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STAR and STARx – Smouldering Remediation of PFAS-Impacted Soils

Presented by: Laura Kinsman, M.E.Sc.

Overview

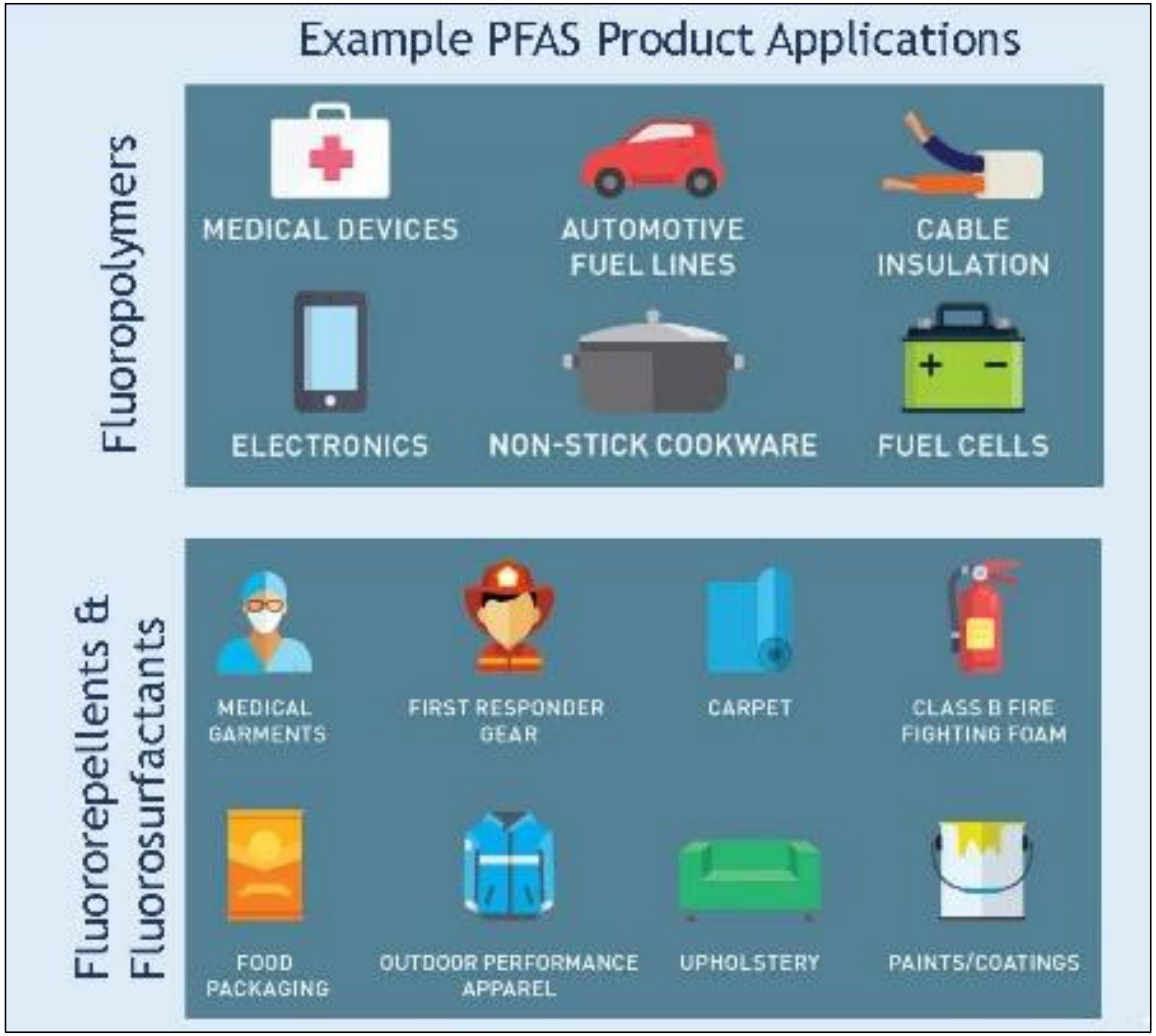
- **PFAS Overview**
- **Smouldering Combustion Basics**
  - Hydrocarbon Applications
  - Applicability to PFAS
- **PFAS Smouldering**
  - Lab Results
  - Scale Up Testing Program
- **Summary**

PFAS Overview

No natural source

Thousands of chemicals

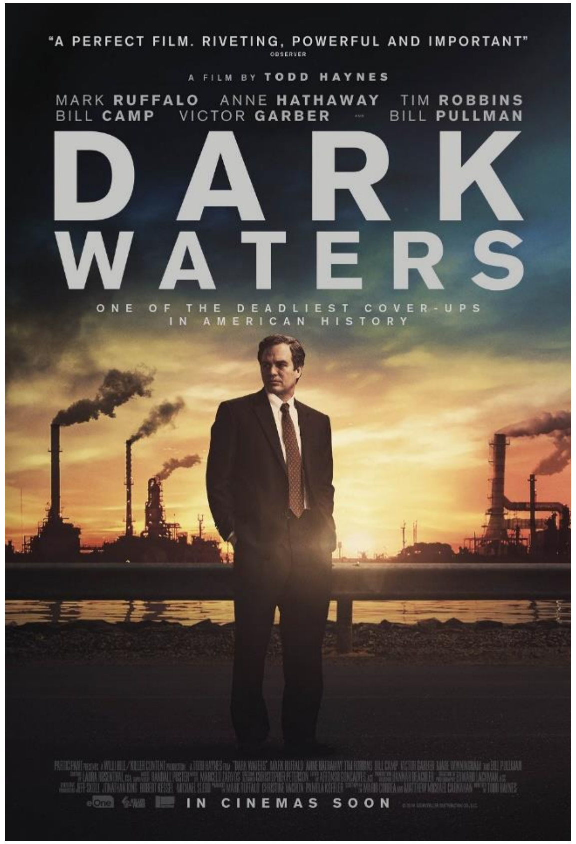
Thermally and chemically stable



Resist water, heat, and grease and reduce friction

Linked to cancer, immune and reproductive system toxicity

PFAS in the Media



abcNEWS VIDEO LIVE SHOWS CORONAVIRUS

'Ticking time bomb': PFAS chemicals in drinking water alarm scientists over health risks

EPA under pressure to regulate PFAS, found in the water of nearly 2,800 cities.

By Devin Dwyer, Stephanie Ebbs, and Jacqueline Yoo
10 August 2021, 15:33 • 17 min read

US EPA Interim Guidance

United States Environmental Protection Agency

Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials That Are Not Consumer Products

