Biogenic compound quantification and removal by use of comprehensive GCxGC

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Who We Are

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Service Beyond Analysis  www.agatlabs.com
What is GCxGC?

Many different names, GCxGC, Multi-dimensional GC, 2-D GC, GC² ....

Amounts to the same thing, 2 GC columns for multiple levels of separation.
How it works... (roughly)

Start!  Non-Polar column

Modulator

Polar column
Why GCxGC?

Traditional GC can delineate some constituents in an oil sample, but not the details—compounds with similar properties can merge together into an Unresolvable Complex Mixture or “hump”
Clear separation of typically co-eluting compounds. This is a Diesel
GCxGC Chromatography

In 1-D these compounds are actually stacking up.

With 2D we can cleanly separate these compounds.

Plus it looks cool!
Large Unresolved Complex Mixture (UCM)

Routine GC-FID CCME

Routine Scans
Cost: Low
Accuracy: Low
Pro: Quantify regulatory Hydrocarbons
Information: Limited
Signature Recognition
- Accuracy: Medium
- Multiple points of ID
  X, Y, Pressure, Curvature, Acceleration
- Cost: Marginal
- Interpretation dependant

GC-FID/MS ‘Signature’
- Resolution: Medium
- Multiple points of ID
  Ratios, profile matches, PCA...
- Multiple Runs
- Cost: Marginal
- Interpretation dependant

Product Fingerprinting

45+ min
Fingerprinting GCxGC

**Fingerprint Scan**
- Accuracy: High
- Multiple points of ID: Ridges, Crossover, Core
- Less ambiguous interpretation

**GCxGC FID Scan**
- Resolution: Very High
- Multiple points of ID in Single run: Homohopanes, Steranes, etc.
- Less ambiguous interpretation
- Better product and structure determination

Middle Distillate-Diesel GCxGC-FID
Petroleum Hydrocarbons (PHCs)

- Petroleum Hydrocarbons (PHCs) are one of the most widespread soil contaminants in Canada.

- CCME/CSR method does not differentiate PHC from Biogenic compounds which are co-extracted with PHCs.

- Possible overestimation of PHC levels in soil samples, interferences can even exceed regulatory levels.

PHC Fractions analysis cannot discern biogenic from petrogenic signals
Biogenic Organic Compounds

Organic compounds biosynthesized by living organisms:
- Fatty Acids and Alcohols
- Sterols, Steranes
- Alkanes
- Waxes and esters

Sources are diverse and include Plants, Algae, Bacteria, and animals. Bioremediation can actually result in BOCs through microbial action.
Volatile Hydrocarbons Identification

- Drilling Fluid
- Middle Distillates/Diesel
- Biogenic Hydrocarbons
- Gasoline
- Lube Oils/Bitumen/Tar
- Crude Oil

- C6
- C10
- C16
- C22
- C34
- ++
PHC interference

Petrogenic
• Petroleum or Anthropogenic origin
• Oil, Gasoline, Diesel, etc

Biogenic
• Naturally present hydrocarbons
• Muskeg rich areas
• Typically F3 some F4

Biogenic HCs can cause regulatory exceedances. Are we meant to “remediate” natural areas back to guideline?
Peatland Distribution

Peatlands in Canada
High Organic content
TOC >28% = F3 exceedance
TOC Peat >40%

Significant natural role
Carbon Sink

Sensitive Ecosystem. Peat Wetlands can take up to 10,000 years to form. No engineered is equivalent to natural.
Volatile Hydrocarbons Identification

- VPHs
- EPHs

- F1: Biogenic
- F2: Mixed
- F3a: Biogenic
- F3: Gasoline
- F3b: Diesel
- F4: Crude Oil

- C6 - C34
This is good chromatography of a peat sample; it should be, it is pristine, clean, and fresh.

- Clear even odd ratios are visible
- Little F2, whole lot of F3.
A little less clear. Sample with F3 exceedance of 2150mg/kg
→ Little F2; lots F3
→ This is actually a mixed sample.
Addressing False PHC positives

Forensic methods conclusively identify sites that are contaminated and those that are not, to ultimately limit liability and reduce unnecessary impacts on environment from extensive excavation activities.

False PHC detections may be addressed by the following approaches:

**Subtraction of Background PHC Concentrations** – CCME: Clean background soil concentrations can be subtracted from contaminated soil concentrations. Can generate highly variable concentrations due to the non-homogeneity.

