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November 17, 2020

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Subject: Emerging Contaminant/PFAS Scoping Document

Ashview Terrace Apartments

988-1020 Willard Drive, Ashwaubenon, Wisconsin

BRRTS #: 02-05-564043

Mr. LeRoy,

Georgia-Pacific LLC (GP) is submitting the enclosed document in response to your letter dated September 14, 2020 regarding the above-referenced matter.

Please feel free to let me know if you have questions or wish to discuss.

Sincerely,

Michael Hassett

cc: Greg Council, Tetra-Tech

Michael Healt

Michael Savale, Tetra-Tech

PFAS Site Investigation Work Plan

Ashview Terrace Apartments Ashwaubenon, Wisconsin





#117-4124161November 16, 2020



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PFAS Site Investigation Work Plan

Ashview Terrace Apartments Ashwaubenon, WI

#117-4124161 November 16, 2020

PRESENTED BY

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Prepared by:

Michael Savale Project Manager Date

11/16/2020

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11/16/2020

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TABLE OF CONTENTS

1.0 INTRODUCTION	1
2.0 SITE BACKGROUND	
2.1 Project Contacts	1
2.2 Site Location	1
2.3 Site Description and Setting	2
2.4 Site History	2
2.5 Previous Environmental Investigations	2
3.0 PFAS INVESTIGATION	4
3.1 Pre-Drilling Preparations	4
3.2 Soil Borings	5
3.3 Monitoring Well Installation	5
3.4 Water-Level Measurement	6
3.5 Groundwater Sampling	6
3.6 Quality Assurance/Quality Control (QA/QC) Samples	7
3.7 Sample Handling	8
3.8 Decontamination Procedures	8
3.9 Investigation-Derived Waste Management	8
4.0 REPORTING	10
5.0 REFERENCES	11

LIST OF FIGURES

- Figure 1 Site Location Map
- Figure 2 Proposed Monitoring Well Location Map
- Figure 3 Surrounding Features

APPENDICES

- Appendix A Standard Operating Procedures and Safe Work Practices
- Appendix B Groundwater Water Quality Data Sheet
- Appendix C Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Expectations

CERTIFICATION

Hydrogeologist:

I hereby certify that I am a hydrogeologist as that term is defined in s. NR712.03(1), Wis. Adm. Code, and that, to the best of my knowledge, all information contained in this document is correct and the document was prepared in compliance with all applicable requirements in chs. NR700 to 726, Wis. Adm. Code.

Mark A. Manthey, P.G, Associate Hydrogeologist

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ACRONYMS/ABBREVIATIONS

Acronyms/Abbreviations	Definition
amsl	Above Mean Sea Level
bgs	Below Ground Surface
BRRTS	(Wisconsin) Bureau for Remediation and Redevelopment Tracking System
DO	Dissolved Oxygen
EPA	United States Environmental Protection Agency
HDPE	High density polyethylene
IDW	Investigation Derived Waste
LLC	Limited Liability Corporation
mg/L	Milligrams per Liter
NR 140	Wisconsin Administrative Code, Department of Natural Resources Chapter 140
NR 292	Wisconsin Administrative Code, Department of Natural Resources Chapter 292
NR 716	Wisconsin Administrative Code, Department of Natural Resources Chapter 716
ORP	Oxidation-Reduction Potential
PCBs	Polychlorinated Biphenyls
PE	Professional Engineer
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
PG	Professional Geologist
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
SIWP	Site Investigation Work Plan
SVOC	Semi-volatile organic compound
SOP	Standard Operating Procedure
TCLP	Toxic Characteristic Leaching Procedure
USCS	Unified Soil Classification System
USGS	United States Geologic Survey
VOCs	Volatile Organic Compounds
WDHS	Wisconsin Department of Health Services
WDNR	Wisconsin Department of Natural Resources
WTM	Wisconsin Transverse Mercator Co-ordinate Plane

1.0 INTRODUCTION

On behalf of Georgia-Pacific LLC, Tetra Tech, Inc. (Tetra Tech), has prepared this PFAS Site Investigation Work Plan (Work Plan) to detail the groundwater investigation of the potential presence of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in groundwater at the Ashview Terrace Apartments site located at 988-1020 Willard Drive, in the Village of Ashwaubenon, Brown County, Wisconsin 54304 (Site). A Site location map is presented in **Figure 1**. The Site is being managed as a Wisconsin Department of Natural Resources (WDNR) Bureau for Remediation and Redevelopment Tracking System (BRRTS) Site (Site # 02-05-564043).

The goal of this Work Plan is to determine if PFAS compounds are present in the Site groundwater. This Work Plan has been prepared in response to the WDNR August 17, 2020 *Reminder to Include Evaluation of Emerging Contaminants in Site Investigation* letter and their September 14, 2020 *Review of Site Investigation Work Plan* letter. Both letters requested that the Site be evaluated for the potential presence of PFAS. This Work Plan includes a scoping evaluation and presents the scope of work to satisfy the PFAS site investigation requirements outlined in the WDNR's two letters and has been prepared in accordance with the site investigation requirements prescribed in Chapter NR 716 Wisconsin Administrative Code (Wis. Admin. Code).

A Site Investigation Work Plan (SIWP) was submitted to the WDNR by Wood Environment and Infrastructure Solutions, Inc. of Minneapolis, MN (Wood) on June 8, 2020. The goal of the Wood SIWP was to define areas of the Site where paper sludge may be present and to evaluate surficial soils at the Site for the presence of polychlorinated biphenyls (PCBs), lead, and mercury. This PFAS Site Investigation Work Plan has been prepared as a supplement to the scope of work proposed in the Wood SIWP to address the WDNR's request that the Site be evaluated for emerging contaminants.

2.0 SITE BACKGROUND

This section presents Tetra Tech's understanding of the Site history, location, geologic setting, and a brief summary of previous environmental Site investigations.

2.1 PROJECT CONTACTS

Responsible Party: Georgia-Pacific LLC., Mike Hassett, 133 Peachtree Street NE, Atlanta, GA 30303

Environmental Consultant: Tetra Tech, Michael Savale, 710 Avis Drive, Suite 100, Ann Arbor, MI 48108

WDNR Project Manager: BJ LeRoy, PG., Hydrogeologist Northeast Region, Remediation and Redevelopment Program, WDNR, 2894 Shawano Avenue, Green Bay, WI

54313

Property Owner: Perry Charles and Marilyn J Living Trust, 1360 Greenway Terrace, Elm Grove WI 53122

Drilling Contractor: Cascade Drilling and Technical Services, 6215 Lehman Drive, Flint, MI 48507

Public Utility Locator: Wisconsin 811, Diggers Hotline

Private Utility Locator: GLS Utility LLC., 1756 Tam-O-Shanter Trail, Sun Prairie, WI 53590

Analytical Laboratory: Vista Analytical Laboratory, 1104 Windfield Way, El Dorado Hills, CA 95762

Analytical Laboratory: Pace Analytical, 1241 Bellevue St, Suite 9, Green Bay, WI 54302

2.2 SITE LOCATION

Site Name: Ashview Terrace Apartments

Site Address: 988-1020 Willard Drive, Ashwaubenon, Brown County, Wisconsin 54304

Wisconsin Transverse Mercator (WTM91) Location:

X Coordinate: 673295 m

Y Coordinate: 448028 m

Latitude: 44.4993009

Longitude: -88.0720701

USGS Topographic Map: SE 1/4 of the SE 1/4 of Section 4, Township 23 North, Range 20 East, Brown

County, WI.

Wisconsin Tax Parcel ID: VA-120-5

See Figure 1.

2.3 SITE DESCRIPTION AND SETTING

The Site is approximately 3.3 acres in size; 2 acres are covered by apartment buildings and associated hardscapes (parking lots, sidewalks, etc.) and the remaining 1.3 acres are covered by grass (**Figure 2**). The Site is in a mixed commercial and residential area in the northeast portion of Ashwaubenon. To the south of the Site is Willard Drive followed by the Parkview Middle School. To the east is the Playmates Childcare and Preschool commercial business followed by another apartment complex. To the north is Bel Aire Court followed by a Target Corporation commercial business. To the west is an Animal Hospital followed by a private medical practice.

The topography of the Site is relatively flat with a slight slope downward to the southeast. The approximate elevation of the Site is 650 feet above mean sea level (amsl). No wetlands or other bodies of surface water exist on the Site and the nearest surface waters are the Dutchman Creek and the Fox River, located approximately 0.75 southwest and 1.5 miles southeast of the Site, respectively (**Figure 3**).

Per prior soil investigations, much of the Site is within the boundary of a former borrow pit and is underlain by fill materials consisting of sandy clay, silty sand, gravel, and paper sludge. The fill materials encountered below 1 to 2 feet of topsoil or asphalt/concrete extend to 16 feet below ground surface (bgs). The extent of the fill material is depicted on **Figure 2**. The western portion of the Site is underlain by native sandy clay and/or silty sands (Amec Foster Wheeler 2017). Groundwater is expected to be encountered between 4 to 8 feet bgs and groundwater is assumed to flow to the southeast, towards the Fox River (OMNNI 2015).

2.4 SITE HISTORY

Review of previous environmental investigations indicate the Site was an agricultural field until the 1930s. From the 1930s through the 1950s the Site served as a borrow pit. Beginning in approximately 1952, paper-mill wastes were disposed of in the borrow pit. The Site overlays a portion of the filled borrow pit.

2.5 PREVIOUS ENVIRONMENTAL INVESTIGATIONS

To date, five environmental investigations have been conducted at the Site from February 2015, when the potential for hazardous substance spill was discovered during a records search, through August 2017. The historical Site investigations have been undertaken by OMNNI Associates of Appleton WI (OMNNI), and Amec Foster Wheeler Environment & Infrastructure, Inc. of Minneapolis, MN which has since become Wood Environmental & Infrastructure Solutions, Inc. The historical Site investigations have consisted of:

- Advancement of hand auger, hand probe, and Geoprobe soil borings to various depths,
- · Installation and sampling of two temporary monitoring wells, and
- Collection of 43 soil and 2 groundwater analytical samples.

The previous Site investigations, conducted on or in close proximity to the former borrow pit area, were performed primarily to assess the subsurface soils and shallow groundwater for the presence of PCBs and metals. These investigations have identified PCBs, arsenic, mercury, and lead above their WDNR Industrial

site direct-contact residual contaminant levels (RCLs), Non-Industrial site direct-contact RCLs, and Soil-to-Groundwater pathway RCLs in the soil and fill material samples collected from the central and southeastern portions of the Site. No PCBs or metals have been detected above Chapter 140 Wis. Admin. Code Enforcement Standards or Preventative Action Limits in the groundwater samples collected at the Site. It has been concluded that the contaminants present in the Site soils are consistent with those expected to occur from wastepaper sludge, however, additional contaminants were detected that are not associated with paper sludge (Amec Foster Wheeler 2017). To date, no environmental samples collected at the Site have been submitted for PFAS analysis.

3.0 PFAS INVESTIGATION

Groundwater sampling will be conducted at the Site to determine if PFAS impacts are present in the groundwater. There are many sources of PFAS in the environment. Paper wastes are known to be a potential source of PFAS; some types of paper were treated with PFAS-containing products to make them water- and grease-resistant.

PFAS are considered to be emerging contaminants and the potential health effects from environmental exposures (primarily via drinking water) are not yet well understood. The United States Environmental Protection Agency (EPA) has set a health advisory concentration of 70 nanograms per liter (ng/L) for the sum of two PFAS compounds: perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). In 2019, the Wisconsin Department of Health Services (WDHS) recommended enforcement standards of 20 ng/L for each of these compounds. Enforcement standards have not yet been adopted in Wisconsin.

Due to the nature of PFAS, their prevalence in many consumer products, and the low concentrations that are of potential concern, special precautions will be taken to avoid introducing PFAS during drilling and sampling. Groundwater sampling activities will be conducted according to methods and protocols for collecting and handling groundwater samples analyzed for PFAS as outlined in Tetra Tech Standard Operating Procedure (SOP) 1. SOP 1 is consistent with EPA prescribed sampling methods. All SOPs referenced throughout this document are Tetra Tech SOPs, unless specified otherwise, and are included in **Appendix A**. Site features and proposed soil boring/monitoring well locations are presented on **Figure 2**. The planned field activities include the following:

- Pre-drilling coordination with property owners and Ashwaubenon, permitting, and utility clearing
- Collection of continuous soil cores to a maximum depth of 40 feet bgs for geologic logging
- Installation and development of three groundwater monitoring wells:
 - One monitoring well will be installed upgradient of the Site to evaluate groundwater PFAS concentrations not impacted by Site sources
 - Two monitoring wells will be installed downgradient of the Site to evaluate Site-related groundwater PFAS concentrations
- Collection of groundwater samples using minimal drawdown (low-flow) techniques from the monitoring wells for PFAS analysis
- Handling and disposal of investigation derived waste (IDW) in accordance with local, state and federal regulations

3.1 PRE-DRILLING PREPARATIONS

Prior to advancing soil borings at the Site, Georgia-Pacific and Tetra Tech will coordinate property access with the current property owner and will communicate with the Village of Ashwaubenon to determine if

permits are required. Utility locating will be completed by utilizing the Wisconsin 811 Diggers Hotline. Following the public utility locating, private utility locating will be performed by GLS Utility LLC at each of the three soil boring locations. The private utility locate will utilize ground penetrating radar and other subsurface scanning tools, as needed, to determine if any underground utilities are in proximity to the proposed soil boring locations.

3.2 SOIL BORINGS

The first five feet of each soil boring will be completed using a hand auger. The remainder of each soil boring will be completed using sonic drilling methods. A core barrel assembly will be advanced into the subsurface to obtain continuous soil cores. The soil borings will be advanced to a maximum depth of 40 feet, or until groundwater is encountered, whichever comes first. The exact depth will be determined based on field observations. All non-disposable drilling equipment will be decontaminated in accordance with procedures detailed in **Section 3.8** below.

As the soil cores are brought to the surface, they will be placed on plastic sheeting so that they can be logged by the on-Site Tetra Tech geologist. Each soil core will be described including sample recovery and lithology description using the Unified Soil Classification System (USCS). Signs of contamination (staining and odor), moisture content, and other notable observations/information will be noted. Photographs will be taken of the soil cores in their entirety and close-up photographs will be taken where essential information requires greater detail (lithologic contacts, staining, grain size differences, etc.). The photographs will include a scale and written details to convey the important aspects of the soil cores. Soil boring installation is discussed in SOP 4 and Safe Work Practice SOP 5-4. Soil logging procedures are described in SOP 6.

3.3 MONITORING WELL INSTALLATION

Following the completion of the soil boring advancement, a monitoring well will be installed at each of the three soil boring locations. The monitoring wells will be installed in accordance with the procedures and specifications described in Chapter NR 141 Wis. Admin. Code. Monitoring well installation procedures are also discussed in SOP 4. Each monitoring well will be constructed as follows:

- A 2-inch diameter Schedule 40 polyvinyl chloride (PVC) casing with 5 feet of 0.010-inch slot PVC screen will be installed to three feet below the top of the observed water table.
- A locking well cap will be installed.
- A sand filter pack will be placed to a minimum of 2 feet above the well screen. If the depth to
 groundwater is less than 7 feet bgs, the filter pack height above the top of the well screen will be
 reduced to 6 inches to accommodate the placement of the annular space seal.
- Two feet of clean fine sand will be placed above the filter pack. If the depth to groundwater is less than 5 bgs, the fine sand thickness will be reduced to allow for a minimum 2-foot thick bentonite annular space seal.

A bentonite pellet seal (hydrated in-place) will be placed on top of the find sand to the bottom of
the flush-mount protective well casing. Per s. NR 141.13 Wis. Admin. Code, bentonite granules will
be used as the annular space seal if the depth to groundwater is less than 7 feet bgs. The ground
surface seal around the flush-mount protective well casing will be constructed of concrete.

Following the installation of the three monitoring wells, they will be developed in accordance with the well development requirements specified in s. NR 141.21 Wis. Admin. Code to remove fines from the sand filter pack, well screen and casing. All water purged from the monitoring wells during development will be containerized for off-Site disposal. In addition, a professional survey will be performed to establish the horizontal and vertical location of each well location, as well as the top of each well casing.

WDNR Soil Boring Logs (WDNR Form 4400-122), Monitoring Well Construction Forms (WDNR Form 4400-113A) and Monitoring Well Development Forms (WDNR Form 4400-113B) will be completed for the three monitoring wells. Copies of the forms will be submitted to the WDNR within 60 days after the monitoring wells have been installed per the requirements of s. NR 141.23 Wis. Admin. Code.

3.4 WATER-LEVEL MEASUREMENT

Depth to water will be measured to 0.01-foot from the newly installed monitoring wells using an electronic water level meter in accordance with SOP 10 prior to the collection of groundwater samples. The depth to water measurements will be relative to the top of the well casing (at north side) and will be used to determine the direction of groundwater flow across the Site. The depth to water will also be monitored during the purging of the monitoring wells to monitor drawdown during groundwater sampling.

3.5 GROUNDWATER SAMPLING

Groundwater samples will be collected after the monitoring well installations are completed. Groundwater sampling will be conducted in general accordance with EPA low-flow (minimal drawdown) sampling procedures (SOP 9), sample acquisition for PFAS analysis (SOP 1), and groundwater sampling procedures (SOP 8). Groundwater sampling will be performed using a peristaltic pump with high density polyethylene (HDPE) and silicone tubing. New tubing will be used for each monitoring well to avoid cross-contamination between wells.

Prior to sampling, groundwater will be purged using low-flow purging techniques. During the purging of each well, water level drawdown, flow rate, and water quality readings will be recorded on the groundwater water quality data sheet, **Appendix B.** Groundwater will be pumped through a flow-through cell and water quality parameters of pH, conductivity, temperature, dissolved oxygen (DO), oxidation-reduction potential (ORP), and turbidity will be measured with a YSI DSS Pro multi-parameter water quality meter or equivalent. The instrument will be calibrated according to the manufacturer's specifications prior to sampling and

equipment calibration will be documented in the field staff's field notes, per SOP 3. The water quality parameters will be collected at 3- to 5-minute intervals until all parameters have stabilized for three consecutive readings and are within the following limits:

- Turbidity (10% if greater than 5 Nephelometric Turbidity Units)
- DO (10% for values greater than 2 milligrams per Liter (mg/L); 0.5 mg/L for values less than 2 mg/L)
- Specific conductance (3%)
- Temperature (3%)
- pH (0.1 unit)
- ORP (10 millivolts)

Drawdown will be maintained at 0.3 feet or less during purging and sampling. If water quality parameters do not stabilize or meet the limits within a 1-hour time period, three well volumes will be removed from the well and a groundwater sample will be collected.

Groundwater samples will be collected into clean, pre-labeled, laboratory supplied bottles. These sample containers will be placed in a cooler for shipment to Vista Analytical Laboratory where the samples will be analyzed for the WDNR list of 36 PFAS found in the *Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Expectations* (**Appendix C**) via a modified EPA Method 537 utilizing isotope dilution. Laboratory reporting will also include a Level IV data package in addition to the standard laboratory report.

