



DRINKING WATER SAMPLE COLLECTION GUIDANCE FOR PER- AND POLY-FLUOROALKYL SUBSTANCES (PFAS)



Photo by Valerie Gregory

STATE WATER RESOURCES CONTROL BOARD DIVISION OF DRINKING WATER

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SWRCB PFAS Website: <https://www.waterboards.ca.gov/pfas/>

DDW PFAS Website https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html

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SWRCB Division of Drinking Water
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I. INTRODUCTION

Obtaining representative samples and maintaining their integrity are critical elements of any monitoring program. Analytical methods may be standardized but the results of analyses are only as good as the sampling and the sample preservation methods. Sampling is the first key element in a monitoring program that must be performed properly to assure valid data. The goal of this sampling guidance is to present the steps for sampling drinking water¹ for per and poly-fluoroalkyl substances (PFAS).

PFAS are a large group of synthetic fluorinated chemicals widely used in industrial processes and consumer products. These synthetic compounds are very persistent in the environment. People are exposed to these compounds through food, food packaging, textiles, electronics, personal hygiene products, consumer products, air, soils, and drinking water. Studies indicate that continued exposure to low levels of PFAS may result in adverse health effects.

California water utilities tested drinking water supplies for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS) between 2013 and 2015, as required by the United States Environmental Protection Agency (USEPA) under the third Unregulated Contaminant Monitoring Rule (UCMR3). In May 2016, the USEPA issued a lifetime health advisory for PFOS and PFOA in drinking water, advising municipalities that they should notify their customers of the presence of levels over 70 parts per trillion (ppt) of PFOS and PFOA, individually or combined, in community water supplies. USEPA recommended that the notification of customers include information on the increased risk to health, especially for susceptible populations. On July 13, 2018, the State Water Resources Control Board's (SWRCB) Division of Drinking Water (DDW) issued a drinking water notification level (NL) of 14 ppt for PFOA and a NL of 13 ppt for PFOS due to liver toxicity and cancer risks (for PFOA) and immunotoxicity risks (for PFOS). On August 22, 2019, the NLs were reduced to 5.1 ppt for PFOA and 6.5 ppt for PFOS. On February 6, 2020, DDW released a new set of response level² of 10 ppt for PFOA and 40 ppt for PFOS. This amendment is based on updated health

¹ Water of sufficiently high quality that it can be consumed or used without risk of immediate or long term harm. Water that is free from disease-producing organisms, chemical, biological, and radioactive contaminants which would make it unfit for human consumption

² The response level represents a recommended chemical concentration level at which water system consider taking a water source out of service or provide treatment before the deliver to public.

recommendations by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA). Currently, OEHHA is developing a public health goal (PHG) for both PFOA and PFOS. Establishing a PHG is the first step in the development of a drinking water standard.

The collection of PFAS drinking water data can support future regulatory determinations and other actions to protect public health. The analytical methodology approved by DDW for use to assess the presence of PFAS in drinking water is EPA Method 537.1 (November 2018). This is the only method acceptable to the DDW for drinking water analyses.

II. PURPOSE OF SAMPLING GUIDANCE

Due to the prevalent nature of PFAS in commonly used sampling materials and personal protective equipment, as well as in clothing, food packaging, and personal care products, careful procedures should be implemented to prevent cross-contamination of field samples. The detection of PFAS at the low concentrations that pose a health risk requires careful planning, sampling, and shipping techniques that ensure the integrity of the sample. This sampling guidance provides recommendations to reduce such cross-contamination sources and provides information for samplers to ensure the collection of a valid sample. Water samplers should make every effort to implement these sampling recommendations, recognizing that there may be different protocols and procedures recommended by the laboratory, or standard operating procedures already in place by the water utility. Analytical results from the sampling of drinking water sources should be reported electronically by the analytical laboratory to DDW.

III. TYPES OF QUALITY CONTROL FIELD SAMPLES

Due to the required low detection limits of PFAS in drinking water, DDW is specifying the use of a field reagent blank sample and is recommending the collection of a field duplicate sample from the source, at the same time that the field sample (source sample) is collected. These special quality control (QC) samples must be discussed with the laboratory prior to sampling to ensure proper sample containers and materials are on hand when sampling begins in the field.

FIELD REAGENT BLANK (Required)

A Field Reagent Blank (FRB) is analyzed to assess the potential for PFAS cross-contamination being introduced during the sampling process. The FRB consists of a pre-preserved sample bottle filled by the laboratory with PFAS-free water and shipped to the site with the other sample bottles. For each FRB, an empty sample bottle (with no preservative) must also be included. At the sample site, the sampler will open the FRB and pour it into the empty sample bottle. An FRB must be

collected at each sample site (i.e., each source being sampled) and placed in the ice chest used to store and transport samples.

