrated for each individual calibration level. Meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. **Compounds not meeting criteria should be considered estimated. If the RF of any compound is <0.01 data is to be qualified, as it affects all non-detected results.**

Additional Calibration Criteria for samples run by CT RCP protocols:

The %RSD for all target analytes compounds over the working range must be **<20%** for the average RRF to be used for subsequent calculations.

If %RSD is >20% for any target analyte, then a linear regression must be established using the calibration data for that compound (see EPA Method 8000D, Section 11.5.2). For the linear regression to be acceptable for quantitative purposes, when using r must be ≥0.995 and when using r^2 must be ≥0.99. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results. When calculating the calibration curves using linear regression, a minimum quantitation check should be performed by re-fitting the response from the low concentration calibration standard back into the curve (SEE Method 8000D). The recalculated concentration of the low calibration point should be within **± 30%** of the standard's true calculation. Analytes which do not meet the minimum quantitation calibration criteria should be considered "Out of control" and corrective action such as redefining the lower limit and/or reporting "Out of control" analytes as estimated.

For all 8260 methods:

If any initial calibration standard analysis is determined to be unusable (e.g., a bad injection), the standard may be re-analyzed before any samples are run. The re-analysis results may be incorporated into the initial calibration in their entirety, in place of the original analysis. If the initial calibration still does not meet acceptance criteria, even with the replacement standard, then the entire initial calibration should be performed again.

If the initial calibration still does not meet acceptance criteria for a particular analyte, the analyst may consider dropping the lowest or highest point for that analyte and recalculating the average RRF and %RSD or linear regression. Note that ONLY the lowest or highest data point may be dropped – a data point from the middle of the calibration range may NOT be dropped. Note also that if the low standard is dropped, the RL for that analyte must be adjusted so that the lowest standard used for the calibration is less than or equal to the RL.

When the instrument data system is updated to reflect the new initial calibration, the analyst verifies that it has been properly set up to calculate each target analyte according to the actual model used to establish the initial calibration (i.e., average RRF or linear regression) and to reflect any abbreviated ranges established for individual analytes.

High level soil surrogate calibration for MeOH preservation samples is run on a 7pt curve: 1ppb, 2ppb, 5ppb, 10ppb, 25ppb, 50ppb, and 100ppb. The criteria are the same as initial calibration curve for method 8260.

The initial calibration curve is verified immediately, using a second source standard. The acceptable limits are 70-130%. Analytes outside of criteria should be considered estimated.

Note: ICV for MA MCP & CT RCP does allow for difficult compounds to exhibit percent recoveries of 40-160%. However, data is still to be qualified.

11.3.3 Continuing Calibration Check (CCC/CCV)

Continuing Calibration Criteria for samples run by Method 8260 D protocols:

At the start of each 12-hour analysis sequence, before any samples are analyzed, a 10ppb calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be ±20%. Exceedances are noted in a case narrative.

Additional Continuing Calibration Criteria for samples run by MA MCP protocols:

At the start of each 12-hour analysis sequence, before any samples are analyzed, a 10ppb calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be ≤20%. **"Difficult" analytes must exhibit %D of ≤60%.** Exceedances are noted in a case narrative.

A minimum response factor for compounds in TABLE 4.0, must be demonstrated for the calibration level. Compounds not meeting criteria should be considered estimated.

Additional Continuing Calibration Criteria for samples run by CT RCP protocols:

A minimum response factor for compounds in TABLE 4.0, must be demonstrated for the calibration level. Compounds not meeting criteria should be considered estimated.

For all 8260 methods:

If the minimum RRF or percent difference/drift criteria are not met for any target analyte based on the data quality objectives for the samples, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, compressed gas cylinders, syringes, column fittings, etc.; clean the MS source, changing an injector port or filament, cleaning the inlet, etc.). If corrective action that may affect instrument response is taken, then the calibration verification standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration verification standard, then a new initial calibration must be performed.

Any non-conformance associated with initial or continuing calibration that affects the usability of the data or otherwise as specified in an associated QAPP or the data quality objectives must be narrated and the data qualified.

Internal Standard (IS) retention times must be evaluated in the calibration check standard. The IS retention times should be within ± 30 seconds of the retention times from the midpoint standard of the initial calibration. If the retention times shift more than

30 seconds, the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is run.

IS areas must be evaluated in the calibration check standard. If the IS areas change by more than a factor of two (-50% to +100%) from the areas in the midpoint standard of the most recently analyzed initial calibration, then the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is run.

If corrective action requires major instrument maintenance, then performing a new initial calibration is automatically required.

If two calibration check standards are run in succession, one immediately following the other, and neither is deemed to have been a bad injection, then the one closest in injection time to the associated sample analyses, or both standards, must be evaluated for and pass method performance criteria for sample analyses to continue. In addition, the two calibration check standards are documented by the analyst for evaluation of reproducibility.

11.3.4 Surrogates

Surrogates are added to all blanks, standards, client samples, and quality control samples. The surrogates are checked and documented. Percent recoveries must be 70-130% for individual surrogate compounds. If the %R is outside of control limits, the sample must be reanalyzed unless interference is noted. One high surrogate standard recovery associated with a sample that has all target compounds “non-detected” is permissible.

11.3.5 Internal Standards

Internal standards are monitored in each client sample, blank, quality control sample analysis. Acceptable criteria for the internal standards response is 50-200% of the response in the associated continuing calibration standard. Retention times of internal standards must be within ±30 seconds of retention times in the associated continuing calibration standard.

The internal standard selected for calculation of the RRF for the concentration of each target analyte should be the internal standard with a retention time closest to the analyte being measured.

11.3.6 Method Blank (MB)

A matrix-specific method blank must be analyzed 1 per batch of 20 samples or less, prior to running samples and after calibration standards. Target analytes must be <RL except for common laboratory contaminants (such as acetone, chloroform, methylene chloride, toluene, and MEK which must be <5x the RL). Flag any contamination to qualify the sample results.

If the method blank does not meet these criteria, appropriate corrective action is taken (bake the trap or column, flush the transfer lines, etc.). An acceptable method blank must be analyzed prior to sample analyses.

11.3.7 Laboratory Control Sample (LCS)

A matrix specific LCS and duplicate is analyzed 1 per batch of 20 samples or less, or for each new window. The LCS is prepared from a different stock than that of the calibration curve, and is matrix matched to the samples of that batch. The concentration should be between the low and mid-level standard and must contain all analytes. The percent recoveries must be 70-130%R for most compounds (document exceedances for "difficult compounds"). Difficult compounds are evaluated regularly. Reduction in the number of difficult compounds is a laboratory goal through corrective action and technical improvements. No greater than 10% of the total targets can be outside of control limits for analysis to proceed.

8260D states that matrix spikes and laboratory control samples should be prepared from the **same source as the ICAL**(Section 7.12 of 8260D Method). When the LCS is prepared in the same manner as the CCV, the same standard can be used as both LCS and CCV. However, when done this way MA MCP & CT RCP requires it to pass same criteria as CCV. 8260D only suggests to use the CCV criteria.

11.3.8 Matrix Spike (MS)

Analyzed at a frequency equivalent to 1 per batch of 20 samples or less. The MS working stock is prepared at a concentration of 20 ug/mL (from a source different than that of the calibration curve). Must contain all the target analytes.

Water prep: 20uL working stock into 40 mL sample (when enough sample is collected) True value = 10 ppb

Soil prep: 5uL working stock into sample vial with either DI or Bisulfate (when enough sample is collected). The Archon adds another 5mL purge&trap water; final volume = 10mL. True value = 10 ppb

The %R must be 70-130. If percent recoveries exceed these limits, check the LCS: if recoveries are acceptable in the LCS, narrate nonconformance.

11.3.9 Matrix Spike Duplicates (MSD)

Analyze MS in duplicate at a frequency of 1 per batch of 20 samples or less when additional VOA vial is available. RPDs must be <20% for waters and <30% for solids.

11.3.10 TCLP Method Blank

A TCLP method blank must be analyzed with each set of TCLP extracts. The TCLP method blank is diluted 10x with zero headspace in a 40 ml volumetric VOA vial, I.S./Surr. Std. is added via autosampler and the sample is purged.

11.3.11 TCLP Matrix Spike

A representative TCLP matrix spike must be analyzed with each set of TCLP samples. The TCLP matrix spike is diluted 10x with zero headspace in a 40ml VOA vial, 40uL of the matrix spike solution and I.S./Surr. Std. is added via autosampler and the sample is purged.

12.0 DATA REVIEW & CORRECTIVE ACTION

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-ELON-0035_Data Review for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

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

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

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

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have not been modified from the reference test method(s) cited.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.
- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015 *Document Management* and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: Routine Analyte List and LOQ
- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev.4, June 2018, Method 8260D.
- MA DEP, MCP Data Enhancement Program, “Quality Control Requirements and

  Performance Standards for the Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in support of Response Actions under the Massachusetts contingency Plan (MCP)”, Rev.1, July 1, 2010.
- CT DEP. Recommended Reasonable Confidence Protocol. Quality Assurance and Quality Control Requirements. VOC Method 8260, SW-846, Ver. 3.0, July 2006.
- EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev 1, July 2002, Method 5035A.
- EPA, Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods, SW-846, Rev. 3 May 2003, Method 5030C.
- EPA, Test Methods 8000D, Determinative Chromatographic Separations, Rev. 5, March 2018.
- HP 5890 Gas Chromatograph Operating Manual, Edition 5, October 1991.
- HP 5970 Gas Chromatograph Operating Manual, 1991
- Encon Purge & Trap Operating Manual, EST Analytical, 2002
- Archon Purge & Trap Autosampler System Operating Manual, Varian, 2000, p/n 03-914642
- ELON QA Manual Doc#610

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Catherine Rouleau	Volatiles Supervisor	05/18/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
All	Updated to Pace SOP template
2.0 + 8.2.3	Addition of VOA7
6.0	Note added that samples not collected in VOA vials in field will be prepped in lab and qualified
7.1	HP 7890/5977 added
9.2	Note added that tune limits are tighter than method
10.6	TIC criteria changed to ≥80% for 8260D and ≥85% for MA MCP
11.3.2	Updated entire Cal section
11.3.3	Updated entire CCV section
11.3.7	Added 8260D criteria for LCS
11.3.8	Added Bisulfate
11.3.9	Added RPD criteria
11.3.10+11.3.11	Added IS/Surrogate

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
Doc#50 Rev 15	SOP 8260	03/11/2021

Appendix A: Target Analyte List and LOQ

Table 1: Standard Analyte List and LOQ

Analyte	CAS #	LOQ[1] Aqueous (ug/L)	LOQ[1] Soils and P/S (mg/kg)
1,1,1,2 TETRACHLOROETHANE	630-20-6	1.0	0.002
1,1,1 TRICHLOROETHANE	71-55-6	1.0	0.002
1,1,2,2 TETRACHLOROETHANE	79-34-5	0.5	0.001
1,1,2 TRICHLOROETHANE	79-00-5	1.0	0.002
1,1,2TRICHLORO-1,2,2 TRIFLUOROETHANE "NR"	76-13-1	1.0	0.01
1,1 DICHLOROETHANE	75-34-3	1.0	0.002
1,1 DICHLOROETHENE	75-35-4	1.0	0.004
1,1 DICHLOROPROPENE	563-58-6	2.0	0.002
1,2,3 TRICHLOROBENZENE	87-61-6	5.0	0.002
1,2,3 TRICHLOROPROPANE	96-18-4	2.0	0.002
1,2,4 TRICHLOROBENZENE	120-82-1	1.0	0.002
1,2,4 TRIMETHYLBENZENE	95-63-6	1.0	0.002
1,2 DIBROMO-3-CHLOROPROPANE	96-12-8	5.0	0.002
1,2 DIBROMOETHANE	106-93-4	0.5	0.001
1,2-DICHLOROBENZENE	95-50-1	1.0	0.002
1,2 DICHLOROETHANE	107-06-2	1.0	0.002
1,2 DICHLOROETHENE (TRANS)	156-60-5	1.0	0.002
1,2 DICHLOROPROPANE	78-87-5	1.0	0.002
1,3,5-TRICHLOROBENZENE	108-70-3	1.0	0.002
1,3,5 TRIMETHYLBENZENE	108-67-8	1.0	0.002
1,3-DICHLOROBENZENE	541-73-1	1.0	0.002
1,3 DICHLOROPROPANE	142-28-9	0.5	0.001
1,4-DICHLORO-2-BUTENE(trans) "NR"	110-57-6	2.0	0.004
1,4-DICHLORO-2-BUTENE(cis) “NR”	1476-11-5	1.0	0.002
1,4-DICHLOROBENZENE	106-46-7	1.0	0.002
1,4-DIOXANE	123-91-1	50.0	0.1
2,2 DICHLORPROPANE	594-20-7	1.0	0.002
2 BUTANONE (METHYL ETHYL KETONE, MEK)	78-93-3	20.0	0.04
2 CHLOROTOLUENE	95-49-8	1.0	0.002
2 HEXANONE	591-78-6	10.0	0.02
4 CHLOROTOLUENE	106-43-4	1.0	0.002
ACETONE	67-64-1	10.0	0.1
ACRYLONITRILE "NR"	107-13-1	5.0	0.006
BENZENE	71-43-2	1.0	0.002
BROMOBENZENE	108-86-1	1.0	0.002
BROMOCHLOROMETHANE	74-97-5	1.0	0.002
BROMODICHLOROMETHANE	75-27-4	0.5	0.002
BROMOFORM	75-25-2	1.0	0.002

