Thank you for signing in early

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

SERDP
DOD • EPA • DOE

ESTCP

SERDP and ESTCP Webinar Series

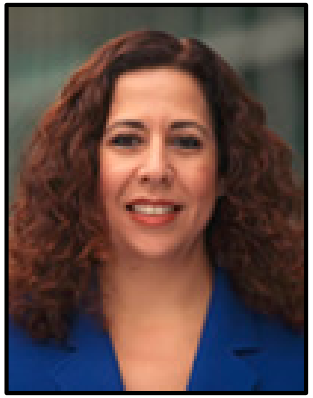
- The webinar will begin promptly at 12:00 pm ET, 9:00 am PT
- Options for accessing the webinar audio
  - Listen to the broadcast audio if your computer is equipped with speakers
  - Call into the conference line
    - (669) 900-6833 or (929) 205-6099
    - Required webinar ID: 718-735-670
  - YouTube live stream
    - https://www.youtube.com/user/SERDPESTCP
- For questions or technical issues, please email serdp-estcp@noblis.org or call 571-372-6565

Innovative Technologies for PFAS Destruction in Investigation Derived Wastes

May 7, 2020

SERDP DOD • EPA • DOE | ESTCP

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
- **Electrochemical Oxidation of PFAS Using a Novel Reactive Electrochemical Membrane Technology** (25 minutes + Q&A)
  Dr. Brian Chaplin, University of Illinois
- **Plasma Based Treatment Processes for PFAS Investigation Derived Waste** (25 minutes + Q&A)
  Dr. Thomas Holsen, Clarkson University
- **Final Q&A session**

Zoom Instructions

- Download Zoom
  - https://zoom.us/download
- If you cannot download Zoom, you can view the slides using an internet browser
  - Create a free Zoom account (https://zoom.us/signup)
  - Use a compatible browser (Firefox, IE or Edge)
  - View the webinar at https://success.zoom.us/wc/718735670/join
- If the material is not showing on your screen or if screen freezes
  - Key in Ctrl + F5 to do a hard refresh of your browser

Zoom Instructions (Cont'd)

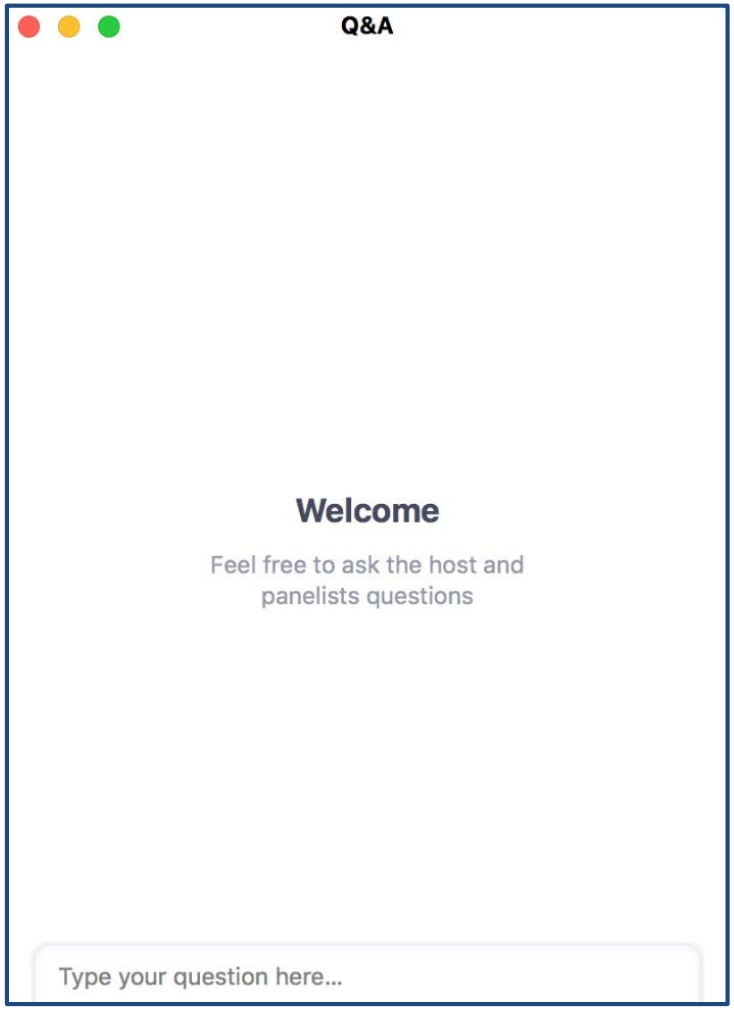
- If you are connecting to computer audio
  - Click the arrow next to the "Join Audio" button
  - Select test "Speaker and Microphone"
  - Follow prompts
- If you experience difficulties with the audio, call into the conference line
  - (669) 900-6833 or (929) 205-6099
  - Required webinar ID: 718-735-670

In Case of Continued Technical Difficulties

- Download a PDF of the slides at https://serdp-estcp.org/Tools-and-Training/Webinar-Series/05-07-2020 and call into the conference line
  - (669) 900-6833 or (929) 205-6099
  - Required webinar ID: 718-735-670
- We will also be live streaming the webinar on the SERDP and ESTCP YouTube channel
  - https://www.youtube.com/user/SERDPESTCP

How to Ask Questions

- 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

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

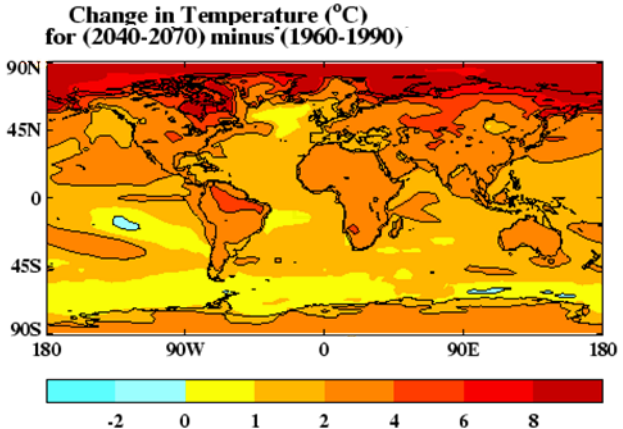
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

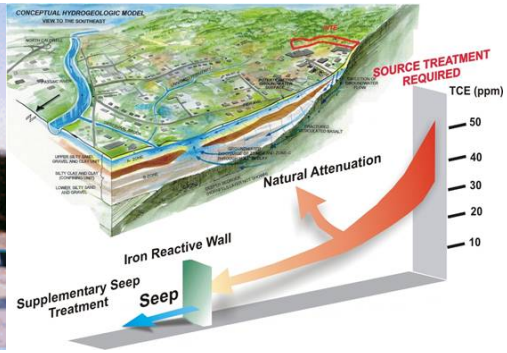
Sustainable FOB



Environmental Drivers

Reducing Current and Future Liability

Contamination from Past Practices



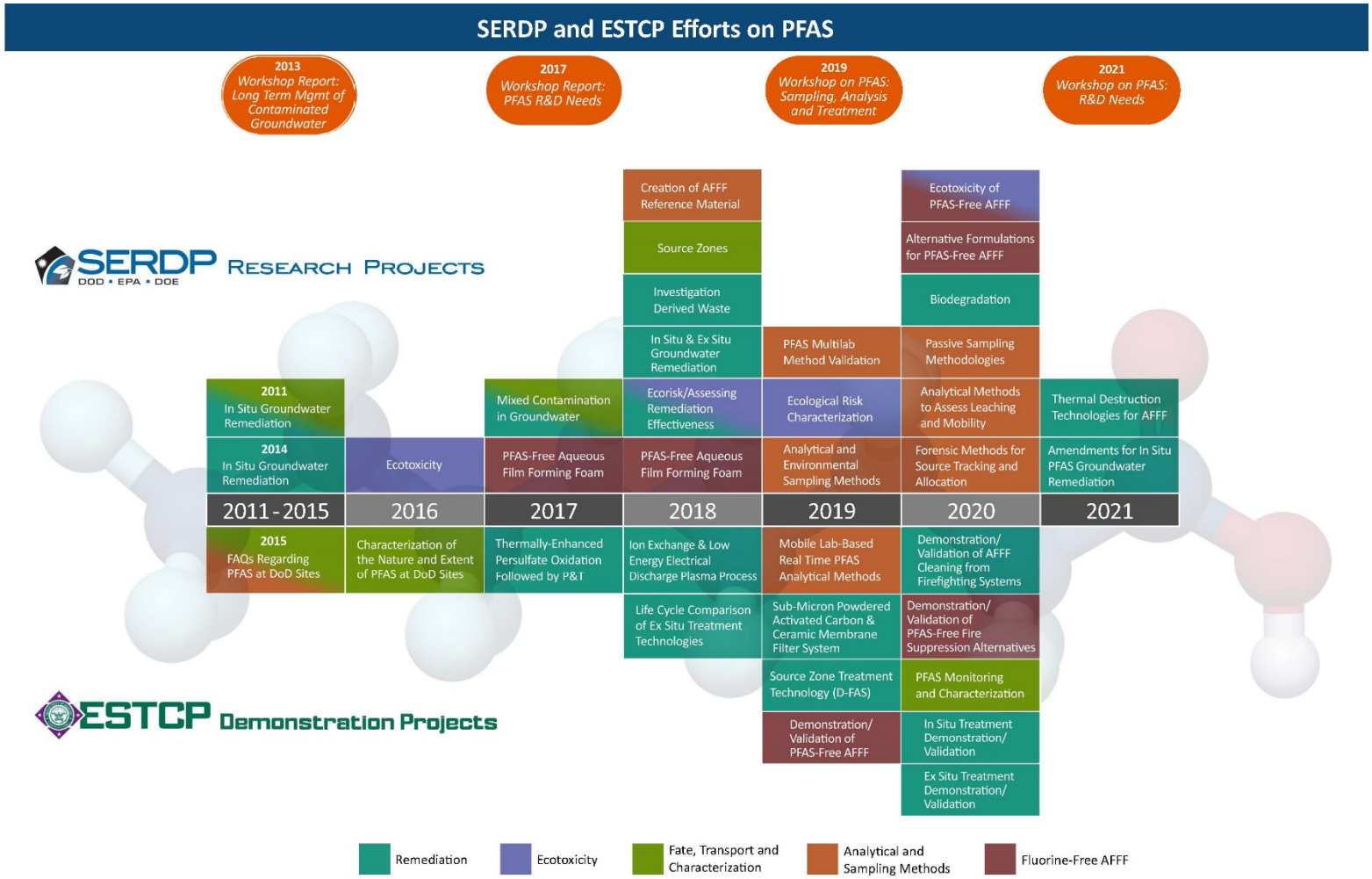
- Groundwater, soils and sediments
- Large UXO liability
- Emerging contaminants

Pollution Prevention to Control Life Cycle Costs

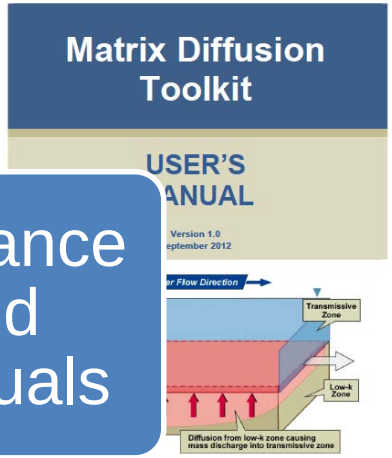
- Elimination of pollutants and hazardous materials in manufacturing, maintenance, and operations
- Achieve compliance through pollution prevention

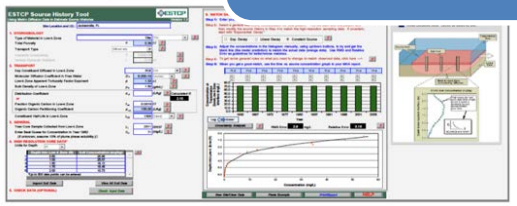
PFAS Online Resource

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



www.serdp-estcp.org





Webinars

In Person Training

EnviroWiki

Videos

Technology Transfer

Guidance and Manuals

SERDP and ESTCP Webinar Series

Date	Topic
May 21, 2020	Analysis of Defense Related Ecosystem Services
June 4, 2020	Waste Reduction and Treatment in Armed Forces Vessel Environments
June 18, 2020	Predicting PFAS Fate and Transport in Subsurface Environments, and Treatment
July 9, 2020	Software and Hardware Solutions for Securing DoD Control Systems and Infrastructure from Cyber Threats
July 23, 2020	PFAS Fate, Transport and Treatment
August 20, 2020	Addressing Threatened and Endangered Species on DoD Lands

