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Hydrocarbon Treatability Study of Antarctica Soil with Fenton's Reagent

Sam Beal, Ashley Mossell, and Jay Clausen

July 2021

Cold Regions Research and Engineering Laboratory

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Final report

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Preface

This study was conducted for the U.S. Army Corps of Engineers under the Engineering for Polar Operations, Logistics, and Research (EPOLAR) Program, EP-ANT-18-80. The technical monitor was Dr. Jay Clausen.

The work was performed by the Biogeochemical Sciences Branch (Mr. Nathan Lamie, Chief) of the of the Research and Engineering Division (Dr. George Calfas, Chief), U.S. Army Engineer Research and Development Center, Cold Regions Research Engineering Laboratory (ERDC-CRREL). At the time of publication, the Deputy Director for ERDC-CRREL was Mr. David Ringelberg and the Director was Dr. Joseph Corriveau.

This material was originally presented at the Association for Environmental Health and Sciences Foundation (AEHS) *30th Annual International Conference on Soil, Water, Energy, and Air* (Virtual) on March 25, 2021.

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

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Dr. Sam Beal, Ashley Mossell, and Dr. Jay Clausen
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Study Objectives

Determine the effectiveness of Fenton's Reagent and Modified Fenton's Reagent in reducing Total Petroleum Hydrocarbon (TPH) concentrations in petroleum-contaminated soil from McMurdo Station, Antarctica

$$Fe(II) + H^2O^2 \longrightarrow Fe(III) + HO^- + HO$$

Introduction

- McMurdo Station, Antarctica has large quantity of hydrocarbon contaminated soils
- Present remediation approach is dig and haul with shipment of contaminated soils to CA
- Remediation costs exceed $1M annually
- McMurdo Station is looking for inexpensive soils management solutions
- Hydrocarbons persist in the organic carbon limited soils and low temperature and soil moisture environment of Antarctica
- Prior bioremediation and Fenton's field treatability study efforts were ineffective

Previous Fenton's Reagent Treatability Studies

- Room temperature laboratory studies with Fenton's or Modified Fenton's typically yield > 50% TPH contaminant reduction (Lu et al. 2010; Tsai et al. 2009; Mater et al. 2007)
- Complete TPH reduction using Fenton's during laboratory studies at 4ºC with Arctic soils (Sherwood and Cassidy 2014)
- Field study using Fenton's reagent on hydrocarbon contaminated soils at Old Casey Station, Antarctica found no significant contaminant reduction (Ferguson et al. 2004)
- No prior laboratory studies have been conducted with Antarctica TPH contaminated soils

Site Information

- McMurdo Station, Antarctica served as logistics hub, 60+ years
- Soils contaminated with fuel and lubricating oils
- Two contaminated soils collected, TPH > 1,000 mg/kg
  - ITC F1 - predominantly mid-range (n-C8 to n-C16) hydrocarbons (1,250 mg/kg)
  - Soil Pile - predominantly heavy molecular weight (> n-C21) hydrocarbons (3,500 mg/kg)