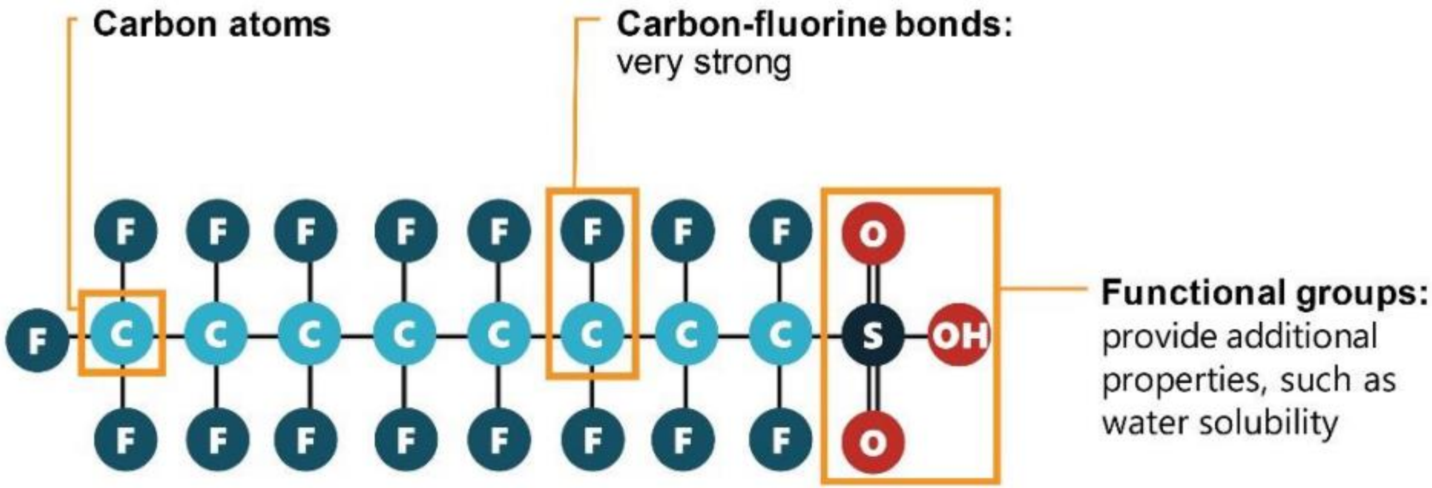
On December 18, 2020, EPA released for public comment new interim guidance that will help protect the public from exposure to these emerging chemicals of concern. Specifically, the new interim guidance outlines the current state of the science on techniques and treatments that may be used to destroy or dispose of PFAS and PFAS-containing materials from non-consumer products, including aqueous film-forming foam (for firefighting).

Presents three destruction / disposal methods that may be effective and are commercially available:

- Thermal treatment
- Landfilling
- Underground injection (for liquid wastes)

Thermal Treatment of PFAS

$$PFAS \xrightarrow{HEAT} HF + shorter\ chain\ compounds$$



(AAAS, 2021)

Mineralization

- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

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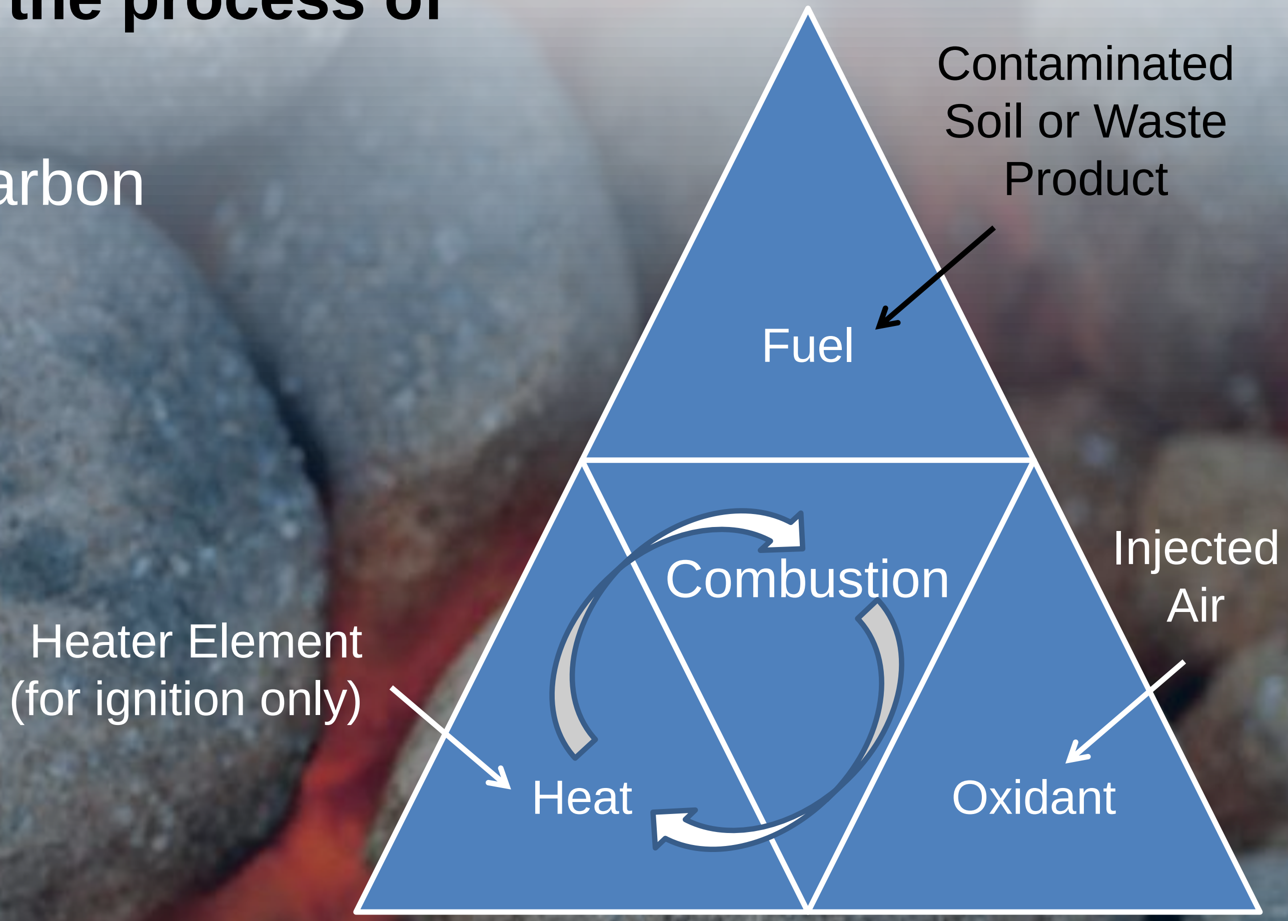
Vecitis et al., 2009; Wang et al., 2011; Watanabe et al., 2015; Yamada et al., 2005

Smouldering Combustion

Smouldering Combustion

STAR and STARx are based on the process of smouldering combustion:

Exothermic reaction converting carbon compounds to CO_2 + H_2O



STAR / STARx is a flameless combustion process: only smouldering is possible within a porous matrix (i.e., soil)

