REPORT

Summary Report: Strategic Workshop on Management of PFAS in the Environment

NOVEMBER 2022

SERDP ESTCP

DISTRIBUTION STATEMENT A
This document has been cleared for public release.

TABLE OF CONTENTS

List of Tables

Appendices

LIST OF AUTHORS

Andrea Leeson, Ph.D.
SERDP & ESTCP

David Adamson, Ph.D.
GSI Environmental Inc.

Lisa Alvarez-Cohen, Ph.D.
University of California, Berkeley

Hunter Anderson, Ph.D.
Air Force Civil Engineer Center

Frank Barranco, Ph.D.
EA Engineering, Science, and Technology

Christopher Bellona, Ph.D.
Colorado School of Mines

Jens Blotevogel, Ph.D.
Colorado State University

Mark Brusseau, Ph.D.
University of Arizona

Michelle Crimi, Ph.D.
Clarkson University

Brian Crone
U.S. Environmental Protection Agency

Rula Deeb, Ph.D.
Geosyntec Consultants

Dominic Di Toro, Ph.D.
University of Delaware

Craig Divine, Ph.D.
Arcadis

Jennifer Field, Ph.D.
Oregon State University

Rajat Ghosh, Ph.D.
Alcoa

Philip Gschwend, Ph.D.
Massachusetts Institute of Technology

Jennifer Guelfo, Ph.D.
Texas Tech University

Paul Hatzinger, Ph.D.
APTIM

Damian Helbling, Ph.D.
Cornell University

Heather Henry, Ph.D.
National Institute of Environmental Health Sciences

Christopher Higgins, Ph.D.
Colorado School of Mines

Peter Jaffe, Ph.D.
Princeton University

Detlef Knappe, Ph.D.
North Carolina State University

Paul Koster van Groos, Ph.D.
APTIM

Linda Lee, Ph.D.
Purdue University

Jinxia Liu, Ph.D.
McGill University

Shaily Mahendra, Ph.D.
University of California, Los Angeles

Carrie McDonough, Ph.D.
Stony Brook University

Selma Mededovic, Ph.D.
Clarkson University

Marc Mills, Ph.D.
U.S. Environmental Protection Agency

Charles Newell, Ph.D.
GSI Environmental Inc.

Carla Ng, Ph.D.
University of Pittsburgh

Dung (Zoom) Nguyen
CDM Smith

Bonnie Packer, Ph.D.
Army National Guard

Cara Patton
Noblis

Graham Peaslee, Ph.D.
University of Notre Dame

Kurt Pennell, Ph.D.
Brown University

Jovan Popovic, Ph.D.
Naval Facilities Engineering and Expeditionary Warfare Center

Philip Potter, Ph.D.
U.S. Environmental Protection Agency

Joseph Quinnan
Arcadis

Maya Rabinowitz
Noblis

Jessica Reiner, Ph.D.
National Institute of Standards & Technology

Stephen Richardson, Ph.D.
GSI Environmental Inc.

Charles Schaefer, Ph.D.
CDM Smith

David Sedlak, Ph.D.
University of California, Berkeley

Erin Shields, Ph.D.
U.S. Environmental Protection Agency

Jason Speicher
Naval Facilities Engineering Systems Command Atlantic

Thomas Speth, Ph.D.
U.S. Environmental Protection Agency

Timothy Strathmann, Ph.D.
Colorado School of Mines

Hans Stroo, Ph.D.
Stroo Consulting LLC

Timothy Thompson
SEE LLC

Paul Tratnyek, Ph.D.
Oregon Health & Science University

Janice Willey
Naval Sea Systems Command

ACRONYMS

AEC	anion exchange capacity
AFFF	aqueous film-forming foam
BCF	bioconcentration factor
BTEX	benzene, toluene, ethylbenzene, and xylenes
CAC	colloidal activated carbon
CIC	combustion ion chromatography
CSM	conceptual site model
DOC	dissolved organic carbon
DoD	Department of Defense
DOM	dissolved organic matter
ECD	electron capture detector
EDX	energy-dispersive X-ray spectroscopy
ELAP	Environmental Laboratory Accreditation Program
EPA	Environmental Protection Agency
EPS	extracellular polymeric substances
ESTCP	Environmental Security Technology Certification Program
EU	European Union
FRTR	Federal Remediation Technologies Roundtable
FTIR	Fourier transform infrared
GAC	granular activated carbon
GC	gas chromatography
GC/LC-HRMS	gas and liquid chromatography-high resolution mass spectrometry
HAL	Health Advisory Level
HALT	hydrothermal alkaline treatment
HRMS	high-resolution mass spectrometry
IDW	investigation-derived waste
ITRC	Interstate Technology and Regulatory Council
IX	ion exchange
LC-MS/MS	liquid chromatography with tandem mass spectrometry
LEAF	Leaching Evaluation Assessment Framework
LOQ	limits of quantification
LSER	linear solvation energy relation
MCDA	multi-criteria decision analysis
MGP	manufactured gas plant

MIL-SPEC	U.S. military specification
MTBE	methyl tert-butyl ether
NDAA	National Defense Authorization Act
NMR	nuclear magnetic resonance
O&M	operation and maintenance
OTM	Other Test Method
PAC	powdered activated carbon
PA/SI	Preliminary Assessment/Site Inspection
PChPs	physical-chemical properties
PEARL	Pesticide Emission Assessment at Regional and Local scales
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate
PFCA	perfluoroalkyl carboxylates
PFHxS	perfluorohexane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFSA	perfluoroalkyl sulfonate
PID	product of incomplete destruction
PIGE	particle-induced gamma emission
POE	point-of-entry
pp-LFER	polyparameter linear free energy relation
ppt	part(s) per trillion
PRZM	Pesticide Root Zone Model
PTFE	polytetrafluoroethylene
QPL	Qualified Products List
QSAR	quantitative structure activity relationship
RI	Remedial Investigation
RPM	remedial project manager
RSSCT	rapid small-scale column test
SCWO	supercritical water oxidation
SERDP	Strategic Environmental Research and Development Program
SPLP	Synthetic Precipitation Leaching Procedure
SVOC	semi-volatile organic compounds
TCLP	Toxicity Characteristic Leaching Procedure
TDS	total dissolved solids
TFA	trifluoroacetic acid
TOC	total organic carbon

TOF	total organic fluorine
TS	total solids
VOC	volatile organic compound
XRD	X-ray diffraction

1.0 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) have been widely detected in soils and waters throughout the United States (U.S.). The majority of PFAS detections at U.S. Department of Defense (DoD) facilities are associated with the use of aqueous film-forming foam (AFFF) formulations to extinguish fuel-based fires since the 1970s. As a result of training and fire suppression, the DoD may have thousands of sites impacted by PFAS, with a current estimated cost for managing these sites of approximately $2 billion.

The AFFF mixtures used by the DoD contained significant quantities of perfluorooctane sulfonate (PFOS) and related perfluoroalkyl sulfonates such as perfluorohexane sulfonate (PFHxS), as well as a suite of other PFAS. In 2016, the U.S. Environmental Protection Agency (EPA) issued drinking water Health Advisory Levels (HALs) for PFOS and perfluorooctanoic acid (PFOA), both of which have been found at AFFF-impacted sites. The 2016 HAL was 70 parts per trillion (ppt or ng/L) for the sum of PFOS and PFOA in drinking water or either compound individually. In June 2022, the EPA released updated HALs for PFOS and PFOA, and added HALs for perfluorobutane sulfonic acid (PFBS) and GenX chemicals. The current HAL is 0.004 ppt for PFOA, 0.02 ppt for PFOS, 10 ppt for GenX chemicals, and 2,000 ppt for PFBS in drinking water. In addition, numerous states have begun to promulgate their own drinking water standards. PFOS and PFOA advisory levels are sufficiently low that large volumes of groundwater exceed these criteria by several orders of magnitude at many sites.

Due to their chemical structure, many PFAS (especially perfluoroalkyl acids [PFAAs] such as PFOA and PFOS) are stable in the environment and resistant to treatment by biodegradation, direct photolysis, and hydrolysis. However, some PFAS, notably the polyfluoroalkyl compounds, can be transformed in the environment, producing PFOA and PFOS, as well as other PFAAs. Complicating the understanding of PFAS fate and transport in the environment is the varying composition of AFFF depending on the manufacturer, formulation, and date of manufacturing. AFFF manufactured by 3M is known to have contained PFOS and other perfluoroalkyl sulfonates (PFSAs) such as PFHxS. Multiple formulations of AFFF were commonly used at any given DoD site over the years. Both PFOS and PFOA are relatively soluble, migrate readily in groundwater, and therefore are capable of forming large and dilute groundwater plumes. The stability of PFAAs (particularly the PFSAs) limits the effectiveness of in situ treatment approaches. Thus, ex situ treatment using granular activated carbon (GAC) or other media are commonly used and then these media must be disposed securely. As a result, management of AFFF-impacted sites can be very costly.

Reducing the magnitude of the DoD's legacy PFAS liability will require a sustained effort to identify the best technologies to characterize, treat, and manage these sites. The DoD initiated preliminary assessments and site inspections (PA/SIs) at nearly all of their U.S. facilities in 2017 to determine the extent of PFAS impacts; Remedial Investigations (RIs) have subsequently begun at a number of DoD sites. Efficient and meaningful investigations will require significant improvements in the current understanding of PFAS behavior in the environment, as well as improvements in sampling and analytical methods for PFAS. A substantial fraction of the impacted sites will likely require treatment. Given the recalcitrance and complexity of PFAS, as well as the low cleanup levels likely to be required, advances in current treatment technologies are needed to improve effectiveness and greatly reduce costs (Newell et al., 2022).

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) have been funding research on PFAS for several years, to improve PFAS analytical methods and AFFF site characterization, to understand ecotoxicological effects, to develop tools for assessing the fate of PFAS in the subsurface, and to develop and validate in situ and ex situ treatment technologies. Descriptions of all projects addressing PFAS issues that have been funded under SERDP and ESTCP can be found at https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs.

To provide strategic guidance for future research and demonstrations on management and treatment of AFFF-impacted sites, SERDP and ESTCP conducted a workshop on March 29-30, 2022 in Chicago, IL. The objectives of the workshop were as follows: (1) to review the current state of the science regarding PFAS in the environment; (2) to evaluate currently available and developing characterization and treatment technologies; (3) to identify research and demonstration needs to improve our ability to manage and treat PFAS effectively in the environment, ultimately reducing site management costs; and (4) to determine methods to improve the dissemination and transfer of these new technologies to the user communities.

2.0 METHODS

The workshop was attended by approximately 60 invited personnel, representing DoD remedial project managers (RPMs), federal and state regulators, engineers, researchers, industry representatives, and consultants. The agenda for the workshop is provided in Appendix A, and the attendee list is provided in Appendix B. A steering committee composed of representatives from the various sectors assisted SERDP and ESTCP in defining the meeting's scope and format.

The agenda was designed to identify the most pressing needs in a focused manner, while ensuring that all participants could express their views. The workshop opened with several presentations that summarized efforts to address research and demonstration needs at sites impacted by PFAS, as well as provide insight into the status of the DoD's and EPA's efforts to manage PFAS at these sites.

Two breakout sessions, each with five working groups, were conducted to facilitate discussions of the current state of the science of management of PFAS-impacted sites. Working group participants discussed several aspects of PFAS management and response at DoD sites, including specific tools, demonstrations, and/or information transfer that would facilitate more cost-effective PFAS management and response. The five working groups covered the following PFAS-related areas: (1) fate and transport; (2) sampling and analysis; (3) thermal treatment technologies; (4) non-thermal destructive treatment technologies; and (5) concentration technologies.

On Day 1, each working group addressed overall focus questions as well as topic-specific charges for their group. Key questions were formulated by the SERDP and ESTCP, as well as the steering committee, with input from some attendees. Working groups identified key research, demonstration, and technology transfer needs to improve the overall management of PFAS-impacted sites. The overall focus questions, which were provided in advance to the participants, were as follows:

- What is the current state of the science regarding PFAS-impacted matrices?
- What are the major opportunities to improve management of PFAS-impacted sites?
- What are the most promising technologies and advances in PFAS characterization and treatment?
- What are the key research and demonstration needs over the next five years?

The second breakout session built on the first by prioritizing the identified research, demonstration, and technology transfer needs. Needs were prioritized as either critical or high priority, largely based on the sequence of events required to improve DoD site management within 3 to 5 years of initiating research and demonstrations (Table 1).

The entire group then participated in a final discussion to select critical and high priority research, demonstration, and technology transfer needs. Following the meeting, several participants contributed to written sections of this report describing specific issues and needs.

Table 1. Definition of Need Prioritization

	Critical	High
Research	Research that potentially could have a significant impact on cost-effective management of PFAS-impacted sites.	Research that cannot be initiated or clearly defined until critical research needs are addressed.
Demonstration	Field demonstrations or assessments that can improve cost-effective management of PFAS-impacted sites.	Field demonstrations or assessments that cannot be implemented until critical demonstrations or assessments are completed.
Technology Transfer	Specific actions or documents that could be undertaken immediately to promote technology transfer of key concepts or technologies.	Actions or documents that should be undertaken to promote technology transfer of key concepts or technologies once specific research and/or demonstrations have been completed.

3.0 DATA NEEDS OVERVIEW

In the following sections, each of the needs identified by the breakout groups is described in more detail and is assigned a priority, either high or critical. Provided in Table 2 is a top-level summary of the identified needs. A substantial number of research needs were identified, indicative of the complexity of addressing PFAS in the environment; however, as technologies are further developed, there is a clear need for additional efforts in field demonstrations.

A small number of technology transfer needs were identified, primarily associated with developing summaries and decision guides based on the available research and demonstrations to date. As the research progresses, such technology transfer needs will increase.

Table 2. Summary of Identified Research, Demonstration, and Technology Transfer Needs
(C- Critical Priority; H = High Priority)

Fate and Transport Needs		
Determine physical-chemical properties of PFAS by measurement and predictive modeling to support assessments of PFAS fate, transport, bioavailability, and remediation (C)	Assess processes impacting migration and fluxes of source zone-derived PFAS (C)	Understand impact of AFFF composition on fate and transport of PFAS (C)
Determine microbial impacts on PFAS transport and/or transformation (C)	Evaluate rate-limited processes with respect to PFAS release and migration in saturated and unsaturated soils (C)	Evaluate relevance of PFAS vapor transport (C)
Develop understanding of fate and transport processes in aquatic environments: PFAS bioaccumulation to fish and shellfish (C)	Assess applicability of current vadose zone models for quantitative prediction of PFAS migration (C)	Develop understanding of PFAA precursors, intermediates, and compounds diagnostic of extent of AFFF plume development at AFFF-impacted field sites (C)
Interrogate PFAS transport and fate at the capillary fringe (C)	Evaluate role(s) of varying redox conditions on PFAS groundwater transport and transformation (H)	Improve fundamental understanding of PFAS interactions with biofilms (H)
Determine suitability of groundwater fate and transport models for simulating migration of PFAS plumes (C)	Advance understanding of how AFFF source zones age (C)	Evaluate role of low-permeability zones on PFAS transport (C)
Conduct meta-studies of PFAS field distributions as function of site characteristics (C)	Assess behavior of PFAS in wetlands (H)	Assess rhizosphere/plant influences on PFAS distribution and ecological exposure(H)
Evaluate role of solid versus dissolved phases in stormwater runoff (H)	Assess role of gas/aerosol transport during and after AFFF application (H)	Determine effects of episodic storm events and other climate effects on fate and transport (H)
Sampling and Analysis		
Develop field methods to rapidly screen or monitor PFAS (C)	Develop better laboratory preparation and analysis methods for inclusion of understudied types of PFAS (C)	Develop and validate new sampling methods relative to thermal treatment, stormwater sampling, surface water, and sediment fractionation sampling (C)
Evaluate PFAS sampling protocols (H)	Develop methods to assess leaching and mobility of polymeric PFAS and polymer-associated low molecular weight PFAS (H)	Develop ancillary real-time sensors for monitoring PFAS transport in treatment systems, discharge flows, and environmental waters (H)

Table 2. Summary of Identified Research, Demonstration, and Technology Transfer Needs
(C- Critical Priority; H = High Priority)

Create materials to support existing and developing methods (C)	Standardize and validate methods for sample collection of foam and surface water microlayer (C)	Standardize and validate analytical methods to close mass balance (C)
Optimize and validate SW-846 methods 1311 and 1312 for use with PFAS (C)	Evaluate effects of sample storage on quantitation of PFAS in biota (H)	Collect and disseminate current state of knowledge of PFAS analysis (C)
Thermal Treatment		
Develop understanding of transformation mechanisms, pathways, and kinetics for thermal processes (C)	Develop vapor phase analytical methods to measure PFAS emissions from thermal treatment processes (C)	Improve understanding of incineration process operating conditions (C)
Develop predictive models to estimate PFAS destruction and products as a function of incineration conditions (H)	Improve understanding of important process operating conditions for non-incineration thermal destruction technologies (H)	Develop best practice incineration conditions (C)
Demonstrate and validate on-site thermal treatment technologies for management of PFAS-containing media (H)		
Non-Thermal Destructive Treatment		
Improve understanding of biodegradation processes and biological treatment strategies for PFAS (C)	Develop more complete fundamental understanding of mechanisms of PFAS degradation during non-thermal physicochemical treatment processes (C)	Improve understanding of effect of field conditions on outcomes of non-thermal destructive treatment technologies (C)
Develop fundamental understanding of how technologies function for a variety of PFAS-impacted sources (C)	Conduct side-by-side comparisons of promising treatment technologies or combinations of technologies at select field locations (C)	Develop framework for selecting PFAS treatment technologies for impacted environments (C)
Concentration Technologies		
Develop framework to predict performance of full-scale sorption processes for PFAS removal from bench-scale data (C)	Develop systematic guidance for implementing and evaluating in situ PFAS adsorption by colloidal activated carbon (C)	Develop understanding of fundamentals of PFAS adsorption-desorption behavior in mixtures for commercially available sorbents (C)
Develop and test conventional or novel adsorbents for capture of treatment off-gases containing PFAS and reaction byproducts	Develop novel and existing adsorbents to capture PFAS poorly adsorbed by GAC (H)	Develop and validate novel soil amendments for larger-area applications in PFAS secondary source areas (H)
Develop drinking water system alternatives for affected communities (H)	Assess soil washing for treatment of PFAS-impacted soils and sediments (H)	Evaluate performance of novel adsorbents for management of PFAS-impacted media at field-scale (C)
Demonstrate combined concentration-destructive technologies for remediation of mixed PFAS streams (C)	Improve insights into and removal of AFFF from firefighting foam delivery systems (H)	Develop decision framework for ex situ PFAS treatment of impacted groundwater and surface water (C)
Improve commercial water treatment technologies for PFAS (H)		

4.0 FATE AND TRANSPORT

As the pervasiveness of PFAS in environmental systems becomes more apparent, along with the inherent challenges associated with PFAS treatment, improved insight into PFAS fate and transport is becoming increasingly necessary. Key research is needed with respect to PFAS subsurface, aquatic, and vapor fate and transport. A wide range of research efforts are needed, ranging from the development of predictive models to bench-scale studies identifying and elucidating fundamental processes. Further efforts to demonstrate and validate our understanding of the PFAS migration and transformation processes at the field scale also will be critical to future site assessment and remediation efforts.

4.1 Research Needs

4.1.1 Determine Physical-Chemical Properties of PFAS by Measurement and Predictive Modeling to Support Assessments of PFAS Fate, Transport, Bioavailability, and Remediation (Critical Priority)

Any quantitative approach to analyzing the behavior of PFAS in treatment systems or in the environment requires knowledge of the distribution of the PFAS of interest in the multiple phases that comprise the system being considered. For example, a successful treatment system should be designed such that the PFAS of interest is primarily associated with the treatment phase and not sequestered in other phases in the system such as soil or other matrix materials. This requires that the PFAS speciation be considered (e.g., the relative quantities of free or complexed anionic or neutral species, cation-anion ion pairs, larger molecular aggregates, or pure phase if the solubility limit is exceeded). All of this information is required to build a reliable model of PFAS fate and transport within any media. If PFAS is primarily associated with stationary phases, its mobility is much less than if it is in the vapor or aqueous phases. Evaluation of the bioaccumulation and toxicity of PFAS also requires consideration of its phase distribution and speciation. PFAS bound to phases not exposed to the organism or distributed among multiple chemical species will accumulate differently in organisms depending on the bioavailability of each species and their toxic potential. This is not a new requirement for understanding the transport, transformations, and toxicity of environmental contaminants, but the challenges and unknowns are extreme for PFAS.

Such issues result in a critical need to determine the necessary physical-chemical properties (PChPs) of PFAS, not only of the neutral forms of PFAS, but also of their charged monomeric species. Since there are too many PFAS in legacy AFFF and new firefighting formulations for each to be evaluated experimentally, a parallel critical need is for models that can predict these properties as a function of chemical structure. These models will require experimentally-measured PChPs to calibrate structure-activity relationships such as linear solvation energy relationships (LSERs) and polyparameter linear free energy relationships (pp-LFERs). Additionally, further understanding is needed regarding the potential confounding/competing effects in complex PFAS mixtures.

Specific research needs are as follows:

- Evaluate data on conventional PChPs for PFAS that have been reported and summarized in various places (e.g., Interstate Technology and Regulatory Council

[ITRC]). These parameters include density, melting point, boiling point, vapor pressure, aqueous solubility, critical micelle concentration, Henry's Law constant, K_{OW}, and pKa. Often these values have been estimated; having measures of the same would be particularly helpful. An important goal is to clarify what PFAS speciation is in the solutions used to measure values so that it is clear what the reported data represent, thereby also resolving inconsistencies spanning wide ranges in the reported values, and filling gaps where few if any data are available. This information is needed for non-ionic and ionic PFAS.

- Determine the environmental phases/interfaces and corresponding phase distribution behavior required for fate and transport modeling. These include partitioning between environmental phases such as air and water, water and specific soil phases such as natural organic matter, bulk water and the air-water interface, vapors and aerosols (both on the surface and inside bulk air/water volumes), and should include assessment of complex mixtures.. As these are not pure phases in environmental settings, it is necessary to characterize and determine which components/phases are controlling partitioning in the subsurface and prioritize processes for further study. For example, neutral hydrophobic compounds partition primarily to soil organic matter and black carbon. For charged compounds, additional mechanisms likely need to be considered including cation-anion complexation, association with ion exchange sites on soil minerals, mineral surface adsorption, and distribution into organic matter with variable cationic and anionic charge densities.
- Determine the most important organism compartment(s) for accumulating PFAS mass. This includes the corresponding partition coefficients for neutral and ionic PFAS species from water to fish (the bioconcentration factor [BCF]), but also for organisms ranging from aquatic plants to soil and sediment-dwelling invertebrates as well as upper trophic level animals like shellfish, fish, and birds. The challenge is analogous to partitioning into environmental phases. While organism lipid content has proven useful for binding neutral hydrophobic organic compounds, charged chemical species also can bind to proteins, cellular membrane components, and other charged biomaterials. These components and PFAS distribution coefficients need to be evaluated.
- Construct fundamental chemistry-based models (i.e., dependent on chemical structures) to estimate PFAS distributions between environmental phases (e.g., water) and organism phases (e.g., proteins, membrane components) for individual PFAS in legacy and modern fluorotelomer AFFF (note: straight-chain and branched isomers should be handled in separate components). As an alternative approach, toxicokinetic models that account for PFAS-specific protein binding and transcompartment transport (e.g., organic anion transport proteins) also may need to be considered. Quantitative structure activity relationships (QSARs)—such as the Abraham ppLFERs—must consider the three complicating factors for PFAS (that they are charged, poly- or per-fluorinated, and surfactants). In addition to assessing PChP values (and uncertainties), research needs to identify surrogate phases, develop distribution coefficients, and validate these models using PFAS phase distribution data from laboratory and field environmental phases.

It is critically important that experiments and modeling be completed in parallel to identify model shortcomings early on and design experiments to elucidate the cause(s) and provide the necessary information for the iterative cycle of generating data and building reliably accurate models.

4.1.2 Assess Processes Impacting Migration and Fluxes of Source Zone-Derived PFAS (Critical Priority)

Investigations of DoD sites impacted by AFFF have indicated significant retention of PFAS in the vadose zone, particularly in unsaturated soil and deeper horizons. The longevity of PFAS in source zones is a critical component when assessing management and remediation approaches for AFFF-impacted sites; significant uncertainties remain with respect to the key processes impacting the distribution and flux of AFFF-derived PFAS during vertical migration (and lateral dispersion) to groundwater. Given the diversity of hydrogeologic and climatic conditions throughout the DoD portfolio of AFFF-impacted sites, it is likely that migration and flux of water, and associated PFAS transport, are highly variable. If quantitative models of source zone longevity are to be developed, there is a need to assess and validate the fundamental processes and parameters impacting both water and PFAS flux through the vadose zone. Specific factors that will need to be considered include the following:

- the role of site stratigraphy (e.g., clay lenses) in 3-dimensional water and PFAS flux;
- the function of site-specific recharge dynamics (e.g., recharge event variability, seasonal effects);
- how site-specific recharge dynamics impact PFAS flux to groundwater;
- the significance in PFAS in local precipitation;
- the extents to which air-water interfaces impede, or perhaps enhance, the transport of surface-active PFAS;
- the controlling factors affecting the transport of anionic PFAS, particularly the relative importance of hydrophobic versus ionic interactions with the solid phase;
- the role sediment beds and hyporheic exchange processes play in long-term PFAS fate and transport for direct AFFF surface water discharge scenarios; and
- the roles of colloid-facilitated transport, dissolved organic carbon (DOC) complex transport, mixed micelle formation, and ion pairs under variably saturated conditions near source zones (specifically differentiated from those that may have occurred during the initial release of PFAS present in AFFF).