BROMOMETHANE	**74-83-9**	**2.0**	**0.01**
N-BUTYL BENZENE	**104-51-8**	**1.0**	**0.002**
CARBON DISULFIDE	**75-15-0**	**5.0**	**0.01**
CARBON TETRACHLORIDE	**56-23-5**	**5.0**	**0.002**
CHLOROBENZENE	**108-90-7**	**1.0**	**0.002**
CHLOROETHANE	**75-00-3**	**2.0**	**0.02**
CHLOROFORM	**67-66-3**	**2.0**	**0.004**
CHLOROMETHANE	**74-87-3**	**2.0**	**0.01**
CIS-1,2-DICHLOROETHENE	**156-59-2**	**1.0**	**0.002**
CYCLOHEXANE	**110-82-7**	**5.0**	**0.01**
CIS 1,3 DICHLOROPROPENE	**10061-01-5**	**0.5**	**0.001**
DIBROMOCHLOROMETHANE	**124-48-1**	**0.5**	**0.001**
DIBROMOMETHANE	**74-95-3**	**1.0**	**0.002**
DICHLORODIFLOUROMETHANE	**75-71-8**	**2.0**	**0.02**
DIETHYL ETHER	**60-29-7**	**2.0**	**0.02**
DIFLUOROCHLOROMETHANE	**75-45-6**	**1.0**	**0.002**
DIISOPROPYL ETHER	**108-20-3**	**0.5**	**0.001**
ETHYL ACETATE	**141-78-6**	**10.0**	**0.01**
ETHYLBENZENE	**100-41-4**	**1.0**	**0.002**
ETHYL TERT-BUTYL ETHER	**637-92-3**	**0.5**	**0.001**
FLUORODICHLOROMETHANE	**75-43-4**	**1.0**	**0.002**
HEXACHLOROBUTADIENE	**87-68-3**	**0.6**	**0.002**
IODOMETHANE	**74-88-4**	**20.0**	**0.04**
ISOPROPYLBENZENE	**98-82-8**	**1.0**	**0.002**
METHYLCYCLOHEXANE	**108-87-2**	**1.0**	**0.002**
METHYL ACETATE	**79-20-9**	**1.0**	**0.002**
M/P XYLENES	**108383/ 106423**	**2.0**	**0.004**
METHYL TERT BUTYL ETHER(MTBE)	**1634-04-4**	**1.0**	**0.004**
METHYLENE CHLORIDE	**75-09-2**	**5.0**	**0.02**
METHYL ISOBUTYL KETONE (MIBK)	**108-10-1**	**10.0**	**0.02**
NAPHTHALENE	**91-20-3**	**2.0**	**0.004**
O XYLENE	**95-47-6**	**1.0**	**0.002**
P ISOPROPYLTOLUENE	**99-87-6**	**1.0**	**0.002**
N-PROPYLBENZENE	**103-65-1**	**1.0**	**0.002**
SEC-BUTYLBENZENE	**135-98-8**	**1.0**	**0.002**
STYRENE	**100-42-5**	**1.0**	**0.002**
TERT-AMYL METHYL ETHER	**994-05-8**	**0.5**	**0.001**
TERT-BUTYL ALCOHOL "NR"	**75-65-0**	**20.0**	**0.1**
TERT-BUTYLBENZENE	**98-06-6**	**1.0**	**0.002**
TETRAHYDROFURAN	**109-99-9**	**10.0**	**0.01**
TETRACHLOROETHENE	**127-18-4**	**1.0**	**0.002**
TOLUENE	**108-88-3**	**1.0**	**0.002**
TRANS 1,3 DICHLOROPROPENE	**10061-02-6**	**0.5**	**0.001**
TRICHLOROFLUOROMETHANE	**75-69-4**	**2.0**	**0.01**
TRICHLOROETHENE	**79-01-6**	**1.0**	**0.002**
VINYL ACETATE	**108-05-4**	**20.0**	**0.05**
VINYL CHLORIDE	**75-01-4**	**2.0**	**0.01**

[1] Values as of effective date of this SOP. LOQ are subject to change, contact quality personnel for most current information.

"NR" = not required for Massachusetts Contingency Plan (MCP)

Appendix B: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failures	Must meet one of curve fit options presented in Section 11.3.2. For any curve fit other than Average RF (RSD), curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 30% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
CCV	Daily, before sample analysis, after every 20, and at end of analytical window.	Opening CCV: All analytes within ± 20 %D	See Section 11.3.3 for required corrective actions based on circumstance.	Qualify analytes with CCV out of of criteria.
Internal Standards	Every field sample, standard and QC sample	Must meet criteria specified in Section 11.3.5.	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Surrogate	Every field sample, standard and QC sample	Must meet criteria specified in Section 11.3.4.	Troubleshoot instrument performance. Reanalyze samples or note if permissible	Qualify outages and explain in case narrative
Method Blank	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.6.	Flag any contamination	Qualify outages and explain in case narrative
LCS	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.7.	Troubleshoot instrument performance. Reanalyze samples or note if permissible	Qualify outages and explain in case narrative
MS/MSD	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.8 and 11.3.9.	If LCS is acceptable, narrate nonconformance	Qualify outages and explain in case narrative
Trip Blank	Client Request	<RL	Flag any contamination	Qualify outages and explain in case narrative

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure used by Contest, A Pace Analytical Laboratory (ELON) for the determination of Volatile Organic Compounds (VOCs) in air collected in specially prepared canisters and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) by Method EPA TO-15.

This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants listed in Title III of the Clean Air Act Amendments of 1990. The Air is collected in specially prepared canisters (silco steel, silonite or summa), separated by a gas chromatograph and measured by mass spectrometry. The VOCs in this method have been tested and determined to be stable in pressure and sub ambient canisters at low ppbv ranges.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided in Table 1, Appendix A.

2.0 SUMMARY OF METHOD

Air samples are collected in precleaned, evacuated Summa passivated stainless steel canisters either by sub-atmospheric pressure or pressurized sampling modes. Once the air sample is collected, the canister valve is closed and labeled and sent to the laboratory for analysis. Upon receipt of the sample, the sample is logged into the LIMS and delivered to the Air lab for analysis.

The pressure in the canister is checked and documented. All cans are pressurized 1.5X with compressed ultra-zero air and recorded in the air dilution logbook located at F:\Lab\Air\Airlogbooks\4700 Pressure Log as an excel spreadsheet. (Summa cans are pressurized 1.5X unless lower RL's are needed. All new ultra-air gas cylinders are lot checked before use and stored on the F: F:\CTAL-Laboratory\Air\CLEANING CHECKS\02 TANK CHECKS. Some summa cans may need to be more pressurized more than 1.5X if below 10in. of Hg. Target pressure to run from can is 14-18psia). A specified amount of sample is then withdrawn from the canister and introduced on to the gas chromatograph for separation of the volatile organic compounds. The VOCs thus separated, are detected by a quadruple low-resolution mass spectrometer in full scan mode, or SIM or simultaneous SIM/SCAN. Upon completion of analysis and data review, the sample is removed from the auto sampler and held for at least two weeks. When ready to clean, it is hooked up to the can cleaner for cleaning and then stored away for future use.

3.0 INTERFERENCES

Interferences may be caused by the following sources of contamination:

- purge gas
- contaminated sampling canister
- sample cross contamination: column or trap (bake-out to eliminate contamination)

- high methane and/or carbon dioxide levels in the sample

4.0 DEFINITIONS

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

- Gauge Pressure: Pressure measured with reference to the surrounding atmospheric pressure, usually expressed in psig.
- Absolute Pressure: Pressure measured with reference to absolute pressure, usually expressed in psia.
- Cryogen: A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator 7100 from Entech. The cryogen used is Liquid Nitrogen.
- Fill gas: Is ultra-zero air. Usually used to dilute the air samples and blanks.
- Dynamic dilution: Is a process by which Calibration mixtures are prepared by blending fill gas continuously with standard gases from pressurized cylinders so that a flowing stream of calibration mixture is available at the inlet of the analytical system. We use Entech's 4700 Static Dilution System.
- MS-Scan: Is the mass spectrometric mode of operation in which a mass spectrometer is programmed to scan all ions over a specified mass range.

5.0 HEALTH AND SAFETY

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

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides Summa Canisters for the collection of samples upon client request.

The laboratory does not perform sample collection or field measurements for this test method. Samples should be collected in accordance with a sampling plan and sampling procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

Samples can be collected in the canisters by two techniques namely sub-atmospheric sampling and pressurized sampling.

Sub-atmospheric Sampling: In preparation to the sub-atmospheric sampling the canister is evacuated to 50mTorr. When the can is opened to the atmosphere containing the air to be sampled, the differential pressure causes the sample to flow into the canister. This technique could be used to collect grab samples or time-weighted average samples through a flow restrictive inlet with a critical orifice flow restrictor regulator.

Pressurized Sampling: Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical final canister pressure.

Time-Weighted-Average samples with flow regulators: Passive air sampling kits designed by Restek are used to collect time-weighted-average samples. These regulators are pre cleaned in the air laboratory by passing ultra-high pure Nitrogen at 10 psig and the flows are preset for various times from 1-24 hrs of sampling depending upon the volume of the canister.

Sample Collection: As explained earlier, samples are collected either by opening the valve on the summa canister (grab sample) and listen to a hissing noise (when air enters the evacuated zone) and closing the valve once the hissing noise stops or attaching a precleaned, preset flow regulator onto the canister and keeping the valve open for the duration of the sampling period. At the end of the sampling period the valves are closed, regulators are detached from the setup and the can, and the regulator are both sent back to the lab via a courier service. Flow regulators are calibrated before sending out to clients with flow meters and checked when received back in the laboratory.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Air	Summa Canister – various sizes	400mL for Inst. G/H 200mL for Inst. J/K	Thermal: None Chemical: None	Collection to Analysis: 30 days

[1] *Amount of sample required for each discrete test.*

Tedlar bags must be analyzed as soon as possible, preferably within 72 hours of sampling. There is no documented holding time for Tedlar bags. Note: Sample collection in Tedlar bags for TO-15 is not permitted for New Jersey samples

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

- Concentration System: Sys “G” - Entech 7100 Preconcentrator/ Sys “H” and “J” +” K” Entech 7200 Preconcentrator
- Autosampler: Entech 16 position 7016 CA Canister Autosampler – for System “G”. Entech 7016D Autosampler for System “H” and “J” and “K”
- Entech 4700 Static Diluter
- GC/MS System: HP 6890/ Agilent 7890B/5977B (System J and K), 7890A/HP5975C (sys G), Agilent 7890A/5975C (Sys H)
- GC/MS Data System: Enviroquant/Windows NT/2000/Windows XP/Windows 10
- Ashcroft NIST-certified test gauge (send out for calibration at least every five years)
- Flow meters – Primary Flow Meter (Bios Dry Cell) is sent out for calibration at least every five years. Other flow meters are calibrated against the primary flow meter at least annually as well as every time the battery is changed.
- Passive Flow Controllers

7.2 Supplies

- Summa Canister-6L, 3L, 1L and 0.4L
- GC Column: For Instruments “G” and “H”: Restek RXi-1ms 60m x 0.32mmID x 1um (or equivalent) and for Instruments “J” and “K”: Agilent Column DB-1 30m x 0.25mmID x 0.50um column is used.

8.0 REAGENTS & STANDARDS

8.1 Reagents

- Liquid Nitrogen
- Chromatographic grade Helium

8.2 Standards

- Calibration Mix: Spectra Gases TO-15 mix containing 65 compounds conc. 1 ppm, cat # 34436
- Internal Standard/Surrogate Stock: certified gas mix from Restek containing 4 compounds cat# 34408 - Statically dilute the standard by adding 60uL of purged H2O and filling with ultra- zero air; final pressure 35 psia, final concentration 40ppbv. Expires one month from preparation.
- Quality Control Std. – Purchased from Air gas – a mix with different vendor and different lot than calibration standards 1 ppm. The LCS is a separate secondary source TO-15 canister that has been prepared exactly like the 5ppbv standard used for calibration. It is analyzed at the 5ppbv level.

Note: Working standards prepared in canisters are to only be stored for 30 days.

9.0 PROCEDURE

9.1 Canister Cleaning

All canisters are cleaned after sample analysis and prior to reusing them. They are cleaned on a 10-position heated Nutech Canister Cleaner 3650A, or a 24-position Holman Engineering Canister Cleaner. The canisters are heated to 75℃ on the 24-slot cleaner, or 75℃ on the 10-slot cleaner, valves are opened, and canisters are evacuated with a roughing pump. The roughing pump and molecular drag pump are both vented into hood ducting.

The canister cleaner is cycled four to six times of pressurization of the canisters with humidified synthetic air followed by evacuation of the canisters. At the completion of the final cycle, the molecular drag pump is activated, and the canisters are brought to a vacuum of < 50 millitorr. The pump-down with the molecular drag pump is typically 1.5hrs to 3 hrs.

At the completion of the process, one or more canisters are chosen for batch certification analysis as per the method. These cans are pressurized to 35psia on 4700 Precision Static Diluter with ultra-pure air and sit for 12hours before being analyzed to age them. If there are no compounds detected above 0.2ppbV for a 400- ml sample, (except for ethanol, IPA, propene, and acetone as these are not on the TO-15 list, which must be below the reporting limit of 2.0ppbv, but are still documented if over 0.2ppbv); the batch is considered clean and the cleaning check can is put on the cleaner and pulled to < 50millitorr to be certified clean. However, if there are compounds above 0.2ppbv (or the reporting limit for acetone, ethanol and IPA) the cans go for a second round of cleaning and will be cleaned until all the targeted compounds in the can are below the detection limit. Once certified, clean the cans are labeled, documented in the cleaning log, and placed in storage at <50mTorr to await future sampling. Before cans are sent out, they are leak checked. All clean checks are documented at F:\Lab\air\Logbooks\Clean Check Log in an excel spreadsheet.

