PFAS Environmental Sampling Guidance (ESG)

DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

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ADONA	4,8-Dioxa-3H-perfluorononanoic Acid
AFFF	Aqueous Film-forming Foam
ANPRM	Advance Notice of Public Rulemaking
AOF	Adsorbable Organic Fluorine
ARAR	Applicable or Relevant and Appropriate Requirement
ASP	DOE Analytical Services Program
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BET	Brunauer/Emmett/Teller
bgs	Below Ground Surface
BMP	Best Management Practice
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulation
CIC	Combustion Ion Chromatography
CMS	Corrective Measures Study
COPC	Chemical of Potential Concern
CSM	Conceptual Site Model
CWA	Clean Water Act
DNAPL	Dense Nonaqueous Phase Liquid
DoD	Department of Defense
DOE	United States Department of Energy
DOECAP	Department of Energy Consolidated Audit Program
DOECAP-AP	DOECAP-Accreditation Program
DQI	Data Quality Indicator
DQO	Data Quality Objective
EOF	Extractable Organic Fluorine
EPA	United States Environmental Protection Agency
ESG	Environmental Sampling Guidance
ESTCP	Environmental Security Technology Certification Program
ESV	Ecological Screening Values
FOSA	Fluoroalkyl Sulfonamide
FS	Feasibility Study

FTS	Fluorotelomer Sulfonic Acid
GenX	Hexafluoropropylene Oxide Dimer Acid
HAL	Health Advisory Level
HAP	Hazardous Air Pollutant
HBWC	Health Based Water Concentration
HDPE	High-density Polyethylene
HFPO-DA	Hexafluoropropylene Oxide Dimer Acid
HI	Hazard Index
HQ	Hazard Quotient
IDW	Investigation Derived Waste
IRIS	Integrated Risk Information System
ITRC	Interstate Technology and Regulatory Council
LC-MS/MS	Liquid Chromatography Mass Spectrometry
LC-QTOF	Liquid Chromatography Quadrupole Time-of-flight Mass Spectrometry
LDPE	Low-density Polyethylene
LNAPL	Light Nonaqueous Phase Liquid
LOQ	Limit of Quantitation
MassDEP	Massachusetts Department of Environmental Protection
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
mg/L	Milligrams Per Liter
MIP	Membrane Interface Probe
mm Hg	Millimeter Mercury
MRL	Minimum Reporting Level
NAPL	Nonaqueous Phase Liquid
NFI	No Further Investigation
NFRAP	No Further Remedial Action Planned
ng/L	Nanograms Per Liter
NPDES	National Pollutant Discharge Elimination System
NPDWR	National Primary Drinking Water Regulation
OECD	Organization for Economic Cooperation and Development
OTM-45	Other Test Method-45
PA	Preliminary Assessment
Pace	Pace Analytical Services

PAL	Project Action Level
PFAA	Perfluoroalkyl Acid
PFAS	Per- and Polyfluoroalkyl Substances
PFBA	Perfluorobutanoic Acid
PFBS	Perfluorobutanesulfonic Acid
PFCA	Perfluoroalkyl Carboxylic Acid
PFDA	Perfluorodecanoic Acid
PFDoA	Perfluorododecanoic Acid
PFHpA	Perfluoroheptanoic Acid
PFHpS	Perfluoroheptane Sulfonic Acid
PFHxA	Perfluorohexanoic Acid
PFHxS	Perfluorohexane Sulfonic Acid
PFNA	Perfluorononanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonic Acid
PFPeA	Perfluoropentanoic Acid
PFSA	Perfluoroalkane Sulfonic Acid
PFUnA	Perfluoroundecanoic Acid
PIGE	Particle-induced Gamma-ray Emission
POD	Porewater Observation Device
ppb	Parts Per Billion
PPE	Personal Protective Equipment
ppt	Parts Per Trillion
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
QSM	Quality Systems Manual
RAI	Response Action Investigation
RBSL	Risk-based Screening Level
RCRA	Resource Conservation and Recovery Act
RFA	RCRA Facility Assessment
RfD	Reference Dose
RFI	RCRA Facility Investigation

RI	Remedial Investigation
RL	Reporting Limit
RML	Removal Management Level
RPF	Relative Potency Factor
RSL	Regional Screening Level
SAP	Sampling and Analysis Plan
SDS	Safety Data Sheet
SDWA	Safe Drinking Water Act
SERDP	Strategic Environmental Research and Development Program
SI	Site Inspection
SMART	Specific, Measurable, Attainable, Relevant, and Timebound
SOP	Standard Operating Procedure
SRR	Sustainable and Resilient Remediation
TBC	To-be-considered Value
TCRA	Time-critical Removal Action
TOF	Total Organic Fluorine
TOP	Total Oxidizable Precursor
TSCA	Toxic Substances Control Act
TSDF	Treatment, Storage, and Disposal Facility
U.S.	United States
UCMR	Unregulated Contaminant Monitoring Rule
UCMR3	Unregulated Contaminant Monitoring Rule 3
UCMR5	Unregulated Contaminant Monitoring Rule 5
VOC	Volatile Organic Compound

1. INTRODUCTION

This Environmental Sampling Guidance (ESG) outlines a framework for the environmental investigation of per- and polyfluoroalkyl substances (PFAS), emerging contaminants at United States Department of Energy (DOE) owned or operated entities complex-wide. The investigative techniques outlined herein are designed to help identify the nature and extent of contamination, including sources of PFAS contamination in the environment, the concentrations of PFAS in those sources, and the areas impacted by PFAS migration from those sources. In addition, the ESG includes considerations for risk communication, sustainability, risk assessment, adaptive management, and decision-making. The ESG is intended to satisfy the goals and objectives presented in the first pillar of DOE's PFAS Strategic Roadmap: DOE Commitments to Action 2022-2025 (DOE 2022). Specifically, the first pillar of the Roadmap seeks to develop information concerning PFAS uses and environmental releases to characterize and assess DOE's liabilities and risks.

This ESG addresses Objective 4 of the DOE PFAS Strategic Roadmap (DOE 2022), "Understand the presence of PFAS in drinking water and the environment," and the following Roadmap actions:

- Action 1.6: Publish environmental sampling guidance to support determining the nature and extent of PFAS releases at DOE sites, following the Data Quality Objective (DQO) process.
- Action 1.7: Perform Site field assessments, as appropriate.

The ESG is intended to support PFAS investigation such as a preliminary assessment, site investigation, or a response action investigation, and support risk assessment under CERCLA, RCRA, or state corrective action requirements to determine the need for PFAS response action(s).

Using this ESG and referenced regulatory information will support the development and use of a structured PFAS investigation program. This ESG will be managed as a "living" document and will be updated periodically with the release of new regulations, approved analytical methods, and guidance. However, not all DOE sites are the same. The implementation of the ESG should be tailored to meet site-specific circumstances (e.g., Comprehensive Environmental Response, Compensation, and Liability Act [CERCLA] versus non-CERCLA sites), needs (e.g., site mission), and agreements (e.g., Federal Facility Agreement). The focus of this document is on PFAS assessments or investigations considering the evolving science and regulatory environment and the unique and challenging characteristics of this widespread and complex class of emerging contaminants.

1.1 Incorporating PFAS Sampling Program into Site Regulatory Framework

PFAS are emerging contaminants that potentially include more than 12,000 (and counting) chemicals that are widespread in the environment. They were first synthesized in 1890 (Hendricks 1953) and are widespread due to their extensive industrial, commercial, and household use in thousands of product formulations. In addition, millions of tons of PFAS have been mass-produced since the 1930s (Glüge 2020).

The first consideration in developing a PFAS assessment strategy is the regulatory framework under which the site is managed. **Table 1-1** summarizes the investigation goals and steps under CERCLA or the Resource Conservation and Recovery Act (RCRA). Four scenarios have unique considerations in developing the PFAS assessment strategy under DOE authority (e.g., DOE Order 458.1) (DOE 2011) as follows:

1. Scenario 1: Implementing environmental remediation programs that include CERCLA.
2. Scenario 2: Implementing environmental remediation programs under RCRA.
3. Scenario 3: Implementing environmental remediation programs under state authority.
4. Scenario 4: Assessing PFAS at sites not currently under an environmental remedial program; for example, some DOE sites are not comprised of operational facilities; do not have legacy environmental issues; do not generate, store, treat, or dispose of hazardous waste; or have been remediated or cleared of environmental liability.

Table 1-1. PFAS environmental investigations under Scenarios 1 and 2 (i.e., federal) prog rams

General Environmental Investigation Steps	Overarching Investigation Goal	CERCLA	RCRA	Decisions Supported
Preliminary Assessment[1]	To determine the potential for historical use and release of PFAS	Preliminary Assessment (PA)	RCRA Facility Assessment (RFA)	Distinguish between sites that pose little or no threat to human health and the environment and sites that require further investigation or no further investigation (NFI)
Site Investigation	To conduct sampling and analysis to evaluate the presence or absence of PFAS and complete a risk evaluation	Site Inspection (SI)	RCRA Facility Investigation (RFI)	Determine whether PFAS impacts and risks warrant: 1. No further remedial action planned (NFRAP) 2. Listing on the National Priorities List (CERCLA only) 3. Interim action (RCRA) or removal (CERCLA) 4. Response action investigation

General Environmental Investigation Steps	Overarching Investigation Goal	CERCLA	RCRA	Decisions Supported
Response Action Investigation	To conduct sampling and analysis to define nature and extent of PFAS contamination, evaluate PFAS fate and transport, and complete a risk assessment	Remedial Investigation (RI) [2]	RFI	Determine whether PFAS impacts and risk warrant: 1. NFRAP 2. Response action 3. Feasibility Study (FS), Corrective Measures Study (CMS), or state equivalent

[1] DOE Historical Use Guide 2023, a PFAS-specific PA-like guidance document for early PFAS investigation activities at DOE sites, can be used here.

[2] Federal facilities on the National Priorities List, Superfund Alternative Approach, and sites deferred for response under other laws in accordance with CERCLA §120(d) require an RI (United States Environmental Protection Agency [EPA] 2023a), and the PA/SI conducted are considered part of the RI by EPA.

DOE recommends using the historical use investigation guidance to conduct the first step, preliminary assessment (DOE 2023) for Scenarios 1-4 listed previously. The preliminary assessment includes an initial compilation of existing information about the site and its surrounding area to identify the need for next steps (e.g., an SI or Response Action Investigation [RAI]). DOE recommends a multiphase evaluation process to determine if further action at a site is necessary, or if a site can be removed from further consideration for a response.

If the preliminary assessment concludes that further investigation is warranted, then a site investigation (e.g., SI or RI [EPA 1988] under CERCLA or RFI [EPA 1989] under RCRA) is performed. The primary purpose of an SI is to collect and analyze environmental samples to identify if PFAS are present, determine whether PFAS were released into the environment, determine whether PFAS have impacted specific receptors (EPA 2005a), determine anthropogenic background or non-site related PFAS impacts, and determine whether contamination at the site potentially poses a threat to human health or the environment (thus warranting a response action). Combining the preliminary assessment/site investigation phases for PFAS investigations should be considered. For instance, under CERCLA, the combined PA/SI integrates activities typically performed during the PA (i.e., information gathering, site reconnaissance) with activities typically performed during the SI (i.e., reviewing data, developing field work plans, field sampling, filling data gaps) to achieve one continuous site investigation (EPA 1999a).

If the preliminary assessment and site investigation phases have determined that a response action is necessary, an RAI is initiated. The RAI contributes to the site characterization and subsequent conceptual site model (CSM) development, risk assessment, and next phases (e.g., feasibility study [FS], CMS, or state equivalent). The PFAS RAI supports human health and ecological risk assessments (refer to **Section 11.3.1**) used to document the magnitude of risk at a site, and the primary causes of that risk, to determine whether additional response action is necessary. Environmental risk assessments are site-specific and, therefore, may vary or may not be feasible depending on the complexity and particular circumstances of the site, as well as the availability of applicable or relevant and appropriate requirements (ARARs) and other criteria, advisories, and guidance.

This ESG may be consulted when conducting a preliminary assessment, site investigation, or RAI. In addition, information provided herein (i.e., sampling and analytical methods) can also be used to support sampling required for EPA compliance and American Society for Testing and Materials (ASTM) standards Phase I Site Assessment (E1527) and the Phase II Environmental Site Assessment (E1903):

- Under Scenario 1, if a DOE site is subject to CERCLA cleanup, then the PA/SI and RI should be documented in consultation with regulators. For federal facilities on the National Priorities List, Superfund Alternative Approach, and sites deferred for response under other laws in accordance with CERCLA §120(d), PFAS investigations require an RI as discussed in EPA guidance (2023a). Therefore, EPA considers the PA/SI as part of the RI, unless such documents are separately listed as primary documents in a Federal Facility Agreement.
- Under Scenario 2, DOE sites with operations and facilities regulated under RCRA, PFAS preliminary assessments should be documented using the RFA/RFI as dictated by agreements with and in consultation with regulators. In some instances, it may be appropriate to provide supplemental information to ensure that PFAS at the facility are addressed.
- Under Scenario 3, DOE sites with operations and facilities managed under state programs should follow the relevant entity’s guidance for conducting a preliminary assessment, site investigation, or RAI. If there is insufficient guidance to support PFAS assessment, DOE recommends using the CERCLA process (PA/SI/RI) for PFAS investigation as a methodical and defensible approach.
- Under Scenario 4, DOE sites are not currently under an environmental remedial program. However, historical investigations/remediations completed at these sites may have been performed prior to industry understanding of PFAS as emerging chemicals of concern. Under Scenario 4, DOE recommends using the CERCLA PA/SI/RI process for PFAS investigation as a methodical and defensible approach, if necessary.

Until recent years, PFAS were not widely investigated and were not considered a risk to the environment or human health, with PFAS sampling and analytical procedures unavailable. As a result, PFAS sources may have had years to develop and migrate without detection or characterization. For sites lacking an identified source/release, a complete understanding of the site timeline, or a general understanding of potential PFAS use, the investigation approach should start with a review of available site information and the completion of an investigation consistent with DOE *Guidance for Investigating Historical and Current Uses of Per- and Polyfluoroalkyl Substances at Department of Energy Sites* (DOE 2023).

2. REGULATORY LANDSCAPE FOR SITE CHARACTERIZATION

PFAS-regulations are rapidly evolving and vary between individual states and the federal government, with human health protection driving most PFAS regulations, guidance, and advisories developed to date. In addition, regulations have focused mainly on perfluoroalkyl acids (PFAAs; for more discussion on PFAS characteristics, refer to **Section 3.4**). However, human health and environmental toxicity evaluations are ongoing for many PFAS. In addition, EPA's 2021 Strategic Roadmap describes the intent to categorize PFAS based on toxicokinetic data and treatment capabilities (EPA 2021a). As the regulatory landscape continues to evolve rapidly, regulatory stakeholders must be engaged early in the planning phase of the investigative process to identify the current and relevant criteria that will be used to evaluate the investigation data and for decision-making following the investigation. The federal and state regulatory programs and links to resources for determining the specific values in use at the time this ESG was prepared are described within this section and in **Appendix A**.

As of October 2022, regulatory human health–based guidance values and standards had been derived for 17 PFAAs and five precursors and replacement PFAS chemicals by one or more state or federal agencies in the United States (U.S.). The values for these PFAS vary across programs, with differences due to the selection and interpretation of key toxicity studies, choice of uncertainty factors, exposure assumptions, and approaches used for animal-to-human extrapolation. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have the most regulatory guidance and standards available. The DOE is planning to issue a memorandum on the identification and selection of risk screening levels, which will include additional information on this topic.

2.1 Federal

The EPA has the authority to regulate PFAS under several different acts and programs, including RCRA, CERCLA, the Emergency Planning and Community Right-to-Know Act, the Clean Water Act (CWA), and the Clean Air Act. In addition, through the Office of Regulatory Affairs, the Office of Management and Budget maintains a list of regulatory actions initiated by the EPA and other federal agencies. The regulatory actions list is updated periodically to give the status of the regulations and is available here.

EPA has issued several documents outlining its strategy for regulating PFAS:

- EPA issued a PFAS Action Plan in February 2019 (EPA 2019a) with an update a year later (EPA 2020a). The plans outline a process with timelines for establishing PFOA and PFOS maximum contaminant levels (MCLs) for drinking water, and they include a few main actions that encompassed more than just safe drinking water issues.

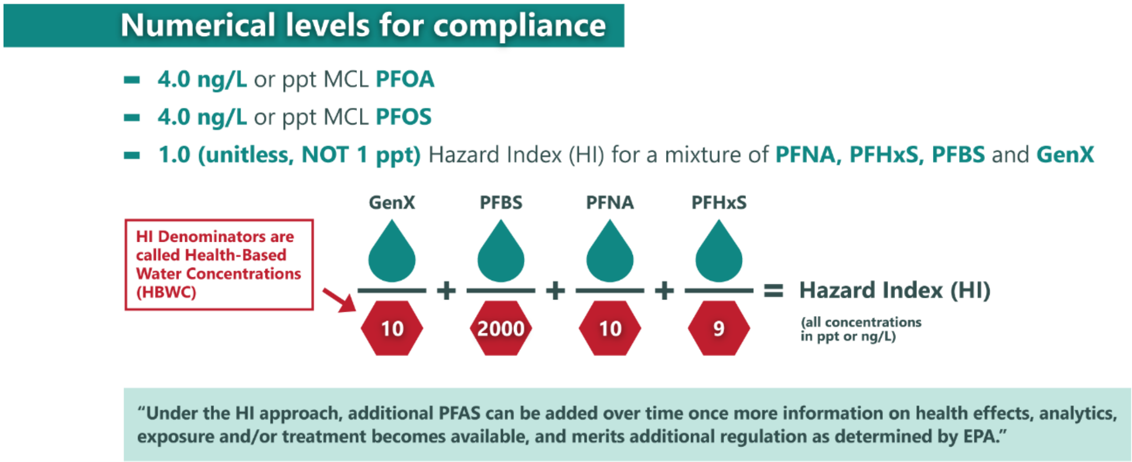
- In October 2021, the EPA published the PFAS Strategic Roadmap: EPA's Commitments to Action 2021–2024 (EPA 2021a). The EPA's stated goals for addressing PFAS are focusing on research, restriction, and remediation. The strategic roadmap includes actions across the different divisions of EPA under its Toxic Substances Control Act (TSCA), Safe Drinking Water Act (SDWA), RCRA, CERCLA, CWA, and Clean Air Act authorities.

While the actions being taken at the federal level are broad, the focus of the following subsections is on regulations in place as of May 2023 that affect investigation programs.

2.1.1 Safe Drinking Water Act

On March 14, 2023, the EPA released the pre-publication draft of the PFAS National Primary Drinking Water Regulation (NPDWR) Proposed Rule (EPA 2023b). This was published in the Federal Register on March 29, 2023. The proposed rule includes MCLs and maximum contaminant level goals for six PFAS. PFOS and PFOA are proposed to be regulated individually, while the other four PFAS (perfluorobutanesulfonic acid [PFBS], perfluorononanoic acid [PFNA], perfluorohexanesulfonic acid [PFHxS], and hexafluoropropylene oxide dimer acid [HFPO-DA, commonly referred to as GenX]) are proposed to be regulated as a mixture using a hazard index (HI) approach. The HI approach is shown graphically in **Figure 2-1**. Measured concentrations of the four PFAS will be compared to the health-based water concentrations (HBWCs) stipulated in the proposed rule, with the quotients for each analyte summed to provide a total HI. The HI is unitless; an exceedance of 1.0 would be a considered a violation under the proposed rule.

The final rule is anticipated to be published in late 2023 or early 2024.



Numerical levels for compliance

- **4.0 ng/L** or ppt MCL **PFOA**
- **4.0 ng/L** or ppt MCL **PFOS**
- **1.0 (unitless, NOT 1 ppt)** Hazard Index (HI) for a mixture of **PFNA, PFHxS, PFBS** and **GenX**

"Under the HI approach, additional PFAS can be added over time once more information on health effects, analytics, exposure and/or treatment becomes available, and merits additional regulation as determined by EPA."

Figure 2-1. Proposed numerical MCLs for compliance (EPA 2023b).

Prior to the proposed NPDWR EPA issued non-enforceable interim health advisory levels (HALs) in June 2022 for PFOA and PFOS (EPA 2022d), and final health advisories for PFBS and GenX in drinking water. The HALs for GenX and PFBS are equal to the HBWCs in the NPDRW proposed rule.

Under the SDWA, the Unregulated Contaminant Monitoring Rule (UCMR) program was developed to collect data for suspected chemicals in drinking water that do not have health-based standards. The third UCMR (UCMR3) included six PFAS (PFOS, PFOA, PFBS, PFNA, PFHxS, and perfluoroheptanoic acid [PFHpA]).

EPA required water utilities to collect samples during any consecutive 12-month monitoring period between 2013 and 2015 from public water systems serving more than 10,000 people and from a limited number of smaller systems to be nationally representative. Based on the UCMR3 reported limits of between 10 and 90 nanograms per liter (ng/L), depending on the specific PFAAs, at least one of the six PFAAs listed above was detected in 194 out of 4,920 public water systems tested (~4%), which serve about 16.5 million people in 36 states and territories (Hu 2016).

On December 27, 2021, the EPA published the fifth UCMR (UCMR5) for large and small public water systems. It includes a list of 29 PFAS, shown in **Table 2-1**. Sampling for UCMR5 will be conducted between 2023 and 2025.

Table 2-1. PFAS included within the UCMR5 Monitoring Program

Perfluorocarboxylic Acids	Perfluorosulfonic Acids/ Fluorotelomer Sulfonates (FTS)	Precursor and "Replacement" PFAS
Perfluorobutanoic acid (PFBA)	Perfluorobutane sulfonic acid (PFBS)	N-ethyl Perfluorooctanesulfonamidoacetic acid (NEtFOSAA)
Perfluoropentanoic acid (PFPeA)	Perfluoropentane sulfonic acid (PFPeS)	N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)
Perfluorohexanoic acid (PFHxA)	Perfluorohexane sulfonic acid (PFHxS)	Hexafluoropropylene oxide dimer acid (HFPO-DA) (GenX)
Perfluoroheptanoic acid (PFHpA)	Perfluoroheptane sulfonic acid (PFHpS)	4,8-dioxa-3H-perfluorononanoic acid (ADONA)[1]
Perfluorooctanoic acid (PFOA)	Perfluorooctane sulfonic acid (PFOS)	Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)
Perfluorononanoic acid (PFNA)	1H, 1H, 2H, 2H-perfluorohexane sulfonic acid (4:2 FTS)	Perfluoro-3-methoxypropanoic acid (PFMPA)
Perfluorodecanoic acid (PFDA)	1H, 1H, 2H, 2H-perfluorooctane sulfonic acid (6:2 FTS)	Perfluoro-4-methoxybutanoic acid (PFMBA)
Perfluoroundecanoic acid (PFUnA)	1H,1H, 2H, 2H-perfluorodecane sulfonic acid (8:2 FTS)	Perfluoro (2-ethoxyethane) sulfonic acid (PFEESA)
Perfluorododecanoic acid (PFDoA)		11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)

Perfluorocarboxylic Acids	Perfluorosulfonic Acids/ Fluorotelomer Sulfonates (FTS)	Precursor and "Replacement" PFAS
Perfluorotridecanoic acid (PFTrDA)		9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)
Perfluorotetradecanoic acid (PFTA)		

[1] Although the abbreviation is ADONA, indicating the ammonium salt, 4,8-dioxa-3H-perfluorononanoic acid is the parent acid.

2.1.2 CERCLA

CERCLA requires that Superfund response actions ensure the protectiveness of human health and the environment and compliance with laws and regulations that constitute ARARs. The lead agency (as defined in 40 Code of Federal Regulations [CFR] 300.5) identifies potential ARARs and to-be-considered values (TBCs) based on the timely identification of potential ARARs by states. As such, promulgated state PFAS standards (e.g., MCLs) can be identified as ARARs. Risk-based goals may be calculated to determine cleanup levels when chemical-specific ARARs are unavailable or not sufficiently protective (EPA 1997). The ARAR process can be complex and impact the scope, budget, and public acceptance components of a project (EPA 2019b).

As of April 2023, no PFAS are listed as CERCLA hazardous substances, but they may be addressed as CERCLA pollutants or contaminants, as defined by section 101 (33) of CERCLA (40 CFR 300.5). However, on September 6, 2022, EPA proposed listing PFOA and PFOS as hazardous substances on the Federal Register. On April 12, 2023, EPA provided advance notice of public rulemaking (ANPRM) seeking input regarding potential future hazardous substance designation under CERCLA of seven additional PFAAs; precursors to the nine PFAS (seven PFAAs and PFOS and PFOA); and/or categories of PFAS.[1] In addition, the EPA Action Plan (EPA 2019a) includes a priority action to develop interim cleanup recommendations for groundwater contaminated with PFOA and PFOS. PFAS actions can be initiated based on evaluating historical uses (DOE 2023), and PFAS may be included in a CERCLA site's 5-year review when supported by site-specific information.

State and federal guidance values have been issued and are frequently updated for PFAS in water and soil; a summary of links to the federal and state websites is provided in **Appendix A**, and an overview of current regulatory levels is provided by the Interstate Technology and Regulatory Council (ITRC) (updated approximately monthly). However, state-specific values are not necessarily automatically recognized as ARARs and must be evaluated to determine their ARAR status. In the Superfund program, EPA regions evaluate potential ARARs, including state

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[1] EPA is defining a group or category as a set of PFAS that share one or more similar characteristics, including, but not limited to, chemical structure (e.g., carbon chain length, functional group), physical and chemical properties, mode of toxicological action, precursors or degradants, or co-occurrence.

standards, on a site-specific basis to determine whether a specific standard or requirement is an ARAR for response decision and implementation purposes. Determining if a state requirement is promulgated, substantive, and enforceable are some factors in evaluating whether a specific standard may constitute an ARAR or TBC (40 CFR 300.5, 2001; 40 CFR 300.400, 2019; EPA 1988; EPA 1991a).

As mentioned previously, risk-based cleanup goals may be calculated when chemical-specific ARARs are not available or are determined not to be protective (EPA 1997). The EPA's Regional Screening Levels (RSLs) Generic Tables (EPA 2023c) and the RSL online calculator (EPA 2017a) may be used by risk assessors to identify screening levels and preliminary remedial goals for contaminants of potential concern at a site.

In May 2023, eight PFAS were in the RSL generic tables: PFBS, PFOA, PFOS, PFNA, PFHxS, GenX, PFHxA, and PFBA. Non-cancer reference doses (RfDs) are available for these eight analytes, with a cancer slope factor available for PFOA only. Available RSLs, as of May 2023 (EPA 2023c), and their toxicological basis are summarized in **Table 2-2**. The online RSL calculator supports site-specific calculations for multiple PFAS in tap water and soil. The EPA also provides tables and a calculator for removal management levels (RMLs). In general, RMLs are not final cleanup levels but can provide a reference when considering the need for a removal action (e.g., drinking water treatment or replacement) (EPA 2016a).

Table 2-2. November 2022 PFAS RSLs

PFAS	**Available RSLs**	**Basis of Toxicity Values**	**Reference**
PFBS (and potassium salt)	Resident soil, industrial soil, tap water, and protection of groundwater	EPA Provisional Peer-Reviewed Toxicity Value	EPA 2021c
PFHxS		ATSDR	ATSDR 2021
PFOS (and potassium salt)		ATSDR	ATSDR 2021
PFOA		ATSDR	ATSDR 2021
PFNA		ATSDR	ATSDR 2021
PFHxA		IRIS	IRIS 2023
PFBA		IRIS	IRIS 2022
GenX	Resident soil*, industrial soil*, tap water, and protection of groundwater^	EPA Office of Water	EPA 2021d

ATSDR – Agency for Toxic Substances and Disease Registry
IRIS – Integrated Risk Information System
*Soil RSLs are slightly different between the two isomers
^Protection of groundwater value only available for the anion
RSLs are updated in May and November. The most recent tables should be consulted.

Because RSLs and RMLs are periodically updated, they should be reviewed for revisions and additions before use. RSLs based upon a hazard quotient (HQ) of 0.1 should be used in SIs and

RIs. If exposure to multiple PFAS (and other chemicals of potential concern) is likely, RSLs and RMLs are not ARARs, but they may be evaluated as TBCs. The EPA has emphasized that RSLs and RMLs are not cleanup standards (EPA 2016b) and suggests that final remedial goals be informed by a baseline risk assessment so that site-specific information can be incorporated. **Section 11.3.1** provides more information on site-specific risk assessment for PFAS.

CERCLA requires that remedies also be protective of the environment. Protective risk-based cleanup goals are site-specific and depend in part on identifying the receptors to be protected.[2]

Under the Superfund Amendments and Reauthorization Act of 1986 amendment to CERCLA (or Superfund; 42 U.S.C. 9601 et seq.), the United States Department of Health and Human Services, ATSDR was established to assess the potential public health risk from exposure to hazardous substances commonly found at National Priorities List facilities. CERCLA authorizes ATSDR to develop toxicological profiles that describe these hazardous substances' health effects and support site-specific response actions through public health assessments, health consultations, or exposure assessments. A description of ATSDR's actions regarding PFAS is on its web page (ATSDR 2022). In May 2021, ATSDR released a final Toxicological Profile for Perfluoroalkyls (ATSDR 2021). In this revision, the agency discussed potential human health risks related to 14 specific PFAS and derived "provisional intermediate Minimal Risk Levels" for PFOA, PFNA, PFOS, and PFHxS. ATSDR stated that these provisional Minimal Risk Levels are intended to serve as "screening levels" for identifying contaminants and potential health effects that may be of concern at hazardous waste sites and are not intended to be used for regulatory action, including to define cleanup or action levels.

2.1.3 RCRA

RCRA authorizes EPA to regulate hazardous waste management, nonhazardous solid waste facilities and practices, and underground storage tanks holding petroleum or certain hazardous substances. No PFAS have been formally listed as RCRA hazardous waste for regulation under this program. However, some states (e.g., Texas) regulate certain PFAS under their RCRA permits and require investigation and cleanup.

On June 23, 2021, New Mexico Governor Michelle Lujan Grisham petitioned EPA Administrator Michael Regan to designate PFAS as "hazardous waste" under RCRA, citing imminent and substantial endangerment. On October 26, 2021, EPA Administrator Regan responded to the governor's petition (EPA 2021b). This response announced that EPA would be initiating the process to add four PFAS (PFOA, PFOS, PFBS, and GenX) as RCRA Hazardous Constituents. In addition, there will be a rulemaking effort to clarify that RCRA has the authority to require the cleanup of wastes that meet the definition of hazardous waste. This will mean that "emerging

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[2] As of fall 2022, no U.S. regulatory agency has established ecological criteria for PFAS.

contaminants such as PFAS can be cleaned up through the RCRA corrective action process" (EPA 2021b).

2.1.4 Clean Water Act

The CWA requires EPA to regulate pollutant discharges and water quality standards for surface waters. According to the EPA Strategic Roadmap (EPA 2021a), a validated method (Method 1633) to measure 40 PFAS compounds in eight environmental matrices will be promulgated under the CWA. Method 1633 is currently in draft as discussed in **Section 5.3.2**. In addition, the CWA authorizes EPA to set pollutant limits and monitoring and reporting requirements for contaminants in biosolids if sufficient evidence indicates potential harm to human health or the environment.

2.1.5 Clean Air Act

The Clean Air Act requires EPA to regulate emissions of hazardous air pollutants (HAPs), which are pollutants that are known or suspected to cause cancer or other serious health effects. According to the EPA Strategic Roadmap (EPA 2021a), EPA actively works with Tribal, state, and local governments to reduce air emissions of 187 HAPs to the environment. While PFAS are not listed as HAPs under the Clean Air Act as of February 2023, EPA is building the technical foundation on PFAS air emissions to inform future decisions. EPA is conducting ongoing work to evaluate PFAS emissions, and EPA will evaluate mitigation options, including listing certain PFAS as HAPs.

2.2 State

As of fall 2022, promulgated standards for one or more PFAAs have been passed in numerous states (including Alaska, Colorado, Indiana, Iowa, Massachusetts, Michigan, Minnesota, Montana, New Hampshire, New Jersey, New York, North Carolina, Oregon, Rhode Island, Texas, Vermont, and Washington), and are under development in several other states.

Some states have developed screening levels for PFAS in soils or water assuming direct contact and ingestion (see ITRC PFAS water and soil values table on the fact sheets page). In addition, certain states (e.g., Connecticut, Florida, Hawaii, Maine, and others) and EPA have developed soil-specific screening levels for groundwater protection.

Numerous states in which DOE has facilities have state-specific guidance. ITRC's guidance, which contains links to state guidance, can be consulted with the project state regulator to ensure that investigations are undertaken per state-specific requirements.