Soil Pile

ITC F1

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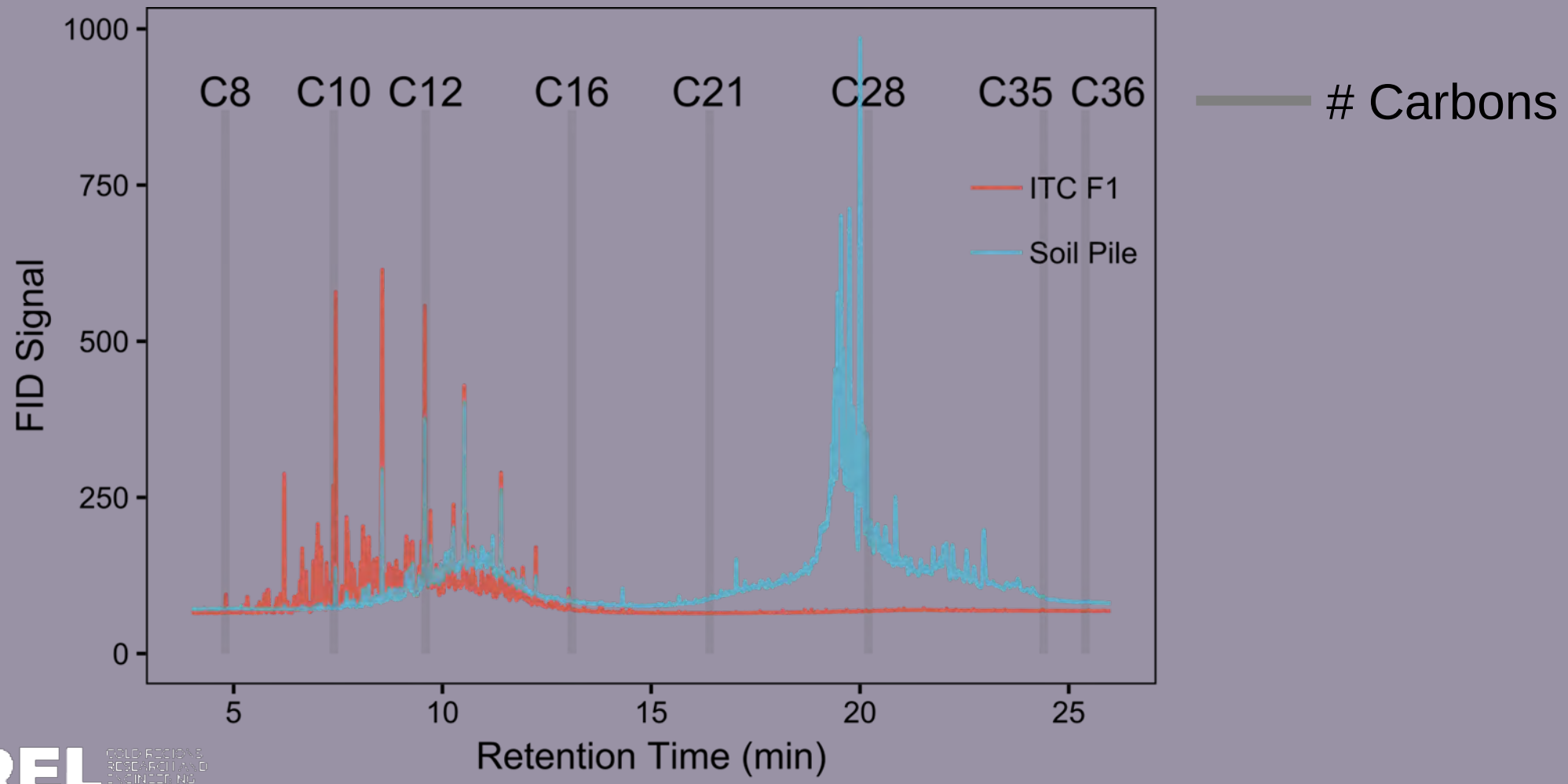
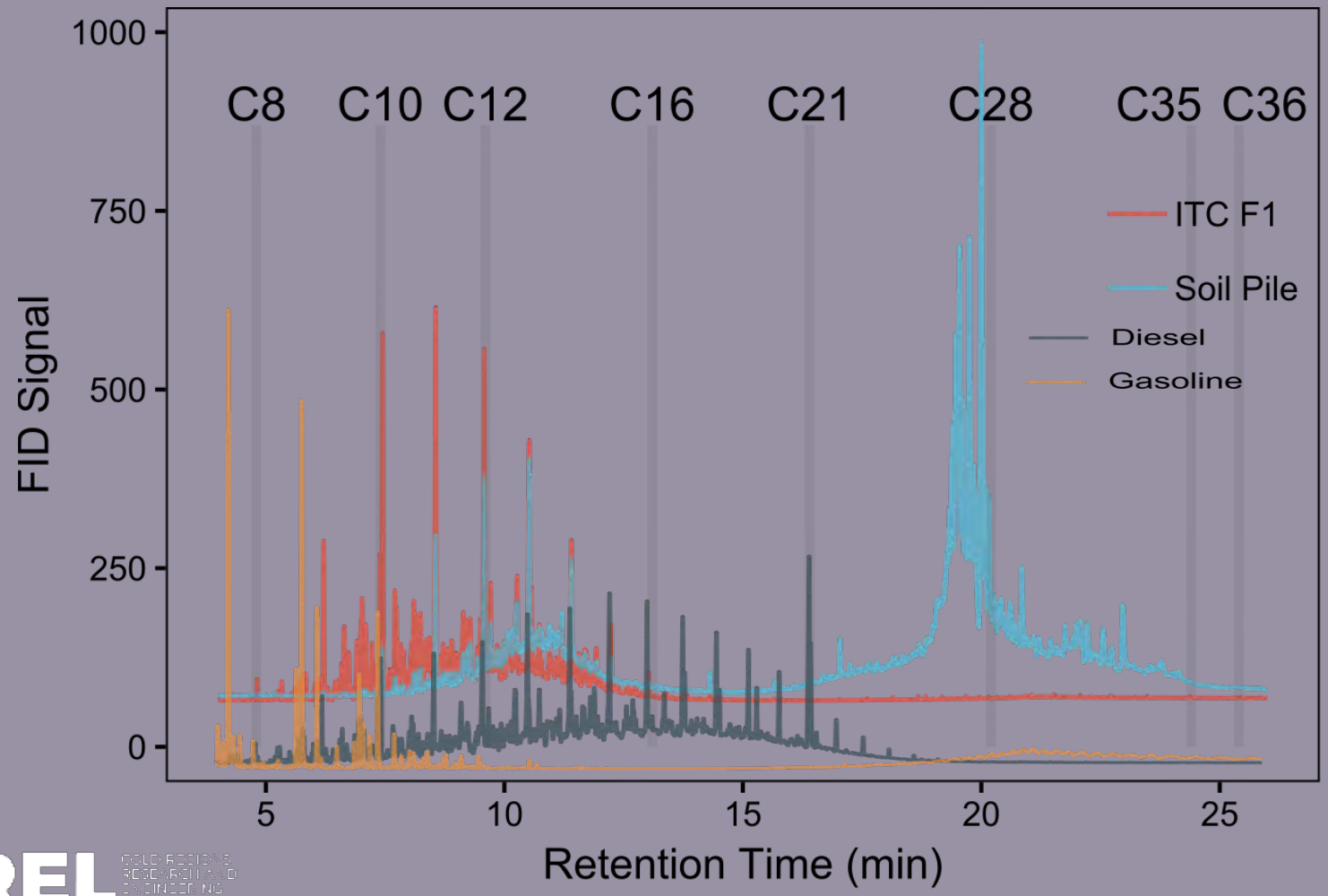
Representative GC-FID Chromatograms



