Phytogenic vs. Petrogenic Contamination: *A Swampy Issue*

Applying Petroleum Biomarkers as a Tool for the Confirmation of Petroleum Hydrocarbons in High Organic Content Soils

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Abstract

The Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil acknowledges that high organic carbon content may create positive interferences for the determination of petroleum hydrocarbons in certain instances. The standard does not stipulate the analytical techniques required for confirmation of the positive interferences. Natural attenuation of petroleum hydrocarbons in highly organic soil will often cause severe alteration of the original product. Degradation of the petroleum product, although desirable, can hinder the identification and quantification of the target contaminants. This work describes the measurement of chemical fossils termed "Petroleum Biomarkers" in high organic content soil extracts. Petroleum biomarkers are used to positively identify or confirm the presence of petroleum products in a significant background of phytogenic (naturally occurring) organic material. The biomarker compounds cover the range of CCME PHC fractions F2 and F3, where interference from phytogenic hydrocarbons is most problematic. Specialized GC/MS techniques are employed that allow for unambiguous identification of key biomarker compounds. The biomarkers targets sought in this work include acyclic isoprenoid compounds, PAH compounds, terpanes, hopanes and triaromatic steranes. The presentation will provide a description of basic principles of biomarker analysis including example chromatograms and mass spectra. The presentation will also include data from a case study completed in early 2007 where biomarker analysis was used to provide environmental forensic data in support of an environmental remediation project in central Alberta.

The site in question was an active oil well from the 1960's to the 1990's, and is currently under lease by Nexen Inc. Subsequent reclamation activities undertaken at the site identified residual impact, which prompted additional assessment activities to be undertaken. During the investigation, large quantities of organic material were noted which raised concerns surrounding analytical bias. Routine petroleum hydrocarbon analysis revealed that "impacts" appeared to be widespread across the site, including background areas. Trium consulted with Maxxam, and through the internal resources of both companies determined an amendable approach to forensically differentiate the naturally occurring phytogenic from the non-naturally occurring petrogenic petroleum hydrocarbon contributions. The results of this forensic investigation revealed that although detectable petroleum hydrocarbon concentrations were still present above the applicable criteria, the petrogenic contributions were marginal

Outline

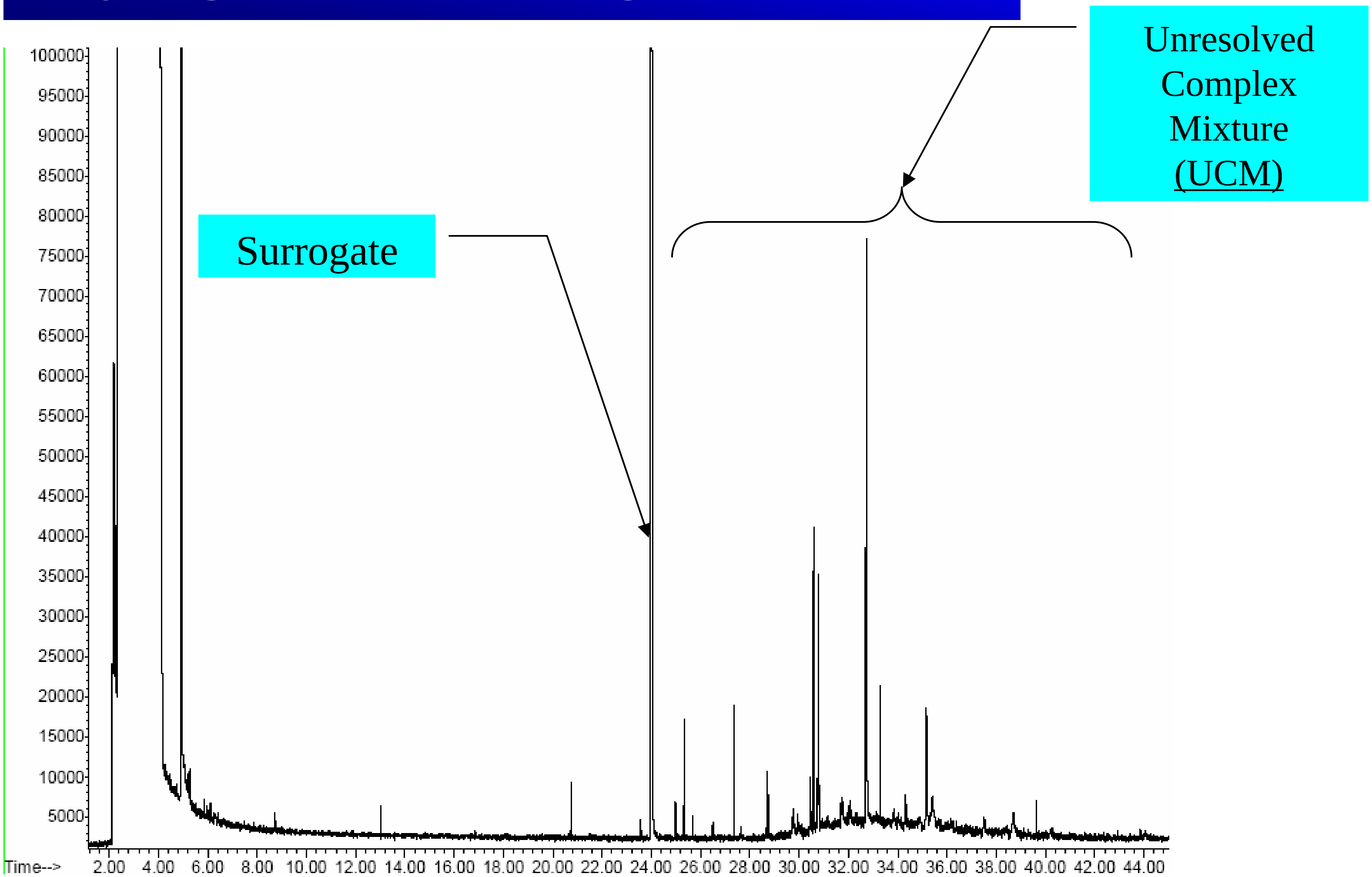
- Biomarkers – Phil Heaton, Maxxam
  - Definitions/Guidance
  - Methodology
  - Biomarkers and Interpretation
- Case Study – Jevins Waddell, Trium
  - Background and analytical data
  - Remedial approach
  - Conclusions
- Questions

