Advancing the Use of Indirect Thermal Desorption/Thermal Oxidation Technology to Address Treatment of PFAS Associated with Solid Media, Including Soil and Investigative-Derived Waste

Prepared for: Northeast Conference on the Science of PFAS: Public Health & the Environment

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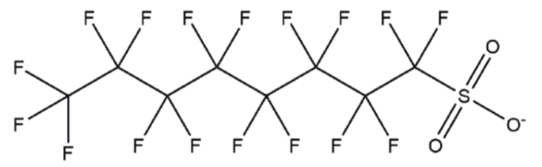
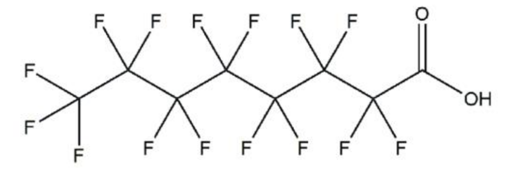
06 April 2022

PFAS Summary Background

- Per- and polyfluoralkyl substances (PFAS) are a group of synthetic fluorinated chemicals use since the 1940s in a wide array of consumer and industrial product manufacturing (e.g., non-stick cookware, stain- and water-resistant fabric, aqueous film-forming foam [AFFF] for firefighting).
- Most widely known PFAS are perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA).



Perfluorooctane sulfonate (PFOS)



Perfluorooctanoic acid (PFOA)

- Both chemicals highly persistent in the environment and the human body. Resistant to breakdown and can accumulate.
- Studies indicate that PFOS and PFOA and now other PFAS can, at extremely low levels, are linked in humans to:
  - Reproductive, developmental, immunological, and hormonal effects in humans
  - Liver and kidney ailments in humans
  - Tumors in animals

Per- and Polyfluoroalkyl Substances (PFAS)

Polymers

- Fluoropolymers [8]
- Perfluoropolyethers (PFPE) [9]
- Side-chain fluorinated polymers [10]
  - Fluorinated urethane polymers
  - Fluorinated acrylate/methacrylate polymers
  - Fluorinated oxetane polymers

Non-Polymers

Perfluoroalkyl Substances
(All H atoms on all C atoms in alkyl chain attached to a functional group have been replaced with F)

- Perfluoroalkyl acids (PFAAs)[a]
  - Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs) [1,a]
  - Perfluoroalkane sulfonic acids/ Perfluoroalkane sulfonates (PFSAs) [1,b]
  - Perfluoroalkane sulfinic acids (PFSiAs) [2,b]
  - Perfluoroalkyl phosphonic acids (PFPAs) [1,c]
  - Perfluoroalkyl phosphinic acids (PFPiAs) [1, c]
  - Perfluoroalkyl ether carboxylic acids (PFECAs)/ Perfluoroalkyl ether sulfonic acids (PFESAs) [5, c]
- Perfluoroalkane sulfonamides (FASAs) [4, b]
- Perfluoroalkane sulfonyl fluorides (PASFs) [3, b]
- Perfluoroalkanoyl fluorides (PAFs) [4, b]
- Perfluoroalkyl iodides (PFAIs) [4, c]
- Perfluoroalkyl aldehydes (PFALs) [2, c]

Polyfluoroalkyl Substances
(all H atoms on at least one (but not all) C atoms have been replaced with F)

- Polyfluoroalkyl ether carboxylic acids [5, c]
- Fluorotelomer-based substances [6, f]
  - n:2 Fluorotelomer sulfonic acids (FTSAs) [1, 2, c]
  - n 2: Fluorotelomer carboxylic acids (FTCAs) [2, (2‡), c]
  - n:2 Fluorotelomer alcohols (FTOHs) [7, (2‡) c]
  - n:2 Fluorotelomer iodides (FTIs) [7, c]
  - n:2 Fluorotelomer olefins (FTOs) [7, c]
  - Semifluorinated-N-alkanes (SFAs) / alkenes (SFAenes) [6, c]
  - n:2 Fluorotelomer acrylate/methacrylate (FTACs/FTMACs) [7, c]
  - n:2 Fluorotelomer aldehydes (FTALs) [2, (2‡), c]
  - Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates (PAPs) [10, c]
- Perfluoroalkane sulfonamido substances [2, 11, b]
  - (N-alkyl) -, Perfluoroalkane sulfonamides (N-Ethyl perfluorooctane sulfonamide (EtFOSA)) [2,11, b]
  - (N-alkyl) -, Perfluoroalkane sulfonamidoethanols (MeFASEs, EtFASEs, BuFASEs),(FASEs) [2,11, b]
  - N-alkyl Perfluoroalkane sulfonamidoethyl acrylates / Methacrylates (MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs) [2,11,b]
  - N-alkyl -, Perfluoroalkane sulfonamidoacetic acids (MeFASAAs, EtFASAAs, BuFASAAs)/(FASAAs) [2, b]

PFAS Soil Remediation Trends

Treatment Technology	Technical and Cost Information	
	Selection Considerations	**Relative Costs Compared to Thermal**
Transport and disposal to landfill	• Landfilling transfers PFAS and is not destruction • Safety and liability considerations for transport over long distance • Hazardous waste (Subtitle C) versus non-hazardous waste landfill • Waste and potential groundwater contamination remain a potential long-term liability	Slightly Higher than *Ex Situ* Thermal Desorption
Ex Situ Thermal Desorption	• Can be conducted on site or offsite at nearby facility • Can utilize multiple fuel options for thermal oxidation • Permitting process is well understood for Thermal Desorption Coupled with Thermal Oxidation for **complete destruction of PFAS** • Can control and monitor emissions • Treated material can be reused onsite or offsite	N/A
Ex Situ Soil washing	• Uses very large volumes of water • Requires large footprint for treatment and processed material dewatering • Relies on physical particle separation and may require additional treatment or offsite disposal of fines fractions • Requires treatment of large liquid waste stream and transfers but does not destroy PFAS	Comparable, but not likely as standalone technology to achieve treatment for fines
In Situ or Ex Situ Thermal Conductive Heating	• Electric heated *in situ* soil is 5-10 times higher on a per ton basis than a fuel oil or natural gas-fired thermal desorption unit • Requires extended time (if ever reached) to bring to treatment temperature required for complete PFAS destruction • Requires treatment media to be maintained over periods of months during treatment and transfers but does not destroy PFAS	Comparable, though monitoring treatment performance more difficult.
Hydrothermal/ Supercritical Water Oxidation Process	• Uses complex system of high-pressure vessels and elevated temperature • Cannot handle large throughput necessary to treat large soil volume • Still in R&D stage, not ready for scale up • Likely more suitable to smaller high concentrated volume of liquid	Not feasible for large soil volumes
Other thermal processes (e.g., smoldering)	• Requires the presence of, or addition of, organic matter as primary energy source • Requires emissions control • Relies on lower temperatures maintained over longer period	May be comparable but still in development for PFAS

Sources: SERDP/ESTCP 2021 PFAS Workshop, San Pedro, CA, July 19-22 and Grant et. al,.2016.

