BENCH AND PILOT-SCALE OPTIMIZATION OF FRACTIONATION TECHNOLOGY TO TREAT PFAS IMPACTED WASTE STREAMS

April 5th 2022, NEWMOA Northeast Conference -The Science of PFAS

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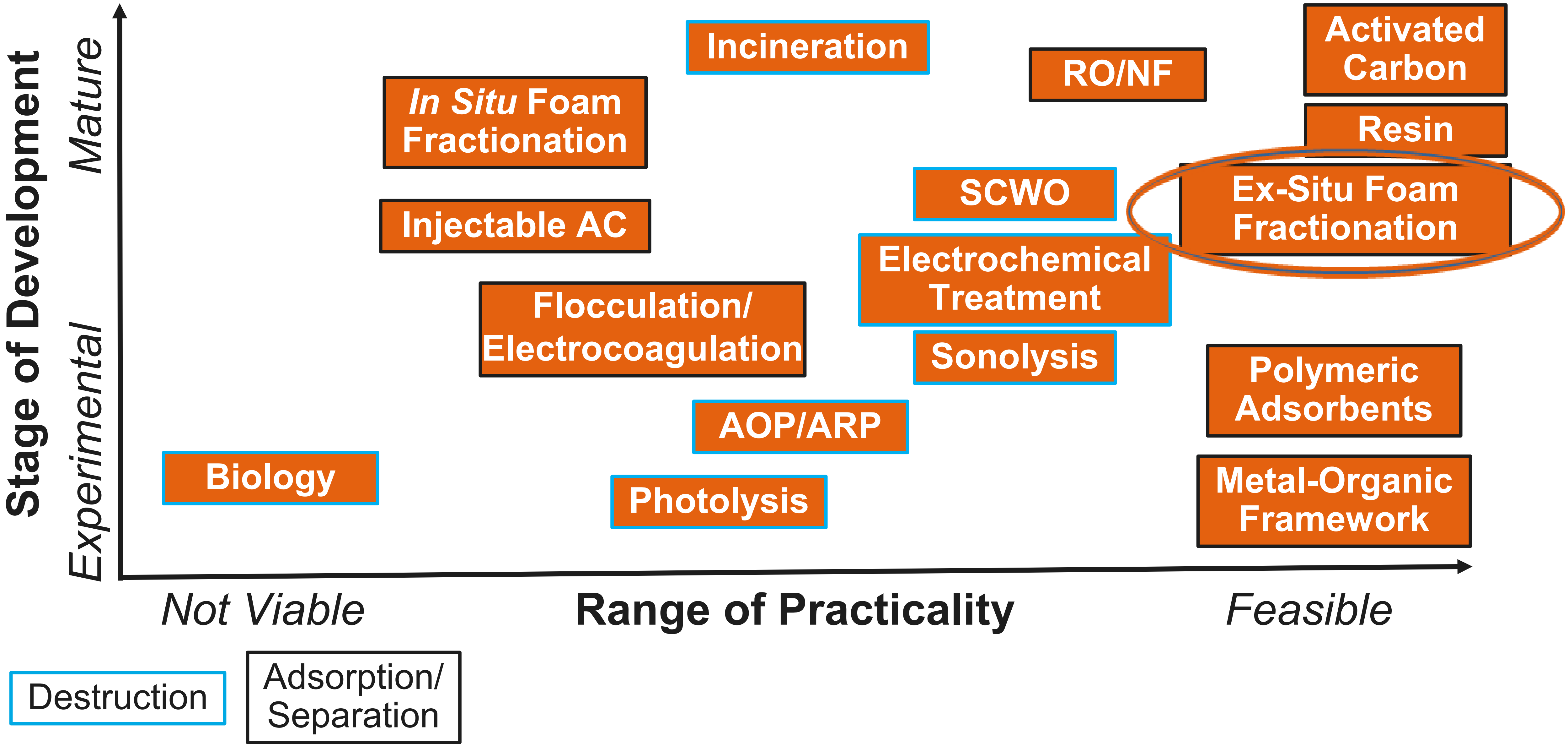
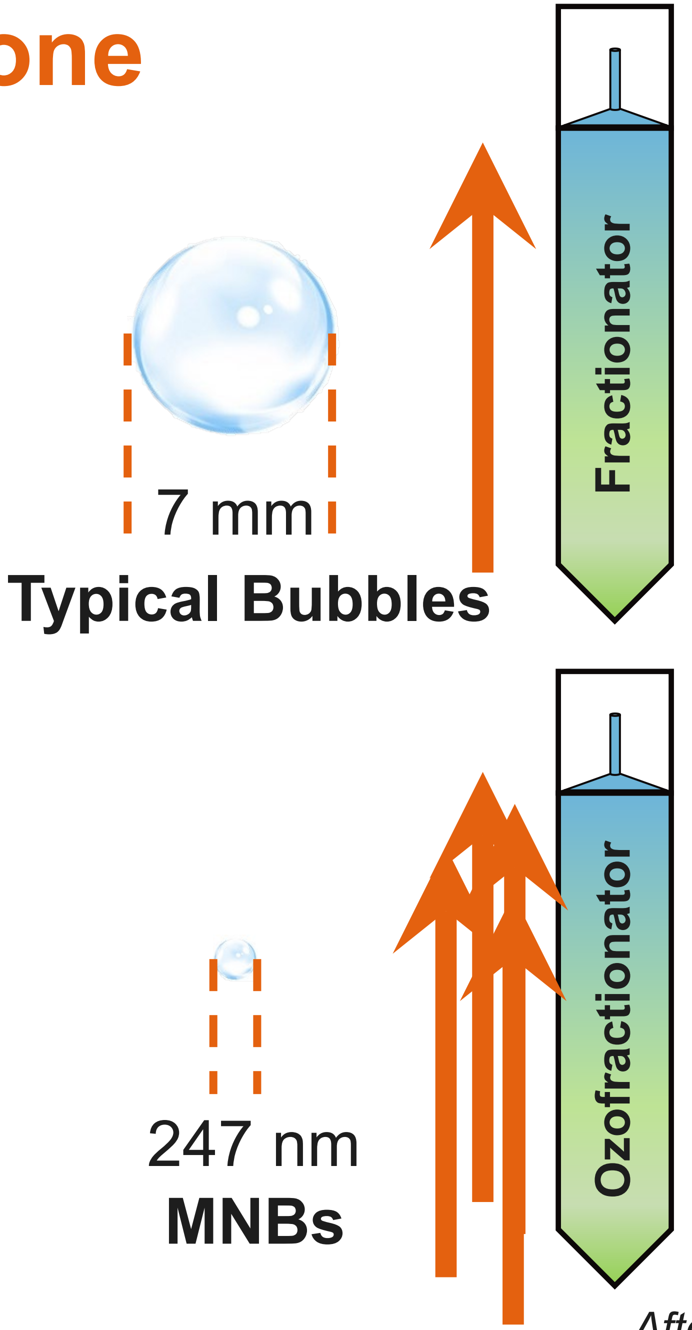
PFAS Water Treatment Technologies



