ESTCP

FINAL REPORT

Ex Situ Thermal Treatment of PFAS-Impacted Soils

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ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
ADEC	Alaska Department of Environmental Conservation
AFB	Air Force Base
Brown	Brown University
COC	chain-of-custody
DOD	Department of Defense
EPA	US Environmental Protection Agency
ESI	electrospray ionization
EOF	extractable organofluorine
E-Stop	emergency stop
ft bgs	feet below ground surface
GAC	granular activated carbon
gpm	gallons per minute
HRMS	high resolution mass spectrometry
kVA	kilovolt amperes
kV	kilovolt
kW	kilowatt
kWh	kilowatt hour
LC-MS	liquid chromatography-mass spectrometry
LGAC	liquid-phase granular activated carbon HAL Health Advisory
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
MB	method blank
MRL	minimum reporting level
MS	matrix spike
MSD	matrix spike duplicate
m/z	mass to charge
NDFA	National Defense Authorization Acts
NELAP	National Environmental Laboratory Accreditation Program
ng/L	nanograms per liter
NS	not specified

OSHA	Occupational Safety and Health Administration
OTM-45	Other Test Method-45
Paragon	Paragon Professional Services, LLC
PCU	power control unit
PFAS	perfluoroalkyl and polyfluoroalkyl substances
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PIR	prediction interval of result
PLC	programmable logic controller
ppm	parts per million
ppt	parts per trillion
RPD	relative percent difference
RSL	risk screening level
RTD	resistance temperature detector
SOP	standard operating procedure
TCH	thermal conduction heating
TMP	temperature monitoring point
TOC	total organic carbon
TQ-S	tandem quadrupole mass spectrometer
TRS	TRS Group, Inc.
UHPLC	ultra-high performance liquid chromatograph
UPLC	ultra-performance liquid chromatograph
USAF	United States Air Force
USEPA	United States Environmental Protection Agency
VGAC	vapor-phase granular activated carbon
VR	vapor recovery
yd^3	cubic yards

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Kevin Thomas, AFCEC

Jennifer Wehrmann, AFCEC

Roy Willis, Eielson AFB Restoration Team Lead

ABSTRACT

INTRODUCTION AND OBJECTIVES

This report provides a summary of the thermal conduction heating (TCH) remediation performed by TRS Group, Inc. (TRS), in conjunction with Paragon Professional Services, LLC (Paragon) and Brown University (Brown) at Eielson Air Force Base (AFB), located near Fairbanks, Alaska (the Site). Using TRS's patented FlexHeater® Thermal Conduction Heating (TCH) technology, the removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from *ex situ* soil stockpiles was demonstrated.

TECHNOLOGY DESCRIPTION

During TCH application, the heater itself was raised to temperatures up to 900°C. The radiant heat from the FlexHeater® then heated the casing and the surrounding soil is then slowly heated by conduction. The PFAS-containing soil was heated to a minimum temperature of 350°C throughout the treatment volume. Soil vapor extraction (SVE) screens were installed in between the heater casings. The SVE screens were put under vacuum using a positive displacement blower. Recovered steam and soil vapors were then transported via stainless steel piping headers to a wet scrubber and a condenser and on to a vapor/liquid separator and heat exchanger. Condensate and non-condensable air were treated using activated charcoal filtration.

PERFORMANCE AND COST ASSESSMENT

Soil sampling performed before and after thermal treatment showed substantial reductions in PFAS, including PFOS and PFOA. The predominant PFAS, PFOS, experienced a 95.3% average percent reduction from thermal treatment. All soil samples collected post thermal treatment were below detection limits for PFOA. Post thermal treatment soil showed a PFOS concentrations average of 4.1 µg/kg, with the highest levels found at the top of the pile where the soil reached 350°C. Samples heated to 400°C were below Alaska Department of Environmental Conservation (ADEC) soil cleanup levels for PFOA and PFOS, 1.7 ug/kg and 3.0 ug/kg, respectively. The implementation cost of the technology was evaluated for soil volumes up to 15,000 cubic yards (yd^3). Treatment costs ranging from $550-800 per cubic yard are projected, with lower unit costs for large volumes. Site location (climate and mobilization distance) and local electricity costs were identified as the main cost drivers.

IMPLEMENTATION ISSUES

For future ex situ PFAS soil treatments, sufficient power availability and reliability are important considerations when considering implementation. If sufficient power is not available, additional electricity sources can be installed, however scheduling and funding evaluations should be performed to assess project feasibility.

Water source availability for the vapor and liquid treatment process equipment should be considered for implementation. Treated process water discharge and treated vapor emission requirements are also important implementation issues to consider to ensure the sampling methodology and process treatment equipment is sufficient to be in compliance with all regulatory requirements.

A working area sufficient for the ex situ soil treatment and process equipment will be required for implementation. Weather impacts during installation and system operations should also be considered, including winterization requirements and whether shelter for the equipment and ex situ cell are necessary.

The ultimate disposal requirements for PFAS impacted carbon that is generated from the vapor and liquid treatment system is a potential implementation issue. The identification of a viable source for PFAS impact carbon should be considered for implementations.

The planned use for soil after thermal treatment should be considered to ensure a plan is in place for necessary moisture, nutrient, and organics addition to allow reuse of the soil.

PUBLICATIONS

Multiple publications are being prepared. A public visitor day was arranged, and the results of the demonstration have been presented at technical conferences.

EXECUTIVE SUMMARY

INTRODUCTION

This report provides a summary of the thermal conduction heating (TCH) remediation performed by TRS Group, Inc. (TRS), in conjunction with Paragon Professional Services, LLC (Paragon) and Brown University (Brown) at Eielson Air Force Base (AFB), located near Fairbanks, Alaska (the Site). Using TRS's patented FlexHeater® Thermal Conduction Heating (TCH) technology, the removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from *ex situ* soil stockpiles was demonstrated.

OBJECTIVES

Primary objectives included:

- Evaluation of PFAS removal and fate – targeting 95% concentration reduction and achieving Alaska standards for PFOS and PFOA without accumulation of harmful by-products.
- Demonstration of the TCH technology and ability to achieve temperatures above 300ºC and average above 350ºC.
- Demonstrate effective vapor capture and treatment of both vapor and condensate to safe levels for discharge.
- Demonstration of an energy balance and the ability to predict energy demand for effective treatment.
- Gathering of cost data and scale-up cost analysis.

Additional quantitative and qualitative performance objectives were evaluated.

TECHNOLOGY DESCRIPTION

The FlexHeater® TCH process uses TRS' patented FlexHeater® to deliver energy to the designated treatment interval at easily controllable rates. During TCH application, the heater itself is raised to temperatures up to 900°C. The radiant heat from the FlexHeater® then heats the casing and the surrounding soil is then slowly heated by conduction. The PFAS- containing soil is heated to a minimum temperature of 350°C throughout the treatment volume. This is verified by measuring temperatures at the coolest locations farthest away from the heaters. The layout of the system is summarized in Figure ES1 below.

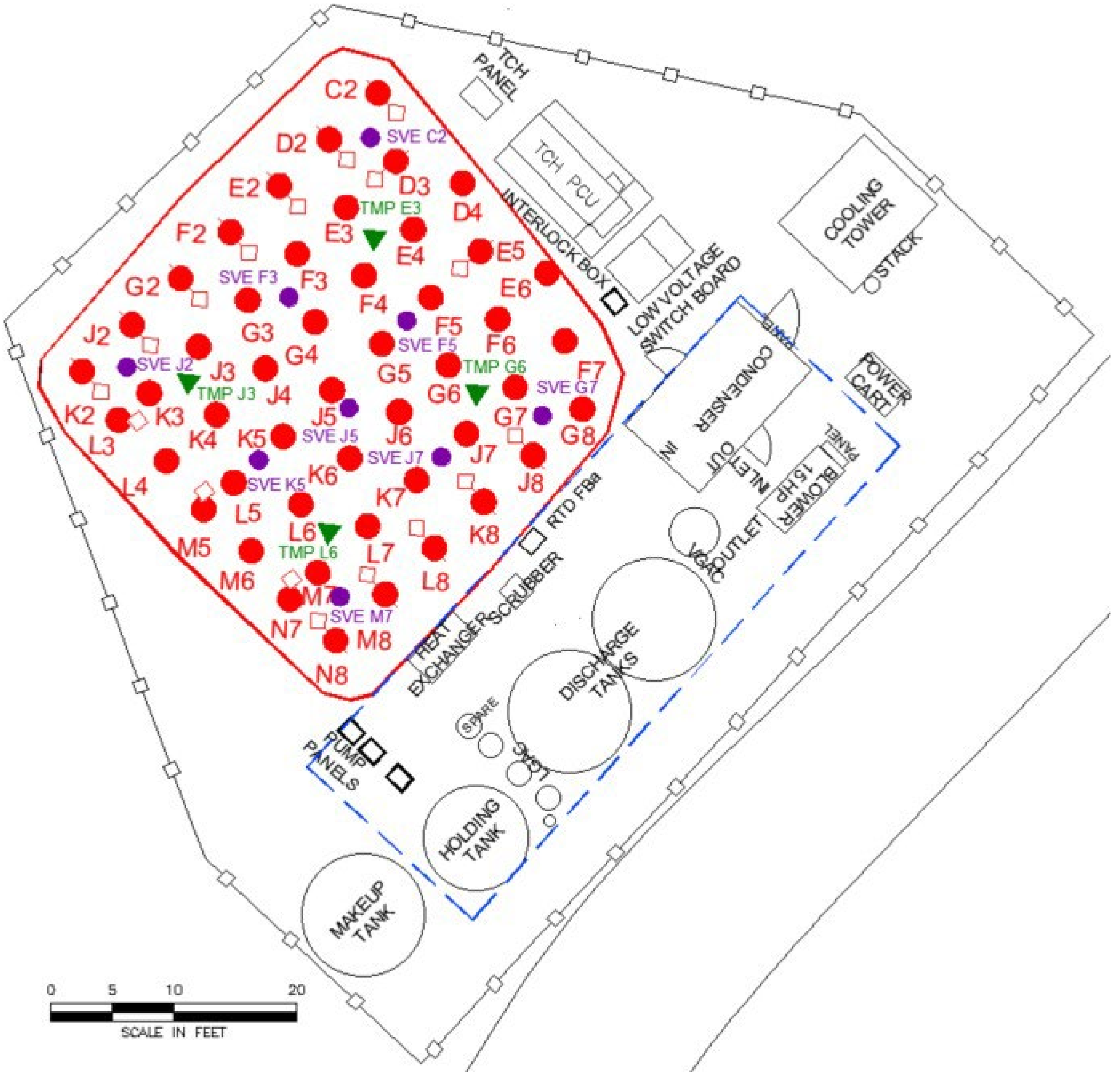


Figure ES-1. Site Layout with Heating Infrastructure.

The stockpile is 40 ft wide. TCH borings are shown as red dots.

In addition to the FlexHeater® well casings, soil vapor extraction (SVE) screens were installed adjacent to or in between the heater well casings (purple circles in Figure ES1). During the TCH application, the VR screens were under vacuum using a positive displacement blower. Recovered steam and soil vapors were then transported via stainless steel piping headers to the scrubber (Figure ES2). From the scrubber the vapors were transported to the condenser where the recovered mixture was passed through a vapor/liquid separator and heat exchanger. Any condensate generated following the heat exchange process was captured and conveyed for subsequent treatment and the extracted air was treated using the best applicable technology or methods, such as vapor-phase granular activated carbon (VGAC) or thermal oxidation. For this demonstration, VGAC was used.

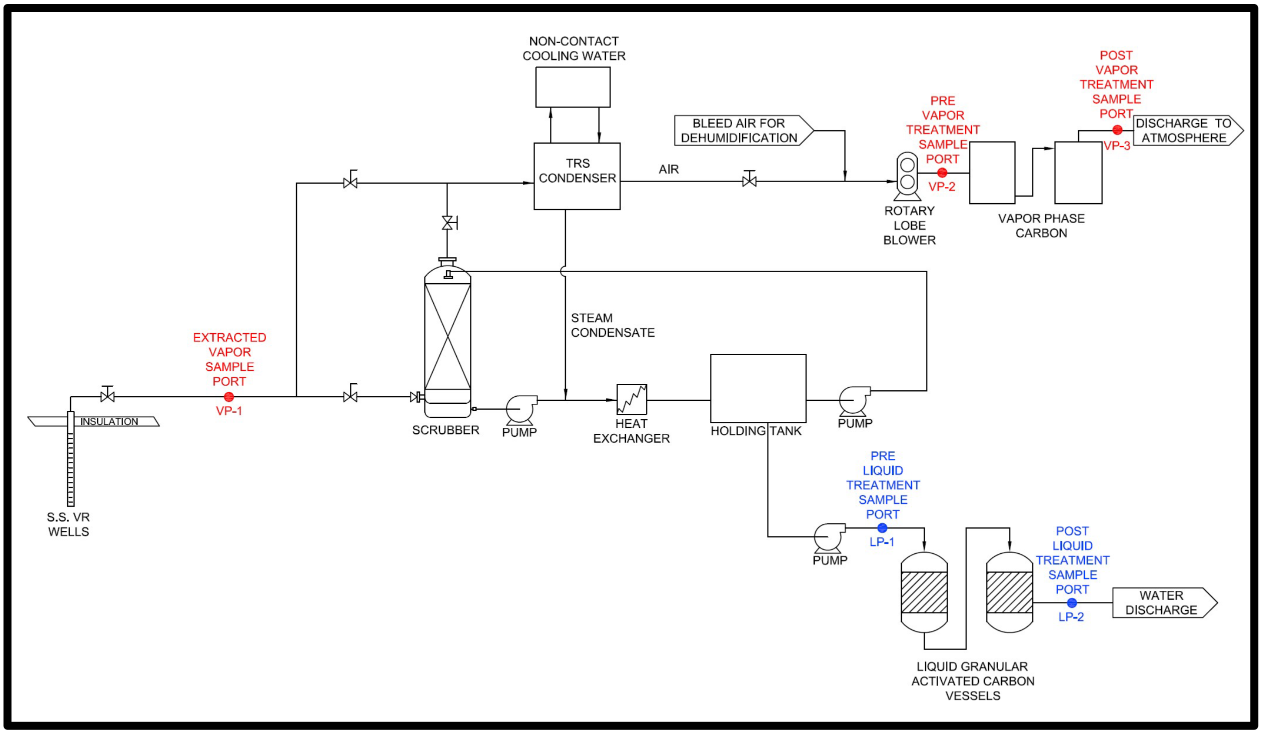


Figure ES-2. Process Flow Diagram of Thermal Treatment System.

Temperature monitoring points are shown as green triangles in Figure ES1. A total of 16 sensors were used to track heating progress.

PERFORMANCE ASSESSMENT

The heating and treatment progressed almost entirely as expected based on prior experience. The 48 heaters delivered approximately 80-120 kW of power to the heaters. A cumulative energy balance is shown in Figure ES3. Note that an average soil temperature of over 400°C was achieved – the coolest sensors reached 350°C at the time heating was turned off.

The energy used or the heating was within 5% of the modeled value, illustrating the ability to closely predict energy usage and utility costs. The energy used was equal to 775 kWh per cubic yard of soil, including heat lost through the surfaces of the relatively small and thin soil pile. Modeling shows that larger soil volumes with less significant heat loss can achieve the same level of treatment with 20-30% less energy.

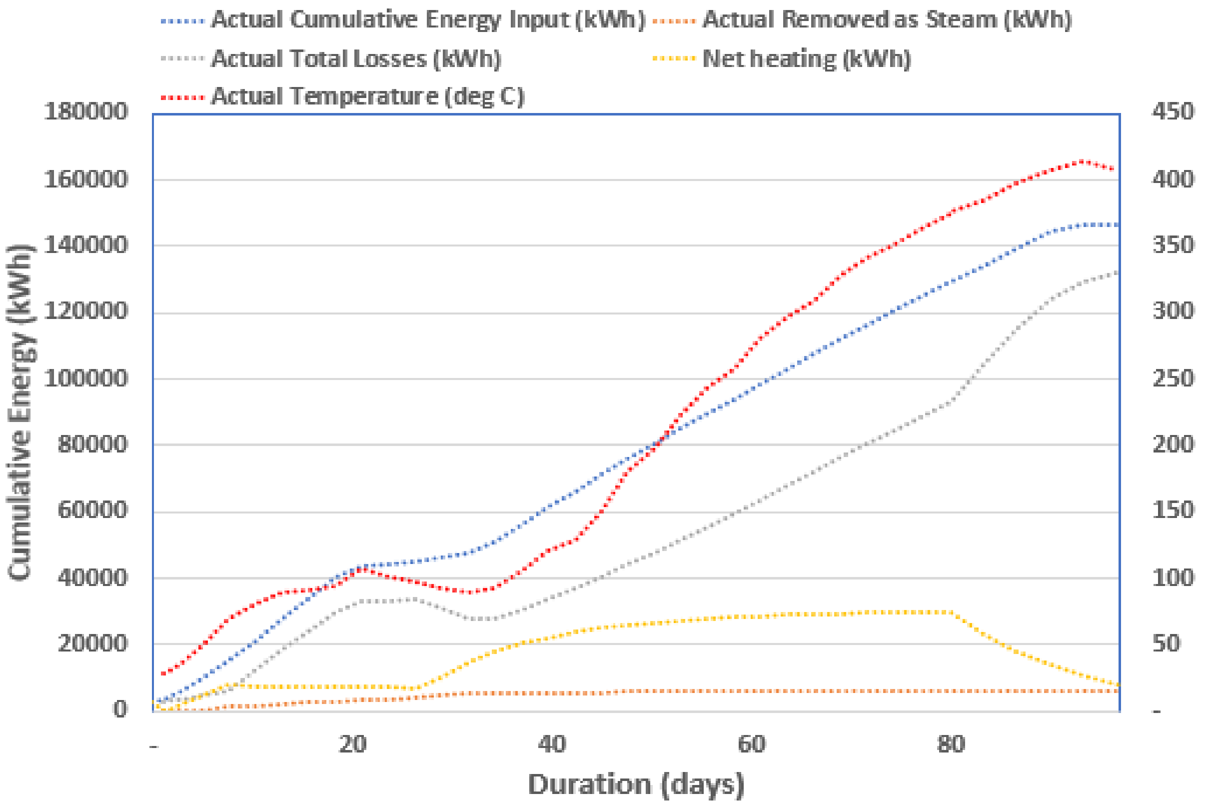


Figure ES-3. Energy Balance for the TCH Demonstration.

Analytic laboratory data collected for extracted vapor and condensate samples showed a peak in mass removal during the heating period and non-detect PFAS levels in treated water and air.

Laboratory analyses of soil sampling performed before and after thermal treatment showed reductions in PFAS, including PFOS and PFOA. All soil sample results collected post thermal treatment were below detection limits for PFOA. PFOS concentrations of 4.1 µg/kg was achieved as an average. All soils treated to 400°C or higher were non-detect for all targeted PFAS compounds.

COST ASSESSMENT

An analysis of scale-up costs for soil volumes up to 15,000 yd^3 was performed. Larger volumes have lower unit treatment costs. Figure ES4 shows the cost break-down for TCH treatment of a 15,000 yd^3 soil pile. The installation and operations costs are the largest items, with the electricity contributing 11% of the total cost. This percentage may be higher in states with higher power costs.

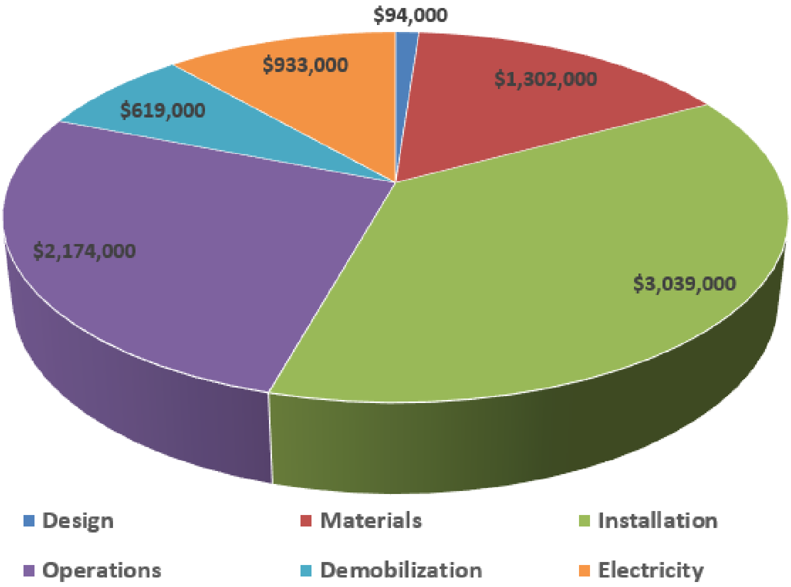


Figure ES-4. Modeled Scale-up Cost for TCH Treatment of a 15,000 yd^3 Stockpile.

The estimated cost, assuming treatment in moderate climate and a power cost of $0.08/kWh is approximately $8.2 million, equaling a unit cost of $540/yd^3. For smaller volumes, a treatment cost range of $550-800 was predicted.

IMPLEMENTATION ISSUES

Procurement delays and increased material prices due to COVID-19 supply chain disruptions posed challenges during the TCH implementation at Eielson AFB.

Power interruptions at Eielson AFB impacted the heating infrastructure, which required repairs before the system was fully operational. Following a 36-hour power outage, a back- up generator was rented and mobilized to the site to ensure that the system could remain operational if a future power interruption were to occur.

Extreme cold temperatures and snow required that winterization measures be installed on the system, which included a tent enclosing the vapor and liquid treatment system, circulating pumps, heat trace, and diesel-powered ambient heating system. The location of future PFAS thermal treatments should impact the design considerations to ensure the system can remain operational through all anticipated weather conditions.

Overall, this demonstration was successful and indicated that TCH is an effective option for treatment of PFAS-laden soil.

1.0 INTRODUCTION

This report provides a summary of the thermal conduction heating (TCH) remediation performed by TRS Group, Inc. (TRS), in conjunction with Paragon Professional Services, LLC (Paragon) and Brown University (Brown) at Eielson Air Force Base (AFB), located near Fairbanks, Alaska (the Site). Using TRS's patented FlexHeater®, the removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from *ex situ* soil stockpiles was demonstrated. The FlexHeater® TCH process is described further in **Section 4.0**.

