Electrochemical Treatment of Perfluoroalkyl Acid (PFAA) Precursors and PFAAs in Groundwater Impacted with Aqueous Film Forming Foams

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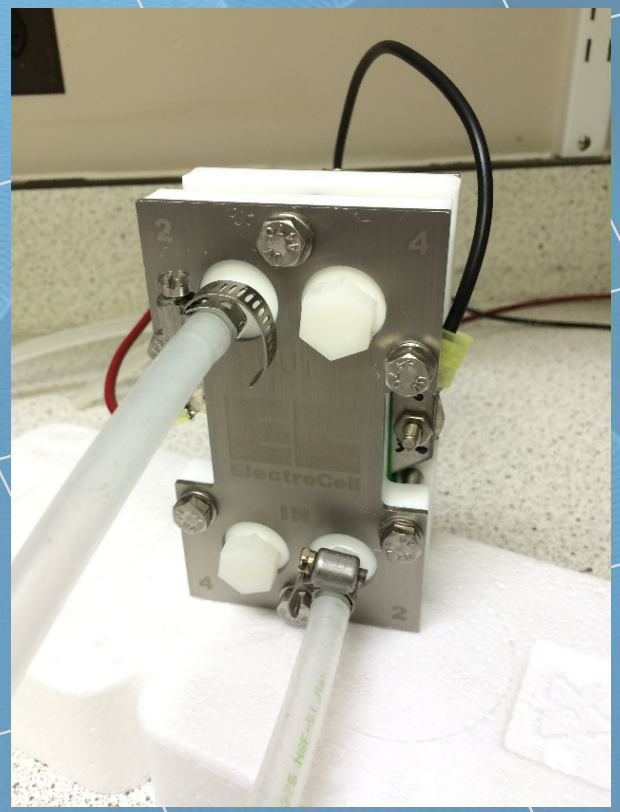
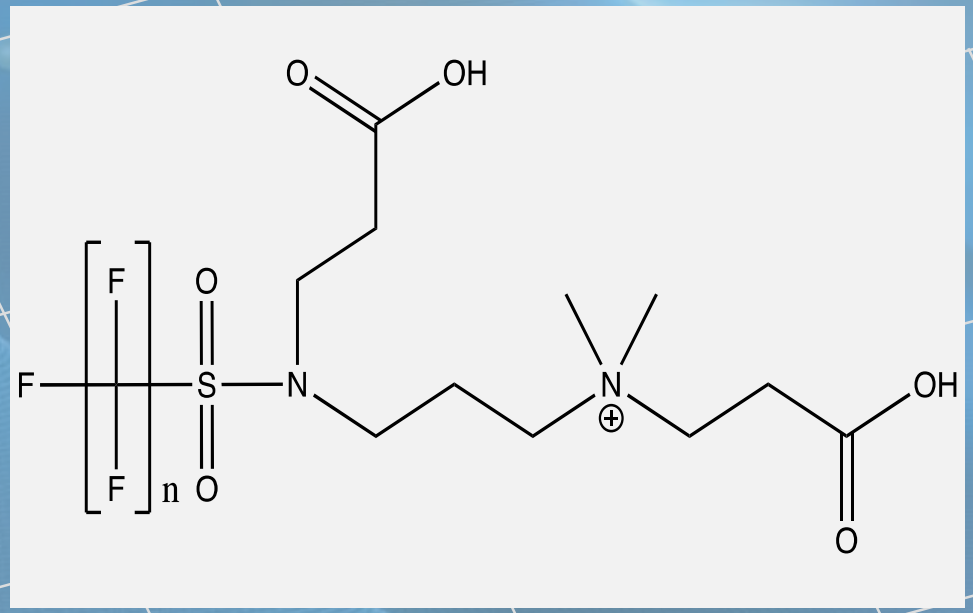




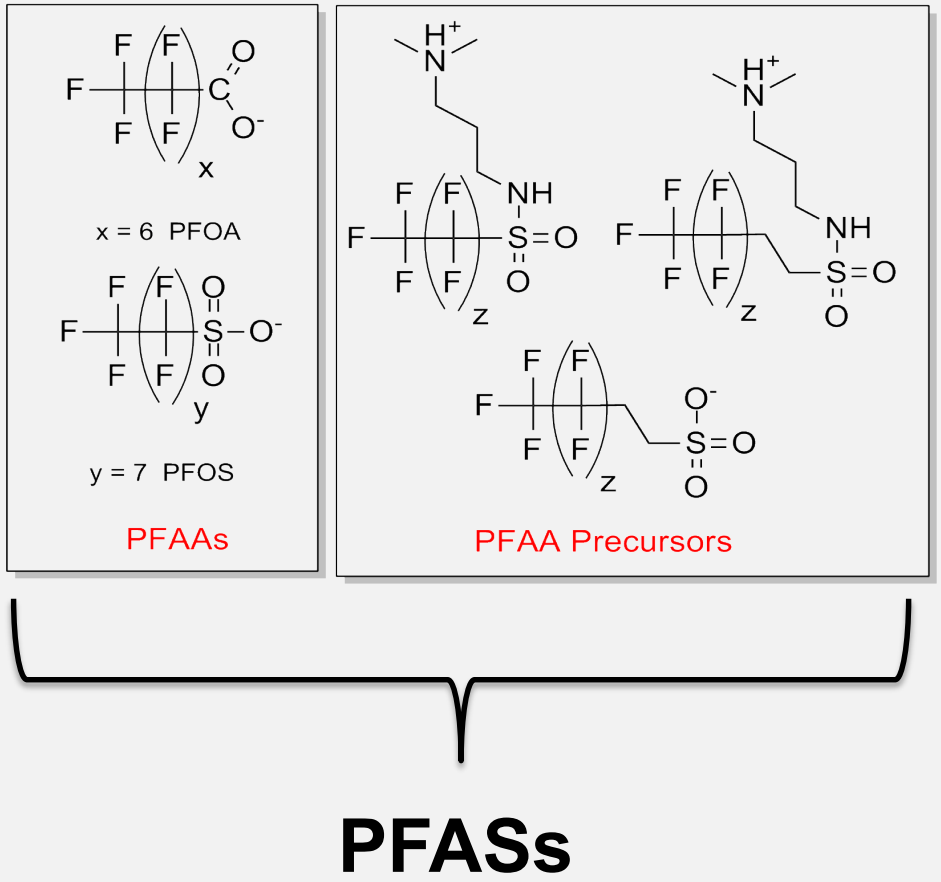
April 17, 2019

Per- and Polyfluoroalkyl Substances (PFASs)

Perfluoroalkyl acids (PFAAs)

Carboxylates

Sulfonates



USEPA Health Advisory

70 ng/L (PFOS+PFOA)

Electrochemical Treatment of PFASs

- **Several studies evaluating EC treatment of PFASs (most for PFAAs)**

- **Several different anode materials**
  - Doped mixed metal oxide
  - Magnéli phase (Ti_4O_7)
  - Boron Doped Diamond

- **Perchlorate generation**
  - Biotic reduction
  - Chloride-free solutions

- **Areas for continued study**
  - Limited studies in real groundwater
  - Treatment for the wide range of PFASs present
  - Electrode longevity with respect to PFAS treatment
  - Energy consumption

