Rapid removal of poly- and perfluorinated compounds (PFAS) from aqueous streams by electrical discharge plasma

Selma Mededovic Thagard[1], Thomas Holsen[1], Poonam Kulkarni[2] and Stephen Richardson[2]

[1]Clarkson University, Potsdam, New York, USA

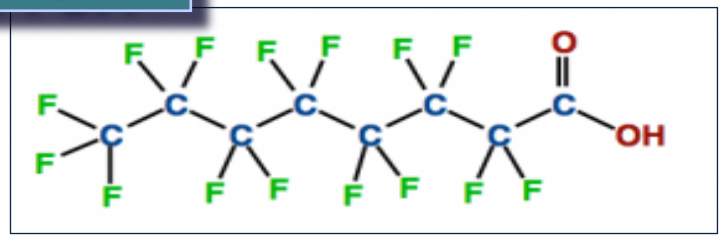
[2]GSI Environmental Inc., Texas, USA

SERDP • ESTCP SYMPOSIUM 2019 | Enhancing DoD's Mission Effectiveness

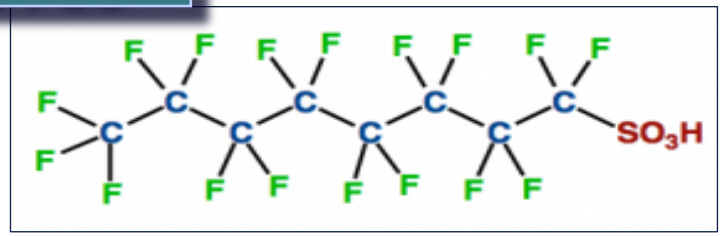
Background

- Historical use of aqueous film forming foams containing PFAS for firefighting and training activities at DoD sites, commercial airports and industrial facilities.
- Potential for groundwater contamination at up to 600 sites.
- PFOA/PFOS concentrations measured in groundwater at several AF bases are often ***several orders of magnitude higher*** than federal drinking water health advisories.
- PFAS are difficult to remove using traditional treatment approaches.
- PFAS are ***very recalcitrant*** because of the stability of the C-F bond.

PFOA



PFOS

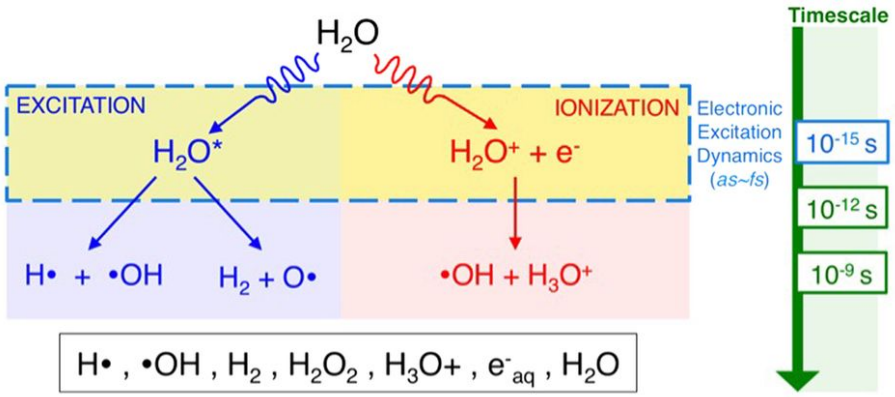


SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

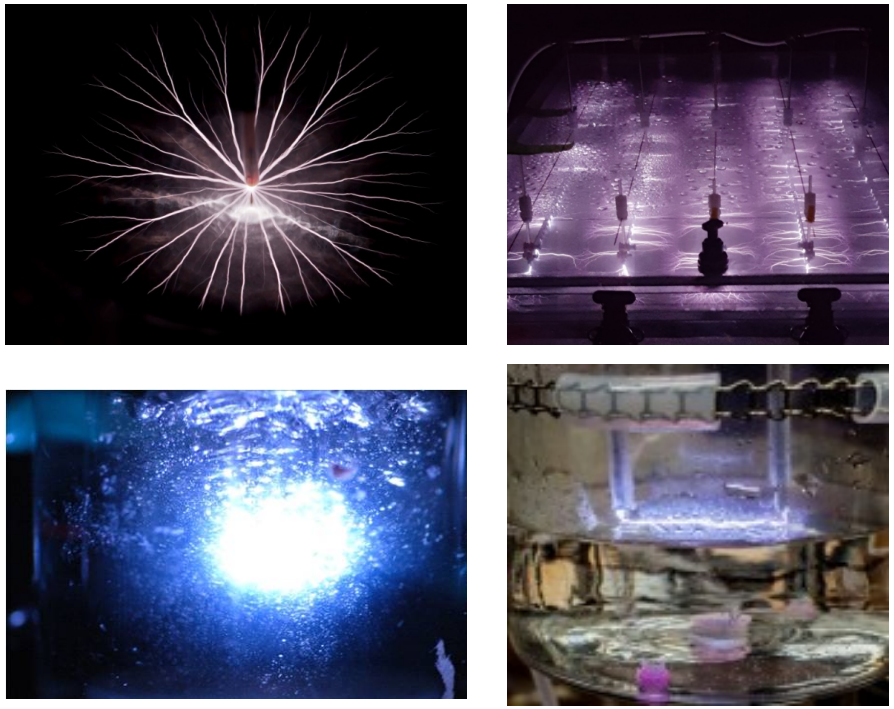
Plasma-based Water Treatment

Plasma-based water treatment uses electricity to convert water into a mixture of highly reactive species (i.e., plasma) that rapidly and non-selectively degrade recalcitrant organic contaminants.

Electrical discharge plasma formed *directly in* or *above* water makes use of OH radicals to oxidize and aqueous electrons to chemically reduce organic and inorganic compounds.



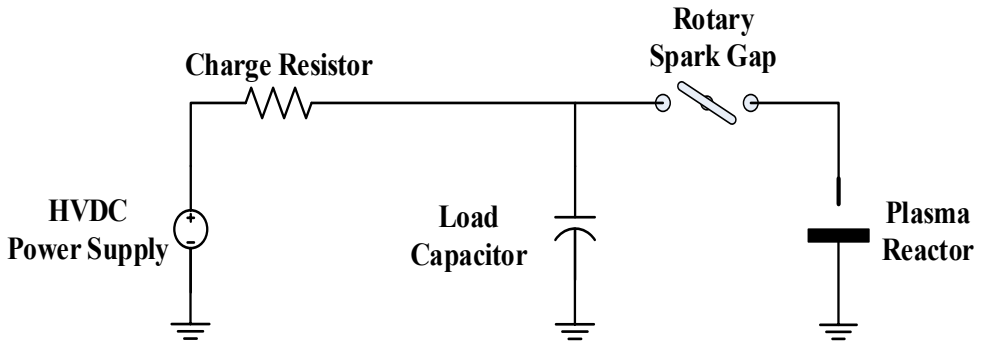
https://www.nature.com/articles/srep40379



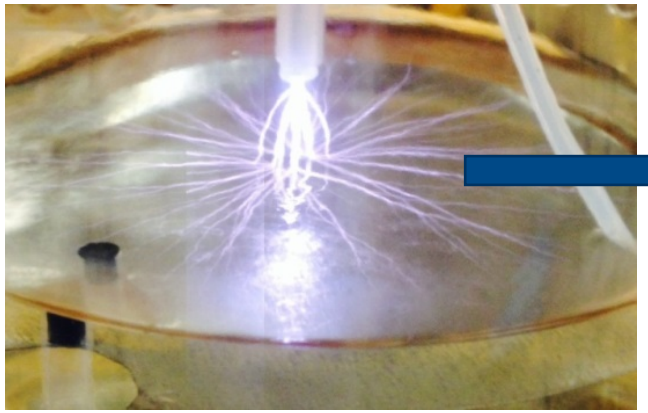
Pictures courtesy of Plasma Research Laboratory, Clarkson University

SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

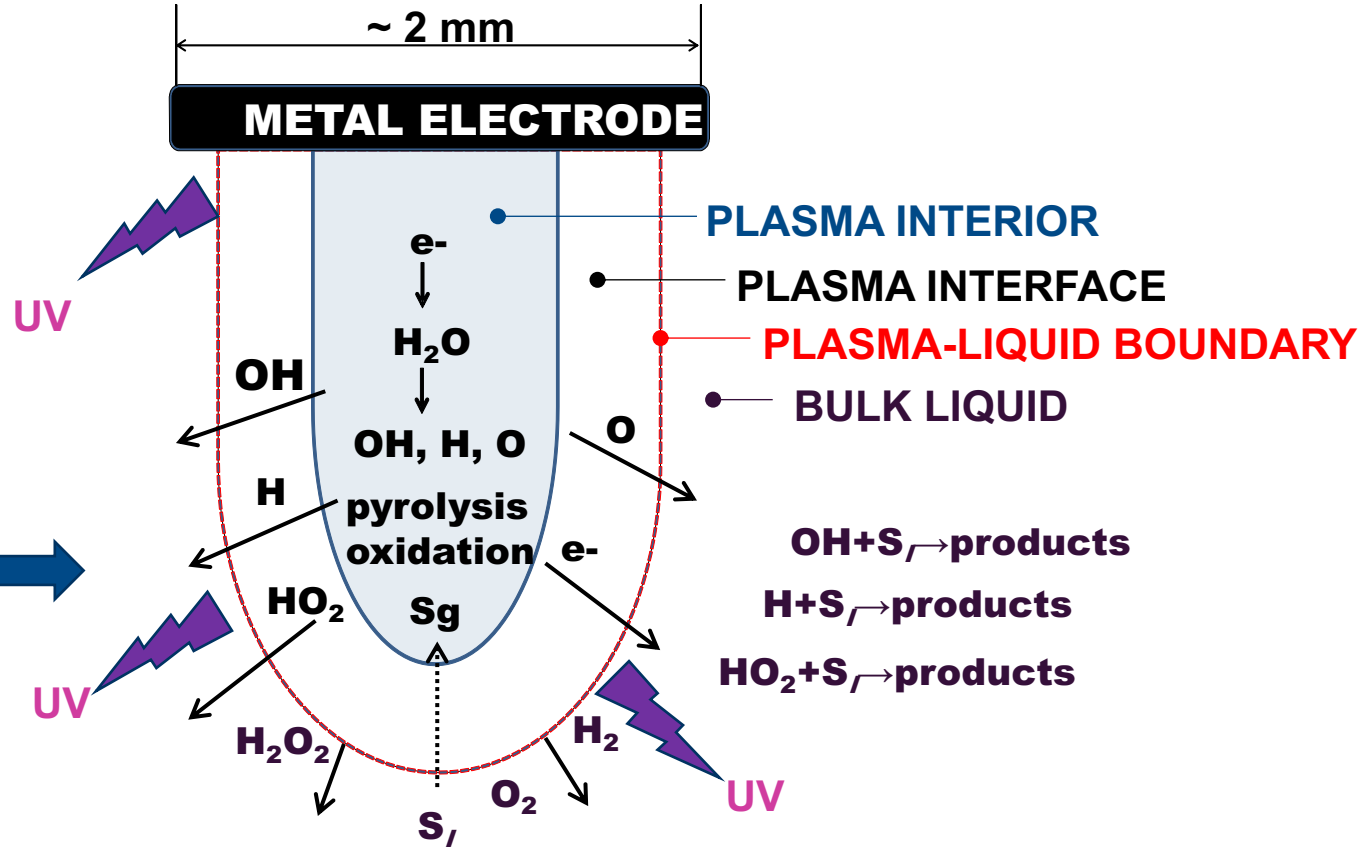
Plasma Formation



Circuit diagram for a pulsed power supply

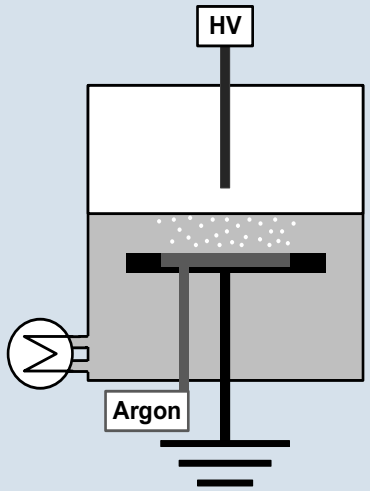


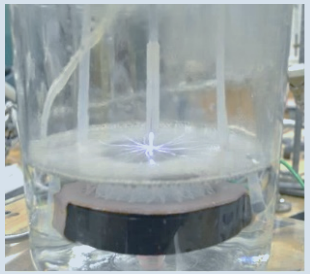
Plasma in argon gas contacting water

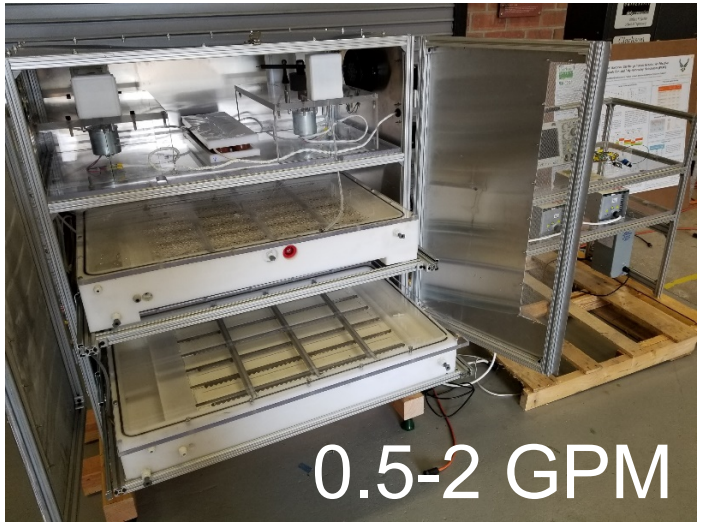


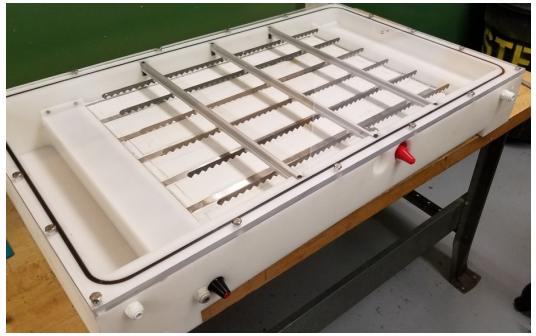
S_l =liquid solute S_g =gas solute

Plasma PFAS Treatment



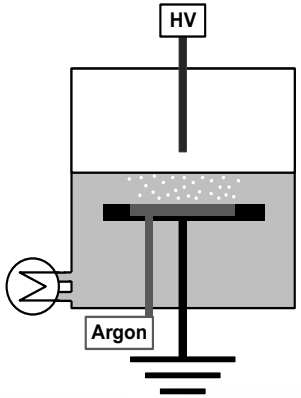


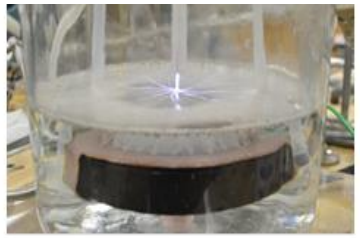


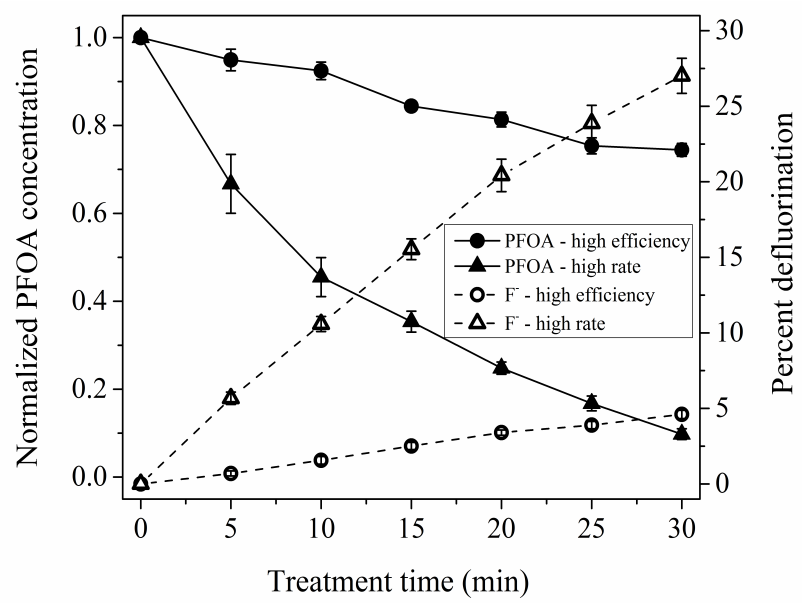


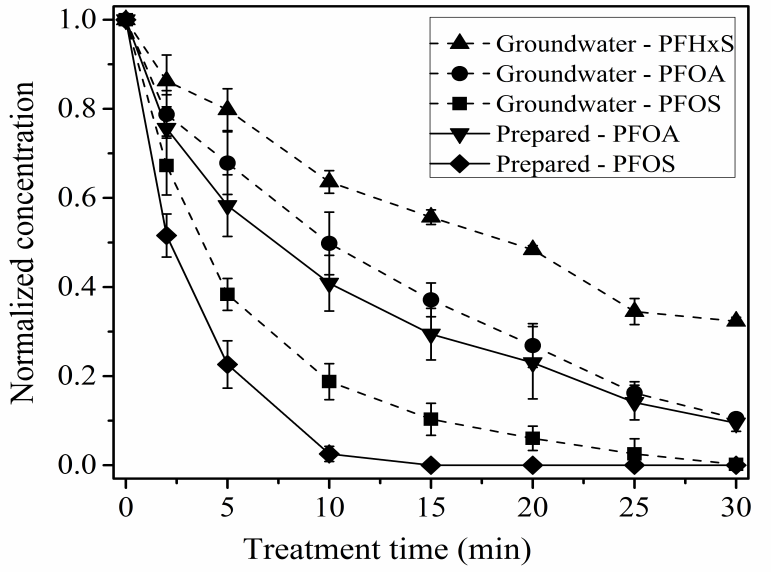
Selma Mededovic Thagard, Gunnar Stratton, Christopher Bellona, and Thomas Holsen, Enhanced Contact Electrical Discharge Plasma Reactor for Liquid and Gas Processing, US Patent Number 10, 357, 753 B2, Issued on July 23, 2019.

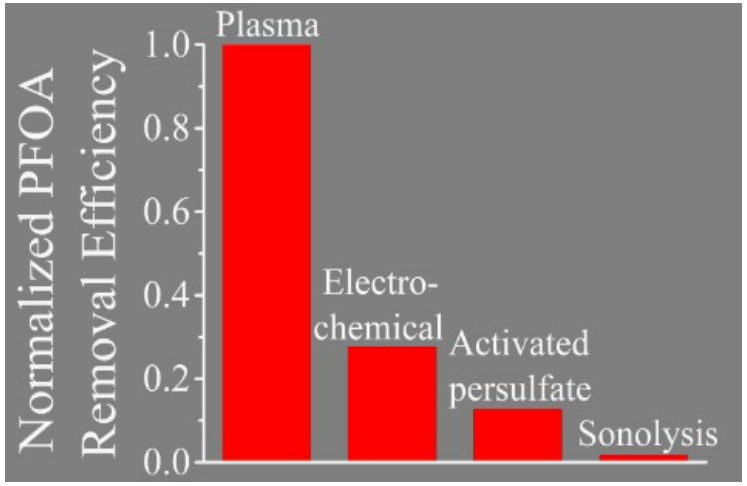
Bench-scale Degradation of PFOA and PFOS in the Enhanced Contact Plasma Reactor





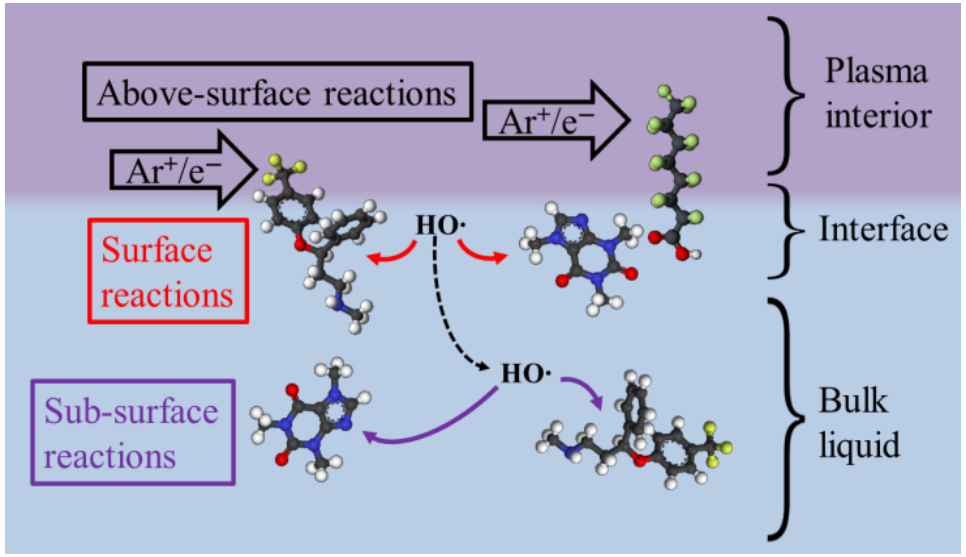


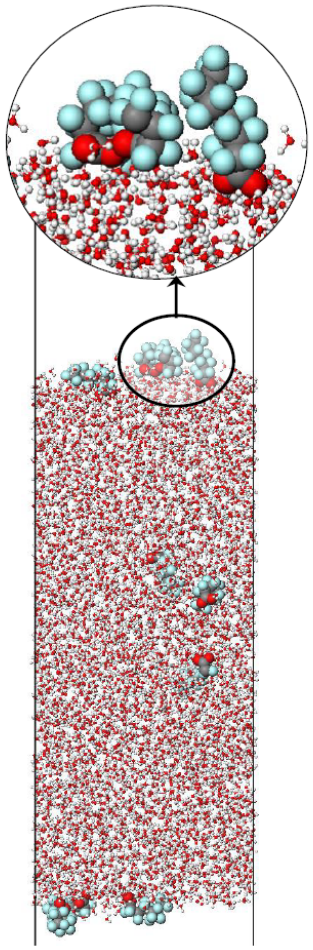


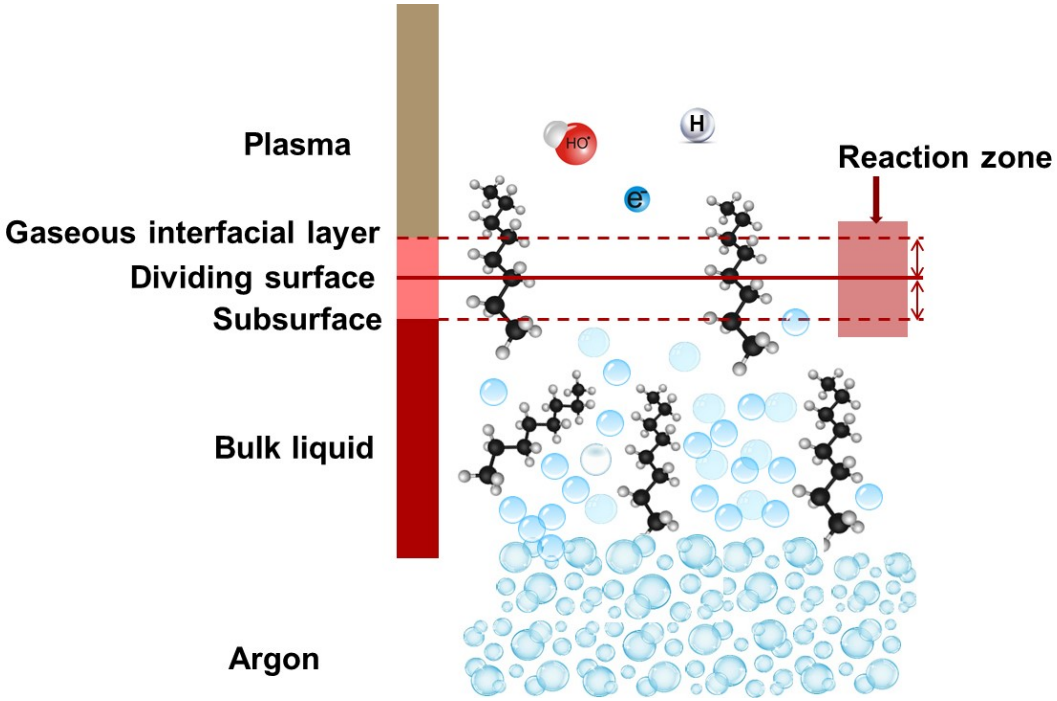


Stratton, G.R., Dai, H., Bellona, C.L., Holsen, T.M., Dickenson, E.R.V., Mededovic Thagard, S. (2017). Plasma-based water treatment: Demonstration of efficient perfluorooctanoic acid (PFOA) degradation and identification of key reactants. *Environmental Science & Technology*, 51, 1643-1648.

