# EXECUTIVE SUMMARY

## Evaluation of Indirect Thermal Desorption Coupled with Thermal Oxidation Technology to Treat Solid PFAS-Impacted Investigation-Derived Waste

SERDP Project ER18-1572

FEBRUARY 2020

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# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| °C | Degrees Celsius |
| % | Percent |
| AFFF | Aqueous film forming foam |
| DRE efficiency | Destruction and removal |
| DT | Demonstration test |
| EA | EA Engineering, Science, and Technology, Inc., PBC |
| EPA | United States Environmental Protection Agency |
| ESTCP | Environmental Security Technology Certification Program |
| FTS | fluorotelomer substances |
| HF | Hydrogen fluoride |
| ITD | Indirect Thermal Desorption |
| kg | Kilogram(s) |
| mg/kg | Milligrams per kilogram |
| PFAS | Per- and polyfluoroalkyl substances |
| PFBS | Perfluorbutane sulfonate |
| PFCA | Perfluoroalkyl carboxylic acids |
| PFHxS sulfonate | Perfluorohexane |
| PFNA | Perfluorononanoic acid |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctane sulfonate |
| PFPeA | Perfluoropentanoic acid |
| PFSA | Perfluoroalkyl sulfonic acids |
| ppb | Parts per billion |
| QC | Quality Control |
| SERDP Program | Strategic Environmental Research and Development |
| TO | Thermal oxidizer |
| TOP | Total Oxidizable Precursor Assay |

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## ACKNOWLEDGEMENTS

EA Engineering, Science, and Technology, Inc., PBC (EA) would like to acknowledge the contributions of TestAmerica and TD*X Associates. Collaboration with TestAmerica was key in ensuring that usable and defensible data were obtained in the exhaust gas during execution of the Demonstration Test (DT) Program. TestAmerica completed this laboratory method development and validation, demonstrating that the six per- and polyfluoroalkyl substances (PFAS) evaluated in the DT Program could be adequately recovered from the Method 0010 sampling train media (i.e., XAD- 2 sorbent resin, condensate impingers, and a second XAD-2 resin trap) following analyses by Environmental Protection Agency (EPA) Method 537. TD*X Associates was vital in development and operation of the DT pilot system used to execute this project and provided extensive knowledge and expertise on the implementation of thermal technologies.

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# 1.0 INTRODUCTION

In May 2017, participants of a Strategic Environmental Research And Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) workshop identified a critical priority to demonstrate the effectiveness and sustainability of thermal destruction technologies for per- and polyfluoroalkyl substances (PFAS) waste streams (soils, spent granulated activated carbon, and resins). This report presents the results a pilot-scale demonstration test (DT) program to assess the performance of an Indirect Thermal Desorption (ITD) system and the destruction and removal efficiency (DRE) of a Thermal Oxidizer (TO) when treating PFAS-spiked soil and aqueous film forming foam (AFFF) (that includes Perfluorooctane sulfonate [PFOS]-based pre 2002 formulations)-spiked soil. The activities in this contract include the development and government approval of a detailed test plan to evaluate the performance of the system; provisioning of the equipment, materials and trained personnel to perform the tests; execution of the tests in the test plan; and the generation of a report that documents the findings and conclusions of the tests.

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## 2.0 OBJECTIVES

Previous studies have shown that thermal technologies (including ITD) can reduce PFAS levels in soil, combust PFAS contained in commercial products, and thermally mineralize PFAS-based industrial chemicals. However, uncertainties remain regarding ITD parameterization for application to treatment of specific PFAS-impacted waste as well as information regarding the DRE that can be achieved through off-gas treatment by TO. **The overall objective of this study was to advance the current understanding of ITD/TO's effectiveness for the treatment of soil containing a typical suite of PFAS found in, but not limited to, AFFF formulations manufactured and heavily utilized prior to 2002.**

A hypothesis-driven, two-phase pilot-scale treatment regime (referred to as the Demonstration Test [DT] Program) was conducted on PFAS-spiked and AFFF-spiked soils at two different thermal desorption temperatures (500 degrees Celsius [°C] and 650°C) with off-gas TO treatment at 1,000°C for a subset of test runs that included a quantitative fluorine mass balance. The DT Program was designed to answer the following four technical questions:

1. Is thermal desorption capable of treating a selected suite of PFAS to low parts per billion (ppb) levels in soil that would potentially allow for unrestricted reuse, discharge, or disposal of treated soil?
2. Does thermal desorption treatment effectively remove/treat/destroy potential precursors within soil?
3. During thermal desorption treatment, can TO achieve a DRE of 99.99 percent (%) for the selected suite of PFAS for the range of temperatures tested?
4. Can onsite ITD/TO treatment be a cost-effective alternative to current offsite disposal methods?

