PFAS Mobile Treatment and Rapid PFAS Measurements of Highly Contaminated Fire Runoff Water from Chemical Plant Fire

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ABSTRACT

To avoid costly transport and disposal of Polyfluoroalkyl Substances (PFAS) runoff water from a chemical plant fire by deep well injection or incineration, on-site pre-treatment and final treatment by the Publicly Owned Treatment Works (POTW) was evaluated as a disposal option for the impacted water. Remtech conducted pilot treatability tests on 440,000 gallons of fire runoff water that was contained in twenty-two frac tanks from a chemical plant fire that was extinguished with (AFFF) foam. Samples were collected and independent treatment efficacy laboratory (Eurofins) analysis reported by Keith Cole, Ramboll Americas Engineering Solutions, Inc.[1, 2] Pilot tests and design specifications were prepared by Mark Ryckman, Remtech Engineers.[3] PFAS concentrations ranged from 253,649 ng/l to 13,185,500 ng/l in six of the 22 frac tanks. Waste from all 22 tanks were equalized/blended to reduce the wide range of concentrations and treated through a pilot treatment train consisting of screening, equalization, sedimentation, fine bubble aeration, sand filtration, and three-stage liquid Granular Activated Carbon Filtration (GAC). By aeration 27.97% of PFAS was removed, and 99.99% were removed by all unit operations. The treatment method demonstrated that both long and short chain PFAS analytes were effectively removed. Powdered Activated Carbon (PAC) dosed at a self-flocculating 1,000 mg/l concentration was considered as a treatment option that removed 34.50% of PFAS following 48 hours of clarification. This treatment method was ruled out. To reduce the laboratory testing frequencies and costs, correlation curves with a field COD meter (REALTECH BOD/COD Field Meter) were developed with laboratory data to predict PFAS concentrations approaching EPA target PFAS treatment values.

BACKGROUND

Remtech developed a mobile treatment system design to treat runoff water from a chemical plant fire that had total PFAS concentrations ranging from 253,649 ng/l to 13,185,500 ng/l in 6 of 22 frac tanks. Household products, fragrances, sports drinks, tapes, and road-paving materials were manufactured from processed pine tree stumps into resins, rosins, waxes, and gums at the treatment plant. To avoid costly transport and disposal of the wastewater, on-site pre-treatment and final treatment by the Publicly Owned Treatment Works (POTW) was assessed as an option for the impacted water. Pilot/bench-scale tests were evaluated to properly design a full-scale wastewater treatment system.[4]

WASTE CHARACTERIZATION & PREPARATION

Initial samples were collected from six (6) of the 22 frac tanks and tested for PFAS (using EPA Method 533) and general chemistry analytes. The results are presented in Tables 1a and 1b. Herbicides, heavy metals, mercury, and organochlorine pesticides were also tested on the initial 6 frac tank samples. These analytes were below pretreatment requirements of the Publicly Owned Treatment Works (POTW) and were not run on Pilot Runs 1 and 2. EPA methods employed for PFAS and General Chemistry analyses are summarized below:

- ◆ pH - Method: (SM-4500-$^{+}$)
- ◆ VOCs - Method: 8260D GC/MS
- ◆ Organochlorine Pesticides - Method: SW846 8081B (GC)
- ◆ Herbicides - Method: SW846 8151A (GC)
- ◆ Metals (ICP) - Total Recoverable - Method: EPA 200.7 Rev 4.4
- ◆ Total Hardness (as $CaCO_3$) by calculation - Method: SM 2340B-2011
- ◆ Mercury (CVAA) - Method: EPA 245.1-1994 R3.0
- ◆ Oil & Grease - HEM (1664A)
- ◆ Total Suspended Solids - (SM 2540D-2015)
- ◆ Chemical Oxygen Demand (SM 5220D-2011)
- ◆ Total Organic Carbon TOC (SM 5310 B-2011)
- ◆ PFAS - EPA Method 533 was used for testing PFAS in the first 6 frac tanks
- ◆ PFAS - EPA Method 1633 was used for pilot testing. EPA recommends this method, and it is currently the only PFAS method that has been validated for wastewater, surface water, and groundwater by 10 laboratories in 12 diverse and challenging aqueous matrices [5]

The frac tanks contained a floating layer of resins/oils, a suspension of suspended solids, and settled solids. Samples from individual frac tanks had highly variable pHs (ranging from 4.25 to 11.96), general chemistry analytes and PFAS concentrations that required equalization. Results of initial testing are presented in Tables 1a & 1b.

Due to the wide variation of analyte concentrations, one-gallon samples from all 22 frac tanks were collected and a 22-gallon equalized composite sample was prepared for pilot testing. This resulted in significantly lower analyte concentrations. The "Raw Equalized" sample is depicted in the "blue highlighted" portions of Tables 1a & 1b and Table 2. The equalized raw wastewater had a pH of 10.1

TREATMENT METHOD & GOALS

Environmental releases from chemical fires are known to produce toxic vapor clouds, contaminated runoff from firefighting operations, partially burnt chemicals and residues, heavy resins, and fire extinguishing agents. Past treatment unit operations used by Remtech on contaminated chemical plant fire runoff water included flow/concentration equalization, aeration, sedimentation, GAC filtration, and PAC addition at self-flocculating dosages of 1,000 mg/l combined with bentonite.[6]

Remtech's treatment train design was based on the following documented PFAS treatability information:

- Complex organics, dissolved organic carbon (DOC), surfactants, suspended solids, TOC, and COD interfere with and compete for GAC and PAC absorption sites for PFAS and therefore, needs to be removed first [7]
- Aeration/foam fractionation is an effective pretreatment to remove some PFAS analytes and to enhance post treatment with carbon or ion exchange filtration [8,9]
- Foam fractionation produces extremely high concentrations of toxic vapors mists that requires mist treatment [10]
- Soluble PFAS analytes on particulates can be desorbed and transferred to the aqueous phase by mixing for treatment [11]
- Particulate matter needs to be removed prior to filtration to reduce carbon column backwashing that decreases PFAS removal efficiencies by channeling of bed media [7]
- PFAS removal efficiencies may increase with decreasing pH's in the 3 to 7 range [12]
- Aqueous and vapor phase coal-based GAC effectively removes PFAS and can be regenerated for reuse

Two of the preferred PFAS coal based GACs are Calgon's F400M and General Carbon's 12 X 40PF. General Carbon's GAC was selected since this vendor claimed that their product outperformed Calgon's carbon for PFAS removal.

Remtech's mobile pretreatment system was designed to reduce total PFAS concentrations to less than 200 ng/l with a pH of 10.12 so a local POTW could accept the wastewater for further treatment.

Six (6) EPA proposed PFAS analytes to be regulated are PFOA, PFOS, PFNA, PFHxS, PFBS, HFPO-DA/GenX. Two of the most toxic long chains analytes are PFOS and PFOA. Activated carbon filtration has been reported to be more effective in removing long chain rather than short chain PFAS analytes.[4] Of the six proposed regulated compounds, HFPO- DA and PFBS were the only short chain compounds detected in initial testing.

Treatment Goals

- Reduce PFAS concentrations down to a POTW pretreatment goal of less than 200 ng/l
- Determine if 12 x 40PF carbon is effective in removing very high concentrations of long and short chain PFAS analytes
- Determine treatment efficiency of sedimentation, aeration, GAC, and PAC
- Determine if a field COD test kit could be used to develop correlations to predict trending final PFAS concentrations to reduce the frequency of expensive PFAS lab costs

PILOT PLANT SETUP

Wastewater was first passed through a 35 mesh (50 micron) screen to remove floating and suspended scum. Selected unit operations were screening, sedimentation, non-harvesting aeration, sand filtration, and three GAC columns in series.

Sand media selected was Filtersil which is a high-purity monocrystalline industrial quartz sand for mixed media and pressure filters for potable, process, and wastewater filtration. Filtersil specifications are Grade 0.85, Effective Size (mm) 0.78, Uniformity Coefficient 1.47, Prior Grade designation WG#1, Approximate Screen Slot Size (inches) 0.030), bulk density 79-80 lb/cf loose, 83-85 lb/cf compacted.

