MEMO

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1 Project Background

Due to the presence of per- and polyfluoroalkyl substances (PFAS) at the RACER Trust Coldwater Road Facility and the need to prevent untreated discharges containing perfluorooctanesulfonic acid (PFOS) from on-site ponds, surface water from the ponds require treatment prior to discharge to the municipal storm sewer system. Therefore, a bench scale testing program was conducted to assess overall feasibility of technologies, which will be used to identify estimated operational expenses, including, but not limited to granular activated carbon (GAC) and anion exchange resin (IX) consumption rates (i.e., estimated change out rates). The bench testing was organized in a logical and stepwise fashion to ensure each treatability test yielded information useful to the path forward of the treatment of PFAS impacted surface water at the Site. All wastewater collected to support this study was characterized to understand baseline concentrations of parameters of interest.

Because of difficulties encountered during operation of the temporary treatment system at the site the treatability testing consisted of evaluating chemical precipitation and dissolved air flotation (DAF) testing with coagulant and flocculant as surface water pretreatment technologies to evaluate pretreating the surface water prior to either GAC or IX treatment to remove PFOS.

In addition, isotherm testing and rapid small-scale column testing (RSSCT) were conducted to evaluate the removal efficacy of four GAC products and two IX products. Isotherm testing consisted of dosing 1-L aliquots of the site surface water with varying masses of adsorbent. The site surface water and adsorbent media were tumbled at a constant speed and temperature for 24-hours to reach adsorption equilibrium. Upon completion of the 24-hour period, each isotherm was filtered to remove the adsorbent media and analyzed for PFAS. The analytical data was then modeled to generate isotherm curves to assess each media's adsorption capacity and adsorption intensity. The results of the isotherm modeling were used to select the media to be used in the RSSCT.

RSSCT consisted of three individual columns, two columns were packed with GAC, and the third column was packed with PFAS selective anion exchange resin. The media used in the column was modified to be of a particle size that was between US mesh size 60x80. The purpose of the RSSCT was to predict the full-scale breakthrough of PFOS by utilizing the accelerated treatment afforded by the small-scale columns. Further explanation of the RSSCT set-up is provided in the Treatability Testing Results section. This technical memorandum provides a summary of the results of the treatability testing.

At this time RACER Trust and Ramboll are still evaluating how best to apply the treatability study results and the data and experienced gathered during the recent three-month long operation of the temporary surface water treatment system (SWTS) at the Site to further evaluate and possibly design and construct a more permanent SWTS for the Site to address discharges from the on-site ponds. In conjunction with the planned updating of the options analysis a separate technical memorandum will be prepared with our conclusions and recommendations from both this treatability study and the lessons learned from the operation of the temporary SWTS, which will guide potential future treatment of discharges from the on-site ponds.

2 Treatability Testing Results

2.1 Chemical Precipitation

Chemical jar testing was performed to evaluate the extent to which suspended solids can be precipitated out of solution. 1% alum was added to 2-L aliquots of the Site pond water (site surface water) in various increments, combined with 0.25 mg/L of 0.1% Aries 3644 polymer in a 2-L square beaker. The samples were well-mixed and measured with a pH probe. A control jar test was performed using site surface water that was not chemically conditioned. Upon completion of the chemical screening, it was observed that the most effective chemical combination was 50 mg/L of commercial alum and 0.25 mg/L of Aries 3644 polymer. The results are shown in Table 1.

Table 1: Coagulation/Flocculation

Sample I.D.	Volume	Alum	Aries 3644	pH	Supernatant TSS
	L	mg/L	mg/L	S.U.	mg/L
1	2	30	0.25	6.9	10
2	2	50	0.25	6.6	3
3	2	70	0.25	6.4	3
Control	2	0	0	7.4	10
Raw	2	0	0	7.4	210

Note: Alum dosed as product received

Testing results indicate that the use of the coagulant and flocculant independently had a significant impact on the precipitation of TSS, with Test No. 2 visually displaying the clearest treated surface water (see Attachment 1 for treatability testing photographs), largest floc aggregates, and one of the lowest concentrations of supernatant TSS, followed by Test No. 3. The control test had a significantly lower supernatant TSS concentration compared to the raw site surface water but was parametrically similar to Test No. 1 that was treated with a coagulant and flocculant.