Additional Can Cleaning details found in ENV-SOP-ELON-0042_Can Cleaning.

9.2 Instrument Set Up Conditions

Entech 7100 Preconcentrator

	Micro Scale Purge and Trap	**Cold Trap Dehydration**
Module 1:	Trap at –130 ℃ to -160℃	Trap at –20 ℃ to -50℃
	Preheat to 0 ℃ to 20℃	Preheat to 0 ℃ to 10℃
	Desorb at 0 ℃to 20 ℃	Desorb at 0 ℃ to 10 ℃
Module 2:	Trap at –40 to -10 ℃	Trap at –50 to -60 ℃
	Desorb at 180 ℃ to 190 ℃	Desorb at 180 ℃ to 190 ℃
	Bake at 190 ℃	Bake at 190 ℃
Module 3:	Focus at –180 to –150 ℃	

Inject for 2 min to 4 min

Bake for 3-10 min

Wait 20-28 minutes before starting next analysis

Column: For Instruments G+H: Restek RXi-1ms, 60m x 0.32mmI.D. x 1um

For Instruments J+K: Agilent DB-1 30m x 0.25mmID x 0.50um

All Systems

GC 5890-7890

Oven equilibration time: 0.5 min

System "G" MS5975

Column program = 35℃ for 4 min., ramp at 8℃/min to 170℃, 30℃/min to 220℃ for 4.45 min

Run time: 24 min - 27 min
Split ratio: Splitless
Sampling rate: 2
Threshold: 200
Mass Range: 35-300 amu
Scans per second: 2.82
Scan start time: 4.0 min
Number of A/D samples: 4

System "H" MS 5975C

Column program = 35℃ for 4 min., ramp at 8℃/min to 170℃, 30℃/min to 220℃ for 5.0 min

Run time: 24 min - 28 min
Split ratio: 30:1
Sampling rate: 2
Threshold: 150
Mass Range: 35-300 amu
Scans per second: 2.73
Scan start time: 4.2 min
Number of A/D samples: 3

System "J" and "K" MS 5977B

Column program = 35℃ for 2 min., ramp at 25℃/min to 260℃, 50℃/min to 180℃ for 2 min.

Run time:14 min – 15 min
Split ratio: Splitless
Sampling rate: 1
Threshold: 50
Mass Range: 35-300 amu
Scans per second: 9.4
Scan start time: 1.5 min
Number of A/D samples: 4

9.3 Step by Step Start-up

9.3.1 Pressurizing Samples:

Open 4700 software 2) open Air, He or N2 valve 3) select pressurize 4) attach sample to 4700 5) Flush if necessary 6) select pressure by factor or pressure to absolute 7) select Start tab and wait until done. Record initial and final pressure in the Air Dilution Logbook 9) Be Sure to note the pressurization in the Misc Info in the GC sequence.

9.3.2 Setting up GC Sequence

- System G:

  Open GC software 2) open sequence 3) save as current date 4) edit in sequence vial #, sample name, method, file ID# and misc info/comment 5) save sequence 6) select position and run 7) select line to start on 8) change Data File Directory to current date 8) select Run Sequence to start and select No to run keywords.

- System H, J, K:

  Open GC software 2) open sequence 3) save as current date 4) edit in sequence vial #, sample name, method, file folder, file ID# and misc info/comment 5) save sequence 6) select position and run 7) select line to start on 8) change Data File Directory to current date 8) select Run Sequence to start and select No to run keywords

9.3.3 Setting up 7100 Concentrator

- System G:

  Open 7100 software 2) load last sequence 3) save sequence as current date 4) edit in sequence Sample Name, Samp Inlet #, Auto Pos #, Samp Vol, Method and Internal Std Vol 5) save sequence 6) highlight starting position 7) select Start (GO) tab 8) select View tab to see current state of 7100 concentrator.

- System H, J, K:

  Open 7100 software 2) load last sequence 3) save sequence as current date 4) edit in sequence Sample Name, Samp Inlet #, Auto Pos #, Samp Vol, Method, Internal Std Vol and set to Queue 5) save sequence 6) select Run to start

9.4 MS Calibration and Tuning

Auto-tune with PFTBA with Instrument idle at 35℃.

Tuning is performed by injecting 28.6ng of BFB (for G+H) or 14.3ng of BFB (for J+K) in the gaseous state (like a regular sample) with column temperature ramped from 35℃ to 220℃ or 230℃ depending on system “J”, “K” and “F”, “G” and “H” respectively, with the following acceptance criteria:

Mass	m/z Abundance Criteria
50	8 to 40 % of Mass 95
75	30 to 66% of Mass 95

95	Base Peak, 100% relative abundance
96	5 to 9% of Mass 95
173	<2% of Mass 174
174	>50% but <120% of Mass 95
175	4 to 9% of Mass 174
176	>93% but <101% of Mass 174
177	5 to 9% of Mass 176

The mass spectrum of BFB that is evaluated against the acceptance criteria is obtained in the following manner: three scans (the peak apex and the scans immediately preceding and following the apex) are averaged, and a single scan no more than 20 prior to the BFB peak is subtracted. No part of the BFB peak itself may be background-subtracted. This is done through the software program "Autofind BFB"

The BFB relative abundance criteria must be met before any standards, samples, or quality control samples are analyzed at least once every 24 hours.

9.5 Scan Analysis Table

Compound Name	Ions Used	Compound Name	Ions Used
Propene	41,42,39	Cyclohexane	84,69,41
Dichlorodiflouromethane	85,87	1,2-Dichloropropane	63,62,76
Chloromethane	50,52	Bromodichloromethane	83,85,129
Freon 114	85,135,87	Trichloroethene	95,130,132
Vinyl Chloride	62,64	Heptane	57,71,100
1,3-Butadiene	54,53,50	MIBK	43,57,100
Bromomethane	94,96	Cis-1,3-Dichloropropene	75,110
Chloroethane	64,66	Trans-1,3-Dichloropropene	75,110
Acetone	43,58	1,1,2-Trichloroethane	97,83,85
Trichlorofluoromethane	101,103	Toluene	91,92
Ethanol	45,46	2-Hexanone (MBK)	43,57,100
1,1-Dichloroethene	61,63,96	Dibromochloromethane	129,127,131
Methylene Chloride	49,84,86	1,2-Dibromomethane	107,109
Freon 113	101,151	Tetrachloroethane	166,168,129
Carbon Disulfide	76,78	Chlorobenzene	112,77,114
Trans-1,2-Dichloroethene	61,96,98	Ethylbenzene	91,106
Methyl tert-butyl-ether	73,57	M/P-Xylenes	91,106
Isopropyl Alcohol	45,43,59	O-Xylene	91,106
2-Butanone (MEK)	43,72,57	1,1,2,2-Tetrachloroethane	83,131,85
Cis-1,2-Dichloroethene	61,98,96	4-Ethyltoluene	105,120
Vinyl Acetate	43,86	1,3,5-Trimethylbenzene	105,120
Hexane	41,56,86	1,2,4-Trimethylbenzene	105,120
Ethyl Acetate	61,70,88	1,3-Dichlorobenzene	146,148,111
Chloroform	83,85	Benzyl Chloride	91,126
Tetrahydrofuran	71,72	1,4-Dichlorobenzene	146,148,111
1,2-Dichloroethane	62,64,98	1,2-Dichlorobenzene	146,148,111
1,1,1-Trichloroethane	97,99,61	1,2,4-Trichlorobenzene	180,182,145
Bromoform	173,175	Styrene	104,78
Benzene	78,51,77	Hexachlorobutadiene	225,260

Carbon Tetrachloride	117,119	1,1-Dichloroethane	63,65,83
Acrylonitrile	53,52	*4-phenylcyclohexane(4-PCH)	104,158
Acrolein	56,55	Naphthalene	128,102
1,4-Dioxane	88,58,43		

Full scan parameters:

Low Mass: 35.0
High Mass: 300.0
Threshold: 200
Sample Number: 2
A/D samples: 4

9.6 Calibration

Static Dilution of Calibration standards for the initial calibration. Three precleaned canisters are picked for preparing the working standards. One canister is blended with the calibration mix to represent a lower concentration at 0.1ppbv, one is at 1.0ppbv and last one is the 20ppbv standard using the Entech4700 Static Diluter. (Other levels may be used). These three cans will be used to run the calibration curve. The first 4-5 points of the curve are run from the canister blended with the standard at 1.0ppbv level and the remainder from the 20ppbv and 0.1ppbv cans. These standards are prepared by opening the 4700 software. Once in the program open the saved files and use 0.1std, 20std and 1.0std for the appropriate stock standard. Attach the Summa canister to the 4700. Open the valve and fill the can up to 35psia for the 20ppbv can and 25psia for the 0.1ppbv and 1.0ppbv cans. The following amounts are used for each instrument.

When prepping a new calibration curve, typically the 20ppbv canister is prepped first, allowed to sit for 12hours, then the 1.0ppbv can is prepped from the 20ppbv can and allowed to sit for 12 hours, and then finally the 0.1ppbv can is prepped from the 1.0ppbv can and allowed to sit for 12 hours. The ICAL will then be analyzed. Each point is allowed to sit as it assures stability and better results.

All Systems (A minimum of five points used to establish initial calibration.)

Systems “G” and “H”:

STD.	AMOUNT
0.025ppbv	10 mL of 1.0 ppbv
0.05ppbv	20 mL of 1.0 ppbv
0.10ppbv	40 mL of 1.0 ppbv
0.20ppbv	80 mL of 1.0 ppbv
0.5 ppbv	200 mL of 1.0 ppbv
1.0 ppbv	20 mL of 20 ppbv
2.0 ppbv	40mL of 20 ppbv
5.0 ppbv	100 mL of 20 ppbv
10 ppbv	200 mL of 20 ppbv
20 ppbv	400 mL of 20 ppbv
50 ppbv	1000mL of 20 ppbv

Note: Larger volumes may be injected to reduce RL’s for samples.

Note: Calibration point 40ppbv not always analyzed.

Systems "J" + "K":

STD.	AMOUNT
5pptv	10mL of 0.1 ppbv
10pptv	20mL of 0.1 ppbv
20pptv	40mL of 0.1 ppbv
25pptv	50mL of 0.1 ppbv
50pptv	100 mL of 1.0 ppbv
100pptv	20 mL of 1.0 ppbv
200pptv	40 mL of 1.0 ppbv
250 pptv	50 mL of 1.0 ppbv
500 pptv	100 mL of 1.0 ppbv
1.0 ppbv	200 mL of 1.0 ppbv
2.0 ppbv	20 mL of 20 ppbv
5.0 ppbv	50 mL of 20 ppbv
10 ppbv	100 mL of 20 ppbv
20 ppbv	200 mL of 20 ppbv
50 ppbv	500 mL of 20ppbv

A 5ppbv Standard is used for the daily continuing calibration

9.7 Analysis

Samples upon receipt are logged into the laboratory LIMS by the sample management department. Once the Summa canisters and or the Tedlar bags are labeled, they are transported to the air laboratory for storage. Containers are generally shipped by courier or express service. Note: Tedlar bags are not permitted for New Jersey work by EPA TO-15.

Each canister pressure is recorded upon arrival in psia. The pressure in the canister should be between 0-15 inches of Hg to obtain a significant amount of sample for analysis by the 7100 preconcentrator. All cans are pressurized 1.5X with compressed ultra-zero air and recorded in the air dilution logbook. (Summa cans are pressurized 1.5X unless lower RL's are needed. Some summa cans may need to be more pressurized more than 1.5X if below 10in. of Hg. Target pressure to run from can is 14-18psia). The canister will be pressurized with the fill gas through the 4700 Entech static dilutor and the resulting dilution factor is recorded for result calculations in (F:/CTAL Laboratory/Air/Air logbooks/Airdilutionlogbook.xl). Prior to analysis all positions are flushed with purge gas to prevent contamination of lines. The canisters or tedlar bags are then attached to a 16-position auto-sampler for analysis.

Analysis of samples begins after an acceptable performance standard, calibration, blanks and QCs are run. A sequence for the 7100 system is written and saved to the Entech operating system. This is done by opening the 7100 through the smartlab menu. Put in sample description, sample volume and method. All systems are based on a 400ml injection. A GC run sequence is also needed to be written and saved in the HP Chemstation/Enviroquant software.

Initially, Module 1 on the 7100 is cooled down to approximately –40 to -20℃, the empty SC Trap for Cold Trap Dehydration (see section 9.2 for CTD parameters) and 100mL for G+H and 50mL for J+K (of the Internal Standard and Surrogate mix is collected and the defined volume of air

sample (400mL for G+H and 200mL for J+K for standard injections) is trapped. The concentrated sample is then transferred to Module 2 (Tenax) at approximately -30 to –50℃. The cryogenic trapping system acts as the third module prior to the GC. Water is removed at the transfer from Module #1 to Module #2. CO2 is removed at Module #2 to Module #3. The third Module is cooled to approximately -150 to -180℃ and focuses the plug onto the column improving chromatography. The GC temperature is ramped for separation of components. Prior to switching from autosampler#1 to autosampler#2 a cleanup blank is run on the auto-sampler being switched too. (clup)

All the sample results are checked for Surrogate, Internal Standard criteria and saturation of compounds following analysis. If targeted compounds exceed linear range of the curve, a dilution of the sample is necessary.

