

*Thank you for signing in early*

The webinar will begin promptly at  
12:00 pm ET, 9:00 am PT



# SERDP and ESTCP Webinar Series

***The webinar will begin promptly at 12:00 pm ET,  
9:00 am PT***

- You have two options for accessing the webinar
  1. Listen to the broadcast audio if your computer is equipped with speakers
  2. Call into the conference line: 303-248-0285  
Required conference ID: 6102000
- For any question or issues, please email [serdp-estcp@noblis.org](mailto:serdp-estcp@noblis.org) or call 571-372-6565

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

September 7, 2017



## Welcome and Introductions

Rula A. Deeb, Ph.D.  
Webinar Coordinator



# Webinar Agenda

- **Webinar Logistics** (5 minutes)  
**Dr. Rula Deeb**, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)  
**Dr. Andrea Leeson**, SERDP and ESTCP
- **PFOS and PFOA: Department of Defense Policy and Management Issues** (10 minutes + Q&A)  
**Ms. Maureen Sullivan**, Office of the Assistant Secretary of Defense  
(Energy, Installations and Environment)
- **SERDP and ESTCP Efforts to Gain a Better Understanding of Issues Associated with PFASs in the Subsurface** (20 minutes + Q&A)  
**Dr. Andrea Leeson**, SERDP and ESTCP
- **Fighting the Unbeatable Foe: Remediation of Groundwater Contaminated by PFASs with ISCO** (20 minutes + Q&A)  
**Dr. David Sedlak**, University of California, Berkeley
- **Final Q&A session**

# How to Ask Questions

Type and send questions at any time using the Q&A panel

Chat with Presenter:

# In Case of Technical Difficulties

- Delays in the broadcast audio
  - Click the mute/connect button
  - Wait 3-5 seconds
  - Click the mute/connect button again
  - If delays continue, call into the conference line
    - Call into the conference line: 303-248-0285
    - Required conference ID: 6102000
- Submit a question using the chat box

# SERDP and ESTCP Overview

Andrea Leeson, Ph.D.  
SERDP and ESTCP



# SERDP

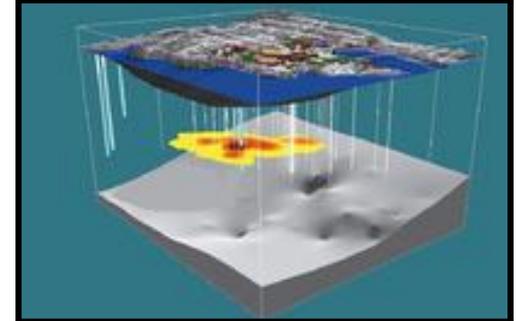
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

# ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

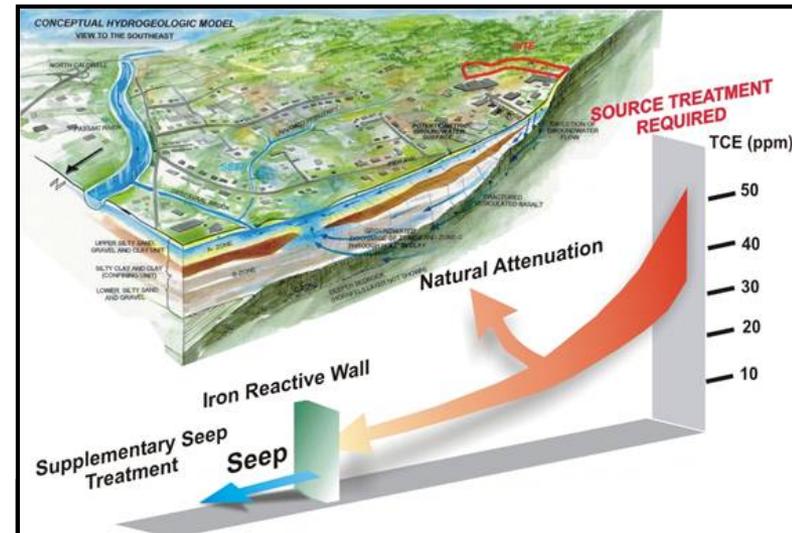
# Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Resiliency
5. Weapons Systems and Platforms



# Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment



# SERDP and ESTCP Webinar Series

Date	Topic
October 5, 2017	New Resource Conservation Insights to Desert Environments
October 19, 2017	Laser De-Paint and Surface Preparation Mechanism and Technologies
November 2, 2017	Platforms for Underwater and Near-Shore Munitions Surveys
November 16, 2017	Building Envelop Technologies
December 7, 2017	Management of Novel Hawaiian Ecosystems

**For upcoming webinars, please visit**

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



# SERDP • ESTCP SYMPOSIUM

2017 | Enhancing DoD's Mission Effectiveness

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

- November 28 - November 30, 2017
- Washington Hilton Hotel  
1919 Connecticut Avenue, NW  
Washington, DC 20009
- ***Registration is open***