3. INVESTIGATING PFAS

3.1 Investigative Process Overview

The general principles of contaminant investigation for PFAS and other contaminants are similar in that the physical setting, release specifics, proximity to receptors, and fate and transport characteristics are used to develop the sampling and analysis strategy, including sampling media, locations, and requirements. However, PFAS investigations are challenging due to the following factors:

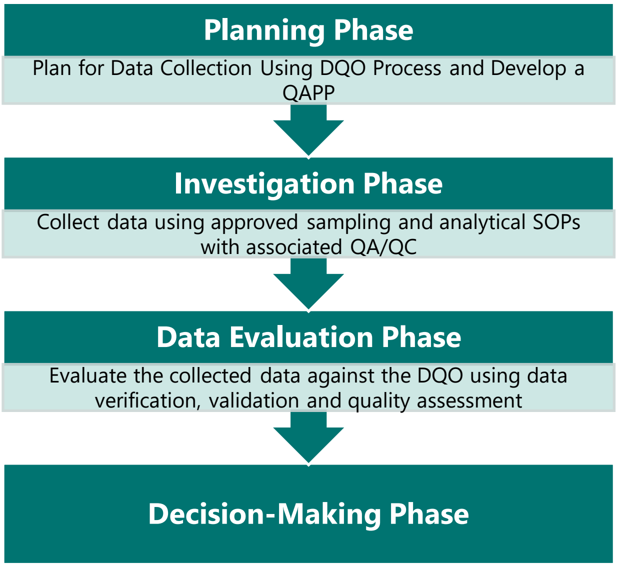
- A large chemical class with thousands of PFAS emerging, many coming under regulatory scrutiny as analytical methods capable of measuring them are developed.
- Dynamic regulatory environment, including quickly evolving environmental state and federal regulations (i.e., MCLs) with analytical methods for measuring and regulating PFAS in development. In addition, trends in regulated concentrations and health advisories are coming out in the low parts per trillion (ppt) levels or sub-ppt levels for many PFAS, which may be lower than the current analytical limits of detection.
- Widespread PFAS presence due to expansive uses involving all environmental media (ATSDR 2021) with low-level (i.e., ppt) anthropogenic background often observed due to PFAS persistence, accumulation in the environment, and diverse transport mechanisms, including atmospheric deposition.
- PFAS uses are increasingly revealed as materials, products, and industries come under progressively more stringent reporting requirements (e.g., new TSCA reporting requirements for manufacturers [including importers] of materials containing and using certain PFAS, and addition of PFAS to the Toxics Release Inventory), and exemptions to reporting are removed (e.g., eliminating the *de minimis* exemption under TSCA).

As discussed in **Section 1.1**., this ESG supports PFAS environmental investigations (see **Table 1-1**). Because of the complexity of PFAS and the evolving regulatory environment, the environmental investigation strategy should be a dynamic, flexible process tailored to the specific circumstances of individual sites; it is not a standardized process to be repeated at every site. The investigation team is responsible for the design and execution of the PFAS investigation(s) and should use concepts of adaptive management (**Section 10**) to establish the DQOs (**Section 3.1)**, collect data of sufficient quality to evaluate the site, and support the decisions being made in that phase (e.g., determine if additional data gaps warrant more investigation or if sufficient data exist to complete risk evaluation). These adjustments involve balancing a wide variety of factors and exercising professional judgment. Upon completion of the PA/SI, a report is prepared to document the findings, and, at a minimum, the results documented in the report should accomplish the following:

- Define the source(s) and nature of the release
- Describe pathways for contaminant migration
- Identify potential human and ecological receptors
- Conclude, as applicable, with:
    1. An NFI or NFRAP determination, or
    2. An interim or removal action as necessary (e.g., removal action or PFAS removal in drinking water systems), or
    3. An RAI (e.g., RI/FS or RFI/CMS) including a risk (e.g., screening-level or baseline) assessment if warranted.

Collaboration with site regulators to settle on a site-specific PFAS investigation process is recommended to meet existing and potential future regulatory requirements, and to ensure appropriate review, comment, concurrence, and dispute in accordance with the regulatory process. Several states have implemented PFAS investigative and regulatory initiatives. In addition, some DOE sites have completed initial PFAS investigations and are proceeding with advanced CERCLA mechanisms, such as remedial actions in response to existing requirements imposed by host states. Therefore, the DOE Field Manager and appropriate external regulators should be confident that the proposed approach meets regulatory requirements.

Planning Phase. The PFAS investigation strategy is developed and documented using the DQO process. Quality assurance and quality control (QA/QC) procedures are developed and written in a Sampling and Analysis Plan (SAP) or Quality Assurance Project Plan (QAPP). The QAPP is the principal product of the planning process that incorporates the DQO while integrating all technical and quality aspects for the project life cycle, including planning, implementation, and assessment. The QAPP documents planning results for the PFAS investigation and provides a specific format for obtaining the type and quality of data needed for decision-making. The development of the QAPP is described in **Section 7.2**.



Investigation Phase. The investigation design is carried out in accordance with the PFAS sampling and analysis standard operating procedures (SOPs) and QAPP/SAP, resulting in the generation of raw data. **Sections 4, 5, 6, 7** and **Appendix A** provide information on the selection of data collection techniques, QA and QC requirements, and other important information that will be used during the investigation.

Data Evaluation Phase. The data generated during the Investigation Phase are first verified to ensure that the SOPs specified in the QAPP/SAP were followed and that the measurements were performed in accordance with the criteria specified in the QAPP. Then the data are validated to ensure that the results of data collection activities support the objectives of the investigation as documented in the QAPP or help determine that these objectives should be modified. The data quality assessment process is then applied using the validated data to determine if the data quality satisfies the data user's needs. Data verification and validation are described in **Section 7.3.2**.

Decision-Making Phase. Decisions are made in coordination with the responsible regulatory agency based on the technically defensible conclusions drawn from the investigation process. The ultimate objective is to make technically defensible decisions with a specified level of confidence. For instance, under CERCLA, the findings of the PA/SI are used to determine whether the site (especially a National Priorities List site) should fall under an NFI or NFRAP (or equivalent), be identified as potentially requiring a removal action to address actual or imminent threats to human health or the environment, or undergo further investigation (e.g., risk assessment and RI) with regulatory concurrence. The following are the potential decision outcomes of the PFAS investigation:

1. **NFRAP or equivalent:** The site does not pose an unacceptable risk to human health and the environment.
2. **NFRAP with decision document:** The sites designated NFRAP from the investigation may also be included in a decision document (e.g., Record of Decision) for the relevant site, or in other decision documents at the same installation, if acceptable to the stakeholders.
3. **Early Response Action:** An early response action can be a Removal Action under CERCLA or Interim Action under RCRA (or equivalent under a state program). Under CERCLA, EPA categorizes removal actions in three ways: (1) emergency removal actions, (2) time-critical removal actions (TCRAs), and (3) non-time critical removal actions (see the CERCLA/Superfund Orientation Manual [EPA/542/R-92/005]). When implementing a removal action, whether it is an interim or final action, it is recommended that the site be characterized in enough detail to perform risk screening, define the limits of the removal action in advance, and develop an exit strategy. For PFAS, TCRAs may include installation of point of use treatment systems on impacted potable wells or drinking water systems to protect receptors.

4. **Initiate next phases (e.g., select a remedy):** Under CERCLA, potential next phases could include initiating an FS for the site, and under RCRA, initiating an RCRA CMS or equivalent response action investigation under a state program. The RI/FS and RFI/CMS typically support selecting a remedy by determining the nature and extent of contamination, evaluating risk at the site, testing whether certain technologies can treat the contamination, and evaluating the cost and performance of technologies that could be used to clean up the site.

3.2 PFAS DQO Process

Developing a plan for data collection using the DQO process is the first step in the planning phase when conducting an initial PFAS investigation. During initial PFAS investigations, actions are taken to understand uses and environmental releases to characterize and assess a site's liabilities and risks using the DQO process. Initial PFAS investigations address important questions that inform the development and refinement of the CSM necessary to complete the DQO process, such as the following:

- Has there been a PFAS release? Knowledge of historical uses of PFAS (DOE 2023) can provide insight into where materials were used and where releases might have occurred.
- Where are PFAS likely to exist following a release? Knowledge of PFAS fate and transport informs site investigation by providing insight into where efforts should be focused and developing an appropriate CSM.
- What media are impacted by PFAS? Understanding PFAS sources, fate, and transport provides a basis for evaluating what media may be affected.
- How far have PFAS migrated in the developed and natural environment? An understanding of fate and transport provides the basis for understanding migration routes and the extent of impacts from sources.
- Have media (e.g., water, soils, concrete, sediments) potentially impacted by a PFAS release been relocated, disturbed, or redistributed? Relocation and redistribution of PFAS-contaminated media may result in establishing additional sources to be investigated and potentially remediated.
- Is there potential for anthropogenic background presence or sources? Where may these sources be located? Understanding drivers of anthropogenic background can help refine CSMs.
- What human health or ecological receptors may be affected by a PFAS release? Understanding where receptors may be located can impact where samples are collected (i.e., bias sampling toward locations along the migration path between PFAS source and receptors).

The DQO process (**Figure 3-1**) involves completing seven steps to establish performance and acceptance criteria for executing environmental investigations. The DQO process is considered flexible and can be tailored to support the goals of any PFAS investigation. Historically, it has been deemed effective for determining appropriate resources, quality, and quantity of data required to meet project goals and develop a documented action plan. Further, the DQO process described in this section only summarizes each step and is not intended to cover all details described in the Guidance on Systematic Planning Using Data Quality Objectives Process (EPA QA/G-4). The information described within each step shown in **Figures 3-2** through **3-9** is provided as example(s).

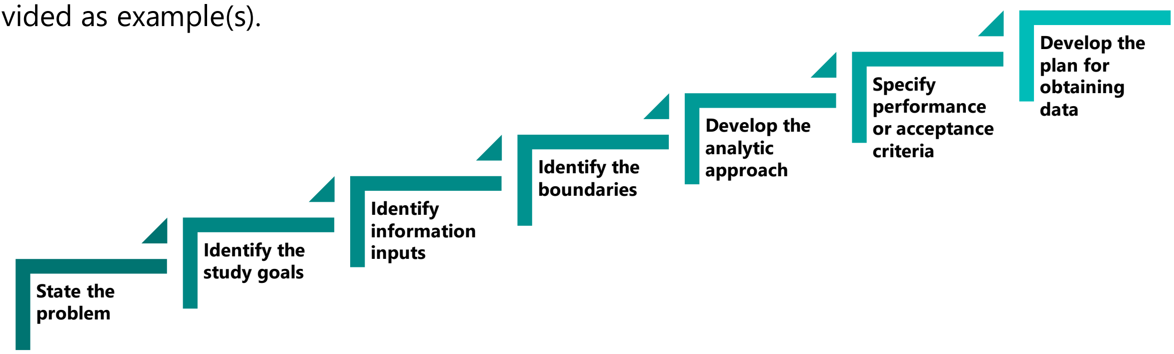
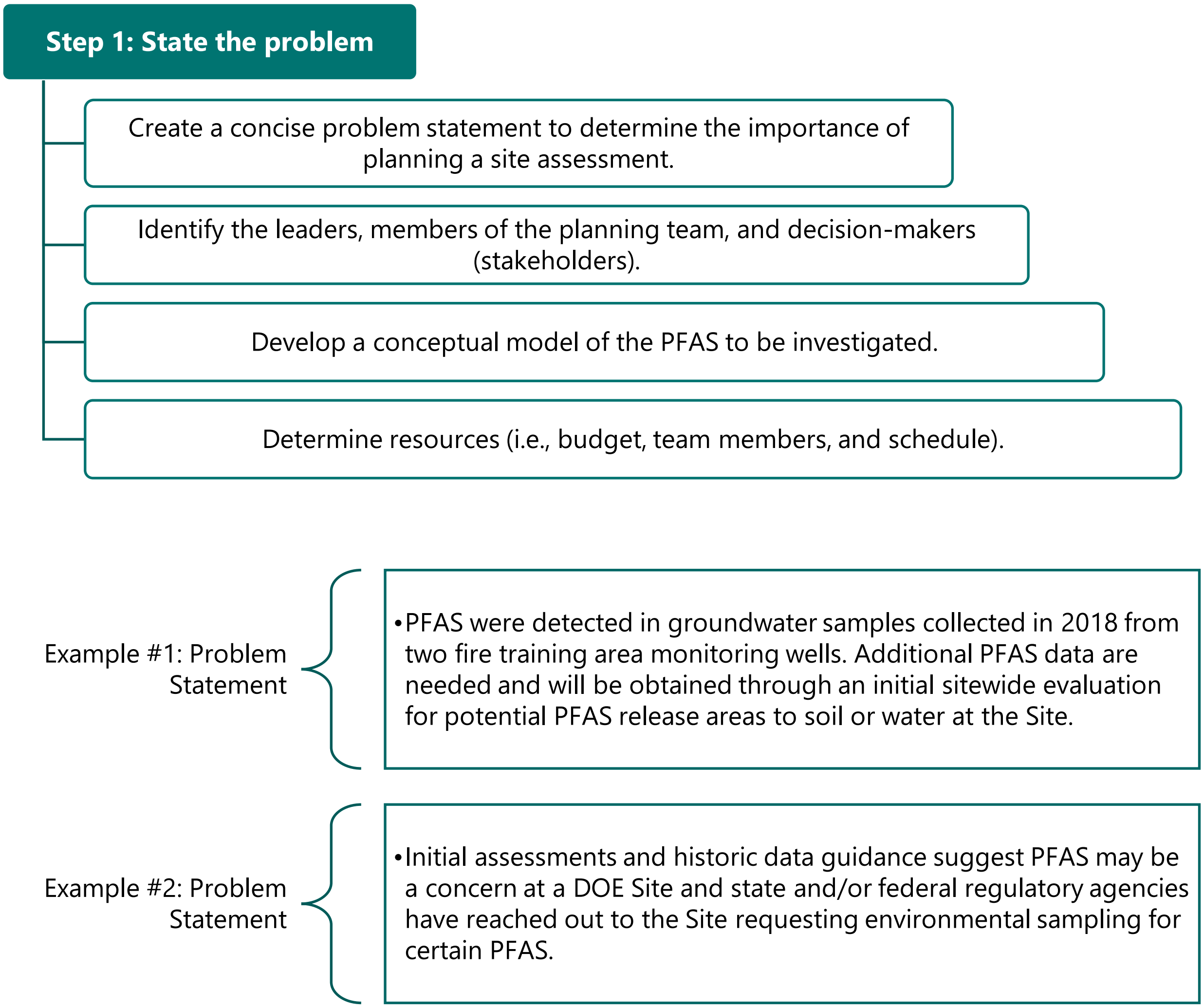


Figure 3-1. Data quality objective 7-step process (EPA 2006).



Step 1: State the problem

- Create a concise problem statement to determine the importance of planning a site assessment.
- Identify the leaders, members of the planning team, and decision-makers (stakeholders).
- Develop a conceptual model of the PFAS to be investigated.
- Determine resources (i.e., budget, team members, and schedule).

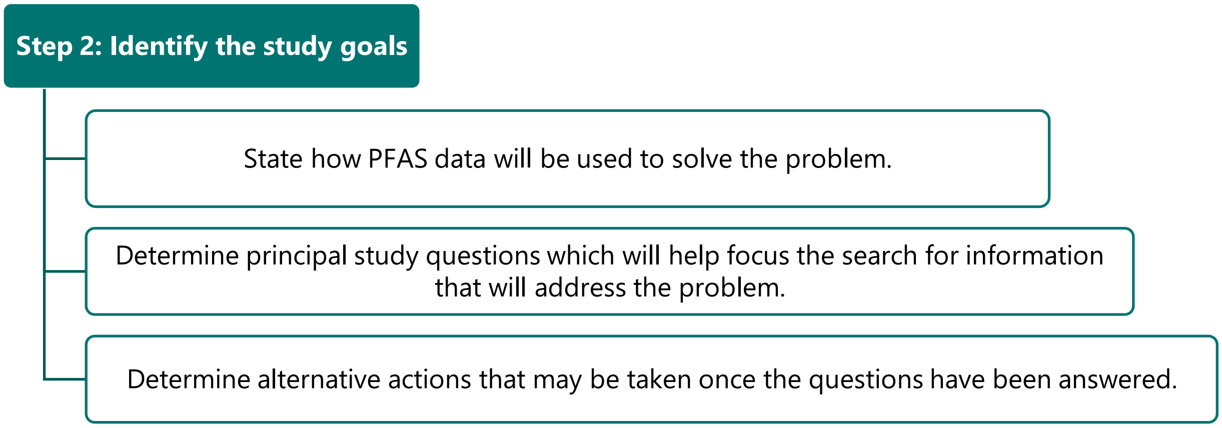
Example #1: Problem Statement

- PFAS were detected in groundwater samples collected in 2018 from two fire training area monitoring wells. Additional PFAS data are needed and will be obtained through an initial sitewide evaluation for potential PFAS release areas to soil or water at the Site.

Example #2: Problem Statement

- Initial assessments and historic data guidance suggest PFAS may be a concern at a DOE Site and state and/or federal regulatory agencies have reached out to the Site requesting environmental sampling for certain PFAS.

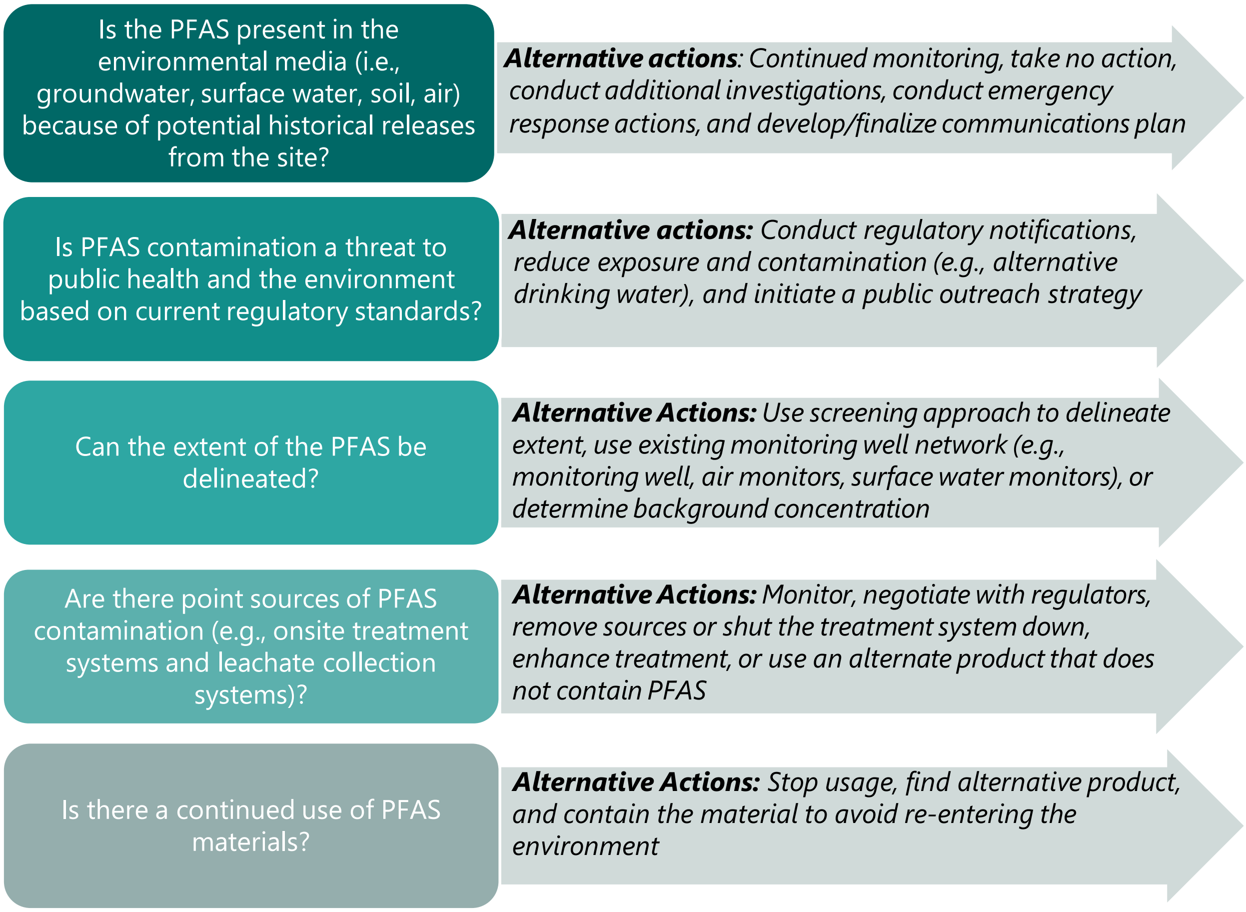
Figure 3-2. DQO Step 1: State the problem and examples.



Step 2: Identify the study goals

- State how PFAS data will be used to solve the problem.
- Determine principal study questions which will help focus the search for information that will address the problem.
- Determine alternative actions that may be taken once the questions have been answered.

Figure 3-3. DQO Step 2: Identify the study goals.



Is the PFAS present in the environmental media (i.e., groundwater, surface water, soil, air) because of potential historical releases from the site?

***Alternative actions**: Continued monitoring, take no action, conduct additional investigations, conduct emergency response actions, and develop/finalize communications plan*

Is PFAS contamination a threat to public health and the environment based on current regulatory standards?

***Alternative actions:** Conduct regulatory notifications, reduce exposure and contamination (e.g., alternative drinking water), and initiate a public outreach strategy*

Can the extent of the PFAS be delineated?

***Alternative Actions:** Use screening approach to delineate extent, use existing monitoring well network (e.g., monitoring well, air monitors, surface water monitors), or determine background concentration*

Are there point sources of PFAS contamination (e.g., onsite treatment systems and leachate collection systems)?

***Alternative Actions:** Monitor, negotiate with regulators, remove sources or shut the treatment system down, enhance treatment, or use an alternate product that does not contain PFAS*

Is there a continued use of PFAS materials?

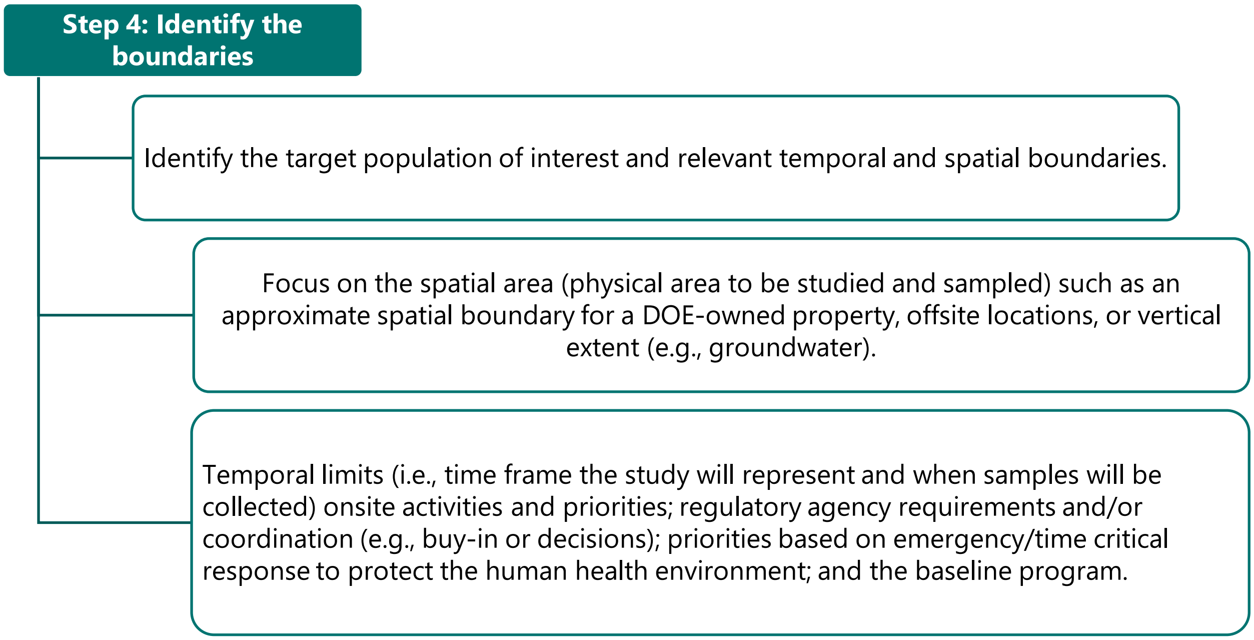
***Alternative Actions:** Stop usage, find alternative product, and contain the material to avoid re-entering the environment*

Figure 3-4. Example principal study questions and alternative actions.

Step 3: Identify information inputs - Determine the types and potential sources of information needed to conduct the PFAS investigation

- Compile existing information
    - Results from historical use assessment (e.g., site information, physical/geologic characteristics per the historical use guide)
    - Previous PFAS data (e.g., methods used, PFAS reported, and quality assessment)
    - Other database(s) of PFAS information (e.g., Department of Defense, state, others)
    - PFAS data for existing treatment systems (e.g., permit compliance)
- Determine potential off-site sources
- Determine the decision makers (e.g., regulators) and engage as early as possible in the process to obtain buy-in on the type, quantity, means, and methods to support the decision outcomes
- List sample locations and environmental media as well as potentially impacted media
- Determine analytical test methods
- Determine fate and transport
- Identify the current suite of PFAS analysis, reported PFAS and reporting limits
- Characterize investigation derived wastes (IDW)

Figure 3-5. DQO Step 3: Identify the information inputs and example data needed.



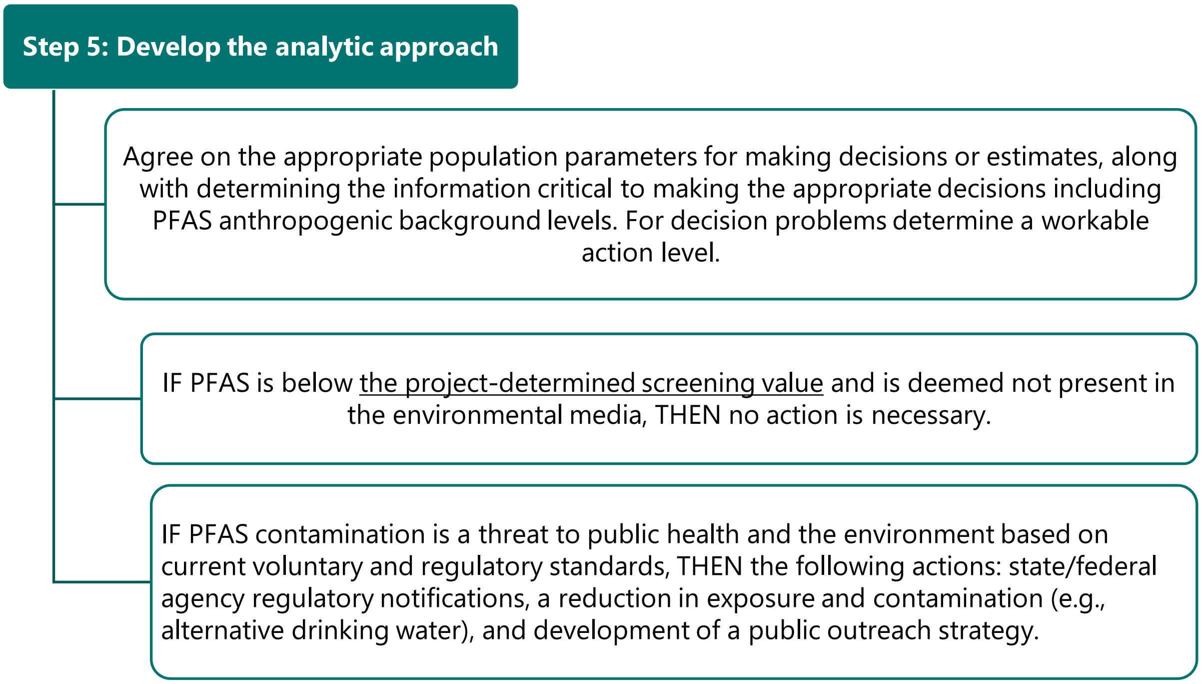
Step 4: Identify the boundaries

Identify the target population of interest and relevant temporal and spatial boundaries.

Focus on the spatial area (physical area to be studied and sampled) such as an approximate spatial boundary for a DOE-owned property, offsite locations, or vertical extent (e.g., groundwater).

Temporal limits (i.e., time frame the study will represent and when samples will be collected) onsite activities and priorities; regulatory agency requirements and/or coordination (e.g., buy-in or decisions); priorities based on emergency/time critical response to protect the human health environment; and the baseline program.

Figure 3-6. DQO Step 4: Identify the boundaries.



Step 5: Develop the analytic approach

Agree on the appropriate population parameters for making decisions or estimates, along with determining the information critical to making the appropriate decisions including PFAS anthropogenic background levels. For decision problems determine a workable action level.

IF PFAS is below the project-determined screening value and is deemed not present in the environmental media, THEN no action is necessary.

IF PFAS contamination is a threat to public health and the environment based on current voluntary and regulatory standards, THEN the following actions: state/federal agency regulatory notifications, a reduction in exposure and contamination (e.g., alternative drinking water), and development of a public outreach strategy.

Figure 3-7. DQO Step 5: Develop the analytic approach and example decision rules.

Step 6: Specify performance or acceptance criteria - Define the criteria that will be needed to minimize the possibility of either making erroneous conclusions or failing to keep uncertainty in estimates within acceptable levels.

- Sampling and field screening will be conducted by field personnel experienced in collecting environmental PFAS samples using sampling, analytical, and quality procedures described in the SAP.
- PFAS samples must be sent to laboratories that are certified/accredited to perform the most recent EPA test methods related to PFAS that are appropriate for the media being sampled (**Section 5.6).**
- Groundwater, treated groundwater, surface water, treated wastewater, and landfill leachate samples will be analyzed using EPA Method 1633.
    - Drinking water samples will be analyzed using EPA Method 537.1 and533 (or more recent).
    - The data will be subject to X% percent verification/assessment and Y% percent validation. This step is project-specific, and a decision concerning the level of validation will need to be made.
- Only data with QC results that meet the applicable methodology and data use criteria will be considered usable for supporting the study's goals.

Figure 3-8. DQO Step 6: Specify performance or acceptance criteria.

Step 7: Develop the plan for obtaining the data - Develop an acceptable and efficient sample and analysis plan including identifying the constraints that will impact the plan.

- Output from the DQO Steps 1-6
- Cost-effective design alternatives
- Elements of the Uniform Federal Policy-QAPP worksheets/SAP
- Standard operating procedures
- Laboratory reports
- Data verification/validation reports
- Process and decision criteria, e.g., the Triad approach for multiphase investigation
- Identification of certified laboratories

Figure 3-9. DQO Step 7: Develop the plan for obtaining the data and the level of QA/QC needed to ensure defensible results.

QA/QC procedures are developed and written in an SAP or QAPP. The QAPP is the principal product of the planning process and defines the DQOs that are used to develop performance or acceptance criteria, also referred to as data quality indicators (DQIs). The development of the QAPP is described in **Section 7.2.**

3.3 PFAS Sources

DOE published a summary of historical uses of PFAS that identifies common activities potentially involving PFAS use and environmental release at DOE sites (DOE 2023, **Appendix C**). Potential sources are generally categorized from greatest to least likelihood of PFAS release. However, some categories may have used PFAS in *de minimis* applications, depending on the site. A non-exhaustive list of keywords is associated with each category to assist in records research. The categories of activities with potential for PFAS usage or release include the following:

- Category 1: Fire Training Facility, Fire Department, aqueous film-forming foam (AFFF) use
- Category 2: Wastewater Treatment Plants and Landfills
- Category 3: Uranium Enrichment, Plutonium Production, Nuclear Operations
- Category 4: Metal Plating Processing
- Category 5: Explosives and Munitions
- Category 6: Electronics Manufacturing
- Category 7: Equipment Fuel/Maintenance
- Category 8: Well Drilling
- Category 9: Pesticides
- Category 10: Laboratory
- Category 11: Other

3.4 PFAS Characteristics

PFAS are characterized as fluorine aliphatic and cyclic compounds (Buck 2011), having carbon atoms linked to each other and bonded to fluorine atoms. The carbons may be partially fluorinated (i.e., polyfluorinated) or fully fluorinated (i.e., perfluorinated). The carbon-fluorine bond is the strongest single bond to carbon in chemistry, which results in high persistence in soil and water once released into the environment. PFAS moieties are hydrophobic and oleophobic, making many PFAS effective surfactants or surface protectors. In addition, they impart oil, water, stain and soil repellency, chemical and thermal stability, and/or friction reduction properties. Due to these desirable properties, PFAS have been widely used in firefighting foams, uranium enrichment, paper and packaging, textiles, production of plastic and rubber, paints and coatings, fluoropolymer production, metal-plating, and the semiconductor industry (to name a few).

One recent study (Glüge 2020) identified over 200 uses in 64 use categories for more than 1,400 PFAS, summarized in **Table 3-1.** PFAS use is extensive, with a myriad of use categories identified (over 210). Industries and applications with the most PFAS use categories include the photographic industry, semiconductor industry, coatings, paints and varnishes, firefighting foams, medical utensils, personal care products, and printing. This suggests that the media impacted by releases of PFAS chemicals used in these industries are particularly diverse, widespread, and complex, and likely include PFAS that are not quantified with analytical methods available as of May 2023.

A summary of compiled sources of PFAS contamination associated with DOE facilities is provided in **Section 3.3** (DOE 2023).

