GUIDANCE DOCUMENT

Lines of Evidence and Best Practices to Assess the Effectiveness of PFAS Remediation Technologies

SERDP Project ER18-1633

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14. ABSTRACT

The goal of this project was to produce guidelines, checklists, best practices, and metrics for evaluating the effectiveness of PFAS treatment technologies. This guidance provides researchers with evaluation criteria that can inform research and demonstration plans. Ultimately, this guidance will help DoD site managers and contractors by providing them with accurate and more complete information about the effectiveness of remedial technologies for PFAS, resulting in more realistic treatment expectations. This project will therefore aid DoD with site management and accelerate the development of promising technologies for PFAS remediation. Because new PFAS treatment technologies are being brought to market or tested without adequate documentation to demonstrate successful treatment, these criteria can be used to standardize the review of technology effectiveness and inform conclusions about technology effectiveness, knowledge gaps, and priorities for further testing.

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List of Acronyms

<	less than
>	more than
°C	degrees Celsius
β-CD	beta-cyclodextrin
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
^{19}F NMR	fluorine-19 nuclear magnetic resonance
4:2 FtS	fluorotelomer sulfonic acid 4:2
6:2 FtS	fluorotelomer sulfonic acid 6:2
8:2 FtS	fluorotelomer sulfonic acid 8:2
AFFF	aqueous film-forming foam
AOF	absorbable organic fluorine
DFT	density functional theory
DOC	dissolved organic carbon
DoD	U.S. Department of Defense
eBeam	electron beam
ELAP	Environmental Laboratory Accreditation Program
EOF	extractable organic fluorine
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FOSAs	perfluorooctane sulfonamides
FOSEs	perfluorooctanesulfonamide ethanols
FTOH	fluorotelomer alcohol
GAC	granular activated carbon
GC/MS	gas chromatrography and mass spectrometry

IC	ion chromatography
ISCO	in situ chemical oxidation
ITRC	Interstate Technology and Regulatory Council
LC-MS/MS	liquid chromatography and tandem mass spectrometry
LC-QTOFMS	liquid chromatography with quadrupole time of flight mass spectrometry
LC-Orbitrap MS	liquid chromatography and Orbitrap mass spectrometry
LDPE	low density polyethylene
MIP	molecularly imprinted polymer
MS	mass spectrometry
NAPL	non-aqueous phase liquid
NEtFOSAA	N-ethyl perfluorooctane sulfonamido acetic acid
NMeFOSAA	N-methyl perfluorooctane sulfonamido acetic acid
PFAAs	perfluoroalkyl acids
PFAS	per- and polyfluoroalkyl substances
PFBS	perfluorobutane sulfonic acid
PFCAs	perfluorocarboxylic acids
PFHpA	perfluoroheptanoic acid
PFHxS	perfluorohexane sulfonic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFSAs	perfluorosulfonic acids
PIGE	particle induced gamma emission
QA	quality assurance
QC	quality control
QSM	quality system manual
R&D	research and development
SERDP	Strategic Environmental Research and Development Program
SON	statement of need
SOP	standard operating procedure
TOP	total oxidizable precursors
UCMR	Unregulated Contaminant Monitoring Rule
U.S.	United States
UV	ultraviolet

Keywords: lines of evidence, per- and polyfluoroalkyl substances, PFAS, PFOS, PFOA, treatment, remediation, technology evaluation, research and development, decision-making tools.

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1. Introduction

1.1. Background

Aqueous film-forming foams (AFFFs) are complex and proprietary mixtures of hydrocarbon surfactants, organic solvents, and per- and polyfluoroalkyl substances (PFAS) (Field et al., 2017). PFAS presence at U.S. Department of Defense (DoD) sites is primarily a result of widespread use of AFFF over the past 50 years. Because AFFF effectively extinguishes flammable liquid fuel fires, AFFF releases are known to have occurred at hundreds of DoD fire training areas and crash sites.Site investigations conducted by the Air Force have confirmed PFAS occurrence at other militarysites including emergency response areas, AFFF lagoons, hangar-related AFFF storage tanks and pipelines, and fire station testing and maintenance areas. The DoD has taken a proactive approach towards PFAS site assessments, site investigation, and risk management, and has conducted PFASremediation on a case-by-case basis. Per the Government Accountability Office, the DoD has spent at least $200 million on PFAS investigations and response as of December 2016 and could face billions in cleanup costs (GAO, 2018). The National Aeronautics and Space Administration and other Federal organizations are also conducting PFAS investigations.

Because the chemistry of AFFF is complex and perfluoroalkyl substances are highly stable in the environment, PFAS are extremely difficult to treat using any single proven remediation technology. Full-scale treatment typically relies on granular activated carbon (GAC) or ion exchange to sequester PFAS from extracted groundwater, followed by off-site regeneration or incineration. Destructive treatment technologies for remediating PFAS are still in the development stage and there are no in situ destructive remedial options for site managers that are clearly effective at full-scale. Technology developers may need to consider technologies that work together in series over time or concurrently as ex situ treatment trains.

In response to the need for PFAS treatment technologies, there has been an influx of research and development (R&D) funding to develop innovative treatment technologies for PFAS. In this environment, vendors and technologydevelopers promote claims of success to attract additional funding dollars and demonstration opportunities. Without understanding the big picture, researchers may miss confounding factors and generate ambiguous results. In order to develop robust science-based and effective treatment technologies for PFAS, site managers need clear standards to assess technology performance, andtechnology developers need clearer direction on how to demonstrate the effectiveness of promisingtechnologies.

1.2. Objectives

The goal of this project was to produce guidelines, checklists, best practices, and metrics for evaluating the effectiveness of PFAS treatment technologies. This guidance provides researchers with evaluation criteria that can inform research and demonstration plans. Ultimately, this guidance willhelp DoD site managers and contractors by providing them with accurate and more complete information about the effectiveness of remedial technologies for PFAS, resulting in more realistic treatment expectations. This project will therefore aid DoD with site management and accelerate the development of promising technologies for PFAS remediation. Because new PFAS treatment technologies are being brought to market or tested without adequate documentation to demonstrate successful treatment, these criteria can be used to standardize the review of technology effectiveness and inform conclusions about technology effectiveness, knowledge gaps, and priorities for further testing.

1.3. Approach

The project team was led by principal investigator Dr. Rula Deeb of Geosyntec Consultants. The co-principal investigator was Dr. David Sedlak from the University of California at Berkeley. Dr. Jennifer Field from Oregon State University, Dr. Chris Higginsfrom the Colorado School of Mines, and Dr. Michael C. Kavanaugh of Geosyntec Consultants served as technical advisors.

A collaborative approach was used to develop lines of evidence and best practices for the assessment of PFAS treatment technology effectiveness as follows:

- Conducted brainstorming and open discussion within the project team to create and refine draft lines of evidence;
- Surveyed individuals who are conducting or evaluating PFAS R&D projects. Survey participants were asked to rate the importanceof each line of evidence on a scale of 1 to 5, for each stage of technology development;
- Conducted a workshop in conjunction with the 2018 Strategic Environmental Research and Development Program (SERDP)/Environmental Security Technology Certification Program (ESTCP) Symposium to discuss survey results and prioritize lines of evidence more broadly, regardless of technology or stage of technology development. Three lines of evidence were identified as an outcome of the workshop, as well as other important considerations;
- Reviewed over 100 relevant peer-reviewed articles related to PFAS remediation or treatment to identify examples of lines of evidence and other practices;
- Developed a series of fact sheets summarizing lines of evidence, best practices, and other considerations for evaluating the effectiveness of PFAS treatment;
- Conducted a working group discussion in conjunction with the September 2019 Interstate Technology and Regulatory Council (ITRC) PFAS Team meeting and group discussion at the Michigan PFAS Action Response Team Treatment Technologies Roundtablemeeting in October 2019 in Lansing, Michigan. Follow-up was conducted with interested participants to solicit feedback on fact sheets describing lines of evidence; and
- Developed criteria for decision-making and technology assessment, followed by beta testing of draft decision tools by PFAS researchers and technology developers. Completed evaluations for specific technologies will be compiled and posted to SERDP’s website along with fact sheets.

2. Lines of Evidence for Demonstrating the Effectiveness of PFASRemediation Technologies

This section provides a detailed discussion of three lines of evidence for assessing PFAS remediation efficacy:

- A decrease in target PFAS concentrations is observed and is explained in the context of a mass balance;
- A treatment mechanism is proposed that is consistent with previous studies and is supported by data; and
- Transformation products have been identified and quantified, if applicable (i.e., if the treatment technology transforms or destroys rather than sequesters PFAS).

2.1. Decrease in Target PFAS Concentrations is Observed and Explained in the Context of a Mass Balance

A statistically quantifiable decrease in concentrations of aqueous-phase and/or particle-associated PFAS is the primary line of evidence for assessing the effectiveness of remedial technologies in sequestering or destroying PFAS. A concentration decrease is commonly reported and is easily understood. This section describes how an assessment of this line of evidence can be more rigorous. References to exemplary studies in which concentration decreases were documented and for additional details related to this line of evidence are included throughout this section.

2.1.1. Definition of Target PFAS

The first step in assessing this line of evidence is to define target PFAS. There are over 3,000 PFAS on the global market. Currently, verified analytical techniques are available for a tiny fraction of total PFAS. To date, public and regulatory attention has primarily focused on two PFAS: perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Both are persistent, bioaccumulative, and potentially toxic. However, other homologous perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) are also present in AFFFs. These are collectively referred to as perfluoroalkyl acids (PFAAs). In addition, AFFFs also contain polyfluorinated substances that can degrade to form PFAAs and are often referred to as *precursors*. There are two classes of polyfluorinated compounds found in AFFFs: those generated using perfluoroalkyl sulfonamide chemistry (3M AFFF compounds), and those produced using fluorotelomer-based chemistry (fluorotelomer AFFF compounds) (Field et al., 2017). Additional information on AFFF chemistry has been published by Field and colleagues (Place and Field, 2012; Backe et al., 2013; Houtz et al., 2013; Barzen-Hanson and Field, 2015; Barzen-Hanson et al., 2017).

Families of compounds included in the term PFAS are summarized in Figure 1.

