



GROUNDWATER PFAS SAMPLING

Guidance

Introduction

This sampling guidance discusses the processes and acceptable items and materials that should be used when sampling groundwater monitoring wells for per- and polyfluoroalkyl substances (PFAS). The guidance primarily addresses the collection of representative water samples from the subsurface saturated zone. In addition, this guidance will be used to support the sampling objectives and procedures based on the Quality Assurance Project Plan (QAPP) developed prior to sampling activities. This guidance assumes staff has basic familiarity with and/or understanding of basic groundwater sampling procedures.

NOTE: Review the **General PFAS Sampling Guidance** document prior to reviewing this guidance document.

This sampling guidance may be varied or changed as required, depending on site conditions, equipment limitations, or limitations imposed by the procedure. The ultimate procedures used should be documented in the final report.

The MDEQ intends to update the information contained within this Groundwater PFAS Sampling Guidance document as new information becomes available. The user of this Groundwater PFAS Sampling Guidance is encouraged to visit the Michigan PFAS Action Response Team (MPART) webpage (www.michigan.gov/PFASresponse) to access the most current version of this document.

PFAS has been detected in groundwater in Michigan at concentrations over 810,000 parts per trillion (ppt). Many commercial laboratories have extremely low PFAS detection limits of about 1 ppt. Therefore, there is a high potential of false positives if proper procedures are not followed during sample collection.

This Groundwater PFAS Sampling Guidance discusses the collection of groundwater samples and methods to prevent cross-contamination that can occur from:

- Field clothing and personal protective equipment (PPE)
- Personal care products (PCPs)
- Food Packaging
- Sampling equipment
- Equipment decontamination
- Filtering of surface water
- Sample collection and handling
- Sample shipment

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1. Potential Sources for PFAS Cross-Contamination

Potential sources for PFAS cross-contamination include items and materials used within the sampling environment, such as sampling equipment, field clothing, personal protective equipment (PPE), sun and biological protection products, personal hygiene, personal care products (PCPs), and food packaging. A detailed discussion about potential sources for PFAS cross-contamination is included in the **General PFAS Sampling Guidance**, which should be reviewed before reading this document. However, a high-level summary is presented in this guidance.

All of the items and materials discussed in each of the MDEQ's PFAS Sampling Guidance Documents are divided into three major groups:

- Prohibited (●) identifies items and materials that should not be used when sampling. It is well documented that they contain PFAS or that PFAS are used in their manufacture.
- Allowable (■) identifies items and materials that have been proven not to be sources of PFAS cross contamination and are considered acceptable for sampling.
- Needs Screening (▲) identifies items and materials that have the potential for PFAS cross-contamination due to a lack of scientific data or statements from manufacturers to prove otherwise. These items and materials are further sub-divided into two categories:
 - **Category 1:** Items and materials that will come in direct contact with the sample. These should not be used when sampling unless they are known to be PFAS-free, by collecting an equipment blank sample prior to use.
 - **Category 2:** Items and materials that will not come in direct contact with the sample. These should be avoided, if possible, unless they are known to be PFAS-free by collecting an equipment blank sample prior to use.

Please note that at this time no published research is available that documents the use of various materials and effect on sample results. Therefore, a conservative approach is recommended, and the guidance is based on the collection of multiple environmental samples at various PFAS sites. Sampling staff should take practical and appropriate precautions to avoid items that are likely to contain PFAS at the sampling site as well as avoid specific items during the sampling event.

A general overview of PFAS contamination sources during sampling can be found in **Section 4.2** of the **General PFAS Sampling Guidance**. Any items or materials utilized that are not identified in this guidance or not discussed in **Section 4.2** should be evaluated as described in **Section 4.2.1 of the General PFAS Sampling Guidance**.

Sampling staff should take practical and appropriate precautions to avoid items that are likely to contain PFAS at the sampling site as well as avoid specific items during the sampling event (see below).

1.1 Field Clothing and PPE

Materials, field clothing, and equipment screening should be performed during the QAPP development or the planning phase of sampling programs. The screening should be performed on all items and materials that are expected to come into contact with the samples and are defined as **Category 1**. Due to the extensive use of PFAS in many industries and

products, PPE may contain PFAS. During a PFAS investigation, PPE containing PFAS should be avoided to prevent cross-contamination.

As with any field mobilization, it is the responsibility of all personnel to be aware of the physical, chemical, and biological hazards associated with a particular site. Personal safety is paramount. The safety of staff should not be compromised by fear of PFAS-containing items or materials without any scientific basis. Any deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel, should be recorded in field notes and discussed in the final report.

Any additional field clothing and/or PPE items that might be required for groundwater sampling and not discussed in this sampling guidance should be evaluated as described in **Sections 4.2.1** and **4.2.2** of the **General PFAS Sampling Guidance**.

NOTE: Special attention should be given to clothing that has been advertised as having waterproof, water-repellant, or dirt and/or stain characteristics. They are likely to have PFAS in their manufacturing.

Field sampling during wet weather (e.g., rainfall and snow) should be conducted while wearing the proper field clothing.