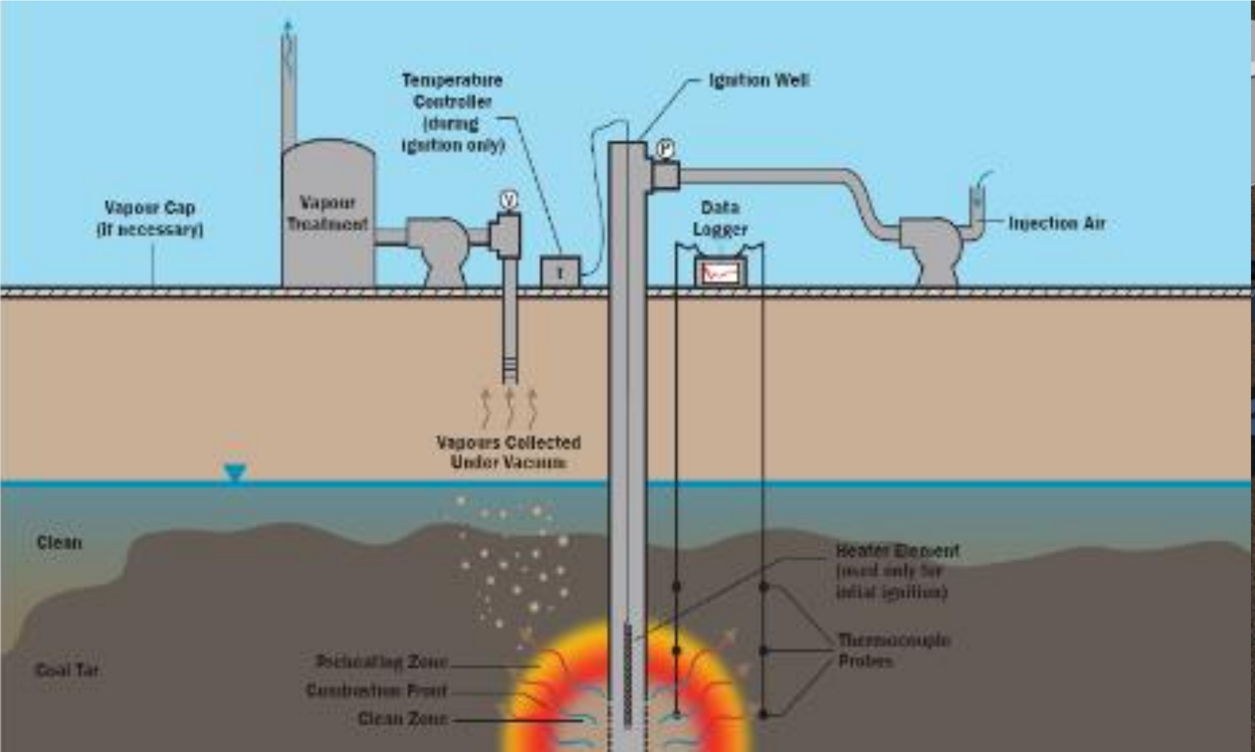
Modes of Application

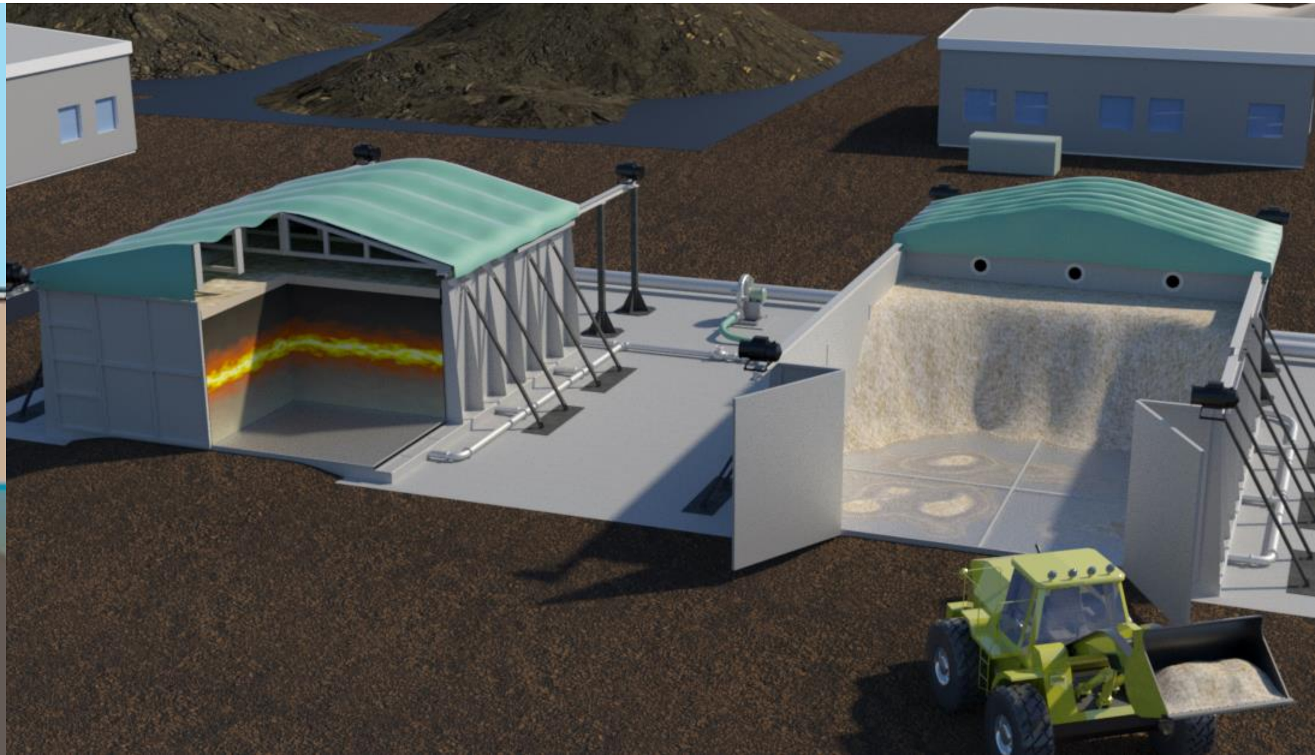
STAR

- **In situ (below water table)**
  - Applied via wells in portable in-well heaters

STARx

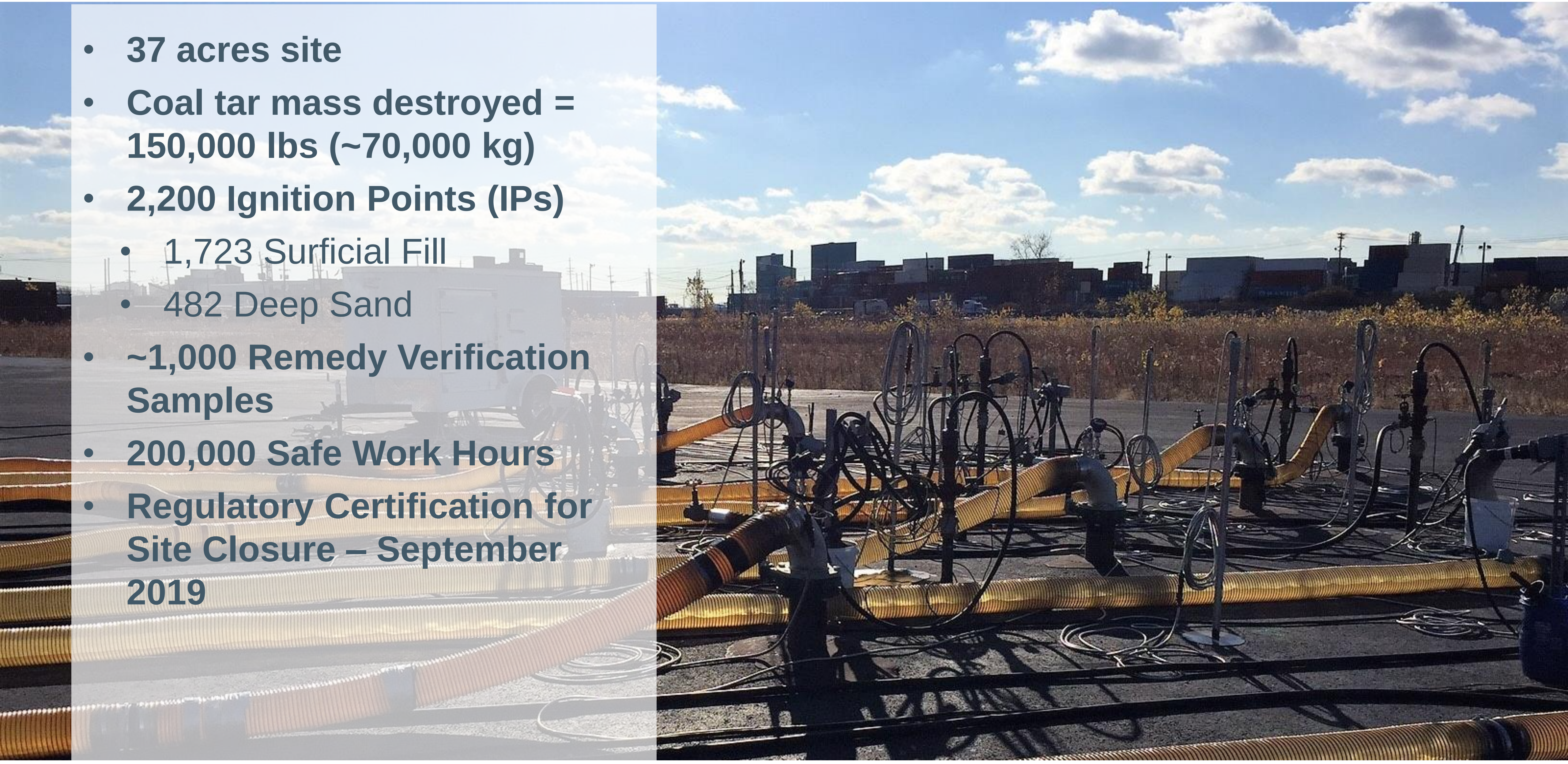
- **Ex situ (above ground)**
  - Soil piles placed on "Hottpad" system





