What is Really in Aqueous Film Forming Foam & Does it Matter?

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Outline

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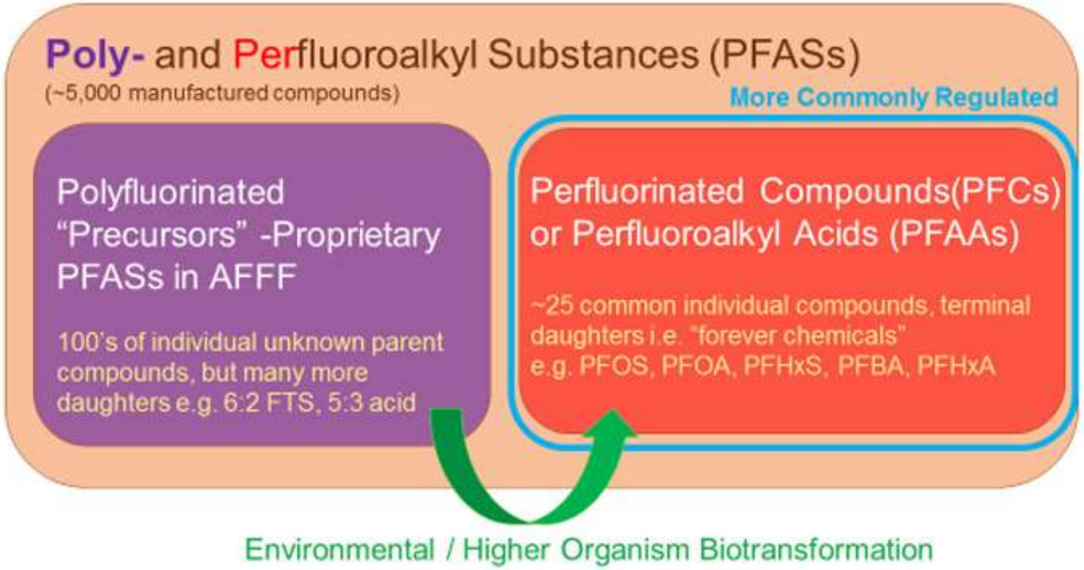
  - ➢ PFAS classification
  - ➢ Background
  - ➢ Motivation
- AFFF Characterization
- What happen upon AFFF oxidation
- AFFF treatment approach
- Plasma based water treatment
  - ➢ Plasma treatment for PFAS
  - ➢ Plasma treatment results
- Conclusion

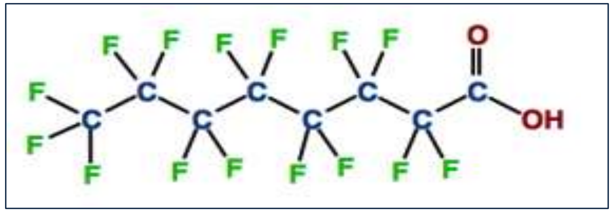
Per- and Polyfluorinated alkyl substances (PFAS)

Group of synthetic chemical compounds

PFAS
- PFAAs — **Perfluoro alkyl acids (C_4 – C_n)**
- Precursors

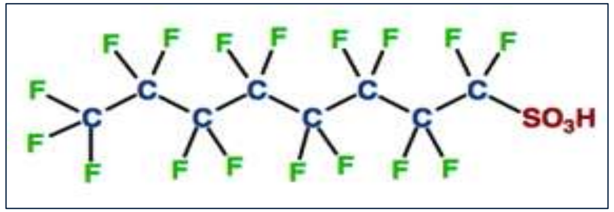


Carboxylic acid



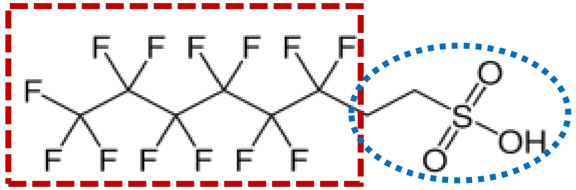
Perfluorooctanoic acid (PFOA)

Sulfonic acid

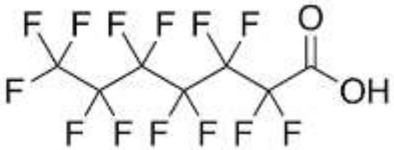


Perfluorooctane sulfonate (PFOS)

Surfactant-like compounds



6:2 Fluorotelomer sulfonate (6:2 FTS)



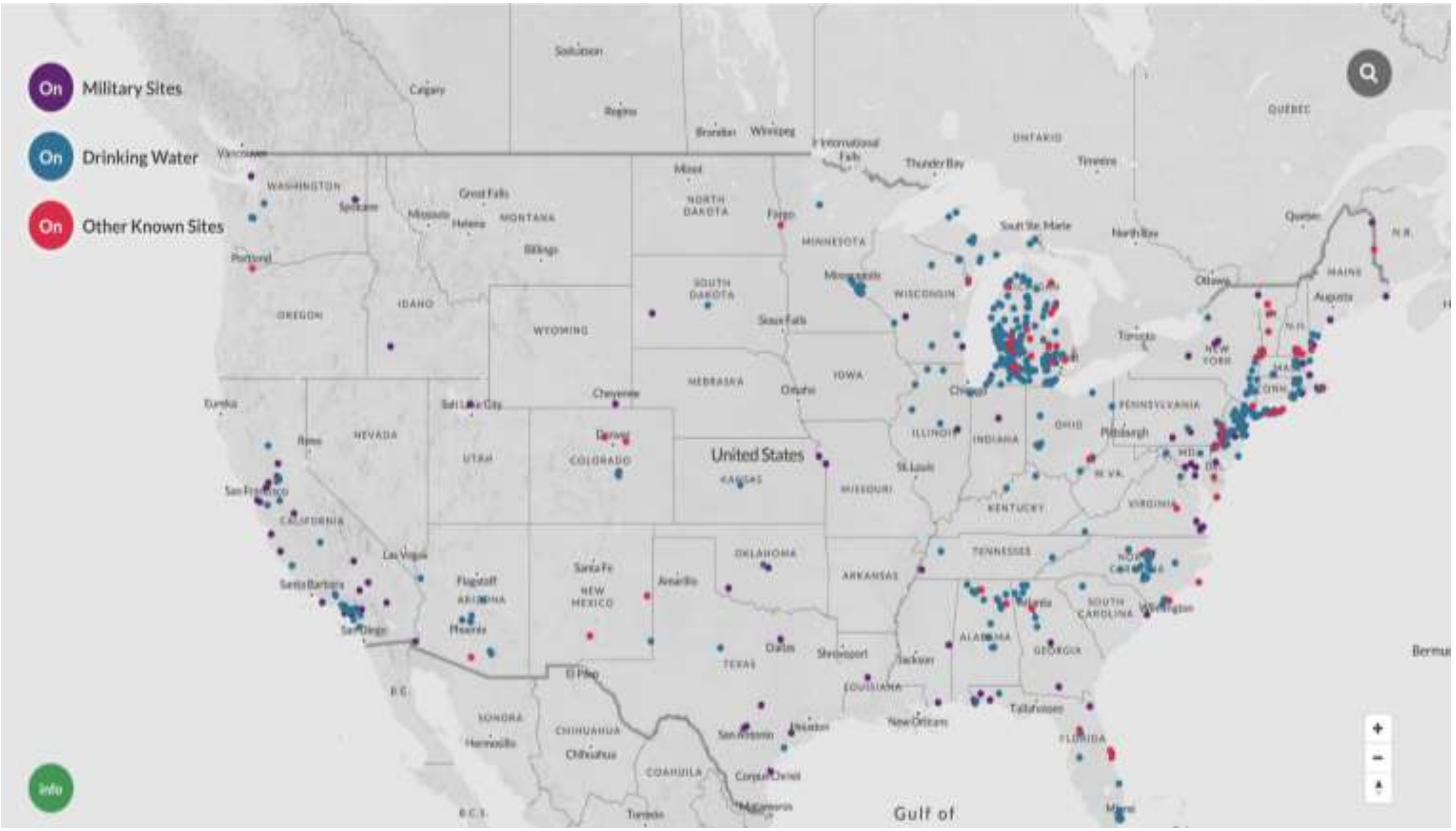
Perfluoro heptanoic acid (PFHpA)

Per- and Polyfluorinated alkyl substances (PFAS)