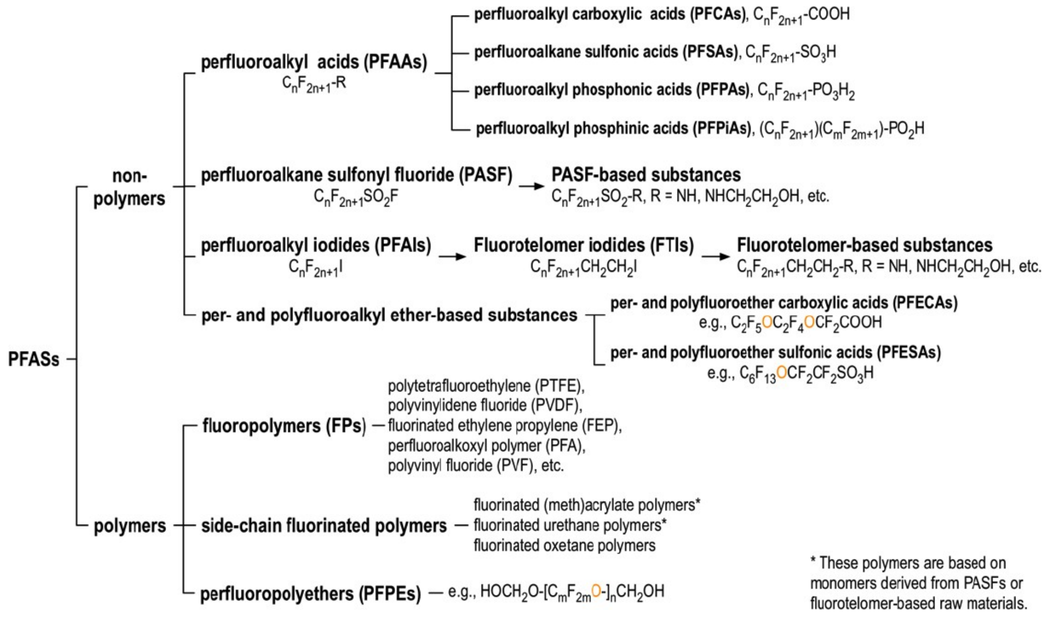

Figure 1. PFAS families of compounds (OECD, 2015)

The selection of PFAS of interest for research projects depends on available analytical techniques and the intended application of the treatment technology. Preliminary research may focus on a subset of PFAS with published toxicity values (e.g., PFOS, PFOA), draft toxicity assessments (e.g., GenX and perfluorobutane sulfonic acid [PFBS]), advisory levels (e.g., PFOS, PFOA, perfluorononanoic acid [PFNA], perfluorohexane sulfonic acid [PFHxS], perfluoroheptanoic acid [PFHpA]), or PFAS included on the third Unregulated Contaminant Monitoring Rule (UCMR3) occurrence database (i.e., PFOS, PFOA, PFNA, PFHxS, PFHpA, PFBS). More targeted research may address specific PFAS that are known to be recalcitrant, difficult to treat, or may contribute substantially to potential health risks at a specific site.

For drinking water samples, the standard analytical method, U.S. Environmental Protection Agency (EPA) Method 537.1, can be used to quantify 18 PFAS, primarily PFAAs as well as several perfluoroether acids (e.g., GenX, ADONA). Note that GenX is the trade name forthe ammonium salt of hexafluoropropylene oxide dimer acid; ADONA is the trade name for 4,8-dioxa-3H-perfluorononanoic acid. Modifications of this method can be used for soil,groundwater, and other aqueous and solid samples to quantify the following PFAS:

- PFOA and homologous compounds of varying carbon chain lengths (C4 to C14), known as PFCAs (11 individual compounds);
- PFOS and homologous compounds of varying carbon chain lengths (C4 to C10), known as PFSAs (7 individual compounds);
- Perfluorooctane sulfonamide (PFOSA), a perfluorosulfonic acid derivative that can undergo transformation to form PFOS (1 compound); and

- Several polyfluorinated compounds that are environmental transformation products of fluorotelomer-based AFFFs, including three fluorotelomer sulfonic acids (8:2 FtS, 6:2 FtS, and 4:2 FtS), N-ethyl perfluorooctane sulfonamido acetic acid (NEtFOSAA), and N-methyl perfluorooctane sulfonamido acetic acid (NMeFOSAA) (5 individual compounds).

A summary of the suite of 24 PFAS compounds is provided in Table 1. Commercial laboratories have developed methods to quantify additional PFAS but the list of 24 provided in Table 1 provides a common foundation for PFAS research. SERDP and ESTCP researchers have been directed to use this list of 24 compounds as a baseline and provide technical justification for any deviations from this list (SERDP & ESTCP, 2020).

Table 1. Suite of 24 PFAS Commonly Included in Laboratory Analyses

PFAS Chemical Name	Abbreviation	Chemical Abstracts Service (CAS) No.
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorododecanoic acid	PFDoDA	307-55-1
Perfluoroundecanoic acid	PFUnDA	2058-94-8
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorodecane sulfonic acid	PFDS	335-77-3
Perfluorononane sulfonic acid	PFNS	474511-07-4
Perfluorooctane sulfonic acid	PFOS	1763-23-1
Perfluoroheptane sulfonic acid	PFHpS	375-92-8
Perfluorohexane sulfonic acid	PFHxS	355-46-4
Perfluoropentane sulfonic acid	PFPeS	2706-91-4
Perfluorobutane sulfonic acid	PFBS	375-73-5
Perfluorooctanesulfonamide	PFOSA	754-91-6
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4
N-Ethyl perfluorooctane sulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-Methyl perfluorooctane sulfonamidoacetic acid	NMeFOSAA	2355-31-9

Researchers may expand this list by using more specialized analytical methods (described in Section 3) to focus on unique or signature PFAS associated with specific products or manufacturing methods. For example, PFAS products may have entirelylinear fluorinated carbon chains or both branched and linear isomers depending on the manufacturer. As a result, techniques that differentiate between linear and branched PFAS can be useful for source tracking (e.g., Benskin et al., 2010).

The list of target PFAS can also vary based on the research objectives. Preliminary research may focus on screening of samples for a subset of PFAS chosen based on published toxicity values, draft toxicity assessments, advisory levels, or UCMR3 occurrence data. This may be followed by more targeted research focused on the treatment of aspecific compound that is either hard to remove or contributes substantially to potential health risks.

Many treatment technologies partially degrade PFAS. Therefore, the potential for transformation of one PFAS to another during treatment needs to be considered in the study design. This may necessitate an expansion of the list of target analytes or create a need to measure PFAA precursors (e.g., total oxidizable precursor [TOP] assay) or total concentrations of fluorinated organic compounds. Additional backgroundinformation on PFAS transformations in treatment systems and under conditions with substantial microbial activity (e.g., landfills) is available in prior publications (e.g., ITRC, 2017; Hamid et al.,2018).

2.1.2. PFAS Mass Balance

The second step in assessing the line of evidence is to measure decreases in target PFAS concentrations in the context of a PFAS mass balance. Concentrations of PFAS in the aqueous phase may decrease during treatment for a variety of reasons other than transformation or removal by a treatment system. Possible reasons for decreasing concentrations unrelated to successful treatment include the following:

- **Sorption of PFAS on the surface of soil or sediments** – PFAS can adsorb onto soil or sediments. In particular, the organic carbon that coats soil and sediment surfaces can be a particularly important PFAS sorbent. Therefore, experiments carried out in the presence of soils or sediments should account for changes in partitioning of PFAS between the liquid and solid phase. This is particularly important when a treatment technology alters the soil pHor ionic strength or if the mineral surface is altered by treatment (e.g., through the precipitationor dissolution of minerals on the soil surface). The effect of partitioning of PFAS to surfaces increases as the soil-to-water ratio increases. Therefore, this effect is best evaluated under conditions approximating those encountered in the treatment system (e.g., solid-to-water mass ratios of one or higher).

- **Association of PFAS with non-aqueous phase liquid (NAPL) and interfaces** – PFAS can also associate with NAPL (e.g., McKenzie et al., 2016). Because PFAAs exhibit surfactant properties (i.e., they have a carbon-fluorine *tail* that is hydrophobic and a nonfluorinated *head* that is hydrophilic), they commonly accumulate at media interfaces (e.g., water/air, water/soil, water/NAPL). PFAS can readily adsorb to the walls of sample bottles and other materials that may contact sample media (e.g., filters, low density polyethylene [LDPE] tubing). PFAS can also adsorb to the air-water interface, and so a change in conditions leadingto the formation of additional air-water interfacial area could masquerade as a loss process or lead to overestimations of the affinity of PFAS for solid phases. For this reason, control experiments are needed to assess the importance of these phenomena as possible explanationsfor PFAS loss (e.g., vacuum degassing of adsorbents prior to experiments to remove residual air [Meng et al., 2014]). PFAS sampling and analytical methods should be consistent with bestpractices, (e.g., state guidance and criteria listed in DoD Quality System Manual (QSM) (version 5.4), Table B-15, as described in more detail in Section 3).

- **Volatilization** – Some non-ionic PFAS (e.g., fluorotelomer alcohols (FTOHs), fluorotelomer acids, perfluorooctane sulfonamides [FOSAs], perfluorooctanesulfonamide ethanols [FOSEs]) havea tendency to volatilize from aqueous solutions (Ahrens et al., 2012). In addition, under acidicconditions, PFAAs are also capable of volatilizing. The tendency of PFAS to volatilize increases with increasing temperature and decreasing pH (Bruton and Sedlak, 2017). Therefore, special attention should be paid to technologies that involve treatment under elevated temperatures and/or low pH. Finally, the mass of PFAS volatilized as two and three carbon-chain PFAAs may be significant and are not currently included in typical analytical suites. A recent review highlights current data gaps in the current state of knowledge on short- and ultrashort-chain PFAS (Ateia et al., 2019).

- **Dilution** – Field demonstration of PFAS treatment needs to account for dilution due to reagent injection or reinjection of treated groundwater into the treatment zone. At sites with brackish groundwater, chloride has been used as a tracer for dilution and displacement of water due to injection of reagents as part of treatment (e.g., Eberle et al., 2017). Such systems are complicated by the potential for PFAS desorption from surfaces after fluid is displaced.

Conversely, aqueous-phase concentrations of PFAS may increase after treatment due to the following reasons:

- **Transformation of PFAS precursors** – PFAS are typically present in mixtures in the environment. Upon exposure to strong oxidants, reductants, or microbes, some PFAS may be converted to PFAAs and other PFAS (Harding-Marjanovic et al., 2015; Yi et al., 2018; Bruton and Sedlak, 2017; 2018). As a result, concentrations of certain PFAS may actually increase during treatment as other compounds are converted.

- **Desorption/release from surfaces or NAPL** – PFAS can be released from the solid phase with an increase in pH. If treatment conditions facilitate the degradation of a NAPL co-occurring chemical, PFAS can also be released from association with the NAPL, increasing aqueous-phase PFAS concentrations (McKenzie et al., 2016).