This study addresses ITD/TO treatment effectiveness, optimized operating parameters, air permitting requirements, and other practical considerations and attempts to validate the destruction pathway through calculation of DRE for residual PFAS as well as a fluorine mass balance.

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# 3.0 TECHNICAL APPROACH

The subject demonstration tests were performed in Robstown, Texas using a pilot-scale thermal desorption system owned and operated by TD*X Associates under contract to EA Engineering, Science, and Technology, Inc., PBC (EA). Tests were initially planned to be conducted by treating soil spiked with the six PFAS included in the third Unregulated Contaminant Monitoring Rule and pre-2002 formulation AFFF solution diluted in water. However, due to a discrepancy when ordering, perfluoropentanoic acid (PFPeA) was received and ultimately used instead of perfluorononanoic (PFHpA) during the DT Program. PFPeA, like PFHpA is a perfluoalkyl carboxylic acid (PFCA), but a shorter 5 versus 7 chain PFCA. Use of this analyte as an alternate did not affect the overall project. The six PFAS used in these tests included: perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), PFPeA, and perfluorbutane sulfonate (PFBS). Tests were conducted in strict accordance with a sampling and analysis plan that specified samples per test run to be collected and analyzed (including quality control [QC] sampling), laboratory analytical methods and procedures, and data quality requirements.

The ITD/TO treatability testing was performed in two phases. During the first phase, a pilot- scale thermal desorber was used to treat PFAS-spiked and AFFF-spiked soils at two different temperatures (500°C and 650°C). The first phase evaluated the performance of ITD technology to remediate AFFF-contaminated soils to low ppb levels and to determine if thermal desorption of AFFF-contaminated soils will desorb (i.e., remove) PFAS and potential PFAS precursors. The second phase of testing designed to demonstrate that an ITD unit (operating at temperature and residence time conditions optimal for PFAS removal from soil) combined with a TO for off- gas emissions control can achieve a DRE of 99.9997% for the PFAS-contaminant mass desorbed from the PFAS-spiked soil.

A series of ten tests were conducted on sand spiked with PFAS at concentrations ranging from approximately 6 to 19 milligrams per kilogram (mg/kg). Pre-treated spiked feed soil samples as well as thermally treated soil samples were collected for each test run. Over 60 pre-and post-treatment soil samples were collected and analyzed. PFAS analyses of pre- and post-treatment soil samples were conducted utilizing United States Environmental Protection Agency (EPA) Method 537 Liquid Chromatography/ Tandem Mass Spectrometry. Total Oxidizable Precursor (TOP) Assay analyses of pre- and post-treatment AFFF-spiked samples were also conducted. Two samples were collected and analyzed for TOP Assay with each test run.

The TO was operated at a nominal temperature of 1,000ºC for the DRE demonstration test runs. Four comparative test runs were conducted with two runs analyzing the TO exhaust gas for PFAS via EPA Method 0010/Method 537 and two runs analyzing the exhaust gas for Hydrogen Fluoride (HF) via EPA Method 26A. Figure ES-1 schematically illustrates the DT Program, how data was collected, synthesized, and used.

