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Hydrocarbon Forensics (Product Characterization)

Maxxam

Overview

- Some of the tools used in Hydrocarbon Forensics
- Application of analytical data to answer:
 - “What is it?”;
 - “How old is it?”; and
 - “Is it mine?”

Available Analytical Tools

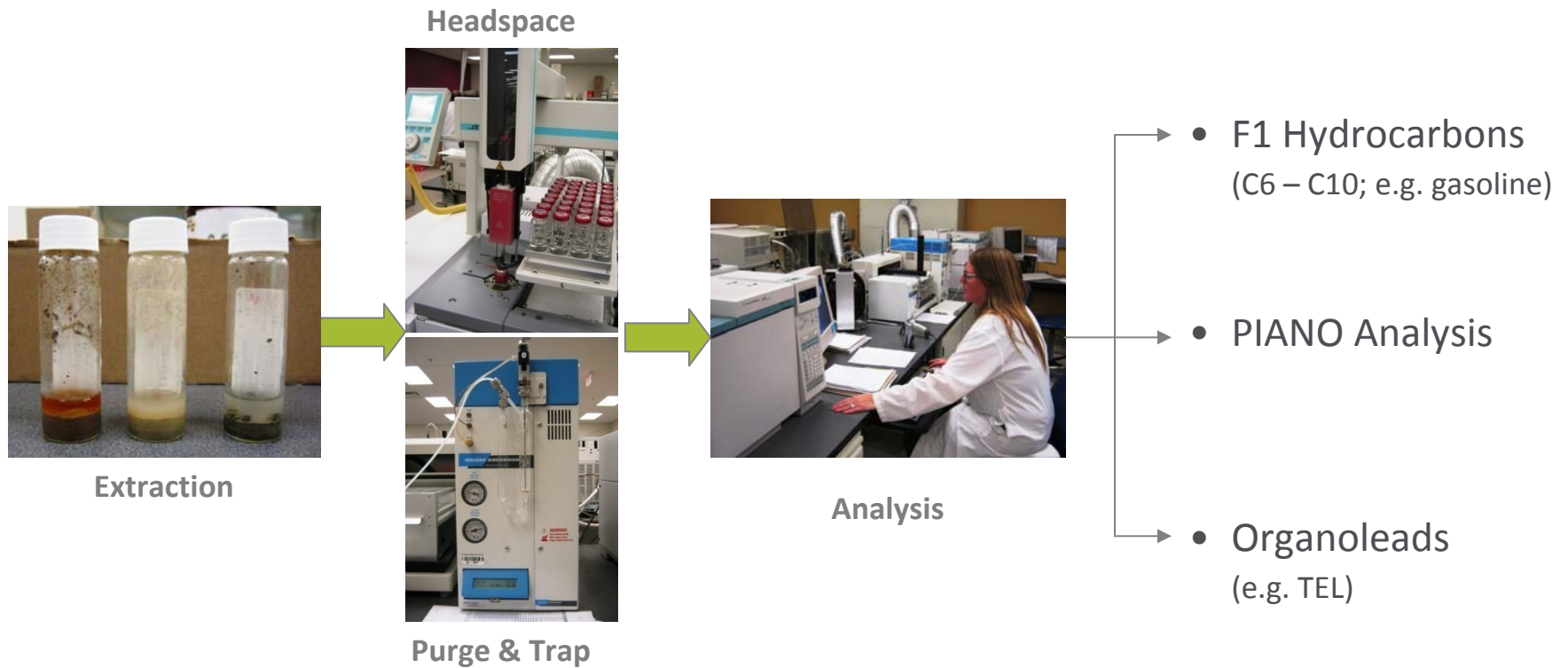
Background Information: “Detective Work”

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- History
 - Background Information
 - Manifests/Phase I ESA information
 - Past use of the property or location
 - Compounds of concern
- Geology/Geochemistry
 - What is the nature of the soil environment? Is it aggressive or passive?
- Hydrogeology
 - Groundwater flow
- Where were the samples collected?
 - Relative to surface
 - Relative to water table
 - Relative to potential sources of impact

Volatile Hydrocarbon Analysis

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Semi-Volatile Hydrocarbon Analysis

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Extraction



in-situ Clean-up
(...or not)



Analysis

- F2-F4 Hydrocarbons (C10 – C50+; fingerprinting)
- Biomarkers: (age estimation)
 - nC17/pristane
 - nC18/phytane
 - Norpristane
- Biomarkers (source determination)
 - Steranes
 - Hopanes
 - Terpanes
 - ...etc.

