PFAS Treatment with EradiFluor™: An Innovative Destruction Technology

Session Code TH-F1

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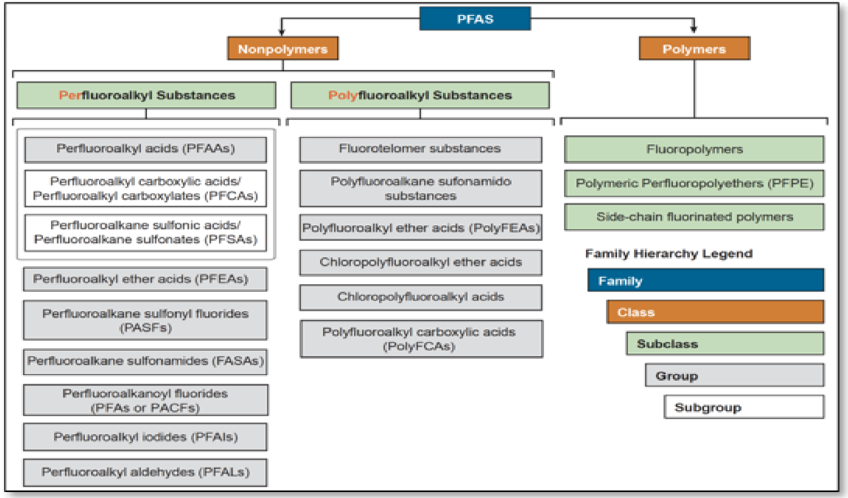
Outline

1. Background
2. PFAS Treatment Technologies
3. Introduction of EradiFluor
4. Field Test Results
5. Additional and Future Work

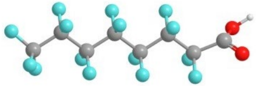
BACKGROUND

Per- and polyfluoroalkyl substances

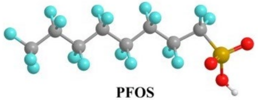
- Thousands of different compounds
- Two compounds most persistent in environment
  - PFOA: Perfluoro octanoic acid (C-8)
  - PFOS: Perfluoro octane sulfonic acid (C-8)
- Resistant to water, oil, and grease, persistent, bioaccumulative
- Analytical methods can reliably measure ng/L or ppt levels
  - 1 ppt = 30 seconds in one million years or one drop of water in 20 Olympic swimming pools



Source: ITRC Fact Sheet 2-2: Chemistry, Terminology, and Acronyms. https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/



PFOA



PFOS

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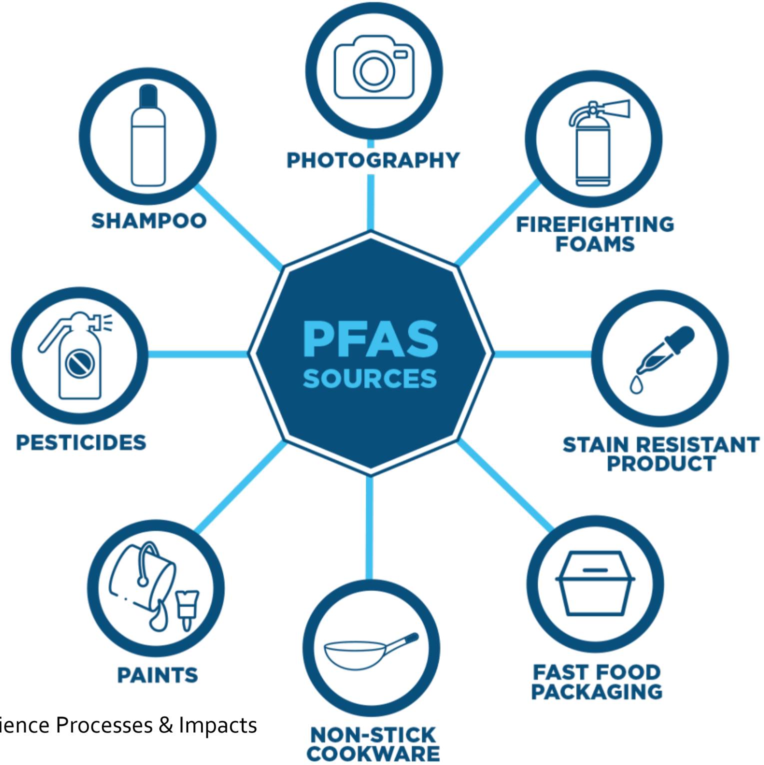
PFAS are widely used in our society

- More than 200 use categories and subcategories for more than 1400 PFAS
- Both industrial processes and consumer products
  - Non-stick cookware
  - Pizza box
  - Firefighting foams
  - Plating fume suppressant

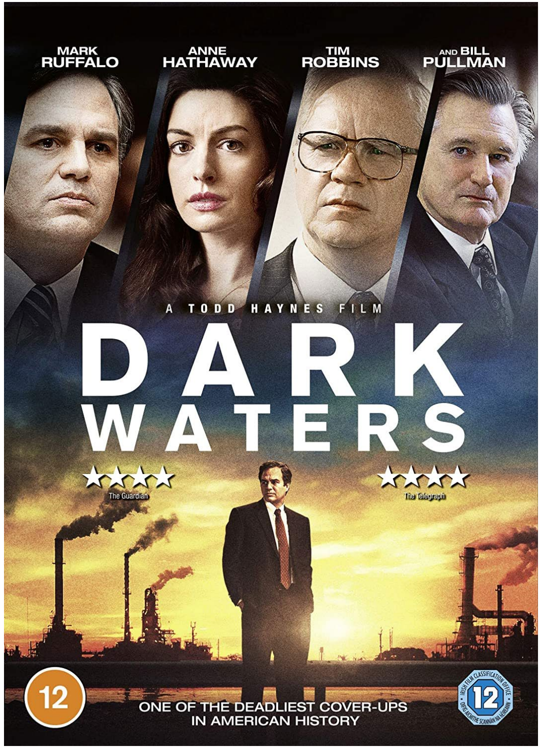


Source: Gluge et al., 2020. An overview of the uses of PFAS, Environmental Science Processes & Impacts

http://smchd.org/pfas/

PFAS – It's not just nerdy scientist paying attention

- Readily leach from soil, migrate in groundwater, do not degrade, and may bioaccumulate
- Limited treatment options
- Heightened public and regulatory focus
  - 3M & Dupont settlements $12 Billion
  - In news and movies



Dark Waters (2019 film)

Final maximum contaminant levels (MCLs) for drinking water

Chemical	Maximum Contaminant Level Goal (MCLG)	Maximum Contaminant Level (MCL)
PFOA	0	4.0 ppt
PFOS	0	4.0 ppt
PFHxS	10 ppt	10 ppt
HFPO-DA (GenX chemicals)	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
Mixture of two or more: PFHxS, PFNA, HFPO-DA, and PFBS	Hazard Index of 1	Hazard Index of 1

*Compliance is determined by running annual averages at the sampling point

ppt = parts per trillion or nanograms per liter (ng/L)

$$HI\ MCL = \left(\frac{[HFPO\text{-}DA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFBS_{water}]}{[2000\ ppt]}\right) + \left(\frac{[PFNA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFHxS_{water}]}{[10\ ppt]}\right) = 1$$

- MCLs become Applicable or Relevant and Appropriate Requirement under CERCLA

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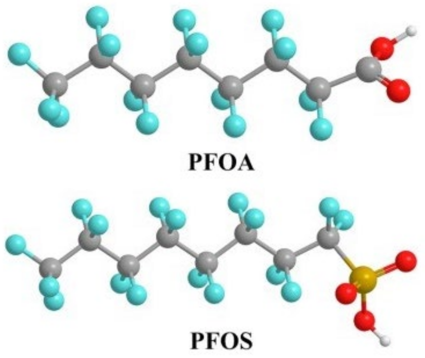
FINAL rule to designate PFOA and PFOS as hazardous substances – **Effective July 8, 2024**

- **“In-scope”** for EPA’s all appropriate inquiry (AAI) rule/ASTM E1527 Phase I standard
- New PFAS CERCLA/Superfund sites; Implications to existing **litigation and settlements**
- EPA or other agencies could seek **cost recovery** from PRPs for PFOA/PFOS at contaminated sites; stated focus on manufacturing sources
- Immediately reportable quantity of **one pound** of PFOS or PFOA
- Entities **do not need to report past releases** of PFOA or PFOS following the requirements of CERCLA section 103 and 111(g) or EPCRA section 304 **if they are not continuing** as of the effective date of the rule.