Phytogenic vs. Petrogenic

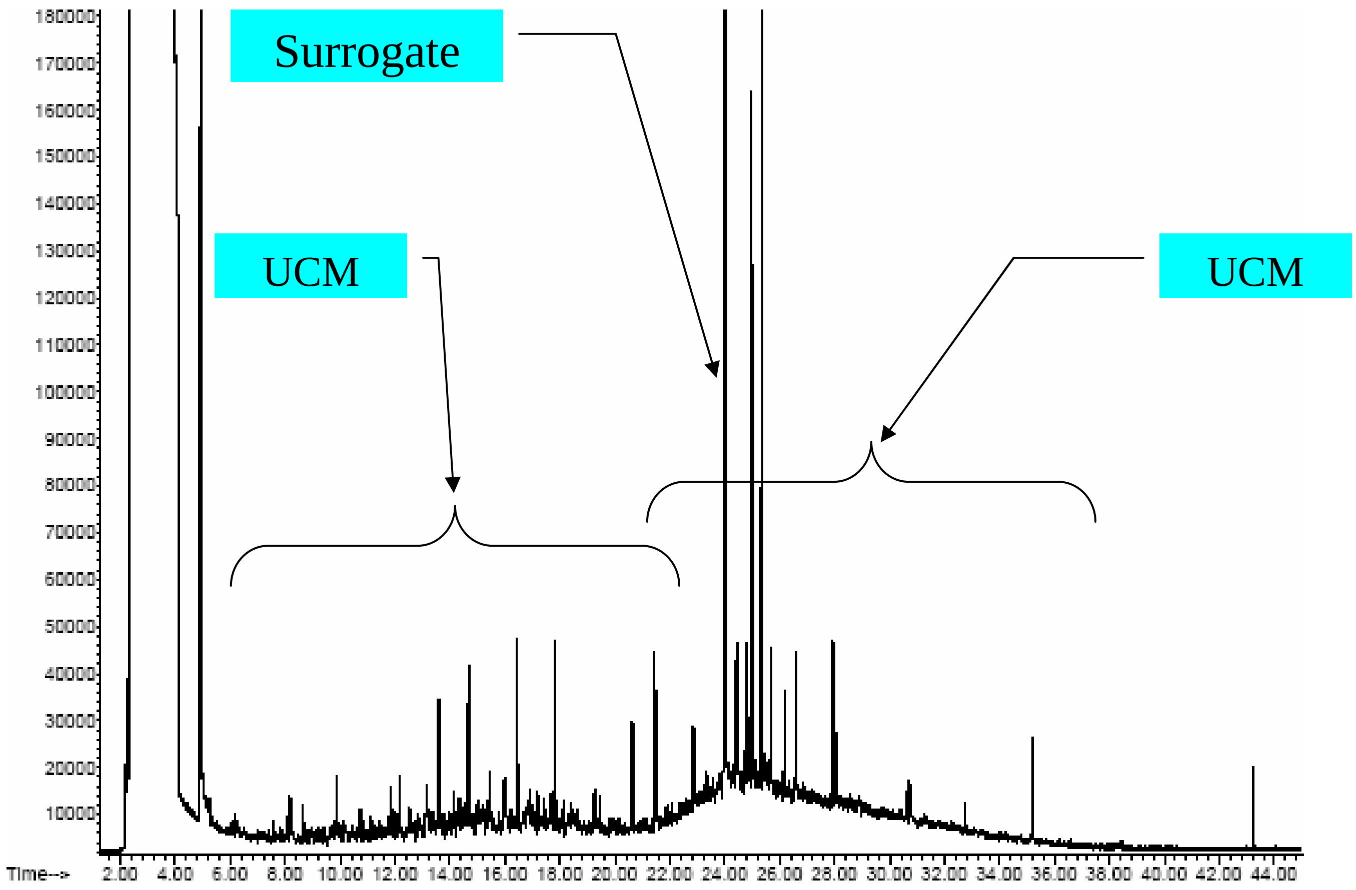
- **Phytogenic hydrocarbons:** hydrocarbon compounds derived from plants.

- **Petrogenic hydrocarbons:** hydrocarbon compounds associated with petroleum products or petroleum sources.

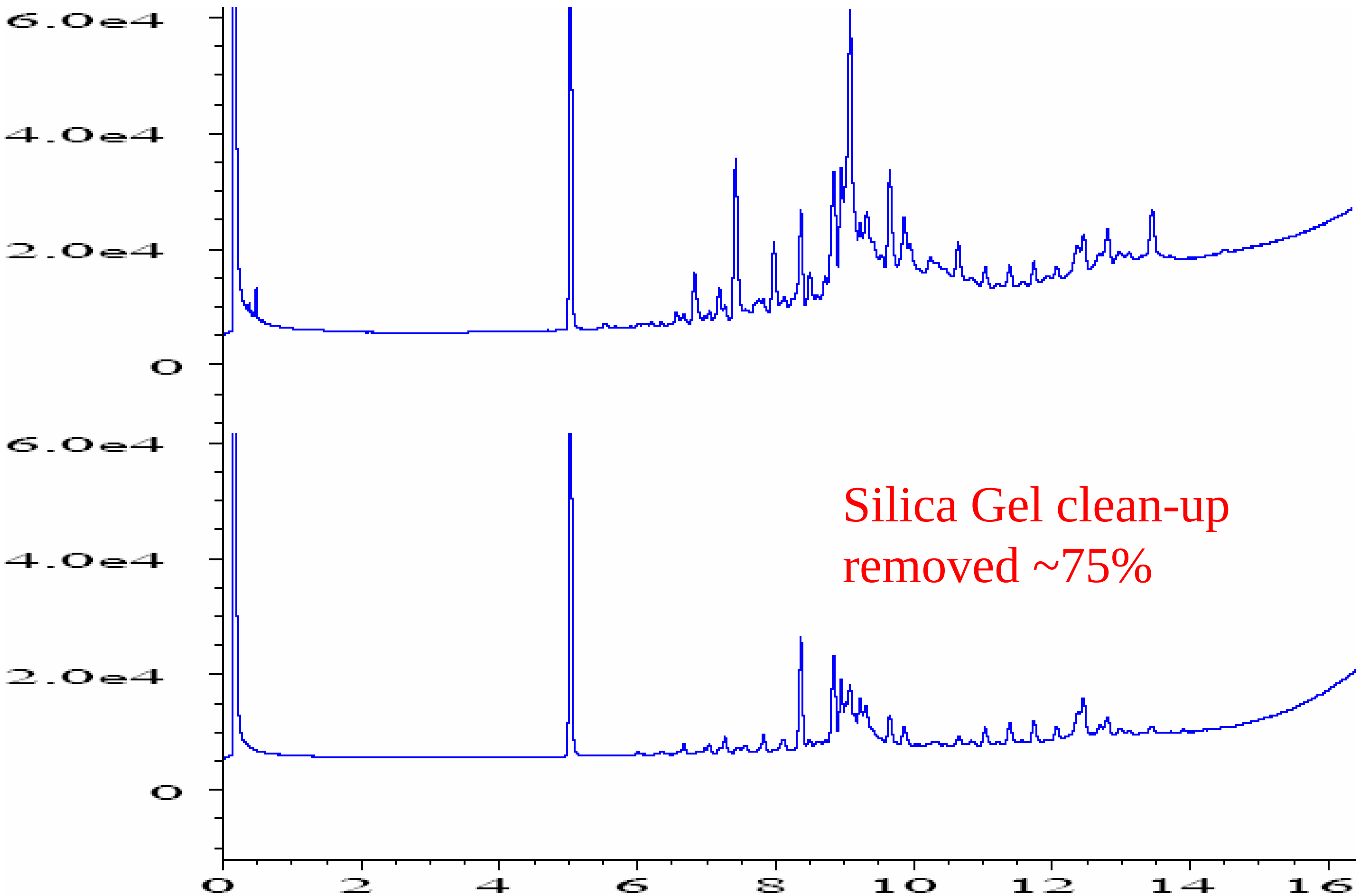
Phytogenic or Petrogenic??