PFAA Electrochemical Oxidation Mechanism

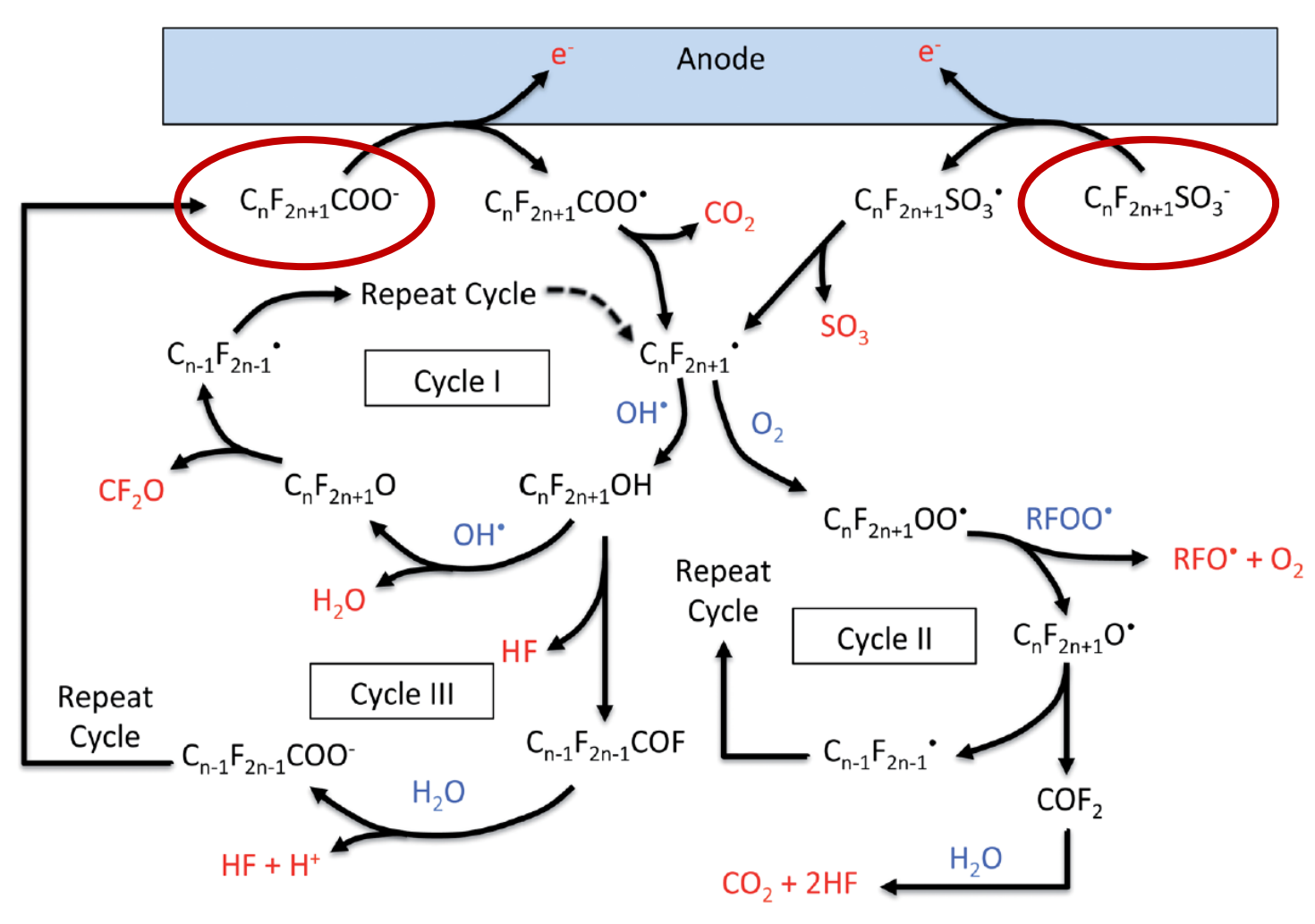
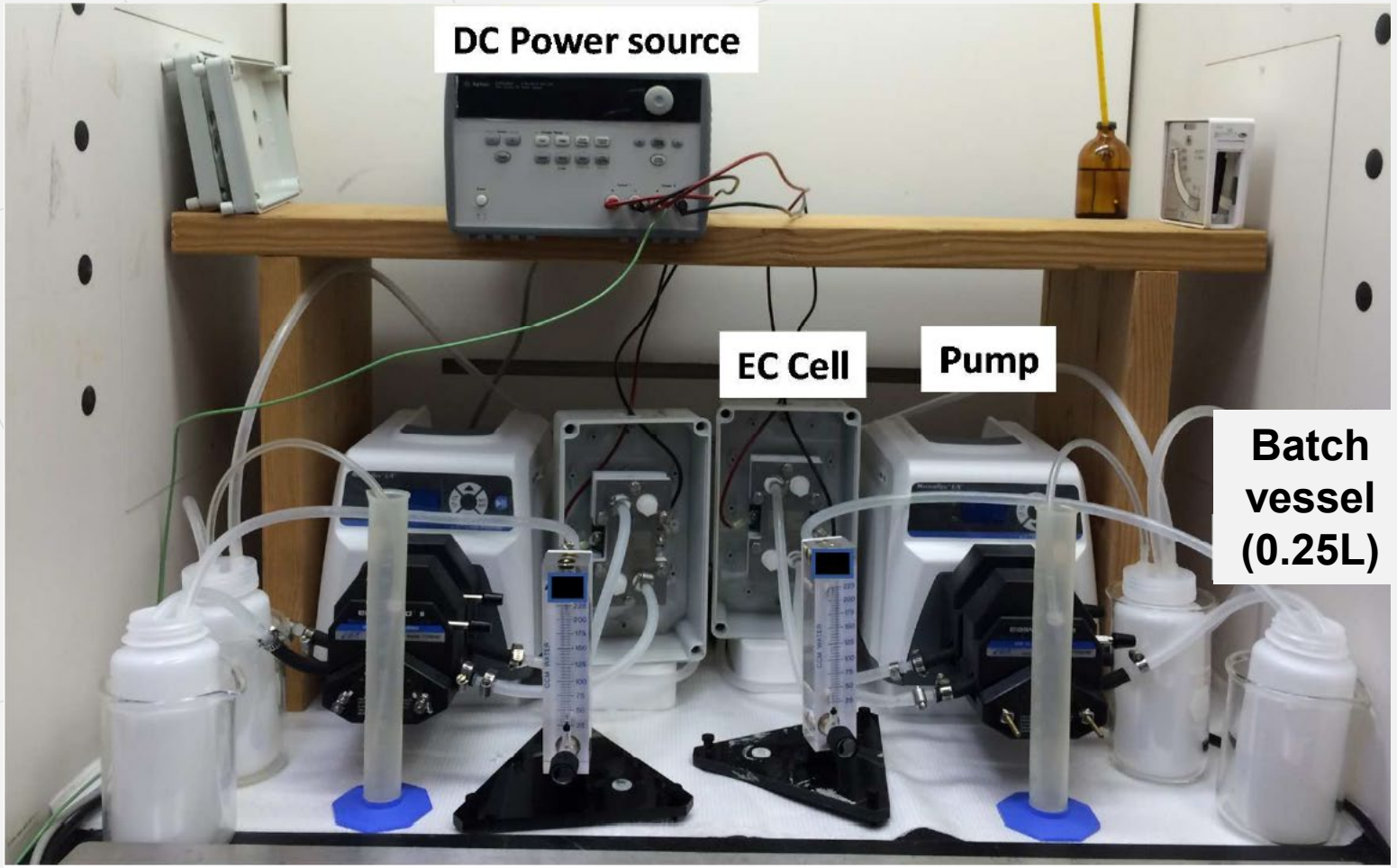


figure from: Chaplin, *Environ. Sci.: Processes*, 2014

- Transformation of both PFOA & PFOS begins with direct electron transfer at anode
- Functional groups removed, forming perfluoro radicals
- Unzipping process yielding shorter chain carboxylates and fluoride *(not always observed)*