3.6 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) SAMPLES

QA/QC samples will be collected to assure PFAS contamination is not introduced to the investigation samples from the drilling equipment or water used for equipment decontamination. QA/QC samples and collection methodology is provided below.

- Drilling Activities
 - Once after the drilling tooling is decontaminated, an equipment blank will be collected. The
 equipment blank will be collected by pouring laboratory provided reagent-free water over
 the decontaminated drilling tooling. The rinsate will be collected and poured into laboratory
 supplied containers.
- Sample Collection Events
 - One laboratory blind field duplicate groundwater sample will be collected concurrently with one of the groundwater samples.
 - One equipment blank sample will be collected during groundwater sampling. Prior to sample collection, reusable sampling equipment will be decontaminated. Following decontamination, laboratory provided reagent-free water will be run through or over

- disposable sampling equipment (sample tubing and nitrile gloves) and over reusable sampling equipment (water level meter). The rinsate will be collected into laboratory supplied containers.
- One field blank sample will be prepared in the field using laboratory supplied reagent-free water. The reagent-free water will be poured into a laboratory supplied sample container. The field blank will be marked for laboratory hold and will only be analyzed if one of the equipment blank samples contains significant levels of PFAS.

The QA/QC samples collected will be analyzed for the WDNR list of 36 PFAS (**Appendix C**) via a modified EPA Method 537 utilizing isotope dilution. The QA/QC sample analytical results will be included in the laboratory analytical report for the groundwater samples.

3.7 SAMPLE HANDLING

Procedures for sample handling, including the field-related considerations concerning sample preservation, packaging, and shipping are described below. As stated previously, due to the nature of PFAS and their prevalence in many consumer products, special precautions and procedures will be required for the handling, packaging, and shipment of samples analyzed for PFAS. These protocols are provided in SOP 1. Samples will be collected directly into clean, laboratory provided bottles. Sample bottle sets will be placed into sealed plastic bags and placed on ice for preservation from the time of collection through shipment to the analytical laboratory. Custody of the samples will be maintained and documented through chain-of-custody forms as described in SOP 11. Chain-of-custody begins with the collection of the samples in the field and ends at the analytical laboratory receiving department. The samples will be shipped to the analytical laboratory via overnight courier service.

3.8 DECONTAMINATION PROCEDURES

All drilling equipment will be decontaminated before being brought to the work site and between each of the boring locations. All decontamination water will be containerized for offsite disposal as described in **Section 3.9**. Alconox detergent and a steam pressure washer will be used with clean water to decontaminate drilling equipment.

All non-disposable sampling equipment will be decontaminated prior to use and after each use. Non-disposable sampling equipment will be decontaminated using Alconox detergent and distilled water. All decontamination water will be containerized for off-Site disposal.

3.9 INVESTIGATION-DERIVED WASTE MANAGEMENT

Purge water, decontamination water, and well development water generated during monitoring well installation and groundwater sampling will be containerized and stored in 55-gallon drums. SOP 12

describes drum and container handling procedures. Soil cutting IDW generated during soil boring advancement and monitoring well installation will be containerized in 55-gallon drums. IDW containers will be properly labeled identifying the contents. While awaiting disposal, IDW will be staged at a location that is agreeable to/and approved by, the property owner. Composite samples will be collected from both the liquid and solid IDW for waste characterization. The IDW composite samples will be submitted to Pace Analytical (Pace) for analysis of:

- Resource Conservation and Recovery Act (RCRA) Toxicity Characteristic Leaching Procedure (TCLP) volatile organic compounds (VOCs),
- RCRA TCLP Semi-VOCs,
- RCRA TCLP Metals,
- PCBs, and
- PFAS (soil sample for PFAS to be submitted to Vista separately).

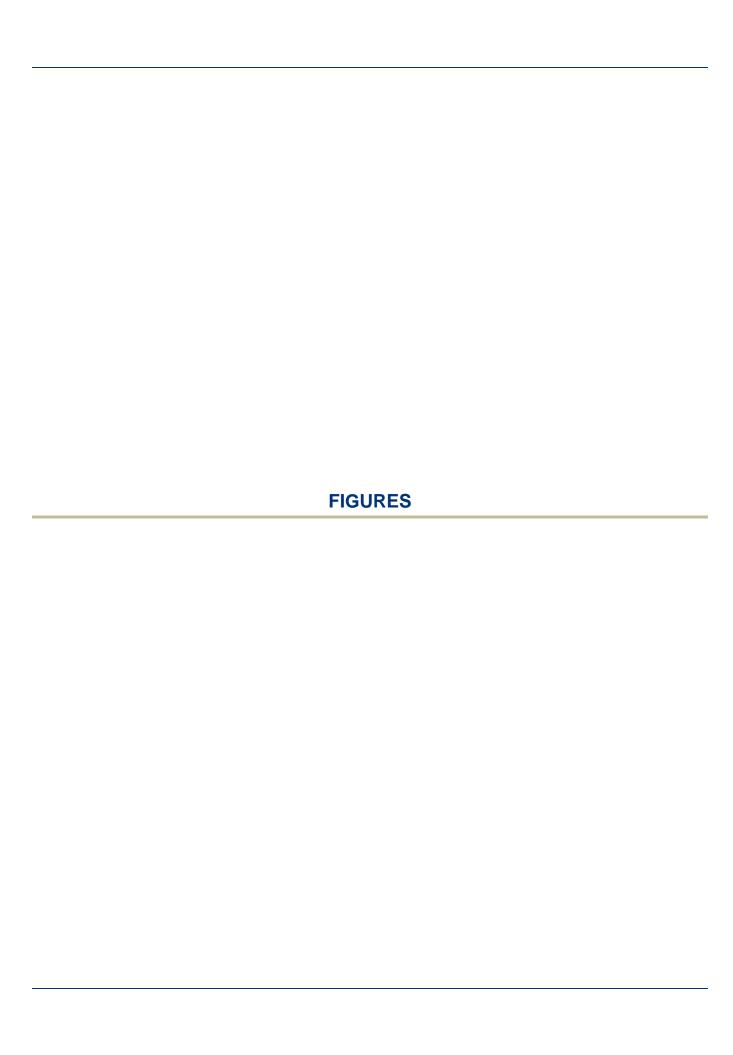
Analytical results will be used to coordinate off-site transportation and proper disposal at an appropriate facility in accordance with local, state and federal regulations. Disposable sampling supplies and materials (i.e., nitrile gloves and sample tubing) will be bagged and disposed of as general refuse/garbage.

4.0 REPORTING

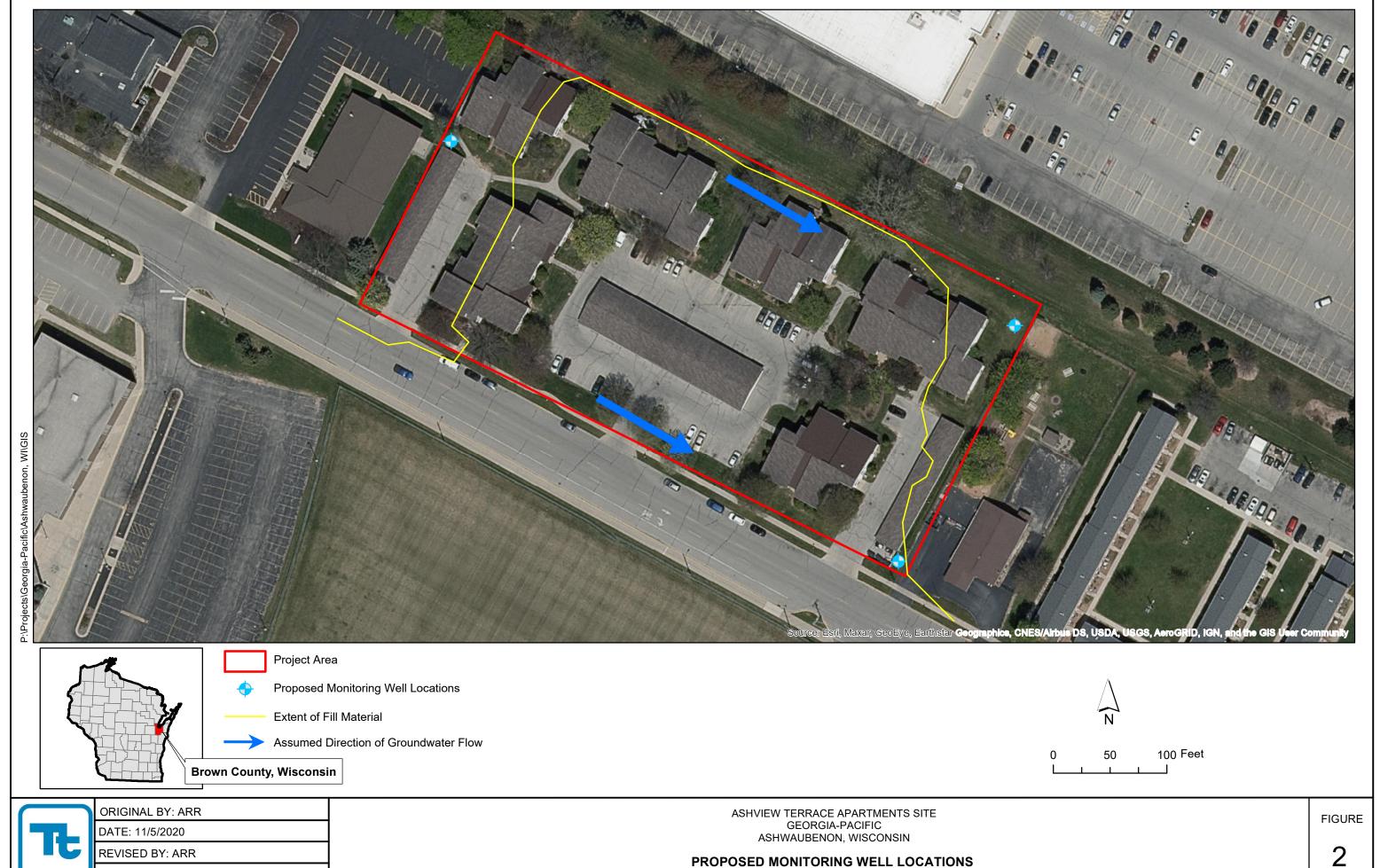
An Investigation Summary letter report will be prepared following the receipt of the analytical results for samples collected during the execution of this work plan. The Investigation Summary report will provide a summary of field activities performed that will include soil boring logs and well installation details. Groundwater sampling results will be summarized in table format and on a Site-area concentration map. Laboratory reports, data verification reports, and monitoring well sampling logs will be included as attachments. The Investigation Summary report will be prepared and submitted to the WDNR within 60 days of receipt of the analytical results, in compliance with s. NR 716.15(1)(a) Wis. Admin. Code.

5.0 REFERENCES

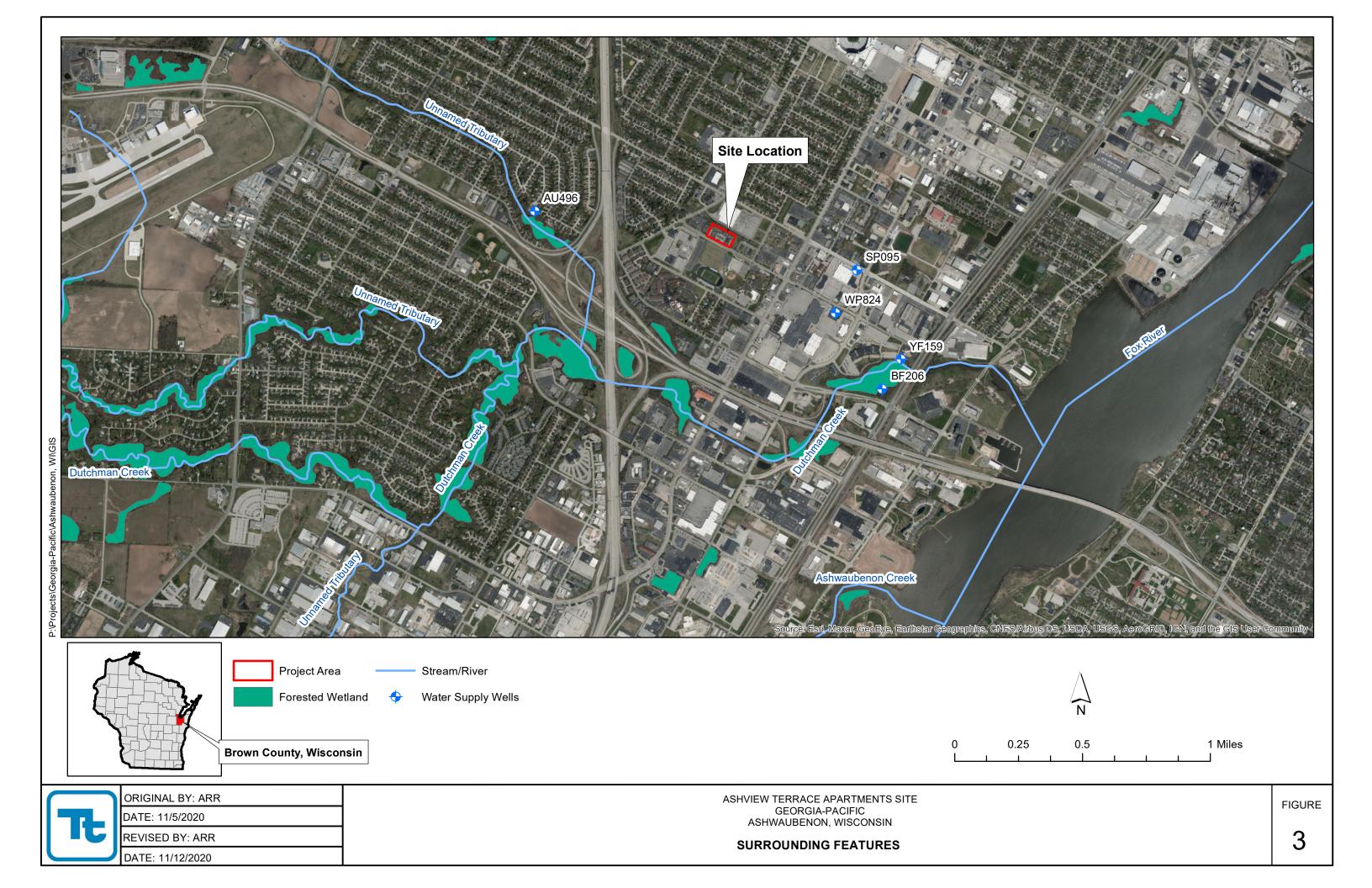
- Amec Foster Wheeler, (June 2017). Site Investigation Report, Ashview Terrace Apartments Site, Ashwaubenon, Brown County, Wisconsin.
- Amec Foster Wheeler (January 2018a). Supplemental Site Investigation Report, Ashview Terrace Apartments Site, Ashwaubenon, Brown County, Wisconsin.
- OMNNI, (February 2015). Phase II Subsurface Investigation at the Perry Property, 988-1020 Willard Dr., Parcel VA-120-5, Ashwaubenon, Brown County, Wisconsin Report.
- WDNR, (November 2013). Chapter NR 716, Site Investigations.
- WDNR, (2015). Chapter NR 292, Remedial Action.
- WDNR, (January 2020). Chapter NR 140, Groundwater Quality.
- WDNR, (August 2020). Reminder to Include Evaluation of Emerging Contaminants in Site Investigations letter.
- WDNR (September 2020). Review of Site Investigation Work Plan letter.
- Wood (June 2020). Site Investigation and Remediation Work Plan for the Ashview Terrace Apartments Site, Ashwaubenon, Wisconsin (WDNR Site # 02-05-564043).

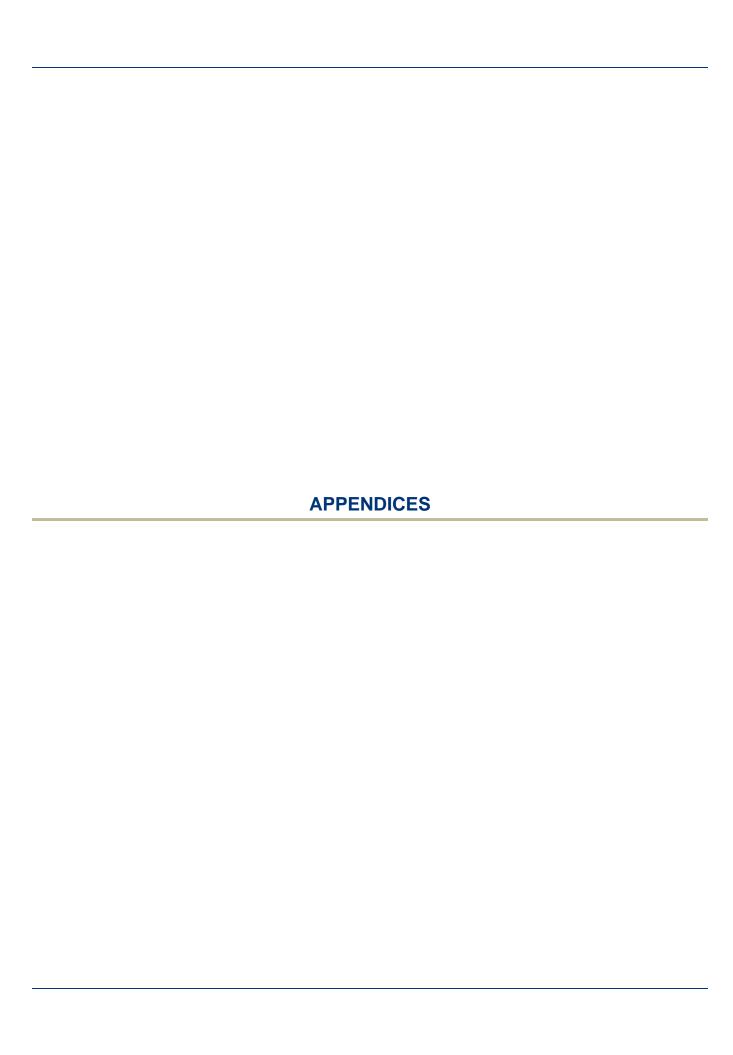


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DATE: 11/12/2020







SOP 1

Sample Acquisition for Polyfluorinated Compounds (PFCs) and Other Polyfluoroalkyl Substance Analysis



1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the methods and protocols to be used for collecting and handling samples to be analyzed for perfluorinated chemicals (PFCs), and other polyfluoroalkyl substances (PFASs). PFAS are present in many consumer products including some typical sampling equipment and are ubiquitous in the environment. Because regulatory screening criteria are very low, measurements of very low PFAS concentrations are required. These two conditions make the collection of samples for accurate quantitation of PFAS concentrations difficult unless special precautions are taken to avoid introducing contaminants into the samples. Instructions are provided herein for collection of environmental samples without contaminating them. This SOP is designed to supplement but not replace existing sampling SOPs. In addition, some clients and/or projects may have specific PFAS-related sampling requirements that extend beyond the procedures described in this SOP.