A minimum 5-point calibration curve is used to calibrate the system for all target analytes and surrogates. The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the low initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates.

The percent relative standard deviation (%RSD) for all target analytes over the working calibration range must be <30% (with an allowance for up to two analytes to have %RSDs as high as 40%) for the average relative response factor (RRF) to be used for subsequent calculations. All analytes that do not meet the <30% RSD criteria will be narrated. (MA MCP allows %RSD for Naphthalene to be <40%).

If %RSD is >30% for any target analyte, then a linear regression must be established using the calibration data for that compound. For the linear regression to be acceptable for quantitative purposes, the correlation coefficient must be greater than or equal to 0.99. If this criterion is met, the linear regression analysis must be incorporated into the curve used to calculate results. This is done by the software by setting the curve fit of analyte in question to linear regression instead of average response. If these criteria are not met, the analytes that do not meet these criteria will be narrated.

If any initial calibration standard analysis is determined to be unusable (e.g., a bad injection), the standard may be re-analyzed within eight hours of the last initial calibration standard analyzed and before any samples are run. The re-analysis results may be incorporated into the initial calibration in their entirety, in place of the original analysis. If the initial calibration still does not meet acceptance criteria, even with the replacement standard, then the entire initial calibration should be performed again.

If the initial calibration still does not meet acceptance criteria for a particular analyte, the analyst may consider dropping the lowest or highest point for that analyte and recalculating the average RRF and %RSD or linear regression. Note that ONLY the lowest or highest data point may be dropped – a data point from the middle of the calibration range may NOT be dropped. Note also that if the low standard is dropped, the RL for that analyte must be adjusted so that the lowest standard used for the calibration is less than or equal to the RL.

When the instrument data system is updated to reflect the new initial calibration, the analyst verifies that it has been properly set up to calculate each target analyte according to the actual model used to establish the initial calibration (i.e., average RRF or linear regression) and to reflect any abbreviated ranges established for individual analytes.

At the start of each 24-hour analysis sequence, before any samples are analyzed, a 5-10ppbv calibration check standard is analyzed to check the calibration curve. The percent difference or percent drift must be <30% for all target analytes.

If the minimum percent difference/drift criteria are not met for any target analyte, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, compressed gas cylinders, syringes, column fittings, etc.; clean the MS source, changing an injector port or filament, cleaning the inlet, etc.). If corrective action that may affect instrument response is taken, then the calibration verification standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration verification standard, then a new initial calibration must be performed.

If two calibration check standards are run in succession, one immediately following the other, and neither is deemed to have been a bad injection, then the one closest in injection time to the associated sample analyses, or both standards, must be evaluated for and pass method performance criteria for sample analyses to continue. In addition, the two calibration check standards are documented by the analyst for evaluation of reproducibility.

The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound, and compounds quantitated by SIM must be noted in the final report.

9.8 SIM Analysis Summary

Synchronous SIM/Scan Analysis:

With the extremely low reporting limits required by new federal and state regulations for air analysis, the Air lab at ELON has implemented new procedures using synchronous SIM/Scan to meet the criteria. With Agilent 5973/5975 MSD coupled with the 6890/7890 GC and properly chosen acquisition parameters, both scan data and SIM data are collected in a single run using the MSD ChemStation D.02.00.275. Fast scan rates of up to 6250 amu/s by 5973/5975 MSD enables analysts to acquire high quality full scan data which are library searchable against NIST spectral data base and to collect SIM data with significantly high sensitivity.

The synchronous SIM/Scan takes advantages of the fast electronics in the 5973/5975 MSD to collect SIM and full scan signals in a single analysis without sacrificing performance. Full scan data covers all 65 compounds specified in EPA TO-15 method, 20 chlorinated and aromatic target compounds have been chosen for SIM analysis. Table 1 shows the compounds and the ions in SIM/Scan run method.

Table 1:

➢ Compound Name	➢ Ions used in SIM	➢ SIM Group Number
Bromochloromethane (IS)	49	Group 4
Vinyl Chloride	62,64	Group 1
1,1-Dichloroethene	61,63,96	Group 2
Trans-1,2-Dichloroethene	61,63,96	Group 3
1,1-Dichloroethane	63,65	Group 3
Cis-1,2-Dichloroethene	61,63,96	Group 4
Chloroform	83,85	Group 4
1,2-Dichloroethane	62,64	Group 5

1,4-Difluorobenzene (IS)	114	Group 6
Carbon Tetrachloride	117,119	Group 6
1,2-Dichloropropane	63,76	Group 7
Bromodichloromethane	83,85	Group 7
Trichloroethene	95,130	Group 7
Cis-1,3-Dichloropropene	75,110	Group 8
Trans-1,3-Dichloropropene	75,110	Group 9
1,2-Dibromoethane	107,109	Group 10
Chlorobenzene-D5 (IS)	117	Group 11
1,1,2-Trichloroethane	97,83,85	Group 9
Naphthalene	128,102	Group 14
1,1,2,2-Tetrachloroethane	83,85	Group 12
4-Bromofluorobenzene (Surr)	95	Group 13

Table 2: SIM

➢ **Group Number**	Ion	Dwell Time (msec)	Star Time (min)
1	62,64	40	1.45
2	61,63,96	25	2.24
3	61,63,65,83,96,98	15	2.48
4	49,61,83,85,96,98,128,130	10	2.76
5	62,64,98	25	3.07
6	88,114,117,119	20	3.30
7	62,63,76,83,85,95,129,130,132	10	3.60
8	75,110	40	3.95
9	75,83,85,97,110	20	4.14
10	107,109	40	4.55
11	82,117	40	5.00
12	83,85,131	25	5.40
13	95,174,176	25	5.70
14	102,128	25	7.60

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Qualitative Identification

A minimum signal-to- noise ratio of 3:1 (based on peak height) must be achieved for any peak used in a calibration standard, client sample, or quality control sample.

10.1.1 Tentatively Identified Compounds (TICs)

Initially include all the non-target compounds that have a peak area count of ≥ 10% of the nearest internal standard.

- Use the following guidelines for making tentative identification:
- Check the spectral library match to make tentative identification.
- The 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.
- The relative intensities of the major ions should agree within ± 20%.
- The special library match should be >85% or based on Analyst interpretation for a tentative identification to be made.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- 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.
- 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.
- Experience of the analyst is also considered when small molecule fragments are not apparent in the spectrum due to scan range limitations.

Quantitative analysis:

- The nearest internal standard shall be the one that is used to calculate concentration, and the RF for the compound should be assumed to be 1.
- The resulting concentration should be reported indicating that the value is an estimate.

10.1.2 Manual Integration

Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are justified and proper all manual integrations must be performed, documented, reviewed, and approved in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration and local ELON Manual Integration SOP.* Refer to these SOPs for guidance on manual integration techniques and required procedures.

When performing manual integration of any peak in a calibration standard, client sample, or quality control sample, the integration must be performed in conformance with the procedures outlined in the SOP for chromatographic integration procedures. In summary:

The most appropriate instrument parameters should be used during method development to allow for automatic integration by the data system in most cases.

All data must be integrated consistently for all standards, samples and QC samples.

In those instances when the automated software does not integrate a peak correctly, manual integration may be used to correct the improper integration performed by the data system. Manual integration should always be performed to create the analyst's best estimate of the actual peak area discerned from the chromatogram.

All manual integrations must be documented by printing, initialing, and dating the manual integrations as well as by recording the reasons for the manual integrations.

10.2 Data Processing

10.2.1 Reporting Package

The reporting package that is delivered to clients consists of the sample results, the surrogate results, and any quality control measures that the client has specifically asked for.

10.2.2 Data Filing

Data to be saved on CD

All the runs, methods, and standards, from each day of analysis.

Sequence and bench sheets to be filed in Data Boxes and all raw data stored electronically on the Archive drive (A: drive). Including:

BFB tuning files
Daily method blanks
Calibration curves
Daily calibration checks
Surrogate recoveries
Lab spikes
Duplicate results
Quality control spikes

10.3 Calculations

All calculations are based on the internal standard technique.

Results must be reported in ppbv as well as ug/m3

Cx = AxCisDF/AisRRF

Cx = Compound concentration, ppbv
Ax = Area of the characteristic ion for the compound to be measured, counts
Ais = Area of the characteristic ion for the specific internal standard, counts
Cis = Concentration of the internal standard spiking mixture, ppbv
RRF= Relative Response Factor is the average Response factor for the compound from the initial calibration
DF = Any applicable dilution factors

10.3.1 Relative Retention Times (RRT)

Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RTc}{RTis}$$

Where: RTc= Retention time of the target compound, seconds

Rtis= Retention time of the internal standard, seconds.

10.3.2 Mean of the Relative Retention Times $\overline{(RRT)}$

Calculate the mean of the relative retention times for each analyze target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

Where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT= Relative retention time for the target compound at each calibration level.

10.3.3 Mean Retention Times (RT)

Calculate the mean of the retention times (RT) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RTi}{n}$$

Where: $\overline{RT}$ = Mean retention time, seconds

RT= Retention time for the internal standard for each initial calibration standard, seconds.

10.3.4 Conversions

ppbv to ug/m3

ug/m3 = (ppbv)(MW)/24.45

11.0 Quality Control & Method Performance

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix B for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
RL Verification	RL	Daily
Sample Duplicate	SD	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Surrogate	SSTD	Added to all samples and QC samples.
Internal Standards	ISTD	Added to all samples and QC samples.

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Appendix B for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Tune (MS Only)		Daily
Initial Calibration Verification	ICV	After each new calibration
Continuing Calibration Verification	CCV	Daily

11.3 Method Performance

An analytical batch is defined as up to 20 client samples of a similar matrix for the same analysis. All quality control samples are assigned to and associated with a particular analytical batch, which is designated at the time client samples are logged-in or at the time of sample preparation. All quality control samples must be traceable to the associated analytical batch for review and evaluation purposes.

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

11.3.2 Calibration Curve

A minimum 5point calibration curve is used to calibrate the system. Please refer to section 9.6 of this document for exact concentrations. An extra point at the low (MDL) level (0.5ppbv) is also run for demonstration purposes and all NJ-based clients. The lowest point in the curve is used as the RL. The response factor variation over the working range must be ≤30 %RSD, with two compounds allowed to 40%. (MA MCP allows Naphthalene to be <40%) If linear calibration is used for any compound, it must be ≥ 0.99 or better. The relative retention time (RRT) for each target compound must be within 0.06 units of the mean RRT for the compound over the initial calibration. The

area response for each Internal Standard at each calibration level must be within 40% of the mean area response over the initial calibration range.

An ICV, second source is analyzed immediately after the calibration and all compounds must recover 70-130%.

11.3.3 Calibration Check Verification (CCV)

Each working day, a 5ppbv calibration check standard is analyzed to check the calibration curve. The calibration check standard is inspected and the response factor for each analyte must be within ±30% for the calibration curve. The retention time shift of each of the internal standards in all calibration check standards must be within 20 secs of the mean response over the Initial Calibration for each Internal Standard. If these criteria are not met, the analytes that do not meet these criteria will be narrated. MA MCP allows 20% of the list compounds to be outside criteria, needs to be qualified.

11.3.4 Method Blank (MB)

A Laboratory Method Blank is prepared by hooking up a clean evacuated canister to the 4700static diluter and pressurizing it with fill gas to a final pressure of 35psia. This is pressurized from the canister cleaner.

The Laboratory Method Blank must be an unused certified canister that has not left the laboratory. It must contain the same amount of Internal Standard as the samples. One LMB must be run every 24 hours or per batch of analysis.

The LMB is analyzed with each batch prior to sample analysis to prove that the instrument is free of any contamination. Any background contamination should be <MDL. Low levels of <2ppbv (less than 5 times the MDL) for common laboratory contaminants (Methylene chloride, Ethanol, Acetone) are acceptable.

11.3.5 Laboratory Control Sample (LCS)

Daily a 5ppbv QC Check standard, prepared from a different stock, is analyzed to check the calibration curve. All compounds must be within the ±30% for NJ and CT RCP samples. All other samples follow 70-130% except for the deemed 11 difficult compounds which have limits of 50-150%. (Difficult compounds include Acetone, 1,4-Dioxane, Hexachlorobutadiene, Naphthalene, 1,2,4-Trichlorobenzene, Propene, Isopropanol, Ethanol, 2-Hexanone, 1,2-Dichloro-1,1,2,2-tetrafluoroethane, and Cyclohexane) QC Check samples are analyzed after the continuing calibration and before samples.

An LCS that fails on the low side or fails on the high side with samples having detections must be rerun. If LCS still fails, then qualify the outlier. Analyst should perform corrective actions to ensure failure doesn't happen again. Any LCS that fails on the high side, with all samples being non-detected can be qualified.

11.3.6 Sample Duplicate

Duplicates are analyzed with every sequence. Results will be reported in LIMS with RPD values. The allowable criterion for an acceptable duplicate is the percent RPD being ≤ 25.

11.3.7 Surrogate

4-Bromofluorobenzene at 8ppbv is the single surrogate spike added to each analysis. A combined mix of three internal standards and a surrogate (4-BFB) are added to each analysis automatically at the beginning of the purge cycle of the 7100 run. The recovery of this spike must be within ±30%.

11.3.8 Internal Standard

Three Internal standards namely Bromochloromethane, 1,4-Difluorobenzene and Chlorobenzene-D5 are used to quantitate the blanks and samples. Internal standards are monitored throughout the analysis. Acceptable criteria for the internal standard area responses are ± 40% of the most recent calibration standard. The retention time criteria for all the internal standards are + or – 0.33min from the mean retention time of the most recent calibration.

