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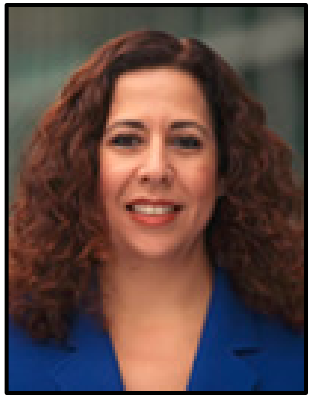
Improved Approaches for PFAS Sampling and Treatment

January 28, 2021

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)
  Dr. Andrea Leeson, SERDP and ESTCP
- **Developing PIGE into a Rapid Field-Screening Test for PFAS** (25 minutes + Q&A)
  Dr. Graham Peaslee, University of Notre Dame
- **PFAS Transformation and Mitigation with nNi^0Fe^0-Activated Carbon Nanocomposites** (25 minutes + Q&A)
  Dr. Linda Lee, Purdue University
- **Final Q&A session**

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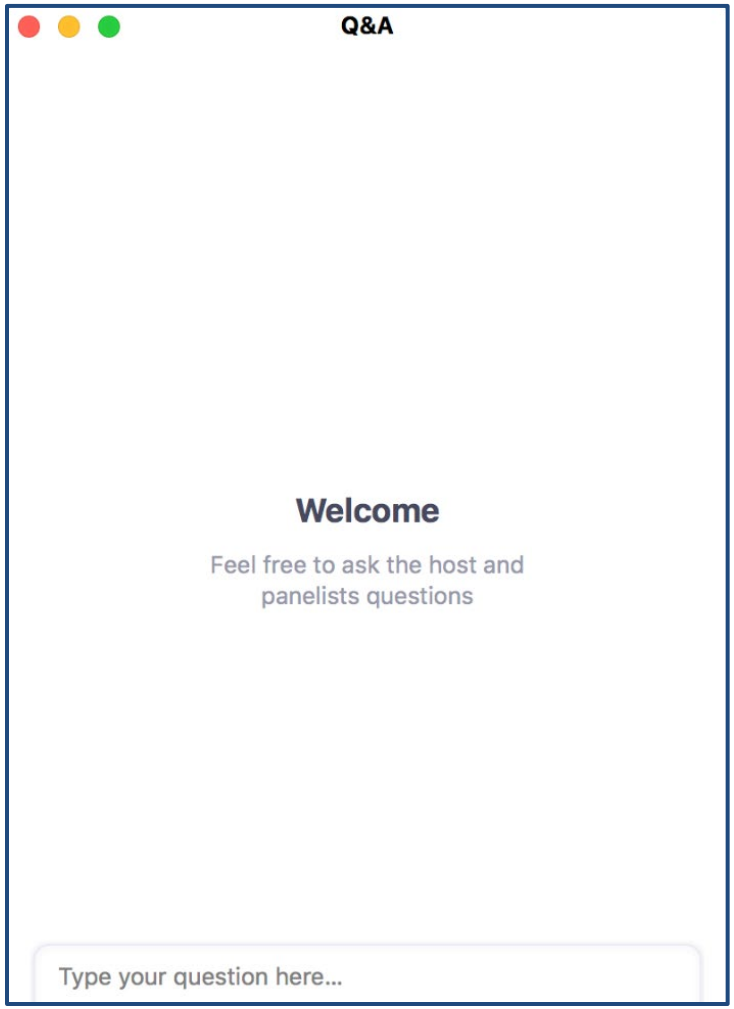

SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
SERDP and ESTCP

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DoD's Environmental Technology Programs

Science and Technology

- Statutory program established 1991
- DoD, DOE, EPA partnership
  - Advanced technology development to address near-term needs
  - Fundamental research to impact real world environmental management

Demonstration and Validation

- Demonstrate innovative cost-effective environmental and energy technologies
  - Transition technology out of the lab
  - Establish cost and performance
  - Partner with end user and regulator
  - Technology transfer
    - Accelerate commercialization or broader adoption
    - Direct technology insertion

Environmental Drivers

Sustaining Ranges, Facilities and Operations

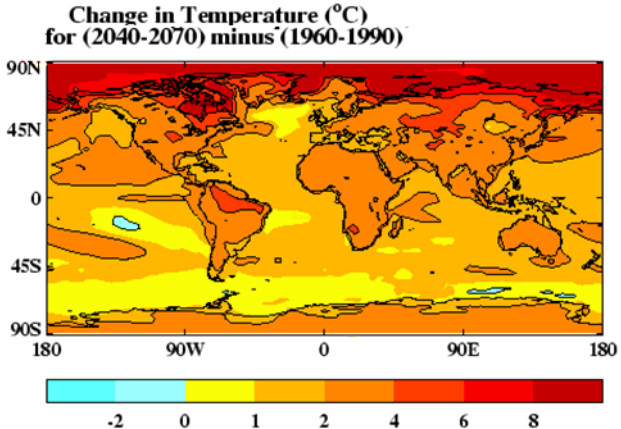
Maritime Sustainability
Threatened and Endangered Species

Toxic Air Emissions and Dust

UXO and Munitions Constituents

Noise

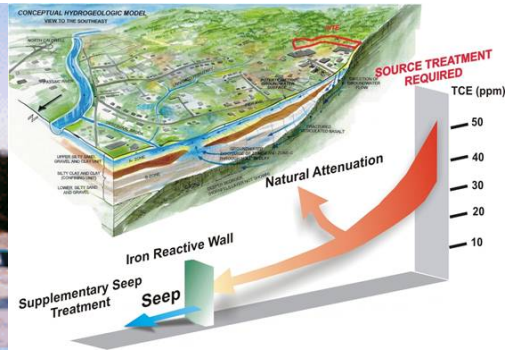
Sustainable FOB



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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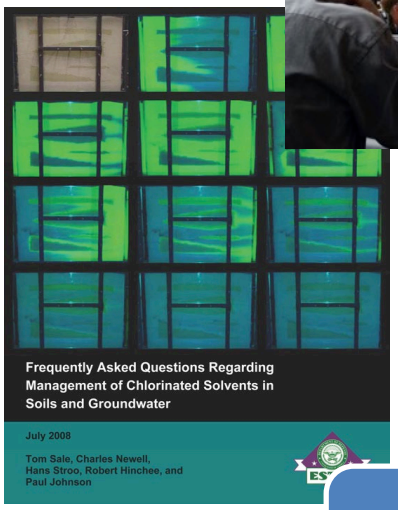


Webinars

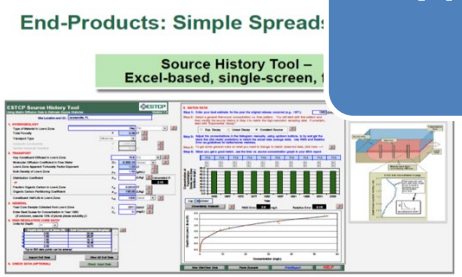
In Person Training

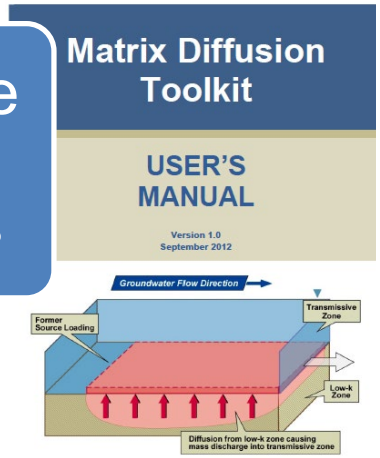
EnviroWiki

Technology Transfer

Videos

Guidance and Manuals





SERDP and ESTCP Webinar Series

Date	Topic
February 11, 2021	Advances in the Detection of Submerged Unexploded Ordnance in Marine Environment
February 25, 2021	Managing Chlorinated Solvents in Groundwater Using Biological Treatment
March 11, 2021	New Resource Conservation Paradigms on DoD Lands
March 25, 2021	Safer Alternatives for Surface Engineering and Structural Materials in Weapons Systems and Platforms: A Fred Lafferman Tribute Webinar
April 8, 2021	Advances in Understanding PFAS Ecological Risks
April 22, 2021	Innovative Approaches to Monitor and Survey At-Risk Species on DoD Lands

For upcoming webinars, please visit

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Developing PIGE into a Rapid Field-Screening Test for PFAS

Graham F. Peaslee, Ph.D.
University of Notre Dame

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Agenda

- Total fluorine methods
  - Useful surrogate for PFAS in fieldwork
- Making PIGE spectroscopy portable
- Risk to build and field test a prototype system minimized by limited scope research project
- Developing novel filters as PIGE targets

Note: *PFAS = per- and polyfluoroalkyl substances; PIGE = particle-induced gamma ray emission*

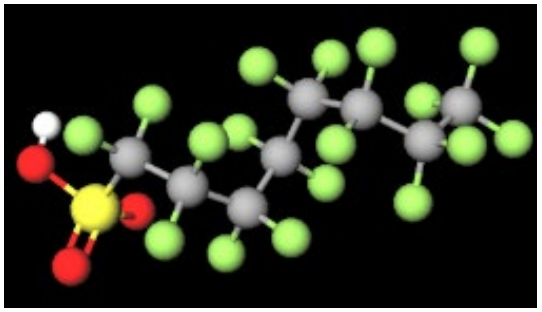
Background

- High-priority need
  - Identified by the ER19-C2 Statement of Need for “in-situ and ex-situ remediation of PFAS-contaminated groundwater”
- LC-MS/MS used to measure some PFAS analytes
  - Used in site characterization, remediation effectiveness, and routine follow-up assessments
  - Usually < 10% of all PFAS
  - Slow and costly, but excellent sensitivity
- Concept: Field-deployable PFAS screening technique
  - Rapid and sensitive
  - Includes all organofluorine
  - “Game-changer” on-site

Portable PIGE concept

Background

- PFAS are highly fluorinated molecules
  - Very few other sources of fluorine in the environment (such as inorganic fluoride)
- LC-MS/MS
  - "Gold standard" for detection and identification
  - Slow
  - Only measures small fraction of PFAS in field unless TOP assay performed
  - Most precursor mass missed
- Total F methods developed
  - Combustion Ion Chromatography, TOP assay and LC-MS/MS, PIGE
  - All are quantitative
  - PIGE is spectroscopic (rapid)

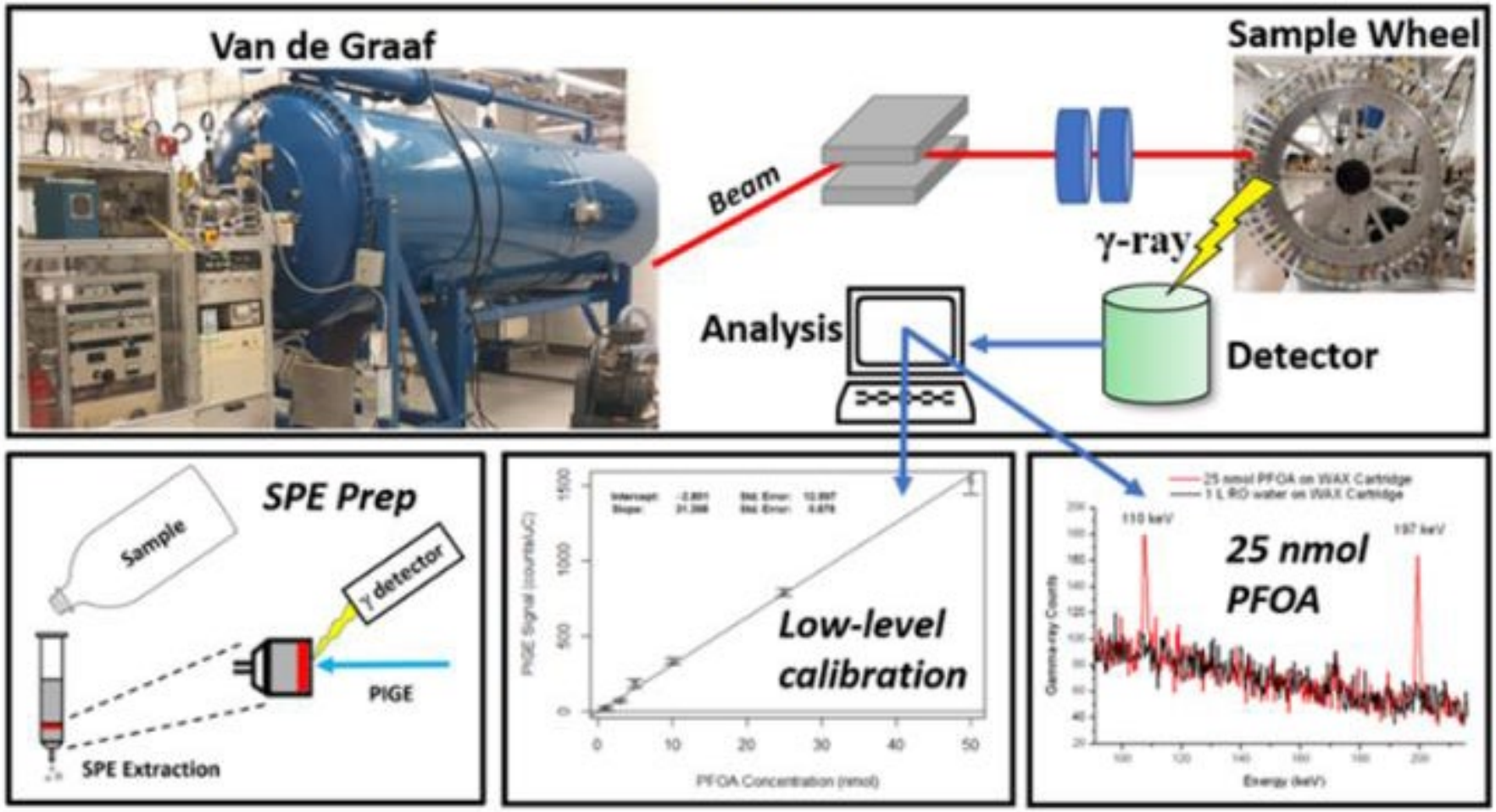


PFOS (65% F)

