THE EMERGENCE OF STABLE ISOTOPES IN ENVIRONMENTAL AND FORENSIC GEOCHEMISTRY STUDIES

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Forensic Geochemistry

- Environmental forensic studies generally involve a product, typically organic, released into some type of environment, such as lakes, rivers, oceans, or groundwater. However with any incident the questions asked are almost always the same.

SO WHO DID IT?

Important questions: What is it? Where did it come from? Who did it?

Bottom line: Who is going to pay to clean it up?

Forensic Geochemistry

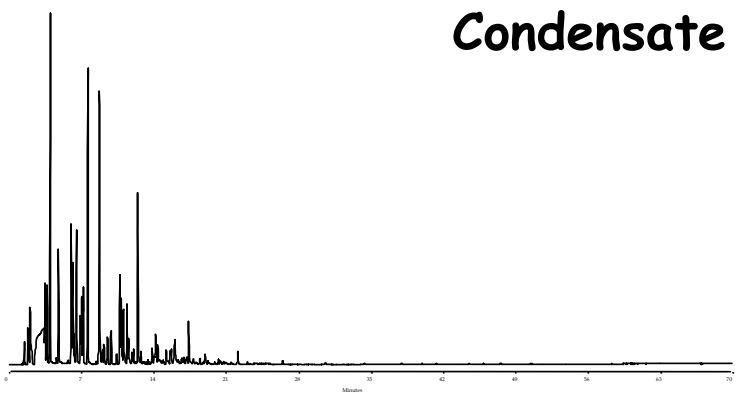
- Techniques commonly used to answer these questions:

  Gas Chromatography (GC)

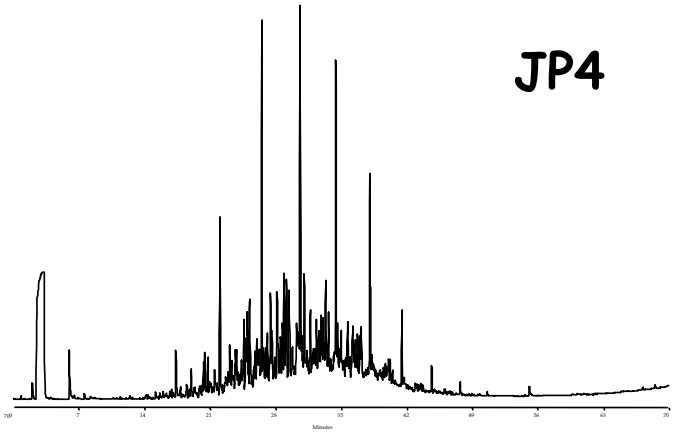
  Gas Chromatography-Mass Spectrometry (GCMS)