Hydrocarbon Fingerprinting: Visual Comparison and Characterization

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- Canadian Council of Ministers of the Environment: “Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier I Method” 2001
- F1 information is helpful for light hydrocarbons
- F2 – F4 is useful for mid-range to heavy hydrocarbons
- Be consistent in the analysis
 - Same instrument
 - Same GC program

Gas Chromatography/Mass Spectrometry: Biomarkers

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- Biomarkers are chemical “fossils” that can act as unique tracers for petroleum contaminants which are structurally very similar to natural products (i.e. plants/chlorophyll) and are one of the last group of compounds to degrade in a petroleum product
- Isoprenoids (e.g. pristane and phytane) are found in middle distillates and are considered “biomarkers”
- GC/MS peak patterns for specific biomarker compounds can be used to:
 - Evaluate degree of weathering under specific soil conditions
 - Differentiate petrogenic and biogenic impacts
 - Identify crude oil sources
- GC/MS analysis for biomarkers is not trivial nor is it routine

Gas Chromatography/Mass Spectrometry: PIANO Analysis

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- Gasoline contains several hundred compounds
- Gasoline hydrocarbons (non additives) typically fall into one of five categories:
 - Paraffins, Isoparaffins, Aromatics, Napthenes or Olefins
- Typically conducted on a NAPL...less commonly on groundwater samples
- Specialized GC/MS analysis on a specialized column with a very long run time
- PIANO results are expressed as relative % concentrations
- Diagnostic ratios can be calculated to assess:
 - Weathering
 - Biodegradation
 - Octane Rating (do you have a premium gas, mid grade, regular)

Stable Isotope Analysis

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- Analysis of stable isotopes by Isotope Ratio Mass Spectrometry (IRMS)
- There are two types of isotopes: stable and radioactive. Carbon has a stable isotope with 7 neutrons (^{13}C) and a radioactive isotope with 8 neutrons (^{14}C).
- The approximate ratio of ^{12}C to ^{13}C is 99:1
- The carbons contained within hydrocarbon compounds will have a $^{13}\text{C}/^{12}\text{C}$ isotopic signature that can be significantly different based on factors such as: the formation of the fuel (source and the refining process); and the changes that occur once it is released to the environment
- Biodegradation will effect the $^{13}\text{C}/^{12}\text{C}$ signature

Any other relevant information...

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...you can get your hands on

- % Moisture
 - can be used as a line of evidence in differentiating biogenic from petrogenic impacts
- Background samples
 - can be used as a line of evidence in differentiating biogenic from petrogenic impacts

Any other relevant information...

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...you can get your hands on

- Other marker compounds
 - Gasoline additives
 - Organoleads
 - MMT (methylcyclopentadienyl manganese tricarbonyl)
 - MTBE (methyl-*tert*-butyl ether)
 - EtOH (ethanol)
- Lead scavengers
 - EDB/1,2-DCA
- Other Oxygenates
- Amines
- Dyes
- Anti-Icing Compounds (e.g. glycols) “Winter Gas”

“What is it?”

(characterization)

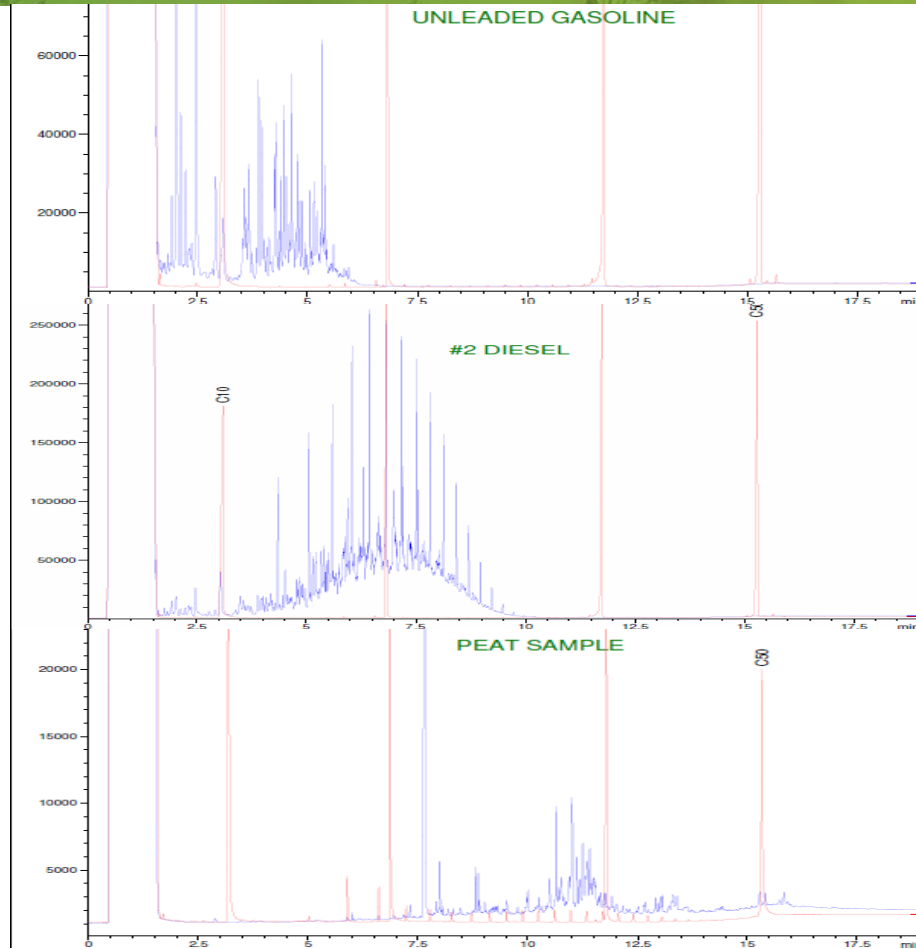
Nature of Impact: Look for Indicator Compounds

