



Standard Operating Procedure

Sampling for Per- and Polyfluoroalkyl Substances (PFAS)

Final

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Authors:

Kathryn Makarowski, Water Quality Division Quality Assurance Specialist
Patrick Skibicki, Cleanup, Protection, and Redevelopment Section

Contributors:

Scott Gestring, Cleanup, Protection, and Redevelopment Section
Libby Murray Henrikson, Public Water Supply Monitoring and Reporting Section

Approvals:

/s/ Kathryn Makarowski	8/31/21
Kathryn Makarowski, Water Quality Division Quality Assurance Specialist, DEQ	Date
/s/ Galen Steffens	2/18/2022
Galen Steffens, Water Quality Planning Bureau Chief, DEQ	Date
	2/18/2022
Greg Olsen, Public Water Supply Bureau Chief, DEQ	Date
	2/18/2022
Terri Mavencamp, Contaminated Site Clean-Up Bureau Chief, DEQ	Date

Signatures on file

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Although DEQ follows this SOP in most cases, there may be situations where an alternative methodology, procedure, or process is used to meet specific project objectives. In such cases, the project manager is responsible for documenting deviations from these procedures in the Quality Assurance Project Plans (QAPPs), Sampling and Analysis Plans (SAPs), and end of project summary reports.

Document Revision and Version History

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ACRONYMS

AFFF	Aqueous film-forming foam
COC	Chain-of-custody
DEQ	Montana Department of Environmental Quality
DI	Deionized
DO	Dissolved oxygen
EPA	Environmental Protection Agency
ETFE	Ethylene-tetrafluoro-ethylene
FEP	Fluorinated ethylene propylene
FRB	Field reagent blank
HAZWOPER	Hazardous waste operations and emergency response
HDPE	High density polyethylene
IDW	Investigation derived waste
ITRC	Interstate Technology & Regulatory Council
LDPE	Low density polyethylene
LRB	Laboratory reagent blank
LRL	Lower reporting level
MT-eWQX	Montana EQUIS Water Quality Exchange
NTNC	Non-transient non-community
ORP	Oxidation/reduction potential
PCPs	Personal care products
PCTFE	Polychlorotrifluoroethylene
PE	Polyethylene
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PTFE	Polytetrafluoroethylene
PP	Polypropylene
PPE	Personal protective equipment
ppt	Parts per trillion
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PWSS	Public water supply system
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
SAP	Sampling and analysis plan
SC	Specific conductance
SDS	Safety data sheets
SOP	Standard operating procedure
UV	Ultraviolet
WQPB	Water Quality Planning Bureau

1.0 PURPOSE

This document describes the Montana DEQ standard operating procedure (SOP) for sampling for per- and polyfluoroalkyl substances (PFAS). The document covers cautions, sampling procedures, decontamination procedures, and acceptable materials to be used during PFAS sample collection and handling.

PFAS are a group of man-made chemicals that have been used since the 1940s to produce nonstick cookware, food packaging, protective coatings, water-repellent clothing, stain-resistant fabrics and carpets, cosmetics and personal healthcare products, cleaning products, architectural resins, some firefighting foams, and other products (ITRC, 2018a). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two most studied PFAS and are used in many industrial and consumer products.

Health effects of PFAS being studied include reproduction and development, kidney and liver function, immunological effects, possible carcinogenic effects, and others. In 2016, EPA adopted a lifetime drinking water health advisory of 70 nanograms/liter (ng/L), or parts per trillion (ppt) for the sum of PFOS and PFOA (EPA, 2016a; 2016b). Montana DEQ added PFOS and PFOA to Circular DEQ-7 Numeric Water Quality Standards for groundwater at the EPA Health Advisory level of 70 ppt, individually or combined (DEQ, 2019).

Since 2000, the US has been phasing out the use of these chemicals because of health impact concerns. However, PFAS, including PFOS and PFOA, tend to be extremely persistent, bioaccumulative, highly soluble, and mobile and can be transported long distances (ITRC, 2018a). Therefore, sampling environmental media for PFAS is increasingly common.

Four major sources of PFAS are (ITRC, 2018a):

1. Fire training/fire response sites (e.g., military installations, civilian airports, fire-fighting training sites, airplane crash sites, oil and gas refineries, fire stations, or other places where aqueous film-forming foam (AFFF) may be found),
2. Industrial sites,
3. Landfills, and
4. Wastewater treatment plants or biosolids applications sites.

Other possible sources include textile and paper mills and manufacturing facilities which produce or use various PFAS-containing surfactants, resins, molds, plastics, textiles and leather, or paper products (ITRC, 2018a).

2.0 APPLICABILITY

This SOP describes the collection of samples for analysis of PFAS. Methods for multiple sample media are described, including surface water, benthic sediment, groundwater, drinking water, and biological tissue.

Sampling procedures for surface water and benthic sediment are intended primarily for use in rivers, streams, lakes and reservoirs; sample collection methods for wadeable zones as well as at depths (e.g., from a boat) are discussed.

Groundwater sampling methods are applicable to groundwater monitoring wells and unfiltered private drinking water wells. Public drinking water sampling methods are applicable to raw water source or finished drinking water (i.e., chlorinated or filtered) sampled from the tap.

When collecting biological tissue samples for PFAS analysis, the cautions to prevent contamination (**Section 6.1**) and procedure to decontaminate field equipment (**Section 10.2**) described in this document must be applied, though sample collection procedures are detailed in other documents:

- Collection of fish tissue samples, including whole fish, fillet, and biopsy plugs, should adhere to DEQ's *Fish Tissue Sampling Standard Operating Procedure* (DEQ, 2015).
- Collection of macroinvertebrate tissue samples for chemistry (e.g., organics) analysis is described in DEQ's *Standard Operating Procedure for Sample Collection for Chemistry Analysis: Water, Sediment, and Biological Tissue* (Makarowski, 2019).

Samples for PFAS analysis may be collected at any time of year.

3.0 METHOD SUMMARY

Products containing PFAS are prolific and persistent. PFAS samples are analyzed and screened at very low concentrations (ppt or ng/L) and extra precautions must be taken when collecting and handling PFAS samples to prevent contamination. Many of these cautions, including products and materials to use or avoid, are summarized in **Section 6.0**.

This document details standardized procedures for collecting, handling, and storing samples for PFAS analysis (**Section 10.0**). Detailed procedures are included for ambient surface water, benthic sediment, groundwater, public water supply, and private water supply wells. Biological tissue sampling procedures are detailed in other SOPs but, if collecting fish or other biological tissue for PFAS analysis, many of the same cautions to prevent contamination and ensure data quality detailed in this SOP apply. Recommended data management and quality assurance and quality control measures associated with PFAS sampling efforts are also included.

4.0 DEFINITIONS

Benthic: Of, relating to, or occurring at the bottom of a body of water.

Blank: A sample of analyte free water used to detect sources of contamination during sampling, transport, storage or analysis of environmental samples (EPA, 2009).

Chain of custody form: A custody record which provides a mechanism for tracking physical samples through sample collection, processing and analysis and document the "chain of custody," the date and person responsible for the various sample handling steps associated with each sample (EPA, 2017).

Decontamination: The neutralization or removal of dangerous substances, radioactivity, or germs from an area, object, or person (dictionary.com, 2019).

Duplicate samples: Two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner; used to assess variance of the total method including sampling and analysis (EPA, 2019).

Field blank: An aliquot of reagent water sample of analyte free water poured into the container in the field, preserved and shipped to the laboratory with field samples; used to assess contamination from field conditions during sampling (EPA, 2009).

Holding time: The maximum time allowed between sampling and analysis for results to still be considered valid.

PFAS-free water: Water that does not contain significant concentrations of any compound in a specific PFAS analyte list that is being analyzed at a project-defined level (Michigan DEQ, 2018a).

Rinsate/Equipment Blank: A sample of analyte free water poured over or through decontaminated field sampling equipment prior to the collection of environmental samples; used to assess the adequacy of the decontamination process or to assess contamination from the total sampling, sample preparation and measurement process, when decontaminated sampling equipment is used to collect samples (EPA, 2009).

Sample: A finite part of a statistical population whose properties are studied to gain information about the whole (Merriam-Webster Dictionary, 2019).

Surfactant: A substance which tends to reduce the surface tension of a liquid in which it is dissolved.

5.0 HEALTH AND SAFETY WARNINGS

Field personnel should be aware of job hazards associated with collecting samples that could result in personal injury or loss of life. Contamination prevention, driving, boating, wading, and chemical safety hazards are especially pertinent to this SOP. Consult the Water Quality Protection Bureau (WQP) Job Hazard Analysis form and DEQ's Waterborne Operations Procedure (DEQ, 2016). Personnel must be familiar with health hazards associated with fixing or preserving agents and must always use caution when using them. Safety Data Sheets (SDS) for all chemicals used must be available to sampling team members. Personal protective equipment should be worn or used as needed, including gloves, eye protection, respirators, or fume hoods. If sampling will be performed in an exclusion or contaminant reduction zone of a hazardous waste site, sampling personnel are required to have Hazardous Waste Operations and Emergency Response (HAZWOPER) training.

6.0 CAUTIONS

This section describes measures to prevent possible invalidation of results and equipment damage.

6.1 PREVENTING CONTAMINATION

Since there is limited published research or guidance on how certain materials used by field staff affect PFAS sample results, a conservative approach is recommended to exclude materials known or suspected to contain PFAS (ITRC, 2018b). To minimize the risk of contamination, project managers and field personnel must take precautions when selecting sampling equipment and supplies, field clothing, personal care products, and other items used while sampling PFAS, especially materials that come into direct contact with the sample media.

Recommendations in this SOP pertaining to equipment and supplies to use or avoid during PFAS sampling are compiled from the Interstate Technology & Regulatory Council (ITRC) and several states (ITRC, 2018b; Michigan DEQ, 2018a; Michigan DEQ, 2018b; Michigan DEQ, 2019a; Florida DEP, 2019; Maine DEP, 2019; Massachusetts DEP, 2020; New York State DEC, 2020; New Hampshire DES, 2019). Generally, items listed as “prohibited” are well-documented to contain PFAS or that PFAS are used in their manufacture, “allowable” items have been proven not to be sources of PFAS cross-contamination, and other items may “need additional screening” if there is insufficient information from the manufacturer to verify risk of contamination.