For upcoming webinars, please visit

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

SERDP DOD • EPA • DOE | ESTCP

Electrochemical Oxidation of PFAS Using a Novel Reactive Electrochemical Membrane Technology

Brian P. Chaplin, Ph.D.
University of Illinois at Chicago

SERDP DOD • EPA • DOE | ESTCP

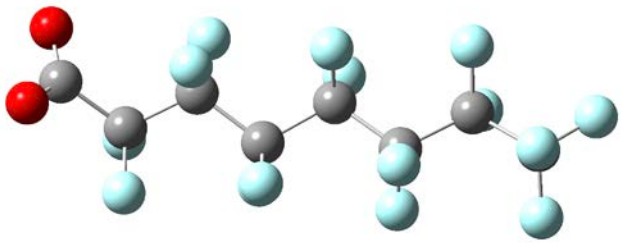
Agenda

- Problem statement
- Technology description: Reactive Electrochemical Membrane (REM)
- Technical objectives
- Electrochemical oxidation results
- Conclusions
- Benefits to DoD

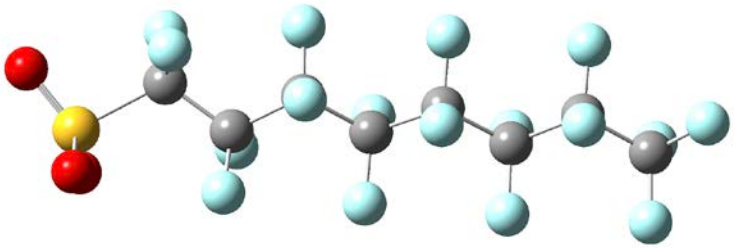
Problem Statement

- Per- and polyfluoroalkyl substances (PFAS) are toxic at low levels
  - EPA has set health advisory levels (< 70 ng/L)
  - States have set lower limits
- Presence at DoD sites
  - Contamination from aqueous film forming foams (AFFF)
  - Groundwater contamination migrating off site
- Resistant to traditional treatment processes

Perfluorooctanoic acid (PFOA)



Perfluorooctanesulfonic acid (PFOS)



Technology Description

Direct Oxidation/Reduction of PFAS (Estimated by DFT Calculations)

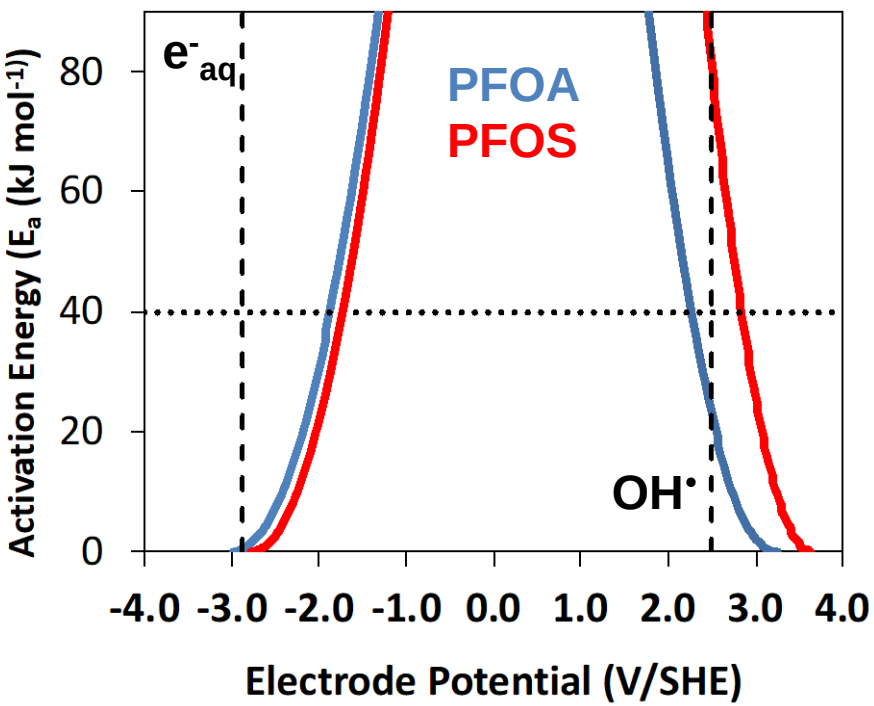
$PFOS + e^- \rightarrow PFOS^-$ $E^o = 3.25$

$PFOS^- + e^- \rightarrow PFOS^{2-}$ $E^o = -2.13$

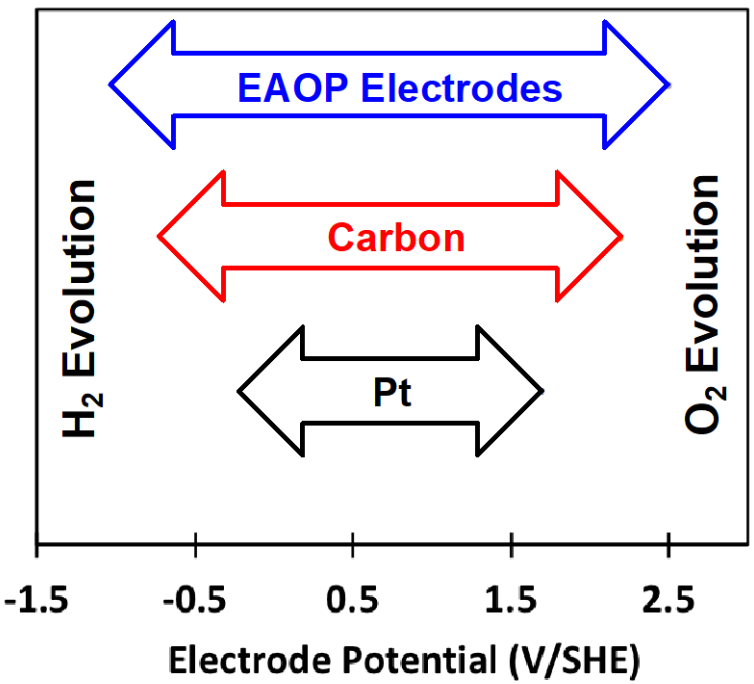
$PFOA + e^- \rightarrow PFOA^-$ $E^o = 2.65$

$PFOA^- + e^- \rightarrow PFOA^{2-}$ $E^o = -2.25$

Activation Energy

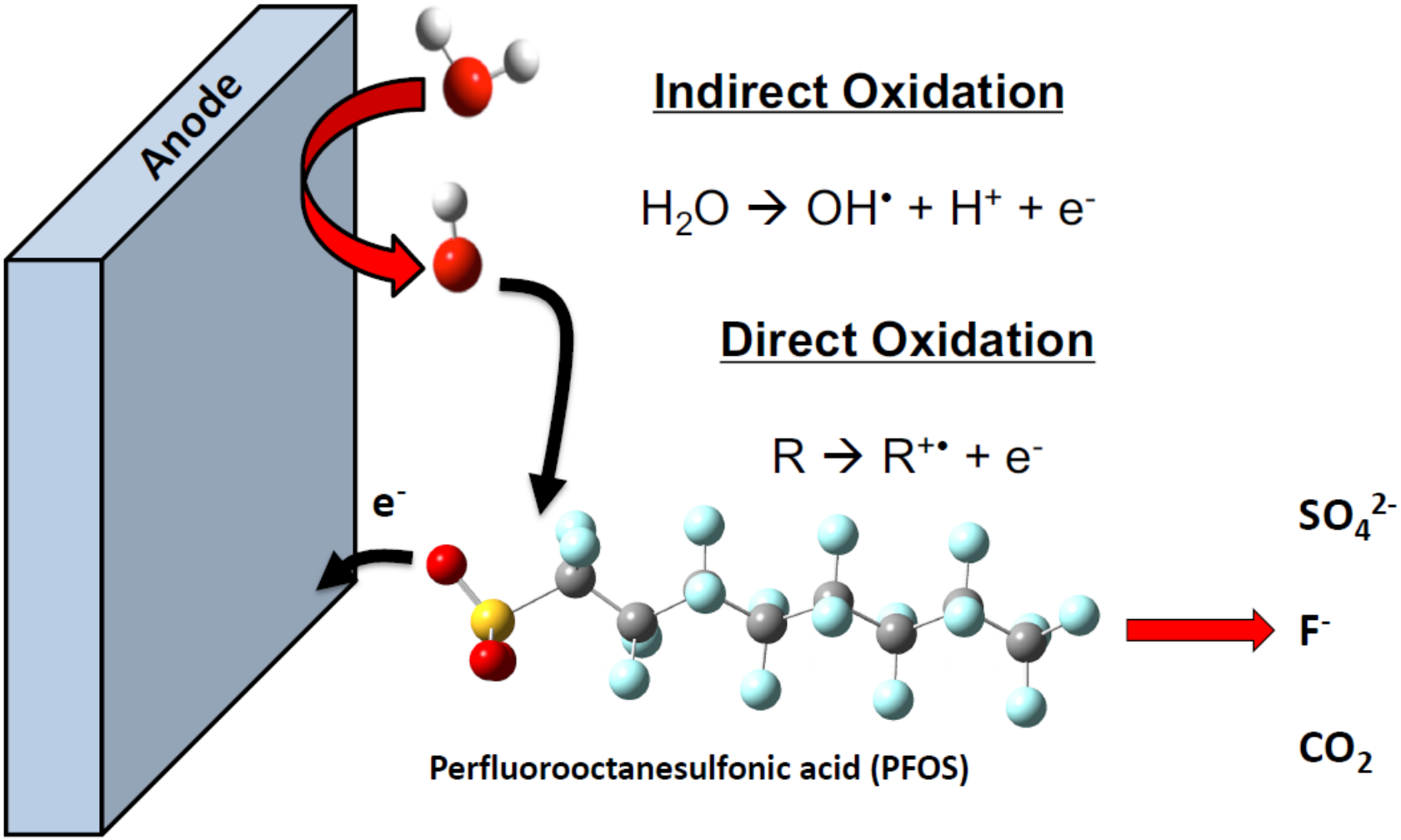


Potential Window



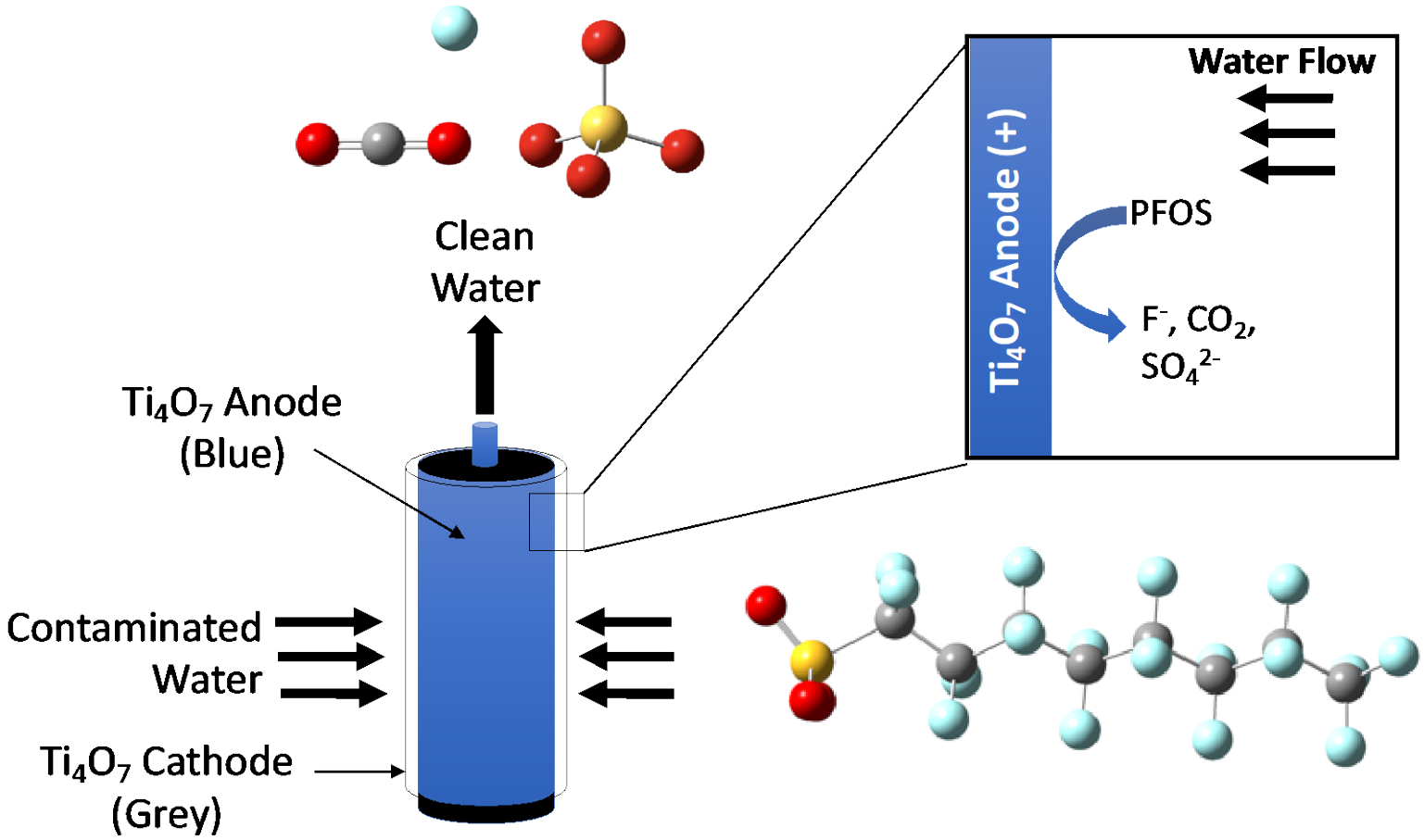
***Notes**: DFT = density functional theory; V/SHE = volts vs. standard hydrogen electrode*