Experimental



8 hour batch experiments
25 mA/cm^2 current density

BDD Anode (Condias)

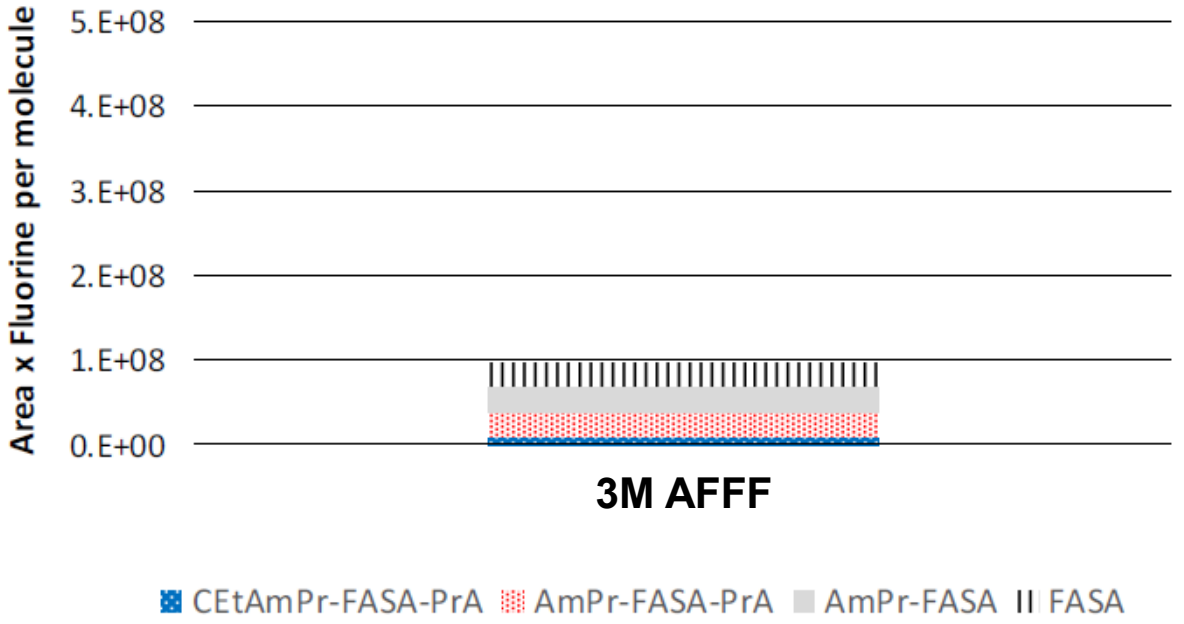
- BDD on Nb
- SS cathode
- 4mm spacing

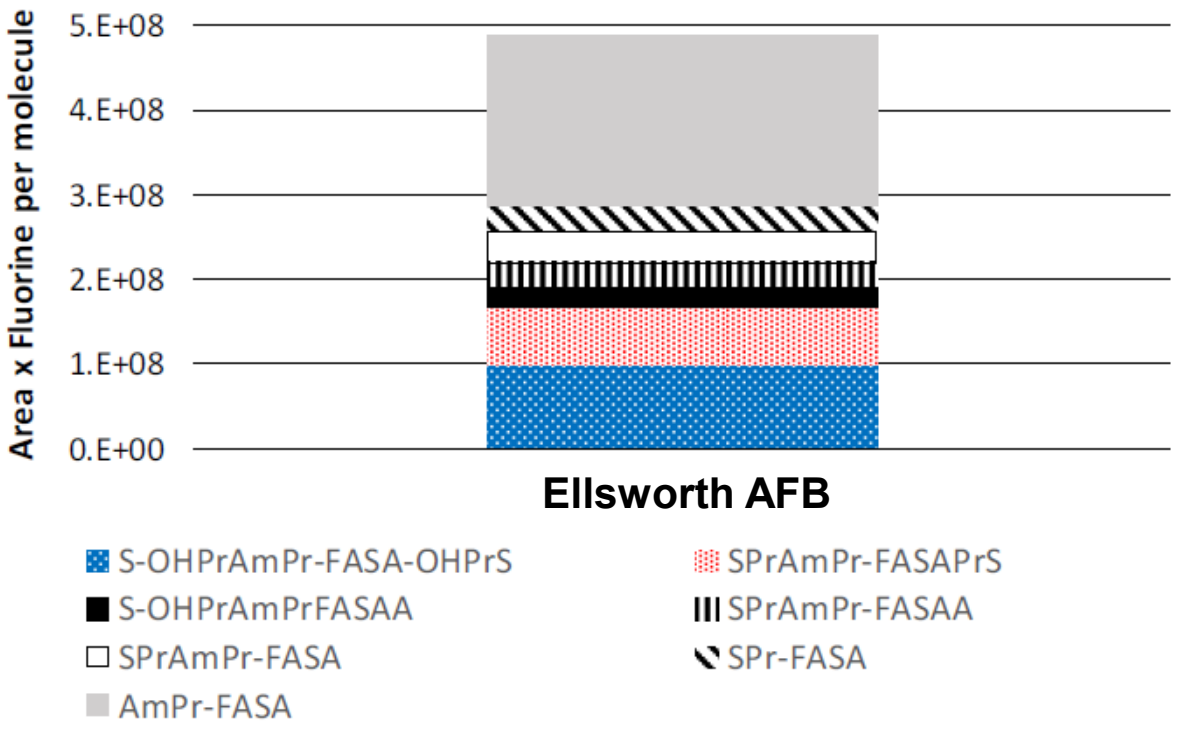
- Natural groundwater (spiked with 3M AFFF)
- AFFF-impacted groundwater (Ellsworth AFB)
- LC-MS/MS and HR-MS
- F mass balance
- Long-term experiment

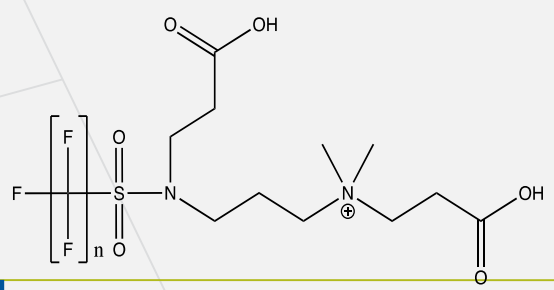
	3M AFFF in GW	Ellsworth AFB GW
Fluoride (mg/L)	<0.2	0.9
Chloride (mg/L)	18	160
Sulfate (mg/L as SO_4)	25	14
Nitrate (mg/L as N)	5.5	<0.2
Total Organic Carbon (mg/L)	11	5.1
Turbidity (NTU)	1.8	6.3
Alkalinity (mg/L $CaCO_3$)	352	890
Conductivity (µmhos/cm)	769	2120
pH	6.7	7.1
Hardness (mg/L $CaCO_3$)	363	1,030