NOTE: Manufacturers can change the chemical composition of products and there is no guarantee that materials considered “allowable” in this SOP will always be PFAS-free (Michigan DEQ, 2019a). Items may be screened and ruled PFAS-free by collecting equipment blanks prior to use; SDS or text fragments such as “perfluoro,” “fluoro,” or “fluorosurfactant” may also help identify products containing PFAS (Michigan DEQ, 2018b).

General

The following basic precautions will help to minimize the risk of contamination during sampling and sample handling:

- Collect samples upstream of any disturbance to the water column or substrate (e.g., upstream of the collector while wading, the boat, or other sources of disturbance).
- Keep sample bottles closed whenever possible and avoid touching the inside of the bottle lid or lip; do not insert tubing or any materials inside the sample bottle.
- Keep dust and fibers out of sample bottles; it is recommended that, before use, sample bottles be transported in clean, PFAS-free containers in a clean environment (e.g., in a designated cooler inside the cab of a clean field vehicle rather than a bag in the truck bed).
- Never place sample container caps directly on the ground during sampling. If sampling staff must set the sample bottle cap down during sample collection and a second member of the sampling crew wearing a fresh pair of powderless nitrile gloves is not available, set the cap on a clean surface (cotton sheeting, HDPE sheeting, triple rinsed cooler lid, etc.).
- Use only the sample containers provided by the laboratory for samples.
- Store and transport sample containers with the lids secured.
- Adequately clean or decontaminate equipment between use at different sites.
- Perform field rinsing of sample containers (e.g., triple-rinse with ambient water if samples are not pre-preserved).
- Drain sample storage coolers frequently so sample containers are not submerged in water.

Nitrile Gloves and Handwashing

Before each sampling event, field personnel must thoroughly wash their hands and put on a new pair of disposable powderless, nitrile gloves (Maine DEQ, 2019; Florida DEP, 2019; Michigan DEQ, 2018b; New York State DEC, 2020; New Hampshire DES, 2019). Gloves should be changed frequently during and between sampling events, including at each sampling location, between collecting routine, duplicate, and blank samples, and before and after field equipment decontamination. Gloves must also be changed any time there is an opportunity for cross-contamination including, but not limited to, handling anything other than approved PFAS sampling equipment, eating or drinking, applying personal care products like sunscreen or bug spray, or retrieving items from vehicles.

Sample Containers

Sample containers should be provided by the laboratory and certified as PFAS-free (Michigan DEQ, 2018b; ITRC, 2018b; Massachusetts DEQ, 2020). Sample container material and volumes should be specified in each project's SAP. Typically, sample containers are made of polypropylene (PP) or high-density polyethylene (HDPE) bottles with unlined PP screw caps (ITRC, 2018b), with 250 ml bottles and 4-ounce jars used for water and sediment samples, respectively. Sample containers with Teflon® lids or lid liners are prohibited. Glass sample containers should be avoided as PFAS has been found to bind to glass especially when the sample is in contact with the glass for a long period of time (e.g., being stored in a glass container) (Michigan DEQ, 2018b; Florida DEP, 2019).

Field Sampling Equipment

Extra precautions should be taken to ensure that any equipment or supplies that come into direct contact with the samples (e.g., samplers, tubing, containers) are PFAS-free. It may not be sufficient to assume that sampling items or materials are PFAS-free based on composition alone; additional screening, such as analyzing an equipment blank before use of new equipment, may be necessary. Precautions should also consider the containers and surfaces used to store equipment and samples (e.g., equipment cases, vehicle upholstery) (Michigan DEQ, 2018b). Tubing should be stored in the original cardboard or bag in which it was shipped and in a clean location free of dust and fibers (Michigan DEQ, 2018b).

Allowable materials include:

- Polypropylene (PP)
- High density polyethylene (HDPE)
- Stainless steel
- Low density polyethylene (LDPE) bags (e.g., Ziploc®) that do not come into direct contact with the sample media
- Silicone
- Acetate
- Natural rubber
- Nylon
- Powderless Nitrile

Prohibited materials include:

- Anything with fluoro in the name.
- Polytetrafluoroethylene (PTFE), including Teflon® and Hostaflon® (e.g., lining of some hoses and tubing, wiring, gears, and some objects that require the sliding action of parts).

- Polyvinylidene fluoride (PVDF), including Kynar® (e.g., tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries).
- Polychlorotrifluoroethylene (PCTFE), including Neoflon® (e.g., valves, seals, gaskets, and food packaging).
- Ethylene-tetrafluoro-ethylene (ETFE), includes Tefzel® (e.g., wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps).
- Fluorinated ethylene propylene (FEP), includes Teflon® FEP and Hostaflon® FEP and may include Neoflon® (e.g., wire and cable insulation and covers, pipe linings, and some labware).
- Low density polyethylene (LDPE) that comes into direct contact with the sample (e.g., containers, bottles, tubing). Note: LDPE does not contain PFAS in the raw material but may contain PFAS cross-contamination from the manufacturing process; LDPE may be used in some cases if it does not come into direct contact with the sample and/or if an equipment blank has confirmed it to be PFAS-free (Michigan DEQ, 2018b).
- Aluminum foil (PFAS are sometimes used as a protective layer on aluminum foil) (Maine DEP, 2019; Michigan DEQ, 2018b; New York State DEC, 2018).
- Pipe thread seal tape.

Decontaminating Field Equipment

Where possible, dedicated or disposable sampling equipment should be used (Maine DEP, 2019). Non-dedicated field equipment (i.e., used at multiple sampling locations) must be decontaminated prior to use at each site using PFAS-free materials (**Section 10.2**) (ITRC, 2018b; Michigan DEQ, 2018b; Maine DEP, 2019; Tetra Tech, 2018; Florida DEP, 2019; New York State DEC, 2020).

Detergents or soaps used during decontamination should be checked to ensure fluoro-surfactants are not listed as ingredients (Florida DEP, 2019). Laboratory-certified PFAS-free water must be used for the final rinse during decontamination of sampling equipment (ITRC, 2018b). Any other water used for decontamination should be checked via field equipment blanks to verify that it does not contain PFAS.

Allowed materials include:

- Alconox®, Liquinox®, or Citranox®
- Cotton cloth or untreated paper towel
- Polyethylene or Polyvinyl chloride (PVC) brush

Prohibited materials include:

- Decon 90®
- PFAS-treated paper towel

Materials that need screening include:

- Water used for rinsing that has not been laboratory-certified PFAS-free
- Recycled paper towels or chemically treated paper towels

PFAS-Free Water

Deionized water used to prepare field blanks and equipment rinsate blanks (**Section 12.2.3**) and for rinsing during decontamination (**Section 10.2**) should be certified by a laboratory as PFAS-free. If lab-certified PFAS-free water is not available, commercially available deionized water in an HDPE container

may be used for decontamination if the water is verified to be PFAS-free through the analysis of one or more blanks (**Section 12.2**). PFAS-free water is defined as water that does not contain significant concentrations of any compound in a specific PFAS analyte list that is being analyzed at a project-defined level (Michigan DEQ, 2018a).

Equipment Storage

Textiles and fabrics treated with PFAS, such as carpets, car interiors, raincoats or GORE-TEX materials, and any other surfaces that repel water or are stain resistant have the potential of being treated with PFAS. Sample containers and equipment that will be used for sampling should not be stored on or come into direct contact with materials suspected to contain PFAS (Michigan DEQ, 2018a). Before use, sample bottles should be stored in a clean, designated PFAS-free container (e.g., cooler with sealed lid) which is kept in a clean environment (e.g., in the cab rather than the bed of a field truck). Use coolers made of PP or PE or other allowable material listed in the Field Sampling Equipment section. Sampling equipment should also be kept in a clean, designated PFAS-free container between uses to minimize incidental contact with substances containing PFAS.

Sample Storage and Preservation

Store PFAS samples in a separate, designated cooler away from sampling containers that may contain PFAS (Massachusetts DEQ, 2020; New Hampshire DES, 2019). Double-bag sample container sets using resealable LDPE bags (i.e., Ziploc®) before storing them in a cooler.

Use regular wet ice to maintain water and sediment samples at or below 6 °C until they are received at the laboratory. Double-bag ice into resealable LDPE storage bags (e.g., Ziploc®) before packing around samples in the cooler. Do not use chemical ice (i.e., blue ice packs) (Michigan DEQ, 2018b; Florida DEP, 2019; Massachusetts DEQ, 2020). Biological tissue samples must be kept frozen until they are delivered to the analytical laboratory.

Field Documentation

Use caution when selecting materials used for field documentation.

Allowed materials include:

- Loose paper (non-waterproof)
- Rite in the Rain® paper and notebooks (paper is preferred; newly purchased products are recommended)
- Aluminum, PP, or Masonite field clipboards
- Pencils
- Ballpoint pens
- Fine or Ultra-Fine point Sharpies®
- Paper sample labels

Prohibited materials include:

- Plastic clipboards, binders, spiral hard cover notebooks
- Post-It® Notes or other adhesive paper products
- Waterproof labels (Massachusetts DEQ, 2020)
- Waterproof field notebooks or paper other than Rite in the Rain®
- Permanent markers (Sharpie® or otherwise) and writing instruments other than those allowed

Field Clothing and Personal Protective Equipment (PPE)

The safety of field personnel is paramount and should not be compromised by fear of PFAS-containing materials. However, effort should be made to avoid clothing and personal protective equipment (PPE) that contain PFAS. Any deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel, should be recorded in field notes. The coatings used on waders are of particular concern and effort should be made to ensure that waders are made from PFAS-free materials before use (Michigan DEQ, 2018b; ITRC, 2018b; Florida DEP, 2019).

Allowed materials include:

- Clothing, footwear, waders, and wet weather gear made of polyurethane, PVC, wax coated fabrics, rubber, neoprene, uncoated Tyvek®, or other PFAS-free materials.
- Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners
- Life jackets made of PE foam and nylon shell fabric

Prohibited materials include:

- Clothing, footwear, and wet weather gear containing Gore-Tex®, coated Tyvek®, or PTFE
- Clothing chemically treated for ultraviolet protection.
- New or unwashed clothing
- Anything applied with or recently washed with fabric softeners or fabric protectors, including UV or stain protection.

