Combined In Situ/Ex Situ Treatment of Per- and Polyfluoroalkyl Substance (PFAS)-Contaminated Groundwater

Michelle Crimi, Ph.D
Clarkson University
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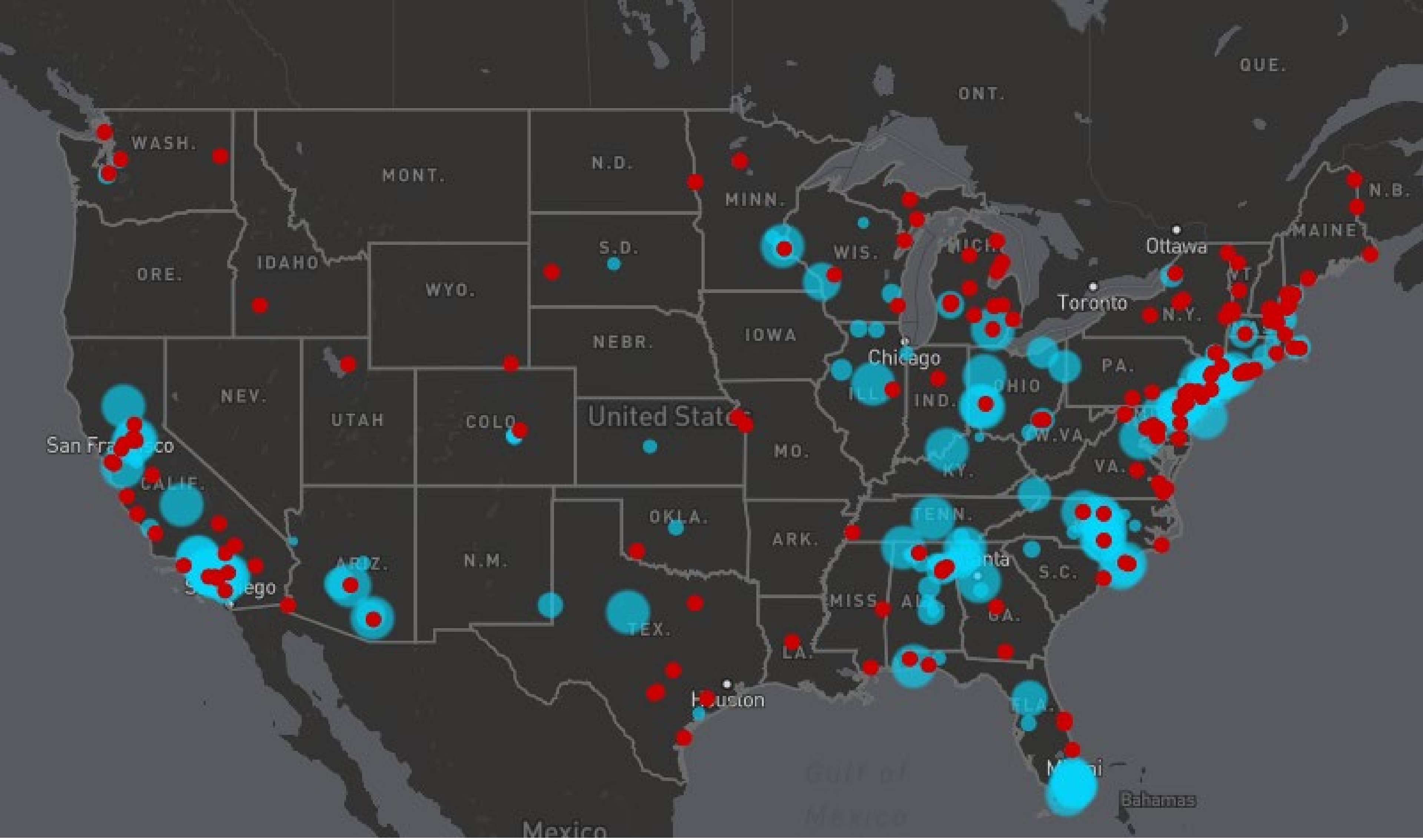
Baltimore, MD

