Source Water Evaluation Guide for PFAS

Technical Support on Per- and Polyfluoroalkyl Substances Policy

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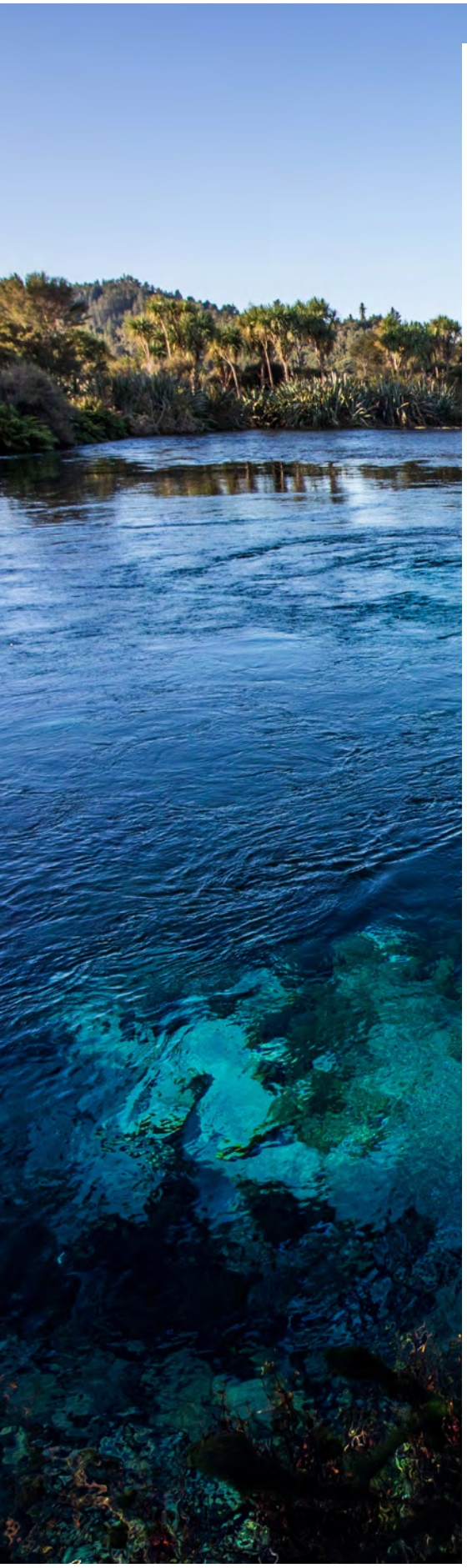

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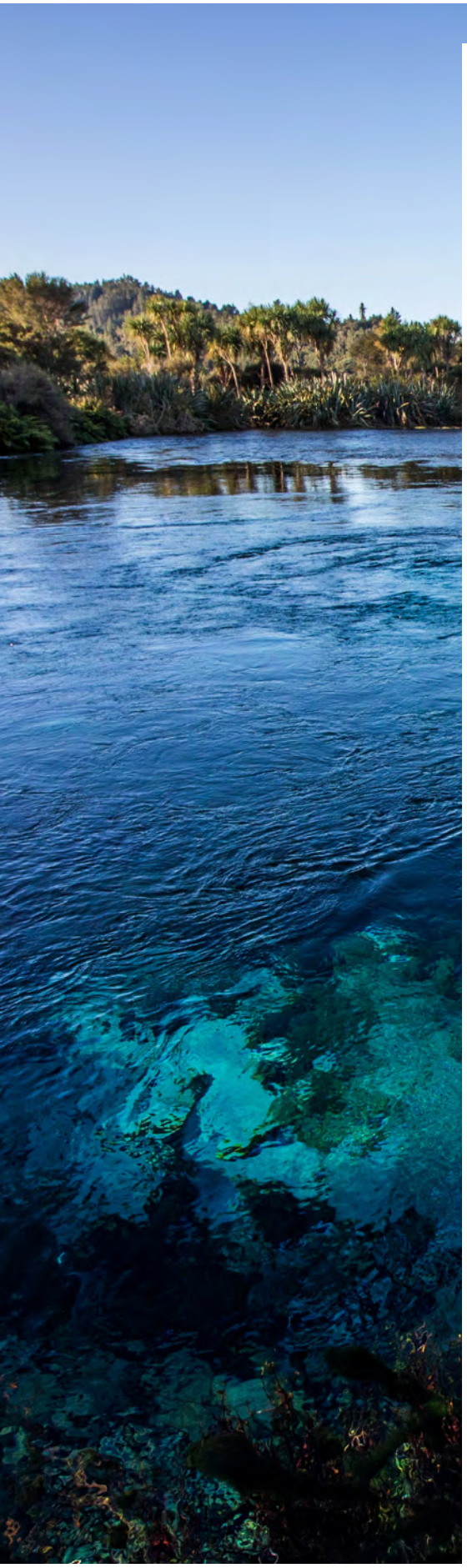

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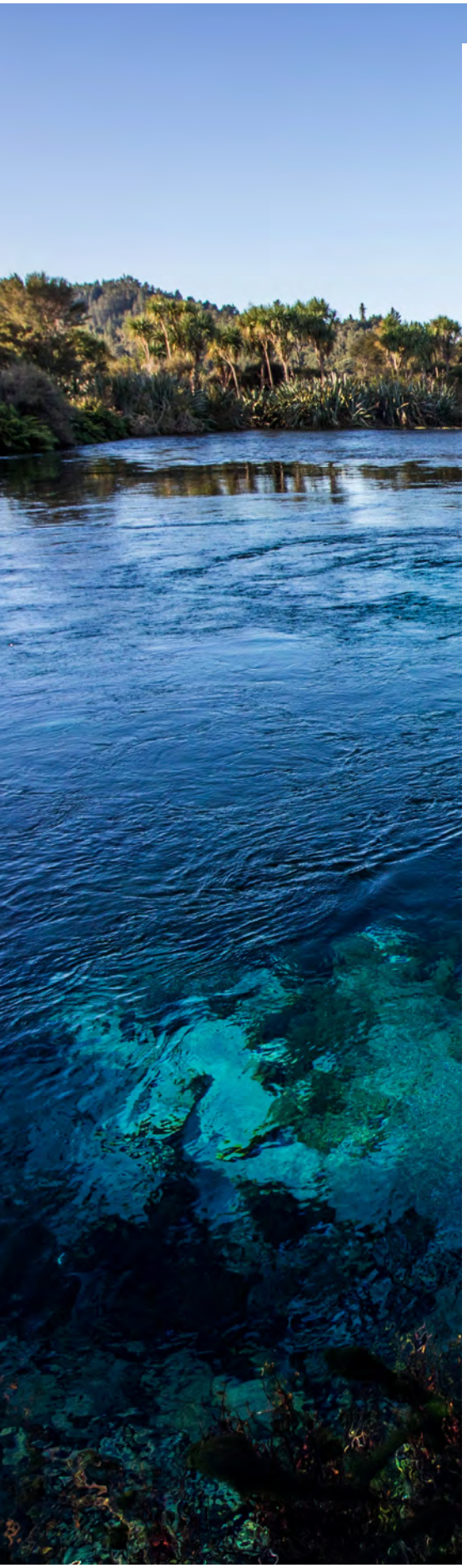

Foreword

This report is not intended to be, nor is it a summary of, best practices for monitoring per- and polyfluoroalkyl substances (PFAS) in drinking water sources. This report does not provide advice to meet legal or regulatory obligations regarding PFAS and should not be used to create any legal or regulatory obligations for water systems. Rather, AWWA hopes this report will help communities consider what potential actions may be appropriate for them to use to identify and manage PFAS in drinking water.

Glossary of Abbreviations and Acronyms

6:2 FTS	6:2 Fluorotelomer sulfonate
AWWA	American Water Works Association
AFFF	Aqueous film-forming foam
DOD	Department of Defense
FAA	Federal Aviation Administration
GenX	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate
GPS	Global positioning system
MCL	Maximum Contaminant Level
MRL	Minimum reporting level
ng/L	nanogram per liter
NPDES	National Pollutant Discharge Elimination System
PFAS	Per- and Polyfluoroalkyl Substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoic acid
PFPeA	Perfluoropentanoic acid
PFDoA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFMOAA	Perfluoro-2-methoxyacetic acid
PFNA	Perfluorononanoic acid
PFO2HxA	Perfluoro(3,5-dioxahexanoic) acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFSA	Perfluoroalkyl sulfonic acid
PTFE	Polytetrafluoroethylene
PWS	Public water system
SDWA	Safe Drinking Water Act
TOF	Total organic fluorine
TOP	Total oxidizable precursor
UCMR 3	Third Unregulated Contaminant Monitoring Rule
USEPA	US Environmental Protection Agency
WWTP	Wastewater treatment plant
WTP	Water treatment plant

Introduction

The presence of per-and polyfluoroalkyl substances (PFAS) in drinking water is a potential health concern and consequently an area of state and federal regulatory activity. Water system managers, water system customers, and local community decision makers want to know if PFAS are a potential challenge for their community. This report is intended to help local water systems evaluate their water supply for PFAS contamination and identify potential sources of PFAS contamination. Understanding and controlling exposure to PFAS in drinking water begins with source water protection.

