

Silica Gel Cleanup of Extractable Petroleum Hydrocarbons – Do you know what you are removing?

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Spill Response and Mobile Lab Services

- Field and Laboratory Response
 - Mobile Lab
 - After Hours Service
 - 24hr Availability
 - Capacity Management
- Logistics
 - Sample Transportation
 - Courier Management
 - Command Center
 - Supply Management



Who We Are



AGAT Forensic Science Team

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Forensic analytical: Environmental Forensics

- Is this contamination related to my activities or from another source?
- My site has multiple land use histories; what is the main product and when did the release occur?
- Are my exceedances related to natural hydrocarbon—or are they petrogenic?
- Is my site commingled?

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Forensic analytical: Environmental Forensics

The Fingerprint Samples interpretation

Enables product type ID

To find the likely culprit it helps to have suspects



The usual suspects: While we have a large hydrocarbon library on hand, exemplars provided from a site enable more definitive and eloquent analysis.



Forensic analytical: Environmental Forensics

The Fingerprint

Exemplars (suspects) help to narrow the field. Especially when related products are involved.



Total Ion Chromatograms (TIC) comparison of the Turbine Fuel Pot sample and comparison samples from the Agat Oil Forensic Library. The Turbine Fuel Pot sample is distinct from the other other types and most closely resembles the Hydraulic Fluid standard. The match is not exact and a further search of Hydraulic Fluids and Gear Oils used at the sample site may identify the unknown matching product.

Forensic analytical: Environmental Forensics

Diagnostics

- Comparison of signature compounds
- Similar to ILR work
- Biogenic toluene/peat





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"



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Routine GC-FID EPH

Stop Light Interpretation: Subjective "Can I make the yellow?" Pro: Simple Information: Limited







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Product Fingerprinting



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



CA GCA

45+ min



GCxGC Chrom



Typical oil—This is a Gulf of Mexico standard run on our system with PAH separation. Circled are the mono- and tri- aromatic sterane biomarkers.

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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.



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GCxGC Chrom



Carbon Number

GCxGC FID Scan

- Resolution: Very High
- Multiple points of ID in Single run:
 PAHs, Homobonanos, Storanos

PAHs, Homohopanes, Steranes, etc.

- Less ambiguous interpretation
- Better product and structure determination
- FID = common response factor; quantitative





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 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?



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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.



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/CSR: 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.

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Addressing False PHC positives

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?

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.

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What About in a Release?



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Fuel Oil #6 (spiked in Boreal Soil)



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Peat Moss



Clear separation of typically co-eluting compounds

Multiple lines of evidence of Biogenic origin.

Easily interpreted

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Diesel plus Peat



Boreal soil sample plus Diesel Clear biogenic signature evident.

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Diesel plus Peat



Subtraction Chromatogram: Peat removed

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Peat Spiked with Motor Oil



This is a motor oil, to demonstrate obvious Petrogenic signals. Clearly petrogenic, but also biogenic. BIC not applicable

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Peat Spiked with Motor Oil



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

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Peat Spiked with Motor Oil



Subtraction Chromatogram: Peat signature removed; clear Motor oil signature

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SGC Evaluation

- Polar compounds removed following Silica gel cleanup
- Aliphatic compounds remain
- Aliphatics not specific to biogenic

C23 C25C33 Peat F3b after SG C25 $C^{2}7$ C29 C33 C31**Carbon Number**

Peat F3b prior to SG



Polarity



Evaluation of SGC



Aliphatic

This is a Heavy Fuel Oil (HFO #6) and following SG.

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Evaluation of SGC



Subtraction Chromatogram: Diesel in Peat moss after Silica Gel

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What about in an old release?

"In a study of two crude oil spill sites, the USGS found that the extracted DRO (Diesel Range Organics) compounds represent **one-third** to **one-half** of the total concentration of petroleum oxidation products found in groundwater (Bekins et al. 2016)"

A number of Studies have demonstrated PM's are significant contributors to overall toxicity (Barron et al. 1999; Zemo et al. 2017; Khan et al. 2018)



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PAH determination

EPA 16 list created in 1970's based on :

- Availability of standards and detection by GC MS or FID
- Environmental occurrance
- Proxy for other hard to detect or unknown toxicity
- *Known to be toxic

 Requires detection, isolation and characterization.
 Holistic approach typically unknown/difficult analytically and experimentally.

List has expanded to 23 routine; sometimes 34—but is far from comprehensive or representative of total PAHs

Uncharacterized A-PAHs can be present in variable amounts

QSARS; TEST

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PAH determination

".....209 theoretical isomers of chlorinated biphenyls are possible......"

".....(for PAHS) isomers ranged from 2 for C-1 naphthalene up to 19 502 for C-6 dibenzo(ah)anthracene. Heterocyclic PACs had similar numbers ranging from 4 isomers for C1 dibenzothiophene to 13 938 for C6 dibenzo[a,i]carbazole..."

Enumeration of the constitutional isomers of environmental relevant substituted polycyclic aromatic compounds – Johnson et al. March 2018 Chemosphere 202

Hundreds of thousands of substituted PAHs. Ecotoxicity? Carcinogenicity? QSARS?

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Fuel Oil #6 (spiked in Boreal Soil)



The sheer number of different PAHs that exist is difficult to comprehensively evaluate by any method. However, it is far more possible with GCXGC.

Laboratories

Not realistic or practical to look at each and every PAH There are not standards available for the 100 000+ compounds for MS

....But what if we could identify quantify groups of PAHs easily?

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Fuel Oil #6 (spiked in NEBC Soil)



Characterization by class as well as unique identification and quantification as needed for tracking petroleum metabolites

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Benefits Using GCxGC

- 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.

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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.

Biodiesel SQL TYPE Condensate Peat Bog



Thank you!

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QUESTIONS AND DISCUSSION Thank you!!

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