Fingerprinting by Gas Chromatography

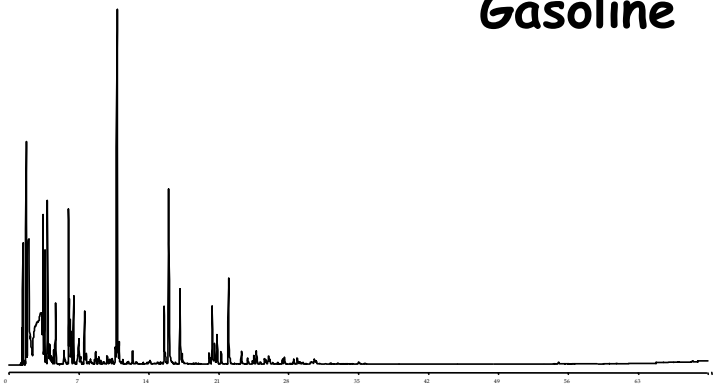
Condensate



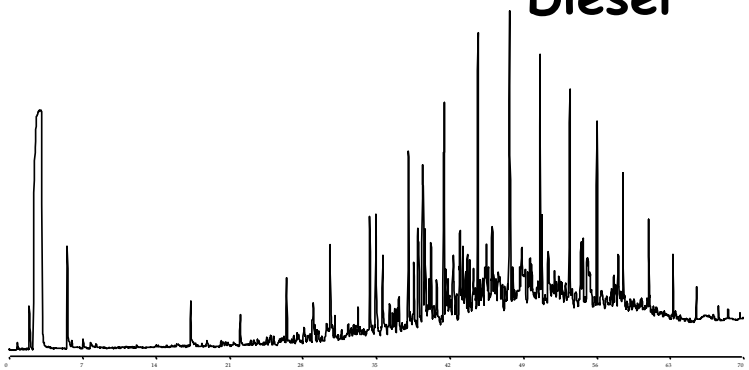
JP4



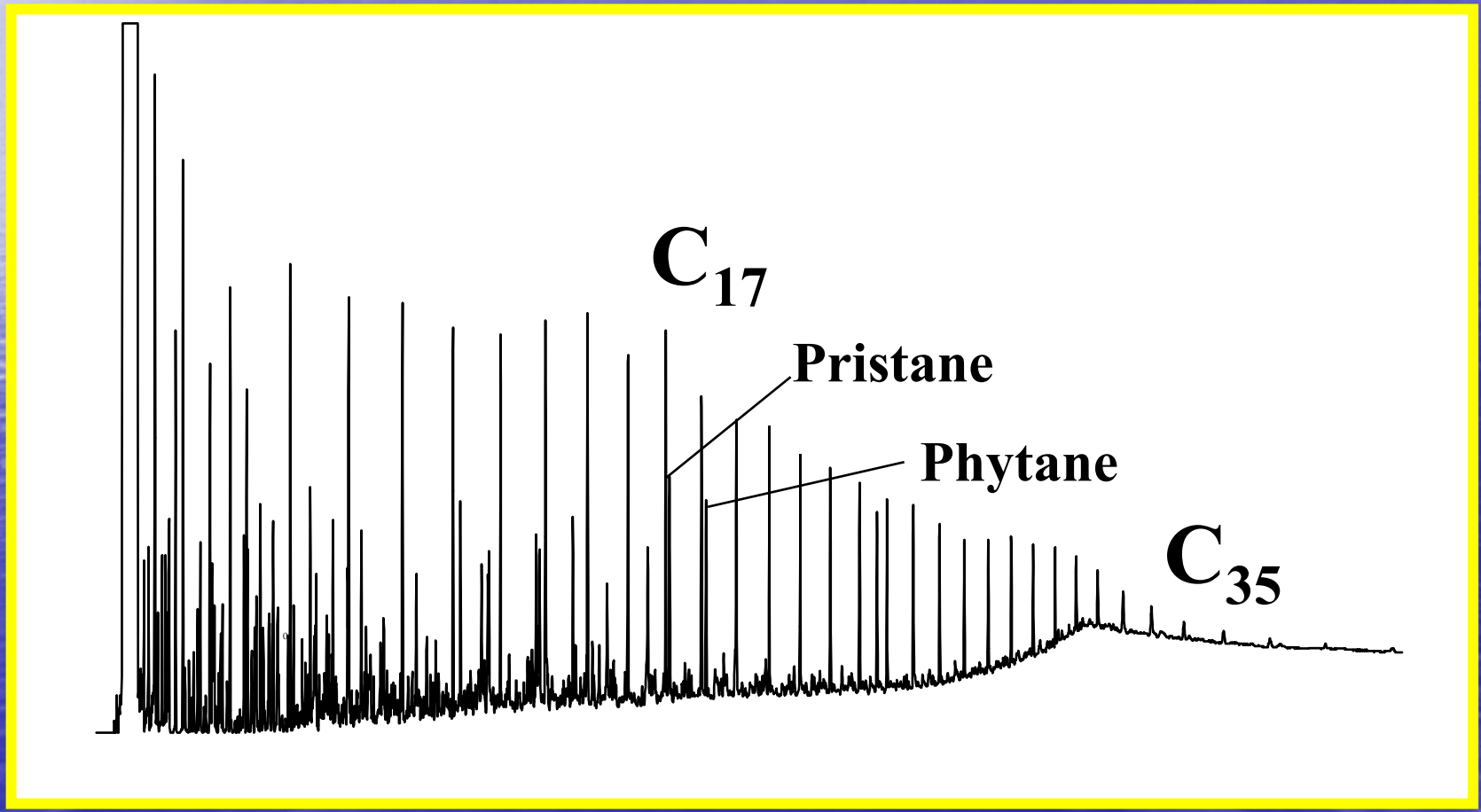
Gasoline



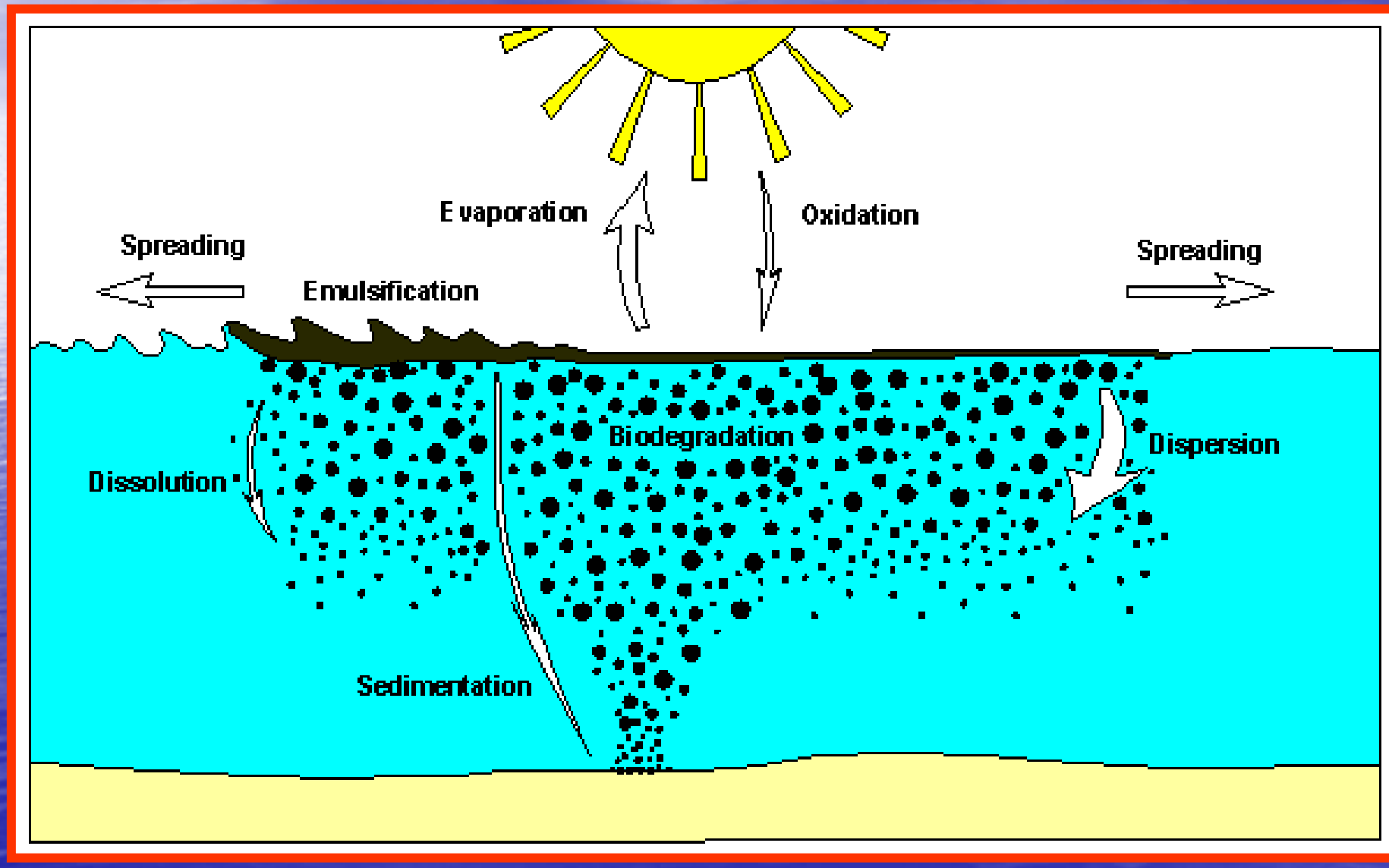
Diesel



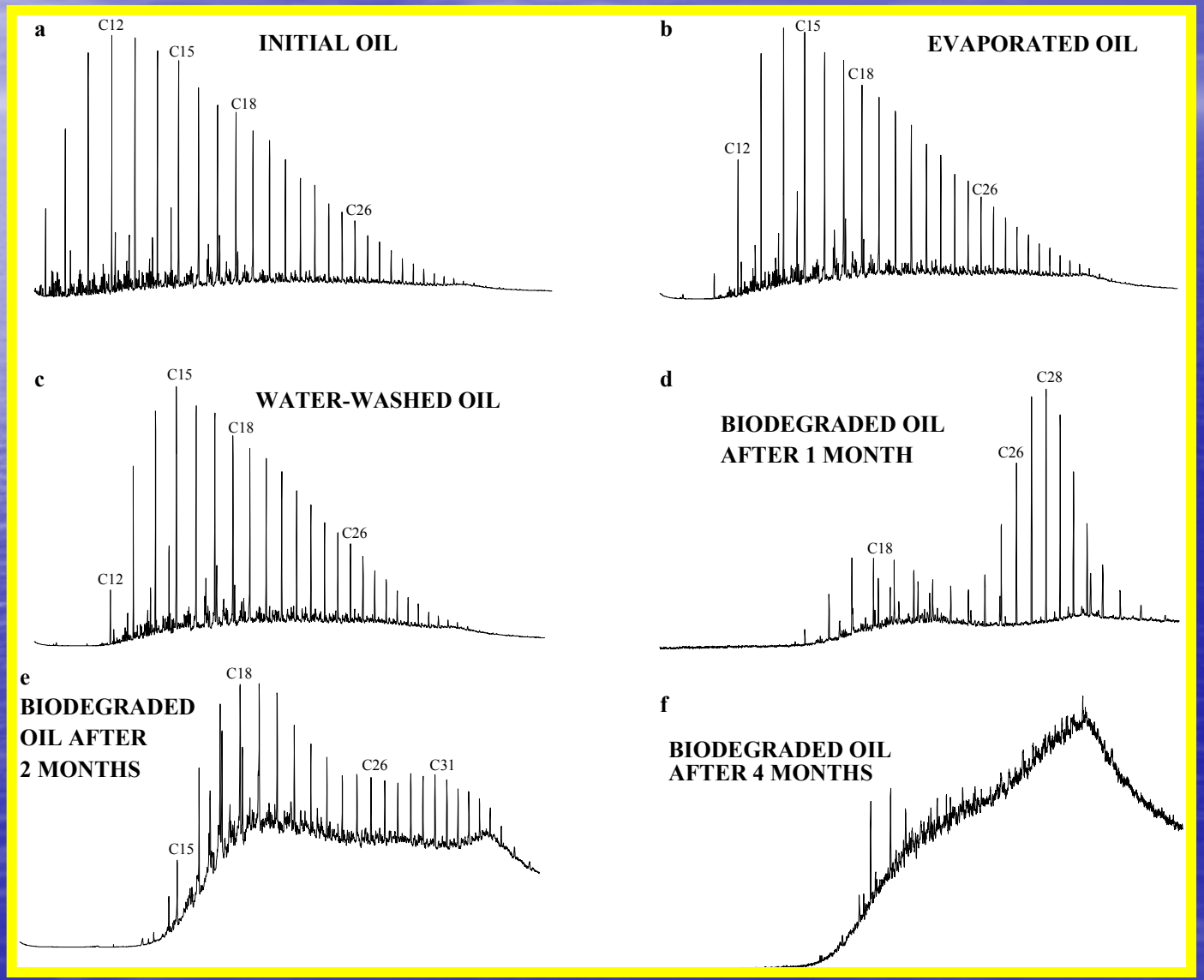
Crude Oil Chromatogram



Processes acting on spilled products



Weathering Effects of Crude Oils

