Remediation of PFAS Contaminated Groundwater

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SERDP DOD ▪ EPA ▪ DOE | ESTCP

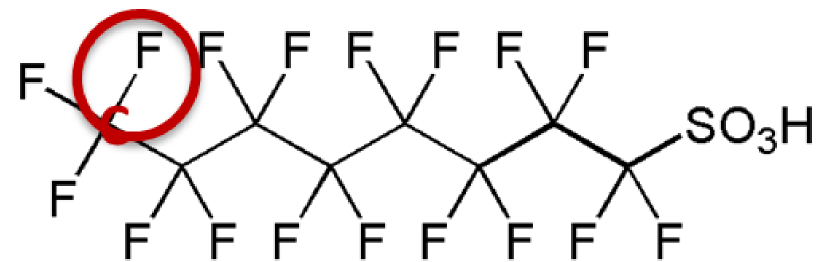
Agenda

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

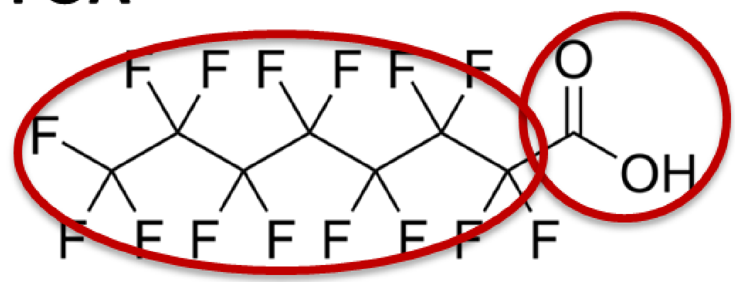
Challenges

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