This approach provided the United States Air Force (USAF) with an innovative technology that can be executed on-site at Eielson AFB and other installations to support the mission to protect human health and the environment. Success in Alaska has demonstrated success at other locations in the United States and internationally is possible.

1.1 BACKGROUND

PFAS are resistant to most biotic and abiotic degradation processes and therefore accumulate in the environment. Eielson AFB has approximately 130,000 yd^3 of potentially PFAS-impacted waste soils stockpiled and awaiting further characterization, treatment, and off-site transportation and disposal. The Department of Defense (DOD) is supporting research and demonstration projects to identify solutions to address PFAS-impacted soils at military bases throughout the United States.

Alternative technologies for treatment of PFAS-impacted soil are largely experimental. Soil washing has been shown to effectively treat the coarser fractions, but leaves large quantities of fines untreated. Thermal destruction by incineration is an option, but temperatures above 600 degrees Celsius (°C) are typically necessary to initiate PFAS mineralization. Thermal destruction of PFAS also produces hydrofluoric acid which quickly corrodes process piping and vapor treatment equipment. As an alternate approach, PFAS can be removed from soil at temperatures around 350°C by heating the stockpiles over a period of months, allowing time for the PFAS to vaporize and be extracted. Removal requires lower treatment temperatures and less energy usage than incineration and does not aggressively destroy PFAS, which may generate hydrofluoric acid. The hot effluents produced during thermal treatment can be neutralized and condensed in a scrubber. The scrubber water and vapors can be treated using granular activated carbon (GAC), other media, or a destructive process. Excavation and off-site transportation costs would also not be incurred.

1.2 OBJECTIVE OF THE DEMONSTRATION

The field demonstration was conducted in an approximately 134 yd^3 soil stockpile to demonstrate that FlexHeater® TCH can provide greater than 95 percent reduction of PFAS concentrations from soil and reduce concentrations to below ADEC soil cleanup levels of 1.7 ug/kg PFOA and 3.0 ug/kg PFOS. The soil was heated to temperatures between 350 and 400°C to dissociate PFAS from the soil and temperatures above 350°C were targeted for a minimum of 10 days. Effluent vapors and process water were treated on-site using GAC. Volatilized PFAS were concentrated into a low volume solution with the scrubber prior to treatment with GAC which significantly reduced the amount of carbon needed for vapor and liquid treatment. The demonstration included an evaluation of PFAS soil removal efficiency and extracted vapor and condensate treatment efficiency.

All field activities were conducted in accordance with the Site Health and Safety Plan. Detailed performance objectives are presented in Section 3.0.

1.3 REGULATORY DRIVERS

Both the Alaska Department of Environmental Conservation (ADEC) and the United States Environmental Protection Agency (USEPA) have established clean-up and/or screening levels for several, but not all, of the PFAS compounds being addressed as part of this project. In 2016, ADEC promulgated clean-up levels for perfluorooctanoic acid (PFOA) and perflouorooctane sulfonate (PFOS). In 2018, ADEC set action levels for six PFAS compounds, including PFOS and PFOA. In 2019, ADEC published a revised Technical Memorandum on Action Levels for PFAS that supersedes the 2018 action levels memorandum and aligns the action levels with EPA's Health Advisory (HAL) levels for PFOS and PFOA. EPA Action Levels serve as thresholds for determining when responsible parties need to provide water treatment or alternative water sources for impacted water supplies (ADEC, 2019). Proposed clean-up levels to PFAS substances in soil were on hold. **Table 1** presents the compound list and the established clean-up levels endorsed by ADEC and the USEPA.

The state of Alaska has adopted soil cleanup levels of 1.7 ug/kg PFOA, and 3.0 ug/kg PFOS, for protection of ground water. For protection of human health, recommended thresholds are 1.3 mg/kg for both PFOA and PFOS. No other PFAS are currently regulated by ADEC.

Table 1. ADEC and EPA Clean-Up Levels for PFAS in Soil

		ADEC Clean-Up Levels[1]		**EPA[2]**
Compound Name (Abbreviation)	**CAS Number**	**Human Health[3] (mg/kg)**	**Migration to Groundwater[4] (mg/kg)**	**RSL (mg/kg)**
Perfluorobutanoic acid (PFBA)	375-22-4	NS	NS	NS
Perfluoropentanoic acid (PFPeA)	2706-90-3	NS	NS	NS
Perfluorohexanoic acid (PFHxA)	307-24-4	NS	NS	NS
Perfluoroheptanoic Acid (PFHpA)	375-85-9	NS	NS	NS
Perfluorooctanoic Acid (PFOA)	335-67-1	1.6	0.0017	0.13
Perfluorononanoic Acid (PFNA)	375-95-1	NS	NS	NS
Perfluorodecanoic acid (PFDA)	335-76-2	NS	NS	NS
Perfluoroundecanoic acid (PFUnA)	2058-94-8	NS	NS	NS
Perfluorododecanoic acid (PFDoA)	307-55-1	NS	NS	NS
Perfluorotridecanoic acid (PFTriA)	72629-94-8	NS	NS	NS
Perfluorotetradecanoic acid (PFTreA)	376-06-7	NS	NS	NS
Perfluorobutane Sulfonic Acid (PFBS)	375-73-5	NS	NS	1.9

Table 1. ADEC and EPA Clean-Up Levels for PFAS in Soil (Continued)

		ADEC Clean-Up Levels[1]		EPA[2]
Compound Name (Abbreviation)	**CAS Number**	**Human Health[3] (mg/kg)**	**Migration to Groundwater[4] (mg/kg)**	**RSL (mg/kg)**
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	NS	NS	NS
Perfluorohexanesulfonic acid (PFHxs)	355-46-4	NS	NS	NS
Perfluoroheptanesulfonic acid (PFHpS)	375-92-8	NS	NS	NS
Perfluorooctanesulfonic Acid (PFOS)	1763-23-1	1.6	0.0030	0.13
Perfluorononanesulfonic acid (PFNS)	68259-12-1	NS	NS	NS
Perfluorodecanesulfonic acid (PFDS)	335-77-3	NS	NS	NS
Perfluorooctanesulfonamide (PFOSA)	754-91-6	NS	NS	NS
Fluorotelomer sulfonic acid 4:2 (FtS 4:2)	757124-72-4	NS	NS	NS
Fluorotelomer sulfonic acid 6:2 (FtS 6:2)	27619-97-2	NS	NS	NS
Fluorotelomer sulfonic acid 8:2 (FtS 8:2)	39108-34-4	NS	NS	NS
2-(N-Ethylperfluorooctanesulfonamido) acetic acid (NEtFOSAA)	2991-50-6	NS	NS	NS
2-(N-Methylperfluorooctanesulfonamido) acetic acid (NMeFOSAA)	2355-31-9	NS	NS	NS

Notes:

[1] ADEC Soil Clean-up Levels (2022), 18 Alaska Administrative Code 75.341 Table B1, Method 2

[2] EPA May 2022 Risk Screening Levels (RSLs) for PFBS (target hazard quotient of 0.1) for resident soil as presented on the website: https://www.epa.gov/risk/regional-screening-levels-rsls

[3] The "Human Health" exposure pathway is the cumulative exposure pathway through dermal contact, ingestion, and inhalation of volatile and particulate compounds from hazardous substances in the soil but excludes the vapor intrusion pathway of indoor inhalation.

[4] The "Migration to Groundwater" exposure pathway is the potential for hazardous substances to leach to groundwater where they may result in a completed human health exposure pathway through dermal contact, ingestion, or inhalation of contaminants at or above levels listed in Table C at 18 AAC 75.345(b)(1); soil clean-up levels protective of migration to surface water must be determined on a site-specific basis. The cleanup levels shown are for the under 40-inch precipitation zone.

[5] NS – not specified

Recent National Defense Authorization Acts (NDAA), from both 2019 and 2020, include provisions on PFAS with specific remedial requirements for the DOD.

On December 20, 2020, Section 330 of S. 1790 stipulated:

- Incineration be conducted at a temperature range adequate to break down PFAS chemicals while also ensuring the maximum degree of reduction in emission of PFAS, including elimination of such emissions where achievable;
- All incineration be conducted in accordance with the requirements of the Clean Air Act (42 USC 7401 et seq.), including controlling hydrogen fluoride;
- Any materials containing PFAS that are designated for disposal are stored in accordance with the requirement under Part 264 of Title 40, Code of Federal Regulations; and
- All incineration be conducted at a facility that has been permitted to receive waste regulated under Subtitle C of the Solid Waste Disposal Act (42 USC 6921 et seq.).

On July 21, 2020, Section 330 of H.R.6395 stipulated:

- Establishment of an interagency working group to coordinate federal activities to advance research and development to address PFAS.
- Require the Secretary of Defense to meet the most stringent of state PFAS clean-up and federal standards or health advisories for clean-up.
- Require the results of drinking and groundwater testing for PFAS conducted on military installations or former defense sites be published.

2.0 TECHNOLOGY DESCRIPTION

Thermal remediation has been used in the environmental remediation industry for over 30 years with well-established TCH field applications targeting soil temperatures in the 300-400°C range (Crownover et al., 2019; and DiGuiseppi et al., 2019).

2.1 TECHNOLOGY DESCRIPTION

The FlexHeater® TCH process uses TRS' patented FlexHeater® to deliver energy to the designated treatment interval at easily controllable rates. During TCH application, the heater itself is raised to temperatures up to 900°C. The radiant heat from the FlexHeater® then heats the casing and the surrounding soil is then slowly heated by conduction. The PFAS-containing soil is heated to a minimum temperature of 350°C throughout the treatment volume. This is verified by measuring temperatures at the coolest locations farthest away from the heaters.

In addition to the FlexHeater® well casings, vapor recovery (VR) screens are installed adjacent to or in between the FlexHeater® well casings. During FlexHeater™ TCH application, the VR screens are put under vacuum using a positive displacement blower. Recovered steam and soil vapors are then transported via stainless steel piping headers to the scrubber. From the scrubber the vapors are transported to the condenser where the recovered mixture is passed through a vapor/liquid separator and heat exchanger. Any condensate generated following the heat exchange process is captured and conveyed for subsequent treatment and the extracted air is treated using the best applicable technology or methods, such as vapor-phase granular activated carbon (VGAC) or thermal oxidation. For this demonstration, VGAC was used.

2.2 TECHNOLOGY DEVELOPMENT

Thermal remediation has been used in the environmental remediation industry for over 30 years with well-established TCH field applications targeting soil temperatures from 100°C to 400°C range and targeting contaminants of concern such as volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and polychlorinated biphenyls (PCBs). More than 600 thermal projects have been completed. Approximately 100 of these have involved TCH.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantages of using thermal conduction heating are that the technology is capable of removing PFAS from soil and thereby reducing the volume of PFAS-impacted waste by extracting PFAS from the soil and transferring it to a low process water volume and adsorbing to GAC. The process is effective for all soil fractions, including the fines.

Treatment directly in the stockpiles also eliminates excavation, transportation, and disposal of the soils. This greatly reduces the overall cost of solving the PFAS stockpile issue.

The disadvantage of using thermal conduction heating is the energy usage and cost associated with implementing the technology. However, if compared to alternative solutions for solving the problem, this may not be critical.

Compared to lower cost solutions such as excavation and disposal, or soil washing, the TCH process completely removes the PFAS from the soils and concentrates the mass in a small volume of waste which can be destroyed on site or at a controlled facility. A critical and objective comparison of the proven alternatives should be carried out – preferably focused on effectiveness, cost and sustainability.

3.0 PERFORMANCE OBJECTIVES

The quantitative and qualitative performance objectives for ER20-5198 Ex Situ Thermal Treatment of Perfluoroalkyl and Polyfluoroalkyl Substances project are summarized in **Table 2**. Details of each performance objective are summarized in respective subsections below.

Table 2. Performance Objectives

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Evaluate PFAS release rate and byproduct formation	PFAS removal and byproduct formation evaluation in flow- through reactor studies	• >95% PFAS reduction considered successful, with concentrations below state of Alaska guidelines • Confirmation of *de minimus* • byproduct accumulation in heated soil
Determine remediation effectiveness soil concentrations	Pre- and post- treatment soil PFAS concentrations in stockpile	• >95% PFAS reduction considered successful, with concentrations below state of Alaska guidelines • PFOA and PFOS soil concentrations below Alaska DEC cleanup levels • Average concentration for each compound detected*
Determine remediation effectiveness stockpile temperatures	Achievement of stockpile temperature of 350 °C or higher for a minimum of 10 days	• >90% of sensors reaching 350 °C • No sensor below 300 °C • Average in target volume exceeding 350 °C
Determine remediation effectiveness vapor treatment	Treatment efficiency for extracted vapor	• Vapor samples at stack below acceptable level • Removal efficiency above 95% when inlet concentrations are high • Capture the peak for extracted PFAS compounds
Determine remediation effectiveness condensate treatment	Treatment efficiency for condensate	• Treated liquid samples below acceptable level • Removal efficiency above 95% when inlet concentrations are high • Capture the peak for extracted PFAS compounds
Determine energy efficiency	Establishment of an energy balance for the subsurface and tracking of energy usage	• Energy balance data recorded • Modeling adjusted to accurately represent losses and energy removal (calibration)
Qualitative Performance Objectives		
Ease of use	Feedback from field technician on usability of technology and time required	A single field technician able to effectively take measurements
Safety	Daily safety meetings and detailed log of all near misses and SOPs	No incidents or OSHA recordables
Timing	Sampling frequency matched to periods when most PFAS is extracted	Capture of the peak mass removal rate and total mass of PFAS compounds removed

3.1 EVALUATE PFAS RELEASE RATE AND BYPRODUCT FORMATION

The laboratory-scale treatability tests described herein are intended to:

a. Provide data to demonstrate the amount of PFAS that is expected to be recovered from the impacted soils during heating
b. Assess the potential for reaction byproduct formation during the thermal treatment process.

3.1.1 Data Requirements

PFAS-contaminated soils from Eielson AFB were placed in a tube furnace and heated to a temperature of 400°C for 10 days. Off gas was collected and analyzed for parent PFAS and reaction byproducts using high resolution mass spectrometry (HRMS). Solid-phase samples were extracted before and after the heating process to determine the change in PFAS concentrations and to assess byproducts that were associated with the solid phase.

Soil samples and effluent samples were analyzed for PFAS using targeted and non-targeted methods to identify and quantify both parent compounds and reaction byproducts. For targeted analysis of PFAS, analyte separation was achieved using a Waters Acquity H-Class ultra-performance liquid chromatograph (UPLC) equipped with a Waters BEH C-18 column with an eluent gradient of ammonium acetate in water or methanol, similar to that described in EPA Method 537.1. Quantification of PFAS was achieved using a Waters Xevo tandem quadrupole mass spectrometer (TQ-S) separated by a mass filter utilizing StepWave ion optics technology to increase sensitivity. The Waters Xevo TQ-S was operated in negative electrospray ionization (ESI) mode using multiple reaction monitoring mode tuned to unit mass resolution to isolate precursor and product ions that are specific to each substance (i.e., transition ions) for quantitation and identification. Mobile phases were prepared from liquid chromatography-mass spectrometry (LC-MS) grade water, methanol, and ammonium acetate. The initial instrument calibration was performed using at least five concentrations of PFAS obtained from Wellington Laboratories, covering the range of expected concentrations. Prior to sample analysis, the initial calibration must achieve the following criteria:

a. Signal to noise ratio of 10:1 for all quantification ions
b. Percent RSD of the response factors for all analytes is less than 30 percent
c. Calibration curve is linear with an $r^2 = 0.99$
d. Peak asymmetry factors at the mid-level CAL standard between 0.8 and 1.5

A method blank (MB) was included with each analytical batch to demonstrate that the experimental systems were free of background PFAS contamination. A matrix spike (MS), matrix spike duplicate (MSD), and laboratory control sample (LCS) were prepared with each batch. The MS and MSD were used to demonstrate that the percent recovery was within 70 percent to 130 percent, and the relative percent difference (RPD) was less than 30 percent.

Isotopically-labelled PFAS extraction standards paired with each PFAS (e.g., M8-PFOA when PFOA is present) were added to each sample as an internal standard to monitor the extraction process. Instrument response to the labelled PFAS was used to show recoveries were between 50 percent and 150 percent of added amounts. If recoveries were outside these limits, the sample result was discarded.

The analytical systems were able to detect 40 PFAS, precursors, and C-13 labeled standards with a total run time of approximately 10 minutes and detection limits ranging from 5 to 50 nanograms per liter (ng/L)(or parts per trillion [ppt]).

Non-targeted analysis PFAS transformation products collected from effluent gas phase samples and extracted from solid samples were performed using a Thermo Scientific Qexactive HF-X Orbitrap MS equipped with a Vanquish ultra-high performance liquid chromatograph (UHPLC). Analytes were separated during liquid chromatography using a Thermo Hypersil GOLD™ VANQUISH™ C18 UHPLC column (1.9 µm x 2.1 mm x 50 mm) and mobile phase prepared from LC-MS grade water, methanol, and ammonium acetate. The compounds were ionized in either negative or positive ion mode using ESI. The resulting ions were trapped in in the Orbitrap mass analyzer, where current was detected and converted to m/z values using Fourier transform. The Orbitrap MS is a high-resolution mass analyzer, providing up to 120,000 resolving power, 1 part per million (ppm) mass accuracy, and mass range from 30 to 3,000 m/z to deliver accurate, distinguishable masses for high confidence identification. LC-Orbitrap mass spectral data were collected in full-scan mode with resolution of at least 60,000, which provided sufficient selectivity and sensitivity. Untargeted data analysis was performed using Compound Discoverer Software (Version 3.2). Compounded Discoverer allowed for automated identification and matches mass spectra using the mass lists, spectral libraries and databases, and a custom high- resolution library collected from certified standards in-house.

3.1.2 Success Criteria

Following thermal treatment of PFAS-impacted soil from Eielson AFB at a temperature of 400°C for 10 days, Success Criterion 1 was achieved when the total PFAS solid-phase mass was reduced by 95 percent. The solid-phase mass was estimated based on the PFAS concentrations measured in soil samples before and after thermal treatment across the 16 volumes for each sample across the 134 yd^3 soil stockpile. In addition, project success was based on the ability to reduce concentrations of PFOA and PFOS in soil to be at or below concentrations limits established by the state of Alaska for protection of surface waters and groundwater.

Success Criterion 2 was based on the detection of less than 5 percent of the initial PFAS mass as reaction byproducts in the soil following heating to 400°C for 10 days based on the average PFAS byproduct concentrations measured in three replicate soil samples before and after thermal treatment.

3.2 DETERMINE REMEDIATION EFFECTIVENESS SOIL CONCENTRATIONS

The field demonstration was intended to confirm the field scale findings observed in the laboratory reactivity studies. An existing PFAS-impacted stockpile at Eielson AFB was heated to 350°C to 400°C using TCH. PFAS removal from the stockpile was evaluated during the field demonstration.

3.2.1 Data Requirements

The treatment area was divided into four quadrants as shown in **Figure 1**.

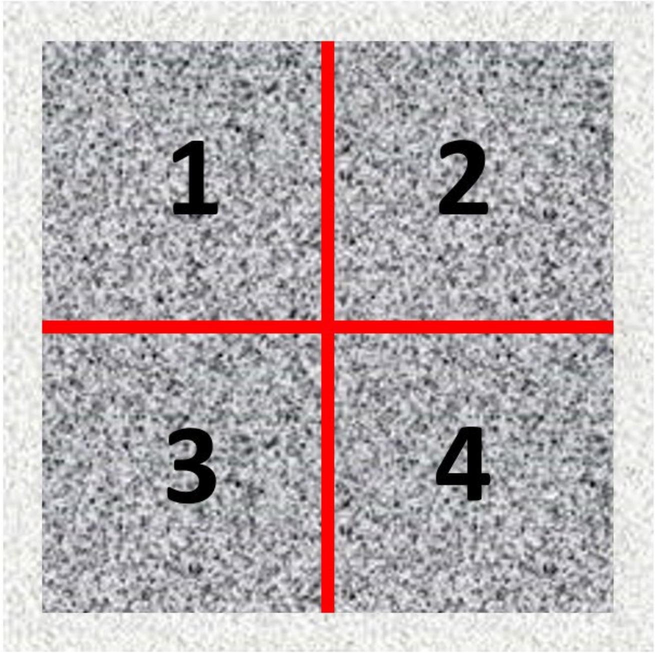


Figure 1. Top View of Stockpile Indicating Quadrant Boundaries for Soil Sampling

Discrete soil samples were collected from the center-point of each quadrant at four depths for initial analyses of 24 target PFAS compounds listed in **Table 3** prior to treatment.

