Collection of Public Drinking Water Samples for Per- and Poly FluoroAlkyl Substances (PFAS)

Standard Operating Procedures

Iowa Department of Natural Resources

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Overview

Scope and Application:

The purpose of this Standard Operating Procedure (SOP) document has been developed to establish a uniform procedure for collecting raw and finished drinking water samples from public water supplies for analysis of per- and poly fluoroalkyl substances (PFAS), while minimizing cross contamination.

References:

Michigan Department of Environmental Quality Groundwater PFAS Sampling Guidance:
https://www.michigan.gov/documents/pfasresponse/Groundwater_PFAS_Sampling_Guidance_637871_7.pdf

Michigan Department of Environmental Quality General PFAS Sampling Guidance:
https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf

CALIFORNIA STATE WATER QUALITY CONTROL BOARD DIVISION OF WATER QUALITY
Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines for Non-Drinking Water:
https://www.waterboards.ca.gov/pfas/docs/sept_2020_pfas_sampling_guidelines.pdf

EPA method 533:
https://www.epa.gov/sites/production/files/2019-12/documents/method-533-815b19020.pdf

Sample Storage Requirements:

- All filled sample bottles and QA/QC samples will be maintained in a cooler on wet ice only
- Cooler with ice for storage at < 6° C

Materials Required:

Field Supplies and Equipment::

- Sample bottles (HDPE or polypropylene bottles with Teflon-free lids, pre-numbered, as provided by the laboratory)
- Cooler for collection and transport
- Wet Ice
- Powderless nitrile gloves
- Chain-of-Custody forms
- Ultra-fine tip Sharpie®
- Data collection sheet
- Shipping labels (if necessary)
- Packing tape
- PFAS-free water for QC samples as provided by the laboratory
- Large LDPE bag for sample bottles

Personal Protective Equipment Required / Waste Disposal:

New powder-free nitrile gloves will be used for every sample collected. There are no special waste disposal requirements. Dispose of waste with general refuse.

Important Notes:

PFAS Cross-Contamination Potential Sources

Potential sources of PFAS cross-contamination in the typical sampling environment include water used during drilling or decontamination, materials used within the sampling environment, sampling equipment, field clothing and personal protective equipment (PPE), sun and biological protection products, personal hygiene and personal care products (PCPs), food packaging, and the environment itself. 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.

Avoid PPE and field supplies that may include PFAS which could cross-contaminate field samples.

- PCPs such as shampoos, moisturizers and cosmetics may contain PFAS and should be used with care the day of sampling unless on a portion of the body that will be covered by PFAS-free clothing.
- Sunblock and insect repellent ingredients need to be verified to ensure that they do not contain PFAS before use in the field. Clothing chemically treated for ultraviolet protection should be avoided.
- Food and food packaging within the sampling zone should be avoided during sampling for PFAS.
- Several brands of waterproof field books contain PFAS and should not be used. Documentation of field activities should be on loose paper on an aluminum clipboard or in a waterproof field book that does not use PFAS. Field notes should be taken with a ballpoint pen and not any type of felt tip marker.
- Some adhering materials contain PFAS, including sticky notes, and should be avoided. Pre-printed labels should be verified as PFAS-free.
- Chemical ice packs should not be used unless it is verified that they are PFAS-free. Samples for PFAS analysis should be placed on water ice immediately and should ideally be received by the laboratory at a temperature less than 6º Celsius.
- Disposable, powderless, nitrile gloves must be worn during PFAS sampling and handling activities and should be changed frequently during and between sampling activities.
- Water resistant, waterproof, or stain-treated clothing, and clothing recently washed with fabric softeners, and new clothing should be avoided.

Field Clothing, Personal Protection Equipment (PPE), and Well Sampling Materials and Equipment

Materials, field clothing, and equipment screening for possible PFAS should be performed during 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. Due to the extensive use of PFAS in many products, some PPE may contain PFAS. However, the safety of staff is our primary concern and should not be compromised by fear of PFAS-containing 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.

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

- Polytetrafluoroethylene (PTFE) that includes the trademarks Teflon® and Hostaflon®.
- Polyvinylidene fluoride (PVDF) that includes the trademark Kynar®.
- Polychlorotrifluoroethylene (PCTFE) that includes the trademark Neoflon®.
- Fluorinated ethylene propylene (FEP) that includes the trademarks Teflon® FEP, Hostaflon® FEP, and Neoflon® FEP.
- Ethylene-tetrafluoro-ethylene (ETFE) that includes the trademark Tefzel®.
- 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, such as plastic bags, tubing, and containers, including some sample bottles.

