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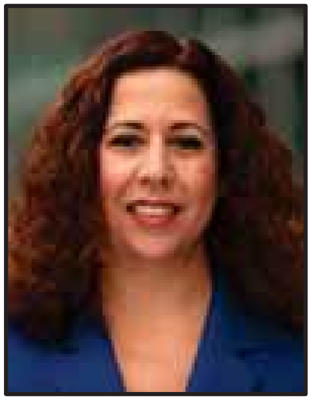
Managing AFFF Impacts to Subsurface Environments and Assessment of Commercially Available PFAS-Free Foams (Part 2)

October 22, 2020

Welcome and Introductions

Rula A. Deeb, Ph.D.
Webinar Coordinator



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Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Understanding and Improving PFAS Degradation with Advanced Reduction and Oxidation** (25 minutes + Q&A)
  Dr. Jinyong Liu, University of California, Riverside
- **Assessment of Commercially Available PFAS-Free Firefighting Foams and Agents** (25 minutes + Q&A)
  Mr. Jerry Back, Jensen Hughes
- **Final Q&A session**

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- Find the Q&A button on your control bar and type in your question(s)
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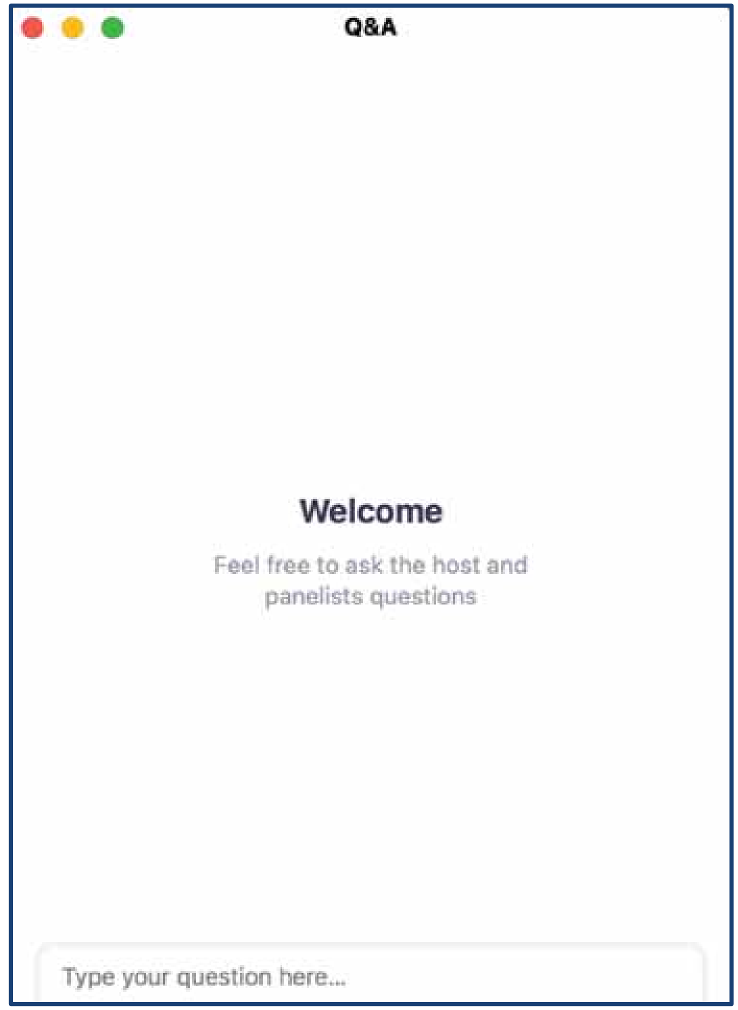


SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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

Sustaining Ranges, Facilities and Operations

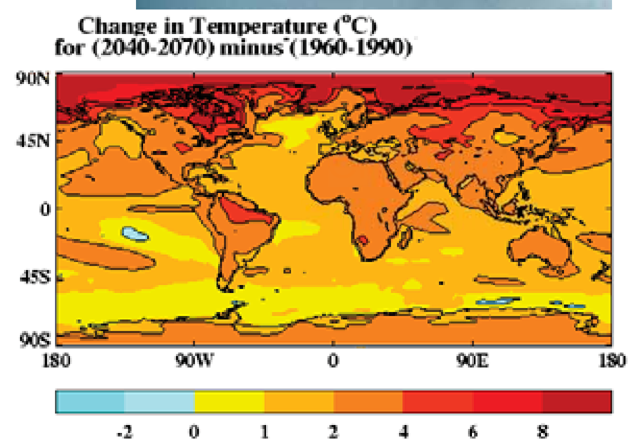
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

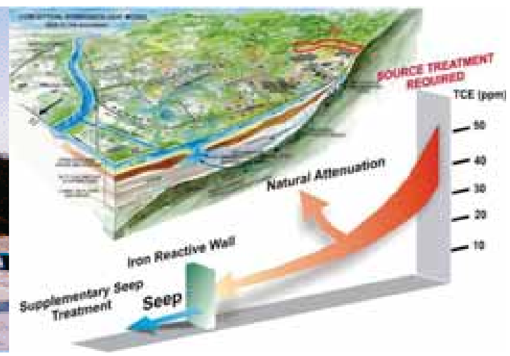
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