***Note**: TOP = Total Oxidizable Precursor*

Particle Induced Gamma-ray Emission

Schematic of Current PIGE Measurements



Technical Objectives

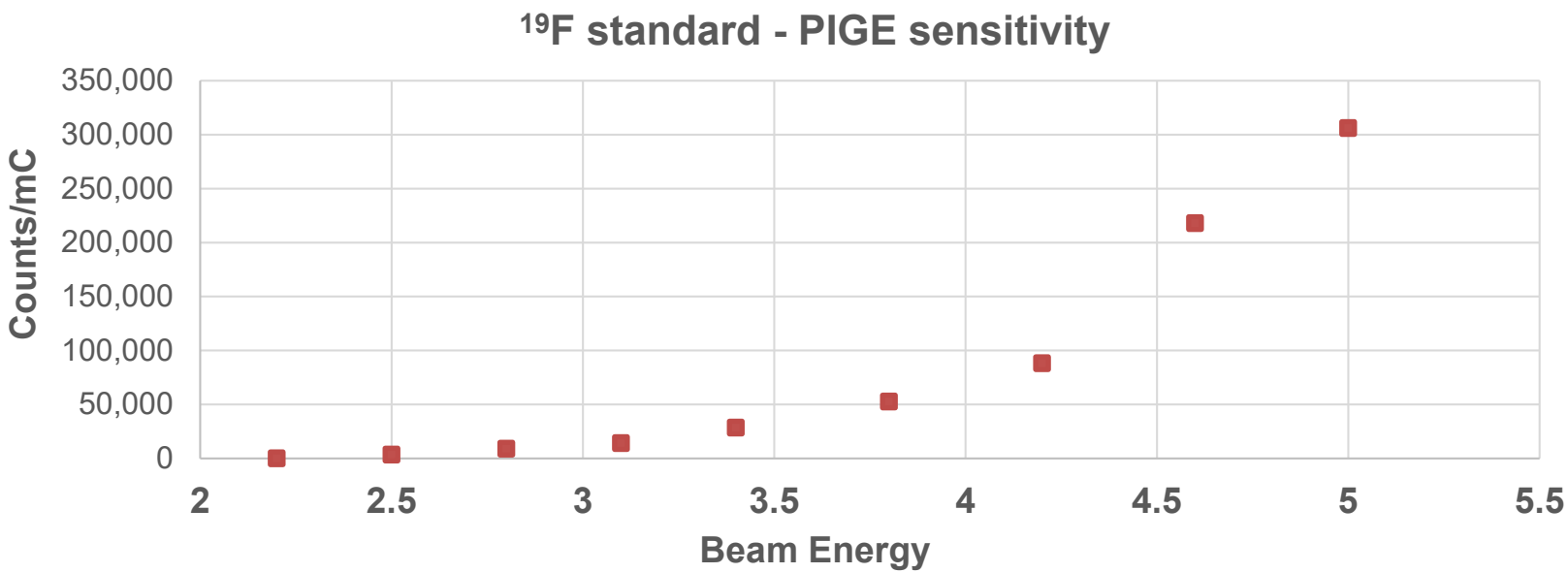
- Take established total F method (PIGE) and develop it into a PFAS field-screening method
  - Task 1: Determine beam-energy dependence of F signal
  - Task 2: Optimize and determine MDL achievable for PFAS
- Based on successful outcome of tasks 1 and 2
  - Take advantage of DARPA-funded construction of a prototype field-deployable accelerator that could be adapted to run PIGE
  - Task 3: Re-design Centurian™ RFQ accelerator system that could provide PIGE as a field-deployable unit

***Notes**: DARPA = Defense Advanced Research Project Agency; MDL = method detection limit; RFQ = radio-frequency quadrupole*

Results – Task 1

Beam-Energy Dependence

- Use existing lab at ND to measure F sensitivity
- Successful: every 0.5 MeV is ~factor of 2-3 increase
- Discovered protons above 5 MeV began to activate N_2, O_2



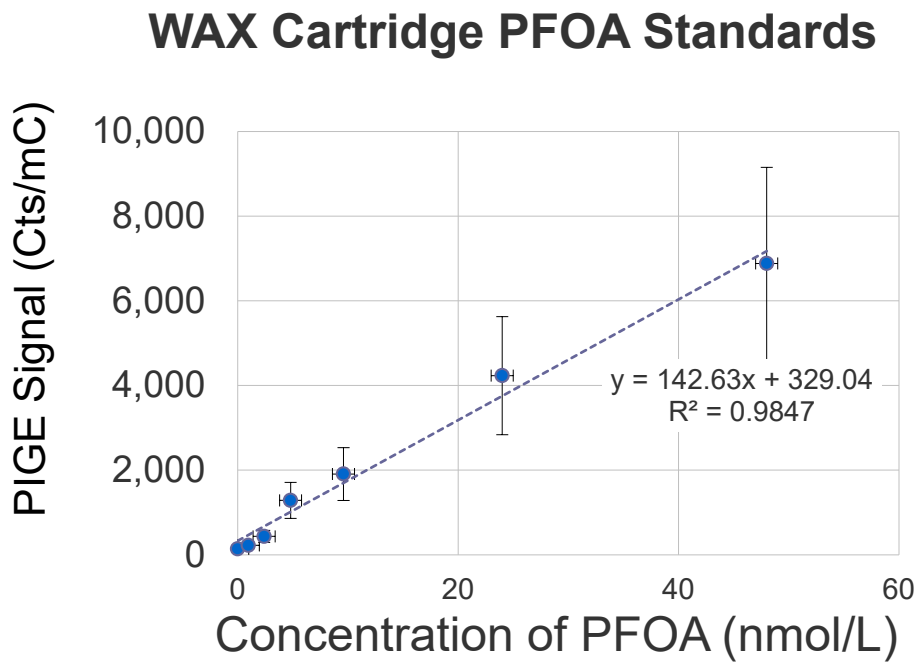
F signal as a function of beam energy

***Note**: ND = University of Notre Dame; MeV = megaelectron volt;*

Results – Task 2a

Optimize MDL

- Measure MDL with 50 mL samples on WAX
- Successful MDLs
  - PFOA – 1.2 ppb F
  - PFOS – 1.1 ppb F
  - PFHxS – 1.4 ppb F



MDLs also scale linearly with volume
1L samples → ~ 50 ppt total F

***Notes**: PFOA = perfluorooctanoic acid; PFOS = perfluorooctanesulfonic acid; PFHxS = perfluorohexanesulfonate; WAX = weak anion exchange*

Results – Task 2a

Optimize MDL

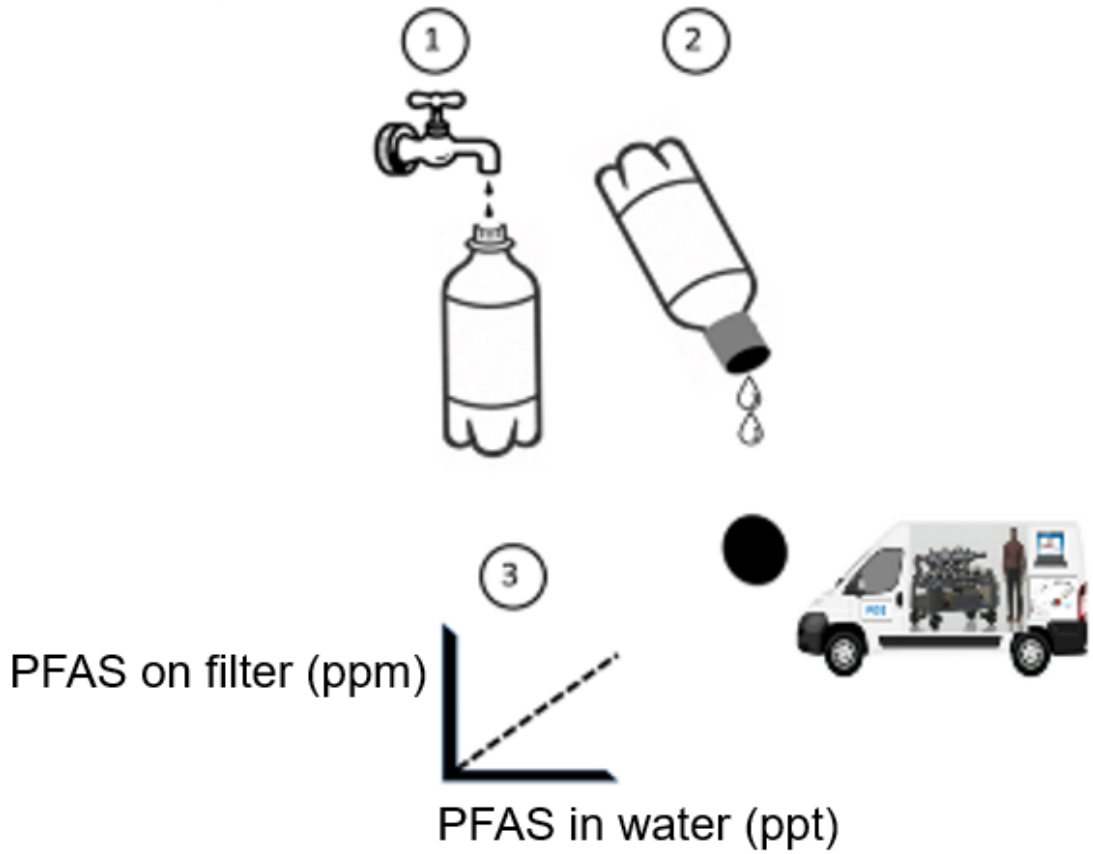
- PIGE screening data in groundwater
  - Range of ppb FI from multiple sample depths
- High, but AFFF-impacted sites have lots of fluorine

***Note**: Contour is approximate, not all locations sampled; some locations not included in contouring*

Results – Task 2b

Optimize MDL

- Discovered new SPE media
  - GAC felt
- Used as an in-line filter
  - Gravity filter 2L in ~2 minutes



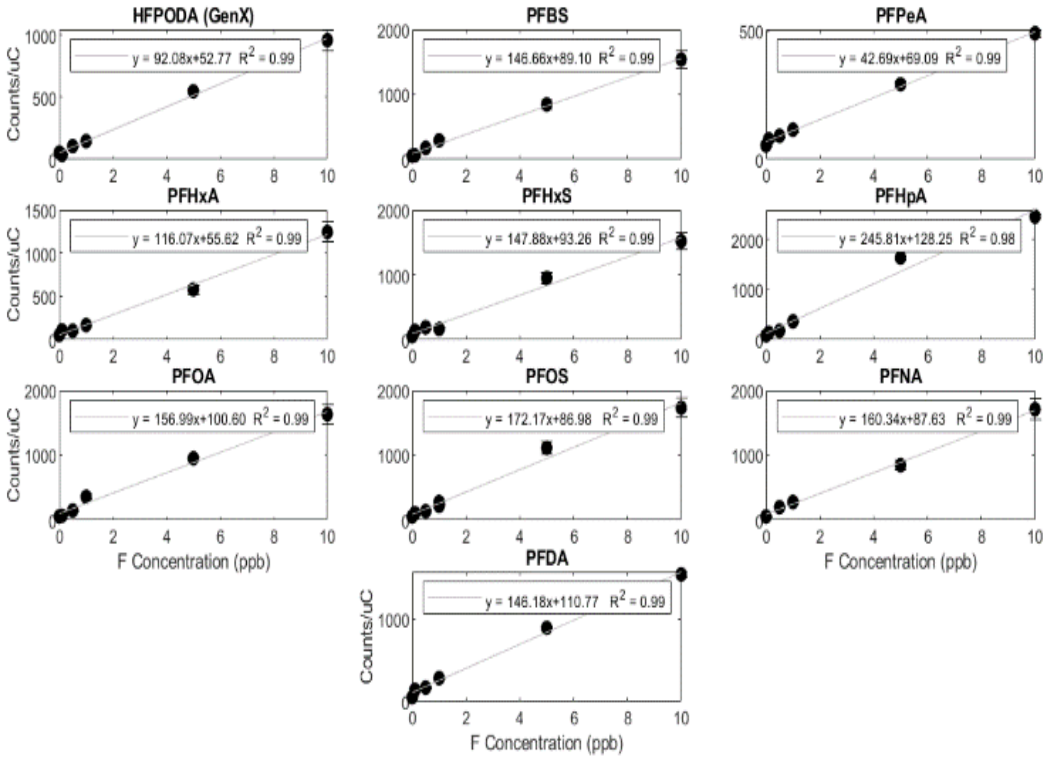
Notes: *GAC = granular activated carbon; SPE = solid phase extraction*