Materials that need screening include:

- Gloves other than disposable powderless nitrile gloves (including latex, water- or dirt- resistant leather gloves, or any special gloves required by a hazard assessment program)

Personal Care Products (PCPs)

Personal care products (PCPs) such as sunscreen, insect repellent, cosmetics, shampoos, moisturizers, and cosmetics may contain PFAS and should be avoided or be used with care the day of sampling, especially if not covered by PFAS-free clothing. The following precautions should be taken when dealing with PCPs before sampling (Michigan DEQ, 2018b):

- Do not handle or apply PCPs in the sampling area.
- Do not handle or apply PCPs while wearing PPE that will be present during sampling.
- Move to the staging area and remove PPE if applying personal care products.
- Wash hands thoroughly after the handling or application of PCPs and, when finished, put on a fresh pair of powderless nitrile gloves.

Allowed materials include:

Sunscreen

- Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30
- Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30
- Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Banana Boat® Sport Performance Sunscreen Stick SPF 50
- Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
- Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30
- Coppertone® Sunscreen Stick Kids SPF 55
- L'Oréal® Silky Sheer Face Lotion 50

- Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50
- Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30
- Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
- Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
- Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70
- Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30
- Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+
- Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30
- Alba Organics Natural
- Yes to Cucumbers
- Aubrey Organics
- Jason Natural Sun Block
- Kiss My Face
- Baby-safe sunscreens ('free' or 'natural')

Insect repellent

- OFF® Deep Woods insect repellent
- Sawyer® Permethrin insect repellent
- Avon Skin So Soft Bug Guard
- Jason Natural Quit Bugging Me
- Repel Lemon Eucalyptus
- Herbal Armor
- California Baby Natural Bug Spray
- BabyGanics

Prohibited materials include:

- Do not use cosmetics, moisturizers, hand cream, or other related products the day of sampling.
- Do not use prohibited sunscreen or insect repellent (Massachusetts DEP, 2020).
- Avoid hand sanitizer, especially foaming varieties, as some are known to contain PFAS; if hand sanitizer must be used during the day of sampling, wash hands thoroughly with PFAS-free soap and don new powderless nitrile gloves just prior to sampling.

Food and Beverage

Food and beverage packaging materials may contain PFAS (e.g., fast food wrappers, candy bar wrappers, microwave popcorn bags, pizza boxes). Field personnel should not handle, consume, or otherwise interact with food items in the sampling area. If food or drink consumption is necessary while on-site during sampling, field personnel must move away from the sampling area and remove PPE prior to eating or drinking and must wash hands and put on a fresh pair of powderless nitrile gloves before resuming sampling (Michigan DEQ, 2018b; ITRC, 2018b). Chemical ice (i.e., blue ice) packs should be avoided (Massachusetts DEQ, 2020).

6.2 EQUIPMENT USE AND MAINTENANCE

Proper use, maintenance, and storage of all equipment or instruments associated with procedures described in this SOP is the responsibility of the field personnel using it. Adhere to user manuals, clean and calibrate as needed, inspect prior to use, and store in a secure location when not in use. DEQ may provide SOPs and field guides for specific pieces of equipment. When using DEQ equipment and supplies, report any problems to DEQ staff responsible for inventorying and maintaining these items.

7.0 INTERFERENCES

This section describes components of the procedure or environmental factors that may interfere with the accuracy of the final product.

7.1 SAMPLING LOCATIONS AND SAMPLING FRAMES

Each sampling site needs to be selected and sampled in a manner that minimizes bias caused by the collection process and that best represents the intended environmental conditions at the time of sampling (USGS, 2006). Sampling site locations are selected based on a project's monitoring objectives. Proposed sites are often subject to change pending landowner permission, access, safety, or other site-specific considerations. Latitude and longitude coordinates of proposed sites, as well as the rationale for site selection, are specified in each project's SAP. Always consult with the project manager before changing site locations to ensure that alternative sites align with project objectives. Landowner permission to access sites must be confirmed prior to any data collection on private lands.

In addition to latitude and longitude coordinates, project SAPs may include guidance for determining exact location(s) within a site where to physically collect samples for chemistry analysis. Samples may be collected at multiple locations or depths to capture spatial variability in physical and chemical properties. For example, SAPs may specify:

- Depth(s) where samples will be collected
- Allowable distance from the site coordinates
- Preferred locations in the water column
- Sampling frames, grids, transects or profiles
- Whether samples are composited and, if so, minimum number of sub-samples per composite
- Primary or contingent monitoring well or private water supply well locations

Upon arrival at each site, field personnel should consult the SAP for guidance and use site-specific considerations when selecting exact locations to collect samples.

Examples of site-specific considerations for surface water and benthic sediment samples include:

- Near the latitude/longitude coordinates of the proposed site in the project SAP.
- In the main channel (i.e., the channel with the most flow) for surface waters.
- In a straight reach where water column is well-mixed with laminar, unidirectional flow (near the thalweg, and avoid stagnant pools, eddies, high turbulence, backwater, side channels, tributary inflows, etc.).
- In a place where field personnel can safely access, wade, and stand.
- Upstream from recent disturbances to the substrate or water column.
- Upstream from bridges, other structures, roads, crossings, or other on-site disturbances.
- Where the water is sufficiently deep so water sample bottles can be fully submerged below the water surface and so the mouth of the bottle is elevated away from the bottom substrate.
- Where samples can be collected consistently throughout the period of the study regardless of discharge, stage, or other conditions.

- Avoid mixing zones of tributaries or point source discharges or structures unless the SAP specifically targets these areas.

Examples of site-specific considerations for sampling groundwater monitoring wells include:

- Inspect designated groundwater-monitoring wells to verify that they are in good condition, properly sealed, and not compromised in a way that would allow surface runoff to enter the well either through a loose well cap or broken (cracked) well casing.
- Verify that the well diameter and well depth correspond with the monitoring well log. In some cases, multiple monitoring wells are clustered and may be completed at different depths.
- Collect samples from designated groundwater-monitoring wells, only after following proper purging and sampling procedures identified in a SAP.
- For most sites, and at wells with screens 10 feet long or shorter, the pump intake/inlet should be located at approximately the midsection of the saturated screened interval (DEQ, 2018a).
- For wells with screens longer than 10 feet, the primary flow zones and contaminant concentration intervals should be identified and the pump intake location should be considered in consultation with the DEQ technical contact (DEQ, 2018a).

Examples of site-specific considerations for sampling private drinking water wells include:

- Verify that you are sampling the private potable drinking water well that is targeted for sampling and that it corresponds with the well completion log. Some property locations may have multiple water wells that are used for different purposes (drinking water, irrigation, stock water, etc.)
- Verify if a cistern is present and if it is connected to the well; avoid potential cistern-related impacts when selecting the sampling location.
- Verify if the well has a water treatment system; if so, the sampling location should allow for the collection of raw, untreated well water if possible.

7.2 SAMPLE VOLUME AND SORPTION

Coordinate with the laboratory to determine appropriate sample container volumes for various media. Not all PFAS are hydrophilic and some are volatile; as a result, these chemicals may sorb to sampling equipment and supplies or be lost from samples during sample collection. Until losses from sorption or volatilization are better quantified, sampling efforts should consider whether these losses would affect project objectives and adjust accordingly; to minimize effects from analyte sorption on sample containers, the laboratory must analyze the entire sample including the sample container rinsate (ITRC, 2018b). For soil or sediment, obtaining a representative subsample in the laboratory is critical, so the entire sample should be homogenized in the laboratory prior to subsampling (ITRC, 2018b).

8.0 PERSONNEL QUALIFICATIONS/RESPONSIBILITIES

All field personnel conducting sampling must be familiar with proper sampling techniques, sample handling, safety procedures, and record keeping. New staff and student interns will be provided written SOPs and in-person training at the start of their employment and must be trained and accompanied in the field by experienced staff until competence is demonstrated and verified.

Sampling at public water supply systems (PWSS) will only be conducted by the Certified Operator for that PWSS, in the presence of the Certified Operator, or the representative for that system.

9.0 EQUIPMENT AND SUPPLIES

Due to the widespread use of PFAS, many materials normally used in field and laboratory operations contain PFAS. In addition, many consumer goods brought to a sampling site may contain PFAS that can contaminate samples. Field sampling and laboratory hygiene protocols are critical to ensuring that testing results reflect actual PFAS levels in the analyzed media (EPA, 2020). Refer to **Section 6.0** for additional guidance pertaining to materials that are allowed or prohibited during PFAS sampling.

A separate set of sampling equipment, laboratory sample containers, and sample storage coolers is recommended for PFAS sampling.

Field Equipment Decontamination

- PE or PVC scrub brush for cleaning/scrubbing
- HDPE or PP squeeze or spray bottle with 1% Liquinox soap solution
- HDPE or PP squeeze or spray bottle with PFAS-free DI water
- HDPE or PP bucket for washing pump or other sampling equipment
- Plenty of extra PFAS-free DI water
- Shallow, broad-bottomed stainless-steel pan over which to conduct rinsing and used to capture rinsate during decontamination (e.g., roasting pan or cookie sheet).
- Wide-mouth container for storing soapy wastewater.

NOTE: The SDS indicates that Liquinox should not be released into the environment, and should be prevented from reaching drains, sewers, or waterways (i.e., direct-to-environment pathways). The Alconox company clarifies that Liquinox is “drain-safe,” referring to sink drains and other drains leading to water treatment, and notes that Liquinox is a neutral range pH, phosphate-free, and biodegradable detergent without any added dyes, fragrances, brighteners, or softeners. When planning PFAS sampling projects involving the use of Liquinox to decontaminate equipment, care should be taken to consider appropriateness of capturing soapy wastewater for later disposal down a drain versus on-site disposal on the ground, especially when working near waterways or other sensitive environments.

