# Remediation of Petroleum Impacted Soils with Electron Beam Irradiation

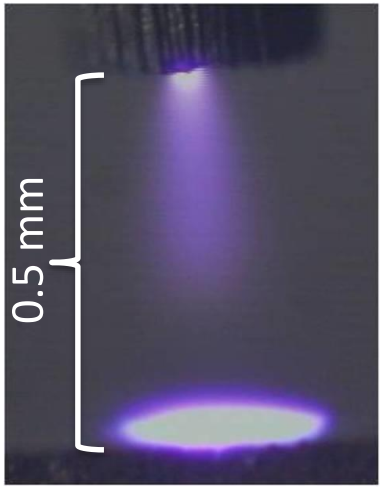
John Lassalle[1], Bob Rodi[1], Kenneth Briggs[1],Thomas Thompson[1]
*PIs: David Staack[1], Andrea Strzelec[1]*
*Thomas P. Hoelen[2], Paul Bireta[2], Deyuan Kong[2], Gabriel P. Sabadell[2]*
*[1]Texas A&M University J. Mike Walker '66 Department of Mechanical Engineering*
*[2]Chevron Energy Technology Company, USA*

International Petroleum Environmental Conference 2019-Oct. 8, 2019

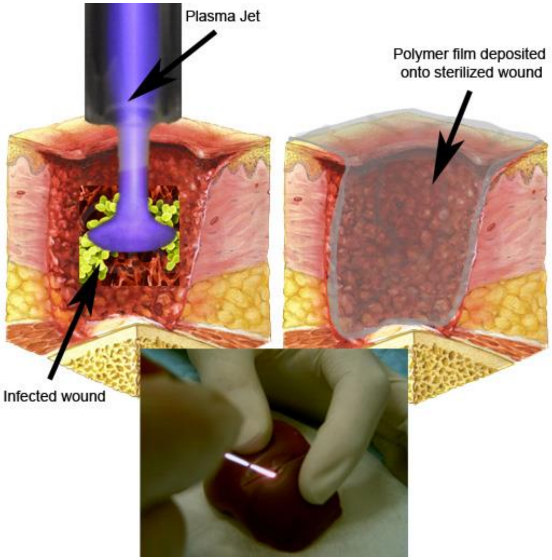
# Plasma Engineering and Non-equilibrium Processing Laboratory

- PI: David Staack
- Basic and applied research concerning plasmas (ionized gases) and non-equilibrium processes (e-beam)
- Application areas include materials processing, waste management, oil upgrading, and plasma medicine

pedl.tamu.edu



Atmospheric pressure microplasma



Plasma jet for wound sterilization and sealing


Plasma actuator for flow control

# Electron Beam Research

- Electron beam: bombardment of material with high-energy electrons (10 MeV, 10 eV to ionize)
- Contributes thermal energy and free radicals to modify materials
- Used to treat medical devices, scrap metals, and remove oil and trace organics (PFOS/PFOA) from soil and water

# Motivation and Objectives

ENGINEERING
TEXAS A&M UNIVERSITY

- Pollution of soils by petroleum hydrocarbons is a major global environmental issue
- Remediation technologies must be fast, efficient, and economical at large scales
- Intermediate range hydrocarbons (~$C_{12}$-$C_{40}$) pose the greatest threat:
  - Degrade slowly
  - Mobile in soils
- Leads to contamination of the water table.

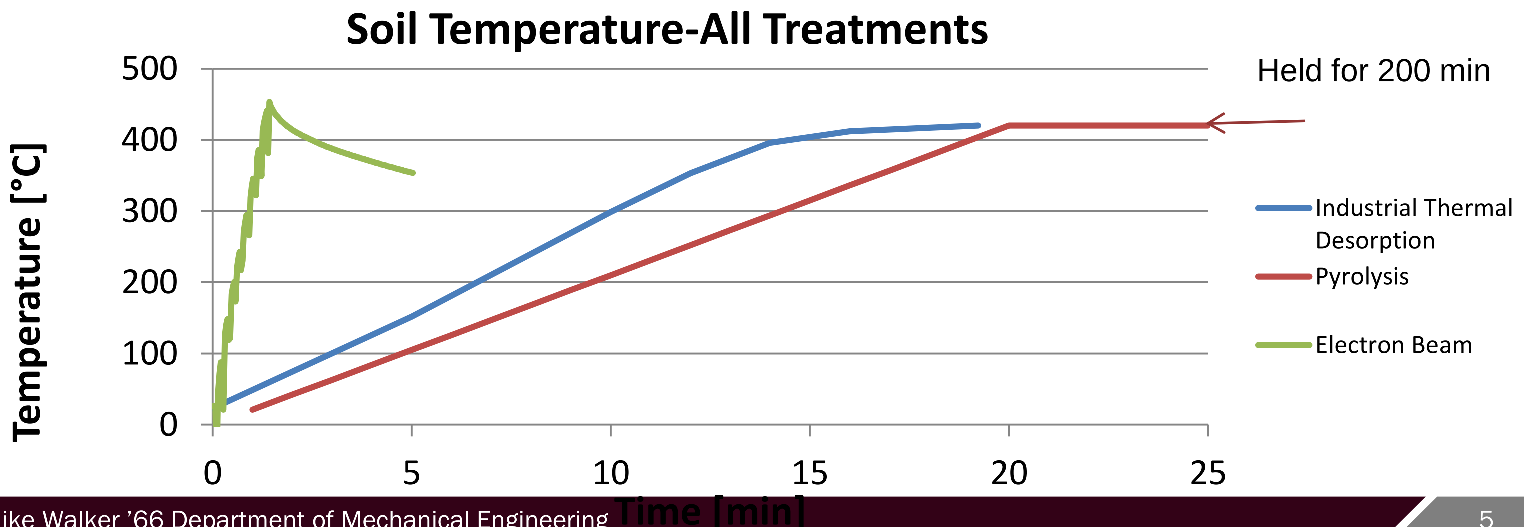
Crude Oil Impact Site

**Objectives:**

- Show proof of concept (TPH reductions to <1%)
- Impact of test parameters such as dosage
- Design of experiment setup
- Validation at high throughput rates required for industrial remediation projects

# Why e-beam?

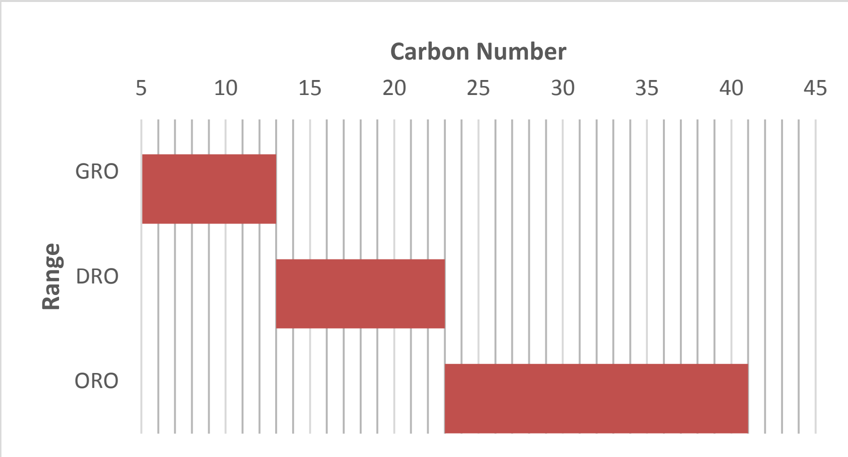
- Energetic Remediation Methods:
  - Industrial thermal desorption: Heat addition to 420°C in 10% $O_2$, ~900 kJ/kg
  - Pyrolysis: Heat addition to 420°C in inert gas, ~1400 kJ/kg
  - e-Beam: Heat addition, radiation chemistry, ~2200 kJ/kg
  - Ozone: Ozone generated and applied to soil, ~1800 kJ/kg (theoretical value)
  - Incineration: Heat addition to 650°C in 10% $O_2$



