



10 Site Characterization

The intent of this section is not to present general site characterization principles, but to highlight unique considerations for this family of emerging contaminant. It is assumed that site characterization will follow all applicable state and federal (CERCLA or RCRA) guidelines. The general principles of site characterization are similar for PFAS as for any contaminant, in that the physical setting, release specifics, proximity to receptors, and fate and transport characteristics will determine the sampling locations and requirements. Because of the toxicity, persistence, mobility, ubiquity, the large number of compounds in this family of chemicals, the variability and uncertainty of specific compounds and their criteria being regulated, and the emerging nature of PFAS, it is necessary to consider specific concerns in PFAS site characterization efforts.

Section Number	Topic
10.1	Site Characterization Issues Relevant to PFAS
10.2	Initial Steps
10.3	Site Investigation
10.4	Data Analysis and Interpretation
10.5	Source Identification

Exposure to PFAS can occur through a variety of transport pathways involving all environmental media, as is described in [Section 5](#). Because ingestion of water is deemed a major route of exposure in humans, current regulatory concerns are centered on this pathway. In turn, this focus has led to an increased emphasis on investigation of the connection between drinking water sources and groundwater, including direct use of groundwater as drinking water and connections between surface water and groundwater. Because of this regulatory and investigatory focus, this section concentrates on the characterization of groundwater plumes. Although groundwater is the most common medium sampled in PFAS investigations, site characterization may require data from soil, sediment, surface water, stormwater, air, biota, or other media depending upon the nature, duration, and time of the release.

The guidelines below include general considerations for the most common types of PFAS sites.

10.1 Site Characterization Issues Relevant to PFAS

Historical investigations may have missed the potential for PFAS contamination at a site because, until recently, these chemicals were not regulated, were not considered a health or environmental concern, or PFAS sampling and analytical procedures may not have been available. As a result, PFAS plumes had years to develop and migrate without detection or characterization. Comparing a site timeline (for example, processes, layout, chemical use, and release history, and fire training and/or firefighting events when AFFF was used) with the timeline of PFAS development and use, and existing drinking water data (for example, UCMR3) can be helpful in evaluating the types and potential occurrences of PFAS releases. Once a potential source has been identified, a site investigation would step out from the source to characterize the nature and distribution of the release. However, if a PFAS site is like one of the many without an identified source ([ATSDR 2018e](#)), an understanding of the site timeline or a general understanding of potential PFAS use may not be available. For sites without a known source release, the investigation approach starts with a review of available site information.

The following are some important considerations that are specific to PFAS sites.

10.1.1 Evolving Science and Regulations

State of the science: Understanding of many aspects of PFAS, such as toxicology and behavior in the environment, is changing rapidly. This may require reevaluation of earlier assumptions and conclusions throughout the site characterization process.

Analytical methodologies: Analytical methodologies continue to be developed and improved. Specific attention must be paid to a wide variety of factors, such as analytical methods, detection/reporting limits, and parameter lists that are continuing to expand. See [Section 11.2](#), Analytical Methods/Techniques, for more details.

Sampling methodologies: Questions exist regarding cross-contamination potential due to the presence of PFAS in consumer products; many regulatory agencies require a precautionary approach to sampling prohibiting the use of materials that may be treated with PFAS. See [Section 11.1](#), Sampling, for more details.

Regulatory environment: The regulatory environment remains in flux, with changing regulatory limits, sampling procedures, and compounds of interest. Investigators must remain vigilant to identify impacts to the site characterization. See [Section 8](#), Basis of Regulations, for more details.

10.1.2 Source, Fate, and Transport Properties

Sources: PFAS sources are discussed in [Section 2.6](#), PFAS Releases to the Environment. There are also “secondary sources,” such as PFAS concentrating into one portion of a plume (for example, groundwater into surface water) that then acts as a source to further groundwater contamination.

Pathways: PFAS may be present or migrate via pathways that are not often encountered with other constituents. For example, PFAS may be present in groundwater at a site via air deposition and no direct on-site release.

Complex transitions between media: The behavior of PFAS compounds in the environment may deviate greatly from typical contaminants. Transitions between media may be complex because of specific characteristics of these compounds. For example, PFAS compounds may disperse more upon reaching the water table than is typical for most other compounds, or a groundwater plume discharging into a surface water body may continue into groundwater elsewhere, with contamination in the surface water acting as a secondary source. See [Sections 5](#) and [6](#) for additional detail.

Partitioning: Binding of PFAS to organic carbon is not as strong as traditional hydrophobic compounds (for example, PCBs, PAHs). So K_{oc} alone may be a poor predictor of binding of PFAS to organic carbon ([Section 4.2.9](#)). Because various factors can affect sorption of PFAS to organic carbon, published K_{oc} values for PFAS cover a very broad range. To properly understand the context of PFAS analytical results, it is often important to collect additional parameters, such as total organic carbon (TOC) and pH, and consider the partitioning behavior of specific compounds.

10.1.3 Other Considerations

Historical view: Historical investigations may not have assessed PFAS contamination because it was not regulated, not a potential contaminant of concern, or analytical methods were unavailable at the time. Plumes may be extensive, having years or decades to develop before being discovered or addressed.

Balancing priorities: Because drinking water is a major pathway of exposure for PFAS and established plumes may have spread to downgradient areas, priority might be given to managing drinking-water exposure pathways over site characterization.

Monitoring-point construction: Investigators must be mindful of ways that monitoring-point construction may influence sampling results. For example, historical wells might have employed fluoropolymer tape ([Section 2.6.1.8](#)), or have screened intervals that make data interpretation difficult (owing to the uneven distribution of PFAS throughout a water column).

