### Research Initiatives and the Challenges of Technical and Risk Assessment

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## **DoD's Environmental Technology Programs**



#### **Science and Technology**

- Statutory Program Established 1991
- DoD, DOE, EPA Partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management



#### **Demonstration and Validation**

- Demonstrate Innovative Cost-Effective Environmental and Energy Technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology Transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion



### Environmental Drivers: Reduction of Current and Future Liability

#### **Contamination from Past Practices**



- Groundwater, Soils and Sediments
- Large UXO Liability
- Emerging Contaminants
  - ♦ PFASs
  - 1,4-dioxane
  - Perchlorate

#### Pollution Prevention to Control Life Cycle Costs



- Elimination of Pollutants and Hazardous Materials in Manufacturing, Maintenance, and Operations
- Achieve Compliance Through Pollution Prevention
- Develop and Assess Alternative Technologies



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#### Characterization of the Fate and Biotransformation of Fluorochemicals in AFFF-Contaminated Groundwater at Fire/Crash Testing Military Sites

#### Professor Jennifer A. Field - Oregon State University







#### Results

- Developed analytical tools, including methods for quantifying individual perfluoroalkyl substances (PFASs) as well as precursors
- Provided analytical advances for more complete characterization of aqueous film forming foam (AFFF)contaminated media
- Significantly improved understanding of the PFASs present at AFFF-contaminated sites

#### **Benefits**

- Identifying precursors will lead to a better understanding of the effectiveness of treatment technologies
- Biotransformation pathway of polyfluoroalkyl substances in fluorotelomer-based AFFF provides a framework for understanding the fate of the precursor and insight into the conditions that lead to high concentrations of persistent fluorotelomer sulfonates















#### FY18 Statement of Need Defining Knowledge Gaps in the Understanding of PFASs in the Subsurface

- Objective: Address specific knowledge gaps identified in the May 2017 PFAS Workshop. The knowledge gaps of interest are those that require collection and analysis of existing data on PFASs, not additional experimental work. Specific areas of interested are as follows:
  - Develop basis for an approach for assessing PFAS risks to TES.
  - Form the basis for future development of innovative on-site technologies for concentrated PFAS waste streams by summarizing characteristics of waste streams from common approaches as well as theorizing the waste composition of potential innovative approaches.
  - Define lines of evidence for assessing effectiveness of proposed remediation technologies based on the current state of the science. 11



# FY18 Statement of Need Defining Knowledge Gaps in the Understanding of PFASs in the Subsurface

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  - ♦ Develop basis for an approach for assessing PFAS risks to TES.

Four proposals selected; projects will be initiated this year with results within 12 – 24 months



### FY19 Statement of Need: Ecological Risk Characterization of PFASs in the Subsurface

- Objective: Improve our understanding of bioavailability, bioaccumulation & biomagnification of PFASs in the subsurface. Specifically:
  - Improved understanding of uptake & excretion rates of PFASs by organisms throughout the food web
  - Determine rate
     Proposals rcvd March 2018
     biover-trophic lev
     Final selections July 2018
     biotransformation of PFAA precursors
  - Identification of physical and geochemical factors affecting bioavailability of PFASs in sediments and soils.
  - Compare potency of PFASs in relation to chain length (C8 vs. C6 sulfonates), functional group (carboxylic acid vs. sulfonate), and varying levels of fluorination.
  - Assess PFAS bioaccumulation/biomagnification throughout a food web.







### **PFAS Workshop**

- In May 2017, SERDP and ESTCP sponsored a two-day workshop: Research and Development Needs for Management of DoD's PFAS Contaminated Sites to:
  - Review the current state of the science regarding PFAS contamination in general, and AFFF in particular
  - Evaluate current and potential characterization and remediation technologies
  - Prioritize research and demonstration opportunities that can improve remediation performance and officiency, and 28 Research, Demonstration and ultimately reduced Technology Transfer Needs Identified S.
  - Summarize findings in a workshop report.



### **PFAS Workshop – Major Findings**

- Fate and transport properties
- Bioavailability, biomagnification
- Toxicity
- Development of on-site technologies for concentrated PFAS waste streams
- PFAS forensics
- Sampling
- Treatment technology demonstrations
- Technology transfer needs



### FY18 Statement of Need: Improved **Understanding of PFAS Source Zones**

- Objective: Improve our understanding of PFASs in source zones resulting from the use of Aqueous Film Forming Foam (AFFF) formulations by the DoD. Proposed ollowing objectives:
  - Increase un areas (vad risk that PF
  - Developme zone prope
  - Investigate and the po attenuation
  - Fill key dat. in AFFF sour

- Funded five projects:
  - ER18-1204: Vadose zone (Schaefer, CDM Smith)
  - ER18-1259: Saturated phase (Field, **Oregon State**)
  - ER18-1389: Air/water Interface (SEED) (Silva, GSI)
  - ER18-1149: Predictive tools & decision support (Abriola, Tufts)
  - ER18-1280: Field sampling & assessment (Sunderland, Harvard)

FFF source zone eas) that affect the

ize the key source

dation mechanisms, br enhanced

transport of PFASs

 Develop analytical or mathematical tools to predict the fate and impacts of PFASs in source zones and the potential for continuing releases to groundwater plumes.