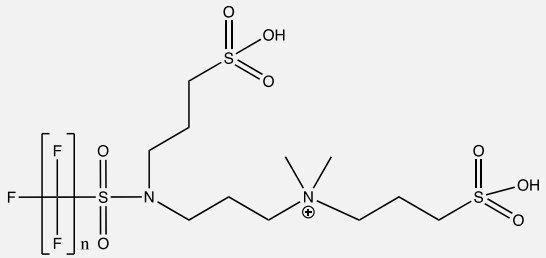
	3M AFFF in GW	Ellsworth AFB GW
PFAAs (µg/L)		
PFBA	<0.074	25
PFPeA	4.0	61
PFHxA	9.0	130
PFHpA	2.6	12
PFOA	15	58
PFBS	33	45
PFHxS	76	160
PFHpS	11	26
PFOS	300	22

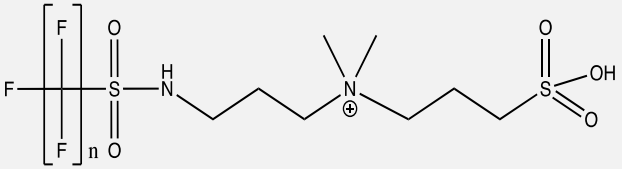
Potential PFAA Precursors











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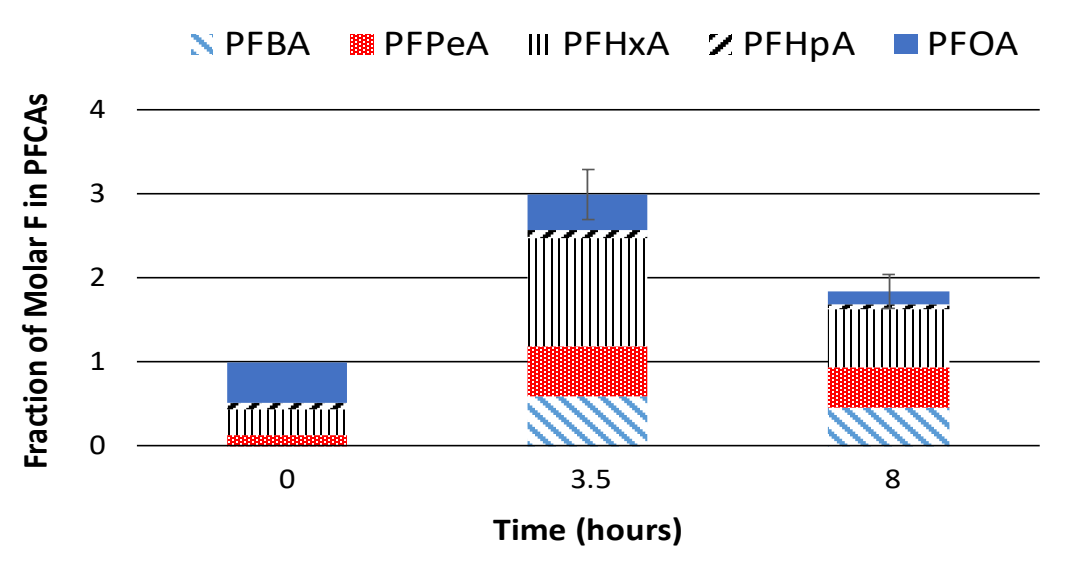
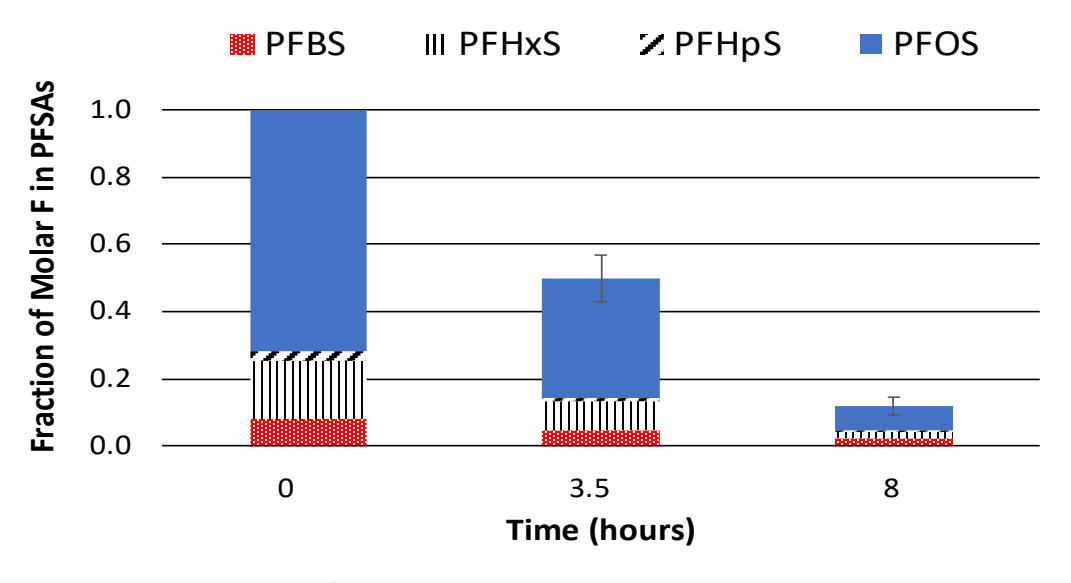
EC Treatment (3M AFFF)



PFCAs show transient increases, but no increases in PFSAs



<u>Total Oxidizable Precursor assay</u>

Showed substantial PFCA generation for untreated 3M AFFF-spiked water

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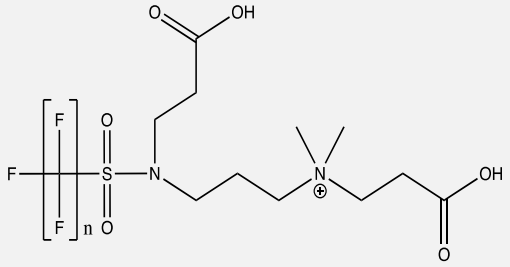
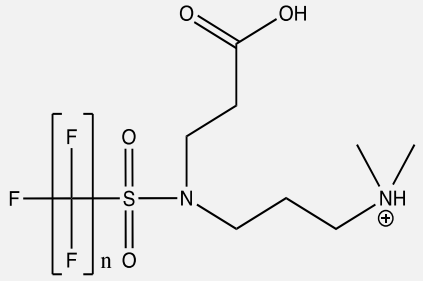
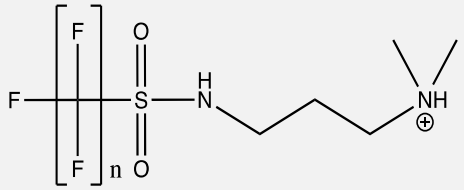
Identified Pre-Cursors in 3M AFFF Spiked Groundwater