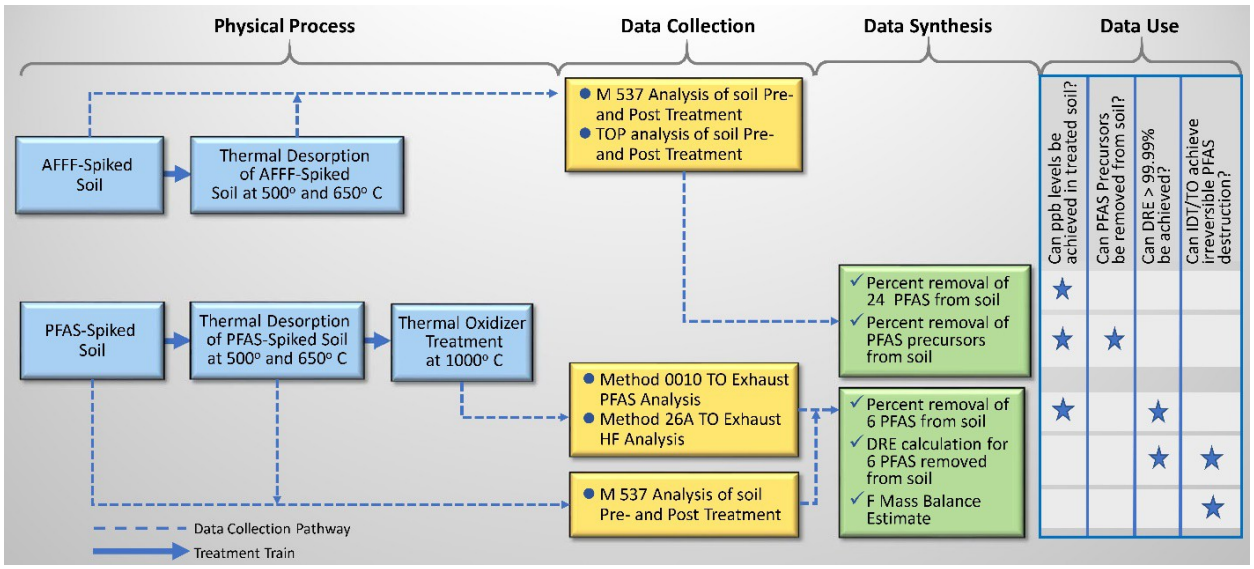



**Figure ES-1. Title Summary of Demonstration Test Program**

## 4.0 RESULTS AND DISCUSSION

Based on the arithmetic average of the compilation of all AFFF-spiked soils tested at 500°C, PFAS removal exceeded 97% for the total of 24 quantifiable PFAS. The percent reduction for perfluoroalkyl sulfonic acids (PFSA), PFCA, and fluorotelomer substances (FTS) subgroups are shown below in Figure ES-2.

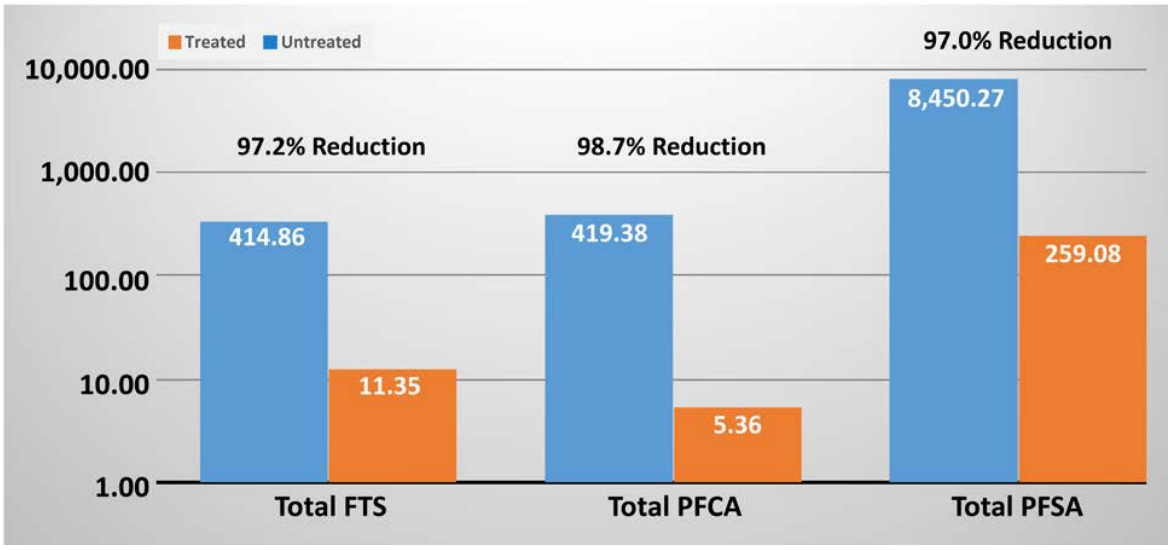



**Figure ES-2. Thermal Desorption Treatment Results of AFFF in Soil (500° C)**

Based on the arithmetic average of the compilation of all AFFF-spiked soils tested at 650°C, the PFAS removal exceeded 99.7% for all 24 of the total quantifiable PFAS. The percent reduction for PFSA, PFCA, and FTS subgroups are shown below in Figure ES-3.