Table 3. Target PFAS Analytes

Compound Name	Abbreviation	CAS#	Labelled Surrogate
Perfluorobutanoic acid	PFBA	375-22-4	MPFBA
Perfluoropentanoic acid	PFPeA	2706-90-3	M5PFPeA
Perfluorohexanoic acid	PFHxA	307-24-4	M5PFHxA
Perfluoroheptanoic acid	PFHpA	375-85-9	M4PFHpA
Perfluorooctanoic acid	PFOA	335-67-1	M8PFOA
Perfluorononanoic acid	PFNA	375-95-1	M9PFNA
Perfluorodecanoic acid	PFDA	335-76-2	M6PFDA
Perfluoroundecanoic acid	PFUnA	2058-94-8	M7PFUnDA
Perfluorododecanoic acid	PFDoA	307-55-1	MPFDoA
Perfluorotridecanoic acid	PFTriA	72629-94-8	
Perfluorotetradecanoic acid	PFTreA	376-06-7	M2PFTeDA
Perfluorobutanesulfonic acid	PFBS	375-73-5	M3PFBS
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	
Perfluorohexanesulfonic acid	PFHxS	355-46-4	M3PFHxS
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	

Table 3. Target PFAS Analytes (Continued)

Compound Name	Abbreviation	CAS#	Labelled Surrogate
Perfluorooctanesulfonic acid	PFOS	1763-23-1	M8PFOS
Perfluorononanesulfonic acid	PFNS	68259-12-1	
Perfluorodecanesulfonic acid	PFDS	335-77-3	
Perfluorooctanesulfonamide	PFOSA	754-91-6	M8PFOSA
Fluorotelomer sulfonic acid 4:2	FtS 4:2	757124-72-4	M24:2FTS
Fluorotelomer sulfonic acid 6:2	FtS 6:2	27619-97-2	M26:2FTS
Fluorotelomer sulfonic acid 8:2	FtS 8:2	39108-34-4	M88:2 FTS
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	NEtFOSAA	2991-50-6	D3-N- EtFOSAA
2-(N-Methylperfluorooctanesulfonamido) acetic acid	NMeFOSAA	2355-31-9	D3-N- MeFOSSA
N-methylperfluorooctanesulfonamide	MeFOSA	31506-32-8	

Baseline concentrations of target PFAS analytes in stockpile 377-2 were sufficient enough to detect anticipated post-heating concentrations above the detection limits. For a statistically valid population, 16 samples were analyzed before and after thermal treatment (for a total of 32 samples) using targeted and untargeted analytical methods as described in **Section 2.0**. Eighty percent of PFAS sample analysis were performed in the Pennell laboratory at Brown University. The soil samples underwent shake extraction with ultrasound bath extraction with the extract analyzed by a QSM Table B-15 compliant method, a modified EPA Method 537 procedure involving liquid chromatography and mass spectrometry. Twenty percent (20%) of the field samples were analyzed by the Battelle Memorial Institute (Norwell, MA), which is a National Environmental Laboratory Accreditation Program (NELAP) Battelle Lab and DoD ELAP accredited laboratory to verify the targeted PFAS analysis performed at Brown University.

Soil samples were also analyzed for total organic carbon (TOC) by ASTM Method 2974 Method C. In addition, twenty percent (20 %) of soil samples were analyzed by a DoD ELAP accredited laboratory (Eurofins Lancaster Laboratories Environmental, LLC) for extractable organofluorine (EOF) using combustion ion chromatography (IC). EOF provided information for determining the contributions of different sources to the overall contamination, in addition to, understanding the total mass present before and after thermal treatment. The technique used combustion of concentrated extracts, followed by downstream analysis of fluoride ion by ion chromatography. A limit of quantitation of 0.02 mg F/kg was generally achievable for solid samples.

To monitor PFAS reductions following thermal treatment, soil confirmation samples were collected from each of the four grids within close proximity to the location of the original sampling as shown in **Figure 1**. Soil sampling can occur once the heater wells were turned off. Hot soil sampling standard operating procedures (SOPs) were used. Soil samples were analyzed by a QSM Table B-15 compliant, modified EPA Method 537, to evaluate the reduction concentration for the targeted PFAS compounds. Following thermal treatment, samples were also analyzed for non-targeted PFAS, EOF, and TOC.

3.2.2 Success Criteria

Following thermal treatment, soil sample results from four decision units were compared to baseline soil concentrations prior to heating the stockpile. A greater than 95% reduction of targeted PFAS, with PFOA and PFOS present at soil concentrations below the limits established by the state of Alaska for protection of ground and surface waters (1.7 ug/kg PFOA, and 3.0 ug/kg PFOS), was considered successful with an overall sample average for each decision unit. Ideally the baseline PFAS concentrations were high enough to aim for total targeted PFAS <1 ug/kg in heated soils. If starting PFAS concentrations were very low, less than a 95% reduction may be observed. With higher starting PFAS concentrations, more than 95% reduction in soils would be expected. In addition, project success is based on the ability to reduce concentrations of PFOA and PFOS in soil to be at or below concentrations limits established by the state of Alaska for protection of groundwater. With the reduction in PFAS, an anticipated reduction in TOC and EOF was also considered part of the success criteria.

3.3 DETERMINE REMEDIATION EFFECTIVENESS STOCKPILE TEMPERATURES

The stockpile was subjected to a power density of approximately 428 watts per cubic yard of soil during heating. At this power density, the boiling point of water was expected to be reached within the first 40 days of heating. Once the water was boiled off, stockpile temperatures were further increased reaching the target temperature range of 350°C to 400°C.

3.3.1 Data Requirements

An average temperature of 350°C was expected to be reached approximately 65 days after heating began. The system was to be held at the 350°C to 400°C temperature range under vacuum until 80 total days of heating operations were reached. Soil moisture content was evaluated prior to heating to ensure the operations period was sufficient to allow for moisture to be boiled off and the targeted temperature range to be achievable.

While heating the stockpile, temperatures within the stockpile were recorded daily and continuously monitored. Twenty individual sensors were installed within the stockpile consisting of four strings of sensors with five sensors across the depth of the stockpile. The accuracy of the temperatures needed to be within +/- 1°C. Data were automatically logged and stored in a database for long-term viewing and analysis.

3.3.2 Success Criteria

For the stockpile temperature evaluation, criteria considered to be successful was no sensor in the stockpile was below 300°C with greater than 90 percent of the sensors reaching 350°C and a 350°C stockpile average temperature maintained for 10 days.

3.4 DETERMINE REMEDIATION EFFECTIVENESS VAPOR TREATMENT

As shown in the process flow diagram in **Figure 4**, the first step in the treatment process consisted of a scrubber followed by vapor treatment using VGAC. As the scrubber process water is indicative of the amount of PFAS extracted from the stockpile, the water sampling approach was relevant for the vapor treatment analysis. **Sections 3.4** and **3.5** therefore overlap considerably.

3.4.1 Data Requirements

During the field demonstration, the concentration of PFAS in the extracted vapors from the stockpile was monitored. Other Test Method-45 (OTM-45) was used to monitor for PFAS in stockpile extracted vapors. OTM-45 is an analytical method developed by the EPA, with Ray Merrill and Jeff Ryan as primary investigators. Vapor samples were collected from location VP- 1 in **Figure 4**, the vapor manifold before scrubbing, condensation and treatment. For each OTM- 45 vapor sampling event at Eielson AFB, specialized glassware was mobilized to the Site. Seven sample fractions were collected from the OTM-45 sampling train for each sample collection.

These sample fractions include:

1) Particulate filter
2) Solvent probe rinse
3) XAD-2 resin tube
4) Coil condenser and filter holder
5) Condensate and impinger contents
6) Impinger glassware rinses
7) Breakthrough XAD-2 resin tube

The hot vapors were routed to a scrubber to transfer the majority of the extracted PFAS to a low volume aqueous solution.

Mass removal rates are typically expressed in grams/day or a similar unit. Estimates were derived by multiplying a volume of the media sampled by the concentration measured in it. Therefore, both flow rates, extracted volumes, and PFAS content in the scrubber effluent streams were measured.

Both process water and vapor streams were treated using granular activated carbon. The vapor stream flow rate was measured using pitot tubes placed within the vapor recovery piping. The differential pressure was measured manually at the time of sampling.

Vapor treatment efficiency was estimated based on inlet and outlet sample pairs for the GAC systems. In this process, the stack effluent vapor was sampled for PFAS compounds (it is the outlet of the VGAC system).

Over the 80-day heating period, vapor sampling occurred approximately every 14 days. Vapor samples were captured in summa cannisters and analyzed using liquid chromatography tandem mass spectrometry (LC-MS/MS).

Table 4. Total Number and Types of Samples Collected

Component	Matrix	Number of Samples	Analyte	Location
Pre-demonstration sampling	Soil	16	PFAS (QSM Table B-15 compliant), EOF	Four quadrants within stockpile
	Soil	16	Grain size/hydrometer ; moisture content	Four quadrants within stockpile
	Soil	16	Total organic carbon	Four quadrants within stockpile
Technology performance sampling	Stockpile extracted vapors	6	OTM-45, Targeted and non-targeted analysis	VP-1
	Scrubber water effluent	12	PFAS (QSM Table B-15 compliant)	Post- scrubber sample port (LP-1)
	Liquid treatment effluent	12	PFAS (QSM Table B-15 compliant)	Post liquid treatment sample port (LP-2)
	Vapor treatment effluent	12	PFAS (QSM Table B-15 compliant), Total F	Post-vapor treatment sample port (VP-3)
	Ambient air	6	PFAS (QSM Table B-15 compliant), Total F	Ambient air within close proximity to heated stockpile
Post-demonstration sampling	Soil	16	PFAS (M 537), ETOF	Four quadrants within stockpile
	Soil	16	Grain size/hydrometer ; moisture content	Four quadrants within stockpile
	Soil	16	Total organic carbon	Four quadrants within stockpile

Table 5. Analytical Methods for Sample Analysis

Matrix	Analyte	Method	Container	Preservative	Holding Time
Soil	Targeted PFAS	QSM Table B-15 compliant	Brass sleeve	None	14 days until extraction, 28 days after extraction
	Non-targeted PFAS	LC-Orbitrap MS	Brass sleeve	None	14 days until extraction, 28 days after extraction
	Extractable Total Organic Fluorine	Combustion IC	Brass sleeve	None	14 days until extraction, 28 days after extraction
	Moisture Content	ASTM	Brass sleeve	None	14 days until extraction, 28 days after extraction
	Particle Size	11 sieve	1 L glass jar	None	14 days until extraction, 28 days after extraction
Scrubber effluent (water treatment system influent)	Targeted PFAS	QSM Table B-15 compliant	Polypropylene bottle	None	14 days until extraction, 28 days after extraction
Scrubber effluent (water treatment system influent)	Non-targeted PFAS	LC-Orbitrap MS	Polypropylene bottle	None	14 days until extraction, 28 days after extraction
Water treatment system effluent	Targeted and Non-targeted PFAS	QSM Table B-15 compliant LC-Orbitrap MS	Polypropylene bottle	None	14 days until extraction, 28 days after extraction
Water treatment system effluent	Non-targeted PFAS	LC-Orbitrap MS	Polypropylene bottle	None	14 days until extraction, 28 days after extraction
Air	Targeted and Non-targeted PFAS	QSM Table B-15 compliant LC-MS; LC-Orbitrap MS	Summa Cannisters	None	14 days until extraction, 28 days after extraction

3.4.2 Success Criteria

Success criteria for vapor treatment were to observe PFAS vapor concentrations below an acceptable level as defined by local regulators. To the authors' knowledge, there were no existing vapor standards at the time. Sampling data would be used to determine acceptable vapor emission concentrations approximately every 14 days.

It was an objective to capture the peak for extracted PFAS from the stockpile and thereby establish an estimate of PFAS mass removal. When temperatures in the soil approached 300°C, PFAS concentrations in the extracted system were expected to rise. The sampling frequency was reduced to weekly, or potentially more frequently, when the combined data indicate that the PFAS removal rate is peaking. This was expected to occur between day 50 and 70 of heating.

The key stream to sample during this time was the liquid effluent from the scrubber as the cooling process allows for most of the PFAS to condense in the water. PFAS removal efficiency was above 95 percent for the liquid-phase GAC (LGAC) systems when inlet concentrations were high and treated water concentrations were below 13 micrograms per liter (µg/L) throughout.

3.5 DETERMINE REMEDIATION EFFECTIVENESS OF CONDENSATE TREATMENT

Condensate treatment effectiveness was important not only to ensure that liquid discharges were acceptable, but also for the vapor treatment evaluation described in **Section 3.4**.

3.5.1 Data Requirements

Treatment efficiency for PFAS in the condensate was established by comparing PFAS concentrations in the influent and effluent streams of the LGAC treatment system. This sampling occurred approximately every 14 days during the heating period.

Water samples were analyzed using a QSM Table B-15 compliant method. Flow rates and volumes of water treated by the LGAC system were quantified using an in-line totalizer with automatic logging once daily with continuous monitoring.

3.5.2 Success Criteria

The success criteria for process water treatment were considered a removal efficiency above 95 percent when influent PFAS concentrations high and below 13 µg/L throughout heating of the stockpile. It was important that the sample frequency be such that the peak for extracted PFAS was captured, as described in **Section 3.4.2**.

3.6 DETERMINE ENERGY EFFICIENCY

A proprietary numerical model was developed to quantify heat losses, energy removal rates, and subsurface power delivery. The numerical model indicated the required components of the system included a total of 48 heater borings installed to a depth of 4 feet below stockpile 377-2 with a vapor cover R value of at least 30. The total predicted energy to operate the heaters was estimated to be 154,000 kilowatt-hours (kWh) with the power input ranging from 75 to 125 kilowatts (kW).

The average soil temperature predictions and resultant energy balance are shown in **Figure 2**. As noted in the figure, TRS anticipated that the success criteria would be met following approximately 80 days of subsurface heating if continuous heating can be maintained.

Energy usage for heating the pilot test pile volume was electronically tracked and logged. Using TRS' HeatWave model, the net amount of energy used to treat the soil pile was estimated, as energy removal and heat losses were tracked and monitored. The energy density defined as the energy delivered to the soil per unit volume was calculated and extrapolated to larger treatment volumes where heat loss percentages were much lower.

Based on the derived minimum energy density for PFAS soil treatment to acceptable levels, full-scale site parameters, local utility costs, and HeatWave modeling of the full-scale scenarios enabled relatively accurate predictions of power usage and cost.

3.6.1 Data Requirements

When establishing an energy balance for the subsurface and tracking of energy usage, it is important to monitor for key parameters that include:

- Electrical power used to deliver heat via the TCH heaters that were recorded automatically and stored in a database. This energy usage is compared to a totalizing power meter and estimated energy usage by the treatment system and other on-site sources.
- Energy removed in extracted steam estimated based on condensate production rates and the enthalpy of vaporization for water.
- Energy extracted in non-condensable air estimated based on the flow rate, temperature, and heat capacity of the air.

Heat losses cannot be measured directly. An energy balance was maintained with estimates for heat losses. This energy balance returns an average target treatment zone temperature, which can be compared to the subsurface temperatures measured.

3.6.2 Success Criteria

When energy balance data was recorded, the model was updated and calibrated with observed temperatures and energy fluxes. The thermal model was updated periodically during the heating period. At the end, success criteria were an accurate account for the energy used for heating provided in kilowatt hours with an expected accuracy of +/- 2,500 kWh so the unit energy used can be estimated (in units of kWh/yd^3) with an accuracy of +/- 10 kWh/yd^3 or better. Thermal modeling was adjusted to accurately represent losses and energy removal (calibration). The calibrations described above allowed for improved future energy predictions.

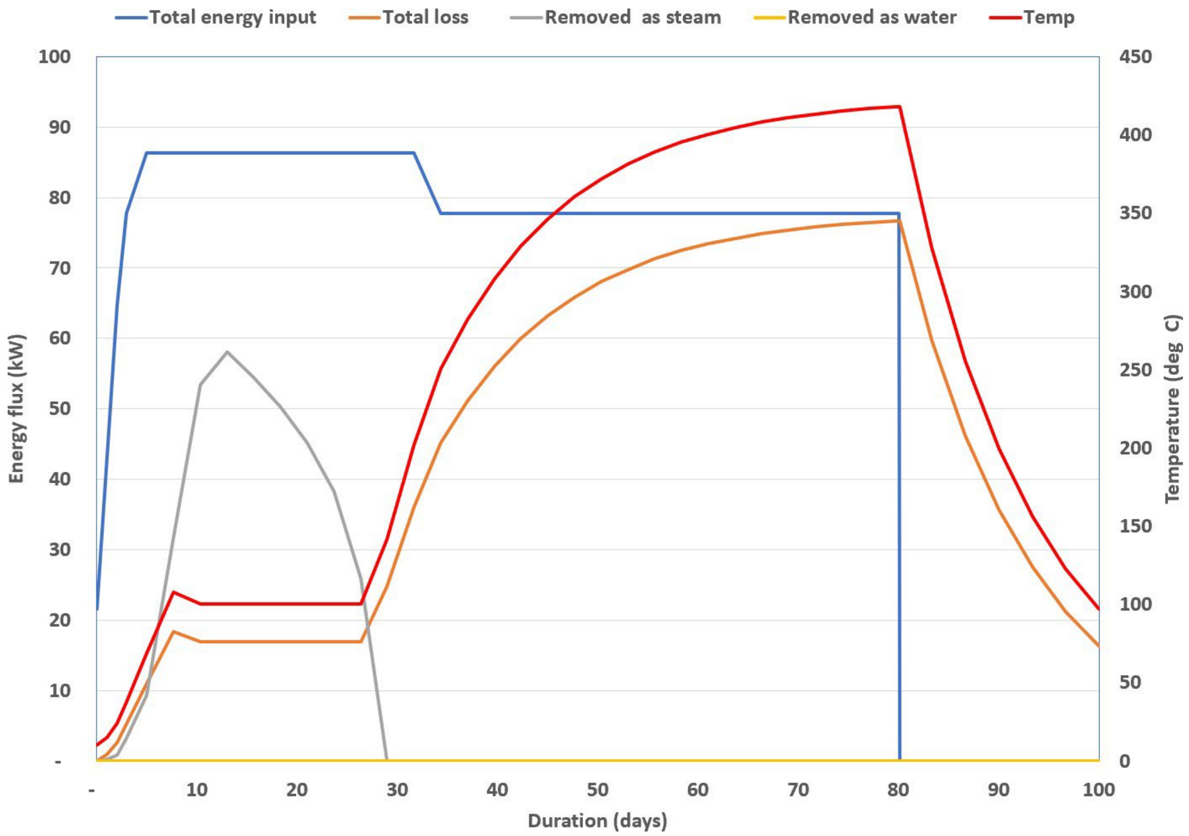


Figure 2. Modeled Energy Balance and Average Temperature for Stockpile

3.7 EASE OF USE ASSESSMENT

For future *ex situ* thermal remediation implementations, it was important that the systems were designed for ease of use.

3.7.1 Data Requirements

To evaluate the ease of use of the PFAS thermal treatment system, feedback from the field technician was required on the usability of the technology and the amount of time that was required to operate and monitor the system.

To assess ease of use, the hours required by the field technician to operate and monitor the system were recorded. Following completion of the field demonstration, the hours required for training and optimal operations were assessed and the need for any further training documentation was evaluated.

3.7.2 Success Criteria

Success for the ease-of-use assessment was determined with confirmation that site data collection could be completed by a single on-site field technician.

3.8 SAFETY EVALUATION

It was essential that a safety evaluation was performed throughout and upon completion of the field demonstration.

3.8.1 Data Requirements

The data required to perform the safety evaluation for the system was collected to conduct daily safety meetings and maintain a detailed log of all standard operating procedures and near misses.

3.8.2 Success Criteria

The success criteria for the safety evaluation were considered to be the occurrence of zero incidents or Occupational Safety and Health Administration (OSHA) recordables.

3.9 TIMING ANALYSIS

The timing analysis was an important qualitative performance objective to help ensure that the peak PFAS removal from the stockpile was observed and quantified through sampling.

3.9.1 Data Requirements

The data required to evaluate timing analysis was to monitor whether the sampling frequency matched the periods during which the most PFAS was extracted from the stockpile.

3.9.2 Success Criteria

Timing analysis success criteria was that the peak mass removal rate and total mass of PFAS compounds removed was captured during operations of the thermal treatment system.

4.0 SITE DESCRIPTION

The demonstration was staged at Eielson AFB near Fairbanks, Alaska. An estimated 130,000 yd^3 of potentially PFAS-impacted soils are stockpiled at Eielson AFB and awaiting further characterization, treatment, or off-site transportation and disposal. Stockpile 377-2 was thermally treated for the field demonstration. It was approximately four to five feet high, 40 feet by 40 feet at the base, with a calculated volume of 134 yd^3.

Table 6 summarizes the quantity of FlexHeater® well casings, treatment interval, and treatment volume.

Table 6. TCH Treatment Details

	FlexHeater® Well Casing (Quantity)	Treatment Interval (ft bgs)	Treatment Volume (yd^3)
TCH Remediation Zone	48	0 to 4.5	134

4.1 SITE LOCATION AND HISTORY

Eielson AFB is located in the east-central portion of interior Alaska, approximately 2 miles east of the Tanana River and approximately 25 miles southeast of Fairbanks. Eielson AFB is within the Fairbanks North Star Borough.

Eielson AFB was established in 1944 to train and equip military personnel for air support of ground troops in an arctic environment, and encompasses an area of approximately 19,700 acres, most of which is forest, wetlands, lakes, and ponds. Approximately 3,650 acres have been improved or partially improved. Operations at Eielson AFB have generated varying quantities of hazardous and non-hazardous wastes from industrial and airfield operations, fire training, and fuel management activities. In 2017, construction on base ramped up significantly with the announcement that a new F-35 fighter squadron would be stationed at Eielson AFB. Due to all the construction, a significant volume of potentially PFAS-contaminated soil has been excavated and stockpiled at Environmental Restoration Program site LF003 – Former Base Landfill. LF003 is located east of the southern threshold of the base runway.

4.1.1 Site Selection

Eielson AFB was chosen due to the large volume of stockpiled soil awaiting treatment, the logistical challenges inherent in treating and removing soil from Alaska, and the harsh local climate (hot summers, extremely cold winters). Existing stockpiles were evaluated to identify the stockpile(s) with the highest PFAS contamination that contained both PFOA and PFOS concentrations well above detection limits to help detect the highest percent reduction. Stockpile 377-2 met the criteria and was selected for this field demonstration therefore providing the maximum benefit of PFAS removal while providing the most cost-effective approach to demonstrating thermal PFAS removal in the field.

4.2 SITE GEOLOGY/HYDROGEOLOGY

Eielson AFB occupies part of a tectonic basin filled with alluvium, primarily shed from the Alaska Range, to the south. Along the eastern edge, metamorphic bedrock (the Birch Creek Schist) crop out as the Yukon-Tanana Uplands. Moose Creek Bluff, a metamorphic bedrock inselberg, rises above the floodplain 3.5 miles to the northwest. Tanana River deposits fill the basin beneath Eielson AFB and consist of unconsolidated fluvial sands and gravels, with rare silt. Where unmodified by human activity, the uppermost 10 to 15 feet of basin fill commonly consists of silts and sands (Pewe and Reger 1983). Below this, the basin fill consists of subequal proportions of well-graded sand with variable amounts of gravel interbedded with poorly graded sand and rare intervals of silt. Even at depth, this material is unconsolidated and lacking any degree of cementation.