Phytogenic or Petrogenic??



Silica Gel Treatment



F2 = ND

F3 = 5500 mg/kg

F4 = 4200 mg/kg

F2 = ND

F3 = 1800 mg/kg

F4 = 760 mg/kg

CCME PHC CWS Section 15.1

Section 15.1 from the CCME CWS for PHC states the following:

High Organic Carbon Soils

Soils containing high organic carbon content may give rise to false positives. This can occur if a high organic carbon soil is extracted as for the C10 to C50 fraction. The chromatogram will contain peaks that may appear to be hydrocarbons. In such cases, it is recommended that the extract be analyzed by GC-MS to confirm that there are hydrocarbons present. Alternatively, a comparison soil should be sampled from a site known to be free of contamination. This second or "blank" soil should be extracted in a manner similar to the contaminated sample. After analysis, the two chromatograms should be compared. If possible, the "blank" chromatogram should be subtracted from the "contaminated" chromatogram, either by physical comparison of the two chromatograms or by using a computer. If the results from the blank are similar or higher than the contaminated sample, then it must be assumed that there is no hydrocarbon present.

If there is evidence of hydrocarbon present, the best approach may be to conduct the analysis without silica gel cleanup on both the contaminated soil and an uncontaminated soil of the same type from a nearby location. Subtraction of the "blank" soil from the contaminated soil will give an estimate of the hydrocarbon levels. Normally there is some other evidence of hydrocarbon contamination, such as a distinct odour or definite information regarding a spill. Furthermore, it is recommended that in assessing high organic carbon soils, the organic content should be measured. Various techniques are given in reference [10]. The consensus is that methods based on the Leco furnace (or equivalent) are the most reliable [11].

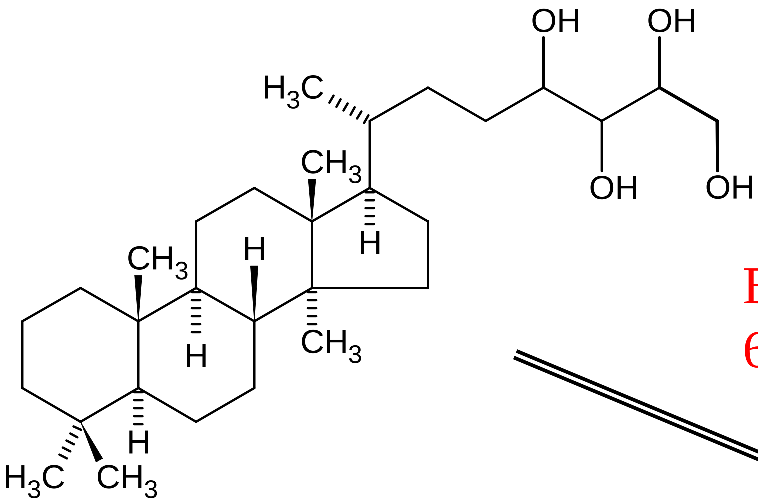
CCME PHC CWS Section 15.1 (summary)

- **Recommends the use of GC/MS to confirm if hydrocarbons are present.**
  - Does not acknowledge the complexity of phytogenic and petrogenic hydrocarbons
- **Recommends the collection and analysis of background soils from areas known to be free of contaminants.**
  - Background samples are used as blanks?
  - Does not acknowledge the heterogeneity of large sites.
- **Recommends analysis with and without silica gel clean-up**
  - Does not acknowledge the the variability in clean-up “success”.
- **Recommends the use of other indicators such as odor.**
  - Does not acknowledge the challenge of aged sites.
- **Recommends the samples be analyzed for total organic carbon**
  - Does not acknowledge that the TOC may be >50% of the mass on a dry basis.

Petroleum Biomarkers

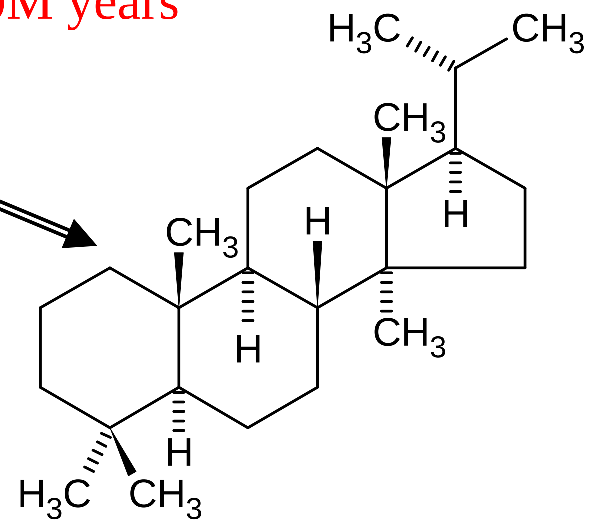
- **Petroleum Biomarkers** are chemical fossils that can act as unique tracers for petroleum contaminants.
- They originate from formerly living organisms.
- They closely resemble their parent molecules found in living organisms.