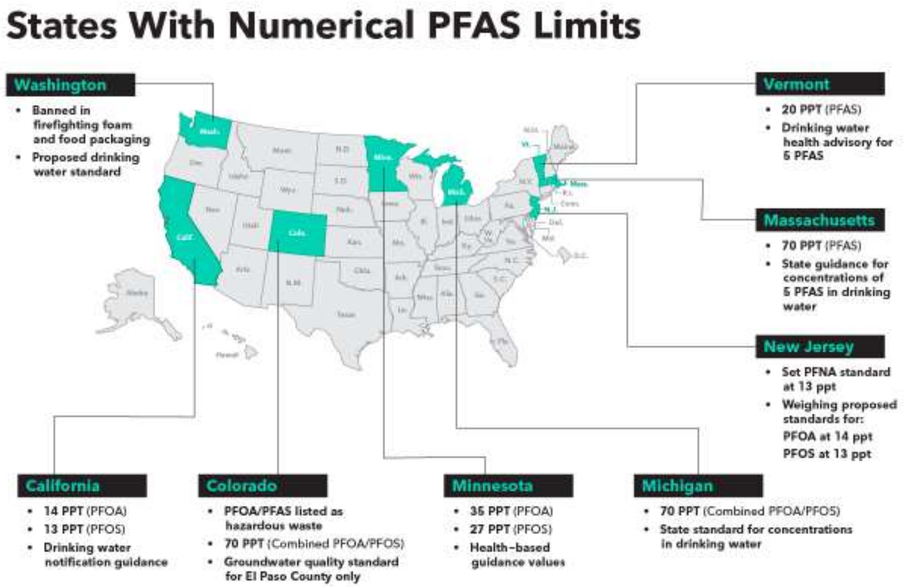
- PFAS sources in the environment:
  - ➢ **Aqueous film forming foams (AFFF)** for firefighting activities at DoD sites, commercial airports, and industrial facilities
  - ➢ Industrial spills and dumping
  - ➢ Wastewater effluents
  - ➢ Leaky landfill
  - ➢ Disposal of household products
- Current drinking water health advisory levels for PFAS are ***3-4 orders of magnitude lower*** than concentrations measured at several U. S. Department of Defense sites.
- Long-chain PFAS (C≥8) are bio-accumulative and toxic. Therefore, manufacturing and usage of C8 AFFF is phased out.
- PFAS are ***very recalcitrant*** because of the stability of the C-F bond.
- USEPA requires AFFF to be free of long-chain PFAAs.

Source: midwestadvocates.org

PFAS contaminated sites: Current status



Source: saferchemicals.org



Source: Bloomberg Environment

US EPA – no standards

US EPA health advisory limit: 70 ng/L for PFOA and PFOS

Massachusetts PFAS standard: 20 ng/L for six PFAS (PFHxS, PFHpA, PFOA, PFOS, PFNA and PFDA

Motivation

Activated carbon – relatively short breakthrough time and disposal of adsorbent.

Ion exchange – concentrated brine solution.

Advanced oxidation processes (UV/H_2O_2/O_3) – ineffective and/or prohibitively expensive.

Plasma: Generates both oxidants and reductants – reported to be more effective than other leading technologies for removal of PFAS from water.[1]

Literature gap:

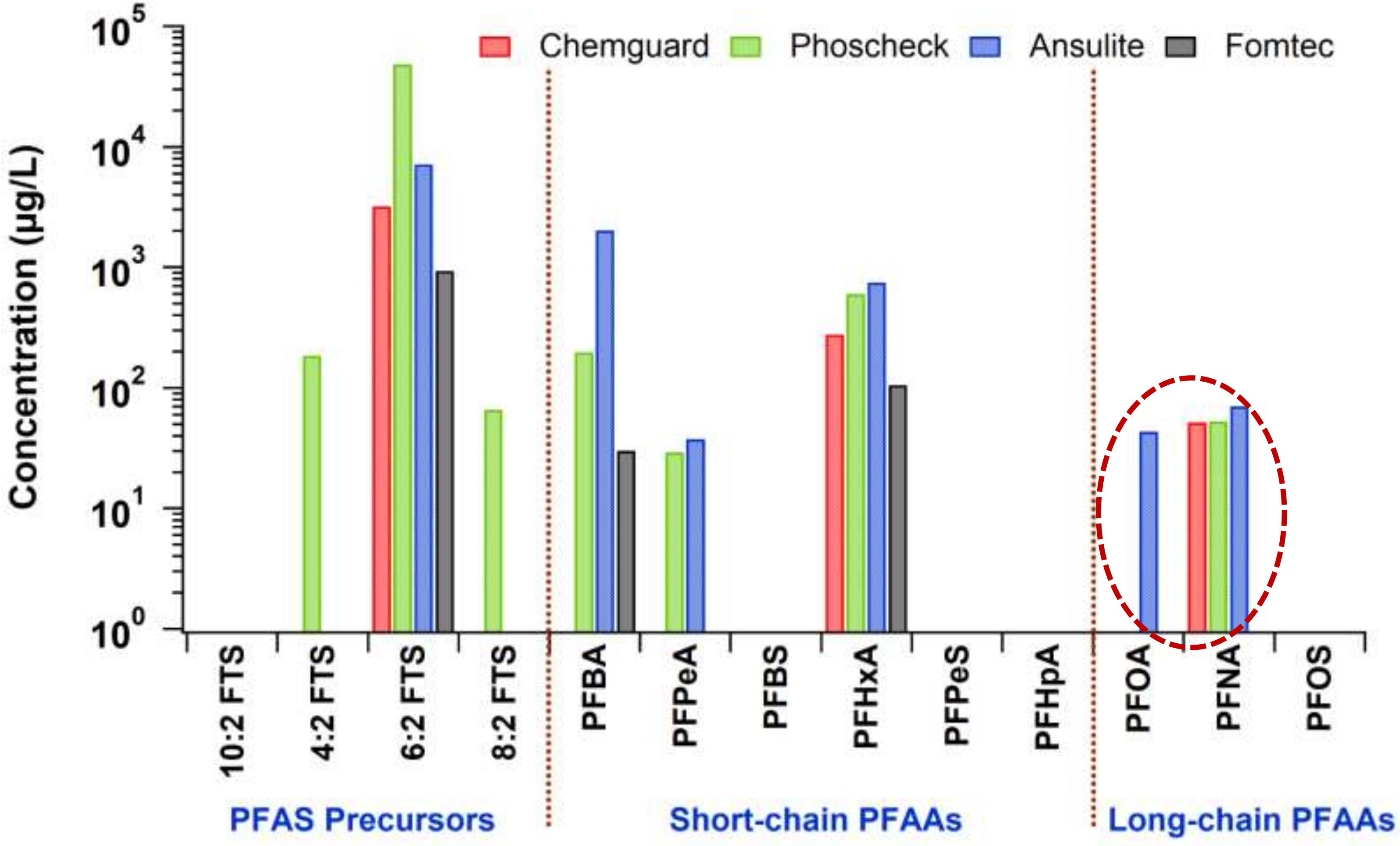
- No treatment technology available to **degrade** PFAS at **large-scale**.
- Efficient treatment of aqueous film-forming foams (AFFF).

Rationale:

- Can a pre-oxidation option prior to plasma be more efficient and cost effective?