Background

PFAS are a group of industrial chemicals that have been used largely for their water and oil repellent properties in several applications, including consumer products (e.g., raincoats, food packaging, nonstick cookware), and aqueous film-forming foam (AFFF) to fight petroleum-based fires. PFAS can be present in wastewater effluent and biosolids as a result of residential and industrial activities. Communities across the United States and in other countries have detected PFAS in drinking water and drinking water sources. When detected in drinking water supplies, occurrence is typically at nanogram per liter (ng/L) concentrations. Detection of PFAS has been associated with point-source discharges resulting from the manufacturing, use, and disposal of these chemicals.

The chemical properties of PFAS are such that the compounds are mobile in both groundwater and surface water. PFAS also bioaccumulate. Their properties result in PFAS representing a unique challenge for water and wastewater treatment processes. The water sector's understanding of PFAS is growing rapidly, but much of what is known at present, particularly about the toxicity of PFAS, draws on research conducted on legacy PFAS. These tend to be long-chain perfluoroalkyl carboxylic acids (PFCAs) with eight or more carbons and perfluoroalkyl sulfonic acids (PFSAs) with six or more carbons. Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are the most well-known PFAS in these two groups. The US Environmental Protection Agency (USEPA) updated its drinking water health advisories for PFOS and PFOA in 2016, setting 70 ng/L for either compound individually or combined as a level of concern based on health risks of lifetime exposure.

INTRODUCTION TO PFAS

For those in search of an introductory overview of PFAS chemistry, resources include:

- EPA's Basic Information on PFAS (www.epa.gov/pfas).
- ITRC, PFAS Fact Sheets, Introductory Document (pfas-1.itrcweb.org/fact-sheets/)

While much of our knowledge about PFAS is based on PFOS and PFOA, the production of PFOS was voluntarily phased out of production in the United States by its primary manufacturer from 2000 to 2002. Additionally, in 2006, eight major companies agreed to phase out the production of PFOA and PFOA-related chemicals. There are some circumstances where PFOS is still used (photography and film products, fire resistant aviation hydraulic fluids, etc.) because alternatives are not available. There are also inventories of PFAS-based Class B firefighting foams still in use due to the success of the foams. And importantly, there are ground and surface waters that are being contaminated from historical release sites.

Recognizing that water supply contamination warranted evaluation, the USEPA included six PFAS under the Third Unregulated Contaminant Monitoring Rule (UCMR 3). UMCR is a monitoring program through which USEPA assesses the occurrence of contaminants that may warrant regulation or guidance to state drinking water programs and public water systems. The data is intended to be a nationally representative sample of occurrence in drinking water as it is distributed to customers for consumption. Between 2013 and 2015, approximately 4,920 public water systems (PWS) sampled for perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), PFOS, PFOA, and perfluorononanoic acid (PFNA). Very few samples exceeded the USEPA's lifetime health advisory (not established yet). Approximately two percent of systems detected PFOA and/or PFOS above the UCMR 3 reporting limits.

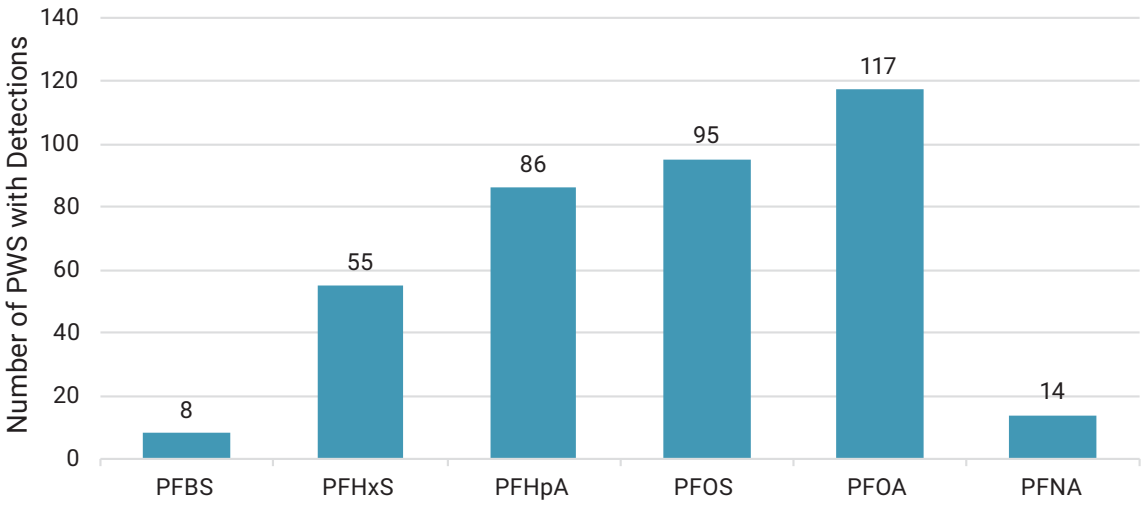

Figure 1 *UCMR 3 PWSs with Detections*

Several states subsequently engaged in occurrence studies after recognition of PFAS in UCMR 3, instances of gross contamination of drinking water supplies by industrial facilities, or in response to information from the Department of Defense (DOD) that showed hundreds of DOD facilities either had or were likely to have PFAS contamination. Data from these studies show similar trends to what was found in UCMR 3 but include larger lists of contaminants. Some of these studies also extended beyond finished drinking water to water supplies and industrial effluent.

USEPA will require additional PFAS monitoring in the Fifth UCMR (UCMR 5). Monitoring is expected to occur over three years beginning in 2022. USEPA has improved the existing analytical method used in UCMR 3 method (USEPA Method 537) and replaced it with method 537.1, which was validated for more compounds than method 537. Additionally, USEPA has developed a new analytical method to detect short-chain PFAS (USEPA Method 533). Together, USEPA Methods 537.1 and 533 can provide information on 29 PFAS.

Before Getting Started

Initiating a source water evaluation for PFAS requires proper planning. Before monitoring for PFAS, a water system should have a clear understanding of the objectives of the source water evaluation, how results will be communicated with public interest groups, and what resources will be committed to the evaluation.

Be Prepared to Communicate

PFAS is a challenging topic for water systems to address with their customers and community decision makers. There is limited and inconsistent information to guide risk communication. However, managing PFAS requires active communication with local decision makers and the public. A water system that engages in an effort to better understand levels of PFAS and potential sources contributing to PFAS in a community's water supply must be prepared to be transparent about its intentions, observations, and subsequent actions. The water system must also be prepared to listen to and understand community concerns. This requires prior planning and preparation in concert with preparations for the technical work that must be accomplished.

TRENDING IN AN INSTANT

AWWA has created Trending in an Instant: A Risk Communication Guide for Water Utilities to enhance your ability to communicate effectively and supporting resources. They are available at www.awwa.org/Policy-Advocacy/Communications-Outreach.

Identify Objectives

Before starting, setting clear objectives for a source water evaluation are essential to guide the effort. Determine what questions the evaluation will be asking. Questions can be broken down into phases of effort drawing on findings and available resources.

Example objectives might be

- Determine the ongoing PFAS challenge (loading) for a system's water sources

- Determine where PFAS are entering the water sources
- Prioritize sources of PFAS contamination for efforts at mitigation

Allocate Appropriate Resources

While analytical services can be a significant expense in source water evaluations, they are not the only resources to consider in planning. Water systems will need to allocate resources for

- Planning the monitoring effort
- Adequately training technicians to collect samples from locations that are appropriate for the study objectives
- Quality assurance and quality control
- Timely analysis
- Effective communication of the occurrence analysis to decision makers and the public

Develop a Robust Monitoring Plan

A robust and defensible monitoring plan should be developed to achieve desired objectives. A monitoring plan should be structured so that sampling results will answer the questions that stakeholders may ask.

Examples of components that make a monitoring plan defensible include

- Sampling upstream and downstream of a potential contamination point to determine PFAS contribution from this source
- Sampling in phases to avoid inefficient use of time and resources
- Taking replicate samples to ensure that results are accurate
- Assigning a minimal number of sample collectors to safeguard consistency in sampling procedure

Identifying Which PFAS to Evaluate

PFAS are a very large group of compounds and consequently, the focus has been on individual PFAS or families of PFAS structures that pose a clear risk to public health. The toxicology and risk assessment communities are still coming to grips with this question. There are some PFAS that federal agencies and individual states have evaluated. There are two regularly updated references that provide the status of these evaluations:

- Interstate Technology Regulatory Council PFAS Regulations, Guidance and Advisories, Section 4 and Section 5 Tables (ITRC, 2020a)
- AWWA Summary of State Policies to Protect Drinking Water PFAS Fact Sheet (AWWA, 2020)

KEY REFERENCE FOR PFAS CHEMICAL STRUCTURES

USEPA's Computational Toxicology Program's Chemical Dashboard contains ten lists of PFAS compounds. Information about individual chemicals in these lists varies based on the state of knowledge but is periodically updated. Data includes available chemical properties, chemical structure, synonyms, and available toxicity data. The dashboard is at comptox.epa.gov/dashboard. Use the "list" feature to locate the PFAS list most helpful to your search.

