

SUMMARY REPORT

SERDP and ESTCP Workshop on Research and Demonstration Needs for Management of AFFF-Impacted Sites

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TABLE OF CONTENTS

ACRONYMS	iii
1.0 INTRODUCTION	1
2.0 WORKSHOP APPROACH	3
3.0 RESEARCH NEEDS	5
3.1 FATE AND TRANSPORT PROPERTIES.....	5
3.1.1 <i>Evaluate PFAS Fate and Transport Processes Relevant to AFFF Sites (Critical Priority)</i>	5
3.1.2 <i>Evaluate the Influence of Phase Partitioning on Fate and Transport (Critical Priority)</i>	6
3.1.3 <i>Develop Predictive Fate and Transport Models and Identify Key Parameters (High Priority)</i>	6
3.1.4 <i>Develop Leachability Methods for PFASs in Soils and Sediments (High Priority)</i>	6
3.2 ECOLOGICAL RISK CHARACTERIZATION: RESEARCH INTO BIOAVAILABILITY, BIOMAGNIFICATION, AND TOXICITY OF PFASs	7
3.2.1 <i>Basic Research on Bioavailability of PFASs (Critical Priority)</i>	8
3.2.2 <i>Determine Toxicity of PFAS Mixtures Based on Available Site Data (Critical Priority)</i>	9
3.2.3 <i>Basic Research on Bioaccumulation and Biomagnification Pathways from Soils and Sediments to Higher Trophic Levels (Critical Priority)</i>	10
3.2.4 <i>Evaluate Exposure Pathways to Threatened and Endangered Species of Concern (Critical Priority)</i>	11
3.2.5 <i>Determine Population Level Impacts of PFASs on Aquatic and Terrestrial Ecosystems (High Priority)</i>	12
3.2.6 <i>Develop and Validate Models for Bioaccumulation and Biomagnification for Soils, Sediments, and Water (High Priority)</i>	12
3.2.7 <i>Evaluate Bioaccumulation and Biomagnification Processes and Exposure Pathways for Key PFASs Based on Data from Existing DoD Sites (High Priority)</i>	12
3.3 PFAS TREATMENT TECHNOLOGIES	12
3.3.1 <i>In Situ Treatment (Critical Priority)</i>	13
3.3.2 <i>Ex Situ Treatment (Critical Priority)</i>	13
3.3.3 <i>On-Site Technologies for Concentrated PFAS Waste Streams (Critical Priority)</i>	14
3.3.3.1 GAC or Other Carbon-Based Sorbents	15
3.3.3.2 Ion Exchange Resins.....	15
3.3.3.3 Concentrates from Membrane Filtration Processes.....	15
3.3.4 <i>Reductive Technologies (High Priority)</i>	16
3.4 SAMPLING AND ANALYTICAL PROCEDURES.....	16
3.4.1 <i>Develop and Demonstrate Standardized Sampling Procedures for PFASs (Critical Priority)</i> ...	17
3.4.2 <i>Develop and Validate Analytical Methods for PFASs (Critical Priority)</i>	17
3.4.2.1 Organofluorine Methods.....	18
3.4.2.2 Rapid Field Screening Methods.....	18
3.4.2.3 Additional Analytical and Sampling Needs.....	19
3.4.3 <i>Develop Forensic Methods for Source Tracking and Allocation of Emerging Contaminants (High Priority)</i>	19
4.0 DEMONSTRATION NEEDS	21
4.1 TREATMENT TECHNOLOGY DEMONSTRATIONS.....	21
4.1.1 <i>Demonstrate the Effectiveness and Sustainability of Thermal Destruction Technologies for Soils and Spent GAC and Resins (Critical Priority)</i>	21
4.1.2 <i>Validate Destruction Technologies and their Applicability to Treat Concentrated PFAS Waste Streams (Critical Priority)</i>	22
4.1.3 <i>Side-by-Side Comparisons of Treatment Technologies (High Priority)</i>	23
4.1.4 <i>In Situ and Ex Situ PFAS Treatment (High Priority)</i>	24
4.2 MEASUREMENT & PREDICTION.....	24

4.2.1 Measurement of PFAS Mass Flux Relative to Source Mass in the Vadose Zone and in Groundwater (Critical Priority)	24
4.2.2 Development and Validation of a Fate and Transport Model for PFASs (High Priority)	25
5.0 TECHNOLOGY TRANSFER NEEDS	26
5.1 TECHNOLOGY TRANSFER WHITE PAPER (CRITICAL PRIORITY)	26
5.2 TECHNOLOGY TRANSFER EFFORTS (HIGH PRIORITY)	27
5.3 RISK COMMUNICATION TOOLS (HIGH PRIORITY)	28
5.4 GRANULAR ACTIVATED CARBON STATUS PAPER (HIGH PRIORITY)	28
6.0 SUMMARY AND CONCLUSIONS	29
7.0 REFERENCES	30
APPENDIX A: AGENDA	A-1
APPENDIX B: ATTENDEE LIST	B-1

LIST OF TABLES

Table 1. Definition of Need Prioritization	4
Table 2. SERDP-Funded Ecotoxicity Projects as of September 2017	9

LIST OF FIGURES

FIGURE 1. Representative PFAS Structures and Formulas	2
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ACRONYMS

AFFF	aqueous film forming foam
BAF	bioaccumulation factor
CSIA	compound specific isotope analysis
CSM	conceptual site model
CUL	cleanup level
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FAQ	Frequently Asked Question
FTOH	fluorotelomer alcohol
FTSA	fluorotelomer sulfonate
GAC	granular activated carbon
HAL	Health Advisory Level
HRMS	high resolution mass spectrometry
ITRC	Interstate Technology Regulatory Council
LOEL	Lowest Observed Effect Level
MOOC	massive open online course
NARPM	National Association of Remedial Project Managers
NF	nanofiltration
NOEL	No Observed Effect Level
PIGE	particle induced gamma-ray emission
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substance
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate
PFCA	perfluoroalkyl carboxylate
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonate
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate

PFNA	perfluorononanoic acid
PFNS	perfluorononane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFSA	perfluoroalkyl sulfonate
RI	remedial investigation
RO	reverse osmosis
RPM	Remedial Project Manager
SERDP	Strategic Environmental Research and Development Program
T&E	threatened and endangered
TEQ	toxic equivalent
TOP	total oxidizable precursor
TRV	toxicity reference value
TSERAWG	Tri-Services Environmental Risk Assessment Working Group
UCMR	Unregulated Contaminant Monitoring Rule

1.0 INTRODUCTION

Contamination of soils and waters by per- and polyfluoroalkyl substances (PFASs) is a widespread problem. The majority of the liability facing the U.S. Department of Defense (DoD) is a result of the use of Aqueous Film Forming Foam (AFFF) formulations that have been used since the 1970s to extinguish fuel-based fires. As a result of training and fire suppression, DoD may have thousands of sites contaminated with PFASs, with a current estimated cost for managing these sites of approximately \$2 billion.

The AFFF mixtures used by DoD contained significant quantities of perfluorooctane sulfonate (PFOS) and related perfluoroalkyl sulfonates such as perfluorohexane sulfonate (PFHxS), as well as a suite of other PFASs. Research on AFFF sites is timely given the U.S. Environmental Protection Agency's (EPA's) recent drinking water Health Advisory Levels (HALs) for PFOS and perfluorooctanoic acid (PFOA), both of which have been found at AFFF sites. The current HAL is 70 parts per trillion (ng/L) for the sum of PFOA and PFOS in drinking water, or either compound individually. In addition, numerous states are beginning to promulgate their own drinking water standards. These advisory levels are sufficiently low such that large volumes of groundwater can exceed these criteria by several orders of magnitude at many sites.

Due to their chemical structure (Figure 1), PFASs (especially perfluoroalkyl acids [PFAAs] such as PFOA and PFOS) are stable in the environment and resistant to treatment by biodegradation, photooxidation, direct photolysis, and hydrolysis. However, some PFASs, 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 fact that the composition of AFFF varies with 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 apt to form 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. As a result, management of AFFF sites can be very costly.

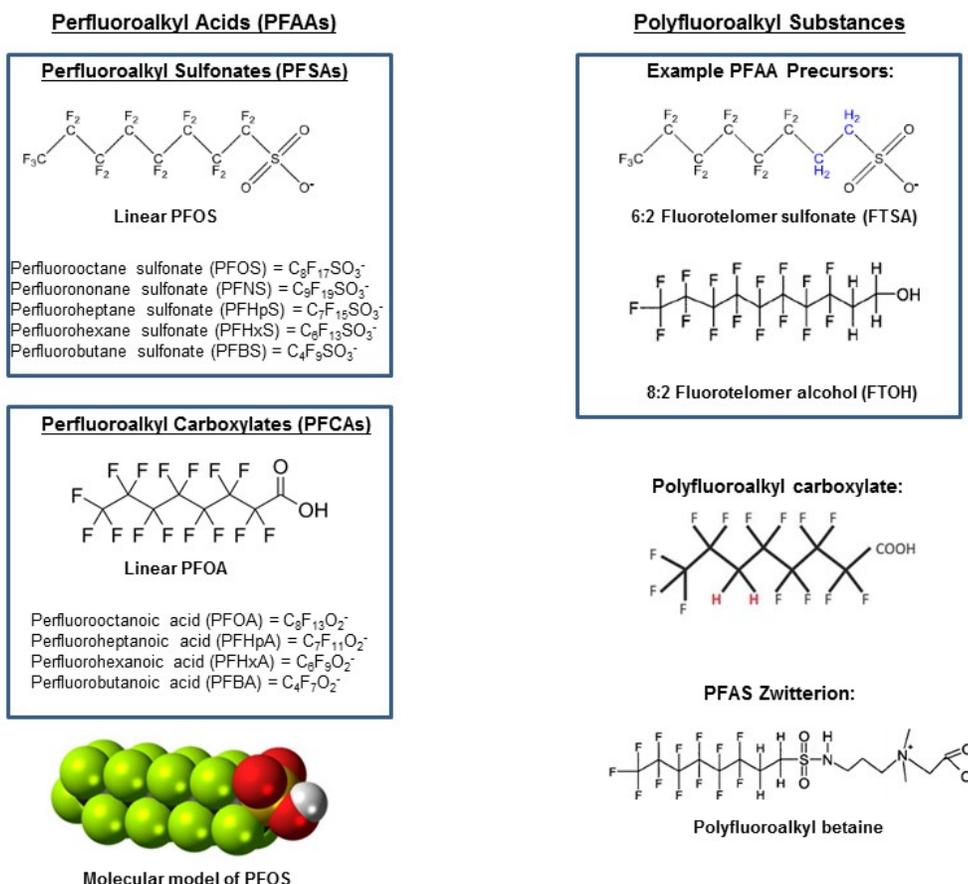
Reducing the potential magnitude of the DoD's PFAS liability will require a sustained effort to identify the best technologies to characterize, treat, and manage these sites. The DoD is currently performing initial site investigations at nearly all of their U.S. facilities to determine the extent of PFAS contamination. It is anticipated that Remedial Investigations (RIs) will begin at many DoD sites in the next few years. Efficient and meaningful investigations will require significant improvements in the current understanding of PFAS toxicity and behavior in the environment, as well as improvements in sampling and analysis of PFASs. A substantial fraction of the impacted sites will likely require remediation. Given the recalcitrance and complexity of PFAS contamination, as well as the low cleanup levels likely to be required, advances in current remediation technologies are needed to improve effectiveness and greatly reduce costs.

The Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) have been funding research

on AFFF contamination for several years, to improve PFAS analysis, to develop tools for assessing the fate of PFASs in the subsurface, and to evaluate the potential for in situ remediation. Research is ongoing to evaluate a range of potential remediation technologies, ecotoxicological effects, and improved AFFF site characterization and technology transfer regarding PFAS contamination. Recent Statements of Need have focused on improving the characterization of AFFF source zones and improving ex situ and in situ groundwater treatment. A description 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 remediation of AFFF sites, SERDP and ESTCP conducted a workshop on May 2-3, 2017 in Washington, D.C. The objectives of the workshop were (1) to review the current state of the science regarding sources of PFAS contamination, particularly AFFF, (2) to evaluate currently available and developing technologies for characterization and remediation of AFFF sites, and (3) to identify research and demonstration needs to improve remediation performance, efficiency, and ultimately reduce the cost of managing AFFF sites.

Figure 1. Representative PFAS Structures and Formulas



2.0 WORKSHOP APPROACH

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 the Program 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 intended to summarize efforts supported to date to address research and demonstration needs at sites impacted by PFASs as well as provide insight into the status of DoD's efforts to manage these sites.

Two breakout sessions, each with four working groups, facilitated discussions of the current state of the science of management of PFAS contaminated sites, reviewed where DoD facilities are in their management of these sites, and determined what specific tools, demonstration, or information transfer needs existed that would facilitate cost effective management.

On Day 1, each working group addressed the same charge comprised of a list of key questions formulated by the Program Office and steering committee with input from some attendees. These questions, which were provided in advance to the participants, are as follows:

- What are the major opportunities to improve management of AFFF sites?
- What are the most promising technologies and advances in PFAS characterization and remediation?
- How would you quantitatively develop site-specific soil thresholds protective of groundwater?
- What sediment concentrations are protective of the cumulative risk of biomagnification in higher trophic organisms?
- Are real-time field analytical methods available to qualitatively or semi-quantitatively assess soil and groundwater contamination?
- How do we account for precursors in both risk assessment and delineation?
- What is the likely regulatory scenario in the future and how may this impact site management?

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

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

Table 1. Definition of Need Prioritization

	Critical	High
Research	Research that potentially could have a significant impact on cost-effective management of PFAS contaminated sites.	Research that is of high priority but may not be able to be initiated until critical research needs are addressed or may be more clearly defined after critical research needs are addressed.
Demonstration	Field demonstrations or assessments that can improve on cost-effective management of PFAS contaminated sites.	Field demonstrations or assessments that are of high priority but may not be able to 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 RESEARCH NEEDS

The research needs identified during the workshop are described in this section; demonstration and technology transfer needs are described in Sections 4.0 and 5.0, respectively. The needs are categorized as either critical priority needs (most urgent), followed by high priority needs. The order in which the needs are listed does not imply any prioritization. These needs were grouped into broad categories, including fate and transport properties, ecological risk characterization, treatment, and sampling and analytical procedures.

3.1 Fate and Transport Properties

Understanding the fate and transport of PFASs in the environment is critical for assessing their risks and developing accurate conceptual site models (CSMs). Fate and transport evaluations are complicated by the sheer number of PFASs present in complex AFFF formulations, and further complicated by the differences between linear and branched forms (i.e., isomers) of many PFASs. A large number of different isomers can be found at AFFF sites, and isomers can have pronounced differences in key fate and transport properties (Prevodorous et al., 2006), as well as in bioaccumulation potential (Houde et al., 2008) and susceptibility to different treatment technologies (Rahman et al., 2014). The basic chemical information needed to predict fate and transport is not available for most PFASs, and there are large ranges in the chemical properties for PFASs that have been studied.

Complicating the issue is that there are probably significant mixture effects and interactions with co-contaminants that can alter fate and transport properties in situ. In addition, a variety of abiotic and biotic processes can transform PFAA precursors under specific environmental conditions into the more problematic PFAAs (e.g., PFOA and PFOS), and these processes should be considered in risk assessments, model predictions, and CSMs. Four fate and transport research needs were identified during the workshop, as shown below, and described in the following subsections.

- Critical priority research needs
 - Evaluate PFAS fate and transport processes relevant to AFFF sites
 - Evaluate the influence of phase partitioning on fate and transport
- High priority research needs
 - Develop predictive fate and transport models and identify key parameters
 - Develop leachability methods for PFASs in soils and sediments

3.1.1 Evaluate PFAS Fate and Transport Processes Relevant to AFFF Sites (Critical Priority)

A better understanding of the long-term fate and transport of PFASs (including precursors) in soil and groundwater would improve the ability to predict contaminant migration and longevity, and thus improve the management of AFFF sites. Ideally, this knowledge could be incorporated in current and planned site investigations that are designed to identify sites that need further investigation and remediation. This knowledge would lead to more efficient site characterizations, and improve DoD's ability to assess the full extent of contamination at AFFF sites. A scientifically sound approach to performing these initial characterizations is urgently needed to facilitate efficient investigations.

In particular, reliable predictions of AFFF source depletion rates within vadose zones, aquifers, and sediments are not currently possible. As a result, the mass discharge from these sources over time is difficult to measure and model. For example, cationic and zwitterionic PFASs are likely to remain in the source zones due to relatively strong sorption, but it is not known if they persist over time or to what extent they may be degraded or transformed. PFAS releases may occur largely near and within the capillary fringe in contaminated aquifers, but under some conditions PFASs may migrate deeper into the subsurface, and the conditions controlling migration are not understood. Processes responsible for long-term sorption and desorption of PFASs from aquifer solids within sources and plumes are of particular interest.

Issues associated with PFAA precursors are also of concern. A large number of PFAA precursors are present in AFFF formulations, and their transformation pathways and rates are not well understood, especially in the presence of co-contaminants and under biogeochemical conditions encountered at contaminated sites. Comprehensive studies on the biotransformation of precursors could significantly improve risk assessments and the characterization of AFFF sites.

3.1.2 Evaluate the Influence of Phase Partitioning on Fate and Transport (Critical Priority)

The phase partitioning of PFASs is complex and strongly affects environmental fate and transport, as well as site characterization and remediation. The partitioning of PFASs to solids, water, and air may affect the remedial technology selection and the success of remediation; remediation methods also may affect PFAS mobility. Understanding the factors controlling partitioning to aquifer solids is also critical for site management. Fundamental information on the underlying partitioning processes is not available for many PFASs. PFASs are surface-active substances and therefore tend to accumulate at interfaces (e.g., air/water, water/solvent, and soil/water interfaces). Depending on concentrations and PFAS composition, PFAS mass may be predominantly present as monomers, hemimicelles, or micelles, affecting fate and transport characteristics.

3.1.3 Develop Predictive Fate and Transport Models and Identify Key Parameters (High Priority)

Predictive fate and transport models are needed to assess the risks posed by PFASs in all media. Such models are essential to evaluating the potential migration of PFASs, and the concentrations and composition of the PFAS mixtures over time. These models should incorporate precursor transformations, and the effects of environmental conditions such as redox, pH, salinity, organic carbon content, interface effects, and presence of co-contaminants on fate and transport. Identifying and quantifying the key soil and sediment parameters controlling these models is also necessary. Development and validation of such models will improve CSMs and decisions regarding the need for further investigations and/or remediation.

3.1.4 Develop Leachability Methods for PFASs in Soils and Sediments (High Priority)

Given the complexity of PFAS mixtures, the range in the operation histories of most fire-training areas, and the difficulty in predicting mobility, it will be important to develop methods and tools to measure the potential for, or extent of, PFAS migration in unsaturated or saturated zones. It is particularly important to assess the potential for migration to groundwater from residual contamination located in the vadose zone. Determining whether residual sources pose a continuing risk after the most mobile constituents have been depleted requires validated leachability methods for use in soils and sediments. Laboratory methods to measure the leachability of PFAS mixtures

in environmental samples would be valuable, as would methods to measure mass discharge/flux in situ. A credible leachability protocol should address the impacts of co-contaminants, PFAA precursors, as well as soil and water geochemical conditions. Related basic research on the effects of soil and sediment parameters on transport also is needed.

