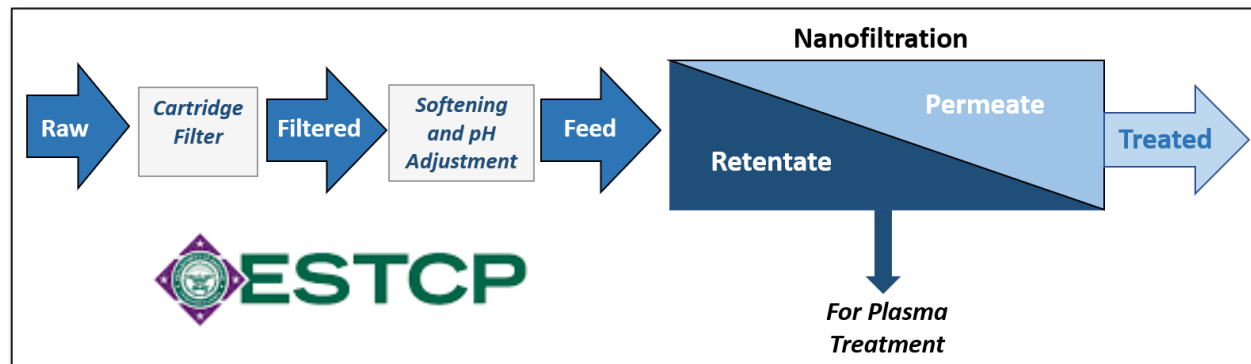


# Nanofiltration Followed By Electrical Discharge Plasma for Destruction of PFAS and Co-Contaminants in Groundwater: A Treatment Train Approach



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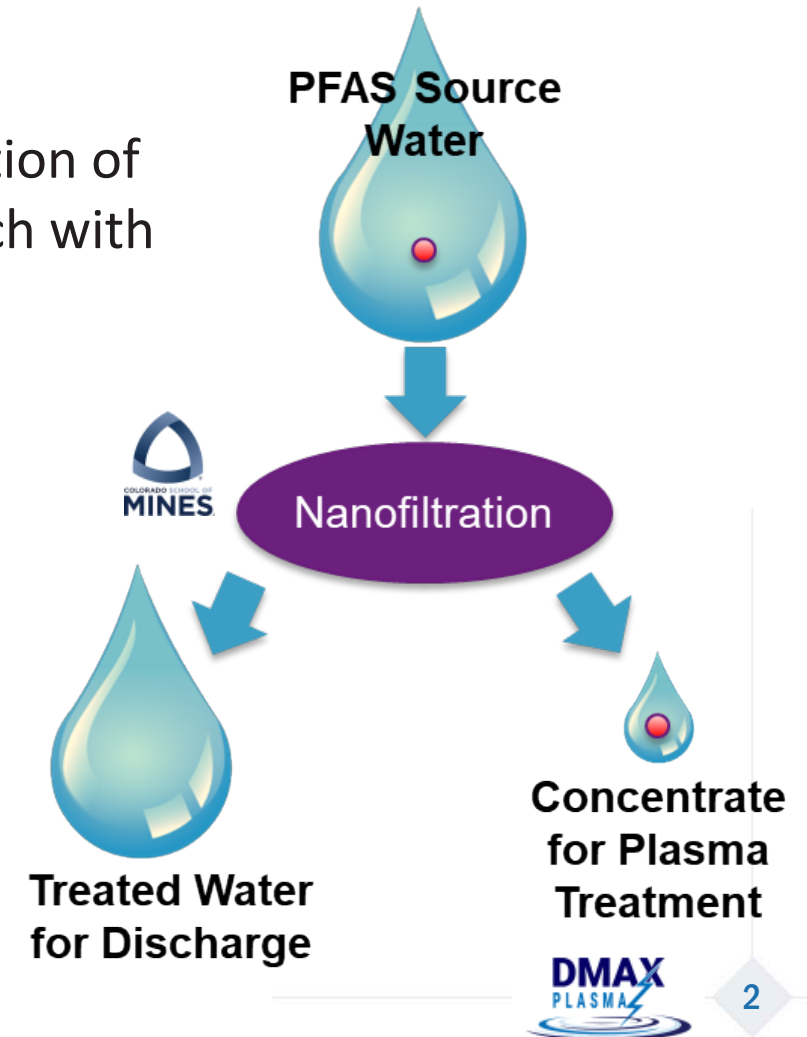
# Technical Objectives

## What's Needed?

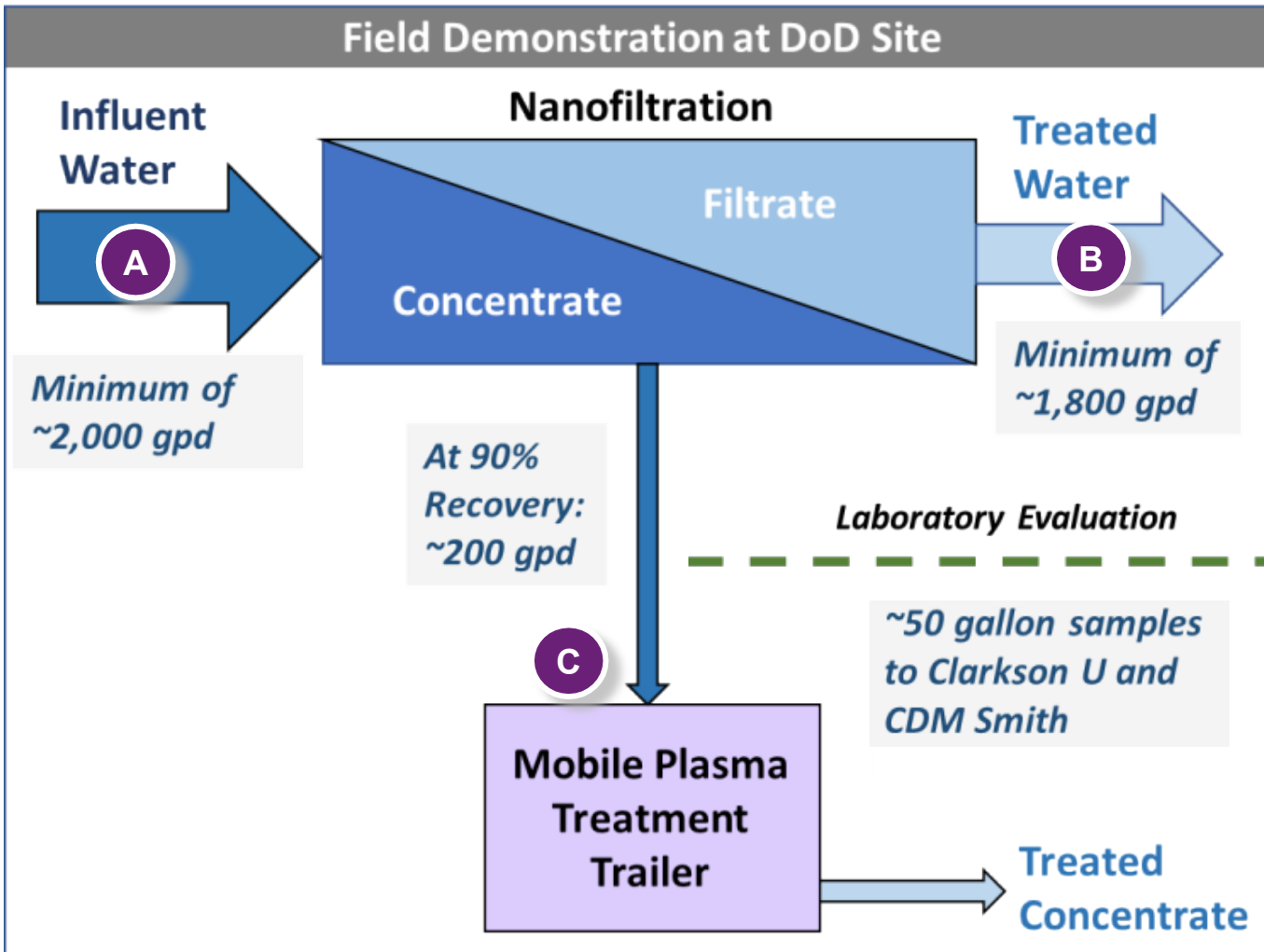
- › Since PFAS plumes are generally dilute (often a few ppb), remediation of PFAS-impacted water best lends itself to a treatment train approach with integrated **PFAS concentration and destructive steps**

