1 Introduction

This fact sheet provides an overview of site characterization for PFAS and media-specific occurrence of PFAS. Additional information is available in the Guidance Document.

The intent is not to present general site characterization principles, but to highlight unique considerations for this family of emerging contaminants. 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. PFAS 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, must be considered in PFAS site characterization efforts. Current regulatory and investigatory focus has been on use of groundwater as drinking water and connections between groundwater and surface water, accordingly Section 10 of the Guidance Document concentrates on the characterization of groundwater plumes.

Media-specific occurrence of PFAS in the environment is an active area of research. The material presented in this fact sheet and in Section 6 of the Guidance Document is not the result of an exhaustive literature review but is included to provide a general understanding of PFAS concentrations. Because analytical methods are still being optimized and standardized, it is often difficult to compare results between studies and the reported data may offer various levels of confidence. Media types considered in a site investigation include air, soil and sediment, groundwater, surface water, and biota.

2 Site Characterization Issues Relevant to PFAS

Evolving Science and Regulations

The state of the science and regulatory environment are evolving rapidly. Many aspects of PFAS, such as toxicology and behavior in the environment, sampling and analytical methodologies, and the regulatory environment including regulatory limits and compounds of interest need to be reevaluated during the course of characterizing a PFAS site. Section 11 of the Guidance Document covers sampling and analysis for PFAS and Section 8 includes information about regulations.

Source, Fate and Transport Properties and Other Considerations

Sources: An overview of PFAS sources is discussed in Section 2.6 of the Guidance Document. In addition to the main sources that include industrial discharges and AFFF releases, there are also “secondary sources,” such as sources created through movement of contaminated media into an area that was previously uncontaminated, or an area where physical or chemical processes have concentrated PFAS (for example, multi-media interfaces).

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

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

Complex transitions between media: The behavior of PFAS in the environment may deviate greatly from typical contaminants. Transitions between media may be complex because of specific characteristics of these compounds.

Partitioning: PFAS will bind to soils and sediments, with an affinity that may be correlated to the amount of organic carbon present. However, 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. Because various factors can affect sorption of PFAS to organic carbon, published $K_{oc}$ values for PFAS cover a very broad range.
**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 such as historical wells with fluoropolymer tape.

**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 are often detected in low levels in samples from locations without an obvious source; there may be a need to evaluate 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 for understanding potential effects of precursor degradation. Note that with currently available analytical methods, even a broad compound suite will not detect all PFAS.

**Geologic heterogeneity:** Because of the low regulatory limits that are used for delineation of groundwater impacts and the mobile nature of certain PFAS, extra emphasis should be placed on understanding the effects of hydrogeologic heterogeneity on the groundwater plume.

**Initial Conceptual Site Model (CSM)**

CSMs are useful tools for the presentation and evaluation of site characteristics, releases, contaminant fate and transport, and exposure pathways and can help focus a site investigation. An example generalized industrial CSM is presented in Figure 1.

**Figure 1. CSM for industrial sites.**

*Source: Adapted from figure by L. Trozzolo, TRC. Used with permission.*

The CSM presents most known and potential PFAS source areas, transport mechanisms, and pathways on a simplified physical setting. The CSM also illustrates exposure routes and receptors. CSM development is an iterative process over the duration of the project that will incorporate information obtained during site investigation, remedy design, and remedy implementation and optimization.

Some specific challenges related to identifying the nature and extent of impacts for CSM development for PFAS sites are cases of surface water creating very large dilute groundwater plumes through recharge (ATSDR 2008) and identification of potential ecological and human receptors in the context of risk-based evaluations for PFAS.
Site Investigation

Development of Site Investigation Work Plan

PFAS investigation work plans should take into consideration the initial CSM and a comprehensive site preliminary assessment and incorporate applicable information and concepts from the Guidance Document. A few such items are 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.

In addition, 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.

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 becoming more available. Other field-screening methodologies have either been tried or are in the research and development phase (Deeb 2016).

Key factors related to secondary sources to consider in development of a work plan include: leaching from the vadose zone to the saturated zone; back-diffusion; desorption; nonaqueous phase liquids (NAPL) dissolution; non-site sources; atmospheric deposition; overland runoff; groundwater seepage into surface water or surface water seepage into groundwater; subsurface features, including utility lines; multicomponent mixtures; and the PFAS precursors that may be present.

As with other compounds, a site investigation for PFAS relies upon understanding the extent of sources as well as the extent of contaminant transport. At some sites, plumes of more mobile, shorter chain PFAS have been observed to be relatively more extensive than longer chain PFAS due to less retardation in groundwater. The partitioning behavior of PFAS is discussed in Section 5.2 of the Guidance Document. Further, comingling of contaminants has a potential to impact PFAS extent.