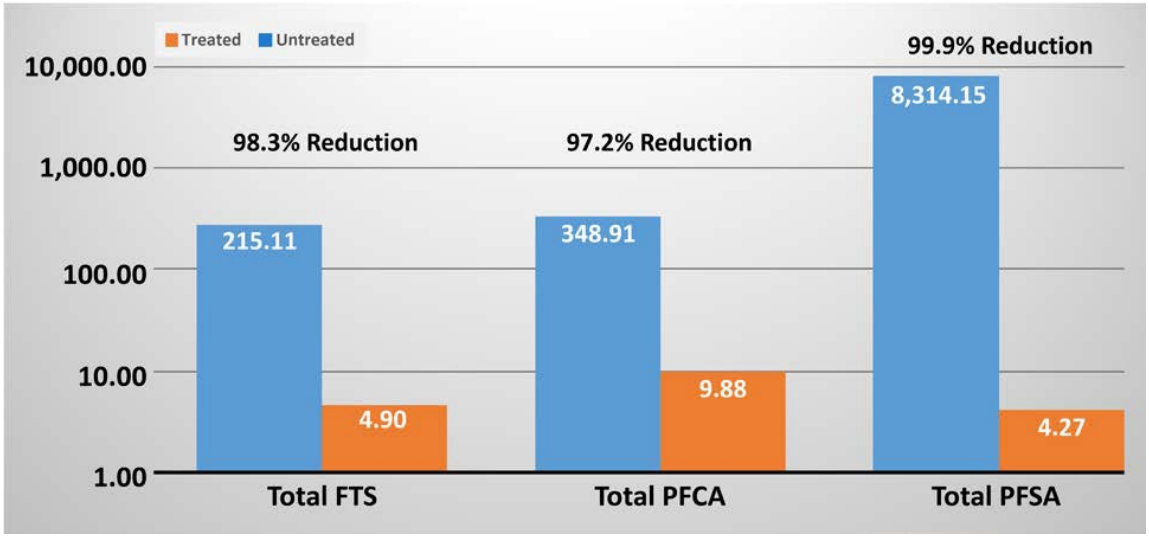



**Figure ES-3. Thermal Desorption Treatment Results of AFFF-Spiked Soil (650°C)**

TOP analyses was conducted on AFFF-spiked soils prior to and after thermal treatment at 500 and 650°C. The purpose was to evaluate if any precursors present in feed soil would be removed, and to what degree, by thermal treatment. As expected with the TOP procedure, pre-treated feed samples were oxidized, whereby the total PFCA mass increased in untreated samples by more than an order of magnitude (an indication of the significant presence of precursors in AFFF soil tested). However, after IDT treatment, TOP analyses of oxidized samples compared to non-oxidized samples show insignificant increases in PFCA and overall reduction of PFCA precursors by at least 99% and 99.9 % respectively at 500°C and 650°C for treated samples.

Figure ES-4 illustrates the arithmetically averaged PFCA levels prior to and after TOP, illustrating the presence of precursors in feed soil compared to pre- and post- oxidation results of process (treated) soil for tests operated at the ITD temperature of 650°C. These findings indicate that although AFFF contains a significant precursor burden that is subject to transformation, thermal removal efficiencies of greater that 99% were achieved, leaving little to no additional precursors remaining within the treated soil.

