Innovation that provides sustainable solutions to complex challenges worldwide

Thermal Treatment of Per- and Polyfluoroalkyl Substances (PFAS) in Soil

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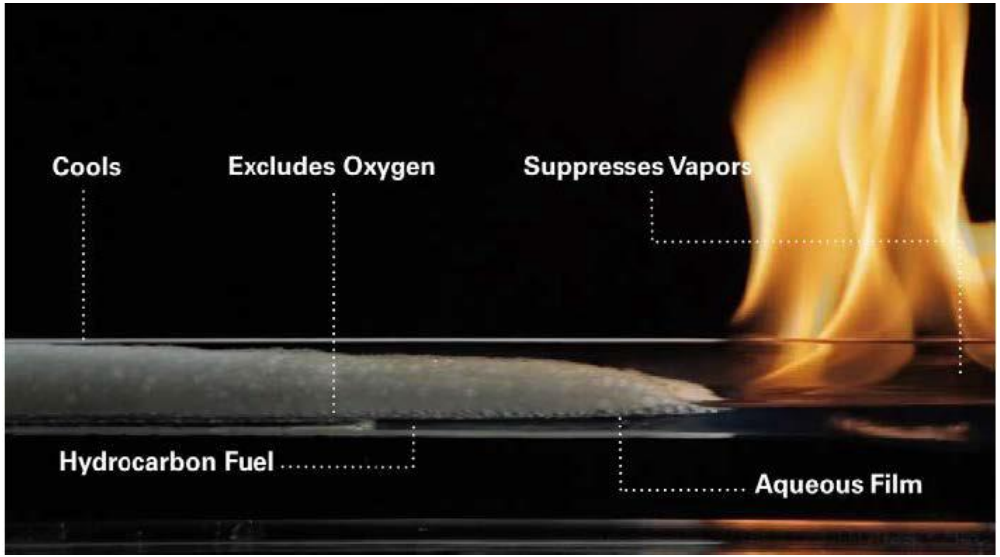
Outline & Acknowledgements

- Background
- Thermal Treatment Testing Data
- Implications
- Future Plans

- Jacobs
  - Katie Rabe
  - Laura Cook
  - Bill DiGuiseppi
- Iron Creek: Roger Richter
- SGS
  - Tim Fitzpatrick
  - Richard Grace
  - Sean Campbell
- Battelle: Ramona Darlington

Aqueous Film Forming Foam (AFFF)

- Military Use
  - Crashes
  - Fire Training Areas
- Commercial Fire Fighting
  - Rail
  - Airports
  - Fire Training Areas
- Industrial Fire Fighting
  - Tank Farms
  - Refineries



http://williamsfire.com/files/PDFs/TFPP-C8-to-C6-Transition-Bulletin.pdf

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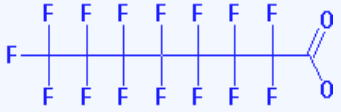
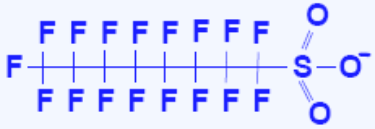
AFFF Chemistry

- Per and polyfluorinated alkyl substances (PFAS)
- >300 individual PFAS
  - ~80% of PFAS mass in AFFF
- Major Components of AFFF
  - PFOA
  - PFOS
  - PFBS
  - 6:2 FtS

Perfluorooctanoic acid (PFOA)

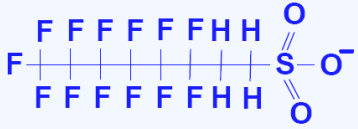


Perfluorooctane sulfonate (PFOS)



Perfluorobutane sulfonate (PFBS)

6:2 Fluorotelomer sulfonate (6:2 FtS)



