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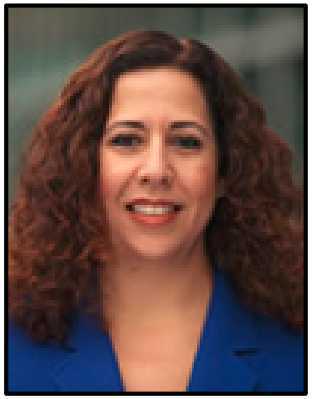
Managing Aqueous Film Forming Foam (AFFF) Impacts to Subsurface Environments and Assessment of Commercially Available Fluorine-Free Foams

October 17, 2019

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions



Rula A. Deeb, Ph.D.
Webinar Coordinator

SERDP DOD • EPA • DOE | ESTCP

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Mr. Timothy Tetreault, SERDP and ESTCP
- **Remediation of PFAS Contaminated Groundwater** (25 minutes + Q&A)
  Dr. Michelle Crimi, Clarkson University
- **Assessment of Commercially Available Fluorine-Free Firefighting Foams and Agents** (25 minutes + Q&A)
  Mr. Jerry Back, Jensen Hughes
- **Final Q&A session**

In Case of Technical Difficulties

- Use a compatible browser (Firefox, IE or Edge)
- If material is not showing on your screen or if screen freezes
  - Key in Ctrl + F5 to do a hard refresh of your browser
- If connecting to computer audio
  - Click the arrow next to the “Join Audio” button
  - Select test “Speaker and Microphone”
  - Follow prompts
- If you continue to experience difficulties, call into the conference line
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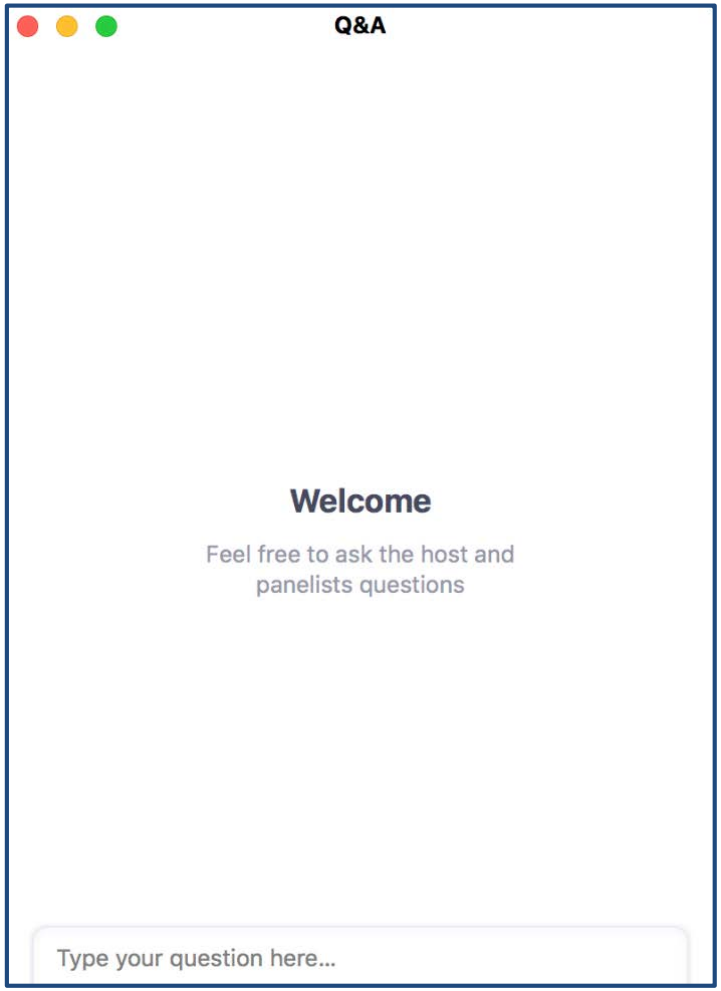
- Find the Q&A button on your control bar and type in your question(s)
- Make sure to add your organization name at the end of your question so that we can identify you during the Q&A sessions



SERDP and ESTCP Overview

Timothy Tetreault
Installation Energy and Water
Program Manager

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SERDP

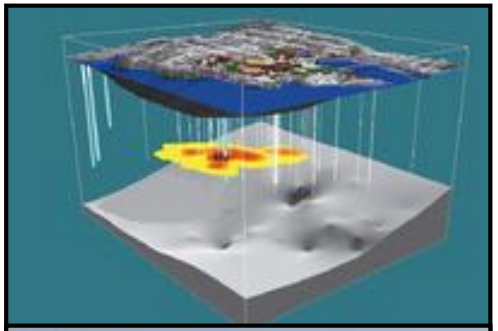
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced 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

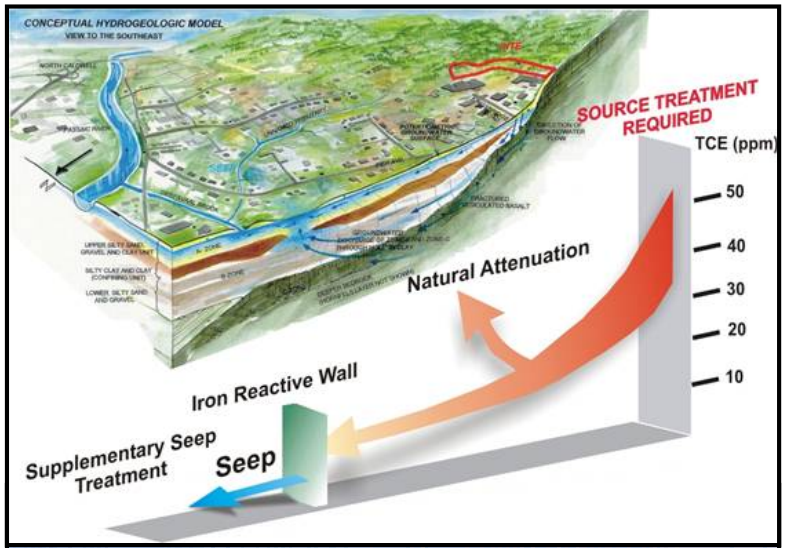
Program Areas

- Environmental Restoration
- Installation Energy and Water
- Munitions Response
- Resource Conservation and Resiliency
- Weapons Systems and Platforms



Environmental Restoration

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



Weapons Systems and Platforms

- Major focus areas
  - Surface engineering and structural materials
  - Energetic materials and munitions
  - Noise and emissions
  - Waste reduction and treatment in DoD operations
  - Lead free electronics

SERDP and ESTCP Webinar Series

Date	Topic
October 24, 2019	Advances in Managing Contaminated Groundwater Using High Resolution Site Characterization and Contaminant Mass Flux Reduction
October 31, 2019	Developing and Demonstrating Non-Toxic and Sustainable Coating Systems for Military Platforms
November 7, 2019	Overview of SERDP and ESTCP Efforts on Developing and Demonstrating PFAS Treatment Technologies
December 12, 2019	Monitoring and Remediating Groundwater Contaminated with Chlorinated Solvents