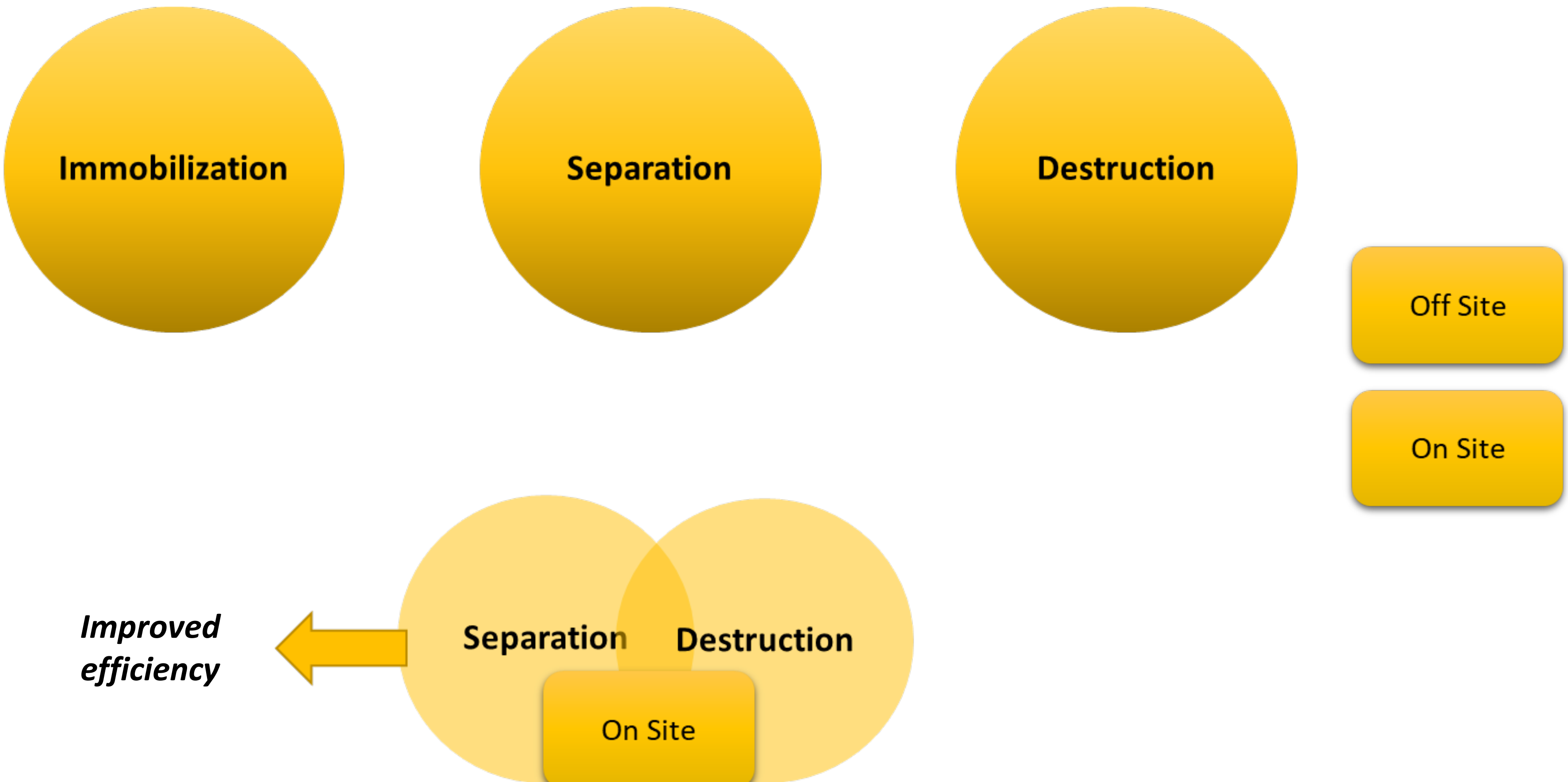
PFOS



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

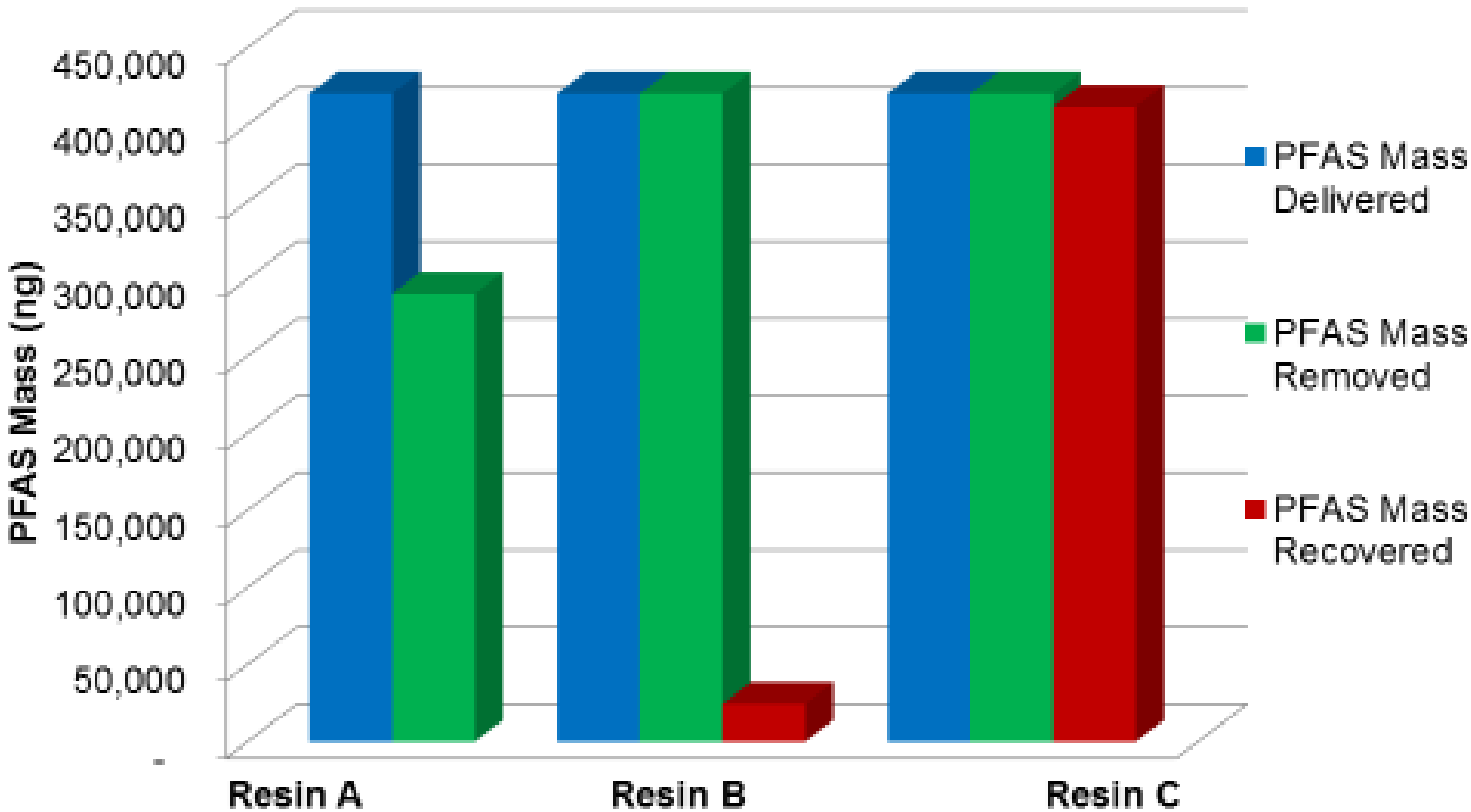
- Treatability testing essential
- Co-contaminants and precursors compete
- Less effective for small chain compounds
- Hemi-micelle and micelle formation
- Granular activated carbon (GAC) reuse

