

Environmental Forensics in the Context of the Oil and Gas Industry*

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Abstract

It is inevitable that any industrial operation at some stage of development or production will have some sort of environmental problem. The oil and gas industry is no exception to this - some problems are clearly visible as manifested by the recent incident in the Gulf of Mexico or more subtle as in the case of issues involved with shale exploration and development. However, with all of these issues there are two major questions: what is the source of the contaminant, and is it undergoing natural attenuation or degrading? There are many analytical techniques that have been used to address these issues in the past, but one tool that has seen an exponential increase in application in the area of environmental forensics in the past decade has been the utilization of stable isotopes. Whilst analytical techniques such as gas chromatography and gas chromatography mass spectrometry are powerful fingerprinting techniques, they can easily provide ambiguous results in the case of groundwater contaminants. While these techniques can identify groundwater contaminants, they are of little use in distinguishing sources. However, incorporation of stable isotopes, both C and H, introduce another element of characterization that may enable differentiation of one source from another. Furthermore, it is also important to note that as a groundwater contaminant undergoes degradation it will become isotopically enriched providing an ideal tool for monitoring this process.

In the case of shale gas problems, one area where stable isotopes can play an immediate role is first distinguishing sources of microbial and thermogenic gas on the basis of the isotopic compositions. In addition, gases from different sources and thermal maturity regimes can be differentiated through this approach.

So in brief, this presentation will provide a number of examples where stable isotopes have been used in the manner described above, including oil spills, groundwater contamination with a variety of products, and environmental issues associated with shale gas development. It should be noted that it is not being suggested that stable isotopes will solve every single environmental problem. However, it does provide an extremely powerful tool that may provide the difference between solving a problem and obtaining an ambiguous solution.

Environmental Forensics in the Context of the Oil and Gas Industry

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AAPG Conference

April 2012



Environmental Forensics

- The major purpose of this talk is to provide an overview of some major environmental forensic topics.
- The aim being to demonstrate to those of you not so familiar with environmental forensics, particularly in the oil and gas industry, what can be done and how it is relevant to oil and gas problems.

Environmental Forensics

- Environmental Forensics-basically trying to answer the following questions:
- What is the product?
- Is there more than one source (point of release) and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?

Environmental Forensics

- Environmental Forensics - Available Analytical Techniques:
- Gas Chromatography
- Mass Spectrometry
- Isotope Ratio Mass Spectrometry
- (Plus various combinations of the above)

Major Uses of Stable Isotopes

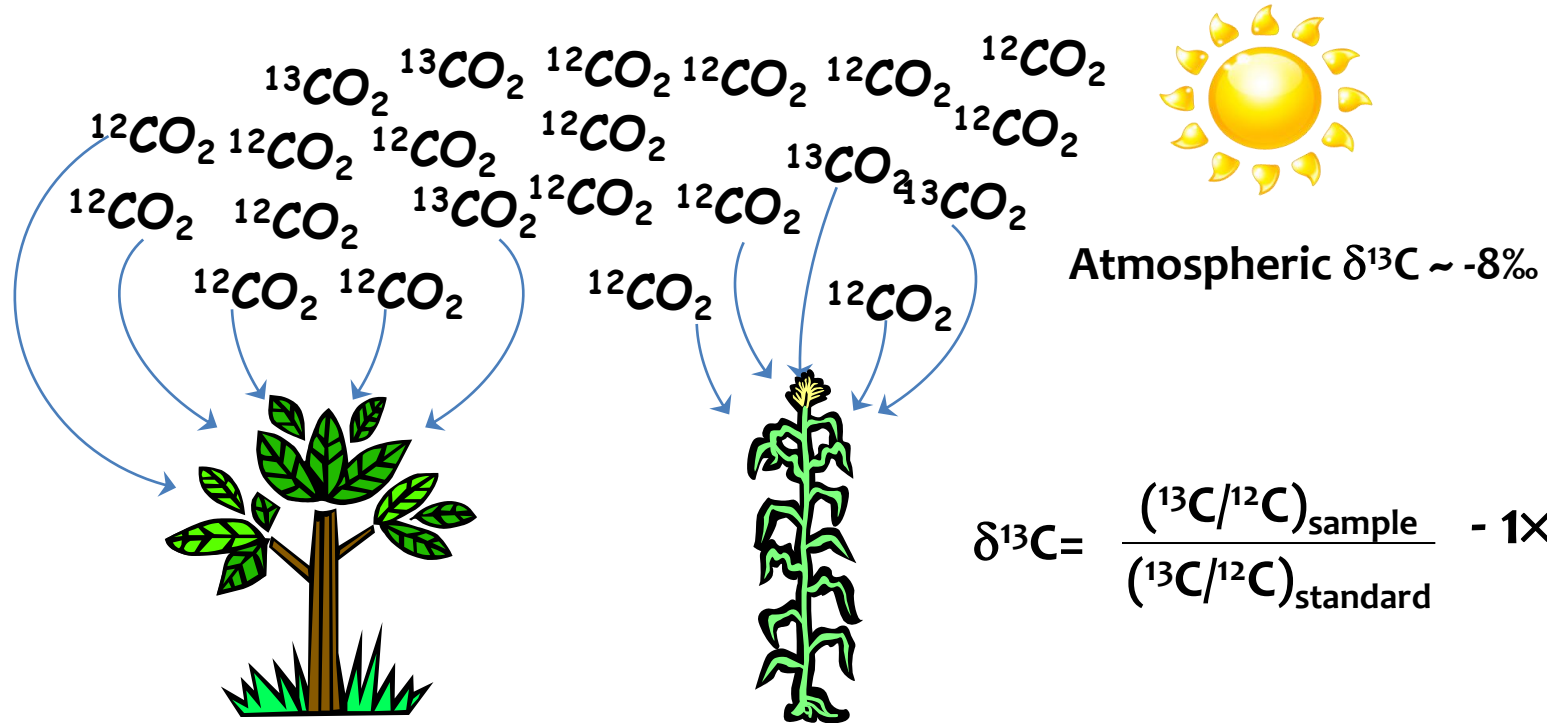
- **Source Correlation or Discrimination**
- **Natural Attenuation**

Stable Isotopes and Source Discrimination

- Carbon in fossil fuels is derived from atmospheric CO_2 . Hydrogen is primarily derived from H_2O . During photosynthesis, fractionation of the two isotopes occurs with preferential assimilation of the lighter isotopes.

Photosynthesis

Carbon isotope fractionation during photosynthesis



$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \times 1000$$

C3 plants : >85% of plant species
 (all trees, wheat, sugar beat, tobacco, a lot of herbaceous...)
 C3 plant $\delta^{13}\text{C} \sim -26\text{‰}$

C4 plants : <5% of plant species
 (corn, sorghum, millet, sugarcane)
 C4 plant $\delta^{13}\text{C} \sim -12\text{‰}$

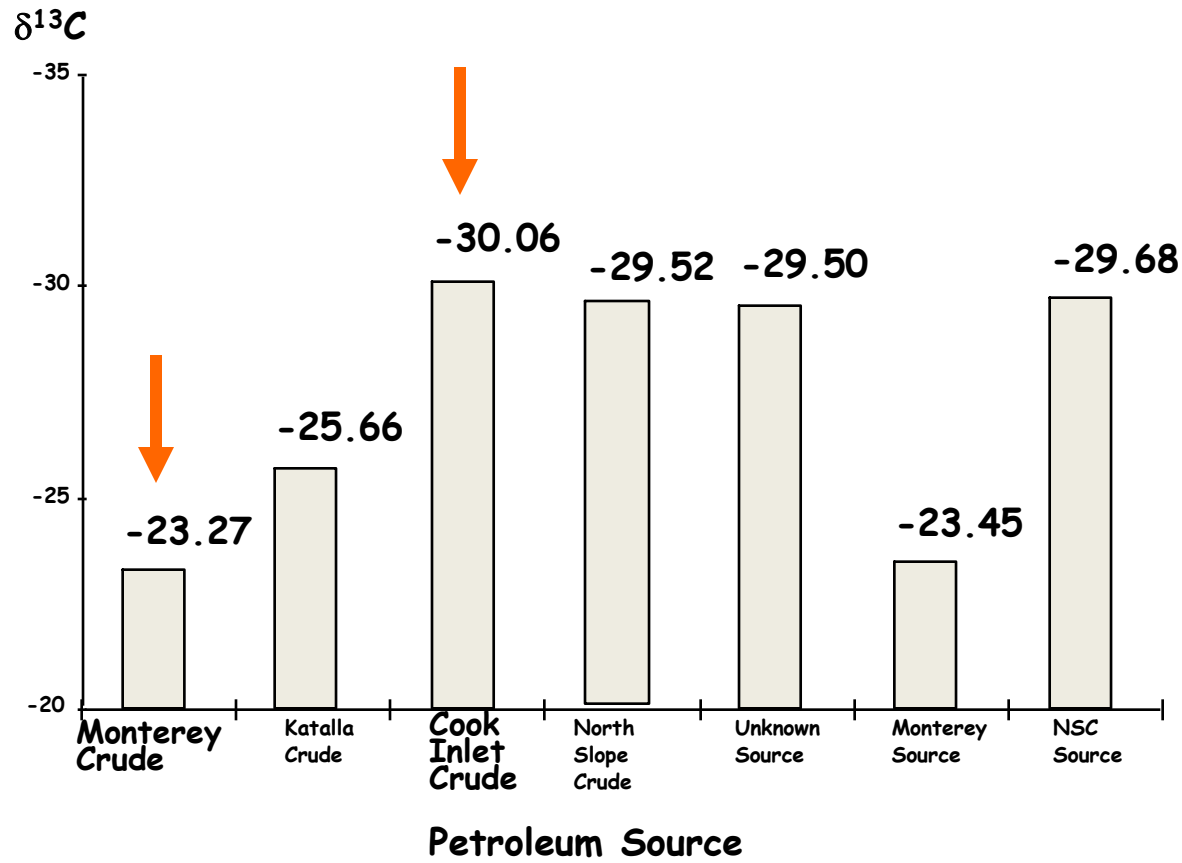


Stable Isotope Determinations

ISOTOPIC VALUES CAN BE MEASURED IN TWO WAYS:

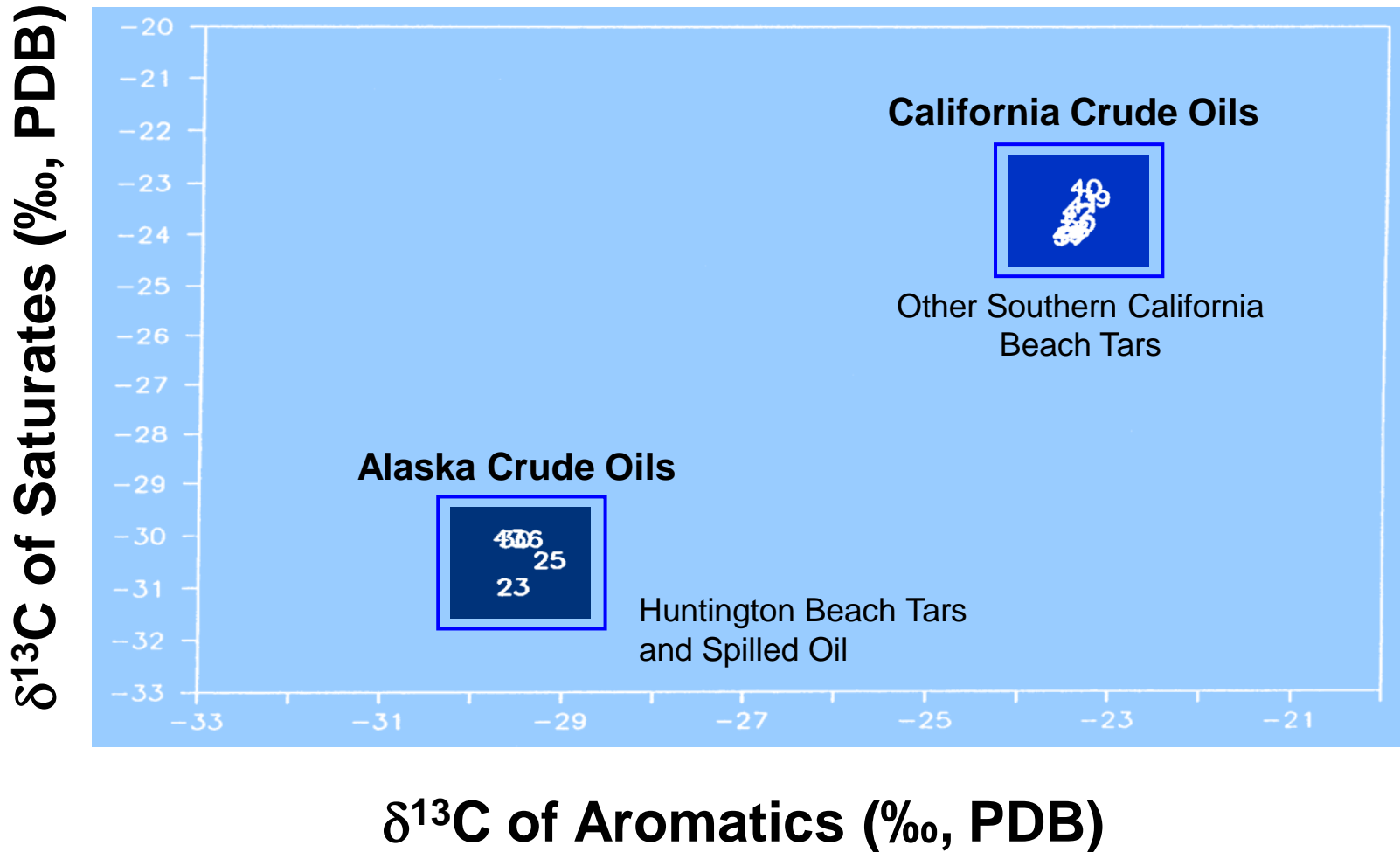
- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS

Isotope Values of Crude Oils Vary with Source



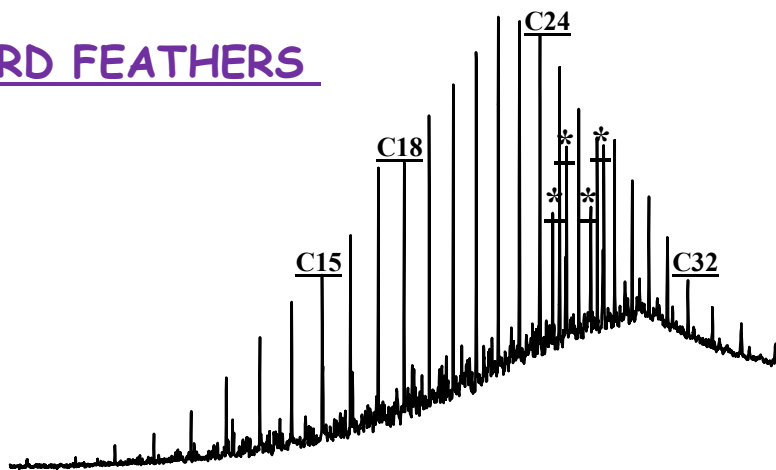
Correlations Using Carbon Isotopes

BP "American Trader" Accident 5/7/90 - Huntington Beach, CA

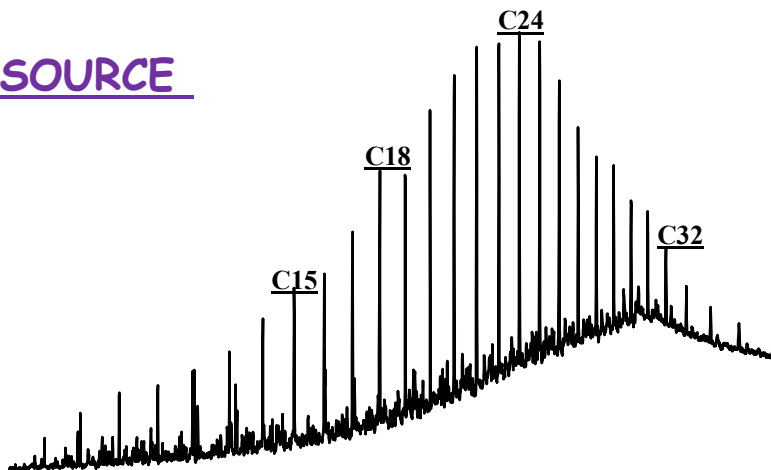


GC Comparison between Feathers and Oil Source

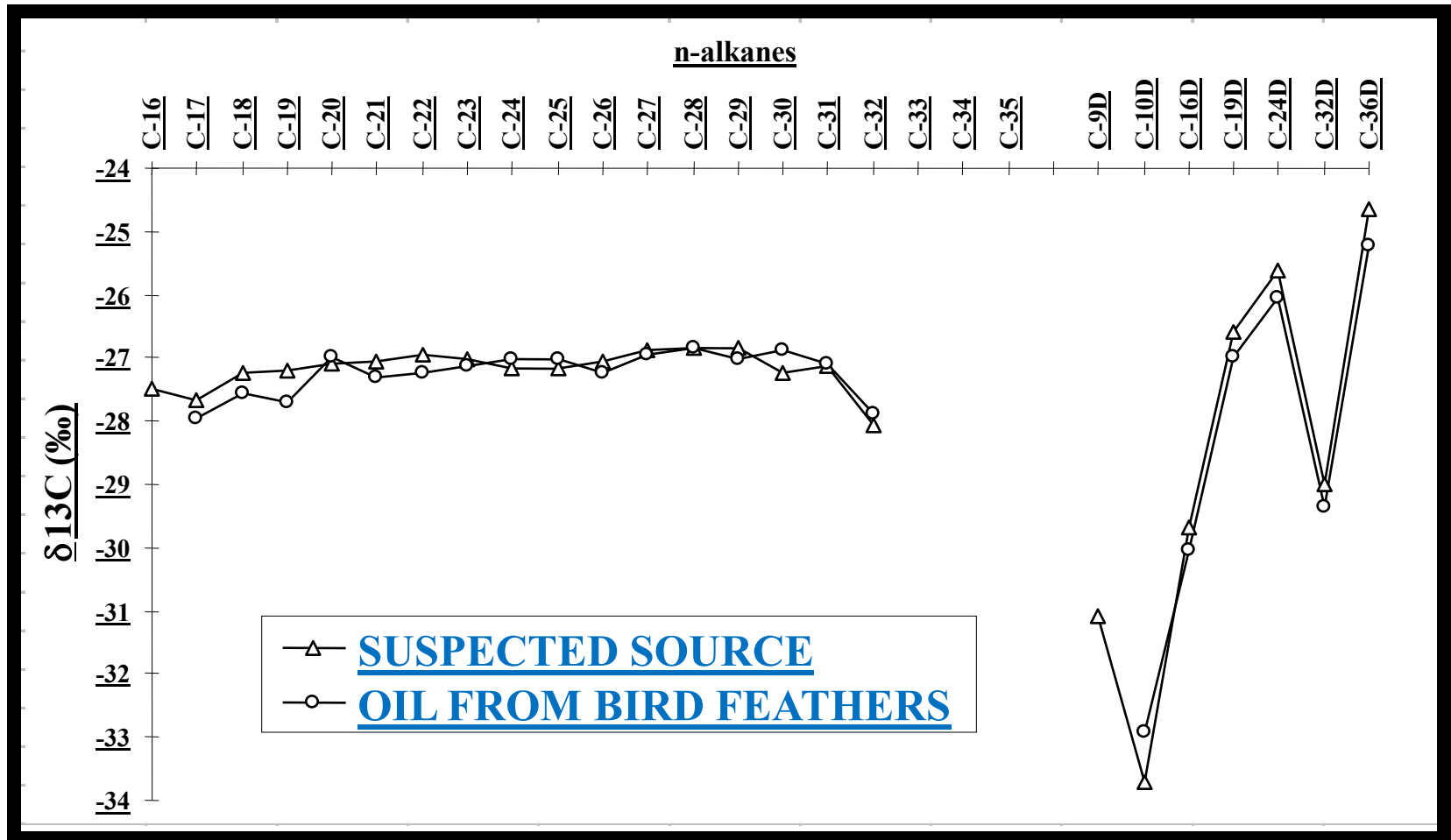
OIL FROM BIRD FEATHERS



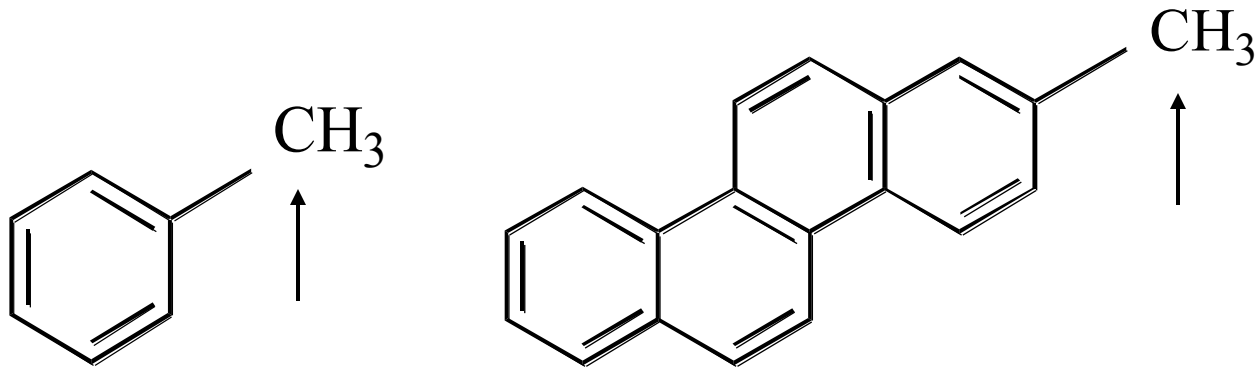
SUSPECTED SOURCE



Isotopic Signatures from Feathers and Oil



Large vs. Small Molecules



1:7

1:19

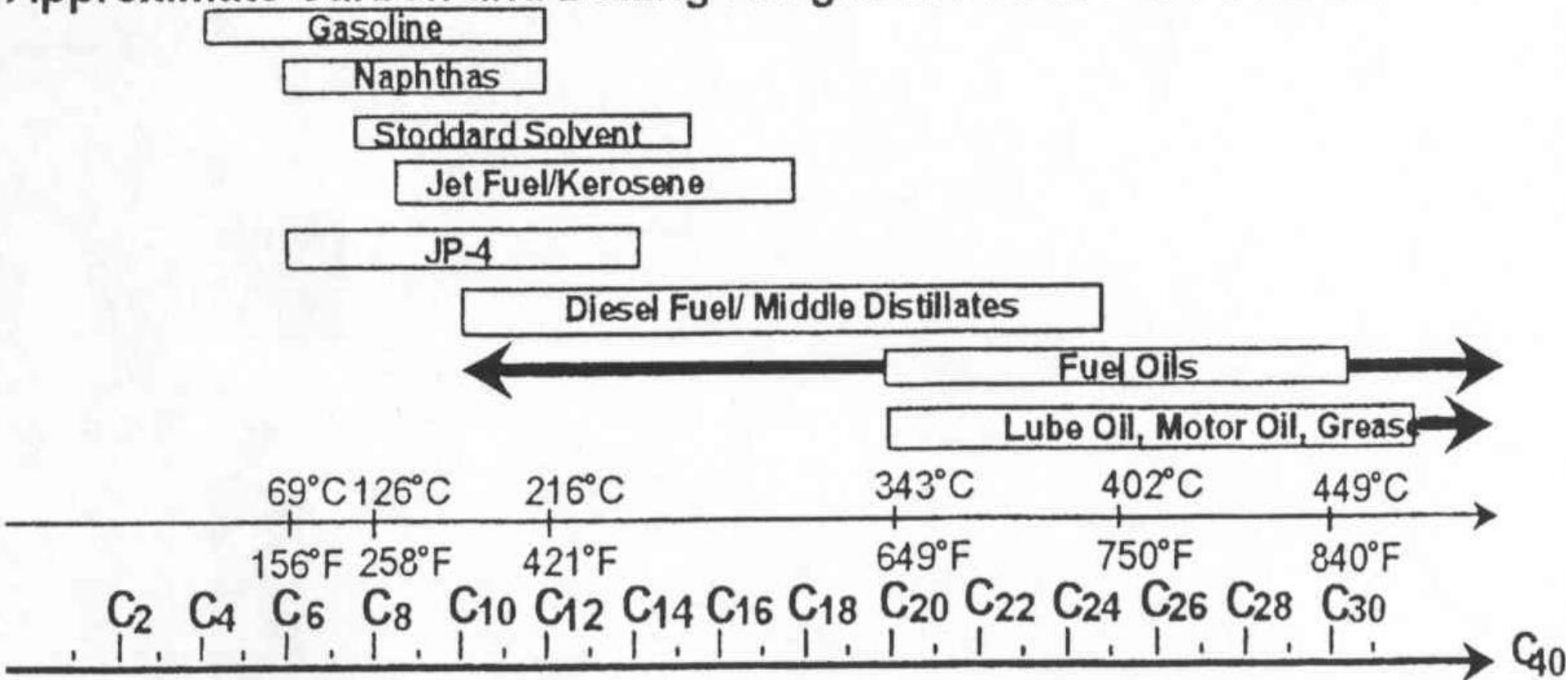
Biodegradation will induce larger isotopic fractionation in smaller molecules which have lower ratio altered to non-altered carbons- (intrinsic isotopic effects).

Environmental Forensics

- Are all techniques applicable to all products?
 - No!
- What are the problems?
 - Weathering
 - Evaporation
 - Water washing
 - Biodegradation

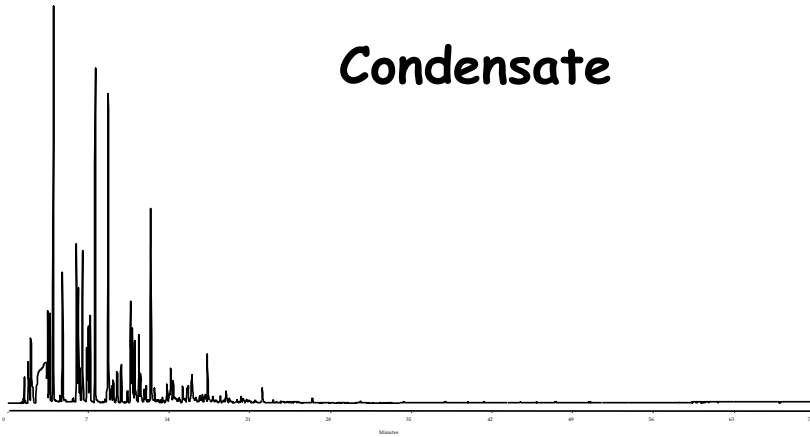
Carbon Number Distribution of Hydrocarbon Products