- **Sample contamination** – PFAS are potentially present in a variety of materials; field work plans often include a list of restrictions on field equipment and sampling materials to avoid cross-contamination. Sampling guidance for PFAS is in its infancy; however, some states (e.g., Michigan, California) and organizations (e.g., ITRC) have released PFAS sampling guidance documents. Because analytical method detection limits are low, sample cross-contamination can be detected and may generate false positive results if adequate precautions are not taken. Generally, materials that contain fluorochemicals should not be used in proximity to samples whenever possible. If avoiding these materials is not possible (e.g., practicality, health and safety, or economic concerns), then quality assurance/quality control (QA/QC) samples (e.g., equipment blanks) can be collected to identify whether sample cross-contamination is occurring.

These processes can result in multiple potential reasons for a change in aqueous-phase and/or solid-phase PFAS concentrations. Therefore, a measured decrease in the concentration of one PFAS compound does not necessarily indicate PFAS destruction or sequestration. By working within controlled study conditions and collecting additional data, researchers can assess alternative explanations for a decrease in PFAS concentrations. A mass balance on fluorinated organic compounds provides strong evidence for successful treatment.

2.2. Treatment Mechanism Proposed that is Consistent with Previous Studies and Supported by Data

Another line of evidence for assessing PFAS treatment effectiveness is the identification of the treatment mechanism. The mechanism should be scientifically plausible, i.e., consistent with the known chemistry of PFAS and the treatment system employed. This section describes ways in which kinetic and mechanistic data can be used to support a proposed treatment mechanism. Examples of data used to support assertions about PFAS destruction and sequestration mechanisms are also provided, along with references for additional detail.

2.2.1. How Do PFAS Treatment Technologies Work?

PFAS treatment technologies are intended to transform or employ a physical process to remove PFAS from the media of concern (e.g., groundwater). Transformation of some PFAS has been shown to occur (i.e., biotransformation of polyfluoroalkyl compounds to perfluoroalkyl compounds under aerobic conditions); the objective of many treatment technologies is complete PFAS transformation, i.e., mineralization. Examples of treatment technologies that transform PFAS include oxidation of PFCAs by sulfate radicals under acidic conditions (Bruton and Sedlak, 2017; 2018), reduction of PFOS by solvated electrons (Qu et al., 2010; Song et al., 2013), and destruction of PFAS by thermal methods such as high-temperature incineration (Yamada et al., 2005). Examples of sequestration technologies include adsorption of PFAS in groundwater onto GAC or ion exchange resins (Dudley et al., 2015; Xiao et al., 2017), removal by reverse osmosis and nanofiltration (Appleman et al., 2013; 2014), and in situ immobilization (e.g., RemBind™).

2.2.2. Evaluating PFAS Transformation and Destruction

The transformation of polyfluoroalkyl substances to form perfluoroalkyl substances is well documented. Chemical oxidation has been shown to be broadly effective in converting PFAA precursors to PFAAs (e.g., Bruton and Sedlak, 2017; Houtz and Sedlak, 2012). In the natural environment, the rate of transformation is typically much slower (e.g., summaries provided by Ross et al., 2018; Kucharzyk et al., 2017). PFAS transformations are not typically the focus of treatment strategies. Research into transformation mechanisms and kinetics may be valuable to quantify natural rates of PFAS transformation (e.g., Harding-Marjanovic et al., 2015). In addition, treatment processes that are designed to address co-occurring chemicals (e.g., trichloroethene) may stimulate PFAS precursor degradation, forming more mobile or recalcitrant PFAS. Finally, the presence of PFAS can inhibit co-occurring chemicals degradation (e.g., Yi et al., 2018).

Studies of PFAS transformation are typically supported by experimental data that document decreases in the mass of the PFAS accompanied by formation of a stable product, such as fluoride. Fluoride generation has been measured as a line of evidence in support of PFAS destruction (e.g., Bruton and Sedlak, 2018) and is discussed in more detail in other sections. In some cases, it may not be possible to measure fluoride due to analytical limitations. In these situations, it is important that the experiments include controls to assess whether the loss of PFAS is attributable to physical loss from the system or an analytical artifact.

To support the assertion that PFAS has been transformed, the proposed mechanism should be consistent with those described in prior peer-reviewed publications. This includes detection of transformation products that are consistent with the proposed reaction mechanisms. For example, the proposed mechanism of the sequential removal of CF_2 groups from PFCAs during persulfate oxidation at low pH is consistent with the appearance of shorter-chain PFCAs observed in laboratory experiments (Bruton and Sedlak, 2018; Yin et al, 2016). In some cases, it might not be possible to detect transformation products under the conditions employed during treatment. Additional experiments designed to verify the production of transformation products (e.g., experiments conducted at higher initial PFAS concentrations or in a simplified matrix) might support this line of evidence.

Another consideration for examining potential reaction mechanisms is bond strengths/energies. Calculations of bond energies can provide insight into which bonds are most susceptible to cleavage and which reactants can initiate the proposed reaction. For example, based on estimated bond strengths for PFAAs, cleavage of a C-C bond is more likely to occur than a C-F bond, particularly the C-C bond of the carboxylic acid head group of PFOA (Fang et al., 2017).

Density functional theory (DFT), the method that serves as the basis for estimating bond strength, can also be used to simulate the relative probability of radicals to attack PFAS molecules at different locations. DFT can provide insight into the rate-limiting step in a reaction or the effect of carbon chain length or branched versus linear configurations on compound reactivity (e.g., Fang et al., 2017; Liu et al, 2017). For example, a recent article by van Hoomissen and Vyas (2019) details proposed mechanisms for reductive dehalogenation of linear PFAS at a molecular level. It should be noted that predictions made with DFT do not always yield accurate results, especially when reactions occur at surfaces or when PFAS are adsorbed or interact with other ions.

The following examples illustrate PFAS transformation reactions that have been supported by research conducted to date and provide a starting point for considering destructive PFAS mechanisms:

- **Chemical oxidation** – Based on bond strengths/energies and empirical studies, PFOS and PFOA are not susceptible to degradation by hydroxyl radical. However, some PFAS may be transformed by hydroxyl radical and other strong oxidants (see, for example, a recent review by Trojanowicz et al., 2018). For example, polyfluoroalkyl groups are susceptible to oxidation by hydroxyl radical (i.e., this is the basis of the PFCA precursor method, which transforms polyfluoroalkyl substances into PFCAs). Advanced chemical oxidation processes can also generate persulfate radicals that can oxidize PFOA and other PFCAs under acidic conditions. For chemical oxidation using sulfate radicals at low pH, the proposed mechanism for PFOA degradation consists of stepwise degradation of CF2 units and the temporary formation of shorter-chain PFCA transformation products.

- **Chemical reduction** – Certain PFAS are also susceptible to reduction. PFOS and other PFSA have been reduced by solvated electrons generated using ultraviolet (UV) light or other activation methods and reducing agents (e.g., UV light and aqueous iodide [Park et al., 2011] or UV light and sodium dithionite [Vellanki et al., 2013]). These studies have demonstrated that solvated electrons attack C-F bonds, which initiates the defluorination process. Several laboratory-scale studies have used irradiation technologies to produce solvated electrons to destroy PFAS, including electron beam (eBeam) (Wang et al., 2016), gamma radiation (Zhang et al., 2014), and photocatalysis methods such as ultraviolet or vacuum ultraviolet radiation in combination with modified photocatalyst materials (e.g., Ti_4O_7, Wang et al., 2017; Sabu et al., 2018) or vacuum ultraviolet radiation under alkaline conditions (Jin and Zhang, 2015). Factors evaluated in these studies have included light wavelength and energy, the concentration and type of photocatalyst, surface area, PFAS concentration, pH, pressure, and temperature (Wang et al., 2017). The proposed mechanism of solvated electrons facilitating PFOS reduction is consistent with the results of controlled experiments that have examined the effect of adding oxygen and other electron scavenging agents. Studies have also added carbonate (Wang et al., 2016) or formate in side-by-side studies to form other oxidizing or reducing radicals and assess their ability to degrade PFAS. PFAS reduction has also been achieved using zerovalent nickel and iron nanoparticles supported by activated carbon where zerovalent nickel is used as a catalyst to enhance reactivity (Zenobio et al., 2019). Because solvated electrons react with dissolved oxygen, nitrate and other solutes, the solution composition has a major effect on the efficacy of the treatment process. Laboratory studies have also used elevated temperatures, elevated pressure, and/or elevated pH to facilitate reduction.

- **Electrochemical mechanisms** – For PFOS oxidation, a similar mechanism has been proposed that involves cleavage of the C-S bond and formation of a perfluorinated radical to also achieve stepwise degradation of CF_2 groups (Lin et al, 2018). PFAS have been oxidized using various types of anodes of electrochemical treatment systems (see, for example, a review summarizing recent advances in electrochemical oxidation by Fang et al., 2017). In electrochemical oxidation, mineralization at the anode surface has been proposed to explain the scarcity of detection of shorter-chain PFAA transformation products in solution (Niu et al., 2012).

- **Thermal degradation mechanisms** – Incineration has been used to destroy PFAS (Yamada et al., 2005). This is typically accomplished in two stages: thermal desorption of PFAS into the vapor phase at temperatures of 500 to 600 degrees Celsius (°C) followed by catalytic oxidation in an afterburner at temperatures greater than 1000 °C. The required temperature for PFAS degradation varies with chain length (longer chain length increases the required degradation temperature) and branched versus linear composition, with greater temperatures needed for linear isomers (Rayne and Forest, 2009). Multiple potential mechanistic pathways for PFOA degradation were presented by Rayne and Forest (2009), who stated that the complexity of starting waste mixtures and various thermal degradation mechanisms precluded a more definitive assessment. PFAS hydrodefluorination reactions to form calcium fluoride can be facilitated by the addition of calcium hydroxide (lime) and other agents prior to waste thermal treatment (see Wang et al., 2015). More recently, smouldering combustion has been found to be effective in degrading PFAS in soil to below detection limits, using GAC as a carbonaceous soil amendment to sustain combustion over time (e.g., Major, 2019).

In contrast, other mechanisms have been proposed but not fully supported or peer-reviewed prior to publication. For example, researchers have suggested the conversion of PFOS to PFOA toexplain variability in concentration data over time (Yao et al., 2016). The mechanism was proposedprior to ruling out other more likely explanations. For example, controls did not evaluate the effectsof changes in pH as a result of reagent addition, although changes in pH are known to affect PFAS sorption to soils. Researchers did not quantify a reduction in total PFAS concentrations or attempt to present a mass balance (e.g., using the TOP assay). Error bars were not used to communicate uncertainty in the experimental results.