Fractionation and Ozone

ARCADIS

- Fractionation uses bubbles to separate PFAS from the aqueous solution
- Ozone can create micro-nano-bubbles (MNBs) ranging from 10s nm to 10s µm
- MNBs increase bubble quantity and **available surface area** for treatment
- Ozone bubbles may have a high zeta potential which lessens bubble coalescence and **improves stability**



2.1×10^6 bubbles/100 gal

3,400 ft^2/100 gal

>28,000,000% surface area increase, less incidence of coalescence; more stability

4.8×10^{22} bubbles/100 gal

9.9×10^8 ft^2/100 gal

After Hu and Xia 2018

Ozone Fractionation Process - OCRA

- Patented process by Evocra, Australia
- Uses ozone bubbles in a multiphase process to extract PFAS
- Reagent can be added to increase efficiency of process
- PFAS removed is collected as a concentrate "foam"
- Volume of foam target is less than 1% of the raw influent (will vary depending upon initial water quality)
- Potential for significant cost savings in disposal volumes
- Additional foam reduction via subsequent processing

Target Structural Collapsing Foam – Optimized Fractionate Flow

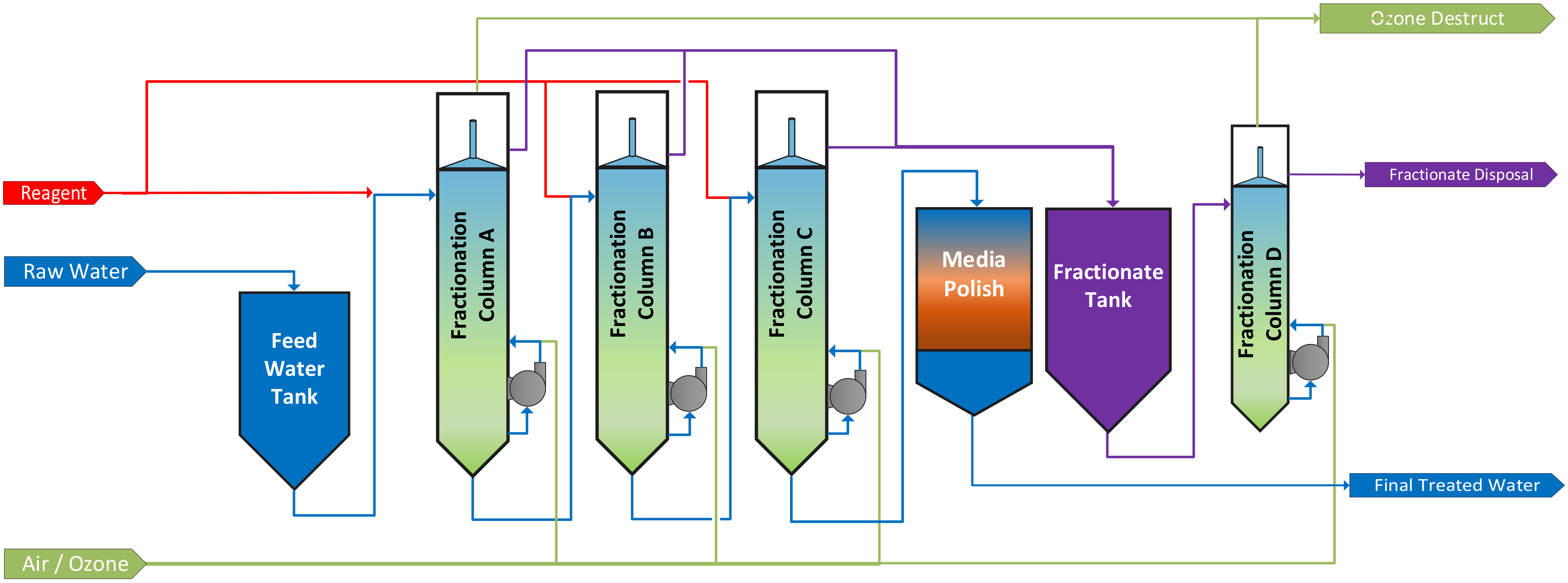
Fractionation and Ozone

ARCADIS

- Addressing ozone concern of creating ultra-short chain PFAS
- Optimized concentrations through rigorous testing and trials
- Lower risk of ultra-short chain PFAS
- Maximize waste removal effectiveness with lower volumes
- Zero-waste outcome possible with destruction technologies for foam

“Ozonated air fractionation showed the best PFAS removal efficiency, which was more than 95%, as a result of the enriched OH radicals in the gas bubbles.”
Comparative study of PFAS treatment by UV, UV/ozone, and fractionations with air and ozonated air (Dai et. al 2019)

Fractionation Process



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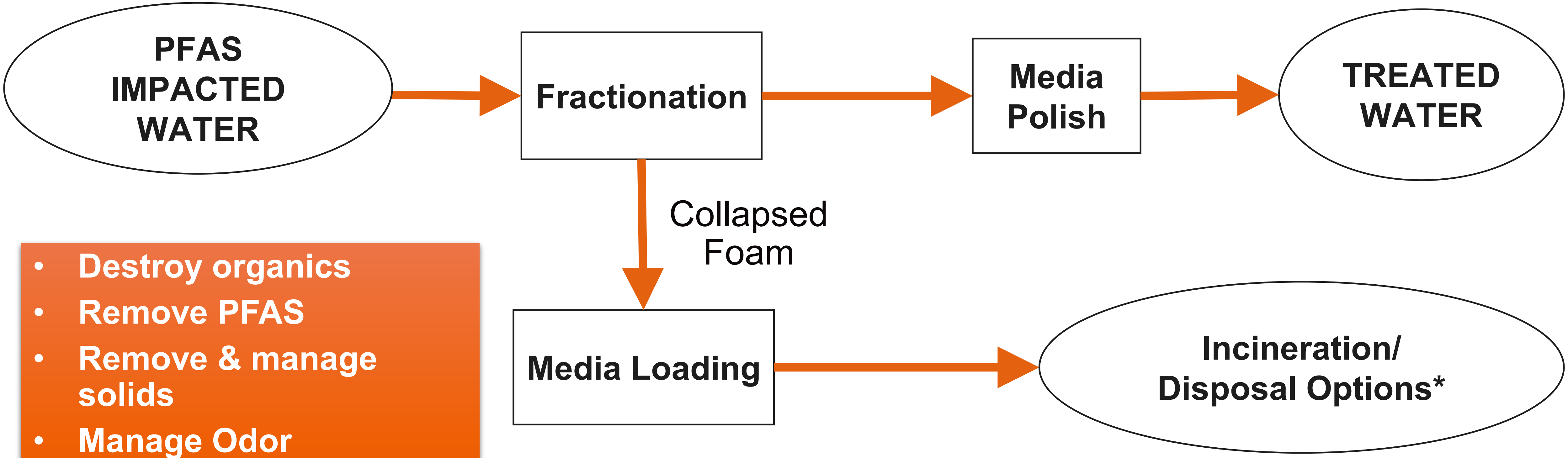
Example of PFAS Treatment Train



