

Per- and Polyfluoroalkyl Substances (PFAS) Laboratory Testing Primer for State Drinking Water Programs and Public Water Systems

This document provides guidance and an overview of options and issues for state drinking water programs that are associated with testing for Per- and Polyfluoroalkyl Substances (PFAS) in water samples collected from public water systems. The document provides information on:

- 1) Selecting an analytical method;
- 2) Finding a qualified laboratory;
- 3) Specifying a list of compounds and the form that each PFAS needs to be reported in;
- 4) Specifying reporting limits;
- 5) Technical issues that cause variability in testing results;
- 6) Sample collection procedures;
- 7) Interpreting results; and
- 8) USEPA's ongoing work to develop new analytical methods

Topic 1: Selecting an Analytical Method

Different laboratories provide different options for measuring PFAS in drinking water. These include:

- 1) EPA Method 537 Rev. 1.1 - Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)(2009);
- 2) EPA Method 537.1 Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) Version 1.0 (2018); and
- 3) Determination of PFAS Using Isotope Dilution - The name of the lab method varies from laboratory to laboratory. Although this lab method is completely different from EPA Method 537 Rev. 1.1, some laboratories refer to their isotope dilution method as "EPA 537 modified."

Both analytical methods provide reliable results if a qualified laboratory is used. However, the water system should follow any requirements or guidance from their state drinking water program, as some individuals and entities have expressed varying preferences over which analytical method to use.

Comparing USEPA Method 537 Rev 1.1, USEPA Method 537.1 and Isotope Dilution

Until USEPA issued Method 537.1 in November of 2018, USEPA Method 537 Rev 1.1 and was the only analytical method approved by USEPA and provided a single verified methodology that can be used by any laboratory. The use of consistent methodologies among laboratories is desirable because it reduces variability introduced by using alternative analytical methods. The method guidelines

provide some flexibility in the liquid chromatography tandem mass spectrometry (LC-MS/MS). This flexibility could optimize certain aspects of the method, such as column chemistry, gradient profile, and MS/MS transitions. However, USEPA Method 537 currently only applies to fourteen compounds and is only applicable to a drinking water matrix. While the cost per sample can vary, the cost per sample analyzed via USEPA Method 537 is typically \$175-\$275 per sample and is generally 25%-50% less than the cost per sample analyzed via isotope dilution.

In November 2018, USEPA issued Method 537.1 which updates Method 537 Rev 1.1 to test for an additional four PFAS in drinking water, including the GenX chemical hexafluoropropylene oxide dimer acid (HFPO-DA), 11-chloroeicosafuoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS), 9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS), and 4,8-dioxa-3H-perfluorononanoic acid (ADONA)]. USEPA Method 537.1 also achieves lower reporting and detection limits than USEPA Method 537 Rev 1.1. As USEPA Method 537.1 was just recently released, very few commercial laboratories are accredited for or utilize this method at this time. The cost per analysis will likely be slightly higher than Method 537 Rev. 1.1.

Isotope dilution analytical techniques are generally considered to be the best analytical approach for PFAS for drinking water and other media. This method would probably be recommended by more regulatory agencies if there was an USEPA approved method that could be used by all laboratories. Samples that are analyzed by isotope dilution are spiked with a known amount of isotopes that are substantially the same as each of the PFAS being analyzed. The water sample is then analyzed and the concentration of the PFAS compound and the added isotope is estimated using standards for each compound. If the measured concentration of isotope that was added to the sample is above or below the actual amount added, the PFAS result is corrected by a proportional amount. The benefit

Method Comparison Study - New Hampshire Department of Environmental Services (NHDES)

NHDES conducted a split sample study on water samples collected from private and public water systems. The water samples were analyzed by the same laboratory using both isotope dilution and Method 537. The measured concentration of PFAS samples analyzed by Method 537 and isotope dilution were similar, meaning that matrix interference was not an issue for the samples that were included in this study.

of making the correction is that the analysis can account for analytical errors associated with the matrices of the samples. Water samples possess chemical and physical properties other than just the concentration of PFAS, and these properties can alter the response of the instrument that is measuring PFAS and produce errors. Isotope dilution corrects for matrix interferences or errors. For this reason, isotope dilution is often utilized on other media such as wastewater, solids and groundwater samples.

