

AFFF Source Area Groundwater PFAS Treatment with Foam Fractionation Bench and Pilot Scale Demonstration

Wednesday June 5, 2024, Battelle Chlorinated Conference

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Roadmap

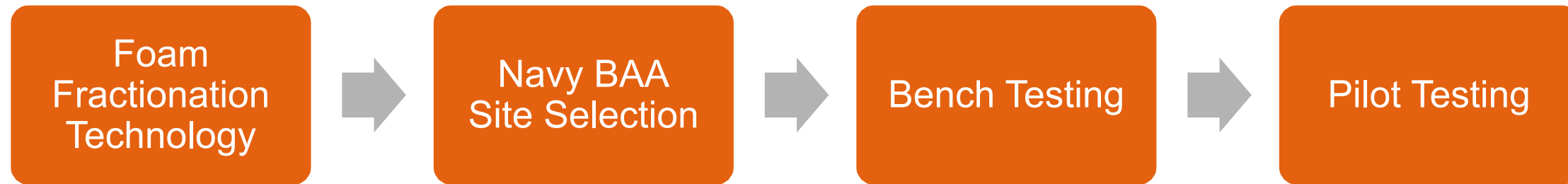


Photo Source: Evocra 2020



Photo Source: Arcadis 2022

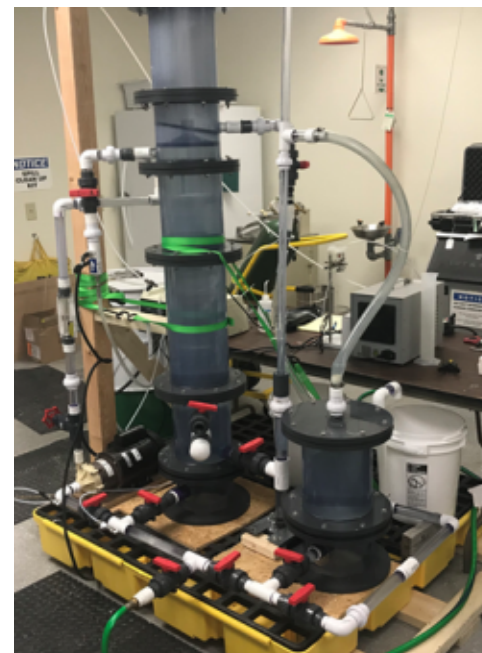


Photo Source: Arcadis Treatability Lab 2023



Photo Source: Arcadis 2023

Navy EXWC BAA Site Selection

Navy EXWC BAA

- Broad Agency Announcement (BAA) For Innovative Environmental Technologies and Methodologies Solicitation Number N3943021S2201 (2021)
- Need Topic NO. 4: Technologies and Methodologies Addressing Emerging Contaminants



Navy BAA Target Objectives



Use foam fractionation with varying gasses (i.e., air and air/ozone) to optimize the removal of PFAS from groundwater extracted from an AFFF-impacted source zone



Demonstration of the removal efficiency of PFAS from groundwater, with greater than 90% removal originally anticipated



Target the volume of foam fractionate waste to be less than 1% of the raw influent



Potential variation from target objective values due to water quality would be documented during demonstration

Site Selection Process

- Evaluated several Navy sites for the demonstration
- Site to remain un-named at request of client
- Existing groundwater extraction and treatment system on site (GAC/Resin)
- Total PFAS Concentrations >90 ppb targeted
- No restricted access / clearance needed
- No active base operations



- ☒ **DRAFT report submitted to EXWC on 5/1/2024**
- ☒ **FINAL report to be issued Summer 2024**

Bench Test

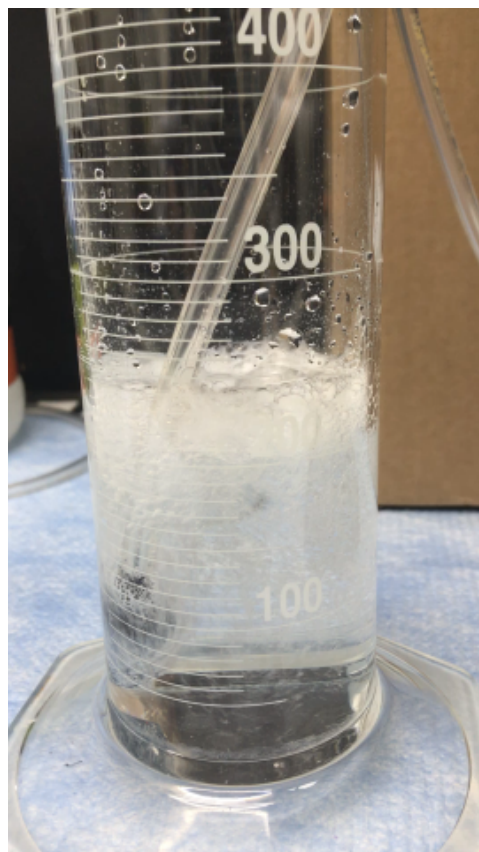
March 2023

DRAFT Results

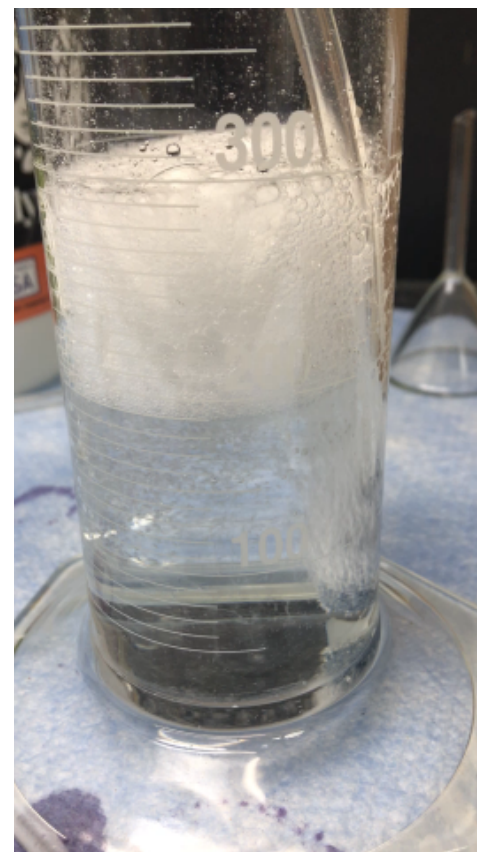
Grad Cylinder Screening – 45% Acetic Acid (Vinegar) Solution



Native pH 8.2



pH 4.0 – Acetic Acid

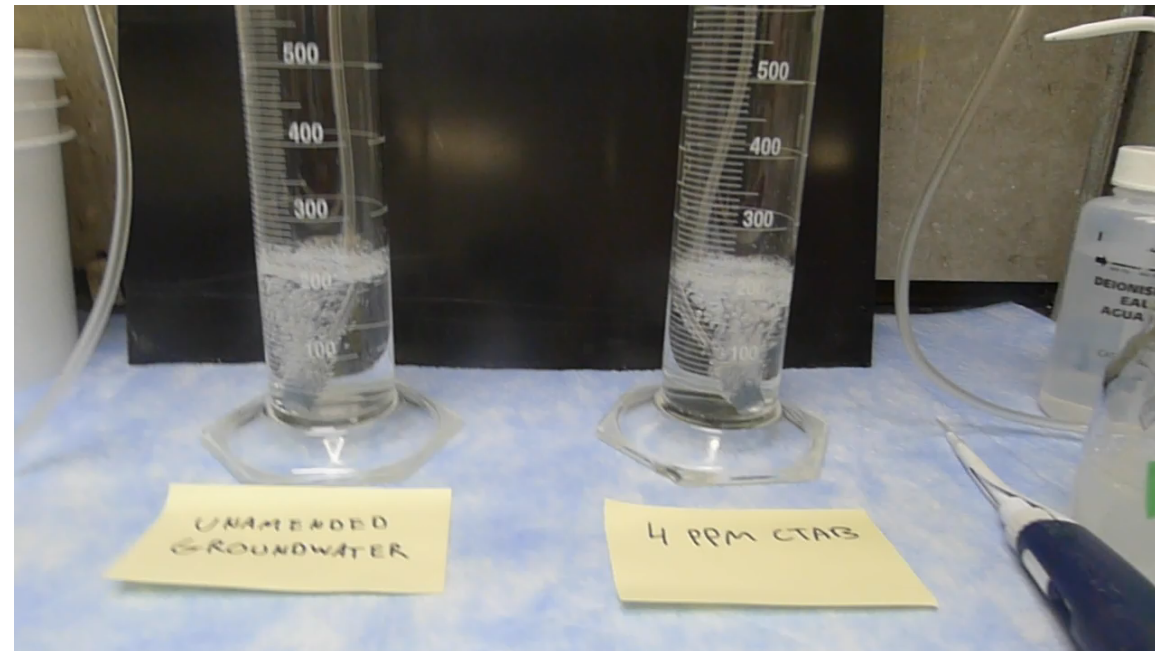


pH 3 – Acetic Acid

Cetyltrimethylammonium bromide (CTAB) Screening



Untreated GW (left), CTAB 1 ppm (right)



Untreated GW (left), CTAB 4 ppm (right)

- CTAB- ~\$150 per kg (Spectrum Chemical 2024)
- **Acetic Acid ~\$0.44 per kg (Acetic Acid price index 2024)**

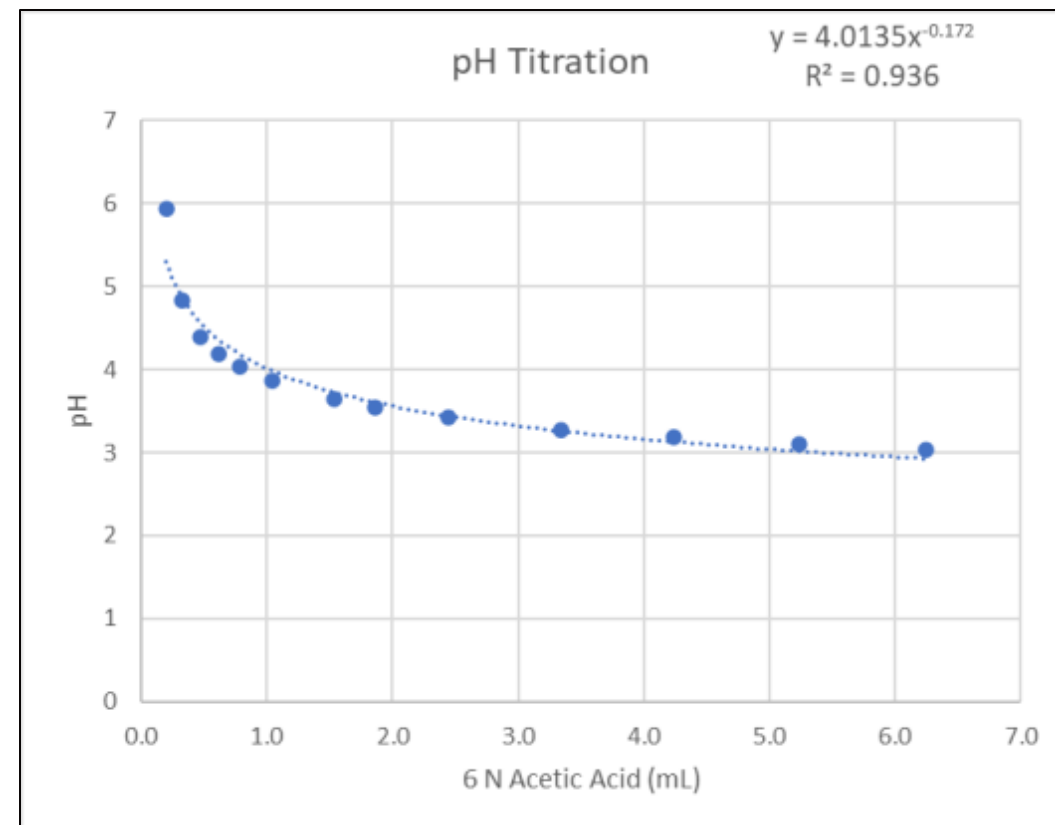
Other Reagents and Co-surfactants Considered