2.2 Dissolved Air Flotation (DAF) Testing with Coagulant and Flocculant

The objective of the DAF testing was to assess the extent to which solids may be separated from the site surface water matrix via air flotation as opposed to gravity settling. Site surface water was saturated with compressed air at 45 psi. The air-saturated pressurized water was then introduced slowly to allow the tiny air bubbles to adhere to solids in the raw unsaturated surface water sample in an open reservoir.

The bench scale DAF unit was operated at a pressure of 45 psi, air saturated surface water was preconditioned with alum and Aries 3644 and tested at 50 and 75% recycle ratios. For example, if 1 L of raw site surface water is placed in the open reservoir, 500 mL of air saturated site surface water will be added to obtain a 50% recycle ratio. The results of the DAF testing are shown in Table 2.

Table 2. DAF treatability testing results

Test	Volume	Alum*	Aries 3644	Pressure	Air Saturated Water#	Recycle Ratio	Subnatant TSS
	L	mg/L	mg/L	psi	L	%	mg/L
1	1	50	0.25	45	0.5	50	5
2	1	50	0.25	45	0.75	75	6

Note: Alum dosed as product received

Air saturated surface water used for DAF testing was chemically conditioned supernatant of site surface water

The results of DAF testing indicate that test No. 1, with a recycle ratio of 50%, removed the most concentration of subnatant TSS.

2.3 Isotherm Testing

Isotherm testing was performed in order to evaluate a variety of adsorbent material with respect to their ability to remove PFAS from the site surface water. In total, six adsorbent media were tested, four granular activated carbons (GAC) and two PFAS selective anion exchange resins (AER). The media tested include Filtrasorb 400 (F400) from Calgon Carbon Corp., Ultracarb-1240 (UC1240) from Evoqua Water Technologies Inc., Gl65RG (virgin) and L900R (reactivated) from Carbon Activated Corp., Dowex PSR2+ (PSR2+) produced by Dupont and supplied by Evoqua, and PFA694 produced by Purolite. Each media was used to perform batch equilibrium isotherms. Isotherms were dosed with adsorbent on a TOC basis for GAC, on the basis of 100 mg TOC/g GAC. For example, if the TOC of the water being tested was measured to be 100 mg/L, 1g of GAC would be added to the sample. The AER dosages used for isotherm testing were based on previous project experience, best practices for accurately measuring small resin volumes, and minimum exchange capacity. The adsorbent dosages used for testing are shown in Table 3.

Table 3: Adsorbent dosages used for batch equilibrium isotherms

Media	0.1X	0.25X	0.5X	0.75X	1.0X
GL65RG	0.0031	0.00775	0.0155	0.02325	0.031
L900R	0.0031	0.00775	0.0155	0.02325	0.031
F400	0.0031	0.00775	0.0155	0.02325	0.031
UC1240	0.0031	0.00775	0.0155	0.02325	0.031
PFA694	0.003	0.105	0.2625	0.525	1.05
PSR2+	0.00036	0.11	0.275	0.55	1.1

Note: units for dosage are reported in grams/liter

Due to low concentrations of PFAS in the site surface water collected for testing, the compound that exhibited the results most suitable for modeling was PFOS. Analytical noise, resulting in PFAS concentrations in the isotherms being slightly higher than the control, sometimes with differences in the single digit ng/L, made modeling PFOA, PFHxA, and PFHxS non-ideal.

The results of the PFOS model for each adsorption media tested is shown below in Table 4:

Table 4: Langmuir and Freundlich model for PFOS adsorption

PFOS Isotherm Model Parameters						
	Langmuir			Freundlich		
	Smax	K	R^2	K	n	R^2
GL65RG	*6068*	*0.56*	*0.86*	*2441*	*0.26*	*0.97*
L900R	4934	0.18	0.92	1515	0.29	0.95
F400	**6927**	**0.47**	**0.94**	**2624**	**0.26**	**0.98**
UC1240	4814	0.7	0.86	2521	0.17	0.73
PFA694	370	0.38	0.95	131	0.25	0.82
PSR2+	336	0.27	0.92	100	0.30	0.95

Table 4 shows that the highest performing carbon was Calgon F400 in both the Langmuir and Freundlich model. The second-best carbon was the GL65RG from Carbon Activated Corp. For the Langmuir model, high Smax and K values indicate better adsorption. For the Freundlich model, High K values and Low n values indicate better adsorption. The R^2 value was also taken into consideration, as it indicates how well the model fits the experimental data.