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

December 3-5, 2019

Washington Marriott Wardman Park

Registration is open

Remediation of PFAS Contaminated Groundwater

Michelle Crimi, Ph.D.
Clarkson University

SERDP DOD • EPA • DOE | ESTCP

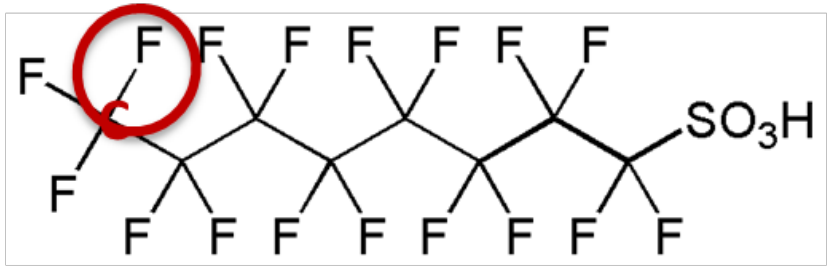
Agenda

- PFAS-contaminated groundwater
  - Treatment challenges
- Remediation approaches
  - Carbon-based sorption
  - Ion exchange
  - Destructive treatment
- Considerations for remedy selection
- Benefits to DoD

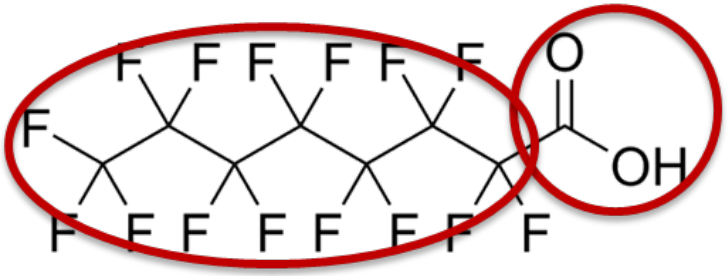
Challenges

- Chemical properties
- Mixtures
  - Can't detect/quantify some PFAS
  - Range of properties
- Precursors → Compounds of concern
  - Many can undergo transformation

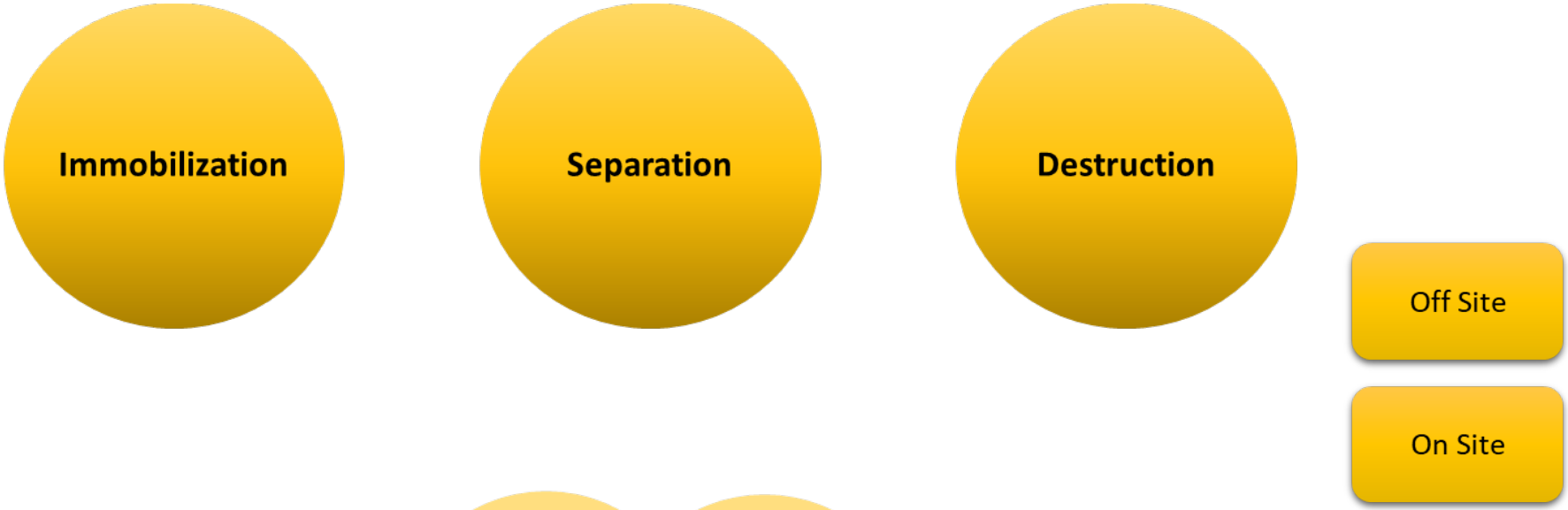
PFOS

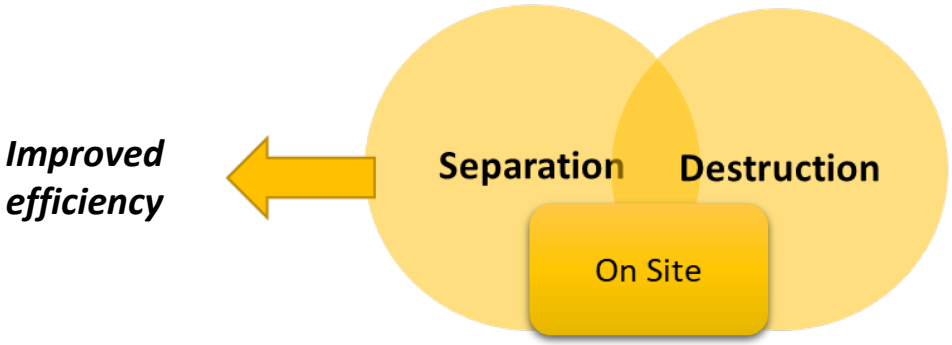


PFOA



Treatment Options





Treatment Options

- Separation
  - Filtration
    - Nanofiltration, reverse osmosis
  - Coagulation
  - Sorption
    - Granular activated carbon (GAC)
    - Carbon nanotubes, biomaterials
  - Ion exchange
    - Resins
    - Polymers, mineral materials
- Destruction
  - Chemical oxidation
  - Customized reductants
  - Electrochemical
  - Photochemical
  - Sonolytic
  - Plasma

TREATMENT TRAINS and COMBINED REMEDIES!