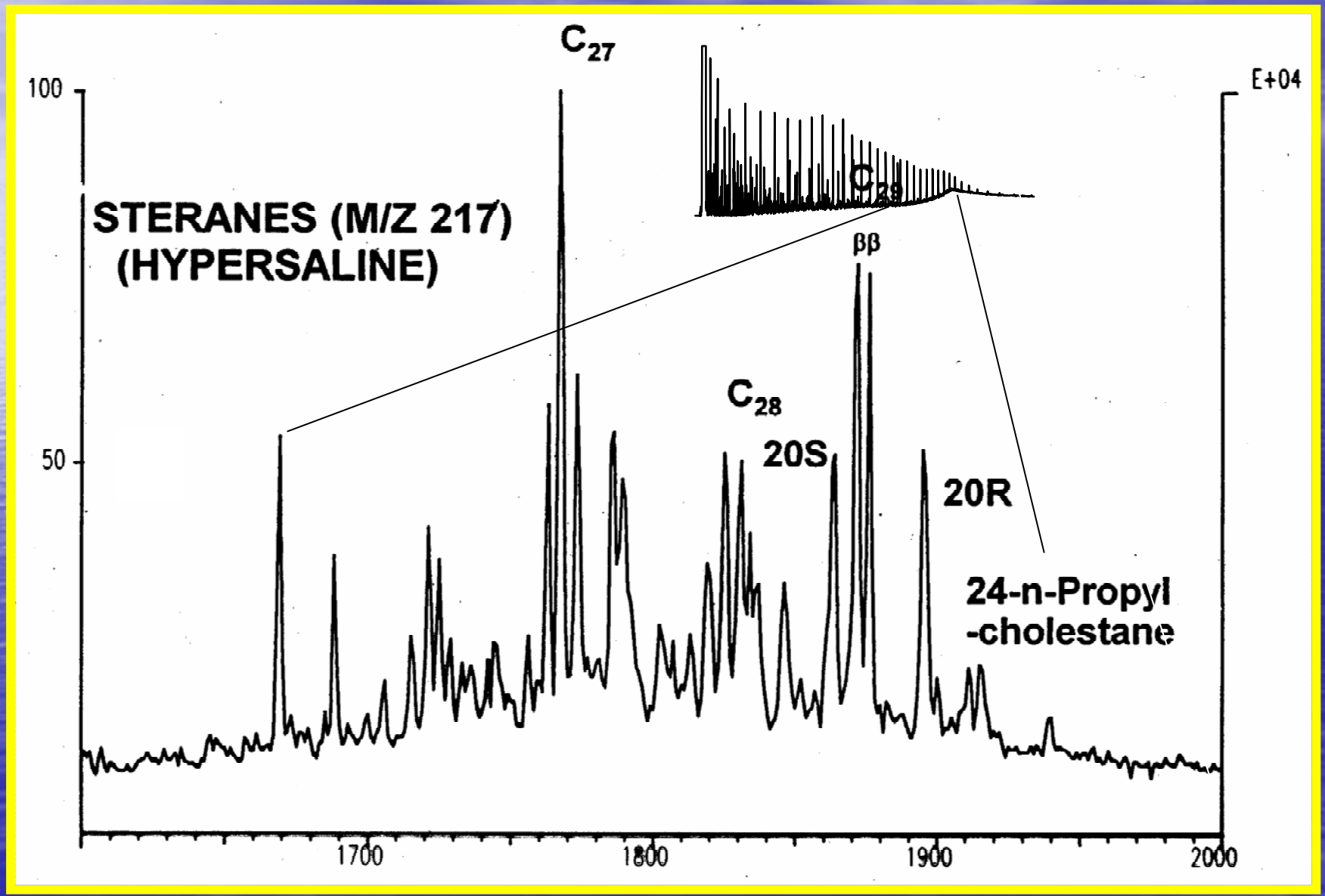


STEROL/STERANE BIOMARKERS

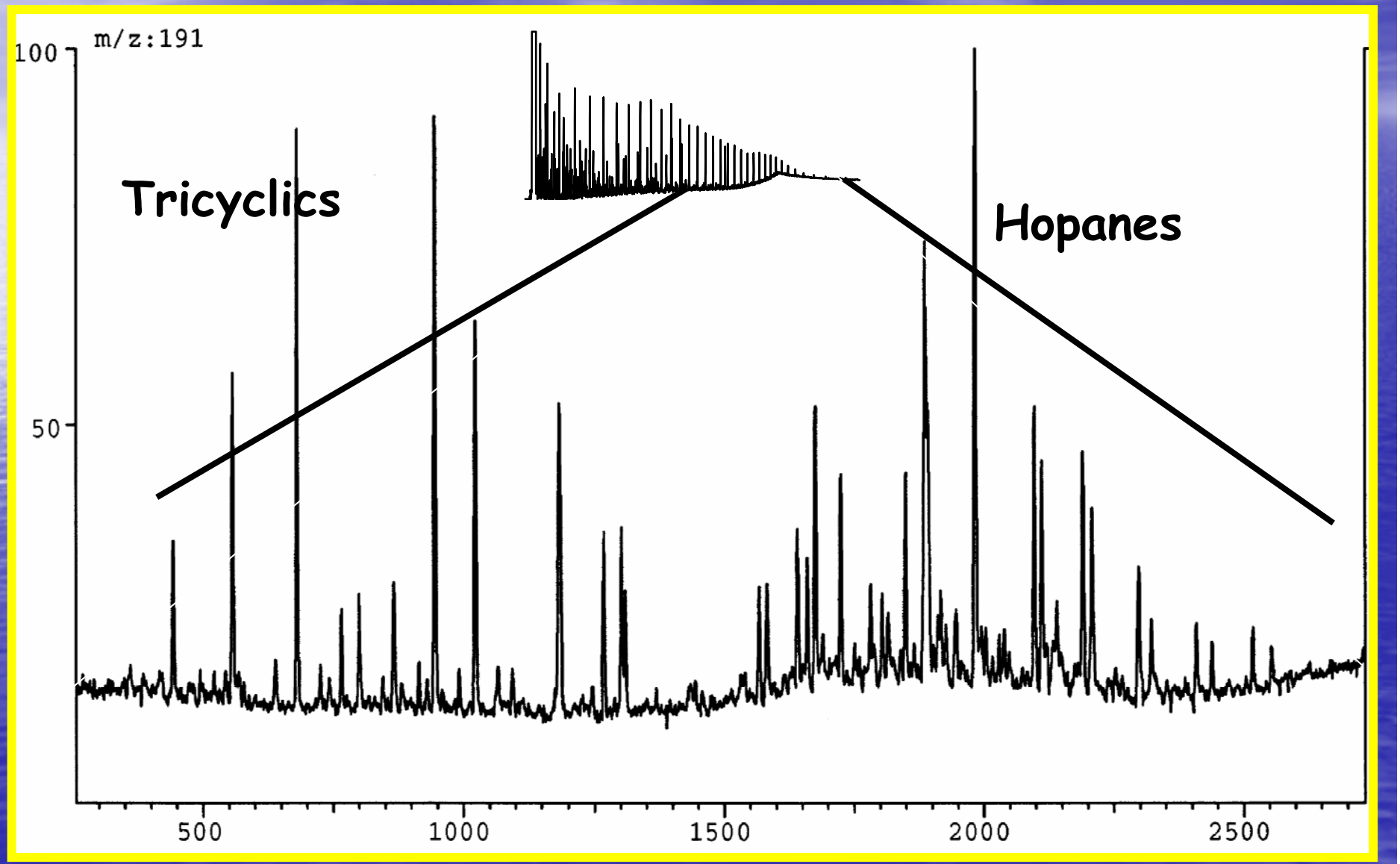
STEROL

STERANE

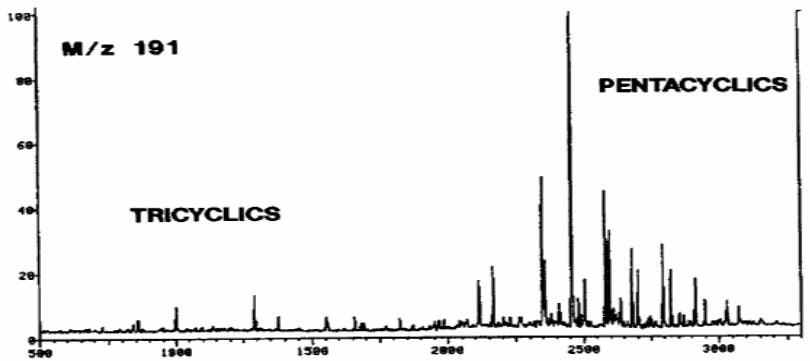
M/z 217 Sterane Chromatogram

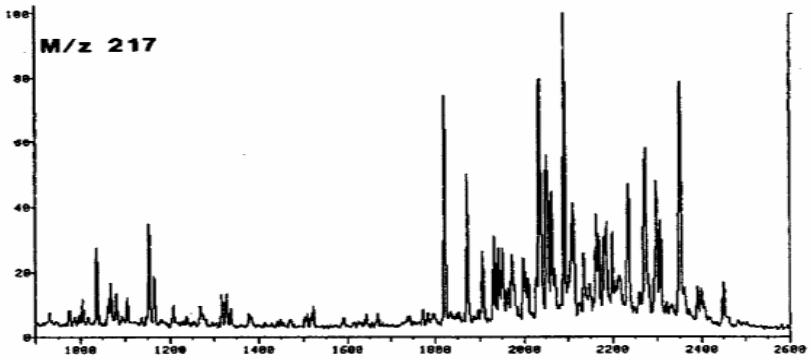


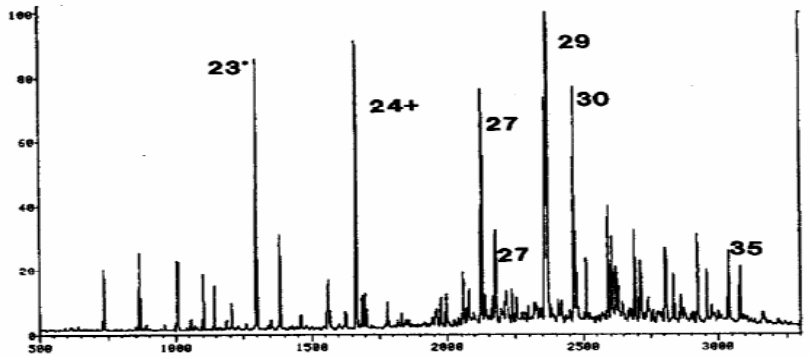
M/z 191 Terpane Chromatogram

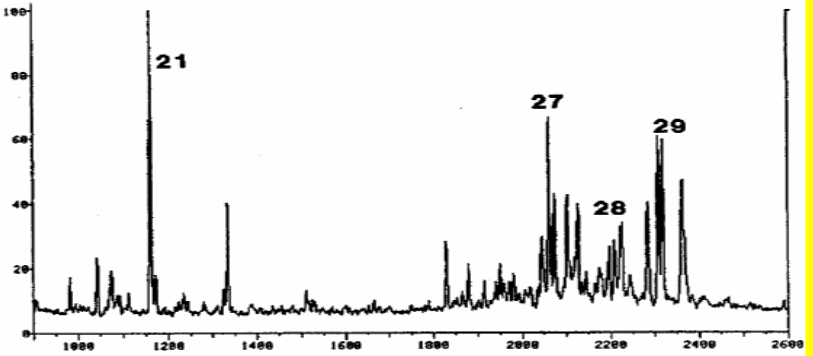


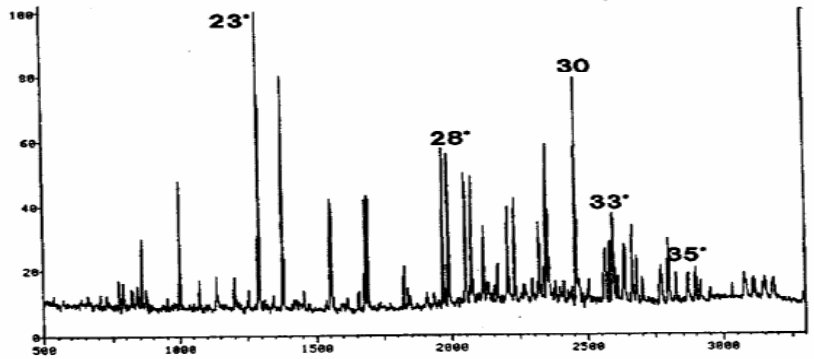
Biomarker Distributions