Based on the isotherm data it may appear that carbon greatly outperformed resin, however, resin dosing is based on volume (mL resin/L sample). When compared on a mass dosage to carbon, resin received a much higher mass loading. Due to the higher mass of resin added, it appears to have performed more poorly in the static isotherm test versus a more dynamic column test. Based on the isotherm data between the two resins, Purolite PFA694 performed slightly better than the Dowex PSR2+.

Figures 1 & 2 show the modeled isotherm curves.

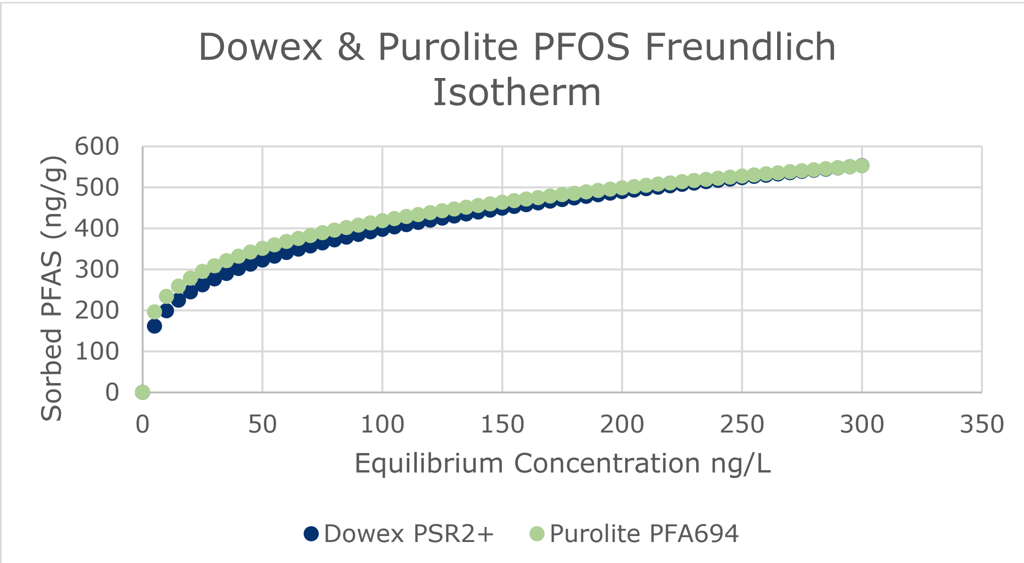


Figure 1: Comparison of the two modeled isotherms for the resins tested

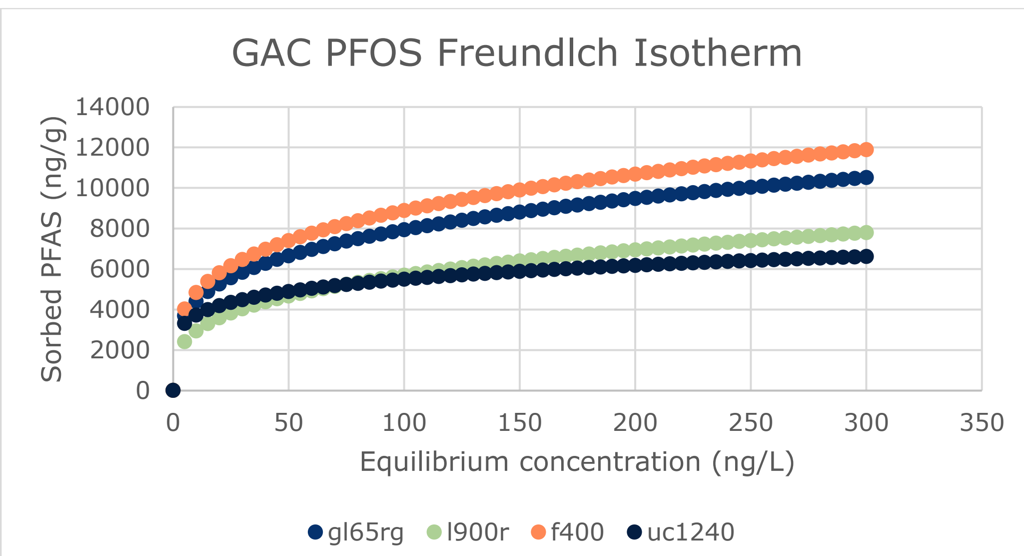


Figure 2: Comparison of the modeled isotherms for the GACs tested

Figures 1 and 2 are graphical representations of the data provided in Table 4. It is shown in figure 1 that the PFA694 resin slightly outperformed the PSR2+ resin. Figure 2 illustrates that the best performing carbon was F400 followed by GL65RG, L900R, and UC1240. Due to significantly lower product costs it was decided to test GL65RG and L900R GAC, and PFA694.

2.4 Rapid Small-Scale Column Testing (RSSCT)

Upon completion of the batch isotherm testing, Ramboll performed three dynamic RSSCT test to simulate approximate bed life of a full-scale contactor vessel. The purpose of this testing was to build upon information gained in the isotherms by using the selected media in a dynamic, flow through test to give an approximation of the frequency vessels would need to be changed-out at full scale. The three media tested included GL65RG, L900R, and PFA694.

Important parameters related to the design of the RSSCT column include hydraulic loading and empty bed contact time (EBCT), which are used to scale the small column operation to approximate full-scale operation. The column test was designed to meet the demands of an average daily flow of 288,000 gallons, or approximately 200 gpm. This flowrate was selected to simulate treatment for an 8' diameter single GAC contactor containing 10,000 lbs of GAC. For the resin vessel, the same flow values were used, however a 5' diameter vessel was simulated. The simulation period was planned to simulate approximately 200 days of full-scale run time testing simulated approximately 7 months of full-scale run time at this hydraulic loading.