# Why e-Beam?

- Advantages:
  - Higher rate of energy addition than some energetic methods
  - Production of char (fixed carbon with potential benefits for soil health)
  - Radiation chemistry volatilizes (easier to remove) or polymerizes (reduces mobility) some medium-heavy hydrocarbons
  - Volumetric heating simplifies material handling, potentially enables separation of liquid crude oil
- Disadvantages:
  - Higher specific energy requirements than some methods for some applications
  - Need radiation shielding during operation

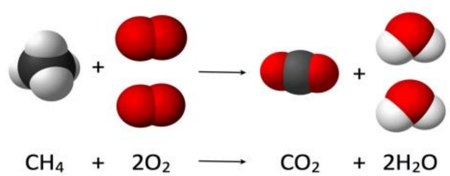
# Background



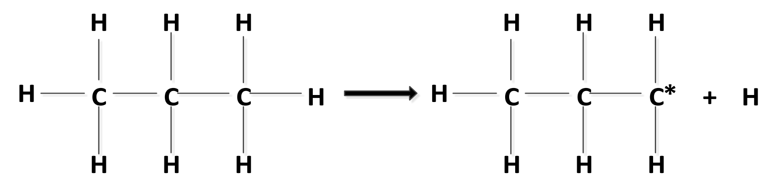

**Carbon number ranges**[9]

- Acceptable TPH level is 1 % by soil mass, but may vary depending on jurisdiction [2].
- Remediation methods are inefficient, and may not achieve this clean-up level [3-5].
- E-beam remediation could generate physical/chemical changes leading to remediation [4,6-8].
- Primary reaction types are pyrolysis, combustion, and evaporation

$$\Delta T = \frac{D - h_{fg}}{c}$$




**Combustion [P3]**



**Pyrolysis**

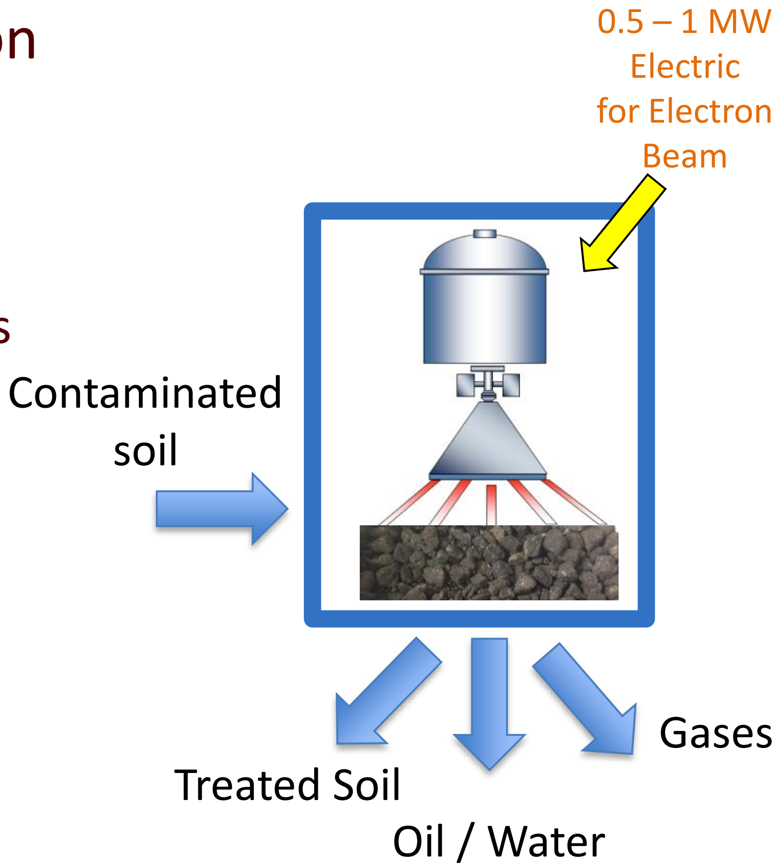
| Range | Boiling (°C) | Outcome |
|---|---|---|
| GRO | -0.2 – 216 | Evaporation, combustion |
| DRO | 234 – 367 | Evaporation, cracking, combustion |
| ORO | 379 – 524 | Cracking, combustion, polymerization |

| Parameter (↑) | Effect |
|---|---|
| Dose | Higher temp; more energy for reactions |
| Temperature | Enhance removal: 480 kGy results in DRO boiling |
| Water Content | Decrease removal efficiency |
| TPH | Increase removal efficiency [7] |
| Additive | Enhances phase separation |

Soil specific heat = 1.4 kJ/kg*K. "kGy" is specific energy, or "kJ/kg".
Estimate of temp. increase based on U=c$\Delta T$, where dose is considered as the change in internal energy.

# Process Overview

- Layout is similar to Thermal Desorption Unit
- <u>Differences Are:</u>
  1. Lower temperature
  2. Non-thermal / electron induced effects
     - Radiation Chemistry
     - Cracking / Polymerization
     - Volumetric heating
     - Non-uniform temperature
     - Targeted beam process
  3. Electrical Energy Input




- Key operation parameter for cost of processing is Required Specific Energy Input: ~ 500 kGy = 500 kJ/kg = 50 Mrad

# Conceptual Process Overview Schematic



E-beam Processing
(mobile facility brought to site)

Excavation

Crushing & Sizing


Conveyor

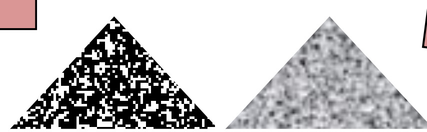
TPH measured at starting point and desired for end point determine conveyor feed rate and administered dose. Monitoring points can be used to maximize efficiency and throughput.

0.5 – 1 MW Electric for Electron Beam

Radiation Shielding Necessary only when beam is on. No residual radiation.