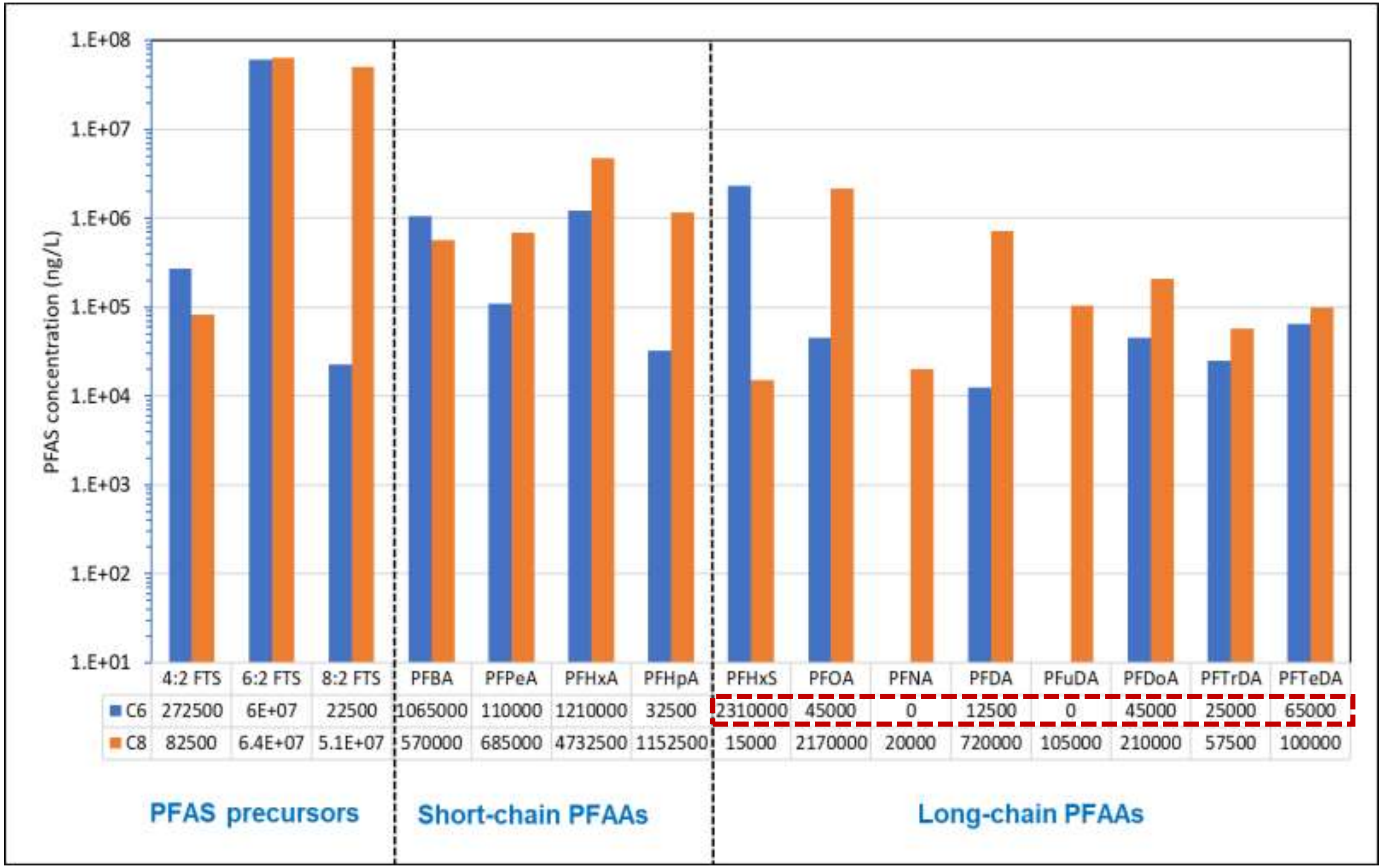
[1]Nzeribe et al., 2019 *Critic. Rev. Env. Sci. Tech.* **2019**, *49*, 866 – 915.

C6 AFFF Characterization



	Total fluorine (mg/L)	TOP (mg/L)
Chemguard	430	2900
Phoscheck	380	1500
Ansulite	6140	10000
Fomtec	-	3000

Comparison between C8 and C6 AFFF



	4:2 FTS	6:2 FTS	8:2 FTS	PFBA	PFPeA	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFDA	PFUDA	PFDoA	PFTrDA	PFTeDA
C6	272500	6E+07	22500	1065000	110000	1210000	32500	2310000	45000	0	12500	0	45000	25000	65000
C8	82500	6.4E+07	5.1E+07	570000	685000	4732500	1152500	15000	2170000	20000	720000	105000	210000	57500	100000