There are ongoing efforts at USEPA to evaluate the toxicity of a much larger list of PFAS (approximately 150); however, the timeframe for obtaining actionable information from the Agency's work is not currently clear. As the understanding of the health consequences of PFAS continues to develop, this report suggests the following guiding considerations:

- Is there a well-established toxicological basis for specific PFAS or groups?
- Is the individual PFAS compound currently being evaluated by federal or state agencies for regulation?
- Is there a substantial history of use and has use been linked to contamination of water supplies?
- Are there robust analytical methods available for systems to use in their investigations?

History of PFAS in Manufacturing

PFAS were first invented in the 1930s and their use in nonstick coatings began in the 1940s. By the 1950s, PFOS and PFOA were incorporated into products to provide protective coatings as well as stain and water resistance. In the 1960s, PFOS was first used in the production of Class B firefighting foam. PFHxS has historically been used for stain-resistant fabrics, AFFF, food packaging, and as a surfactant in industrial processes. Over time, manufacturers incorporated PFAS into a wide range of industrial activities and commercial products ranging from metal plating and finishing to electronics and paper packaging. Consumer products where PFAS were used include cookware, fabric protector, waterproof clothing, pizza boxes, fast food wrappers, popcorn bags, waxes, paints, and cleaning products. Not only did the number and diversity of PFAS expand to fill new commercial applications, there were also notable decisions to deliberately stop production of certain PFAS.

HISTORY OF PFAS USE

ITRC's PFAS Fact Sheets provides a succinct summary of the history of PFAS use in manufacturing and a summary of the relevant industrial sector applications.

- ITRC, PFAS Fact Sheets, History and Use (pfas-1.itrcweb.org/fact-sheets/)

- Use of PFOS, PFOA, and PFHxS began to be phased out in 2000 with a decision by 3M, the principle manufacturer, and was completed by 2008. However, these chemicals are still actively used by others.
- PFNA was introduced into production in the 1970s and use has declined with voluntary and mandatory phase outs in the early 2000s.
- The initial phase out was expanded in 2006 with a deliberate halt to the new use of 183 PFAS.
- Fluorotelomer production continues today and USEPA continues to approve new PFAS on a routine basis.

This history of manufacture and use means that evaluating whether any contamination is present would involve identifying current and historical

1. Production facilities that may have produced legacy PFAS
2. Manufacturing and use sites from sectors that use PFAS
3. Disposal sites for relevant industrial or manufacturing wastes

Water systems that have taken on this task have encountered mixed results, for some of the following reasons:

1. Association of a particular PFAS contamination to a specific manufacturing/discharge facility, especially in groundwater aquifers can be challenging.
2. The presence of a known use site (e.g., an airport or fire-foam training facility) does not assure that a sample today will detect PFAS with available methods and sampling opportunities.
3. PFAS may be present from diffuse sources, such that low-level concentration cannot be traced to a point of release.

These experiences reflect in part that while PFAS are remarkably stable, evaluating where releases may have occurred may be impacted by

- The lack of information on historical PFAS manufacture and use
- The presence of PFAS as a byproduct of production chemistry or subsequent degradation
- The degradation in the environment

Currently, analytical techniques can quantify nanograms per liter (ng/L) levels of a small group of individual PFAS. These concentrations are one thousandth of those typically used when assessing industrial discharges or contamination of drinking water for most other contaminants of potential concern. Detecting PFAS at such low levels means that some systems have found it difficult (impossible) to associate levels of PFAS with particular PFAS sources. Given this challenge, a focus on known high-risk contamination sources may be appropriate, which will be discussed in greater detail in subsequent sections.

Aqueous Film Forming Foam

One application of PFAS is a component of Class B AFFF. AFFF is used to suppress hydrocarbon fuel fires. It may be used within buildings, for exteriors, or mobile fire suppression systems. While only an estimated three percent of fluorochemicals produced are used in AFFF, they are a particularly problematic application from a drinking water perspective. The Department of Defense (DOD) has located more than 400 current or former facilities where there are known or suspected AFFF release sites, where the AFFF contained PFOA or PFOS.

AQUEOUS FIRE FIGHTING FOAM

References include:

- ITRC, PFAS Fact Sheets, Aqueous Film-Forming Foam (pfas-1.itrcweb.org/fact-sheets/)
- DOD, PFAS: A National Issue That Needs National Solutions (www.defense.gov/Explore/Spotlight/pfas/)
- FAA, National Part 139 CertAlert (www.faa.gov/airports/airport_safety/certalerts/media/part-139-cert-alert-19-01-AFFF.pdf)

In testimony to Congress, DOD has indicated that at more than 90 of these sites, the contamination of on-base or off-base water supplies were affected (DOD, 2020). **Importantly, the Federal Aviation Administration (FAA) regulations and guidance have required the use of AFFF containing PFAS; this requirement will be revised in 2021** (FAA, 2019). Consequently, municipal airports, hospital helipads, and other aviation facilities where there was a risk of a hydrocarbon fuel fire used this same type of AFFF. Application extends beyond aviation-related facilities to municipal fire departments, oil refineries and storage facilities, flammable liquid storage and processing facilities, etc. There are known examples of AFFF contamination associated with: emergency response use of AFFF, required fire suppression system testing, use of AFFF in training, and disposal of AFFF/AFFF-contaminated materials.

AFFF composition has changed over the past several decades as legacy compounds were phased out and replaced with new compounds (ITRC, 2020b).

Waste Management Facilities

Waste management facilities including wastewater treatment plants (WWTPs), landfills, and incineration facilities can potentially release PFAS to the environment. These may be through wastewater or leachate discharges to the environment, biosolids applications, or air emissions as well.

WWTPs receive wastewater flows from domestic and industrial sources. Given the ubiquity of PFAS in our environment, WWTPs receive PFAS in wastewater influent. The PFAS challenge posed by industrial and manufacturing facilities is more significant, but these facilities could potentially discharge quantities of PFAS in their wastewater and consequently release more PFAS to surface waters or septic fields.

Additionally, PFAS-laden biosolids (the solids that are produced from WWTPs) may be land-applied as fertilizer to improve and maintain productive soils and stimulate plant growth. Land application of biosolids often requires permitting though state agencies, therefore studies are ongoing to characterize the impact of PFAS in biosolids. To determine where biosolids are land-applied, interested parties can reach out to state contacts. Additionally, some municipalities, states, and universities keep current and historical biosolids application databases (City of Marinette, n.d.; Florida Department of Environmental Protection, 2020; Nielsen, 2011).

BIOSOLIDS

References include:

- NACWA, A Clean Water Utility's Guide to Considering Source Identification, Pretreatment, and Sampling Protocols for PFAS (www.nacwa.org/docs/default-source/resources---public/2019-11-25-pfas-3-consideration.pdf?sfvrsn=5771fd61_4)
- NEBRA, Guidance – PFAS Sampling & Analysis for Maine DEP (www.nebiosolids.org/guidance-pfas-sampling-for-maine-dep)

While the state of knowledge for PFAS in wastewater is still under investigation, preliminary studies conducted by some individual utilities' pretreatment programs, biosolids monitoring programs, and state monitoring programs, indicate that (Michigan Department of Environment, Great

Lakes, and Energy, 2020; Rainey, 2018; Venkatesan & Halden, 2013b)

- PFAS are not efficiently removed in municipal WWTPs.
- PFAS can increase in WWTPs, suggesting precursor compounds can degrade and release persistent PFCAs and PFSAs.
- Biosolids have been shown to potentially contaminate soil, groundwater, and surface waters.
- PFOS and PFOA are the most highly detected PFAS in biosolids.
- PFAS levels in biosolids have no seasonal variations.
- PFAS levels show no significant difference in biosolids samples collected 2001 versus years 2004 through 2007, after the phase-out of certain PFAS.

Landfills may also contribute to PFAS occurrence in the environment through collection in landfill leachates, which is topic of ongoing research. There have been various contamination sites that are linked to landfills that received industrial waste from PFAS manufacturers or users. Landfill leachate may contribute to PFAS contamination through leachate discharges to nearby surface or groundwater as well as indirectly by discharges to local wastewater facilities (USEPA, 2019b).

Source Water Evaluation

Determining presence, abundance, and source characterization of PFAS in a drinking water supply can be summarized in the four-step process shown in Figure 2.