Examples of 2018 SERDP Projects

- Remediation of PFAS Contaminated Groundwater Using Cationic Hydrophobic Polymers as Ultra-High Affinity Sorbents
- Regenerable Resin Sorbent Technologies with Regenerant Solution Recycling for Sustainable Treatment of PFASs
- Electrically Assisted Sorption and Desorption of PFASs
- Molecular Design of Effective and Versatile Adsorbents for Ex Situ Treatment of AFFF-Impacted Groundwater
- Ex Situ Treatment of PFAS Contaminated Groundwater Using Ion Exchange with Regeneration
- Electrochemical Oxidation of Perfluoroalkyl Acids in Still Bottoms from Regeneration of Ion Exchange Resins
- Treatment of Legacy and Emerging Fluoroalkyl Contaminants in Groundwater with Integrated Approaches: Rapid and Regenerable Adsorption and UV-Induced Defluorination
- Combined In Situ / Ex Situ Treatment Train for Remediation of PFAS Contaminated Groundwater

CARBON-BASED SORPTION

Carbon-Based Sorption

- Ex situ pump-and-treat
- In situ injectable
- Large installations and point-of-entry or point-of-use

- Granular or powdered activated carbon
- Clays or blends
- Synthetics

Carbon-Based Sorption

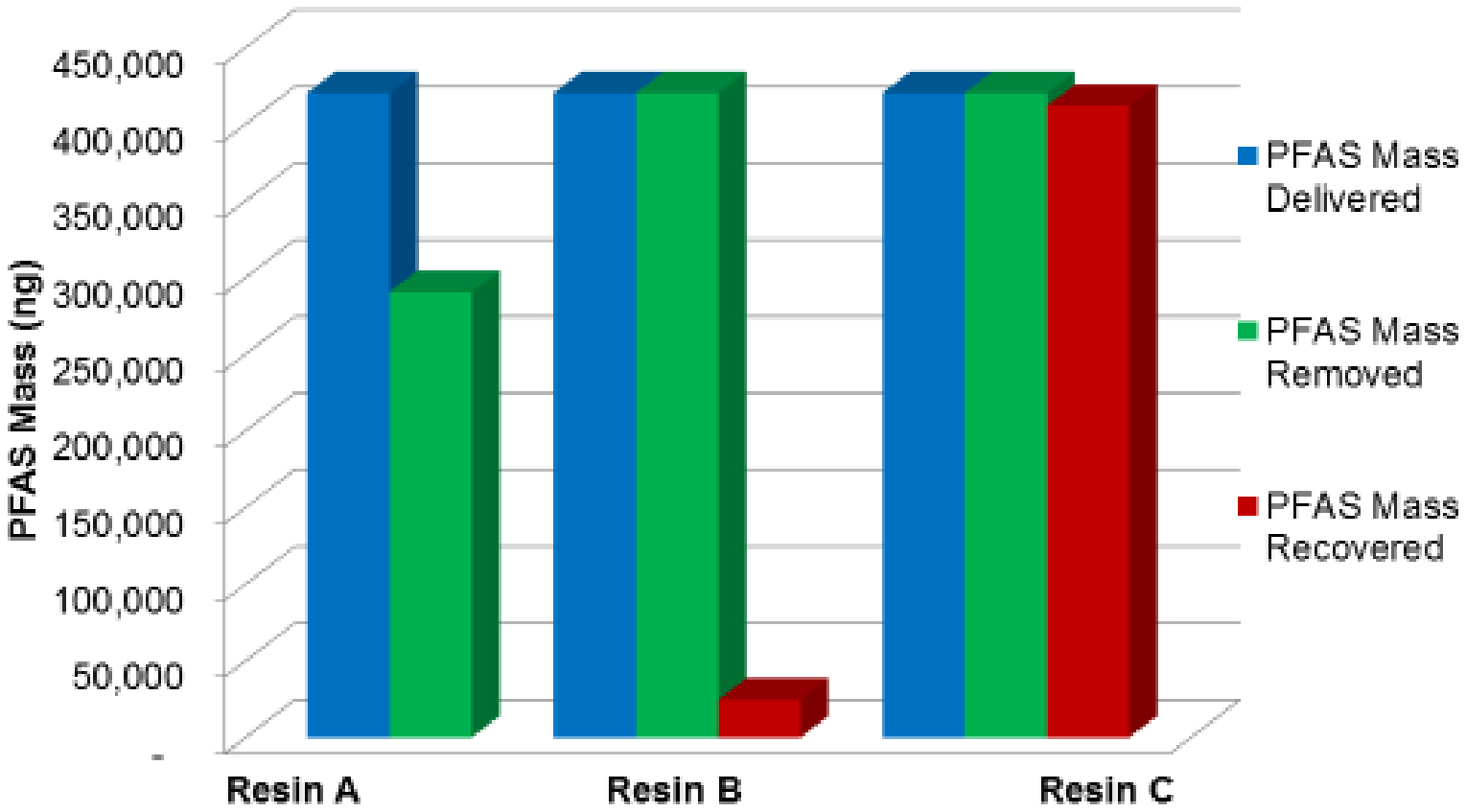
- Treatability testing essential
- Co-contaminants and precursors compete
- Less effective for small chain compounds
- Hemi-micelle and micelle formation
- Granular activated carbon (GAC) reuse

Carbon-based sorption is effective, but challenging to predict

ION EXCHANGE

Ion Exchange

Resin Adsorption/Regeneration from Column Testing

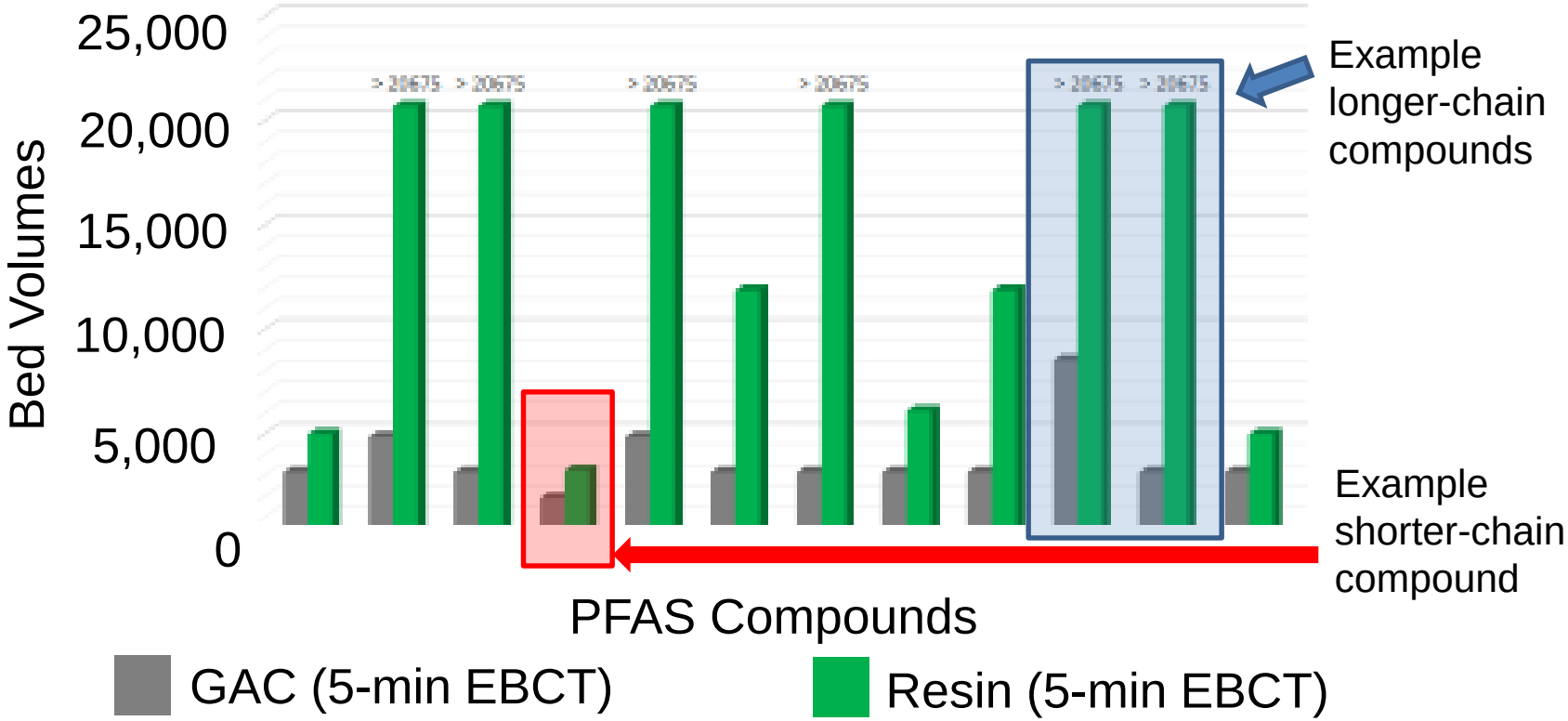


Sustainable Removal of Poly- and Perfluorinated Alkyl Substances (PFAS) from Groundwater Using Synthetic Media