11.3.9 MDL and On-going RL/LOQ Verification

An MDL study must be performed as per 40 CFR 136 Appendix B Rev2. The MDL Definition is as follows, “The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results” The value calculated from the spike samples is called the MDLS. The MDL spikes are both prepared and analyzed over a three-day period. The MDLS calculation is the same as the MDL calculation in Revision 1.11. The method blank samples are used to calculate the MDLb, which is a very similar calculation that also calculates 99% confidence level that the result is derived from the sample rather from contamination/noise. The MDL is the higher of the two values (either the MDLs calculated using spiked samples or the MDLb, calculated using method blanks). EPA considers this change important because as detector sensitivity improves, the background contamination of the laboratory, consumable supplies, and equipment can be more important in determining the detection limit than the sensitivity of the instrument.

The MDL now requires that the samples used to calculate the MDL are representative of laboratory performance throughout the year, rather than on a single day.

A laboratory has the option to pool data from multiple instruments to calculate one MDL that represents multiple instruments.

Additionally, a streamlined approach to determine whether a new instrument can be added to a group of instruments with an already established MDL, and Laboratory have the option to use only the last six months of method blank data or the fifty most recent method blanks, whichever yields the greatest number of method blanks to calculate the MDL value derived from method blanks (MDLb)

After initial MDL is established, every year thereafter quarterly 2 RL/LOQ samples are performed. At the end of the year the points are tabulated in an MDL-S and compared to current MDL.

Note: For method EPA TO-15 the calculated MDL must be < 0.5ppbv for each analyte listed in the method.

*For AIHA-LAP, LLC a daily RL/LOQ verification is analyzed with limits of 50-150%. Quarterly, each canister type has an RL/LOQ verification performed that is analyzed just like a sample would be run. This shall be spiked at the reporting limit.

11.3.10 Mechanical Gauges

All pressure on outbound and inbound canisters (before and after sampling) are checked and the pressures recorded in the Outbound-Inbound log.

11.3.11 Qualifiers

Any data that fails to meet method requirements will be qualified. For example, if cans return with a pressure of zero.

12.0 Data Review & Corrective Action

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-ELON-0035_Data Review for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix B for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

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

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

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

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have not been modified from the reference test method(s) cited.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0 RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.
- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in

corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.

- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: Routine Analyte List and LOQ
- Appendix B: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- ELON QA Manual, current version.
- Compendium of methods for the determination of toxic organic compounds in Ambient Air, 2nd Edition, USEPA JAN 1999, Method TO-15.
- MA DEP Bureau of Waste Site Cleanup, “Quality Control Requirements and Performance Standards for the Analysis of Volatile Organic Compounds in Air Samples (TO-15) by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP”, Rev 0, July 1, 2010.
- CT DEP QA/QC Work Group, “State of CT Dept. of Environmental. Protection Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements Volatile Organics by Method TO-15”, Version 2.0, December 2006.
- HP 5890/6890/7890 Series Gas Chromatograph Operating Manuals.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Catherine Rouleau	Air Lab Supervisor	09/01/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change

All	Reformatted using Pace SOP Template
2.0	Added air tank checks
6.0	Added 400mL or 200mL sample amounts
7.2	Specified which columns go with each inst.
8.2	Added I.S./Surr. mix one month expiration date
9.1	Changed can cleaning temp to 75℃ from 95℃
9.3	Added parameters for H, J, K
9.4	Added BFB inj. 14.3ng for J+K
9.7	Added new amounts for J+K
9.8	Addition of Sim analysis and added Napthalene
10.1.1	Addition of TICs

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
Doc #45 Rev 24	SOP EPA TO-15	06/16/2021

Appendix A: Target Analyte List and LOQ

Table 1: Standard Analyte List and LOQ

Analyte	CAS #	LOQ[1] Air (ppbv)	LOQ1 Air (ppbv) Sim
Propene *	115-07-1	2.0	
Dichlorodifluoromethane (Freon 12)	75-71-8	0.05	
Chloromethane	74-87-3	0.1	
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	76-14-2	0.05	
Vinyl Chloride	75-01-4	0.05	0.01
1,3-Butadiene	106-99-0	0.05	
Bromomethane	74-83-9	0.05	
Chloroethane	75-00-3	0.05	
Acetone *	67-64-1	2.0	
Trichlorofluoromethane (Freon 11)	75-69-4	0.2	
Ethanol *	64-17-5	2.0	
1,1-Dichloroethene	75-35-4	0.05	0.01
Methylene Chloride	75-09-2	0.5	
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	0.2	
Carbon Disulfide	75-15-0	0.5	
trans-1,2-Dichloroethene	156-60-5	0.05	0.01
Methyl tert-butyl-ether (MTBE)	1634-04-4	0.05	
Isopropyl Alcohol (Isopropanol) *	67-63-0	2.0	
2-Butanone (MEK)	78-93-3	2.0	
cis-1,2-Dichloroethene	156-59-2	0.05	0.01
Vinyl Acetate	108-05-4	1.0	
Hexane	110-54-3	2.0	
Ethyl Acetate *	141-78-6	0.5	
Chloroform	67-66-3	0.05	0.01
Tetrahydrofuran *	109-99-9	0.5	
1,2-Dichloroethane	107-06-2	0.05	0.01
1,1,1-Trichloroethane	71-55-6	0.05	
Bromoform	75-25-2	0.05	
Benzene	71-43-2	0.05	
Carbon Tetrachloride	56-23-5	0.05	0.01
Acrylonitrile *	107-13-1	0.288	
Acrolein	107-02-8	1.0	
1,4-Dioxane	123-91-1	0.5	
Cyclohexane *	110-82-7	0.05	
1,2-Dichloropropane	78-87-5	0.05	0.01
Bromodichloromethane	75-27-4	0.05	0.01
Trichloroethene	79-01-6	0.05	0.01
Heptane *	142-82-5	0.05	
4-Methyl-2-pentanone (MIBK)	108-10-1	0.05	
cis-1,3-Dichloropropene	10061-01-5	0.05	0.01
trans-1,3-Dichloropropene	10061-02-6	0.05	0.01
1,1,2-Trichloroethane	79-00-5	0.05	0.01
Toluene	108-88-3	0.05	

2-Hexanone (MBK) *	591-78-6	0.05	
Dibromochloromethane	124-48-1	0.05	
1,2-Dibromomethane (EDB)	106-93-4	0.05	0.01
Tetrachloroethylene	127-18-4	0.05	
Chlorobenzene	108-90-7	0.05	
Ethylbenzene	100-41-4	0.05	
m/p-Xylenes	179601-23-1	0.1	
o-Xylene	95-47-6	0.05	
1,1,2,2-Tetrachloroethane	79-34-5	0.05	0.01
4-Ethyltoluene *	622-96-8	0.05	
1,3,5-Trimethylbenzene	108-67-8	0.05	
1,2,4-Trimethylbenzene	95-63-6	0.05	
1,3-Dichlorobenzene	541-73-1	0.05	
Benzyl Chloride	100-44-7	0.05	
1,4-Dichlorobenzene	106-46-7	0.05	
1,2-Dichlorobenzene	95-50-1	0.05	
1,2,4-Trichlorobenzene	120-82-1	0.05	
Styrene	100-42-5	0.05	
Hexachlorobutadiene	87-68-3	0.05	
1,1-Dichloroethane	75-34-3	0.05	0.01
*4-phenylcyclohexane(4-PCH)	4994-16-5	0.097	
Naphthalene	91-20-3	0.05	
* Not listed in Method TO-15 Table 1, considered “difficult analytes”			
**Reporting limits subject to change based on calibration.			

[1] Values as of effective date of this SOP. LOQ are subject to change, contact quality personnel for most current information.

Appendix B: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet one of curve fit options presented in Section 11.3.2. For any curve fit other than Average RF (RSD), curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 30% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
CCV	Daily, before sample analysis	All analytes within 70-130%	See Section 11.3.3 for required corrective actions based on circumstance.	Qualify analytes with CCV out of criteria.
Internal Standards	Every field sample, standard and QC sample	Must meet criteria specified in Section 11.3.8. 60-140%	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Surrogate	Every field sample, standard and QC sample	Must meet criteria specified in Section 11.3.7. 70-130%	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Method Blank	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.4. <MDL	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
LCS	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.5. 70-130% and 50-150% for difficult.	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Sample Duplicate	1 per batch of 20 or less samples	Must meet criteria specified in Section 11.3.6. RPD ≤25	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Tune Standard	Daily	Must meet criteria specified in Section 9.4	Identify and correct source of problem, repeat	None. Do not proceed with analysis

Pace ANALYTICAL SERVICES	**ENV-SOP-ELON-0060 v01_1,4-Dioxane EPA 8270E Sim**	
	Effective Date: 07/27/2022	COPYRIGHT© 2019, 2021, 2022 Pace®

Management Approval:
Katherine Allen Approved on 7/25/2022 10:44:24 AM
Tod Kopyscinski Approved on 7/27/2022 7:30:55 AM

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the laboratory procedure used by Contest, A Pace Analytical Laboratory (ELON) for the determination of low-level 1,4-Dioxane in ground water, surface water, and soils by GC/MS based on method EPA 8270E SIM.

1.1 Target Analyte List and Limits of Quantitation (LOQ)

The target analytes that can be determined by this SOP and the associated LOQ is provided below:

RL/LOQ for aqueous samples = 0.2 µg/L

RL/LOQ for soil/solid samples = 0.05 mg/kg

2.0 SUMMARY OF METHOD

For water samples, approximately one liter of sample is extracted with methylene chloride at a neutral pH using a separatory funnel (In accordance with SW-846 Method 3510C). For soil samples, 20 g of sample is weighed and extracted with a methylene chloride/acetone mixture in accordance with SW-846 method 3546. The methylene chloride extract is dried and concentrated to a volume of 1.0 mL and analyzed by GC/MS SIM using GC/MS equipped with an LVI/PTV (Large volume injection/programmable temperature vaporization inlet). Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitation is accomplished by using the response of a major ion relative to an internal standard and a response factor generated from a minimum five-point calibration curve.

3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and or cause elevated baselines in the total ion current profiles.

Interferences by phthalate esters can pose a problem, usually the result of contamination during extraction. Avoiding the use of plastics in the laboratory can best minimize these interferences.

Matrix interferences may be caused by contaminants that are co-extracted from the sample.

4.0 DEFINITIONS

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

5.0 HEALTH AND SAFETY

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

The following sections provide general health and safety information about chemicals and materials that may be present in the laboratory.

- The toxicity or carcinogenicity of each chemical material used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.
- The laboratory maintains documentation of hazard assessments and OSHA regulations regarding the safe handling of the chemicals specified in each method. Safety data sheets for all hazardous chemicals are available to all personnel. Employees must abide by the health, safety and environmental (EHS) policies and procedures specified in this SOP and in the Pace® Chemical Hygiene / Safety Manual (COR-MAN-0001)
- Personal protective equipment (PPE) such as safety glasses, gloves, and a laboratory coat must be worn in designated areas and while handling samples and chemical materials to protect against physical contact with samples that contain potentially hazardous chemicals and exposure to chemical materials used in the procedure.
- Concentrated corrosives present additional hazards and are damaging to skin and mucus membranes. For procedures that require use of acids, use acids in a fume hood whenever possible with PPE designed for handing these materials. If eye or skin contact occurs, flush with large volumes of water. When working with acids, always add acid to water to prevent violent reactions. For procedures that that emit large volumes of solvents (evaporation/concentration processes), these activities must be performed in a fume hood or apparatus that reduces exposure.

6.0 .SAMPLE COLLECTION, PRESERVATION, HOLDING TIME & STORAGE

The laboratory provides containers for the collection of samples upon client request. Refer to laboratory SOP ENV-SOP-ELON-0017_Bottle Prep for procedures related to preparation of bottle kits for the test method(s) associated with this SOP.

The laboratory does not perform sample collection or field measurements for this test method. Samples should be collected in accordance with a sampling plan and sampling procedures appropriate to achieve the regulatory, scientific, and data quality objectives for the project.

Container Type, Minimum Sample Amount, Preservation, and Holding Time Requirements:

Matrix	Container Size & Type	Required Sample Amount[1]	Preservation	Holding Time
Water	1-Liter Amber with Teflon lined cap	1-Liter	Thermal: 4°C Chemical: If residual chlorine suspected, 80mg Sodium thiosulfate per 1-Liter.	Collection to Ext: 7 Days Ext to Analysis: 40 Days
Soil	8 oz amber glass jar	8 oz	Thermal: 4°C	Collection to Ext: 14 Days Ext to Analysis: 40 Days

[1] *Amount of sample required for each discrete test.*

Thermal preservation is checked and recorded on receipt in accordance with laboratory SOP Login. Chemical preservation is checked and recorded at time of receipt or prior to sample preparation.

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

After analysis, samples are retained as stated in the Pace® standard terms and conditions, unless otherwise specified in the analytical services contract. Samples are then disposed of in accordance with Federal, State, and Local regulations.

7.0 EQUIPMENT & SUPPLIES

7.1 Equipment

- HP7890GC/MS
- Enviroquant data system (HP ChemStation)

7.2 Supplies

- Capillary column: Restek Rtx-PCB; 60m, 0.25mm ID, 0.25 µm, cat # 13226
- Gas Tight syringes
- Vials: 2mL snap cap and crimp top, and 4mL screw cap vials

8.0 REAGENTS & STANDARDS

8.1 Reagents

- Reagent Water: interferent free
- Methylene Chloride: Pesticide quality or equivalent
- Methanol, Acetone: Pesticide quality or equivalent
- Nitrogen: Ultra high purity
- Helium: Ultra high purity

8.2 Standards

Note: All Standards must be stored in amber vials, for protection from light.