## PFOS and PFOA: Department of Defense Policy and Management Issues

Maureen Sullivan  
Office of the Assistant Secretary  
of Defense



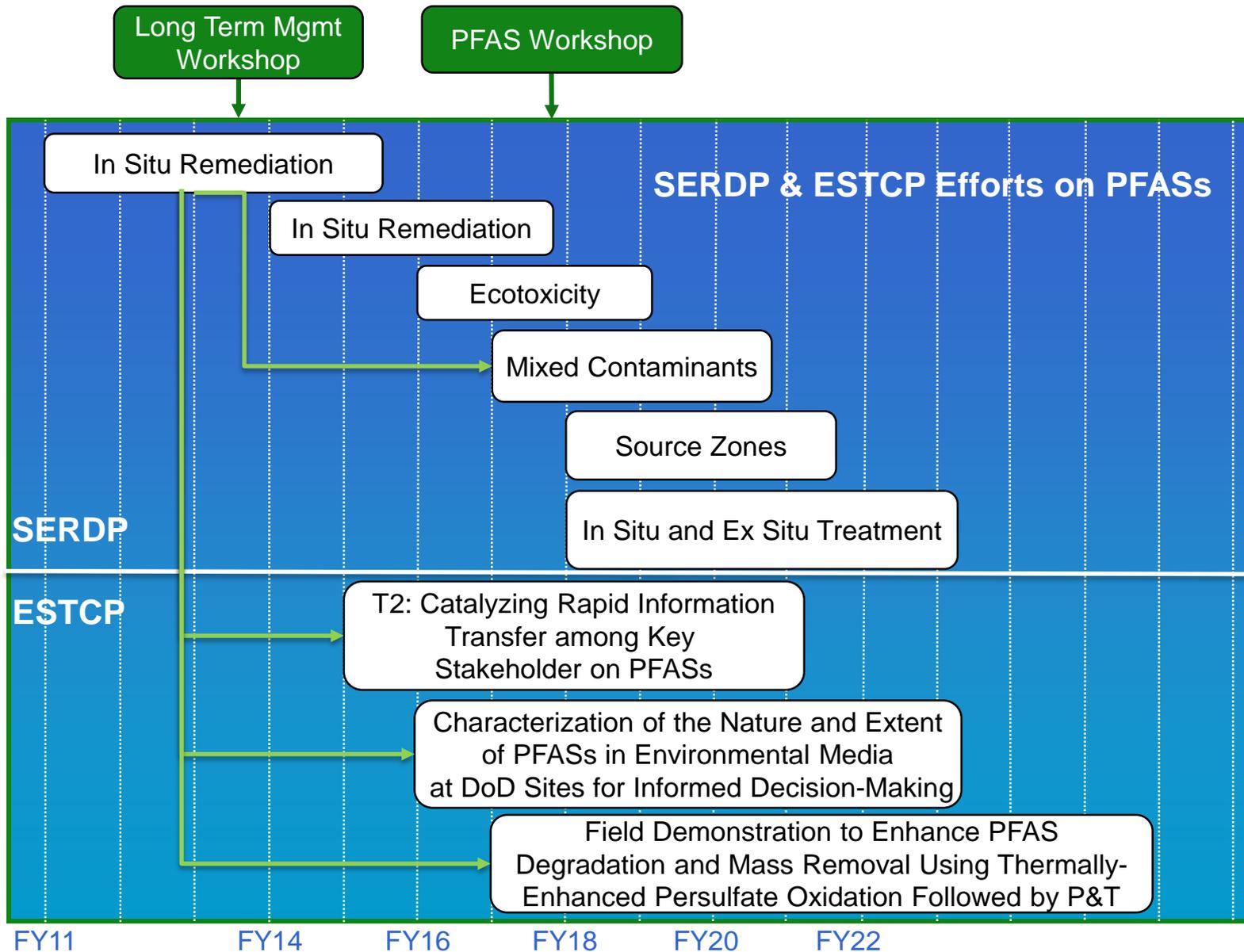
## Q&A Session 1

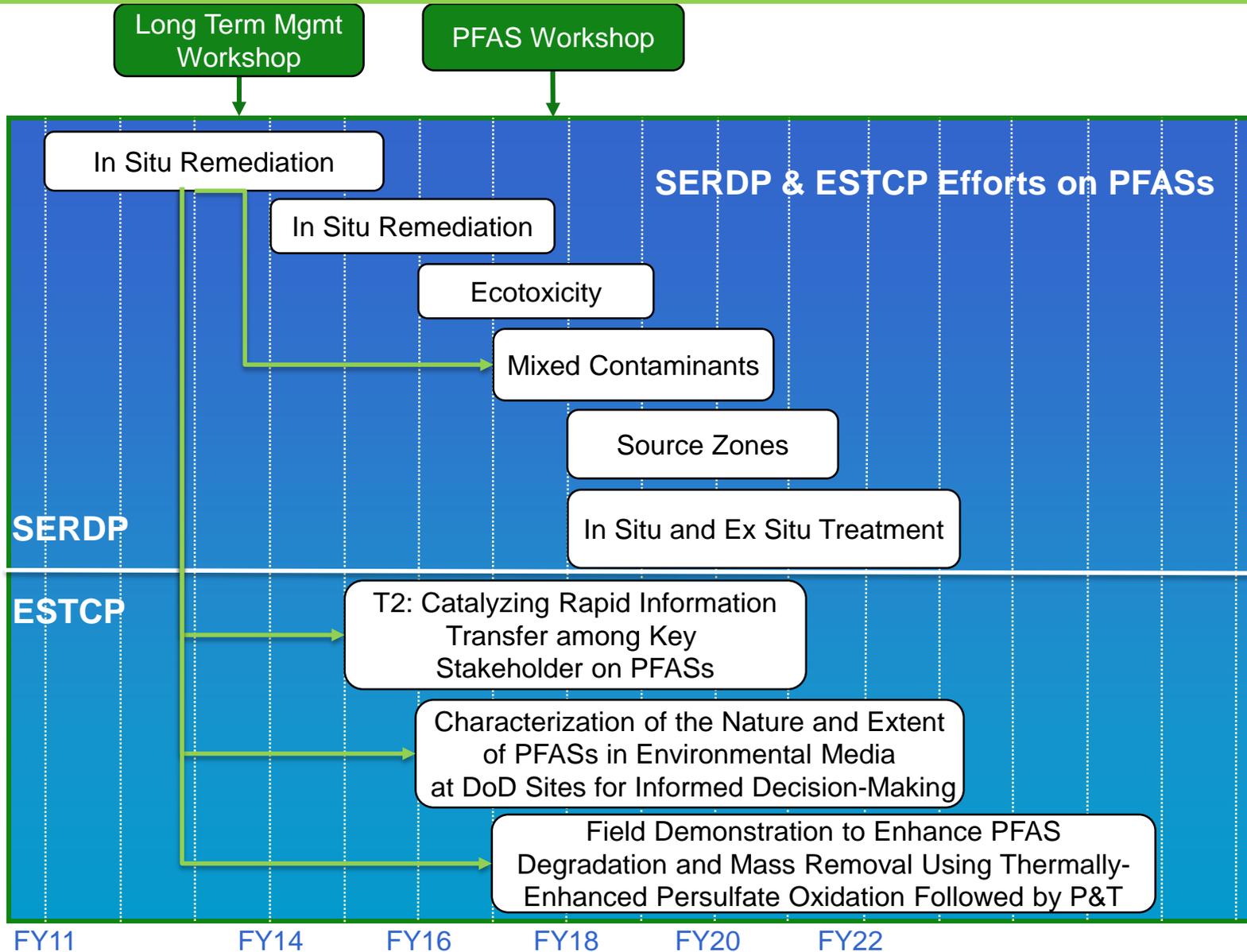


# SERDP and ESTCP Efforts to Gain a Better Understanding of Issues Associated with PFASs in the Subsurface

Andrea Leeson, Ph.D.  
SERDP and ESTCP







In Situ Remediation

SERDP & ESTCP Efforts on PFASs

Released shortly after the EPA released the Provisional Health Advisories for PFOS (0.2 µg/L) and PFOA (0.4 µg/L)

Funded three projects

1. ER-2126: Fate and transport under varying conditions (Higgins, CSM) **(complete)**
2. ER-2127: SEED, remediation technology (Huang, Georgia) **(complete)**
3. ER-2128: Delineate fluorochemicals that persist in AFFF-contaminated matrices and evaluate impact on priority pollutant transport and bioremediation (Field, OSU) **(complete)**

FY11

FY14

FY16

FY18

FY20

FY22

In Situ Remediation

## SERDP & ESTCP Efforts on PFASs

In Situ Remediation

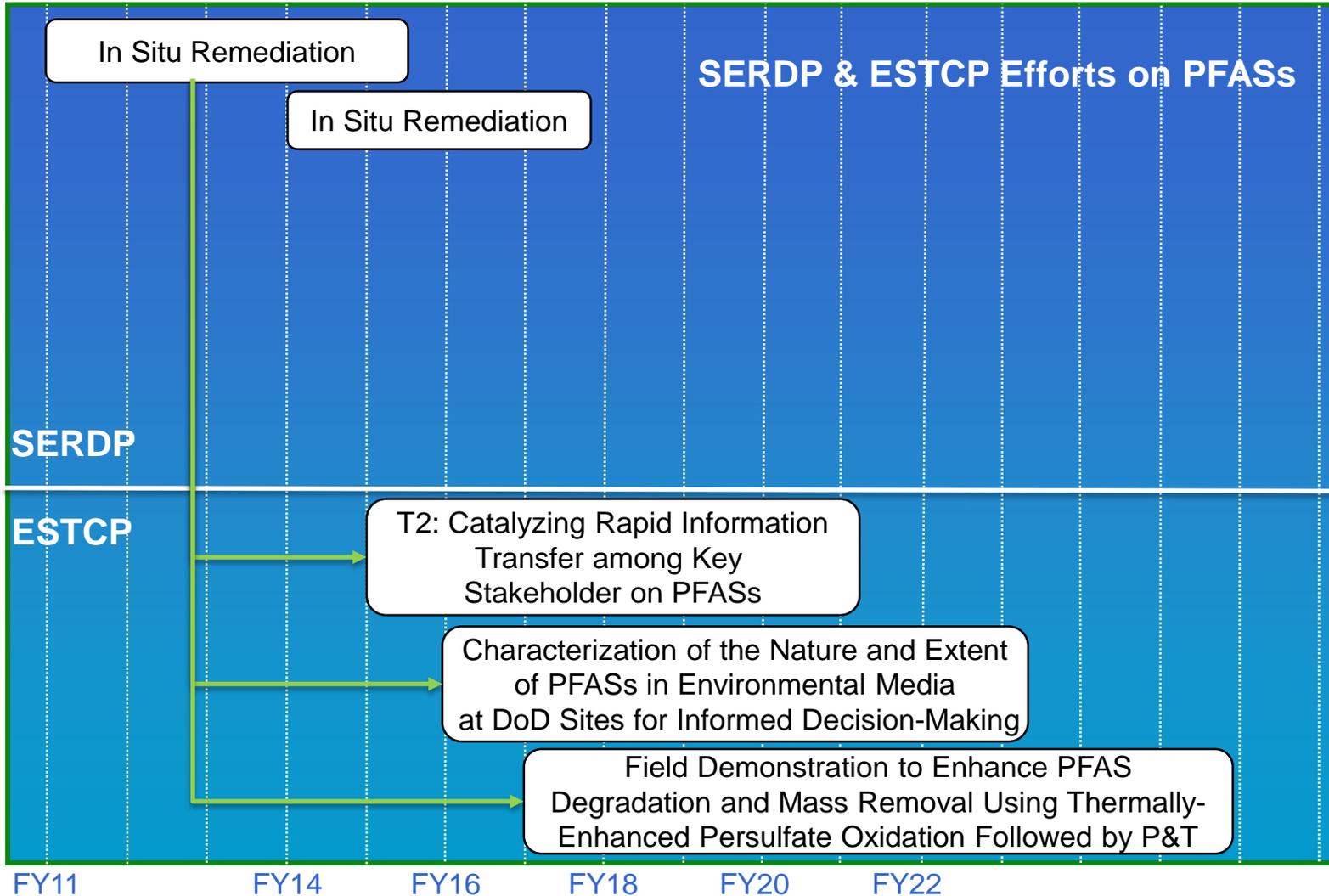
Follow on SON intended to address development of remedial technologies more directly

Funded five projects

1. ER-2422: SEED: Bioaugmentation with vaults (Mahendra, UCLA) **(one year follow on)**
2. ER-2423: ISCO of sorbed contaminants (Crimi, Clarkson) **(complete)**
3. ER-2424: Electrocatalytic and catalytic (Schaefer, CDM Smith) **(in progress)**
4. ER-2425: Coagulant enhanced sorption (Simcik, Minnesota) **(in progress)**
5. ER-2426: In situ chemical reductive defluorination (Lee, Purdue) **(in progress)**

