Optimization of Regenerable Ion Exchange for PFAS Groundwater Treatment: Outcomes from Two SERDP and ESTCP Projects

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Project Team

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ECT_2

Ion exchange, synthetic media for contaminant treatment, resin regeneration

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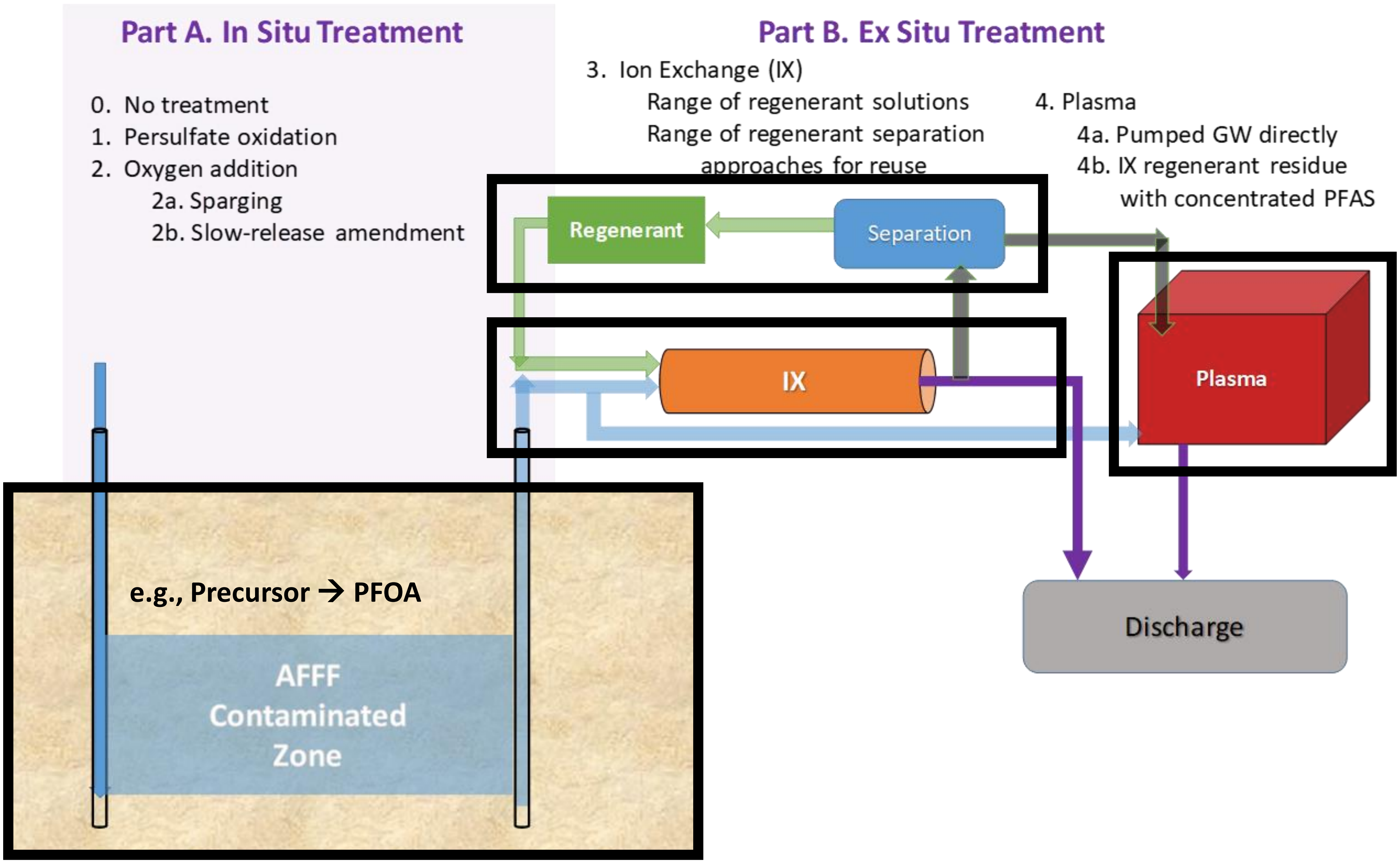
PFAS characterization and treatment


Part A. In Situ Treatment
0. No treatment
1. Persulfate oxidation
2. Oxygen addition
2a. Sparging
2b. Slow-release amendment
Part B. Ex Situ Treatment
3. Ion Exchange (IX)
Range of regenerant solutions
Range of regenerant separation approaches for reuse
4. Plasma
4a. Pumped GW directly
4b. IX regenerant residue with concentrated PFAS
Regenerant
Separation
IX
Plasma
Discharge
e.g., Precursor → PFOA
AFFF Contaminated Zone

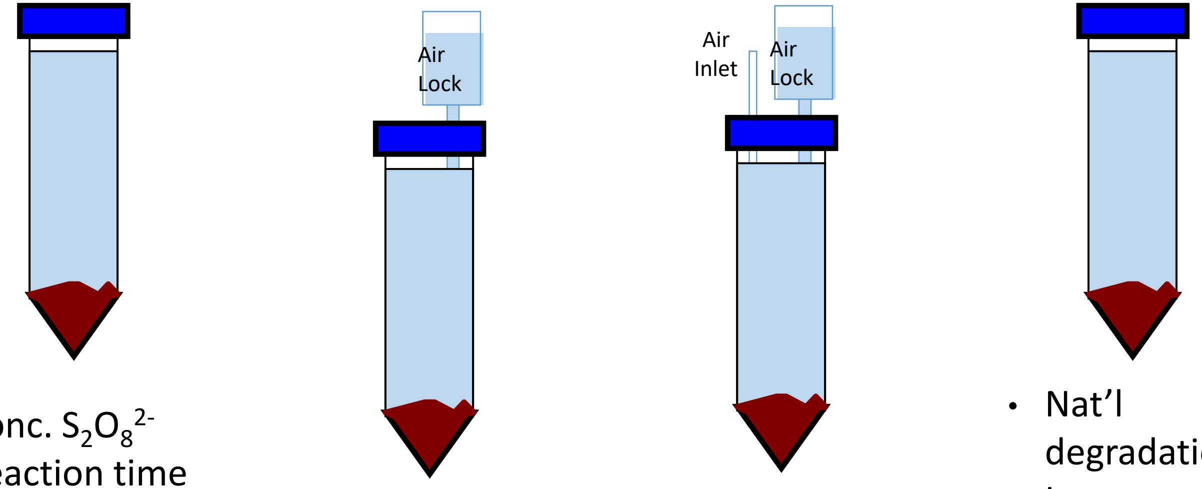
Pre-treatment - Batch Reactor Tests

Treatment 1:
Persulfate

Treatment 2:
Slow-release O_2

Treatment 3:
O_2 sparge

Control
No Treatment



Treatment 1:
- Conc. $S_2O_8^{2-}$
- Reaction time

Treatment 2:
- CaO_2 amount
- Reaction time

Treatment 3:
- Sparge rate
- Reaction time

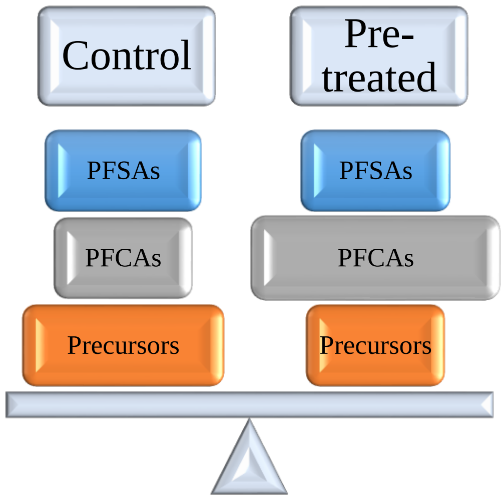
Control:
- Nat'l degradation
- Losses to vial