Approximate Carbon and Boiling Ranges of Petroleum Products

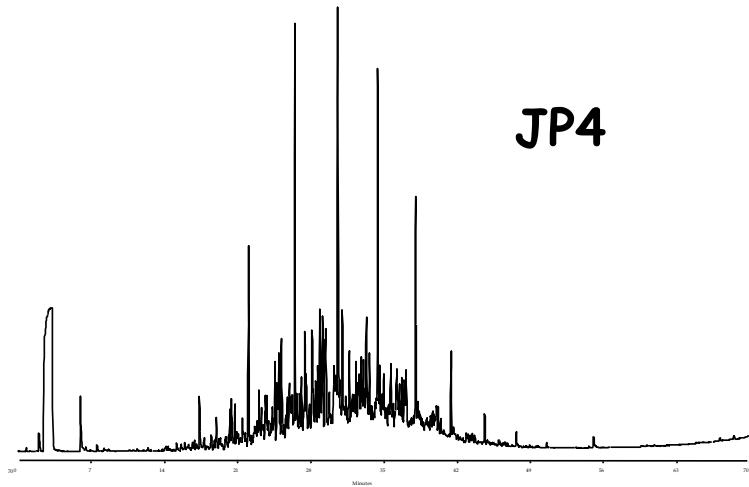


Gas Chromatography

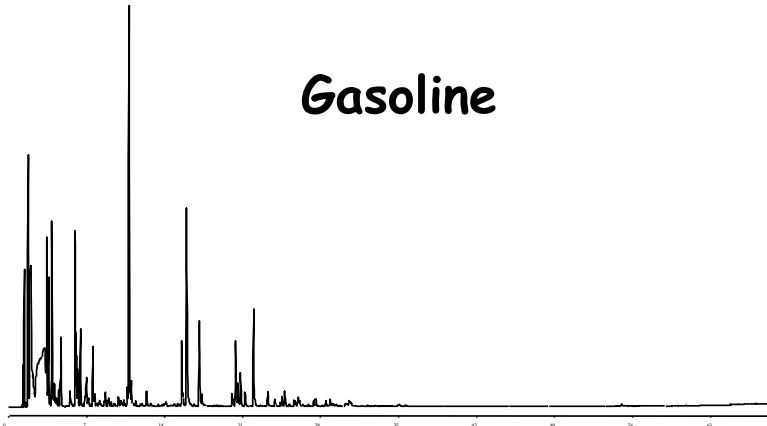
Condensate



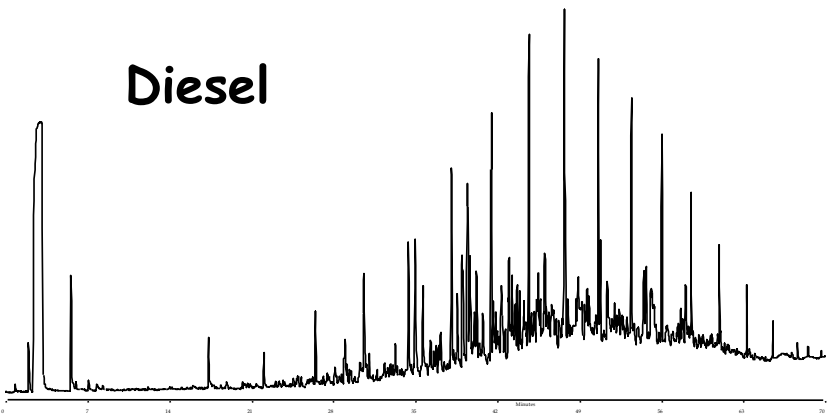
JP4



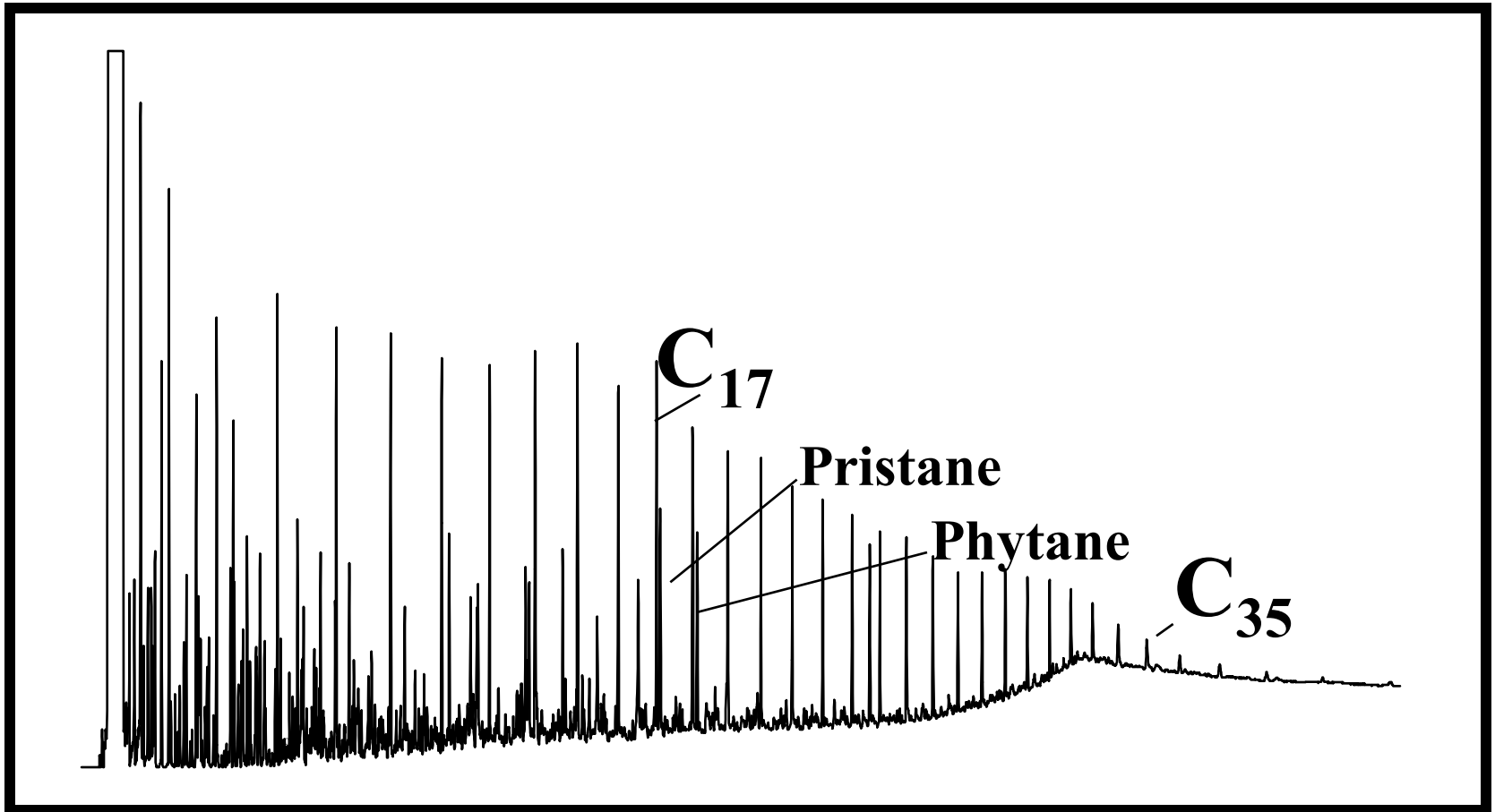
Gasoline



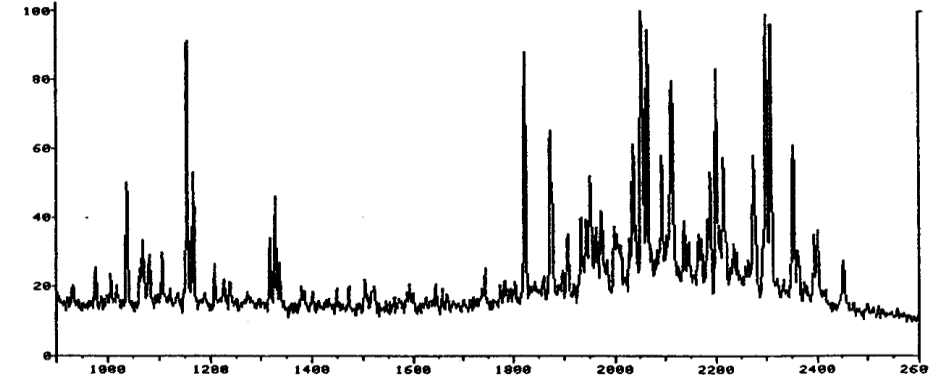
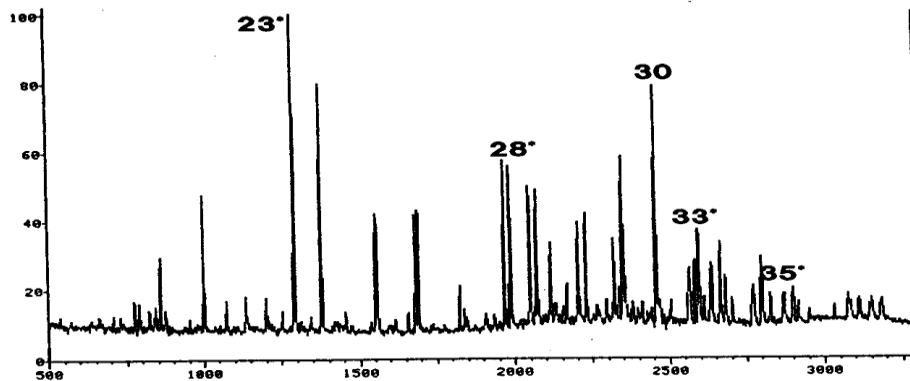
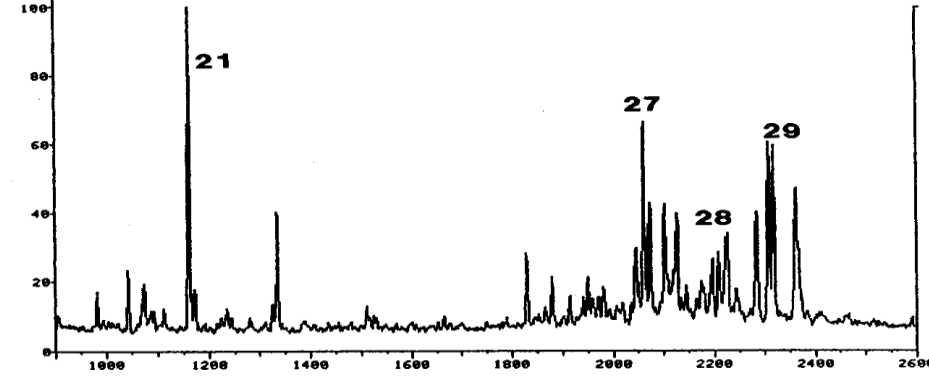
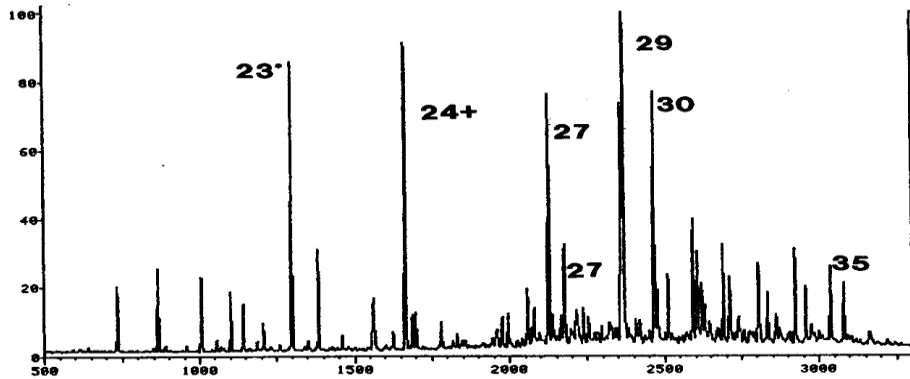
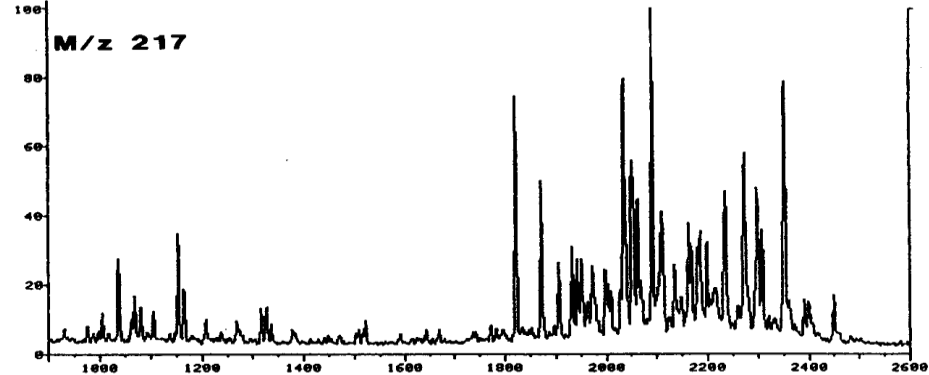
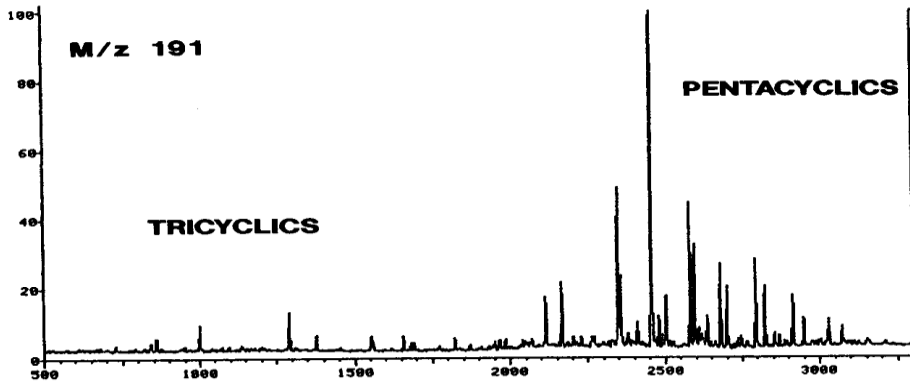
Diesel



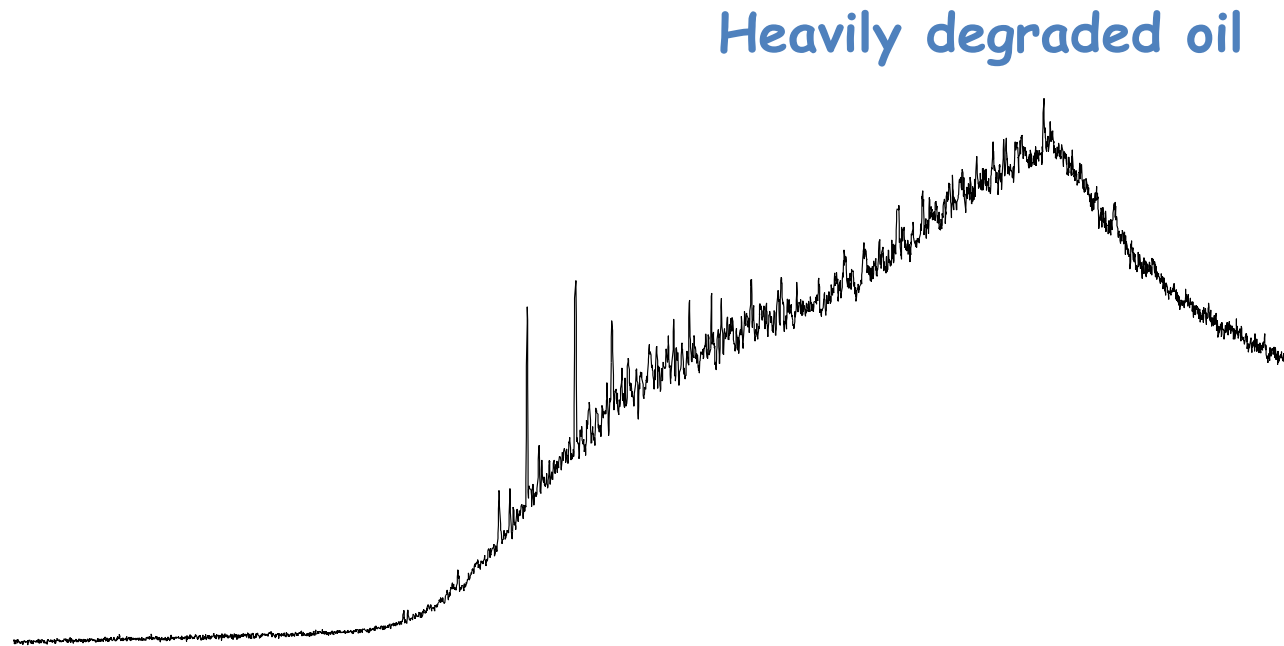
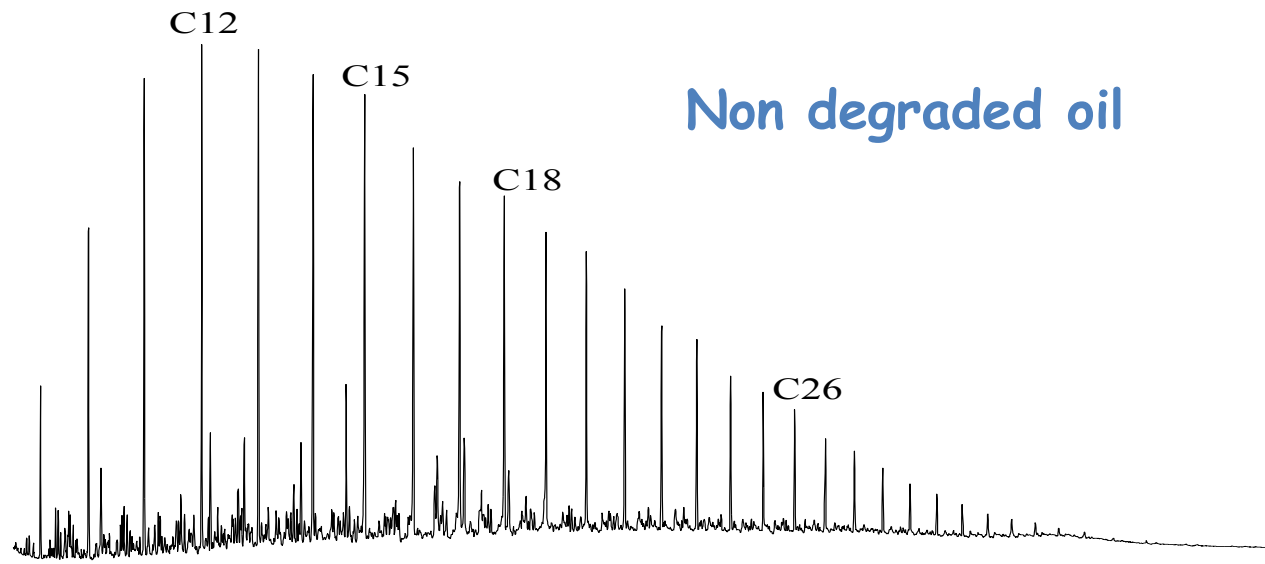
Crude Oils and Biomarkers