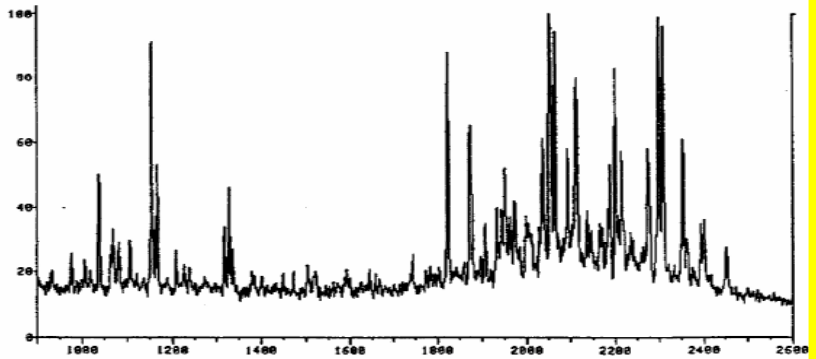










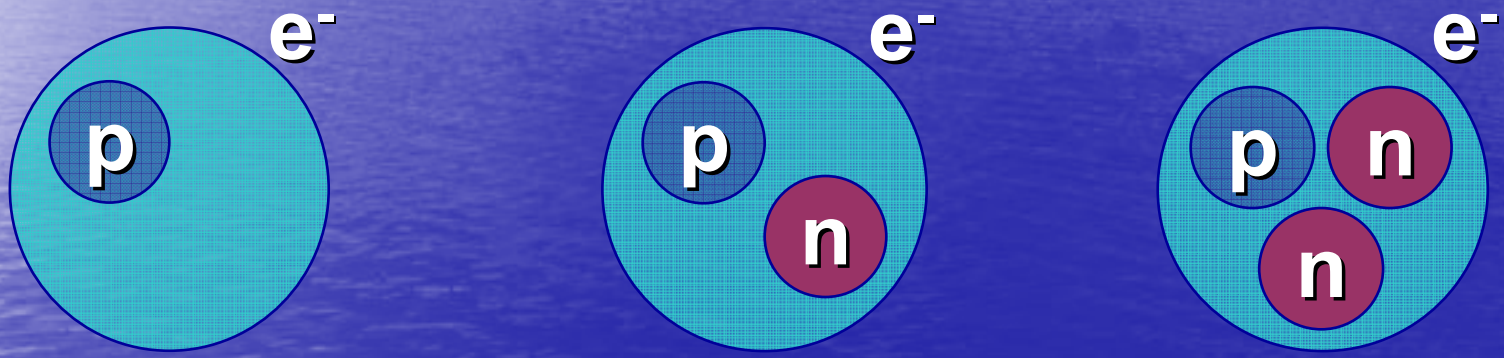


Forensic Geochemistry

- GC and GCMS-powerful, well established, used extensively in litigation.
- Additional evidence required when GC and GCMS are of limited, or no, use-(i.e. single components or refined products.)
- In these situations stable isotopes are being used to provide additional information.