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

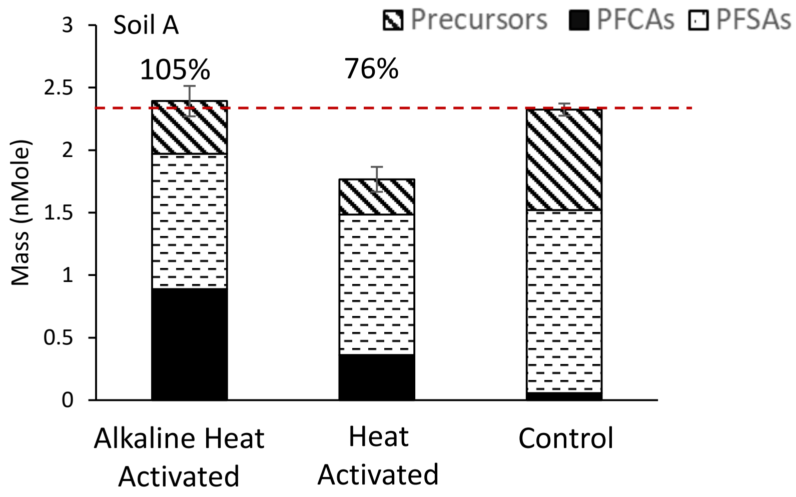
Pre-treatment - Batch Reactor Tests

Results: persulfate pre-treatment

Total PFAS recovery



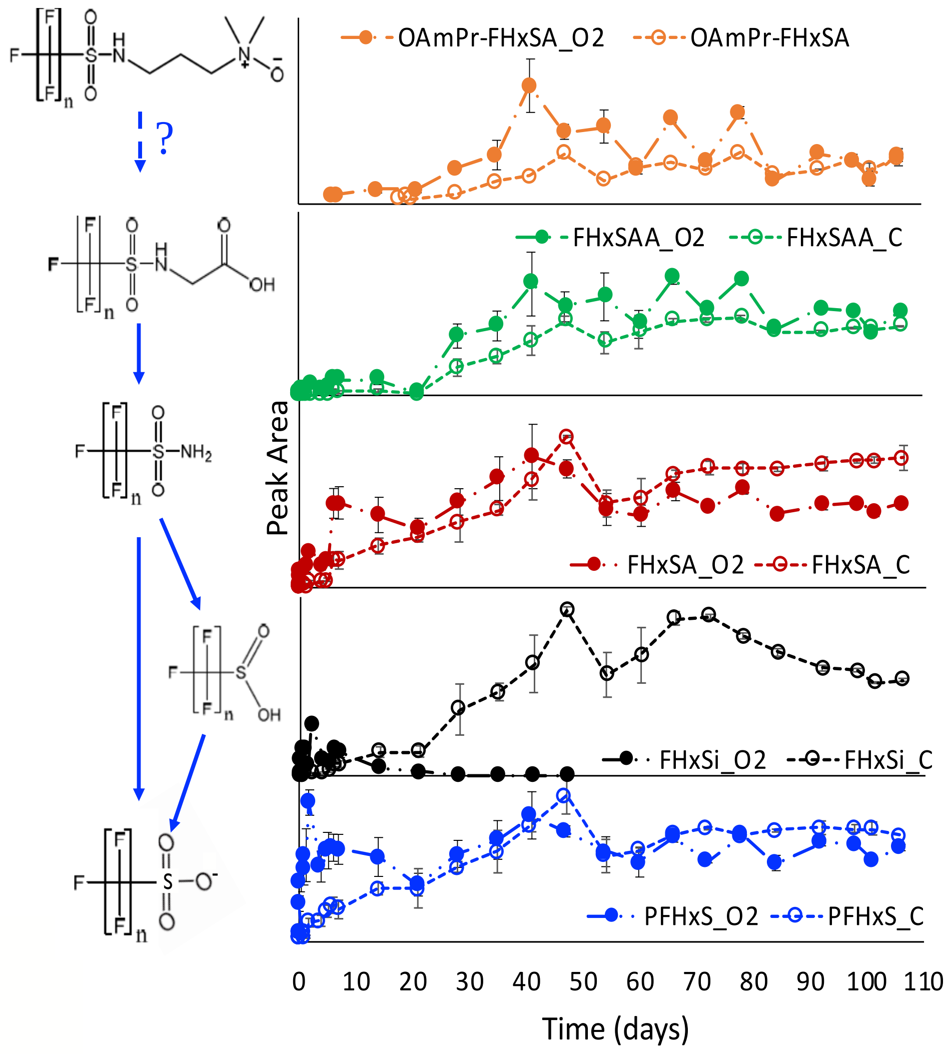
Total PFAS recovery



- Shift from precursors to PFCAs ($OH^{\cdot}$)
- Full recovery in alkaline heat activated and heated controls (heated not shown)
- Low recovery in $SO_4^{\cdot-}$ = PFCA degradation
- 47-57% precursor oxidation

Pre-treatment - Batch Reactor Tests

Results: O_2 pre-treatment



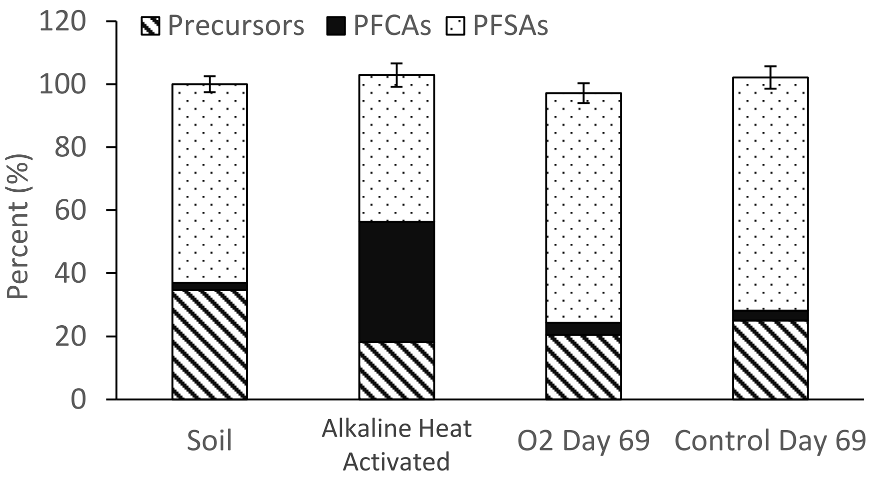
- Some transformation intermediates appeared earlier in sparged (OAmPr-FHxSA)
- Some degraded faster (FHxSi, FHxSA) in sparged

Accelerated precursor transformation using O_2 amendment is supported by individual precursor data.

Pre-treatment - Batch Reactor Tests

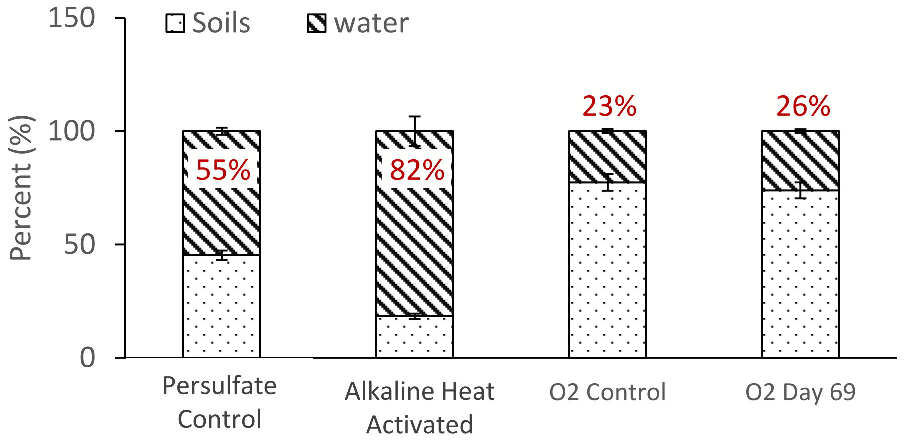
Results: Persulfate vs. O_2

Persulfate v. O_2 composition:



- Composition reflects treatment technique
- Persulfate generates PFCAs
- O_2 generates predominantly PFSAs, minor PFCAs

Persulfate v. O_2 aqueous fraction:

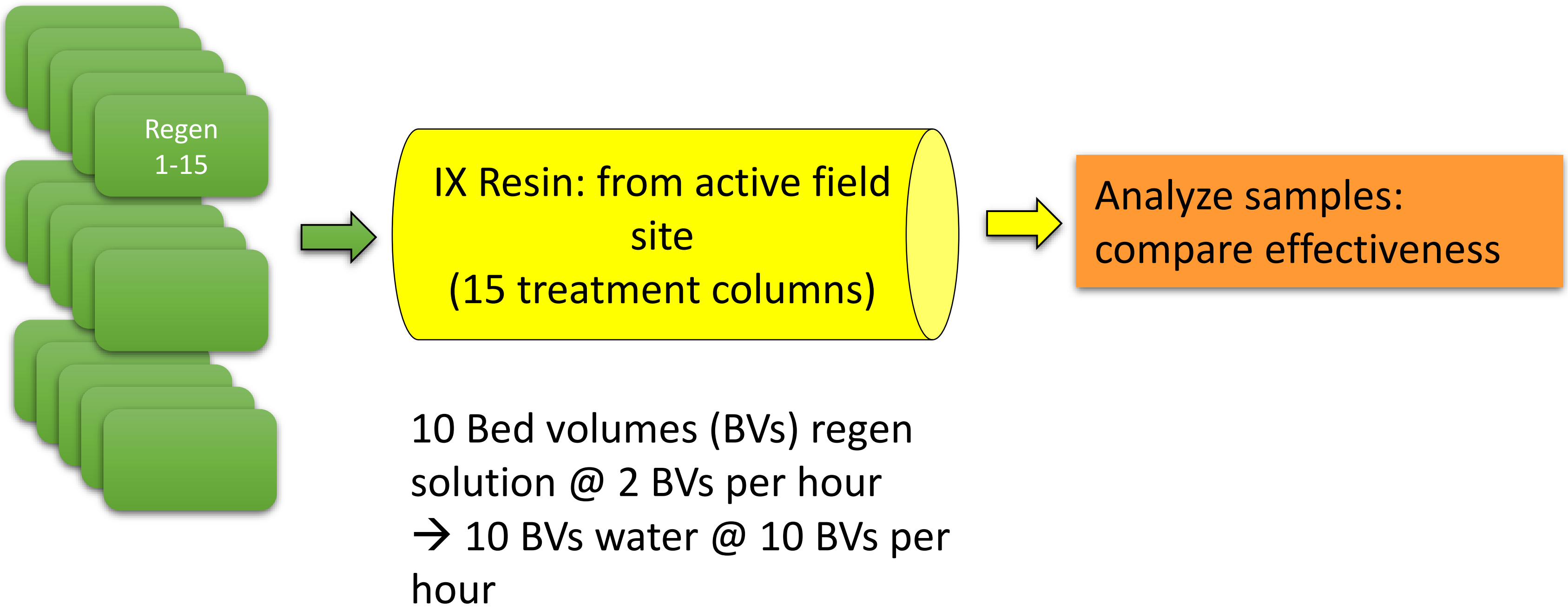


- Aqueous fraction in persulfate > O_2 as of Day 69
- Only ~50% of the O_2 experimental duration

Persulfate favorable for fraction of total PFAS mobilized; additional time points are needed to determine mobilization in O_2 experiments