Eielson AFB is underlain by lenses of discontinuous permafrost up to hundreds of feet thick and beginning as shallow as approximately 15 feet below ground surface (ft bgs). Groundwater was encountered at shallow depths of 10 to 15 ft bgs over the developed area of the base. Groundwater generally flowed northwesterly, roughly parallel with the flow of the Tanana River.

4.3 CONTAMINANT DISTRIBUTION

PFAS contamination was widespread at Eielson AFB. A plume of PFAS-contaminated groundwater has reached approximately 4 miles downgradient of the base and encompassed an area of over 6 square miles. Active mitigation measures are in place to prevent contaminated drinking water from reaching local residents.

The stockpile 377-2 was staged with multiple stockpiles primarily located to the east of the southern end of the runway. These stockpiles were assumed to be contaminated with PFAS. Surveying and sampling of the stockpiles occurred under a separate contract to confirm the quantity/volume of impacted material stockpiled and to characterize the contaminant concentrations in the stockpiled material. Analytical results from samples collected from stockpile 377-2 in October 2019 indicated that it was contaminated with PFAS, predominantly PFOS.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENT DESIGN

The laboratory reactivity studies were first performed on PFAS-impacted stockpile soil samples collected from Eielson AFB. The laboratory-scale treatability tests were completed by Brown University and were intended to demonstrate the amount of PFAS expected to be recovered from the impacted soils during heating and to assess the potential for reaction byproduct formation during the thermal treatment process. In addition, 10 percent of the field samples were sent to Battelle Memorial Institute (Norwell, MA), a ELAP-accredited laboratory, to perform verification of the targeted analysis performed at Brown University.

Following the laboratory reactivity studies, stockpile 377-2 was characterized and prepared for the field demonstration. Once the heaters and insulation were installed on the *ex situ* pile and the vapor and water treatment equipment were connected to the system, operations began. The progress of heating the *ex situ* pile was monitored using temperature and energy balance measurements. A site layout and process flow diagram are provided in **Figure 3** and **Figure 4.**

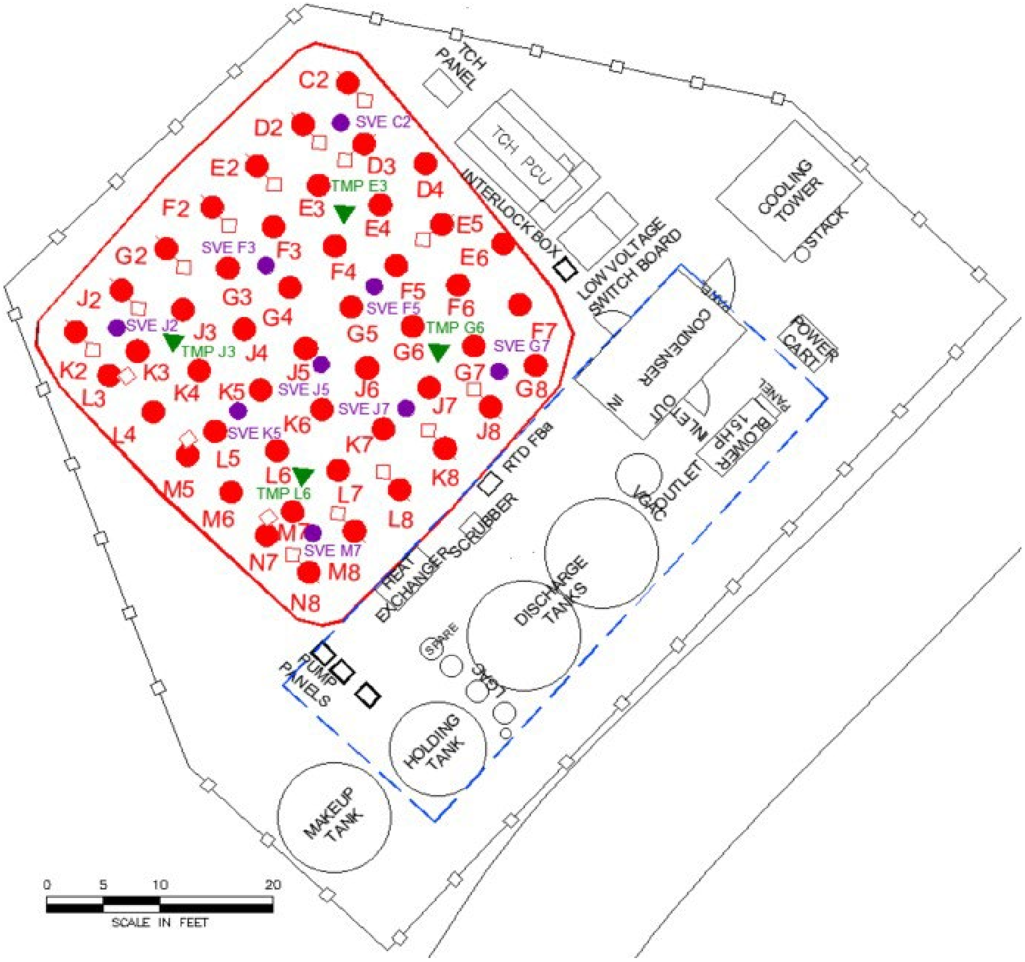


Figure 3. Site Layout with Heating Infrastructure.

The stockpile is 40 ft wide.

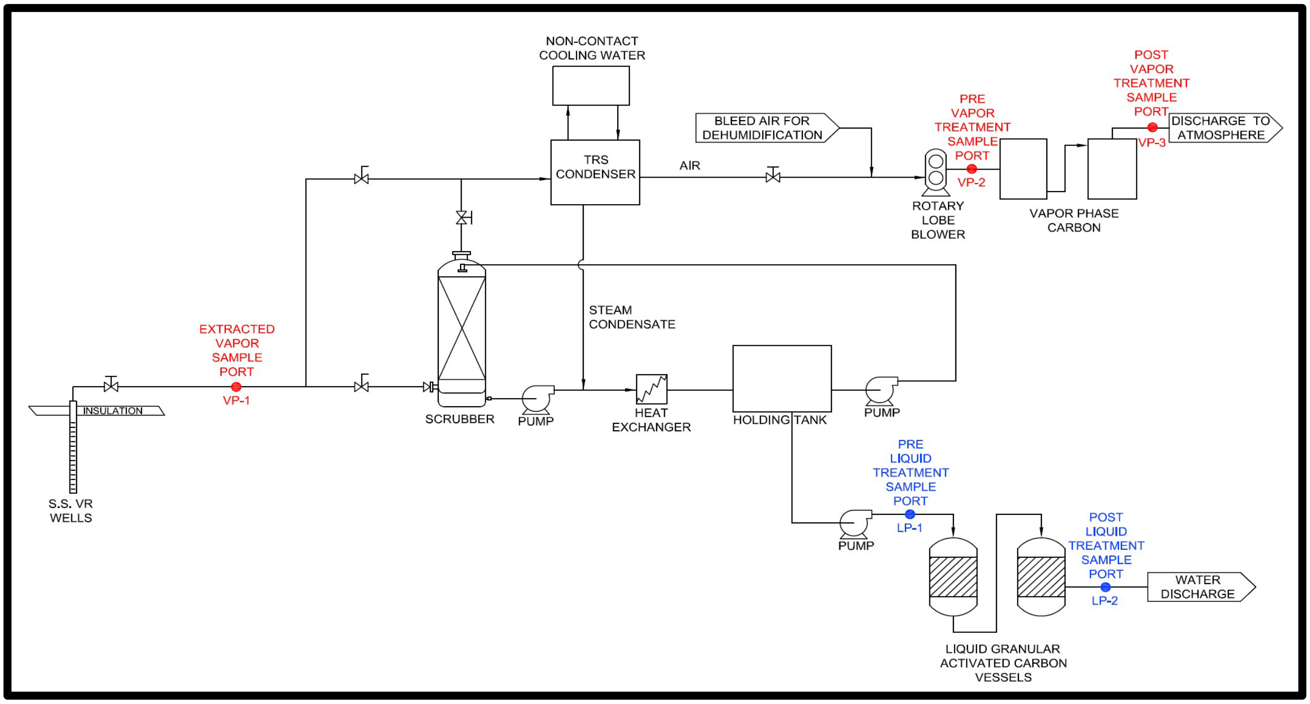


Figure 4. Process Flow Diagram of Thermal Treatment System

5.2 BASELINE CHARACTERIZATION ACTIVITIES

The treatment area was divided into four quadrants as shown on **Figure 1.** Four discrete soil samples were collected from a single borehole in the center of each quadrant. Within each borehole, a discrete soil sample was collected at the planned depth of the four temperature monitoring points: one at the surface, two spaced within the pile, and one at the bottom of the pile. A total of 16 baseline samples were collected from the stockpile for initial analyses of 24 target PFAS compounds prior to treatment. The final design incorporated the sampling methodology for extracting comparable baseline and confirmatory samples from the stockpile. The soil samples underwent shake extraction with ultrasound bath extraction with the extract analyzed by a QSM Table B-15 compliant, modified EPA Method 537 procedure involving liquid chromatography and mass spectrometry as described in the Supporting Technical Data. Twenty percent of the samples were analyzed by the Battelle Memorial Institute (Norwell, MA), which is a member of the National Environmental Laboratory Accreditation Program (NELAP) and a DoD-ELAP accredited laboratory facility. The samples were also analyzed for TOC by ASTM Method 2974, Method C.

5.3 LABORATORY TREATABILITY TEST

The Pennell Lab conducted thermal treatability tests using AFFF-impacted soil that will be treated as part of the field test at Eielson Air Force Base (AFB). The treatability tests involved heating approximately 50 g of air-dry soil in a tube furnace operated with the following sequential temperature ramp, 1 hr at 100 ºC, followed by 1 hr at 200 ºC, 1hr at 300 ºC, and 1 hr at 400 ºC. Four separate treatability tests were conducted, terminating at each temperature (e.g., the second experiment was conducted for 1 hr at 100 ºC + 1 hr at 200 ºC), followed by destructive sampling and targeted analysis of the soil (in triplicate) for 24 per- and polyfluoroalkyl substances (PFAS).

The following 6 PFAS were detected in the soil at quantifiable concentrations prior to treatment: perfluorooctane sulfonic acid (PFOS), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), and perfluoropentanoic acid (PFPeA). Separation of PFAS was achieved using a Waters Acquity H-Class ultra-performance liquid chromatograph (UPLC) equipped with a Waters BEH C-18 column with an eluent gradient of ammonium acetate in water as described in EPA Method 537.1. Quantification of PFAS was achieved using a Waters Xevo TQ-S micro consisting of a tandem quadrupole mass spectrometer. The Waters Xevo TQ-S micro was operated in negative electrospray ionization using multiple reaction monitoring mode tuned to unit mass resolution to isolate precursor and product ions that are specific to each substance (i.e., transition ions) for quantitation and identification. A method blank (MB) was included with each analytical batch to demonstrate that the experimental systems are free of background PFAS contamination. A matrix spike (MS) and a matrix spike duplicate (MSD) were prepared with each batch of extracts by adding a trace-level PFAS standard to the background solids used in each experiment. Isotopically labelled PFAS extraction standards paired with each PFAS (e.g., M8-PFOA for PFOA) were added to each sample as an internal standard to monitor the extraction process. Verification samples were sent to the Battelle Memorial Institute Laboratory in Norwell, MA. Concentrations of 15 PFAS measured in pre- and post-heating (to 400oC) were within 25% between the two laboratories as reported in the February 2021 IPR Meeting.

Prior to heating, the initial concentrations of PFOS, PFHxS, PFOA, PFHxA, PFHpA, and PFPeA ranged from approximately 5 ug/kg to 0.6 ug/kg. After heating for 1 hr at 100ºC, or heating for 1 hr at 100oC + 1 hr at 200ºC, the concentrations of PFOS and PFHxS were reduced by approximately 15%, but the other four PFAS exhibited minimal concentration reductions. After heating for 1 hr at 100ºC + 1 hr at 200ºC + 1 hr at 300oC, the concentrations of all six PFAS decreased, with 75% reductions in PFOS and PFHxS, and only trace levels of PFOA, PFHxA, PFHpA, and PFPeA detected. For the final heating sequence (1 hr at 100ºC + 1 hr at 200ºC + 1 hr at 300ºC + 1 hr at 400ºC), all six PFAS were below the detection limit measured by both the Pennell Lab and Battelle Memorial Institute Laboratory. These results demonstrate the ability of the thermal treatment to 400ºC to remove PFAS from AFFF-impacted soil.

The second phase of the treatability tests focused on identifying reaction byproducts that may be formed during the thermal treatment process. Targeted and non-targeted high-resolution mass spectrometry methods were used to analyze residual soil and off-gas liquid trap samples. Several different trapping methods were evaluated including methanol + water traps, acid traps, and activated carbon traps. Untargeted analysis of volatile and semi-volatile organic transformation products was performed using a Thermo Scientific Q Exactive HF-X Orbitrap MS equipped with a Vanquish ultra-high-performance liquid chromatograph (UHPLC). Compounds were first separated during liquid chromatography using a Thermo Hypersil GOLD™ VANQUISH™ C18 UHPLC column (1.9 µm x 2.1 mm x 50 mm) and mobile phase prepared from LC-MS grade water, methanol, and ammonium acetate. The compounds are ionized in either negative or positive ion mode using electrospray ionization (ESI). The ions are trapped in in the Orbitrap mass analyzer, where current is detected and converted to m/z values using Fourier transform.

The Orbitrap MS is a high-resolution mass analyzer, providing up to 120,000 resolving power, 1 ppm mass accuracy, and mass range from 30 to 3,000 m/z. Mass spectral data were collected in full-scan mode with resolution of at least 60,000, which provides sufficient selectivity and sensitivity.

Untargeted analysis of m/z features was performed using Compound Discoverer Software (Version 3.2). Compounded Discoverer allows for automated identification and matches mass spectra using the mass lists, spectral libraries and databases, and a custom high- resolution library collected in house using certified standards. Nontargeted analysis of soil samples analyzed before and after treatment to 400oC indicated a marked shift from higher m/z features to primarily lower m/z features, including 2-fluoropropene (MW = 60.03723), fluoro-N- methylidynemethanaminum (MW = 60.02464), and fluorocyclopropane (MW = 60.03719). We are currently analyzing the off-gas liquid traps using targeted and non-targeted methods, and refining the sample collection procedures to improve mass recovery.

Mass Balance Using Targeted Monitoring of PFOS and PFOA:

Deionized water was added to separate Ottawa sand samples, prior to spiking with either PFOS or PFOA, to create sand-spike slurries. Slurry spiking was chosen to help ensure adequate coverage of all sand particles with spiked compound. After mixing, and prior to thermal treatment, sands were allowed to dry at ambient temperature in a chemical fume hood. For thermal treatment, spiked reference sands were subjected to 4 hr heating, from 100oC to 400oC, with off-gas collection conducted using deionized water and methanol in sequential off-gas traps. In these experiments we monitored spiked compound concentrations in soil before and after thermal treatment, and in off-gas trapping solvents. Results showed no remaining PFOA, or PFOS, in soil after treatment. After treatment, results showed only 25% spiked compound was collected in the first, aqueous off-gas trap. PFOA and PFOS were not detected in the second, methanol off-gas trap. The remaining fluorine mass existed as shorter chain length byproducts condensed on soil.

Mass Balance Using Targeted and Non-targeted Monitoring:

Non-targeted analysis focused on three “classes” of PFAS compounds: (a) the 28 compounds monitored during targeted PFAS analysis, (b) PFAS compounds present in soil but are not normally targeted (i.e., beyond the 28 targeted PFAS), and (c) unknown reaction byproducts formed during the thermal treatment process. Non-targeted analysis by high resolution LC-Orbitrap MS was used to detect fluorinated organic compounds before and after thermal treatment. Experiments performed for this project consistently show generation of a large number of unknown organofluorine compounds present in soil and collected in off-gas traps. Recent experiments seek to quantify these organofluorine organic species in solids before and after treatment and collected in off-gas samples. For these experiments, a total of seven solids were treated, including three soils collected from U.S. Air Force bases (Eielson, Loring, Robins), and separate Ottawa sand samples spiked with either PFOA, PFOS, 13C-labelled PFOA, or 13C-labelled PFOS. Non-targeted data processing, PFOS- and PFOA-spiked sand samples were compared with samples collected from treatment of sands spiked with the deuterium-labelled analogue to improve mass balance tracing capability. With non-targeted monitoring data acquired and processed to produce a target list of precursor ion mass-to-charge ratios, we migrated methods and analyses for used for monitoring unknown organofluorine compounds to the triple quadrupole mass spectrometry platform. Selected ion recording (SIR) analyses were performed by transferring precursor ion mass-to-charge ratios identified during non-targeted monitoring.

Additional Heating of Field Samples to Confirm Ability to Remove PFOS

A limited number of post-treatment field soil samples indicated that low concentrations of PFOS and PFHxS remained in some zones of the treated soil pile. Therefore, a post-treatment soil subsample (BH2 0/6) was subjected to additional heating studies using the laboratory furnace system. The heating regime for this experiment involved a temperature ramp to 400ºC over 24 hours, followed by a temperature hold at 400ºC for a period of 5 days. No gas flow was applied during heating. Analysis of the contaminated sample after 1 week of additional heating at 400ºC showed no measurable PFOS or PFHxS remaining in the soil. An additional 5-day soil heating experiment with air flow at 350ºC for 5 days was initiated at the end of this quarter. A second 5- day laboratory soil heating experiment using soil subsample BH2 0/6 was undertaken to determine if a lack of air flow would impact the treatment results. After five days of heating at 400ºC under static air flow conditions, no measurable PFOS or PFHxS remained in the soil, consistent with the results obtained last quarter for BH2 0/06 heated to 400ºC for 5 days with air flow.

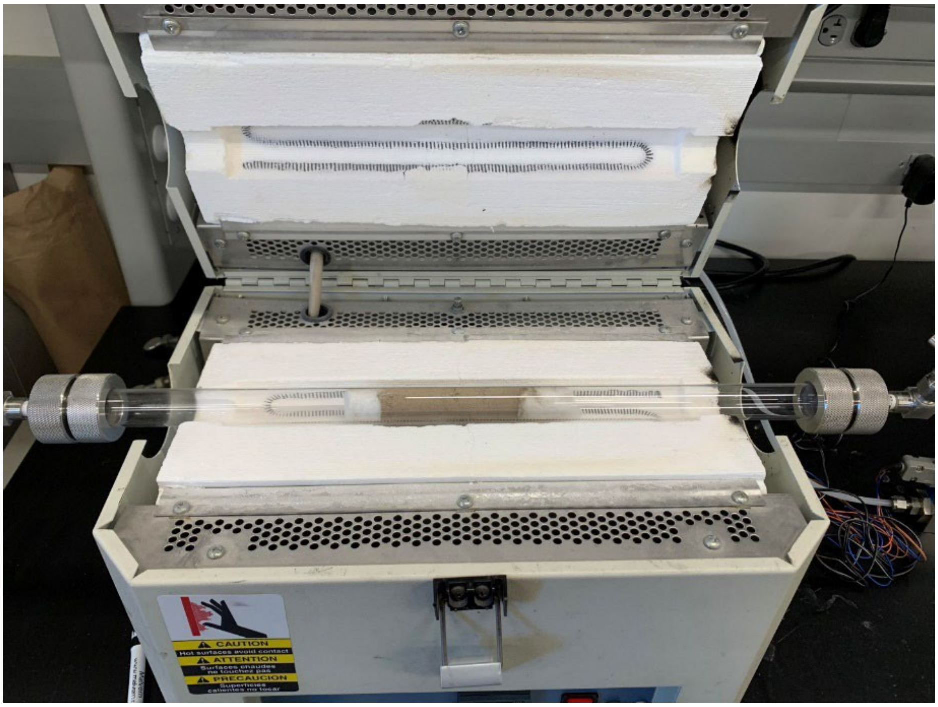


Figure 5. Laboratory Reactivity Study Setup

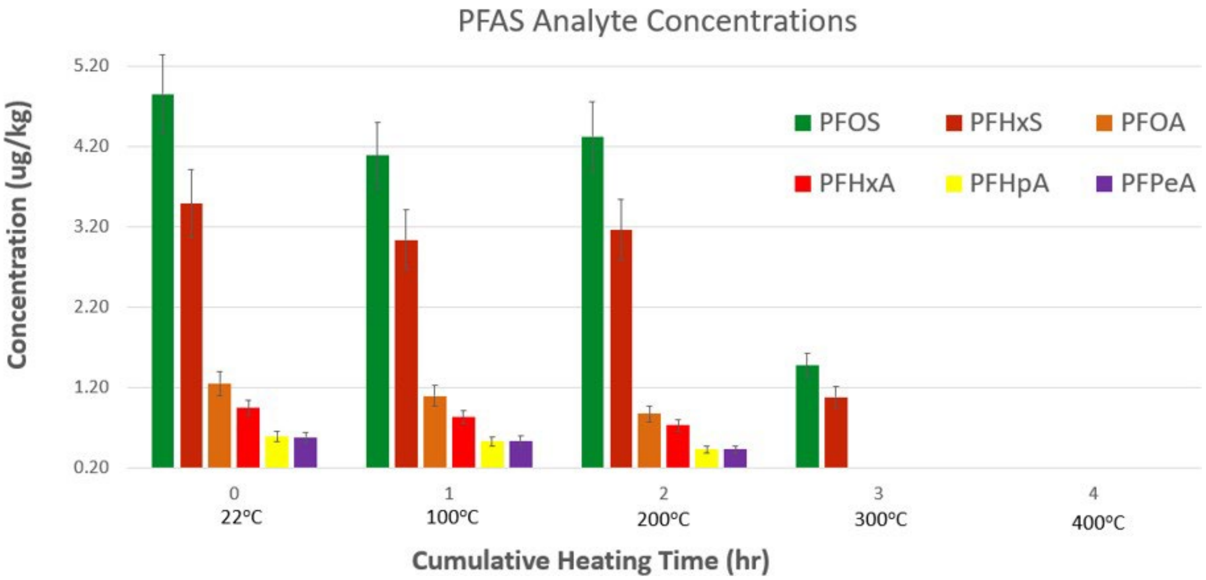


Figure 6. Laboratory Reactivity Study Analyte Concentrations

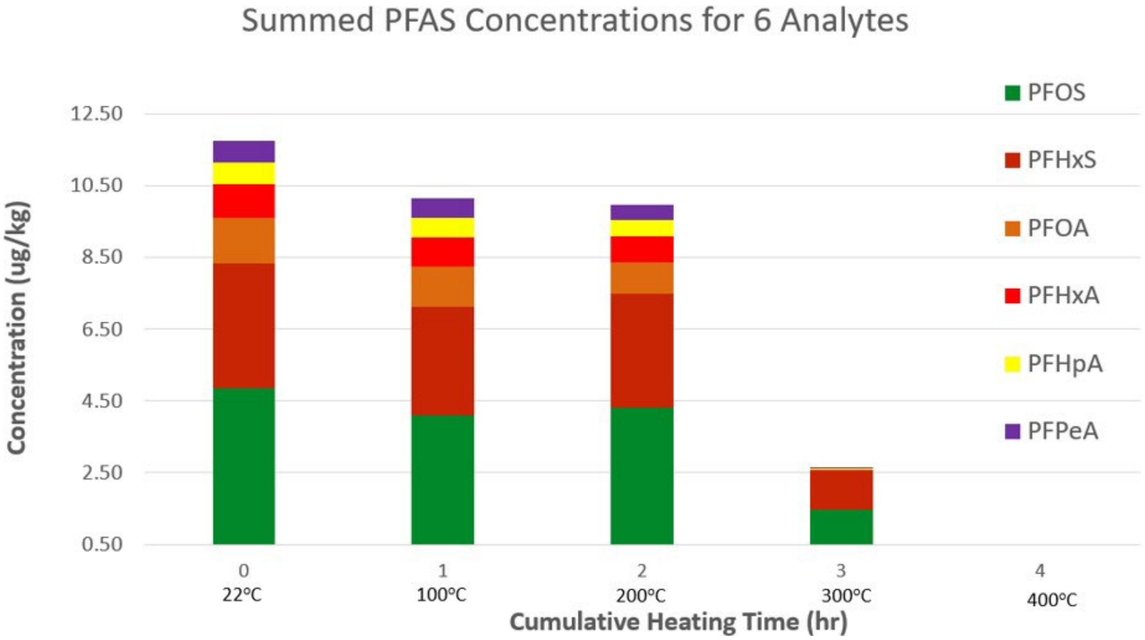


Figure 7. Laboratory Reactivity Study Summed Soil Concentrations

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The TCH target volume at the Site was approximately 134 yd^3. The design package is included in **Appendix A**. The TRS FlexHeater® TCH system consisted of the components identified in **Table 7**. The components are described in detail in subsequent sections.