Results – Task 2b

Optimize MDL

- Successful MDLs
  - PFOA – 330 ppt F
  - PFOS – 550 ppt F
  - PFHxS – 200 ppt F
- MDLs still scale linearly with volume
  - 20 L samples → ~20-50 ppt total F

Calibration Curves for Various PFAS Using PIGE

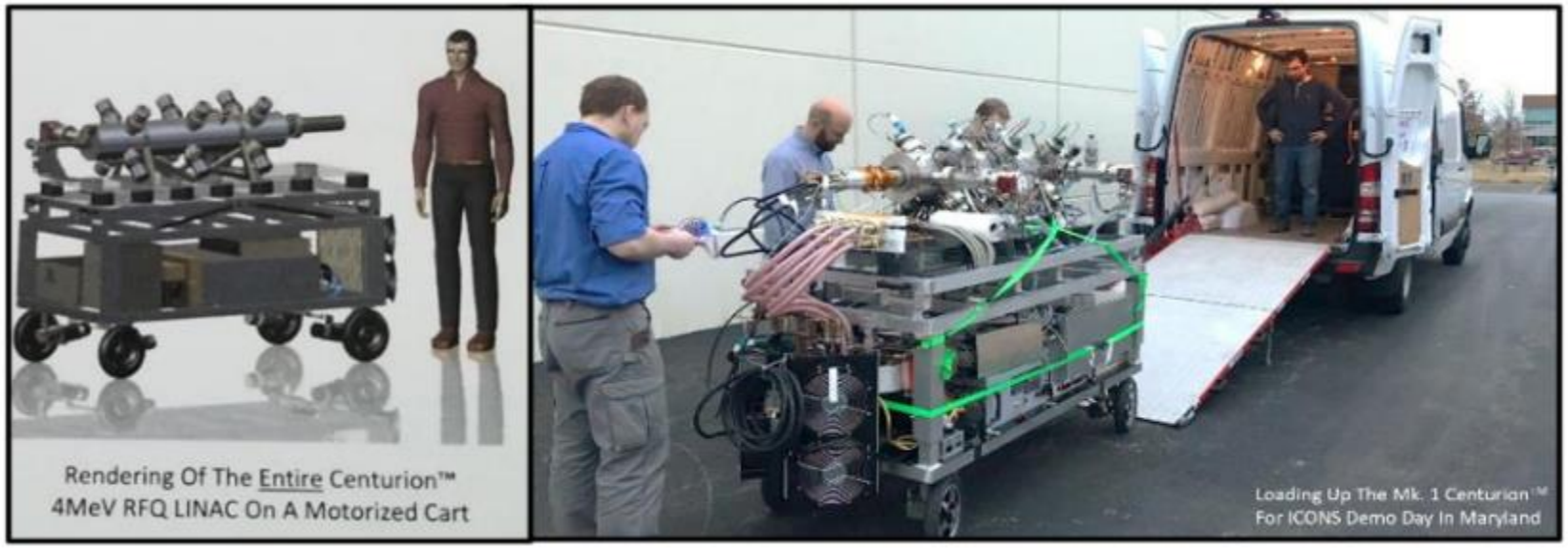


Linear response for all PFAS

Results – Task 3

Accelerator Re-Design

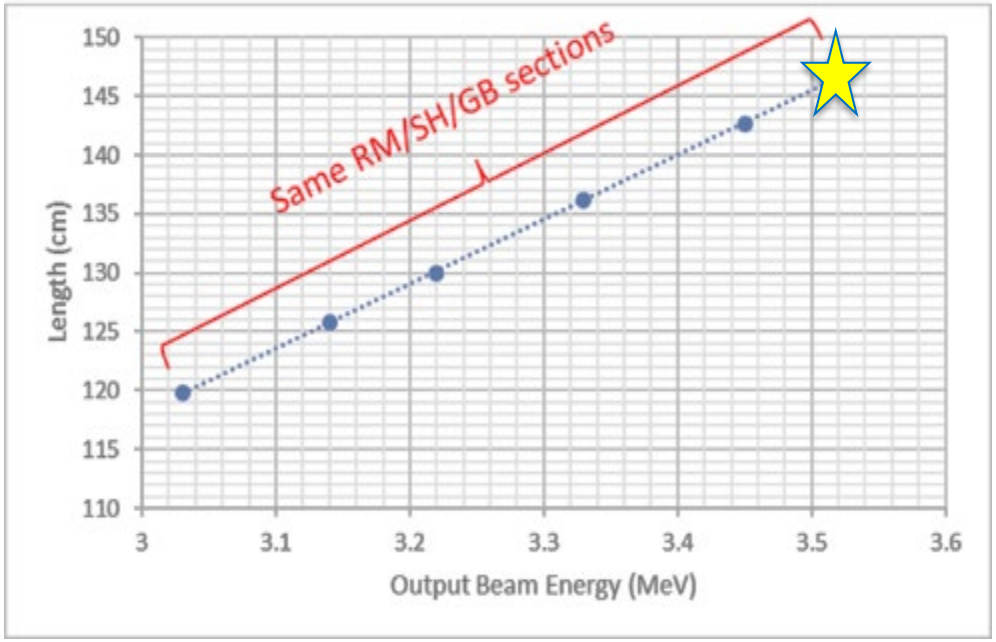
- Successful
  - Existing RFQ accelerator: delivers 4 MeV deuterons
  - Field tested at Aberdeen



Results – Task 3

Accelerator Re-Design

- Successful
  - Length of accelerator cavity chosen to maximize beam energy
  - Still fit within footprint that is field-deployable and can be powered on-site



Results – Task 3

Accelerator Re-Design

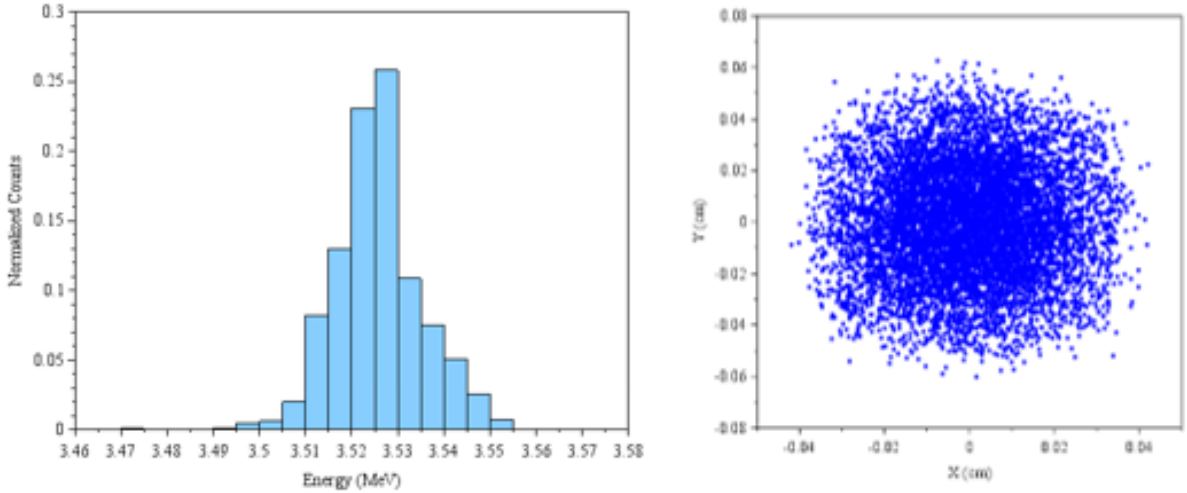
Parameter	Value
Final beam energy	3.52 MeV
Transmission at 10 mA	82.00%
Input transverse emittance (normalized)	0.20 π mm-mrad
Output emittance (normalized)	0.14 π mm-mrad
Output beam FWHM energy spread at 10 mA	15 keV
Linac operating repetition rate	60 Hz
Output beam width	100 μs
Vane length	147 cm
Pulse cavity RF power	212 kW
Pulsed beam power (10 mA)	35 kW
Pulsed RF input power	247 kW
Average RF power requirement	1.5 kW

Notes: *eV = electron volt; mrad = milliradian; mA = milliampere; RF = radio frequency*

Results – Task 3

Accelerator Re-Design

- Successful
  - mA of beam available at 3.5 MeV
  - 20X ND facility = more sensitivity

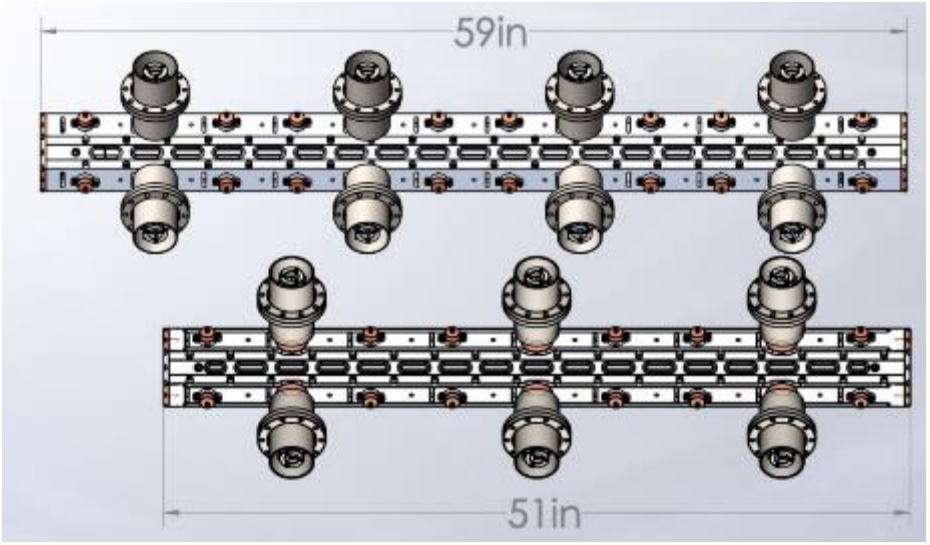


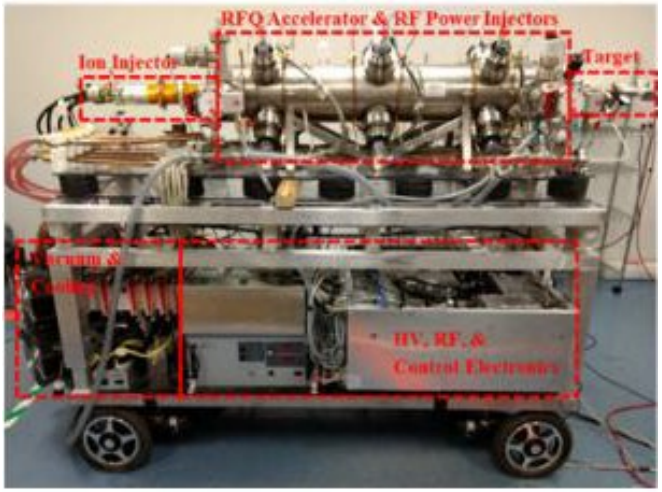
Histogram (left) of energy distribution of proton beam, and beam spot output size (right)

Results – Task 3

Accelerator Re-Design

- Successful
  - Fits inside light truck
  - Can make the measurements!