Technical Objective of SERDP ER18-1572

- ✓ Overall Objective: To advance the current understanding of ITD/TO technology for the treatment of soil containing the typical suite of PFAS found in, but not limited to, Aqueous Film Forming Foam (AFFF) formulations manufactured prior to 2002.
- ✓ Prior studies performed indicate TD can remove PFAS from solid media over a wide range of temperatures ~500-1,750°F; though limited efforts made to treat/destroy PFAS once desorbed.
- ✓ Study designed at pilot-scale under highly controlled experimental conditions to determine optimal thermal operating parameters.
- ✓ Attempted to answer four technical questions:
  - Is ITD capable of treating a selected suite of PFASs to low parts per billion (ppb) levels in soil that would potentially allow for unrestricted reuse, discharge or disposal of the treated soil?
  - Does ITD treatment effectively remove/treat/destroy potential PFAS precursors within soil?
  - During ITD/TO treatment, can TO achieve a destruction and removal efficiency (DRE) of 99.99% for the selected suite of PFASs studied?
  - Can on-site ITD/TO treatment be a cost-effective alternative to current off-site disposal methods?

TECHNICAL/REGULATORY GUIDELINES

TECHNICAL REQUIREMENTS

FOR

ON-SITE THERMAL DESORPTION

OF

SOLID MEDIA CONTAMINATED WITH

HAZARDOUS CHLORINATED ORGANICS

-FINAL-

September 18, 1997

Prepared by

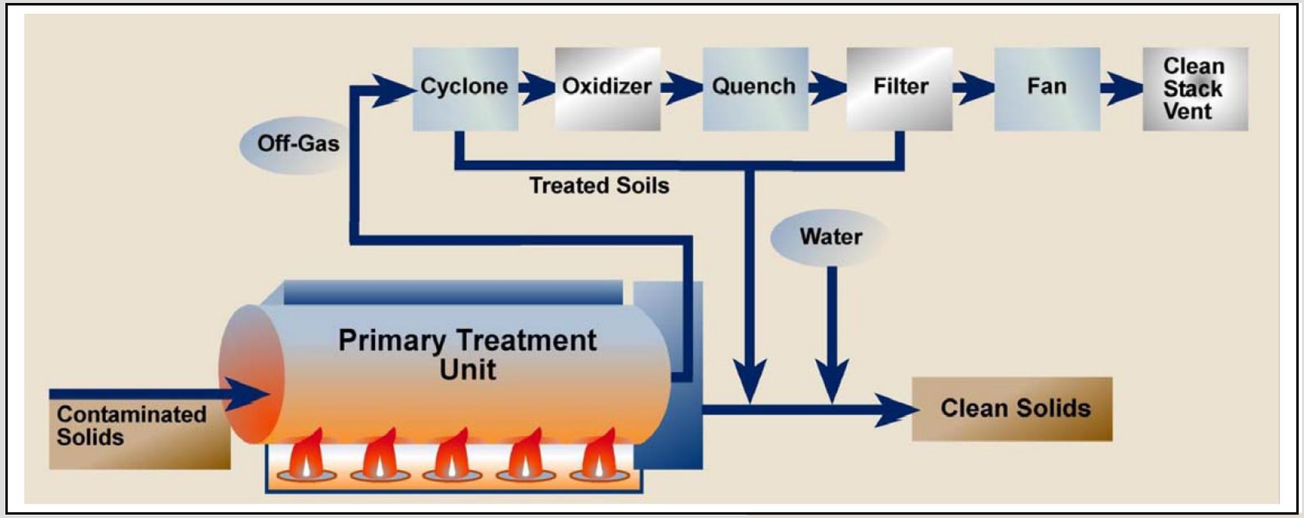
The Interstate Technology and Regulatory Cooperation Work Group

Low Temperature Thermal Desorption Work Team

EA Team Member Carl Palmer Co-Authored ITRC's Technical Requirements Document for On-Site Thermal Treatment of Impacted Soil