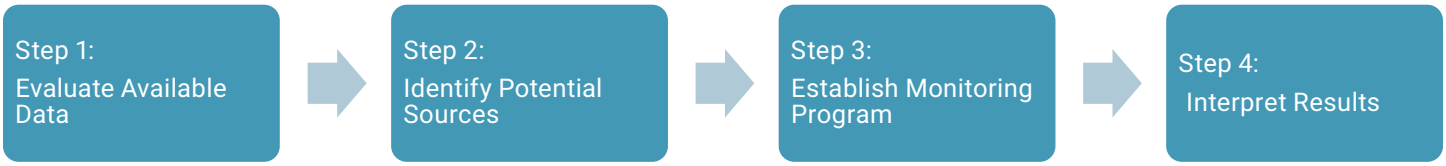

Figure 2 – *Determining if PFAS Sources Threaten Your Water Supply*

Step 1 – Evaluate Available Data

If there is existing occurrence data, a water system can draw on that information to guide its monitoring effort. Aside from monitoring raw or finished water, additional data may be available to characterize the following PFAS sampling locations:

1. Raw water concentrations near a system's well or upstream from its surface water intake location
2. Point source discharges into an aquifer or surface water supply
3. Local land discharges (such as AFFF runoff) that are associated with PFAS releases

The system itself may have information from UCMR 3 or state-required monitoring. There may also be data that has been collected by other water systems, state environmental agency sampling campaigns, wastewater water utilities, stormwater utilities, and Department of Defense facility sampling. If data are available, it is important to understand the datasets.

CHALLENGES ASSOCIATED WITH USING EXISTING DATA

- Detection limits change as new analytical methods become available
- Not all entities use laboratories that measure PFAS using EPA-approved methods
- Poor documentation of sampling protocols
- Poor documentation of weather at sample collection time
- Inconsistent sampling procedures

1. What PFAS observations are available?
2. Where were the samples collected?
3. What sampling protocols were used?
4. What analytical methods were used?
5. What replication of sampling was conducted, if any?

6. Do the organizations responsible for collecting the data draw any conclusions or express any caveats on how the observations should be used?

Data of uncertain quality need not be discarded, but data quality is an important consideration for data that may inform subsequent PFAS mitigation strategies. Drawing inferences from existing data can be complicated by factors including

1. Much available PFAS data is monitoring of finished drinking water rather than potential sources of contamination.
2. Analytical method detection levels have changed substantially so "non-detects" can be based on what are now considered measurable levels.
3. PFAS use and discharge patterns have changed and the use of replacement PFAS, such as PFBS, may have changed since sampling occurred.
4. Little may be known about sampling protocols at the time of collection (e.g., was the use of water-resistant clothing prohibited?).
5. Little may be known about weather conditions at the time of collection, and heavy rain can impact PFAS levels.
6. The exact sample location or collection procedure, such as water depth in a surface water source or groundwater well purge time, may not be documented.

Step 2 – Identify Potential Sources

If the evaluation's purpose is to move beyond the initial evaluation of influent PFAS levels, identification of potential sources is the next step. Existing occurrence data can suggest whether a water body or aquifer is contaminated; however, beyond that data, land uses exist where there are known examples of PFAS contamination. Examples include

- Airports (military and civilian)
- Firefighting training facilities
- Industrial and commercial facilities associated with PFAS manufacture or use
- Waste management facilities (landfills)
- Wastewater residual disposal sites where there is an industrial source known to use PFAS

Importantly, PFAS manufacture and use began in the 1940s, so identifying relevant land uses may entail identifying sites that are no longer in active use (e.g., landfills) and no longer engage in practices that release PFAS (e.g., industrial sites).

AQUEOUS FILM FORMING FOAM (AFFF)

AFFF uses are not limited to military and civilian airports and fire training centers; however, these are the applications that have been most frequently recognized to-date as sources of PFAS-contaminated AFFF impacting water supplies. Researchers have correlated AFFF contamination with elevated PFAS concentrations in wastewater, drinking water, groundwater, and surface water from runoff that occurs when AFFF are used (Høisæter et al., 2019; Houtz et al., 2016).

AFFF

References include:

- Appendix C to Report to Congress, DOD, Inventory of Fire/Crash Training Area Sites
- Installations Where DoD is Performing an Assessment

If AFFF contamination is suspected, several key pieces of information should be identified. The estimated time of contamination should be known to understand the likelihood of PFAS degradation as well as PFAS movement through soils. If possible, the type and amount of foam used with the AFFF dischargers should be discussed to understand which individual PFAS can be expected. During PFAS sampling, the groundwater well depth and purge time should be noted, as well as surface water characteristics such as flow, depth, and sample depth. It is also important to note the location where PFAS contamination occurred and sample location coordinates. Sampling both groundwater and surface water near the point(s) of contamination can also provide information relative to PFAS travel through the environment. The PFAS analyzed at the laboratory should be discussed to ensure at least a portion of PFAS typically found in AFFF will be analyzed. Once PFAS results are received, analysts should review the contribution of individual PFAS to the total PFAS concentration and the level of PFAS that are typically found in AFFF.

One study in Norway investigated an AFFF-contaminated site to identify the percentage of individual PFAS detected in an AFFF sample (as a fraction of the total measured PFAS in AFFF), as shown in Figure 3 (Høisæter et al., 2019). In this study, 23 PFAS were measured. The study also evaluated the transport of individual PFAS through soil and showed that the short-chain PFAS, such as PFBS, moved quickest

through the soil, while long-chain PFAS took longer to breakthrough during a column experiment (Høisæter et al., 2019). However, this research found that PFHxS was not decreased to the same degree as other long-chain PFAS. At the end of their experiment, Høisæter et al. (2019) found that PFHxS was the most dominant PFAS in the water after their soil filtration experiment. While this study may not be representative of PFAS fractions found in other AFFF contamination sites, the method of investigation could be applied to other locations with suspected or known AFFF discharges.

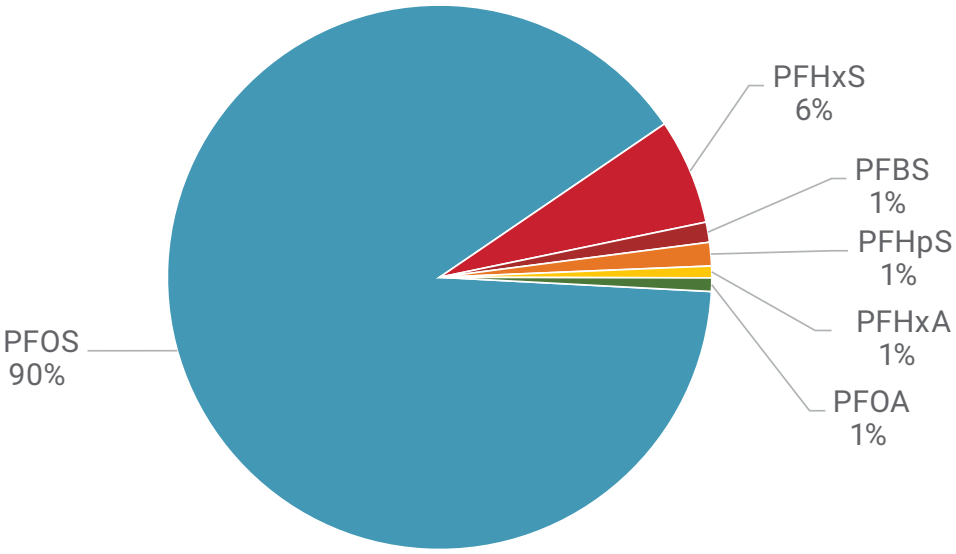

Figure 3 – *Percentage by mass of individual PFAS identified in an AFFF-contaminated soil sample near an as part of a Norwegian AFFF Study (Source: Høisæter et al., 2019)*

INDUSTRIAL USE

PFAS released into the environment have reached water supplies through direct discharges to water as well as air emissions (Bao et al., 2019; Domingo & Nadal, 2019; Hopkins, Sun, DeWitt, & Knappe, 2018; Y. Sun et al., 2018). In addition to work showing release of long-chain PFAS, Sun et al. (2016) illustrated that short-chain PFAS, including ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy) propanoate (GenX), were released and could be more abundant than long-chain PFAS in some manufacturing effluents. In addition to direct discharges, industrial facilities can be responsible for PFAS contamination of wastewater effluent and biosolids from WWTPs and landfill leachate (Loganathan et al., 2007; Sinclair & Kannan, 2006).

USEPA TOXICS RELEASE INVENTORY TRACKING TOOL

Prior to 2020, little data on PFAS use and release was publicly available. As part of the National Defense Authorization Act for Fiscal Year 2020, the USEPA was required to add 172 PFAS to the Toxics Release Inventory (TRI) for immediate inclusion beginning January 1, 2020 (US EPA, 2019a). The TRI is a useful tool that will help the USEPA and water systems better understand the users and dischargers of PFAS. The reports on facility releases for 2020 will be

due to the USEPA in mid-2021. The applicable reporting threshold is 100 pounds.

Table 1 provides a summary of common PFAS that currently are covered by water analytical methods that will be reported in 2021 and thereafter.

Table 1. PFAS Added to TRI Reporting in 2020 and Associated Analytical Methods

ANALYTE	ABBREVIATION	CASRN	METHOD 533	METHOD 537.1	EPA TARGET SW846	US DOD QSM 5.2	TRI PFAS
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	x	x			x
Perfluorodecanoic acid	PFDA	335-76-2	x	x	x	x	x
Perfluorododecanoic acid	PFDoA	307-55-1	x	x	x	x	x
Perfluorohexanesulfonic acid	PFHxS	355-46-4	x	x	x	x	x
Perfluorononanoic acid	PFNA	375-95-1	x	x	x	x	x
Perfluorooctanoic acid	PFOA	335-67-1	x	x	x	x	x
Perfluorooctanesulfonic acid	PFOS	1763-23-1	x	x	x	x	x
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	x				*
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	x				*
Perfluorotetradecanoic acid	PFTA	376-06-7		x	x	x	x
Perfluorodecanesulfonic acid	PFDS	335-77-3			x	x	*

* PFHpS, PFPeS, and PFDS are not specifically included in the TRI because they are not actively used in the US. However, their actively used salts are included on the TRI.