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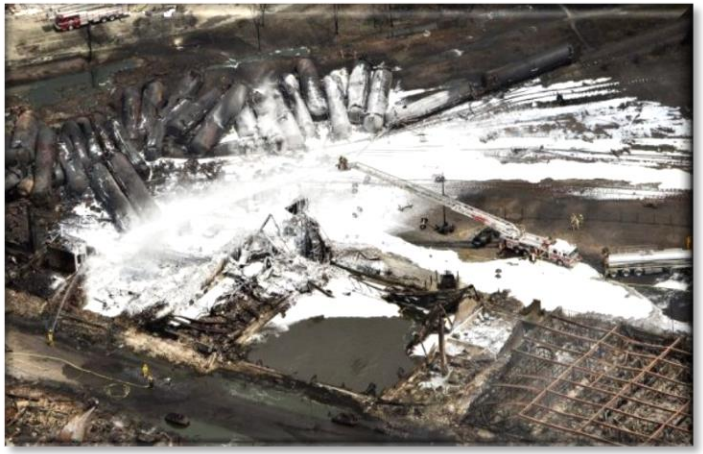
Concerns with Major AFFF Components

- Recalcitrant
  - Carbon-Fluorine bond is strong and stable
- Highly mobile in the environment
  - Both hydrophobic & oleophobic
  - Infiltrate readily to the groundwater
- Chemical structure similar to fatty acids
  - Readily absorbed into blood serum
  - C8 Panel identified effects on human health
    - Half-life: 5.4 yrs for PFOS / 3.8 yrs for PFOA



Lac-Mégantic derailment in Quebec

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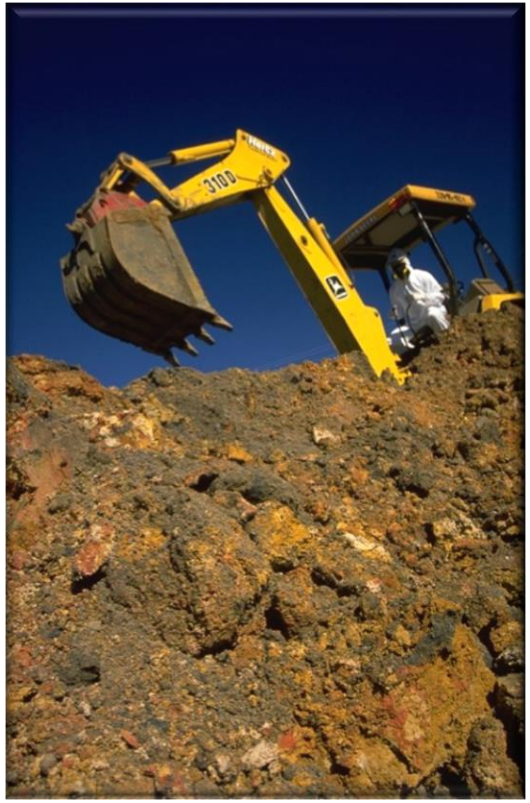
Soil Remediation - Practiced

- Excavation
  - Landfilling retains liability
  - Incineration: energy/carbon footprint concerns
- Stabilization/Sorption
  - RemBind (Ziltek's carbon, AA, kaolin clay)
  - Longevity?
- Soil washing
  - Waste stream handling



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Thermal Desorption

- **Low temperature (100-300 C)**
- **Medium temperature (300-600 C)**
- **High Temperature (600-1000 C)**

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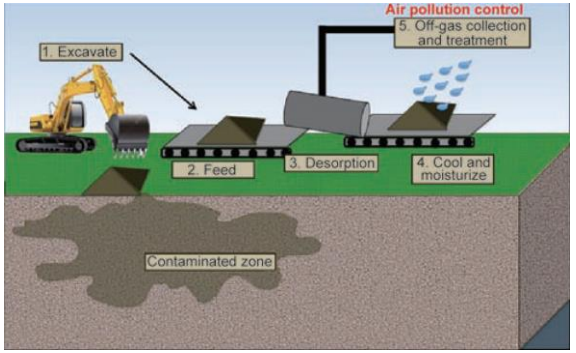
Thermal Desorption – Ex-Situ

- Typical Configurations
  - Rotary Kiln
  - Rotary Screw
  - Batch
- Heat Methods
  - Direct fired (Heated air in contact with soils)
  - Indirect fired (Heated Surface in contact with soils)
  - Flame
  - Infrared
- Air Emission
  - Capture and mitigate