Description of Thermal Desorption Coupled with Thermal Oxidation

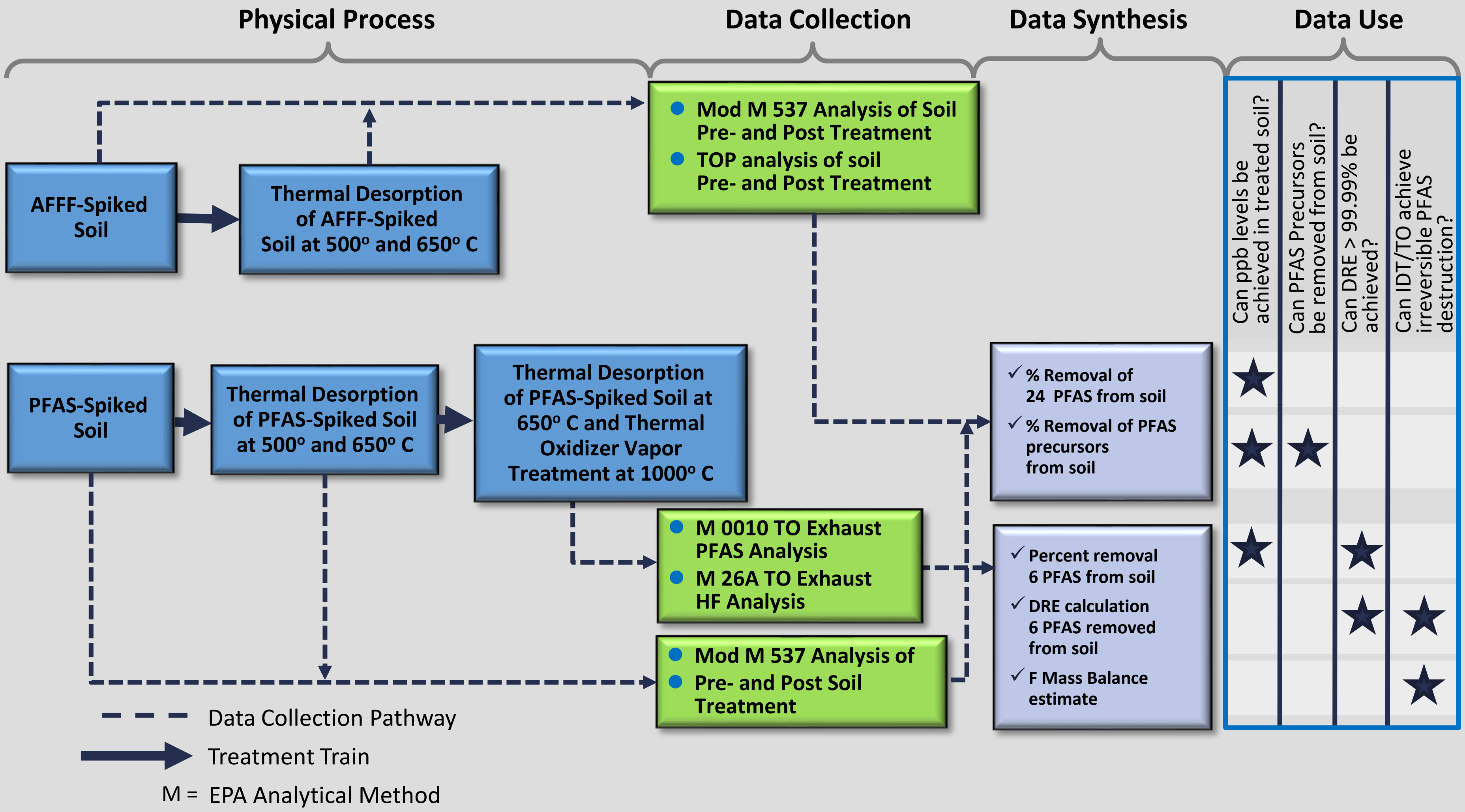
- Thermal Desorption coupled with Thermal Oxidation (TD/TO) has been widely applied to treatment of contaminated soils; however, application to PFAS-impacted media is novel.
- Soil treatment performed in Primary Treatment Unit, or Thermal Desorption Unit (TDU), where contaminants aggressively desorbed, vaporized, and transferred via off-gas to a Secondary Treatment Unit (STU), comprised of a high-temperature propane- or liquified natural gas-fueled TO.
- TO just one feature of a robust Air Pollution Control (APC) train consisting of a cyclone separator (for initial particulate control), TO (for contaminant destruction), a quench chamber (for exhaust gas cooling), and baghouse dust filters (dust removal).
- For SERDP and ESTCP demonstration projects, both direct-fired and indirect-fired TDUs are being tested at target temperatures of 500°C to 650°C and soil residence times in the TDU ranging from 20 to 75 mins.



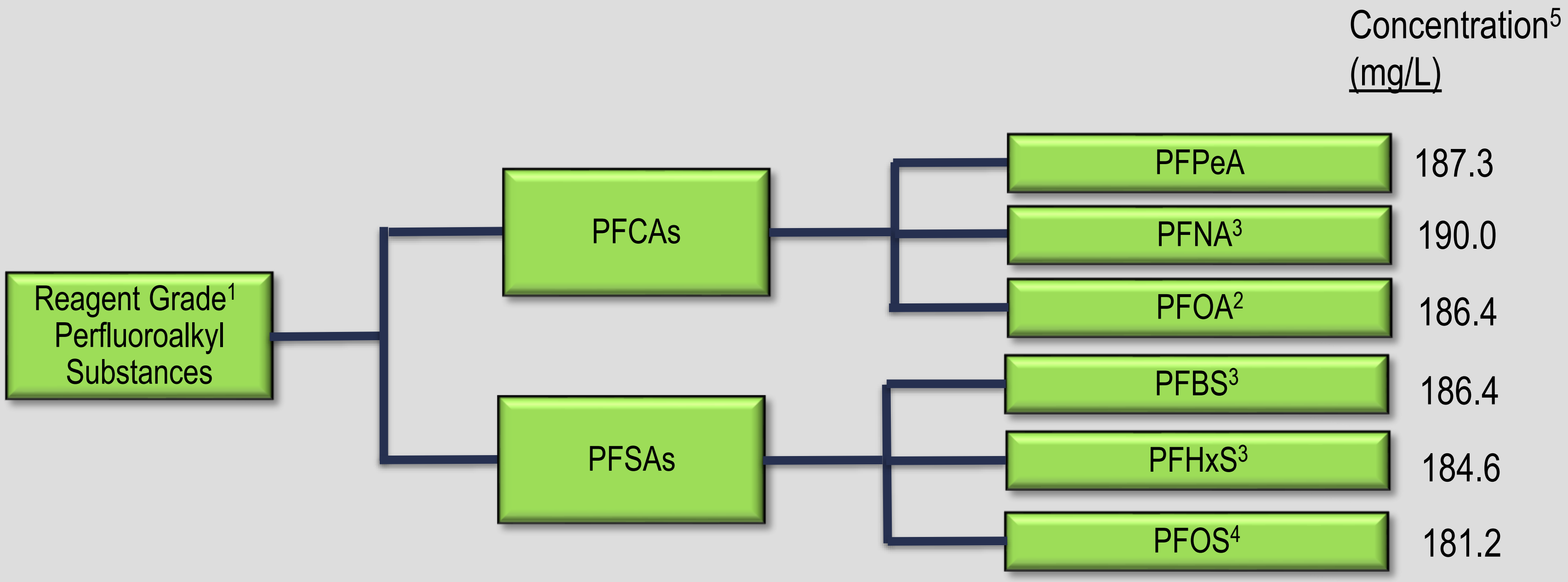
Process Flow for a Typical TD/TO System

Typical Layout of a Thermal Desorption Project

SERDP ER18-1572 Proof of Concept Approach



PFAS Study Materials



1. Reagent-grade PFAS ordered from Sigma Aldrich and Thermo Fisher Scientific. PFAS compounds included: perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), perfluoropentanoic Acid (PFPeA), and perfluorbutane sulfonate (PFBS).
2. Dissolved fast.
3. Dissolved slow.
4. Dissolved very slowly. Twenty-four hours mixing required.
5. Dissolved aqueous concentrations in stock solutions,

