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

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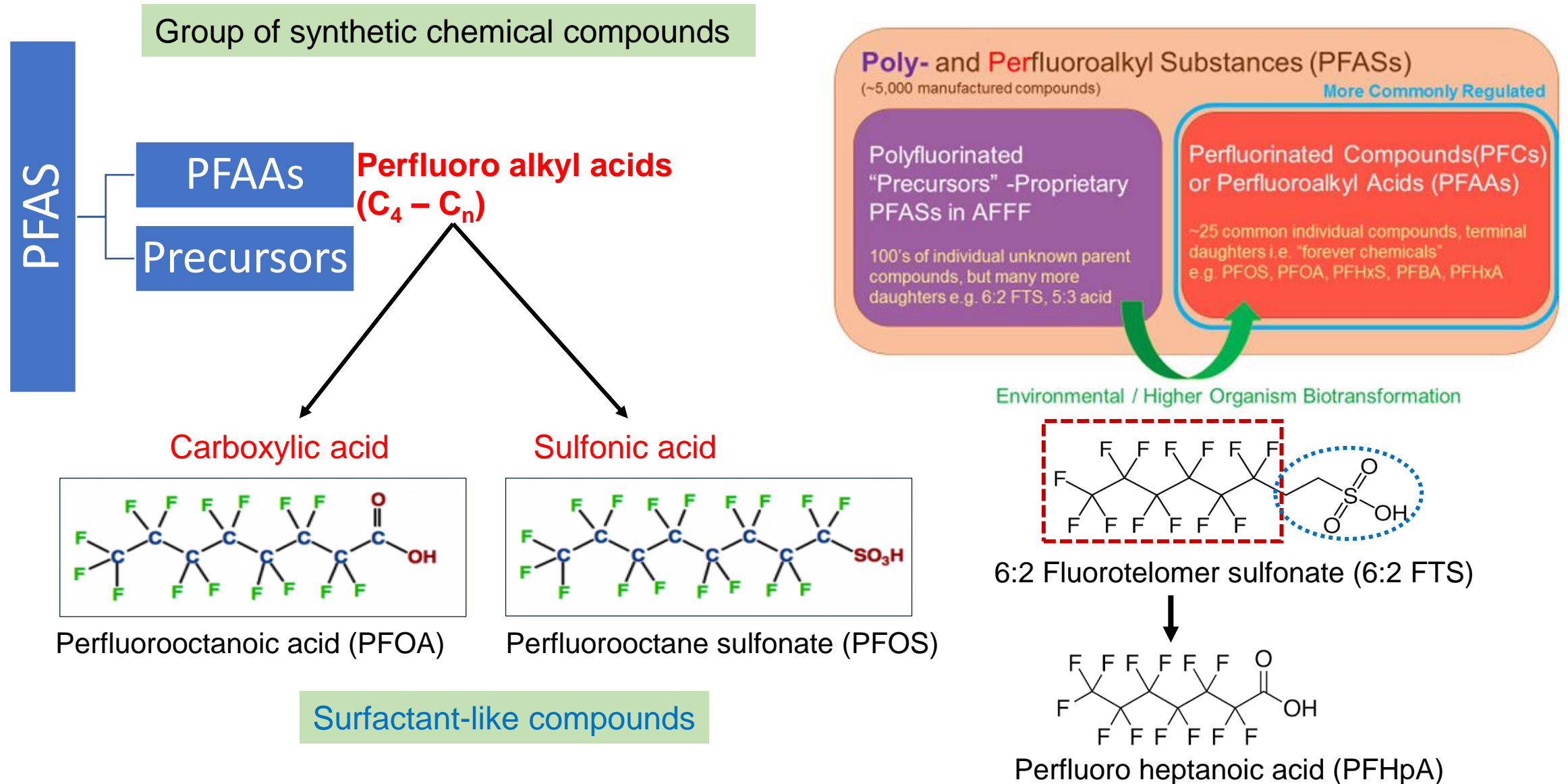
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Outline

- Introduction
 - 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)



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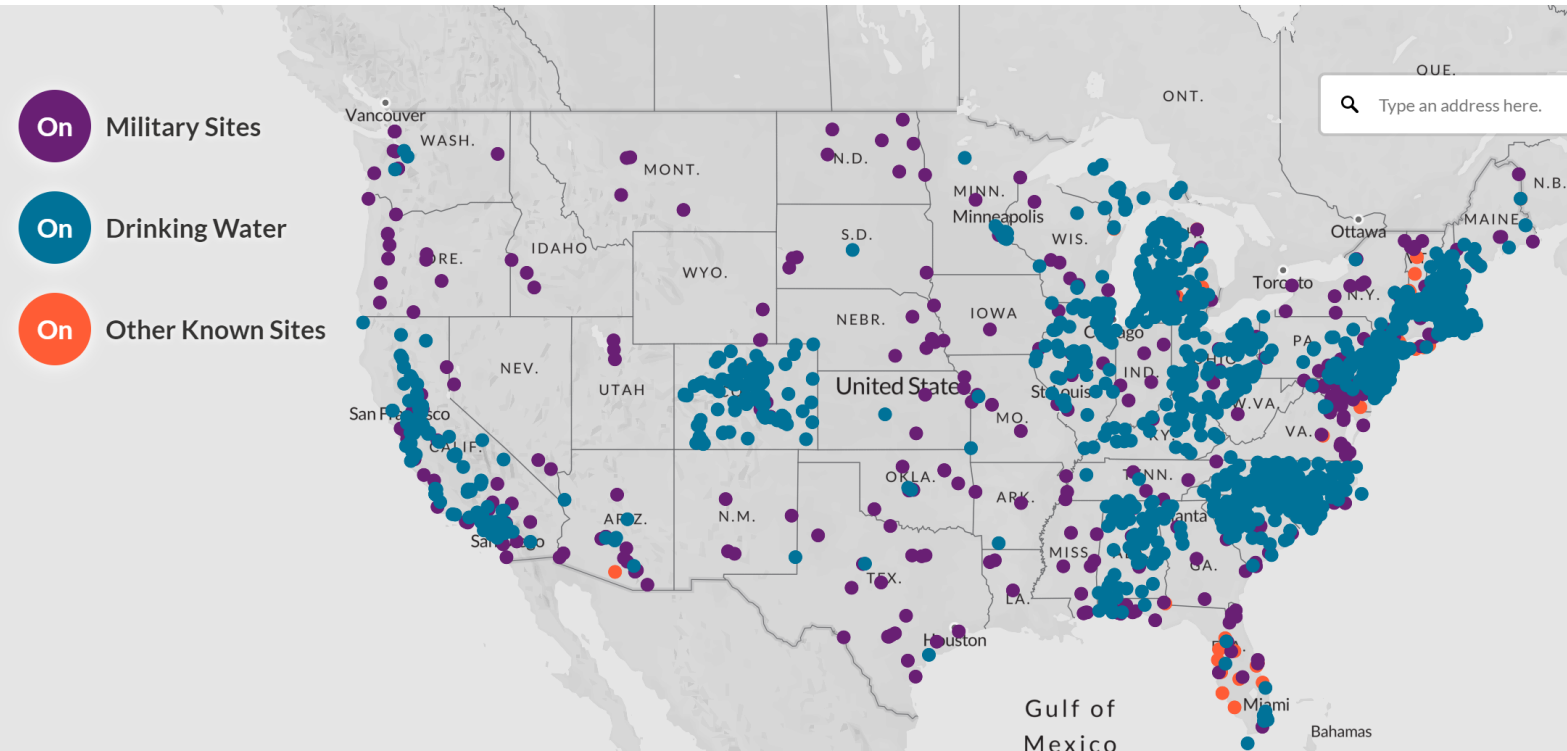
- PFAS sources in the environment:
 - **Aqueous film forming foams (AFFF)** for firefighting activities at DoD sites, commercial airports, and industrial facilities
 - Industrial spills and dumping
 - Wastewater effluents
 - Leaky landfill
 - Disposal of household products
- Current drinking water health 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.