3.2 Ecological Risk Characterization: Research into Bioavailability, Bioaccumulation, Biomagnification, and Toxicity of PFASs

Ecological risk characterization for PFASs was recently identified as a clear and immediate information gap by the Tri-Services Environmental Risk Assessment Working Group (TSERAWG) and the EPA, as well as by the participants in this workshop. Due to their high water solubility and high to moderate mobility in soils and sediments (Zareitalabad et al., 2013), PFASs persist in aquatic and terrestrial environments and accumulate in fish and wildlife. Management of PFAS-contaminated sites requires ecological risk evaluations for listed and non-listed wildlife species. Consequently, the lack of basic PFAS ecotoxicological data is a significant gap that must be addressed.

Ecological risk assessments at AFFF sites are complicated by the fact that the PFASs occur in complex mixtures, with over 200 different fluorinated organic chemicals having been identified in AFFF-impacted waters and soils so far. Biota are exposed to a mixture of PFASs, but what remains a critical research need is the bioaccumulation, food-web biomagnification, and the relative potency of both individual PFASs and the mix of constituents present at AFFF sites. Determining these relationships for additional PFASs in comparison to PFOS and PFOA will allow a more thorough assessment of risks for AFFF sites.

The TSERAWG identified a series of fundamental research and development questions and needs, including:

- What approaches and methods can be developed to identify whether PFOS and PFOA drive ecological risk assessment, or whether PFAS mixtures must be accounted for? How should ecological risk assessments account for PFAA precursors? At a minimum, scientifically-defensible ecological toxicity reference values (TRVs), fate and transport, and bioaccumulation/biomagnification data are needed for the six PFAS identified by the Unregulated Contaminant Monitoring Rule (UCMR 3)¹.
- Should a Toxic Equivalent (TEQ) approach be developed for PFASs to account for PFAS mixtures – at a minimum, the six PFAS included in UCMR 3?
- What approaches and/or models could be developed to support derivation of surface water, sediment, and soil cleanup levels? Approaches for establishing cleanup levels are needed for immediate receptors (e.g., phytoplankton/zooplankton, benthos and epibenthos) and to protect upper trophic species from PFAS biomagnification.
- Do PFASs accumulate at sufficient levels to pose risks to threatened and endangered (T&E) species, or to humans consuming fish? What are the mechanisms and transfer pathways in the food web? There is currently insufficient information to (1) document food web transfer, (2) develop food web models, or (3) assess PFAS bioavailability.

¹ UCMR 3 lists six PFASs that must be monitored for in drinking water. Of these, only PFOS and PFOA have health advisory levels. The other four PFASs are perfluorononanoic acid (PFNA), PFHxS, PFHpA, and PFBS.

- Accepted and validated analytical methods for sediments, soils, or biological tissues are not available, but are needed to develop defensible TRVs, food web models, or ecologically protective soil/sediment or surface water values.

Building on the prior work, this workshop identified four critical and three high priority ecotoxicity research needs, listed below and described in subsequent sections. Given the current state of the science for PFASs relative to ecological receptors, all are basic research needs, and no immediate demonstration or technology transfer needs were identified. The workshop participants did anticipate that successful completion of the research needs would lead to later demonstration and technology transfer needs.

- Critical priority research needs
 - Basic research on bioavailability of PFASs
 - Determine toxicity of PFAS mixtures based on available site data
 - Basic research on bioaccumulation/biomagnification pathways from soils and sediments to higher trophic levels
 - Evaluate exposure pathways to threatened and endangered species of concern
- High priority research needs
 - Determine population level impacts of PFASs on aquatic and terrestrial ecosystems
 - Develop and validate models for bioaccumulation and biomagnification for soils, sediments, and water
 - Evaluate bioaccumulation and biomagnification processes and exposure pathways for key PFAS based on data from existing DoD sites

Note that there are currently four SERDP projects that are determining PFAS TRVs for amphibians, birds, and reptiles (Table 2). While these projects will produce essential data for ecological risk assessments at PFAS sites, they do not directly address the needs summarized in this section.

3.2.1 Basic Research on Bioavailability of PFASs (Critical Priority)

Basic research on bioavailability of PFASs to ecological receptors in water, sediments, and soils is a critical research need. That PFASs are bioaccumulative in water is well-established, as all published Bioaccumulation Factors (BAFs) are > 1 . However, to date the only BAFs in the scientific literature are for individual PFASs to soil/sediment invertebrates and to fish. Additional work establishing bioaccumulation (uptake) to organisms at the base of the food chain is needed for soil invertebrates, sediment infauna, and phytoplankton/zooplankton. Specific research areas of interest include:

- The uptake, retention, and excretion (loss) rates of PFASs by these food web base organisms in water, sediments, and soils need to be assessed. Initially this work should focus on the six UCMR-3 PFASs, both singly and as mixtures. The potential impacts of competitive uptake and/or selective retention of PFASs will be important to assess.
- The rate and extent of PFAS uptake from soils and water by organisms should be evaluated, along with the potential biotransformations of PFAA precursors after uptake in order to determine the relevant mixtures for further study with higher trophic level organisms.

Table 2. SERDP-Funded Ecotoxicity Projects as of September 2017

Project Number	Title	Target Ecological Receptors	Principal Investigator
ER-2624	Development of TRVs for Birds Exposed to PFOS, PFOA and Associated Mixtures of Fluorinated Compounds	Japanese quail (<i>Coturnix japonica</i>) as a surrogate for wild avian species. Develop acute and chronic TRVs for PFOS and PFOA	Matt Simcik, University of Minnesota
ER-2625	Development of Toxicity Data to Support Toxicity Reference Values for Perfluorinated Compounds	White footed mouse (<i>Peromyscus leucopus</i>). Develop reproductive/population-based oral dose TRVs for PFOA, PFOS, PFHxS and PFBS.	Michael Quinn U.S. Army Public Health Command
ER-2626	Development of Amphibian PFASs TRVs for Use in Ecological Risk Assessment at AFFF Sites	Amphibians including the Northern Leopard Frog (<i>Lithobates pipiens</i>), American Toads (<i>Anaxyrus americanus</i>), and Eastern Tiger Salamanders (<i>Ambystoma tigrinum</i>). Develop TRVs using 1) Aquatic chronic larvae; 2) Sediment subchronic larvae; 3) Terrestrial dermal chronic adults; and 4) Terrestrial oral chronic adults.	Maria Sepulveda Purdue University
ER-2627	Advancing the Understanding of the Ecological Risk of PFASs	Avian and reptile species are being evaluated in this oral-dose study. Target bird species include Bobwhite quail (<i>Colinus virginianus</i>) and mallard ducks (<i>Anas platyrhynchos</i>); endpoints include acute and chronic (growth, egg production, survival) to yield oral-dose TRVs. Representative reptile is the on Western fence lizards, <i>Sceloporus occidentalis</i> .	Christopher Salice Towson State University

- Physical and geochemical factors affecting bioavailability of PFASs in sediments and soils. Factors such as organic and/or black carbon, pH, cation/exchange capacity (in soils), dissociation constants (*k*), or other factors influencing uptake will be critical in developing food-web modeling.
- Bioavailability measures, either as direct tissue measurements or from tools such as passive samplers, are important needs. Whether passive samplers could function as biological surrogates for uptake in invertebrates, or up to and including fish species, is of specific interest.

3.2.2 Determine Toxicity of PFAS Mixtures Based on Available Site Data (Critical Priority)

PFASs are found in complex mixtures and ~ 200 different fluorinated organic chemicals have been identified in the environment at AFFF sites. Therefore, biota are likely to be exposed to a mixture of PFASs. However, to support the assessment of risk from mixtures, it is necessary to first understand the relative potency of its constituents. Determining these relationships for additional PFASs in comparison to PFOS and PFOA will allow assessment of risks for AFFF sites.

Toxicity and kinetics of PFASs are, at least in part, driven by their physical and chemical properties. For instance, in mammals, shorter-carbon chain PFASs (such as PFHxA and PFBA)

are less overtly toxic than longer-carbon chains (PFOS and PFOA) (Kudo et al., 2006). Differences in chain length also drive bioaccumulation rates since in general, the rate of elimination decreases with increasing chain length (Conder et al., 2008).

The toxicity of PFASs has been evaluated in mammals (rodents) and in a few model fish species, such as zebrafish and rainbow trout. However, other aquatic taxa, including native amphibians, have been largely overlooked. Similarly, almost no PFAS toxicity data are available for birds and reptiles. Importantly for SERDP, studies need to focus on PFASs and ecological receptors that are of relevance to AFFF sites. Specific research topics of interest include:

- Compare the potency of PFASs in relation to chain length (C8 vs. C6 sulfonates), functional group (carboxylic acid vs. sulfonate), and varying levels of fluorination (complete vs. partial fluorination). Chemicals of interest for testing include understudied PFASs (i.e., excluding PFOS and PFOA). Studies should target PFASs commonly found at AFFF sites, including PFAA precursors (parent and transformation intermediates) and PFAAs. Persistent co-contaminants and non-fluorinated AFFF components found at AFFF sites may also require study.
- Using potency data from single chemical exposures, determine whether a TEQ approach would be relevant for assessing the ecotoxicology of PFASs. The TEQ approach would only be feasible if the mechanism of toxic action is consistent among the various PFASs. Therefore, use of “high-throughput” experimental (e.g., in vitro tests with fish embryos or cell lines) and computational approaches would be ideal for rapid results that can then be partially validated at higher levels of biological organization (e.g., using whole animals that are relevant and representative of AFFF sites).

3.2.3 Basic Research on Bioaccumulation and Biomagnification Pathways from Soils and Sediments to Higher Trophic Levels (Critical Priority)

Basic and applied research is needed to understand and model bioaccumulation and biomagnification in aquatic and terrestrial environments. The critical need addressed by this research is the ability to derive soil or sediment-based clean-up levels (CULs) for site remedial actions. While single-compound CULs can be derived using standard soil or sediment toxicity tests, CULs for the protection of higher trophic level organisms (e.g., T&E species) – or human health based on fish consumption – requires a more complete understanding of conceptual site models, physical/geochemical fate and transport processes, and trophic transfer factors.

