Life Cycle Stage 2: Site Investigation

Remediation PFAS Guidance

Site investigation goals

The initial decision to sample for PFAS is made during the Initial Site Review (Life cycle stage 1), where a site's current and historical industrial practices, nearby off-site sources, and potential risk exposure pathways are evaluated to assess the need for a site investigation.

Once it is determined that there is an actual or potential release of PFAS, collect and analyze samples of all potentially impacted environmental media for the presence of PFAS. If a release is identified at a site, it must be reported to the Minnesota Duty Officer. Minnesota Statute § 115.061 requires that a person notify the Duty Officer immediately when any amount of any substance is released into the environment that may cause pollution of waters of the state. Note that independent, additional reporting requirements may exist under Federal Law. When in doubt, **report.** If there is an immediate threat to life or property, call 911 first!

- MPCA Incident Response: https://www.pca.state.mn.us/about-mpca/incident-response
- MN Duty Officer: https://dps.mn.gov/divisions/bca/bca-divisions/administrative/Pages/minnesota-duty-officer-program.aspx

The actions outlined in this section are applicable during all life cycle stages during which an investigation is required. For nuances related to non-responsible parties, refer to the Brownfield section of this document.

2.1 Site Investigation Milestone 1: Investigation Planning

2.1.1 Investigation Planning Action 1: Receptor Evaluation

A responsible party for a PFAS release, or a state-led investigation of a PFAS release, must complete a full receptor survey to identify all on-site and off-site potential exposure pathways related to the PFAS release. A non-responsible party must complete a receptor survey within the boundary of the Brownfield site, taking to account the current and proposed use of the property.

- A receptor survey should be completed to identify all human and ecological receptors within a specific radius of the release area. This release area is dependent on the impacted media and the area hydrogeology. The receptor survey will identify all potential receptors and the contaminant migration pathways whereby receptors are impacted, including but not limited to:
    - Utility corridors and conduits
    - Surface water bodies
    - Soil and sediment
    - Drinking water supply management areas
    - Wells
    - Vulnerable hydrogeological conditions such as fractured bedrock, springs, seeps and sinkholes

Water supply receptor survey

The water supply receptor survey identifies water supply areas that may be at risk and provides information regarding the geology, groundwater, and surface water use near the release site.

For the water supply receptor survey, complete the following:

I. Generate a map of all water supply locations including:
   a. All wells within the search radius of identified groundwater contamination.
   b. All irrigation, industrial wells, and wells with a water appropriation permit within the search radius of ground water contamination.
   c. Drinking Water Supply Management Areas (DWSMAs) and Surface Water DWSMAs
   d. Monitoring well information from adjacent contaminated sites is not required to be mapped or submitted for the receptor evaluation.

II. Prepare a base map showing property boundaries and relevant features, such as buildings, roads, and surface water within the search radius of the source.

III. Identify property ownership.

IV. Contact residents, property owners, and business owners within the search radius of the source and obtain the following information for each property:
   a. Presence of a water supply well(s) or connection to a public water supply. Include a description of how this information was obtained, such as visual observation, personal contact, telephone conversation, returned postcard, or assumed.
   b. Type of well usage, such as private, domestic, or irrigation
   c. Possible PFAS sources that residents/owners may be aware of at the property

V. Document sources used to conduct well search.

VI. Determine if groundwater contamination is in a well head protection area.
   a. If contamination is within a designated area, the next step is to determine the aquifer’s susceptibility to contamination.

Land use survey

I. Identify all current land use at the site and within the search radius of the site boundary.
   a. Provide a map and a table with the address of each of the following located within the search radius of site boundary:
      i. Residence
      ii. School
      iii. Childcare center
      iv. Subsistence food communities
      v. Environmental Justice communities
      vi. Other sensitive population

II. Identify and describe all proposed/planned changes to land use at the site or within the search radius of site boundary

The decision to limit the evaluation of land use must be based on existing site data and on best professional judgment.

Utility survey

Migration Pathway Identification: Identify and indicate the depth of all subsurface utilities and structures that may serve as preferential migration pathways.

I. Locate all underground utility lines and conduits within the area of known or likely soil and groundwater impacts, for both on-site and any off-site properties, to which a release may have migrated or to which a release may migrate in the future (includes communications lines, water lines, sanitary sewers, storm sewers, and natural gas lines).