AFFF[1] Study Materials

Dilute 1997 3M AFFF

Group	Compound	Concentration (mg/L)
Fluorotelomers	4:2 FTS	<2.5
Fluorotelomers	6:2 FTS	<2.5
Fluorotelomers	8:2 FTS	<2.5
PFCAs	PFOA	1.1
PFCAs	PFHxA	1.3
PFCAs	PFPeA	0.3
PFCAs	PFHpA	0.3
PFCAs	PFNA	0.5
PFCAs	PFBA	0.2
PFSAs	PFOS	78.0
PFSAs	PFHxS	7.4
PFSAs	PFHpS	1.3
PFSAs	PFBS	1.5
PFSAs	PFPeS	1.6
PFSAs	PFNS	0.06

1. Dilute AFFF formulation (1997 3M variety) obtained from M Simcik at University of Minnesota.

Technical Approach – AFFF and PFAS Soil Spiking

Test Run	Soil Type	Spike Constituent(s)	Target PFAS Concentration (mg/kg, each)	Actual PFAS Concentration (mg/kg, each)	Soil Treatment Temperature (°C)
DT1-1	Sand	(6) PFAS	10	6.0 - 10.1	500
DT1-2	Sand	(6) PFAS	10	5.9 - 9.4	500
DT2A-1[1]	Sand	(6) PFAS	20	11.6 - 15.6	650
DT2A-2[1]	Sand	(6) PFAS	20	13.4 - 18.7	650
DT2B-1[1]	Sand	(6) PFAS	20	11.4 - 19.0	650
DT2B-2[1]	Sand	(6) PFAS	20	11.5 - 17.7	650
DT3-1	Sand	AFFF	10[2]	8.4 - 9.2	500
DT3-2	Sand	AFFF	10[2]	8.9	500
DT4-1	Sand	AFFF	10[2]	8.3 - 9.4	650
DT4-2	Sand	AFFF	10[2]	8.1 - 9.2	650

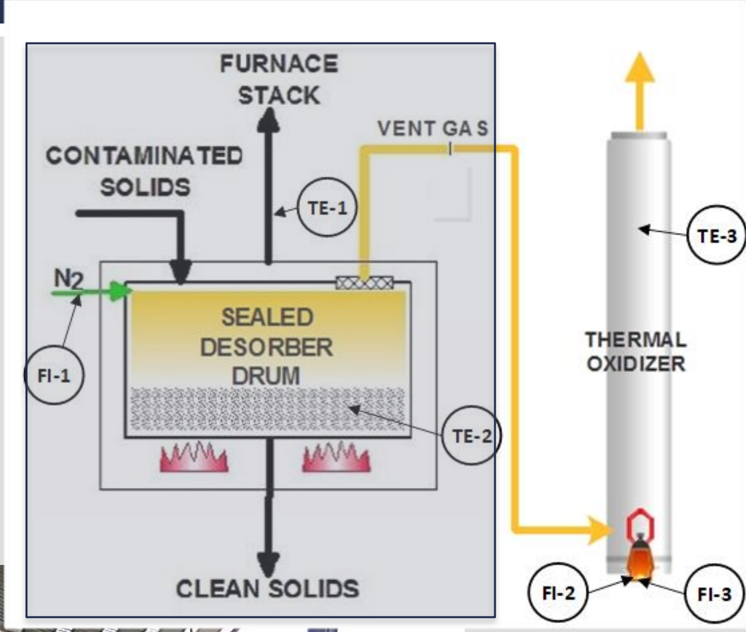
1. During test run DT2A sampling of the TO exhaust was performed for PFAS.
   During test run DT2B, sampling of the TO exhaust gas was performed for Hydrogen Fluoride (HF).
2. Estimated from stock AFFF concentration of PFOS.

Technical Approach – AFFF and PFAS Soil Spiking

- Testing with clean, well sorted, medium sand (USCS: SP).
- PFAS weighed on laboratory balance and dissolved in 5.5 liters of DI water (equating to ~10% soil moisture) to achieve target concentration.
- PFAS (or AFFF), DI water, and sand mixture loaded per batch (~50 kg) into 3 cu ft electric cement mixer and homogenized until uniform soil moisture content.
- Spiked soil mixture divided for test run into aliquots of 20.7 to 25.5 kg and top loaded into thermal separation drum (desorber).
- AFFF analyses of pre-treatment soils conducted by modified EPA Method 537 (LC/MS/MS) and TOP Assay. PFAS analyses of pre-treatment soils conducted by modified EPA Method 537 (LC/MS/MS).