Technology Description



Technology Description

Reactive Electrochemical Membrane (REM)

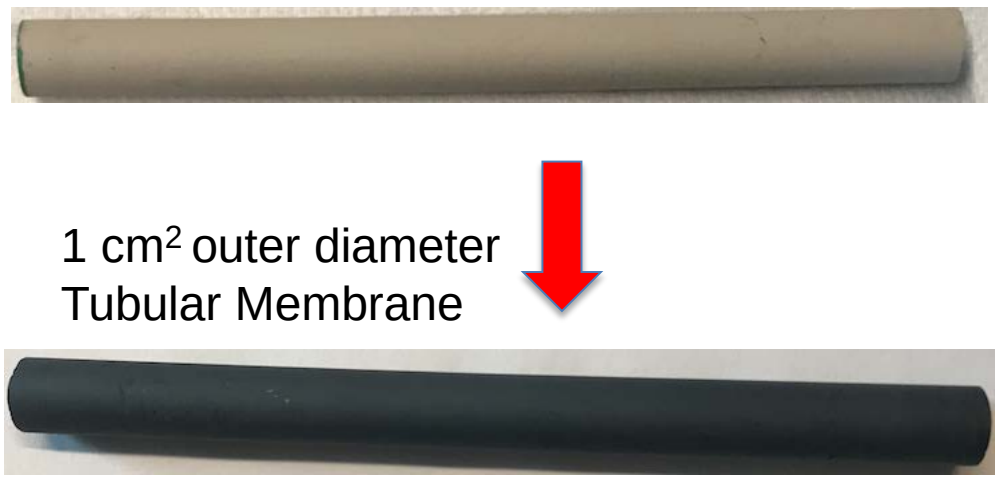


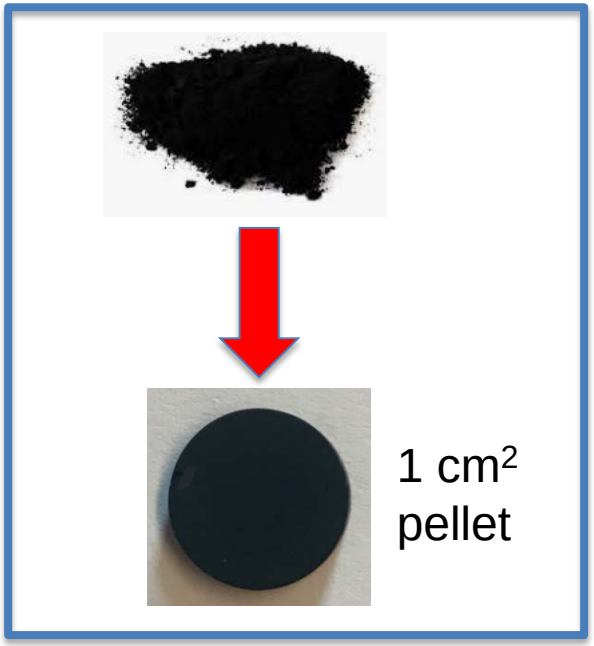
Technical Objectives

- Specific technical objectives
  - Development of REMs for destructive PFAS removal to < 70 ng/L
  - Determination of the optimal operational mode
  - Calculation of energy requirements for the REM-based system

Results: REM Synthesis

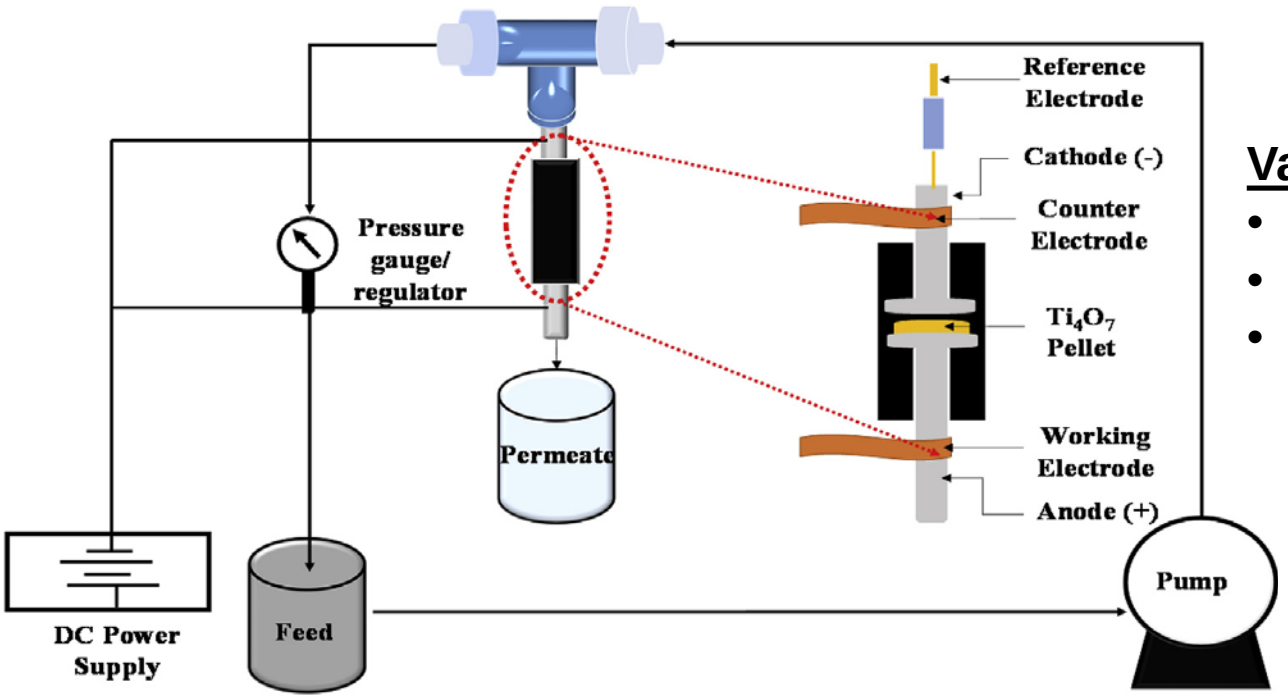
- Reduction of non-conductive TiO_2 to conductive Ti_4O_7
- Fabrication of tubular and disk REMs





Results: REM Reactor

Schematic of the Flow-Through Reactor



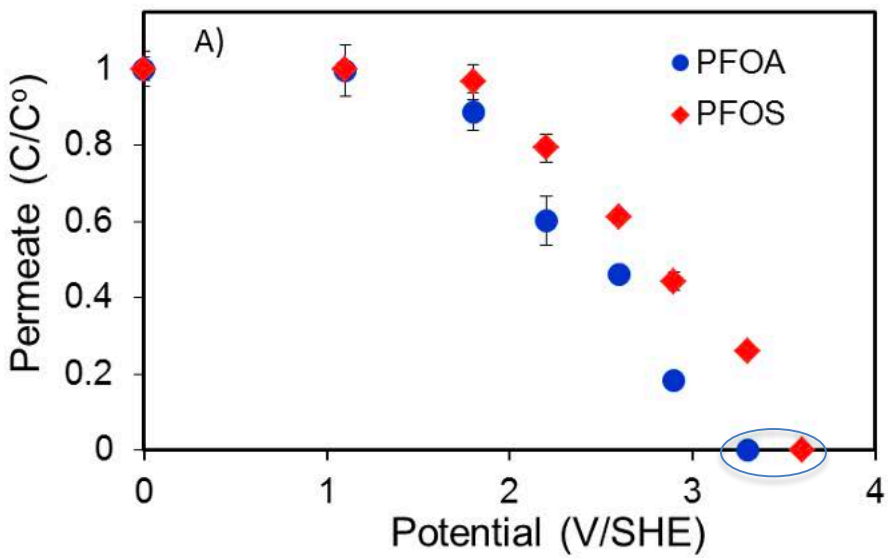
Variables to test

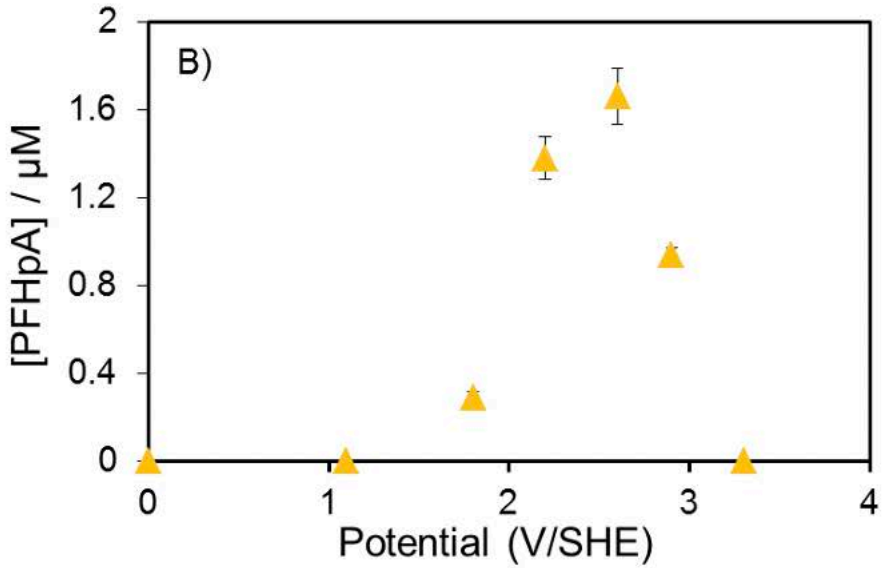
- Potential
- Flow rate
- Operational mode (single-pass vs. recycle)

Results: Effect of Potential

PFOA/PFOS in Synthetic Solutions

(10 μM PFAS, 100 mM K_2HPO_4, pH ~ 7, flux = 240 LMH [(liters/m^2/hour)])