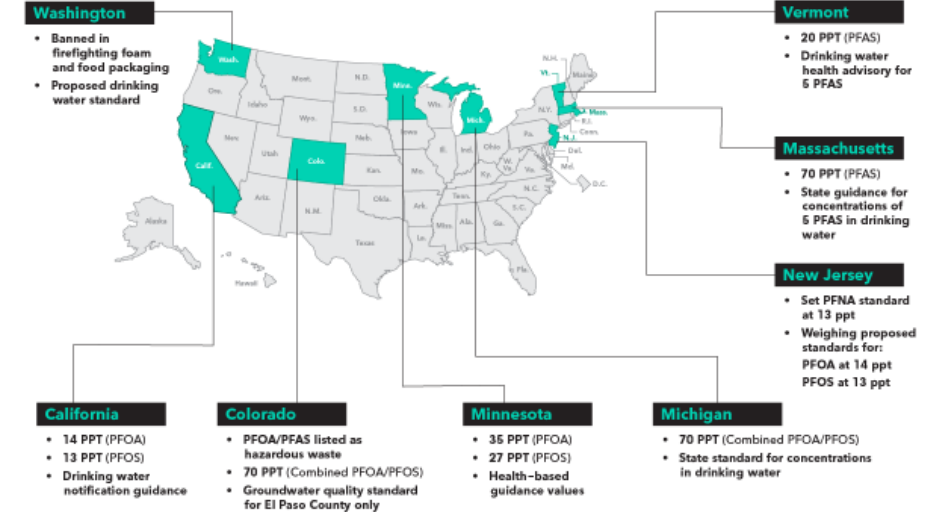
[Source: midwestadvocates.org](http://midwestadvocates.org)

PFAS contaminated sites: Current status

October 2021



States With Numerical PFAS Limits



Source: Bloomberg Environment

Source: ewg.org

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/H₂O₂/O₃) – 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, 2}

Literature gap:

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

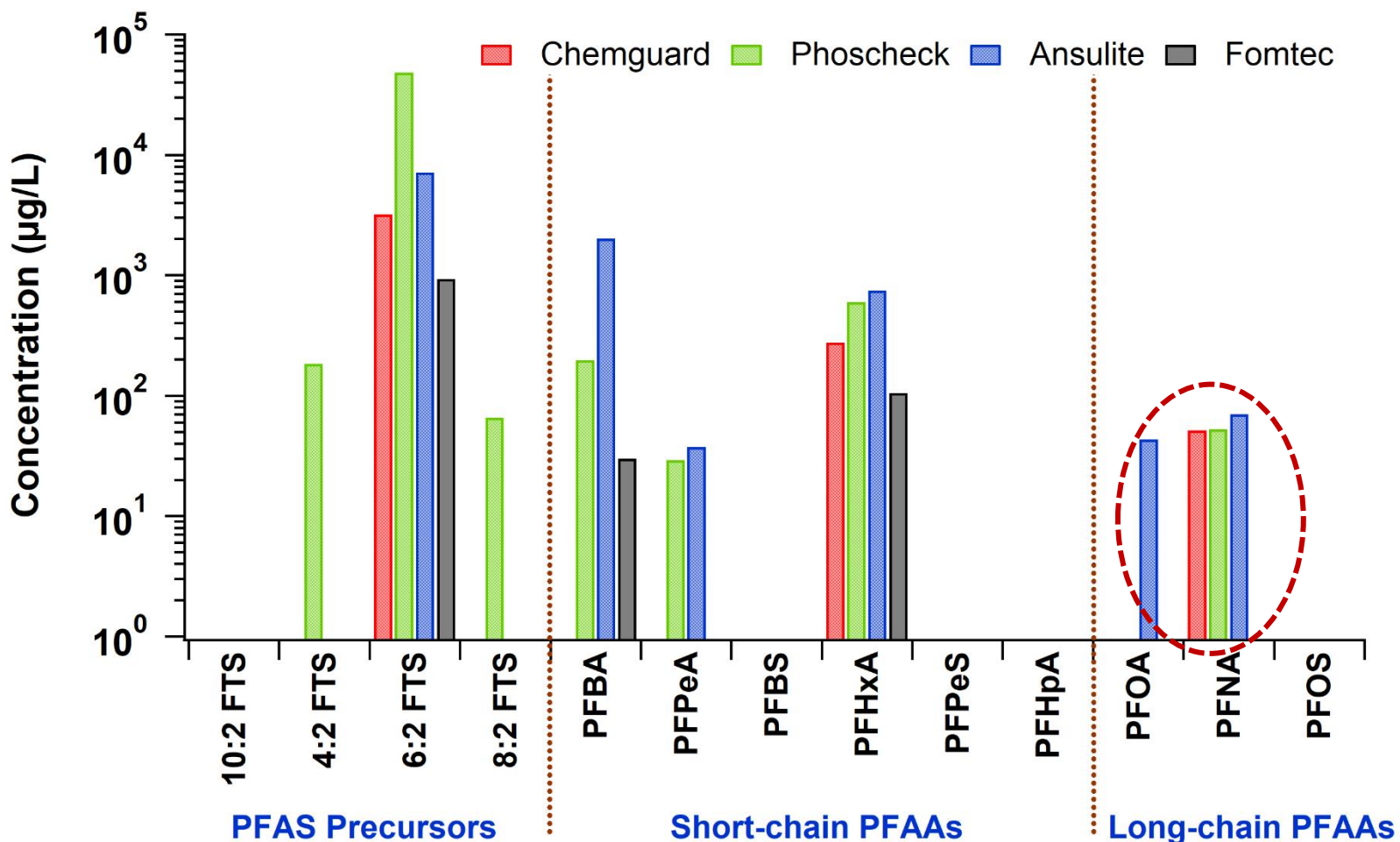
Rationale:

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

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

²Singh et al., (2019) *Environmental Science & Technology*, 53, 2731 – 2738

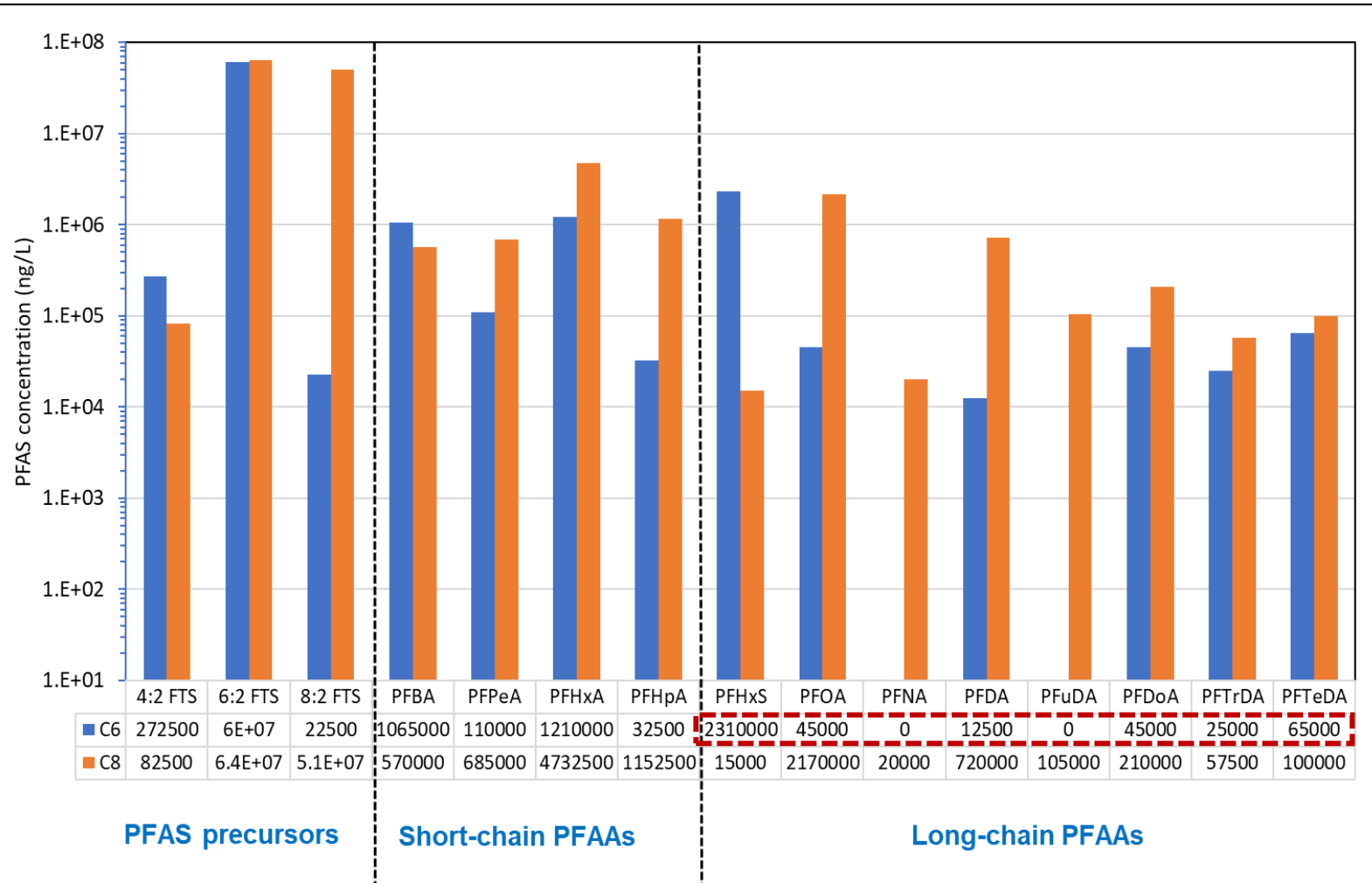
C6 AFFF Characterization



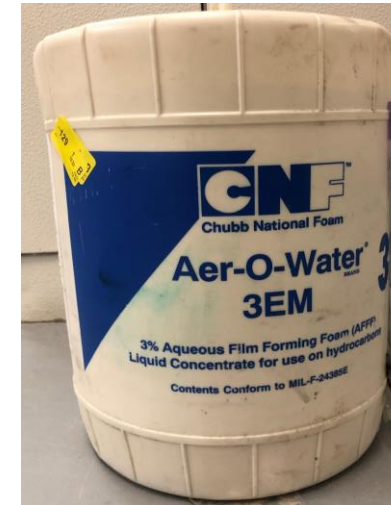
	Total fluorine (mM)	TOP (mM)
Chemguard	230	11
Phoscheck	200	6
Ansolite	320	40
Fomtec	-	12

TOP – Total Oxidizable Precursors

Comparison between C8 and C6 AFFF



C6 Foam



C8 Foam

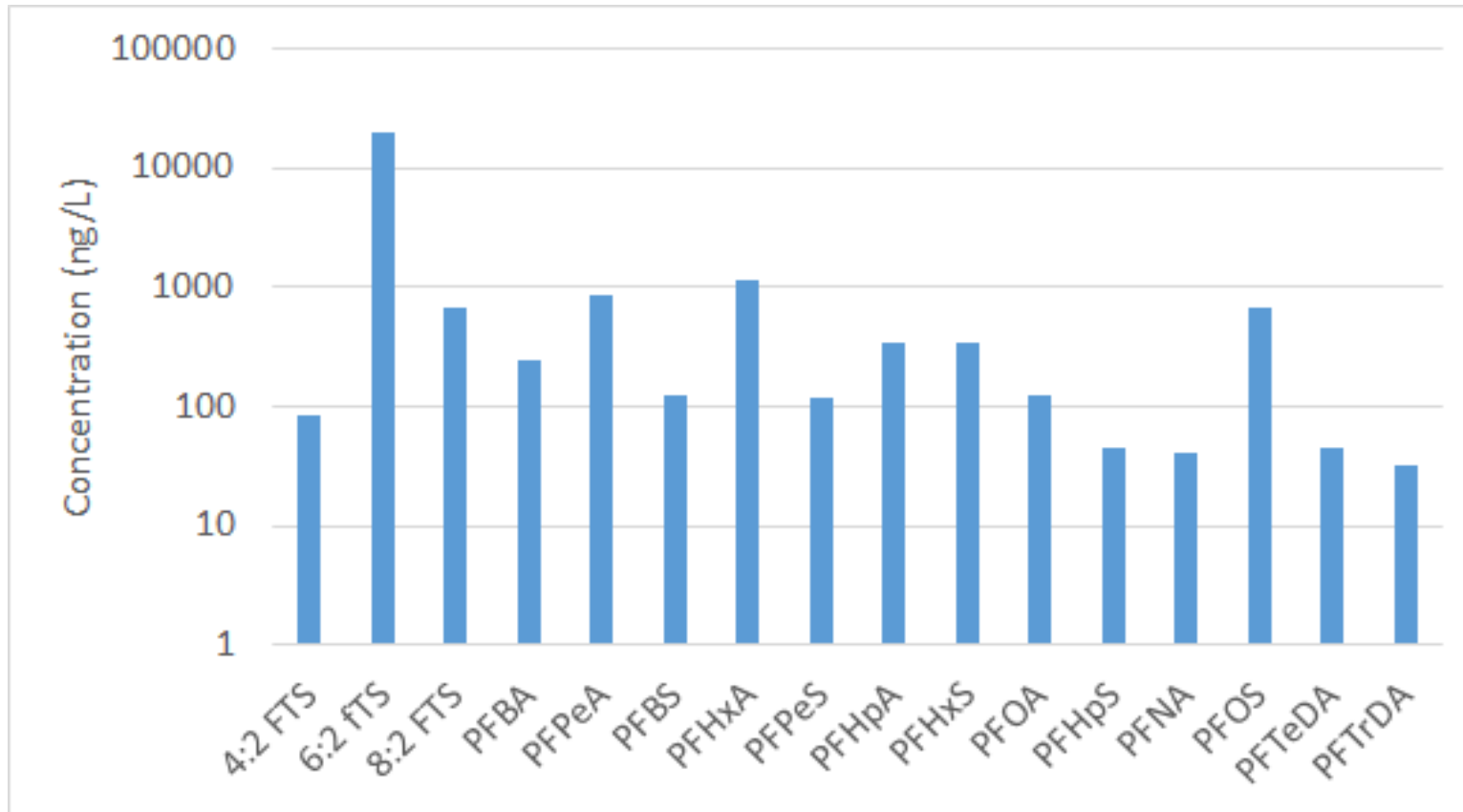


	TF (mM)	TOP (mM)
Phos-Chek 3% AFFF MilSpec (C6)	68	21
Aer-O-Water 3EM (C8)	55	22.3

