A Storm is Brewin': Results of LSPA WES Grant Study of PFAS in Rain

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Why did we conduct the study?

PFAS found in rain in other areas

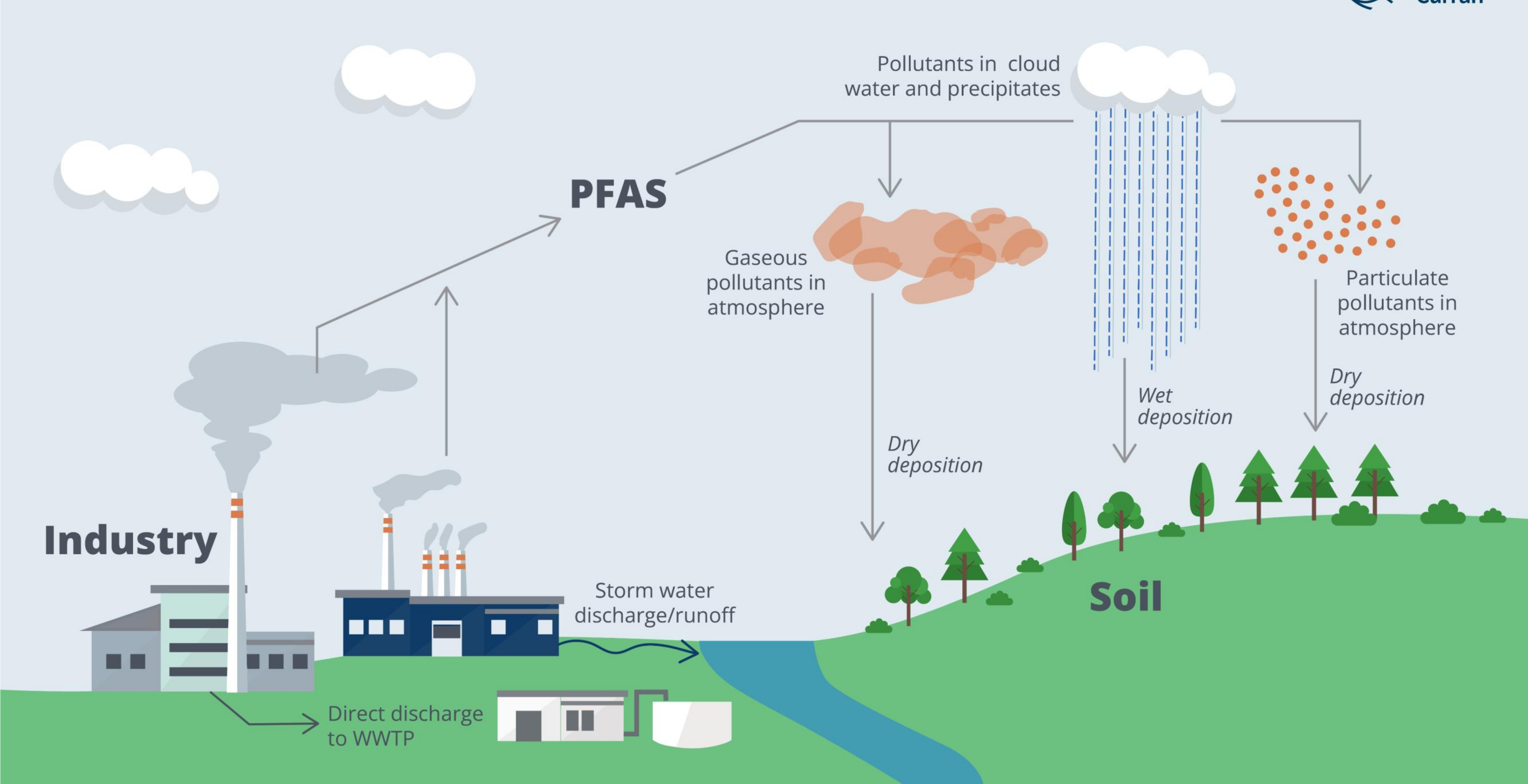
Understand if PFAS is present in rain in Massachusetts

Study Overview

- Received LSPA WES Grant to help cover costs
- Teamed with Alpha Analytical
- Collected rain samples from across Massachusetts

- Evaluated both high intensity (convective) and low intensity (stratiform)

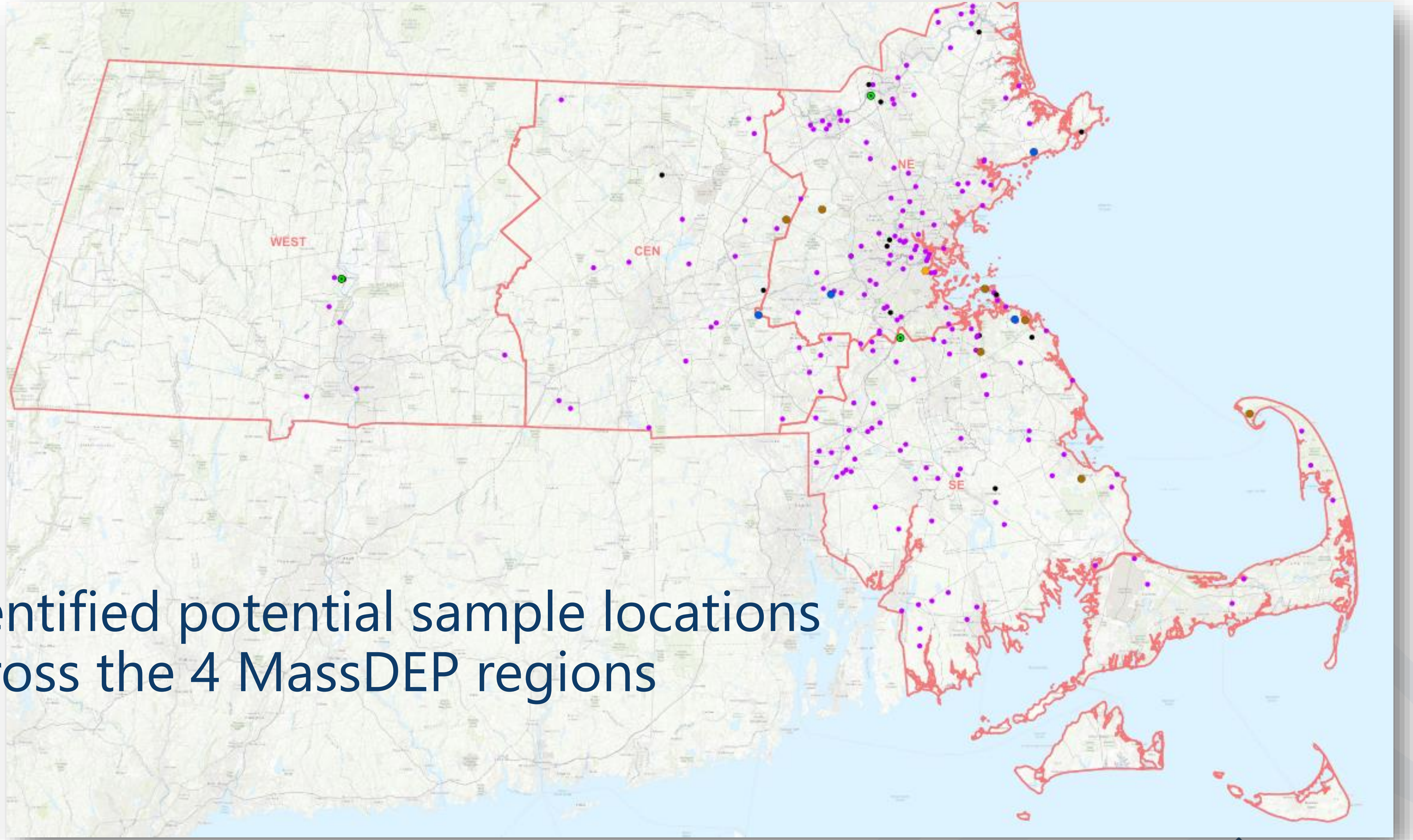
Massachusetts PFAS in Rain Study | **Conceptual Model**



Evaluate both high intensity and longer low intensity rain events

Precip Type	Precip Intensity	Spatial Scale	Lifetime over an area
Stratiform	Lower	Larger	Longer – hours to days

Precip Type	Precip Intensity	Spatial Scale	Lifetime over an area
Convective	Higher	Smaller	Shorter – min to hours



Identified potential sample locations across the 4 MassDEP regions

What we were looking for at sample locations

Good

Unobstructed rainfall into collection device

Better

Unobstructed rainfall + no irrigation, fertilizer or herbicide use

Best

Trees & buildings >20 feet away + >35 feet away from roads

25 rain collection stations were selected based location and setting

Massachusetts PFAS in Rain Study

Woodard & Curran

25
Collection Stations across Massachusetts

21
Woodard & Curran Employees

5
Offices

2
Plants

Next: PFAS Sampling Training for our Volunteers!