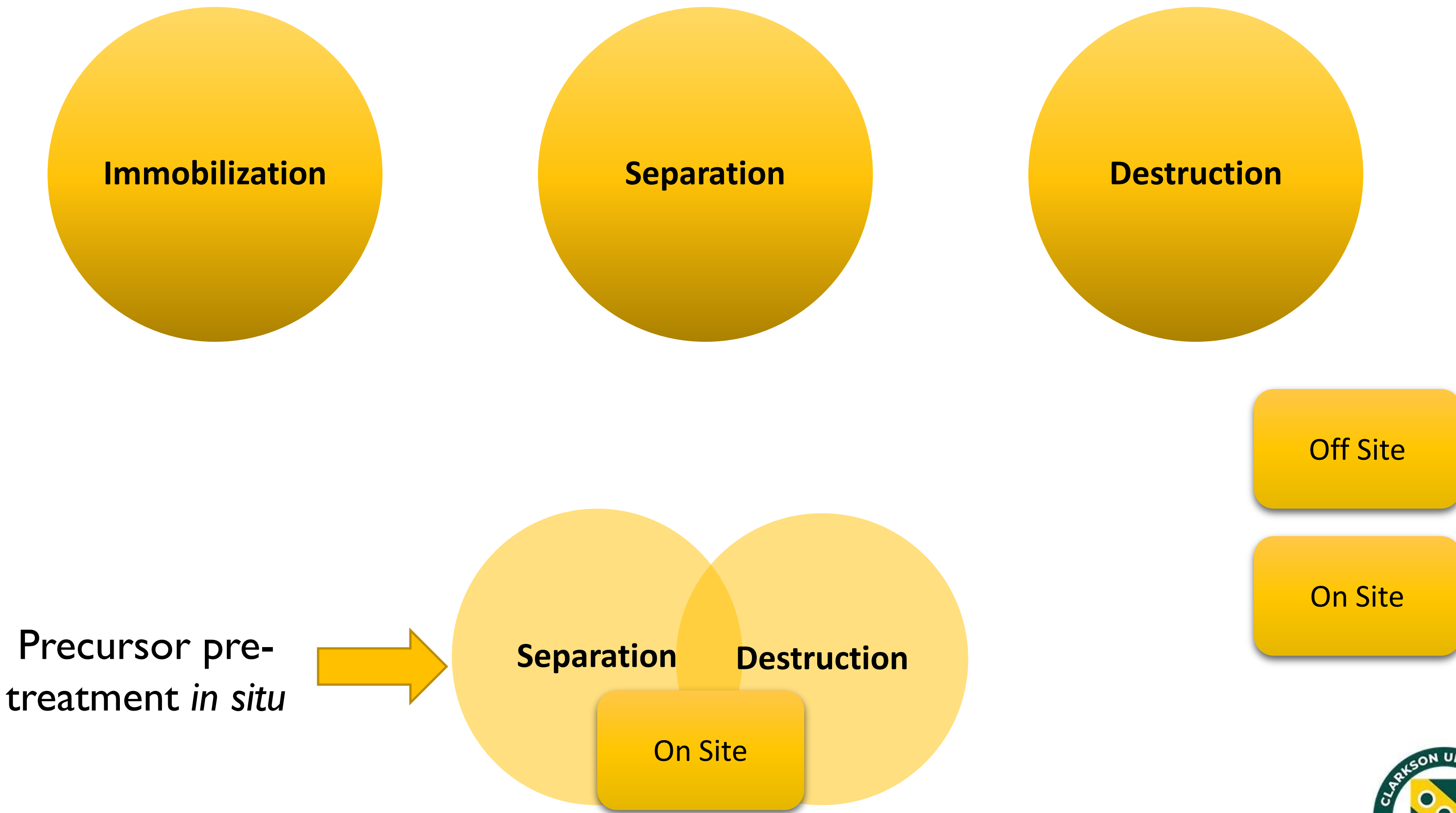


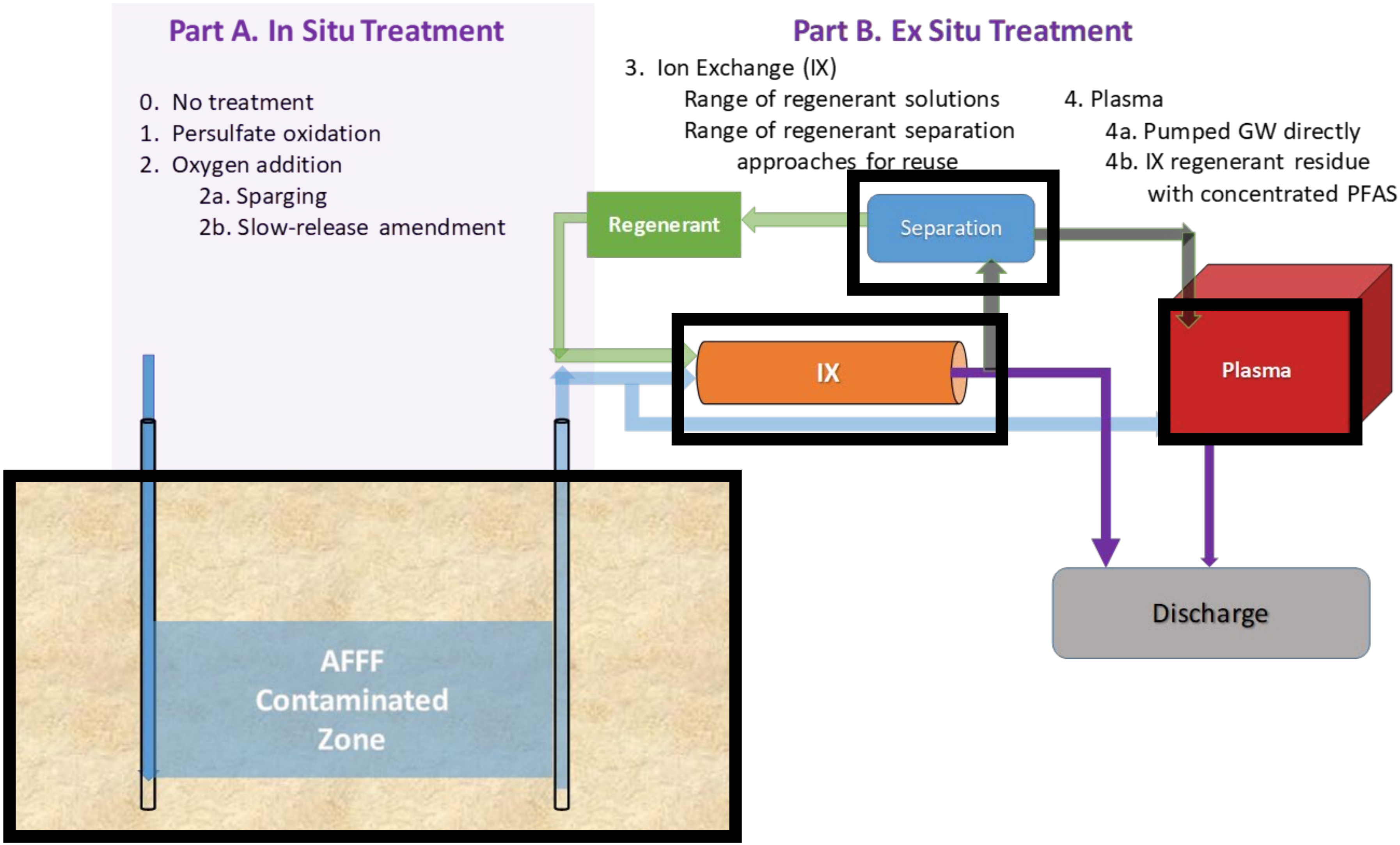
Public Water Supply

Federal & Industrial Sites

Credit: Environmental Working Group and SSEHRI at Northeastern University

Remediation Options

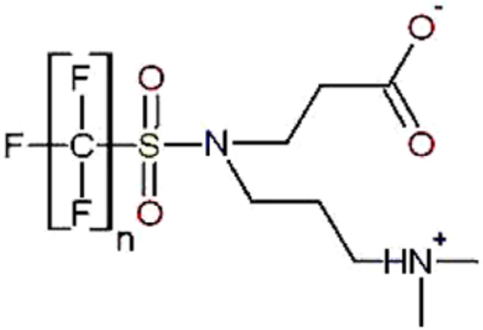




PFAS Treatment Train

SERDP ER18-1306

Precursors



- Cationic, anionic, zwitterionic
- Many expected to sorb strongly to soil based on their properties
- Many can undergo transformation
  - Extended treatment time and cost
- Oxidizable → recalcitrant perfluoroalkyl acids
  - Oxygen
  - ISCO (heat-activated persulfate)

Houtz, E.F., D.L. Sedlak (2012). Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environmental Science & Technology*, 46:9342-9349.