Carbon-based sorption is effective, but challenging to predict

ION EXCHANGE

Ion Exchange

Resin Adsorption/Regeneration from Column Testing

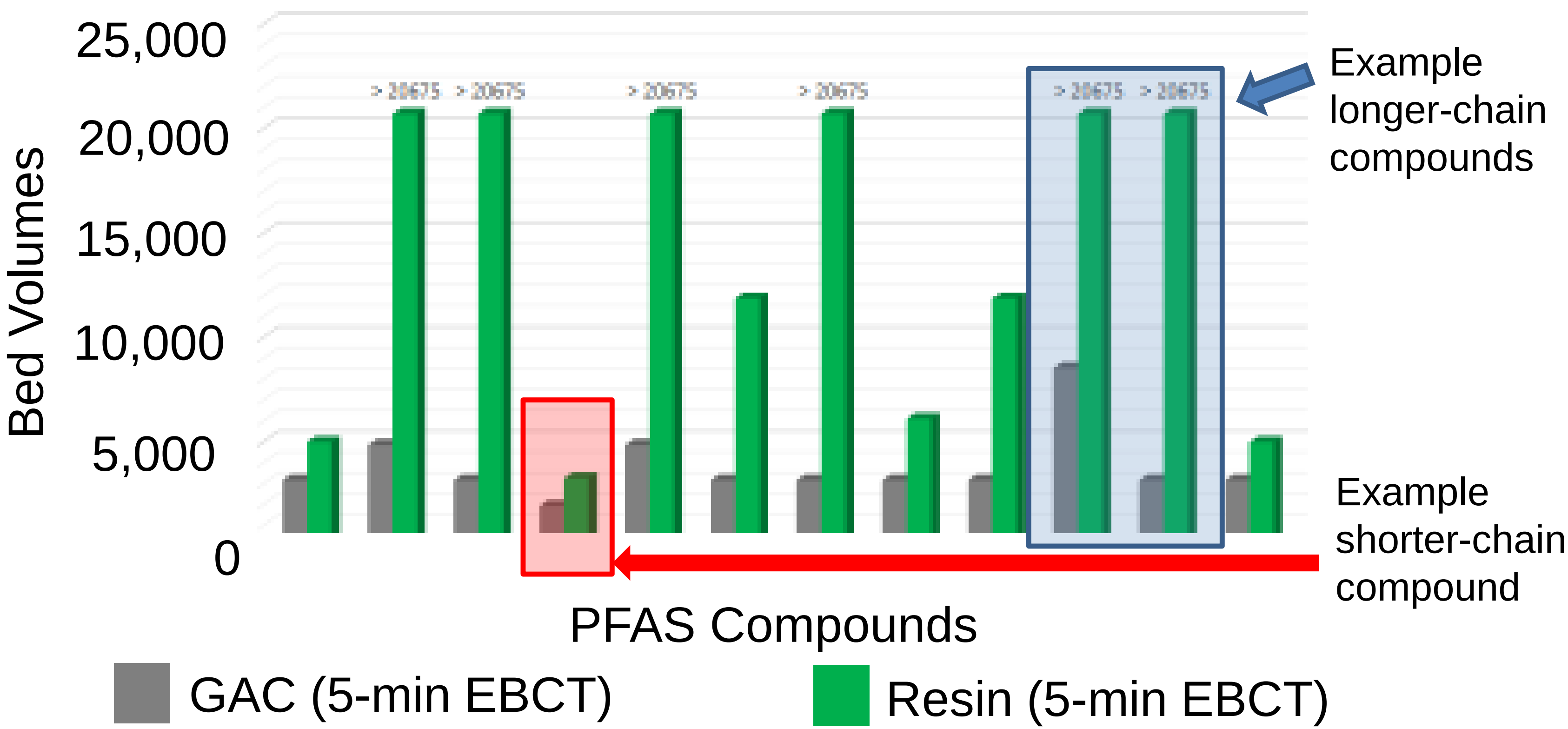


Sustainable Removal of Poly- and Perfluorinated Alkyl Substances (PFAS) from Groundwater Using Synthetic Media