FIELD SAMPLE (Required)

The Field Sample is the sample collected from the source at a location prior to any treatment, to qualify as a “source sample”. Samples may be collected after treatment to confirm PFAS concentration in the water delivered to customers

FIELD DUPLICATE (Recommended)

The Field Duplicate (FD) is a sample collected from the source at the same time and place under identical circumstances as the Field Sample and treated exactly the same throughout field and laboratory procedures.

TRIP BLANK (Not Required)

The Trip Blank sample is generally used to evaluate potential cross-contamination from sample shipping and handling procedures. The Field Reagent Blank provides the same quality assurance under this sampling guidance, and therefore the Trip Blank is not a required sample for PFAS monitoring.

IV. SAMPLING ACTIVITIES

Become thoroughly familiar with sample collection and shipping requirements before proceeding to the site to collect water samples. Ensure adequate sample containers are on hand to sample each site, including the FRB per each site.

Keep clear and precise written field records. Make every effort to implement the methods described in this document conscientiously and consistently.

Samples collected from a well to represent the “source sample” should be collected directly from a sample tap on the well discharge line, with the well operating and at a location prior to any treatment. The sample should not be taken from a hose. The well should be allowed to flow either to the system or to waste (if it has not been in operation recently) for at least 15 minutes before sample collection. The tap should be flushed for at least 5 minutes before sample collection.

Use of a laboratory accredited to analyze for PFAS using EPA Method 537.1 is required for samples reported to DDW. A list of laboratories accredited by the California Environmental Laboratory Accreditation Program (ELAP) can be found at this internet site:

https://www.waterboards.ca.gov/water_issues/programs/pfas/docs/ddw%20pfas%20042120.pdf

AVOID SAMPLE CROSS-CONTAMINATION

PFAS compounds are detected at very low levels (parts per trillion). Therefore, there could be materials used by the sampler, or present at the sampling site, that could contaminate the sample. PFAS are used in many personal care products and in food packaging and wrappers, especially fast food and snack products. As a precaution, all persons involved in the sampling event should use every effort to minimize exposure to certain products, ensure proper handwashing at each site and wearing powderless nitrile gloves. Samplers should take efforts to implement the following recommendations when sampling for PFAS:

- Minimize use of the following products on the day of the sample event, preferably **24 hours prior to the event**:
 - Cosmetics, moisturizers, sun-blocks, insect repellants, fragrances, creams, or other personal care products (including hair products). Exceptions: Products that are known to be 100% natural.
- Other items that are likely to contain PFAS and to be avoided include:
 - Paper packaging for food or fast food.
 - New or unwashed clothing.
 - Clothing washed with fabric softeners or dried with anti-static sheets.
 - Synthetic water-resistant/or stain-resistant materials (such as waterproof clothing and shoes such as Gore-Tex), waterproof or coated Tyvek® material (special attention to boots).
 - Teflon® and other fluoropolymer-containing materials (e.g., polyvinylidene fluoride [PVDF], Kynar®, Neoflon®, Tefzel®).
 - Waterproof /treated paper on field notebooks.
 - Waterproof markers (such as Sharpie®, etc.).
 - Chemical or blue ice, which may contain PFAS and may not reduce and/or maintain the temperature of the samples adequately.
- Avoid sampling in the rain if possible (if necessary, please use vinyl or polyvinyl chloride [PVC] rain gear).
- Fill the vehicle with gasoline the day before sampling.
- Avoid consuming food or beverages in the sample site area. If food, drink or other activities, such as smoking, are necessary during the sampling event, first move away from the sample site. Before returning to the sampling site, wash hands thoroughly and put on fresh powderless nitrile gloves.

BEFORE SAMPLING

- Complete materials and supplies checklist (Attachment A).

- Familiarize yourself with each site being sampled.
- Coordinate the sampling event with the accredited laboratory. The laboratory will provide containers, sample preservative, chain-of-custody (COC) forms, ice chest, QC samples, and shipping instructions. Note: It is preferable to receive pre-preserved bottles from the laboratory.
- Bottle labels and the COC should be completed before sample collection with the exception of the sample time.
- Ensure a sufficient number of pre-preserved sample bottles are provided by the laboratory before departure to the site. It is recommended to request extra bottles, in case of damage to bottles during shipping or handling during the sampling event.
- Ensure that the interior of the ice chest is clean.
- Fill the ice chest with wet ice in double-bagged resealable storage bags (not dry ice, blue ice or reusable chemical ice) before departure for the sample collection event. Keep water drained from the ice chest to avoid soaking the containers.
- Ensure an adequate number of resealable bags are available to store all sample bottles.

