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Analysis of TPHd in soil by Portable GC-MS

Rachel Mohler, Karen Gonzalez, Kyle Hench, Brian Morlan, Catalina Espino Devine

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Outline

Background
Description of Portable GC-MS
Analytical Approach
Results
Future work

Motivation

- Chevron has large sites where remediation is required for soils containing more than 1 wt% total petroleum hydrocarbons (TPH).
  - Some sites have more stringent cleanup objectives (100s of ppb)
- Site assessment tools are needed to distinguish between clean and contaminated soils
  - Simple, easy to use method required
  - Some sites want information on gasoline or diesel range organics
- Soil remediation costs can be significant millions/year

Standard EPA Methods 3540 (or other 3500) and 8015

- Solvent extraction
  - Weigh out at least 2 g
  - Extract with solvents such as
    - acetone/hexane
    - acetone/methylene chloride

- Analyze on a GC/FID (some may use GC/MS)
  - Requires
    - a large gas cylinder
    - Significant power

- Report out results

Portable Technology

Portable IR

- Advantages
  - Extremely easy to use
  - Quick measurement
- Disadvantages
  - Reduced sample size
  - Chemometric model required
  - Not sensitive enough to measure in the 100s of ppm
  - Natural organic matter can interfere
  - Site specific calibration required

GC-MS

- Advantages
  - Easy to use
  - Sensitive down to 100s of ppm
  - Uses a technology similar to standard EPA method
  - Sufficient sample size
- Disadvantages
  - Consumables required
  - Boiling point limitations
  - Response factors vary by class of compound and carbon number
  - Sample extraction based on equilibrium
  - Site specific calibration required

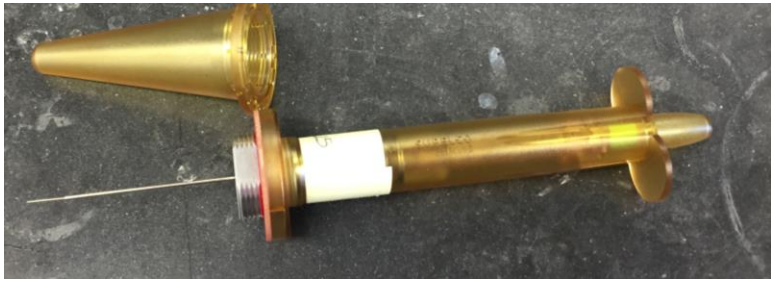
Tridion-9 Portable GC-MS

- Easy to use
- Full portable
  - Helium cylinder
  - Battery
  - Data analysis
- Low thermal mass GC system
  - Column: MXT-5 (5m x 0.1mm x 0.4 um)
  - Split/Splitless Injection
  - Temperature Program: 40-300°C at 2.5°C/second
  - Run time: < 5 minutes (including cooling and data analysis)
- Mass Range: 45 to 500 Daltons

Portable GC-MS
31 lbs
50 sample battery life

T-9 Sample Introduction

- Solid Phase Microextraction (SPME)



  - 19 gauge needle
  - DVB/PDMS coated fiber
  - compatible with direct measurements in aqueous or vapor phase
  - competitive sorption

- Needle Trap (NT)

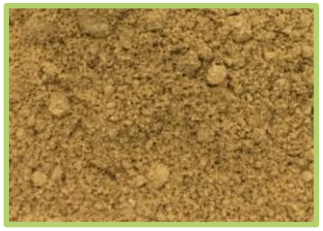
  - 19 gauge needle
  - tri-bed
  - retains compounds from C2-C30