There is a clear need to provide data to address the above issues to enable more quantitative, site-specific modeling of source zone PFAS transport through the vadose zone to groundwater. Laboratory- and field-scale studies that identify the data needed (e.g., geology, recharge) and advance our fundamental understanding of PFAS mass flux using field materials/sites are particularly needed.

4.1.3 Understand Impact of AFFF Composition on Fate and Transport of PFAS (Critical Priority)

AFFFs are complex proprietary mixtures that contain PFAS (D'Agostino and Mabury, 2014; Place and Field, 2022) and many other components including organic solvents, hydrocarbon surfactants, and additives such as corrosion inhibitors (Martin, 2012; Pabon et al., 2002). The Qualified Products List (QPL) provides the AFFF formulations that met the U.S. military specification (MIL-

SPEC), but does not reflect the actual AFFFs purchased on large military contracts. Thus, the QPL is a rough guide for the AFFFs that may have been used. In 1970, the QPL included Type 6 AFFFs and in 1982, Type 3 AFFFs. Type 3 and Type 6 MIL-SPEC AFFFs that date from 1982 to 2000 include those made by 3M, Ansul, and National Foam. Single entries from Angus and Chemguard appear on the Type 3 QPL and date from 1994 and 1998, respectively. For legacy DoD sites, most discharges of AFFFs for routine firefighter training ceased in the late 1990s. Thus, it is quite likely that the dominant AFFFs used at firefighter training areas were manufactured by 3M, Ansul, and National Foam.

Many other manufacturers had MIL-SPEC AFFFs after 2000, including Buckeye, ICL Performance Products, Amerex/Solberg, Dafo Fomtec, and Fire Service Plus. Although the use of these AFFFs at former firefighter training areas cannot be ruled out, the volumes used may be limited relative to products used before 2000. Current research is underway to better define volatile and non-volatile PFAS present in MIL-SPEC AFFFs on the QPL prior to 2000 (e.g., 3M, Ansul, and National Foam) (SERDP Project ER20-1375); the compositions of non-MIL-SPEC AFFFs from the same three manufacturers are being characterized to determine if MIL-SPEC and non-MIL-SPEC AFFFs from the same manufacturer can be differentiated for forensic purposes.

Although there is some information on the PFAS composition of MIL-SPEC AFFFs (1989-2010) (Backe et al., 2013; Houtz et al., 2013), less is known about the composition of current-use AFFFs (undergoing MIL-SPEC testing) (Ruyle et al., 2021). Recent versions of the MIL-SPEC limit the PFOA and PFOS content and restrict chain length to C6 or less (U.S. DoD, 2020). Thus, current-use MIL-SPEC AFFFs may differ significantly in their chemical composition from those on the QPL up to 2000.

SERDP and ESTCP have funded several projects that provide field data indicating PFAS are present in AFFF-impacted groundwater, particularly in ‘source areas’ associated with former firefighter training areas (Adamson et al., 2020; 2022; Liu et al, 2022; Nickerson et al., 2021). Although the focus of field studies is to determine the spatial distributions of PFAS and their potential impact on subsurface water supplies, there are few data to determine if biodegradable AFFF components such as butyl carbitol and some hydrocarbon surfactants remain under the prevailing biogeochemical conditions of AFFF-impacted soil and/or groundwater. Knowledge of the AFFF manufacturer, date, and type is needed to understand the potential impacts of additives on PFAS transport and transformation at the time of AFFF discharge. However, to characterize processes (natural or engineered) that are occurring at field sites today, the additives present in intact AFFFs, which may no longer be present at sites, may alter the experimental results in a way that are not relevant to current field conditions. Field data are needed to determine if additives remain at field sites and may influence PFAS transport and transformation, as well as the concentrations of AFFF-related chemicals in water-supply wells and receiving surface waters. Identified research needs include the following:

- Determine how components of AFFF mixtures, as used in past firefighting and training, affect the transport of PFAS at field sites both (a) vertically from the ground surface into unsaturated soils and deeper unsaturated horizons and (b) horizontally with groundwater and overland flows.

- Assess how transport of specific PFAS change due to evolution of the AFFF mixtures including other surfactants and organic co-solvents with which PFAS are co-transported. How do such cooperative/competitive or synergistic associations change with AFFF weathering? What PFAS properties and soil properties do we need to be able to quantify such as potentially competitive sorptive processes affecting PFAS transport?
- Determine whether PFAS mixtures from AFFF experience changing biogeochemical conditions in the subsurface (e.g., pH, oxygen presence/absence) due to transformations of non-PFAS components of AFFF. Do these changes enhance or inhibit transformations of PFAS?

4.1.4 Determine Microbial Impacts on PFAS Transport and/or Transformation (Critical Priority)

There are significant knowledge gaps regarding PFAS biotransformation that have relevance for PFAS treatment as well as for assessment of their fate and transport. Determining the (geo)chemical conditions and biological agents (e.g., bacteria/fungi/plants) that affect transformation rates and quantifying these rates and pathways for polyfluoroalkyl precursors are important to understanding PFAS accumulation and attenuation in the environment and treatment systems. However, the complexity of many sites, including the presence of PFAS mixtures with individual components having diverse transformation rates and pathways, present real challenges in quantifying biotransformation rates from in situ measurements, especially for the slower transformation rates. In addition, elucidating the role(s) that polyfluoroalkyl substance biotransformations play in the sorption and release of PFAS from solids is important to improving our understanding of the fate and transport of PFAS in the subsurface and in formulating strategies for how to control and remediate those compounds. Hence, in addition to PFAS biotransformation knowledge gaps for treatment, the following questions are of key importance in the assessment of PFAS fate and transport:

- What are generalizable field-relevant biotransformation rates for polyfluoroalkyl substances in a variety of environmental settings (e.g., variable soil geochemistry, oxidation-reduction [redox] conditions, salinity, temperature, soil moisture, vadose zone versus saturated zone, low permeability versus transmissive zone, etc.)? What are the relative rates and pathways for different classes of polyfluoroalkyl substances (e.g., branched versus linear, ultrashort versus moderate or long-chain, cationic versus anionic versus zwitterionic) under a range of geochemical conditions?
- What role do microorganisms that transform polyfluoroalkyl substances (i.e., polyfluorinated compounds that likely degrade to form perfluorinated sulfonic and carboxylic acids) play in the sorption and release of PFAS from solids? What effects do biotransformation reactions have on weathering of PFAS in source zones? How are these biotransformations affected by geochemical conditions such as redox, salinity and specific metals, buffering, or pH? What are the effects of biotransformations on the size and composition of downstream groundwater plumes?
- To what extent are coupled biotic-abiotic processes important with respect to precursor transformation?

- How can the effects of polyfluoroalkyl substance biotransformation be integrated into fate and transport models to better inform site management and potential remediation strategies?
- Are there biological markers/tests (e.g., specific genes expressed, presence of specific organisms, enzyme assays, compound-specific isotope analyses, relatively rapid laboratory incubation tests, etc.) that can aid in determining whether polyfluoroalkyl substance biotransformation is occurring in the field at specific sites and the pathways and products involved? Is it possible to quantify such biotransformation rates in the field?

4.1.5 Evaluate Rate-Limited Processes with Respect to PFAS Release and Migration in Saturated and Unsaturated Soils (Critical Priority)

Several recent studies have shown that PFAS release from soils is a rate-limited process, and equilibrium models may be inappropriate for describing PFAS transport under many relevant field conditions. These rate limitations can be due to mechanisms at the grain scale (e.g., Brusseau et al., 2019; Maizel et al., 2021; Schaefer et al., 2021), and/or due to mass transfer between advective and non-advective domains (e.g., Brusseau, 2020). While these rate-limited processes are recognized, there are several fundamental issues that remain unresolved, including:

- the mechanisms controlling rate-limited PFAS desorption from soil, including the potential role of aggregated PFAS molecules, the changing structures of aged soil solids, and releases of PFAS in associated colloids;
- the soil and PFAS properties that impact rate-limited adsorption/desorption — specifically, the behavior of anionic, cationic, and zwitterionic PFAS (and mixtures thereof) should be considered;
- the extent to which mass transfer between advective and non-advective domains impact PFAS sorption to solid-fluid and fluid-fluid (i.e., NAPL-water and air-water) interfaces in both the saturated and unsaturated zone;
- the impacts of rate-limited processes on PFAS subsurface transport at multiple scales and timeframes;
- the impact of rate-limited processes on remedial technologies; and
- the development of quantitative models to describe and predict rate-limited processes influencing PFAS fate and transport in the subsurface.

Further research at both the bench-scale and field-scale are needed to address the issues identified above. There is a critical need to understand the role of rate-limited processes in AFFF-impacted soils, as is the ability to distinguish between non-linear sorption and partitioning behavior. Finally, guidance as to how these rate-limited processes impact conceptual site models and overall site management should be a key component of this research.

4.1.6 Evaluate Relevance of PFAS Vapor Transport (Critical Priority)

Recent SERDP-funded research indicates the presence of volatile PFAS in mg/L levels in MIL-SPEC AFFFs dating from 1974 to 2010. Given the wide range in estimated and measured Henry's Law constants (as well as aqueous solubilities) for the PFAS present in AFFF, the uncertainty in the potential for volatile PFAS to partition from water to air, both in soil and indoor spaces (e.g., vapor intrusion) is large. Analytical methods, field sampling methods, and measurement of volatile

PFAS are needed for soil gas, porewater, groundwater, and indoor air associated with AFFF releases to better understand if volatile PFAS associated with AFFF represent a potentially significant source of human exposure (see Section 6.1.2). In addition, despite current low estimates of the acid dissociation constants of the perfluoroalkyl carboxylates (PFCAs) and sulfonates (PFSAs), there is concern that PFCAs and PFSAs are, at least in significant fractions, in their free acid, volatile forms in environmental matrices at environmental conditions (e.g., pH 4-9).

The following represent critical research needs:

- develop more definitive determinations of the volatility of PFAS, including PFCAs and PFSAs, along with better estimates of critical physicochemical properties (e.g., Henry's Law constants, pKa values) to narrow the uncertainty around potential human exposure to gas-phase PFAS;
- collect field measurements of PFAS in soil gas to determine if there is potential for exposure to soil gas — air sampling methods for PFAS are under development by the EPA and EPA-funded projects could be adapted for use with soil and improve the ability to address these research needs (see Section 5.0 for further discussion);
- determine the impacts of capillary fringe processes, including a fluctuating water table, on PFAS vapor transport;
- critically evaluate existing air and vapor intrusions models and develop new models as needed for their application to PFAS vapor intrusion;
- determine the potential importance of aerosolization of PFAS and other additives in historic AFFFs on long-range PFAS transport at sites; and
- collect field data as as to bound typical spatial distributions (e.g., meters to kilometers) of PFAS beyond firefighter training areas, impacting soils, sediments, and potentially groundwater.

4.1.7 Develop Understanding of Fate and Transport Processes in Aquatic Environments: PFAS Bioaccumulation to Fish and Shellfish (Critical Priority)

PFAS fate and transport in fresh and marine surface waters and sediments, and specifically the pathways leading to fish and shellfish uptake, was identified as a critical need. Over the last 30 years of managing aquatic-impacted sites for metals, pesticides, and hydrophobic organic compounds (e.g., Hg, 2,4-dichlorophenoxyacetic adic [2,4-D], polycyclic aromatic hydrocarbons [PAHs], polychlorinated byphenyls [PCBs], dioxins), human health risks associated with fish consumption have been the primary drivers of cleanup levels. These human health-based cleanup levels have been derived principally using bioaccumulation modeling to back-calculate sediment, surface water, or even groundwater concentrations of chemicals that would result in unacceptable risks associated with consumption of impacted fish or shellfish. Ankley et al. (2021) argue that "[U]nderstanding bioaccumulation is arguably the most significant exposure challenge relative to PFAS, with critical ramifications not only for ecological but also for human health effects." That there are already PFAS fish-consumption advisories in several states (Maryland, Massachusetts, Michigan, Pennsylvania, and Wisconsin) reinforces that notion.

There is a growing body of literature relative to PFAS in aquatic organisms (e.g., De Silva et al., 2021; Gobas, 2020; Valsecchi et al., 2020). Many of the studies conducted to date are compartment-to-compartment measures (i.e., water to fish tissue or sediment to water to fish tissue), and for relatively limited individual PFAS (Burkhard, 2021). Less is known about mass transfer processes, the role of precursors in uptake, or the physicochemical metrics of gradients driving PFAS uptake. Relative contributions of PFAS from groundwater, surface runoff, or even from air are also poorly understood. Some bioaccumulation modeling has been undertaken (Burkhard, 2021; Gobas, 2020; Ng and Hungerbühler, 2013), but this work has been principally done with a small number of individual PFAS and has not advanced to the level needed to support setting cleanup levels in water or sediments.

To provide a framework to understand PFAS fate and transport in aquatic environments ahead of upcoming and expected remedial management decisions, research is critically needed in the following areas:

- understand partitioning equilibria and kinetics driving PFAS exchanges between particulate, colloidal, and dissolved phases in sediments and the water column;
- advance our understanding of PFAS benthic/pelagic coupling including relationships between the water column and the sediments;
- determine the fate, transport, and transformation processes of PFAA precursors into fish and shellfish;
- elucidate the extent to which PFAS bioaccumulation data in fish and shellfish can inform site-specific source locations and fluxes of PFAS to surface waters;
- determine whether there are seasonal impacts in lakes due to phenomena such as stratification and turnover; and
- evaluate whether precursor transformations in surface waters are distinct from those in soil vadose zones.

4.1.8 Assess Applicability of Current Vadose Zone Models for Quantitative Prediction of PFAS Migration (Critical Priority)

To date, field-scale modeling of PFAS fate and transport in the vadose zone has been limited. Shin et al. (2011) employed several models to simulate the environmental distribution of a PFOA release in Parkersburg, WV. The authors used PRZM (Pesticide Root Zone Model), a pesticide leaching model developed by the EPA, but no attempt was made to validate the model or incorporate additional processes relevant to PFAS transport. A second model has been adapted for simulating PFAS leaching in agricultural systems is PEARL (Pesticide Emission Assessment at Regional and Local scales). This model is frequently used for assessment of pesticide leaching as part of the European Union (EU) evaluation process. HYDRUS, a commonly employed contaminant transport model, includes unsaturated and saturated water flow and can account for up to five species exhibiting nonlinear and nonequilibrium sorption processes, as well as capillary hysteresis. The HYDRUS model currently has a provision to account for root uptake of water, but does not account for plant uptake of solutes, which may be necessary for some PFAS. Recently, compositional relationships developed for sorption, interfacial accumulation of mass, and capillary pressure-saturation are being incorporated into HYDRUS (Silva et al., 2020). Additional flow and transport models have been developed to simulate PFAS transport in the vadose zone (Brusseau et al., 2019, Guo et al., 2020). These models incorporate interfacial adsorption and other processes that may influence PFAS behavior in unsaturated soils.

Despite the availability of these models, there is a lack of model validation at the field scale, particularly for multi-dimensional systems that are likely to be important due to the potential effects of PFAS and AFFF constituents on water flow and retention. There is also a lack of model simulations that directly link PFAS mass discharge from the vadose zone with groundwater flow and transport, making it difficult to simulate the effects of fluctuating water tables and potential impacts on downgradient receptors (e.g., residential wells, surface water bodies). Further, most of the model simulations conducted to date focus on single PFAS, and the effects of potential competitive or synergistic interactions between multiple PFAS are not considered. In addition, abiotic and biotic reactions have not been considered to date and may be particularly important for PFAA precursors. Models that can be used to assess impacts of PFAS source remediation (full or partial) also are needed to better assess the impacts on PFAS flux to groundwater. Ultimately, it is important that these models are useful for assessing the value of source remedial actions and predicting benefits, including benefits of partial/incremental actions, on reduced loading to groundwater and future changes in plume mass discharge, concentrations, and geometry.

The comprehensive models needed to incorporate these preceding factors are complex and have significant input requirements that are often difficult or impractical to fully meet for field-scale applications. Simplified screening-level models are being developed for PFAS leaching that can be employed with less input-parameter burden (Guo et al., 2022). Conditions under which these simplified models can be successfully used have to be determined for field-scale applications. Finally, with the exception of PRZM, the mathematical models discussed above are only available as compiled programs or the source code is not available to the general public, and therefore, users are not able to modify the source code to incorporate additional processes that may be relevant to PFAS fate and transport. Critical data gaps include:

- conduct an independent evaluation of the ability of current vadose zone models to simulate PFAS fate and transport in multi-dimensional, variably saturated systems using data collected from laboratory and field studies that specifically include measured pore-water concentrations;
- develop and validate vadose zone models that can account for multiple PFAS as well as co-occurring chemicals of concern and co-constituents relevant to AFFF releases;
- develop and validate vadose zone models that can account for effects of chemical or biological reactions on PFAS, and in particular PFAA precursors;
- develop comprehensive mathematical models that link the unsaturated and saturated zones, allowing for simulation of PFAS migration subject to fluctuating water tables and prediction of impacts on receptors (e.g., wells, surface water bodies);
- test screening models at field-scale to determine conditions applicable for their use to predict PFAS leaching and mass discharge; and
- provide open-source vadose zone models so that users can modify the code to account for additional processes (e.g., reactions) and release scenarios.

4.1.9 Develop Understanding of PFAA Precursors, Intermediates, and Compounds Diagnostic of Extent of AFFF Plume Development at AFFF-Impacted Field Sites (Critical Priority)

Modern analytical methods, coupled with improved sample preparation methods, are capable of detecting a broad array of target and suspect PFAS at AFFF-impacted field sites. Laboratory microcosm studies provide insights into (bio)transformation pathways and intermediates of polyfluoroalkyl precursors under well-controlled redox conditions. Moving forward, beyond identifying PFAS of original AFFF components and their transformation intermediates in field samples, new data and knowledge on the occurrence of select PFAS and their correlation with redox conditions and/or plume development are needed to identify if specific PFAS are indicative of various stages of AFFF-derived PFAS groundwater plume development. For example, it would be desirable if the specific PFAS ("indicator" PFAS) can be used to indicate the extent to which in situ biotransformation of precursors has occurred or to predict the potential for further biotransformation in the future. Aside from fluorinated substances, AFFF additives — including solvents, hydrocarbon surfactants, and corrosion inhibitors — also may serve as indicators, which has not been explored and deserves further investigations. They may be used to assist identification of the types of AFFF used at a site and to understand what other components also may be released or be present in groundwater or other receiving bodies.

Further research is needed to understand the following:

- the prevalence and occurrence of PFAS transformation intermediates and other indicators as a function of site age and redox conditions;
- the potential for indicator organisms that can be assessed during site characterization to inform the extent of transformation or redox state in groundwater (e.g., perfluorinated sulfonates), given that redox potential likely controls PFAS transport through affecting geochemical phase (e.g., iron oxyhydroxides) and PFAS transformations;
- the potential for use of real-time sensors for soil moisture, pH, oxygen, redox potential, or organic content to characterize the extent of ongoing PFAS transport and transformations; and
- the potential to use (bio)transformation intermediates or other indicator PFAS to indicate the extent of in situ transformation of precursors that has already occurred or to predict the potential for further biotransformation in the future.

4.1.10 Interrogate PFAS Transport and Fate at the Capillary Fringe (Critical Priority)

The capillary fringe is a highly dynamic zone in which fluctuations of the groundwater table constantly change its position and thickness along with gas/water saturations, flow conditions, and biogeochemical gradients. The capillary fringe is typically considered fully saturated with respect to water, but under negative fluid pressures (i.e., less than atmospheric pressure conditions, where atmospheric pressure defines the water table), may have entrapped soil gas (Berg and Gillham, 2010; Fetter, 1999). Similarly, isolated loci of water-filled pore spaces also may exist in the vadose zone immediately above the capillary fringe. Neither the entrapped water nor the entrapped soil gas phases in and around the capillary fringe are typically captured in most subsurface sampling plans. As many PFAS are surface-active chemicals, a potentially significant fraction of their mass may be at the gas-water interface. Furthermore, transient redox conditions may impact the transformation rates of less mobile PFAA precursors into more mobile PFAAs. In addition, concentrated PFAS mass present in the capillary fringe may serve as a long-term source that may be difficult to detect or quantify by conventional monitoring wells and other field conventional sampling methods. A better understanding of PFAS distribution, fate, and transport at the upper boundary of the capillary fringe or within the capillary fringe is therefore critically needed through interrogating issues and questions such as those listed below:

- How do temporal fluctuations of the water table affect PFAS accumulation at the capillary fringe and PFAS transport along (laterally, see Freitas and Barker, 2011) or through (vertically) the capillary fringe?
- Due to retention of either AFFF or other non-aqueous phases within the capillary fringe, does this zone serve as a potential PFAS source for underlying groundwater?
- Which subsurface coring approaches are useful for the delineation of the capillary fringe and allow for high-resolution spatial correlations of PFAS distribution and speciation with parameters such as gas saturation, pH and redox potential, mineral phase composition, and eventually functional microbial genes involved in PFAA precursor transformation and possibly other related relevant processes?
- How important is vapor transport of PFAS, with or without a fluctuating water table, and how could this be quantified? Are semi-volatile PFAS present and is their presence a function of redox potential and/or pH that warrant additional evaluation of fate and transport processes? Please also see Section 4.1.6 regarding the broader relevance of PFAS vapor transport.

The extent of PFAS retention adjacent to or within the capillary fringe has critical implications for risk management and remedial actions. There is a clear need to investigate and demonstrate the viability of appropriate sampling, analysis methods, and potential product recovery (long studied for floating petroleum products, see Blake and Lewis, 1983) at the field scale under ambient conditions.

4.1.11 Evaluate Role(s) of Varying Redox Conditions on PFAS Groundwater Transport and Transformation (High Priority)

Groundwater sites exhibit widely varying redox conditions from aerobic (E_H = +0.8 V) to methanogenic (E_H < - 0.4V). The redox state is largely dependent on biogeochemical conditions, including soil mineralogy and microbial activity. Such conditions likely affect the transport of PFAS in groundwater, as well as the transformation of polyfluorinated precursors. For example, soil surface charges and/or coatings can change under iron reducing conditions, which can subsequently impact PFAS sorption:

> Si-Fe(III)-OH_2^+ (surface coating) => >Si-O^- + Fe(II)^{+2} (aq) => change from a soil with elevated anion exchange capacity to a soil with elevated cation exchange capacity

In another example, Yi et al. (2018) observed the biotic transformation of 6:2 fluorotelomer thioether amido sulfonate (6:2 FtTAoS) to 6:2 fluorotelomer thioether propionate (6:2 FtTP) under sulfate reducing conditions, while Harding-Marjanovic et al. (2015) observed biotic transformation of 6:2 FtTAoS to 6:2 fluorotelomer sulfonate and perfluorinated carboxylates; the 6:2 FtTAoS transformation rate under sulfate reducing conditions was approximately 20 times less than that observe under aerobic conditions.

Different redox conditions also lead to different biotransformation pathways that result in changes in polyfluoroalkyl substance molecular charges. Thus, redox conditions can determine if transformed PFAS are cationic, zwitterionic, or anionic. As a result, such transformations could either increase or decrease affinity to charged soil surfaces, and ultimately impact PFAS mobility.

In light of these data, research is needed to address the following:

- To what extent does varying redox conditions have on PFAS adsorption to iron-based coatings (similar to the $Si\text{-}Fe(III)\text{-}OH_2^+$ example shown above)? Can this effect be predicted using formulations of K_d values based on sorption models with combinations of parameters like f_{oc} and anion exchange capacity (AEC)?
- What functional groups in AFFF-derived PFAS are redox sensitive (e.g., thiols), and can we understand their equilibrium distributions as a function of groundwater redox potential?
- Are oxidations of thiol moieties on PFAS abiotic, biotic, or both? Can the rates of these transformations be predicted from information on microbial species and numbers?
- Do polyfluoroalkyl substance biotransformations under different redox conditions produce products with different mobility in groundwater? Can the rates of these transformations be predicted from information on microbial species and numbers?

4.1.12 Improve Fundamental Understanding of PFAS Interactions with Biofilms (High Priority)

Most current research on the adsorption characteristics of PFAS has been conducted with pure solids (e.g., mineral surfaces, activated carbon). However, in many environments, natural or man-made solids are colonized by microorganisms, which subsequently produce extracellular materials and form a complex matrix, termed a "biofilm". Such films can dramatically alter the sorptive and reactive properties of the underlying solid. Biofilms are potentially present in many different PFAS-impacted environments including groundwater aquifers, aquatic sediments, surface and vadose soils, and drinking water conveyance piping, among others. Biofilms also can influence the efficiency and operation of traditional groundwater treatment systems (e.g., ion exchange and GAC systems), and potentially impact the efficacy of in situ remedial amendments for PFAS, such as colloidal activated carbon (CAC).

Historically, biofilms were thought to consist of microbial cells in a matrix of extracellular polymeric substances (EPS), which was composed primarily of polysaccharides (Fleming, 2016). Given that biofilms are 98% water and often negatively charged (Tourney and Ngwenya, 2014), sorption of many common PFAS (also negatively charged at neutral pH), would be expected to be minimal; however, a few recent studies indicate significant accumulation or "bioconcentration" of PFAS, including anionic PFAS, in natural biofilms present in aquatic ecosystems (Munoz et al., 2018; Zhang et al., 2022). While this seems counterintuitive based on the simple biofilm model, studies conducted over the past forty years reveal that biofilms are diverse, dynamic, and highly complex structures composed of not only microbial cells and polysaccharides, but also variably of proteins, including amyloids and extracellular enzymes, extracellular nucleic acids, surface-active substances, inorganic ions including sulfate and phosphate, membrane vesicles, and lipopolysaccharides, among other materials (Fleming, 2016). Moreover, they are often characterized by high biodiversity, and strong geochemical gradients, often having both oxidizing and reducing microzones.