HR-MS data: semi-quantitative

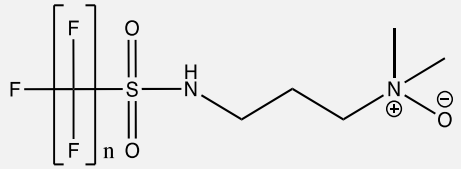
Rapidly Removed

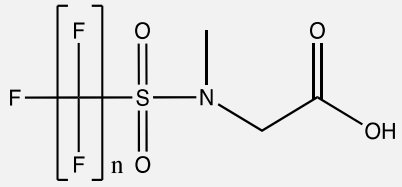


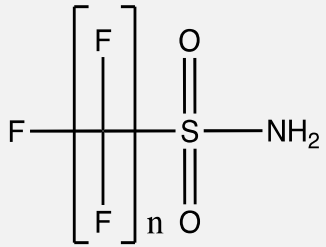


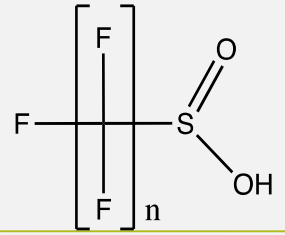


Transient Increase

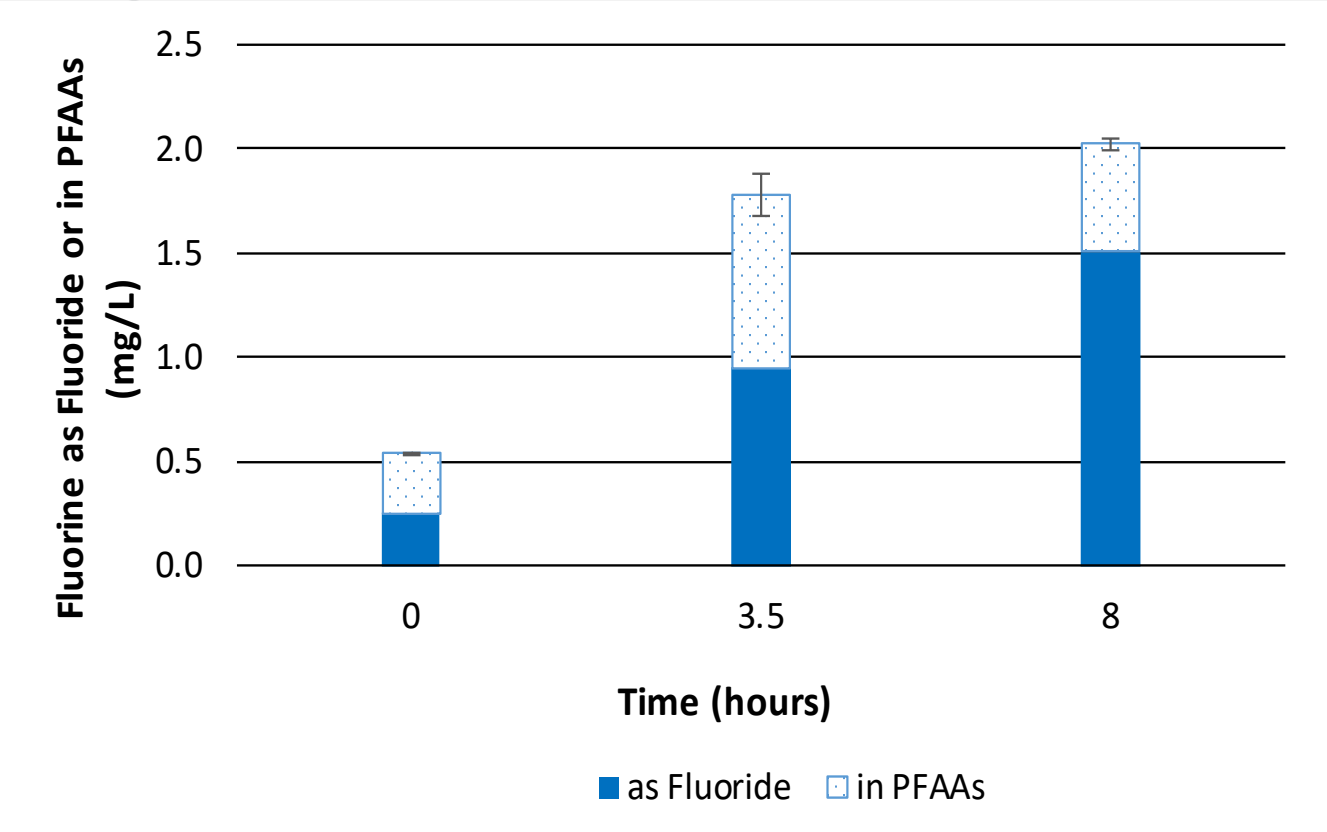








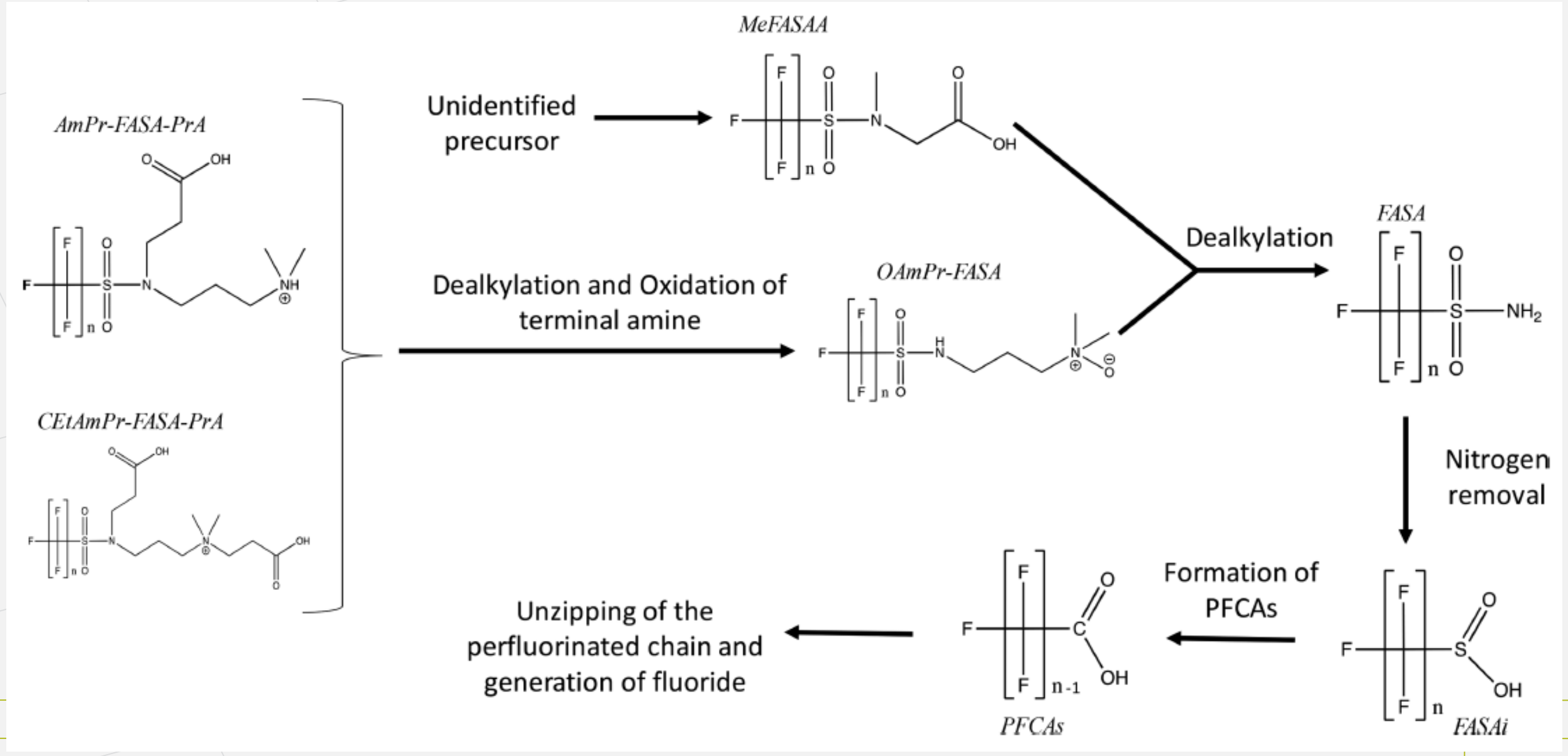
F Mass Balance (3M AFFF)