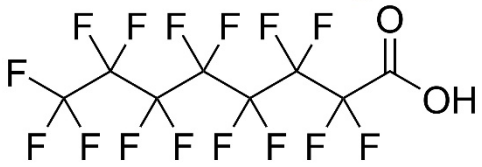
Mechanism of PFOA and PFOS Degradation and Liquid and Gas Byproducts







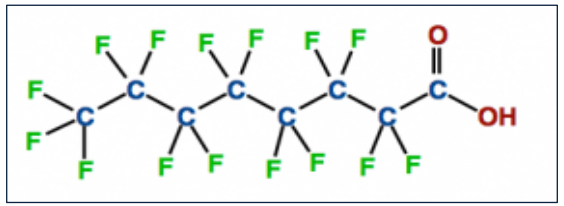
PFOA



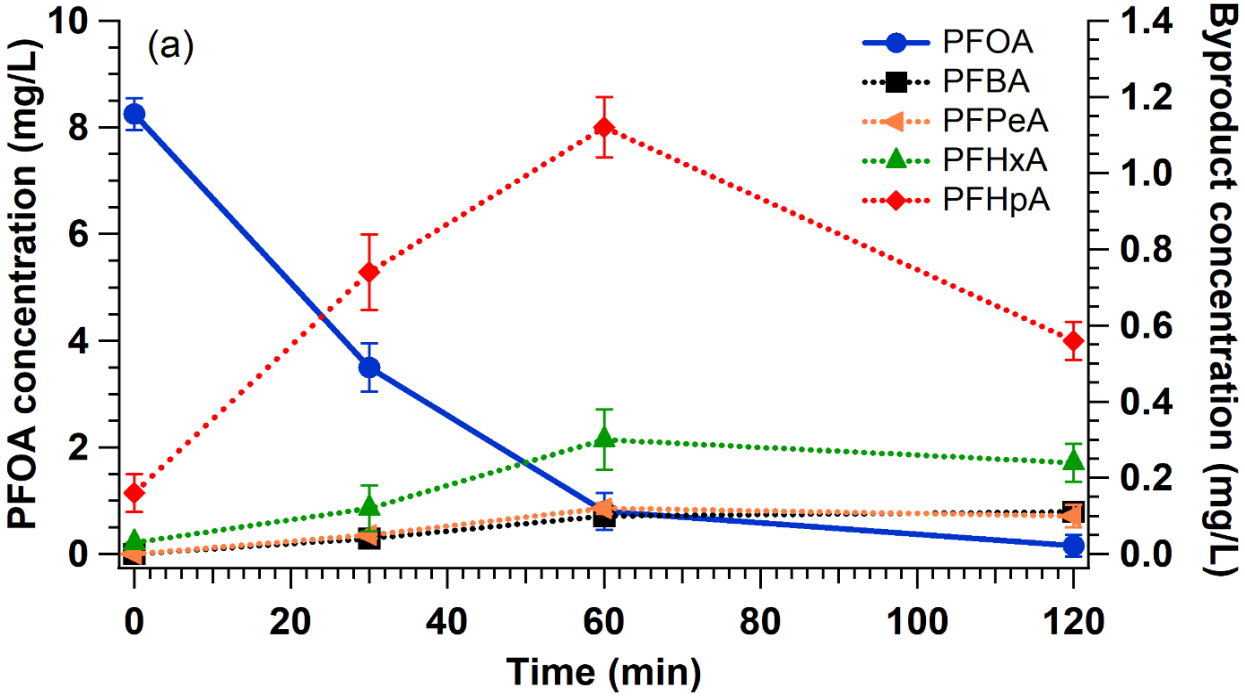
> 98% of PFOA at the interface protrudes out into the plasma

SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

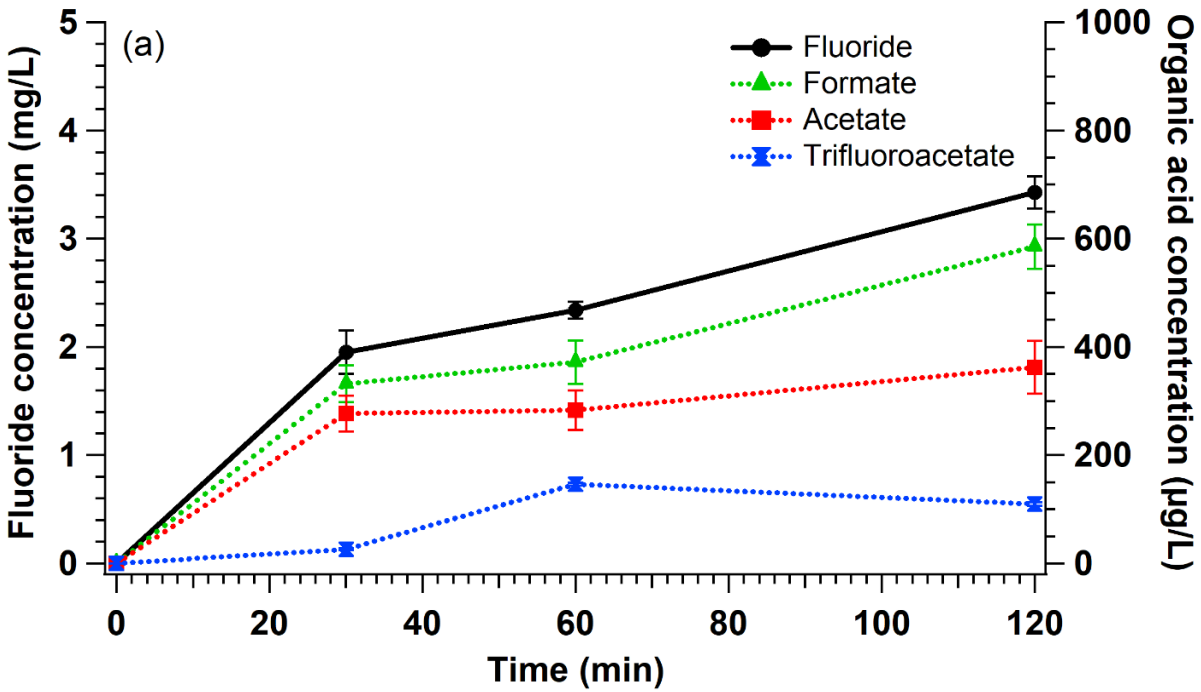
Liquid Byproducts - PFOA



PFAA byproducts



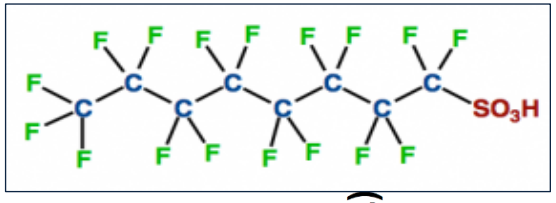
Non-PFAA byproducts



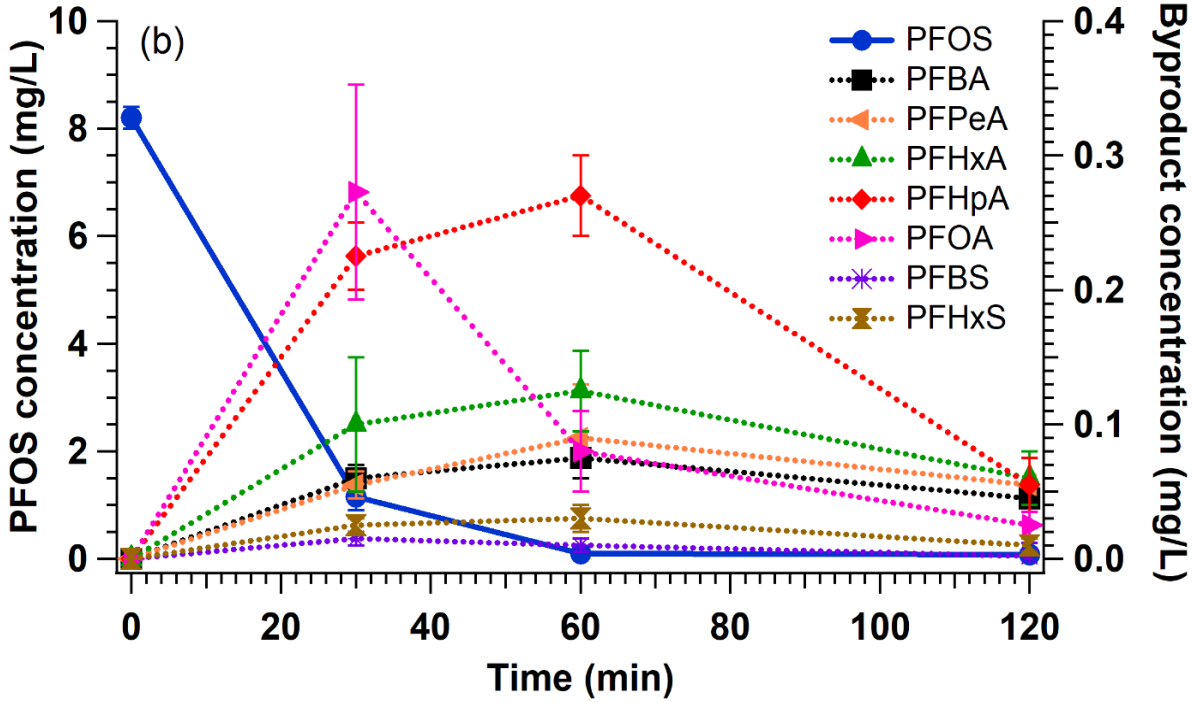
F in organic byproducts ~ 10% of initial F (PFOA)

Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

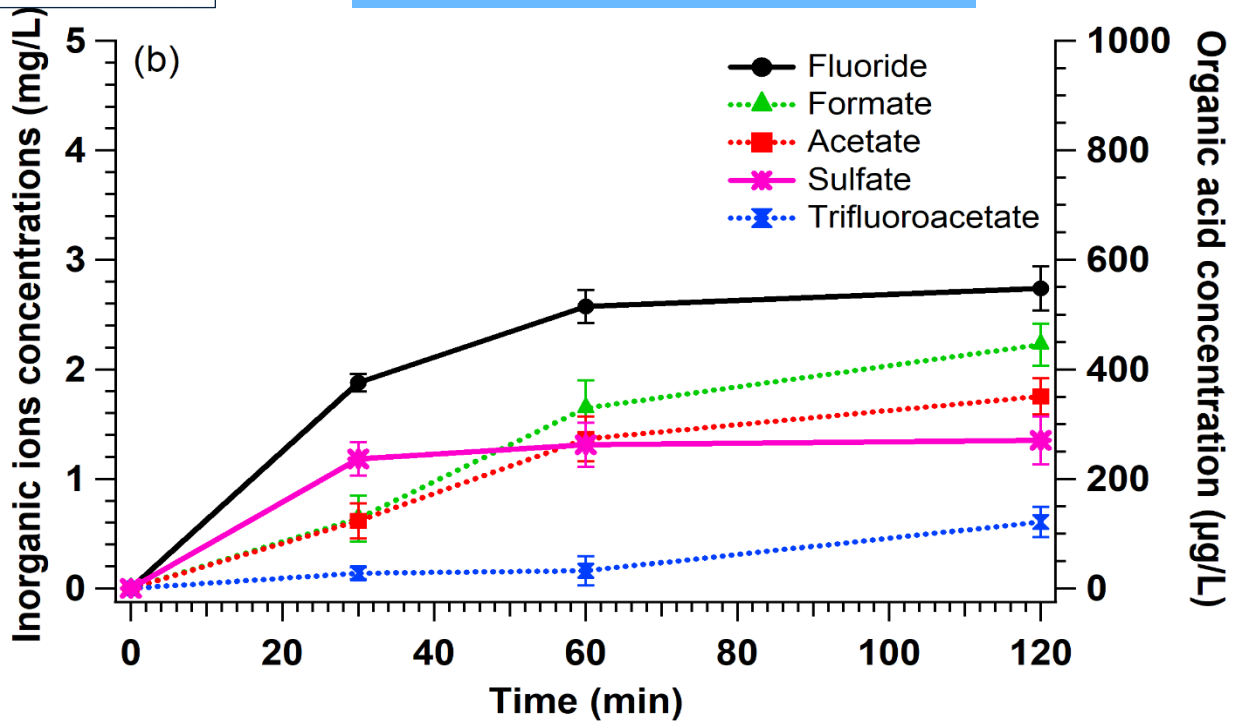
Liquid Byproducts - PFOS



PFAA byproducts



Non-PFAA byproducts

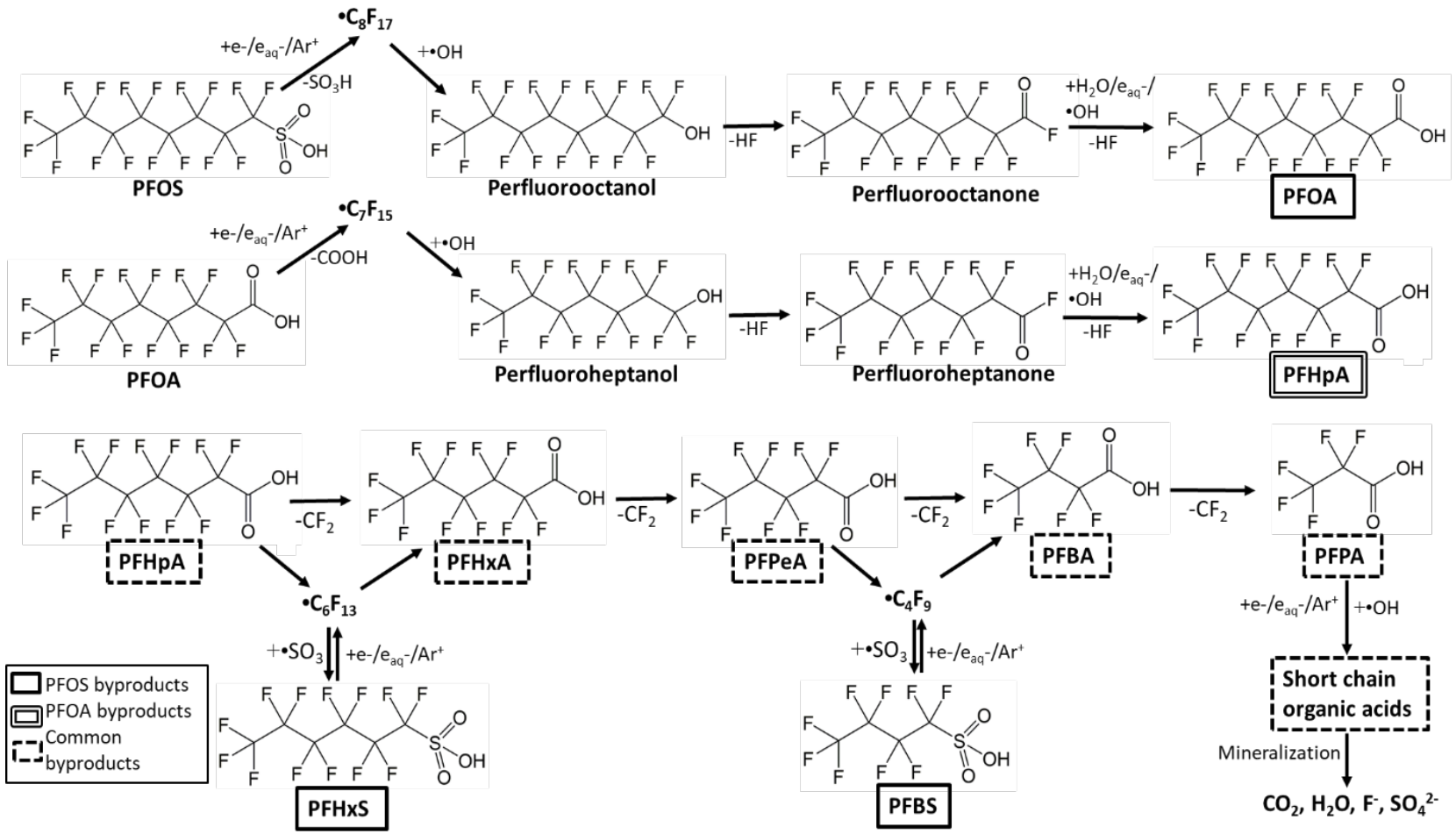


F in organic byproducts < 2% of initial F (PFOS)