Comparison of Contaminated Soil to Fuel Standards



- ITC F1 and Soil Pile signals don't appear to match diesel or gasoline

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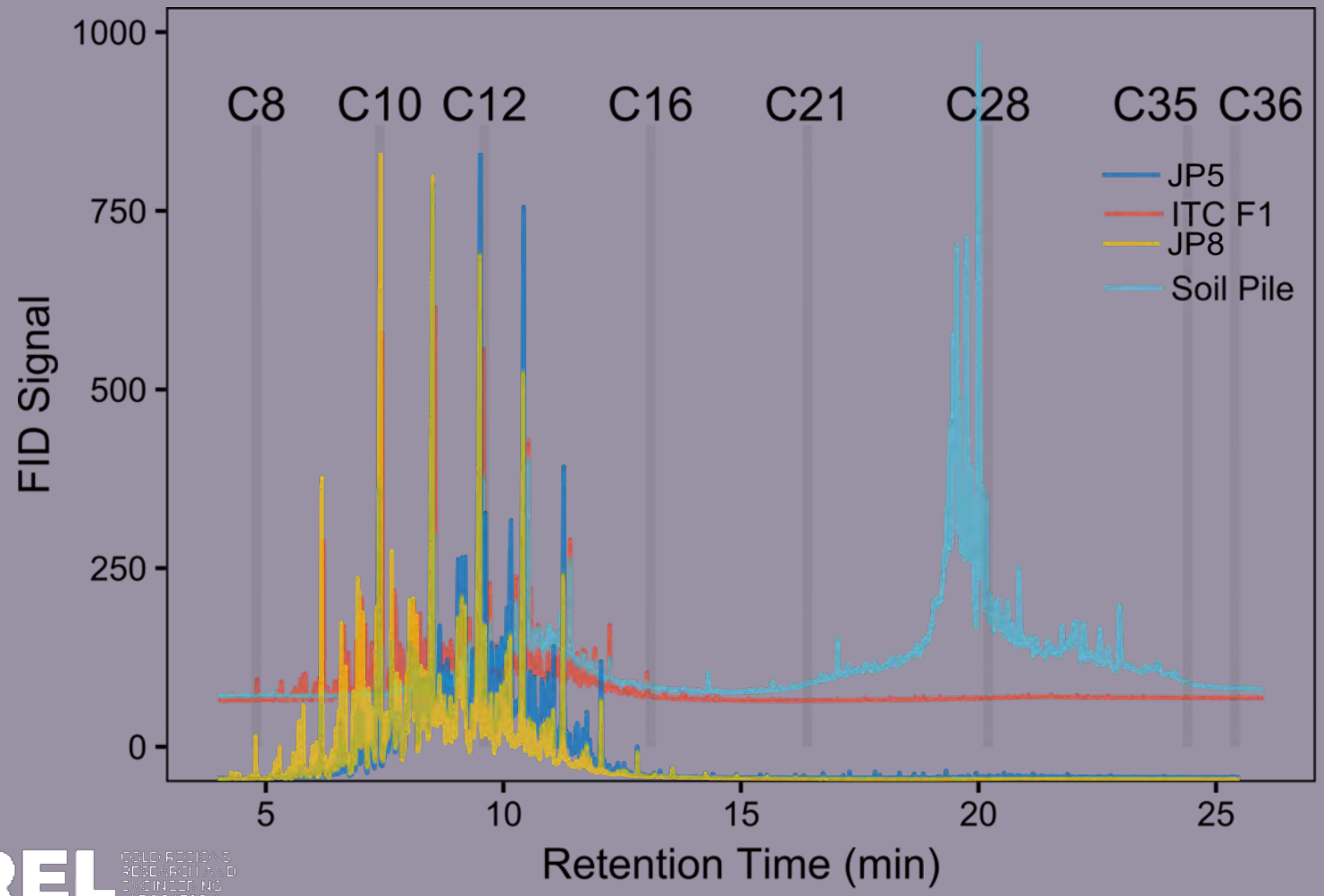
Comparison of Contaminated Soil to Jet Fuel Standards