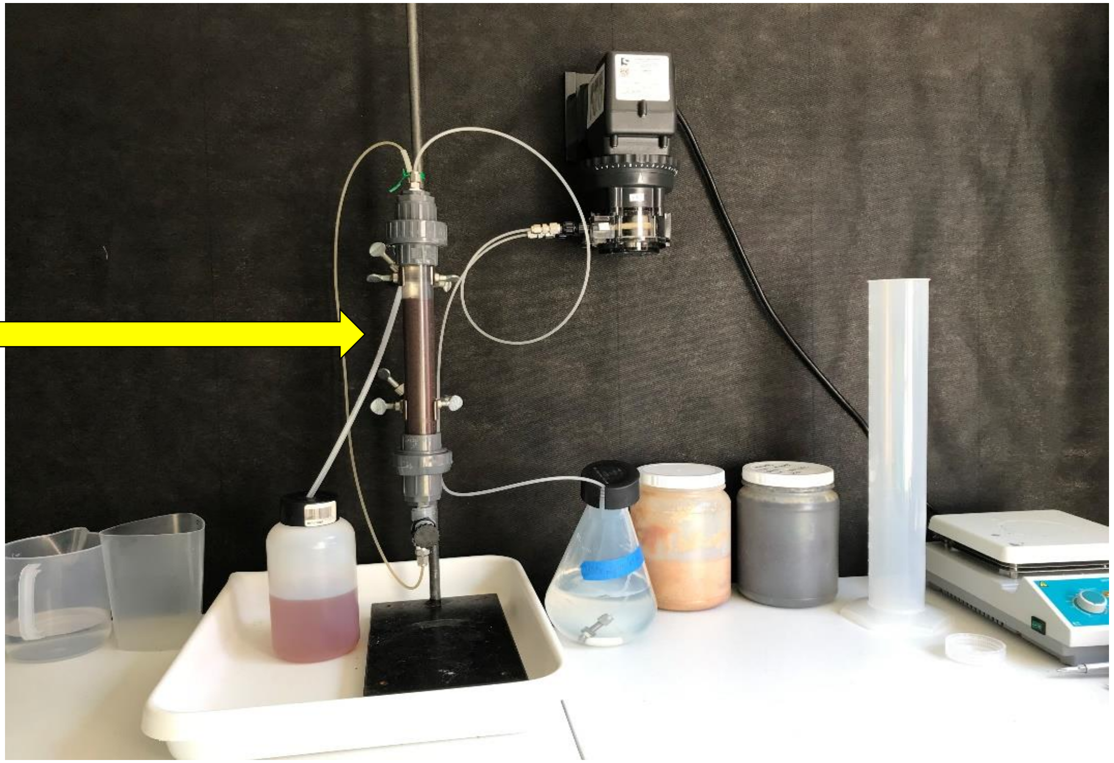
Regeneration

- Screen regeneration solutions

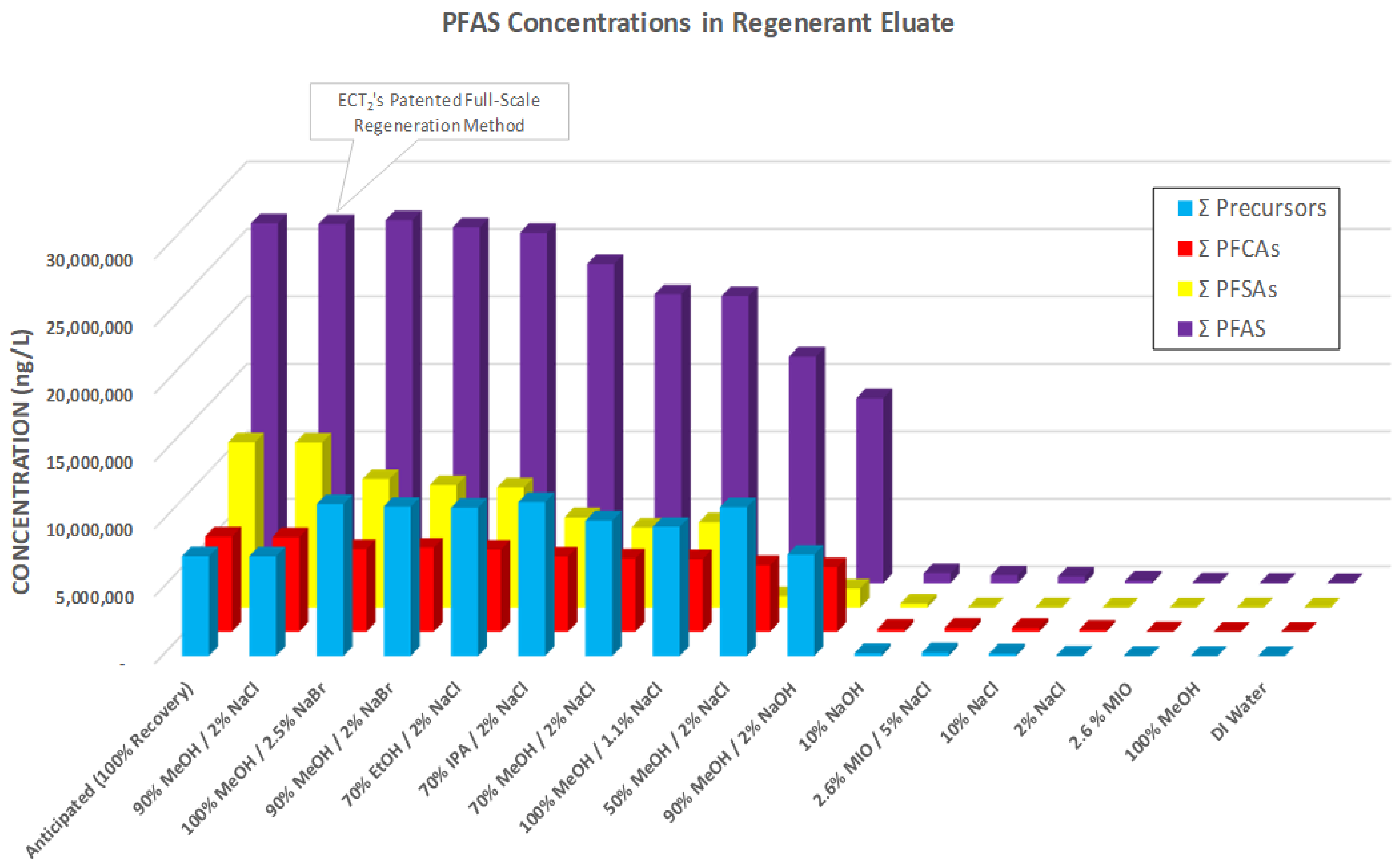


Regeneration

100 mL resin

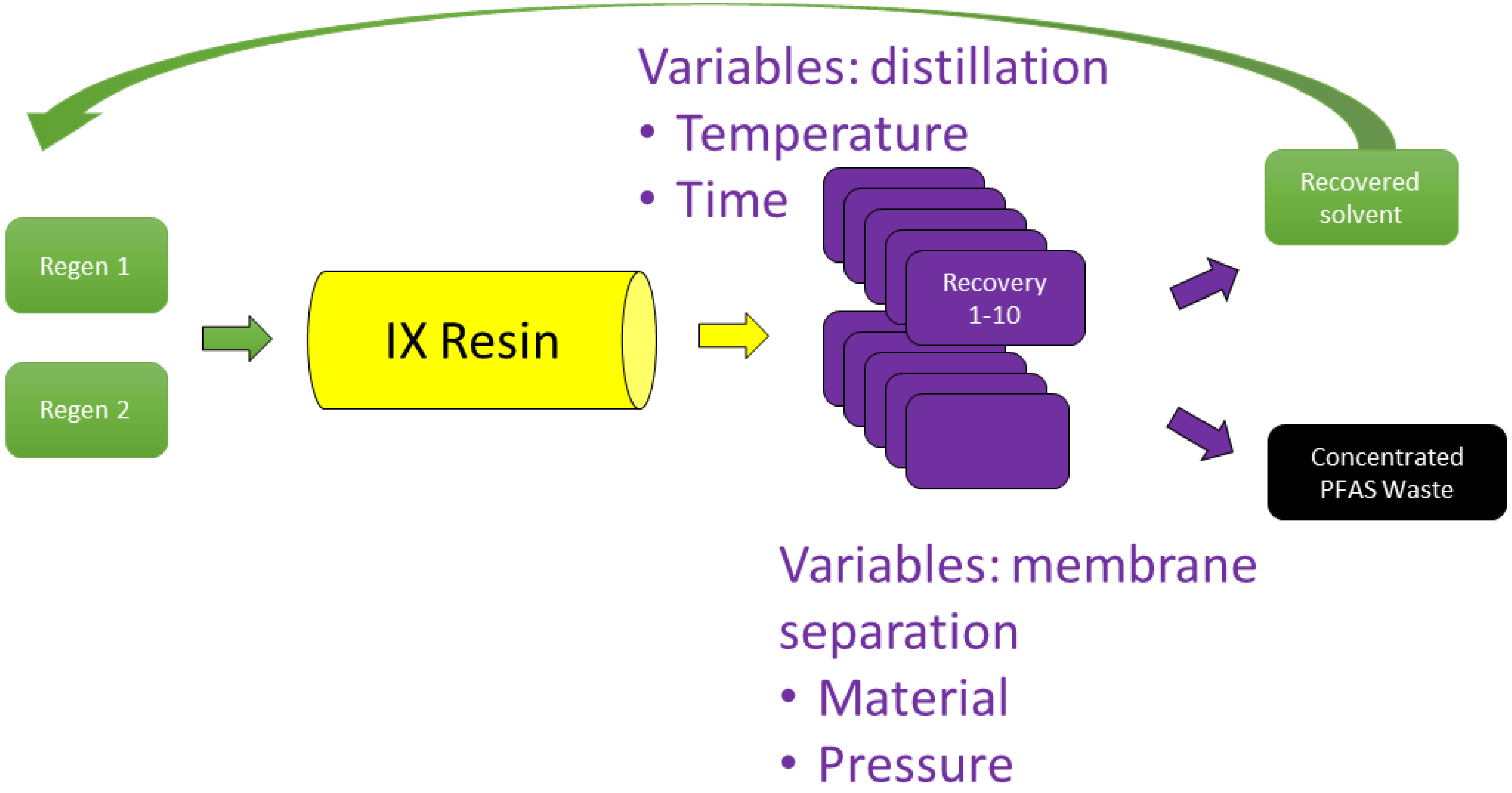


10 Bed volumes (BVs) regen solution @ 2 BVs per hour

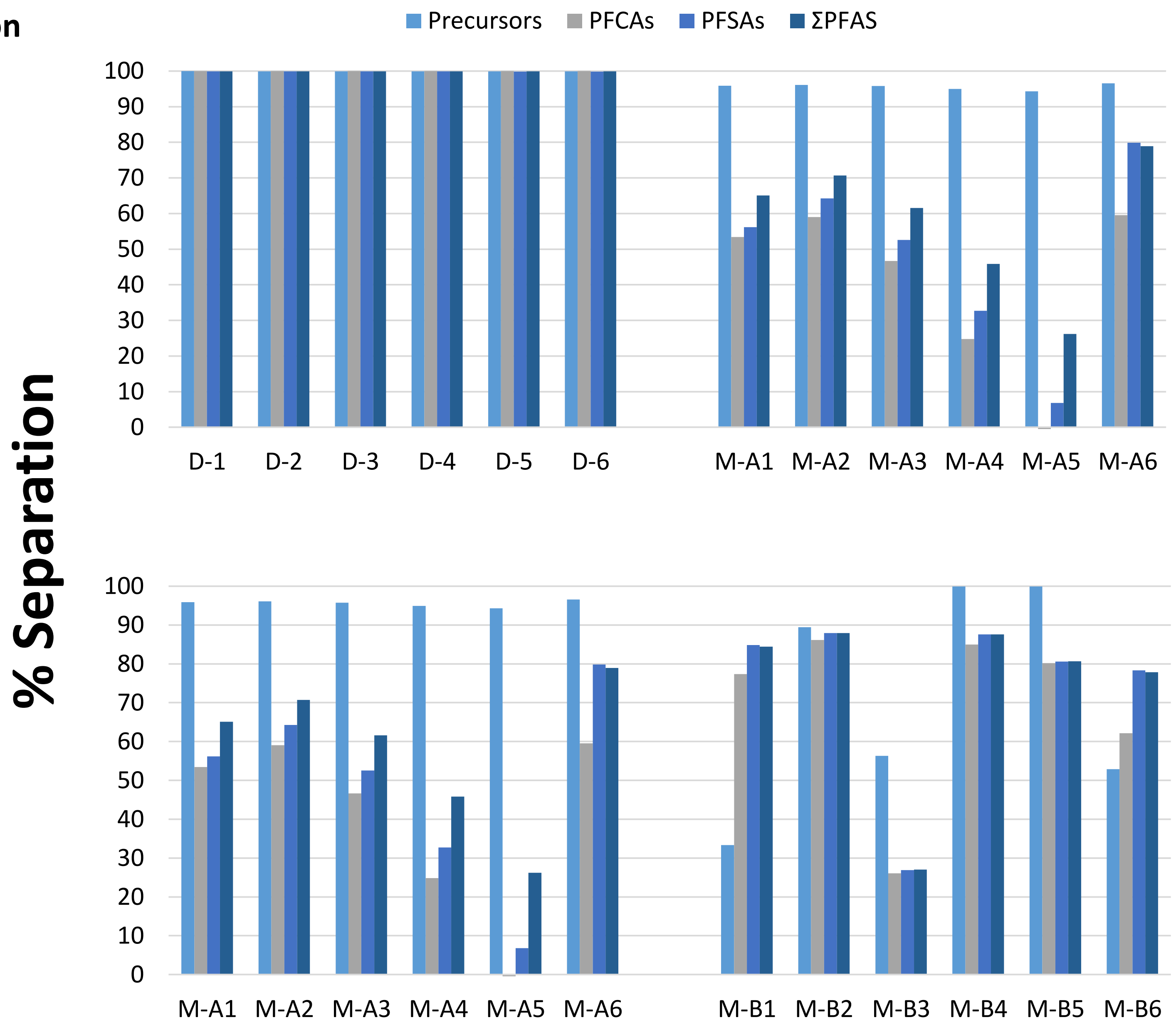

PFAS Concentrations in Regenerant Eluate
ECT2's Patented Full-Scale Regeneration Method
CONCENTRATION (ng/L)
30,000,000
25,000,000
20,000,000
15,000,000
10,000,000
5,000,000
-
Σ Precursors
Σ PFCAs
Σ PFSAs
Σ PFAS
Anticipated (100% Recovery)
90% MeOH / 2% NaCl
100% MeOH / 2.5% NaBr
90% MeOH / 2% NaBr