While preparing for sampling, particular focus should be made on NOT wearing clothing that has been advertised as having waterproof, water-repellant, or dirt and/or stain resistant characteristics. These types of clothing are most likely to have had PFAS used in their manufacturing. Field Clothing and PPE that should be avoided in the immediate sampling environment include the following:

- Do not use clothing that has been washed with fabric softener which may contain PFAS.
- Do not use clothing that has been made with or washed with water, dirt, and/or stain resistant chemicals.
- Do not use clothing chemically treated for insect resistance and ultraviolet protection.

Personal Care Products (PCP)

Several sampling guidance documents recommend that personal hygiene and PCPs (e.g., cosmetics, shampoo and other hair products, 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 sampling guidance documents are followed, these items should not come into contact with the sampling equipment or the sample being collected. Field personnel should be aware of the potential of cross contamination of the sampling equipment or actual samples coming 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 PCPs becomes necessary.
- Wash hands thoroughly after the handling or application of PCPs. When finished, put on a fresh pair of powderless nitrile gloves.

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 area 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.

Sample Collection Methods

Public Wells and Surface Water Intakes

To obtain a representative sample of raw water in a public water supply well, it is important to avoid extremes in the pumping regime, such as stagnant water from a well that has not been actively pumped for several hours, or a well that is being pumped at a much higher rate than under normal use conditions. Therefore, a discussion with the water operator about these requirements is necessary prior to sampling the well. Ideally, the well should be run for at least 30 minutes prior to sampling. Then, the raw-water sampling tap (prior to any treatment) should be opened and allowed to run for a minimum of 5 minutes in order to ensure that water that has been sitting in the pipes is flushed sufficiently.

Surface water sources should be sampled to avoid sampling the surface of a stagnant water body. Samples should be obtained from a sampling port, if available, or from well-mixed/flowing water.

No filtering of samples should be conducted in the field to avoid contamination.

Quality Assurance/Quality Control:

The typical method reporting level for several PFAS chemicals is 2-10 ng/L. The Health Advisory established by the USEPA for PFOA and PFOS is 70 ng/L. The very low concentrations that are required to evaluate the impacts of PFAS chemicals in drinking water is unprecedented in the environmental field. Sampling conducted in other states by various groups has shown that the sampler can influence the results by cross contaminating the sample during collection. Several best practices have been recommended to minimize this issue.

A two-person crew will sample each facility. One person will be designated the sampler, and only handle sampling bottles, sample collection, and sample storage in LDPE plastic bags. The other person will be designated the support person and will complete the COC, labels, and record field notes on site conditions.

An incremental approach to implementing this SOP will ensure that the best possible steps are taken to minimize cross contamination of samples.

QA/QC Samples

The ability to understand the impacts of collection, transport and laboratory preparation and analysis is essential in establishing the veracity of the results collected by this SOP.

Sample blanks and duplicates are the primary means of assuring and assessing quality control during sample collection and transport. For the purposes of the IDNR's PFAS Action Plan monitoring, field blanks, trip blanks, and duplicate samples will be integral to the QA/QC evaluation. Equipment blanks may be needed in future sampling efforts.

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 (e.g., 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).

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.

Trip blanks are used to evaluate the potential cross-contamination present in 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.

If an atmospheric source of PFAS is suspected, collect the equipment blank downwind of the suspected source.

At least one field blank will be obtained per sampling location during the initial phase of sampling. This may be reduced to one field blank per sampling trip depending on the results of the initial phase of sampling.

Field duplicates

Sample duplicates are two samples collected sequentially from the same sampling location. Duplicate samples should be labeled to prevent anyone, other than the sample collector, from knowing which specific well(s) or intake(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.

At least one duplicate will be collected per sampling location during the initial phase of sampling. This may be reduced to one field duplicate per sampling trip depending on the results of the initial phase of sampling.

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 (wet ice only) and at the proper temperature.
    - Refresh with wet ice (double bagged in LDPE resealable storage bags) if needed.
- Shipping coolers should be packed with enough laboratory-approved PFAS-free 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 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 laboratory-supplied 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.

Procedure:

Ensure the sampler and support staff understand their roles and responsibilities.

1.0 Purge well

1.1 Record time well pumping started and pumping rate
1.2 Ensure well has purged for more than 30 minutes
1.3 Take a picture of the sampling area

2.0 Prepare and sample.

2.1 Inventory primary and QA bottles, add appropriate information as necessary
2.1.1 Ensure only laboratory-provided HDPE or polypropylene sample bottles with Teflon® -free caps are used.