Existing Centurion™ System

Conclusions

- Principle of scaling to field-deployable size proven
  - Existing accelerator with modifications will work
- SPE media identified (GAC felt)
  - Purchased commercially without modification will work as in-line filters for PFAS
  - Delivers < 50 ppt for ALL anionic organofluorine when connected to a bore pump for 20 minutes
- Risk to build and field test a prototype system minimized by limited scope research project

Future Research

- Surface modification of GAC felt filters
- Addition of existing SPE media (WAX cartridges) and polyvinyl alcohol (PVA)
  - Makes flow-through filters ~50x more sensitive to PFAS
  - More for short-chain PFAS
- Potential applications for ground water, drinking water, blood

Future Research

- Current project successful to demonstrate proof-of-principle
  - For both accelerator design and sample preparation
- Potential follow-on proposal
  - Construct a prototype system with Starfire Industries, LLC
  - Starfire would construct modified Centurian system equipment vehicle
- ND would provide PIGE detection, target system and sample processing station to fit within vehicle

Benefits to DoD

- Environmental consulting firm (Jacobs) would provide site access and personnel to field-test system
- Applicability examples
  1. On-site characterization of plumes while bores drilled
  2. On-site measurement of in-situ and ex-situ of PFAS sequestration and destruction technologies
  3. Long-term screening of remediation, or remediated sites; complementary to LC-MS/MS screening

Acknowledgments

- Principal Investigator
  - Graham Peaslee, University of Notre Dame
- Co-performers
  - Brian Jurczyk, Tom Houlihan, Starfire Industries, LLC
- Students
  - Meghanne Tighe, John Wilkinson, Sean McGuinness, Yukun Jin, Alec Gonzalez

For additional information, please visit
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Speaker Contact Information

gpeaslee@nd.edu; 574-631-7554

Q&A Session 1

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PFAS Transformation and Mitigation with nNi^0Fe^0-Activated Carbon Nanocomposites

Linda S. Lee, Ph.D.
Purdue University

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Agenda

- Problem statement
- Technology description: nNi^0Fe^0-AC
- Batch studies
- Column studies
- Conclusions
- Benefits to DOD

Note: *nNi^0Fe^0-AC = activated carbon-supported zero valent iron-nickel nanoparticles*

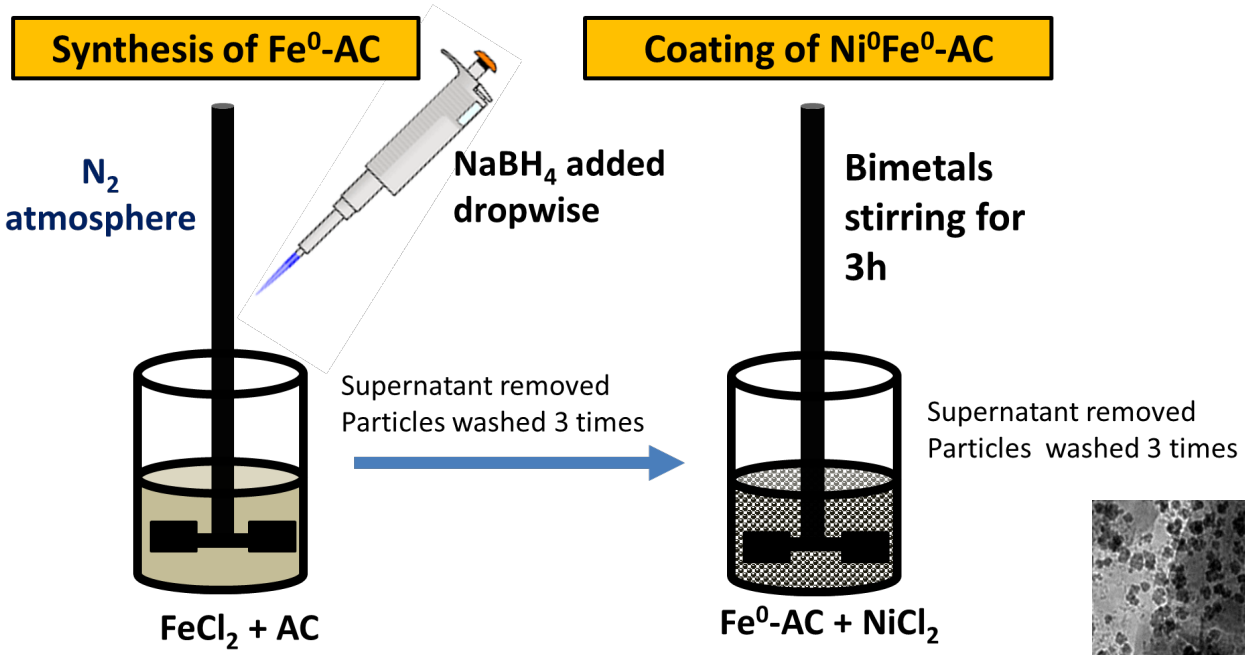
Problem Statement

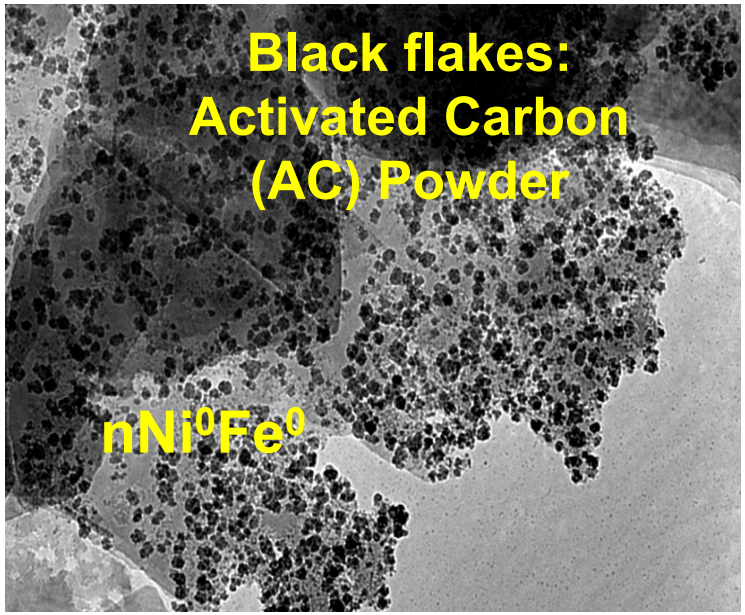
- Low ppt health advisory levels for several per- and polyfluoroalkyl substances (PFAS)
- PFAS presence at numerous DoD sites
- Off-site migration in large diffuse groundwater plumes
- Need for viable in-situ treatment options
- Advanced oxidation approaches have not shown sufficient promise

In-Situ Reductive Treatment Technologies

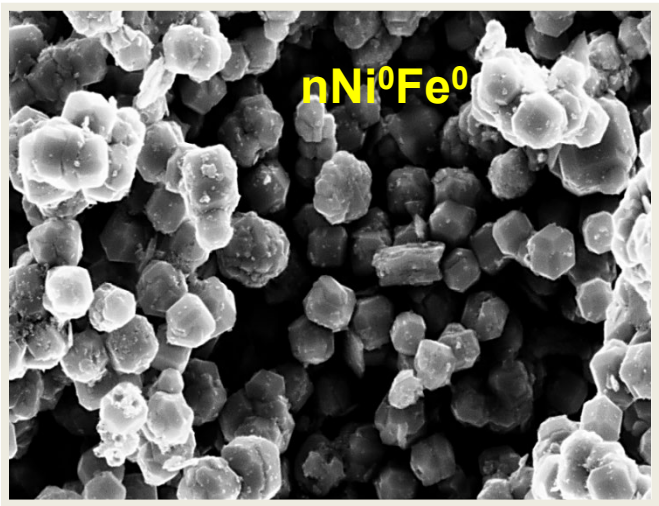
- Zero-valent iron (ZVI, Fe^0) already used in-situ for other halogenated chemicals
- ZVI alone not successful for PFAS treatment
- ZVI modifications needed to enhance reactivity
  - Decrease particle size - nanoscale
  - Add catalyst to decrease energy barrier
  - Add support to reduce particle aggregation
- Catalyst and support options
  - Nickel (Ni) proved to be the most promising
  - Activated carbon support low cost

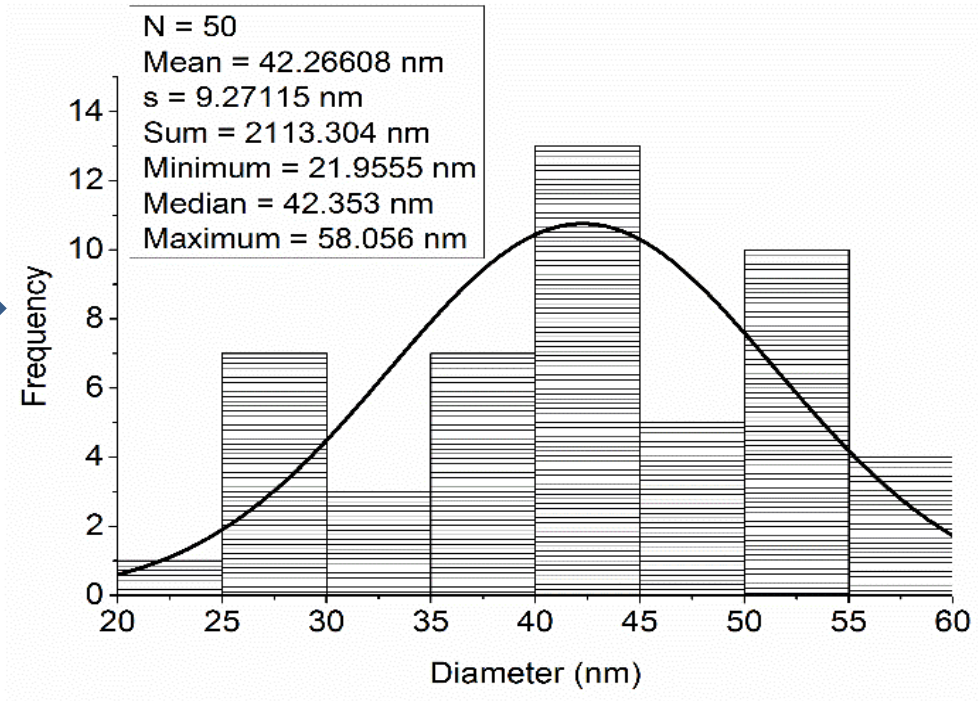
Technology Description: Synthesis





Technology Description: Synthesis

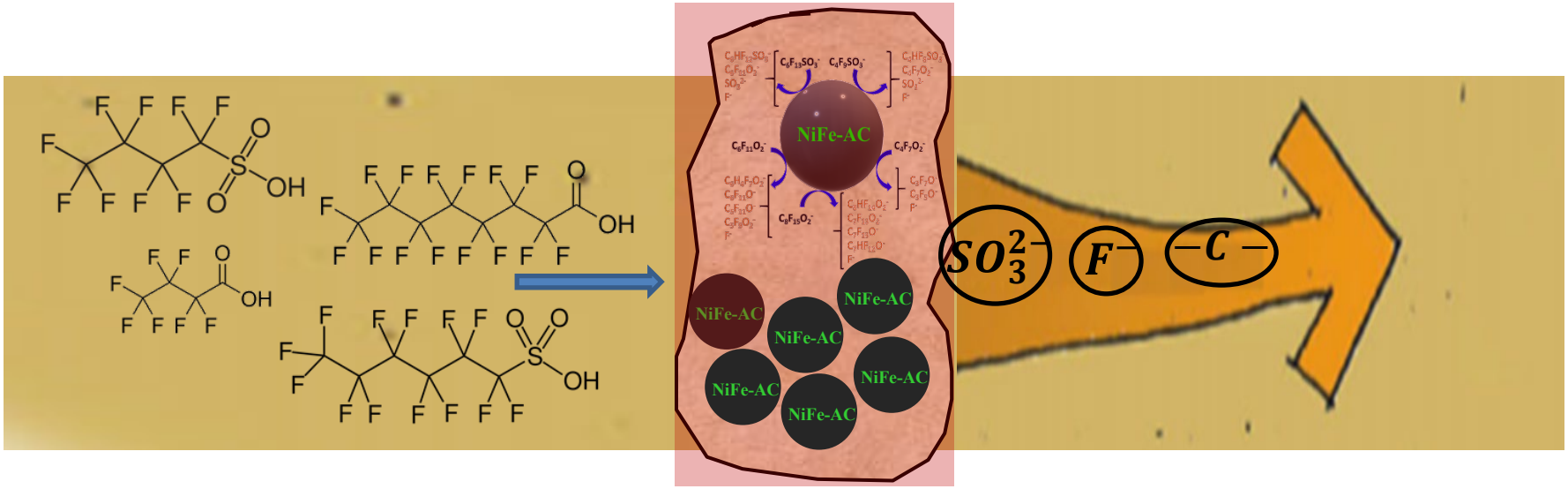




- nNi^0Fe^0-AC deposits on the activated carbon
  - Mean: 42.3 nm
  - Dominant Range: 25-60 nm

Technology Description

PFAS Destruction with Heated nNi^0Fe^0-AC

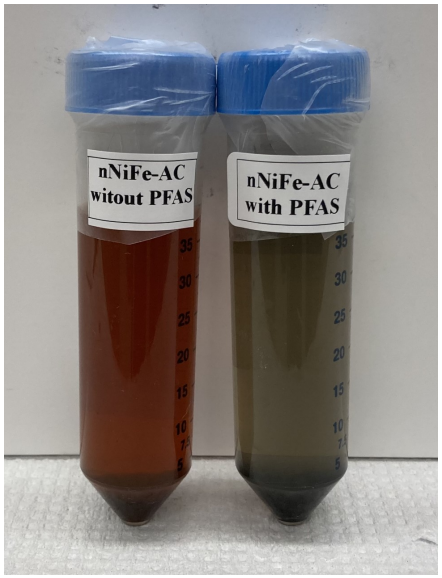


- nNi^0Fe^0-AC nanocomposites transform and mineralize PFAS
- First report of PFOS mineralization by any Fe-based particles
- Provisional patent (2018), active patent application