Vidonish et. al., 2016

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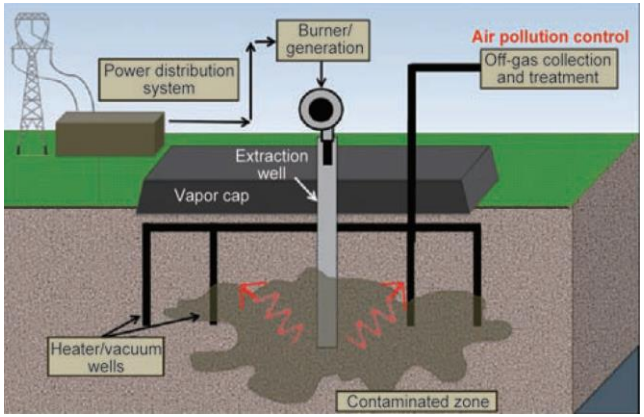
Thermal Desorption – In-Situ

- In place
  - Vadose Zone
  - Groundwater table depression
- Soil Piles
  - Sprung Structure for vapor capture
- Heat Methods
  - Indirect fired (Heated Surface in contact with soils)
- Air Emission
  - Capture and mitigate



Vidonish et. al., 2016

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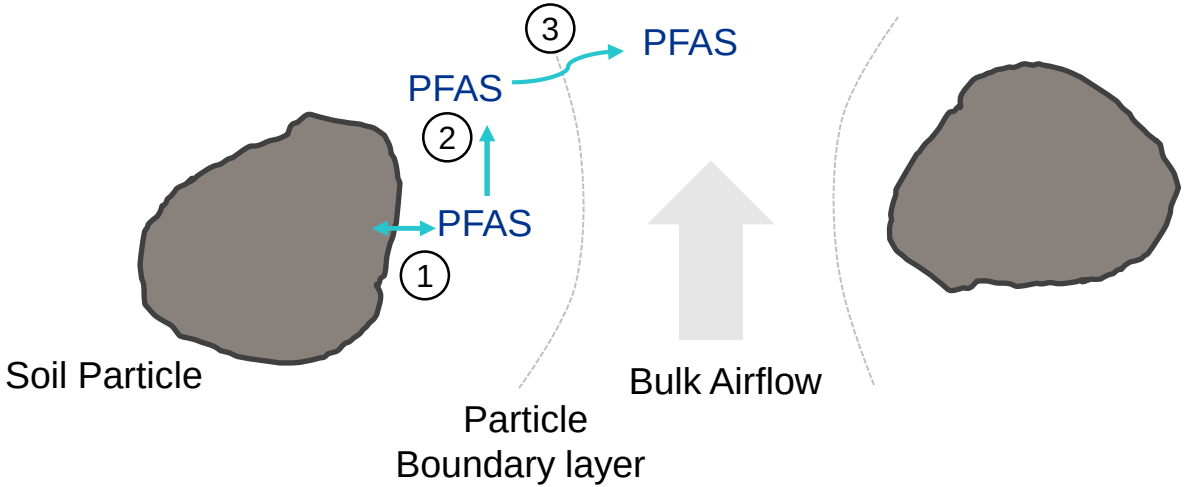
Conceptual Model for Desorption



1. Desorption: Impart energy to overcome sorption
2. Sublimation: Impart Energy to drive into gas phase
3. Diffusion: from boundary layer to bulk air phase

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Previous Low (250 C) and High Temperature (>450 C) Studies

Study	Thermal Method	Initial Total PFAS Conc. (µg/kg)	% Reduction in Total PFAS	Exposure Temperature/Time	PFAS Analyzed
Iron Creek/ Jacobs	Infrared Heating	200	26	250˚C for 8 days	24 PFAS analyzed
Endpoint/ Jacobs	Vapor Energy Generator	40	Minimal 50 >99.9	482˚C for 15 mins 593˚C for 15 mins 954˚C for 30 mins	10 PFAA analyzed
Iron Creek/ Jacobs	Infrared Heating	290	89.3-99.8 97.3-100 99.8-100	400˚C for 60 mins 550˚C for 50 mins 700˚C for 80 mins	24 PFAS analyzed
Confidential	Rotary Kiln	175	>99.9	450˚C for <20 min	20 PFAS analyzed
Confidential	Rotary Kiln	1200	>99	700˚C for <20 min	16 PFAS Analyzed