What are Isotopes?

Atoms of same element with differing masses;
same # of protons, different # of neutrons



Hydrogen,
^{1}H
Lighter

Deuterium,
^{2}H, D

Tritium,
^{3}H, T
Heavier

Sum of protons and neutrons is the atomic mass

What are Stable Isotopes?

- Carbon exists as two stable isotopes, ^{12}C and ^{13}C which differ in the number of neutrons they contain. ^{12}C has 6 electrons, 6 protons and 6 neutrons; ^{13}C has 7 neutrons. ^{1}H has 1 electron and 1 proton and ^{2}H has 1 electron, 1 proton and 1 neutron.

Other Isotopes of Environmental Interest

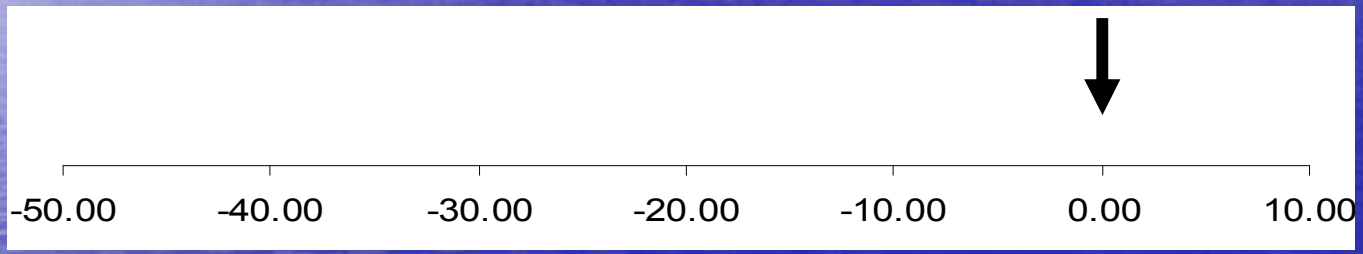
- Chlorine ($^{35}Cl/^{37}Cl$- 75.53/24.47)
- Sulfur ($^{32}S/^{34}S$-94.02/3.21)
- Nitrogen ($^{14}N/^{15}N$-99.64/0.36)

Data Output-Isotope Scale

$$\delta^{13}C = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$

$R = {}^{13}C/{}^{12}C$

PDB Standard



Isotopically lighter

Isotopically depleted

More negative

Forensic Geochemistry

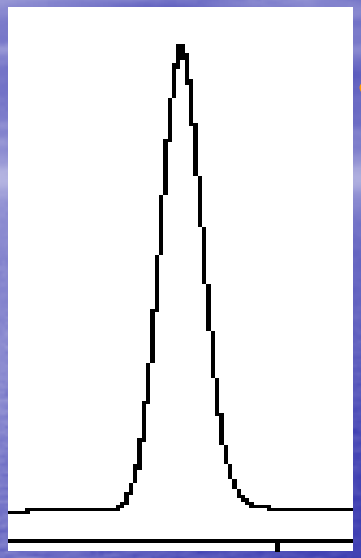
- Stable isotopes utilized in geochemical applications for more than 50 years.

Single Component Contaminants

GC-FID

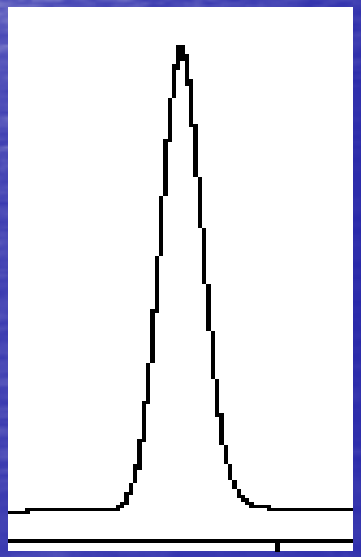
or

GCMS



Source A

Toluene



Source B

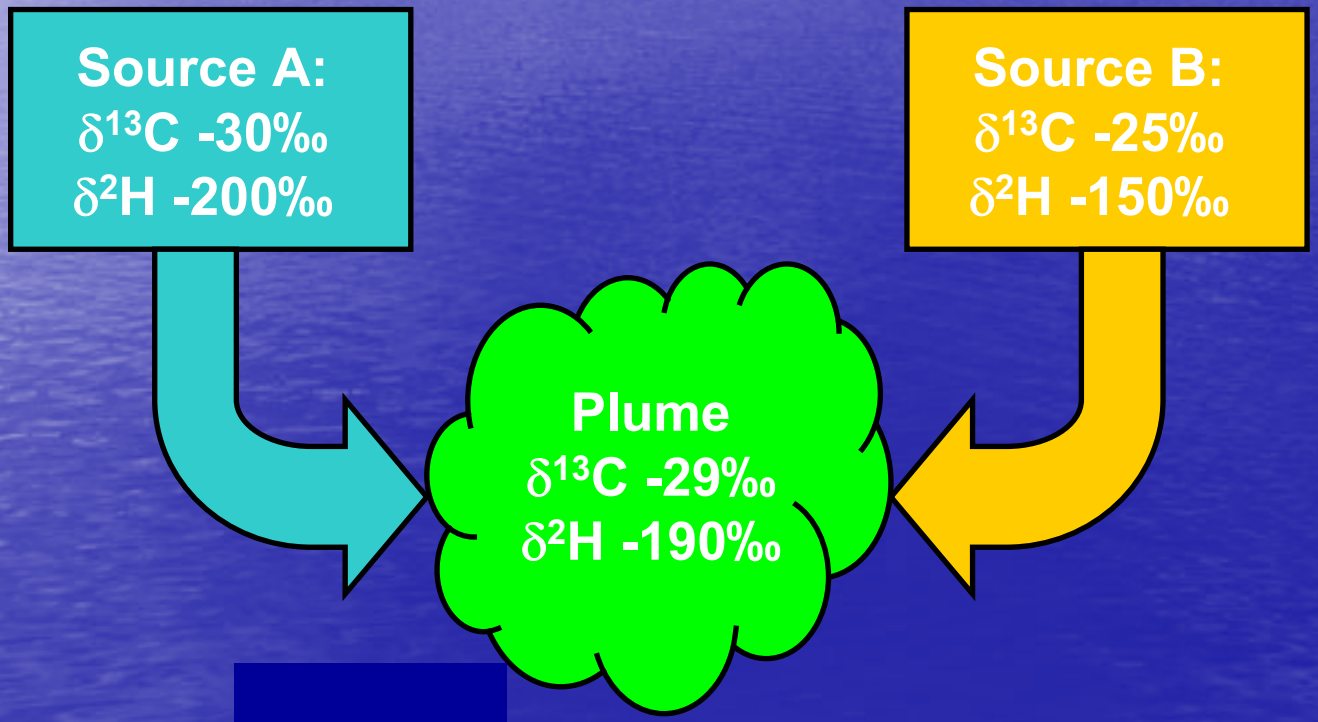
Toluene

When the contaminant is a single component- how can you distinguish one from another? GC and GCMS no help.