Analytical Approach

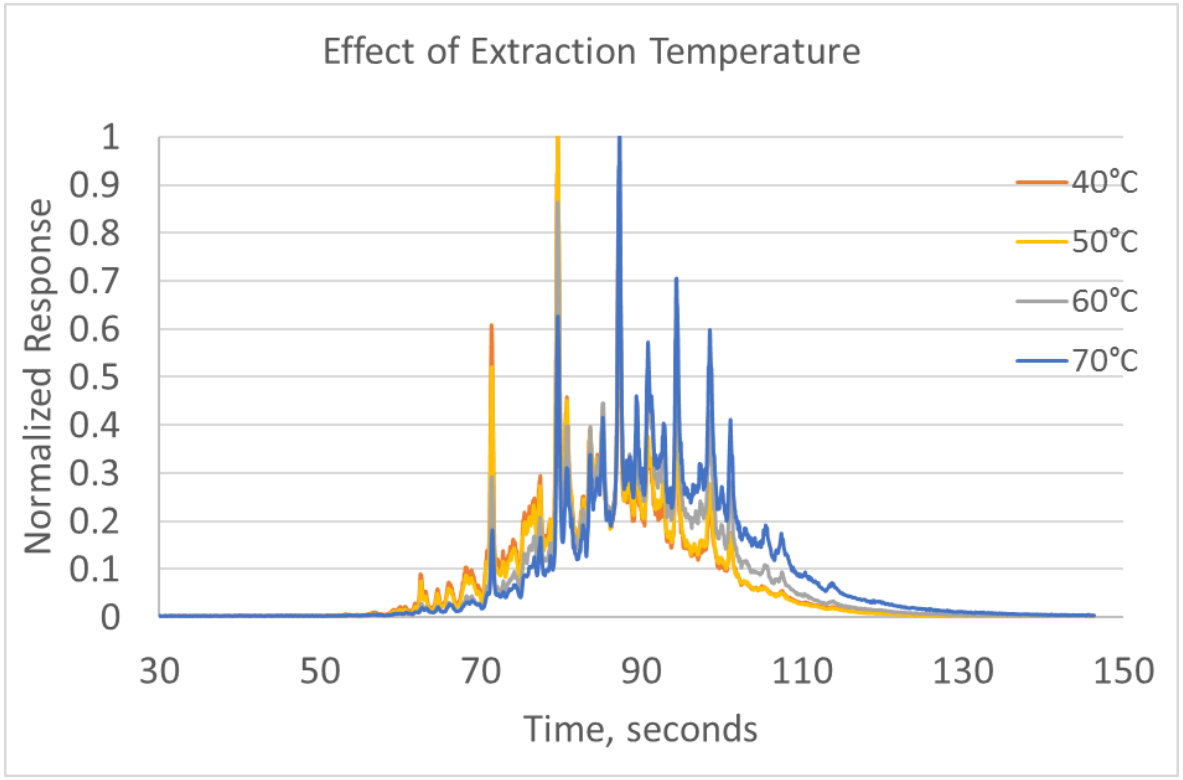
- Homogenize soil
- Place a known amount in a VOA vial
- Heat VOA
- Extract hydrocarbons using SPME
- Analyze on T-9
- Integrate signal and convert to concentration
- Validate method using samples collected from a variety of locations