Publication	Applied Co-surfactant	Surfactant Type
McCleaf et al. (2023)	MONTALINE™ C 40 (Cocamidopropyl Betainamide MEA Chloride)	cationic (L)
Vo et al. (2023), Buckley et al. (2023), Li et al. (2021)	Cetyltrimethylammonium bromide (CTAB)	cationic (L)
Li et al. (2021)	Dodecyl-trimethyl-ammonium bromide (DTAB)	cationic (L)
Li et al. (2021)	Tetra-n-butyl-ammonium bromide (TBAB)	cationic (B)
Li et al. (2021)	N-octyl-trimethyl-ammonium bromide (OTAB)	cationic (L)
McCleaf et al. (2023)	Marlinat™ 242/28 (Sodium Laureth Sulfate)	anionic (L)
McCleaf et al. (2023)	Linear alkylbenzene sulfonate (LAS)	anionic (L)
Vo et al. (2023), Buckley et al. (2023), Buckley et al. (2022), Li et al. (2021)	Sodium dodecyl sulfate (SDS)	anionic (L)
McCleaf et al. (2023)	SIMULSOL™ SL 10 (Alkylpolyglucoside)	non-ionic (L)
Meng et al. (2018)	N-Octyl-β-D-glycopyranoside	non-ionic (L)
Vo et al. (2023), Buckley et al. (2023)	Triton X-100	non-ionic (L)
Vo et al. (2023), Buckley et al. (2023)	N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (SB3-12)	zwitterionic (L)
Smith et al. (2023)	Neutral Hand Dishwash	mixture of anionic, zwitterionic, and non-ionic

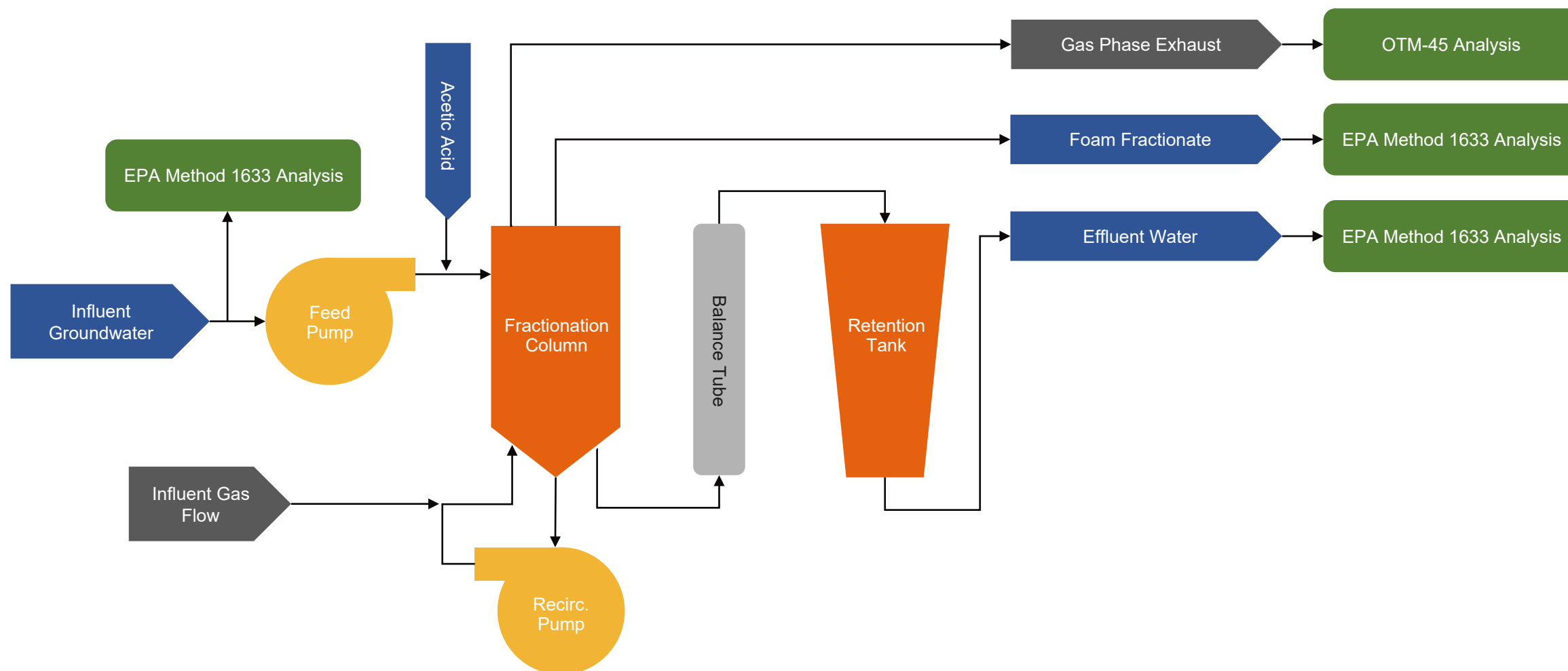
Consider cost, availability, toxicity, and effectiveness

Acetic Acid Dosing

- Determined acetic acid dosing would be tested to promote foaming
- Titration curves performed
- Target pH 3.5 as an economic compromise
- 25% Acetic Acid Solution for Column Testing
- Dosing rates: 3.6 to 8 mL/min