Reactors, pumps, valves, fittings, and tubing selected were PFAS free. Following screening, wastewater was allowed to settle in a 30-gallon poly overpack for 24 hours for Run 1. Water was pumped with an agricultural diaphragm pump (Pentair Shurflo,12-volt,1.8 gpm) into a 10-gallon covered glass reactor (12" L x 6" W x 8" H) that was aerated for 1 hour at a flowrate of 6 standard cubic feet/hour (scfh) with 40-micron diffusers prior to running through four identical PVC columns (3" D x 26" H). Flowrates were measured with a King Liquid Flow meter (1 to 12 gph). Flowrates were controlled with a recirculation valve. Filter volumes and media charge weights are listed in Table 3.

Two GAC runs (Runs 1 & 2) were conducted at two flowrates (0.0277 and 0.0555 gpm) for carbon contact times of 10 and 20 minutes. Sample were collected from the raw wastewater, post aeration, and after each filter and were analyzed to determine removal efficiencies. The pilot test setup is depicted in Figures 1 and 2. Analytical results for Run 1 and Run 2 are presented in Tables 4, 5, 6 & 7.

Raw wastewater was also treated with 1,000 ppm of PAC. PAC was mixed with air at 6 scfh for 1 hour then allowed to settle for 48 hours then one sample was collected for analysis of PFAS by a certified laboratory. Results are depicted in Tables 8 & 9. PAC was most effective in removing PFBS, PFPeS, PFHxS, PFOS, and 6:2 FTS.

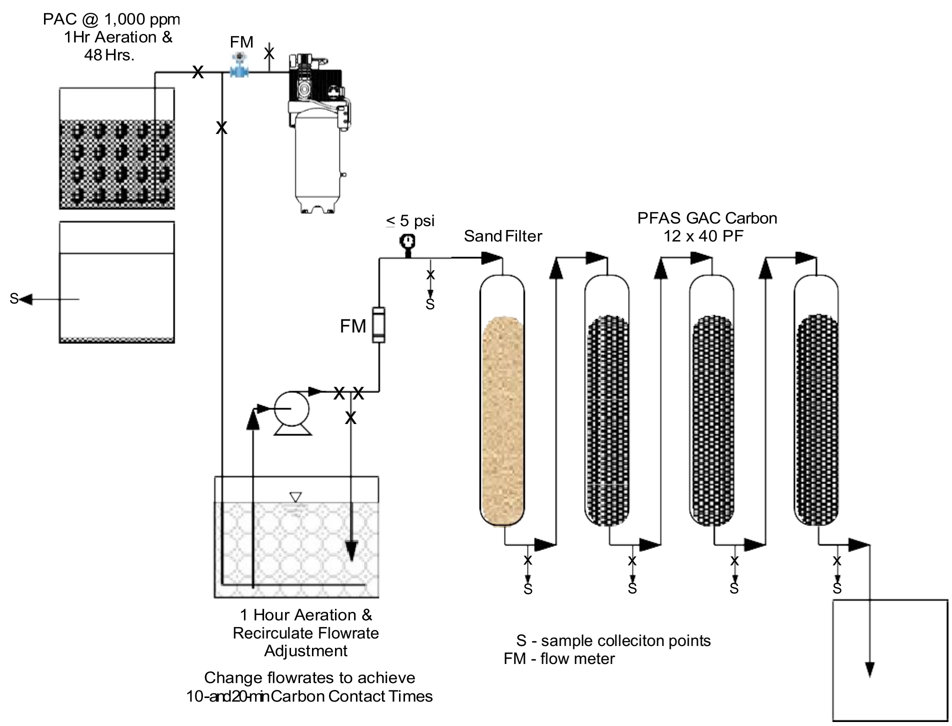

Figure 1: Pilot PID Drawing

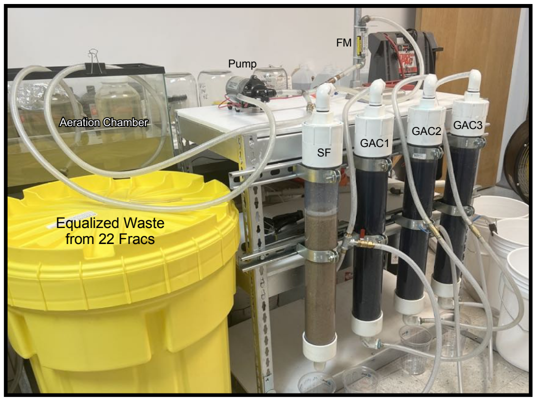

Figure 2: Pilot Plant Setup

Discussion & Results

GAC Run 1

Run 1 was conducted at a flowrate of 0.0277 gpm and carbon contact time of 20 minutes. Clarified wastewater was introduced into the aeration chamber (Figure 3). A significant finding was that 27.97% of PFAS was removed by aeration. Lab VOC analytes removed by aeration were 46.17%. Off-gas VOC emissions during aeration were measured with a MultiRae PID (10.6 e.v. lamp) with a chlorine sensor - 3.5 ppm Photo-ionization detector (PID) and 1 ppm chlorine. The average correction factor for VOC analytes (reported by method SW846 8260D GC/MS) with this meter is 0.56 or approximately 1.2 ppm. The total lab reported VOC was 1.46 mg/l (Table 9). Considerable foam was generated during aeration (Figure 4). To prevent the need for foam harvesting, the aeration rate was controlled at 6 scfh.

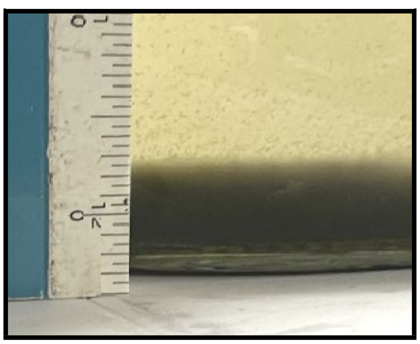
Figure 3: Solids Removed by Clarification

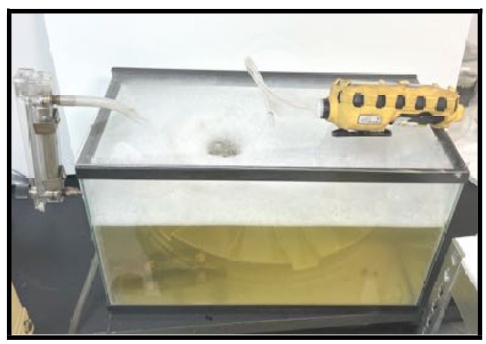
Figure 4: Non-Harvested Foam & Off-Gas Measurement by MultiRae PID with Chlorine Sensor

The first GAC column removed all the following short chain PFAS analytes below laboratory detection limits; PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS, 4:2 FTS, GenX, PFMBA, 3:3 FTCA, and PFMPA were removed.

The long-chain PFAS analytes (PFHpS, 8:2 FTS, and 5:3 FTCA) were also removed by the first GAC column. Only PFOS remained after the 3rd GAC column. Each GAC column removed a reduced amount of PFOS; first column - 99.84%, second column - 81.38%, and 12.58% by the 3rd column. A final concentration of 139 ng/l remained for an overall PFAS removal efficiency of 99.993% through the complete treatment train (Table 4).

Total removal efficiencies for VOCs were 95.05%, COD 99.56%, TOC 96.44%, Oil & Grease 92.86%, and TSS 100% (Table 5). When either lab COD or TOC concentrations are less than 10 mg/l, PFAS concentrations approach EPA's proposed treatment goals.

GAC Run 2

Run 2 was at twice the flowrate (0.0555 gpm) and a carbon contact time of 10 minutes. Foam was removed by the first GAC column (Figure 5). This test was initiated with mixed wastewater from the 30-gallon overpack that introduced suspended solids into the aeration chamber and increased loadings on the sand filter (Figure 6). This produced a higher raw wastewater concentration of PFAS due to desorption of soluble PFAS from suspended solids - 2,647,815 ng/l. An estimated 577,625 ng/l PFAS were likely desorbed from the increased suspended solids loading.