Widespread use: Because use of PFAS-containing products is widespread, there may be multiple sources in a given area that may act as additional or alternative sources of PFAS at a site. In addition, PFAS is often detected in low levels in samples from locations without an obvious source; there may be a need to evaluate

Secondary Sources

Sources created through movement of contaminated media into an area that was previously uncontaminated, (for example, contaminated water from irrigation wells or reuse and application of biosolids), or an area where physical or chemical processes have concentrated PFAS, resulting in an additional source (for example, multi-media interfaces; see [Sections 5](#) and [6](#)).

Site-Specific Anthropogenic Background

Concentrations of PFAS present in environmental media at the site that are not the result of or influenced by site activities or releases.

site-specific anthropogenic background to determine contributions in groundwater or soils that are not due to an on-site release. See, for example, [Strynar et al. \(2012\)](#).

Compound suite: Selection of a broad suite of compounds may prove useful for applications such as fingerprinting (if multiple sources are suspected) or understanding potential effects of precursor degradation ([Section 10.5](#)). Note that with currently available analytical methods, even a broad compound suite will not detect all PFAS.

Geologic heterogeneity: Because of the low delineation limits and mobile nature of certain PFAS, extra emphasis should be placed on understanding the effects of hydrogeologic heterogeneity on the groundwater plume.

10.2 Initial Steps

A comprehensive site preliminary assessment commonly starts with developing an understanding of potential PFAS uses in the area, history of the site operations that potentially used the chemicals, air deposition patterns where PFAS may have been produced or processed (for example, manufacturer with PFAS emissions), and the regional geologic and hydrologic framework as it relates to contaminant transport to surface waters or drinking water wells. Following the preliminary assessment, a series of site investigations may be required at a sufficient resolution to capture the effects of the heterogeneities that direct contaminant distribution, fate and transport, and remediation effectiveness. However, there may be a need to prioritize the evaluation of certain exposure pathways (for example, drinking water wells) during the beginning investigations to quickly assess potential human exposures and because of constraints on resources and schedule.

When historical PFAS releases occur upgradient of drinking water sources, drinking water sampling may be the first indication that there is a problem. In areas where there is a concern that a PFAS source may be present, it is common to identify and sample nearby drinking water sources (for example, groundwater and surface water) to determine if PFAS are present in potable water sources and evaluate the potential exposure to human receptors. This approach is a policy for the Department of Defense ([USDOD 2014b](#)). In cases where sources are not well defined, reconnaissance sampling may be useful to inform the development of the CSM and site investigation. In these instances, drinking water source sampling has preceded typical site investigation work. Prior to further site characterization, proper notification to consumers and evaluating options to reduce or eliminate PFAS exposures, including alternative drinking water sources, may be required.

10.2.1 Initial Conceptual Site Model

CSMs are useful tools for the presentation and evaluation of site characteristics, releases, contaminant fate and transport, and exposure pathways. Generalized CSMs are presented in Figures [9-1](#), [9-2](#), and [9-3](#). The CSMs present most known and potential PFAS source areas, transport mechanisms, and pathways on a simplified physical setting. The CSMs also illustrate exposure routes and receptors. CSM development is an iterative process over the project life cycle with information obtained during site investigation, remedy design, and remedy implementation and optimization. Similar to the USEPA's data quality objectives (DQOs), it relies on a systematic objectives-based site characterization process ([ITRC 2015b](#)). The CSM for a PFAS site is developed with information on PFAS sources and releases (whether occurring on site or off site from groundwater, surface water, sediment, or air), site characterization, pathways, and potential receptors.

Some specific challenges related to identifying the nature and extent of impacts for CSM development for PFAS sites are described in the following sections.

10.2.1.1 Surface Water Body Secondary Sources

Because certain PFAS are mobile and resistant to breakdown in the environment, there have been cases of surface water creating very large dilute groundwater plumes through recharge ([ATSDR 2008](#)). Infiltration of PFAS along the course of surface water systems, including tidal zones, may result in widespread secondary sources to groundwater, further enlarging the contamination area. In situations where PFAS-contaminated surface water is recharging groundwater, investigation of the potentially impacted groundwater should be conducted to fully characterize site-related contamination. Complicating surface water being a secondary source is that PFAS compounds have been shown to concentrate at the surface water-air interface ([Ju et al. 2008](#)). PFAS contamination may also concentrate in naturally occurring surface water foam (due to an affinity to organic material in the foam and the higher PFAS concentrations at the surface water-air interface where the foam is formed). Therefore, site characterization must consider whether or not surface water bodies are the most downgradient extent of contamination.

10.2.1.2 Receptor Identification

Identification of potential ecological and human receptors as part of development of the CSM first includes identification of potential exposure pathways (for example, PFAS migration in groundwater to downgradient drinking water wells, creating human exposure to PFAS; or water containing PFAS entering surface water bodies, creating aquatic life exposure to PFAS). See [Section 9](#) for additional information on receptor identification in the context of risk-based evaluations for PFAS.

10.3 Site Investigation

10.3.1 Development of Site Investigation Work Plan

PFAS investigation work plans should take into consideration the information provided in this guidance document (for example, Sections [2](#), [4](#), [5](#), [6](#), [9](#), and [11](#)), including items such as sampling procedures and equipment to prevent cross-contamination, analytical methods and compounds to be reported, geographically variable and changing regulatory requirements and criteria, and site-specific environmental setting. From a general perspective the work plan will depend on the type of PFAS source and subsequent transport via various media. Attention should be paid to potential secondary sources from irrigation, sludge, or biosolid application, the use of soils not recognized to be contaminated, and other anthropogenic factors affecting fate and transport of PFAS-contaminated media, such as discharge from landfills or wastewater treatment plants (WWTPs).