## Our Objective

- › Demonstrate and validate a field-scale integrated treatment approach:
  - 1 **Nanofiltration** to concentrate PFAS and co-contaminants
  - 2 **Electrical Discharge Plasma** to treat concentrate
  - 3 “Apple to Apples” Bench-scale comparison of **Electrochemical Oxidation and Plasma**



# Technical Objectives



- (A) Nanofiltration can process a **minimum** of 2,000 gpd of influent water (Feed)
- (B) ~1,800 gpd will be a treated effluent stream (Filtrate, ~90% of Feed)
- (C) ~200 gpd will be treated by plasma (Concentrate, ~10% of Feed)

**Laboratory Comparison of Destructive Technologies**

Electro-Chemical Oxidation	vs.	Plasma Reactor
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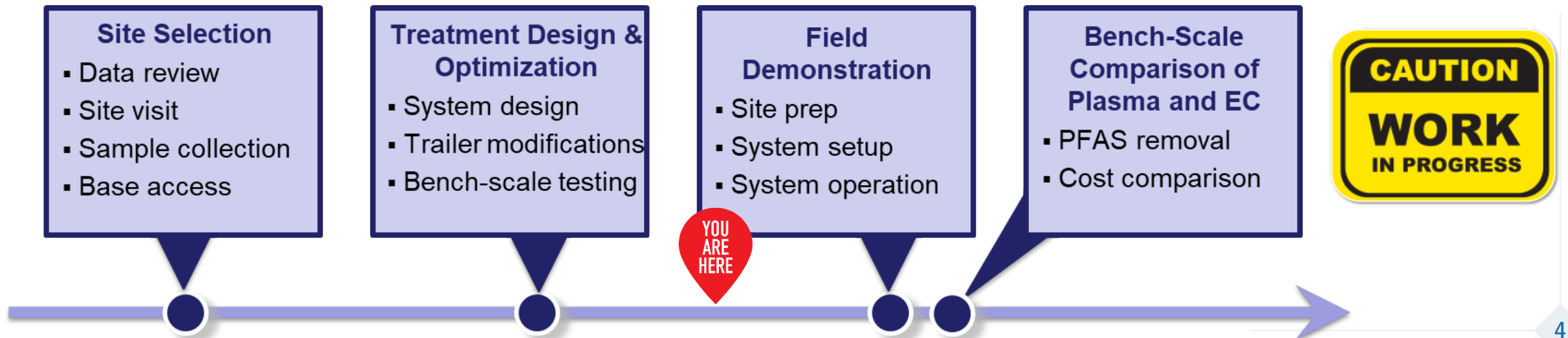
**Study Variables:**

- PFAS Removal Efficiency
- Recirculation
- Energy Use & Treatment Cost (\$/gal)



# Today's Presentation...

- 1 Overview: Nanofiltration and Enhanced Contact Plasma technologies
- 2 Source water characterization
- 3 Treatability testing results
- 4 Next steps



# Coupling Concentration & Destruction

## Concentration

- Activated carbon
- Ion exchange resins
- Novel polymer adsorbents
- Silica coatings
- Zeolites
- Foam Fractionation
- Colloidal Gas Aphrons
- Nanofiltration
- Ultrafiltration
- Reverse Osmosis

## Destruction

- Electrochemical Oxidation
- Enhanced Contact Plasma
- Hydrothermal Alkaline Treatment
- Photochemical Oxidation
- Supercritical Water Oxidation
- Sonolysis
- Thermal Oxidation

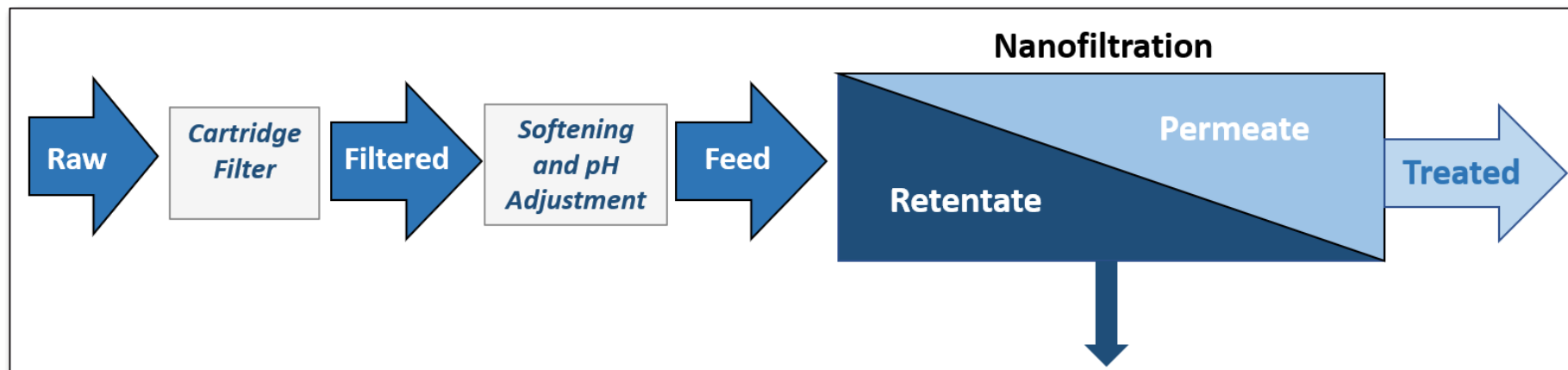
**KEY POINT:**

There are numerous opportunities to combine concentration and destructive technologies for the treatment of PFAS-impacted waters

# Nanofiltration: *The Basics*

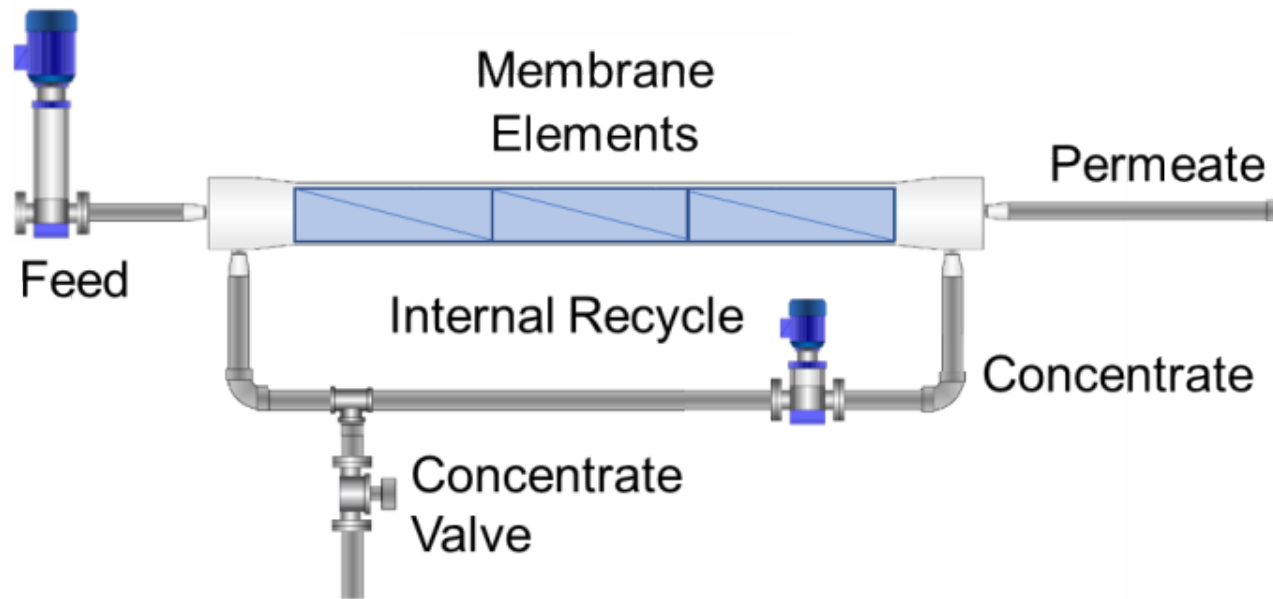


- › High-pressure separation process where solutes are retained by membranes and concentrated into a smaller volume of water (*retentate or concentrate*)
- › Majority of feed water exits system as treated *permeate (or filtrate)*
- › **% Recovery:** proportion of feed water recovered as permeate
- › **% Rejection:** proportion of solute (PFAS) retained by the membranes



# Closed-Circuit Desalination (CCD)

- › Newer membrane systems such as closed-circuit desalination (CCD) can achieve >20x concentration of PFAS-impacted waters