Gas Treatment / Air Quality Control
(Bag house, scrubber)

Treated Soil



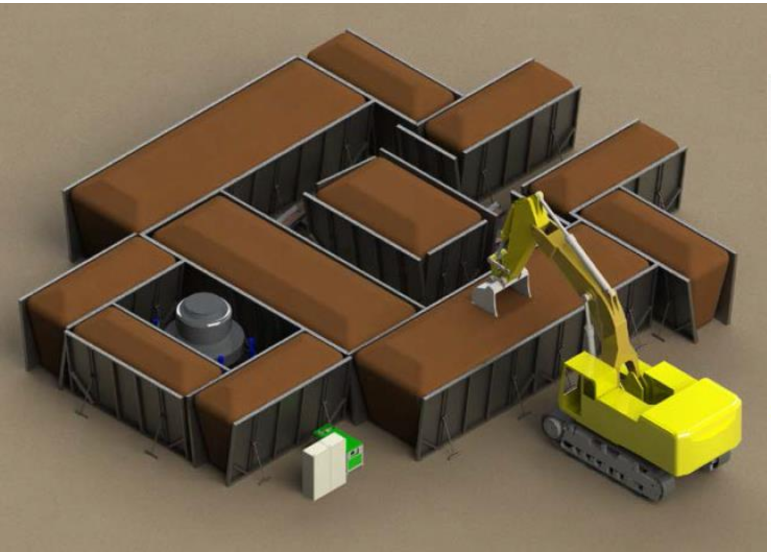
Condensation of desorbed vapors

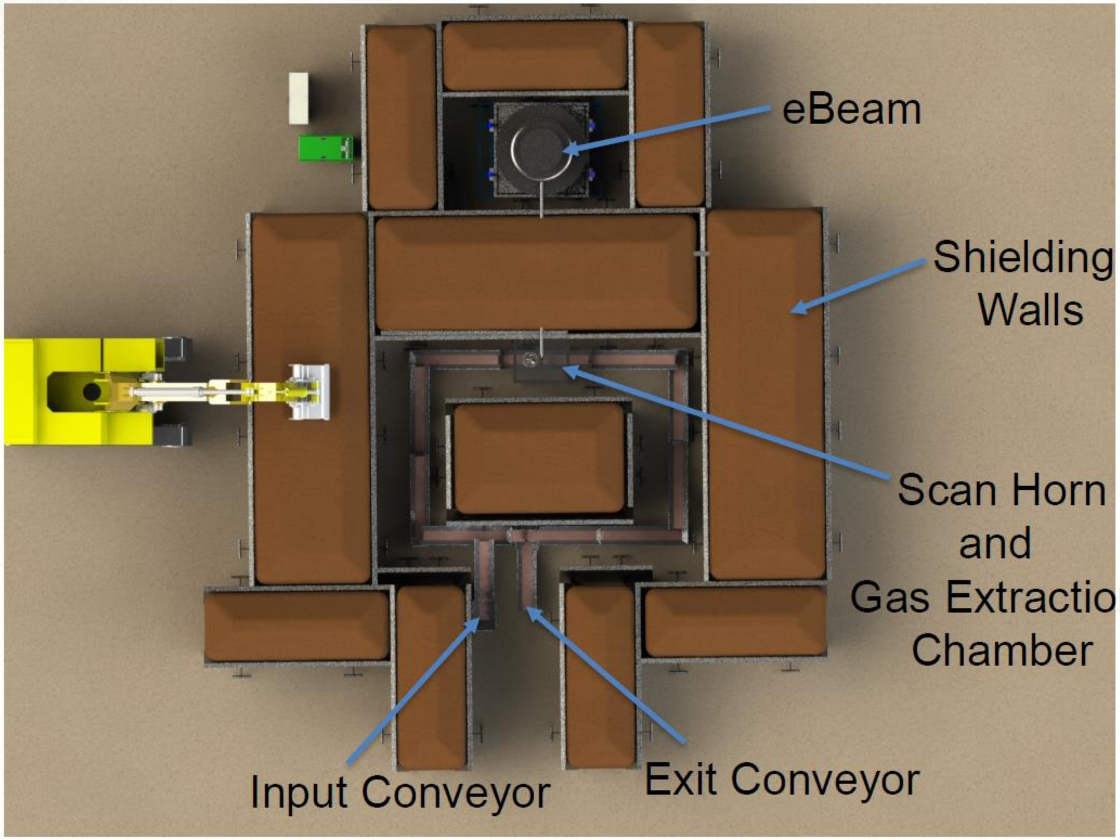

Soil stays on site

Water

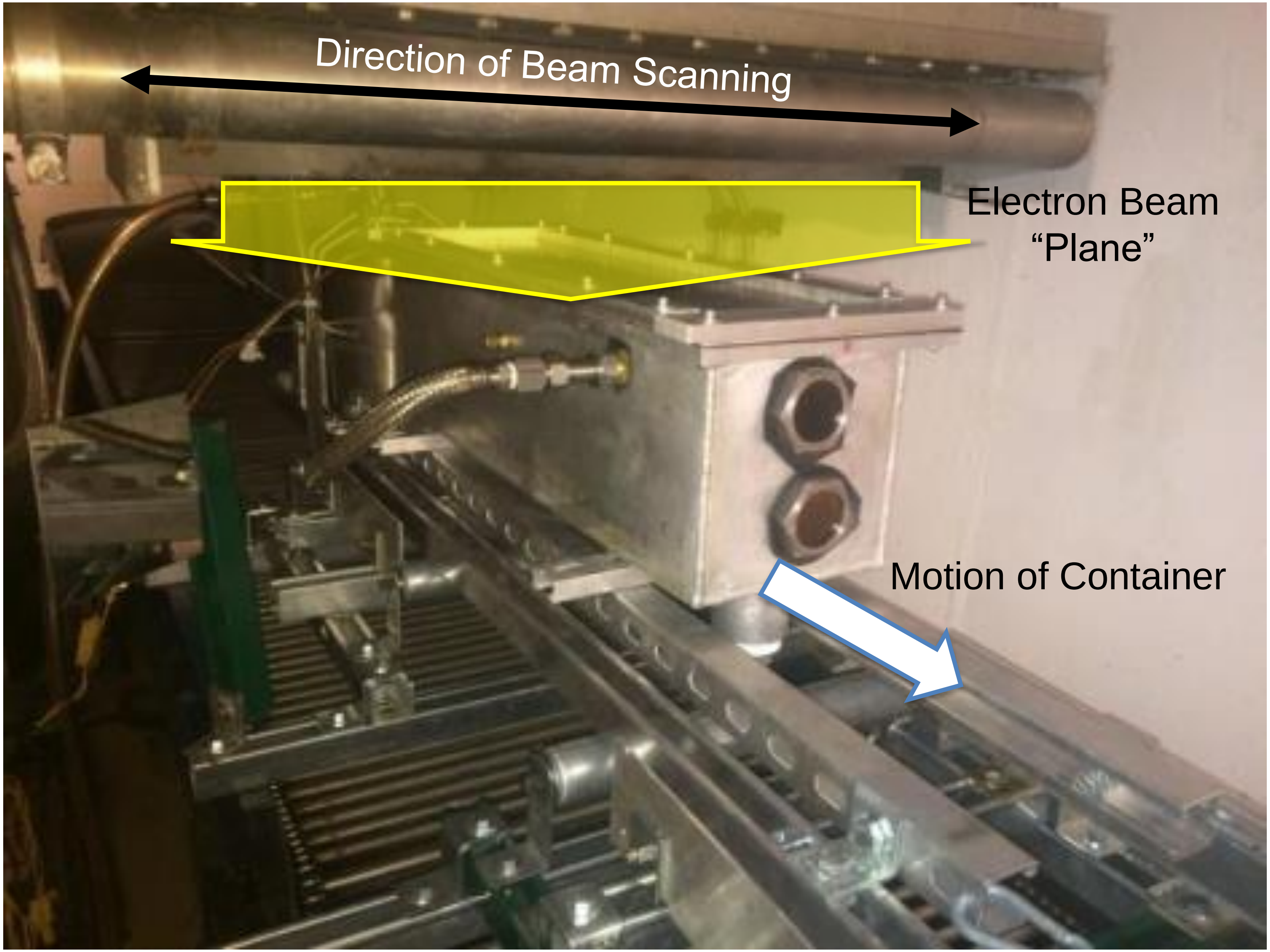

Oil

# Conceptual Field Implementation





# Experimental Setup

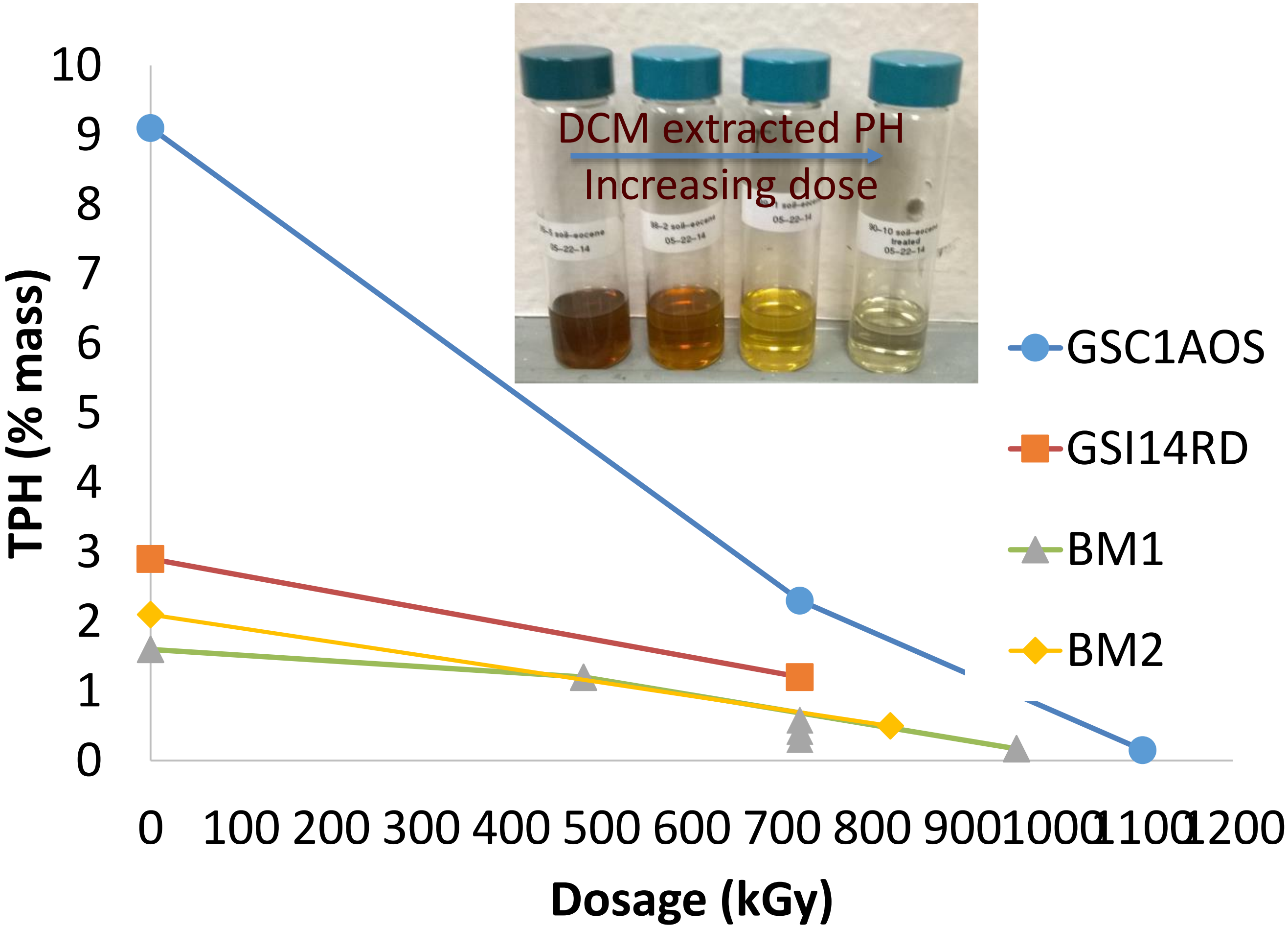


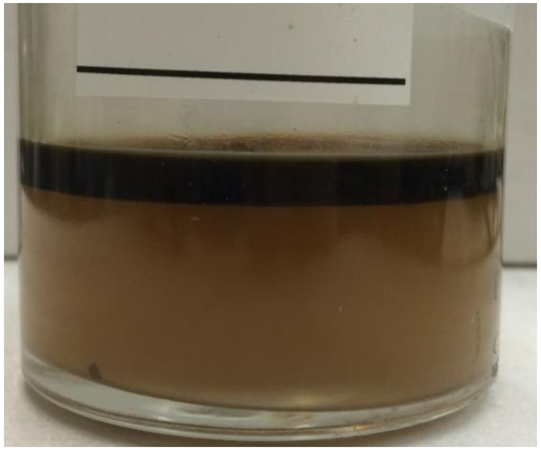
# Experimental Methods

- Experimental configurations
  - Small batch 100g preliminary experiments
  - Stationary large batches for dose matching
  - Conveyed 3 kg samples (1 to 5 inches/minute)
- Various Soils Tested
  - Synthetic Manufactured Mixtures (crude + soil)
  - Field Attained Soils (GSC1AOS, GSI14RD)
  - Benchmark Soils (BM1, BM2, TX-1)
- Dose ranges from 200 to 1200 kJ/kg at 6-100 kGy/s
- Diagnostics: UV-Vis Absorption, Colorimetry for screening tests, GC-FID (including evaluation by Eurofins Lancaster Labs for Third Party evaluation of TPH)