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



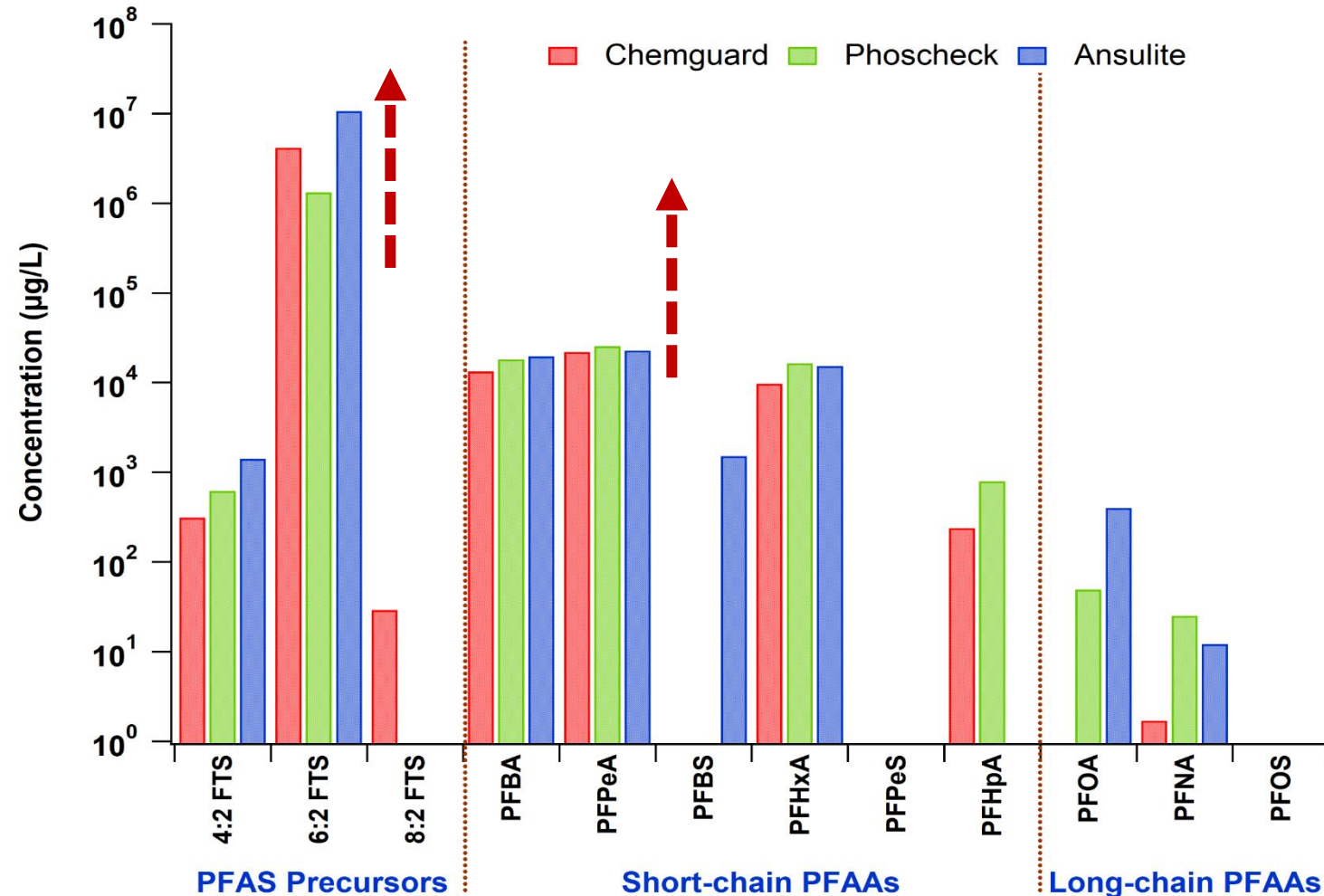
PFAS precursors, Long- and short-chain PFAAs were detected in rinsate sample.

6:2 FTS detected in highest concentration.

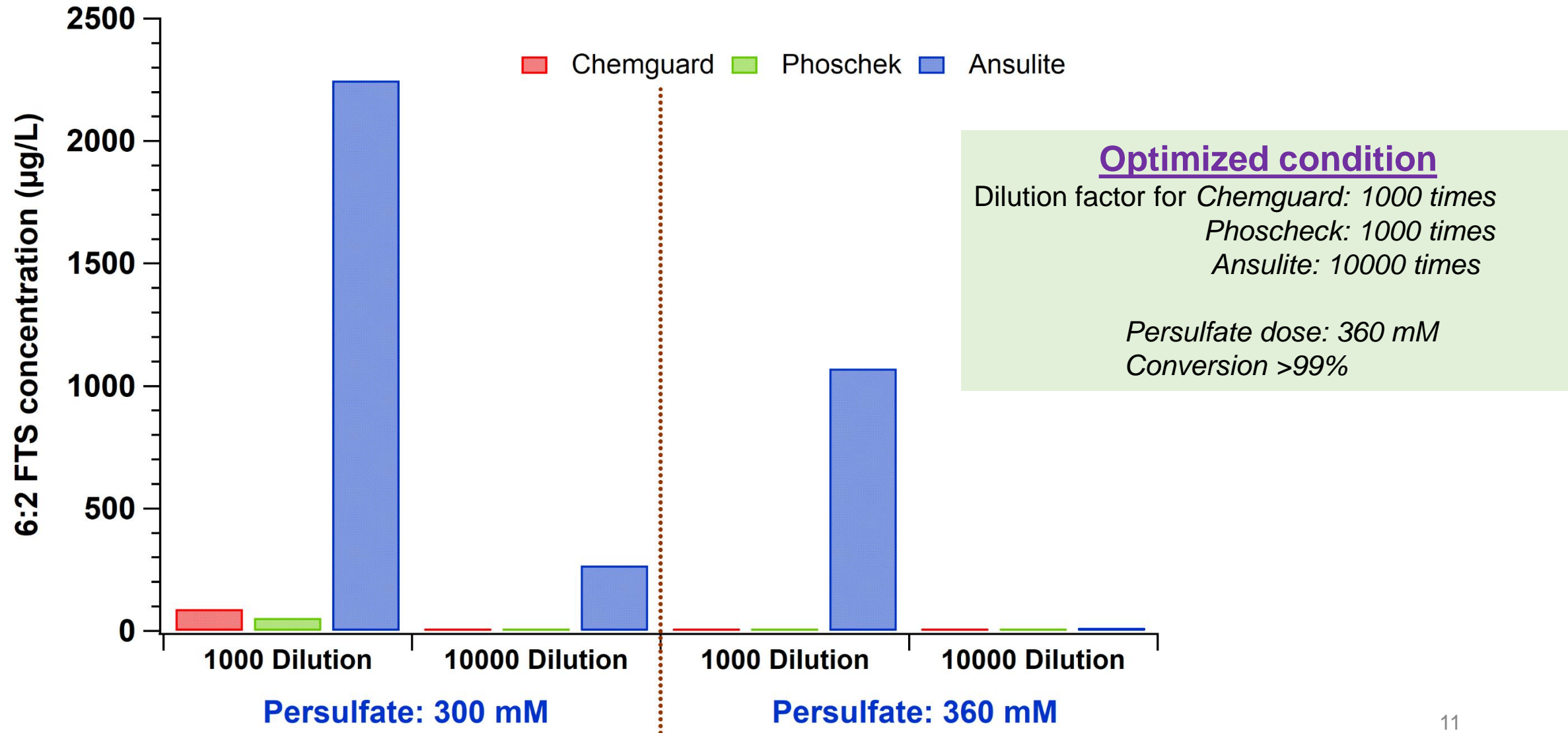
What happen upon oxidation of AFFF?