<u>PFOA</u> < 86 ng/L @ 3.3 V/SHE

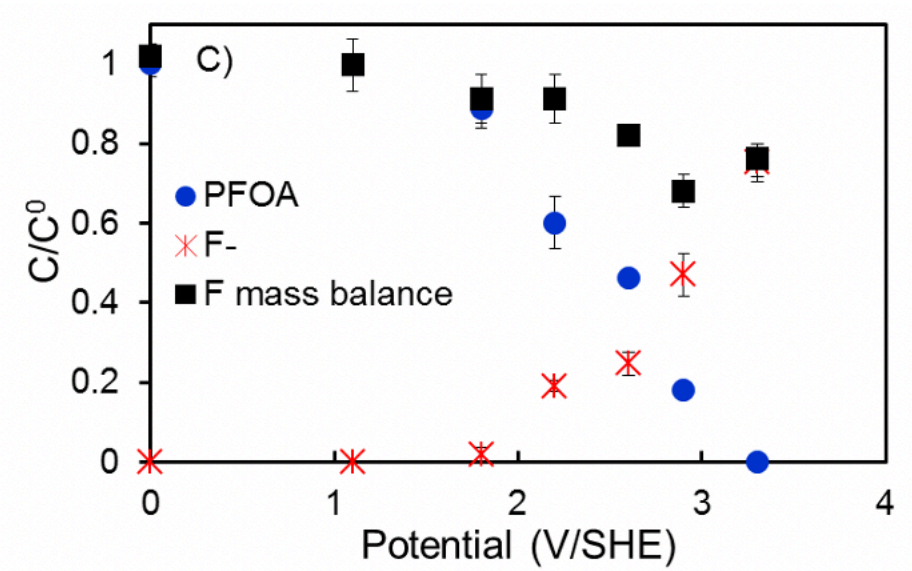
<u>PFOS</u> < 35 ng/L @ 3.6 V/SHE

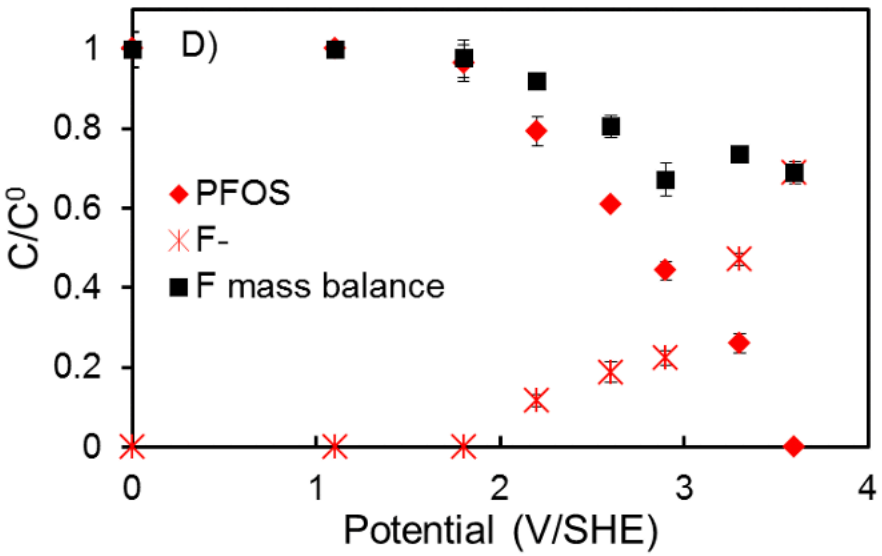
PFHpA primary detected product of PFOA oxidation

Results: Effect of Potential

PFOA/PFOS in Synthetic Solutions

(10 μM PFAS, 100 mM K_2HPO_4, pH ~ 7, flux = 240 LMH [(liters/m^2/hour)])





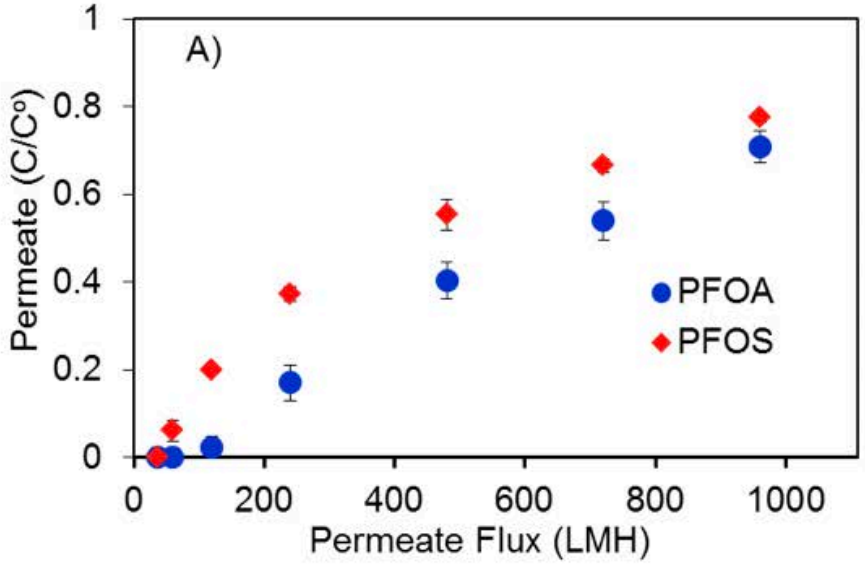
F-mass balances: (67 - 98%)

Results: Effect of Flux

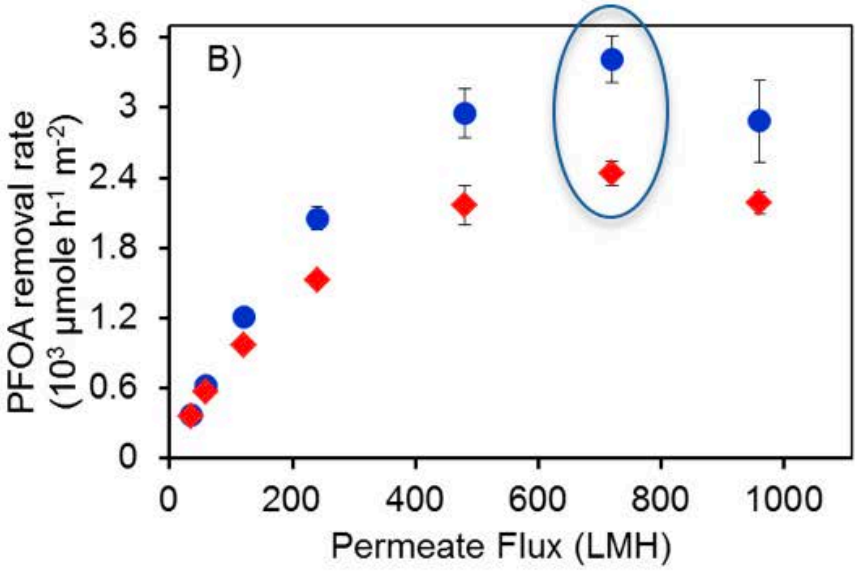
PFOA/PFOS in Synthetic Solutions

(10 μM PFAS, 100 mM K_2HPO_4, pH ~ 7)

PFOA and PFOS versus flux (2.9 V/SHE)



Rates from (A)



- PFOA and PFOS < detection limits at 36 LMH (86 and 35 ng/L)
- ~ 5-log removal with residence time (t_r = 75 s)
- Maximum rate observed at 720 LMH (t_r = 3.8 s)
- Rate constants (k = 210 and 607 h^{-1})

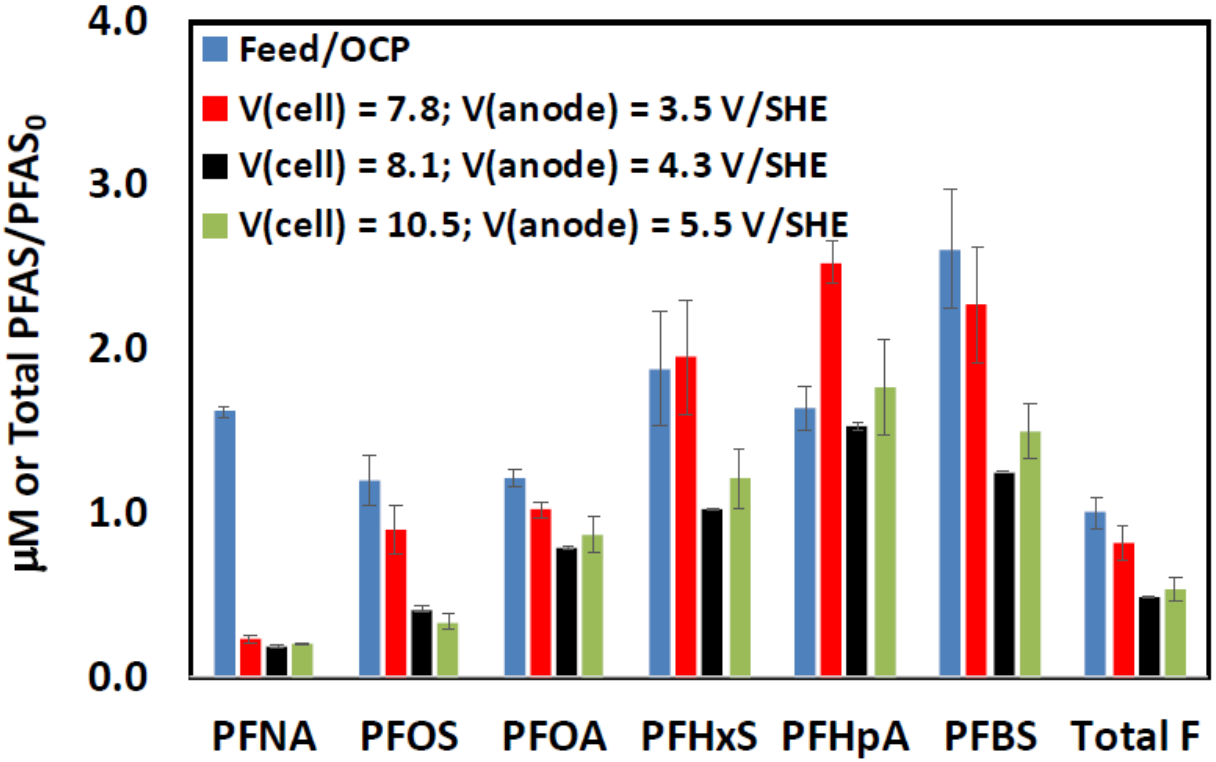
Results: Groundwater Samples

General water quality analyses for groundwater samples

	GW1	GW2
Constituent	**mg/L**	**mg/L**
F^-	1.06	15.7
Cl^-	51.5	27.1
NO_3^-	8.18	< 0.1
SO_4^{2-}	10.8	< 0.1
HPO_4^{2-}	7.78	< 0.1
HCO_3^-	228	87.7
Na^+	72.6	25.3
K^+	13.7	30.1
Ca^{2+}	25.7	34.5
Mg^{2+}	21.4	8.75
pH	6.8	6.5
Conductivity (µS/cm)	788	337
COD (mg/L)	**43.3**	4.35
Alkalinity (mg/L $CaCO_3$)	373	144

- Groundwater 1 (GW1)
  - Geosyntec client in Jacksonville, FL
  - Generally PFAS free
  - Spiked with 1.0 - 2.5 µM of PFAS (PFNA, PFOS, PFOA, PFHxS, PFHpA, PFBS)
- Groundwater 2 (GW2)
  - Willow Grove Naval Base in collaboration with Jason Speicher
  - µg/L levels of PFAS: (PFNA, PFOS, PFOA, PFHxS, PFBS)

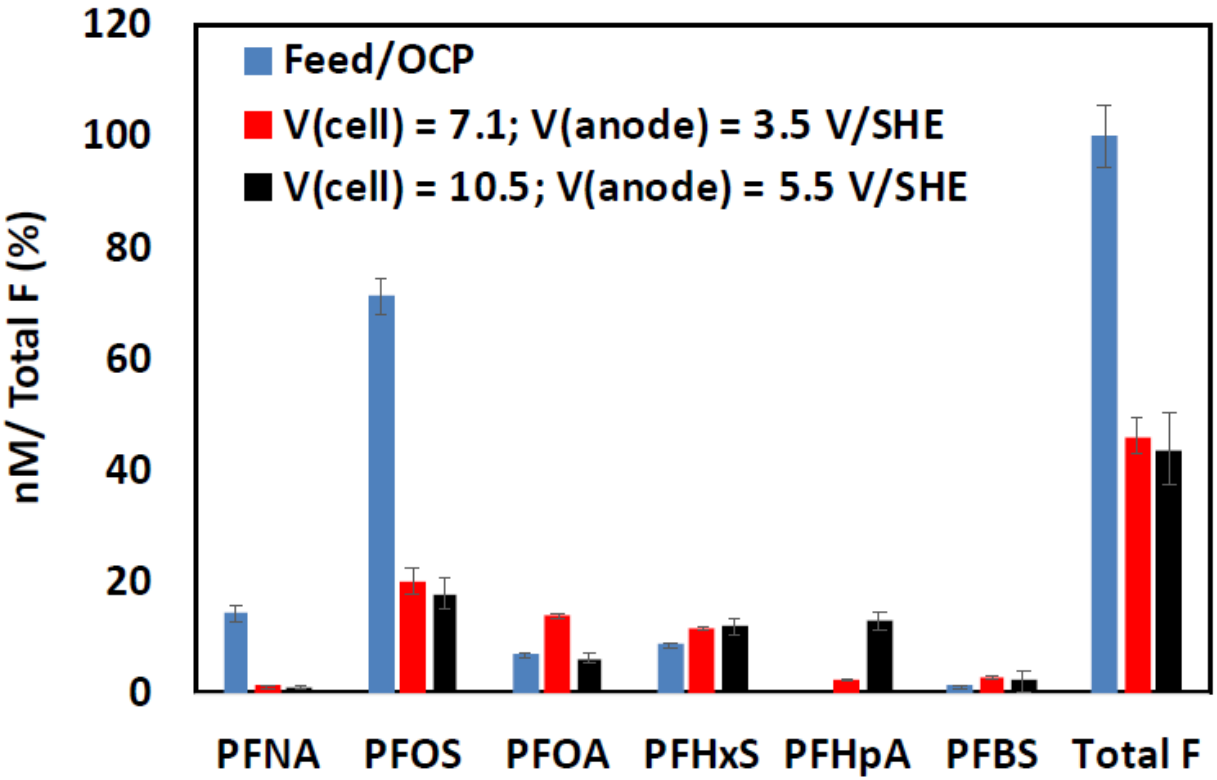
Results: GW1 Oxidation



Low flux
J = 60 LMH
t_r = 45 s

- Shorter chain PFAS formed
- ~50% total PFAS removal
- Moderately high energy consumption: E_{EO} = 13.2 - 23.8 kWh/m^3
- **High COD content: 43 mg/L (competition)**