Avoid

Waterproof clothing

Chemical ice packs

Sunscreens, insect repellants, moisturizers immediately before or during sampling

Food or drink near/during sample collection

Use Instead

Cotton clothing & shoes

Regular ice in plastic bags

Always wear nitrile gloves when handling samples

What Was Provided

Rain Collection Equipment

- Collection Tray
- Debris Screen
- Rain Gauge

Sample Collection Equipment & Supplies

- Sample Bottles & Cooler
- Gloves
- Chain of Custody
- Shipping Labels & Packing Tape

Copy of the Sample Collection SOP for reference

You Will Supply

- Ice
- Ziplock Bags for ice

Rain Collection Station Set-Up and Sampling

3 Steps as detailed in the Sample Collection SOP

1. Locating & Setting Up Your Collection Station

2. Collecting a Sample

3. Recording Field Observations

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Data Collection Form

https://forms.office.com/r/ZcsWsipFuu

Massachusetts PFAS in Rain Study Data Collection Form - Saved

Questions

Responses 57

8. How would you characterize the precipitation? *

- Heavy (i.e. larger drops with wider separation)
- Light (i.e. drizzle, fine drops with less separation)
- Did Not Observe (i.e. you weren't home during the rain event, the rain event occurred overnight)
- Other

9. Did you observe any of the following during the rain event? *

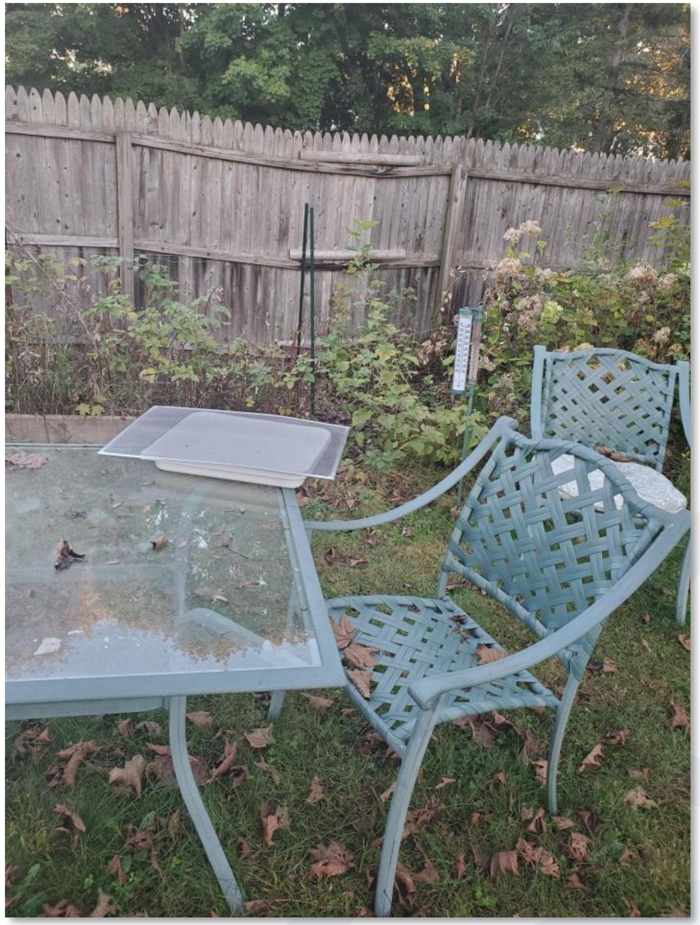
- Thunder
- Hail
- High Winds
- Did Not Observe (i.e. you weren't home during the rain event, the rain event occurred overnight)
- Other

10. How would you describe the clouds during the rain event? *

- Nimbostratus (i.e. gray cloud layer - thick enough to obscure the sun, low ragged clouds beneath a somewhat uniform sheet)
- Cumulonimbus (i.e. heavy dense cloud in the form of a mountain or huge tower, upper portion usually smooth, or striated; underneath very dark, with low ragged cloud fragments)

5 mins

Collection Stations



Collection Stations

Collection Stations

Collection Stations

Woodard & Curran

Collection Stations

Woodard & Curran

Collection Stations

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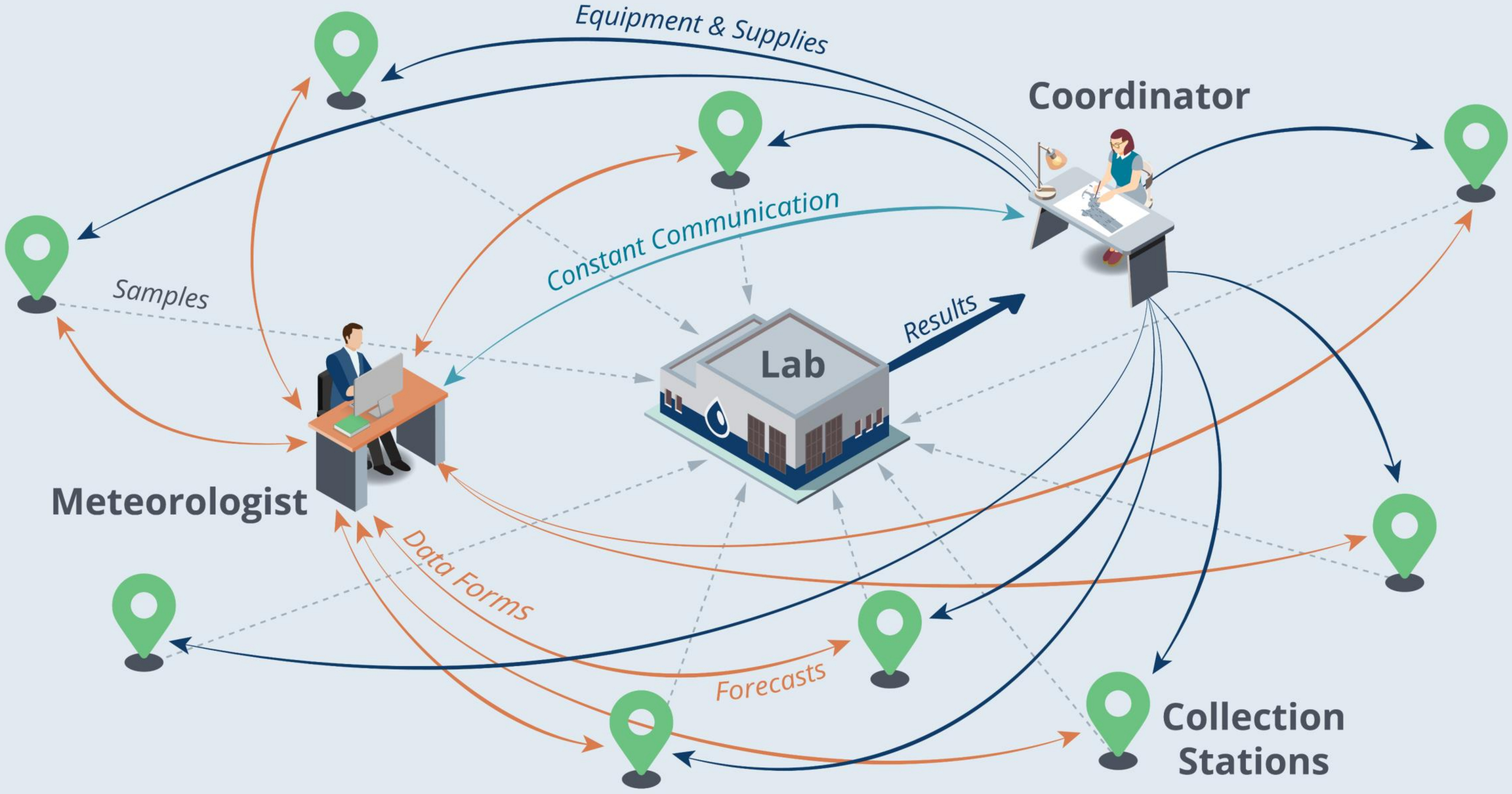
Massachusetts PFAS in Rain Study | **Sample Collection Logistics**



Weather forecasting!

SUNDAY EVENING WEATHER BRIEFING

LITTLE / NO
SLIGHT
MED
HIGH

Likelihood of sampleable event (≥ 0.25" precipitation)

Area Forecast Discussion
National Weather Service Boston/Norton MA
740 PM EDT Sun Aug 29 2021

Much warmer and more humid Monday ahead of a cold front, that will produce scattered thunderstorms. A few strong to severe storms are possible in the afternoon and early evening. The cold front moves through Monday night. High pressure then briefly returns Tuesday with drier and less humid air. Tropical moisture associated with the remnants of Hurricane Ida arrives Wednesday into Thursday with the risk of heavy rain and flooding, but axis of heaviest rainfall remains uncertain. Drier and cooler conditions arrive heading into Labor Day weekend with a touch of fall.

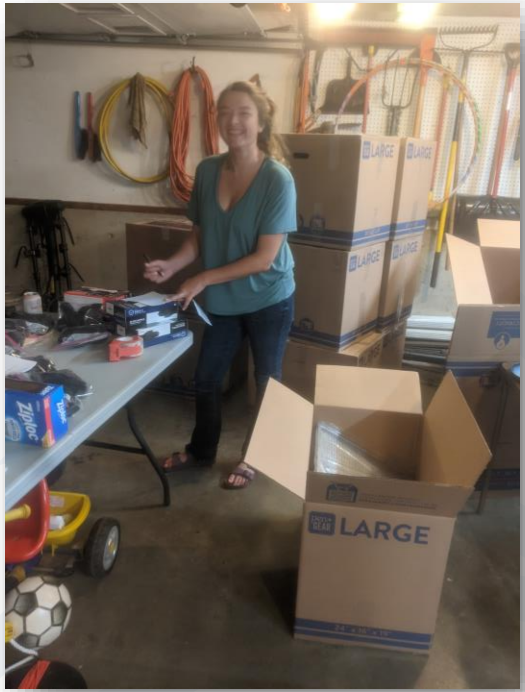
	Monday, August 30, 2021				Tuesday, August 31, 2021				Wednesday, September 1, 2021				Thursday, September 2, 2021			
	MORNING	AFTERNOON	EVENING	OVERNIGHT	MORNING	AFTERNOON	EVENING	OVERNIGHT	MORNING	AFTERNOON	EVENING	OVERNIGHT	MORNING	AFTERNOON	EVENING	OVERNIGHT
	8am-12pm	12pm-4pm	4pm-8pm	8pm-8am	8am-12pm	12pm-4pm	4pm-8pm	8pm-8am	8am-12pm	12pm-4pm	4pm-8pm	8pm-8am	8am-12pm	12pm-4pm	4pm-8pm	8pm-8am
WEST		SLIGHT								MED	MED	HIGH	HIGH	MED	SLIGHT	
CENTRAL			SLIGHT							MED	MED	HIGH	HIGH	MED	SLIGHT	
NORTHEAST			SLIGHT								MED	HIGH	HIGH	HIGH	MED	
SOUTHEAST										SLIGHT	MED	HIGH	HIGH	HIGH	MED	

- Delivered to inbox **Sunday evening** and **Thursday evening**
- Likelihood of a **sampleable event (0.25")** in the region
- Both event types (**stratiform and convective**)

Woodard & Curran

Study Overview: Quick Facts

- 50 Primary Samples Collected
  - 27 Stratiform Samples from 5 Stratiform Rain Events
  - 23 Convective Samples from 6 Convective Rain Events
- QA/QC Samples
  - 3 Field Duplicates
  - 2 Field Blanks (all ND)
  - Equipment Blank on Sampling Equipment (ND)
- September 13 – October 30, 2021