2.2.3. Evaluating PFAS Sequestration Mechanisms and Kinetics

For treatment systems that utilize sequestration, understanding the mechanism(s) can inform an assessment of aspects of treatment effectiveness such as the capacity for sequestration under a variety of environmental conditions and reversibility/potential for PFAS to desorb or leach back into solution, thereby affecting long-term treatment system performance. The following provides examples of research that is needed to better understand PFAS sequestration mechanisms and their implications for treatment effectiveness:

- **GAC and other sorbents** – Researchers have characterized sorption characteristics of PFAS to various media and developed sorption isotherms. Sorption to organic carbon and minerals is predominantly a function of the hydrophobicity of the perfluorocarbon chain. The breakthrough of shorter-chain PFAAs has been well-documented; some research on the sorption characteristics of polyfluoroalkyl substances has also been published (e.g., Xiao et al., 2017). Because PFAAs are strong acids, sorption is also influenced by surface charge, pH, ionic strength, and temperature. The formation of hemimicelles at GAC surfaces may explain increased removal efficiency following initial GAC loading. The effect of aging on PFAS sorption to nanoscale zerovalent iron was recently studied to assess the effect of formation of a mixed layer of iron sulfides and iron oxides on PFAS sorption (Zhang et al., 2018). Other sorbents such as mesoporous organosilica rely solely on hydrophobic adsorption to remove PFAS from water and may improve sorption of shorter-chain PFAS.

- **Complexation** – Alternatives to GAC have been developed that can be engineered specifically to complex PFAS. Molecularly imprinted polymers (MIPs) using beta-cyclodextrin (β-CD) can form stable inclusion complexes with PFAS of varying chain lengths (Karoyo and Wilson, 2015). β-CD is a toroid-shaped macrocyclic molecule with a hydrophilic exterior due to the alcohol functionalities and a hydrophobic interior. MIPs offer the potential advantages of engineered high specificity for PFAS, faster equilibration times, and a well-defined surface area and capacity for PFAS. A detailed fluorine-19 nuclear magnetic resonance (^{19}F NMR) investigation attested to strong encapsulation of six-chain PFAS and longer by β-CD by van der Waals interactions. pH, ionic strength and the presence of humic acid had a small influence on the complexes (Weiss-Errico and O'Shea,2017). β-CD polymers rapidly sequester a variety of micropollutants and can be regenerated using a washing procedure with no loss in performance (Alsbaiee et al., 2016).

- **Ion exchange** – Ion exchange systems have been used to remove a variety of PFAS and have several advantages over GAC systems, including significantly longer run-times prior to the need for resin regeneration or disposal as well as a shorter residence time which translates into a smaller footprint. Ion exchange systems have been used for decades and the general removal mechanisms are well understood. For PFAS that are not anionic (e.g., zwitterionic, cationic, or neutral polyfluoroalkyl substances), removal is not anticipated via anion exchange processes. However, adsorption due to hydrophobic interactions can also occur in ion exchange resin systems, enhancing removal (Carter and Farrell, 2010); most publications on PFAS removal in ion exchange systems do not differentiate between these two removal mechanisms. In addition, formation of hemimicelles may also contribute to removal.

- **Foam fractionation** – The surfactant nature of PFAS make them prone to accumulate at surface interfaces. Fractionation processes generate fine air bubbles that rise through a narrow water column and deliver PFAS to the top of the water column, where foam will form provided PFAS concentrations are sufficiently high (>0.5 micrograms per liter [µg/L]) (Burns, 2018; Ross et al., 2018). In an ex situ treatment process, the PFAS-containing foam can be vacuumed off for separate disposal. A similar mechanism has been proposed for ozofractionation – sparging withnanobubbles of ozone (Ross et al., 2018). Peer-reviewed studies have not yet been conducted to evaluate the proposed mechanism in detail, e.g., evaluate the relative efficacy of ozone versus air or different sizes of bubbles.

2.3. PFAS Treatment Transformation Products Have Been Identified and Quantified

The third line of evidence relates to the identification and quantitation of treatment transformation products. This section provides examples of potential treatment transformation products that have been identified and quantified by PFAS researchers, as well as references for additional detail.

There are several reasons to evaluate transformation products generated by a PFAS treatment technology. First, it can help establish that a treatment technology was successful in mineralizing PFAS, as opposed to converting some PFAS to a potentially toxic, more mobile, or more recalcitrant transformation product. Second, quantifying treatment transformation products, such as fluoride, can close the mass balance and provide an additional line of evidence supporting PFAS destruction. Third, it can inform our understanding of the treatment mechanism. Finally, PFAS treatment processes can lead to secondary water quality impacts, such as the dissolution of naturally occurring metals from soil at low pH.

Common PFAS treatment transformation products are described below, along with methods for identifying and/or quantifying them:

- **Shorter-chain PFAS** – The detection of shorter-chain PFAS (i.e., PFAAs with carbon chains ranging from 2 to 6 [Buck et al., 2011]) can help researchers evaluate reaction kinetics and mechanisms. When subjected to oxidation, PFAS may degrade by undergoing the sequential loss of -CF_2 groups (Bruton and Sedlak, 2017). As a result, PFCAs or PFSAs with a shorter perfluoroalkyl chain may be produced during the treatment process (Buck et al., 2011). Short-chain individual PFAS can be identified with existing analytical methods. It is also possible to identify and quantify PFAS collectively as total fluoride species. The detection of shorter-chain transformation products may indicate that an unzipping process is occurring. The lack of detection of shorter-chain transformation products also can occur when the shorter-chain compounds are transformed more readily than the parent compound, the reaction occurs on a surface (i.e., products are not released back into to bulk solution), and if transformation products are produced that are not readily detected by existing analytical methods (e.g., liquid chromatography and tandem mass spectrometry [LC-MS/MS]). Non-targeted analysis using high resolution mass spectrometry may be useful in identification of shorter-chain PFAS species (McCord and Strynar, 2019).

- **Volatile shorter-chain PFAS** – The detection of volatile shorter-chain PFAS can provide researchers with insight into degradation mechanisms and help close the mass balance. Several volatile shorter-chain PFAS, such as FTOHs, fluorine-containing hydrocarbons such as perfluoroheptene-1, and shorter-chain PFCAs such as trifluoroacetic acid can be detected using gas chromatography and mass spectrometry (GC/MS). For example, Liu et al. (2017) identified perfluoroheptene-1 as a byproduct of thermally induced PFOA degradation at 80 °C under acidic pH conditions. The formation of perfluoroheptene-1 was consistent with a decarboxylation mechanism (Liu et al., 2017). A new analytical method using LC-MS/MS was recently developed and validated to quantify PFCAs with two to eight carbons (Janda et al., 2019a).

- **Fluoride** – The generation of fluoride can be measured over time to provide evidence that PFAS mineralization is occurring. Researchers commonly track fluoride generation (e.g., Bruton and Sedlak, 2018; Hori et al., 2005; 2008; Liu et al., 2012) and may report a defluorination ratio, defined as the moles of fluoride produced per mole of PFAS degraded. Fluoride is typically measured using ion chromatography (IC). Given the value of fluoride as a line of evidence, appropriate quality controls also need to be employed in the measurement of fluoride, including matrix overspikes to check for interferences, determination of limits of detection and quantification, accuracy, and precision. Because IC is a nonspecific method for quantifying fluoride based on retention time, the method is susceptible to a variety of different potential interferences. Matrix spikes for fluoride can be useful to confirm that fluoride is actually being measured.

2.4. Technology Evaluation Checklist

PFAS researchers, technology developers, and practitioners (collectively referred to here as technology evaluators) often face the task of evaluating the performance of PFAS treatment technologies and determining whether a technology is effective or demonstrates promise in destroying or sequestering PFAS. These technology evaluators also ask the question of what data gaps or uncertainties remain and are priorities for additional research. A related question is identifying whether a PFAS treatment technology is ready to advance to the next stage of R&D (e.g., move from laboratory studies to a field demonstration).

Tools and decision criteria are presented in this section to help address these questions, based on the lines of evidence that were presented earlier. Section 7.1 describes a technology-specific evaluation of treatment performance and data gaps. Section 7.2 describes a tool to identify whether a technology is a good candidate for the next stage of research and development.

The project team developed a checklist of questions to facilitate reviewing the status of a PFAS treatment technology with respect to each line of evidence (**Table 2**). Each question pertains to the three lines of evidence. The checklist is meant to be applied to a specifictechnology. Examples of completed checklists are posted on the SERDP project website for various PFAS treatment technologies. Because the checklist was developed to be useful in assessing a variety of different technologies, it is not tailored for any one technology and is therefore provided as an example of a tool to facilitate decision-making. Questions can be adjusted to reflect technology-specific needs and technology development status.

Table 2. Lines of Evidence Evaluation Checklist

Checklist Item	Response (Yes, No, NA)	Notes/ Explanation
Decrease in Target PFAS Concentrations in Context of Mass Balance		
Were target PFAS defined?		
List of 24 individual PFAS		
Subset of the list of 24 PFAS (e.g., PFOS and PFOA)		
PFAS precursors		
Other		
Do studies to date show that the technology decreases aqueous-phase concentrations of target PFAS?		
Do studies to date account for potential apparent sources and losses of target PFAS? See below.		
PFAS transformations (e.g., precursor conversion to target PFAS)		
PFAS sorption/desorption onto soil or sediments		
PFAS association with NAPL		
PFAS association with media interfaces		
PFAS volatilization		
Dilution, particularly in field settings		
Cross-contamination from lab or field materials or equipment		
If the technology will be applied in situ, do studies show a decrease in aqueous-phase PFAS concentrations in the presence of sediments/soils?		
Treatment Mechanism is Proposed that is Consistent with Previous Studies and Supported by Data		
Is the proposed treatment mechanism well-known and demonstrated? **If yes, continue on to the third line of evidence.**		
Sequestration:		
Has a mechanism been proposed? (e.g., hydrophobic sorption, ionic interaction, surface interaction, complexation)?		
Have the kinetics of sorption/sequestration been evaluated?		
Has reversibility, potential for desorption, or leaching back into solution been evaluated?		
Has the lifetime/longevity of sorption/sequestration been evaluated, if appropriate?		
Transformation/destruction:		
Has a transformation mechanism been proposed?		
If yes, is the proposed mechanism consistent with and supported byother peer-reviewed publications?		
Is the detection of intermediates (e.g., shorter-chain PFAS) or lack of detection of intermediates consistent with the proposed mechanism?		
Is the formation of fluoride or other end products documented?		
Is the proposed mechanism consistent with chemical bond strength/susceptibility to cleavage?		
PFAS Transformation Products have been Identified and Quantified (Transformation/Destruction Technologies Only)		
Were shorter-chain aqueous-phase PFAS detected?		
Were shorter-chain volatile-phase PFAS detected?		
Was fluoride generation measured?		
If so, were controls used to assess interference and confirm fluoride isthe analyte being measured (e.g., matrix spikes of fluoride)?		
Were other PFAS-related transformation products identified or quantified?		
Were secondary water quality effects evaluated (e.g., metalsmobilization, perchlorate formation)?		