Results: GW2 Oxidation



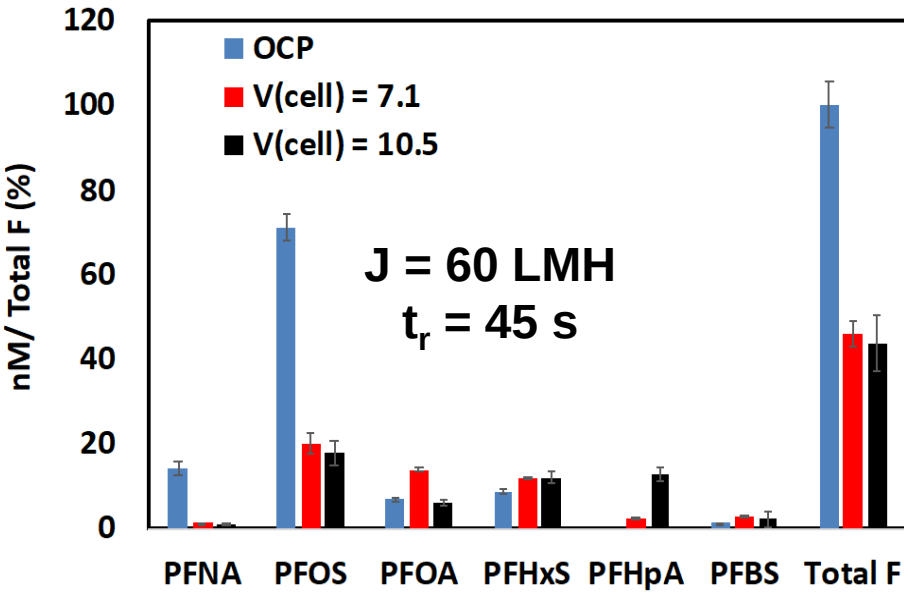
Low flux
J = 60 LMH
t_r = 45 s

- Shorter chain PFAS formed
- ~50% total PFAS removal
- Lower energy consumption: E_{EO} (per log removal) = 11 - 15 kWh/m^3
- **Low COD content: 4.4 mg/L** (less competitive reactions than GW1)

Results: Operational Mode

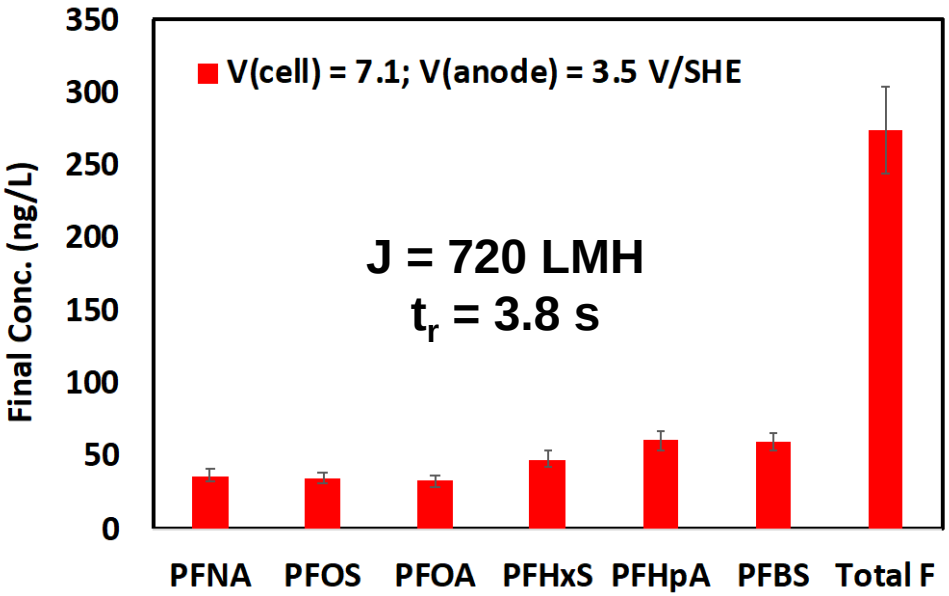
Single Pass vs. Recycle Mode (GW2)

a) Single-pass Mode: Low Flux



- Total PFAS destruction ~ 50%
- Final individual [PFAS] at nM (μg/L) levels
- E_{EO} (per log removal) = 11-15 kWh/m^3

b) Recycle Mode: High Flux



- Total PFAS destruction > 99%
- Individual [PFAS] < 61 ng/L
- E_{EO} (per log removal) = 2.9 kWh/m^3

Results: Energy Calculations

Energy consumption (E, kWh m^{-3}) per log removal:

$$E_{EO} = 10^{-3} \times \frac{V_{cell} I}{Q \log\left[\frac{C_f}{C_p}\right]}$$

Solution	V (Cell)	E_{EO} (kWh m^{-3})	Operational Mode
PFOA	6.0	5.1	Single pass
PFOS	6.1	6.7	Single pass
GW1	7.8 - 10.5	13 - 24	Single pass
GW2	7.1 - 10.5	11 - 15	Single pass
GW2	**7.1**	**2.9**	**Recycle**

- Low E_{EO} values for electrochemical oxidation
- Order of magnitude lower than most other destructive technologies

Conclusions

- PFOA/PFOS oxidized from mg/L to ng/L levels in single-pass mode
- Organic composition of GW samples made single-pass mode less efficient
- Recycle mode (high flux) removed PFAS by 99% and final individual concentrations were < 61 ng/L
- Energy consumption for groundwater treatment
  - E_{EO} = 2.9 kWh m^{-3}
- Rate constants
  - k = 210 and 607 h^{-1}

Benefits to DoD

- Understanding of the capabilities of using electrochemical technologies for groundwater remediation
- Low energy, destructive technology for PFAS remediation
- Next step
  - Field-scale prototype REM for remediation of PFAS-contaminated groundwater

For additional information, please visit
https://serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1491

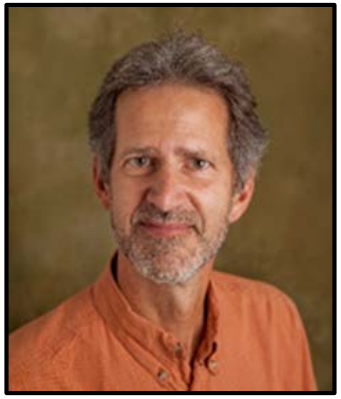
Speaker Contact Information

chaplin@uic.edu; 312-996-0288

Q&A Session 1

SERDP DOD • EPA • DOE | ESTCP

Plasma Based Treatment Processes for PFAS Investigation Derived Waste



Thomas M. Holsen, Ph.D.
Clarkson University

SERDP DOD • EPA • DOE | ESTCP

Presentation Outline

- Project objectives
- Soil washing
  - Methods and materials
  - Results
- Plasma treatment
  - Description of the plasma process
  - Results
- Conclusions and DoD benefits

Project Objective

- Investigate soil washing followed by treatment of the soil washing solution in an enhanced contact plasma reactor to destroy desorbed PFAS
- Limited-scope proposal

Soil Washing Methods

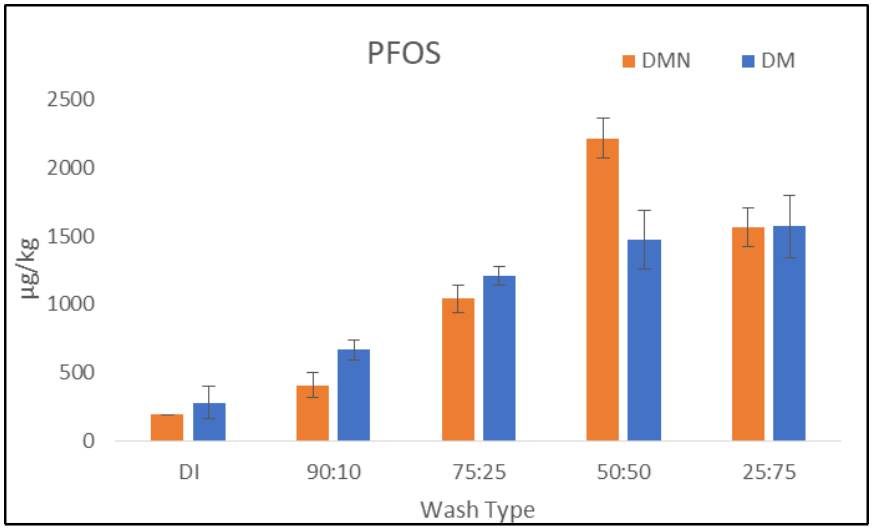
- Dry sample in polypropylene dish
  - 104°C for 8 hours
- Pulverize sample with mortar and pestle
- Add 2 grams of soil and 10 mL wash solution to 50 mL polypropylene centrifuge tube
- Vortex 30 seconds
- Tumble end-over-end
- Centrifuge for 30 minutes at 9000g
- Transfer aliquot to autosampler vial
- Add labelled injection standard
- Analyze by LC/MS/MS (isotope dilution)

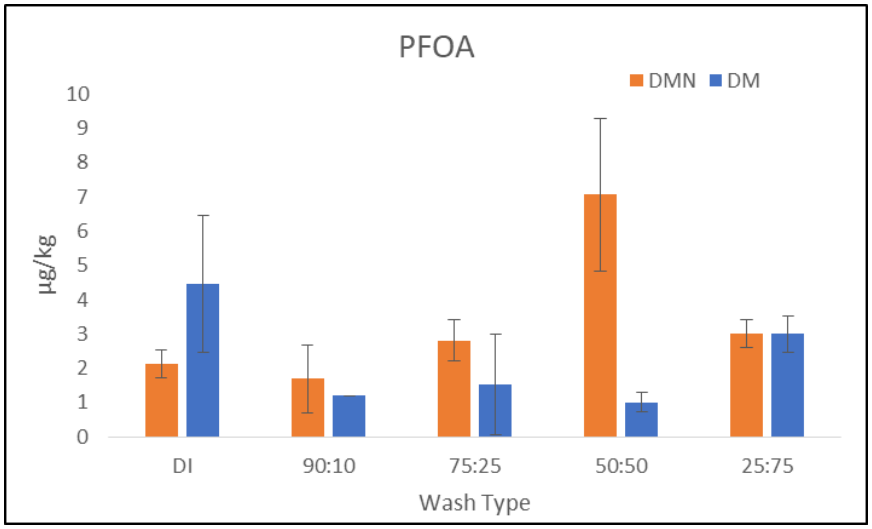
Soil IDW

- Sample sources
  - Jacksonville
    - Highest organic carbon content (0.9%)
  - Willow Grove
  - Wurtsmith
    - Lowest organic carbon content (0.07%)
  - Joint Base San Antonio
- PFAS and precursor concentrations varied significantly
- Anion exchange concentrations pending

Soil Washing Results

Impact of Wash Solution





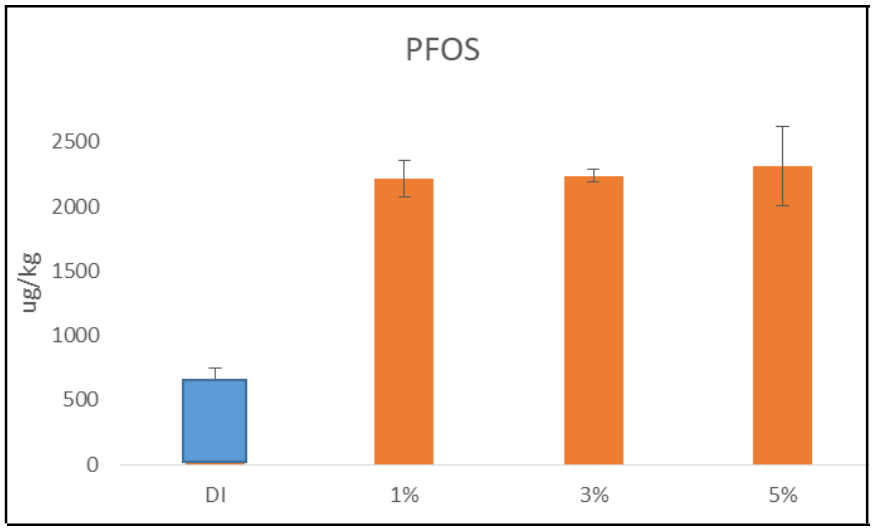
Legend:
Orange Bars (DMS): 1% NaCl in DI:MeOH
Blue Bars (DM): DI:MeOH