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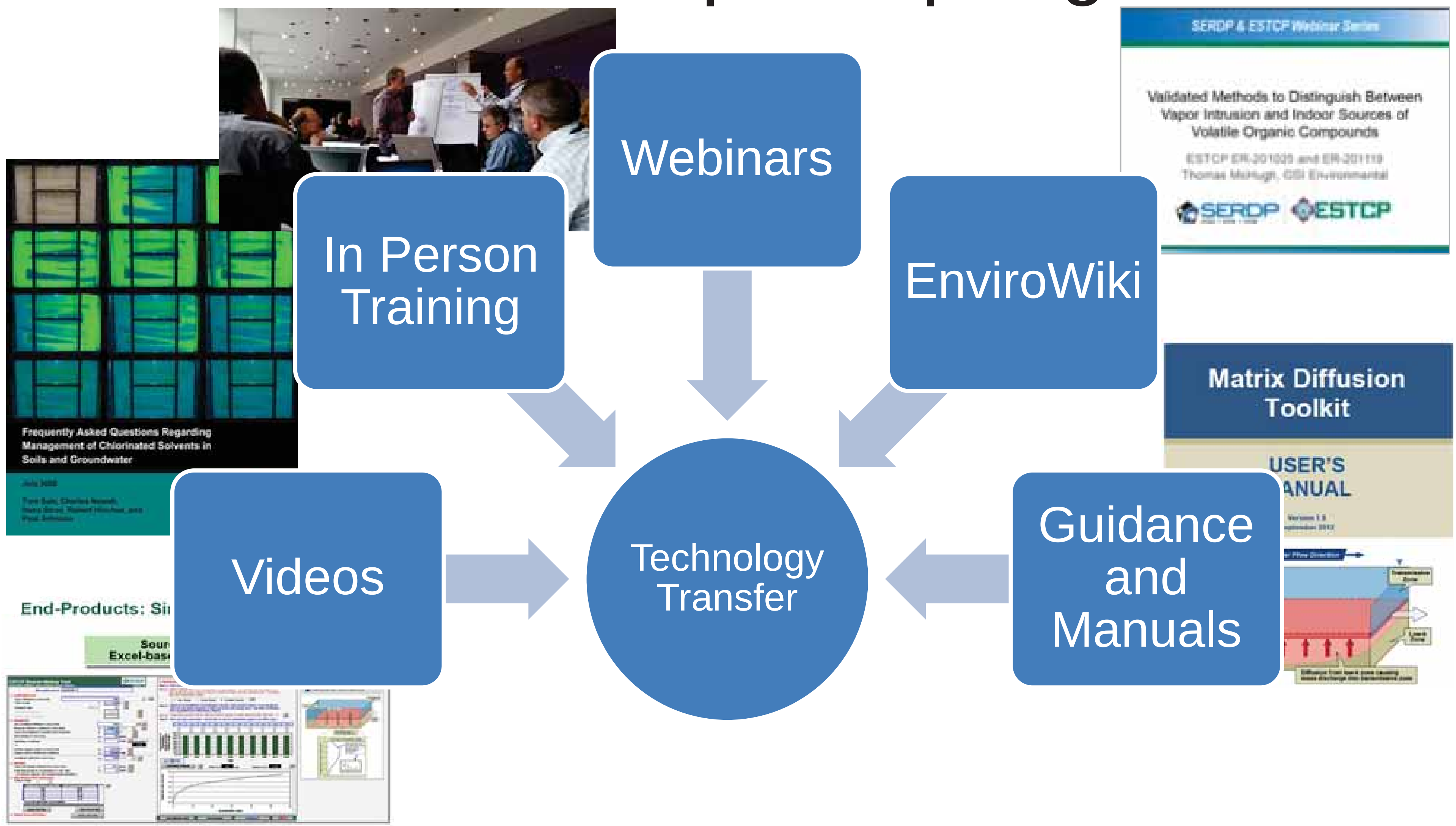

SERDP and ESTCP PFAS Efforts

https://map.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/pfas_efforts.pdf

SERDP and ESTCP Webinar Series

Date	Topic
November 5, 2020	Pathways under Non-Stationary Conditions and Their Implications for Wildlife and Human Exposure on Department of Defense Lands
November 19, 2020	Abiotic Degradation of Chlorinated Solvents in Subsurface Environments
December 10, 2020	Approaches for Managing Contaminated Sediments
January 14, 2021	Improving Energy Efficiency through Advanced Building Controls
January 28, 2021	Improved Approaches for PFAS Sampling and Treatment
February 11, 2021	Advances in the Detection of Submerged Unexploded Ordnance in Marine Environment

For upcoming webinars, please visit

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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Save the Date

SERDP • ESTCP SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

November 30 - December 4, 2020

Registration for the virtual event is open!

Understanding and Improving PFAS Degradation with Advanced Reduction and Oxidation

Jinyong Liu, Ph.D.
University of California, Riverside

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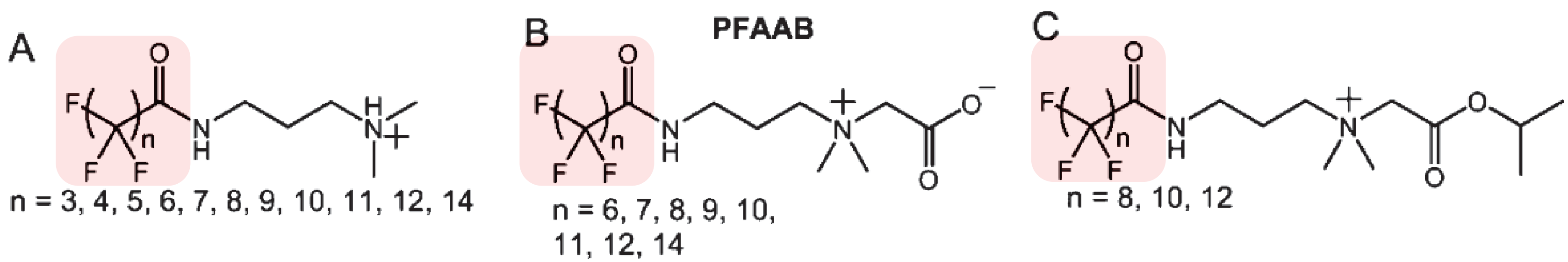
Agenda

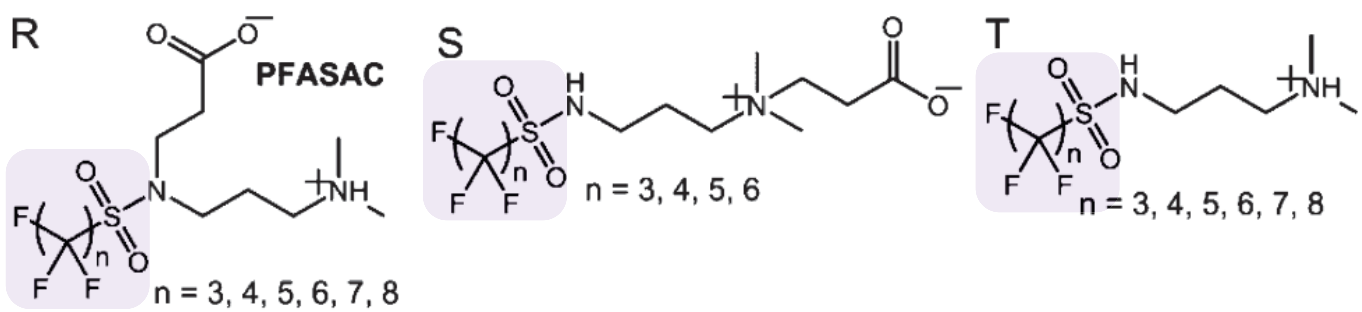
- Structure of PFAS pollutants
- Advanced reduction and oxidation
- Structure-reactivity relationship
- Complete destruction of PFAS
- Implications to remediation and management
- Benefits to DoD