Nathan Hagelin, Amec Foster Wheeler; Steve Woodard, ECT

Ion Exchange

Volume Treated Before Breakthrough



Resin outperformed GAC for many, but not all, compounds

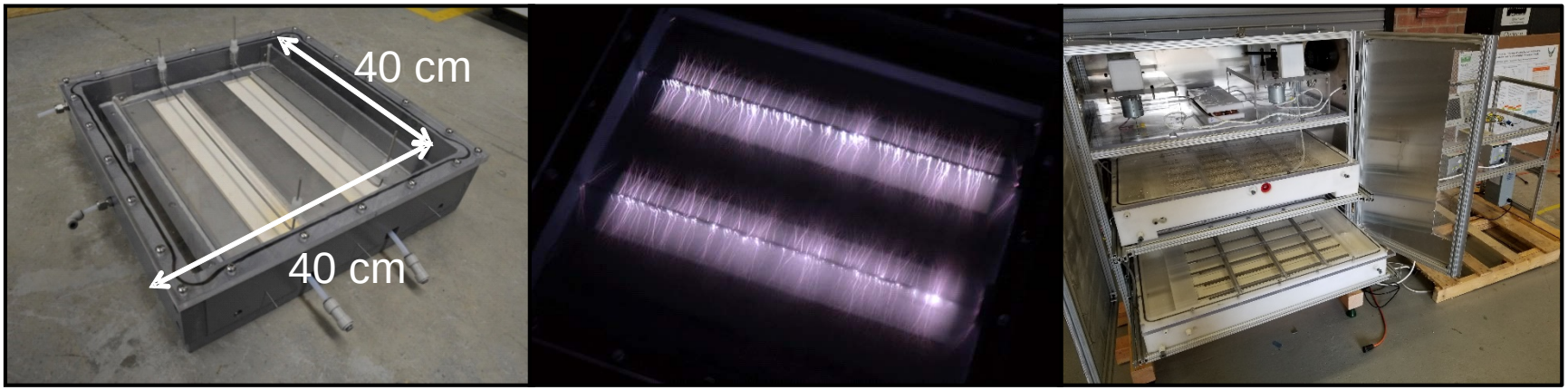
Note: EBCT = empty bed contact time

REDOX MANIPULATION

- Plasma
- Sonolysis
- Activated Persulfate
- Electrochemical
- Chemical Reduction
- Combinations

Plasma

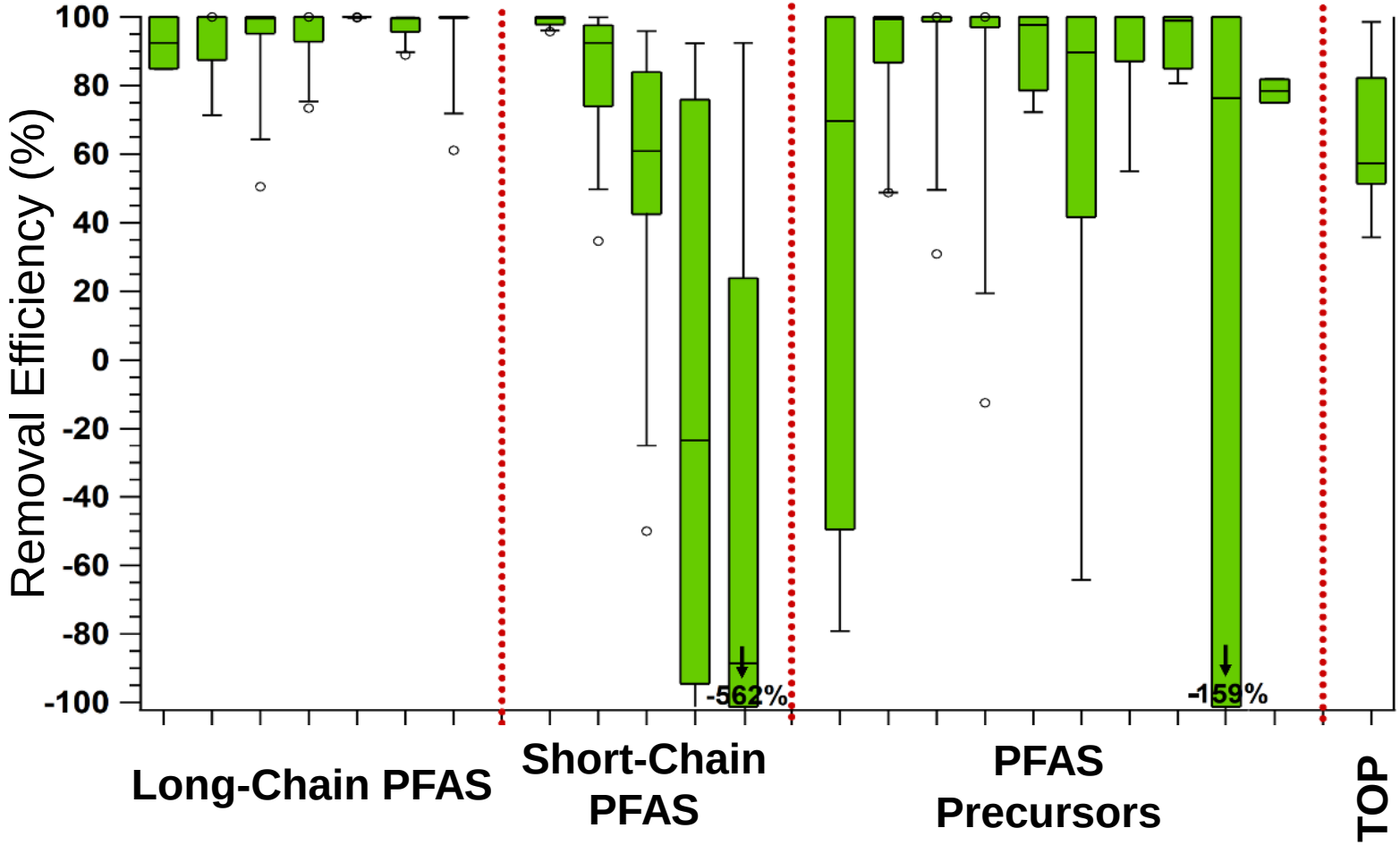
- Uses electricity to convert water into mixture of highly reactive species
  - $OH\bullet$, O, $H\bullet$, $HO_2\bullet$, $O_2\bullet^-$, H_2, O_2, H_2O_2 and aqueous electrons (e^-_{aq})