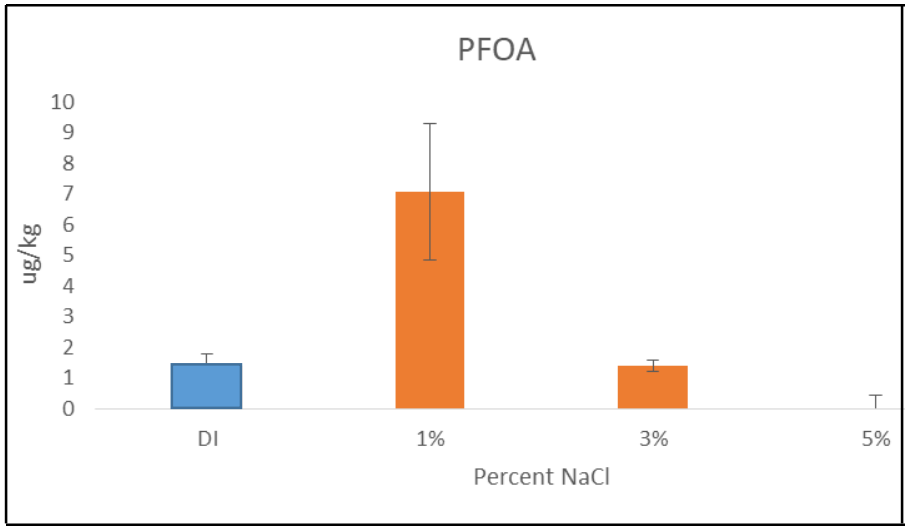
50:50 DI:MeOH optimum ratio

Notes: *DI = deionized water; MeOH = methanol*

Soil Washing Results

Impact of Salt Content



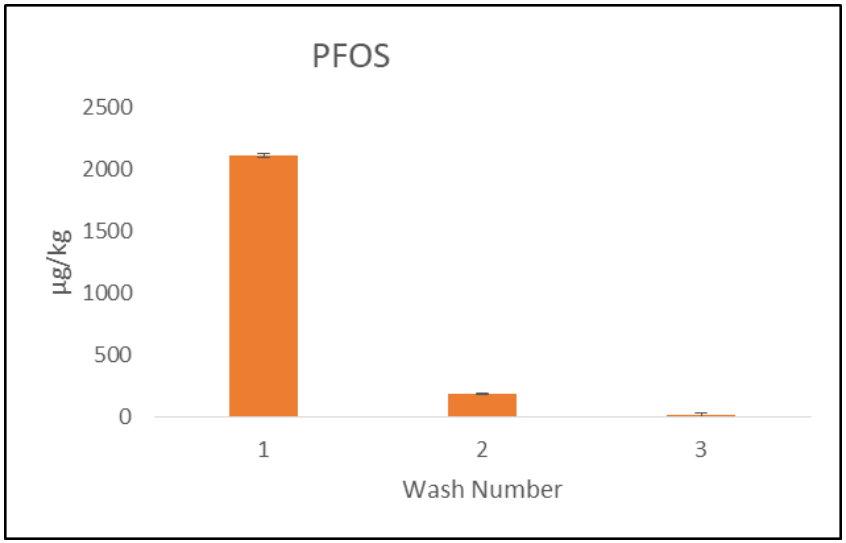


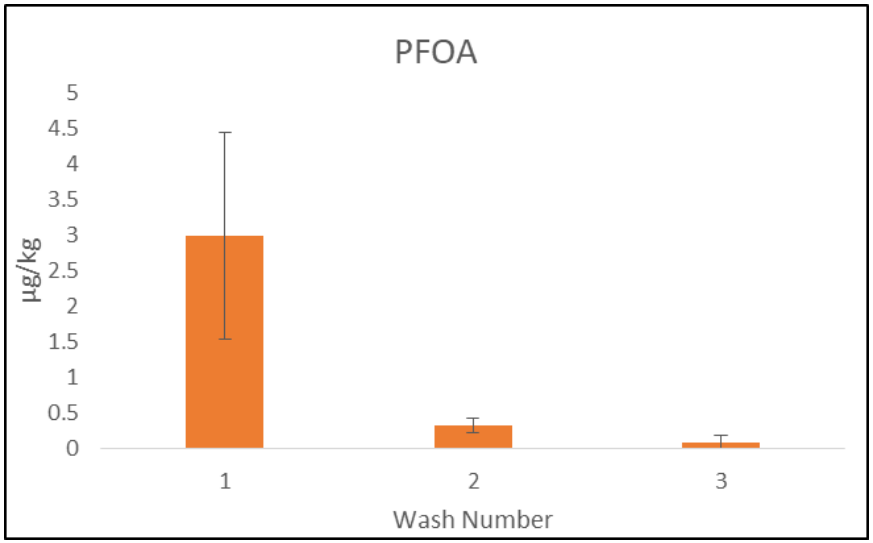
Legend:
Orange Bars: 50:50 DI:MeOH
Blue Bars: DI only

1% NaCl optimal concentration

Soil Washing Results

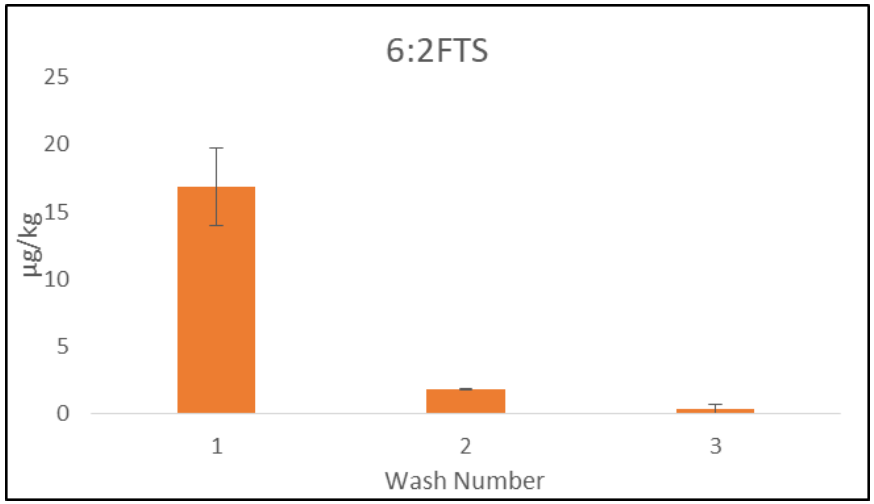
Impact of Number of Washes





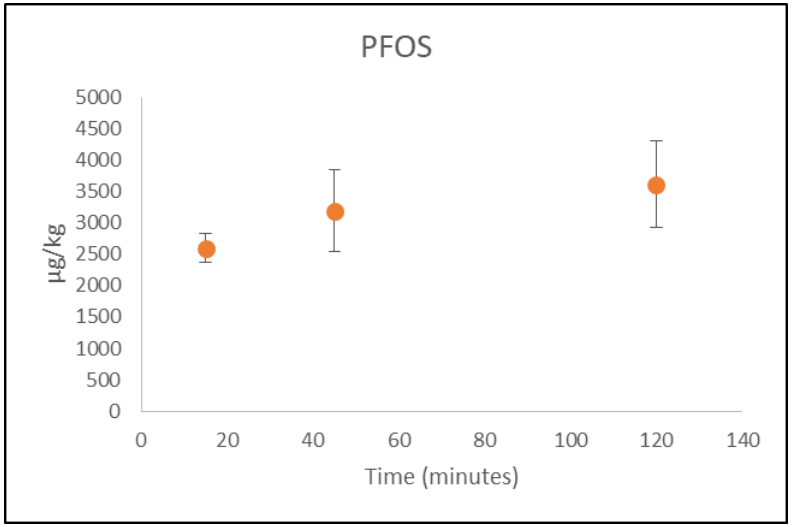
Legend:
Orange Bars: 50:50 DI:MeOH 1% NaCl

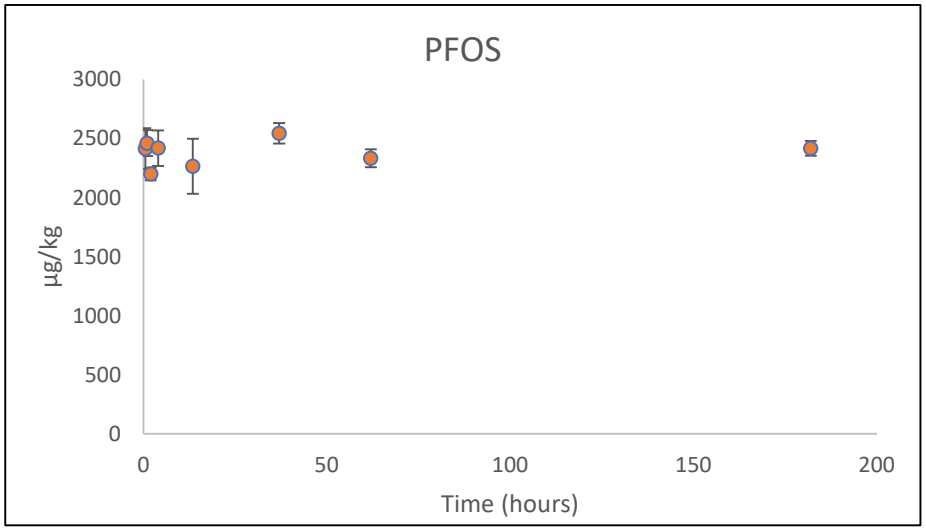
>90% removed with one wash



Soil Washing Results

Kinetics





Legend:
50:50 DI:MeOH 1% NaCl

Desorption was fast (minutes)

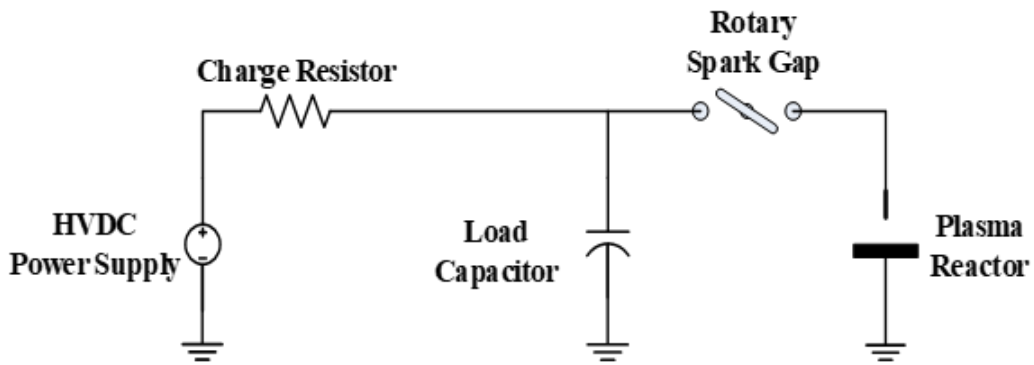
Overview of Soil Washing Results

- Water alone removed a large amount of PFAS
- Increasing MeOH content up to 50% MeOH improved removal
- Salt addition increased removal
  - No difference between 1 and 5% NaCl
- Vast majority (>90%) of the PFAS removed in the first wash
- Fast PFAS removal
  - Minutes not hours
- pH had minor impact on PFAS removal
  - Data not shown

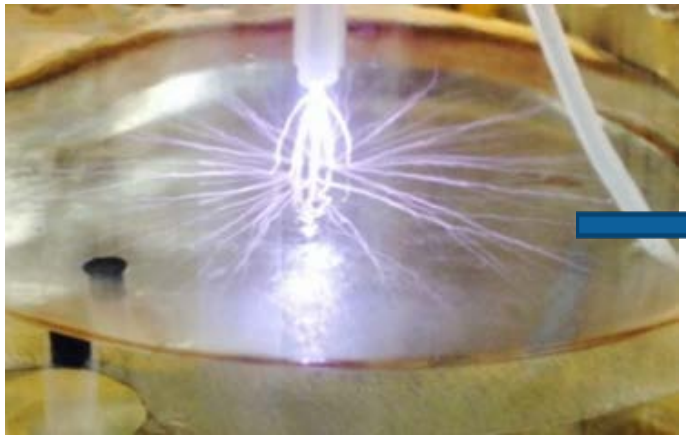
Plasma Treatment

- Limited volumes of soil washing solution available after soil washing experiments
  - Large percentage of MeOH
  - MeOH likely distilled and reused for full-scale soil washing applications
- Plasma experiments
  - Laboratory prepared brine
  - Still bottoms from IX regenerant solutions
    - Former Pease AFB, courtesy of ECT2
  - Simulate soil washing solutions after MeOH recovery