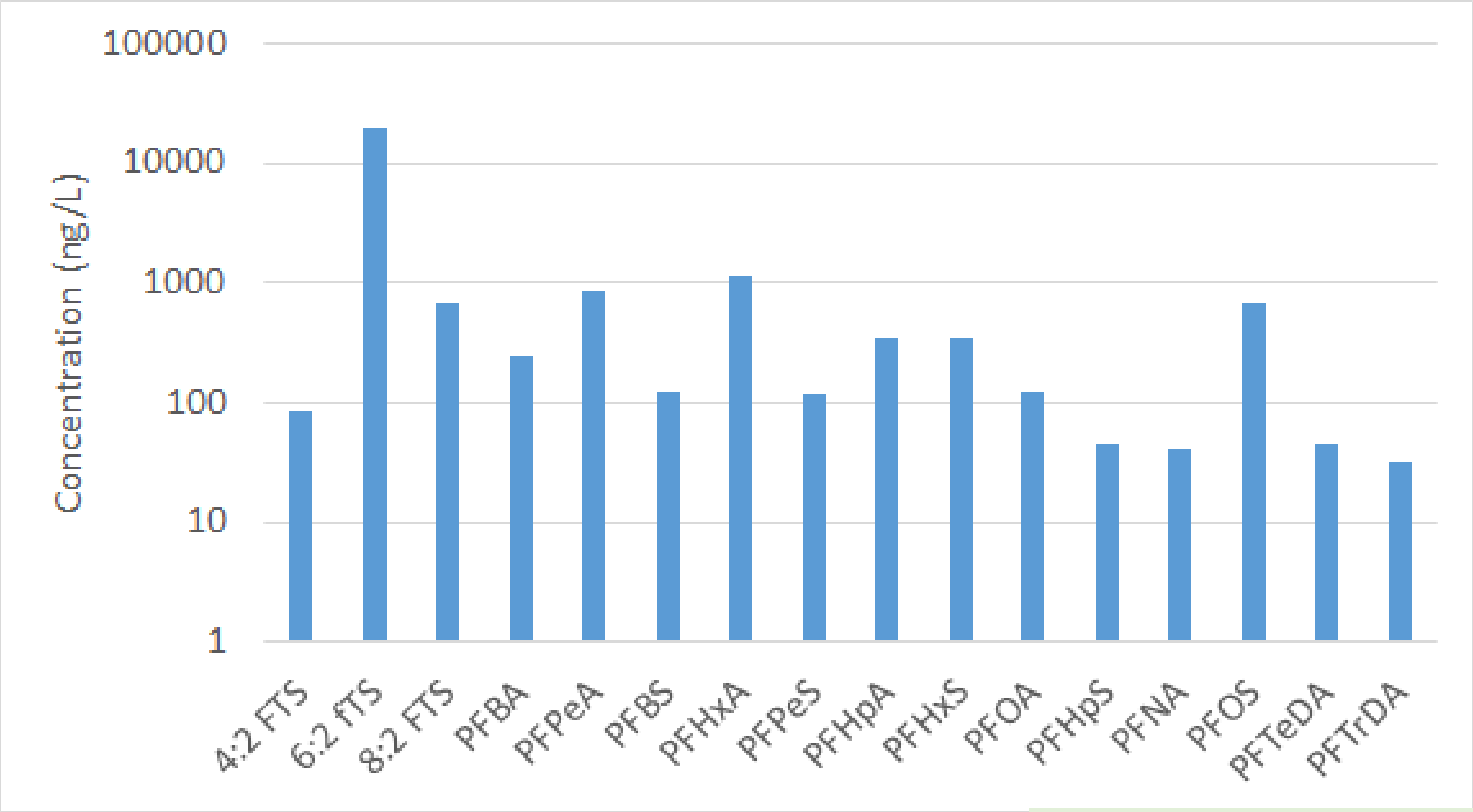
C6 Foam

C8 Foam

Very high concentration of PFHxS (C6) = 2.3 mg/L

Significant concentration of C8, C10, C12, C13 and C14 acids = 12 to 65 µg/L

PFAS Concentrations in AFFF Rinsate



AFFF Rinsate

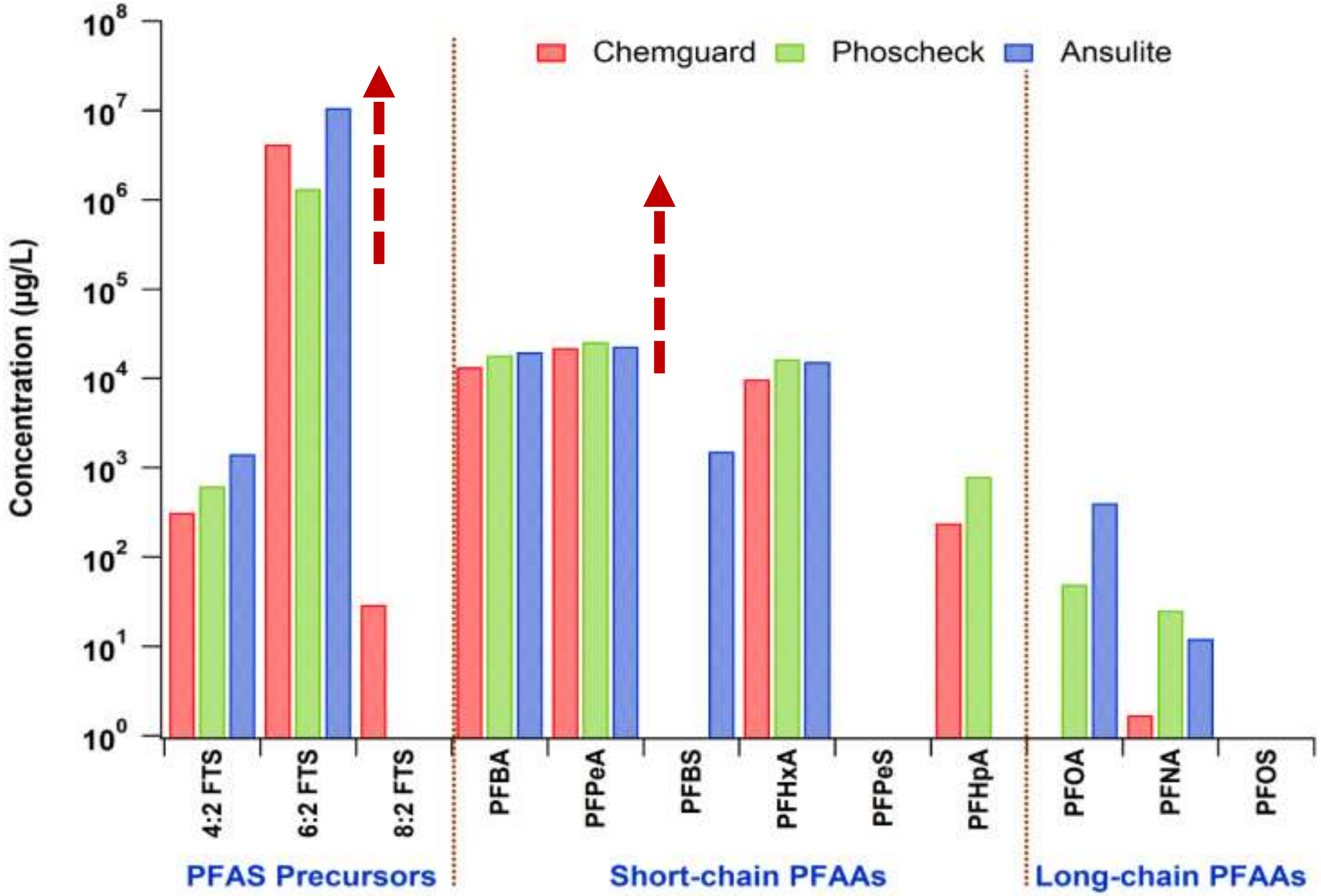
PFAS precursors, Long- and short-chain PFAAs were detected in rinsate sample.

6:2 FTS detected in highest concentration.

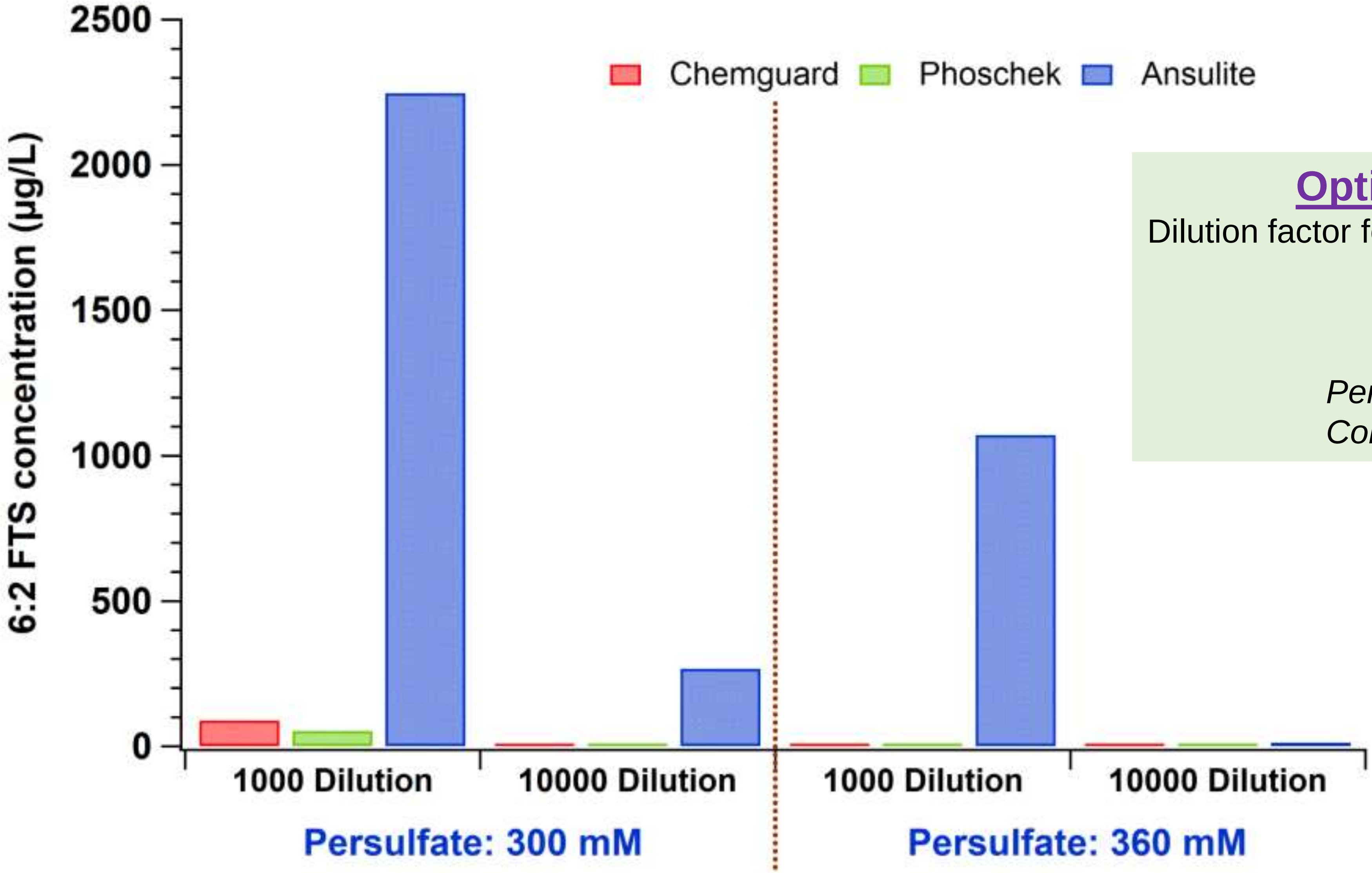
What happen upon oxidation of AFFF?