- Dust and fibers must not be allowed to collect on field clothing or PPE.
- Do not use clothing that has been advertised as waterproof, dirt and/or stain repellent that has not been verified to be made of PFAS-free materials.
- Use powderless nitrile gloves
- Only use clothing/PPE that has been verified to be made of PFAS-free materials.
- ▲ Latex gloves should be screened before use.

Powderless nitrile gloves should be changed frequently any time there is an opportunity for cross-contamination. See **Section 5** of this guidance for additional glove instructions.

1.2 Personal Care Products (PCPs)

A number of sampling guidance documents recommend that personal hygiene and PCPs (e.g., cosmetics, shampoo, sunscreens, dental floss, etc.) not be used prior to and on the day(s) of sampling because the presence of PFAS in these products has been documented (OECD, 2002, Fujii, 2013, Borg and Ivarsson, 2017). However, if the MDEQ's sampling SOPs are followed, these items should not come into contact with the sampling equipment or the sample being collected. As of the date of this sampling guidance, cross-contamination of samples due to the use of PCPs has not been documented during the collection of thousands of samples. However, field personnel should be aware of the potential of cross-contamination of the sampling equipment or actual samples would come into contact with these products. The following precautions should be taken when dealing with personal hygiene or PCPs before sampling:

- 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 becomes necessary.
- Wash hands thoroughly after the handling or application of PCPs and, when finished, put on a fresh pair of powderless nitrile gloves.

1.3 Food Packaging

PFAS has been used by the paper industry as a special protective coating against grease, oil, and water for paper and paperboards, including food packaging since the late 1950s (Trier et al., 2018). PFAS application for food packaging includes paper products that come into contact with food such as paper plates, food containers, bags, and wraps (OECD, 2002). Pre-wrapped food or snacks (such as candy bars, microwave popcorn, etc.) must not be in the sampling and staging areas during sampling due to PFAS contamination of the packaging. When staff requires a break to eat or drink, they should remove their gloves, coveralls, and any other PPE, if worn, in the staging area and move to the designated area for food and beverage consumption. When finished, staff should wash their hands and put on a fresh pair of powderless nitrile gloves at the staging area, before returning to the sampling area.

- Do not handle, consume, or otherwise interact with pre-wrapped food or snacks, carry-out food, fast food, or other food items while on-site during sampling.
- Move to the staging area and remove PPE prior to leaving the sampling and staging areas if consuming food on site becomes necessary.

2. Groundwater Sampling Equipment

Do not use any equipment that contains any known fluoropolymers including, but not limited to:

- Do not use polytetrafluoroethylene (PTFE), that includes the trademark Teflon® and Hostaflon®, which can be found in many items, including but not limited to ball check-valves on certain bailers, the lining of some hoses and tubing, some wiring, certain kinds of gears, lubricant, and some objects that require the sliding action of parts.
- Do not use Polyvinylidene fluoride (PVDF), that includes the trademark Kynar®, which can be found in many items, including but not limited to tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries.
- Do not use Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon®, which can be found in many items, including but not limited to valves, seals, gaskets, and food packaging.
- Do not use Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®, which can be found in many items, including but not limited to wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps.
- Do not use Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP, and may also include Neoflon®, which can be found in many items, including but not limited to wire and cable insulation and covers, pipe linings, and some labware.
- Do not use low density polyethylene (LDPE) for any items that will come into **direct contact** with the sample media. LDPE can be found in many items, including but not limited to containers and bottles, plastic bags, and tubing.
 - ▲ **However**, LDPE may be used if an equipment blank has confirmed it to be PFAS-free. LDPE does not contain PFAS in the raw material but may contain PFAS cross-contamination from the manufacturing process.
- LDPE bags (e.g., Ziploc®) that **do not** come into direct contact with the sample media and do not introduce cross-contamination with samples may be used.

NOTE: Manufacturers can change the chemical composition of any product. As a result, all materials that will come into direct contact with the sample media (defined as Category 1) should be tested to confirm they are “PFAS-free,” i.e. will not contaminate samples at detectable levels. **There is no guarantee that materials in the “Allowable” category will always be PFAS-free.**

- Use items and materials that are either made of high-density polyethylene (HDPE), polypropylene, silicone, polyvinyl chloride(PVC), or acetate.
- Keep tubing in the original cardboard or bag in which it was shipped.
- Store tubing in a clean location free of dust and fibers.
- Use nylon line, cotton string, or other PFAS-free material when raising and lowering bailers.
- When using bladder pumps, use pumps made of stainless steel with polyethylene bladders.
- Glass bottles or containers may be used if they are known to be PFAS-free, however, PFAS have been found to adsorb 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). If the sample comes into direct contact with the glass for a short period of time (e.g. using a glass container to collect the sample, then transferring the sample to a non-glass sample bottle), the adsorption is minimal.
- ▲ In many submersible pumps, the O-Rings do not come into contact with the groundwater sample, and in this case, the O-Rings should be treated as internal pump components. The O-Rings present a low possibility of cross-contamination. Equipment blanks should be collected simulating actual field sampling procedures and not for individual pump components.

Field rental equipment companies offer “PFAS-free” bladder pumps; however, caution is advised, and an equipment rinsate blank is required. Rental equipment should be treated as being contaminated and only used after proper decontamination has been done.

Staff should follow the **MDEQ PFAS Sampling Quick Reference Field Guide** at the end of this document for approved and prohibited items for documenting and sampling groundwater for PFAS.