2.1.2 Ensure only Ultra-Fine tip Sharpie® markers are used for labeling purposes.

2.1.3 The type of label used will be determined in consultation with the certified laboratory.

2.2 Turn on sampling tap and let run until the system is sufficiently flushed.
2.3 Don new powder-free nitrile gloves
2.3.1 Hands should be well washed and gloved.

2.3.2 Do not sample without powderless nitrile gloves.

2.4 Remove sample container cap with one hand and keep the top of the cap up while sampling
2.4.1 Bottles should only be opened immediately prior to sampling.

2.4.2 Dust and fibers must be kept out of sample bottles.

2.4.3 The sample container cap should never be placed on the bare ground during sampling.

2.4.4 If sampling staff must set the sample container 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 (HDPE sheeting, triple rinsed cooler lid, etc.).

2.5 Tip the bottle to a 45 degree angle and place under the sampling tap, minimize aeration to the extent possible. slowly fill the bottle and at the same time slowly rotate the bottle to a vertical position.

2.6 Replace cap on bottle. Record sample container filling start time.

2.6.1 Bottles should be capped immediately after collecting the sample.

2.6.2 Bottles for EPA method 533 will contain ammonium acetate as a preservative. Once capped, containers should be agitated by hand to ensure preservative is fully dissolved.

2.6.3 Place all primary and QA samples in a resealable low density polyethylene (LDPE) bags (e.g., Ziploc®).

2.6.4 Place label on the outside of the first LDPE bag.

2.6.5 Samples should be double bagged using resealable LDPE bags.

2.6.6 Place double bagged samples into the supplied cooler with wet ice.

2.6.7 Verify all information on the labels and chain-of-custody and note in the field book.

2.6.8 Samples must be chilled during storage and shipment and must not exceed 50°F (10° C) during the first 48 hours after collection.

Training:

The following individuals have read this procedure, have been trained on how to perform the steps, and have been warned of the personal hazards involved.

Name	Date
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Appendix 1: Labeling requirements

Labels and chain-of-custody format to be determined upon laboratory selection.

Appendix 2: Sampling approach to collecting PFAS samples from public drinking water supplies

The very low concentrations that are required to evaluate the impacts of PFAS chemicals in drinking water and its widespread use in society is new in the environmental field. Sampling conducted in other states and by various groups has shown that the sampler can influence the results by cross contaminating the sample during collection. Several best practices have been recommended by other groups to minimize this issue (see the DNR SOP).

To address this concern, an incremental approach to implementing the DNR's Sampling Standard Operating Procedure (SOP) will ensure that the best possible steps are taken during sample collection in the field.

Initial Round

1. Use the established SOP to sample 5-10 wells or surface water intakes at ~5 facilities. (About 1 month for sample collection plus 1 month for data review)
    a. Use the highest level of Quality Assurance (QA) including: blind duplicates at every sampling point, field blanks at every sampling point, and a trip blank at every facility (used to indicate potential lab issues) using separate coolers for each facility.
    b. Use two DNR staff for every sample collected so only one person handles the sample collection while the other handles all the logistics and field documentation at the sampling site. Note the same person should do the sample collection during each day.
    c. Samples mailed to the approved laboratory no later than the morning after collection. Sample custody will be maintained 24 hours a day and documented on the approved chain-of-custody form.
    d. Review analytical results and field notes to evaluate possible QA issues, update SOP if needed.
2. Use the revised SOP to sample 10-20 wells at ~10 facilities (About 1 months-sample collection; 1 month-data review)
    a. Use appropriate QA based on laboratory recommendations and analytic results, at a minimum consider: duplicates at each facility, field blanks at each facility, and a trip blank in the cooler using one cooler per day.
    b. Use two people at each facility, the operator may be used to handle logistics so DNR staff can focus on sampling.
    c. Samples submitted as a batch to laboratory (weekly)
    d. Review analytical results to evaluate possible cross contamination, update SOP if needed, and finalize the document.
3. Use final SOP to sample remaining Tier 1 wells (About 1 month)

a. Use appropriate QA based on laboratory recommendations and analytic results: at a minimum consider 1 blind duplicate and 1 field blank each day. Others as deemed appropriate based on data review.

4. Based on the results of the Tier 1 sampling, timelines and resources for Tier 2 will be planned. Sampling of other tiers will be based on the detected concentrations and prevalence of elevated concentrations reported in the analytical reports of the Tier 1 and 2 sampling and in consultation with the Director and other agencies as appropriate.