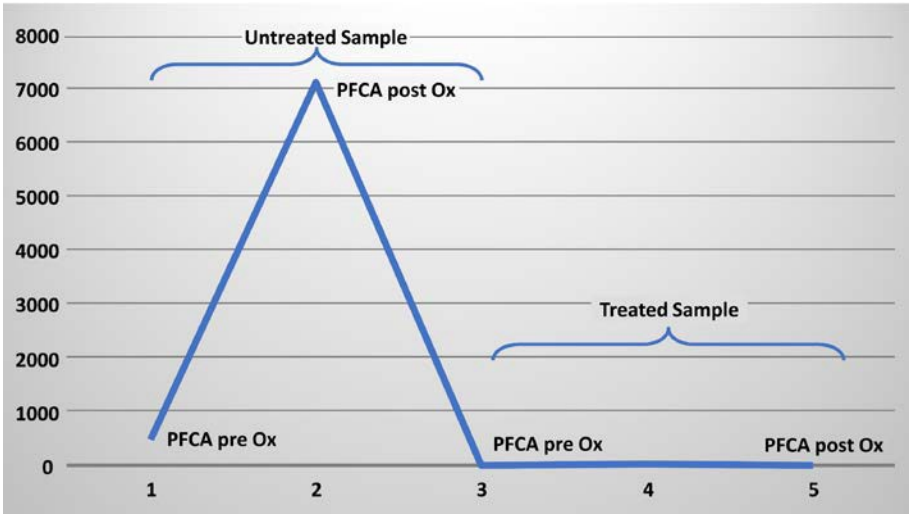



**Figure ES-4. Total PFCA (ug/kg) for AFFF-Spiked Soil Treated at 650°C**

In addition to treatment of AFFF-spiked soil, six PFAS were spiked at known quantities to soils that were then treated at 500°C (Figure ES-5) and 650°C (Figure ES-6). These experiments were performed to assess, under highly controlled conditions, PFAS reduction in soils and TO exhaust gas when combining thermal desorption and thermal oxidation in the treatment train. Thermal oxidizer exhaust gas was analyzed for the six PFAS as well as HF, respectively, to calculate DRE and to complete a mass balance on fluorine. Based on the arithmetic average of PFAS-spiked soils (i.e., 3 PFCA and 3 PFSA) tested at 500°C, total PFAS removal exceeded 94%. The PFCA removal exceeded 99.8% while the PFSA removal was approximately 89%. With an approximate initial feed concentration of 45 ppm for the total of the 6 spiked PFAS (i.e., individual PFAS feed levels in the 6 to 9 ppm range), treated levels ranged from less than 20 ppb for PFCAs and between 500 and to approximately 1000 ppb for select PFSAs.

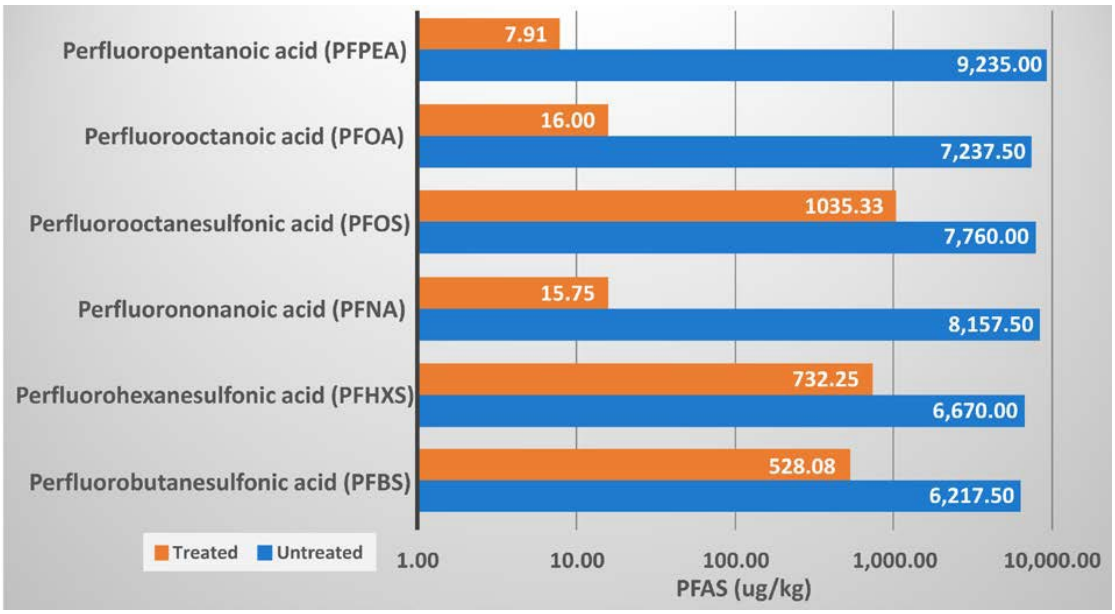



**Figure ES-5. Thermal Desorption Treatment Results of 6 PFAS-Spiked Soil (500°C)**

Based on the arithmetic average of all 6 PFAS-spiked soil (i.e., 3 PFCA and 3 PFSA) tested at 650°C, the PFAS removal exceeded 99% for PFAS, as well as the 3 PFCA and 3 PFSA. With an approximate initial feed concentration of 86 ppm for the total of 6 PFAS (i.e., individual PFAS feed levels in the 13 to 17 ppm) treated levels ranged from less than 2 ppb all PFAS.