3. Equipment Decontamination

It is customary with groundwater sampling that the equipment is decontaminated before the sampling event. If the previous user of the equipment is not known, and it is unclear how the equipment was handled—especially rental equipment—decontaminate the equipment before sampling. Any **Category 1** non-dedicated sampling equipment (equipment used for more than one location) must be verified as PFAS free before use.

For non-dedicated **Category 1** sampling equipment, the following materials and procedures must be used for decontamination:

- Do not use Decon 90®.
- Laboratory supplied PFAS-free deionized water is preferred for decontamination.
- Alconox®, Liquinox®, and Citranox® can be used for equipment decontamination.
- Sampling equipment can be scrubbed using a polyethylene or Polyvinyl chloride (PVC) brush to remove particulates.
- Decontamination procedures should include triple rinsing with PFAS-free water.
- Commercially available deionized water in an HDPE container may be used for decontamination if the water is verified to be PFAS-free.
- ▲ Municipal drinking water may be used for decontamination purposes if it is known to be PFAS-free.

NOTE: All samples must be collected using PFAS-free High-Density Polyethylene (HDPE), glass, or polypropylene bottles provided by the laboratory, with Teflon®-free caps.

4. Groundwater Sample Collection Methods

4.1 Method summary

Before a well is sampled, stagnant water in the well casing must be removed or purged in order to obtain a representative groundwater sample. The instruments most commonly used for purging by the MDEQ are bailers, submersible pumps, and inertia pumps. MDEQ staff may oversee purging and sampling conducted by noncontact gas bladder pumps, suction-lift pumps, and other pumps, but the MDEQ does not typically use these pumps. The MDEQ typically samples groundwater using bailers, or by low-flow methods utilizing a peristaltic pump.

Prior to purging, the water level in the well and the total depth of the well should be measured, using the procedures described in the QAPP to determine the volume of water in the well. When using a bailer, a minimum of three well volumes should be purged, unless the well runs dry. When using low-flow methods, purging should continue until the selected indicator parameters have stabilized (see **Section 4.7 Low-Flow Methods**).

Once purging is completed or the groundwater in the well recovers, the groundwater pH, temperature, specific conductance, and turbidity should be measured using the procedures described in the QAPP. After the correct sample containers have been prepared, sampling may proceed. Care should be taken when choosing the sampling device, since some devices may affect the integrity of the sample.

NOTE: Purging is mandatory in all cases where there is the potential for the data to be used for enforcement purposes.

Purging and sampling should occur in a progression from the least contaminated well to the most contaminated well, if this information is known; disposable equipment should be used for each well or equipment must be decontaminated prior to use and between each well.

4.2 Calculations

If it is necessary to calculate the volume of water in the well, use the following equation:

$$\text{Well volume (gallons)} = \pi r^2 h (\text{cf})$$

where:

r = radius of monitoring well (feet)

h = height of the water column (feet) (This may be determined by subtracting the depth to the water from the total depth of the well as measured from the same reference point.)

cf = conversion factor (gallons/linear foot) = 7.48 gal/ft³

If the diameter of the monitoring well is known, standard conversion factors can be applied to simplify the equation above. Monitoring well diameters are typically two, three, four, or six inches.

Well volumes, in gallons per linear foot, for these common monitoring well diameters are as follows:

Well diameter	2-inches	3-inches	4-inches	6-inches
Volume (gal/ft.)	0.1632	0.3672	0.6528	1.4688

The volume of water in the well can then be calculated by multiplying the appropriate value of gallons per linear foot by the height of the water column in feet (h).

This well volume is typically tripled to determine the volume to be purged.

4.3 Preparation Procedures

The success of any sampling effort depends on thorough preparation. The following steps should be followed in preparing for groundwater well sampling:

1. Determine the extent of the sampling effort, the sampling methods to be used, and the types and quantities of equipment and supplies needed.
2. Develop and implement a site-specific sampling plan.
3. Prepare the schedule and coordinate with the laboratory, staff, contractors, and the regulated facility, as appropriate.
4. Obtain necessary sampling and monitoring equipment and supplies.
5. Decontaminate or preclean equipment, and ensure that it is in working order.
6. Perform a general site survey prior to site entry in accordance with the site-specific Health and Safety Plan (HASP), if appropriate.
7. Identify all monitoring wells to be sampled.
8. Start at the least contaminated well, if known.
9. Powderless nitrile gloves should be changed between each discrete task in the well purging and sampling process.
10. Remove the locking well cap; note the location, time of day, date and general weather conditions in the field logbook or Monitor Well and Groundwater Data Sheets.
11. Remove the well casing cap.
12. Lower the water level measuring device into the well until the water surface is encountered. Refer to the QAPP for specific water level measurement procedures.
13. Measure the distance from the water surface to a known reference measuring point on the well casing or protective barrier post and record the distance in the field logbook or Monitor Well and Groundwater Data Sheets. Alternatively, if no known reference point is available, note that the water level measurement is from the top of the steel casing, top of the riser pipe from ground surface, or some specific position on the well head.
14. Measure total depth of the well and record the depth in the field logbook or Monitor Well and Groundwater Data Sheets.
15. Calculate the volume of water in the well and the volume to be purged using the equations in **Section 4.2 Calculations**.