SAMPLE COLLECTION PROCEDURE

- Sampling taps and plumbing should be free of materials containing Teflon® and other fluoropolymer-containing materials (such as Teflon® tape at plumbing joints). If these cannot be avoided, ensure the tap has been flushed for at least 5 minutes. The presence of Teflon® and other fluoropolymer-containing materials should be clearly noted in the field notebook. Be sure to remove aerators, screens, washers, hoses, and water filters from the tap prior to flushing.
- Wash hands before and after each sampling event.
- Wear powderless nitrile gloves while filling and sealing the sample bottles, using a new pair of nitrile gloves at each sample site.
- Samples should be collected in a wide mouth 250 mL polypropylene or high-density polyethylene (HDPE) bottle (provided by the laboratory) fitted with a polypropylene or HDPE screw cap.
- Each bottle should be preserved before sample collection with 5 g/L Trizma®³ unless the preservative has already been added to the bottles by the laboratory.

³ Trizma® is a buffering agent and removes free chlorine.

- Ensure that the sample container is labeled appropriately, check that the label ID number on the sample container matches the COC form.
- Indelible pens that are ballpoint or gel and pencils are acceptable to use to add the sample collection times on the labels and the COC.

FRB Procedure:

- Collect the FRB prior to the collection of the Field Sample and Field Duplicate.
- At the sampling site, the sample personnel must open the empty FRB sample bottle, pour the pre-preserved PFAS-free reagent water into the sample bottle, and seal and label this bottle as the FRB. Record the FRB identification number on the COC form.
- The FRB is shipped back to the laboratory along with the site samples. The empty container that the field reagent water was poured out of must also be shipped back to the laboratory in the same shipment.

Field Sample & Field Duplicate Procedure:

- Activate the well and flush until the water temperature has stabilized, or until a minimum of one well casing volume has been flushed out. **Wells should be allowed to flow for a minimum of 15 minutes** before sampling to ensure that the sample reflects the water quality of the source. The **sample tap should be flushed for a minimum of 5 minutes** to ensure the impact of local sources of PFAS cross-contamination, such as Teflon® tape and valve seats, are minimized.
- Reduce the flow to a slow laminar stream to reduce air entrainment and overfilling of the bottle.
- Uncap the sample bottle. Do not place the bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.
- Fill the sample bottle, taking care not to flush out the sample preservation reagent. Samples do not need to be collected headspace free, but a volume of 250 mL is necessary for the sample analysis. Do not overfill.
- After collecting the sample(s), cap the bottle(s) and gently agitate by hand until preservative is dissolved.
- The Field Duplicate should be collected in the same manner as the Field Sample. Preferably, you may use a container with twice the volume necessary to fill the sample bottles. Aliquots of this volume are then equally

distributed in two sets of sample containers for the Field Sample and Field Duplicate. As a result, there are two equal volumes of sample collected from one sampling location. In this case two bottles with 250 ml volume.

- Place the sample bottle(s) in individual re-sealable plastic bags (provided by the laboratory), and then into the ice chest with ice surrounding the bottles.
- A two-person sample team is recommended: One team member obtains the samples, and the other team member records the samples on the COC form with the sample collection information. If only one person is conducting the sampling, ensure care is taken to properly record all samples on the COC, and follow all the precautions noted in this guidance.
- Record field site observations in the field notebook (such as types of pipes and fittings, time well operated prior to sample, site characteristics, atmospheric conditions, personal items such as whether a break was taken for food, etc.). Take pictures documenting the specific conditions encountered and how the sample was collected. Record this information at the time of sampling.

Table 1 shows the sampling summary information for PFAS

Table 1. PFAS Sample Summary Information

Parameters	Minimum Requirements
Sample Volume	(2)x250 mL
Container/cap	Polypropylene or HDPE bottle/screw cap
Sample preservation	Trizma®
Field Reagent Blank (FRB)	One per sample site
Field Duplicate (FD)	One per sample site
Temperature	
After sample collection	<10°C (50°F) within 48 hours but not frozen
Sample stored	<6°C (42.8°F) but not frozen
Holding Time	
Extraction	Within 14 days of collection
Analyses	Within 28 days of extraction
Minimum Reporting Limit (MRL)	Report MRL with analytical results

AFTER SAMPLING

All team members coming out of the site sampling area must immediately conduct personal decontamination.

- Remove your gloves and place them in a sealable plastic bag to be disposed at the end of the sample collection.
- Wash your hands after sampling.