Summary of Results

11
Samples with Detections of PFAS

5
Different PFAS Compounds Detected

Woodard & Curran

Detected PFAS

	% Detected	Minimum Detected	Maximum Detected
1H,1H,2H,2H-Perfluorooctanesulfonic Acid (6:2FTS)	6%	1.82	3.48
Perfluorobutanoic Acid (PFBA)	13%	2.3	3.36
Perfluorohexanoic Acid (PFHxA)	2%	1.94	1.94
Perfluorononanoic Acid (PFNA)	2%	2.86	2.86
Perfluoropentanoic Acid (PFPeA)	6%	2.08	2.35

Results in ng/l

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Summary of Results

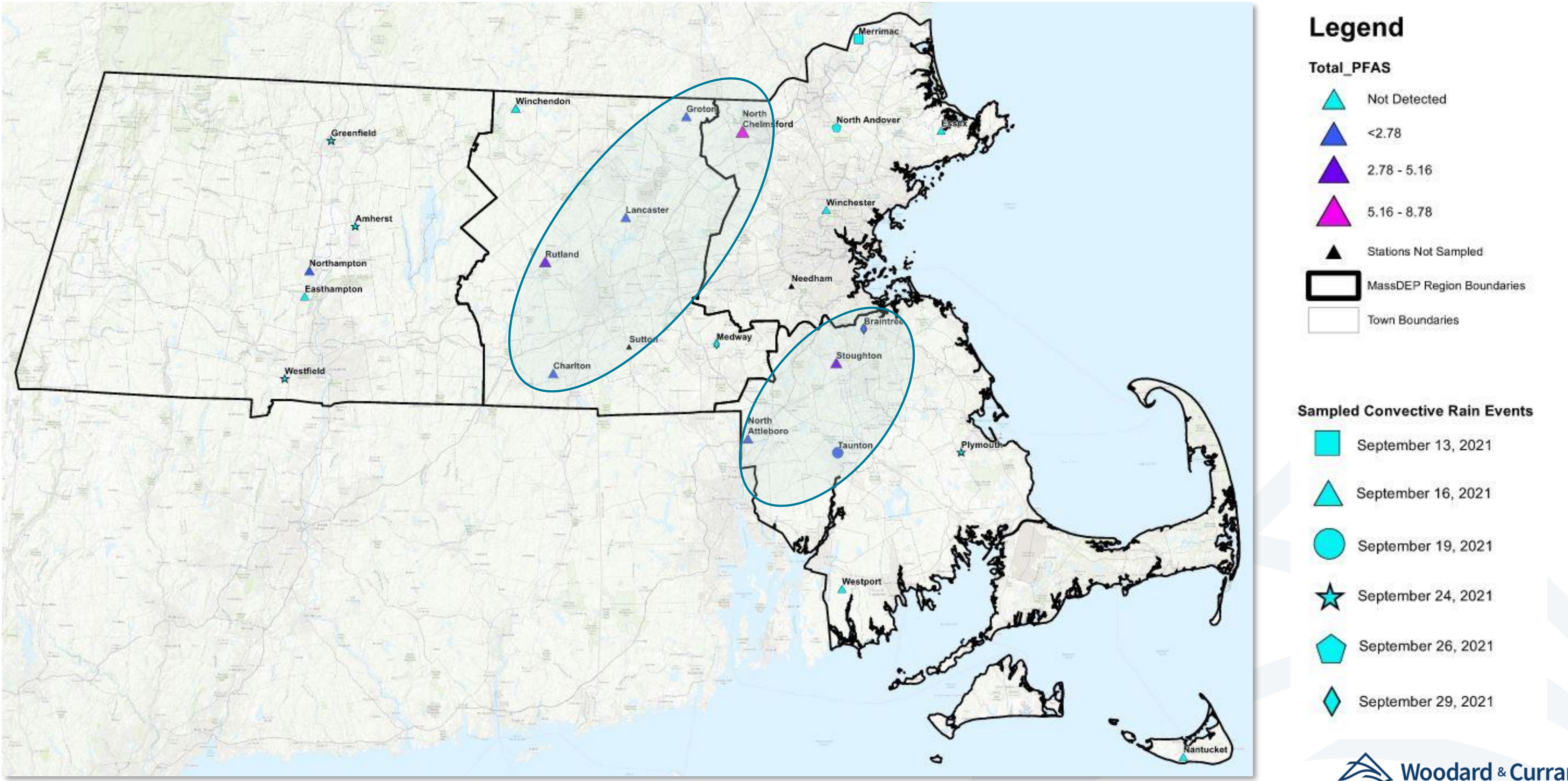
11
Samples with Detections of PFAS

5
Different PFAS Compounds Detected

10
Samples from Convective Rain Events with Detections

1
Sample from Stratiform Events with Detections

Results: Convective Rain Events



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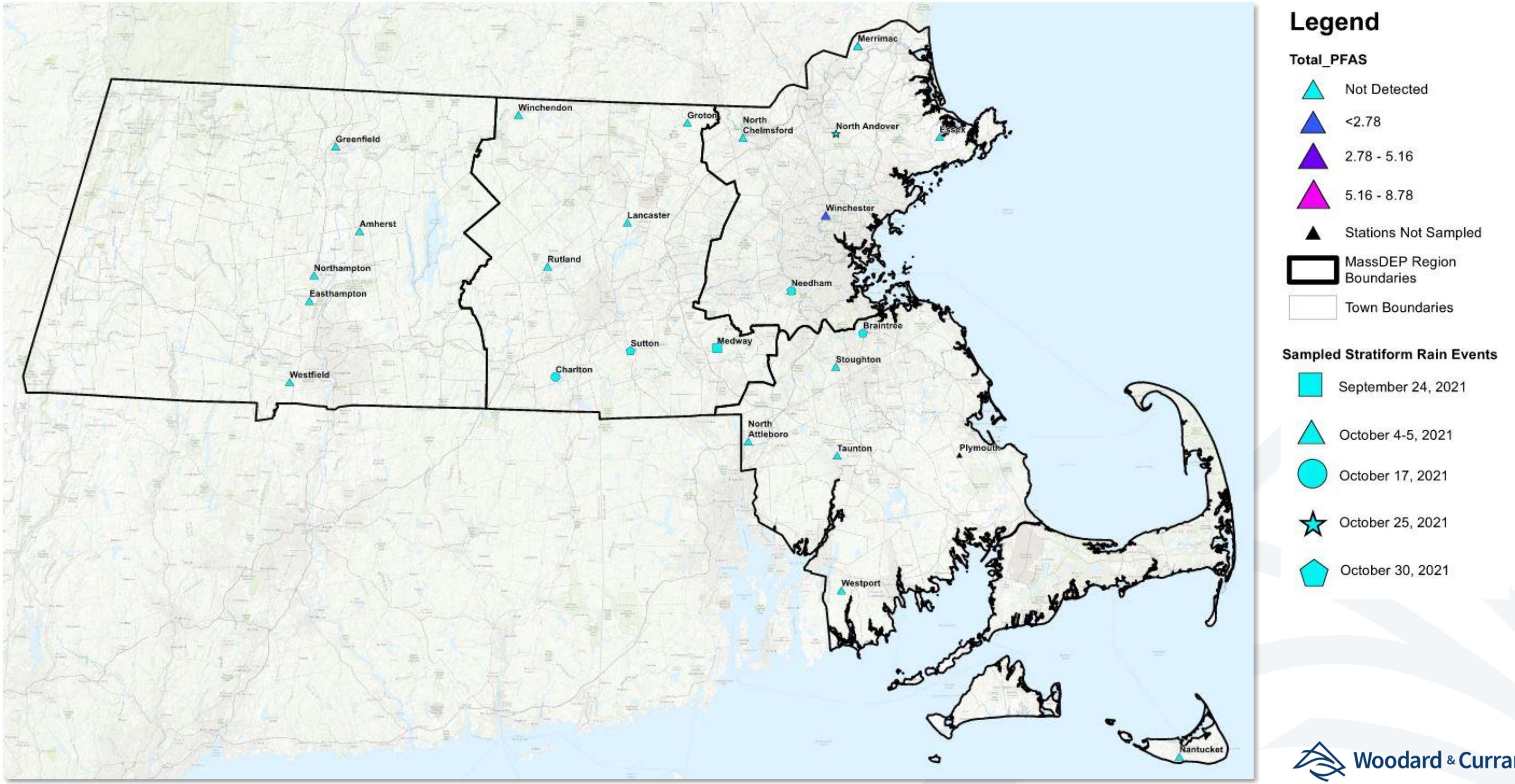
Results: Stratiform Rain Events