Technology Description

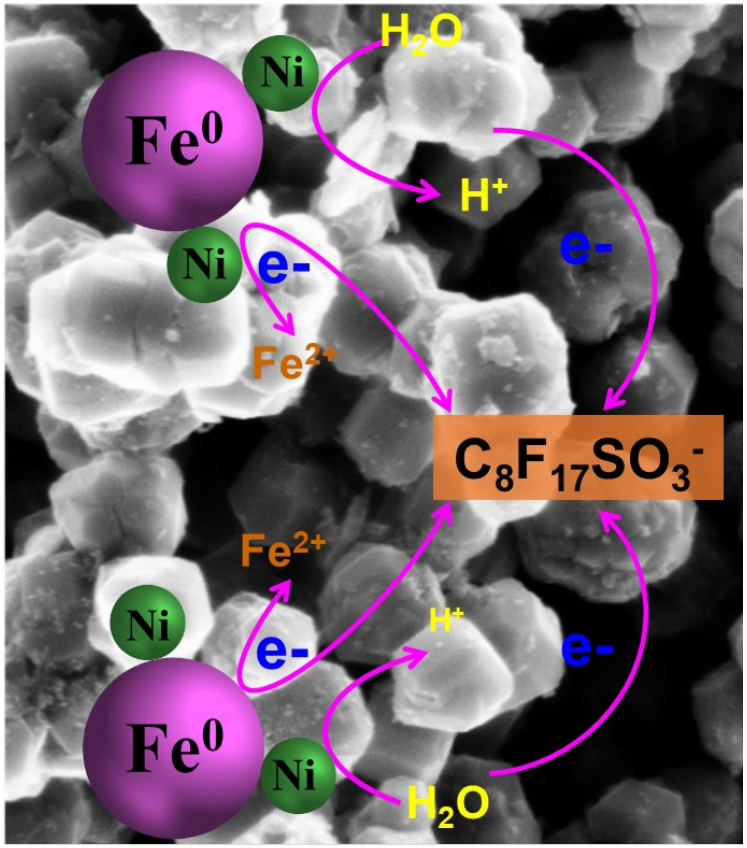
Mechanistic Exploration: Ni and Fe

- Ni and Fe (XPS data)
  - Pre-reaction – both zero valent
  - During reaction with PFAS both convert to oxides
  - Both donate e- in PFAS reaction



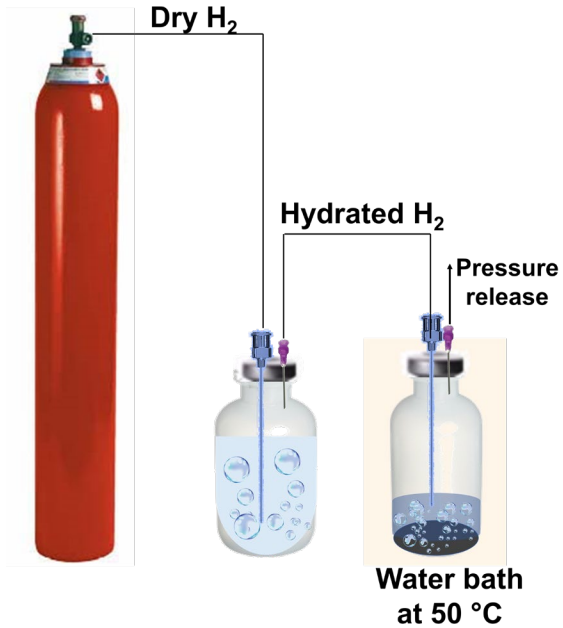
Note: *XPS = X-ray photoelectron spectroscopy*

- H_2 generation with Fe0 corrosion greater during PFOS reactions



Technology Description

Mechanistic Exploration: Ni, Fe, and AC

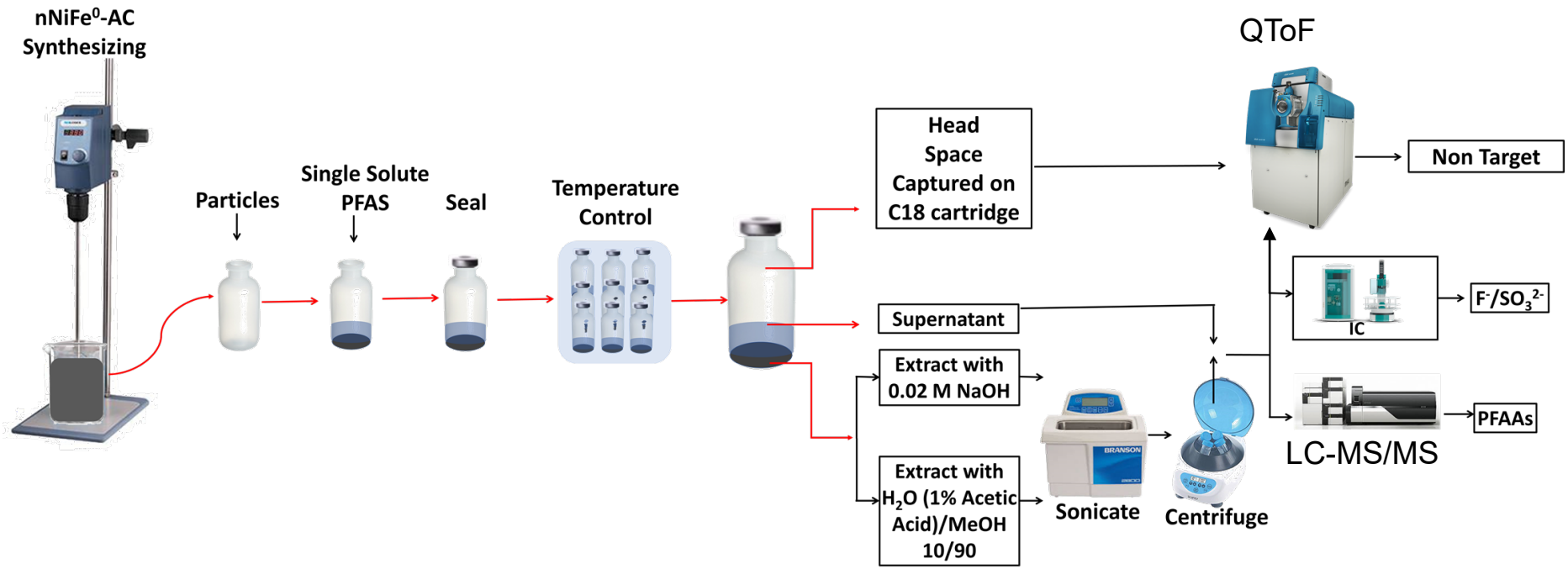


- H_2-bubbling with Ni or Ni^0-AC particles: 50% less PFOS transformation than with nNi0Fe0-AC
- Fe's role more than generating H_2

- AC prevented flocculation
- No changes in carbon functional states (e.g., C=0, C-C, etc.) - no apparent role in e- transfer

Technical Approach

Batch Reactors

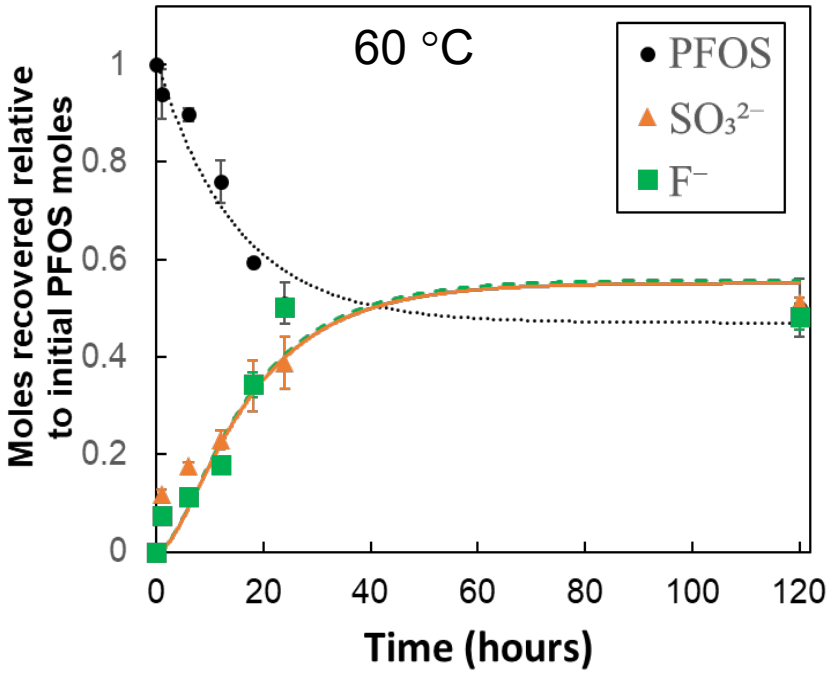


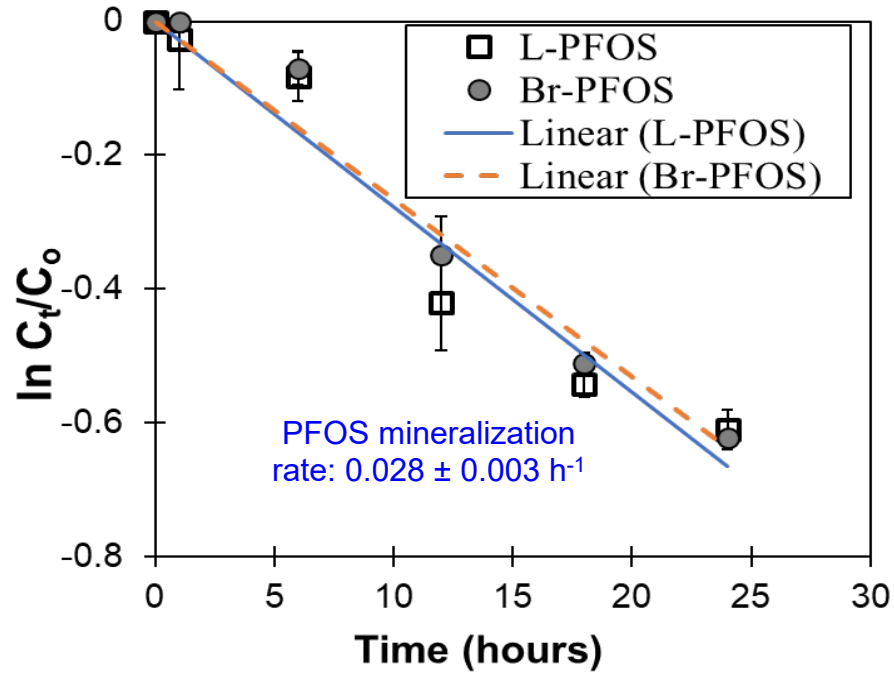
Variables: Single solute, mixtures, temperature

Note: *QToF = Quadrupole Time-of-Flight*

Results: Batch Studies 60 °C

Linear and Branched PFOS Degradation Kinetics

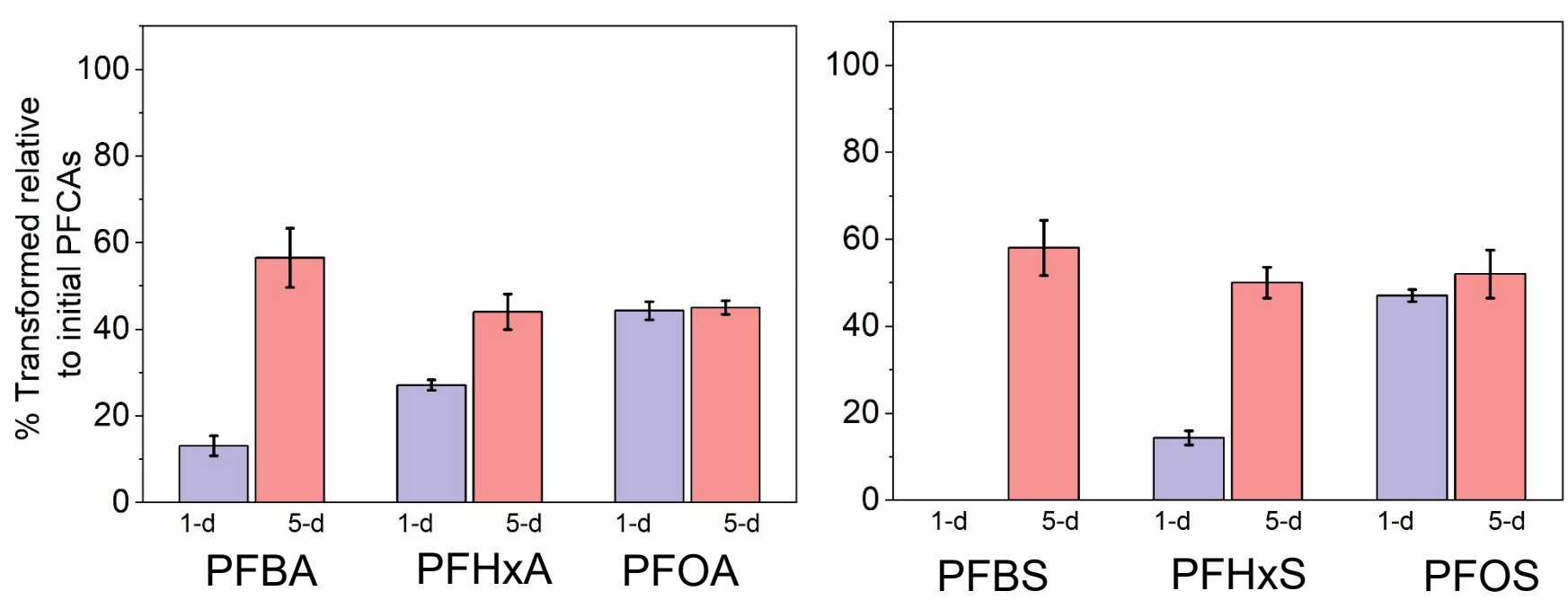




- Rapid degradation of both linear (L) and branched (Br) PFOS
- 53 ± 1% PFOS was unrecovered at 60 °C
- Essentially all unrecovered PFOS was mineralized