Nathan Hagelin, Amec Foster Wheeler; Steve Woodard, ECT

Ion Exchange

Volume Treated Before Breakthrough



Resin outperformed GAC for many, but not all, compounds

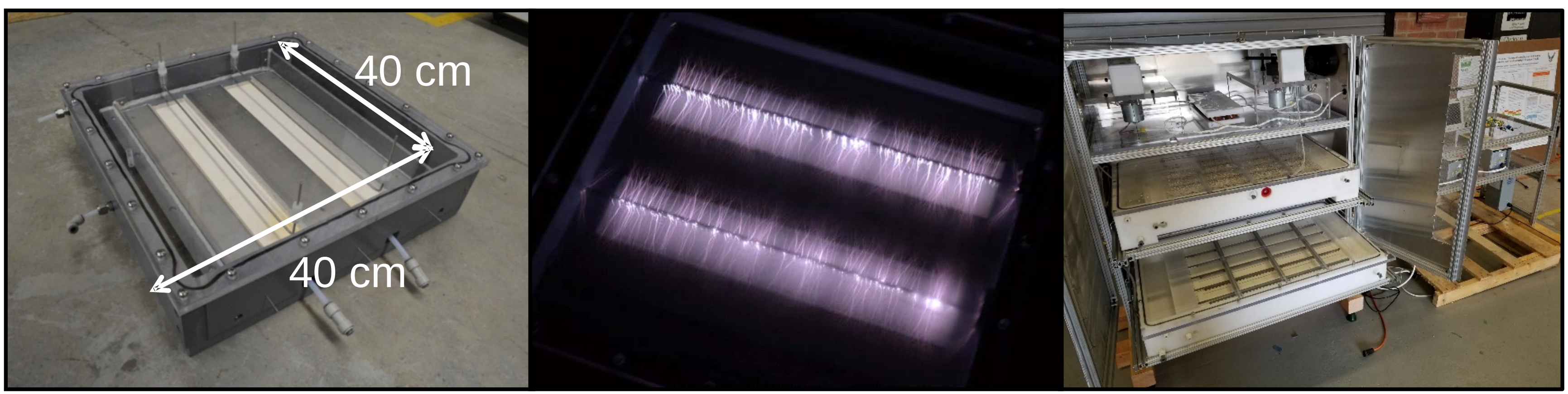
Note: EBCT = empty bed contact time

REDOX MANIPULATION

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

Plasma

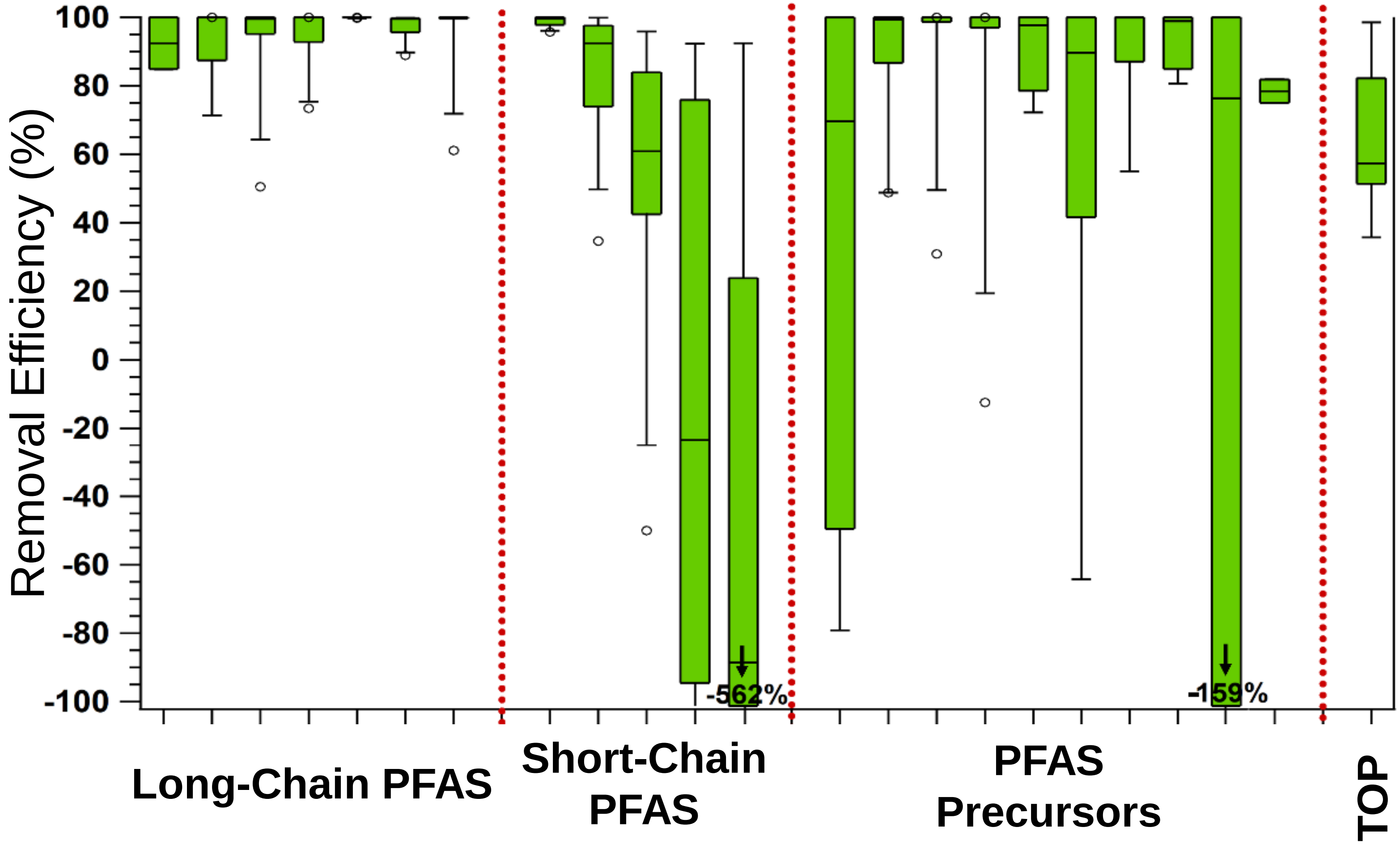
- Uses electricity to convert water into mixture of highly reactive species
  - $OH\bullet$, O, $H\bullet$, $HO_2\bullet$, $O_2\bullet^-$, H_2, O_2, H_2O_2 and aqueous electrons (e^-_{aq})