Biomarker Examples



Bacteriohopanetetrol in Prokaryotic Organisms

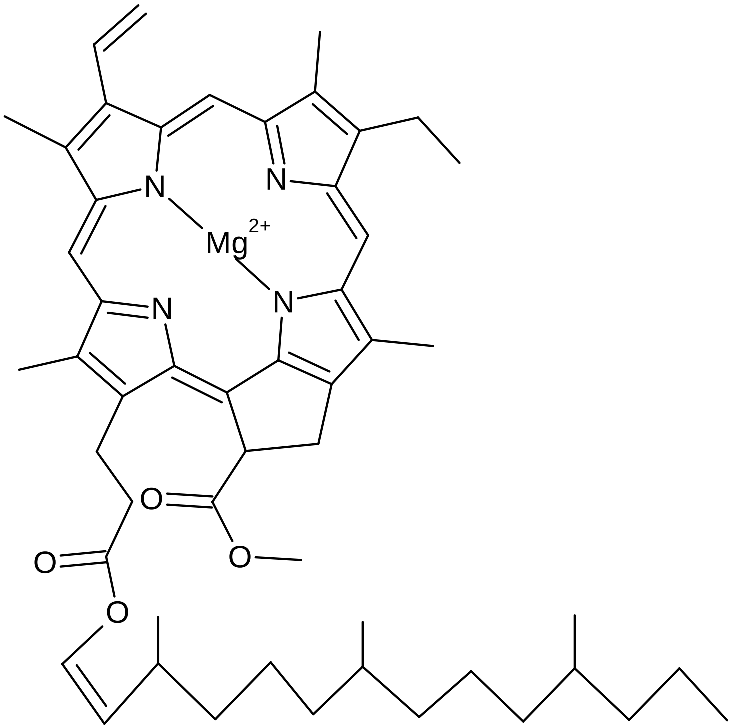
Bake under pressure @ 60C for 200M years