There is no exhaustive list of the types of industrial facilities that contribute to PFAS contamination in the environment. For the purposes of a source water evaluation, and in the absence of comprehensive TRI data, PFAS contamination have been previously reported to be linked with facilities involved in the manufacturer of

- Leather and leather products, such as tanneries,
- Coated or laminated packaging paper and plastics film,
- Carpets and rugs,
- Electroplated metal products, and
- Semiconductors or other electronic equipment.

LANDFILLS AND LEACHATES

Landfills have the potential to be sources of PFAS due to their acceptance of waste, both consumer and industrial, that may contain PFAS. PFAS from solid waste can enter landfill leachate, which may be collected (and treated) through landfill leachate management systems. Legacy dumps and waste disposal sites that were in use prior to regulatory requirements, may also leach PFAS-containing leachate into groundwater if no liner is present.

In a survey of landfills throughout the U.S., the mass of PFAS in leachate sent to WWTPs was estimated to be between a total of 563 kg and 638 kg in 95 samples in 2013 (Lang et al., 2017). The PFAS with the highest concentration in most of the leachate samples was 5:3 fluorotelomer carboxylic acid (FTCA). One of the major conclusions of this study was that landfill age impacts the type of PFAS present in leachate. Higher concentrations of PFNA, 8:2 FTCA, 5:3 FTCA, PFBS, N-methyl perfluorobutane sulfonamido acetic acid, and N-methylperfluorooctane sulfonamidoacetic acid were detected in younger landfills, which could be due to decreases in concentrations with type or changes to PFAS used in products because PFNA and PFBS are alternatives to PFOA and PFOS. Additionally, PFAS present in leachate is impacted by climate. PFAS were found in higher concentrations in wet climates, indicating leaching governed PFAS release (Lang et al., 2017).

Groundwater impacted by currently operating landfills has been shown to have cumulative PFAS concentrations ranging from 26 to 5,200 ng/L (Hepburn, Northway, et al., 2019). Individual studies show that the dominant PFAS in landfill leachate varies from landfill-to-landfill but that PFOA and PFOS continue to be observed along with other PFAS that are quantified with current analytical methods. In 2019, a study of 32 landfill leachates in Michigan found PFOA levels ranging from 16 to 32,000 ng/L and PFOS ranging from 9 to 960 ng/L (deSilva, 2019).

Hamid et al. (2018) also found that PFOA was one of the most abundant PFAS detected in landfill leachates. Hepburn consistently found PFOA (25%–45%) but observed lower concentrations at older landfills. Gallen et al. (2017) demonstrated the site-specific nature of PFAS distributions in landfill leachate, observing perfluorohexanoic acid (PFHxA) as the predominant PFAS, with an average concentration of 1,700 ng/L (37% of the total PFAS concentration). In the same study, five PFAS (PFHxA, PFHpA, PFOA, PFHxS, and PFOS) were detected in all samples in all 27 landfills. Hamid et al. (2018) also found that short-chain PFAS were routinely detected in landfill leachate.

Typical indicators of landfill leachate impacting groundwater include ammonia, ammonium, bicarbonate, potassium, total organic carbon, and dissolved methane (Eschauzier et al., 2013). If a water system is in close proximity to a landfill and has detected elevated levels of these constituents in groundwater or surface water that is impacted by groundwater, they are at greater risk for PFAS contamination as well (Eschauzier et al., 2013).

Hepburn et al. (2019) showed a relationship between ammonium in groundwater impacted by landfill leachate and the ratio of PFOA to the sum of perfluoroalkyl acids (PFAAs). As ammonium increased, the ratio of PFOA: ΣPFAA also increased. One of the outcomes of this research was a framework for determining the extent of PFAS groundwater contamination originating from landfills. Results showed that if there are elevated levels of landfill indicators (e.g., ammonia, ammonium, bicarbonate, etc.) and a PFOA: ΣPFAA value greater than 10%, PFAS contamination is likely caused by the municipal landfill (Hepburn, Madden, et al., 2019).

WASTEWATER TREATMENT AND LAND APPLICATION OF BIOSOLIDS

AFFF runoff, industrial discharge, and landfill leachate can all be discharged to a WWTP through sewage and stormwater collection systems. If PFAS is not removed in the receiving WWTP processes, it will be discharged as effluent, air emissions, or biosolids disposal. Primary, secondary, and tertiary WWTP treatment technologies do not significantly reduce PFAS prior to release in final effluent (Chen et al., 2018; Coggan et al., 2019). A survey of nineteen WWTPs in Australia showed PFAS detections in every influent and effluent sample collected (Coggan et al., 2019). Research has shown that perfluorobutanoic acid (PFBA), PFHxA, PFOS, PFOA, and perfluoropentanoic acid (PFPeA) are commonly found in high concentrations at WWTPs, although these findings are limited to specific WWTPs (Chen et al., 2018; Houtz et al., 2016; Nguyen et al., 2019).

Measurable levels of PFAS have been found in WWTP biosolids. According to the 2001 National Sewage Sludge Survey, the mean load of total PFAS in U.S. biosolids was estimated at 2,749 kg/yr to 3,450 kg/yr, where 1,375 kg to 2,070 kg was land applied and 467 kg to 587 kg was transported to landfills for disposal (Venkatesan & Halden, 2013a), although biosolids can also be incinerated. Zareitalabad et al. (2013) reported concentrations of 36 ug/kg and 69 ug/kg in biosolids found in Germany for PFOA and PFOS, respectively. According to one study, land application of biosolids that contain PFAS have contaminated soil, groundwater, and surface waters. This study found that 22% of surface and groundwater samples collected in the vicinity of local agricultural fields where biosolids were applied had PFOA concentrations > 400 ng/L (Lindstrom et al., 2011).

Surface water and groundwater contamination from biosolids application will be highly dependent on

- Type and concentration of PFAS in applied biosolids
- The amount of biosolids land applied
- How long biosolids have been applied
- Soil properties
- Water table level
- Rainfall

Types of PFAS in groundwater due to biosolids application would be dependent on the source of contamination to the original WWTP, and research is ongoing to understand fate and transport in biosolids, among other matrices. For example, contamination from industrial discharge would likely yield different PFAS compared to WWTP contamination from AFFF, which would subsequently impact biosolids PFAS speciation.

Biosolids may pose a risk of PFAS contamination for drinking water systems using groundwater or surface in the vicinity of biosolids land application sites. Systems performing an evaluation for PFAS should coordinate with nearby WWTPs to identify biosolids land application sites. Measurement of PFAS levels in WWTP effluent and discharge locations would be beneficial. While PFAS are not yet covered under the Clean Water Act, and therefore are not required under National Pollutant Discharge Elimination System (NPDES) permits, some states have enacted ambient groundwater quality criteria and discharge limits.

For example, the state of Michigan now requires WWTPs to monitor for PFOS and PFOA, with the goal of reducing or eliminating these compounds in municipal WWTPs. Part of this initiative is to identify sources of PFAS entering municipal WWTPs, and classify WWTPs into one of four bins based on PFAS data (Michigan Department of Environment, Great Lakes, and Energy, 2019). Drinking water systems should review AWWA's Fact Sheet "Summary of State Policies to Protect Drinking Water" to determine if there are applicable state policies in place (AWWA, 2020). This information may help to determine the extent of PFAS discharge upstream of a surface water plant or within the proximity of groundwater wells.

Step 3 – Establish a Monitoring Program

MONITORING PROGRAM OVERVIEW

The findings of Step 2 may indicate the need for a water system monitoring program. Critical components of a successful monitoring program include selecting sampling locations, sample frequency, and appropriate analytical methods. In developing a monitoring program, each of these components should be balanced while keeping in mind the budgetary considerations and expectations of stakeholders. For instance, it may not be valuable to have sampling conducted at numerous locations across the watershed or at multiple groundwater wells if the sampling is only conducted annually or for one compound. Water systems must consider the trade-offs of each component of their monitoring program against the budget and objectives to maximize the efficacy of the program.

STATE SUPPORT FOR SOURCE WATER MONITORING

As a response to industrial PFAS contamination in a river used as a water source to several drinking water municipalities, the North Carolina Department of Environmental Quality (NC DEQ) routinely performs PFAS testing throughout the Cape Fear River, groundwater wells, nearby utilities, and industries. This information provides PFAS occurrence and concentration data to nearby and downstream municipalities.

IDENTIFYING SAMPLING LOCATIONS

Drinking water contamination by PFAS is often localized, meaning that contamination is likely to occur where a point source enters the source water. For example, a water system's risk of being exposed to PFAS increases depending on proximity to one or more pollution sources, as PFAS concentrations are always highest in areas closer to the source of pollution (Hale et al., 2017; Hansen et al., 2002).