2.0 SCOPE AND APPLICABILITY

This document provides information on proper sampling equipment and techniques for groundwater, surface water, sediment, and soil sampling for PFAS analysis. Sampling of air or biota is not addressed in this SOP, but the same principles would apply for those media.

3.0 BACKGROUND

PFAS have been used since the 1940s as manufacturer-applied oil and water repellants on products such as clothing, upholstery, paper, and carpets; and in making fluoropolymers for non-stick cookware. They are found in textiles and leather products, mist suppressants for metal plating, the photography industry, photolithography, semi-conductors, paper and packaging coatings, cleaning products, pesticides, and cosmetics. They have been used in well-known consumer products including Teflon®, StainMaster®, Scotchgard®, and GoreTex®. In the 1960s, aqueous film-forming foam (AFFF) containing PFAS was developed for fighting flammable liquid fires, particularly petroleum-fueled (Class B) fires (ATSDR, 2009). The two most researched and most prevalent PFAS in the environment are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) (ATSDR, 2009).



PFAS are persistent in the environment, tend to bioaccumulate, and demonstrate toxicity in laboratory animals, enough to raise concerns about their presence in the environment. Some areas where PFAS may have been released to the environment include the following:

- Firefighting training areas
- Areas where firefighting products/materials are stored
- Aircraft crash sites
- Metal coating and plating facilities
- Water treatment systems and receiving water bodies
- Airport hangars and other facilities storing fire-fighting foams
- Fluorochemical manufacturing, use, and disposal facilities

PFAS are ubiquitous in consumer products and some materials used in environmental sampling (Teflon® tubing, waterproof logbooks, or GoreTex® field clothing). There are many potential sources of PFAS that are independent of media being sampled; therefore, it is essential to take special precautions to minimize the potential for contaminating environmental samples with PFAS during collection and handling. Laboratory detection limits are low for these compounds and contact of sample material or sampling equipment with any one of the multitude of PFAS sources could result in detectable contamination. In addition, PFAS tend to adsorb to glass so glass sample collection containers are inappropriate. Adsorption to glass sample containers may result in a low bias for measured PFAS concentrations.

Collection and analysis of Quality Control blanks is an important aspect of verifying that samples have not been contaminated during sample collection and handling. Use of additional blanks or blanks of a different type than usual may be required and the governing project planning documents should be consulted. Consult Section 7.7 of this SOP for instructions regarding collection of field reagent blanks (FRBs).

4.0 DEFINITIONS AND ABBREVIATIONS

<u>AFFF</u> – Aqueous film-forming foam.

<u>FRB</u> – Field Reagent Blank. A blank sample prepared in the field by transferring laboratory-supplied, chemically-preserved deionized water to an empty, laboratory-supplied collection bottle.



FRBs are typically analyzed only for PFAS and are treated as a site sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all PFAS analytical procedures. The purpose of FRBs is to indicate whether PFAS measured in corresponding site samples may have been introduced during sample collection and handling.

<u>PFASs</u> – Per- and polyfluoroalkyl Substances. A reference term currently in use, replacing "PFCs" in recent scientific and other technical literature. The term is inclusive of both perfluorinated chemicals like PFOA and PFOS and polyfluoroalkyl substances like fluorinated telomers.

<u>PFCs</u> – Perfluorinated Compounds or Chemicals. PFCs are a family of man-made chemicals that have been used for commercial, industrial, and military applications because they resist thermal degradation, and they repel oil, stains, grease, and water.

<u>PFOA</u> – Perfluorooctanoic Acid. PFOA is used as an aqueous dispersion agent and in the manufacture of fluoropolymers (including Teflon®) that are used in industrial components such as electrical wire casings, fire- and chemical-resistant tubing, and plumbing seal tape. PFOA is used in surface treatment products to impart oil, stain, grease, and water resistance. PFOA can also be produced by the breakdown of some fluorinated telomers.

<u>PFOS</u> – Perfluorooctane Sulfonate. PFOS was a key ingredient in Scotchgard® and used in the manufacture of Class B AFFF used per DoD military specifications. Phase out of AFFF by 3M occurred in 2002.

5.0 SAFETY PRECAUTIONS

Sample acquisition activities shall be conducted in accordance health and safety requirements identified in the project-specific Health and Safety Plan (HASP), corporate health and safety policies, and individual sampling SOPs, as applicable.

6.0 PERSONNEL RESPONSIBILITIES, QUALIFICATIONS, AND TRAINING

<u>Project Manager (PM)</u> – The PM is responsible for determining sampling objectives, initial sampling locations, and field procedures used in the collection of samples of environmental



media. Additionally, in consultation with other project personnel (geologist, hydrogeologist, etc.), the PM is responsible for selecting and detailing the specific sampling techniques, equipment to be used, and providing detailed input in this regard to the project planning documents. The PM has the overall responsibility for ensuring that sampling activities are properly conducted by appropriately trained staff.

<u>Site Safety Officer (SSO)</u> – The SSO (or a qualified designee) is responsible for providing the technical support necessary to implement the project HASP, AP or equivalent. The SSO or SSO designee may also be required to advise the Field Operations Leader (FOL) on safety-related matters regarding sampling, such as measures to mitigate potential hazards from hazardous objects or conditions. The SSO may be referred to as the Site Safety and Health Officer (SSHO).

<u>Project Geologist/Sampler</u> – The project geologist/sampler is responsible for the proper acquisition of samples in accordance with this SOP or other project-specific documents. In addition, this individual is responsible for the completion of all required paperwork (e.g., sample log sheets, field notebook, boring logs, container labels, custody seals, and chain-of-custody forms) associated with the collection of those samples.

<u>Field Operations Leader (FOL)</u> – This individual is primarily responsible for the execution of the field sampling program in accordance with the project planning documents. This is accomplished through management of a field sampling team for the proper acquisition of samples.

- General personnel qualifications for environmental media sample collection include the following:
- Occupational Safety and Health Administration (OSHA) 40-hour HAZWOPER and applicable refresher training.
- Ability to perform field work under the expected physical and environmental (i.e., weather)
 conditions
- Familiarity with appropriate procedures for sample documentation, handling, packaging, and shipping
- Familiarity with chemical-specific requirements for collection and handling of samples for PFAS analysis as described in this procedure.



 Personnel implementing this SOP must read and understand this SOP prior to collection of samples designated for PFAS analysis.

7.0 PROCEDURES

All personnel involved in sample acquisition must strive to prevent contact of sample media with potential sources of PFAS contamination. Given the widespread use of PFAS in products including those typically preferred for environmental sampling, all samples for PFAS analysis are to be collected using precautions to avoid inadvertent contamination of the sample media. These precautions are identified below for selection of sampling equipment and general field equipment, field personnel clothing and protective gear, sample containers and sample handling activities.

7.1 Selection of Equipment

It is important to research available equipment and materials at the planning stage to avoid last minute problems in the field; for example, ensuring compatibility of high-density polyethylene (HDPE) tubing with fittings for use in a peristaltic or other pump; or ensuring that equipment does not contain Teflon®.

Sampling Equipment:

- Avoid using any sampling equipment constructed of or containing polytetrafluoroethylene (PTFE) or Teflon® (DuPont brand name) or fluorinated ethylene propylene (FEP) during sample handling or mobilization/demobilization.
- Avoid using low-density polyethylene products (LDPE) if contamination from those products can be transferred to environmental samples or QC samples.
- Use sampling equipment made of stainless steel, acetate, silicone, high-density polyethylene (HDPE), or polypropylene. This applies to tubing, pumps and pump components, tape for plumbing fittings, trowels, mixing bowls or other equipment that could contact the sample media. Gasket and O-ring components of sampling equipment may contain fluoropolymers.

Non-Sampling Field Equipment:

 Avoid using waterproof field books or paper during sampling activities. Non-waterproof loose-leaf paper or notebooks are acceptable. Do not use plastic clipboards, binders, or



spiral hard cover notebooks that may be coated; use Masonite or aluminum clipboards instead.

- Avoid using Post-it® notes or similar removable notes during sample handling or mobilization/demobilization activities.
- Avoid using Sharpies® or similar indelible markers; do use ball-point pens or pencils for note taking and sample bottle labeling.

Field Personnel Clothing and Protective Gear:

- Avoid wearing new clothing due to the possible treating of fabric with PFAS for stain
 resistance. Wear clothing made from natural fibers (e.g. cotton) to the extent possible.
 Clothing should have been washed at least several times between time of purchase and
 time of first use during sampling activities. Avoid using fabric softener when laundering
 clothing to be worn during sample collection.
- During wet weather, use rain gear made from polyurethane or wax-coated materials.
- Avoid wearing water-resistant (e.g., Gore-Tex® or similar material) clothing or footwear (i.e., boots) immediately prior to or during sample collection and management.
- Avoid wearing cosmetics, shampoos, moisturizers, or other similar personal hygiene products on the day of sampling.
- Use sunscreens and insect repellants with 100% natural ingredients. The following items
 are acceptable for use, but the suitability of these items has not been independently
 verified:
 - Sunscreens Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are "free" or "natural."
 - Insect Repellents Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus
 Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics
 - Sunscreen and insect repellant Avon Skin So Soft Bug Guard Plus SPF 30
 Lotion
- Avoid wearing Tyvek® suits.
- Wear un-powdered nitrile gloves at all times while collecting and handling samples and change gloves often.



 Avoid unnecessary contact with automobile upholstery that may have been treated with PFAS. If practical, cover clothing and skin that has been in contact with such upholstery within non-fluorinated clothing.

Sample Containers and Shipping Materials

- Avoid the use of glass sample containers, which are believed to result in loss of PFAS from samples through adsorption to the container.
- Collect samples in laboratory-supplied plastic bottles only, typically polypropylene or HDPE.
- Confirm that Teflon®-lined caps are not used in sample containers; unlined polypropylene screw caps must be used.
- Avoid using Blue Ice® or similar items to cool samples and avoid placing such items in sample coolers for shipping. Use commercially available (e.g., from convenience stores or supermarkets) double-bagged ice instead.

7.2 Other Precautions for Sample Handlin

- Avoid handling or bringing pre-wrapped food or snacks (e.g., fast food, candy bars, microwave popcorn, etc.) into the sampling area before or during sampling, because many food and snack products are packaged in wrappers treated with PFAS. Only water or hydrating drinks (e.g., Gatorade) should be brought onsite or allowed in vehicles used for PFAS sampling activities.
- Wash hands thoroughly after handling fast food, carryout food, or snacks, or other items that may contain PFAS.
- Assume that shipping tape used for securing coolers could contain PFAS; therefore, take care not to transfer PFAS from tape to samples.

These precautions should be observed during sampling activities, especially during water sample collection (groundwater and surface water), given the high solubility of PFAS in water. Examples of how these precautions may be applied to sampling of specific media are provided in the following sections.



7.3 Groundwater Sample Acquisition

The precautions and requirements identified in the previous sections must be observed for groundwater sampling. Do not proceed any further without reviewing each of those precautions and requirements.

- Collect groundwater samples for PFAS analyses in accordance with this SOP, and/or project- or client-specific requirements.
- If non-dedicated, non-disposable equipment is used between sampling locations, it should be decontaminated with Alconox® or Liquinox®, unless 1,4-dioxane (a potential component of these detergents) is also a contaminant of concern. In that case Liquinox® should not be used. Products such as Decon 90 should not be used.
- If samples are to be collected for analysis of PFAS and other analytes, determine whether the same equipment can be used for all sample analyses. If Teflon® or LDPE materials are required for the non-PFAS analytes, then use multiple sets of equipment and determine a suitable sample collection sequence and protocol for collecting the groundwater samples for the analyte groups of interest. For example, purge and sample a monitoring well for PFAS first using a peristaltic pump with HDPE and silicone tubing. Then use a bladder pump with Teflon® tape on air-line fittings to purge the well and sample for VOCs with Teflon tubing, if the VOC protocol requires it. Or use silicone tubing for all parameters, if appropriate. Protocols and order of sampling should be clearly identified in the SAPs. If the sampling sequence is unclear, consult the FOL or Project Manager and record the actual sequence in the field notes.
- If tasked to sample monitoring wells that have or had dedicated Teflon® or FEP tubing
 that potentially contained PFAS, after removing the tubing, evacuate at least one well
 volume prior to sampling using silicone or HDPE tubing. This will ensure that standing
 water that was in contact with the tubing is removed from the water column prior to
 sampling.

7.4 Soil Sample Acquisition

The precautions and requirements identified in Sections 7.1 and 7.2 must be observed for soil sampling. Do not proceed any further without reviewing each of those precautions and requirements.



- Collect soil samples for PFAS analyses in accordance with this SOP, and/or project- or client-specific requirements.
- Soil sampling equipment should not be constructed of or contain Teflon® materials.
 Acceptable materials for sampling include stainless steel, acetate, or polypropylene. If non-dedicated, non-disposable equipment is used between sample locations, it should be decontaminated with Alconox® or Liquinox®.
- Collect samples in laboratory-provided containers specifically designated for PFAS analysis. Do not use glass jars typically used for soil sample collection.

7.5 <u>Surface Water and Sediment Sample Acquisition</u>

The precautions and requirements identified in Sections 7.1 and 7.2 must be observed for surface water and sediment sampling. Do not proceed any further without reviewing each of those precautions and requirements.

- Collect surface water and sediment samples for PFAS analysis in accordance with this SOP, and/or project- or client-specific requirements.
- Surface water and sediment samples should be collected in laboratory-supplied bottleware specifically designated for PFAS analysis (not glass). If transfer bottles are required for collection of surface water samples, the transfer bottles used should be the same material as the containers designated for submission to the laboratory.
- Surface water and sediment sampling equipment should not be constructed of or contain Teflon® or LDPE materials. Acceptable materials for sampling include HDPE, silicone, stainless steel, acetate, or polypropylene. If non-dedicated, non-disposable equipment is used between sample locations, it should be decontaminated with Alconox® or Liquinox®.

7.6 Water Supply Sampling

This section applies to sampling from taps, spigots, faucets, or similar devices. The precautions and requirements identified in Sections 7.1 and 7.2 must be observed for water supply sampling. Do not proceed any further without reviewing each of those precautions and requirements.

- Collect water supply samples for PFAS analysis in accordance with applicable portions of this SOP, and/or project- or client-specific requirements.
- Water supply samples should be collected in laboratory-supplied bottleware specifically designated for PFAS analysis (not glass).



- Ensure that sample bottles used to collect chlorinated water samples contain the proper preservative; non-chlorinated water does not require chemical preservatives designed to remove chlorine.
- Water supply sampling equipment (if needed) should not be constructed of or contain Teflon® or LDPE materials. Acceptable materials for sampling include HDPE, silicone, stainless steel, acetate, or polypropylene. If non-dedicated, non-disposable equipment is used between sample locations, it should be decontaminated with Alconox® or Liquinox®.
- Locate the sampling point. If a specific sampling point has already been designated (e.g., a kitchen tap), plan to collect the sample from that point; otherwise, identify a location in the water supply line that is as close as possible to the water's point of origination (e.g., a well or other water source) and upstream of any local water treatment unit(s) that could affect PFAS levels (e.g., water softeners, activated carbon, or reverse osmosis treatment units). If a treatment unit is in use, a post-treatment sample may also be required in some cases, per project requirements.

Note: If treatment that could affect PFAS levels (e.g., carbon filtration or reverse osmosis) is part of the water distribution system, often a spigot will be present in the plumbing line between the water source and the treatment unit and this spigot should be used

- Remove any aerator/diffuser from the faucet, if possible. If removal is not possible, record this observation in the field notes.
- Allow the water to run freely from the tap until parameter stabilization per project-specific requirements is achieved, or as otherwise required by project-specific requirements. This will often require purging for 3 to 5 minutes.
- Reduce the water flow rate to minimize aeration of the sample. The water stream should be no wider than the diameter of a pencil.
- Fill the sample bottle (typically 250 mL) directly from the tap to the bottom of the neck of the bottle and cap the bottle immediately.
- After collecting the sample, cap the bottle and, if preservative is included, agitate by hand until the preservative is dissolved.



STANDARD OPERATING PROCEDURE <u>SAMPLE ACQUISITION FOR PERFLUORINATED COMPOUNDS (PFCs) AND OTHER</u> POLYFLUOROALKYL SUBSTANCE ANALYSIS

7.7 Field Reagent Blank Collection

Note: EPA Method 537 and modifications thereof for PFAS analysis require an FRB to be handled along with each sample set. A sample set is described as samples collected from the same sample site and at the same time, but "sample site" and "same time" are not precisely defined. Therefore, it is important to verify that the correct number of FRBs will be collected. *Collection of an FRB at every sampling point may be required.*

- Verify the number of FRBs to be collected for the project and where those samples must be collected. This should be described in the project planning documents such as work plans or sampling and analysis plans. If it is not, consult the PM.
- At the sampling site, when ready to collect an FRB, open the bottle of chemically
 preserved FRB reagent water provided by the laboratory and a corresponding empty
 bottle, also provided by the laboratory.
- Pour the preserved FRB reagent water into the empty sample bottle, close the cap, and label this filled bottle as the FRB.
- Pack and ship the FRB along with site samples and the required documentation (e.g., chain of custody form) to the laboratory.

Note: Although chain of custody forms will indicate that FRBs must be analyzed for PFAS, analysis of an FRB will be required only if site samples contain PFAS above a certain concentration. If an FRB is analyzed and any PFAS concentration in the FRB exceeds 1/3 the laboratory MRL, then all samples collected with that FRB may be considered invalid and may require recollection and analysis of the recollected samples. Consult the project planning documents governing sample collection for specifics as to whether resampling is necessary. Care in collection and handling of site samples and FRBs in a way that avoids contamination cannot be overemphasized.

SOP 2

Field Documentation



1. PURPOSE

To set environmental group criteria for content and form for Daily Report Sheets or projectspecific field logbooks.

The standard procedure for field documentation requires the use of Daily Report Sheets. Part A of this standard operating procedure (SOP), Daily Report Sheet Content and Control, addresses use of the Daily Report sheet. For special cases, as may be required by the client, project-specific field logbooks may be used for field documentation. Part B of this SOP, Site-Specific Field Logbook Content and Control, addresses use of the project-specific field logbook.

Information recorded on daily report sheets or in field logbooks may include identification of field team personnel, visitors on-site, date, time, weather conditions, observations, data, calculations, description of the data collection or sampling activity, methods, instruments used, instrument calibration data, and results. In addition, the daily report sheets or logbooks may contain descriptions of geologic material, wastes generated or disposed, biota, and site features including sketches, maps, or drawings as appropriate. Entries will be described in as much detail as practical.