The current SERDP-funded ecotoxicity projects (Table 2) will provide oral (as well as aqueous and dermal in the case of amphibians)-dose based TRVs for individual PFASs, as well as the relative toxicity of mixtures of PFASs that occur in AFFF. While results from these studies may be used for future development of an upland/terrestrial exposure model to develop site-specific screening values and/or risk estimates, those currently cannot account for trophic transfer and biomagnification. These studies evaluate steady-state exposure and uptake only, but exposure modeling will involve many other parameters that are all highly variable (e.g., consumption rates, area use, etc.). The development of an exposure model to use in risk assessments, and its field-testing and validation remain future research needs.

For aquatic environments, only PFOS has been found to significantly biomagnify up the food chain (Ahrens and Bundschuh, 2014). The degree to which other compounds (e.g., PFHxS) bioaccumulate and biomagnify remains unknown. As noted previously, uptake and elimination kinetics, absorption/binding efficiency, in vivo precursor transformation rates, and competitive bioaccumulation effects from PFAS mixtures remains relatively uncertain. There are some data that suggest PFOS is more toxic to wild tree swallows with effects observed at lower concentrations than those reported from laboratory feeding trials or egg injection studies in other avian species (Custer et al., 2014). Those data suggest that field-caught organisms exposed largely via diet may be experiencing mixture toxicity due to cumulative exposure to other PFASs. Specific research areas of interest include:

- Demonstration of PFAS bioaccumulation/biomagnification throughout a food web using existing empirical site data or project-specific collected data. Questions that could be addressed include:
 - Are PFASs accumulating in biota within areas of known AFFF use?
 - What PFASs biomagnify? Does the relative distribution of PFASs change with each subsequent trophic transfer? What is the relative role of PFAA precursors in determining total body burdens?
 - Do the collective data show direct pathways from soils/sediments to higher trophic levels? For example, is there a clear sediment-to-biota transfer (e.g., sediment-to-benthos-to-prey fish-to-top predatory fish), or are there gaps in the PFAS transfer that suggest other uptake pathways and/or precursor transformation?
 - How important are these pathways to potential human exposure? For example, are PFASs in fish accumulating to levels that could pose risks to humans consuming those fish?

3.2.4 Evaluate Exposure Pathways to Threatened and Endangered Species of Concern (Critical Priority)

Evaluating chemical risks to T&E species is a required component for Superfund ecological risk assessments. For PFASs, there is little information on the uptake and toxicity to T&E species. T&E species cannot be used to develop TRVs, and therefore suitable surrogate species are needed to develop toxicity thresholds. Towards articulating a defensible approach for assessing risks to T&E species the following critical needs were identified:

- Prepare a white paper summarizing available information on uptake and toxicity assessments for T&E species found on DoD sites. The white paper should first identify the most common T&E species found on DoD sites where AFFF has been used. From that list of species, the white paper will identify exposure factors for PFASs and suitable surrogate (non-T&E) species, and will review the available toxicological information including the No Observed and Lowest Observed Effect Levels (NOEL and LOEL, respectively) for the surrogate species.
- Develop TRVs and bioaccumulation/biomagnification factors for surrogate T&E species. The results of the white paper can be used to establish what species should be targeted for TRV development, and those toxicity tests should then be conducted.

3.2.5 Determine Population Level Impacts of PFASs on Aquatic and Terrestrial Ecosystems (High Priority)

Almost no data are available on population-level effects of PFASs. Observational field studies could provide insight into PFAS exposure of ecologically relevant species and potential impacts on population dynamics. Specific research areas of interest include:

- Conduct laboratory studies that evaluate population-level effects of PFAS exposure in aquatic and terrestrial species.
- Conduct field population dynamic studies that examine endpoints of interest (survival, age to maturity, reproduction) in sentinel species found in AFFF sites in relation to PFAS tissue concentrations.

3.2.6 Develop and Validate Models for Bioaccumulation and Biomagnification for Soils, Sediments, and Water (High Priority)

A high priority research need is to develop and validate food web models. To that end, specific research is needed on the physiochemical and biological parameters needed to support development of food web models for both terrestrial and aquatic systems. The resulting models may be based on simple transfer factors for well-understood trophic pathways (e.g., surface-to-water-to-insect, and soil-to-insect bioaccumulation factors), or they may consist of more complex kinetic models that predict tissue concentrations using data on sediment-water exchanges, ingestion and uptake rates, growth, dilution, and other physiological factors.

3.2.7 Evaluate Bioaccumulation and Biomagnification Processes and Exposure Pathways for Key PFASs Based on Data from Existing DoD Sites (High Priority)

This high priority research need would evaluate toxicity, bioaccumulation, and food web transfer processes for other PFASs identified in EPA Method 537 (USEPA, 2009). This would include laboratory uptake and toxicity studies, and field measures at DoD sites in tissue with the goal of validating a food web model for these additional compounds.

3.3 PFAS Treatment Technologies

Development of improved PFAS treatment technologies is needed (particularly those that transform and defluorinate PFASs into less harmful products) for both long- and short-chained PFAAs. PFAS treatment technologies must be able to achieve the low part per trillion (ng/L) cleanup criteria required while remaining as sustainable and cost effective as possible. PFAS treatment technologies are needed for the wide range of PFASs present in AFFF, including PFAA precursors, rather than technologies that focus solely on the compounds that currently have health advisory levels or other regulatory limits. It is recognized that a treatment train, rather than a single stand-alone treatment technology, may be required to address the unique challenges and wide range of compounds associated with AFFF-impacted media.

Whether treatment involves PFAS transformation, separation, or both, the treatment mechanism(s) must be appropriate under typical field conditions, considering geochemistry, the presence of likely co-contaminants (with respect to the impacts of treatment on the co-contaminants, as well as the impact of the co-contaminants on PFAS treatment), and the relatively low concentrations of PFASs that are present at many of the DoD's AFFF sites.

For treatment approaches that are based on PFAS transformation, careful assessment and demonstration of a mass balance (including defluorination) should be performed to assess the risks associated with the final products. In addition, as aggressive reaction conditions are typically needed to degrade PFAAs, the potential generation of toxic byproducts (e.g., perchlorate) should be a key component of the research effort. Finally, PFAS treatment approaches must include an assessment of overall energy requirements, estimated cost, and sustainability assessment. Four research needs were identified under this area as shown below and described in the following subsections. In addition, closely related to these research needs are specific demonstration needs for PFAS treatment; these are described in Section 4.1.

- Critical priority research needs
 - In situ treatment
 - Ex situ treatment
 - On-site technologies for concentrated PFAS waste streams
- High priority research needs
 - Reductive technologies

3.3.1 In Situ Treatment (Critical Priority)

In situ treatment technologies for PFASs in both soil (source area) and groundwater (source area and/or dilute plume) are urgently needed. Effective treatment of the unsaturated zone, where much of the AFFF source mass may reside, is of particular interest. Unsaturated zone treatment approaches must consider PFAS phase partitioning behavior that is likely to be influenced by elevated concentrations of soil organic matter and fluid-fluid interfaces. Source zone technologies may transform, flush, or immobilize/stabilize PFASs.

Ongoing or recently completed SERDP and ESTCP projects have advanced several in situ treatment methods, including enzyme based approaches (ER-2127 and ER-2422), coagulant enhanced sorption (ER-2425), zerovalent metals (ER-2426), permeable barriers (sorption) (ER-2714), persulfate oxidation coupled with bioremediation (ER-2715), and thermally-enhanced persulfate oxidation coupled with pump-and-treat (ER-201729). In situ technologies that facilitate PFAS transformation should be able to demonstrate a mass balance (with defluorination), maintain sufficient reaction longevity and rates to achieve treatment goals in situ for the wide range of PFAS concentrations, and be reasonably implementable under a wide range of hydrogeologic conditions. In situ technologies based on sequestration/immobilization must be able to demonstrate irreversibility (or near-irreversibility) and long-term stability of the treatment process. In situ technologies meeting these criteria have yet to be demonstrated.

Cost-effective in situ treatment approaches for downgradient dissolved plumes also are needed, especially at DoD facilities where PFASs are migrating offsite or approaching receptors. However, treatment technologies that target PFAS sources are desired as a key aspect of site remediation. PFAS sources may include vadose zone soils, non-aqueous phases, and/or other low permeability materials. The impact of mitigating PFAS sources on long-term dissolved plume behavior and overall PFAS mass discharge is currently unknown.

3.3.2 Ex Situ Treatment (Critical Priority)

Pump-and-treat systems using GAC and/or ion exchange resins are currently being implemented, either in full or pilot scale, at several locations to treat PFASs. These technologies have limitations

with respect to their ability to efficiently remove small chain and hydrophilic PFASs. In addition, PFASs partitioned to the GAC or resins eventually require additional treatment (for regeneration and reuse) or disposal, thereby adding to the costs and liability incurred by the DoD. For these reasons, ex situ technologies that are able to transform and defluorinate PFASs (particularly the recalcitrant PFASs) to inert species are desired. While electrochemical approaches (including those being studied as part of on-going SERDP projects ER-2424, ER-2717, and ER-2718), generation of hydrated electrons (ER-2424), and high pressure filtration continue to show promise, challenges regarding oxidation by-products, waste/concentrate streams, and energy demand persist. These challenges remain a barrier to the wide implementation and acceptance of these approaches.

To mitigate and overcome these challenges associated with ex situ treatment of PFASs, several approaches are considered:

- Alternate sorbents with extended lifetime and selectivity for PFASs, with reduced costs and effort associated with regeneration or disposal
- Improvements to GAC and ion exchange resins that extend lifetime and/or facilitate regeneration
- Treatment trains, considering combinations of PFAS separation and/or transformation processes
- Improvements in electrochemical processes or in generation of hydrated electrons
- Development of novel processes for effective and efficient transformation/defluorination of PFASs

For all of the above approaches, energy demand, treatment rates, treatment longevity, the ability to treat the wide range of PFASs present in AFFF (including PFAA precursors), and life-cycle cost need to be considered. Finally, the overall water quality of the treatment effluent (including salinity, turbidity, pH, and other water quality criteria) needs to be considered for final discharge.