Houtz, E.F., C.P. Higgins, J.A. Field, D.L. Sedlak (2013). Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil." *Environmental science & technology* 47(15):8187-8195

McGuire, M.E., C. Schaefer, T. Richards, W.J. Backe, J.A. Field, E. Houtz, D.L. Sedlak, J.L. Guelfo, A. Wunsch, C. Higgins (2014). Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area. *Environmental Science & Technology*, 48:6644-6652.

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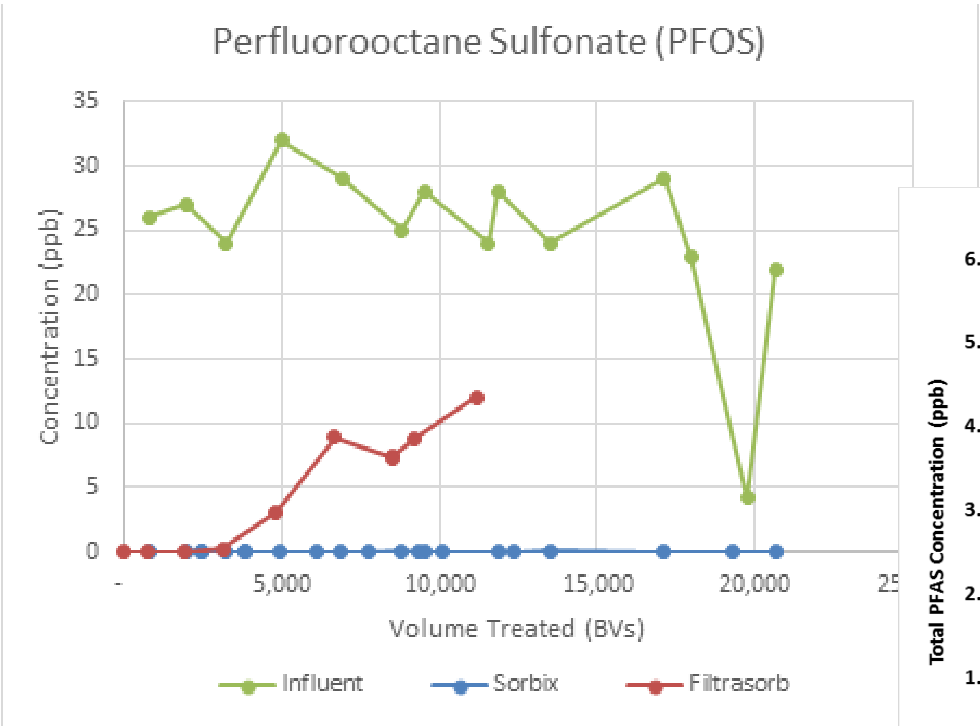
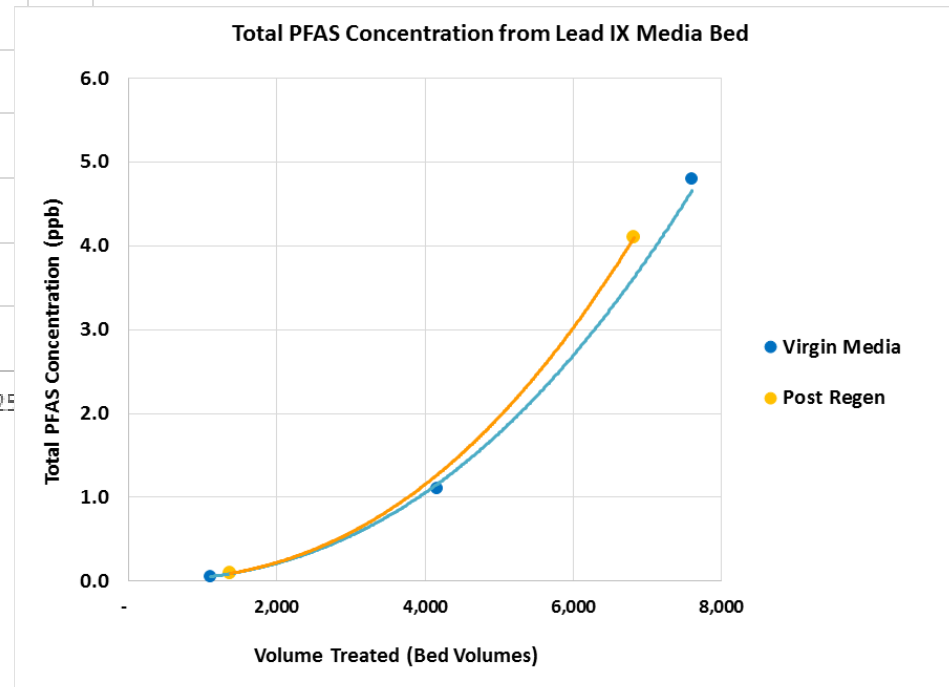
Ion Exchange (IX)





Nickelsen, M. and S. Woodard, A Sustainable System and Method for Removing and Concentrating Per- And Polyfluoroalkyl Substances (PFAS) From Water, US Patent Application Serial No. 15/477,350. April 2017: USA.

Woodard, S., T. Mohr, and M.G. Nickelsen, Synthetic Media: A Promising New Treatment Technology for 1,4-Dioxane. Remediation Journal, 2014. 24(4): p. 27-40.

Plasma treatment

- 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})



Stratton, G., Bellona, C., Dai, F., Holsen, T., Dickenson, E., Mededovic Thagard, S. (2015). Plasma-based Water Treatment: Conception and Application of a New General Principle for Reactor Design. Chemical Engineering Journal, 273: 543-550.

Stratton, G. R., F. Dai, C. Bellona, T. Holsen, E.R.V. Dickenson E. R. V. S. Mededovic Thagard, (2017). Plasma-Based Water Treatment: Efficient Transformation of Perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater. Environmental Science & Technology 2017, 51(3):1643-1648.