- ITC F1 and Soil Pile appear to contain JP5
- Soil Pile may contain some JP8

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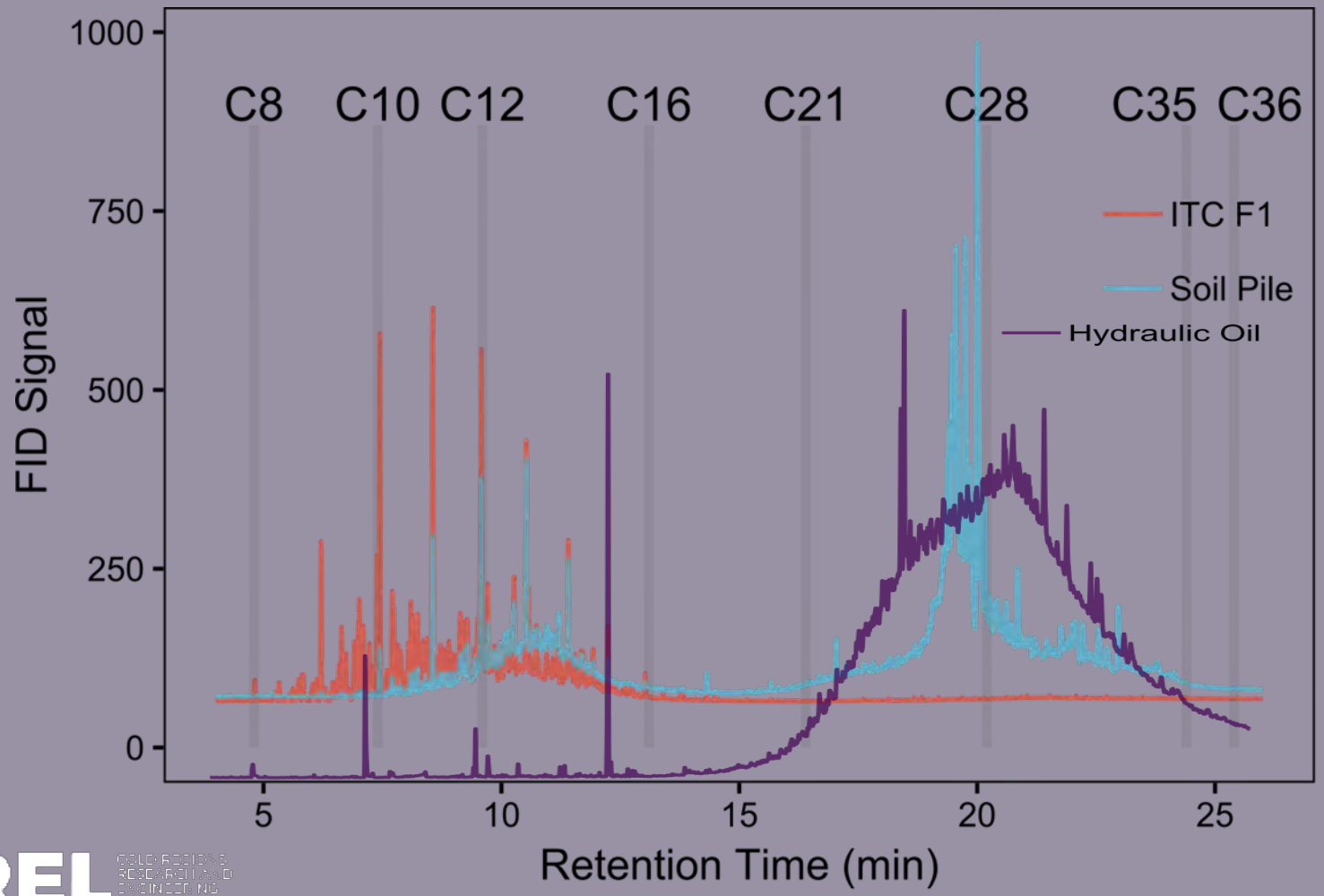
Comparison of Contaminated Soil to Hydraulic Oil Standards