ENGINEERING
TEXAS A&M UNIVERSITY

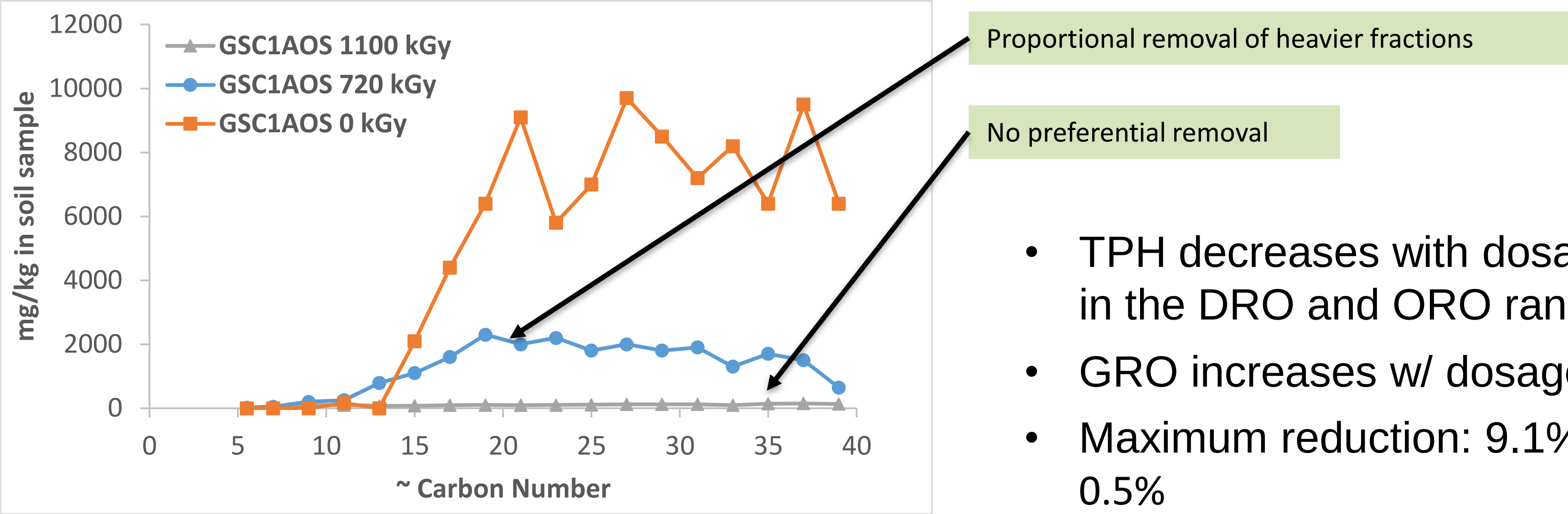
# Preliminary Results

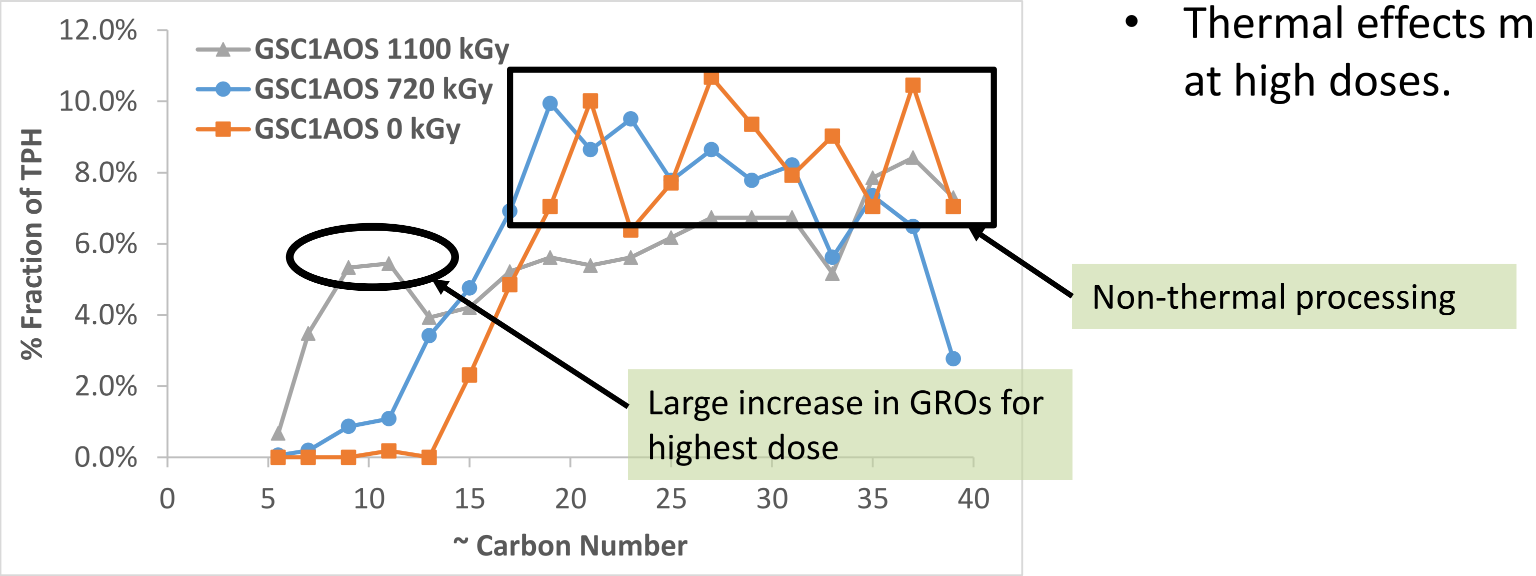


Recovered Oil and Water

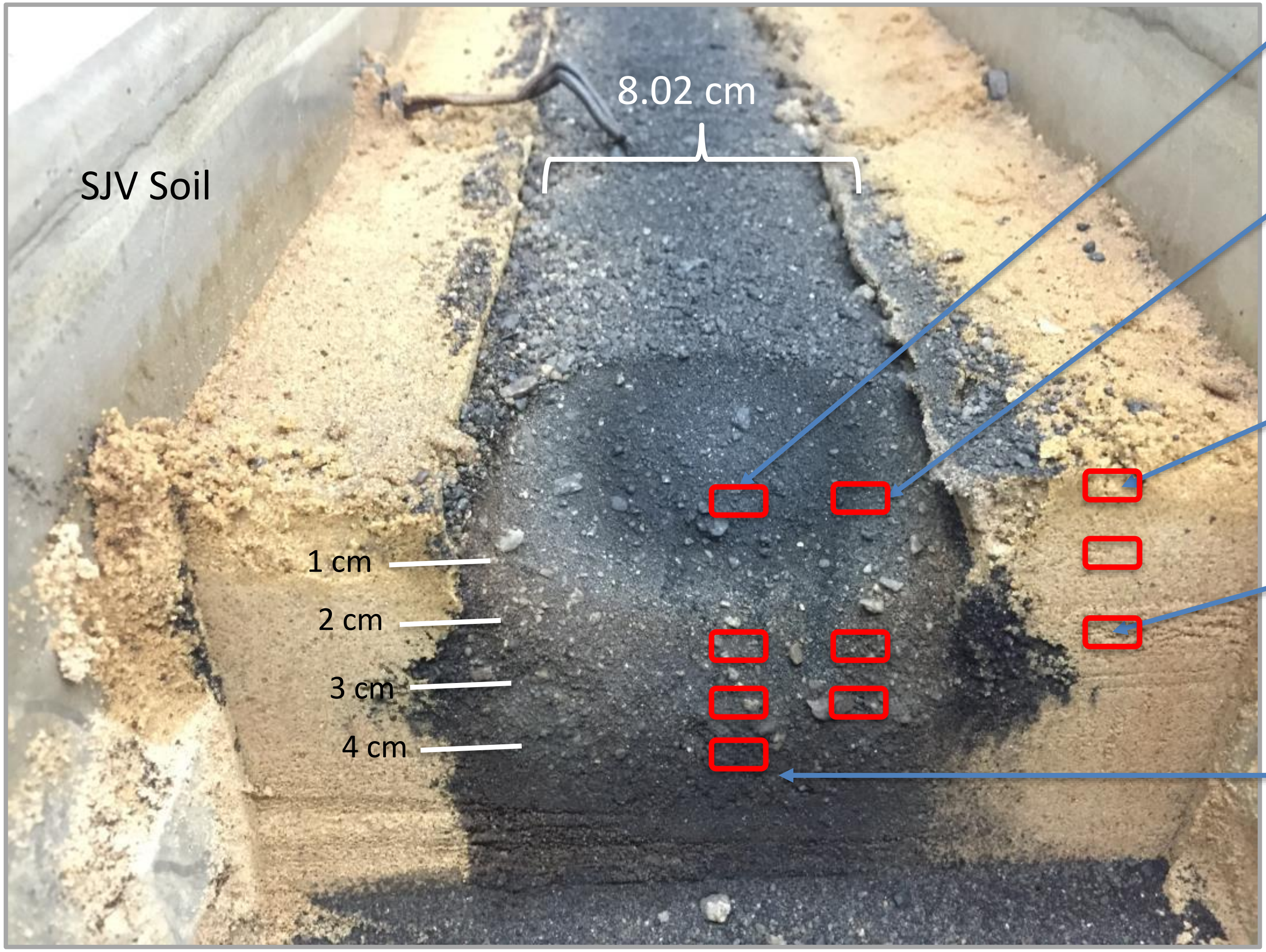
# TPH Results: GSC1AOS Soil




- TPH decreases with dosage in the DRO and ORO ranges.
- GRO increases w/ dosage
- Maximum reduction: 9.1% → 0.5%
- Thermal effects more dominant at high doses.

# Treatment Cross Section




Heavily treated

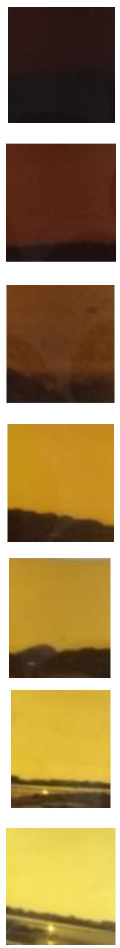
Moderately treated

Got oily from condensation

Still clean