Effect of dilution prior to heat-activated persulfate oxidation

100x diluted samples



Optimization of heat-activated persulfate oxidation



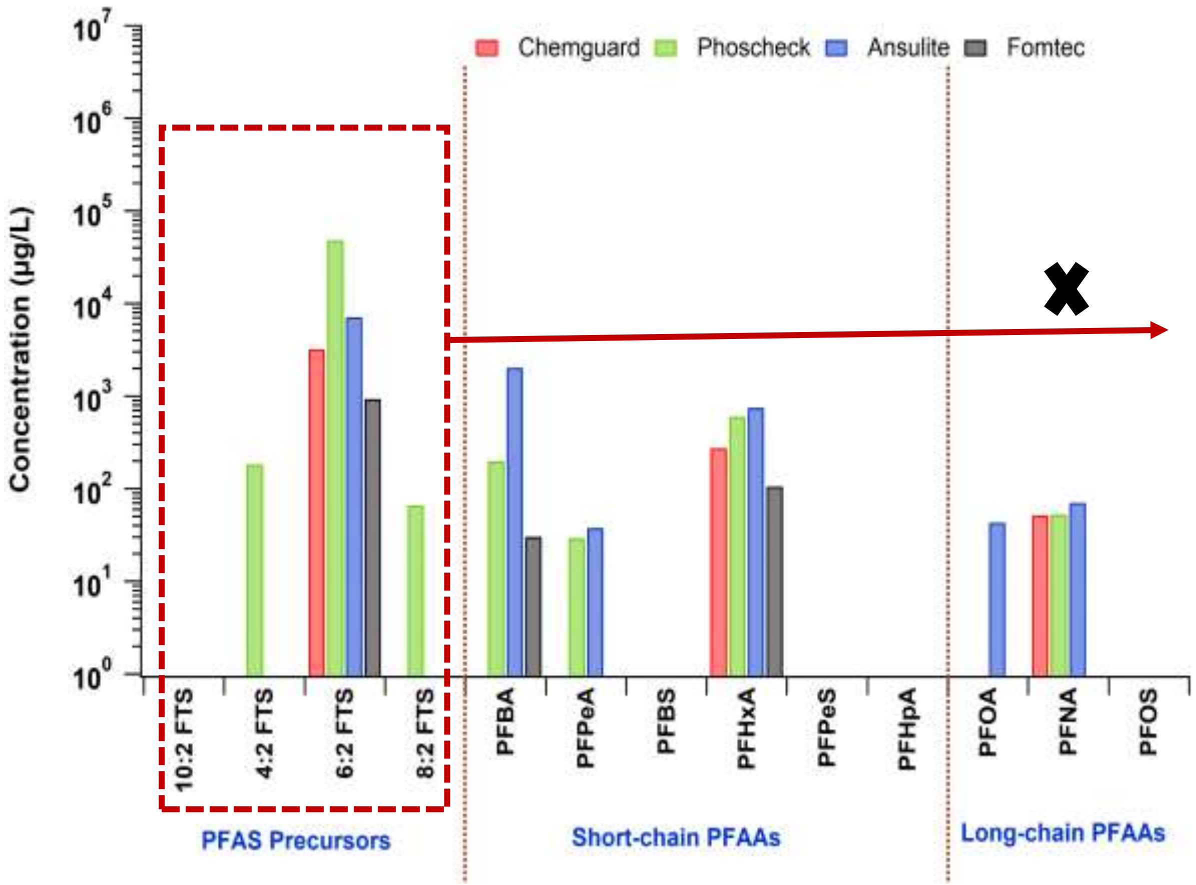
Optimized condition

Dilution factor for *Chemguard: 1000 times*
Phoscheck: 1000 times
Ansulite: 10000 times

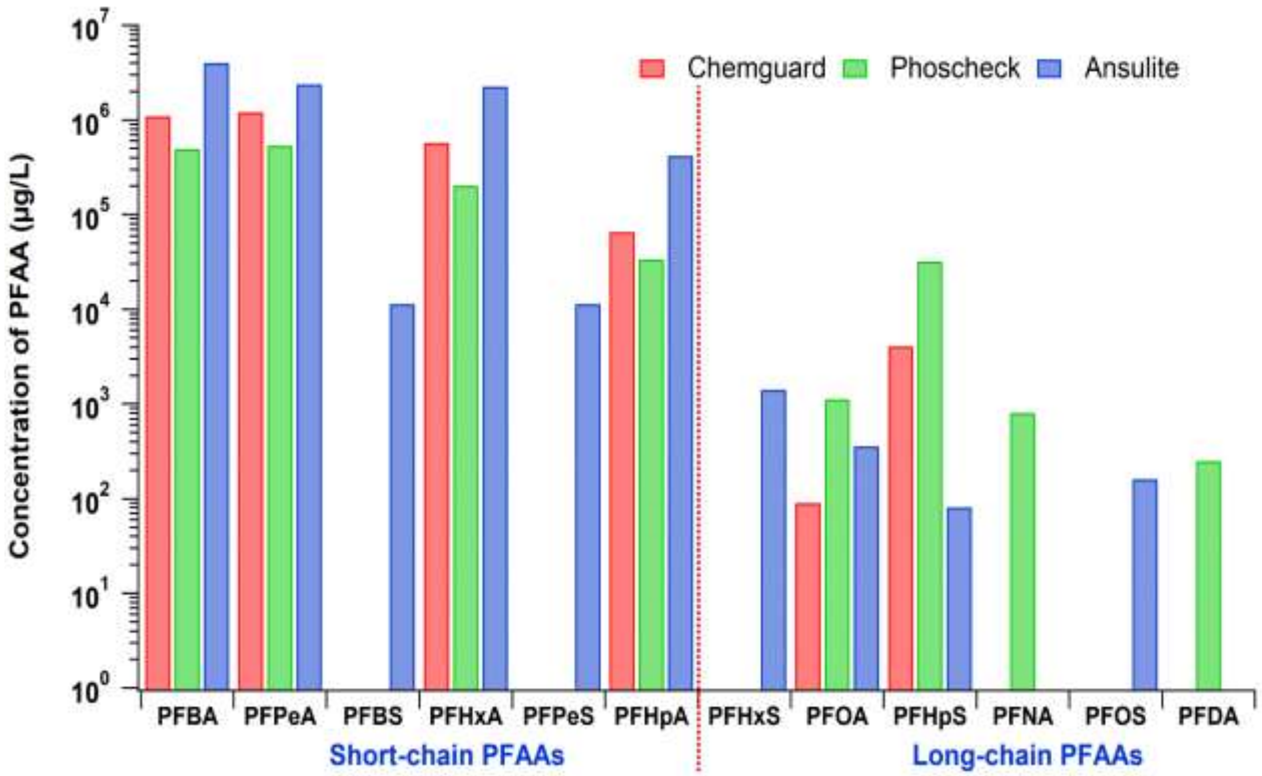
Persulfate dose: 360 mM
Conversion >99%

PFAS concentrations in pre- and post-oxidized AFFF samples

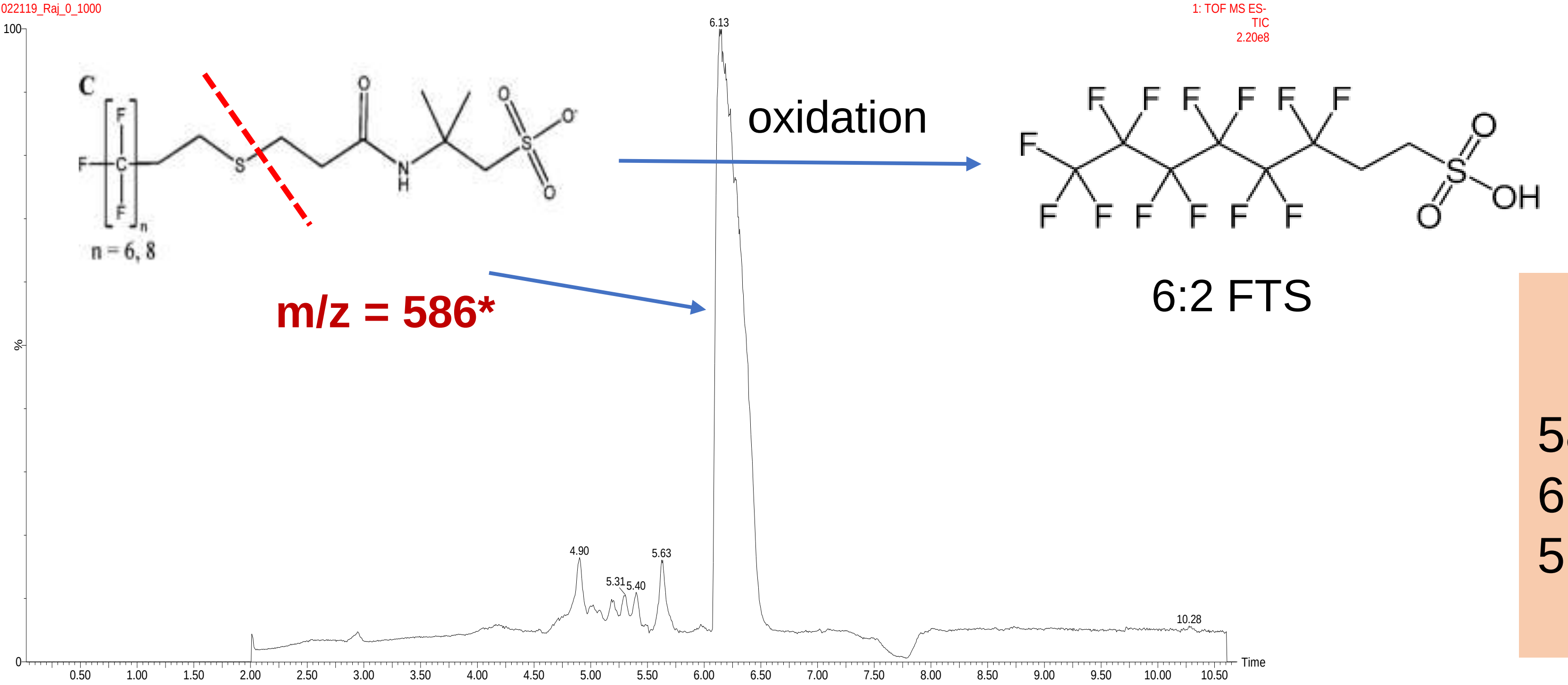
Pre-oxidation



Post-oxidation



Insight from non-targeted (LC-QToF-MS) analysis: Hunting for Unknowns



<u>Unknown compounds of detected mass (m/z)</u>

586, 567, 638, 709, 780, 602, 569, 618, 451, 541, 686, 467, 483, 461, 510, 542, 581, 597, 483

Most abundant unknown PFAS precursor in Ansulite (1000x diluted) sample

***Place and Field., 2012**

Treatment approach

Characterization of four AFFF samples

- PFAS – 20 PFAAs, 10 precursors
- Total oxidizable precursors (TOP)
- Total Fluorine (TF)

Optimization of heat-activated persulfate and other oxidation options

- Oxidant dose
- Dilution factor
- Treatment time

Plasma-treatment of oxidized AFFF samples

Optimization of reactor geometry and power input for degradation of PFAAs

Plasma-based Water Treatment (PWT)

- Plasma is a mixture of neutral species, positive ions, negative ions, and electrons.