70% EtOH / 2% NaCl
70% IPA / 2% NaCl
70% MeOH / 2% NaCl
100% MeOH / 1.1% NaCl
50% MeOH / 2% NaCl
90% MeOH / 2% NaOH
10% NaOH
2.6% MIO / 5% NaCl
10% NaCl
2% NaCl
2.6 % MIO
100% MeOH
DI Water

Regenerant Solution Recovery

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

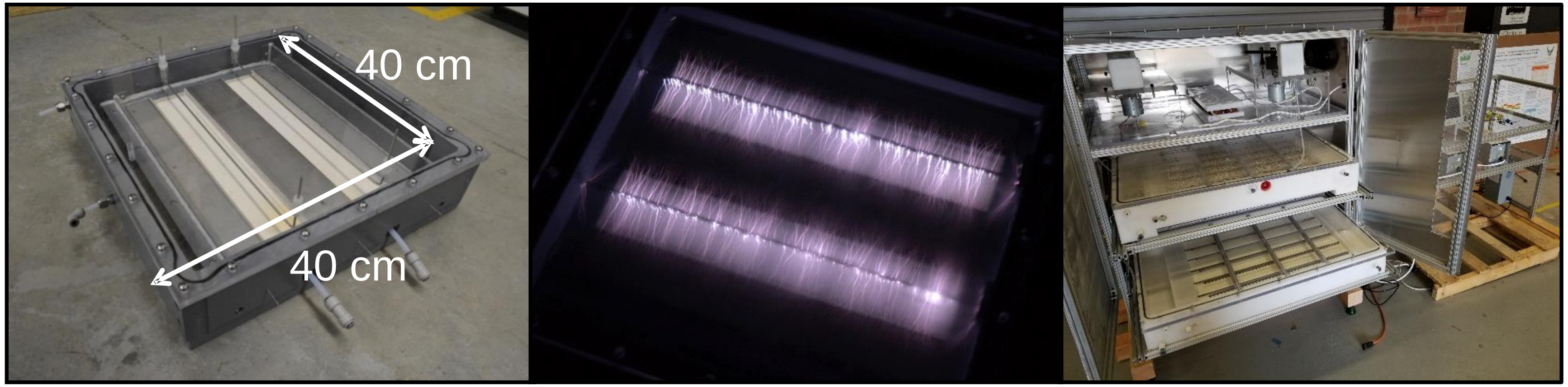


D = Distillation
M = Membrane Separation
A = Site A; B = Site B



Plasma Destruction

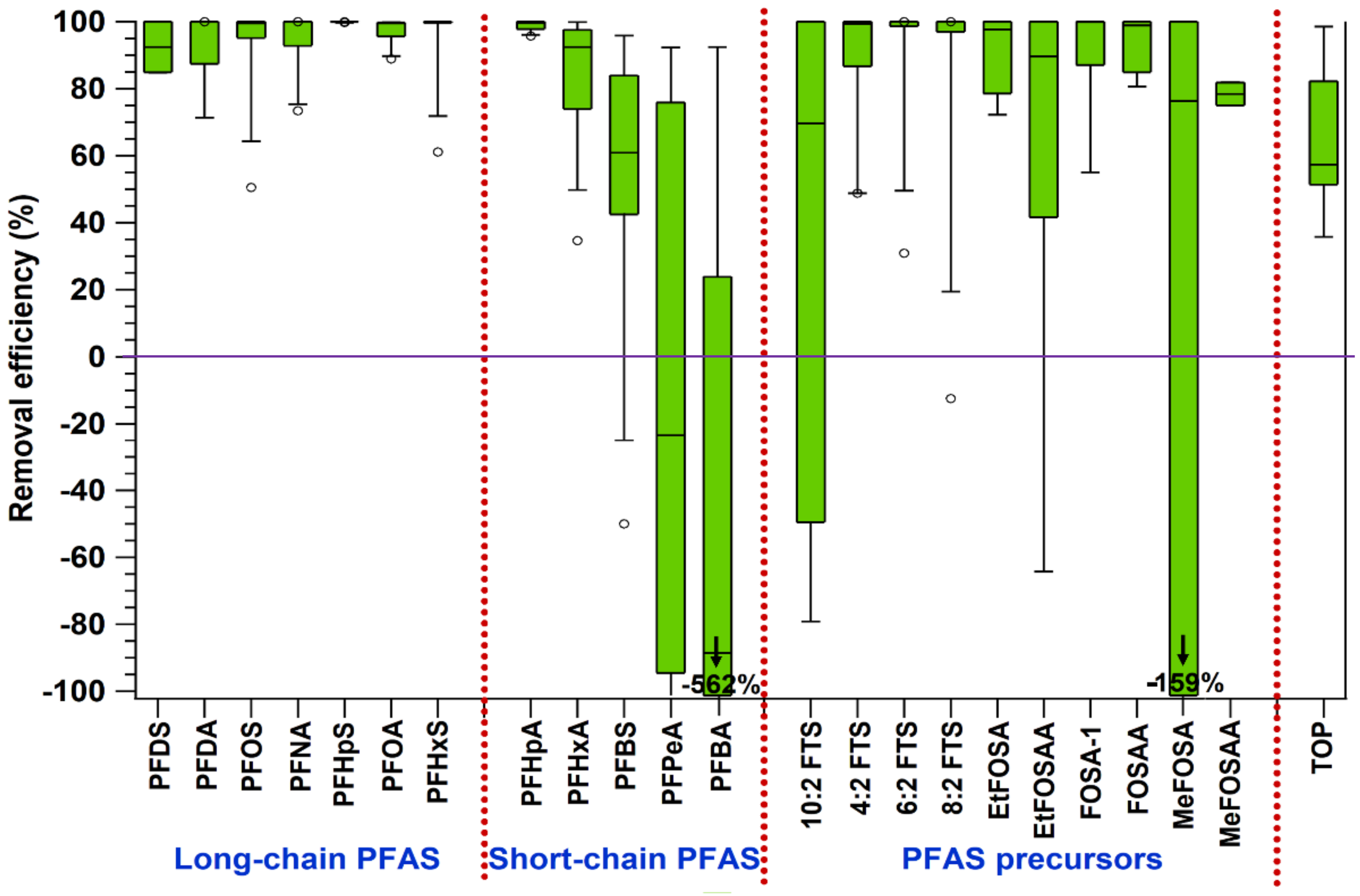
- Uses electricity to convert water into mixture of highly reactive species
  - OH•, O, H•, HO_2•, O_2•⁻, H_2, O_2, H_2O_2 and aqueous electrons (e^-_{aq})