- Destroy organics
- Remove PFAS
- Remove & manage solids
- Manage Odor
- Extend Media Polish Performance
- Reduce Waste Disposal Volumes and Cost

*Other Alternatives i.e. Super Critical Water Oxidation

Demonstration Field Pilot Case Study (Australia 2017)

- **>4 Million Gallons-** Sewage, Trade waste, Brackish Creek Water, Chemical Flush Fluids, and Stormwater
- **Emergency Response –** full-scale onsite in three weeks
- FF Foam Concentrate – Precursors, 5,000 µg/L PFAS
- Multiple Contaminants (1,500 mg/L COD)
- Small Footprint
- Treatment Objective: 0.25 µg/L sum of PFASs measured by TOP assay
- Fractionation with Ozone and Media Polish achieved 99.96% PFAS removal as measured by TOP

Demonstration Field Pilot Case Study (Australia 2017)

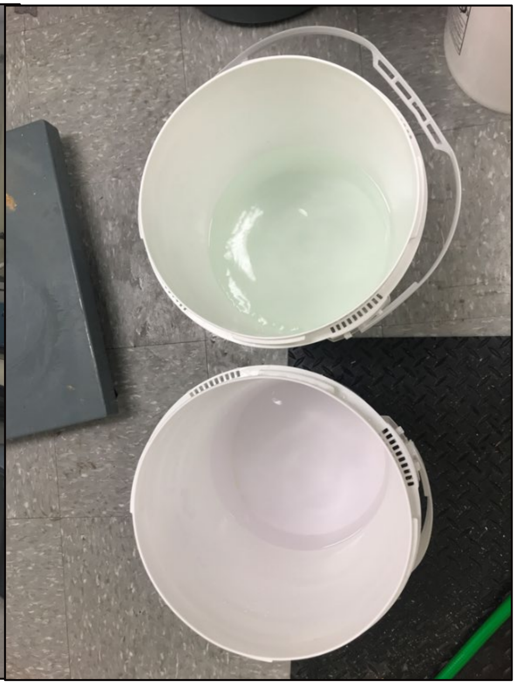
Photo Source: Evocra 2017

Current Bench-Scale Work

ARCADIS

- Arcadis Treatability Lab, North Carolina, US
  - Performing fractionation bench-scale studies for over a year now
- Providing proof of concept of various waste streams
  - Wastewater, Leachate, AFFF Impacted Streams
- Removal has shown removal of PFOS>99%, PFNA>99%, PFHxS>96%

Top -Foam Concentrate
Bottom- treated Effluent



Photos courtesy of Arcadis Treatability Lab

Bench-Scale Testing Optimization

- Single column from Evocra with additional capabilities
  - Increased column diameter
  - Foam collection cup angled for easier foam collection
  - Retention tank and recirculation loop added
  - Venturi modified for optimal gas flow into system
  - Balance tube added for level control within column
  - Dosing Reagent Capabilities on Influent

Photo- (top)
Optimized Fractionate Flow

Photo (right)
Single fractionation column set-up

Bench-Scale Testing Optimization

Optimization Parameter	High Structural Foam	Low Structural (Wet) Foam	No Foam
Reactor volume adjustment	Reduce liquid volume in column	Reduce liquid volume in column	Increase liquid volume in column
Recirculation Flowrate	Reduce recirculation flowrate	Reduce recirculation flowrate	Increase the recirculation flowrate
Gas Flowrate	Reduce gas flowrate	Increase gas flowrate, increase ozone gas for smaller bubbles	Increase gas flowrate, use ozone gas for smaller bubbles
Pre-Treatment Dosing	Inorganic or organic defoaming agent to break down undesired foam structure	Add a reagent for increased foam structure	No pre-treatment dosing required

- Fractionation operation varies dramatically depending on influent water quality
- Industrial wastewater presents largest challenge to fractionation to handle additional inputs

Bench-Scale Testing
Case Study 1 – Proof of Concept

- Industrial Wastewater with AFFF trial
- 300 Minute Test (5-hour)
- 23 gallons of water treated
- Additional dosing reagent added to manage foaming of industrial wastewater source

- **PFOS – >99% Reduction**
- **<5% volume of influent foam waste**

Trial 4 Extended Residence Time, Inorganic Reagent Pre-treatment		Average Influent Concentration	Treated Water Effluent	Removal Efficiency
Parameter	Units	Result	Result	Percent
PFOS	ng/L	**310,000**	**740**	**99.7%**
PFOA	ng/L	< 11,000	**370**	NC
NEtFOSAA	ng/L	< 24,000	**2.7**	NC
NMeFOSAA	ng/L	< 39,000	<3.0	NC
PFBS	ng/L	< 2,500	**970**	NC
PFDA	ng/L	< 3,900	**3.1**	NC
PFDoA	ng/L	< 6,900	**3.2**	NC
PFHpA	ng/L	**5,900**	**2,900**	**49.1%**
PFHxS	ng/L	**38,500**	**1,500**	**96.1%**
PFHxA	ng/L	**310,000**	**47,000**	**84.8%**
PFNA	ng/L	**6,550**	**28**	**99.6%**
PFTeA	ng/L	< 3,600	**6.1**	NC
PFTriA	ng/L	< 16,000	**5.6**	NC
PFUnA	ng/L	< 14,000	**6.2**	NC