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- Gasoline (C6 – C13/14)
 - BTEX
 - Isooctane
- Diesel/Fuel Oils (C8 – C22)
 - Linear and branched alkanes
(may or may not be there depending on degree of weathering)
 - Biomarker Compounds
 - Isoprenes, steranes, hopanes, bicyclic sesquiterpanes
- Biogenic Organic Material (peat)
 - Characteristic peak pattern (C28 – C34)
 - Is F3 reduced with additional silica gel clean-ups

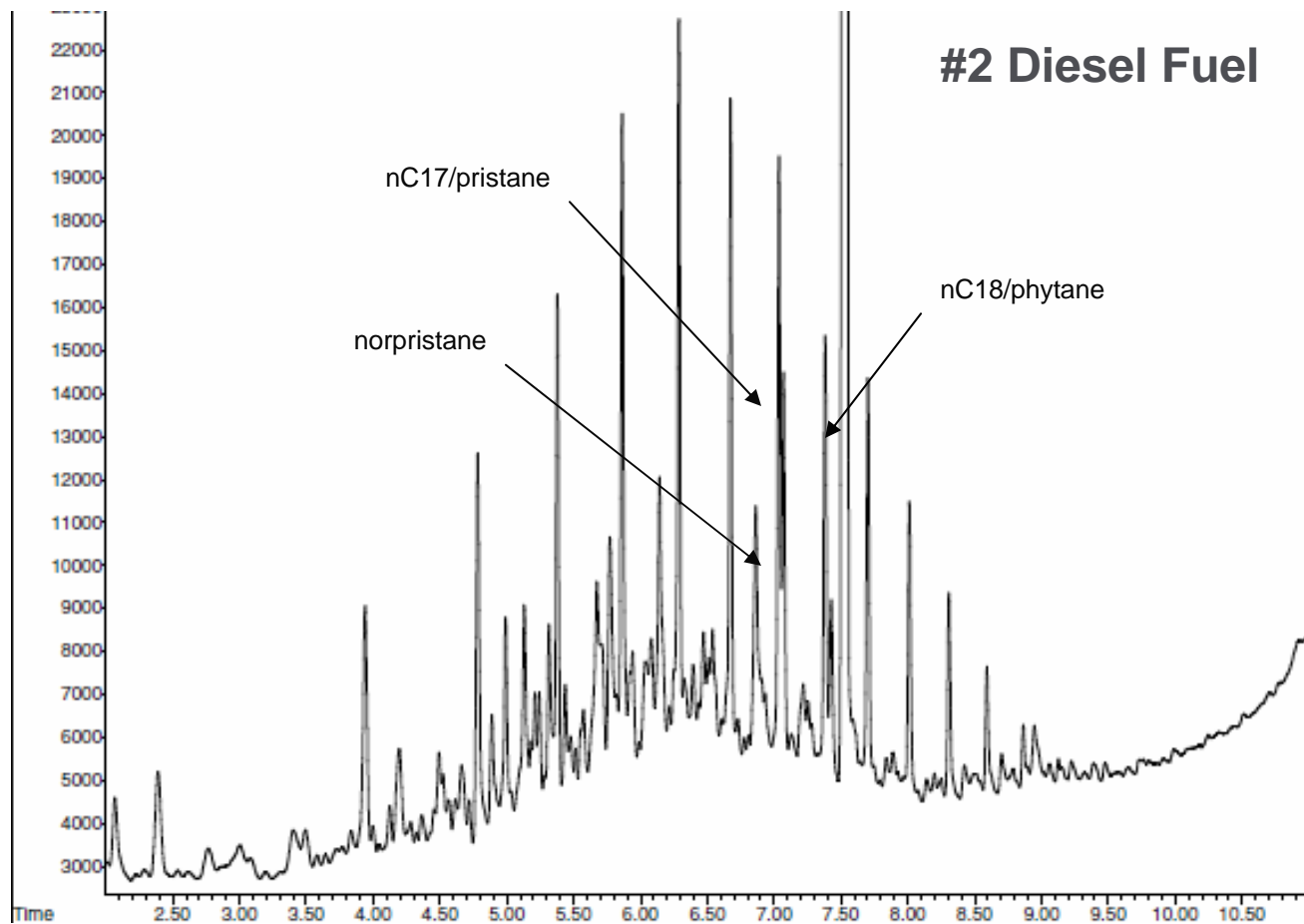
Hydrocarbon Characterization: Visual Evaluation