85% of the theoretical sulfate that could be produced from the oxidation of sulfur present in 8.3 mg/L of PFOS

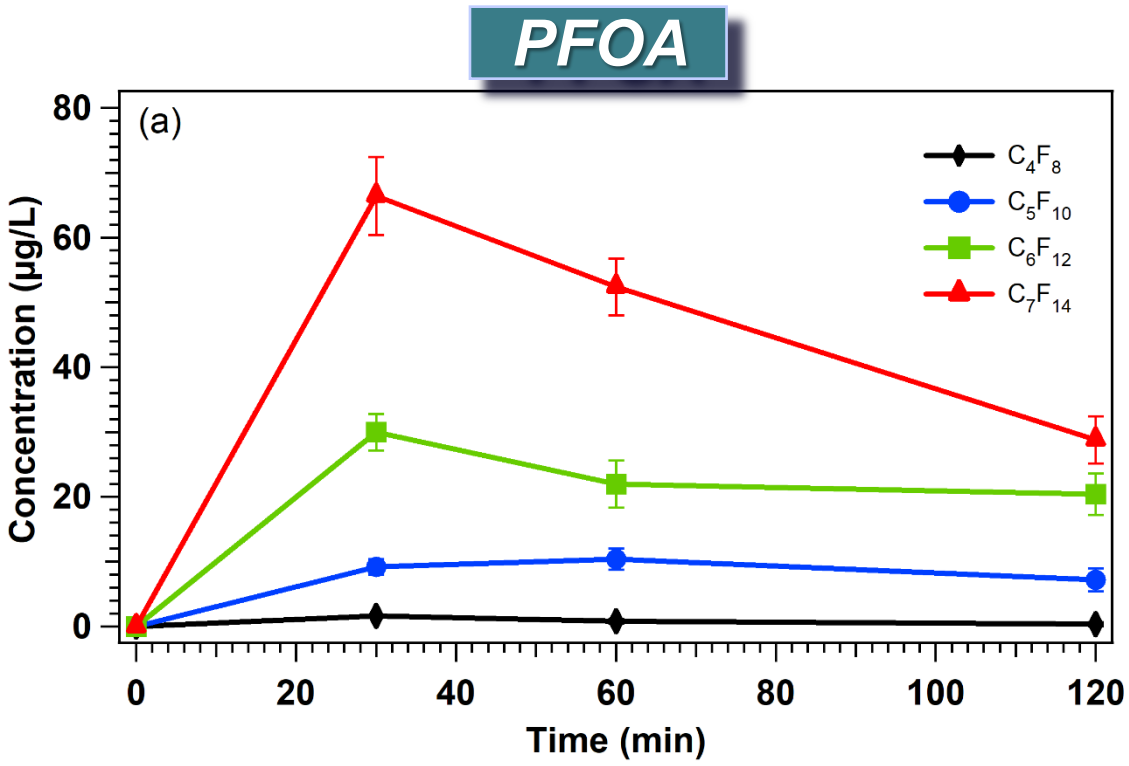
Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

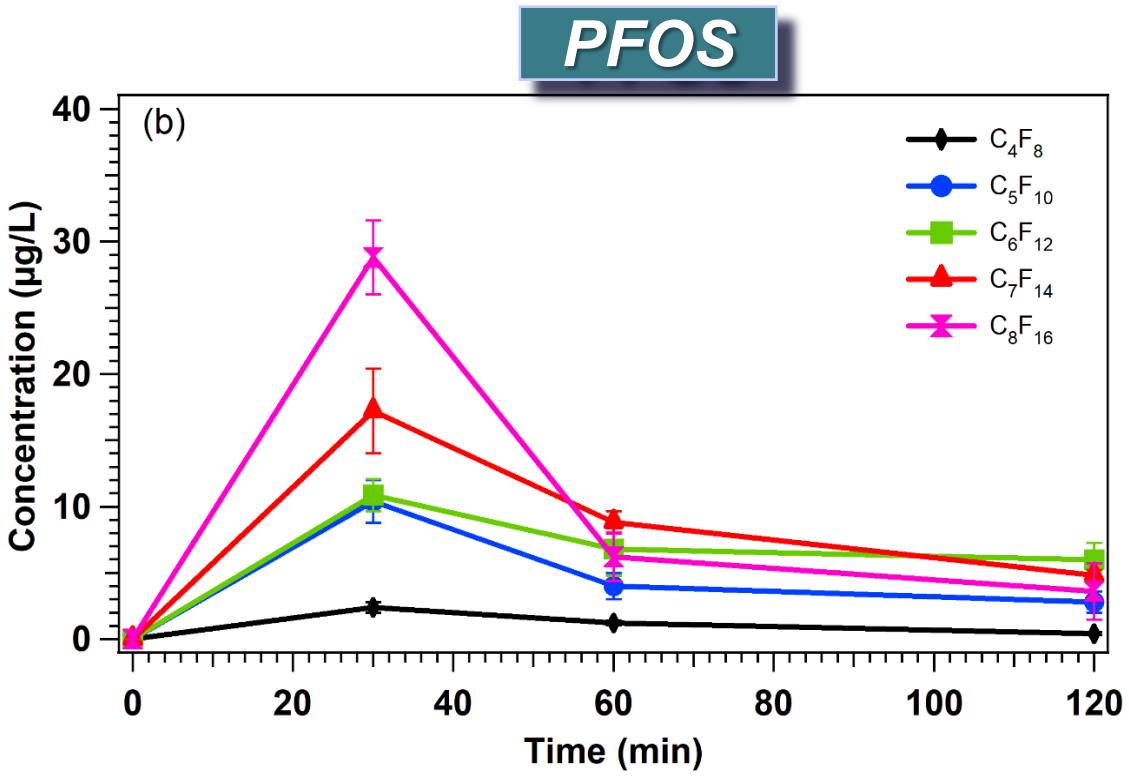
Mechanism of PFOA and PFOS Degradation and Liquid-phase Byproducts



Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

Gaseous Byproducts

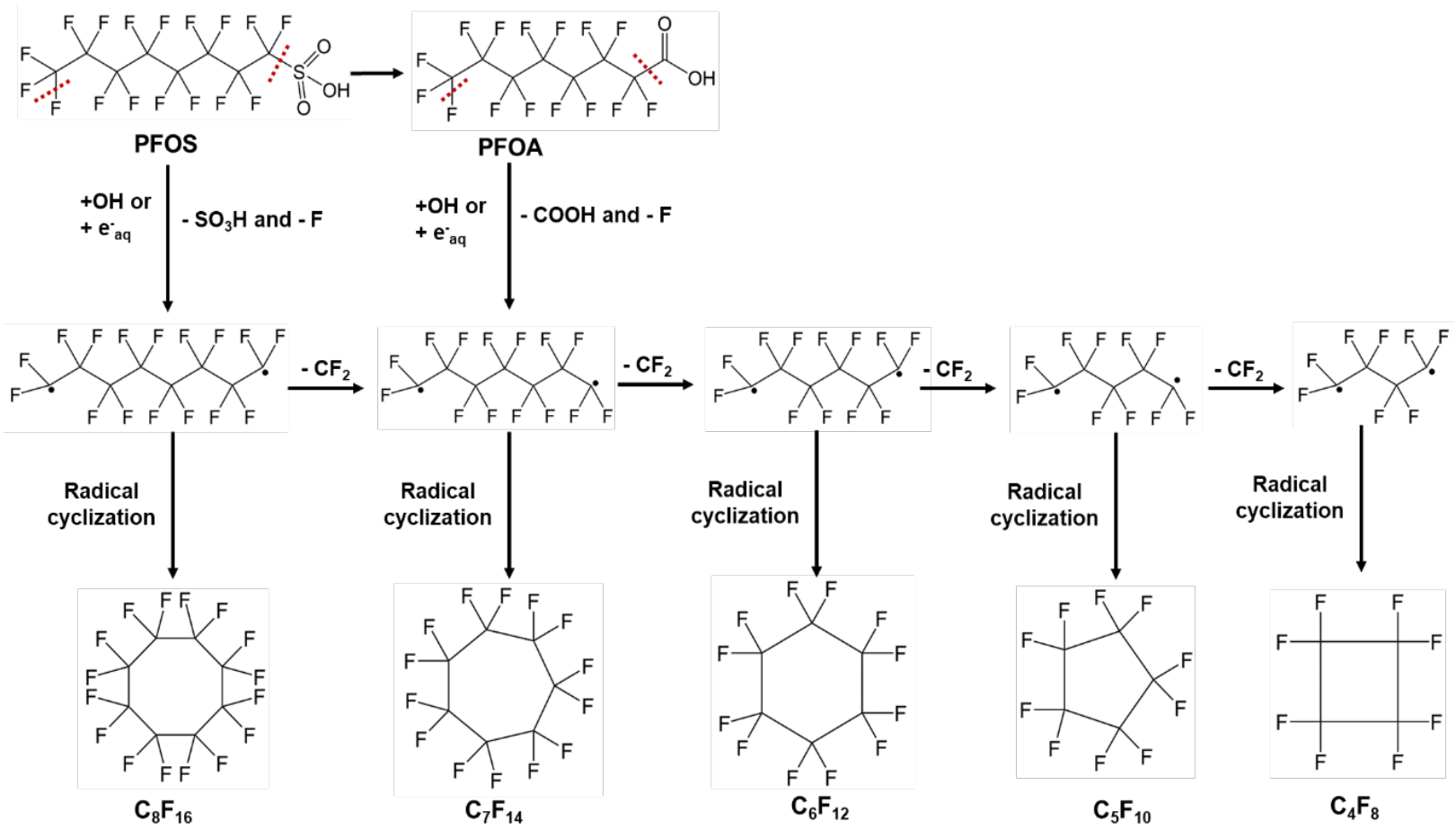




F in cyclic fluoroalkanes ~1% of initial F

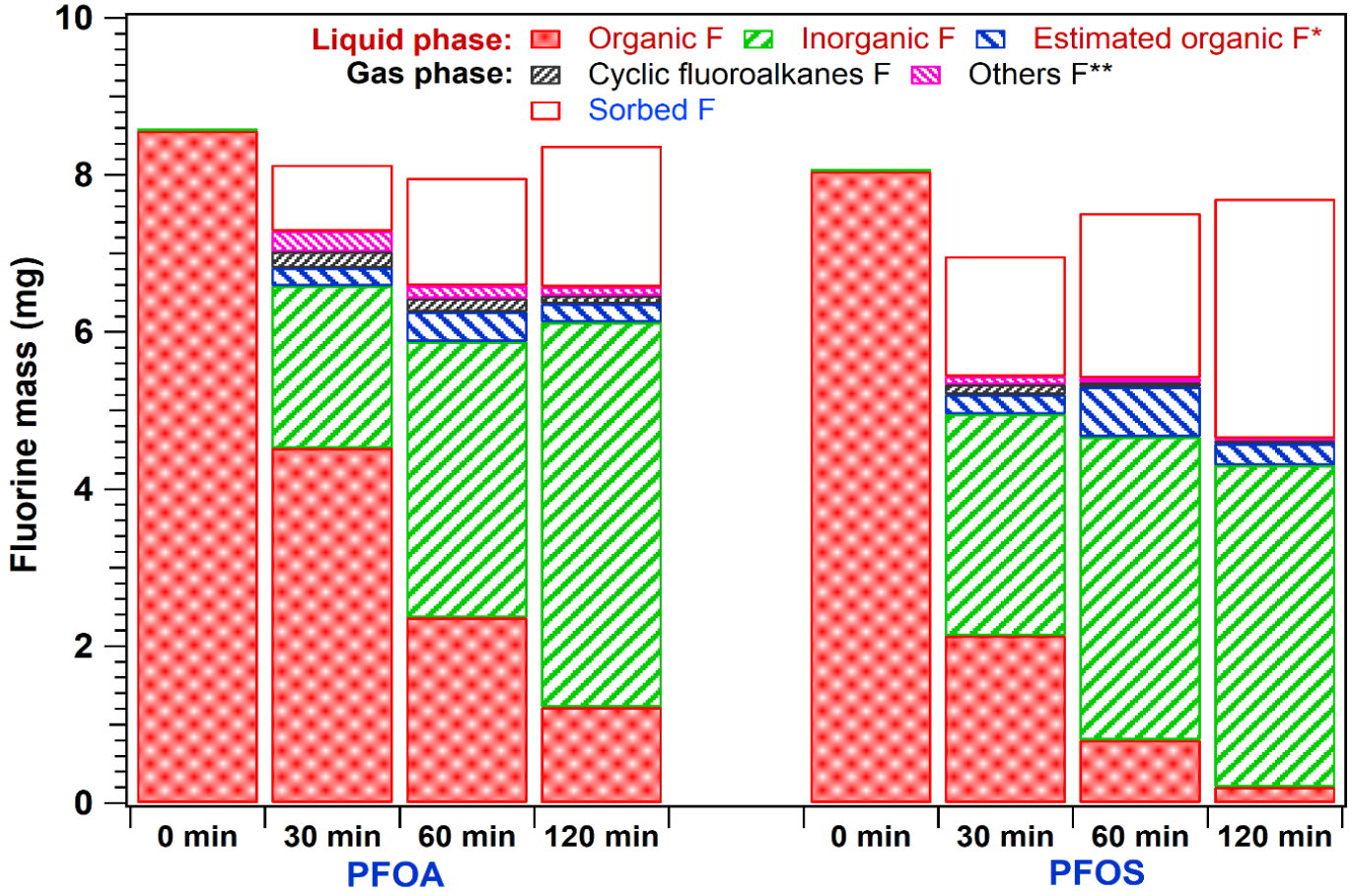
Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