The diversity and complexity of biofilms, combined with their ubiquity, provides impetus for research on their overall role in PFAS fate. This understanding is critical for both natural environments and the long-term performance of systems prone to bacterial growth and biofilm formation such as traditional GAC and ion exchange (IX) systems.

Areas of primary interest for research include the following:

- determination of mechanisms, equilibrium partition coefficients, and mass transfer kinetics for PFAS sorption by biofilms in natural environments and engineered systems (e.g., drinking water piping, media used for PFAS adsorption in pump-and-treat systems);
- identification of biofilm properties and environmental conditions that control PFAS sorption-desorption processes;
- determination of physiochemical properties of PFAS that control their sorption by biofilms, and predictive models of this behavior;
- ascertainment of whether biotransformation of polyfluoroalkyl substances occurs in biofilms;
- determination of biomagnification potential to aquatic organisms of PFAS present in biofilms (i.e., in surface waters); and
- mathematical modeling of PFAS sorption by biofilms and modeling of PFAS transport in sediments, soils, and aquifers in the presence and absence of natural biofilms; including measurable metrics of biofilm presence affecting such transport at field sites.

4.2 Demonstration Needs

4.2.1 Determine Suitability of Groundwater Fate and Transport Models for Simulating Migration of PFAS Plumes (Critical Priority)

Groundwater fate and transport models have been valuable tools for managing conventional groundwater contaminant plumes (e.g., hydrocarbon and chlorinated solvent plumes). However, knowledge of PFAS fate and transport processes is still evolving, and there is some uncertainty if existing fate and transport models are suitable for modeling PFAS plumes. The limited modeling studies conducted to date in the peer-reviewed literature generally assume simple PFAS source histories, linear sorption/desorption isotherms (Gefell et at., 2022), and non-degrading PFAAs (Raschke et al., 2022; Shin et al., 2011). Recent modeling efforts also have considered the important role of matrix back-diffusion on PFAS concentrations in groundwater (Kulkami et al., 2022). Because several of the key PFAS constituents are recalcitrant to naturally occurring transformation processes, other processes (e.g., dispersion, matrix diffusion, sorption) become much more important for understanding potential PFAS plume stability compared to conventional chemicals of concern.

There is a critical need to understand whether existing and developing fate and transport models are able to simulate the migration of PFAS plumes. Key issues include demonstrating the following:

- determine whether PFAS sorption can be simulated using existing standard sorption model terms (e.g., distribution coefficient with linear or Freundlich isotherms) or if the

sorption processes for key PFAS are so distinct that new mathematical sorption models are needed;
- determine whether co-located soil and groundwater samples can yield reliable distribution coefficients for sorption models;
- demonstrate matrix diffusion processes and whether surface diffusion effects on clays or other novel diffusion processes are strong enough to render conventional matrix diffusion models ineffective, or if existing models are sufficiently accurate; and
- demonstrate a more quantitative basis for documenting PFAA precursor transformation to PFAAs, determine if reaction packages available in existing models can be adapted for precursor transformation, and determine how modeling these complex processes might differ from approaches used for other chemicals of concern (e.g., sequential first-order biodegradation kinetics used for chlorinated solvents).

Finally, because the PFAAs in groundwater plumes are unlikely to undergo substantial degradation, an increased focus on how to develop reliable dispersion and matrix diffusion input data would likely improve the accuracy of PFAS modeling. For example, better tools to convert high-resolution geohydrologic field data (e.g., hydraulic profiling data) to reliable input data for matrix diffusion models is a critical need. Newer PFAS vadose zone models are already being developed to help define the PFAS source term and there is an opportunity to couple these approaches with groundwater transport modeling. As a result, developing improved or new models that incorporate complex input data and provide more refined approaches for simulating PFAS behavior in groundwater should be an overarching priority.

4.2.2 Advance Understanding of How AFFF Source Zones Age (Critical Priority)

AFFF use as part of fire training activities typically resulted in releases that consisted of a complex mixture of PFAS, hydrocarbon surfactants, cosolvents, and residual fuels. Upon entering the subsurface, this likely led to changes in subsurface redox and transformation of many of the AFFF constituents (e.g., transformation of PFAA precursors). Source weathering and flushing (either via infiltration through the vadose zone or groundwater flow through the saturated zone) likely play important roles in these redox and transformation processes, and ultimately in overall source longevity and subsequent impacts to groundwater. However, the extent to which a source has been weathered is likely dependent on the history of AFFF release and/or climatic conditions.

Focused research is needed to better understand how AFFF sources age, and the subsequent impacts on redox conditions, precursor transformation, and long-term impacts to groundwater. Specific research areas of interest include:

- determine whether source history methodologies based on high-resolution matrix diffusion sampling could be adapted to reconstruct AFFF source histories;
- develop better probes and sensors to monitor future long-term redox changes in AFFF source zones;
- compare the conditions of AFFF sites with similar site characteristics but with a range of release dates, from older sites to more recent releases;
- identify key indicator compounds that could be used to understand and monitor AFFF source zone aging (see also Section 4.1.9);

- determine the extent to which non-PFAS constituents persist in AFFF source areas, and what potential impact they have on site conditions; and
- develop better conceptual and mathematical models to predict the long-term persistence of AFFF source zones.

Studies of source zone aging at large scales could provide direct measures of PFAS release rates over time, a better ability to model the impacts of changes in environmental conditions, improved models and risk assessments at AFFF sources, and possibly diagnostic markers of source aging processes (e.g., PFAS composition, contaminant mass distribution within the source zone, or key biogeochemical parameters). A dynamic conceptual site model (CSM) of AFFF sites, incorporating key aging effects, could lead to more cost-effective management of AFFF source zones.

4.2.3 Evaluate Role of Low-Permeability Zones on PFAS Transport (Critical Priority)

The importance of low-permeability materials on the retention and subsequent long-term release of non-PFAS chemicals of concern in aquifer formations has been well studied and has been identified as a frequent cause of sustained plumes (Berns et al., 2019; Mundle et al., 2007; West and Kueper, 2010). For chlorinated solvents, even relatively thin clay lenses can control the longevity of groundwater plumes (Parker et al., 2008). Recent modeling studies suggest that low permeability zones may play a similarly important role for PFAS migration (Kulkarni et al., 2022). However, despite the fact that substantial PFAS accumulation in low permeability soils has been observed at AFFF-impacted sites (e.g., Adamson et al., 2020), several critical unknowns persist regarding PFAS transport in low permeability media, including:

- the role of mineralogy, aging, co-occurring chemicals of concern, soil water content, and water geochemistry on adsorption-desorption processes for a wide range of PFAS present at AFFF-impacted sites;
- the extent of PFAS aggregation, surface diffusion (e.g., Schaefer et al., 2021), fluid-fluid interfaces, and compound structure/charge on diffusive transport and overall diffusive flux of PFAS;
- the extent to which PFAA precursor transformation may occur in low permeability materials, and subsequent impacts on PFAS transport;
- the extent to which low-permeability zones contribute to or mitigate groundwater plumes at AFFF-impacted sites; and
- the impacts of low permeability materials with respect to remediation technology effectiveness.

Studies to address these knowledge gaps should include coupled laboratory- and field-based approaches, as well as relevant empirical data and verified models. Understanding these processes for the wide range of PFAS present at many AFFF-impacted sites, including anionic, zwitterionic, and cationic species, also is needed.

4.2.4 Conduct Meta-Studies of PFAS Field Distributions as a Function of Site Characteristics (Critical Priority)

Historically, meta-studies of groundwater plumes at multiple sites have provided key insights about the behavior regarding chemicals of concern in the subsurface and the impacts of remediation on plume intensity and longevity (or lack thereof). Since 1995, researchers have performed meta-studies for a variety of groundwater contaminants such as hydrocarbons (Mace et al., 1997; Newell and Connor, 1999; Rice et al., 1995), chlorinated solvents (Aziz et al., 2000; McGuire et al., 2004; McNab et al., 1999; Newell et al., 2006), manufactured gas plant (MGP) constituents (EPRI, 2012); oxygenates such as methyl tert-butyl ether (MTBE) (Kamath et al., 2012; McDade et al., 2015), and stabilizers like 1,4-dioxane (Adamson et al., 2014; 2015). Some studies have compiled data from thousands of plumes and tens of thousands of monitoring wells. For example, McHugh et al. (2015) analyzed a database with 12,000 sites and 2.1 million groundwater samples. Through these types of studies, it was discovered that leaking underground-storage-site plumes comprised of benzene, toluene, ethylbenzene, and xylenes (BTEX) are substantially controlled by natural attenuation. Exceptionally long MTBE plumes in the early 2000s had diminished in length by 2015; and, contrary to expectations, most 1,4-dioxane plumes were not longer than their associated chlorinated solvent plumes due to remediation and natural attenuation processes.

Meta-studies of multiple well-characterized PFAS plumes also may provide new insights into key PFAS fate and transport knowledge gaps such as the following:

- the approximate distribution of PFAS plume lengths in groundwater as a function of the groundwater hydrology (Darcy flow, dispersivity) and sorption factors (e.g., f_{oc}, AEC, dissolved anions, water temperature);
- the distribution of historical plume expansion rates;
- the nature of PFAA plume stability and the general distribution of shrinking, stable, and expanding plumes for individual key PFAAs;
- whether the observed length of individual PFAA plumes generally follow their expected behavior based on chemical factors such as functional group and chain length (e.g., expected K_ds);
- for sites with PFAA precursor measurements, the relative historical migration rates of PFAAs versus PFAA precursors and whether PFAA precursor biodegradation and concomitant PFAA production can be detected in the multi-site data;
- the relative importance of different PFAA attenuation factors (e.g., dispersion, sorption, and/or matrix diffusion); and
- whether passive attenuation-based remedies can be applied successfully at specific sites.

At this time, there are only a limited number of PFAS groundwater plumes that have been well characterized. With the current DoD focus on ramping up remedial investigations at PFAS-impacted sites, the number of well-characterized plumes will quickly increase over the next few years. Ancillary factors such as pH, oxidation-reduction potential (ORP), dissolved oxygen, solids mineralogy and properties (e.g., AEC), and dissolved organic carbon also will be gathered depending on the design of the RI study. Overall, meta-studies of multiple PFAS sites could be mined to identify "common denominator" processes that occur at many PFAS sites that could increase our understanding of how PFAS plumes migrate in the subsurface, improve our ability to assess risks associated with specific plumes, and improve remediation decision-making.

4.2.5 Assess Behavior of PFAS in Wetlands (High Priority)

At this point, little is known about the fate of PFAS in wetlands. PFAS, particularly cationic species and those with long perfluoroalkyl chains, are expected to sorb onto wetland sediments. Wetlands are distinguished by the presence of hydric soils and plants adapted to live in such conditions. Wetlands often are at the boundary between upland soils and open waters and may therefore process a significant amount of surface runoff before it is discharged to streams and lakes. Shallow groundwater can also discharge into wetlands. As such, wetlands may be the recipients of PFAS from impacted sites and/or discharged by groundwater to surface waters. Wetlands are important habitats for wildlife—including some threatened and endangered species—and are furthermore characterized by a high level of biological productivity and a wide range of biogeochemical processes. Engineers have taken advantage of this wide range of processes to design treatment wetlands for a wide range of chemicals of concern, although a better understanding of the mechanisms for the removal of specific organic contaminants in wetlands is still warranted (Jasper et al., 2013).

Given the high biological productivity of wetlands, crucial questions remain on how PFAS might enter the food chain in these ecosystems. PFAS may be taken up by emergent vegetation (Pi et al., 2017; Wang et al., 2020a, b), which is expected to vary between surface and subsurface wetlands as well as the route of entry of PFAS into wetlands (i.e., groundwater discharge versus surface runoff). In terms of PFAS biotransformation, the high levels of microbial activity (e.g., nitrate, iron, and sulfate reduction) may convert polyfluoroalkyl substances into PFAAs in wetlands. However, little information is available at this point on the transformation or persistence of PFAS in wetland environments. There also is an absence of data on fluxes of PFAS to open water bodies from wetlands. Many wetlands are located close to U.S. Navy installations, U.S. Army bases, and commercial airports. Given the high biological productivity in these wetlands, there is a need to understand PFAS fate and transport in these settings and possible pathways to the food chain.

Specific questions of interest include:

- Are PFAS sequestered in wetlands?
- Do PFAS, particularly PFAA precursors, undergo biotic or abiotic transformation to an appreciable degree in wetlands? If so, which organisms, microbial communities, or other mechanisms are responsible for these transformations?
- While some wetlands are permanently flooded, others have extended time periods without standing water, where they resemble upland soils. How do these changes, with significant changes in redox conditions and microbial activity, affect the transport and transformation of PFAS?
- Can wetlands be engineered to protect surface waters from PFAS-impacted runoff?
- Do wetlands (natural and constructed) serve as an important source of exposure of wildlife to PFAS and as a pathway to enter the food chain?

4.2.6 Assess Rhizosphere/Plant Influences on PFAS Distribution and Ecological Exposure (High Priority)

The long-term impact of high levels of PFAS in vadose zone soils remains unclear. In particular, given the potential for some PFAS to be taken up by plants (Xu et al., 2022) and for other PFAA precursors to be transformed by plants (Bizkarguenaga et al., 2016), the role of the rhizosphere and complex interactions of plants (including trees, but also perennial grasses) in the cycling, transport, and transformation of PFAS at and near the soil surface remains understudied. Such interactions may be particularly important given the accumulation of PFAS at the air-water interface in the subsurface. Topics warranting additional investigations include:

- the role of plant uptake and cycling (i.e., leaf litter) of PFAS at the source as well as at downgradient or downwind locations (i.e., the potential for biotransport);
- potential contributions of rhizosphere microbial and mycorrhizal activity and/or plant and endophyte metabolism on transformation of polyfluorinated substances and release of PFAAs; and
- the relative role of terrestrial plant accumulation and PFAS cycling on terrestrial ecological exposures (particularly for higher trophic organisms as a result of food web accumulation) — this may include investigations of *in planta* PFAS distribution (e.g., which compartments accumulate PFAS) and fate (e.g., does phytovolatilization play a role for individual PFAS).

Field-scale studies, perhaps coupled with green-house studies, that develop a better understanding of the importance of these processes with respect to PFAS fate and transport and terrestrial ecological exposures are of particular interest.

4.2.7 Evaluate Role of Solid Versus Dissolved Phases in Stormwater Runoff (High Priority)

The presence of PFAS in stormwater at DoD installations has raised concerns about discharges to local receiving water bodies, including sediments. To design adequate stormwater control measures, characterization of the type of PFAS and form of PFAS (i.e., dissolved or particle-bound) is needed. Specifically, PFAS affinity to particulates is poorly understood, especially as it relates to particulate size, surface charge, and composition among the various anionic, zwitterionic, and cationic species that are present. Topics warranting additional investigations include:

- quantify the interactions between various PFAS classes and particulate/colloidal species commonly found in stormwater runoff — both mineral and organic-based particles should be considered, as well as particle sizes that range from the millimeter scale to colloidal;
- evaluate how PFAS distribution between dissolved and particulate phases vary as a function of storm conditions and other site-specific factors (e.g., terrain, nature of AFFF source);
- determine how water chemistry (pH, ionic strength, dissolved organic carbon) and co-occurring chemicals of concern impact PFAS partitioning to particles;
- identify seasonal or other temporal impacts on PFAS distribution between dissolved and particulate phases;
- determine the extent to which particle-bound PFAS impact stormwater treatment approaches (e.g., filtration, sorption); and
- develop models to describe the coupled dissolved and particle-associated migration of PFAS in stormwater, and the subsequent fate of PFAS in stormwater treatment systems

Field-based studies that develop a better understanding of the importance of these topics and inform potential treatment technologies are of particular interest.

4.2.8 Assess Role of Gas/Aerosol Transport during and after AFFF Application (High Priority)

During historic AFFF use events, foams were discharged in outdoor conditions such that wind-blown overspray was possible. Identification of neutral and volatile PFAS in MIL-SPEC AFFFs at mg/L levels, along with recent work that implicates the relevance of aerosol transport (non-AFFF scenarios) (Titaley et al., 2022) emphasizes the need for research on the potential importance of such PFAS transport during historic AFFF discharges.

At present, it is not known to what spatial extent firefighter training activities impacted surrounding area soils and sediments beyond the footprint of foam infiltration due to transport of PFAS via the gas and aerosol phases. If these transport processes were important during the initial release of PFAS at a site, this has important implications with respect to site assessments. Specifically, health-based soil screening levels are being used to delineate the extent of impact, which are generally much greater (~ 10x) than typical "background" surface soil levels reported in the literature. Therefore, the potential exists for additional marginal soil impact beyond the typical "hotspot" observed in the vicinity of the original footprint of infiltration.

The following specific demonstration needs are of importance:

- collect basic data to understand the potential importance of volatile and non-volatile PFAS during AFFF releases including data on medium- to long-range transport of non-volatile PFAS in aerosols and volatiles in the gas phase as well as additives in historic AFFF;
- collect field data to determine typical spatial distributions (e.g., meters to kilometers) of PFAS beyond firefighter training areas, impacting soils, sediments, and potentially groundwater; and
- evaluate efficacy of existing models for predicting observed spatial distributions due to gas/aerosol transport, and develop modifications to the models if needed.

4.2.9 Determine Effects of Episodic Storm Events and Other Climate Effects on PFAS Fate and Transport (High Priority)

There is substantial evidence that climate change is associated with more frequent and intense extreme weather events (Blunden and Arndt, 2014; Coumou and Rahmstorf, 2012; Intergovernmental Panel on Climate Change, 2013; Najjar et al., 2010), and that this increased variability does affect the transport of some compounds, such as nitrogen species, in the environment (Lee et al., 2016). In the saline littoral settings, seawater influx, be it from either groundwater pumping or raising sea levels/increased tidal flooding, is expected to alter the salinity and hence PFAS transport at sites that are affected by increasing salinity.

Extreme storm events also are likely to have important impacts on PFAS transport. Enhanced leaching and stormwater runoff, along with flooding, could result in episodic PFAS migration that is not typically considered in current modeling approaches. "Background" PFAS levels in rainwaters or floodwaters might also be an important consideration during episodic storm events.

The need to account for climate change and extreme weather events on site cleanup has recently been explored in a two-part series by the Federal Remediation Technologies Roundtable (FRTR), [FRTR 2021]. At this point, it is unknown how such climatological changes might be affecting the fate and transport of PFAS in the environment. Specific questions include:

- Do prolonged droughts result in soil drying that alters the soil redox potential and hence possible PFAA precursor biotransformation?
- Can such prolonged drying events result in changes in soil PFAS concentrations due to enhanced volatilization of select PFAS?
- Do higher and/or more intense precipitation events result in more PFAS transport from shallow soils to surface waters?
- How do major flood events affect PFAS that have accumulated in riverine sediments?
- What other PFAS transport processes are affected by more extreme precipitation events and a higher amplitude between extreme events?
- How does increased salinity in the near shore environment due to sea level rise or increased tidal flooding affect the fate and transport of PFAS?

While the focus here is on episodic storm events and other climate induced effects, it is recognized that some of these questions are closely related to issues related to PFAS fate and transport in the vadose zone discussed in Section 4.1.2.

5.0 SAMPLING AND ANALYSIS

The use of sampling and analytical methods that are fit for their intended purpose is critical to support decision-making at DoD facilities as well as to support ongoing research efforts. While some EPA PFAS methods have been published in the past few years (e.g., EPA Methods 533, 1633, and 1621), these methods fall short of addressing all sample matrices and classes of PFAS that currently warrant evaluation. Beyond published methods, there exists a host of analytical techniques that researchers, commercial instrument vendors, and laboratories are exploring for application to PFAS. With the discovery of PFAS and ever-changing regulatory landscape, sampling and analysis method needs are and will continue to be in a constant state of flux.

5.1 Research Needs

5.1.1 Develop Field Methods Designed to Rapidly Screen or Monitor PFAS (Critical Priority)

The traditional analysis of anionic PFAS in environmental samples via liquid chromatography with tandem mass spectrometry (LC-MS/MS) is used to identify and quantify a number of specific PFAS in impacted sites for both site characterization and long-term environmental monitoring. While extremely sensitive and accurate, sample collection, shipment, processing, analysis, and validation result in long wait times for data. There are many reasons why novel technologies that could rapidly screen for the presence of PFAS, or routinely monitor for all water-soluble PFAS would be valuable both in the initial site evaluations and long-term monitoring applications. Rapid or near-real-time monitoring on site could guide the site characterization efforts, significantly reducing the amount of time needed and costs incurred to perform a site characterization that includes the entire source zone(s). Similarly, once the precise constituents of a PFAS-impacted site have been determined and measured by traditional methods, real-time monitoring of all PFAS at each location would be much more valuable that trying to assess remediation or sequestration efforts quarterly with the inherent time delay of high-precision methods.

To this end, a number of novel total fluorine detection methods have been developed to measure total fluorine, or total organic fluorine as a surrogate for all water-soluble PFAS. These methods are typically faster and cheaper than LC-MS/MS analysis and provide quantification of total PFAS (but not individual PFAS); however, the PFAS accounted for can be limited by the sample extraction technique used (e.g., sorbents used in adsorbable organic methods typically have difficulty retaining short chain [C4 or less] PFAS). If there is no total fluorine measured in a sample, there can be no PFAS present, which allows unimpacted samples to be excluded from further analysis. Similarly, if total fluorine could be directly compared via split sampling with a traditional measurement of targeted PFAS, then subsequent long-term monitoring could be on total fluorine concentrations. A rapid change in total fluorine could be used to trigger site-specific responses to events such as remediation system break-through, hydrologic events, etc.

All of these new methods for total fluorine, or some other understudied type of PFAS, will need method validation studies, reference materials for interlaboratory comparisons, and identification of strengths and limitations for each method, and associated sample preparation in the field.

Specific areas of need have been identified as follows:

- conduct method validation studies to demonstrate rapid (near real time) screening capability, and sensitivity in the field;
- develop reference materials that can be used for interlaboratory studies to support rapid screening methods;
- search for more limited technologies that could be repurposed for all PFAS (e.g., returning to gas chromatography [GC] with electron capture detectors [ECDs] to screen for volatile PFAS);
- better define the mass balance of fluorine at impacted sites to understand the difference between total fluorine concentrations and the sum of targeted PFAS (which typically accounts for 1 – 10% of total F);
- for total fluorine methods, develop better methods to discriminate or eliminate inorganic fluoride background from typical environmental matrices such as drinking water, soils and sediments; and
- develop rapid methods for total organofluorine that would be able to monitor incineration efforts in real-time to reduce smokestack emissions.

5.1.2 Develop Better Laboratory Preparation and Analysis Methods for Inclusion of Understudied Types of PFAS (Critical Priority)

While there have been tremendous technological advances in detection and quantification of water-soluble anionic PFAS in environmental samples, there are several other types of PFAS that are currently understudied because rigorous preparation and analysis methods have not been established. Any PFAS that are not readily accessible by traditional LC-MS/MS methods such as those described in EPA Method 537.1 or draft EPA Method 1633 are included in this list, such as those PFAS that are too volatile for liquid chromatography (e.g., ultra-short-chain, ethers, telomer alcohols), PFAS that are polymeric in nature (side-chain fluoropolymers), or non-anionic PFAS (e.g., zwitterions). All of these understudied types of PFAS have been observed in the environment, and many may act as precursors to the more readily detected PFAS. Some of these may be of regulatory interest in the future in their own right. New laboratory methods to prepare environmental samples from a variety of matrices need to be developed and standardized for these types of PFAS. This would include the creation of reference materials to quantify PFAS in these matrices. Additionally, new analysis methods are required for some of these PFAS, and those methods also need interlaboratory validation.

Specific areas of need have been identified and include examples as follows:

- GC-MS methods for volatile PFAS;
- ultrashort PFAS (C2-C3) characterization/capture methods (e.g., trifluoroacetic acid [TFA]);
- use of pyrolysis GC (which is used commercially for microplastics) for PFAS;
- comparison of acidic versus basic sample extraction methods (adds complexity);
- development of clean-up steps for common LC-MS/MS interferences (MRM limits);
- development of novel solid-phase extraction methods/media (e.g., vacuum assisted sorptive extraction);

- development of extraction and measurement methods for dissolved PFAS in oils and bilge water;
- development of better clean-up steps for water mixed with other matrices; and
- standardization of methods to eliminate inorganic fluoride from samples in total fluorine methods (e.g., to obtain total extractable organofluorine values).