Biomarker Distributions

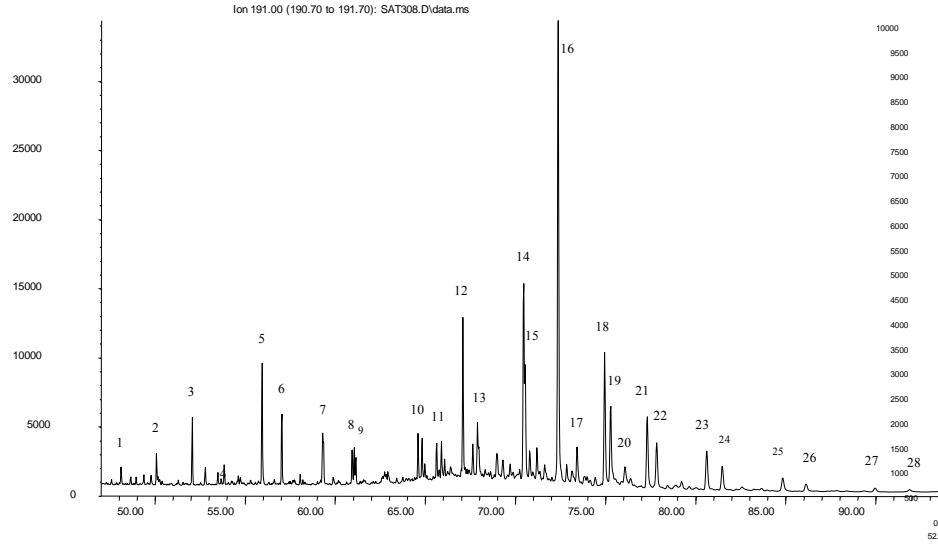


Weathering Effects of Crude Oils

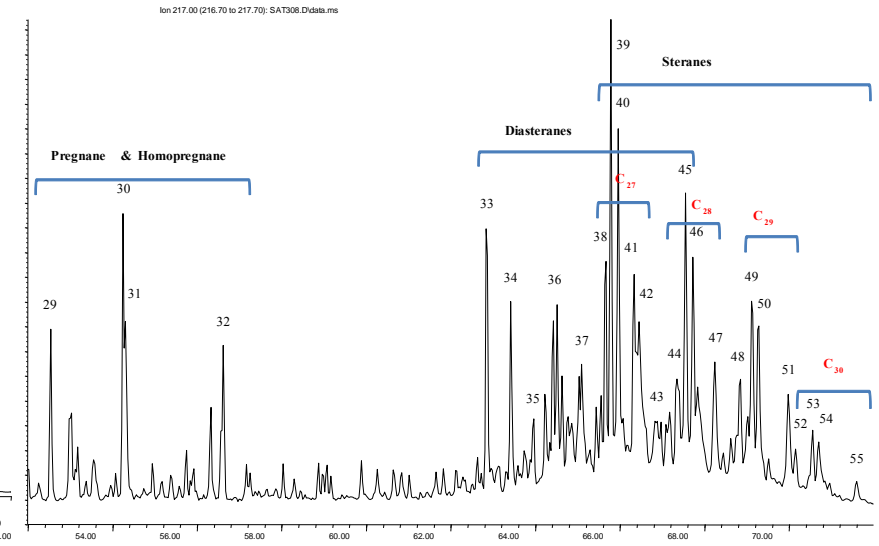


Weathering Effects of Crude Oils

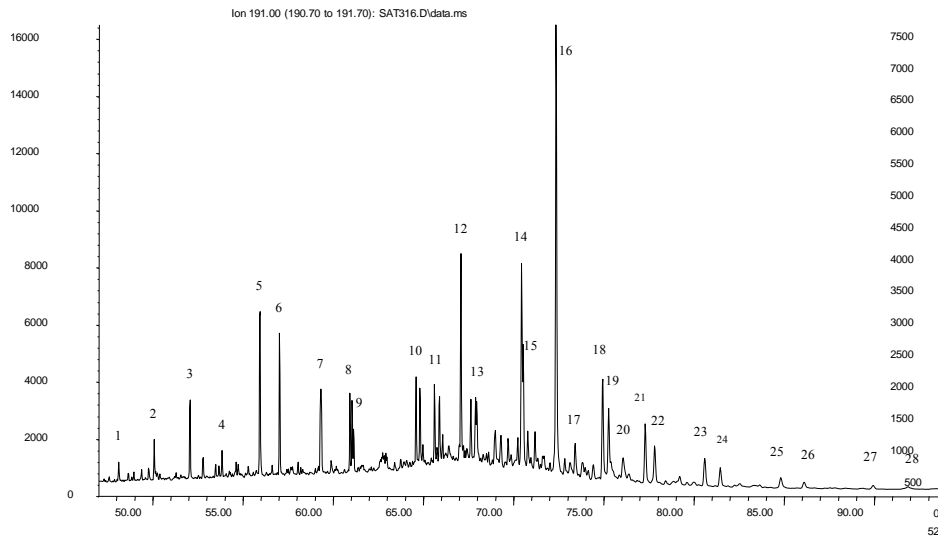
Abundance



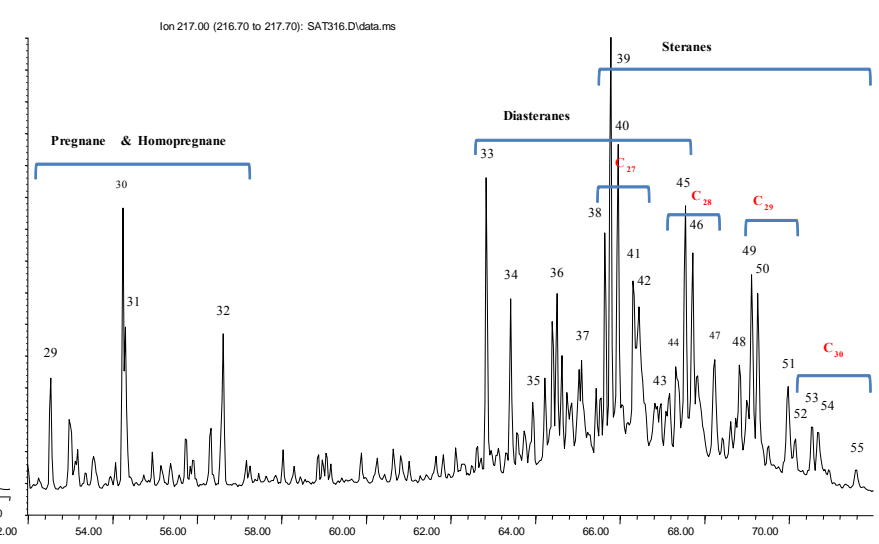
Abundance



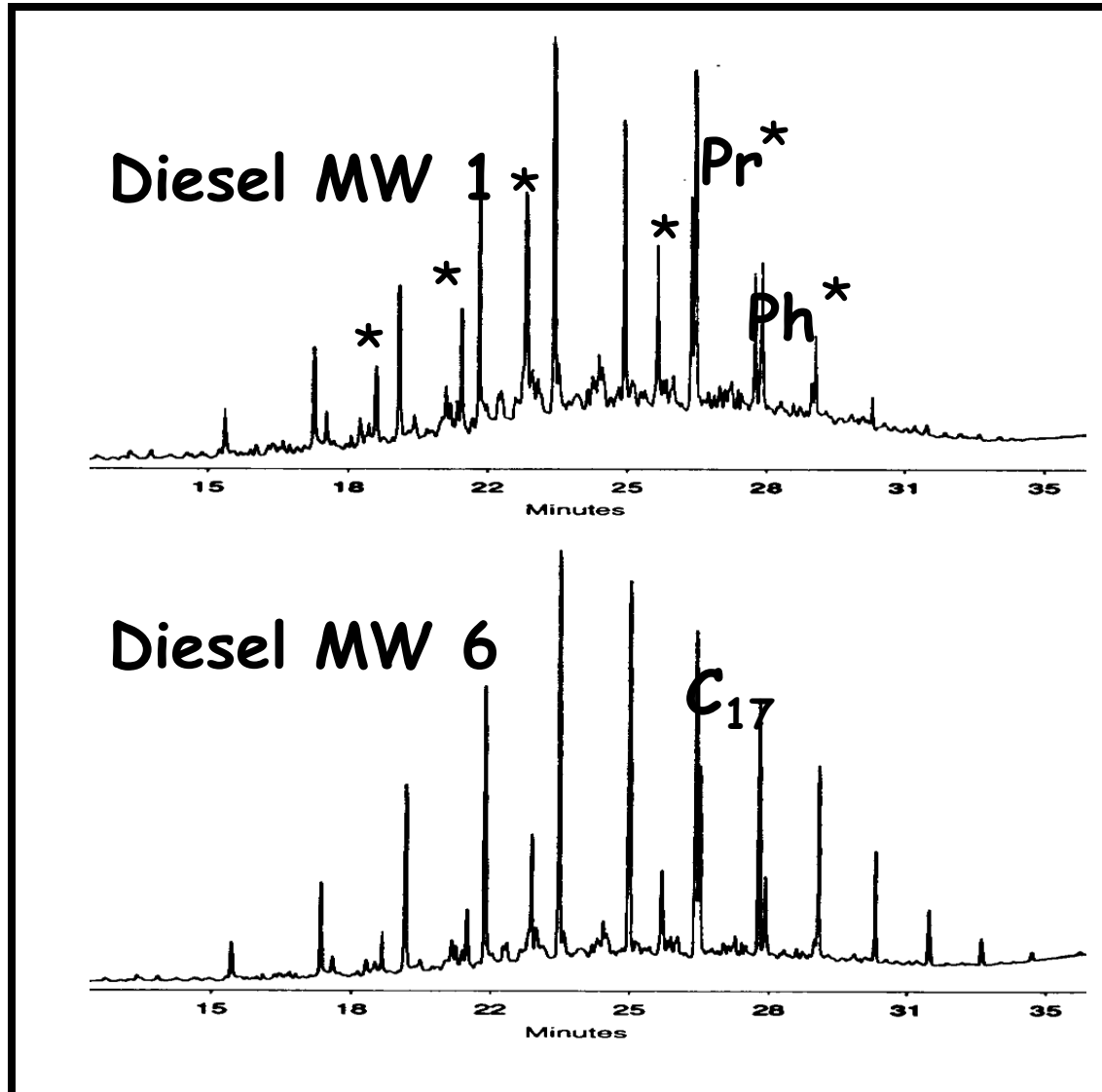
Abundance



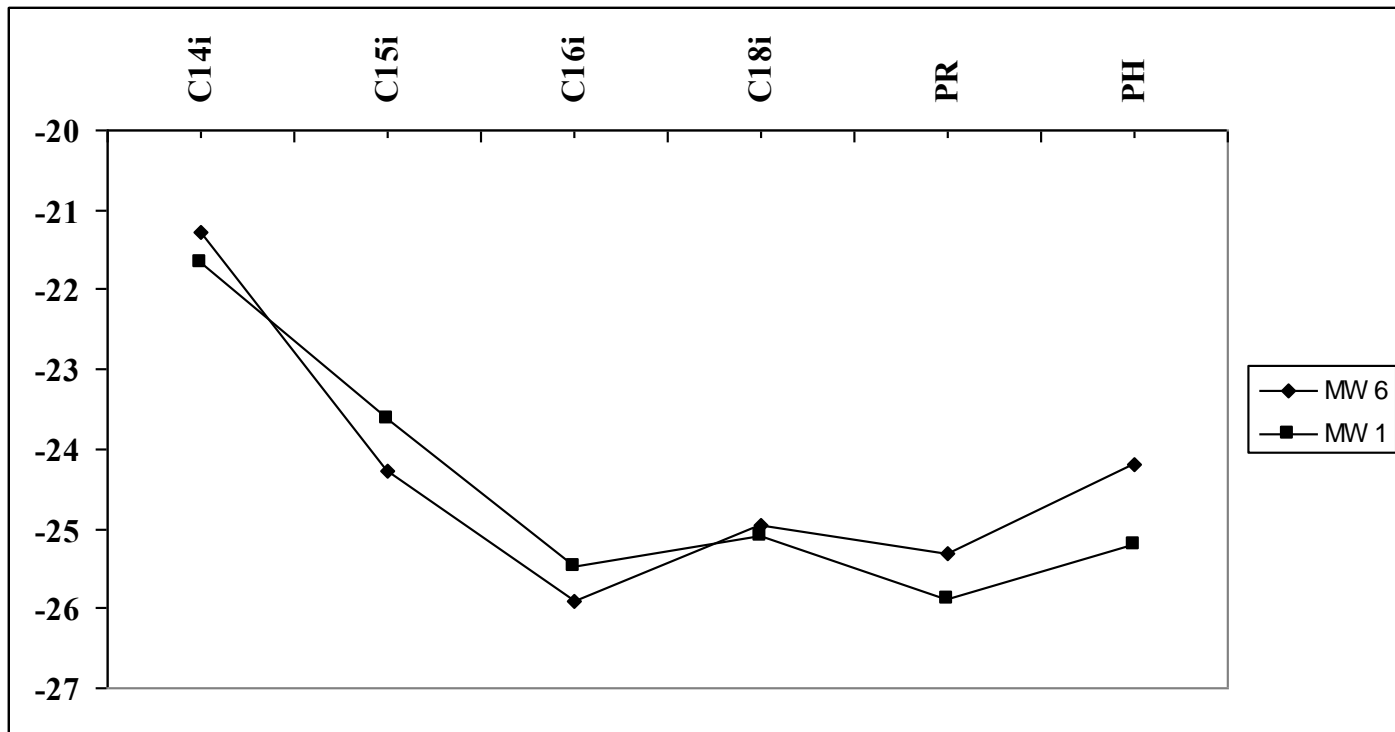
Abundance



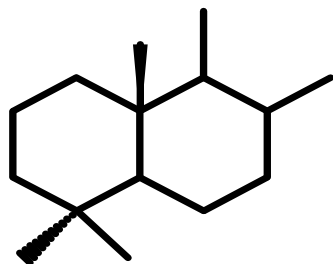
Weathered and Unweathered Diesel



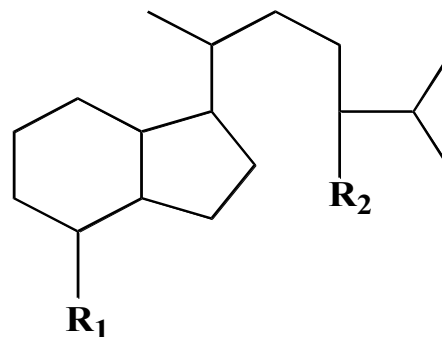
Carbon Isotope Values for Isoprenoids



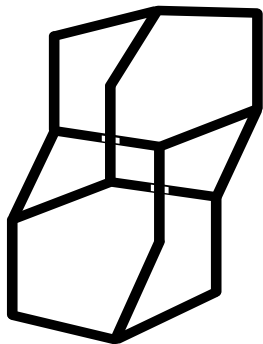
Diesel Correlations



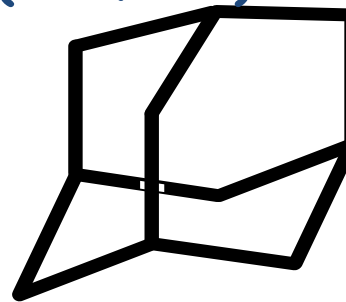
Sesquiterpanes(123)



Degraded steranes
(110;124)

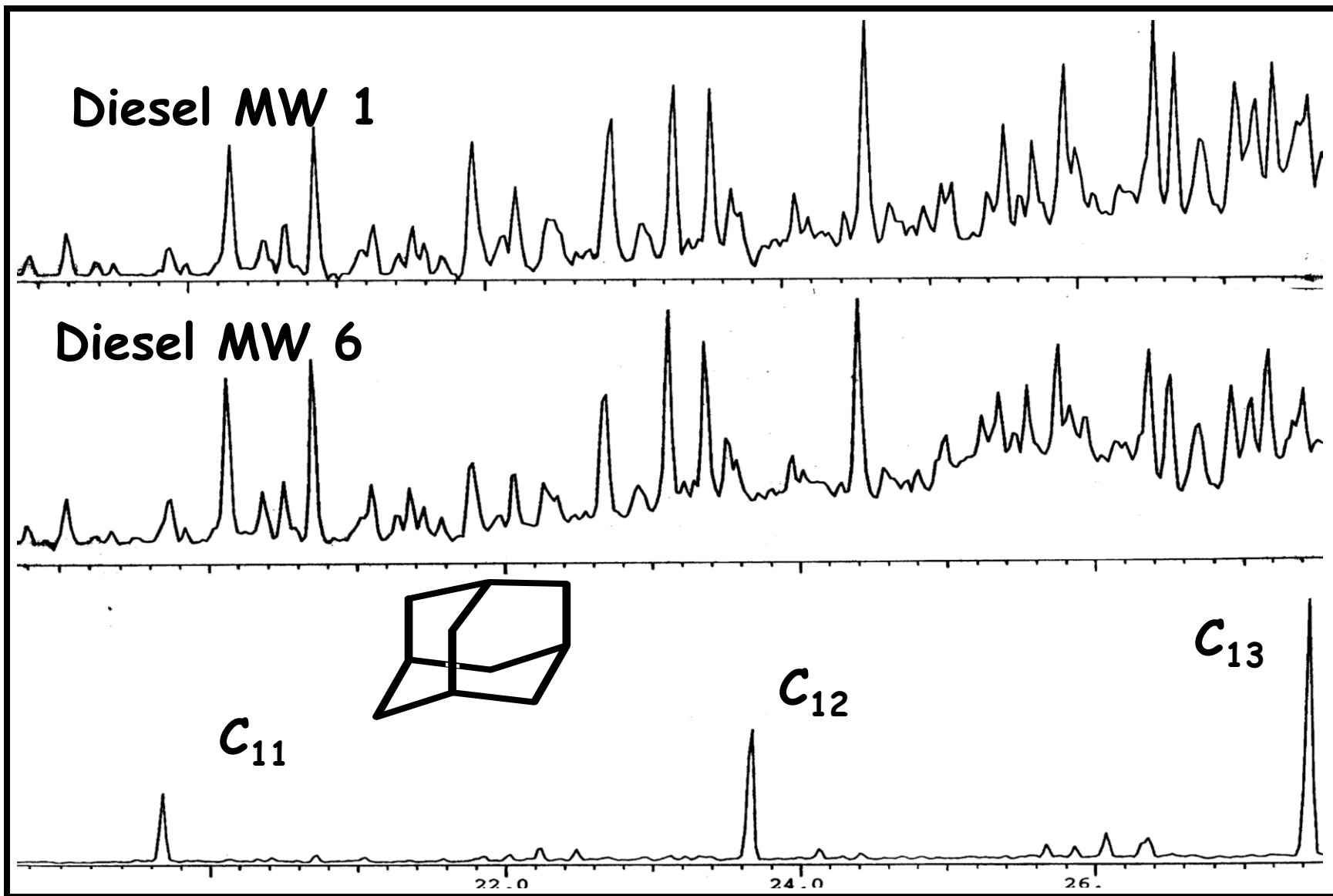


Diamantane (135)

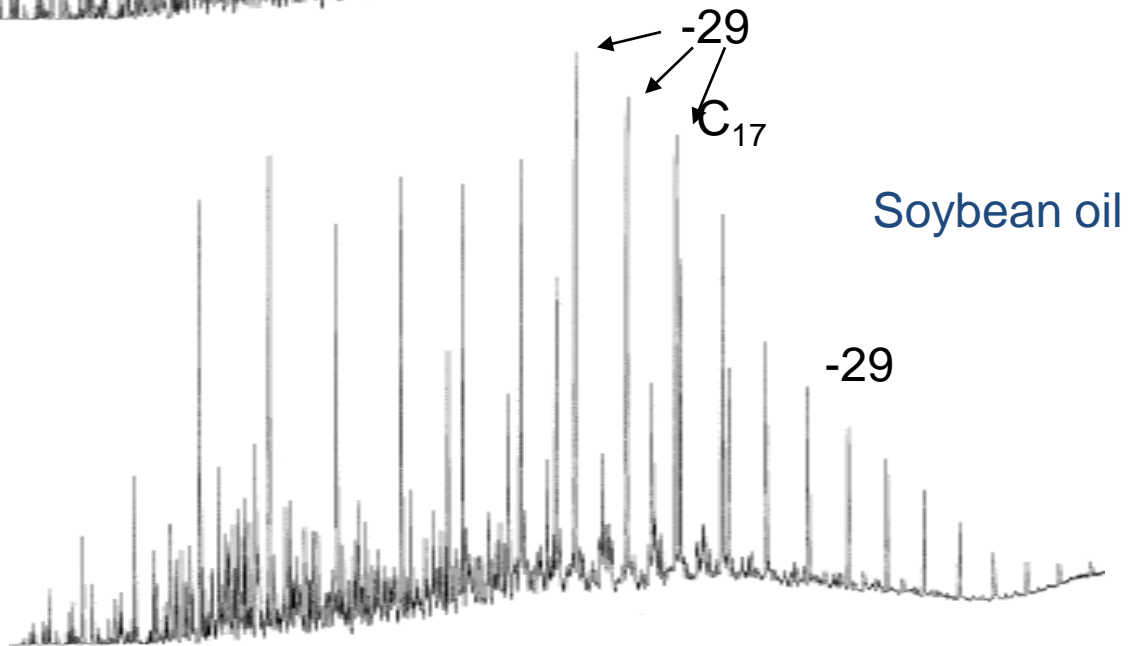
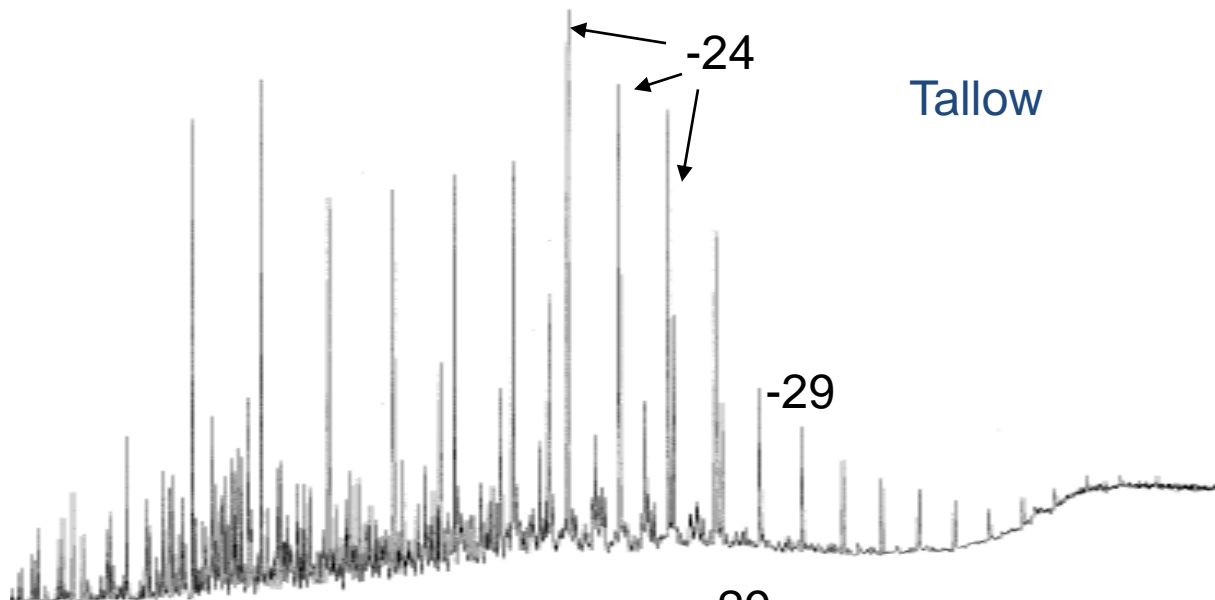