Isotopes may be different

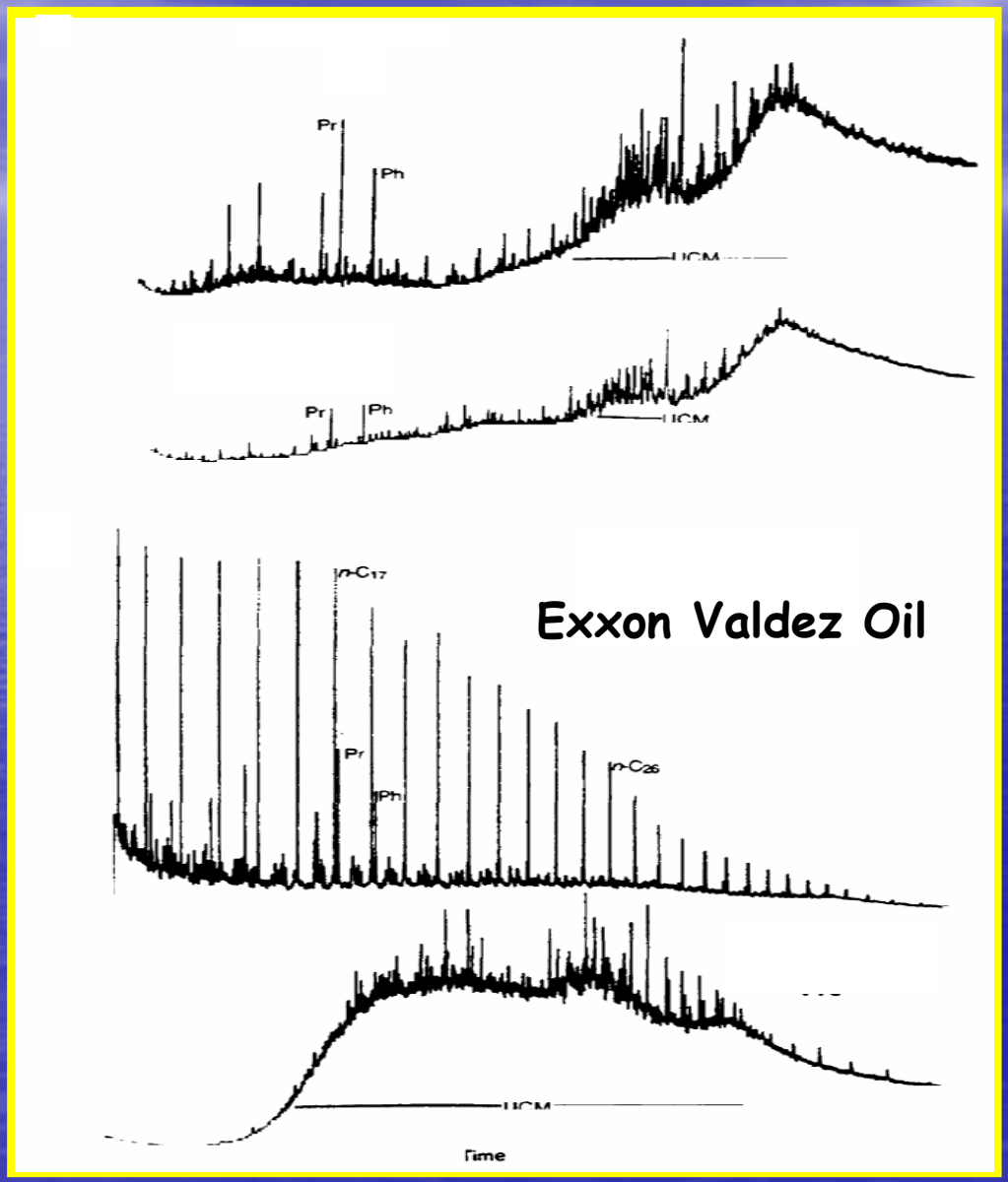
Allocation – 2 Sources

Toluene $\delta^{13}C$ or $\delta^{2}H$: 2 sources, single tracer

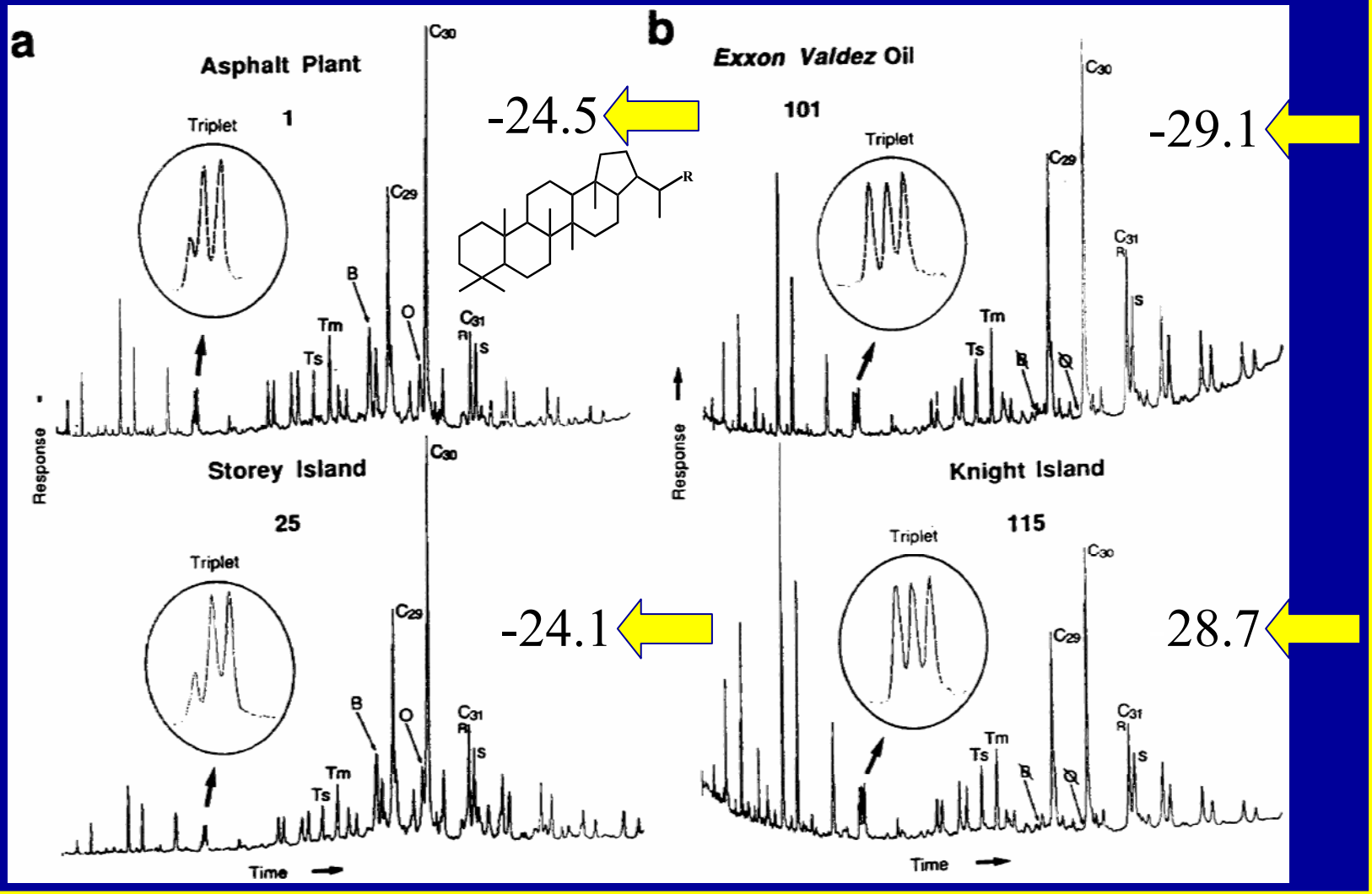


Plume = 80% Source A, 20% Source B

Prince William Sound Residues



Terpanes in Prince William Sound Residues



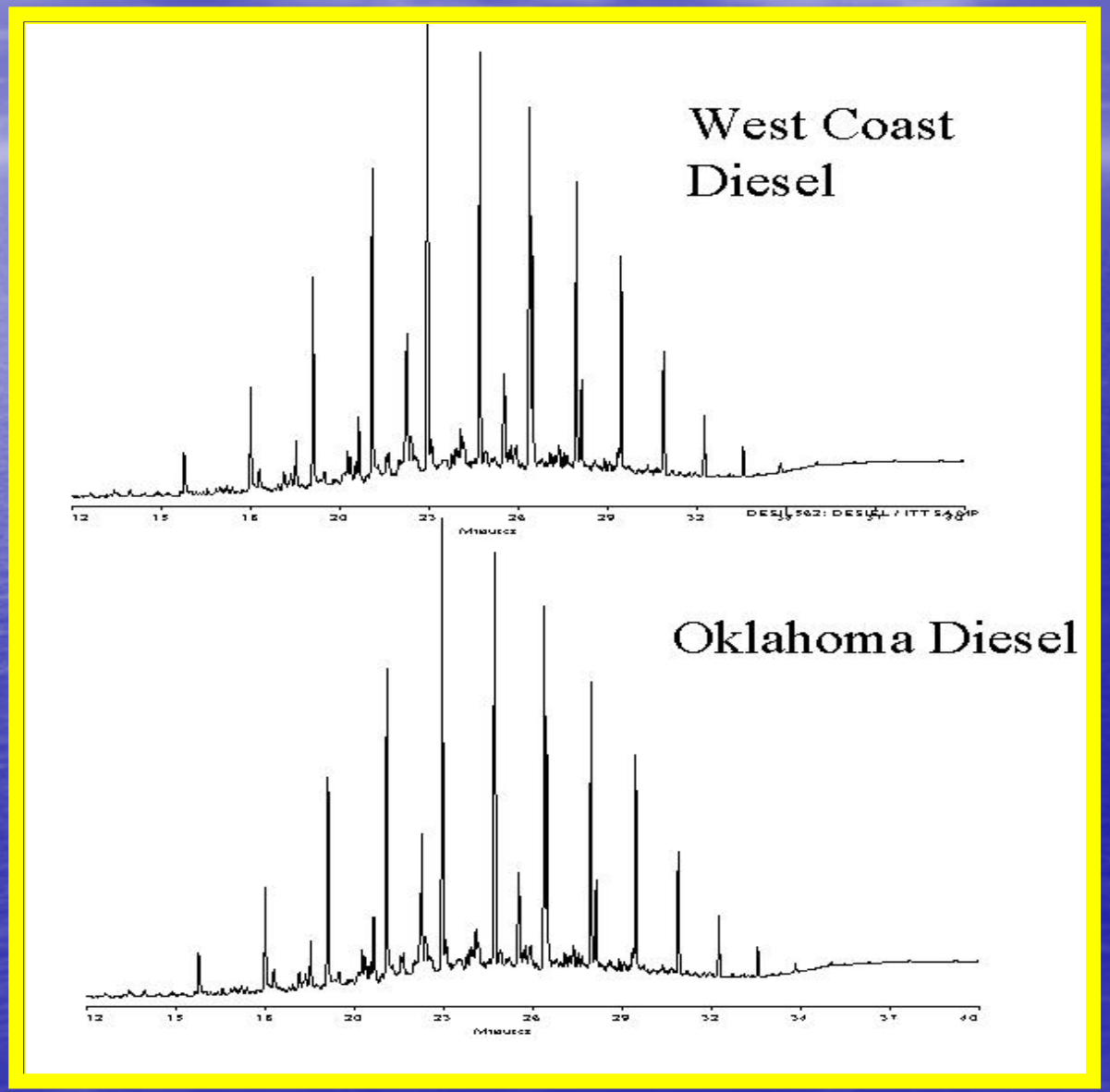
Forensic Geochemistry