PFAS Contamination from AFFF

- Perfluorocarboxylate-based surfactants, $C_nF_{2n+1}-CO-X$



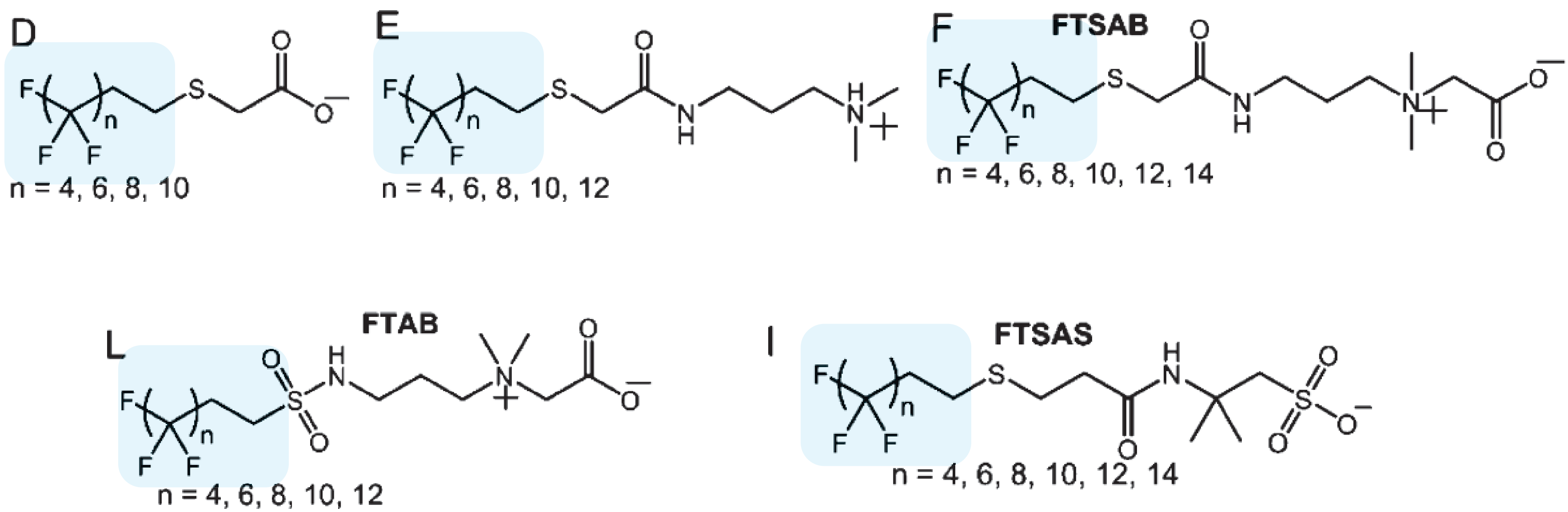
- Perfluorosulfonate-based surfactants $C_nF_{2n+1}-SO_2-X$



***Source**: D'Agostino and Mabury. ES&T 2014, 48, 121*

PFAS Contamination from AFFF

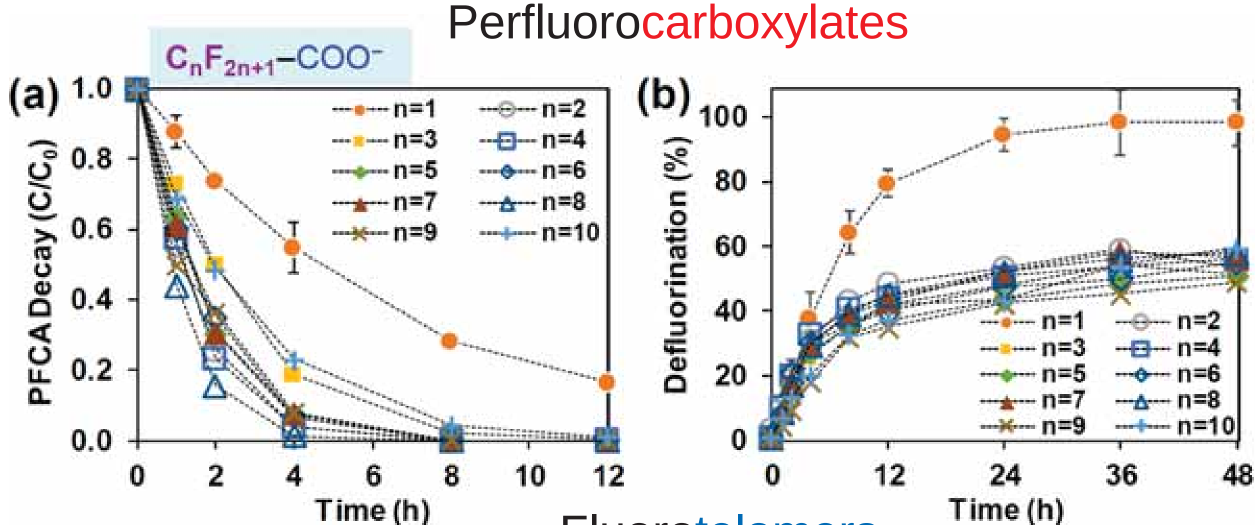
- Fluorotelomer-based surfactants, $C_nF_{2n+1}{-}CH_2CH_2{-}X$