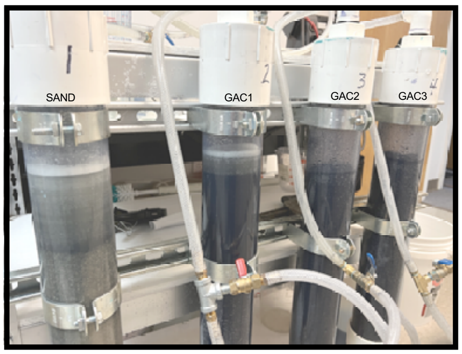

Figure 5: PFAS Foam Removed by 1st GAC Column

Figure 6: Increased Solids Loading Removed by Sand Filter

Two analytes remained after the 3rd GAC column, PFOS at 386 ng/l, and 6:2 FTS at 134 ng/l. Short chain PFAS analytes removed below detection limits by the first GAC column were PFBA, PFPeA, PFHxA, PFHpA, PFBS, PFPeS, 4:2 FTS, GenX, PFMBA, 3:3 FTCA, and PFMPA. Long chain analytes removed by the first column were PFOA, PFNA, PFDA, PFHpS, PFOSA, NEtFOSE, 5:3 FTCA, and PFDS. A final concentration of 520 ng/l or 386 ng/l PFOS (of the proposed regulated PFAS analytes) remained for an overall PFAS removal efficiency of 99.985% (Table 7). A higher filter backpressure of 5 psi was observed due to the additional TSS loadings on the sand and GAC filters.

Run 2 had higher General Chemistry values across the board except for Total VOCs which were about the same as Run 1; +78.93% Oil & Grease, +78.005% TSS, +15.67% COD, and +31.05% TOC, that resulted in slightly lower treatment efficiencies (Tables 7 & 9). If clarified raw wastewater had been used in Run 2, the total raw PFAS concentration would have been 21.82% less and it is likely that similar overall treatment efficiencies to Run 1 would have been achieved at twice the flowrate and half the carbon contact time (10 min).

Optional PAC Treatability Test

Mixed raw waste with suspended solids (Figure 7) was dosed with 1,000 mg/l PAC, aerated for 1 hour at 6 sdfh, and allowed to settle for 48 hours (Figure 8) to see if a synergistic removal of particulate and solution phase PFAS could be achieved. The overall PFAS removal was 34.5% (Table 8) with an estimated 28% removed by aeration. Note that TOC and COD final clarified concentrations were approximately 30 to 90 times higher respectively, than 3rd GAC column effluent concentrations for the same analytes. Consequently, an elevated concentration of PFAS remained in the clarified effluent. Coagulation with alum or other polymers should be investigated to determine if PAC treatment would perform better at a reduced pH.[12]

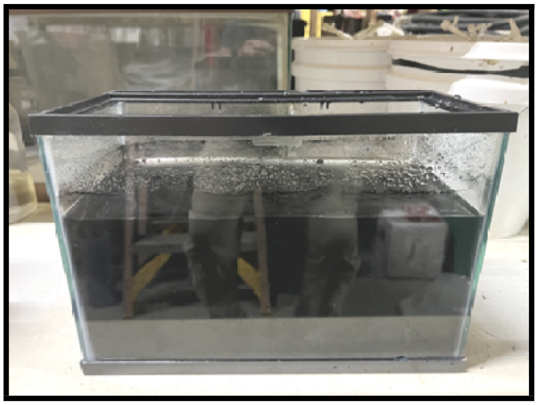

Figure 7: 1,000 mg/l PAC Treatment after 1 hr aeration @ 6 scfh

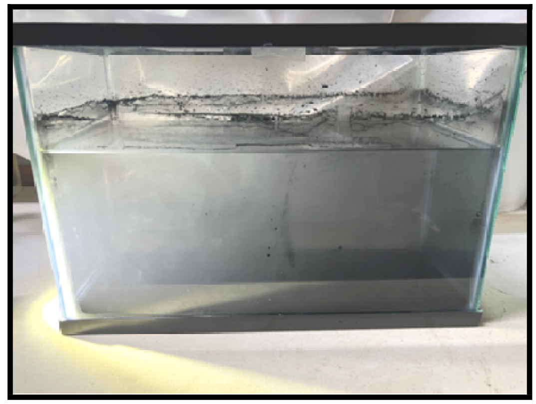

Figure 8: Post 48-Hour Clarification after 1,000 mg/l PAC Treatment

FIELD COD METER PFAS CORRELATIONS

PFAS concentrations in landfill leachates have significant correlations with TOC, alkalinity, ammonia, and COD.[13] Remtech set out to determine if similar PFAS laboratory and field meter COD correlations could be established for the chemical plant fire wastewater matrix. AFFF foam is manufactured by combining organic solvents, hydrocarbon surfactants, fluorosurfactants, polymers and other additives which are analytically detectible by COD.

COD data correlation curves with a field COD meter resulted in an acceptable R^2 value of 0.9987 (Figure 9). PFAS versus field COD meter correlations resulted in a R^2 values ranging from 0.9992 to 1.0 (Figures 10 & 11). Correlations with higher COD values resulted in a slightly lower R^2 value of 0.965 (Figure 12). Field analysis with field COD meters has the potential to reduce PFAS lab costs by identifying trends that suggest required lab PFAS treatment efficiencies have been reached when field meter COD values approach 0.0 mg/l.

Typical turnaround times for PFAS lab analysis may be 15 days for some labs. Shorter turnarounds can increase unit charges by 1.5 to 2 times. For 5-day rush turnarounds, estimated lab costs (prices may vary significantly between labs) are presented below:

- EPA PFAS Method 533 - $600/sample
- EPA PFAS Method 1633 - $700/sample
- For VOC, Oil and Grease, TSS, COD, and TOC - $217.80/sample (for all 5 parameters)

Additional parameters that may need to be evaluated for certain matrices include alkalinity, heavy metals, pesticides, herbicides, and organochlorines.

When lab COD or TOC values for waste streams on this project were less than 10 mg/l after GAC filtration, PFAS concentrations were in the range of 4 to 100 ng/l. Correlation curves need to be prepared for each waste stream to determine when field COD meters can be used to predict total PFAS analyte concentrations.