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

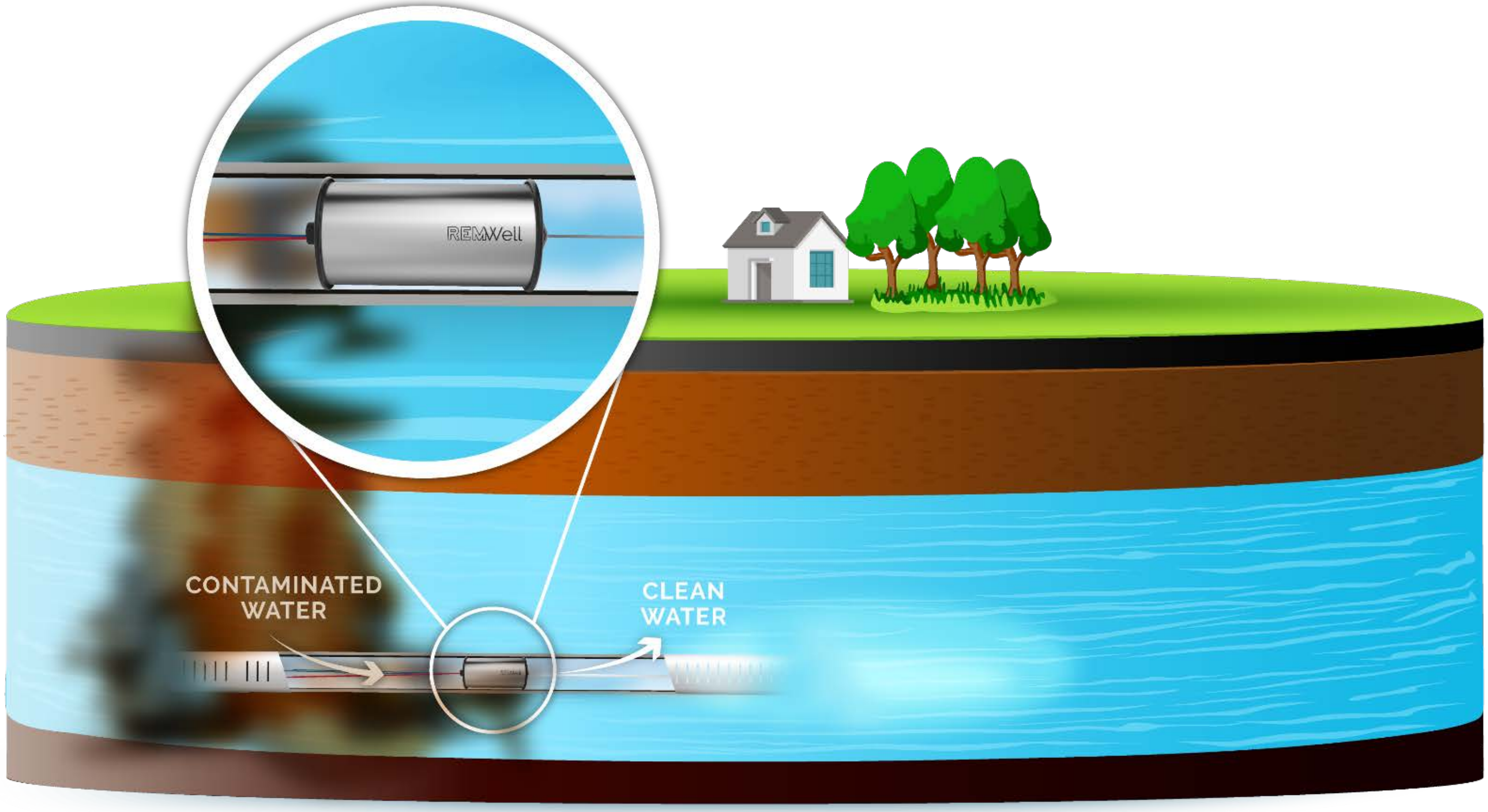
Plasma



Plasma treats PFAS rapidly, proceeding through short-chain intermediates

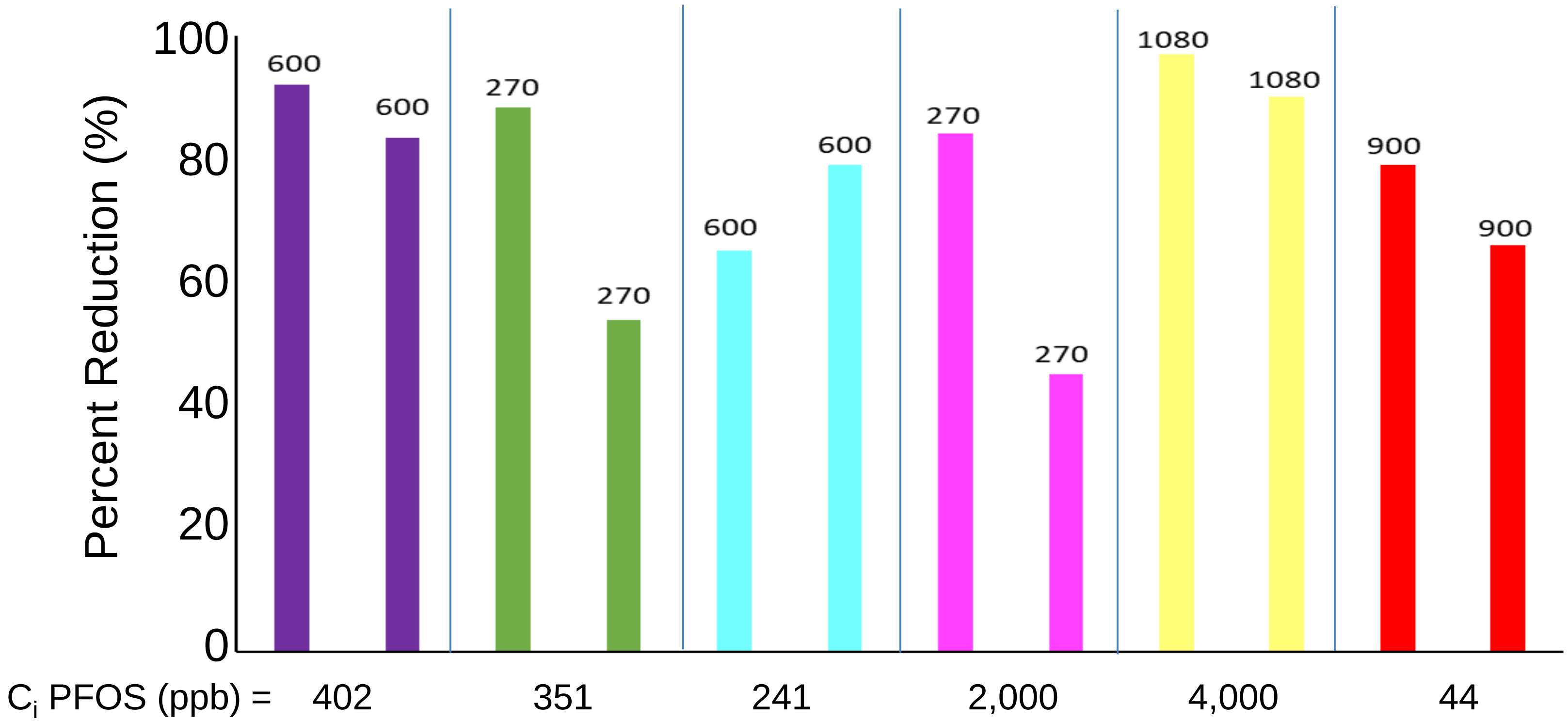
Sonolysis