5.1.3 Develop and Validate New Sampling Methods Relative to Thermal Treatment Processes, Stormwater Sampling, Surface Water, and Sediment Fractionation Sampling (Critical Priority)

Significant advancements have been made in the sampling and analysis of PFAS in some environmental and engineered settings. However, several systems remain to be rigorously characterized, beginning with the development and standardization of sampling methods. Of highest priority are systems such as incinerators, surface water, and sediment. PFAS may differentially partition to suspended sediment and accumulate along various phase interfaces present in surface water. Moreover, stormwater discharges into surface water may complicate surface water characterization and discharge permit compliance monitoring. It is therefore necessary to further develop sampling technologies and methods. Critical issues to be addressed include:

- Evaluation of the thermal destruction of PFAS-containing or -impacted media requires an understanding of both the processes inside thermal reactors and the composition of stack emissions. Sampling and analysis methods are needed to characterize radical and/or volatile fluorine species with the ultimate goal of closing the fluorine mass balance (for details, see Section 6.1.1 and 6.1.2).
- Real-time and total PFAS measurements are needed to allow process monitoring and screening sites for further characterization using definitive methods.
- Standardization of surface water, stormwater, and sediment sampling, including the use of passive samplers for PFAS.
- Development of sampling strategies to address the potential for time-variable PFAS concentrations in stormwater flows.
- Demonstration of real-time electrochemical PFAS sensors for ultra-low concentrations in the presence of complex and variable geochemical conditions and co-occurring chemicals of concern.
- Determination of the appropriate sample size of impacted environmental media. What is the lowest sample volume/mass that is representative, and what are the limitations?
- Methods for and standardization of foam and surface microlayer collection.

There is a clear need for the development of these sampling methods to appropriately manage and remediate environmental impacts. Laboratory- and field-scale studies that enable a fundamental understanding of the occurrence, speciation, fate, and transport of PFAS in these systems are of interest.

5.1.4 Evaluate PFAS Sampling Protocols (High Priority)

A number of PFAS sampling guidance documents have been published by federal and state government entities as well as commercial organizations over the past few years. These documents detail the equipment, supplies, techniques, timing, and specific requirements for location of sampling for a wide range of environmental media. Often, there are significant differences in these published protocols; however, the impact of these differences on the resulting site characterization, or the representativeness of the collected samples, has not been evaluated.

While sampling that follows a published method is the minimum criterion needed for any site characterization, determination of which of these protocols provides the most accurate, complete characterization requires comparison of existing sampling protocols. In particular, there is a high need to provide objective data to address the following:

- evaluate the impact of differing sample volumes/masses collected on the limit of quantitation (LOQ) and characterization;
- evaluate the impact of varying techniques for the collection of various sample types such as microlayer and AFFF foam samples;
- evaluate the impact of sample collection location, in particular sampling depth in a surface water sample;
- evaluate the impact of in-field sample processing steps such as homogenization/splitting, and filtering; and
- evaluate the applicability and limitations of incremental sampling to PFAS site investigations.

Field-scale studies that provide a thorough comparison of sampling protocols at multiple sites with varying geochemical/geophysical properties are needed.

5.1.5 Develop Methods to Assess Leaching and Mobility of Polymeric PFAS and Polymer-Associated Low Molecular Weight PFAS (High Priority)

To date, studies on leaching and mobility of PFAS have focused primarily on low-molecular-weight (i.e., nonpolymeric) PFAS such as PFAAs and a limited number of polyfluoroalkyl substances (e.g., fluorotelomer-based PFAS). Few studies have investigated the potential for generation of low-molecular-weight PFAS from fluorinated polymers. Polymeric PFAS can be divided into fluoropolymers, side-chain fluorinated polymers, and poly- or perfluoropolyethers (Buck et al., 2010). Fluoropolymers have a carbon backbone with fluorine attached, poly- and perfluoropolyethers have a carbon and oxygen backbone with fluorine attached, and side-chain fluoropolymers have a non-fluorinated backbone with fluorinated side-chains attached (Buck et al., 2010). DoD-related uses of fluorinated polymers include munitions, aerospace applications (e.g., flight controls, communication equipment), building materials (e.g., piping, sealants), protective clothing, lubricants, surface coatings, consumer products, and others (Olsavsky et al., 2020).

Due to challenges associated with extraction and analysis, few researchers have investigated the occurrence of fluorinated polymers in the environment; however, side-chain fluorinated polymers have been detected in sediment, soil, and biosolids (Chu et al., 2017; Letcher et al., 2020). In addition to polymeric PFAS, a key concern is the potential for fluorinated polymers to contain residual low-molecular-weight PFAS. Researchers have reported that volatile PFAS (e.g., n:2 fluorotelomer alcohols) and non-volatile PFAS (e.g., PFAA) are associated with polymers such as polytetrafluoroethylene (PTFE) and side-chain fluorinated polymers (Muensterman et al., 2022; Peaslee et al., 2020). Further, low-molecular-weight PFAS may be generated during polymer weathering. Studies of the conversion of fluorinated polymers to low-molecular-weight PFAS have focused on a subset of materials and have yielded vastly different estimates of polymer half-lives (i.e., decades to millennia) in part due to varied methods of evaluating polymer degradation (Lohmann et al., 2020; Rankin et al., 2014; Russell et al., 2008; Russell et al., 2010; Washington et al., 2015a; 2015b). As a result, standardized approaches to evaluate the release of fluorinated polymers and polymer-associated low-molecular-weight PFAS are needed. Specific areas of need include:

- methods of extraction and analysis of PFAS from fluorinated polymers (some methods have been published, but they are not standardized);
- development of standardized approaches or optimization of existing leaching protocols for assessment of leaching and mobility of polymeric PFAS and polymer-associated, low-molecular-weight PFAS from matrices including soils, biosolids, and consolidated materials;
- demonstration of developed/optimized approaches on varied fluorinated polymers or polymer-impacted materials to ensure repeatable evaluations of leaching under a range of environmentally relevant conditions; and
- validation of leaching protocols through comparison to field data.

Additional factors that should be considered include assessment of which fluorinated polymers and release scenarios (e.g., surface release, disposal) are most relevant to the DoD and which low molecular weight PFAS are most likely to be generated or leach from common fluorinated polymers during these release scenarios. Development of these methods will allow a more in-depth understanding of the environmental risk associated with DoD uses and application of fluorinated polymers or fluorinated polymer-containing materials.

5.1.6 Develop Ancillary Real-Time Sensors for Monitoring PFAS Transport in Treatment Systems, Discharge Flows, and Environmental Waters (High Priority)

There is a need to develop real-time, continuous monitoring PFAS sensors for use in ex situ treatment systems and discharge flows to provide a continuous record of treatment performance and compliance, and to give early warning of potential PFAS breakthrough and/or exceedences. There is also a need for real-time, continuous monitoring of key ancillary parameters that could improve both initial site characterization and long-term monitoring for PFAS. Acknowledging that there are technical constraints that have frustrated the development of real-time sensors for directly measuring PFAS concentrations in water, the development and verification of real-time sensors for other in situ parameters could result in better tools for measuring the PFAS source zone strength over time (e.g., mass discharge) and for monitoring changes in environmental conditions (e.g., changing from anaerobic to aerobic geochemical environment which could increase precursor transformation).

As an example, source strength in terms of mass discharge is determined by multiplying a water flowrate through a control area by PFAS concentration measurements. In the vadose zone, there are no accepted methods for estimating annual infiltration through a control area, and in some cases, it is assumed to be constant at a rate equal to some fraction of the annual precipitation. However, an alternate conceptual model suggests that the mass discharge from vadose zone to groundwater is episodic, greatly complicating the measurement of mass discharge to groundwater.

Use of existing or new real-time sensors is one approach to generate real-time estimates of this episodic vertical water flow in the unsaturated zone for calculation of vertical mass discharge. With continuous data collection, this type of sensor array could also be used to trigger the sampling of PFAS in leachate from these larger events, further increasing the accuracy of the mass discharge measurement.

Other examples include the measured groundwater flux in the saturated zone, which is often estimated using slug tests, resulting in measurement uncertainties ranging over an order of magnitude, and a related uncertainty that directly carries over into mass discharge estimates, and the need to measure redox geochemistry spatially and temporally in the field.

Critical issues to be addressed include:

- development of real-time water sensor arrays and analysis methodology for field sites that can be used to measure vadose zone saturation as a function of depth and time;
- development of novel groundwater-flow sensors or novel adaptations of existing sensors to provide high-frequency continuous groundwater data that can yield more accurate and precise estimates of the groundwater flowrate entering or leaving PFAS source zones; and
- development of reliable, real-time redox sensors that can identify if underlying geochemical conditions have changed in PFAS source zones and plumes — while novel new sensors have recently emerged and are being evaluated at some sites, more verification studies are needed to confirm accuracy and long-term reliability at PFAS sites.

5.2 Demonstration Needs

5.2.1 Create Materials to Support Existing and Developing Methods (Critical Priority)

The EPA has published EPA Method 1633, an LC-MS/MS method, for the analysis of PFAS in environmental matrices such as aqueous samples, soils/sediments, biosolids, and tissue samples. This method measures 40 PFAS; however, PFAS as a group contain thousands of synthetic chemicals. With only 75 to 100 chemical standards commercially available, a major concern is the lack of chemical standards for PFAS measurement. In addition, reference standards to assess the quality of data provided are needed as are analytical methods for the assessment of understudied PFAS (e.g., volatile, semi-volatile, zwitterions). The development of reference standards will be especially valuable in supporting the current and future measurement methods. Critical areas that need to be addressed are listed below:

- Since chemical synthesis can be a time consuming and costly process, prioritization of PFAS standards is necessary. A comprehensive understanding of understudied PFAS (based on overall extent of detection in environmental samples) should be undertaken to adequately inform the synthesis of new PFAS standards.
- Chemical standard creation will aid in the identification and quantification of PFAS tentatively identified by suspect screening analysis, but where there currently are no standards. Chemical standards which are ionizable using ESI positive and their matching mass labeled internal standards, branched isomers, zwitterions, volatile and

semi volatile PFAS (GC-MS standards), and additional internal standards are of critical importance to address the identification and quantification.

- Comparability and validation of analytical data continuously needs to be evaluated for PFAS measured in environmental samples. There is a clear need to provide reference materials, including research grade test materials, certified reference materials, reference materials, and matrix-matched interlaboratory samples, to assess laboratory data quality on an ongoing basis.
- Detection of PFAS in the air (gas or particulate phase) has implications for emissions, transformation, degradation, transport, and exposure. An improved understanding of the PFAS present in the environment requires the development of standards and methods for the measurement of volatile and semi-volatile PFAS.

5.2.2 Standardize and Validate Methods for Sample Collection of Foam and Surface Water Microlayer (Critical Priority)

In addition to groundwater, surface water, leachate, and wastewater sampling, there is a critical need to evaluate other aqueous matrices such as foam, aerosol spray, and the surface water microlayer to determine the distribution of PFAS throughout a water column. Various techniques, such as surface skimming and hand collection (Michigan Department of Environment, Great Lakes, and Energy, 2019) have been utilized for the collection of foam from surface water or spillage. For example, Zhang and Liang (2020) used a column apparatus to collect foam generated during dissolved air flotation experiments, while Sha et al. (2020) employed a staged impactor to collect sea spray containing PFAS. However, such methods have yet to be fully evaluated with respect to representativeness, robustness and repeatability. While published methods, such as the Langmuir trough (Schaefer et al., 2019), also exist for the collection of surface water microlayer samples, their applicability to PFAS sampling have yet to be rigorously evaluated. Standardized and validated methods are critical to the evaluation of the frequency of occurrence and significance of PFAS-containing microlayer formation in the environment.

In order to evaluate PFAS concentrations in foam and the surface water microlayer, there is a critical need to standardize and validate sample collection protocols for these matrices. Component critical to this standardization and validation include:

- evaluation and optimization of published sampling methods for the collection of the surface water microlayer;
- comparison study of sampling protocols for the collection of foam samples for the determination of the most appropriate sampling protocol via laboratory- and field-scale pilot studies;
- development of methods to integrate the results of foam and microlayer samples with water column samples to understand total PFAS mass and mass discharge in surface water systems;
- optimization of sampling methods for the determination of, at a minimum, the 40 PFAS included in EPA Method 1633;
- formatting of sampling methods to ensure translation of the methods to the commercial laboratory community; and
- evaluation of sampling methods with respect to repeatability, robustness, accuracy, and precision.

There is a clear need to provide objective quality evidence such that procedures used to collect complex matrices such as foam and surface water microlayer samples are fit for their intended use. Existence of standardized methods will aid in determining the relevance of these matrices in site characterization and remediation efforts.

5.2.3 Standardize and Validate Analytical Methods Designed to Close Mass Balance (Critical Priority)

Development and demonstration of standardized, fully validated procedures for closing the fluorine mass balance in various environmental matrices has been identified as a critical need. This is driven by the need to know where the reservoirs and sources of PFAS exist in site characterization and remediation processes (e.g., thermal treatment processes). Established methods for PFAS analysis quantify a small fraction of PFAS analytes (e.g., 40 PFAS via EPA Method 1633) compared to the number of PFAS that have been observed in the environment. Identifying and quantifying the full suite of PFAS that are known to occur in some environmental matrices (e.g., AFFF-impacted soil and groundwater) is challenged by a lack of analytical standards. Currently, routine PFAS analysis focuses on compounds captured using liquid chromatography (LC) with high-resolution mass spectrometry (HRMS). While GC-based techniques are capable of identifying and quantifying many additional PFAS not amenable to LC-based separation, standard methods are lacking. Further, standardized methods that can quantify total PFAS or total organic fluorine (TOF) concentrations are critical to understand the fraction of PFAS not captured in routine analysis. These PFAS not currently measured in PFAS-impacted sites and remediation processes could become future sources of PFAS when environmental transformations occur, or when regulatory interest changes.

Recent studies have used particle-induced gamma emission (PIGE) and combustion ion chromatography (CIC)-based methods to evaluate TOF, but these approaches are conducted largely in research settings and lack standardization and validation. In order to provide high quality evidence of complete destruction of PFAS, there is a critical need to accomplish the following:

- optimize existing techniques designed to detect and quantify polar, semi-volatile, and volatile individual PFAS in a range of media using instruments that are readily available to commercial laboratories such as GC-MS;
- standardize optimized techniques for polar, semi-volatile, and volatile individual PFAS to facilitate adoption by the EPA and commercial laboratories — this includes the development of verified standard reference materials;
- develop, validate, and optimize novel methods for analysis of total PFAS or TOF;
- standardize any novel methods as well as existing methods for total PFAS and TOF analysis — this includes the development of verified standard reference materials; and
- conduct validations (single-laboratory at least) of each standardized method developed for individual or total PFAS/TOF analysis following EPA Office of Water Validation Guidelines.

5.2.4 Optimize and Validate SW-846 Methods 1311 and 1312 for Use with PFAS (Critical Priority)

Standard methods for the evaluation of contaminant leaching in liquids, solids, and multiphasic wastes include EPA Methods 1311 and 1312 in SW-846 (EPA, 1991; 1999). Method 1311 is the Toxicity Characteristic Leaching Procedure (TCLP) and is intended to assess the leaching potential of select inorganic and organic compounds present in liquid, solid, and multiphasic wastes under conditions representative of landfills (EPA, 1999). Results are used to classify waste as hazardous or non-hazardous, which determines the type of solid waste facility (i.e., RCRA or municipal) appropriate for disposal. Method 1312 is the Synthetic Precipitation Leaching Procedure (SPLP), and it is designed to assess the risk to surface water and groundwater due to mobilization of select organic and inorganic constituents in liquids, soils, and wastes as a result of precipitation (EPA, 1991). In the case of solids, both TCLP and SPLP assess leaching using batch extractions of solids at a liquid to solid ratio (L/S) of 20.

TCLP and SPLP were developed, optimized, and validated for use with volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), mercury, and other metals (EPA, 1991; 1999). Neither method has been optimized or validated for use with PFAS. Additionally, Both TCLP and SPLP assess leaching under one set of test conditions representing a single pH and mode of water contact, and they cannot capture material evolution with time. As a result, prior studies based on inorganic constituents have found that these methods can overestimate leaching of inorganic constituents relative to anticipated field conditions (Clavier et al., 2019; Intrakamhaeng et al., 2019; Kosson et al., 2002). In such cases, methods will still offer a worst-case assessment of leaching (Clavier et al., 2019). However, studies have also concluded that TCLP and SPLP do not always represent the most conservative (i.e., worst-case scenario) estimates of leaching. For example, TCLP was found to underestimate contaminant leaching under conditions representative of the mining and metallurgic industries (Cohen et al., 1999). As summarized by Clavier et al. (2019), shortcomings and concerns regarding these leaching methods were reported in the EPA Scientific Advisory Board (SAB) Leaching Subcommittee documents starting soon after inception of TCLP and SPLP (EPA, 1991; 1999). The SAB advocated for use of scenario-specific leaching evaluations such as Methods 1313-1316 in SW-846, which comprise the Leaching Evaluation Assessment Framework (LEAF) (EPA, 1991, 1999; Kosson et al., 2017, 2019). Regardless, TCLP and SPLP are still implemented in state and federal regulatory frameworks.

Optimization of TCLP and SPLP should be able to draw from ongoing efforts in SERDP to optimize batch leaching methods that are included in LEAF (i.e., Methods 1313, 1316). Although these methods collectively use varied pH and L/S, other factors such as the experimental apparatus and sample collection procedures should be consistent with 1311 and 1312. Demonstration of 1311 and 1312 for use with PFAS will inform leaching scenarios for which test results may yield conservative or relevant estimates of mobility and will inform the limitations that apply to these tests. The latter will be critical to appropriate interpretation of test results, particularly when TCLP or SPLP is required despite evidence that suggests scenario-specific leaching assessments are more appropriate.

Because use of TCLP and SPLP may be appropriate and/or required in certain scenarios, their applicability for use with PFAS needs to be established. Specific areas of need include:

- optimization and demonstration of Methods 1311 and 1312 for use with a variety of PFAS-impacted liquid, solid (including soil), and waste materials;
- estimation of achievable LOQs in various media types;
- validation of Methods 1311 and 1312 through comparison to field data (e.g., lysimeter data);
- identification of leaching scenarios wherein TCLP or SPLP will provide a conservative estimate of PFAS leaching; and
- identification of scenarios including source type and aspects of site geochemistry and hydrogeology wherein TCLP or SPLP will underestimate PFAS leaching.

5.2.5 Evaluate Effects of Sample Storage on Quantitation of PFAS in Biota (High Priority)

The conditions under which environmental samples to be analyzed for a chemical constituent are stored and the duration that they can be stored while maintaining site representativeness is a critical component of any analytical method. Given the risk of increased adsorption of PFAS to container walls over time and the potential for the transformation of precursors, this determination is a crucial component of PFAS methods. Published PFAS methods, such as those for drinking water analysis (EPA Methods 537.1 and 533) and other matrices (EPA Method 1633) identify storage conditions and durations for samples and extracts based on holding time studies that evaluated PFAS concentrations in samples and extracts under various temperatures over various time intervals. While EPA Method 1633 is applicable to tissue samples, a holding time evaluation was not conducted for this matrix. There is an immediate need to evaluate the potential impact of PFAS on organisms that are relevant to DoD facilities; therefore, there is a high need to determine the appropriate thermal preservation for tissue samples. In addition, the evaluation of food sources such as plants is needed. Key components of holding time studies that can fulfill this high need are as follows:

- include the evaluation of the 40 PFAS included in method analyte list of EPA Method 1633, at a minimum;
- utilize EPA Method 1633 sample preparation and analysis;
- evaluate multiple types of tissue, such as fish with varying lipid content;
- evaluate the thermal options presented in EPA Method 1633, at a minimum;
- evaluate the use of freeze-drying techniques; and
- evaluate PFAS concentrations over the intervals evaluated in the EPA Method 1633 holding time study, at a minimum.

The data resulting from these studies must be of the quantity and quality needed to establish scientifically valid holding time and preservation requirements for biota matrices using EPA Method 1633.

5.3 Technology Transfer Needs: Collect and Disseminate Current State of Knowledge of PFAS Analysis (Critical Priority)

In recent years, both the research community and the commercial laboratory community have gained considerable experience and expertise relative to PFAS analysis. As a result of research aimed at answering questions beyond the focus of the commercial laboratory community, the research community has acquired knowledge that can be used to improve data quality. This includes, for example, identification of known interferences and techniques to identify, account for, and/or eliminate matrix interferences. Transfer of this current state of knowledge to the laboratory community that serves the DoD is a critical need as it facilitates the collection of data of improved quality, especially with respect to problematic matrices. With the current increase in DoD projects transitioning to the site investigation stage, there is an increased need to evaluate matrices beyond those evaluated at the remedial investigation stage, many of which can prove to be challenging. It is therefore critical to transfer to the commercial laboratory community the current state of knowledge relative to the analysis of PFAS in a wide range of matrix types. Key elements for inclusion are:

- information on known matrix interferences relative to the 40 PFAS included in the EPA Method 1633 analyte list;
- techniques for detecting, compensating for, and or eliminating matrix interferences;
- techniques for enhancements to EPA published methods;
- training on methods such as Other Test Method 45(OTM-45) that are less commonly used in the commercial sector; and
- an understanding of the limitations and advantages of evolving analytical techniques.

This knowledge transfer can take the form of reference documents, videos, or online/onsite workshops. Solutions and techniques discussed must be relevant to the DoD commercial laboratory community in that they must be allowed under the limitations for method modifications specified in the applicable EPA method and the DoD Environmental Laboratory Accreditation Program (DoD ELAP).

6.0 THERMAL TREATMENT

In this report, thermal processes are defined as processes in which the temperature of the bulk medium (e.g., water, air, soil) is purposefully raised to greater than 100°C. Example technologies include incineration, pyrolysis, supercritical water oxidation, and hydrothermal alkaline treatment.

PFAS represent a highly diverse imultaneously occur across a range of temperatures and other operating conditions within thermal-based reactors. In general, studies have demonstrated that desorption and volatilization of PFAS occur at relatively lower temperatures (e.g., <700ºC), but the possibility exists for some PFAS to transform within the thermal desorption range of others (e.g., Altarawneh et al., 2022; Crownover et al., 2019; Khan et al., 2020; Krusic and Roe, 2004; LaZerte et al., 1953; Riedel et al., 2021). For a specific suite of conditions, understanding the temperature range where more recalcitrant PFAS become volatile and desorb relative to where other more labile PFAS begin to transform is of critical importance since most AFFF-impacted sites are often characterized by the presence of highly complex mixtures of many PFAS (Anderson et al., 2021). Figure 1 conceptually illustrates the range in temperatures where the various processes applicable to the thermal destruction of PFAS and regeneration of sorbent media have been studied and shown to occur, but much additional research is needed to define the regions of overlap and the impact of various operational factors.

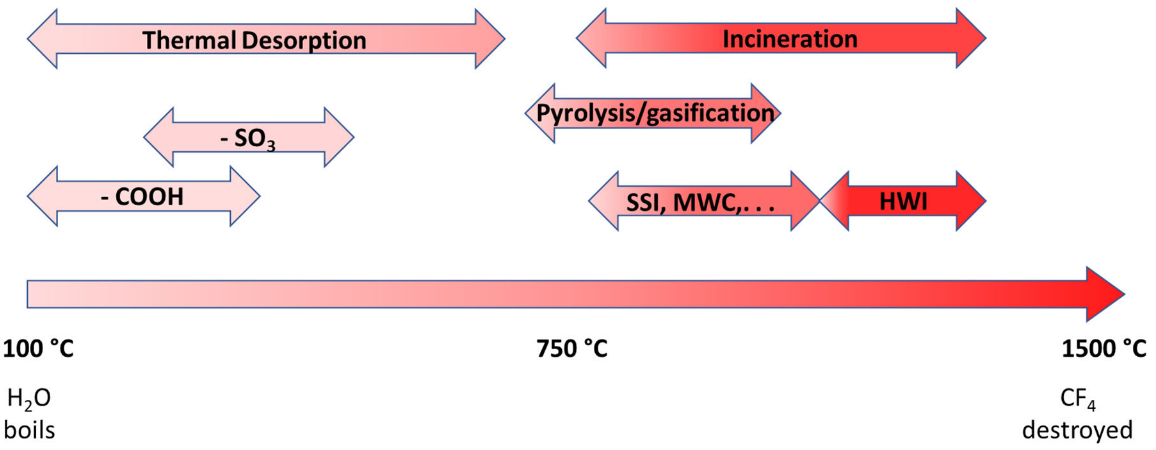

Figure 1. Thermal treatment techniques are shown over the temperature ranges at which they occur, from water boiling to tetrafluoromethane's destruction, 100 to 1500°C. Volatilization occurs in the thermal desorption temperature range, but other chemical changes, such as the loss of a functional group, can start to occur at low temperatures too. SSI, MWC, and HWI refer to sewage sludge incinerators, municipal waste combustors, and hazardous waste incinerators, respectively.

Much research funded under SERDP related to the various processes relevant to thermal destruction of PFAS-impacted media is underway with additional data gaps identified herein as critical basic research requirements. Expected outcomes should ultimately culminate in a comprehensive understanding of all operative mechanisms and their kinetics related to desorption, transformation and mineralization processes as well as relevant factors that affect or in some way modify these processes. These additional factors could include, for example, feedstock composition, processing rate, temperature, residence time, oxygen level, and the presence of additives/catalysts.