4.4 Purging Procedures

Wells should be purged to ensure that a representative sample is obtained. Generally, at a minimum, purging of three well volumes is effective. Bailers, submersible pumps, and inertia pumps are the purging devices most commonly used.

NOTE: Reference and utilize the *MDEQ Purge Water Disposal Policy* for detailed purge water disposal procedures.

- Purge water should be containerized, characterized, and properly disposed of. Sample results for the well can be used to assist in waste characterization.

If no other option is available and only a small volume of purge water has been generated, purge water may be disposed of on the ground near the well.

- Do not dispose of purge water in a way that the disposal will exacerbate existing contamination.

4.4.1 Bailers

Bailers are the simplest purging device used and have many advantages. They generally consist of a rigid length of tube, with a ball check-valve at the bottom. A line is used to lower the bailer into the well and retrieve a volume of water.

Manual purging with bailers is best suited to shallow and/or narrow-diameter wells. For deep, larger-diameter wells that require purging large volumes of water, other devices may be more appropriate.

Procedures for purging with a bailer are as follows:

1. Determine the volume of water to be purged as described in **Section 4.2 Calculations**.
2. Attach the line to the bailer and slowly lower the bailer until it is completely submerged. Be careful not to drop the bailer to the water, as it causes turbulence and the possible loss of volatile organic contaminants. On the bailer's first trip down the well, it is good sampling practice to gently lower it to the bottom of the well casing so that the sampler has an adequate length of line in hand to bail the well dry, should it be needed.
3. Pull the bailer out in a manner that the line never touches the ground.
4. Empty the bailer into a graduated pail.
5. Collect and dispose of purge water in accordance with the *MDEQ Purge Water Disposal Policy* and any additional requirements in the site-specific sampling plan. If purge water is disposed of on the ground, this should be done away from the base of the well.

4.4.2 Submersible Pumps

The use of submersible pumps for purging is permissible, provided they are constructed of suitably noncontaminating materials. The chief drawback, however, is possible cross-contamination between wells. Although some units can be disassembled easily to allow surfaces contacted by contaminants to be cleaned, field decontamination may be difficult and require solvents that can affect sample analysis.

NOTE: Submersible pumps may be the only practical sampling device for extremely deep wells (greater than 300 feet of water). Under those conditions, it is recommended that dedicated pump systems be installed to eliminate the potential for cross-contamination of well samples.

The use of submersible pumps in multiple well-sampling programs should be carefully compared to other sampling mechanisms (e.g., bailers, peristaltic pumps). In many cases, a sample can be collected by a bailer after purging with a submersible pump.

Submersible pumps generally use one of two types of power supplies: electric or compressed gas. Electrically powered pumps can run off a 12-volt DC rechargeable

● - Prohibited ■ - Allowable ▲ - Needs Screening

battery, or a 110 or 220-volt AC power supply. Pumps powered by compressed air normally use a small electric or gas-powered air compressor. They may also utilize compressed gas (i.e., nitrogen) from bottles. Differently sized pumps are available for different depth or diameter monitoring wells.

Procedures for purging with a submersible pump are as follows:

1. Determine the volume of water to be purged as described in **Section 4.2 Calculations**.
2. Assemble the pump, hoses, and safety cable, then lower the pump into the well. Make sure the pump is deep enough so that all the water is not evacuated (running the pump dry may cause damage).
3. Determine the volume of water purged by discharging purged water into a graduated pail or by attaching a flow meter to the outlet hose.
4. Use a ground fault circuit interrupter or ground the generator to avoid possible electric shock.
5. Connect the power supply and purge the well until the specified volume of water has been evacuated. If the pumping rate exceeds the well recharge rate, lower the pumping rate, lower the pump further into the well, and continue pumping.
6. Collect and dispose purge waters in accordance with the *MDEQ Purge Water Disposal Policy* and any additional requirements in the site-specific sampling plan. If purge water is disposed on the ground, this should be done away from the base of the well.

4.4.3 Inertia Pumps

Inertia pumps, such as the WaTerra® pump and piston pump, are manually operated. They are the most appropriate to use when wells are too deep to bail by hand, or too shallow, narrow, or inaccessible for a submersible pump. Inertia pumps are made of plastic or stainless steel and may be either decontaminated or discarded.

Procedures for purging with an inertia pump are as follows:

1. Determine the volume of water to be purged as described in **Section 4.2 Calculations**.
2. Assemble the pump and lower it to the appropriate depth in the well.
3. Begin pumping manually, discharging the water into a graduated pail. Purge until the specified volume of water has been evacuated.
4. Collect and dispose purge waters in accordance with the *MDEQ Purge Water Disposal Policy* and any additional requirements in the site-specific sampling plan. If purge water is disposed on the ground, this should be done away from the base of the well.

4.5 Representative Sample Collection

The primary goal in performing groundwater sampling is to obtain a representative sample of the aquifer or water-bearing zone. Groundwater sampling results can be compromised in two primary ways: collecting a non-representative sample or handling the sample incorrectly.