Table 3-1. Industry branches and other use categories in which PFAS were or are employed

Industry Branches	
Aerospace (7)	Mining (3)
Biotechnology (2)	Nuclear industry
Building and construction (5)	Oil and gas industry (7)
Chemical industry (8)	Pharmaceutical industry
Electroless plating	Photographic industry (2)
Electroplating (2)	Production of plastic and rubber (7)
Electronic industry (5)	Semiconductor industry (12)
Energy sector (10)	Textile production (2)
Food production industry	Watchmaking industry
Machinery and equipment	Wood industry (3)
Manufacture of metal products (6)	
Other Use Categories	
Aerosol propellants	Metallic and ceramic surfaces
Air conditioning	Musical instruments (3)
Antifoaming agent	Optical devices (3)
Ammunition	Paper and packaging (2)
Apparel	Particle physics
Automotive (12)	Personal care products
Cleaning compositions (6)	Pesticides (2)
Coatings, paints, and varnishes (3)	Pharmaceuticals (2)
Conservation of books and manuscripts	Pipes, pumps, fittings, and liners
Cook and bake ware	Plastic, rubber, and resins (4)
Dispersions	Printing (4)
Electronic devices (7)	Refrigerant systems
Fingerprint development	Sealants and adhesives (2)
Firefighting foam (5)	Soldering (2)
Flame retardants	Soil remediation
Floor covering including carpets and floor polish (4)	Sport article (7)
Glass (3)	Stone, concrete, and tile
Household applications	Textile and upholstery (2)
Laboratory supplies, equipment, and instrumentation (4)	Tracing and tagging (5)
Leather (4)	Water and effluent treatment
Lubricants and greases (2)	Wire and cable insulation, gaskets and hoses
Medical utensils (14)	

Modified from Glüge 2020.
Numbers in parentheses indicate the number of subcategories identified for PFAS use within the industry branch or other use categories. No parentheses indicates no subcategories.

PFAS can be divided into two major classes: nonpolymers and polymers (see **Figure 3-10,** ITRC 2022a). The PFAS polymer class includes fluoropolymers, polymeric perfluoropolyethers, and side-chain fluorinated polymers (Henry 2018, Buck 2011; Wang 2013). In general, most polymer PFAS pose lower risks to human health and the environment than nonpolymer PFAS. In addition, some polymer PFAS can transform into nonpolymer PFAS, including PFAAs.

Nonpolymer PFAS encompass two major subclasses: per- and polyfluoroalkyl substances (as shown in **Figure 3-10**), which include many groups and subgroups of chemicals as follows:

- Perfluoroalkyl substances are fully-fluorinated alkane molecules and include the persistent PFAAs (most commonly detected at PFAS investigation sites), perfluoroalkyl ether acids, perfluoroalkane sulfonyl fluorides, perfluoroalkane sulfonamides, perfluoroalkanoyl fluorides, perfluoroalkyl iodides, and perfluoroalkyl aldehydes.
- Polyfluoroalkyl substances are partially fluorinated aliphatic molecules. They include predominantly PFAA precursors, including, but not limited to, polyfluoroalkyl ether acids, fluorotelomer substances, perfluoroalkane sulfonamido substances, chloropolyfluoroalkyl ether acids, and chloropolyfluoroalkyl acids.

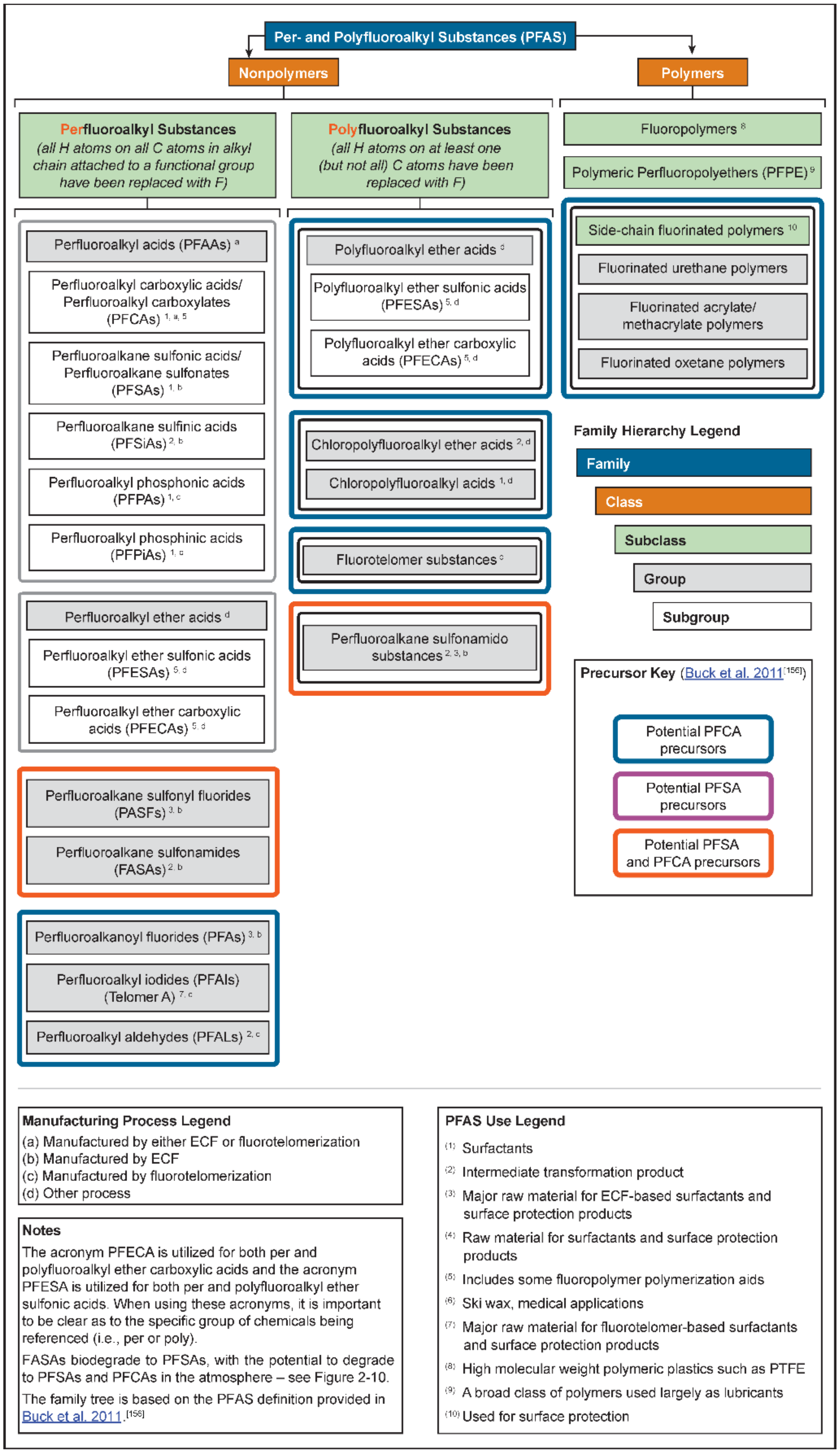
PFAAs are often considered "terminal PFAS" because they are not subject to biotic or abiotic degradation under normal environmental conditions, persist for decades, and generally include two groups:

- Perfluoroalkyl carboxylic acids (PFCAs), or perfluoroalkyl carboxylates (e.g., PFOA).
- Perfluoroalkane sulfonic acids (PFSAs), or perfluoroalkane sulfonates (e.g., PFOS).

PFOA and PFOS are two of the most widely studied and regulated PFAS, have been manufactured for decades, and are ubiquitous in the environment, having been detected in the deep sea and in the Arctic (Evich 2022). Although these two compounds are no longer produced in the U.S. (ATSDR 2021) since the phase-out of PFOS in 2002 and PFOA in 2015, chemical manufacturers have replaced them with alternative PFAS, such as polyfluoroalkyl precursors and GenX. In addition, PFOS and PFOA are still produced in China, which remains a major producer and user (HAES 2017; Li 2015; Lim 2011).

Many PFAS still in wide use globally are precursors to PFAAs and are subject to biotic or abiotic transformation to PFAAs (Washington 2015a). For example, some precursor polyfluoroalkyl substances, such as fluorotelomer alcohols and perfluoroalkane sulfonamido ethanols, transform to PFOA or PFOS, respectively, as a terminal degradation product. Due to the restrictions on the manufacture of PFOS and PFOS-related substances (e.g., precursors), manufacturers have replaced these compounds with short-chain analogs, including precursors that can transform into PFBS and PFHxS, two additional PFAS that are also coming under U.S. regulatory purview, as discussed in **Section 2**. In one study, approximately 4,700 PFAS were evaluated (The Organization for Economic Cooperation and Development [OECD] 2018), of which about 90%

were potential precursors to PFAAs. The potential for polyfluoroalkyl precursor transformation may be an under-represented source of PFAAs in many environments impacted by PFAS. The potential for precursors to act as future sources of PFAAs should be considered in site investigations, particularly at locations with known historical releases of complex PFAS mixtures, such as AFFF.



Manufacturing Process Legend

(a) Manufactured by either ECF or fluorotelomerization
(b) Manufactured by ECF
(c) Manufactured by fluorotelomerization
(d) Other process

Notes

The acronym PFECA is utilized for both per and polyfluoroalkyl ether carboxylic acids and the acronym PFESA is utilized for both per and polyfluoroalkyl ether sulfonic acids. When using these acronyms, it is important to be clear as to the specific group of chemicals being referenced (i.e., per or poly).

FASAs biodegrade to PFSAs, with the potential to degrade to PFSAs and PFCAs in the atmosphere – see Figure 2-10.

The family tree is based on the PFAS definition provided in Buck et al. 2011.[156]

PFAS Use Legend

(1) Surfactants
(2) Intermediate transformation product
(3) Major raw material for ECF-based surfactants and surface protection products
(4) Raw material for surfactants and surface protection products
(5) Includes some fluoropolymer polymerization aids
(6) Ski wax, medical applications
(7) Major raw material for fluorotelomer-based surfactants and surface protection products
(8) High molecular weight polymeric plastics such as PTFE
(9) A broad class of polymers used largely as lubricants
(10) Used for surface protection

Figure 3-10. PFAS classification and polyfluoroalkyl precursors to PFAAs.

Modified from ITRC 2022b.

3.4.1 Physical and Chemical Properties

The physical and chemical properties of PFAS affect their distribution, fate, and transport in the environment (ITRC 2022b). **Table 3-2** summarizes important chemical properties for characterizing PFAS.

Table 3-2. Physical, chemical, and partitioning properties to consider when characterizing PFAS

Physical Properties	Chemical Properties	Partitioning in Environmental Media
Physical state (e.g., liquid, solid, gas)	Solubility	Partitioning to fluid-fluid interfaces
Density	Volatility	Partitioning to air-water interfaces
Ionic state (e.g., acid, neutral, cation, anionic, zwitterionic at the pH in the environment)	Critical micelle concentration	Sorption onto soil
Extent of fluorination (e.g., polyfluorinated or perfluorinated)	Boiling point	Sorption onto organic carbon
Carbon-fluorine chain length	Melting point	Partitioning to biota and their chemical properties
Functional groups	Chemical stability	
	Thermal stability	

Because of the number and diversity of PFAS, there is considerable variation in the quantity and quality of chemical and physical properties data, with only some PFAS having been extensively characterized. In contrast, there is almost no information available for others. The physical and chemical properties available for 45 PFAS, including those quantified via EPA Methods 1633, 533, or 537, can be found on the ITRC website (ITRC 2022b). The physicochemical properties of PFOS and PFOA are provided in **Table 3-3.**

Table 3-3. Physicochemical properties of PFOS and PFOA

Property	PFOS	PFOA
Molecular Weight (grams per mole [g/mol])	500.13	414.09
Color/Physical State	White powder (potassium salt)	White powder (ammonia salt)
Boiling Point	133 – 249 °C (experimental) 219 – 244 °C (predicted)	188 – 199 °C (experimental)
Melting Point	15.2 – 185 °C (predicted)	47.5 – 59.5 °C (experimental) ≥400 °C (potassium salt)[#]
Vapor Pressure	2.48 x 10^{-6} millimeter mercury (mm Hg) at 25 °C (experimental and predicted)	1.65 x 10^{-2} – 10.0 mm Hg at 25 °C (experimental) 0.111 – 0.345 mm Hg at 25 °C (predicted)
Henry's Law Constant	1.8 x 10^{-11} atm-m^3/mole (predicted)	1.92 x 10^{-10} atm-m^3/mole (predicted)
Log K_{ow}: Octanol-Water partition coefficient	4.30 – 7.03 (experimental)	1.92 – 3.6 (experimental)
Organic carbon-water partition coefficient (K_{oc})	2.57	2.06
Solubility in Water	680 milligrams per liter (mg/L)	9.50 x 10^{-3} mg/L at 25 °C
Half-life in Water	Stable (41 years)[#]	Stable (92 years) [#]
Half-life in Air	Stable (114 days)[#]	Stable (130 days)[##]

All data adapted from EPA's CompTox website (accessed March 20, 2021) except data marked # which was sourced from ATSDR 2021, and ## from Hurley 2004.
Atm-m^3/mole – standard atmosphere cubic meter per mole

Increasingly, estimating properties of PFAS for which data are unavailable relies on predictive mathematical techniques, such as quantitative structure-activity relationship models. Therefore, EPA is pursuing a categorization approach for PFAS informed by structural, mechanistic, and toxicokinetic information discussed in the PFAS Strategic Roadmap (EPA 2021a) to estimate the physicochemical properties of PFAS, model PFAS biodegradation, map PFAS to parent substances, and use in related data generation, integration, modeling and analytics, and development of toxicity parameters.

3.4.2 Comingling of PFAS and Other Contaminant Considerations

Because PFAS impart desirable characteristics to chemical mixtures, PFAS may be comingled with multiple PFAS analytes and other contaminants. PFAS have been widely used in specialized chemical formulations such as oil surfactants; leveling agents in paints, coatings, and sealants; lubricants; mist suppressants; and firefighting foams. Release of PFAS along with co-contaminants (e.g., solvents, petroleum products) in sources such as industrial sites and fire training areas also influences the fate and transport of PFAS.

For example, fire training often co-released PFAS and petroleum fuels as nonaqueous phase liquid (NAPL), resulting in a mixed contamination source area. In PFAS-NAPL mixtures (Brusseau 2018), PFAS mass may be entrained in NAPL or adsorbed onto the NAPL/water interface resulting in increased retardation and persistence of PFAS (Guelfo 2013, McKenzie 2016). The contribution of NAPL partitioning relative to other PFAS partitioning mechanisms (e.g., solid phase, and air-water interface) will vary based on site-specific conditions.

PFAS mixtures have unique chemical properties, and obtaining site-specific measurements of their chemical and physical properties (e.g., solubility) is suggested to facilitate a better understanding of how these mixtures are distributed and migrate in the environment. However, because of the nature of PFAS releases (i.e., age and use in various complex mixtures), obtaining site-specific measurements may be infeasible or impractical. In these cases, the investigation to evaluate the nature and extent of the release impacts may require more locations and samples.

3.5 Fate and Transport of PFAS in the Environment

Once released into the environment, PFAS can be transported in the atmosphere and in terrestrial and aquatic (i.e., surface water, stormwater, and groundwater) systems. PFAS fate and transport describes how PFAS move through the environment within and between different media and how they might change chemically, physically, or biologically in doing so. Factors that influence PFAS fate and transport can be broadly divided into the following categories (ITRC).

Nature of PFAS sources: PFAS sources are important to evaluating fate and transport and vary depending on the nature of the site operations and release(s). Types of PFAS uses and sources are discussed in **Section 3.3.** Significant sources include facilities that use PFAS products in manufacturing or processing (e.g., uranium enrichment); areas where fluorine-containing Class B firefighting foams are used, stored, or released; waste management facilities (i.e., landfills); and wastewater treatment facilities. The PFAS composition, properties, and release mechanisms will vary for each source type.

PFAS properties: The PFAS properties also dictate their mobility in the environment and vary widely depending on the nature of the source, the type of PFAS released, and co-contaminants in PFAS mixtures, as discussed in **Section 3.4.2.** These properties strongly influence the type and extent of PFAS partitioning, migration routes, and transformations that can be expected to occur.

Environmental conditions: Environmental conditions include characteristics that impact how PFAS partition between and migrate through different media, as well as the forces that drive migration (e.g., precipitation, recharge, advective gradients, surface water or stormwater flows) when PFAS are released, including the following:

1. Soil and sediment properties (e.g., permeability, surface charge, organic carbon content, exchange capacity, mineralogy, water content, **Section 3.5.2**)
2. Nature of migration routes from sources to receptors (e.g., unconsolidated material vs. bedrock, depth of the vadose zone, transmissivity, stormwater route to surface water)
3. Properties of groundwater geochemical conditions (e.g., oxidation-reduction conditions, pH, hardness, tritium, or alkalinity), and hydraulic properties (e.g., hydraulic conductivity, seepage, Darcy velocity) (**Section 3.5.4**)
4. Properties of stormwater or surface waters (e.g., geochemical conditions, flow rates) (**Section 3.5.6**)
5. Climate and weather conditions (e.g., precipitation/infiltration rates)
6. Prevailing atmospheric conditions
7. Anthropogenic background
8. Previous and current remedial efforts
9. The presence of co-contaminants

The characteristics of sites with releases of PFAS often share many similarities with sites having releases of other contaminants. However, widespread PFAS use has resulted in impacts on receiving facilities, such as wastewater treatment plants and landfills, that are relatively unique to PFAS. This has resulted in PFAS in waste streams and resulted in anthropogenic background concentrations. In addition, PFAS persistence often results in a more complicated life cycle than other contaminants. Understanding the PFAS cycle (**Figure 3-11**) is the first step in developing a framework for understanding potential PFAS sources and migration routes, which can then be used to inform a site investigation. In addition, each migration route (e.g., soil, surface water, leaching to groundwater, sediment, stormwater, air) should be considered when identifying data gaps and developing the DQOs for the investigation or sampling plan.

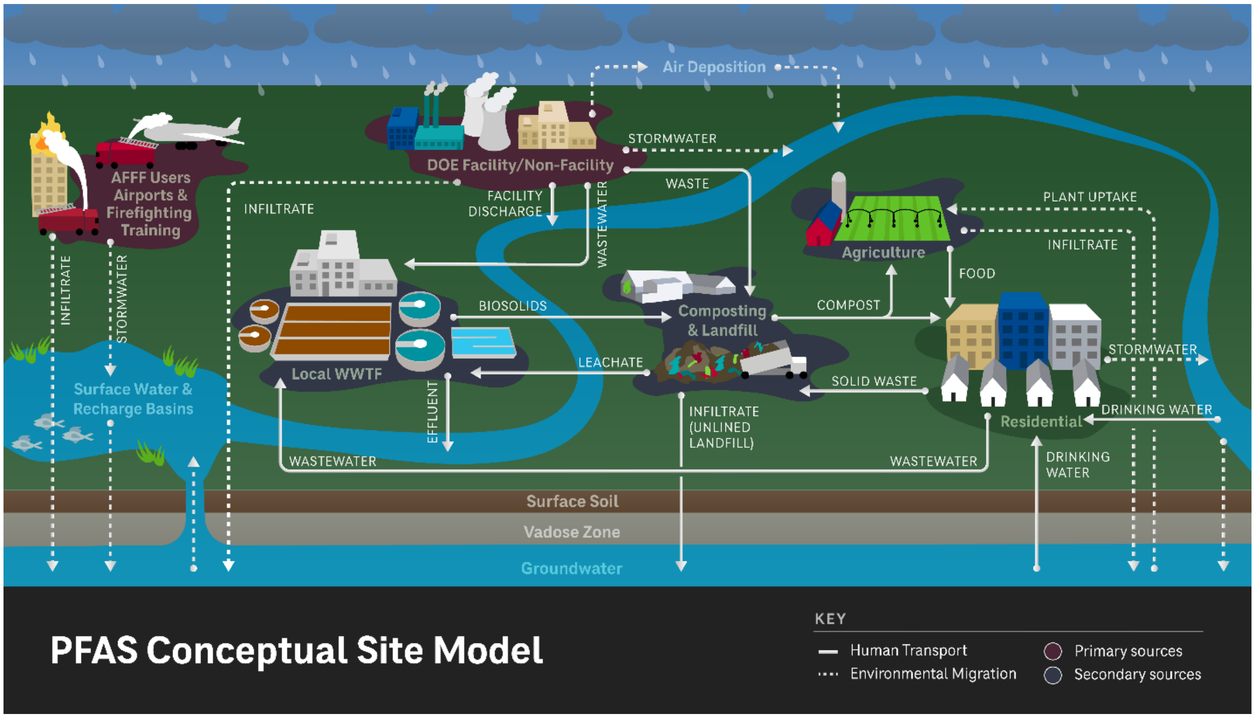


Figure 3-11. PFAS life cycle.

3.5.1 *PFAS Conceptual Site Model*

A CSM is a comprehensive graphical and written summary of what is known or hypothesized about environmental contamination at a site and the relationships among key site information pertinent to decision-making. A CSM represents the source, release, migration, and potential exposure pathways and provides a platform for evaluating data gaps. The EPA defines the six stages of CSM maturity (EPA 2011b) as preliminary-, baseline-, characterization-, design-, remediation/mitigation-, and post-remedy-stages. This ESG provides information on developing a CSM for the first three stages (summarized in **Table 3-4**), which are the most relevant to the early phases of PFAS investigations:

- Preliminary CSM Stage – A project milestone or deliverable based on existing data; developed before systematic planning to provide the fundamental basis for the planning effort as discussed in the Historical Use Guidance (DOE 2023).
- Baseline CSM Stage – A project milestone or deliverable used to document stakeholder consensus or divergence and to identify data gaps, uncertainties, and needs. The CSM is informed by the PFAS life cycle so that decisions can be made regarding sampling and analysis based on what is known about PFAS migration and transport from likely sources within different media.
- Characterization CSM Stage – Provides iterative improvement of the CSM as new data become available from investigation efforts. This stage supports risk screening, risk assessment, and remedial action decision-making.

Table 3-4. PFAS assessment CSM stages

General Environmental Cleanup Steps	CSM Stage	Level of Data Density and Quality	Primary Questions Informed by the CSM
Preliminary Assessment	Preliminary	Low-conceptual	Could PFAS use at the facility have resulted in releases to the environment?
Site Investigation	Baseline	High-quantitative	What environmental media have potential PFAS contamination? How could site receptors (human or ecological) be exposed to impacted environmental media? Do PFAS potentially pose a risk to human health or the environment? Do PFAS pose an imminent threat?
Response Action Investigation	Characterization	High-quantitative	What is the nature and extent of PFAS present in environmental media? Are PFAS levels above anthropogenic background? What are the migration pathways for PFAS within and between different media? Do PFAS pose a risk to human health or the environment? Is remedial action(s) needed?

Figure 3-11 illustrates a conceptual PFAS life cycle showing PFAS migration in the environment from the discharge of PFAS from primary or secondary sources in waste streams, environmental releases or spills, and disposal of PFAS-containing or PFAS-treated materials. The volume, concentration, and mixture of PFAS released to the environment depend on the nature of the source (primary or secondary), release mechanism(s), and environmental or process controls employed throughout this life cycle. Exposure to PFAS at DOE facilities may occur through use of or contact with PFAS-containing chemicals, materials, or products, or through exposure (human or ecological) to environmental media or waste streams impacted by PFAS. Additional discussion about PFAS exposures and risk assessment is provided in **Section 11.3**.

3.5.2 Sorption (Soils and Other Materials) Pathway

Migration of PFAS in soils depends on the nature of PFAS release, PFAS properties, any conditions or events that may mobilize PFAS (e.g., heavy precipitation, irrigation), and the properties of the soils and sediments through which PFAS are migrating. When PFAS is partitioned to solid phase minerals, retention and migration in the soil are driven through the following processes and factors:

- Electrostatic interactions between PFAS and soil/sediments, especially those with a surface charge (e.g., clay) (Higgins 2006)
- Hydrophobic sorption of PFAS onto soil organic carbon
- PFAS partitioning to air-water interfaces
- PFAS partitioning to other co-contaminants, such as petroleum hydrocarbon NAPLs (e.g., at fire-training areas)
- PFAS partitioning (e.g., dissolving) into water
- PFAS volatility

These processes affect migration in the environment by promoting or deterring retardation and leaching from soil/sediment to porewater and groundwater. The pH of the environment also dictates the charge on PFAS, and, ultimately, the extent of sorption. Other site-specific conditions that increase PFAS sorption generally include high levels of organic carbon, surface area, surface charge, and increasing air content in the vadose zone (Guelfo 2013). However, PFAS sorption characteristics are complex and affected by phenomena such as the following:

- Nonlinear sorption (Guelfo 2020; Brusseau, 2020b), with PFAS adsorbing more strongly at low concentrations than high
- Nonideal sorption/desorption with desorption isotherms measured an order of magnitude higher than sorption isotherms (Xiao 2019; Schaefer 2021), suggesting irreversible sorption or very slow desorption
- Nonlinear PFAS partitioning due to electrostatic interactions (Xiao 2019)
- Sorption at air-water interfaces, particularly in vadose zones (Brusseau 2018; Brusseau 2019)
- Partitioning into and sorption onto NAPLs and formation of microemulsions (Brusseau 2018; Kostarelos 2020)
- Formation of supramolecules, PFAS self-assemblies (Riess 2018)

Investigations in release areas sample soil, sediment, or NAPL as the primary means of assessing the presence, extent, and strength of PFAS source(s). In addition, migration from soil, sediment, or NAPL sources to groundwater and surface water occurs through various solubilization, leaching, desorption, and back-diffusion processes. Therefore, to assess PFAS fate and transport, site-specific sorption and retention parameters shown in **Table 3-5** should be considered.

Construction materials (e.g., concrete, pipework) may adsorb or entrain PFAS and act as secondary sources of contamination to stormwater or groundwater, which is the subject of ongoing research by the Department of Defense's (DoD) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program

(ESTCP). Areas receiving multiple and ongoing exposures to concentrated PFAS, such as AFFF in fire-training areas, may have impacted concrete or asphalt. In addition, systems exposed to concentrated PFAS may have impacts from PFAS "supramolecules" formed from the self-assembly of surfactant PFAS onto solid surfaces (Riess 2018); this phenomenon may contribute to the difficulty in cleaning out AFFF systems and their propensity for rebound. Contaminated materials (e.g., soil, concrete) that are disturbed or moved during remediation and other disruptive activities can then act as sources of PFAS at their new locations and should be considered in the investigation program, if applicable. The need to evaluate impacts in construction materials should be considered on a site-specific basis.

3.5.3 Leaching to Groundwater Pathway

PFAS in unsaturated soils are subject to downward leaching during porewater percolation, which promotes dissolution and migration of PFAS mass (Sepulvado 2011; Ahrens 2014; Sharifan 2021). In addition, leaching can result in PFAS transport from the surface or subsurface soil and sediments to groundwater or surface water because PFAS releases often involve surface applications or atmospheric deposition (Borthakur 2022; Gellrich 2012; Anderson 2019; Galloway 2020).

PFAS and soil and sediment characteristics influence PFAS leaching to groundwater, as do climatic conditions and partitioning between the different media (e.g., air, water, solid, NAPL), as shown in **Figure 3-12**. Therefore, investigation programs should define the characteristics of the media with a sufficient vertical resolution to represent the system's heterogeneity. The PFAS leaching potential will be affected by the following:

- Precipitation and infiltration rates, which may arise from both natural precipitation and irrigation
- Thickness of the vadose zone (depth to the water table)
- PFAS soil sorption and partitioning characteristics (discussed in **Section 3.5.2**)
- PFAS sources (discussed in **Section 3.3**)
- PFAS physical and chemical properties (discussed in **Section 3.5.1**)
- Biotic or abiotic transformation
- Relevant transport processes within and between media (e.g., air, soil, water)
- Presence of co-contaminants

The structure of different PFAS will also influence their transport, including the tendency for longer-chain PFAAs to be less soluble and exhibit larger partitioning coefficients than shorter-chain PFAAs. In addition, linear PFAS isomers tend to be more sorptive and less mobile in porewater than branched isomers. Several of these partitioning processes within the vadose zone are nonlinear, such that their relative contribution to leaching may change over time as concentrations change because of dilution, sorption, or transformation (Zeng 2021). Finally, site conditions influencing the degree of flushing (e.g., precipitation rates and depth to groundwater) should be considered when evaluating the potential for PFAS to leach from soil to groundwater.

Generally, any soil or chemical properties that enhance PFAS sorption reduce soil-to-groundwater (or to surface water) leaching. Investigation programs should consider sufficient vertical profiling to understand the distribution of PFAS and soil/sediment properties for leaching potential. For instance, increased sorption/retention has been shown in shallow soils, attributed to the higher organic content, and at the capillary fringe of the groundwater table due to the smearing across air-water interfaces (Van Glubt 2021) and formation of PFAS-entrained light nonaqueous phase liquid (LNAPL) microemulsions (Kostarelos 2020) in some systems.

Table 3-5. Soil parameters collected during investigations to understand PFAS soil sorption and leaching to groundwater

Parameter	Data Quality Objective	Example Methods
Lithologic characterization	Evaluate soil types and characterize geologic heterogeneity	ASTM D2487
Ionic exchange capacity	Evaluate whether it may serve as a positive indicator of the importance of electrostatic interactions with minerals for anionic PFAS such as PFOS and PFOA	Cation/anion exchange capacity by ASTM D7503-18
Soil organic carbon	Evaluate PFAS sorption	Total organic carbon by Walkley-Black
Soil properties	Evaluate PFAS transport characteristics of soil or sediment, often used for fate and transport modeling	Permeability by ASTM D5084-90 Porosity, grain size, or sand/silt/clay ratio by ASTM D422-63 Surface area by Brunauer/Emmett/Teller [BET] Soil pH Bulk density by ASTM D2937-94 or D7263, Troxler Borehole geophysics (e.g., gamma, and induction resistivity)
Soil-water partition coefficient (K_d)	Estimate soil sorption	Standard batch sorption testing
Air-water partition coefficient (K_{aw})	Estimate air-water sorption	Film method (Schaefer 2019), ppQSPR estimation (Stults 2023)
Porewater PFAS concentration	Measure PFAS leaching in porewater	Lysimeter sampling (Schaefer 2022a; Anderson 2022)
PFAS leachate	Estimate PFAS leaching in porewater	Synthetic Precipitation Leaching Procedure (EPA 1312)

Parameter	Data Quality Objective	Example Methods
		Leaching Environmental Assessment Framework (EPA SW 846, 1313-1316)
Soil PFAS concentrations	Evaluate PFAS impacts on soils	EPA Method 1633 Total organic fluorine (TOF) Extractable organic fluorine (EOF) Particle-induced gamma ray emission (PIGE) spectroscopy Liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QTOF)
Co-contaminant concentrations and phases (e.g., NAPL)	Evaluate PFAS partitioning to separate phases (e.g., NAPL) and leaching characteristics of mixed contaminants (e.g., total petroleum hydrocarbons/PFAS from sources)	NAPL Free Product Mobility Package (Mod. ASTM D425/API RP40) Total petroleum hydrocarbons (EPA 8015D)
NAPL water partitioning coefficient (K_{nw})	Estimate PFAS partitioning into NAPL	Surface tension (Liao 2022)
Vadose zone saturation/water retention monitoring	Unsaturated hydraulic conductivity, validation of satellite data accuracy	Meter Group Sensors: ATMOS 41 Weather Station ZL6 Pro Data Logger Soil moisture sensors Field tensiometers Groundwater transducers

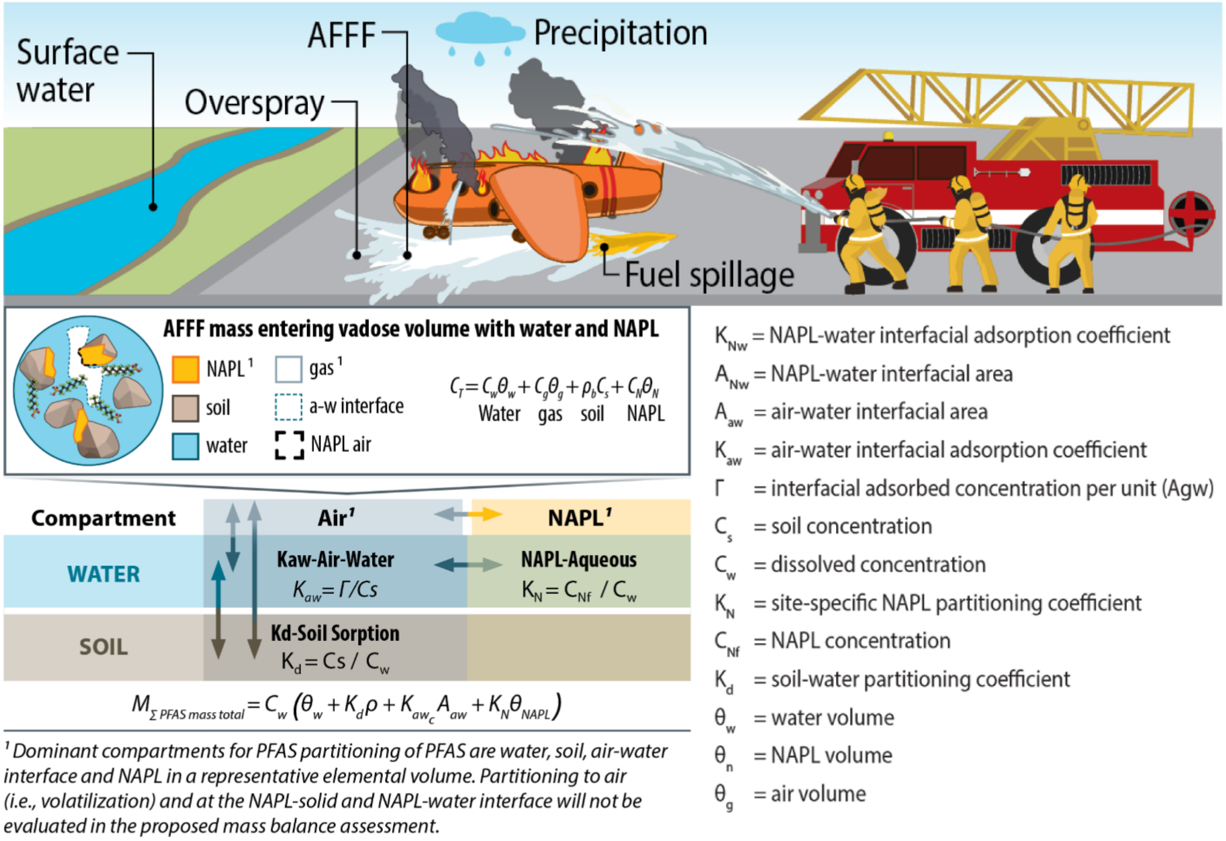


Figure 3-12. Conceptual depiction of PFAS partitioning compartments in the unsaturated zone following releases, such as release of firefighting foams, as a basis for evaluating transport in the vadose zone.