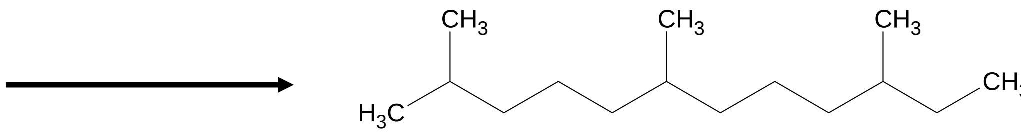
Hopanes found in Crude Oil

The Biomarker Guide, Volume 1, Peters, Walters & Moldowan

Biomarker Examples

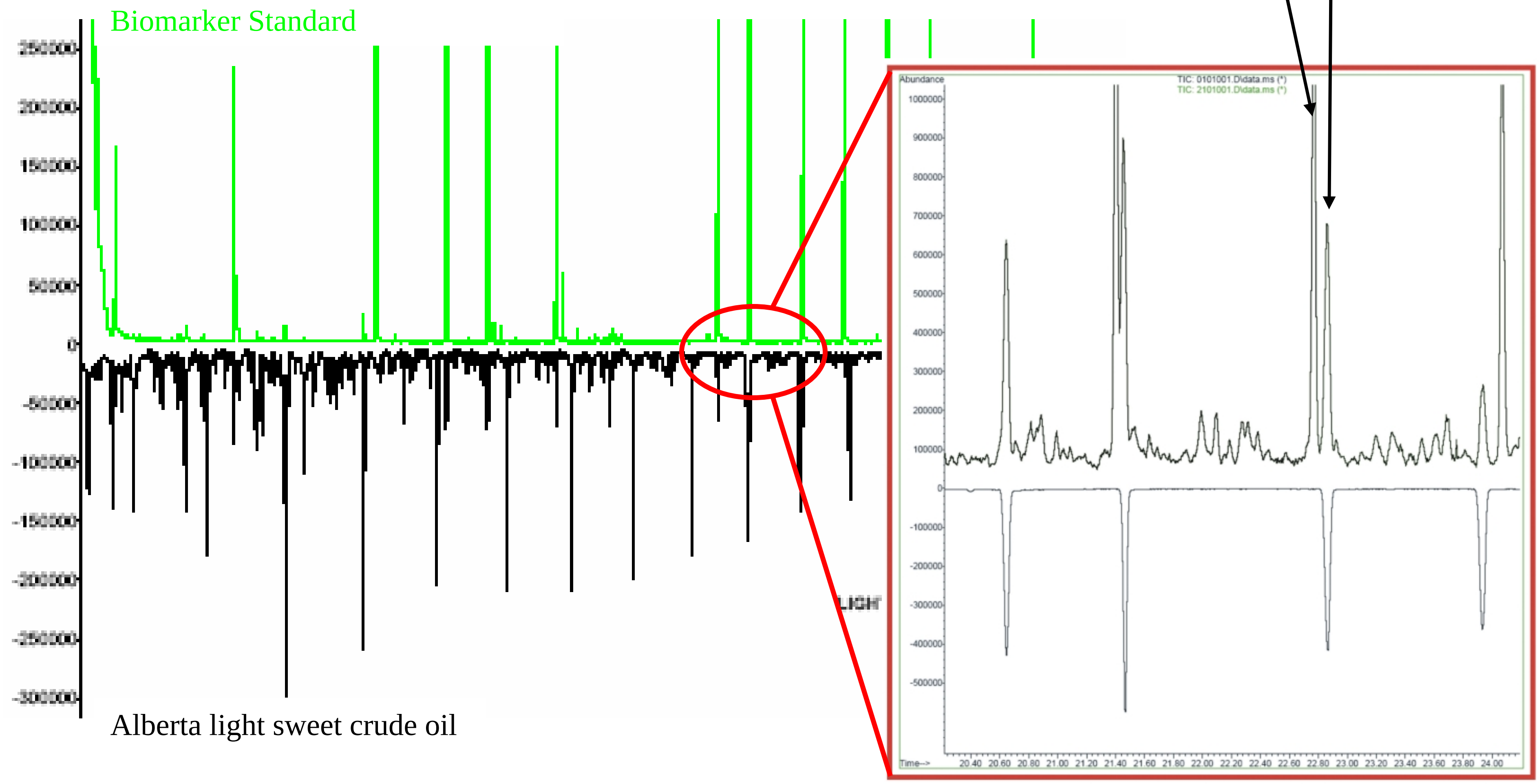


Chlorophyll a



Farnesane

Biomarkers in Crude Oil



Susceptibility to Weathering

Susceptibility to weathering

Most

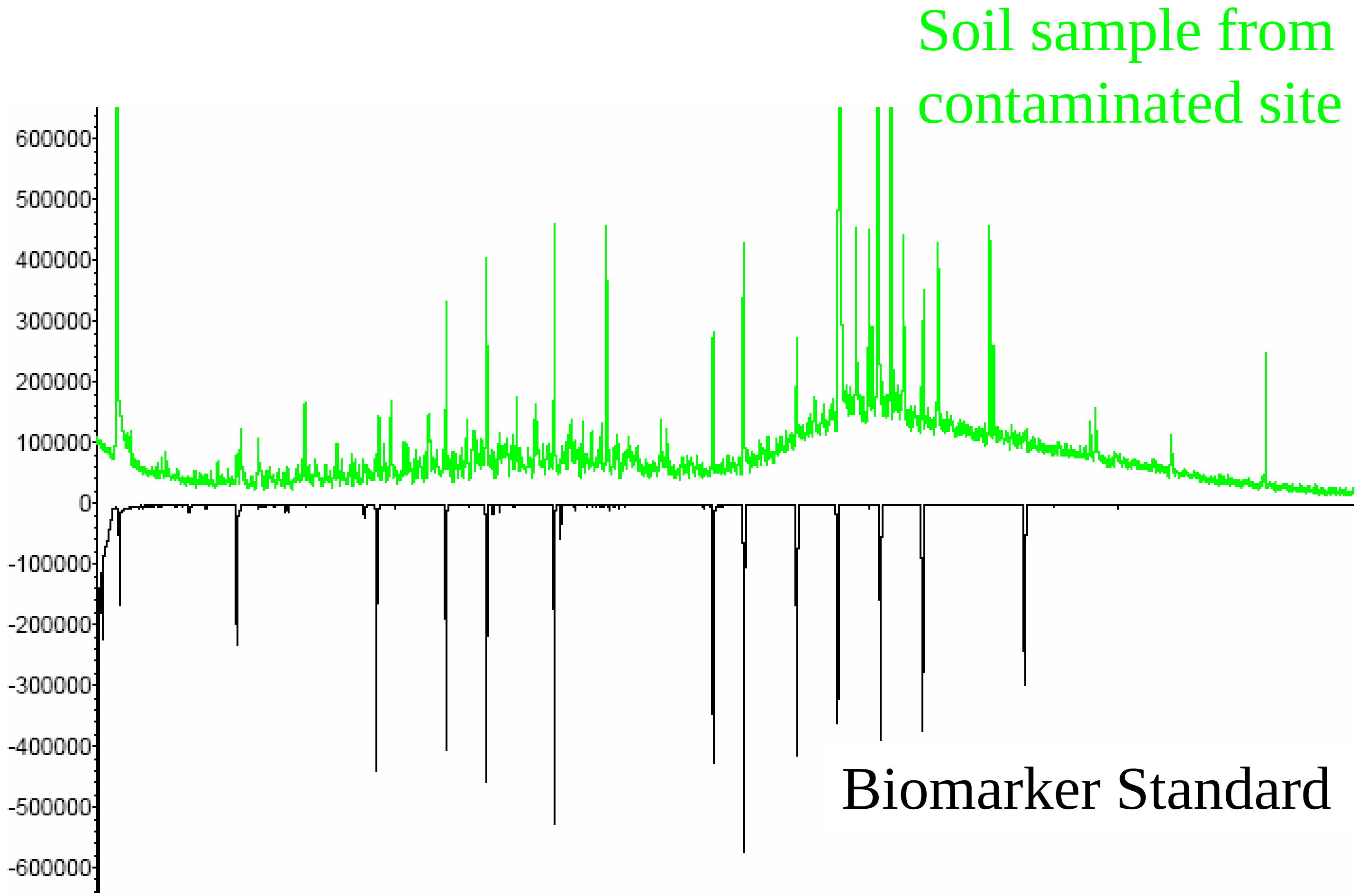
- Light hydrocarbons
- Olefins
- N-Alkanes
- Monoaromatics
- Isoalkanes
- Parent PAH > 2-ring
- C1, alkyl PAH → C4 alkyl PAH
- Triterpanes
- Diasteranes → Aromatic Steranes
- Porphyrins

Least

Introduction to Environmental Forensics, Murphy and Morrison

Biomarkers in weathered samples

- Note that the sample is severely weathered.
- Biomarkers have become the predominant peaks
- Indication of some phytogenic hydrocarbons also