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PFAS discharge regulations are evolving

- EPA withdrew ELG for PFAS manufacturers in Jan 2025
  - technology-based effluent limitations
  - manufacturers in the Organic Chemicals, Plastics, and Synthetic Fibers category
- Several states are using NPDES permitting process to regulate PFAS discharges
  - CA, MA, MI, NY

Groundwater General Permit

Order R2-2025-XXXX
NPDES Permit CAG912002

Parameter	Units	Receiving Waters Used as Drinking Water [1]		Other Receiving Waters	
		Average Monthly	Maximum Daily	Average Monthly	Maximum Daily
Per- and Polyfluoroalkyl Substances (PFAS)					
Perfluorooctanoic acid (PFOA)	ng/L	4.0	-	4.0	-
Perfluorooctane sulfonic acid (PFOS)	ng/L	4.0	-	4.0	-
Perfluorohexane sulfonic acid (PFHxS)	ng/L	10.	-	10.	-
Perfluorononanoic acid (PFNA)	ng/L	10.	-	10.	-
Hexafluoropropylene oxide dimer acid (HFPO-DA)	ng/L	10.	-	10.	-

Footnotes:

[1] "Receiving Waters Used as Drinking Water" are surface waters with existing or potential beneficial uses of "Municipal and Domestic Supply" or "Groundwater Recharge," or both. Groundwater recharge beneficial uses may include recharge areas to maintain salt balance or to halt saltwater intrusion to freshwater aquifers.

ELG = Effluent Limitation Guidelines

NPDES = National Pollutant Discharge Elimination System

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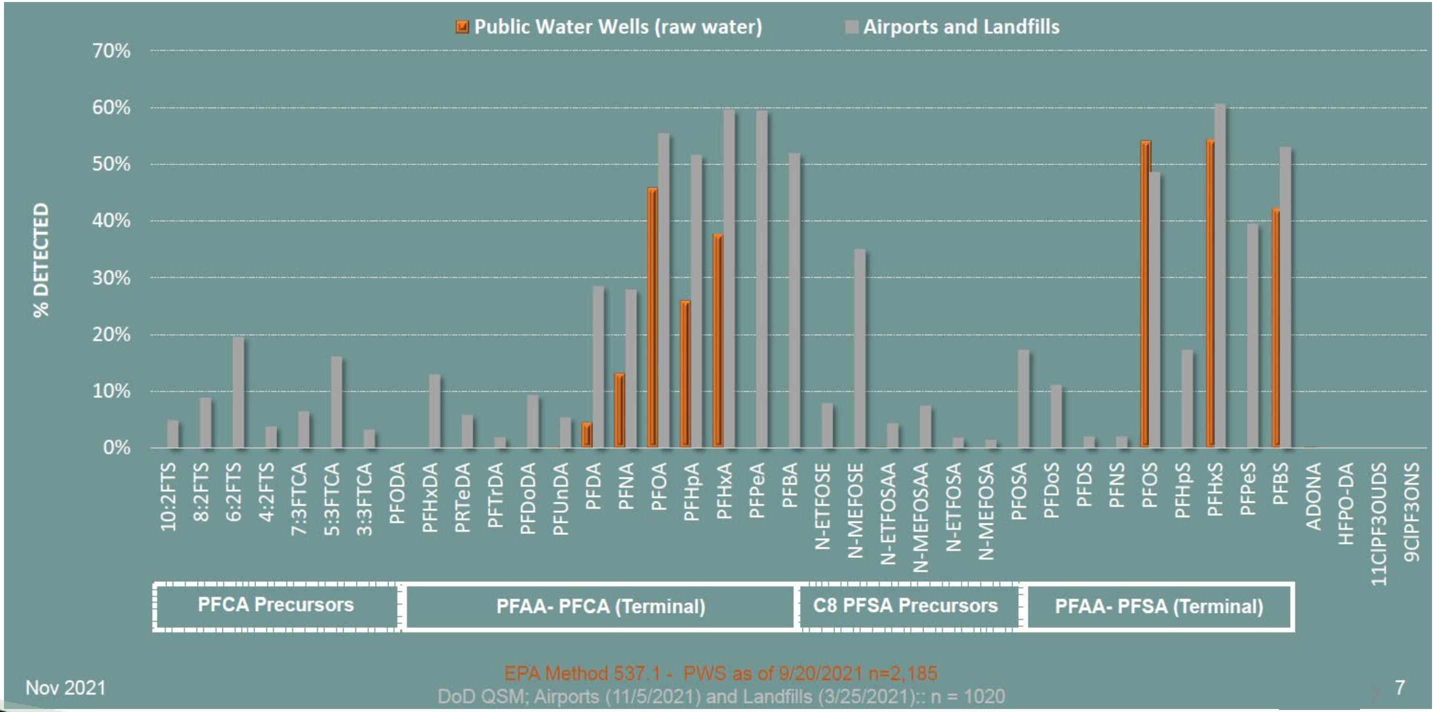
State water board issued PFAS Investigative Orders (Water Code 13267)

- CA Water Boards are implementing a phased investigation approach
- Phase I, started in March 2019 targets:
  - 31 airports
  - 252 municipal solid waste landfills
  - >1,000 drinking water wells/sources near the above-listed facilities
- Phase II and III target:
  - manufacturing facilities (271 chrome platers; Oct 2019)
  - refineries, bulk terminals, and non-airport fire training areas
  - wastewater treatment & pre-treatment plants
  - domestic wells

https://www.waterboards.ca.gov/pfas/

PFAS are frequently detected in CA groundwater



Source: Palmer, 2021

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PFAS TREATMENT TECHNOLOGIES

Existing separation technologies leave behind concentrated waste

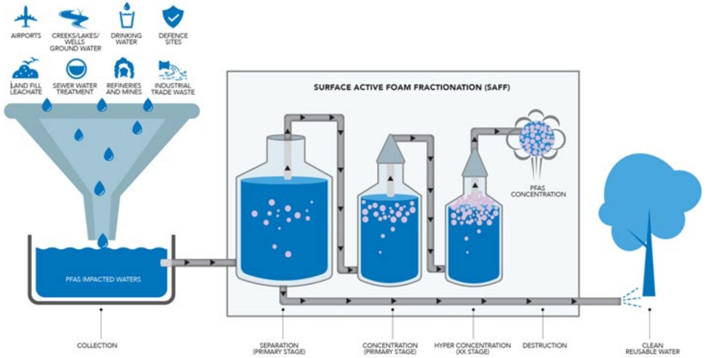
Conventional technology

Granular activated carbon

Membrane filtration

Ion exchange resin

Recent developments



OPEC

Foam fractionation

In situ sequestration of PFAS with colloidal carbon

- Injectable activated carbon
  - Colloidal particles: 1 – 2 microns
  - Can be injected to subsurface
  - Remain as a suspension
- Remove PFAS and others
  - Sequestration technology
  - Dese not degrade PFAS
- Pilot scale field application conducted
- Several studies underway to evaluate effectiveness

There are few options for disposal of PFAS waste

Source: EPA, 2024. Interim guidance on the destruction and disposal of perfluoroalkyl and polyfluoroalkyl substances and materials containing perfluoroalkyl and polyfluoroalkyl substances – Version 2 (2024).