3.5.4 Groundwater Pathway

PFAAs in U.S. public drinking water sources were evaluated in response to the 2013 to 2015 UCMR3, which required sampling of treated water that originated from groundwater wells (n = 22,624), surface water (n = 12,733), and mixed sources (n = 792) (EPA 2017b). One or more PFAAs were detected in 4% of the reporting public water systems (EPA 2017b), and groundwater sources had approximately double the detection rate of surface water sources (Hu 2016). In addition, 59 out of 4,905 public water systems reported PFOA and PFOS at combined concentrations that exceed the 2016 EPA health advisory of 0.07 micrograms per liter (µg/L; EPA 2016a; EPA 2016c). Detections were geographically widespread but showed quantifiable associations with suspected sources, including industrial sites, military fire training areas, AFFF-certified airports, and wastewater treatment facilities (Hu 2016).

PFAS can be leached to groundwater from original releases and vadose zone sources and discharged from PFAS-impacted surface water to groundwater. Groundwater transport of dissolved PFAS is dictated primarily by groundwater advection, dispersion, diffusion, sorption, and transformation as well as by the elements discussed in **Section 3.5.3** for leaching to groundwater (e.g., geology, hydrogeology, partitioning, PFAS sources, transformation).

PFAAs can form significant groundwater plumes due to their relatively high solubility (Ney 1995, e.g., PFOA has a reported solubility of 9,500 mg/L at 25°C [EPA 2017c]), surfactant properties, and persistence in the environment.

Groundwater advection is the primary mechanism that governs PFAS transport with groundwater flow and dispersion in the groundwater matrix. Groundwater advection is a function of the hydraulic gradient and the properties of the groundwater matrix (e.g., permeability, porosity). Therefore, the advective characteristics of the groundwater system (e.g., Darcy and seepage velocities) should be considered when designing an investigation, particularly the distance that samples should be collected from the source area to evaluate PFAS nature and extent.

PFAS are not typically observed as a separate phase in the environment (e.g., solid, LNAPL, or dense nonaqueous phase liquids [DNAPL]). Instead, they are typically observed as dissolved solutes in groundwater systems. However, at sites where PFAS mixtures are present as separate phases (e.g., at fire-training facilities where petroleum hydrocarbon LNAPL was released along with AFFF foams), PFAS interactions with co-contaminants (e.g., NAPL) within the subsurface have been reported and can impact migration in groundwater.

PFAS sorption onto the groundwater matrix (i.e., soil, sediment, or bedrock) is often the most significant retardation mechanism in dissolved plumes (as discussed in **Section 3.5.2**). Sorbed PFAS can act as a long-term secondary source of PFAS to groundwater, with the desorption rate often much slower than the sorption rate. Preliminary investigation programs should consider sampling saturated soils to evaluate them as potential future sources of PFAS to groundwater.

3.5.5 Surface Water and Sediment Pathway

PFAS (specifically PFOS and PFOA) were widely detected in surface water samples collected from various rivers, lakes, and streams in the United States (ATSDR 2021). PFAS can be released to surface water in several forms, including direct discharges to surface water (e.g., stormwater runoff), PFAS-contaminated effluents (e.g., wastewater treatment plant or industrial wastewater), PFAS-contaminated groundwater, or aerial deposition. PFAS concentrations in surface water usually depend on proximity to the point of release and source concentrations but are also complicated by PFAS gradients at the water surface due to partitioning at the air-water interface, colloidal and suspended solid transport, and sediment sorption/desorption. In addition to releases associated with identified sources, stormwater runoff from nonpoint sources may contribute significant loads of PFAS to surface water (Wilkinson 2017, Zushi 2009).

PFAS-impacted surface water can also contaminate groundwater through recharge or be transported to larger receiving water bodies such as rivers, lakes, or oceans. Once in surface water, long-chain PFAAs such as PFOS and PFOA tend to stay in solution, although they can also sorb to the organic fraction of suspended solids, soil, or sediment. PFAS may also partition into mobile colloids, resulting in facilitated transport (Brusseau 2019, Schaefer 2022b). Therefore, surface water migration routes should be considered in the sampling strategy for a site investigation. Sediment can also be a significant sink for PFAS in surface water systems and should be considered as well.

Due to the surfactant properties of PFAS, at concentrations that exceed the critical micelle concentration, PFAS can form a visible separate phase floating on a water surface (Costanza 2019). In addition, the propensity of PFAS to partition to air-water interfaces can result in enrichment at the water surface relative to concentrations in bulk solution (Costanza 2019). Enrichment of PFAS at the water surface, coupled with winds, waves, or other turbulent forces that introduce air into the water, can also lead to foam formation at the water surface (Schwichtenberg 2020, Schaefer 2022b). Therefore, the potential for PFAS partitioning at the water surface into foams and facilitated transport onto organics should be considered in the surface water sampling strategy for a site investigation.

3.5.6 Stormwater Pathway

Stormwater represents a significant PFAS migration pathway, particularly in or near PFAS point sources (e.g., AFFF release areas) where highly impacted shallow soils or hardstand such as concrete may be exposed to rainwater resulting in sheet flow. Due to the high mobility of most PFAS in water, stormwater can be a significant mobilization mechanism (Codling 2020). In addition, PFAS migration in stormwater via dissolved and colloidal/particulate pathways (which have not been well studied) can contaminate surface water, sediment, and suspended particulates.

Groundwater infiltration into stormwater infrastructure can also create preferential/alternative pathways. For example, PFAS-impacted groundwater can potentially infiltrate into stormwater infrastructure through cracks and joints, particularly in older, degraded infrastructure. This can result in the discharge of PFAS-impacted groundwater from source zones into stormwater networks, with impacts distal to the sources in directions not expected from groundwater flow alone.

Additionally, studies have shown PFAS can persist in the atmosphere causing PFAS to be measured in rainfall and snow, with local point sources influencing PFAS profiles in the rain over that specific area (Pike 2021). Investigation programs should also consider the potential for "background" PFAS levels in rain/stormwater. Sites with a higher density of paved streets and buildings typically result in higher volumes and greater accumulation of anthropogenic contaminants (e.g., PFAS) during dry periods. During rain events, these contaminants are transported by rainwater through conveyance systems into the surrounding environment (Olmsted 2021).

Other approaches to protecting against PFAS in stormwater pathways include the following:

- Conduct facility inspections to identify sources of PFAS and conduct PFAS sampling, where applicable.
- Employ stormwater best management practices (BMPs) for PFAS to meet any relevant permit limits.
- Update stormwater pollution prevention plans to include monitoring and BMPs specific to PFAS.

3.5.7 Air Pathway

PFAS can be transported to the atmosphere by industrial stack emissions, incineration, or combustion processes, as well as during fire suppression activities. Transported PFAS can include low volatility compounds such as PFOA and PFOS that are transported through association with aerosols (Barton 2006). The role of atmospheric transport is complex and depends on PFAS-specific properties such as volatility, vapor-particle partitioning, and air-water partitioning mechanisms. Aerosols, representing a suspension of solid particles and liquid droplets in the air, provide a variety of environmental media and surfaces within or upon which PFAS can partition, adsorb, and migrate (Johansson 2019). Some precursors, including fluorotelomer alcohols and fluoroalkyl sulfonamides, have higher volatility and tend to partition into the air (Xie 2015) to a greater extent than PFAAs. More volatile PFAA precursors are subject to photooxidation during air transport, which can result in terminal PFAA formation in the atmosphere (Makey 2017).

Wet and dry deposition are the significant mechanisms of PFAS removal from the atmosphere (Dreyer 2010; Barton 2007; Hurley 2004). During dry deposition, PFAS in air can be deposited onto surfaces via settling, diffusion, or other processes. Wet deposition occurs when precipitation contributes to PFAS deposition. Wet or dry deposition depends on the amount of PFAS emissions, particle size distributions, local topography, weather patterns, meteorological data, land use characteristics, and release factors such as stack height, effluent flow rate, and effluent temperature. These parameters should be included in the investigation of potential sources of PFAS from stack emissions or other processes that generate aerosols (e.g., cooling towers, shower facilities, dust suppression). Short-range atmospheric transport near sites of significant emissions may result in PFAS contamination of terrestrial and aquatic systems.

Long-range transport processes are also responsible for the wide distribution of PFAS across the globe (Muir 2019) and can contribute to the anthropogenic background of PFAS. Therefore, investigation programs should consider evaluating the potential for anthropogenic background in contaminated soil, surface water, sediment, biota, and groundwater due to PFAS air transport (Davis 2007, Shin 2011).

3.5.8 PFAS Transformation

Transformation of PFAS precursors to PFAAs, such as PFOS and PFOA, can complicate CSMs and should be considered during comprehensive site investigations (ITRC 2022c). For example, atmospheric emissions of volatile precursors can result in long-range transport and subsequent transformation and deposition that can yield detectable levels of PFAAs in environmental media. The extent to which precursors at a site transform into detectable PFAAs is relevant to site investigations, particularly if transformation occurs after initial site characterization. Different transport rates between precursor PFAS and the corresponding terminal PFAA could also complicate CSMs if transformation rates are slower than transport rates, as has been suggested (Weber 2017). There are still many unknowns regarding PFAS precursor transformation, including mechanisms, rates, and transformation products. Therefore, the scientific community continues to study PFAS precursor transformation, and CSMs/risk assessments are based on available information.

Abiotic Pathways. Abiotic processes that can transform precursors in soil, air, or water under ambient environmental conditions include the following:

- **Hydrolysis** of some precursors, followed by subsequent biotransformation, such as the production of PFOS from perfluorooctane sulfonyl fluoride (Martin 2010) and PFOA from fluorotelomers (Washington 2015b).
- **Oxidation** of precursors by hydroxyl radicals can occur in natural waters, with the fluorotelomer-derived precursors being oxidized more rapidly than electrochemical fluorination-derived precursors (Gauthier 2005; Plumlee 2009). In addition, shorter-chain PFCAs and PFSAs such as PFBS can be produced by oxidation reactions between hydroxyl radicals and sulfonamido derivatives (D'Eon 2006).
- **Photolysis** of the more volatile PFAA precursors, such as fluorotelomer alcohols and FOSAs that once released into the air, can result in the formation of PFOA (Makey 2017).

Aerobic Biotic Pathways. Several aerobic biotransformation processes that can transform precursors in soil or water under ambient environmental conditions have been identified:

- All polyfluorinated precursors studied to date have the potential to biotransform to PFAAs (OECD 2018) aerobically.
- Aerobic biotransformation of various fluorotelomer-derived precursors exclusively results in the formation of PFCAs, including PFOA.
- Aerobic biotransformation of various electrochemical fluorination-derived precursors primarily results in the formation of PFSAs, including PFOS.

Anaerobic Biotic Pathways. A few studies have shown the anaerobic biotransformation of PFAS. Fluorotelomer alcohols have shown slow anaerobic transformation with the production of stable polyfluorinated acids under methanogenic conditions with much slower kinetics relative to aerobic biotransformation (Zhang 2013; Allred 2015). PFOA and PFOS were recently demonstrated to be defluorinated by a specialized microbe, *Acidimicrobium* sp. Strain A6, under conditions of ammonium oxidation with iron reduction, in a process called Feammox (Huang 2019).

Investigation programs can elucidate the role of PFAS precursors as future sources of PFAAs using several surrogate analytical methods, including the following:

- Combustion ion chromatography (CIC) methods for TOF, adsorbable organic fluorine (AOF), and EOF (Wagner 2013, **Sections 5.4.1-5.4.3**)
- Total oxidizable precursor (TOP) assay (Houtz 2012; **Section 5.4.4**)
- Non-target LC-QTOF (**Section 5.4.6**)
- PIGE (Schaider 2017; **Section 5.4.5**)

Natural processes and remediation activities, such as those involving advanced oxidation processes, aerobic bioremediation, or chemical oxidation, can result in PFAS precursor transformation reactions. This should be considered when designing investigation programs.

4. SAMPLING

Sampling conducted to determine PFAS concentrations in environmental media is similar to sampling performed for other organic contaminants, but with additional considerations. Project specific QAPP and SAP work control documents are developed to describe sampling and analysis procedures and special considerations for PFAS, including QA/QC samples, discussed in more detail in **Section 5.6.** Special considerations for PFAS may vary from site to site, depending on logistics, necessary sampling equipment, and the comprehensiveness of the sampling program as determined by the project's DQOs. The QAPP or SAP should include historical PFAS uses, handling of PFAS, and past remediation activities, or reference to documents that discuss this information, such as DOE's *Historical Use Investigation Guide* (DOE 2023).

4.1 Introduction

Environmental investigation guidance and procedures used for other contaminants are also the basis for PFAS investigations (such as ASTM International D 4823-95 and D 4448-01 or EPA compendium EPA 540/P-87/001a, OSWER 9355.0-14, EPA SESDPROC-513-R2, EPA SESDPROC-305-R3). This section will discuss false positive cross-contamination considerations, false negative considerations, sampling preparation, decontamination, sample location considerations, and PFAS sampling by media.

Examples of special considerations and challenges with PFAS sampling include the following:

- Developing a program that balances the cost of using PFAS-free materials/equipment, necessary for limiting cross-contamination and false positives, against the need to achieve low quantitation limits (ppt, as discussed in **Section 2**)
- Field and equipment blanks above and beyond what is usually required
- Need for modified decontamination measures
- Nuances of sample holding times/temperature caused by continuous target and non-target analytical method development

Appendix A includes a compendium of references and guidance on sampling and analysis for PFAS.

4.2 Sample Location and Type Considerations

Identifying the appropriate locations to sample for PFAS is crucial to understanding the extent of the PFAS contamination and meeting project-specific DQOs. The location where a sample is to be collected is a project-specific decision that could be based, in part, on where the PFAS is known to collect. Sample locations for different projects will differ depending on the goals of the project.

At a minimum, sample locations must be representative of PFAS contamination (within all phases, solid/liquid/gas) and help define a boundary for the PFAS contamination. Understanding the manufacturing history of PFAS, historical and current applications, and release mechanisms/subsequent disposal of products at a site can help identify potential direct and indirect PFAS sources (discussed in more detail in **Section 3.3**) and specific geographical locations to sample. Then, a sampling technique (**Table 4-1**) can be used to select sampling locations that meet project-specific DQOs.

Table 4-1. Techniques for determining PFAS sampling locations

Name	Definition	Pros	Cons
Non-Probability Techniques			
Judgmental Sampling	Sampling location based on prior information/ professional experience	• Economical • Time efficient • Effective as screening approach	• No randomization • Does not support statistical interpretation of sampling results
Convenience/ Haphazard Sampling	Random sampling with potential bias to one area; samples selected based on easy access/proximity	• Economical • Time efficient	• Not representative of area
Probability Techniques			
Random Sampling	Arbitrary sample collection providing each sample same probability of selection	• Statistical analysis straightforward (mean, standard deviation, variance) • Time efficient	• Not adequate for heterogeneous systems (assumes variability of media is not significant)
Stratified Random Sampling	Area divided into non-overlapping and mutually exclusive subareas to sample	• Efficient and manageable • Cheaper than random sampling • Used when number of samples is limited	• Assumes variability of media is not significant • Preliminary knowledge of contamination required to be representative
Systematic Sampling (grid, random)	Sample location chosen from larger area based on random starting point and fixed, periodic interval	• Provides consistent data over time • Provides control/sense of process	• Greater risk of data manipulation • Defined area of site/ contamination needed
Transect Sampling	Samples collected along one or more lines in area	• Used to establish linear gradient of contamination and visualize concentration changes	• Time consuming • May not be representative of full contamination

Location selection can also be governed by preexisting site conditions, types of PFAS sources identified, and subsequent type of media to be sampled. Selection of sampling locations should consider the surfactant nature of some types of PFAS (as discussed in **Section 3.4**). PFAS concentrate at interfaces (soil/water, water/air), and soil depth profiles in the literature indicate significant retention of PFAS in the vadose zone over decadal time frames and subsequent leaching to groundwater (Brusseau 2020a). Similarly, precursor breakdown into terminal PFAS should be considered when selecting PFAS sampling locations. PFAS precursors have been found more frequently in and near source zones, while intermediary and terminal PFAS compounds are more often found farther from source zones. Concentrations of PFAS also generally decrease with distance from known sources (Dasu 2022). Short-chain PFAS have also been shown to be more mobile than long–chain PFAS (Brusseau 2020a).

Sample type should also be considered in designing a PFAS sampling program:

- Grab samples are one-time samples that only reflect site conditions at the time of sampling.
- Composite samples are a collection of numerous individual discrete samples taken at regular intervals (spatial, temporal, or flow proportional) and combined into one larger sample.

Composite samples are often chosen to account for temporal or spatial differences in the environmental media to be sampled (e.g., integrated temporal samples of a treatment system effluent) and to fulfill the DQOs. However, composite samples can lose information in some cases. For example, some temporal information may be lost for a composite sampling of water (e.g., effluents), and composite samples of soil may lose some spatial information. The sample type must be weighed against project-specific DQOs to select the best approach to meet the DQOs.

4.3 False Negative Sampling Considerations

Special considerations should be taken to avoid false negative PFAS results when sampling. False negative results could prevent the identification of PFAS present above concentrations that might cause harm to a receptor (e.g., above a health-based screening level or regulatory limit). False negatives can arise for several reasons. First, they can be caused by elevated method reporting limits. PFAS analytical methods are designed to limit false negatives with continual advancements to limit matrix interferences (e.g., steps to clean up or remove interferences in a sample). For instance, multiple analytical runs on diluted and undiluted samples may be necessary to quantify individual PFAS in mixtures across a range of concentrations. Second, false negatives can occur if the sampling program does not accurately reflect environmental conditions and ensure representativeness with the number and types of samples collected.

Third, some types of equipment and certain materials used during sampling can also remove PFAS from a sample, leading to false negative results. This is one reason why only using approved equipment and materials is crucial.

4.4 False Positive Sampling Considerations

Special steps should also be taken to manage false positive PFAS results from PFAS cross-contamination when sampling. Having false positives in a sampling program can increase costs of cleanup when cleanup is not necessary. This is more challenging to manage because: (1) PFAS are found in thousands of materials and products (as discussed in **Section 3.3**), and (2) investigation screening levels and state and future federal regulatory levels tend to be in the low or sub-parts per trillion range (as discussed in **Section 2**). Recent studies suggest focus should be on limiting PFAS-containing materials/equipment that come into direct contact with the sample during sample collection, with less focus on PFAS-containing material/equipment that is in indirect contact with the sample (Rodowa 2020). To reduce the potential of false positive PFAS cross-contamination, samplers should change gloves immediately before taking the sample, avoid contact with PFAS-containing materials/equipment around them, and minimize the time that PFAS sample bottles are open to the environment. Labels should be placed on the bottles after collection and capping/sealing.

General potential sources of PFAS cross-contamination include water used during drilling or decontamination, materials used within the sampling environment, sampling equipment, field clothing and personal protective equipment (PPE), sun and biological protection products, personal hygiene and personal care products, food packaging, and the environment itself. A thorough review of federal and state PFAS sampling guidance should be conducted with appropriate processes and procedures chosen for the site documented in the work control document (e.g., QAPP), including field documentation procedures for possible PFAS containing materials found while sampling for reporting and verification (as discussed in **Section 7.3**).

Sometimes it is impossible or financially infeasible to eliminate PFAS-containing materials/equipment from sampling. For example, these materials might be needed at sites where hazards warrant the use of specific PPE, such as Tyvek suits, where such materials are necessary to properly sample non-PFAS co-contaminants (e.g., radiological sampling), or when sampling occurs before a formal PFAS sampling program can be developed. In these cases, the following actions should be conducted:

- Collect an equipment blank for any material/equipment in direct contact with the sample by running "PFAS free" water over the item and collecting the water, if possible. Once the specific material/equipment is determined "PFAS free" (as discussed in **Section 4.6**), then future equipment blanks for that material/equipment do not need to be collected unless there has been a potential for the equipment to become PFAS-contaminated.

- For materials/equipment that may be used long-term near PFAS sampling sites (e.g., dedicated equipment at a sampling location), more vigorous analyses may be warranted. For these cases, the material/equipment may be sent to a laboratory for more in-depth leachate analysis.
- Consider the overall impacts of using PFAS containing materials to the project-specific DQO and note in work control documents the use of any materials that may potentially contain PFAS. Any variation to work control documents in the field should be recorded appropriately on field forms.

More detail on specific sources of PFAS cross-contamination is discussed below and in **Appendix A**. **Table 4-2** lists known PFAS-containing products to avoid. Again, a tiered approach should be taken to prevent PFAS cross-contamination. The first tier minimizes PFAS-containing material/equipment that comes into direct contact with the sample. The second tier minimizes PFAS-containing material/equipment in indirect contact with the sample.

Table 4-2. Field clothing and PPE brand and product names to avoid

PFAS-containing Materials/Equipment to Avoid (DEPA 2015)[1]:	
Polytetrafluoroethylene (PTFE) that includes the trademark Teflon® and Hostaflon®	Ethylene tetrafluoroethylene (ETFE) that includes the trademark Tefzel®
Waterproof coatings containing PFAS	Aluminum foil (particularly the shiny side)
Fluorinated ethylene-propylene (FEP) that includes the trademark Teflon® and Hostaflon®	Refrigerators with Freon leaks
Low-density polyethylene (LDPE)	Pipe thread compounds and tape
Polychlorotrifluoroethylene (PCTFE) that includes the trademark Neoflon®	Polyvinylidene fluoride (PVDF) that includes the trademark Kynar®
Oleophobol CP®	RUCOSTAR®
Bionic Finish®	RUCO® includes other brands
GreenShield®	Resists Spills and Releases Stains™
Lurotex Protector RL ECO®	Scotchgard™ Fabric Protector
Repellant KFC®	Resist Spills™
PFAS-containing Field Clothing to Avoid:	
Clothing washed with fabric softener	Clothing made with or washed with water-, dirt-, and stain-resistant chemicals
Clothing chemically treated for insect resistance and ultraviolet protection	Clothing that has any of the brand or product names mentioned above

10. This list should not be considered comprehensive.

As discussed in **Section 3.3**, the ongoing discovery of PFAS-containing materials/equipment requires updating lists and inventories regularly. An evaluation of materials and equipment should be conducted before any sampling event to understand what equipment may contain

PFAS. Obtaining and reviewing all Safety Data Sheets (SDSs) before considering materials for use during PFAS sampling is greatly encouraged, as product manufacturing formulations can change over time. If PFAS are listed on the SDS, it is recommended that equipment/material not be used. Text such as "perfluoro," "fluoro," or "fluorosurfactant" may identify PFAS.

PFAS might not be documented on SDSs. In this case, understanding the general materials and coatings PFAS are found in is important to avoid these materials when sampling. This may include sample containers (such as PTFE lids) and sampling equipment. Adopting a thorough QA/QC program can help to understand and manage uncertainties related to PFAS cross-contamination, as discussed more in detail in **Section 5.6** and **Section 7.**

4.5 PFAS Anthropogenic Background Considerations

The ubiquitous nature of PFAS, as discussed in **Section 3.5**, has motivated discussions to assess and adopt PFAS anthropogenic background levels. Background levels are chemical concentrations likely to be found on site that are not site-related. Even though PFAS chemicals are entirely manmade, it is apparent that locations worldwide have some level of PFAS that may not be associated with a local point source release (Cousins 2022).

The United States Geological Survey is working on guidance for handling PFAS background concentrations, and in the interim, various techniques can be used to determine PFAS background levels and how they play a role at PFAS contaminated sites. Method OSWER 9285.7-41 can also be referenced until more PFAS specific guidance is published. Other common techniques include the following:

1. Using publicly available PFAS data collected in general proximity of the site to compare to on-site PFAS samples.

   PFAS data are becoming more readily available for all matrices (e.g., surface water, groundwater, soil, air, and other media) and are compiled into PFAS databases that are often publicly available. These databases can evaluate PFAS background concentrations for a given area or type of waste stream. One example is the California Geotracker database, which has published PFAS concentrations for different releases, including landfills, DoD facilities, and airports in the state. A 2020 study compiled PFAS concentrations found in soil in a literature review and compared these values to a curated database of PFAS soil concentrations at contaminated sites (Brusseau 2020a). The study showed that background levels of PFAS existed separate from site contamination.

2. Collecting additional samples upgradient and upwind of the site to compare to on-site PFAS samples.

   Establishing off-site specific PFAS concentrations that are upwind and upgradient can show what PFAS concentrations may be anthropogenic background that is not attributed to site-specific PFAS releases. These samples can serve as “reference samples,” with only contamination above “reference samples” deemed to be actionable.

PFAS background levels may also fluctuate over time and need to be recalculated over a set period; this may be especially relevant for surface water bodies that receive or are sources of PFAS.

4.6 Sampling Preparation and Decontamination Considerations

Some primary steps that should be taken to prepare for PFAS sampling include developing a QAPP, SAP, and work control documents including SOPs. PFAS specific items to mention in QAPP, SAP, and work control documents have been discussed throughout this guidance. It is also important to check and account for all items included in the PFAS bottle kits sent from analytical laboratories. This may include appropriate bottles, bottle labels, chain of custody forms, “PFAS Free” water, and QA/QC samples. The analytical laboratory should be contacted prior to mobilization if anything is missing from the bottle kits.

Special decontamination procedures for PFAS should also be reviewed and outlined in the work control documents. One primary consideration is verifying whether the decontamination water used is “PFAS Free” or does not contribute to PFAS contamination of the sample. The analytical laboratory selected for the analysis should provide laboratory-certified “PFAS-free” water for QA/QC samples (e.g., field blanks/equipment blanks). However, this source may not be practical or available in the quantities needed for decontamination. If that is the case, a water source that can provide sufficient volume for decontamination should be identified and then sampled for PFAS to verify that it can be used before initiating the investigation. “PFAS Free” should also be defined in the project’s DQO, including what detection limits are acceptable to deem the water as “PFAS Free.”

Obtaining a single, large-volume bottle of “PFAS-free” water may not always be appropriate to support sampling at different locations over time. Extended handling and use could expose the water to ambient/airborne PFAS. Decontamination water can be placed in multiple bottles for one or a few sampling locations. Laboratory-grade detergent (such as Alconox®) is preferred for decontaminating equipment and supplies, followed by a deionized water rinse or water deemed to be “PFAS Free”. Rinsing tooling in methanol, while employing proper controls and waste handling, is another option for decontamination.

Once PFAS samples are collected, the samples should be sealed in LDPE zip-style bags and stored in the sample cooler, ensuring the LDPE outer barrier does not come into direct contact with the PFAS sample. PFAS contamination from the LDPE is not expected because it does not come into direct contact with the environmental sample. Ice packs (e.g., “blue ice” type freezer packs) should be avoided in PFAS sample coolers; sealed bags of water-based ice should be used instead. Sample coolers should be shipped overnight, and contents must remain at the temperature specified by the method (e.g., 0 – 6°C is the standard temperature range for most PFAS sample matrices). Sample holding times and shipping requirements should be verified with the analytical laboratory. Sample collection techniques or sample volumes other than those listed in analytical methods may be used if documented and determined they will meet the DQO.

4.7 Solid Matrices

Solid matrices are defined as environmental media in solid form, such as soils, sediments, and biosolids.

4.7.1 Soil

Soil PFAS sampling can vary by program and by source, geology, and other environmental characteristics. At a minimum, the requirements discussed in approved PFAS analytical methods for regulatory compliance should be followed, as discussed in more detail in **Section 5.3.**

Collecting PFAS soil samples at depth may require using equipment that could come into direct contact with the sample. Identifying drilling contractors who have adopted PFAS protocols, such as using specific drill tooling and dedicated crews for PFAS sites, can be helpful in reducing PFAS cross-contamination. Requesting SOPs/SDSs from the drilling contractors who do not have special PFAS programs is recommended, because lubricants and other standard materials may contain PFAS. The use of drilling fluids (such as mud rotary) should be minimized or omitted unless these fluids are tested for PFAS and verified to be PFAS-free. Other methods include locating a local water source that is verified "PFAS free" or noting in field documentation that drilling fluids and unverified water were used during sampling.

Stainless steel is preferred for tooling material, as the coatings found on stainless steel generally are accepted as being "PFAS free." Only stainless-steel split spoons should be used with hollow stem augers. Geoprobe was recently included in a PFAS study that performed leaching tests on a handful of its drilling materials, including polyvinyl chloride soil liners, membrane interface probe (MIP) membranes, and sonic core bags; the study determined these materials to be PFAS-free (i.e., showed no detections of PFAS [Rodowa2020]).

4.7.2 Sediments

Sediment PFAS sampling should generally follow the same considerations as soil sampling, as discussed in **Section 4.7.1.** Most core, grab, and composite sampling devices are constructed of stainless steel. Some core samplers include a high-density polyethylene (HDPE) sleeve inserted in the core barrel to retain the sample. Ensure that materials in contact with the sampling media do not have water-resistant coatings or other PFAS-containing materials or substances. Approach the sampling location from downstream. Personnel conducting sampling may require additional PPE, such as waders and personal flotation devices.

4.7.3 Biosolids

Biosolid PFAS sampling should generally follow the same considerations as soil sampling, as discussed in **Section 4.7.1.**

4.8 Aqueous Matrices

Aqueous matrices are defined as environmental media in liquid form. Special considerations for sampling aqueous matrices include the following:

- Sample bottles should be filled to the shoulder, and not past that point, to allow for the full volume to be extracted and for expansion during frozen storage.
- At a minimum, sampling equipment should be chosen to minimize PFAS cross-contamination (as discussed in **Section 4.4).**
- Samples should not be filtered because filters may be a source of PFAS or PFAS may be adsorbed/lost to the filter (Ahrens 2009; Arp 2009).

4.8.1 Potable water

Potable water PFAS sampling procedures should follow the requirements of approved PFAS analytical methods for regulatory compliance purposes (see **Section 5.3.1**) and meet project-specific DQO. Current methods require the addition of a preservative to all sample containers to remove free chlorine from potable water sources that have disinfecting agents added to them. If a potable water source is known to not use disinfecting agents in the water purification process, then the addition of preservatives to sample bottles can be omitted. The sample bottle needs to be agitated afterward to dissolve the preservative.

4.8.2 Landfill Leachate

Landfill leachate samples can present significant analytical challenges due to increased matrix effects and high concentrations of PFAS, as documented in the literature. A reduced sample volume may be collected for these samples compared to other aqueous samples. The analytical method requirements should be checked prior to PFAS leachate sampling.