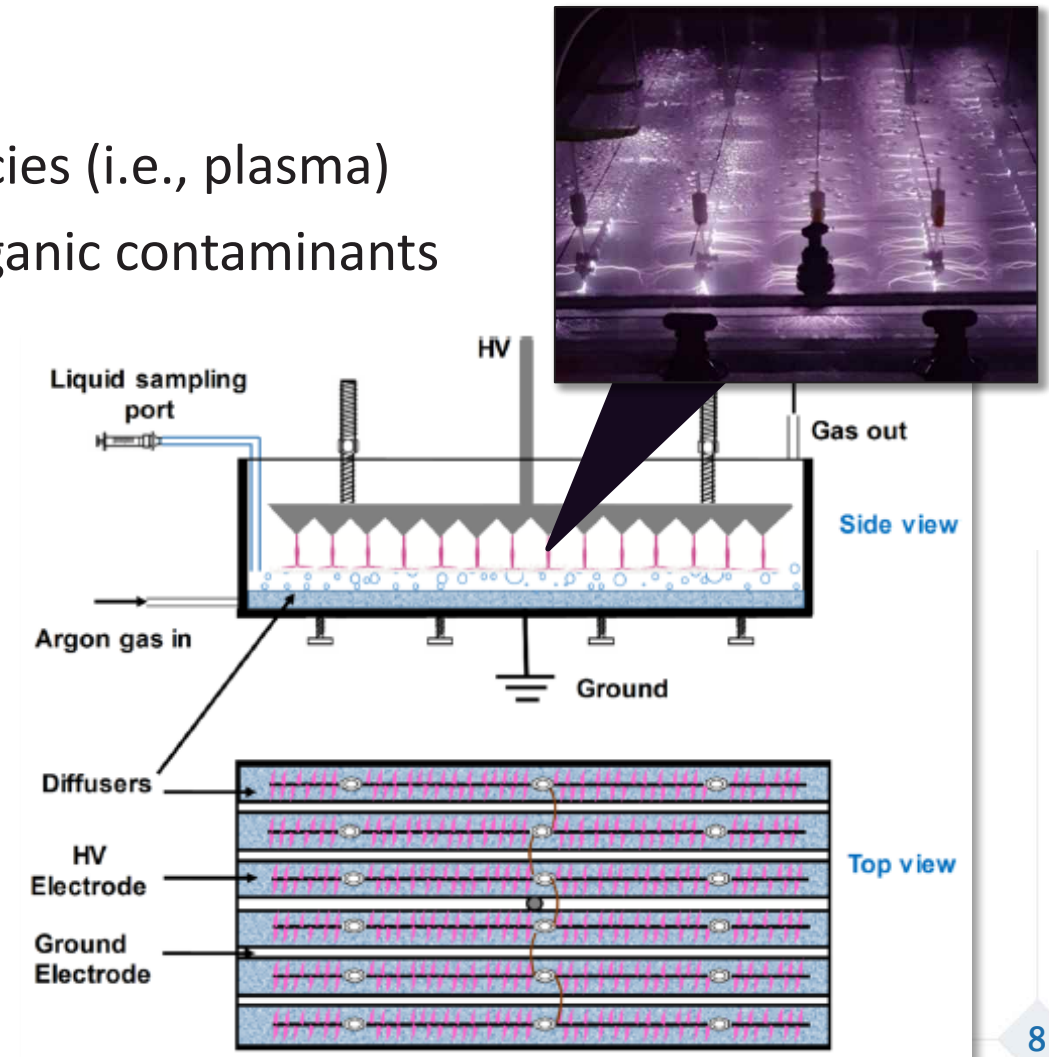
## *Semi-Batch Treatment Process*

- › During filtration, concentrate recirculated internally, concentrate valve closed
- › Once a recovery (proportion of feed water recovered as permeate) setpoint is reached, concentrate valve opens
- › With concentrate valve open, plug-flow flush displaces concentrate in system
- › Concentrate valve closes, new cycle starts

# Enhanced Contact Plasma: *The Basics*

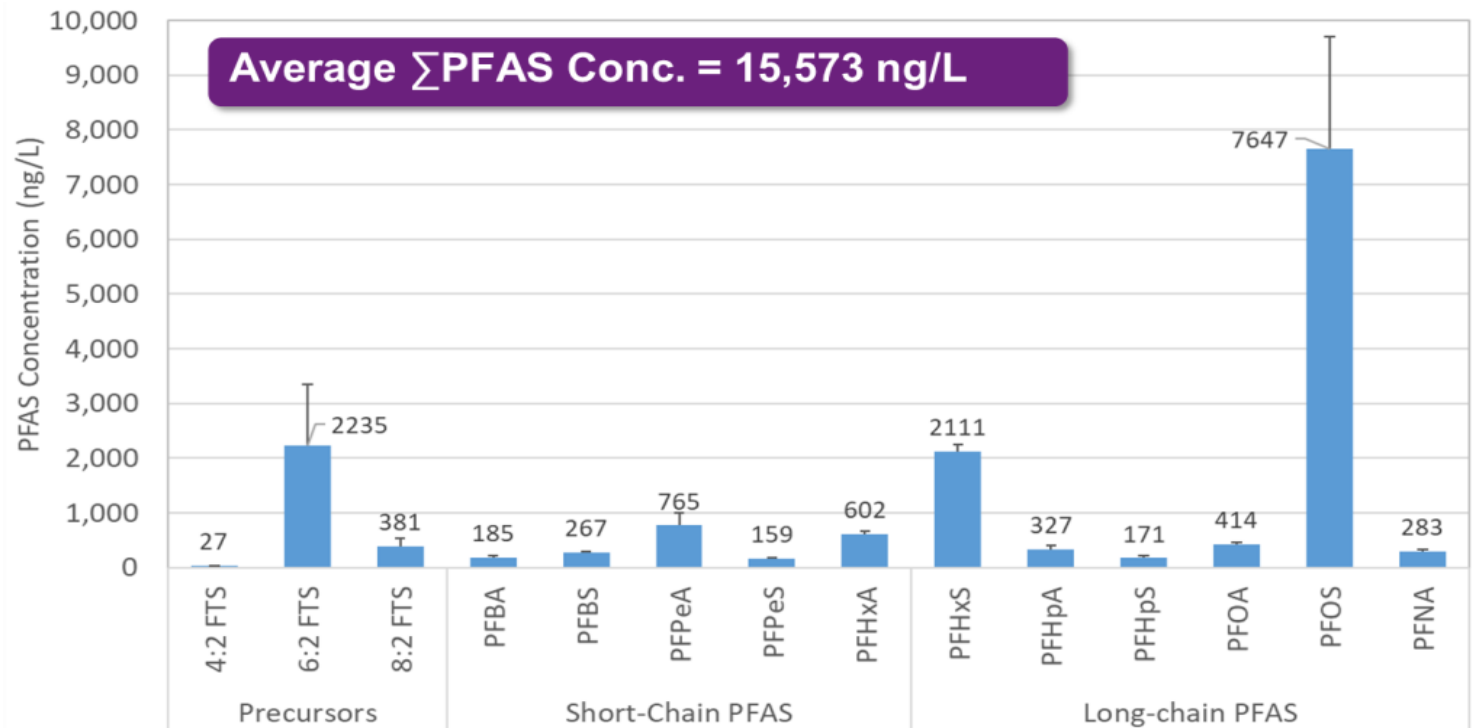
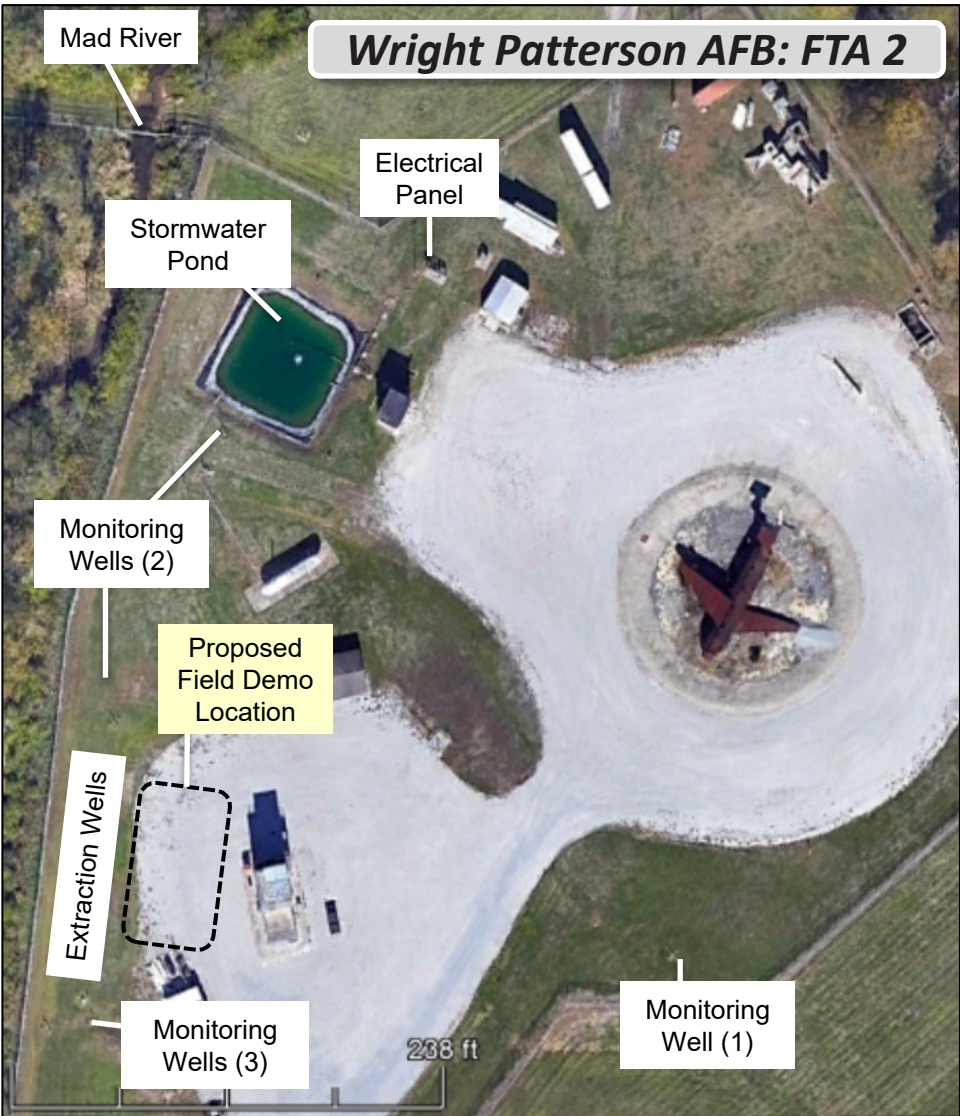