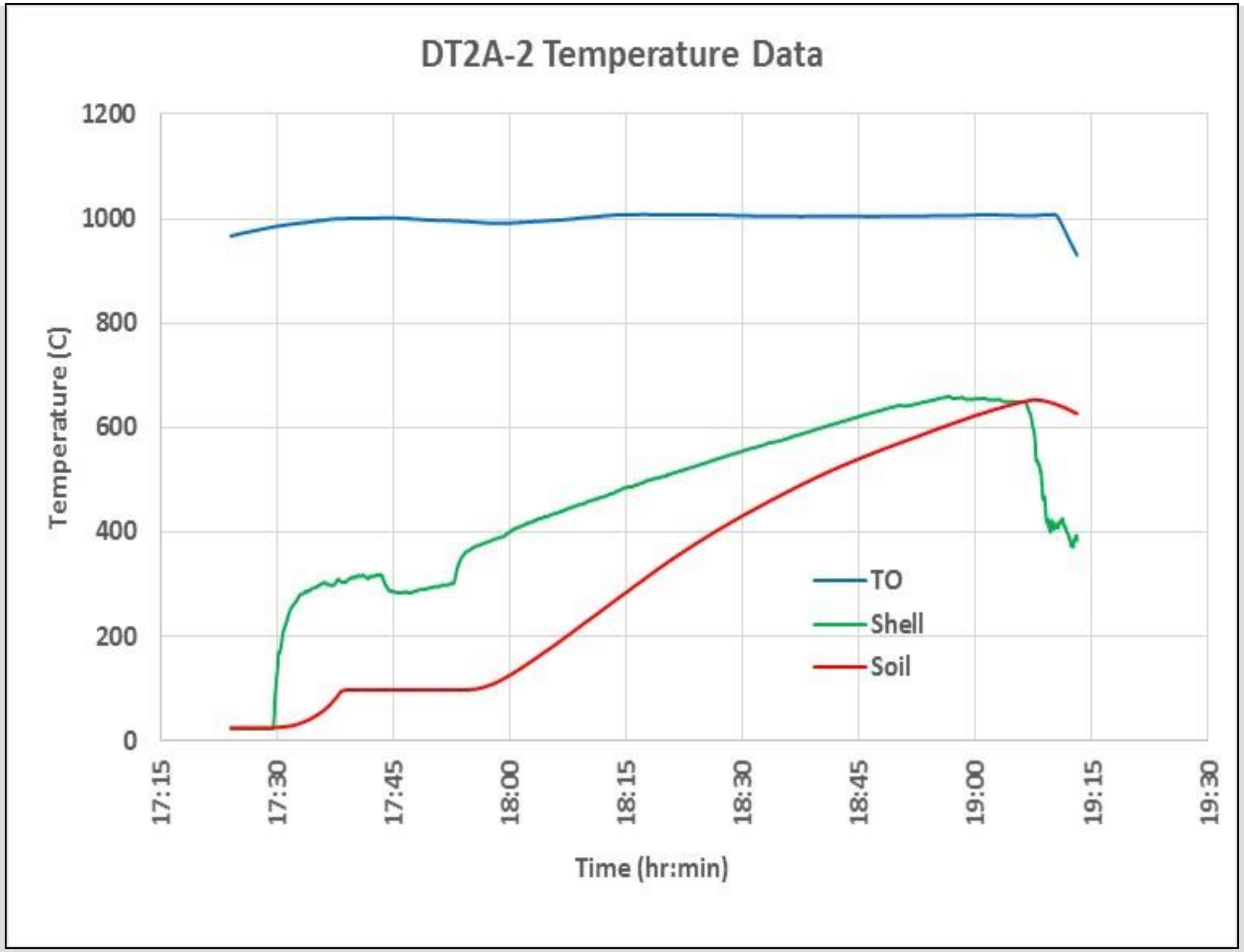
Technical Approach – ITD

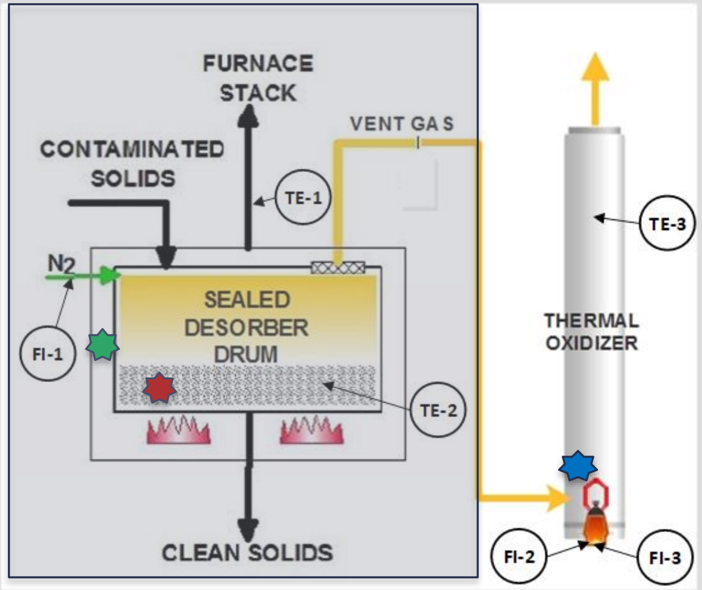
- Soil batch loaded to sealed dryer (desorber) through airlock and heated by thermal conduction and radiation from propane-fueled steel cylinder.
- Internal paddles rotated in dryer to mix the solids and desorb PFAS (or AFFF) constituents as vapors, which were then transported to a TO via inert carrier gas (nitrogen). Two target ITD treatment temperatures tested (500º and 650º C).

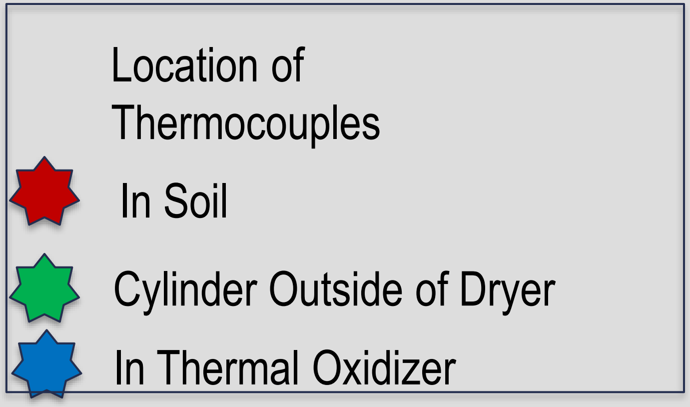


- AFFF analyses of post-treatment soil samples conducted by modified EPA Method 537 (LC/MS/MS) and TOP Assay. PFAS analyses of post-treatment soil samples conducted by modified EPA Method 537 (LC/MS/MS).
- Replicate test runs conducted for each test condition (each temperature) and two samples were collected and analyzed for each test run.