4.8.3 Surface Water and Stormwater

Surface water PFAS sampling follows traditional methods, such as those described in the EPA’s Compendium of Superfund Field Operations Methods (EPA 1987) (as discussed in **Section 5.3.2**). Runoff and stormwater conveyance systems can impact surface water locations downstream of the actual source, or groundwater along the course of the conveyance system. Therefore, sampling stormwater may help in determining PFAS sources. Special considerations for PFAS surface water sampling include the following:

- The presence of any foam on the surface of the water body should be determined prior to sampling, and sampling should be adjusted appropriately to meet project specific DQOs. Surface water foams have shown to serve as potential reservoirs for PFAS caused by extensive air/water interfaces (Schwichtenberg 2020).
- If other characteristics of the water, such as percent solids, are desired for analysis, surface water to support non-PFAS analyses must be collected in separate containers from the PFAS sample.
- For samples collected via container immersion, the sample bottles should be held above the water surface and inverted (positioning the container opening downwards into the water). Then, once fully submerged, invert the sample bottle upright to collect the sample. If foam is present on the water surface, it should be cleared away so it does not contact the container and is not included in the sample.
- When container immersion is not feasible due to insufficient water depth, collecting surface water using a peristaltic pump with HDPE/silicon tubing is preferred. The tubing volume should be purged before taking the sample, and IDW should not be disposed of in the area where the sample is taken. Pumping of sediment and other particulates into the sample container should be avoided.
- Personnel who must enter the water body to collect a sample should enter and stand downstream of the sample collection point.
- The sample location in the water column should be described and noted in the field logbook or other field form. The sample location in the water column must consider the potential stratification of PFAS and their tendency to accumulate at the air/water interface (as discussed in **Section 3.5.5**).
- If the surface water location is to be sampled repeatedly, collect each sample from the same location.
- If the surface of the water is frozen, then the ice may be broken or drilled through to access the water beneath. Be sure to allow time for any disturbed sediments or other particulates to settle before collecting samples, again avoiding collecting sediments or surface water. Reschedule sampling if liquid water is not present. Collecting surface water PFAS samples during wet and dry periods is preferred to assess seasonal fluctuations.
- PPE worn during surface water sampling may differ from that worn when sampling other media, such as groundwater from monitoring wells. It may be necessary for sampling personnel to wear PFAS-free booties or waders over other footwear (such as field boots) in case the footwear is treated with PFAS-containing substances.

4.8.4 Porewater

The porewater SOP (EPA 2013) describes the purging and sampling equipment available for porewater sampling in sediment or soil. For sampling sediment porewater, peristaltic pumps with silicon and HDPE tubing are typically used, along with push-point samplers, porewater observation devices (PODs), and drive-point piezometers. Push-point samplers and drive-point piezometers are made of stainless steel, while PODs consist of slotted polyvinyl chloride pipe and silicon tubing. PODs and drive-point piezometers are permanent, or dedicated, sampling points typically installed and used for multiple sampling events, whereas push-point samplers are used as temporary sampling locations. Otherwise, the standard procedure for porewater purging and sampling using a peristaltic pump, as described in the Compendium of Superfund Field Operations Methods (EPA 1987), can be followed. Porewater samplers are now available that can be deployed over time and then retrieved, with the collected water submitted for analysis.

Lysimeters

Lysimeters can be used for porewater sampling in the vadose zone and have been used for site characterization to elucidate PFAS leaching to groundwater (see **Section 3.5.3**) within source zones. Specifically, suction lysimeters were used at an AFFF-impacted site at two depth intervals and sampled quarterly for a year to determine if PFAS porewater concentrations varied. The data showed that PFAS porewater concentrations did not fluctuate significantly and that PFAS specific soil to porewater ratios increased with PFAS soil concentrations, contrary to concentration dependence of saturated sorption sites (Anderson 2022). Also, lysimeters were used in an in situ field setting with spiked soils to understand how incorporating air-water interfacial sorption improves methods for predicting PFAS porewater concentrations (Schaefer 2022a).

Passive Samplers

Passive samplers can be used to measure PFAS concentrations in water matrices over prolonged periods. The benefits of using passive samplers include obtaining time-weighted average concentrations and the ability to concentrate large volumes of water, resulting in lower detection limits. Passive samplers can be used to evaluate time-integrated PFAS in stormwater and can easily be deployed before rainfall. Some limitations of using passive samplers are weather effects on results, possible invariable uptake rates, and few validated methods to provide consistency across data sets (Horst 2022).

Some PFAS passive samplers have recently launched in the market, such as the Battelle PFAS passive samplers and SiREM's PFASsive^{TM} sampler. EON Products now offers a PFAS-specific dual-membrane passive diffusion bag. More recently, others have developed a sediment bed passive flux meter (SBPFM) that can measure vertical contaminant flux at groundwater-surface water interfaces (Horst 2022). DoD is also working on solid-phase passive samplers to avoid the cost of shipping water samples to laboratories (Horst 2022).

4.8.5 Groundwater

Groundwater PFAS sampling is conducted by traditional methods (ASTM 2007; EPA 1987) (more details are in **Section 5.3**). Special considerations for PFAS groundwater sampling include the following:

- Low-flow sampling is preferred. Peristaltic pumps for depths less than 25 feet (using PFAS-acceptable tubing) and bladder pumps for depths greater than 25 feet (using PFAS-acceptable components) are recommended to minimize materials in direct contact with the PFAS sample. If dedicated bladder pumps are used, an equipment blank should be collected after first use to rule out the possibility of PFAS leaching.
- When possible or as appropriate for project DQOs, remove dedicated tubing from wells. Dedicated tubing is commonly made of Teflon™-, PTFE-, and LDPE-containing material. In these circumstances, the dedicated tubing should be pulled from the well, and disposable HDPE tubing should be used for PFAS sampling. Dedicated HDPE tubing should be avoided, as some HDPE tubing may leach PFBA over time (Denly 2019). If dedicated HDPE tubing is the only option, then an equipment blank may be collected for the tubing.
- No-purge sampling devices (such as HydraSleeves) can be used. However, these devices may contain HDPE. Efforts should be made to select no-purge sampling devices made of materials that have been verified not to leach PFAS.
- Consider the sample location in the water column for potential stratification of PFAS and their tendency to accumulate at the air/water interface. However, this is less critical for groundwater than for surface water (Rodowa 2020), likely due to the ratio of the bulk water volume to surface area and methods that typically require sampling beneath the water table (e.g., in the middle of a well-screened interval).
- Consider the presence and form of NAPL (e.g., LNAPL or DNAPL), and use methods for sampling either NAPL or bulk water that represent the sample target and minimize sample bias in order to measure PFAS partitioning into these media.
- For wells that are sampled for PFAS more than once, samples should be collected from the same depth interval each time unless the specific objective requires otherwise (for example, to evaluate PFAS at the water table or stratification in the well).
- Groundwater sampling equipment, at a minimum, should be chosen to minimize PFAS cross-contamination, as discussed in **Section 4.3.** The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants in the well(s), should be used whenever possible. The various types of purging and

sampling equipment available for groundwater sampling are described in the ASTM International Standard Guide for Sampling Ground-Water Monitoring Wells, D 4448-01 (ASTM 2007) or Compendium of Superfund Field Operations Methods (EPA 1987).

- When replacing equipment with "PFAS free" equipment is impractical or cost-prohibitive, such as for deep wells or sites with co-contaminants, various field and equipment blanks can be collected to determine if the current equipment may be a source of PFAS, resulting in false positives. Samples can also be collected in duplicate with and without existing dedicated equipment to discern if the equipment could be a source of PFAS contamination. Specific equipment blanks for a project should be listed in the work control documents.
- When sampling for co-contaminants requires the use of PFAS materials, sampling events should be separated to avoid contamination from these materials. For example, the PFAS sampling event should be completed first, followed by the sampling event for the co-contaminants. In some cases, using the same equipment at a concurrent sampling event may be acceptable.

Passive Fluxmeters

Passive fluxmeters have been developed to evaluate groundwater and contaminant flux in groundwater (Annable 2005). The technology relies on placing a sock filled with sorbent material(s) and impregnated with an internal tracer in a well screen. As groundwater migrates through the media, contaminants are adsorbed and the tracer desorbs to provide estimates of contaminant and groundwater flux. Currently, Enviroflux is developing and validating sorbents for PFAS (Horst 2022).

4.9 Gas Matrices

Gas matrices are defined as environmental media in gaseous form. As of May 2023, there are no multi-laboratory-validated, published sampling methods for PFAS in air emissions. In their absence, emissions measurements have been performed using modifications to EPA SW846 Method 0010 (Modified EPA Method 5 Sampling Train) (EPA 1986), a method designed to measure semivolatile organic compounds.

5. ANALYTICAL METHODS

5.1 Introduction

Precise, accurate, representative, comparable, and complete quantitative analytical methods are necessary to discern the extent of PFAS burden in the environment. Selecting the appropriate analytical method defines the level of confidence for the data set (extent to which the numbers in the data set can be trusted). Choosing the wrong analytical method could result in under- or over-reporting of PFAS concentrations and lead to misinformed decision-making. PFAS encompasses over 12,000 different chemicals (and counting); as such, the analytical methods discussed below focus on the following actions:

1. Quantifying by targeting specific individual PFAS compounds
2. Quantifying to some level of fluorine or oxidizable precursors in the tested media
3. Conducting non-targeted analyses to understand the full spectrum of PFAS in the tested media

The selection of specific PFAS chemicals mentioned in some of the current EPA methods (537.1, 533, 1633) has been driven by available toxicity information, the availability of commercial standards, and the known frequency of use.

Analytical methods discussed in this guidance may be at various validation steps for final publication in the Federal Register. The federal rulemaking process establishes analytical methods for the analysis of pollutants through a formal notice and public comment rulemaking process. Usually, a draft method is made available for public comment. Then, depending on the extent of comments, EPA either (1) creates another updated draft method for the public to provide additional comments, or (2) finalizes the draft for final publication. Creating a final analytical method is an iterative, lengthy process with multiple validation steps. EPA's PFAS Strategic Roadmap discusses updating the drinking water method (537.1) in the next couple of years and publishing the first EPA-approved PFAS analysis method (1633) under 40 CFR Part 136.

The following sections will discuss how to select an analytical laboratory, specific quantitative methods, and the sampling procedure(s) that should be followed to ensure proper QA/QC.

5.2 Laboratory Selection and Data Qualification

Selecting an analytical laboratory for PFAS analysis is critical in ensuring a high-confidence data set. One rule in obtaining high-confidence quantitative data is to remain as consistent as possible. Therefore, laboratory certification programs are established to ensure laboratory results are consistent with the method and are comparable and reproducible across laboratories. Some other key considerations are described below.

5.2.1 Laboratory Accreditation/Certifications

The DOE Analytical Services Program (ASP) provides environmental management-related services and products to DOE Program Offices and field element sites, including the National Nuclear Security Administration and their contractors, in support of environmental regulatory compliance programs, remediation and cleanup efforts, and waste management. The ASP is coordinated through the DOE Office of Environment, Health, Safety and Security and the Office of Sustainable Environmental Stewardship.

A component of the ASP is the DOE Consolidated Audit Program (DOECAP), which is comprised of the DOECAP Treatment, Storage, and Disposal Facility (TSDF) Audit Program and the DOECAP-Accreditation Program (DOECAP-AP). The TSDF audit program helps ensure that the treatment and disposal of DOE low-level radioactive and mixed waste are accomplished in a manner that protects human health and the environment. The DOECAP-AP aids in assuring DOE managers, workers, and the public that the data results acquired from analytical environmental laboratories are valid, reliable, and defensible. In addition, it provides DOE sites assurance that a contracted commercial laboratory can provide accurate sample analysis. The DOECAP-AP requires third-party assessments that ensure that environmental sample analysis is performed using proven methods, provide valid, reliable, and defensible data, and manage sample waste streams responsibly. The assessments are conducted by one of three DOECAP-approved third-party accreditation bodies (Abs) and are assessed to the most recent version of the DoD/DOE Quality Systems Manual (QSM). The QSM has strict QA/QC and detection limit requirements for PFAS analyses.

The DOECAP-AP maintains a list of accredited laboratories for PFAS analyses, including laboratories that can analyze a sample with potential radiological components. To obtain a current list of PFAS-accredited laboratories, contact the ASP Manager at doecap@hq.doe.gov or PFASInfo at pfasinfo@hq.doe.gov.

5.2.2 Laboratory Capacity

Most accredited PFAS laboratories continue to experience a high volume of requests for PFAS analysis, resulting in excessive delays in the analyses. Thus, it is important when formulating project-specific DQOs and selecting a laboratory to confirm with the laboratory that it can meet the method-required holding times and turnaround times. Commercial laboratories (e.g., Pace Analytical Services [Pace], Eurofins) have reported they do not expect turnaround times will increase as demand ramps up and will rather decrease as full integration of Method 1633 is complete in the next year.

More evidence is being published showing that precursor degradation can occur within method storage times at temperatures between 0 – 6 °C (Woudneh 2019). If understanding PFAS precursors is an important part of a project’s DQOs, then this should be discussed with the laboratory to determine appropriate holding times and temperatures.

5.2.3 Screening Levels against Method Detection Limits and Reporting Limit

As discussed in **Section 2.1**, RSLs available within the CERCLA framework use different toxicity information as of May 2023. Consensus should be reached with the project-specific regulators on the appropriate project action levels (PALs) to adopt (e.g., health-based values such as RSLs). This should be considered when (1) selecting analytical limits (detection limit, quantitation limit, etc.), and (2) using the resulting data.

PFAS data summarized in laboratory reports may be reported as follows:

- Below the method detection limit (MDL), also referred to as detection limit and limit of detection
- Below limit of quantitation (LOQ), also referred to as the reporting limit (RL) and limit of reporting
- As a true quantified value based on the intended use of the data

These three types of reported PFAS data must be handled and interpreted differently. Individual laboratories can consider the MDL differently based on nuances in the definitions used and what type of noise contributes to the measurement. Understanding how MDLs and data are interpreted is important. For instance, the proposed MCLs for PFOS and PFOA are at the MDLs of current analytical methods. **Figure 5-1** shows an infographic of the different types of PFAS data.

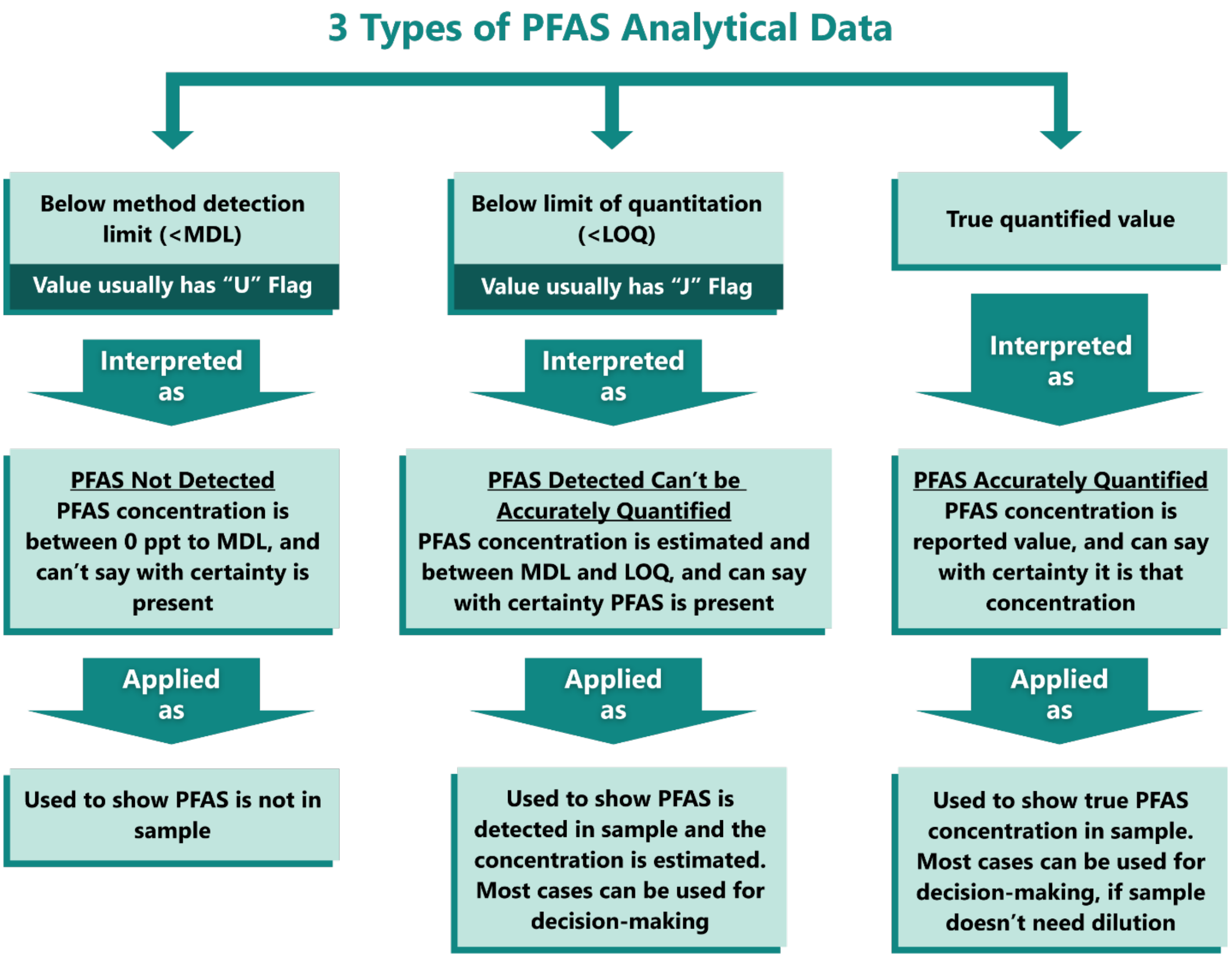


Figure 5-1. Infographic describing the types of PFAS data.

Analytical detection limits (i.e., Instrument Detection Limit or Lowest Level of Detection) are determined based on evaluating the significance of a response in the analytical instrument against background (also referred to in this context as noise). For example, direct injection of a specific PFAS compound must produce a signal greater than three times the standard deviation of the noise level to be considered a detection. Additional steps to process and extract PFAS from media generally increase measured detection limits (Long 1983). MDLs are influenced by sample matrix, preparation steps, instrument (age, maintenance), technology, analyst skill, and environmental conditions. Each laboratory establishes its specific MDLs for each method following its procedures and methods (e.g., 40 CFR Part 136, Appendix B). A laboratory's MDL is generally updated annually.

The LOQ is the lowest PFAS signal the instrument can produce to quantify the compound in the sample with a degree of certainty. The LOQ is commonly calculated as follows:

- Lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99% (EPA Method 537.1 rev 2 and EPA Method 533)

- Smallest concentration that produces a quantitative result with known and recorded precision and bias and must be above the concentration of the lowest calibration standard (EPA Method 1633)

If the PFAS signal falls below the MDL, it is interpreted as not detected and commonly reported with a U flag. However, a result below the MDL may mean PFAS is present in the sample at concentrations below what the method detects. If the PFAS signal falls between the MDL and LOQ, it is interpreted as detected with an estimated value and commonly reported with a J flag. J flag results indicate a likely concentration between MDL and LOQ. These estimated values depend on the specific laboratories' standard operating procedures for handling these values. Common ways to report values below LOQ (<LOQ) include the following:

- Drop <LOQ values from consideration (biases PFAS results/statistics high since low values are eliminated).
- Replace <LOQ values with new values such as 0, LOQ/2, LOQ/√2, LOQ (where using 0 value will bias PFAS results/statistics low, and using LOQ value will bias PFAS results/statistics high).
- Use a value estimated by the analytical method.
- Use a value estimated by statistical analysis such as a maximum likelihood or linear regression.

Estimated values between MDL and LOQ can in most cases be used for decision-making and to determine more focused sampling efforts.

5.2.4 Definitive Data vs. Screening Data

DQIs can vary depending on the project-specific DQOs that need to be met. Generally, there are two types of data: definitive and screening. The type of PFAS analytical method selected also determines how the data can be used for interpretation and decision-making. Definitive data, or data with highest confidence, can be generated through using PFAS methods such as 537.1 (**Section 5.3.1**), 533 (**Section 5.3.1**), and 1633 (**Section 5.3.2**) if method QA/QC standards are met. Screening data, on the other hand, include less confident data sets but still provide useful information to further environmental investigations. Screening data are commonly used in environmental investigations to understand the presence or extent of contamination. Screening data are generated from PFAS methods such as Method 8327 (**Section 5.3.3**), OTM-45 (**Section 5.3.4**), and methods described in **Section 5.4**. Other drivers that determine if a data set is definitive or screening include the sampling technique, handling technique, and analytical technique, where specific QA/QC standards must be met to characterize a data set as definitive.

5.3 Quantitative (Target) Analytical Methods

The following provides a general overview of analytical methods accepted for PFAS quantification. The method chosen for analysis depends upon the type of media (solid/liquid/gas) under investigation, the type and number of PFAS compounds to be analyzed, and project-specific DQOs. **Table 5-1** gives an overall summary of targeted PFAS methods, including differences between methods, to enable discernment of the most appropriate PFAS analysis for a job. The ITRC maintains tables that provide details of published methods, draft methods, and analyte lists beyond what is provided in this guidance. Some commonalities among all methods include the following:

- Samples containing organic material can enhance ionization of PFAS precursors. One way to manage this is to measure the TOC of the sample.
- Samples containing large amounts of inorganic salts (chloride/sulfate/hardness as $CaCO_3$) can cause the method performance to be outside the acceptable range.
- All branched and linear PFAS isomers are summed as a single value.

Table 5-1. Summary of analytical methods and differentiating factors

Method Name[1]	**EPA Method 537.1 Rev 2.0**[2]	**EPA Method 533**	**SW-846 EPA Test Method 8327 Rev 0**	**EPA Third Draft Method 1633**	**Draft EPA Other Test Method-45**
Released	March 2020	December 2019	July 2021	December 2022	January 2021
Data Type	Definitive	Definitive	Screening	Definitive	Screening
Matrix Analyzed	Drinking water	Drinking water	Surface water, groundwater, wastewater	Surface water, groundwater, wastewater, soils, biosolids, sediment, landfill leachate, fish tissue	Source air emissions
Number of PFAS Quantified	18	25	24	40	50
Sample Holding Time	14 days, not to exceed 10 °C (do not freeze)	28 days, not to exceed 10 °C (do not freeze)		Aqueous – 28 days (not to exceed 6 °C) Solid – 90 days (dark storage at 20 °C)	28 days (room temperature)
Technology	Liquid Chromatography Mass	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS

Method Name[1]	EPA Method 537.1 Rev 2.0[2]	EPA Method 533	SW-846 EPA Test Method 8327 Rev 0	EPA Third Draft Method 1633	Draft EPA Other Test Method-45
	Spectrometry (LC-MS/MS)				
Application to PFAS Monitoring Programs	Used for UCMR5	Used for UCMR5	Not used in upcoming monitoring programs	Used in CWA for National Pollutant Discharge Elimination System (NPDES) permits	Not yet subject to the federal rulemaking process
Multi-Laboratory Validation	Multi-laboratory validated	Multi-laboratory validated	Multi-laboratory validated for RCRA program	Currently under multi-laboratory validation for CWA	None
Notes		Focus on "short-chain" PFAS (4-12C) Can't measure all 18 PFAS in 537.1; compliments 537.1	Guidance providing general information Will be phased out in lieu of final 1633	Future versions including final (tentative launch winter 2023) unlikely to involve substantive changes	Provides a consistent method with best available analytical practices

[1] Table updated as of February 2023

[2] List of specific PFAS compounds to be analyzed can be viewed by clicking each method link

5.3.1 Drinking Water Methods (537.1 and 533)

As of February 2023, two EPA-approved drinking water analytical methods are required for use during UCMR5 analyses occurring from 2023 to 2025 (see **Table 2-1**). EPA Method 537.1 Rev 2.0 (Method 537.1) is the primary method to quantify 18 PFAS, and EPA Method 533 (Method 533) was published to compliment 537.1 and focus on shortef r-chain compounds (C4-C12), quantifying 25 PFAS. Method details of note include the following:

- Determination of MDL is not required by Method 537.1 and Method 533; however it may be required by various regulatory bodies associated with compliance monitoring. It is the laboratory's responsibility to determine if detection limit determination is required based on intended use of data. MDL can attain PALs.
- Method 537.1 and Method 533 must establish target concentration for minimum reporting level (MRL) based on intended use of method. MRL may be established by the laboratory for a specific purpose or set by the regulatory agency. Establishing an MRL concentration that is too low may cause repeated failure of ongoing QC requirements.

- Method 537.1 and Method 533 both use concepts of adsorption for extraction. Thus, if a sample has greater frequency of long-chain PFAS, it may cause shorter-chain PFAS concentrations to be biased low based on PFAS chemical characteristics described in **Section 3.4**.
- Method 533 uses a different solid phase extraction cartridge than 537.1, resulting in an increased level of confidence for smaller chain (4 to 12 carbons) PFAS concentrations. **Table 5-2** provides a list of PFAS compounds found in both methods (537.1 and 533) for which higher confidence in results can be achieved using Method 533.
- Method 533 uses the analytical technique of isotope dilution to account for matrix interferences, whereas Method 537.1 does not. This may result in minor differences in PFAS concentrations reported from the two methods, with Method 533 yielding greater accuracy from carrying concentration ratios, rather than concentration values, all the way through to quantification.
- Method 537.1 uses Trizma® (only available through Sigma Aldrich) for free chlorine removal, whereas Method 533 uses ammonium acetate (a popular general laboratory reagent) for free chlorine removal.

Table 5-2. PFAS analytes in Methods 537.1 and 533, with higher confidence achievable in Method 533

Target Analyte Name[1]	Abbreviation	CAS Registry Number
Perfluoroalkyl Carboxylic Acids (PFCA)		
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroalkane Sulfonic Acids (PFSA)		
Perfluorobutane sulfonic acid	PFBS	375-73-5
Perfluorohexane sulfonic acid	PFHxS	355-46-4
Perfluorooctane sulfonic acid	PFOS	1763-23-1
Perfluoroalkyl Ether Carboxylic Acids (PFECA)		
Hexafluoropropylene oxide dimer acid	HFPO-DA (GenX)	13252-13-6
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
Ether Sulfonic Acids (PFESA)		
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OudS	763051-92-9

[1] Methods measure all forms of the compounds as anions.

5.3.2 EPA Third Draft Method 1633 (Revised Draft Released December 2022)

EPA's third Draft Method 1633 (Method 1633) contains all required quality control procedures for use under the CWA, including NPDES permits (with conditions subject to further revision). The DoD has accredited 15 laboratories to run draft Method 1633 as the method was written to comply with all 40 CFR Part 136.7 method quality controls. Looking forward, the EPA has stated it will publish the fourth draft method and then publish the final method in 40 CFR 136 by the end of 2023. Future versions are unlikely to involve substantive changes to procedures and will likely include the QC criteria for the ifferent matrices, obtained from reviewing results of the multi-laboratory validation study that started in late 2021.

Method 1633 is a robust method that quantifies 40 PFAS in surface water, groundwater, wastewater, soils, biosolids, sediment, landfill leachate, and fish tissue; the final 1633 method should address extraction in soils. This method is performance-based, allowing modifications to be made to improve performance provided all performance criteria in the method are met. Other method details include the following:

- Determination of MDL for all target analytes must be established using the procedure in 40 CFR Part 136, Appendix B. MDL can attain PALs
- A minimum level of quantitation may be established by (1) calculating the equivalent to the concentration of the lowest calibration standard or (2) multiplying MDL by 3.18
- Uses adsorption for extraction.
- Uses isotope dilution analytical technique to account for matrix interferences

5.3.3 SW-846 EPA Test Method 8327 Rev 0 (Released July 2021)

SW-846 EPA Test Method 8327 Rev 0 (8327) is not a required method for use under the CWA and is not recommended for PFAS analysis. However, until a final analytical PFAS method (1633) is published in 40 CFR 136, applicants may use any suitable method if a description for using the method is provided. This method can be used to obtain screening data only, because it does not meet all QA/QC requirements for definitive data. Screening data are discussed more in detail in **Section 5.2.3,** and methods that produce definitive or screening data are provided in **Table 5-1**.

Method 8327 provides general information on how to perform an analytical procedure that quantifies 24 PFAS compounds in surface water, groundwater, and wastewater. The method has gone through multi-laboratory validation for the RCRA program, testing only in one wastewater matrix (wastewater treatment plant final effluent). Other method details include the following:

- Determination of MDL established by signal to noise ratio ≥3. MDL cannot attain PALs
- A minimum level of quantitation may be established by (1) calculating the equivalent to the concentration of the lowest calibration standard or (2) multiplying MDL by 3.18
- Uses adsorption for extraction
- Recommends laboratories adopt additional QA/QC practices beyond those listed in the specific method

5.3.4 Air Emission Methods (e.g., OTM-45)

Draft EPA Method Other Test Method-45 (OTM-45) was created to provide federal, state, and local agencies a consistent method to measure PFAS released into the air and begin the discussion for developing validated PFAS emission measurement methods. This is the first air emission test method introduced for PFAS. Method OTM-45 has not yet been subject to the federal rulemaking process but has been reviewed by the Emission Measurement Center to promote consistency with current best analytical practices. This method can only be used to obtain screening data only, as it does not meet all QA/QC requirements for definitive data.

Method OTM-45 (released January 2021) measures 50 target PFAS compounds in air emissions from stationary sources. The method also has a non-target component that can help identify other PFAS compounds beyond the 50 that may be present in an air sample. Method OTM-45 is a performance-based method that mentions analytical techniques discussed in 533 and 537.1. Other method details include the following:

- It uses isotope dilution analytical technique to account for matrix interferences during different steps of the process
- The MDL is calculated as signal in laboratory analyses above background for a target compound with 99% confidence

Other non-PFAS source air emission analytical methods include SW-846 Test Method 0010: Modified Method 5 Sampling Train and Modified Method TO-15; however, these methods were not created to measure PFAS specifically. Until a formal PFAS source air method is approved and published, laboratories are recommended to use any suitable alternate methods if they provide a description for use and meet specified QA/QC standards.

Ambient air emission analytical methods for PFAS are still under development. Applications for these methods will include deposition, receptor exposure, and fugitive emissions. Specifically, an ambient/near-source field deployable method, semi-volatile PFAS method, and volatile PFAS method will be available in the next few years. This guidance will continue to be updated as new methods are introduced.

5.4 Semi-Quantitative or Qualitative Analytical Methods

Semi-quantitative and qualitative analytical methods are also very important tools to understand PFAS in the environment. A major drawback of targeted PFAS analyses is they only provide data on a small number PFAS compounds that may be present in environmental media. As discussed in **Section 3.4**, there are thousands of PFAS, and many PFAS precursors transform, generating regulated PFAAs. Therefore, a mass balance that includes future sources of PFAAs is important for understanding fate and transport and selecting and designing remedies. Semi-quantitative and qualitative analytical methods, or non-target analyses, can be used to accomplish the following:

- Provide information that is otherwise not available (e.g., presence of PFAS precursors, presence of patented PFAS with no analytical standard, total fluorine), as shown in **Figure 5-2**
- Provide information at higher resolution, more quickly, or more cost effectively for decision-making

- Provide information to evaluate dynamic parameters such as integrated mass flux or discharge that is more difficult to collect/understand with traditional sampling and analysis

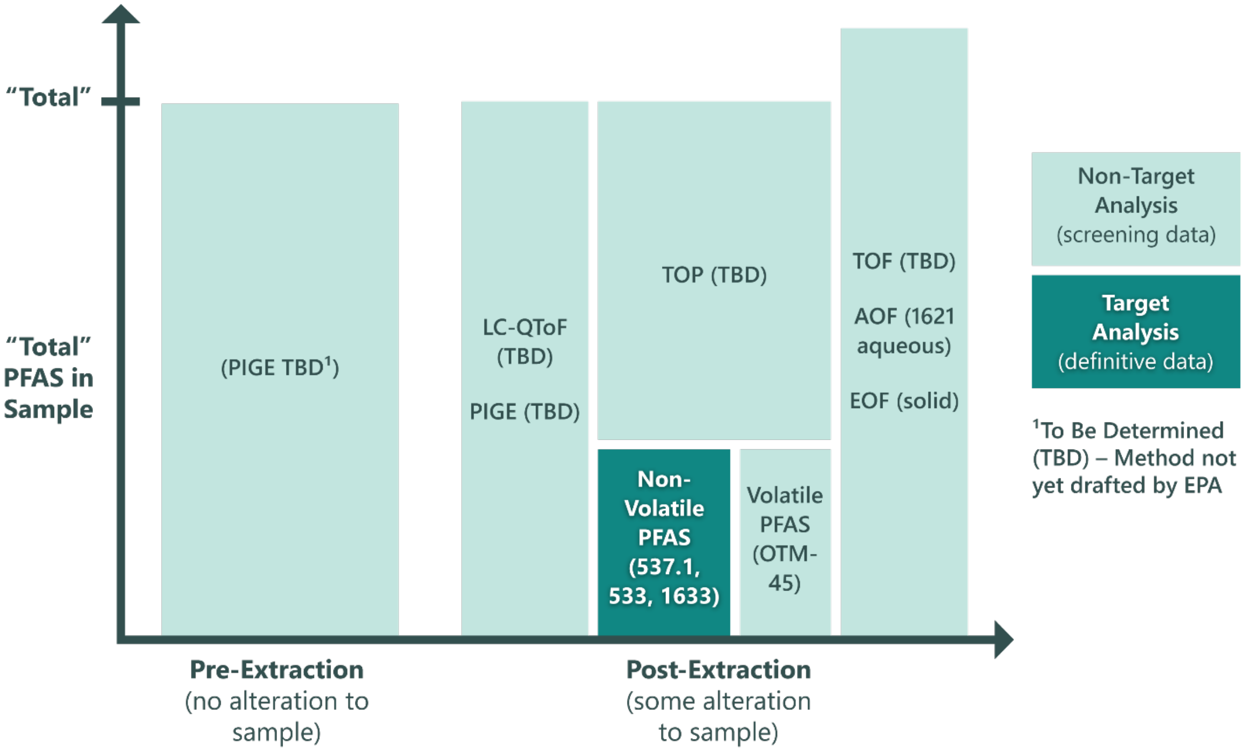


Figure 5-2. Conceptual mass balance for full PFAS spectrum in environmental samples, available with analytical techniques as of March 2023.