STAR Example Project – New Jersey

- **37 acres site**
- **Coal tar mass destroyed = 150,000 lbs (~70,000 kg)**
- **2,200 Ignition Points (IPs)**
  - 1,723 Surficial Fill
  - 482 Deep Sand
- **~1,000 Remedy Verification Samples**
- **200,000 Safe Work Hours**
- **Regulatory Certification for Site Closure – September 2019**



STARx Example Project – SE Asia

Before

After

Thermal Treatment of PFAS

$$PFAS \xrightarrow{HEAT} HF + shorter\ chain\ compounds$$

Mineralization

- Increases with Temp > 700°C
- Maximizes at Temp > 900°C

But PFAS not a smoulderable fuel

- Requires a surrogate fuel

What About Spent GAC?

- A potential waste product that contains PFAS

Vecitis et al., 2009; Wang et al., 2011; Watanabe et al., 2015; Yamada et al., 2005

SERDP Project

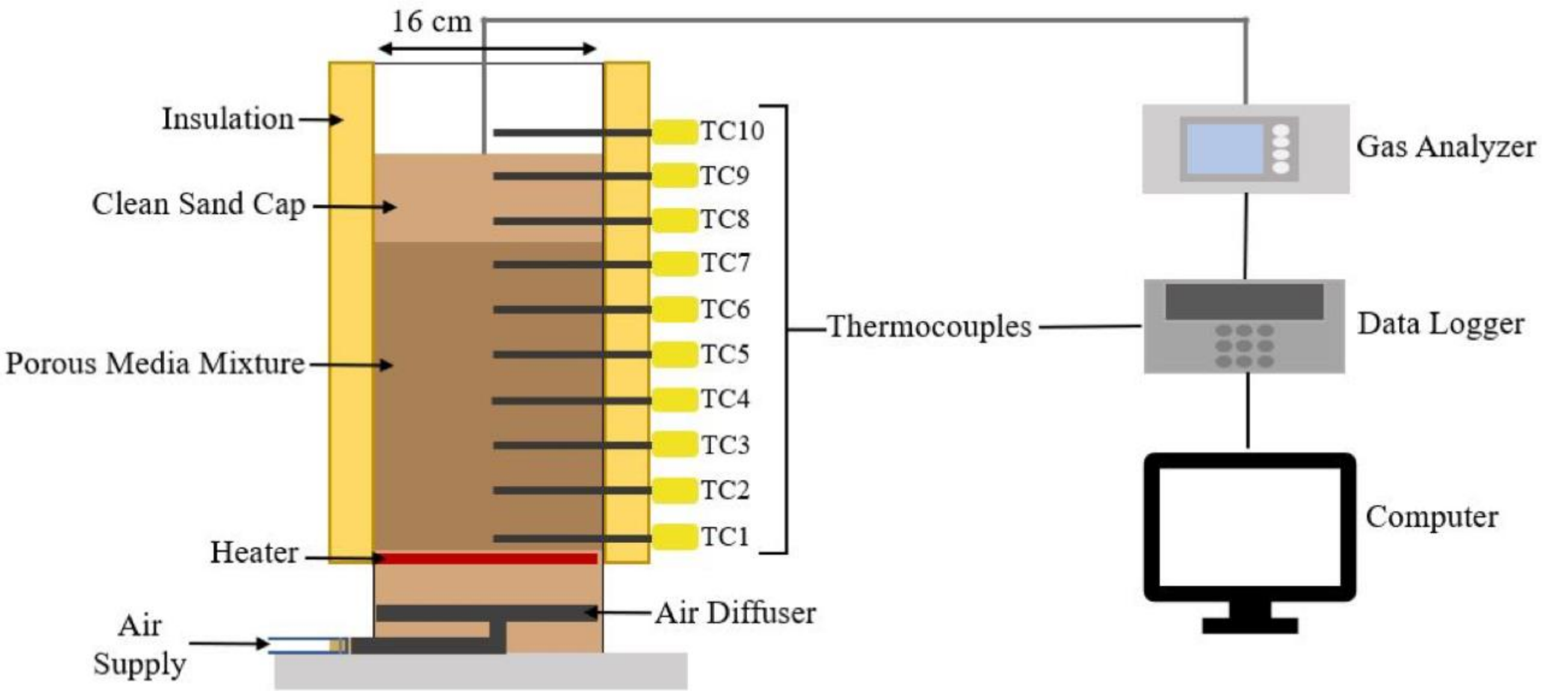
Goal: Can smouldering GAC remediate PFAS?

- Phase I (no PFAS)
    - What is the relationship between GAC concentration and smouldering temperature?

