A per- and polyfluoroalkyl substances (PFAS) investigation is headed for a site near you… State and federal regulators are increasingly issuing PFAS investigation orders and requiring the addition of PFAS to site characterization plans. Further, some parties are opting to conduct voluntary PFAS site investigations as a means of managing future risk and liability. PFAS investigations can be daunting given the heightened scrutiny required of sampling procedures, the state-by-state patchwork of ever-lower regulatory criteria and the financial and legal implications potentially associated with investigation results.

Site investigations are used to answer fundamental questions such as: What is the extent of the contaminant footprint? Is the contamination migrating off-site? What is the source of contamination? Do contaminant levels exceed regulatory criteria? While PFAS site investigations generally follow the same principals as those for other environmental contaminants, they also pose unique challenges and require PFAS-specific considerations stemming from the ubiquity of PFAS and the evolving state of the scientific, regulatory, and legal landscape. Taking these considerations into account is a step towards achieving a PFAS investigation that produces accurate, defensible data and meets the investigation’s overall objectives.

Sampling is the crux of site characterization

When it comes to PFAS sampling, the precautionary principle applies. With high financial and legal implications tied to site investigation results, the last thing a party needs is for the credibility of the results to be undermined by an issue associated with sample collection.

The ubiquitous presence of PFAS has been well established. Several materials associated with sample collection, including water-resistant clothing and field gear, sunscreen, insect repellent, and plastic clipboards, potentially contain PFAS. The potential presence of PFAS in these materials, juxtaposed with near-detection limit regulatory levels, warrants precaution against cross contamination during sampling. Therefore, sampling for PFAS requires additional considerations beyond those applied during sampling for other chemicals. While PFAS sampling techniques that take these considerations into account can increase time and cost requirements to site characterization efforts, they help ensure the collection of accurate and defensible data.

Site characterization 101

This article outlines the key components that form the foundation of a successful PFAS site characterization. Included in the discussion are useful resources ranging from websites specifically maintained to provide the most recent PFAS regulations, to guidance for field personnel to minimize the potential for cross-contamination during sampling. Careful planning and execution of the PFAS site characterization is paramount to identifying and mitigating the risks and liabilities associated with PFAS contamination.
Understand the regulatory environment

Considering ever-mounting regulatory scrutiny, PFAS site characterization may be warranted, and in some cases required, depending on the state in which a site is located. Understanding PFAS regulations, or lack thereof, that are relevant at a given site is a crucial step towards a successful PFAS investigation, as regulatory, screening or guidance levels are key in developing the data quality objectives of the investigation. For example, sites undergoing PFAS investigation in California may pursue the lowest possible detection limits for soil or groundwater in light of stringent screening levels for two of the most widely studied PFAS constituents, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), recently issued by a regulatory authority in that state. Other states have opted to regulate PFAS beyond the federal drinking water health advisory limits. No matter where PFAS are located, one thing for certain is that the regulatory environment is in flux. For example, while state-level regulation has dominated the landscape in lieu of federal activity, the U.S. Environmental Protection Agency (EPA) may be listing PFOS and PFOA as hazardous substances under the federal Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), otherwise known as Superfund, in the near future. The implications of this pending hazardous substance designation are far reaching as discussed in the April 2020 Godfrey & Kahn Environmental Strategies FLASH.

To keep current on PFAS regulations, visit the Interstate Technology Regulatory Counsel (ITRC) website and download the updated tables of state, federal and international PFAS criteria.

Pre-sampling considerations

The objectives of the site investigation will be driven by the rationale for pursuing the data:

- **Investigation performed as part of due diligence:** Emerging contaminants of concern, like PFAS, are often viewed as a potential threat to human or ecological health, but because they are not yet listed under CERCLA, they are therefore not considered by EPA to meet the definition of a “hazardous substance.” If conducting a Phase I Environmental Site Assessment (ESA) per the ASTM E1527-13 Standard, consideration of PFAS is currently outside the scope of the Standard, even if a local (or state) regulatory agency has established PFAS guidance or cleanup requirements. While it may not be required to evaluate PFAS in a Phase I ESA, parties are becoming more aware of potential liabilities as states conduct their own water supply investigations and enact standards. A Phase I ESA including “non-scope” considerations may be completed, or a separate report prepared, if a specific use or occupant of the site is suspected of discharging PFAS to the environment. A PFAS investigation conducted as part of due diligence under attorney-client privilege may also be a means of managing risk by learning of potential PFAS impacts at a site. How do you decide whether or not to sample for PFAS? The important topics of attorney-client privilege, confidentiality, opportunities for “exploratory” investigations and spill reporting will be addressed in a subsequent article.