Technical Approach – ITD (Cont'd)



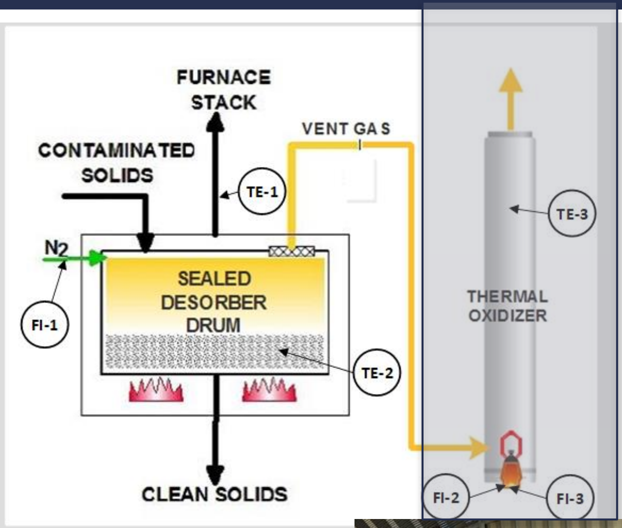




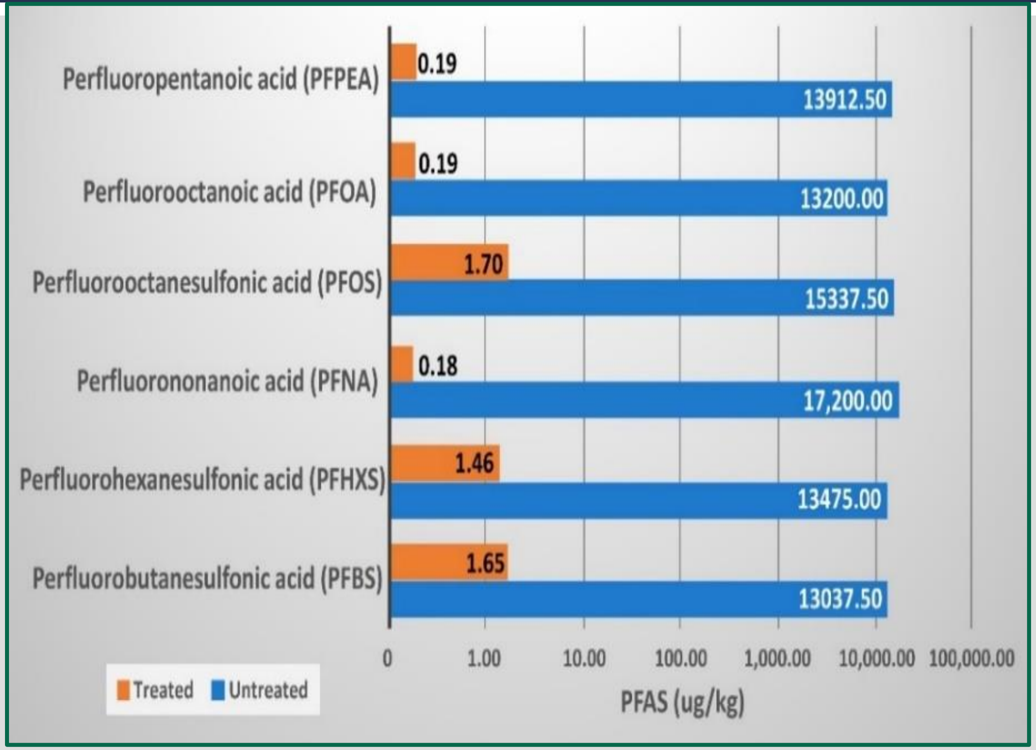
- **Temperature data electronically logged via multiple thermocouples to a data logger every minute. Other data manually recorded by plant operators on data sheets.**

Technical Approach – TO

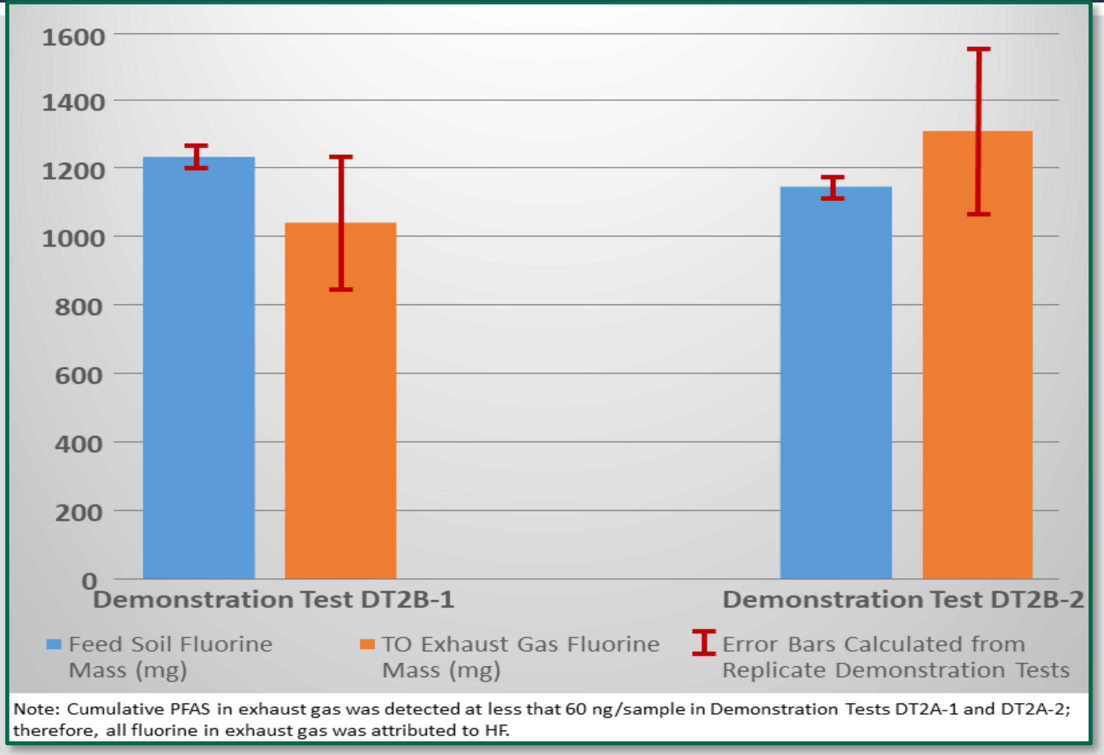
- Comparative test sets conducted at optimal ITD temperature condition (650^{o} C) for analyses of TO exhaust gas sampling train (EPA Method 2, 3, 4, 0010, and 26A).
- TO tests conducted at operating temperatures in range of 750 to 1000^{o} C for 2 second residence.
- PFAS spiking/mixing conditions as well as ITD parameters same as previously defined.
- Test set included PFAS analyses of TO exhaust gas conducted via EPA Method 0010/modified Method 537 (LC/MS/MS). Air sampling train composed of particulate filter, XAD-2 resin, and impinger condensates.
- Alternate test set included Hydrogen Fluoride (HF) analyses of TO exhaust gas conducted via EPA Method 26A (IC). Air sampling train composed of impingers with H2SO4/NaOH/Silica Gel Reagents.
- Replicate test runs conducted for each set. Two exhaust samples analyzed for each test run.