- Determine how moisture content effects the extraction and T-9 response

Homogenize Soil

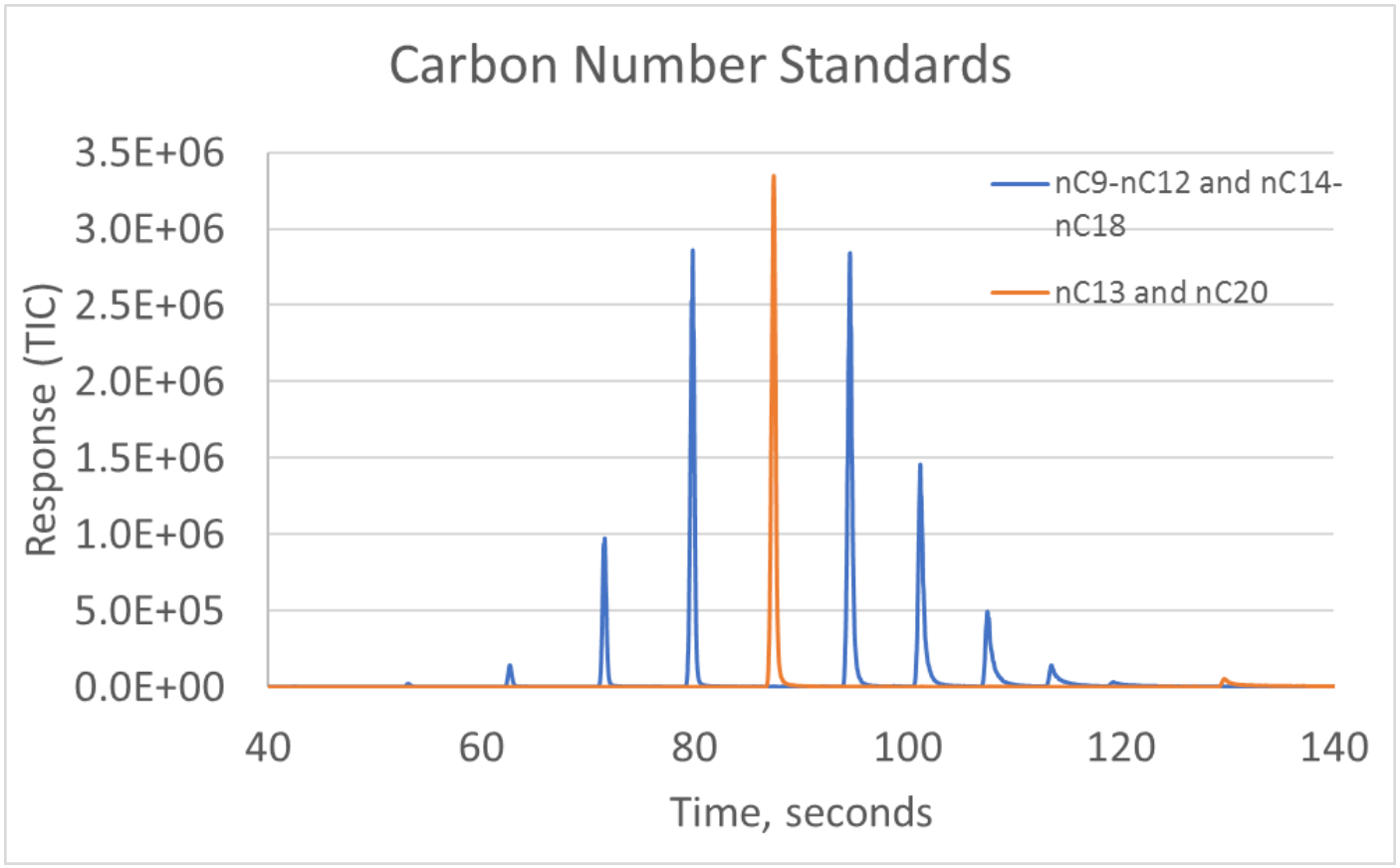


Extraction Parameters



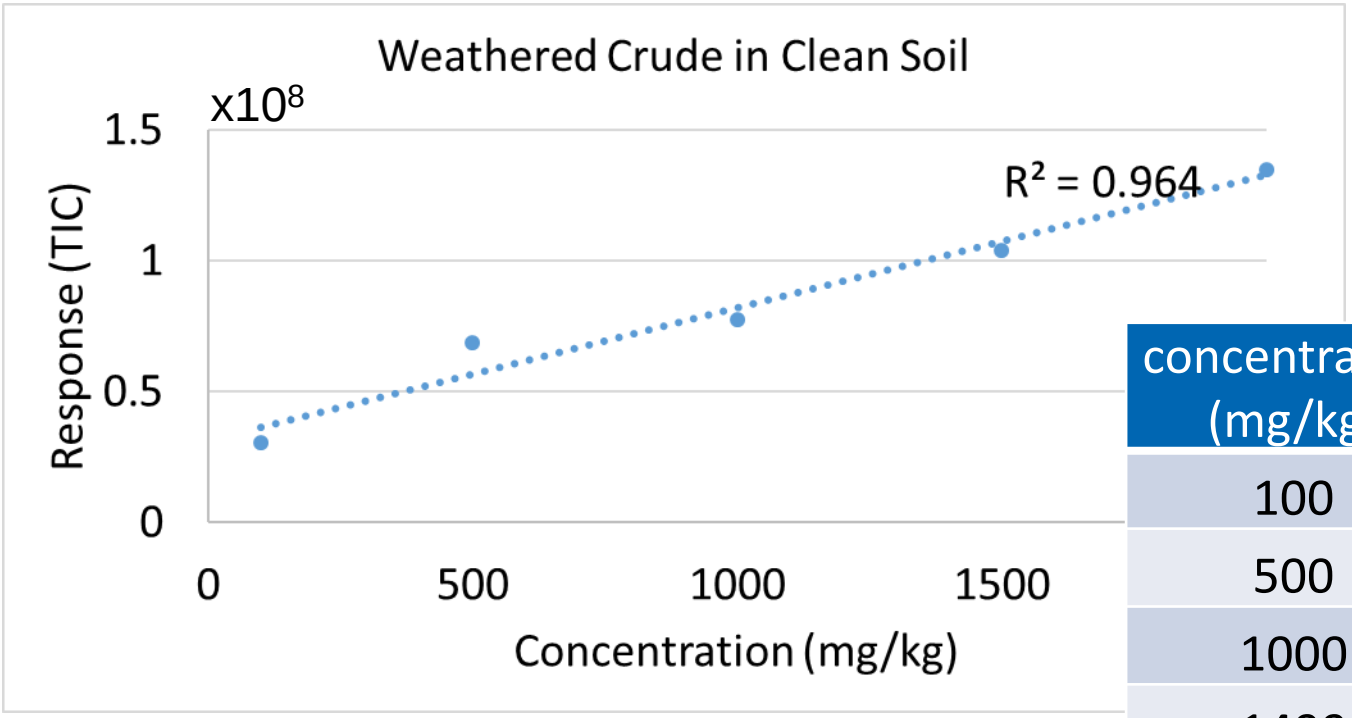
- Elevated Temperature is required to transfer the diesel range hydrocarbons into the headspace of the vial
- Sufficient time at elevated temperature is required to reach equilibrium in the headspace
- Sufficient extraction duration is required to allow equilibrium on the SPME fiber