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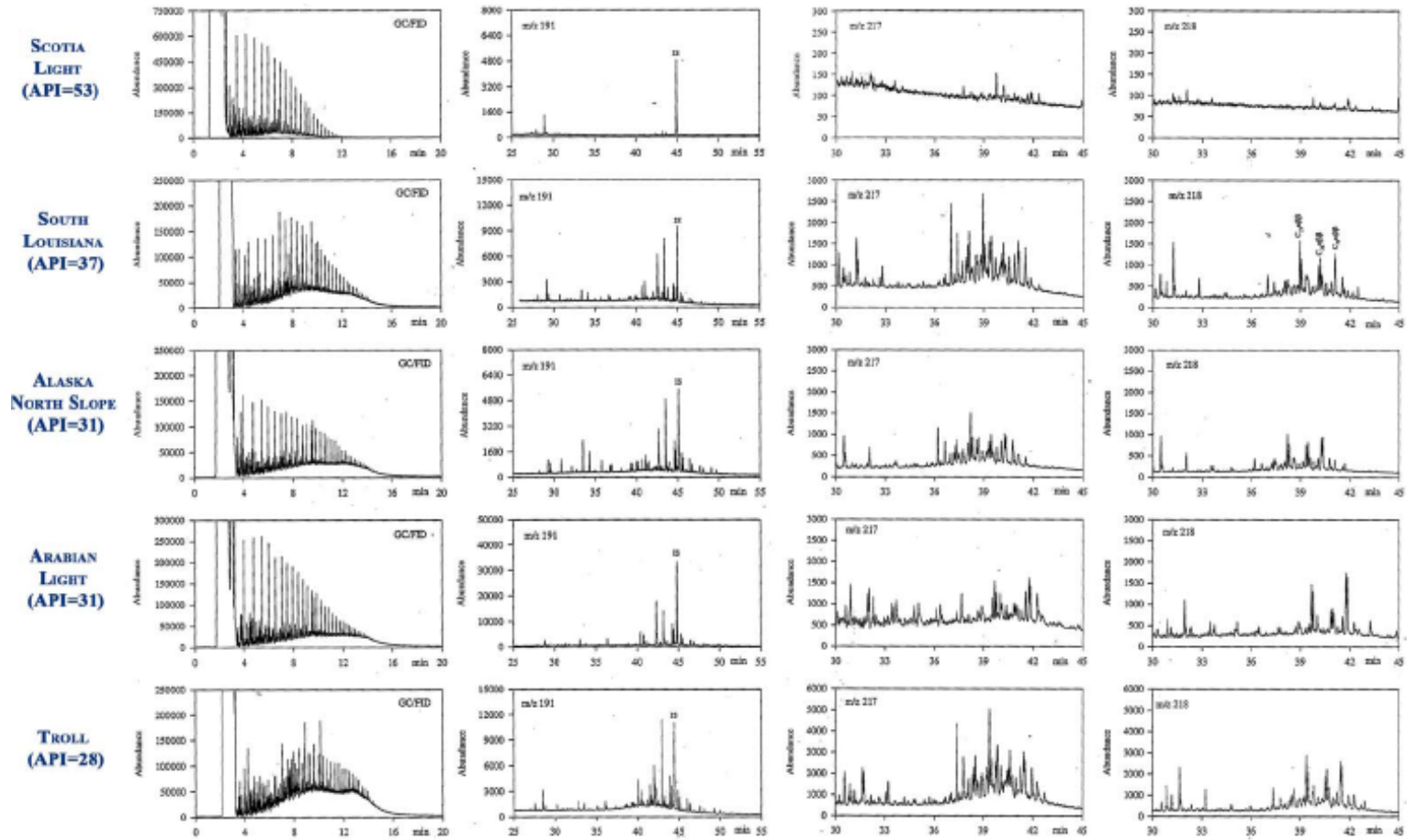
Isoprenoid Biomarkers: Pristane and Phytane

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Biomarker Signatures in Crude Oils: Steranes, Hopanes and Terpanes