10.3.1.1 Geologic and Hydrogeologic Investigation

Evaluation of the geologic and hydrogeologic framework associated with the site is critical, and sometimes that framework may need to be addressed on a regional basis, as the PFAS impacts may extend significant distances from the site.

In development of a work plan, consideration should be given to obtaining adequate information to allow for applying Environmental Sequence Stratigraphy (ESS). ESS is an emerging best practice for understanding the geologic framework and related subsurface contaminant transport pathways, both regionally and underlying a site. The ESS approach is presented in USEPA Groundwater Issue Paper “Best Practices for Environmental Site Management: A Practical Guide for Applying Environmental Sequence Stratigraphy to Improve Conceptual Site Models” ([USEPA 2017c](#)).

Geochemical parameters that may be pertinent to potential PFAS migration and possible remedies also require consideration during the investigation. The understanding of soil and groundwater chemistry at the site (parameters such as pH, TOC, redox) is needed to assess transformation and migration in groundwater or desorption from soil. These and other geochemical data can be used to assess the viability of PFAS remedy options should remediation be necessary. For example, the groundwater’s general chemistry, including cations, anions, total dissolved solids, and fouling parameters (for example, iron, manganese, hardness, biofoulants), as well as other organic compounds in groundwater, may have a significant impact on the selection, design, and implementation of potential groundwater remedies.

10.3.1.2 PFAS-Specific Tools for Site Screening or Characterization

Investigative techniques to characterize source soils and determine the three-dimensional extent of soil and groundwater contamination should be considered. High-resolution site characterization techniques beyond those that provide lithologic or hydrologic information and are *specific* to PFAS are currently limited because reliable analytical procedures that are cost-effective and can be used for field screening are not readily available. However, analytical procedures that can be used in a mobile laboratory and achieve ng/L detection limits are available. Use of a mobile laboratory can be expensive and is cost-effective only in specific situations when a sufficient number of samples can be collected in a short time period to keep the mobile laboratory at or near its capacity. Use of a mobile laboratory and the quick turnaround of results they provide allow for adaptive selection of additional sampling locations for delineation or other objectives. Other field-screening methodologies have either been tried or are in the research and development phase, including ion selective electrodes to quantify PFOS and a mobile field-screening unit for PFOS and PFAS, both of which are attempting quantification to ng/L levels ([Deeb 2016](#)). One of the main drawbacks associated with current field-screening methods is the inconsistency of results related to varying soil types and compositions.

10.3.2 Nature of PFAS Sources

The nature of primary and secondary PFAS sources at a site will largely determine the extent of PFAS contamination at the site. Multiple factors may contribute to the nature of PFAS sources at a site. Key factors related to secondary sources to consider in development of a work plan include:

- Leaching from the vadose zone to the saturated zone: PFAS present in unsaturated soils are subject to downward leaching during precipitation or irrigation events that promote desorption of soil-bound contaminant mass ([Sepulvado et al. 2011](#); [Ahrens and Bundshuh 2014](#); [Milinovic et al. 2015](#)).
- Back-diffusion: PFAS dissolved in groundwater that accumulated in lower permeability silt/clay layers below the water table may diffuse into the higher permeability zones due to changing relative concentrations ([Section 5.3.1](#)).
- Desorption: PFAS resulting from desorption from solids in the vadose or saturated zones and resolubilizing in porewater or groundwater could occur when adsorption (that is, partitioning) is reversible ([Milinovic et al. 2015](#)); such desorption would have the effect of sustaining PFAS concentrations in porewater or groundwater.
- Nonaqueous phase liquids (NAPL) dissolution: PFAS entrained in NAPL in the subsurface may be associated with releases of chlorinated solvents and/or petroleum hydrocarbons.
- Other sources: Given the widespread use of some PFAS, additional sources upgradient or within a plume may be contributing to PFAS concentrations at a site. Site-specific anthropogenic background may be a contributing factor.
- Atmospheric deposition: PFAS are sometimes associated with stack or other air-emission sources and may contribute to regional PFAS concentrations.
- Overland runoff: Runoff and stormwater conveyance systems can impact surface water locations downstream of the actual source or groundwater along the course of the conveyance system.
- Groundwater seepage into surface water or surface water seepage into groundwater: Groundwater elevations surrounding surface water bodies (that is, gaining or losing) may influence the extent of a plume. Seepage rates and directions may change seasonally, with extreme weather events, or during periods of drought or precipitation.
- Subsurface features, including utility lines: Preferential pathways may result from subsurface features. For example, flow may seep into or out of nonwatertight sewer lines based upon groundwater elevations relative to the utility. The bedding material of a subsurface line may also convey groundwater.
- Multicomponent mixtures: At some sites, numerous PFAS compounds may be present in one or more source zones. Mixtures may be present for several reasons, including, but not limited to, the following: multiple sources, varying time frames, and a mixture of compounds introduced during production ([Sections 5 and 10.5](#)).
- Precursors: Delineating, as practicable, the extent of precursors that may degrade to PFASs and PFCAs will help the investigator understand sources and potential long-term concentrations.