Mechanism of PFOA and PFOS Degradation and Gas-phase Byproducts



Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

Fluorine Mass Balance



PFOA

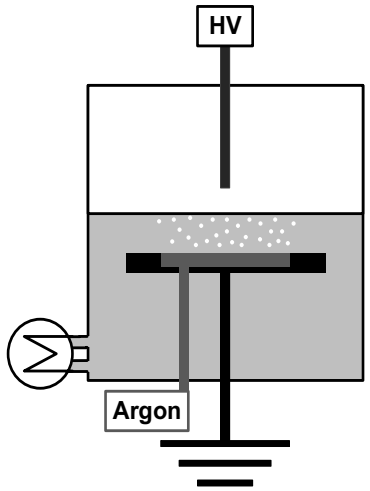
Liquid byproducts – 74%
Gas-phase byproducts – 2.5%
Sorption – 22%

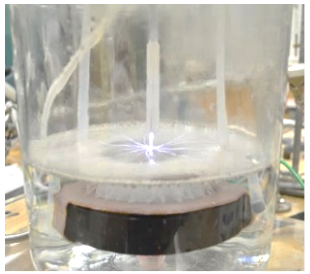
PFOS

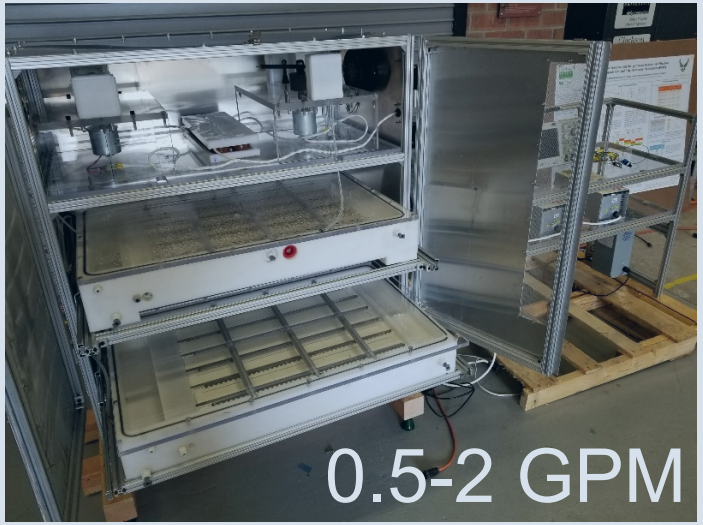
Liquid byproducts – 57%
Gas-phase byproducts – 1%
Sorption – 38%

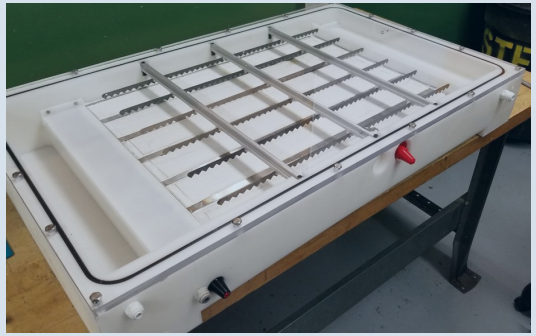
Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Mededovic Thagard, S., Holsen, T. M. (2019). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environmental Science & Technology,* 53, 2731 – 2738.

Plasma PFAS Treatment



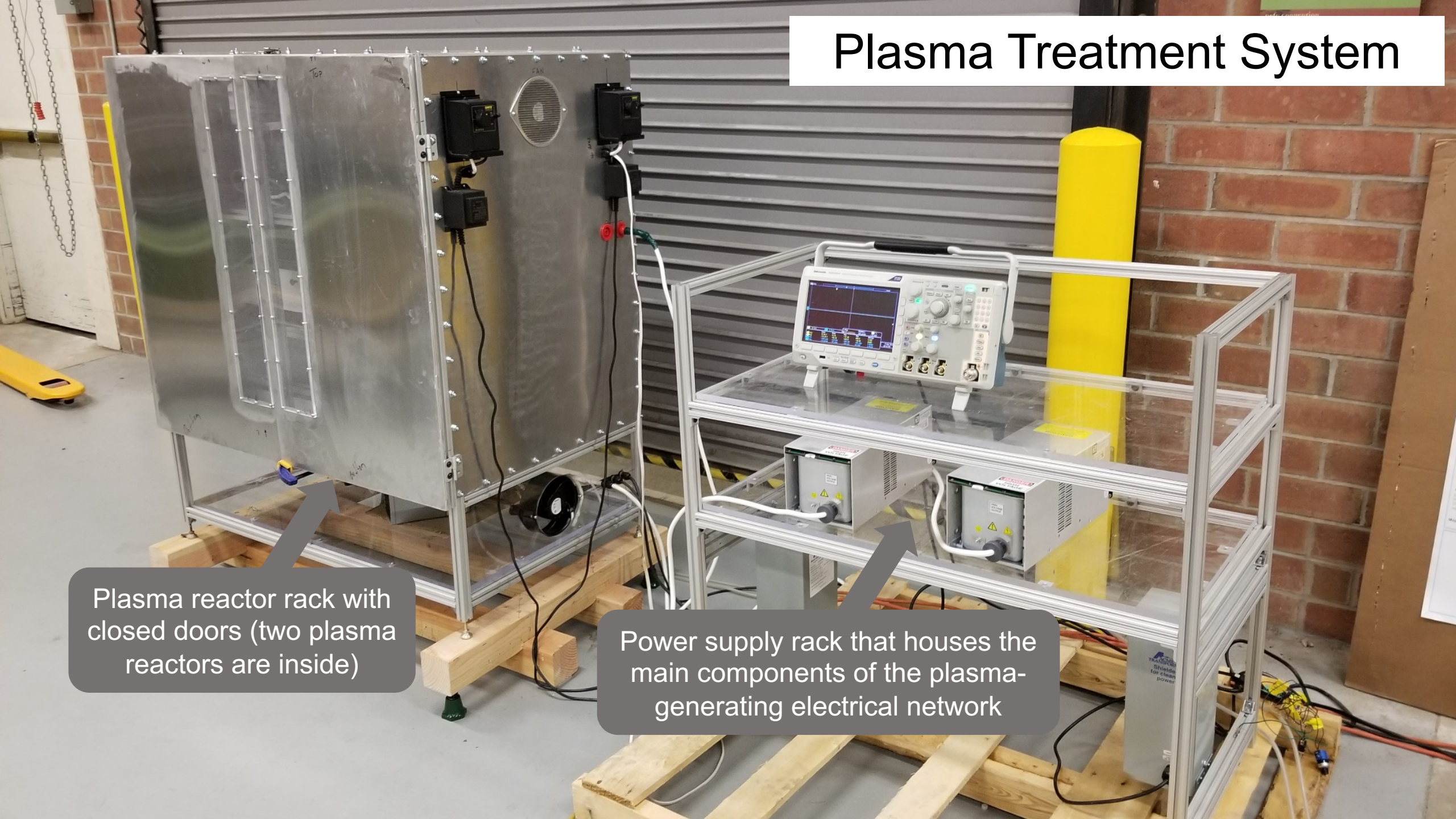


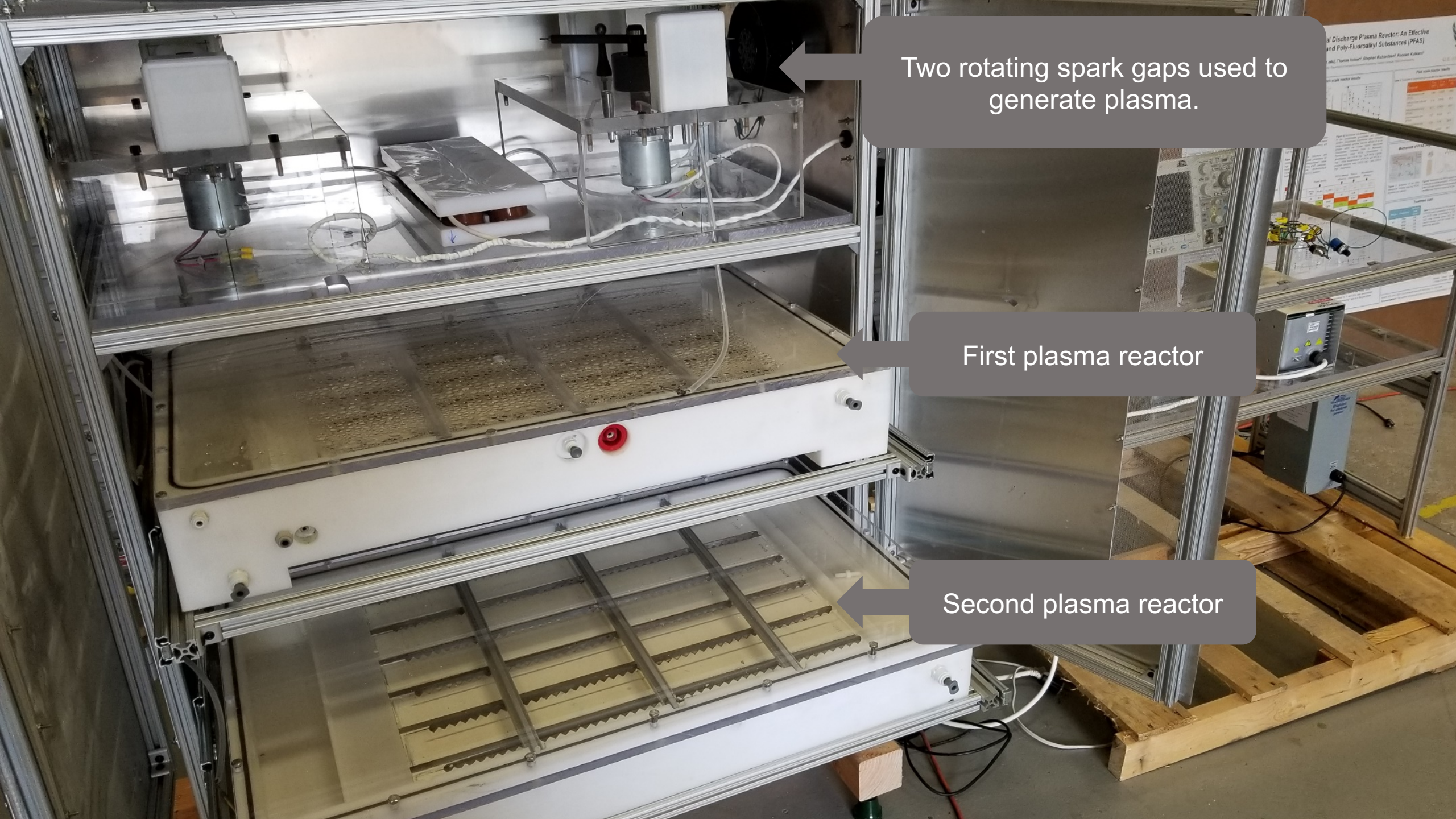




Selma Mededovic Thagard, Gunnar Stratton, Christopher Bellona, and Thomas Holsen, Enhanced Contact Electrical Discharge Plasma Reactor for Liquid and Gas Processing, US Patent Number 10, 357, 753 B2, Issued on July 23, 2019.