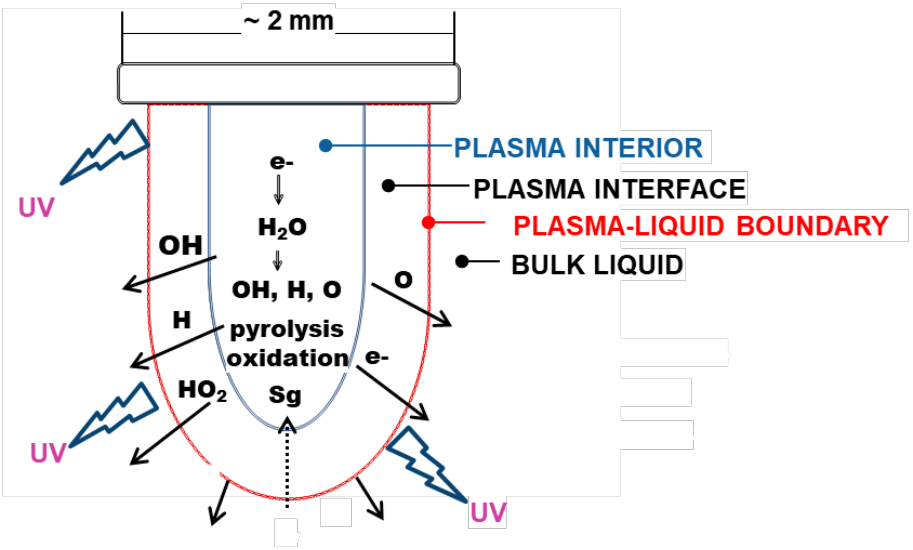
Plasma Formation



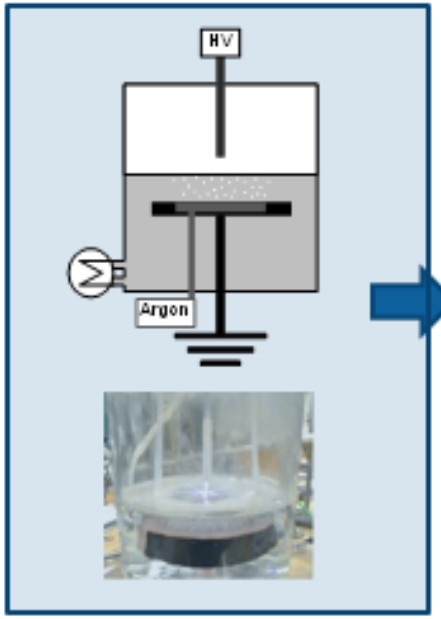
Circuit diagram for a pulsed power supply

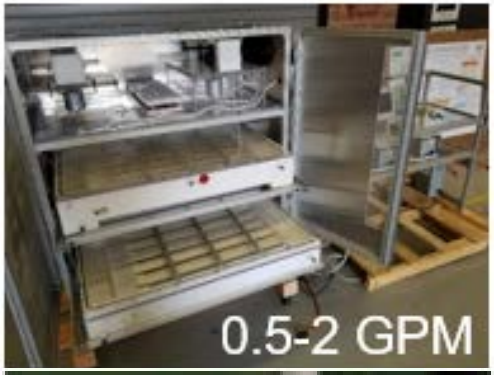


Plasma in argon gas contacting water



Plasma PFAS Treatment

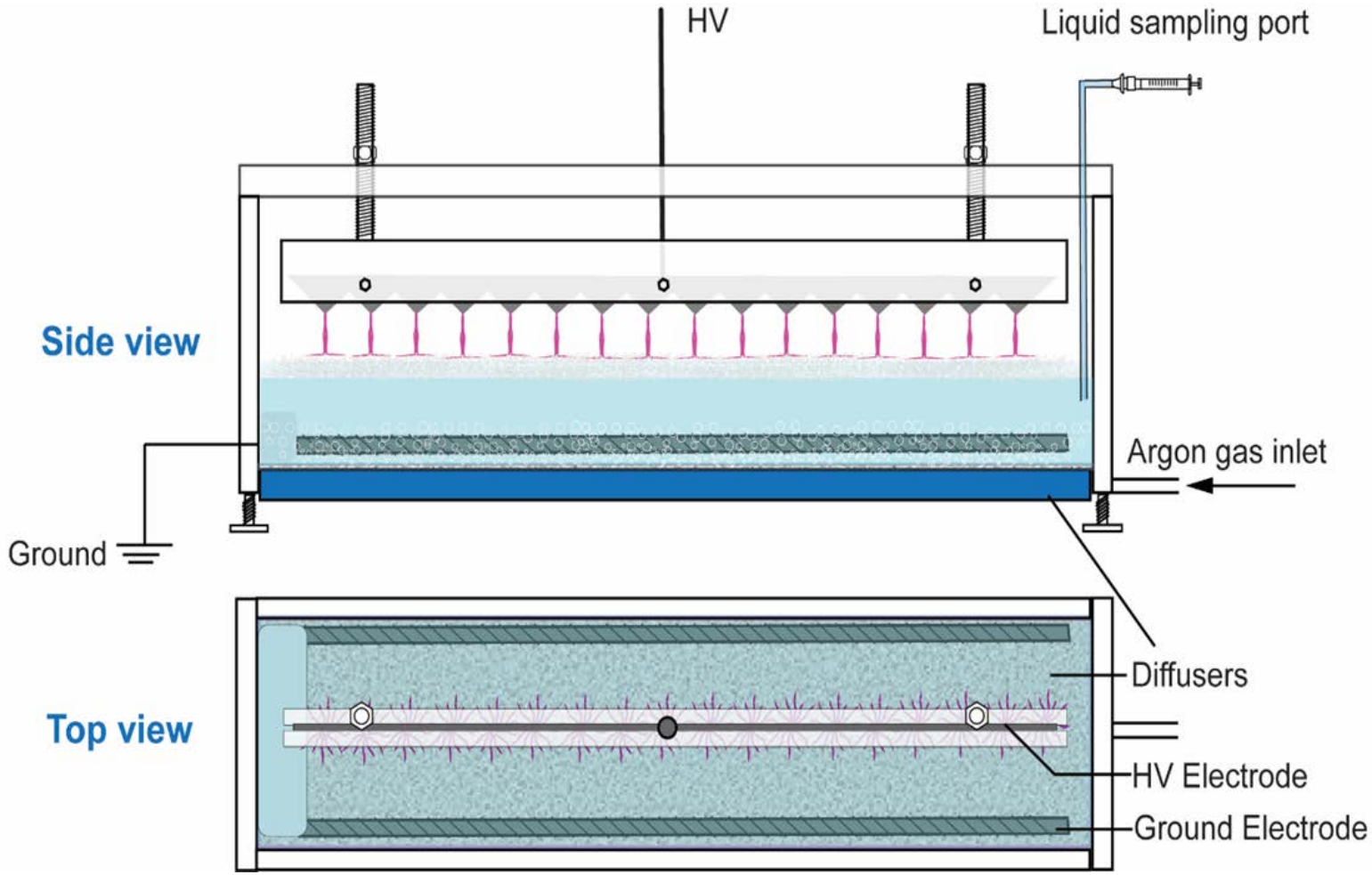




Current generation reactor – 10 gpm

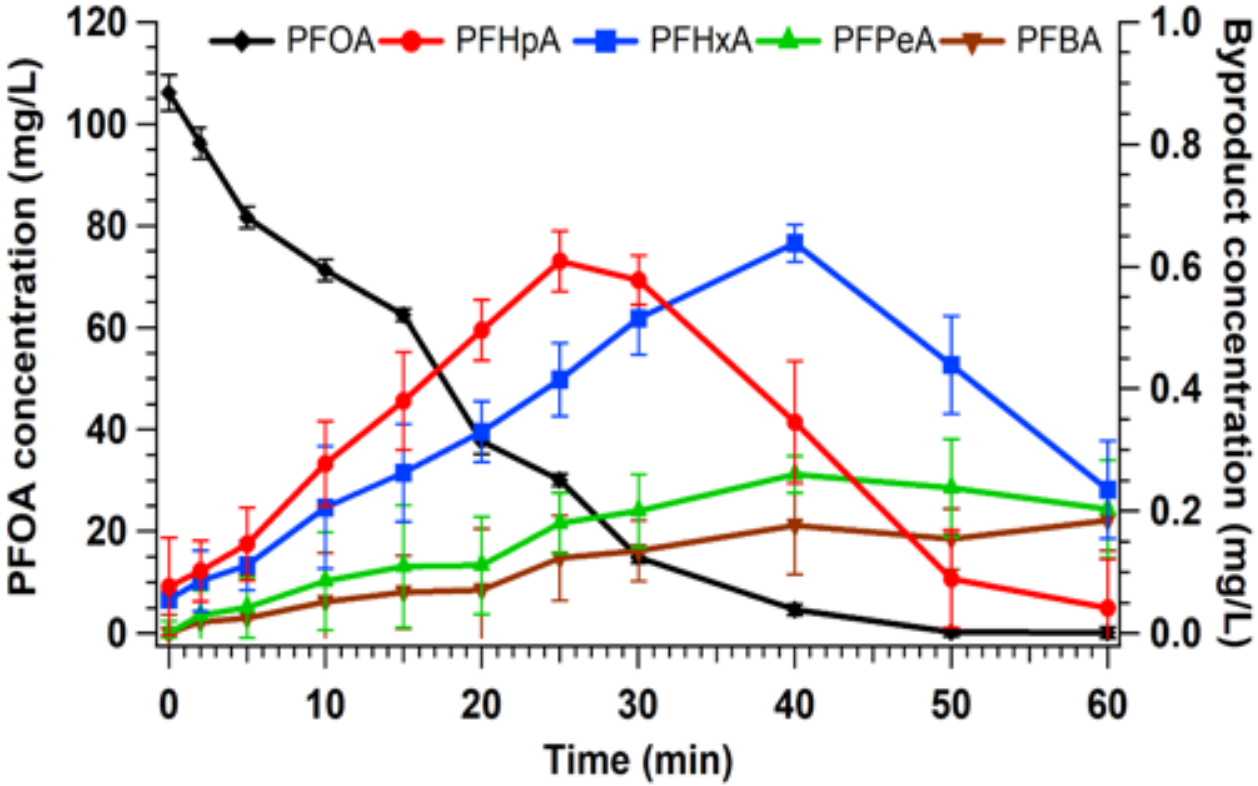
***Source**: Selma Mededovic Thagard, Gunnar Stratton, Christopher Bellona, and Thomas Holsen, Enhanced Contact Electrical Discharge Plasma Reactor for Liquid and Gas Processing, US Patent Number 10, 357, 753 B2, Issued on July 23, 2019*

IDW Reactor


HV
Liquid sampling port
Side view
Argon gas inlet
Ground
Diffusers
Top view
HV Electrode
Ground Electrode

Plasma Treatment Results

PFOA Containing Lab Water, 4% NaCl Concentration



1.5 L of solution

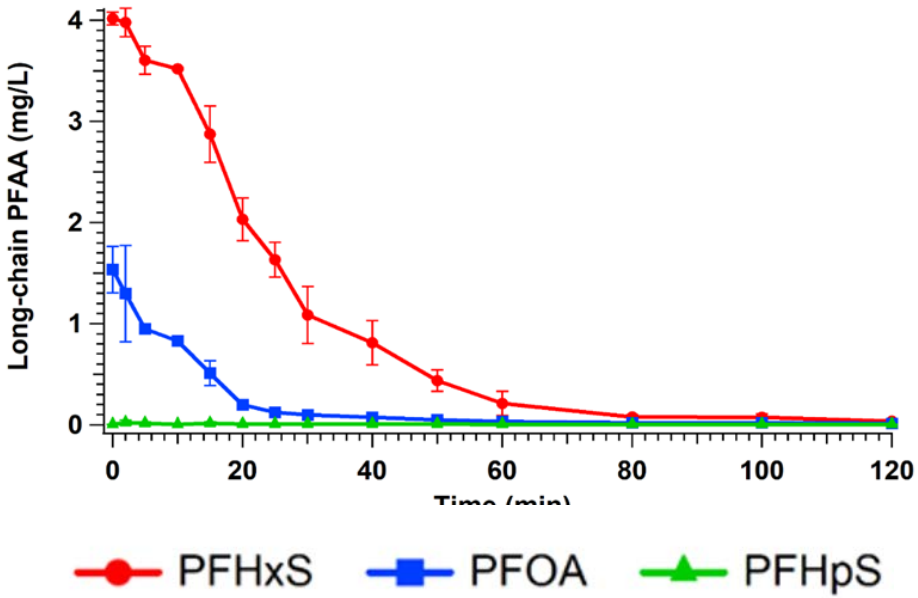
PFOS removal faster than PFOA.