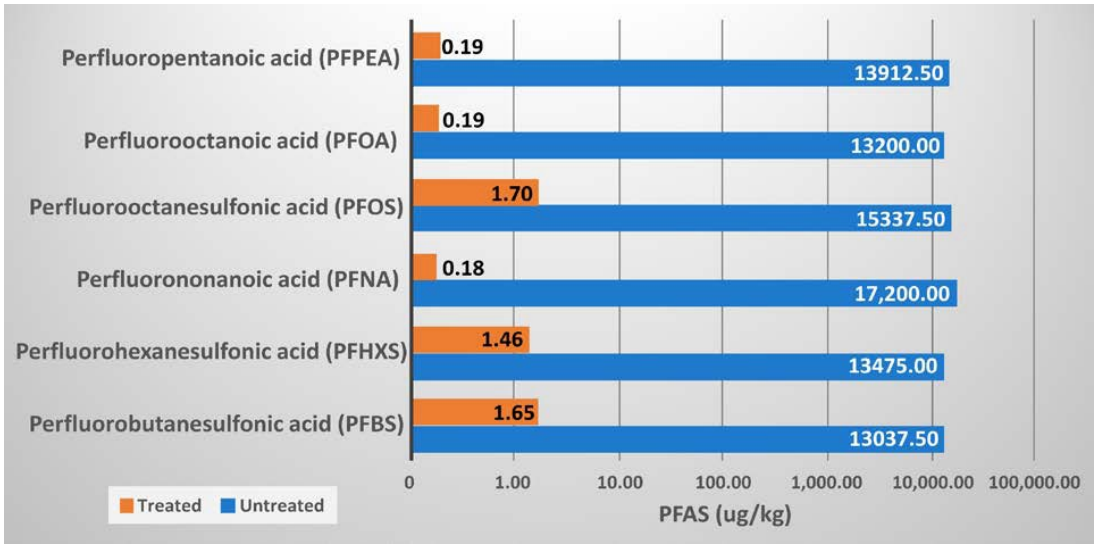
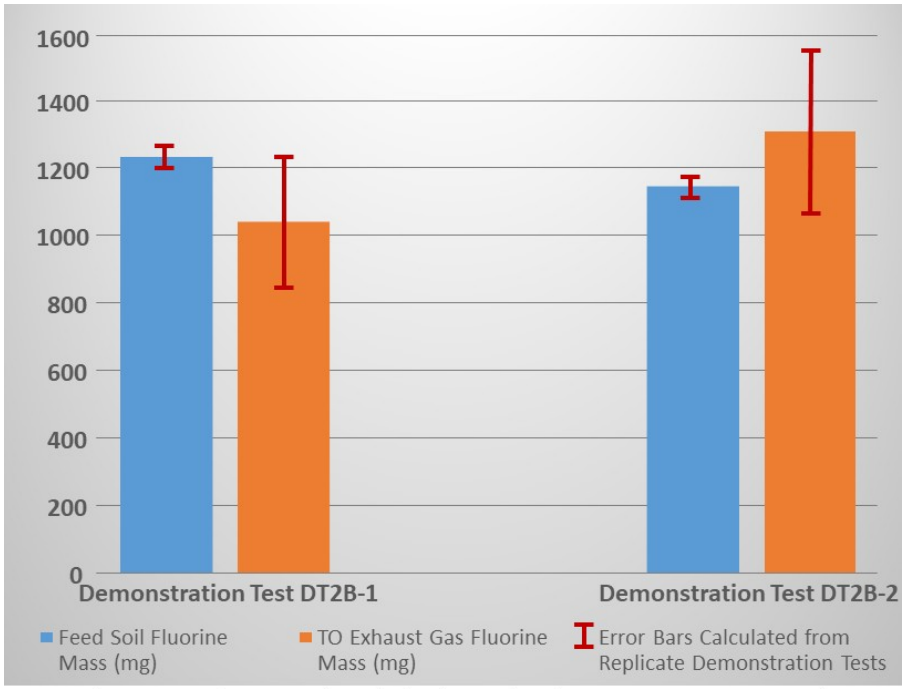