USEPA Method 537.1

Field Blanks and USEPA Method 537

It is important to note, that EPA Method 537 Rev 1.1 requires water systems to collect a field blank at each sampling location. This requirement addresses the concern that the sample collection process could introduce PFAS contamination because of the ubiquitous nature of these compounds in the environment coupled with the part-per-trillion reporting limits that are utilized. Collection of QA/QC (field blank, trip blank, and method blank) samples can be useful to assess field contamination from

materials such as Tyvek PPE that might include PFAS residues. However, with sound sampling protocols, PFAS are not routinely detected in field blanks associated with the sampling of public water systems. This means that the sample collection process is not regularly introducing contaminants into the water sample and thus a field blank only needs to be collected when there is a detection in a corresponding sample. Some laboratories performing EPA Method 537 Rev. 1.1 continue to request a field blank with each water sample and charge for both the drinking water sample and the field blank sample which may double the overall cost. The cost of running the field blank should be included in the cost of the analysis, not added on for each field blank sample.

Topic 2: Finding a Qualified Laboratory

A water system should check with their state drinking water program to see if their state has established a list of approved, certified or accredited laboratories for completing PFAS analyses. If the state has not established a list, water systems can identify laboratories that have been accredited by:

- 1) National Environmental Laboratory Accreditation Program (<http://lams.nelac-institute.org/Search>) by selecting a common PFAS chemical such as perfluorooctanoic acid (PFOA) under the “Analyte” pulldown tool; and
- 2) The Department of Defense <https://www.denix.osd.mil/edqw/accreditation/accreditedlabs/> by selecting EPA 537 or EPA 537 Mod under the “Method” pull down tool.

The laboratories that water systems routinely do business with may already have or can establish subcontracts with laboratories listed with the two accreditation programs. State drinking water programs should also consider the advantages and challenges associated with using state laboratories.

Topic 3: Which PFAS Chemicals Should Be Analyzed?

A water system should check with their state drinking water program to see if their state has established a list of PFAS compounds that should be analyzed for. There are thousands of PFAS compounds. Commercial laboratories can typically analyze for only approximately 6 to 30 compounds. A laboratory may offer multiple options on the number of PFAS compounds that will be reported. If EPA Method 537 is utilized, as many as 14 compounds may be included. If lab methods based on isotope dilution are utilized, the number of compounds could approach 30. Generally, the cost per sample increases when more compounds are measured. However, the cost increase is often relatively minor and is not usually proportional to the increased number of compounds.

Lab analyses that include a longer list of compounds provide more information on how PFAS contamination is impacting drinking water. The additional compounds may assist in fingerprinting sources of contamination. While there may be no health guidance at this time for some of the PFAS compounds that are analyzed for, there may be guidance or toxicity information available in the future.

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Six PFAS (PFOS, PFOA, PFNA, PFHxS, PFHpA and PFBS) were included in USEPA's Third Unregulated Contaminant Monitoring Rule (UCMR3) and for this reason, as a minimum, states and water systems should always consider including all six compounds in the analysis requested from the lab. Compounds included in the UCMR sampling were selected based on current research pertaining to potential occurrence and health risk factors. Three additional PFAS (PFBA, PFPeA and PFHxA) have been regularly detected in drinking water systems throughout the nation and it is suggested that these compounds be included along with the six UCMR compounds (PFOS, PFOA, PFNA, PFHxS, PFHpA and PFBS) in the PFAS analysis.

Labs Should Report PFAS Compounds in the Acid Form

It is critical that laboratories be instructed to report PFAS compounds in the acid form and that the PFAS Chemical Abstracts Service (CAS) number and compound name shown on written reports and electronic data deliverables also reflect the acid form of the PFAS compound.