Surface Water Sampling

- Three 250 ml PP or HDPE sample containers with unlined lids (provided by the laboratory)
- Resealable LDPE bags (e.g., Ziploc®) for bagging sample containers and ice
- Regular ice
- Powderless nitrile gloves
- Designated cooler for PFAS sample storage
- Kemmerer or Van Dorn water sampler (if applicable)
- Extension rod with clamp for laboratory-provided sample bottle (if applicable)
- PFAS-free water for preparing field blanks

Benthic Sediment Sampling

- 4 oz. PP or HDPE sample container with unlined lid (provided by the laboratory)
- Stainless-steel bowl (large mixing bowl)
- Stainless-steel pail (or second large mixing bowl)
- Stainless-steel spoon or ladle
- Stainless-steel Ponar or Ekman grab sampler (if applicable) plus associated rope or cables, winches, etc. used to deploy and retrieve the sampler from the boat.
- Stainless-steel sieve (2 mm, U.S. standard #10)
- Stainless-steel funnel
- Resealable LDPE bags (e.g., Ziploc®) for bagging sample containers and ice.
- Designated cooler for PFAS sample storage
- Regular ice
- Powderless nitrile gloves.
- PFAS-free plastic sheeting (to be used as a clean surface near the sampling location)

Groundwater Sampling

- Three 250 ml PP or HDPE sample containers with unlined lids (provided by the laboratory)
- Powderless nitrile gloves
- Socket set or speed wrench and large flathead screwdriver (for removing well cover)
- Electronic water level tape
- Sonic water level meter (optional)
- Water quality meter(s) (e.g., pH, DO, SC, ORP, temperature, turbidity)
- Water quality meter calibration solutions
- Flow-through cell
- Stainless-steel low-flow sampling pumps, including submersible bladder pumps, and/or a peristaltic pump
- Power source (e.g., 12-volt battery) to operate selected pump
- Battery charger (e.g., 12-volt)
- Extra batteries for water quality meters/equipment
- Stainless-steel or disposable HDPE bailers (ensure check valve material is also PFAS-free)
- HDPE tubing, PE bladders, and Buna-Nitrile O-rings for use with submersible bladder pumps (see manufacturer recommendations for PFAS sampling)
- Silicone (or manufacturer recommended PFAS-free flexible tubing) and HDPE tubing (for use with peristaltic pumps)
- PFAS-free twine (cotton or nylon; MI DEQ, 2020) for lowering and retrieving submersible pumps or bailers into wells
- Utility knife and/or cutting tool (for cutting tubing, twine, etc.)
- 5-gallon bucket with graduated markings
- Watch and calculator (for calculating purge volume) or a cell phone

- PFAS-free plastic sheeting (for placement at sampling area (monitoring well) to provide a clean surface during sampling)
- Resealable LDPE bags (e.g., Ziploc®) for bagging filled sample containers and ice
- Regular ice
- Designated cooler for PFAS sample storage
- Laboratory-provided field reagent blanks
- Replacement well plugs

Public Water System Sampling

- Three 250ml PP or HDPE sample containers with unlined lids (provided by the laboratory)
- Trizma preservative (5 g/L) per sample bottle (1.25 g per 250ml bottle)
- Powderless nitrile gloves.
- Resealable LDPE bags (e.g., Ziploc®) for bagging sample containers and ice.
- Regular ice
- Designated cooler for PFAS sample storage
- Laboratory-provided field reagent blanks

Private Well Sampling

- Three 250ml PP or HDPE sample containers with unlined lids (provided by the laboratory)
- Powderless nitrile gloves
- Water quality meter(s)
- Water quality meter calibration solutions
- Watch and calculator (for calculating purge volume) or a cell phone
- PFAS-free plastic sheeting (for placement at sampling area (hydrant or spigot) to provide a clean surface during sampling)
- Resealable LDPE bags (e.g., Ziploc®) for bagging sample containers and ice
- Regular ice
- Designated cooler for PFAS sample storage
- Laboratory-provided field reagent blanks

10.0 PROCEDURAL STEPS

This section describes procedural steps for collecting samples of various media for PFAS analysis.

NOTE: The selected analytical laboratory may provide PFAS sampling instructions; this SOP should be referenced in conjunction with the laboratory-provided instructions.

10.1 ORDER OF OPERATIONS

Field personnel should be aware of how the order of operations of field activities may affect the quality of samples and should take care not to cross contaminate PFAS samples.

To reduce the risk of cross-contamination, a preferred sampling sequence should be established in which sampling begins in areas expected or known to be least contaminated, then proceeds to areas expected or known to be more contaminated. If analytical results from past sampling events are not available, sampling sequence should begin upgradient from the impacted area or suspected source then proceed to those furthest downgradient (Michigan DEQ, 2018b; Michigan DEQ, 2019a; Maine DEP, 2019).

Collect PFAS samples before collecting other types of samples at a sampling site. Collect samples in order of most sensitive to least sensitive to disturbance. Sample media should generally be collected in the following order: 1) drinking water (e.g., residential wells), 2) surface water, 3) groundwater, then 4) sediment (Michigan DEQ, 2018a).

Collect samples upstream from previous disturbance, especially those collected at flowing-water sites. To minimize disturbance, collect samples from downstream to upstream and, when sampling from boats, collect samples on the upgradient side of the boat (Michigan DEQ, 2018b).

Decontaminate field equipment, as necessary, shortly before it is to be used to collect samples at a site; avoid storing clean equipment for extended periods before it is used for sampling. Change gloves frequently, including between decontamination and sampling and between sampling for non-PFAS contaminants and PFAS (Florida DEP, 2019).

Prior to and during sampling at a site, remove and avoid any clothing, personal care products, food and beverage, or other products (**Section 6.1**) which may introduce risk of PFAS contamination.

10.2 DECONTAMINATING FIELD EQUIPMENT

Field sampling equipment that is used at multiple sampling locations (i.e., non-dedicated equipment such as spoons, bowls, pails, pans, sieves, funnels, dippers, Kemmerer® or Van Dorn® samplers, pumps, water level meters, sediment grab samplers) must be decontaminated prior to use at each site to avoid cross contamination. Equipment must be verified as PFAS-free (Michigan DEQ, 2019a; Florida DEP, 2019). Sample bottles must not have Teflon or other lid liners. Decontamination must be completed using PFAS-free materials and PFAS-free water (ITRC, 2018b; Michigan DEQ, 2018b; Maine DEP, 2019; Tetra Tech, 2018; Florida DEP, 2019):

1. Put on nitrile gloves.
2. Thoroughly rinse the equipment with deionized water over a stainless-steel broad-bottomed pan or pail.
3. Thoroughly wash/scrub all equipment with phosphate-free detergent solution (1%; Alconox or Liquinox detergent) and a PE or PVC brush to remove particulates (Michigan DEQ, 2018b) over the stainless-steel broad-bottomed pan or pail.
4. Rinse all equipment thoroughly with laboratory-certified PFAS-free water over the broad-bottomed stainless-steel pan or pail until agitated rinse water on the equipment produces no more suds. Pour soapy wastewater from the pan wash basin into the wide-mouth storage container to be held for later discard down a drain (see cautions in **Section 6.1 – Decontaminating Field Equipment**).

NOTE: If decontaminated equipment is not to be used immediately, allow to air dry and store in a covered container or resealable plastic bag until use. Rinse equipment with PFAS-free water immediately before use (ITRC, 2018b).

10.3 SURFACE WATER SAMPLE COLLECTION FOR PFAS ANALYSIS

The following protocol is used to collect unfiltered grab samples of surface water for PFAS analysis. Each sample set typically requires three 250 ml sample bottles collected from the same location at the same time; project SAPs should specify the volume required for laboratory analysis.

1. Put on powderless nitrile gloves.
2. Prior to use, clean and decontaminate all equipment using approved decontamination procedures (**Section 10.2**), then rinse all equipment with ambient water at the site.
3. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.
4. Carry the sample bottles to a suitable sampling location (**Section 7.2**).
5. Triple-rinse each bottle and lid: facing upstream (if flowing water), collect a small volume of water in the bottle, replace the lid, and shake gently. Discard the rinse water downstream from the sampling location. Repeat two more times to triple-rinse.
6. Collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml:
 - For stream/river sites, face upstream and submerge each sample bottle so the mouth is below the water surface but elevated above the substrate, and fill each bottle.
 - Only when site conditions require (e.g., unsafe flow conditions prevent direct access to the water's edge), clamp the sampling container onto the end of a clean extension rod that is made of PFAS-free material and has been decontaminated before use at each site, and submerge to fill each bottle (ITRC, 2018b).
 - For surface sampling at lake/reservoir sites, field personnel grasp each sample bottle in their hand and slowly submerge it vertically down through the water column to the depth where their elbow is at the water surface (Egge, *et al.*, 2018), then bring the full bottle back up to the surface.
 - For deep-water sampling at lake/reservoir sites, secure a Kemmerer or Van Dorn water sampler to a sturdy line, open the rubber end seal(s) and secure into place using the cables provided, attach the metal weight called a "messenger" to the line, hold the messenger above the water surface and lower the water sampler to the desired depth. Once the desired depth is reached, hold in place and drop the "messenger" down the line to trigger the rubber end seals to release and snap shut. Raise the water sampler to the surface and use the drain valves to release water to perform rinsing and to fill each bottle.

NOTE: Use only sample collection equipment (e.g., extension rods, submersible devices) made of materials such as stainless steel, glass, HDPE, PVC, silicone, or aluminum, that has been identified as being PFAS-free (Michigan DEQ, 2018b).

NOTE: The sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface (ITRC, 2018b).

NOTE: Sample collection directly into the laboratory-provided sample bottles is strongly recommended. If transfer bottles are necessary for surface water sample collection (e.g., to composite grab samples collected from multiple depths, or when using an extension pole sampler that does not allow the sample bottle itself to be clamped to it) the transfer bottles must be made of the same PFAS-free material as the laboratory-provided sample containers and must be decontaminated before every use (Florida DEP, 2019; Michigan DEQ, 2018b).

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5 g/L) for buffering and free chlorine removal for drinking water samples only.

NOTE: Samples collected for PFAS analysis do not have to be headspace free (Maine DEP, 2019).

7. Securely tighten the lid of each sample bottle.
8. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).
9. Record the samples on the Site Visit/Chain-of-Custody form (**Appendix A**).
10. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

10.4 BENTHIC SEDIMENT SAMPLE COLLECTION FOR PFAS ANALYSIS

The sample collection strategy for benthic sediment focuses on obtaining samples of fine-grained surficial sediments from natural depositional zones during low-flow conditions and on compositing samples from several depositional zones; this strategy is designed to yield a representative sample of fine-grained surficial bed sediments (USGS, 1994). Benthic sediment samples should be collected during low flow/baseflow conditions to provide maximum direct access to the stream bed and to minimize seasonal streamflow variability (USGS, 1994).

At each sampling site, sub-samples of benthic sediment are collected from at least five depositional zones and sub-samples are composited into a single sample unless otherwise noted in the project SAP. For organic contaminants, benthic sediment samples should be sieved and the sand and silt-clay fraction smaller than 2.0 mm should be saved for analysis (USGS, 1994). Benthic sediment sampling for organic constituents is conducted using all stainless-steel equipment.

The following protocol is used to collect benthic sediment samples for PFAS analysis. Each sediment sample typically requires a 4 oz. sample jar; project SAPs should specify the volume required for laboratory analysis.