Appendix A, Figure Y-1 shows the TCH treatment area and pertinent surface features. The site-specific TCH system was designed to deploy 48 FlexHeaters®, installed within FlexHeater® well casings, spaced apart in 5.5-foot increments. FlexHeater® well casing construction details are provided in **Appendix A, Figure M-1**.

A total of four temperature monitoring points (TMPs) with four sensors each were installed to monitor heating progress through the heated depth to help guide optimization and confirmation sampling efforts. TMP details are provided in **Appendix A, Figure M-2**.

Table 7. FlexHeater® TCH System Components

Primary System Component	Quantity
TCH Power Control Unit	1
Monitoring, control, and data acquisition system	1
Remote access and control system	1
FlexHeaters®	48
Soil Vapor Extraction Points	9
Temperature Monitoring Points (TMPs)	4 (16 sensors)
TCH Condenser & Cooling Tower Unit	1
Vapor Recovery Blowers	1
Vapor Treatment System – Vapor-Phase Granular Activated Carbon (VGAC)	1

The FlexHeater® TCH VR system brought the steam and volatilized PFAS compounds from the treatment volume to the vapor treatment system. The VR system consisted of a VR header connected to the scrubber and the condensing unit where steam was condensed into water.

Condensate water was treated with LGAC and discharged to a water storage tank. The vapors continued through the VR blower and were sent through VGAC for treatment prior to discharge to the atmosphere. A FlexHeater® TCH system process flow diagram is presented in **Appendix A, Figure P-2**.

5.4.1 FlexHeater® TCH Power Control Unit and Data Acquisition

The FlexHeater® TCH Power Control Unit (PCU) delivered electrical power to the FlexHeaters® to heat the treatment volume. A PCU is best described as a variable transformer system capable of providing a variable power output by adjusting voltage levels to the FlexHeaters®.

Three-phase, 480-volt electrical power was brought in to provide power to the PCU. There was a power pole in the vicinity of the soil stockpiles equipped with pole-mounted, 75-kilovolt (kV) transformers. These transformers were capable of providing up to 225 kilovolt amperes (kVA) for the PCU and auxiliary equipment. Electrical one-line details are presented in **Appendix A, Figure E-1.**

The FlexHeater® TCH PCU was individually housed in a weather-tight steel enclosure that provides both security and electrical insulation. During FlexHeater® TCH operation, the output voltage was reduced to the appropriate level for optimum subsurface heating. As the subsurface was heated, this optimum voltage typically changed, and the PCU was adjusted to match those changes.

PCU control and data acquisition was performed on dedicated computers and associated programmable logic controllers (PLC). Remote data acquisition software was used to collect and store subsurface temperatures, power, voltage, amperage, and operational status data for the entire FlexHeater® TCH system. Off-site project personnel can view and download this information in real time using a high-speed, wireless modem. The software also allowed for control and/or monitoring of power application, vapor condensation, and wastewater pumping functions (as applicable).

The PCU was equipped with an emergency stop (E-Stop) button on the exterior of the PCU, at the operator control panel. Depression of the E-stop immediately terminated power application to the FlexHeaters®. All other functions, such as control computer operation and the VR and treatment system, would not be affected and would remain operational if activated. An additional E-stop button was made available at the main entrance of the equipment compound.

Power delivery to the FlexHeaters® was accomplished directly from circuit breaker panels which were fed from the PCU. Connections between the PCU, circuit breaker panels, and the FlexHeaters® were accomplished using fine strand, weather-rated power cable.

5.4.2 FlexHeater® and FlexHeater® Well Casings

A direct push rig with a vibratory post driver attachment advanced 48 borings and installed 48 casings into the stockpile. The casings were installed to four feet below the bottom of the stockpile. The top of the casing extended 3 feet above the stockpile to allow for the insulating cover. The casings were installed with an approximate 5.5-foot spacing.

5.4.3 Temperature Monitoring Points

Four TMPs provided temperature data collection within the treatment volume. Temperature data from the TMPs was automatically recorded at least once per day. The TMP casing was schedule 80 black iron, installed via direct push rig with 3 feet of casing at the surface. A string of five resistance temperature detector (RTD) sensors were placed in the TMPs casing. TMP details are provided in **Appendix A, Figure M-2**.

5.4.4 Vapor Recovery with Vapor and Water Treatment System

A vacuum was applied to the stockpile during heating and the extracted vapors collected from the stockpile passed through a scrubber and condenser to transfer the majority of extracted PFAS from the vapor phase to a low process water volume. A total of nine vapor extraction points were installed in the stockpile. Granular activated carbon was used for PFAS treatment in both vapor and water. Vapor recovery screen details are provided in **Appendix A, Figure M-3**.

5.5 FIELD TESTING

5.5.1 FlexHeater® TCH System Operations

During initial heating, the vapors consisted mostly of air, but the steam content in the vapors continued to increase during the heat-up period. By the time the soil stockpile reached an average temperature of 100°C, the recovered vapors were expected to contain approximately 60 percent steam and 40 percent air. During the next phase of operations, the steam content slowly decreased and the extraction flow rate at the blower was modified to achieve optimal soil heat-up rates.

Significant removal of water vapor occurred at 100°C; however, the water was expected to have very low levels of PFAS, as most PFAS volatilize at significantly higher temperatures and have strong sorptive characteristics. Once the soil moisture depleted, temperatures increased from 100°C towards the target of 350°C, and PFAS concentrations in the gas phase increased. Once treatment approached completion, the removal rate for PFAS also diminished.

The extracted vapors collected from the stockpile during heating passed through a scrubber where a recirculating flow of 10 to 20 gallons per minute (gpm) of water from a 5,000-gallon storage tank was used to quench and condense the steam from the vapors and capture the volatilized PFAS. A vacuum was applied to the *ex situ* stockpile as soon as the heater borings were turned on to ensure vapor collection throughout operations. The storage tank initially was filled with 2,500 gallons of water before heating started. During the pilot test, the volume of water in the tank began to increase with time by water boiled from the soils condensing inside the scrubber. During heating, the water temperature inside the 5,000-gallon storage tank increased from the recirculation of hot scrubber water. The energy balance model predicted that the temperature of the water in the storage tank could reach 80°C during the phase of the project where water is boiled from the soil, and such temperatures were observed. Temperature of the water of the storage tank was regulated by the scrubber heat exchanger by the site operator.

As the operating temperature of the 5,000-gallon storage tank increased, the temperature inside the scrubber would also increase. This resulted in an increase in the humidity of the exhaust gas from the scrubber. A condenser was located in-line after the scrubber to cool and condense remaining steam from the vapors to allow the vapors to be effectively treated by VGAC.

Although PFAS were not expected to be in the vapors after the scrubber, the VGAC served as a contingency polish vapor treatment method. Bleed air was introduced into the 15 horsepower blower to help reduce the overall humidity before the vapors enter the VGAC, and the heat of compression at the blower also increased the temperature by approximately 8 to 10°C and further drop the relative humidity to approximately 50 percent for effective VGAC treatment.

5.6 SAMPLING METHODS

Scrubber water accumulated inside the water storage tank during operations. Samples of the water from the storage tank were collected bi-weekly and analyzed by modified EPA Method 537 for 24 target PFAS compounds in the Pennell lab at Brown University. The volume of water and concentration data were used to determine the amount of PFAS mass captured by the scrubber during operations.

At various times and temperatures throughout thermal treatment, liquid- and vapor-phase sampling occurred of all compounds listed in Method 537.1 to monitor mass removal and to confirm the absence of PFAS fugitive emissions. Soil samples before, during and after treatment, liquid condensate generated during thermal treatment, and the gas phase samples collected with summa cannisters were analyzed using liquid chromatography tandem mass spectrometry (LC- MS/MS).

PFAS soil sample analysis was performed in the Pennell lab at Brown University. For the field demonstration, 64 field samples were analyzed for PFAS using targeted and untargeted methods in an effort to identify and quantify both parent compounds and reaction byproducts. To perform verification of the targeted analysis performed at Brown University, 20 percent of the field samples was sent to Battelle Memorial Institute (Norwell, MA), a NELAP-certified laboratory,

Sixteen baseline samples were collected and analyzed by modified EPA Method 537 to evaluate the reduction concentration for 24 target PFAS compounds for each soil sampling event. To monitor PFAS reductions following thermal treatment, four soil confirmation samples were collected from each of the four quadrants in close proximity to the location of the original sampling (16 total samples). Soil sampling occurred in accordance the TRS' SOP and final design drawings once the heater wells were turned off.

Stainless steel hand augers were used to collect hot soils. Sample trays containing hot soil were covered immediately and placed on a dedicated sample storage table outdoors to cool in sub-zero temperatures. An infrared thermometer was used to monitor sample temperature. The cooled soils were transferred to laboratory containers once near-ambient temperatures were reached.

5.6.1 Calibration of Analytical Equipment

Separation of PFAS was achieved using a Waters Acquity H-Class ultra-performance liquid chromatograph (UPLC) equipped with a Waters BEH C-18 column with an eluent gradient of ammonium acetate in water or methanol, the same as described in EPA Method 537.1 (Shoemaker et al., 2009). Prior to sample analysis, the initial calibration must achieve the following criteria:

- Signal to noise ratio of 10:1 for all quantification ions
- Percent RSD of the response factors for all analytes is less than 20 percent
- Calibration curve is linear with an r2 = 0.99
- Peak asymmetry factors at the mid-level CAL standard between 0.8 and 1.5.

The minimum reporting level (MRL) for each PFAS was established by fortifying, extracting, and analyzing seven (7) replicate samples at the proposed MRL. The MRL was determined based on the prediction interval of result (PIR) using the mean and standard deviation of the replicates as described in EPA Method 537.1 (Shoemaker et al., 2009).

5.6.2 Quality Assurance Sampling

A MB was included with each analytical batch to demonstrate that the experimental systems were free of background PFAS contamination. A MS and an MSD were prepared with each batch of extracts by adding a trace-level PFAS standard to the background solution or solids used in each experiment. The MS and MSD were used to demonstrate that the percent recovery was within 70 percent to 130 percent, and the RPD was less than 30 percent. Isotopically labelled PFAS extraction standards paired with each PFAS (e.g., M8-PFOA when PFOA is present) were added to each sample as an internal standard to monitor the extraction process. Instrument response to the labelled PFAS were used to show that recoveries were between 50 percent and 150 percent of added amounts, if recoveries were outside these limits, the sample result was discarded. The Pennell lab was able to detect 40 PFAS, precursors, and C-13 labeled standards with a total run time of approximately 10 minutes and detection limits ranging from 5 to 20 ng/L (ppt). Non-targeted analysis of high molecular weight, low volatility PFAS were analyzed in triplicate using UPLC interfaced to a high-resolution mass spectrometer (Thermo Qexactive HFX Orbitrap) which provided resolution of 70,000 over mass-to-charge (m/z) range of 85-1,250 (Go et al., 2015). To achieve a broad range of PFAS coverage, separation was achieved using a dual column chromatography scheme that incorporates a C-18 column with negative ESI and hydrophilic interaction liquid chromatography (HILIC) column with positive ESI. Due to these high-resolution capabilities, the need for analyte separation or fragmentation was minimized, allowing for identification of specific byproducts in full scan mode. Details of the analytical approach and data analysis methodologies used to identify unknown species were presented in Walker et al. (2016). The SOP for PFAS Sample Collection, Preparation, and Analysis are included in **Appendix B**.

5.6.3 Documentation Procedures

Daily entries in field sampling logbooks included, at a minimum, names and affiliations of personnel on-site, the day's goals or objectives, the day's weather conditions, the level of personal protective equipment being donned that day, and a chronological account of the day's sampling-related events.

5.6.4 Sample Documentation

At the time of collection, sample information was recorded into the field logbook and onto the sample collection jar. Information recorded included:

- Sample ID
- Sample location
- Collection date and time
- Depth interval of the sample

Sample information was entered into a master sample summary spreadsheet daily. Entry of sample information to digital media allowed for a quality control check of sample information.

A chain-of-custody (COC) was submitted inside the cooler containing the samples. The COC included for each sample, at a minimum, the sample identifier, a location identifier, sample collection date and time, samplers' initials, preservative, and analysis requested. The COC was signed by the individual packing the cooler and placed in the cooler inside of a resealable plastic bag and attached to the inside of the lid. Coolers were sealed with signed custody seals to provide evidence of tampering with the contents of the cooler. Custody seals were signed by the individual signing the COC. Coolers were expedited to the lab as quickly as possible by air courier (*e.g.*, FedEx overnight). A technician at the laboratory ensured custody seals displayed no evidence of tampering before opening the cooler. The technician then signed the COC as recipient of the samples. They immediately recorded the temperature of the cooler's temperature blank on the COC or cooler check-in form.

Sample processing and transfers were monitored within the Brown mass spectrometry laboratory using a sample handling log. The log included the name of the individual(s) handling the sample(s), identifiers for the sample(s) being handled, amount of material removed or transferred, and the reason for handling. Samples were stored at or below 4°C until extraction but was not frozen. Samples were extracted and analyzed as outlined in Table 4 above. Acquired data were processed by the individual performing the analysis and submitted to the Brown Mass Spectrometry Laboratory manager for review and subsequent distribution. A portion of samples (see **Section 5.5**) were shipped to a NELAP-approved reference laboratory (Battelle Memorial Institute, Norwood, MA) to confirm the accuracy of analytical results. Shipment of samples to the reference laboratory was accompanied by the COC form required by the reference laboratory. Reference laboratory results were submitted to the Brown Mass Spectrometry Laboratory Manager for review, comparison, and distribution.

5.7 SAMPLING RESULTS

5.7.1 Pre-Demonstration Sampling

The soil stockpiles at Eielson AFB have been characterized extensively (Brice and AECOM, presentation: F35 PFOS/PFOA Stockpile Characterization, Eielson RPM Meeting, 26 Aug 2020). Stockpile 377-2 is among the ones characterized, showing 31% fines, which is a typical value for the many soil piles. Fines are defined by the fraction passing a #200 sieve (openings of 0.075 mm, passing particles smaller than 0.063 mm). Data showed that 24% passed the #200 sieve, so the soil had slightly less fines than the sample in the Brice/AECOM report. It is still in range with the average soils in the many stockpiles.

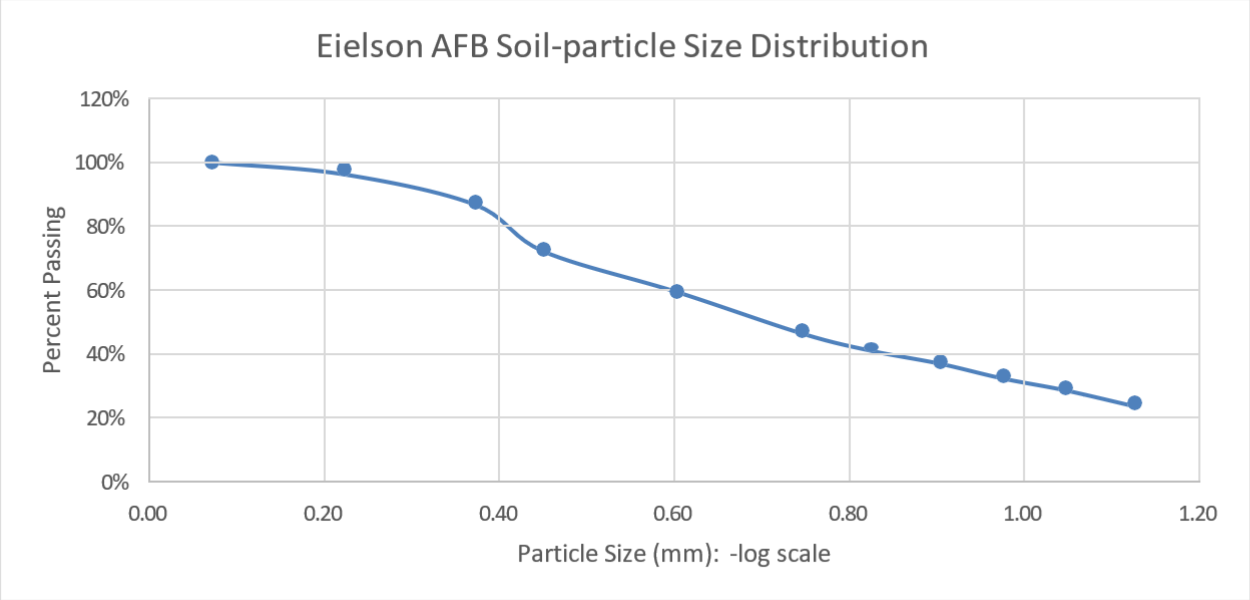


Figure 8. Particle Size Distribution from Dry-Sieving

As shown in **Figure 8**, the #200 mesh sieve passed 24% of the soil as fines.

The soil from stockpile 377-2 was analyzed for organic carbon (triplicate samples) at Brown University. Measured TOC was 1.66 g/kg (0.166%) with a standard deviation of +/- 0.22 g/kg (0.022%). There was no measurable inorganic carbon (the soil weight before and after acidification was identical). The Brice/AECOM report did not contain TOC data for comparison, but the measured value is typical for non-organic topsoil.

Soil data on PFAS concentrations is presented in Section 5.7.3.

5.7.2 Technology Performance Sampling

As shown in **Figure 9**, stockpile extracted vapors collected with OTM-45 were analyzed with targeted analysis showing the highest PFAS removal on October 22, 2021, and November 5, 2021, primarily composed of PFHxA, although PFPeA, PFOA, FOSA, and 6:2 FTS were also detected at higher concentrations.

Results from OTM-45 sampling are provided in **Appendix C**.

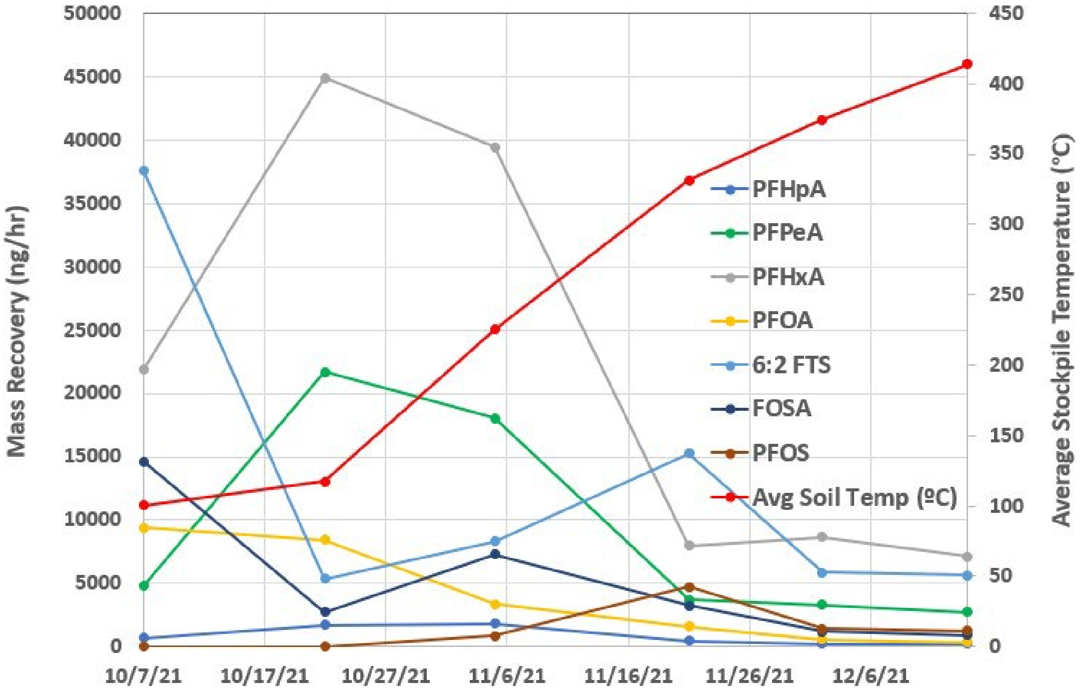


Figure 9. PFAS Mass Recovery Detected by OTM-45

As shown in **Figure 10**, the high concentration in the first samples (September 24, 2021, and September 30, 2021) were primarily due to FOSA which made up 98% of the high starting value (7,413 ng/min on September 24). Note that the soil temperature at this time was approaching 100ºC where we would expect the lighter PFAS compounds to volatilize.