10.3.3 Extent of PFAS

As with other constituents, a site investigation for PFAS relies upon understanding the extent of sources as well as the extent of contaminant transport. A PFAS release can be localized or highly extensive, both horizontally and vertically. PFAS may be highly mobile in groundwater. In addition, PFAS plumes may have had years to develop, as discussed above. Therefore, PFAS plumes may be larger than expected. At some sites, plumes of more mobile, shorter chain PFAS have been observed to be relatively extensive due to limited attenuation and minimal retardation in groundwater. The partitioning behavior of PFAS is discussed in [Section 5.2](#).

Depending upon site-specific conditions, several pathways need to be considered to assess potential upgradient sources. PFAS migration in air from industrial or commercial sources can influence soil or groundwater a great distance from larger sources ([Section 6.1](#)) (for example, ([Barton 2010](#)) and ([Shin et al. 2011](#))). Data from urban soils and groundwater indicate that for sites near metropolitan areas, there may be measurable contributions of PFAS from other sources, unrelated to site-specific sources ([Xiao et al. 2015](#)).

Comingling of contaminants has a potential to impact PFAS extent. For example, for PFAS sites associated with industry, fire training, or emergency response that have a chlorinated solvent or other NAPL source, investigators need to consider potential effects on PFAS in the subsurface and related data collection requirements. Laboratory studies have demonstrated that sorption or partitioning of perfluoroalkyl acids may increase in the presence of trichloroethene DNAPL in bench-scale tests ([McKenzie et al. 2016](#)). Conceptual modeling of published PFAS data suggests that NAPL-water partitioning and NAPL-water interface interactions may significantly increase retardation of some PFAS in source zones ([Brusseau 2018](#)). This research suggests that if PFAS and NAPL are present in media that make effective source treatment unlikely—for example, in low-permeability soils or fractured rock—that fraction will represent a long-term contributor to groundwater plume persistence. At older sites where in situ (for example, oxidation) or pump and treat methods have been employed to reduce NAPL source areas prior to awareness of PFAS, those remedies may complicate characterization and distribution of PFAS. Depending upon the method employed, mobilization of PFAS may have increased (oxidative) or decreased (reductive)

following treatment, and remedial actions may affect distribution and relative concentrations of individual PFAS ([McKenzie et al. 2016](#); [McGuire et al. 2014](#)).

10.4 Data Analysis and Interpretation

There are a number of methods and tools available for characterizing a wide range of contaminated sites. Examples of methods and tools that may be relevant to PFAS sites are described below.

10.4.1 Retardation Coefficients and Travel Time

It may be helpful to estimate retardation coefficients for PFAS compounds to evaluate contaminant-specific velocity and travel time in groundwater, particularly for longer PFAS plumes. As discussed in [Section 5.2.3](#), a linear sorption isotherm is typically assumed for PFAS sorption to organic matter in soil, and sorption coefficients. The Physical and Chemical Properties Table ([Table 4-1](#)) provided as a separate Excel file presents a range of available organic carbon partitioning coefficients for environmentally relevant PFAS.

However, as noted in [Section 5.2](#), while common PFAS appear to be appropriately defined by linear sorption relative to organic carbon concentration when sufficient organic carbon is present, the current state-of-science supports K_{oc} being reported in relatively broad ranges on a compound-specific basis. [Section 4.2.9](#) presents a discussion of potential limitations in using K_{oc} values as a predictor of sorption and PFAS mobility. It is also important to note that other geochemical factors (for example, pH, presence of polyvalent cations, and electrostatic processes) may also impact PFAS sorption to solid phases ([Section 5.2.3](#)). Due to the uncertainty regarding K_{oc} , it may be appropriate to evaluate transport of an individual PFAS using a range of partitioning coefficients to account for uncertainties in this parameter. In addition, empirical estimation of site-specific K_{oc} values in different areas of a site (for example, source zone versus downgradient plume) may be necessary if quantification of the retardation coefficient is important to its characterization.

For example, [McGuire et al. \(2014\)](#) described the calculation of site-specific K_{oc} values for various PFCAs and PFSAAs at an AFFF-impacted site. These site-specific K_{oc} values were calculated based on seven pairs of co-located groundwater and soil samples, and fraction of organic carbon (f_{oc}) measurements at each sampling location. The soil samples were collected near or at the water table, which was about 4.6–6.1 m below ground surface. [McGuire et al. \(2014\)](#) found that there was a range of between one and three orders of magnitude in site-specific K_{oc} values for the PFAAs analyzed. This may reflect the enhanced sorption of PFAS that occurs at the NAPL-water or air-water interface ([Brusseau 2018](#)). There may be smaller ranges in K_{oc} values for PFAAs at greater depths below the water table and downgradient of a source zone (where NAPL is not present). When using this type of site-specific K_{oc} analysis method, it is also important that the groundwater samples be representative of conditions where the point soil samples are collected.

As another alternative to the use of K_{oc} values and the assumption of a linear sorption isotherm, in situ or ex situ studies may be used to develop parameters for simulation of PFAS transport. Such studies could allow development of pseudo-constants to use in model simulations. For example, lysimeter studies were used to establish relative rates of transport of PFOA and shorter chained PFCAs, and PFSAAs as compared with PFOS ([Stahl et al. 2013](#)).

Desorption of PFAS from solids in the vadose zone or below the water table could occur when partitioning is reversible; such desorption would have the effect of maintaining PFAS concentrations in porewater or groundwater. There is uncertainty regarding the extent to which sorption is irreversible and rate-limited versus an equilibrium process ([Section 5.2.3](#)). It may be important to characterize the extent and kinetics of desorption that may occur as a result of remedial activities at the site.