- **Investigation mandated by regulatory authority:** While some states have taken little action with respect to PFAS while awaiting EPA guidance, others have proposed or promulgated stringent standards for certain PFAS, established task forces for toxicology studies, and initiating widespread PFAS investigation efforts. For instance, in June 2020, the New Jersey Department of Environmental Protection (NJDEP) adopted Ground Water Quality Standards for PFOA of 14 parts per trillion (ng/L) and PFOS (13 ng/L), joining the previously adopted standard for perfluorononanoic acid (PFNA) of 13 ng/L in 2018. In 2019, NJDEP issued guidance that for sites with remediation under NJDEP regulation, an evaluation or Preliminary Assessment must be conducted to evaluate if there is the potential that PFOA and/or PFOS “may have been manufactured, used, handled, stored, disposed or discharged at the site or area of concern.” If PFOA/PFOS are identified as contaminants of concern, then a groundwater investigation is required. Similarly, in 2019, New York began requiring sites entered into the Brownfield Cleanup Program and Superfund Program to incorporate a specific suite of PFAS into investigations. Other states are taking tiered approaches as they first inventory facilities that may impact drinking water supplies. In California, the State Water Resources Control Board (SWRCB) is taking a phased approach to investigating sites, starting in 2019 with source investigation and nearby drinking water supply sampling within certain radii of airports and municipal solid waste landfills, followed by chrome plating facilities, refineries, bulk terminals, fire training areas, secondary manufacturing sites, and wastewater
treatment and pre-treatment plants.

- **Investigation performed as part of ongoing litigation** – State attorneys general, environmental organizations, drinking water suppliers and other parties are filing lawsuits against primary manufactures and downstream users of PFAS. Investigations stemming from these lawsuits may need to be tailored to compare and contrast specific compounds used at a property versus compounds identified in the local environment, and evaluate potential facilities in the surrounding area that may be potentially responsible parties contributing to the contaminant plume.

### Doing your homework

A PFAS conceptual site model is key to assessing potential sources, transport pathways and receptors of PFAS in various media. Due diligence, whether in the form of a Phase I ESA or targeted evaluation, should consider numerous factors. When evaluating the potential sources of PFAS, consider the following:

- Is the site a current or former primary manufacturer or secondary PFAS manufacturer? Primary manufacturers include locations where PFAS are or were manufactured from other raw chemical ingredients. Secondary manufacturers are locations where PFAS were incorporated into finished products. Secondary manufacturing sites can include paper product manufacturers, semiconductors, textiles/leather manufacturing, surfactant production, and production of resins, molds, coatings, and plastics.

- Is there current or former handling, storage and/or use of aqueous film-forming foam (AFFF) at the site? PFAS is a key component of AFFF, which has been used to combat liquid fuel fires since the 1970s. Therefore, sites such as fire training facilities, airports, military bases and locations of bulk fuel storage likely used AFFF historically or may continue to do so today.

- Is the site a current or former metal plating facility? PFAS is a known component in the surfactants used as mist-suppressants used in the chrome plating industry, and possibly in other types of metal plating applications.

- Is the site associated with wastewater treatment effluent, landfill leachate or biosolids application? These substrates can contain PFAS derived from the activities and uses described above.