SERDP ER18-1572 Results – Indirect Thermal Desorption (ITD) of PFAS-Spiked Soils



PFAS Removal Efficiency at 650°C



Fluorine Mass Balance at 650°C

- PFAS removal efficiency of 99.7% from PFAS spiked soils tested at 650° C.
- Fluorine balance averaging 99% for two replicate trials with duplicate quality control sampling per test for 6 spiked constituents.
- Experimental error (+/-30%) associated with the measurement of exhaust gas flux.
- PFAS results reflect soil treatment to sufficiently low ug/kg levels and show capability to meet unrestricted use soil treatment criteria.

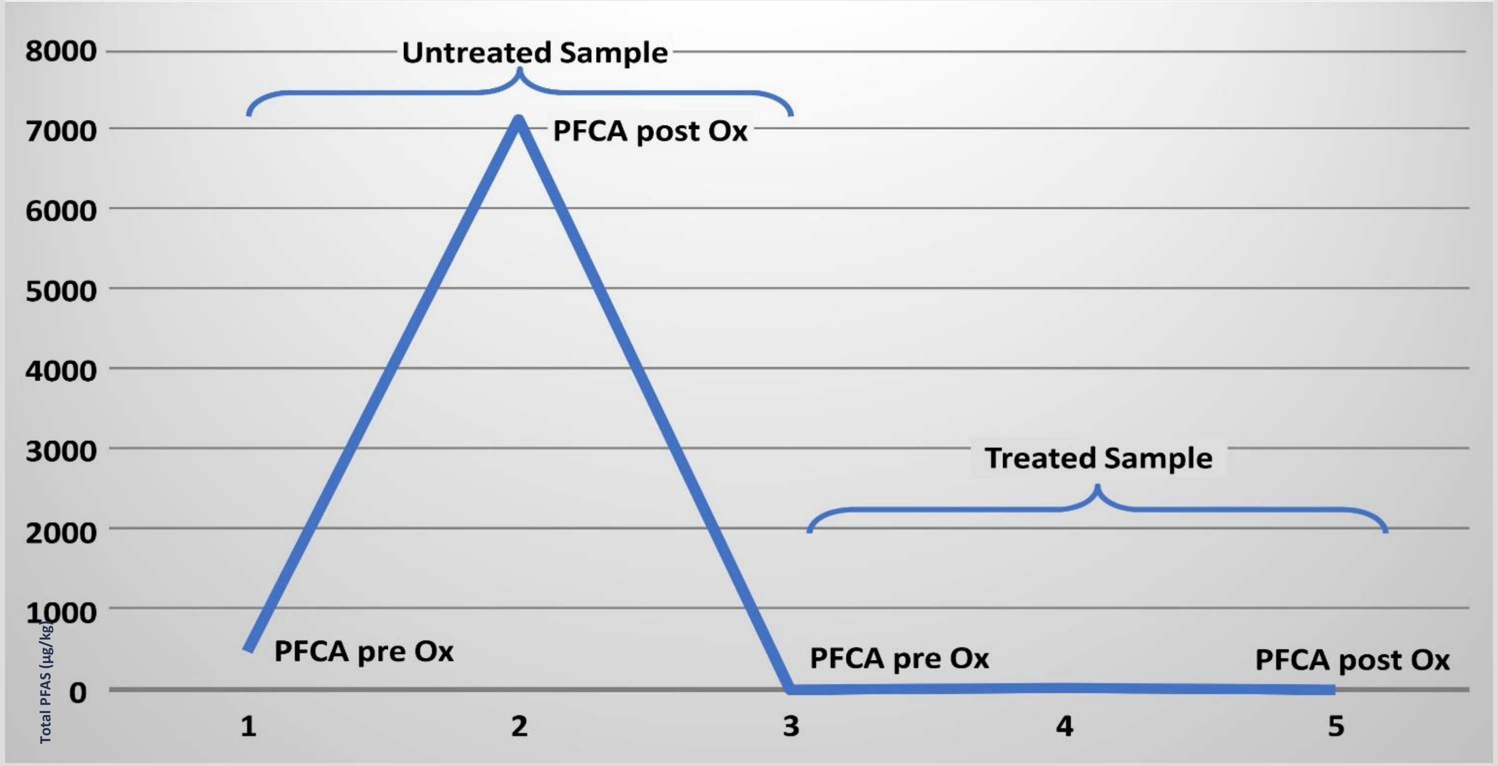
Thermal Treatment Results Versus Soil Screening Levels (SSLs) and/or Standards

- **Upon initiation of SERDP ER18-1572 in 2019, only AK and TX had established SSLs or Standards.**
- **As of March 2022, eight States and the EPA now have SSLs or Standards.**
- **More States likely to join on and SSLs or Standards will be race to the bottom.**
- **EPA is developing (or floating revisions) to seven PFAS that will lower human health reference doses (RfDs) by four orders of magnitude. This development will likely lead to lowering of SSLs or Standards by the same magnitude.**
- **Achievement of thermal cleanup standards as low is possible but will come with additional time and cost.**

State	Standard	PFOA ug/kg	PFOS ug/kg	PFPeA ug/kg	PFNA ug/kg	PFHxS ug/kg	PFBS ug/kg
EPA	RSL	0.172	0.378				130
Alaska	CL	1.7	3				
Florida	PSTCL	2	7				
Maine	RAG	9.5	21				7100
Massachusetts	S-1,2,3/GW-1	0.72	2		0.32		
Michigan	GSIPC	350	0.22				
Nebraska	RG	0.6	0.78				
North Carolina	PSRG	17					910
Texas	PCL	3	50	0.32	3		110
SERDP ER18-1572	**Post-treatment**	**0.19**	**1.7**	0.19	0.18	1.46	1.65