3.3.3 On-Site Technologies for Concentrated PFAS Waste Streams (Critical Priority)

Improved technologies for on-site PFAS waste treatment is a separate need. Concentrated waste streams are a product of the most widely applied approach for treating PFAS-contaminated waters (groundwater extraction and ex situ separation using GAC or ion exchange resins). In addition, concentrated waste streams will result from several innovative technologies that are under development, including high pressure filtration (using reverse osmosis [RO] or nanofiltration [NF]) or alternate sorbents. Each of these treatment processes generates one or more residual or concentrate streams that require careful management and can substantially increase the overall cost of treatment. For example, regeneration of spent ion exchange resins produces a concentrate stream enriched in PFASs, co-contaminants, salts, and possibly co-solvents such as short-chained alcohols. A first step should be a white paper detailing what kinds of waste streams are expected, including PFAS concentrations and any co-contaminants of concern, and any results to date on treatment of such waste streams.

Current approaches to manage these concentrated streams are energy intensive, and require high-temperature (1000°C) incineration or disposal of concentrated PFASs (which poses a continuing liability for the DoD). Likewise, thermal regeneration/reactivation and reuse of GAC is a common

practice, but there is a lack of data on any residual contaminants and other potentially toxic byproducts that may remain in the reactivated material.

There is a critical need to research and develop cost-effective and sustainable approaches for managing residuals and concentrate streams from ex situ treatment technologies. Ideally, these technologies could be employed for on-site treatment or regeneration of these streams. Research in this area is needed to ensure that treatment objectives are met and DoD liabilities are eliminated.

Specific needs related to individual concentrated PFAS waste streams are described in the following subsections. For each of these materials, research should address the wide range of PFASs present in AFFF-impacted waters, including short-chained PFAAs and potential precursor compounds. Treatment train approaches may be required to treat the wide range of PFASs present in the regeneration/concentrate streams. In addition, particularly for treatment processes that rely on transformation of PFASs within these concentrated waste streams, transformation products must be identified and defluorination should be confirmed. Other reaction byproducts not involving PFASs (e.g., perchlorate formation from chloride present in the waste stream) should be carefully identified. Treatment longevity (with respect to reaction rates or sorbent capacity) should be understood, and the overall energy requirements for treating concentrated waste streams should be determined. Finally, assessments of the life cycle costs and environmental impacts of residual streams and management approaches is also of interest. The concentrated waste materials of interest are as follows.

3.3.3.1 GAC or Other Carbon-Based Sorbents. Improved understanding is needed regarding PFAS fate during thermal reactivation of GAC and other carbon-based sorbents. The extent to which reactivation impacts the long-term effectiveness of the sorbent also requires further study, as does the extent to which any hazardous or toxic products are formed and subsequently released from the sorbent. In addition, there is a need to develop novel or modified sorbents that facilitate less intensive reactivation, or to develop less energy intensive reactivation approaches that can be implemented on-site. Lastly, development of improved, higher-capacity adsorbents may be important for advancing the capability of concentrate PFAS wastes onto smaller volumes of media.

3.3.3.2 Ion Exchange Resins. Improved approaches may be needed to treat waters effectively using ion exchange resins, while also reducing the effort needed for resin regeneration or reactivation. Current regeneration approaches for ion exchange resins involve accumulating PFAS-rich waste streams containing brine and/or alcohol. Technologies to cost-effectively transform and/or remove PFASs from these regeneration waste streams so that the regeneration fluids can be reused are desired. Such technologies might involve development of alternative regeneration fluids and methods, and/or novel or improved technologies for transforming or separating PFASs from the regeneration fluid. Coupled with this may be the need for alternate or modified resins that are designed to facilitate regeneration. How the regeneration process impacts the long term effectiveness of the ion exchange resin with respect to PFAS removal from water also needs to be carefully considered. Development of improved single-use ion exchange resins also may be important for advancing the capability of concentrate PFAS wastes onto smaller volumes of media.

3.3.3.3 Concentrates from Membrane Filtration Processes. Membrane filtration processes, such as RO or NF, generate a high salinity/high PFAS concentration waste stream that requires further

management. A treatment approach for this concentrate is needed that ideally can be performed on site, with zero or minimal off-site disposal of PFAS mass and volume. Strategies might include reducing the volume of the PFAS concentrate stream or developing improved methods to treat PFAS in the concentrate stream. Separation or transformation technologies could be used to treat PFAS in the concentrate stream. Elevated salt levels in the concentrate should be considered when developing a treatment approach, as these may either inhibit or facilitate a specific treatment approach.

3.3.4 Reductive Technologies (High Priority)

The vast majority of technologies being studied or tested for PFAS transformation (defluorination) involve oxidative treatment. Exceptions are the use of zerovalent metals (ER-2426) and generation of hydrated electrons via the UV-sulfite process (ER-2424). Oxidative approaches may be less effective for PFASs than for PFCAs (e.g., Park et al., 2016), while reductive approaches may be more effective for PFASs (Park et al., 2009; Arvaniti et al., 2015).

In addition, oxidative treatment approaches for PFAS often produce undesirable reaction byproducts such as perchlorate and shorter-chain PFAAs. In situ oxidative approaches also may impact soil organic carbon, thereby diminishing the naturally occurring retardation of PFAS in aquifers. Thus, identification and development of reductive PFAS transformation technologies are of interest, either as in situ or ex situ technologies. Compared with oxidative transformation of PFASs, particularly PFAAs, relatively little is known regarding reductive pathways and kinetics. Possibilities for reductive treatment technologies include, but are not limited to:

- Cathodic electrochemical treatment, including cathodically generated coagulants (electrocoagulation)
- Catalysts/zerovalent metals
- Hydrated electrons
- Treatment trains involving sequences of reductive, oxidative, and/or separation processes

Transformation pathways for reductive processes must be clearly understood, as well as how the reductive technology impacts water chemistry and other co-contaminants that might be present. The longevity and energy consumption associated with reductive technologies also need to be assessed to determine the overall potential for implementation.

3.4 Sampling and Analytical Procedures

Three critical priority needs were identified related to the development and demonstration of standardized sampling and analytical procedures for PFASs. These are summarized below and described in the following subsections.

- Critical priority research needs
 - Develop and demonstrate standardized sampling procedures for PFASs
 - Develop and validate PFAS analytical methods
 - Develop forensic methods for source tracking and allocation of emerging contaminants

3.4.1 Develop and Demonstrate Standardized Sampling Procedures for PFASs (Critical Priority)

The development and demonstration of standardized, fully validated procedures for the field sampling of environmental waters (groundwater, surface water, storm water run-off), AFFF products, soils and sediments, biological tissues, and vegetation media for analyses of 24 PFASs (USEPA, 2017) and total PFASs has been identified as a critical priority research need. Currently, no single document or source exists for these procedures.

The EPA's Office of Research and Development is currently leading an effort to create and validate sampling procedures for environmental water and sediment/soil media. However, the timeframe for full validation of sampling procedures is unknown and their applicability to DoD projects is yet to be determined. Environmental programs within the EPA and DoD are utilizing previous PFAS sampling experience, current research conclusions, and the current state of knowledge of analyte properties and behavior. Although sampling guidance documents are publicly available, they contain a limited amount of information, and often include limitations on applicable sampling supplies and equipment that are not based on scientific evidence and may complicate field sampling plans and increase sampling costs. Further, existing guidance does not reflect the fact that more precautions may be needed when sampling certain media (e.g., drinking water) or when concentrations of interest are expected to be low than in other instances (e.g., when working in a contaminated plume). Once developed, any guidance should be validated through demonstration at various types of EPA and DoD sites.

Examples of specific research and demonstration needs related to standardized sampling procedures include, but are not limited to, the following:

- Development of sampling techniques to evaluate soil and water columns.
- Evaluation of the potential biases when using different sampling supplies and equipment.
- Research on the most appropriate sample bottles for each matrix (environmental waters, soil/sediment, animal and vegetation) to eliminate/minimize potentially irreversible bias, and the associated holding times and preservation requirements when sampling for the EPA's list of 24 PFAS analytes or for total PFASs.
- Research and development of decontamination procedures for use at both minimally and highly contaminated sites.
- Validation of sample procedures through demonstration at DoD/EPA sites with varying levels of PFAS contamination, geological properties, and co-contaminants.
- Evaluation of possible media to be used for passive samplers and their performance.

3.4.2 Develop and Validate Analytical Methods for PFASs (Critical Priority)

The development and eventual demonstration of standardized, fully validated procedures for the analysis of environmental waters (groundwater, surface water, stormwater run-off), AFFF products, soil/sediment, biological tissue, and vegetation for determination of concentrations of 24 PFASs and total PFAS is a critical need. Currently, there are no EPA published procedures for PFAS analyses in media other than drinking water. Commercial laboratories offer analysis of these media using in-house developed method that are based on EPA Method 537.

Modifications include, but are not limited to, the addition of sample preparation steps to accommodate solids, clean-up process to eliminate matrix interference, and changes to or elimination of quality controls, and changes to calibration and calibration verification techniques. Since the modifications made are not consistent among laboratories, the resulting data between laboratories can be highly variable. In an attempt to minimize this variability, the DoD has implemented requirements (DoD Quality Systems Manual for Environmental Laboratories, Version 5.1) for these modified Method 537 methods for environmental restoration projects. Regulatory acceptance of such performance-based methods is much more difficult than a standardized, fully validated published method.

The USEPA Office of Research and Development (ORD) is currently leading an effort to create and validate analytical procedures for environmental water and sediment/soil. However, the timeframe for full validation of these methods is unknown, and their applicability to DoD projects is not yet clear, given their limitations with regard to achievable quantitation limits.