2. PROCEDURE

2.1 FIELD PREPARATION

2.1.1 Forms

Daily Report Sheets or field logbook

2.1.2 Equipment

- Waterproof pen or marker (black ink preferable) and pencils for emergency backup
- Ruler or similar scale (in some circumstances)
- Watch or other timepiece
- Compass (in some circumstances)

2.1.3 Documents

Any site-specific plans required for field activities



2.2 FIELD PROCEDURES

2.2.1 Part A – Daily Report Sheet Content and Control

Upon arrival on-site and before the start of field activities, the following information shall be recorded in the heading section of the Daily Report sheet (see attached):

- Project name
- Tetra Tech Project number
- Date of site activity
- Site location
- Weather
- Contractors working for Tetra Tech
- Contractor's employees
- Contractor's equipment
- Equipment
- Visitors presently on-site

Daily Report sheets should be used to record a "summary" of daily field information. The following is a list of requirements that must be followed when using a Daily Report sheet:

- Record the following on a daily basis or if any conditions change on any given day:
 - Name of individual making entry and names of all field team members present
 - Date
 - Weather conditions (i.e., temperature, cloud cover, precipitation, wind direction and speed) and other pertinent data
 - Level of personal protection to be used
 - The names of all visitors to the site and the purpose of their visit
- Record the work performed, observations, data, quantities of materials, calculations, drawings, and related information directly on the Daily Report sheet.
 If data collection forms are specified by SOP, this information need not be duplicated; however, any forms used to record site information or measurement



data must be included with the Daily Report sheet and delivered to the Project Manager for review and filing.

- Do not skip lines on the Daily Report sheet. Do not start a new page until the
 previous one is full or has been marked with a single diagonal line so that
 additional entries cannot be made.
- Do not erase or blot out any entry at any time. Before an entry has been signed and dated, changes may be made but care must be taken not to obliterate what was written originally. Indicate any deletion by a single line through the material to be deleted.
- Record as much information as practical.
- Other events and observations that should be recorded include:
 - Changes in the weather that impact field activities or personal health and safety
 - Deviations from and reasons for deviations from procedures outlined in work plans or SOPs
 - Problems, down-times, or delays
 - Upgrade or downgrade of personal protective equipment

Post-Operation:

To guard against loss of data due to damage or disappearance of Daily Report sheets, completed pages shall be copied periodically (weekly, at a minimum) and securely stored at the appropriate office in two locations, project file and a separate field documentation file. Documents which are separated from the Daily Report sheets shall be copied and submitted regularly and as promptly as possible to the appropriate office with the Daily Report sheets for similar review and filing. This includes all automatic data recording media (print-outs, logs, or disks) and activity-specific data collection forms required by other SOPs.

Comments:

Daily Report Sheets constitute the official record of on-site technical work, field investigations, and data collection activities. Their use, control, and ownership are restricted to activities pertaining to specific field operations carried out by Tetra Tech personnel and their subcontractors. They are documents that may be used in court to indicate and defend dates and times, personnel, procedures, and techniques employed during site activities. Entries made in these notebooks and on these sheets should be factual, clear, precise, and as non-subjective as possible.



In some adverse weather or work conditions, Daily Report sheets may become wet and will not accept ink. If this situation arises, attempt to dry the pages. If drying attempts fail, use a graphite pencil to continue with field documentation entries. Document this occurrence on the sheet and resume ink use when possible.



2.2.2 Part B – Site-Specific Field Logbook Content and Control

Preparation:

Field log information will be recorded in Tetra Tech field survey books or Project Managerapproved notebooks. Logbooks shall be bound and all pages must be numbered prior to initial use of the logbook.

The following information should be recorded inside the front cover prior to initial use of the logbook:

- Person to whom the logbook is assigned
- Office address and telephone number
- Logbook number
- Project name
- Project number
- Project start date

The first five pages of the logbook shall be reserved for a table of contents. Mark the first page with the heading and enter the following:

TABLE OF CONTENTS

Date/Description	Page
(Start Date)/ Reserved for TOC	1-5

The remaining pages of the Table of Contents will be designated as such with "TOC" written on the top-center of each page.



Procedure:

The following is a list of requirements that must be followed when using a site-specific field logbook:

- Record the following on a daily basis or if any conditions change on any given day:
 - Name of individual making entry and names of all field team members present
 - Date and time
 - Weather conditions (i.e., temperature, cloud cover, precipitation, wind direction and speed) and other pertinent data
 - Level of personal protection to be used
 - The names of all visitors to the site and the purpose of their visit
- Record the work performed, observations, data, quantities of materials, calculations, drawings, and related information directly in the logbook. If data collection forms are specified by another standard operating procedure (SOP), this information need not be duplicated in the logbook; however, any forms used to record site information or measurement data must be referenced in the logbook.
- Do not skip lines in the logbook. Do not start a new page until the previous one is full or has been marked with a single diagonal line so that additional entries cannot be made. Use both sides of the logbook page.
- Do not erase or blot out any entry at any time. Before an entry has been signed and dated, changes may be made but care must be taken not to obliterate what was written originally. Indicate any deletion by a single line through the material to be deleted.
- Do not remove any pages from the logbook.
- Record as much information as practical.
- Initial and date each page.
- Sign and date the final page entries for each day.
- Initial and date all changes.



Multiple authors must sign out the logbook by inserting the following:

Above notes authored by:

- (Sign name)
- (Print name)
- (Date)
- A new author must sign and print his/her name before additional entries are made.
- Draw a diagonal line through the remainder of the page at the end of the day.

Entries into the field logbook shall be preceded with the time (written in military units) of the observation. The time should be recorded frequently and at the point of events or measurements that are critical to the activity being logged. All measurements made and samples collected must be recorded unless they are documented by automatic methods (e.g., data logger) or on a separate form required by an SOP. In these cases the logbook entry must reference the automatic data record or form.

At each station where a sample is collected or an observation or measurement is made, a detailed description of the station location is required. Use a compass, scale, or nearby survey markers, as appropriate. A sketch of station location may be warranted. All maps or sketches made in the logbook should have descriptions of the features shown and a direction indicator. It is preferred that maps and sketches be oriented so that north is towards the top of the page. The number of photographs taken of the station or activity, if any, will also be noted.

Other events and observations that should be recorded include:

- Changes in the weather that impact field activities
- Deviations from and reasons for deviations from procedures outlined in work plans or SOPs
- Problems, down-times, or delays
- Upgrade or downgrade of personal protective equipment

Post-Operation:

To guard against loss of data due to damage or disappearance of site-specific field logbooks, completed pages shall be copied periodically (weekly, at a minimum) and securely stored at the appropriate office in two locations, project file and a separate field documentation file. Documents which are separated from the site-specific field logbooks shall be copied and submitted regularly and as promptly as possible to the appropriate office with the field logbook



copies for similar review and filing. This includes all automatic data recording media (print-outs, logs, or disks) and activity-specific data collection forms required by other SOPs.

Comments:

Field logbooks constitute the official record of on-site technical work, field investigations, and data collection activities. Their use, control, and ownership are restricted to activities pertaining to specific field operations carried out by Tetra Tech personnel and their subcontractors. They are documents that may be used in court to indicate and defend dates and times, personnel, procedures, and techniques employed during site activities. Entries made in these logbooks should be factual, clear, precise, and as non-subjective as possible.

In some adverse weather or work conditions, field logbooks become wet and will not accept ink. If this situation arises, attempt to dry the pages. If drying attempts fail, use a graphite pencil to continue with field documentation entries. Document this occurrence on the sheet and resume ink use when possible.

SOP 3

Field Equipment Use and Calibration



STANDARD OPERATING PROCEDURE FIELD EQUIPMENT USE AND CALIBRATION

1. PURPOSE

The purpose of this procedure is to set criteria for field equipment use and calibration.

2. PROCEDURE

A significant number of field activities involve usage of electronic instruments to monitor for environmental screening and heath and safety purposes. It is imperative the instruments are used and maintained properly to optimize their performance and minimize the potential for inaccuracies in the data obtained, and to insure worker's health and safety is not compromised.

This SOP provides guidance on the usage, maintenance and calibration of electronic field equipment, whether for equipment owned by the Consultant or Contractor, or equipment obtained from a rental agency.

2.1 FIELD PREPARATION

2.1.1 Forms

Field Calibration Forms

2.1.2 Equipment

- Monitoring equipment specific to work plan tasks.
- Associated calibration gases, aqueous standards, etc.
- Appropriate shipping containers to facilitate transport without damage to equipment.

2.1.3 Documents

Manufacturer's instructions, operation and maintenance information.

2.2 FIELD PROCEDURES

All monitoring equipment will be in proper working order, and operated for the purpose for which it was intended, in accordance manufacturer's recommendations.

Field personnel will be responsible for insuring the equipment is maintained and calibrated in the field to extent practical, or returned for office or manufacturer maintenance or calibration if warranted. Calibration is discussed in greater detail below.

A copy of the Operating Instructions, Maintenance and Service manual for each instrument used on a project will be kept on site at all times.



STANDARD OPERATING PROCEDURE FIELD EQUIPMENT USE AND CALIBRATION

Instruments will be operated only by personnel trained in the proper usage and calibration. In the event certification of training is required, personnel will have documentation of such certification with them on site at all times.

Personnel must be aware that certain instruments are rated for operation within a limited range of conditions such as temperature and humidity. Usage of such instruments in conditions outside these ranges will only proceed with proper approval by a project manager and/or Health and Safety supervisor as appropriate.

Instruments that contain radioactive source material, such as x-ray fluorescence analyzers or moisture-density gauges require specific transportation, handling and usage procedures that are generally associated with a license from the Nuclear Regulatory Commission (NRC) or an NRC-Agreement State. Under no circumstance will operation of such instruments be allowed on site unless by properly authorized and trained personnel, using the proper personal dosimeter badges or monitoring instruments.

Calibration

Calibration of an electronic instrument is critical to insure it is operating properly for its intended use. Such instruments are often sensitive to changes in temperature or humidity, or chemical vapors in the working atmosphere, and as a result their response and ability to monitor conditions and provide data can change significantly.

Parameters

Calibration of instruments shall be performed in accordance with the manufacturer's recommendations. This includes the following parameters:

- Frequency
- Use of proper calibration Gases or Chemical Standards
- Requirements for Factory Calibration

Calibration Gas Safety

Several instruments such as photoionization detectors (PIDs), flame ionization detectors @!IDS), oxygen meters, explosimeters, combustible gas indicators and many others require use of calibration gasses contained in compressed gas cylinders. Many of these gases are combustible or explosive. Care shall be taken to minimize the potential for injury from the use of such compressed gases. Transport, handling and storage of cylinders, where necessary, shall be performed in accordance with applicable DOT regulations and site requirements.



STANDARD OPERATING PROCEDURE FIELD EQUIPMENT USE AND CALIBRATION

Calibration will only be performed in areas free of sources of spark, flame or excessive heat. Smoking will not be allowed in the vicinity of calibration gas usage areas.

Documentation of Calibration

Instrument Calibration activities will be documented on the field calibration form.

Intrinsically Safe Requirements

Certain work locations may be such that dangerous, ignitable or explosive conditions exist. In such cases, it may be necessary to utilize only equipment that is rated as "Intrinsically Safe." Intrinsically safe instrumentation is designed with limited electrical and thermal energy levels to eliminate the potential for ignition of hazardous mixtures.

For site work requiring operation of monitoring instruments in Class I, Division I locations (as defined by the National Fire Protection Agency (NFPA)) only instrumentation rated as Intrinsically Safe will be used. Such equipment (including all accessories and ancillary equipment) must be rated to conform to Underwriter's Laboratories (UL) Standard 91 3, for use in a Class I, Division 1 Groups A, B, C, and D locations. It is also recommended the equipment conform to CSA Standard 22.2, No. 157-92.

Upon completion of the field activities, equipment shall be returned to the possession of the Consultant, Contractor or Rental Agency accompanied by a written summary of any problems encountered with its use or calibration.

Equipment shall be properly prepared for shipping, including insuring that residual gases (if applicable) are removed from the instrument, and accompanying containers of compressed gases or fluids are properly labeled and sealed.

Equipment Decontamination

Equipment that comes in contact with Site media (water level meters, water quality meters) must be cleaned before removal from the site to ensure that chemicals are not transferred to other sites. It is the responsibility of the person who requisitioned the equipment to ensure appropriate cleaning before returning the equipment. Equipment decontamination procedures are typically site-specific for unique site compounds.

SOP 4

Soil Boring and Monitoring Well Installation



STANDARD OPERATING PROCEDURE SOIL BORING AND MONITORING WELL INSTALLATION

1. PURPOSE

The purpose of this procedure is to install a soil boring or groundwater monitoring well to obtain soil and groundwater data. Monitoring wells are constructed to ensure that groundwater accessed is representative of in-situ conditions.

2. PROCEDURE

2.1 FIELD PREPARATION

Call Miss Dig at 1-800-482-7171 more than 72 hours in advance of field activity commencement to identify buried utilities in the area of subsurface activity.

Notify the client, property owner, and MDEQ as necessary.

2.1.1 Forms

- Soil Boring and Monitoring Well Logs
- Purchase order form to ensure payment of the drillers
- Field Service Request
- Tailgate Health and Safety
- Daily Report Sheets

2.1.2 Equipment

- Well caps expanding, locking
- Locks (keyed alike)
- Latex or nitrile gloves
- Typically provided by the drillers:
- Well screen and casing
- Sand, bentonite chips/grout
- Concrete



STANDARD OPERATING PROCEDURE SOIL BORING AND MONITORING WELL INSTALLATION

2.1.3 Documents

- Site Access Agreements (if necessary)
- Site maps
- Workplan
- Health and Safety Plan

2.1.4 Other

- Cellular telephone
- First aid kit
- Personal comfort items
- Stakes and flagging to mark location

2.2 FIELD PROCEDURES

Build a berm or dike, if necessary, around the drilling area to divert surface water and run-off from the borehole, and avoid entry of surface water and run-off into the hole during drilling and well installation. Boreholes should not be left open (unsupported by casing, auger, or drilling fluid) if advanced through contaminated material to prevent contaminated soils from caving to the area of the well screen.

Segregate all well materials and drilling tools from potential sources of contamination. The drilling contractor should use new well casing and screen that has been sealed at the factory, or decontaminated and wrapped before arrival at the site. Handle casing and screen only while wearing clean gloves (this is most important if the wells are not expected to be in an affected area). Be sure to decontaminate all drilling tools and equipment before each well installation using a high-pressure steam cleaner.

Soil boring and monitoring well depth should be determined before field activity commencement, if appropriate. Reference the Field Service Request Form for the method to be used for field depth determination.

If nested wells (two or more closely spaced wells, screened at different depths) are installed, the deepest well in the grouping should be installed first. This allows for complete vertical characterization of the geology and verification of the proper depths for any shallower well. It also reduces the possibility of grout intrusion into the shallower wells.

For installing groundwater monitoring wells in unconsolidated geologic materials, hollow stem auger drilling is the method of choice, as vertical cross-contamination between depth intervals and extraneous handling of contaminated materials is avoided.



STANDARD OPERATING PROCEDURE SOIL BORING AND MONITORING WELL INSTALLATION

- Determine position and depth of well to be installed.
- Complete the Soil Boring and Monitoring Well Log using military time and recording sample recovering in inches. Samples submitted for laboratory analysis are recorded on the log in parenthesis and are named as the soil boring or monitoring well name followed by the depth (ex. SB-02-4 30 feet). Split spoon (SS) samples are recorded consecutively starting with SS-1.
- As soils are retrieved from the split spoon sampling tool (or Shelby tube), the borings must be characterized based on their color, moisture content, odor, cohesive properties, grain size, and lithology (see soil classification SOP).
- Well materials may be schedule 40, 2" or 4" diameter with # 10 (or 0.010-inch) slot well screen with a schedule 40, 2" or 4" diameter PVC casing or a stainless steel screen with galvanized steel casing.
- If the well hole is advanced too far, backfill the bottom with sand before positioning the screen (unless a confining unit has been breached then seal the breach with bentonite and grout the boring). Deposit appropriate sand filter pack around the well screen until measured at one foot above the screen. Then seal the top of the sand pack with a bentonite slurry (approx. 1-1.5 feet), bentonite chips or a grout mixture to the surface.
- A well cap with a watertight seal and lock must be affixed to the well top. For flush-mounted wells, have the drillers use a neat cement grout to form the annular seal surrounding the well casing. They should bring the grout to within 3 inches of the top of the monitoring well casing, tapering the grout away from the monitoring well to the edge of the bore hole. Place and center the metal manhole cover (minimum diameter 8") over the monitoring well casing. Cement the cover in place inside a square 2 x 2 foot (or 12" diameter round pad) 6-inch deep pad. Slope the concrete surface away from the well to promote surface drainage away from the monitoring well.
- Develop the well before conducting sampling or performing hydraulic conductivity tests by surging, pumping, or bailing, depending on the well depth, yield, diameter, contaminants present, and depth to water.

SOP 5.4

Safe Drilling Practices



STANDARD OPERATING PROCEDURE SAFE DRILLING PRACTICES

This document establishes safe work practices (SWP) to follow during drilling operations. These SWPs are based on suggested safety procedures provided in the National Drilling Association's "Drilling Safety Guide." Procedures to follow before, during, and after drilling are listed below.

Before beginning any drill operation, each employee must conform to the following requirements:

- Wear a hard hat, safety glasses or goggles, steel-toed work boots, a shirt and full-length pants when working with or near the drill rig. Shirts must be tucked in at the belt.
- Do not wear loose or frayed clothing, loose long hair, or loose jewelry while working with rotating equipment.
- Do not eat, drink, or smoke near the drill rig.
- Identify all underground utility and buried structure locations before drilling.
- Ensure that drill masts or other projecting devices will be farther than 25 feet in any direction from overhead power lines.
- Ensure that the drill rig and any other machinery used is inspected daily by competent, qualified individuals. The site safety coordinator (SSC) will ensure compliance with this precaution.
- Drill rig operators will be instructed to report any abnormalities, such as equipment failure, oozing liquids, and unusual odors, to their supervisors or the SSC.
- Establish hand-signal communications for use when verbal communication is difficult.
 One person per work team will be designated to give hand signals to equipment operators.

While the drill rig is operating, employees must:

- Wear appropriate respiratory and personal protective equipment (PPE) when conditions warrant their use.
- Avoid direct contact with known or suspected contaminated surfaces.
- Move tools, materials, cords, hoses, and debris to prevent tripping hazards and contact with moving drill rig parts.

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STANDARD OPERATING PROCEDURE SAFE DRILLING PRACTICES

- Adequately secure tools, materials, and equipment subject to displacement or falling.
- Store flammable materials away from ignition sources and in approved containers.
- Maintain adequate clearance of the drill rig and mast from overhead transmission lines.
 The minimum clearance is 25 feet unless special permission is granted by the utility company. Call the local utility company for proper clearance.
- Only qualified and licensed personnel should operate drill rigs.
- Workers should not assume that the drill rig operator is keeping track of the rig's exact location. Workers should never walk directly behind or beside heavy equipment without the operator's knowledge.
- Workers should maintain visual contact with drill rig operators at all times.
- When an operator must maneuver equipment in tight quarters, the presence of a second person is required to ensure adequate clearance. If much backing is required, two ground guides will be used: one in the direction the equipment is moving, and the other in the operator's normal field of vision to relay signals.
- Auger sections and other equipment are extremely heavy. All lifting precautions should be taken before moving heavy equipment. Appropriate equipment, such as chains, hoists, straps, and other equipment, should be used to safely transport heavy equipment too heavy to safely lift.
- Proper personal lifting techniques will be used. Workers should lift using their legs, not their backs.
- Workers will not use equipment they are not familiar with. This precaution applies to heavy as well as light equipment.
- All personnel not essential to work activities will be kept out of the work area.
- Workers will be aware of their footing at all times.
- Workers will remain alert at all times.