Ecological receptor survey

I. Determine if any environmentally sensitive natural resources are present on or adjacent to the site or AOC that may be, have been, or are impacted by contamination from the site.
II. Determine if contamination is present at the site or AOC in excess of any ecological screening criterion or aquatic-life (toxicity) based surface water quality criterion or standard.
III. Prepare a map showing the locations of all surface water and wetland features within the search radius of the site.
    a. Obtain surface water information from a variety of sources, including United States Geological Survey (USGS) topographical maps and in-field surveys.
    b. Identify any potential pathways such as ditches, drain tiles, and storm sewers that may lead to an identified surface water feature.

2.1.2 Investigation Planning Action 2: Identify media and locations to sample

In general, the following approach should be taken to determine baseline sampling requirements at a Site. For nuances related to non-responsible parties, refer to the Brownfield section of this document:

- Use the information from the initial site review to develop a conceptual site model (CSM) for the Site. The CSM should incorporate historical PFAS usage, pathways, and receptors throughout the site. Use the CSM to assist in selecting the appropriate number and location of potentially impacted media to sample.
- Baseline sampling requirements will be determined by potential impacted environmental media (soil, groundwater, sediment, or surface water) that have likely been impacted as a result of current or historical use of the site and/or from off-site sources (i.e., groundwater flow, surface drainage runoff, etc.), as identified during the initial review stage. At this time, sampling for air deposition of PFAS from off-site sources and soil vapor from on-site sources is not included in baseline sampling.
- If the Site has previously been investigated for PFAS, existing data should be evaluated further to inform the baseline sampling requirements and determine if previous data were sufficient to meet current guidance or regulatory criteria. Examples: evaluate boring logs for soil types, evaluate any potential subsurface conduits for PFAS migration, identify data gaps such as areas of the Site where potential pathways/receptors have not been investigated. Compare historical laboratory reporting limits for PFAS to current risk-based criteria.
- If the site has not previously been investigated, more comprehensive data collection (e.g., soil types, geology, depth to groundwater, etc.) will be required.
- Impacts to aqueous media will require sampling in affected groundwater and surface water units and drinking water wells (see the receptor evaluation milestone). If the extent of impacts is unclear, further consideration of potential or likely hydrogeological pathways, including but not limited to site-specific groundwater flow direction, and the physical characteristics of known water-bearing units should be evaluated. It may be necessary to include sampling of potentially impacted drinking water wells and municipal water supply wells during the initial sampling event. See the communications section for additional details about property access for off-site sampling.
- If permanent monitoring wells are not present or available, initial groundwater samples can be collected from temporary wells. In a preliminary groundwater investigation, potable use of all groundwater is assumed, so the quantity and locations of samples is not solely receptor dependent.

- Surface water sampling is necessary if there was a known direct release of PFAS to the surface water body or if there is a confirmed or likely PFAS contaminant migration pathway to the surface water via surface runoff, impacted groundwater discharge to surface water, aerial deposition from an on-site source, or effluent discharge.
- Impacts to solid matrices are assessed through the collection and laboratory analysis of soil and sediment samples.
- Within unconsolidated units, soil intervals will require careful logging to determine where PFAS is likely to be present based on its known characteristics, such as preferential soil adsorption. Soil types identified during the investigation will help determine which interval(s) to sample.
- Assessment of potential impacts from facility operations may include sampling sumps, wastewater, and stormwater discharge.

2.1.3 Investigation Planning Action 3: Prepare SAP/QAPP/Work Plan

- Prepare a site-specific Sampling and Analysis Plan (SAP) to define the goal of investigative activities (e.g., current site usage is residential/industrial/commercial and future site usage will be residential/industrial/commercial).
- If required by the MPCA or regulated party, a site-specific Quality Assurance Project Plan (QAPP) will be prepared.
- PFAS sampling when other contaminants of concern (CoC) are present may require alternative sampling collection and analysis methods. In cases where PFAS and another CoC are present, separate sampling procedures as outlined in the MPCA Guidance for PFAS field sampling should be observed.
- An important functional aspect of project planning is the data quality objective (DQO) process. It is necessary to formalize these planning steps to inform the type, quantity, and quality of PFAS data used in decision-making. Thoughtfully derived DQOs provide the qualitative and quantitative framework by which data collection activities are successful in terms of achieving project objectives. The qualitative aspect of DQOs seeks to encourage good planning for field investigations. The quantitative aspect of DQOs involves designing an efficient field investigation that reduces the possibility of incorrect decision-making.
- The DQO process is defined in MPCA guidance document p-eao2-14: Data Quality Objectives (state.mn.us). The DQO process consists of seven steps. Note that every project is different, and the DQO process should yield project-specific objectives.
- Refer to MPCA's PFAS analytical guidance and sampling guidance for information on selecting appropriate DQO's: Guidance for Per- and Polyfluoroalkyl substances (PFAS): Sampling (state.mn.us), Guidance for Per- and Polyfluoroalkyl Substance: Analytical (state.mn.us). Data quality objectives should be established prior to data collection and sampling and the prescribed quality assurance/quality control (QA/QC) procedures followed throughout sampling, laboratory analysis, and data analysis.
- The ongoing, expanding nature of PFAS environmental awareness and the need for more comprehensive investigations have caused increased demand for PFAS environmental sampling and analysis. There are limited analytical method options available, particularly across the full spectrum of environmental media for a range of PFAS compounds. In many cases, the primary source in the search for available analytical methods for any environmental application is the U.S. Environmental Protection Agency (EPA). The USEPA has published analytical methods for the analysis of select PFAS analytes in drinking water, non-potable water, soil, sediment, biosolids, and tissue.
- There are several accepted analytical methods that may be utilized for various media; the most appropriate analytical method selection depends on the following key inputs:
  - Is a **specific** method required or cited for use, e.g., drinking water compliance, NPDES permit, MPCA regulation?
  - What are the project DQOs?
  - Is the laboratory certified by MDH for a specific method (where certification is required)?