USEPA health advisories for PFOA and PFOS are based on the concentration of these two compounds in the acid form. A review of hard copy lab reports and electronic data deliverables across multiple commercial laboratories have shown that: 1) Laboratories reports PFAS results for some compounds in the salt form; 2) Laboratory reports and electronic data deliverables sometimes have discrepancies whereby the CAS number reflects the salt form of a PFAS compound but the chemical name in the report or data file reflects the acid form and vice-versa. While sometimes the concentration of a PFAS compound in the salt form and acid form are substantially the same, in some instances, such as in the case for PFOS, there can be up to an 8% difference in the analytical result when comparing the salt form to the acid form of the compound. Ensuring labs report the acid form of the PFAS compound and include the correct nomenclature and CAS number will ensure that the results are reported in the form that can be associated with health advisories as well ensuring the integrity and consistency of the PFAS data record.

Drinking water sources that are located near fluoropolymer manufacturing facilities should potentially be tested for two chemicals that are used to manufacture PFAS chemicals that replaced PFOA. These two compounds are referred to as GenX and Adona. GenX and Adona are much more likely to be detected in water where fluoropolymers are manufactured as these chemicals are used in the fluoropolymer manufacturing process but are not substantially present in the final products. For this reason, these two compounds are less likely to be detected where chemicals containing PFAS are actually used. Commercial labs require a separate test to analyze for both GenX and Adona. The price per sample to obtain results for just GenX and Adona is generally similar to a PFAS analysis that includes a full panel of compounds.

The PFAS analyses described above may only quantify a fraction of the PFAS, PFAS precursors and/or total organic fluorine contamination that may be present when PFAS is detected in drinking water. Some water systems have worked with research laboratories to more fully quantify the potential for other highly fluorinated chemicals in drinking water. This work generally exceeds any regulatory guidance or requirements. More information on these testing methods can be found in this factsheet prepared by the Interstate Technology Regulatory Council Factsheet titled, "[Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances \(PFAS\).](#)"

Topic 4: What Reporting Limits Should Be Required?

Laboratory analytical methods with reporting limits (RL) of at least 2-4 nanograms per liter (ng/L) parts-per-trillion (ppt) should be utilized. Many commercial labs are achieving reporting limits of less than 1 ng/L ppt. Additional health studies are rapidly evolving and some states have determined that PFAS health advisory concentrations in drinking water should be based on the additive effect of PFAS compounds. Obtaining water quality results with low RL will improve the utility of the data in the event health guidance or standards are changed or that the state you are in develops health guidance or standards based on the additive effects of PFAS.

It is important to understand the difference between a reporting limit (RL) and a detection limit (DL). An RL or reporting detection limit is the limit of detection in which the concentration of a contaminant can be reliably quantified. In contrast, the DL or method DL is lower than the RL and is below the point of calibration such that results reported below the RL are unreliable and as such, must be qualified as estimated values by carrying a "J" or "E" (NELAP) qualifier/flag.

Typical PFAS Reporting Limits	
Method 537 Rev 1.1 (2009)	Range from 2.9 to 14 ng/L
Method 537.1 (2018)	Range from 0.53-6.3 ng/L
Isotope Dilution	Varies by lab and compound but can be: <ul style="list-style-type: none">• Below 1 ng/L for some compounds and• Up to 3 ng/L for others

Topic 5: Technical Issues that Cause Variability in Testing Results

Sample Results Prior to September 2016 May Be Under Reported

Many PFAS compounds can be present as a linear isomer or a branched isomer. When a compound can have the same chemical formula, but a different arrangement of atoms, it is considered an isomer. Initially, DuPont produced PFOA using telomerization processes that produced PFOA and other PFAS only in the linear isomer form. 3M later produced PFAS compounds using electrochemical processes that produced PFOA that contained linear and branched isomers at the ratio of 70% linear isomer to 30% branched isomer. [SEE PAGE 538 <https://www.atsdr.cdc.gov/toxprofiles/tp200-c5.pdf>]

In September 2016, USEPA issued a technical advisory to laboratories utilizing Method 537 that the concentration of both the linear and branched isomers of PFOA need to be quantified and combined to determine the total PFOA concentration. Prior to the issuance of the technical advisory, USEPA Method 537 did not stipulate this requirement and some laboratories only reported PFOA in the linear isomer form, while others were reporting PFOA in the linear and branched isomer form. This means some PFOA analyses completed prior to September 2016 may be underreported by as much as 30%.