After drilling operations are completed, employees should do the following:



STANDARD OPERATING PROCEDURE SAFE DRILLING PRACTICES

- Shut down machinery before repairing or lubricating parts (except parts that must be in motion for lubrication).
- Shut down mechanical equipment prior to and during fueling operations. When refueling
 or transferring fuel, containers and equipment must be bonded to prevent the buildup of
 static electricity.
- Keep drill rigs in the exclusion zone until work has been completed. Such equipment should then be decontaminated within the designated decontamination area.
- Engage parking brakes when equipment is not in use.
- Implement an ongoing maintenance program for all tools and equipment. All tools and moving equipment should be inspected regularly to ensure that parts are secured, are intact, and have no cracks or areas of weakness. The equipment must turn smoothly without wobbling and must operate in accordance with manufacturer specifications. Defective items should be promptly repaired or replaced. Maintenance and repair logs will be kept.
- Store tools in clean, secure areas to prevent damage, loss, or theft.

Disclaimer: This safe work practice (SWP) is the property of Tetra Tech, Inc. Any reuse of the SWP without Tetra Tech's permission is at the sole risk of the user. The user will hold harmless Tetra Tech for any damages that result from unauthorized reuse of this SWP. Authorized users are responsible for obtaining proper training and qualification from their employer before performing operations described in this SWP.

Revision Date	Document Authorizer	Revision Details
10/1/2008	Chris McClain	Update from 1998 format

SOP 6

Soil Descriptions



1. PURPOSE

The purpose of this procedure is to describe and classify soil samples in the field during soil boring advancement.

2. PROCEDURE

2.1 FIELD PREPARATION

Call Miss Dig (1-800-482-7171) at least 72 hours in advance to arrange utility staking in any subsurface boring or exploration area.

Notify client, property owner, and MDEQ if necessary.

2.1.1 Forms

- Soil Boring and Monitoring Well Logs
- Tailgate Health and Safety
- Field Service Request
- Daily Report Sheets

2.1.2 Equipment

- Knife or spatula
- Ruler, tape measure, or scale
- Latex or nitrile gloves
- Sand gauge and geotechnical gauge, if necessary

2.1.3 Documents

- Health and Safety Plan
- Work Plan
- Maps
- Site access agreements



2.1.4 Other

- Cellular telephone
- First aid kit
- Personal comfort items

2.2 FIELD PROCEDURES

Include the following information in the soil sample description: color (including mottling); moisture; major and minor soil types; content and grain sizes; and other additional descriptors including contaminant observations; bedding and lamination. Particle shape or angularity is also useful for coarse-grained materials.

Record these descriptors in the following order: 1) color, 2) moisture content, 3) density (ONLY IF BLOW COUNTS ARE TAKEN), 4) composition and grain sizes, and 5) other descriptors.

1. **Color:** Use best judgment in describing soil color. Munsell color charts may be used on specific projects if required. Observed mottling should also be reported. Be sure to include corresponding quantity and contrast terms and specify the mottled colors.

Mottling

If Mottling Is:	Use This Contrast Term:
Indistinct	Faint
Easily seen	Distinct
Outstanding	Prominent

2. Moisture Content

Dry	Little or no perceptible moisture
Damp	Some perceptible moisture, not compactable
Moist	Compactable
Wet	Above compactable range
Saturated	Pores, voids filled with water



- 3. Density: Based upon blow counts (Note difference of terms for Sand/Gravel vs. Silt/Clay)
 - ONLY LISTED IF BLOW COUNTS ARE TAKEN

Sand or Gravel	Blows per foot
Very loose	0 - 4
Loose	4 - 10
Medium dense	10 - 30
Dense	30 - 50
Very dense	>50

Silt or Clay	Blows per foot	Thumb Penetration
Very soft	0 - 2	Very easily
Soft	2 - 4	Easily
Medium stiff	4 - 8	Moderate effort
Stiff	8 - 15	Indented easily by nail
Very stiff	15 - 30	Indented by nail
Hard	>30	Difficult by nail

4. USCS Texture/ Grain Size (if gradation within class, list in ascending size order):

Particle Size (mm)	Individual Particle Term
>300	Boulders
75 - 300	Cobbles
75 - 19	Coarse Gravel
19 - 4.8	Fine Gravel
4.8 - 2.0	Coarse Sand
2.0 - 0.43	Medium Sand
0.43 – 0.08	Fine Sand
<0.08	Silt
<0.002	Clay



Percentage Category:	<u>%</u>
Trace	0 – 5
Little	5 - 20
Some	20 - 35
With	35 - 50
And	equal parts (if 2 categories, 50/50; if 3, 1/3 rd of each); list in descending grain-size order.

5. Additional Descriptors, such as:

Lens	Zone equal to or less than 1-inch (2.5 cm) in thickness
Layer	Zone greater than 1-inch (2.5 cm) in thickness
Interbedded	Alternating lenses and/or layers of different media types (The term varved is occasionally applied to some interbedded sediments, but only applies to interbedding that results from annual variation in sediment deposition rates/types.

Examples of soil descriptions:

- Fine to coarse GRAVEL and medium to coarse SAND
- Fine **GRAVEL**, some fine to coarse Sand, little Silt, trace Clay
- Yellowish orange, dry, dense, medium to coarse **SAND**, trace fine Gravel and Silt
- Gray, wet, medium dense, fine to coarse **SAND**, some fine Gravel
- Brown, moist, soft, interbedded SILT and CLAY, trace fine Sand, very thinly bedded Distinct gray mottling



Notes

- Always use ALL CAPITAL LETTERS for the primary constituent, or for all primary constituents if you use "and". The first letter of each subsequent constituent of soil is capitalized. Still use all caps even if the primary constituents are human-made materials, such as ASPHALT and CONCRETE.
- Where there is variation within a texture class (i.e. Gravel, Sand, Silt, and Clay), indicate the entire range of grain size, listed in increasing size order (ex. fine to coarse Gravel).
- Within one percentage category, list in decreasing grain-size (ex. trace fine Gravel and coarse Sand).
- Avoid the temptation to create new categories intermediate to those listed here, such as "damp/moist" or "trace/little." If there is gradation vertically from top to bottom, indicate this with expressions such as "damp to moist;" other heterogeneity should be described in detail, as in "Brown, damp, soft SILT, with pockets of moist, firm Clay."
- Describe unusual features (inclusions, discontinuities, irregularities) in detail in the "remarks" column. If contamination of any kind is encountered, describe its properties instead of simply naming it. For example, instead of "Diesel Oil @ 6.5", it is better to say "Thin layer of oily material @ 6.5"; odor similar to diesel oil."



SOIL LITHOLOGY "CHEAT SHEET":

Soil Color	Moisture Co	ontent:	Density (Based on BLOW COUNTS)			Percentage Category:	"Other"	
(Mottling):	Term:	Features:	Gravel and Sand: Silt and Clay:		(Descending order by prevalence)	Other		
(Faint)	Dry	Little/no moisture	Term:	Blows per foot:	Term:	Blows per foot:	0-5%:Trace	Lens
(Distinct)	Damp	Some moisture, not compactable	Very loose	0-4	Very soft	0-2	5-20%: Little	Layer
(Prominent)	Moist	Compactable moisture	Loose	4-10	Soft	2-4	20 – 35%: Some	Interbedded
	Wet	Moisture content > compactable range	Medium dense	10-30	Medium stiff	4-8	35 – 50% With	Slickensided
	Saturated	Voids filled (water flows from sample)	Dense	30-50	Stiff	8-15	Equal % Parts: And	Pockets
	(Most clay formations cannot contain water above the "Wet" range, as clay micropores hold water with a force greater than can be overcome by gravity alone.)		Very dense	>50	Very stiff	15-30		Residues
				•	Hard	>30	(Do not use "Few")	Olfactory Obs.
								No Recovery

SOIL LITHOLOGY "CHEAT SHEET":

Soil Color	Moisture Co	ontent:	Density (Based on BLOW COUNTS)			Percentage Category:	"Other"	
(Mottling):	Term:	Features:	Gravel and Sand: Silt and Clay:		(Descending order by prevalence)	Otilei		
(Faint)	Dry	Little/no moisture	Term:	Blows per foot:	Term:	Blows per foot:	0-5%:Trace	Lens
(Distinct)	Damp	Some moisture, not compactable	Very loose	0-4	Very soft	0-2	5-20%: Little	Layer
(Prominent)	Moist	Compactable moisture	Loose	4-10	Soft	2-4	20 – 35%: Some	Interbedded
	Wet	Moisture content > compactable range	Medium dense	10-30	Medium stiff	4-8	35 - 50% With	Slickensided
	Saturated	Voids filled (water flows from sample)	Dense	30-50	Stiff	8-15	Equal % Parts: And	Pockets
	(Most clay formations cannot contain water above the "Wet" range, as clay micropores hold water with a force greater than can be overcome by gravity alone.)		Very dense	>50	Very stiff	15-30		Residues
					Hard	>30	(Do not use "Few")	Olfactory Obs.
								No Recovery

SOP 7

Well Development



STANDARD OPERATING PROCEDURE WELL DEVELOPMENT

1. PURPOSE

The purpose of this procedure is to set criteria for well development after installation of new monitoring or production wells or wells than have not been sampled or used for an extended period of time.

2. PROCEDURE

This procedure is for the development of groundwater monitoring wells. Before a newly constructed well can be used for water-quality sampling, measuring water levels, or aquifer testing, it must be developed. Well development refers to the procedure used to clear the well and formation around the screen of fine-grained materials (sands, silts, and clays) produced during drilling or naturally occurring in the formation.

Well development is completed to remove fine grained materials from the well casing, well screen and gravel pack. The time allotted and techniques used for well development will vary by well and depend on drilling method, well construction, geological formation and intended use for the well. In general, well development should continue until the well responds to water level changes in the formation (i.e., a good hydraulic connection is established between the well and formation) and the well produces clear, sediment-free water to the extent practical. In general, the method (disturbance) used to develop the well should be more rigorous than the amount of disturbance the well will experience during its regular or intended use. For example, if a well develops clear, sediment free water using a bailer, it is very well developed for low-flow sampling using a peristaltic pump. Please note that well development is especially important when contaminants of concern are sensitive to suspended solids (e.g., metals, PCBs, SVOCs).

2.1 FIELD PREPARATION

2.1.1 Forms

- Daily Log
- Well Development Form

2.1.2 Equipment

- Required Health and Safety Equipment and PPE
- Well Keys
- General Tools: knife, socket set, vise grips, screwdriver, etc.
- Power Source: generator, extension cord



STANDARD OPERATING PROCEDURE WELL DEVELOPMENT

- Well Development Device: water truck with hoist, surge block, bailer, submersible pump
- Discharge Line: tubing or hose (suitable for expected flow rates and chemicals of concern)
- Purge Water Container: Clear glass jars (e.g., drillers' jars), graduated pail, 55gallon drum, polytank or frac tank
- Cleaning Supplies: non-phosphate soap, buckets, brushes, laboratory-supplied distilled/deionized water, tap water, cleaning solvent, aluminum foil, plastic sheeting, etc.
- Meters: water level, flow
- Water Quality Meter: pH, temperature, conductivity, turbidity, etc.

2.1.3 Documents

- Detailed Scope Work Summary
- Proposal
- Work Plan

2.2 FIELD PROCEDURES

All wells must be developed and well development generally occurs with a few days of installation (please remember that some grouts require time to cure). Well development methods and procedures will vary as described above. In most cases, a monitoring well can be developed in less than one hour using a bailer, submersible pump, surge block and/or check valve and tubing (waterra tubing). Production or extraction wells may need to be developed by more rigorous methods and may require a specialized subcontractor. The following presents the minimum steps required to complete well development for a monitoring well and is generally acceptable for all well development activities. More rigorous methods may be required and will be detailed in project specific SOP.

- 1. Review HASP and don appropriate safety equipment and set up appropriate air monitoring equipment as needed.
- 2. Prior to introduction to a well, all non-dedicated equipment used for development purposes must be cleaned using a soapy wash (laboratory grade), tap water rinse, isopropyl alcohol rinse and distilled/deionized water rinse as appropriate.
- 3. Uncap and gauge well, record initial water level.
- 4. Place well development device (pump, bailer, surge block) into the well.



STANDARD OPERATING PROCEDURE WELL DEVELOPMENT

- 5. Collect a baseline groundwater sample in a glass jar, or purge bucket to determine relative turbidity. Your project manager may also request that you measure and record the temperature, pH, turbidity, specific electrical conductance and other water quality parameters.
- 6. Surge the well.
- 7. Purge the well. If the well runs dry, stop purging and allow the well to recover. Sometimes purge water or distilled water must be added to the well initially to help clear the screen. Additional surging of the screen with the recycled purge water (or distilled water) will allow formation water to flow into the screen. Please make sure that three times the amount of water added is removed during the purging of the well.
- 8. Repeat steps 5 through 7 until groundwater is relatively clear (less than 4 NTUs) and if required, the water quality parameters are stable within 10%.
- 9. After development, the well should be allowed to rest and should not be sampled immediately. The period of rest will vary depending on the hydraulic properties of the aquifer or targeted water bearing unit and the intended use of the sample results obtained from the well. In general, a minimum of 2 to 3 days of rest should be adequate.

Waste Disposal

- All waste generated will be disposed in accordance to the methods and procedures contained in the Waste Disposal SOP.
- All water generated during cleaning and development procedures will be collected and contained in accordance to the site specific disposal requirements.
- All PPE, such as gloves, disposable clothing, and other disposable equipment
 used or generated during the development process, will be placed in plastic
 bags. These bags will be transferred into appropriately labeled 55-gallon drums
 or a covered roll-off box for appropriate disposal.

SOP 8

Water Sampling



STANDARD OPERATING PROCEDURE WATER SAMPLING

1. PURPOSE

The purpose of this procedure is to obtain representative groundwater samples from groundwater monitoring wells or piezometers with a bailer, peristaltic, submersible, or KeckTM pump. Site-specific groundwater sampling requirements, if necessary, will be described in work plans or field sampling plans.

2. PROCEDURE

2.1 FIELD PREPARATION

Notify client, property owner, and MDEQ as necessary.

2.1.1 Forms

- Water Level Data Sheet
- Daily Report Sheets
- Chain of Custodies
- Water Quality Data Sheet
- Field Service Request
- Tailgate Health and Safety

2.1.2 Equipment

- Laboratory provided containers and labels
- Laboratory-cleaned cooler
- Well keys
- Electronic water level indicator
- Interface probe (if free-product is expected at the site)
- Calculator
- Latex or nitrile gloves
- Tools to access wells
- metal detector, turkey baster or plastic cup
- Decontamination equipment including deionized or distilled water, Alconox, graduated cylinders, and paper towel



STANDARD OPERATING PROCEDURE WATER SAMPLING

- Knife or scissors
- Garbage bags
- Two graduated 5-gallon pails to collect purge water
- pH, temperature, and specific conductivity meter

One of:

- Disposable high-density polyethylene sampling bailers and bailer rope
- Peristaltic pump and sufficient disposable Silicon (approximately 10 inches per sample) and Tygon tubing (length measured from pump head to sampling depth)
- Submersible pump and Tygon tubing
- KeckTM pump

If needed:

- DOT-approved sealed drums for storage of purged well water, or a suitable location to disperse of liquid (i.e., on-site treatment system)
- Quantab[™] and Hach[™] Titration kits

2.1.3 Documents

- Well Construction Log
- Well location map/site map
- Work Plan
- Health and Safety Plan
- Signed site access agreement

2.1.4 Other

- Cellular phone
- Replacement locks
- Writing implements and an indelible marker
- Crushed ice
- Bubble wrap if required to protect samples during shipment to the laboratory
- First aid kit



STANDARD OPERATING PROCEDURE WATER SAMPLING

- Personal comfort items
- Machete or other vegetation-clearing tool

2.2 FIELD PROCEDURES

2.2.1 Well Purge

Don a new pair of latex or nitrile gloves

First sample those wells with the lowest historical or suspected concentrations, and then advance to the wells more likely to be contaminated. Set plastic sheeting or a garbage bag near the well to set sample bottles on and to rest sampling equipment.

Obtain the water level measurement, noting any occurrence of LNAPL or DNAPL.

Calculate three or five times the volume of groundwater present in the well casing, as indicated on the *Field Service Request Form*.

Purge the well using a dedicated HDPE disposable bailer and a new length of clean rope, a peristaltic pump with new Teflon and Tygon tubing, a submersible pump with new Tygon tubing, or a KeckTM pump. Purge the groundwater monitoring well of a minimum of 3 to 5 well casing volumes prior to collecting the samples. Measure the volume of purged water using a graduated pail, or other container of known volume. Purging and sampling should be conducted using slow and steady motions to avoid excessive agitation, increased sample turbidity, and sample volatilization. Empty purge water onto the ground, away from the well, or in the event containerizing is required, transfer purged water from the pail into the appropriate storage container for storage until disposal is arranged.

NOTE: If well goes dry before 3 well volumes can be purged from the well, allow groundwater to recharge, then collect sample.

2.2.2 Field Measured Parameters

After at least 3 well volumes have been purged from the well, measure temperature, pH, conductivity, and any other field parameters as specified in the *Field Service Request Form*. Once three measurements are obtained within 10-percent of each other, the groundwater quality may be considered representative of the groundwater as it exists in the formation.

If well goes dry before 3 well volumes can be purged from the well, a single round of field parameter measurements will be obtained following recharge of a sufficient amount of groundwater to complete the sampling activities.



STANDARD OPERATING PROCEDURE WATER SAMPLING

2.2.3 Bottle Preparation

Prior to sample collection; label all appropriate fields on the sample container labels with an indelible marker. Apply labels to appropriate containers.

2.2.4 Sample Collection

2.2.4.1 **Bailers**

Samples will be collected using the same HDPE disposable bailer used for purging. Transfer groundwater samples from the bailer to their appropriate sample bottle, minimizing turbulent flow between the bailer and the sample bottles. Place samples in the appropriate containers in decreasing order of volatility (e.g., purgeables and aromatics first, then PNAs and phenols, then cyanides, and lastly, nitrate, sulfate and metals). Samples for dissolved metals analysis may be field filtered. If there is insufficient sample volume to provide all sampling needs, retrieve additional bailer volumes until all samples are collected.

2.2.4.2 Peristaltic, Submersible, or KeckTM Pump

Samples for laboratory analysis of parameters, other than VOCs, will be collected directly from the pump tubing following purging of 3 to 5 well volumes, and stabilization of field parameter measurements. A 0.45 μ m filter will be used to field filter samples for dissolved metals into a preserved laboratory container.

2.2.5 Sample Preservation

Tighten lids of sample containers and place in coolers

Wrap all glass containers in bubble wrap or foam; then place into large 1-2 gallon zip-lock bags; label the outside of the bag, and place into the coolers.