A spreadsheet version of **Table 2** is provided as a separate spreadsheet file along with this report. The spreadsheet version includes color coding for the response column, with yes responses appearing in blue, no responses appearing in orange, and NA responses appearing gray. The notes column is included to encourage the user to reference supporting citations and provide other explanatory notes to accompany each yes or no response.

Once the technology evaluation checklist has been completed, PFAS technology evaluators can see areas where additional research may strengthen the state of knowledge for a specific technology. This may inform research priorities, comments on a research proposal, or allocation of available funding to research tasks. The completed checklist can also provide PFAS technology evaluators with a way to demonstrate the depth and care of collective research efforts to assess treatment effectiveness for PFAS and demonstrate that a PFAS treatment technology is effective. Another potential outcome of this evaluation may be recognition that a treatment technology's effectiveness is not based on the proposed mechanism (e.g., destruction) but is a result of other factors (e.g., partitioning), pointing researchers in a new direction for technology optimization.

The criteria laid out in Table 2 may prompt technology evaluators to review peer-reviewed studies in detail. Academic PFAS researchers are likely best suited to contribute to the evaluation, as they are more likely to be familiar with the peer-reviewed research literature. As part of technology transfer activities, the project team will continue to contact individuals who volunteer to conduct beta testing of the tables. Beta tested case studies will be compiled and posted to SERDP's website along with fact sheets, following SERDP review.

3. Best Practices for Assessing the Effectiveness of PFAS Remediation Technologies

Several factors have a critical effect on the quality of research to assess PFAS treatment technology effectiveness. The project team identified the following best practices for PFAS treatment technology research:

- Use verified analytical methods for PFAS that are commonly analyzed;
- Use established research methods for PFAS precursors and other PFAS;
- Follow and document laboratory best practices for sample preparation and analysis;
- Include controls in the study design; and
- Account for statistical significance in study design and presentation of results.

Each of these best practices is described in this section with the overall goal of improving the quality of PFAS research and avoiding ambiguous outcomes.

3.1. For Commonly-Analyzed PFAS, Use Verified Analytical Methods

For analysis of drinking water samples, EPA Method 537.1 was released in November 2018 as an update to EPA Method 537. Both methods consist of solid phase extraction followed by LC-MS/MS. EPA is developing another drinking water method to target 25 shorter-chain PFAS (primarily PFAAs) and expects to have this method completed in November 2019 (Speth, 2019). EPA does not have an ongoing laboratory certification process for Methods 537 and 537.1. However, the International Organization for Standardization 17025 accreditation bodies and some states have accreditation processes for EPA Method 537 and/or Method 537.1. In December 2019, EPA published EPA Method 533, another method for analysis of PFAS in drinking water samples. Compared to EPA Method 537.1, EPA Method 533 focuses on shorter-chain PFAS and can be used to test for 11 additional compounds for a total of 29 PFAS. Together, these methods provide a basis for monitoring 29 PFAS in public drinking water systems nationwide under the Unregulated Contaminant Monitoring Rule (UCMR) 5 beginning in 2023.

For groundwater, soil, surface water and other media, several laboratories have developed their own analytical methods as modifications to EPA Methods 537 and 537.1. Because modified versions of Methods 537 and 537.1 have not undergone the type of systematic evaluations that have been conducted for the validated methods, they need to be critically assessed before being employed in a new context (e.g., analysis of samples that contain ions, organic compounds, or organic matter that is not usually present in drinking water). Because most SERDP and ESTCP projects include analyses of PFAS in matrices other than drinking water, researchers need to be vigilant about the potential for the accuracy and precision of the methods to be compromised by matrix effects. In August 2021, EPA finalized draft method SW-846 Test Method 8327 to analyze for 24 different PFAS in surface water, groundwater, or wastewater. This method did not include isotope dilution calibration and may lack the method sensitivity required to meet project objectives. Due to the lack of a marketplace need, many commercial laboratories did not invest resources to offer this PFAS analytical method. In September 2021, EPA and DoD published draft EPA Method 1633 for the analysis of 40 different PFAS in eight different media – wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. The method uses isotopically-labeled standards, similar to the modified methods that commercial laboratories have developed and documented in their standard operating procedures. Once EPA Method 1633 is finalized, commercial laboratories may begin offering it.

QA/QC protocols and guidelines for PFAS analysis in matrices other than drinking water are summarized in Table B-15 of the *Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*, version 5.4 (DoD, 2021). The DoD Environmental Laboratory Accreditation Program (ELAP) accredits PFAS laboratory methods for compliance with Table B-15 of QSM criteria. A DoD ELAP accredited method for PFAS analysis is preferred. The DoD maintains an online database of accredited laboratories. As of May 2019, 14 laboratories were listed as DoDELAP accredited for PFAS analyses (DENIX, 2019). In Spring 2019, the state of California required compliance with DoD QSM criteria for laboratories conducting PFAS analyses in response to statewide orders to assess PFAS occurrence at airports, landfills, and nearby drinking water wells.

3.2. Use Established Research Methods for PFAS Precursors and Other PFAS

Analytical methods are currently being developed and/or verified to quantify a larger number of PFAS in environmental samples in various matrices. Advanced analytical instruments are available at some academic institutions and government agencies to identify a greater number of PFAS than the analytes included in current EPA methods. Examples include the following:

- **Liquid chromatography with quadrupole time of flight mass spectrometry (LC-QTOFMS)**[1] can be used to evaluate both the chemical formula and structure of unknown PFAS in a sample. Unequivocal structural identification is not possible without analytical standards. This assessment is best used to understand the presence and estimated concentrations of PFAS precursors and transformationproducts other than the 24 analytes included in modified EPA Method 537.
- **Liquid chromatography and Orbitrap mass spectrometry (LC-Orbitrap MS)**[2] can be used for high resolution (i.e., low detection limit) targeted analysis of PFAS or non-targeted analysis to determine which PFAS are present in the sample, even if they lack analytical standards.
- **Gas chromatography and mass spectrometry (GC/MS)** can be used to analyze neutral and nonionic volatile PFAS, including FTOHs, perfluoroalkane sulfonamides, and perfluoroalkane sulfonamido ethanols.
- Total oxidizable precursor (TOP) assay is an increasingly common method for quantification of total polyfluorinated PFAS precursors (Houtz and Sedlak, 2012). Samples are exposed to hydroxyl radicals produced by thermal decomposition of persulfate at elevated pH values. Under these conditions, precursors to both PFCAs and PFSAs are converted to PFCAs. Provided that the amount of hydroxyl radicals is sufficient to transform the polyfluorinated alkyl substances into PFCAs, the difference between ≥C4 PFCA concentrations measured before or after oxidation corresponds to the concentration of PFCA precursors.

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[1] PFAS quantification by these instruments is still limited by a lack of high-quality analytical standards available for instrument calibration. In general, these instruments are not routinely used for quantification of chemicals in environmental samples. For target PFAS for which there are no internal standards, a decrease in PFAS concentrations cannot be directly measured and instead typically rely on presentation of peak area counts using mass spectrometry data.

[2] See footnote 1.

Several methods for quantifying the total mass of fluorine in samples are available. These methods may be useful for establishing fluorine mass balances and identifying the presence of PFAS that cannot be detected by validated methods. These methods include the following:

- **Extractable organic fluorine (EOF) assay** – The EOF assay employs combustion to convert PFAS into inorganic fluoride, which is subsequently quantified by IC. The EOF assay has been applied to sediments and soil (Yeung et al., 2013; Codling et al., 2014; Wang et al., 2013) following solid phase extraction, as well as aqueous matrices (Miyake et al., 2007; D'Agostino and Mabury, 2017). Because the detection limit for fluorine by IC is relatively high (e.g., 10 µg/L [Yeung et al., 2013]), this method is not appropriate for samples containing low concentrations of PFAS. This method detects all fluorine-containing compounds that exhibit an affinity for the extraction material and therefore, the EOF assay can include compounds that are not PFAS. This technique is not currently commercially available.
- **Adsorbable organic fluorine (AOF) assay** – Similar to the EOF assay, the AOF assay employs combustion and IC. However, rather than solid phase extraction, organic fluorine is sorbed to activatedcarbon. To date, the AOF assay has only been applied to water (Wagner et al., 2013; Willach et al., 2016; Dauchy et al., 2017; Bach et al., 2017). This technique is also not currently commercially available.
- **Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectroscopy** – Historically used to characterize organofluorine compounds, ^{19}F NMR spectroscopy has recently been used to quantify total organic fluorine (Guy et al., 1976). Because the NMR spectra can be analyzed in a manner that is selective for PFAS, it can be used to differentiate between PFAS and other fluorine-containing compounds. However, ^{19}F NMR spectroscopy has a relatively low sensitivity (e.g., 10 µg/L) and is not widely available. It has been used in at least one PFAS-related study relevant to impacted sites (Moody et al., 2001).
- **Particle induced gamma emission (PIGE) spectroscopy** – PIGE spectroscopy is a surface analysis technique used to measure elemental fluorine that is isolated on a thin surface. The technique consists of exciting ^{19}F nuclei (organic and inorganic) by an accelerated beam of protons (McDonough et al., 2019). Initially used in biological and medical applications, PIGE spectroscopy has been primarily used by PFAS researchers to assess the fluorine content of solids (e.g., consumer products). Its potential use for analysis of water and impacted soil is limited by its low sensitivity and the specialized nature of the instrumentation (i.e., PIGE spectroscopy is not readily available in most commercial or academic laboratories); however, PIGE has been used as a quantitative, high-throughput and inexpensive field screening analytical tool (Ritter et al., 2017).

3.3. Follow and Document Laboratory Best Practices for Sample Preparation and Analysis

Detailed guidelines for laboratory best practices are provided in Table B-15 of the DoD QSM criteria, version 5.3. Several examples of laboratory best practices for sample preparation are as follows:

- **Documentation –** Document media and analytes, equipment, supplies, homogenization and subsampling processes, preparation technique, clean-up procedures, sample preparation QC types and frequency, and sample extract storage and hold time requirements.