1. Put on powderless nitrile gloves.
2. Prior to use, clean and decontaminate all equipment using approved decontamination procedures (**Section 10.2**), then rinse all equipment with ambient water at the site.
3. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.
4. Identify five depositional zones containing fine benthic sediment within the sampling frame.

5. Collect a sub-sample of fine-grained benthic sediment at each of the five depositional zones:
 - When sampling stream/river sites, use a stainless-steel spoon to scoop benthic sediments directly from the channel bottom into a stainless-steel bowl or pail. Target depths less than 0.5 meters deep as a safety measure and to minimize loss (wash-out) of surficial fine sediments as the spoon is drawn up through the water column (USFWS, 2010). Be sure to collect sediment from the channel bed, not the banks.
 - When sampling lake/reservoir sites, navigate via boat to the sampling location and deploy an anchor. Secure a stainless-steel Ponar or Ekman grab sampler to a sturdy line, secure the jaws of the grab sampler open using the spring-loaded pins provided, and steadily lower the grab sampler until it comes in contact with the substrate, triggering closure. Gradually raise the instrument to the boat, detach it from the rope, and place it on a stainless-steel broad, shallow pan. Open the instrument (e.g., remove the stainless-steel screens from the Ponar or pull the Ekman open) and inspect the sample to determine if it is acceptable. Pour overlying water off the sample and use a stainless-steel spoon to scoop sediment from the grab sampler into a stainless-steel bowl or pail.

NOTE: If sub-sampling will take substantial time before the final composite sample is produced (e.g., especially when navigating by boat from place to place), store the bowl or pail of sediments between sub-samplings in a cooler containing regular ice to maintain a cool temperature.

6. After all sub-samples are collected in the stainless-steel bowl or pail, use the stainless-steel spoon to homogenize the composited material by stirring to a uniform consistency and color (ORSANCO, 2002; USEPA, 2003; Puget Sound Water Quality Action Team, 1997; Washington DOE, 2014).
7. Use a stainless-steel spoon to scoop and pass the entire volume of the homogenized sample from the initial stainless-steel bowl or pail through a stainless-steel sieve (U.S. standard #10) into a second stainless-steel bowl or pail to remove particles larger than 2 mm (ORSANCO, 2002).
8. Use a stainless-steel spoon (and stainless-steel funnel if needed) to transfer sieved sediments into a 4 oz. HDPE or PP jar with unlined screw cap.

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5 g/L) for buffering and free chlorine removal for drinking water samples only.

9. Securely tighten the lid of the sample jar.
10. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).
11. Record the samples on the Site Visit/Chain-of-Custody form (**Appendix A**).
12. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at ≤ 6 °C, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

10.5 GROUNDWATER SAMPLE COLLECTION FOR PFAS ANALYSIS

The following protocols are used to collect groundwater samples for PFAS analysis. Each sample set typically requires three 250 ml sample bottles collected from the same location at the same time; project SAPs should specify the volume required for laboratory analysis.

Groundwater Monitoring Wells

See site selection considerations in **Section 7.1**. Access to both the property and the monitoring well must be secured prior to initiating field activities. Some above ground well monuments may be locked. Research the status of the well prior to initiating field work and secure a key if necessary. If it is not possible to drive to the monitoring well location identified for sampling, all sampling equipment must be carried by hand to the monitoring well.

Water Level Measurements in Groundwater Monitoring Wells

Measure and record depth to groundwater (i.e., water level) and total well depth prior to purging or sampling a groundwater monitoring well. Water level measurements should be taken in such a way to minimize disturbance of the water surface and limit the potential to disturb sediments that may have accumulated in the bottom of the monitoring well.

Steps for collecting water level measurements from a groundwater monitoring well include:

1. Put on powderless nitrile gloves.
2. Remove the steel flush mount cover or above ground well monument cover (if present).

NOTE: A socket-set or speed wrench will be needed to remove flush mount cover bolts (typically 3/8th inch or ½ inch). A large flathead screwdriver is also helpful for prying up and removing the steel well monument cover after the bolts have been removed.

3. Verify well diameter to make sure it is consistent with monitoring well log documentation.
4. Remove the monitoring well cap or well plug.

NOTE: Some well plugs may be locked, but generally can be removed and put back on without removing the lock. If field personnel do not have a key and cannot re-insert the well plug, install a new well plug or cap. Do not leave the well open.

NOTE: If the well is under vacuum or pressure when the well plug/cap is removed, allow the well to equilibrate to atmospheric pressure.

5. Measure depth to groundwater with an electronic water level tape or meter:
 - If using an electronic water level tape, turn it on and test it to make sure it is working properly, then lower the probe slowly until the alarm sounds indicating water. Multiple measurements may be needed to verify that the water level has equilibrated.
 - Sonic water level meters sit above the well and use a sonic (sound) wave to collect the water level (there is not a probe to lower into the well).

NOTE: Make sure that the electronic water level tape or meter has been decontaminated (see **Section 10.2**) prior to lowering into a well.

NOTE: Measure from an established measuring point, typically the north end of the well casing or from a black survey mark if present.

6. Record the final depth to groundwater measurement to nearest 0.01 foot in field book and/or field form (**Appendix B**).
7. Slowly lower the water level probe to the bottom of the well to verify the well depth. This is necessary to determine if the well has filled with sediment and to confirm it matches the well log. Record the total well depth in the field book and/or field form (**Appendix B**).

NOTE: If using a sonic water level meter, it may not be possible to record the well depth. An electronic water level tape may also be needed to measure the total well depth.

NOTE: A well that has accumulated sediment in the bottom may affect pump or tubing placement depth. Significant sediment accumulation may also affect sample integrity if a cloudy, silty water sample is collected. A well that has accumulated significant sediment may need to be redeveloped prior to sampling.

8. Slowly remove the water level probe from the well and decontaminate (see **Section 10.2**) it before using it to take measurements in another well.

Groundwater Sample Collection

There are numerous methods and pump types for collecting groundwater samples from groundwater monitoring wells. Four common sampling methods are described below, including 1) low flow sampling using a bladder pump, 2) low flow sampling using a submersible pump, 3) low flow sampling using a peristaltic pump, and 4) groundwater sampling using a disposable bailer. Groundwater samples should be collected in accordance with an approved QAPP and SAP. Additional groundwater sampling information can be found in DEQ's *Groundwater Sampling Guidance* (DEQ, 2018a).

NOTE: Follow manufacturers' instructions for equipment service, maintenance, and operation.

NOTE: All field water quality meters should be calibrated daily prior to use.

NOTE: Before a well is sampled, stagnant water in the well casing must be removed or purged to obtain a representative groundwater sample. Purge water should be disposed of in accordance with DEQ's purge water flow chart (**Appendix C**).

NOTE: Record all relevant field sampling information in a field book and/or field form (**Appendix B**).

NOTE: Samples collected for PFAS analysis do not have to be headspace free (Maine DEP, 2019).

A. Bladder Pump

1. Put on powderless nitrile gloves.
2. Insert new PE bladder into the submersible bladder pump.
3. Determine sampling depth (based on recorded water level measurements, well screened interval, and in accordance with SAP) and cut HDPE tubing to the appropriate lengths needed to reach the target sampling depth.

NOTE: Cut two equal lengths of HDPE tubing, one for the air line and one for the water return line.

4. Attach new HDPE tubing to the bladder pump.
5. Attach safety cable (nylon or cotton line) to the bladder pump to ensure that it does not fall to the bottom of the well in the event the HDPE tubing comes loose.

NOTE: Do not use PTFE (e.g., Teflon®) tubing or bladders.

6. Slowly lower the bladder pump into the well to the target sampling depth (typically the midsection of the saturated screened interval unless otherwise stated in the SAP (**See Section 7.1**)).
7. Slowly lower the water level probe into the well.
8. Attach the HDPE tubing (discharge line) to the flow-through cell using new non PFAS-containing tubing or connector.

9. Ensure that the flow-through cell discharge line discharges to a 5-gallon bucket with graduated markings for the purpose of estimating purge volume.
10. Turn on the bladder pump, verify that it is operating correctly, and adjust purge rate as needed (typically set at 100 to 500 mL/min).

NOTE: The purge rate should be low enough so as not to dewater the well. Water level measurements should be taken throughout well purging to verify that the well is not being dewatered. If the well is being dewatered, reduce the purge rate.

NOTE: If the well pumps dry, allow the well to recover, then reduce the flow rate and continue purging.

11. Purge the well until the field parameters have stabilized and in accordance with the SAP. Readings should be taken every three to five minutes while pumping. Well stabilization parameters may include pH, specific conductance (SC), dissolved oxygen (DO), turbidity, oxidation/reduction potential (ORP), and temperature. Once the well has stabilized, it is ready to sample.

12. **NOTE:** Detach the HDPE tubing (discharge line) from flow through cell prior to sampling. Collect the water samples directly from the HDPE tubing.

13. Put on new powderless nitrile gloves.

14. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.

15. Triple rinse each bottle and lid with groundwater from the well that is being sampled.

16. Collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5g/L) for buffering and free chlorine removal for drinking water samples only.

17. Securely tighten the lid of each sample bottle.

18. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).

19. Record the samples on the Chain-of-Custody form.

20. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

21. Remove the water level probe, bladder pump, and tubing from the well.

22. Put the well cap or plug back on the well.

23. Secure the well monument.

NOTE: Properly dispose of liquid investigation derived waste (IDW) in accordance with DEQ guidance (**Appendix C**). General trash and PPE should be placed in plastic garbage bags and disposed of at a licensed solid waste disposal facility.

B. Submersible Pump

1. Put on powderless nitrile gloves.
2. Determine sampling depth (based on recorded water level measurements, well screened interval, and in accordance with SAP) and cut HDPE tubing (discharge line) to the appropriate length needed to reach the target sampling depth.
3. Attach tubing to submersible pump.

NOTE: Do not use PTFE (e.g., Teflon®) tubing or materials. Verify that the selected pump and tubing do not contain PFAS.

4. Slowly lower the submersible pump into the well to the target sampling depth (typically the midsection of the saturated screened interval unless otherwise stated in the SAP (**See Section 7.1**)).
5. Slowly lower the water level probe into the well.
6. Attach the HDPE tubing (discharge line) to the flow-through cell using new non PFAS-containing tubing or connector.
7. Ensure that the flow-through cell discharge line discharges to a 5-gallon bucket with graduated markings for the purpose of estimating purge volume.
8. Turn on the submersible pump and verify that it is operating correctly. Adjust the purge rate as needed (typically set at 100 to 500 mL/min).