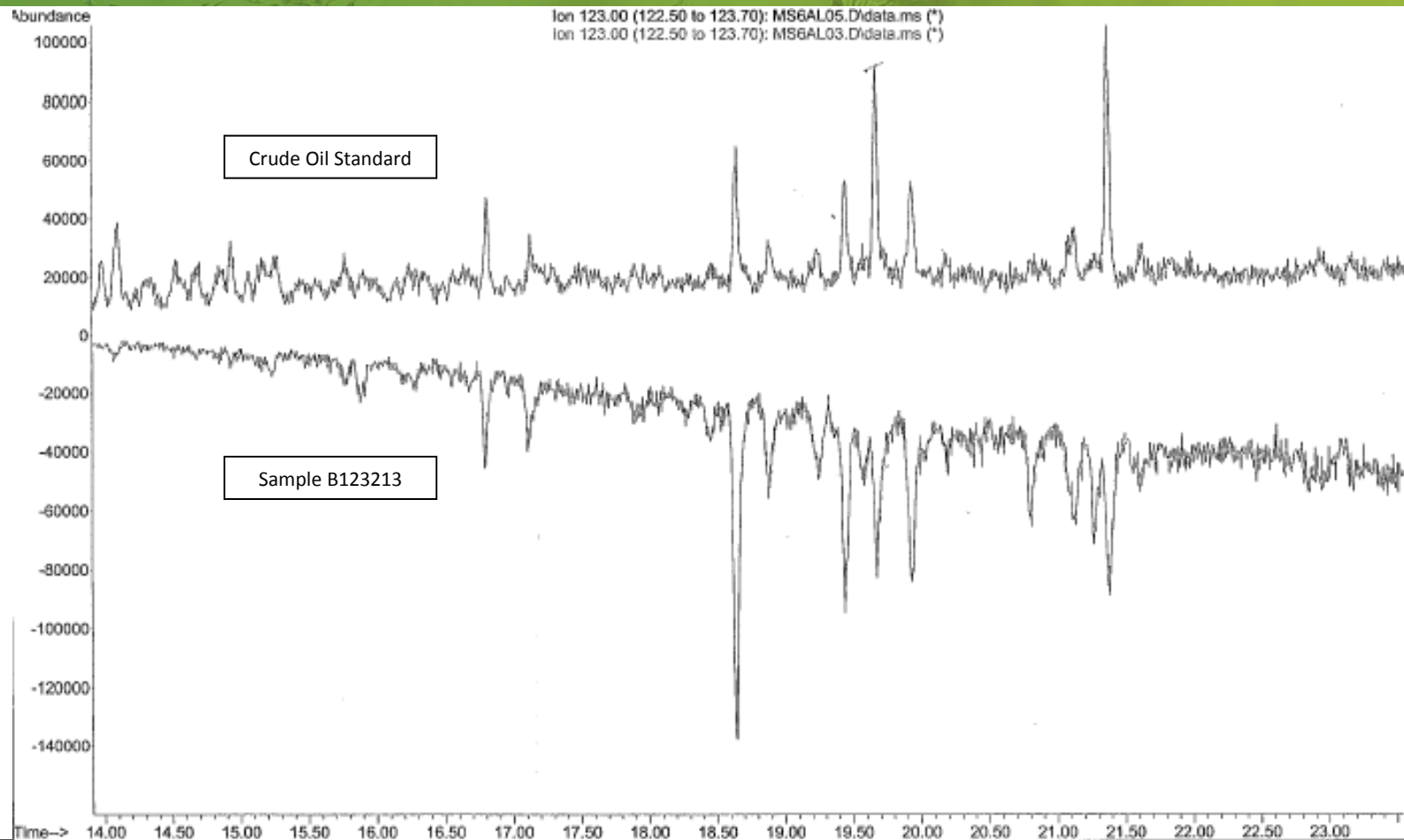
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SOURCE: Oil Spill Environmental Forensics – Fingerprinting and Source Identification, Zhendi Wang and Scott A Stout, ISBN13:978-0-12-369523-9, 2007

Another Class of Biomarkers: Bicyclic Sesquiterpanes ($m/z = 123$)

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“How old is it?”

(weathering)

Age Estimation

("How old is it?")

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- Evaluation of Weathering
- Can you estimate when the impact occurred?