The specific needs include, but are not limited to the following

3.4.2.1 Organofluorine Methods. Development and demonstration of procedures to assess the total organofluorine in environmental waters and soil and sediment has been identified as a critical priority research and demonstration need. Such procedures are needed to help assess transformation and distribution of PFASs, as well as to assess various aspects of PFAS remediation techniques. Currently there is no standardized total organofluorine analytical procedure readily available that has been fully validated and the limitations of such procedures are yet to be determined.

3.4.2.2 Rapid Field Screening Methods. Development and demonstration of rapid field screening procedures for PFASs would prove useful when determining the extent of a plume, as multiple samples could be collected and analyzed in the field quickly so that the results could be used to guide the placement of subsequent samples. Even use of rapid field assays that yield semi-quantitative screening values will be useful to reduce the site investigation and remedial decision making timeframes. Certain methodologies that can be relevant, but not limited to include:

- Colorimetric technique
- Field NMR borehole probes
- Mobile LC/MS/MS tests
- Visual foam indicators
- Total Oxidizable Precursor (TOP) Assay/Particle Induced Gamma-Ray Emission (PIGE) analysis

Eventually, rapid field screening methods could reduce costs by eliminating some fixed laboratory analyses.

3.4.2.3 Additional Analytical and Sampling Needs. Other specific research needs related to sampling and analysis include:

- Evaluate subsampling techniques to determine the process by which the subsample provides results that are the most representative of the entire sample collected.
- Evaluate extraction techniques to determine which produce the most accurate and precise quantitation.
- Evaluate techniques to eliminate matrix interference.
- Evaluate techniques to achieve the lowest limit of quantitation possible when analyzing AFFF formulations and samples containing high concentrations of PFASs while achieving the required precision and accuracy.
- Validate sample preparation and analytical procedures per DoD Quality Systems Manual requirements for non-standard method validation.
- Demonstrate sample preparation and analytical procedures for each media through multi-laboratory validation.
- Compare analytical results using the procedures developed to determine individual PFASs and total PFAS mass.
- Determine the range of PFASs that is included in the total PFAS determination.
- Demonstrate total PFAS analysis procedures at various EPA/DoD site locations.
- Evaluate techniques that could be used to ensure precision and accuracy of total PFAS analytical procedures.
- Evaluate rapid field screening procedures against individual PFASs and total PFAS procedure results.
- Demonstrate rapid field screening procedures at various EPA/DoD site locations.

3.4.3 Develop Forensic Methods for Source Tracking and Allocation of Emerging Contaminants (High Priority)

Demonstrated analytical forensic techniques to differentiate between DoD and non-DoD sources of PFASs are needed. More specifically, the ability to discriminate AFFF from non-AFFF sources would be useful not just in source allocation, but also in delineating plumes and ascertaining when and where AFFF-derived polyfluorinated PFAA precursors are present. Forensics also could provide insight into the time period when the contaminants were introduced to the environment. Different AFFF mixtures were used over time and the presence/absence of certain compounds could be used to date a plume.

As noted earlier, PFASs are unique in the multiple potentially important sources of human and ecological exposure, but also because of the complex chemistry of polyfluorinated PFAA precursors (particularly in AFFF). Though the current regulatory framework is focused primarily on PFOS, PFOA, and to some extent perfluorobutane sulfonate (PFBS), the potential formation of these chemicals (and other PFAAs) will also likely be a key determinant in the successful demonstration of PFAS remediation technologies and risk mitigation.

For these reasons, there is a critical need for forensic tools for PFASs that specifically address the issue of PFAA precursors. Though analysis of individual PFAAs and/or ratios of PFAAs as a means of discerning PFAS sources is attractive, given the complexity of the sources, it is presently unclear as to whether such a simple approach would yield meaningful and defensible results. At

the same time, it is unlikely that pure analytical standards for the myriad of PFASs present in AFFF (as well as their transformation products) will be available in the near future. Advances in forensic analysis are thus needed that do not rely on the availability of a broad suite of analytical standards. Such advances are likely to evolve from either high resolution mass spectrometry (HRMS; i.e., LC coupled to quadrupole time-of-flight MS or orbitrap MS) and/or compound specific isotope analysis (CSIA). The latter has been particularly useful in evaluating the extent of natural attenuation of contaminants at DoD sites, though it is presently unclear as to whether the different sources of PFASs will exhibit different isotopic signatures. Nevertheless, an evaluation of the potential application of CSIA to PFASs is warranted as a potential means to ascribe liability.

As HRMS is a more broadly available technology and is already being used for SERDP and ESTCP PFAS research, this also could provide a more viable path for the development and validation of PFAS forensic tools. Specific HRMS-based activities that would aid tool development are:

- An HRMS spectral library of PFASs, which would need to be HRMS platform independent and would need to include both AFFF-derived PFASs as well as PFASs derived from other sources (i.e., consumer products).
- A validated “map” of the chemical pathways to specific PFASs. Ideally, this would be linked to field-validated (or at least laboratory validated) information on the relative rates of transformation (abiotic and biotic) along these pathways (such as data collected under the needs identified in Section 3.1.1).
- A framework for assessing the relative mass contribution of PFAA precursors in both soil and water. While not necessarily directly linked to source allocation, such a framework will enable RPMs to fully assess the nature and extent of PFAS contamination at impacted sites.

4.0 DEMONSTRATION NEEDS

This section presents the demonstration needs that were identified during the workshop. These relate primarily to treatment and to measurement and prediction – techniques that can be used to improve the CSM, evaluate potential remedial strategies, and effectively predict and monitor remedy performance. Within each category, demonstration needs that were determined to be critical priority (most urgent) are presented first, followed by high priority needs. The order in which the needs are listed does not imply any further prioritization.

4.1 Treatment Technology Demonstrations

During the workshop, working groups identified four demonstration needs, two that were designated as critical priority and two that were designated as high priority. Each topic relates not just to the removal or destruction of PFOS, PFOA and other analogous PFAAs of different carbon chain lengths, but also to the removal or destruction of polyfluorinated compounds that are known PFAA precursors (i.e., they have been shown to transform to PFOA and other persistent PFAAs). The demonstration are listed below and described in the following subsections.

- Critical priority demonstration needs
 - Demonstrate the effectiveness and sustainability of thermal destruction technologies for soils and spent GAC and resins
 - Validate destruction technologies and their applicability to treat concentrated PFAS waste streams
- High priority demonstration needs
 - Side-by-side comparisons of treatment technologies
 - In situ and ex situ PFAS treatment

4.1.1 Demonstrate the Effectiveness and Sustainability of Thermal Destruction Technologies for Soils and Spent GAC and Resins (Critical Priority)

Working group participants identified a need to assess the effectiveness and sustainability of thermal destruction technologies for PFASs in soils and other residuals, including spent GAC and spent ion exchange resins. This need was identified as a critical priority to inform management options and decision making at AFFF sites.

Off-site incineration is the only acceptable and proven technology that destroys PFASs in soil, water, liquid, and remediation wastes generated from PFAS contaminated sites. Currently, spent GAC is returned to the GAC facility for thermal reactivation and spent regeneration waste from regenerating ion exchange resin is sent off-site for incineration. Both can be shipped significant distances. Having local treatment options for incineration or regeneration could save significant transportation costs and carbon emissions. A field demonstration could address treatment effectiveness, operating parameters, air permitting requirements and other practical considerations. Stability of heating temperature and complete destruction of these off-site thermal options have not been evaluated, although any residual PFASs can generate potential ongoing liabilities after final disposal of the treated materials.

On-site destructive technologies involving thermal components (e.g., on-site thermal treatment, sonolysis) have the potential to completely destroy on-site generated wastes but have not been demonstrated. Incomplete regeneration and thermal destruction may result in residual PFASs or PFAS-like products in vapors or sorbed to the regenerated GAC.

This demonstration is intended to evaluate the effectiveness and sustainability of on-site and off-site PFAS destruction technologies. A mass balance capturing PFASs from inlet (different environmental media) and outlet (off-gas, dusts, reactivated GAC) to document the completeness of PFAS destruction should be considered. PFASs and daughter products should be evaluated, and the minimum temperatures sufficient for complete destruction should be documented.

Thermal destruction technologies also may be cost-effective for treating soils contaminated with PFASs. Treatment standards vary for the reuse or management of local Subtitle D disposal of waste soils. Guidelines for assessing the feasibility and cost-effectiveness of soil treatment versus soil reuse or disposal are needed to streamline site managers' decisions to manage contaminated soils. As with the management of spent GAC and resins, options for soil treatment or reuse may be more sustainable than disposal, depending on site-specific green and sustainable remediation considerations. An assessment of the sustainability of different management options for soil treatment, reuse or landfill disposal also is needed.

4.1.2 Validate Destruction Technologies and their Applicability to Treat Concentrated PFAS Waste Streams (Critical Priority)

To date, the most widely applied approach for treatment of PFAS-contaminated sites is ex situ GAC adsorption. SERDP, ESTCP and other DoD programs have supported research and development of innovative ex situ treatment technologies (e.g., ion exchange, nanofiltration, reverse osmosis). Although separation of PFOS, PFOA and other PFAS from contaminated water has been demonstrated to some extent with these technologies, each process also generates one or more residual or concentrate streams that require careful management.

For example, regeneration of spent ion exchange resins produces a concentrate stream enriched in PFAS, co-contaminants, salts, and possibly co-solvents. Incineration or direct disposal of such concentrate streams in a hazardous waste landfill can be both cost-prohibitive and unsustainable. Likewise, thermal regeneration and re-use of GAC is a common practice, but concerns have been raised about residual contaminants and other potentially toxic byproducts that remain in the reactivated material and may be released into water when put back into service.