The RSSCT was conducted according to a modified ASTM D6586-03 method, with the main modification of a bottom-up column feed, rather than top-down, in order to minimize entrapment of air bubbles in the media bed, which can lead to short circuiting (channeling) and decreased contact with the adsorbent media. The RSSCT column was constructed from 1 cm inner diameter clear PVC pipe. Site surface water was preconditioned with 50 mg/L of alum and 0.25 mg/L of polymer, flash mixed, and allowed to settle. The supernatant was decanted and then filtered through a 0.2-micron cartridge filter to remove particulate that would foul the column. Upon completion of the pretreatment step, all of the received surface water for testing was composited. It should be noted that the 0.2-mircon filtration step had no impact on PFAS concentrations in the column feed as compared to Raw sample. The relevant operating parameters are summarized in Table 8 below.

Table 1 – GAC RSSCT Operating Parameters

	Unit	GL65RG	L900R	PFA694
Media Particle Size	-	60 x 80 mesh	60 x 80 mesh	60 x 80 mesh
Bed Depth	cm	10.2	10.1	3.4
Column ID	cm	1.05	1.05	1.05
Empty Bed Contact Time (EBCT)	minutes	12.5	12.5	3
Flow Rate	mL/min	16.5	39.2	39.2
Bed Volume (BV) Rate	BV/hr	112	268	811
Equivalent days of full scale treatment per hour of RSSCT operation	d	0.98	2.33	1.26

Note: Differences between the 2 GAC columns is the product of L900R being an 8x30 mesh carbon and GL65RG being a 12x40 mesh carbon (full-scale size).

The experimental set up of the column is fitted with a pressure gage to measure the backpressure of the column from the packed bed. It is normal and typical for this pressure to rise as the experiment timeline progresses, if pressures exceed 120 PSI the column would be shut down before a failure pressure of 150+ PSI. Two of the three columns experienced pressure that resulted in a shutdown of the column. The GL65RG and PFA694 columns were temporarily turned off on the 4th full day of operation, glass wool and glass bead packing material was removed from the column and restarted. Both columns were able to operate for an additional day before returning to a pressure greater than 120 psi resulting in shutdown. The L900R column reached 150 psi on the final day of testing, however all necessary samples were able to be collected as planned.

Figure 3 illustrates the performance of each column with respect to PFOS breakthrough.