Use of these methods, compared to quantitative analytical methods, carries an inherent higher uncertainty in their data caused by method design and less strict QA/QC parameters. Therefore, these methods are only appropriate for screening-level evaluations to support investigations and are not appropriate for making decisions requiring definitive data (e.g., ensuring compliance with regulations).

The methods discussed in this section have not been promulgated by EPA through rulemaking, and therefore, they are not approved for use in compliance monitoring (e.g., under the CWA). Rather, this section provides other analytical techniques available and a look to the future of PFAS analytical chemistry (summarized in **Table 5-3**). As of March 2023, EPA has released Draft Method 1621 for evaluation of AOF in liquid matrices. The EPA is reviewing other methods for TOF and the TOP assay, and first drafts may become available in the next couple years.

Table 5-3. Non-target PFAS analysis

Method Name[1]	**Total Organic Fluorine (TOF)**	**EPA Draft Method 1621**[2] **(AOF)**	**Extractable Organic Fluorine (EOF)**	**Total Oxidizable Precursor (TOP)**	**PIGE**	**Nontarget Methods (QToF)**
Released	NA	April 2022	NA	NA	NA	NA
Data Type	Screening	Screening	Screening	Screening	Screening	Screening
Matrix Analyzed	Aqueous and solid	Aqueous	Solid	Aqueous and solid	Primarily solids with continued development for aqueous	Aqueous and solid
Analyte	Total organic fluorine	Adsorbable organic fluorine	Extracted organic fluorine	Total PFAS precursor	PFAS on surfaces	Full spectrum of PFAS class
Technology	CIC	CIC	CIC	LC-MS/MS	PIGE	LC-QToF MS/MS
Notes	Available in commercial laboratories Captures short chain PFAS more accurately than 1621/EOF	Multi-laboratory validation is underway Measures carbon/ fluorine bonds with lower detection limits that TOF	Available in commercial laboratories Better suited at mitigating inorganic fluorine interference than TOF	Available in commercial laboratories Measures PFAA precursors		Available in commercial laboratories

[1] Table updated as of March 2023.

[2] Full method can be viewed by clicking each method link.

5.4.1 *Total Organic Fluorine*

The TOF method is a semi-quantitative method in development by the EPA with the first draft not yet published. EPA intends the method to serve as a rapid screening tool to identify total PFAS presence or absence. Until the EPA publishes the method, commercial laboratories (e.g., Eurofins, Pace) offer variations of this method. The method can be used to create screening PFAS data to help explain precursor transformation and complete PFAS mass balances. It may not be the best method to use if naturally occurring fluorine is known to be present near PFAS contamination at the site.

TOF method estimates “total” PFAS in aqueous and solid matrices by measuring concentrations of organic fluorine through CIC. Information on molecular structure can’t be determined in this method, so what is reported is the sum of fluorine from PFAS and other sources (fluorine is the thirteenth most abundant element in the earth’s crust). At DOE facilities, a common source of environmental fluorine (besides PFAS) is fluorine-containing refrigerants. Pace specifically has launched the True-TOF® method quantifying TOF in aqueous matrices without extraction to a granular activated carbon media (used for 1621 and EOF). Other method details include the following:

- Captures short-chain PFAS more accurately than Method 1621
- Less costly method compared to nontarget PFAS analysis (see **Section 5.4.5**)
- MDLs and RL are order(s) of magnitude higher than Method 1621/EOF or TOP assay

5.4.2 Absorbable Organic Fluorine: EPA Draft Method 1621 (Released April 2022)

EPA Draft Method 1621 (Method 1621) is a draft semi-quantitative method that is not yet required for CWA compliance monitoring. It is a single laboratory validated method, with multi-laboratory validation started in summer 2022 and a goal for final publication by the end of 2023. Method 1621 can be used to create screening PFAS data to help explain precursor transformation and complete PFAS mass balances.

Method 1621 estimates AOF (e.g., “total” fluorine) in aqueous matrices by measuring the amount of carbon-fluorine bonds that are present in the sample through CIC. Information on molecular structure can’t be determined in this method, so what is reported is the sum of carbon-fluorine bonds from PFAS and other sources, which are rarely naturally occurring (e.g., pesticides and pharmaceuticals). Other method details include the following:

- Uses adsorption for extraction (may bias short-chain PFAS low)
- Less costly method compared to nontarget PFAS analysis (**Section 5.4.5**)
- Better suited for mitigating inorganic fluorine interferences than TOF, and generally has lower method detection limits (2-4 parts per billion [ppb] range) compared to TOF (>400 ppb)

5.4.3 Extractable Organic Fluorine

The EOF Method is a semi-quantitative method offered by several commercial laboratories (e.g., Eurofins, Pace), and the EPA is evaluating this method under the formal rule-making process. The method can be used to create screening PFAS data to help explain precursor transformation and complete PFAS mass balances.

The EOF method estimates extractable organic fluorine (e.g., “total” fluorine) in solid matrices by measuring the amount of carbon-fluorine bonds that are present in the sample through CIC.

Information on molecular structure can't be determined in this method, so what is reported is the sum of carbon-fluorine bonds from PFAS and other sources (e.g., pesticides and pharmaceuticals), which are rarely naturally occurring. Other method details of note include the following:

- Uses adsorption for extraction (may bias short chain PFAS low)
- Less costly method compared to nontarget PFAS analysis (**Section 5.4.5**)
- Better suited for mitigating inorganic fluorine interferences than TOF, and generally has lower method detection limits
- Detection limits are significantly lower than those achieved by TOF, however still higher than AOF

5.4.4 Total Oxidizable Precursor Assay

The TOP Assay is a semi-quantitative method with a specific EPA draft method forthcoming. Commercial laboratories (e.g., Eurofins, Pace) do offer this method, and the EPA is considering the need for a thorough multi-laboratory validation study. The method can be used to create screening PFAS data to help explain potential level of PFAS precursors present and precursor transformation.

The TOP assay estimates total precursors in aqueous and solid matrices by evaluating polyfluorinated precursor PFAS (as discussed in **Section 3.3**) oxidation into known PFAAs that can be quantified via target PFAS methods. The target assay (e.g., Method 1633) is run before and after a robust oxidation used to drive transformation, and the difference is used to evaluate presence and relative quantities of polyfluorinated precursors. Other method details of note include the following:

- Uses adsorption for extraction (may bias short-chain PFAS low)
- More costly method as target analyses must be run twice (pre- and post-oxidation)
- Total PFAS concentration post-TOP assay should be greater or equal to the total PFAS concentration in the pre-TOP assay, which signifies no material losses observed in preparation steps, noting a decrease of up to 10% might be expected due to normal analytical variability (Ventia 2019)
- Sum of PFCA post-TOP assay should be equal to or greater than the sum of PFCA pre-TOP assay, which signifies any precursors being converted to PFCA products (Ventia 2019)
- Complete oxidation should be verified in that no PFAA precursors (e.g., 6:2 FTS, FOSA) are detectable post oxidation, unless near complete oxidation is acceptable as defined in project specific work control documents (Ventia 2019)

- Sum of PFSA post-TOP assay should approximate the sum of PFSA pre-TOP assay, signifying that precursors did not convert to PFSA products.
- For situations in which near complete oxidation is acceptable, minimal PFAA precursors are detectable post-oxidation, signified by (for aqueous samples), the sum of [PFAA precursors] divided by the sum of [total PFAS] is less than 5%

5.4.5 Particle-Induced Gamma Ray Emission

The PIGE spectroscopy method is a semi-quantitative technique that is not required for compliance monitoring under any federal rulemaking, with no standard method being drafted by the EPA. This method is also still only offered in research laboratories. The method can be used to create screening PFAS data to help explain potential PFAS on solid surfaces (such as textiles, paper, food packaging).

PIGE rapidly estimates “total” PFAS on the surface of environmental media by using a proton ion beam and measuring the gamma-ray wavelength emission of organic fluorine (Ritter 2017; Xia 2022). Applications for aqueous matrices are being evaluated with the understanding that the method can only measure fluorine within the depth of beam penetration. Information on molecular structure can’t be determined by this method; the sum of fluorine from PFAS and other sources is reported. Other method details include the following:

- Non-destructive method with minimal sample processing
- Can reach desired sensitivity within 1 to 3 minutes per sample with possible application in the field for in situ PFAS screening
- Laboratory-based (as of May 2023) with multiple research programs (e.g., SERDP/ESTCP) developing PIGE for possible field scale applications; however, proton beam accelerator systems are costly and may limit application
- For applications in paper and textiles, it is assumed the concentrations of inorganic fluoride are negligible; however, inorganic fluoride must be considered when using this technique for aqueous matrices

5.4.6 Non-Target Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry

Liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QtoF method) is a nontargeted technique that is not required for compliance monitoring under any federal rulemaking with no standard method being drafted by the EPA. Commercial laboratories (e.g., Eurofins, Pace) do offer this method. The method can be used to create screening PFAS data to help identify PFAS sources, explain precursor transformation, and complete PFAS mass balances for high resolution conceptual site models.

The LC-QtoF method can identify PFAS compounds that do not have an analytical standard in aqueous and solid matrices by way of looking at known, structurally similar PFAS compounds (Liu 2019; Adamson 2022; Nickerson 2020; Koelmel 2022). The method provides more data to create a PFAS "fingerprint" of the different PFAS chemicals found within specific environmental media. Other method details include the following:

- The main drawbacks of the technique include: (1) lack of data-processing and interpretation standards, (2) labor- and time-intensiveness, (3) susceptibility to error, and (4) non-comprehensive PFAS mass spectral libraries, resulting in analytical laboratories adopting individual nontarget workflows creating unavoidable biases in results (Koelmel 2022).
- Some nontarget techniques use a suspect screening approach to identify unknown PFAS. Suspect screening uses libraries of cataloged data (exact mass, retention time, isotope pattern) from standards and information found in the literature to tentatively identify suspect compounds with similar structure to known compounds. This approach biases nontarget PFAS results toward PFAS compounds that are similar to those known to the analytical community.
- More advanced nontarget techniques use no pre-existing knowledge for comparison before analysis and thus enhance the identification and discovery of known, uncommon, and unknown PFAS. For example, FluoroMatch 2.0 funded by the United States Department of Agriculture (USDA), EPA, and Agilent Technologies, is the first software to automate nontarget identification workflow for PFAS not using the suspect screening approach to help harmonize reporting across laboratories (Koelmel 2022). The new software release increases coverage of likely PFAS more than tenfold compared to FluoroMatch Flow, and when applied to AFFF matrices, it found more than one thousand likely PFAS, including previously unreported compounds.
- Continued method advancements are likely to facilitate new PFAS compounds being identified in environmental samples.

5.5 Mobile Laboratories and Sensors

Validated commercially available on-site PFAS measurement methods are still scarce and often do not meet the DQO requirements of many investigations because of their low PFAS sensitivity and selectivity. Reliance on these types of methods to accurately represent actual site conditions is not recommended until the technology is further developed to reach desired QA/QC standards. Currently, these methods should be used to create screening data only.

Advantages of using on-site measurement methods include the ability to screen PFAS on-site, to obtain real-time results for rapid decision-making, to keep hazardous or radiological materials on-site, and to reduce cost. On-site measurements can also help screen PFAS compounds to determine the appropriate selection of compounds for routine off-site analysis. General disadvantages of on-site measurement methods include higher PFAS detection limits, reduced compound selectivity, stronger influences of environmental factors on method performance, and stronger likelihood of field sample contamination. On-site measurement methods are appropriate for semi-quantitative and qualitative approaches. This section gives a highlight of where the research is going, and what on-site PFAS measurements are most promising for commercialization as of May 2023.

5.5.1 Field (Mobile) Laboratories

Field (mobile) laboratories are simpler robust versions of off-site commercial laboratories that are in the general vicinity of field sampling and are appropriate for screening-level investigations. Some considerations for setting up a mobile laboratory include determining type of instruments to use, weight of instruments, application (leakage detection/screening/area monitoring), and site conditions. Pace is the first to offer DoD's Environmental Laboratory Accreditation Program—an accredited mobile PFAS laboratory service that can quantify PFAS in the single digit, part-per-trillion range with same-day results possible.

In March 2021, a case study funded by ESTCP (ER19-5203) was conducted to investigate the efficacy of using an accelerated method in a PFAS mobile laboratory deployed at an airfield. The study used Pace's mobile laboratory method for comparison to the accelerated method. Generally, the accelerated method modified extraction steps for shorter analytical run times and allowed relaxed QC tolerances to provide higher analytical throughput while still providing defensible analytical data. Conclusions of the study proved generally that no significant biases running the accelerated method were introduced other than differences in results for shorter chain compounds (PFHpA, PFPeA, PFHpS). Running accelerated PFAS methods in mobile laboratories allows for near real-time decision-making in the field for dynamic work strategies. Methods used in mobile PFAS laboratories will continue to be optimized to improve accuracy and precision and to shorten run times.

5.5.2 Sensors

Sensor-based approaches offer a faster, more affordable on-site PFAS detection option; however, many challenges still exist, including understanding (1) PFAS selectivity, (2) sample preparation and preconcentration, (3) sensitivity, and (4) portability for PFAS detection (Menger 2021). Areas of promising growth for PFAS sensors include transitioning the use of optical sensors from the laboratory to full-scale field implementation, continued development of molecularly imprinted polymers for specific PFAS, and immunosensors based on how PFAS act in the human body.

Fluorescence sensor approaches enable relatively easy measurements, are more sensitive than colorimetry, and can discern complex photochemical behavior (Rodriguez 2020). However, combining methods showed better results and enhanced PFAS sensitivity in water samples. For example, Chen (2018) developed a sensing method for detecting PFOS using a colorimetric method that involves using Nile blue A as a probe with fluorescence, resonance light scattering, and ultraviolet-visible absorption detection. Combining three techniques enhanced the accuracy; however, the lowest limit of detection was still 1.6 ppb. Small molecule complexation-based methods are limited by sensitivity and specificity, but with a pretreatment step to lower the detection limits, and the advancements of smart phones with high-resolution cameras with custom applications to analyze images of a test and compare them to built-in calibration curves (Fang 2018), this route gives promise for on-site PFAS detection. Additionally, a recent example of molecularly imprinted polymer sensor development is Glasscott's (2020) success in fabricating a molecularly imprinted polymer on a gold microelectrode selective for GenX with a limit of detection of 0.086 ppt.

While progress is being made in developing PFAS sensors in laboratory settings, commercialization of these sensors for real world use has lagged. The technology transfer process needs to be considered early in the development cycle. For example, immunoassay sensors require a microplate reader that is not field-compatible in its traditional form. Identifying this problem early in immunoassay sensor development is crucial to leverage the technology for commercialization. Understanding the limits of PFAS sensors in a laboratory can help water quality managers and the public influence current research to leverage technology for its intended end-use purpose.

5.6 Method Quality Control/Quality Assurance

Commercial laboratories accredited under the DOECAP-AP are subject to strict QA/QC and detection limit requirements in the QSM for PFAS analyses. DOE strongly recommends that a DOCAP-AP accredited laboratory be used for PFAS analyses. If a non-DOECAP-AP accredited laboratory is selected, the laboratory must go through a formal certification process meeting specific DQOs to receive accreditation to perform the PFAS methods in accordance with EPA orders. Usually, the process includes successfully analyzing a set of proficiency testing samples for each PFAS method the laboratory wants to be certified for and maintaining a formal QA program. Each method also requires the laboratory to show initial demonstration of capability and continue to meet standard analytical data quality checks.

Project-specific work control documents should list QA/QC samples that are required for the analytical method and sampling program. **Table 5-4** provides a list of all possible environmental data quality samples, which samples are required in each EPA method, and how samples may fit within the DQI framework.

Table 5-4. QA/QC samples for PFAS

General Sample Name	Method Sample Required	Purpose of the Sample	DQI
Field Reagent Blank	537.1; 533; OTM-45	Used to determine whether on-site contamination is introduced into samples during collection and handling. A field reagent blank, sometimes called a field blank, is a sample of clean water (or other environmental matrices) processed (i.e., collected, filtered, preserved, stored, or assayed) the same way as field samples.	Accuracy
Trip Blank	NA[1]	Used to determine whether contamination is introduced during transport to and from the laboratory. A trip blank is a sample of clean water (or other environmental matrices) shipped like the field samples but not exposed to an outside sampling environment, and sampled and analyzed the same way as field samples.	Accuracy
Laboratory Fortified Blank	537.1; 533; OTM-45	Used to determine whether the unknown sample matrix causes any analytical effects. A laboratory blank sample spiked with known quantities of both native and isotopically labeled standards is analyzed the same way as the field samples. This control sample is also occasionally referred to as a laboratory-fortified blank.	Accuracy
Laboratory Reagent Blank	537.1; 8327; 1633; OTM-45	Used to determine whether contamination is introduced from the laboratory environment, chemical mixtures, glassware, or extraction equipment. A laboratory blank is spiked with an isotopically labeled standard and analyzed the same way as the field samples. This control sample is also referred to as a method blank or laboratory sample media blank.	Accuracy
Instrument Blank	1633	Used to determine whether contamination is introduced from the laboratory instrument. A laboratory blank is analyzed before running field samples or after analysis of a high-concentration sample.	Accuracy
Equipment Blank	NA	Used to determine whether contamination is introduced from a specific type of equipment used during sampling. An equipment blank is collected by running PFAS-free water over equipment in direct contact with an unknown sample. An equipment blank is important when sampling equipment that can't be certified as PFAS-free.	Accuracy
Refrigerator Blank	NA	Used to determine whether PFAS used in refrigerants are introduced to the sample during storage in a refrigerator.	Accuracy
Laboratory Fortified Sample Matrix	537.1; 533; 8327; OTM-45	Used to detect any potential bias in analytical results caused by the sample matrix. A field sample is spiked with both native and isotopically labeled standards. This control sample is also referred to as a matrix spike.	Precision

General Sample Name	Method Sample Required	Purpose of the Sample	DQI
Laboratory Fortified Sample Matrix Duplicate	537.1*; 533*; 8327; OTM-45	Used to assess the precision of the analytical method instead of a field duplicate when the occurrence of a method analyte is infrequent. A field sample is spiked with both native and isotopically labeled standards. This control sample is also referred to as a matrix spike duplicate.	Precision
Field Duplicate	537.1*; 533*	Used to assess the precision of the sampling and analytical methods. Duplicate field samples are collected and analyzed.	Precision
Quality Control Standard	533; OTM-45	Used to verify the integrity of the primary calibration standards used to create calibration curves.	
Continuing Calibration Check	537.1; 533; 8327; 1633; OTM-45	Used to verify the accuracy of the existing analytical instrument calibration. A calibration standard is analyzed during or at the end of the analytical batch.	

*Either QA/QC sample can be used

[1] NA- not applicable. Samples not explicitly required for analytical methods but can be included in sampling program based on site-specific DQOs and field methods planned for sampling.

5.7 Analytical Measurement Uncertainty

Analytical measurement uncertainty in PFAS analyses continues to be identified and managed among the analytical community and relayed to the environmental industry. Recently, a paper was published discussing how PFAS “total” parameters (TOF, EOF, TOP) are not able to identify ultra-short chain PFAS (C2 and C3); in the study, ultra-short chain PFAS comprised 98% of sum target PFAS concentrations in aqueous samples (Neuwald 2022).

Steps to manage analytical measurement uncertainty should be discussed in the project specific QAPP. For example, pre-existing PFAS source information at a site can be helpful in selecting the most appropriate PFAS analytical method. TOP and AOF/EOF may be better for sites with PFAS sources primarily made of PFAS precursors or patented PFAS. Targeted PFAS analyses may be better for sites with PFAS sources primarily made of terminal PFAS (PFCAs, PFSAs), such as wastewater effluent.

6. INVESTIGATION DERIVED WASTE

6.1 DOE Disposal Policy and Guidance

IDW poses waste management challenges to environmental sampling efforts when PFAS are present. DOE has developed a waste policy framework for sites to characterize wastes and make disposition determinations, which aids in IDW management. The September 2021 Deputy Secretary memorandum on PFAS authorizes the Head of the Departmental Element to make waste disposal determinations on PFAS-containing wastes. The DOE PFAS Disposal Guide (https://www.energy.gov/pfas/pfas-and-polyfluoroalkyl-substances) provides waste characterization strategies, potential disposal options, and key information to include in the disposal request to the Head of Departmental Element. Departmental Elements may develop their own management policies as long as they are approved by the Head of the Departmental Element.

6.2 Soil, Sludge, and Water/Wastewater

Sampling work plans should address IDW. Prior to a sampling event that is expected to generate PFAS-containing IDW, site personnel should secure a disposal determination from the Head of Departmental Element or identify a waste treatment process. If it is unknown or uncertain whether the sampling event will generate PFAS-containing IDW, sites should prepare in advance for IDW to be stored while the waste is analyzed and any necessary disposal determination is made. Characterization of PFAS-containing waste should follow the established approach for IDW. Care should be taken not to comingle PFAS IDW with PFAS-free IDW; this may require using separate roll-off bins or wastewater tanks, for example. Appropriate planning and preparation for sampling events will help sites to avoid noncompliance with DOE guidance and requirements.

6.3 PPE and Sampling Equipment

As discussed in **Section 4.4**, PFAS may be found in certain PPE, such as coated Tyvex and water/stain repellent clothing, as well as in sampling equipment, such as Teflon tubing. When environmental media are being sampled and assessed for the presence of PFAS, only PFAS-free tools, equipment, and gear should be used to avoid producing false positive results.

Workers should attempt to limit the generation of PFAS-contaminated disposable equipment and PPE gear to the extent practical during sampling events. Because PPE and sampling equipment are considered consumer products, it is recommended to dispose of these wastes in a sanitary landfill.

7. QUALITY ASSURANCE/QUALITY CONTROL

7.1 Introduction

QAPPs document the outcomes of DQO planning (for example, how the collected data will be used to make decisions) and show how QA/QC requirements are applied to environmental data to ensure that the quality and type of data needed are obtained.

7.2 Development of a Quality Assurance Project Plan

QAPPs will be wwritten in accordance with EPA QA/G-5, *Guidance for Quality Assurance Project Plans*, and EPA QA/R-5, *Requirements for Quality Assurance Plans*, using the Uniform Federal Policy-QAPP guidelines. Per this guidance, QAPPs will be composed of standardized, recognizable elements covering the entire project from planning through implementation to assessment. The four main groups of elements include project management, data generation and acquisition, assessment and oversight, and data validation and usability. QAPPs will be developed for activities involving both primary and existing data (e.g., PFAS historical use data). The evaluation process for existing data is based on EPA's *Guidance for Quality Assurance Project Plans* (EPA 2002a).

7.3 Data Assessment

The quality of data used to characterize environmental processes and conditions must be evaluated and confirmed per the intended use of the data. The unique nature of PFAS sampling and analytical procedures makes following and verifying the procedures as discussed in **Sections 4 and 5** imperative.

7.3.1 Field Quality Assurance/Quality Control

As discussed in **Sections 4.3 and 4.4,** special considerations for PFAS investigations include training of sampling personnel, equipment requirements, sample preparation and decontamination, and applicable QC sampling to evaluate the potential for false positives or negatives and anthropogenic background. **Table 5-4** details the QC samples considered in the sampling program and documented in the work control documents (i.e., QAPP) to evaluate false positives or negatives associated with field sampling and analytical methods. The QC program should verify and document that applicable procedures were followed, QC sample collection was completed, and data satisfactorily meet the DQOs.

7.3.2 Data Verification and Validation

Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements. Specifically, for PFAS, data verification/validation across sampling events may include identifying that similar PFAS patterns/trends exist across the data set, understanding that there may be some variability caused by the analytical methods being used.

Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set. In general, data validation is the process of reviewing data and accepting, rejecting, or qualifying it based on nationally accepted or project-approved criteria. Data validation must occur soon after data collection and be objective in its approach. It is particularly important that newly generated sampling and analysis data are technically reviewed to ensure they are valid and were collected and analyzed following appropriate processes and procedures. QAPPs for sampling and analysis will identify the validation criteria and the staff members who will validate the data.

Data verification and validation activities will be conducted in accordance with the following documents and requirements:

- EPA QA/G-8, Guidance on Environmental Data Verification and Data Validation
- EPA-540-R-08-005, Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use
- DoD Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories – Version 5.4 (2021)
- DoD Data Validation Guidelines Module 3: Data Validation Procedure for Per-and Polyfluoroalkyl Substances Analysis by QSM Table B-15 (May 2020)
- DoD Data Validation Guidelines Module 3: Data Validation Procedure for Per-and Polyfluoroalkyl Substances Analysis by QSM Table B-15 (May 2020)
- DoD Data Validation Guidelines Module 6: Data Validation Procedure for Per-and Polyfluoroalkyl Substances Analysis by QSM Table B-24 (October 2022)
- DoD Data Validation Guidelines Module 6: Data Validation Procedure for Per-and Polyfluoroalkyl Substances Analysis by QSM Table B-24 (October 2022)
- National and regional data validation functional guidelines and directives
- Laboratory SOWs, routine analytical services, and modified analyses contract protocols and performance requirements
- Laboratory contracts, protocols, and performance requirements
- Analytical methods

Throughout the data verification/validation process, coordination with laboratories will be conducted, as appropriate, regarding any analytical support and reporting of QA issues if necessary.

8. SUSTAINABILITY CONSIDERATIONS

Sustainable and resilient remediation (SRR) is the practice of developing and implementing "an optimized solution to cleaning up and reusing hazardous waste sites that limits environmental impacts, maximizes social and economic benefits, and creates resilience against the increasing threat of extreme weather events, sea-level rise, and wildfires" (ITRC 2021).

SRR principles and practices should be integrated through all parts of the project lifecycle starting at the site screening investigation planning step, including relevant stakeholder engagement processes described in **Section 9**. During earlier stages of project planning, SRR principles can inform development of DQOs, data collection, and subsequently performance and acceptance criteria. Establishing the anticipated end use of the site or cleanup area can help inform the site risk assessment investigation planning step (ITRC 2021).

Several resources are available to help guide SRR planning and implementation:

- The ITRC SRR Toolkit provides detailed guidance for planning and implementation, including an interactive state resource map to help identify regulations, executive orders, guidance, resources, and case studies relevant to each state.
- The EPA CLU-IN Green Remediation Focus website provides case studies, detailed analysis of BMPs, and training/continuing education resources.
- ASTM E2893 Standard Guide for Greener Cleanups and E2876 Standard Guide for Integrating Sustainable Objectives into Cleanup.

As site investigation activities proceed, development of the CSM should include consideration of whether SRR DQOs were achieved, a summary of the SRR BMPs implemented (refer to the following subsections) and the associated benefits/impacts, how PFAS were considered, and how project resilience was supported by the BMPs. Site investigation activities can be planned to be in alignment with federal, state, and local sustainability-based and resiliency-based policies, objectives, and targets. These activities should also consider environmental justice and social equity consistent with DOE environmental justice best practices (as discussed in **Section 9.2**).

Implementation of SRR principles helps manage multiple types of risk, including risk associated with climate and severe weather event impacts via resilient risk management; risk associated with adverse environmental, social, and economic impacts via sustainable risk management; and risk associated with other unintended adverse impacts from cleanup activities via remediation risk management (RRM) (ITRC 2021). Consideration of these risks and related drivers during project planning and CSM development can help inform schedule and prioritization of site activities.

The following subsections summarize PFAS-specific sustainable BMPs to consider when developing the project-specific QAPP/SAP and SOPs by integrating them into data collection procedures, waste handling, and other site investigation activities (ITRC 2021). Sustainable BMPs are categorized based on the triple bottom line (environmental, economic, and social). Selection of SRR BMPs should consider the overarching goal of PFAS investigation and remediation and should not conflict with that goal.

8.1 Minimize Environmental Footprint

Waste handling and the use of consumables, natural resources, and earthwork equipment typically have large environmental footprints. Minimizing their use will result in lower overall greenhouse gas and criteria air pollutant emissions, among other environmental footprint metrics. Substitute materials and media that have a lower environmental footprint should be confirmed to be also PFAS-free.

Site investigation planning, especially DQO development and data collection to inform the CSM, should consider factors such as current AFFF storage and uses, potential secondary PFAS sources such as stormwater and drainage infrastructure, and source area delineation to streamline and optimize site investigation activities. This BMP will facilitate a site investigation with a low overall environmental footprint by avoiding redundancy in PFAS data collection.

If there are other contaminants at the site, ongoing sampling can be optimized to be PFAS-free program wide, for example by removing PFAS-containing sampling equipment from wells (e.g., some bailers, pump bladders, tubing).

PFAS-laden IDW should be properly disposed of or treated to mitigate long-term environmental impacts and achieve PFAS destruction if possible.

8.2 Maximize Economic Benefits

Creation of employment opportunities can advance the local community’s skill set to help perform PFAS site investigation and public outreach activities. Use of environmental justice community screening tool(s) (as discussed in **Section 9.1.2**) during site investigation and outreach planning can identify whether any environmental justice communities may have been impacted by PFAS contamination, thus requiring additional support and engagement as site investigation activities proceed. For example, if drinking water sources are impacted by PFAS released at the site, alternative drinking water sources and treatment devices may need to be provided during site investigation activities. Such interim risk mitigation measures could pose a financial burden on affected communities.

8.3 Maximize Social Benefits

On- and off-site site activities, including sampling, can create stress on a community. This scenario is highly likely if the affected community has been involuntarily exposed to PFAS in its workplaces, in drinking water or food sources, or through other environmental exposure pathways. Development and implementation of a public and community outreach plan can help promote well-being within the affected community by addressing needs and concerns during site investigation activities (as discussed in **Section 9**).

If community resources are impacted by PFAS released at the site, communities may be interested in alternative water and food sources during site investigation activities. These alternative sources, including bottled water and municipal water, should be tested for PFAS. Some state agencies, such as Massachusetts Department of Environmental Protection (MassDEP), have a list of licensed bottlers who can sell or distribute bottled water or beverages that comply with drinking water standards for PFAS and other contaminants established by MassDEP, EPA, and the United States Food and Drug Administration (MassDEP 2023). If community municipal water source(s) have reported PFAS in the water supply, outreach efforts may require an educational campaign on publicly available water source alternatives and whether they are PFAS-free.

9. COMMUNICATION APPROACH

As part of the remediation project life cycle process, DOE works with multiple public and community stakeholders to inform site investigation activities and educate the general public. DOE is committed to fostering meaningful public involvement in all aspects of environmental remediation decision-making. Depending on the cleanup site's regulatory compliance framework, the DOE project team may need to develop a regulatorily required communication approach, such as EPA's CERCLA community involvement plan or state environmental agency's public involvement plan.

This section provides guidance on understanding PFAS-specific stakeholder needs and concerns, presents examples of PFAS-specific community outreach strategy and engagement, and summarizes PFAS-specific outreach resources.

9.1 Align with Stakeholder Expectations

Stakeholder acceptance of site investigation PFAS-specific DQOs, data collection, and subsequently performance and acceptance criteria are influenced by whether stakeholder expectations have been adequately identified and addressed. Development of a stakeholder and community outreach or engagement plan, followed by implementation of outreach and/or engagement activities, helps understand and integrate stakeholder PFAS-related needs, concerns, and values into site investigation activities and decision-making. The following subsections provide a broad overview of how to assess stakeholder PFAS expectations and achieve alignment of the PFAS site investigation approach with stakeholder expectations, while addressing common challenges in implementing PFAS communications.

9.1.1 Align with Decision Maker Stakeholder Expectations

Decision-maker stakeholders could include site owners or occupants, local, state, and federal elected officials, and regulators, among others. Due to the evolving state of the science and regulatory framework of PFAS issues and concerns, the expectations of these stakeholders may vary. For example, uncertainty surrounding the toxicity of PFAS and associated exposure risks can lead to a lack of consensus on how to evaluate risk and proposed risk management strategies. The ITRC Risk Communication Toolkit (ITRC 2020) provides the following guidance to help align site cleanup objectives and activities with the expectations of decision-maker stakeholders:

- Avoid both downplaying and embellishing risk due to lack of consensus on PFAS risk levels among decision-makers.
- Instead, strategies should be implemented to navigate disagreements and craft an approach to communicate a PFAS risk management strategy that is most likely to be reasonable and protective from the perspective of the stakeholders.

- One strategy is to consider and incorporate stakeholder needs and values, placing greater weight on those factors (e.g., specific risk assessment exposure pathways) when risk management is considered.
- A second or complementary strategy is to develop secondary risk management objectives or DQOs (e.g., understand and reduce PFAS bioavailability and sourcing) that evaluate how site investigation activities will lead to and inform measurable increased protection from PFAS impacts for public health and the environment.