**Figure ES-6. Thermal Desorption Treatment Results of 6 PFAS-Spiked Soil (650°C)**

The DRE was calculated for PFAS captured from TO exhaust by a modified EPA Method 0010. The findings indicate a DRE of 99.9997%. When performing EPA Method 26A to capture HF from TO exhaust gas, findings indicate fluorine mass recovered from TO exhaust is closely comparable to total fluorine mass added (as calculated molecular mass to PFAS) to feed soils.

Mass balance calculations yield fluorine mass recovery of 84% and 114%, respectively, for the two trial tests conducted with 6 PFAS-spiked soil runs combining ITD and TO (Figure ES- 7).




Note: Cumulative PFAS in exhaust gas was detected at less that 60 ng/sample in Demonstration Tests DT2A-1 and DT2A-2; therefore, all fluorine in exhaust gas was attributed to HF.

**Figure ES-7. Fluorine Mass Balance Results**

The demonstration tests show conclusively that for 650°C, the ITD technology will effectively remediate PFAS in soil to a concentration of less than 1-10 µg/kg. Furthermore, ITD combined with TO can achieve a DRE of greater than 99.9997% for off-gas emissions from ITD-treated PFAS feed material. Moreover, findings of this DT Program have demonstrated that ITD technology effectively desorbs PFAS precursors when treating soils that were recently spiked with AFFF. Prior to this study, the knowledge of how PFAS behaves in combustion or thermal processes was scarce. One of the more important aspects of this study was to advance the understanding of the capability of ITD/TOs (at the temperatures tested) to achieve "irreversible destruction" of PFAS-containing materials (including investigation-derived waste) and if other unintentional and unwanted degradation products will potentially be formed during the ITD/TO process. During the tests where TO was utilized and exhaust gas was analyzed separately for PFAS and HF, the mass balance performed on fluorine effectively demonstrates and confirms the destruction of the PFAS without the creation of unwanted byproducts. The extremely low detection of PFAS in the treated exhaust (at part per trillion levels) and recovery of the molar equivalent of F added to feed material during the mass balance provide complimentary lines of evidence for complete and irreversible PFAS thermal mineralization.

## 5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Full-scale treatment of PFAS-impacted soil and spent sorbents from groundwater cleanup is currently limited to costly measures including transport to/disposal at a permitted landfill, transport to/destruction at an incineration facility, and high-temperature regenerative methods of spent treatment sorbents. Anticipating that future demand will only increase for treatment of PFAS-impacted media, this study has direct benefits on advancing the state-of-the-industry by employing a mature technology (ITD/TO) to provide "innovative" treatment of an emerging contaminant. Based on these preliminary results of this study, which are very promising, additional scale-up study is warranted on ITD/TO technology for PFAS treatment to better define the routine application of this technology with respect to PFAS destruction and more completely assess the costs associated with full-scale implementation of this technology for PFAS treatment.

Transportable indirect thermal desorption systems intended for on-site soil treatment can be designed over a wide range of throughput capacity, from small batch units with a treatment capacity of approximately 0.5 ton/hr to large continuous-feed units with a 15 ton/hr capacity. Equipment selection and sizing is generally based on the quantity of soil requiring treatment at a given site; for example, higher capacity units are generally more cost-effective at sites with large quantities of soil and vice versa. Unit treatment costs are inversely proportion to soil quantity and can range from $600/ton for sites containing 1,000 cubic yards of soil, to less than $300/ton for a 100,000 cubic yard site. Direct-fired units have higher throughput capacity compared to indirect units, given similar capital and operating costs, and are therefore more cost-effective.

Throughput capacity of direct fired units generally range from 5 ton/hr to in excess of 30 ton/hr. A highly engineered feasibility study coupled with a more extensive onsite full-scale, onsite demonstration pilot is recommended.