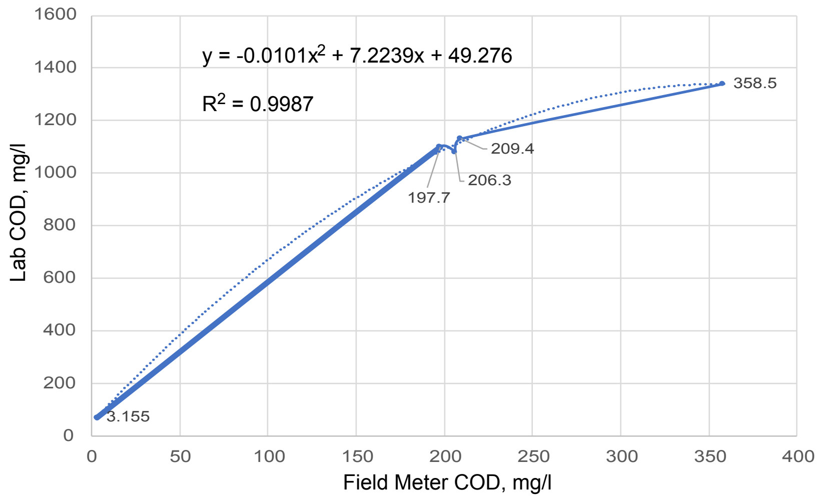

Figure 9: Field COD Meter vs Lab COD, mg/l

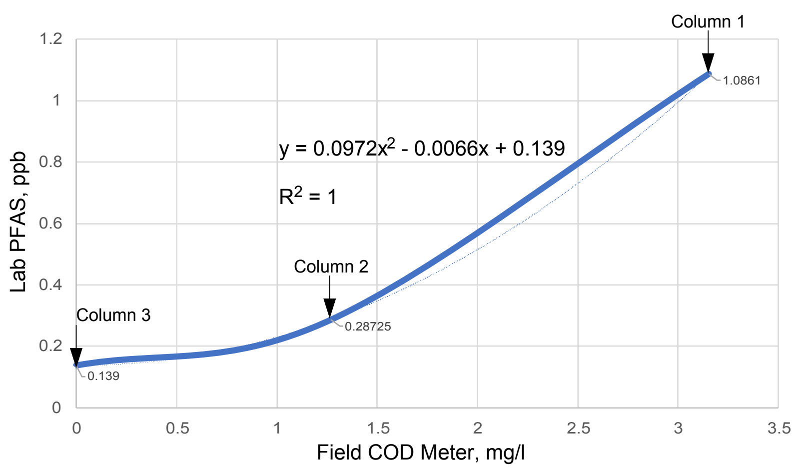

Figure 10: Field COD Meter vs Lab PFAS, ppb

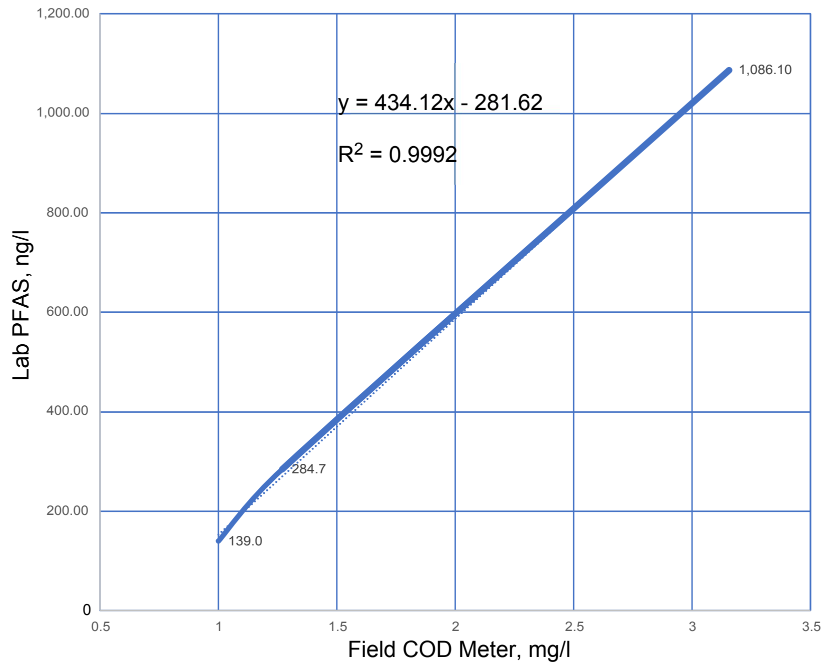

Figure 11: Field COD Meter vs Lab PFAS, ng/l

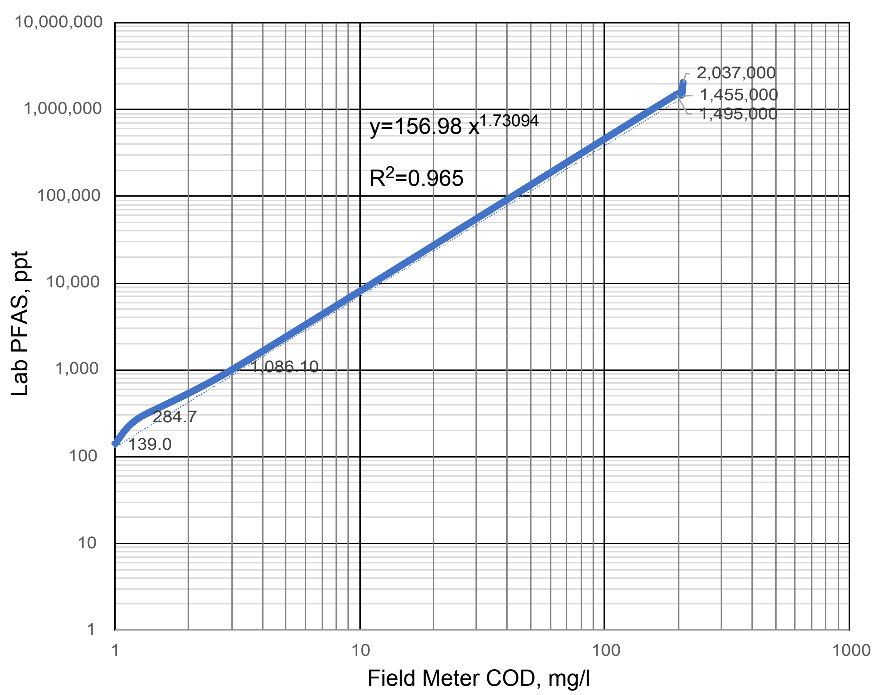

Figure 12: Field COD Meter vs Lab PFAS, ppt

TREATMENT SYSTEM DESIGN

Carbon Column Design Criteria

Table 3 displays the mass loading, reactor volumes, and flowrates for pilot Runs 1 & 2. Scaling up to a flowrate of 35 gallons for Run 1, an estimated 2,448 lbs of GAC are required for each full-scale carbon filter or a total of 7,344 pounds for all three GAC filters. When the flowrate is doubled in Run 2, an estimated 1,745 lbs of GAC was required for each full-scale filter or a total of 5,236 lbs for all three GAC filters at a flowrate of 50 gpm.

Surface loading rates for the two runs are summarized below:

- Pilot carbon column area = ((3.14 x 9)/4)/144 in^2 = 0.049 sf
- Run 1; Surface Loading Rate = 0.0277/0.049 = 0.565 gpm/sf @ 20 min contact time
- Run 2; Surface Loading Rate = 0.0555/0.049 = 1.133 gpm/sf @ 10 min contact time

GAC pressurized filter design criteria for much lower PFAS feed concentrations suggest surface loading rates ranging from 2 to 10 gpm/sf for treatment plant flowrates ranging from 1 - 12 MGD and empty bed contact time ranging from 10 to 20 minutes.[7,14] GAC surface loading rates for the treatment of PFAS contaminated fire runoff water for this matrix appears to be in the range of 0.56 to 1.13 gpm/sf with an untreated PFAS concentration ranging from 2 to 2.6 mg/l if clarification, aeration, and sand filtration is provided upstream (Table 10).

Suitable activated carbons show incipient breakthrough for PFOS at 30,000 to 40,000 Bed Volumes (BV) and for PFOA at 20,000 to 30,000 BV. GAC absorbers are effective and feasible considering operational and economic factors so long as a specific throughput of at least 15,000 BV can be achieved.[15,16] Actual BVs prior to media changeout for this highly contaminated PFAS matrix is unknown.

Using 3 carbon columns that contain 2,000 lbs of carbon with dimensions of 4 ft diameter and 6 ft tall, the BV would be 7,328 gallons for each filter (Figure 14). If 15,000 to 40,000 BV would result in PFAS breakthrough, then the volume of water treated prior to media changeout could be between 109,920 to 293,120 gallons. With 440,000 gallons to be treated, one to two media changeouts may be required. Actual BVs needs to be field verified to determine media changeouts.

Sand Filter Design

For Runs 1 & 2; approximately 7,266 lbs and 5,180 pounds of sand were respectively required. An average of 6,203 lbs of sand was selected to be placed in one of the 2,000 lb carbon reactors. Back pressures near 10 psi may require filter back-washing.

Aeration Chamber Design

Using a 21,000-gallon frac tank for batch aeration for 1 hour operating at 18,000 gallons with Remtech's *Magnetic Aeration System* - installed through a 20" manhole[17], the non-harvesting foam aeration rate is calculated below:

- 6 scfh/60 - 0.1 cfm, 40-micron diffusers, volume of wastewater treated = 5 gallons (reactor volumes including sample volumes removed for lab testing)
- 0.1 cfm/5 gal = X/18,000 gal = 360 cfm. Aeration/mixing requirements demonstrated by Remtech on previous projects - 60 to 120 cfm for each frac tank. 120 cfm was selected

Actual aeration rates to produce non-harvesting foam generation rates needs to be field verified.