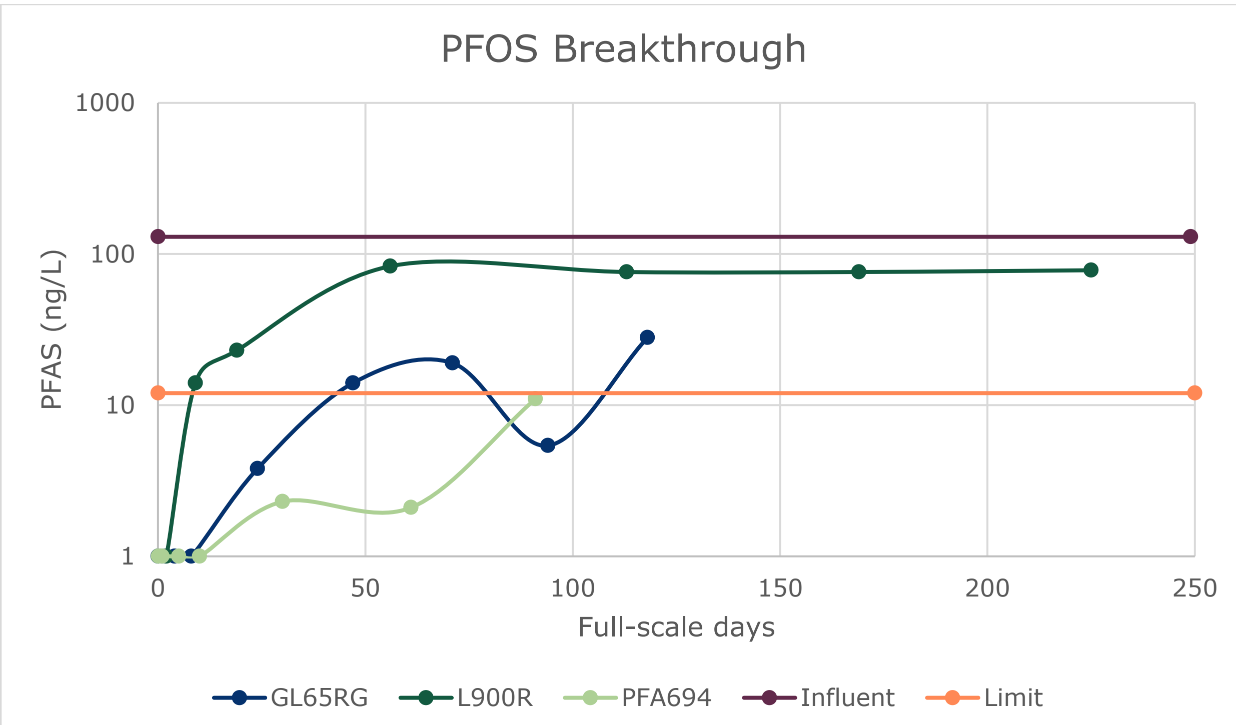


Figure 3: PFOS breakthrough for three RSSCT columns

The data indicates that L900R, the reactivated carbon, exhibited near instantaneous breakthrough with respect to PFOS. This data is contradictory to the field data that was generated during operation of the temporary treatment system. GL65RG exhibited improved PFOS removal in comparison to the L900R media, reaching the PFOS effluent limit of 12 ng/L after approximately 45 days of simulated full-scale operation. PFA694 performed greater than both GAC products, with a PFOS concentration in the column effluent reaching 11 ng/L after 91 days of simulated full-scale treatment.