Results: Batch Studies 60 °C

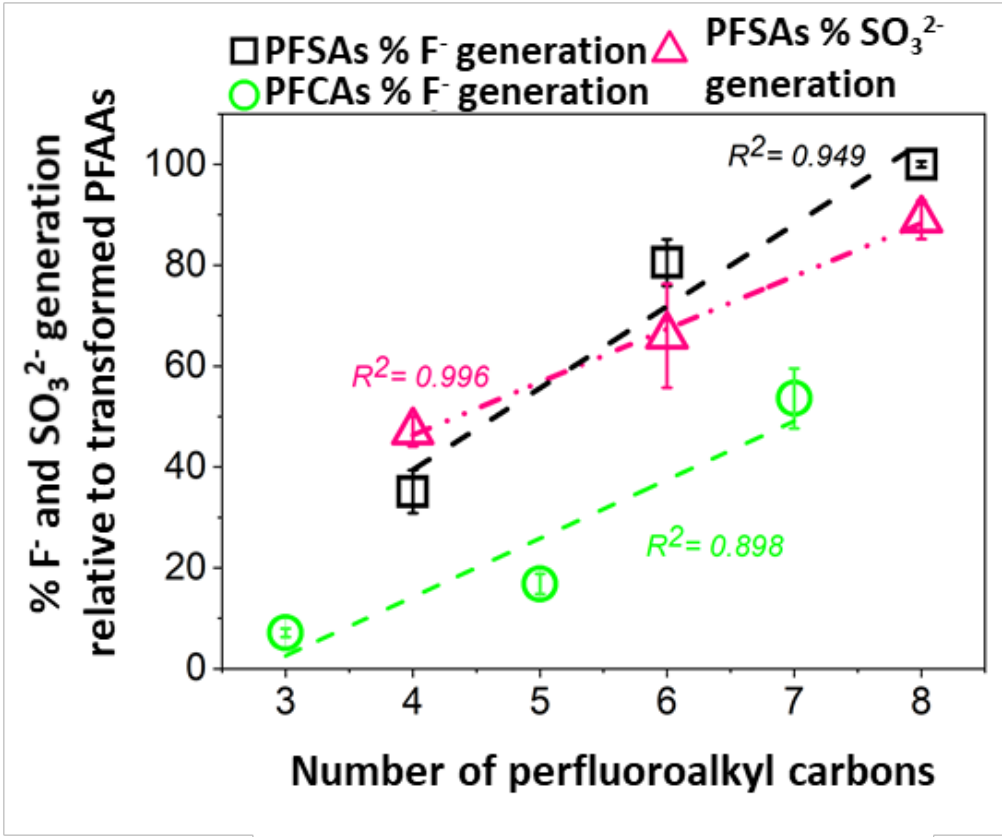
% Perfluoroalkyl Acid (PFAA) Transformed Chain Length Effect



- Slower kinetics (1-d vs. 5-d) for shorter chain PFAAs
- After 5 days, similar % transformation of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs)

Results: Batch Studies 60 °C

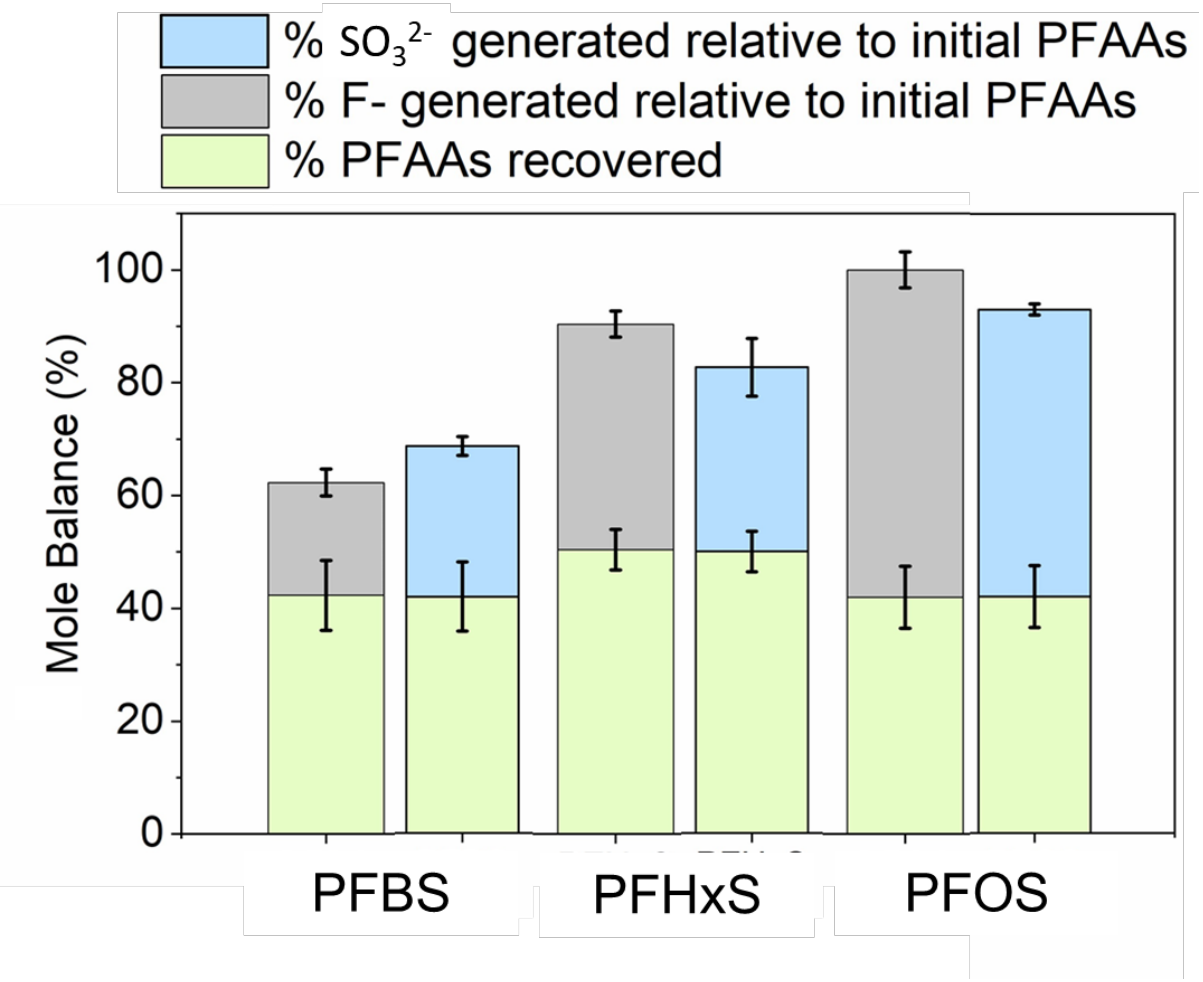
F^- and SO_3^{2-} Generation with Perfluorocarbons



- PFSAs – strong positive linear correlations with both % defluorination and % desulfonation
- PFCAs - similar but weaker correlation with % defluorination
- PFCAs % defluorination lower than for PFSAs

Results: Batch Studies 60 °C

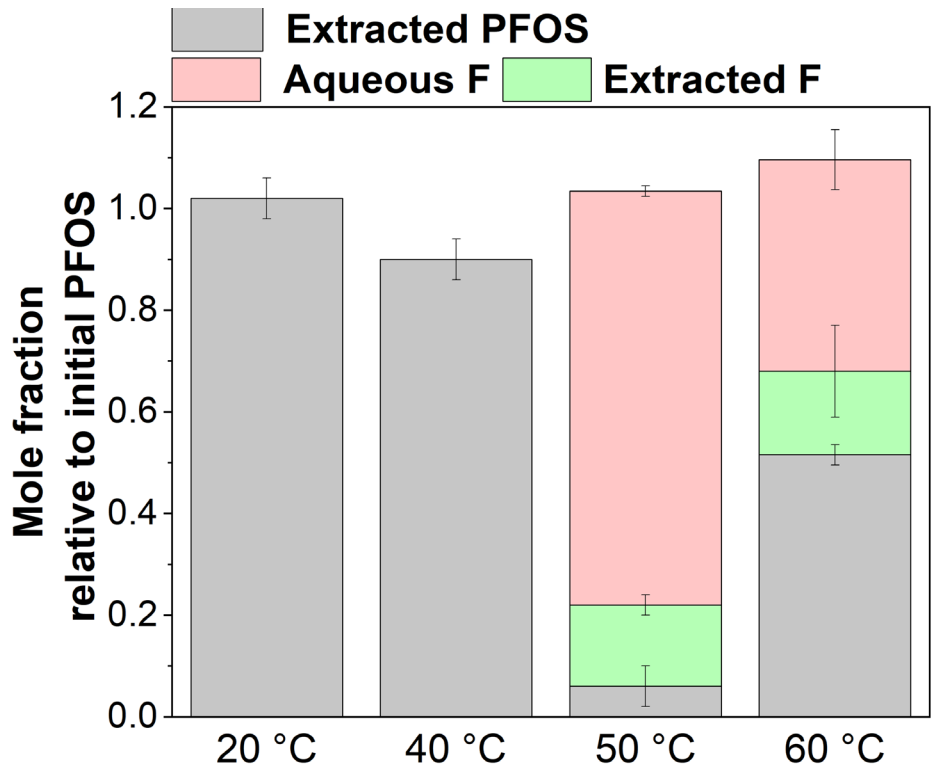
5 Days Fluorine Mole Balance



- Low F mole balance for PFCAs and shorter chain PFSAs
- Nontarget analysis revealed several intermediates

Results: Batch Studies

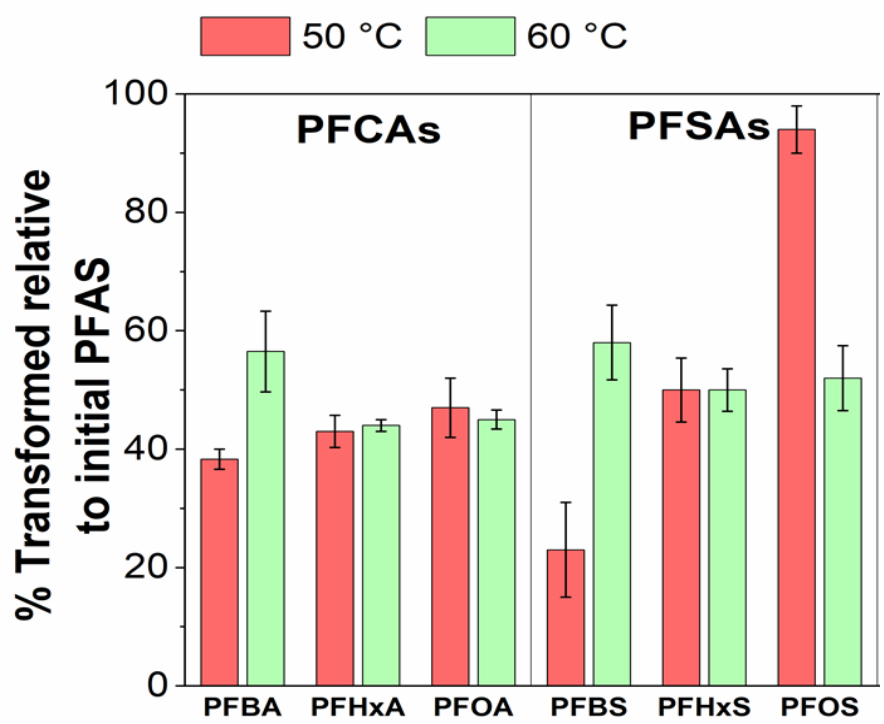
Temperature Effect on PFOS Transformation

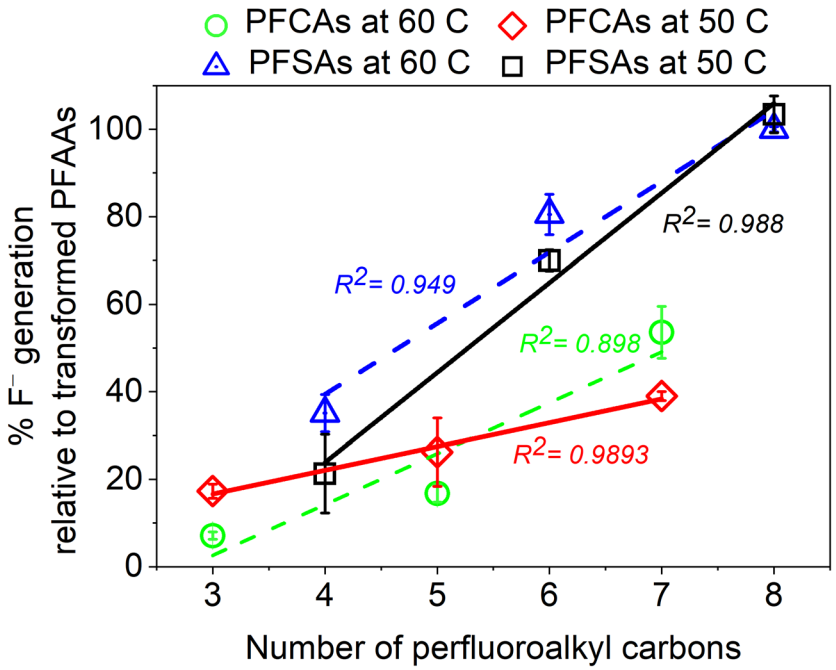


- Optimal transformation at 50 °C (94 ± 4.1%)
- Fluoride recovered ~ equaled F moles in PFOS not recovered, essentially complete defluorination
- All PFOS recovered at 20 °C
- No apparent transformation at 40 °C