Vapor Off Gas Mist Treatment Design (optional, not currently regulated)

- 579,126 ng/l (579.13 ug/l) of PFAS were removed in Run 1 and 1,456 ug/l VOCs were removed in Run 2 yielding a total of 2,035 ug/l of volatiles removed from 5 gallons of wastewater
- 394.5 lbs of volatiles need to be removed from 440,000 gallons of wastewater
- Assume that 1 pound carbon removes 0.4 lbs of VOCs or 986.2 pounds of carbon required
- Selected three (3) 300 lb carbon vapor absorbers operating at 150 cfm
- Vapor off-gas carbon requirements and media change outs needs to be field verified.

FULL-SCALE MOBILE TREATMENT TRAIN DESIGN

Diaphragm pumps with 25 ft suction lifts were selected to remove wastewater from 22 frac tanks from the top manholes with adjustable depth suction hoses with inlet screens. Withdrawing wastewater from mid- depths will leave floating and settled solids in each tank. Wastewater is then pumped to a 21,000 frac tank for settling, then pumped to another frac tank with Remtech's *Magnetic Aeration System* for pulsed aeration for 1 hour at 120 scfm (Figure 13).

After settling and aeration, wastewater is pumped through the mobile treatment trailer with sand and tri-GAC filters. Initial flowrates to be increased from approximately 5 gpm with PFAS removal efficiencies demonstrated as flowrates are increased.

Field COD vs Lab correlation curves can be used as predictive final lab PFAS concentrations to minimize lab analytical costs. Additional Frac holding tanks may be used to hold treated water until discharge limits are verified by lab analysis. Backwash media filter water is pumped to a 9,000-gallon mini-frac settling tank with clarified water directed back to the initial 21,000 gallon settling fractank.

Spent GAC media is removed and sent for regeneration and reuse (which is still allowed by EPA at the time of this paper and thermal recycling is included in the purchase of GAC). Spent sand filter and solids from the 22 fracs will be removed by vacuum truck, dewatered, tested and disposed of at an approved disposal facility.

A schematic of the full-scale system is presented in Figures 13 & 14. The estimated cost of this system for one month of operation is $450,000 plus disposal of remaining solids in frac tanks. Note that 50% of estimated costs are associated with labor intensive efforts to operate multiple pumps and manifolds required to remove blended wastewater from 22 frac tanks that is transferred to the initial clarification frac tank.

SUMMARY

Remtech has demonstrated that this type of mobile treatment system is effective in removing very high concentrations of short and long chain PFAS analytes using a combination treatment train consisting of screening, sedimentation, non-harvesting foam aeration, sand filtration, and tri-GAC filtration using General Carbon's 12 x 40PF PFAS carbon.

PFAS expensive laboratory costs can be reduced by using a field COD test meter by developing correlation curves between laboratory COD and PFAS data for each specific waste stream.

This same mobile treatment process can be used for landfill leachates, wastewater, drinking water, and other more dilute PFAS waste streams. Pilot/bench scale tests are required to determine appropriate carbon mass, flowrate loadings, carbon contact times, aeration times, and sand filter loading rates for each waste stream to meet discharge limits.

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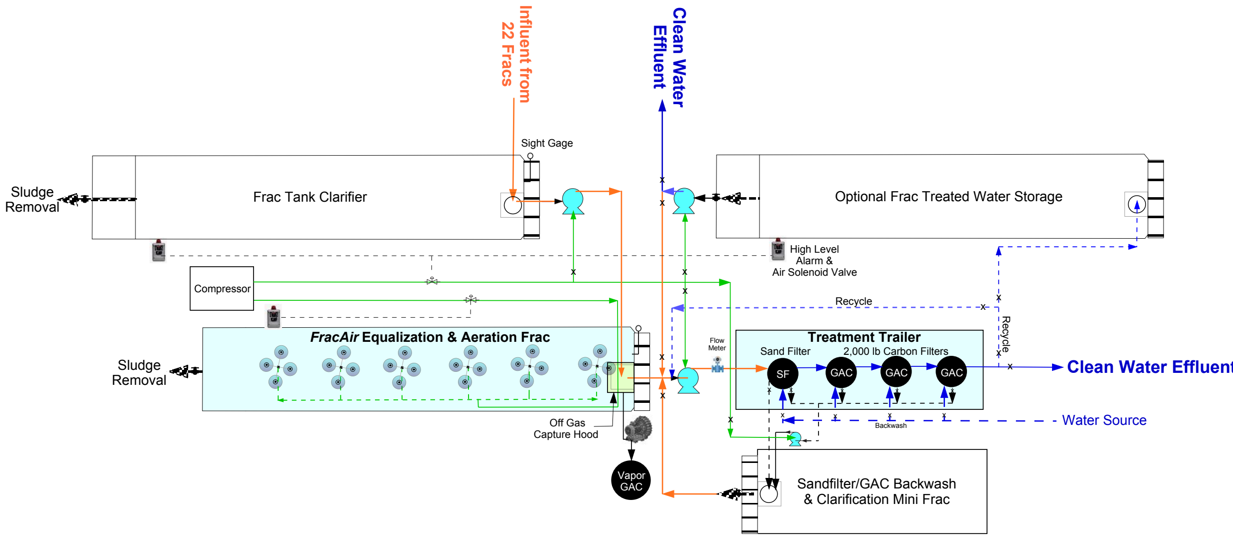

Figure 13: Mobile PFAS Treatment System

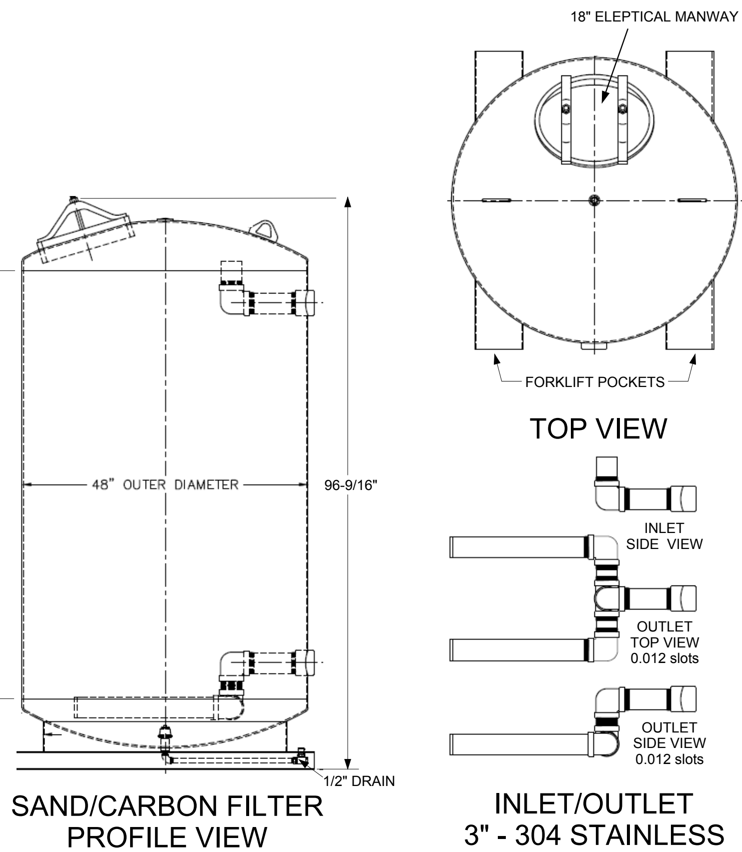

Figure 14: Sand/GAC Filter Detail

REFERENCES

1. Cole, Keith, Senior Managing Consultant, Ramboll Americas Engineering Solutions, Inc., *Sample Collection and Laboratory Analysis Reporting*, 2023.

2. Eurofins Environmental Testing, Savannah, GA, 2023

3. Ryckman, Mark, Principal Engineer, Remtech Engineers, *Pilot Plant Design, Testing, and Full-Scale Design*, 2023.

4. AWWA, *Drinking Water Treatment for PFAS Selection Guide - Technical Support on Per- and polyfluoroalkyl Substances Policy*, 2020

5. USEPA, Office of Water (4303T), Office of Science and Technology Engineering and Analysis Division, Washington, DC, EPA 821-D-23-001, *4th Draft Method 1633* Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS*, July 2023.