Research Objectives

- Evaluate the feasibility and effectiveness of a range of treatment train approaches
- Estimate and compare the scaled-up cost and design challenges for implementation

Pre-treatment *in situ*

1. Determine if in situ pre-treatment can eliminate precursors
2. Quantify precursor transformation
3. Quantify change in PFAA mass flux following pre-treatment
4. Compare persulfate, slow release O_2, and O_2 sparging

Ion exchange (IX) *ex situ*

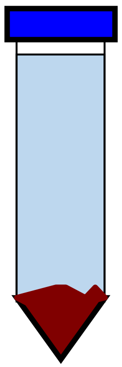
5. Screen IX regenerant solutions
6. Compare regeneration procedures
7. Compare effectiveness of regenerant solution recovery for reuse

Plasma treatment *ex situ*

8. Quantify destruction of PFAS under varied conditions
9. Compare treatment of groundwater, pre-treated groundwater, and concentrated IX regenerant residue

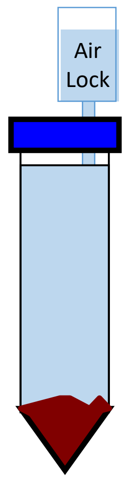
Precursor treatment

Treatment 1:
Persulfate



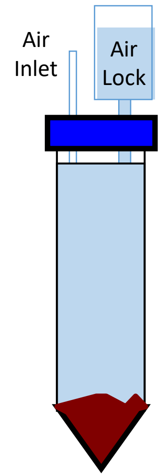
- Conc. $S_2O_8^{2-}$
- Reaction time

Treatment 2:
Slow-release O_2



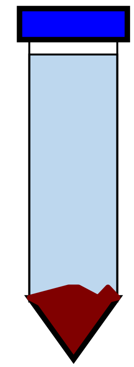
- CaO_2 amount
- Reaction time

Treatment 3:
O_2 sparge



- Sparge rate
- Reaction time

Control
No Treatment

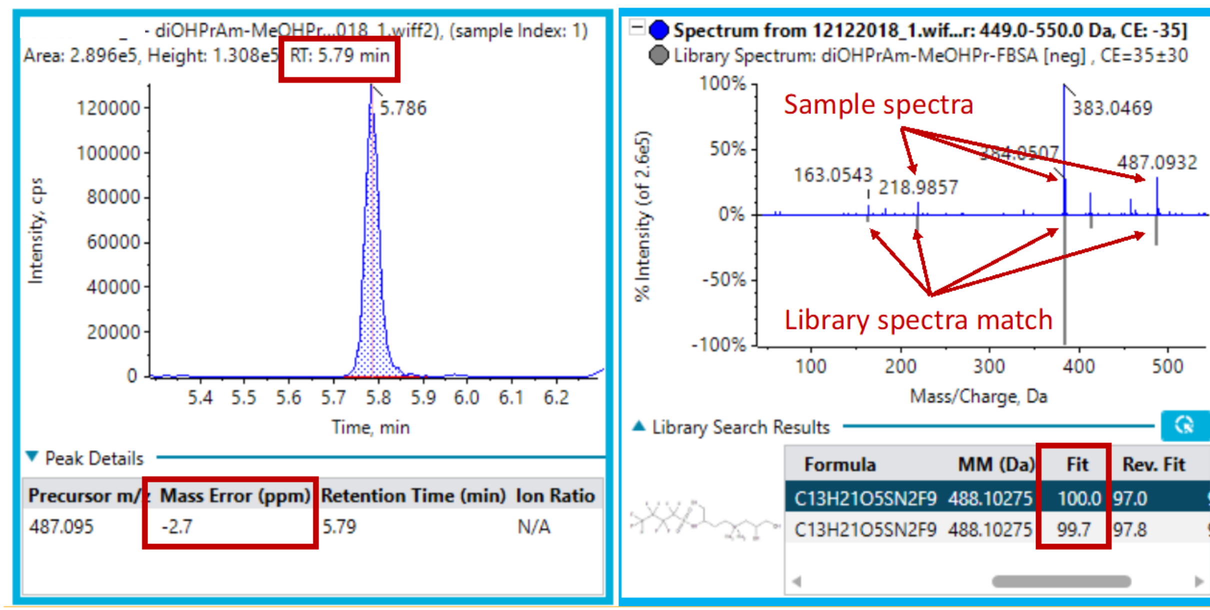


- Nat'l degradation
- Losses to vial

Use batch reactors (3x per treatment) to optimize treatment conditions for elimination of precursors as secondary source of PFAAs in groundwater.

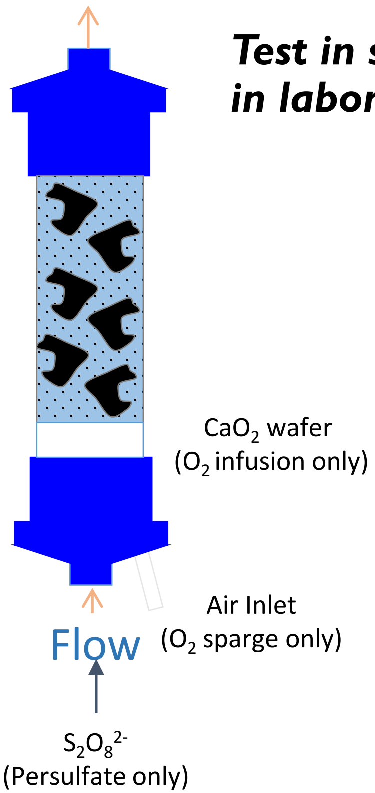
Precursor treatment

- TTU screening for occurrence of ~325 PFAS
- Utilize spectral library generated in prior SERDP projects
- Library matches help identify the composition of the precursor fraction
- TOP (in progress) measures total precursor concentration



N-dihydroxy propyl dimethyl ammonio hydroxymethyl propyl-perfluorobutanesulfonamide (diOHPrAm-MeOHPr-FBSA) in groundwater

Precursor treatment



Test in situ treatments under field-relevant conditions in laboratory transport cells (2x per treatment)

Pretreatment Questions:

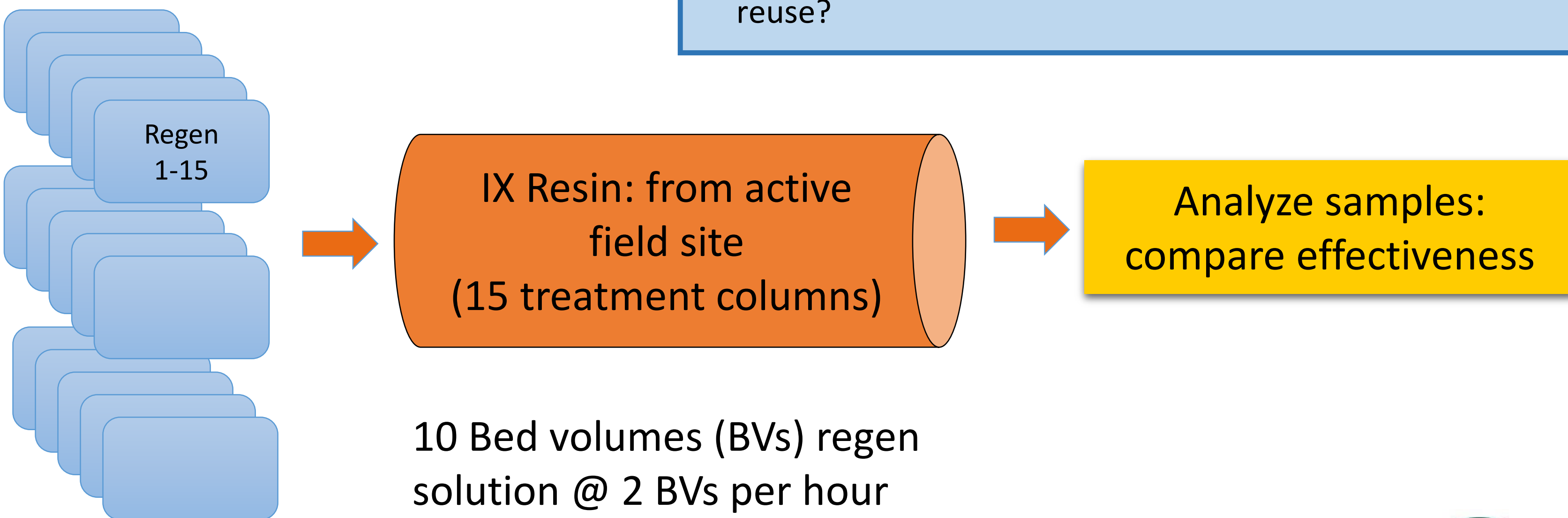
- Can pre-treatment eliminate precursors as a secondary source of PFAAs in groundwater?
- How much of precursors are transformed, how long does it take, and what are the transformation products?
- What is the change in PFAA mass flux into groundwater following pre-treatment?
- How do treatments compare?

IX Regeneration

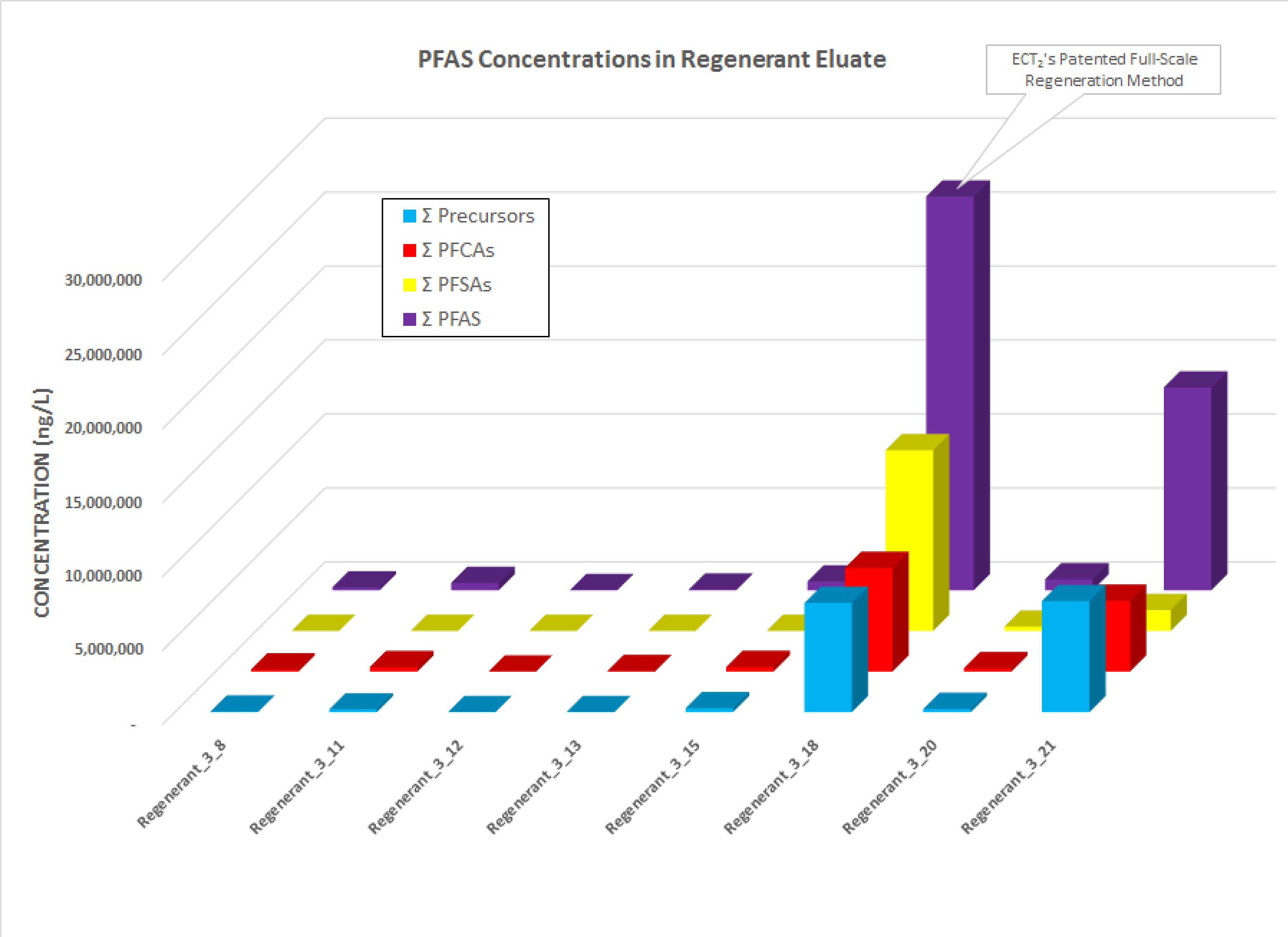
- Screen regeneration solutions

Regeneration & Recovery Questions:

- ♦ What regeneration approaches most effectively remove PFAS from IX resin while maintaining IX performance?
- ♦ How consistent is regeneration across resin types and site conditions?
- ♦ To what extent can regenerant solution be recovered for reuse?