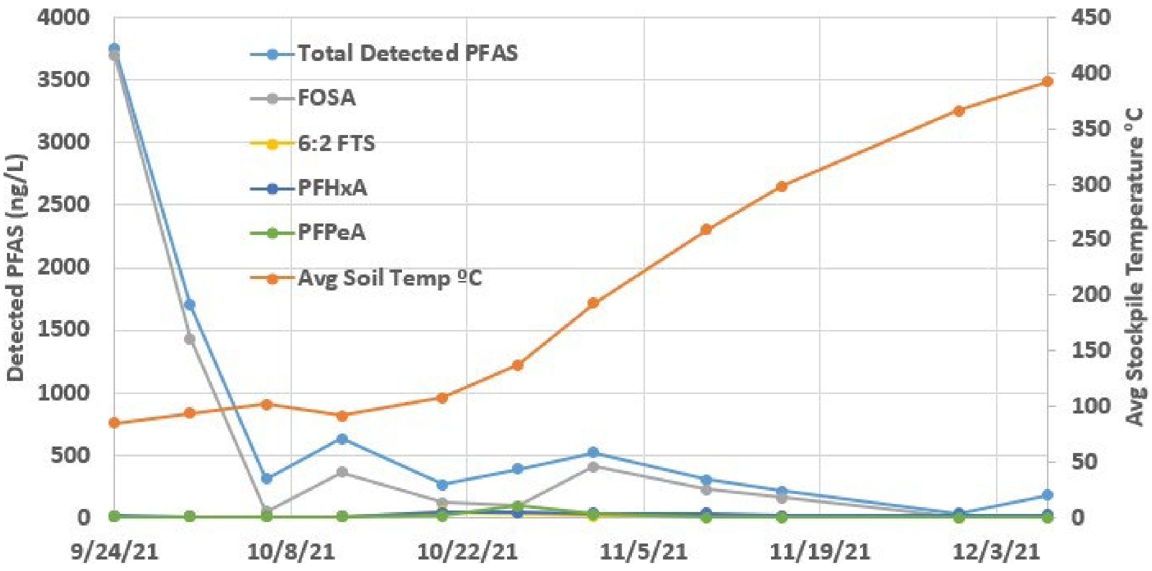


Figure 10. Detected PFAS in Scrubber Effluent Prior to GAC Treatment

Figure 11 shows the mass flux of detected PFAS in the water from the scrubber. The early high numbers represent the time where FOSA dominated. Later in the heating period, as temperatures rose above the boiling point of water to the 150-200ºC range in early November, a small peak seems to be observed. The FOSA fraction was still 75-78%, but other PFAS such as PFOA, 6,2-FTS, PFHxA and PFPeA were detected in significant concentrations (**Figure 10**). Note that the scrubber water contained very little PFOS during all sampling events other than the final one where PFOS made up less than 8% of the detected PFAS.

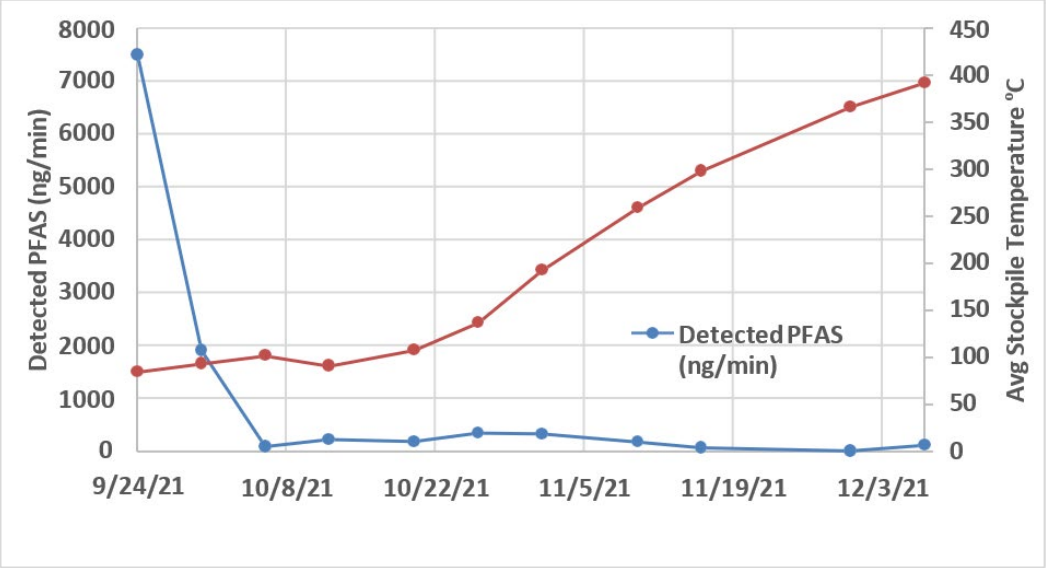


Figure 11. Mass Flux of Detected PFAS in Scrubber Effluent Prior to GAC Treatment

All post water treatment samples (LP-2) analyzed by Brown and Battelle were below detection limits.

The secondary stockpile temperature axis in **Figure 9**, **Figure 10**, and **Figure 11** represents the average measurement of all temperature sensors distributed across the soil stockpile, with some sensors above and below the average temperature. The decrease from 9/24 to 10/8 is presumed to be due to PFAS that would more readily removed in moisture laden vapors near or at the boiling point of water being extracted and depleted.

5.7.3 Post-Demonstration Sampling

Soil sampling performed before and after thermal treatment showed reductions in PFAS, including PFOS and PFOA. All soil samples collected post thermal treatment were below detection limits for PFOA. The concentrations of PFOS before and after thermal treatment area shown in **Figure 12**. Substantial reductions were observed across the stockpile. Post thermal treatment average discrete PFOS concentrations across the stockpile aligned well with the composite concentration shown in **Figure 13**. Post thermal treatment, a composite 4.1 µg/kg was achieved.

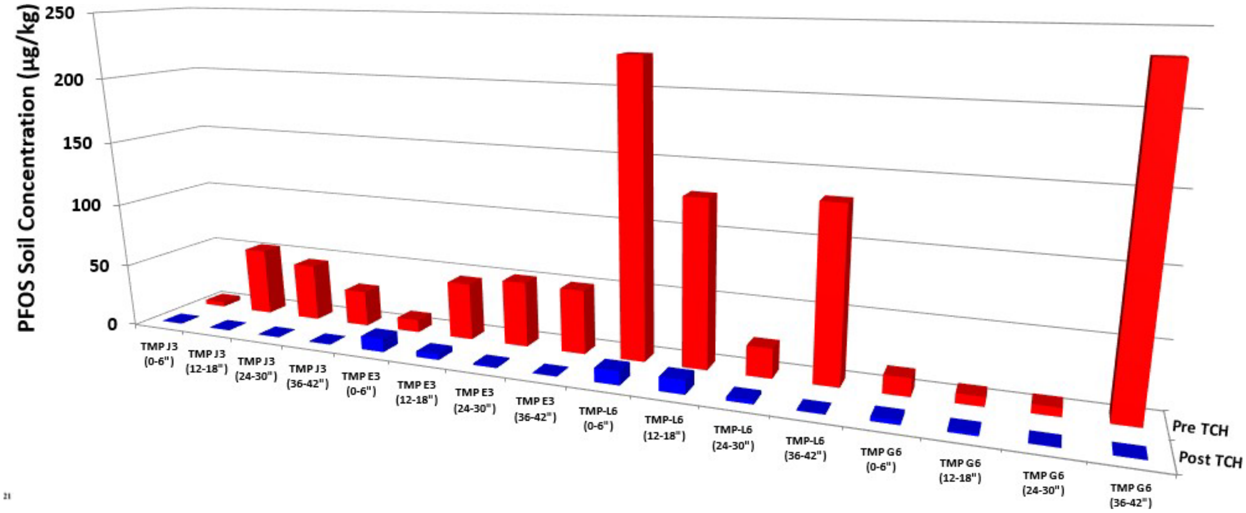


Figure 12. PFOS Soil Concentrations Before and After Thermal Treatment

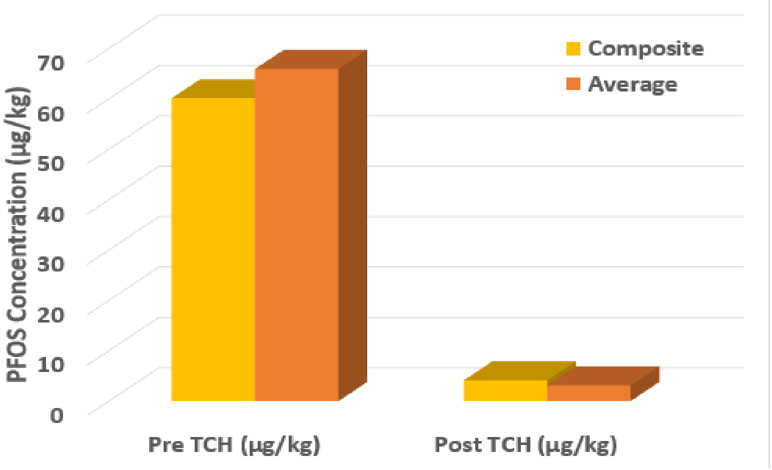


Figure 13. PFOS Concentration in Soil Samples Before and After Thermal Treatment (average of 16 samples and a composite sample shown)

The highest concentrations detected post thermal treatment were at the shallowest locations in the stockpile, which were the slowest locations to heat. The soil sample with the highest PFOS concentration at TMP E3 0 – 6”, was subsequently heated to 400ºC in the laboratory, resulting in a concentration less than detection limits of 1 µg/kg.

In **Figure 14,** the PFOS concentrations of all soil samples were plotted against days above 400ºC. It is noteworthy that samples exposed to temperatures above 400ºC for the most amount of time were below PFOS detection limits.

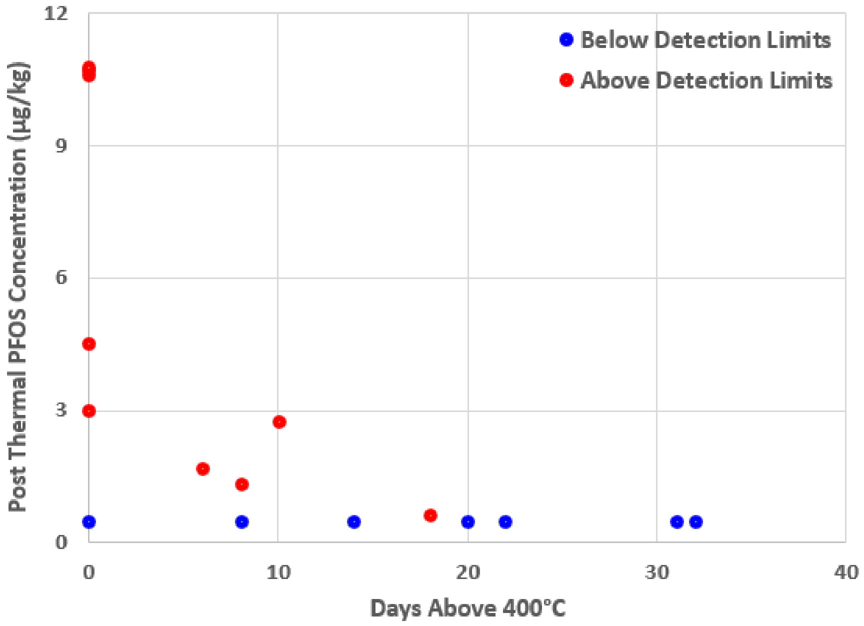


Figure 14. Post-Thermal PFOS Concentration Analysis

5.8 DATA ANALYSES

Data collection and corresponding analytical methods are described in the Performance Objectives sections. Data were analyzed to evaluate PFAS removal from the stockpile and efficiency of PFAS treatment in vapor and aqueous phases using GAC. The energy balance evaluated during operations was calibrated based upon actual heat-up trends observed in the stockpile for empirical verification and calibration of the thermal model.

6.0 PERFORMANCE ASSESSMENT

6.1 EVALUATE PFAS RELEASE RATE AND BYPRODUCT FORMATION

Additional analysis is underway to complete the assessment of this performance objective.

6.2 DETERMINE REMEDIATION EFFECTIVENESS SOIL CONCENTRATIONS

The remediation effectiveness soil concentration performance assessment showed the following:

- Substantial PFAS concentration reduction can be achieved at or near 350ºC. Treatment at this temperature should occur for more than a week to optimize reductions.
- Reaching 400ºC at all locations is optimal to achieve PFOS concentrations below detection limits.
- PFOA concentrations below detection limits can be achieved at slightly lower temperature ranges
- No accumulation of other targeted PFAS compounds in the soil was found.

6.3 DETERMINE REMEDIATION EFFECTIVENESS STOCKPILE TEMPERATURES

As shown in **Figure 15** and **Figure 16**, the remediation effectiveness stockpile temperature performance assessment showed the following:

- The stockpile achieved the boiling point of water at atmospheric pressure by day 36 of operations.

- A 36-hour power outage on day 20 of operations impacted the heating infrastructure which required repairs. Once the heaters were fully operational, the stockpile continued heating up at the anticipated rate, achieving an average stockpile temperature of 415.8ºC.

- The shallowest temperature sensors experienced the greatest heat losses that were impacted by the level of vacuum applied to the stockpile and were the slowest locations to heat up.

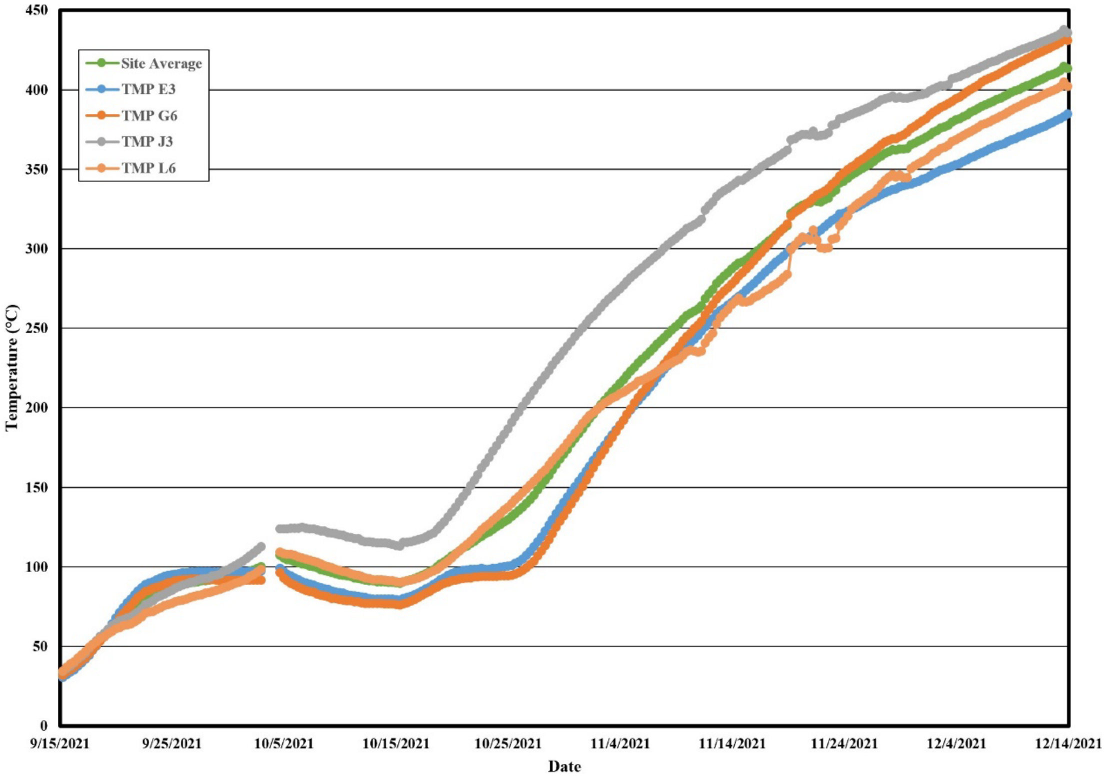


Figure 15. Average Temperature at Each Monitoring Point

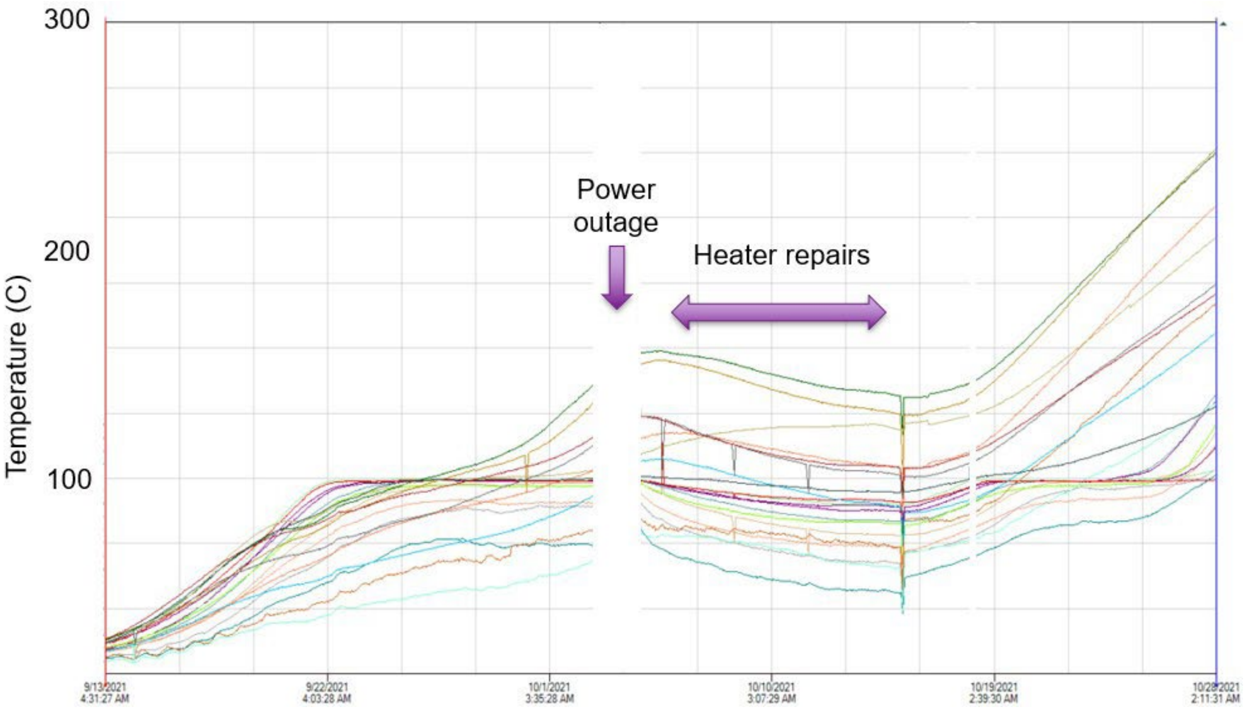


Figure 16. Soil Stockpile Temperatures for the Period Where a Power Outage Affected the Heating (individual sensors shown).

6.4 DETERMINE REMEDIATION EFFECTIVENESS VAPOR TREATMENT

Additional analysis is underway to complete the assessment of this performance objective. We note that no detectable PFAS was emitted through the stack and that the peak in PFAS concentrations was captured.

6.5 DETERMINE REMEDIATION EFFECTIVENESS OF CONDENSATE TREATMENT

The condensate treatment performance assessment showed the following:

- Treated liquid samples below acceptable level: All effluents from the water treatment system showed PFAS below the detection limits.
- Removal efficiency above 95% when inlet concentrations are high: This was demonstrated, as there was never detectable PFAS in the treated effluent.
- Capture the peak for extracted PFAS compounds: Per **Figure 10**, a detailed picture of the variation in different PFAS compounds was obtained. A peak in concentration was observed near the middle of the operational period.

All performance objectives related to condensate treatment were satisfied.

6.6 DETERMINE ENERGY EFFICIENCY

TRS applies our proprietary HeatWave™ model to calculate the heat-up rate and treatment timeframe required to achieve project goals. The model performs energy balance calculations to determine how much energy is required to successfully heat up and strip contaminants from the subsurface, while accounting for surrounding heat losses. TRS has refined and calibrated the model with over 20 years of site data from more than 160 ISTR projects.