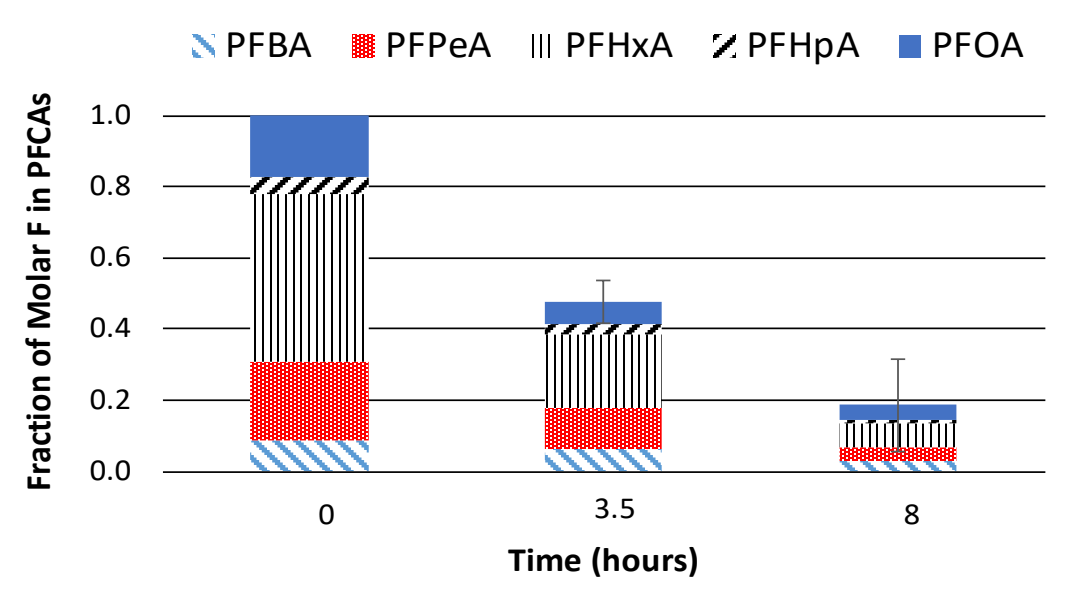
PFAAs in untreated water could only account for about 1/3 of the fluoride generated

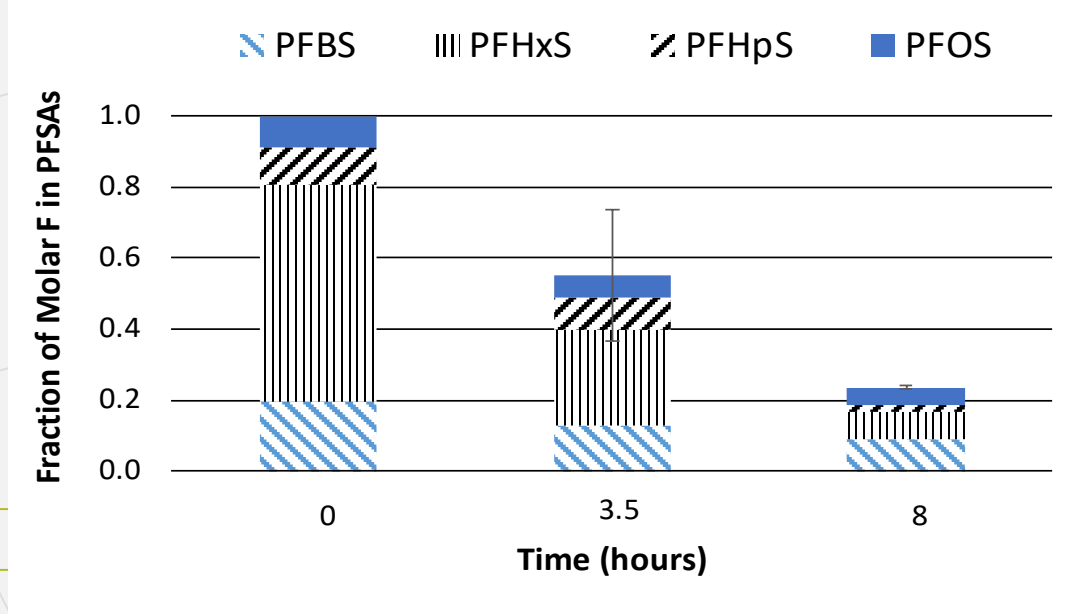
Based on TOP assay, 64% of the F present as PFAS accounted for

Oxidation Pathway during EC Treatment: 3M AFFF



EC Treatment (Ellsworth AFB GW)