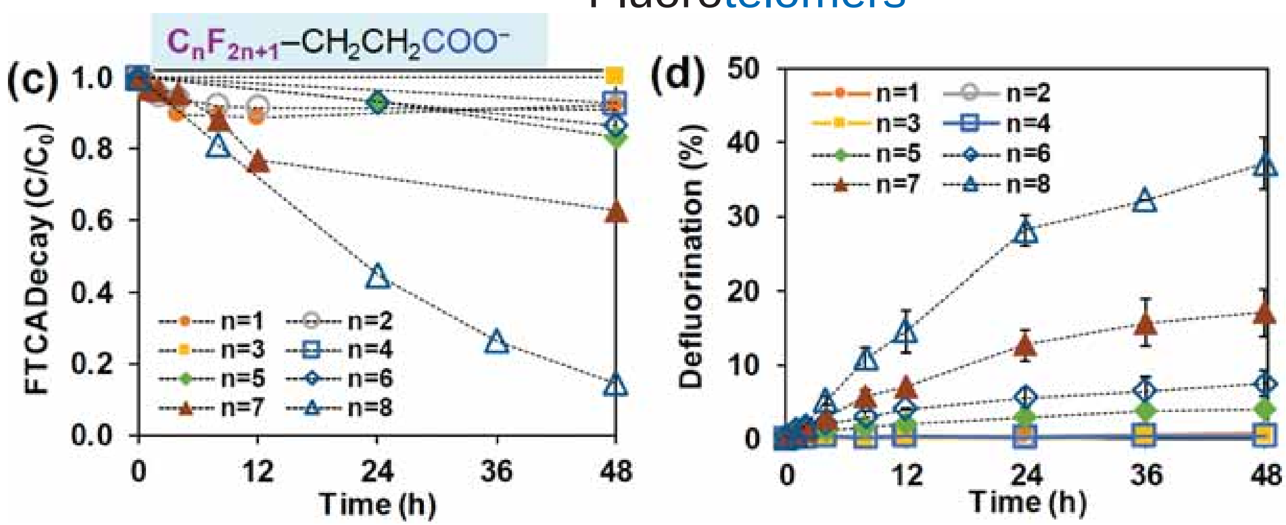
Source: *D'Agostino and Mabury. ES&T 2014, 48, 121*

Reduction with UV/Sulfite System

Perfluorocarboxylates

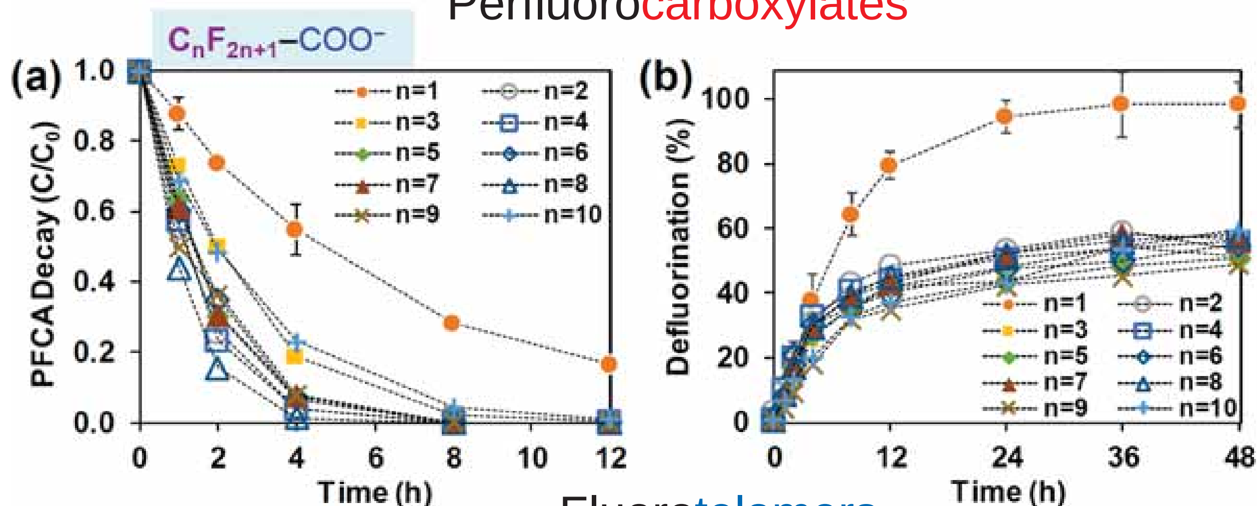


Fluorotelomers

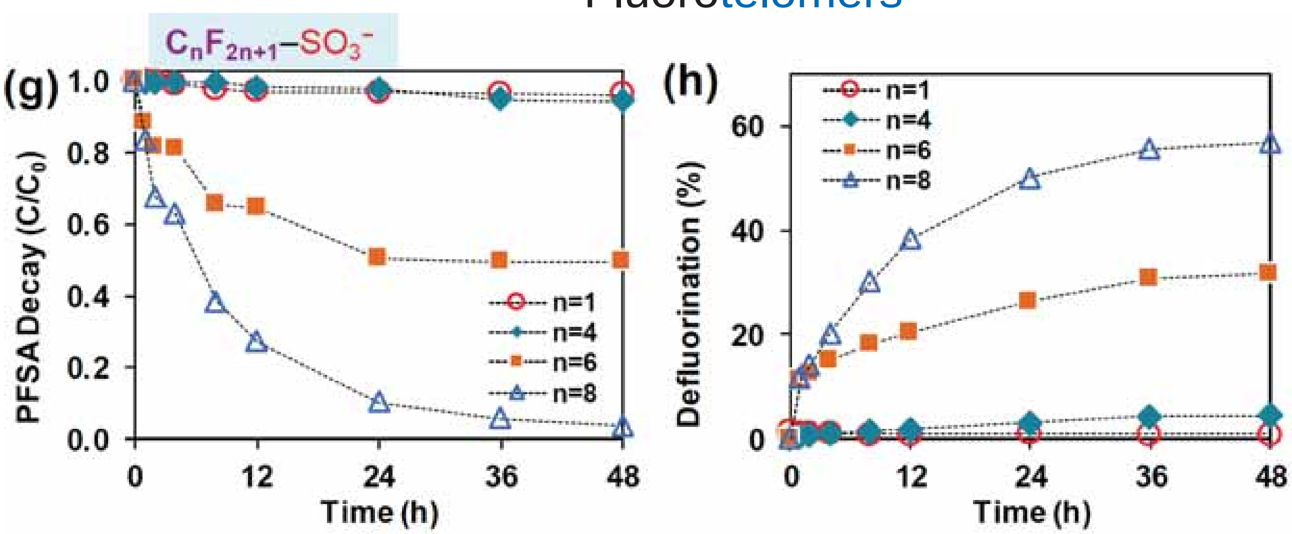


Reduction with UV/Sulfite System

Perfluorocarboxylates



Fluorotelomers



Reduction with UV/Sulfite System

- All perfluorocarboxylates can be effectively treated
- Short-chain fluorotelomers are recalcitrant
- Short-chain perfluorosulfonates are recalcitrant

Improving the Performance of UV/Sulfite System

pH 9.5 (traditional setting)