- Soil Pile may contain some weathered hydraulic oil

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Treatability Study Methods

- Samples maintained under freezing conditions until treatability test
- Samples thawed for disaggregation, sieving, and subsampling
- Fenton's Reagent (pH < 3 w/ Fe^{2+}) with 3% and 10% H_2O_2
- Modified Fenton's (chelated Fe^{2+}) with 3% and 10% H_2O_2
- Soils slurried and utilized shaker table (100 rpm) for 21 days at 4ºC
- Utilized 11 sampling event per treatment including control

Treatment	Iron/Chelate	pH Modifier	Oxidizer
FR 3%	2.5 ml 0.1 M Fe	TBD µl 1 M H_2SO_4	2.5 ml 3% H_2O_2
FR 10 %	2.5 ml 0.1 M Fe	TBD µl 1 M H_2SO_4	2.5 ml 10% H_2O_2
MFR 3%	2.5 ml 0.1 M Fe/EDTA	-	2.5 ml 3% H_2O_2
MFR 10%	2.5 ml 0.1 M Fe/EDTA	-	2.5 ml 10% H_2O_2
Control	-	-	5 ml MilliQ

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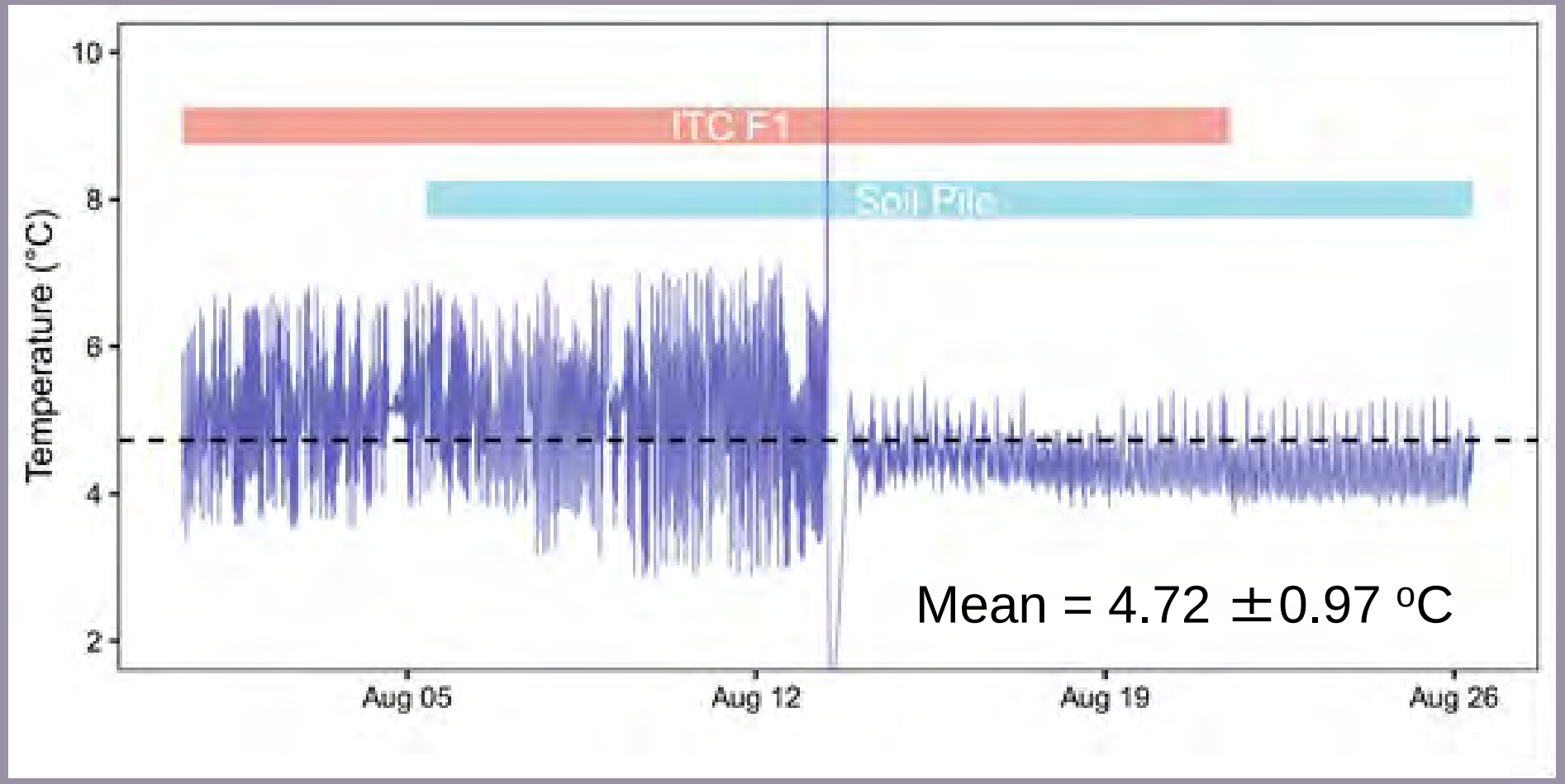
Air Temperature During Treatability Study