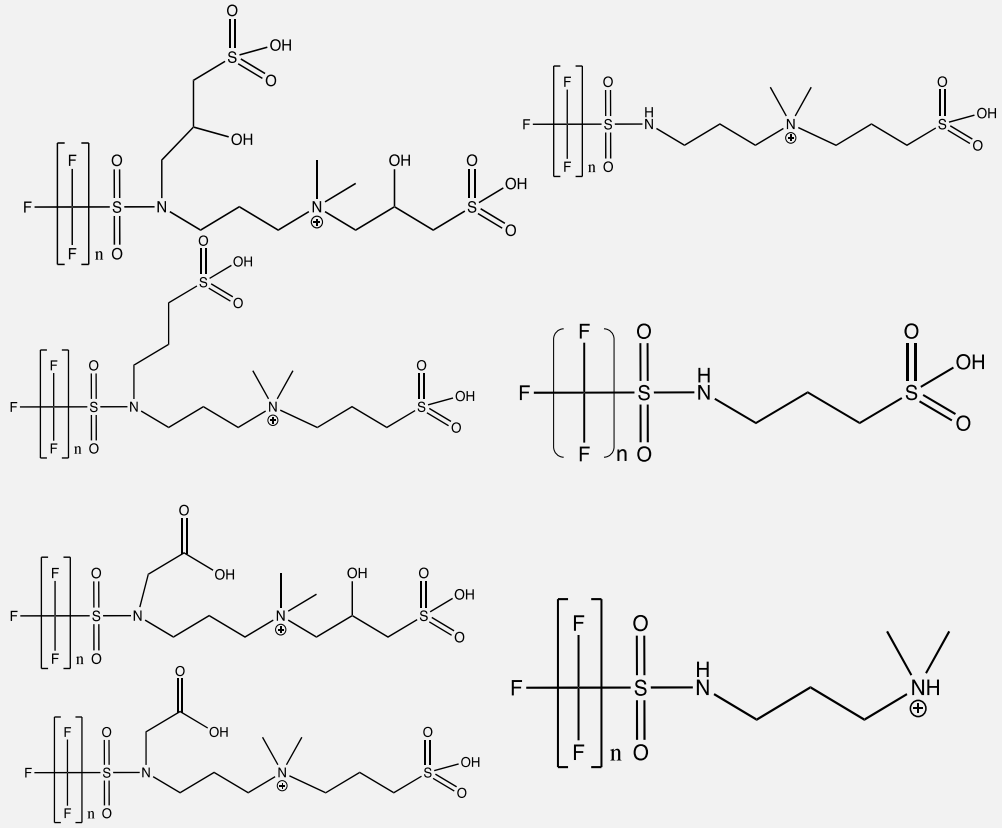
NO transient increases in PFCAs or PFSAs

<u>Total Oxidizable Precursor assay</u>

No PFCA or PFSA generation for untreated Ellsworth AFB groundwater

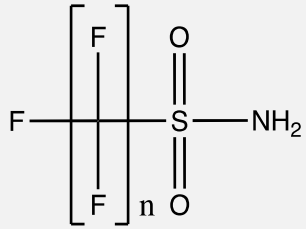
Fate of Identified Pre-Cursors in Ellsworth AFB Groundwater during EC Treatment

Rapidly Removed

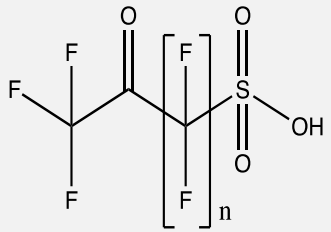


Transient Increase

10 to 100x
Less than in 3M
AFFF GW



Not observed
in 3M AFFF GW



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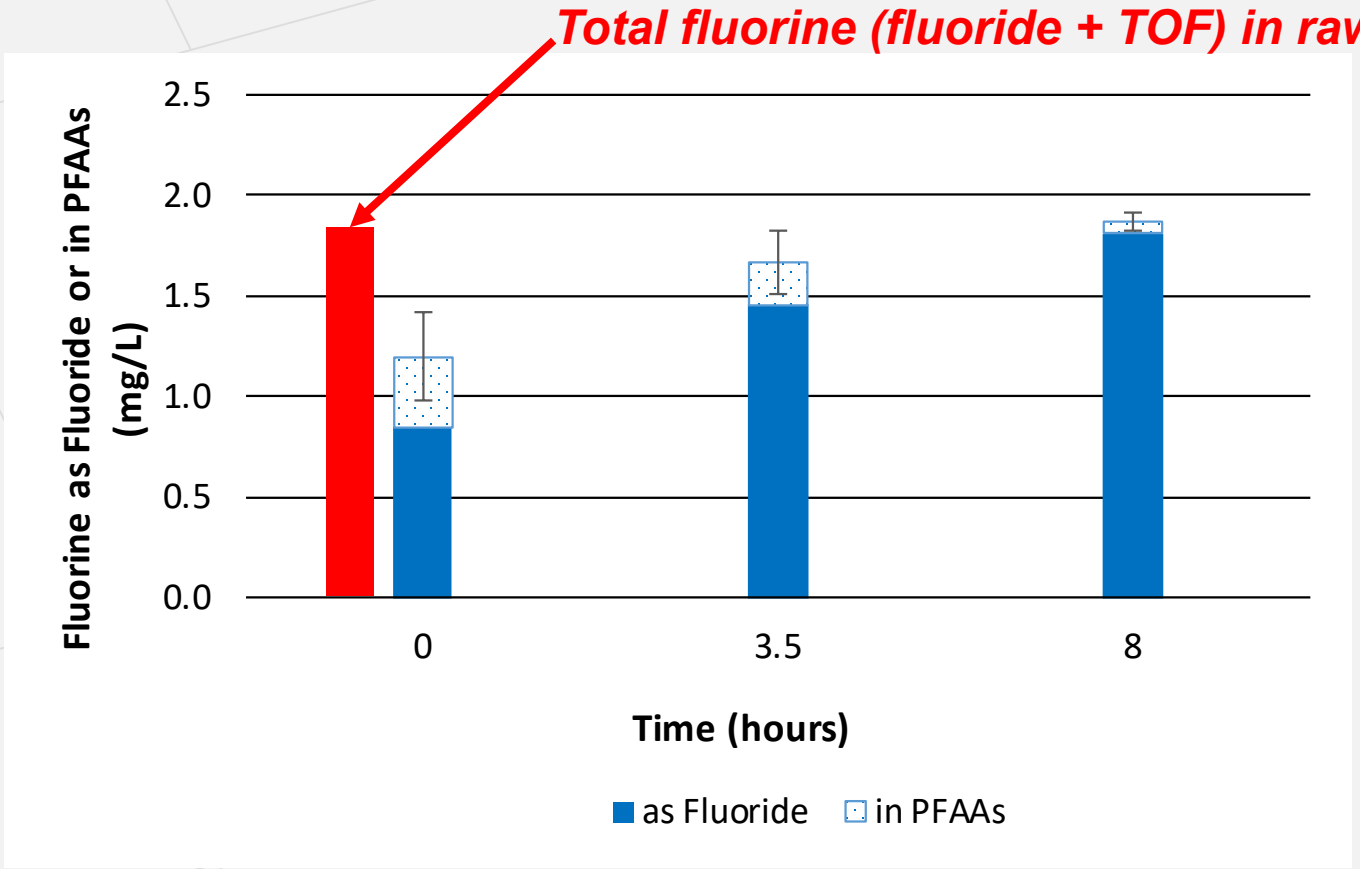
F Mass Balance (Ellsworth AFB Groundwater)



Only 1/3 of the fluoride generated could be accounted for by the PFAAs initially present

TOP analysis or standard PFAS analysis did not capture ~65% of organic fluorine present