SAMPLE SHIPPING

- Samples should be stored in ice chests at least 1/3 filled with wet ice⁴ which do not exceed 10°C (50°F) until analyzed at the laboratory. If immediate delivery to the laboratory is not possible, samples should be stored at 10°C (50°F) while enclosed in their individual sealed bag but must not be frozen or stored with blue ice/chemical ice. Use fresh ice for packaging and shipping.
 - Samples must arrive at the laboratory within 48 hours of sampling and at a temperature between 10°C (50°F) and 0°C (32°F) but not frozen.
 - If samples are received at the laboratory more than 48 hours after sampling, they must be between 6°C (42.8°F) and 0°C (32°F) but not frozen.
- Pack the bottles (which are placed inside sealable plastic bags provided by the laboratory) upright in the ice chest. Ensure that the bottles cannot move sideways at all. Any extra space around the bags should be packed with ice to 1/3 the depth of the ice chest.
- Put additional ice inside of double plastic bags and place these on top of the bottles.
- The COC form will accompany all samples and be filled out at the same time samples are collected. The COC form is an integral part of sample quality assurance/QC; each ice chest should include a COC.
 - Ensure that the COC is complete and ready to be signed by shipping company personnel or laboratory courier prior to sealing the ice chest. Retain the sender's copy.
 - Place the COC in a sealed plastic bag (1 gallon) inside of the cooler.
 - NOTE: The general information in the COC could be filled out in advance of the field sample event

⁴ The use of chemical or blue ice is not recommended, as it may not maintain the necessary temperature of the samples during the shipping process, and it may contain PFAS.

- Seal the ice chest firmly with PFAS-free shipping tape, wrapping it around multiple times.
- Attach plastic overnight carrier tags to the ice chest's handle, retain the marked sender's copy for the record tracking number.
- Provide the shipping information to the laboratory and communicate the potential time of arrival of the samples.

V. LABORATORY METHODS AND DATA REPORTING

The analytical method used to assess the presence of PFAS in drinking water is EPA Method 537.1 (November 2018). This is the only method acceptable to DDW for drinking water analyses. Use of a laboratory accredited for this method is required for samples to be reported to DDW.

A list of laboratories that are ELAP accredited for EPA Methods 537.1 can be found at this link:

https://www.waterboards.ca.gov/water_issues/programs/pfas/docs/ddw%20pfas%20042120.pdf

Laboratories accredited by ELAP are certified to analyze for the entire suite of target analytes listed in the method. For sampling intended to be reported to DDW, the 18 analytes must be reported with each set of sample results. Reporting to DDW must be through the EDT (Electronic Data Transfer) process. The water utility should obtain the hard copy results that include the QC information and make it available to DDW on request.

This guidance recommends the collection of Field Duplicate. If the laboratory analyzes the Field Duplicate for any reason, the results must be reported by EDT along with the Field Sample results. The laboratory must report the FRB and the FD (if analyzed) using the Storet Codes shown in Table 2. The laboratory should report results down to the minimum reporting limit (MRL) for each PFAS analyte with each sample.

Table 2. EPA PFAS Method and associated with the Storet Codes

**EPA 537.1
18 Analytes Storet Code**

Analytes	Field Sample	Field Reagent Blank	Field Duplicate
PFBS	C2801	F2801	D2801
PFHpA	C2802	F2802	D2802
PFHxS	C2803	F2803	D2803
PFNA	C2804	F2804	D2804
PFOS	C2805	F2805	D2805
PFOA	C2806	F2806	D2806
NEtFOSAA	C2807	F2807	D2807
NMeFOSAA	C2808	F2808	D2808
PFDA	C2809	F2809	D2809
PFDoA	C2810	F2810	D2810
PFHxA	C2811	F2811	D2811
PFTA	C2812	F2812	D2812
PFTTrDA	C2813	F2813	D2813
PFUnA	C2814	F2814	D2814
HFPO-DA	C2815	F2815	D2815
9Cl-PF3ONS	C2816	F2816	D2816
11Cl-PF3OUdS	C2817	F2817	D2817
ADONA	C2818	F2818	D2818

ATTACHMENT A: Recommended Materials and Supplies Checklist

- Sampling procedure document (Methods for sampling)
- Site location information
- Chain-of-custody forms
- Extra sample labels for each sample
- Sample bottles
 - Number of sites to be sampled: _____
 - Number of Field/Duplicate Sample bottles: _____
 - Number of Field Reagent Blanks: _____
- Trizma® (preservative, unless added to the bottles by the laboratory)
- Cooler (ice chest) and ice
- Packing material if samples are to be shipped
- Field notebook, but not waterproof paper
- Office supplies (indelible ballpoint or gel pens, PFAS-free tape)
- Powderless nitrile gloves, M, L or XL
- Paper towels
- Scissors/cutter
- Resealable bags [(jumbo (2.5 gal); large (1 gal); and medium (1quarter)]
- Alconox® or Liqui-Nox® soap
- Deionized water (DI)
- Folding table
- Field clipboard
- Overnight carrier shipping forms
- Temperature/pH/EC meter
- Safety glasses
- Camera and charger – ensure time and date stamps are on the digital camera image