Effect of dilution prior to heat-activated persulfate oxidation

100x diluted samples

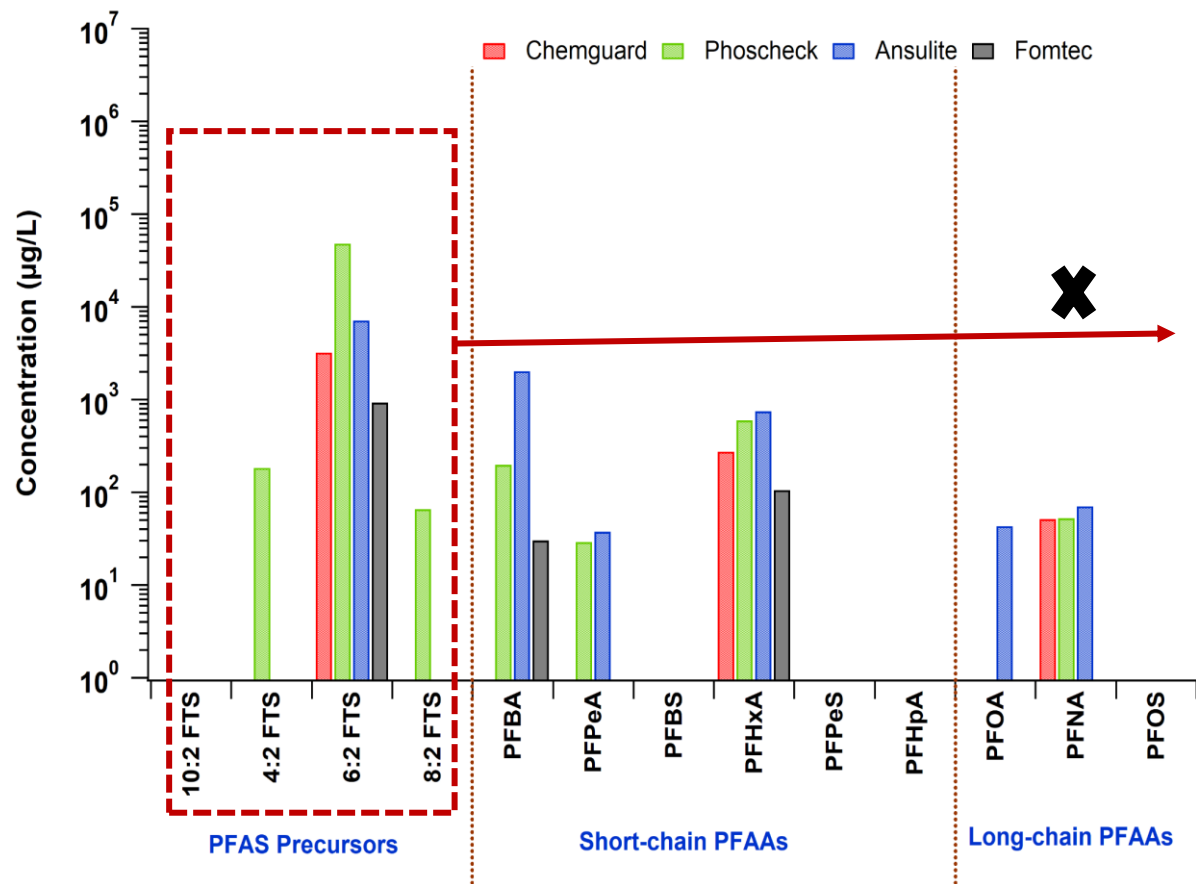


Optimization of heat-activated persulfate oxidation

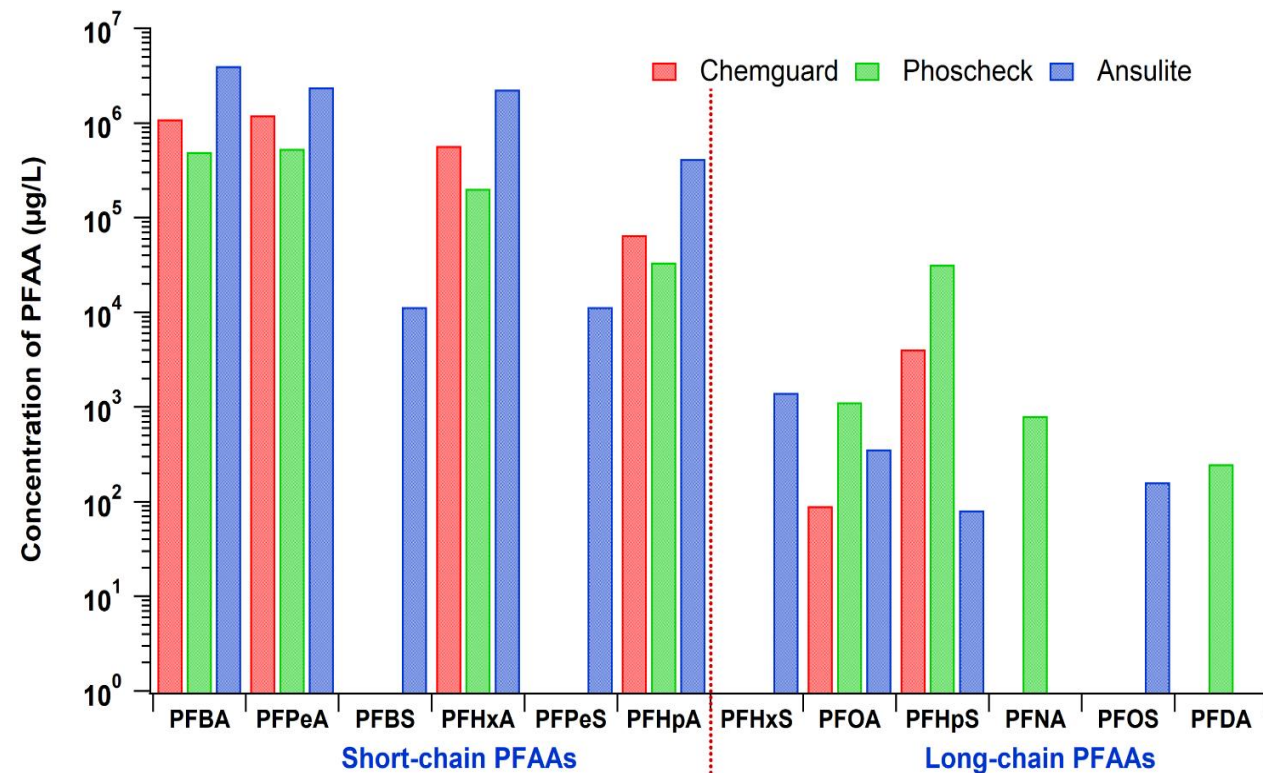


PFAS concentrations in pre- and post-oxidized AFFF samples

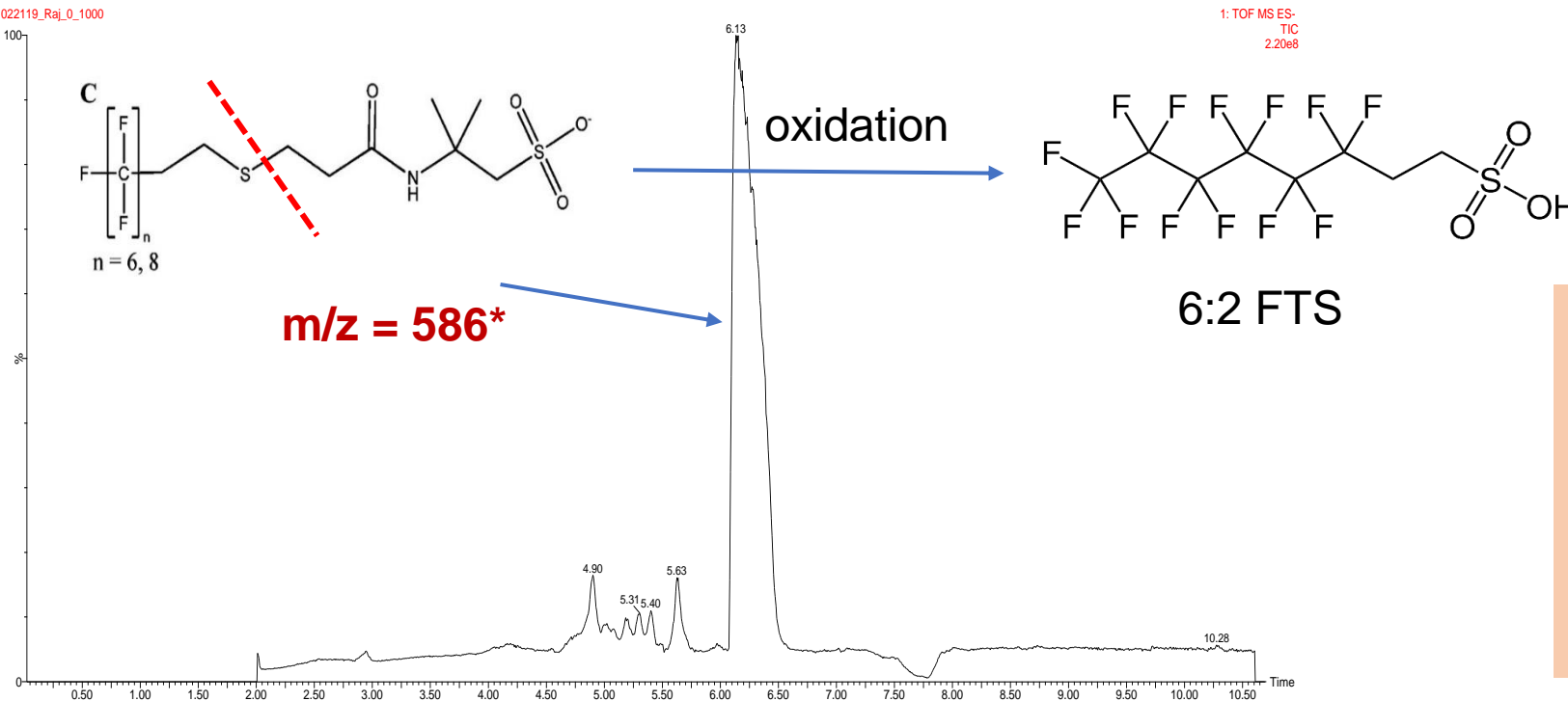
Pre-oxidation



Post-oxidation



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



Unknown compounds of detected mass (m/z)

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 Ansilite (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

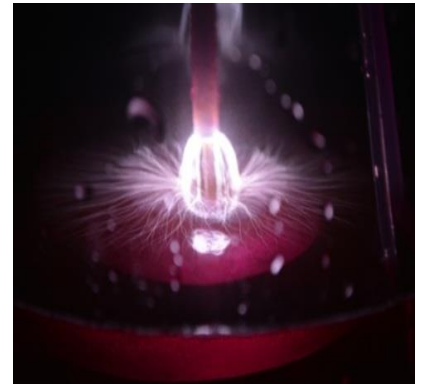
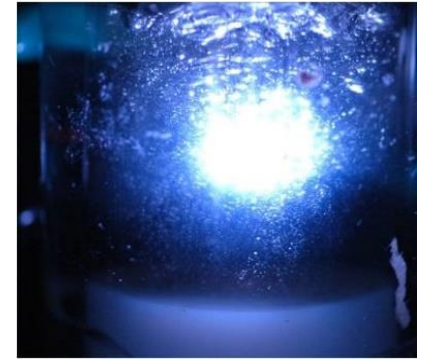