NOTE: The purge rate should be low enough so as not to dewater the well. Water level measurements should be taken throughout well purging to verify that the well is not being dewatered. If the well is being dewatered, reduce the purge rate.

NOTE: If the well pumps dry, allow the well to recover, then reduce the flow rate and continue purging.

9. Purge the well until the identified field parameters have stabilized and in accordance with the SAP. Readings should be taken every three to five minutes while pumping. Field well stabilization parameters may include pH, SC, DO, turbidity, ORP, and temperature. Once the well has stabilized, it is ready to sample.

NOTE: Detach the HDPE tubing (discharge line) from flow-through cell prior to sampling. Collect water samples directly from the HDPE tubing.

10. Put on new powderless nitrile gloves.
11. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.
12. Triple rinse each bottle and lid with groundwater from the well that is being sampled.
13. Collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5g/L) for buffering and free chlorine removal for drinking water samples only.

14. Securely tighten the lid of each sample bottle.
15. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).
16. Record the samples on the Chain-of-Custody form.

17. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

18. Remove the water level probe, submersible pump, and tubing from the well.
19. Put the well cap or plug back on the well.
20. Secure the well monument.

NOTE: Properly dispose of liquid investigation derived waste (IDW) in accordance with DEQ guidance (**Appendix C**). General trash and PPE should be placed in plastic garbage bags and disposed of at a licensed solid waste disposal facility.

C. Peristaltic Pump

1. Put on powderless nitrile gloves.
2. Cut a short length (approximately 4 – 6 inches) of new flexible silicone (or other manufacturer recommended PFAS-free tubing) and install it onto the peristaltic pump head.
3. Determine sampling depth (based on recorded water level measurements, well screened interval, and in accordance with SAP) and cut HDPE tubing to the appropriate length needed to reach the target sampling depth. In addition, cut an appropriate length (4 - 6 feet) of HDPE tubing to be used for the water discharge line.

NOTE: Peristaltic pumps will only work for wells where the static water level is less than approximately 28 feet.

4. Attach both lengths of HDPE tubing to the silicone or other selected tubing.

NOTE: Do not use PTFE (e.g., Teflon®) tubing.

5. Slowly lower HDPE tubing into the well to the target sampling depth (typically the midsection of the saturated screened interval unless otherwise stated in the SAP (**See Section 7.1**)).
6. Slowly lower the water level probe into the well.
7. Attach the HDPE tubing (discharge line) to the flow-through cell using new non PFAS-containing tubing or connector.
8. Ensure that the flow-through cell discharge line discharges to a 5-gallon bucket with graduated markings for the purpose of estimating purge volume. Turn on the peristaltic pump and verify that it is operating correctly. Adjust flow rate as needed (typically set at 100 to 500 mL/min).

NOTE: The purge rate should be low enough so as not to dewater the well. Water level measurements should be taken throughout well purging to verify that the well is not being dewatered. If the well is being dewatered, reduce the purge rate.

NOTE: If the well pumps dry, allow the well to recover, then reduce the flow rate and continue purging.

9. Purge the well until the identified field parameters have stabilized and in accordance with the SAP. Readings should be taken every three to five minutes while pumping. Field well stabilization parameters may include pH, SC, DO, turbidity, ORP, and temperature. Once the well has stabilized, it is ready to sample.

10. **NOTE:** Detach the HDPE tubing (discharge line) from flow-through cell prior to sampling. Collect water samples directly from the HDPE tubing.
11. Put on new powderless nitrile gloves.
21. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.
22. Triple rinse each bottle and lid with groundwater from the well that is being sampled.
23. Collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5g/L) for buffering and free chlorine removal for drinking water samples only.

24. Securely tighten the lid of each sample bottle.
25. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).
26. Record the samples on the Chain-of-Custody form.
27. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

28. Remove the water level probe and HDPE tubing from the well.
29. Put the well cap or plug back on the well.
30. Secure the well monument.

NOTE: Properly dispose of liquid investigation derived waste (IDW) in accordance with DEQ guidance (**Appendix C**). General trash and PPE should be placed in plastic garbage bags and disposed of at a licensed solid waste disposal facility.

D. Disposable Bailers

NOTE: Do not use PTFE (e.g., Teflon®) bailers or bailers with PTFE check valves.

1. Put on powderless nitrile gloves.
2. Determine sampling depth (based on recorded water level measurements, well screened interval, and in accordance with SAP).
3. Attach nylon or cotton line to the top of the disposable bailer (HDPE or PFAS free material) and attach the other end to your wrist.

NOTE: Leave the bailer in its plastic sleeve until the line is attached and you are ready to begin bailing.

4. Slowly lower the bailer down the well until you hear it hit water; continue to lower the bailer until it has filled with water.
5. Gently retrieve the filled bailer from the well.

NOTE: Avoid lowering the bailer to the bottom of the well and disturbing sediment that may have accumulated in the well.

NOTE: Do not allow the bailer to free-fall down the well casing; this can also increase sample turbidity.

6. Empty the water from the bailer into a 5-gallon bucket with graduated markings and slowly lower the bailer down the well again. Repeat this process until well purging is complete (in accordance with the SAP) and field parameters have stabilized. Readings should be taken every three to five minutes during well purging. Well stabilization parameters may include pH, SC, DO, turbidity, ORP, and temperature. Once the well has been purged and stabilized, wait several minutes prior to collecting water samples with a bailer to allow for stirred up sediment to settle out.

NOTE: Do not allow the bailer to contact the ground surface anything that might cross-contaminate the sample.

NOTE: Do not allow the bailer or twine to contact the sample bottles.

NOTE: If the well bails dry, allow the well to recover prior to continuing with well purging.

NOTE: Check knots frequently to ensure that the bailer will not come loose and fall to the bottom of the well. If it does, it must be removed. A treble hook connected to fishing line is a good option for removing the bailer.

7. Put on new powderless nitrile gloves.
8. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®; if using labels other than those provided by the laboratory, adhere a label to each sample bottle.
9. Triple rinse each bottle and lid with groundwater from the well that is being sampled.
10. Slowly pour water from the bailer to collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

NOTE: USEPA Method 537.1, Version 1.0 and USEPA Method 537, Version 1.1 requires chemical preservation using Trizma (5g/L) for buffering and free chlorine removal for drinking water samples only.

11. Securely tighten the lid of each sample bottle.
12. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).
13. Record the samples on the Chain-of-Custody form.
14. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

15. Remove the bailer from the well.
16. Put the well cap or plug back on the well.
17. Secure the well monument.

NOTE: Properly dispose of liquid investigation derived waste (IDW) in accordance with DEQ guidance (**Appendix C**). General trash and PPE should be placed in plastic garbage bags and disposed of at a licensed solid waste disposal facility.

10.6 PUBLIC DRINKING WATER SAMPLE COLLECTION FOR PFAS ANALYSIS

The following protocol can be used to collect samples from potable raw water sources or finished (i.e., chlorinated or treated) drinking water for PFAS analysis. When sampling from raw water sources, collection from entry points to the distribution system of public water systems is the preferred sampling location. For groundwater systems, the sampling location will be the designated raw water entry point(s). For groundwater PWSS that have multiple wells, the common header should be used after isolating the other active wells from the entry point. For surface water systems, the sampling location will be before treatment or filtration. Only the certified operator may sample for a community or non-transient non-community (NTNC) PWSS.

Each sample set typically requires three 250 ml sample bottles collected from the same location at the same time, plus a field reagent blank (**Section 12.2**); project SAPs should specify the volume required for laboratory analysis.

1. Put on powderless nitrile gloves.
2. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®.

NOTE: 250 ml sample bottles for drinking water samples must be pre-preserved with 1.25 g Trizma (5 g/L), a preservative reagent which functions as a buffer and removes free chlorine in chlorinated finished waters (Shoemaker and Tettenhorst, 2018; Shoemaker, *et al.*, 2009).

3. Carry the sample bottles to a designated sampling location:
 - If sampling from a system with multiple groundwater wells, the operator will need to isolate the additional wells and may sample at the common header if possible. The sampling location for the designated well should be at the pump house or the first entry point prior to any treatment or storage. Do not sample from the pressure tank(s) discharge faucet. If the system has storage or a cistern, a raw water sampling location should be selected before raw water enters these facilities. A frost-free hydrant may be used for raw water sampling, but the system must be sure the hydrant is located before a cistern or treatment.
 - If sampling from a drinking water faucet from a location in the distribution, remove the faucet aerator, run water for 5 to 15 minutes, slow water flow to the size of a pencil to avoid splashing.
 - Distribution sample site selection can be from a business, school or residential home.
4. From the flowing system, collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: To prevent the Trizma preservative from flushing out of the sample bottle, do not triple rinse the sample bottle before collection and do not allow the sample bottle to overflow.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

NOTE: Samples collected for PFAS analysis do not have to be headspace free (Maine DEP, 2019).

5. Securely tighten the lid of each sample bottle.
6. Gently invert each bottle five times to mix the preservative into the sample.
7. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).

- When sampling finished drinking water a field reagent blank (FRB) is required and will be provided in the sampling kit; other project SAPs may also specify a requirement for FRBs. Prepare the FRB by carefully pouring the provided PFAS-free water and preservative into the provided FRB sample bottle, labelling it, and storing it with the other samples (**Section 12.2**). Include the FRB on the Chain-of-Custody (COC) form as a separate sample.
8. Record the samples on the Chain-of-Custody form.
 9. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.
10. **NOTE: DO NOT ALLOW SAMPLES TO FREEZE!**

10.7 PRIVATE WATER SUPPLY WELLS

Water samples collected from private water supply wells should be collected in accordance with an approved QAPP and SAP. Additional sampling information can be found in DEQ's *Groundwater Sampling Guidance* (DEQ, 2018a).