Plasma: Groundwater

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)	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: Groundwater

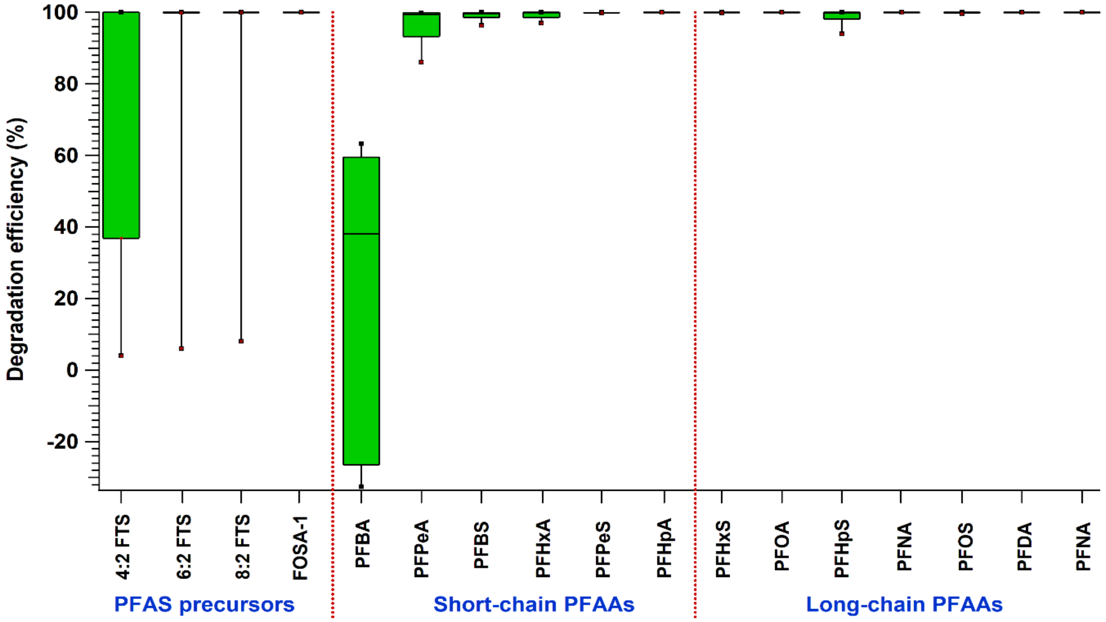


Treatment time = 5 - 60 min; 4L reactor

Plasma: Concentrated IX Distillate

“High-concentration” plasma reactor results

PFAS degradation efficiency in six SBs

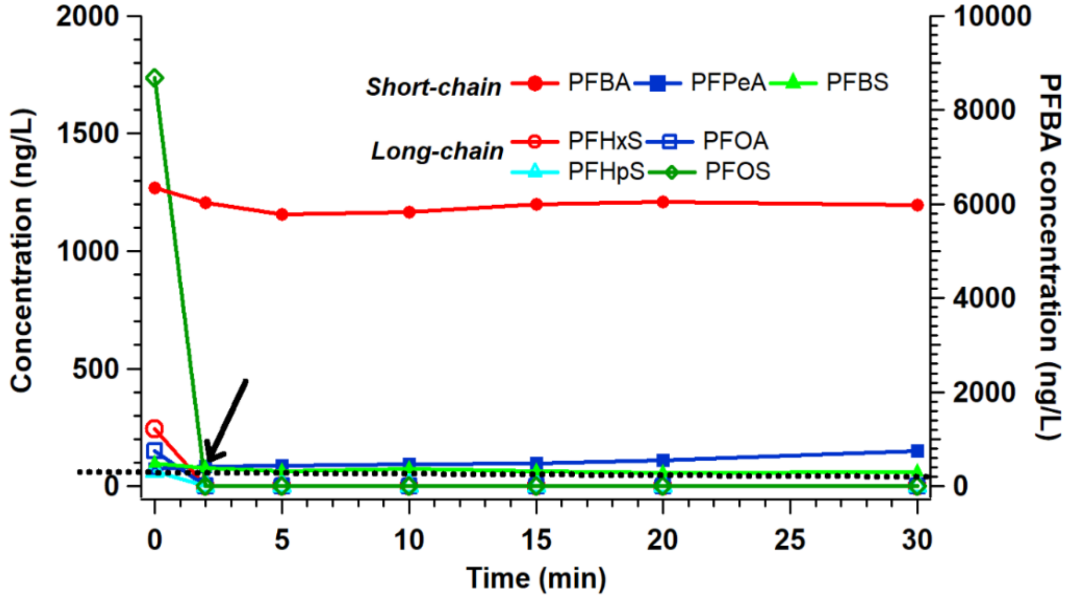


Total oxidizable precursors (TOP) removal

	TOP Initial (mg/L)	TOP final (mg/L)	TOP removal (%)
HC1A	3870	2	99.95
HC1B	9260	34	99.63
HC1C	6870	13	99.81
A3FA	4380	10	99.77
A3FB	6360	11	99.83
A3FC	9440	15	99.84

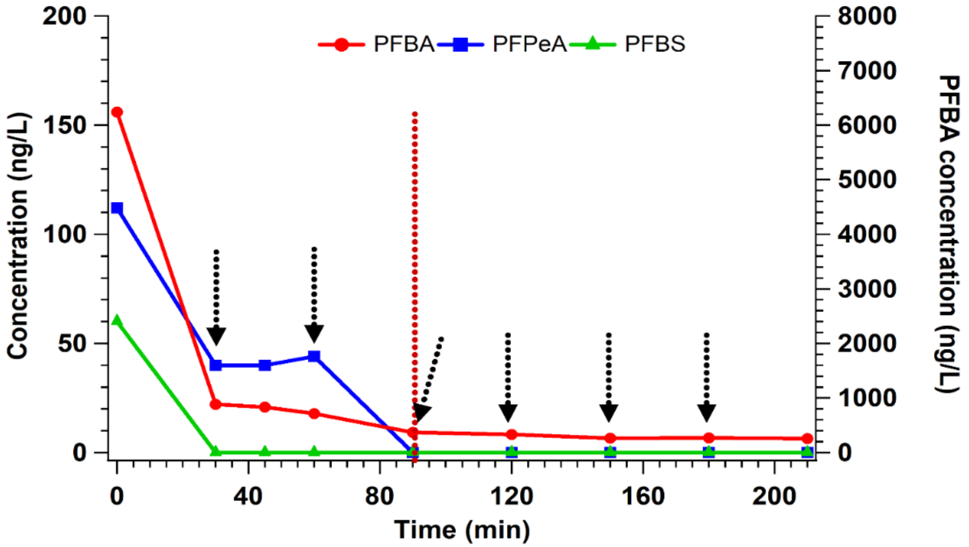
Plasma: IX Distillate

"Low-concentration" plasma reactor results



All the long-chain PFAAs were removed to BDL

Short-chain degradation by addition (0.2 mM) of CTAB (cationic surfactant)



All the short-chain PFAAs (except PFBA) were removed to BDL by the addition of CTAB

Field Demonstration

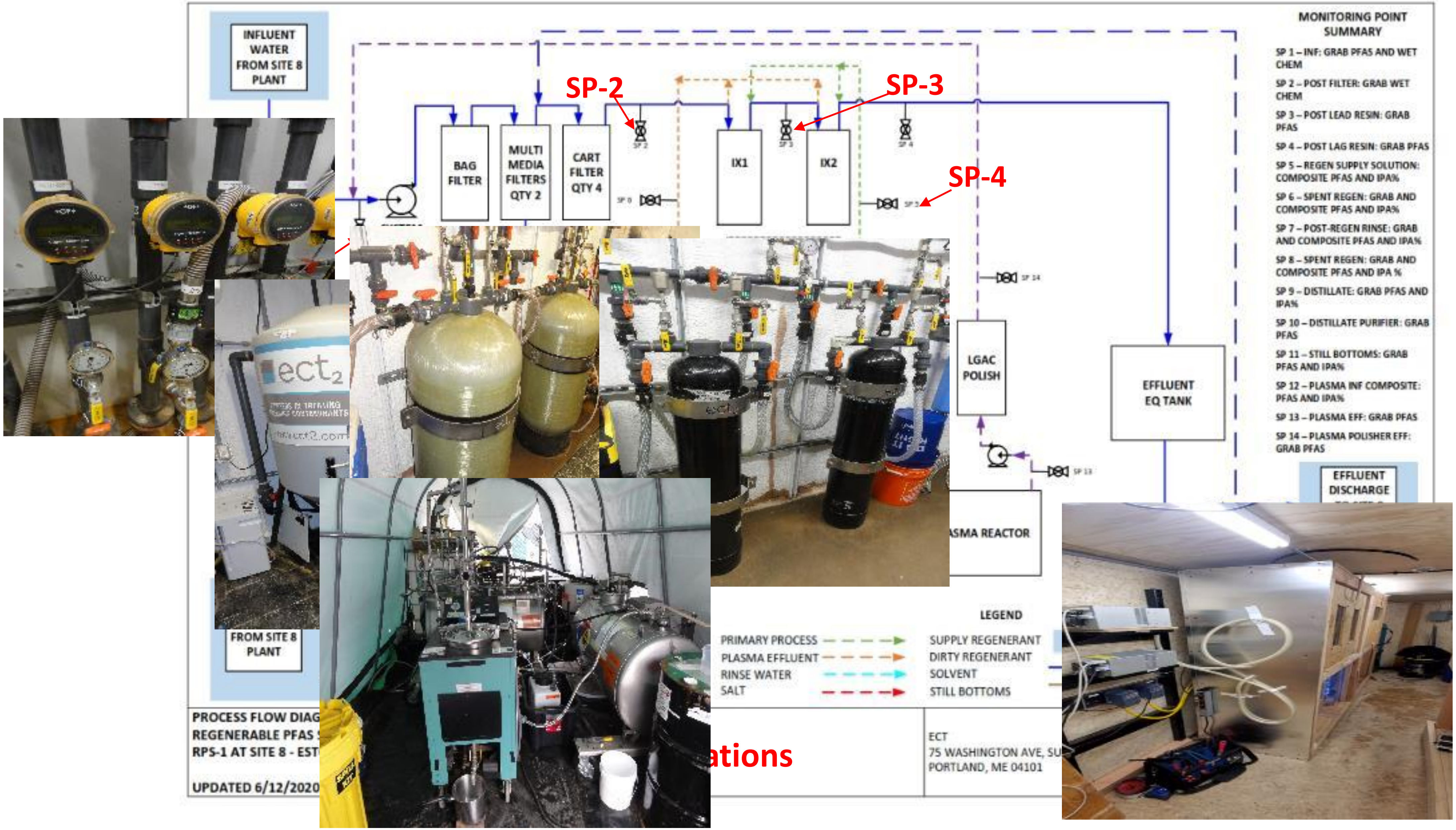
- Former Pease AFB in Portsmouth, NH
  - Contaminated public and private water supply wells – high priority site
  - [PFAS] > 10 μg/L + co-contaminants
- High-level objectives to refine the regenerable IX treatment train
  1. Determine performance characteristics during subsequent IX loading and regeneration cycles
  2. Refine regeneration and distillation process requirements
  3. Optimize plasma system configuration and destruction efficiency