FY11

FY14

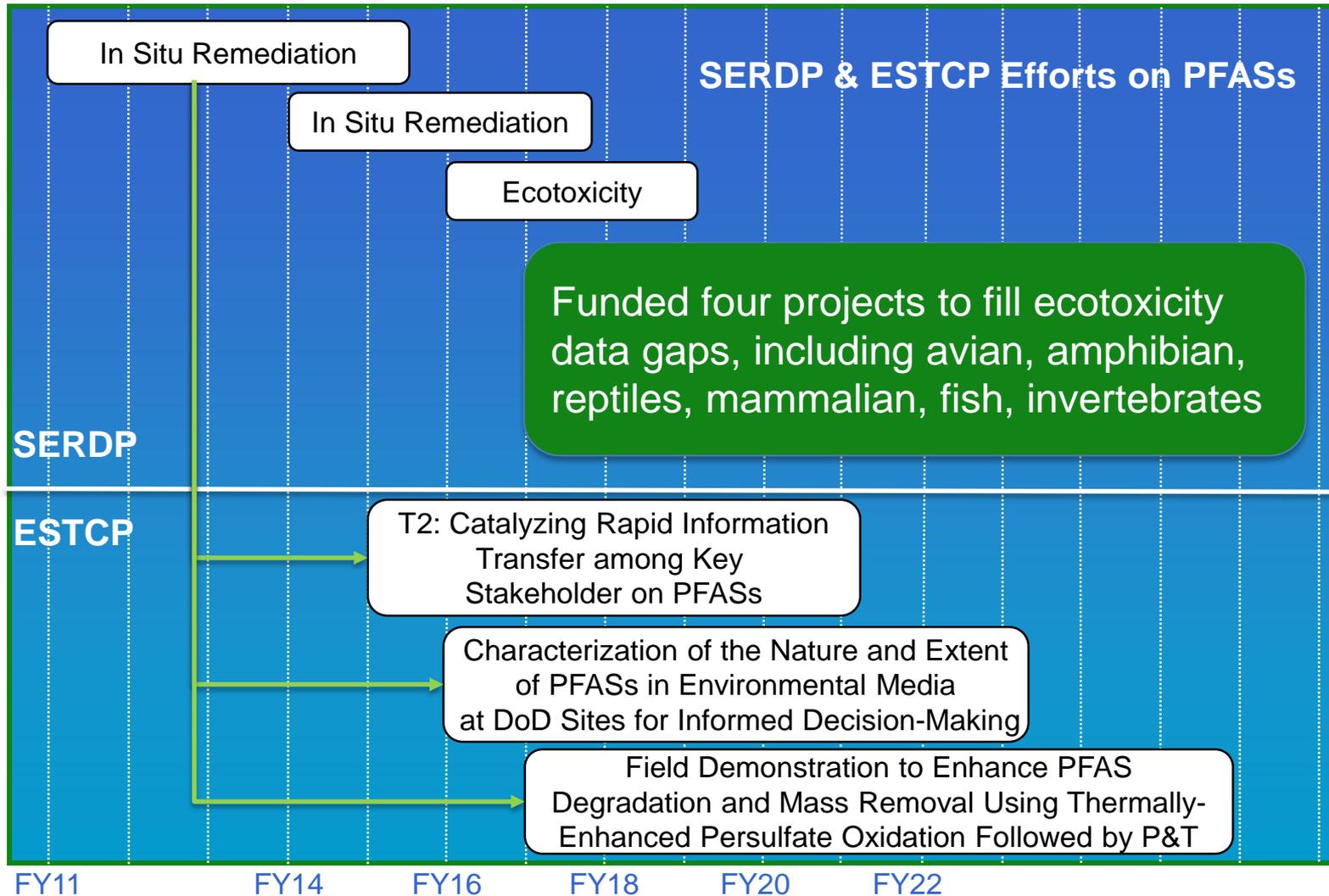


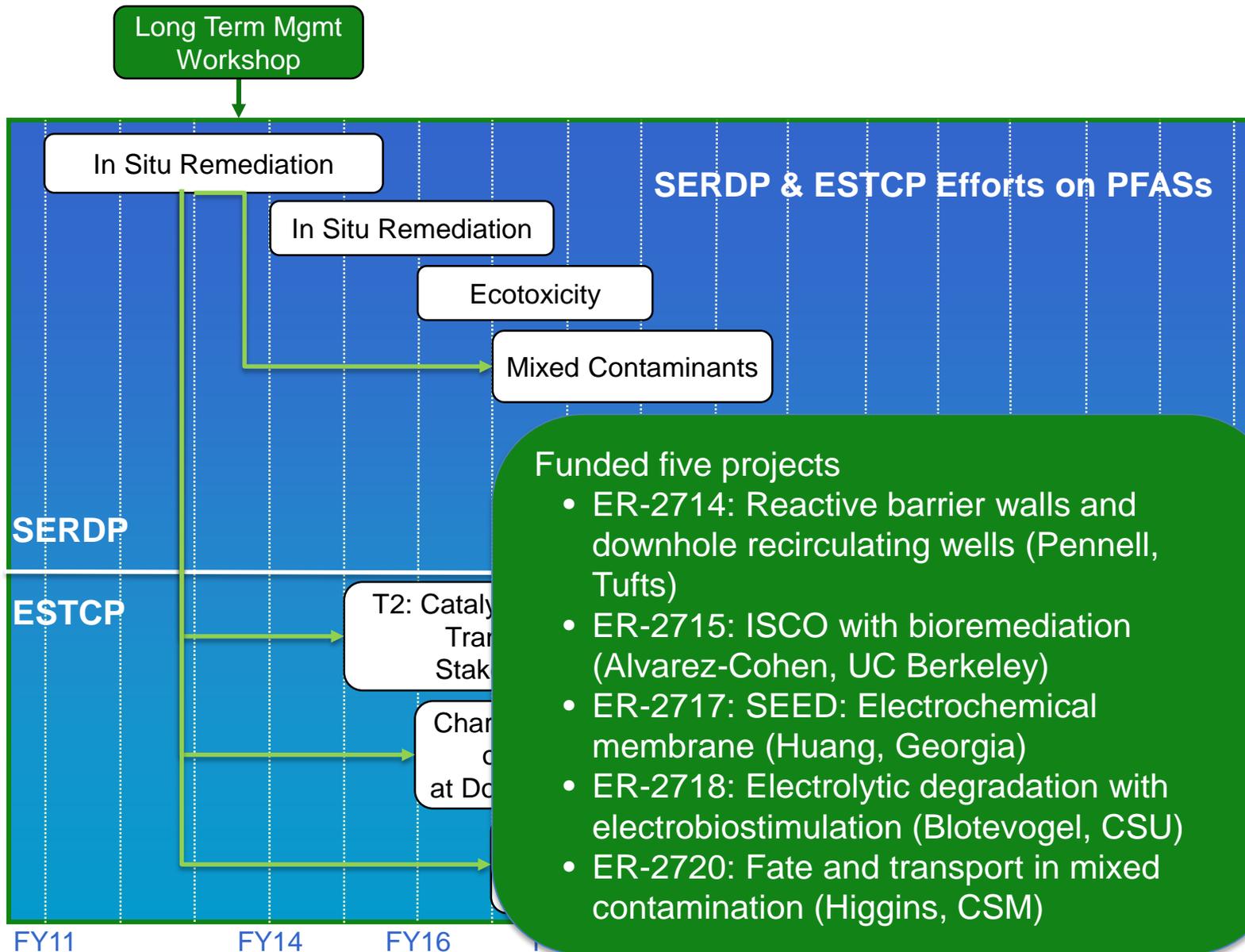
# Catalyzing Rapid Information Transfer Among Key Stakeholders on PFASs at Contaminated Military Sites

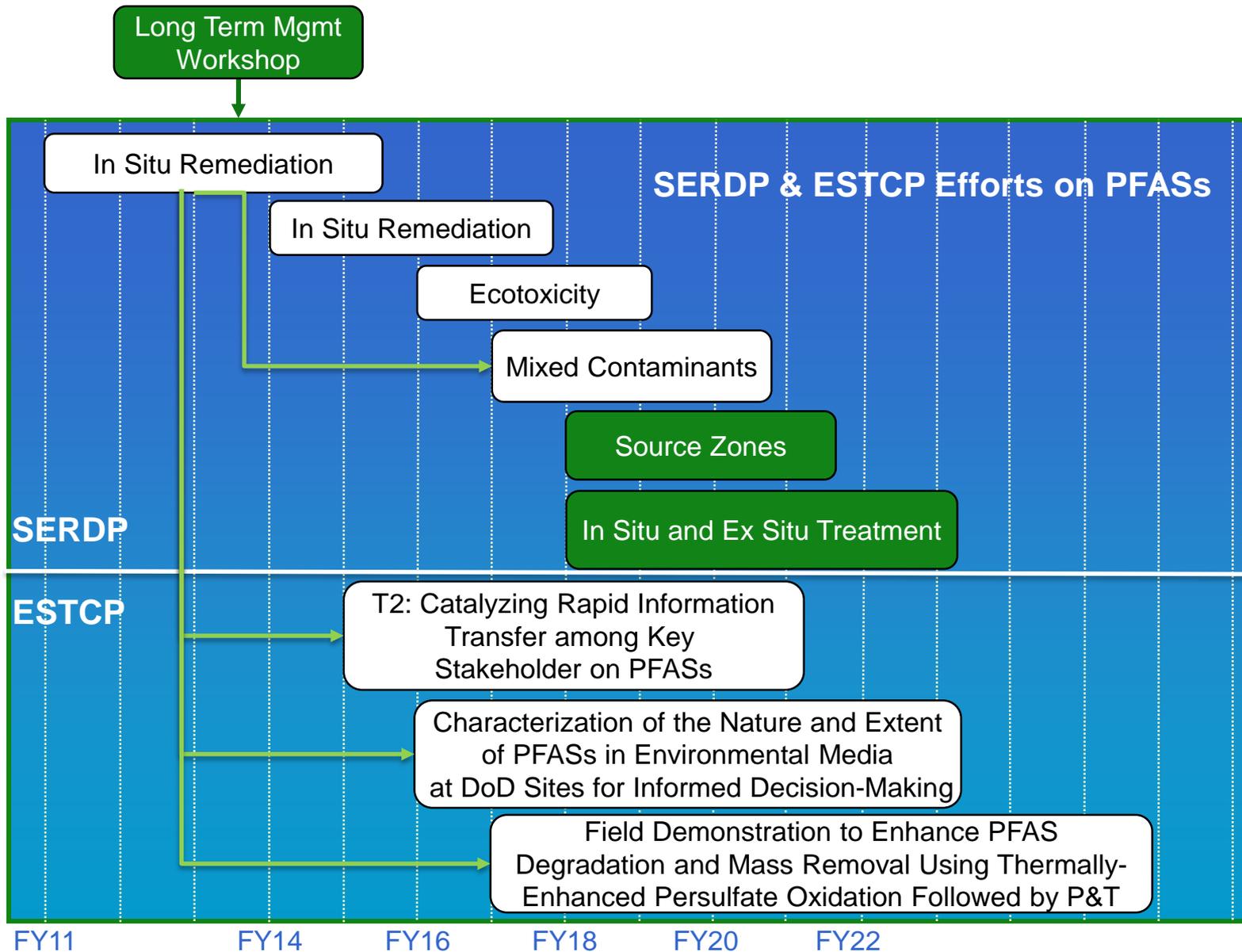
- Performers
  - Jennifer Field, OSU; Chris Higgins, CSM; Rula Deeb, Geosyntec Consultants
- Objectives
  - Expedite the transfer of knowledge regarding PFASs that occur at military sites as well as how PFASs can be reliably measured in environmental media
- Project benefits
  - FAQ and Reference Document provide efficient transfer of basic knowledge on PFASs and awareness of issues to RPMs
  - Improved coordination between vendor laboratories and synthesis labs (Wellington) to bring requisite materials for quality data to market faster
  - Uniform understanding of site characterization targets for improved remedial design that minimize future liabilities
  - Implementation of analytical strategies will result in improved interactions with regulators
  - With +10 locations at each military site impacted by PFASs, project likely to impact all sites
  - FAQ Documents to be posted soon
  - Short course at upcoming SERDP & ESTCP Symposium

# Characterization of the Nature and Extent of PFASs in Environmental Media at DoD Sites for Informed Decision-Making

- Performers
  - John Kornuc, NAVFAC EXWC; Tim Appleman, NAVFAC EXWC; Chuck Newell, GSI; Jennifer Field, OSU; Chris Higgins, CSM; Graham Peaslee, University of Notre Dame
- Demonstration objectives
  - Determine presence of PFAS source zone(s), differentiate AFFF and non-AFFF sources, and demonstrate particle-induced gamma ray emission spectroscopy (PIGE) as cost-effective field screening tool
- Project benefits
  - Assist RPMs to develop more accurate conceptual site models (CSMs) by identifying PFASs that define source zones and the composition of plumes. These CSMs can help inform the selection of mitigation and remediation strategies, not just at the sites studied, but at all DoD sites
  - Final documents and training material to be completed in 2018







# SON: Improved Understanding of PFAS Source Zones

- **Objective:** *Improve our understanding of PFASs in source zones resulting from the use of AFFF formulations*
  - Increase understanding of key characteristics of AFFF source zone areas that affect the risk that PFASs pose to groundwater quality
  - Develop tools and methods to better characterize key source zone properties
  - Investigate nature and permanence of PFAS retardation mechanisms, and potential use of these mechanisms in natural or enhanced attenuation
  - Fill key data gaps regarding biotransformation and transport of PFASs in AFFF source zones
  - Develop analytical or mathematical tools to predict fate and impacts of PFASs in source zones and potential for continuing releases to groundwater plumes

# SON: Improved Understanding of PFAS Source Zones

- **Objective:** *Improve our understanding of PFASs in source zones resulting from the use of AFFF formulations*

## 5 proposals selected subject to SAB approval

- Better understanding of source impact of air-water interface
- Characterization of transport, phases, and mobility as a function of key hydraulic parameters
- Understand how processes change over time and with AFFF composition and mass
- Better understand sequestration mechanisms and abiotic/biotic transformations
- Capitalize on large field database to understand transport and biotransformation
- Develop and validate models and decision tools for key processes