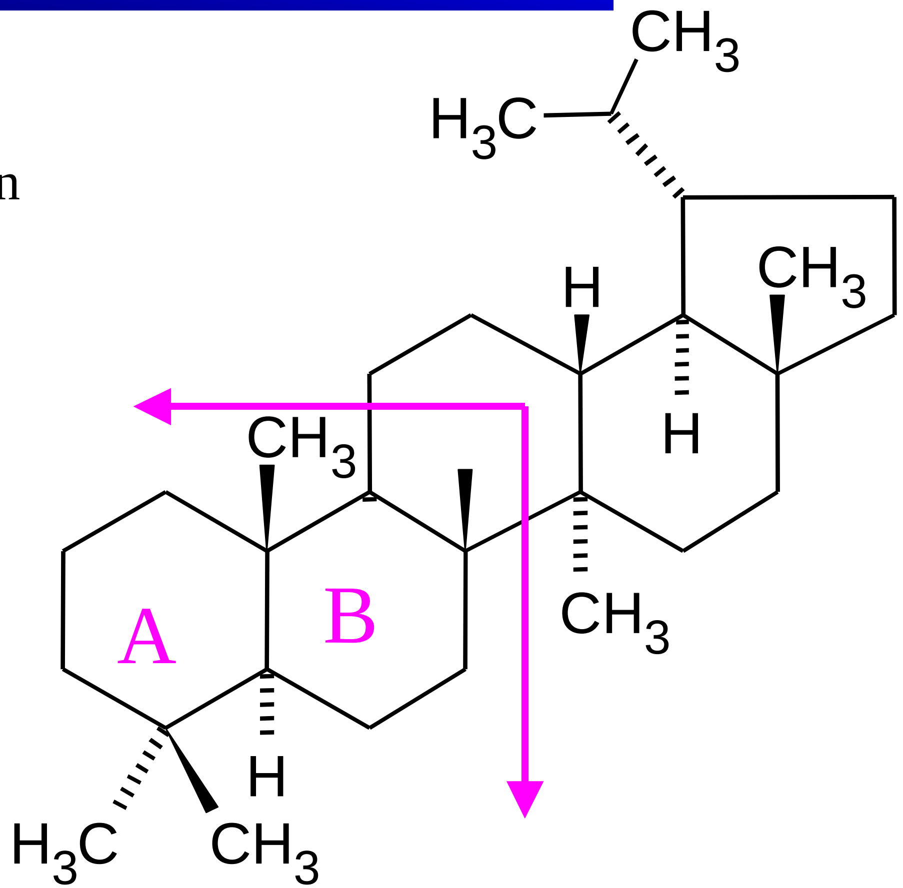


Petroleum Biomarker Groups

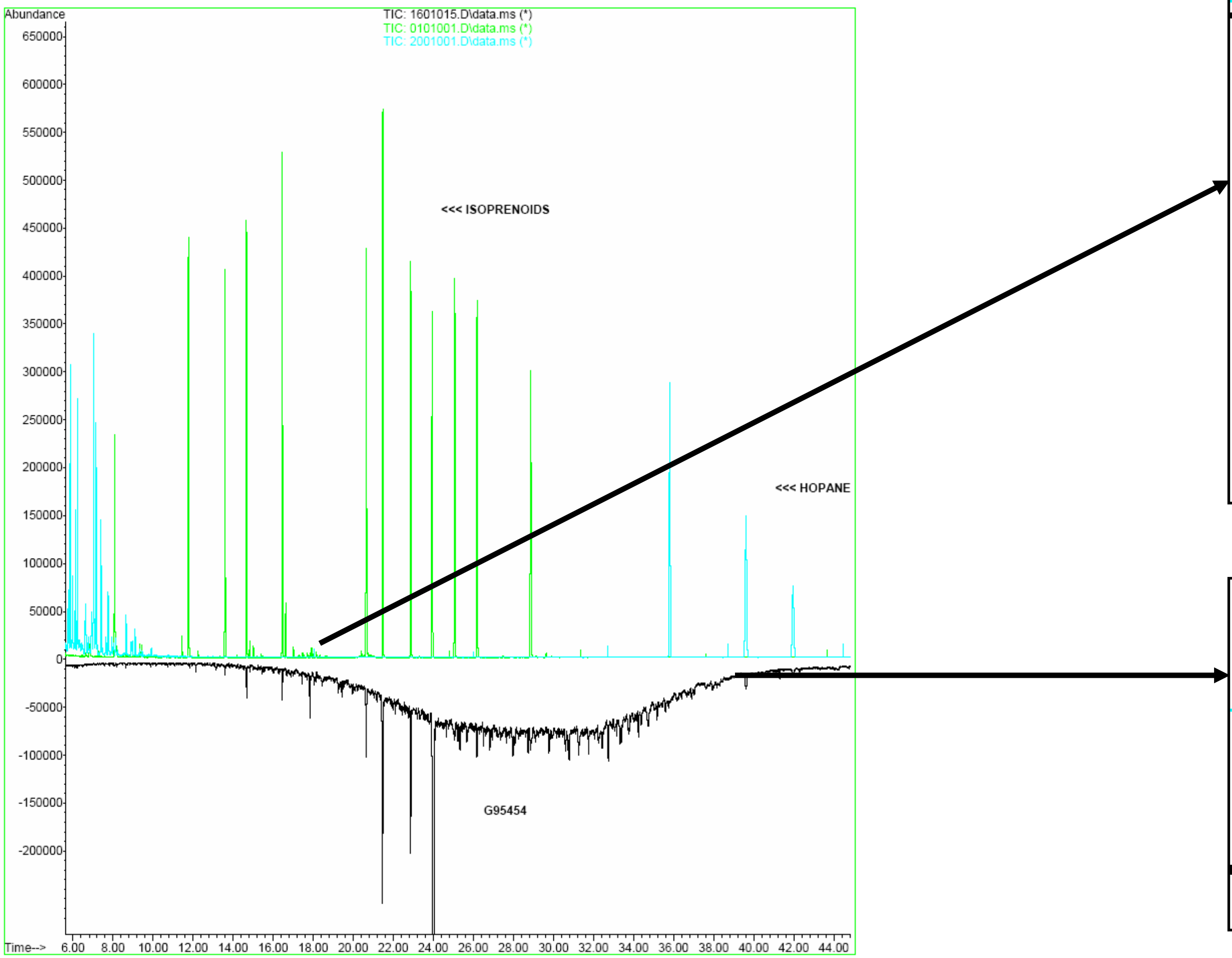
Biomarker Class	Carbon number	Target Ion
Isoprenoids	12 - 26	57, 113, 127
Triterpanes (Hopanes)	27- 30	191
Steranes	20 - 29	217, 218