Pilot Test Design

- Pilot Testing for Proof of Concept
  - Isolated EW-6028 at influent manifold
  - Equalization tank and pumping system
  - Multimedia and cartridge filters for removal of iron and solids
  - 2 regenerable HC1 IX Columns (Lead/Lag) operated at 2 GPM
  - Regeneration system using isopropyl alcohol and salt
  - Distillation system for recovery of alcohol and concentration of PFAS compounds (still bottoms)
  - Approx. four weeks to load lead vessel
  - Plasma destruction currently performed at Clarkson University (due to COVID concerns)

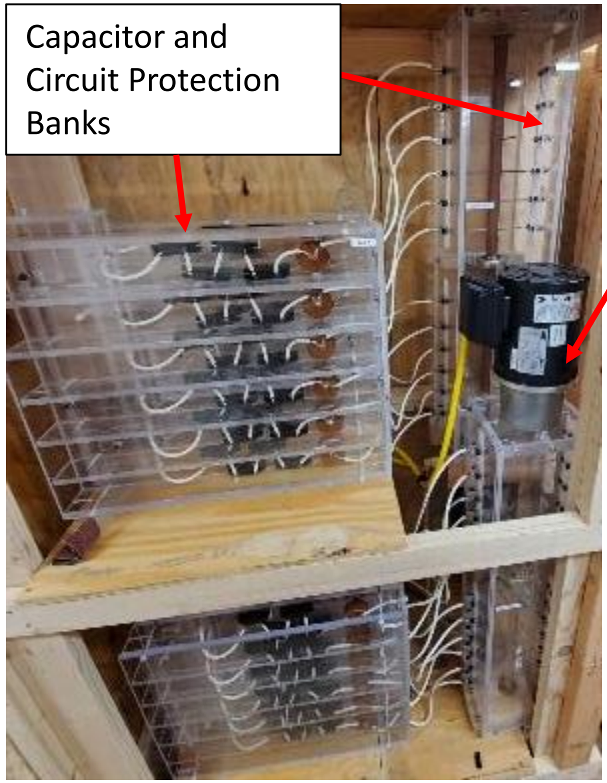
EW-6028

Pilot Study Process Flow Diagram



Plasma Reactor Configuration Detail

Capacitor and Circuit Protection Banks

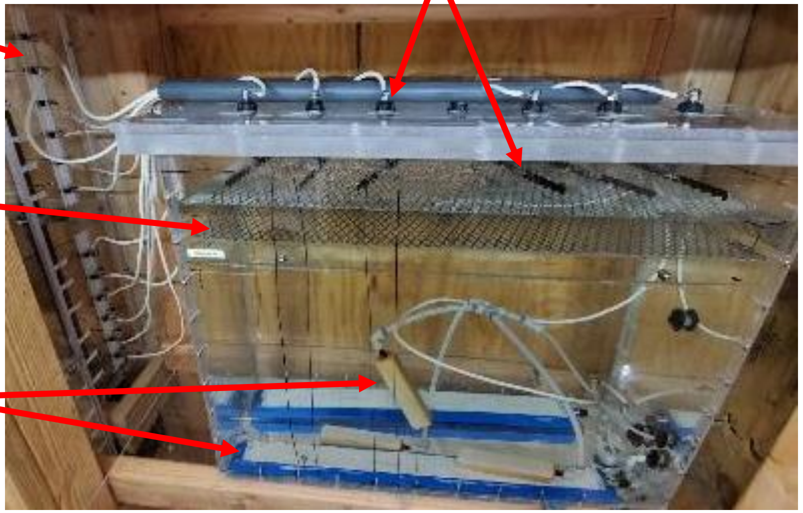


12 Channel Spark Gaps

Electrodes

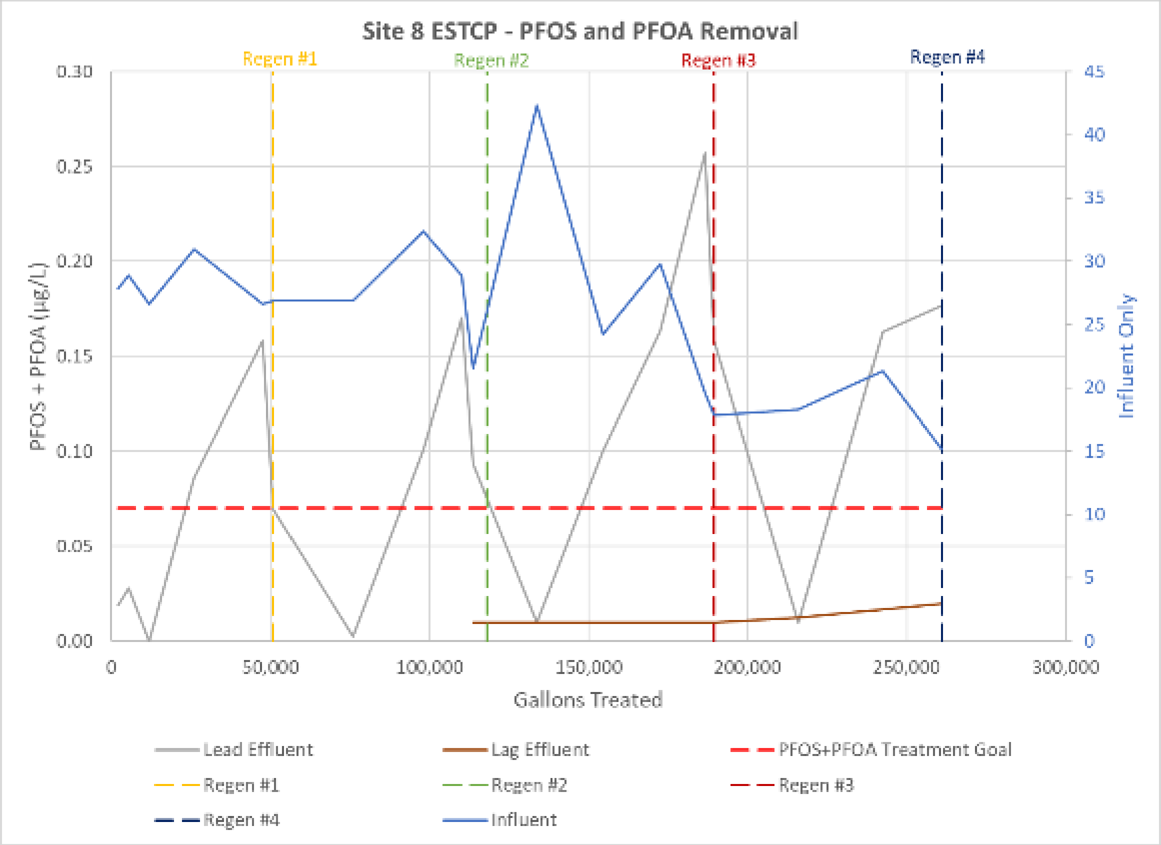
Grounding mesh

Macro and micro diffusers sets



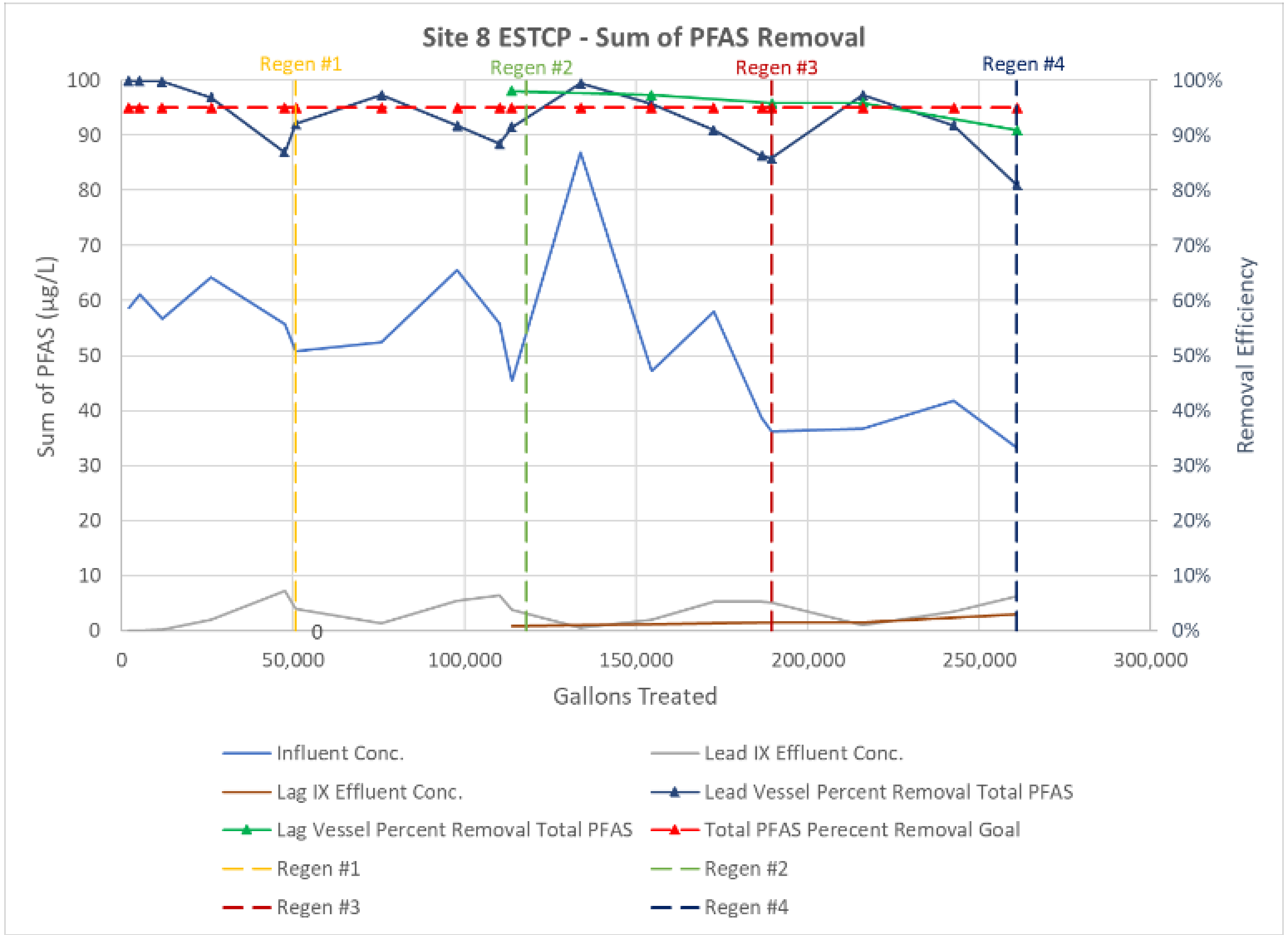
35-gallon reactors

Performance Assessment – IX Resin: PFOS and PFOA Removal



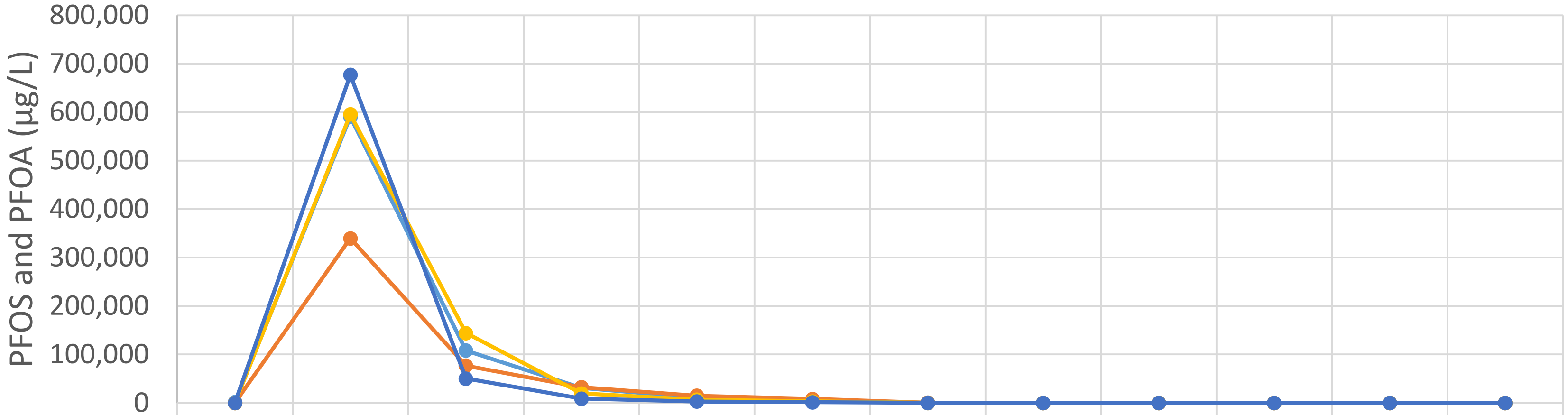
- Data available up through completion of regen #4
- HC1 lead vessel producing consistent treatment between regeneration cycles
- Similar breakthrough curves running both more ~2,000 bed volumes treated (loading cycles 2, 3, and 4) and higher PFOS and PFOA influent concentration (loading cycle 3)
- **Lag vessel has remained below PFOS and PFOA treatment goals through test to date**

Performance Assessment – IX Resin: Sum of PFAS Removal



Performance Assessment – Regeneration

Site 8 ESTCP - Regeneration Performance Cruves

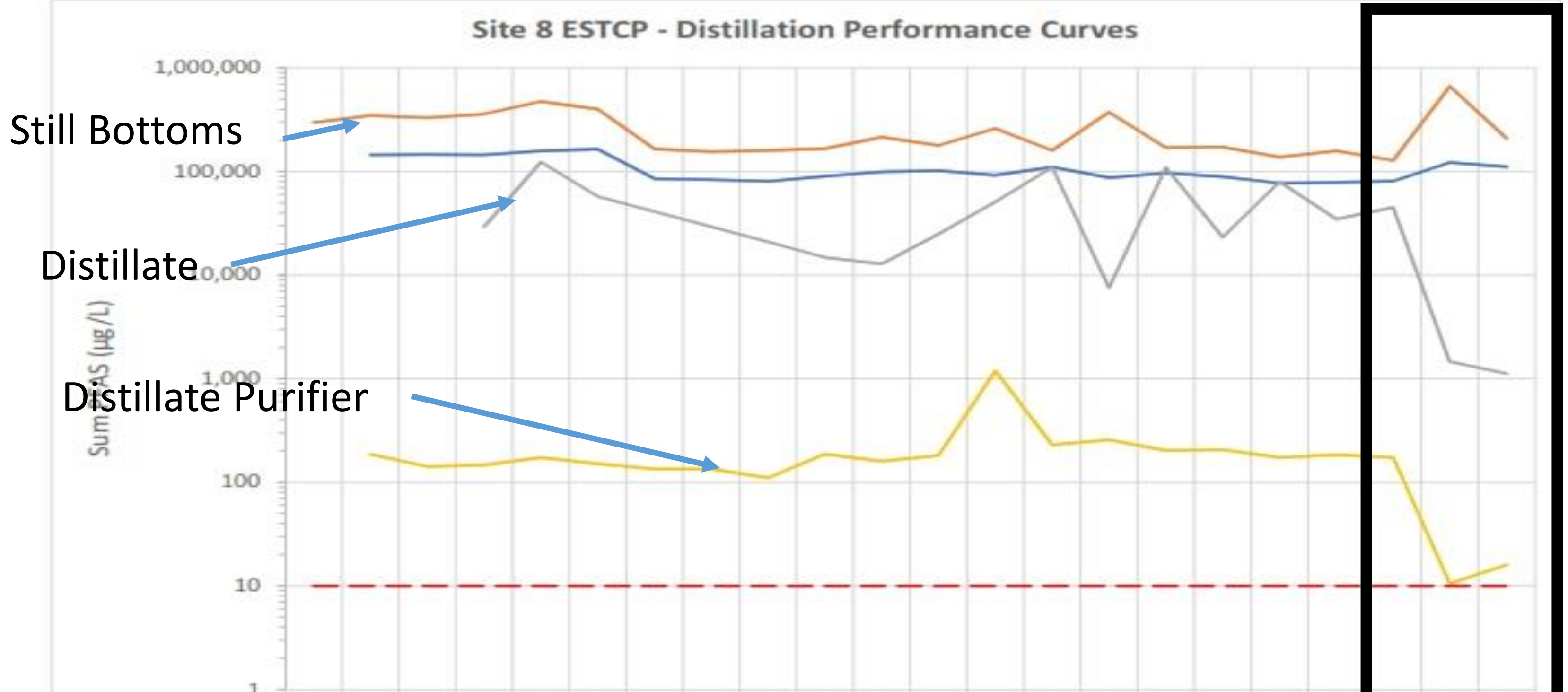


	Regen Supply	Regen BV1	Regen BV2	Regen BV3	Regen BV4	Regen BV5	Rinse BV1	Rinse BV2	Rinse BV5	Rinse BV10	Rinse BV15	Rinse BV20
Regen 1	1,930	590,516	108,003	31,069	10,830	6,792	298	117	94	93	106	106
Regen 2	121	339,659	76,843	32,452	14,762	8,099	237	162	113	106	112	112
Regen 3	138	595,657	144,120	19,545	6,620	3,119	20	15	9	4	2	1