Plasma Treatment System

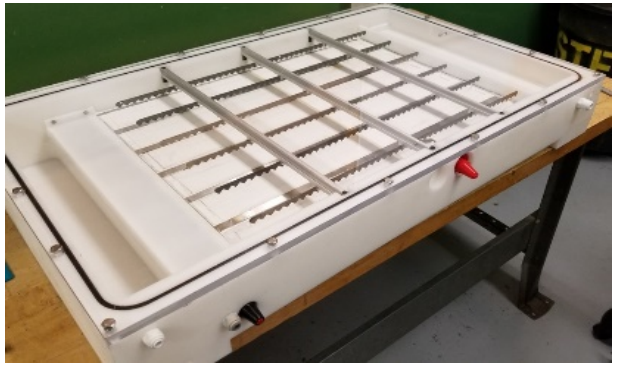


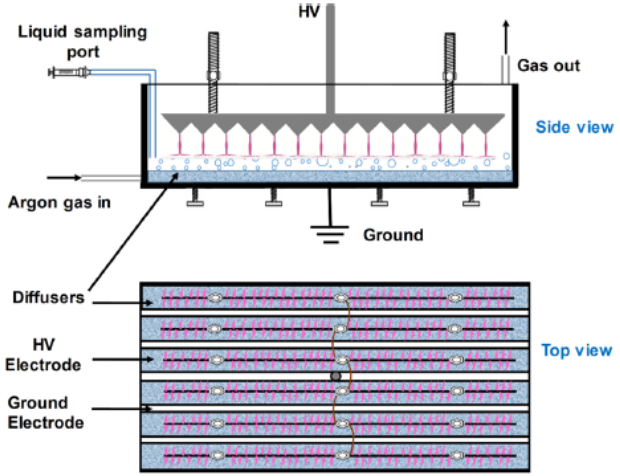

Two rotating spark gaps used to generate plasma.
First plasma reactor
Second plasma reactor

Measurement of power in the plasma reactors
External power supplies
Tektronix
DANGER
HIGH VOLTAGE
HIGH VOLTAGE OUTPUT
ACME TRANSFORMER
Shielded for cleaner power
An Enhanced Contact Electrical
Technology to Degrade Per- and
Objective

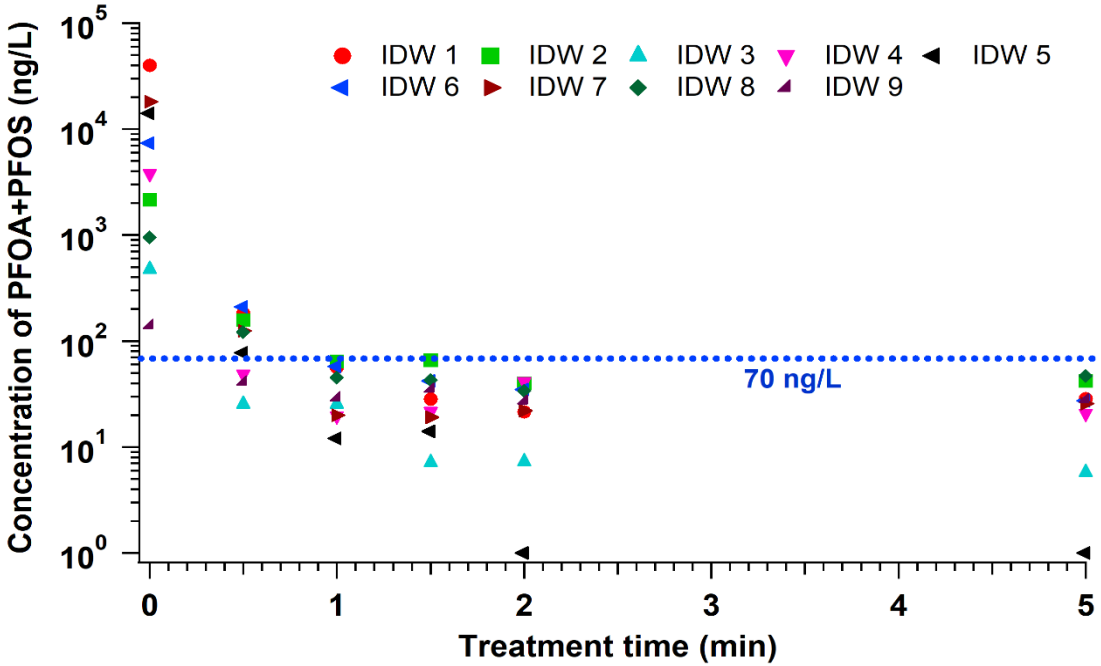
Video of one of the plasma reactors in operation

Scaled-up Plasma Reactor Performance





Degradation profiles of combined PFOA and PFOS concentrations in investigation derived waste (IDW) obtained from 9 different Air Force site investigations. Treatment volume is 4 L. No pre-treatment.



Singh, R. K., Multari, N., Chase Nau-Hix, Richard H. Anderson, Stephen D. Richardson,, Holsen, T. M., Mededovic Thagard, S. (2019). Rapid removal of poly- and perfluorinated compounds from investigation- derived waste (IDW) in a pilot-scale plasma reactor. *Environmental Science & Technology,* 53, 11375 – 11382.

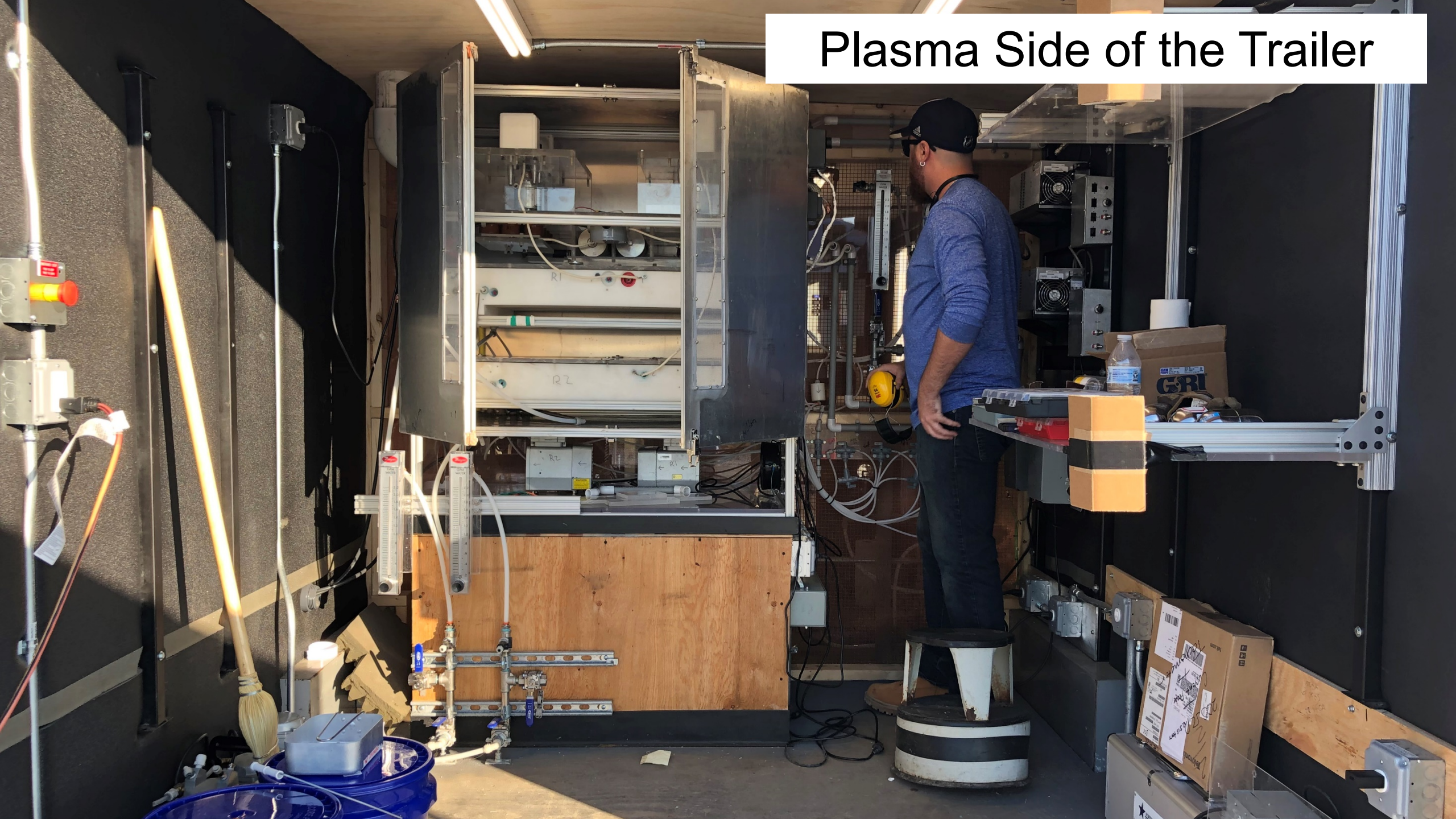
Field Demonstration of the Scaled-up Plasma Reactor

- Designed as a mobile unit for treatment of stored IDW purge water or other sources of PFAS-impacted water
- The trailer houses two plasma reactors operated in parallel
- Samples collected at ports before and after each reactor
- Monitor system parameters: flow rates, pressures, and voltage
- Field demonstration was performed September 16-27, 2019 at former Fire Training Area 2, Wright-Patterson AFB

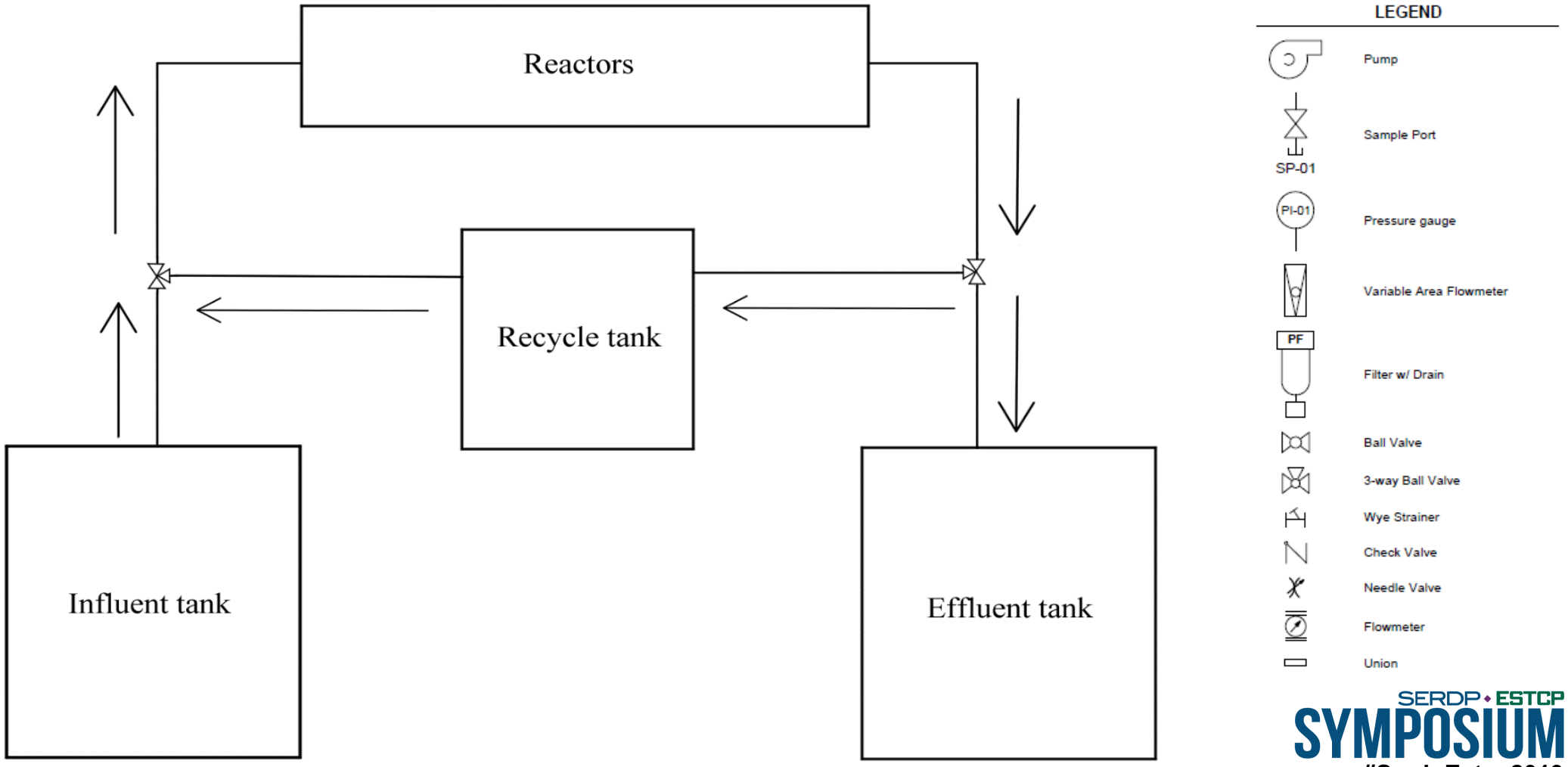
Mobile Plasma Trailer

Sample Collection Side of the Trailer

Plasma Side of the Trailer



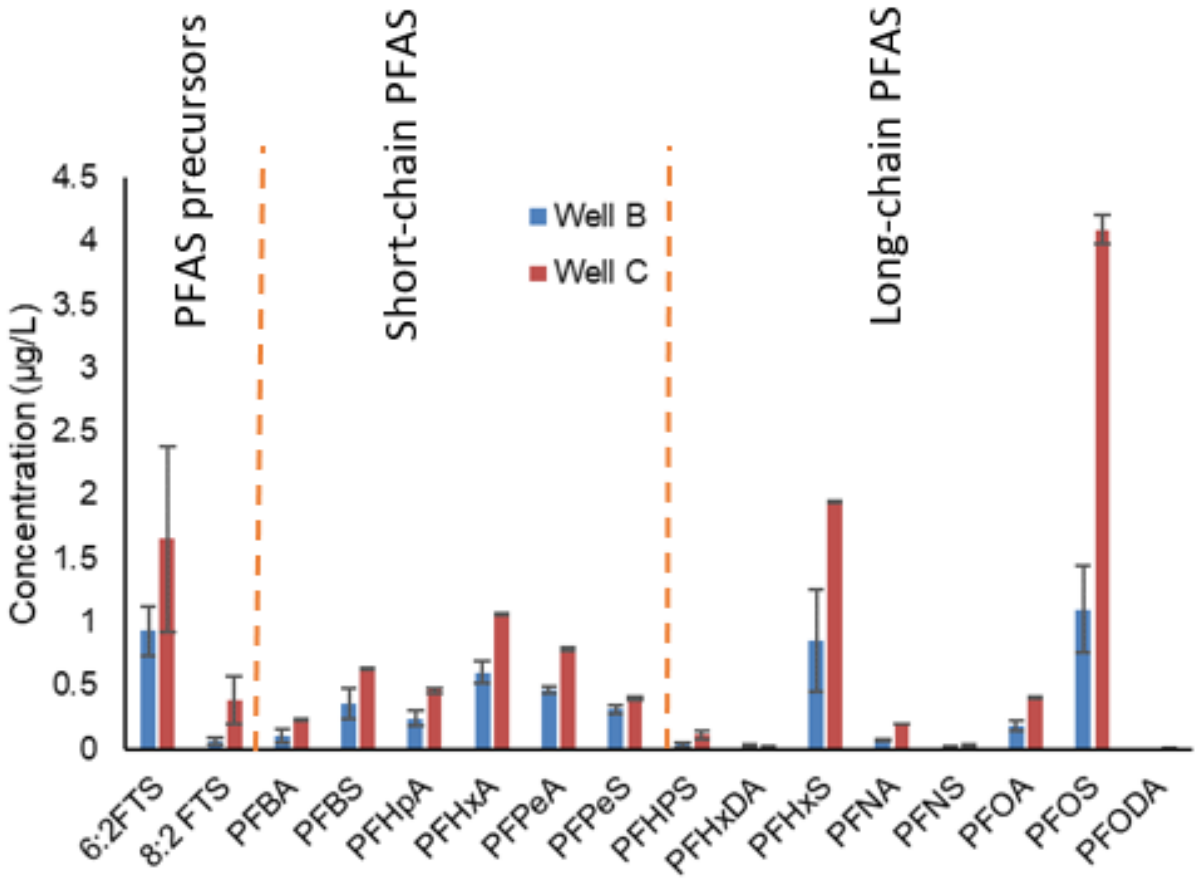
Trailer Process Flow Diagram



Field Demonstration-Water Composition

- PFAS-impacted water was pumped from two monitoring wells, FTA2-MW02B (Well B) and FTA2-MW02C (Well C)
- PFOA and PFOS concentrations:

	PFOA (ppt)	PFOS (ppt)
FTA2-MW02B	185	1100
FTA2-MW02C	416	3944



SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Trailer Operating Conditions

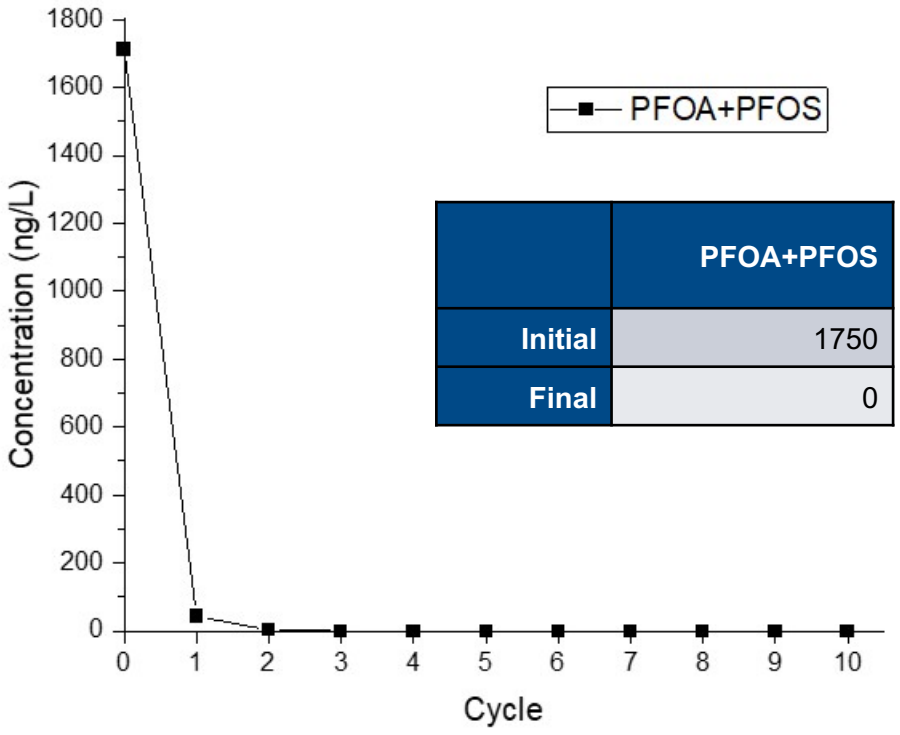
~350 gallons of PFAS-impacted groundwater were treated at various reactor operating conditions (flowrates, no. of recycle events*)

- Well B conditions: 0.3 GPM, 0.6 GPM and 0.9 GPM per reactor treated for 8 cycles, 8 cycles and 10 cycles respectively.
- Well C conditions: 0.3 GPM and 1.1 GPM per reactor treated for 8 cycles each.

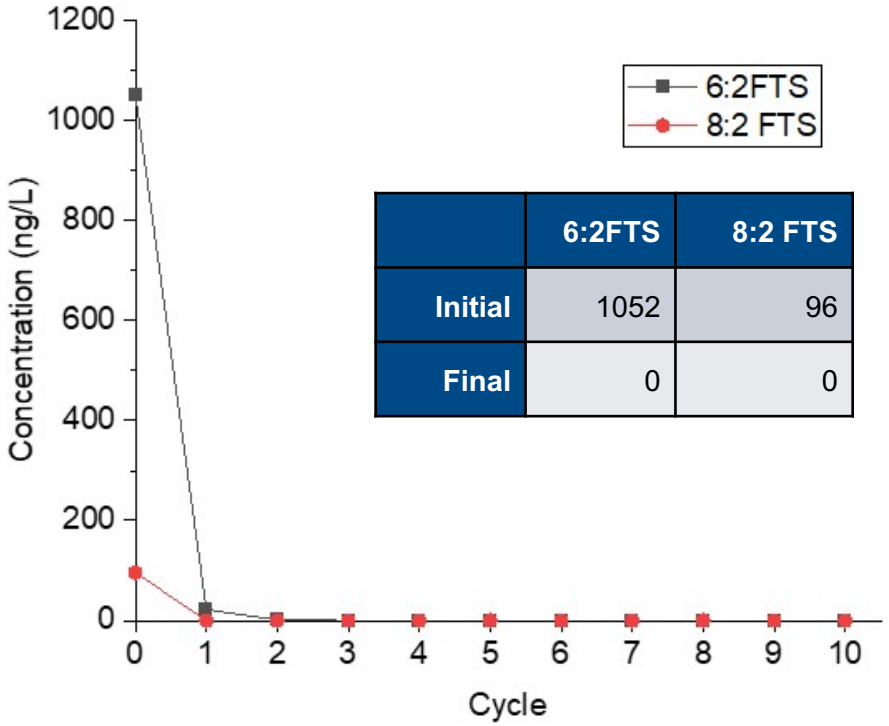
**One cycle (18 gal of water) is defined as a single pass through the reactor from the influent tank.*

SERDP • ESTCP SYMPOSIUM
#SerdpEstcp2019

Trailer Performance Results: Well B at 0.9 GPM for 10 Cycles



	PFOA+PFOS
Initial	1750
Final	0



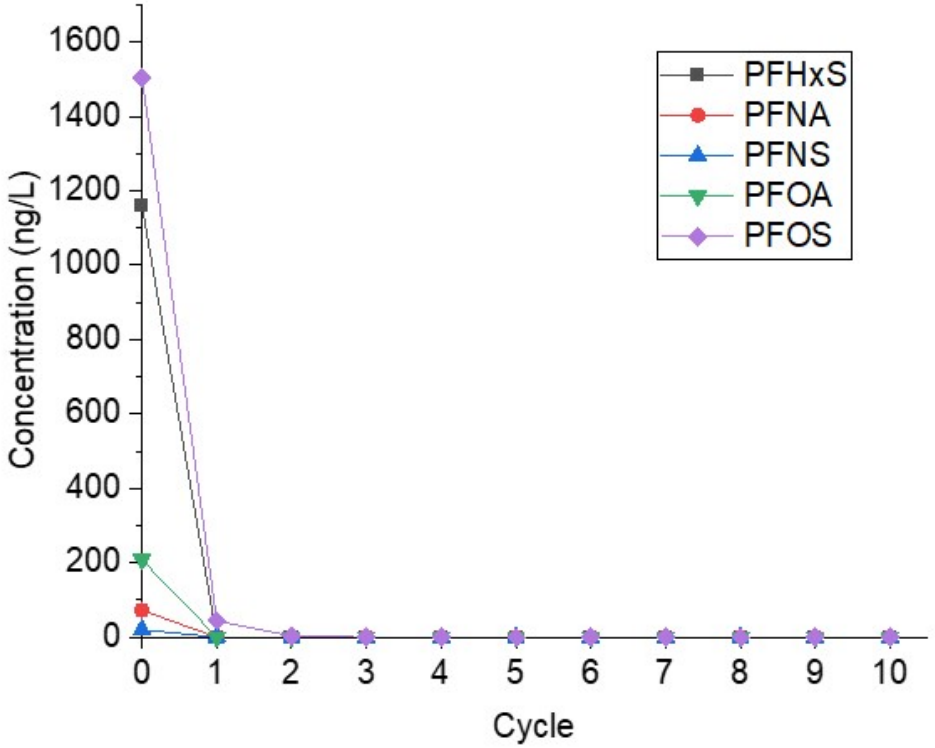
	6:2FTS	8:2 FTS
Initial	1052	96
Final	0	0

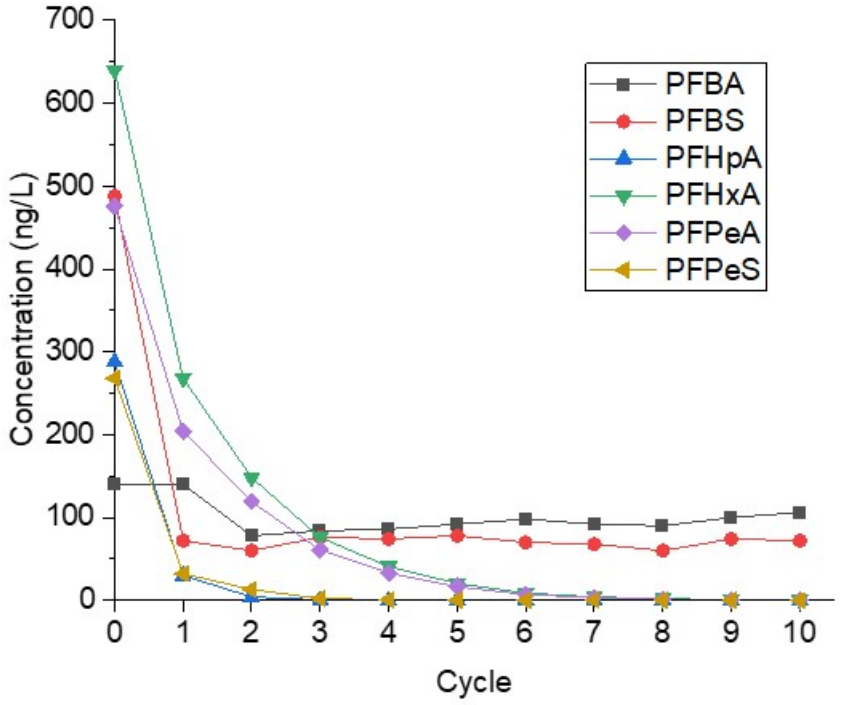
One cycle is defined as a single pass through the reactor from the influent tank.

Trailer Performance Results: Well B at 0.9 GPM for 10 Cycles

	PFHxS	PFNA	PFNS	PFOA	PFOS
Initial	1160	72	20	208	1504
Final	0	0	0	0	0

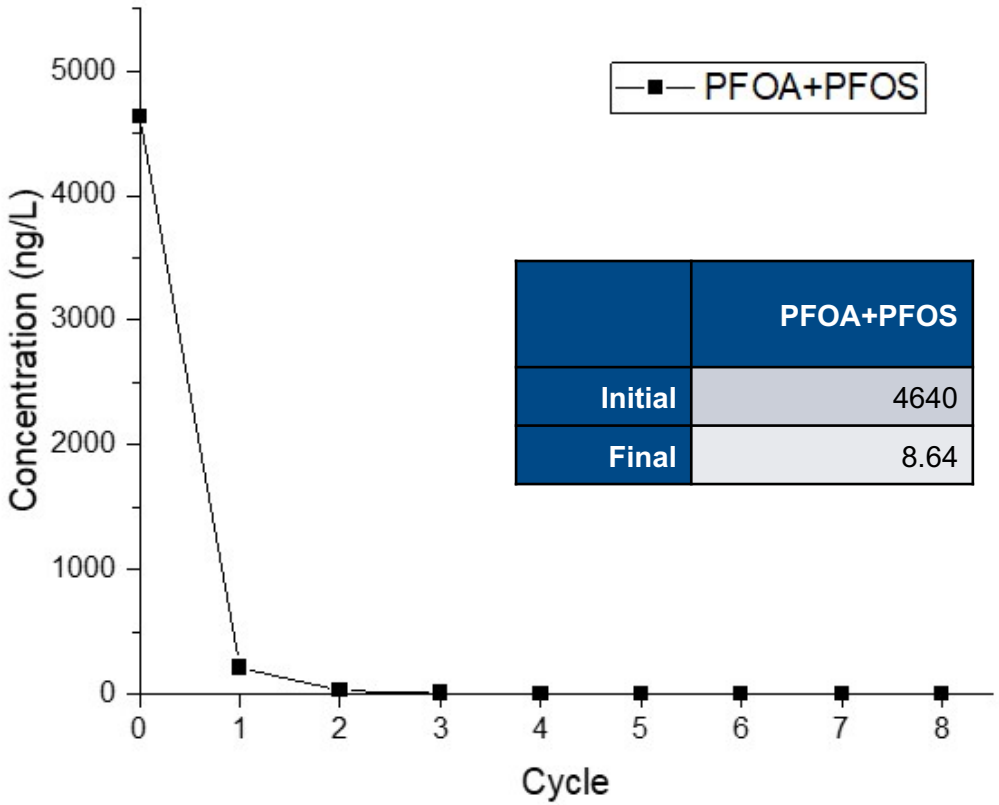
	PFBA	PFBS	PFHpA	PFHxA	PFPeA	PFPeS
Initial	140	488	288	640	476	268
Final	106	72	0	0	0	0