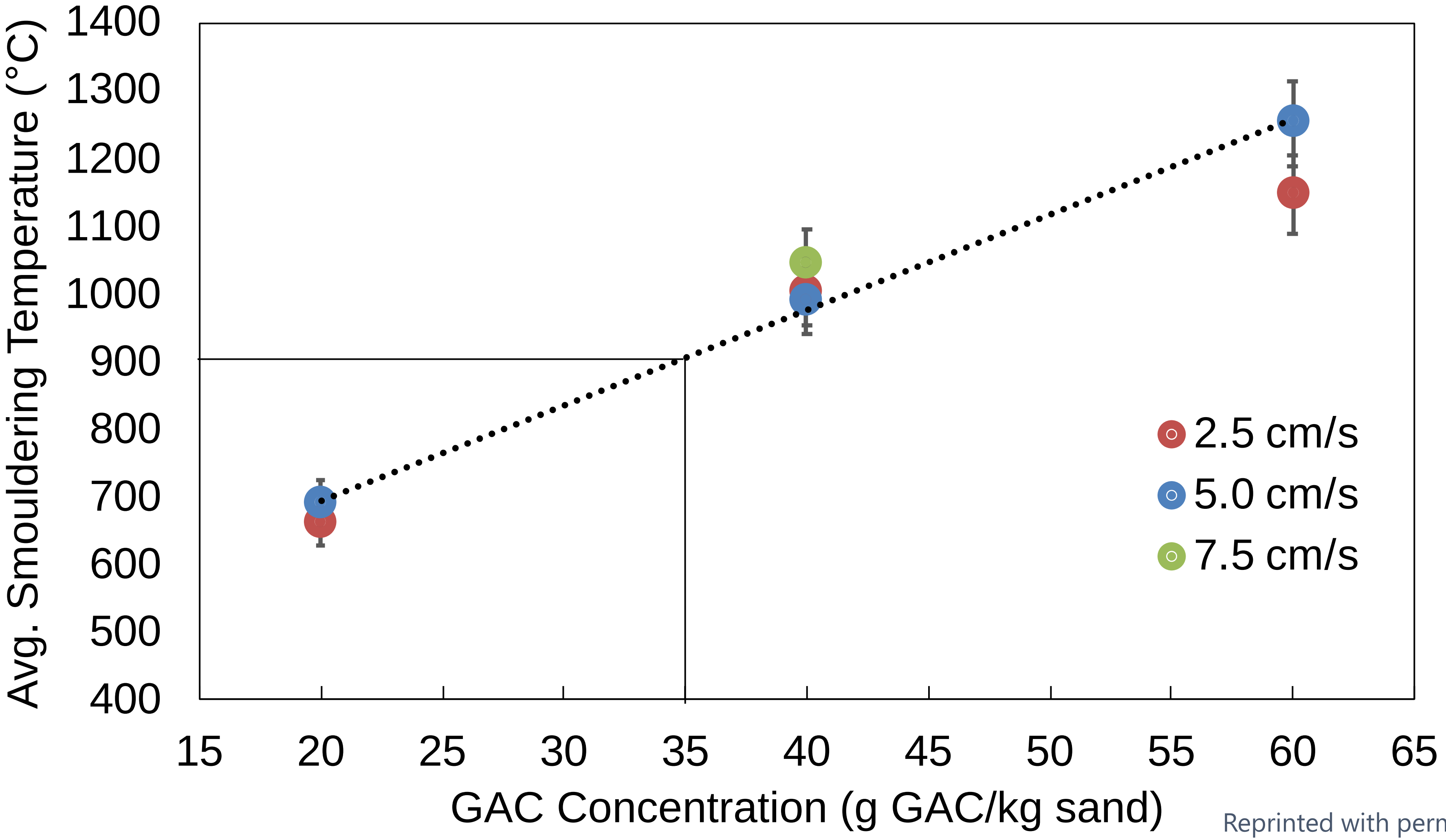
Can smouldering GAC remediate PFAS?

- Phase II: PFAS-contaminated GAC
- Phase III: PFAS-contaminated surrogate soil
- Phase IV: PFAS-contaminated field soil

Experimental Setup



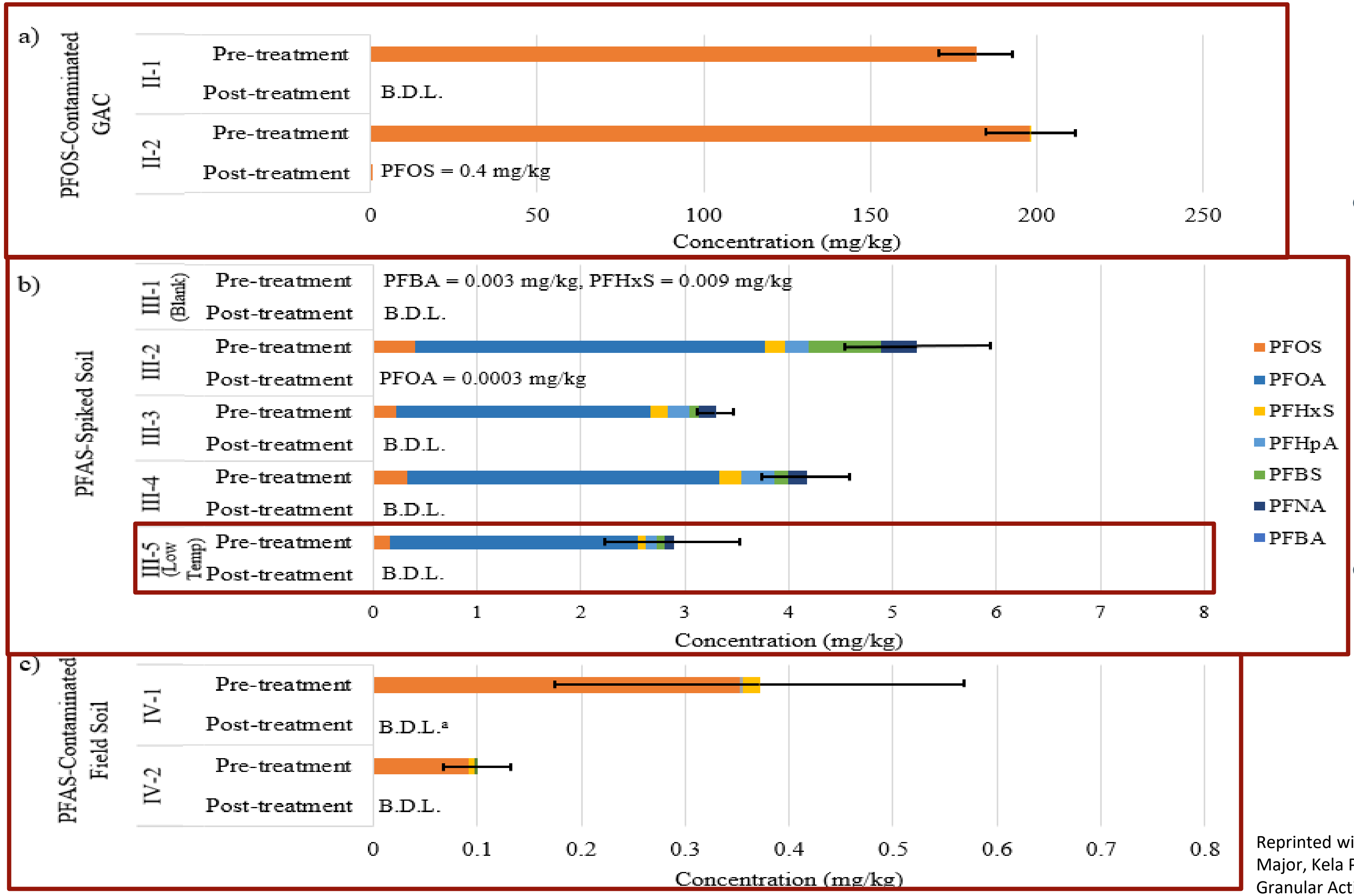
Smouldering Temperatures



Key Takeaways

- Temp ∝ to [GAC]
- Small impact of air flux on temp
- Smouldering front velocity increases with increased air flux (data not shown)

PFAS in Soil and GAC



[a]PFHxS, PFOA, and PFOS were B.Q.L.

B.D.L. = 0.0005 mg/kg (III-2 B.D.L. = 0.0002 mg/kg) and B.Q.L. = 0.001 mg/kg.