Electrochemical Efficiency

Coulombic Efficiency for Defluorination

$$CE = FVe\frac{C_F}{MW_F At} \sim 2 \times 10^{-4}$$

3M AFFF-Spiked GW

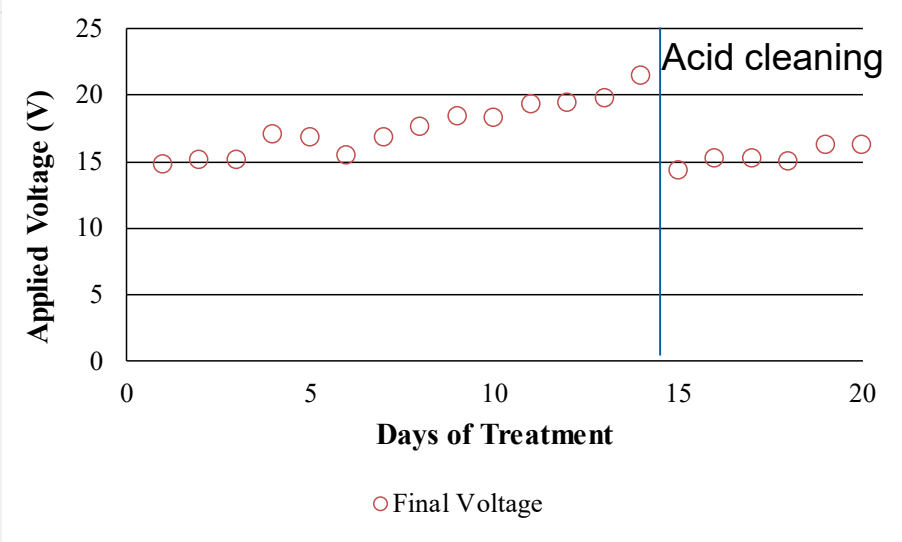
PFAS	% Removal	Energy (W-h/L)
PFOS	91	
PFHpS	94	
PFHxS	87	
PFBS	78	99
PFOA	71	
PFHpA	45	
PFHxA	(increase)	
PFPeA	(increase)	
PFBA	(increase)	

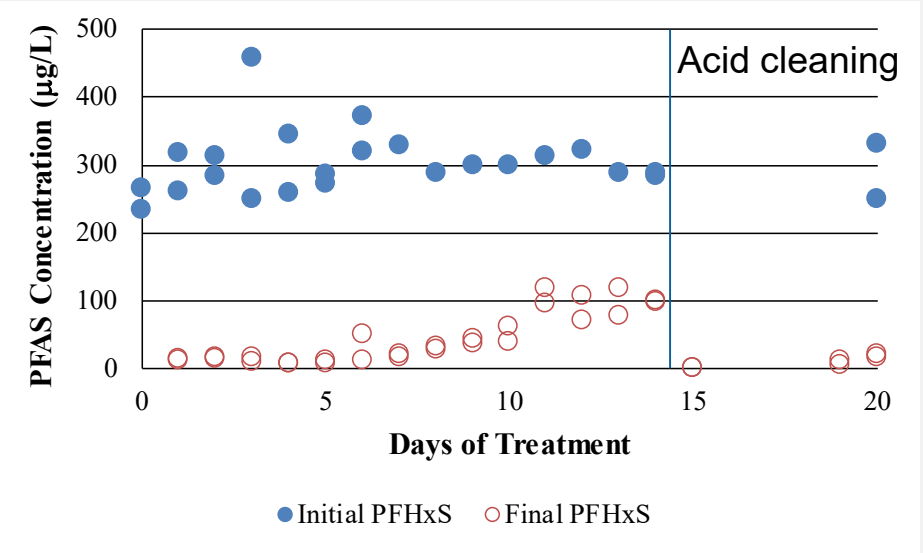
Ellsworth AFB GW

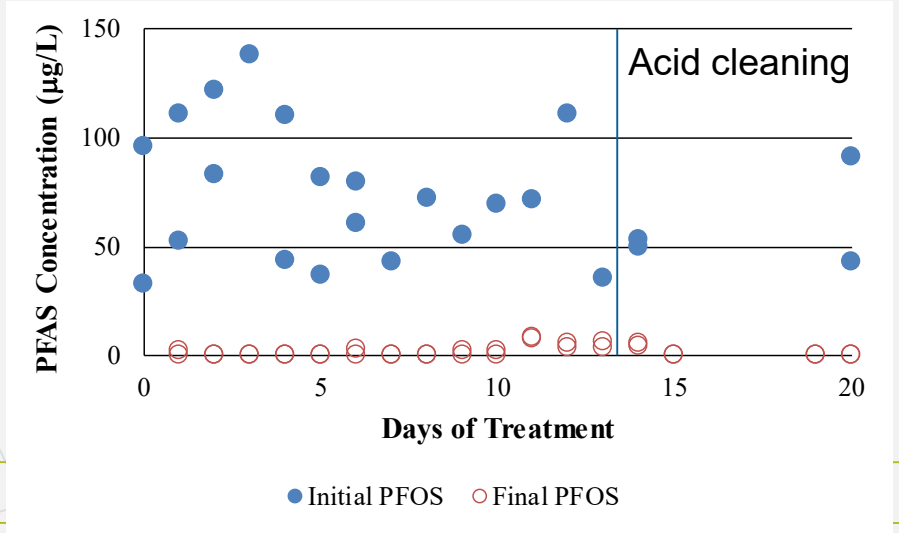
PFAS	% Removal	Energy (W-h/L)
PFOS	40	
PFHpS	85	
PFHxS	89	
PFBS	63	136
PFOA	75	
PFHpA	59	
PFHxA	81	
PFPeA	67	
PFBA	57	

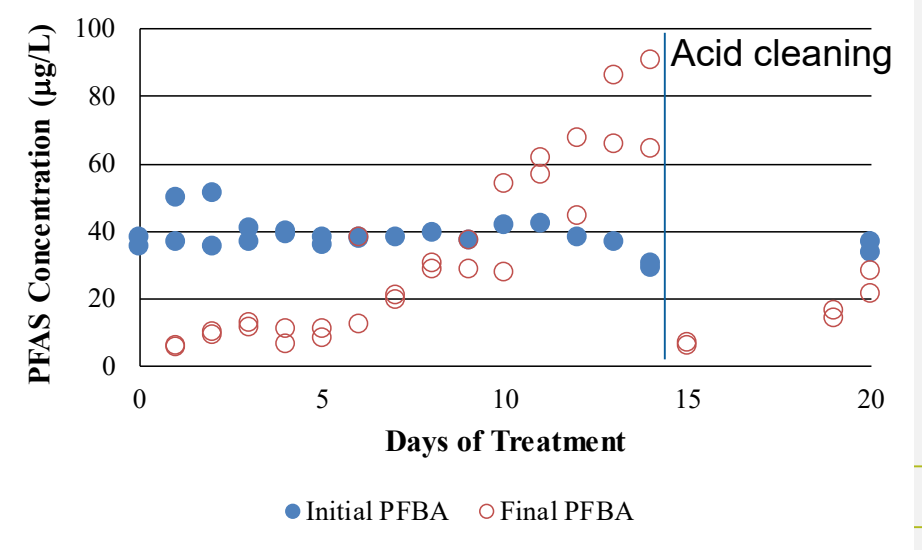
Long Term Testing

(Successive 24-hour batch tests using Ellsworth AFB Groundwater)









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Summary

- EC treatment remains a promising technology for PFAS, esp. for high PFAS concentrations
- Poly fluorinated compounds, and their oxidation pathways, are important and not yet fully understood
- The TOP assay may not be a good indicator of polyfluorinated compounds present in water. Total organic fluorine via CIC may be a better indicator.

Research Funding