A monitoring well will have little or no vertical mixing of the water, and stratification will occur. The well water in the screened section will mix with the groundwater due to normal flow patterns, but the well water above the screened section will remain isolated, become stagnant, and may no longer be representative of the groundwater quality. Also, stagnant water may contain foreign material inadvertently or deliberately introduced from the surface, resulting in a non-representative sample. To safeguard against collecting non-representative stagnant water, the following guidelines and techniques should be adhered to during sampling:

1. As a general rule, all monitoring wells should be purged prior to sampling; see **Section 4.3 Purging Procedures**. To obtain a representative sample, a minimum of three volumes of water in the well casing should be purged. When using low-flow methods, purging should continue until the selected indicator parameters have stabilized. Indicator parameters typically used in low-flow purging include groundwater pH, specific conductivity, turbidity, temperature, dissolved oxygen and oxidation-reduction potential. The appropriate set of indicator parameters for the specific sampling event should be chosen by the project manager in advance of the sampling event. Alternatively, for low-yielding groundwater formations, the well can be pumped dry. For deeper wells, packers can be used to isolate a portion of the screened interval, minimizing the volume of groundwater that must be purged. In a high-yielding groundwater formation and where there is no stagnant water in the well above the screened section, purging is not as critical.
2. When purging with a pump, the pump should be set within the screened interval. When sampling a screened well, the sample should also be collected from the same depth within the screened interval at which the pump was set.
3. The well should be sampled as soon as possible after purging.
4. For wells that are pumped or bailed to dryness prior to the purging procedure being completed, the well should be allowed to recover (for up to, but no longer than, 24 hours) prior to collecting a sample.
5. A non-representative sample can also result from excessive pre-pumping of the monitoring well. Stratification of the constituent concentration in the groundwater formation may occur, or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping can dilute or increase the constituent concentrations relative to those at the sampling point of interest.
6. A sampling methodology must be used that accounts for the effects of aquifer heterogeneities, while minimizing alterations in water chemistry that could result from sampling disturbances. The MDEQ will accept properly conducted purging methods designed to minimize drawdown, by controlling the flow from the well while monitoring stabilization indicator parameters, commonly referred to as low-flow methods. Available low-flow procedures include:
 - United States Environmental Protection Agency (USEPA), Office of Research and Development, Office of Solid Waste and Emergency Responses, EPA/540/S-95/504, April 1996, USEPA Ground Water Issue, [Low-Flow \(Minimal Drawdown\) Ground-Water Sampling Procedures](#), Robert Puls and Michael Barcelona
 - USEPA, Region 1, July 30, 1996, Revision 3, [Low Stress \(Low-Flow\) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells](#)

4.6 Low-Flow Methods

Low-flow sampling involves the slow removal of a minimal amount of water from a well to ensure that stagnant water is removed and that water in the well is representative of water in the formation. The advantage of low-flow sampling is that, when conducted properly, it avoids

● - Prohibited ■ - Allowable ▲ - Needs Screening

disrupting the formation and minimizes turbidity that can be introduced by other purging and sampling devices, such as bailers. Instead of removing a set volume of water from the well, low-flow sampling uses a pump (typically a peristaltic pump), set at a low rate of flow, to continuously remove water until a set of indicator parameters are stabilized.

Flow rates are typically on the order of 100 to 200 milliliters per minute (ml/min) and should never exceed 500 ml/min. Indicator parameters are measured using probes inside a flow through cell and may include pH, specific conductance, dissolved oxygen, oxidation-reduction (redox) potential, temperature, and turbidity. Not all indicators may be used for a specific sampling; staff is most likely to use pH, specific conductivity, temperature, and turbidity.

NOTE: For a detailed discussion of low-flow methods, see USEPA, Office of Research and Development, Office of Solid Waste and Emergency Responses, EPA/540/S-95/504, April 1996, USEPA Ground Water Issue, *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, Robert Puls and Michael Barcelona

5. Groundwater Sample Collection Procedures

Groundwater samples can be collected using bailers, submersible pumps, inertia pumps, and peristaltic pumps used for purging. Several factors must be considered when choosing a sampling device, and care should be taken when reviewing the advantages or disadvantages of any one device (see **Section 2 Groundwater Sampling Equipment**). It may be appropriate to use a sampling device different than that used to purge. The most common example of this is the use of a submersible pump to purge and a bailer to sample.

The following considerations should be taken during sample collection to prevent contamination:

- Dust and fibers must be kept out of sample bottles.
- The sample cap should never be placed 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.).
- Do not sample without powderless nitrile gloves.
- Regular/thick size markers (Sharpie® or otherwise) are to be avoided; as they may contain PFAS.
- Fine and Ultra-Fine point Sharpie® markers are acceptable to label the empty sample bottle while in the staging area provided the lid is on the sample bottle and gloves are changed following sample bottle labeling.
- Ballpoint pens may be used when labeling sample containers. If ballpoint pens do not write on the sample container labels, preprinted labels from the laboratory may be used.
- Hands should be well washed and gloved.
- Use HDPE or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory.
- Commercially bought sample bottles used with automatic sampling equipment should be decontaminated prior to sampling and equipment blank samples should be collected using laboratory supplied PFAS-free water.
- Glass bottles or containers may be used if they are known to be PFAS-free, however, PFAS have been found to adsorb 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). If the sample comes into direct contact with the glass for a short period of time (e.g. using a glass container to collect

the sample, then transferring the sample to a non-glass sample bottle), the adsorption is minimal.