Expected Accuracy of Testing Results and Common Biases

In a recent proficiency testing program that included four commercial labs contracted by the New Hampshire Department of Environmental Services, USEPA established accuracy acceptance limits of 50% to 150% of the expected value meaning the expected accuracy of PFAS analyses using Method 537 or isotope dilution is +/-50%. The results of the proficiency testing programs determined: 1) Testing

results for split samples sent to the laboratories were generally similar; 2) Testing results for split samples analyzed using Method 537 and isotope dilution were similar; 3) Results were generally accurate within 20% of the expected value but were almost always 20% underreported from the expected value; and 4) Occasional significant over or under reporting of PFAS concentrations occurred.

Existing PFAS analytical methods use an “extraction” process to isolate the PFAS in an aqueous sample so that it can be then measured by the instrument. This can be accomplished by using solvents to concentrate the compounds or an absorbent material to capture PFAS. Extraction methods are designed to minimize losses, but generally are not able to completely extract all PFAS that is in a water sample. Under reporting of PFAS results is likely associated with losses that occur during the analytical extraction process. Proficiency testing for other chemicals such as pesticides which rely on analytical methods that also use extraction processes show similar under reporting outcomes.

Certified Standards Are Source of Variability

Laboratories purchase certified standards for PFAS analytes from different vendors. Certified standards purchased from different sources have been shown to vary by as much as 20%. Additionally, PFAS standards that contain both branched and linear isomers of some PFAS compounds are not available, and laboratories have to estimate the concentration of a PFAS compound in the branched form using the linear standard.

Laboratory Analytical Methods May Vary

Laboratories performing EPA Method 537 utilize the same analytical method and sample container, preservatives and processing protocols because the method developed by USEPA is being applied. Although laboratories are utilizing the same method, some variability may be introduced based on how laboratories interpret chromatograms for the branched isomers because there may be several peaks that are less defined for branched isomers relative to the single pronounced peak associated with a linear isomer.

At this time, USEPA has not issued a laboratory method for isotope dilution. Laboratories using isotope dilution are utilizing proprietary methods developed in-house and sample preparation, analysis, sample container material, preservatives and processing protocols vary from laboratory to laboratory.

Topic 6: Sample Collection Procedures

PFAS is analyzed down to ng/L or ppt on levels opposed to part-per-billion (ppb) or (µg/L) or part-per-million (ppm) or (mg/L) r levels that a typically used for drinking water analyses. Additionally, there are numerous sources of PFAS at any given location due to their wide-spread domestic, commercial and institutional uses. This means that there is a greater potential for introducing PFAS contamination into a drinking water sample during the sample collection process. While in most instances, certified drinking water operators are qualified to sample water systems for PFAS compounds, additional training may be required to ensure that they understand proper PFAS sampling collection procedures.

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Depending on the objective of the sampling, the water sample may be collected after treatment at the entry point to the distribution system or at a raw water sampling tap. Existing water treatment systems generally would not affect the concentration of PFAS in the water unless carbon treatment is in use. If a single entry-point to the distribution system receives an irregular blend water from multiple sources of water, a sampling strategy that characterizes the concentration of PFAS in each potential blend or from each source should be utilized. The plumbing associated with each sampling tap should be examined to ensure Teflon tubing is not in use.

Category	Prohibited Items/Actions that could introduce PFAS Sample Contamination	Allowable Items
Pumps and Tubing	Teflon® and other fluoropolymer containing materials	High-density polyethylene (HDPE), low density polyethylene (LDPE) or silicone tubing
Sample Container Storage	Containers should not come in to contact with carpeting or upholstery inside buildings or vehicles	Containers should be stored in a zip-lock bag and transported in coolers.
Stacked Glassware	Foil should not be used as a layer between stacked glassware	Plain paper
Field Documentation	Waterproof/treated paper or field books, plastic clipboards, non- Sharpie® markers, Post-It® and other adhesive paper products	Plain Paper, metal clipboard, Sharpies®, pens
Clothing	Clothing or boots made of or with Gore-Tex™ or other synthetic water resistant and/or stain resistant materials, Tyvek® material	Synthetic or cotton material, previously laundered clothing (preferably previously washed greater than six times) without the use of fabric softeners
Personal Care Products (for day of sample collection)	Cosmetics, moisturizers, hand cream and other related products	<p>Sunscreens:</p> <ul style="list-style-type: none"> Alba Organics Natural Yes to Cucumbers Aubrey Organics Jason Natural Sun Block Kiss My Face Baby-safe sunscreens ('free' or 'natural') <p>Insect Repellents:</p> <ul style="list-style-type: none"> Jason Natural Quit Bugging Me Repel Lemon Eucalyptus Herbal Armor California Baby Natural Bug Spray BabyGanics <p>Sunscreen and Insect Repellents:</p> <ul style="list-style-type: none"> Avon Skin So Soft Bug Guard-SPF 30
Food and Beverage	Pre-packaged food, fast food wrappers or containers	