Carbon Number Range with Extraction Temperature of 70°C



- Carbon numbers up to nC20 can be detected in the headspace above a soil and elute in a predictable pattern

Calibration using weathered crude oil



concentration (mg/kg)	% RSD
100	13%
500	2%
1000	18%
1499	19%
2000	4%

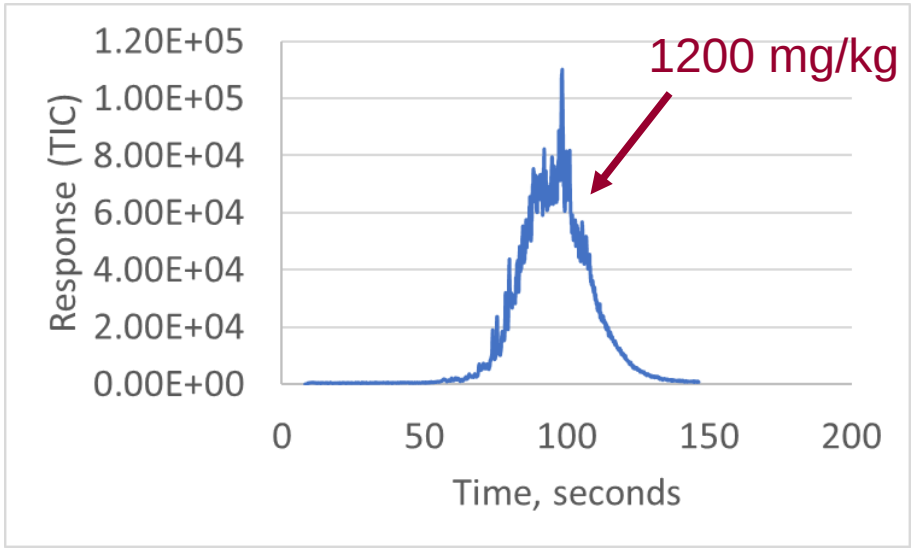
- %RSD for all measurements excellent with all values below 20%

Overview of Field Method for DRO

- Homogenize the sample by stirring and breaking up any clumps
- Weigh out 2 g of soil into a 40 ml VOA
- Heat the sample for 20 minutes at 70°C
- Expose the SPME to the headspace in the vial for 3 minutes
- Place the SPME in the injection port and follow the instructions on the screen
- Export the file to Excel and process using the macro

Field Test

- Site in California
- 27 soil cores were collected, homogenized, and analyzed on the T-9
  - ~27% of the cores had a measurable amount of TPH on the T-9
  - ~7% had a measurable amount by commercial lab



Limitations and Future Work

- Limitations
  - Site specific calibration required
  - Soils with concentrations greater than 4000 mg/kg will contaminate the T-9
  - Method can not detect hydrocarbons with carbon numbers greater than nC20 (so a site calibration might be required)
  - Moisture content impacts results
- Future work
  - Develop a QC protocol
  - Implement surrogate spike
  - Validate method with various types of soils
  - Modify method to create a linear response with concentration