Completely fill out the *Chain-of-Custody*. When shipping samples, seal *Chain-of-Custody* in a watertight zip-lock bag, and attach to the underside of the cooler lid with packaging tape. Ship coolers or arrange delivery to the laboratory as soon as possible and before the sample "hold-time" expires.

2.2.6 Decontamination

Decontaminate electronic water level indicator, pH, temperature, and specific conductivity meter between sampling points.

If peristaltic pump is used, dispose used flow-through tubing and filters.

If submersible or KeckTM pump is used, place pump in a graduated cylinder filled with a solution of Alconox and deionized or distilled water. Allowing the soap and water solution to re-circulate through the pump and tubing for a maximum of five minutes. Rinse cylinder and outside of



STANDARD OPERATING PROCEDURE WATER SAMPLING

pump and tubing with deionized or distilled water. Fill cylinder with deionized or distilled water and allow at least 4 liters to run though the pump and tubing and onto the ground away from the well.

NOTE: During pump use and decontamination, take care to assure tubing and pump does not come in contact with the ground or other surfaces. Following sampling of the last well, remove and throw away submersible pump tubing prior to decontamination of the pump.

Dispose of all gloves, bailers, rope/string, tubing, and filters used to collect the sample prior to accessing the next well.

3. QUALITY ASSURANCE

Avoid cross-contamination of wells with the water level indicator, and sampling equipment by conducting proper decontamination procedures described above.

Take care in labeling the samples, and the corresponding *Chain-of-Custody* with the correct sample date, time and well identification. All labeling must be consistent between samples and the *Chain of Custody*.

Keep samples on ice following collection, and be conscience of "hold-times" for the samples. It is imperative that samples are submitted to the laboratory prior to the exceedence of hold times.

SOP 9 EPA Low-Flow (Minimum Drawdown) Groundwater Sampling Procedures

Office of Solid Waste and Emergency Response

EPA/540/S-95/504 April 1996

Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls¹ and Michael J. Barcelona²

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing

units were identified and sampled in keeping with that objective. These were highly productive aguifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic units. With time it became apparent that conventional water supply generalizations of homogeneity did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

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chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aguifer heterogeneity and colloidal transport. Aguifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry. hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third phase as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria.

These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

- Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;
- Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and
- 3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term representativeness applies to chemical and hydrogeologic data collected via wells, borings, piezometers. geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few

feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-

flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxida-

tion-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the mobile load of contaminants present (dissolved and colloid-associated):
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- · reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water.
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- · higher initial capital costs,
- · greater set-up time in the field,
- need to transport additional equipment to and from the site.
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a change in conditions and trigger an action.

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). Highquality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and fresh screen waters during insertion of the sampling device or groundwater level measurement device: disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g., pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well:
- maximize tubing wall thickness, minimize tubing length:
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- · monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are illsuited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a $\it fix$ for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally $\it dissolved$ [i.e., samples filtered with 0.45 μ m filters]) concentrations of major ions and trace metals, 0.1 μ m filters are recommended although 0.45 μ m filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO $_2$ composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and nondisposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality

indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe²⁺, CH₄, H₂S/HS⁻, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or

introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon $^{\text{TM}}$ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C .

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

- (1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.
- (2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.
- (3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of

the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

- a. "portable or non-dedicated mode" Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.
- b. "dedicated mode" Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described herein as part of its in-house research program and under Contract No. 68-C4-0031 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Figure 2. Ground Water Sampling Log

Project	Site	Well No	Date	
Well Depth	Screen Length	Well Diameter	Casing Type	
Sampling Device	Tubing type		Water Level	
Measuring Point	Other Inf	or		
Sampling Personnel				

Time	рН	Temp	Cond.	Dis.O ₂	Turb.	[]Conc		Notes

Type of Samples Collected			

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi \ r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project	Site	Well No	Date	
Well Depth	Screen Length	Well Diameter	Casing Type	
Sampling Device	Tubing type		Water Level	
Measuring Point	Other Int	for		
Sampling Personnel				

Time	Pump Rate	Turbidity	Alkalinity	[] Conc	Notes

Type of Samples Collected
Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi r^3$

SOP 10

Water Elevations



STANDARD OPERATING PROCEDURE WATER ELEVATIONS

1. PURPOSE

The purpose of this procedure is to obtain groundwater level measurements from wells and piezometers to assist in defining site hydrogeologic conditions.

2. PROCEDURE

2.1 FIELD PREPARATION

Notify client, property owner, and MDEQ as necessary.

2.1.1 Forms

- Water Level Data Sheet
- Daily Report Sheets
- Tailgate Health and Safety
- Field Service Request

2.1.2 Equipment

- Well keys
- Electronic water level indicator
- Calculator
- Latex or nitrile gloves
- Tools to access wells
- Metal detector, turkey baster or plastic cup
- Decontamination equipment including deionized or distilled water, Alconox®, and paper towel
- Garbage bags



STANDARD OPERATING PROCEDURE WATER ELEVATIONS

2.1.3 Documents

- Well Construction Log, or total well depth and previous water level measurements
- Well location map/site map
- Work Plan
- Health and Safety Plan
- Signed site access agreement, as applicable

2.1.4 Other

- Cellular phone
- Replacement locks
- Writing implements and an indelible marker
- First aid kit
- Personal comfort items
- Machete or other vegetation-clearing tool

2.2 FIELD PROCEDURES

Don a new pair of latex or nitrile gloves and open the well with a socket set if it is a flush grade manhole cover or a key if it is an above grade cover.

Beware of insects (particularly wasps and bees) that may be nesting within the protective casing. Bail out any standing water with a turkey baster or cup in flush-grade manholes. Note on presence and appearance of standing water, insects, and well condition.

Unlock, loosen, and carefully remove locking expandable well cap.

Well may be under pressure. Always face away from well when removing well cover. Allow groundwater elevation to stabilize for a minimum of five minutes prior to measuring depth to groundwater. When working on smaller sites, it may be appropriate to open all of the wells first, and then gauge them.

2.2.1 Identify the Monitoring Point for the Well

The well monitoring point may be the north side of the riser casing and marked with an indelible marker, or on the highest side of the top of casing. The top of an above-grade protector or flush-grade manhole should never be used as a reference point due to frost heave and settling. Note the reference point used on the *Water Level Data Sheet*



STANDARD OPERATING PROCEDURE WATER ELEVATIONS

2.2.2 Obtain the Water Level Measurement

Water levels will be measured from suspected cleanest (up-gradient) well to the suspected most contaminated (down-gradient or near source) well.

Use a consistent sensitivity setting for all wells.

Lower the decontaminated probe into the well until a "beep" sound is heard. The probe should be raised and lowered to confirm the exact water level. NOTE: condensation inside the well casing can result in a premature sounding and contaminants can result in incorrect confirmatory measurements. Refer to previous depths to groundwater recorded on the *Field Groundwater Sample Form* to verify measurement, if available. When a false reading is suspected, gently shake the tape of the electronic water level indicator until the audible sound stops. Then proceed to lower the probe to confirm.

Read the tape at the monitoring point and recorded the measurement to the nearest 0.01-foot on the *Water Level Data* Sheet.

Lower probe to bottom of well and record total depth on *Field Groundwater Sample Form*, if necessary.

Complete all information on the Water Level Data Sheet.

2.2.3 Decontamination

The measuring device shall be decontaminated immediately after each use. The decontamination procedure should be initiated while reeling in the tape and probe: wipe tape with clean paper towel soaked with deionized or distilled water and Alconox® solution, rinse probe with deionized or distilled water and Alconox® solution, rinse tape and probe with deionized or distilled water, and dry probe with clean paper towel. Apply decontamination fluids with a labeled spray bottle.

SOP 11

Transfer of Sample Custody and Shipping



STANDARD OPERATING PROCEDURE TRANSFER OF SAMPLE CUSTODY AND SHIPPING

1. PURPOSE

The purpose of this procedure is to set criteria for transfer of sample custody and shipping of samples to the laboratory.

2. PROCEDURE

2.1 FIELD PREPARATION

2.1.1 Forms and Documents

Chain of custody

2.1.2 Equipment

- Sample labels and containers
- · Waterproof pen or marker
- Coolers and packing materials
- Ice

2.2 FIELD PROCEDURES

- A chain-of-custody (COC) record will be completed during sample collection and will
 accompany each shipment identifying the contents of the shipment. The COC record will
 accompany the samples to the laboratory. The field personnel collecting the samples will
 be responsible for the custody of the samples until the samples are relinquished to the
 laboratory. Sample transfer will require the individuals relinquishing and receiving the
 samples to sign, date and note the time of sample transfer on the COC record. As few
 people as possible should handle the samples.
- Samples will be shipped or delivered in a timely fashion to the laboratory so that holding-times and/or analysis times as prescribed by the methodology can be met.
- Samples will also be transported in containers (coolers) packaged with ice to maintain the temperature prescribed in RRD Operational Memorandum No. 2 Attachment # 4. Samples will be packaged for shipment and shipped to the appropriate laboratory for analysis with a separate signed chain-of-custody record enclosed in each sample cooler. Water VOC samples will be placed in bubble wrap bags while soil VOC samples will be placed in sealed sample pouches. The remaining samples in glass containers will be wrapped in bubble wrap and placed in the sample cooler. Samples in polyethylene containers will be placed upright directly in the sample cooler. All samples will be placed



STANDARD OPERATING PROCEDURE TRANSFER OF SAMPLE CUSTODY AND SHIPPING

in an upright position and limited to one layer of samples per each cooler. Additional bubble wrap or packaging material will be added to fill the cooler. Shipping containers will be secured with strapping tape and custody tape for shipment to the laboratory.

- When samples are split, a separate chain-of-custody will be prepared for the samples and marked to indicate to whom the samples are being split. The person relinquishing the samples to the spilt-sample representative will require the representative's signature acknowledging sample receipt.
- If samples are sent by a commercial carrier, a bill of lading will be used. A copy of the bill
 of lading will be retained as part of permanent documentation. Commercial carriers are
 not required to sign the custody record as long as the custody record is sealed inside the
 sample cooler and the custody tape remains intact.
- Samples will be picked up by a laboratory courier or transported overnight by a courier to
 the laboratory the same day they are collected or within twenty-four hours unless
 collected on a weekend or holiday. In these cases, the samples will be stored in a
 secure location until delivery to the lab. Additional ice will be added to the cooler as
 needed to maintain proper preservation temperatures.

SOP 12

Drum and Container Handling Practices



This safe work practice (SWP) establishes procedures to protect field personnel and the public from exposure to hazardous materials resulting from the handling, opening, sampling, transferring, overpacking, and shipping of drums.

All drum and container handling operations must adhere to all applicable federal, state, local, contractual, and company requirements. Preparation and shipping of containers of hazardous materials must comply with applicable U.S. Environmental Protection Agency (EPA) and U.S. Department of Transportation (DOT) regulations. All drums and containers used during hazardous waste operations must meet appropriate DOT regulations for the materials they contain.

Drum and container handling should be approached in a systematic, stepwise manner, especially when the contents are unknown or containers are in poor condition. Inspection, opening, sampling, overpacking, and staging requirements for drums and containers are described below

1.0 RESPONSIBILITIES

Operating unit health and safety managers (HSMs) are responsible for providing technical guidance to project managers and site safety coordinators (SSC) on drum and container handling procedures. Project managers are responsible for ensuring implementation of this SWP, when warranted, on their projects. SSCs are responsible for enforcement of this SWP at the work site. Field personnel are required to adhere to drum and container handling guidelines and procedures.

2.0 DRUM AND CONTAINER INSPECTION

Drums or containers must be visually inspected before any work is conducted in order to gain as much information as possible about their contents. Field personnel should document in the field logbook the following information:

- Any labels or other markings indicating possible contents;
- Drum or container condition (such as rusted, leaking, or dented);
- Signs of pressure (such as bulging or swelling);



- Drum or container size, construction, and type; and
- Configuration of drum or container head (open or closed top).

After observations are documented in the field logbook, each drum or container should be labeled with an identification code for future tracking.

3.0 DRUM AND CONTAINER OPENING

For efficient and safe drum or container opening, personnel must adhere to the guidelines below.

- If available, remote-controlled drum or container opening equipment should be used.
- In order to protect the employee, a suitable shield shall be placed between the employee and the drum being opened.
- Only spark-proof tools should be used to open drums and containers.
- Drums or containers containing unknown materials should be opened using Level B
 personal protection, including splash protection.
- Drums or containers containing radioactive material should not be opened or handled until the appropriate personnel with expertise in this area have been consulted.
- Air monitoring equipment should be available near the drum or container being opened, such as combination oxygen and combustible gas meters, colorimetric tubes, and photoionization detectors.
- Tools used for drum or container opening should be decontaminated after each use to avoid mixing incompatible wastes.
- Drums or containers should be resealed as soon as possible to minimize vapor generation.
- If possible, drums or containers exhibiting signs of pressure should not be opened.



4.0 DRUM AND CONTAINER SAMPLING

Drum and container sampling poses a variety of potential hazards to worker health and safety, including direct contact with hazardous materials, inhalation of hazardous vapors, and the possibility of drum or container explosion or rupture. The guidelines below should be used to properly sample drums and containers.

- Prior to sampling, a sampling plan must be developed that includes the following information:
- Background information on the waste;
- Which drums or containers will be sampled;
- Appropriate sampling devices; and
- Sample containers to be used,
- Sampling personnel should not stand on drums or containers or lean over other drums or containers to obtain samples.
- All phases in the vertical cross section of each drum or container should be sampled.
- Disposable glass tubing or other disposable sampling devices should be used to sample liquid.
- When sampling liquids, absorbent pads should be placed on drum tops to collect spillage that may occur while transferring samples into containers.
- Sampling personnel should document container number, any container labeling, sampling date and time, and number and color of different phases.

5.0 DRUM AND CONTAINER OVERPACKING

During an emergency, drums and containers should be handled as detailed below.

Leaks should be plugged or patched immediately if this can be done without risk.



- Damaged drums and containers should be placed in an overpack container with absorbent pads to collect any spilled material or the contents transferred into a clean, compatible drum or container.
- Absorbent material should be used to collect any leakage that may occur during shipment.

During remedial actions, the procedures below apply to drum and container handling.

- Drums or containers should be placed in overpack containers, and any identification number assigned to the drum or container should be placed on the outside of the overpack container.
- If drum or container contents are to be bulked with other drum or container contents, the compatibility of the contents should be verified by a field characterization study prior to bulking.

6.0 DRUM AND CONTAINER STAGING

Staging refers to moving drums or containers in an organized manner to predesignated areas. Drums or containers may be staged to facilitate characterization and remedial action and also to protect drums or containers from potentially hazardous site conditions (such as high temperatures and proximity to ignition sources or heavy equipment). To ensure that staging is conducted in a safe and efficient manner, the guidelines below should be followed.

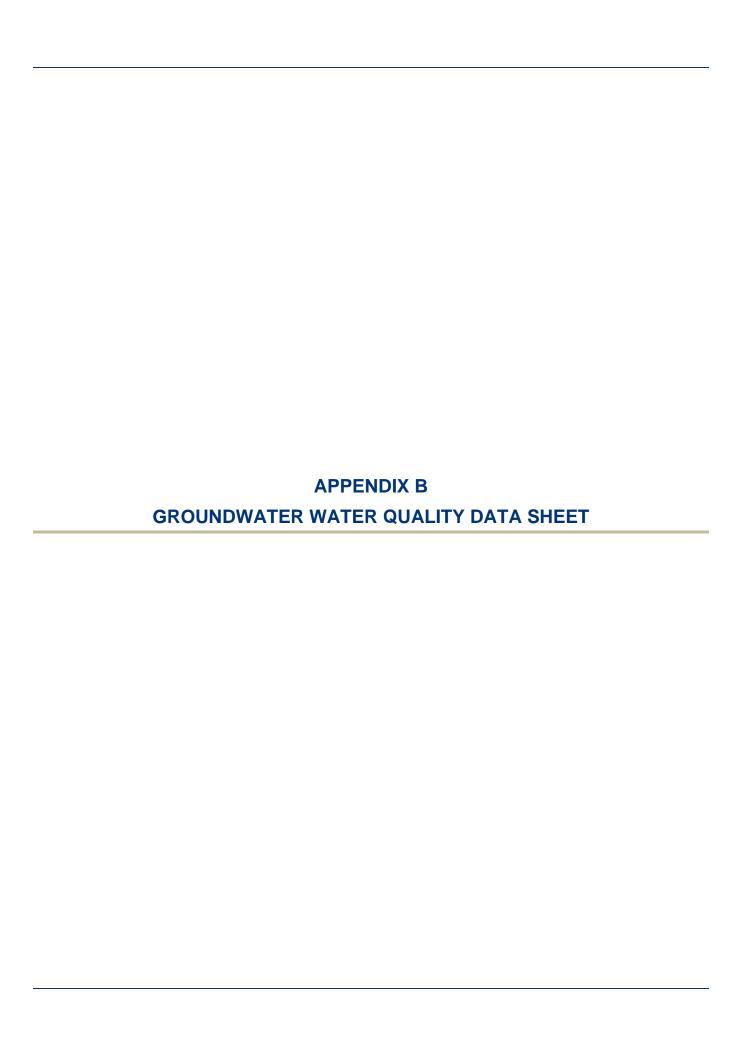
- Staging activities should be kept to a minimum to prevent hazards associated with increased handling of drums or containers.
- The staging area should be as close as possible to the site exit.
- The staging area should be level and covered with plastic sheeting or absorbent material.
- The staging area should be diked to contain possible spills.



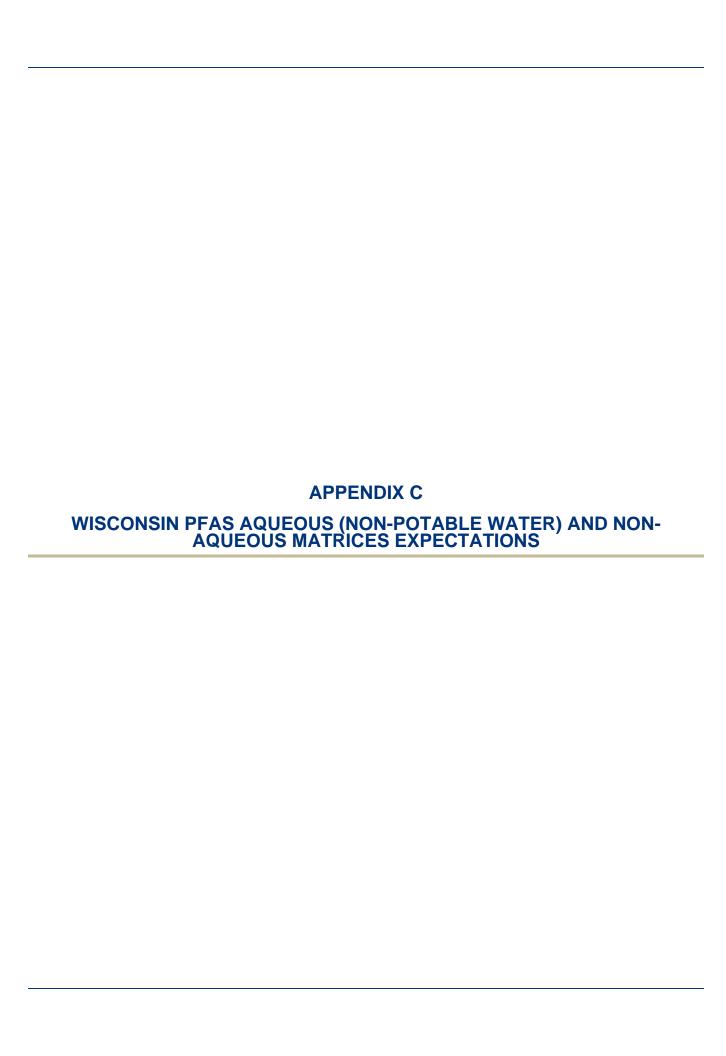
- Drums or containers should be secured on pallets whenever possible to aid in the safe movement of drums or containers and to isolate the drums or containers from the soil surface.
- Drums or containers should not be stacked on top of each other.
- Drums or containers should be staged according to chemical composition of the contents. Drums or containers containing incompatible materials should be kept segregated.
- Drums and containers should be staged far enough apart to allow for the movement of equipment and personnel.