Although PFAS contamination is usually caused by a point source, a few studies have reported migration of contaminants to remote areas several miles away from the point of release. In some instances, determining the exact origin of PFAS contamination may be challenging, especially when PFAS is present at low concentrations. For example, there are reports of PFAS travelling 90 miles downstream of an industrial source at discernable concentrations (Hopkins, Sun, DeWitt, & Knappe, 2018). PFAS, especially short-chain PFAS, can be transported through precipitation and dry atmospheric deposition. Additionally, different types of PFAS migrate through soils at different rates (Xiao et al., 2015). Air emission of GenX, other PFAS, and their precursors from manufacturing strongly influence contamination (NC DEQ, 2019). Short-chain PFAS can travel to other parts of the environment more easily compared to long-chain PFAS because they are more hydrophilic (Westreich et al., 2018).

As PFAS are not only persistent but can easily migrate, the following sampling considerations are suggested.

1. Evaluating sources of PFAS contamination – multiple locations of contaminated soil/water can be sampled at the point of discharge, if located, as well as, downstream/down gradient locations in keeping with the evaluation goals set in Step 1. Initially, sampling may be conducted up to several miles upstream of a point source to confirm whether PFAS contamination could be coming from elsewhere.

2. Testing at source water intake locations or groundwater wells – can involve testing at several points upstream of the intake point, such as varying reservoir locations or nearby wells.

APPLY ADAPTIVE MANAGEMENT WHEN MONITORING

Sampling and analysis of samples can be costly, making effective planning of the monitoring program important. Likewise, when monitoring program objectives have been achieved, there is an opportunity to shift resources either to new monitoring goals or targeting/reducing ongoing monitoring. Recognizing success or failure relative to objectives requires ongoing assessment.

3. Engaging state regulatory agencies – once point sources are identified, regulatory agencies should be apprised of observations. Regulatory agencies can also be helpful for understanding and communicating to stakeholders when upstream sampling (1) does not identify clear sources of PFAS contamination, (2) indicates a more distant source (e.g., higher in watershed, air deposition), or (3) repeat low-level concentrations (e.g., *de minimus* levels). (Hopkins et al., 2018).

Considerations when establishing sampling locations include

- Ensure monitoring personnel can reliably access the sample location. Site constraints to consider include legal access, safety issues, water level changes, future construction, etc.
- Sample locations should be mapped and global positioning system (GPS) coordinates recorded, so that samples can be taken from the same location over time and observations can be reliably communicated.
- Prioritize monitoring effort relative to the water system's dependence on specific sources and ability to use alternative sources. Considerations include overall dependency on a source and seasonal criticality.
- Phase the monitoring program to prioritize specific water sources with known or suspected primary sources of PFAS contamination before monitoring water sources without known or suspected sources of contamination.
- Monitoring of a specific water supply can be phased where initial monitoring determines both the placement and frequency of subsequent monitoring.
- Monitoring plan should consider seasonality in flow. Like other contaminants, flow and precipitation events can also lead to marked change in occurrence.
- Sampling finished or intermediate samples from the water treatment plant (WTP) treatment train should be evaluated relative to the monitoring plan's objectives. Sampling between treatment processes can help inform evaluating treatment changes.

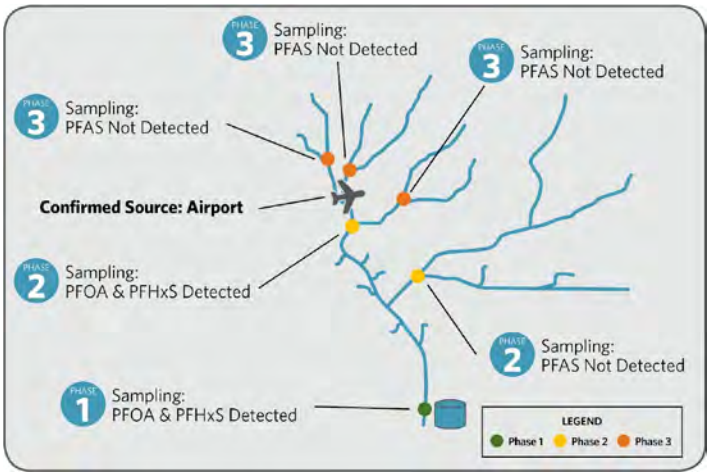

Figure 4 – *Example of an Implemented Phased Approach to PFAS Sampling*

SAMPLING FREQUENCY CONSIDERATIONS

Many sampling programs have focused on collecting a limited number of samples once to identify contamination hot spots. However, there are cases of more frequent, active monitoring. Some water systems may choose to monitor as often as weekly or biweekly. For example, one utility collects weekly samples from their intake with a rush turnaround time to determine if they need to operate their powdered activated carbon (PAC) treatment system to ensure management of PFAS.

For water quality with variable PFAS concentrations, sample frequency should be higher than areas where concentrations are constant (Bartram & Ballance, 1996). Frequency of sampling will be a case-by-case decision based on the monitoring plan objectives. Cost and logistics are factors to consider when setting sample frequency. Michigan requires quarterly monitoring of PFAS for drinking water (Michigan Department of Environment, Great Lakes, and Energy, 2019). Sampling requirements were phased in and PFAS levels will be based on a running average of the four previous quarterly sampling results.

WATER SYSTEMS ARE NOT THE ONLY ENTITY THAT CAN CONDUCT MONITORING

- Some states are conducting sampling for PFAS contamination.
- NPDES permittees can monitor discharges regularly (e.g.,1–2 times per month).
- Monitoring can be incorporated into operating procedures when PFAS contaminated fire foam is released.
- Universities and other research groups can monitor PFAS occurrence

ANALYTICAL METHOD CONSIDERATIONS

At present, there are various methods available to measure PFAS that were developed by the USEPA, ASTM, independent laboratories, and university researchers. It is important to understand which methods are most appropriate for a given situation as each method offers its own advantages and disadvantages.

USEPA Method 537 revision 1.1 is the most commonly used analytical method for PFAS in drinking water. The water sector is currently transitioning to use of USEPA Method 537.1 in drinking water and source water instead of the previously established USEPA Method 537. USEPA 537.1 uses solid phase extraction (SPE) with liquid chromatography/tandem mass spectrometry (LC/MS/MS). Method 537.1 and its predecessor measure commonly identified long-chain PFAS. Method 537.1 has low detection limits for these PFAS, and this method is widely available in laboratories across the country. USEPA Method 533 is a newer drinking analytical method that was developed to measure short-chain PFAS. Released in late 2019, there are not many laboratories currently using USEPA Method 533. With anticipated use of USEPA Method 533 in UCMR 5, laboratory capacity will likely increase rapidly in 2020 and 2021.

USEPA Method 8327 uses LC/MS/MS but does not incorporate the use of an isotope dilution technique. USEPA Method 8327 can be used in surface water, groundwater, and wastewater matrices. Detection limits are higher than those in USEPA Method 537.1, ranging from 10 ng/L to 40 ng/L, depending on the compound. At present, USEPA Method 8328 has not been released but according to the USEPA, it is expected to be used to measure PFAS in surface water, groundwater, and wastewater matrices. Unlike USEPA Method 8327, USEPA Method 8328 will use SPE for nondrinking water aqueous samples and solvent extraction for solid matrices as well as isotope dilution.

ASTM 7979 can be used to measure PFAS and PFAS surrogates in biosolids (total dissolved solids less than 20,000 mg/L) in addition to surface water, groundwater, and wastewater matrices. Like USEPA Method 8327, ASTM 7979 has relatively high minimum reporting limits, ranging from 10 ng/L to 50 ng/L. ASTM 7968 can be used to analyze PFAS in biosolids as well as soil matrices, although the minimum reporting limits for individual PFAS ranges from 25 ng/L to 50 ng/L.

Another method for detecting PFAS is a modified version of the USEPA Method 537 or 537.1. The modifications may vary between laboratories making it difficult to know what parts of the method the lab may have changed. Usually the modifications include shorter run times, use of different SPE or elution solvents, analysis of additional compounds, and quantification using isotope dilution. These drinking water methods are commonly modified for the extraction and analysis of wastewater and soil. There is significant laboratory-to-laboratory variability in the analyte list, analytical recovery, and accuracy of analytical results when

using modified USEPA 537 that must be considered anytime labs modify methods.

Total oxidizable precursor (TOP) and total organic fluorine (TOF) assays can be used to measure "total" PFAS concentrations. TOP assay uses heat and alkaline activated persulfate to oxidize polyfluorinated compounds into PFAAs. The TOP assay has the potential advantage of measuring precursor PFAS that might otherwise be excluded from sampling. TOF assay is based on a direct combustion method where samples undergo pyrohydrolysis at 900 °C to 1000 °C in an oxygen rich environment and can be used in conjunction with an USEPA method to better characterize the extent of PFAS in a sample. This is not yet a standardized method, and thus interpretation and inter-laboratory variability may be of concern.