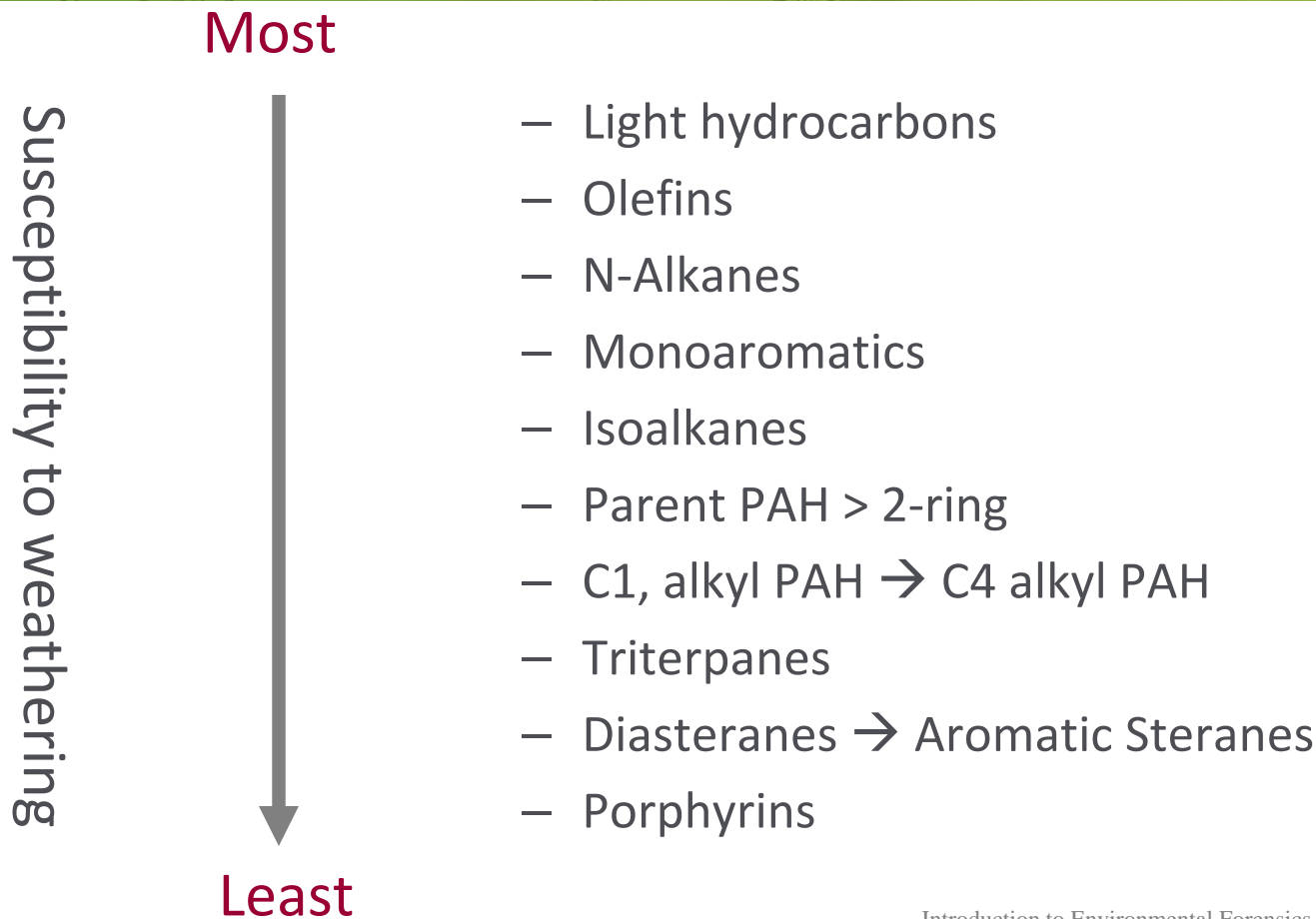
Weathering Mechanisms

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- Volatilization
- Solubilization or Dissolution
- Biodegradation

Impact of Weathering

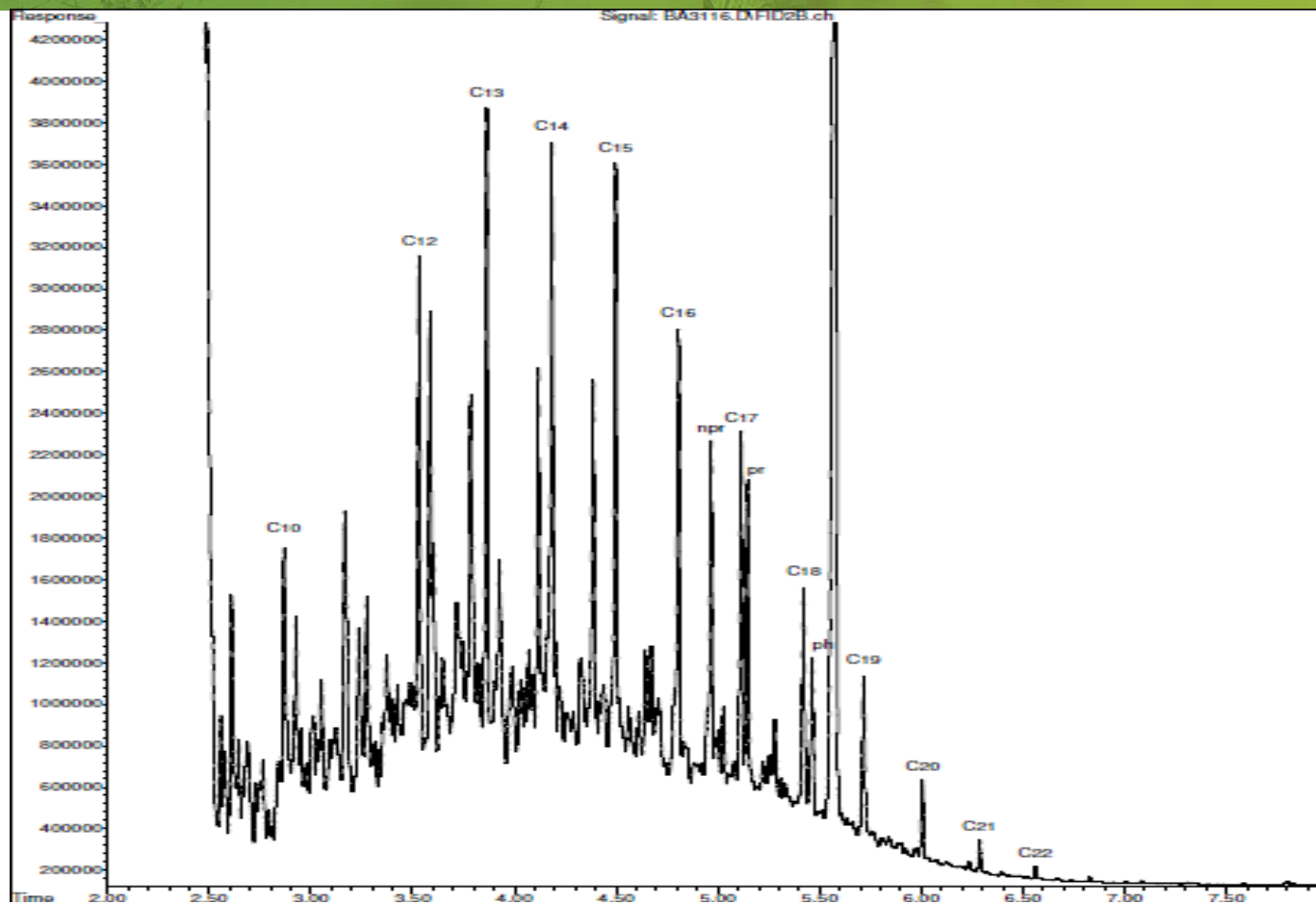
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Introduction to Environmental Forensics, Murphy and Morrison