Key Takeaways

- BDL (except as noted) after treatment regardless of initial PFAS mass over orders of magnitude
- Low Temp (III-5) was also BDL

Publication

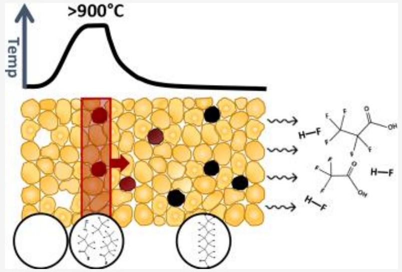
Environmental Science & Technology

pubs.acs.org/est Article

Remediation of PFAS-Contaminated Soil and Granular Activated Carbon by Smoldering Combustion

Alexandra L. Duchesne, Joshua K. Brown, David J. Patch, David Major, Kela P. Weber, and Jason I. Gerhard*

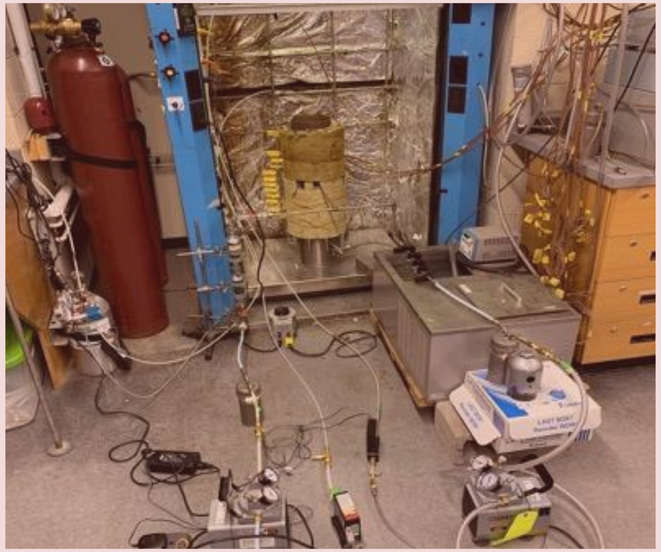
Cite This: https://dx.doi.org/10.1021/acs.est.0c03058 Read Online



ABSTRACT: This study explored smoldering combustion for remediating polyfluoroalkyl substance (PFAS)-impacted granular activated carbon (GAC) and PFAS-contaminated soil. GAC, both fresh and PFAS-loaded, was employed as the supplemental fuel supporting smoldering in mixtures with sand (≈175 mg PFAS/kg GAC-sand), with PFAS-spiked, laboratory-constructed soil (≈4 mg PFAS/kg soil), and with a PFAS-impacted field soil (≈0.2 mg PFAS/kg soil). The fate of PFAS and fluorine was quantified with soil and emission analyses, including targeted PFAS and suspect screening as well as hydrogen fluoride and total fluorine. Results demonstrated that exceeding 35 g GAC/kg soil resulted in self-sustained smoldering with temperatures exceeding 900 °C. Post-treatment PFAS concentrations of the treated soil were near (2 experiments) or below (7 experiments) detection limits (0.0004 mg/kg). Further, 44% of the initial PFAS on GAC underwent full destruction, compared to 16% of the PFAS on soil. Less than 1% of the initial PFAS contamination on GAC or soil was emitted as PFAS in the quantifiable analytical suite. Results suggest that the rest were emitted as altered, shorter-chain PFAS and volatile fluorinated compounds, which were scrubbed effectively with GAC. Total organic fluorine analysis proved useful for PFAS-loaded GAC in sand; however, analyzing soils suffered from interference from non-PFAS. Overall, this study demonstrated that smoldering has significant potential as an effective remediation technique for PFAS-impacted soils and PFAS-laden GAC.

For more details: https://dx.doi.org/10.1021/acs.est.0c03058

On-Going Work



Phase 1:

Lab Column Tests

Mass Balance / Optimization

Phase 2:

Intermediate Scale Reactor

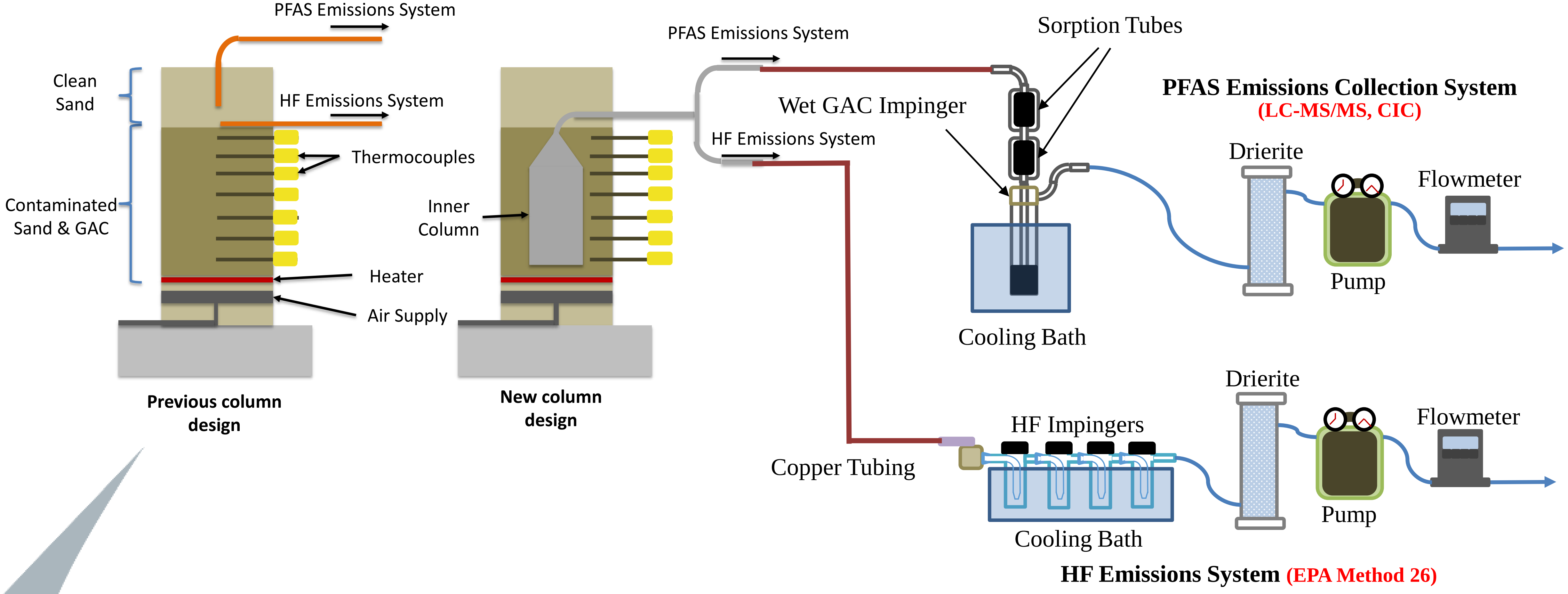
Heterogeneity

Phase 3:

Pilot Scale Tests

Field Deployable

Phase 1 – Lab Column Tests



Key Takeaways

- $PFAS_{13}$ reduced to below detection limits in soils
- <1% of $PFAS_{13}$ found in the emissions
  - Majority of PFAS is destroyed (converted to HF)
  - No breakthrough of PFAS in emissions collection system
- PFAS are altered during smouldering
  - Formation of carboxylate PFAS
  - Conversion from C4-C9 to C2-C3
- HF data suggests ~70 - 80% mass balance

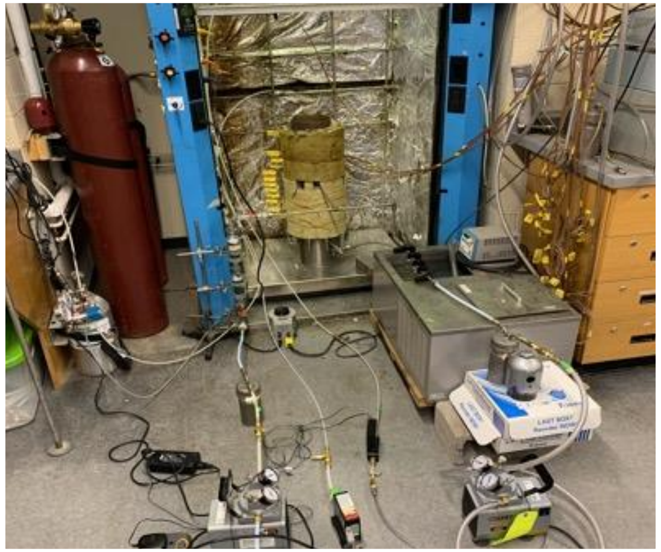
Phase 1 – Enhanced Destruction

- Calcium Oxide (CaO) found to exhibit pseudo-catalytic effect promoting PFAS destruction at lower temperatures (Wang et al., 2011, 2013, 2015)
- Column tests using PFOS loaded on GAC at known concentrations