Incineration

Landfill

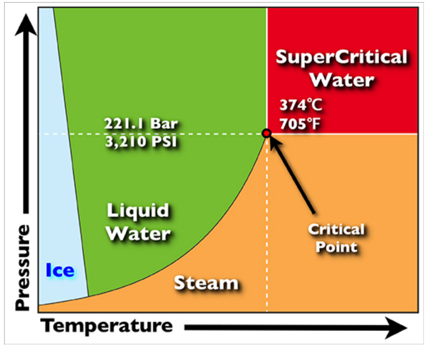
Deep well injection

There is a growing need for destructive technologies

- Regulations on PFAS are evolving
- Several destructive technologies are under development, and some have moved to commercial application:
  - Supercritical water oxidation
  - Hydrothermal alkaline treatment
  - Electrochemical oxidation
  - Plasma technology
  - [illegible] beam

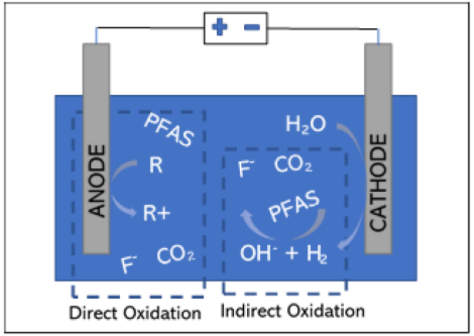
EPA launched a technical challenge
for innovative ways to destroy PFAS in 2020

Destructive technologies under development



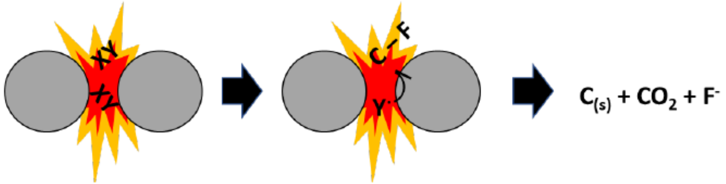
Supercritical water oxidation

- Chemical oxidation process
- Used to treat other organic waste
- High energy consumption
- Generate corrosive HF



Electrochemical Oxidation

- Low energy costs
- No chemical oxidants needed
- Generate toxic by-products
- Incomplete of destruction of some PFAS



Ball-Milling: Ball impacts create radicals, heat, and even plasma from co-milling materials and localized high temperatures that mineralize PFA

Pyrolysis and Gasification: Decomposes materials at moderately elevated temperatures in an oxygen-free or low-oxygen condition. Treating PFAS-containing sewer and biosolid.

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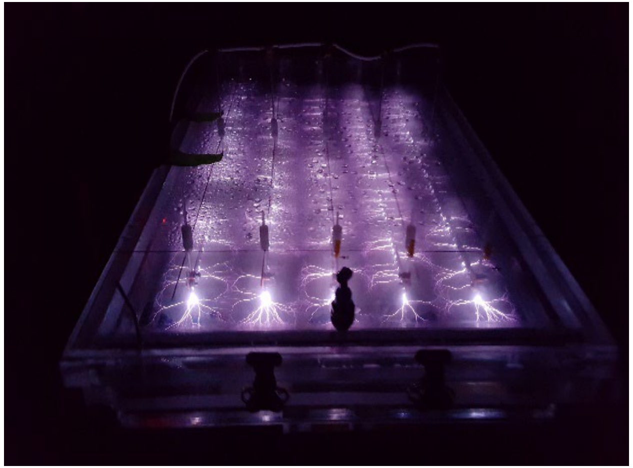
Source: https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt

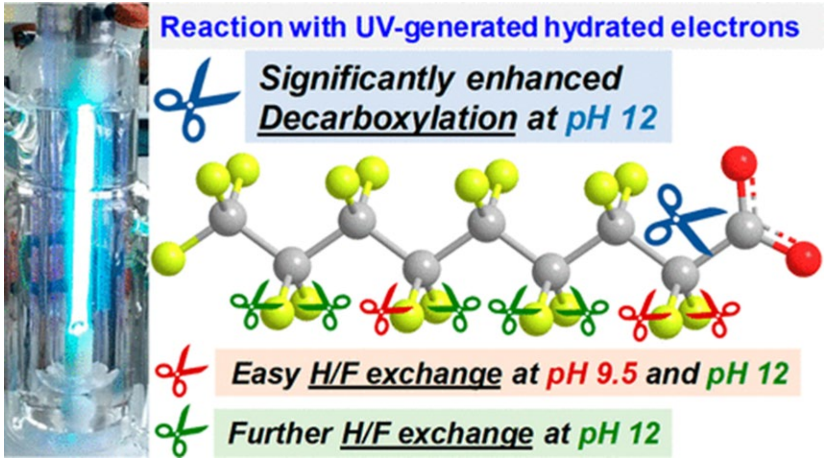
Destructive technologies under development (cont'd)



Plasma Technology

- Field pilot tests have been conducted
- Promising field data have been collected
- Have difficulty in destructing short-chain PFAS

Source: Singh et al., ES&T 2019



Hydrated Electrons

- Near complete defluorination for both long- and short-chain PFAS
- Extensively studied in bench-scale
- Field study under an ESTCP-funded project

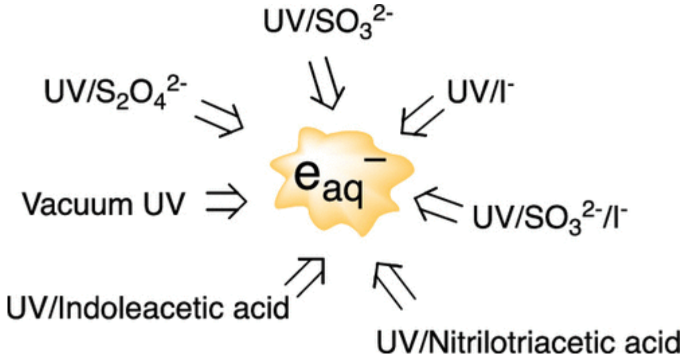
Source: Bentel et al., ES&T Letter 2020

BREAK TIME!

INTRODUCTION OF ERADIFLUOR

A new approach: UV-based advanced reduction process

- This process is based on the production of highly reducing hydrated electrons, e_{aq}^-
  - Different from UV/H_2O_2 used in water treatment
  - e_{aq}^- is a strong reductant (standard potential = −2.9 V)
  - Key reactant for PFAS destruction by non-thermal plasma and electron beam
- e_{aq}^- can be generated under UV irradiation
  - Several ways to produce e_{aq}^-
  - As shown in the figure on the right



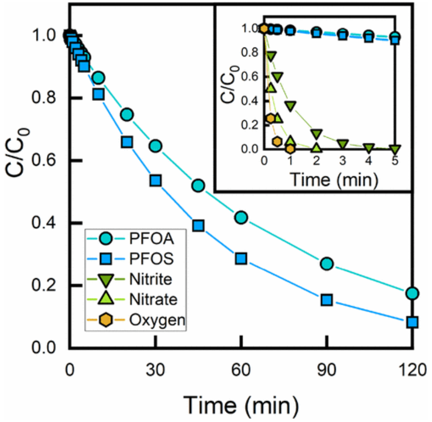
Source: Fennell et al., 2022

A new approach: UV-based advanced reduction process

- e_{aq}^- break C-F bond and degrade PFAS compounds
  - Highly effective in PFAS destruction
- e_{aq}^- highly effective for treatment
  - Chlorinated solvents, perchlorate, nitrate, chromium (VI)
- Certain water constituents may scavenge e_{aq}^-
  - Oxygen
  - Nitrate/nitrite