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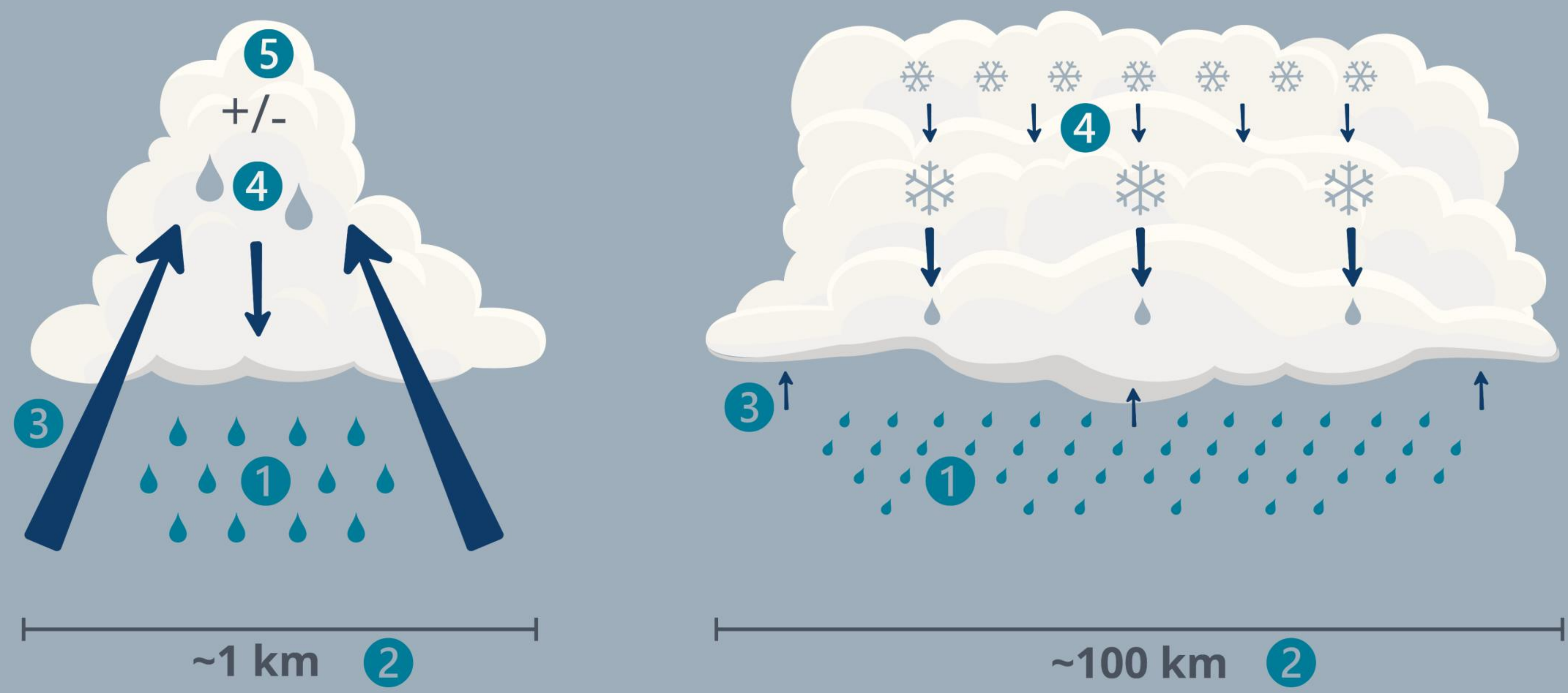
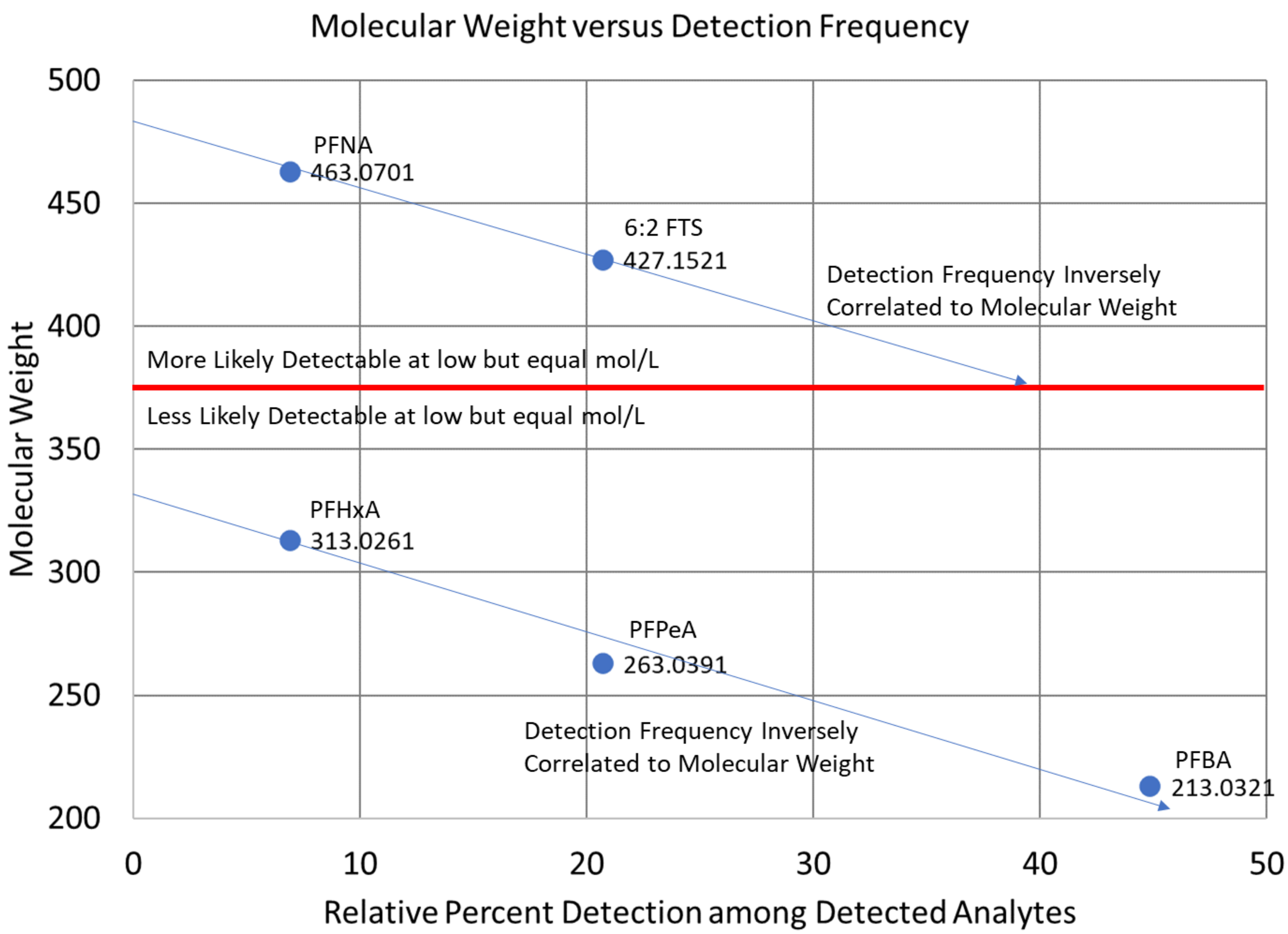
Massachusetts PFAS in Rain Study | **Precipitation Types**



1 Intensity 2 Scale 3 Vertical motion 4 Precipitation growth 5 Ionization



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Key Take Aways

Very low concentrations

total PFAS <8.78 ng/L

No regulatory or personal health implications

Demonstrates widespread nature

recycling of molecules in the water cycle

Next steps

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LSP Association assess. advise. restore.

ALPHA ANALYTICAL World Class Chemistry

Thank you!

Questions?

www.battelle.org/pfas

18 May 2022

BATTELLE

It can be done

PFAS Annihilator™

Supercritical Water Oxidation (SCWO) for PFAS Destruction

Presented to: LSP Association

Analytical Services | Health Assessment | Novel Chemistries | Remediation & Treatment | Site Characterization | Toxicology

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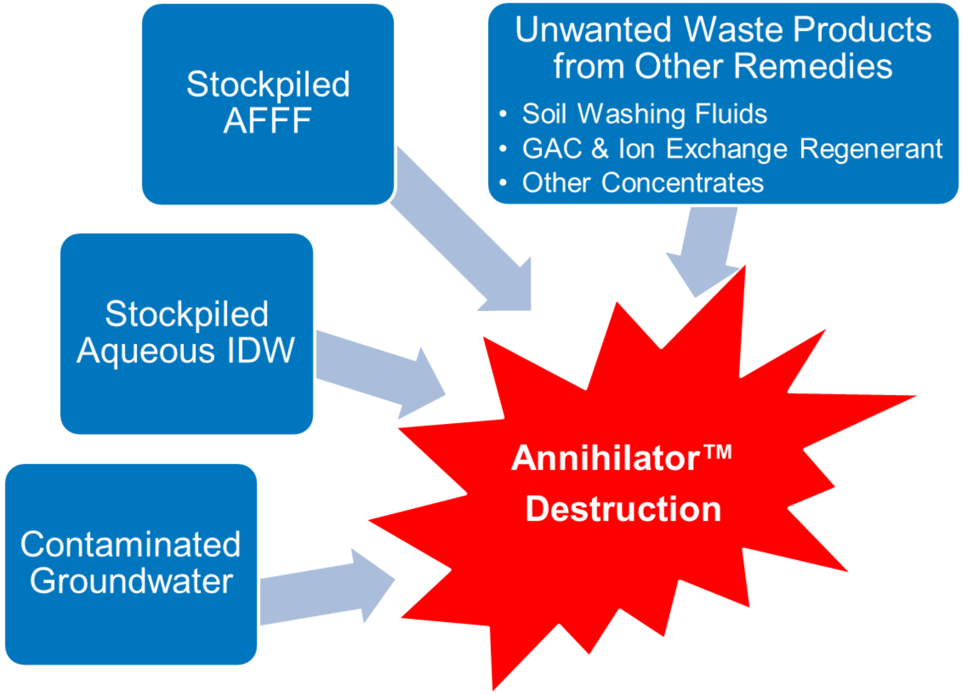
What is PFAS Annihilator™?

Challenge: To meet the growing need for effectively and efficiently treating water for per- and polyfluoroalkyl substances (PFAS), we must destroy the substances, prevent them from transferring elsewhere, and avoid creating harmful byproducts.

Solution: Battelle has created a closed-loop, on-site destruction solution powered by supercritical water oxidation (SCWO) that does exactly that.

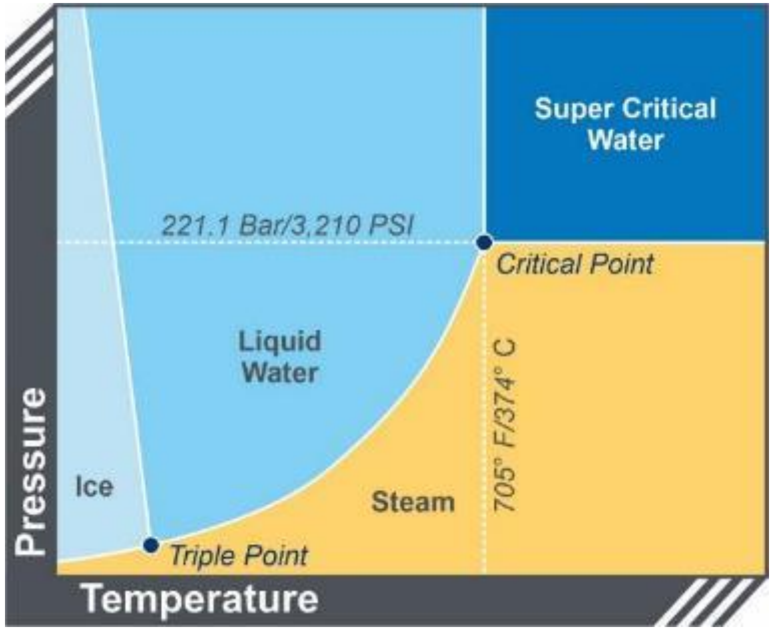
- Utilizes supercritical water oxidation (SCWO) proven to break the PFAS carbon-fluorine bond.
- SCWO has been used successfully to treat other recalcitrant waste including nerve agents, radioactive waste, and polychlorinated biphenyls (PCBs).