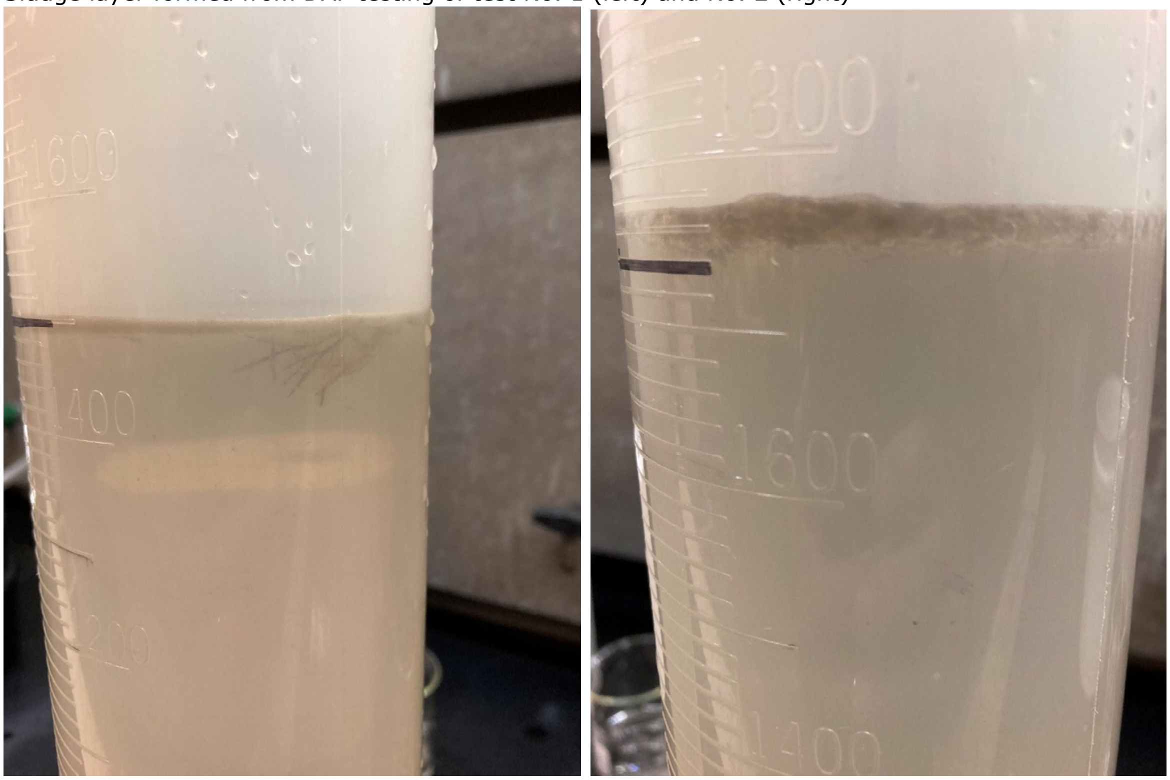
Since PFOS is the predominant PFAS compound present in the site surface water, graphical representation of total PFAS breakthrough follows the same trend as the PFOS breakthrough curves. Due to column pressure, and early shutdown of the RSSCT columns, full breakthrough was not observed.

3 Summary of Treatability Test Results

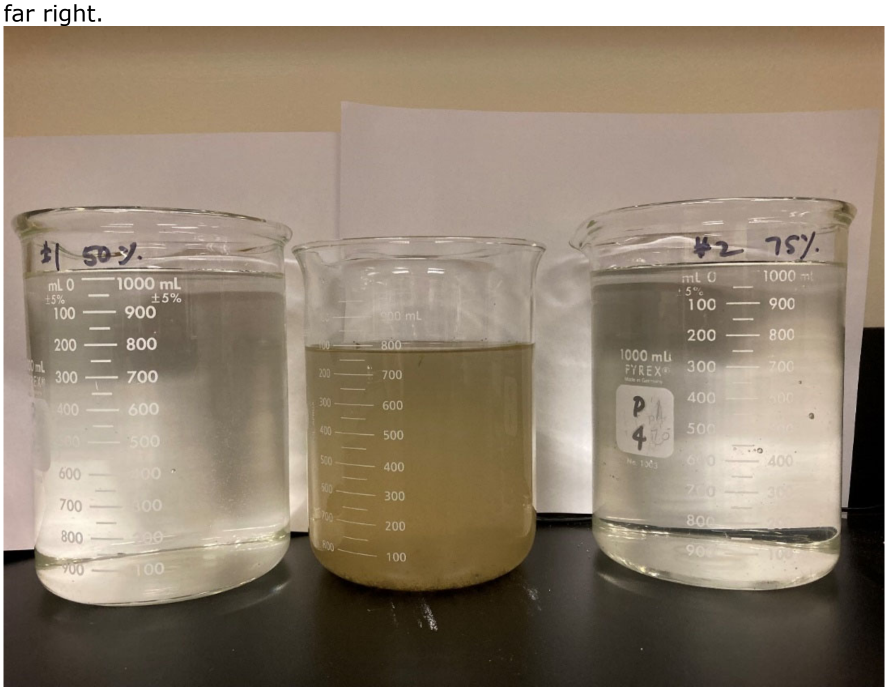
- Chemical precipitation and DAF testing exhibited similar removal of TSS from the site surface water. Ramboll will further evaluate what technology will be the simplest to implement on site with the lowest capital (i.e., equipment) and operations and maintenance (O&M) costs.
- PFA694 exhibited the longest time for PFOS breakthrough to occur, followed by GL65RG, and L900R.
- L900R showed near immediate breakthrough of PFOS during the RSSCT, which contradicts the field data generated during operation of the temporary treatment system.
- Further evaluation of the treatability study and temporary treatment system operational/performance data and costing of the system are still required.