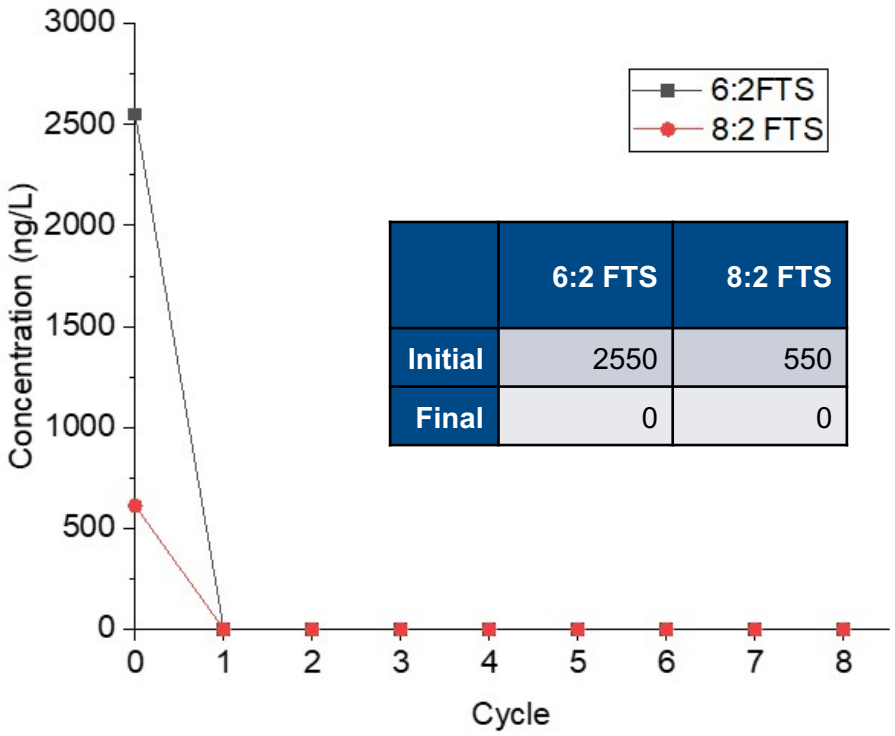


One cycle is defined as a single pass through the reactor from the influent tank.

Trailer Performance Results: Well C at 1.1 GPM for 8 Cycles



	PFOA+PFOS
Initial	4640
Final	8.64



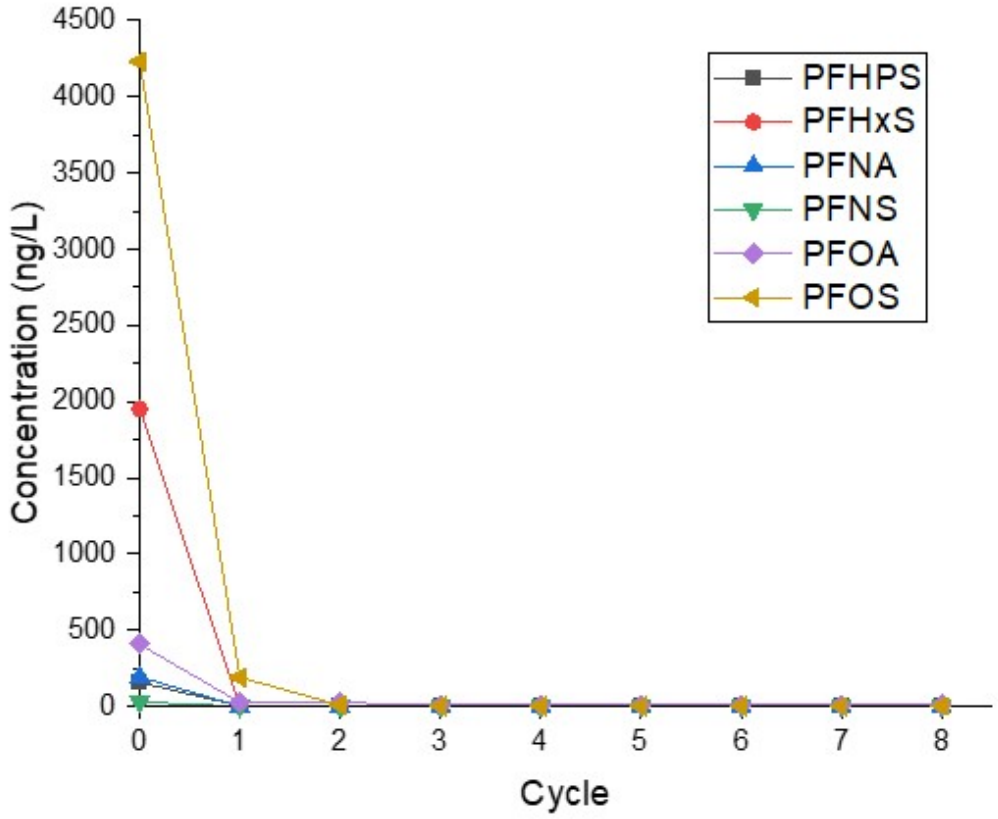
	6:2 FTS	8:2 FTS
Initial	2550	550
Final	0	0

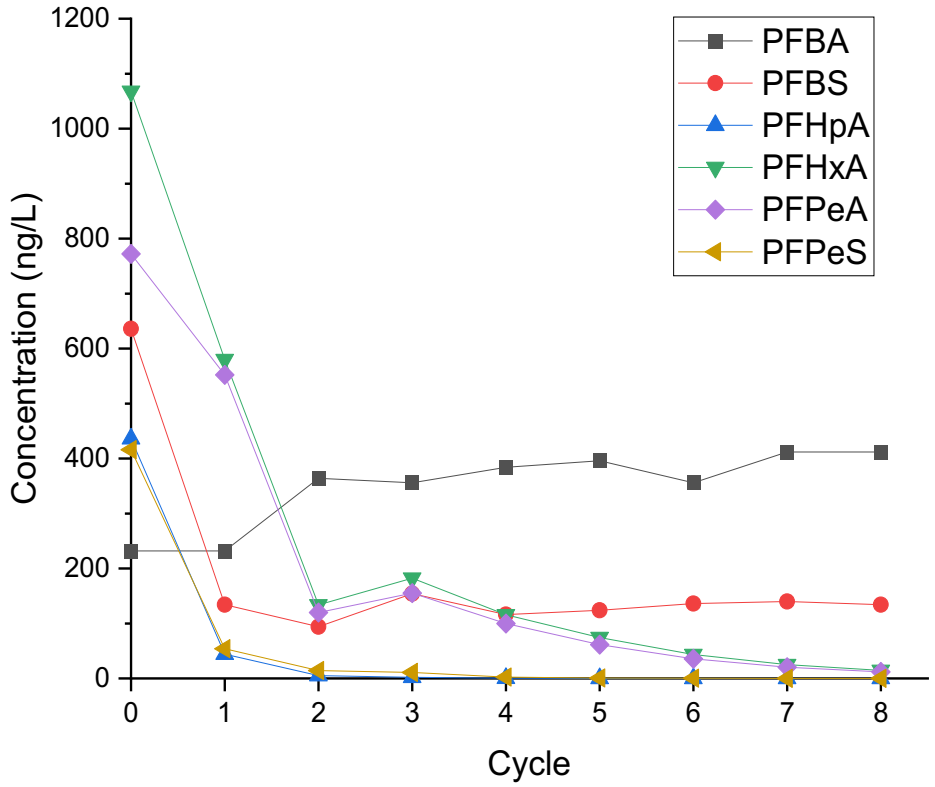
One cycle is defined as a single pass through the reactor from the influent tank.

Trailer Performance Results: Well C at 1.1 GPM for 8 Cycles

	PFHPS	PFHxS	PFNA	PFNS	PFOA	PFOS
Initial	156	1952	192	28	408	4232
Final	0	0	0	0	8.64	0

	PFBA	PFBS	PFHpA	PFHxA	PFPeA	PFPeS
Initial	232	636	436	1068	772	416
Final	412	134	0	14	11	0

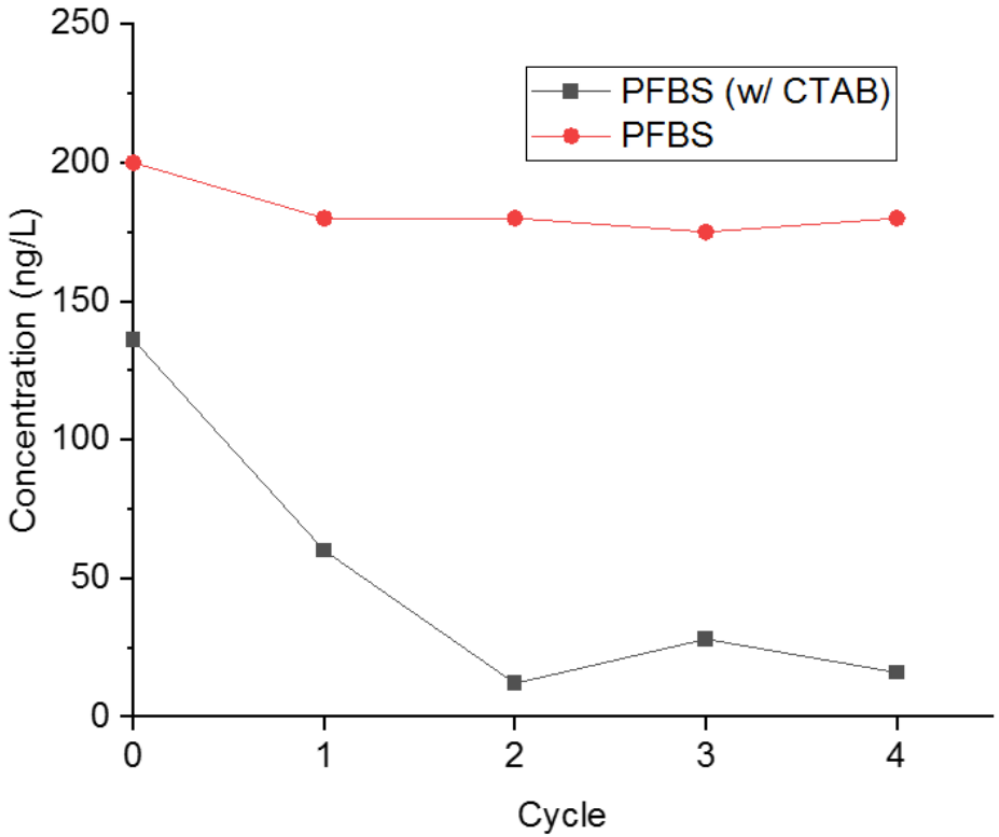


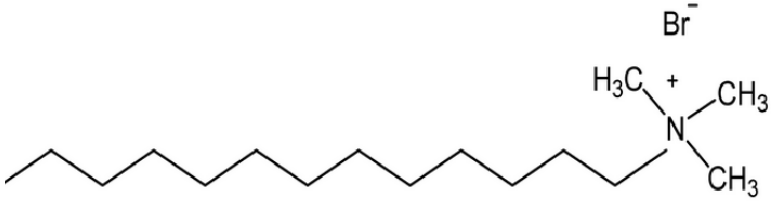


One cycle is defined as a single pass through the reactor from the influent tank.

Removal of Short-chained PFAS with the Addition of a Surfactant

Cationic surfactants (CTAB) electrostatically and hydrophobically interact/associate with short-chained PFAS and transport them to the plasma-liquid interface.





Cetyletrimethylamonium bromide (CTAB)

In the CTAB addition experiments (0.9 GPM for 4 cycles) the CTAB concentration was increased to 0.04 mM before each cycle.

Trailer Performance Results: Energy Use

- Energy requirements and calculated costs for reducing the initial PFOA+PFOS concentration to below 70 ng/L (argon and recycling costs included)

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		

Summary

- Plasma-based water treatment is an effective technology for the treatment of various sources PFAS-impacted water.
- Co-contaminants have no effect on the PFAS treatment efficiency.
- Higher volumetric flowrates reduce the treatment time.
- Long term treatment of PFOA and PFOS results in the formation of a range of liquid byproducts and minor concentrations of cyclic gas-phase byproducts.
- The technology is highly scalable and is more efficient than leading alternative destructive processes for treatment of PFAS-contaminated water.

ONGOING PFAS RESEARCH EFFORTS INCLUDE PLASMA TREATMENT OF: PFAS-contaminated groundwater, ion exchange regenerant brine, landfill leachate, AFFF formulations and foam fractionate.

Clarkson University

Selma Mededovic

315-268-4423

smededov@clarkson.edu

Tom Holsen

315-268-3851

tholsen@clarkson.edu

GSI Environmental

Stephen Richardson

512-346-4474

sdrichardson@gsi-net.com

Poonam Kulkarni

713-522-6300

prkulkarni@gsi-net.com