Projects									
Electrocata (ER2424; CDN	In situ coa (ER2425; M	In situ coagulents (ER2425; Minnesota)				luctive e)	Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)		
In situ chemical o bioremediatior contamina (ER2715; UC E	Electrolytic deg electrobiostimu contami (ER2718; Colo	Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)	
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex situ treatment train: & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially available regenerable resins Ex situ (1063; CSM)		sins, electrochemical Iltrasonic treatment for regenerant Ex situ (1027; Aptim)
Proof of Concept	(Ex situ/d	rinking water or pump	-and-	treat)					
Protein based adsorbents (1417; U.S. Army)	Elec adsorptic disch	Electrically enhanced ption onto AC, electrically scharge to regenerate (1395; NCSU)		ctrochemic oxidation 20; Univ of GA)	Mesopo organosilica Ex sit (1300; Wo	orous Cationic po sorbents (PANI) & po (PANI) & po (PPy) pc ooster) (1052; Un		olyaniline olypyrrole lymers iv of AZ)	Electrocoagulation (1278; AECOM)
Proof of Concept	(Investiga	tion Derived Waste)							
Advanced oxidation- reduction & membrane concentration (1 (1497; UC Riverside)		Modified SiC based catalysts (1513; Research Trian Institute)	Modified SiC based catalysts 513; Research Triangle Institute)		ductive ination by d electrons s; Miami)	Thermal treatment (1556; Aptim)		Nonthermal plasma technology (1570; Drexel)	
Combined Ele photo/electrochemical reduction (1595; UCLA)		Electron beam technol (1620; Texas A&M)	Electron beam technology (1620; Texas A&M) (1624;		na based atment Clarkson)	Hydrothermal technologies (1501; Colorado Scho of Mines)		Indirect thermal desorption with thermal oxidation I (1572; EA Engineering)	



Projects										
Electrocata (ER2424; CDN	In situ coa (ER2425; N	In situ coagulents (ER2425; Minnesota)			In situ chemical reductive defluorination (ER2426; Purdue)			Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)		
In situ chemical o bioremediatior contamina (ER2715; UC E	Electrolytic deg electrobiostimu contam (ER2718; Cole	Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)		
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex situ treatment train: & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially available regenerable resins Ex situ (1063; CSM)		esins, electrochemical Iltrasonic treatment for regenerant Ex situ (1027; Aptim)	
Proof of Concept	(Ex situ/d	inking water or pump	-and-	treat)						
Protein based adsorbents (1417; U.S. Army)	Elec adsorptic disch	ectrically enhanced tion onto AC, electrically charge to regenerate (1395; NCSU)		ctrochemic oxidation 20; Univ of GA)	Mesopo organosilica Ex sit (1300; Wo	orous Cationic poly sorbents (PANI) & poly itu (PPy) poly ooster) (1052; Univ		olyaniline olypyrrole olymers iv of AZ)	Electrocoagulation (1278; AECOM)	
Proof of Concept	(Investiga	tion Derived Waste)								
Advanced oxidation- reduction & membrane concentration (1 (1497; UC Riverside)		Modified SiiC based catalysts (1513; Research Triar Institute)	Modified SiiC based catalysts 513; Research Triangle Institute)		Reductive defluorination by hydrated electrons (1526; Miami)		Thermal treatment (1556; Aptim)		Nonthermal plasma technology (1570; Drexel)	
Combined El photo/electrochemical reduction (1595; UCLA)		Electron beam technol (1620; Texas A&M)	(1526) Electron beam technology (1620; Texas A&M) (1624; (		na based atment Clarkson)	Hydrothermal technologies (1501; Colorado Schoo of Mines)		ol (15	Indirect thermal desorption with thermal oxidation (1572; EA Engineering)	