Results: Batch Studies (5 Days)

Temperature Effects of Other PFAAs

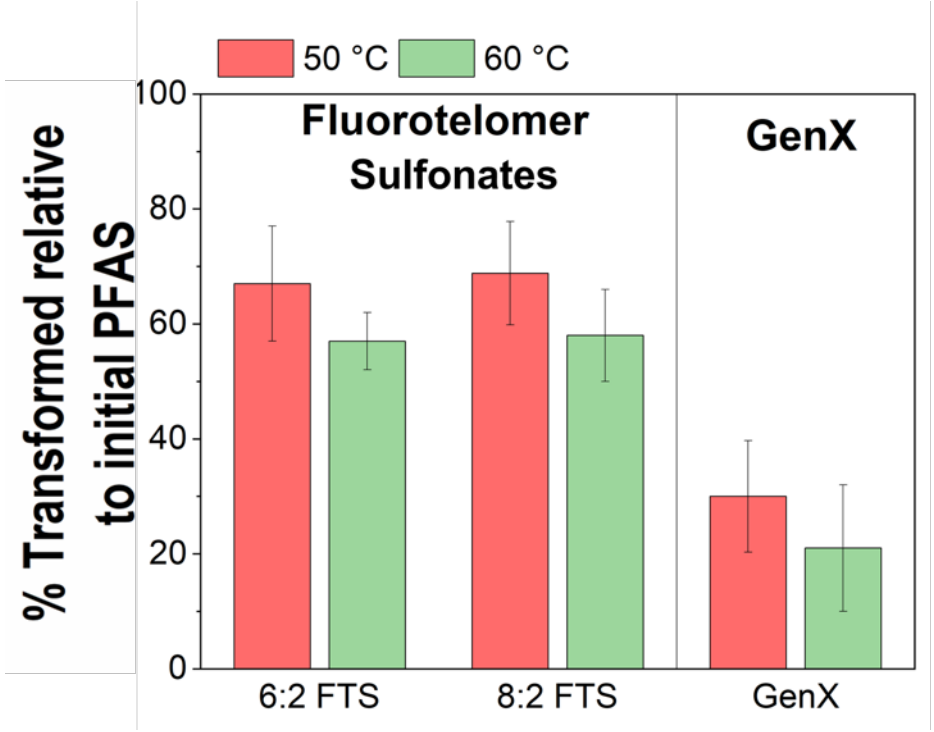


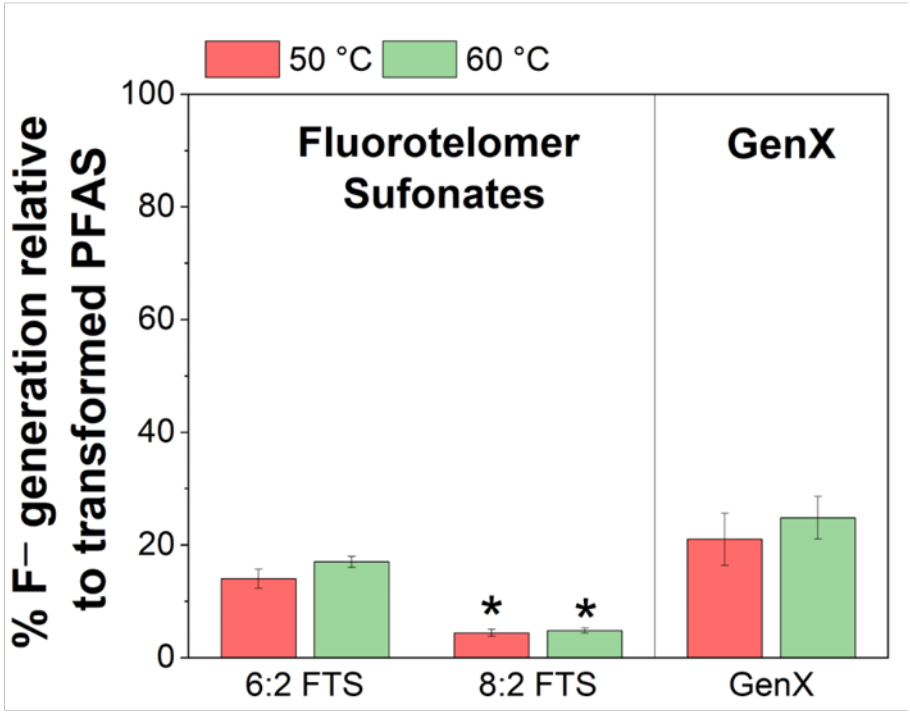


- Transformation of C4 PFAAs higher at 60 °C
- All other PFAAs, equal or higher transformation at 50 °C
- For a given PFAA, no consistent trend between temperatures
- Both temperatures: linear trend between F- generation and chain length

Results: Batch Studies (5 days)

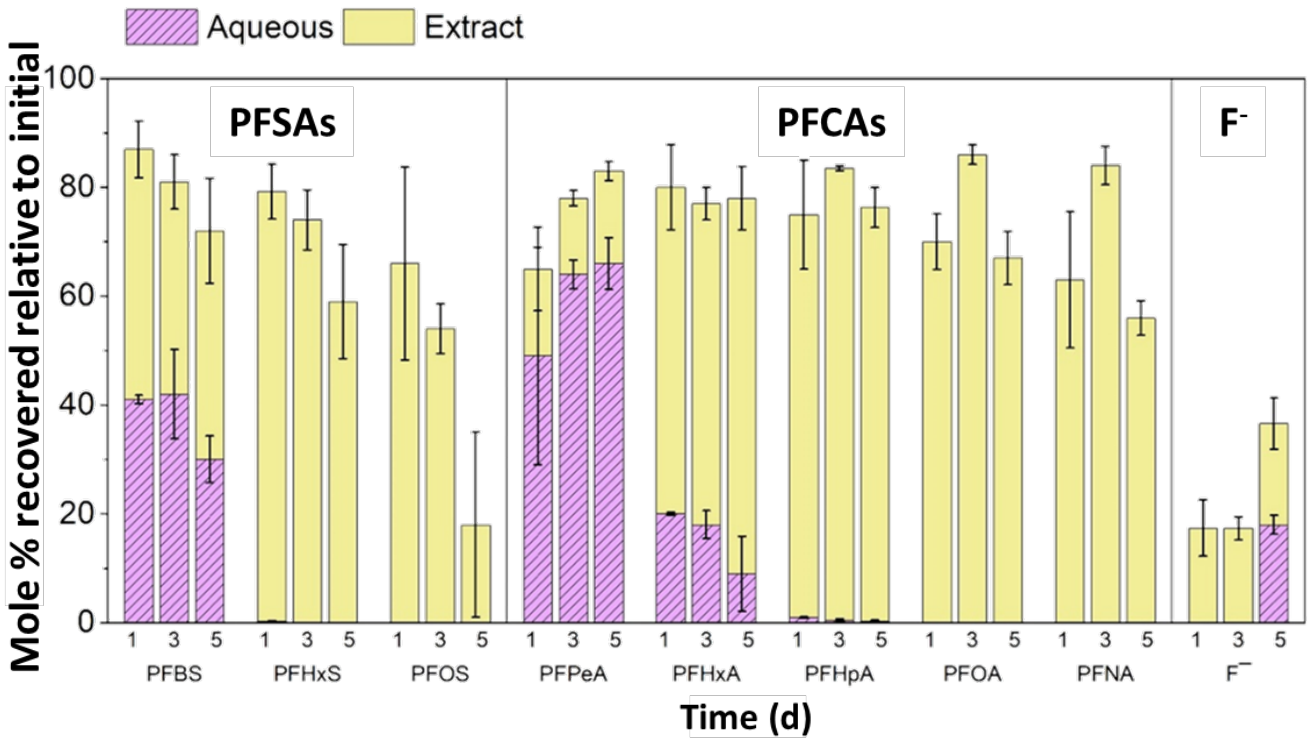
More PFAS Structure Effects on Transformation





- Fluorotelomer sulfonates (6:2 & 8:2 FTS) – high transformation but low defluorination
- Mole balance: FTSs < 50%; GenX > 75%

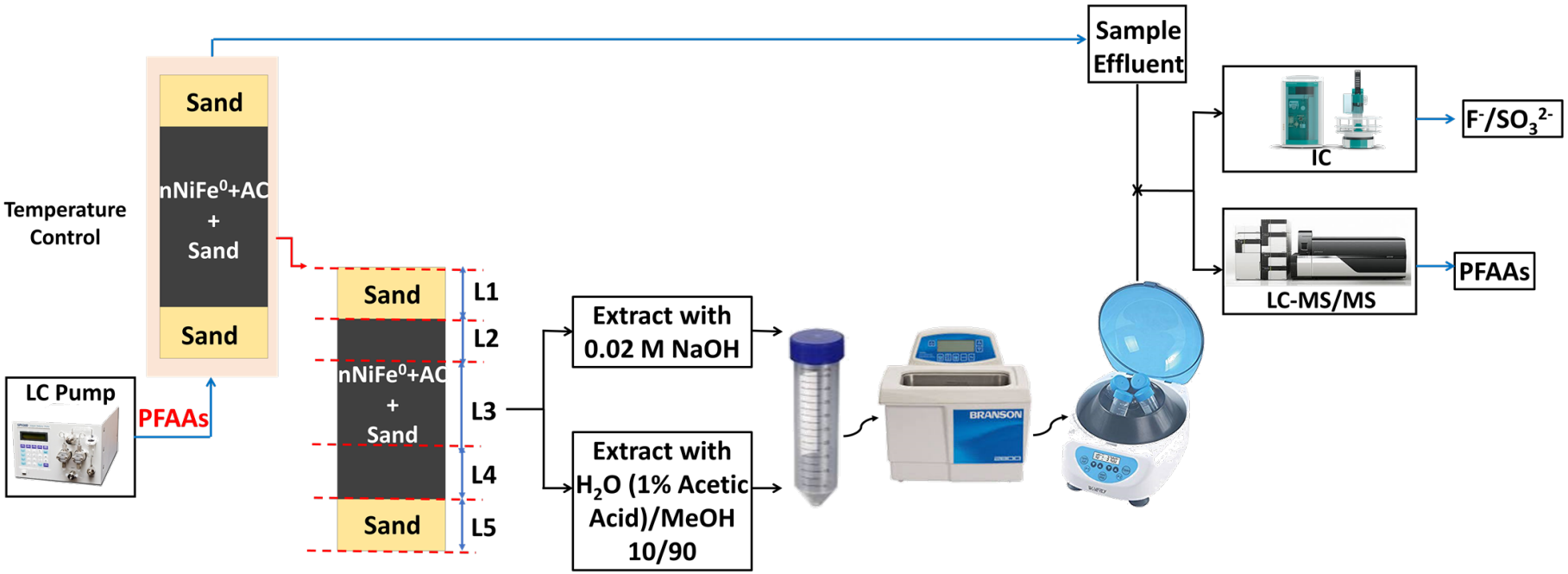
Results: Batch Studies 50 °C Transformation of a PFAA Mixture



- Long chains recovered in only extracts
- PFSAs – single and mixtures similar transformation
- PFCA generation from PFSA and other PFCA transformation
- Similar results with an AFFF-impacted groundwater sample (Cape Cod)