# SON: In Situ and Ex Situ Remediation of PFAS Contaminated Groundwater

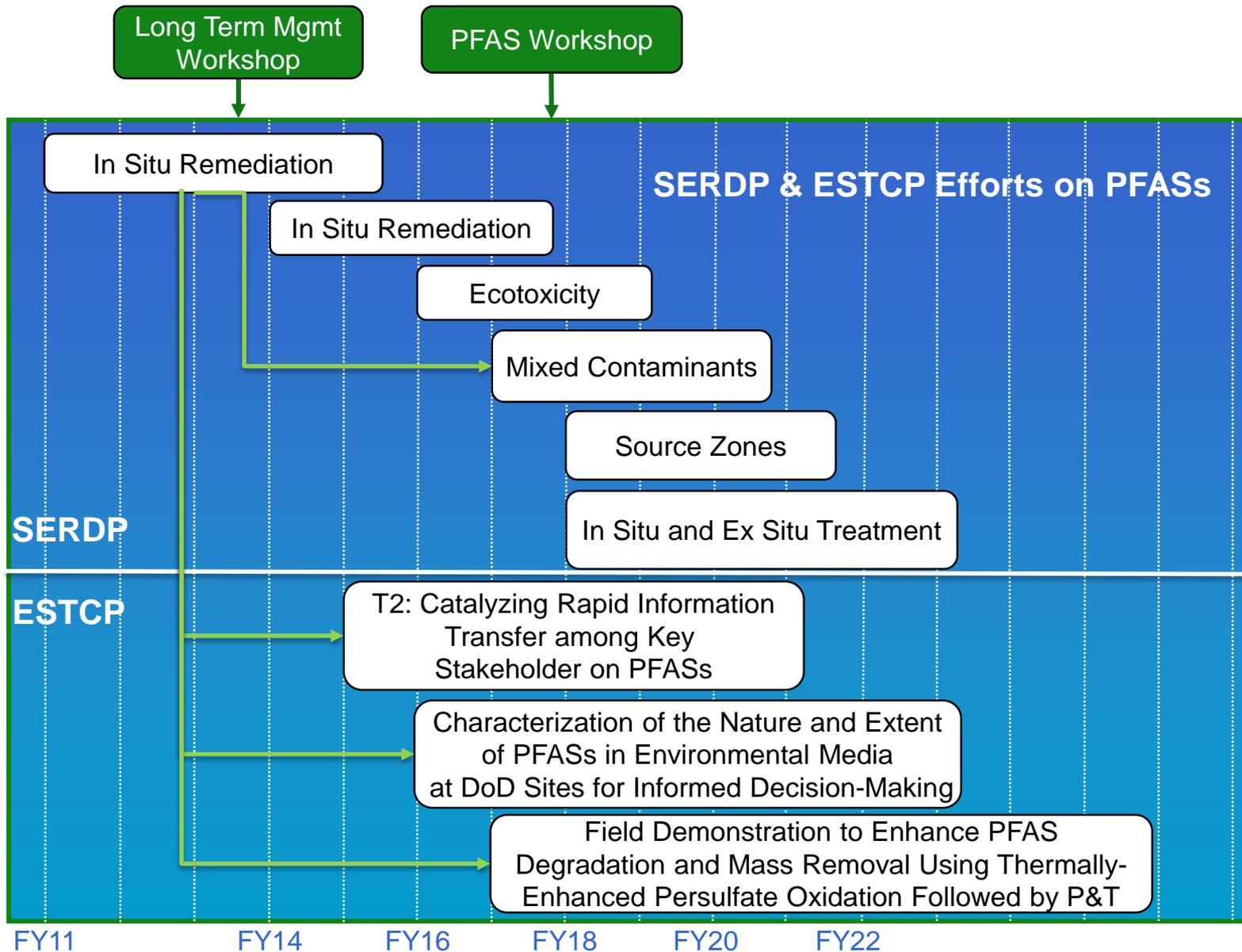
- **Objective:** *Develop cost-effective in situ or ex situ remedial technologies for groundwater contaminated with PFASs resulting from use of AFFF formulations*
  - Include consideration of impact of common co-contaminants on the remedial process
  - Develop treatment train approaches that cost-effectively treat PFASs and facilitate treatment of co-contaminants

# SON: In Situ and Ex Situ Remediation of PFAS Contaminated Groundwater

- **Objective:** *Develop cost-effective in situ or ex situ remedial technologies for groundwater contaminated with PFASs resulting from use of AFFF formulations*

## 11 proposals selected subject to SAB approval

- Combination of regenerable resin sorbents
- Treatment train using ion exchange with electrochemical or ultrasonic destruction
- Novel polymer adsorbents
- Electrochemical oxidation
- Electrocoagulation
- Cationic hydrophobic polymers
- Oxidation-organoclay adsorption-defluorination treatment train
- Electrically enhanced adsorption onto activated carbon
- Treatment train of in situ oxidation followed by direct plasma treatment and ion exchange
- Mesoporous organosilica sorbents
- Adsorption to proteins



# PFAS Workshop Overview

- In May 2017, SERDP and ESTCP sponsored a two-day workshop titled “Research and Development Needs for Management of DoD's PFAS Contaminated Sites”
  - 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 efficiency, and ultimately reduce the costs to manage sites
  - Summarize findings in a workshop report

# PFAS Workshop Major Findings

- Fate and transport properties
- Ecological risk characterization
- Treatment: Research needs
- Sampling and analytical procedures
- Treatment technology demonstrations
- Measurement and prediction
- Technology transfer needs

<https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/2017-Workshop-Report-on-Per-and-Polyfluoroalkyl-Substances>

# Fate and Transport Properties

- Evaluate PFAS Fate and Transport Processes Relevant to AFFF-Impacted Sites (Critical Priority)
- Evaluate Influence of Phase Partitioning on Fate and Transport (Critical Priority)
- Develop Predictive Fate and Transport Models and Key Parameters (High Priority)
- Develop Leachability Methods for PFAS in Soils and Sediments (High Priority)

# Ecological Risk Characterization

*Research into Bioavailability, Biomagnification and Toxicity of PFAS*

- Basic Research on Bioavailability of PFAS (Critical Priority)
- Determine Toxicity of PFAS Mixtures Based on Available Site Data (Critical Priority)
- Basic Research on Bioaccumulation and Biomagnification Pathways from Soils and Sediments to Higher Trophic Levels (Critical Priority)
- Evaluate Exposure Pathways to Threatened and Endangered Species of Concern (Critical Priority)
- Determine Population Level Impacts of PFASs on Aquatic and Terrestrial Ecosystems (High Priority)
- Develop and Validate Models for Bioaccumulation and Biomagnification for Soils, Sediments, and Water (High Priority)
- Evaluate Bioaccumulation and Biomagnification Processes and Exposure Pathways for Key PFASs Based on Existing DoD Sites (High Priority)

# Treatment

- In Situ Treatment (Critical Priority)
- Ex Situ Treatment (Critical Priority)
- On-Site Technologies for Concentrated PFAS Waste Streams (Critical Priority)
- Reductive Technologies (High Priority)

# Sampling and Analytical Procedures

- Develop and Demonstrate Standardized Sampling Procedures for PFAS (**Critical Priority**)
- Develop and Validate PFAS Analytical Methods (**Critical Priority**)
- Develop Forensic Methods for Source Tracking and Allocation of Emerging Contaminants (**High Priority**)

# Treatment Technology Demonstrations

- Demonstrate the Effectiveness and Sustainability of Thermal Destruction Technologies for Soils and Spent GAC and Resins (**Critical Priority**)
- Validate Destruction Technologies and their Applicability to Treat Concentrated PFAS Waste Streams (**Critical Priority**)
- Side-by-Side Comparisons of Treatment Technologies (**High Priority**)
- In Situ and Ex Situ PFAS Treatment (**High Priority**)

# Measurement and Prediction

- Measurement of PFAS Mass Flux Relative to Source Mass in the Vadose Zone and through Groundwater (Critical Priority)
- Demonstration and Validation of a Fate and Transport Model for PFAS (High Priority)

# Technology Transfer

- Technology Transfer White Paper (Critical Priority)
- Technology Transfer Smorgasbord (High Priority)
- Risk Communication Tools (High Priority)
- Granular Activated Carbon Status Paper (High Priority)

# Resources

- Workshop report  
<https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs/2017-Workshop-Report-on-Per-and-Polyfluoroalkyl-Substances>
- Summary of SERDP and ESTCP efforts  
<https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs>
- Future PFAS solicitations
  - Special SERDP solicitation (mid-September release)
    - Full proposal due in late October
  - SERDP regular solicitation (October 2017 for FY19 funding)
    - Preproposals due early January 2018
  - ESTCP solicitation (January 2018 for FY19 funding)
    - Preproposals due March 2018
  - Webinars will be provided shortly after solicitation release to summarize details and answer questions

# *SERDP & ESTCP Webinar Series*

For additional information, please visit  
<https://www.serdp-estcp.org/Featured-Initiatives/Per-and-Polyfluoroalkyl-Substances-PFASs>