Test Name	Average Peak Temperature (°C)	GAC Concentration (g/kg)	CaO Concentration (g/kg)	Total F^- Captured as HF (mg)
II-2	940	50	-	73.8%
II-3	887	50	-	48.1%
II-4	908	50	-	55.7%
II-6	795	50	50	2.3%
II-8	890	50	10	4.8%

- Preliminary results suggest CaO also removes HF from emissions

On-Going Work



Phase 1:

Lab Column Tests

Mass Balance / Optimization

Phase 2:

Intermediate Scale Reactor

Heterogeneity

Phase 3:

Pilot Scale Tests

Field Deployable

Phase 2 – Intermediate Scale Reactor

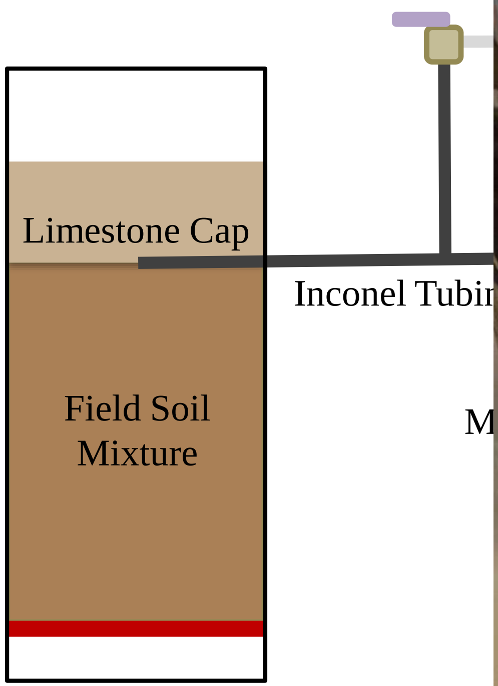
Limestone cap

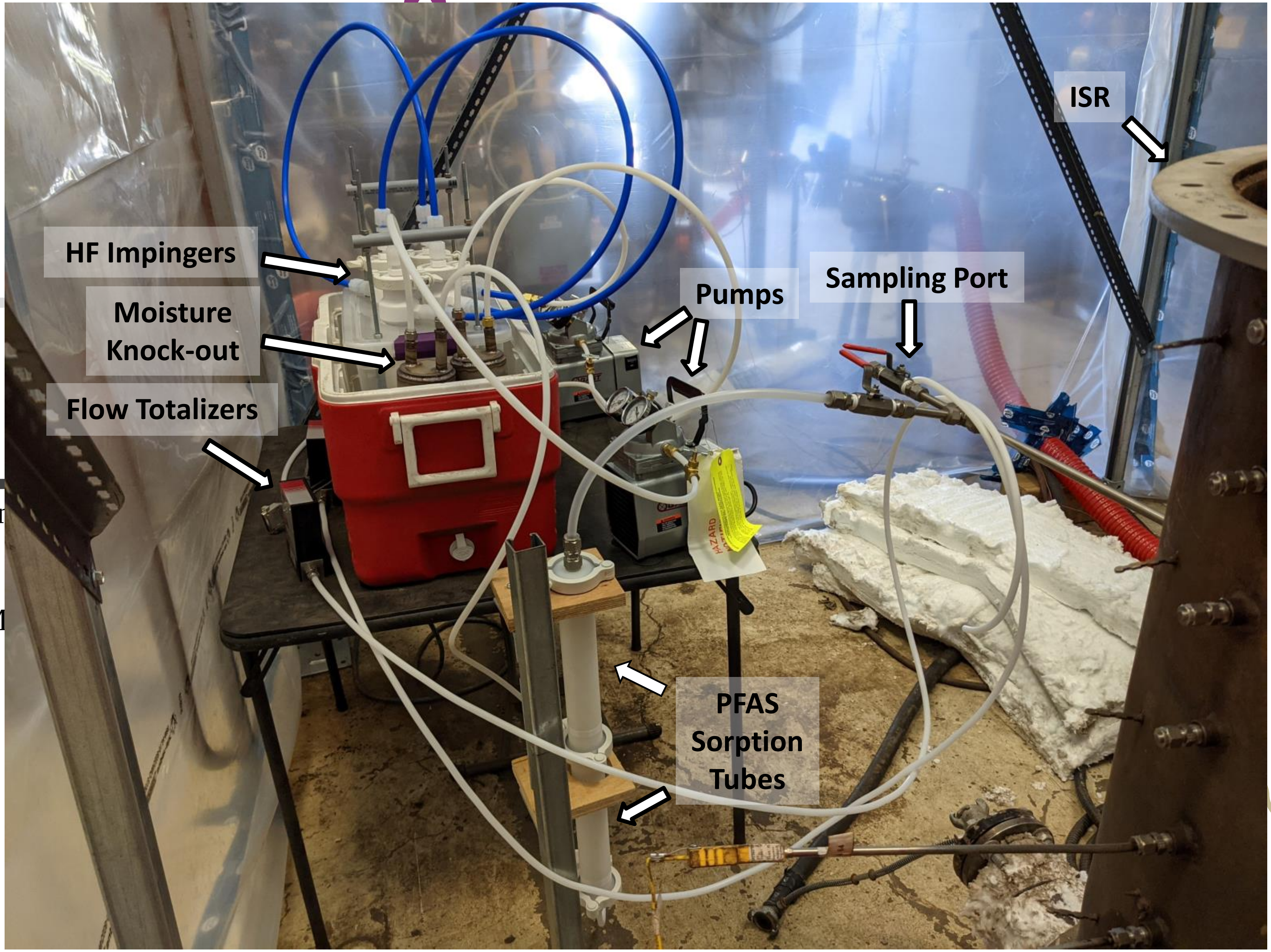
PFAS-Impacted Field Soil
+ 40 g/kg GAC + 10 g/kg CaO

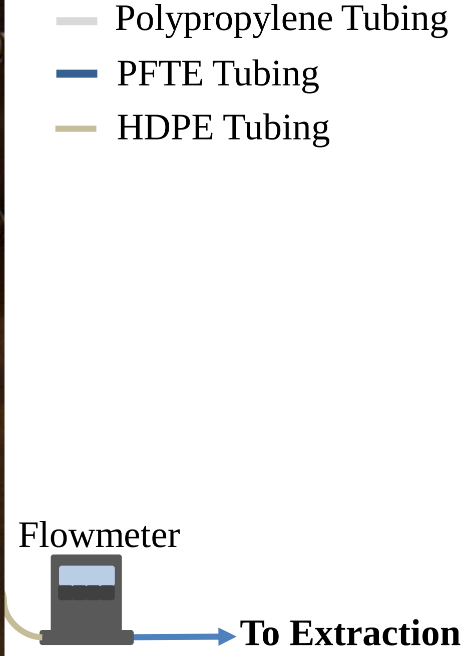
Objectives:

- Track peak combustion temperatures (centerline and radial)
- Evaluate effectiveness of CaO / limestone at removing HF
- Pre-/post-treatment soils analysis
- Emissions analysis