Plasma

Parameter	Range for 13 Samples
pH	5.3 - 8.0
Conductivity (uS/cm)	17.3 - 26,300
Turbidity (NTU)	< 1 - 20
Alkalinity, as $CaCO_3$ (mg/L)	10 - 550
Hardness, as $CaCO_3$ (mg/L)	BD - 1,130
Total organic carbon (mg/L)	0.11 - 10.8
Iron (mg/L)	BD - 2600
Manganese (mg/L)	8.6 - 5000
∑acids (mg/L)	0.3 - 500
∑sulfonates (mg/L)	0.3 - 950
Individual PFAAs (mg/L)	0.003 - 650
Total fluorine (mg-F/L)	98 - 4,900

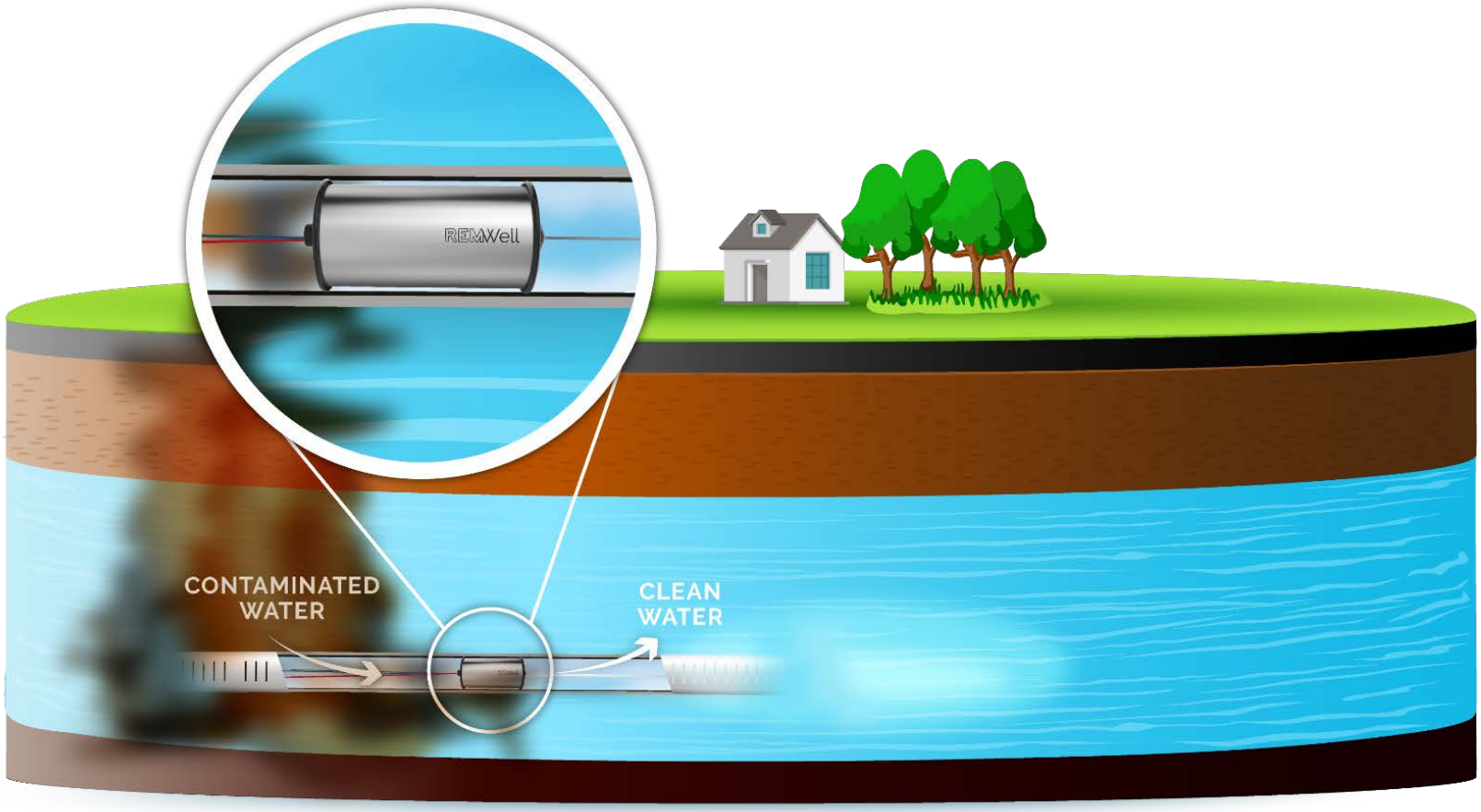
Plasma



Plasma treats PFAS rapidly, proceeding through short-chain intermediates