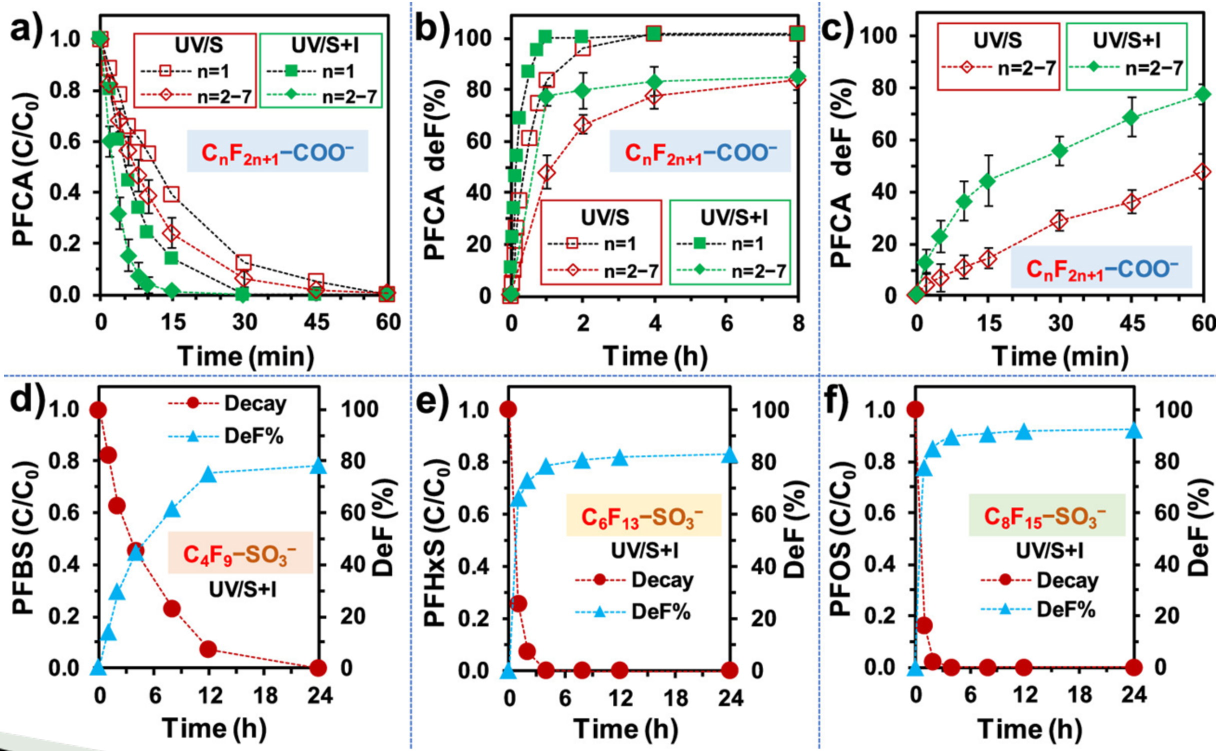
$$SO_3^{2-} \xrightarrow{UV} SO_3^{\bullet -} + e_{aq}^-$$

NHE = −2.9 V



Source: Fennell et al., 2022

Laboratory study results showed effective destruction of various PFAS



Source: Liu et al., 2022

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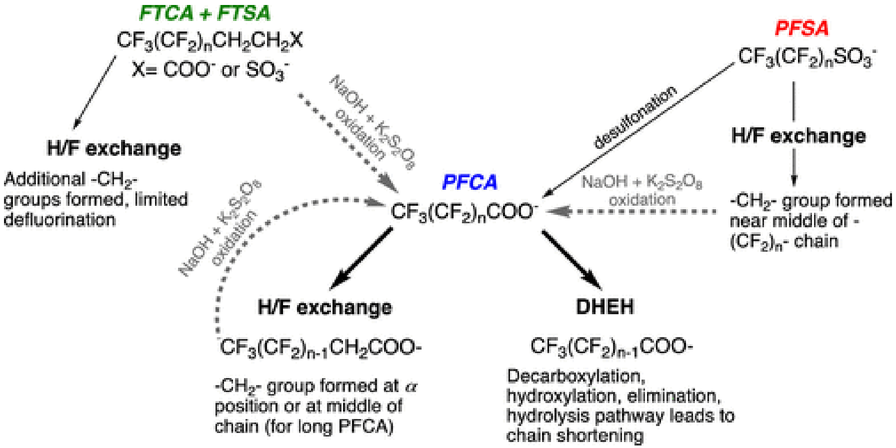
Mechanism of PFAS destruction by hydrated electrons

- Two PFAS defluorination pathways are identified:
  - H/F atom exchange
    - $-CF_2-$ group to $-CH_2-$ group
    - Produces polyfluorinated products
  - DHEH
    - Shorten one $-CF_2-$ group each step
    - Deeper defluorination
    - Mostly occur to PFCAs



DHEH = Decarboxylation, hydroxylation, elimination, hydrolysis

Source: Fennell et al., 2022

Findings from laboratory tests

- Hydrated electrons are highly effective in destroying PFAS
- Near-complete destruction of various short-chain and long-chain PFAS
- No harmful byproducts (e.g., perchlorate, bromate)
- The reactive mechanisms are well understood
- Not affected by high salt concentration
- Mild reaction conditions (e.g., temperature, pressure)

EradiFluor - PFAS destruction system

- A PFAS treatment system has recently been designed and constructed
  - UV/sulfite-based treatment process
  - Mobile, on-site treatment unit
  - Ambient reaction conditions
  - Control/monitoring components

- Concentrated PFAS streams to be treated and destroyed

View from the rear of the trailer

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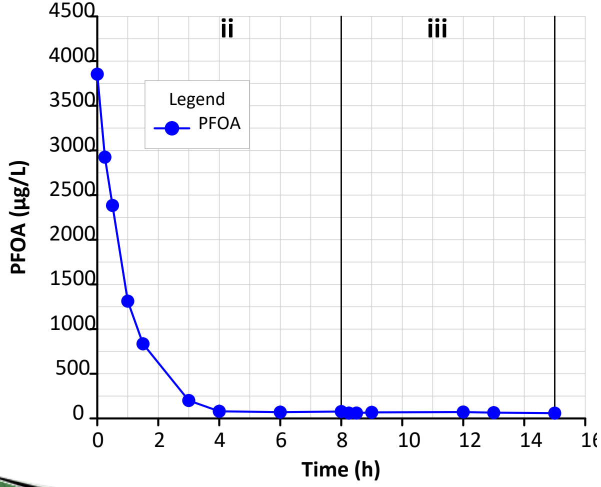
Simulated waste test results

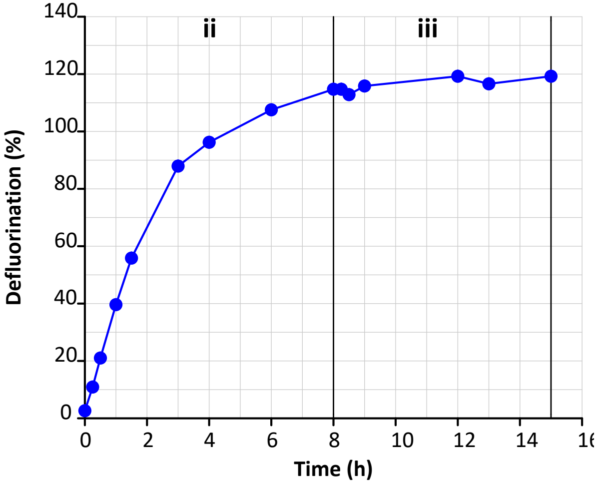
Method:

- **PFOA:** Consumer products, food packaging, firefighting foam, and other industrial processes
- 30-gallon batch liquid waste
- Treatment: (II) reduction, (III) post-oxidation



Results:

- 99% PFOA degradation
- >100% defluorination was achieved
- Post-oxidation didn't improve defluorination efficiency