- Time for complete removal of PFCA
  - 8−12 h
- EE/O
  - 77 − 174 kWh m^{-3}
- Maximum defluorination percentage
  - 52 − 61%

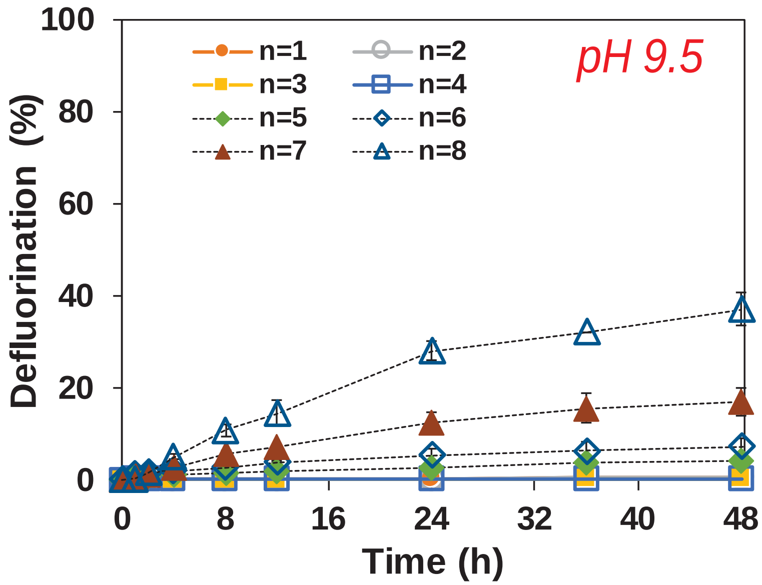
pH 12 (new results)

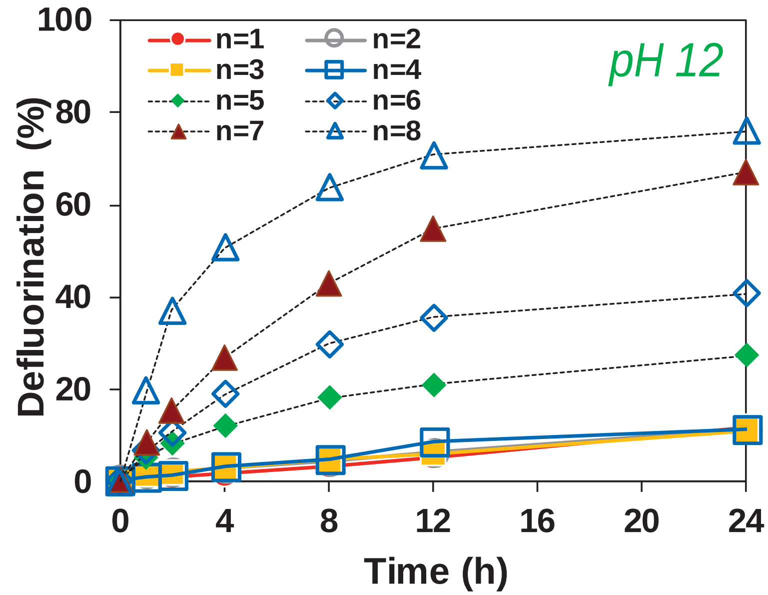
- Time for complete removal of PFCA
  - 0.5−1 h
- EE/O
  - 5.3 − 8.9 kWh m^{-3}
- Maximum defluorination percentage
  - 73 − 92%

***Note**: EE/O = **e**lectrical **e**nergy consumed when the pollutant concentration is lowered for one **o**rder of magnitude (i.e., 10% remaining or 90% removal)*

Treatment of Fluorotelomers

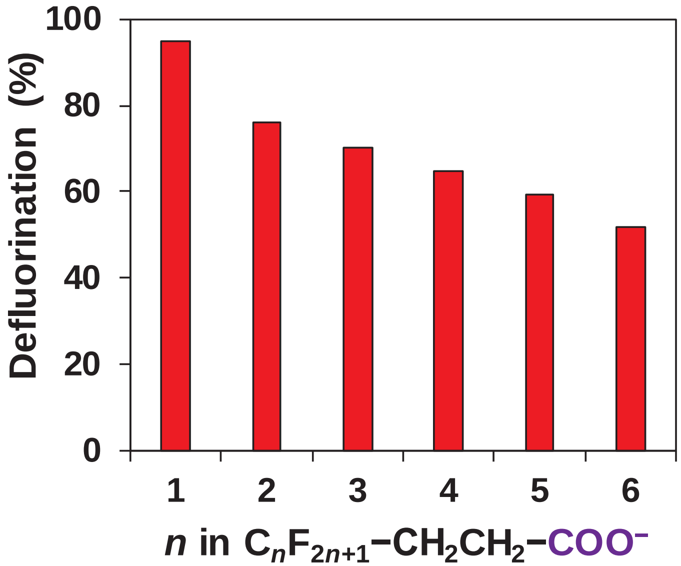
$C_nF_{2n+1}-CH_2CH_2-COO^-$

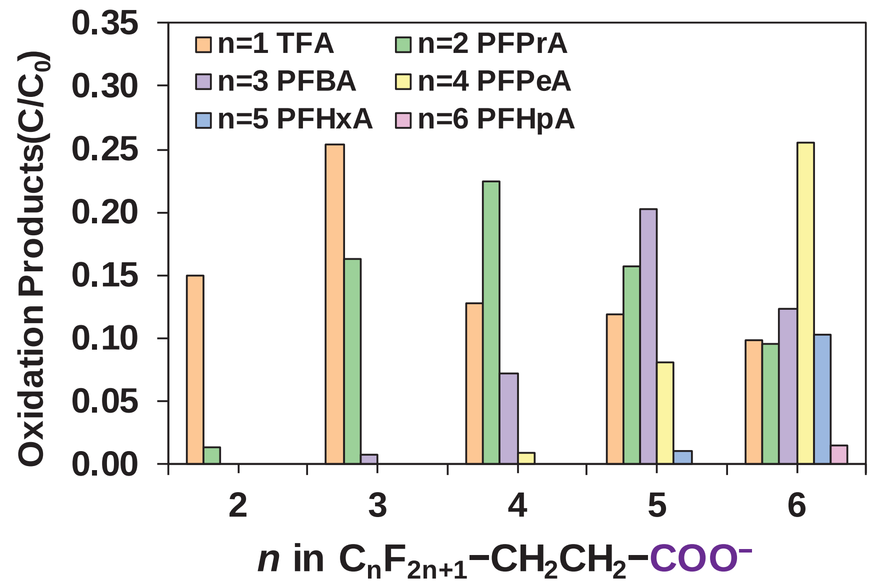




- Short-chain telomers are still recalcitrant
- Oxidation is used to generate PFCA