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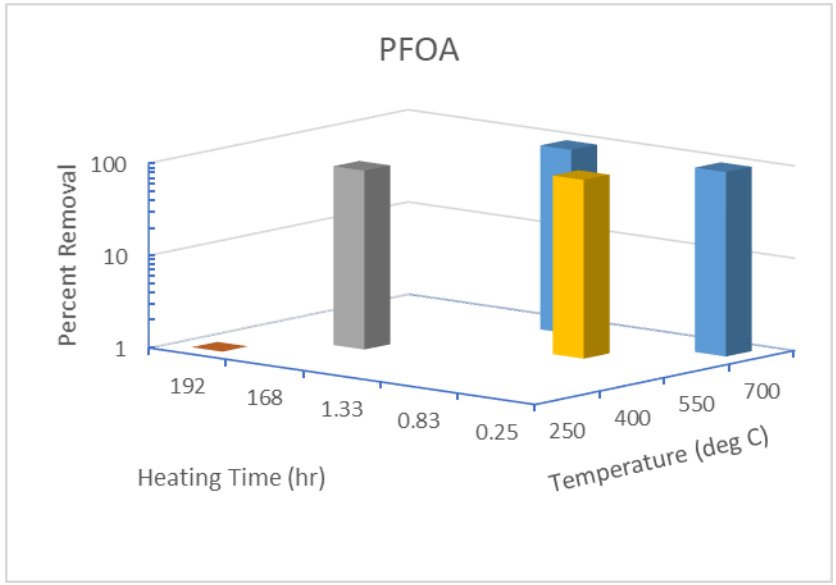
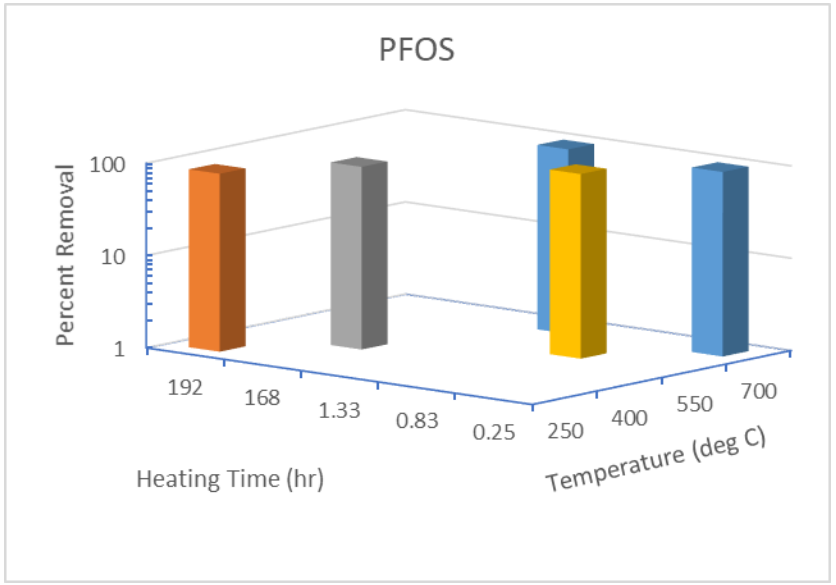
Time-Temperature Data: Thermal Desorption





- Clear threshold in the medium temperature range:

  >250 ºC and <400 ºC

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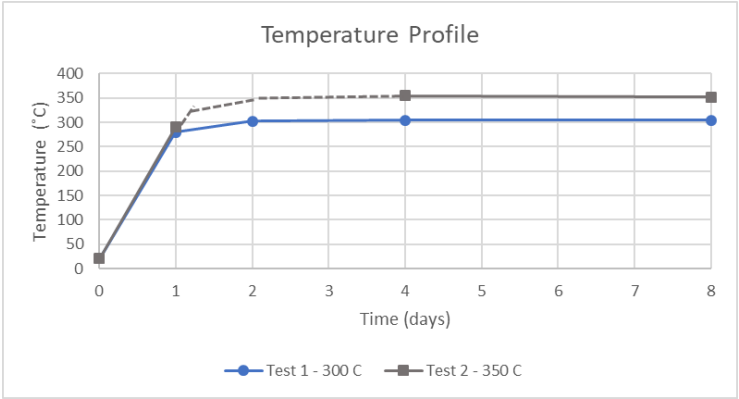
Pilot Study : Medium Temperature Testing

- Tested infrared thermal treatment
- 1 cubic foot bench test chamber
- Soil samples collected after heating to 300˚C and 350˚C.
- Samples collected at 1, 2, 4, and 8 days
- Samples analyzed for 24 PFAS compounds by SGS AXYS.