Note: All working standards have an expiration date of 6 months from when prepared or manufacturer's documented expiration date, whichever comes first.

Note: After opening Stock Standards, transfer the stock standard into vials with PTFE lined caps. Store protected from light at -10°C or less. Stock standard solutions should be checked frequently for signs of degradation or evaporation and expire 1 year from open date unless manufacturer's documented expiration date comes first.

Note: All standards are purchase as certified solutions

- Surrogate Stock: 1,4-dioxane-d8 Standard, 2000 µg/mL in p&t methanol, 1.0 mL ampule; Restek cat# 30614
- **Surrogate Prep:**

Compound	Vendor	Volume	Final Volume (mL)	Final Concentration (µg/mL)
1,4-Dioxane-d8	Restek	500 µL	10 mL	100

- Add 5.0 mL of Acetone to 10 mL volumetric flask.
- Add 500 µL of 1,4-Dioxane-d8 at 2000 µg/mL
- Bring up to final volume with Acetone.

- Spike Stock: 1,4-dioxane, 1000 µg/mL in MeCl2, Absolute #79216
- **Matrix Spike Prep**:

Compound	Vendor	Conc. (µg/mL)	Volume (mL)	Final Volume (mL)	Final Conc. (µg/mL)
1,4-Dioxane Spike Stock	Absolute	1,000	1.0	10.0 mL in acetone	100

- Add 5.0 mL Acetone to 10 mL Volumetric flask
- Add 1.0 mL 1,4-Dioxane spike stock @ 1000 µg/mL
- Bring to volume with Acetone

- Internal Standard Stock: 1,4-dichlorobenzene-d4 @ 1000 µg/mL in Methanol, Absolute Standards Cat# 70118.
- **Internal Standard Prep**:

Compound	Vendor	Init. Conc. (µg/mL)	Volume or weight (mL or g)	Final Volume (mL)	Final Conc. (µg/mL)
1,4-dichlorobenzene-d4 I.S.	Absolute Standard	1,000	1.2mL	3.0 mL in MeCl2	400

Cal Std Level	Amount of 1,4-Dioxane-d8 Stock (mL)	Amount of I.S. 1,4-Dioxane-d8 mL)	Final Volume (mL)	Final Conc. I.S. (µg/mL)	Final Conc. 1,4-Dioxane-d8 (µg/mL)
1	0.01	0.125	5.0	1.0	0.2
2	0.05	0.125	5.0	1.0	1.0
3	0.125	0.125	5.0	1.0	2.5
4	0.25	0.125	5.0	1.0	5.0
5	0.025**	0.125	5.0	1.0	10
6	0.0625**	0.125	5.0	1.0	25
7	0.125**	0.125	5.0	1.0	50
8	0.25**	0.125	5.0	1.0	100

**Use 1,4-dioxane-d8@2000 µg/mL, not the intermediate stock @ 100 µg/mL

An internal standard is made from 1,4-dichlorobenzene-d4 and is added to all samples and QC. Add 5.0 µL of internal standard at 400 µg/mL to 200 µL of room temperature sample extract.

- Tuning standard: Semi-volatiles GC/MS Tuning Standard, 1000 µg/mL each in methylene chloride; Agilent cat# GCM-150-1
- **DFTPP Tuning Solution Prep:**

Compound	Initial Conc. (µg/mL)	Amount (mL)	Final Volume (mL)	Final Conc. (µg/mL)
Tuning Standard	1000	0.125	5.0 mL in $MeCl_2$	25.0

Prior to running an initial calibration, DFTPP Tuning solution must be injected and evaluated. It is up to the analyst's discretion to run a tune at times other than prior to an ICAL, however it is recommended to evaluate the overall performance of the system.

The DFTPP Tuning Solution consists of four compounds: DFTPP (Decafluorotriphenylphosphine), Benzidine, Pentachlorophenol, and DDT, and is purchased from Agilent.

- Calibration Stock – 1,4-Dioxane, 2000 µg/mL in MeCl2, Restek #31853

  Stock standards are purchased as certified solutions from Restek. They are used to prepare calibration standards, which are used to create the calibration curve.

- **Working Standard Stock Prep**:

Compound	Initial Conc. (µg/mL)	Amount (mL)	Final Volume (mL)	Final Conc. (µg/mL)
1,4-Dioxane	2000	0.25	5.0	100
1,4-Dioxane-d8	2000	0.25	5.0	100

Bring up to Final Volume of 5mL with Methylene Chloride.

Final Concentration = 100 µg/mL

- **Calibration Curve Prep** for 1,4-Dioxane with 1,4-Dioxane-d8 as internal standard:

Cal Std Level	Amount of 1,4-Dioxane Stock (mL)	Amount of I.S. 1,4-Dioxane-d8 mL)	Final Volume (mL)	Final Conc. I.S. (µg/mL)	Final Conc. 1,4-Dioxane (µg/mL)
1	0.01	0.025	5.0	10	0.2
2	0.05	0.025	5.0	10	1.0
3	0.125	0.025	5.0	10	2.5
4	0.25	0.025	5.0	10	5.0
5	0.025**	0.025	5.0	10	10

6	0.0625**	0.025	5.0	10	25
7	0.125**	0.025	5.0	10	50
8	0.25**	0.025	5.0	10	100

**Use 1,4-Dioxane@2000 µg/mL, not intermediate stock @ 100 µg/mL

9.0 PROCEDURE

9.1 Extraction

- Water samples – Extract by method EPA 3510C. Refer to ENV-SOP-ELON-0005_3510C Water Extraction.
- Soil samples – Microwave extraction by method EPA 3546. Refer to ENV-SOP-ELON-0001_Microwave Extraction SW846 3546.

9.2 Analysis

9.2.1 Instrument Set Up

AGILENT TECHNOLOGIES – 7890 GC/MS

Column: RESTEK Rtx-PCB; 60m, 0.25mm ID, 0.25µm

Column flow: constant; 0.9 mL/min

Injection Temperature: 250°C

Transfer Line Temperature: 290°C

Injection Volume: 1.0 µL Splitless

Temperature Program:

35°C for 3 min.
Ramp @ 25°C/min to 200°C for 0 min.
Ramp @ 50°C/min to 300°C for 3.4 min.
Total run time: 15 min.

Purge Flow: 20 mL/min @ 2.0 min.

9.2.2 DFTPP tuning

Prior to running an initial calibration, DFTPP Tuning solution must be injected and evaluated. It is recommended that DFTPP solutions are prepared at 50 ng/µL or less in methylene chloride. Alternate concentrations may be used so long as the total amount injected is 50 ng or less. It is up to the analyst's discretion to run a tune at times other than prior to an ICAL, however it is recommended to evaluate the overall performance of the system.

The DFTPP Tuning Solution consists of four compounds: DFTPP (Decafluorotriphenylphosphine), Benzidine, Pentachlorophenol, and DDT, and is purchased from Agilent.

The mass spectrum of DFTPP must meet the performance criteria established by the method (listed below). If it does not, analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. Benzidine must also be evaluated for excessive tailing, and the tailing must be < 2. If this criterion is not met, instrument maintenance should be performed to correct.

The mass spectrum of DFTPP that is evaluated against the acceptance criteria is obtained in the following manner: Three scans (the peak apex and the scans immediately preceding and following the apex) are averaged, and a single scan no more than 20 scans prior to the DFTPP peak is subtracted. No part of the DFTPP peak itself may be background-subtracted.

MASS	M/Z ABUNDANCE CRITERIA
68	<2% of m/z 69
69	Present
70	<2% of m/z 69
197	<2% of m/z 198
198	Base peak or present
199	5-9% of m/z 198
365	>1% of base peak
441	<150% of m/z 443
442	Base peak or present
443	15-24% of m/z 442

9.2.3 Daily Maintenance

Maintenance may need to be performed to bring instrument back within calibration criteria or to satisfy mass ion abundance criteria. Daily maintenance includes replacement of the following: Injection liner, wool, inlet base seal and clipping head of guard column.

9.2.4 Initial Calibration

Initial calibration is performed before any samples are analyzed. A new initial calibration must be performed whenever the following corrective action or maintenance procedures are performed: Changing the electron multiplier or ion source chamber, column replacement, or if the calibration check standard criteria cannot be met.

The initial calibration requires a minimum of five different concentrations of all target analytes and surrogates. The calibration standards routinely used in this method are listed in Section 8.2.

The low concentration initial calibration standard must be less than or equal to the reporting limit (RL). Target analytes detected in a sample at concentrations below the concentration of the lowest

initial calibration standard should not be reported as quantitative results. If reported, they must be qualified as estimates or “J” flags.

Initial Calibration requirements for samples run by Method 8270E protocols:

The % RSD for all target analytes over the working calibration range must be less than or equal to 20% for the average RRF or "r" > 0.99 to be used for subsequent quantitations. If any of the target compounds exceed the 20% RSD limit or when the compound is calibrated by linear regression where the correlation coefficient < 0.99 alternative (SEE EPA METHOD 8000D), cannot be achieved, the system is considered too reactive, and the calibration must be repeated.

In some cases, the detector response may not be linear because of the broad range of the standards. Data points for individual target analytes at either extreme end of the calibration range may be discarded and the %RSD recalculated. Discarding an individual point in the middle of the calibration range is not permitted. If the low concentration standard is discarded, the reporting limits must be adjusted so that the lowest standard used for the calibration is less than or equal to the reporting limit.

Note: No points may be dropped from the initial calibration curve for any surrogate compound.

If any initial calibration standard is determined to be unusable (e.g., bad injection), the standard in question may be rerun within eight (8) hours of the last initial calibration standard analyzed and before any samples are run. The rerun standard may be incorporated into the initial calibration in its entirety, replacing the original standard. If the initial calibration still does not meet acceptance criteria, even with the replacement standard, then the entire initial calibration should be performed again.

All changes made to the calibration curve are documented with the reason given for the change.

When the instrument data system is updated to reflect the new initial calibration, the analyst verifies that it has been properly set up to calculate each target analyte according to the actual model used to establish the initial calibration (i.e., average RRF or Linear Regression) and to reflect any abbreviated ranges established for individual analytes.

The initial calibration is verified by analyzing a secondary source (ICV)- (Same solution as the LCS source). Criteria is 70-130% recovery.

9.2.5 Continuing Calibration Verification (CCV)

The calibration relationship established during the Initial Calibration is verified at the beginning of analytical sequence.

The analysis sequence is documented on an analysis run log maintained by the analyst.

At the start of each 12-hour analysis sequence, before any samples are analyzed, a mid-point calibration standard is analyzed to check the calibration curve.

Continuing Calibration requirements for samples run by Method 8270E protocols:

The percent difference or percent drift must be less than or equal to 20% for all target compounds

If the percent difference criteria are not met for any target analyte, then the analytical system should be evaluated for problems and corrective action taken as appropriate (change septa, check compressed gas cylinders, syringes, column fittings, etc., clean MS source, change the injector port or check filament, clean the inlet.)

If corrective action that may affect instrument response is taken, then the calibration check standard must be rerun before samples are analyzed. If the corrective actions do not resolve the problem(s) with the calibration check standard, then a new initial calibration must be performed.

Note: Additional Method 8270E Quality Assurance Requirements – Quantitation Check

When calculating the calibration curve using linear regression, a minimum quantitation check, on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration standard back into the curve (SEE METHOD 8000D). The recalculated concentration of the low calibration point should be within + 30% of the standards' true concentration. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered "out of control" and corrective action such as redefining the lower limit of quantitation and/or reporting those "out of control" target analytes as estimated.

Internal Standard (IS) retention times must be evaluated in the calibration check standard. The IS retention times should be within + 30 seconds of the retention times from the midpoint standard of the initial calibration. If the retention times shift more than 30 seconds, the system is inspected for malfunctions and corrections made as required. When corrections are made, a new calibration check standard is to be run.

I.S. areas must be evaluated in the calibration check standard. If the IS areas change by more than a factor of two (50-200%) from the areas in the midpoint standard of the most recently analyzed initial calibration, proceed as follows:

a. If I.S. is failing high, run the CCAL a 2nd time; (re-prep CCV) if results confirm, then the system needs to be inspected for malfunctions and corrections made as required. A new ICAL would need to be run.

b. If I.S. is failing low, adjust the tune and begin a new window with CCAL and blank; if maintenance and tune do not correct the failure, make corrective actions and re-calibrate.

If corrective action requires that the column be replaced, or that the electron multiplier or ion source be replaced, then performing a new initial calibration is automatically required.

If two calibration check standards are run in succession, one immediately following the other, and neither is deemed to have a bad injection, then the one closest in injection time to the associated sample analysis, or both standards, must be evaluated for and pass method performance criteria for sample analyses to continue.

10.0 DATA ANALYSIS & CALCULATIONS

10.1 Qualitative Identification

Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a

relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component. (i.e. broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes co elute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the co eluting compound.

Because target organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

All raw data must be properly identified with initials of the proper analyst and date analyzed.

10.1.1 Manual Integration

Manual integration is sometimes necessary to correct inaccurate automated integrations but must never be used to meet QC criteria or to substitute for proper instrument maintenance and/or method set-up. To assure that all manual integrations are justified and proper all manual integrations must be performed, documented, reviewed, and approved in accordance with corporate SOP ENV-SOP-CORQ-0006, *Manual Integration and Local SOP ENV-SOP-ELON-0058_Manual Integrations.* Refer to these SOPs for guidance on manual integration techniques and required procedures.