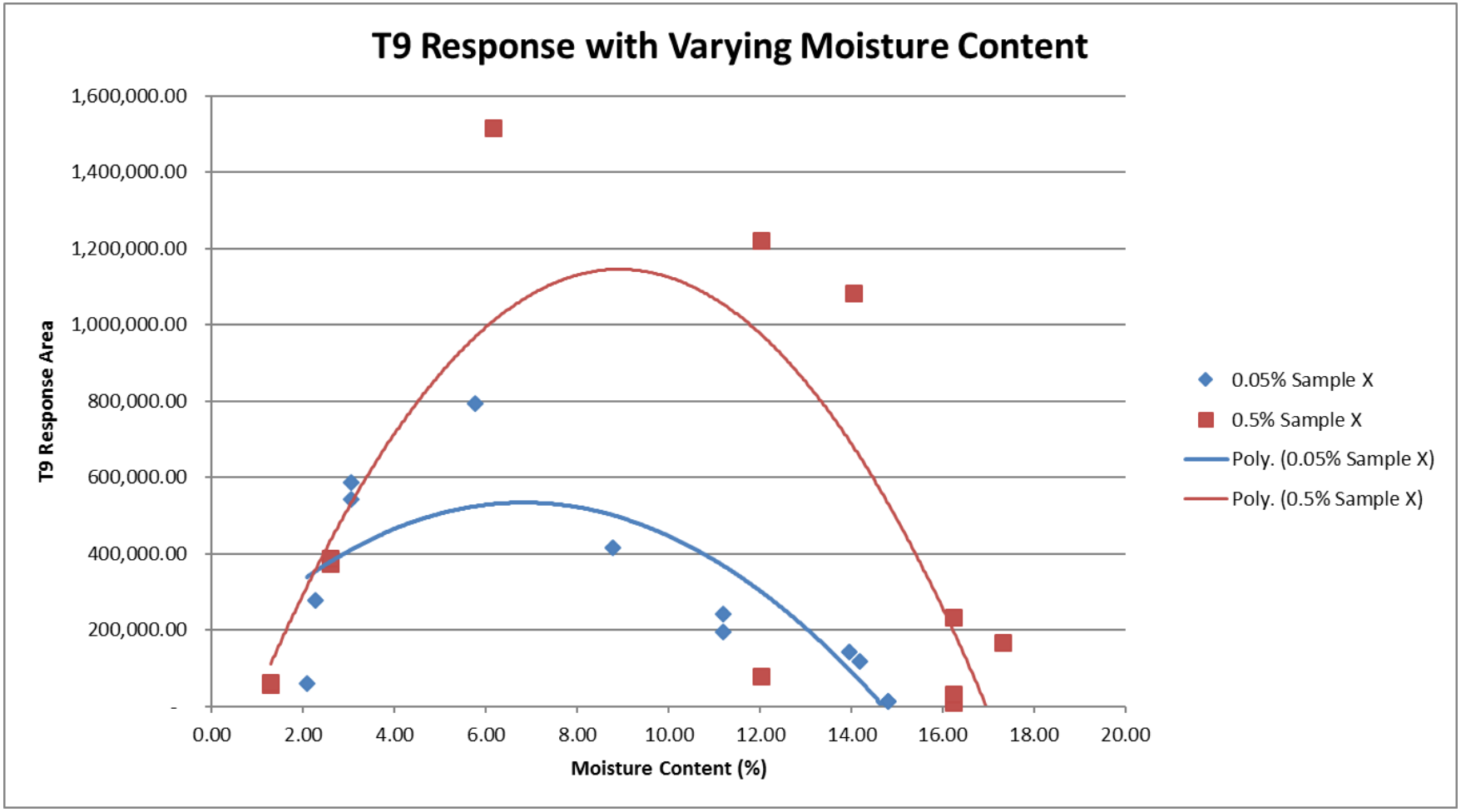
Summary

- Portable GC method is extremely easy to implement and shows potential
  - Even a junior in high school can perform the method!
- Additional method development is required to transition from a screening method to precise method
- Portable GC is complementary to IR based technology
  - IR can measure higher concentrations (% levels) without contaminating the instrumentation

Acknowledgements

- Funding and Support:
  - Chevron Environmental Management Company

Effects of Moisture Content



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