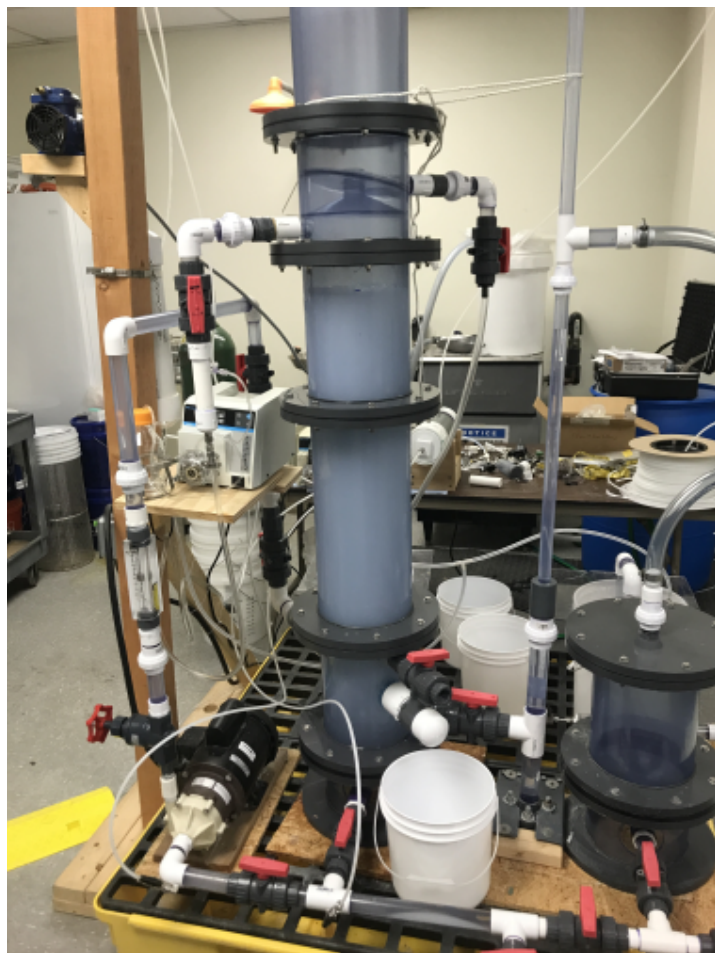


Bench Test Process

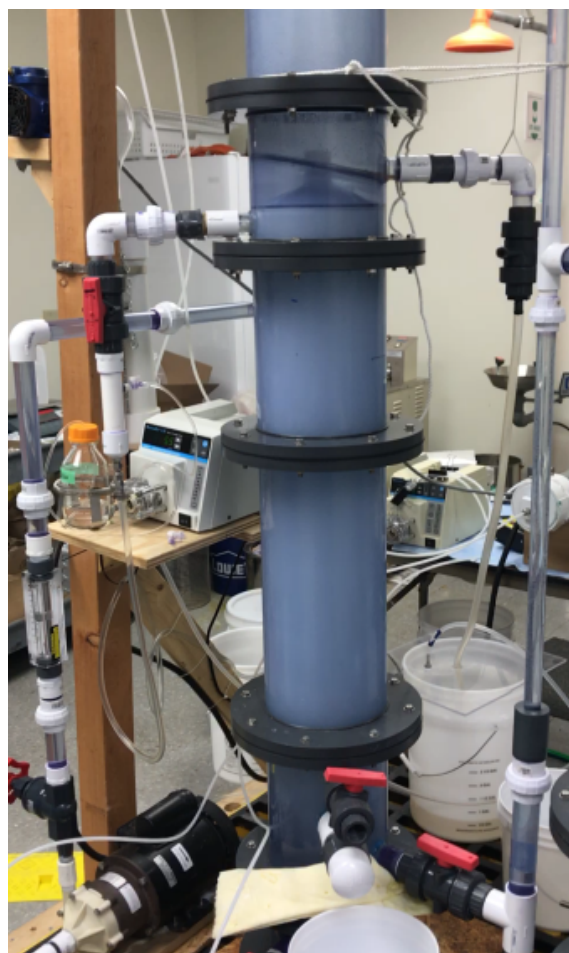


System Operation

Priming Column
with Groundwater



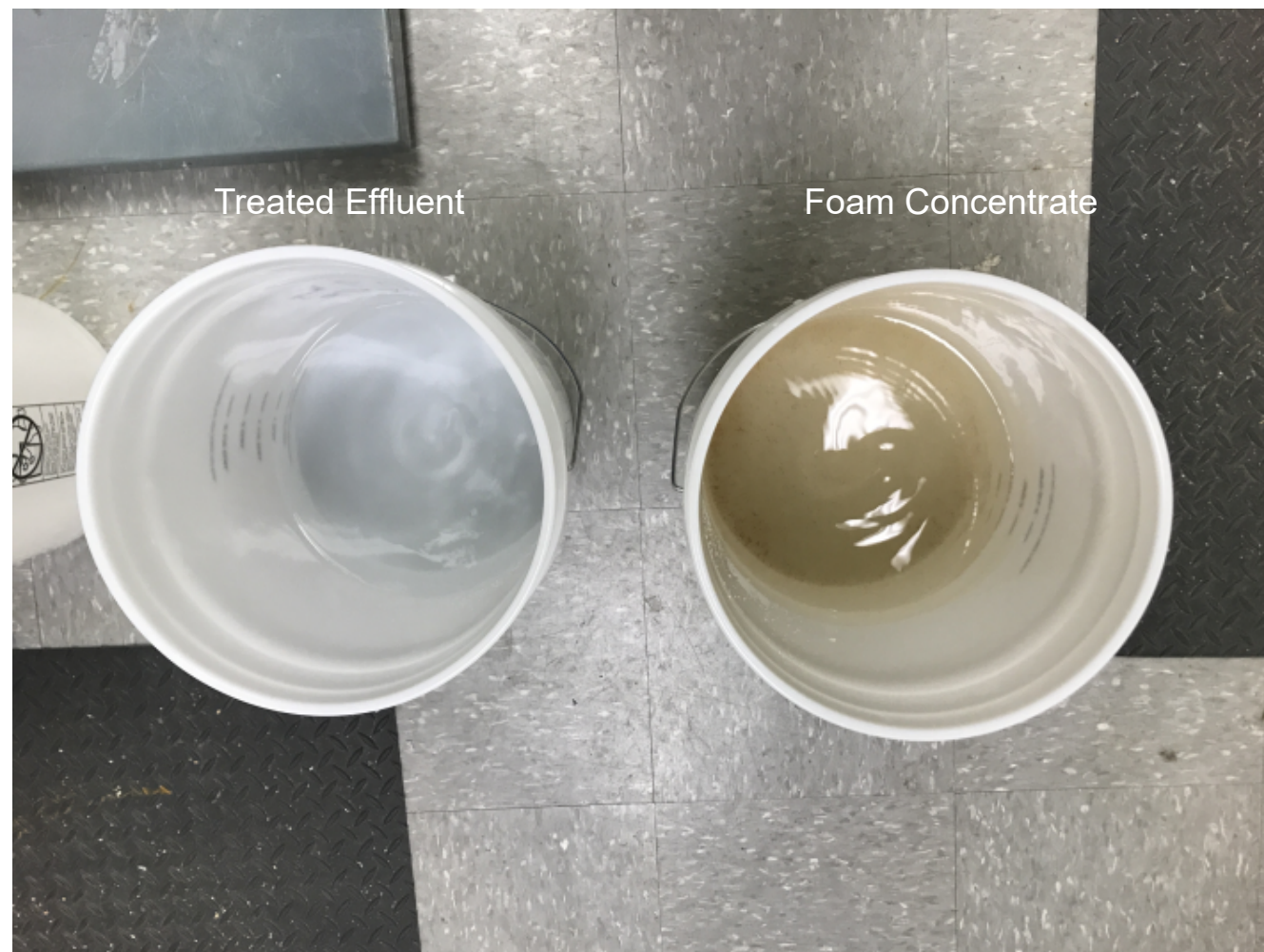
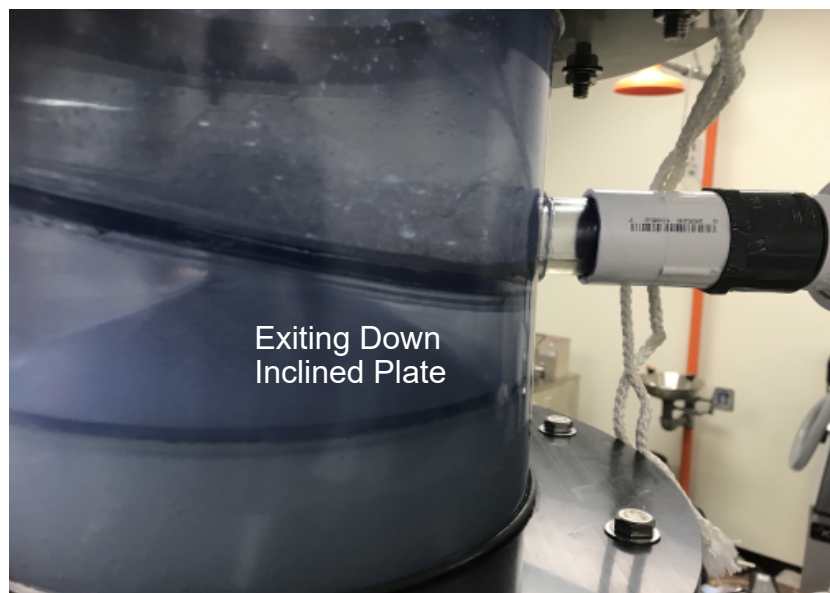
Full Column During
“Air Test” Trial



Acetic Acid
Feed System



Foam Production



Sample Collection



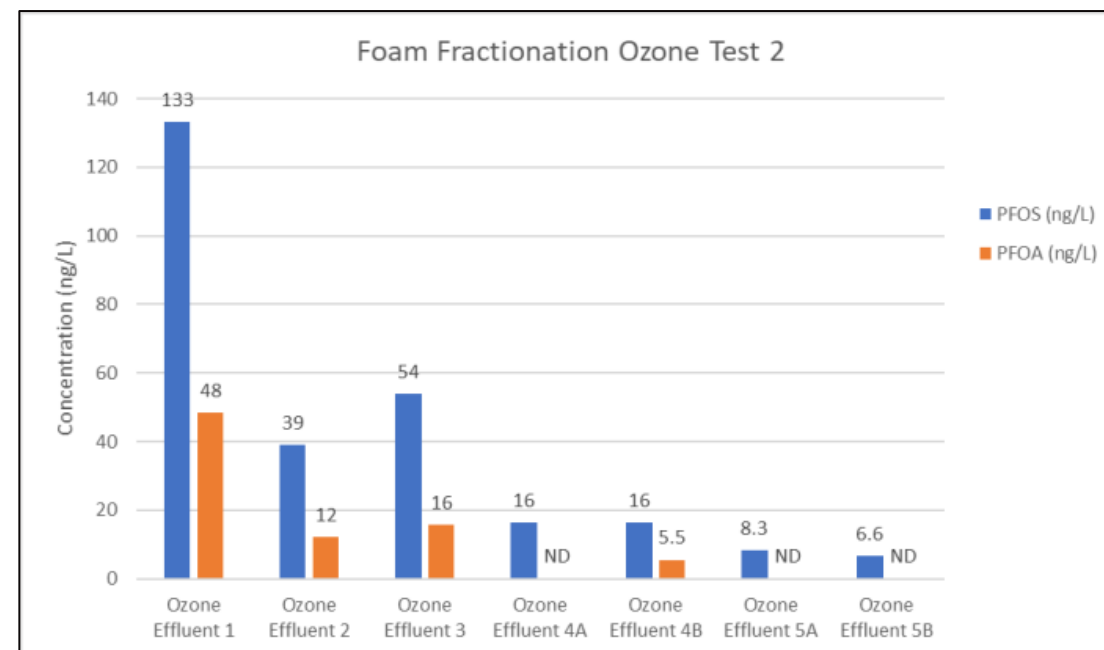
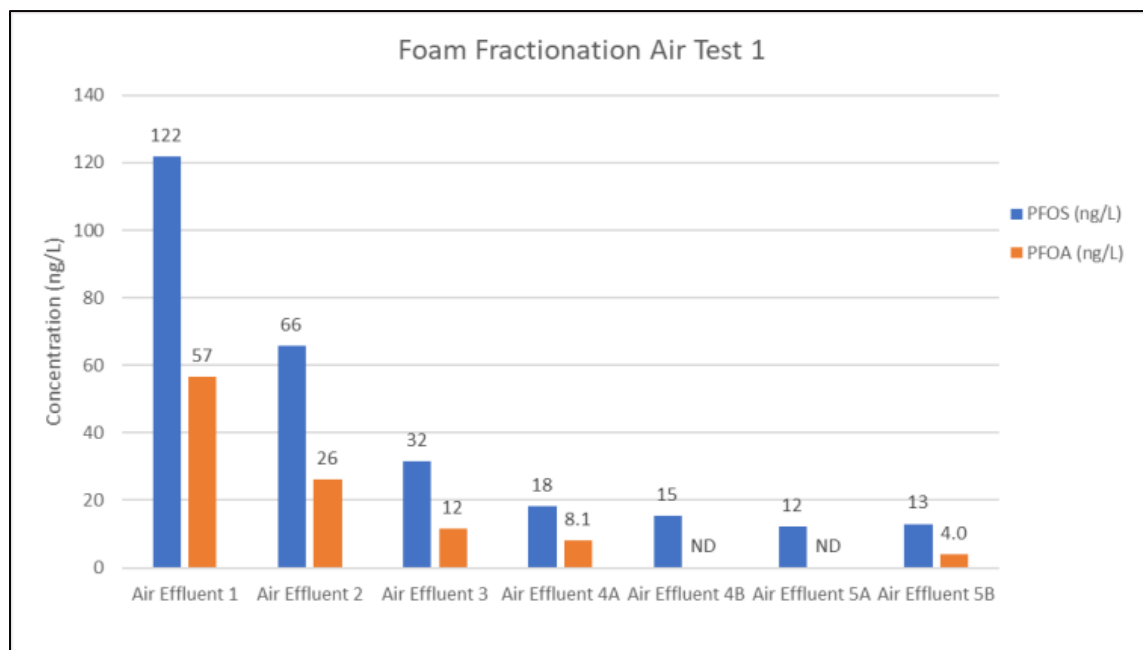
Collecting Treated Effluent Sample



All PFAS Samples (Method 1633, TOP Assay, AOF) Prior to Shipment to SGS Axys

Bench Results

- PFOS Average Influent: 48,340 ng/L
- PFOA Average Influent: 2,562 ng/L



All samples are at a 50-minute HRT taken during steady state operation continuous flow through.