## **Speaker Contact Information**

571-372-6398



## Q&A Session 2



# Fighting the Unbeatable Foe: Remediation of Groundwater Contaminated by PFASs with In Situ Chemical Oxidation

Dr. David Sedlak  
University of California, Berkeley



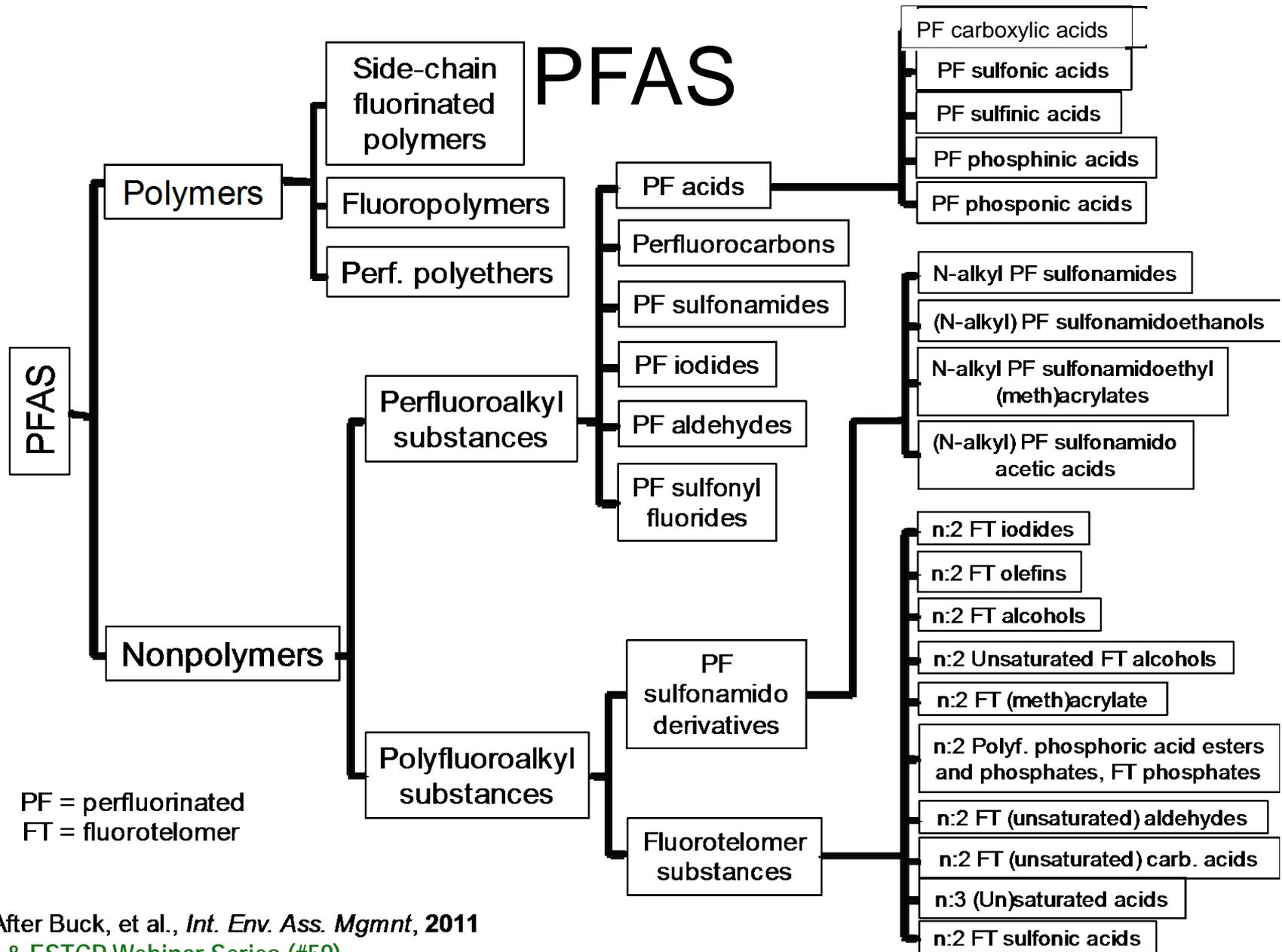
# Overview

- Background: PFAS, AFFF and ISCO
- Stepwise treatment
  - Conversion of polyfluoroalkyl substances to perfluoroalkyl carboxylic acids (PFCAs)
  - Mineralization of PFCAs
- Moving toward field application

PFAS: poly- and perfluoroalkyl substances

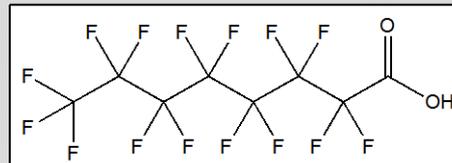
AFFF: aqueous film forming foams

ISCO: in situ chemical oxidation

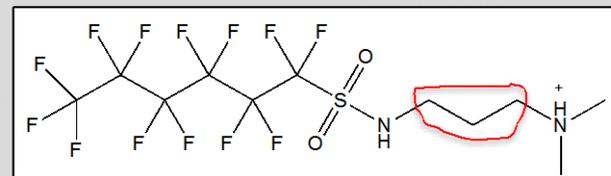
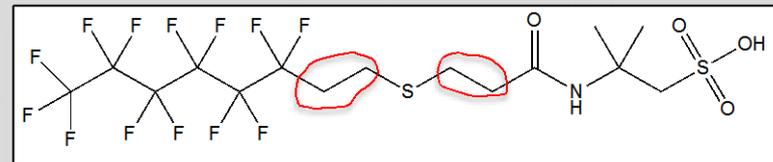


After Buck, et al., *Int. Env. Ass. Mgmt*, 2011

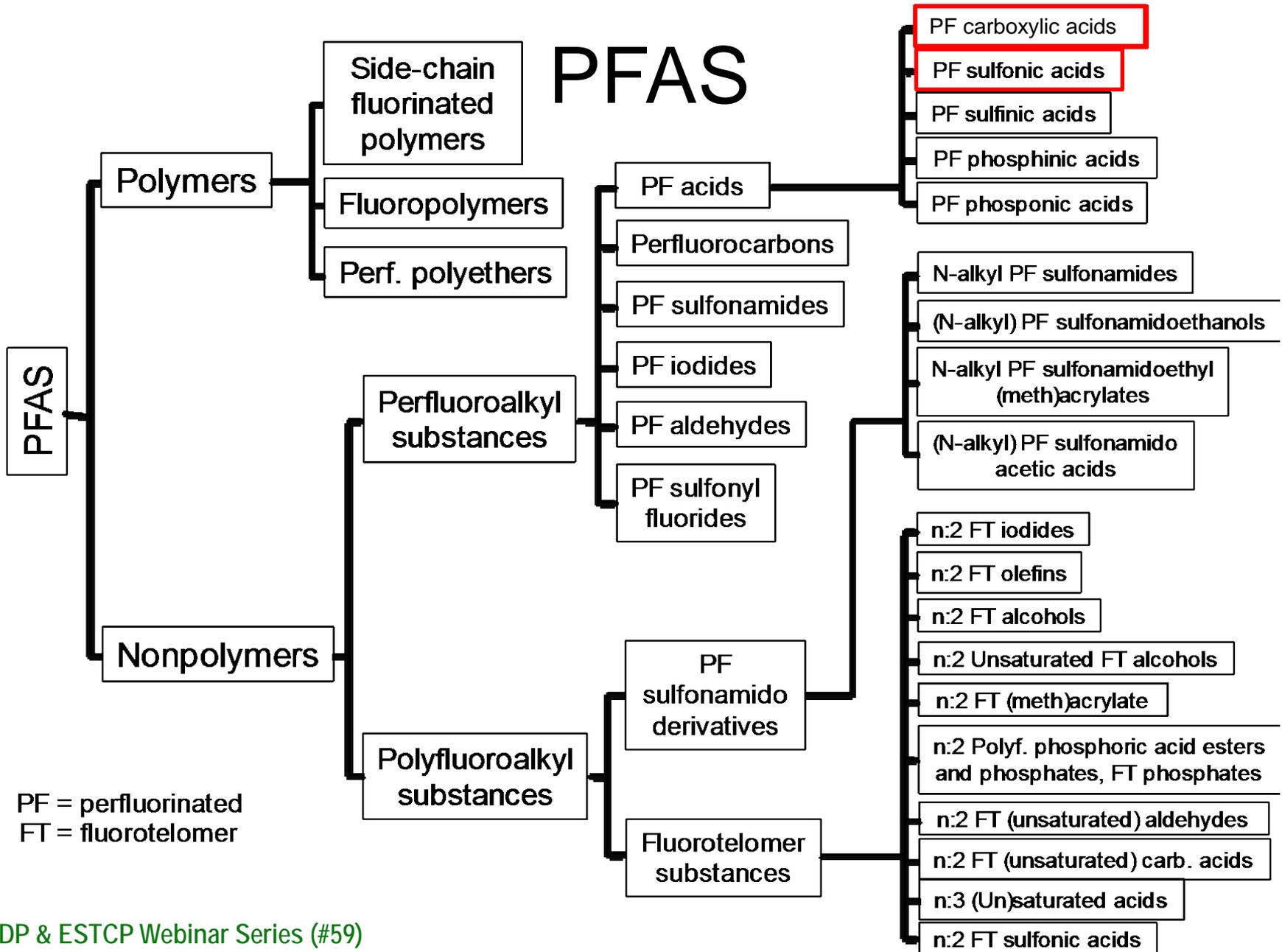
Perfluoroalkyl  
substances



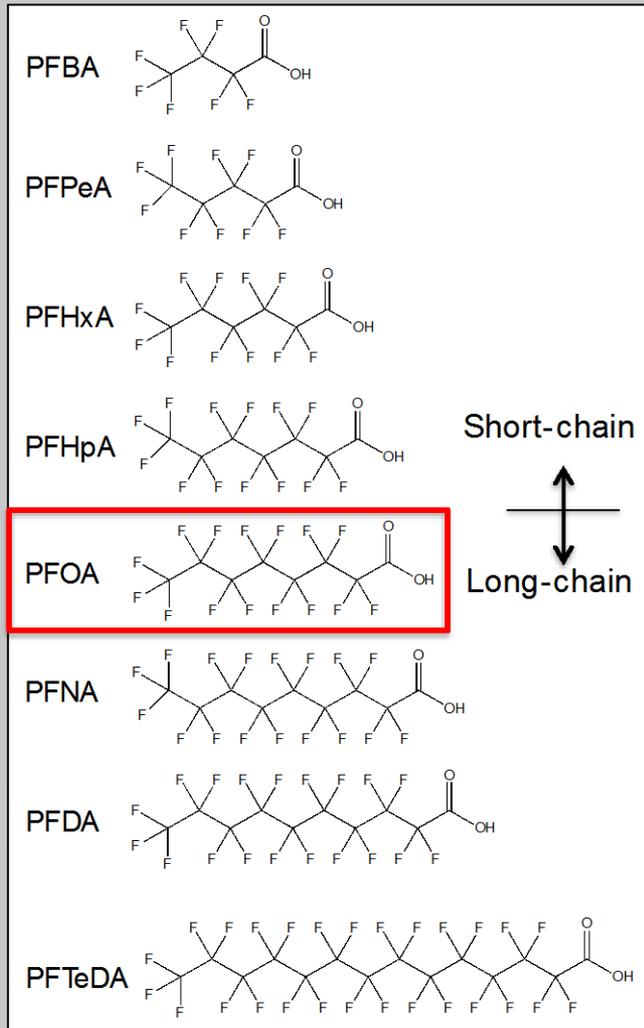
Polyfluoroalkyl  
substances



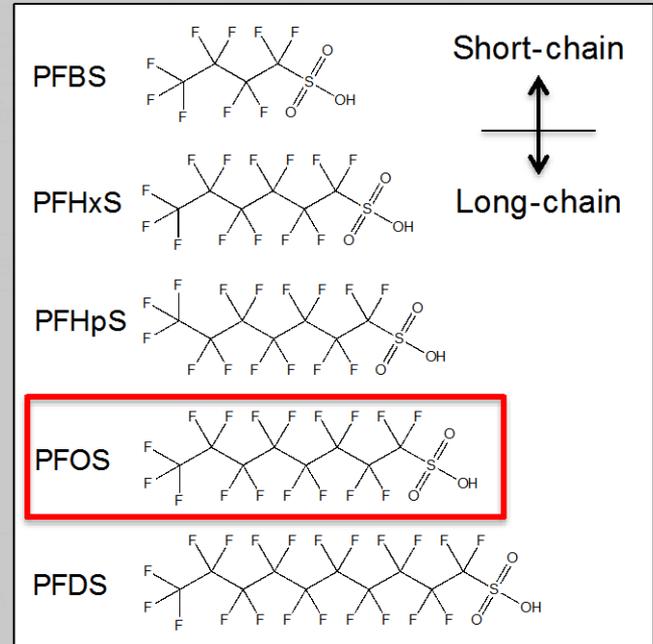
# PFAS



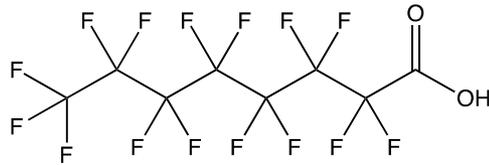
PF = perfluorinated  
 FT = fluorotelomer