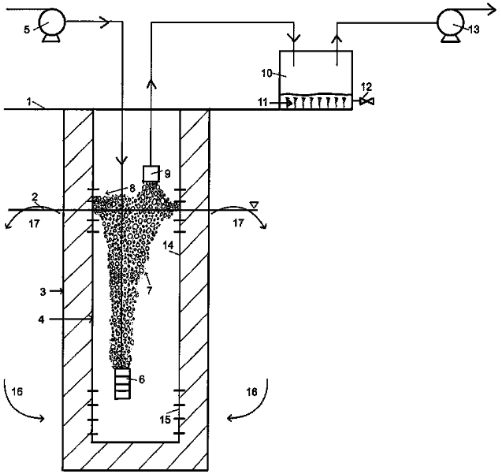


ii = Reduction **iii = Post-oxidation**

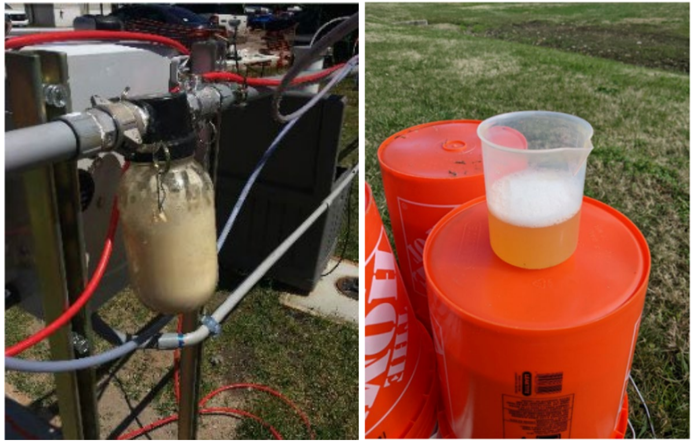
FIELD TEST RESULTS

Treatment of waste concentrate: in situ foam fractionation

- Foamate produced from an in situ foam fraction groundwater remediation system from a Navy site
  - Tens of ppm level of PFAS
  - PFOS and 6:2 FTS dominant
  - Low level of TOC and nitrate/nitrite



In situ foam fractionation system for groundwater remediation



PFAS concentrate produced from an in situ foam fractionation system for groundwater remediation (Source: Nelson 2022)

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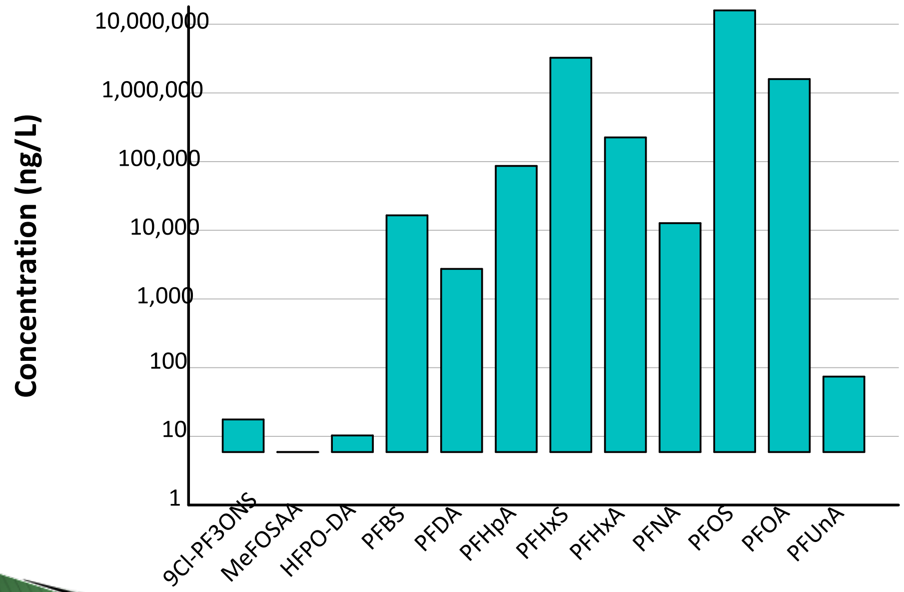
Constituents of the foam fractionate



Parameter	Concentration	Unit
Alkalinity	28.4	mg $CaCO_3$/L
Total Dissolved Solids	92	mg/L
Nitrogen, Nitrite	ND	mg/L
Nitrogen, Nitrate	ND	mg/L
Total Organic Carbon	16	mg/L
Sulfate	34.3	mg/L

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Field demonstration at a Navy site

- Treatment system was mobilized to the site this summer.
  - Simple setup
  - 24/7 operation
  - Ambient conditions
  - Near complete PFAS destruction

EradiFluor trailer was transported to the Navy site in the East Coast with a pickup truck.

EradiFluor system and a temporary tent was set up for the field demonstration

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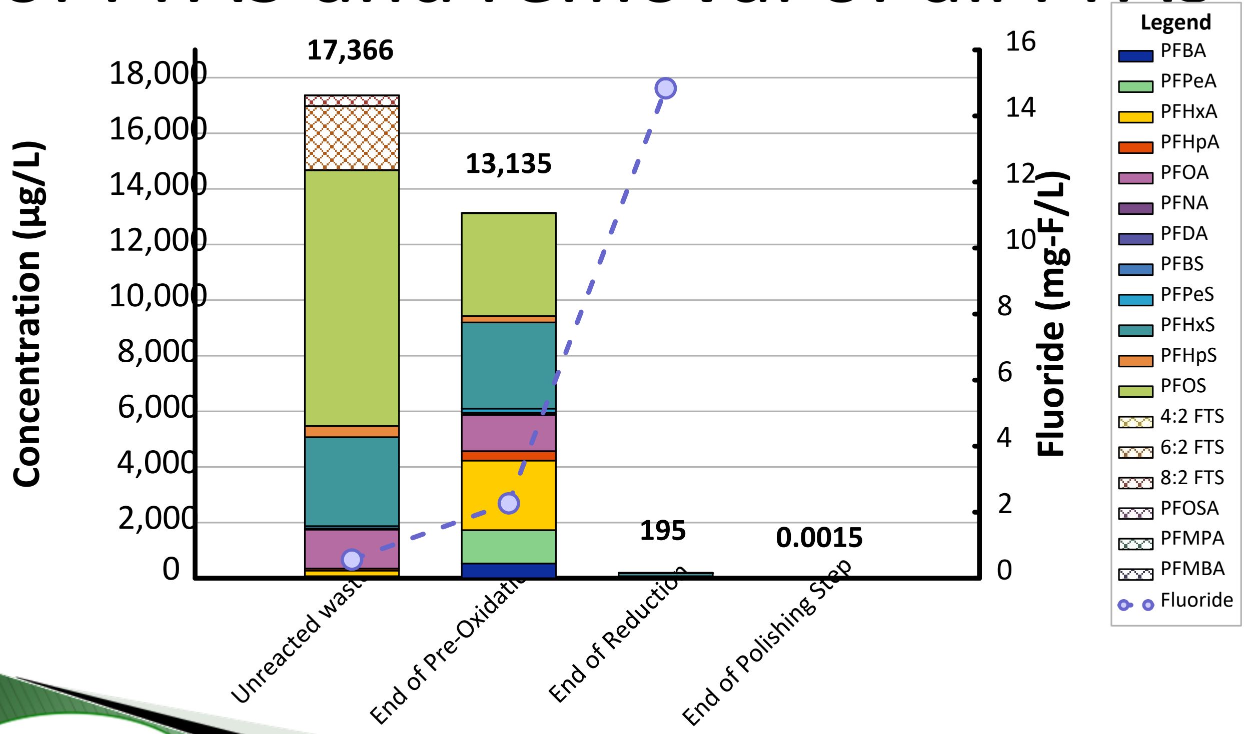
Field results show near-complete destruction of PFAS and removal of all PFAS



About 99 percent of PFAS were destroyed at the end of the reduction step.

After the polishing step, all residual PFAS were removed to the Not-Detect level, except one compound PFOS reported as 1.5 ng/L (below MCL of 4 ng/L).