6. Ryckman, M.D., *Emergency Response to a Major Agricultural Chemical Warehouse Fire*, Proceedings of the 36th, Industrial Waste Conference, Purdue University, May 12, 13, and 14, 1981., https://www.remtech-eng.com/downloads/remtech-environmental-publications.html

7. Black and Veatch Project No. 409850, *WITAF 56 Technical Memorandum PFAS National Cost Model Report,* prepared for the American Water Works Association, March 7, 2023.

8. Smith, Sanne J., et. al, *Pilot-Scale Continuous Foam Fractionation for the Removal of Per and Polyfluoroalkyl Substances (PFAS) from Landfill Leachate*, Environmental Science and Technology, 2022, 2, 841-851.

9. Yuan, Shideng, et.al., *Contribution of Air-Water Interface in Removing PFAS from Drinking Water: Adsorption, Stability, Interaction and Machine Learning Studies*, Water Research, Volume 236, June 1, 2023, 119947.

10. Smith, Sanne J., et.al., *Foam Fractionation for Removal of Per- and Polyfluoroalkyl Substances: Towards Closing the Mass Balance*, Science of the Total Environment, 871 (2023) 162050.

11. Grimison, Charles, et., al, *The Efficacy of Soil Washing for the Remediation of Per and Poly-fluoroalkyl Substances (PFASs) in the Field*, Journal of Hazardous Materials, Volume 445, March 5, 2023, 130441.

12. Zhang, Zhiming, et. al. *Adsorption of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) by Aluminum-based Drinking Water Treatment Residuals,* Journal of Hazardous Materials Letters, 2021 100034.

13. Zang, Hekai, et., al., *Relationships Between Per- and Polyfluoroalkyl Substances (PFAS) and Physical-Chemical Parameters in Aqueous Landfill Samples*, Chemosphere, Volume 329, July 2023, 138541.

14. Newton, Jim, *Introduction to PFAS D175/D175*, PDHonline.com, PE Continuing Education Course, 2023

15. McMnamara, James D, et., al., *Comparison of Activated Carbons for Removal of Perfluorinated Compounds from Drinking Water*, https://doi.org/10.5942/jawwa.2018.110.0003.

16. Riegel, Marcel, et., al., *Sorptive Removal of Short-chain Perfluoroalkyl Substances (PFAS) during Drinking Water Treatment using Activated Carbon and Anion Exchanger*, Environmental Sciences Europe (2023) 35:12, https://doi.org/10.1186/s12302-023-00716-5.

17. Remtech's FracTank Mobile Magnetic Aerations System, *https://www.remtech-eng.com/store-/frac-tank-magnetic-aeration-system-frac-tank-temporary-wastewater-treatment-system-.html., 2023.*

18. Morrison, Anthony L*., Impact of Salinity and Temperature on Removal of PFAS Species from Water by Aeration in the Absence of Additional Surfactants: A Novel Application of Green Chemistry Using Adsorptive Bubble Fractionation,* Industrial & Engineering Chemistry Research, 2023, 62, 5635−5645

19. Nguyen, Thi Minh Hong, et. al., *Influences of Chemical Properties, Soil Properties, and Solution pH on Soil−Water Partitioning Coefficients of Per- and Polyfluoroalkyl Substances (PFASs)*, Environmental Science & Technology, 2020, 54, 15883-15892.

20. Krogerstrom, Axel, *Removal of per- and Polyfluoroalkyl Substances (PFAS) from Contaminated Leachate using Aeration Foam Fractionation*, Department of Aquatic Sciences and Assessments, Swedish University of Agricultural Sciences (SLU) UPTEC 21020. ISSN 1401-5765. Digitally published in DIVA, 2021 at the Department of Earth Sciences, Geotryckeriet, Uppsala University, Uppsala.

21. USEPA, *Proposed PFAS National Primary Drinking Water Regulation*, March 29, 2023.

22. AECOM, *Evaluation of PFAS in Influent, Effluent, and Residuals of Wastewater Treatment Plants (WWTPS) in Michigan*, Proj. No. 60588767, Prepared in association with Michigan Department of Environment, Great Lakes, and Energy, April 2021.

23. Realtech BOD/COD BP200-meter, Water and Wastewater, COD Range 0 - 700 mg/l.

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Table 1a: Initial Raw Frac Tank PFAS Testing

Analyte, ng/l	Frac 1	Frac 1 Dup	Frac 4	Frac 5	Frac 9	Frac 11	Frac 15	Frac 21	Avg	Raw Equalized Run 1 Clarified
PFBA	**11,400**	ND	**27,700**	<60,000	**112**	**18,400**	<24,000	**55,000**	22,522	33,500
PFPeA	**16,800**	**33,200**	**33,800**	<12,300	**692**	**36,200**	<4 900	**30,600**	25,215	16,500
PFHxA	**46,400**	**99,100**	**79,300**	<14,500	**786**	**89,800**	**89,800**	**91,100**	70,898	43,400
PFHpA	**12,600**	**16,000**	**28,900**	**122,000**	**328**	**17,400**	**18,800**	**14,800**	28,854	9,950
PFOA	**33,700**	**45,000**	**75,900**	**214,000**	**589**	**46,000**	**64,200**	**38,700**	64,761	31,100
PFNA	**81.7**	**800**	**218**	**762**	**36.8**	**338**	**747**	**956**	492	<600
PFDA	**72.2**	**557**	**400**	**400**	**23.6**	**230**	**263**	**504**	306	<800
PFBS	**54,800**	**53,600**	**104,000**	**4,0**	**212**	**56,000**	**40,600**	**32,000**	48,745	89,900
FFPeS	**66,200**	**83,500**	**121,000**	**91,300**	**331**	**71,800**	**126,000**	**47,100**	75,904	66,400
PFHxS	**324,000**	**149,000**	**708,000**	**2,200,000**	**3,500**	**426,000**	**589,000**	**316,000**	589,438	367,000
PFHpS	**27,900**	**64,700**	**70,700**	**179,000**	**3,100**	**61,000**	**66,600**	**59,600**	66,575	21,200
PFOS	**1,860,000**	**3,990,000**	**2,950,000**	**4,680.00**	**236,000**	**3,180,000**	**2,950,000**	**3,750,000**	2,365,085	933,000
PFNS	**646**	**790**	**227**	**3,110**	**97.3**	**540**	<185	**668**	868	<475
4:2FTS	**36.3**	**36.3**	<120	<6 000	**2.02**	**219**	<2,400	**205**	100	<2,230
6:2 FTS	**17400**	**796,000**	**327,000**	**5,610,000**	**7,370**	**402,000**	**1,130,000**	**726,000**	1,126,971	444,000
8:2 FTS	**1,540**	**20,900**	**10,700**	**295,000**	**960**	**10,600**	**19,200**	**29,000**	48,488	7,120
PFOSA	**1,040**	**9,170**	**2,770**	**6,520**	ND	**5,280**	**4,320**	**8290**	5,341	<225
NEtFOSE	**52.1**	**52.2**	<425	**910**	<4.25	<425	<425	<700	338	<875
GenX	ND	<7.50	<750	**37,000**	**51.7**	<750	<15,000	<750	18,526	7,120
PFMBA	ND	ND	ND	ND	ND	ND	ND	ND	ND	<675
3:3 FTCA	ND	ND	ND	ND	ND	ND	ND	ND	ND	<1200
5:3 FTCA	ND	ND	ND	ND	ND	ND	ND	ND	ND	<9,500
PFDS	**913**	**913**	ND	ND	<1.60	<160	ND	ND	913	<275
PFMPA PFMOPrA	ND	ND	ND	ND	ND	ND	ND	ND	ND	<725
PFAS Total	2,475,581	5,363,319	4,540,615	8,764,682	254,191	4,421,807	5,099,530	5,200,523	4,560,340	2,070,190

[shaded] EPA Proposed Regulated PFAS   ND - Non-Detect

Table 1b: Initial Frac Tank General Chemistry Testing

Parameter	Frac 1	Frac 4	Frac 5	Frac 21	Avg	Raw Run 1
Oil & Grease, mg/l	32.7	10.7	59.6	39	35	24
TSS, mg/l	<4.17	44	76	112	94	58
COD, mg/l	874	632	4,300	1,460	1,817	1,130
TOC, mg/l	172	228	1,150	444	499	262
Total Volatiles, ug/l	58,591	975	16,024	15,772	22,841	940