Bench Results

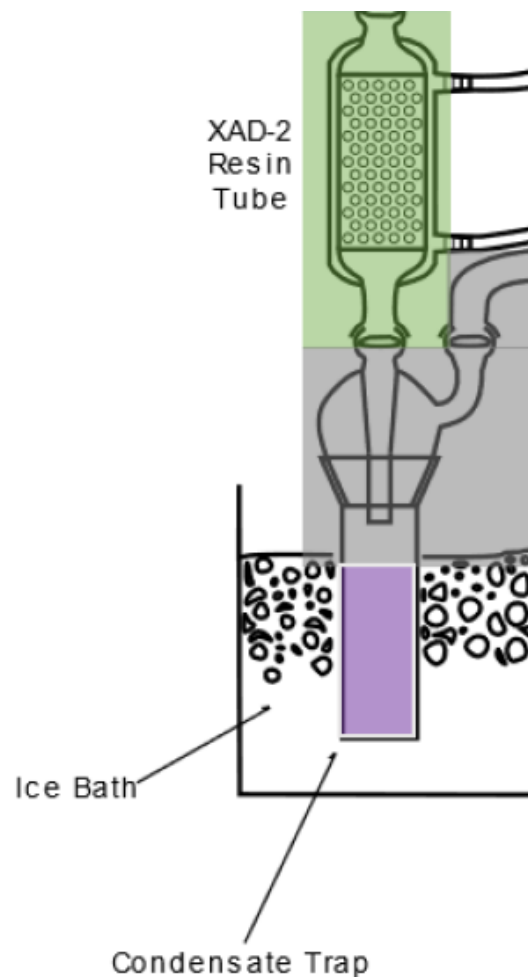
PFAS: SGS Axys MLA-110 (Method 1633)	Air % Removal	Ozone % Removal
PFBA	61%	65%
PFPeA	65%	72%
PFHxA	76%	92%
PFHpA	98%	99.0%
PFOA	99.88%	99.89%
PFBS	67%	81%
PFPeS	92%	98%
PFHxS	99.5%	99.7%
PFHpS	99.7%	99.7%
PFOS	99.97%	99.98%
6:2 FTS	99.7%	95%
PFOSA	98.5%	98%
Total detected:	97.4%	98.2%

- Only detected PFAS shown
- Air Column Test vs. Ozone Column Test
 - Same feed rate, operating volume, HRT for each test
- PFOA and PFOS had high 99.9% removal with both gasses
- PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS had higher percent removal with ozone compared to air

Bench TOP Assay Results

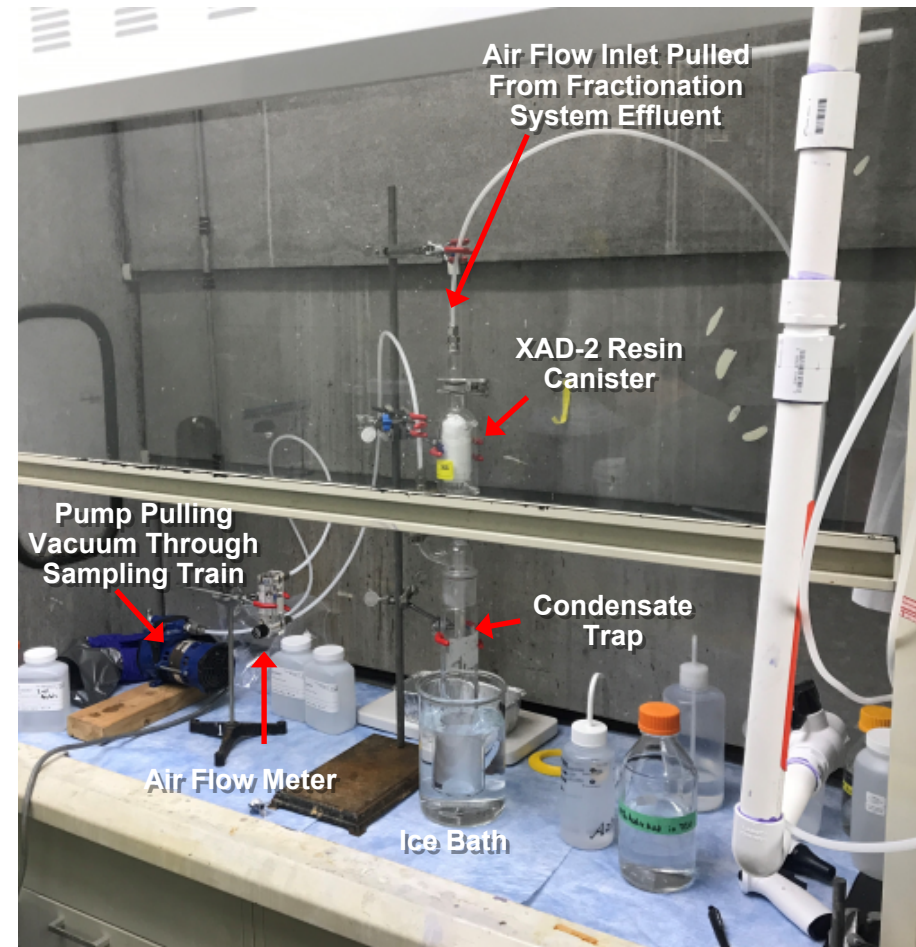
PFAS: SGS MLA-111 (ng/L)	Influent PRE-TOP (ng/L)	Influent POST-TOP (ng/L)	Air Treated Effluent POST-TOP (ng/L)	Air % Removal (POST-TOP)	Ozone Treated Effluent Post TOP (ng/L)	Ozone % Removal (POST-TOP)
PFBA	715	18,300	6,940	62%	1330	93%
PFPeA	1155	14,350	1,960	86%	548	96%
PFHxA	2,287	23,000	2,140	91%	314	98.6%
PFHpA	458	<4,570	33	99.3%	<9.68	99.8%
PFOA	2,747	4,935	15	99.7%	<9.68	99.8%
PFBS	1,387	<4,570	1,730	62%	387	92%
PFPeS	1,345	<4,595	378	92%	48.4	99%
PFHxS	7,517	9,685	127	98.7%	40.7	99.6%
PFHpS	1,017	<4,570	<9.1	99.8%	<9.68	99.8%
PFOS	49,200	65,600	85	99.9%	85.9	99.9%
6:2 FTS	4,182	<16,500	<33	99.8%	<34.9	99.8%
PFOSA	193	<4,570	<9.1	99.8%	<9.68	99.8%

Air Sampling Overview



Components of OTM-45 Train Used in Modified Method

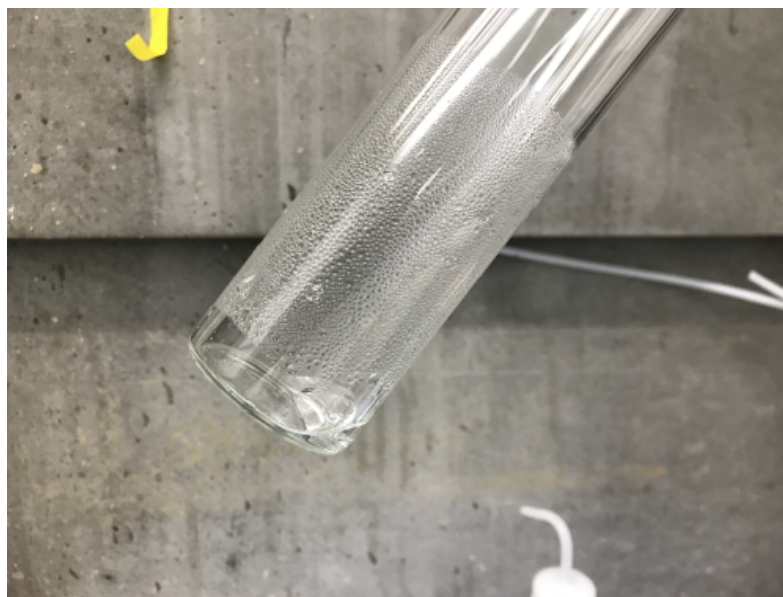
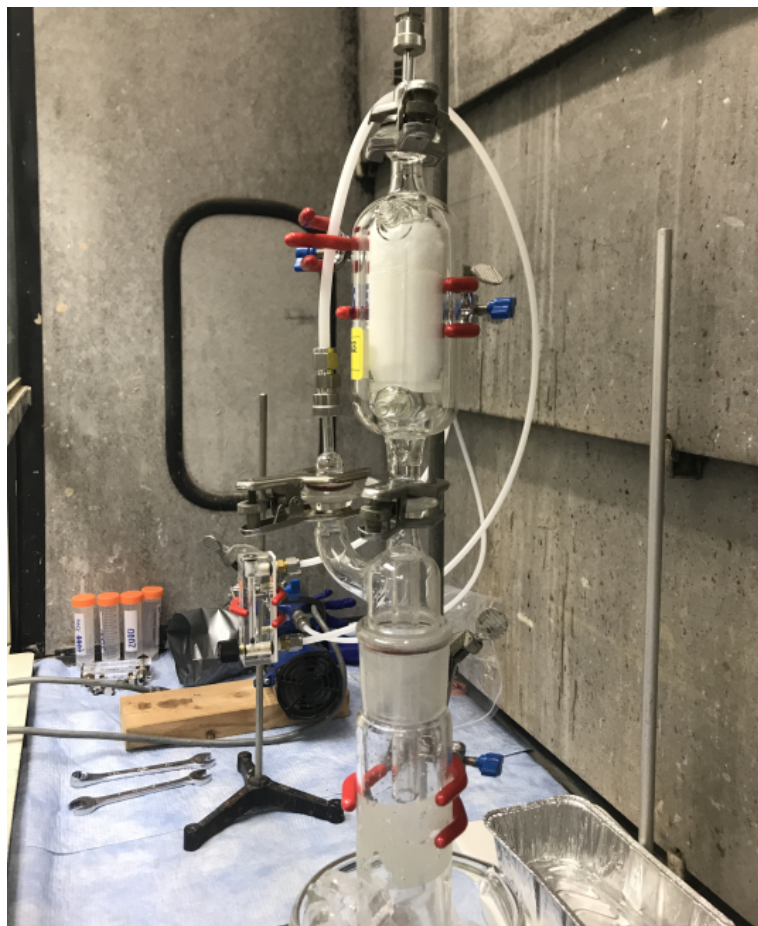
Air Sampling Train Overview During “Air Test”



“Air Test” Air Phase Sampling

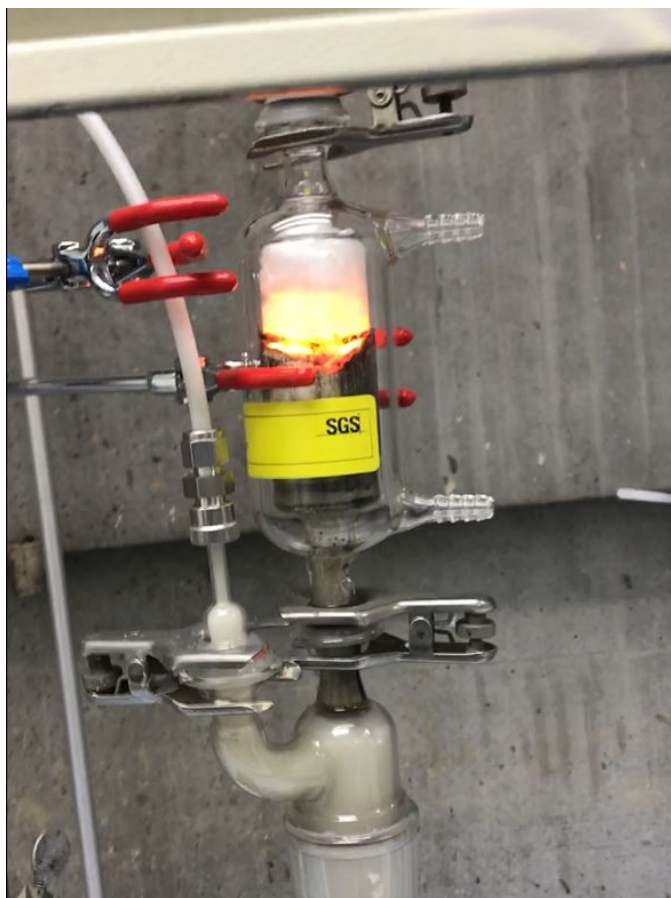
XAD-2 Canister & Impinger During “Air Test”

