Use of Two-Dimensional Gas Chromatography to Supplement the Evaluation of Natural Attenuation at Petroleum Release Sites

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Battelle Symposium
Miami, FL
May 24, 2017
Presentation Overview

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Project Objectives

• Evaluate petroleum biodegradation by GCXGC-TOF-MS technology and study how important it is at sites with historical releases
• Present a case study on the application of the technology and interpretation of the results consistent with the multiple lines of evidence approach to evaluate Natural Attenuation

Key points:
• GCXGC-TOF-MS is a cutting edge tool to show natural attenuation/biodegradation is occurring.
• GCXGC-TOF-MS is an (expensive) tool in the toolbox that may not be needed for the majority of petroleum release sites.

TOF-MS - Gas Chromatography by gas chromatography, time of flight, mass spectrometry.
Quick Theoretical Background: What is Extractable TPH?

“TPH” is not total, not only petroleum and not only hydrocarbons

TPH is defined by the method

- TPH has been measured by very different analytical methods that quantify in different ways petroleum hydrocarbons as well as non-hydrocarbons as a bulk “TPH” concentration. Results depend on the solvent used, type of detector and fuel standard.
- Non-hydrocarbons (polars) are compounds with oxygen, sulfur and/or nitrogen
- Non-hydrocarbons can be separated from hydrocarbons in the extractable TPH by a silica gel cleanup step (e.g. EPA Method 3630c; SGC)

ITRC TPH Team expected to publish TPH guidance in 2018

- TPH is a measure of extractable organics.
- TPH methods vary across different regulatory jurisdictions, labs and methods.
- SGC can separate the polar from the hydrocarbon fraction
- Non-hydrocarbons = NSO compounds = Polar compounds

TPH – Total Petroleum Hydrocarbons
NSO compounds – Nitrogen, Sulphur and Oxygen containing compounds
“TPH” plumes measured as Extractable TPH in groundwater and natural attenuation

1. Upgradient from HC plume: TPH = Background organics + Naturally occurring organics + Background anthropogenic contamination + Lab/sampling artifacts

2. Dissolved HC plume: TPH = + HC + HC metabolites + Background organics

3. Dissolved metabolites from HC biodegradation: TPH = + HC metabolites + Background organics

4. Downgradient from HC metabolite plume: TPH = + Background organics

LNAPL – Light Non Aqueous Phase Liquids
HC – Hydrocarbons
NSO compounds – Nitrogen, Sulphur and Oxygen containing compounds
Collection of groundwater samples from monitoring wells from 16 fuel terminals and 5 service station sites with biodegrading sources and shrinking/stable plumes

Extraction (3) with DCM (EPA Method 3510)

Silica gel cleanup (EPA Method 3630)

Extract (hydrocarbon + polars fraction) DRO Method 8015 & Method 8270C

Methanol eluate from the SGC (polars fraction)

Three extracts and one methanol eluate analyzed by GCXGC-TOFMS (Mohler et al., 2013)

All extractable organics and organics in the SGC were tested by GCXGC-TOF-MS

SGC – Silica Gel Cleanup
Collection of groundwater samples from monitoring wells from 16 fuel terminals and 5 service station sites with biodegrading sources and shrinking/stable plumes

Extraction (3) with DCM (EPA Method 3510)

Silica gel cleanup (EPA Method 3630)

Extract (hydrocarbon +polars fraction) DRO Method 8015 & Method 8270C and GC-MS Targeted Search

Methanol eluate from the silica gel column (polars fraction)

Three extracts and one methanol eluate analyzed by GCXGC-TOFMS List of TIC classified by:

- Molecular family
  - Alcohols/diols
  - Acids/esters
  - Ketones
  - Aldehydes
  - Phenols

- Molecular structural class
- Name, chemical formula
- Oxygen, carbon and hydrogen ratios
- SMILES designation

TIC – Tentatively Identified Compounds with a similarity number >750
(Zemo et al., 2016)
GCXGC
SMILES - Simplified Molecular Input Line Entry System
SGC – Silica Gel Cleanup

GCXGC –TOFMS result gives you compound family/structural class identification
GCXGC results: detections, not concentration
Case Study