VOC Breakdown, ug/l	Frac 1	Frac 4	Frac 5	Frac 21	Avg	Raw Run 1
1,2,4-Trimethylbenzene	ND	2.42	16.7	59.7	26.3	ND
2-Butanone (MEK)	ND	17.6	1040	ND	528.8	ND
Acetone	ND	241	4440	2460	2380.3	ND
Benzene	ND	8.69	2.65	43.3	18.2	ND
Ethylbenzene	ND	1.67	2.42	ND	2.0	ND
Isopropylbenzene	ND	0.355	2.15	ND	1.3	ND
Methyl isobutyl ketone (MLBK)	ND	8.77	50.7	ND	29.7	ND
m-Xylene and p-Xylene	ND	4.8	9.74	ND	7.3	ND
N-Propylbenzene	ND	1.24	7.45	ND	4.3	ND
o-Xylene	ND	1.93	3.64	ND	2.8	ND
p-Isopropyltoluene	57,900	651	10,400	13,000	20487.8	917
Styrene	ND	8.41	4.54	ND	6.5	14
Toluene	ND	19.1	29.1	ND	24.1	8.53
Trichloroethene	321	0.346	1.47	ND	107.6	ND
Xylenes, Total	ND	6.73	13.4	184	68.0	ND
cis-1,2-Dichloroethene	185	ND	ND	25.4	105.2	ND
1,2-Dichloroethene	185	ND	ND	ND	185.0	ND
1,3,5-Trimethylbenzene	ND	0.6	ND	ND	0.6	ND
Total VOCs, ug/l	58,591	975	16,024	15,772	23,986	939.53

Table 2: Raw Equalized Wastewater PFAS Analytes from 22 Frac Tanks

Formula	Analyte	Clarified Equalized Raw Wastewater, ng/l
Short Chain, $C_4HF_70_2$	Perfluorobutanoic acid (PFBA)	**33,500**
Short Chain, $C_5HF_90_2$	Perfluoropentanoic acid (PFPeA)	**16,500**
Short Chain, PFHxA, $C_5F_{11}COOH$	Perfluorohexanoic acid (PFHxA)	**43,400**
Short Chain, degradation product of long chain with characteristics of long chain, $C_7HF_{13}0_2$	Perfluoroheptanoic acid (PFHpA)	**9,950**
Long Chain, $C_7F_{15}COO$, most toxic	Perfluorooctanoic acid (PFOA)	**31,100**
Long Chain, $C_9HF_{17}0_2$	Perfluorononanoic acid (PFNA)	<600
Long Chain, $C_{10}HF_{19}0_2$	Perfluorodecanoic acid (PFDA)	<800
Short Chain, $C_4F_9S0_3H$	Perfluorobutanesulfonic acid (PFBS)	**89,900**
Short Chain, $C_5HF_{11}0_3S$	Perfluoropentanesulfonic acid (PFPeS)	**66,400**
Long Chain, more bioconcentration, PFHxS $C_6F_{13}S0_3H$	Perfluorohexanesulfonic acid (PFHxS)	**367,000**
Long chain, $C_7F_{15}S0_3H$	Perfluoroheptanesulfonic acid (PFHpS)	**21,200**
Long chain, $C_8F_{17}S0_3H$, most toxic	Perfluorooctanesulfonic acid (PFOS)	**933,000**
Long chain, $C_9F_{19}S0_3H$	Perfluorononanesulfonic acid (PFNS)	<475
Short Chain, $C_4F_9CH_2CH_2S0_3H$	1 H, 1 H,2H,2H-Perfluorohexane sulfonic acid (4:2 FTS)	<2,230
Long Chain, $C_8H_5F_{12}0_3S$	1 H, 1 H,2H,2H-Perfluorooctane sulfonic acid (6:2 FTS)	**444,000**
Long Chain, $C_{10}H_5F_{17}0_3S$	1 H, 1 H,2H,2H-Perfluorodecane sulfonic acid (8:2 FTS)	**7,120**
Long Chain $C_8H_2F_{17}N0_2S$	Perfluorooctanesulfonamide (PFOSA)	<225
Long Chain, $C_{12}H_6F_{21}$ $N0_3S$	N-ethylperfluorooctane sulfonamidoethanol (NEtFOSE)	<875
Short Chain, $CF_3CF_2CF_2OCF(CF_3)COO-NH4+$	Hexafluoropropylene Oxide Dimer Acid (HFPO-DAGenX)	**7,120**
Short Chain, $C_5HF_90_3$	Perfluoro-4-methoxybutanoic acid (PFMBA)	<675
Short Chain, $C_6H_5F_70_2$	3-Perfluoropropylpropanoic acid (3:3 FTCA)	<1200
Long Chain, $C_{15}H_5F_{25}0_2$	3-Perfluoropentylpropanoic acid (5:3 FTCA)	<10,500
Long Chain, $C_{10}HF_{21}0_3S$	Perfluorodecanesulfonic acid (PFDS)	<275
Short Chain, $C_4HF_70_3$	Perfluoro-3-methoxypropanoic acid (PFMPA) or PFMOPrA	<725
	TOTAL PFAS, ng/l	**2,070,190**

EPA Proposed Regulated PFAS

Table 2a: pH Range of Frac Tank Composite Samples

5 Gal Sample Pail No.	Frac Composite Sample	pH
1	1 to 4	9.29
2	5 to 8	9.59
3	9 to 12	9.68
4	13 to 16	11.96
5	17 to19	4.25
6	20-22	7.69

Table 3: Filter Size and Media Charge

Media	Vol. Liters	Weight, gms
Sand	1.85	2,610.80
Sand+Water	2	N/A
GAC	2.1	879.2
GAC+Water	2.1	N/A

N/A Water added to reach reactor volume

Table 4: Run 1 PFAS Results

Analyte, ng/l	Raw PFAS Clarified	Post Air Conc.	% Air Removal	Post Sand Conc.	Post GAC1 Conc.	% Removal GAC1	Post GAC2 Conc.	% Removal GAC2	Post GAC3 Conc.	% Removal GAC3	% Total System Removal
PFBA	33,500	36,800	-9.851	34,800	<170	100	<170	0	<170	0	100
PFPeA	16,500	22,500	-36.364	19,600	<61	100	<61	0	<61	0	100
PFHxA	43,400	42,600	1.843	50,600	<54	100	<54	0	<54	0	100
PFHpA	9,950	11,500	-15.58	11,200	<25	100	<25	0	<25	0	100
PFOA	31,100	32,500	-4.502	36,900	<34	100	105	N/A	<34	100	100
PFNA	<600	176	N/A	171	<24	100	41.52	N/A	<24	100	100
PFDA	<800	<32	N/A	<32	<32	N/A	<32	N/A	<32	0	100
PFBS	89,900	74,700	16.91	80,900	<13	100	<13	0	<13	0	100
PFPeS	66,400	57,400	13.554	58,500	<15	100	<15	0	<15	0	100
PFHxS	367,000	346,000	5.722	311,000	44.4	99.9857	20.7	53.3784	<13	100	100
PFHpS	21,200	26,700	-25.943	26,600	<30	100	<30	0	<30	0	100
PFOS	933,000	522,000	44.051	529,000	854	99.839	159	81.382	139	12.58	99.9851
PFNS	<475	<19	N/A	<19	<19	N/A	<19	N/A	<19	0	100
4:2 FTS	<2230	308	N/A	289	<89	100	<89	0	<89	0	100
6:2 FTS	444,000	301,000	32.207	351,000	166	99.953	<100	100	<100	0	100
8:2 FTS	7,120	5,950	16.433	7,880	<85	100	<85	0	<85	0	100
PFOSA	<225	1,360	N/A	1,180	21.7	98.161	<9	100	<9	0	100
NEtFOSE	<875	<35	N/A	<35	<35	N/A	<35	N/A	<35	0	100
HFPO-DA/GenX	7,120	9,570	-34.41	9,770	<25	100	<25	0	<25	0	100
PFMBA	<675	50	N/A	37	<29	100	<29	0	<29	0	100
3:3 FTCA	<1200	115	N/A	<48	<48	100	<48	0	<48	0	100
5:3 FTCA	<10500	659	N/A	673	<420	100	<420	0	<420	0	100
PFDS	<275	<11	N/A	<11	<11	100	<11	0	<11	0	100
PFMPA or PFMOPrA	<725	44	N/A	38	<29	100	<29	0	<29	0	100
PFAS Totals	2,070,190.00	1,491,932.00	27.9326	1,530,138.00	1,086	99.9290	326.22	69.9613	139	57.3907	99.9933