6.1 Research Needs

6.1.1 Understand Transformation Mechanisms, Pathways, and Kinetics for Thermal Processes (Critical Priority)

It is critical to elucidate the mechanisms and pathways that underlie conventional and innovative thermal technologies for PFAS destruction. Both experimental and theoretical studies are needed to better understand the mechanisms, rates, and products of the most important pathways by which PFAS transform and mineralize under process-relevant operating conditions (temperature, residence time, reactant concentrations, waste stream composition, gaseous/ condensed phases). Important thermal decomposition mechanisms include combustion, pyrolysis, oxidations, radical reactions such as H abstractions, hydrolysis, elimination, and others. Information on the formation and stability of products of incomplete destruction (PIDs) and other byproducts is particularly important to support the design and operation of thermal technologies, ensure that treatment targets are met, and undesired product formation is minimized. Understanding PID and byproduct formation may also inform the characterization of source zones at firefighting training sites and inhalation exposure of firefighters using AFFF. It is therefore critical to conduct studies focusing on information gaps associated with the following:

- Development of sample collection protocols and analytical methods to identify and quantify specific products (PIDs, byproducts) generated in thermal processes. These products are expected to exhibit a wide range of boiling points and polarities, and protocols are needed that effectively capture PIDs over a range of scales (bench-scale experiments to full-scale sampling campaigns). Furthermore, complementary analytical approaches (e.g., gas and GC/LC-HRMS, ^{19}F-nuclear magnetic resonance [NMR] spectroscopy, Fourier transform infrared [FTIR] spectroscopy) are needed to characterize PFAS degradation pathways. Development of applicable standards and reference materials to support these methods also are needed. See also Sections 5.1.3 and 6.1.2.
- Development of sample collection protocols and analytical methods to support closure of the fluorine mass balance [e.g., ion chromatography, combustion ion chromatography, X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX)]. See also Sections 5.1.3 and 6.1.2.
- Experimental determination of the effects of process-relevant operating conditions such as temperature, residence time, PFAS structure, PFAS concentration, co-occurring chemicals of concern (e.g., chlorinated solvents), and matrix composition (e.g., silicates, calcium) on PFAS destruction mechanisms, mineralization rates, and formation of PIDs and byproducts.
- Coupling experiments with theoretical and kinetic modeling to support mechanistic foundations for optimizing thermal decomposition of PFAS and minimizing PID and byproduct formation. Identification of quantitative structure-activity relationships that can be used to predict reactions of PFAS occurring in AFFF.

- Identification and development of surrogate measurement parameters and analytical approaches (e.g., FTIR) for real-time assessment of PFAS destruction/mineralization efficiencies, as well as stack emission contents.
- Assessment of PFAS destruction efficiencies in thermal processes at multiple scales.

To address these knowledge gaps, data from controlled bench- and pilot-scale experiments are needed that delineate PFAS destruction pathways and PID formation. Data need to be developed with verified sampling and analytical approaches that target PIDs and byproducts with a wide range of polarities and boiling points. Information developed in these experiments is expected to (1) define conditions that assure effective mineralization of PFAS and minimize PID emissions for different PFAS-containing matrices, (2) validate models designed to predict PFAS fate in thermal processes, and (3) serve as a basis for validation studies conducted in pilot- and full-scale systems. See also Section 6.1.4 for related research needs to develop process models.

6.1.2 Develop Vapor Phase Analytical Methods to Measure PFAS Emissions from Thermal Treatment Processes (Critical Priority)

Various methods of thermal treatment can be used for the removal and destruction of PFAS from solids, liquids, and gases. The strong carbon-fluorine bond can require temperatures over 1400°C for complete destruction (Tsang et al., 1998). The functional groups of many PFAS can be removed at temperatures as low as 100°C (LaZerte et al., 1953) creating molecules with physical properties very different than the starting materials. To thoroughly investigate thermal treatment processes for PFAS, it is necessary to have sampling and analytical methods to measure a wide variety of molecules that may persist or form during treatment such as polar, nonpolar, volatile, semi-volatile, and non-volatile molecules. Currently, the analysis of PFAS in liquid and solid matrices is well developed with methods such as EPA Method 1633, but methods for the analysis of PFAS in the vapor phase is lacking with only OTM-45 being released to sample stack emissions for the polar PFAS common to EPA Method 1633. The nonpolar, semi-volatile, and volatile PFAS do not currently have a validated detection method and provide an analytical challenge.

Vapor-phase methods should target the measurement of volatile and semi-volatile PFAS emissions and associated reaction byproducts that may form over a wide range of operating temperatures (i.e., ~100 – 1,200°C) and a wide range of boiling points (i.e., -130 to over 300°C). To accurately identify and quantify this broad suite of compounds, there is a critical need to address the following (see also Sections 5.1.3 and 6.1.1):

- Develop and validate methods to collect gas phase samples and quantitatively introduce them into analytical instrumentation, mainly GC-MS platforms.
- Establish analyte lists of both parent PFAS and possible byproducts formed during treatment and determine the LOQs for targeted methods.
- Develop and validate total organic fluorine or similar methods to analyze gas-phase emissions and establish protocols for closing the fluorine mass balance of gas-phase samples.
- Establish high-resolution GC-MS analytical and data processing approaches, including non-targeted compound libraries.
- Assess analyte integrity under GC-MS operating conditions (e.g., thermal transformations).

- Develop real-time monitoring systems to sample gas streams and detect volatile PFAS and relevant reaction byproducts.

6.1.3 Improve Understanding of Incineration Process Operating Conditions (Critical Priority)

Incineration is commonly employed to destroy hazardous organic wastes. The organic molecules react with oxygen at high temperatures to produce the preferred thermodynamic products, CO_2 and H_2O (Linak and Lee, 2021). The addition of fluorine to the wastes complicates this process in several ways. The fluorine radical is unstable and readily bonds to carbon or hydrogen radicals thereby halting the chain reactions that happen during incineration. This radical suppression property can inhibit combustion and lead to the formation of fluorine containing PIDs. The carbon-fluorine and hydrogen-fluorine bonds are very strong while the oxygen-fluorine and fluorine-fluorine bonds are very weak. This leads to the need for unimolecular bond dissociation or the abstraction of fluorine by a hydrogen radical as the initiating processes to start the destruction of the fluorinated molecule. Both processes require high temperatures and flame conditions are needed for the presence of a hydrogen radical (Tsang et al., 1998). Hazardous waste incinerators likely have temperatures, residence times, and the turbulence necessary to destroy all the carbon-fluorine bonds in PFAS. Incinerators possess different properties and conditions brought about by the complicated reactions as well as thermal and mass transfer processes specific to each incinerator and waste stream, so one set of operating conditions is unlikely to apply to every system. A comprehensive analysis of the emissions for all types of fluorinated PIDs would be necessary to test each incinerator. However, it may be possible to use a process like other performance tests for hazardous compounds in an incinerator, such as the use of a conservative surrogate. To apply this procedure, a substance (e.g., C_2F_6, or another fluorocarbon) is added to the waste feed stream as a PFAS surrogate and the destruction of the surrogate molecule would indicate that the hazardous PFAS will be destroyed too. The surrogate would provide an easily measurable molecule and allow for potential real-time monitoring.

With appropriate temperatures, residence times, and turbulence, incineration is likely to be a safe, effective, and available method to destroy stockpiled PFAS wastes. There is a critical need to identify the optimal operating parameters for full-scale incinerators to ensure the complete destruction of concentrated PFAS waste streams, including AFFF, PFAS-laden sorbents such as GAC and IX resins, as well as residuals from concentration treatment systems. Critical operating parameters can be generally classified into directly-controlled, indirectly-controlled, and emissions assessment type, and can be categorized as the following:

- Directly-controlled parameters
    - What temperatures, residence times, and mixing are needed to fully destroy PFAS?
    - What are the ideal fuel : oxygen : PFAS ratios to destroy PFAS?
- Indirectly-controlled parameters
    - What are the radicals and their concentrations during incineration (fluorine versus other radical reactions)? What are the most common radicals and mechanisms to aid in simulations and understanding of the incineration process?
    - Additive/catalytic enhancements: Are there practical substances that can lower the temperature requirements and increase the kinetic rate of destruction?

  - Matrix effects: Does the incinerator waste matrix as well as nature of PFAS phase (liquid, adsorbed or solids, gas phase) change the conditions needed for complete destruction?
- Emissions assessment
  - What are the possible surrogate types and the most effective measurement methods?
  - Byproduct identification: What PIDs are formed? Are there common PIDs between different PFAS wastes? Are the PIDs volatile, or are the deposited around the incinerator?
  - How does contribution from atmospheric deposition factor into emissions assessment when assessing efficacy of an incineration process?

6.1.4 Develop Predictive Models to Estimate PFAS Destruction and Products as a Function of Incineration Conditions (High Priority)

While the DoD is developing several new PFAS treatment technologies, incineration is currently the most readily available technology for PFAS destruction at full-scale. Additional data is needed to develop thermal PFAS transformation models and to date have only been collected experimentally for a small number of specific PFAS (see Section 6.1.1). Variability in waste stream composition, and therefore in the nature and concentration of reactive species during incineration, further complicates the picture. It is therefore critical to develop accurate models that utilize and leverage our developing an understanding of relevant chemical reactions to predict the behavior of diverse PFAS during incineration, focusing on issues such as those listed below:

- determine relevant thermal reaction pathways and mechanisms for various PFAS classes, including radical formation, propagation, and recombination/termination reactions;
- assess and simulate the reaction order of the kinetic processes involving reactions with fuel-, waste-, and PFAS-derived radicals as a function of concentration;
- quantify treatment of the formation and quasi steady-state concentrations of key radical species (e.g., ●OH, H●, F●...) as a function of waste stream composition and time;
- identify rate-limiting mechanisms governing thermal decomposition of PFAS;
- characterize possible catalytic processes on surfaces such as incinerator walls, carbonaceous solids, and soil components;
- assess formation of possible products of incomplete destruction such as fluorinated dioxins or fluorocarbons with high global warming potential (e.g., CF_4 and C_2F_6) as well as incineration by-products such as fluorinated dibenzofurans;
- assess the fate of fluorine in the presence of Si, Ca, and other inorganics abundant in matrices such as soil within the thermal reactor (e.g., formation of SiF_4);
- assess the fate of fluorine in the presence of co-occurring chemicals of concern, such as chlorinated solvents and the potential formation of chlorofluorocarbons; and
- calibrate and validate model predictions with experimental observations.

To address these knowledge gaps, *ab initio* calculations, thermo-kinetic models, structure-activity linear free-energy relationships, and other models are needed that can predict the behavior of individual PFAS under relevant conditions. Models are expected to predict the extent of mineralization, the formation of products of incomplete destruction, and byproducts of concern as a function of temperature, residence time, and co-introduced materials such as soils.

6.1.5 Improve Understanding of Important Process Operating Conditions for Non-Incineration Thermal Destruction Technologies (High Priority)

There is a growing need for alternative thermal destruction technologies, especially those that can be implemented on-site to treat highly impacted media from source zones (e.g., soils, waste pond fines, fire training area collection waste), investigation-derived wastes, and PFAS byproduct streams derived during site remediation (e.g., exhausted adsorbents, sorbent regenerant waste streams, soil washing wastes, foam fractionates). A variety of non-incineration thermal treatment processes have been proposed that range from established treatment systems to emerging technologies, including pyrolysis/gasification, hydrothermal alkaline treatment (HALT), supercritical water oxidation (SCWO), plasma, and dry catalyzed thermal treatment (Hao et al., 2021; Krause et al., 2022; Singh et al., 2019; Wang et al., 2015). Although these technologies are not currently as widely available as incineration, such treatment processes may provide advantages over incineration depending on the feed material, volume of impacted material, and treatment objective. Ultimately, the goal is to identify processes and conditions that maximize complete mineralization of PFAS and minimize generation of hazardous byproducts. To advance individual technologies, critical information is needed to establish their suitability and feasibility for mineralizing PFAS, and to identify important process design constraints and performance criteria. Potential data gaps and research questions include the following:

- assess the influence of important operational conditions on the extent of PFAS destruction and mineralization, including temperature, residence time, pressure, and the addition of amendments, oxidants, and co-fuels — identification of catalysts and amendments that accelerate PFAS destruction or sequester byproducts (e.g., HF) from these processes is also of interest;
- compare energy requirements and life cycle environmental impacts for achieving target levels of PFAS destruction (e.g., >99%) to established incineration practices;
- assess effects of the PFAS-impacted matrix (e.g., soil, water, solid waste) on required operational conditions needed to achieve targeted levels of PFAS destruction — the influence and behavior of common AFFF co-occurring chemicals of concern during these processes should also be assessed;
- establish fluorine mass balance and quantify fluorochemical residuals in process effluents, including potential for gas phase emissions of HF and volatile fluorochemical products (e.g., CF_4, C_2F_6);
- investigation coupling of non-incineration thermal treatment processes with other technologies designed to separate and concentrate PFAS (e.g., foam fractionation, soil washing, membranes, sorption);
- provide supporting evidence for underlying reaction mechanisms and pathways that can be applied to maximize PFAS mineralization while minimizing formation of undesirable byproducts; and
- investigate application of non-incineration thermal treatment to the growing suite of PFAS identified at AFFF-impacted sites, including shorter-chain structures that have replaced legacy formulations.

There is a clear need to advance the development of effective on-site alternatives to off-site centralized incineration. Achieving this goal requires independent and objective evaluations of the promising non-incineration thermal treatment technologies before they can be broadly applied at PFAS-impacted sites. Laboratory and field studies including side-by-side comparisons for treatment of common wastes are of interest, as is research focused on the upscaling of novel technologies and the effect on treatment performance and costs.

6.2 Demonstration Needs

6.2.1 Develop Best Practice Incineration Conditions (Critical Priority)

Demonstration projects funded under ESTCP that systematically transfer the mechanistic knowledge gained during addressing the research needs described above into validated guidance is needed to provide a universal suite of operational conditions and/or compliance protocols for adoption by regulatory agencies to permit safe and effective destruction of PFAS-containing wastes at fixed industrial hazardous waste incineration facilities and/or on-site alternatives.

6.2.2 Demonstrate and Validate On-Site Thermal Treatment Technologies for Management of PFAS-Containing Media (High Priority)

Many thermal technologies (e.g., thermal desorption coupled with thermal oxidation for solids, SCWO for liquids) may be suitable for on-site treatment of PFAS, but field demonstration and validation of these treatment technologies are needed. Such on-site systems are used for limited durations (i.e., until all desired materials are treated), and often involve mobile or otherwise easily deployable components, and are distinct from stationary permanent facilities that receive diverse materials from many locations, sometimes at great distance. In contrast to permanent facilities, on-site thermal treatment systems may benefit from targeted optimization addressing site-specific needs (e.g., contaminant as well as media profiles and/or volumes), and some on-site thermal technologies may also be considered for in situ applications (e.g., in situ thermal desorption).

Demonstration and validation of on-site thermal treatment technologies are needed to inform several concerns:

- To date, thermal technologies have been shown to remove or reduce quantities of select PFAS (e.g., perfluoroalkyl acids such as PFOS and PFOA) from media, but efficacy for treating a wider variety of AFFF-relevant PFAS must be demonstrated. Disposition of treated materials (e.g., unrestricted on-site use) should be considered.
- Complete transformation of PFAS to benign products is strongly desired, but collection and concentration of PIDs may also be considered (e.g., through use of appropriate air pollution control devices) if these are suitable for subsequent treatment by other means. The extent of PFAS transformation can be evaluated through examination of the fluorine mass balance, which requires careful consideration of fluorine before and after treatment in all relevant phases (i.e., gas/liquid/solid). As described in Section 6.1.2, there is a clear need for improved analytical approaches to evaluate all possible treatment by-products, including targeted and non-targeted PIDs.
- Approaches for assessing and documenting thermal system performance, preferably in real-time, need to be improved, demonstrated, and validated. This may include measurements of PFAS or other relevant indicators (e.g., surrogates or hydrofluoric

acid) related to treatment performance, as well as real-time monitoring and logging of operating conditions (e.g., temperature, time, mixing). Predictive models may be useful for defining appropriate operating conditions, but empirical evidence is also needed to demonstrate that air emissions, water discharges, and solids are not of concern.

- The behavior of co-occurring chemicals of concern (e.g., metals, volatile organic compounds) during thermal treatment should be considered. Co-occurring chemicals of concern may be transformed during thermal treatment; or co-occurring chemicals of concern may otherwise impact system requirements, performance, and emissions. Unintended and undesired byproducts of thermal processes (e.g., mobilization of toxic metals) should be evaluated.
- There is significant uncertainty regarding the scalability of different on-site thermal treatment technologies. For example, the size and scale of required on-site systems may vary widely based on treatment volumes, material disposition, and co-occurring chemicals of concern. Better information is needed to project performance and costs of competing technologies at a range of scales.

7.0 NON-THERMAL DESTRUCTIVE TREATMENT

Non-thermal physicochemical processes are aimed at destroying PFAS through a variety of mechanisms resulting from different approaches to manipulating oxidation-reduction conditions. Examples of such approaches include biological, electro- and/or photolytic, electro- and/or photochemical, sonolytic, microwave, electron beam, chemical, manipulation of temperature and pressure, and plasma. In general, such treatment approaches produce a suite of highly reactive free radicals that can break down PFAS. While research has provided evidence of PFAS destruction, there remains limited understanding and validation of specific reaction mechanisms and pathways, as well as the effects of PFAS source and reaction conditions on treatment efficiency and effectiveness that would guide optimization and ultimate site-specific technology selection and implementation.

7.1 Research Needs

7.1.1 Improve Understanding of Biodegradation Processes and Biological Treatment Strategies for PFAS (Critical Priority)

Current research provides evidence regarding the microbial biotransformation of subsets of PFAA precursor compounds, such as perfluorooctane-sulfonamides and fluorotelomer alcohols (e.g., Harding-Marjanovic et al., 2015; Zhang et al., 2021). However, there are relatively limited data concerning the potential for significant biodegradative losses of PFAAs by isolated bacterial species (e.g., Huang and Jaffé, 2019), and particularly bacterial processes that could result in defluorination of these compounds, as would be required for the development of bioremediation strategies for PFAS. Moreover, these compounds are structurally diverse and occur in natural environments at exceedingly low concentrations compared to many traditional chemicals of concern, such as chlorinated solvents, where growth-linked biodegradative processes are widely used for site remediation. At present, no organism has been isolated with the capability of using any PFAS as either a carbon and energy source or a terminal electron acceptor.

Relatively few bacterial or fungal species have been tested for their ability to degrade PFAAs or many of the different precursor compounds. Confirmed reports of the biological removal of fluorine atoms from PFAS are few (Shahsavari et al., 2020), and as such, little is known about the biodegradation potential of most PFAS. One recent finding concerning PFAS biotransformation has been the suggestion that some fungal ligninolytic enzymes (e.g., laccases, peroxidases) have been demonstrated to transform PFOA and PFOS as well as some precursors in the laboratory (e.g., Huang, 2013). There is a clear need to further explore the biodegradation of PFAS, focused on both PFAAs and precursor compounds. Important research areas include the following:

- Identify new bacterial and/or fungal species capable of biodegrading PFAAs, particularly those that result in substantial defluorination and backbone cleavage. Determine what environmental/geochemical conditions (microbial communities, salinity, temperature, redox, pH, etc.) favor the presence of such organisms.
- Identify intracellular and extracellular enzymes capable of catalyzing PFAA defluorination and/or structural cleavage. Are they constitutively expressed or inducible by PFAS or other organics? Do they require mediators or electron shuttles?

What are the optimal conditions for these enzymes to be present and to significantly biotransform PFAS?

- For organisms and/or consortia where PFAS biotransformation has been observed, determine intermediates and end products. Can mechanism-dependent concentration thresholds below which PFAS biodegradation is difficult to achieve be identified?
- Determine whether there are markers (i.e., gene expressions, rapid assays) that can be used to predict or determine if PFAS biotransformation/defluorination is occurring.
- Given the large number of PFAS that have been synthesized and are present in the environment, determine whether biotransformation pathways can be generalized and likewise, whether end products can be predicted by grouping PFAS into different categories, each with similar chemical properties, but with correction factors for linear/branched chain lengths. Can we draw general conclusions about the relative rates and pathways for certain classes of PFAS (e.g., branched versus linear, ultrashort versus moderate or long-chain, cationic versus anionic or zwitterionic)?
- Determine which compounds are suitable as electron donors, enzyme inducers, mediators, cofactors, vitamins, etc. for PFAS biotransformation. Which primary substrates will support PFAS cometabolism? Which co-occurring chemicals of concern are most inhibitory for PFAS biotransformation processes? Which co-occurring chemicals of concern are stimulatory for PFAS biotransformation processes?
- Bioaugmentation has been used successfully to degrade chlorinated solvents at impacted sites. Can this be reproduced for PFAS degradation once proper organisms have been identified? Are there reactions in PFAS transformation equivalent to the 'stalling' of chlorinated solvent degradation at vinyl chloride that would need to be prevented?

Although there are some promising results showing that PFAS can be degraded, a much deeper understanding of the overall PFAS biodegradation process is needed to evaluate the feasibility of PFAS bioremediation schemes and their general applicability.

7.1.2 Develop More Complete Fundamental Understanding of Mechanisms of PFAS Degradation during Non-Thermal Physicochemical Treatment Processes (Critical Priority)

The chemical composition of PFAS includes a unique combination of structures with highly variable susceptibility to degradation under non-thermal physicochemical treatment conditions. While some of these structures are readily degraded by well-known reactions (e.g., oxidation of unsubstituted and unbranched alkyl moieties), others are less labile and/or less well-studied, such as the ether and sulfonate moieties in the head-group area of some PFAS. Most notably, the (per)fluoroalkyl moieties are exceptionally recalcitrant to degradation under all but the most extreme conditions.

As a result, the non-thermal physicochemical treatment processes that have demonstrated effectiveness on other refractory compounds may be suitable for treatment and destruction of PFAS. These are primarily advanced oxidation and reduction processes that involve extremely reactive free radical intermediates (e.g., hydroxyl radicals, solvated electrons, etc.); however, limited research has been conducted to date to validate reaction mechanisms, particularly in systems where multiple destructive treatment mechanisms are suspected.

The lack of knowledge on the fundamental chemistry of PFAS degradation under conditions of non-thermal physicochemical treatment processes is an impediment to the evaluation, optimization, and application of existing and emerging technologies and the invention of novel ones. Therefore, more research on the fundamental chemistry of these processes is needed. This should include:

- identification and quantification of the reactive species that are directly responsible for PFAS degradation;
- characterization of the pathways and mechanisms by which these reactive species breakdown PFAS molecules;
- development of mechanistically-based kinetic models and rate constants that can describe the breakdown of PFAS parent compounds;
- extension of these kinetic models to describe the network of reactions that determine the distribution of intermediates and products from PFAS degradation;
- coordinated experimental and kinetic modeling analyses to explain and predict differences between measured (target and non-targeted) species and mass balance;
- determine the fundamental basis for the dependence of treatment performance on operational factors such temperature, pH, and dissolved oxygen;
- develop deterministic, quantitative models for the complications caused by mixtures of co-occurring chemicals of concern, matrix materials such as aquifer solids, multiphase media, etc.;
- define the fundamental basis for combination of treatment technologies (e.g., preconcentration, pretreatment, serial treatments [i.e., treatment trains], etc.); and
- apply background on the fundamental aspects of PFAS treatment to explain/predict performance under full-scale field conditions.

7.1.3 Improve Understanding of Effect of Field Conditions on Outcomes of Non-Thermal Destructive Treatment Technologies (Critical Priority)

A variety of non-thermal destructive treatment technologies have been developed to treat PFAS in water and soils. Many of these technologies have proven to destroy PFAS, but primarily in the laboratory and under a limited set of conditions. To move these technologies forward to larger scales, an improved understanding is needed on how different waste stream characteristics and physical and biogeochemical conditions affect the efficiency and effectiveness of PFAS destruction. Specific areas requiring study include the following:

- evaluate how different waste streams that vary in electrolyte composition and contain a range of PFAS (precursors to byproducts), as well as the presence of common co-occurring chemicals of concern, impact treatment effectiveness;
- evaluate how soil properties and pH impact treatment effectiveness;
- evaluate how geologic permeability and hydrology impact treatment effectiveness and efficiency;
- identify indicators of operational and treatment success and how they can be leveraged to improve treatment efficiency and avoid unintended consequences; and
- identify the range of applicability and limitations of the technology as well as where it may fit into a treatment train.

Laboratory and pilot-scale studies conducted under a range of solution and geologic conditions will aid in identifying which technologies are best suited for a full field demonstration alone or as part of a treatment train. Data collected in these studies will also identify parameters within those technologies that can be optimized to allow more effective and efficient treatment at the field scale. Technology evaluations and their role within a treatment train need to include quantifying fluorine mole balances and considering formation of secondary byproducts (e.g., perchlorate, chlorate), ease of implementation, technical and economic scalability, and energy requirements.

7.1.4 Develop Fundamental Understanding of How Technologies Function for Variety of PFAS-Impacted Sources (Critical Priority)

Numerous treatment technologies for the destruction of PFAS have been and are currently being developed for a variety of PFAS-impacted matrices relevant to the DoD. These technologies are at varying stages of development (e.g., technology readiness level) ranging from bench-scale (e.g., microcosms, columns, single reactors) to field-scale units (e.g., mobile treatment trailers, packed bed systems, etc.). Despite these different development stages, it is critical that we gain a fundamental or holistic understanding of how these technologies function for a variety of PFAS-impacted sources including 1) aqueous streams (groundwater, surface water), 2) soils and sediments, and 3) concentrates (AFFF, reject water, regenerants). By using consistent sources of PFAS-impacted matrices to test these technologies, we will gain an “apples to apples” comparison of treatment technologies. The benefits of this approach include facilitation of greater inclusivity of new technologies, avoiding hurdles related to site access, and avoiding inconsistencies between comparisons due to different sources.

7.2 Demonstration Needs (Critical Priority): Conduct Side-by-Side Comparisons of Promising Treatment Technologies or Combinations of Technologies at Select Field Locations

Research and demonstration of promising treatment technologies for PFAS impacted sites and/or materials have made substantial progress under SERDP and ESTCP funded efforts. These technologies include ex situ filtration of aqueous media (e.g., groundwater, stormwater, surface water); in-situ treatment of PFAS-impacted soils and groundwater; and PFAS-destructive technologies for spent investigation-derived waste, soils or legacy AFFF stock concentrate.