- Bottles should only be opened immediately prior to sampling.
- Bottles should be capped immediately after collecting the sample.
- Samples should be double bagged using resealable low density polyethylene (LDPE) bags (e.g., Ziploc®).
- Follow any guidance or requirements in the PFAS analytical reference method that will be used for testing samples, for sample collection, storage, preservation, and holding times.
- In the absence of formal USEPA guidance for PFAS groundwater sample storage, the documentation in USEPA Method 537 Rev. 1.1 should be used as a guide for thermal preservation (holding temperature) and holding times for groundwater or other samples. Samples must be chilled during storage and shipment and must not exceed 50°F (10° C) during the first 48 hours after collection. Samples stored in the laboratory must be held at or below 50°F (10°C) until extraction but should not be frozen.
- Groundwater samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction.
- ▲ Off-brand markers should be known to be PFAS free prior to use.
- ▲ Latex gloves should be screened before use.

NOTE: USEPA Method 537 Rev. 1.1 was developed for the analysis of finished drinking water samples **only**.

5.1 Bailers

1. Complete purging. Measure the groundwater pH, temperature, and specific conductance using the procedures described in the QAPP.
2. Assemble the appropriate sample containers, and label with appropriate sample labels.
3. Attach a nylon or cotton line to the bailer.
4. Lower the bailer slowly and gently into the well, attempt to minimize contact with the casing, and avoid splashing the bailer into the water. Stop lowering at a point adjacent to the screen.
5. Allow the bailer to fill and then slowly and gently retrieve the bailer from the well. Attempt to minimize contact with the casing, to ensure that flakes of rust or other foreign materials are not knocked into the bailer.
6. Remove the cap from the sample container and keep it in a gloved hand (two sample collection personnel may be needed).
7. Begin slowly pouring groundwater from the bailer into the sample container.
8. Replace the well cap once all sample containers are filled.
9. Cap the sample container tightly, label the container, and place the container in a temperature-controlled carrier.
10. Log all samples in the field logbook and on Monitor Well and Groundwater Data Sheets.
11. Package the samples for transport to the analytical laboratory. Complete chain-of-custody records.
12. Properly dispose of the bailer and line.

NOTE: For bailers especially, two sample collection personnel may be needed.

5.2 Submersible Pumps (Low-Flow Sampling)

1. Complete purging, keeping the pump approximately in the middle of the screened interval. Measure the groundwater pH, temperature, and specific conductance using the procedures described in the QAPP.
2. Assemble the appropriate sample containers, and label with the appropriate sample labels.
3. Reduce the purge water flow rate to a manageable sampling rate by adjusting the control box or by attaching a gate valve to the tubing (if not already fitted).
4. If the flow rate cannot be adjusted, run the water down the side of a clean jar and fill the sample containers from the jar.
5. Remove the pump and assembly. Dedicate the tubing to the monitoring well.
6. Replace the well cap once all sample containers are filled.
7. Cap the sample container tightly, label the container, and place it in a temperature-controlled carrier.
8. Log all of the samples in the field logbook and/or the Monitor Well and Groundwater Data Sheets.
9. Package the samples for transport to the analytical laboratory. Complete chain-of-custody records.
10. Decontaminate equipment in accordance with **Section 3 Equipment Decontamination**.

5.3 Inertia Pumps

1. Complete purging, keeping the pump approximately in the middle of the screened interval. Measure the groundwater pH, temperature, and specific conductance using the procedures described in the QAPP.
2. Assemble the appropriate sample containers, and label with appropriate sample labels.
3. Manually regulate the flow rate and discharge the sample from the pump outlet directly into the appropriate sample container.
4. Remove the pump from the well.
5. Replace the well cap once all sample containers are filled.
6. Cap the sample container tightly, label the container, and place it in a temperature-controlled carrier.
7. Log all samples in the field logbook and/or the Monitor Well and Groundwater Data Sheets.
8. Transport the samples to the decontamination zone, and package them for transport to the analytical laboratory. Complete chain-of-custody records.
9. Decontaminate equipment in accordance with **Section 3 Equipment Decontamination**.

5.4 Peristaltic Pumps (Low-Flow Sampling)

1. Determine that the indicator parameters (see **Section 4.4**) have stabilized. Complete purging, keeping the pump approximately in the middle of the screened interval. Record indicator parameters at 3-minute intervals.
2. Assemble the appropriate sample containers, and label with appropriate sample labels.
3. Collect samples.
4. Remove the pump and assembly. Dedicate the tubing to the monitoring well or properly dispose.
5. Replace the well cap once all sample containers are filled.
6. Cap the sample container tightly, label the container, and place it in a temperature-controlled carrier.
7. Log all samples in the field logbook and/or the Monitor Well and Groundwater Data Sheets.
8. Package the samples for transport to the analytical laboratory. Complete chain-of-custody records.
9. Decontaminate equipment in accordance with **Section 3 Equipment Decontamination**.

● - Prohibited ■ - Allowable ▲ - Needs Screening

When the depth to the water table exceeds 25 feet below grade, suction-lift mechanisms, such as peristaltic pumps, cannot be used to sample groundwater. A bladder or submersible pump can be used in the case when groundwater is located deeper than 25 feet below grade. Both of these pumps are submerged beneath the water table and will come into contact with the groundwater being sampled.