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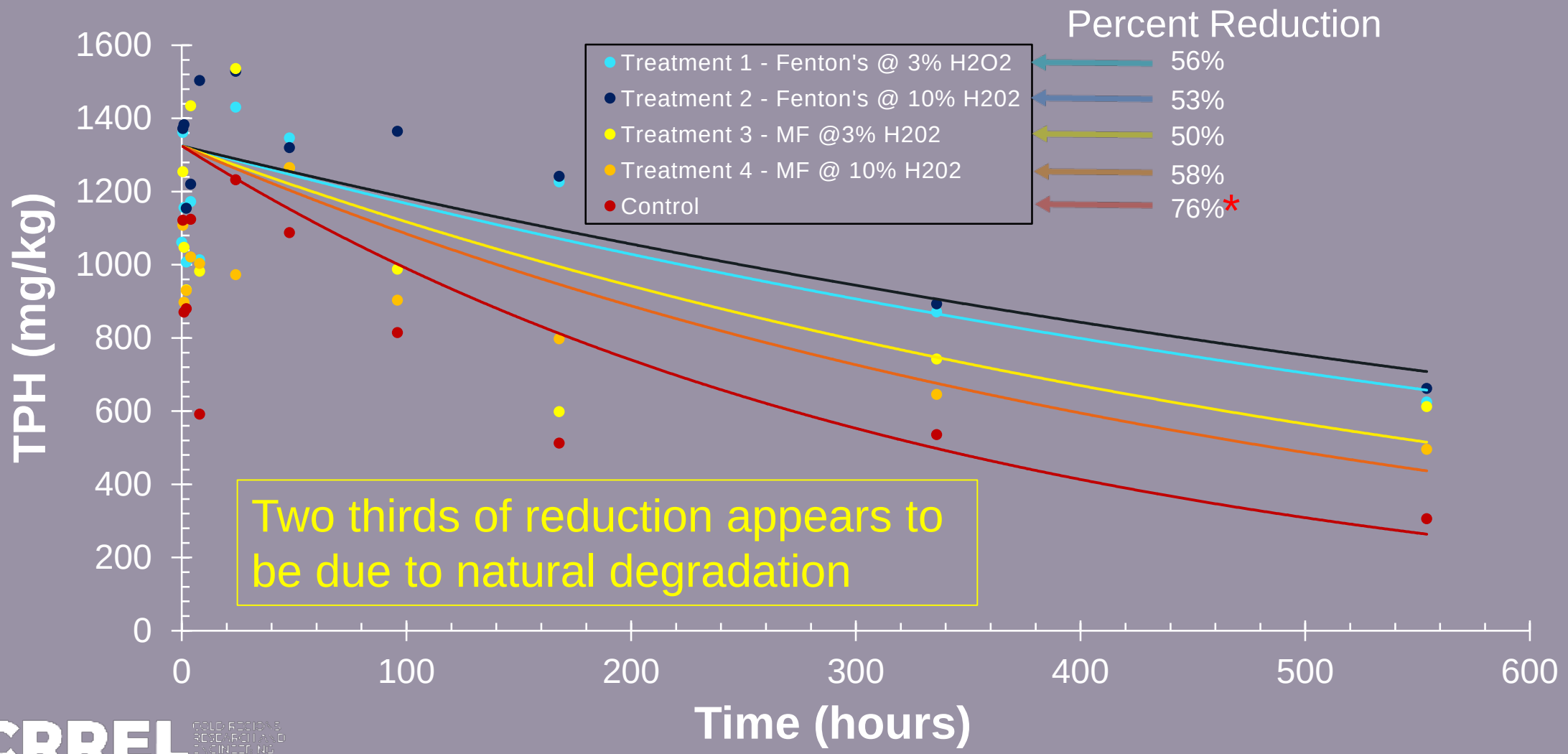
ITC Soil TPH Concentrations by Treatment