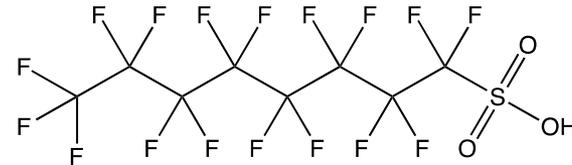
PF carboxylic acids  
PF sulfonic acids



# Treatment of Perfluoroalkyl Acids with Persulfate

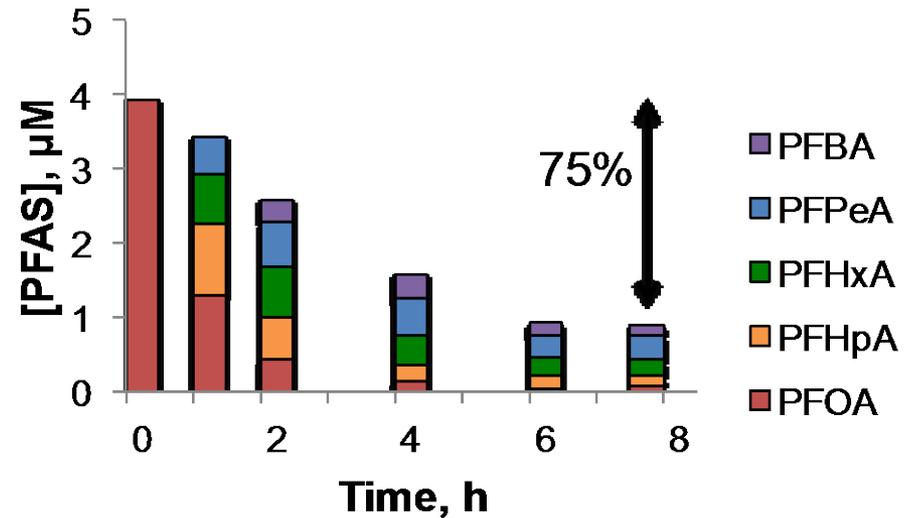
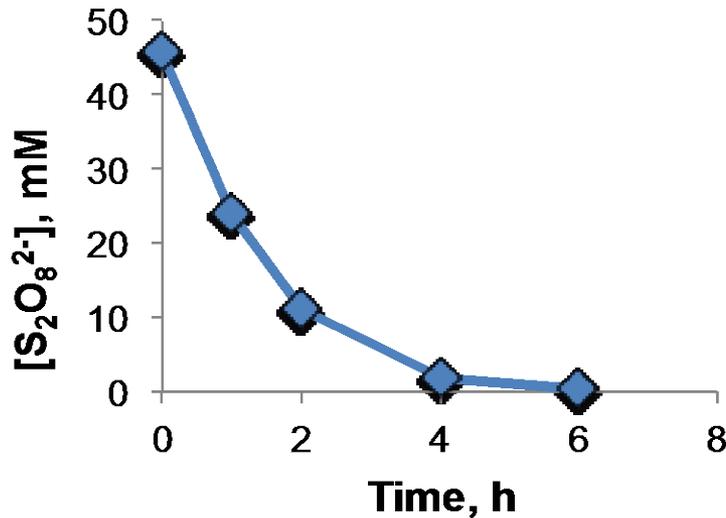


PFOA



PFOS

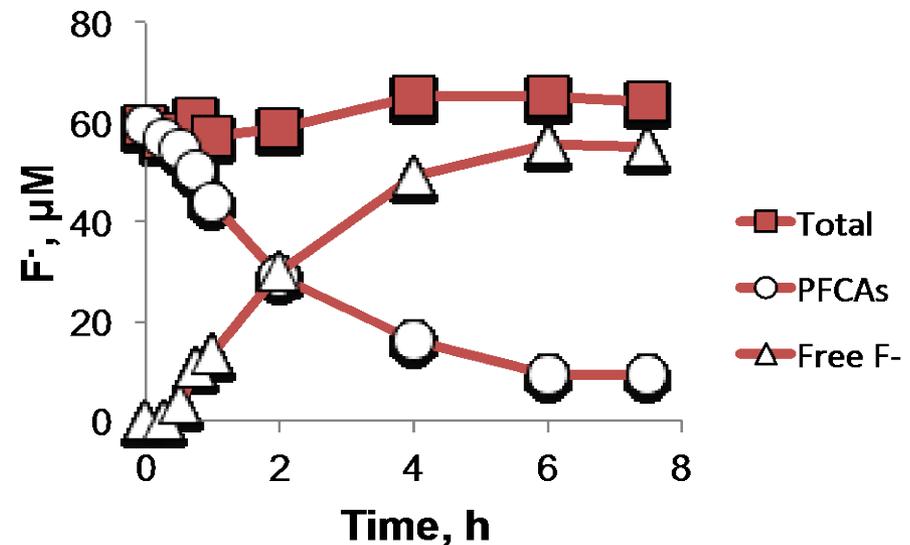
# PFOA in Deionized Water



## Conditions:

[S<sub>2</sub>O<sub>8</sub><sup>2-</sup>]<sub>0</sub> = 50 mM,  
 [PFOA]<sub>0</sub> = 4 μM  
 unbuffered (pH < 3) H<sub>2</sub>O,  
 T = 85° C

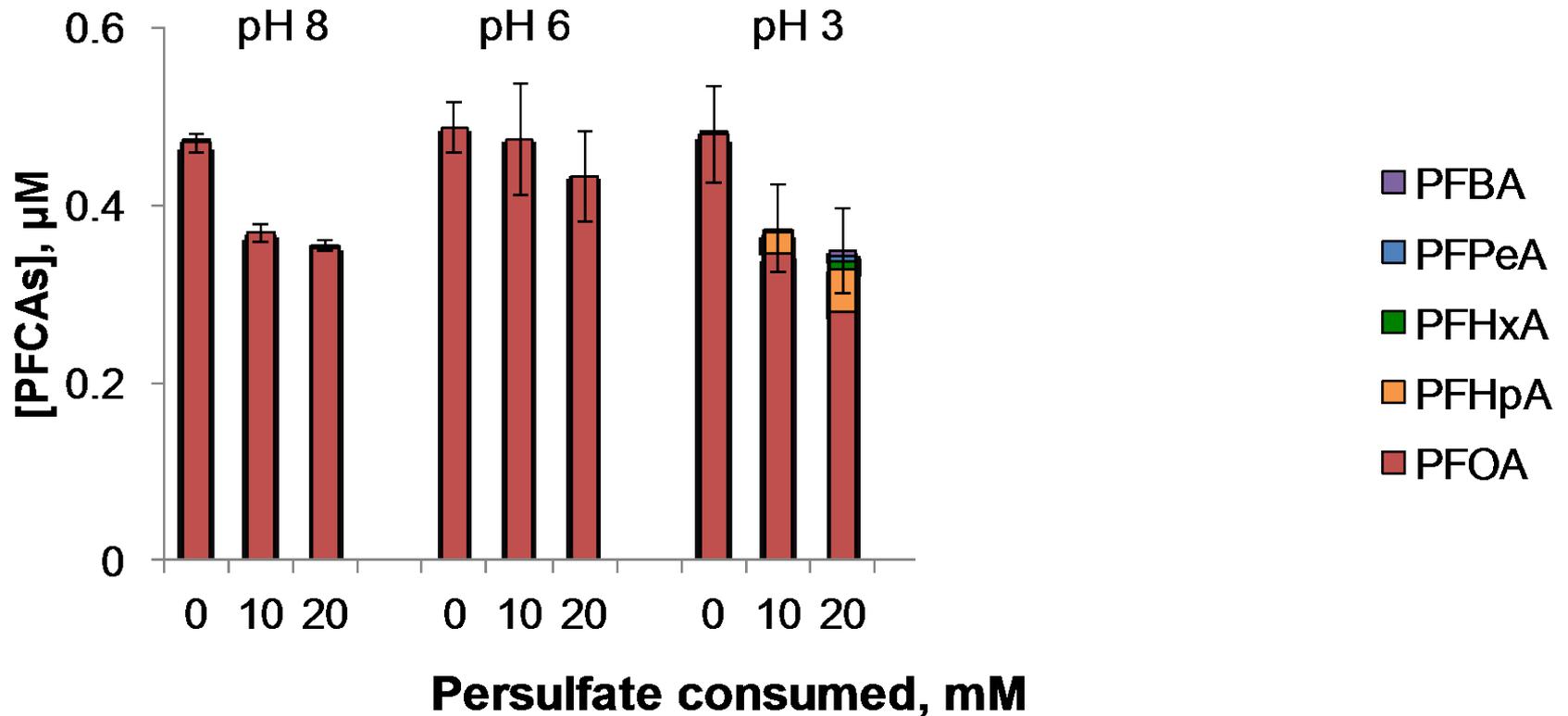
Bruton and Sedlak, in review



# Effect of pH

## Conditions:

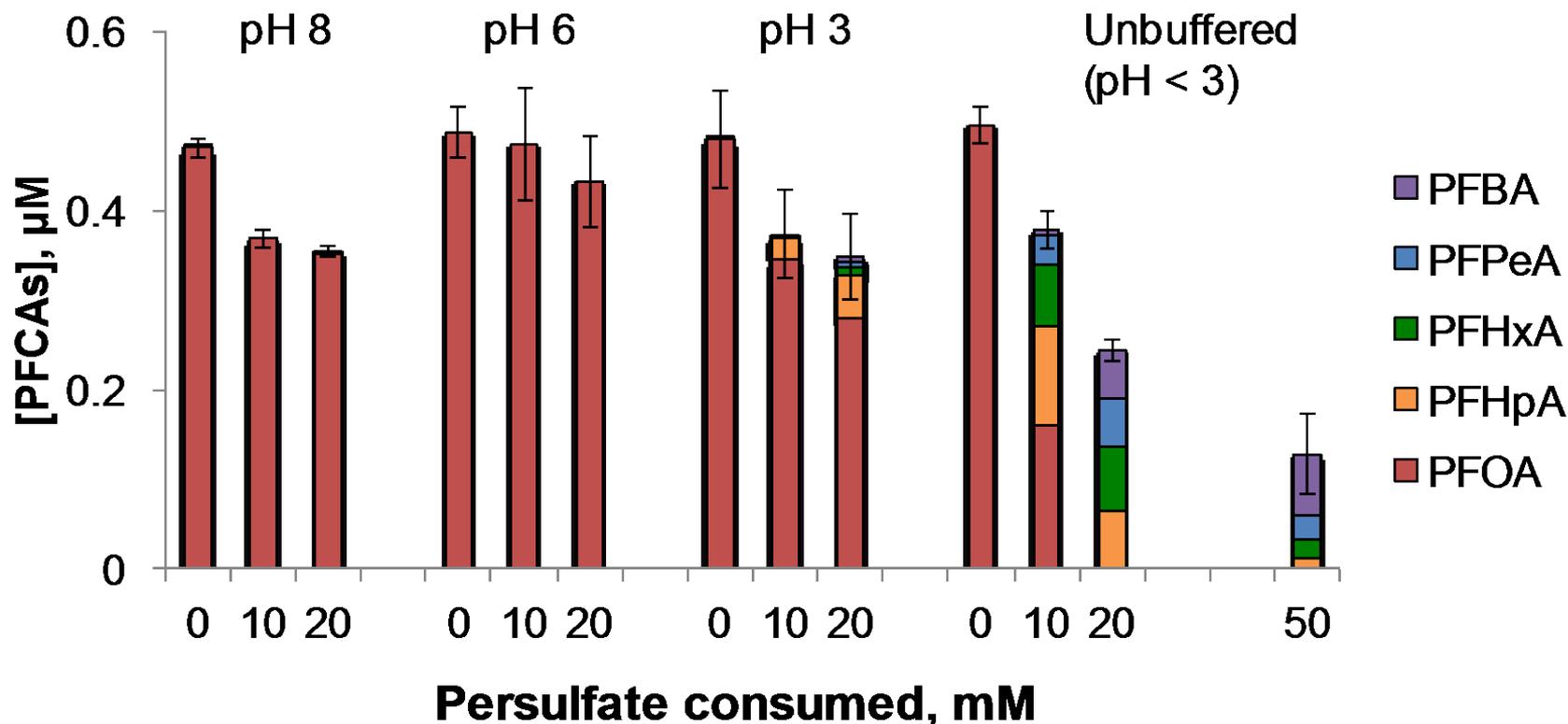
pH 8 borate (50 mM) or pH 3 H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O, T = 85° C