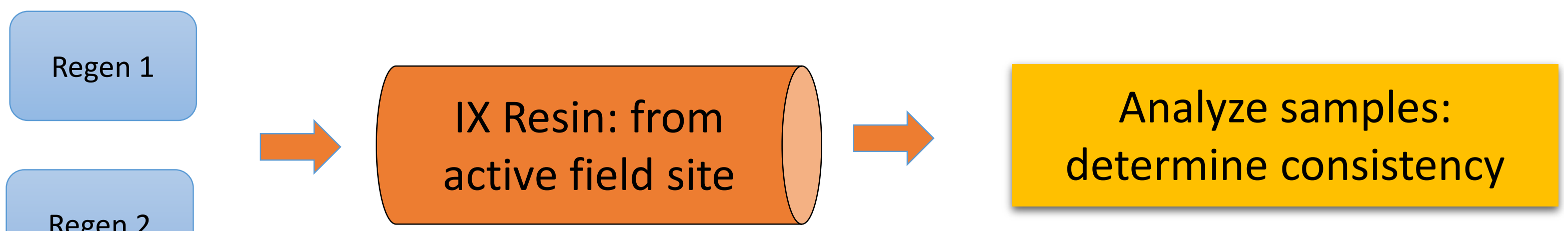


10 Bed volumes (BVs) regen solution @ 2 BVs per hour
→ 10 BVs water @ 10 BVs per hour


PFAS Concentrations in Regenerant Eluate
ECT₂'s Patented Full-Scale Regeneration Method
Σ Precursors
Σ PFCAs
Σ PFSAs
Σ PFAS
CONCENTRATION (ng/L)
30,000,000
25,000,000
20,000,000
15,000,000
10,000,000
5,000,000
-
Regenerant_3_8
Regenerant_3_11
Regenerant_3_12
Regenerant_3_13
Regenerant_3_15
Regenerant_3_18
Regenerant_3_20
Regenerant_3_21

Consistency of Regeneration

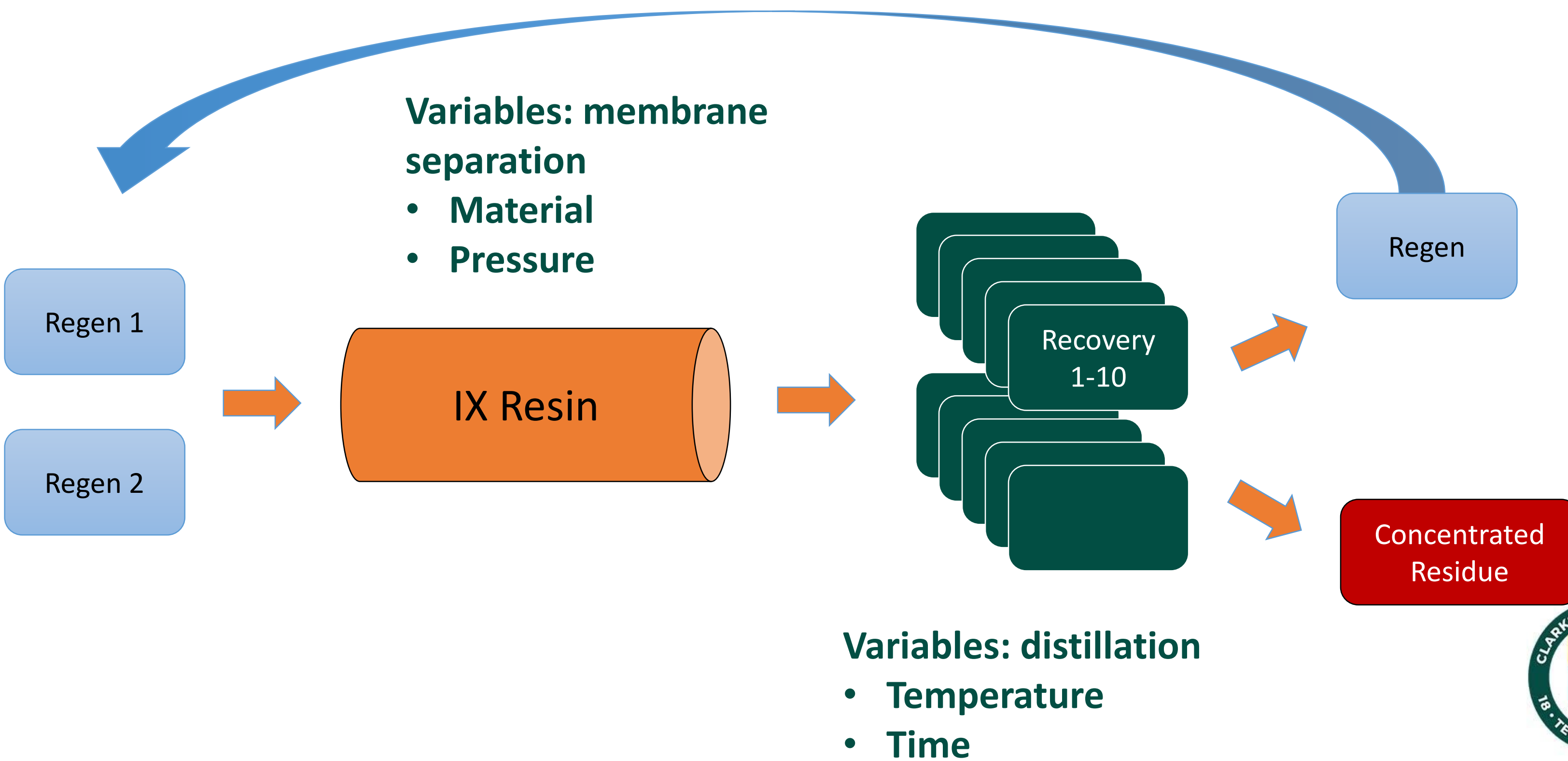
- Determine consistency of top performing regeneration approaches



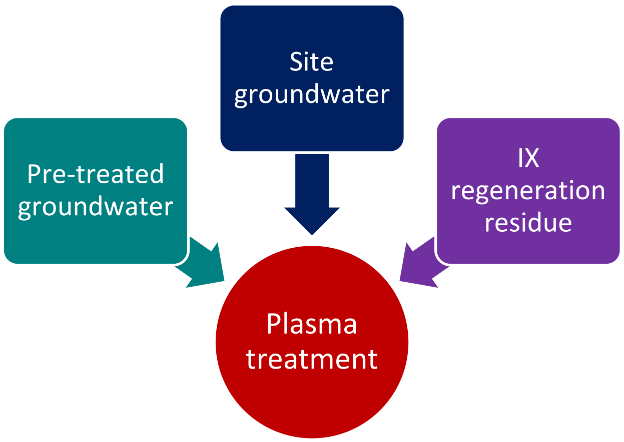
Repeat in triplicate
Repeat with a second field resin