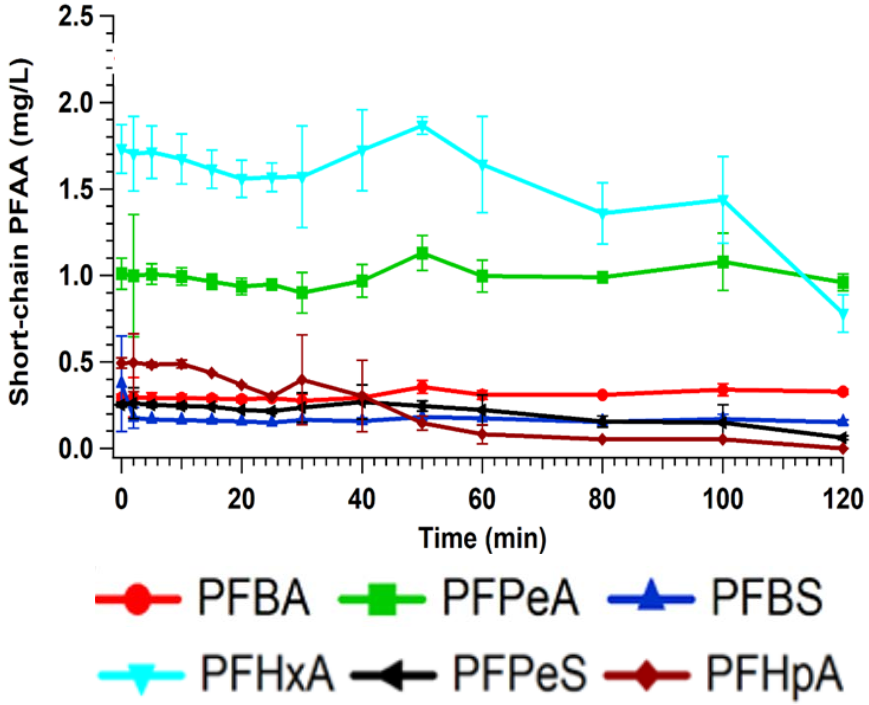
400 Watt reactor

PFOA concentration decreased rapidly
Shorter chain PFAAs were produced and then destroyed

Plasma Treatment Results

Still Bottoms from Pease





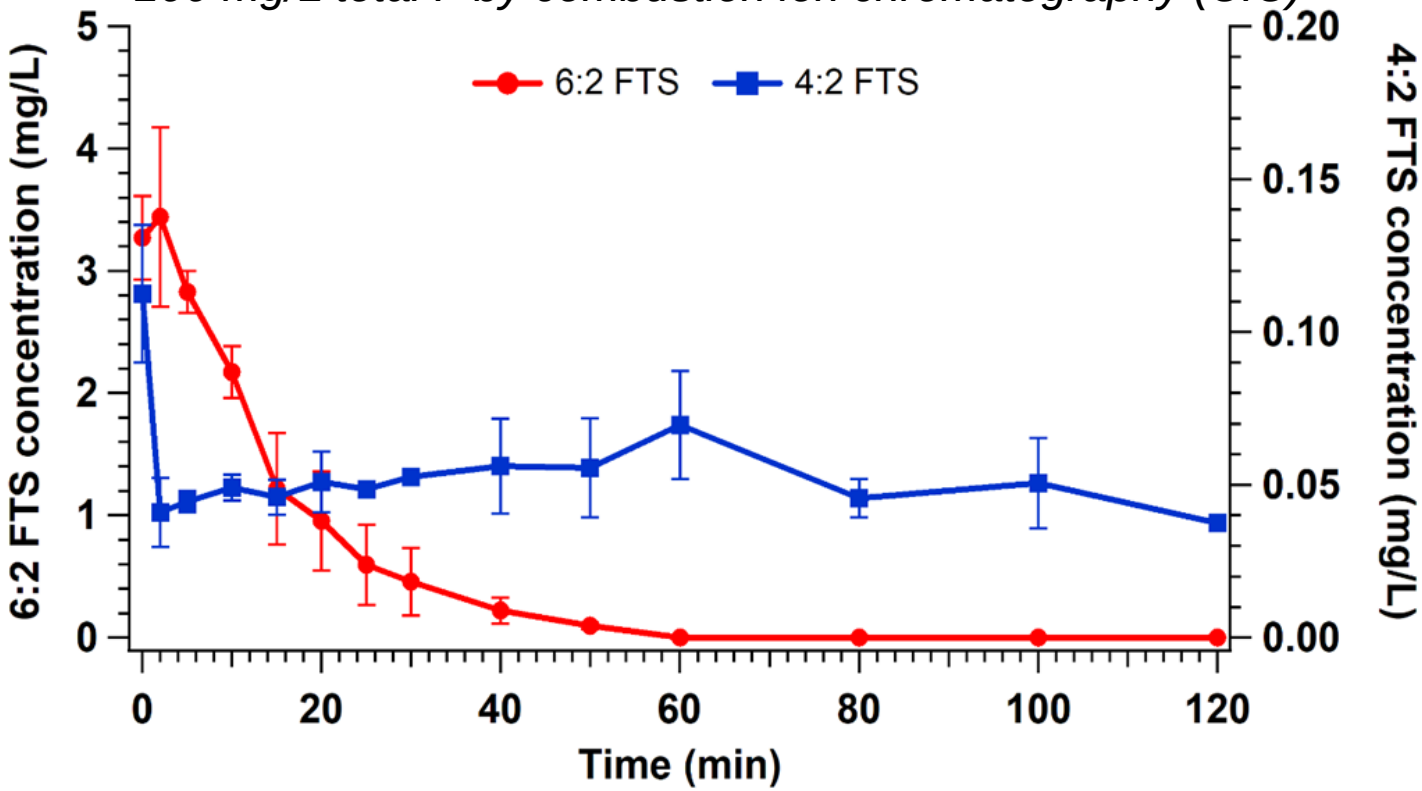
Long-chain PFAAs removed faster than short-chain PFAAs

Plasma Treatment Results

Still Bottoms from Pease

50 mg/L total organic precursors (TOP)

100 mg/L total F by combustion ion chromatography (CIC)

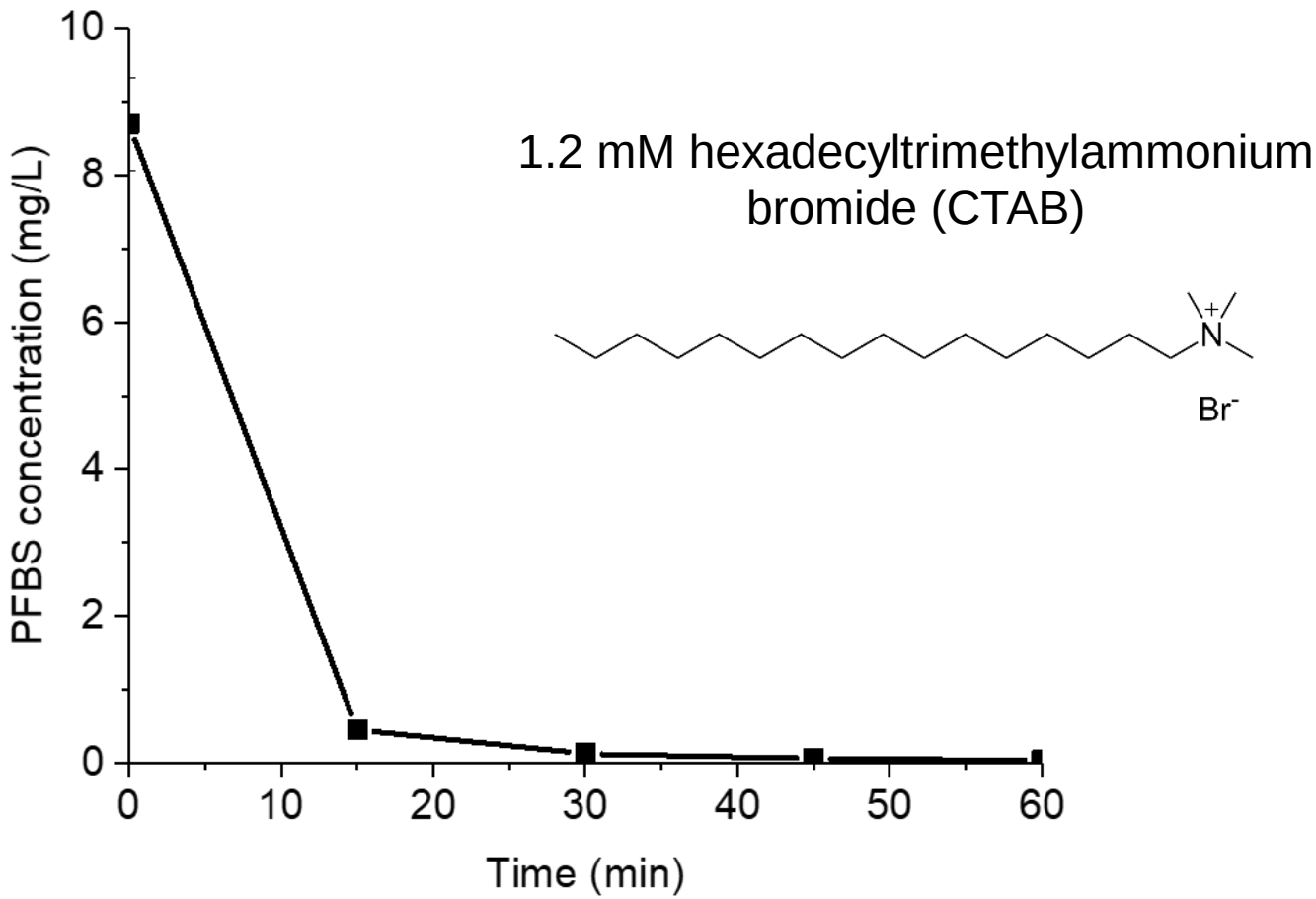


Precursors removed during treatment and converted to PFAAs

Unidentified precursors also present in high concentration

Plasma Treatment Results

Short-Chain Acid Removal with Cationic Surfactant Addition



Cationic surfactant addition significantly increased PFBS removal

Plasma Treatment Results

- Plasma treatment of brine solutions is effective at destroying PFAS
- Precursors in soil washing solution will extend required treatment times
- Plasma treatment is relatively insensitive to salt concentration and small amounts of MeOH (data not shown)

Conclusions

- Soil washing with MeOH + NaCl is effective at removing PFAS
  - Water alone is fairly effective
- PFAS are removed from soil quickly
  - Minutes in these experiments
- Plasma treatment from high concentration salt solutions is effective
- Precursor concentrations drive treatment times
  - Precursor oxidation before plasma treatment would decrease treatment times and may be economically beneficial

Benefits to DoD

- A significant amount of PFAS containing IDW will be generated in the coming years
- On-site destructive treatment would accomplish the following
  - Decrease IDW disposal costs
  - Limit DoD future liability

Acknowledgments

- Clarkson University
  - Selma Thagard Mededovic
  - Michelle Crimi
  - Justin Miceli
  - Sujan Fernando
  - Raj Singh
- GSI Environmental
  - Stephen Richardson
  - Poonam Kulkarni
- ECT2
  - Steve Woodard
  - Mike Nickelsen
- Andrea Leeson and her team

For additional information, please visit

https://serdp-estcp.org/Program-Areas/Environmental-Restoration/ER18-1624

Speaker Contact Information

tholsen@clarkson.edu; 315-268-3851

Q&A Session 2

SERDP DOD • EPA • DOE | ESTCP

The next webinar is on May 21, 2020

Analysis of Defense Related Ecosystem Services

SERDP DOD • EPA • DOE | ESTCP

Survey Reminder

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

SERDP DOD • EPA • DOE | ESTCP