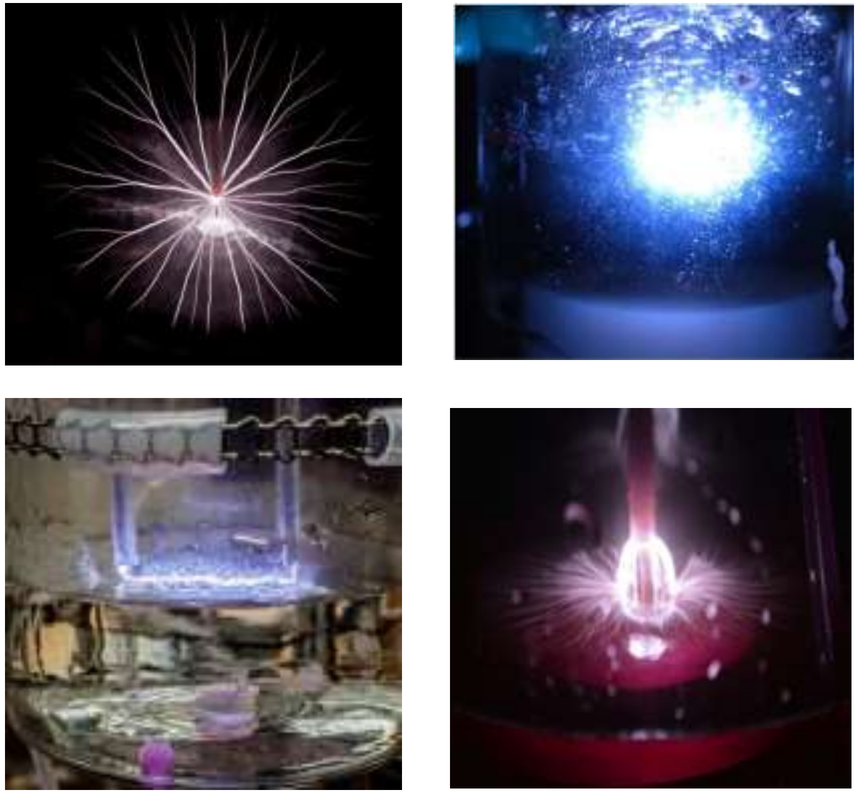
- Electrical discharge plasmas are generated *directly in* or *above* water.

Advanced oxidation process (AOP)

Plasma →

- Oxidative species ($^{\cdot}OH$, O, H_2O_2, O_2, $^{\cdot}HO_2$)
- Reductive species (e_{aq}^-, e^-, H)
- Physical effect (UV, electric field, shock wave, locally high temperature)

Oxidative and reductive species: Can oxidize and reduce organic and inorganic compounds



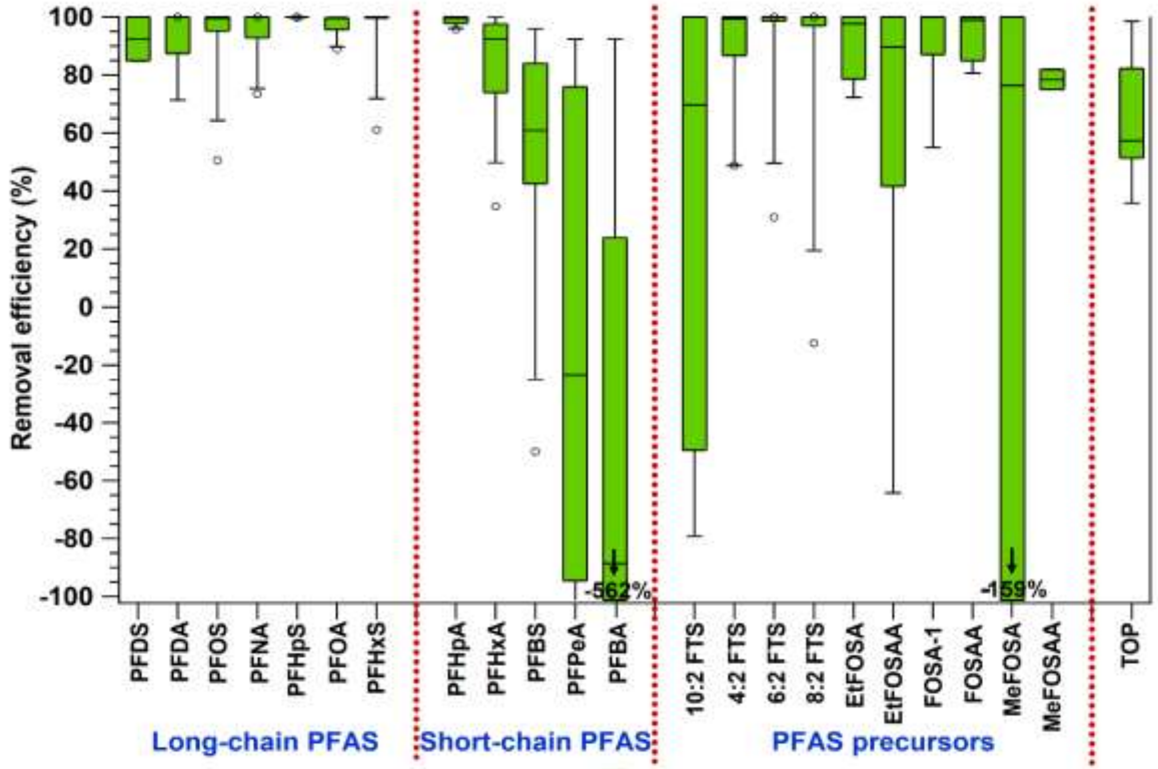
Pictures: Plasma Research Laboratory, Clarkson University

- PWT does not require chemical additives and produces no residual waste.

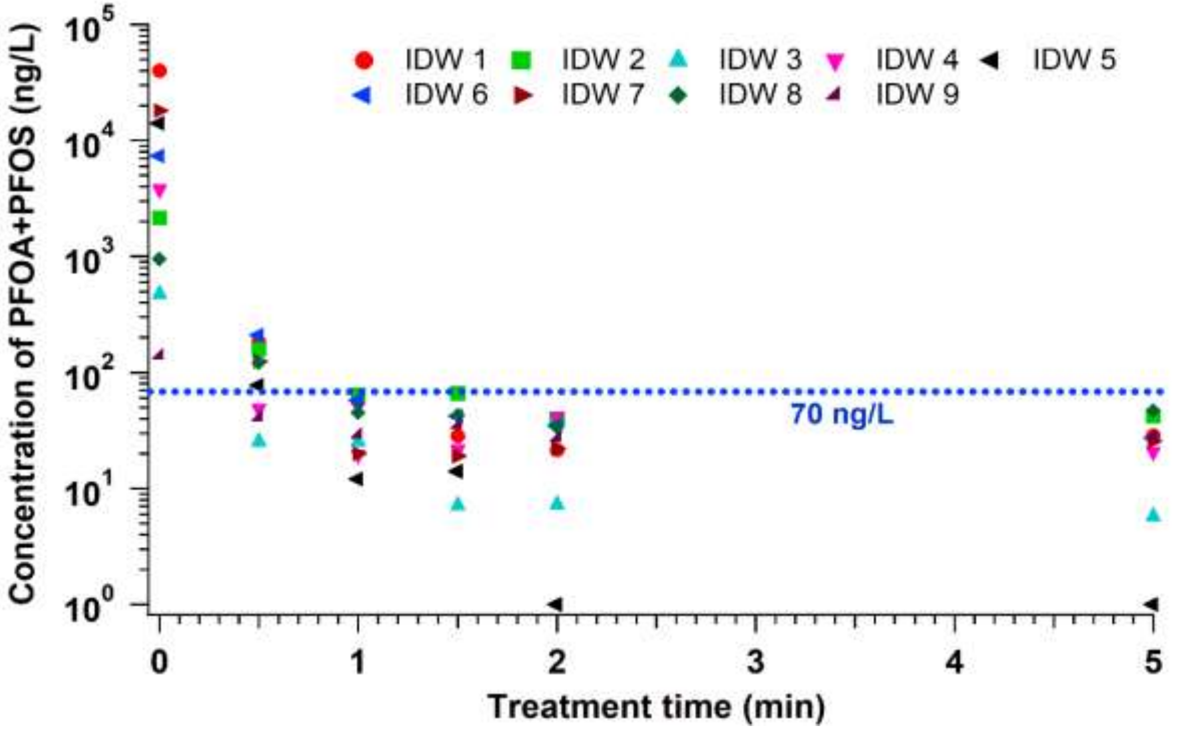
Performance of Pilot-scale Plasma Reactor