#### Destruction



Projects											
Electrocatalytic (ER2424; CDMSmith)			In situ coa (ER2425; M	its ota)	In situ chemical reductive defluorination (ER2426; Purdue)			Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)			
In situ chemical oxidation & bioremediation; mixed contaminants (ER2715; UC Berkeley)			Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally oxidati (El	Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)	
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex : a	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially available regenerable resins Ex situ (1063; CSM)		<ul> <li>IX resins, electrochemical &amp;/or ultrasonic treatment for regenerant Ex situ (1027; Aptim)</li> </ul>		
Proof of Concept	(Ex situ/d	irinki	ing water or pump-	-and-	treat)						
Protein based adsorbents (1417; U.S. Army)	Ele adsorpti discl	ectrically enhanced tion onto AC, electrically charge to regenerate (1395; NCSU)		Electrochemic al oxidation (1320; Univ of GA)		Mesopo organosilica Ex sit (1300; Wo	orous Cationic p sorbents (PANI) & p itu (PPy) p ooster) (1052; Ur		olyaniline olypyrrole lymers v of AZ)	Electrocoagulation (1278; AECOM)	
Proof of Concept	(Investiga	ation	Derived Waste)								
Advanced oxidation- reduction & membrane concentration (1 (1497; UC Riverside)		(15	Modified SiiC based catalysts 513; Research Triangle Institute)		Rec defluor hydratec (1526	luctive ination by d electrons ; Miami)	Thermal treatment (1556; Aptim)		N	Nonthermal plasma technology (1570; Drexel)	
Combined El photo/electrochemical reduction (1595; UCLA)		Ele	ectron beam technology (1620; Texas A&M) (1		Plasma based treatment (1624; Clarkson)		Hydrothermal technologies (1501; Colorado School of Mines)		Indire wit ol (15	Indirect thermal desorption with thermal oxidation (1572; EA Engineering)	

#### **Sequestration**



Projects										
Electrocata (ER2424; CDN	In situ co (ER2425; M	In situ coagulents (ER2425; Minnesota)			In situ chemical reductive defluorination (ER2426; Purdue)			Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)		
In situ chemical o bioremediatior contamina (ER2715; UC E	Electrolytic de electrobiostim contam (ER2718; Co	Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)		
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex situ treatment train & post oxidation, adsorption, adsorpti material regeneratio (1289; UC Riverside	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially available regenerable resins Ex situ (1063; CSM)		sins, electrochemical Iltrasonic treatment for regenerant Ex situ (1027; Aptim)	
Proof of Concept	(Ex situ/d	rinking water or pum	o-and-	treat)						
Protein based adsorbents (1417; U.S. Army)	Elec adsorptic disch	Electrically enhanced ption onto AC, electrically scharge to regenerate (1395; NCSU)		ctrochemic oxidation 20; Univ of GA)	Mesopo organosilica Ex sit (1300; Wo	orous Cationic po sorbents (PANI) & po itu (PPy) po ooster) (1052; Un		olyaniline olypyrrole lymers iv of AZ)	Electrocoagulation (1278; AECOM)	
Proof of Concept	(Investiga	tion Derived Waste)								
Advanced oxidation- reduction & membrane concentration (15 (1497; UC Riverside)		Modified SiiC base catalysts (1513; Research Tria Institute)	Modified SiiC based catalysts 513; Research Triangle Institute)		Reductive defluorination by hydrated electrons (1526; Miami)		Thermal treatment (1556; Aptim)		Nonthermal plasma technology (1570; Drexel)	
Combined Ele photo/electrochemical reduction (1595; UCLA)		Electron beam techno (1620; Texas A&N	(1526) (1		na based atment Clarkson)	Hydrothermal technologies (1501; Colorado Schoo of Mines)		Indire wit ol (15	Indirect thermal desorption with thermal oxidation (1572; EA Engineering)	

#### **Treatment Trains**



Projects										
Electrocatalytic (ER2424; CDMSmith)			In situ coa (ER2425; M	ts ota)	In situ chemical reductive defluorination (ER2426; Purdue)			Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)		
In situ chemical oxidation & bioremediation; mixed contaminants (ER2715; UC Berkeley)			Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)	
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex a r	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially available regenerable resins Ex situ (1063; CSM)		IX resins, electrochemical &/or ultrasonic treatment for regenerant Ex situ (1027; Aptim)	
Proof of Concept	(Ex situ/d	lrink	ing water or pump	-and-	treat)					
Protein based adsorbents (1417; U.S. Army)	Ele adsorpti discł	Electrically enhanced corption onto AC, electrically discharge to regenerate (1395; NCSU)		Electrochemic al oxidation (1320; Univ of GA)		Mesopo organosilica Ex sit (1300; Wo	orous Cationic po sorbents (PANI) & po itu (PPy) po ooster) (1052; Uni		lyaniline blypyrrole ymers v of AZ)	Electrocoagulation (1278; AECOM)
Proof of Concept	(Investiga	ation	Derived Waste)							
Advanced oxidation- reduction & membrane concentration (19 (1497; UC Riverside)		(15	Modified SiiC based catalysts 513; Research Triangle Institute)		Reductive defluorination by hydrated electrons (1526; Miami)		Thermal treatment (1556; Aptim)		Nonthermal plasma technology (1570; Drexel)	
Combined Ele photo/electrochemical reduction (1595; UCLA)		(1526) (1526) Electron beam technology (1620; Texas A&M) trea (1624; 1		na based atment Clarkson)	Hydrothermal technologies (1501; Colorado Schoo of Mines)		Indire wit ol (15	Indirect thermal desorption with thermal oxidation (1572; EA Engineering)		