- **Sample transfer** – Transfer of samples from various containers should be minimized. This will limit potential analyte loss to sample bottles and to the atmosphere.
- **Sample filtration** – Filtration of samples is generally not recommended due to potential PFAS adsorption to filters. Turbid samples can be left allowed to settle or centrifuged and then decanted. Samples can also be sub-sampled, diluted, and then centrifuged and decanted.
- **Solid phase extraction** – Solid-phase extraction cartridge capacities should not be exceeded.
- **Materials** – PFAS sorb to many common laboratory materials, including glass and porous LDPE plastics, making it important to test laboratory materials as potential sinks and sources of PFAS and adopt laboratory practices such as whole-bottle extraction when possible. Laboratories should avoid potential cross-contamination with common laboratory materials, such as aluminum foil, if possible. More guidance on the measurable effects of common field and laboratory materials on PFAS is forthcoming from SERDP project ER19-1205 titled *Assessing and mitigating bias in PFAS levels during ground and surface watersampling*.

Several examples of laboratory best practices for sample analysis are as follows:

- **Documentation** – Document analytical equipment and supplies, type of standards utilized, calibration procedure, instrument cleanliness requirements (e.g., instrument blank criteria), calibration verification procedure, known interferences, and verification of numeric detection/ quantitation values. Documentation is typically in the form of SOPs followed by a research laboratory.
- **Isotope dilution standards and internal standards** – Appropriate, high-quality, internal standards and isotope-labeled PFAS standards should be used throughout the sample preparation process to assess potential analyte loss.
- **Analytical standards** – High-quality (i.e., high purity) analytical standards and stock solutions of PFAS should be used if they are available. The purity of a stock solution can be confirmed by laboratory analysis of starting materials and the use of control conditions to assess the potential presence of polyfluoroalkyl compounds that may degrade to form measurable PFAS transformation products during the laboratory study. Standards containing linear and branched isomers are only commercially available for some PFAS. The type of isomers used in the analysis should be reported. If PFAS standards are not available for purchase, results cannot be calibrated to concentrations but need to be reported as relative concentrations or estimated concentrations based on recovery of PFAS with known standards.
- **Field QC samples –** Analyze field blanks, equipment rinsate (decontamination) blanks, and field duplicates in order to assess the potential for artifacts related to sample contamination during sampling and sample handling.
- **Laboratory QC samples** – Analyze method blanks, laboratory control samples, and matrix spikes in order to assess accuracy (e.g., recovery) and precision.
- **Detection limit and/or quantitation limit** – Provide information to derive and validate reported detection limits and quantification limits for the various matrices included in a study. Detailed recommendations are included in Table B-15 of the DoD QSM criteria (DoD, 2021).

It is the nature of research to develop new methods and improve on existing methods. For example, to further evaluate all PFAS, DoD's SERDP released the Fiscal Year 2020 Statementof Need (SON) ERSON-20-C3 titled *Development of analytical methods to assess leaching and mobility of PFAS from soils, sediments, and solid wastes*. This SON states that SERDP is specifically looking for methods to address “solid waste, concrete, biosolids, emergency response wastes, and other materials of commerce.” Researchers should consult with SERDP and ESTCP PFAS project guidelines (SERDP & ESTCP, 2020) and updates to DoD QSM criteria (DoD, 2021) for the most up-to-date information.

3.4. Include Controls in the Study Design

In a laboratory setting, experimental elements other than the independent variables will ideally be kept constant throughout the study, especially if these elements may influence the effectiveness of the remedial technology (e.g., temperature, pH). Controls can be conducted to further screen out the effects of other test conditions. For example, a control may assess differences between test results using deionized water versus natural water to examine the potential effects of carbonate, organic carbon, or dissolved minerals. Whole-bottle analysis is less likely to be biased compared with the analysis of aliquots; sacrificial samples are therefore preferable from a study design perspective. If aliquots of samples will be collected, controls can also to incorporated to assess the effect of different mixing methods prior to analysis of aqueous-phase PFAS concentrations. Controlled elements should be measured, documented, and published along with other experimental data.

Controls can be used to differentiate between the purported mechanism and others. For example, laboratory studies of unbuffered thermally enhanced persulfate on PFAS degradation included controls acidified to the same low pH using sulfuric acid as well as heated controls (Bruton and Sedlak, 2018). In contrast, ozone was initially thought to be effective for PFAS destruction based on field test results that did not include controls for PFAS partitioning (Ross et al., 2018).

Two of the most overlooked controls are sorption controls and air-water interface controls. For example, PFAS can sorb or desorb from the solid phase with changes in pH (Pereira et al., 2018). pH changes can also affect the mechanisms governing treatment system performance. If treatment conditions facilitate the degradation of a NAPL co- occurring chemicals, PFAS can also be released from association with the NAPL, increasing aqueous-phase PFAS concentrations (McKenzie et al., 2016). PFAS can also concentrate to the air-water interface (Brusseau, 2018), and so a change inconditions leading to the formation of additional air-water interfacial area could masquerade as a loss process or lead to overestimations of the affinity of PFAS for solid phases. For this reason, controlled experiments are needed to assess the importance of these phenomena as possible explanations for PFAS loss (e.g., vacuum degassing of adsorbents prior to experiments to remove residual air [Meng et al., 2014]).

In a field environment, the opportunity to set up controls is more limited. For in situ treatment technologies, upgradient or background samples are typically collected to compare with samples from the target treatment zone. For ex situ treatment technologies, influent samples or samples from a split stream that is untreated are typically collected. Blank samples are collected to assess potential cross-contamination during field sampling and handling processes. Treatment study design may also be phased to provide an opportunity to assess the effect of multiple changes one at a time (e.g., monitoring following a heating phase prior to addition of chemical reagents).

Consideration of additional controls is warranted during field studies if PFAS treatment technologies have not been rigorously tested in the laboratory. Examples include controls to assess the presence and transformation of PFAS precursors during treatment, controls to assess the effect of PFAS dilution, displacement, sorption, or phase transfer, and the effect of key parameters such as changes in pH or temperature.

3.5. Account for Statistical Significance in Study Design and Presentation of Results

The statistical significance of study results is also an important consideration when designing and assessing results of a PFAS treatability research study.

- **Size of the data set** – When conducting a study, consideration should be given to the sample size. While a large and statistically significant sample size is ideal, economic and time limitations may inhibit the number of representative samples. The sample size of the study should be considered when study conclusions are made.
- **Sample replicates** – Working in duplicate, triplicate, or even quadruplicate can greatly increase the statistical significance and confidence in study results. Similar to sample size, economic and time constraints may limit the number of sample replicates. The fact sheet titled *Analytical Techniques and Laboratory Best Practices for PFAS* discusses the need for replicates to reduce data variability, particularly replicates of final data points and throughout an experiment when using field materials (e.g., aquifer solids).
- **Statistical analyses** – Statistical analyses can be used to assess whether PFAS removal is statistically significant, or whether it is within the range of uncertainty (e.g., analytical error). Basic relevant statistical analyses include standard deviations, confidence intervals (Student's *t*-Test), relative percent difference, and regression analyses (coefficient of determination).

A summary of best practices is provided in Table 3 for use as an evaluation checklist.

Table 3. Best Practices Evaluation Checklist

Checklist Item	Response (Yes, No, NA)	Notes/ Explanation
Use Verified Analytical Methods for PFAS that are Commonly Analyzed		
Were verified analytical methods used?		
Drinking water samples – EPA Method 537.1 or Method 533		
Other samples – PFAS by LC-MS/MS consistent with DoD QSM criteria Table B-15 or EPA Method 8328		
Other (describe under Notes/Explanation)		
Use Established Research Methods for PFAS Precursors and Other PFAS		
Were established research methods used?		
Liquid chromatography and quadrupole time of flight mass spectrometry (LC-QTOFMS)		
Liquid chromatography and Orbitrap mass spectrometry (LC-Orbitrap MS)		
Gas chromatography and mass spectrometry (GC/MS)		
Total oxidizable precursor (TOP) assay		
Extractable organic fluorine (EOF) assay		
Adsorbable organic fluorine (AOF) assay		
Fluorine-19 nuclear magnetic resonance (^{19}F NMR)spectroscopy		
Particle induced gamma emission (PIGE) spectroscopy		
Other (describe under Notes/Explanation)		
Follow and Document Laboratory Best Practices for Sample Preparation and Analysis		
Were criteria in DoD QSM Table B-15 followed?		
Sample preparation		

Checklist Item	Response (Yes, No, NA)	Notes/ Explanation
Documentation of sample preparation methods		
Minimal number of sample transfers from containers		
Settling or centrifuging in lieu of filtration		
Solid phase extraction cartridge capacities are not exceeded		
Materials are appropriate to minimize sorption/losses		
Sample analysis		
Documentation of analytical equipment, supplies, standards, calibration procedures, and more in a laboratory SOP		
Isotope dilution standards and internal standards were used toassess potential analyte loss		
High purity analytical standards and stock solutions		
Field QC samples including field blanks,equipment rinsate blanks, and field duplicates		
Laboratory QC samples including method blanks, laboratory control samples, and matrix spikes to assess accuracy andprecision		
Detection limit and/or quantitation limit provided		
SERDP & ESTCP PFAS projects		
Consult SERDP & ESTCP PFAS project guidelines (e.g., SERDP & ESTCP, 2020) for requirements for SERDP & ESTCP projects addressing PFAS-related issues		
Include Controls in the Study Design		
For laboratory studies, did the study include controls for the following?		
Differentiate between the purported mechanism and others		
Presence and transformations of PFAS precursors, if applicable		
PFAS sorption/desorption, if applicable		
PFAS volatilization, if applicable		
Changes in PFAS association with NAPL, if applicable		
Effect of PFAS partitioning to air/water interface, particularly at high concentrations		
PFAS accumulation on lab bottle surfaces and other equipment losses prior to extraction		
For field studies, did the study include controls for the following?		
Definition of upgradient, background conditions, or influent concentrations		
Field QC samples including field blanks, equipment rinsateblanks, and field duplicates		
Phased design to assess the effect of multiple changes one at atime		
Controls to assess the presence and transformation of PFAS precursors during treatment		
Controls to assess the effect of PFAS dilution, displacement, sorption, or phase transfer		
Effect of key parameters such as changes in pH or temperature		
Account for Statistical Significance in Study Design and Presentation of Results		
Does the size of the data set allow for statistically significant results?		
Were samples analyzed in triplicate or duplicate? Did laboratorystudies evaluate variability of results?		
Were statistical analyses performed and error bars provided? Are study results statistically significant?		
Have study results been confirmed or reproduced by others?		

4. Other Considerations for Assessing the Effectiveness of PFAS Remedial Technologies

A variety of other factors may impact the performance of PFAS remedial technologies. These considerations are typically evaluated after proof-of-concept has been established. There is typically a progression of technology development from laboratory proof-of-concept testing to full-scale field testing. During laboratory proof-of-concept testing, academic researchers, trained in the scientific method, design research studies to control for many external variables. For example, researchers will often try to eliminate variability by working with a simple matrix (e.g., ultrapure water spiked with high concentrations of PFOA and/or PFOS). If a treatment technology is successful in treating PFAS under simplified conditions, researchers will then conduct follow up experiments to evaluate technology effectiveness under environmentally relevant conditions.