Regenerant Solution Recovery

- Optimize recovery of regenerant solution for reuse
  - Up to 10 recovery techniques for two regenerant solutions



Plasma treatment



- Compare removal efficiencies
- Optimize reactor
- Identify byproducts
- Confirm reliability, energy requirement, cost

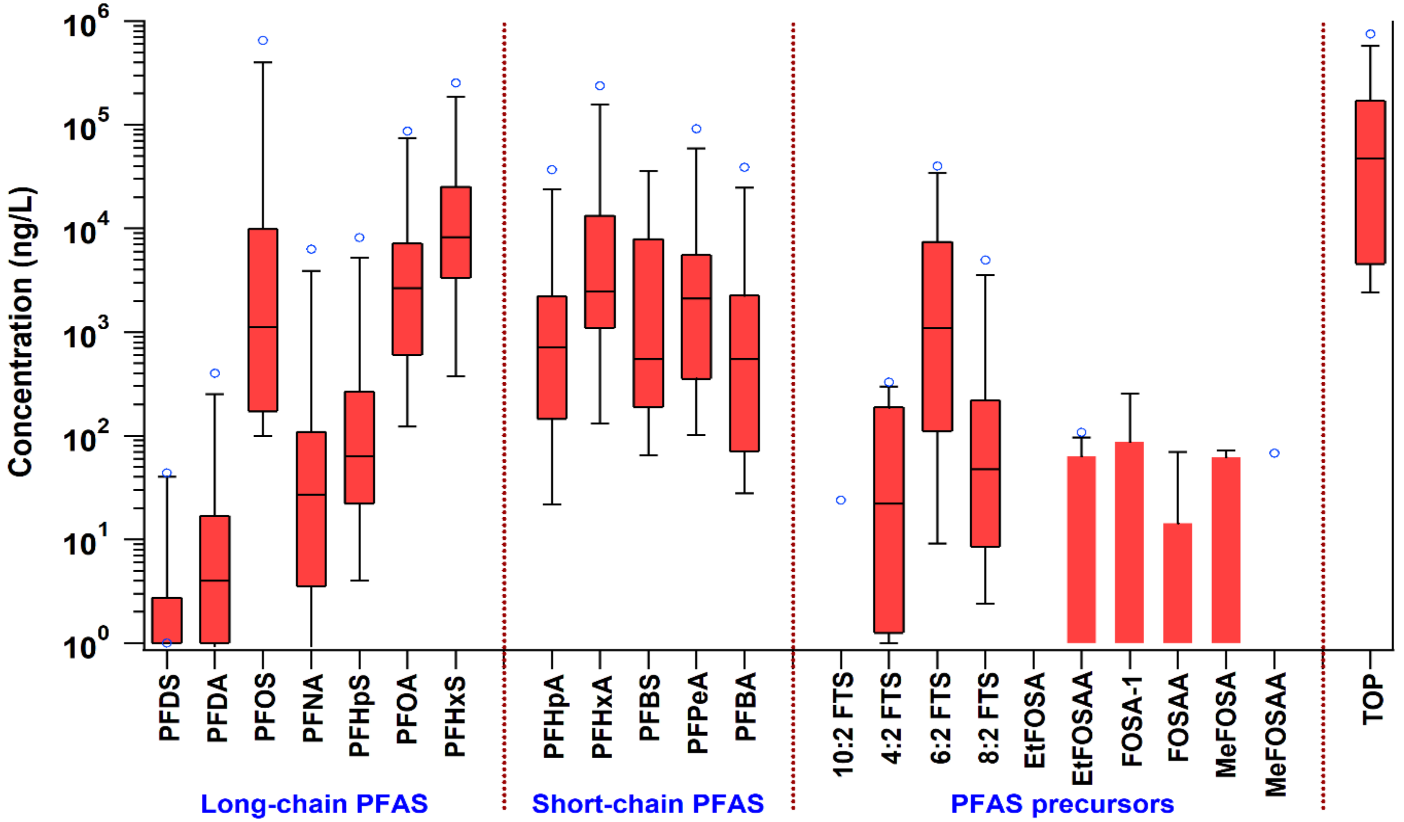
Plasma Questions:

- ♦ Does plasma effectively treat a range of PFAS concentrations within varied matrices (groundwater, pretreated gw, IX regeneration residue)?
- ♦ What design and site factors do plasma treatment efficiency and effectiveness depend on?
- ♦ What byproducts are formed during plasma treatment of PFAS?
- ♦ What is the energy demand and cost of plasma treatment?