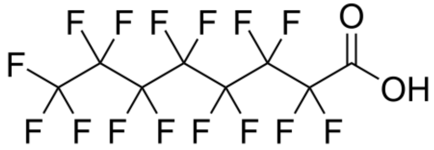
The Annihilator Effectively Addresses PFAS-Contaminated Media

SCWO Destruction of PFAS

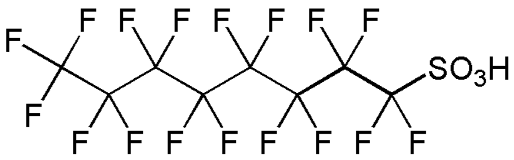
- Supercritical water exhibits unique properties
  - Gas and liquid phases become indistinguishable
  - Density is about 10% of water above the supercritical point
  - Water no longer behaves as a polar solvent
  - Fast transport properties result in increased reaction kinetics
- High temperature in an oxidizing environment overcomes activation energy to break C-F bond



PFOA

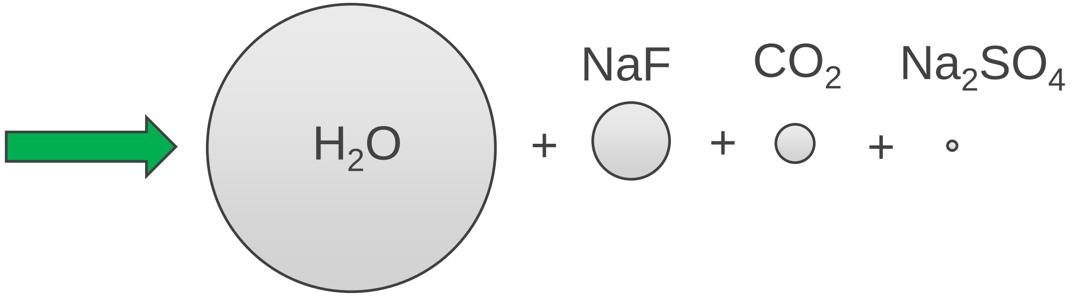


PFOS



+ H_2O_2 (oxygen source)

+ NaOH (Neutralization)



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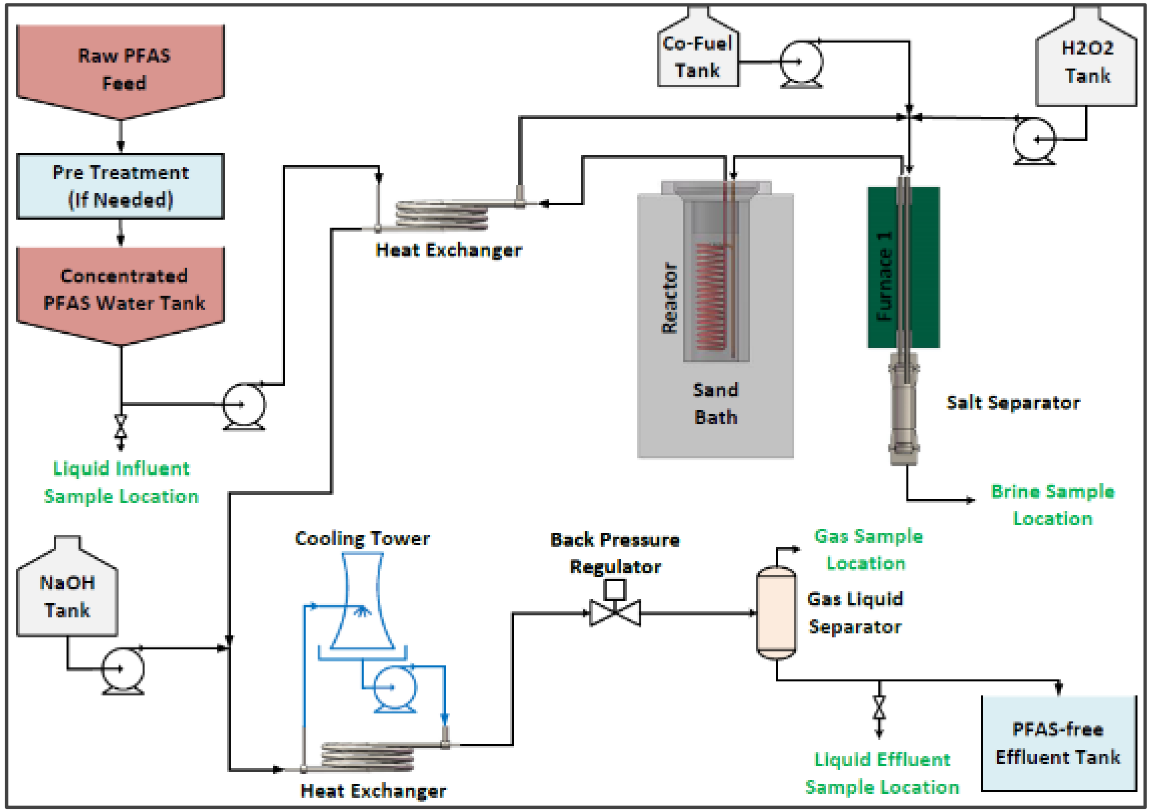
PFAS Annihilator™ Process Flow

- Water is pretreated and concentrated (if necessary)
- The water is heated to supercritical temperature and pressure using one or more heat sources
- Feed is oxygenated with H_2O_2 or air
- A neutralizing agent (NaOH) is added to remove hydrofluoric acid in effluent
- The effluent is cooled
- Generated gas is separated from the liquid
- Effluent streams are further treated (if necessary) and discharged



Battelle's Bench-Scale Systems have Effectively Treated AFFF and Aqueous Investigation Derived Waste

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PFAS Annihilator™ Discriminating Factors

- Not a new technology
- Results in destruction of PFAS rather than transferring them from one media to another
- Fast. <10 second residence time
- Effective on short- and long-chain PFCAs and PFSAs
- Not inhibited by organic co-contaminants
- Operates at lower temperature than thermal treatment technologies
- Treats dilute and highly-concentrated PFAS-impacted media
- Generates little waste

Landfill Leachate

SCWO-treated Landfill Leachate

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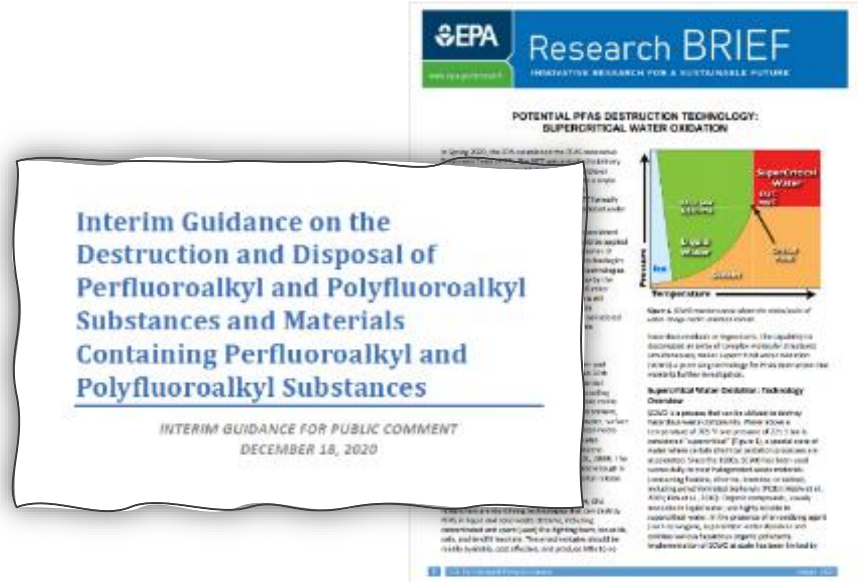
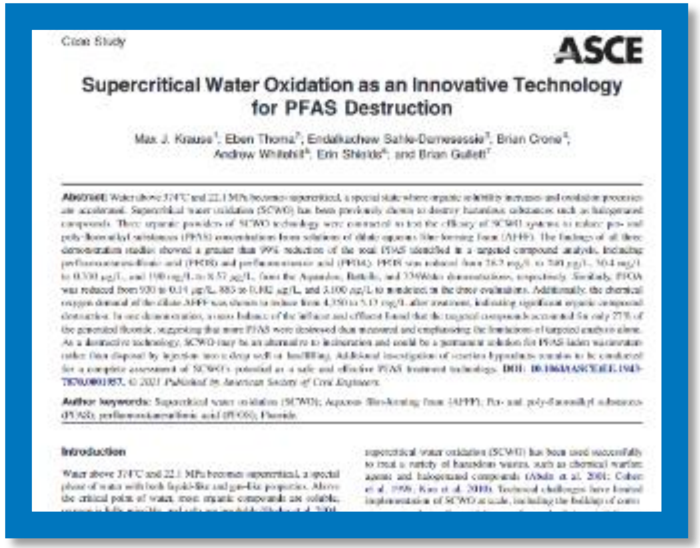
SCWO is an established technology for difficult-to-treat compounds that is validated by EPA for PFAS

- PFAS Annihilator™ demonstrated to > 99.99% destruction
- EPA peer-reviewed publication December 2021
- EPA is a co-PI with Battelle on Navy-led FY22 ESTCP proposal pending award



Research Brief: Potential PFAS Destruction Technology: Supercritical Water Oxidation | US EPA



Supercritical Water Oxidation as an Innovative Technology for PFAS Destruction | Journal of Environmental Engineering | Vol 148, No 2 (ascelibrary.org)