Other factors that are relevant for assessing the performance and further consideration of PFAS treatment includes the following:

- Effect of PFAS mixtures, concentrations, co- occurring chemicals, and other water qualityparameters;
- Long-term treatment system performance;
- Generation of harmful byproducts; and
- Value relative to other available technologies.

An evaluation of these factors is needed as technology development progresses in order to foresee limitations to the technology applications and identify conditions under which treatment will be effective.

4.1. Effect of PFAS Mixtures, Concentrations, Co-Occurring Chemicals, and Other WaterQuality Parameters

4.1.1. *PFAS Mixtures*

Because PFAS were often manufactured and used as mixtures, multiple PFAS are typically present in samples collected from impacted environments. To gain insight into the potential for applying the technology, research is needed on the effect of PFAS mixtures on treatment efficacy. For example, PFAS can compete for the same active sites on GAC and ion exchange resins (Crimiet al., 2017; Rahman et al., 2014; Maimaiti et al., 2018). PFAS also can compete with each other during in situ chemical oxidation (ISCO) (Dombrowski et al., 2018). The transformation of one PFAS may result in the production of another (e.g., oxidation of polyfluoroalkyl substances to a shorter-chain perfluoroalkyl substance).

Researchers studying PFAS mixtures often use dilute solutions of AFFF as a surrogate for a complex PFAS mixture found in the environment. When using AFFF, it is important to specify the manufacturer and the year of production because the relative amounts of PFAS in AFFF vary considerably (Backe et al., 2013). Other AFFF components, such as the solvent diethylene glycol butyl ether (also known as butyl carbitol) (Pabon and Corpart, 2002) or hydrocarbon surfactants (Garcia et al., 2019) are not typically measured at field sites and may impact experimental systems. For example, butyl carbitol is known to support reductive dechlorination of trichloroethene (Harding-Marjanovic et al., 2016).

To properly interpret results from studies conducted with AFFF or other mixtures of PFAS, it is important to quantify the “hidden” mass of PFAS precursors that were present prior to and after treatment. Researchers can assess polyfluoroalkyl precursors as well as the identity of transformation products. In these types of studies, researchers often attempt to close the fluorine mass balance by tracking the mass of fluorine present as measurable PFAS compounds, PFAS precursors (e.g., measured with the TOP assay) and inorganic fluoride. When the mass balance cannot be closed (i.e., when PFAS compounds removed from the impacted matrix cannot be recovered or accounted for by quantifying precursors or fluoride, it may be necessary to use more specialized analytical techniques, such as LC-QTOFMS, to identify transformation products.

4.1.2. *PFAS Concentrations*

Another factor for PFAS treatment effectiveness is the range of PFAS concentrations evaluated. Treatment may work at high PFAS concentrations and be less effective at low concentrations or vice versa. Following proof-of-concept testing, researchers typically evaluate treatment performance at environmentally relevant PFAS concentrations (i.e., µg/L or microgram per kilogram [µg/kg] concentrations in source zone soils and nanogram per liter concentrations in drinking water).

Because treatment kinetics, mechanisms, and overall effectiveness can vary with PFAS concentrations, technologies should be tested at environmentally relevant PFAS concentrations (i.e., µg/L or µg/kg for remediation technologies). Sometimes laboratory detection limits require higher PFAS concentrations to be used (i.e., in order to measure fluoride release and present a fluoride mass balance). Studies conducted early on in a treatment technology’s development may also employ higher PFAS concentrations. Micelle formation and aggregate behavior have been observed at concentrations below the critical micelle concentration and have the potential to affect measured aqueous-phase concentrations. Early studies of a technology may be conducted with extremely high reagent concentrations or high radiation doses/energy usage. These studies need to be followed by studies at environmentally relevant concentrations to demonstrate proof-of-concept.

4.1.3. *Co-Occurring Chemicals*

Co-occurring chemicals are present at many PFAS sites due to the use of AFFF for firefighting or historical practices at firefighter training areas. AFFF contains a variety of organic compounds in addition to PFAS (e.g., butyl carbitol, hydrocarbon surfactants). At airports or firefighter training facilities chlorinated solvents and/or hydrocarbons and/or methyl tertiary-butyl ether may also be present as co-occurring chemicals. Sometimes PFAS remediation technologies will address these co-occurring chemicals; for other processes, co-occurring chemicals may interfere with or complicate the remedial approach. For example, co-occurring chemicals may compete for GAC sorption, especially if they are present at much higher concentrations than PFAS or have a stronger affinity for GAC. The co-occurring chemicals can also affect microbial communities or act as scavengers of oxidants and reductants during chemical treatment.

Although PFAAs are recalcitrant with respect to microbial degradation, they can affect microbial activity or have toxic effects on bacterial communities. For example, Harding (2014) showed that the presence of PFAS inhibited trichloroethene dechlorination and that inhibition was a result of PFAS structure (i.e., high concentrations of PFCAs but not PFSAs) and PFAS concentration.

4.1.4. *Other Water Quality Parameters*

Temperature

Environmental remedial technologies are typically tested and implemented at ambient temperatures. However, due to the high stability of PFAS, matrices may be heated to accelerate the rates of chemical reactions. Similarly, temperatures in the subsurface or in surface waters are often considerably lower than those studied in the laboratory. Equilibrium partitioning of PFAS and rates of mass transfer are impacted by temperature; consequently, the effectiveness of many remedial technologies may be affected by temperature. Bench-scale evaluations are typically conducted at the anticipated field-scale temperature and yield data to assess the technical and economic feasibility of field-scale treatment. For GAC, advanced oxidation, and bioremediation of polyfluorinated substances, treatment efficacy generally increases with temperature due to a higher diffusion rate, number of active sorption sites, and/or bioactivity (Qian et al., 2017; Liu et al, 2017; Bruton and Sedlak, 2018; Yin et al., 2016). For reverse osmosis and nanofiltration, separation decreases to a small degree at higher temperatures. PFAS volatilization will occur to a greater extent at elevated temperatures, underscoring the need for researchers to account for volatilized PFAS mass as part of study design (Bruton and Sedlak, 2018).

pH

Groundwater pH can vary significantly from one site to another, depending on naturally occurring geochemical characteristics and historical releases. Groundwater pH can also be altered intentionally to enhance the treatment process or as a result of treatment (e.g., batch studies of remedial methods including ISCO or bioremediation). Buffers may need to be added to avoid generating extreme pH conditions that may be harmful. For example, boron-doped diamond electrodes will degrade at high pH values (Lin et al., 2018). At neutral pH values, most PFAAs are strong acids and are present as anions. Several examples of the impact of pH on treatment effectiveness are presented below:

- **Sorption** – PFAS sorption is affected by hydrophobic and electrostatic interactions, which vary greatly with pH. Under acidic pH conditions, PFAAs have a greater affinity to the negatively charged surfaces of GAC and other sorbents (e.g., RemBind). Sorbentcharacteristics such as the pH point of net zero charge are also important to consider.Published pKa values for PFAAs vary over several orders of magnitude, from -0.1 toapproximately 2.8 (Liu et al., 2017). Researchers have suggested that PFAS-cation complexes may form at low pH and facilitate PFAS sorption to negatively charged GAC surfaces (Du et al., 2014).

- **Ion exchange** – The effectiveness of ion exchange resins can also vary with pH, although it is a function of the type of resin. Maimaiti et al. (2018) reported that a change in pH altered both the properties of the ion exchange resin (IRA910 with quaternary ammonium functional groups) and PFAS, resulting in pH-independent sorption. Dudley et al. (2015) reported that weak base anion exchange resins were expected to perform more effectively at lower pH values. Variations within the typical range of drinking water treatment pH (6 to 9) is not expected to affect PFAS removal rates by ion exchange (Rahman et al., 2014).

- **Reduction** – The kinetics of chemical reduction has been shown to be a function of pH as well as carbon chain length (Liu et al., 2017). Studies on the reductive photolysis of PFOA using ultraviolet radiation in the presence of iodide indicated a strong effect of pH on degradation with the highest efficiency achieved at pH above 8.0. The concentration of hydrated electrons increased with pH (Qu et al., 2014). Wang and Zhang (2014) also documented the effect of pH on PFOA degradation by hydrated electrons.

- **Oxidation** – Heat-activated persulfate has been shown to be effective in mineralizing PFCAs as well as PFAA precursors, but only under acidic conditions (pH ≤ 3) (e.g., Bruton and Sedlak, 2018) due to the protonation of PFAA species under highly acidic pH conditions.

Dissolved Ions/Ionic Strength

Ionic strength is another variable that may affect PFAS treatment (Zhang et al., 2019). For example, PFAS sorption onto powdered activated carbon has been shown to decrease in ultrapure water when ionic strength was increased from 0.002 to 0.02 (Dudley, 2012; Dudley et al., 2015). Dissolved anions can block or occupy sites on GAC or ion exchange resins, reducing treatment effectiveness for PFAS. Specifically, chloride, bromide, sulfate, and nitrate have been shown to sorb to GAC, reducing the time before breakthrough (Kirisits et al., 2000). Electrolyte ions can also affect adsorption equilibrium as well as kinetics. Redox conditions (i.e., concentrations of oxygen and other electron acceptors) will affect PFAS biotransformation processes (e.g., Yi et al., 2018).

Dissolved anions can also react with oxidants and reductants that are produced with the intention of transforming PFAS. Chloride, which is one of the anions typically present at the highest concentrations in natural waters, reduces treatment efficacy by scavenging oxidants or reductants. Chloride can lower the efficacy of treatments that rely upon sulfate radicals (e.g., Bruton and Sedlak, 2018) as well as electrochemical processes, decreasing rates by <20% (Schaefer et al., 2017). The efficacy of electrochemical processes is also affected by ionic strength due to the role of dissolved ions in electron migration. Therefore, electrochemical treatment technologies should consider the role of ionic strength and the nature of the ions (e.g., experiments conducted in a 0.1 molar sodium sulfate solution may exaggerate the efficiency of an electrochemical treatment process intended for impacted groundwater).

With the exception of water that has undergone treatment to remove dissolved ions (e.g., reverse osmosis), all PFAS-impacted water will contain dissolved ions. As a result, experiments conducted to assess treatment technologies should include representative concentrations of the types of salts likely to be present in the water that the technology is designed to treat.