- 1 Plasma-based water treatment** uses electricity to:
  - › convert water into a mixture of highly reactive species (i.e., plasma)
  - › rapidly and non-selectively degrade recalcitrant organic contaminants
- 2 Plasma Formation:** High voltage is applied between suspended electrodes (above the water surface) and submerged grounded electrodes
- 3 Plasma Reactor Components**
  - › High voltage electrodes for generation of plasma
  - › Stainless steel strips as grounded electrodes
  - › Gas diffusers for bubble formation to drive PFAS to liquid surface





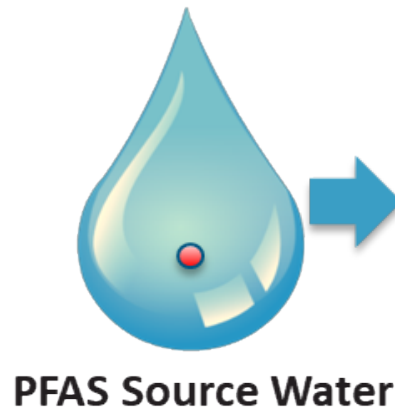
# Source Water Characterization



- › Samples collected from several extraction wells
- › Most abundant PFAS: PFOS, 6:2 FTS, and PFHxS
- › Elevated alkalinity, calcium, and iron

# Bench-scale Treatability Testing

60 gallons of PFAS-impacted groundwater collected from WPAFB and shipped to Mines



Concentrate



1 gallon of concentrate shipped to Clarkson for analysis and DMAX for plasma testing

Permeate sample shipped to Clarkson for analysis

**Treated Water for Discharge (Permeate)**

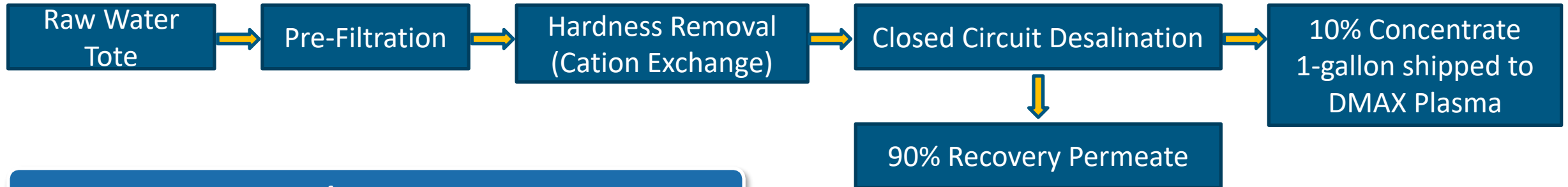


**Treated Water for Discharge**



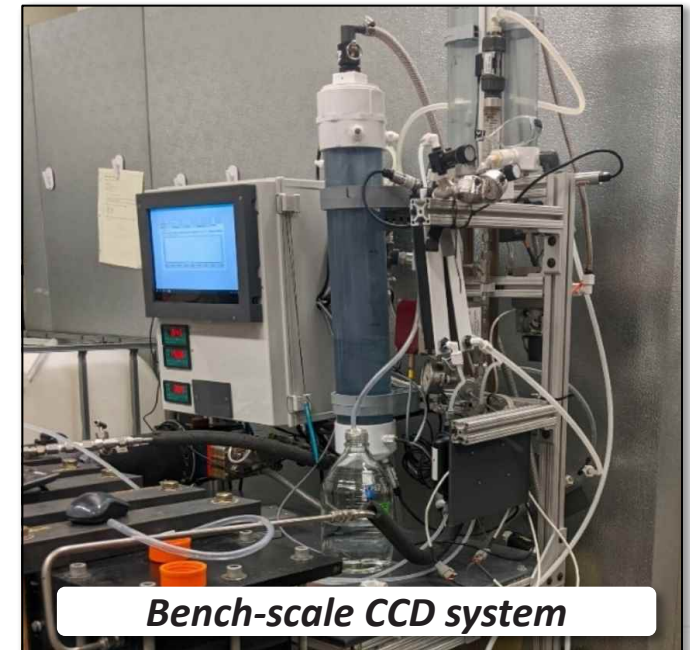
Treated water samples analyzed at Clarkson

# Nanofiltration: *Membrane Concentration Tests*



## *Membrane System/Experiment Specifications:*

- › Tested two membranes: NF-90 (tight NF) and CR-100
- › System uses 0.14 m<sup>2</sup> of flat-sheet membrane in two cells
- › Each sequence produced ~3.6 L of permeate, ~0.4 L of concentrate
- › SCADA logs flow rate, pressure, conductivity, temperature
- › Performed approximately 30 sequences up to 90% recovery
- › Collected permeate and concentrate samples



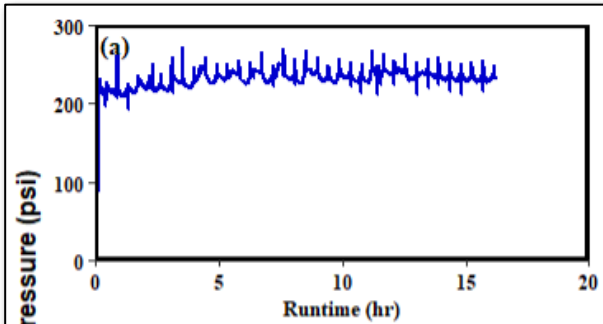
*Bench-scale CCD system*

# Nanofiltration: *Operational Results*

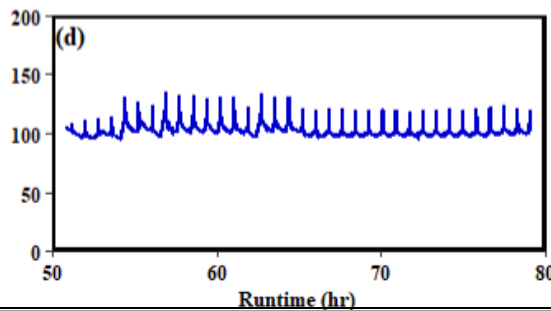
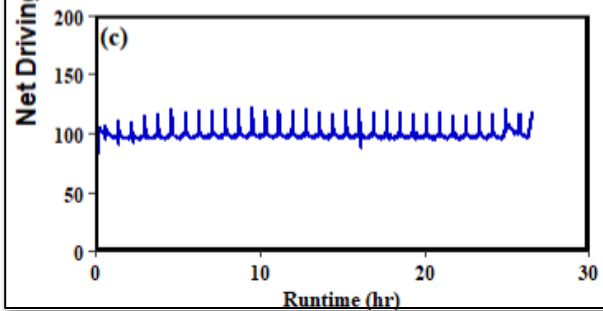
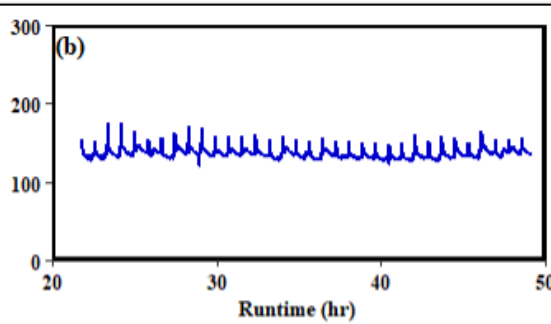