The goal of initial PFAS due diligence should be to establish potential on-site source areas. While the standard resources used in due diligence\(^1\) can provide insight on historical occupants and operations (topographic maps, aerial photographs, fires insurance maps, city directories) additional information can be captured by reviewing chemical inventories, Right To Know submittals and safety data sheets to obtain a better understanding of chemicals that may have been used/stored that contain PFAS, and the timeframe these chemicals were used. Review of these documents may find products are composed of PFAS, or may identify trade names, or indicators on SDS like “fluoro,” “fluorosurfactant” or “fluoroprotein.” This information would then be compared to the timeframes PFAS began to be produced (various PFAS were generally first developed in 1940’s to 1970’s). Fire department/emergency management files may be reviewed to determine if fires have occurred at the site that were extinguished using AFFF, or if foam fire suppression systems have been used at a site. Industrial sites may have historically had on-site landfilling, oil/water separators or wastewater treatment plants that may have received PFAS-containing waste that was subsequently released to the environment.

Because PFAS are not currently classified as hazardous substances, the management and disposal of PFAS-containing materials, including AFFF, were not commonly documented and tracked. Therefore, in addition to the due diligence activities noted above, interviews with site personnel with knowledge of current and historical site operations can be useful to capture information pertaining to potential PFAS-sources that are not captured in site documentation.

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\(^1\) As previously noted, PFAS is not listed as a CERCLA hazardous substance (and therefore not required to be included in a Phase I ESA) and PFAS have not historically been amongst contaminants required to be investigated as part of site investigation/remedial activities; therefore, a new evaluation focused specifically on PFAS may be warranted.
Transport and exposure pathways

Once there is an understanding of potential on-site PFAS source areas, transport and exposure pathways can be evaluated to determine if there is a complete pathway from a potential PFAS source to receptors. This evaluation considers several factors including PFAS volume, potential for discharge during storage and handling (floor drains, septic system versus public sewer service, exposure to stormwater, lined versus unlined landfill), and potential for atmospheric deposition of PFAS from industrial air emissions. Site-specific topography, geology, hydrogeology and stormwater/surface water flow generally should be evaluated as part of the fate and transport evaluation to determine how PFAS may infiltrate into soils, sediment and groundwater, runoff into surface water, and in turn impact human and/or ecological receptors. Fate and transport of PFAS can also be influenced by the geochemistry of potentially impacted environmental matrices (e.g., soil, groundwater, surface water) and presence of pure- or dissolved phase co-contaminates, such as petroleum hydrocarbons or volatile organic compounds, as identified in previous remedial activities.

Strategic placement of sampling locations can incorporate the findings of PFAS due diligence and fate and transport evaluation, as well as publicly available resources for potential PFAS sources in the vicinity of the site, especially upgradient of the site. States like Michigan and New Hampshire have begun to compile results of PFAS drinking water sampling and investigations which can be compared to or referenced to understand site area concerns.

But how do we sample?

Once a decision is made to conduct a PFAS investigation, there are still many factors to consider as part of the sampling plan, including selection of sampling equipment and supplies and determination of the appropriate analytical method. While the sections below are not intended as a comprehensive “how-to” of PFAS sampling, they address these and other key considerations for successful sample collection and analysis.

Much ado about sampling equipment and supplies

With such low levels of PFAS currently considered a concern, and the presence of PFAS in so many products, there is a concern of cross contamination from sampling equipment and supplies. Materials considered acceptable for PFAS sample due to low risk of cross contamination include stainless steel, polypropylene, high density polyethylene (HDPE), polyvinylchloride (PVC), silicone, acetate and polypropylene. Materials to avoid due to a higher potential for cross contamination include low density polyethylene (LDPE), glass or polytetrafluoroethylene (PTFE, Teflon™). Sample bottleware is commonly HDPE containers, as PFAS can adhere to glass.

In addition, unacceptable secondary field materials include water-resistant paper, notebooks and labels (PFAS may be in water-resistant inks and coatings), sticky notes, plastic clipboards and binders, felt pens and markers, and aluminum foil (protective layer may contain PFAS). Food wrappers and packaging must be kept out of sampling areas. Unacceptable materials that have been identified for sampling crew clothing and personal products include water- or stain-resistant boots and clothing (such as GORE-TEX®), latex gloves, clothing recently laundered with fabric softener, and moisturizers and hand creams. California has even identified in their sampling guidance examples of sunscreens and insect repellants that are PFAS-free.