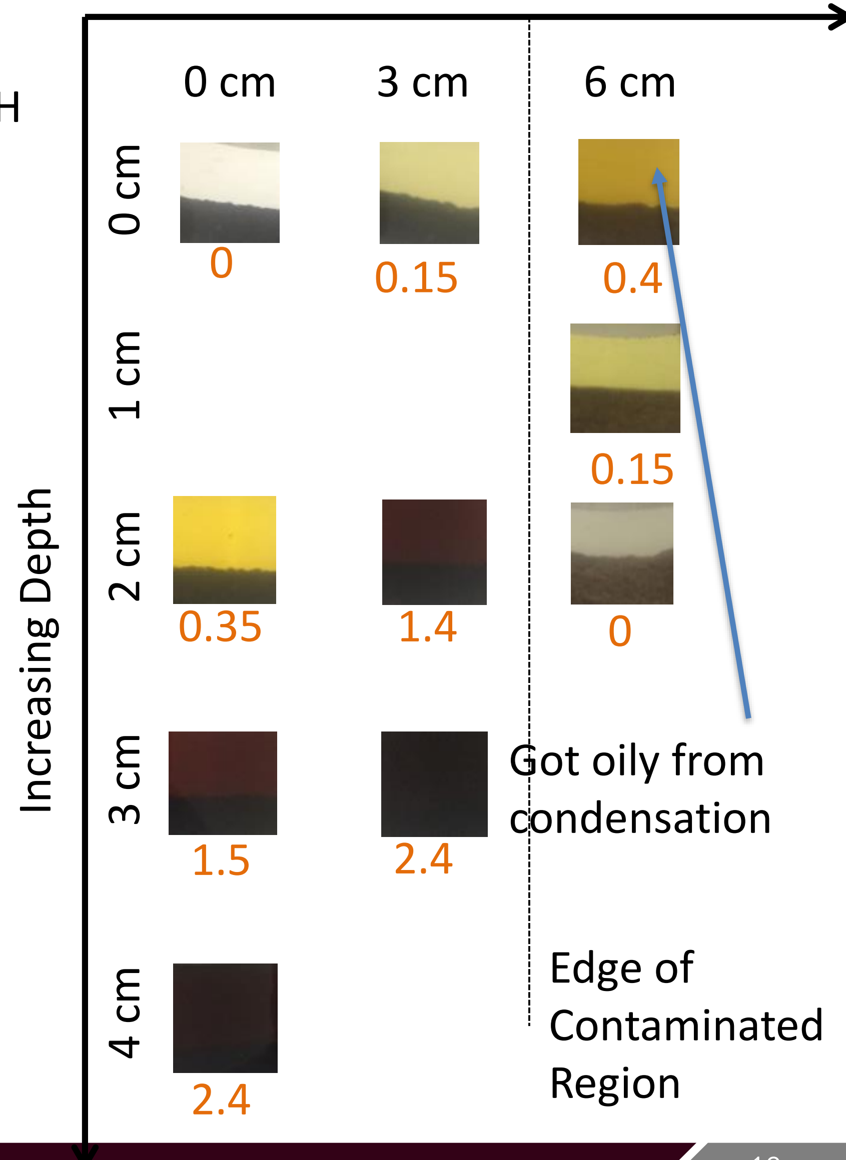
Unaffected

# Treatment Profile



| Dilution (Soil:DCM) | TPH |
|---|---|
| 1:10 | 2.4 |
| 1:20 | 1.2 |
| 1:40 | 0.6 |
| 1:50 | 0.48 |
| 1:60 | 0.4 |
| 1:80 | 0.3 |
| 1:100 | 0.24 |

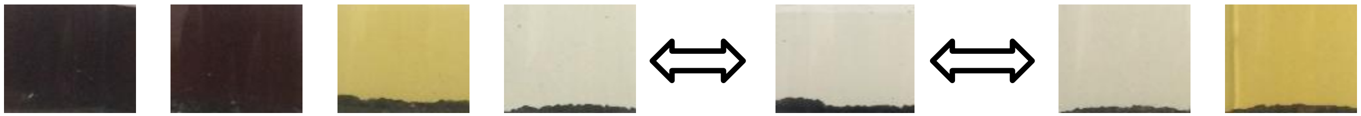
Estimated TPH from colorimetry



# Continuous Treatment

ENGINEERING
TEXAS A&M UNIVERSITY

| 0” | 1” | 2” | 3” | 9” | 16” | 17” |
|---|---|---|---|---|---|---|

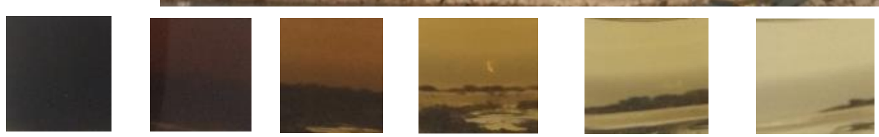


| Estimated TPH: | 2.28% | 1.25% | 0.25% | <0.1% | <0.1% | <0.1% | 0.3% |
|---|---|---|---|---|---|---|---|