## Net Driving Pressure

NF-90 (tight NF)

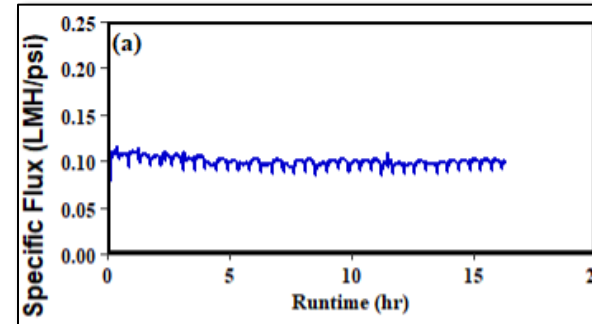


CR-100

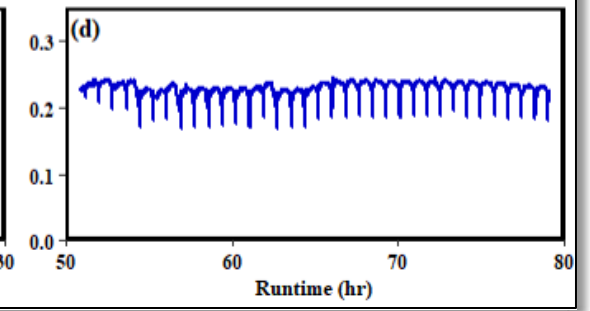
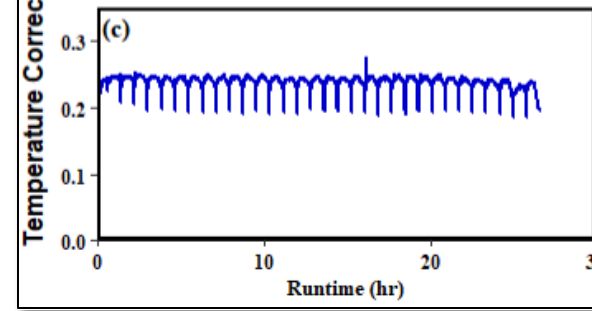
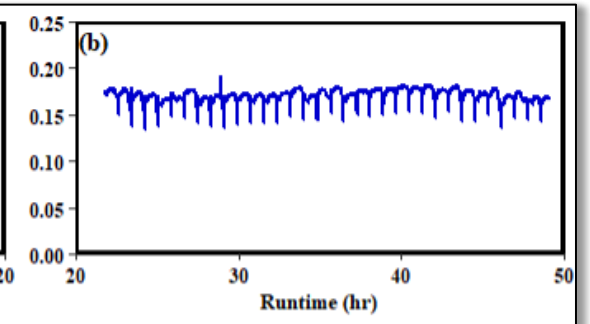


## Temperature Corrected Specific Flux

NF-90 (tight NF)



CR-100

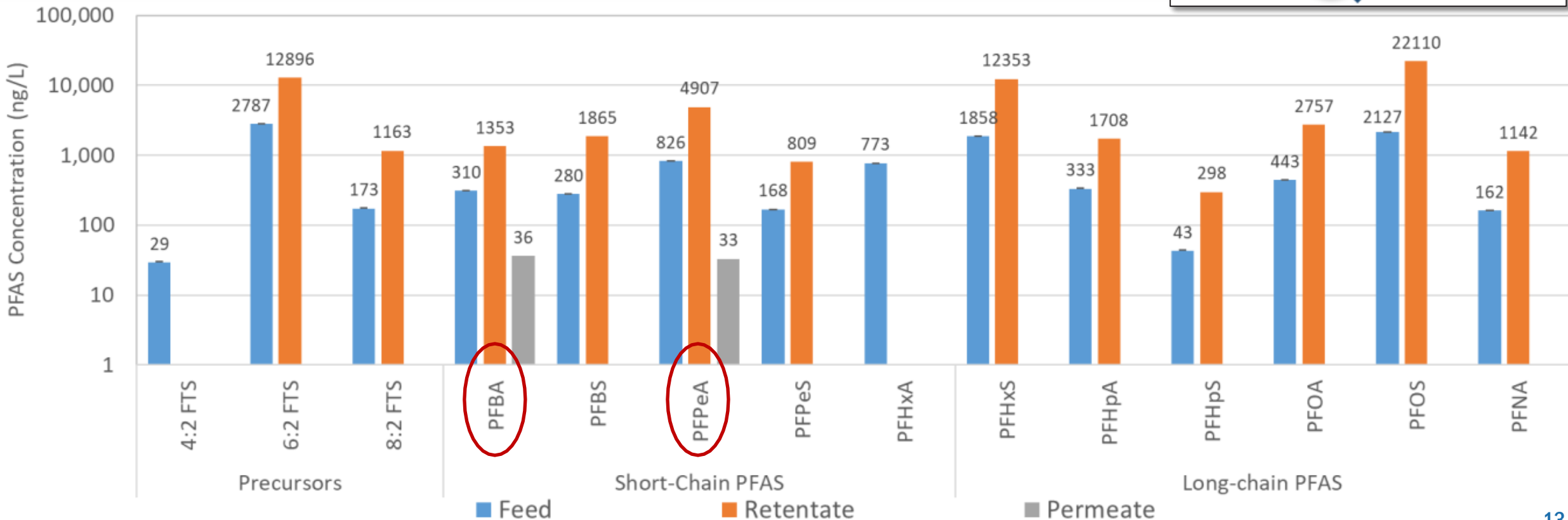
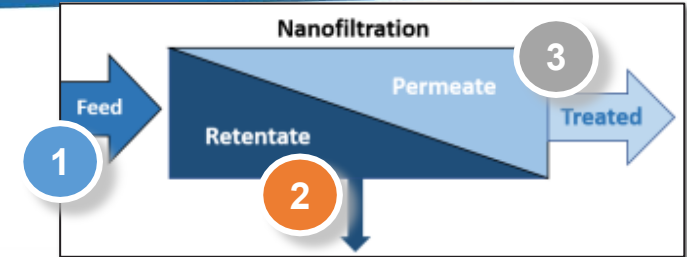


### **KEY POINT:**

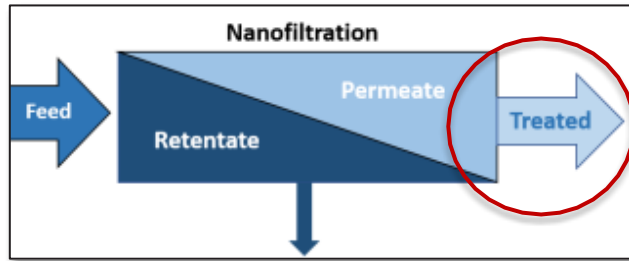
No decrease in permeability was observed for both membranes indicating that CCD treatment of pretreated groundwater did not result in membrane fouling.