# Effect of pH

## Conditions:

pH 8 borate (50 mM) or pH 3 H<sub>2</sub>SO<sub>4</sub> in H<sub>2</sub>O, T = 85° C

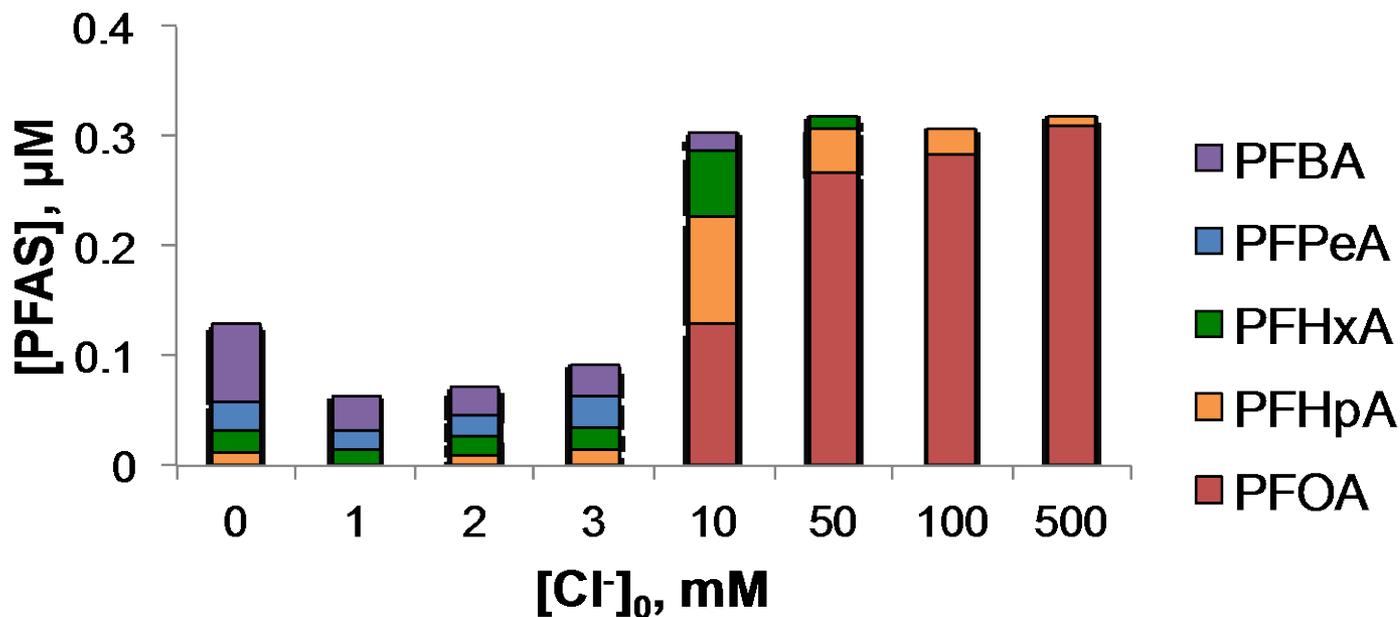


# Effect of Chloride

## Conditions:

$[S_2O_8^{2-}]_0 = 50 \text{ mM}$ , unbuffered ( $\text{pH} < 3$ )  $H_2O$ ,

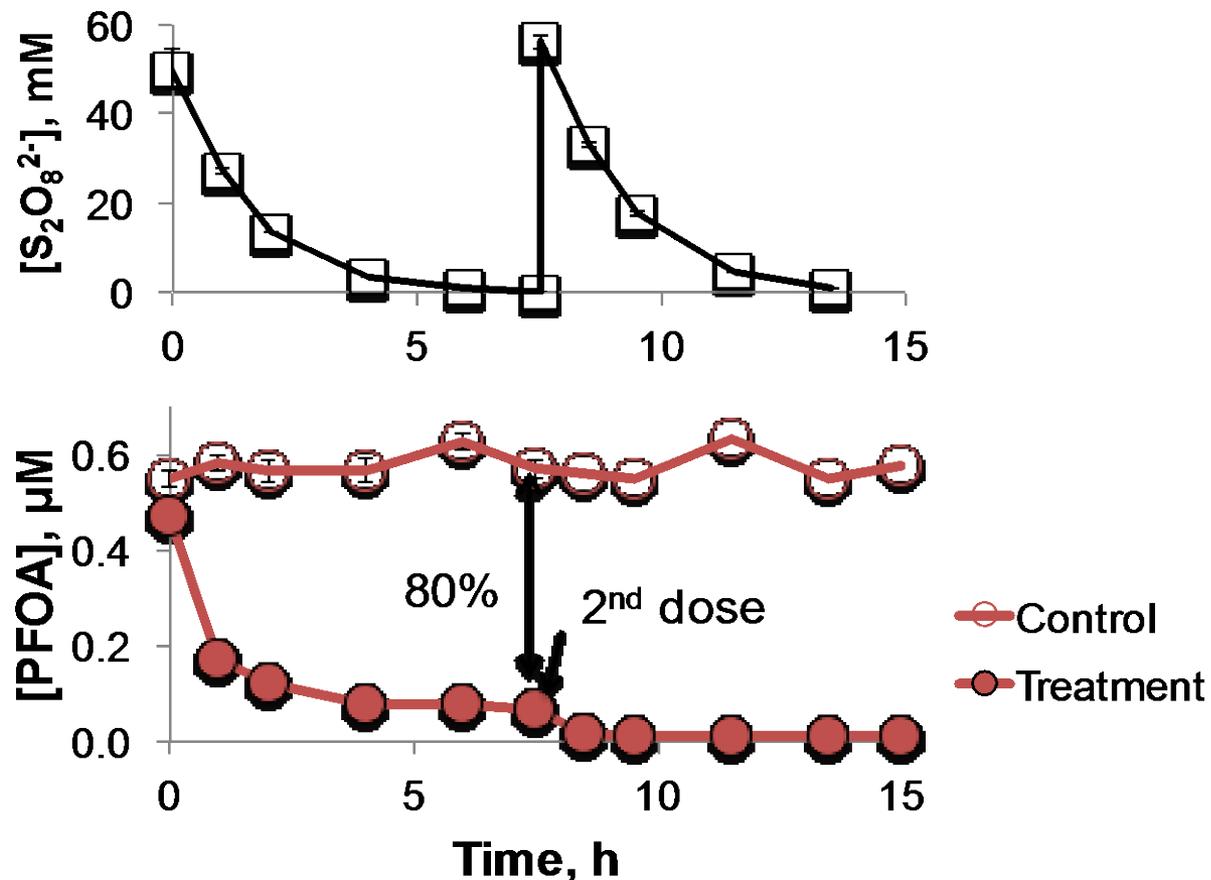
$T = 85^\circ \text{C}$



# Effect of Sediments

## Conditions:

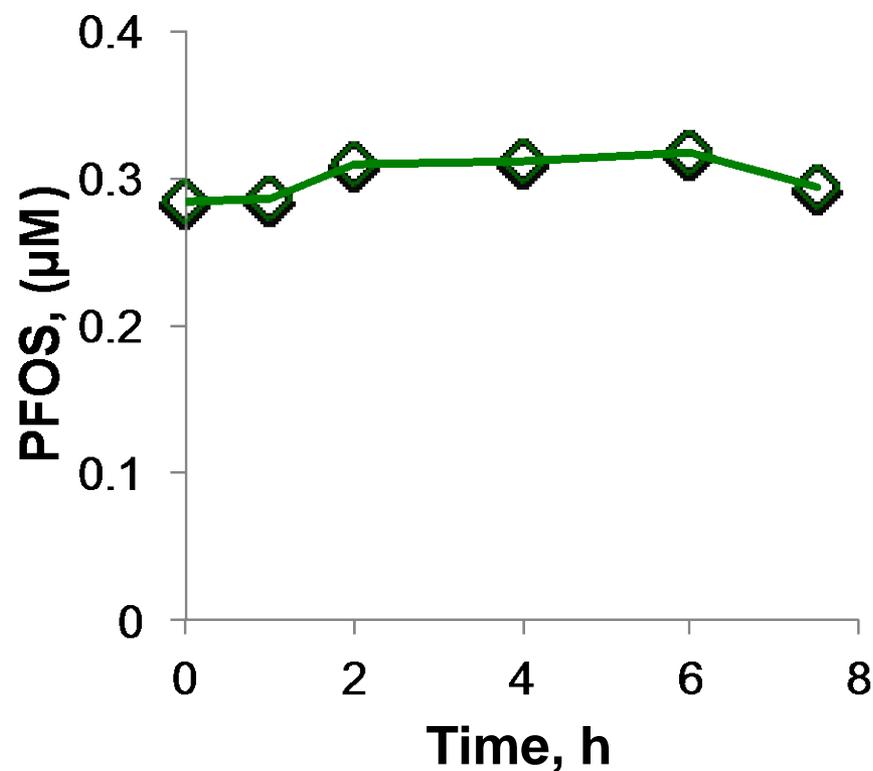
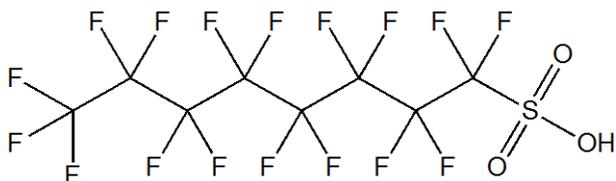
$[S_2O_8^{2-}]_0 = 50 \text{ mM} \times 2$ , unbuffered ( $\text{pH} < 3$ ),  $H_2O$ , 200 g/L aquifer sediments,  $T = 85^\circ\text{C}$