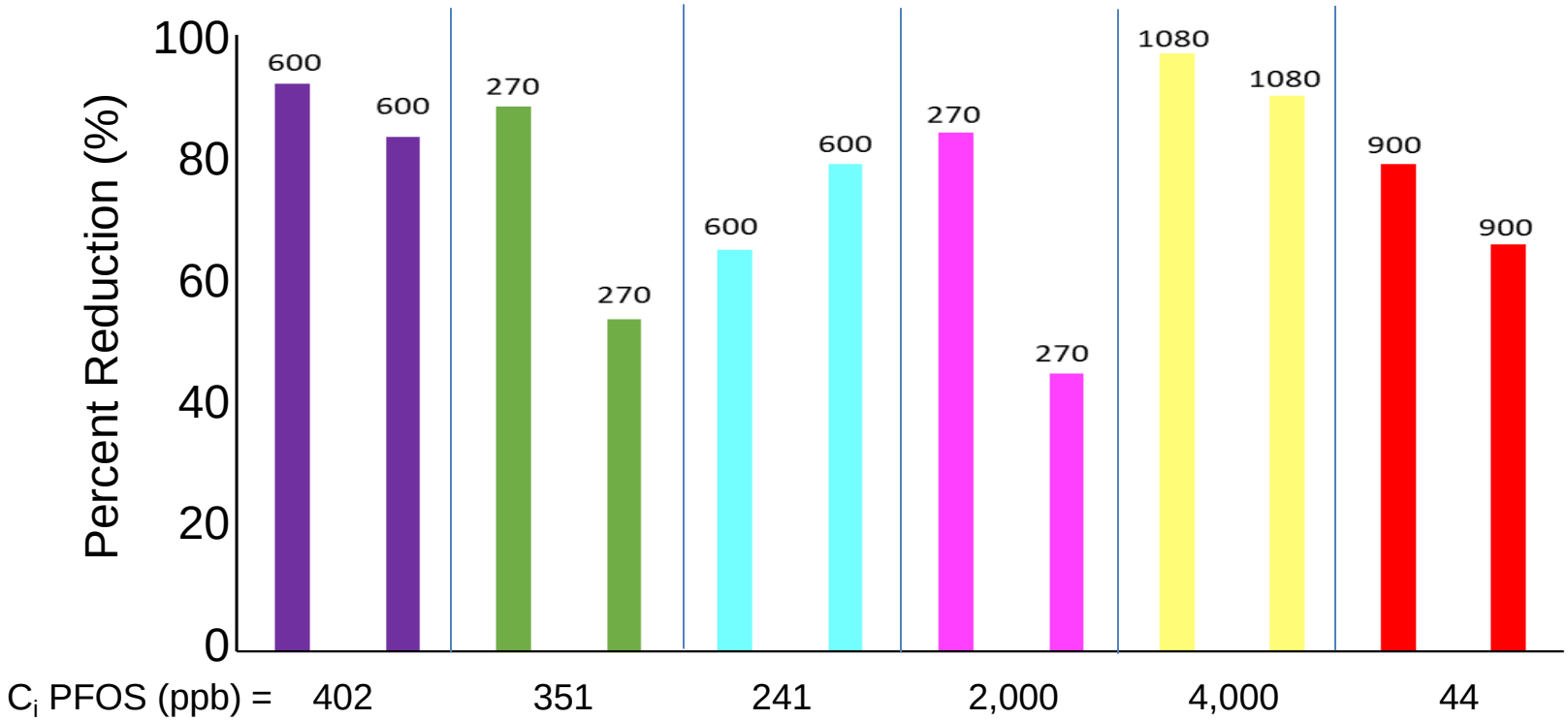
Sonolysis

In Situ Sonolytic Reactor for PFAS Treatment



Contaminated water → Clean water

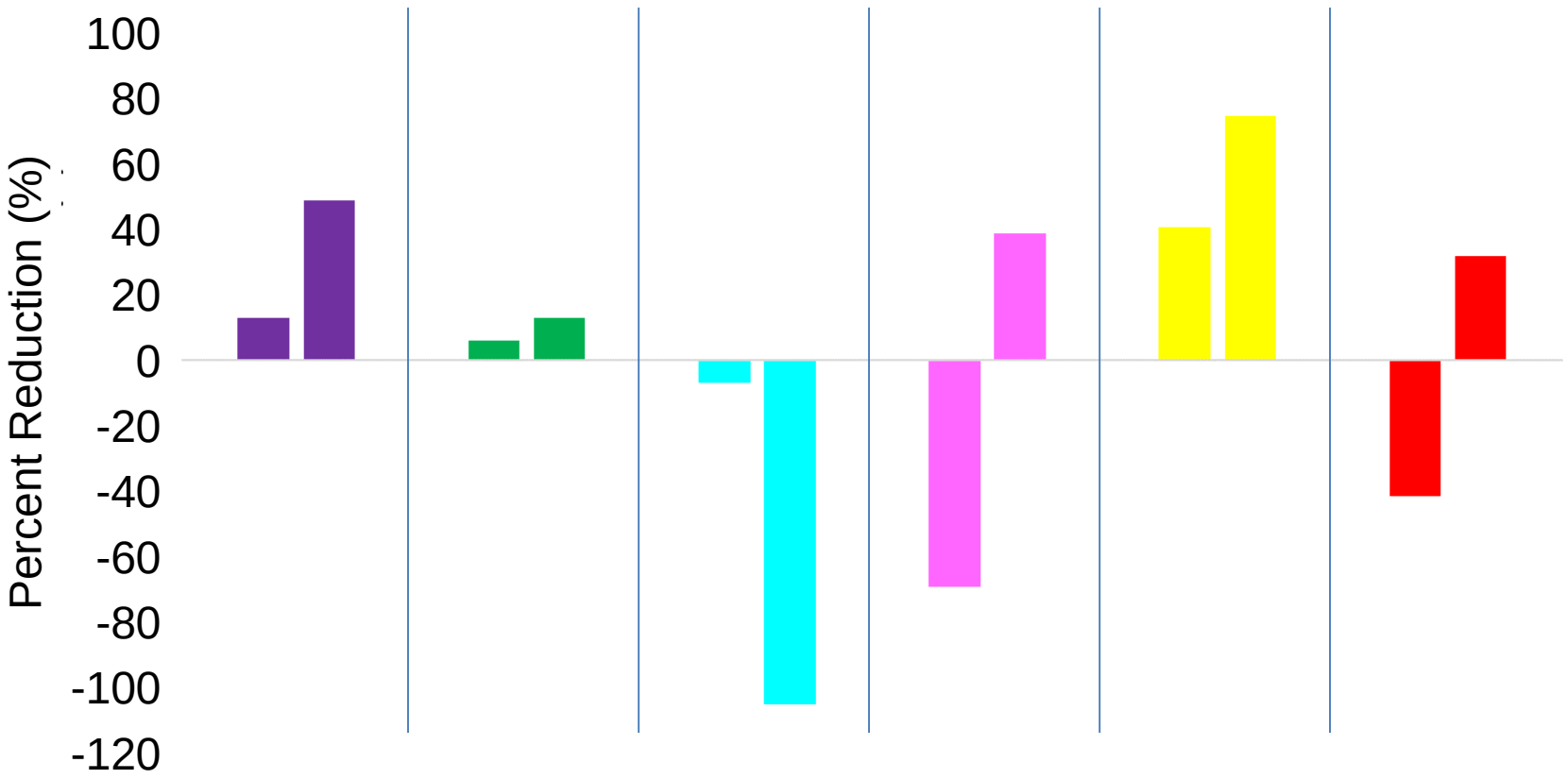
Sonolysis



Sonolysis effectively treats PFAS, with potential for in situ application

Notes: Values above bars represent treatment time in minutes. Each color represents a different contaminated field site with PFOA (perfluorooctanoic acid) on the left and PFOS (perfluorooctane sulfonate) on the right