Regen 4	12	677,122	50,191	8,965	2,844	1,288	2	1	1	0	1	0

Regen 1 Regen 2 Regen 3 Regen 4

- Data available up through completion of regen #4
- Similar removal of PFAS from the regenerated vessel, with most of the removal occurring in the first and second bed volumes
- Regeneration #2 impacted by combination of lower IPA solution makeup (estimated at 65% vs. 70% target) and difficulty mixing IPA solution up to 2% salt by weight. Vessel still performed well in loading cycle 3

Performance Assessment – Distillation



	C1B1	C1B2	C1B3	C1B4	C1B5	C1B6	C2B1	C2B2	C2B3	C2B4	C2B5	C2B6	C2B7	C2B8	C2B9	C2B10	C2B11	C2B12	C2B13	C2B14	C3B3	C3B10
Distiller Feed		144,48	146,15	144,92	158,20	164,13	85,357	83,225	80,474	89,836	99,114	101,99	91,905	110,47	87,100	96,771	89,217	77,099	78,490	80,928	121,95	110,90
Still Bottoms	297,14	347,99	329,98	358,47	474,58	400,43	164,56	155,51	159,81	166,27	214,46	178,65	260,94	159,70	374,28	170,17	172,27	138,13	158,16	127,80	664,36	208,34
Distillate				29,355	123,78	57,553			20,965	14,787	12,817	24,962	50,889	110,21	7,551	109,57	23,149	79,804	34,773	45,150	1,462	1,120
Distillate Purifier		186	142	147	173	151	134	134	110	187	160	181	1,192	230	258	203	207	174	184	[illegible]	[illegible]	[illegible]
Dist. Pur. Goal	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

- Data available up through start of distillation cycle #3
- Distillation cycles #1 and #2 successfully produced concentrated still bottoms. However, the distiller unit's construction caused it to foam over and carry PFAS over in the distillate. PFAS concentrations in the distillate were too high to be treated by the distillate purifier.
- Before starting cycle #3, we installed a distillation column on top of the distiller and replaced the distillate purifier resin. The first two samples results from cycle #3 show increased still bottoms concentration and decreased distillate concentrations, indicating the distiller unit modifications are working and the improved performance of the distillate purifier.