ATTACHMENT 1 – TREATABILITY TESTING PHOTOGRAPHS

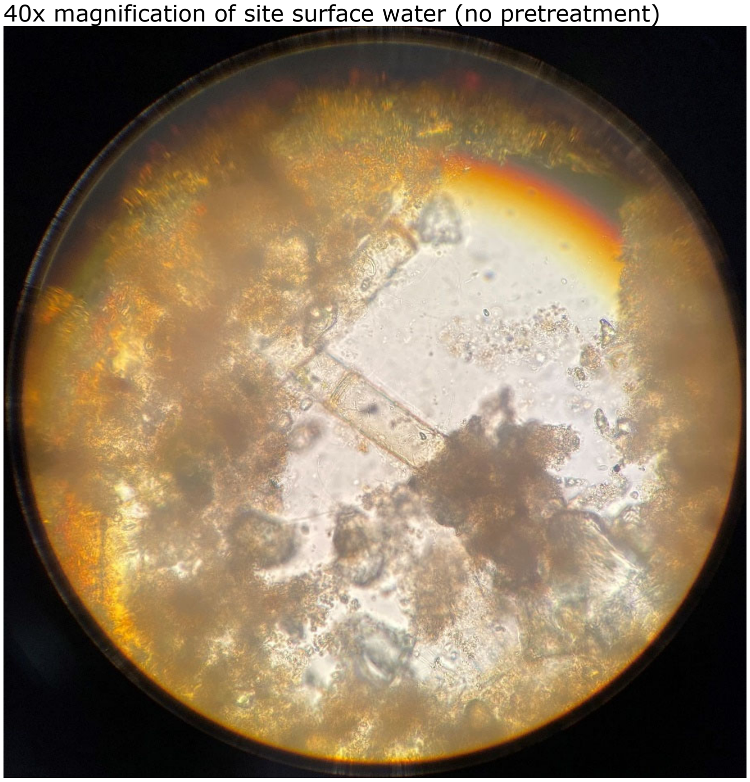
Sludge layer formed from DAF testing of test No. 1 (left) and No. 2 (right)



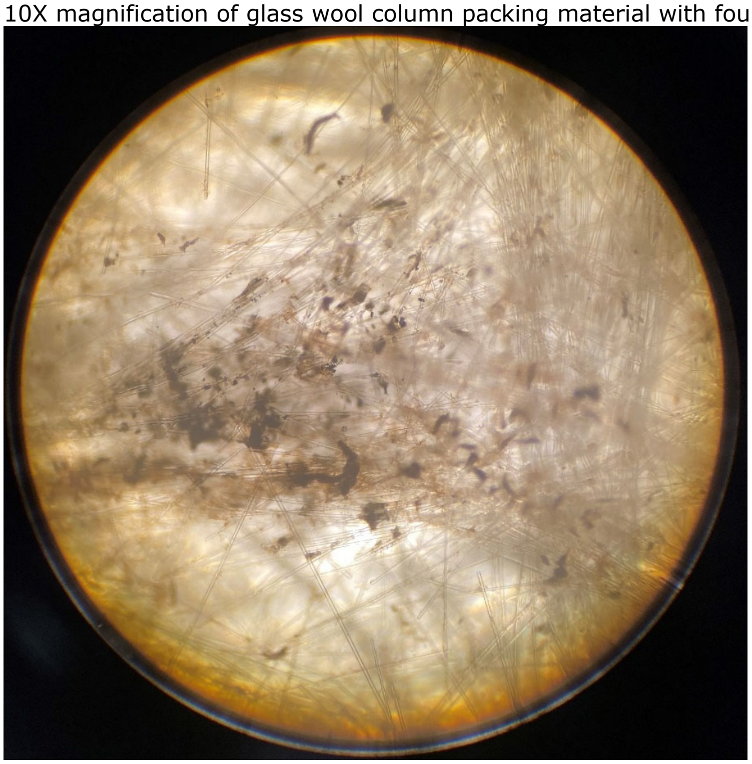
Pre-DAF testing with test No. 1 on the left, raw site surface water in the center, and test No. 2 on the far right.