- Former oil field ~2800 acre site at the Pacific Ocean shoreline
- Oil field operations from late 1940s to early 1990s
- Historical releases of a mid-distillate product (C10-C28) and heavy crude
- Active remediation and LNAPL recovery has been conducted at several locations of the site
- TPH in unconfined aquifer is evaluated under MNA

- MNA evaluated with multiples lines of evidence, in a tiered approach.
  1. Concentration in GW vs. time (TPH w/wo SGC)
  2. Geochemistry (not shown here)
  3. GCXGC-TOFMS for metabolites in groundwater, soil and LNAPL
TPH without SGC in Groundwater  
(191 monitoring wells)  

TPH (mg/L)  
0.05 – 0.5  0.5 – 1.0  1.0 – 2.5  LNAPL  

TPH – Total Petroleum Hydrocarbons  
SGC – Silica gel cleanup by EPA Method 3630
TPH with SGC in Groundwater

- 54% of the samples with TPH detections were non-detect (<50 ug/L) with TPH with SGC
- TPH concentrations with SGC showed more than 85% were polars

Dissolved “TPH” plume is mostly metabolites

TPH (mg/L)

- **0.05 – 0.5**
- **0.5 – 1.0**
- **1.0 – 2.5**
- ![LNAPL](symbol)

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TPH w/o SGC - trends in Transect 1

Historical Groundwater Elevation and TPH

TPH w/o SGC is a poor metric of biodegradation

TPH: mg/L
Groundwater (GW) Elevation: feet above mean sea level
GCXGC data - approx. % TIC in Transect 1

HC biodegradation occurring across the flow path

TPH/TPHwSGC (ug/L)

- 5000 / 620
- 4900 / 420
- 400 / <50

Alcohols  Acids/Esters  Ketones  Aldehydes  Phenols

TPHwSGC – Total Petroleum Hydrocarbons with Silica Gel Cleanup
Most downgradient wells show complete HC biodegradation.

TPH/TPHwSGC (ug/L)

260 / <50
210 / <50
320 / <50
1400 / 79
400 / <50
620 / <50

GCXGC data - % TIC in Transect 2

Alcohols  Acids/Esters  Ketones  Aldehydes  Phenols

67%  33%  33%  33%  0%
67%  33%  33%  33%  0%
50%  50%  50%  50%  50%
50%  50%  50%  50%  50%
34%  33%  33%  33%  33%
Soil Biodegradation

• Results from 24 soil samples show samples with higher % Polars have a higher % of less biodegraded metabolite classes
Interior LNAPL attenuation

• **3 out of 4 samples** - The n-alkanes have been completely removed, and only the isoprenoids remain as resolvable peaks.

• **1 out of 4 samples** - The 2014 sample has lost the C11-C13 n-alkanes; and the nC17/Pristane and nC18/Phytane ratios are slightly lower than in 1995.

Note – Chromatograms and GCXGC results by % TIC detections after Zemo, 2016

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Conclusions

• Biodegradation of petroleum hydrocarbons occurs in groundwater, soil and LNAPL phases. GCXGC-TOF-MS is a tool that can show natural attenuation/biodegradation.
  – GCXGC-TOF-MS can provide family and structural class information relevant for toxicity evaluation

• Biodegradation indicators are useful: Biodegradation indicators (higher presence of acids/esters and alcohols) are present in LNAPL and are more prevalent in the outer edges of the plume (metabolite plume vs. source zone).

• SGC can help evaluate natural attenuation:
  – The difference between TPH without SGC and TPH with SGC is a good indicator of polars (non-hydrocarbons) load in soil and groundwater.
  – SGC can serve to evaluate naturally occurring organics and background and lab/sampling contamination.
Co-Authors and Acknowledgements

• Renae Magaw, MPH and Rachel Mohler PhD - Chevron
• Dawn Zemo, MS, PG, CEG - Zemo & Associates
• Kirk O’Reilly PhD, Asheesh Tiwary PhD, DABT, DVM and Sungwoo Ahn PhD – Exponent

• Karen Synowiec – retired

• Research funded by Chevron Environmental Management Company
• Consulting and field work conducted by Padre Associates, Inc.
Thank you

Questions?

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References