# Nanofiltration: *Performance Results*

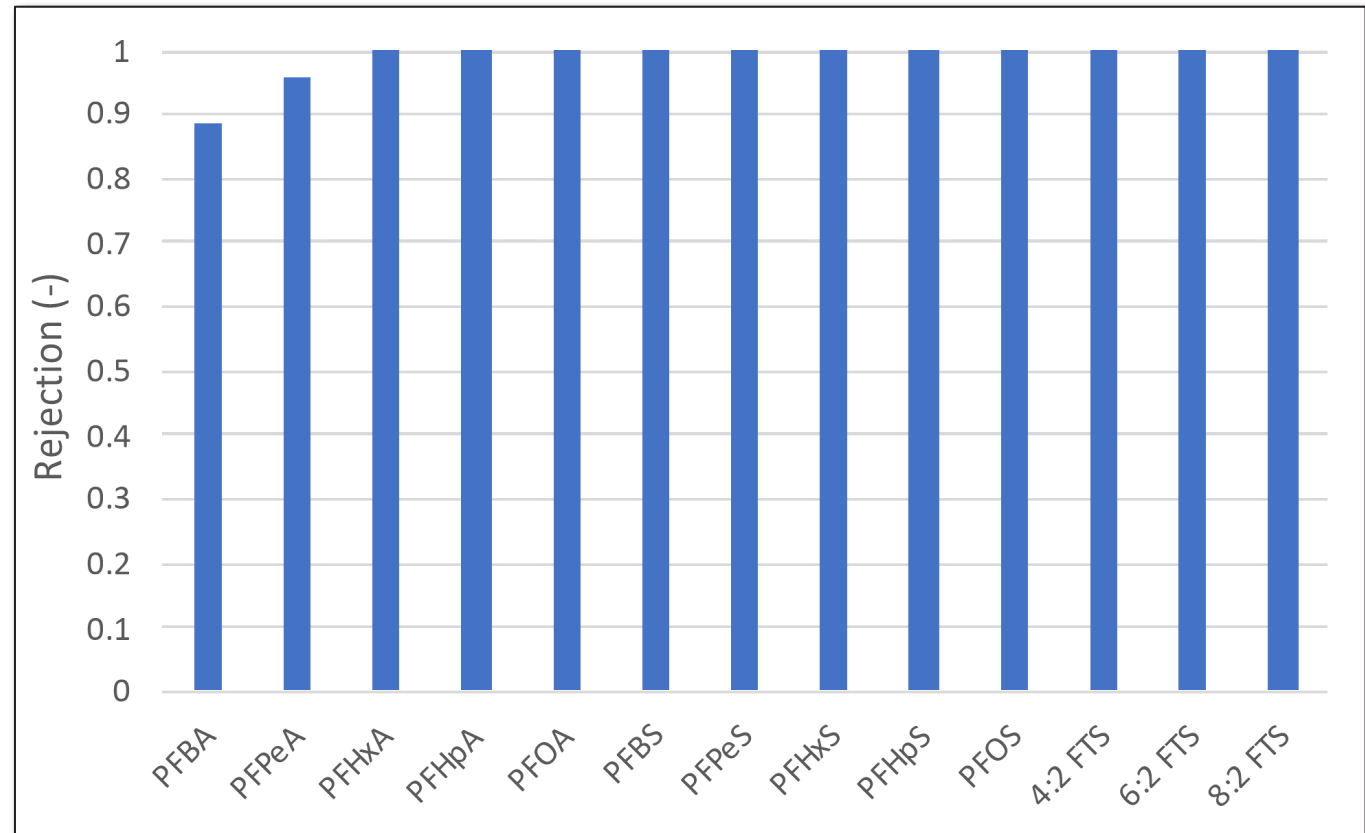
## CR100 Membrane



# Nanofiltration: *Performance Results*

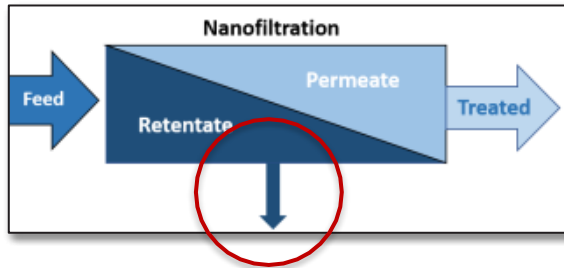


**CR100 Membrane**



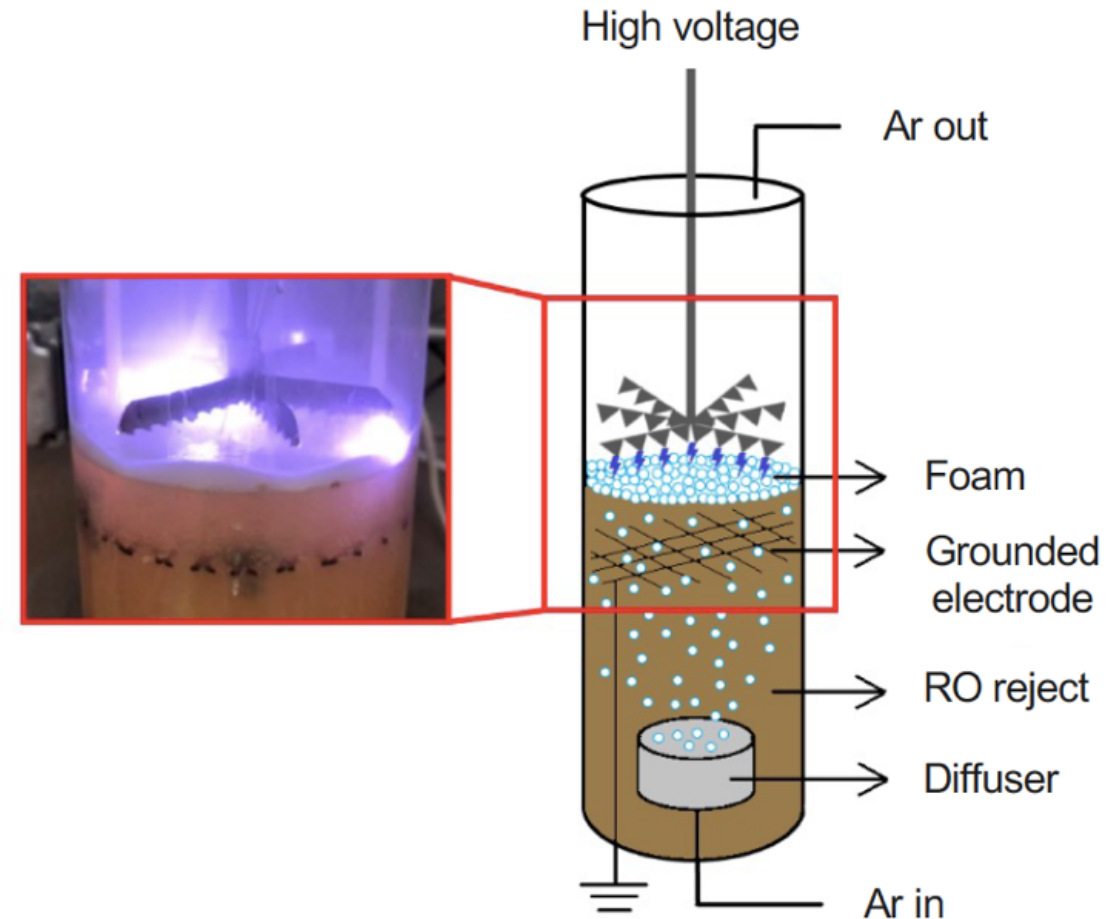
- › Concentrations of most PFAS in the CR100 permeate were below respective detection limits (Rejection  $\approx 1$ )
- › Two exceptions: PFPeA and PFBA (Rejection = 0.96 and 0.88, respectively)
- › Smaller solutes are harder to remove with membranes
- › Bench-scale systems tend to underpredict rejection