The risk of cross contamination from various materials typically used or applied during sampling is the subject of ongoing research. While limited, some research findings have suggested that PFAS can leach into water over an extended period of time from sampling materials such as tubing and bailers; however, initial testing did not find evidence of quantifiable concentrations of common individual PFAS in select materials used in sample collection, such as putty caulk, resin and polyethylene bladders, and some shipping/packaging materials. The cautionary principal is being adopted for PFAS sampling efforts in the absence of supporting evidence to verify the need for extensive PFAS sampling “do’s and don’ts.”

2 When comparing to applicable standards that exist, the USEPA drinking water health advisory levels for PFOA and PFOS are 70 parts per trillion (nanograms per liter [ng/L]) individually or combined when both compounds are present, and states have established drinking water and/or groundwater standards generally between 5 and 750 ng/L.
Establishment and use of a standard operating procedure (SOP) that outlines sampling methodology, equipment, quality assurance/quality control (QA/QC) samples, proper sample storage and handling, and lists of acceptable and unacceptable PFAS sampling materials is a key step to manage the challenges associated with current precautionary practices surrounding PFAS sampling. An SOP is a means of reducing the risk of cross contamination and generating results that meet the data quality objectives of the investigation.

QA/QC samples should include equipment blanks and field blanks as applicable. Equipment blanks are prepared by pouring PFAS-free water over or through decontaminated reusable field sampling equipment and collecting the rinsate in a sample container. Field blanks are prepared by filling a sample container with PFAS-free water in the field in the same manner as environmental samples. Field blanks and equipment blanks are an effective means of assessing potential cross-contamination as a result of sample collection and handling. Trip blanks, typically reserved for samples designated for analysis of volatile organic compounds (VOCs), can also be included PFAS sample coolers to assess the potential for cross contamination during sample transport. Certified PFAS-free water can be obtained from an analytical laboratory, typically for a fee, or can be obtained from an on-site source once that source is verified as PFAS-free through laboratory analysis. The latter option may be a cost-efficient solution when large volumes of PFAS-free water are needed for decontamination.

Analytical method selection

Current EPA approved methods for analyzing PFAS in drinking water are EPA Methods 533 and 537.1. However, there is no standard method for analyzing PFAS in other media such as surface water, groundwater, soil and sediment. For these media, a modification of EPA Method 537 is available for a limited suite of PFAS constituents. For example, the U.S. Department of Defense (DOD) Quality Systems Manual for Environmental Laboratories (QSM)\(^3\) has quality control requirements for PFAS analysis in non-drinking water samples. An SOP may specify the use of a modified 537 method compliant with the most recent DOD QSM requirements as a defensible analytical technique in lieu of an EPA-approved method.

If elevated levels of PFAS are identified in soils, testing via Synthetic Precipitation Leaching Procedure may help determine the potential for PFAS leaching from soil into groundwater. Another potentially beneficial analysis for risk evaluation is the Total Oxidizable Precursor (TOP) assay which can help identify PFAS breakdown products that may be oxidized downgradient and/or off-site in the contaminant plume over time.

Because states are at varying milestones for establishing PFAS guidance values or standards, the current focus has been on two media: drinking water and groundwater. As the understanding of PFAS toxicology is continuously changing and states are at various stages of promulgating standards, it is important to review the most recent state PFAS screening levels prior to any investigation. This will ensure that the SOP will identify appropriate analytical methods and associated reporting limits and that the investigation will generate data that is comparable to applicable regulatory screening levels.

Key takeaways

There is not a “one size fits all” approach to PFAS site characterization. Because PFAS is omnipresent in our lives and current guidance values area extremely low, a tailored approach should be taken when developing a PFAS sampling plan. Careful consideration of specific locations and receptors suspected of contamination, and methodology to generate high quality data and avoid cross contamination are key.

\(^3\) Table B-15 of the Quality Systems Manual address PFAS analysis.