Parameter	PFAS	PFCA	PFOA	PFSA	PFOS
Initial Conc. (µg/Kg)	151	24.7	5.52	118	96



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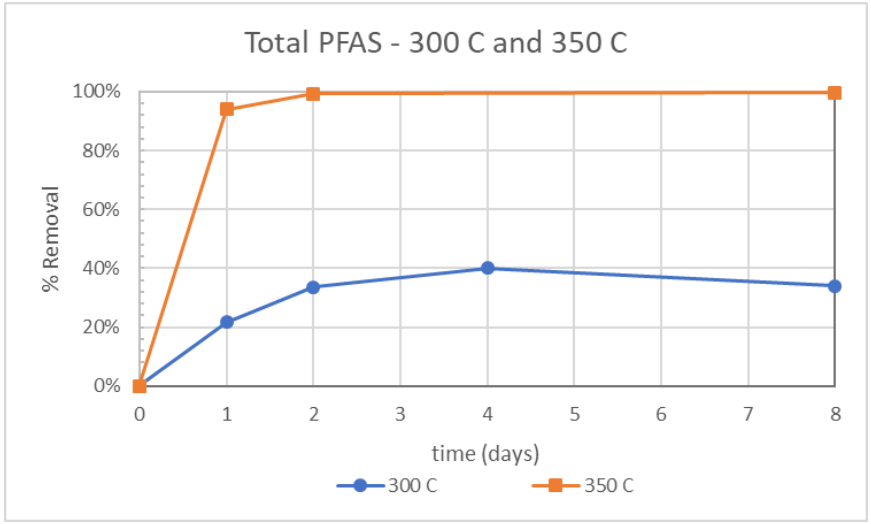
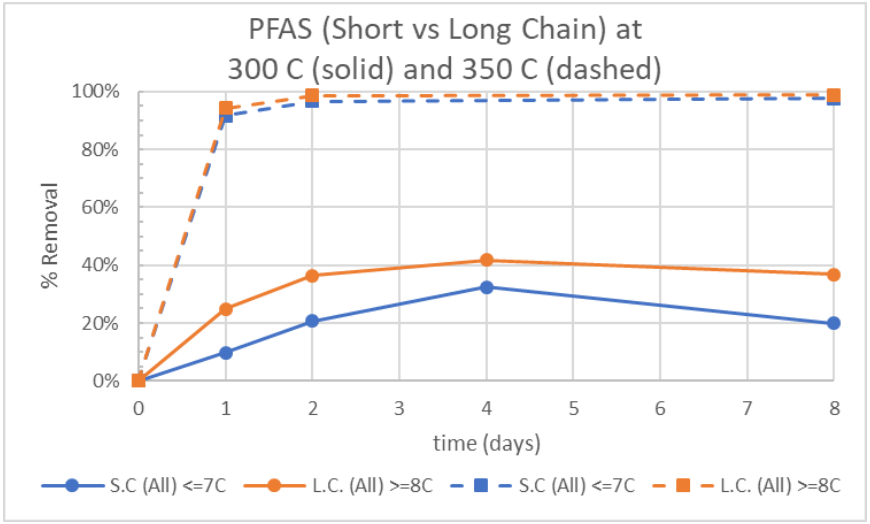
Medium Temperature Results – Total PFAS