Small Amount of Moisture Condensation in Impinger Following “Air Test”

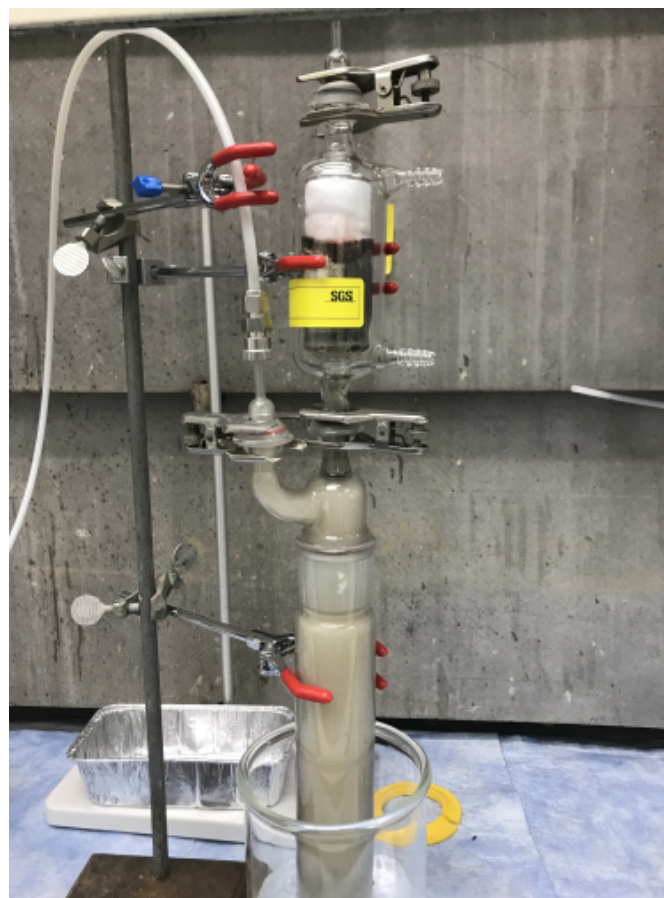


“Ozone Test” Air Phase Sampling

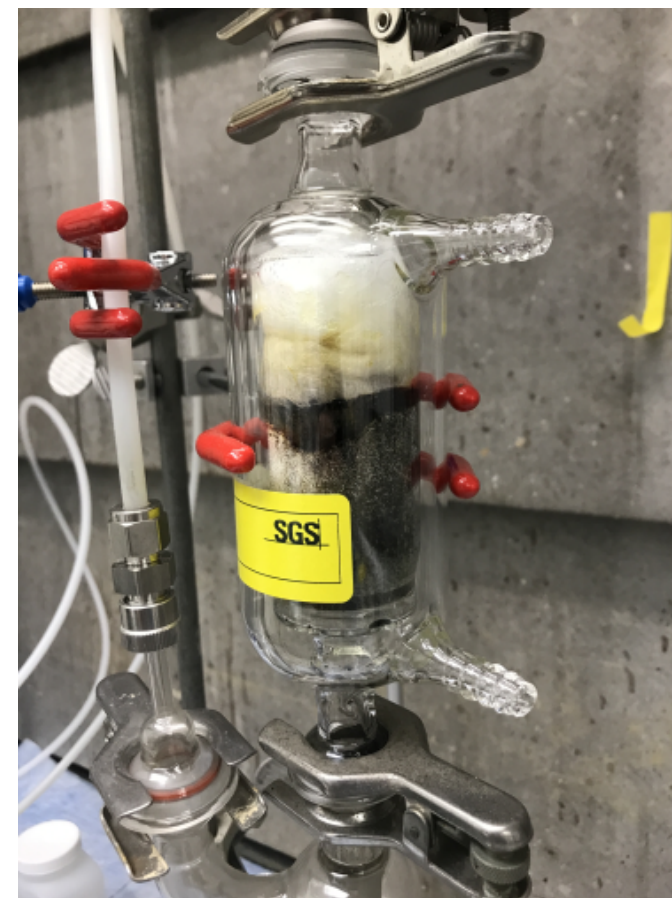
XAD-2 Ignites During
“Ozone Test”



Sampling Train Filled With Smoke/Soot
Following Cessation of Pump

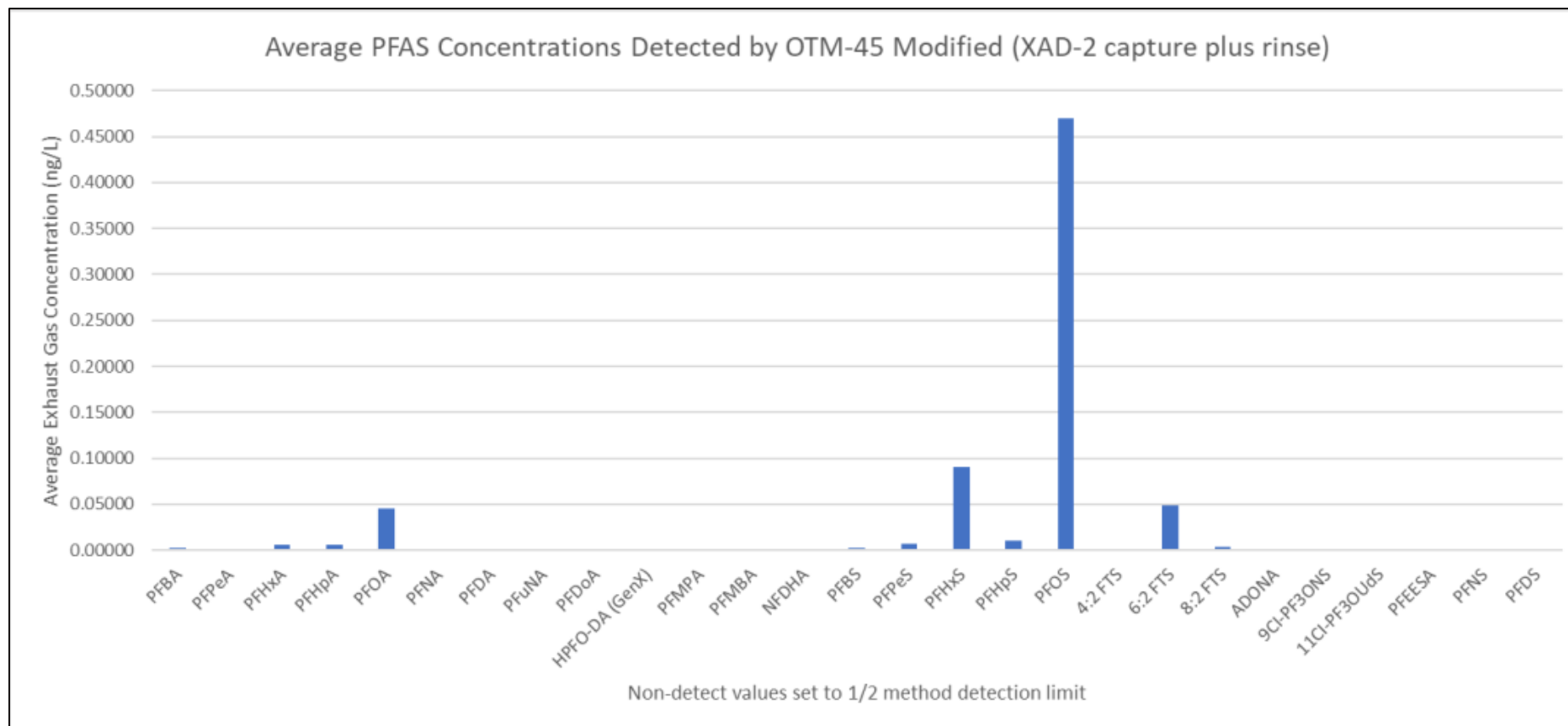


Residual Burned XAD-2
Resin in Canister



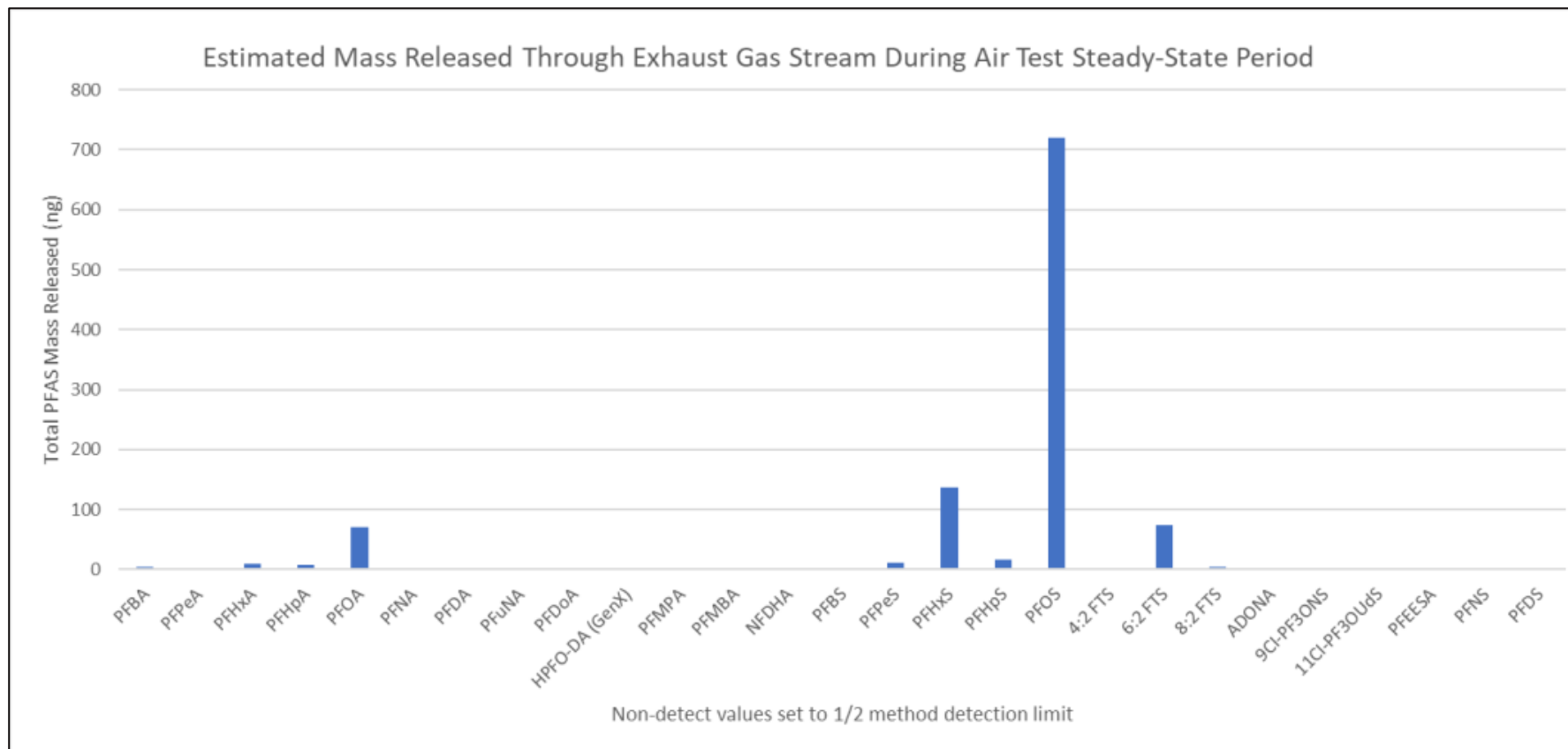
Air Sample Results

Air samples taken during Ozone Test 2 could not be used due to XAD resin failure. Results shown below for Air Test 1 only.