# Enhanced Contact Plasma: *Retentate Treatment*

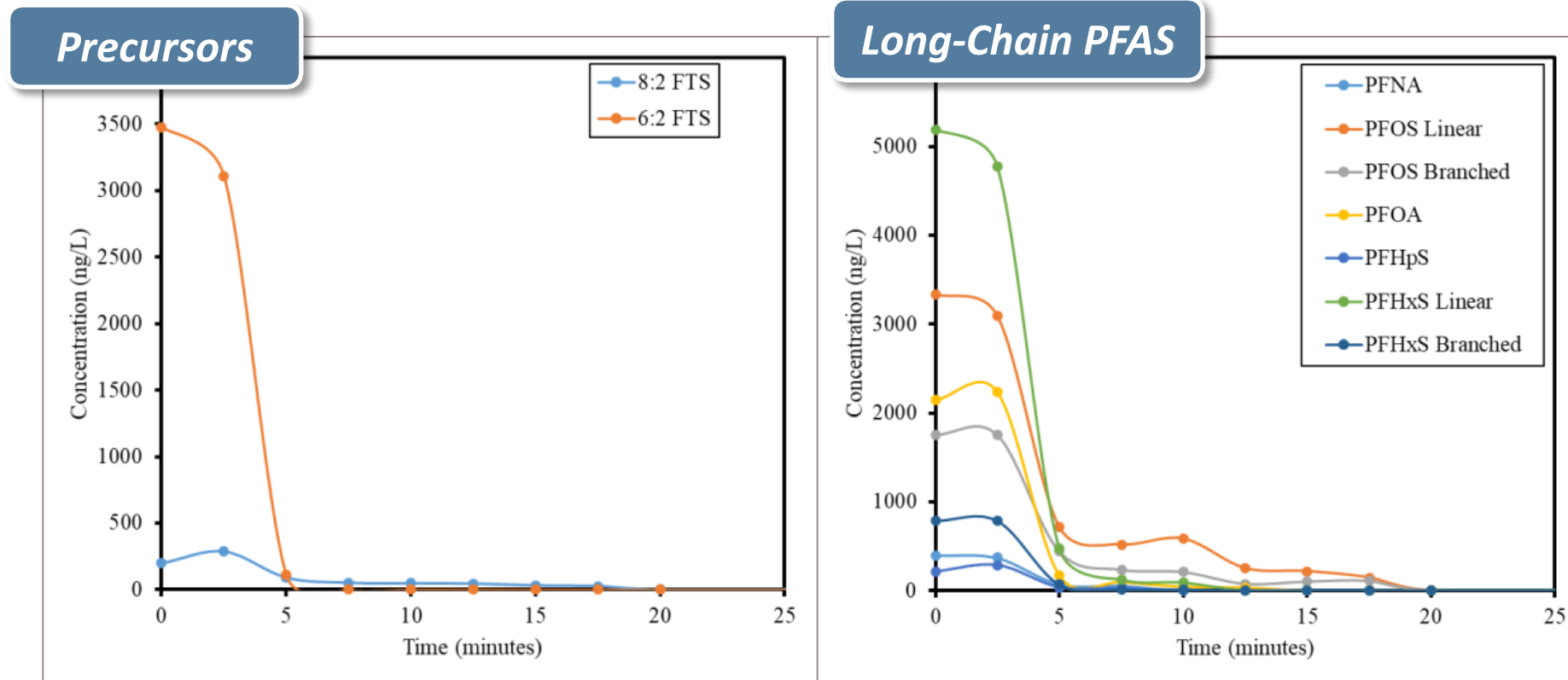


## Batch bubble column reactor with liquid recirculation

- › Treated liquid volume: 3.1 L
- › Treatment time: 180 min
- › Gas flowrate adjusted to maintain foam height
- › Proprietary surfactant addition every 15 min
- › Solution recirculated through heat exchanger at 10°C



# Enhanced Contact Plasma: *Performance Results*



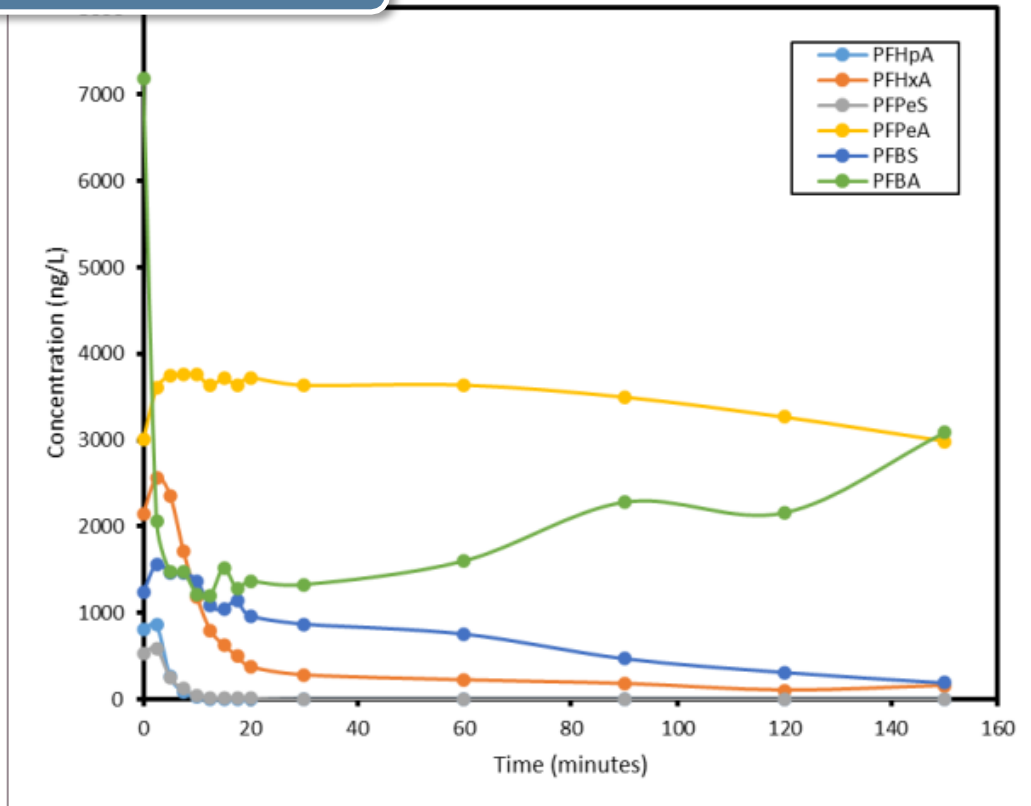
- Concentrations of all identified precursors and long-chain PFAS were below respective detection limits (2-7 ng/L) within 20 minutes; many within 5 minutes of treatment



# Enhanced Contact Plasma: *Performance Results*



## Short-Chain PFAS



- › Short-chain PFAS removal varied from 57% to >99% within 150 minutes of treatment
- › Sulfonates readily degrade over course of treatment while carboxylates exhibit greater treatment times
- › Production of PFBA and slow decline of PFPeA can be attributed to the degradation of long-chain PFAS and unidentified precursors
- › For the field demo, lower flowrates and/or multiple passes will be necessary to achieve short-chain PFAS removal

# Key Points

- › Nanofiltration achieved up to 10x concentration of source water and 88->99% PFAS separation using closed circuit desalination
- › Both membranes (NF90 and CR100) operated well with little to no reductions in permeability
- › Plasma achieved complete removal of identified PFAS precursors and long-chain PFAS to below detection limits; longer treatment times required for short-chain PFAS

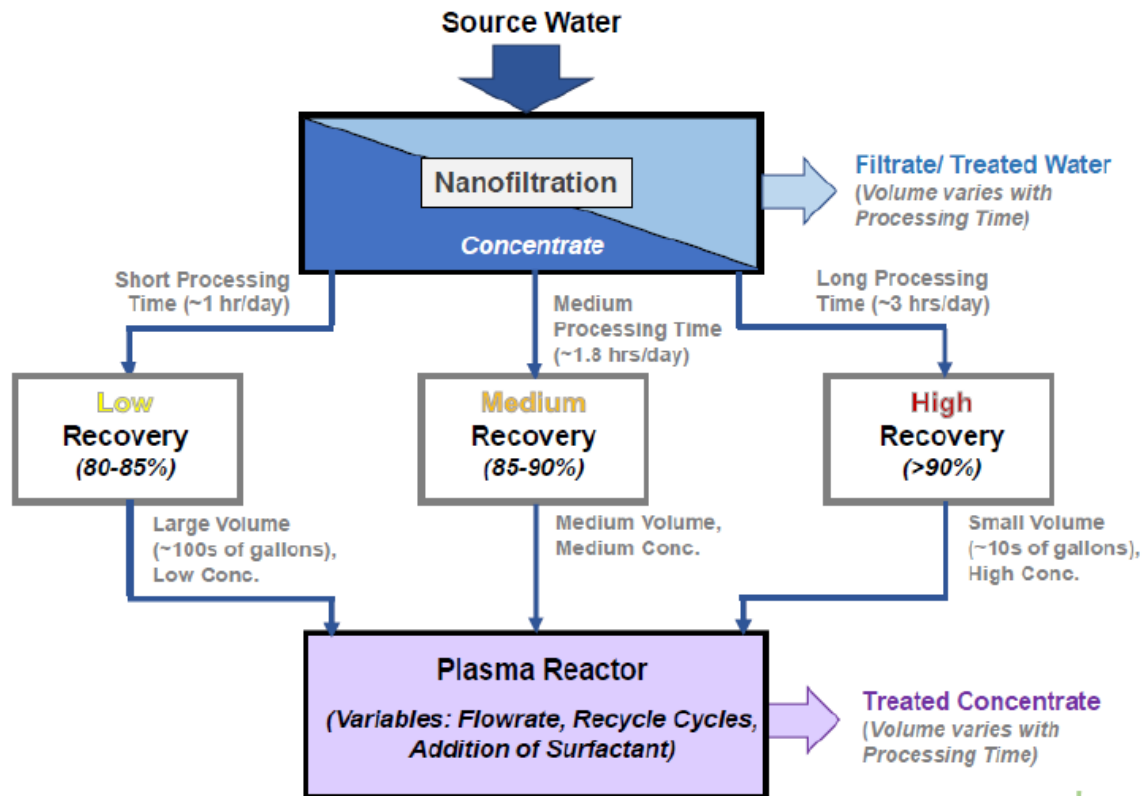
For the field demonstration...