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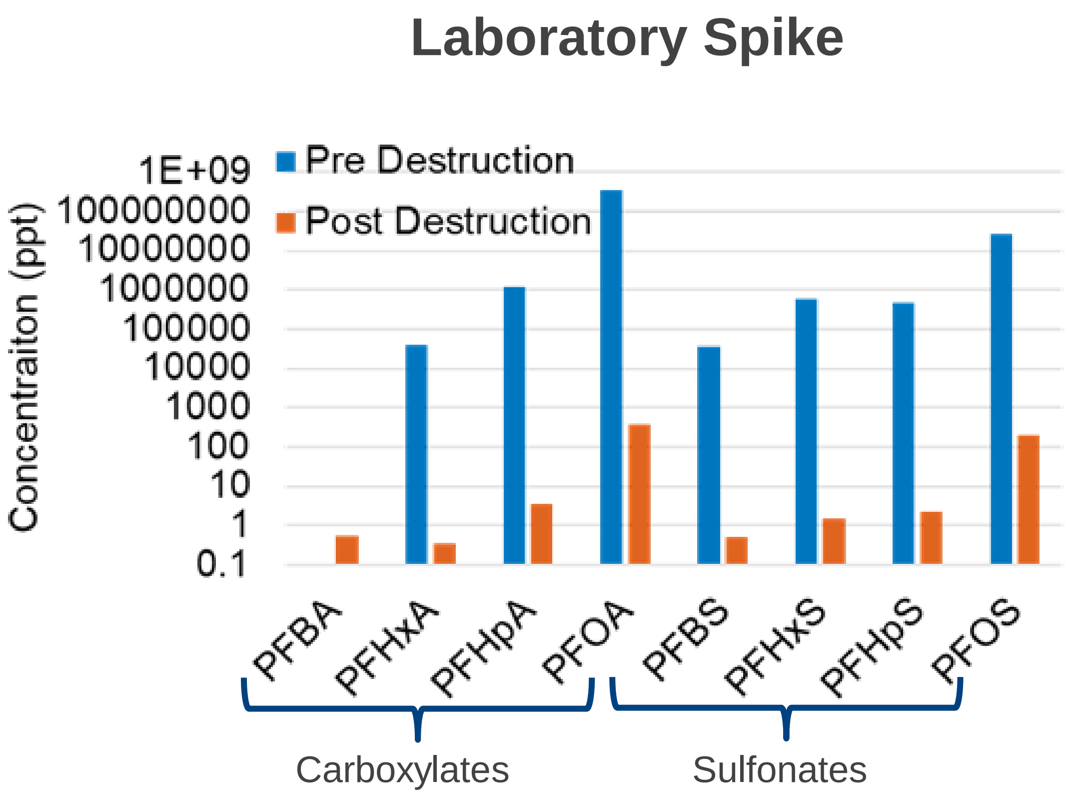
Bench-Scale Demonstration of Performance – Laboratory Spike Water

Lab Sample	Pre-Destruction (ppt)	Post-Destruction (ppt)	Annihilation
Total PFAS	386,301,393	580	99.9998%

- Single run of a high-level spiked sample to simulate AFFF concentrations
- Reduced concentration of 6 out of 8 PFAS analytes (that were initially present) to below 5 ppt
- Overall destruction efficiency was better than 99.999% (5 logs)



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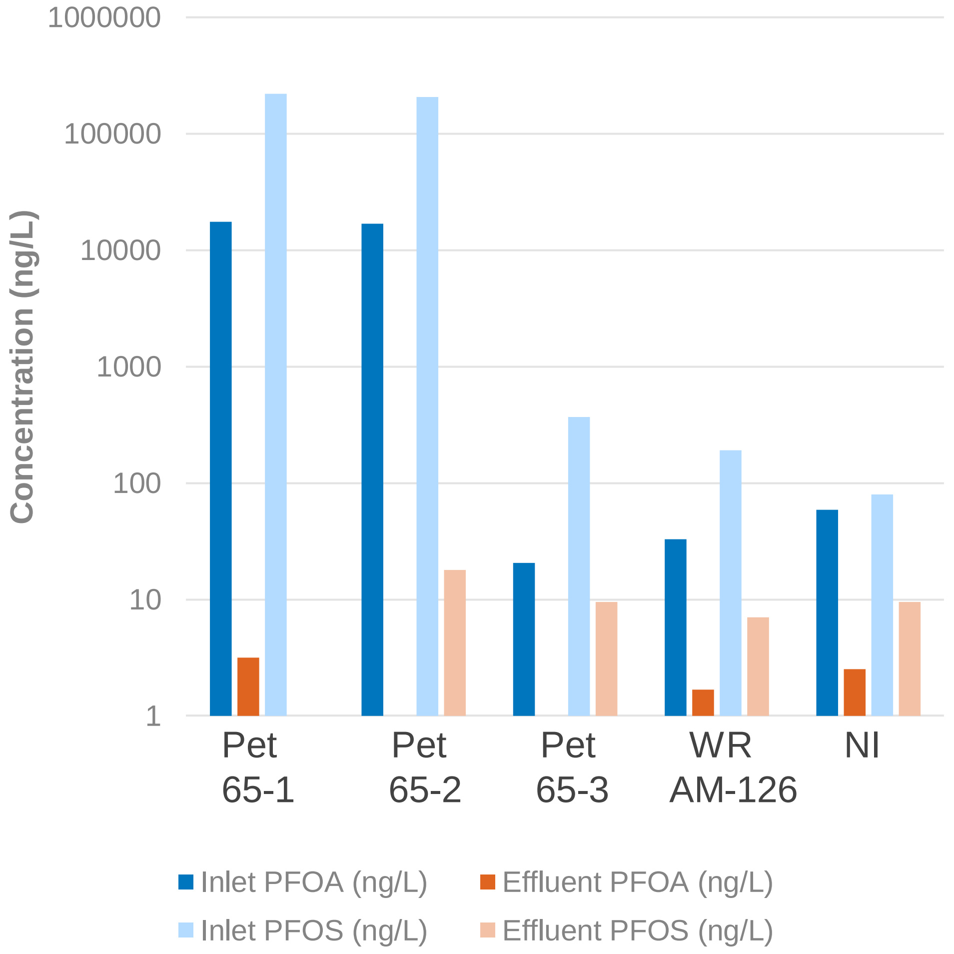
PFAS Annihilator™ Groundwater & IDW Destruction

Sample	Inlet PFOA (ng/L)	Effluent PFOA (ng/L)	Inlet PFOS (ng/L)	Effluent PFOS (ng/L)	% Destruction Target PFAS
Pet 65-1	17,590	3.16	221,300	< 5	99.998
Pet 65-2	16,820	< 5	207,800	17.8	99.996
Pet 65-3	20.62	< 5	369.0	9.51	92.601
WR AM-126	33.00	1.68	190.0	7.03	98.751
NI	59.20	2.51	80.20	9.51	98.334



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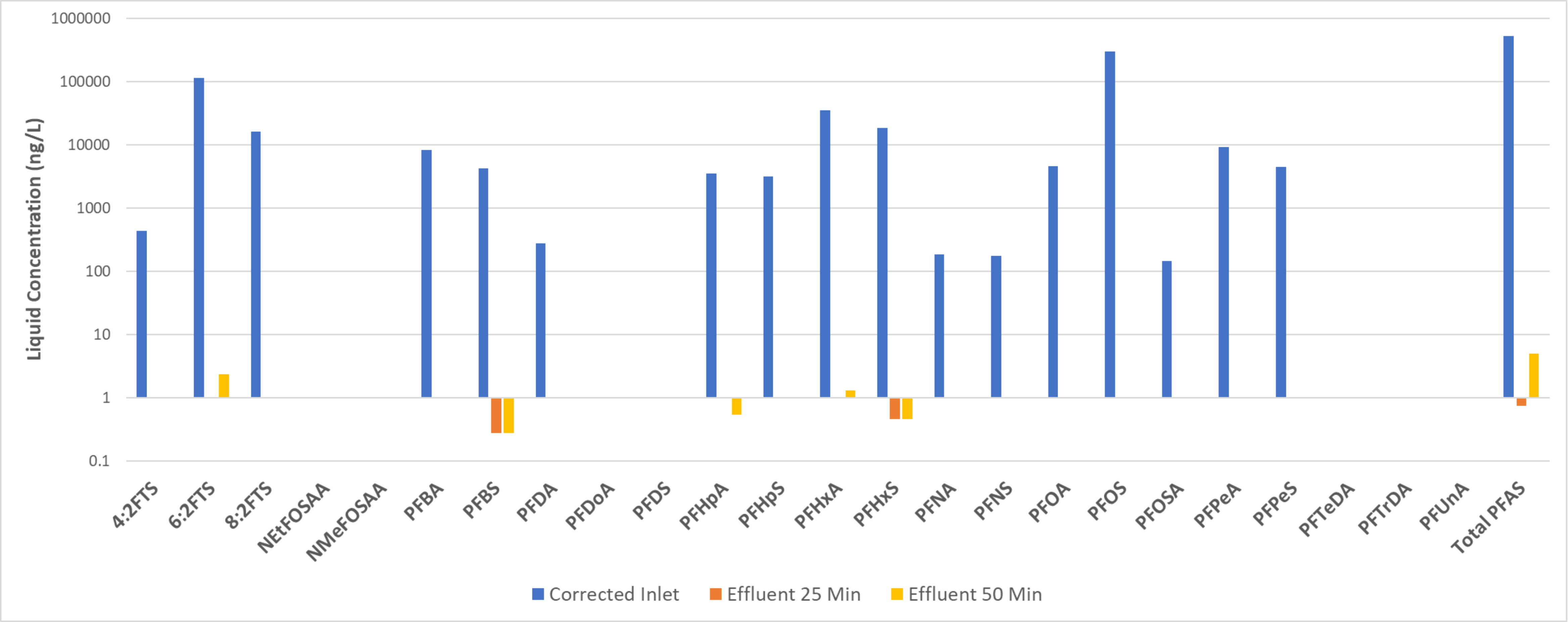
PFAS Destruction in IDW