Disclaimer: This safe work practice (SWP) is the property of Tetra Tech, Inc. (Tetra Tech). Any reuse of the SWP without Tetra Tech's permission is at the sole risk of the user. The user will hold harmless Tetra Tech for any damages that result from unauthorized reuse of this SWP. Authorized users are responsible for obtaining proper training and qualification from their employer before performing operations described in this SWP.

Revision Date	Document Authorizer	Revision Details
10/1/2008	Chris McClain	Update from 1998 format



Tetra Tech 710 Avis Dr., Suite 100, Ann Arbor, MI 48108 (734) 213-2204						WATER QUALITY DATA SHEET				
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WISCONSIN DEPARTMENT OF NATURAL RESOURCES NOTICE OF FINAL GUIDANCE & CERTIFICATION

Pursuant to ch. 227, Wis. Stats., the Wisconsin Department of Natural Resources has finalized and hereby certifies the following guidance document.

DOCUMENT ID

EA-19-0001

DOCUMENT TITLE

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

PROGRAM/BUREAU

Certification Services / Environmental Analysis & Sustainability

STATUTORY AUTHORITY OR LEGAL CITATION

Wis. Stats. s. 299.11 and Wis. Admin. Code s. NR 149.41 (2)

DATE SENT TO LEGISLATIVE REFERENCE BUREAU (FOR PUBLIC COMMENTS)

9.16.19

DATE FINALIZED

12.16.19

DNR CERTIFICATION

I have reviewed this guidance document or proposed guidance document and I certify that it complies with sections 227.10 and 227.11 of the Wisconsin Statutes. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is not explicitly required or explicitly permitted by a statute or a rule that has been lawfully promulgated. I further certify that the guidance document or proposed guidance document contains no standard, requirement, or threshold that is more restrictive than a standard, requirement, or threshold contained in the Wisconsin Statutes.

Signature

Date

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations



- Version 12.16.2019 -



Per- and Polyfluorinated Alkyl Substances (PFAS) Analysis Using Isotope Dilution by LC/MS/MS

The purpose of this document is to provide the expectations that will help the Program determine if a laboratory's method is considered suitable for analysis of PFAS in aqueous (non-potable water) and non-aqueous matrices for Wisconsin.

The Program has the legal authority under NR 149.41 (2) to determine whether the method selected by a laboratory is suitable for the matrix, type of analyte, expected level of analyte, regulatory limit, and anticipated interferences in the sample, when methods are not prescribed by covered programs under NR 149 or permits issued by the department.

Once the EPA publishes their 1600 series isotope dilution method, the Program will defer to that method for certification.

Potable water samples are analyzed utilizing EPA 537.1.

{F} = when "{F}" is listed after an expectation and the expectation is not met, then qualify the associated results on the test report. The qualifier can refer the data user to the narrative where detail is provided that indicates what the non-conformance was, and if known, the possible effects on the sample results.

Definitions are provided in Section X, "Definitions," of this document.

I. Sample Handling

- 1. Instruct sample collectors to collect grab samples in high density polyethylene or polypropylene containers. **{F}**Avoid polytetrafluoroethylene (PTFE) containers and contact with PTFE surfaces.
- 2. Instruct sample collectors to collect an equipment blank when using equipment in the field to collect samples. {F}
- 3. Instruct sample collectors not to fill aqueous sample containers completely.
- 4. There is no chemical preservation necessary, just temperature preservation. Instruct sample collectors to ship aqueous and solid samples at above their freezing point to 6 °C. {F} Instruct sample collectors to ship tissue samples frozen. {F} Measure and document the temperature of aqueous and solid samples at sample receipt. Tissue samples received frozen can be documented as "frozen" at sample receipt.
- 5. Store aqueous and solid samples at above their freezing point to 6 °C at the laboratory. {F} Store tissue samples at less than or equal to -10 °C at the laboratory. {F} Store all extracts at 0 6 °C at the laboratory. {F}
- 6. Aqueous and solid sample holding times are within 28 days from collection to extraction and within 30 days from extraction to analysis. {F} Tissue sample holding times are within 1 year from collection to extraction and within 30 days from extraction to analysis. {F}
- 7. Rinse aqueous sample containers and all extract containers after transfers with one or more rinses of polar solvent to remove any PFAS that may have been adsorbed to container walls.
- 8. Thoroughly vortex or mix extracts and standards before transfer or aliquoting to remove any PFAS that may have been adsorbed to container walls.
- 9. Thoroughly vortex autosampler vials before loading the autosampler to remove any PFAS that may have adsorbed to container walls.



II. Initial Demonstration of Capability (IDC)

- 1. All analysts performing testing are expected to pass an IDC. If analysts perform only the extraction steps, then they are expected to pass the extraction portion of an IDC. If analysts perform only the analysis steps, then they are expected to pass the analysis portion of an IDC.
- 2. Analyze standards of all target (native) analytes and extracted internal standards (EIS) to determine retention times of the linear and branched isomers.
- 3. Analyze a method blank. The results are expected to be less than one-half the method reporting limit (MRL).
- 4. Assess precision and recovery by performing the entire procedure on four laboratory control samples (LCS) spiked at a midrange concentration of the initial calibration for each target (native) analyte. The average recovery is expected to be within 65-135%, and the RSD is expected to be less than or equal to 30%.
- 5. Assess recovery of the extracted internal standards (EIS) in each LCS. Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 50–150%. For FOSA, NMeFOSA, NMeFOSE, and NEtFOSE, EIS recoveries are expected to be within 20 150%.

III. Field Quality Control Samples

- 1. **Equipment blanks** (one per sampling event when equipment is used in the field to collect samples) The results are expected to be less than the highest of the following {F}:
 - a. 1/2 the MRL
 - b. 1/10 the sample concentration

It is not necessary to qualify equipment blank detections between the MDL and one-half the MRL.

- 2. **Field blanks** (one per sampling event for each sampling site) The results are expected to be less than the highest of the following **F**:
 - a. 1/2 the MRL
 - b. 1/10 the sample concentration

It is not necessary to qualify field blank detections between the MDL and one-half the MRL.

3. **Field duplicates** (one per sampling event for each sampling site) – The RPDs are expected to be less than or equal to 30% when analyte concentrations are greater than twice the MRL. **{F}** The RPDs are expected to be less than or equal to 50% when analyte concentrations are the MRL and twice the MRL. **{F}**



IV. Batch Quality Control Samples

- 1. **Method blank** (one per batch) The results are expected to be less than the highest of the following {F}:
 - a. 1/2 the MRL
 - b. 1/10 the sample concentration

It is not necessary to qualify method blank detections between the MDL and one-half the MRL.

Method blanks are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

2. Laboratory control sample (one per batch) – Spike with all target (native) analytes.

Laboratory control samples are processed along with and under the same conditions, including all sample preparation steps (i.e. filtering, centrifuging), as the associated samples in the preparation batch.

For aqueous and solids batches, spike the LCS at a low range (1 - 2x MRL) in each batch, or the laboratory may rotate spike concentrations between three consecutive batches alternating low range, midrange, and high range. Midrange and high range are relative to the initial calibration range. For aqueous and solid batches, the recoveries are expected to be within 60-135%, except for the low range (1 - 2x MRL) where the recoveries are expected to be within 50-150%. {F}

For tissue batches, spike the LCS at midrange. For tissue batches the recoveries are expected to be within 60-135% with the following exceptions: for PFHxDA, PFODA, and NMeFOSA, the recoveries are expected to be within 50-135%; for PFDS, PFDoS, and 4:2 FTS, the recoveries are expected to be within 40-135%. **{F}**

3. **Extracted internal standards (EIS)** – Spike field samples and all quality control samples (preparation and instrument) with internal standards. The recoveries of these internal standards are used to adjust target (native) analyte concentrations. These isotopically labeled internal standards are added to the sample at the very beginning of the procedure, before extraction, centrifuging, filtering or phase separation takes place.

In order to report quantitative results for the target (native) analytes using the EIS, a minimum signal to noise ratio of 10:1 is expected for each EIS. Do not report results with a qualifier if this minimum is not achieved.

Except for FOSA, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE, the EIS recoveries are expected to be within 25-150% in samples. For FOSA, NMeFOSA, NMeFOSE, and NEtFOSE, these EIS recoveries are expected to be within 10-150% in samples. Once enough data points have been collected, the laboratory may develop their own statistical limits for these five EIS in samples. The statistical limits can be different than 10–150% as long as the expected minimum 10:1 signal to noise ratio is maintained for each EIS.

If any EIS recoveries are outside of limits in a sample, reinject the sample. If the EIS recovery fails again, the data may be reported with a qualifier. **{F}**

Use exact isotopically labeled analogs for the EIS where commercially available. As of December 2019, at least 25 of the 36 PFAS for which Wisconsin is offering certification are available as exact isotopically labeled analogs of the target (native) analytes. As of December 2019, the following 11 PFAS do not have exact isotopically labeled analogs commercially available and are therefore not currently necessary: PFTriA, PFODA, PFPeS, PFHpS, PFNS, PFDS, PFDoS, 10:2 FTSA, DONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS.



For these 11 PFAS without an exact isotopically labeled analog commercially available, use an alternate EIS. The alternate EIS is expected to be isotopically labeled and is expected to be a chemically similar analyte that is close in retention time to the target (native) analyte. The alternate EIS may be from the same functional group as the target (native) analyte or have the same chain length as the target (native) analyte (whichever gives better performance). Typically, the alternate EIS comes from those EIS that are already in use. The same EIS can be used for more than one target (native) analyte.

V. Calibration (Initial and Continuing)

- 1. Perform initial calibration at setup and after an ICV or CCV standard failure. If an ICV or CCV standard fails, the laboratory may immediately analyze two additional consecutive ICV or CCV standards. If either of the two fails, or if immediate analysis is not possible, it is expected that a new initial calibration is performed. If both pass, then sample analysis can continue without a new initial calibration. If a CCV fails high and there are no detections in the associated samples, then analysis can proceed.
- 2. Initial calibration functions are expected to be as follows:
 - a. Calibration factors have an RSD that is less than or equal to 20%.
 - b. Linear regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of five non-zero concentration standards.
 - c. Quadratic regressions have a coefficient of determination that is greater than or equal to 0.99 and use a minimum of six non-zero concentration standards.
 - d. Do not force linear and quadratic regressions through zero.
 - e. For each calibration standard, reprocess the target (native) analyte against the chosen calibration function. The reprocessed recoveries are expected to be within 70–130% of their actual concentrations, except for the lowest concentration standard, whose reprocessed recoveries are expected to be within 50–150% of their actual concentrations.
- 3. It is expected that sample analysis is not performed if the initial calibration fails.
- 4. Analyze standards of all target (native) analytes and EIS to determine retention times of the linear and branched isomers. Analyze branched isomers that have commercially available standards. As of December 2019, the following PFAS are commercially available as branched isomer analytical (quantitative) standards: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA. As of December 2019, PFOA is commercially available as a branched isomer technical grade (qualitative) standard.
- 5. When an initial calibration is performed, it is expected that the midrange standard is used to establish absolute retention times. When an initial calibration is not performed, it is expected that the first CCV is used to establish absolute retention times.
- Retention times of the target (native) analytes and the EIS are expected to fall within 0.4 minutes of the established
 absolute retention times. Comparison of the target (native) analyte and EIS retention times can help determine if
 analyte shifts occurred due to matrix effects.
- 7. **ICV (2nd source)** It is expected that the ICV is performed with each new initial calibration before sample analysis. The ICV is analyzed after the ICB. As of December 2019, the following PFAS may be difficult to find as second sources and are therefore not currently necessary: PFHxDA, PFODA, PFDOS, NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE. Recoveries in the ICV are expected to be within 70-130%. It is expected that sample analysis is not performed if the ICV fails.



- 8. **ICB** It is expected that the ICB is analyzed immediately after the highest standard in the initial calibration and before the ICV to demonstrate the instrument is free from levels of contaminants that would bias results. The results of the ICB are expected to be less than one-half the MRL.
- 9. **CCV** It is expected that CCVs are performed at the beginning and end of each analysis batch and after every 10 field samples.
 - a. It is expected that the concentrations in the first CCV on non-initial calibration days are at the MRL.
 - b. Target (native) analyte recoveries are expected to be within 50-150% for the CCV analyzed at the MRL.
 - c. Target (native) analyte recoveries for all other CCVs are expected to be within 70-130%.
 - d. It is expected that samples results are only reported when bracketed by passing CCVs unless the recovery failure is high and there are no detections of that analyte in the associated samples.
- 10. **CCB** It is expected that the CCB is analyzed immediately after each CCV to demonstrate the instrument is free from levels of contaminants that would bias results. If method blanks or reagent blanks are analyzed after a CCV instead of a CCB, then it is expected that the CCB limits are used for assessment. The results of the CCBs are expected to be less than one-half the MRL.
- 11. It is expected that the same EIS as those used in samples are added to the initial calibration standards, ICV, CCVs, ICBs, and CCBs at the same concentration used in samples. The calibration standards (initial and continuing) are not extracted like samples. Since there is no matrix effect or extraction performed on these instrument quality control samples, the recoveries of the EIS are expected to be within 50 150%.

VI. Aqueous Sample Extraction

- 1. Extract the entire sample received in the sample container in which it was collected unless the exceptions listed below apply.
 - a. Samples received at extremely high PFAS concentrations may be subsampled. {F}
 - b. If more sample volume is received than what can be extracted through the solid phase extraction (SPE) cartridge, then subsampling is allowed. {F}

Adsorption of target (native) analytes to sample collection container walls is known to occur in aqueous samples. Extract the entire aqueous sample volume. Subsampling of aqueous samples from the sample collection container is discouraged and can result in significant loss of longer-chain PFAS (e.g. carboxylic acids \geq C9, sulfonic acids \geq C7).

2. Spike the sample in the sample bottle it was received in by adding the EIS. Cap, invert and mix. It is expected that the EIS that are spiked into the sample are provided sufficient time to equilibrate in the sample before further processing. This allows the EIS time to disperse proportionally into the liquid phase and solid phase – same as the target (native) analytes and thereby providing a more accurate result. Add the EIS before any extraction, centrifuging, filtering or phase separation takes place.

Biphasic and problematic sample matrices may have to use a different spiking procedure. It is best for the laboratory to contact the client prior to spiking and extraction to determine the best course of action to meet their data quality objectives. In these events, include detail in the narrative as to why spiking into the sample bottle was not possible, what was done instead, and if known, the possible effects on the sample results. **{F}**

Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

- 3. If particulates in the sample have to be removed before using SPE, centrifuge the sample and take the liquid phase through the SPE. Samples should only be centrifuged when the suspended solids content visually appears to be high enough, by chemist inspection, that it would cause the SPE cartridge to clog.
 - The laboratory could consider creating a "percent solids reference sample" that would include the minimum solids the laboratory has tested that would clog the SPE cartridge and use it to compare it to field samples. For reference, the Department of Defense has indicated that samples with percent solids greater than one percent may require centrifuging before performing the SPE procedure. Ideally, the entire sample is extracted, including the suspended solids.
- 4. If aqueous samples with a solid phase are centrifuged, the solid phase of the sample is expected to be a plug at the bottom of the container. 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 the polar elution 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.
- 5. If a total sample concentration is needed and there are significant solids in the sample, the initial spike of EIS into the sample container is sufficient for both phases. There is no need to re-spike the solid phase with EIS if it is being extracted separately.
- 6. Using filters to separate the solid phase from the liquid phase is discouraged <u>unless there is data</u> to demonstrate that the filters used do not result in contamination greater than one-half the MRL.
- 7. In the cases where a filter is used to separate the solid phase from the liquid phase, it is expected that the filter would also be rinsed to remove any potentially adsorbed PFAS. The filtrate is then added to the SPE cartridge during the elution step.
- 8. The data quality objectives from the data user should determine whether the solid phase of the sample has to be extracted or not. Not analyzing the solid phase may lead to a low bias in total sample concentration. Analyzing the liquid phase only would provide a liquid sample concentration result. It is expected that the laboratory would make it clear to the data user whether the reported concentrations are a total or liquid concentration sample result.
- 9. Determine sample volume by marking the sample level on the bottle or by weighing. It is expected that sample volumes would not be measured with a graduated cylinder. Sample volumes are expected to be measured and not assumed by container size.
 - 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 and include this information in the test report.
- 10. Use an appropriate SPE cartridge for the target (native) analytes reported. A weak anion exchange cartridge has been shown to work with the PFAS for which Wisconsin is offering certification.
- 11. 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.
- 12. Bring to a quantitative final volume with the final injection solvent and vortex well.



VII. Non-Aqueous Sample Extraction

- 1. Homogenize the entire solid sample received in the sample container in which it was collected in by stirring the solids with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.
- 2. For tissues (e.g. fish, wildlife), the target tissue (liver, fillet, whole fish) is isolated from the rest of the tissue sample. The target (isolated) tissue is ground and is typically provided to the analyst as a subsample. At the time of sample preparation, the analyst is to further homogenize the subsample by stirring with a clean spatula or other suitable implement. This would help ensure that a representative subsample is taken.
- 3. Spike a portion of the homogenized subsample by adding the EIS directly onto the sample. It is expected that the solvent used to carry the EIS spike onto the sample be allowed to evaporate prior to addition of the extraction solution.
- 4. Extract the PFAS from the non-aqueous samples with an appropriate solution prior to clean-up.
- 5. Use an appropriate clean-up cartridge (i.e. ENVI-Carb, W-AX, ...) to remove the organic analytes extracted from the soil matrix. More than one type of clean-up cartridge can be used.
- 6. Use a clean-up cartridge on the fish tissue extract to eliminate known interferences with PFOS (e.g. bile acids such as taurodeoxycholic acid (TDCA)).
- 7. Ensure that all transfers are quantitative by solvent-rinsing with the elution solvent.
- 8. Bring to a quantitative final volume with the final injection solvent and vortex thoroughly.