(shaded) EPA Proposed Regulated

Table 5: Run 1 General Chemistry Results

Analyte	Raw Clarified	Post Aeration Conc.	% Aeration Removal	Post Sand Conc.	% Post Sand Removal	Post GAC1 Conc.	% Post GAC1 Removal	Post GAC2 Conc.	GAC2 Removal	Post GAC3 Conc.	% Post GAC3 Removal	% Total System Removal
Oil & Grease (mg/l)	23.8	26	-9.244	24.6	5.38	0	100	2.6	N/A	1.7	34.62	92.8571
Total Suspended Solids (TSS) (mg/l)	57.5	53	7.826	17.4	67.17	4.8	72.414	12.2	-154.17	0	100	100
Chemical Oxygen Demand (COD) (mg/l)	1,130	1,080	4.425	1,100	-1.85	71.7	93.482	< 5	100	< 5	100	100
Total Organic Carbon (TOC) (mg/l)	262	391	-49.237	393	-0.51	28.5	92.748	6.8	76.14	8.36	-22.94	96.8092
Total VOCs (ug/l)	1,461	786.5	**46.167**	700.9	**10.88**	5.2	**99.258**	12.2	-134.62	72.3	-492.62	95.0513
pH	10.16	10.16		10.21		9.851		10.39		10.22		N/A

Table 6: Run 2 PFAS Results

Analyte, ng/l	Raw PFAS Clarified	Post Air & Sand Not Clarified	Post GAC1 Conc.	% GAC1 Removal	Post GAC2 Conc.	% GAC2 Removal	Post GAC3 Conc.	% GAC3 Removal	% System Removal
PFBA	33,500	95,700	<170	100	<170	0	<170	0	100
PFPeA	16,500	50,500	<61.0	100	<61.0	0	<61.0	0	100
PFHxA	43,400	52,000	<54.0	100	<54.0	0	<54.0	0	100
PFHpA	9,950	7,530	<25.0	100	<25.0	0	<25.0	0	100
PFOA	31,100	34,300	<34.0	100	<34.0	0	<34.0	0	100
PFNA	<600	682	<24.0	100	<24.0	0	<24.0	0	100
PFDA	<800	89	<32.0	100	<32.0	0	<32.0	0	100
PFBS	89,900	87,300	<13.0	100	<13.0	0	<13.0	0	100
PFPeS	66,400	74,900	<15.0	100	<15.0	0	<15.0	0	100
PFHxS	367,000	398,000	102	99.9744	29.7	70.8824	<13.0	100	100
PFHpS	21,200	19,100	<30.0	100.00	<30.0	0	<30.0	0	100
PFOS	933,000	1,270,000	3370	99.7350	676	79.9410	386	42.8990	99.9696
PFNS	<475	<19.0	<19.0	0.00	<19.0	0	<19.0	0	100
4:2 FTS	<2230	738	<89.0	100	<89.0	0	<89.0	0	100
6:2 FTS	444,000	506,000	373	99.9260	<100	100	134	**SR**	99.9735
8:2 FTS	7,120	19,400	233	98.7990	<85.0	100	<85.0	0	100
PFOSA	<225	3,830	<9.00	100	<9.00	0	<9.00	0	100
NEtFOSE	<875	36.3	<35.0	100	<35.0	0	<35.0	0	100
HFPO-DA/GenX	7,800	25,600	<25	100	<25.0	0	<9.0	0	100 100
PFMBA	<725	115	<27.0	100	<27.0	0	<27.0	0	100
3:3 FTCA	<1200	62.3	<48.0	100	<48.0	0	<48.0	0	100
5:3 FTCA	<10500	1,730	<420	100	<420	0	<420	0	100
PFDS	<275	93.6	<11.0	100	<11.0	0	<11.0	0	100
PFMPA or PFMOPrA	<675	109	<29.0	100	<29.0	0	<29.0	0	100
PFAS Totals	2,070,190	2,647,815	4,078	**99.8460**	705.7	**82.6950**	520	**26.3140**	99.9749

EPA Proposed Regulated PFAS (grey shading)

SR Near detection limit may explain positive PFAS result

Table 7: Run 2 General Chemistry Results

Analyte	Post Aeration Mixed	Post GAC1 Conc.	% Post GAC1 Removal	Post GAC2 Conc.	% Post GAC2 Removal	Post GAC3 Conc.	% Post GAC3 Removal	% Total System Removal
Oil & Grease (mg/l)	112	1.7	98.482	0	100	0	0	100
Total Suspended Solids (mg/l)	262	4.5	98.282	2.8	37.778	3.2	-14.286	98.77863
Chemical Oxygen Demand (mg/l)	1,340	93.1	93.052	15.1	83.781	< 5	100	100
Total Organic Carbon (TOC) (mg/l)	380	43.9	88.447	18.8	57.175	6.83	63.67	98.20263
Total VOCs (ug/l)	1,455.70	2.1	99.856	0.7	66.667	0	100	100
pH	10.2	10.16	N/A	10.04	N/A	9.71	N/A	N/A

N/A Not Applicable

Table 8: PAC PFAS Results

Analyte, ng/l	Raw PFAS Mixed	48 Hr PAC Clarified	% PAC Removal
PFBA	95,700	34,100	64.37
PFPeA	50,500	20,500	59.41
PFHxA	52,000	50,900	2.12
PFHpA	7,530	10,300	-36.7862
PFOA	34,300	36,100	-5.2478
PFNA	682	20	N/A
PFDA	89	<32.0	SR
PFBS	87,300	81,000	7.2165
PFPeS	74,900	63,000	15.8879
PFHxS	398,000	294,000	26.1307
PFHpS	19,100	21,900	-14.6597
PFOS	1,270,000	470,000	62.9921
PFNS	<19.0	494	N/A
4:2 FTS	738	<89.0	SR
6:2 FTS	506,000	260,000	48.6166
8:2 FTS	19,400	3,250	83.2474
PFOSA	3,830	718	N/A
NEtFOSE	36.3	<35.0	SR
HFPO-DA/GenX	25,600	9,610	62.4609
PFMBA	115	40.7	N/A
3:3 FTCA	62.3	<48.0	SR
5:3 FTCA	1,730	<420	SR
PFDS	93.6	<11.0	SR
PFMPA or PFMOPrA	109	37.7	N/A
PFAS Totals	2,647,815	1,355,971	48.7891

(Grey shading) EPA Proposed Regulated PFAS
N/A Measurable PFAS near detection limit
SR Some reduction posible due to reduced detection limit

Table 9: P AC General Chemistry

Analyte	Raw Mixed	48 hr Clarified	% Removed
Oil & Grease (mg/l)	112	8.1	92.77
Total Suspended Solids (TSS) (mg/l)	262	54.5	79.20
Chemical Oxygen Demand (COD) (mg/l)	1,340	891	33.51
Total Organic Carbon (TOC) (mg/l)	380	308	18.95
Total VOCs (ug/l)	1,455.70	692.2	52.45

Table 10: GAC Design Information

Run 1				**Design Flowrate 1 GAC column**			**3 GACs**
Volume	Specific Gravity	Each Column, cf	gpm	gpm	Each Column, cf	lbs GAC	lbs GAC
2.1 liters	26.12 lbs/cf	0.0742	0.0277	35	93.72	2,448.00	7,344.00
Run 2				**Design Flowrate 1 GAC column**			**lbs GAC**
2.1 liters	26.12 lbs/cf	0.0742	0.0555	50	66.82	1,745.00	5,236.00