Wells are purged using the homeowner's dedicated submersible pump to remove stagnant well water prior to sample collection. Considerations for purging:

- Generally, three well volumes will be purged (DEQ, 2018a; USOSMRE, 2012). Obtain a copy of the well log from Montana's Groundwater Information Center (GWIC) or the well owner to determine the well depth, diameter, and estimated static water level and calculate the amount of water per well volume for purging (DEQ, 2018).
- If it is not possible to calculate the well volume (due to lack of well information), purging multiple well volumes would cause water disposal problems or time constraints, or the homeowner does not wish to purge the estimated well volumes (e.g., due to low yielding aquifer or general concerns about water usage), it is recommended that the well be purged for a minimum of 15 minutes to help ensure the water samples are representative of the groundwater source.
- For domestic wells that are consistently used (i.e., daily), extensive purging prior to sampling may not be needed. If the well has been used for normal domestic purposes within the previous 24 hours, this will perform most of the required purging. Instead, water should be run at 1-2 gallons per minute (gpm) for approximately 15 minutes prior to taking a sample to clear the plumbing system and allow for a freshwater sample to be taken (USOSMRE, 2012).
- In residences, determine the size of the holding tank. If it is not possible to collect a sample before the holding tank, then the volume of the holding tank should be purged before sample acquisition, if feasible (DEQ, 2018a).
- During purging, water quality parameters (e.g., pH, SC, DO, turbidity, ORP, and temperature) should be measured and recorded to further ensure that the water samples are representative of the groundwater source.

NOTE: Do not open the wellhead to obtain a static water level measurement. Using a water level tape or probe to measure depth-to-water in a drinking water well is not recommended because they can easily get entangled with the discharge piping or electrical wiring for the submersible pump (DEQ, 2018a).

Static water level information can be obtained from a well log or the well/property owner. There is also potential that the well could become contaminated by bacteria.

The following protocol can be used for collecting water samples from private water supply wells for PFAS analysis:

1. Identify the sampling location:
 - Samples should be collected from as close to the well influent as possible (DEQ, 2018a).
 - Samples should be collected before any type of treatment system, if possible (DEQ, 2018a).
 - Primary consideration should be given to the kitchen faucet (i.e., most likely to represent the water consumed by the resident(s)), but only if the water is unfiltered. Acceptable alternate water sample locations may include other common points-of-use within the home, such as a bathroom sink.
 - If the homeowner is concerned about the sampler being inside their home (i.e., Covid-19, safety, etc.), identify an outside faucet.
 - Collect water from the cold, not the hot, water line (USOSMRE, 2012).
 - Collect samples directly from spigots or faucets (DEQ, 2018a).
 - Avoid sampling through hoses or tubing, or utility sprayers (EGLE, 2020).
 - Sample before the water is stored in a holding (pressure) tank.
2. Put on powderless nitrile gloves.
3. Calculate the well volume.
4. Carry sample bottles to the sample area.
5. Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®.
6. Purge the well (generally 3 well volumes) using the cold water line. Well stabilization water quality parameters (pH, SC, DO, turbidity, ORP, and temperature) should be measured and recorded during well purging to further ensure that the water samples are representative of the groundwater source. Once the well has been purged and the field parameters have stabilized, the well is ready to sample. Record the final well stabilization results on the field form (**Appendix B**).

After flushing the cold water line, decrease the water flow to a small stream for sampling.

NOTE: If sampling a faucet with an aerator (typically a small mesh screen on the end of the faucet), carefully remove the aerator prior to sampling. To prevent faucet damage, wrap a flexible piece of rubber around the aerator before using a pliers to remove it.

7. Put on new powderless nitrile gloves.
8. Triple rinse each bottle and lid using water from the well that is being sampled.
9. Collect the three samples that comprise each sample set, filling each sample bottle to the shoulder or line that denotes the target volume of 250 ml.

NOTE: Do not touch the inside of the cap or around the upper edges of the bottle.

10. Securely tighten the lid of each sample bottle.
11. Collect or prepare any QC samples required by the project SAP (**Section 12.2**).

12. Record the samples on the Chain-of-Custody form.
13. Double-bag the sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory within required holding times as described in **Section 10.8**.

NOTE: DO NOT ALLOW SAMPLES TO FREEZE!

10.8 SAMPLE STORAGE, HOLDING TIME, AND DELIVERY

The thermal preservation, shipping, storage, and holding times contained in EPA Method 537, Version 1.1 should be used for all sample media except biota until additional information is available (ITRC, 2018b). Biological tissue samples must be frozen as soon as is practical and must remain frozen until being processed by the analytical laboratory. From the time of collection, PFAS samples must be stored on regular ice at or below 6°C until delivery to the lab. PFAS samples must not exceed 10°C during the first 48 hours after collection then must be held at or below 6°C until extraction but must not be frozen (Shoemaker, *et al.*, 2009). To chill samples, do not use chemical (blue) ice; use regular ice that is bagged in resealable LDPE bags (e.g., Ziploc®).

Store samples in a designated, clean cooler made of PFAS-free material. Double-bag the sets of sample bottles from each site together using resealable LDPE bags (e.g., Ziploc®). Store sample containers upright in the cooler.

Chain-of-custody of the samples must be maintained from the time of collection in the field to the time of receipt by the analytical laboratory. Signatures, date, and time must be recorded each time the samples are relinquished and received on the site visit forms.

Whenever possible, samples should be delivered to the analytical laboratory within 48 hours of sample collection. The analytical method specifies that water samples should be extracted within 14 days (Shoemaker, *et al.*, 2009) and, therefore, there is flexibility to deliver samples within a 14-day holding time if a 48-hour holding time is unachievable. At the laboratory, extracts must be stored at room temperature and analyzed within 28 days after extraction (Shoemaker, *et al.*, 2009; EPA, 2020).

Hand delivery to the lab is preferred. If samples must be shipped to the lab:

- Ship samples same-day or overnight
- Accompany samples with proper documentation (e.g., chain-of-custody forms)
- Ensure samples will arrive at the lab during business hours (e.g., Monday through Friday, not weekends or holidays) and within holding times specified in the project SAP
- Specify on chain-of-custody forms which shipping method was used (i.e., United States Postal Service, FedEx, UPS)
- Fill out shipping labels carefully and completely to minimize risk of loss
- Place custody seals over opening of cooler or shipping container and secure with tape
- Use package tracking to confirm delivery status
- Notify the lab to expect a delivery
- Ship samples according to packaging instructions provided by the laboratory
- Keep samples cold using plentiful bagged ice and minimize the volume of empty cooler space.

Upon receipt, the lab must confirm that the proper holding temperature was maintained during sample storage and transport.

11.0 DATA AND RECORDS MANAGEMENT

All hardcopy documentation of the data, such as completed field forms and laboratory EDDs, are stored and archived by DEQ. Data is reviewed, validated, and stored according to DEQ's quality assurance and data management systems for environmental data operations.

11.1 SITE DOCUMENTATION, FIELD FORMS AND CHAIN-OF-CUSTODY

All sites where samples are collected must be geo-located (including station name, latitude and longitude, Datum NAD83) and documented on a field form. **Appendix A and B** contains examples (i.e., Site Visit Form for surface water and sediment samples, and Well Sampling Data Sheet for groundwater samples collected from monitoring wells and water supply wells). Alternate field forms may be used instead if they are deemed acceptable by the project manager and database manager.

All samples submitted to an analytical laboratory must be entered onto a Chain-of-Custody Form. Whenever samples are relinquished from one person to another, chain-of-custody signatures must be completed to maintain a record of who possesses and is responsible for the samples at all times, from the time of collection by field personnel to the time samples are received at the analytical laboratory. Chain-of-custody signatures must be accompanied by the date and time when samples were relinquished and received, and the sample delivery method used (e.g., delivery by hand, United States Postal Service, FedEx, UPS).

11.2 SAMPLE LABELING

Each sample container must be labeled with the following information:

- Waterbody name or well location
- Date collected
- Personnel who collected the sample
- Indication if sample was filtered or not filtered
- Preservation method(s)

Fill out sample labels using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®.

11.3 DATABASE COMPATIBILITY

Most PFAS data collected by or for DEQ will be stored in the Montana EQuIS Water Quality Exchange (MT-eWQX) database. Data submitted to MT-eWQX is sent to the national Water Quality Portal (NWQMC, EPA and USGS, 2019). Procedural and formatting requirements (DEQ, 2018b) must be followed to submit Electronic Data Deliverables (EDDs) to MT-eWQX. If other databases are to be used, they should be specified in project SAPs and metadata and formatting requirements for those data systems must be followed. Data validation procedures required by each program for each database being used to store data must be followed.

12.0 QUALITY ASSURANCE AND QUALITY CONTROL

12.1 LABORATORY ANALYTICAL METHODS

Typically, EPA Method 537.1 is used to analyze finished drinking water samples for 18 PFAS compounds (Shoemaker and Tettenhorst, 2018) and, for surface water samples, groundwater, and benthic sediment samples, a modified version of EPA Method 537.1 is used which includes 28 PFAS compounds. Additional methods and compounds may become available through time for PFAS as analytical capabilities advance.

NOTE: Project SAPs will include a table with analytical methods, container, volume, holding times and reporting limits for each sample media being collected. Although USEPA Method 537, Version 1.1 (Shoemaker, *et al.*, 2009) was developed for the analysis of finished drinking water samples only, the method is often used as a guide for thermal preservation (holding temperature) and holding times for other sample media.

12.2 QUALITY CONTROL SAMPLES

Field quality control (QC) samples can be used to evaluate the field equipment and supplies used during sample collection as well as assess the possibility of cross-contamination during sampling, transport, and storage of samples (Michigan DEQ, 2018a). Collection and analysis of QC samples are important for PFAS analyses because of very low detection limits and widespread commercial use (historical and current) of PFAS containing products (ITRC, 2018b). QC samples include but are not limited to field reagent blanks, field duplicates, and equipment rinsate blanks.

This section describes various types of QC samples that are commonly prepared during PFAS sampling activities. Project SAPs USEPA Method 537, Version 1.1 (Shoemaker and Tettenhorst, 2018) contains method quality control requirements, including requirements for field duplicates and field reagent blanks. Refer to project SAPs for specific guidance regarding the type, quantity, frequency, and locations of QC sample collection.

When preparing QC samples:

- New nitrile gloves must be worn.
- Follow sample documentation and labeling protocols used during routine sampling (**Section 11**) except use a separate Site Visit Form and a unique Site Visit Code for each type of QC samples (i.e., duplicates and blanks).
- Submit QC samples to the laboratory at the same time routine samples are submitted.

Field Reagent Blanks (Field Blanks)

USEPA Method 537, Version 1.1 (Shoemaker, *et al.*, 2009) and USEPA Method 537.1, Version 1.0 (Shoemaker and Tettenhorst, 2018) state that a field reagent blank (FRB) must be handled along with each sample set. An FRB, also referred to as field blank, is an aliquot of reagent water that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

Project SAPs should specify the frequency and timing at which FRB samples are required; for most projects, one FRB must accompany each batch of samples submitted to the analytical laboratory. Due to the added expense associated with analyzing FRBs, the lab or a project SAP may require that a FRB always be submitted with each sampling set but may be selectively analyzed only if PFAS are detected at or above the lower reporting level (LRL) in any of the field samples in the batch that the FRB is associated with.

