



## **DRINKING WATER SAMPLE COLLECTION FOR PER AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) SAMPLING GUIDANCE**



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**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](https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html)

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PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS)  
SAMPLING GUIDANCE  
SWRCB Division of Drinking Water  
April 2019**

## **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 drinking water sampling on per and poly-fluorinated alkyl substances.

Per- and polyfluorinated alkyl substances (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 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 total combined PFOS and PFOA 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 Division of Drinking Water 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).

The collection of PFAS drinking water data can support future regulatory determinations and other actions to protect public health. The analytical methodologies used to assess the presence of PFAS in drinking water are EPA Method 537.1 (released in November 2018), and EPA Method 537 Revision 1.1 (2009). These are the only methods validated by the USEPA and acceptable to the Division of Drinking Water 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 must be implemented to prevent cross-contamination of a field sample. 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 collection of a valid sample. Results from sampling of drinking water sources should be reported electronically by the analyzing laboratory to the Division of Drinking Water.

### III. QUALITY CONTROL FIELD SAMPLE TYPES

Due to the low detection limits of PFAS in the drinking water, the Division of Drinking Water 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 time that the field sample (source sample) is collected. These special quality control sample techniques must be discussed with the laboratory to ensure proper sample containers and materials are on hand when sampling begins in the field.

#### **FIELD SAMPLE (Required)**

The Field Sample is the sample collected from the source at a location prior to any treatment.

#### **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 and consists of a sample bottled filled at the sample site using reagent water provided by the laboratory. FRB must be collected at each sample site (i.e., each source being sampled) and stored in the ice chest used to store and transport samples. The laboratory will provide the FRB sample bottle, the reagent water and the preservative (if not already added to the sample bottle).

#### **FIELD DUPLICATE (Recommended)**

The Field Duplicate is a second 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 trip blank and one field blank per site.

Keep clear and precise written field records. Implement the methods described in this document conscientiously and consistently. Departure from these procedures requires documentation in the field notebook.

All samples shall 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 well should be flushed either to the

system or to waste (if it has not been in operation recently) at least 15 minutes before sample collection.

Use of a laboratory accredited to analyze for PFAS using EPA Method 537.1 or EPA Method 537 Revision 1.1 is required for samples reported to the Division of Drinking Water. 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/drinking\\_water/certlic/drinkingwater/PFOA\\_PFOS.html](https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/PFOA_PFOS.html)

### **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 minimize exposure to the following products, and ensure proper hand washing at each site and wearing powderless nitrile gloves:

- Minimize use 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 need to be avoided include:
  - Pre-packaged food, fast food or items wrapped in aluminum foil
  - 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
  - Waterproof /treated paper on field notebooks
  - Waterproof markers (such as Sharpie®, etc.). Indelible pens that are ball point or gel and pencils are acceptable.
  - Adhesive paper products (such as Post-It ®Notes or scotch tape)
  - Sealable bags (e.g., zip-lock ® plastic bags) that are not provided by the laboratory. (Note: only ultra-clean polypropylene or HPDE material sealable bags are allowed)
  - Chemical or blue ice, which may contain PFAS and may not reduce and maintain the temperature of the samples adequately
- Avoid sampling during rain if possible (if necessary please use, vinyl or PVC rain gear)
- Fill gasoline in the vehicle the day before sampling
- No food or beverage should be consumed 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 preservation, Chain of Custody (COC) forms, ice chest, quality control samples, and shipping instructions.
- Bottles should be labeled before sample collection.
- Ensure sufficient number of sample bottles and preservatives before departure. It is recommended to request extra bottles, in case of damage to bottles during shipping or handling during the sampling event.
- Ensure that the ice chest interior is clean.
- Fill the ice chest with wet ice (not dry ice, blue ice or reusable chemical ice) before departure for the sample collection event. Keep water drained from ice chest to avoid soaking the containers.
- Ensure an adequate number of sealable bags are available to store all sample bottles.

### **SAMPLE COLLECTION PROCEDURE**

- Sampling taps and plumbing should be free of materials containing Teflon® (such as Teflon® tape at plumbing joints). If these cannot be avoided, ensure the tap has been flushed for at least 5 minutes.
- Wash hands with prepared Alconox® or Liquinox® soap and deionized water before and after each sampling event.
- Wear nitrile gloves while filling and sealing the sample bottles, using a new pair of nitrile gloves at each sample site.
- Samples must be collected in a wide mouth 250 mL polypropylene bottle (provided by the laboratory) fitted with a polypropylene screw cap.
- Each bottle needs to be preserved before sample collection with 5 g/L Trizma®<sup>1</sup>, unless the preservative has been added to the bottles by the laboratory.
- Ensure that the sample container is labeled appropriately, check that the label ID number on the sample container matches the COC form.
- Field Reagent Blank (FRB) Procedure:

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<sup>1</sup> Trizma® is a buffering agent and removes free chlorine.