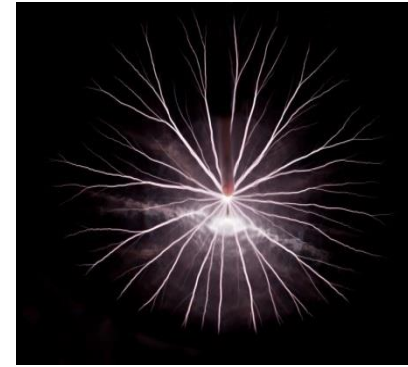
- Oxidant dose
- Dilution factor
- Treatment time

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*.



Pictures: Plasma Research Laboratory, Clarkson University

Advanced oxidation process (AOP)

Oxidative species
($\cdot\text{OH}$, O , H_2O_2 , O_2 , $\cdot\text{HO}_2$)

Reductive species
(e_{aq}^- , e^- , H)

Can oxidize and reduce organic and inorganic compounds

Physical effect
(UV, electric field, shock wave, locally high temperature)

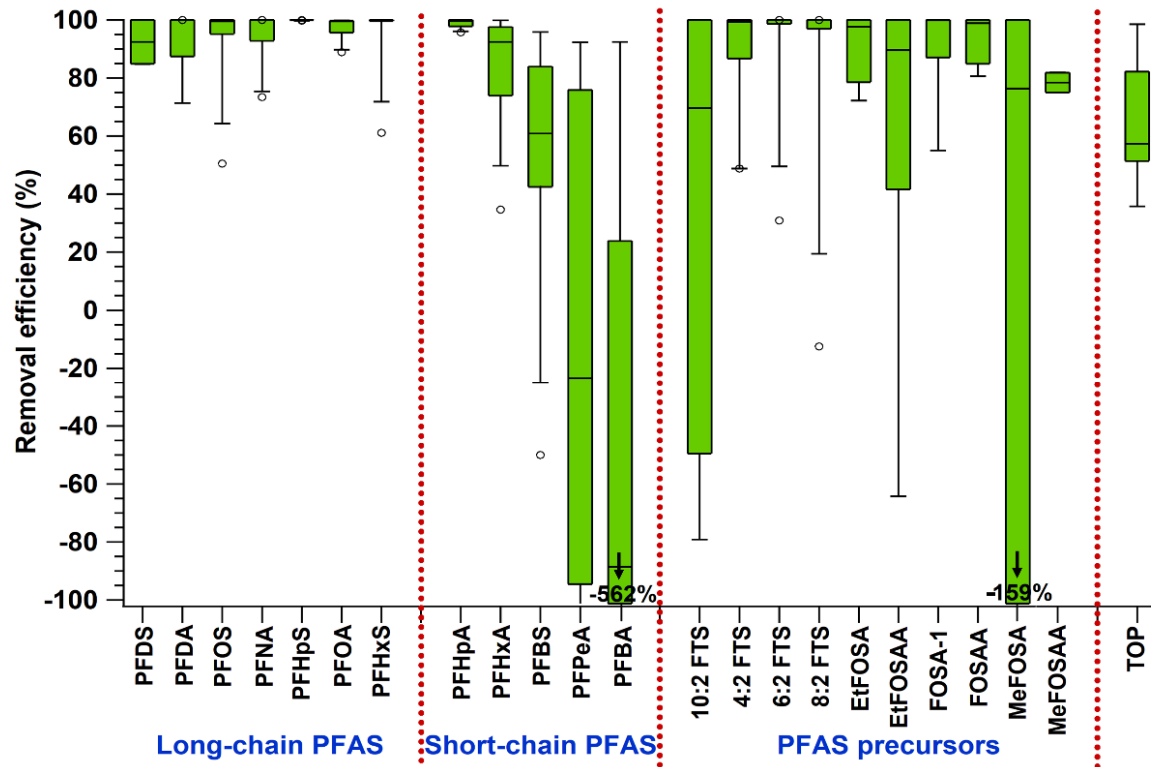
Plasma

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

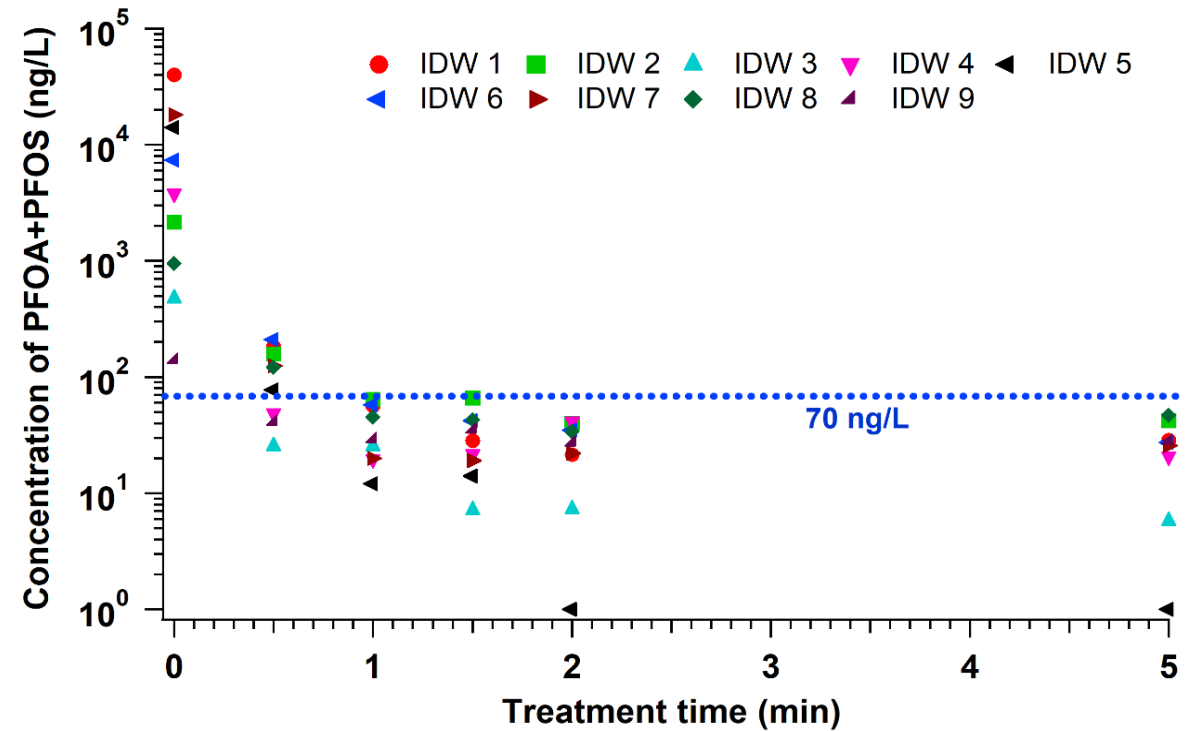
Performance of Pilot-scale Plasma Reactor