10.4.2 Mass Flux/Mass Discharge

Note that it may be challenging to estimate the relative mass flux contribution of multiple sources at some sites due to the low PFAS concentrations present in groundwater. In addition, it is important to consider the potential for increases in dissolved mass flux of some PFAS due to biotransformation reactions or desorption between transects.

[ITRC \(2010\)](#) presented a variety of methods available for estimating mass flux and mass discharge, including the use of transects of temporary or permanent monitoring wells across the width of a plume. Even simple methods such as the use of chemical isoconcentration figures to estimate mass discharge may be applicable for an initial order of magnitude estimate. Calibration of solute transport models is another method that may be used to estimate the mass discharge of PFAS from a source zone or at a point in a plume.

10.4.3 Contributions from Different Sources

The potential impact of multiple sources on a plume, particularly in proximity to urban or developed locations, needs to be accounted for when assessing site data or identifying data gaps. Each source then needs to be assessed in terms of its specific contributions, and their relative importance or magnitude. Although there are no naturally occurring background levels of PFAS, it is critical to gain an understanding of the anthropogenic ambient or “background” concentrations that may be present at a site, as these can have significant implications for site characterization, assessing exposures, evaluating ecological and human health risks, and establishing site action and cleanup levels. Tools available to quantify relevant contributions from different types of sources are discussed below.

10.4.3.1 Atmospheric Deposition

Certain PFAS may be present in ambient air and may be elevated near sources such as landfills, WWTPs, fire training facilities, and manufacturing plants ([Section 2.6](#)). Many PFAS exhibit relatively low volatility; however, airborne transport of some PFAS can be a relevant migration pathway for some industrial releases. Sections [5.3.2](#) and [6.1](#) provide an overview of transport of aerosols and particulates via air. To assess relative contributions from atmospheric sources, air sampling for PFAS compounds can be conducted. Additionally, air dispersion models, such as AERMOD or Industrial Source Complex (ISC3) Model, can be employed to estimate airborne PFAS concentrations and total wet and dry deposition rates at designated receptor locations. Examples where AERMOD could be beneficial during site characterization activities include sites with no obvious source area and sites in industrial areas with multiple potential sources of airborne PFAS. See [Section 2.6](#) for additional details on the most typical PFAS source scenarios.

10.4.3.2 Vadose Zone Percolation

Recent research has illuminated the complexities of PFAS fate and transport in the vadose zone. PFAS surfactant properties can enhance or reduce PFAS sorption, in particular at high concentrations such as those encountered at release locations (Sections [5.2.2.2](#) and [5.2.3](#)). At lower concentrations the air-water interface may have important implications for vadose zone transport ([Section 5.2.4](#)). Therefore, model simulations of PFAS transport in the vadose zone should be performed with appropriate caveats.

Models such as USEPA’s VLEACH and Seview’s Seasonal Soil (SESOIL) compartment model can simulate one-dimensional vertical transport in the vadose zone via diffusion, adsorption, volatilization, biodegradation, cation exchange, and/or hydrolysis; however, these models do not include air-water interface interactions that may be important to the vadose zone migration of PFAS and these models have not been validated for use with PFAS. For these reasons, these models may not be appropriate for use with PFAS at this time. Most PFAS are resistant to biotic or abiotic degradation, and in general PFAS are far less volatile than many other contaminants. However, it is noted that certain PFAS are volatile, for example, the FTOHs ([Section 4.2.3](#) and Table 4-1). With the exception of the few volatile PFAS, the most important vadose zone processes to model are the physical transport processes.

Analytical leaching methods such as Synthetic Precipitation Leaching Procedure (SPLP), USEPA Method 1312; Toxicity Characteristic Leaching Procedure (TCLP), USEPA Method 1311; Leaching Environmental Assessment Framework (LEAF); and others may provide insight into the leachability of PFAS from vadose zone materials. Care should be taken in selecting a method to assess PFAS leachability that is appropriate for the settings and parameters that are present and considers the end use of the data.

Given the complexity of predicting the mass discharge from vadose soils to groundwater, along with modeling and leaching methods, direct measures of mass discharge, including the use of soil lysimeters, may be considered.

10.4.3.3 Back-Diffusion

When evaluating fate and transport of PFAS in a groundwater plume, including time frame for remediation of PFAS, matrix diffusion may be an important process to consider ([Section 5.3.1](#)). As such, the potential impacts of diffusion on PFAS persistence in natural soils are a topic of ongoing research. Diffusion coefficients for PFAS are generally uncertain but are in development using measurements and models ([Pereira et al. 2014](#)). During the characterization of PFAS plumes, it may be beneficial to collect PFAS soil samples from the transmissive zone directly above a silt/clay layer, and at different depths into the silt/clay layer, to evaluate the potential for back-diffusion to be occurring presently or in the future if there is a decline in PFAS concentrations in the transmissive zone (see [Parker, Cherry, and Chapman \(2004\)](#) and [Chapman and Parker \(2005\)](#) for an example of this sampling approach).

10.4.3.4 Upgradient Site Contributions

PFAS persistence in the environment and their use in a multitude of industrial processes and commercial products result in potential for nonsite-related inputs, similar to other mobile contaminants (Figures 9-1, 9-2 and 9-3). Assessment of site-specific background or upgradient site inputs is recommended. The very low health advisory criteria for groundwater only increase the potential importance of identifying what might otherwise be considered “minor” upgradient sources and may result in alternate source identification (Sections 10.3.2 and 10.5). As part of site investigation of an air deposition release, soil data can be statistically compared to background samples, evaluated for vertical stratification, and assessed for spatial distribution relative to the potential source. Groundwater data from the site may be compared to data from other locations using cluster analysis to assess whether there was evidence of other source terms, or if the site in question appeared to be the sole source.