To prepare the FRB, field personnel must put on a new pair of powderless nitrile gloves, fill out the FRB sample label using pencil, ballpoint pen, or fine or ultra-fine point Sharpie®, and pour the PFAS-free water provided by the lab for the FRB into the FRB sample bottle. If the sample set includes drinking water samples being preserved with Trizma, the FRB must also contain Trizma. Double-bag the FRB sample bottles using resealable LDPE bags (e.g., Ziploc®), store them in a cooler on regular ice at $\leq 6^{\circ}\text{C}$, and deliver them to the laboratory alongside the other samples in the sample set within required holding times as described in **Section 10.8**.

The following considerations apply to FRBs:

- Field blanks must be prepared using laboratory-grade PFAS-free deionized water (provided by the analytical laboratory).
- Field blank samples must be prepared while in the field.
- New nitrile gloves must be worn while preparing field blanks.
- The same batch of preservative must be used for the FRBs as for the field samples.
- Field blank samples are often collected at the end of a sampling trip following completion of activities at the final sampling site.
- Field blank sample preparation should follow the same procedures (**Section 10**) used in rinsing, collecting, preserving, handling, and storing routine samples except laboratory-certified PFAS-free water is used rather than ambient water.
- Follow sample documentation and labelling protocols used during routine sampling (**Section 11**). Include FRB samples on the chain-of-custody form as a separate sample.
- Submit field blank samples to the laboratory at the same time as routine samples.

If the method analyte(s) found in the field sample is present in the FRB at a concentration greater than 1/3 the MRL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed. Reagent water used for FRBs must be initially analyzed for method analytes as a laboratory reagent blank (LRB) to ensure samples are not being discarded due to contaminated reagent water or sample bottles rather than contamination during sampling.

Field Duplicates

Field duplicate samples are two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures (including decontamination, rinsing, collecting, preserving, handling, and storage). Field duplicates are used to evaluate precision associated with sample collection, preservation, and storage, as well as laboratory procedures. USEPA Method 537, Version 1.1 (Shoemaker, *et al.*, 2009) and USEPA Method 537.1, Version 1.0 (Shoemaker and Tettenhorst, 2018) recommends extracting and analyzing at least one field duplicate with each extraction batch (20 samples or less). In most cases, DEQ recommends that field

duplicate samples be collected during each sampling event at a rate of 10% of the total number of routine samples collected.

Equipment Rinse Blanks

Equipment rinse blanks are samples of analyte-free water that has been poured over or through field sampling equipment after the equipment has been decontaminated to ensure that decontamination was properly and adequately performed.

- If non-disposable equipment is used during sample collection, at least one equipment rinse blank will be collected and submitted to the laboratory for PFAS analysis (ITRC, 2018b; Florida DEP, 2019; Maine DEP, 2019; Michigan DEQ, 2018a; Tetra Tech, 2018).
- The equipment rinse blank will be collected into laboratory supplied containers (three 250 ml polypropylene sample bottles per sample set).

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APPENDIX A – SITE VISIT FORM FOR SURFACE WATER AND SEDIMENT

The following is an example Site Visit Form; DEQ modifies this form to meet project-specific needs.

Place Site Visit Label Here	Site Visit Form	Project ID: _____
Date: _____ Time: _____ Personnel: _____		
Waterbody: _____ Location: _____		
Station ID: _____ HUC: _____ County: _____ AUID: _____		
Latitude: _____ Longitude: _____ Elevation: _____ ft m		
Field Duplicate to <input type="checkbox"/> Field Blank <input type="checkbox"/> Trip Blank <input type="checkbox"/> Field Equipment Blank <input type="checkbox"/>		
Samples Collected	Sample ID	Sample Collection Information/Preservation
Water <input type="checkbox"/>		GRAB EWI BACT
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Analysis:		0.45µ Filtered HNO ₃ H ₂ SO ₄ H ₃ PO ₄ HCL Ice Frozen
Sediment <input type="checkbox"/>		SED-1
Analysis:		Preserved: None Other:
Benthic Chl-a <input type="checkbox"/>		Sample Method: C=Core H=Hoop T=Template N=None
Composite at Lab <input type="checkbox"/> AFDW <input type="checkbox"/> Visual Est. <50 mg/m2 <input type="checkbox"/>		Sample Location: R=Right C=Center L=Left
Transect: A - B - C - D - E - F - G - H - I - J - K -		
Phytoplankton Chl-a <input type="checkbox"/>		D1 Filtered: _____ mL D2 Filtered: _____ mL
Phytoplankton CNP <input type="checkbox"/>		CN Filtered: _____ mL P Filtered: _____ mL
Algae <input type="checkbox"/>		PERI-1-MOD PERI-1 OTHER:
Macroinvertebrates <input type="checkbox"/>		MAC-R-500 OTHER: _____ # of Jars: _____
Field Measurements	Time: _____ am pm	Field Assessments
Water Temp: _____ °C °F	Air Temp: _____ °C °F	Photos <input type="checkbox"/> Aquatic Plant Visual Assessment <input type="checkbox"/> SAM <input type="checkbox"/>
Bar. Pressure: _____ mm/Hg	SC: _____ uS/cm	Aquatic Plant Tracking <input type="checkbox"/> Rosgen <input type="checkbox"/> NRCS <input type="checkbox"/>
pH: _____ DO: _____ mg/L	Turbidity: _____ NTU	EMAP <input type="checkbox"/> Total Discharge <input type="checkbox"/> Channel X-Section <input type="checkbox"/>
Turbidity: Clear <input type="checkbox"/> Slight <input type="checkbox"/> Turbid <input type="checkbox"/> Opaque <input type="checkbox"/>		Wetland <input type="checkbox"/> Bacteria <input type="checkbox"/> Other:
Flow: _____ ft ³ /sec (Dry Bed <input type="checkbox"/> Stranded Pools <input type="checkbox"/>)		Only Transect F <input type="checkbox"/> Total Site Length _____ m
Meter <input type="checkbox"/> Meter-Auto <input type="checkbox"/> Float <input type="checkbox"/> Gage <input type="checkbox"/> Visual Est. <input type="checkbox"/>		Transect Length _____ m Average Wetted Width _____ m
Data Loggers	Temperature <input type="checkbox"/> YSI <input type="checkbox"/> MiniDOT <input type="checkbox"/> EC <input type="checkbox"/> TruTrack <input type="checkbox"/> AquaRod <input type="checkbox"/> Weather Station <input type="checkbox"/>	
	Deployed <input type="checkbox"/> Cleaned/Checked <input type="checkbox"/> Retrieved <input type="checkbox"/>	
Chemistry Lab Information		
Lab Samples Submitted to: _____	Account #: _____	Term Contract Number: _____
Invoice Contact: _____		
Contact Name & Phone: _____		EDD <input checked="" type="checkbox"/> Format: MT-eWQX Compatible
1) Relinquished By & Date/Time: _____	1) Shipped By: _____ Hand <input type="checkbox"/> FedEx/UPS <input type="checkbox"/> USPS <input type="checkbox"/>	1) Received By & Date/Time: _____
2) Relinquished By & Date/Time: _____	2) Shipped By: _____ Hand <input type="checkbox"/> FedEx/UPS <input type="checkbox"/> USPS <input type="checkbox"/>	2) Received By & Date/Time: _____
Lab Use Only - Delivery Temperature: Wet Ice _____ °C Dry Ice _____ °C		
Rev. 3/9/2017		

Place Site Visit
Label Here

Site Visit Form Continued

Field Meter Calibration

pH Meter:	Manufacturer & Model:	Date of Last Calibration:
	Comments:	
Multiparameter Meter:	Manufacturer & Model:	
	Date of SC Calibration:	DO calibrated at site visit <input type="checkbox"/>
	Comments:	

Site Visit Comments

Data Logger Notes:

Time data logger removed:

Time data logger returned:

Data logger cleaned

Data logger downloaded

Data logger re-launched

Photos:

#

#

#

#

#

#

APPENDIX B – WELL SAMPLING DATA SHEET

Well Sampling Data Sheet

Site Visit Information

Site Name: _____ Date: _____
 Site Address: _____ Time: _____
 Site/Facility ID: _____ Personnel: _____
 Well ID: _____ Well Type (*circle*): Monitoring / Private
 Well Latitude: _____ Screen Interval: _____
 Well Longitude: _____ Measuring Point: _____
 Analysis: _____ Preservative: _____

Site Characterization

Well Box (*circle*): Above ground / Flush mounted Measureable Product: Y / N
 Product Sheen: Y / N Silty: Y / N
 Odor: Y / N Clear: Y / N

Weather Conditions

Wind Direction & Speed: _____ Surface Conditions (*circle*): wet / dry / snow cover
 Precipitation: None Other (describe): _____ Temperature: _____ °C °F
 Overcast / Clear

Well Information

Total Depth of Well (feet): _____ One Well Volume of Water (gallons/lineal foot in well)
 Depth to Water (feet): Initial: _____ Final: _____ 6" well: 1.5 x height of water column
 Height of Water Column (feet): _____ 4" well: 0.66 x height of water column
 Well Casing Diameter (inch): _____ 2" well: 0.17 x height of water column
 One Well Volume (gallons): _____ 0.75" well: 0.023 x height of water column
 Total Purge Volume (gallons): _____ Purge Rate: _____
 Pump intake depth: _____

Purge Method (*circle*): Disposable bailer Peristaltic pump Submersible Pump Bladder Pump

Sample Collection Method (*circle*): Disposable bailer Peristaltic pump Submersible Pump Bladder Pump

Field Parameters:

Time	Purge Volume (gal)	Water Level	SC (mS) ± 3%	DO (ppm) ± 10%	pH ± 0.1	Temp (°C) ± 0.5° c	ORP ± 10 mV	Turbidity (NTU) ± 10%

Final Sample Time: _____
 Field Instrument(s): _____ Date Calibrated: _____

Comments:

Decontamination (*circle all that apply*): Liquinox Methanol DI water

APPENDIX C – PURGE WATER DISPOSAL GUIDANCE



DISPOSAL OF UNTREATED PURGE WATER FROM MONITORING WELLS 7/27/2015