Moderately Weathered Diesel

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- Using weathering as an indicator of age may be subject to considerable scrutiny
- Be careful with statements like “this groundwater sample contained diesel, but many of the low boiling point hydrocarbons are absent, so this is an older release”
- What impacts weathering?
 - Volume of contaminant released
 - Time of release (one event / leak over time)
 - Depth of spill (or depth of where the sample was collected)
 - Subsurface conditions (oxygen content, microbiological populations)

Using Weathering to Estimate Impact Age

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It can be done, but weathering information must be considered in the context of other available information including:

- Soil environment
- Volume of contaminant released
- Time of release (one event / leak over time)
- Depth of spill (or depth of where the sample was collected)
- Subsurface conditions (oxygen content, microbiological populations)
- Diagnostic ratios of specific hydrocarbon compounds

“Is it mine?”

(source determination)

Source Determination

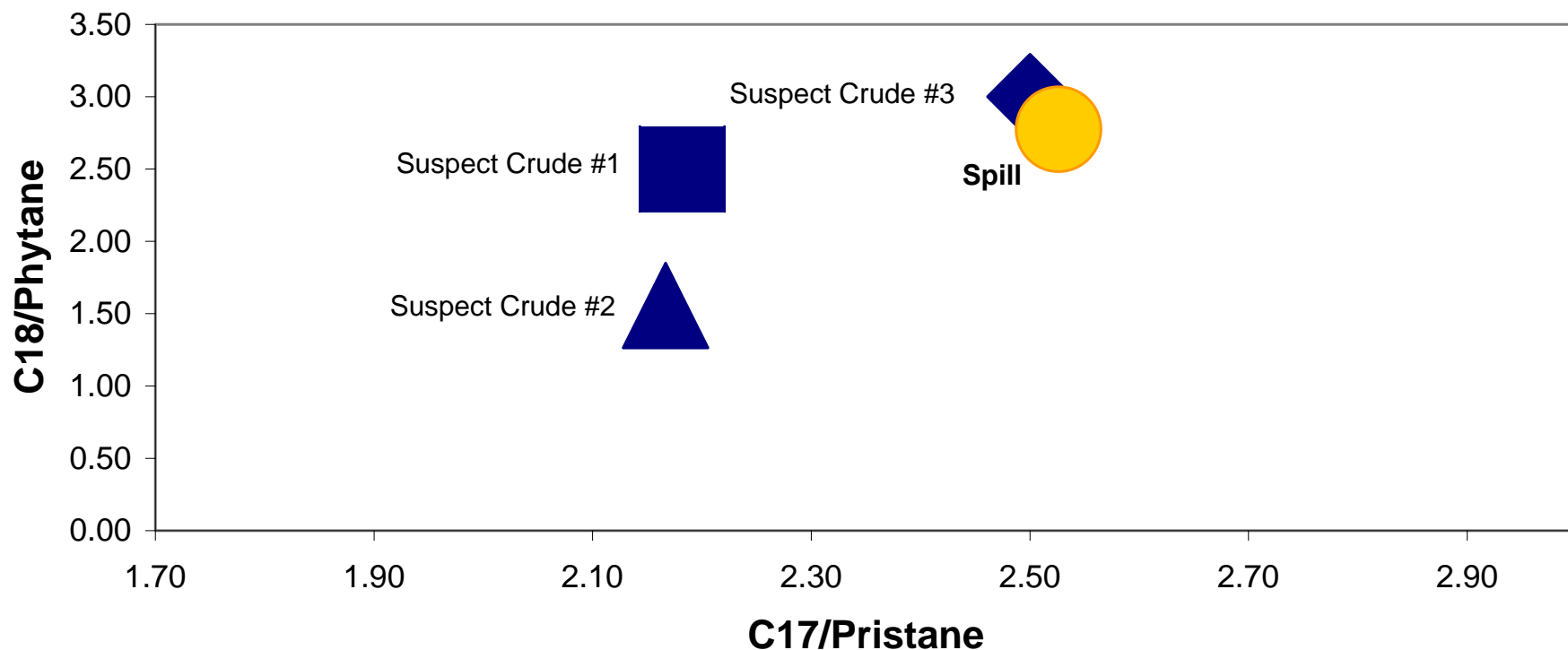
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- This is probably the most difficult question to answer
- All of the tools described need to be considered (if data are available) to provide a reasonable judgment about “source”
- Multiple “lines of evidence” need to be established in order to build a compelling case