VIII. Sample Analysis

- 1. Use an LC/MS/MS that is capable of negative ion ESI, produces unique product ions within retention time windows, and is able to provide a minimum of 10 scans across each peak.
- 2. Perform mass calibration such that the range of masses associated with all precursor and product ions are bracketed for both the primary and confirmation transitions. Documentation is expected to be available to demonstrate that the mass calibration covers this range. Calibrate the mass scale using the calibration analytes and procedure from the instrument manufacturer.
- 3. Analyte identification is performed using retention times, Signal/Noise ratio, Quantitation Parent Ion to Quantitation Daughter Ion (Quantitation Ion Transition), Confirmation Parent Ion to Confirmation Daughter Ion (Confirmation Ion Transition) and the Ion Transition Ratio.
- 4. Calculate sample results for the target (native) analytes that have exact isotopically labeled standards using isotope dilution (recovery correction using the EIS).
- 5. Calculate sample results for the target (native) analytes that do not have exact isotopically labeled standards using an alternate extracted isotopically labeled standard and internal standard quantitation recovery correction (recovery correction using the alternate EIS).
- 6. Use analytical (quantitative) standards containing both branched and linear isomers where commercially available. The analytical branched isomer standards are included in the initial calibration the same as the linear isomer





standards. Branched isomers in samples are quantitated against these analytical branched isomer standards. To calculate the target (native) analyte result, sum the resulting concentrations of all branched and linear isomers that have corresponding analytical standards.

7. Where analytical standards are not available for the branched isomers, use qualitative (technical grade) standards to identify the branched isomer using retention times, transitions, and ion transition ratios. Quantitate target (native) analytes that use qualitative branched isomer standards by integrating the branched and linear isomer peaks and sum the peak areas to get a total area. Calculate the target (native) analyte concentration using the linear isomer.

Do not include branched isomer peaks in the initial calibration when qualitative standards are used, and do not use calibration functions from the qualitative branched isomer standards to quantitate branch isomer concentrations.

- 8. It is expected that the target (native) analytes that have exact labeled analogs would elute within 0.1 min of their analogs. {F}
- 9. Have a written policy on how retention time windows are established.
- 10. It is expected that the method reporting limit (MRL) concentration would not be below the lowest standard concentration in the initial calibration.
- 11. The MDL is expected to be less than the MRL.
- 12. Report sample results and all quality control blank results to the MDL and include the MRL with each result. Qualify results reported between the MDL and MRL as estimated concentrations.

Example 1: MDL = 0.6, MRL = 2, sample result = 0.4. Report as:

Example 2: MDL = 0.6, MRL = 2, sample result = 0.8. Report as:

- 13. The MDL for PFOS and PFOA in non-potable waters are each expected to be no higher than 2 ng/L.
- 14. It is expected that high density polyethylene or polypropylene autosampler vials are single injection use only unless they are immediately recapped.
- 15. It is expected that all sample results are reported from a response that is no higher than the highest response in the initial calibration, except for samples that saturate the instrument. If supplemental EIS is needed to quantitate dilutions, qualify the results that used the supplemental EIS (in this case, true isotope dilution was not achieved).
- 16. It is expected that sample results that saturate the instrument are reported with "E" flags. {F}
- 17. For target (native) analytes, the Signal to Noise (S/N) ratio is expected to be greater than or equal to 3:1 for quantitation ions and confirmation ions. If the S/N is not achieved, it is expected that the peak would not be used in any way and the analyte would be reported as "not detected."



- 18. All analytes that have two transitions are expected to include two transitions ions in the analysis (precursor ion to quantitation ion and precursor ion to confirmation ion). Use the confirmation ion for positive analyte identification. The department has provided a list of target (native) analytes and confirmation ions in section XII, "Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with lons," of this document.
- 19. Assess primary and secondary ion transition ratios. It is expected that recoveries be within 50–150% of the value calculated from the midrange standard in the ICAL on ICAL days or from the beginning CCV on non-ICAL days. {F}

The transition ratio = <u>quantitation ion abundance</u> or <u>confirmation ion abundance</u> or <u>confirmation ion abundance</u> quantitation ion abundance

Either ratio protocol presented above can be used, but it is expected that the protocol is consistently used for all analytes.

When the ion ratio fails, it is expected that the target (native) analytes would still be reported but qualify them as failing the ion ratio. {F} The ion transition ratio can help identify if bias is present. Ratios can be outside of limits due to interferences or the presence of branched isomers that are in the sample but not in the quantitation standards.

- 20. Document the primary and confirmation transitions and the ion transition ratio.
- 21. It is expected that the following transitions are used for quantitation of the following analytes [precursor product] unless a technically justified reason is used and documented:
 - a. PFOA 413-369
 - b. PFOS 499-80
 - c. PFHxS 399-80
 - d. PFBS 299-80
 - e. 4:2 FTS 327-307
 - f. 6:2 FTS 427-407
 - g. 8:2 FTS 527-507
 - h. NEtFOSAA 584-419
 - i. NMeFOSAA 570-419
- 22. The laboratory is expected to determine at what concentration the instrument has carryover at concentrations greater than one-half the MRL. The laboratory is expected to have a documented procedure to bring the instrument back in control after encountering a sample with carryover. PFAS have demonstrated a delayed release in the system.
- 23. Report results in acid form.
- 24. Verify standard purity and ensure that any standards with less than 98% purity are corrected for in the calculations.
- 25. Mass correct salt content in all calibration standards purchased as salts.
- 26. Perform a moisture analysis on solid samples (on a subsample different than that used for extraction) and adjust the final concentration of solid samples for the percent moisture.
- 27. If only the liquid phase of a biphasic sample was extracted, report the results as liquid concentration results instead of total sample concentration results. The lab should report the weight of the solid phase not prepared in this case. This can be detailed in the narrative.



Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

- 28. If the data quality objective is to obtain a total sample concentration and the sample is biphasic, then extract and analyze both phases.
- 29. Do not subtract quality control blank values from sample result values.
- 30. Integrate linear and branched isomers in the samples in the same manner as the standards.
- 31. Include the following elements in the laboratory SOP:
 - a. The extracted internal standards used to calculate the result of each target (native) analyte reported.
 - b. The mass used for the precursor ion for each analyte.
 - c. The mass used for the product quantitation ion for each analyte.
 - d. The mass used for the product confirmation ion for each analyte.
 - e. Instructions for conditioning and elution of the SPE cartridge.
 - f. Indicate which branched isomers are calculated using the linear isomer standard.
- 32. PFOA and PFOS WP PT samples are necessary for aqueous (non-potable water) certification of PFOA and PFOS. To obtain the 36-analyte group for aqueous (non-potable water) or non-aqueous from Wisconsin, analyze a PT with a minimum of 6 PFAS that include PFOA and PFOS. It is expected that 80% of the spiked analytes pass.
- 33. Requirements in NR 149 still apply to this analysis unless otherwise specified in this document.

AS NEW INFORMATION IS PROVIDED BY THE EPA, THIS DOCUMENT WILL BE UPDATED.



IX. Other Considerations

- 1. Screen a separate aliquot of sample received prior to preparation of a quantitative analysis.
- 2. Prior to any quantitative analysis, at least one, if not multiple instrument blanks should be analyzed to assess the system for potential contamination. These instrument blanks should include EIS to enable quantitation of the contamination.
- 3. Evaluate all containers, water, reagents, solvents, materials, SPE cartridges, and equipment as sources of contamination. The lab should be able to demonstrate that these items are not introducing unacceptable positive or negative bias.
- 4. Supplies should be tested on a lot-by-lot basis.
- 5. Avoid contact with glassware.
- 6. Avoid any Teflon including Teflon lined caps.
- 7. Flush water purification system with 3 liters of reagent water before using.
- 8. Use LC PEEK tubing and stainless-steel frits.
- Use polypropylene transfer lines.
- 10. Replace mobile phase after 48 hours of preparation.
- 11. Store standards in the containers they were received in and at the storage conditions recommended by the manufacturer.
- 12. Store solid PFSA standards in a desiccator as they can hydrate over time.
- 13. PFCA standards in methanol solution may undergo esterification to methyl esters. Ideally, purchase PFCA standard solutions in methanol that contain four mole equivalents of NaOH. Use basic methanol (0.3% NH₄OH v/v in methanol) rather than straight methanol for all standard dilutions to avoid this potential problem.
- 14. PFSA standards that are ¹⁸O-labelled may exchange with water and therefore reducing purity.
- 15. To establish retention times, analyze individual standards of each analyte. Analyze a mixed standard of all analytes to confirm their separation and identification.
- 16. Validate each individual standard and labeled standard by analysis to confirm its identity and the absence of significant impurities.
- 17. Certified standards have been known to vary by as much as 20% between vendors. The laboratory should be able to demonstrate that the standards being used are of known and defensible quality.
- 18. Some certified standards are less than 90% pure and often contain impurities that are other PFAS being analyzed.
- 19. EIS should be 96% or greater purity. When the impurity consists of an unlabeled analyte, the EIS can result in a background artifact that is present in every sample, standard, and blank if the EIS is spiked at excessive concentrations.
- 20. Different certified standards can have different isomer content.
- 21. Calibration standards are solvent based only. Matrix matched calibration standards (such as those that include sand or fish tissue) should not be used for isotope dilution methods.
- 22. If the site where samples are being collected is considered a "newer" spill and source apportionment is one of the data quality objectives, ship the samples with dry ice. PFAS transformation can occur if the samples are not frozen.
- 23. Although matrix spikes and matrix spike duplicates (MS/MSDs) are not necessary, analyzing them would help with assessing measurement bias for those target (native) analytes that do not have exact labeled isotope analogs.
- 24. Solid samples should not be air dried unless required by a QAPP.
- 25. Perform solid and fish tissue PT samples.



X. Definitions

Confirmation Ion - one of the fragment ions (product ions) used to help qualitatively confirm presence of the analyte. The product ion chosen is typically one of the remaining ions with high sensitivity and minimum interferences, after the quantitation ion has been chosen. Not all precursor ions provide confirmation ions.

Extraction batch – a set of one to 20 environmental samples of the same certification matrix with a maximum time of 24 hours between the start of processing of the first and last samples in the batch.

Extracted Internal Standards (EIS) - isotopically labeled internal standards that undergo the same extraction and analysis as the other analytes in the sample. The EIS are added to the sample at the very beginning of the procedure before extraction, centrifugation, filtering, or phase separation. Ideally, these are exact isotopically labeled analogs of the target (native) analyte so that identical behavior can be assumed. The recoveries of these standards are used to adjust the target (native) analyte results.

Internal Standard Dilution Quantitation - measurement of native analytes using an alternate analog (surrogate) isotope (one that has the same chemical behavior and is close in retention time to the native analyte) thus providing a close approximation of matrix effects and losses that can occur during the preparatory and analytical procedures. The native analyte concentration is adjusted for the recovery of the alternate analog isotope. An alternate analog isotope is typically used when an exact analog isotope is not available.

Method Detection Limit (MDL) – the minimum measured concentration of a substance that is reported with 99% confidence that the measured concentration is distinguishable from method blank results. The MDL is generated according to the procedure specified in the latest revision of 40 CFR Part 136, Appendix B. The MDL is expected to meet S/N ratio, ion transition ratio, and both quantitation and confirmation ions.

Method Reporting Limit (MRL) – the minimum concentration reported as a quantitative value for a method analyte in a sample following analysis. This defined concentration is expected to be no lower than the concentration of the lowest calibration standard for that analyte and is only used if the recovery in the lowest standard is within 50 - 150%.

Native Analyte - the analyte being tested in the matrix of interest. It is also the analyte for which a result would be reported. It is defined as native to distinguish it from analyte standards added during the test procedure. Native analyte is also referred to as "target analyte" or "reported analyte."

Precursor Ion – the deprotonated molecule of the analyte. The precursor ion is mass selected and fragmented to produce distinctive product ions of smaller m/z.

Product Ion – one of the fragment ions produced from the precursor ion.

Quantitation Ion – one of the fragment ions (product ions) used to quantitate analyte concentrations. The product ion chosen is typically one of high sensitivity and minimum interferences.

True Isotope Dilution Quantitation – measurement of native analytes using an exact analog (surrogate) isotope of the native analyte thus eliminating differences in chemical behavior. The native analyte concentration is adjusted for the recovery of the exact analog isotope that has been included in the preparatory and analytical procedures.



XI. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings – 5.1.19

#	Acronym	Name	CAS#	# carbons	Acronyms (other)
		Carboxylic Acids		l .	
1	PFBA	Perfluorobutanoic acid	375-22-4	4	
2	PFPeA	Perfluoropentanoic acid	2706-90-3	5	
3	PFHxA	Perfluorohexanoic acid	307-24-4	6	
4	PFHpA	Perfluoroheptanoic acid	375-85-9	7	
5	PFOA	Perfluorooctanoic acid	335-67-1	8	
6	PFNA	Perfluorononanoic acid	375-95-1	9	
7	PFDA	Perfluorodecanoic acid	335-76-2	10	
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	11	PFUdA, PFUnDA
9	PFDoA	Perfluorododecanoic acid	307-55-1	12	PFDoDA
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	13	PFTrA, PFTrDA
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	14	PFTeDA
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	16	
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	18	
		Sulfonic Acids	1		
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	4	
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	5	
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	6	
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	7	
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	8	
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	9	
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	10	
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	12 PFDoDS	
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	6	
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	8	
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	10	
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	12	
		Sulfonamides, Sulfomidoacetic acids, Sulfonam	nidoethanols		
26	FOSA	Perfluorooctane sulfonamide	754-91-6 8		PFOSA
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	9 MeFOSA	
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	10	EtFOSA
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	11	MeFOSAA
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	12	EtFOSAA
		<u> </u>			-



Wisconsin PFAS Aqueous (Non-Potable Water) and Non-Aqueous Matrices Method Expectations

31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	11	MeFOSE	
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	12	EtFOSE	
	Replacement Chemicals					
33	HFPO-DA	Hexafluoropropylene oxide dimer acid ¹	13252-13-6	6	PFPrOPrA	
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid ²	919005-14-4	7		
35	9CI-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid ³	756426-58-1	8	F-53B Major	
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid ⁴	763051-92-9	10	F-53B Minor	
	1 - Also referred to as "GenX"					
	2 - Also available as the ammonium salt = ADONA (Ammonium 4,8-dioxa-3H-perfluorononanoate) # 958445-44-8					
	3 - Also available as the potassium salt = Potassium, 9-chlorohexadecafluoro-3-oxanone-1-sulfonate # 73606-19-6					
	4 - Also available as the potassium salt = Potassium, 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate # 83329-89-9					

XII. Wisconsin Laboratory Accreditation Program PFAS Certification Offerings with Ions – 10.27.19

The masses presented are expected to be used, although if other masses are used for the <u>precursor or product ions</u>, the reason is expected to be documented (such as interferences). If the confirmation ion is weak (S/N < 3), it does not have to be used but instrument optimization can increase the S/N.

#	Acronym	Name	CAS#	Precursor Ion Mass	Primary Product Ion Mass	Suggested Confirmation Product Ion Mass		
	Carboxylic Acids							
1	PFBA	Perfluorobutanoic acid	375-22-4	213	169	None		
2	PFPeA	Perfluoropentanoic acid	2706-90-3	263	219	69, None		
3	PFHxA	Perfluorohexanoic acid	307-24-4	313	269	119		
4	PFHpA	Perfluoroheptanoic acid	375-85-9	363	319	169		
5	PFOA	Perfluorooctanoic acid	335-67-1	413	369	169		
6	PFNA	Perfluorononanoic acid	375-95-1	463	419	219		
7	PFDA	Perfluorodecanoic acid	335-76-2	513	469	219		
8	PFUnA	Perfluoroundecanoic acid	2058-94-8	563	519	269		
9	PFDoA	Perfluorododecanoic acid	307-55-1	613	569, 319	569, 369, 319, 269, 169		
10	PFTriA	Perfluorotridecanoic acid	72629-94-8	663	619	369, 319, 269, 169		
11	PFTeA	Perfluorotetradecanoic acid	376-06-7	713	669	369, 319, 269, 169		
12	PFHxDA	Perfluorohexadecanoic acid	67905-19-5	813	769	369, 319, 269, 219, 169		
13	PFODA	Perfluorooctadecanoic acid	16517-11-6	913	869	369, 319, 269, 219, 169		
	Sulfonic Acids							
14	PFBS	Perfluorobutanesulfonic acid	375-73-5	299	80	99		
15	PFPeS	Perfluoropentanesulfonic acid	2706-91-4	349	80	99		
16	PFHxS	Perfluorohexanesulfonic acid	355-46-4	399	80	99		
17	PFHpS	Perfluoroheptanesulfonic acid	375-92-8	449	99, 80	99, 80		
18	PFOS	Perfluorooctanesulfonic acid	1763-23-1	499	80	99		
19	PFNS	Perfluorononanesulfonic acid	68259-12-1	549	80	99		
20	PFDS	Perfluorodecanesulfonic acid	335-77-3	599	99, 80	99, 80		
21	PFDoS	Perfluorododecanesulfonic acid	79780-39-5	699	80	99, 62		
22	4:2 FTSA	4:2 Fluorotelomer sulfonic acid	757124-72-4	327	307	81, 80		
23	6:2 FTSA	6:2 Fluorotelomer sulfonic acid	27619-97-2	427	407	81, 80		
24	8:2 FTSA	8:2 Fluorotelomer sulfonic acid	39108-34-4	527	507	81, 80		
25	10:2 FTSA	10:2 Fluorotelomer sulfonic acid	120226-60-0	627	607	587, 81, 80		



	Sulfonamides, Sulfomidoacetic acids, Sulfonamidoethanols					
26	FOSA	Perfluorooctane sulfonamide	754-91-6	498	78	478, 169, None
27	NMeFOSA	N-Methyl perfluorooctane sulfonamide	31506-32-8	512	169	219
28	NEtFOSA	N-Ethyl perfluorooctane sulfonamide	4151-50-2	526	169	219
29	NMeFOSAA	N-Methyl perfluorooctane sulfonamidoacetic acid	2355-31-9	570	419	512, 483
30	NEtFOSAA	N-Ethyl perfluorooctane sulfonamidoacetic acid	2991-50-6	584	419	526, 483
31	NMeFOSE	N-Methyl perfluorooctane sulfonamidoethanol	24448-09-7	616	59	122, None
32	NEtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol	1691-99-2	630	59	136, None
	Replacement Chemicals					
33	HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	329	285, 169	285, 169, None
34	DONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	377	251	85, None
35	9CI-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	531	351	83, None
36	11Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	631	451	99, None

NOTE: ISO 21675, SW 8327, and Wellington Laboratories provide precursor, product and confirmation ions for many of the extracted internal standards

Mass Source
EPA 537.1
DoD QSM 5.3
Janice Willey
EPA-821-R-11-007, PFAS in Sludge/Biosolids
ISO 21675
SW 8327
Wellington Laboratories
Confirmation mass have multiple sources