Phase 2 – Intermediate Scale Reactor



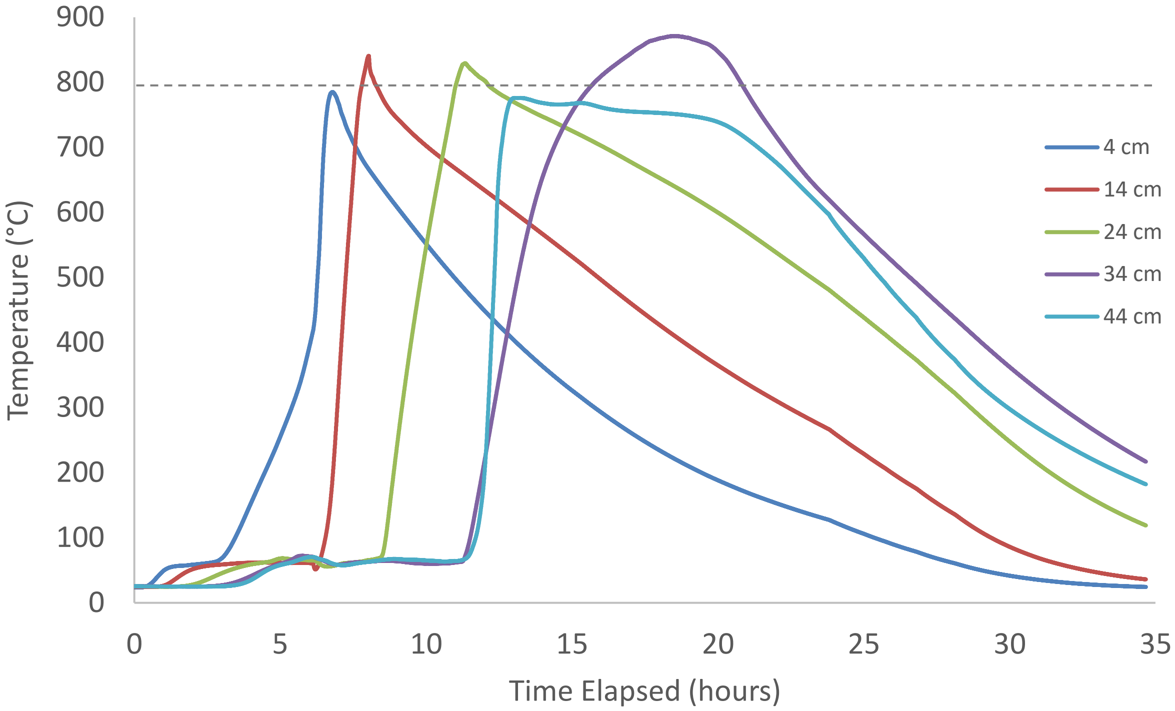




Phase 2 – Intermediate Scale Reactor

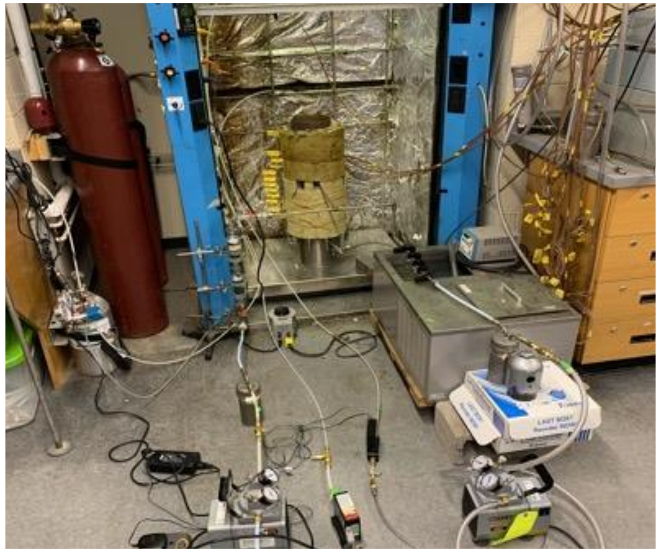
Pre-treatment

Post-treatment



- **Consistent peak temperatures (~800°C)**
- **HF not detected in emissions after limestone cap**
- **PFAS in soil and emissions analytical results pending**

On-Going Work



Phase 1:

Lab Column Tests

Mass Balance / Optimization

Phase 2:

Intermediate Scale Reactor

Heterogeneity

Phase 3:

Pilot Scale Tests

Field Deployable

Phase 3 – Pilot Test

- **CFB Trenton**
- **Mobilizing equipment late October 2021**

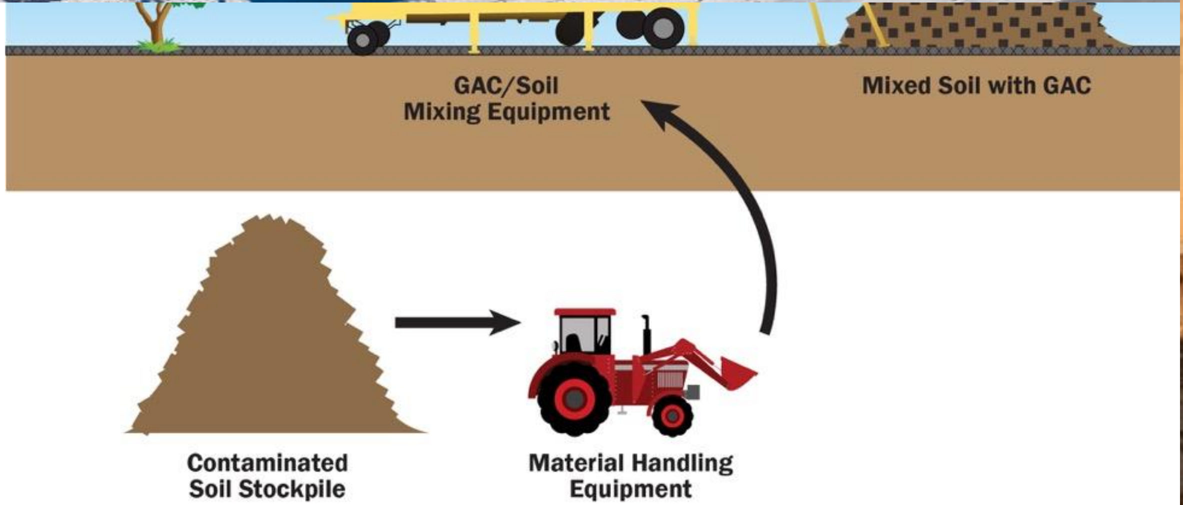
Two tests planned:
1. Virgin GAC
2. Spent GAC

Implications

- **Smouldering is very promising treatment option for:**
  - PFAS-contaminated soil mixed with clean GAC
  - PFAS-contaminated GAC

- **Potential for low-cost, combined treatment facility**
  - Contaminated GAC and soil can be combined for increased net treatment
  - GAC used in emissions treatment system can be used as fuel once spent

Potential Application
Ex Situ: Soil or Waste GAC



Potential Application
In Situ Source Treatment

Summary

- **STAR / STARx is a rapid, sustainable, and cost-effective method for treatment of coal tar, creosote, and petroleum hydrocarbons**
- **Significant potential for treatment of PFAS**
  - $PFAS_{13}$ reduced to below detection limits in soils
  - Majority of PFAS is destroyed (converted to HF)
  - CaO can promote destruction at lower temperatures and may remove HF from emissions
- **Larger scale tests to assess heterogeneity and ex situ field implementation in progress**

Acknowledgements

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Questions?

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