These and other issues highlight the critical needs for development of cost-effective and sustainable approaches for managing residuals and concentrate streams from ex situ treatment technologies to ensure that remedial treatment objectives are met and that DoD liabilities are eliminated. Research is needed on the fate and behavior of PFAS and co-contaminants during the production and processing of residual product streams. New technologies for concentrate management of interest include those designed to mineralize PFAS and co-contaminants, recycle important regenerant components (e.g., salts, solvents) and/or minimize waste volumes. Assessment of the life cycle costs and environmental impacts of residual streams and competing management approaches is also of interest.

This demonstration topic is similar to a critical priority research need to develop on-site technologies for concentrated PFAS waste streams (Section 3.3.3). Both the research and validation needs were prioritized as critical over the next 1 to 3 years. Following the development of advanced technologies for concentrated waste streams, as outlined in Section 3.3.3, field validation will be needed. There are multiple types of concentrated waste streams, including, but not limited to, GAC regeneration solutions, ion exchange regeneration solutions, high pressure filtration concentrates and fluids extracted from AFFF spills or other release areas. A mass balance approach is needed to assess treatment byproducts and predict the fate of PFAS under relevant field conditions. Advanced technologies could be developed for treating waste streams on site, but they would have to be shown to be more cost-effective than off-site treatment of concentrated PFAS wastes.

Field validation of existing technologies for PFAS destruction from waste streams and other waste media also is also needed. Examples of these technologies include thermal oxidation, electrochemical oxidation, and chemical reduction. Technologies and approaches are needed to address chemical reduction of PFOS-impacted groundwater at DoD sites. Reductive approaches have shown some promise at the laboratory scale. Additional information is needed to assess the readiness of PFOS destructive technologies at the bench and field scales. Field demonstrations would gauge the ability of these technologies to treat concentrated PFAS waste and technology cost-effectiveness compared with other options.

4.1.3 Side-by-Side Comparisons of Treatment Technologies (High Priority)

Numerous technologies are being developed for the remediation of PFAS-contaminated sites through SERDP and ESTCP or other funding sources. Because the technologies have been piloted or demonstrated at field sites with different characteristics (e.g., PFAS sources, water chemistry or hydrogeology), it is difficult to make cost and performance comparisons among methods. Furthermore, there is often a perception among potential users that technology developers seek to feature their remedial solutions in the best possible light. To facilitate efficient technology selection and to identify the most promising remedial solutions for different types of sites, side-by-side comparisons should be conducted of promising treatment technologies. Comparisons could involve the following:

- Ex situ groundwater treatment (e.g., GAC, ion-exchange, membrane filtration)
- Treatment of concentrates from RO or ion exchange systems (e.g., electrochemistry, incineration, photochemical bisulfite)
- Methods to enhance PFAS extraction from soils (e.g., soil washing with different reagents)

Comparative analyses should include costs, ability to achieve stringent guidelines, and ability to remove PFAA precursors and compounds beyond PFOS and PFOA. If possible, demonstration sites should include common PFAS co-contaminants and conditions typical of most AFFF sites.

In addition, it may be useful to compile existing treatment performance data in a white paper prior to developing the performance objectives for these demonstrations. These performance objectives should be as uniform as possible, and be applicable across multiple technologies, to facilitate direct

comparisons of the applicability and cost-benefit of one technology relative to another at a given site.

4.1.4 In Situ and Ex Situ PFAS Treatment (High Priority)

Long-term assessment, treatment optimization and treatment validation are needed for the wide range of PFASs present at AFFF sites. Development and validation of novel treatment and/or combined treatment technologies are needed to address PFASs (including PFAA precursors) in soil and groundwater. Both source areas and downgradient plumes should be considered. Treatment in the presence of co-contaminants and under field-relevant conditions is needed. Transformation pathways and defluorination, or stability of PFAS sequestration, should be clearly demonstrated. There is a need to determine and compare the cost and performance of established ex situ and in situ technologies based on the current state of knowledge.

Potential technologies and advances in remediation technologies include barrier walls, coagulants, in situ thermal remediation, plasma treatment, sonolysis, and a variety of concentration technologies including membranes, GAC, and ion exchange. Developing and articulating standards for validating the success of technologies using environmentally relevant concentrations and compounds (adequate and quality controls, mass balances, co-contaminants, dissolved organic matter, etc.) is a promising topic for demonstration. Another example of a demonstration need to improve PFAS treatment is the development and demonstration of better sorbent and hybrid technologies with concentrate management methods.

4.2 Measurement and Prediction

Improved measurements and predictive models for PFAS contamination are needed to characterize risks. The greatest needs identified are for 1) better measurements of PFAS mass flux from source areas and 2) a validated fate and transport model for PFASs in the subsurface. These needs are described in the following subsections.

4.2.1 Measurement of PFAS Mass Flux Relative to Source Mass in the Vadose Zone and in Groundwater (Critical Priority)

Mass flux measurements can improve CSMs, improve understanding of PFAS concentration data, and support communication of technical information to technical and non-technical audiences. Mass flux measurements for a PFAS release are complicated by the mixture of per- and poly-fluorinated chemicals, with individual compounds exhibiting differing behaviors in the subsurface, and the range of subsurface hydrogeological conditions.

A combination of tools and methods have been promoted for mass flux measurements including flux meters, pump tests, and transects based on isocontours (ITRC, 2010). A mass flux measurement approach using an appropriate combination of tools/methods for PFASs is needed. Applied research should address the strengths and limitations of mass flux measurement methodologies for PFASs, the data requirements for each (including data quality), resource requirements, and applications of the approach to the various sub-classes of PFASs. Additionally, research should identify hydrogeological conditions that significantly affect vadose zone and groundwater fluxes.

Primary PFASs of interest are those that are currently subject to state and federal regulations as well as PFAA precursors that could make significant contributions to the regulated chemical mass.

4.2.2 Demonstration and Validation of a Fate and Transport Model for PFASs (High Priority)

PFASs are released to the environment in AFFF as mixtures of many compounds, and the fate and transport of these substances is highly complex. As mentioned earlier, a predictive model of PFAS fate and transport in the subsurface needs to be developed (Section 3.1.1). This model should initially focus on PFAAs and a few PFAA precursors that may be transformed into the more persistent PFAAs currently regulated or under regulatory review. Developing a unified groundwater fate and transport model is a complex undertaking that must not only consider the various chemical forms in foam mixtures but also transformations that occur in the subsurface that are dependent on site specific conditions.

Following model development, demonstration and validation under field conditions will be needed before the model can be used with confidence. A validated model would be very helpful for making risk management decisions at AFFF sites. Model validation efforts should include model calibration, identification of sensitive parameters, and an uncertainty analysis to assist users in interpreting modeling results.

5.0 TECHNOLOGY TRANSFER NEEDS

SERDP and ESTCP have an established technology transfer program that includes, but is not limited to, a webinar series, on-demand videos, environmental remediation wiki articles, conferences and workshops, software, protocols, user manuals, guidance documents, and technical fact sheets and summary reports. SERDP and ESTCP also have published monographs on several technical topics and have worked in collaboration with environmental experts, Federal agencies and the Interstate Technology and Regulatory Council (ITRC) to disseminate practical and trustworthy information. Technology transfer needs identified in this section are expected to dovetail with or expand upon existing approaches and partnerships.

5.1 Technology Transfer White Paper (Critical Priority)

Workshop participants recommended preparing a white paper presenting lines of evidence for demonstrating technology success. Current Federal contracting practice is to define the requirements and inform the contractor how they will be evaluated. To assess the effectiveness of proposed remediation technologies, clearly defined metrics of success are necessary. A white paper could be developed that defines these metrics for treatment of PFASs. Metrics could include criteria specific to PFAS treatment including, for example, the disappearance of targeted PFAS species which correlate with fluorine and the appearance of transformation products. The analysis of fluorine is particularly important and an assessment of these methods also could be considered in the white paper. Quality assurance objectives and performance criteria should be developed for each stage of the demonstration. This paper would provide the metrics that define a successful demonstration. The white paper should consider lessons learned from previous demonstrations, and input from various stakeholders should be requested and considered.

Furthermore, the white paper would review potential remediation technologies and summarize lessons learned for each, based on previous technology testing at the laboratory scale and field demonstrations. The white paper also would describe potential performance objectives and metrics that could be used to assess the performance of different treatment technologies.

This technology transfer topic may be relevant to other environmental remediation projects and contaminants beyond PFASs.

The transfer of the information resulting from the research and development of standardized, fully validated procedures for the sampling and analysis (both fixed laboratory and rapid field screening) of environmental waters, soil/sediment, animal tissue, and vegetation used to determine concentrations of 24 PFASs, as well as total PFAS concentration has been identified as a critical priority technology transfer need. Technology transfer work is needed to develop the following:

- Summary documents describing the advantages and limitations of the standardized field sampling, analytical procedures, and rapid field screening procedures
- On-line workshops for sampling personnel and RPMs on standardized sampling and rapid field screening procedures. Workshops and subsequent follow-up must a question and answer process.

- On-line workshops for commercial and government laboratories and government agencies on standardized analytical procedures. Workshops and subsequent follow-up must be a question and answer process.
- Presentations on standardized sampling and analysis procedures for PFASs to be given at applicable conferences and workshops.
- Frequently Asked Questions (FAQ) documents which are derived from on-line workshops and conference feedback.

5.2 Technology Transfer Efforts (High Priority)

Numerous technical and regulatory developments are relevant for PFASs and are ready for technology transfer. These developments can improve understanding of PFAS analytical methods, site characterization, health effects and risk assessment practices, risk management, and remediation. For example, user-friendly summaries of sampling and analytical methods and forensic techniques for characterizing PFASs would be valuable for the environmental remediation industry.

Other topics of interest include factors affecting PFAS fate and transport, a review of ecotoxicity data, criteria for assessing the performance of PFAS treatment technologies, and standardized performance data and costs. The working groups elaborated on potential content as separate research needs.