Alternate Sources

Sources that may exist within, upgradient, or near a PFAS plume under investigation, that come from releases of PFAS separate from the source being investigated.

10.4.4 Transformation Pathways and Rates

As discussed in Section 5.4, the transformation of precursors may result in increasing concentrations of PFAAs such as PFOS and PFOA along the flow path of a dissolved plume. Transformation reactions may occur due to aerobic biological or chemical oxidation. For example, McGuire et al. (2014) concluded that infusion of dissolved oxygen to bioremediate hydrocarbons downgradient of a former burn pit also likely caused the transformation of precursor compounds to PFAAs such as PFHxS. Some methods that may be used to assess the degree to which transformation is affecting PFAS plume extent and stability include:

- plotting concentration isopleths for precursors and various PFAAs (for example, McGuire et al. (2014))
- use of the total oxidizable precursor (TOP) assay to identify whether precursors are present that may be available for transformation to PFAAs at a point in the plume (Section 11.2.2)
- assessment of ratios of precursor and daughter product species at monitoring wells situated along the centerline of a plume, or the ratio of various PFAAs in various portions of a plume. For example, McGuire et al. (2014) plotted an isopleth map for the ratio of PFHxS to PFOS to show that in areas where dissolved oxygen was injected this ratio was as high as 50, and in other areas where bioremediation was not conducted this ratio was less than 1.
- use of concentration trends along a plume centerline and quantitative methods described in USEPA (1998) to estimate precursor transformation rates
- groundwater modeling to demonstrate that the relative plume lengths of different PFAAs with different retardation coefficients can be explained only through the transformation of precursors (for example, McGuire et al. (2014))
- a literature review to identify potential precursor transformation mechanisms and evaluate whether site geochemistry and redox conditions are favorable for the occurrence of these mechanisms.

Another method that may be used to illustrate the occurrence of these transformations is radial diagrams. See the case study in Section 15.1.1.

Figure 10-1 shows three radial diagrams based on data from an AFFF release site (McGuire et al. 2014). Each radial diagram compares groundwater concentrations at a monitoring well within the oxygen infusion zone to concentrations at a well approximately 76 m upgradient. The radial diagram shown at the left of Figure 10-1 compares concentrations for five PFCAs between these two wells; the middle diagram shows concentrations from the TOP assay conducted using samples from each well; and the radial diagram on the right compares concentrations for four PFSAs.

These radial diagrams illustrate that oxygen infusion into groundwater likely stimulated the production of mainly PFHxA,

PFPeA, PFHxS, and PFBS. The middle radial diagram shows that the difference in TOP assay results between the upgradient well and the well in the oxygen infusion zone does not explain the large PFAAs concentration increases that were observed at the well in the oxygen infusion zone. The TOP assay results were low at both wells throughout the area. This suggests that desorption and subsequent transformation of precursors were occurring within the oxygen infusion zone. These radial diagrams are also useful for evaluating relative concentrations of various PFAAs at each monitoring well. The use of radial diagrams for additional types of trend analysis is discussed further in [Section 10.4.7](#).

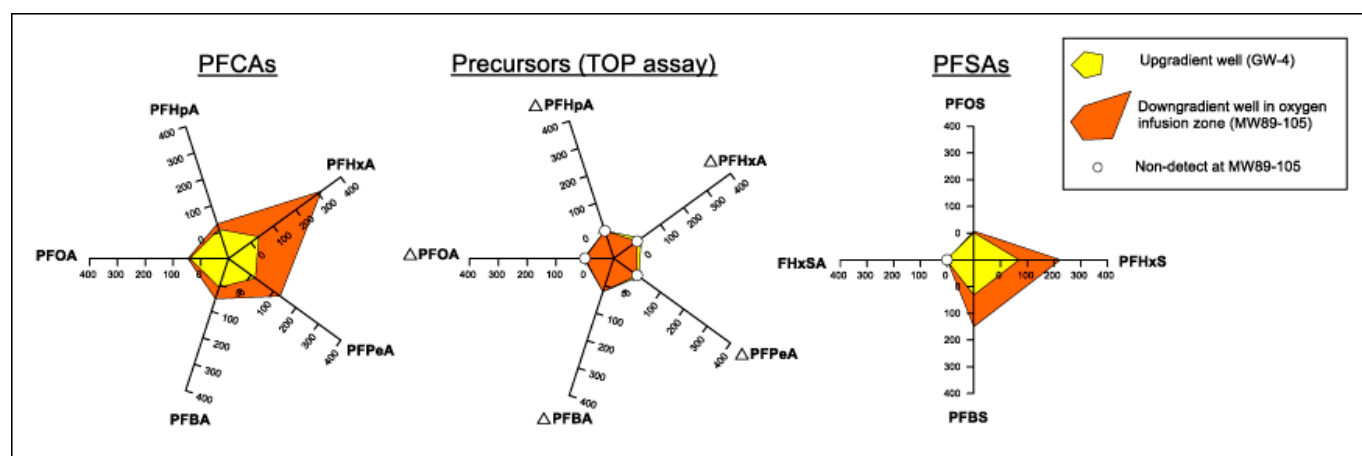


Figure 10-1. Radial diagrams showing the production of various PFAAs in the vicinity of an oxygen infusion zone at an AFFF release site remediated for hydrocarbons in groundwater.