Adamantane (187)

Adamantanes in Diesel Fuels



Biodiesel

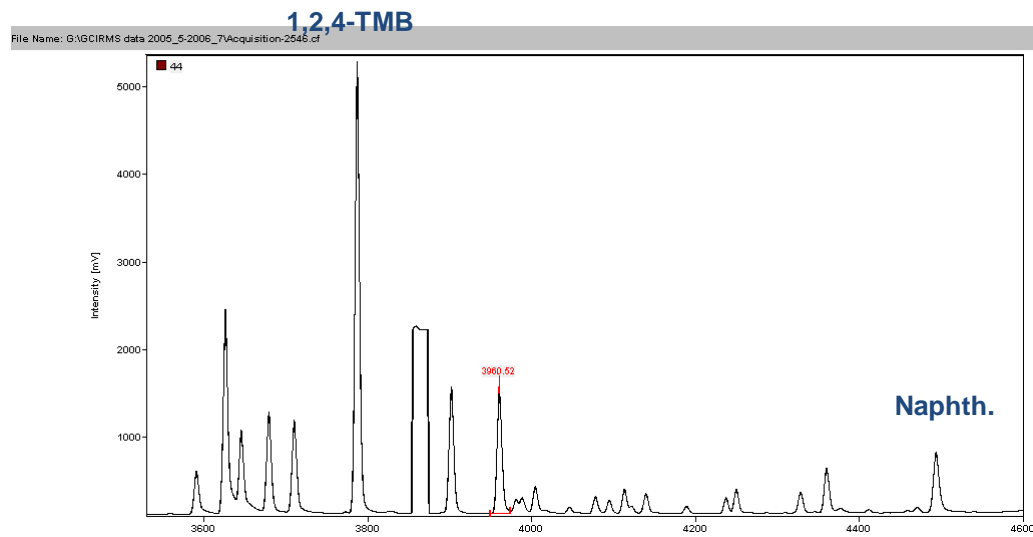


Gasolines

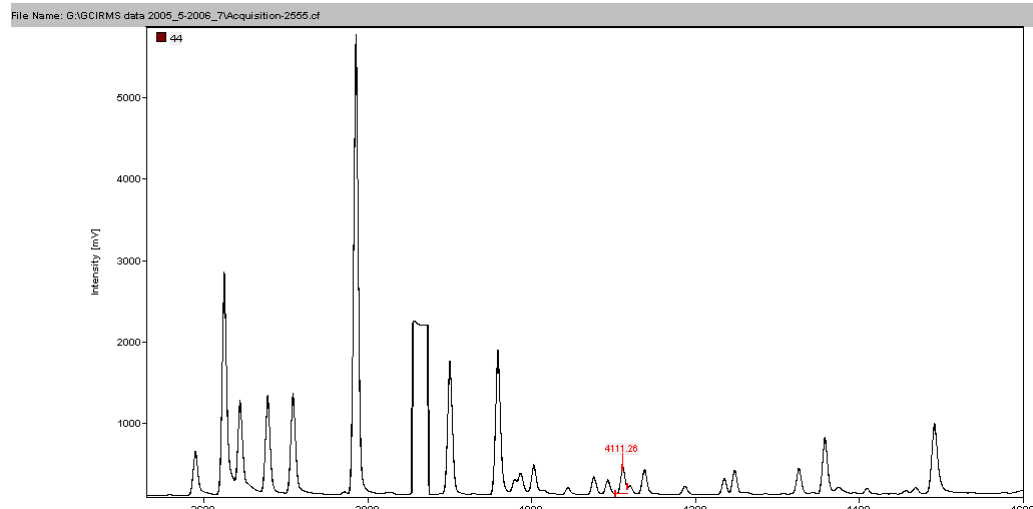
- Gasolines from different sources often have very similar chromatograms, making it difficult to distinguish such samples. Gasolines are also devoid of biomarkers, further limiting correlation possibilities.
- One solution here is to use GCIRMS for both the hydrocarbons and additives.

Gasolines - Identical GC Signals

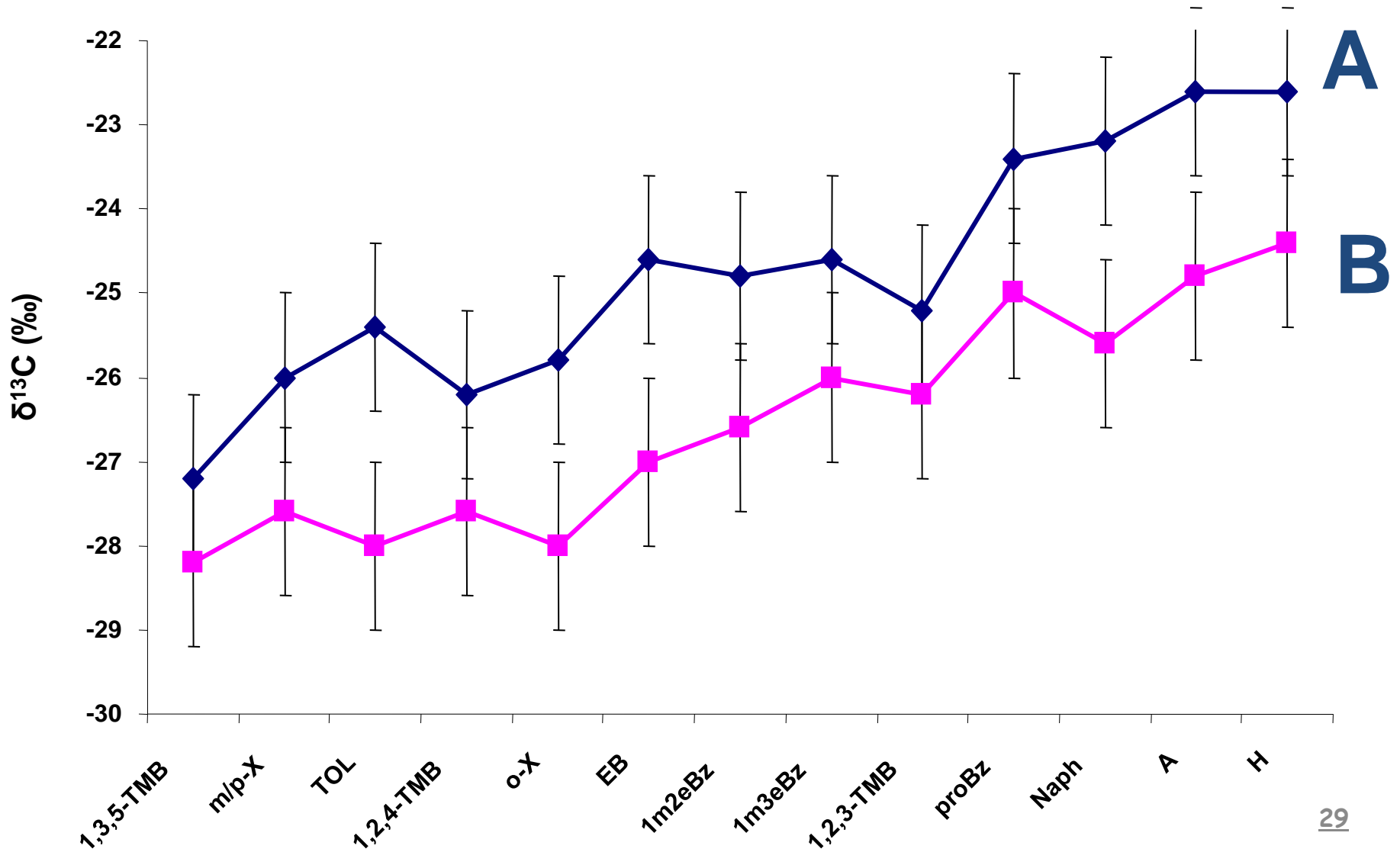
A



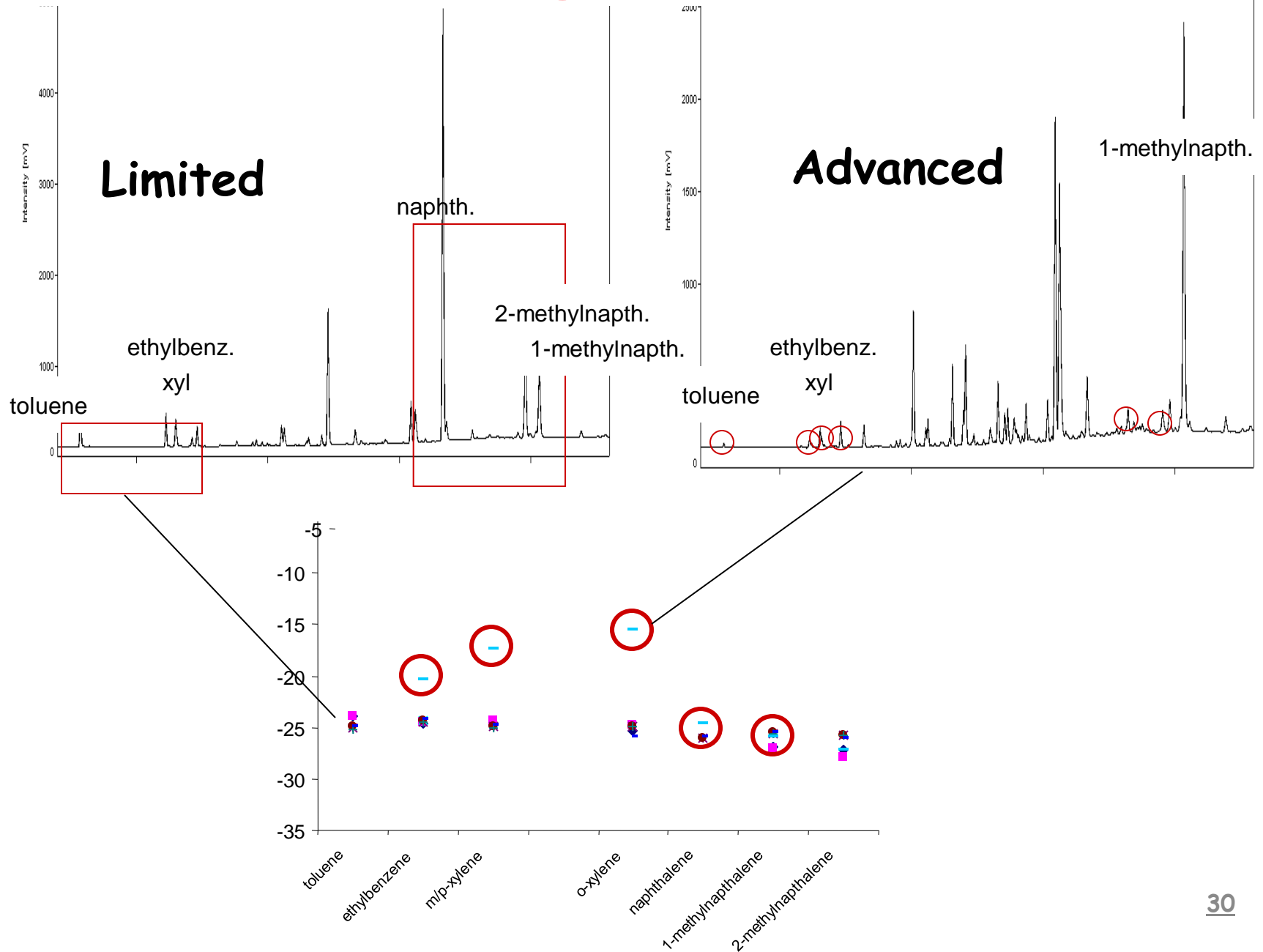
B



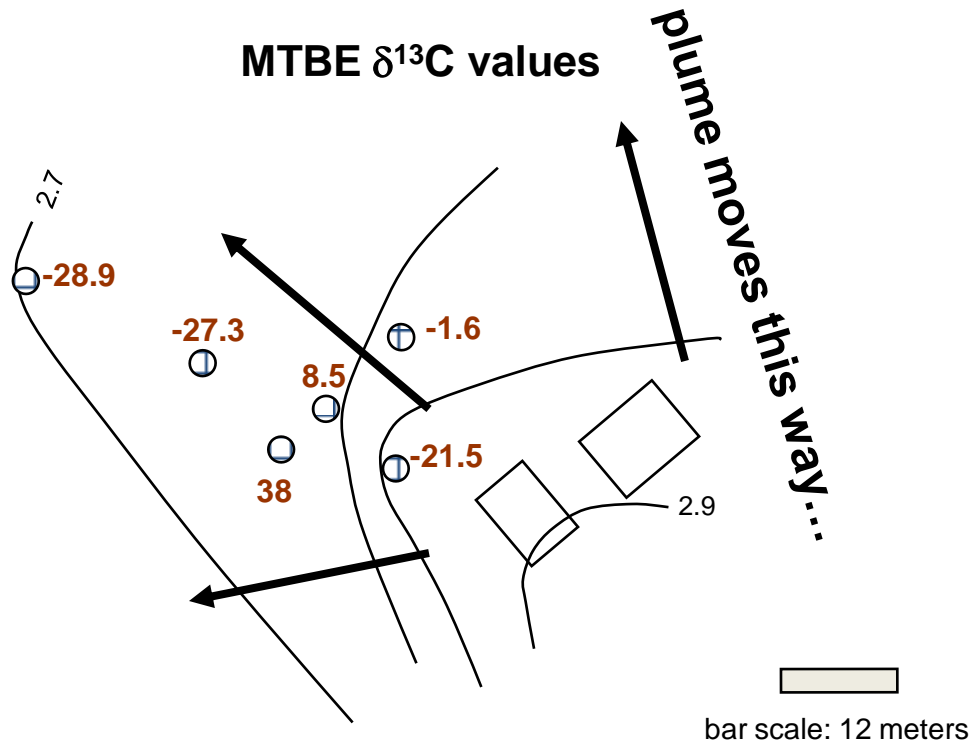
Gasolines - Different $\delta^{13}\text{C}$ Fingerprints