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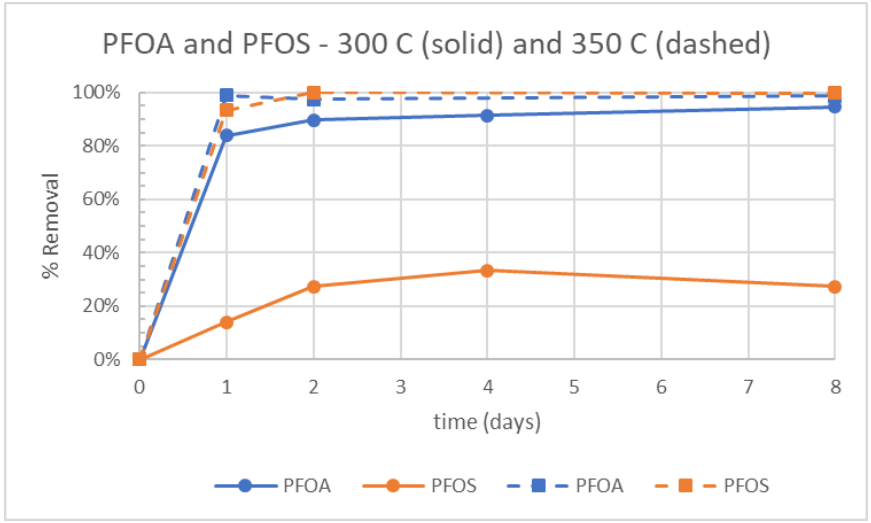
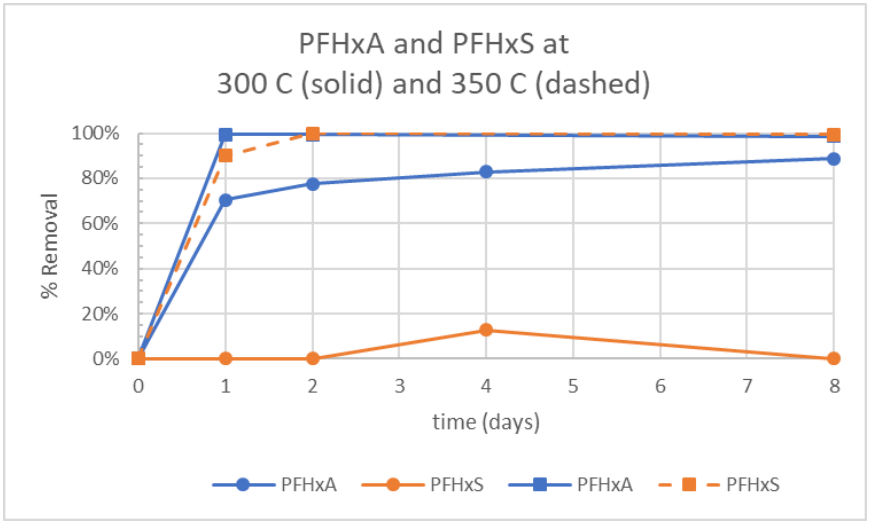
Medium Temperature Results





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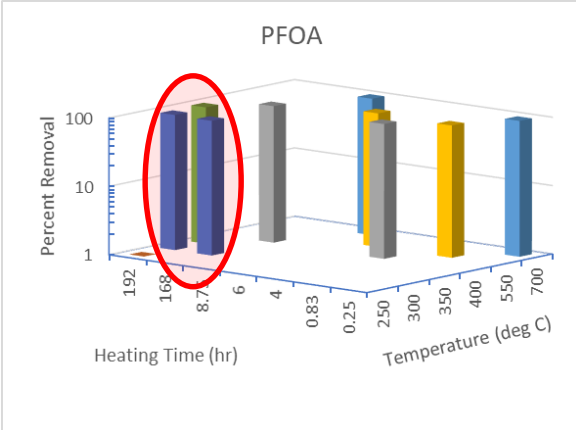
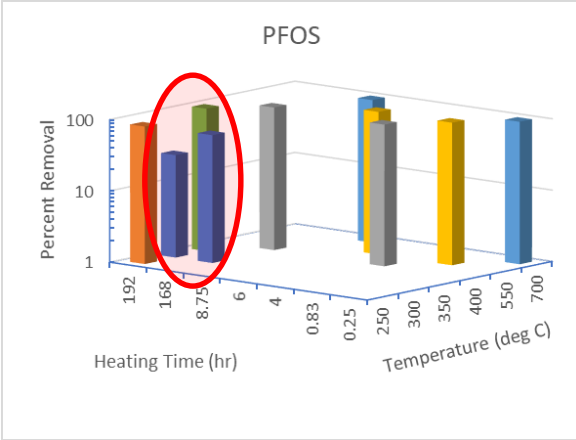
Testing Summary

- Appears PFSA are more strongly bound
  - require higher temperature (more energy) for desorption
- Data supports excellent removal at 350 C
  - Reaches maximum removal in >2 days of heating
  - >99.4% removal of total PFAS
- Low end of “Medium temperature” Thermal Desorption
  - Cost savings for lower energy input
  - Options for both ex-situ and in-situ application