NC= not calculated

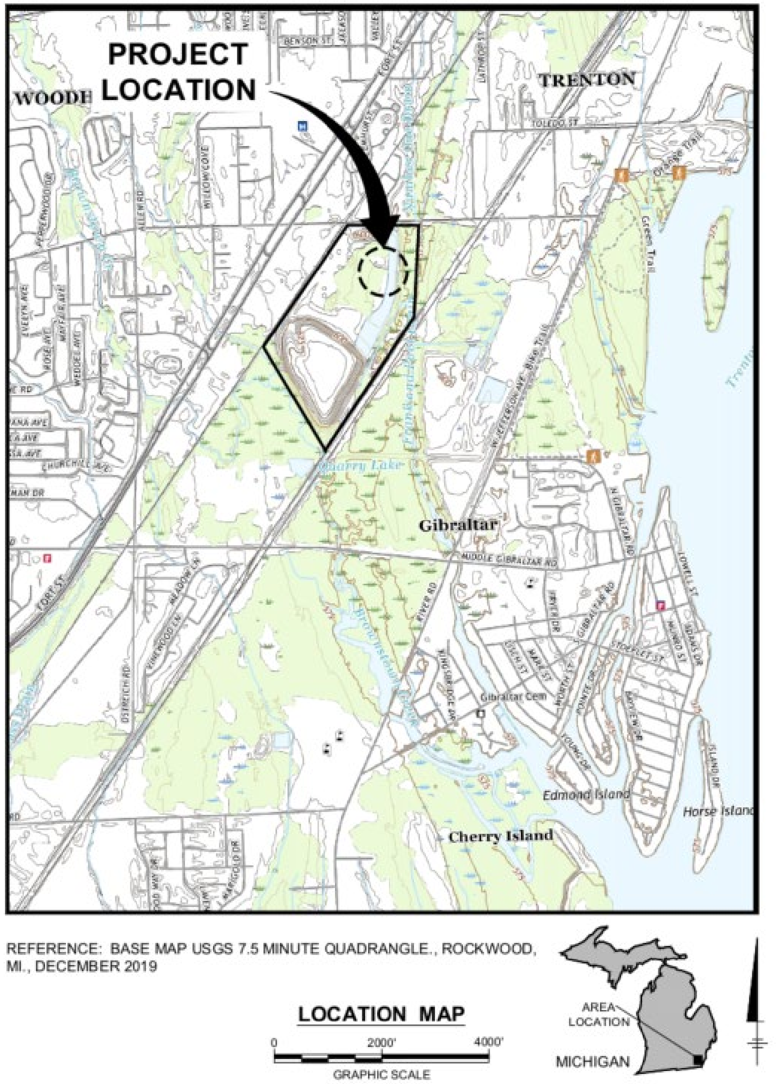
Photo- (right)
Target Structural Collapsing Foam – Optimized Fractionate Flow

Fractionation Case Study 2 – Bench to Pilot

Countywide Landfill (CWLF), Michigan

Site Location and Background

- 330-acre site
- Historically operated as steel finishing operation
  - 3 landfills
  - Leachate treatment lagoon system
- Countywide Landfill (CWLF)
  - Steel manufacturing waste (Trenton and Gibraltar McLouth Steel)
  - Construction and demolition debris
- Added to National Priorities List on March 26, 2015
- Discovered PFAS in leachate in 2018
- Leachate collection system along west and south sides of landfill (partially blocked?) – installed by USEPA Contractor in 2011
- Gravity fed to collection sump
- 2019 Arcadis hired for Feasibility Study



Site Conditions

- Current system:
  - EGLE Contract with leachate hauler
  - Off-site treatment and disposal
  - 10,000-20,000 gallons/day
  - $0.15 per gallon, subject to increase
  - ~$700,000 annual cost
- Electrical power not accessible near sump
- Targets for surface water discharge (rule 57)
  - 11 ppt PFOS
  - 420 ppt PFOA
  - 3.2 mg/L winter, 1.2 mg/L summer ammonia-N (FCV, Final Chronic Value)
  - Volatiles and Semi-Volatiles under Rule 57
  - Metals under Rule 57

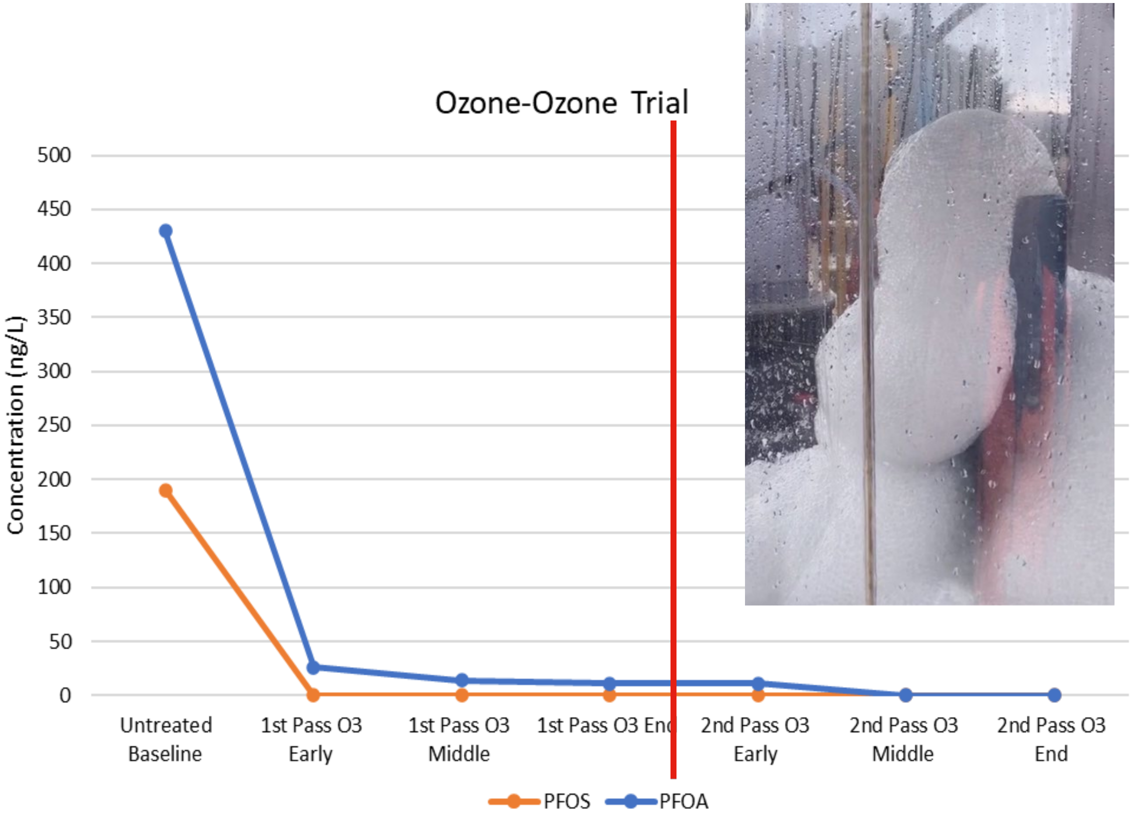
Bench-Scale Testing
Case Study 2 – Landfill Leachate