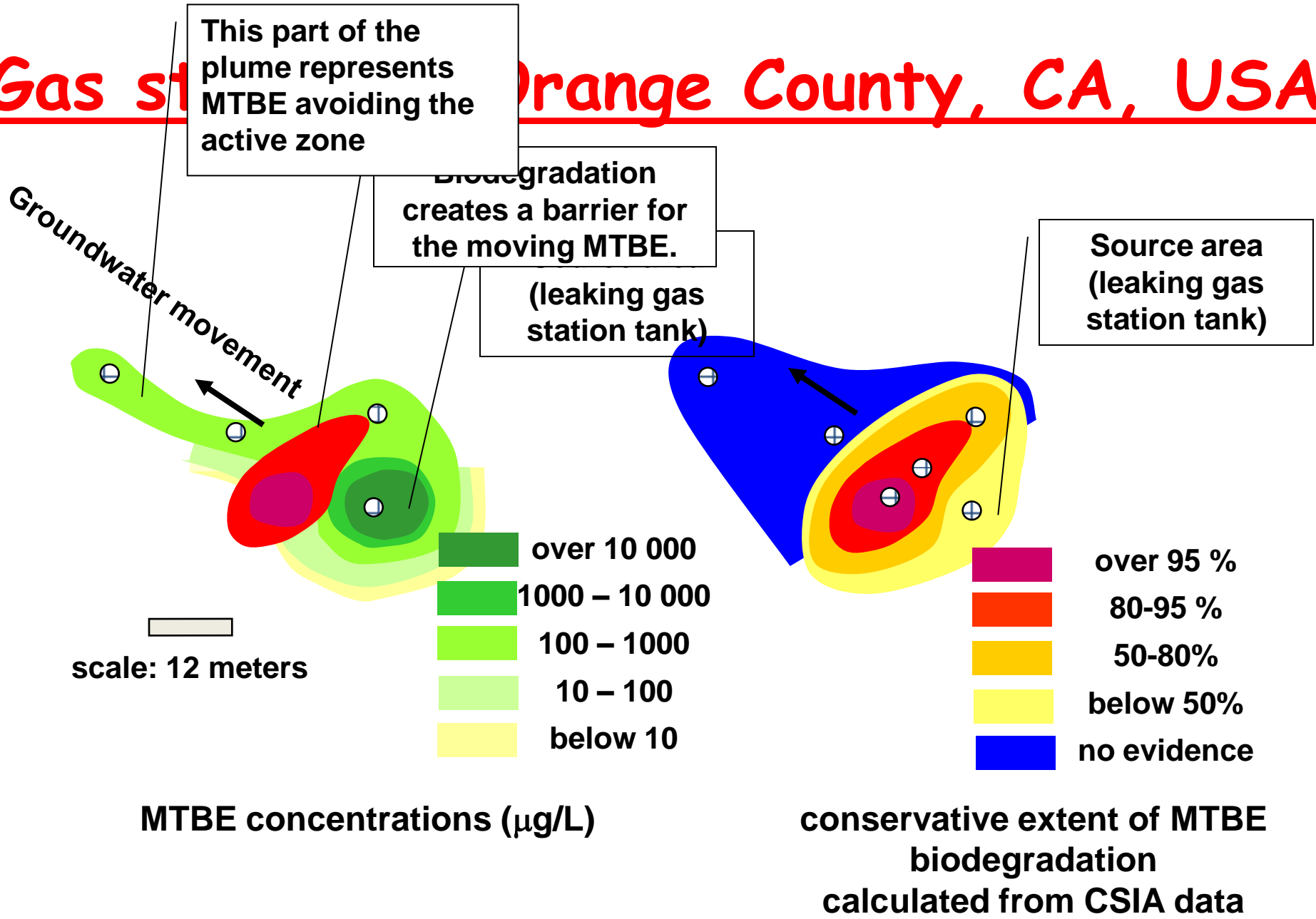
Biodegradation



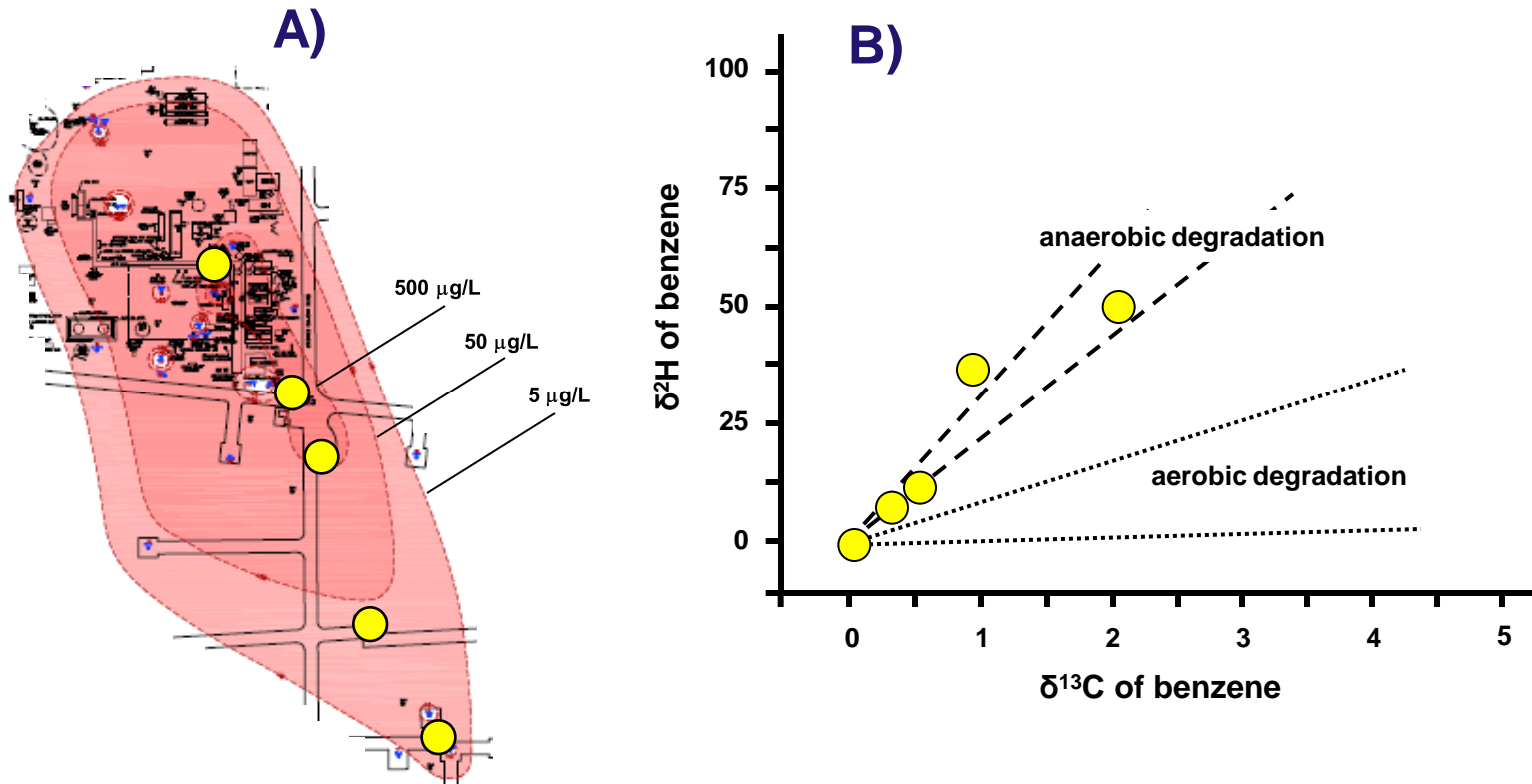
Dana Point, Orange County, CA



Gas station plume Orange County, CA, USA

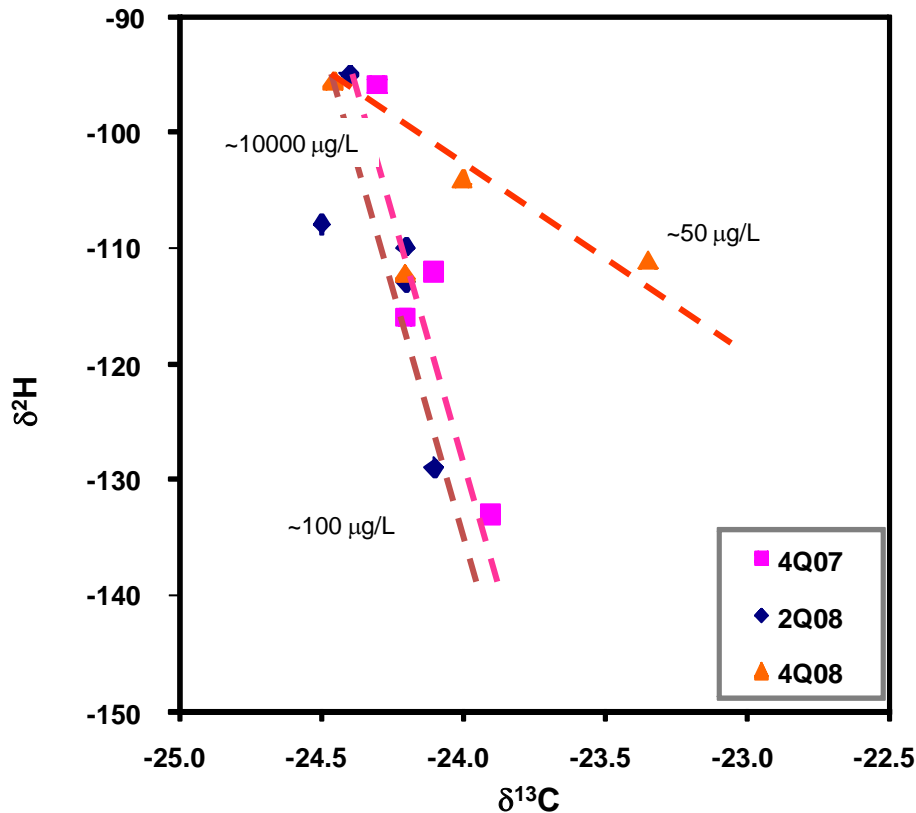


2D-CSIA Discrimination of Benzene Degradation Pathways



Application of CSIA at an industrial site. A) Locations of monitoring wells within a benzene plume; B) 2D-CSIA of benzene from the five monitoring wells. Note that net fractionation is larger for hydrogen than for carbon by a factor of ~ 20 . This is consistent with anaerobic degradation in the core of the plume, but not consistent with aerobic degradation. At this site, the extent of isotope fractionation accounts for 50-60% of benzene mass removal in the distal monitoring well. The apparent attenuation trend of benzene concentration is larger (see the "Caveat" below).

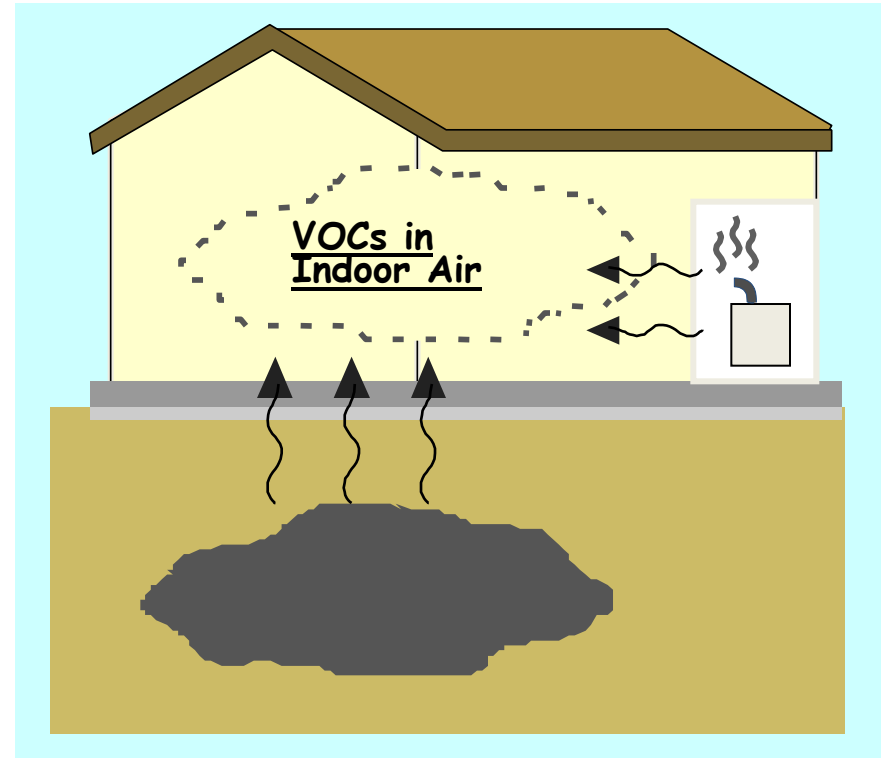
2D-CSIA Discrimination of Benzene Degradation Pathways



2D-CSIA plot of data from a benzene site in California. Three quarterly sample sets are shown. Note the inverse H fractionation, similar to the trends observed for volatilization of MTBE from NAPL phase. The difference between 4Q08 vs. the two other sets may represent relatively less prominent volatilization in 4Q08.

Vapor Intrusion

- At vapor intrusion site, testing of indoor air is most direct way to identify VI impacts.
- Indoor sources of VOCs are ubiquitous: cleaners, glues, plastic, etc
- Detection of VOCs in indoor air does not necessarily indicate vapor intrusion.

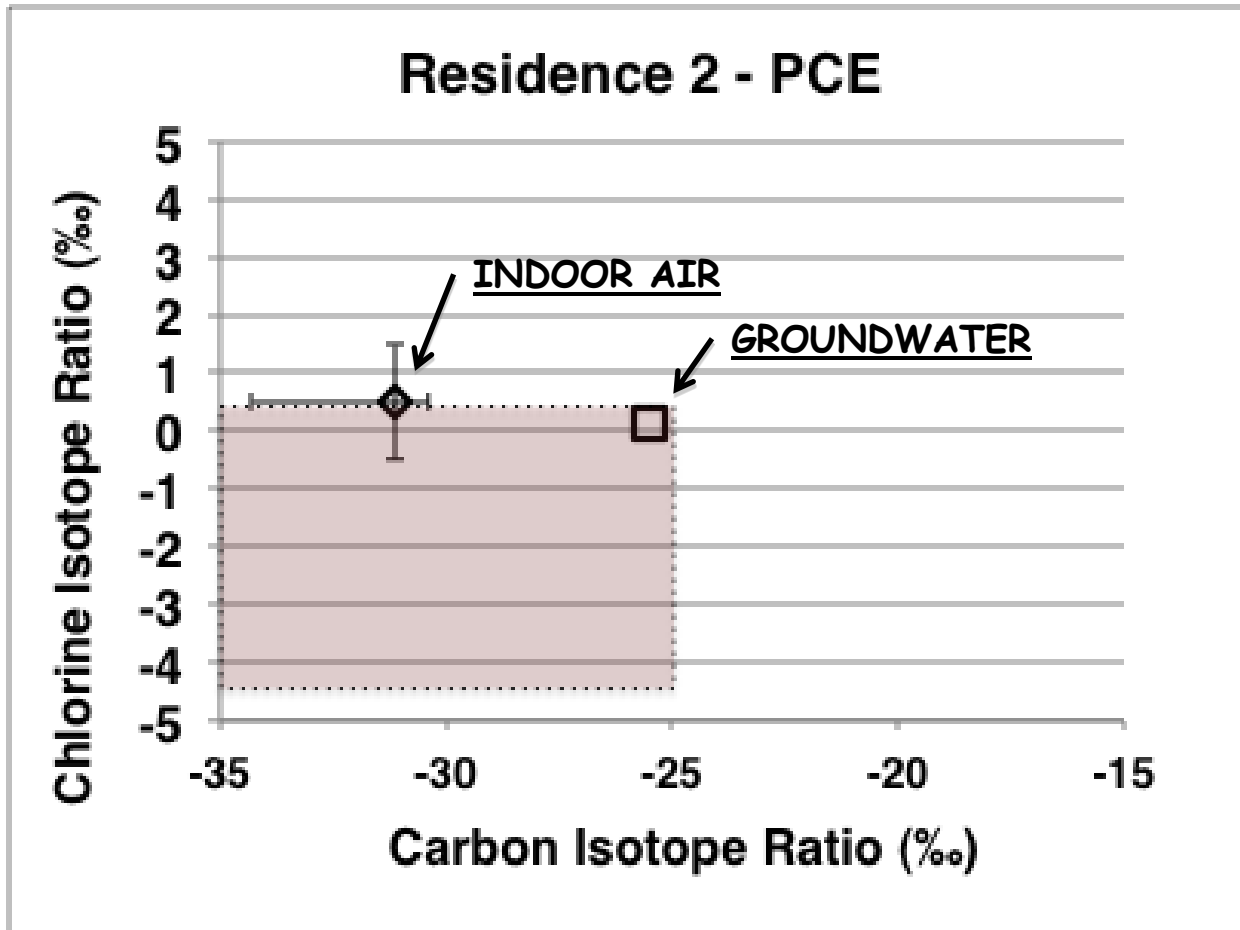


**Key
Point:**

Critical need for reliable methods to distinguish between vapor intrusion and indoor sources of VOCs.