IDW – Investigation derived waste; 13 samples from different Air Force base

Removal efficiency



PFOA and PFOS removal

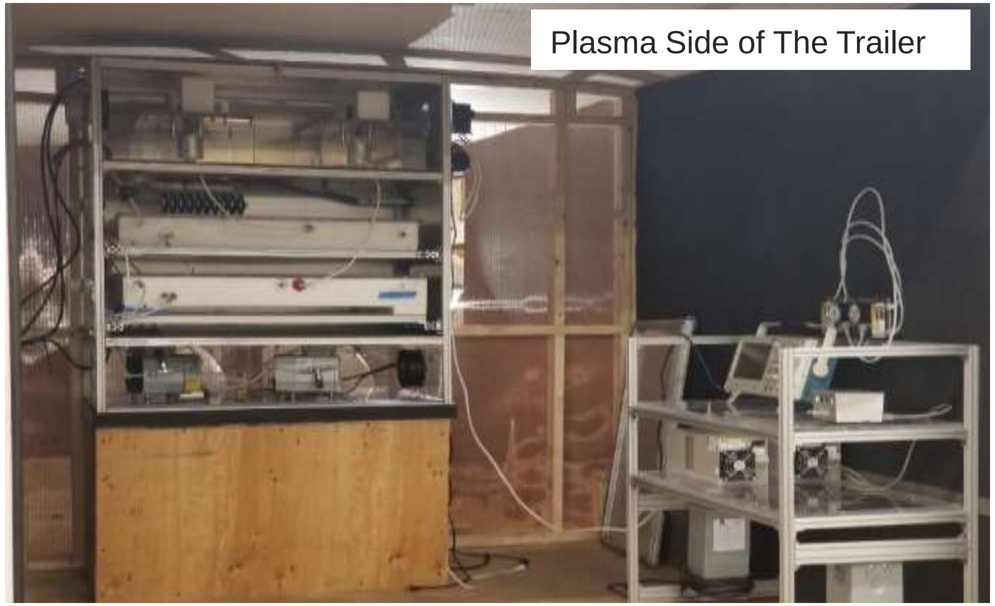


TOP – Total Oxidizable Precursors

Within 1 minute, PFOA and PFOS was degraded to below USEPA health advisory concentration (70 ng/L)

Singh et al., (2019) *Environmental Science & Technology, 53*, 2731 – 2738

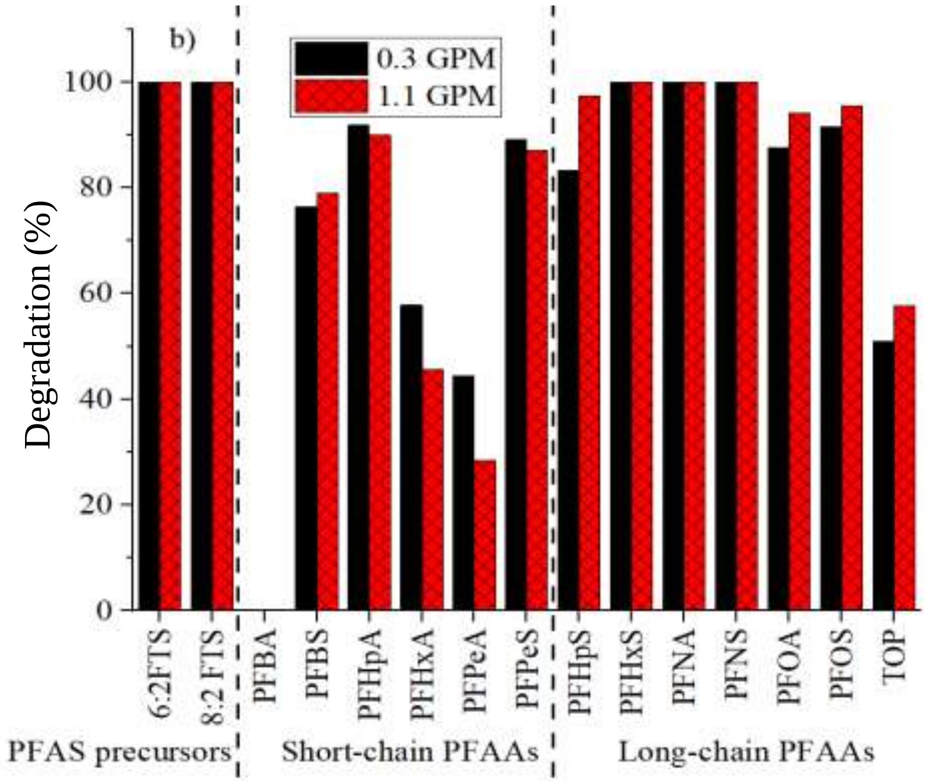
Mobile Plasma Trailer


Plasma Side of The Trailer


Sample Collection Side of the Trailer

Field Demonstration

~350 gallons of PFAS-impacted groundwater were treated at various reactor operating conditions (flowrates, no. of recycle events*)



Trailer Performance: Energy cost

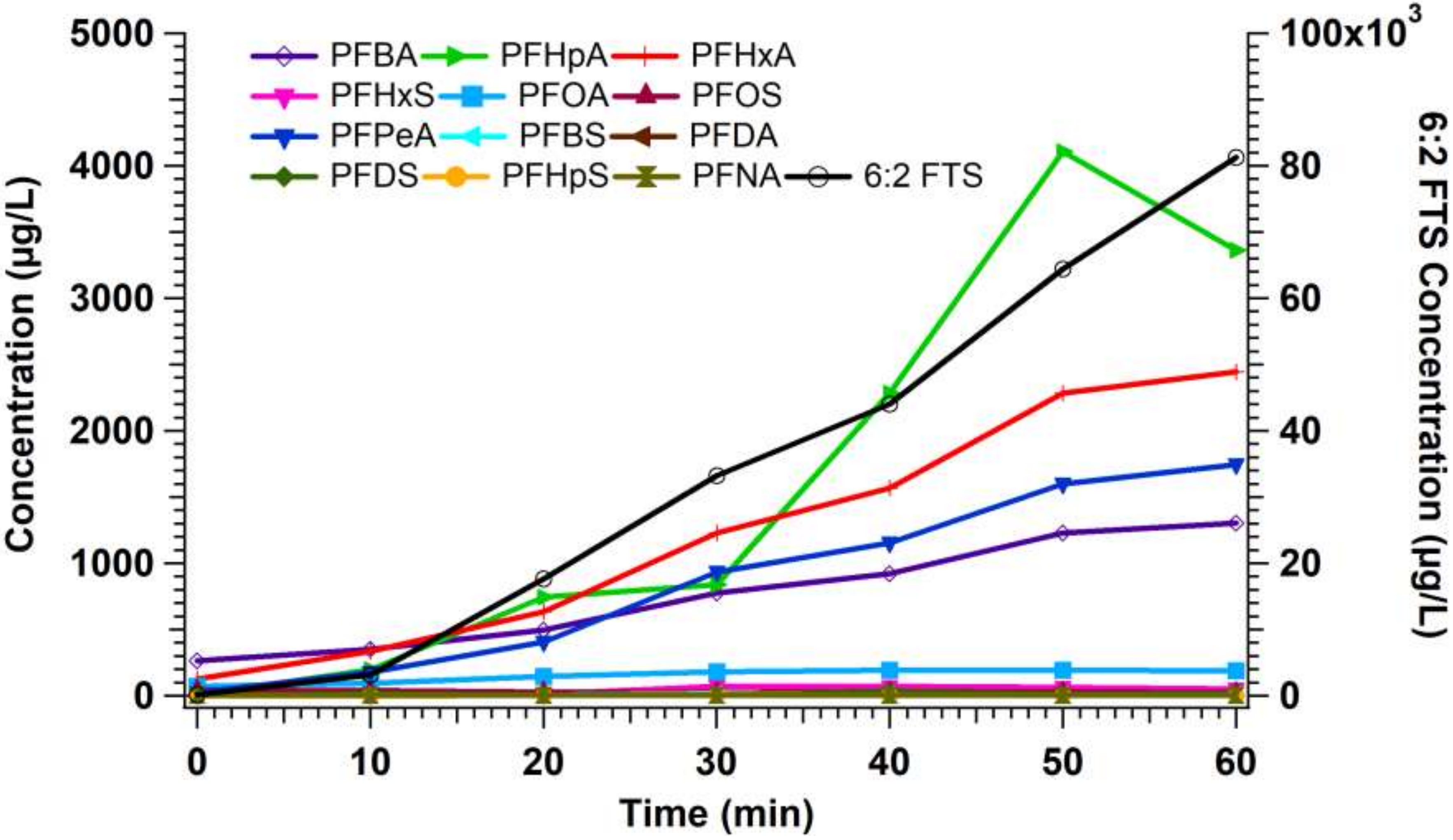
Energy Requirements and Calculated Costs for Reducing the Initial PFOA+PFOS Concentration to below 70 ng/L