Principal Component Analysis (PCA) Plots

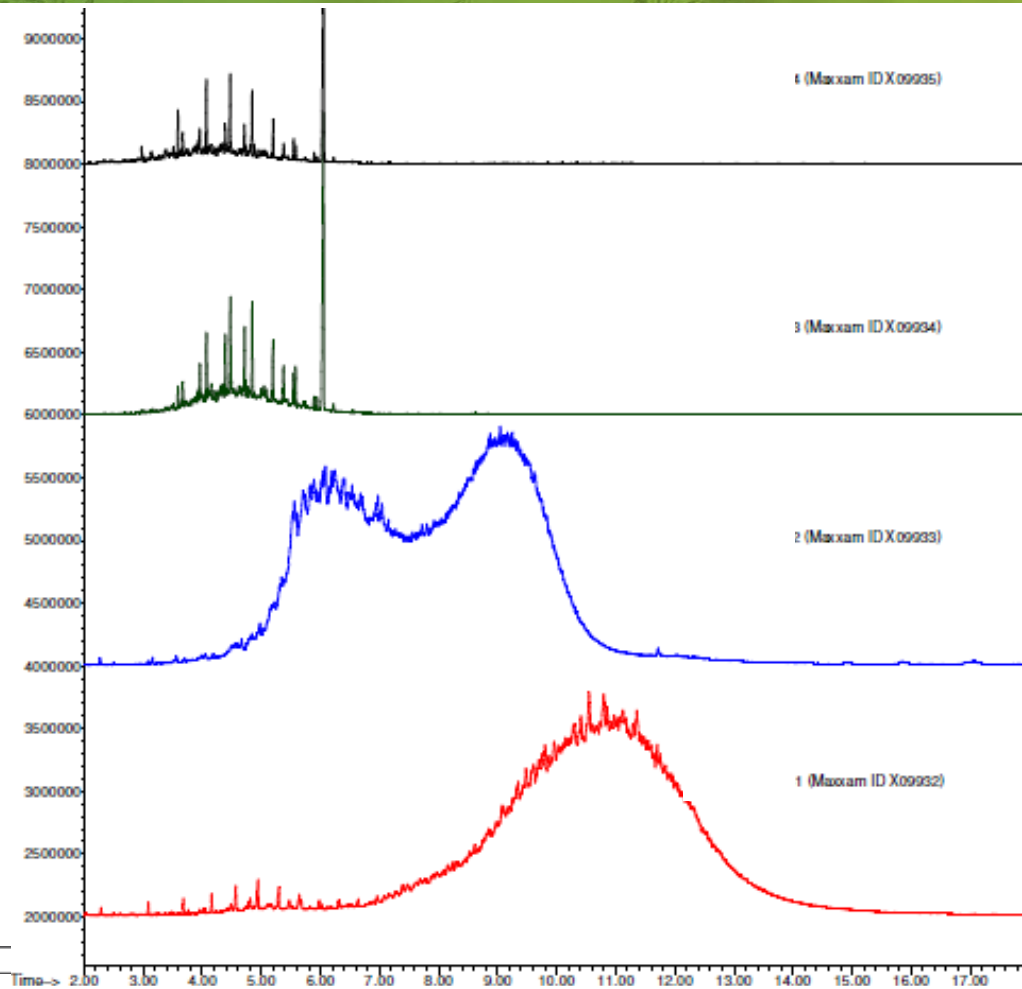
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Chemometric plot of isoprenoid ratios



Source Determination: Visual Evaluation

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BP Deepwater Horizon Spill

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Coast Guard: Tar balls found in Keys not from BP spill

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Tar balls discovered on the Florida Keys shoreline are not connected to the oil spill in the Gulf of Mexico, the Coast Guard said Wednesday.

Tests done "conclusively show" that the tar balls found on the shoreline do not match the type of oil from the Deepwater Horizon oil spill. The source of the tar balls remains unknown at this time.

"The conclusion that these tar balls are not from the Deepwater Horizon oil spill incident in no way diminishes the need to continue to aggressively identify and clean up tar ball-contaminated areas in the Florida Keys," Capt. Pat DeQuattro, commanding officer of the Coast Guard's Key West sector said. "We will continue to operate as a Unified Command and utilize funding through the Oil Spill Liability Trust Fund until we have successfully identified any additional tar balls on the shoreline and completed cleanup efforts."

Recognize...

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- There is no single test that provides a “smoking gun” when it comes to characterizing the nature, age and source of hydrocarbon contamination
- Multiple “lines of evidence” need to be established in order to build a compelling case
- Data and information from each of the lines of evidence need to be considered in proper context to draw any conclusions
- Sometimes with available data the evaluation will be...
“data are inconclusive...additional detailed analyses are required”

Process