- › Pretreatment required to manage water chemistry at the site
- › Lower flowrates and/or multiple passes will be necessary to achieve short-chain PFAS removal



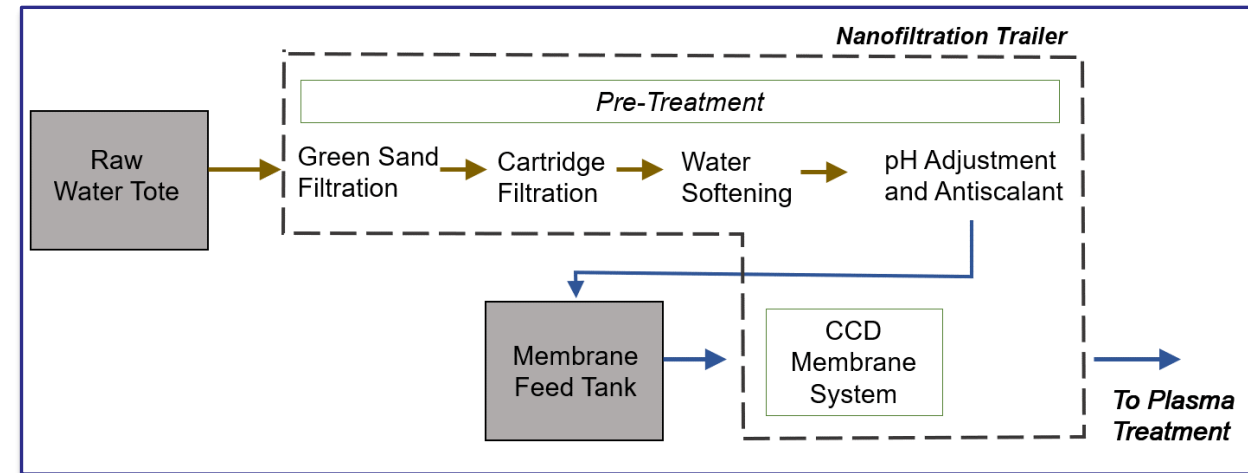
# Next Steps: *Field Demonstration*

## Experimental Plan



Integrated Continuous Operation Under Optimal Conditions

## Trailer Modifications



# Acknowledgements



**Poonam Kulkarni, Whitney Bailey, & Alison Denn**  
*Project Design Engineer*



**Christopher Bellona, Tzahi Cath**  
*Nanofiltration Design & Modifications*



**Selma Mededovic & Tom Holsen**  
*Plasma Reactor Testing & Analytical*



**Ken Camarco, Chase Nau-Hix, Will Knudson, Tom Holsen, and Selma Mededovic**  
*Plasma Reactor Design & Operation*



**Charles Schaefer**  
*Electrochemical Oxidation Testing*

**QUESTIONS?**



# Technical Resources

## Nanofiltration

- › Liu, C.J. et al. (2021). Rejection of Per- and Polyfluoroalkyl Substances (PFASs) in Aqueous Film Forming Foam by High-Pressure Membranes. *Water Research*, 188, 116546.

## Enhanced Contact Plasma

- › Nau-Hix, C. et al. (2021). Field Demonstration of a Pilot-Scale Plasma Reactor for the Rapid Removal of Poly- and Perfluoroalkyl Substances in Groundwater. *Environmental Science & Technology: Water*, 1(3), 680-687.
- › Singh, R. K. et al. (2019). Rapid Removal of Poly- and Perfluorinated Compounds from Investigation-Derived Waste (IDW) in a Pilot-Scale Plasma Reactor. *Environmental Science & Technology*, 53(19), 11375–11382.

## Electrochemical Oxidation

- › Fang, Y. et al. (2022). Removal and destruction of perfluoroalkyl ether carboxylic acids (PFECAs) in an anion exchange resin and electrochemical oxidation treatment train. *Water Research* 230, 119522.

The screenshot shows the top portion of a research article. The journal title 'Environmental Science & Technology' is at the top left. The article title is 'Rapid Removal of Poly- and Perfluorinated Compounds from Investigation-Derived Waste (IDW) in a Pilot-Scale Plasma Reactor'. The authors listed are Raj Kamal Singh, Nicholas Multari, Chase Nau-Hix, Richard H. Anderson, Stephen D. Richardson, Thomas M. Holsen, and Selma Mededovic Thagard. The abstract begins with 'ABSTRACT: A pilot-scale plasma reactor installed into an 8 x 20 ft mobile trailer was used to rapidly and effectively degrade poly- and perfluoroalkyl substances (PFAS) from liquid investigation-derived waste (IDW)'. There is a small image of a plasma reactor in operation. The page number '23' is visible in the bottom right corner of the article preview.

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Page Discussion

### PFAS Treatment by Electrical Discharge Plasma

Plasma-based water treatment is a technology that, using only electricity, converts water into a mixture that can simultaneously oxidize and reduce organics by producing a mixture of hydroxyl radicals and other reactive species. Additionally, the plasma process produces no residual waste and requires no chemical additions, although increasing removal efficiency.

#### Related Article(s):

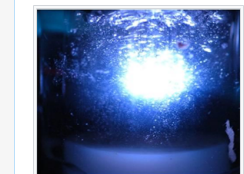
- Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
- PFAS Ex Situ Water Treatment
- PFAS Soil Remediation Technologies
- PFAS Sources
- PFAS Transport and Fate
- Supercritical Water Oxidation (SCWO)

**Contributor(s):** Dr. Selma Mededovic Thagard, Dr. Thomas Holsen, Dr. Stephen Richardson, P.E., Ph.D.

#### Key Resource(s):

- Interstate Technology Regulatory Council (ITRC), PFAS – Per- and Polyfluoroalkyl Substances: 1
- Physico-Chemical Processes for the Treatment of Per- And Polyfluoroalkyl Substances (PFAS): A
- Low Temperature Plasma for Biology, Hygiene, and Medicine: Perspective and Roadmap<sup>[10]</sup>

#### Introduction



Plasma processing plays an essential role in various management<sup>[1][11][12][13][14]</sup>. Plasma is a gaseous state with the temperature of the background gas, plasmas thousand Kelvins (K). Non-thermal plasmas are formed by commercial ozone generation. Plasma that is applied in water treatment (Figure 1) is over a hundred different plasma reactors have been developed for various compounds (VOCs), 1,4-dioxane, herbicides, pesticides, and liquid. Different excitation sources including AC, nano-plasma processing for water treatment applications h

# Next Steps:

## *Destructive Technology Comparison*

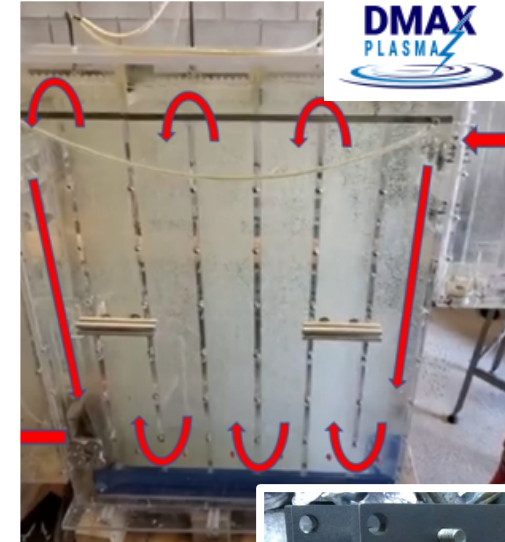
### *Objective*

Direct comparison of two PFAS destructive technologies based on:

- › PFAS removal efficiency
- › Energy use & treatment cost (\$/gal)

### *“Apples to Apples” Comparison*

- › Both technologies will use nanofiltration concentrate generated during the field demonstration.
- › Technologies will be tested under similar controlled operating conditions.
- › Key elements: i) assessing PFAS defluorination relative to the applied current density ( $\text{mA}/\text{cm}^2$ ) and ii) verifying the longevity of the technologies.





# Enhanced Contact Plasma: *Performance Results*



- › Concentrations of most PFAS in the CR100 permeate were below respective detection limits (Rejection = 1)
- › Two exceptions: PFPeA and PFBA (Rejection = 0.96 and 0.88, respectively)

## Pre-treatment:

■  $\Sigma$ PFAS = 55.8  $\mu\text{g/L}$

■ TOPA = 24.2  $\mu\text{g/L}$

## Post-treatment:

■  $\Sigma$ PFAS = 6.4  $\mu\text{g/L}$

■ TOPA = 6.3  $\mu\text{g/L}$