Water systems can refer to Table 2 for a comparison of analytical methods for PFAS to determine the analytical method that is most appropriate. Water systems should refer to the analytical method and the supporting laboratory for information on the appropriate sample volumes, sample storage requirements, and to confirm the number of analytes tested, because not all laboratories can run all analytes listed in a method.

COLLABORATING WITH A RESEARCH COMMUNITY

Universities and research groups use TOP and TOF to measure PFAA precursors, which cannot be done using currently USEPA-approved methods. Collaborating with a university or research group can be a cost-effective way to gather and analyze PFAS data. These entities can provide additional information beyond traditional PFAS results that would be obtained from a commercial laboratory. Examples of additional information can include modeling, treatability, or correlation with alternative parameters.

Table 2 – Test Methods Used for PFAS Quantification (AWWA, 2019)

METHOD	TYPE OF SAMPLE*	NUMBER OF ANALYTES	TYPES OF PFAS OBSERVED	STANDARD PROCEDURE	PROS AND/OR CONS	ANALYTICAL LIMITS**** (NG/L OR NG/KG)	PERCENT RECOVERY
USEPA Method 537.1	DW	18	PFCAs, PFSAs, sulfonamides, sulfonamidoacetic acids	Yes	Limited capture of short-chain PFAS	PFBS: 6.3 PFOA: 0.82 PFOS: 2.7 PFHxS: 2.4 PFHpA: 0.63 PFNA: 0.83	70 – 130%
USEPA Method 533	DW	26	On short-chain PFAS	Yes	Effective capture of short-chain PFAS	PFBS: 3.5 PFOA: 3.4 PFOS: 4.4 PFHxS: 3.7 PFHpA: 2.6 PFNA: 4.8	70 – 130%
USEPA Method 8327	SW, GW, WW	24	PFCAs, PFSAs, sulfonamides, sulfonamidoacetic acids	Yes	Procedure used commercially	PFBS: 10 PFOA: 10 PFOS: 10 PFHxS: 40 PFHpA: 40 PFNA: 10	70 – 130%
USEPA Method 8328	SW, GW, WW	28	PFCAs, PFSAs, sulfonamides, sulfonamidoacetic acids, GenX	Yes	Effective capture of long-chain PFAS	Draft Phase	Draft Phase
ASTM 7979	SW, GW, WW, Biosolids	21***	PFCAs, PFSAs, perfluorotelomer acids, perfluoroalkyl sulfonamides	Yes	Higher Minimum reporting level (MRL)	PFBS: 50 PFOA: 10 PFOS: 10 PFHxS: 10 PFHpA: 10 PFNA: 10	70 – 130%
ASTM 7968	Soil	21***	PFCAs, PFSAs, perfluorotelomer acids, perfluoroalkyl sulfonamides	Yes	Suitable for biosolids and soil	PFBS: 25 PFOA: 25 PFOS: 50 PFHxS: 25 PFHpA: 25 PFNA: 25	70 – 130%
TOP Assay	SW, GW, WW, Biosolids, Soil	Total	PFAAs	Yes	Captures all PFAAs	2	N/A
TOF Assay	SW, GW, WW, Biosolids, Soil	Total	Organic fluorines	Yes	Surrogate measurement of fluorine compounds	1	N/A
Modified USEPA Method 537	SW, GW, WW	24**	PFCAs, PFSAs, sulfonamides, sulfonamidoacetic acids	No	Faster runs but methods are not validated or consistent	Varies	Varies

*DW = drinking water, SW = surface water, GW = groundwater, WW = wastewater; **Varies, most labs quantify 24 analytics with this method; ***Representative of PFAS. ASTM methods also capture surrogates ****Analytical limits for are based on lowest concentration minimum reporting limits for EPA Methods 533 and 537.1 and ASTM Methods and the lower limits of quantification for EPA Methods 8327.

SAMPLING PROCEDURES

Obtaining sound observations from field monitoring requires implementation of sampling procedures to reduce the potential for sample contamination and measure to recognize if inadvertent contamination has occurred.

EXAMPLE PROCEDURES

- Michigan PFAS Sampling Guidance
- California PFAS Sampling Guidelines
- Ohio EPA Sampling at Public Water Systems

Care should be taken when collecting PFAS samples to avoiding cross contamination. PFAS-free or high-density polyethylene or polypropylene containers should be used to collect PFAS samples, and samples should be shipped on ice to preserve integrity before analysis. Generally, sampling personnel should avoid clothing that has been waterproofed, contact with food wrappers or containers that may contain PFAS, personal care products, and materials and equipment that may contain PFAS products (e.g., Teflon™ tape). Prior to sampling, water systems should consult with the laboratory that will be analyzing PFAS to determine laboratory-specific sampling requirements (such as field and travel blanks), as these requirements may vary by state or by laboratory.

SELECTING A LABORATORY

The analytical methods commonly use have progressed beyond those used in UCMR3. Consequently, the laboratory analyzing samples should be appropriately skilled and experienced with these updated methods. Analytical laboratory certification is one of the ways that laboratory performance can be benchmarked.

States are responsible for certifying drinking water laboratories for monitoring of regulated drinking water contaminants. At present laboratory certification is available to laboratories through states that have existing monitoring requirements. At present most of those certifications are limited to USEPA method 537, 537.1, and 533.

LABORATORIES

NELAC Institute List of Accredited Labs (lams.nelac-institute.org/)

USEPA State Certification Program and Certified Laboratories List (www.epa.gov/dwlabcert/contact-information-certification-programs-and-certified-laboratories-drinking-water#state-labs)

Department of Defense (www.denix.osd.mil/edqw/accreditation/accreditedlabs/)

OTHER IMPORTANT SAMPLING CONSIDERATIONS

In addition to determining sampling locations, frequency, and analytical methods, there are several important considerations when collecting PFAS samples to ensure robust and defensible results are obtained. Other parameters should be measured and recorded when collecting PFAS samples, as shown in Table 3. This list is not meant to be exhaustive, and water systems should add or remove parameters as appropriate for their sample location(s).

Table 3 – Parameters Evaluated Alongside PFAS

PARAMETER	EXAMPLE
Weather Conditions	Rainy, cloudy, sunny, etc.
Environmental Conditions	Stream flow, water depth, distance from shoreline, water type (e.g., lake or river), etc.
Water Quality	pH, temperature, turbidity, organics (e.g., TOC or UV254), etc.
Groundwater Well Conditions	Well depth, time purged, water table characteristics, well material, etc.
Location Characteristics	GPS coordinates, groundwater well name, etc.

Step 4 – Interpret Results

For water systems that conduct monitoring programs, it can be difficult to interpret the results to determine the likely source of PFAS contamination and to determine appropriate follow-up action. The following sections provide an overview of approaches to interpret PFAS results in a way that helps determine the sources of the contamination in the system's watershed. This section may also be useful for systems sampling as required by the UCMR 5 monitoring.

INDIVIDUAL PFAS FINGERPRINTING

Water systems may use sampling and monitoring program results to determine the causes of PFAS in their source

water. Knowing which PFAS are present in a water sample can help water systems determine a "PFAS fingerprint," allowing them to gain a better understanding of a contamination source or sources. Table 4 presents a variety of PFAS and possible PFAS contamination sources in drinking water. This table was generated using occurrence data with known PFAS contamination sources. This list is not intended to be complete but represents the primary PFAS identified in drinking water to date.

Table 4 – Possible Sources of PFAS Contamination

PFAS	ASSOCIATED SOURCE
Perfluoro-2-methoxyacetic acid	Industrial discharge
Perfluoro(3,5-dioxahexanoic) acid	Industrial discharge
Perfluoro-3-methoxypropanoic acid	Industrial discharge
Perfluorobutane-sulfonate	AFFF discharge, industrial discharge, landfills
Perfluoro(3,5,7-trioxaoctanoic) acid	Industrial discharge
Perfluoropentanoic acid	AFFF discharge, landfills
Perfluoro(3,5,7,9-tetraoxadecanoic) acid	Industrial discharge
Perfluorohexanoic acid	AFFF discharge, landfills
Perfluoroheptanoic acid	AFFF discharge, industrial discharge, landfills
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	Industrial discharge
Fluorotelomer sulfonate 6:2	AFFF discharge
Nafion Byproduct 1	Industrial discharge
Nafion Byproduct 2	Industrial discharge
Perfluorohexane-sulfonate	AFFF discharge, landfills
Perfluorooctane-sulfonate	AFFF discharge, industrial discharge, landfills
Perfluorooctanoic acid	AFFF discharge, industrial discharge, landfills
Perfluorononanoic acid	Industrial discharge, landfills

Because of research on common sources of PFAS contamination in the environment, known PFAS fingerprints can be used to trace measured PFAS in source water to a specific type of PFAS source. The following figures illustrate how individual PFAS can be used to help identify the source of contamination. Figure 5 represents PFAS from water samples collected near a known historical AFFF discharge location. A majority of the total PFAS concentration is 6:2 fluorotelomer sulfonate (6:2 FTS) (35%), followed by PFPeA (21%) and PFHxA (14%). These three types of PFAS are primarily used in AFFF as opposed to industrial or manufacturing applications.