Test	Energy required (kWh)	Total cost	Cost/cycle	Cost/gallon
Well B				
0.3 gpm	4 (4 cycles)	$ 0.48		
0.6 gpm	1 (1 cycle)	$ 0.12	$ 0.12/cycle	**$0.0067/gal**
0.9 gpm	1 (1 cycle)	$ 0.12		
Well C				
0.3 gpm	3 (3 cycles)	$ 0.36	$ 0.12/cycle	**$ 0.0067/gal**
1.1 gpm	2 (2 cycles)	$ 0.24		

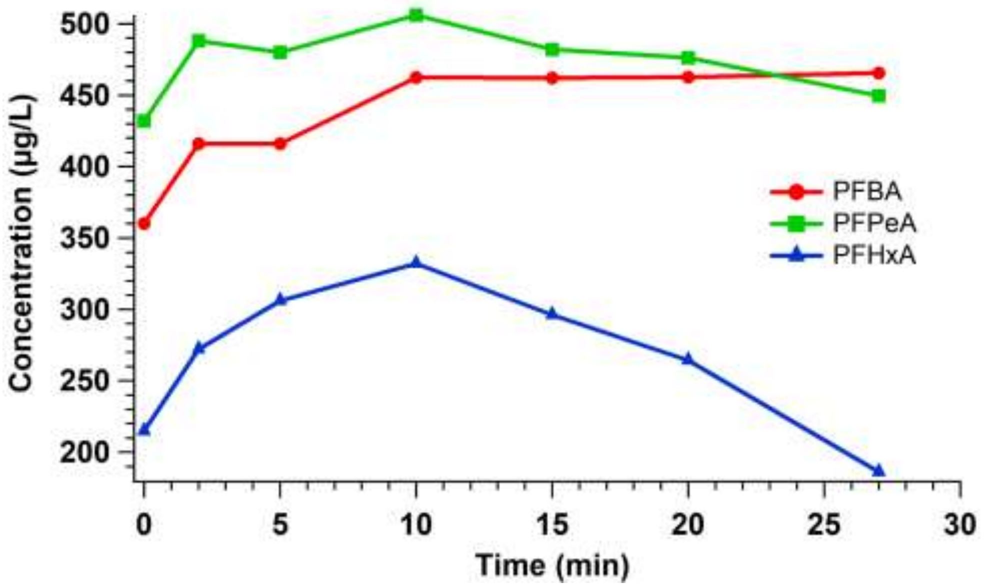
*One cycle (18 gal of water) is defined as a single pass through the reactor from the influent tank.

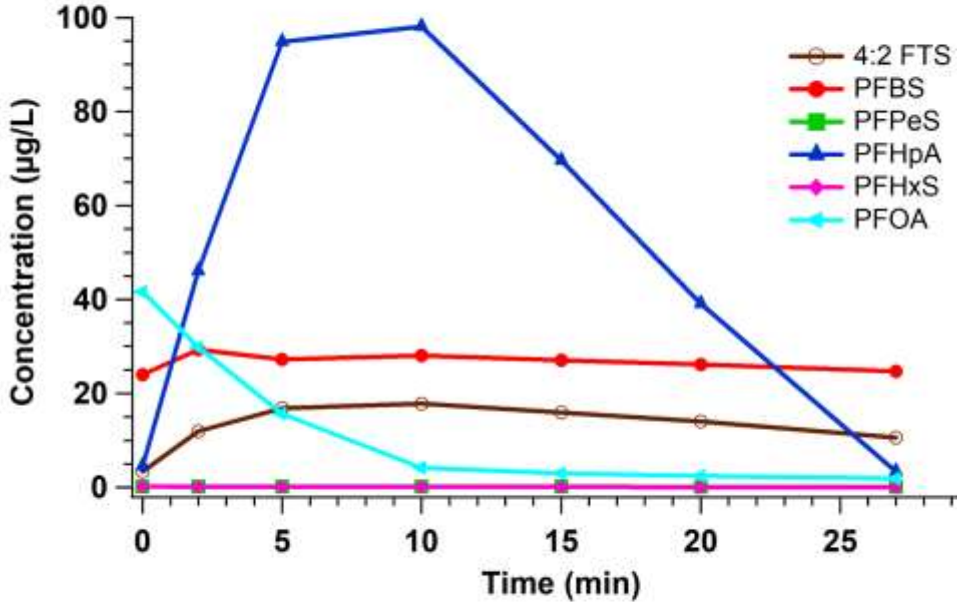
Nau-Hix, et al. (under preparation)

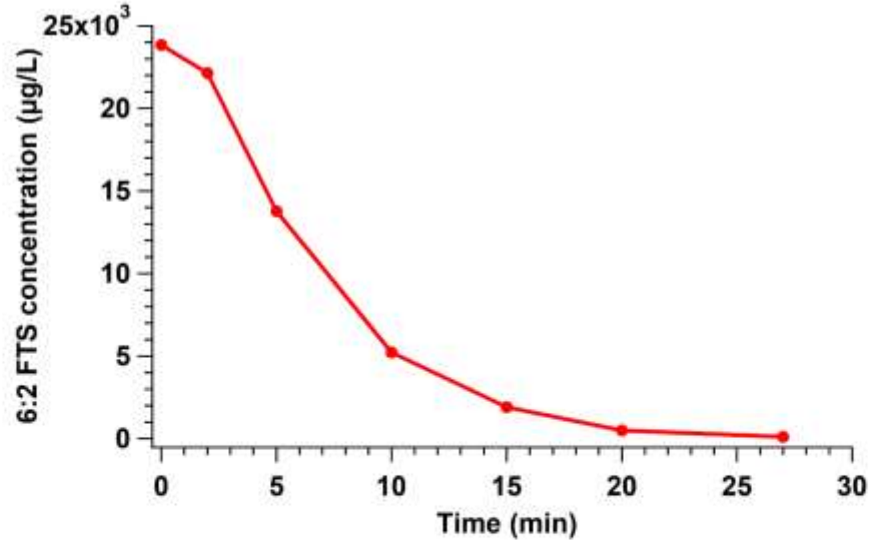
Plasma treatment: Without pre-oxidation



Plasma Treatment: with Pre-oxidation







Conclusion

- Analysis of 20 PFAAs and 10 precursors in 4 different AFFF samples showed:
    - high concentrations of short-chained PFAAs
    - traces of long-chain PFAAs
    - a significant amount of PFAS precursors
- 6:2 FTS was present at high concentrations in all four AFFF samples.
- The AFFF sample with the highest concentrations of PFAS precursors can be fully oxidized (>99%) when diluted 10^3 to 10^4 times with a 360 mM $K_2S_2O_8$.
- After oxidation significantly higher concentrations of long-chain PFAAs were found (for PFOA concentrations increased by up to 700%).
- LC-QToF-MS analysis showed the presence of many unknown PFAS compounds in AFFF samples.
- To fully convert PFAS precursors to PFAAs, pre-oxidation of AFFF samples **may be required** prior to plasma treatment, which was proven to be an effective technology to destroy AFFF.

Acknowledgements

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