Oxidation of Fluorotelomers with Hydroxyl Radicals (Pre-Oxidation)





- Oxidation can release F^- from fluorotelomers
- Products are perfluorocarboxylate mixtures

Oxidation of UV/Sulfite Residues (Post-Oxidation)

(C−F bond dissociation energy, kcal/mol)

118.1 108.7 109.0 106.9

$CF_3{-}CF_2{-}CF_2{-}CF_2{-}COO^-$

Not reactive with HO•

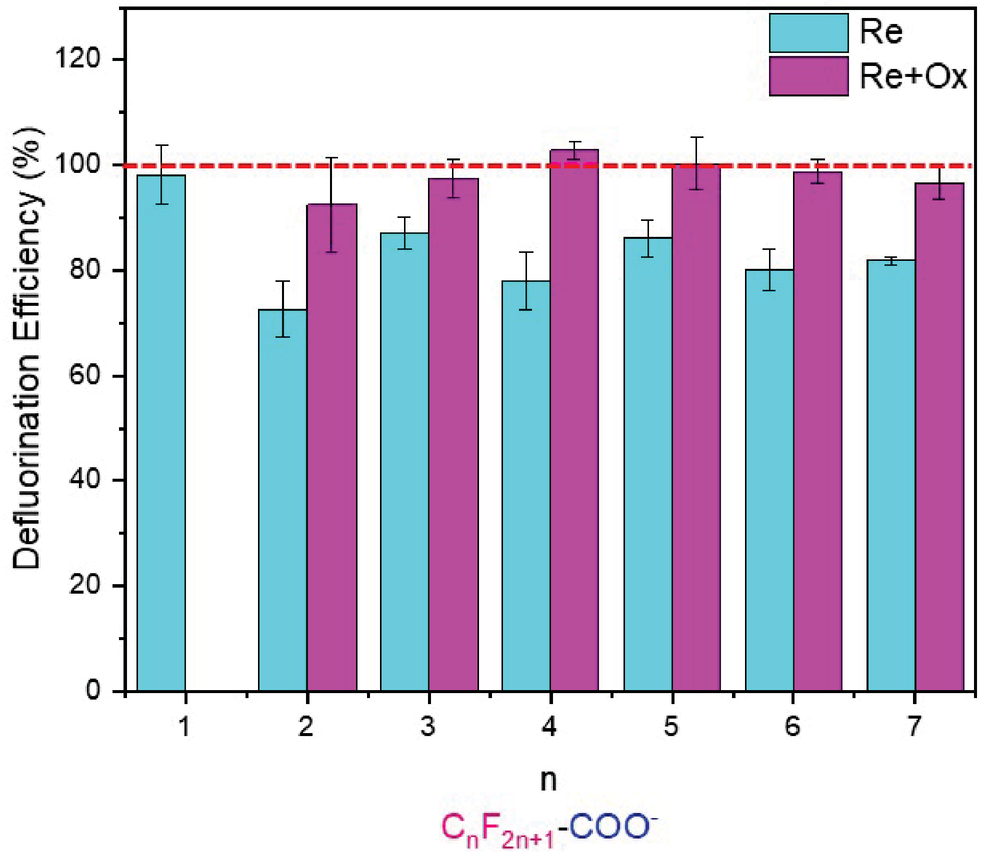
122.4

$CF_3{-}CH_2{-}CH_2{-}CH_2{-}COO^-$

Can be fully destroyed by HO•

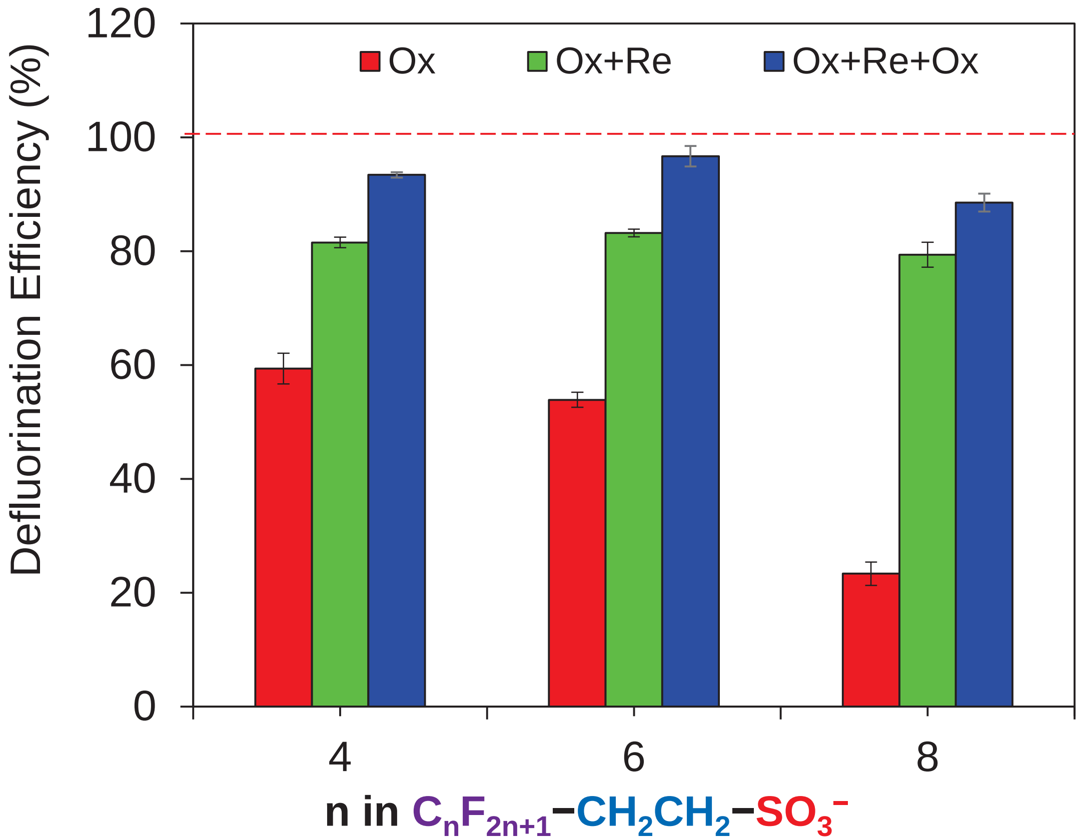
- Remaining C−F bonds are in the H-rich residues
- Oxidation releases most remaining C−F bonds