When performing manual integration of any peak in a calibration standard, client sample, or quality control sample, the integration must be performed in conformance with the procedures outlined in the SOPs for Manual integration procedures.

In Summary:

The most appropriate instrument parameters should be used during method development to allow for automatic integration by the data system in most cases.

All data must be integrated consistently for all standards, samples, and QC samples.

In those instances, when the automated software does not integrate a peak correctly, manual integration may be used to correct the improper integration performed by the data system. Manual integration should always be performed to create the analyst's best estimate of the actual peak area discerned from the chromatogram.

All manual integrations must be documented by printing, initialing, and dating the before and after reports with manual integrations as well as by recording the reasons for the manual integrations.

To prevent overwriting manual integrations, the analyst should not re-quantitate calibration standard files.

A minimum signal to noise ratio of 3:1 (based on peak height) must be achieved for any peak used in a calibration standard, client sample, or quality control sample.

When preparing to establish a new initial calibration, to prevent carry-over of numbers from previous calibrations, the analyst should “Clear all response factors “(which is a function in the software) from old calibration curves prior to running the new curve.

10.2 SIM – Selective Ion Monitoring Mode

A GC/MS system is operated in the SIM mode to increase sensitivity. In the SIM mode, the mass spectrometer repeatedly scans a smaller number of pre-selected masses rather than the typical mass range (35 to 500 amu) utilized in the full scan mode. In the GC/MS SIM acquisition mode, the masses to be monitored are selected based on the mass spectra of compounds to be analyzed.

GC/MS SIM improves detection limits without compromising positive identification of analytes. Sample preparation, chromatographic conditions, analyte identification, analyte quantification are the same whether the GC/MS system is operated in the full scan or SIM Mode.

SIM Parameters:

SIM Group	Ions (m/z) / Dwell in Group
#1	43.0, 46.0, 64.0, 88.0, 96.0, 58.0
	115.0, 150.0, 152.0
#2	56.0, 82.0, 83.0, 111.0, 54.0

10.3 Calculations

10.3.1 Calculation #1

$$\frac{\text{Final Extract Volume}}{\text{Sample Volume Extracted (L)}} \text{ X Dilution Factor X Instrument Value (µg/mL) = µg/L}$$

10.3.2 Calculation #2

All calculations are based on the internal standard technique.

$$Cx = \frac{AxCis}{AisRRF}$$

Cx = Compound concentration = instrument value
Ax = Area of the characteristic ion for the compound to be measured, counts
Ais = Area of the characteristic ion for the specific internal standard, counts
Cis = Concentration of the internal standard spiking mixture, ppm
RRF = Relative Response Factor is the average Response factor for the compound from the initial calibration

- **Relative Retention Times (RRT)** Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RTc}{RTis}$$

Where: RTc = Retention time of the target compound, seconds

Rtis = Retention time of the internal standard, seconds

- **Mean of the Relative Retention Times (RRT)** Calculate the mean of the relative retention times (RRT) for each target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

Where:

$\overline{RRT}$ = Mean Relative Retention time for the target compound for each initial calibration standard

RRT = Relative Retention time for the target compound at each calibration level.

- **Mean Retention Times (RT)** Calculate the mean of the retention times (RT) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RTi}{n}$$

Where:

$\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds

11.0 Quality Control & Method Performance

11.1 Quality Control

Prepare the following QC samples with each batch of samples. Refer to Appendix A for acceptance criteria and required corrective action(s).

QC Check	Acronym	Frequency
Method Blank	MB	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Laboratory Control Sample	LCS	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
LCS Duplicate	LCSD	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Matrix Spike/Matrix Spike Duplicate	MS/MSD	1 per batch of 20 or fewer samples. If batch exceeds 20 samples, every 20 samples.
Surrogate	SSTD	Added to every QC and client sample

Internal Standards	ISTD	Added to every QC and client sample

11.2 Instrument QC

Perform the following checks to verify instrument performance. Refer to Appendix A for acceptance criteria and required corrective action.

Instrument Check	Acronym	Frequency
Tune (MS Only)		Analyzed prior to ICAL and analyst discretion
Initial Calibration Verification	ICV	Immediately after ICAL
Continuing Calibration Verification	CCV	At the start of each 12 hour window

11.3 Method Performance

11.3.1 Method Validation

Refer to corporate SOP ENV-SOP-CORQ-0011 for general requirements and procedures for method validation.

Establish detection limits (DL) and limits of quantitation (LOQ) at initial method set up and verify the DL and LOQ on an on-going basis thereafter. Refer to corporate policy and/or SOP for DL and LOQ requirements and procedures.

12.0 Data Review & Corrective Action

12.1 Data Review

The data review process of Pace® Analytical Services includes a series of checks performed at different stages of the process by different people to ensure that SOPs were followed, the analytical record is complete, and properly documented, QC criteria were met, proper corrective actions were taken for QC failure and other nonconformance(s), and test results are reported with proper qualification, when necessary.

The review and checks that are performed by the employee performing the task is called primary review.

All data and test results are also peer reviewed.

This process, known as secondary review is performed to verify SOPs were followed, that calibration, instrument performance, and QC criteria were met and/or proper corrective actions were taken, qualitative ID and quantitative measurement is accurate, all manual integrations are justified and documented, and approved in accordance with the Pace® Analytical Services SOP for manual integration, calculations are correct, the analytical record is complete and traceable, and that results are properly qualified.

Lastly, a third-level review, called a completeness check, is performed by reporting or project management staff to verify the test report is complete.

Refer to laboratory SOP ENV-SOP-ELON-0035_Data Review for specific instructions and requirements for each step of the data review process.

12.2 Corrective Action

Corrective action is required when QC or sample results are not within acceptance criteria.

Refer to Appendix A for a complete summary of QC, acceptance criteria, and recommended corrective actions for QC associated with this test method.

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

Corrective action is also required when carryover is suspected and when results are over range.

Samples analyzed after a high concentration sample must be checked for carryover and reanalyzed if carryover is suspected. Carryover is usually indicated by low concentration detects of the analyte in successive samples analyzed after the high concentration sample.

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

13.0 POLLUTION PREVENTION & WASTE MANAGEMENT

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

The EPA requires that laboratory waste management practices comply with all applicable federal and state laws and regulations. Excess reagents, samples, and method process wastes are characterized and disposed of in an acceptable manner in accordance with the Pace® Chemical Hygiene Plan / Safety Manual. Refer to this manual for these procedures.

14.0 MODIFICATIONS

The procedures in this SOP have not been modified from the reference test method(s) cited.

When applicable, comparability and/or equivalency studies necessary to validate the modification as required per corporate SOP ENV-SOP-CORQ-0011 are retained by local quality personnel for historical reference.

15.0RESPONSIBILITIES

- All employees of Pace® Analytical Services that perform any part this procedure in their work activities must have a signed Read and Acknowledgement Statement (R&A) in their training file for the version(s) of the SOP that were in effect during the time the employee performed the activity.
- Local quality personnel are responsible for tracking the currency of the R&A on this SOP for employees at the locations they are assigned to and for notifying the General Manager (GM), however named, when R&A are overdue or outstanding. The GM and the employee's direct supervisor are responsible for ensuring the employee completes the R&A assignments as required.

- The supervisors and managers of Pace® Analytical Services, however named, are responsible for training employees on the procedures in this SOP, implementing the SOP in the work area, and monitoring on-going adherence to the SOP the work area(s) they oversee.
- All employees of Pace® Analytical Services are responsible for following the procedures in this SOP. Unauthorized deviations or departures from this SOP are not allowed except with documented approval from the local Quality Manager and only when those deviations do not violate the Pace® Code of Ethics or Professional Conduct (COR-POL-0004) or associated policy and procedure(s). Hand-edits or manual change to the SOP are not permitted. If a change is desired or necessary, Pace® employees must follow the procedures for document revision specified in corporate SOPs ENV-SOP-CORQ-0015 *Document Managemen*t and ENV-SOP-CORQ-0016 *SOP for Creation of SOP and SWI*.
- Local quality personnel are responsible for monitoring conformity to this SOP during routine internal audits of work areas that utilize this SOP and for communicating gaps and deviations found during monitoring to the work area supervisor, who is responsible for correction of the situation.

16.0 ATTACHMENTS

- Appendix A: QC Summary & Corrective Action Table

17.0 REFERENCES

- ENV-SOP-CORQ-0006, *Manual Integration*, current version.
- ENV-SOP-CORQ-0011, *Method Validation*, current version.
- ENV-SOP-CORQ-0015, *Document Management*, current version.
- ENV-SOP-CORQ-0016, *SOP for SOP and SWI,* current version.
- ENV-TMP-CORQ-0007, *Quality Manual Template*, current version.
- COR-POL-0004, *Code of Ethics and Professional Conduct*, current version.
- COR-MAN-001, *Pace® Safety Manua*l, current version.
- ENV-MAN-ELON-0001, *Quality Assurance Manual*, current version.
- SW-846 Method 8270E, Test Methods for Evaluating Solid Waste, “Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry”, June 2018, Revision 6.
- Connecticut DEP, RCP, Quality Assurance and Quality Control Requirements, Semi-Volatile Organic Compounds by method 8270E, SW-846, Version 6, June 2018.
- USEPA – “Determinative Chromatographic Separations”, SW846, 5th edition, March 2018, Method 8000D.
- Instrument Manuals, HP GCMS 5975.

18.0 REVISION HISTORY

Authorship

Primary Author[1]	Job Title	Date Complete
Christian Merchant	R&D	07/25/2022

[1]The primary author is the individual / role responsible for the content of this SOP. Send questions or suggestions for content to the primary author. See the Quality Manager for questions or concerns related to implementation of this SOP.

Revisions Made from Prior Version

Section	Description of Change
All	Updated using Pace SOP Template
2.0	Updated to include soil prep information.
6.0	Changed soil hold time.
9.2.1	Replaced pulsed splitless injection technique with splitless.
9.2.2	Added DFTPP injection guidelines.

Document Succession: This version replaces the following documents:

Document Number & Version	Document Title	Effective Date:
Doc #314 Rev5	SOP 1,4-Dioxane 8270E	12/14/2021

Appendix A: QC Summary and Corrective Action Table

QC Item	Frequency	Acceptance Criteria	Corrective Action	Qualification
ICAL	At instrument set up, after CCV failure	Must meet one of curve fit options presented in Section 9.2.4. For any curve fit other than Average RF (RSD), curve must also pass RSE test at the low and midpoint calibration standard.	Identify and correct source of problem, repeat	None. Do not proceed with analysis
ICV	After Each ICAL	All analytes must be within ± 30% of the true value. (%R)	Identify source of problem, re-analyze. If repeat failure, repeat ICAL. Analysis may proceed if it can be demonstrated that the ICV exceedance has no impact on analytical measurements. For example, the ICV %R is high, CCV is within criteria, and the analyte is not detected in sample(s).	Qualify analytes with ICV out of criteria.
CCV	Daily, at the start of each 12-hour sequence	All analytes within ± 20 % of the true value (%R)	See Section 9.2.5 for required corrective actions based on circumstance.	Qualify analytes with CCV out of of criteria.
Internal Standards	Every field sample, standard and QC sample	15-130%	Troubleshoot instrument performance. Reanalyze samples.	Qualify outages and explain in case narrative.
Surrogate	Every field sample, standard and QC sample	15-130%		
Method Blank	Every 20 samples or less	<RL		
LCS/LCSD	Every 20 samples or less	40-140%		
MS/MSD	Every 20 samples or less	30-140%		
Tune Standard	Prior to ICAL and analyst descretion	Meet criteria in section 9.2.2		

APPENDIX D
Resumes of Key Personnel

PROJECT MANAGER

PATRICK MONTUORI, PG

Mr. Montuori is an environmental consultant with over 6 years of experience involving a wide range of environmental and geologic projects across New York State. Mr. Montuori provides expertise in all phases of environmental investigation including New York State Department of Environmental Conservation (NYSDEC) Site Characterizations, Remedial Investigations, and Soil Vapor Intrusion (SVI) investigations. He has prepared Site Management Plans, Site Characterization and Remedial Investigation Work Plans, Remedial Action Work Plans, Health and Safety Plans. Mr. Montuori has managed remedial excavations, subsurface investigations, groundwater injections, and soil vapor extraction pilot testing. His responsibilities at HRP Associates include project management, environmental sampling, field oversight, data interpretation, and report preparation.

EXPERIENCE

Site Characterization, Various Sites, Brooklyn, Queens, & New York, NY
As Project Manager, developed and implemented investigations at thirteen brownfield sites located throughout Brooklyn and Queens. The investigations focused on protecting offsite receptors through the delineation of chlorinated volatile organic compound (CVOC) contamination in groundwater and soil vapor. Responsibilities included development of site-specific soil vapor intrusion (SVI) sampling plans in coordination with the NYSDEC and NYSDOH; use of data visualization techniques to identify potential exposure pathways; obtaining NYCDOT and MTA permits required for the investigation drilling program; obtaining property access for residential and commercial properties for SVI sampling; completion of SVI investigation at dozens of off-site properties, coordination and oversight of subcontractors, data analysis and preparation of Site Characterization reports.