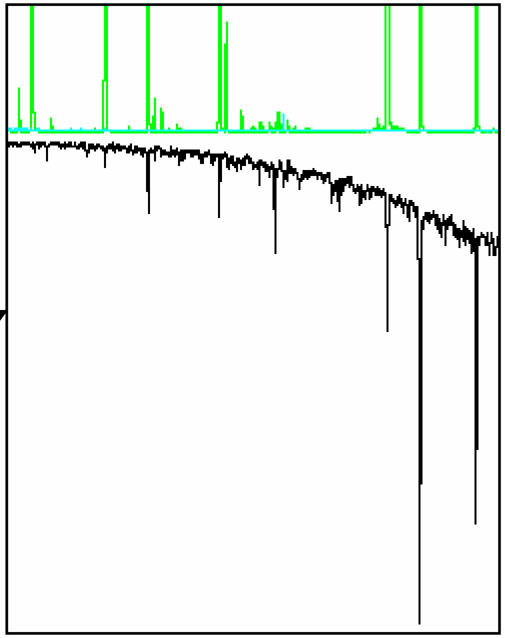
Characteristic Biomarker Ions

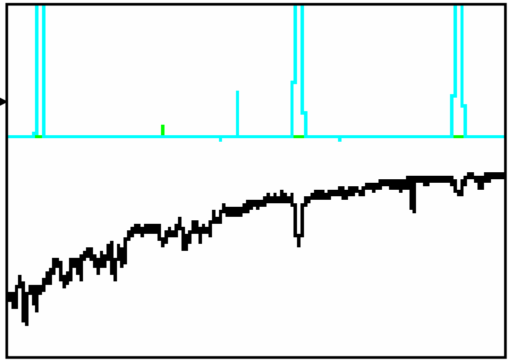
Cleavage of the A and B rings creates a 191 m/z ion



Locating Petroleum Biomarkers



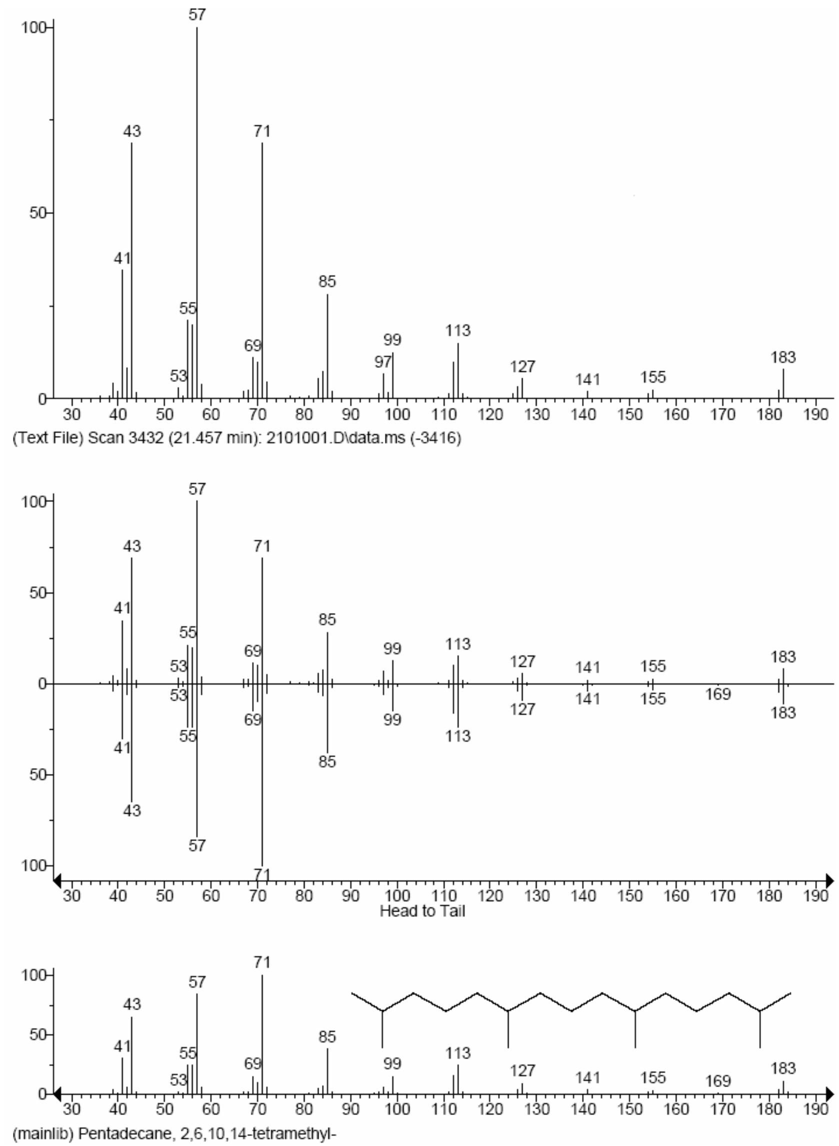




Biomarker Peak Identification

Library spectra are available for a limited number of petroleum biomarker compounds.

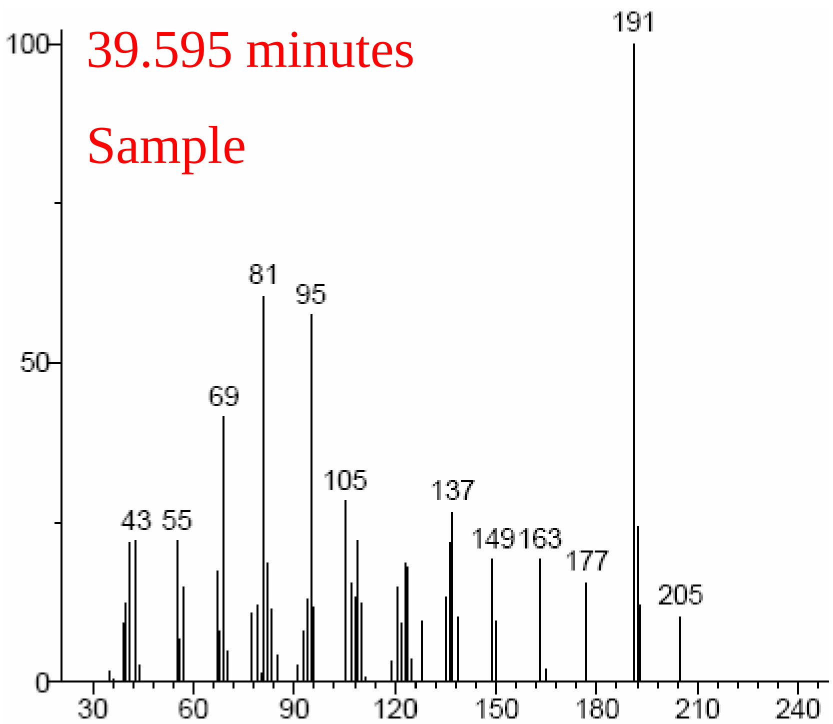
In this case the sample showed a perfect match!