The model predicts heat losses in all directions, energy removed in water and vapor streams and net energy delivered to the subsurface. The energy balance accounts for energy delivered into the subsurface in the categories listed below. The heating and heat losses are described in **Figure 17**. The model accounts for:

- Specific heat: the amount of energy required to heat the subsurface to the target temperature
- Latent heat: the amount of energy used to create steam and remove the soil moisture such that temperatures can increase above the boiling point of water
- Conductive heat loss: the energy lost to the surroundings by conductive heat transfer (through the cover, the sides, and to the soil below the pile)
- Convective heat loss: the energy lost at the surface due to natural and forced convection
- Advective heat removal: energy removed by hot air removal

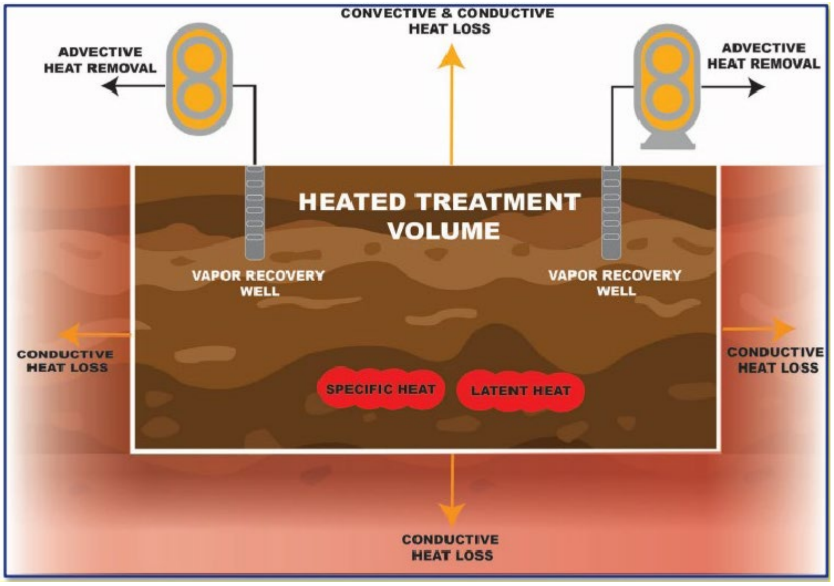


Figure 17. Energy Balance Illustration

The energy delivered by the heaters is not shown is **Figure 17**. Using recorded field data, an actual energy balance was made. This actual balance was based on:

- TCH power delivered to the subsurface, as recorded using electrical meters and near real-time recorded voltage and current data for the Power Control Unit. Losses in cables and connections were considered (these were minimal).
- Energy used to vaporize pore water (steam extracted along with air). This energy was estimated based on the quantity of condensate produced in the scrubber system.
- Energy stored in the heated pile and the zone below it. This energy was estimated based on the heat capacity of both soil grains and pore water and the observed subsurface temperatures. After all pore water was removed from the soil, the only stored energy was that in the heated soil matrix/grains.
- Heat losses were estimated as the balance – the energy delivered minus the extracted and stored energy.

Figure 18 shows the predicted energy balance modeled and **Figure 19** shows the actual energy balance observed based on operational data. The total energy delivered was 1.47 million kWh, quite close to the estimated 1.54 million kWh. The energy lost to the surroundings was nearly identical to the predicted value. The only parameter which was significantly different than the predicted value was the energy in the steam – less than expected condensate was recorded. This may be explained by the soil being drier than expected but could also be associated with uncertainty related to the totalizing flow-meter used to quantify the condensate volume and the fact that fluids circulate through the condensing system, making accurate quantification of the separate streams challenging.

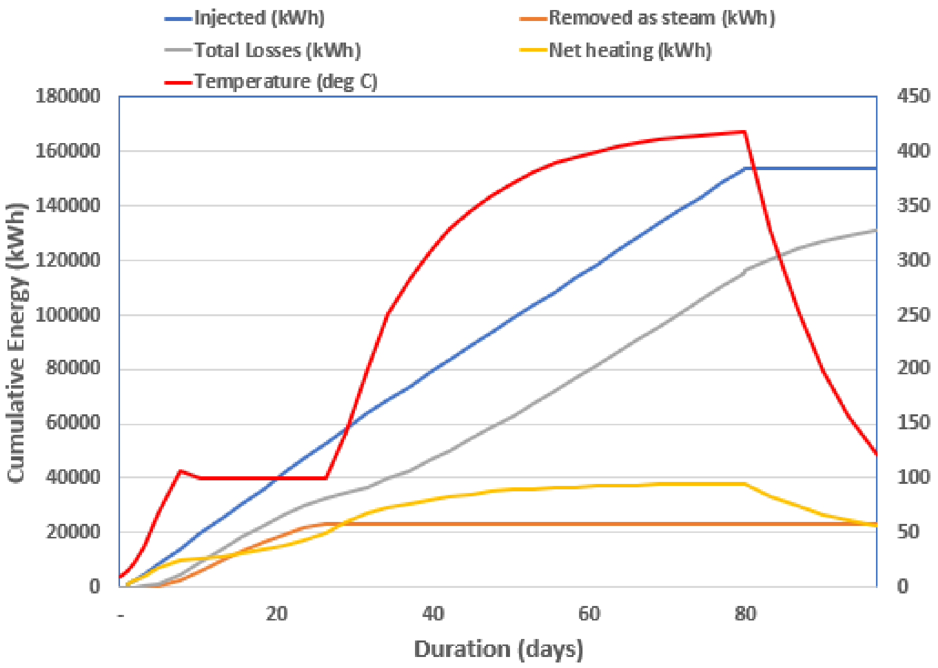


Figure 18. Predicted Eielson ESTCP Field Demonstration Energy Balance

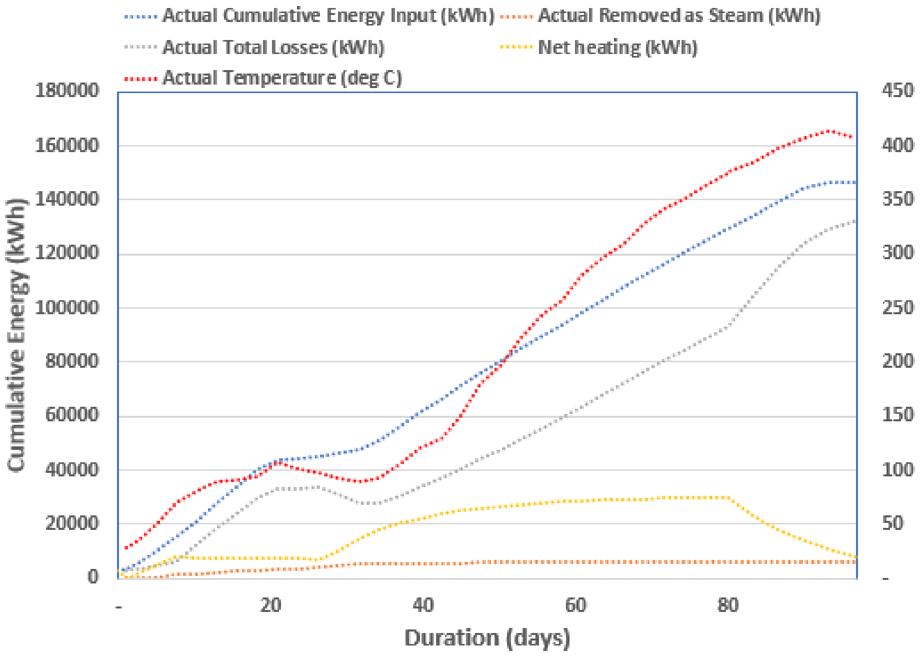


Figure 19. Actual Eielson ESTCP Field Demonstration Energy Balance

Overall, the energy balance shows that the power and energy required for the TCH process to treat PFAS is readily predictable if good data on starting moisture content is available.

6.7 EASE OF USE ASSESSMENT

For this qualitative performance assessment, the field demonstration was shown to be successfully implemented with primarily one field technician on site. While the power outage induced challenges to the heating infrastructure, subsequent repairs allowed successful completion of the remediation. The majority of challenges for field technicians were related to operation of the system during winter at Eielson AFB, including water management, snow removal, and maintaining warm conditions within the treatment compound.

6.8 SAFETY EVALUATION

The safety evaluation qualitative performance assessment showed that the field demonstration was safely implemented.

6.9 TIMING ANALYSIS

The timing of the sampling during operations successfully identified the peak PFAS mass removal during operations.

7.0 COST ASSESSMENT

To the extent possible, the expected operations costs of the technology were evaluated. Installation, operations, demobilization, and electricity costs were evaluated at locations, primarily in the contiguous United States for the cubic yard rates in **Table 8** of stockpiles in reasonable range for treatment.

Table 8. Cost Model for *Ex Situ* Thermal Remediation

Cost Element	Data to be Tracked	Costs
Design, Site Preparation & Installation	• System design • Preparation of stockpile and surrounding area • Dig permit/utility locates • Installation of remediation system – Onsite labor and equipment – Drilling – Electrical system connection – Insulating cover – System installation	• $295/yd^3$ - $375/yd^3$
Operations, Sampling & Analysis	• Field technician to support operations • Equipment rental for operations • Carbon usage for vapor and liquid treatment • Collection of soil, condensate samples • Shipment of samples to laboratory(ies) • Analysis by the laboratory(ies) • Data reporting	• $145/yd^3$ - $185/yd^3$
Decommissioning & Waste Disposal	• Equipment operator and equipment to decommission and dismantle the treatment system • Soil disposal not required • Recycling of reusable parts • Local landfill for all other materials	• $40/yd^3$ - $50/yd^3$
Electricity	• Electricity to power the thermal treatment system	• $30/yd^3$ - $175/yd^3$

7.1 COST MODEL

To provide a simple cost model for remediation professionals to understand costing implications, key cost drivers were analyzed, including soil volume to be treated, energy requirements, and electricity rates.

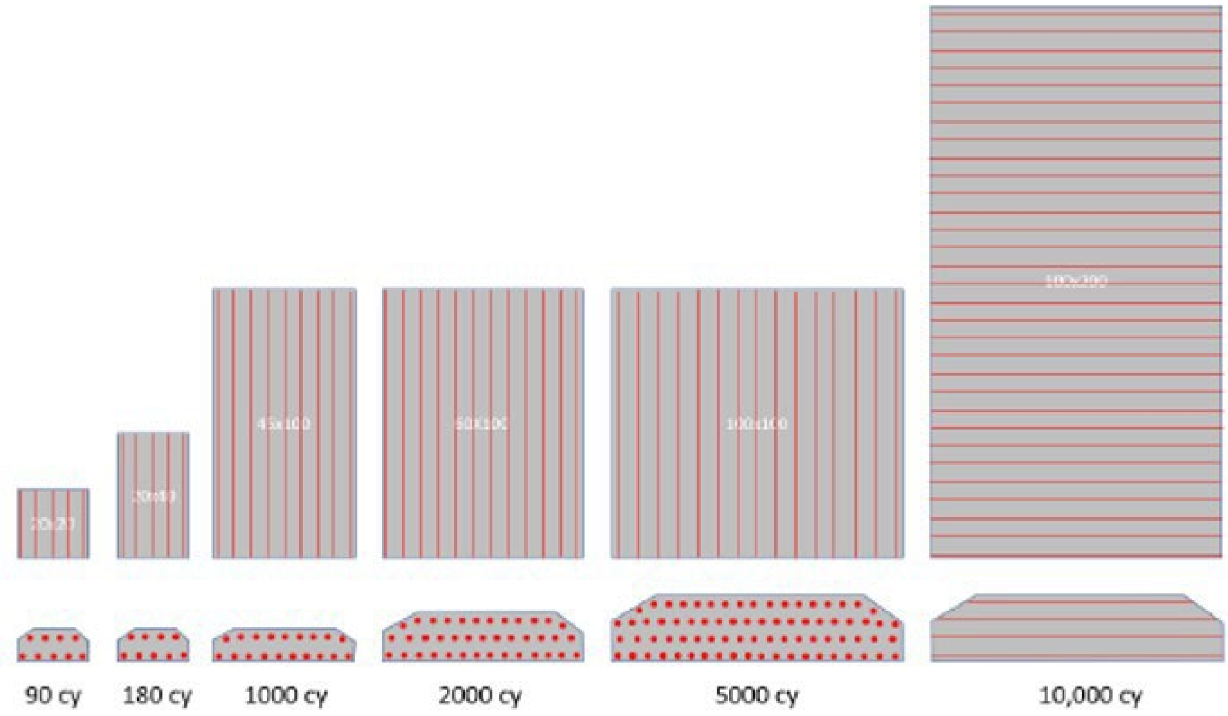


Figure 20. Cost Model Soil Volume Scenarios Showing Cross-sectional Concepts.

Heaters are shown as red dots and lines.

Multiple soil volumes and stockpile dimensions were evaluated, which are shown in **Figure 20**.

The impact of the *ex situ* soil treatment volume on the total heater length required to reach a target temperature of 400ºC is shown in **Figure 21**.

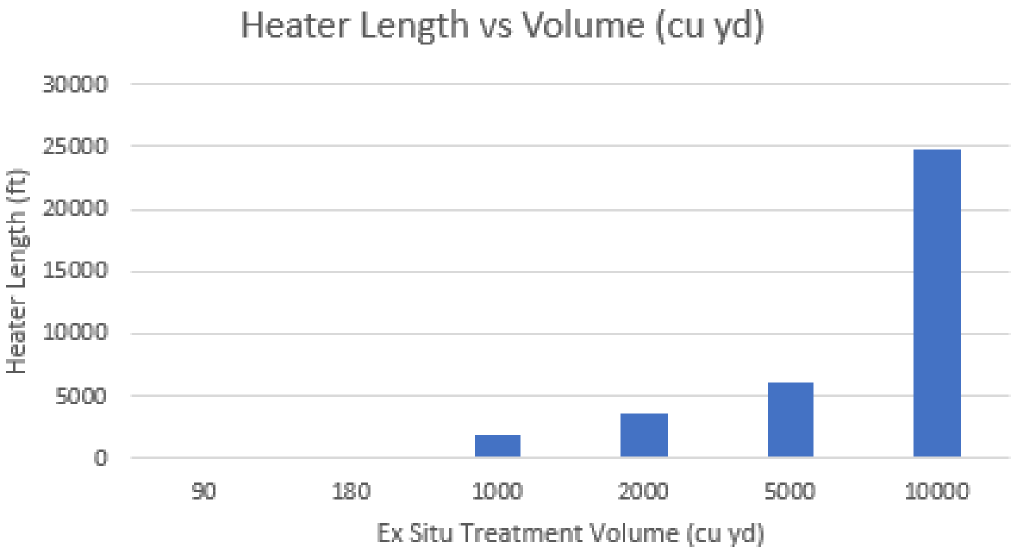


Figure 21. Total Heater Length vs Ex Situ Treatment Soil Volume

The impact of the *ex situ* soil treatment volume on the total energy required to reach a target stockpile temperature of 400ºC is shown in **Figure 22**.

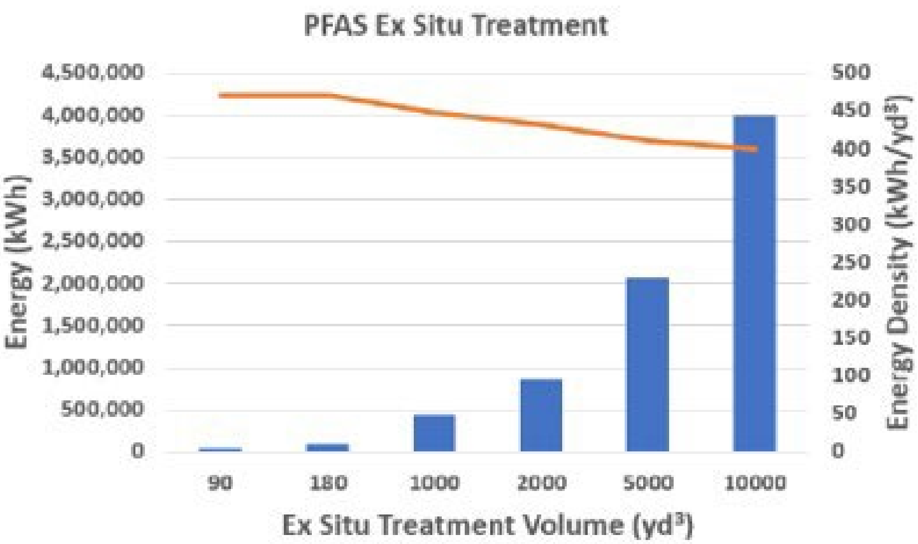


Figure 22. Energy Requirement vs Ex Situ Treatment Soil Volume

Energy is a significant percentage of the overall remediation cost. Increasing the *ex situ* treatment volume shows the economy with scale. The energy density shown in the orange line in **Figure 22**, shows that the overall kilowatt-hours per cubic yard decreases with increasing treatment volume. This is largely due to a decrease in the area to volume ratio of the treated soil and the associated heat losses.

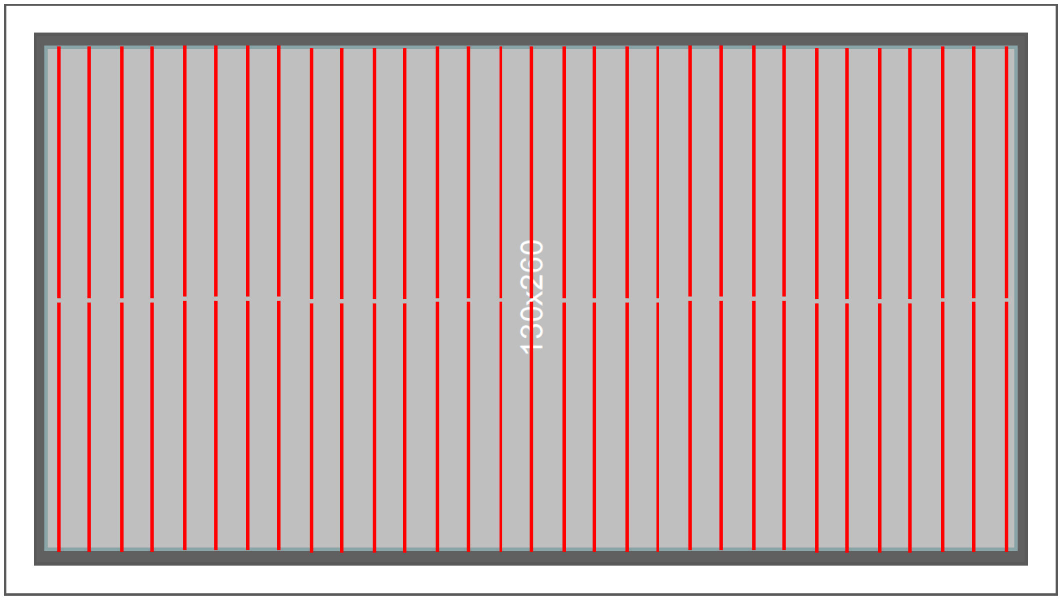
7.2 COST DRIVERS

Location is one of the most significant cost drivers. Particularly for sites that are not part of the contiguous United States, mobilization and shipping costs are substantially higher than the remaining states. Electricity rates also vary significantly by location, ranging between \$0.04/kWh and \$0.22/kWh.

7.3 COST ANALYSIS

For the cost analysis, the following *ex situ* treatment conditions were modeled:

- 15,000 yd^3 soil stockpile
- Area ~ 34,000 square feet
- Pile height ~ 12 ft
- Heating Infrastructure: 208 horizontal heaters, 65 feet long
- Remediation Time Frame: 210 days of heating



Top view of pile. Approximate pile dimensions: 260 feet by 130 feet.

Figure 23. 15,000 yd^3 Stockpile Dimensions and Heater Layout

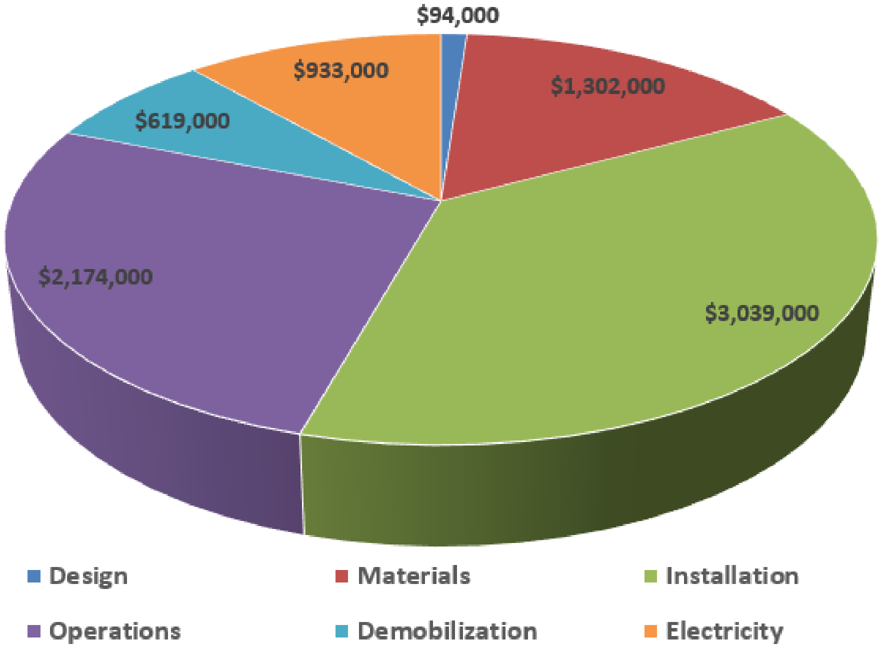


Figure 24. 15,000 yd^3 Cost Scenario Modeling

Table 9 Shows the Cost Modeling Conveyed in **Figure 24** and **Figure 25.**

Table 9. Cost Summary for 15,000 yd^3 *Ex Situ* Thermal Remediation

Ex Situ Treatment Remediation Costs for 15,000 yd^3 Soil Stockpile	
Design	$94,000
Materials	$1,302,000
Installation	$3,039,000
Operations	$2,174,000
Demobilization	$619,000
Electricity	$933,000
Total	$8,161,000

When comparing costs of PFAS thermal treatment to other technologies, it was identified that a traditional technology currently does not exist for PFAS treatment of soil fines. Thermal treatment is an existing technology that has been shown to be successful for other compounds at various temperature ranges. When thermal treatment is applied at temperature ranges up to 400ºC, it is a viable technology for PFAS treatment.

Cost savings were integrated by modeling the system prior to installation, to help ensure that only the necessary heating infrastructure was installed and energy applied to achieve the target temperatures. The energy balance modeling and heat-up rate prediction aligned well with what was observed during the field demonstration.

8.0 IMPLEMENTATION ISSUES

For future ex situ PFAS soil treatments, sufficient power availability and reliability are important considerations when considering implementation. If sufficient power is not available, additional electricity sources can be installed, however scheduling and funding evaluations should be performed to assess project feasibility.

Water source availability for the vapor and liquid treatment process equipment should be considered for implementation. Treated process water discharge and treated vapor emission requirements are also important implementation issues to consider to ensure the sampling methodology and process treatment equipment is sufficient to be in compliance with all regulatory requirements.