- More recently the combination of gas chromatography with isotope ratio mass spectrometry (GCIRMS) has lead to a significant increase in the number of isotopic applications.

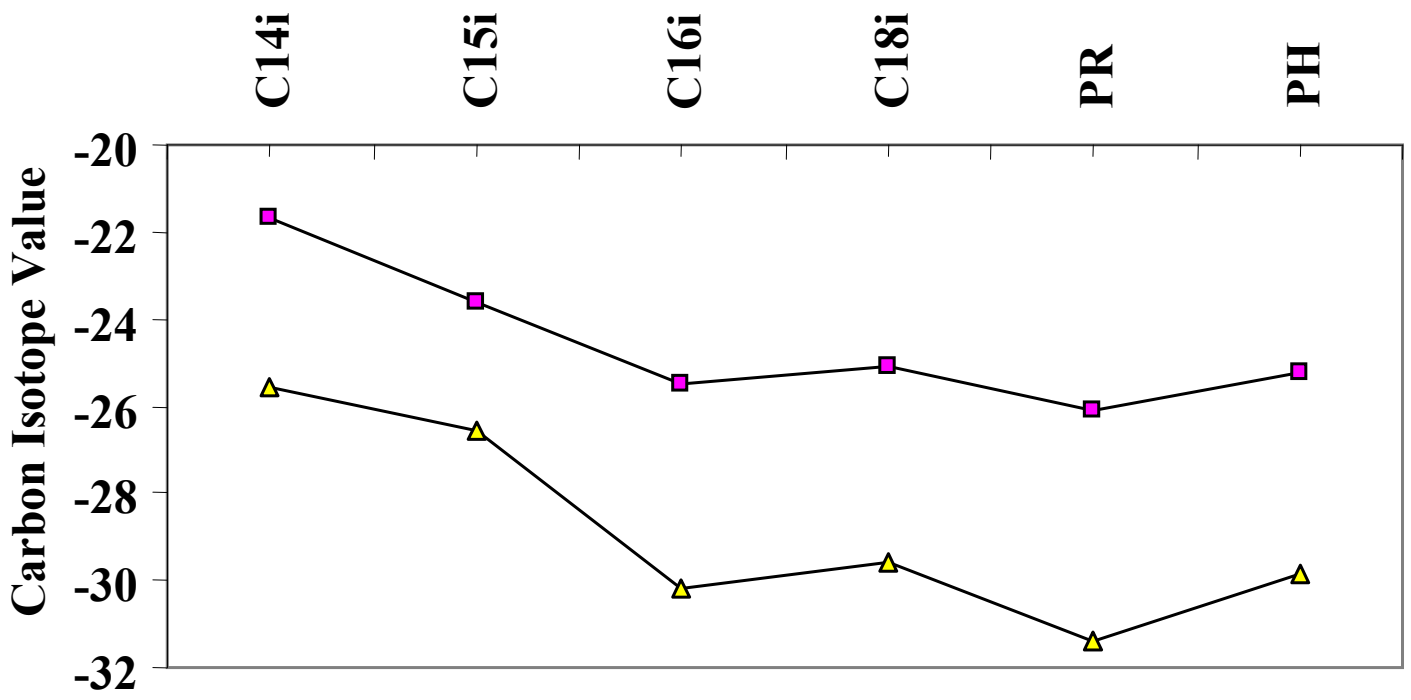
Refined Products

- For example diesel derived from different crude oils can be differentiated using carbon and hydrogen isotopic compositions.
- Isotope data can be supported by various biomarkers not commonly used in environmental studies: sesquiterpanes; adamantanes; and degraded steranes.