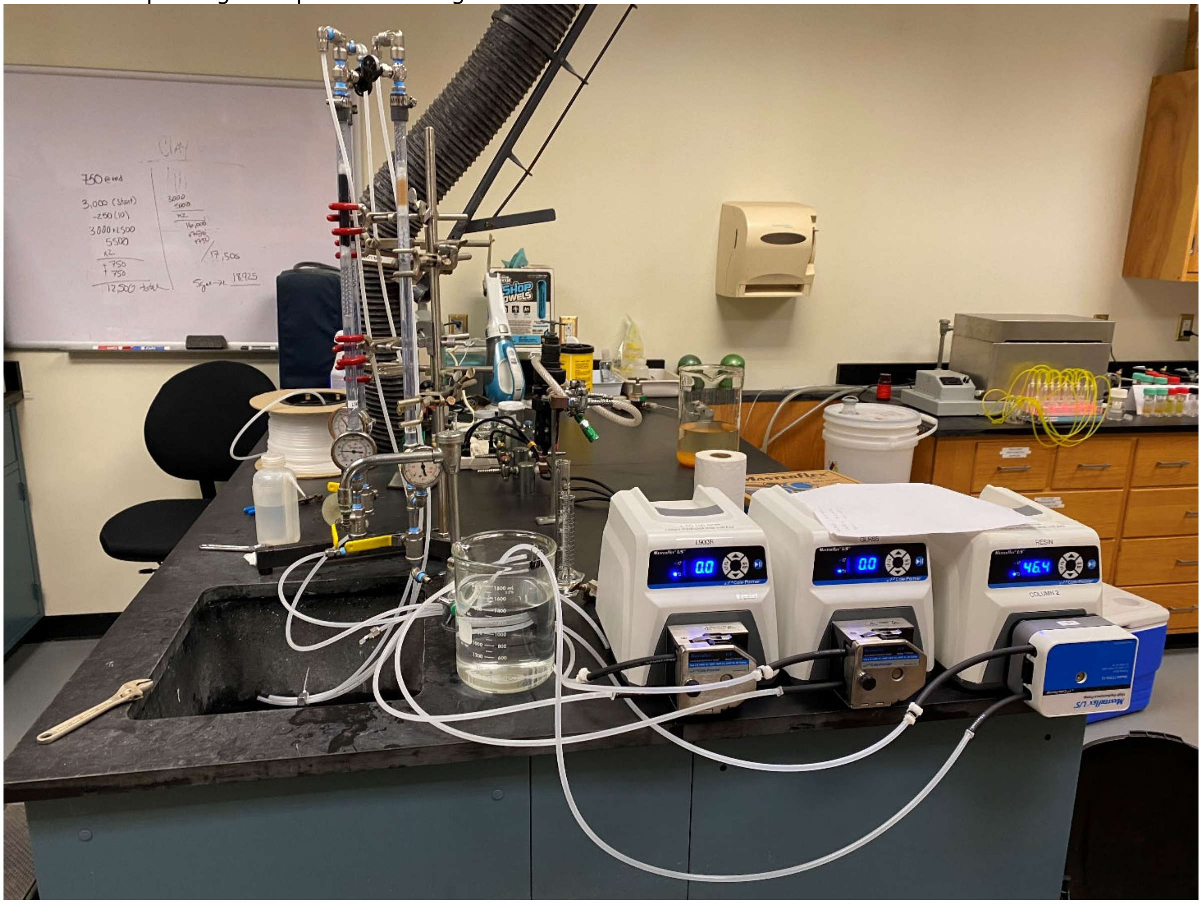
40x magnification of site surface water (no pretreatment)



10X magnification of glass wool column packing material with fouling



RSSCT set-up being built prior to testing



Resin column showing discoloration of resin and movement of the bed caused by high pressure