Many technologies have demonstrated a high degree of efficacy for PFAS treatment. In SERDP, the technologies have shown promise but are often conducted with a single source medium (e.g., PFAS-spiked soils or water, or single-site groundwater or soils). Under ESTCP, several are already commercially available and/or are in the process of becoming so.

A critical need identified at the Workshop is comparisons of these technologies “head-to-head”. These comparisons could be facilitated by providing bench-demonstrated technologies, a series of well-characterized, impacted media from DoD sites with a range of geochemical conditions. For aqueous media, the water quality conditions could include a range of total and dissolved solids (TS, TDS), alkalinity, iron and magnesium, and differing levels of PFAS, and the presence of precursors and co-occurring chemicals of concern. For solid media (soils, sediments, or investigation-derived waste [IDW]), different sourced-material, with a range of conditions such as of organic carbon, grain/particle size, or different treatment media. For ESTCP, demonstrating the technology(ies) at a set of common DoD sites with differing physical/geochemical conditions with side-by-side comparisons of technologies, such as a test bed approach. This may include for example, different levels of TS/TDS, various PFAS compositions, the presence of precursors and/or co-occurring chemicals of concern, operational conditions (e.g., energy demand, flow rate, volume), and water sources (e.g., groundwater, IDW, concentrates, high salinity). There is a need to develop real-time, continuous monitoring PFAS sensors for use in ex situ treatment systems and discharge flows to provide continuous record of treatment performance and compliance, and to give early warning of potential PFAS breakthrough and/or exceedences.

7.3 Technology Transfer Needs (Critical Priority): Develop Framework for Selecting PFAS Treatment Technologies for Impacted Environments

Numerous technologies for PFAS remediation have been and are currently being developed for all PFAS-impacted matrices relevant to the DoD (soils/sediments, groundwater, drinking water, stormwater, rinsates, surface water, legacy stockpiles, investigation-derived waste) and are at different stages of development. Despite these different development stages, it is critical that environmental practitioners have up-to-date technical and practical knowledge on the suitability of these remedial options for different environments and site conditions (e.g., high TDS, depth of chemical mass, high organic content, presence of clays), water sources (e.g., groundwater, stormwater, IDW, concentrates), PFAS composition (e.g., presence of precursors, co-occurring chemicals of concern), safety considerations (feasibility framework criteria under CERCLA), and potential for undesired byproducts (e.g., perchlorate, disinfection byproducts). Further, for those technologies that are field-ready, a summary of detailed operational costs will be a critical factor in remedy selection, specifically energy demand, capital costs, and operational labor.

Workshop participants recommended preparing a decision framework to aid in identification and selection of an appropriate remedy or combination of remedies for treatment of PFAS for a particular site, matrix, or PFAS composition. The framework would provide a detailed description of each known technology or approach, their advantages and limitations under various site conditions, and their suitability for field-scale applications or overall scalability. The framework could take the following formats:

- a white paper including sections on each technology, case studies, and a matrix outlining the suitability of each technology for different environments and scenarios;
- training events focused on selection of PFAS remedies for specific types of sites (e.g., ER Manager Training, Navy RITS, EPA CLU-IN) to Interface with various workgroups (regulatory communities, ITRC, Emerging Chemicals Workgroup); or
- a web-based tool where an environmental practitioner can input site conditions and source characteristics to identify the best approaches under a given set of conditions and aid in decision making. Existing decision support tools (e.g., DECERNS or similar multi-criteria decision analysis [MCDA] tools) also can be adapted to address PFAS. Ideally, the tool would be ground-truthed against current down-selected technologies and feasibility studies, and it would incorporate appropriate statistical methodologies and uncertainty analysis. The user interface would also be tested by RPMs and other end users to receive feedback on the applicability of the tool.

8.0 CONCENTRATION TECHNOLOGIES

In recent years, a number of conventional and novel sorbents have been studied at the bench-scale to evaluate their potential to remove PFAS from water. Many of these studies were designed to support the use of the sorbents in ex situ packed-bed sorption processes. Simultaneously, sorbents have been developed for in situ use, as a means to sequester PFAS in the environment. Such technologies play a critical role in combination with destructive technologies. The key research, demonstration, and technology transfer needs identified by workshop participants are discussed in the following sections.

8.1 Research Needs

8.1.1 Develop Framework to Predict Performance of Full-Scale Sorption Processes for PFAS Removal from Bench-Scale Data (Critical Priority)

It is not always clear what data should be collected at the bench-scale to make accurate predictions of sorbent performance during full-scale applications. One common approach is the rapid small-scale column test (RSSCT) (e.g., Park et al., 2022). The RSSCT approach was developed decades ago and provides scaling equations to enable the design of a small-scale column that simulates the performance (i.e., breakthrough) of a full-scale packed-bed sorption process (Crittenden et al., 1991). The RSSCT scaling equations rely on knowledge of the sorption kinetics and affinity of a sorbent as a function of particle size and the mechanisms that control mass transfer of the sorbate to the binding sites on the sorbent. These scaling equations have previously been developed for activated carbon and for sorbates that exhibit specific mechanisms of mass transfer. It is unclear whether these scaling equations are useful when evaluating other conventional sorbents (i.e., ion exchange resins) or novel sorbents that exhibit unique sorption mechanisms (e.g., Schaefer et al., 2020). It is likewise unclear whether one set of scaling equations will adequately simulate the breakthrough of complex mixtures of PFAS that may have variable diffusion coefficients, or the extent to which background water constituents (e.g., natural organic carbon, anions) impact scale-up in the context of PFAS remediation.

There is a critical need to evaluate existing experimental frameworks (i.e., RSSCTs) or to develop and validate novel experimental frameworks to simulate the performance of full-scale adsorption processes for PFAS. Knowledge gaps that need to be addressed include:

- characterization of sorption kinetics, sorption affinity, and sorption capacity as a function of particle size and water chemistry for multiple sorbents and for mixtures of PFAS;
- development and validation of appropriate scaling equations to design bench-scale experiments that can accurately simulate the breakthrough of pilot- or full-scale packed-bed sorption processes; and
- validation of scale-up approaches, which may consist of a combination of experimental and mathematical modeling protocols, with pilot- and/or full-scale breakthrough data.

In lieu of a fully mechanistic framework to simulate the performance of full-scale sorption processes for PFAS, complementary data from bench-scale and pilot- or full-scale systems will be needed to justify an empirical approach. Data from the pilot- or full-scale systems can be from previous studies where the source water is consistent with water used to conduct the bench-scale experiments. Any pilot-scale study should be completed in a manner that is inherently scalable (e.g., full-scale sorbent particle size, empty-bed contact time, hydraulic loading rate).

8.1.2 Develop Systematic Guidance for Implementing and Evaluating In Situ PFAS Adsorption by Colloidal Activated Carbon (Critical Priority)

While there are currently no proven in situ technologies to destroy PFAS in groundwater aquifers, in situ amendments designed to adsorb and sequester PFAS (e.g., powdered and colloidal activated carbon [PAC and CAC], organoclays, biochar) are now being tested in the laboratory and, in some cases, applied in the field (Carey et al., 2019; Liu et al., 2020). One of these agents in particular, CAC, is presently being applied in situ at PFAS sites at large scale. In that the injection of CAC represents one potential technique to treat source areas, mitigate plume expansion, and reduce costs at PFAS sites that can be applied immediately, specific guidance concerning its application and effectiveness at field scale is of critical importance. This guidance is important for DoD RPMs and other project managers to make objective decisions concerning the application of CAC at their sites. Effective technology transfer will consist of guidance concerning the application of CAC in PFAS-containing aquifers

Specifically, there is a need to understand site-specific considerations that may determine the applicability and effectiveness of CAC including:

- Lithological considerations: How do site-specific characteristics influence injectability and subsurface transport of both the CAC and the water to be treated? What is the maximum depth of application? Under what geological conditions is CAC not recommended as an in situ sequestrant for PFAS?
- Delivery and monitoring: Related to performance comparisons and lithological considerations, what are the most effective approaches to deliver the CAC, evaluate its subsurface mixing, and monitor the sequestration of target PFAS?
- To what extent are design considerations impacted by the extent of PFAS impact as well as the presence of co-occurring chemicals of concern such as chlorinated solvents or petroleum hydrocarbons? Are strategies possible to sequester PFAS and degrade the co-occurring chemicals of concern via biological or abiotic approaches?
- What are the most important cost drivers for application?
- What are potential limitations or negative impacts and how can they be mitigated? For example, if CAC enters monitoring wells during injection, are the data from those wells permanently compromised?
- Comparison to any other injectable adsorbents: What are the metrics to measure performance against other in situ treatment options?
- Guidance on various appropriate applications of this technology and associated design guidance is needed. For example, how should this technology be applied when used to reduce PFAS mass flux in high concentration zones versus when it is used at the edges of a plume to protect potential receptors?
- Regulatory concerns: How can regulatory concerns around impacts on water and surrounding environments be identified and addressed through monitoring? One

important goal of this technology transfer is to educate the regulatory community on the application of CAC, including benefits and limitations.

Guidance concerning the appropriate application and potential limitations of CAC for sequestration of PFAS in groundwater aquifers will provide DoD RPMs, practitioners, and regulators with an improved ability to make informed decisions concerning the field application of this material.

8.1.3 Develop Understanding of Fundamentals of PFAS Adsorption-Desorption Behavior in Mixtures for Commercially Available Sorbents (Critical Priority)

The adsorption behavior of PFAS mixtures on commercially available sorbents, such as activated carbons and ion exchange resins, has received only limited attention in the scientific literature (e.g., Maimaiti et al., 2018). Additionally, the effects of co-constituents (e.g., natural organic matter), solution properties (e.g., pH, dissolved salts), and co-occurring chemicals of concern (e.g., chlorinated organic compounds) on the adsorption characteristics of PFAS mixtures are largely unknown (e.g., Gagliano et al., 2020). To accurately predict competitive adsorption of PFAS mixtures, data are needed for a range of concentrations across a range of molar ratios that are representative of surface and groundwater impacts encountered at DoD sites. Furthermore, there is a need to understand the effects of experimental parameters on PFAS desorption (release), adsorption and desorption kinetics (mass transfer), and non-ideal behavior (hysteresis). Data collected from these studies will support the development of multi-component mathematical models that accurately describe the adsorption-desorption behavior of PFAS mixtures on commercially available sorbents over a range of relevant concentrations and environmental conditions. Models should be validated, to the extent possible, with experiments in well-characterized samples (e.g., DOC, pH, anions, cations) of AFFF-impacted surface water or groundwater. Specifically, there is a need for the following:

- collect adsorption data and determine isotherm parameters for mixtures of PFAS and next generation PFAS on commercially available adsorbents for a range of relative molar ratios and concentrations;
- determine effects of co-constituents (e.g., dissolved organic matter [DOM]), relevant co-occurring chemicals of concern, and solution properties (e.g., pH, ionic strength) on the adsorption performance and longevity of commercially available PFAS adsorbents;
- investigate adsorption kinetics and desorption (release) behavior of PFAS mixtures as a function of co-constituents and solution properties, in particular, the role of competition for adsorption sites; and
- develop and validate mathematical models that are capable of simulating and predicting competitive adsorption of PFAS and co-occurring chemicals of concern, and incorporate the potential effects of solution properties and co-constituents on adsorption parameters.

There is a clear need to provide independent, objective data and mathematical models to estimate and design adsorbent treatment systems for PFAS-impacted surface and groundwater. Laboratory and pilot-scale field studies that provide fundamental knowledge of competitive PFAS adsorption parameters and effects will be critical for cost-effective implementation of adsorption-based systems to manage PFAS-impacted waters at DoD facilities.

8.1.4 Develop and Test Conventional or Novel Adsorbents for Capture of Treatment Off-Gases Containing PFAS and Reaction Byproducts (Critical Priority)

A number of in situ and ex situ treatment technologies that have been proposed to treat PFAS-impacted soil and groundwater (e.g., thermal treatment, air-sparging, advanced oxidation) are likely to generate vapor streams containing volatile PFAS species that will need to be captured to prevent release into the environment. Whereas vapor-phase GAC systems are likely to be used for off-gas treatment, the performance of vapor-phase GAC systems for PFAS and PIDs is largely unknown. Furthermore, vapor-phase GAC systems may not effectively remove short-chain PFAS that may be generated during the treatment process (e.g., in situ thermal treatment) nor fluorocarbon PIDs. Therefore, there is a need to develop and test conventional or novel adsorbents that provide effective removal of PFAS and PIDs generated during remediation activities.

Research activities to better understand the issues listed above include the following:

- characterization of vapor streams generated from in situ and ex situ treatment technologies to identify volatile PFAS species of concern as well as other fluorocarbon products of incomplete destruction with a focus on closing the fluorine mass balance (see also Sections 5.1.3 and 6.1.2);
- evaluation of the performance of vapor-phase adsorption processes for the removal or sequestration of target PFAS through novel or standardized experiments; and
- characterization of the longevity and life-cycle (e.g., regeneration, reuse, disposal) of adsorbent media used in vapor-phase adsorption processes.

Understanding the mechanisms of adsorption of fluorinated compounds from the gas phase is expected to assist in these efforts. Research in this area is also likely to be synergistic with efforts to develop passive-sampling technologies to measure volatile PFAS as well as any other pertinent fluorocarbon products of incomplete destruction captured from the vapor-phase.

8.1.5 Assess Novel and Existing Adsorbents to Capture PFAS Poorly Adsorbed by GAC (High Priority)

Most novel and existing adsorbents were evaluated primarily to remove PFOS and PFOA from water, with some studies considering shorter chain PFAS including PFBS and perfluorobutanoic acid (PFBA) (e.g., McNamara et al., 2018; Yu et al., 2009). The lack of data for a larger number of PFAS was driven at least in part by the current regulatory landscape. We anticipate that short-chain and perhaps even ultrashort-chain PFAS will be of increasing importance as the regulatory landscape evolves and toxicity data become available for a wider range of PFAS. In addition, AFFF formulations containing long-chain PFAS, such as PFOA and PFOS, are currently being replaced with modern formulations containing C6 and shorter chain PFAS (Horst et al., 2021). These PFAS are likely to enter the environment in increasing quantities in the future as the new formulations are used for firefighting and fire training. Further, as PFAS destruction technologies come online, it is likely that short-chain and ultrashort-chain PFAS will be generated due to incomplete mineralization of target PFAS. To meet this need, existing adsorbents are likely to be modified or refined (e.g., carbons and resins), and novel adsorbents with broader specificity will continue to be developed (e.g., graphene, structured polymers, surface modified nanomaterials), and emerging sorbents such as colloidal gas aphrons that show promise for removing short-chained

PFAS (Kulkarni et al., 2022) will be evaluated further at the field scale. To ensure a detailed and unbiased understanding of the adsorptive capacity, efficacy, and performance of novel adsorbents, fundamental research focusing on the following areas will be critical to the advancement and adoption of these materials for treatment of PFAS impacted waters:

- evaluation of novel or modified adsorbents that are capable of removing short-chain PFAS proposed or used as replacements for traditional PFAS in AFFF;
- evaluation of novel or modified adsorbents that are capable of removing short-chain PFAS that are reaction byproducts as a final treatment step of a waste-stream generated from a destructive technology;
- evaluation of non-carbon adsorbents capable of treating PFAS that exhibit limited adsorption by existing carbon adsorbents, including short and ultrashort-chain fluorinated acids and ethers;
- evaluation of novel adsorbents that are designed to capture PFAA precursors that have not been well evaluated to date; and
- evaluation of the performance of regeneration methods for adsorbents that are designed to remove short-chain PFAS and PFAA precursors from surface and ground water and PFAS-impacted waste streams.

There is a critical need to develop an improved understanding of how novel and existing sorbents sorb structurally diverse PFAS, particularly those poorly adsorbed by GAC or that result from other destruction treatment technologies (e.g., short and ultra-short fluorinated acids and ethers).

8.1.6 Develop and Validate Novel Soil Amendments for Larger-Area Applications in PFAS Secondary Source Areas (High Priority)

The focus of PFAS investigations at many DoD installations are fire training areas and other areas with known AFFF use. These efforts have helped to delineate PFAS source areas with high soil concentrations and establish priorities for future remediation efforts; however, these investigations also identify areas with lower PFAS soil concentrations that occupy relatively large footprints and are not necessarily proximate to areas with an established AFFF use history. PFAS in these soils can be related to non-dedicated fire actions, secondary sources (e.g., biosolids), and/or alternative transport pathways (e.g., overland flow). Regardless of the source, addressing PFAS in these areas can be challenging due to the scale and the lack of cost-effective remediation options for soils impacted by lower concentrations of PFAS. For example, there has been a significant effort to develop and commercialize soil amendments for binding PFAS in surface soils to reduce mass discharge to groundwater (e.g., RemBind®; https://rembind.com/), but applications of these amendments may be cost prohibitive to use outside of PFAS source areas.

To address this gap, there is a continued need to develop and validate novel soil amendments that are well suited for large-area surface applications. The goal of any novel amendment would be to reduce PFAS mobility and bioavailability through enhanced stabilization and retention in surface soils. Key considerations for technology development would include:

- cost competitiveness for large-scale application (a few to hundreds of hectares);
- ease of application for larger areas using low-tech methods (e.g., spreading with traditional agricultural equipment);

- maintaining current soil function and compatibility with existing land use;
- little to no toxicity to soil invertebrates, plants, and higher organisms that may be exposed to the amendment;
- long term effectiveness (years to decades), but for specific applications (e.g., agricultural fields), shorter duration materials with high PFAS binding efficacy are of interest — such materials could be important to prevent PFAS uptake in plants and produce grown for human consumption on a seasonal basis; and
- complements other soil amendment strategies.

The application of novel soil amendments would lower potential risks to receptors in these areas and reduce the need to implement more aggressive remediation (e.g., excavation), and complement longer-term site management strategies at DoD installations or neighboring properties. Studies are required to quantify amendment effectiveness and longevity, using PFAS bioavailability, stormwater-driven PFAS mobility, leaching, and/or extractability as key indicators. Reduction of PFAS uptake in plant species is of particular interest.

8.1.7 Assess Drinking Water System Alternatives for Affected Communities (High Priority)

The DoD's strategy for PFAS involves removing drinking water risk from receptors with exceedances of the EPA lifetime health advisory as its top priority. As soon as the DoD receives validated results above the EPA health advisory, the DoD immediately provisions bottled water to the affected drinking water user, which is followed by a 'more durable solution.' The more durable solution chosen has generally been municipal connections where they are possible. In cases where no option exists for municipal water connection, DoD takes an interim action to first supply bottled water with a follow-on action to provide drinking water users a 'point-of-entry drinking water system' (sometimes referred to as whole house filter systems or POE systems). At the moment, GAC systems are the 'off the shelf' point-of-entry option available to the DoD. Novel and effective point-of-entry systems for PFAS impacted water would assist the DoD, its stakeholders, and the affected communities with alternative methods of supplying drinking water to impacted off-installation impacted users.

Drinking water systems must meet all state and federal government requirements under the safe drinking water act and many of the rural areas with no municipal systems must use alternate filtering systems for PFAS. Given that almost 100 percent of these systems utilize well water (raw groundwater), there may be a need to use several media in series to deal with bacteria and sediment, and other minerals that may foul downstream filter media. These systems will be used by residential and commercial customers that may not have physical space to add large systems with large footprints (fitting into the confines of the existing structure). Also, residential customers may not have the knowledge and skill to deal with complex water systems, so the ease of filter operation, monitoring, replacement, and disposal is critically important to users. The DoD considers the capital cost of the system during its CERCLA process as well as the life cycle cost, so costs must be considered for a system to gain widespread use. Residential customers will also be sensitive to replacement media costs. This means that the longevity of the media in these systems must be considered in order to keep the life cycle cost in the competitive range with GAC. Systems should consider the need to minimize biofouling, as this would likely reduce media longevity and introduce biofilms into the premise plumbing. Also important is the need to test preand post-filter systems to identify changes in general water quality and PFAS concentrations. Finally, identifying other classes of possible co-occurring chemicals that would be removed by the proposed system would be valuable for system implementation.

8.2 Demonstration Needs

8.2.1 Assess Soil Washing for Treatment of PFAS-Impacted Soils and Sediments (High Priority)

Soil washing is a relatively mature technology that has been used extensively to treat a variety of chemicals of concern such as chlorinated solvents and petroleum hydrocarbons. Recently, this technology has been adapted to treat PFAS-impacted soil and sediment (e.g., SERDP projects ER18-1624, ER20-5258, Air Force Civil Engineer Center BAA-funded bench-scale treatability studies). These studies have provided insights into the efficacy of water, water/solvent, and water/solvent/salt solutions for soil washing, demonstrated PFAS association with fines and organic/humic material, and assessed PFAS mass balance in laboratory treatability studies using site-specific soils. Work is being conducted at pilot-scale to demonstrate PFAS removal and assess removal efficiency for each size fraction and demonstrate treatment costs.

Despite recent advances, additional research, demonstration, and technology transfer efforts are needed to assess the potential applicability of soil washing at a wider scale. These efforts should include or address the following:

- demonstrate effectiveness of soil washing for PFAS removal for a variety of soils and sediments with varying grain sizes, lithologies, organic and humic material content, cation or anion exchange capacity, PFAS composition and concentrations, and presence of co-occurring chemicals of concern;
- develop a predictive tool to assess the potential effectiveness of soil washing at a specific site;
- develop methods to optimize the design of soil washing processes at field scale to reduce costs and cost drivers — soil washing processes may include initial washing, soil separation, and milling of fines as well as wash water management in a closed loop system;
- evaluate the cost-competitiveness of soil washing alone relative to soil washing paired with destructive aqueous-phase treatment or incineration;
- provide a predictive tool for evaluating the cost of soil washing with other alternatives, presented in the context of site-specific priorities and alternatives — for example, sites may have an onsite PFAS treatment system already operating, a need for onsite soil reuse following soil washing, or a moratorium on incineration of PFAS-impacted media;
- of less importance, explore methodologies to improve soil washing efficacy such as the addition of adsorptive amendments; and
- coordination and outreach efforts to address regulator questions and foster regulatory acceptance are also needed.

8.2.2 Evaluate Performance of Novel Adsorbents for Management of PFAS-Impacted Media at Field-Scale (Critical Priority)

A variety of novel adsorbents have been developed in recent years for the management of PFAS-impacted media. These include organo-clays, natural and synthetic polymers, metal organic frameworks, engineered biological receptors, and many others (Klemes et al., 2019; Li et al., 2021; Ray et al., 2019). Some of these novel adsorbents have undergone extensive testing at the laboratory-scale and show promise for potential implementation in full-scale PFAS remediation processes. There is now an urgent need to transition the most promising novel adsorbents from the laboratory to the field to evaluate their performance for the in situ or ex situ management of PFAS-impacted media.

Media of interest include soil, wastewater, groundwater, drinking water, stormwater, construction runoff, investigation derived waste, and landfill leachate. Some features of promising novel adsorbents include the following:

- potential to sequester a variety of types of PFAS with rapid adsorption kinetics and high adsorption capacity;
- material and operational costs that can be competitive with existing solutions relying on conventional adsorbents;
- technical scalability of the novel adsorbent or the suggested adsorption process for implementation at field-scale; and
- potential for regeneration and reuse or alternate approaches to manage spent adsorbents or regeneration waste streams.

Performance evaluation of novel adsorbents for ex situ management of PFAS-impacted media at the field-scale should consider adsorbent longevity, breakthrough rates of short- and long-chain PFAS, and will ideally be benchmarked against conventional adsorbents. Performance evaluation of novel adsorbents for in situ management of PFAS-impacted media at the field-scale should likewise consider transport of the adsorbent media in the subsurface and distribution in groundwater.

8.2.3 Demonstrate Combined Concentration-Destructive Technologies for Remediation of Mixed PFAS Streams (Critical Priority)

Concentration approaches for PFAS have included sorption, coagulation, filtration, and foam fractionation technologies. For adsorbent technologies, a variety of traditional and emerging sorbents have been developed to address PFAS impact to water with a few showing the potential to both sorb and break down PFAS. Sorbent testing has occurred primarily at the laboratory-scale, although for a few sorbents, field-scale tests are underway. However, questions remain on how to address spent sorbents that are loaded with complex mixtures of PFAS. For regenerable sorbents, the PFAS are washed off into a solution that must be further managed. For non-regenerable sorbents, the spent media constitute a solid waste stream that requires treatment and/or disposal. PFAS in coagulation solids, separated by filtration or in the collected foam in foam fractionation, also need treatment and/or disposal. Therefore, regardless of the PFAS concentration process, one or more destructive treatment steps are needed. Several individual concentration and destruction technologies have been laboratory tested with a few at the pilot scale. Several projects proposing coupled concentration and destruction technologies have recently been funded that are starting to better address matrix effects, but most are still at the laboratory-scale. As this research unfolds, increasingly more of these coupled treatment technologies will need to be tested at the field scale to understand costs of full-scale implementation, as well as any potential implementation challenges. Most will likely include a combination of in situ and ex situ processes.

In order to integrate, optimize, and validate technologically compatible adsorption/concentration and destruction processes, specific research areas needed include:

- integration of existing adsorption and destruction processes to optimize treatment effectiveness and efficiency over a range of potential site conditions, and
- testing of novel sorbents with integrated catalysts for PFAS destruction to streamline PFAS management and ultimately decrease treatment costs.

Within each of the research areas highlighted, several aspects of the technologies should be considered for inclusion including the formation of secondary byproducts (e.g., perchlorate, chlorate) in addition to fluorinated byproducts, fluorine mole balances, hydraulic/media limitations, ease of implementation, technical and economic scalability, and evaluation of energy requirements.