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

Removal efficiency



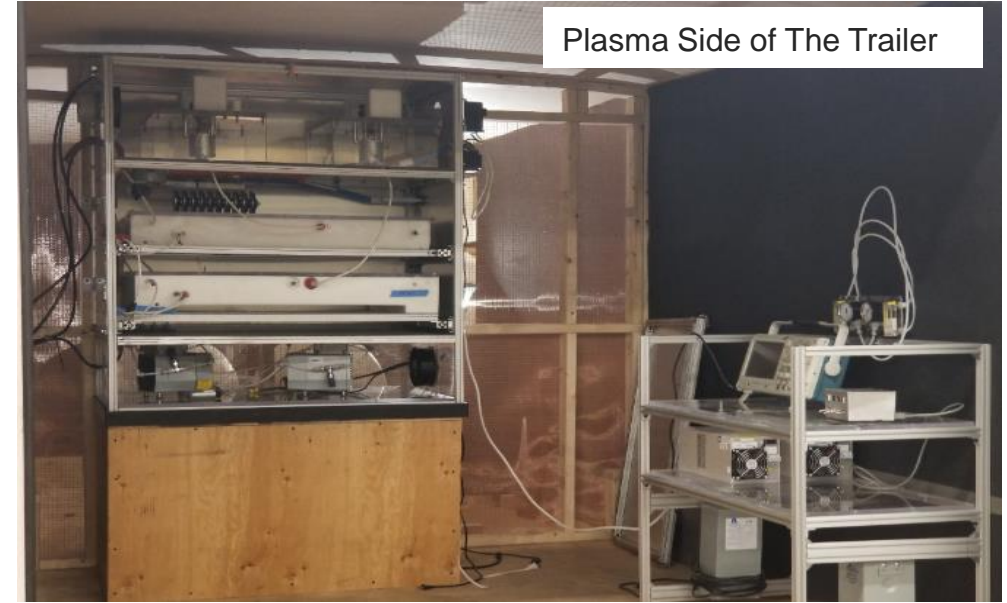
PFOA and PFOS removal



TOP – Total Oxidizable Precursors

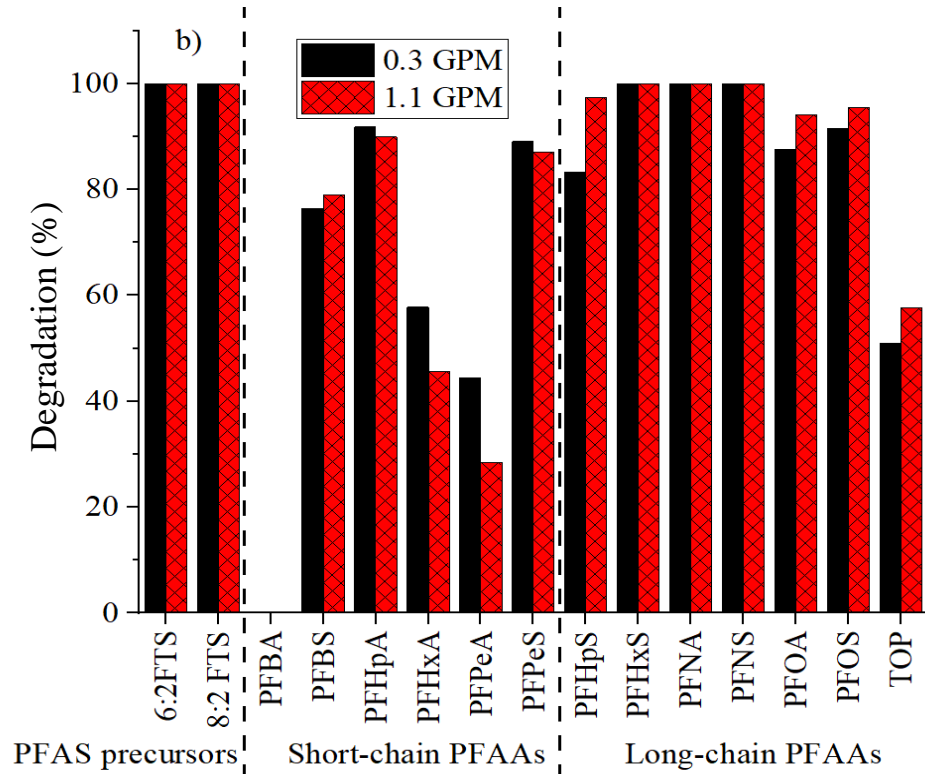
Within 1 minute, PFOA and PFOS was degraded to below USEPA health advisory concentration (70 ng/L)