Total Dose for fully treated regions: 2200 kGy

Initial position of beam at approximately 3” for each round of treatment

Reference DCM Solutions:



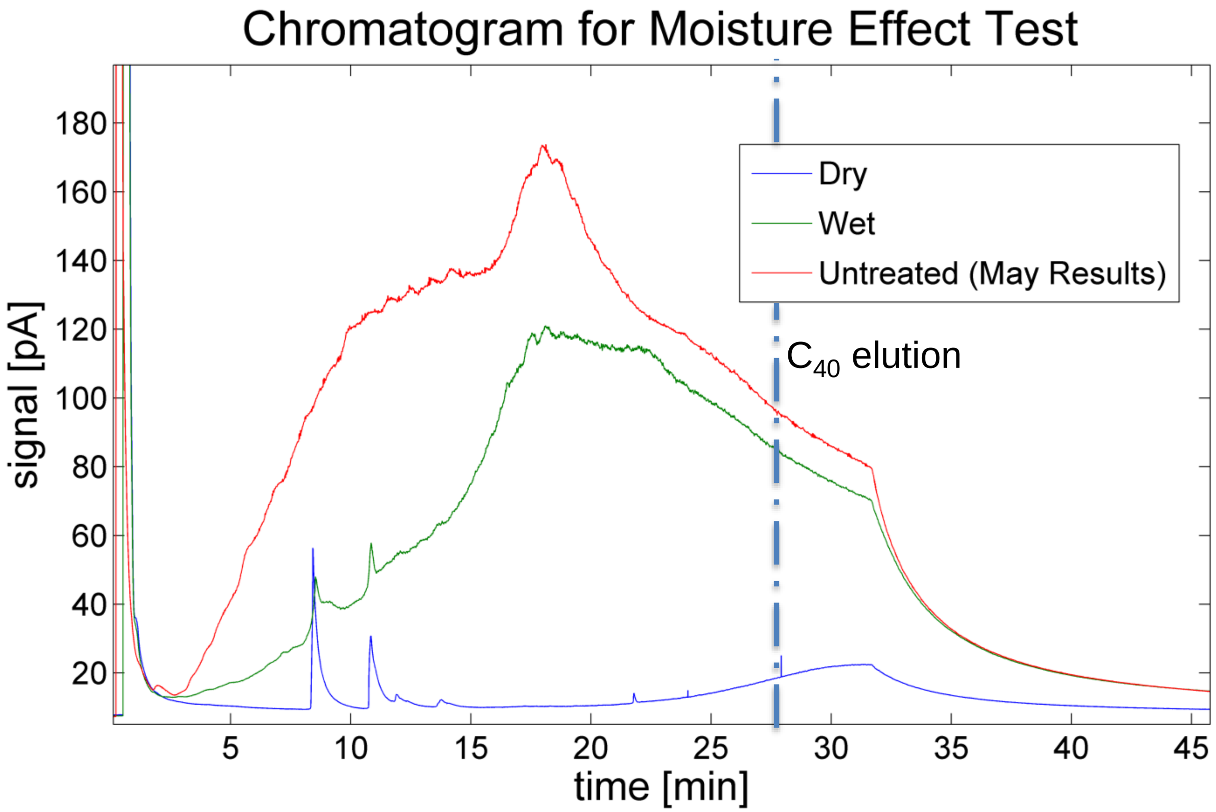
| 1:10 | 1:20 | 1:40 | 1:80 | 1:160 | 1:320 |
|---|---|---|---|---|---|
| 2.28% | 1.14% | 0.57% | 0.285% | 0.1425% | 0.0713% |

# Sensitivity to Water

- An early experiment with the conveyance system was conducted to observe the effect of moisture on the effectiveness of e-beam treatment
- Temperature distributions were also gathered to investigate the prospect of waste heat contributing to treatment of adjacent soil.
- Moisture contents were ~25% water by mass for moist and ~1% water for dry
- Dose: 650 kGy

Dry and moist sections of soil container

# TPH Diagnostics Comparison




Dose: ~ 650 kGy for both tests

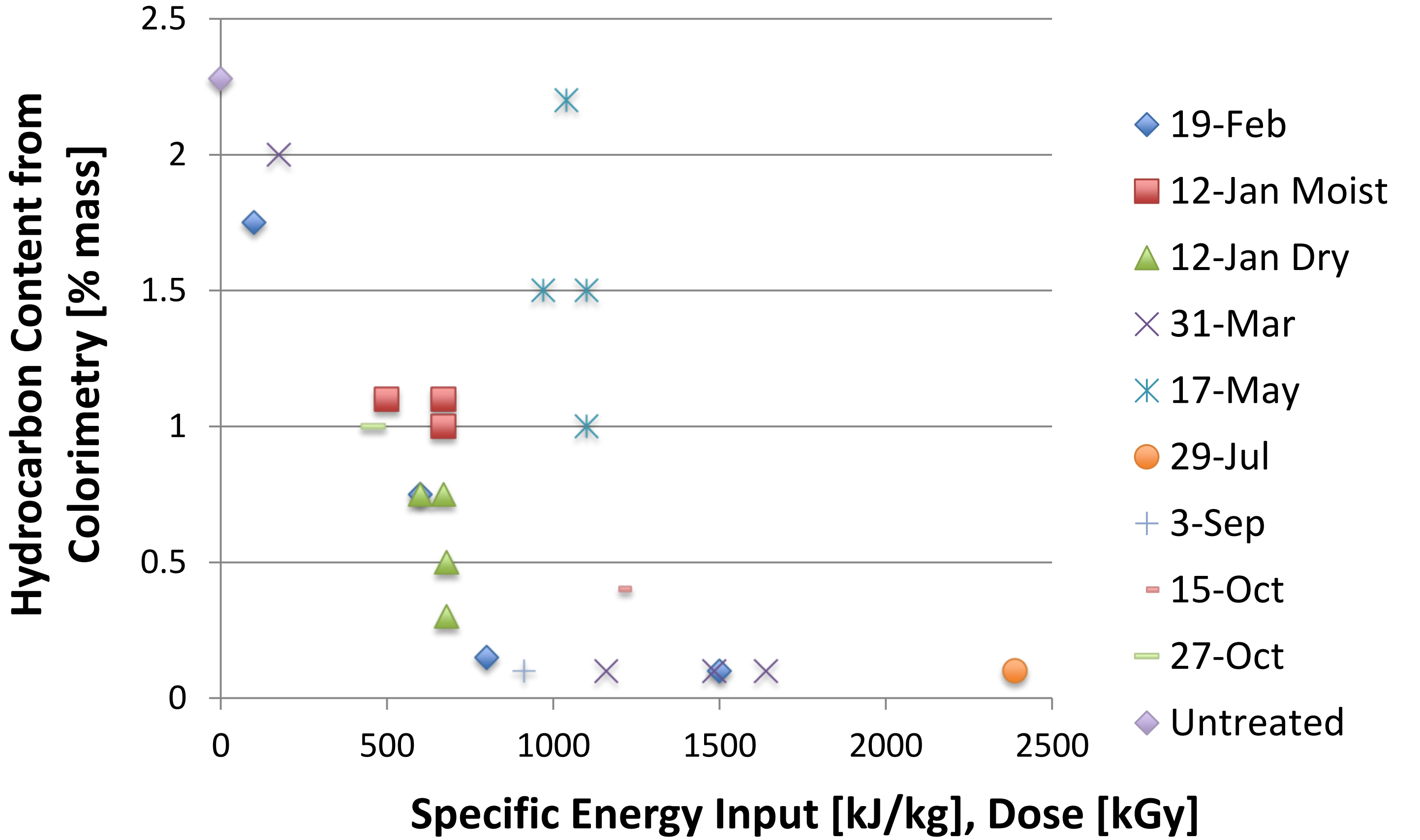
Max T: dry, 520°C

wet, 340°C

TPH:

- calculated from GC:
  - dry, 0.05%
  - wet, 3.3%
- Lancaster value:
  - dry, 0.01%
  - wet, 1.2%
- from colorimetry:
  - dry, 0.3%
  - wet, 1.1%

# Hydrocarbon Content vs. Energy Input

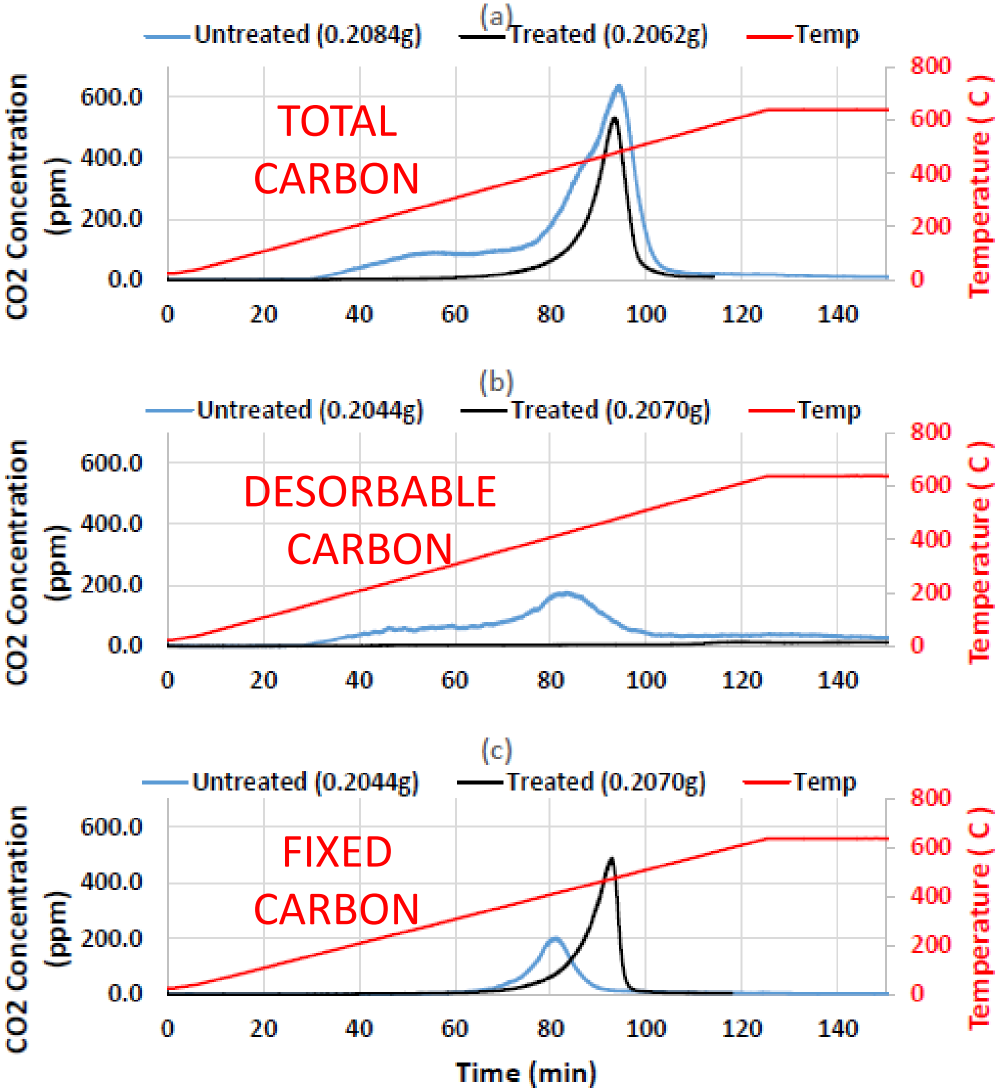


# TPD / TPO Analysis




(a) is TPO (incineration) (b) TPD+O (volatilization) (c) TPD+O then TPO (volatilization then incineration)

There is considerably more fixed carbon in the treated sample as compared to the untreated. However there is over all less carbon. This indicates that the treatment has volatized a portion of the hydrocarbons and converted of the hydrocarbons to a **char**.



# High Power Density TPH Reduction

| Equivalent oil by mass | 5% | 1% | 0.5% |
|---|---|---|---|
| Equivalent TPH | 2.1% | 0.41% | 0.2% |

**Target soil treatment rate: 5 cu. yd./ hr**

4 cu. yd. /hr

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Estimated TPH (% by mass) | 0.2 (top soil only) | 0.3 | 0.2 | 0.5 | <0.2 | 0.5 | 0.5 | 0.3 |
| Average Surface Dose [kGy] | 1370 | 1370 | 1050 | 740 | 1370 | 730 | 708 | 935 |
| Maximum Temperature [°C] | 420 | 540 | 650 | 485 | 730 | 400 | 410 | 555 |
| TPH from GC-FID* | 0.61 | 0.11 | 0.03 | 0.41 | 0.02 | 0.88 | 0.80 | 0.40 |

*calculated based on % TPH reduction for 2.1% initial TPH

# Summary - Electron Beam Remediation of Soils

Proof of Concept

- Benchmark and field attained soils successfully tested. Can extinguish the environmental liability (<1% TPH), conceivably onsite.
- TPH can be reduced to <1% for 500 to 1000 kJ/kg increasing with initial contamination 1.6% to 9.1%.

Mechanisms: Analysis of hydrocarbon distribution indicates

1) Thermal Desorption effect

2) Low temperature pyrolysis effects (char formation)

2) Additional non-thermal process characteristics

i) electron beam initiated cracking and production of GRO

ii) low temperature char formation by e-beam radicals

iii) proportional removal of DRO and ORO components

- Electron beam is safe (not a radiation source) when off, and can be shielded with site materials.
- Progressing toward industrial scales
  - Larger volumes (100g → 3000g)
  - Beam & Treatment profiles
  - Laboratory scale conveying systems
  - High power-density experiments

Thanks for your attention!

We would like to thank Dr. Pillai and the staff at the National Center for Electron Beam Research for their contributions to this work, as well as Chevron for their support for our research.