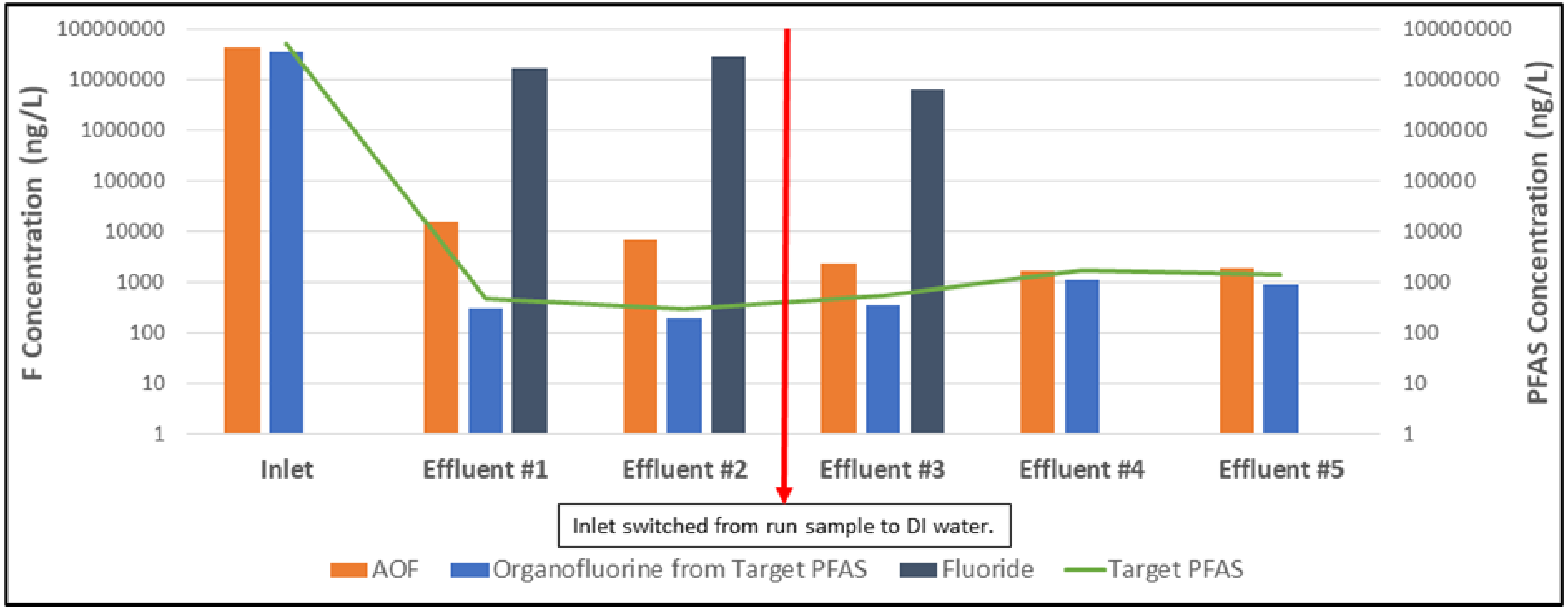


SCWO has been Demonstrated to Effectively Treat a Range of PFAS-Impacted Media

Feed Type	Dilution Factor	TOC (mg/L)	ΣPFAS (µg/L)		% Destruction
			Influent Concentration (Pre-destruction)	Effluent Concentration (Post-destruction)	
AFFF – Legacy PFOS (Lightwater)	~1:25	7,480	471,000	0.100	>99.99
	~1:10	23,900	2,150,000	0.667	>99.99
AFFF – Legacy Fluorotelomer	1:1.63	26,500	13,29	0.171	>99.99
AFFF – Modern Fluorotelomer (C6)	1:1.45	126,000	13,57	3.08	99.9
GAC Regenerant (alcohol-based)	1:15	2.22	23.9	0.0157	99.9
	1:20	2.05	27.3	0.0176	99.9
Soil Wash Rinsate	NA	582	0.709	0.0422	92.8
Landfill Leachate	NA	804	41.0	0.0135	99.9

Mass Balance

- Able to account for >90% of fluorine in system
- Very low levels of fluorine (and target PFAS) in vapor effluent



PFAS Annihilator™

Waste Physical and/or Chemical Characteristics Impact on Performance

Chemical Characteristic	Impact	Mitigation (if applicable)
High chemical oxidant demand	Greater mass of oxidant required	• Dilution of feed may be required
High total organic carbon	Less heat input needed	• Dilution of feed may be required if heating value is greater than heat dissipated
Presence of petroleum hydrocarbons	Less heat input needed	• Dilution of feed may be required if heating value is greater than heat dissipated • Free-phase oil (if present) is removed during pretreatment
Presence of chlorinated solvents	Formation of hydrochloric acid	• Increase dosage of neutralizing agent
High solids content	Reactor plugging	• Perform pre-filtration
High ion concentration	Increase potential for plugging	• Increase frequency of salt removal from salt separator
	Ability to concentrate feed using RO is reduced	• Perform bulk salt removal and/or other types of pre-concentration

Case Study - Background

Objective - Deploy and assess performance of a mobile supercritical water oxidation (SCWO) system to eliminate PFAS in landfill leachate

- 1-week field demonstration (February 2022)
- Waste treatment facility located in Michigan
- Performed bench-scale test to evaluate appropriate operating conditions and confirm destruction efficacy
- Utilized mobile demonstration system
  - 40 to 50 gallons per day (gpd) capacity
  - Utilized hydrogen peroxide as oxidant and sodium hydroxide as neutralizing agent
  - Equipped with prefiltration to remove solids & post ion exchange (IX) system for metals treatment

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Demonstration Highlights

- >99.9% reduction of PFAS for all runs for which samples were collected
- No PFAS detected in reactor effluent except PFOA
- No PFAS detected in vapor
- No VOCs or SVOCs detected in aqueous effluent
- Some metals in effluent, but removed by ion exchange

Feed	Influent PFAS (PFOA) Conc (ppt)	Effluent PFAS (PFOA) Conc (ppt)
1st Stage & Final	7,300	6.97
Concentrate & Final	5,870	9.13
Concentrate	11,500	7.69

Pre- and Post-Treatment Samples

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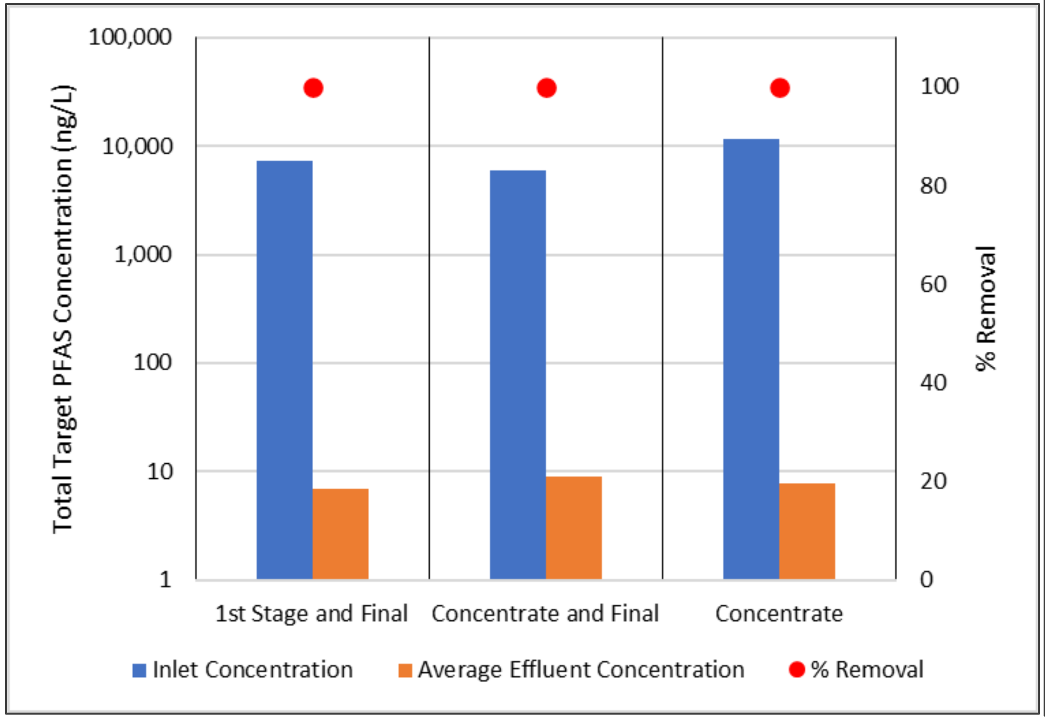
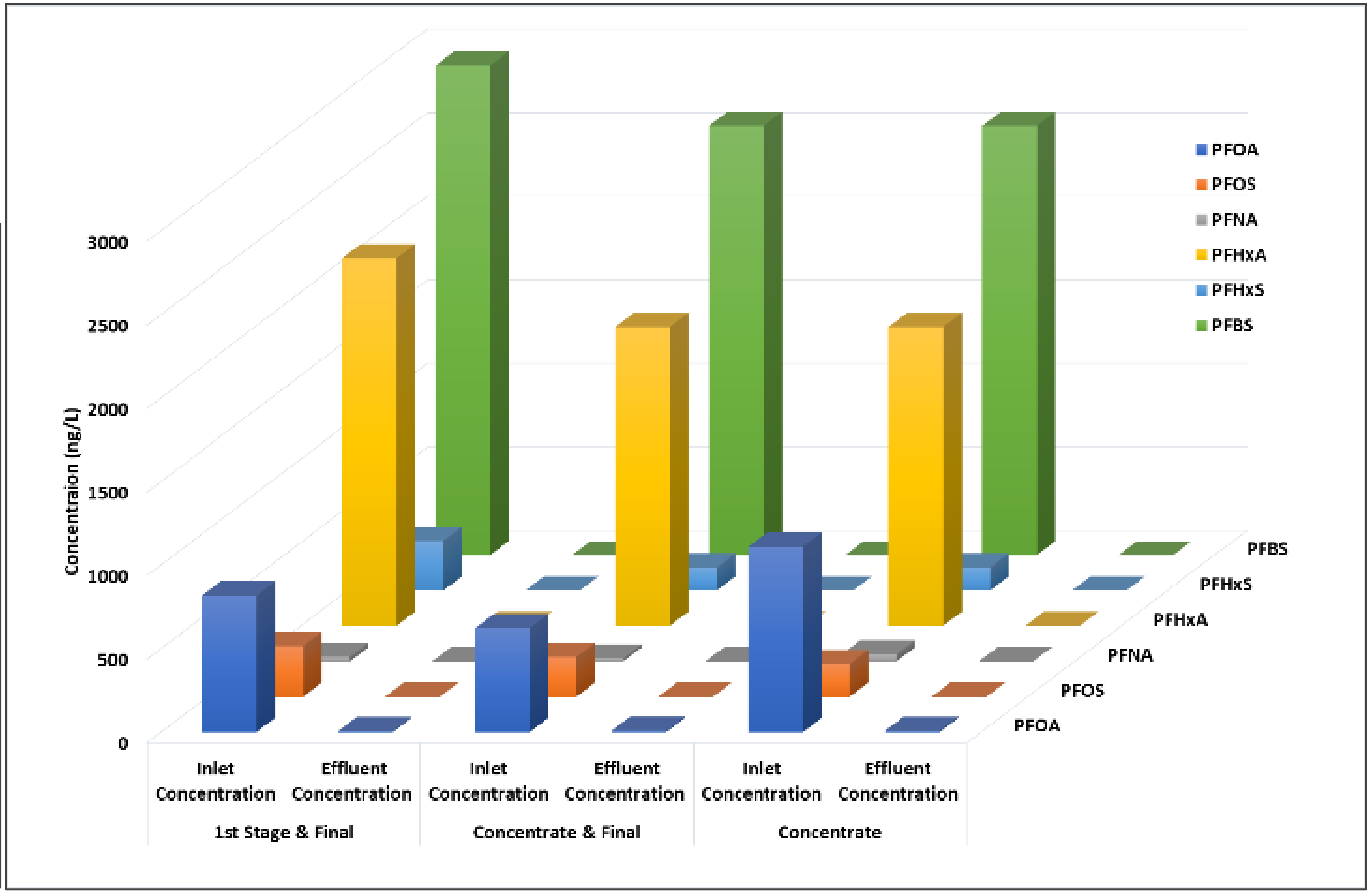
Aqueous Reactor Effluent PFAS Results