FIELD DEMONSTRATION: AFCEE

BAA

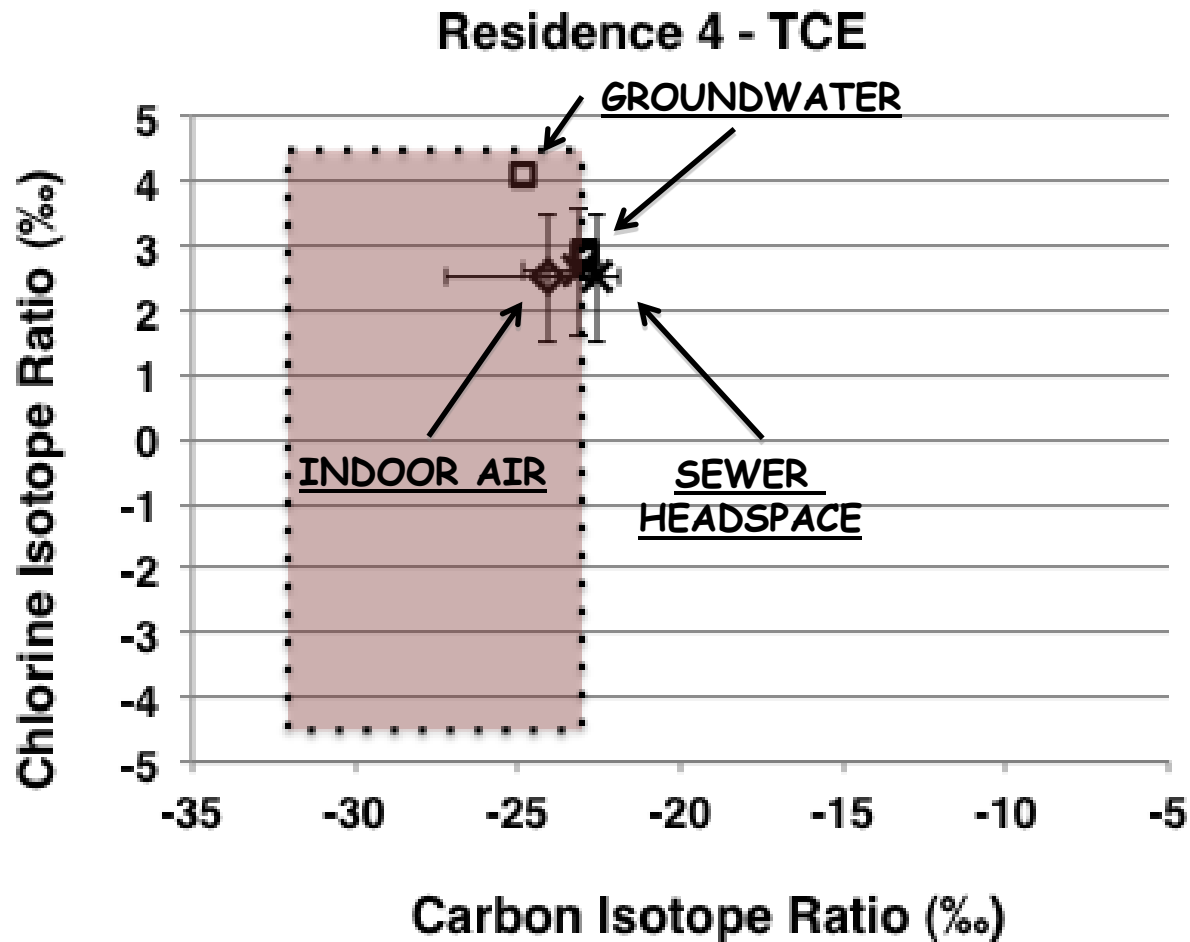


FINDING:

PCE in indoor air is from indoor source.

FIELD DEMONSTRATION: AFCEE

BAA



FINDING:

*GW with TCE
discharged into*

sewer ■

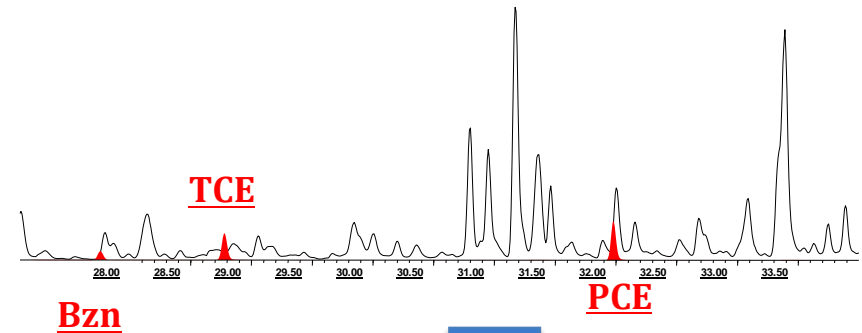
*TCE is moving
from sewer into
house.*

Summary

- Environmental forensics covers many issues directly related to oil and gas issues
- Analytical tools are available to undertake investigations into source of spilled hydrocarbon products in the environment
- Conventional techniques such as GC and GCMS are being complimented by stable isotopes.

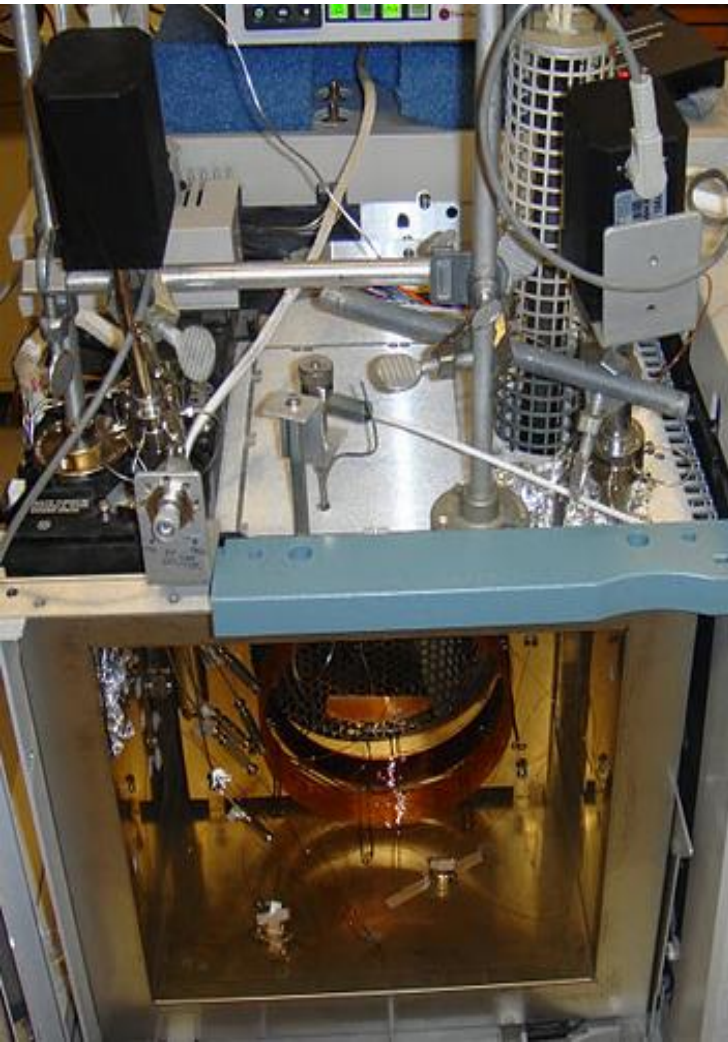
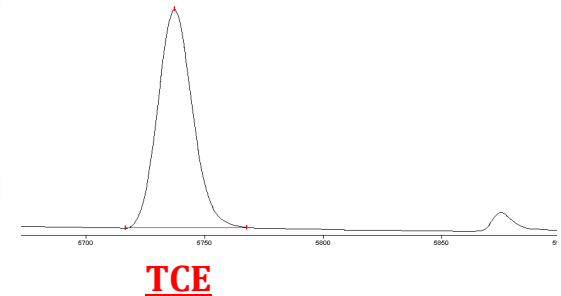
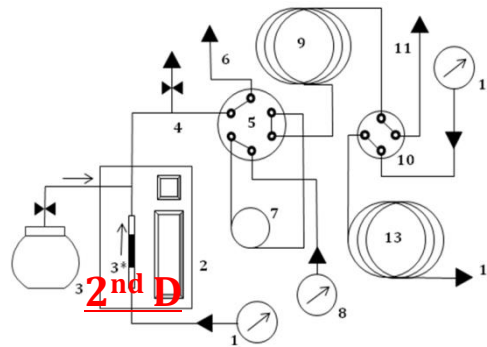
Performance Assessment Optimization of 2D-GC

Indoor air VOCs: conventional GC trace

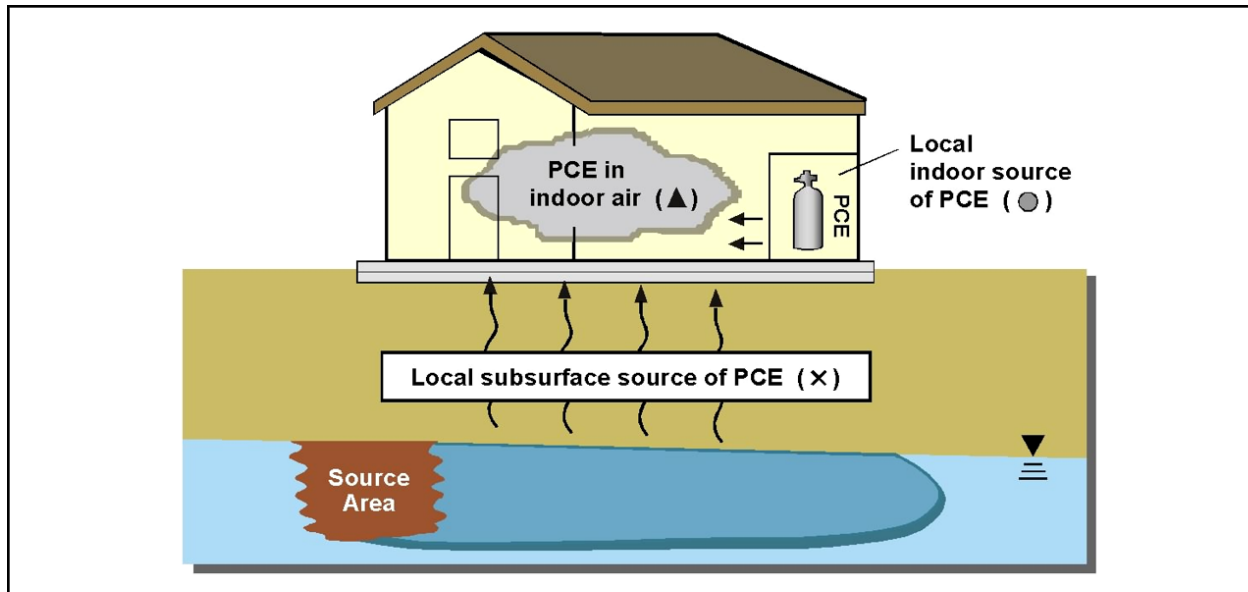


Indoor air VOCs:
resolution of TCE after 2D-GC

1st D

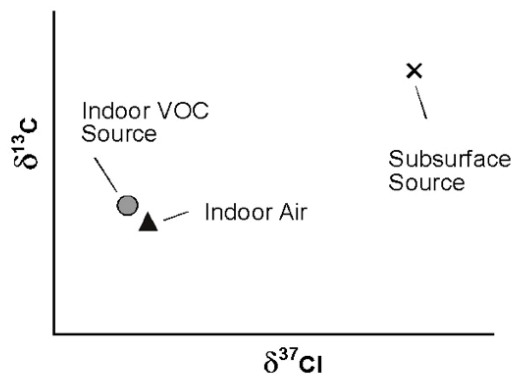


Vapor Intrusion



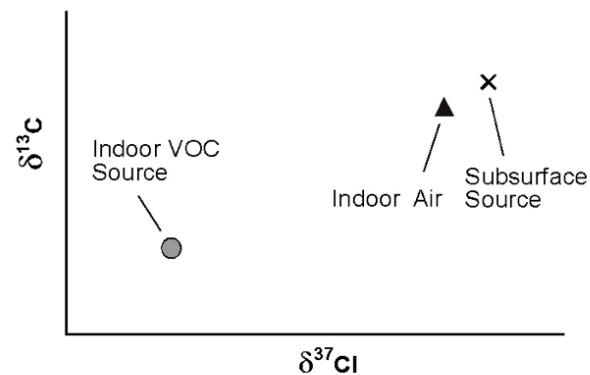
Example A:

Indoor Source is Primary Source of PCE in Indoor Air



Example B:

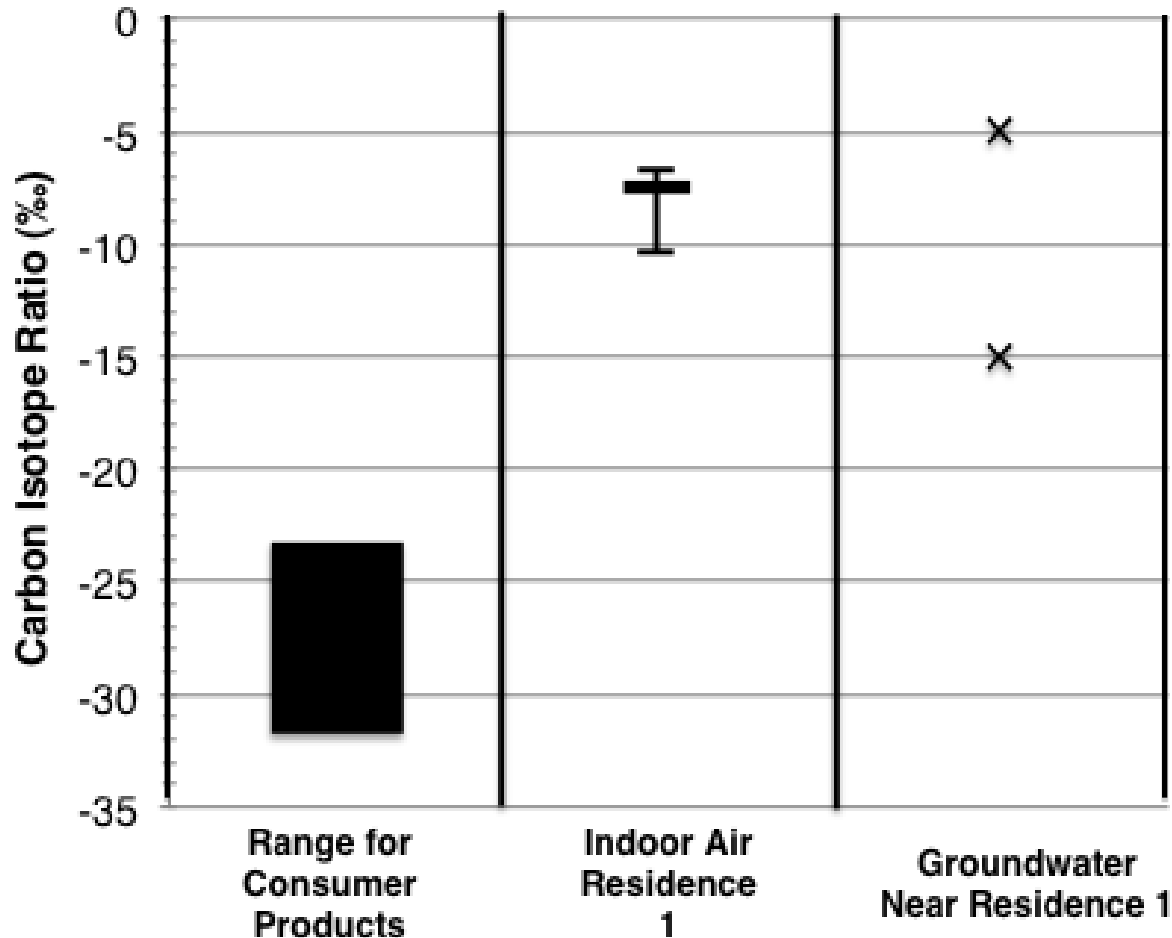
Subsurface Source is Primary Source of PCE in Indoor Air



FIELD DEMONSTRATION: AFCEE

BAA

Residence 1 - TCE



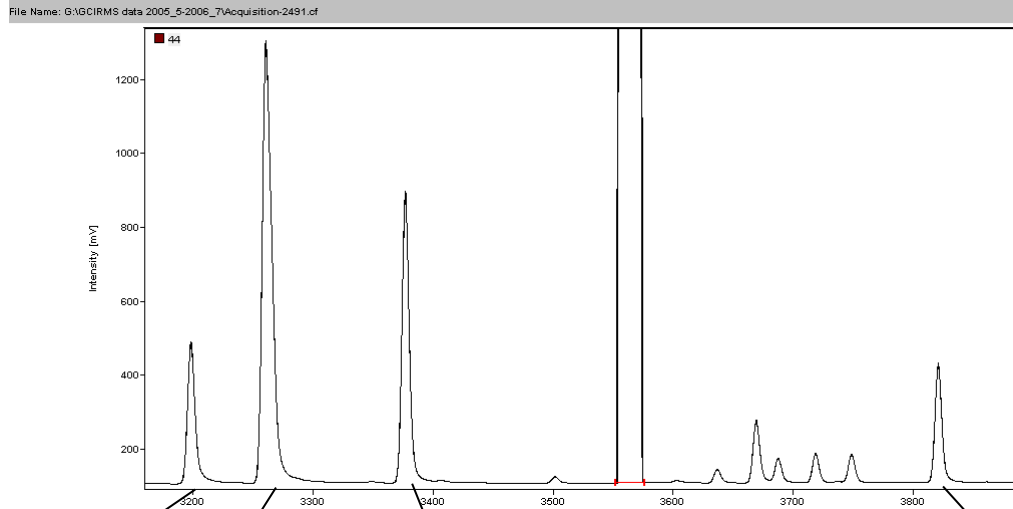
FINDING:

TCE in indoor air matches TCE in GW.