Destruction of PFCAs



Post-oxidation after the UV/sulfite reduction achieved almost complete defluorination of PFCAs

Destruction of FTSAs



Fluorotelomers need pre-oxidation to be converted into PFCAs

Conclusions

- Three major PFAS categories can be effectively degraded
  - PFCA, PFSA and FTA
- PFCAs are the most labile substrates
- The performance and efficiency of the UV/sulfite treatment system are being further improved

Conclusions (Cont'd)

- Advanced oxidation can convert fluorotelomers into PFCAs
- Incomplete defluorination of PFCAs by UV/sulfite is due to the formation of C−H bonds
- Advanced oxidation can release the residual F from H-rich residues

Benefits to DoD

- A structure-reactivity database for PFAS degradation
- Proof-of-concept for a complete PFAS destruction strategy
- Technology development toward a practical treatment system
- Recommendation for the current/future use of PFAS

Additional Resources

- Zekun Liu, Michael J. Bentel, Yaochun Yu, Mei Sun, Yujie Men, Jinyong Liu. Near-Complete Defluorination of PFAS with Combined Reduction and Oxidation. Manuscript in preparation (for submittal to Environmental Science & Technology)
- Michael J. Bentel, Zekun Liu, Yaochun Yu, Jinyu Gao, Yujie Men, Jinyong Liu. Enhanced Degradation of Perfluorocarboxylic Acids (PFCAs) by UV/Sulfite Treatment: Reaction Mechanisms and System Efficiencies at pH 12. Environmental Science & Technology Letters 2020, 7 (5), 351-357. https://doi.org/10.1021/acs.estlett.0c00236
- Michael J. Bentel, Yaochun Yu, Lihua Xu, Zhong Li, Bryan M. Wong, Yujie Men, and Jinyong Liu. Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. Environmental Science & Technology 2019 53 (7), 3718-3728. https://doi.org/10.1021/acs.est.8b06648

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1289

Speaker Contact Information

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Q&A Session 1

Assessment of Commercially Available Fluorine-Free Firefighting Foams and Agents

Jerry Back
Jensen Hughes

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Terminology Clarifications

- SERDP and ESTCP objectives: PFAS-free formulations
  - i.e., PFAS-Free Foams (PFF)
- Fire protection/firefighting industry focused on fluorine
  - i.e, Fluorine-Free Foams (FFF)
  - Products are labeled as FFF
- For this discussion FFF = PFF

Agenda

- Background
- Approach and project plan
  - Six tasks
- Testing and capabilities
- Schedule for completion
- Program summary
- DoD benefits

Introduction

- Background
  - Aqueous Film Forming Foam (AFFF) industry standard 50-year legacy against flammable liquid fires
- Applications
  - Maritime, aviation and petroleum industries
- Problem
  - AFFF is being banned (environmental and health concerns)

Objectives

- Ultimate goal
  - Identify environmentally acceptable AFFF alternative
- Specific objectives
  - Quantify capabilities of available alternatives
  - Begin the development of a database

Technical Approach

Two-Year Program Started February 2019

Task	
1	Literature search (to identify candidates)
2	Environmental analysis (preliminary)
3	Real-scale fire tests
4	Capabilities rankings
5	Approval-scale fire tests
6	Program documentation (database, final report, path forward)

***Note**: Tasks 3 through 5 were conducted in parallel due to COVID related issues*

Overview of Tasks

Task 1: Literature search

- Comprehensive literature review on foams and agents
- Potential candidates/agents (~40 identified)

Task 2: Environmental analysis

- General foam composition environmental assessment
- Life cycle environmental assessments

Testing and Capabilities

Task 5: Approval-scale testing

- 28 ft^2 pan fire
- 2 and 3 gpm
- Gasoline and Jet A
- Aspirating nozzle
- MILSPEC
  - Gasoline / 2 gpm / 30 sec

Task 3: Real-scale testing

- 400 ft^2 pan fire
- 30 gpm nozzle
- With and without foam tube
- Mostly Jet A (some gasoline)

***Note**: 2 gpm / 28 ft^2 = 30 gpm / 400 ft^2 = 0.07 gpm/ft^2*

Task 5: Approval-Scale Test Results

Foam/ Agent	Agent Type	Gasoline		Jet A	
		2 gpm	3 gpm	2 gpm	3 gpm
		Ext (sec)	Ext (sec)	Ext (sec)	Ext (sec)
AFFF	AFFF	30	24	16	12
FFF1	Foam	49	42	19	15
FFF2	Foam	58	37	24	15
FFF3	Foam	57	45	30	20
FFF4	Foam	53	45	33	22
FFF5	Foam	57	52	26	18
FFF6	Foam	77	55	27	15
FFF7	Foam	77	65	25	21
FFF8	Foam	84	67	22	17
FFF9	Foam	126	71	22	16
FFF10	Foam	No	123	26	20
FFF11	Foam	-	No	No	114
WA1	Wetting	No	124	29	20
WA2	Wetting	No	104	32	27
WA3	Wetting	-	No	-	95

- Capabilities
  - 1 AFFF, 2 FFF, 3 WA
  - NF – distant 4th
- Jet A easier than gasoline
  - Gasoline about twice as hard
- 13 of 15 foams/agents extinguish Jet A in <30 sec with 2 gpm
- Some (5) could not extinguish gasoline