In Situ Sonolytic Reactor for PFAS Treatment



Contaminated water → Clean water

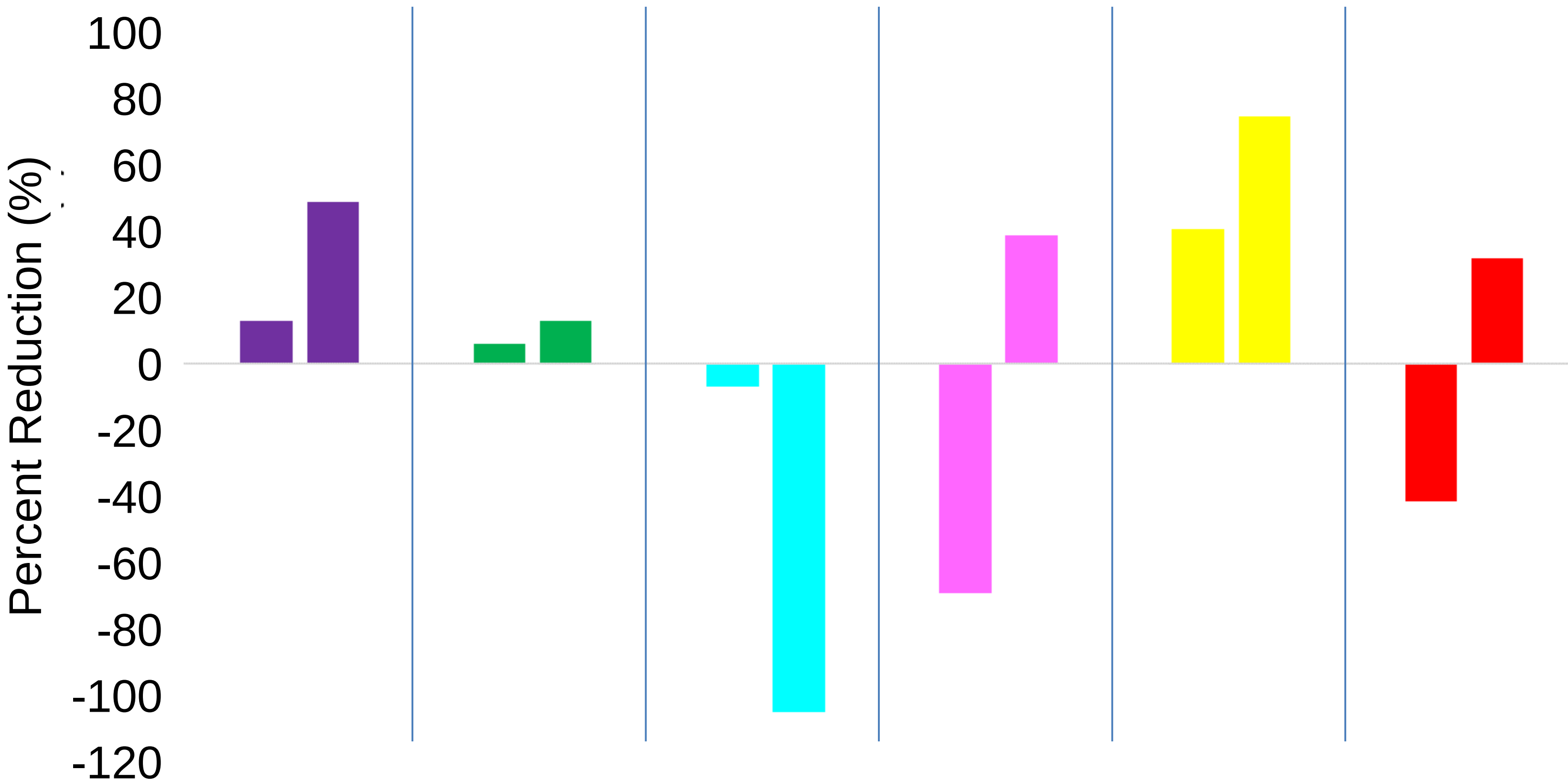
Sonolysis



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

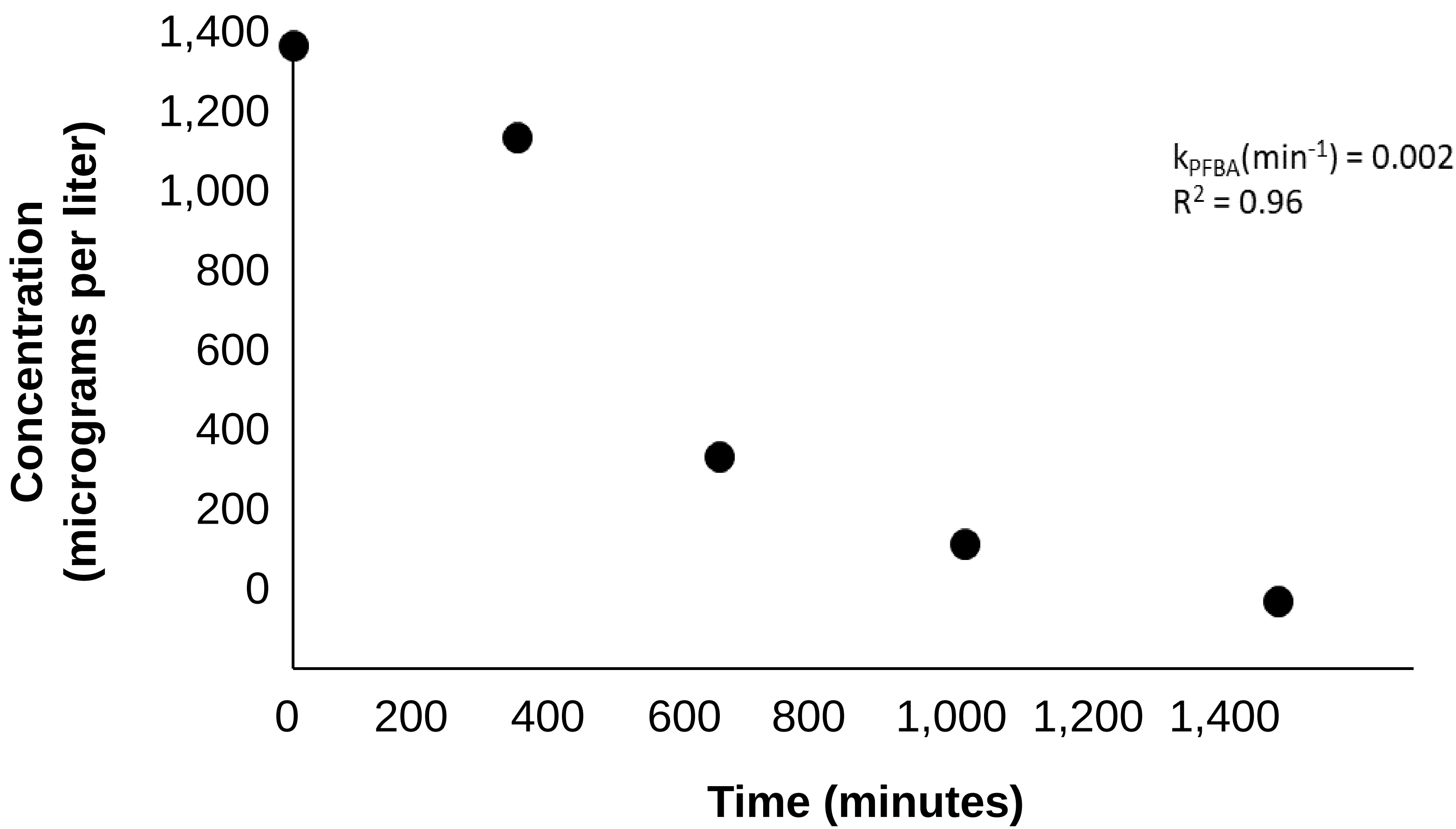
Sonolysis