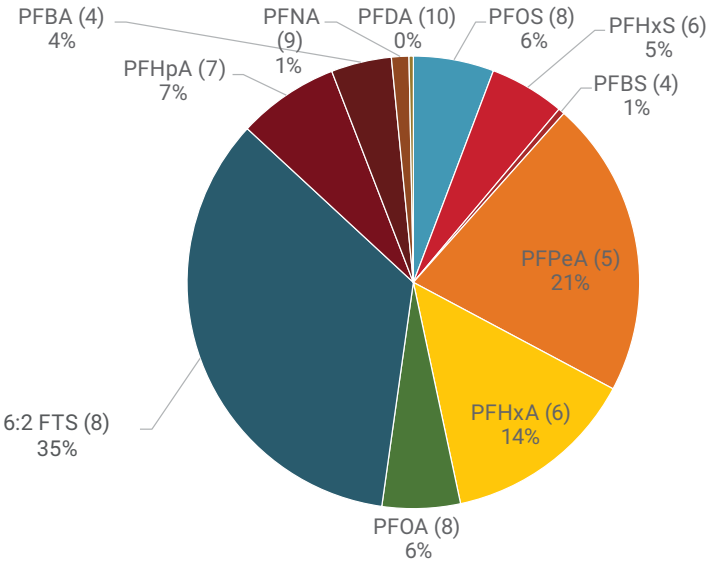

Figure 5 – *PFAS Speciation from Water Samples Contaminated with AFFF (USEPA Method 537)*

Figure 6 presents individual PFAS from surface water samples located near a historical manufacturing facility and downstream of an airport. In this scenario, it is unknown whether the primary source of contamination is due to manufacturing or AFFF discharge. The results presented in Figure 5 and Figure 6 represent samples collected approximately two miles apart but are located in different streams.

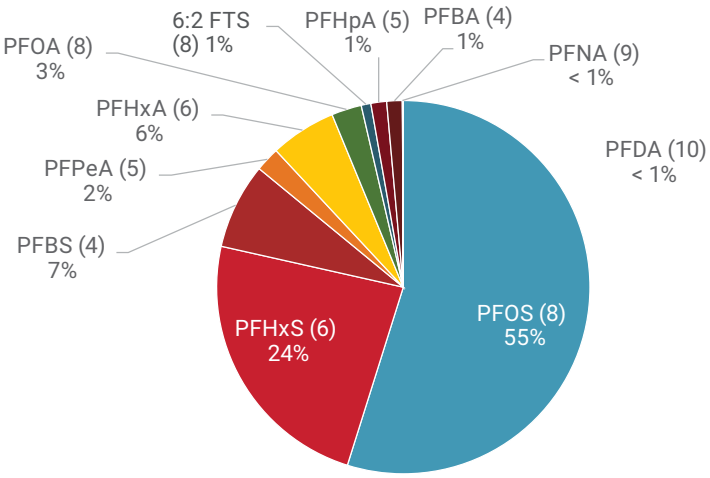

Figure 6 – *Average PFAS Speciation from Water Samples Collected Near a Historical Industrial Site and Downstream of an Airport (USEPA Method 537)*

Figure 7 presents average PFAS results from water samples collected from a river downstream of a known chemical discharge location. PFAS samples collected upstream of the chemical discharge location showed minimal PFAS levels, confirming that the chemical discharge resulted in the PFAS contamination. Short-chain PFAS, including perfluoro-2-methoxyacetic acid (PFMOAA) and perfluoro(3,5-dioxahexanoic) acid (PFO2HxA), comprise a majority of the total PFAS concentration. Alternatively, long-chain PFAS, such as PFOS and PFOA, comprise of < 1% of the total PFAS concentration and reflect the industrial manufacturing phase-out of PFOA and PFOS.

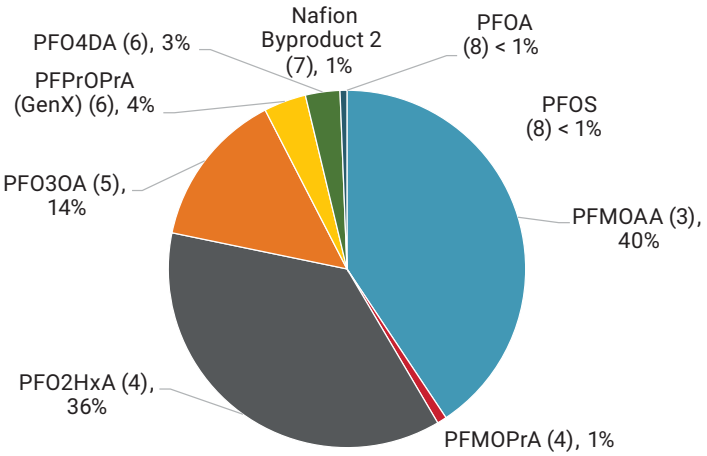

Figure 7 – *Average PFAS Speciation from Samples Collected Downstream of Industrial Discharge (USEPA Method 537)*

Several factors impact individual PFAS present in a water sample other than PFAS type and source. These factors may include water table level, as short-chain PFAS are transported more easily through soil than long-chain PFAS; length of time in the environment, as this impacts PFAS transportation and transformation of individual PFAS to other types (Houtz et al., 2016); and discharge location relative to sample location.

Additionally, multiple sources of PFAS and the fact that PFAS cycle through the environment, WWTPs, and WTPs could result in misleading fingerprint assumptions. For example, according to Table 4, high concentrations of PFOS could indicate contamination from AFFF, industrial facilities, or landfills. The water system or regulatory agency will need to determine if one or more of these sources is located within the area to better understand the source of contamination. If none of these contamination sources is a possibility, a WWTP that receives PFOS from one of these sources and discharges effluent upstream of the WTP could be the cause of PFAS contamination.

Once a water system identifies the type of PFAS present in their water supply, they can use this information to help delineate where contamination is originating. For example, if a water system's water sample contains a majority of 6:2 FTS, it is likely AFFF is at least partially responsible for

PFAS contamination. Alternatively, if most the water sample contains short-chain PFAS, such as PFMOAA, PFO2HxA, and PFMOPrA, the source of contamination is likely from an industrial facility, as these PFAS are known to originate from manufacturing.

Summary of Source Water Evaluation

The strategies recommended in this Source Water Evaluation Guide for PFAS summarize the qualitative and quantitative steps necessary to carry out a PFAS evaluation for a water system's source water, from evaluating existing data to establishing a monitoring program. The difficulty in implementing these steps is determining what considerations should be taken during the investigation. The following sections provide a brief summary of the key points of this guidance.

STEP 1 AND 2 SUMMARY

As noted previously, Steps 1 and 2 of the source water evaluation for PFAS requires collecting any available data and evaluating this data to determine the level of potential for PFAS contamination for a drinking water system. Collection of this data will also help facilitate development of a monitoring and sampling program for the source water. There are a variety of data sources readily available for drinking water systems that can help in this effort, which include

- Occurrence data from historical UCMR 3 monitoring data and/or historical or ongoing state monitoring programs
- Identification of known potential sources within the source water area
    - Primary sources (highest risk), such as civilian and military airports, as well as common industrial facilities associated with PFAS-containing products.
    - Secondary sources (moderate risk), such as landfills, WWTPs, and fields with land applied biosolids.

This report does not provide a definitive approach to determine the level of risk from a PFAS contamination. This decision is subject to the perspective of the water system, the local community, and the other stakeholders. However, the following considerations should be made in determining the level of risk:

- How many potential sources* of PFAS contamination are present within the source water area?
- What proximity are these sources to groundwater wells or surface water intakes?
- What fraction of the source water area are primary and second sources of PFAS?
- Does historical UCMR 3 data or state monitoring data demonstrate existing PFAS contamination? If so, how do these data compare with federal and state guidelines, such as the state's drinking water standards or USEPA's toxicity values?

STEP 3 SUMMARY

A critical step for conducting a source water evaluation is to develop and implement a monitoring program. Given the complex attributes and nature of PFAS, a monitoring program is required to adequately understand the potential contamination hot spots, sources, types of PFAS, and the degree of contamination in the source water. As water systems develop a monitoring program, various critical decisions need to be made, including

- Sampling locations
- Sampling frequencies
- Analytical methods
- Implementation phasing

In addition to a monitoring program, water systems should develop a communications plan prior to implementation to ensure that the results are communicated appropriately.

STEP 4 SUMMARY

This step of a source water evaluation interprets the results. This report is intended to specifically inform water systems on tools to interpret the results with the objective of identifying the originating sources of PFAS contamination. Specifically, the use of evaluating a sample's PFAS speciation and/or fingerprint can be used to help guide this evaluation.

Additionally, a water system should compare the results of their evaluation with relevant risk benchmarks, such as federal guidelines and/or state guidelines. The USEPA and ATSDR have provided risk benchmarks for six PFAS to date (some of which are draft assessments) and are working on additional PFAS. To date, more than 25 states have established policies for PFAS to protect drinking water. The results of the source water evaluation should be compared with these benchmarks, as appropriate, to help determine appropriate mitigation options.

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