The SAP/Work Plan must include analytical sampling of all investigation derived waste to determine the presence and concentration of PFAS for appropriate disposal. See the Disposal section for details regarding appropriate management of investigation derived waste (IDW).

Table 2-1: PFAS Laboratory Analytical Methods and Applications

Method	537.1	533	8327	1633	537.1 Modified	TOP Assay	Draft Method 1621 (AOF)	Non-Targeted Analysis
Author	USEPA ORD	USEPA Office of Water	USEPA Office of Solid Waste	USEPA Office of Water	Lab SOP	Lab SOP	USEPA Office of Water	Lab SOP
Version (Latest)	2	0	0 (2021)	3 (Draft)	NA	NA	0 (Draft)	NA
MPCA/MDOH Offer Certification?	Yes	Yes	Yes	Yes	Yes	No	No	No
Applicable Sample Media	DW	DW (municipal supply)	Non-DW: GW, SW, WW	GW, private and non-municipal DW SW, WW; Solid: Soil, Sediment, Biosolids, Tissue	Non-DW: GW, SW, WW; Solid: Soil, Sediment, Biosolids, Tissue	Non-DW: GW, SW, WW; Solid: Soil, Sediment, Biosolids, Tissue	Non-DW: GW, SW, WW	Non-DW: GW, SW, WW; Solid: Soil, Sediment, Biosolids, Tissue
Compounds Determined	18	25	24	40	Lab-specific	Lab-specific	1	Lab-specific
Preservative	Tris buffer	Ammonium acetate	none	none	none	none	none	none
Hold Time (Extract / Analyze)	14 / 28 days	28 / 28 days	28 / 30 days	28 / 28 days 90/ 28 days (frozen)	28 / 28 days	28/ 28 days	90 days	28/ 28 days
Instrument	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	LC/MS/MS	Combustion-IC	qTOF/ HRMS
Calibration/ Quantification	Internal standard (non-isotope dilution)	Internal standard (isotope dilution)	External standard (non-isotope dilution)	Internal standard (isotope dilution)	Internal standard (isotope dilution)	Internal standard (isotope dilution)	External standard	Exact mass determination via library search
Primary Use/Application	Safe Drinking Water Act compliance		Testing for all matrices except municipal drinking water			Forensic tools (where needed)		

The summary table above provides the current primary methods available for PFAS testing.

DW= Drinking Water, GW = Groundwater, SW = Surface Water, WW = Wastewater

2.2 Site Investigation Milestone 2: Develop the Conceptual Site Model (CSM)

2.2.1 Develop the CSM Action 1: Evaluate Fate and Transport

Many PFAS are resistant to biotic and abiotic degradation except for precursors which can transform into terminal PFAS (final degradation products). They are, therefore, ubiquitous in the environment and subject to long-range environmental transport. Most PFAS can move readily between environmental compartments. The fate and transport of perfluoroalkane sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) has been studied in more detail than other PFAS. In general, PFSAs are more strongly sorbed to solid phases (e.g., soil or sediment) than PFCAs. Similarly, longer chain perfluoroalkyl acids (PFAAs), which contain both PFSAs and PFCAs, are more strongly sorbed than the shorter chain PFAAs (ITRC 2022). Generally, PFAAs are relatively mobile in groundwater, tend to associate with the organic carbon fraction in soil and sediment, and can be generated by transformation of volatile precursors (ITRC 2022). Due to their unique properties as surfactants, containing a hydrophilic head and a hydrophobic tail, PFAAs tend to accumulate along interfaces of environmental media such as soil/water, water/air, and water/non-aqueous phase liquid (ITRC 2022). For additional information about the fate and transport of PFAS refer to the ITRC PFAS technical and regulatory guidance document.