The sampling process typically includes running water through the sampling tap for two to three minutes, washing hands and utilizing a new pair of nitrile gloves with each sample. PFAS samples should be collected first. The table on page 7 identifies some categories of items that could introduce PFAS contamination into the sample during the collection process and appropriate alternatives that can be used to avoid inadvertent sampling contamination.

Field blank samples and trip blank samples should be collected periodically. A trip blank consists of a bottle of water verified as containing no detectable levels of PFAS that is provided by the laboratory. The bottle travels with the PFAS sample containers from the lab to the location of the sampling and then is returned back to the lab with the water samples. The trip blank is analyzed to assess the potential for PFAS contamination being introduced during the shipping and storage of the sampling containers.

A field blank also consists of a bottle of water verified as containing no detectable levels of PFAS that is provided by the laboratory. The bottle travels from the lab to the location of the sampling. At the location where drinking water samples are collected from a sampling tap, the contents of the field blank bottle are transferred into a sampling bottle after the sampler washes his/her hands and wears a new pair of nitrile glove. The field blank is analyzed to assess the potential for PFAS contamination being introduced during the sampling process.

If there are detections of PFAS compounds in trip or field blanks, it is important to assess if the same compounds were detected in lab blanks, which are generally included in all laboratory analyses at no additional cost. If PFAS are detected in lab blanks, then PFAS detections in the field or trip blanks are not likely associated with contamination from the shipping, storage or sampling process.

Topic 7: Interpreting Results

Results are reported by laboratories on written documents and/or electronic data deliverables. USEPA has established a health advisory for two PFAS compounds combined, perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) of 70 nanograms per liter. If the total concentration of PFOA and PFOS added together exceeds 70 nanograms per liter, then USEPA's health advisory is exceeded and USEPA recommends that pregnant women and babies utilize an alternative source of drinking water. USEPA's health advisory is not enforceable, but many states have adopted the health advisory as an action level, guidance or enforceable standard. Many states have also adopted health action levels, guidance or standards that is more or less protective than USEPA's health advisory. Some states have adopted action levels, guidance or standards for additional PFAS compounds as well. A summary from June 2018 of various health-based values established by states and other countries are available for download (in an Excel spreadsheet) on [ITRC's website](#). Please note that some states have changed or developed new values since that time.

The detection of the combined concentration of PFOA and PFOS at levels below 10 nanograms per liter and of total PFAS (the combined sum all PFAS concentrations detected) are not uncommon and does not infer there is a major source of PFAS contamination. Contamination at these levels could be associated with components of the plumbing system, the use of Teflon components in the plumbing

system or chemical feed tanks and tubing, regional septic systems, or other dispersed and relatively minor releases of PFAS from domestic, commercial or industrial uses of products or chemicals containing PFAS compounds.

Topic 8: USEPA's Ongoing Work to Develop New Analytical Methods

USEPA is currently developing several new analytical methods for PFAS. These methods will include isotope dilution and analytical methods for an extended list of PFAS compounds in drinking water, non-potable water, groundwater, wastewater, and solids such as a SW-846 direct injection method for quantifying 24 PFAS analytes in matrices other than drinking water. These new methods will mitigate many of the issues described in this primer. An update on USEPA's work on PFAS analytical methods can be found at <https://www.epa.gov/water-research/pfas-methods-and-guidance-sampling-and-analyzing-water-and-other-environmental-media>.