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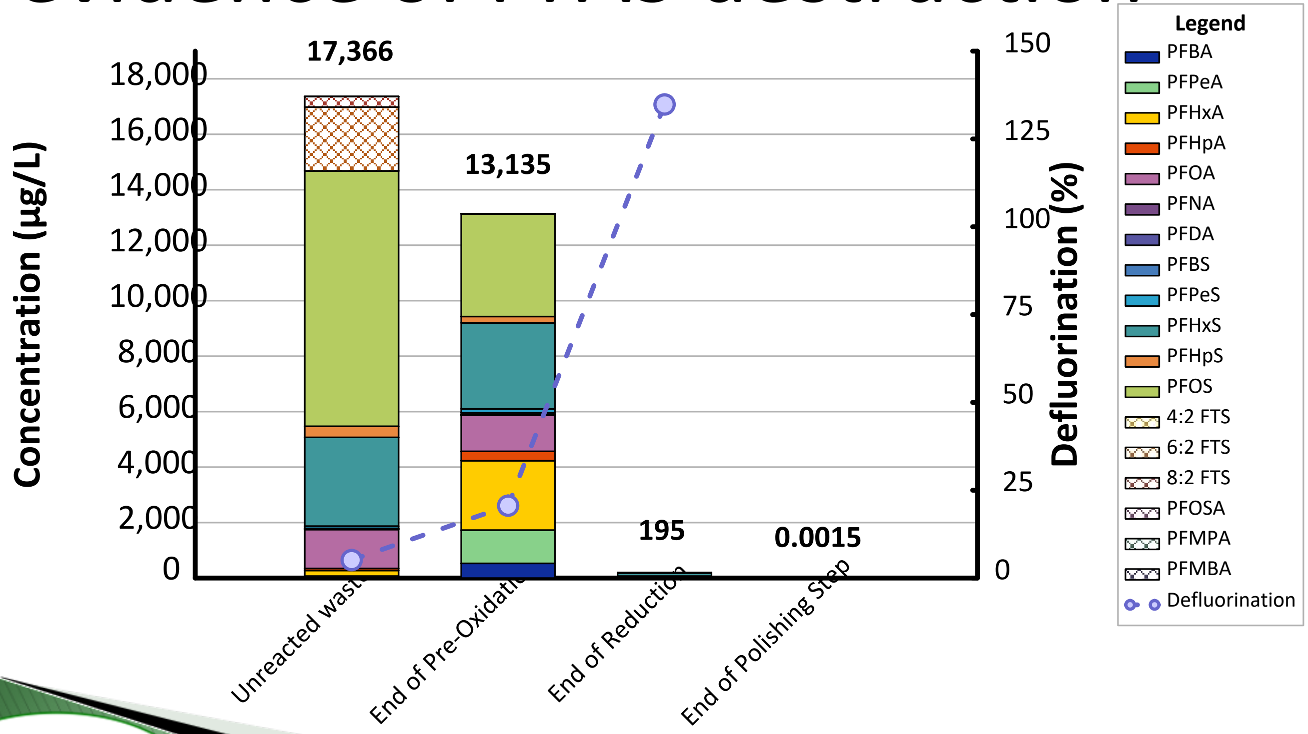
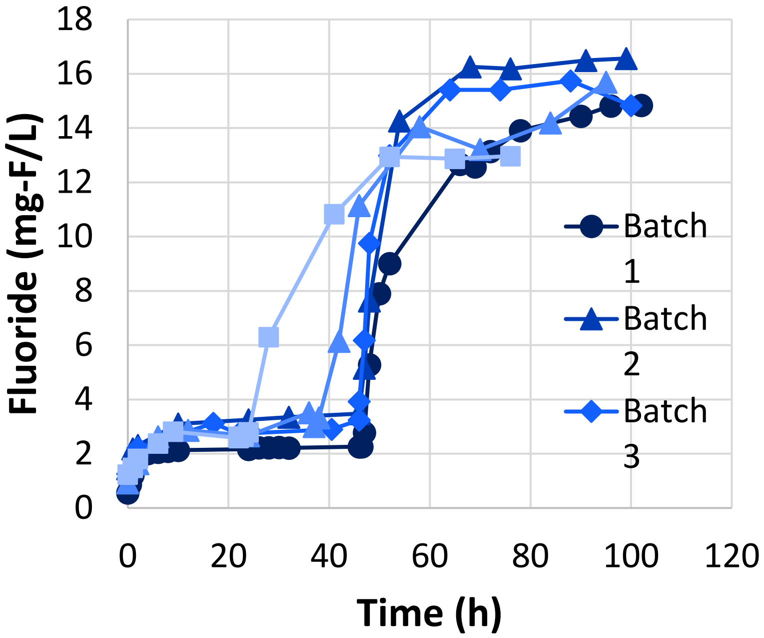
Generation of non-toxic fluoride provides evidence of PFAS destruction



The non-toxic final degradation product, i.e., fluoride, increased to 15 mg/L in concentration, demonstrating complete defluorination or mineralization of PFAS

Substantial fluoride release demonstrated effective PFAS treatment



Fluoride release profiles were consistent between 5 batches

Max fluoride concentration was 15 ±1.3 mg-F/L

Effective destruction of long- and short-chain PFAS

- Average of multiple batches shows > 99% destruction of most PFAS (short- and long-chain)
- PFBS showed slightly less destruction, but still effectively degraded

Destruction (%) (end of reduction)

Batch	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	4:2 FTS	6:2 FTS	8:2 FTS
1	> 99.8	> 99.99	99.96	> 99	> 99.98	> 98	> 99.7	> 99.98	> 99.4	> 99.99	> 97.2	> 99.98	> 99.9
2	99.9	99.8	99.8	> 99.9	99.8	94	99.8	99.8	99.7	99.7	99.6	99.9	99.9
3	99.98	99.96	99.99	> 99.6	> 99.998	95	> 99.98	99.99	99.98	99.97	99.7	99.99	99.97
4	99.98	99.9	99.99	> 99.99	> 99.997	92	> 99.98	99.996	99.98	99.97	99.5	99.997	> 99.99
5	99.9	99.95	99.96	> 99.96	99.99	66	98.7	99.96	99.98	99.9	98	99.99	99.1

Notes:

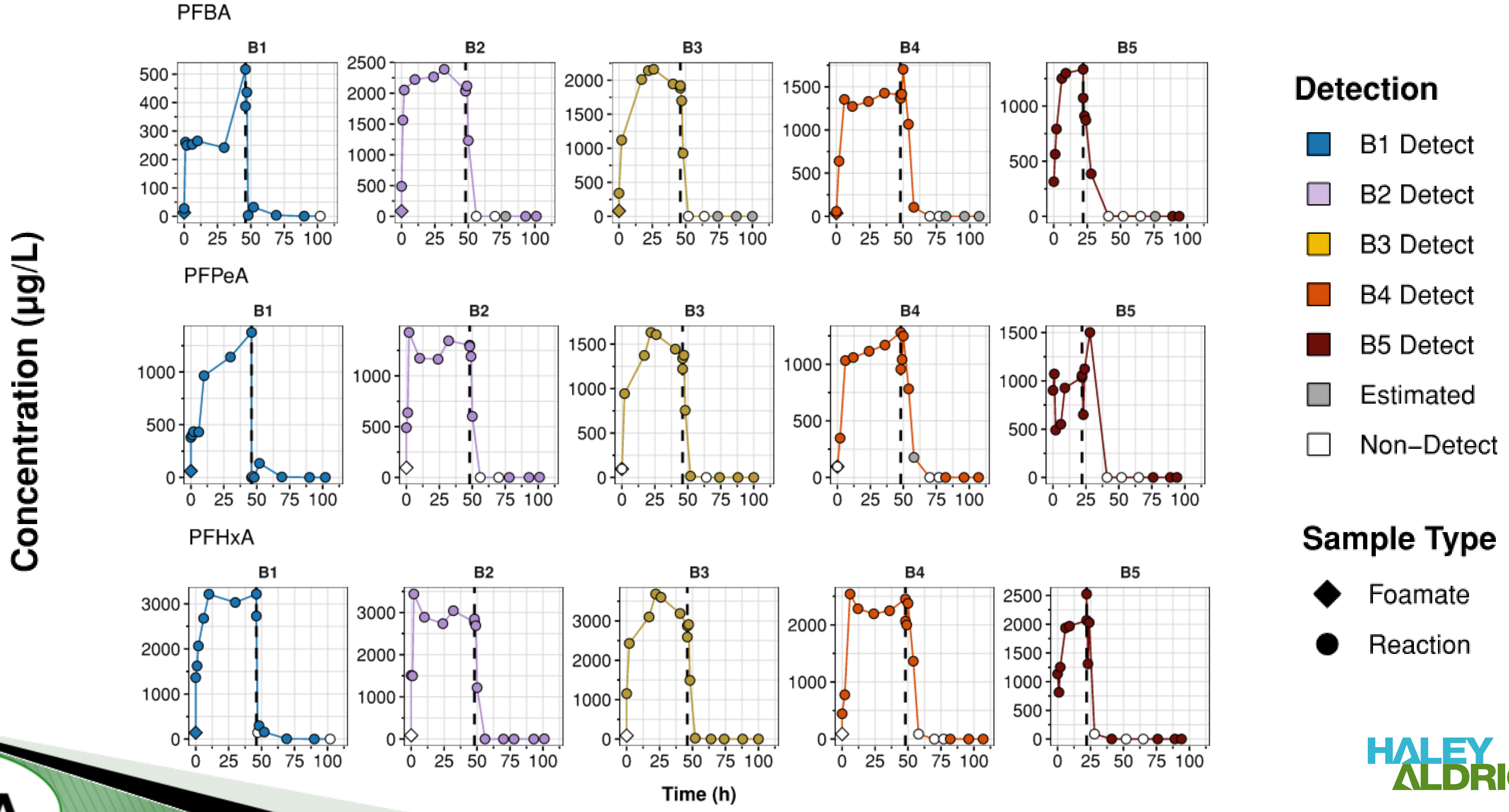
Destruction (%) = 100 x [($C_{max} - C_{end\ of\ reduction}$) / C_{max}]