The focus of this technology transfer need is to identify a variety of communication avenues and formats to reach and expand SERDP and ESTCP's target audiences. By adopting a broad range of technology transfer methods, existing information can be better transferred to users. Examples of technology transfer methods to be considered as part of this effort include the following:

- Developing a PFAS-specific online course, perhaps in partnership with Coursera or another existing Massive Open Online Course (MOOC).
- Creating and posting PFAS-specific videos onto a YouTube channel.
- Hosting an international workshop and/or working group on PFASs.
- Developing and presenting a webinar or invited presentation to groups that are currently interested in PFASs. Examples include the ITRC team and/or National Association of Remedial Project Managers (NARPM)
- Writing white papers, fact sheets, answers to FAQs, and other practical and trustworthy sources of information.
- Publishing manuscripts summarizing research and demonstration findings that are relevant to ecological risk assessment

Several of these methods have already been used in SERDP and ESTCP projects (e.g., PFAS presentations have already been featured on the SERDP and ESTCP webinar series, PFAS articles are posted on the ER wiki website, answers to FAQs on PFAS are under development). Keeping these materials up-to-date and linking or referring to existing synopses where possible will leverage past technology transfer efforts and expand their audiences.

5.3 Risk Communication Tools (High Priority)

Technical, policy, and management issues addressing PFAS releases to the environment are complex due to the ubiquitous nature of PFASs in many commercially available products. Some forms of PFASs can be found in all environmental media where they are generally very mobile among media types and between living organisms and environmental media.

One of the most difficult challenges is communicating complex technical information to various stakeholder audiences outside of the scientific/engineering disciplines involved in basic and applied PFAS research and development. Risk communication should be science-based, providing risk benefit information in a context adapted to intended audience needs. Audiences include site managers, regulators, the press, and the general public.

There is a need for risk communication tools tailored to the needs of target audiences in a variety of formats to optimize information exchange. Formats include hardcopy manuals/handbooks available in pdf format through the internet, websites, web-based tutorials, and social media.

5.4 Granular Activated Carbon Status Paper (High Priority)

The most widely-used technology for treating PFASs in groundwater or other water supplies is GAC. However, existing data from GAC systems currently in operation have not yet been compiled or made widely available. There is a need to compile cost and performance data of full-scale GAC treatment systems as well as design parameters (e.g., isotherm data generated in the laboratory). GAC is the default technology at military sites where plume migration is an issue. Most GAC systems are designed to treat for PFOS and PFOA. Little is known about the efficacy of GAC at removing other compounds of interest including PFAA precursors, short-chain PFAAs, and other PFASs.

A white paper evaluating GAC advantages and limitations is needed. Such an effort would include a careful review of data from operating GAC systems at military installations, together with lessons learned from these systems and potential optimization opportunities to maximize cost effectiveness. Key findings would be communicated in a white paper or a similarly user-friendly and readily accessible format.

6.0 SUMMARY AND CONCLUSIONS

Contamination of soils and waters by PFOS and PFOA, largely resulting from the use of AFFF formulations, represents a significant environmental liability for the DoD, with thousands of sites that require investigation and potential remediation. The regulatory requirements for PFAS contaminated soils and groundwaters are still evolving, with the current HALs being relatively low (70 ng/L for PFOS and PFOA, individually or as the sum of the two). PFASs also are resistant to common treatment technologies, so remediation generally requires ex situ treatment, usually involving capture on GAC or other media and off-site regeneration. As a result, management of PFAS-contaminated sites can be very costly.

DoD has begun an aggressive effort to characterize and ultimately remediate its PFAS-impacted sites. However, the scientific understanding of PFASs is in an early stage of development, with significant uncertainties that complicate this effort. This SERDP and ESTCP workshop was convened to improve the management of PFAS contamination at DoD's facilities. The workshop objectives were to: (1) review the current state of the science regarding PFAS contamination in general, (2) evaluate the current and potential characterization and remediation technologies, and (3) identify opportunities to improve remediation performance and reduce site management costs. The workshop identified and prioritized several promising research, demonstration, and technology transfer opportunities.

The most pressing R&D needs include: 1) a better understanding of PFAS fate and transport in the subsurface; 2) basic research on PFAS toxicity, bioavailability and biomagnification; 3) less costly and more effective treatment technologies, including methods to treat concentrated PFAS wastes on-site and off-site; 4) standardized sampling and analytical procedures; and 5) forensic methods to identify sources and characterize groundwater plumes.

The key demonstration and validation needs included: 1) demonstrations of promising treatment technologies, including technologies to treat concentrated wastes and both in situ and ex situ PFAS remediation strategies; 2) measurements of mass flux and source depletion, particularly from the vadose zone to groundwater; 3) improved tools for field assessment and rapid screening; and 4) validation of PFAS fate and transport models.

The critical technology transfer needs identified were: 1) preparation of a white paper reviewing the current state of remediation technologies and defining appropriate metrics for PFAS treatment success for rapid dissemination of state-of-the-art knowledge to stakeholders and practitioners; 2) development of a guidance document on standardized sampling and analysis procedures for PFASs; and 3) development of effective risk communication tools for stakeholders affected by PFAS contamination at DoD sites.

The scientific community is still in the early stages of development of the underlying science regarding PFAS contamination, so the recommendations from this workshop will require several years of intensive work, with careful thought to the sequencing of research and demonstration efforts. However, given the magnitude of the potential problems associated with PFAS contamination at DoD sites and the high costs of investigations and remediation, the return on investments in research and demonstrations in this area are likely to be significant.

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APPENDIX A

AGENDA



Workshop on Research and Development Needs for Management of DoD's PFAS Contaminated Sites

May 2 – 3, 2017
Washington Navy Yard
Washington, DC 20374

TUESDAY, MAY 2, 2017					
0830	Registration, Coffee/Tea Service & Poster Setup				
0900	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Welcome and Introduction Workshop Objectives and Structure</td> <td style="text-align: center;">Andrea Leeson SERDP and ESTCP</td> </tr> </table>	Welcome and Introduction Workshop Objectives and Structure	Andrea Leeson SERDP and ESTCP		
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0910	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">OSD Policy on PFOS and PFOA at DoD Sites</td> <td style="text-align: center;">Maureen Sullivan Deputy Assistant Secretary of Defense for Environment, Safety & Occupational Health</td> </tr> </table>	OSD Policy on PFOS and PFOA at DoD Sites	Maureen Sullivan Deputy Assistant Secretary of Defense for Environment, Safety & Occupational Health		
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0930	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">SERDP and ESTCP PFOS and PFOA Research and Development</td> <td style="text-align: center;"> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Andrea Leeson SERDP/ESTCP</td> <td style="width: 50%;">Hans Stroo Stroo Consulting</td> </tr> </table> </td> </tr> </table>	SERDP and ESTCP PFOS and PFOA Research and Development	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Andrea Leeson SERDP/ESTCP</td> <td style="width: 50%;">Hans Stroo Stroo Consulting</td> </tr> </table>	Andrea Leeson SERDP/ESTCP	Hans Stroo Stroo Consulting
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0945	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Air Force PFOS and PFOA Contaminated Site Management Issues</td> <td style="text-align: center;">Hunter Anderson U.S. Air Force</td> </tr> </table>	Air Force PFOS and PFOA Contaminated Site Management Issues	Hunter Anderson U.S. Air Force		
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1010	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Navy PFOS and PFOA Contaminated Site Management Issues</td> <td style="text-align: center;">Gunarti Coghlan U.S. Navy</td> </tr> </table>	Navy PFOS and PFOA Contaminated Site Management Issues	Gunarti Coghlan U.S. Navy		
Navy PFOS and PFOA Contaminated Site Management Issues	Gunarti Coghlan U.S. Navy				
1035	Coffee Break				
1050	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Army PFOS and PFOA Contaminated Site Management Issues</td> <td style="text-align: center;">Malcolm Garg Army Environmental Programs</td> </tr> </table>	Army PFOS and PFOA Contaminated Site Management Issues	Malcolm Garg Army Environmental Programs		
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1115	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">U.S. EPA PFAS Contaminated Site Management Issues</td> <td style="text-align: center;">Marc Mills U.S. EPA</td> </tr> </table>	U.S. EPA PFAS Contaminated Site Management Issues	Marc Mills U.S. EPA		
U.S. EPA PFAS Contaminated Site Management Issues	Marc Mills U.S. EPA				
1140	Lunch & Poster Session				
1230	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;"> Breakout Session I Discussions <ul style="list-style-type: none"> • Breakout Session Charge </td> <td style="text-align: center;">Breakout Groups</td> </tr> </table>	Breakout Session I Discussions <ul style="list-style-type: none"> • Breakout Session Charge 	Breakout Groups		
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1430	Refreshment Break				
1445	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Breakout Session I Discussions (Continued)</td> <td style="text-align: center;">Breakout Groups</td> </tr> </table>	Breakout Session I Discussions (Continued)	Breakout Groups		
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1645	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 70%;">Recap of Day/Overview for Next Day</td> <td style="text-align: center;">Andrea Leeson SERDP and ESTCP</td> </tr> </table>	Recap of Day/Overview for Next Day	Andrea Leeson SERDP and ESTCP		
Recap of Day/Overview for Next Day	Andrea Leeson SERDP and ESTCP				
1700	Meeting Adjourn				



WEDNESDAY, MAY 3, 2017		
0830	Coffee/Tea Service	
0900	Report from Breakout Session I	Breakout Session Chairs
1030	Coffee Break	
1045	Breakout Session II Discussions	Breakout Groups
1230	Lunch & Poster Session	
1330	Breakout Session II Discussions (Continued)	Breakout Groups
1500	Refreshment Break	
1530	Reports from Breakout Session II	Breakout Session Chairs
1655	Closing Summary and Remarks	Andrea Leeson SERDP and ESTCP
1700	Workshop Adjourn	

APPENDIX B
ATTENDEE LIST

ATTENDEES

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John Tesner
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Patrick Timm
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Office-Northern

Janice Wiley
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Dave Woodward
AMEC Foster Wheeler

Macrina Xavier
Noblis

Ginny Yingling
Minnesota Department of Health