***Note**: FFF = Fluorine-Free Foam, WA = Wetting Agents; NF = New Formulations*

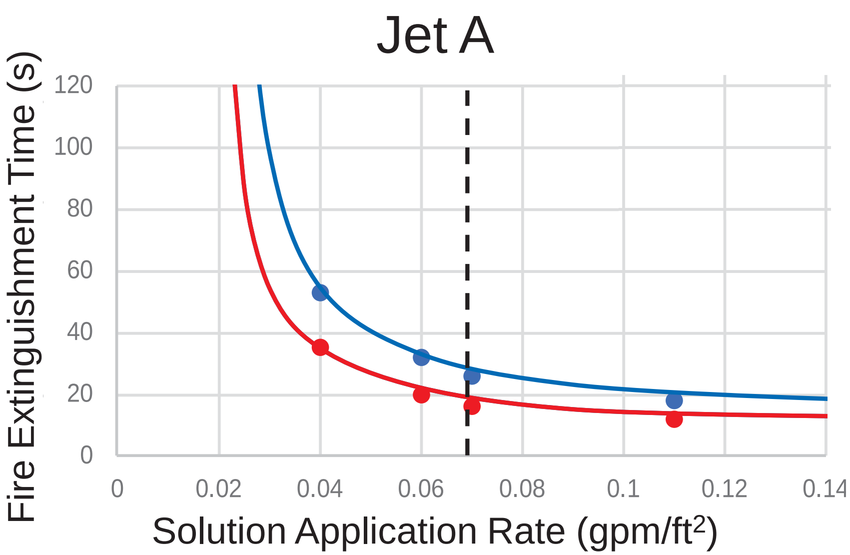
Task 5: Approval-Scale Test Results

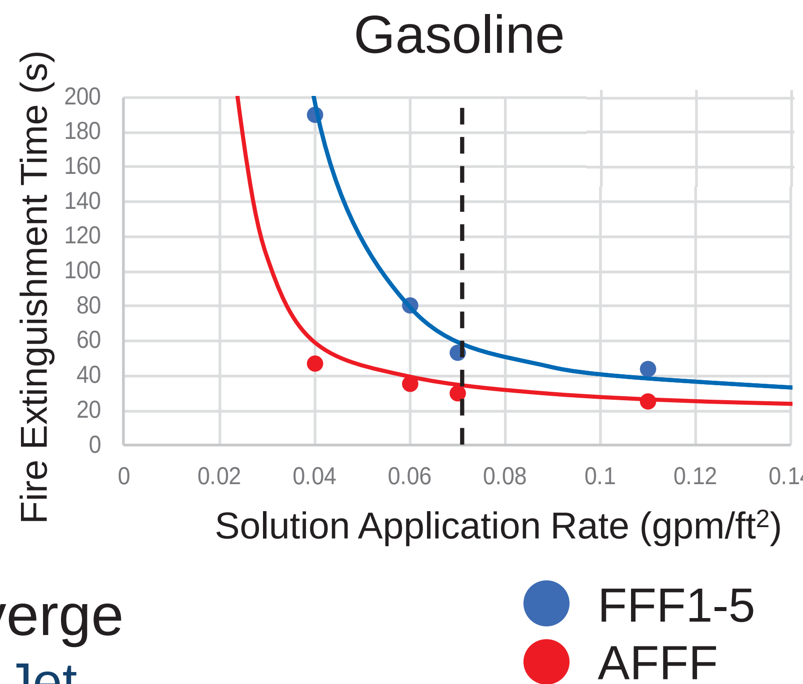
Foam/ Agent	Agent Type	Gasoline		Jet A	
		2 gpm (.07 gpm/ft²)	3 gpm (.11 gpm/ft²)	2 gpm (.07 gpm/ft²)	3 gpm (.11 gpm/ft²)
		Ext (sec)	Ext (sec)	Ext (sec)	Ext (sec)
AFFF	AFFF	30	24	16	12
FFF1	Foam	49-58	37-52	19-33	15-22
FFF2	Foam				
FFF3	Foam				
FFF4	Foam				
FFF5	Foam				
FFF6	Foam	77-82	55-67	22-27	15-21
FFF7	Foam				
FFF8	Foam				
FFF9	Foam	126-No	71-No	22-No	16 -114
FFF10	Foam				
FFF11	Foam				
WA1	Wetting	No	104-124	29-32	20-27
WA2	Wetting				
WA3	Wetting	No	No	No	95

Good | OK | Not so good

Task 5: Approval-Scale Test Results

Extinguishment Times





- Parallel L curves, do not converge
  - Gasoline above 0.07 gpm/ft^2; Jet
- FFF1-5
  - < 1 minute even at 0.04 gpm/ft^2
  - > 0.07 gpm/ft^2 → 1.5 times longer than AFFF
  - < 0.07 gpm/ft^2 → lose capabilities vs. gasoline

Task 3: Real-Scale Test Results

150 gallons of fuel (Gasoline or Jet A)
~80MW; 40 ft flame height; 40 gpm burning rate

Task 3: Real-Scale Test Results

15º pattern
AFFF expansion 5
FFF expansion 6

5º pattern
AFFF expansion 18
FFF expansion 22

***Note**: 30 gpm @ 100 psi = 0.07 gpm/ft^2*

Task 3: Real-Scale Test Results

Foam/Agent	Fuel	STD Nozzle (.07 gpm/ft^2)		Foam Tube (.07 gpm/ft^2)	
		Cont (sec)	Ext (sec)	Cont (sec)	Ext (sec)
AFFF	Jet A	25	45	15	25
FFF1-5 (AVG)	Jet A	45	58	25	44
WA3	Jet A	60	No	60	102
AFFF	gasoline	30	50	30	45
FFF1-5 (AVG)	gasoline	100	135	60	105

- Jet A tends similar as lab-scale test results
  - Consistent and repeatable
- Gasoline is very technique dependent
  - Plunging is detrimental
- Apples to apples FFF1-5 about 1.5-2 times longer than AFFF
- Foam tube reduces ext. time by 30-45%;
  reduces stream reach by 40%

Task 3: Real-Scale Test Results

Task 6: Program Documentation

- All-encompassing final report (review board)
  - Complete data set and analysis
- Consensus topics/issues (review board)
  - Findings/conclusions
  - Path forward
- Early 2021

Conclusions

- AFFF is going away
- DoD needs to address this problem
- Understanding current alternative capabilities is required
- Database on capabilities is a logical first step
- How good is good enough?
  - We may be closer than originally thought

Benefits to DoD

- Database on capabilities of AFFF alternatives
- Links real-scale and approval scale tests
- Potential validation for commercially available alternatives
- Baseline data to begin developing new specification

Acknowledgments

- U.S. Naval Research Laboratory (NRL)
  - John Farley, Director of Fire Test Operations
  - Stan Karwoski, Senior Firefighter
- Jensen Hughes
  - Noah Lieb, Environmental Group
  - Dan Martin, Assistant Project Manager
  - Lindsay Huffert, Test Engineer

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Noise-and-Emissions/WP19-5324

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Q&A Session 2

SERDP & ESTCP Webinar Series

The next webinar is on November 5, 2020

Pathways Under Non-Stationary Conditions and Their Implications for Wildlife and Human Exposure on Department of Defense Lands

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