Detections possible from condensation water droplets seen on XAD resin

Air Sample Results



- 719 ng of PFOS was captured from the exhaust gas, but the system saw a total PFOS throughput during that sampling time of 5,750,000 ng
- 0.013% of the total PFOS mass introduced into the system escaped in the exhaust gas phase

Pilot Test

November – December 2023

DRAFT Results

Pilot Test

- Container delivered/unloaded onto site
- Slip stream connection from single well and back to existing equalization tank
- Slip stream flowrates were 3 gpm during the pilot test as planned, with an equivalent HRT of 22.6 minutes per column; with two columns in series, the total HRT was 45.2 minutes.
- Acetic Acid used for foam optimization
- Sodium bicarbonate used for pH neutralization prior to discharge back to EQ tank
- VGAC and LGAC used for polishing and safety net

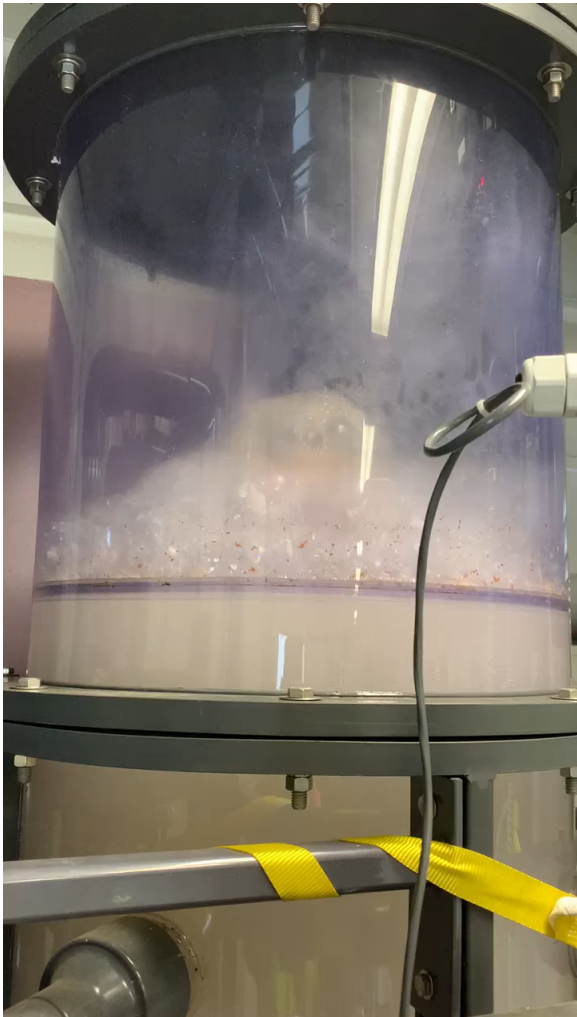


Pilot Test

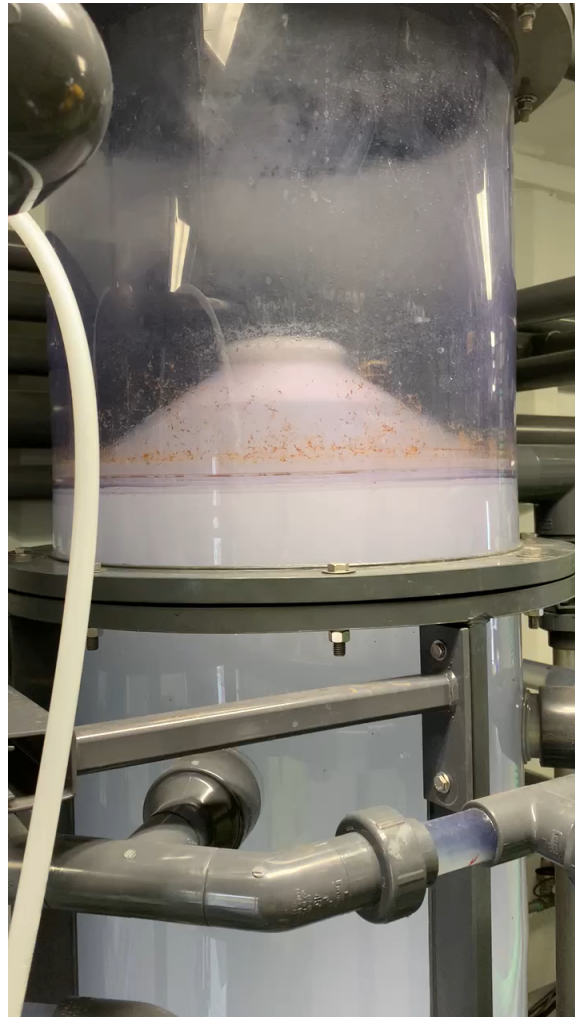
Project Phase	Total PFAS Influent (ppb)	Date
Site Selection Desktop Evaluation Phase	>90	11/4/2022
Bench-Scale Test Phase	72	3/21/2023
Pilot Test Phase	118	11/30/2023
	132	11/30/2023
	113	12/1/2023
	98	12/4/2023
	104	12/5/2023
	24	12/11/2023
	60	12/18/2023
	62	12/20/2023

Existing system operations impacted on 12/11/24 (24 ppb) may be considered an upset/outlier condition

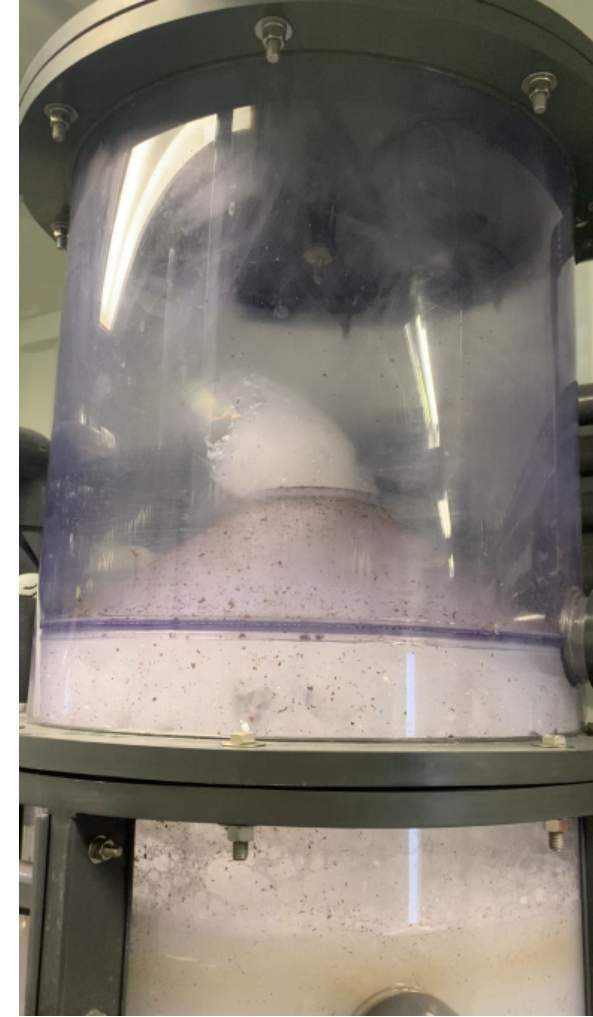
Pilot Test



Column 1 – Ozone
(12/5/23)