8.2.4 Improve Insights into and Removal of AFFF from Firefighting Foam Delivery Systems (High Priority)

As the EPA and many states promulgate increasingly stringent regulations on acceptable concentrations of PFAS in water and soil, pressure is rapidly increasing to replace all PFAS-containing AFFF in DoD firefighting systems. A prerequisite to transition from these firefighting foam delivery systems (including firefighting vehicles) requires thorough cleaning of the systems to remove any PFAS-containing media prior to refilling with next-generation, PFAS-free firefighting formulations. Once the existing foam is removed from the system, current procedures typically require flushing with at least three volumes of potable water to rinse the system. However, results from previous field cleanout efforts in Australia, Canada, and the United States, as well as from ongoing ESTCP laboratory- and field-scale studies (which investigate the use of various cleaning reagents and different application protocols) suggest that 1) thorough cleanout of these firefighting foam delivery systems is very difficult to achieve; 2) PFAS rebounds following the initial cleanout are likely to occur; 3) mechanistic understanding of processes contributing to such rebounds is lacking; and 4) impacts of treatment residuals on the firefighting/foam-forming performance of the PFAS-free firefighting formulations have not been systematically assessed.

Therefore, pending results of the aforementioned ESTCP projects, additional laboratory scale research and field scale demonstration projects will likely be required to identify, as well as further optimize applicable short- and long-term solutions to AFFF cleanout from firefighting foam delivery systems. It will be imperative that optimized methods are effective, low-cost, and sustainable. Critical research and demonstration needs over the next 1-3 years include the following:

- Identification of components within a firefighting foam delivery system that are likely to contribute to the PFAS rebounds often observed during post-cleanout sampling as well as those that can/should be replaced prior to cleanout.

- The role of self-assembling fluorocarbon microlayers present inside firefighting foam delivery system piping on controlling PFAS retention/desorption.
- Impacts of residual treatment chemicals (used during cleanout of firefighting foam delivery systems), residual PFAS, and piping residues (e.g., rust, deposition) on PFAS-free firefighting formulations performance and/or foam forming potential.
- Applicability of different cleaning reagents and/or cleaning protocols for different firefighting foam delivery systems (e.g., AFFF hangars versus firetrucks), different portions of a firefighting delivery system (e.g., concentrated foam versus diluted foam handling, Type 316 stainless steel versus carbon-steel piping), and for delivery systems of varying type, age, conditions, and AFFF used.
- Optimization of various cleanout methodologies (including but not limited to mild heating, pH adjustment, surface scouring.) taking into consideration the relationship between treatment time and performance, costs as well as rinsate and waste generation required to achieve these goals.
- Life-cycle cost analysis of promising cleanout methodologies to allow for proper assessment of clean versus replace for a specific situation.
- Establishment of standardized cleaning protocols that are effective, low-cost, easy to use and readily implementable, as well as post-cleanout confirmation sampling methodologies that can be readily and widely applicable at DoD facilities.

Development of near real-time total fluorine monitoring methods would be valuable to make in situ evaluations of the cleanliness of the system, and to look for PFAS rebounds.

8.3 Technology Transfer Needs

8.3.1 Develop a Decision Framework for Ex Situ PFAS Treatment of Impacted Groundwater and Surface Water (Critical Priority)

There are currently several commercially available ex situ treatment options for PFAS-impacted groundwater and surface water. Most systems utilize GAC and/or IX. Membrane treatment, foam fractionation, and dissolved air floatation are also commercially available and have been shown to remove PFAS and co-occurring chemicals of concern. Regenerable media and other secondary waste streams can be incinerated, landfilled, or treated to destroy PFAS prior to recycling or reuse in the treatment train.

Following the completion of site inspections and remedial investigations, DoD will have an increased need to evaluate and operate efficient and cost-effective treatment systems for PFAS to meet a variety of state-specific and site-specific discharge criteria. DoD users would benefit from a decision framework for evaluating technology performance, optimization, and cost. Key elements that could be included in the framework are as follows:

- best practices for designing and optimizing ex situ treatment systems in the context of short-term and long-term management options (e.g., wellhead vs. centralized treatment, GAC vs. resin vs. combination, treatment trains);
- characterization of water quality parameters to inform technology selection, design, and operation;
- considerations for treatability testing and scale-up evaluations;

- expectations and considerations for spent media volume/secondary waste stream treatment or disposal costs;
- permitting and regulatory considerations (e.g., Clean Water Act, CERCLA, state regulations and considerations for potable water systems);
- operation and maintenance considerations including media fouling, breakthrough of shorter-chain PFAS and/or precursors, co-constituent effects on performance, secondary water quality parameters, etc.; and
- considerations for cost estimation for full-scale operating systems including initial capital costs, energy consumption, operating labor, monitoring costs, spent media regeneration/disposal, and more.

Case studies, including lessons learned and illustrative examples, should be included in the framework. To the extent practical, this framework would incorporate new insights being gained from existing and completed SERDP and ESTCP projects on ex situ treatment of PFAS.

8.3.2 Improve Commercial Water Treatment Technologies for PFAS (High Priority)

There is a continued need to evaluate currently employed PFAS treatment systems to document their performance, operating costs, and any unintended consequences for use in future decision making. This research need will follow on existing SERDP projects to glean additional information that will allow systems to focus on a limited number of processes for implementation. Ideally, enough data and an adequate summary evaluation of source water characteristics can be used to address pre-treatment, PFAS treatment, and post-treatment needs while determining management strategies for impacted systems. It is important to not only consider PFAS, but also other co-occurring chemicals of concern that may be present, to assure that the treated water is fit for its intended purpose. Data harvesting approaches (identifying previously funded efforts) will need to be specifically proposed, as will any approach to simplifying or extrapolating the data. Uncertainties will need to be quantified and incorporated in the final evaluation. It is not expected that a true expert system will be developed, but rather a technology transfer approach that will allow an entity to focus limited resources on a limited number of technologies that will ultimately lead to an optimized treatment system.

The discussion presented herein pertains primarily to GAC and anion exchange resins– arguably the two most proven and widely implemented technologies for PFAS removal from water. Critical technology transfer needs for better communication regarding the selection, design, implementation, and optimization of these commercial water treatment technologies include the following:

- Better knowledge and data transfer among research scientists, consultants, utility operators and managers, and regulators on the use of a timely, cost-effective, and scalable bench-scale treatability testing methodology (i.e., RSSCT) to evaluate PFAS treatment using commercially available GAC and IX products. Guidance is also needed on the regulatory approval process, analytical methodology, testing and monitoring program, and data analysis/reporting during pilot- and full-scale design/implementation of these treatment systems.
- Better communication among various stakeholders on the state-of-the-science, usefulness, and limitations regarding the scaling equations and models used to project

full-scale performance based on bench-scale RSSCT testing for both GAC and IX under a wide range of water quality parameters.

- Comprehensive documentation of lessons learned from pilot- and full-scale design/implementation of GAC and IX for a variety of treatment train combinations, water chemistries and PFAS compositions/concentrations, along with their advantages/disadvantages with respect to treatment efficacy, pre-treatment requirements, capital and operational expenditures, and unintended consequences of treatment to allow for proper selection, design, construction, monitoring, and optimization of these treatment systems.
- Assessment of GAC/IX treatment of PFAS not targeted by standard analytical methods and validation of the appropriate monitoring tools to best capture PFAS mass balance at utilities where these technologies are currently employed.
- Comprehensive evaluation of impacts of water quality parameters (e.g., total organic carbon, hardness, metals), treatment residual (e.g., residual chlorine, residual oxidant, anti-corrosion reagents), and co-occurring chemicals of concern (e.g., volatile and semi-volatile organic compounds) on PFAS treatment effectiveness and media longevity, and transfer of such knowledge to practitioners.
- Assessment of unintended consequences (e.g., transient pH increase and potential for arsenic mobilization during the initial GAC startup, changes in chloride:sulfate mass ratio following IX treatment and associated lead mobilization) as a result of implementing these treatment technologies and corresponding mitigation measures/risk communication methodologies.
- Identification of the most critical pre-treatment requirements for optimal treatment system operations and mitigation measures to address operation and maintenance (O&M) issues such as biological fouling and media clogging/cementation.
- Comprehensive evaluation of the technical and economic merits of employing sacrificial media or combined treatment trains to overcome difficult water chemistries or to extend media longevity.
- Development of a predictive modeling suite, using available bench-, pilot-, and full-scale datasets, to provide regulators and practitioners with guidance on technology and media selection, pre-treatment requirements, treatment efficacy, media longevity, and life-cycle cost for a particular application.
- Better assessment of overall treatment cost from cradle to grave, taking into consideration infrastructure upgrade requirements (e.g., footprint, pumps), pre-treatment requirements (e.g., total organic carbon [TOC] and Fe/Mn removal), and all waste streams generated and their associated disposal costs.

9.0 SUMMARY AND CONCLUSIONS

Research into managing PFAS in the environment has expanded rapidly since 2009 when the EPA first released HALs for PFOS and PFOA. SERDP efforts were initiated shortly after release of the HALs and has expanded to encompass over 200 individual projects and over 250 million dollars in funding at the time of this report. While tremendous progress has been accomplished during this time, many questions remain as evidenced by over 50 research, demonstration, and technology transfer needs identified during this workshop.

While a number of treatment technologies have been developed and commercialized, fundamental questions remain concerning the fate and transport of PFAS, as well as the underlying principles of these treatment technologies. Additional research coupled with thorough field demonstrations will ultimately allow for implementation of more cost-effective management and treatment of PFAS-impacted matrices.

The research, demonstration, and technology transfer needs identified in this report will guide SERDP and ESTCP investments over the next three to five years. Transition of this knowledge into commercial application and daily site management will have a lasting impact on our ability to effectively mitigate the impact of PFAS.

10.0 LITERATURE CITED

Adamson, D.T., R.H. Anderson, S. Mahendra, and C.J. Newell. 2015. Evidence of 1,4-Dioxane Attenuation at Groundwater Sites Contaminated with Chlorinated Solvents and 1,4-Dioxane. *Environ. Sci. Technol*., 49(11):6510-6518. https://doi.org/10.1021/acs.est.5b00964

Adamson, D.T., P.R. Kulkarni, A. Nickerson, C. Higgins, J. Field, T. Schwichtenberg, C.J. Newell, and J.J. Kornuc. 2022. Characterization of Relevant Site Specific PFAS Fate and Transport Processes at Multiple AFFF Sites. *Environ. Adv.,*7:100167.

Adamson, D.T., S. Mahendra, K. L. Walker, S.R. Rauch, S. Sengupta, and C.J. Newell. 2014. A Multisite Survey to Identify the Scale of the 1,4-Dioxane Problem at Contaminated Groundwater Sites. *Environ. Sci. Technol.*, 1(5):254-258. https://doi.org/10.1021/ez500092u

Adamson, D.T., A. Nickerson, P.R. Kulkarni, C.P. Higgins, J. Popovic, J. Field, A. Rodowa, C.J. Newell, P. DeBlanc, and J.J. Kornuc. 2020. Mass-Based, Field-Scale Demonstration of PFAS Retention within AFFF-Associated Source Areas. *Environ. Sci. Technol.,* 54:15768-15777.

Altarawneh, M., M.H. Almatarneh, and B.Z. Dlugogorski. 2022. Thermal Decomposition of Perfluorinated Carboxylic Acids: Kinetic Model and Theoretical Requirements for PFAS Incineration. *Chemosphere*, 286:31685.

Anderson, R.H., T. Thompson, H.F. Stroo, and A. Leeson. 2021. US Department of Defense-funded Fate and Transport Research on Per-and Polyfluoroalkyl Substances at Aqueous Film-Forming Foam-Impacted Sites. *Environ. Toxicol. Chem.,*(1):37.

Ankley, G.T., P. Cureton, R.A. Hoke, M. Houde, A. Kumar, J. Kurias, and S. Valsecchi. 2021. Assessing the Ecological Risks of Per- and Polyfluoroalkyl Substances: Current State-of-the Science and a Proposed Path Forward. *Environ. Toxicol. Chem.,* 40(3):564-605. https://doi.org/10.1002/etc.4869

Aziz, C., C.J. Newell, and J. Gonzales. 2000. BIOCHLOR Chlorinated Solvent Plume Database Report. *Air Force Center for Environmental Excellence, Brooks AFB, Texas*.

Backe, W.J., T.C. Day, and J.A. Field. 2013. Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from US Military Bases by Nonaqueous Large-volume Injection HPLC-MS/MS. *Environ. Sci. Technol.,* 47(10):5226-5234.

Berns, E.C., R.A. Sanford, A.J. Valocchi, T.J. Strathmann, C.E. Schaefer, and C.J. Werth. 2019. Contributions of Biotic and Abiotic Pathways to Anaerobic Trichloroethene Transformation in Low Permeability Source Zones. *J. Contam. Hydrol,* 224:103480.

Bizkarguenaga E., I. Zabaleta, L. Mijangos, A. Iparraguirre, L.A. Fernández, A. Prieto, and O. Zuloaga. 2016. Uptake of Perfluorooctanoic Acid, Perfluorooctane Sulfonate and

Perfluorooctane Sulfonamide by Carrot and Lettuce from Compost Amended Soil. *Sci. Total Environ.,* 571:444-51. doi: 10.1016/j.scitotenv.2016.07.010.

Blake, S.B. and R.W. Lewis. 1983. Underground Oil Recovery. *Ground Water Monit. Rev.,* 3(2): 40-46.

Blunden, J., and D. S. Arndt. 2014. State of the Climate in 2013, *Bull. Am. Meteorol. Soc.*, 95:S1-S279.

Brusseau, M.L. 2020. Simulating PFAS transport Influenced by Rate-Limited Multi-Process Retention. *Water Research,* 168:115179.

Brusseau, M.L., N. Khan, Y. Wang, N. Yan, S. Van Glubt, and K.C. Carroll. 2019. Nonideal Transport and Extended Elution Tailing of PFOS in Soil. *Environ. Sci. Technol.,* 53(18):10654-10664.

Brusseau, M.L., N. Yan, S. Van Glubt, Y. Wang, W. Chen, Y. Lyu, B. Dungan, K.C. Carroll, and F.O. Holguin. 2019. Comprehensive Retention Model for PFAS Transport in Subsurface Systems. *Water Res.,* 148: 41-50.

Buck, R.C., J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. de Voogt, A.A. Jensen, K. Kannan, S.A. Mabury, and S.P.J. van Leeuwen. 2011. Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management*, 7(4):513-541.

Burkhard LP. 2021. Evaluation of Published Bioconcentration Factor (BCF) and Bioaccumulation Factor (BAF) Data for Per- and Polyfluoroalkyl Substances Across Aquatic Species. *Environ. Toxicol. Chem.*, 40(6):1530-1543. doi: 10.1002/etc.5010.

Carey, G.R., R. McGregor, A Pham, and S.G. Hakimabadi. 2019. Evaluating the Longevity of a PFAS In Situ Colloidal Activated Carbon Remedy. *Remediation Journal*, 29:17-31.

Chu, S. and R.J. Letcher. 2017. Side-Chain Fluorinated Polymer Surfactants in Aquatic Sediment and Biosolid-Augmented Agricultural Soil from the Great Lakes Basin of North America. *Sci Total Environ.,* 607–608:262–270. https://doi.org/10.1016/j.scitotenv.2017.06.252.

Clavier, K. A., Y. Liu, V. Intrakamhaeng, and T.G. Townsend. 2019. Re-Evaluating the TCLP's Role as the Regulatory Driver in the Management of Municipal Solid Waste Incinerator Ash. *Environ. Sci. Technol.,* 53 (14):7964-7973. https://doi.org/10.1021/acs.est.9b01370.

Cohen, B., A.E. Lewis, J. Petersen, H. Von Blottnitz, S.C. Drews, and S.I. Mahote. 1999. The TCLP and Its Applicability for the Characterisation of Worst Case Leaching of Wastes from Mining and Metallurgical Operations. *Advances in Environmental Research*, 3 (2):152-165.

Coumou, D., and S. Rahmstorf. 2012. A Decade of Weather Extremes, *Nat. Clim. Change*, 2:491-496.

Crittenden, J.C., P.S. Reddy, H. Arora, J. Trynoski, D.W. Hand, D.L. Perram, and R.S. Summers. 1991. Predicting GAC Performance with Rapid Small-Scale Column Tests. *J. AWWA.* 83:77-87.

Crownover, E., D. Oberle, M. Kluger, and G. Heron. 2019. Perfluoroalkyl and Polyfluoroalkyl Substances Thermal Desorption Evaluation. *Remediation Journal*, 29(4):77-81.

D'Agostino, L.A., and S.A. Mabury. 2014. Identification of Novel Fluorinated Surfactants in Aqueous Film Forming Foams and Commercial Surfactant Concentrates. *Environ. Sci. Technol.*, 48(1):121-129.

De Silva A.O., J.M. Armitage, T.A. Bruton, C. Dassuncao, W. Heiger-Bernays, X.C. Hu, A. Kärrman, B. Kelly, C. Ng, A. Robuck, M. Sun, T.F. Webster, and E.M. Sunderland. 2021. PFAS Exposure Pathways for Humans and Wildlife: A Synthesis of Current Knowledge and Key Gaps in Understanding. *Environ Toxicol Chem.,* 40(3):631-657. doi: 10.1002/etc.4935.

U.S. Environmental Protection Agency (USEPA). 2021. Draft Method 1633, Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf.

U.S. Environmental Protection Agency (USEPA). Method 537.1, Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), https://www.epa.gov/pfas/epa-pfas-drinking-water-laboratory-methods

U.S. Environmental Protection Agency (USEPA). Draft Method 533, Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry, https://www.epa.gov/pfas/epa-pfas-drinking-water-laboratory-methods

U.S. Environmental Protection Agency (USEPA). 1992. Method 1311: Toxicity Characteristic Leaching Procedure; SW-846 1311-1.

U.S. Environmental Protection Agency (USEPA). 1994. Method 1312 Synthetic Precipitation Leaching Procedure; 1312–1.

U.S. Environmental Protection Agency (USEPA). 2021. Other Test Method 45 (OTM-45), Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources, https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf.

U.S. Environmental Protection Agency (USEPA).Environmental Engineering Committee Science Advisory Board. 1999. Waste Leachability: The Need for Review of Current Agency Procedure; EPA-SAB-EEC-COM-99-002.

U.S. Environmental Protection Agency (USEPA).Environmental Engineering Committee Science Advisory Board. 1991. Recommendations and Rationale for Analysis of Contaminant Release by the Environmental Engineering Committee; EPA-SAB-EEC-92-003.

EPRI. 2012. Groundwater Closure Strategy for Former Manufactured Gas Plant Sites. *Electrical Power Research Institute,* Report 1023747 Technical Update.

FRTR. 2021. Meeting, Two Part Series on Remedy Protectiveness and Climate Resilience in Site Cleanups https://clu-in.org/conf/tio/FRTRFall21_110821/,https://clu-in.org/conf/tio/FRTRFall21_111521/.

Fleming, H-C. 2016. EPS-Then and Now. *Microorganisms* 4:41. doi:10.3390/microorganisms4040041.

Freitas J.G. and J.F. Barker. 2011. Monitoring Lateral Transport of Ethanol and Dissolved Gasoline Compounds in the Capillary Fringe. *Ground Water Monitoring and Remediation*, 31:95-102.

Gagliano, E., M. Sgroi, P.P. Falciglia, F.G.A. Vagliasindi, and P. Roccaro. 2020. Removal of Poly- and Perfluoroalkyl Substances (PFAS) from Water by Adsorption: Role of PFAS Chain Length, Effect of Organic Matter and Challenges in Adsorbent Regeneration. *Water Res*., 171:115381.

Gobas, F., B. Kelly, and J. Kim. 2020. Final Report: A Framework for Assessing Bioaccumulation and Exposure Risks of Per- and Polyfluoroalkyl Substances in Threatened and Endangered Species on Aqueous Film Forming Foam (AFFF)-Impacted Sites. *SERDP Project ER18-1502*. https://serdp-estcp.org/content/download/51280/504776/file/ER18-1502%20Final%20Report.pdf

Guo, B., J. Zeng, and M.L. Brusseau. 2020. A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances (PFAS) in the Vadose Zone. *Water Resour. Res*., 56: e2019WR026667.

Guo, B., J. Zeng, M.L. Brusseau, and Y. Zhang, 2022. A Screening Model for Quantifying PFAS Leaching in the Vadose Zone and Mass Discharge to Groundwater. *Adv. Water Resour.,* 160:104102.

Hao, S., Y.J. Choi, B. Wu, C.P. Higgins, R. Deeb, and T.J. Strathmann. 2021. Hydrothermal Alkaline Treatment for Destruction of Per- and Polyfluoroalkyl Substances in Aqueous Film-Forming Foam. *Environ. Sci. Technol*. 55:3283–3295. https://doi.org/10.1021/acs.est.0c06906

Harding-Marjanovic, K.C., E.F. Houtz, S. Yi, J.A. Field, D.L. Sedlak, and L. Alvarez-Cohen. 2015. Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environ. Sci. Technol*., 49:7666-7674. https://doi.org/10.1021/acs.est.5b01219

Horst, J., J. Quinnan, J. McDonough, J. Lang, P. Storch, J. Burdick, and C. Theriault. 2021. Transitioning Per- and Polyfluoroalkyl Substance Containing Fire Fighting Foams to New Alternatives: Evolving Methods and Best Practices to Protect the Environment. *Groundwater Monitor. Remed.,* 41:19-26.

Houtz, E.F., C.P. Higgins, J.A. Field, and D.L. Sedlak. 2013. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environ. Sci. Technol.,* 47:(15) 8187-8195.

Huang, S. and P.R. Jaffe. 2019. Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by *Acidimicrobium* sp. Strain A6. *Environ. Sci. Technol.*, 53:11410-11419. https://doi.org/10.1021/acs.est.9b04047

Huang, Q. 2013. Remediation of Perfluoroalkyl Contaminated Aquifers Using an In-Situ Two-Layer Barrier: Laboratory Batch and Column Study. *SERDP Project ER-2127 Final Report.* https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2127/(language)/eng-US

Huang, S., and P.R. Jaffé. 2019. Defluorination of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) by *Acidimicrobium* sp. strain A6. *Environ. Sci. Technol*., 53(19):11410-11419.

Huang, S., and P.R. Jaffé. 2018. Isolation and Characterization of an Ammonium-Oxidizing Iron Reducer: *Acidimicrobiaceae sp. A6*. *PLOS ONE*, 13(4): e0194007. https://doi.org/10.1371/journal.pone.0194007.

Stocker, F. 2013. Intergovernmental Panel on Climate Change 2013: Detection and Attribution of Climate Change: From Global to Regional. *The Physical Science Basis, Cambridge Univ. Press, Cambridge, U. K.*

Intrakamhaeng, V., K.A. Clavier, J.G. Roessler, and T.G. Townsend. 2019. Limitations of the Toxicity Characteristic Leaching Procedure for Providing a Conservative Estimate of Landfilled Municipal Solid Waste Incineration Ash Leaching. *Journal of the Air & Waste Management Association*, 69 (5):623-632. https://doi.org/10.1080/10962247.2019.1569172.

Jasper, J.T., M.T. Nguyen, Z.L. Jones, N.S. Ismail, D.L. Sedlak, J.O. Sharp, R.G. Luthy, A.J. Horne, and K.L. Nelson. 2013. Unit Process Wetlands for Removal of Trace Organic Contaminants and Pathogens Municipal Wastewater Effluents. *Environ. Engin. Sci.,* 30(8).

Kamath, R., J.A. Connor, T.E. McHugh, A. Nemir, M.P. Le, and A.J. Ryan. 2012. Use of Long-Term Monitoring Data to Evaluate Benzene, MTBE, and TBA Plume Behavior in Groundwater at Retail Gasoline Sites. Journal of *Environ. Engin.*, 138(4):458-469. https://doi.org/10.1061/(asce)ee.1943-7870.0000488

Khan, M. Y., S. So, and G. da Silva. 2020. Decomposition Kinetics of Perfluorinated Sulfonic Acids. *Chemosphere*, 238:124615.

Klemes, M.J., Y. Ling, C. Ching, C. Wu, L. Xiao, D.E. Helbling, and W.R. Dichtel. 2019. Reduction of a Tetrafluoroterephthalonitrile-β-Cyclodextrin Polymer to Remove Anionic Micropollutants and Perfluorinated Alkyl Substances from Water. *Angewandte Chemie*, 58:12049-12053.

Kosson, D. S., A. Garrabrants, S. Thorneloe, D. Fagnant, G. Helms, K. Conolly, and M. Rodgers. 2017. Leaching Environmental Assessment Framework (LEAF) How-To Guide: Understanding the LEAF Approach and How and When to Use It; SW-846 Update VI; *United States Environmental Protection Agency Office of Land and Emergency Management, and Office of Research and Development.*

Kosson, D.S., A.C. Garrabrants, S. Thorneloe, D. Fagnant, G. Helms, K. Conolly, and M. Rodgers. 2019. Leaching Environmental Assessment Framework (LEAF) How-To Guide. https://www.epa.gov/sites/production/files/2017-11/documents/leaf_how_to_guide.pdf

Kosson, D.S., H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants. 2002. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environ. Engin. Sci*., 19 (3):159–204. https://doi.org/10.1089/109287502760079188.

Krause, M.J., E. Thoma, E. Sahle-Damesessie, B. Crone, A. Whitehill, E. Shields, and B. Gullett. 2022. Supercritical Water Oxidation as an Innovative Technology for PFAS Destruction. *Journal of Environ. Engin.,* 148:05021006. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001957

Krusic, P.J., D.C. Roe. 2004. Gas-phase NMR Technique for Studying the Thermolysis of Materials: Thermal Decomposition of Ammonium Perfluorooctanoate. *Anal Chem.,* 76(13):3800-3803.