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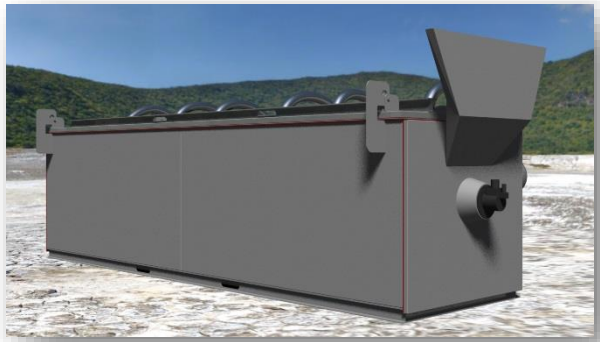
Next Steps: Need for Field Scale Data

- Evaluate PFAS-soil interactions with various soils
  - Clay / humic material / sandy soil
  - Implication to both desorption and diffusion steps
- PFAS Mass Balance on process
  - Wall surface, vapor capture, final emissions
- Air emissions management
  - Collection / Capture
  - Particulate removal
  - Direct Treatment vs Condensation
  - Adsorption vs Oxidation



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Future Work Planned

- SERDP Supplemental Investigation (US DoD Funding)
  - *Field Demonstration of Infrared Thermal Treatment of PFAS-contaminated Soils from Subsurface Investigations*

- Potential soil pile tests at USAF & AU Defence installations
  - Would use excess steam from power plant for electricity generation
  - Supplemented with natural gas
  - Constructed soil pile would be limited in size
  - Ultimate concept would be large soil pile
  - Would test for 30 to 90 days

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Thank you for your time
Questions?

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Consideration of the Limiting Processes

- Desorption
  - Energy to desorb is greater than energy to adsorb {enthalpy ΔH^o}
  - Ionic interactions stronger than physical adsorption

$$-\Delta G° = RT\ ln(K) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

- Sublimation
  - Boiling temperatures of PFAS > H_2O (PFOA = 189 ºC)
  - ex. PFOA: ΔH_{sub} = 90.9 KJ/mol compared to ΔH_{vap} = 46.8 KJ/mol
- Diffusion

$$D \propto \frac{T^{1.75}}{P\ V_d^{0.67}\ M^{0.5}}$$

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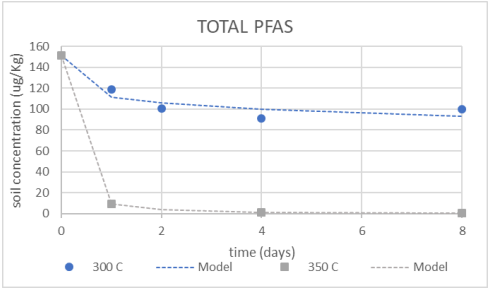
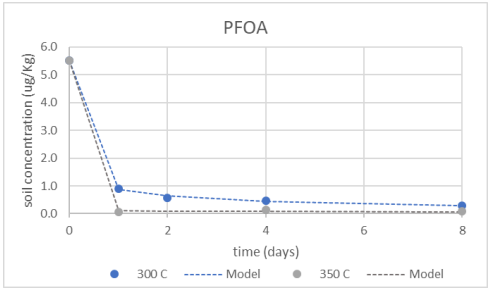
Desorption Rates: 1st Order Kinetics

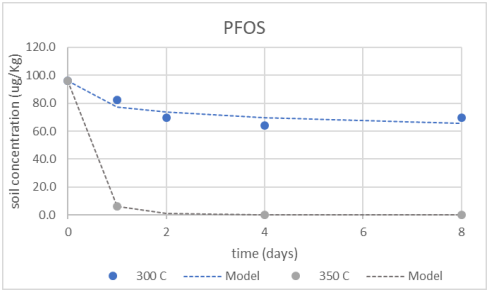
$$C = C_0 e^{-kt^n}$$

k – kinetic desorption rate constant
n – intensity factor

Parameter	PFAS	PFCA	PFOA	PFSA	PFOS
Co (ug/Kg)	151	24.7	5.52	118	96
			300 C		
k	0.306	1.34	1.85	0.176	0.220
n	0.219	0.187	0.225	0.278	0.268
			350 C		
k	2.82	3.29	3.81	2.64	2.72
n	0.402	0.050	0.090	0.47	0.758







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