- Landfill Leachate sent to Arcadis Treatability Lab
- Influent
  - **PFOA- 430 ng/L**
  - **PFOS- 190 ng/L**
  - TOC- 74 mg/L
- Tested both Air and Ozone Treatments
- Multiple Column Passes

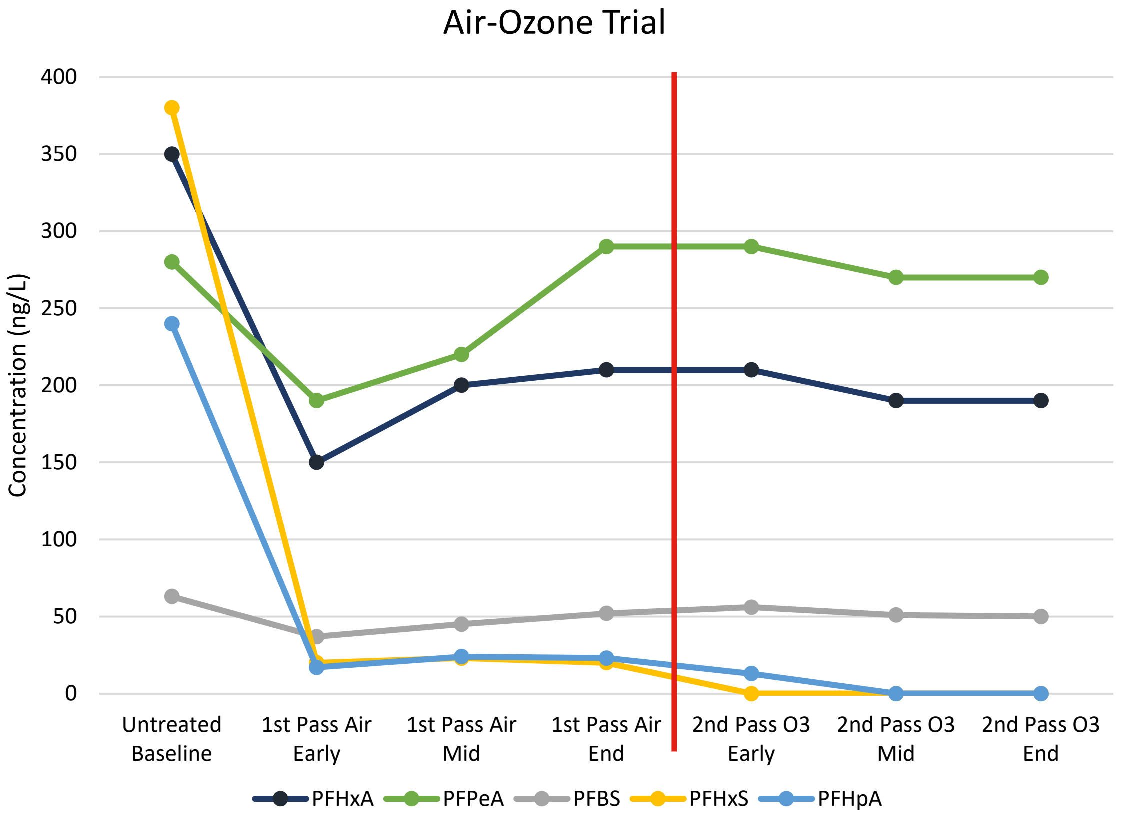
		Influent - Raw Leachate (12/2/2020)
Analyte	**Units**	**Result**
Alkalinity-Total	mg/L	490
Ammonia-N	ug/L	18,000
Chemical Oxygen Demand	mg/L	290
Chloride	mg/L	410
Fluoride	mg/L	0.61
Hexavalent Chromium, Dissolved	ug/L	<50
Nitrate/Nitrite-N	mg/L	<0.2
pH (field)	pH Units	8.7
pH (lab)	pH Units	9.5
Sulfate	mg/L	210
Total Cyanide	ug/L	<0.5
Total Dissolved Solids	mg/L	1,500
Total Organic Carbon	mg/L	74
Total Suspended Solids	mg/L	380

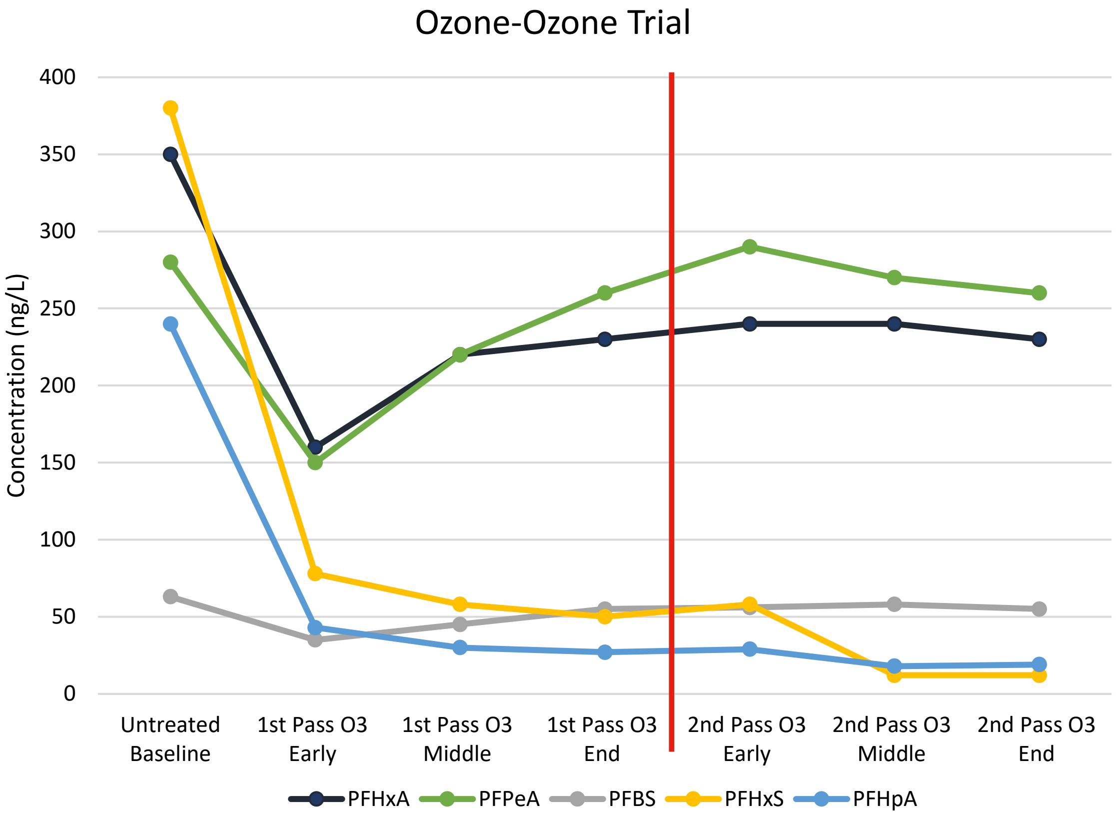
Bench-Scale Testing
Case Study 2 – Landfill Leachate