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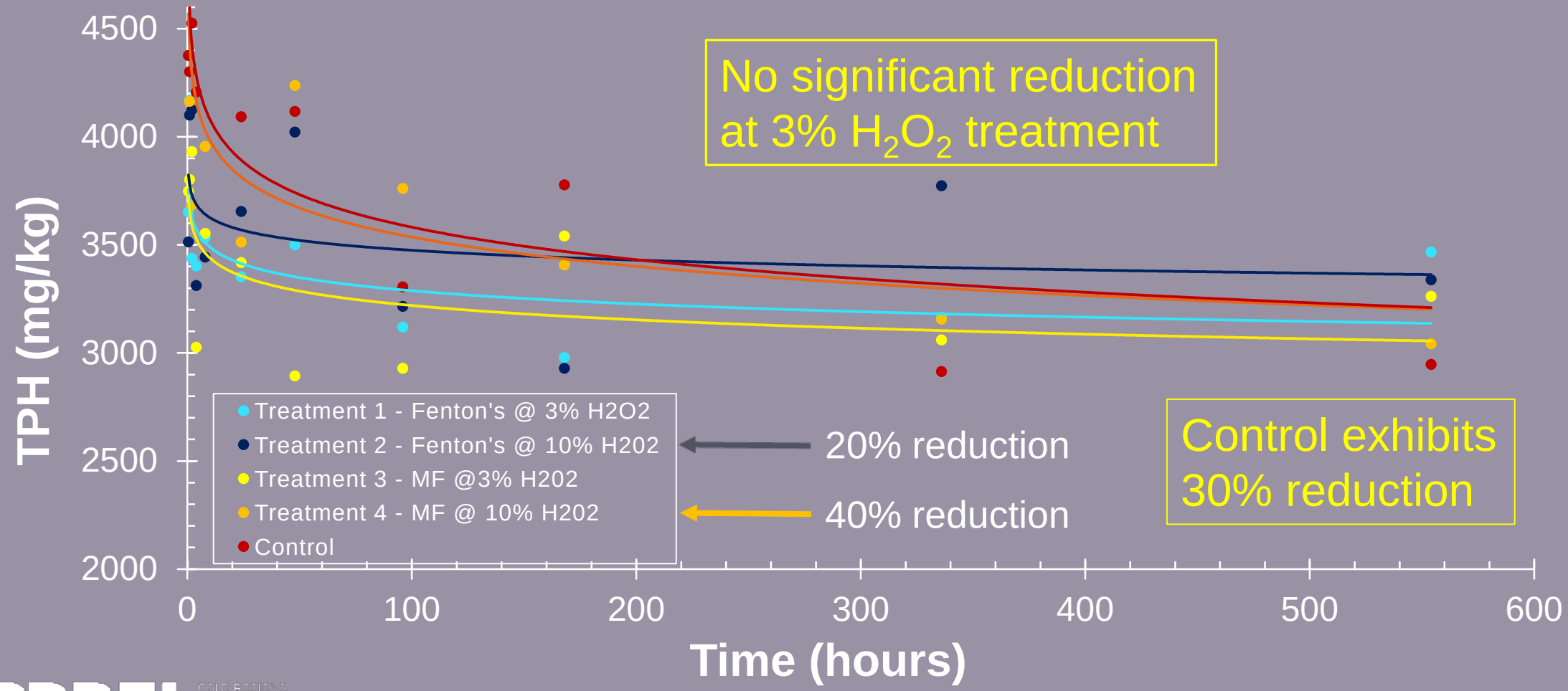
Soil Pile TPH Concentrations by Treatment