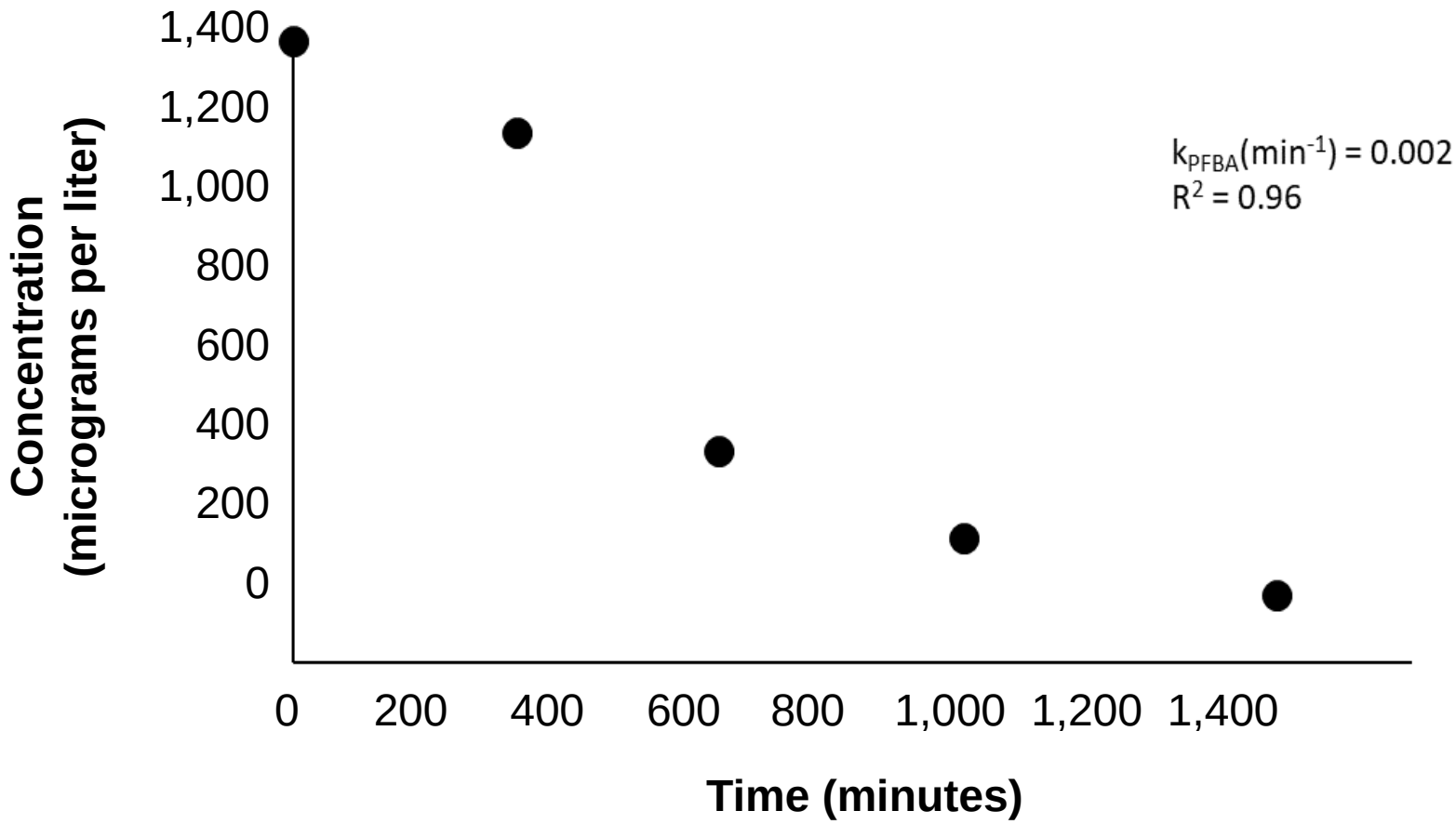
Sonolysis



Notes: Each color shows (PFBA, PFBS); PFBA = perfluorobutyrate; PFBS = perfluorobutane sulfonate

Sonolysis

PFBA Degradation in a Spiked Deionized Water System



Other Approaches

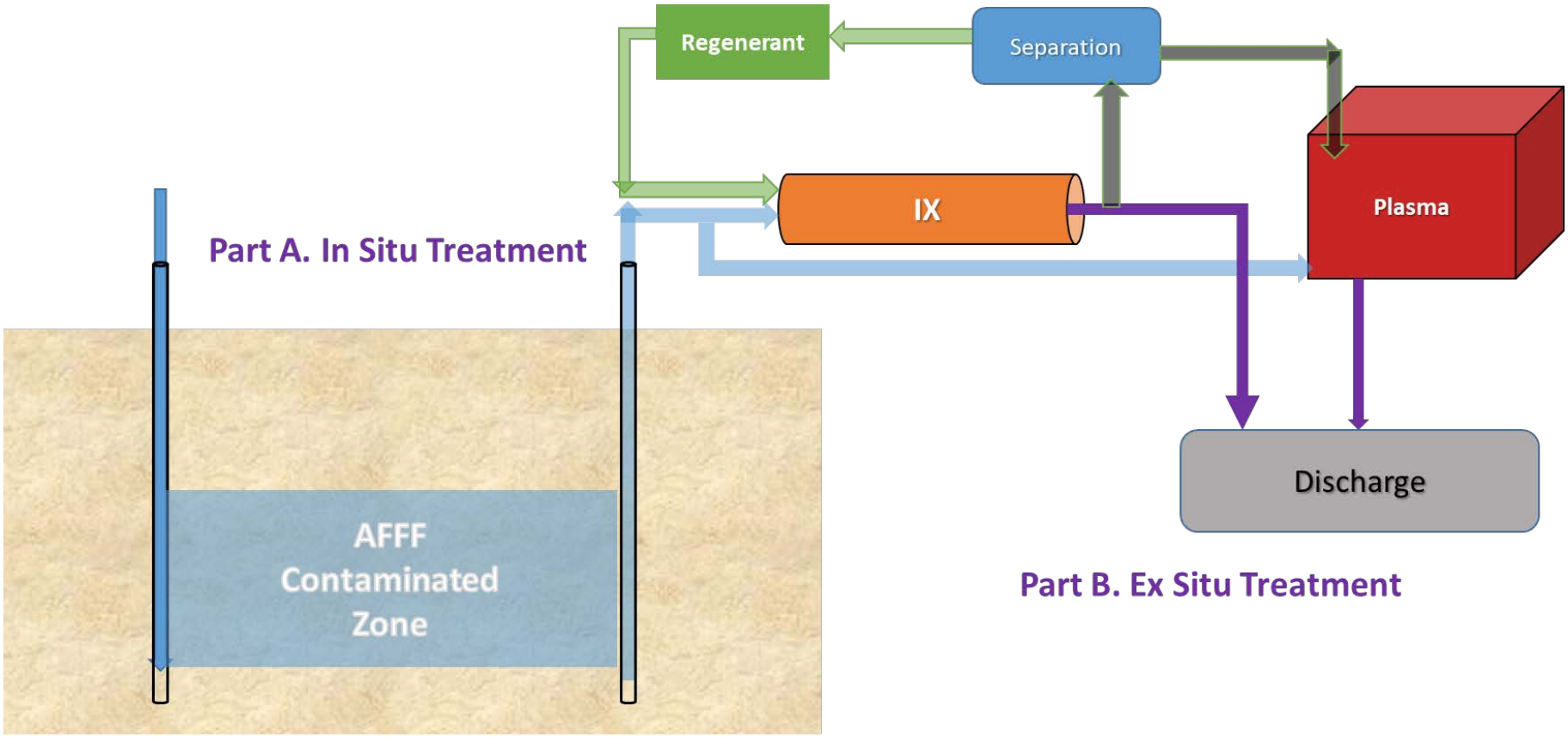
- Electrochemical
- Photochemical
- Reductive
  - Pd_0/nFe_0 nanoparticles
  - Aqueous electrons
- Oxidative
  - Activated persulfate
  - Ozone
  - Different oxidation approaches → different intermediates and byproducts