# PFOS in Deionized Water

## Conditions:

$[S_2O_8^{2-}]_0 = 50 \text{ mM}$ ,  
unbuffered ( $\text{pH} < 3$ )  $H_2O$ ,  
 $T = 85^\circ \text{C}$



# Treatment of AFFF with Persulfate



# AFFF Comes in Two “Flavors”

Manufacturer	3M	Ansul, Others
Process	Electrochemical fluorination	Fluorotelomerization
PFAS used	Perfluoralkane sulfonates <ul style="list-style-type: none"> <li>• PFOS, PFHxS, etc.</li> </ul> Perfluorinated carboxylates  Sulfonamide-based compounds	Fluorotelomer-based compounds

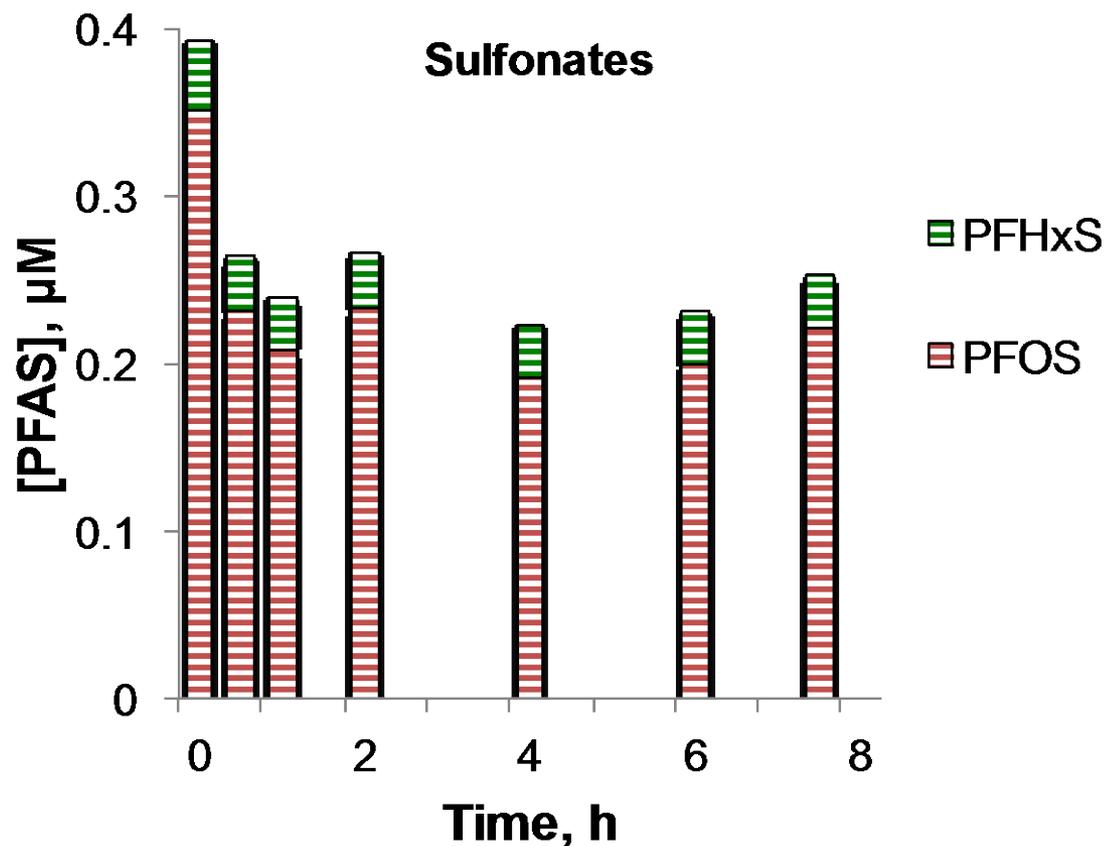
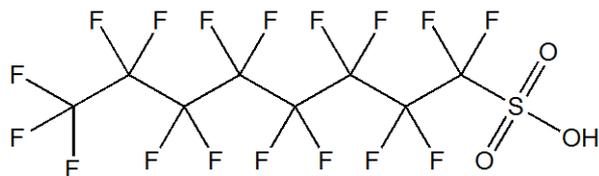


# 3M AFFF: Sulfonates

## Conditions:

$[S_2O_8^{2-}]_0 = 50 \text{ mM}$ ,  
unbuffered (pH < 3) MQ H<sub>2</sub>O

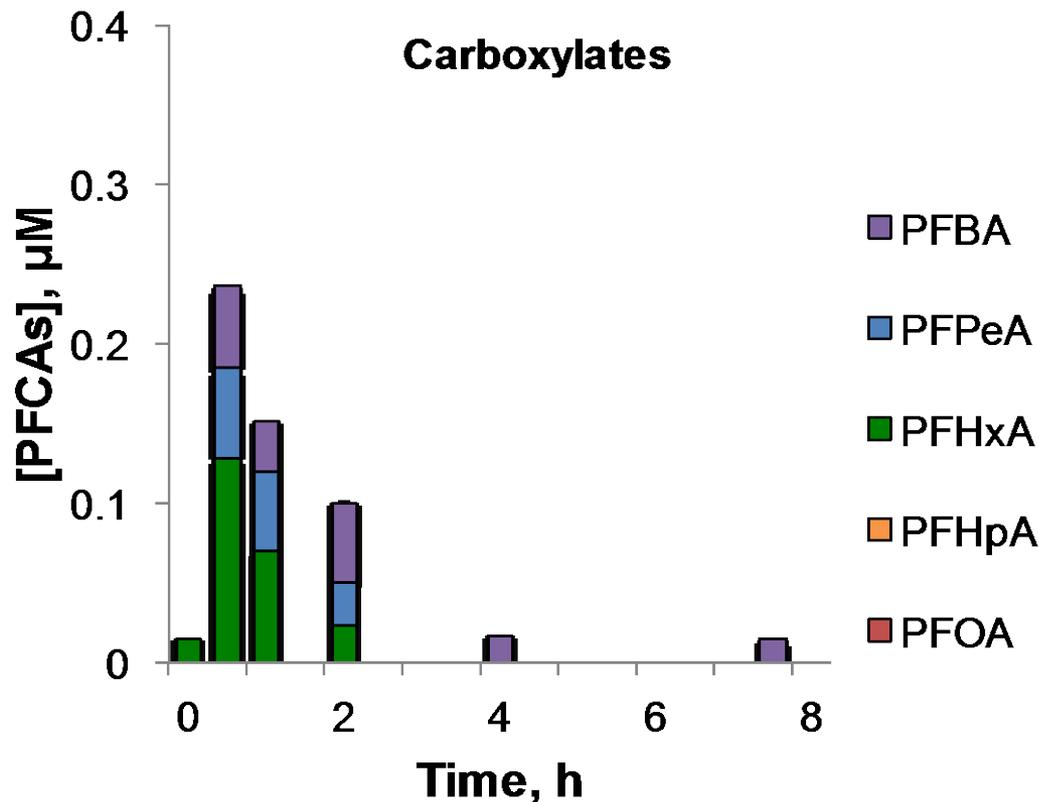
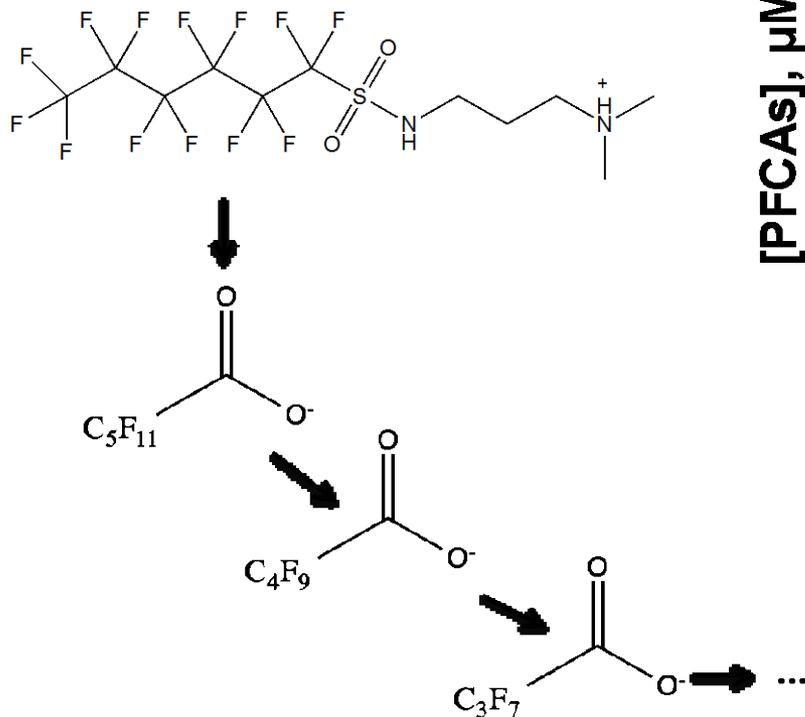
T = 85° C



# 3M AFFF: Carboxylates

## Conditions:

$[S_2O_8^{2-}]_0 = 50 \text{ mM}$ ,  
unbuffered (pH < 3) MQ H<sub>2</sub>O  
T = 85° C



# Next Steps

- ISCO field demonstration (ESTCP17 E-ER1-020)
  - Partners: U.S. Navy (John Kornuc), Geosyntec (Rula Deeb)
  - H<sub>2</sub>O<sub>2</sub> ISCO for heating and PFCA production
  - Acidification and persulfate ISCO for PFCA destruction
- Future field applications
  - PFCA-contaminated sites
  - Ansul AFFF-contaminated sites
  - Coupled ISCO and bioremediation (SERDP ER-2715; Lisa Alvarez-Cohen)

# Summary

- Persulfate or  $\text{H}_2\text{O}_2$  ISCO can convert polyfluorinated compounds into PFCAs
  - Complex AFFF “precursors” converted to PFCAs
  - Benefit: simplifies remediation process
- Persulfate mineralizes PFCAs
  - Only under acidic conditions ( $\text{pH} < 3$ )
  - Interference from chloride
  - Benefit: in situ remediation of PFCAs and Ansol AFFF
- Limitations
  - PFSAs, 3M AFFF, high alkalinity,  $\text{Cl}^-$

# Final Thoughts

*To dream the impossible dream  
To fight the unbeatable foe  
To bear with unbearable sorrow  
To run where the brave dare not go...  
This is my quest  
To follow that star  
No matter how hopeless  
No matter how far*

## The Impossible Dream

Lyrics by Mitch Leigh



**UC BERKELEY**  
**SUPERFUND**  
RESEARCH PROGRAM  
SCIENCE FOR A SAFER WORLD



**NIEHS**



# *SERDP & ESTCP Webinar Series*

For additional information, please visit  
<https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201729>

## **Speaker Contact Information**

sedlak@berkeley.edu; 510-643-0256



# Q&A Session 3



The next webinar is on  
October 5, 2017

*New Resource Conservation Insights  
to Desert Environments*



## Survey Reminder

*Please take a moment to complete the survey that will pop up on your screen when the webinar ends*