**Biomarker Forensics Analysis** - Biomarker forensic analysis involves highly specialized Gas Chromatography Mass Spectrometry (GC-MS) laboratory analysis methods. Can ID presence versus absence of PHCs, but does not allow appraisal of false PHC soil guideline exceedance.
Silica Gel Cleanup – Generally more polar than PHCs. Silica gel is a polar substance; can remove polar BOCs from PHC extracts. CWS PHC standards allow a controlled amount of silica gel removal. BUT organic soils, such as peat, can exceed saturation capacities. = possible false PHC + approval for additional method. Diagenesis of polar biogenic to nonpolar HCs can pass through Silica gel cleanup.

Biogenic Interference Calculation (BIC) Index – Quantitatively determine if sample has falsely exceeded the Tier 1 soil guidelines for PHC F3. PHC F2 and PHC F3 carbon ranges, dividing PHC F3 into two sub-fractions “PHC F3a” (>C16-C22) and “PHC F3b” (>C22-C34)....BUT what if no F3? What if product is similar?

Biogenic Toluene – Application of Forensics techniques including Chromatographic interpretation and diagnostic ratios to distinguish Biogenic and petrogenic origins of Toluene; for example in wetlands potential contamination from oil-based drilling muds, condensate, etc.
Silica Gel Cleanup

In General, biogenic compounds are polar. SPE (Silica Gel) enables clean up of a sample by retaining the polar compounds. SG can also be used to fractionate Aliphatic (Ali) and Aromatics (Aro) relevant for health-based risk assessment

BUT:

• Some Biogenic compounds are not polar.
• Non Biogenic compounds may be removed (ex. Bacterial metabolites)
• Still possible false positives.
• Cannot be used with other techniques without approval.
Silica Gel Cleanup—GCxGC

Peat Moss No SG: 4% F2, 46.3% F3, 49.4% F4

Peat Moss After SG: 3.6% F2, 68.9% F3, 27.6% F4; signal is 48% of no SG
Biomarker Forensics Analysis

Petroleum Biomarkers are chemical Fossils which can be used as unique tracers for petroleum contaminants. Relies on identification of specific biological marker compounds present to identify specific source of HCs.

Highly specialized Gas Chromatography Mass Spectrometry (GC-MS) analysis.

Can differentiate phytogenic and petrogenic contributions requires site knowledge.

Conceptualized Diagnostic Ratio plot.
Example of a Crude Oil

This is an off shore oil, to demonstrate obvious Petrogenic signals. 
→ PAHs in the Chrysenes, Linear alkanes, clearly petrogenic
Unlike in 1 D we can clearly identify individual peaks and develop a peat ‘signature’; separate more polar and aromatic compounds; remove the noise and clearly identify them to help characterize site inputs.
2nd Dimension

Peat Moss

Clear separation of typically co-eluting compounds in the second dimension
Clear separation of typically co-eluting compounds—Peat Moss
Overall for this peat; the biogenic region accounts for roughly 50% of the total. 45% of the total area is found in F3 with 48% in F4.
This is a motor oil, to demonstrate Petrogenic signals.

→ Linear alkanes, clearly petrogenic but also biogenic.
Is about 86% F3 13% F4
Peat spiked with Motor Oil. Clear peat signature. BUT our linear alkanes don’t agree, and we can see some other compounds that do not match the peat. Also our Biogenic region is closer to 30% of our total.
This sample with Peat was 1450mg/kg F3; of this the ‘natural’ or peat equivalent is over half, or 1,015mg/kg
Peat spiked with Diesel. The peat signature is clear and present again. BUT we can easily see the presence of lighter PHC hydrocarbons.
The peat signature is 27% of the total; here F2 is 29%, F3 is 54% and F4 is 15%; F3 is roughly 940mg/kg.
Peat spiked with Diesel. Zoomed in to view the middle distillate pattern. Clearly petrogenic.
The power of GCxGC provides enhanced specificity and peak capacity with increased resolving power that can separate diagnostic biomarkers from potential interferences.

GCxGC provides a structured chromatogram, which allows compound identification that would be impossible with GC due to the complexity of crude oil.
Expert Interpretation

Site assessments require understanding of complex environmental chemical processes—both natural and anthropogenic.

Biogenic and Petrogenic inferences can be made by an experienced chemist and support good field work with informed analyses.

All methods require well thought out sampling programs and sufficient understanding of environmental chemistry and processes.
QUESTIONS AND DISCUSSION

Thank you!!