Source: Nzeribe, B. et al. (2019). *Critical Reviews in ES&T*, *49*(10), 866-915

Verifying Complete Destruction of PFAS

Oxidation Approach	Intermediates and Byproducts
Persulfate	F^-, PFPrA, PFHpA, PFHxA, PFPA PFPeA , PFBA,TFA
UV-Fenton	F^-, Formic acid, PFPrA, PFHpA, PFHeA, PFPeA , PFBA
Fe(III)	F^-, PFPrA, PFHpA, PFHeA, PFPeA
Ferrates	No observed F^-
Fe(III) and oxalate	F^-, PFPrA , PFBA, PFPeA, PFHxA, PFHpA
Plasma	F^-, TFA PFPrA , PFBA, PFPeA, PFHxA, PFHpA, PFBS
UV-Pb-modified TiO_2	PFHpA , PFHeA, PFPrA, TFA PFPeA, PFBA
Sonolysis	PFHpA, PFHxA, PFPA, TFA and F^- ,PFHpS, PFHxS, PFOA
Photocatalysis with Inidium oxide	F^- ,PFHpA , PFHeA, PFPrA, PFPeA, PFBA
TiO_2 photocatalysis	PFHpA, PFHpA, PFPeA, PFBA
Environmental photolysis	PFBA, PFBS, PFOA
Electrochemical oxidation	F^-, TFA, PFPA, PFBA, PFPeA, PFHxA, PFHpA
Photolysis with persulfate	F^-,CO_2, SO_4^{2-} PFBA, PFPeA, PFHxA, PFHpA
Microwave hydrothermal decomposition	F^-,CO_2, PFBA, PFPeA, PFHxA, PFHpA, PFHeA

Treatment Trains



Treatment trains can improve treatment efficiency

Treatment Trains

- Part A: In Situ Treatment
  - No treatment
  - Persulfate oxidation
  - Oxygen addition
    - o Sparging
    - o Slow-release amendment
- Part B: Ex Situ Treatment
  - Ion exchange, range of:
    - o Regenerant solutions
    - o Regenerant separation approaches for reuse
  - Plasma
    - o Pumped groundwater, directly
    - o Ion exchange regenerant residue with concentrated PFAS
    - o Pretreated groundwater

Challenges and Limitations

- Mixtures, precursors, co-contaminants
- Managing materials
- Incomplete mineralization
- Energy intensity
- Technical challenges to in situ treatment
- Limited field-scale examples

Considerations for Remedy Selection

- Does the approach rely on immobilization?
  - Is immobilization irreversible?
- Does the approach rely on separation?
  - How will separated PFAS be managed long-term?
  - What are the challenges, costs, and risks of the long-term management plan?
  - Can removal efficiency be improved at reasonable cost?

Considerations for Remedy Selection

- Does the approach rely on destruction?
  - Can you verify destruction with fluoride recovery? Are the compounds truly destroyed?
  - What intermediates or byproducts may form?
  - What impact do precursors have on mass balance?
  - What is the energy cost?
  - What are the implementation challenges?

Benefits to DoD

- PFAS-related liabilities > $2B
  - Full scope still unclear
- Regulations emerge and evolve
  - Need cost effective PFAS treatment approaches
- Work continues to focus on improving the following:
  - Efficiency
  - Effectiveness
  - Permanence of treatment

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER18-1306

http://serdp-estcp-pfas.com/pfas_efforts/pfas_efforts.pdf

Speaker Contact Information

mcrimi@clarkson.edu; 315-268-4174

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Q&A Session 1

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Assessment of Commercially Available Fluorine-Free Firefighting Foams and Agents

Jerry Back
Jensen Hughes

SERDP DOD • EPA • DOE | ESTCP

Agenda

- Background and problem
- Program objectives
- Approach and project plan
  - Six tasks
- Benefits to DoD
- Status and schedule for completion
- Conclusions

Background

- Special firefighting agents for flammable liquid fires
- AFFF invented by USN/NRL in 60s/70s
  - Industry standard for 50 years
  - DoD AFFF approved per MIL-F-24385F
- MILSPEC foams are best performers

- ***USS Forrestal fire 1967***
- ***USN Fact File***
- ***134 sailors died***
- ***161 injured***

Notes: USN = United States Navy: USS = United States Ship

AFFF Uses

- Shipboard
  - Flight decks
  - Bilges
  - Fuel pump rooms
  - Aircraft hangars
  - Manual firefighting
- Aviation
  - DoD and commercial
  - Land-based aircraft hangars
  - Land-based ARFF
- Petroleum industry
  - Refineries
  - Fueling stations
  - Tank farms

Note: ARFF = aircraft rescue and firefighting

Problem

- Environmental concerns with AFFF
- Human health concerns with AFFF
- DoD needs environmentally acceptable alternative
- AFFF performance is a life safety issue

Objectives

- Ultimate goal
  - Identify environmentally acceptable AFFF alternative
- Specific objective
  - Quantify capabilities of available alternatives

Technology/Methodology Maturity

- Numerous commercially available fluorine free Class B firefighting foams
  - UL, EN, ICAO
- Other agents
  - Wetting/encapsulating
- Chemicals used for other things (e.g. de-icing chemicals)
- Nothing ruled out at this stage

Notes: UL = Underwriters Laboratories ; EN = European Nations ; ICAO = International Civil Aviation Organization

Technical Approach

Two year program started February 2019

Task	
1	Literature Search (to identify candidates)
2	Environmental Analysis (and down-selection 8-10)
3	Real-Scale Fire Tests (two scenarios)
4	Capabilities Rankings (and down-selection)
5	Approval-Scale Fire Tests
6	Program Documentation (database, final report, path forward)

Task 1: Literature Search

- Comprehensive literature review on foams and agents
- Potential candidates/agents (~ 30 identified)
  - 12 - UL listed fluorine-free foams
  - 9 - EN or ICAO tested fluorine-free foams
  - 8 - Wetting and/or encapsulating agents
  - 3-4 - SERDP/ESTCP candidates
- Completed June 2019

Task 2: Environmental Analysis

- General foam composition environmental assessment
- Life cycle environmental assessments
- Ultimate objective
  - Identify any environmental “show stoppers”
  - Down select to 8-10 agents
- In progress - Fall 2019

Task 3: Real-Scale Testing

- Fixed discharge system assessment
- Manual firefighting assessment

- All baselined against MILSPEC AFFF
- Spring 2020

Task 4: Agent Ranking

- Ranking of firefighting capabilities
- Selection of agents for approval scale testing
- Summer 2020

Task 5: Approval-Scale Testing

- MIL-F-24385F fire scenarios
- Increased application rate assessment
- Link between sizes/scales
- Unnecessary elimination
- Fall 2020

Task 6: Program Documentation

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

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

Program Summary

Two year effort to assess AFFF alternatives

Task		Status
1	Literature Search	Complete
2	Environmental Analysis	In Progress/Fall 2019
3	Real-Scale Fire Tests	Spring 2020
4	Capabilities Rankings	Summer 2020
5	Approval-Scale Fire Tests	Fall 2020
6	Program Documentation	Early 2021

Conclusions

- The use of fluorinated foams may be significantly restricted moving forward
- Understanding current fluorine free foam capabilities is important
- A database on alternatives capabilities is a logical first step

Acknowledgments

- U.S. Naval Research Laboratory (NRL)
  - John Farley
  - Director of Fire Test Operations
  - Foam Expert / FF / DC
  - 35 years experience
    - USN firefighting
    - Who's who in MILSPEC foams and DoD systems

Notes: DC = Damage Control; FF = Fire Fighter; MILSPEC = Military Specification

For additional information, please visit

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

Speaker Contact Information

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Q&A Session 2

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Survey Reminder

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

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The next webinar is on October 24, 2019

Advances in Managing Contaminated Groundwater Using High Resolution Site Characterization and Contaminant Mass Flux Reduction

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