Source: G. Carey, Porewater Solutions. Used with permission.

10.4.5 Assessing Plume Stability

In addition to evaluating potential transformations to PFAAs, it may be necessary to evaluate PFAS plume stability - whether the plume is stable, receding, or expanding. Many PFAS plumes are long-lived and highly mobile. Methods for evaluating plume stability include qualitative evaluations of temporal plume trends or statistical evaluations such as Mann-Kendall ([ITRC 2013](#)) ([ITRC 2016](#); [AFCEC 2012](#); [USEPA 2009d](#)). Data uncertainties may have a greater impact on plume stability evaluations because of the low concentrations assessed. As such, more frequent or longer duration monitoring may be required to confirm trends or plume stability.

10.4.6 Modeling PFAS Fate and Transport

Some modeling of PFAS fate and transport has been conducted recently ([Barr 2017](#); [Persson and Andersson 2016](#)). Modeling the fate and transport of PFAS may have significant uncertainty contributed by precursor concentrations, transformation pathways, and biodegradation rates. In addition, desorption kinetics of PFAS are not currently well understood. Although modeling of PFAS transport may be appropriate under certain conditions, the uncertainty of PFAS transport simulations requires that the results be qualified. Site-specific data are important for evaluating some potential model input parameters such as K_{oc} , which can exhibit significant spatial variation. This is particularly true in source zones, the vadose zones, and at or near the water table. There are situations where modeling of PFAS transport may not be appropriate due to a lack of site-specific input parameters.

10.4.7 Visualization Methods

One of the challenges associated with characterization of PFAS sites is the analysis of trends for a number of PFAS constituents that may be sampled in soil and groundwater, and then the communication of the results of these analyses to a less technical audience. Typical site characterization visualization methods such as plume maps, cross-sections, fence diagrams, 3D models may be used to depict the horizontal and vertical extent of PFAS plumes. Several other visualization methods may be helpful when analyzing PFAS data, including:

- bar charts that show the relative concentrations of individual PFAS constituents at each location to help evaluate PFAS composition trends in soil and groundwater (for example, figures 6 and 7 of [Field \(2017\)](#), [Figure 15-1](#))
- radial diagrams to illustrate:
 - transformations of precursors to PFCAs and/or PFSAs along a flow path (for example, see [Section 15.1.1](#))

- relative concentrations of constituents at each sample location to assist with source fingerprinting and to identify potential risk drivers in different parts of a plume
- locations of potential hot spots
- general extent of a PFAS plume.

Case study examples of these different methods are discussed in [Section 15.1](#).

10.5 Source Identification

Source identification is one of the challenges of PFAS investigations. Where records are available that document leaks, spills, and accidents, there may be a direct connection between sources and contaminant plumes. Where there are no documented releases, multiple lines of evidence may be needed for source identification. For example, due to the unique properties of PFAS, it has been observed that soil and sediment concentrations do not always reflect the groundwater concentrations. As such, additional approaches for source identification may be needed to connect releases to contaminated media. Source identification uses the evaluation of both typical and advanced chemical analyses to differentiate among contaminant sources and age-date release events. Advanced techniques can include:

- chemical fingerprinting
- signature chemicals
- isotopic fingerprinting
- contaminant transport models
- molecular diagnostic ratios
- radionuclide dating
- microscopic analysis.

Although these techniques have limitations and are relatively new in application to PFAS, some of these tools have been used to identify regional and local PFAS sources. An overview of PFAS source identification analyses can be found in [Dorrance, Kellogg, and Love \(2017\)](#).

Source identification of PFAS should include all information regarding release mechanisms, as well as fate and transport mechanisms, as they are complementary and can cause environmental fractionation, which can influence chemical profiles. In addition, long-range wind-driven transport and deposition of some PFAS could be considered ([Ahrens, Rakovic, et al. 2016](#); [Davis et al. 2007](#)).

Multiple lines of evidence are needed for reliable source identification because of the complexity of PFAS composition and source formulations, along with the potential for significant formation from precursors within a spill, which diminish the reliability of chemical fingerprinting. Additionally, information related to degradation expected based on case-specific conditions is needed for defensible chemical fingerprinting. With this being said, sources of PFAS could be deduced on a case-by-case basis, in particular when multiple independent lines of evidence are developed and as our knowledge related to fate and transport of different released commercial formulations improves. Library research, preliminary identification of potential PFAS sources, and information gathered from patents can assist in the identification of PFAS.

10.5.1 Source Identification Tools

Chemical fingerprinting involves the evaluation of the relative proportions of different substances in a mixture to link contaminants in the environment back to a source or sources. The data from chemical analyses can be evaluated using various graphical, statistical, or geospatial techniques. These methods have been commonly used for petroleum and chlorinated compound source identification and can potentially be applied to PFAS, because the release of PFAS into the environment generally involves the release of a complex mixture of substances, including different subclasses of PFAS, as well as homologues and isomers of specific PFAS.

PFAAs are produced as a mixture of homologues of different chain lengths ([Section 2.2](#)). PFAAs produced by electrochemical fluorination contain both even and odd chain-length homologues. PFAAs produced by fluorotelomers contain mostly even chain-length homologues. Most commercial laboratories can report PFCA homologues ranging from C4 to C14 and select PFSA homologues between C4 and C12. [USEPA \(2009a\)](#) published PFCA profiles in various commercial products that showed different patterns of PFCA chain lengths. Chemical fingerprinting for source identification may be useful for PFAS sites; however, changes in raw materials and processes over time, as well as environmental fractionation, must be taken into account.