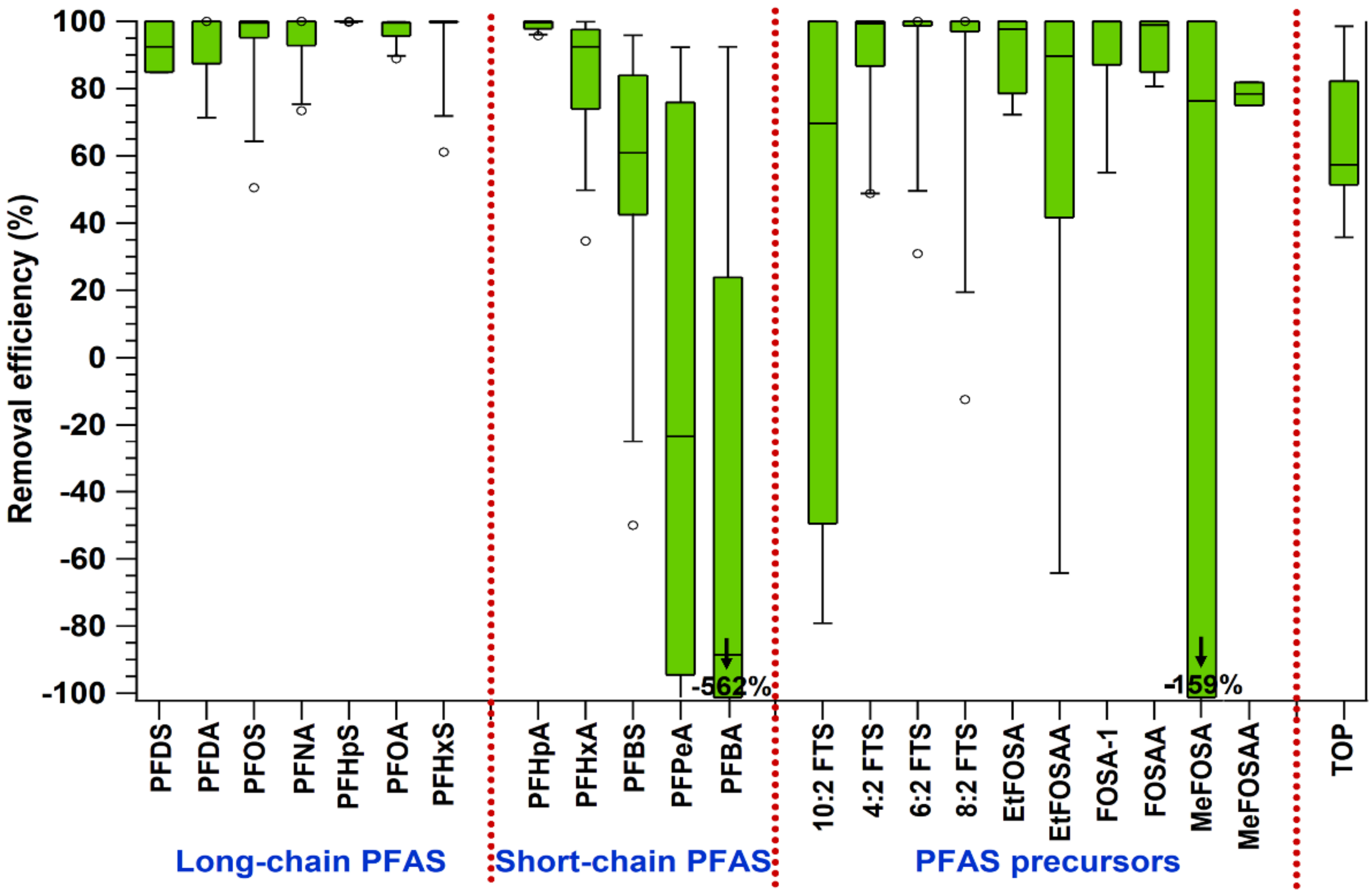
Site media characteristics

Parameter	Range
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)	BDL - 1,130
Total organic carbon (mg/L)	0.11 – 10.8
Iron (mg/L)	BDL - 2600
Manganese (mg/L)	8.6 - 5000

Site media characteristics



Concentrations of PFCAs, PFSAs, precursors and total oxidizable precursors (TOP) in 13 unidentified samples. Ends of the boxes represent the first and third quartiles, horizontal lines marked inside the box represent median, whiskers represent minimum and maximum values, and small hollow circles represent the outliers.



Box and Whisker plot showing the removal efficiency (%) of several long-chain PFAS, short-chain PFAS, PFAS precursors, and total oxidizable precursors (TOP) in unidentified GW samples treated in pilot-scale plasma reactor. Removal efficiency is shown between +100 and -100%, where negative removal efficiency is due to the formation of short-chain PFAS from degradation products of long-chain PFAS. PFBA and MeFOSA have shown negative removal efficiency of -562 and -159%, respectively, which are indicated by down arrows in the figure.

Table 1. Pearson's correlation matrix showing the effect of different water matrices on the PFOA and PFOS removal rate. Statistically significantly correlations are in bold.

	k (min^{-1})	*Total PFAS (ng/L)*	*TOP (ng/L)*	*PFOA+ PFOS (ng/L)*	*TIP (ng/L)*	*PFAS+ TOP (ng/L)*	*PFAS+ TIP (ng/L)*	*Cond. (µS/cm)*	*TOC (mg/L)*
k (min-1)	**1**	-0.44	-0.27	-0.39	**-0.55**	-0.39	-0.45	-0.42	-0.18

Total identified precursors

Table S5 – Concentrations of volatile organic compounds (VOCs) before and after plasma treatment

Samples	VOCs	Concentration (µg/L)	
		Untreated	Treated
IDW1	Met ter-butyl ether	0.26	BDL
	1,2 - dichloroethane	28.00	BDL
IDW4	1,1-dichloroethane	0.72	BDL
	Bromodichloromethane	0.17	BDL
	Chloroform	2.70	BDL
IDW7	1,2 - dichloroethane	0.33	BDL
IDW8	1,1-dichloroethane	0.31	BDL
	1,2 - dichloroethane	2.50	BDL
	Benzene	1.60	BDL
	Ethylbenzene	2.20	BDL
IDW10	1,1-dichloroethane	0.26	BDL
	1,2 - dichloroethane	15.00	BDL
	Trichloroethane	24.00	BDL
IDW12	Acetone	13.00	BDL
	m-xylene & p-xylene	0.44	BDL
	o-xylene	0.27	BDL

BDL – Below detection limit; VOCs concentrations were BDL in IDW 2, 3, 5, 6 and 11; VOCs concentrations in IDW 9 and 13 were not analyzed.

Table S7 – Fluoride concentrations in IDW samples before and after plasma treatment

Samples	Untreated (mg/L)	Treated (mg/L)	% increase
IDW1	0.42	0.55	31.09
IDW2	0.12	0.20	58.11
IDW3	0.74	1.03	39.54
IDW4	0.20	0.41	103.00
IDW5	0.27	0.47	71.85
IDW6	0.20	0.35	71.85
IDW7	0.25	0.36	45.48
IDW8	0.18	0.28	58.11
IDW9	0.18	0.32	79.16
IDW10	0.71	1.22	71.85
IDW11	3.32	3.39	2.10
IDW12	1.12	1.38	23.15
IDW13	2.75	5.24	90.71

System design

- Determine feasible combinations of in situ and ex situ treatment trains
- Prepare conceptual designs for up to 3 representative sites
  - Schematics
  - Diagrams
  - Layouts
  - Considering: effectiveness, implementation challenges, safety, sustainability, cost
- Cost analysis and comparison to current treatment approaches
  - e.g., pump-and-treat using GAC with off-site management of PFAS-contaminated GAC

Summary

- Soil and groundwater samples screened for ~325 PFAS using spectral library generated in prior SERDP work are useful for determining the composition of precursor fraction
- IX regeneration must have regenerant targeted for PFAS and the resin of interest
- Plasma treatment is effective over a broad range of site geochemical conditions
  - Most common intermediates formed during treatment include shorter chain PFAAs

Acknowledgements

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Wood

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ECT_2

Ion exchange, synthetic media for contaminant treatment, resin regeneration

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NAVFAC

PFAS characterization and treatment