- 210 Minute Test (3.5-hour)
- >26 gallons of water treated
- 2 passes simulated to test 2 columns in series
- Both trials with air and ozone successfully treat to ND <10 ng/L PFOS and PFOA
- Ozone had a better lower foam volume of ~7% compared to air of ~25%



Bench-Scale Testing
Case Study 2 – Landfill Leachate





- Less effective on short chain PFAS <C5 (PFHxA, PFPeA, PFBS)
- More effective on longer chain PFAS >C5 (PFHxS, PFHpA)

Bench-Scale Testing
Case Study 2 – Landfill Leachate

Trial 1 & 2 (Air and Ozone)

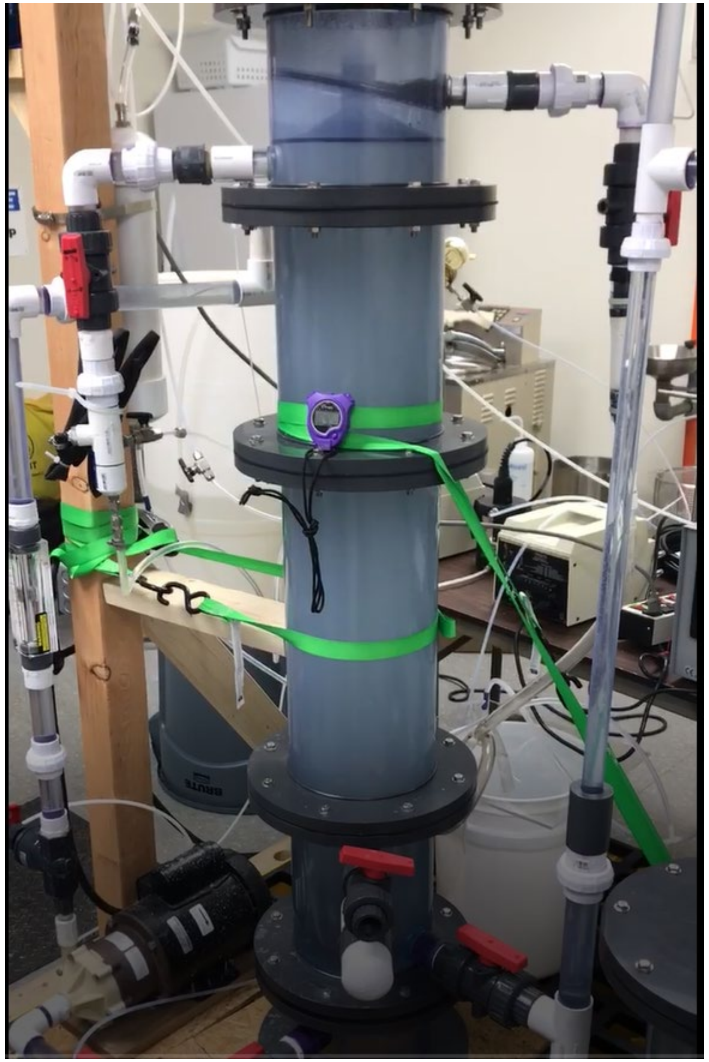
	Volume (L)	6:2 FTS (ng/L)	6:2 FTS (ng)	PFOS (ng/L)	PFOS (ng)	PFOA (ng/L)	PFOA (ng)
Raw Influent	52.1	43	2,238	190	9,890	430	22,382
First Air Pass Treated	39.4	< 10	<394	<10	<613	<10	<613
First Air Pass Foam	12.7	420	5,334	1,300	16,510	2,700	34,290
First Pass Treated- Influent to Second Pass	39.4	<10	<394	<10	<613	<10	<613
Second Pass Ozone Treated	39.5	<10	<395	<10	<400	<10	<400
Second Pass Ozone Foam	1.0	2,000	1,900	200	190	170	162

Trial 3 & 4 (Ozone and Ozone)

	Volume (L)	6:2 FTS (ng/L)	6:2 FTS (ng)	PFOS (ng/L)	PFOS (ng)	PFOA (ng/L)	PFOA (ng)
Raw Influent	57.1	43	2,455	190	10,847	430	24,549
First Ozone Pass Treated	53.4	< 9.8	<523	<10	<834	11	587
First Ozone Pass Foam	3.7	2,100	7,749	4,500	16,605	9,500	35,055
First Pass Treated- Influent to Second Pass	35.1	< 9.8	<344	<10	<834	11	386
Second Pass Ozone Pass Treated	35.0	< 9.8	<344	<10	<834	<10	<350
Second Pass Ozone Pass Foam	0.1	2,900	290	3,500	350	5,600	560

Bench-Scale Testing
Case Study 2 – Landfill Leachate

- Highlighted benefits of ozone fractionation optimization versus air only
- Volume of foam significant differentiator for price point
- There was more overall PFAS removal in the upfront ozone pass than the upfront air pass leaving less to be removed in the 2nd pass
- The two-pass ozone also appears to have removed more total PFAS mass



Pilot Fractionation Testing – December 2021

- System contains 3 main fractionation columns (OCRA A, B, C), but only 2 operated for this test
- Column D is concentrating column for further waste reduction (OSCAR)
- Media polish - Purolite PFA694 resin
- Reactivated GAC (TS8X30CPR) was added later during the test in front of the resin
  - removal of milky coloration from effluent
- Pre-treatment upstream: breakpoint chlorination during select tests
- 4 Scenarios of testing:

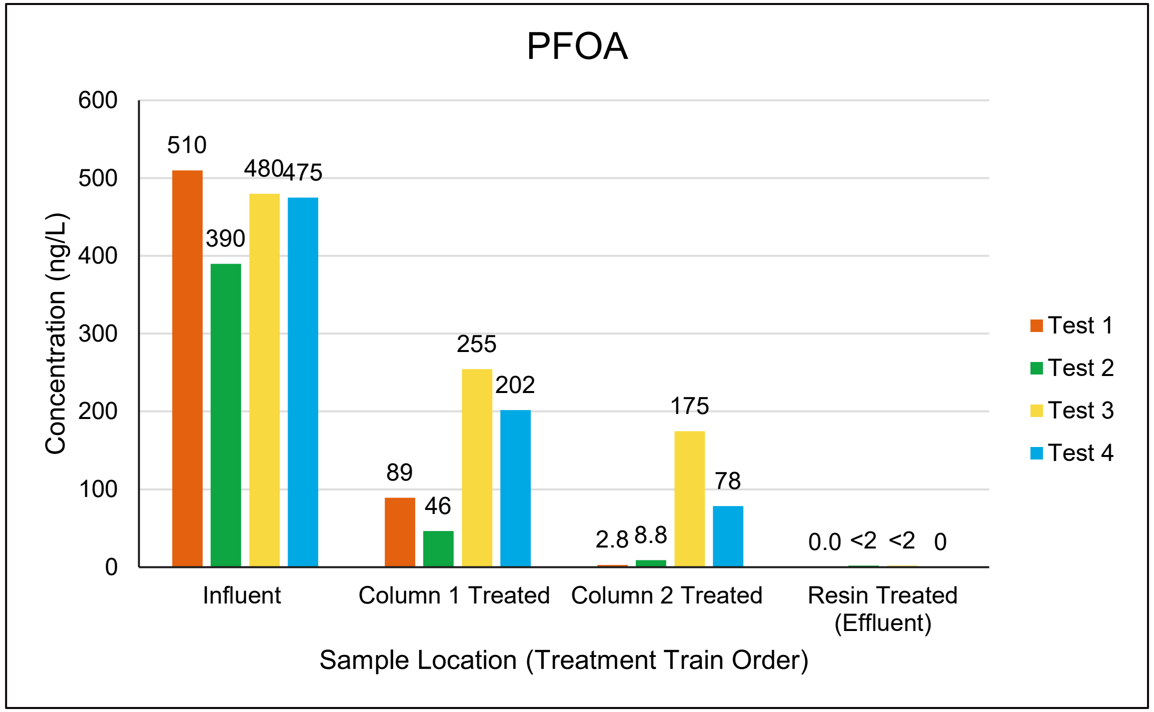
Test	Pretreatment?	OCRA Column A	OCRA Column B
1	No	Air	Ozone
2	No	Ozone	Ozone
3	Yes	Air	Ozone
4	Yes	Ozone	Ozone

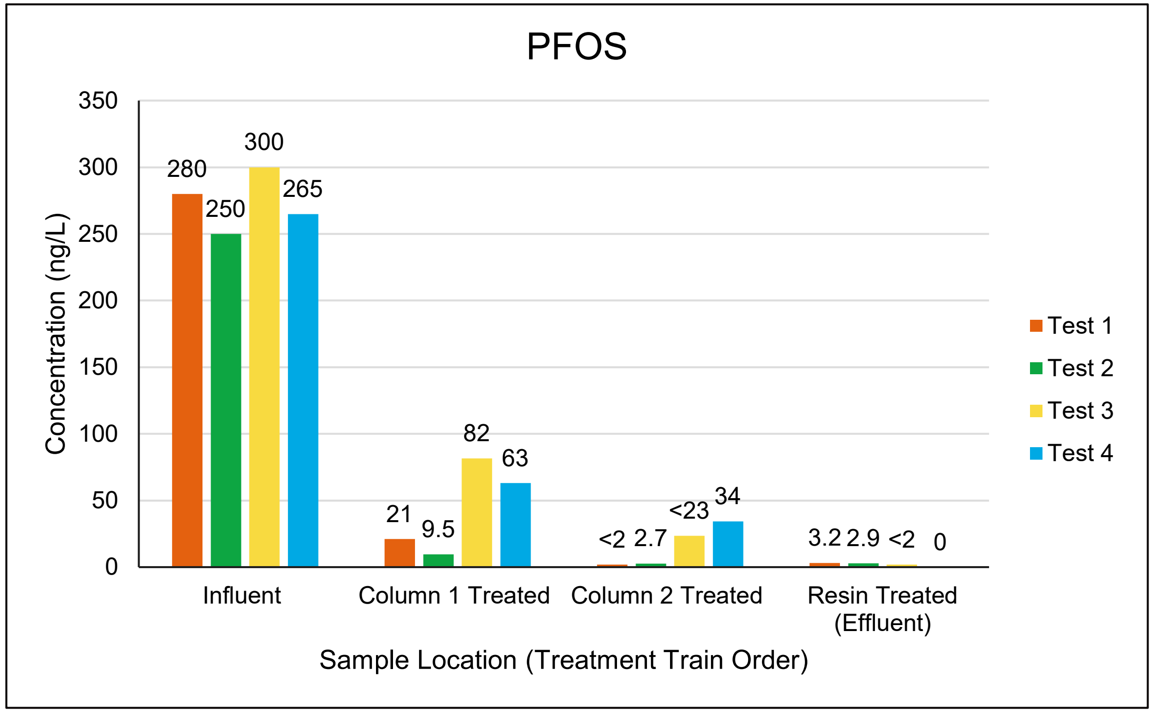
Pilot Test Volumes Summary

- Final concentrated waste to the tote ratios were <5% target range and on target for this test
  - Except Test 1
- Additional volume reduction with concentrating column evident in majority of test days
- 3% to 5% waste volume would be a conservative estimate to use as a basis for full-scale estimates using the concentrating column
- 20,000 gpd influent down to less than 1,000 gpd waste

	Average Influent Flowrate (gpm)	Gallons Treated	Influent to OCRA Waste Ratio	Influent to OSCAR Waste Ratio
Test 1 - Air -Ozone - No Pretreatment	7	1,760	12.6%	**7.8%**
	5	1,940	4.2%	**3.1%**
Test 2 - Ozone-Ozone - No Pretreatment	5	2,126	3.9%	**3.9%**
	5	1,982	4.9%	**4.9%**
	5	1,740	6.9%	**4.3%**
Test 3 - Air-Ozone - With Pretreatment	5	1,974	2.9%	**2.1%**
	8	3,236	4.4%	**4.4%**
	8	4,072	3.4%	**2.8%**
Test 4 - Ozone-Ozone - With Pretreatment	8	4,216	1.9%	**0.7%**
	8	2,432	6.9%	**3.3%**
	8	1,876	7.7%	**1.8%**