Data Analysis and Interpretation

There are a number of methods and tools available for characterizing a wide range of contaminated sites. Examples of data analysis and interpretation approaches discussed in the Guidance Document that may be relevant to PFAS sites are considering: retardation coefficients and travel time, mass flux/mass discharge, contributions from different sources, atmospheric deposition, vadose zone percolation, back-diffusion, upgradient site contributions, transformation pathways and rates, assessing plume stability, modeling PFAS fate and transport, and visualization methods.

Source Identification

Source identification is one of the challenges of PFAS investigations. Where there are no documented releases, multiple lines of evidence may be needed for source identification. Source identification seeks to use the evaluation of both typical and advanced chemical analyses to potentially differentiate among contaminant sources and age-date release events. Advanced techniques continue to be developed. These techniques can include: chemical fingerprinting; signature chemicals; isotopic fingerprinting; contaminant transport models; molecular diagnostic ratios; radionuclide dating; and microscopic analysis. Each technique has inherent levels of uncertainties and a full review of the abilities of each technique and applicability to a specific site should be conducted.

3 Media-Specific Occurrence

PFAS occurrence in various environmental media is an active area of research. The material presented here is not the result of an exhaustive literature review but is included to provide a relative understanding of PFAS concentrations typically found in environmental media. Media types presented here include air, soil and sediment, groundwater, and surface water. Section 6 of the Guidance Document includes figures summarizing the observed concentrations of PFAS that have been reported in the literature. Section 17.1 includes tables summarizing important details concerning each study used in developing the figures.
Air
Certain PFAS are found in ambient air, with elevated concentrations observed or expected in urban areas nearest to emission sources, such as manufacturing facilities, WWTPs, fire training facilities, and landfills (Barton et al. 2006; Ahrens et al. 2011; Liu et al. 2015). Although outdoor air containing PFAS can enter buildings, the presence of indoor sources can cause indoor air concentrations of certain PFAS to be higher than outdoor air concentrations (Fromme et al. 2015; Shoeib et al. 2011).

Soil and Sediment
PFAS are found in soil and sediment due to atmospheric deposition, exposure to impacted media (for example, landfill leachate or biosolids), and direct discharge. PFAS distribution in soil is complex, reflecting several site-specific factors such as total organic carbon (TOC), particle surface charges, and phase interfaces. Properties of individual PFAS, such as alkyl chain length and ionic functional group, are also important factors. PFOS, PFOA, and other long-chain PFCAs are typically the predominant PFAS identified in surface soils and sediments (Zhu et al. 2019; Rankin et al. 2016; Strynar et al. 2012).

Groundwater
USEPA has assembled an extensive data set of the occurrence of six PFAAs in public drinking water through the monitoring of large drinking water systems under the UCMR3 program (USEPA 2017o). One or more PFAAs were detected in 4% of the reporting public water systems (USEPA 2017b). Groundwater sources had approximately double the detection rate of surface water sources (Hu et al. 2016). Groundwater occurrence data collected as part of domestic and international studies have also characterized the range of PFAS concentrations associated with release sites.

Surface Water
Freshwater, marine water, and stormwater PFAS concentrations usually depend on proximity to the point of release and source concentrations. In addition to releases associated with identified sources, stormwater runoff from nonpoint sources may contribute significant loads of PFAS to surface water (Wilkinson et al. 2017; Zushi and Masunaga 2009). The sorption of PFAS to suspended solids may affect surface water PFAS concentrations. Suspended microplastics may also influence PFAS in surface water (Llorca et al. 2018). In addition to PFOS and PFOA, many other PFAS have been observed in surface waters, including compounds other than PFAAs.

Biota
Because PFAS are widespread and have a propensity to bioconcentrate, they have often been found in fish, wildlife, and humans. PFAAs, particularly PFOS, are frequently the dominant PFAS detected in biota (Houde et al. 2011). PFAA concentrations in biota are influenced by uptake and elimination of both PFAAs and their precursors, as well as biotransformation rates of PFAA precursors (Asher et al. 2012; Gebbink, Bignert, and Berger 2016). Therefore, concentrations of PFAAs observed in biota at one location may not reflect concentrations in other environmental media.

4 References and Acronyms
The references cited in this fact sheet and further references can be found at https://pfas-1.itrcweb.org/references/.
The acronyms used in this fact sheet and in the Guidance Document can be found at https://pfas-1.itrcweb.org/acronyms/.