6. Field Quality Assurance/Quality Control

Sample blanks and duplicates are the primary means of assuring and assessing quality control during sample collection or transport.

Field blanks consist of:

- **Equipment blanks**

- Equipment blanks consist of laboratory verified PFAS-free water poured over (for equipment such as static water level indicators) or through (for equipment such as pumps, bailers and flow through cells) the sampling equipment, collected in laboratory-supplied sample containers, and analyzed.
- Equipment blanks should be collected prior to the first use of sampling equipment in the field (particularly if there is any uncertainty as to whether the equipment is constructed from PFAS containing materials) and occasionally after decontamination.
- Equipment blanks should be collected from a representative sample of disposable sampling equipment (one bailer from a box, a length of tubing from a roll) to document that these items are not contributing PFAS to groundwater samples.
- In the field, equipment blanks should be collected at a minimum frequency of one per day (or at a different frequency as specified in the sampling plan).

NOTE: Refer to the specific sampling plan to determine the appropriate number and frequency regarding field quality assurance and quality control.

- **Trip blanks**

- Trip blanks consist of laboratory-verified PFAS-free water in a laboratory-supplied sample container. Trip blanks travel with the field samples and are analyzed in the same batch.
- Typically trip blanks are collected to assess the potential cross contamination from VOCs. The current MDEQ minimum analyte PFAS list does not contain PFAS that are volatile.
- Trip blanks could be used to evaluate the potential cross-contamination present the lab in the containers or deionized water provided from the lab.

- **Field blanks**
 - Field blanks consist of laboratory verified PFAS-free water in a laboratory supplied sample container.
 - A field blank is opened at the sampling site and exposed to ambient conditions for approximately the same amount of time as an actual sampling container (generally 1 to 3 minutes). Alternately, the PFAS—free water can be poured from one sample container into another to mimic sample collection activities. The field blank then travels with the field samples and is analyzed in the same batch.
 - A field blank must be collected once every twenty samples (or at a different frequency as specified in sampling plan) or once during any sampling event, when an ambient source of PFAS (particularly atmospheric) is suspected.
 - If an atmospheric source of PFAS is suspected, collect the equipment blank downwind of the suspected source

- **Field duplicates**
 - Groundwater sample duplicates are two samples collected immediately sequentially from the same well. Duplicate samples should be labeled to prevent anyone, other than the sample collector, from knowing which specific well(s) are being duplicated.
 - Duplicates are analyzed in the same batch and serve as a quality check on the accuracy and precision of sampling procedures.
 - Duplicates are recommended once every ten samples or once per day (whichever is less; or at a different frequency as specified in the sampling plan.

7. Filtration

Filtering of the groundwater samples is sometimes necessary. PFAS can adsorb to particulate matter, and unfiltered samples may result in high biased results. However, the filter material should be carefully evaluated. A study between four different filter materials (PTFE, glass, polyethersulfone [PES], and nylon) found that glass filters adsorbed the least amount of PFAS and nylon adsorbed the most and is therefore not recommended for PFAS sampling.

NOTE: It is recommended that filtering of the samples should **only be performed in the laboratory** in order to reduce the possibility of cross contamination.

The following recommendations should be used when considering filtering of the samples:

- **Field filtration of the sample is generally not advised.**
 - ▲ If filtering is absolutely necessary, if specifically requested by a client or for other reasons:
 - Do not use any filters that contain any PFAS, such as PTFE filters
 - Do not use nylon filters.
 - Glass filters are recommended to be used.
 - Consider use of a centrifuge in the laboratory to reduce the need for sample filtering.

8. Sample Shipment

Once the sample is collected in laboratory-supplied containers, the following recommendations should be used for sample shipment:

- Check the cooler periodically to ensure samples are well iced and at the proper temperature.

- Refresh with regular ice, if needed, double bagged in LDPE resealable storage bags if needed.
- Regular ice should be used to cool and maintain the sample at or below the proper temperature.
 - ▲ Chemical or blue ice may be used if it is known to be PFAS-free and it is absolutely certain that the sample is cooled and maintained at or below the proper temperature during collection and through transit to the laboratory.
- Complete the appropriate Monitor Well and Groundwater Data Sheets.
- Shipping containers should be packed with enough PFAS-free noncombustible, absorbent, cushioning material, such as bubble wrap, to minimize the possibility of breakage.
- Complete a Chain of Custody (COC) form for each separate shipping container. The forms should be hand-carried to the laboratory by the sampler.
- If unable to hand-carry the COC and other forms to the laboratory, forms should be single bagged in LDPE (e.g. Ziploc®) storage bags and taped to the inside of the cooler lid.
- The cooler should be taped closed with a custody seal and, if shipping, shipped by overnight courier.
- Samples should be shipped as soon as possible (e.g. overnight) to ensure the samples arrive within the analytical holding time specified by the lab.

NOTE: Chain-of-custody procedures must be followed and documented.