Examples of chemical fingerprinting for PFAS source identification can be found for wastewater treatment plants ([Clara et al. 2008](#)), differentiating AFFF sources ([KEMI 2015a](#); [Hatton, Holton, and DiGuseppi 2018](#)) ([Section 3](#)), landfills ([Lang et al. 2017](#); [Xiao et al. 2012](#)), surface water ([Xie, Wang, et al. 2013](#)), sediment ([Qi et al. 2016](#)), and groundwater ([Yao et al. 2014](#)). Multivariate statistical analyses (that is, principal components analysis (PCA), cluster analysis, unmixing models) and geospatial analysis have been used extensively to distinguish PFAS sources. [Guelfo \(2017\)](#) emphasized the importance of geospatial distribution of PFAS for source identification. [Qi et al. \(2016\)](#) used PCA–multiple linear regression, positive matrix factorization, and unmix models to identify four PFAS sources (textile treatment, fluoropolymer processing aid/fluoresin coating, textile treatment/metal plating, and precious metals). [Zhang et al. \(2016\)](#) used PCA, hierarchical clustering, and geospatial analysis to determine sources in the northeast United States, and [Lu et al. \(2017\)](#) used factor analysis to classify three categories of PFAS in impacted groundwater. [Pan, Ying, Liu, et al. \(2014\)](#) used PCA in water and sediment samples to distinguish between rural/agricultural and urban/industrial sources.

Evaluation of isomer profiles has been used to assess sources in multiple environments. PFAAs are generally identified as the straight-chain alkyl isomer. However, as discussed in [Section 2.2](#), PFAA that are manufactured by electrochemical fluorination contain about 20–30% branched-chain isomers, while the fluorotelomerization process produces mainly straight-chain isomers ([Prevedouros et al. 2006](#); [Kissa 2001](#); [Parsons et al. 2008](#)). Laboratories generally report the concentration of a given PFAA as the total of the branched and linear forms; however, the concentration of the linear isomer and an estimated concentration for the branched isomers can be reported independently. The concentration of branched isomers must be estimated because standards do not yet exist for most branched-chain PFAA isomers ([Section 11.2.1](#)).

[Benskin \(2011\)](#) used the absence of branched PFCA isomers in dated sediment cores of two lakes to support the conclusion that oxidation of FTOH was the major atmospheric source of PFCAs in the lakes and not direct transport of PFOA. [Fredriksson \(2016\)](#) used isomer profiles along with homologue patterns to assess the sources of PFAS in avian eggs. The potential for environmental fractionation must be taken into account when evaluating isomer profiles because linear and branched-chain isomers have different physical and biological properties, adsorption, and bioaccumulation ([Fredriksson 2016](#); [Miralles-Marco and Harrad 2015](#)). Other examples of isomer analysis for PFAS source identification include [Shi et al. \(2015\)](#), [Benskin, DeSilva, and Martin \(2010\)](#), and [Karrman et al. \(2011\)](#).

PFAS releases into the environment can include fluorinated substances that are not captured by current analytical methods and PFAS target analyte lists. Some of these substances are polyfluorinated and can be oxidized to form PFAAs that can be measured and reported. Such polyfluorinated substances are called “precursors.” The TOP assay, in which the samples are first oxidized and then analyzed for PFAAs, was developed to estimate the mass of these precursors. (See [Section 11.2.2](#) for further information on the TOP assay). The results of PFAS analyses before and after oxidation can be used to generate a two-dimensional PFAS comparison and may be able to support source identification.

In practice, the TOP assay has a number of limitations, and the results are subject to interpretation. Although there is a published TOP procedure ([Houtz and Sedlak 2012](#)), each commercial laboratory has developed its own procedure and quality control steps, and these procedures have not been standardized, nor has interlaboratory validation been conducted. Comparability of TOP assay results between labs may not be possible and should proceed on a case-specific basis after careful review of the methods used and data validation. Another limitation is the potential for incomplete oxidation of precursors during the analysis in the presence of high levels of TOC or other compounds.

Quadrupole time-of-flight mass spectrometry (qTOF/MS) can be used to determine both the chemical formula and structure of unknown PFAS in a sample, but analytical standards are required for unequivocal structural identification ([Newton et al. 2017](#); [Moschet et al. 2017](#)) ([Barzen-Hanson et al. 2017](#)). This method has the potential to greatly increase the number of identified PFAS compounds and provide more accurate source identification.

Chiral fingerprinting through enantiospecific isomer differentiation is a potential method for source identification, although its use is still under development. [Asher et al. \(2012\)](#) applied this method to identify PFAS sources to an aquatic foodweb. However, they noted several limitations and assumptions when using this method for PFAS source identification.

10.5.2 Challenges and Reasonable Expectations

Factors of importance when considering the analysis of source identification of PFAS can include:

- *data quality*, where care must be taken to ensure that analytical results from different time periods, different methods, or different labs are comparable, as older data sets may provide incomplete information when compared to more recent data

- *target compound list*, where a reduced compound list may prevent full differentiation between sources. Linear versus branched (isomer) distinction may also be important.
- *temporal effect*, where an understanding of historical production, use, and release of PFAS becomes important, as is an understanding of differences between samples due to weathering processes that may be interpreted as different sources
- *spatial effect* of long-distance air deposition versus local sources
- *sample collection procedures* to ensure there is no cross-contamination from other sources during sampling
- *weight of evidence* based on multiple lines of inquiry.

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