Dissolved Organic Matter

Dissolved organic carbon (DOC) may also affect treatment system performance. For sorption, McCleaf et al. (2017) described the effect of 1.8 milligrams per liter DOC in drinking water on the removal efficiency using Filtersorb 400 GAC and ion exchange column studies using Purolite resin A600. McCleaf et al. (2017) found a poor correlation between DOC concentrations and PFAS removal efficiency. Appleman et al. (2014) reported a beneficial effect of DOC loading on PFAS treatment as agglomeration of PFAS was apparently facilitated by loading the column with DOC. DOC can also affect the efficacy of treatment processes involving PFAS transformation by serving as a sink for oxidants or reductants, screening ultraviolet light or adsorbing onto the surfaces of electrodes or catalysts. Because natural waters contain some DOC, DOC should be added to any "synthetic" groundwater created and used in laboratory experiments.

Aquifer Soils (In Situ Technologies)

For in situ technologies, treatability studies are typically conducted using a groundwater/solid slurry. Ideally, the same study would be repeated using a variety of matrices. During pilot- and full-scale testing, the site-specific groundwater and other matrices should be well-characterized in order to define operational conditions.

4.2. Long-Term Treatment System Performance

Robust studies consider and evaluate the long-term effects of treatment on PFAS concentrations, therefore providing more confidence in treatment system reliability, frequency of treatment system maintenance, and long-term cost and performance. Examples of research to assess long-term treatment efficacy include the following:

- **Rapid column tests** – Laboratory-scale rapid column tests can be conducted to evaluate the performance of GAC and other adsorbents, ion exchange resins, chemical reduction methods, and photocatalysis methods over time. Results can be used to estimate the number of bed volumes prior to PFAS breakthrough or demonstrate the reliability of PFAS sequestration or destruction during long-term operation.

- **Controlled testing under various conditions** – Long-term effectiveness can also be evaluated by conducting laboratory tests under conditions that are representative of potential future conditions. Examples of controlled test conditions might include increasing the flow rate, altering the PFAS loading rate, adding reagents present in natural waters to simulate mineral deposition onto surfaces (Zhang et al., 2018), and leaching studies to simulate the effect of rainfall on treated soils (e.g., Sörengård et al., 2019).

- **Long-term experiments** – Long-term experiments are not typically conducted in the laboratory or at full-scale to assess PFAS degradation and technology effectiveness over time, presumably due to the limited number of in situ remediation technologies for PFAS as well as their unregulated status. Long-term experiments (e.g., five years) have been conducted to assess PFAS leaching and uptake by plants (e.g., Stahl et al., 2013), and fate after accidental release (e.g., Awad et al., 2011).

4.3. Generation of Harmful Byproducts

The formation of other (non-PFAS) treatment transformation products depends on the type of technology being evaluated. Formation of secondary transformation products may not be identified during initial proof-of-concept technology testing that uses simplified matrix such as PFAS-spiked deionized water. A more comprehensive water quality profile is needed during bench-scale treatability studies and may be site-specific. Several examples from published PFAS literature are as follows:

- Formation of perchlorate using electrochemical treatment (e.g., Trautmann et al., 2015; Schaefer et al., 2018),

- Release of lead from electrochemical treatment of PFAS using lead oxide anode materials (e.g., Niu et al., 2016; Fang et al., 2019), and

- Metals mobilization during in situ persulfate treatment (Bruton and Sedlak, 2018; Gardner et al., 2015).

4.4. Value Relative to Other Available Technologies

Treatability studies or other laboratory studies can be used to estimate chemical doses, energy requirements, and other information that can be used to inform an assessment of the feasibility and practicality of a field application. Examples of factors to consider during technology development in the laboratory includes the following:

- Feasibility of field application (e.g., dosing, energy requirements, reagent quantities, health and safety requirements);
- Number of sites where the technology may be viable/applicable; and
- Potential cost advantage/cost-competitiveness relative to other existing technologies.

Note that there is typically little empirical basis for assessing technology cost-effectiveness prior to a field demonstration. Even after technologies have been field-tested, cost-effectiveness of a remedial technology is highly site-specific.

A summary of these criteria is provided in **Table 4**.

Table 4. Other Considerations to Demonstrate Field Readiness of a PFAS RemedialTechnology

Checklist Item	Response (Yes, No, NA)	Notes/ Explanation
Effect of PFAS Mixtures, Concentrations, Co-Occurring Chemicals, and other Water Quality Parameters		
Were the following factors evaluated to determine their effect on treatment technology performance?		
PFAS mixtures (If AFFF, specify manufacturer and date)		
PFAS concentrations, including environmentally relevant ranges (e.g., µg/L or µg/kg). These studies may supplement earlier ones conducted at higher PFAS concentrations		
Common co-occurring chemicals (chlorinated solvents, hydrocarbons)		
Other water quality parameters		
Temperature		
pH		
Dissolved ions/ionic strength		
Dissolved organic matter		
Aquifer soils (for in situ technologies)		
Other factors that may affect technology performance, based on understanding of the technology mechanism		
Did laboratory studies evaluate matrix effects?		
Assess the effect of natural water matrix (i.e., carbonate, minerals, organic carbon) versus deionized water only		
Assess turbid samples or soil/groundwater slurries		
Assess a variety of matrices		
Were laboratory study conditions environmentally relevant?		
Long-Term Treatment System Performance		
Do studies to date assess long-term treatment system performance?		

Checklist Item	Response (Yes, No, NA)	Notes/ Explanation
Have rapid column tests been performed, if appropriate?		
Has controlled testing to model potential future conditions been performed, if appropriate (e.g., mineral deposition onto surfaces, leaching studies)?		
Have long-term experiments been performed, if appropriate?		
Generation of Harmful Byproducts		
Formation of perchlorate?		
Release of metals?		
Other: ____		
Value Relative to Other Available Technologies		
Feasibility of field application (e.g., dosing, reagent quantities, energy requirements)?		
Health and safety requirements.		
Number of sites where the technology may be viable/applicable.		
Potential cost advantage/cost competitiveness relative to other existing technologies.		

The choice of technology for a specific site is typically made based on criteria such as technology performance, short-term and long-term effectiveness, regulatory acceptance, cost, and other factors. Several additional considerations for evaluating and selecting a full-scale PFAS treatment technology are as follows:

- Complementary nature/synergy with other site processes and operations;
- Effectiveness in meeting project objectives;
- Demonstrated reliability of long-term operation;
- Basis for assessing technology life-cycle impacts;
- Basis for assessing site-specific capital and operating and maintenance costs; and,
- Potential cost advantage/cost-competitiveness relative to other existing technologies.

The goal of full-scale treatment studies is to effectively treat PFAS in a cost-effective manner over the long-term (technology lifetime). Full-scale data is used to demonstrate treatment effectiveness and reliability for PFAS treatment and to identify opportunities to improve technology design and cost-effectiveness. The goals of full-scale operation are typically focused on/driven by the particular site. However, data from multiple full-scale systems that operate effectively at different sites lead a technology to be considered proven. A secondary goal regarding full scale treatment from the perspective of R&D is the collection/synthesis of data from multiple sites to facilitate technology design and performance assessment at other sites.

Practitioners who are facing this decision can use a support tool that is currently being developed under a separate SERDP project titled *Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Per- and Polyfluoroalkyl substances (PFASs) in Groundwater* (SERDP project ER18-5053). The objective of this project is to provide tools for an unbiased assessment of various PFAS treatment technologies in order to compare emerging and established PFAS treatment approaches using a life cycle assessment and life cycle cost analysis. The project team is developing a comprehensive assessment framework, generating a PFAS treatment efficiency database, and developing a decision support tool.

5. Conclusions and Implications for Future Research and Implementation

In summary, this project developed lines of evidence to assess the effectiveness of PFAS treatment technologies. Because new PFAS treatment technologies are being brought to market or tested without adequate documentation to demonstrate successful treatment, these criteria can be used to standardize the review of technology effectiveness and inform conclusions about technology effectiveness, knowledge gaps and priorities for further testing. Best practices for assessing PFAS treatment technologies were developed in consultation with PFAS researchers and technology developers. The following lines of evidence were developed with input from PFAS researchers, technology developers, and practitioners:

- Decrease in target PFAS concentrations;
- Treatment kinetics and plausible mechanism identified; and
- PFAS treatment transformation products have been identified and quantified.

In addition, best practices were identified for evaluation of PFAS treatment technology performance:

- Use verified analytical measures for PFAS that are commonly analyzed;
- Use established research methods for PFAS precursors and other PFAS;
- Use and document laboratory best practices for sample preparation and analysis;
- Include controls in the study design; and
- Account for statistical significance in study design and presentation of results.

Other factors were identified that are relevant for assessing the performance and further consideration of PFAS treatment technologies:

- Effect of PFAS mixtures, concentrations, co- occurring chemicals, and other water quality parameters;
- Long-term treatment system performance;
- Generation of harmful byproducts; and
- Value relative to other available technologies.

This project provides technology evaluators with guidelines, checklists, best practices, and metrics for evaluating the effectiveness of PFAS treatment technologies. Fact sheets were prepared to elaborate on each of the five lines of evidence. A technology evaluation checklist (Table 3) was prepared to allow technology evaluators to summarize the current state of knowledge based on previous research studies and peer-reviewed publications. Table 4 can help a technology evaluator determine the readiness level of a given technology, e.g., whether a technology is ready to advance from the laboratory to the field and data gaps that may need to be filled prior to demonstrating proof-of-concept or providing a site-specific basis for field implementation.

Project deliverables were developed cooperatively with academic researchers, technology developers, and practitioners. Workshops were conducted to discuss and vet preliminary lines of evidence and solicit feedback on draft deliverables. Beta testing of lines of evidence was conducted using specific technologies as examples. Outreach will continue to be conducted to encourage the adoption and broader application of this guidance by stakeholders. Any suggested improvements to the draft decision tools will be incorporated into downloadable spreadsheet tools that will be posted separately on SERDP and ESTCP's website along with fact sheets summarizing each line of evidence. Case studies of technologies tested using the spreadsheet tools will also be posted on SERDP and ESTCP's website as examples that can be used as a starting point for technology evaluators and updated over time. A decision support tool is also being developed under a sister SERDP project ER18-5053 titled *Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Per- and Polyfluoroalkyl substances (PFASs) in Groundwater*.

This guidance provides SERDP and ESTCP and other organizations with tools to communicate expectations for demonstrating the effectiveness of PFAS treatment technologies. This guidance provides researchers with evaluation criteria that can inform research and demonstration plans, as well as inform feedback provided by technology reviewers and strengthen research plans and study designs, improving return on investment.

The guidance will ultimately help DoD site managers and contractors by providing them with accurate and more complete information about the effectiveness of remedial technologies for PFAS, resulting in more realistic treatment expectations. This project will therefore aid DoD and others with site management and accelerate the development of promising technologies for PFAS remediation.

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