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MDEQ PFAS SAMPLING QUICK REFERENCE FIELD GUIDE¹

All Items Used During Sampling Event

● Prohibited

- Items or materials that contain fluoropolymers such as
 - Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon®
 - Polyvinylidene fluoride (PVDF), that includes the trademark Kynar®
 - Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon®
 - Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®
 - Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP
- Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

● Prohibited

- Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)

■ Allowable

- High-density polyethylene (HDPE)
- Low-density polyethylene (LDPE) tubing
- Polypropylene
- Silicone
- Stainless-steel
- Any items used to secure sampling bottles made from:
 - Natural rubber
 - Nylon (cable ties)
 - Uncoated metal springs
 - Polyethylene

▲ Needs Screening²

- Any items or materials that will come into direct contact with the sample that have **not** been verified to be PFAS-free
 - Do not assume that any sampling items or materials are PFAS-free based on composition alone

Sample Storage and Preservation

● Prohibited

- Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps

■ Allowable

- Glass jars⁴
- Laboratory-provided PFAS-Free bottles:
 - HDPE or polypropylene
- Regular wet ice
- Thin HDPE sheeting
- LDPE resealable storage bags (i.e. Ziploc®) that will not contact the sample media⁶

▲ Needs Screening²

- Aluminium foil⁴
- Chemical or blue ice⁵
- Plastic storage bags other than those listed as ■ Allowable
- Low-density polyethylene (LDPE) bottles

Field Documentation

● Prohibited

- Clipboards coated with PFAS
- Notebooks made with PFAS treated paper
- PFAS treated loose paper
- PFAS treated adhesive paper products

■ Allowable

- Loose paper (non-waterproof, non-recycled)
- Rite in the Rain® notebooks
- Aluminium, polypropylene, or Masonite field clipboards
- Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie® markers

▲ Needs Screening²

- Plastic clipboards, binders, or spiral hard cover notebooks
- All markers not listed as ■ Allowable
- Post-It® Notes or other adhesive paper products
- Waterproof field books

Decontamination

● Prohibited

- Decon 90®
- PFAS treated paper towel

■ Allowable

- Alconox®, Liquinox®, or Citranox®
- Triple rinse with PFAS-free deionized water
- Cotton cloth or untreated paper towel

▲ Needs Screening²

- Municipal water
- Recycled paper towels or chemically treated paper towels

Clothing, Boots, Rain Gear, and PPE

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • New or unwashed clothing • Anything made of or with: <ul style="list-style-type: none"> ○ Gore-Tex™ or other water-resistant synthetics • Anything applied with or recently washed with: <ul style="list-style-type: none"> ○ Fabric softeners ○ Fabric protectors, including UV protection ○ Insect resistant chemicals ○ Water, dirt, and/or stain resistant chemicals 	<ul style="list-style-type: none"> • Powderless nitrile gloves • Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners • Made of or with: <ul style="list-style-type: none"> ○ Polyurethane ○ Polyvinyl chloride (PVC) ○ Wax coated fabrics ○ Rubber / Neoprene ○ Uncoated Tyvek® 	<ul style="list-style-type: none"> • Latex gloves • Water and/or dirt resistant leather gloves • Any special gloves required by a HASP • Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

Food and Beverages

● Prohibited	■ Allowable
<ul style="list-style-type: none"> • No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks. <ul style="list-style-type: none"> ■ If consuming food on-site becomes necessary, move to the staging area and remove PPE. After eating, wash hands thoroughly and put on new PPE. 	<ul style="list-style-type: none"> • Brought and consumed only outside the vicinity of the sampling area: <ul style="list-style-type: none"> ○ Bottled water ○ Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection⁶

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • Any PCPs⁶, sunscreen, and insect repellent applied in the sampling area. 	<p>PCPs⁶, sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands:</p> <p>PCPs⁶:</p> <ul style="list-style-type: none"> • Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs⁶ <p>Sunscreens:</p> <ul style="list-style-type: none"> • 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 <p>Insect Repellents:</p> <ul style="list-style-type: none"> • OFF® Deep Woods • Sawyer® Permethrin 	<ul style="list-style-type: none"> • Products other than those listed as <ul style="list-style-type: none"> ■ Allowable

¹ This table is not considered to be a complete listing of prohibited or allowable materials. All materials should be evaluated prior to use during sampling. The manufacturers of various products should be contacted in order to determine if PFAS was used in the production of any particular product.

² Equipment blank samples should be taken to verify these products are PFAS-free prior to use during sampling.

³ **For surface water foam samples:** LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

⁴ **For fish and other wildlife samples:** Depending on the project objectives, glass jars and aluminum foil might be used for PFAS sampling. PFAS has been found to bind to glass and if the sample is stored in a glass jar, a rinse of the jar is required during the sample analysis. PFAS are sometimes used as a protective layer for some aluminum foils. An equipment blank sample should be collected prior to any aluminum foil use.

⁵ Regular ice is recommended as there are concerns that chemical and blue ice may not cool and maintain the sample at or below 42.8°F (6°C) (as determined by EPA 40 CFR 136 – NPDES) during collection and through transit to the laboratory.

⁶ Based on evidence, avoidance of PCPs is considered to be precautionary because none have been documented as having cross-contaminated samples due to their use. However, if used, application of PCPs must be done at the staging area and away from sampling bottles and equipment, and hands must be thoroughly washed after the use of any PCPs prior to sampling.