TCE is too heavy to be an indoor source.

> Vapor Intrusion

CSIA of Gasoline



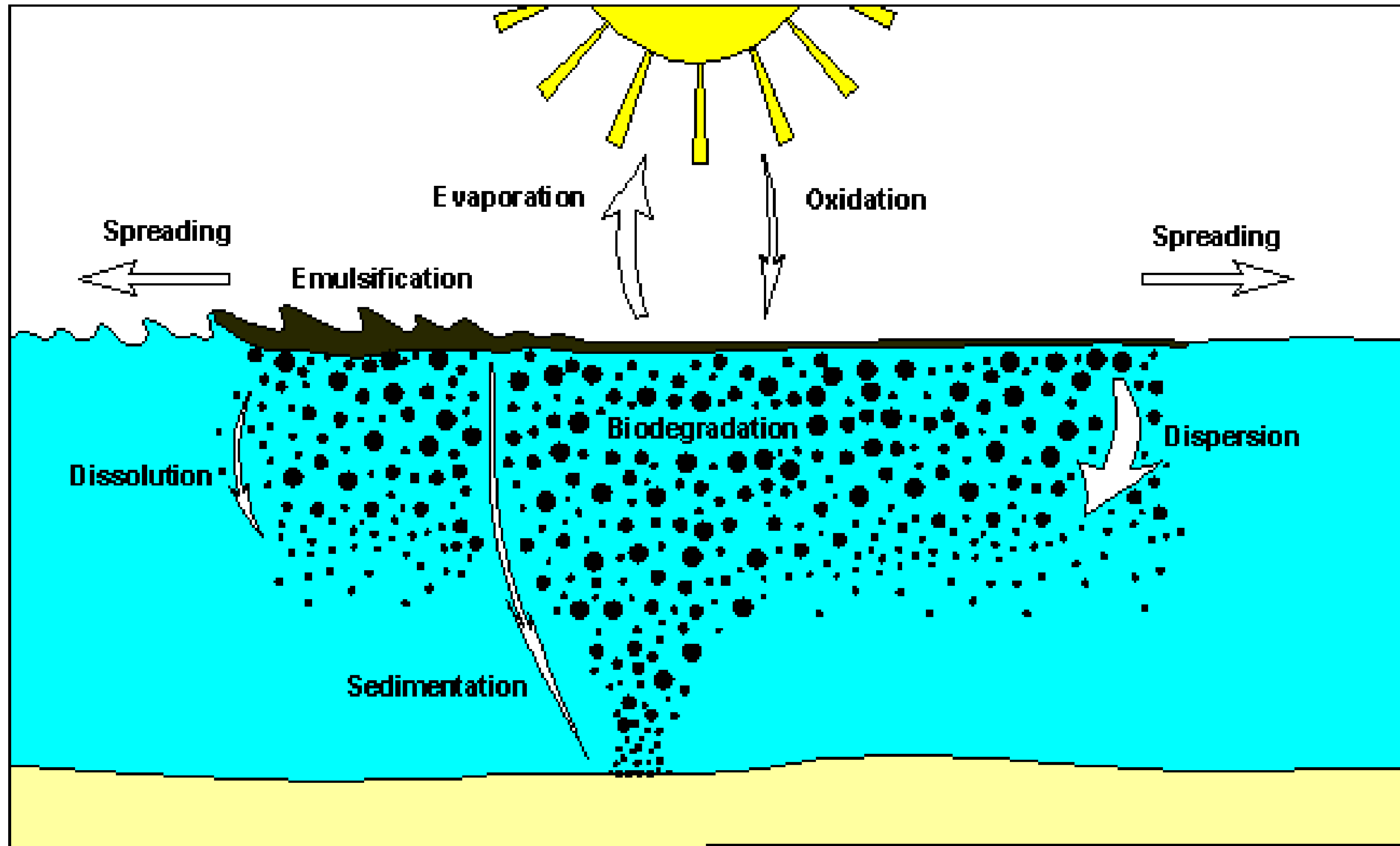
ethylbenzene
 $\delta^{13}C = -24.6$ ‰

m,p-xylene
 $\delta^{13}C = -26.0$ ‰

1,2,4-
trimethylbenzene
 $\delta^{13}C = -26.7$ ‰

o-xylene
 $\delta^{13}C = -25.1$ ‰

Processes acting on Spilled Oils



Environmental Forensics



Friday, October 15, 2004

How investigators track oil culprits

Chemists employ 'fingerprinting' -- but sometimes more is needed

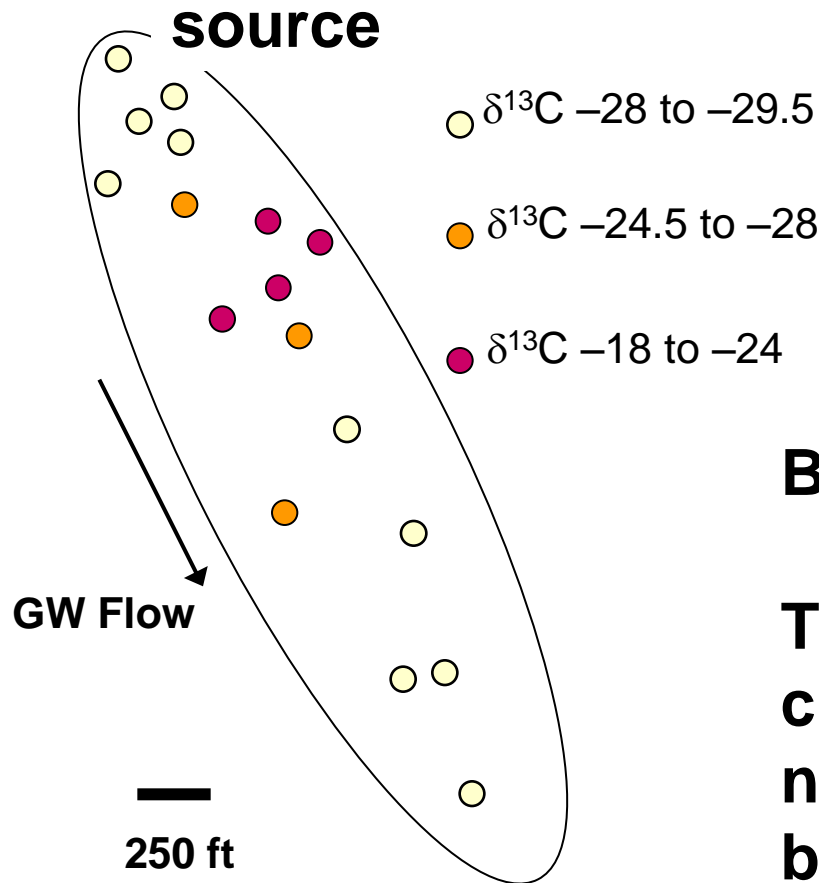
By [ERIC NALDER](#) AND [PHUONG CAT LE](#)

SEATTLE POST-INTELLIGENCER REPORTERS

"To the untrained eye, an oil spill is just a brackish mess speckled with rainbows,

but to a forensic chemist it's a collection of clues pointing to its origin."

Topography of MTBE attenuation

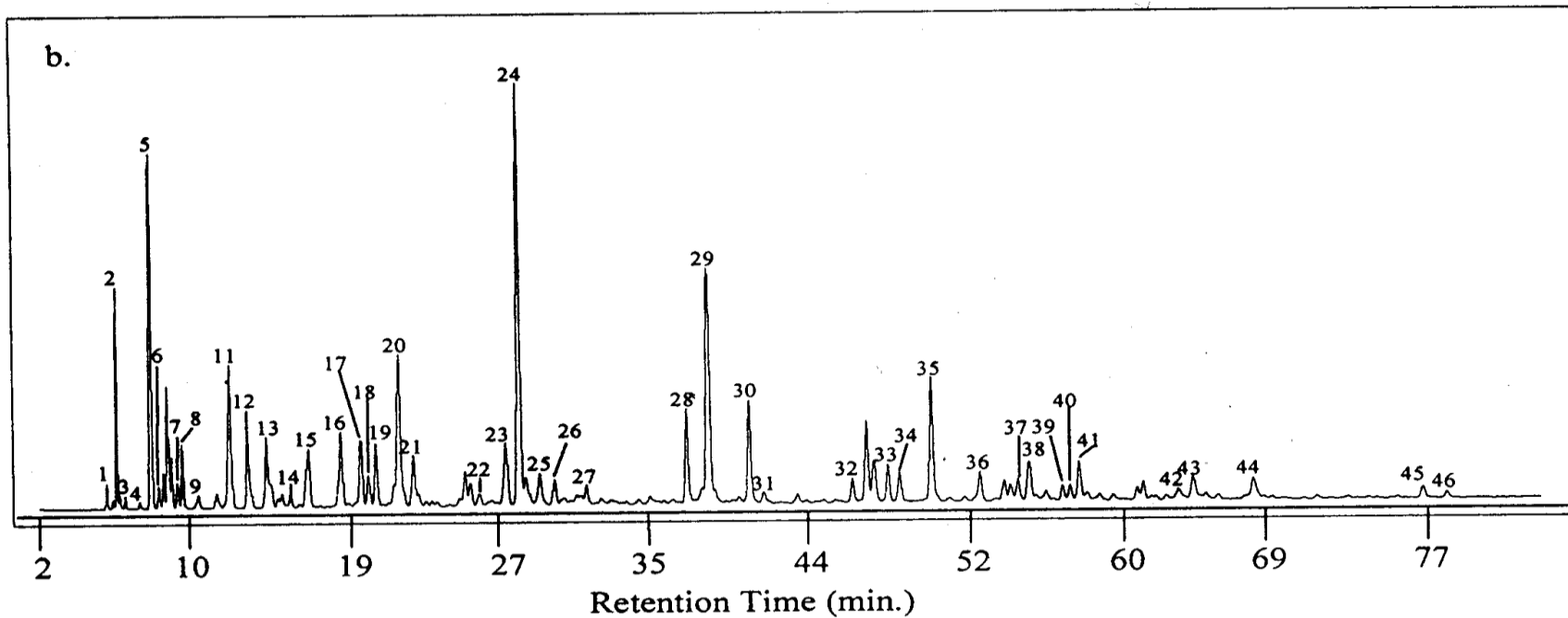
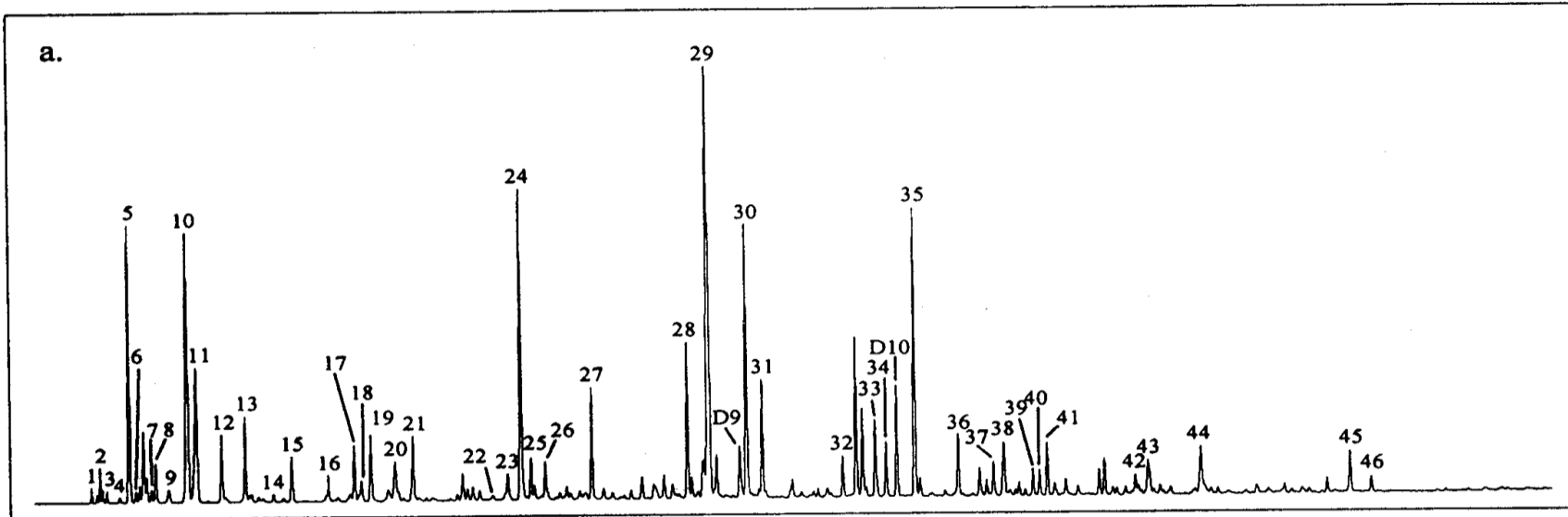


TX, Chevron site

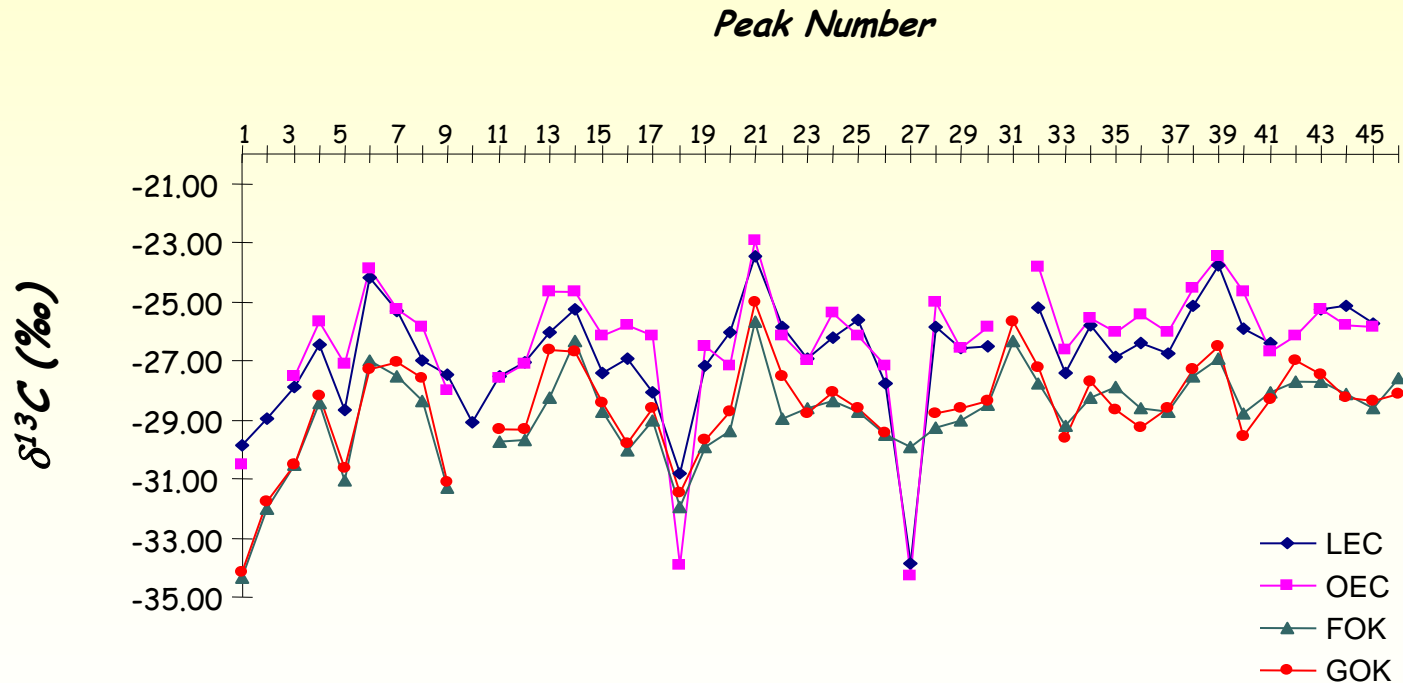
Better site management:

Treatment may be customized to benefit from naturally occurring bioattenuation processes

Comparison of Gasolines by GC



Carbon Isotopic Composition of Gasolines from Oklahoma (FOK, GOK) and the East Coast (LEC, OEC)



This figure shows the carbon isotopic fingerprint of gasolines sampled from Oklahoma and from the East Coast and demonstrates that these gasolines are significantly different in terms of isotopic composition and can be discriminated from each other on this basis. The peak numbers are identified in the section above.

GCIRMS System