9.1.2 Align with Public and Community Stakeholder Expectations

Public and community stakeholders should when practicable include members of the community in which the site is located, neighboring property owners or occupants, users of nearby recreational spaces, disadvantaged or environmental justice communities, and Tribal nations, among others. Identifying and understanding public and community stakeholder expectations is an ongoing process starting at site investigation planning through performance. A community assessment can be performed to identify site-specific community PFAS concerns and values to inform community outreach plan development.

9.1.3 Community Assessment

As part of the PFAS Community Relations Plan, a community assessment may be performed to develop a baseline understanding of the site-specific PFAS community concerns and stakeholder objectives as they pertain to PFAS site investigation activities and risk management, which are used to develop the site-specific outreach strategy (ITRC 2020). The PFAS Community Relations Plan should be considered as an input to project DQOs. The community assessment at the site risk assessment investigation step can be used to develop an understanding of community concerns and values surrounding PFAS-impacted environmental media and potential exposure risks. This understanding can also be used to develop metrics to evaluate the community's response to the site investigation activities and ongoing outreach efforts. Common community concerns related to PFAS exposure have been documented by the ITRC (2022b) and may be a valuable starting point for performing PFAS outreach. The lack of scientific consensus and regulatory uncertainty surrounding PFAS is an overarching community concern affecting PFAS communications. Additional concerns include the following:

- A general lack of comprehensive regulatory PFAS standards or advisories for a diverse array of exposure scenarios (drinking water, food consumption, ecological risk, occupational, other environmental media), along with a desire for consistency in PFAS standards and screening levels between agencies and across media.
- A general limitation of human and/or animal health risk assessment studies to just a few PFAS compounds out of the many thousands of PFAS chemicals that have been identified.

- Current limitations in technical capacity to sample and analyze for the thousands of PFAS compounds, as well as uncertainty about the safety of short-chain substitutes.
- An inability to control various forms of exposure, including: AFFF users, AFFF release sites, unused AFFF disposal, food packaging, contaminated compost and fertilizer, stormwater, and manufacturing discharges.
- Limited programs for PFAS health monitoring and blood testing, lack of PFAS disclosure by product manufacturers, and limited availability of PFAS information on health effects.
- For stakeholders who are familiar with the general site cleanup process, the unique technical challenges of PFAS prompt concerns about how cleanup will proceed.
- Secondary impacts of involuntary exposure, such as fear of public drinking water and economic consequences of local PFAS contamination.

9.1.4 PFAS Risk Communication Challenges

PFAS pose unique challenges to risk communication and public outreach. Misinformation and misinterpretation often stem from limited publicly available and divergent information from different sources about the potential severity and uncertainty associated with PFAS exposure, risk, and need for action. Conventional news media also generally lack sufficient expertise to accurately report on PFAS issues. Section 14.2 of the ITRC PFAS Technical Guidance (ITRC 2022b) discusses six primary PFAS risk communication challenges, which are summarized in **Figure 9-1**.

Figure 9-1. PFAS risk communication challenges.

9.1.5 *Relative Risks and Remediation Funding Priority*

All communities with PFAS risk require assessment, investigation, and remediation, but communities with the greatest risk will be prioritized. Public stakeholder involvement in the decision-making process and participation of affected communities in risk mitigation activities are essential components of identifying, managing, and communicating risk, while informing prioritization of site activities and allocation of funding. As mentioned in **Section 9.1.4**, sustainable risk management is the process of identifying, evaluating, selecting, and implementing actions that mitigate unintended environmental, social, and economic impacts from cleanup and restoration activities. The severity of risk or unintended impact is defined by stakeholder concerns and values that encompass a wide range of physical or environmental, socioeconomic, and risk management drivers and barriers to implementation of site activities and risk-based cleanup. Identifying and assessing these PFAS-specific site drivers and barriers during project planning and CSM development can inform specific, measurable, attainable, relevant, and timely (SMART) goals and performance metrics that integrate stakeholder concerns (ITRC 2020). These SMART goals and performance metrics can then be used as communication tools to inform public stakeholders of relative risk and remediation funding priority.

9.2 PFAS Community Engagement Resources

PFAS community engagement resources are presented in the following subsections. **Section 9.2.1** presents best practices to develop and implement a PFAS-specific outreach strategy that builds upon the community assessment to inform key message topics, affected stakeholders, potential communication methods, and metrics for measuring strategy implementation and performance (such as SMART goals). **Section 9.2.2** presents DOE PFAS-specific community engagement case studies and/or resources. **Section 9.2.3** summarizes practitioner PFAS-specific communication planning and outreach resources.

9.2.1 Outreach Strategy

As an initial step, outreach strategy development should consider the overall objectives for the outreach effort and any community-specific PFAS concerns identified during the community assessment exercise. Before considering implementation details such as key messages and intended audience, outreach strategies should identify the triggers for performing outreach and/or engagement. Communications activities should begin prior to the trigger event occurring, to prepare the public for the event and contextualize site activities for the public. As part of the DOE communications planning during the site investigation stage, common trigger events necessitating outreach and/or engagement may include the following:

- Reopening a previously closed or designated inactive cleanup site
- Off-site sampling in a public right of way, in a public space, on private property, and/or of a public resource (such as drinking water resources)
- Detecting PFAS in potable water supply (public or private) and/or surface water body used for recreational use (non-potable)
- Detecting PFAS above and below applicable screening levels (i.e., HALs, MCL, or state-specific standards)
- Determining the potential of previous, current, or future worker exposure (AFFF use and/or on-site drinking water impacts)
- Periodic and ongoing public communications
- General inquiry from a community stakeholder
- News released from states, regulators, or advocacy groups, which may create a need to increase outreach with communities (e.g., New Mexico assists Clovis family dairy farm with PFAS contamination)
- Requests from stakeholders to present on PFAS topics at monthly-held meetings (e.g., Natural Resource Damage Assessment Trustee Council, pueblo environmental and cultural preservation departments, community and/or citizens advisory boards)

After determining applicable project-specific engagement triggers informed by the CSM, an outreach strategy can be developed. The outreach strategy should include the specific actions to be taken in response to each of the chosen trigger events, and include details such as: key messages, audience (some subset of the identified stakeholders), communication/outreach method(s), party responsible for implementation, and timeline for implementation. An outreach strategy should also be accompanied by specific performance measures for monitoring the implementation and success of the outreach effort, such as SMART goals. A template for developing a site-specific outreach strategy is provided in **Appendix D**.

As new information is collected during strategy implementation, the approach may need to be revised, updated, or supplemented. The comprehensive outreach strategy planning and implementation process is shown in **Figure 9-2**.

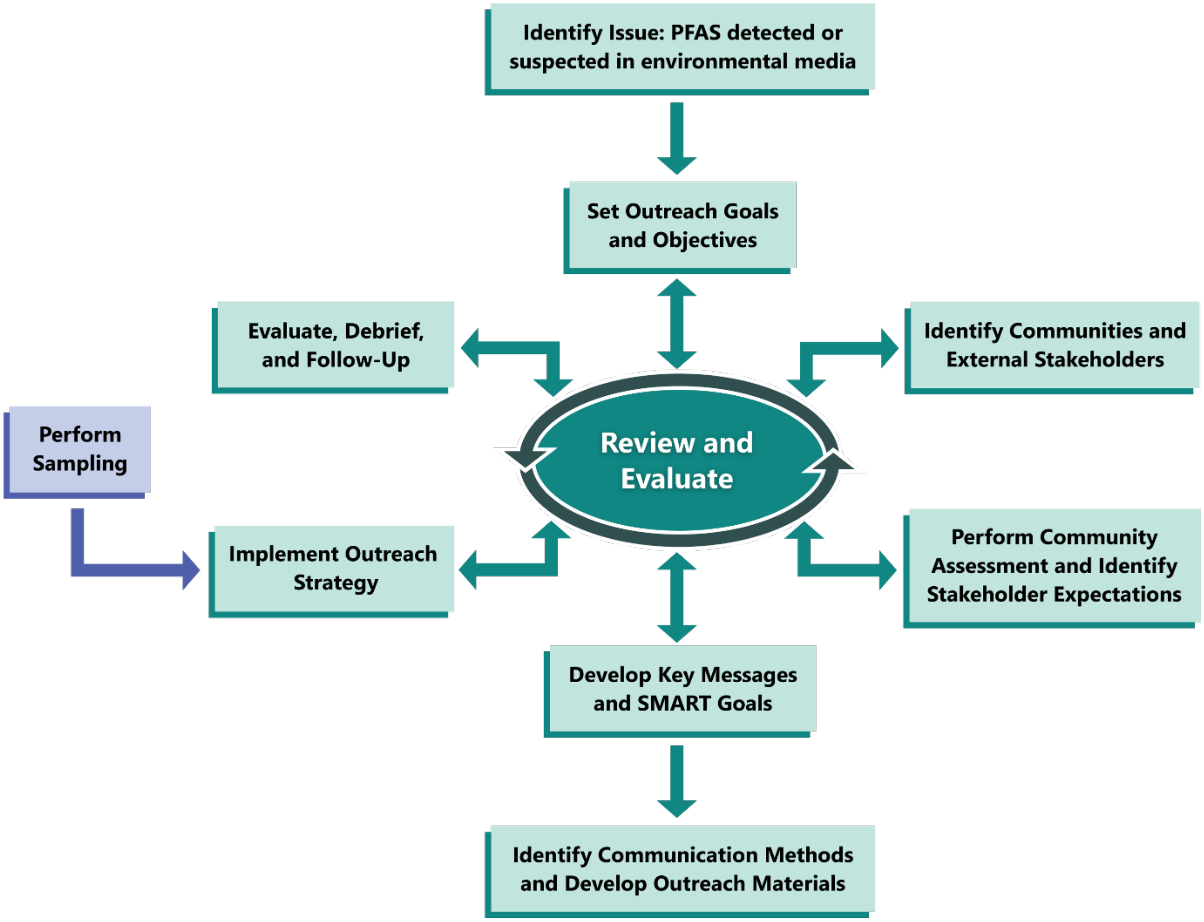


Figure 9-2. Outreach strategy development process.

Modified from New Jersey Department of Environmental Protection (2014).

9.2.2 Existing DOE PFAS-Specific Outreach Resources

Refer to existing DOE PFAS communications plans for examples of key messages, talking points, and FAQs to be used in outreach materials and events. These plans also include key stakeholders and example communications methods and timelines. Plans include the following documents:

- *Draft Communications Plan, Release of DOE PFAS Initial Assessment Report* (dated September 13, 2022). This Communication Plan documents communications activities to guide the *DOE PFAS Initial Assessment Report* release and support development of near-term resources to further inform stakeholders and other key audiences of DOE PFAS activities. Resources include key messages, talking points on the initial assessment, communication schedule (outreach strategy), congressional/governor notification statement, stakeholder/tribal notification statement, media statement, FAQs (general PFAS questions, initial assessment questions) and governmental stakeholder list.
- *Draft Communications Plan, Release of DOE PFAS Strategic Roadmap* (dated August 18, 2022). This Communication Plan documents communications activities to support the *DOE PFAS Strategic Roadmap* document release and support development of near-term resources to further inform stakeholders and other key audiences of DOE PFAS activities. Resources include key messages, communication schedule (outreach strategy), congressional/governor notification statement, stakeholder notification statement, media statement, FAQs (general PFAS questions, roadmap questions) and governmental stakeholder list.

Although not PFAS-specific, the following DOE outreach resources may also be useful:

- Department of Energy 2019 Environmental Justice Second Five-Year Implementation Plan can inform environmental justice best practices.
- Snake River Geothermal Consortium Communications and Outreach Plan is an example of a comprehensive community assessment and outreach strategy process.
- National Energy Technology Laboratory Best Practices: Public Outreach and Education for Geologic Storage Projects can inform community assessment and outreach best practices.

9.2.3 Existing Publicly-Available PFAS Outreach Resources

The following resources may be useful for informing PFAS outreach and risk communication:

- ITRC Risk Communication Toolkit describes general risk communication processes and considerations.

- ITRC PFAS Risk Communication Technical Guidance describes PFAS-specific risk communication considerations.
- AWWA's PFAS resources provide drinking water-specific risk assessment and risk communication guidance.
- North East Biosolids and Residuals Association (NEBRA) resources for PFAS in biosolids.
- Water Environment Federation (WEF) resources for PFAS in wastewater and biosolids.
- Water Research Foundation (WRF) toolkit for PFAS One Water risk communication.

10.ADAPTIVE MANAGEMENT CONSIDERATIONS

Adaptive management approaches for PFAS site investigation steps are particularly relevant due to the evolving science and regulatory environment. Adaptive site management is an iterative process of robust decision-making in which practitioners manage high uncertainty by testing hypotheses and adjusting decisions and outcomes based on experience (Nuclear Regulatory Commission 2003). Because adaptive management is a learning process, it improves management outcomes over the course of a site's investigation activities and overall remedy life cycle. The challenge in using the adaptive management approach lies in finding the correct balance between gaining knowledge to improve management in the future and achieving the best short-term outcome based on current knowledge (Allan 2009).

Concepts of adaptive management can be integrated into project planning and site activities to help inform establishment of PFAS assessment DQOs, including setting short-term interim objectives and long-term site objectives that reflect regulatory, technical, and non-technical PFAS-specific risks (ITRC 2017), such as collecting data of sufficient quality to evaluate the site under current and future conditions, and determining if additional data gaps warrant more investigation. These adaptive management considerations are then tailored to the specific circumstances of individual sites during CSM development to inform design and execution of the PFAS assessment strategy. An integral part of the adaptive management approach is continuous assessment of sources, exposure pathways, and risks during the planning process through site investigation implementation as shown in **Figure 10-1.**

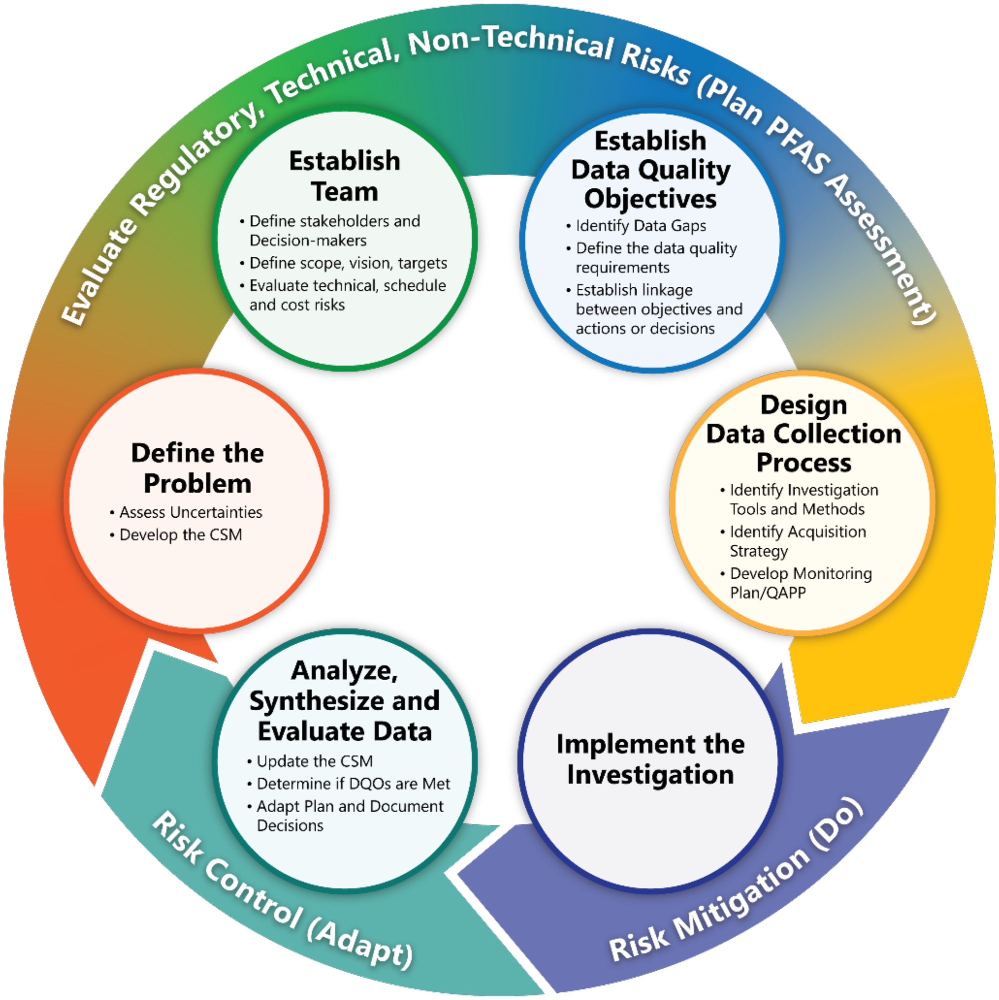


Figure 10-1. Adaptive management for site investigation.

Table 10-1 presents some of these unique challenges with PFAS and how adaptive management strategies can facilitate efficient changes in the investigation program as these challenges arise during the implementation.

Table 10-1. Example technical and non-technical risks to PFAS assessments

Risks	Example of PFAS Adaptive Assessment Approach
Regulatory Risk	
Expanding list of regulated PFAS, revisions to the risk screening levels or promulgated standards	Develop a decision process, documented in the work control documents, that addresses: • Frequency that regulations will be checked for updates (e.g., quarterly). • How new regulated PFAS chemicals, risk screening levels, or promulgated standards will be incorporated into the investigation. • How changes to the investigation plan will be implemented (e.g., delineate extent of PFAS impacts) in response to changes in regulations.
Variance in federal and state standards	Incorporate current federal and state screening levels or standards into DQOs; engage stakeholders (e.g., regulators) early in the planning process to gain acceptance of the standards used for the investigation plan.
Changes in site screening approach	Consider potential for the following in preliminary PFAS CSM development: evolution of PFAS screening levels and policies, laboratory analytical method technical capacity, health advisories for a diverse array of exposure scenarios (e.g., drinking water, food consumption, ecological risk, occupational, other environmental media), waste handling, and PFAS product disclosures.
Changes in the risk assessment approach	Incorporate evolving risk assessment factors (and/or promulgated standards) and a potentially increasing list of PFAS chemicals for which toxicity information is available into the decision process to address these changes; for example: • The EPA Strategic Roadmap notes that five PFAS will be assessed via the Integrated Risk Information System (IRIS): PFBA, PFHxA, PFHxS, PFNA, and PFDA. IRIS assessments have undergone external peer review and are the preferred source of toxicity information for use in risk assessment under CERLCA. • Consider potential updates regarding PFAS carcinogenicity, including development of cancer slope factors for PFAS other than PFOA. At present, no PFAS is a known carcinogen, and most PFAS have toxicity reference doses protective of non-cancer endpoints only.
Technical Risks	
Sampling and analysis methods evolve with quantitative reporting of PFAS in the ppt levels	Engage a project chemist versed in PFAS analysis and develop a strategy in the work control documents that addresses: • Frequency that analytical methods are verified to ensure current methods are used (e.g., when the EPA Method 1633 becomes final for non-potable water, soils, sediments, biosolids). • How PALs will be reviewed and revised as analytical methods are developed or revised. • How changes to the investigation plan and validation will be made in response to changes in analytical methods.

Risks	Example of PFAS Adaptive Assessment Approach
Potential for PFAS precursors, which are not detected with target analytical methods (e.g., EPA Method 533, 537.1 or 1633), as future sources of regulated PFAS	Engage the technical team versed in PFAS analysis and develop a strategy in the work control documents that addresses: • How non-target assays (TOP, AOF or non-target HCMS) will be used. • How changes to the investigation and validation will be made in response to results of non-target assays or if new methods become available to assess precursors.
Anthropogenic background	Engage technical team and develop a strategy in the work control documents that addresses: • Target screening levels relative to anthropogenic background in media to be investigated. • The spatial boundary of the study. • An approach to evaluate anthropogenic background. • A decision process to address the issue if PFAS impacts are observed at the boundary of the study above screening levels but at or below anthropogenic background.
Non-technical Risks	
Increasing public awareness of PFAS risks and stakeholder concerns	Community concerns and values (and the project team's understanding of these factors) may evolve as site investigation activities are implemented; especially as public input is obtained during outreach strategy implementation (refer to **Section 10**). Engage a project communication or public outreach lead to develop a strategy in the work control documents that integrates development and implementation of a community assessment and outreach plan to facilitate active two-way exchange of information between the DOE and affected stakeholders pertaining to site investigation status and evolution of community concerns. As applicable, update CSM and DQOs to address PFAS-specific community concerns.
Overlapping regulatory responsibilities	The state and EPA have concurrent regulatory roles at many large sites. Multiparty agreements at these sites essentially serve to combine the regulatory authorities. At some sites, such as Hanford and Rocky Flats, the division is generally geographic with an overlay of regulatory authority. Assessment programs must comply with state and EPA requirements.

The following subsections further describe additional examples of risks for specific DOE site types:

- **Legacy Sites** and National Laboratories (CERCLA): Regulation of emerging contaminants, such as PFAS, may result in reopening a previously closed or designated inactive cleanup site. Reopening a site may require re-engaging stakeholders, including those that may be receptors, such as the case with drinking water and surface water body impacts. Additional information may need to be collected during the site investigation (e.g., SI or RI) to alleviate concerns. The environmental investigation sampling program should be adaptive to be able to integrate stakeholder concerns as they arise. Development of an outreach plan is recommended to have a formalized strategy to communicate and engage stakeholders (refer to **Section 9**).

- **Operations Facilities** (RCRA): Facilities operating under RCRA may have PFAS stored and potentially used on-site (e.g., PFAS-containing firefighting foams). This scenario can potentially result in new PFAS releases that can re-contaminate or newly pollute areas of the site. Adaptive site management considerations should include PFAS management to avoid redundancy in site sampling and cleanup (and associated environmental footprint; refer to **Section 8**).
- **State Programs:** DOE will implement the site investigation program in compliance with federal PFAS regulations and may also need to comply with regional and local state regulations and programs. These programs may be under development, such as PFAS screening levels, PFAS promulgated standards, or waste handling and product certification, and may require adaptive management considerations to be compliant with state programs.

10.1 Summary of Adaptive Management Guidance

The ITRC *Remediation Management of Complex Site Technical Guidance* (ITRC 2017) is a resource for learning about adaptive management. This approach is particularly useful at complex sites where remediation is difficult, the remediation potential is uncertain, and the remediation may require many years.

Site investigation tools, such as TRIAD, are available to implement a phased sampling program in a manner that utilizes financial, labor, and natural resources in a sustainable manner. The investigation program adaptive management considerations can also be flexible to collect data during key site investigation milestones that will be informative later in the project life cycle (e.g., performing the FS, pilot testing, and remedial design). This proactive adaptive management approach of considering future project phases and site use can help mitigate not having relevant data available to adequately measure performance metrics, integrate stakeholder values, and address public concerns.

Information collected as part of an adaptive investigation is often intended to improve efficiency (including cost) and sustainability of the investigation by expediting remedy decisions. However, there are few regulatory values available for PFAS, and some are non-actionable due to infeasibility of analyzing or cleaning up to low (or sub) ppt levels. As such, PFAS remedial options beyond the use of removal technologies (e.g., excavation for soils and pump and treat for groundwater) are currently limited, requiring additional advancement in the science and regulations before they can be considered with confidence. One approach for managing uncertainty around treatment technology performance and feasibility for PFAS is to use treatability or pilot studies at the remedy selection stage (e.g., FS for CERCLA).

Furthermore, DQOs should be developed that align site investigation activities and data collection with future project phases, including consideration of site reuse. Considering the sampling and analysis needs of future project phases can help minimize the environmental footprint and maximize the sustainable outcome associated with sampling activities integrated across the entire project life cycle. Adaptive management can also consider integration of climate vulnerability and evolution of site conditions over time to ensure adaptive capacity and resiliency of remediation systems. Resilient remediation informs on relative vulnerability of the site and receptors due to climate change impacts, such as sea level rise, storm surge, droughts, wildfires, and severe weather events. The site screening investigation step is an opportunity to collect site-specific sustainability and resiliency data to inform PFAS assessment approach and CSM development.

10.2 Contingency Planning (e.g., Off-site PFAS Impacts)

If sampling programs include off-site areas (i.e., located outside the boundaries of DOE-owned or DOE-managed land) and potential receptors, additional data may be required to understand potential impacts to stakeholders (e.g., owners of potable drinking water wells). Understanding these concerns early in investigation planning and revisiting during investigation implementation will inform DQOs and remedy performance metrics that may require specific data collection activities. The investigation sampling program should be adaptive to be able to integrate stakeholder concerns as they arise and collect relevant data. Addressing risk communication challenges cannot be achieved in a single effort, as project/site information is continuously collected and assessed, and the state of the science and regulations evolve. Adaptative management can be used as a complementary tool alongside risk communication planning to facilitate continuous consideration of site information, state of the science, and community understanding of risk. Development of an outreach plan is recommended to have a formalized strategy to communicate and engage stakeholders (refer to **Section 9**).

11.PFAS ASSESSMENT EVALUATION

11.1 Elevated Measurement Comparison

As discussed in **Section 2**, screening values are evolving rapidly for PFAS. Values are frequently revised, and new values are often added for additional analytes. Consultation with the regulators for a given site should happen early and often to ensure alignment on assessing analytical results in the context of these evolving guidance values. Screening levels/PALs[3] should be defined in the work control documents with appropriate stakeholder involvement/interaction. PALs may include RSLs, state-specific levels, or other relevant guidance. As of November 2022, the RSL tables include screening levels for six PFAS compounds in a variety of media. RSLs are updated approximately biannually, in May and November. The ITRC has compiled state level guidance, which is updated approximately monthly. Consistent with CERCLA and DoD guidance, when multiple PFAS are encountered at a site (as is expected at every site impacted with PFAS), the RSLs based upon an HQ of 0.1 should be used for screening purposes.

In general, all sample results should be screened against the selected PALs. In the event that one or more results exceed the analyte's PAL, additional interrogation of the data using statistical tools (such as the 95th upper confidence level), additional site investigation, emergency action, and/or risk assessment should be considered in consultation with the project regulator, as appropriate.

11.2 Assessment Outcomes

Upon completion of the PA/SI, sufficient data should have been collected to address the DQOs (**Section 3.2**) to allow for informed decision-making. The data should be sufficient to inform the need for additional investigation, emergency action, or no further action. Given the very low toxicity reference values driving the human health and ecological screening levels, many sites may have PFAS concentrations that exceed these initial screening levels (as outlined in **Section 2**). If additional investigation, including a screening level or baseline[4] environmental risk assessment component, is required, PFAS-specific considerations as part of this process are presented below. These considerations are evolving, and the below list is not exhaustive; rather, it serves as an overview of sources of uncertainty that may impact a PFAS risk assessment at a DOE facility.

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[3] PALs may vary based upon the project objectives and should be defined as part of the DQO process. PALs may be regulatory standards (e.g., MCLs), risk-based concentrations (RBCs), or technological limitations (EPA 2015a).

[4] A screening level risk assessment is not designed nor intended to provide definitive estimates of actual risk or to generate cleanup goals, and, in general, is not based on site-specific assumptions (EPA 2015b). It may, however, estimate the likelihood that a particular risk may exist, identify the need for additional data collection, or identify the need for a more detailed and refined baseline risk assessment.

11.3 Risk Assessment

If additional assessment is needed, the site may require additional investigation in the form of removal action (EE/CA) or an RI. Key components of these processes are human health and ecological risk assessments. Significant EPA guidance is available for conducting complete human health (e.g., EPA 1989, 1991b, 1991c, 1992a, 1992b, 1999b, 2001c, 2002b, 2002c, 2002d, 2004, 2009, 2011a, 2014) and ecological risk assessments (e.g., EPA 1992a, 1992b, 1993, 1997, 1998, 2002c, 2003). The risk assessment is an analysis of the potential adverse health effects to a potential receptor (current or future) identified in the project CSM caused by hazardous substance releases from a site in the absence of any actions to control or mitigate these releases (i.e., under an assumption of no action).

Environmental risk assessment comprises four main components: hazard identification, exposure assessment, toxicity assessment, and risk characterization. Hazard identification involves data collection and evaluation, as discussed elsewhere in this ESG. The exposure assessment considers populations of interest, and the pathways by which exposure may occur to assess daily chemical intakes arising from site exposures. Both hazard identification and the exposure assessment should be based upon and support the CSM (as discussed in **Section 3.5**). The toxicity assessment considers the toxicological basis for each chemical of interest (including exposure period of interest, non-cancer effects, and carcinogenic effects), and the target organs. The exposure assessment and toxicity assessments are then assessed together to compare daily intakes against the allowable daily intakes to identify a HQ for non-cancer hazards for each exposure pathway to each chemical, and relative risk owing to carcinogenic endpoints. HQs can be summed to provide an HI, which accounts for cumulative exposures arising from multiple exposure pathways and multiple chemicals. An HI greater than 1 indicates potential for concern arising from exposure to the chemical(s) of interest. Similarly, relative cancer risk can be assessed although limited information is available regarding PFAS carcinogenicity, as discussed below. It is acknowledged that the understanding of PFAS toxicity, exposure, and potential risk is evolving rapidly. The following provides an overview of the process and current state of the science related to PFAS risk assessment, but the site regulator and guidance documents referenced herein should be consulted during risk assessment development.

11.3.1 Human Health

Identify Receptors

Key to any risk assessment is the identification of populations of interest that may be exposed to site related contamination. Understanding the populations of interest allows for accurate selection of screening levels for chemicals of potential concern (COPC). Populations of interest may include, but are not limited to, residents, indoor workers, outdoor workers, construction workers, students, daycare children, recreators, and tribal members.

Characterize Exposure Pathways

Not all exposure pathways for human populations are likely to be of equal concern. A complete exposure pathway consists of the following four elements:

- Source and mechanism of release of chemicals to the environment
- Transport and fate mechanisms (as discussed in **Section 3.4**) for movement of chemicals to a point of human and/or ecological contact (exposure point receptor)
- Exposure point (the point of potential contact between the receptor and medium)
- Exposure route (e.g., inhalation, ingestion, and dermal contact)

If one or more of these elements is missing, the pathway is incomplete, and no exposure will occur.

Drinking water is often the primary source of exposure of PFAS to communities where drinking water is impacted. The general population, however, may receive the majority of PFAS exposure from diet, dust, personal care products, or other sources. Exposure can vary by receptor populations and PFAS analytes (De Silva 2021). Differing exposure route contributions have been reported in different types of occupational situations; for example, inhalation and dermal exposures may be significant in some manufacturing scenarios (Franko 2012). However, dermal contact with AFFF did not appear to be a significant exposure pathway to firefighters[5] (Rotander 2015).

As mentioned, exposure potentials may be variable and significant uncertainty remains regarding dermal and inhalation exposure potential. At the time of this ESG, there are no U.S.-based inhalation reference concentrations (RfCs) for any PFAS to quantify exposures arising from inhalation (Monnot 2022). The EPA RSL tables (EPA 2023c) treat most PFAS as semivolatile organic compounds and use the default dermal absorption fraction of 0.1 (EPA 2004). Some of the anions and short chain PFAS are considered to be volatile (EPA 2023c).

COPC Selection Process

A summary of the regulatory landscape was provided in **Section 2** of this document. As discussed in **Section 5**, target methods for PFAS can quantify up to 40 PFAS analytes. Analytical capabilities far outpace the toxicological understanding of PFAS, and hence, screening levels are only available for a subset of quantifiable analytes.

COPC selection involves identification of the site-specific COPCs that may pose undue risk to a receptor of interest. Typically, this is accomplished by screening the maximum observed concentration against the lowest risk-based PAL. As discussed below, toxicological information

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[5] It is well established that firefighters tend to have elevated blood levels of PFAS such as PFOS, PFHxS, and PFNA.

for PFAS is evolving. The most recent risk-based screening levels should be reviewed to identify any additional PFAS analytes and/or revised toxicity information.

Toxicity Assessment

Non-Cancer Health Effects:

There are significant uncertainties associated with assessing PFAS risk to receptor populations at an impacted site. Chief among them are the current limitations in toxicological data (ITRC 2022b). Of the many thousands of PFAS chemicals, RfDs[6] for non-cancer health hazards are only available for a small subset of PFAS compounds. At the time of this writing, the EPA RSL tables include RfDs for eight PFAS: PFOS, PFOA, PFNA, PFHxS, PFBS, PFBA, PFHxA, and GenX. It is anticipated that RSLs for additional PFAS will become available over time; specifically, the toxicity assessment for PFDA is underway (EPA 2021a).

There are also discrepancies regarding which health effect is the critical effect (e.g., which health outcome is the most sensitive to PFAS exposure). For non-cancer effects, EPA has developed draft RfDs for PFOS and PFOA based upon immune, developmental, cardiovascular, and hepatic outcomes (EPA 2023b). International guidance is variable, spanning several orders of magnitude based upon differences in the selected critical effects, including observed growth, development, or hepatic effects in animal studies (World Health Organization 2022). As of this writing, the RSL tables rely predominantly on toxicity values derived by ATSDR (2021), however EPA is assessing some PFAS through the IRIS (EPA 2021a).