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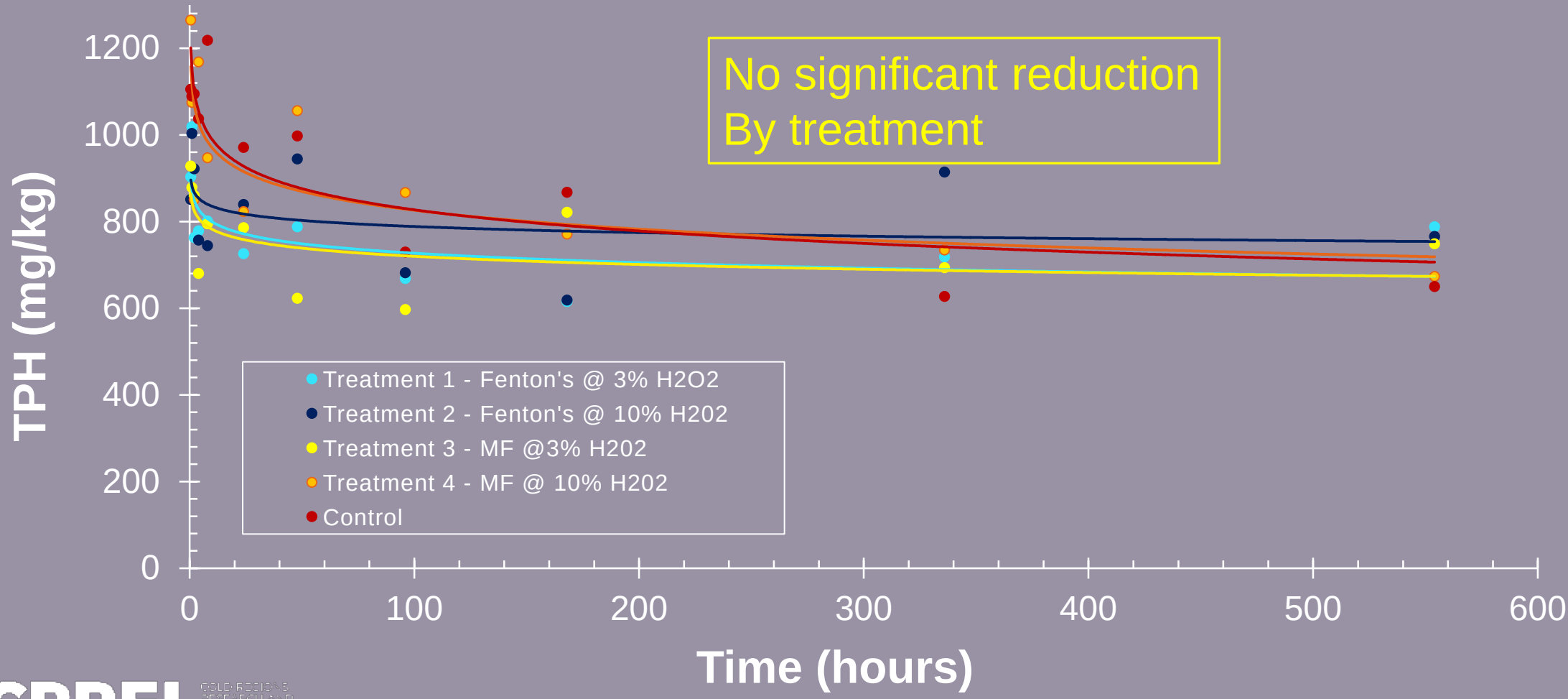
Soil Pile HMW Hydrocarbon Concentrations by Treatment



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Room Temperature Treatability Study

- No significant difference between control and treatments for TPH and High Molecular Weight (HMW) Hydrocarbons
- Results suggest temperature not limiting factor

	TPH (HMW) Concentration (mg/kg)		
Treatment	Room Temperature	20°C	HMW Reduction
FR 3%	2900 (760)	3120 (670)	11%
FR 10%	3060 (770)	3220 (680)	11%
MFR 3 %	3720 (960)	2930 (600)	38%
MFR 10%	3300 (824)	3760 (870)	0%
Control	3930 (1050)	3300 (730)	30%

Results

- ITC F1
  - o Approximately 50%TPH reduction for all treatments
  - o Control exhibited 76% TPH reduction
- Soil Pile
  - o Minimal to 40% TPH reduction
  - o Modified Fenton's at 10% H_2O_2 had greatest TPH reduction
  - o Control exhibited 76% TPH reduction
- Less Soil Pile reduction due to heavier MW hydrocarbons
- Repeating all treatments at room temperature (20^{o}C) had no effect

Discussion

- Explanations for lack of degradation
  - Soil composition, i.e. competitive sorption
  - Weathering of hydrocarbons
  - Experimental approach
    - ► Soil homogenization
    - ► Soil particle size
    - ► Reagent mixture concentration
    - ► Repeated sequential reagent dosing

Conclusions

- Minimal to no significant treatment effect on soil TPH concentrations under cold conditions, i.e. 4^{o}C
- Repeating experimental test at room temperature, i.e. 20^{o}C had no significant effect on soil TPH concentrations
- Future studies should consider homogenization of soil, particle size reduction, and stronger (30 to 50 wt%) H_2O_2 concentrations
- Consideration be given to exploring alternative chemical oxidants

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14. ABSTRACT

The study objectives were to determine the effectiveness of Fenton's Reagent and Modified Fenton's Reagent in reducing Total Petroleum Hydrocarbon (TPH) concentrations in petroleum-contaminated soil from McMurdo Station, Antarctica. Comparisons of the contaminated soils were made, and a treatability study was completed and documented. This material was presented at the Association for Environmental Health and Sciences Foundation (AEHS) 30th Annual International Conference on Soil, Water, Energy, and Air (Virtual) on March 25, 2021.

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