Mobile Plasma Trailer



Field Demonstration

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



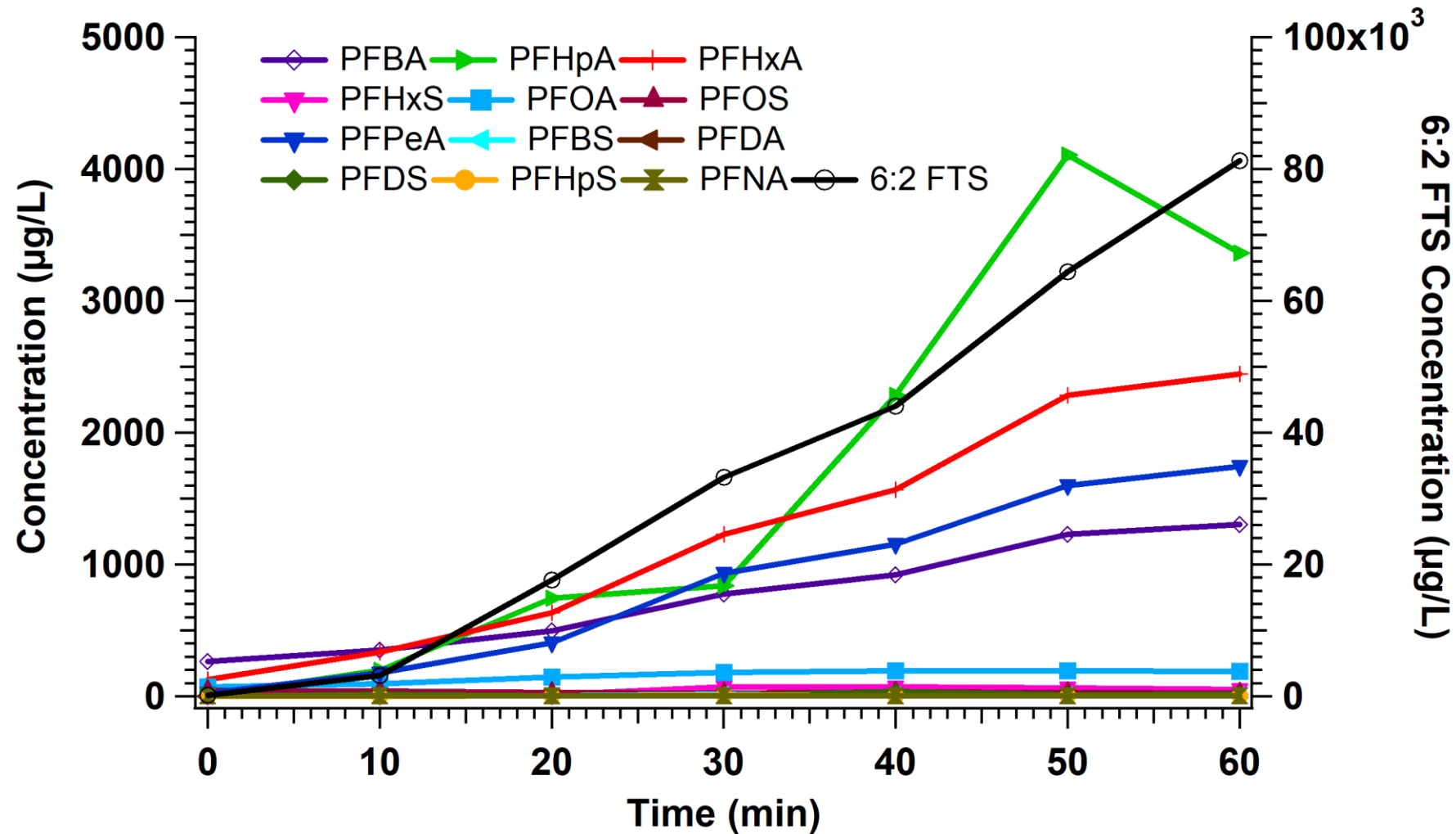
Trailer Performance: Energy cost

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

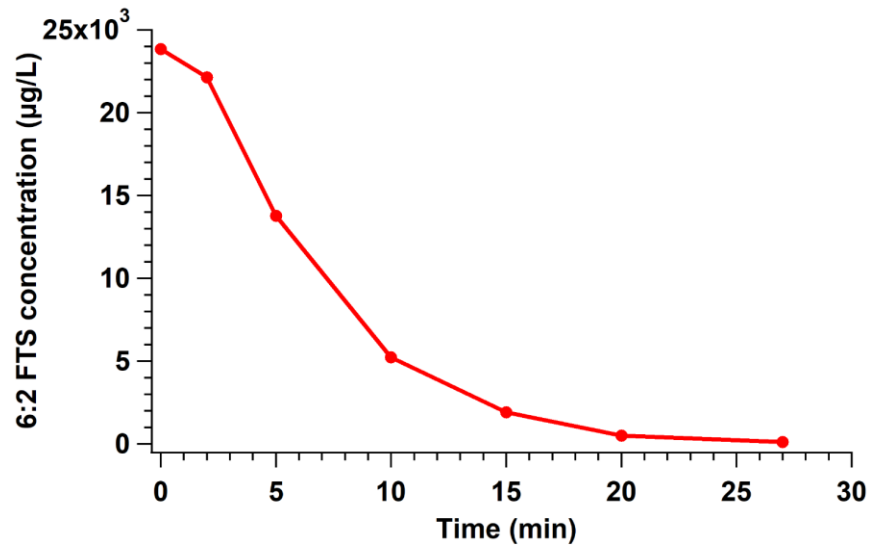
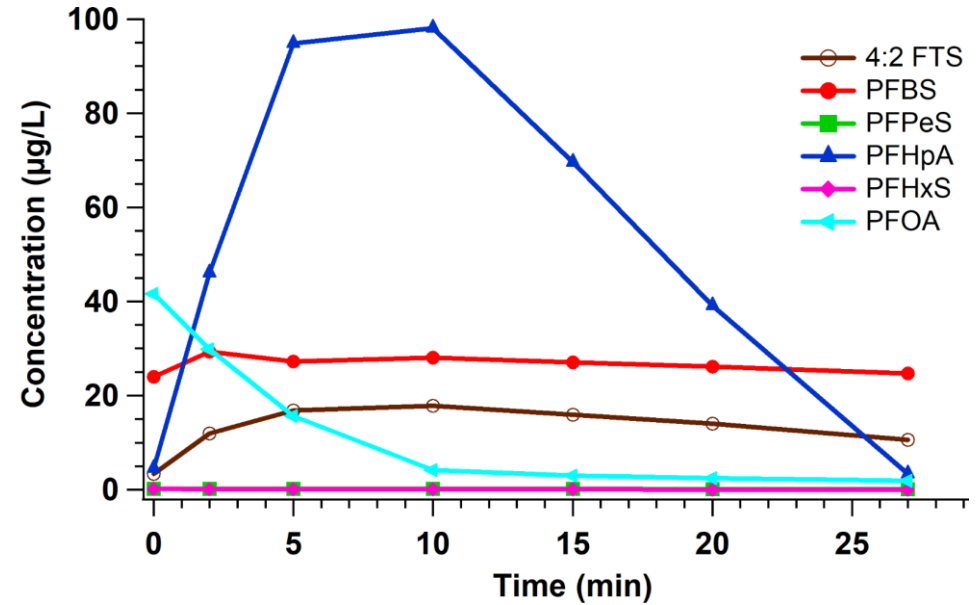
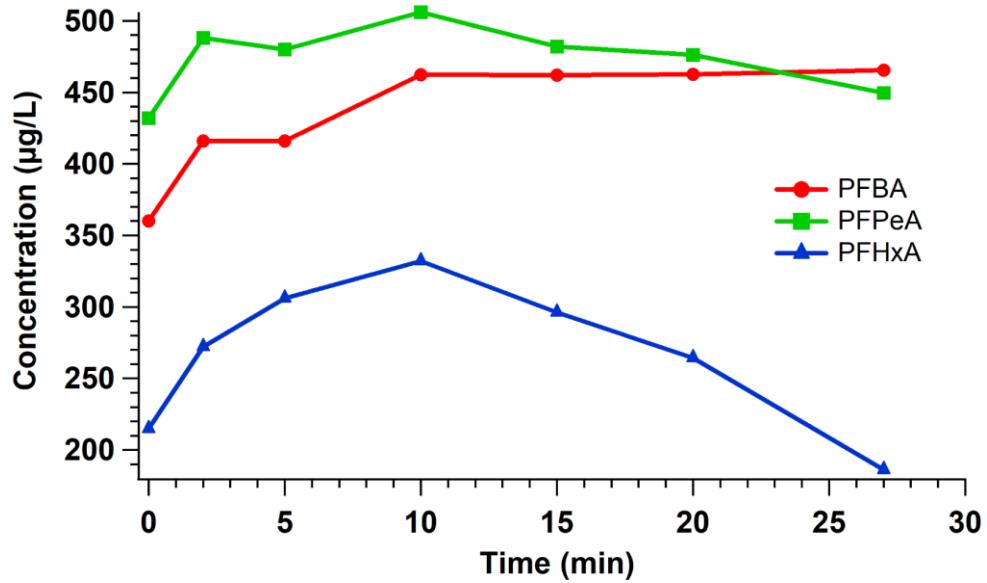
Test	Energy required (kWh)	Total cost	Cost/cycle	Cost/gallon
Well B				
0.3 gpm	4 (4 cycles)	\$ 0.48		
0.6 gpm	1 (1 cycle)	\$ 0.12	\$ 0.12/cycle	\$0.0067/gal
0.9 gpm	1 (1 cycle)	\$ 0.12		
Well C				
0.3 gpm	3 (3 cycles)	\$ 0.36		
1.1 gpm	2 (2 cycles)	\$ 0.24	\$ 0.12/cycle	\$ 0.0067/gal

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

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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