- Collect the FRB prior to collection of the Field Sample and Field Duplicate.
- At the sampling site, the sample personnel must open the empty FRB sample bottle, pour the reagent water into the sample bottle, 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. It is recommended that **wells 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 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.
- The Field Duplicate should be collected immediately following collection of the Field Sample, or as the laboratory instructs.
- After collecting the sample(s), cap the bottle(s) and gently agitate by hand until preservative is dissolved.
- Place the sample bottle(s) in an individual sealed plastic bag (provided by the laboratory), and then into the ice chest with ice surrounding the bottles. (Note: only ultra-clean polypropylene or HPDE material sealed bags are allowed).
- A two-person sample team is recommended: One team member obtains the samples, and other records the samples in the COC form with the sample collection information. If only one person is conducting the sampling, wearing layered nitrile gloves that must be discarded from the transition from dirty hands to clean hands. Ensure care is taken to properly record all samples on the COC, and conduct all the precautions noted in this guidance.
- Record field site observations in the field notebook (not waterproof) - 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. PFAS Sample Summary Information

Parameters	Minimum Requirements
Sample volume	250 mL
Container/cap	Polypropylene bottle/screw cap
Sample preservation	Trizma <sup>®</sup>
Field Reagent Blank	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 with prepared Alconox<sup>®</sup> or Liqui-Nox<sup>®</sup> soap and rinse with deionized water.

### SAMPLE SHIPPING

- Samples should be stored in ice chests at least 1/3 filled with wet ice<sup>2</sup> and do not exceed 10°C (50°F) until analyzed at the laboratory. If the immediate delivery to the laboratory is not possible, samples should be stored or below 6°C (42.8°F) while independently

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<sup>2</sup> The use of chemical or blue ice is not recommended, as it may contain PFAS and may not maintain the necessary temperature of the samples during the shipping process

enclosed to their individual sealed bag provided but must not be frozen or stored in blue ice/chemical ice. Use fresh ice for packing 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.
- Samples stored in the lab must be held at or below 6°C (42.8°F) until extraction. Extraction should be as soon as possible but must be extracted within 14 days.
- 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 QA/QC, each ice chest should include a COC.
  - Ensure that the COC is complete and ready to be signed by shipping company personnel 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. The use of Uline Strapper Tape is recommended to secure the ice chest.
- 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 methodologies used to assess the presence of PFAS in drinking water are EPA Method 537.1 (released in November 2018), and EPA Method 537 Revision 1.1 (2009). These are the only methods validated by the USEPA and acceptable to the Division of Drinking Water (DDW) for drinking water analyses. Use of a laboratory accredited for either of these methods is required for samples to be reported to DDW. The primary differences between EPA Methods 537 Rev 1.1 and 537.1 are the number of constituents and the method detection levels. These are noted in the Table 2 below. Note that laboratories seeking accreditation after April 3, 2019, can only request accreditation for EPA Method 537.1. DDW is phasing out Method 537 Rev 1.1 as an acceptable method for PFAS in drinking water.

Laboratories accredited by ELAP are certified to analyze for the entire suite of analytes in each method. For sampling intended to be reported to DDW, all 14 or 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. The results are due to DDW on the 10<sup>th</sup>

of the month following the date when analysis is completed by the laboratory or reported by the laboratory to the water system.

This guidance recommends the collection of Field Duplicate. If the laboratory analyzes the Field Duplicate for any reason, the results must be reported EDT.

Table 2. EPA Method target analytes and method detection limits

EPA Method 537 Rev 1.1* (14 PFAS analytes)		EPA Method 537.1* (18 PFAS analytes)	
Analyte	Detection Limit <sup>[1]</sup> (ng/L)	Analyte	Detection Limit <sup>[1]</sup> (ng/L)
PFBS	3.1	PFBS	1.8
PFHxA	1.6	PFHxA	1.0
PFHpA	0.5	PFHpA	0.71
PFHxS	2.0	PFHxS	1.4
<b>PFOA</b>	<b>1.7</b>	<b>PFOA</b>	<b>0.53</b>
<b>PFOS</b>	<b>1.4</b>	<b>PFOS</b>	<b>1.1</b>
PFNA	0.7	PFNA	0.7
PFDA	0.7	PFDA	1.6
NMeFOSAA	6.5	NMeFOSAA	2.4
PFUnA	2.8	PFUnA	1.6
NEtFOSAA	4.2	NEtFOSAA	2.8
PFDoA	1.1	PFDoA	1.2
PFTTrDA	2.2	PFTTrDA	0.72
PFTA	1.7	PFTA	1.1
		HFPO-DA	1.9
		ADONA	0.88
		9Cl-PF3ONS	1.4
		11Cl-PF3OUdS	1.5

\*in reagent water

### 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 & de-chlorinator, 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 ball point pens, PFAS free tape)
- Uline Strapper Tape
- Powderless nitrile gloves
- Paper towels
- Scissors/cutter
- Resealable bags [(jumbo (2.5 gal); large (1 gal); and medium (1quarter)] ultra-clear Polypropylene or HPDE material (only).
- 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 digital camera image