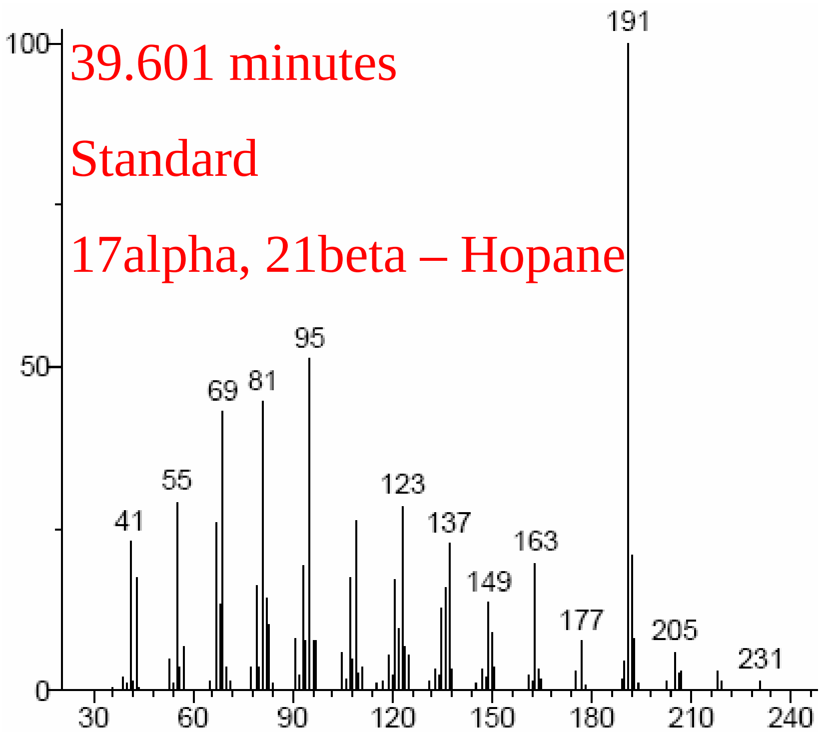


Pristane

2,6,10,14 - tetramethylpentadecane

Biomarker Peak Identification





In many cases biomarker compounds are not found in MS libraries!

Benefits of the approach

- Unambiguous confirmation of petroleum hydrocarbon compounds.
- Not confounded by high backgrounds of phytogenic hydrocarbons.
- Consistent with CCME PHC CWS recommendations.
- Sufficiently sensitive to locate contamination below regulatory PHC limits.
- Particularly effective in aged or weathered sites.

Case Study - The Site

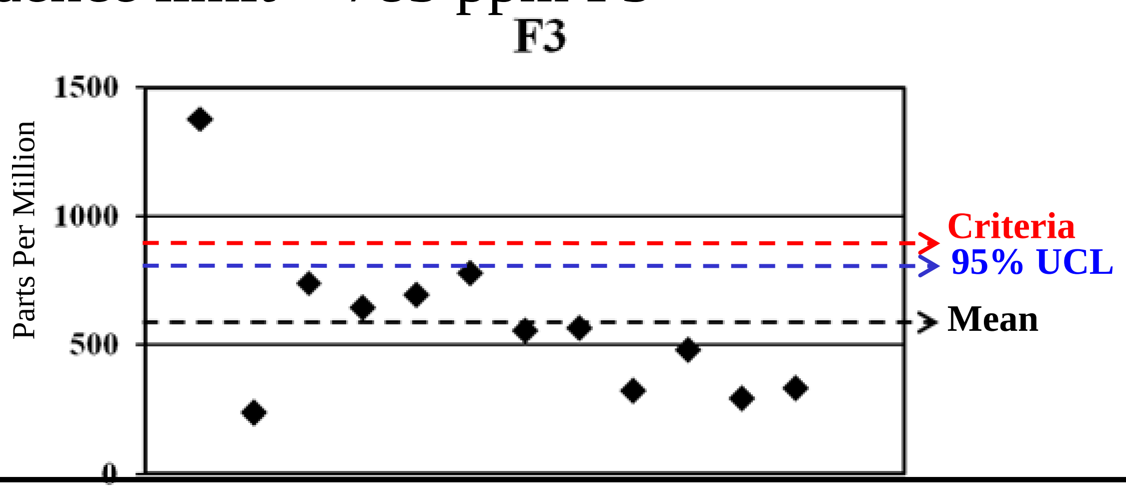
- Former oil well, residual hydrocarbon impacts
- Previous remedial works, admixing of soil
- Organic matter (muskeg) overlying clay
- Client seeking reclamation certificate
- Diverse Ecosystem

Case Study - Initial Assessment

- Previous estimate - 300 cubic meters
- Variable hydrocarbon analytical results
  - non-detect to 9700 ppm F3
- "Background" up to 1380 ppm F3
- What is "Background"?
  - How do we derive it and prove it?
  - What are good scientific practices?

Case study – “Background”

- Consulted with Maxxam, proactive scope development
- 12 samples absent of petrogenic biomarkers
  - Mean = 585 ppm F3
  - 95% upper confidence limit = 783 ppm F3
- Guideline
  - 800 ppm F3



nexen Maxxam Analytics Inc TRIUM Environmental Solutions Inc.

Closure Options

Delineation achieved

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Site Closure

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Guideline Modification

Closure Options

- Guideline Modification
  - Toxicological Profiling
  - Multiple stakeholders
  - Regulatory approval
  - Limited closure

Closure Options

- C ation
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Besides who wants a bunch of scientists pouring over the site when closure is only an excavator bucket away?

- Deemed not cost/time effective for this site

Closure Options

Delineation achieved

↓

Site Closure

Gu[illegible]e
M[illegible]tion

Remediation using
Biomarkers

Biomarker Remediation Option

- Presence/Absence
  - Red Light/Green Light
  - Less emphasize of mass conc.
- Definitive Closure
- Cost/Time Efficient
- Reclamation Certificate & Regulatory Acceptance
- Quick Win

Conclusions

- Biomarker analysis can differentiate
  - Phytogenic vs. Petrogenic impacts
- Resolves "background" uncertainties
- Conclusive assessment and remediation tool
- Everyone Wins
  - Lab - "Good" Science
  - Consultant - Sound Decisions
  - Client - Closure and Assurance
  - Site – Minimal Disturbance in a Diverse Ecosytem

Questions

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