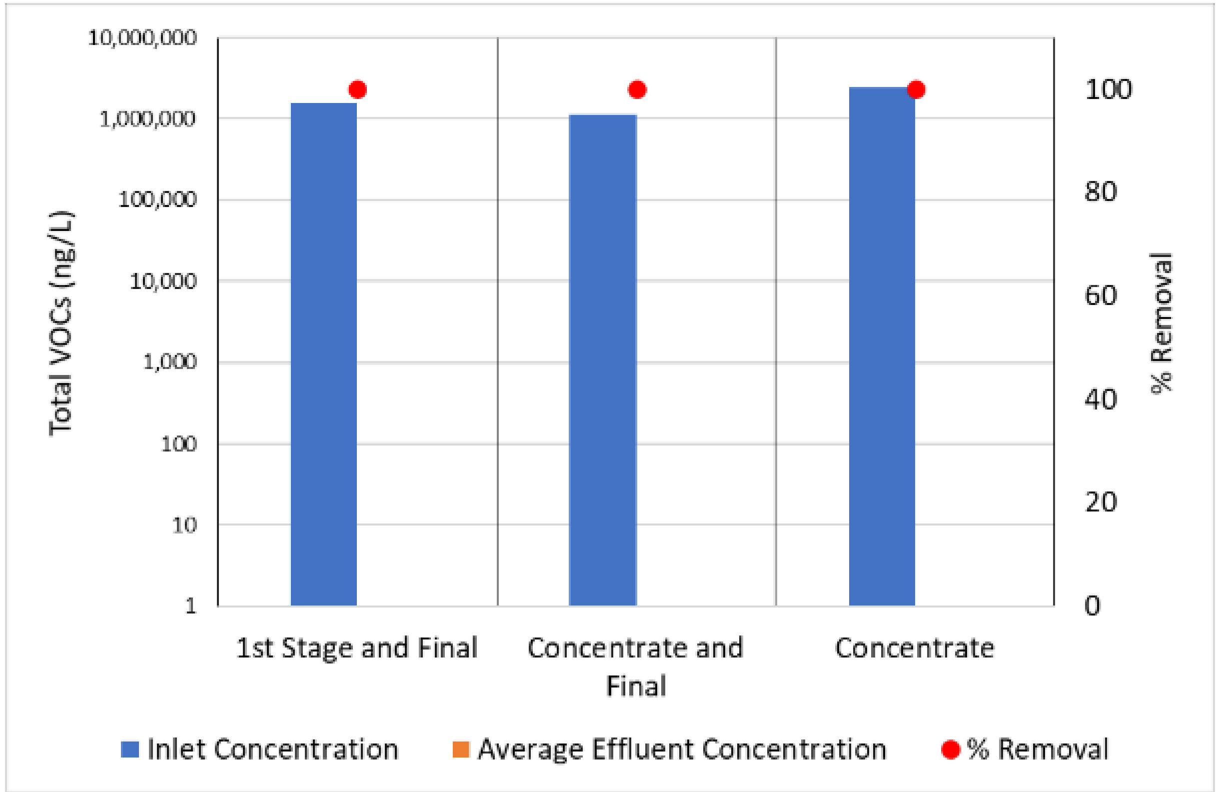




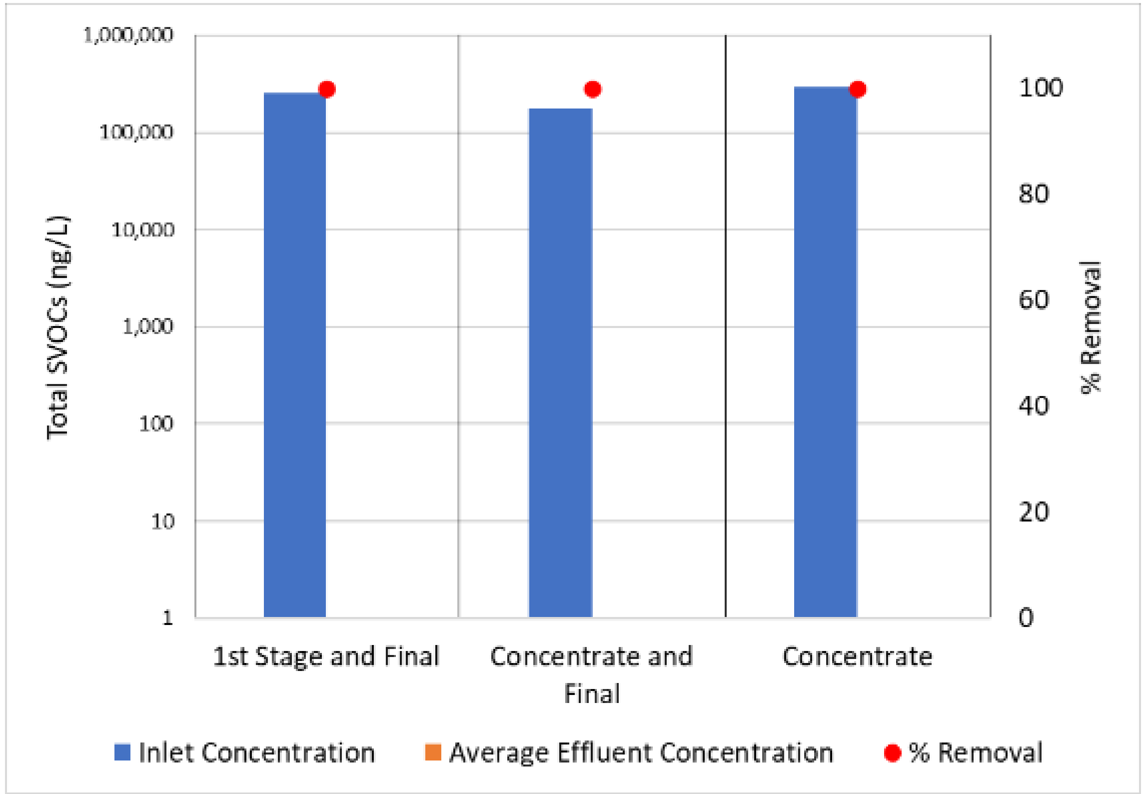
Total PFAS

Select Congeners

Aqueous Reactor Effluent
VOCs & SVOCs Destruction Results



VOCs



SVOCs

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PFAS Annihilator™ is a scalable technology which enables tailored site solutions

Bench/Lab

- Bench-scale testing
- Prepare for field deployment
  - Characterization
  - Optimization
- Develop new applications
  - Solids/Soil Reactor

Mobile 1

- Smaller, finite volumes
- Treatment waste streams
- Concentrated regenerant
- In-situ concentrates

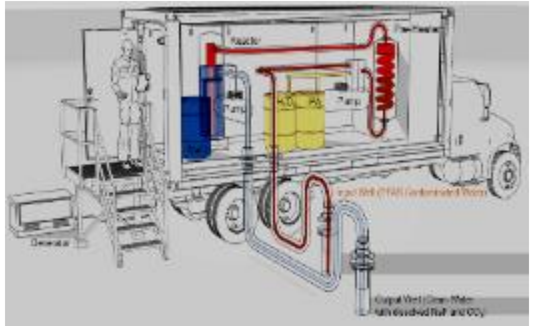
Capacity per unit: 40 – 60 gpd; up to 10x capacity w/ concentration

Mobile 2

- Larger, finite volumes
- Stockpiled waste
- Process water
- AFFF

Capacity per unit: 300 – 500 gpd; up to 10x capacity w/ concentration

Site Scalable



- Mobile or brick and mortar
- Higher volume
- Longer-term operation
- Can be coupled with pump & treat or in-situ treatment

Capacity: scaled to site requirements

Reaction in Seconds

Minimal Waste

Complete PFAS Destruction

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Annihilator™ is being deployed to Air Force and other sites

January 2020	Bench system demonstrated for aqueous
August 2020	Bench system demonstrated for AFFF in US EPA study
December 2021	EPA publication on SCWO
February 2022	Mobile 1 deployed to industrial site
July 2022	Mobile 1 deployed to industrial site
October 2022	Mobile 1 deployed to Hill Air Force Base
January 2023	Mobile 2 deployed to Peterson Air Force Base
FY22-24	ESTCP ER22-7338 SERDP ER22-3384

Q & A with the Presenter

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