Technical Approach

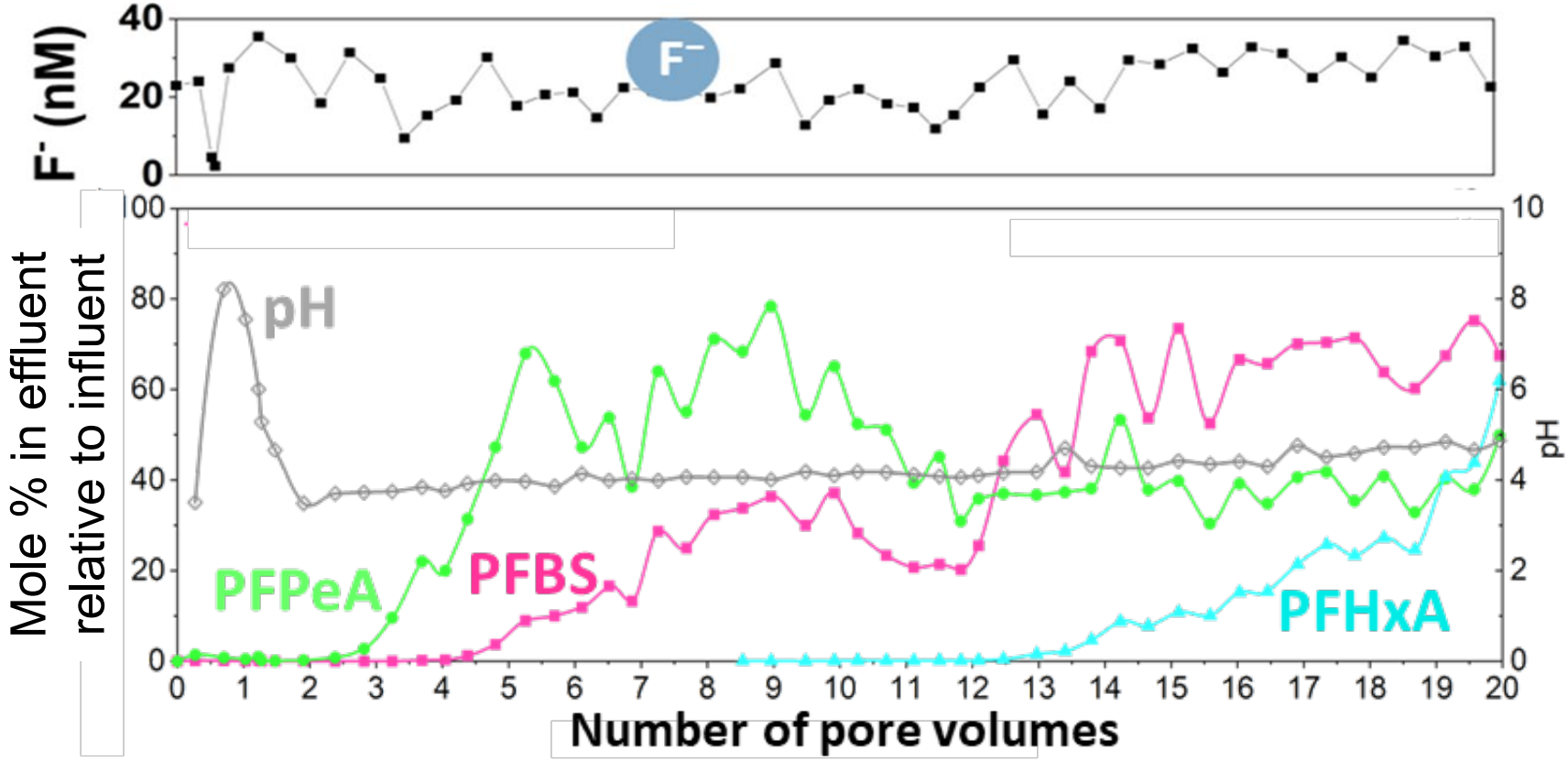
Column Reactors



Variables: Single solute, mixtures, matrix, temperature

Results: Column Studies

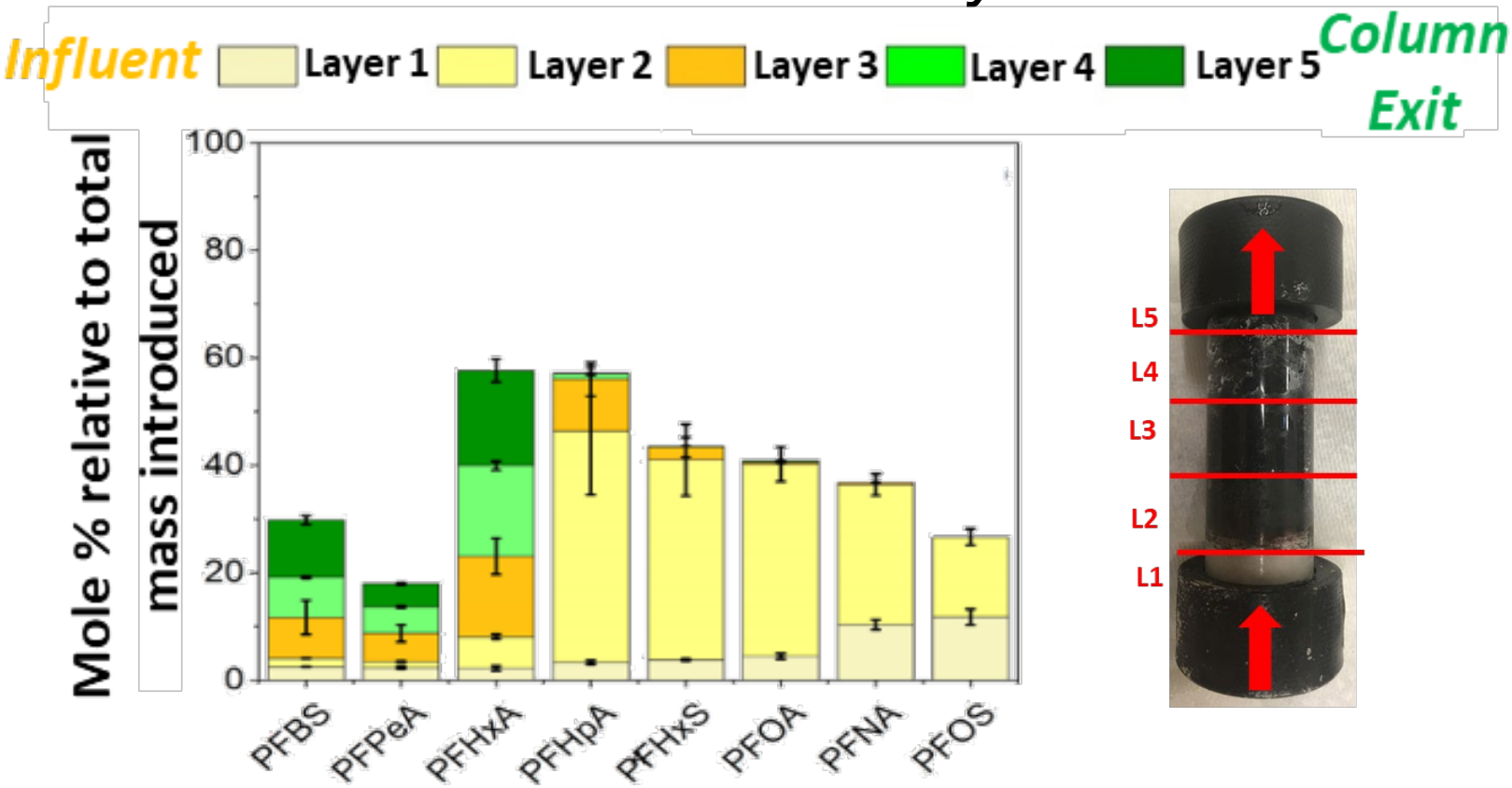
PFAA Breakthrough Example



- Shorter chain PFAAs, shorter residence times, shorter reaction times
- PFAA breakthrough consistent with chain length effects on both mobility and reactivity

Results: Column Studies

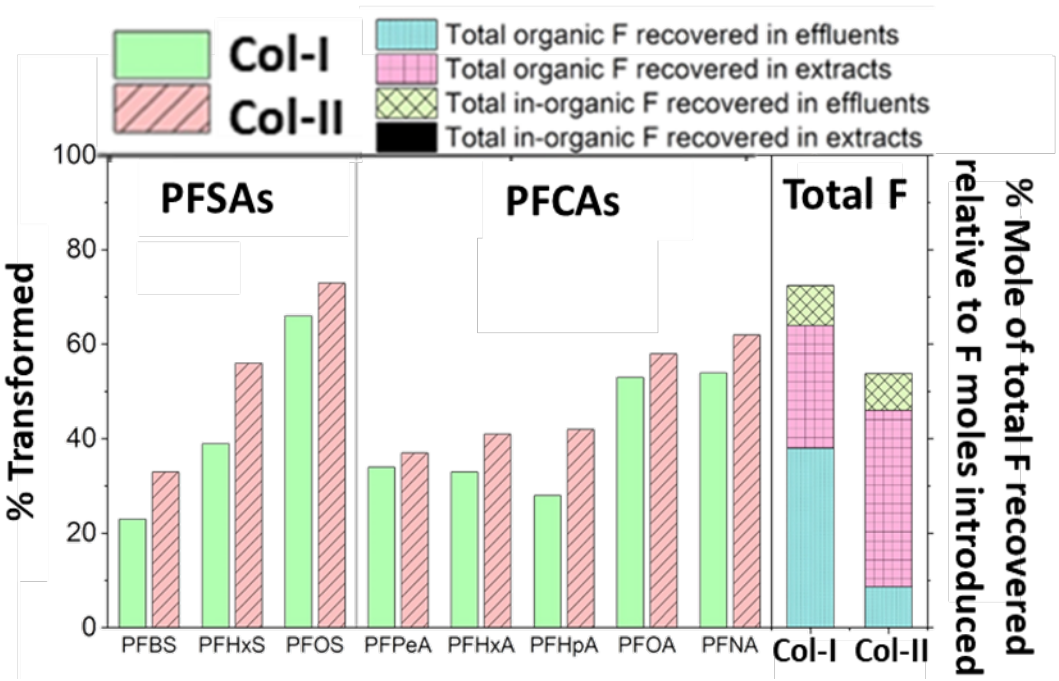
PFAA Recovery



- Most longer chains recovered near column inlet
- Most shorter chains recovered near column exit

Results: Column Studies

PFAA Transformation



	Col-I	Col-II
Flow (mL/min)	0.05	0.005
nNi^0Fe^0-AC to Sand ratio	10:1	7:1
T (°C)	60	50
Hydraulic Residence time	~ 4 h	~ 40 h
Pore Volumes	154	20

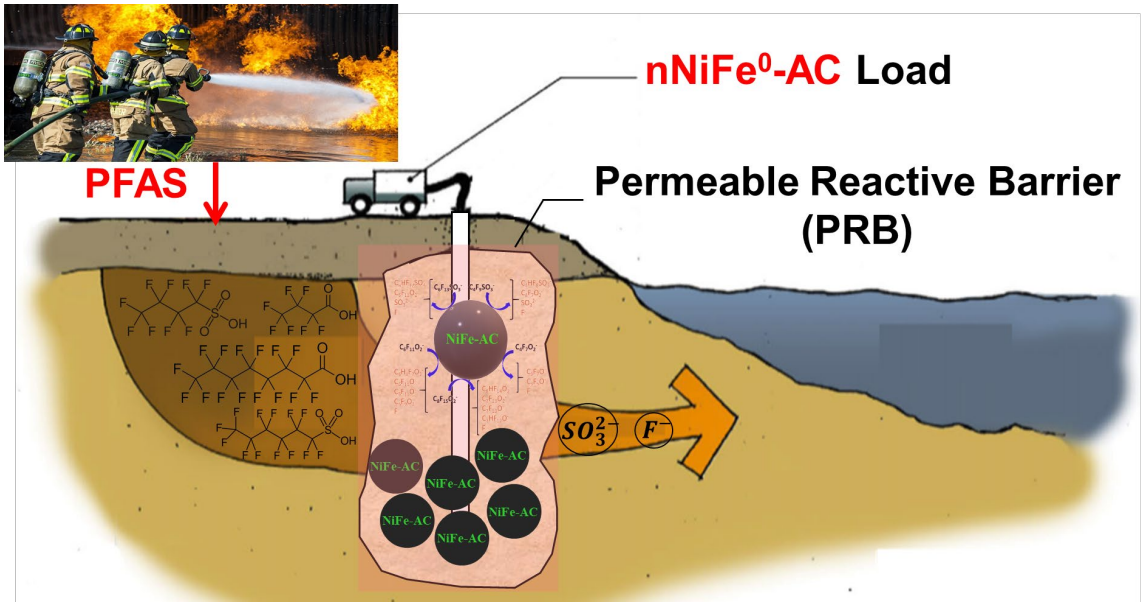
- Transformation: Col-II (~53%) > Col-I (~29%)
- % F^- generation: Col-I > (~23 %) > Col–II (14 %)
- Col-I: No long chain PFAAs in effluent for > 150 pore volumes

Conclusions

- $nNiFe^0$-AC transforms and defluorinates PFCAs, PFSAs, FTSs and GenX to different degrees
- PFSAs and longer chain compounds had higher transformation and defluorination
- PFAS transformation $nNiFe^0$-AC required heat
  - $\geq$ 50 °C
- PFAA mixture transformation higher in column versus batch reactors
- Both Fe and Ni are oxidized as PFAS is reduced; activated carbon improved reactivity to transform PFAS by increasing sorption and preventing particle aggregation
- Additional work column studies underway
  - AFFF-amended water; particle regeneration

Benefits to DoD

- nNi^0Fe^0-AC nanocomposites combine sorption plus destruction to improve PFAS treatment
- Technology use potential
  - In-situ permeable reactive barriers
  - In-situ injection
  - Ex-situ treatment (reactive granular activated carbon)
  - Treatment train module



Additional Resources

- J.E. Zenobio, M. Modiri-Gharehveran, C. de Perre, C. D. Vecitis, and L. S. Lee. Reductive transformation of perfluorooctanesulfonate by nNiFe^0-Activated carbon. JHM, 2020, 397 (122782). https://doi.org/10.1016/j.jhazmat.2020.122782

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2426

Speaker Contact Information

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Q&A Session 2

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The next webinar is on February 11, 2021

Advances in the Detection of Submerged Unexploded Ordnance in Marine Environment

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