Calculation uses C_{max} (and not $C_{initial}$) since certain PFAS were generated during pre-oxidation step

Blue = $C_{end\ of\ reduction}$ was above the method detection limit, but below the reporting limit (i.e., J-flag estimated)

Purple = Outlier. Possibly due to operational adjustments in batch 5.

Effective destruction of short-chain PFAS



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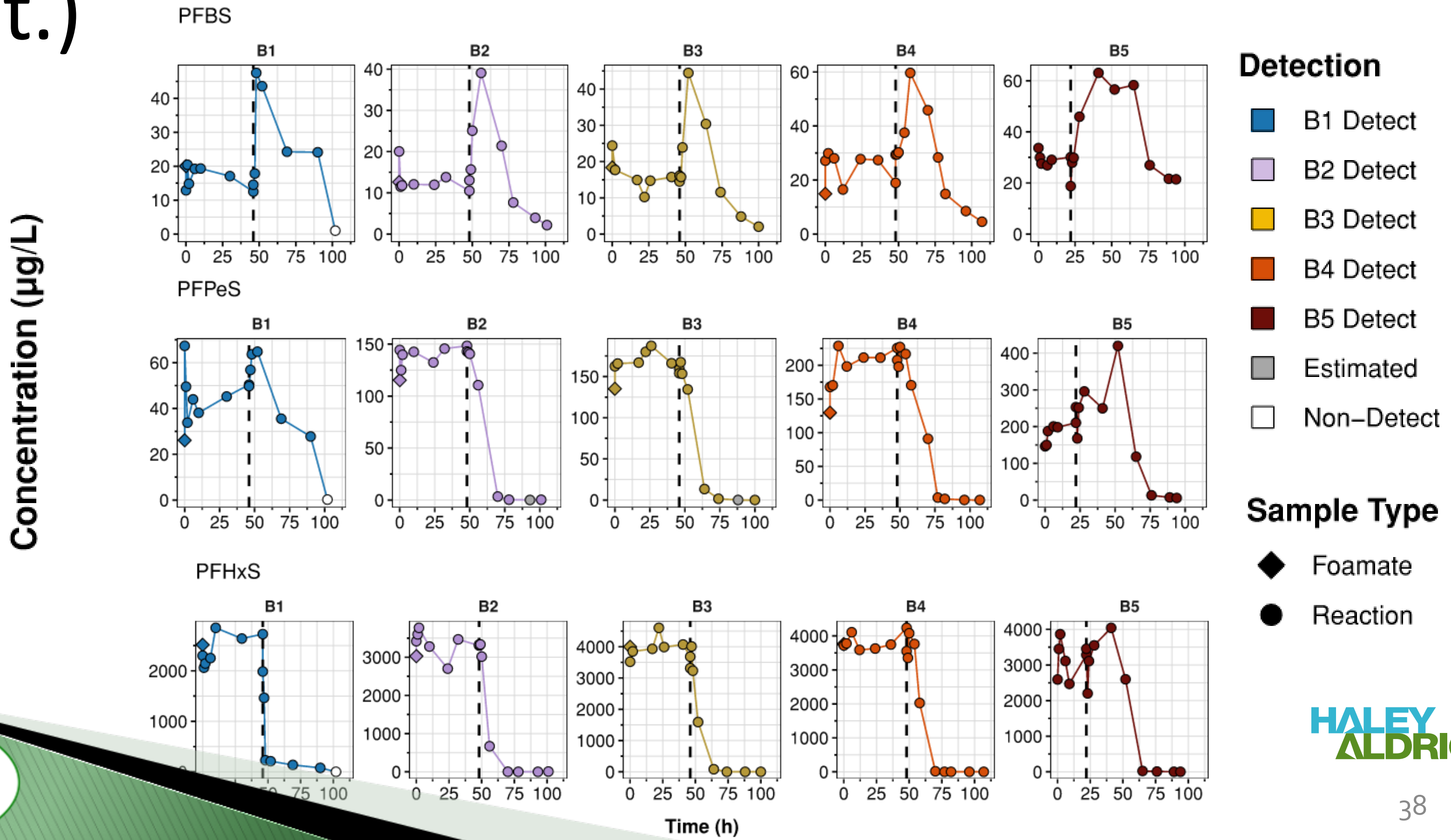
Effective destruction of short-chain PFAS (cont.)



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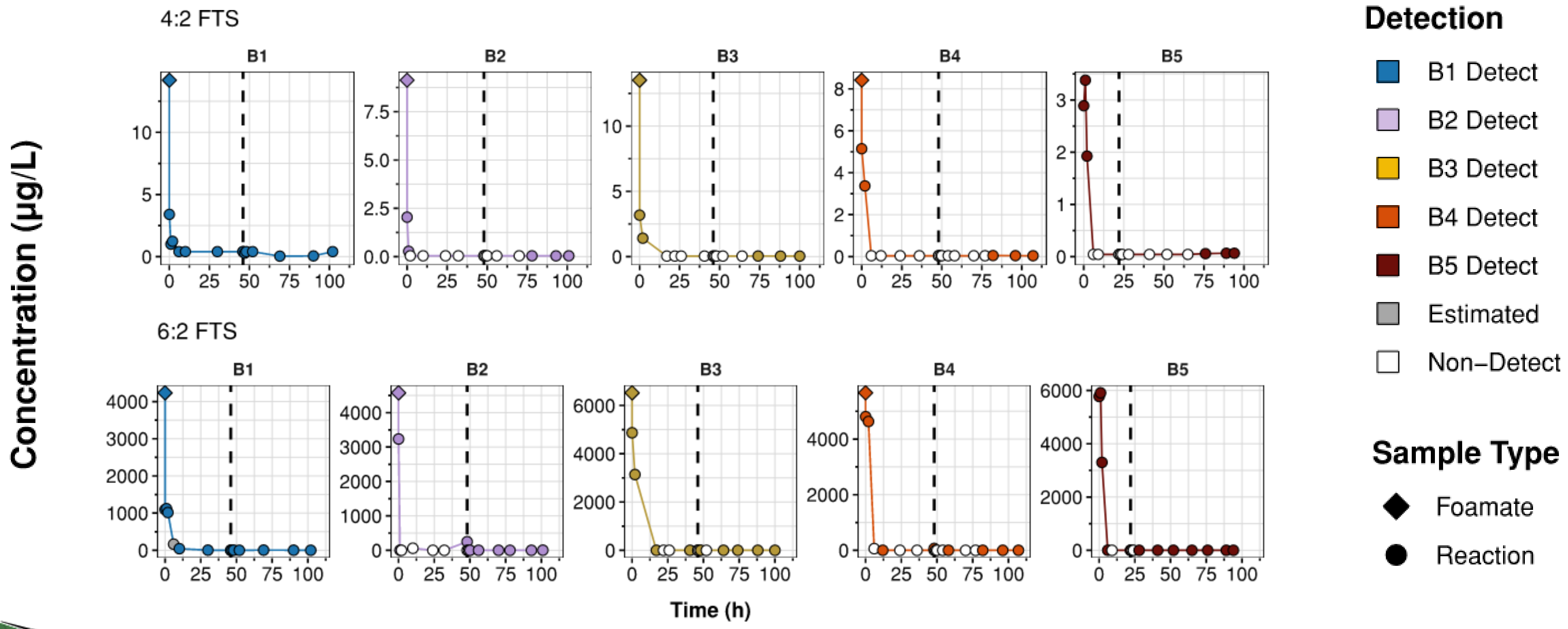
Effective destruction of short-chain PFAS (cont.)