A working area sufficient for the ex situ soil treatment and process equipment will be required for implementation. Weather impacts during installation and system operations should also be considered, including winterization requirements and whether shelter for the equipment and ex situ cell are necessary.

The ultimate disposal requirements for PFAS impacted carbon that is generated from the vapor and liquid treatment system is a potential implementation issue. The identification of a viable source for PFAS impact carbon should be considered for implementations.

The planned use for soil after thermal treatment should be considered to ensure a plan is in place for necessary moisture, nutrient, and organics addition to allow reuse of the soil.

Future evaluation of the addition of calcium oxide (CaO) or calcium hydroxide (CaOH) is an optimization strategy for lowering the target temperature for thermal treatment. Even distribution of these additives would need to be considered for implementation.

9.0 REFERENCES

A list of project contacts is included as **Appendix D**. Works cited are listed below:

Alaska Department of Environmental Conservation. 2018. 18 AAC 75 Oil and Other Hazardous Substances Pollution Control, Formal Proposed Amendments, Public Comment Draft. October 1.

Alaska Department of Environmental Conservation. 2019. 18 AAC 75 Oil and Other Hazardous Substances Pollution Control. January.

Alaska Department of Environmental Conservation. 2019. Technical Memorandum, Action Levels for PFAS in Water and Guidance on Sampling Groundwater and Drinking Water.

Crownover, E., Oberle, D., Kluger, M., Heron, G. 2019. Perfluoroalkyl and polyfluoroalkyl substances thermal desorption evaluation. Remediation Journal, 29, 77-81.

DiGuiseppi, W., Richter, R., and Riggle, M. 2019. “Low Temperature Desorption of Per- and Polyfluoroalkyl Substances.” The Military Engineer, January-February, 2019, vol 111, no. 719, pp 52-53.

Shoemaker, J.A., Grimmett, P.E., Boutin, B.K. Method 537. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). EPA/600/R-08/092. Version 1.1 September 2009.

US Environmental Protection Agency.2020. Regional Screening Levels, Hazard Quotient 0.1. May.

APPENDIX A PILE 377-2 TCH AS-BUILT DESIGN PACKAGE

(Due to confidential information, Appendix A can be accessed by able parties through DTIC)

APPENDIX B STANDARD OPERATING PROCEDURE FOR PFAS SAMPLE COLLECTION, PREPARATION, AND ANALYSIS

Standard Operating Procedures for PFAS Sample Collection, Preparation, and Analysis Ex Situ Thermal Treatment of Perfluoroalkyl and Polyfluoroalkyl Substances

(ESTCP Project ER20-D1-5198)

1. Sample Collection

Samples will be collected from laboratory-scale batch, column, and aquifer cell systems where technical grade PFAS precursors are introduced and degradation products are produced. Aqueous and solid samples will be analyzed to determine concentrations of PFAS precursors and degradation products.

a. Equipment/Supplies

2 mL polypropylene (PP) centrifuge tubes 15 mL PP centrifuge tubes

3 mL PP syringe with rubber plunger and stainless-steel needle 50 mL and 100 mL high-density polyethylene (HDPE) bottles

Isotopically labelled PFAS from Wellington Laboratories LLC (Overland Park, KS)

b. Collection Process

Aqueous effluent samples will be collected with a fraction collector during column experiments in 15 mL PP centrifuge tubes. Additional aqueous samples will be collected from batch and aquifer cell systems using a 3 mL PP syringe with stainless steel needle and placed into 2 mL PP centrifuge tubes. Solid (soil) samples will be collected from batch, column, and aquifer cell systems and transferred into HDPE bottles.

c. Decontamination Procedures

Syringes will be used once and discarded, or they will be rinsed with methanol followed by ultrapure water before collecting each sample. The PP centrifuge tubes and HDPE bottles will be used once and discarded.

d. QC Samples

The isotopically-labelled PFAS extraction standards paired with each PFAS introduced (e.g., M8-PFOA when PFOA is present) will be added to each sample as an internal standard to track the extraction process (i.e., extracted internal standard). The instrument response to the labelled PFAS will be used when recoveries are between 50% and 150% of added amounts (Table B-15, DOD/DOE QSM 5.1.1). If recoveries are outside these limits, the sample result will be discarded.

A method blank (MB) will be collected using the procedures described in section 1.b. during each sampling event from either the uncontaminated background solution or solids being utilized in the experiment. A Laboratory Control Sample (LCS) is a blank spiked with all analytes at a concentration ≥LOQ and mid-level calibration concentration. One LCS is analyzed per preparatory batch. LCS recoveries must be within ±50% true value. When an LCS fails to meet acceptance criteria, correct the problem and then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes if sufficient sample material is available. A matrix spike (MS) and a matrix spike duplicate (MSD) will be prepared with each batch of samples by adding a low-level PFAS standard to the background solution or solids being used in each experiment. The MS and MSD will be used to show that the % recovery is within 70% to 130%, and the relative percent difference (RPD) is less than 30% (Table B-15, DOD/DOE QSM 5.1.1).

e. Sample Preservation, Shipping, and Hold Times

The PP centrifuge tubes and HDPE bottles will be placed in a 4 °C refrigerator immediately after sample collection. Aqueous samples will be analyzed within 28 days of collection. Solid samples will be extracted within 14 days of collection and extracts will be analyzed within 28 days of extraction.

2. Sample Preparation

Aqueous samples used for PFAS analysis will be prepared by collecting a small volume from each PP centrifuge tube and diluting this in a 2 mL autosampler vial to a final 80:20 water to methanol mix. Internal standard is added to the vial immediately following sample transfer. Solid phase extraction (SPE) of the aqueous sample will not be employed as there will be insufficient volume of aqueous sample available (i.e., much less than 250 mL).

Soil samples for PFAS analysis are washed three sequential times and subjected to solid-phase extraction using WAX/GCB cartridges prior to analysis by LC-MS/MS.

a. Equipment/Supplies
LC-MS grade Methanol (Honeywell Burdick & Jackson)
Solid Phase Extraction (SPE) cartridges (e.g. PFAS WAX/GCB) HPLC grade water (Honeywell Burdick & Jackson)
2 mL glass autosampler vials Pipette with PP tips Centrifuge

b. Preparation Technique

For aqueous samples, each PP centrifuge tube containing an aqueous sample will be centrifuged at 4,000 rpm for 20 min to remove suspended solids. Thereafter, a 100 µL aliquot will be transferred from each PP centrifuge tube by pipette with PP tip and placed into a 2 mL glass autosampler vial. The 100 µL aliquot will be diluted by adding 700 µL of HPLC grade water and 200 µL of internal standard in methanol. Each sample will be vortexed for 15 seconds to ensure mixing.

Soil samples are weighed into PP centrifuge tubes. Immediately after transfer, internal standard is added. Soil samples for PFAS analysis are washed three sequential times using 50% methanol. With each addition of methanol wash solution, solid samples are vortexed thoroughly, sonicated at 30^{o}C for 30 minutes, placed on a rotator for 30 minutes, centrifuged, and decanted to a clean PP centrifuge tube. The three combined washes are subjected to solid-phase extraction using WAX/GCB cartridges with 0.5% ammonium hydroxide in methanol used as elution solvent. Elution solvent is evaporated at 65^{o}C under nitrogen. Dried samples are then reconstituted prior to analysis by LC-MS/MS.

Internal standard is added to vapor-phase off-gas collections. Samples are then washed three sequential times using 100% methanol, similar to the soils procedure described above. Samples do not undergo SPE, but are dried and reconstituted identical to the soils procedure.

c. Sample QC

For aqueous samples, a Laboratory Control Spike (LCS) must be present during sample collection. The LCS consists of low-level PFAS analytes in water. The LCS must undergo identical preparation procedures to all samples to ensure the entire collection and preparation procedure is evaluated.

3. Sample Analysis

Samples consisting of 80:20 water to methanol and methanol with 400 mM ammonium acetate will be analyzed by liquid chromatography with tandem mass spectrometry (LC-MS/MS).

a. Equipment/Supplies
Waters Acquity ultra performance liquid chromatograph (UPLC) connected to a Waters Xevo tandem quadrupole (TQ)-S micro mass spectrometer (MS).

Dionex DX500 modular ion chromatography system Isotopically-labelled PFAS from Wellington Laboratories, Inc PFAS analytical standards from Sigma-Aldrich

SPEX CertiPrep standards for fluoride

b. Instrument Conditions

Analyte separation will be achieved with a Waters BEH C-18 column (1.7 µm dia., 2.1 × 50 mm) operated at a flow rate of 0.4 mL/min with an eluent gradient consisting of 10 mM ammonium acetate in water. Large volume injection (50 µL) will be employed to improve sensitivity. The Waters TQ-S micro will be operated in the negative electrospray ionization (ESI) mode with desolvation gas (nitrogen) flow at 450 L/hr and temperature of 55°C. Cone gas flow of 30 mL/min and collision gas (argon) flow at 0.2 mL/min. The source temperature will be maintained at 150°C and the electrospray capillary voltage at 0.6 kV. The multiple reaction monitoring (MRM) conditions for select PFAS are given in **Table 1**. These conditions will be optimized during the mass spectrometer tuning.

c. Analytical Standards and Calibration Procedure

The LC-MS/MS system will be mass calibrated using internal standards (sodium iodide and cesium iodide) and tuned to maximize instrument response using PFAS reference standards obtained from Wellington Laboratories who are accredited to produce reference materials [i.e., American National Standards Institute (ANSI) and American Society for Quality (ASQ) National Accreditation Board (ANAB) accredited reference material producer]. The currently used tune and quantification parameters are given in **Tables 1, 2, and 3** at the end of this document.

The initial calibration (ICAL) will be performed, at a minimum, at instrument set-up and after ICV or CCV failure, prior to sample analysis, using at least 5 concentration levels for analytes. Spectra will be acquired at ≥10 scans across each chromatographic peak. When available, isotopically labeled analogs of an analyte are used for quantitation (Isotope Dilution Quantitation). When a labeled analog is not commercially available, an appropriate, labeled internal standard is applied for quantitation. No unknown samples will be analyzed until the initial calibration has achieved the following criteria:

- Signal to noise ratio of 10:1 for all quantification ions
- Ion ratio tolerance of ±50% of the mean calculated from standards
- The calibration curve is linear with an $r^2 \geq 0.99$
- The %RSD of the RFs for all analytes must be <20%

- Analytes must be within 70-130% of their true value for each calibration standard

The Initial Calibration Verification (ICV) will be performed once after each ICAL using analyte standards obtained from a second source. No samples shall be analyzed until calibration has been verified. To meet acceptance criteria, analyte concentrations must be within ±30% of their true value. If the ICV does not meet acceptance criteria, problems should be corrected and the ICV rerun. If the problem persists, the ICAL must be repeated.

Continuing Calibration Verification (CCV) must be performed immediately following the initial calibration, after every 10 field samples, and at the end of the analytical sequence. Concentrations evaluated must range from the LOQ to the mid-level concentration range. Analyte concentrations must be within ±30% of their true value. When CCV fails to meet acceptance criteria, immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.

d. Instrument Cleanliness

Two checks will be used to verify instrument cleanliness as well as to flush out the system after analyzing samples with high PFAS concentrations. One check is a zero-volume injection (i.e., instrument blank) to determine if there is carry-over on the UPLC column

and the other check is the analysis of a PFAS-free 80:20 water to methanol to evaluate carry-over on the LC injection needle. These two checks will be performed after every 10 to 12 sample are analyzed to determine cleanliness of the instrument.

If the check results after a batch of 10 to 12 samples have significantly elevated PFAS concentrations compared to the other check results ($P > 0.05$) then the batch of samples will be analyzed again with additional blank checks included to determine which sample is causing carry-over.

Instrument Blanks containing internal standards must be analyzed after calibration check samples. Blanks must be quantitatively determined with analyte concentrations measuring <1/3 MRL.

e. **Table 4** below represents current LOQ for water and soil samples. Reporting of results requires demonstration adopted MRLs are achievable according to statistical approaches outlined in “Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods” (Winslow et al., 2006). Concentrations reported that fall between the LOD and LOQ must be noted on any report.

References:

Munoz, G., P. Ray, S. Mejia-Avendaño, S. Vo Duy, D. Tien Do, J. Liu, S. Sauvé. 2018. Optimization of extraction methods for comprehensive profiling of perfluoroalkyl and polyfluoroalkyl substances in firefighting foam impacted soils. Analytica Chimica Acta, 1034: 74-74.

Table 1. Waters TQ-S Multiple Reaction Monitoring Conditions for PFAS: Carboxylates.

Compound	Internal Standard	Molecular Ion	Cone Voltage (V)	Collision Energy (V)	Quant. Ion (m/z)	Cone Voltage (V)	Collision Energy (V)	Qual. Ion (m/z)
PFBA	$[^{13}C_4]$ PFBA	213	10	8	169	--	--	--
PFPeA	$[^{13}C_5]$ PFPeA	263	2	5	219	--	--	--
PFHxA	$[^{13}C_5]$ PFHxA	313	4	4	269	4	20	119
PFHpA	$[^{13}C_4]$ PFHpA	363	20	7	319	20	16	169
PFOA	$[^{13}C_8]$ PFOA	413	2	9	369	2	12	169
PFNA	$[^{13}C_9]$ PFNA	463	8	10	419	8	14	219
PFDA	$[^{13}C_6]$ PFDA	513	11	10	469	6	18	219
PFUnA	$[^{13}C_7]$ PFUnA	563	13	12	519	20	18	269
PFDoA	$[^{13}C_2]$ PFDoA	613	15	12	569	4	26	169
PFTriA	--	663	15	13	619	--	--	--
PFTreA	$[^{13}C_2]$ PFTreA	713	14	13	669	--	--	--
Internal Standards								
$[^{13}C_4]$ PFBA		217	10	8	172	--	--	--
$[^{13}C_5]$ PFPeA		268	10	8	223	--	--	--
$[^{13}C_5]$ PFHxA		318	19	7	273	19	7	120
$[^{13}C_4]$ PFHpA		367	20	8	322	20	20	169
$[^{13}C_8]$ PFOA		421	7	9	276	7	16	172
$[^{13}C_9]$ PFNA		472	10	11	427	10	14	223
$[^{13}C_6]$ PFDA		519	11	11	474	11	16	219
$[^{13}C_7]$ PFUnA		570	13	12	525	13	16	270
$[^{13}C_2]$ PFDoA		615	4	11	570	--	--	--
$[^{13}C_2]$ PFTreA		715	20	14	670	--	--	--

Table 2. Waters TQ-S Multiple Reaction Monitoring Conditions for PFAS: Sulfonates.

Compound	Internal Standard	Molecular Ion	Cone Voltage (V)	Collision Energy (V)	Quant. Ion (m/z)	Cone Voltage (V)	Collision Energy (V)	Qual. Ion (m/z)
PFBS	$[^{13}C_3]$ PFBS	299	2	30	80	2	30	99
PFPeS	--	349	15	32	80	15	32	99
PFHxS	$[^{13}C_3]$ PFHxS	399	2	34	80	2	32	99
PFHpS	--	449	14	38	80	14	38	99
PFOS	$[^{13}C_8]$ PFOS	499	4	50	80	4	40	99
PFNS	--	549	10	43	80	10	43	99
PFDS	--	599	2	55	80	2	48	99
Internal Standards								
$[^{13}C_3]$ PFBS		302	15	25	99	15	25	80
$[^{13}C_3]$ PFHxS		402	25	25	99	25	25	80
$[^{13}C_8]$ PFOS		506	15	32	78	10	33	80

Table 3. Waters TQ-S Multiple Reaction Monitoring Conditions for PFAS: Sulfonamide, Telomer Sulfonates, and Sulfonamidoacetatic Acids.

Compound	Internal Standard	Molecular Ion	Cone Voltage (V)	Collision Energy (V)	Quant. Ion (m/z)	Cone Voltage (V)	Collision Energy (V)	Qual. Ion (m/z)
PFOSA	[$^{13}C_8$] FOSA	498	16	32	78	--	--	--
FtS 4:2	[$^{13}C_2$] FtS 4:2	327	5	17	307	5	25	81
FtS 6:2	[$^{13}C_2$] FtS 6:2	427	5	21	407	5	19	81
FtS 8:2	[$^{13}C_2$] FtS 8:2	527	10	26	507	10	35	81
NMeFOSAA	D3MeFOSA	570	5	18	419	5	20	512
NEtFOSAA	D5EtFOSAA	584	5	18	419	5	17	526
Internal Standards								
[$^{13}C_8$] FOSA		506	15	32	78	--	--	--
[$^{13}C_2$] FtS 4:2		329	5	18	309	5	20	81
[$^{13}C_2$] FtS 6:2		429	5	22	409	5	25	81
[$^{13}C_2$] FtS 8:2		529	10	27	509	10	35	81
D3MeFOSAA		573	10	19	419	5	20	515
D5EtFOSAA		589	10	19	419	10	18	531

Table 4. Limits of Quantitation (LOQ) for PFAS measured in water and soil samples.

Analyte	CAS ID	Limit of Quantitation (LOQ)	
		Water (ng/L)	Soil (µg/kg)
Perfluorobutanoic acid (PFBA)	375-22-4	50	1
Perfluoropentanoic acid (PFPeA)	2706-90-3	50	1
Perfluorohexanoic acid (PFHxA)	307-24-4	50	1
Perfluoroheptanoic acid (PFHpA)	375-85-9	50	1
Perfluorooctanoic acid (PFOA)	335-67-1	50	1
Perfluorononanoic acid (PFNA)	375-95-1	50	1
Perfluorodecanoic acid (PFDA)	335-76-2	50	1
Perfluoroundecanoic acid (PFUnDA)	2058-94-8	50	5
Perfluorododecanoic acid (PFDoDA)	307-55-1	50	5
Perfluorotridecanoic acid (PFTriA)	72629-94-8	50	25
Perfluorotetradecanoic acid (PFTreA)	376-06-7	50	5
Perfluorobutanesulfonic acid	375-73-5	50	1
Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	50	1
Perfluorohexanesulfonic acid (PFHxS)	355-46-4	50	1
Perfluoroheptanesulfonic acid (PFHpS)	375-92-8	50	1
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	50	1
Perfluorodecanesulfonic acid (PFDS)	335-77-3	200	25
Perfluorononanesulfonic acid (PFNS)	68259-12-1	200	5
Perfluorooctanesulfonamide (PFOSA)	754-91-6	200	5
Fluorotelomer sulphonic acid 4:2 (4:2 FTS)	757124-72-4	50	5
Fluorotelomer sulphonic acid 6:2 (6:2 FTS)	27619-97-2	50	5
Fluorotelomer sulphonic acid 8:2 (8:2 FTS)	39108-34-4	50	5
2-(N-Ethylperfluorooctanesulfonamido) acetic acid (EtFOSAA)	2991-50-6	50	25
2-(N-Methylperfluorooctanesulfonamido) acetic acid (MeFOSAA)	2355-31-9	50	25
N-methylperfluorooctanesulfonamide	31506-32-8	50	25

APPENDIX C OTM-45 RESULTS

TRS
Methods 2-4 Analysis

Run Number			1	2	3	4	5	6
DGM Volume	V_m	cubic feet	139.228	137.446	143.56	135.939	133.148	134.908
DGM Y Factor	Y	-	0.988	0.988	0.988	0.988	0.988	0.988
DGM Average Temperature	T_m	Degrees R	521	526	517	514	536	520
Barometric Pressure	P_{bar}	Inches Hg	28.75	29.37	29.46	30.27	30.40	30.10
Delta H	ΔH	Inches Water	1.2	1.2	1.2	1.2	1.2	1.2
Sample Volume at Standard Conditions	**V_{mstd}**	**Standard Cubic Feet**	**134.168**	**133.995**	**143.050**	**139.891**	**131.885**	**136.569**
Total Volume of Water collected	V_{lc}	Milliliters	382	1406	842	1356.5	1306.5	875.5
Standard Volume of Water	V_{wstd}	Standard Cubic Feet	17.981	66.180	39.633	63.850	61.497	41.210
Stack Gas Moisture Content	B_{ws}	-	0.1182	0.3306	0.2169	0.3134	0.3180	0.2318
Pitot Tube Coefficient	C_p	-	0.99	0.99	0.99	0.99	0.99	0.99
Average Pitot differential pressure	ΔP	Inches Water	0.45	0.45	0.60	0.75	0.25	0.24
Square Root of Differential Pressure		-	0.671	0.671	0.775	0.866	0.500	0.490
Average Stack Gas Temperature	$T_{s(ave)}$	Degrees R	530	560	610	790	470	744
Measured Stack Pressure	P_g	Inches Water	-15	-14	-15	-16	-4	-7
Absolute Stack Pressure	P_s	Inches Hg	27.6	28.3	28.4	29.1	30.1	29.6
Stack %O_2		%	20.90	20.90	20.90	20.90	20.90	20.90
Stack %CO_2		%	0.10	0.10	0.10	0.10	0.10	0.10
Stack %N_2 + %CO		%	79.0	79.0	79.0	79.0	79.0	79.0
Stack Gas Dry Molecular Weight	M_d	lb/lb mole	28.9	28.9	28.9	28.9	28.9	28.9
Stack Gas Wet Molecular Weight	M_s	lb/lb mole	27.57	25.26	26.50	25.45	25.40	26.34
Actual Average Velocity	V_s	ft/sec	47.3378	50.20	59.06	75.70	33.17	40.51
Stack Diameter		inches	3.07	3.07	3.07	3.07	3.07	3.07
Stack Area	A	sq ft	0.05	0.05	0.05	0.05	0.05	0.05
Standard Stack Gas Volumetric Flow	**Q_{sd}**	**Standard Dry Cubic Feet/min**	**118.518**	**92.6**	**117.0**	**104.2**	**78.9**	**67.4**
Nozzle Diameter		inches	0.216	0.250	0.216	0.216	0.259	0.281
Nozzle Area		sq ft	0.000254	0.000341	0.000254	0.000254	0.000366	0.000431
Sample Time		min	240	240	240	240	240	240
Iso-kenetics		**%**	**95.341**	**91.00**	**102.96**	**113.09**	**97.95**	**100.90**

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