It is, therefore, important to consider the fate and transport mechanisms that may result in the migration of PFAS contamination from one medium to another. The following examples highlight the primary migration pathways for PFAS:

Groundwater to surface water / surface water to groundwater

Because of their high mobility and persistence, PFAS can travel large distances through migration between groundwater and surface water compartments. If there is potential for a surface water to recharge groundwater or groundwater to discharge to surface water, concentration data should be compared to both MPCA surface water quality standards and MDH drinking water values. This ensures that both surface water and groundwater are protected. Typically, groundwater RBVs are more protective because they are developed for the drinking water pathway. However, for bioaccumulative PFAS, such as PFOS, the surface water RBV is more stringent than the groundwater RBV because it accounts for the fish consumption pathway.

When evaluating the surface water pathway, surface foam samples should be collected when possible. The presence of foam is variable and depends on factors such as seasonal changes and precipitation events. These factors shall be incorporated into the work plan in order to ensure that sampling events occur when foam is most likely to be present.

Soil leaching to groundwater

PFAS present in the unsaturated zone are subject to downward transport during precipitation and irrigation events. While soil leaching values (SLVs) to assess the soil-to-groundwater leaching pathway have been developed for various other contaminants, SLVs are not being developed for PFAS. Given the low risk-based drinking water criteria established by the Minnesota Department of Health and the high mobility of PFAS in the environment, any detection of PFAS in soil is considered to pose a potential risk to groundwater, which should be resolved by groundwater sampling for PFAS.

Atmospheric deposition to terrestrial and aquatic environments

Due to the ubiquity of PFAS in the environment, atmospheric deposition directly impacts the occurrence of PFAS in what would be considered background, unpolluted areas. Background concentrations of PFAS therefore represent “ambient” conditions due to atmospheric deposition, even in the absence of a release. Atmospheric deposition may also have occurred from on-site releases as well which can result in several migration pathways to soil, surface water, and groundwater. Ambient background concentrations may need to be determined if deemed necessary for site evaluation. Refer to the “Ambient background concentrations”, Section 3.5, in the Risk assessment life cycle stage.

Other potential pathways

Subsurface features such as utility lines can provide a preferential pathway for contaminated groundwater. PFAS-contaminated groundwater can infiltrate into sewer lines. PFAS-contaminated wastewater can also exfiltrate into groundwater. The history of remediation efforts at a site should also be evaluated. For example, groundwater pump and treat systems may have changed the plume dimensions, or their discharge could have transported the PFAS to other areas.

2.2.2 Develop the CSM Action 2: Source Evaluations

When developing a work plan for site investigations, consider that more than one PFAS source may be present at a site, both spatially and temporally. The initial site review should indicate if compositions of PFAS changed during the history of operations, locations of facility areas moved, or fire suppression events occurred. It is also important to consider secondary sources of PFAS at a site, such as: sump, wastewater, or stormwater discharges, irrigation, pesticide applications, imported soils, and applications of biosolids. The source evaluation should consider the age, locations, compositions, quantities, and durations of releases.

If a site is impacted by multiple known or suspected sources, there are forensic tools that can be useful in fingerprinting different classes of PFAS. These tools are described in Section 10.5.1 of the ITRC PFAS guidance: 10 Site Characterization – PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org)

Complicating the issue of fingerprinting various sources is PFAS precursors. As previously mentioned, PFAS precursors can also transform into terminal PFAS (i.e., final degradation products) such as PFOS, PFOA, and PFHxS. Many PFAS precursors are polyfluorinated PFAS, meaning they are not fully fluorinated, while the terminal PFAS are perflourinated (i.e., fully fluorinated). Of the thousands of PFAS that currently exist, most are thought to be polyfluorinated. Given the information gaps that still exist for most PFAS, there is much uncertainty regarding the extent to which precursor transformation occurs, which environmental compartments represent the majority of the transformations and the relevant rates and pathways, and relevant environmental conditions that affect transformation processes (ITRC 2022). For an illustration of precursors and how they may impact contaminated sites refer to the ITRC *Figure 5-3*. As shown in Table 2-1 a total oxidizable precursor (TOP) assay can be used to estimate the total precursor content for each terminal degradant. During the TOP assay, precursors are transformed (oxidized) to the end products and the evaluation of pre- and post-TOP assay data offers information on the approximate amount of precursors present in a given sample.