Kulkarni, P.R., D.T. Adamson, J. Popovic, and C.J. Newell. 2022. Modeling a Well-Characterized Perfluorooctane Sulfonate (PFOS) Source and Plume Using the REMChlor-MD Model to Account for Matrix Diffusion. *J. Contam. Hydrol.,* 247:103986.

LaZerte, J.D., L.J. Hals, T.S. Reid, and G.H. Smith. 1953. Pyrolyses of the Salts of the Perfluoro Carboxylic Acids. *Journal of the American Chemical Society*, 75(18):4525-4528.

Lee, M., E. Shevliakova, S. Malyshev, P.C.D. Milly, and P.R. Jaffé. 2016. Climate Variability and Extremes, Interacting with Nitrogen Storage, Amplify Eutrophication Risk, *Geophys. Res. Lett.*, 43(14):7520-7528.

Letcher, R. J., S. Chu, and S.A. Smyth. 2020. Side-Chain Fluorinated Polymer Surfactants in Biosolids from Wastewater Treatment Plants. *Journal of Hazardous Materials*, 388:122044. https://doi.org/10.1016/j.jhazmat.2020.122044.

Li, R., S. Alomari, R. Stanton, M.C. Wasson, T. Islamoglu, O.K. Farha, T.M. Holsen, S. Mededovic Thagard, D.J. Trivedi, and M. Wriedt. 2021. Efficient Removal of Per- and

Polyfluoroalkyl Substances from Water with Zirconium-Based Metal-Organic Frameworks. 33:3276-3285.

Linak, W. and C.W. Lee. Incineration 101 and Issues Related to PFAS Destruction, https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=CEMM&count=10000&dirEntryId=348523&searchall=&showcriteria=2&simplesearch=0&timstype=.

Liu, C., J. Hatton, W.A. Arnold, M.F. Simcik, and K.D. Pennell. 2020. In Situ Sequestration of Perfluoroalkyl Substances Using Polymer-Stabilized Powdered Activated Carbon. *Environ. Sci. Technol*., 54:6929-6936.

Liu, M., G. Munoz, S.V. Duy, S. Sauve, and J.X. Liu. 2022. Per- and Polyfluoroalkyl Substances in Contaminated Soil and Groundwater at Airports: A Canadian Case Study. *Environ. Sci. Technol.,* 56:(2), 885-895.

Lohmann, R., I.T. Cousins, J.C. DeWitt, J. Glüge, G. Goldenman, D. Herzke, A.B. Lindstrom, M.F. Miller, C.A. Ng, S. Patton, M. Scheringer, X. Trier, and Z. Wang. 2020. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? *Environ. Sci. Technol.,* 54 (20):12820-12828. https://doi.org/10.1021/acs.est.0c03244

Mace, R. E., R.S. Fisher, D.M. Welch, and S.P. Parra. 1997. Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas Geologic Circular. *Geologic Circuluar,* 97(1).

Maimaiti, A., S. Deng, P. Meng, W. Wang, B. Wang, J. Huang, Y. Wang, and G. Yu. 2018. Competitive Adsorption of Perfluoroalkyl Substances on Anion Exchange Resins in Simulated AFFF-Impacted Groundwater. *Chem. Eng. J.*, 348: 494-502.

Maizel, A.C., S. Shea, A. Nickerson, C. Schaefer, and C.P. Higgins. 2021. Release of Per-and Polyfluoroalkyl Substances from Aqueous Film-Forming Foam Impacted Soils. *Environ. Sci. Technol., 55*(21):14617-14627.

Martin, T. 2012. Fire-Fighting Foam Technology. In *Foam Engineering: Fundamentals and Application*, Stevenson, P., Ed. John Wiley & Sons Ltd: Pondicherry. 527.

McDade, J. M., J.A. Connor, S.M. Paquette, and J.M. Small. 2015. Exceptionally Long MTBE Plumes of the Past Have Greatly Diminished. *Groundwater*, 53(4):515-524. https://doi.org/10.1111/gwat.12322

McGuire, T.M., C.J. Newell, B.B. Looney, K.M. Vangelas, and C.H. Sink. 2004. Historical Analysis of Monitored Natural Attenuation: A Survey of 191 Chlorinated Solvent Sites and 45 Solvent Plumes. *Remediation*, 15(1):99-112. https://doi.org/10.1002/rem.20036

McHugh, T.E., P.R. Kulkarni, C.J. Newell, J.A. Connor, and S. Garg. 2014. Progress in Remediation of Groundwater at Petroleum Sites in California. *Groundwater,* 52(6):898-907. https://doi.org/10.1111/gwat.12136

McNab, W.W., D.W. Rice, J. Bear, R. Ragaini, C. Tuckfield, and C. Oldenburg. 1999. Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes. *Lawrence Livermore National Laboratory,* UCRL-AR-133361.

McNamara, J. D., R. Franco, R. Mimna, and L. Zappa. 2018. Comparison of Activated Carbons for Removal of Perfluorinated Compounds from Drinking Water. *Journal-American Water Work. Assoc*., 110: E2-E14

Michigan Department of Environment, Great Lakes, and Energy. 2019. Surface Water Foam PFAS Guidance. https://www.michigan.gov/pfasresponse/-/media/Project/Websites/PFAS-Response/Sampling-Guidance/Surface-Water-Foam.pdf?rev=6ad0652c3f4b418ab552c0a3558bbf9c, accessed 20 November 2022.

Miles, C. and J.J. Delfino. 1985. The Fate of Aldicarb, Aldicarb Sulfoxide and Aldicarb Sulfone in Floridan Groundwater. J. Agric. *Food Chem*., 33:455-60.

Muensterman, D. J., I.A. Titaley, G.F. Peaslee, L.D. Minc, L. Cahuas, A.E. Rodowa, Y. Horiuchi, S. Yamane, T.N.J. Fouquet, J.C. Kissel, C.C. Carignan, and J.A. Field. 2022. Disposition of Fluorine on New Firefighter Turnout Gear. *Environ. Sci. Technol.,* 56 (2):974–983. https://doi.org/10.1021/acs.est.1c06322

Mundle, K., D.A. Reynolds, M.R. West, and B.H. Kueper. 2007. Concentration Rebound Following In Situ Chemical Oxidation in Fractured Clay. *Groundwater* 45:692–702.

Munoz, G., L.C. Fechner, E. Geneste, P. Pardon, H. Budzinski and P. Labadie. 2018. Spatio-Temporal Dynamics of Per and Polyfluoroalkyl Substances (PFASs) and Transfer to Periphytic Biofilm in an Urban River: Case-Study on the River Seine. *Environ. Sci. and Pollution Res.,* 25:23574-23582 https://doi.org/10.1007/s11356-016-8051-9

Najjar, R.G., C.R. Pyke, M.B. Adams, D. Breitburg, C. Hershner, M. Kemp, R. Howarth, M.R. Mulhollamd, M. Paolisso, D. Secor, K. Sellner, D. Wardrop, and R. Wood. .2010. Potential Climate-Change Impacts on the Chesapeake Bay. *Estuarine Coastal Shelf Sci.,* 86:1-20.

Newell, C. J., and J.A. Connor. 1998. Characteristics of Dissolved Petroleum Hydrocarbon Plumes. *API Soil and Groundwater Research Bulletin*, 8.

Newell, C. J., I. Cowie, T.M. McGuire, and W.W. McNab. 2006. Multiyear Temporal Changes in Chlorinated Solvent Concentrations at 23 Monitored Natural Attenuation Sites. *Journal of Environ. Eng.,* 132(6):653–663. https://doi.org/10.1061/(asce)0733-9372(2006)132:6(653)

Ng, C.A., and K. Hungerbuehler. 2013. Bioconcentration of Perfluorinated Alkyl Acids: How Important Is Specific Binding?. *Environ. Sci. Technol.,* 47(13):7214-7223. DOI: 10.1021/es400981a

Nickerson, A., A.E. Rodowa, D.T. Adamson, J.A. Field, P.R. Kulkarni, J.J. Kornuc, and C.P. Higgins. 2021. Spatial Trends of Anionic, Zwitterionic, and Cationic PFASs at an AFFF-Impacted Site. *Environ. Sci. Technol.,* 55(1):313-323.

Olsavsky, N. J., V.M. Kearns, C.P. Beckman, P.L. Sheehan, F.J. Burpo, H.D. Bahaghighat, and E.A. Nagelli. 2020. Research and Regulatory Advancements on Remediation and Degradation of Fluorinated Polymer Compounds. *Applied Sciences*, 10(19):6921. https://doi.org/10.3390/app10196921

Pabon, M., J.M. Corpart, and C.A.L. Atofina. 2002. Fluorinated Surfactants: Synthesis, Properties, Effluent Treatment. *Journal of Fluorine Chemistry,* 114:149-156.

Park, M., S. Israel, S.Wu, I.J. Lopez, J.Y. Chang, T. Karanfil, S.A. Snyder. 2020. Adsorption of Perfluoroalkyl Substances (PFAS) in Groundwater by Granular Activated Carbons: Roles of Hydrophobicity of PFAS and Carbon Characteristics. *Wat. Res.,* 170: 115364.

Parker, B.L., S.W. Chapman, M.A. Guilbeault. 2008. Plume Persistence Caused by Back Diffusion from Thin Clay Layers in a Sand Aquifer Following TCE Source-Zone Hydraulic Isolation. *J. Contam. Hydrol.,* 102:86-104.

Peaslee, G.F., J.T. Wilkinson, S.R. McGuinness, M. Tighe, N. Caterisano, S. Lee, A. Gonzales, M. Roddy, S. Mills, and K. Mitchell. 2020. Another Pathway for Firefighter Exposure to Per- and Polyfluoroalkyl Substances: Firefighter Textiles. *Environ. Sci. Technol. Lett.,* 7(8):594-599. https://doi.org/10.1021/acs.estlett.0c00410

Pi, N., J.Z. Ng, and B.C. Kelly. 2017. Uptake and Elimination Kinetics of Perfluoroalkyl Substances in Submerged and Free-Floating Aquatic Macrophytes: Results of Mesocosm Experiments with Echinodorus Horemanii and Eichhornia Crassipes. *Water Res*., 117:167-174.

Place, B.J., and J.A. Field. 2012. Identification of Novel Fluorochemicals in Aqueous Film-Forming Foams Used by the US military. *Environ. Sci. Technol.,* 46(13):7120-7127.

Rankin, K., H. Lee, P.J. Tseng, and S.A. Mabury. 2014. Investigating the Biodegradability of a Fluorotelomer-Based Acrylate Polymer in a Soil–Plant Microcosm by Indirect and Direct Analysis. *Environ. Sci. Technol.,* 48 (21):12783–12790. https://doi.org/10.1021/es502986w

Ray, J.R., I.A. Shabtai, M. Teixidóa, Y.G. Mishael, and D.L. Sedlak. 2019. Polymer-Clay Composite Geomedia for Sorptive Removal of Trace Organic Compounds and Metals in Urban Stormwater. *Water Res.,* 157:454-462.

Rice, D.W., R.D. Grose, J.C. Michaelsen, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.G. Everett, and M.A. Marino. 1995. California Leaking Underground Fuel Tank

(LUFT) Historical Case Analysis. California State Water Resources Control Board Underground Storage Tank Program and Senate Bill 1764 Leaking Underground Fuel Tank Advisory Committee, California Environmental Protection Department, Sacramento, California.

Riedel, T.P., M.A.G. Wallace, E.P. Shields, J.V. Ryan, C.W. Lee, and W.P. Linak. 2021. Low Temperature Thermal Treatment of Gas-Phase Fluorotelomer Alcohols by Calcium Oxide. *Chemosphere*, 272:129859.

Russell, M.H., W.R. Berti, B. Szostek, and R.C. Buck. 2008. Investigation of the Biodegradation Potential of a Fluoroacrylate Polymer Product in Aerobic Soils. *Environ. Sci. Technol.*, 42(3):800-807. https://doi.org/10.1021/es0710499.

Russell, M.H., W.R. Berti, B. Szostek, N. Wang, and R.C. Buck. 2010. Evaluation of PFO Formation from the Biodegradation of a Fluorotelomer-Based Urethane Polymer Product in Aerobic Soils. *Polymer Degradation and Stability*, 95(1):79-85. https://doi.org/10.1016/j.polymdegradstab.2009.10.004

Ruyle, B.J., C.P. Thackray, J.P. McCord, M.J. Strynar, K.A. Mauge-Lewis, S.E. Fenton, and E.M. Sunderland. 2021. Reconstructing the Composition of Per- and Polyfluoroalkyl Substances in Contemporary Aqueous Film-Forming Foams. *Environ. Sci. Technol. Lett.,* 8(1):59-65.

Schaefer, C.E., V. Culina, D. Nguyen, and J. Field. 2019. Uptake of Poly- and Perfluoroalkyl Substance at the Air-Water Interface. *Environ. Sci. Technol*., 53:12442-12448.

Schaefer, C.E., D. Drennan, A. Nickerson, A. Maizel, and C.P. Higgins. 2021. Diffusion of Perfluoroalkyl Acids Through Clay-Rich Soil. *J. Contam. Hydrol.*, 241:103814.

Schaefer, C.E., D. Nguyen, E. Christie, S. Shea, C.P. Higgins, and J.A. Field. 2021. Desorption of Poly-and Perfluoroalkyl Substances from Soil Historically Impacted with Aqueous Film-Forming Foam. *Journal of Environ. Eng.,* 147(2):06020006.

Schaefer, C.E., D. Nguyen, V.M. Culina, J. Guelfo, and N. Kuman. 2020. Application of Rapid Small-Scale Column Tests for Treatment of Perfluoroalkyl Acids Using Anion-Exchange Resins and Granular Activated Carbon in Groundwater with Elevated Organic Carbon. *Ind. Eng. Chem. Res.,* 59:16832-16837.

Sha, B., J.H. Johansson, J.P. Benskin, I.T. Cousins, and M.E. Salter. 2021. Influence of Water Concentrations of Perfluoroalkyl Acids (PFAAs) on Their Size-Resolved Enrichment in Nascent Sea Spray Aerosols, *Environ. Sci. Technol*., 55: 9489–9497.

Shahsavari, E., D. Rouch, L.S. Khudur, D. Thomas, A. Aburto-Medina, and A.S. Ball. 2020. Challenges and Current Status of the Biological Treatment of PFAS-Contaminated Soils. Front Bioeng Biotechnol 2020 5: 602040.. doi: 10.3389/fbioe.2020.602040

Shin, H.-Y., V.M. Vieira, P.B. Ryan, R. Detwiler, B. Sanders, K. Steenland, and S.M. Bartell. 2011. Environmental Fate and Transport Modeling for Perfluorooctanoic Acid Emitted from the Washington Works Facility in West Virginia. *Environ. Sci. Technol*., 45: 1435-1442.

Silva, J.A.K., J. Šimunek, and J.E. McCray. 2020. A Modified HYDRUS Model for Simulating PFAS Transport in the Vadose Zone. *Water,* 12: 2758.

Singh, R.K., N. Multari, C. Nau-Hix, R.H. Anderson, S.D. Richardson, T.M. Holsen, and S.M. Thagard. 2019. Rapid Removal of Poly- and Perfluorinated Compounds from Investigation-Derived Waste (IDW) in a Pilot-Scale Plasma Reactor. *Environ. Sci. Technol*., 53:11375-11382. https://doi.org/10.1021/acs.est.9b02964

Titaley, I.A., J. Khattak, J. Dong, C.I. Olivares, B. DiGuiseppi, C.C. Lutes, and J.A. Field. 2022. Neutral Per-and Polyfluoroalkyl Substances, Butyl Carbitol, and Organic Corrosion Inhibitors in Aqueous Film-Forming Foams: Implications for Vapor Intrusion and the Environment. *Environ. Sci Technol. 56*(15):10785-10797.

Tourney, J. and B.T. Ngwenya. 2014. The Role of Bacterial Extracellular Polymeric Substances in Geomicrobiology. *Chem. Geology*, 386: 115-132. http://doi.org/ 10.1016/j.chemgeo.20 14.08.0 11 0009-2541

Tsang, W., D.R. Burgess, and V. Babushok. 1998. On the Incinerability of Highly Fluorinated Organic Compounds. *Combustion Sci. and Technol.,* 139:385-402.

U.S. Department of Defense. 2020. MIL-PRF-24385F(SH) Performance Specifications Fire Extinguishing Agent, Aqueous Film-Forming Foam (AFFF) Liquid Concentrate for Fresh and Sea Water. https://quicksearch.dla.mil/qsDocDetails.aspx?ident_number=17270

Valsecchi, S., M. Babut, M. Mazzoni, S. Pascariello, C. Ferrario, B. De Felice, R. Bettinetti, B. Veyrand, P. Marchand, and S. Polesello. 2021. Per- and Polyfluoroalkyl Substances (PFAS) in Fish from European Lakes: Current Contamination Status, Sources, and Perspectives for Monitoring. *Environmental Toxicological Chemistry*, 40(3):658-676. DOI: 10.1002/etc.4815

Wang, F., X. Lu, X. Li, and K. Shih. 2015. Effectiveness and Mechanisms of Defluorination of Perfluorinated Alkyl Substances by Calcium Compounds during Waste Thermal Treatment. *Environ. Sci. Technol*., 49:5672-5680. https://doi.org/10.1021/es506234b

Wang, T.T., G.G. Ying, L.Y. He, Y.S. Liu, and J.L. Zhao. 2020. Uptake Mechanism, Subcellular Distribution, and Uptake Process of Perfluorooctanoic Acid and Perfluorooctane Sulfonic Acid by Wetland Plant Alisma Orientale. *Environ. Sci. Technol*., 733:139383.

Wang, T.T., G.G. Ying, W.J. Shi, J.L. Zhao, Y.S. Liu, J. Chen, D.D. Ma, and Q. Xiong. 2020. Uptake and Translocation of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) by Wetland Plants: Tissue- and Cell-Level Distribution Visualization with Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) and Transmission Electron Microscopy

Equipped with Energy-Dispersive Spectroscopy (TEMEDS). *Environ. Sci. Technol*., 54: 6009-6020.

Washington, J.W. and T.M. Jenkins. 2015. Abiotic Hydrolysis of Fluorotelomer-Based Polymers as a Source of Perfluorocarboxylates at the Global Scale. *Environ. Sci. Technol*., 49 (24):14129-14135. https://doi.org/10.1021/acs.est.5b03686

Washington, J.W., T.M. Jenkins, K. Rankin, and J.E. Naile. 2015. Decades-Scale Degradation of Commercial, Side-Chain, Fluorotelomer-Based Polymers in Soils and Water. *Environ. Sci. Technol.,* 49(2):915-923. https://doi.org/10.1021/es504347u

West, M.R. and B.H. Kueper. 2010. Plume Detachment and Recession Times in Fractured Rock. *Groundwater*, 48:416-426.

Xu B., W. Qiu, J. Du, Z. Wan, J.L. Zhou, H. Chen, R. Liu, J.T. Magnuson, and C. Zheng. 2022. Translocation, Bioaccumulation, and Distribution of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Plants. *iScience*, 25(4):104061. doi: 10.1016/j.isci.2022.104061

Yi, S., K.C. Harding-Marjanovic, E.F. Houtz, Y. Gao, J.E. Lawrence, R.V. Nichiporuk, A.T. Iavorne, W. Zhuang, M. Hansen, J.A. Field, D.L. Sedlak, and L. Alvarez-Cohen. 2018. Biotransformation of AFFF Component 6:2 Fluorotelomer Thioether Amido Sulfonate Generates 6:2 Fluorotelomer Thioether Carboxylate under Sulfate-Reducing Conditions. *Environ. Sci. Technol. Lett*., 5:283-288.

Yu, Q., R. Zhang, S. Deng, J. Huang, and G. Yu. 2009. Sorption of Perfluorooctane Sulfonate and Perfluorooctanoate on Activated Carbons and Resin: Kinetic and Isotherm Study. *Water Res*., 43:1150-1158.

Zhang, W. and Y. Liang. 2020. Removal of Eight Perfluoroalkyl Acids from Aqueous Solutions by Aeration and Duckweed. *Sci. Total Environ.,* 724: 138357.

Zhang, W., S. Pang, Z. Lin, S. Mishra, P. Bhatt, and S. Chan. 2021. Biotransformation of Perfluoroalkyl Acid Precursors from Various Environmental Systems: Advances and Perspectives. *Environ. Pollut.*, 272:115908. https://doi.org/10.1016/j.envpol.2020.115908

Zhang, Y., Z. Qv, J. Wang, Y. Yang, X. Chen, J. Wang, Y. Zhang, and L. Zhu. 2022. Natural Biofilm as a Potential Integrative Sample for Evaluating the Contamination and Impacts of PFAS on Aquatic Ecosystems. *Water Research* 215:118233 . https://doi.org/10.1016/j.watres.2022.118233

APPENDIX A: AGENDA

Workshop on Management of PFAS in the Environment

Hyatt Centric Chicago Magnificent Mile, 633 N St Clair St, Chicago IL

Tuesday, March 29, 2022					
0800	**Registration**				
0900	**Welcome and Introduction: Workshop Objectives and Structure**				Andrea Leeson SERDP and ESTCP
0915	**PFAS Efforts under SERDP and ESTCP**				Andrea Leeson SERDP and ESTCP
0940	**NDAA Overview**				Janice Willey NAVSEA
1005	**EPA Perspective**				Marc Mills USEPA
1030	**Break**				
1045	**Breakout Session I Discussions**				
	Thermal Treatment	Non-thermal Treatment	Sampling & Analysis	Fate & Transport	Concentration Technologies
1230	**Lunch**				
1300	**Breakout Session I Discussions (continued)**				Breakout Groups
1500	**Break**				
1515	**Breakout Session I Discussions (continued)**				Breakout Groups
1630	Recap of Day/Overview for Next Day				Andrea Leeson SERDP and ESTCP
1645	**Meeting Adjourn**				

Wednesday, March 30, 2022		
0830	**Coffee/Tea Service**	
0900	**Breakout Session I Reports**	Breakout Session Chairs
1040	**Break**	
1100	**Breakout Session II Discussions** Data Gaps & Priority Ranking	Breakout Groups
1230	**Lunch**	
1300	**Breakout Session II Discussions** (Continued)	Breakout Groups
1400	**Break**	
1415	**Breakout Session II Reports & General Group Discussion**	Breakout Session Chairs
1630	**Closing Summary and Remarks**	Andrea Leeson SERDP and ESTCP
1645	**Workshop Adjourn**	

Thursday, March 31, 2022		
0830	**Coffee/Tea Service**	
0900	**Report Development**	PFAS WG, Chairs, Co-Chairs
1030	**Break**	
1045	**Report Development (continued**	
1200	**Workshop Adjourn**	

APPENDIX B: ATTENDEES

David Adamson
GSI Environmental Inc.

Lisa Alvarez-Cohen
University of California, Berkeley

Hunter Anderson
Air Force Civil Engineer Center

Jens Blotevogel
Colorado State University

Susan Burden
U.S. Environmental Protection Agency

Michelle Crimi
Clarkson University

Brian Crone
U.S. Environmental Protection Agency

Anthony Danko
Naval Facilities Engineering and Expeditionary Warfare Center

Rula Deeb
Geosyntec Consultants

Dominic Di Toro
University of Delaware

Craig Divine
Arcadis

Paul Edmiston
College of Wooster

Jennifer Field
Oregon State University

Robert Ford
U.S. Environmental Protection Agency

Robert George
Naval Information Warfare Systems Command

Rajat Ghosh
Alcoa

Philip Gschwend
Massachusetts Institute of Technology

Jennifer Guelfo
Texas Tech University

Paul Hatzinger
APTIM

Damian Helbling
Cornell University

Heather Henry
National Institute of Environmental Health Services

Christopher Higgins
Colorado School of Mines

Qingguo (Jack) Huang
University of Georgia

Peter Jaffe
Princeton University

Detlef Knappe
North Carolina State University

Paul Koster van Groos
APTIM

Linda Lee
Purdue University

Andrea Leeson
SERDP & ESTCP

Jinxia Liu
McGill University

Michelle Lordemann
U.S. Army Corps of Engineers

David Major
Geosyntec Consultants

Selma Mededovic
Clarkson University

Marc Mills
U.S. Environmental Protection Agency

Charles Newell
GSI Environmental Inc.

Carla Ng
University of Pittsburgh

Dung (Zoom) Nguyen
CDM Smith

Bonnie Packer
Army National Guard

Cara Patton
Noblis

Graham Peaslee
University of Notre Dame

Kurt Pennell
Brown University

Jovan Popovic
Naval Facilities Engineering and Expeditionary
Warfare Center

Phillip Potter
U.S. Environmental Protection Agency

Paul Tratnyek
Oregon Health & Science University

Janice Willey
Naval Sea Systems Command

Joseph Quinnan
Arcadis

Maya Rabinowitz
Noblis

Jessica Reiner
National Institute of Standards & Technology

Stephen Richardson
GSI Environmental Inc.

Charles Schaefer
CDM Smith

David Sedlak
University of California, Berkeley

Erin Shields
U.S. Environmental Protection Agency

Jason Speicher
Naval Facilities Engineering Systems Command
Atlantic

Thomas Speth
U.S. Environmental Protection Agency

Timothy Strathmann
Colorado School of Mines

Hans Stroo
Stroo Consulting LLC

Alison Suess
U.S. Army Corps of Engineers

Timothy Thompson
SEE LLC

Andrea Tokranov
U.S. Geological Survey

Zhong (John) Xiong
Haley & Aldrich