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Potential Byproducts Analysis

- EradiFluor **influent** and **effluent** samples were collected and analyzed for:
  - Total Arsenic (As), Arsenite (III, AsO_3^{3-}), Total Selenium (Se), Selenite (IV, SeO_3^{2-}), Nitrate (NO_3^-), and Nitrite (NO_2^-)
- Results suggest that no harmful byproducts was produced during PFAS destruction

	Metals Speciation				Nitrate/Nitrite	
Sample/Value	Arsenite (As(III)) (µg/L)	Selenite (Se) (µg/L)	As (total) (µg/L)	Se (total) (µg/L)	Nitrate (N) (mg/L)	Nitrite (N) (mg/L)
EPA MCL	10	50	10	50	10	1
Untreated Foamate (Destruction influent)	< 0.5	< 0.2	4.7	0.23	< 0.1	< 0.05
End of Reduction (Destruction effluent)	< 0.5	< 0.2	0.13	0.54	< 0.1	< 0.05

Methods
Total As, Se - EPA 1638
Arsenite – laboratory-specific method (EPA 1632 reference)
Selenite – laboratory-specific method
Nitrate/nitrite – EPA 353.2

Key Points

- A PFAS destruction system (EradiFluor) is constructed. PFAS destruction tests were conducted on simulated waste and real waste samples with effective destruction of various PFAS.

- Field demonstration was successfully conducted
  - 24/7 continuous operation
  - Ambient conditions
  - Effective destruction of long- and short-chain PFAS
  - Near-complete destruction was achieved based on
    - Target PFAS analysis
    - Fluoride generation
    - AOF analytical results
  - Polishing step (ion exchange) further removed residual PFAS

Comparison with other destructive technologies

Strength:

- Does not need special parts
- Low capital cost
- Operate under ambient pressure and temperature (and high pH)
- Low energy use and cost
- Safer operation
- High uptime (rarely shuts down)
- Performance not affected by salt

Limitation:

- Reaction time (to be applied along with concentration technologies)
- Color of liquid waste affects performance (pretreatment is required)

Summary

- Existing technologies produce concentrated PFAS waste
- Growing need for destruction technologies
- Hydrated electrons are effective in destroying various classes of PFAS
- **EradiFluor**™ field demonstration showed that near-complete PFAS destruction based on fluorine mass balance was achieved
- Next steps:
  - additional field demonstration in SoCal
  - study its effectiveness for destruction of un-used AFFF

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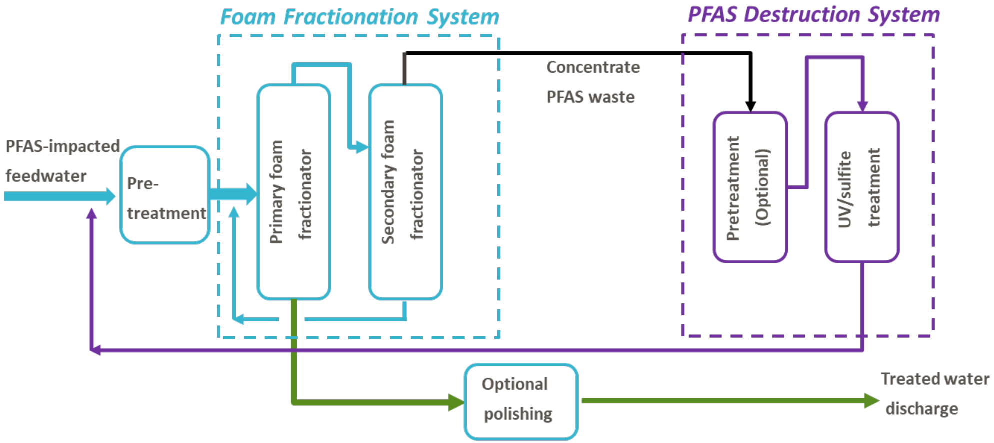
ADDITIONAL AND FUTURE WORK

Ongoing demonstration at a SoCal DoD site



An innovative treatment train combining foam fractionation (SAFF) and EradiFluor is being demonstrated for PFAS removal and destruction in groundwater at a SoCal DoD site.

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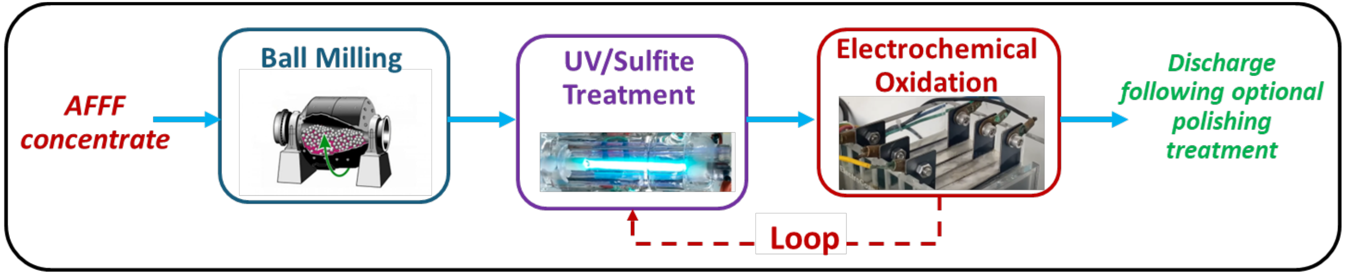
Destruction of unused fire-fighting foam concentrate

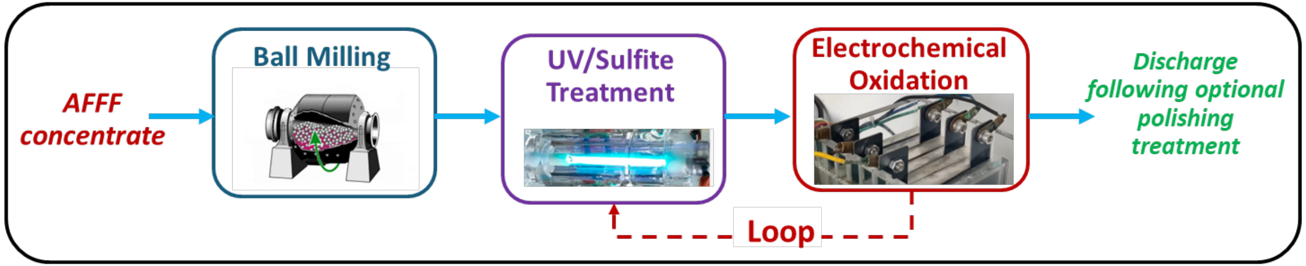
- **<u>Innovative treatment train:</u>**
  - Three novel technologies
  - Non-thermal treatment process



Conceptual Treatment Process

Destruction of unused fire-fighting foam concentrate (cont'd)

- <u>Synergistic effects among the steps:</u>
  - Wet ball-milling reduces foaming and transforms precursors
  - Tandem UV/sulfite and EO are mechanistically complementary for each
  - Chemicals added in the first two steps can be used as electrolytes and source of sulfate radicals in the EO step



Questions?

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Take-home messages

- Existing technologies produce concentrated PFAS waste
- **EradiFluor** effectively and reliably destroys PFAS

Find out more at:

https://serdp-estcp.mil/projects/details/4c073623-e73e-4f07-a36d-e35c7acc75b6/er21-5152-project-overview

https://info.haleyaldrich.com/eradifluor

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