Oftentimes, PFAS may not be the only contaminant released at a site. Consideration needs to be given to how the PFAS source is interacting with other contaminants such as dense and light non-aqueous phase liquids (DNAPLs and LNAPLs). Some research suggests that PFAS partition and accumulate at the NAPL/water interface in both LNAPLs and DNAPLS, possibly resulting in increased retainage and retardation of PFAS where they occur with NAPLs. See ITRC's PFAS guidance *Section 5.2.5*.

Background sources of PFAS are an evolving field of research. Widespread air deposition of PFAS has led to low-level contamination of most environmental media globally. Indoor air sources may also be present due to the numerous household products containing PFAS. Air emission sources of PFAS will be monitored as described in the 2022 PFAS Monitoring Plan. The MPCA will apply knowledge gathered from future research to evaluate how to assess background levels at remediation sites. For more information on background levels, refer to the ITRCs section: 6 Media-Specific Occurrence – PFAS — Per- and Polyfluoroalkyl Substances (itrcweb.org). Background concentrations are further discussed in the "Ambient background concentrations", Section 3.5, in the Risk Assessment life cycle stage.

2.3 Site Investigation Milestone 3: Site Investigations

The general principles of site investigation are similar for PFAS as they would be for other identified chemicals of concern in MERLA and RCRA. As noted above, investigation is necessary to define the full extent and magnitude of contamination in comparison to either risk-based or site-specific criteria. Site investigation work plan(s) will include the approaches outlined in Milestone 1 but will depend on the type of PFAS source and transport via various media. Please note that site investigations will likely undergo an iterative process. For nuances related to non-responsible parties, refer to the Brownfield section of this document.

2.3.1 Site Investigations Action 1: Hydrogeologic investigation strategies

The geologic and hydrogeologic site setting is a key component of the CSM, particularly since PFAS may migrate significantly from a site. An assessment will be site-specific, but an adequate assessment will be one that considers the stratigraphic and lithologic complexity and project objectives.

Effective techniques to meet this need include the application of Environmental Sequence Stratigraphy (ESS) and High-Resolution Site Characterization (HRSC). ITRC has developed guidance on implementing advanced site characterization tools (see https://asct-1.itrcweb.org/).

As noted in ITRC's PFAS guidance, important geochemical parameters include soil characteristics (e.g., fraction of organic carbon (FOC) surface charge, cation exchange capacity, grain size, mineralogy, and water content) and groundwater chemistry (e.g., cation and anion concentrations, ionic strength, oxidation-reduction conditions, pH). These data are used to assess transformation, partitioning (including desorption), and migration in groundwater or soil. These and other geochemical data (e.g., total dissolved solids iron, manganese, hardness) can be used to assess the viability of PFAS remedy options should remediation be necessary.

As noted in ITRC's PFAS Site Characterization Considerations and Media-Specific Occurrence fact sheet (link?), investigations also need to account for the potential for secondary sourcing to occur from the following:

- Leaching from the vadose zone to the saturated zone
- Back-diffusion
- Desorption
- Non-aqueous 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 and drain tiles
- Multicomponent mixtures
- PFAS precursors that may be present

2.3.2 Site Investigations Action 2: Use of PFAS-specific tools for site screening or characterization when available.

In addition to traditional sample collection (i.e., discrete samples), there are a number of available technologies to obtain data. While not a comprehensive list, ITRC's PFAS guidance provides some potential options:

- Use of a mobile laboratory that can be used in conjunction with discrete HRSC sampling.
- Passive and no-purge samplers, which can significantly reduce the amount of Investigation Derived Waste and resources.
- Electrochemical sensors, such as ion selective electrodes (see Rodriguez et al. (2020))
- Passive flux meters and other novel techniques (see Horst et al. 2022).

2.4 Site Investigation Milestone 4 – Site Management Decisions

Actions 1 and 2 are used to facilitate site management, which is the same for PFAS as it would be for other identified chemicals of concern in MERLA and RCRA. Figure 1-2 of ITRC, 2011, while written in mind for DNAPLs, lays out the process for an effective site management strategy.

Questions to ask include but are not limited to:

- Is the conceptual site model well understood?
- Are the extent and magnitude of PFAS adequately defined?

- Has the appropriate media been sampled?
- Have the goals of the investigation been met?
- Is the risk to human health and the environment understood? (See Risk Assessment section)
- Has enough data been collected to determine what the cleanup approach is? Has that been documented? (See Remediation section for information on documenting a cleanup decision.)
- If a remediation or mitigation system is installed, is adequate performance monitoring occurring in order to measure progress toward cleanup goals?

If the answer to any of these questions is no, then additional information and/or data collection is necessary before a site can be "closed."

References and Resources

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