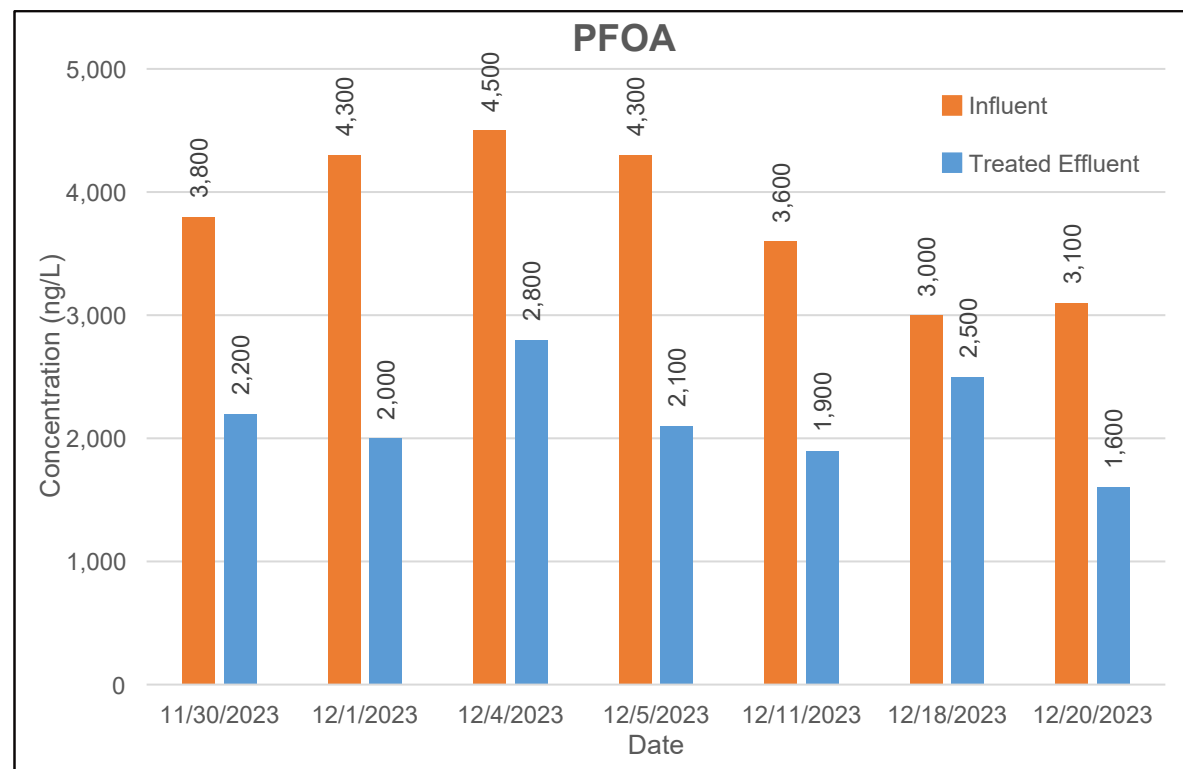
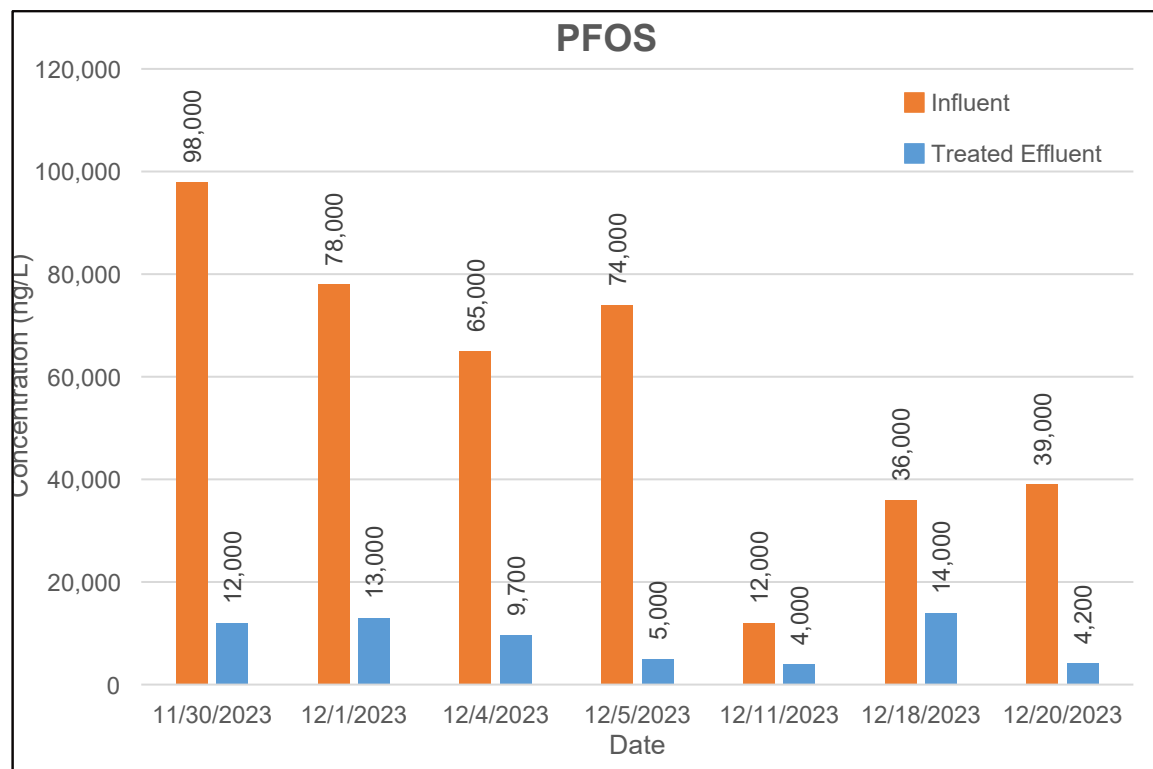


Column 2 – Air
(12/5/23)

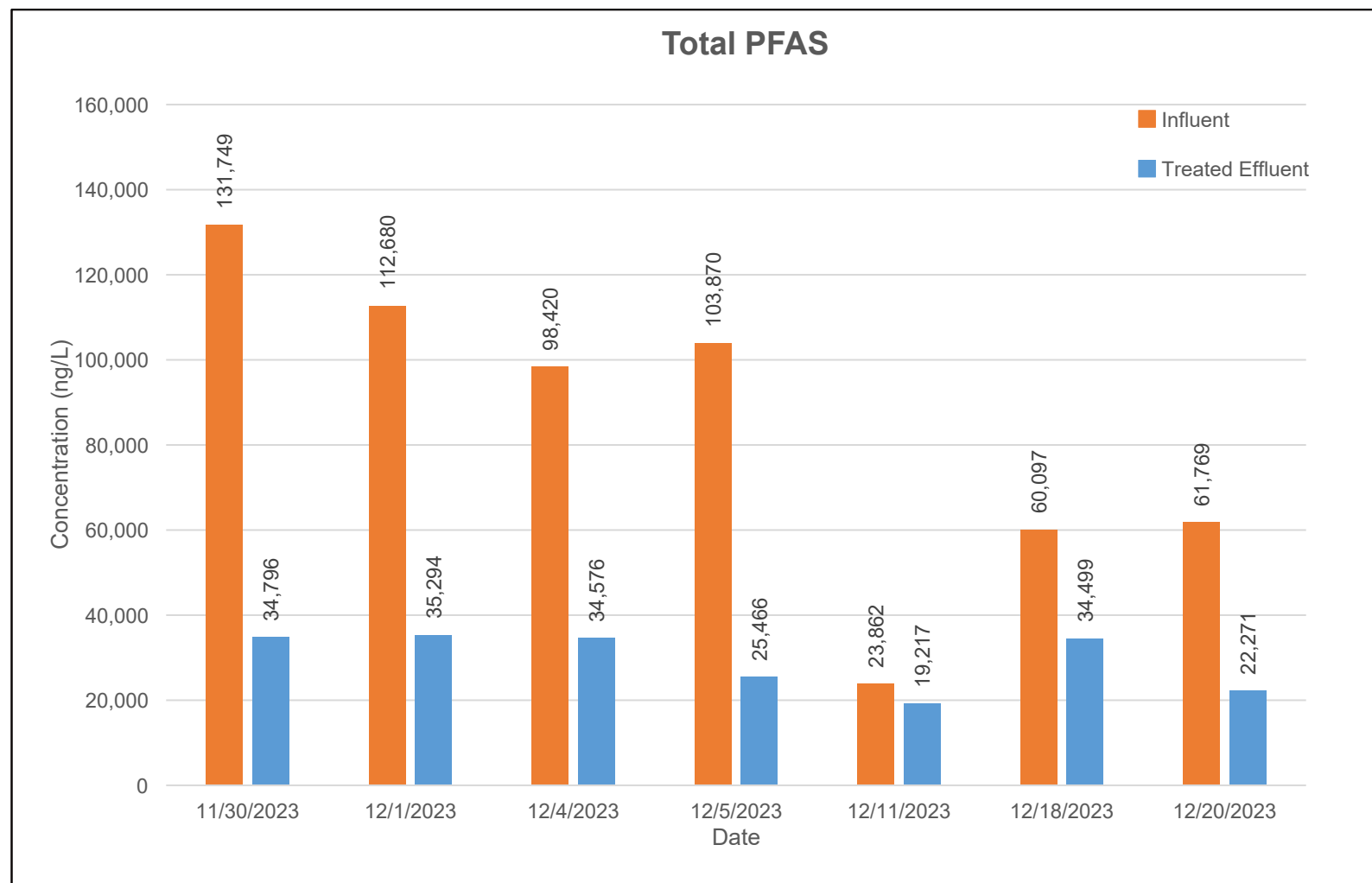


OSCAR Concentrating
Column– Ozone (12/18/23)