Distillation Performance Modifications

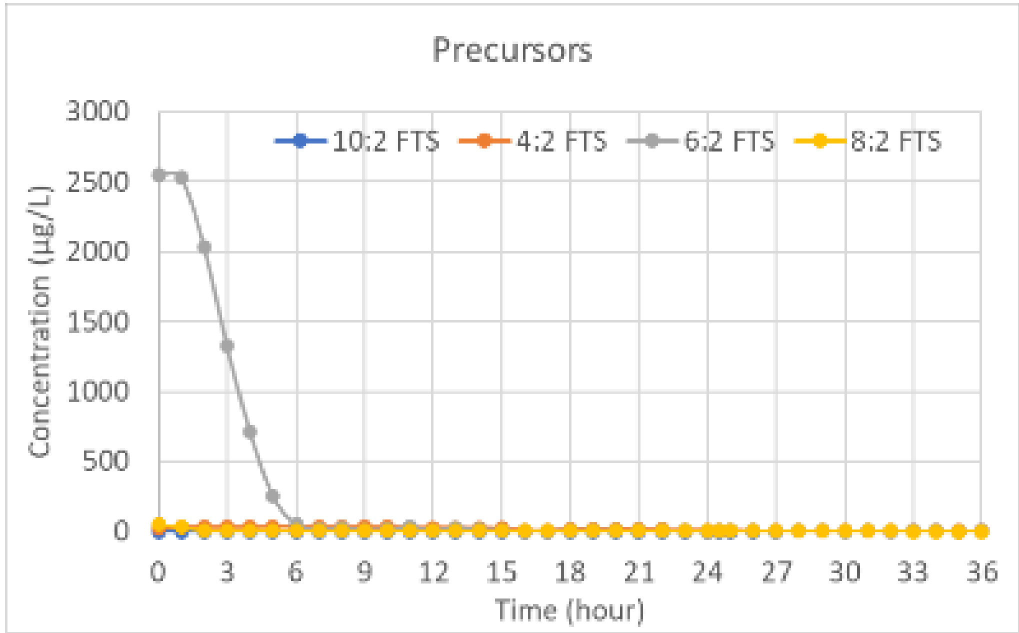
Before – original configuration

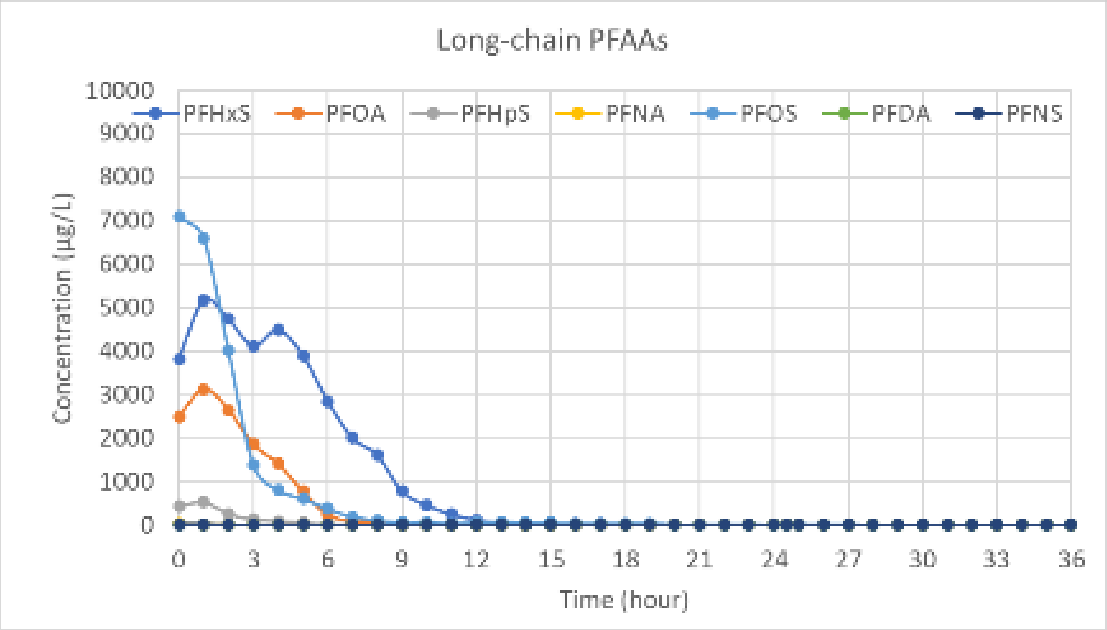
After – with new column

Performance Assessment – Plasma Treatment

- Two regen cycles of still bottoms sent to Clarkson (remaining will be treated on site)
  - Cycle 1
    - 7 gallons treated in 2 batches
  - Cycle 2
    - 14 gallons treated in 3 batches (results pending for third)
- Two reactors in sequence: high concentration (18 hr) → low concentration
- CTAB = 0.2 mM

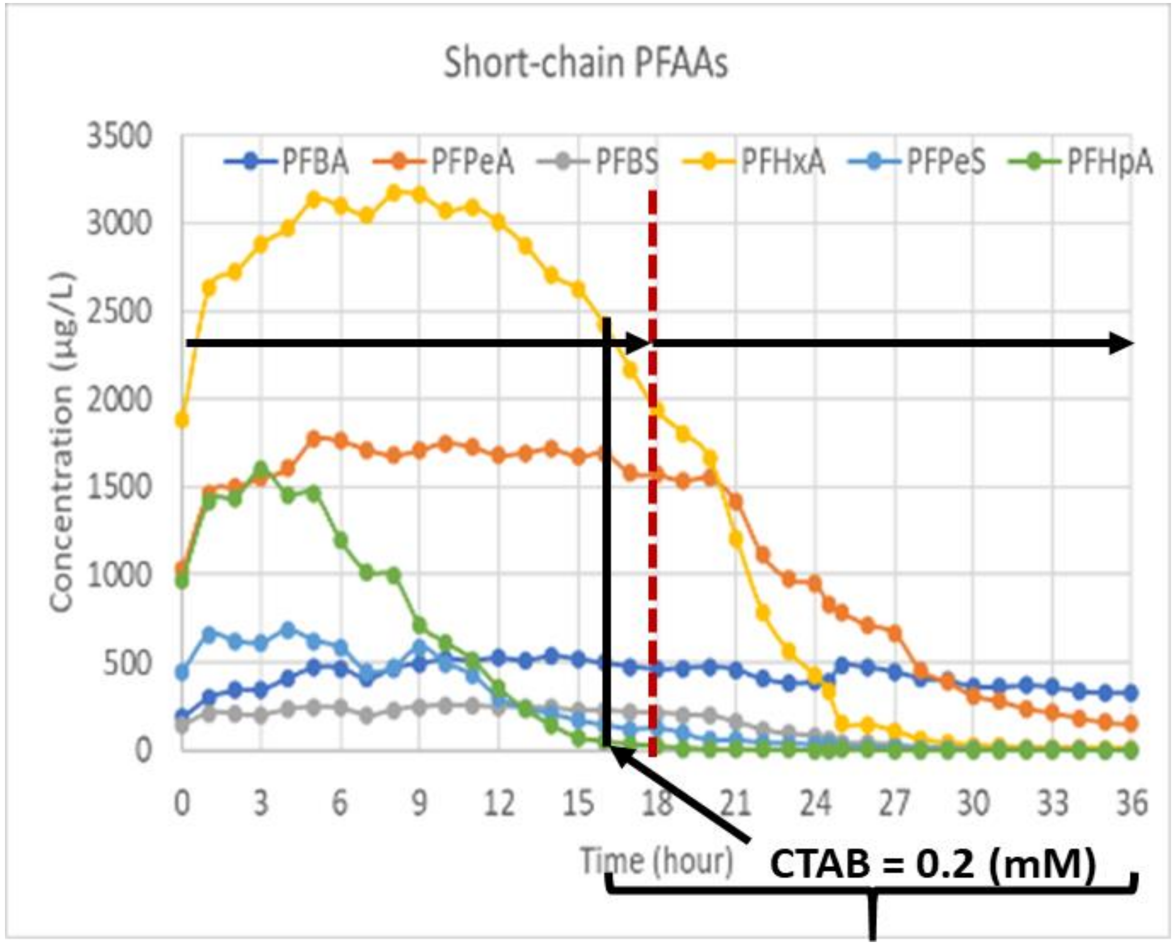
Performance Assessment – Plasma Treatment





Performance Assessment – Plasma Treatment

- PFHpA (C7) and PFPeS (C5) were removed by 99 and 65%, respectively, without CTAB within 16 hours
- Other short-chain PFAAs were not removed without CTAB
- Short-chain PFAAs degradation improved to 99% in the presence of CTAB, except PFBA and PFPeA, after 36 hours of treatment
- PFPeA and PFBA were removed by 85 and 40%, respectively
- Presence of CTAB increases the removal of short-chain PFAAs



Conclusions

- Persulfate and oxygen pretreatment accelerate precursor transformation
  - Products of persulfate oxidation are more mobile/extractable than their precursors
- Regeneration of IX resin can be effectively achieved
  - Distillation effective for solvent recovery
- Plasma treatment is effective over a broad range of site and operating conditions
  - Oxidative pretreatment has limited impact on plasma treatment effectiveness
  - Plasma treatment of high concentration distillate is facilitated by use of staged reactors and addition of cationic surfactant