



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

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, consumer products, and emergency fire response. These synthetic compounds are very persistent in the environment due to the physical and chemical characteristics. 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, USEPA issued a lifetime health advisory for PFOS and PFOA in drinking water, advising water systems that they should notify their customers of the presence of concentrations over 70 parts per trillion (ppt) of PFOS and PFOA, individually or combined, in water supplies. Further, on June 15, 2022, USEPA issued interim updated drinking water health advisories for PFOA and PFOS. The interim health advisory for PFOA is 0.004 ppt and 0.02 ppt for PFOS. At this time USEPA also released the final health advisory for Perfluorobutane sulfonate (PFBS) of 2,000 ppt, and 10 ppt for GenX². USEPA recommended that the notification of customers include information on the increased risk to health, especially for susceptible populations.

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 Hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt are known as GenX chemicals

On July 13, 2018, the State Water Resources Control Board’s (SWRCB) Division of Drinking Water (DDW) issued a drinking water notification level³ (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 levels⁴ of 10 ppt for PFOA and 40 ppt for PFOS. This revision is based on updated health recommendations by the California Environmental Protection Agency’s Office of Environmental Health Hazard Assessment (OEHHA). On March 5, 2021, DDW issued a drinking water notification level for PFBS of 0.5 ppb and a response level of 5 ppb. Furthermore, on October 31, 2022, DDW release a proposed NL for Perfluorohexane Sulfonic Acid (PFHxS) of 3 ppt and a response level of 20 ppt. Table 1, shows the chronological actions taken by SWRCB-DDW on PFAS. Currently, OEHHA is developing a public health goal (PHG)⁵ for PFOA, PFOS and other PFAS compounds. Establishing a PHG is the first step in the development of a drinking water standard.

Table 1. Shows the chronological actions taken by the SWRCB-DDW on PFAS

PFAS Analyte	Notification Level (ng/L)	Response Level (ng/L)	Issue Date
PFOA	14	70	May 13, 2018
PFOS	13		
PFOA	5.1	70	August 22, 2019
PFOS	6.5		
PFOA		10	February 6, 2020
PFOS		40	
PFBS	0.5 ppb	5 ppb	March 5, 2021
PFHxS	3	20	October 31, 2022

³ Notification levels are health-based advisory levels established by DDW for chemicals in drinking water that do not have a maximum contaminant level.

⁴ 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 delivery to public.

⁵ Public Health Goal is the level of a chemical contaminant in drinking water that does not pose a significant risk to health. PHGs are not regulatory standards.

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 (March 2020), and EPA 533 (December 2019).

II. PURPOSE OF SAMPLING GUIDANCE

Due to the prevalence 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 to 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 system. 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, 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 sample bottle filled by the laboratory with PFAS-free water and shipped to the site with the other sample bottles. For each FRB, a second sample bottle containing only the preservative must also be included. At the sample site, the sampler will open the FRB and pour the preserved reagent water into the empty sample bottle. An FRB must be handled along with each sample set. The sample set includes samples collected from the same sample site and at the same time. The FRB is collected 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/ Required)

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 the same throughout field and laboratory procedures. The FD gives a measure of the precision associated with sample collection, preservation, storage, and laboratory performance. When using EPA method 537.1, the FD is recommended. When using the EPA 533 the FD is required to be collected to support potential repeat analyses, such as confirmation results or analyses associated with QC.

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 or EPA 533 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: [PFAS Laboratories \(ca.gov\)](https://www.waterboards.ca.gov/ELAP/PFAS_Laboratories)

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 except for 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®⁶ or ammonium acetate depending on the EPA method selected. Most of the time the laboratories add to the bottles the preservative before shipping.
- 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.

⁶ Trizma® is a buffering agent and removes free chlorine.

- At the sampling site, the sample personnel must open the FRB sample bottle, pour the pre-preserved PFAS-free reagent water into the empty 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 2. PFAS Sample Summary Information

Parameters	Minimum Requirements
Sample Volume	(2)x250 mL
Container/cap	Polypropylene or HDPE bottle/screw cap
Sample preservation	Trizma® for EPA 537.1 Ammonium Acetate for EPA 533
Field Reagent Blank (FRB)	One per sample set
Field Duplicate (FD)	One per sample set
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 as stated on EPA 537.1 and within 28 days of collection in EPA 533
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 ice⁷ 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 or 6°C (42.8°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.

- 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.

⁷ 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.

- 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 methods used to assess the presence of PFAS in drinking water are EPA Method 537.1 (March 2020) and EPA 533. These methods are acceptable to DDW for drinking water analyses. Use of a laboratory accredited for these methods are required for samples to be reported to DDW.

A list of laboratories that are ELAP accredited for EPA 537.1 and EPA 533 methods can be found at [PFAS Laboratories \(ca.gov\)](#):

Laboratories accredited by ELAP are certified to analyze for the entire suite of target analytes listed in the methods. Table 3 shows the analyte codes for PFAS compounds. For sampling reported to DDW under EPA 537.1, the 18 analytes must be reported with each set of sample results. For EPA 533 Method there are 25 analytes that need to be reported. Reporting to DDW must be through the EDT (Electronic Data Transfer) process. The data is submitted through the California Laboratory Intake Portal (CLIP). The water system should obtain the hard copy results that include the QC information and make it available to DDW on request.

When FD and FRB are analyzed, the results must be reported by EDT along with the Field Sample results. To differentiate the results, it is recommended to add FB and FD to the end of the Laboratory Sample ID, as it is described in [California Laboratory Intake Portal Technical Documentation for EDP/EDD](#). The laboratory should report results down to the minimum reporting limit (MRL) for each PFAS analyte with each sample.

Table 3. PFAS in Drinking Water and associated with the Analyte Codes

CAS Number	Analytes	Analyte Code ⁸
375-73-5	PFBS	2801
375-85-9	PFHpA	2802
355-46-4	PFHxS	2803
375-95-1	PFNA	2804
1763-23-1	PFOS	2805
335-67-1	PFOA	2806
335-76-2	PFDA	2807
307-55-1	PFDoA	2808
307-24-4	PFHxA	2809
376-06-7	PFTA	2810
72629-94-8	PFTTrDA	2811
2058-94-8	PFUnA	2812
763051-92-9	11CL-PF3OUdS	2813
756426-58-1	9CI-PF3ONS	2814
919005-14-4	ADONA	2815
13252-13-6	HFPO-DA	2816
2991-50-6	NEtFOSAA	2817
2355-31-9	NMeFOSAA	2818
375-22-4	PFBA	2819
27619-97-2	6:2FTS	2820
757124-72-4	4:2FTS	2821
39108-34-4	8:2FTS	2822
377-73-1	PFMPA	2823
2706-90-3	PFPeA	2824
863090-89-5	PFMBA	2825
113507-82-7	PFEESA	2826

⁸ Analyte Code are designated by EPA



CAS Number	Analytes	Analyte Code ⁸
151772-58-6	NFDHA	2827
2706-91-4	PFPeS	2828
375-92-8	PFHpS	2829

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® or ammonium acetate depending on the method used (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