#### **Mixed Contamination: PFASs & Chlorinated Solvents**



Projects											
Electrocatalytic (ER2424; CDMSmith)			In situ coa (ER2425; M	ts ota)	In situ chemical reductive defluorination (ER2426; Purdue)			Coupled reactive nanoscale materials & bioremediation; mixed contaminants (ER2714; Brown)			
In situ chemical oxidation & bioremediation; mixed contaminants (ER2715; UC Berkeley)			Electrolytic degradation with electrobiostimulation; mixed contaminants (ER2718; Colorado State)			Key F&T properties impacting attenuation & treatment; mixed contaminants (ER2720; Colorado School of Mines)			Thermally enhanced persulfate oxidation followed by P&T (ER201729; Navy)		
In situ & ex situ treatment train: ISCO or amendment, plasma destruction, IX (1306; Clarkson)		Ex a r	situ treatment train: pre & post oxidation, adsorption, adsorption material regeneration (1289; UC Riverside)		Polymer adsorbents In or ex situ (1026; Cornell)		Commercially availabl regenerable resins Ex situ (1063; CSM)		le IX resins, electrochemical &/or ultrasonic treatment for regenerant Ex situ (1027; Aptim)		
Proof of Concept	(Ex situ/d	lrink	ing water or pump	-and-	treat)						
Protein based adsorbents (1417; U.S. Army)	Ele adsorptio disch	ectrically enhanced tion onto AC, electrically charge to regenerate (1395; NCSU)		Electrochemic al oxidation (1320; Univ of GA)		Mesopo organosilica Ex sit (1300; Wo	DrousCationic pointa sorbents(PANI) & pointitu(PPy) pointooster)(1052; Ur		olyaniline olypyrrole lymers iv of AZ)	Electrocoagulation (1278; AECOM)	
Proof of Concept	(Investiga	ation	Derived Waste)								
Advanced oxidation- reduction & membrane concentration (1 (1497; UC Riverside)		(15	Modified SiiC based catalysts 513; Research Triangle Institute)		Reductive defluorination by hydrated electrons (1526; Miami)		Thermal treatment (1556; Aptim)		Nonthermal plasma technology (1570; Drexel)		
Combined Ele photo/electrochemical reduction (1595; UCLA)		Ele	ectron beam technology (1620; Texas A&M) (16		Plasm trea (1624;	Plasma based treatment (1624; Clarkson)		Hydrothermal technologies (1501; Colorado School of Mines)		Indirect thermal desorption with thermal oxidation (1572; EA Engineering)	

#### **Investigation Derived Waste**



### **Funding to Date**

- Total: \$39M (FY11 FY20)
- Ecotoxicity
  - ♦\$5.4M
  - FY19 solicitation associated with bioavailability & bioaccumulation – no funding associated with this yet



### Summary

- Additional research and demonstrations needed in all remediation areas: ex situ (drinking water), in situ groundwater and soil treatments
- Good progress on several fronts
- Toxicology information needed to inform remediation; which PFASs are of most concern

#### Resources

http://map.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/

- Workshop report
  - https://serdp-estcp.org/content/download/45585 /425201/file/PFAS%20Workshop%20Report% 20Final%20September%202017.pdf

#### FAQ and Reference Document

- https://www.serdpestcp.org/content/download/46353/431598/file/FAQ%20ER-201574%20September%202017.pdf
- In what environmental media have PFASs been found?
- What is the fate and transport of PFASs in the environment?
- What characterization & remedial tools are available/effective for PFASs?
- What are human & ecological exposure pathways & health effects?



SERDP

ESTCP

FY11

**FY14** 

**FY16** 

**FY18** 

Analytical Methods

Field Demonstration to Enhance PFAS Degradation & Mass Remova Dem//al of Existing Alternative

**FY22** 

**FY24** 

T2: Catalyzing Rapid Information Transfe Characterization of the Nature & Extent of PFAS

FY20