Standards	
RSL	Regional Screening Level
CL	Cleanup Level
PSTCL	Provisional Soil Cleanup Target Level
RAG	Remedial Action Goal
S-1,2,3/GW-1	Soil Cleanup Levels per Classification Type
GSIPC	Groundwater Surface Water Protection Criteria
RG	Remediation Goal
PSRG	Preliminary Soil Remediation Goal
PCL	Protective Concentration Level

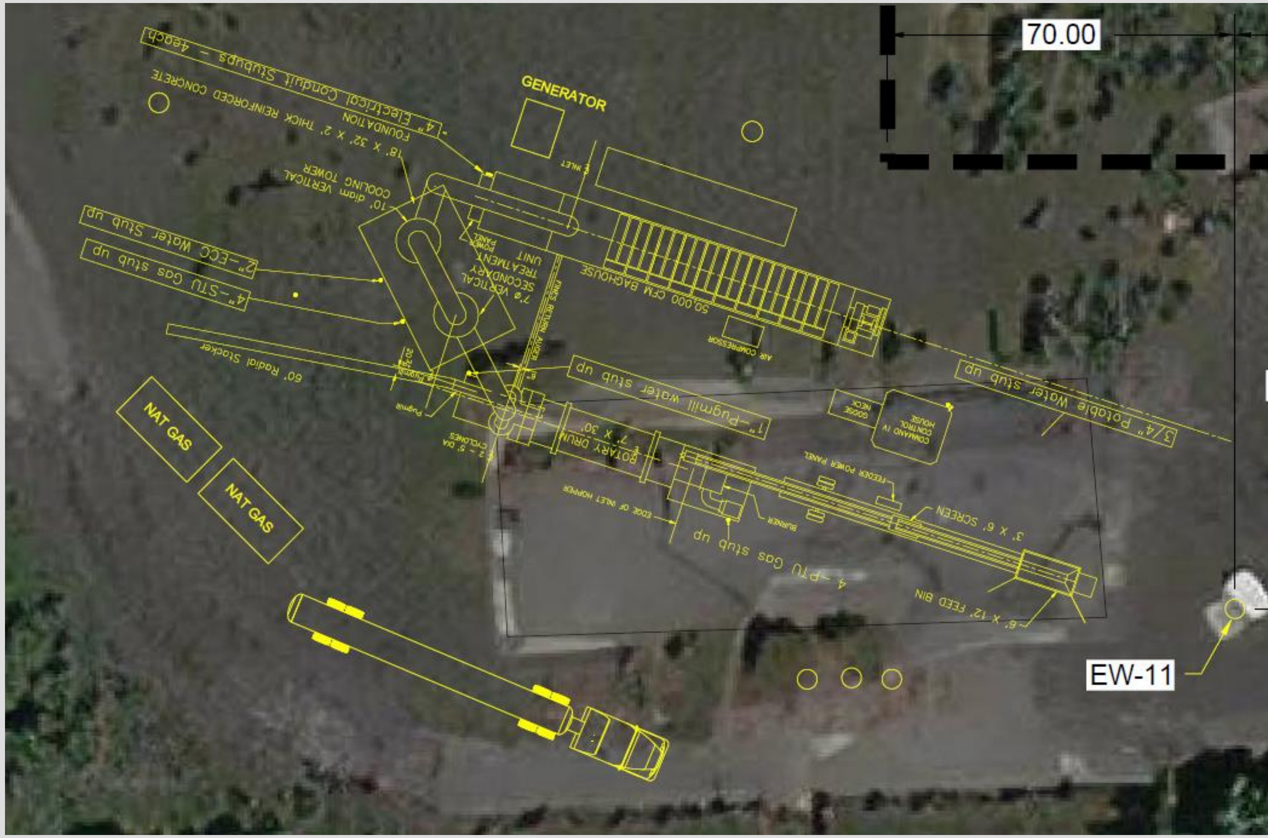
Results – ITD of AFFF-Spiked Soils (cont'd)



- TOP analyses performed pre- and post-ITD treatment at 500 and 650° C.
- Total PFCA mass (arithmetic average) significantly increased in post-TOP pre-treated samples, illustrating presence of precursors in feed soil.
- Post-ITD results show precursor burden eliminated by at least 99% and 99.9%, respectively for 500 and 650 ° C.

Technology Approach and Next Steps

- <u>SERDP Findings:</u> Successfully demonstrated proof of concept to clean up soil to less than 1-10 µg/kg and under controlled pilot conditions to achieve PFAS DREs greater than 99.9997%.
- <u>ESTCP Research:</u> Resolve to extent practicable fluorine material balance as well as Potentially Incomplete Combustion Byproducts (PICs) contribution to exhaust gas emissions.
- <u>Technology Concept:</u> Offer a transportable, onsite full-scale treatment capable of remediating PFAS-impacted soils at sites of AFFF release/discharge (e.g., fire training areas, soil IDW).
- <u>Treatment Target:</u> Target soil volumes ranging from roughly 5K to 100K tons as alternative to current options relying on costly transport/disposal to permitted landfills or transport/destruction at stationary incinerators.
- <u>Air Toxics and Emission Modeling:</u> Perform air quality emissions modeling using air dispersion models and screen for potential impacts exceeding accepted Air Toxic levels/limits.
- <u>Regulatory Acceptance:</u> Engage EPA and MassDEP to provide perspective and guidance on additional data that would be influential in prompting regulatory acceptance of the TD/TO technology to treat PFAS-contaminated soil.
- <u>Sustainability Element:</u> Treat PFAS-impacted soils to unrestricted use levels for onsite reuse.



Concept Layout for Proposed Thermal Treatment System for ESTCP Demonstration Test at JBCC

Questions?

Acknowledgements

- **Lead Organization**
  EA Engineering, Science, and Technology, Inc., PBC (EA): Frank Barranco (Principal Investigator), Nikki Wagner (Lead Scientist), Jason McNew (Responsible Engineer), Paul Caprio (Technical Quality Control), Ivy Harvey (Program Manager)
- **Co-Performers**
  TD*X Associates: George Hay, PE, Carl Palmer, PE, and Gregg Meyers
- AFCEC at JBCC Liason: Rose Forbes
- Developmental Specialty Analytical Services Eurofins/TestAmerica
- EPA Combustion Source Branch: Jeff Ryan and Center for Environmental Measurement and Modeling (CEMM) Team from Research Triangle Park (RTP)