Pilot Test Results for PFOA and PFOS



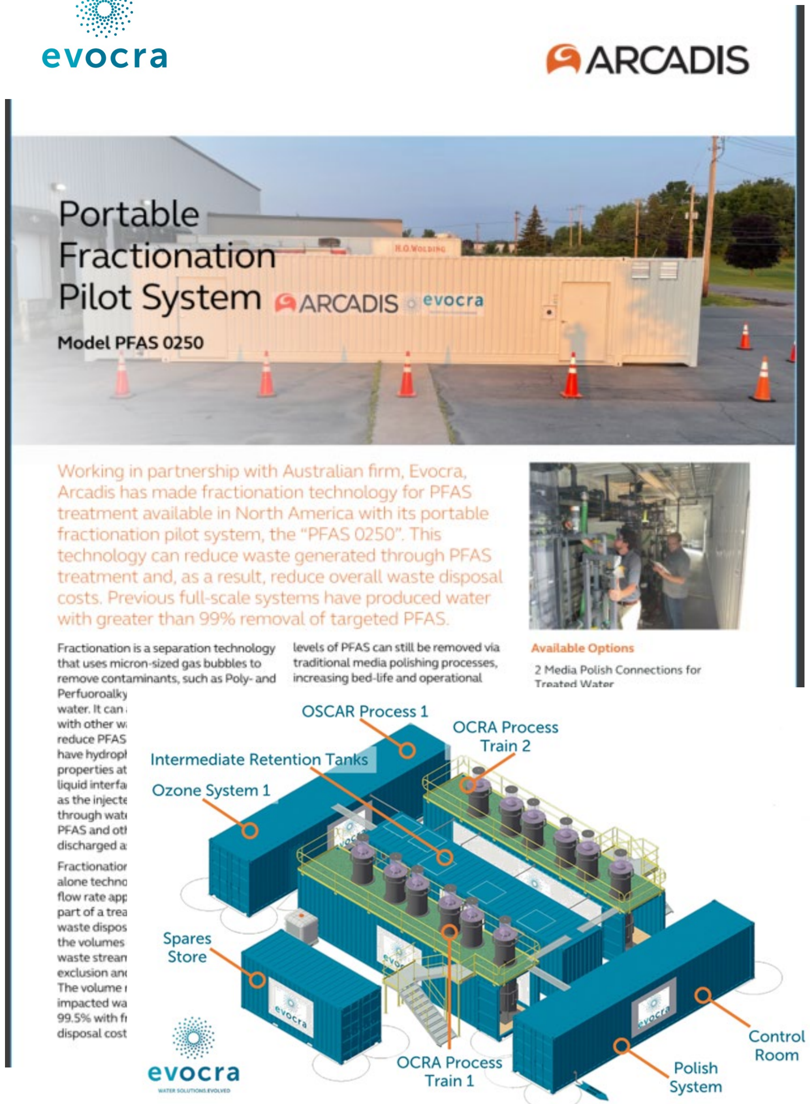


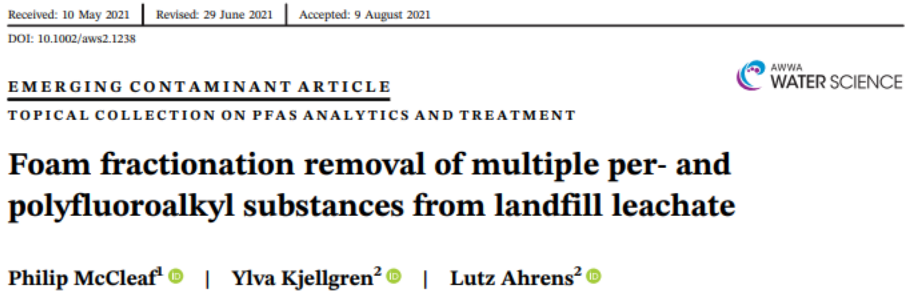
- Surface Water Targets, PFOA – 420 ng/L, PFOS – 11 ng/L
- PFOA and PFOS significantly removed through 2 fractionation columns for each test
- Resin polish significantly treated to non-detect levels post-fractionation

Fractionation More Commercially Available

ARCADIS

evocra





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AWWA WATER SCIENCE

EMERGING CONTAMINANT ARTICLE

TOPICAL COLLECTION ON PFAS ANALYTICS AND TREATMENT

Foam fractionation removal of multiple per- and polyfluoroalkyl substances from landfill leachate

Philip McCleaf[1] | Ylva Kjellgren[2] | Lutz Ahrens[2]

Water treatment

Review of foam fractionation as a water treatment technology

Thomas Buckley, Xiaoyong Xu, Victor Rudolph, Mahshid Firouzi & Pradeep Shukla

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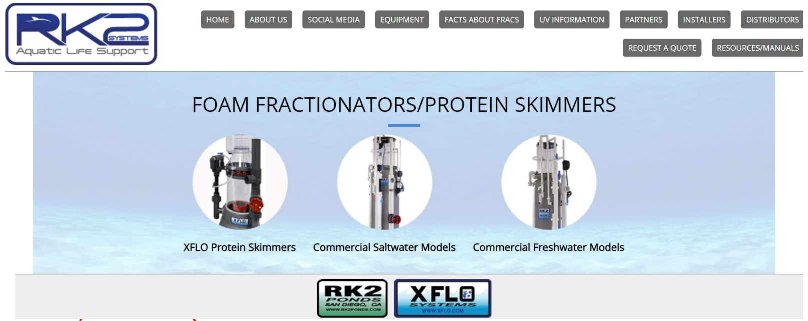

AMSD PFAS Treatment System

Anson Madison Sanitary District in Maine

- PFAS is not treated via standard wastewater secondary treatment technology
- Additional tertiary treatment is necessary
- Proposed at AMSD - Foam fractionation system followed by activated carbon

MAINE DEPARTMENT OF ENVIRONMENTAL PROTECTION www.maine.gov/dep

CONCLUSIONS

Fractionation is a viable PFAS treatment technology to be considered as part of a treatment train approach

U.S. bench scale testing has demonstrated proof-of-concept in lab scale setting with optimized operation parameters

Further optimization to maximize the fractionate-to-treated-water ratio during field pilot applications is possible

Full-scale systems are in operation in Australia with successful PFAS treatment results

Commercialization is becoming available in the U.S. and full scale systems are in progress

Thank You!

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- Michigan EGLE
- Water Tectonics
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PFAS in Perspective

for a closer look at how different stakeholders are approaching PFAS.

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