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

Sonolysis

PFBA Degradation in a Spiked Deionized Water System



Other Approaches

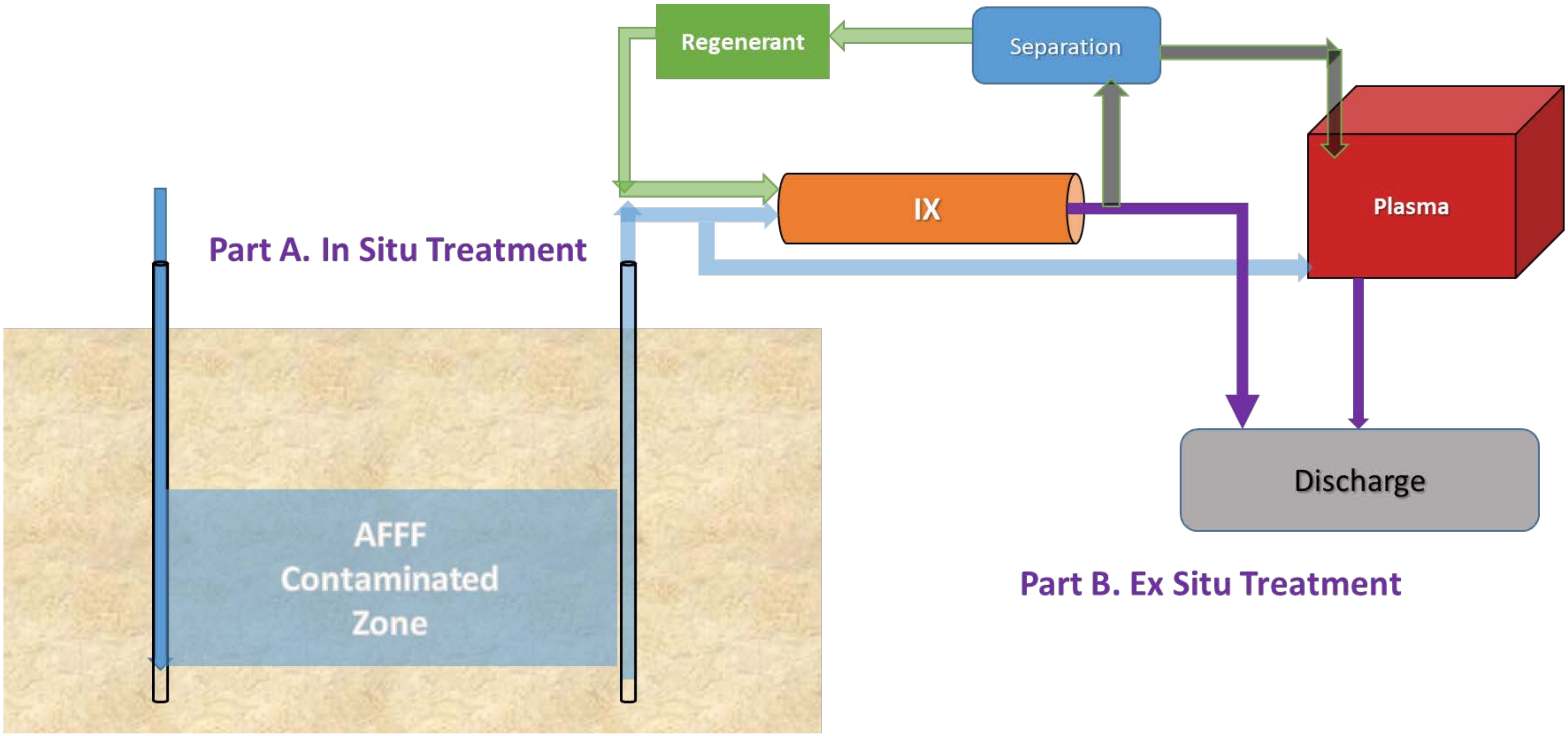
- Electrochemical
- Photochemical
- Reductive
  - Pd_0/nFe_0 nanoparticles
  - Aqueous electrons
- Oxidative
  - Activated persulfate
  - Ozone
  - Different oxidation approaches → different intermediates and byproducts

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

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