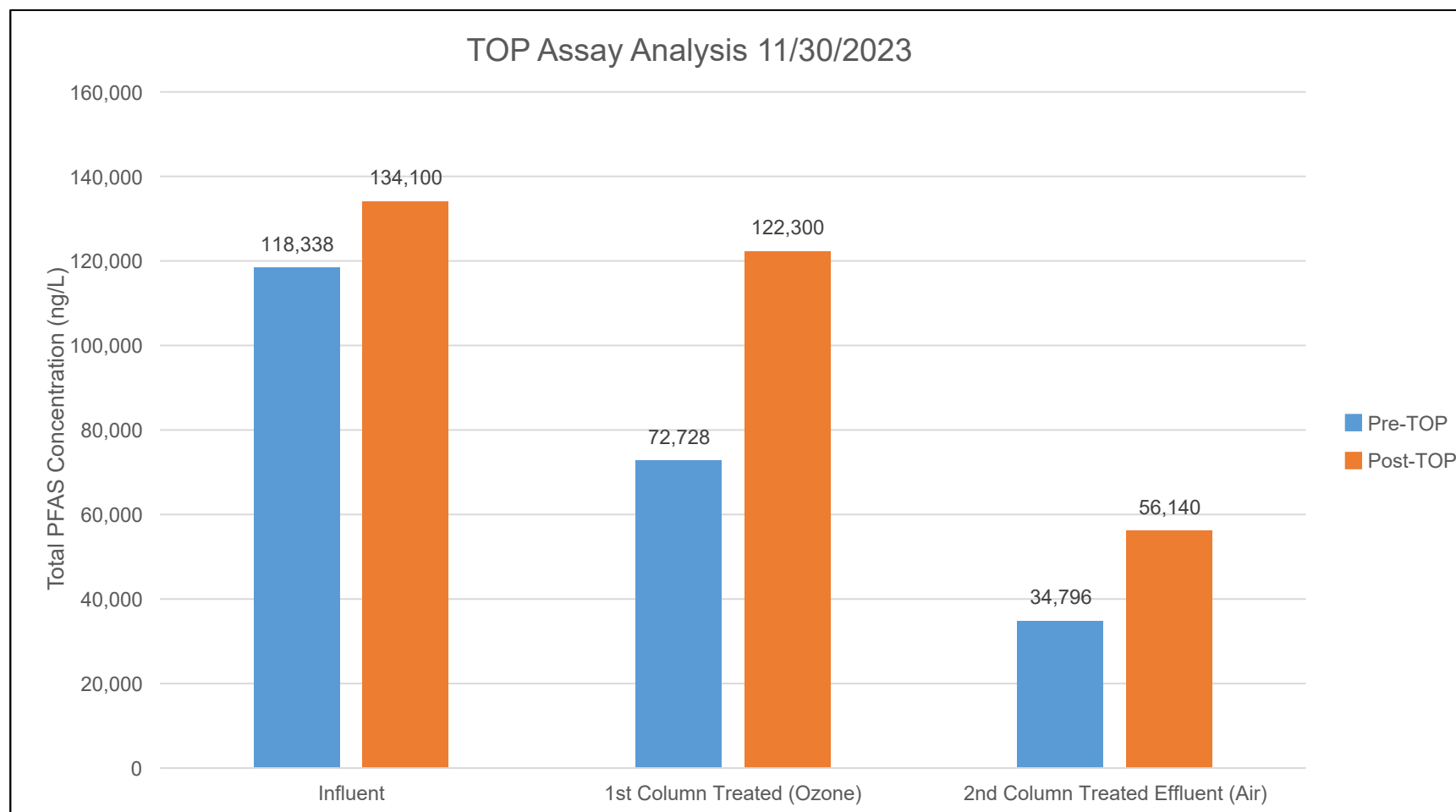
Pilot Results – PFOS / PFOA



Pilot Results –Total PFAS



Pilot Results - TOP Assay

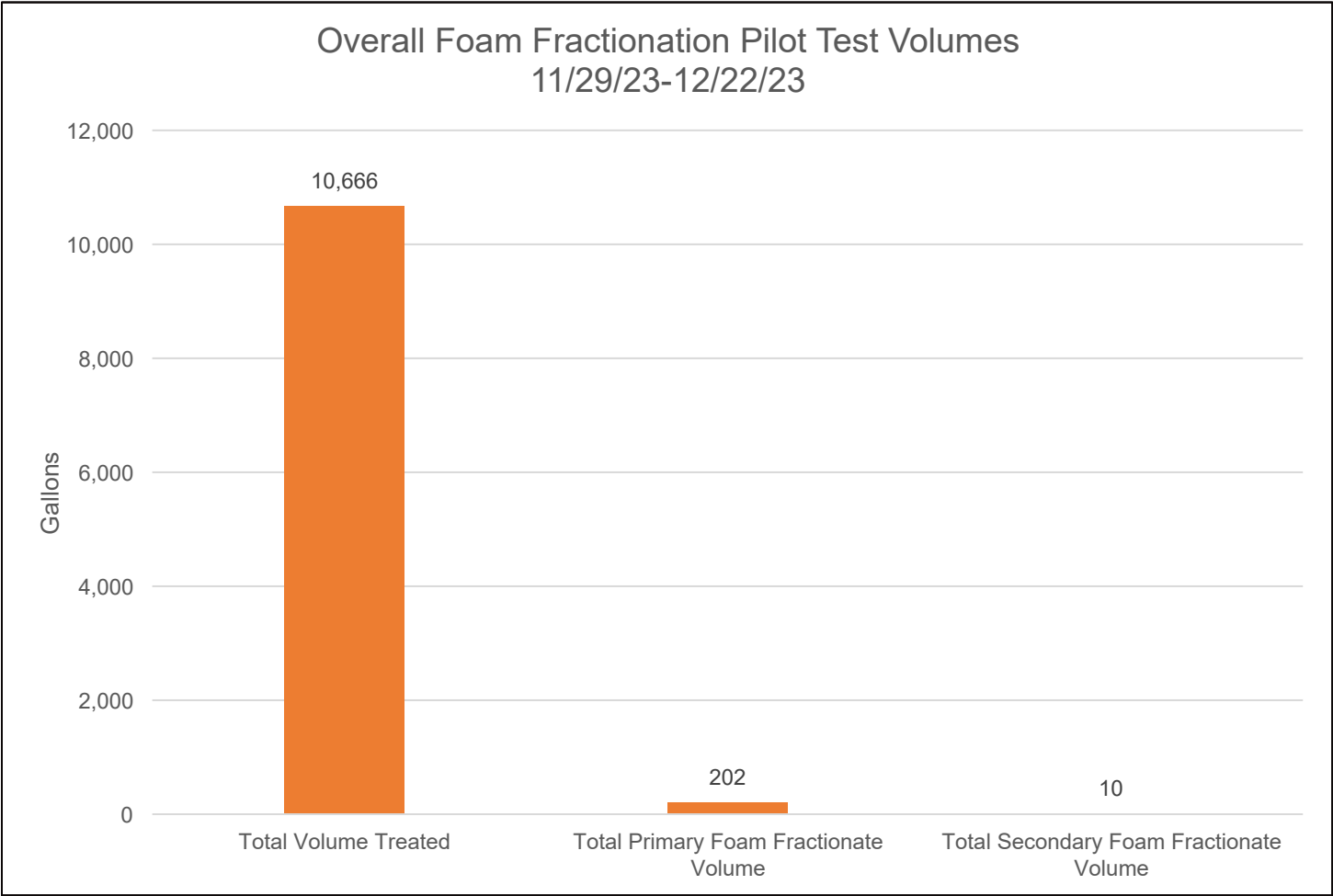


Foam Fractionation Expected Performance

PFAS Analyte	Raw Landfill Leachate Estimated % Removal	Groundwater (90 ppb PFAS) with Reagent Estimated % Removal
PFOA	96% to 99%	38% to 53%
PFOS	96% to 99%	83% to 93%
PFNA	95% to 98%	58% to 87%
PFHxS	93% to 97%	28% to 38%
PFHpA	70% to 81%	0 to 10%
Total PFAS	91% to 95%	64% to 75%

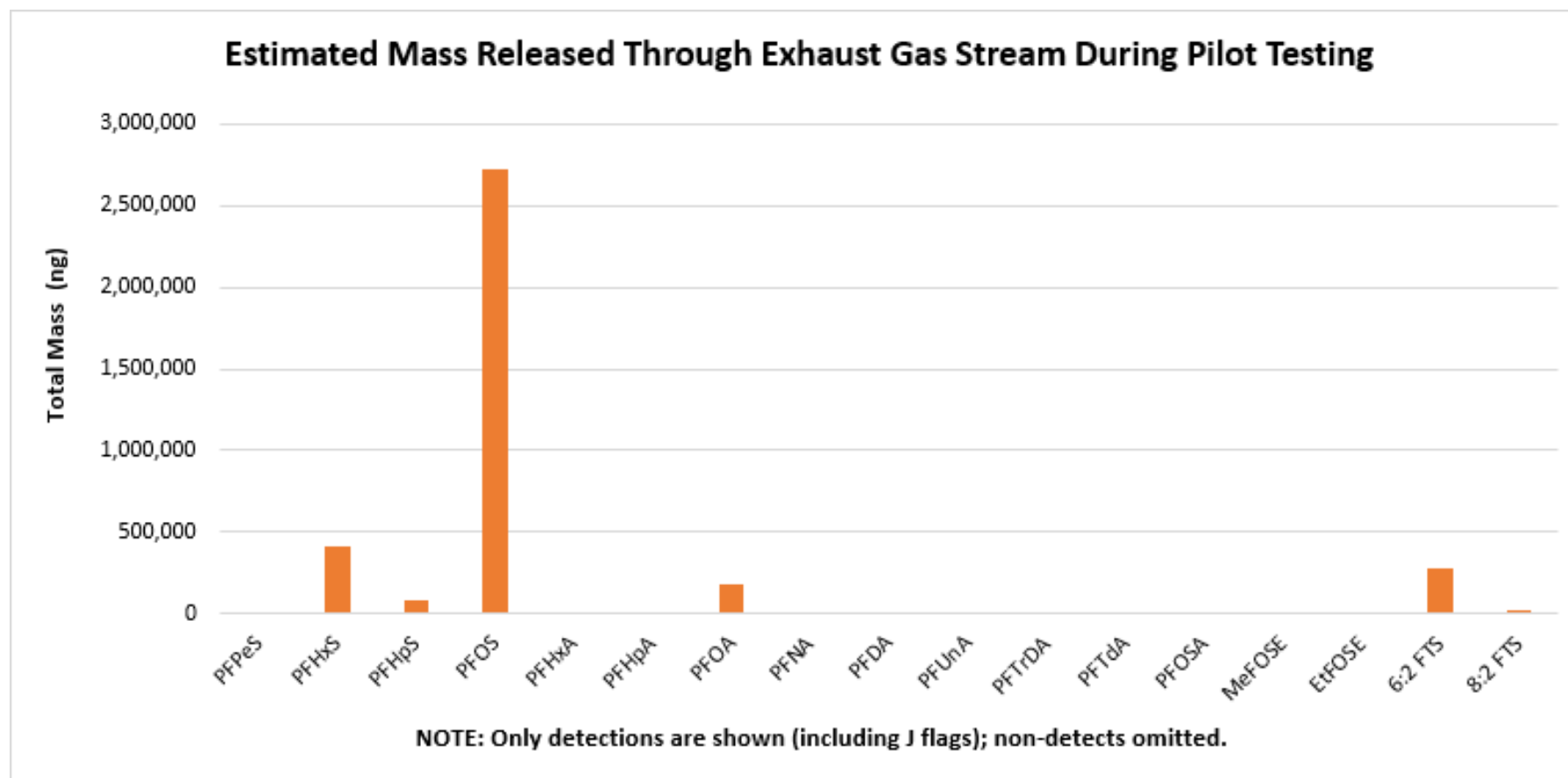
*Based on Landfill Leachate mixed w/ GW 2023 pilot test performed by Arcadis (9/25-10/13). Percent removal varies significantly based on source, PFAS concentrations, surfactant load, hydraulic residence time, and foaming characteristics

Pilot Results – Foam Fractionate Volumes



Statistic	% Foam Primary	% Foam Secondary
Minimum	0.4%	0.04%
Maximum	10.3%	4.7%
Mean	1.9%	0.2%
Median	2.2%	0.1%

Pilot Results- Vapor GAC



~0.121% of the total PFOS and ~0.111% of the total PFAS mass introduced into the system escaped in the exhaust gas phase onto the VGAC

Rough Order of Magnitude Cost Estimates

Technology	Purchased Equipment Capital Cost Estimate* (±50%)	Operations Cost Estimate (±50%)
Foam Fractionation – 10 gpm with Chemical Dosing Pre-Treatment and GAC Polish	\$1.1 million	\$0.52 million

- 3 primary foam fractionation columns in series and 1 concentrating column
- Chemical storage (Acetic acid and sodium bicarbonate) and dosing pumps
- Ozone Generator, destruct unit, and vapor GAC
- Lead/lag post fractionation polish treatment
- 10% contingency on all capital estimate
- Sodium bicarbonate – 455 gallons a year at \$20/gallon
- Acetic acid – 36,372 gallons a year at \$1/gallon.
- Foam fractionate disposal – 21,024 gallons a year at \$3/gallon – may be cheaper with destruction
- Electricity – 365,000 kilowatt-hours at \$0.15/kilowatt-hour
- GAC polish- 200 pounds of GAC with quarterly changeouts at \$10,000/changeout

Foam Fractionation Considerations

- Foam fractionate disposal or destruction
- Injection Gas Selection
- Reagents / Co-Surfactants
- Foam Management- Nozzle cleaning/spray down
- VGAC replacement and air monitoring
- Ozone controls
- Source selection and other treatment train technologies



Conclusions

Bench and pilot testing plays a key role in mitigating the technical risks associated with adopting new technologies.

Foam fractionation can be considered for improving PFAS removal efficiency at a variety of sites

Bench scale and pilot tests have demonstrated foam fractionation can be effective as a stand-alone technology for low- to medium-flowrate applications

Foam fractionation applications include industrial and municipal wastewater treatment plants, landfill leachate, groundwater in firefighting foam impacted source zones or high concentration areas, reverse osmosis rejectate, etc.

Thank You!



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