Carcinogenicity:

EPA (2016a, 2016c, 2021d) has identified PFOA, PFOS, and GenX as having suggestive evidence of cancer effects in humans. The International Agency for Research on Cancer (IARC) has also classified PFOA as a Class 2B carcinogen (possibly carcinogenic to humans). The proposed NPDWR (EPA 2023b) classifies both PFOS and PFOA as carcinogens; however, as of this writing, the RSL tables only include a cancer slope factor for PFOA. Prior to the NPDWR (EPA 2023b), most U.S.-based agencies, except for California EPA's Office of Environmental Health Hazard Assessment (OEHHA 2021), selected non-cancer effects as the more sensitive endpoints in the development of health-based guidance values.

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[6] A reference dose, as defined by the EPA, is "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime."

Mixture Toxicity:[7]

Multiple PFAS compounds and non-PFAS contaminants may be detected within a given medium of interest. The risk assessment approach should be discussed with regulators to identify the best path forward to manage this complexity.

As of fall 2022, there is no national guidance for assessing health risks and hazards arising from PFAS as a class,[8] or accounting for potential mixture toxicity. By comparison, the Netherlands (Zeilmaker 2018) has proposed a relative potency factor (RPF) approach, with PFAS toxicities weighted in comparison to PFOA. By calculating the toxic equivalency of 18 PFAS compounds in relation to PFOA, for which toxicity information is available, risk estimates can be generated for more PFAS than assessing each analyte individually. The authors revised this approach in 2021 (Bil 2021) to include 22 PFAS analytes. As summarized in Bil (2021), the C9, C10, C11, and C12 PFCAs, along with PFOS (C8 PFSA) suggest greater potency than PFOA (as the reference chemical). Notably, PFNA appears to be the most potent PFAS analyte, but few international agencies have determined robust toxicological guidance for this chemical. Very long chain PFCAs (e.g., >C12) as well as short chain and replacement chemicals suggest much lower toxic potential than PFOA.

However, as discussed in Bil (2021), the RPF approach assumes additive effects of the chemicals of interest; in other words, the chemicals act on the same target organ. Liver toxicity, which has been observed consistently across PFAS broadly, was selected as the target organ for this derivation, although recent toxicological guidance elsewhere (e.g., EPA 2023b) has identified other endpoints (e.g., immunotoxicity, cardiovascular effects, and developmental toxicity) as equally or more sensitive to PFOS and PFOA, so it is unknown if this RPF approach would be applicable or appropriate for assessment of risk for non-hepatoxic effects.

The general scientific consensus is that additional information is needed to proceed with using an RPF approach for risk assessment (Rietjens 2022, Goodrum 2021, EFSA 2020), and the current recommendation per the ITRC (2022b) is to assume additivity of PFAS.

Bioaccumulation:

Certain PFAS compounds have the potential to accumulate in biological systems (including humans). In general, short-chain (<C8) PFAAs have been shown to accumulate in plants, while long chain PFAAs accumulate more readily in animals (ITRC 2022b). Conder (2020) provides bioconcentration factors (for aquatic plants, pelagic invertebrates, and fish from surface water), bioaccumulation factors (for benthic invertebrates from sediment, terrestrial invertebrates from

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[7] This section discusses PFAS mixtures. As discussed in **Section 3.4.2**, exposures to other, non-PFAS chemicals may also occur at a given site.

[8] The NPDWR released in March 2023 proposes regulating a mixture of four PFAS (PFBS, PFHxS, PFNA, and GenX) using a hazard index approach. The hazard index is equal to the sum of the individual hazard quotients, with the HBWCs used as denominators (refer to **Section 2.1.1** for more information).

soil, terrestrial plants from soil), and biomagnification factors (for fish from the diet) to support ecological risk assessment. For both human health and ecological risk assessment, however, measured empirical data is preferred for assessment of risk (e.g., collection of fish tissue vs. applying food web modelling) given inherent uncertainties in estimating uptake into biological systems (ITRC 2022b).

Uncertainty

Given how rapidly our understand of PFAS is changing, a robust uncertainty analysis should be included in the risk assessment. As discussed throughout this section, significant uncertainty may exist at all stages of the assessment, including data adequacy (e.g., expanding analytical suites or detection limits of historical data exceeding current screening levels), the exposure assessment (e.g., exposure pathways or parameters, exposure point concentrations, and bioavailability), the toxicity assessment (e.g., limited or no toxicity information for multiple analytes, or discrepancies between critical effects selected by different relevant agencies), and risk characterization (e.g., additive effects vs. synergistic or antagonistic effects). These uncertainties should be acknowledged, with the potential implications of these uncertainties on the risk assessment addressed.

11.3.2 Ecological

Identify Receptors

Identification of ecological receptors that may be exposed to PFAS contamination is also dependent upon the contaminated site media of interest. Most terrestrial and aquatic ecosystems support a variety of organisms that can be exposed to chemicals in the environment. It is not feasible to perform risk evaluations for all species potentially exposed. Such an effort would also be duplicative because of the similarity of exposure patterns among closely related species and those with similar feeding guilds. For these reasons, representative receptor groups are selected for evaluation. Selected receptors groups are intended to be representative of entire classes of organisms (i.e., functional groups).

Selected receptor groups, as well as supporting rationale, are discussed below. Receptor groups of interest may include, but are not limited to, fish, amphibians, invertebrates, plants, birds, and mammals.

Consideration should be given to state or federally protected species that may use the site. Receptor groups encompassing protected species should be selected in ecological risk assessments.

Potential Exposure Pathways of Concern

Aquatic Receptors:

The primary exposure pathway of concern for fish, aquatic plants, water-column-dwelling invertebrates, and early-life-stage amphibians is direct contact with surface water that has been impacted by site-related releases (which may include groundwater discharge). Direct contact with sediment is also an exposure pathway of concern for sediment-dwelling invertebrates.

Another pathway of potential concern to fish and other aquatic predators is ingestion of contaminants that have been taken up into aquatic prey such as periphyton, smaller fish, and emerging aquatic insects. The ingestion of aquatic prey can also result in incidental ingestion of sediment while feeding. Ingestion of aquatic food web items by fish is a pathway of potential concern, but quantitative evaluation of oral exposures is limited by a lack of oral toxicity values for this class of aquatic receptors.

Likewise, some aquatic receptors (mainly amphibians) may be exposed by dermal contact with contaminated sediments, but this pathway is suspected to be relatively minor compared to oral or direct contact with water exposures. Methods are not available to support reliable quantitative evaluation of the dermal contact pathway for sediment for either fish or amphibians.

In addition to ingestion of aquatic food, aquatic wildlife may also be exposed to chemicals via ingestion of surface water and from incidental ingestion of sediment[9] while feeding.

Terrestrial Receptors:

Direct contact with contaminated soil is a primary exposure pathway for terrestrial receptors such as plants and soil invertebrates. Most soil exposures are likely to occur within the top 25 to 30 centimeters of the ground surface (10 to 12 inches below ground surface [bgs]) (EPA 2015b); however, some larger plants, such as bushes and trees, could have roots that extend into deeper subsurface soils.

Exposure in terrestrial plants may also occur because of deposition of dust on foliar (leaf) surfaces; however, this pathway is believed to be small compared to root exposures in surface soils. Depending on the depth to groundwater, it is possible that plant roots could take up shallow groundwater via root exposure. Contact with shallow groundwater is assumed to occur within the top 10 feet bgs.

Terrestrial wildlife are primarily exposed to chemicals in the environment through the ingestion pathway. Wildlife can be exposed via ingestion of terrestrial food items such as plants, small mammals, reptiles, and soil invertebrates; ingestion of surface water as drinking water; and

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[9] Exposure may also occur via ingestion of other, non-food items (such as microplastics), however such exposure remains difficult to quantify at present.

incidental ingestion of soil while feeding. For most wildlife, this contact occurs within the top 6 inches of soil. For some wildlife, such as burrowing mammals, burrowing owls, and reptiles, exposures to chemicals can occur deeper in soil (up to 10 feet bgs).

Depending on the site climate, terrestrial wildlife may be attracted to daylighting seeps/springs or other site-affiliated surface water as a drinking water source when moisture cannot be obtained exclusively from prey or food items.

Direct contact (i.e., dermal exposure) of wildlife to soils may occur in some cases, and inhalation exposure to airborne dusts is possible for all birds and mammals, but these exposures are usually considered to be minor in comparison to exposures from ingestion (EPA 2005b). However, it is possible that burrowing animals could be exposed to relatively high concentrations of volatile organic compounds (VOCs) via inhalation if concentrations accumulate inside their burrows. While PFAAs are not significantly volatile, depending on the PFAS profile in site soils (particularly in source areas), exposures occurring via soil gas to volatile precursor compounds cannot be definitively ruled out.

Ecological Screening Values

Significant limitations exist for assessment of risk to ecological receptors arising from PFAS exposures. As of October 2022, the following documents provide available ecotoxicological data available for PFAS, and provide risk-based screening levels (RBSLs)/ecological screening values (ESVs) for a selection of PFAS compounds:

- EPA (2022b, 2022c) published draft national recommended aquatic life criteria for PFOS and PFOA for acute and chronic water column values for freshwater and marine environments, along with tissue criteria for fish and benthic invertebrates.
- Argonne National Laboratory (2021) developed ecological screening values for eight PFAS for surface water and soil. Ongoing efforts using artificial intelligence (AI) to predict toxicity for 8163 PFAS analytes are underway.
- Divine’s (2020) SERDP Project ER18-1653 assessed risk to five general groups of threatened and endangered ecological receptors and developed RBSLs protective of aquatic life, terrestrial plants, soil invertebrates, and terrestrial and aquatic wildlife.
- Conder’s (2020) SERDP Project ER18-1614 provided guidance to support quantitative ecological risk assessment, providing bioconcentration factors (for aquatic plants, pelagic invertebrates, and fish from surface water), bioaccumulation factors (for benthic invertebrates from sediment, terrestrial invertebrates from soil, terrestrial plants from soil), and biomagnification factors (for fish from the diet), as well as toxicity reference values (TRVs) for mammals and birds.
- A summary of available screening levels available for Argonne (2021), Divine (2020), and Conder (2020) is provided in **Appendix C**.

- Some states (including Michigan, Minnesota, and California) and international agencies (Canada, Australia and New Zealand, and the European Union) have derived additional ecological threshold values (ITRC 2022b).

Ecological Assessment

The challenges discussed above for assessing human health hazards are compounded for ecological receptors, given uncertainties in factors such as ecological receptor viability (e.g., variable sensitivity of different organisms to PFAS), mixture toxicity, and understanding of exposure and bioaccumulation potential. Significant discussion regarding these limitations is provided in ITRC (2022b). Regulators should be engaged prior to pursuing an ecological risk assessment to agree on the best path forward.

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All DOE sites should refer to the EPA PFAS website (https://www.epa.gov/pfas) for current information on CERCLA or RCRA regulatory status.

13. APPENDICES

- Appendix A. Sampling Guidance Compendium
- Appendix B. Best Practices
- Appendix C. Available Ecological Screening Levels
- Appendix D. Example Outreach Strategy Table

Appendix A. Sampling Guidance Compendium

PFAS General Information

1. EPA Current Understanding of PFAS
2. DoD PFAS Factsheet Search by State
3. ITRC PFAS Page (Fact sheets, Naming Convention, Fate and Transport, etc.)
4. DoD PFAS Page
5. EPA TSCA National PFAS Testing Strategy to Identify PFAS for Testing
6. EPA Guidance on Systematic Planning Using the Data Quality Objectives Process (Non-PFAS Specific)
7. DoD Army Guidance for Addressing Releases of PFAS

PFAS Chemistry Resources

1. CompTox Chemicals Dashboard
2. ChemView

PFAS Sampling and Analysis Resources

1. EPA Field Equipment Cleaning and Decontamination (Non-PFAS Specific)
2. EPA Compendium of Superfund Field Operations Methods (Non-PFAS Specific)
3. EPA Pore Water Sampling (Non-PFAS Specific)
4. EPA Potable Water Supply Sampling (Non-PFAS Specific)
5. DoD PFAS SI Sampling and Analysis Plan Example
6. DoD Sampling and Analysis for PFOA and PFOS in AFFF Report
7. DoD PFAS Sampling of Drinking Water Systems Requirements (Policy Memo 2020)
8. DoD PFAS Sampling for Installations with Non-DoD Drinking Water Systems (Policy Memo 2020)
9. DoD AFFF Usage and Spill Reporting (Policy Memo 2020)
10. ITRC Sampling Precautions for PFAS
11. ITRC PFAS Site Characterization Considerations and Media-Specific Occurrences
12. ITRC Data Evaluation Discussion
13. MA State Guidance on Sampling and Analysis for PFAS at Regulated Disposal Sites
14. NH State Lab Testing Guidelines for PFAS for Private and Public Drinking Water Supplies
15. MI State PFAS Sampling Guidance’s (Biosolids, Leachate, Groundwater, etc.)

PFAS Quality Control and Quality Assurance Resources

1. EPA Guidance for Quality Assurance Project Plans (Non-PFAS Specific)
2. DoD Environmental Quality Systems Instructions (Non-PFAS Specific)
3. California Water Board Quality Control/Quality Assurance Program (Non-PFAS Specific)

4. Washington State Quality Assurance Plan for Statewide PFAS Survey in Rivers/Lakes Example

PFAS Databases

1. EPA UCMR 3 (2013 - 2015) Occurrence Data
2. EPA National PFAS Datasets
3. California Water Board GeoTracker PFAS Map
4. DoD Section 345 Data Reporting for Off-Base Potable Water by State

PFAS Regulatory Resources and Future Research Resources

1. EPA PFAS Research
2. SERDP/ESTCP PFAS Research Projects Summary Database
3. ITRC PFAS Water and Soil Values Table Excel File (August 2022)

PFAS Risk Assessment Resources

1. EPA Steps to Reduce PFAS Risk
2. CDCs PFAS Info from Agency for Toxic Substances and Disease Registry (ATSDR)
3. EPA PFAS Resources in Health and Environmental Research Online (HERO)
4. EPA Human Health Toxicity Assessments for GenX Chemicals
5. EPA Human Health Toxicity Assessment for PFBS
6. EPA Toxics Release Inventory (TRI) Program
7. EPA PFAS Collection of References in HERO
8. EPA Superfund Risk Assessment: Human Health Topics
9. ITRC Human Toxicity Assessment

PFAS Treatment Resources

1. EPA Drinking Water Treatability Database
2. EPA Contaminated Site Clean-Up Information
3. DoD PFAS Task Force Reports and Briefings Repository

PFAS Public Outreach Resources

1. DoD PFAS Public Outreach 2022 Questions and Answers
2. DoD PFAS Public Outreach Page
3. DoD Drinking Water Well Sampling Property Owner Questionnaire
4. DoD Example Letter to Request PFAS Sampling in Drinking Water Wells
5. DoD Drinking Water Sampling Frequently Asked Questions
6. MI State Private Residential Well PFAS Sampling Guidance for Residents

Appendix B. PFAS Sampling Best Practices

Rocky Flats

The Rocky Flats Plant near Denver, Colorado, produced plutonium triggers and other nuclear weapons components from 1952 to 1994. Numerous machining and assembly facilities, research and development laboratories, material recovery facilities, a fire department, two landfills, and additional support facilities were present. Rocky Flats was remediated, the land was restored to a near-natural appearance, and it was closed in 2005 under CERCLA and RCRA/Colorado Hazardous Waste Act regulations. Residual contamination is present, and in accordance with a post-closure agreement among the DOE, the Colorado Department of Public Health and Environment (CDPHE), and the EPA, DOE continues to manage and monitor the central 1,300 acres where the research and manufacturing facilities were previously located. The surrounding undeveloped and generally unimpacted land was transferred from DOE to the U.S. Fish and Wildlife Service to become a wildlife refuge. The DOE-retained land is now referred to as the Rocky Flats Site (i.e., the Site).

In 2018, CDPHE formally requested that DOE conduct sampling to investigate for the presence of PFOA and PFOS in groundwater and surface water. Prior to initiating sample activities, DOE conducted a records search to determine if PFAS-containing substances were historically used at Rocky Flats, potentially released to the environment, and/or disposed of as waste. The positive identification of historical use, releases, and waste disposition was used to establish the need and basis for the requested PFAS sampling effort. The records search was initiated by developing an extensive list of search terms, including anticipated misspellings (for example, “flouro-“ instead of “fluoro”). The CERCLA Administrative Record as well as Department of Labor Exposure Records and waste records from the Waste Isolation Pilot Plant (WIPP) (which houses the Rocky Flats waste records) were all searched. These searches preceded the development of the DOE *Guide for Investigating Historical and Current Uses of PFAS*, which contains a more comprehensive list of keywords and other information. In addition, interviews with former workers were conducted, focusing primarily on fire department personnel. A document found on the internet entitled *Estimated Quantities of Aqueous Film Forming Foam (AFFF) in the United States*[10] refers to “a reported estimate of 90 gallons [of AFFF] carried by the on-base department at Rocky Flats, Colorado” (p.8). Site records and interviews confirmed the general validity of this report (i.e., that AFFF was historically present during Rocky Flats operations). The information indicated that AFFF was used in the fire training area, and possibly to extinguish fires at the Rocky Flats Plant. Whether there had been other uses of PFAS at Rocky Flats was not confirmed through this search.

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[10] Darwin, R. L. (Hughes Associates). 2004. Estimated Quantities of Aqueous Film Forming Foam (AFFF) in the U.S. Prepared for the Fire Fighting Foam Coalition. Baltimore, MD.

Following the records search and agreement to proceed with the PFAS sampling efforts, DOE and CDPHE met to outline sampling goals and locations. The result, with which EPA concurred, was to focus sampling efforts at three monitoring wells (all of which present relatively higher concentrations of traditional contaminants [e.g., chlorinated solvents] and a possible association to PFAS or AFFF use), former landfills, the influent of a groundwater treatment system, and surface water points of compliance. A description of each sampling location is provided below:

- One monitoring well in the former fire training area and next to a former oil burn pit.
- One monitoring well that is adjacent to what was a metallurgy and metal plating facility.
- One monitoring well next to another former oil burn pit.
- A seep at the base of one former landfill, and leachate entering a passive treatment system at a second former landfill.
- Influent to one of the groundwater treatment systems for VOCs.
- Two surface water points of compliance, where the associated streams exit the DOE-retained land.

A Sampling and Analysis Plan (SAP) was developed to instruct the sampling. Based on guidance from various states, technical organizations, and technical documentation, the SAP incorporated very conservative measures to minimize the potential for cross contamination resulting from PFAS-containing equipment or through handling. These measures included the following:

- Replacing sampling equipment that incorporated PTFE/Teflon or other PFAS-containing materials.
- Purchasing 100% cotton coveralls and washing them at least six times without fabric softener before use. Sampling personnel did not don these coveralls until they had exited the vehicle at a sampling location (in case vehicle upholstery was treated with stain- or water-resistant PFAS) and then took them off again before getting back into the vehicle to travel to the next location.
- Washing hands with PFAS-free soap and donning multiple pairs of nitrile gloves when preparing to sample at each location.
- Decontaminating equipment (such as the water level indicator) immediately after completing activities at a location and rinsing it again before starting at the next location. Water used for decontamination was obtained from the laboratory and certified PFAS-free, together with PFAS-free laboratory detergent.
- Using dedicated, PFAS-free equipment where appropriate.
- Collecting surface water samples upstream of constructed flumes and installed monitoring equipment, in case those items might contain PFAS. In addition, staff wore disposable rubber booties for surface water and seep sampling.

Additional preventative measures were also identified, as described in the SAP.[11] Following approval of the SAP, sampling activities commenced in 2019, with sampling conducted in the relatively wetter second calendar quarter and drier fourth calendar quarter. Each sample was analyzed by a DOE-accredited analytical laboratory using modified EPA Method 537.1, and the laboratory was requested to report only PFOA and PFOS results because the primary CDPHE interest was on those compounds. Every sample location during the 2019 sampling program reported detections of PFOA, PFOS, or both. The monitoring well in the former fire training area reported the highest concentrations, and the influent to the treatment system for landfill leachate reported the next highest concentrations. In both locations, the sum of PFOA and PFOS exceeded the 2016 EPA Hazard Advisory level of 70 nanograms per liter (ng/L) total.

Following the evaluation of the 2019 data, DOE met with CDPHE and developed a more extensive program in which each of the previously sampled locations would be sampled quarterly for two years. In addition, three additional monitoring wells in the vicinity of the fire training area and the effluent from the landfill leachate treatment system were added to the sampling program. The analytical suite was expanded to include 28 PFAS, reflecting a policy issued by the Colorado Water Quality Control Commission.[12] A new SAP was developed to instruct this effort,[13] which included the same conservatism as the previous SAP. The modified sampling program began in the third calendar quarter of 2021. As summarized in the DOE *PFAS Assessment Report* issued in late 2022, PFOS, PFOA, and other PFAS have been detected; at least one PFAS was detected at every sample location. The modified sampling program, which commenced in 2021, is scheduled to be conclude at the end of the second calendar quarter of 2023.

Throughout these activities, a few issues have stood out:

- To reduce the potential for cross contamination from typical materials, supplies, and equipment, sampling locations and associated dedicated and reusable equipment had to be thoroughly reviewed before scheduling sampling. If a PFAS-containing (such as Teflon) material was present, the item was replaced with a non-PFAS alternative. PFAS-free bladder pumps, tubing, water level sounders, and other equipment as well as suitable PPE and other field supplies were purchased, and in the case of dedicated equipment were installed well in advance of sampling to allow them to acclimate to conditions at the corresponding sampling location. While this process added expense, the cost of false positives (detections of PFAS due solely to cross contamination) would

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[11] DOE (United States Department of Energy). 2019. Sampling Plan for PFOA/PFOS at the Rocky Flats Site, Colorado. LMS/RFS/S22080, Office of Legacy Management. April.

[12] CDPHE (Colorado Department of Public Health and Environment). 2020. Letter "RE: PFOA/PFOS report approval with modifications and future PFAS sampling requirements" issued via email to Scott Surovchak, DOE Site Manager for the Rocky Flats Site at that time. 28 September.

[13] DOE (United States Department of Energy). 2021. Sampling Plan for PFAS at the Rocky Flats Site, Colorado, LMS/RFS/S33207-0.0, Office of Legacy Management. July.

likely be greater. Another alternative would be to collect equipment blanks to test suspect items, but that would have been more involved and time consuming; this option was simpler.

- Much more time, advance preparation, and personnel are needed to effectively and efficiently complete sampling for PFAS. Whereas a normal sampling event at a well requires relatively little advance preparation and can be completed by one person in less than an hour, the same activity focused on PFAS requires much more preparation, three to four individuals, and more time in the field. Due to the sample handling, documentation, and field parameter measurements required, even collecting a simple grab sample at a surface water location requires no fewer than two individuals.
- Immediate review of the analytical results is necessary to confirm the data are of the expected quality. In one case, all samples were run at a dilution, which resulted in detection limits at least three orders of magnitude too high. The laboratory was contacted and asked to reanalyze. Had the results not been immediately inspected, reanalysis may no longer have been feasible.
- Scheduling PFAS sampling and other required sampling requires extra attention to ensure minimal interference between sampling programs. While the regulatory-required routine sampling is a higher priority, PFAS sampling is performed first to help reduce the potential for cross contamination.

The Rocky Flats Site CERCLA Five Year Review (FYR) Report was signed by the EPA in August 2022. While prior FYR Reports had determined the Site to be protective, in this instance the determination was protectiveness deferred. The reason for this is the documented presence of PFAS and uncertainties regarding PFAS distribution and risk to possible receptors. A FYR Amendment is due in 2026 that is to include human health risk evaluation and screening-level ecological risk assessment for PFAS. DOE is in the process of developing the scope of this effort, which will require additional PFAS sampling and is likely to include nonaqueous media.

Brookhaven National Laboratory

In March 2017, Suffolk County Department of Health tested water samples from Brookhaven National Laboratory (BNL)’s potable water supply wells for six PFAS, including PFOA and PFOS. PFAS were identified in three out of five active water supply wells. The presence of PFAS was confirmed by analyzing multiple samples between 2017 and 2019. Although the combined PFOS and PFOA concentrations in the supply wells are typically less than the 70 ng/L HAL, individual PFOS concentrations in three of the wells routinely exceed the 10 ng/L state drinking water standard. In 2018, routine PFAS testing was added to BNL’s potable water monitoring program and samples are now tested for PFAS quarterly. As of 2022, granular activated carbon filters were put back into service on three of the water supply wells.

Groundwater Characterization

In 2018 and 2019, approximately 600 groundwater water samples were tested for 21 PFAS compounds. Most of the samples were collected from temporary monitoring wells installed to characterize PFAS concentrations in supply well source water contributing areas and at known AFFF release areas. Additional samples were collected from existing groundwater treatment systems and extraction wells, and from permanent monitoring wells located in landfill areas, at BNL's wastewater treatment plant and along the BNL site boundary. Samples of the wastewater treatment plant's effluent were also tested for PFAS.

Foam Use Areas

Based upon review of available records and interviews with current long-term firefighters and retirees, eight AFFF release locations were identified and investigated). Most of the AFFF releases were the result of firefighter training (from 1966-2008) and fire suppression system testing and maintenance (from 1970-1980s). PFAS were detected in the groundwater at all eight foam use areas. PFAS were also detected in the groundwater at BNL's wastewater treatment plant, which indicates that AFFF had been released to the sanitary system. The highest PFOS/PFOA concentrations were found in groundwater at the former and current firehouse facilities where routine training with AFFF had taken place. At the former and current firehouse facilities, the maximum combined concentrations of PFOS/PFOA in groundwater were 5,371 ng/L and 12,440 ng/L, respectively. High levels (>1,000 ng/L) of several other PFAS compounds were also detected.

Groundwater Remediation at Source Areas

Additional characterization work is required to determine PFAS distribution in the groundwater downgradient of the source areas. BNL is currently characterizing the extent of the high level PFAS plumes downgradient of the former and current firehouse facilities. These data will be used to design groundwater treatment systems needed to remediate the plumes.

Two groundwater treatment systems utilizing granular activated carbon have been installed to treat three source areas. As of February 2023, startup testing is underway. PFAS analysis received to date has confirmed that treatment system is effectively removing PFAS.

Soil Remediation at Source Areas

PFAS contaminated soils must be controlled or remediated for the planned groundwater remediation systems to be effective. Monitoring results at BNL have demonstrated that even one-time AFFF releases that occurred nearly 50 years ago continue to impact groundwater quality. Because these chemicals do not break down and persist in soil for long periods of time, the distribution of PFAS in soil needs to be characterized from ground surface to the water table.

At BNL, the depth to groundwater in the source areas range from about 10 to 50 feet. There are currently no EPA approved analytical methods for PFAS in soil.

Challenges

Sampling: Sampling protocols for PFAS are evolving. Current protocols recommend eliminating all sources of PFAS from the sampling location to prevent cross-contamination, which includes eliminating Teflon®, low density polyethylene, waterproof rain gear/boots/jackets, waterproof field books, insecticides, sunscreen, etc. Significant attention should be paid to the sampling equipment/ apparatus and personal protective equipment because of the ubiquitous nature of PFAS. BNL has dedicated bladder sampling pumps in all routinely monitored wells. The pumps and discharge tubing contain Teflon®. While Teflon®- free pumps and tubing are available, replacing the existing equipment would result in a significant cost impact to the monitoring program. Furthermore, because many of BNL's monitoring wells are used to track VOC contamination, care must be taken to ensure that the VOCs would not preferentially adsorb onto the materials in the replacement pumps and discharge lines. Teflon® is also commonly used in groundwater treatment system piping systems, where it is used in sample valves and as sealing tape at piping connections. BNL is currently evaluating whether the existing equipment is suitable for continued use and acceptable to the regulators.

Characterizing Extent of PFAS in Groundwater. Characterizing the extent of PFAS contamination at BNL will be challenging due to on-site water pumpage and recharge operations, which have changed over time and have impacted contaminant migration pathways and rates.

Los Alamos Groundwater:

Sampling for PFAS in groundwater at LANL was first conducted in the fall of 2019 at all 195 monitoring locations. The SAP consisted of the three PFAS compounds listed in the New Mexico Water Quality Control Commissions list of toxic pollutants. Specifically, these three compounds are perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), and perfluorooctane sulfate (PFOS). Additionally, historical uses and potential releases and site histories were reviewed to help understand where PFAS might be expected.

Because of the potential for cross-contamination when sampling for these compounds, a task group consisting of the New Mexico Environment Department, N3B, and DOE personnel was established before sampling commenced to determine best sampling practices for collecting these substances. A SOP developed by the California State Water Boards and referenced in the N3B Groundwater Sampling SOP N3B-SOP-ER-3003, Revision 1, established PFAS sampling protocols and continues to be utilized by sampling personnel when collecting PFAS samples. Additionally, all sampling personnel completed a hands-on training course conducted by Tetra Tech to ensure compliance and adherence to this rigorous sampling protocol.

Sampling for PFAS compounds at all monitoring locations was completed in late summer of 2021. Additional sampling at locations with detects for one or more of the compounds listed above continues. As a result of following the sampling practices discussed, of the 231 QA/QC samples collected to date (10 percent of total PFAS samples), less than eight percent have had detected PFAS compounds.

Appendix C. Available Ecological Screening Levels

PFAS Analyte	Argonne (2021)	Divine (2020)	Conder (2020)
Surface Water Screening Levels protective of Aquatic Life			
PFDoA		X	
PFUnA		X	
PFDA	X	X	
PFNA	X	X	
PFOA	X	X	X
PFHpA		X	
PFHxA	X	X	
PFPeA		X	
PFBA	X	X	
PFPrA		X	
PFOS	X	X	X
PFHxS	X		
PFBS	X	X	
10:2 FTCA		X	
10:2 FTuCA		X	
8:2 FTCA		X	
8:2 FTuCA		X	
7:3 Acid		X	
6:2 Cl-PFESA		X	
6:2 FTCA		X	
6:2 FTuCA		X	
6:2 FTAB		X	
5H 4:1 FTOH		X	
FC807		X	
Soil Screening Levels for Terrestrial Plants			
PFDA	X	X	
PFNA	X	X	
PFOA	X	X	X
PFHxA	X		
PFBA	X	X	
PFOS	X	X	X
PFHxS	X		
PFBS	X		
5H 4:1 FTOH		X	
Soil Screening Levels Protective of Invertebrates			
PFDA	X		
PFNA	X	X	

PFAS Analyte	**Argonne (2021)**	**Divine (2020)**	**Conder (2020)**
PFOA	X	X	X
PFHpA		X	
PFHxA	X		
PFBA	X		
PFOS	X	X	X
PFHxS	X	X	
PFBS	X	X	
Surface Water RBSLs protective of Aquatic Wildlife			
PFTeDA			*
PFDoA			*
PFUnDA			*
PFDA	X		* †
PFNA	X	X	*
PFOA	X	X	* †
PFHxA	X	X	*
PFBA	X	X	*
PFOS	X	X	* †
PFHxS	X		*
PFBS	X	X	* †
Sediment RBSLs protective of Aquatic Wildlife			
PFTeDA			*
PFDoA			*
PFUnDA			*
PFDA			* †
PFNA		X	*
PFOA		X	* †
PFHxA		X	*
PFBA		X	*
PFOS		X	* †
PFHxS			*
PFBS		X	* †
Soil RBSLs protective of Terrestrial Wildlife			
PFTeDA			*
PFDoA			*
PFUnDA			*
PFDA	X		* †
PFNA	X	X	*
PFOA	X	X	* †
PFHxA	X	X	*
PFBA	X	X	*
PFOS	X	X	* †

PFAS Analyte	**Argonne (2021)**	**Divine (2020)**	**Conder (2020)**
PFHxS	X		*
PFBS	X	X	* †
Surface Water RBSLs Protective of Terrestrial Wildlife			
PFTeDA			*
PFDoA			*
PFUnDA			*
PFDA	X		* †
PFNA	X	X	*
PFOA	X	X	* †
PFHxA	X	X	*
PFBA	X	X	*
PFOS	X	X	* †
PFHxS	X		*
PFBS	X	X	* †

X - indicates ecological screening level available in the report

* - indicates toxicity reference value available for mammals

† - indicates toxicity reference value available for birds

Appendix D. Example Outreach Strategy Table

Activity	Description (key messages and communication methods)	Audience	Time frame	Responsibility	Performance Measure
Engagement trigger: Off-site sampling on private property					
Letter notification	Notify property owners and tenants of the planned sampling activities, reason for sampling, and timeline for completing the sampling activities. Notification should also include information on how the results will be shared with property owners and tenants once sampling is completed.	Property owners and tenants	One month in advance of sampling activities	Project Manager	Letter notification submitted to property owners and tenants one month in advance of sampling activities. Scheduled sampling with property owner/tenant two weeks prior to site investigation mobilization date.
Engagement trigger: Reopening previously closed or inactive site					
Public workshop	Provide forum for discussing site history and rationale for re-initiating site investigation. Handouts, including a fact sheet and frequently asked questions (FAQs), and posters with site status information, regulatory framework, timeline, and next steps	Community members, adjacent property owners or occupants	Send advertisement of workshop at least two-weeks before event Hold the workshop at least two-weeks before investigation activities begin	Communications Specialist	Project team initiates workshop planning three months before site investigation activities resume. Assess community demographics and attendees to determine if a representative group of the community was engaged. For those not participating, determine an alternate engagement method.