Site Characterization, Francis S. Gabreski Airport, Westhampton, NY
As Senior Project Consultant, developed and implemented an investigation to delineate per- and polyfluoroalkyl substance (PFAS) groundwater contamination related to aqueous film-forming foam (AFFF) releases at the municipal airport and Air National Guard base. Responsibilities included identifying potential AFFF release areas (i.e., firefighting training areas, aircraft crash sites, fueling areas, and landfill/disposal areas) through review of historic maps, records, interviews with staff, and previous investigation results; development and implementation of a sampling plan and scope of work; and obtaining the necessary permits for investigation work from the Federal Aviation Administration (FAA), and contractor oversight during the installation of 100 ft soil borings and collection of vertical profile groundwater samples.

Building Demolition and Remedial Investigation, Former Dry Cleaner, Williamson, NY
As Senior Project Consultant, planned and coordinated the demolition of the former dry cleaner building and developed and implemented an investigation to determine the degree and extent of tetrachloroethylene (PCE) contamination in soil and groundwater beneath the site. Responsibilities included identifying soil boring and monitoring well locations based on historical information and previous investigation results; coordination of project field staff and subcontractors during demolition and investigation activities; analysis of soil and groundwater analytical data to develop a conceptual site model; and development of recommendations for further investigation.

EDUCATION

- BS, Geological Sciences, State University of New York at Plattsburgh, 2016

PROFESSIONAL REGISTRATIONS/ CERTIFICATIONS

- NYS Professional Geologist #1298

TRAININGS

- OSHA - 40-Hour HAZWOPER Health and Safety Training
- OSHA - 8-Hour HAZWOPER Annual Refresher Training
- OSHA - 30-Hour Construction Training
- OSHA - 10-Hour Construction Training
- CPR/First Aid/AED

Site Characterization, Former Howard & Bowen Site, Rochester, NY
As Senior Project Consultant, developed and implemented an investigation to characterize impacts to soil and groundwater and evaluate exposure pathways to potential receptors at the former film processing/silver recovery facility and closed landfill. Responsibilities included assessment of site history through review of previous investigations and available database records; development of investigation strategy in collaboration with the NYSDEC and NYSDOH; oversight of the investigation drilling program, including siting of soil boring and monitoring well locations, selection of sampling intervals and determination of well construction; analysis of soil and groundwater analytical data to develop a conceptual site model, identify exposure pathways to potential receptors, and develop recommendations for site reclassification in the NYS Inactive Hazardous Waste Disposal Site (Sate Superfund) Program; communication of results to the NYSDEC and NYSDOH; and preparation of the Site Characterization Report.

Interim Remedial Measure Monitoring – Inactive Hazardous Waste Site, Schenectady, NY
As Senior Project Consultant, developed, coordinated, and implemented a groundwater monitoring plan to assess the effectiveness of in-situ treatment in mitigating chlorinated solvent contamination in site groundwater. Responsibilities included: development of the groundwater monitoring plan in collaboration with the NYSDEC; preparation of a Construction Completion Report to document in-situ treatment work; conducting groundwater monitoring and sampling; communication of results to the NYSDEC and preparation of quarterly monitoring reports; and development of recommendations for additional in-situ treatment based on review of quarterly monitoring data.

Remedial Investigation – Former Dry Cleaner Site, Milton, NY
As Senior Project Consultant, performed data analysis in support of conceptual site model development, identification of data gaps, and development of recommendations for additional investigation. Responsibilities included: review of soil and groundwater analytical data to determine nature and extent of chlorinated volatile organic compound contamination; development of contaminant isopleth maps and groundwater contour maps; and performing hydraulic conductivity (slug) testing at site monitoring wells.

Remedial Action Implementation – Former Landfill BCP Site, Westchester County, NY
As Project Geologist, conducted oversight, field work, and reporting related to the implementation of a Remedial Action Work Plan on a NYSDEC Brownfield Cleanup Program (BCP) site. Responsibilities included: remedial excavation oversight, excavation end-point soil screening and sampling, and community air monitoring program (CAMP) implementation; overburden and bedrock monitoring wells installation oversight; development and implementation of a groundwater monitoring program, including the sampling of per-and polyfluoroalkyl substances (PFAS); oversight of construction of a soil vapor extraction (SVE) system and two sub-slab depressurization (SSD) systems; SVE and SSD system pilot testing and start-up testing, including collection of air quality and vacuum performance data; groundwater well installation and monitoring; planning and conducting in-situ application of emulsified vegetable oil (EVO) and zero valance iron (ZVI) for treatment of chlorinated solvents in groundwater; installation oversight of a vegetated site cap; presenting at monthly community meetings; correspondence and coordination with NYSDEC; preparation of progress reports, work plans, and documentation related to the site management plan (SMP) and final engineering report (FER).

PROJECT CONSULTANT

ELLIOTT JACKSON

Mr. Jackson is an environmental consultant with experience on an array of Site Characterizations and Remedial Investigations for the New York State Department of Environmental Conservation (NYSDEC) across New York State. He has provided contractor oversight during soil boring and monitoring well installations, soil excavation, and building demolition. Mr. Jackson has prepared Site Characterization and Remedial Investigation Work Plans, Health and Safety Plans, and Site Characterization reports. Mr. Jackson has performed subsurface investigations, groundwater sampling, soil vapor intrusion investigations, and community air monitoring program (CAMP) oversight. His responsibilities at HRP include contractor oversight, environmental sampling, data analysis and interpretation, and report writing. Mr. Jackson has valuable experience in data compilation and presentation using EQuIS, and using GIS to create effective visual representations of site investigation data.

EXPERIENCE

Multiple Sites in Brooklyn/New York, New York, New York
Served as Project Consultant for off-site Site Characterization investigations for multiple DEC Brownfield sites in Brooklyn, Queens, and Manhattan, New York. Responsibilities included reviewing previous investigations, compiling historic use data, writing work plans, site-specific Health and Safety Plans, and use of GIS for data visualization. Drilling oversight and air monitoring, groundwater sampling, and completion of soil vapor intrusion investigations at off-site properties were also a part of his services on these sites.

Former Barthelmes Manufacturing Site, Rochester, New York
Served as Project Consultant for the Site Characterization of the Former Barthelmes Manufacturing Site in Rochester, New York. Responsibilities included the oversight of monitoring well installation, soil logging and sampling, low-flow groundwater sampling, soil vapor intrusion investigations, data analysis and visualizations, and complex report writing.

Newtown Creek, Maspeth, New York
Served as Project Consultant for the Upland Site Characterization of Newtown Creek in Queens, New York. Conducted field activities on two separate occasions to investigate and characterize the impacts to surface water on Newtown Creek related to uplands properties identified as environmental concerns. Responsibilities included operation of FLIR thermal cameras and Trimble GPS units to conduct a shoreline quality survey to identify potential groundwater seeps into the creek during low-tide events, and sampling surface water of identified seeps.

Francis S. Gabreski Airport, Southampton, New York
Served as Project Consultant for the Site Characterization of the Gabreski Airport in Southampton, New York. The Fracis S. Gabreski Airport is a 1,451-acre Site which was investigated for potential surface releases of AFFF from firefighting training exercises and aircraft crash fire response. Responsibilities included characterization of site soils to 100 feet below grade, collection of vertical profile grab groundwater samples, implementation of PFAS decontamination procedures on drill rig and sampling equipment, planning and logistics, data analysis and management, complex GIS compilation, and report writing.

EDUCATION

- BS, Geology, State University of New York, The College at Oneonta, 2022

TRAININGS

- 40-hour HAZWOPER
- NYSDEC 4-Hour Erosion and Sediment Control Training

PUBLICATIONS

- Structural Controls on the Deposition and Stratigraphy of the Canadaway Group (Upper Devonian) in Chautauqua County, Western New York State
- Northeastern Section GSA – 57th Annual Meeting – March 2022

CONTINUING EDUCATION

- The Groundwater Pollution and Hydrology Course: Princeton Groundwater, Inc. (3.8 CEU)

SENIOR PROJECT GEOLOGIST (STAFF)

MICHAEL A. VARNI, LEP

IDENTIFIED WORK ELEMENTS EXPERIENCE

- Site Characterization
- Phased Remedial Investigation/Feasibility Study (RI/FS)
- Soil Vapor Intrusion (SVI) Investigations
- Analytical Quality Assurance/Quality Control Activities (QA/QC)
- Citizen Participation (CP) Activities
- Health and Safety Plan (HASP) Development
- Potentially Responsible Parties (PRP) and Third-Party Oversight

SUMMARY OF QUALIFICATIONS

Mr. Varni has over 10 years of experience in environmental assessment and site investigation. He has performed these services for a number of governmental, municipal, commercial, industrial and private clients. Specifically, Mr. Varni has been responsible for Phase I Environmental Site Assessments at small- to large-scale commercial and industrial facilities. In all cases, the specific manufacturing processes were analyzed and waste streams were defined to identify all potential sources and releases of contaminants to the environment. Mr. Varni has performed numerous Phase II and Phase III investigations involving drilling and test pit supervision, monitoring well installation, and sampling of soils, groundwater, and soil vapor. Mr. Varni has performed numerous site remediation oversight projects including soil excavation, groundwater treatment systems, and vapor extraction systems.

Remedial Actions, West Hartford, CT

This project involved the cleanup and redevelopment of a former large engine break and drill chuck manufacturer contaminated with PCBs, petroleum, and chlorinated solvents. The project involved demolition of the existing industrial building, followed by removal of subslab piping and drainage structures, and finally remediation of soils to achieve compliance with both state and federal regulations. Mr. Varni's responsibilities included supervision of remediation contractors conducting soil excavation, field monitoring and sampling of soil and groundwater, field monitoring of dust and weather conditions according to a project specific remediation and health and safety plan, coordination with construction and remediation crews, and data management and analysis. The project culminated in a successful Brownfields-type redevelopment of the property into a retail shopping center.

Phase I Environmental Site Assessments

- Inspection of a wide variety of commercial and industrial facilities and properties to identify specific site environmental conditions and concerns
- Interviewing site contacts and municipal, state, and federal officials to determine current and former site use and environmental concerns
- Historical research into current and former land use and regulatory history through review of aerial photographs and other published sources and state and local agency records
- Review of published geologic data to determine site setting including surficial and bedrock geology, and groundwater and surface water, and other environmental factors to evaluation contaminant migration potential.

Phase II and III Subsurface Investigations

- Identification of potential contamination sources at sites due to present and historical land uses
- Collection, description, and interpretation of split spoon sediment samples

NSPE LEVEL

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EDUCATION

- MS, Geology, University of Maryland, College Park, Maryland, 2002
- BS, Environmental Earth Science, Eastern Connecticut State University, Willimantic, Connecticut, 1999

TRAINING

- OSHA 40 Hour Hazardous Waste Operations & Emergency Response
- OSHA 8 Hour Refresher Hazardous Waste Operations & Emergency Response

PUBLICATIONS

- The effect of rising atmospheric oxygen on carbon and sulfur isotope anomalies in Neoproterozoic Johnnie Formation, Death Valley, USA. Kaufman, A. J., Corsetti, F.A., and Varni, M.A.

BASE OFFICE LOCATION

Farmington, CT

Environmental Data Services, Inc. (EDS) is a woman-owned, small business providing laboratory data validation and data usability. We have been supporting the environmental industry since 1993 and have worked on hundreds of projects including many in New York State. We are a certified Women's Business Enterprise (WBE) by New York State Division of Minority and Women's Business Development.

We are experienced validating all analytical methods including organic, inorganic and radiological methods. We are experienced validating perfluorintated alkyl substances (PFAS), VOC, SVOC, pesticides, PCBs, herbicides, metals, cyanide, hexavalent chromium, petroleum hydrocarbons, MEE, and volatile compounds in air. As well as many other parameters. We have validated soil, sediment, groundwater, tissue and air samples.

We are experienced in using the USEPA Region 2 data validation SOPs and the USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic and Inorganic Methods Data Review. We have prepared hundreds of DUSRs as specified in NYSDEC DER-10/Technical Guidance for Site Investigation and Remediation; Appendix 2B, Guidance for Data Deliverables and the Development of Data Usability Summary Reports (May 2010).

The following is a brief list of projects completed within New York State. DUSRs were prepared for each project within a 14 or 21 day turn around time.

Preferred Environmental

- Newtown Creek, Maspeth, New York
- Long Island Railroad, Long Island, New York
- Wortman Aveneue, Brooklyn, New York

CDM Smith

- IBM Owego, Owego, New York
- Lubricant Packaging, Middletown, New York
- Charlton Cleaners, Staten Island, New York

Majestic Weaving, Cornwall, New York

Wantagh Cleaners, Wantagh, New York

ERM Northeast

Honeywell, Hoosick, New York

TRW, Union Springs, New York

Lockwood, Kessler & Bartlett

Syossett Landfill, Syossett, New York

110 Sand, Melville, New York

AECOM

East Hampton Airport, Wainscott, New York

64th Street, Woodside, Queens, New York

Kenco Chemical, Glenville, New York

Crystal Cleaners, Pelham, New York

EA Engineering, Science and Technology

Hudson River, Upper Hudson River, New York

Millens Scrapyard, Kingston, New York

Cuba Landfill, Cuba, New York

Corning Materials, Corning, New York

Gannett Fleming

Frito-Lay, Brooklyn, New York, NYSDEC

Salem Fields Cemetary, Queens, New York

Norfolk Southern Railroad, Elmira, New York

Brown and Caldwell

Rensselaer MGP, Rensselaer, New York

Cohoes MGP, Cohoes, New York

Oswego MGP, Oswego, New York

CT Male

Miron Lumber, Kingston, New York

350 Liberty Street, Newburgh, New York

Stratis Consulting

Pelham Bay Landfill, Pelham, New York

Penn & Fountain Landfill, Brooklyn, New York