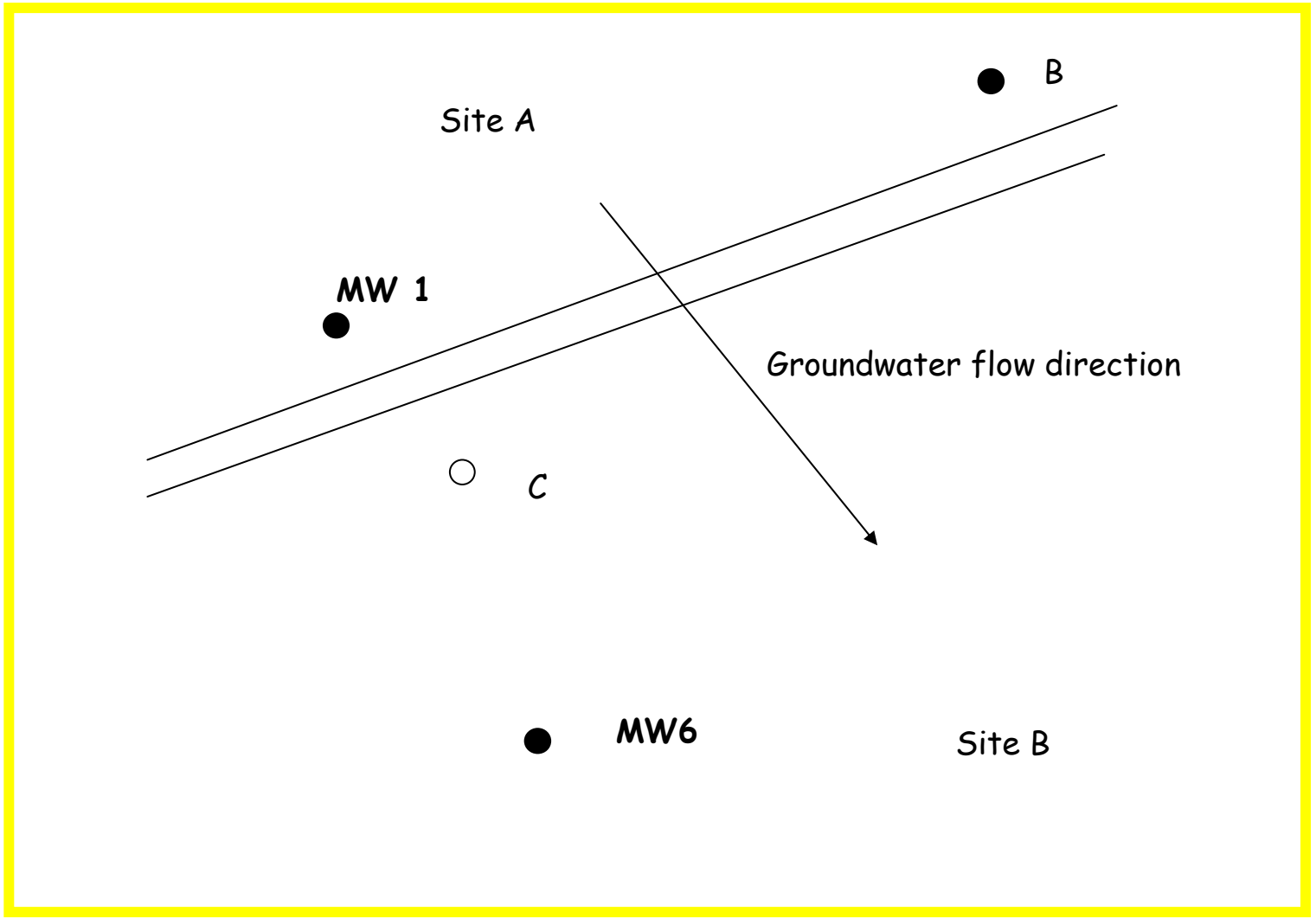
Diesel Fingerprints



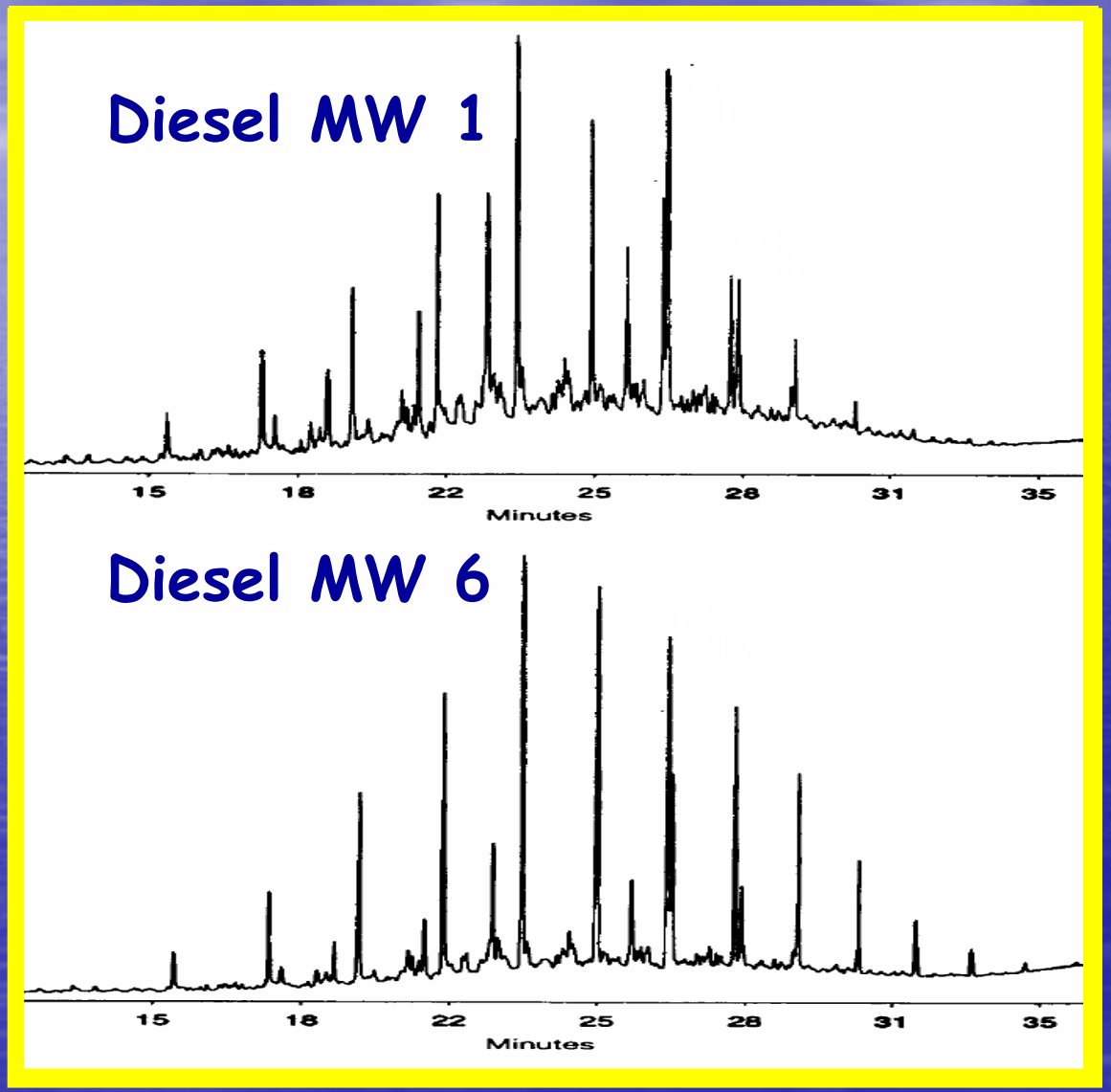
Isoprenoid Isotope Fingerprints



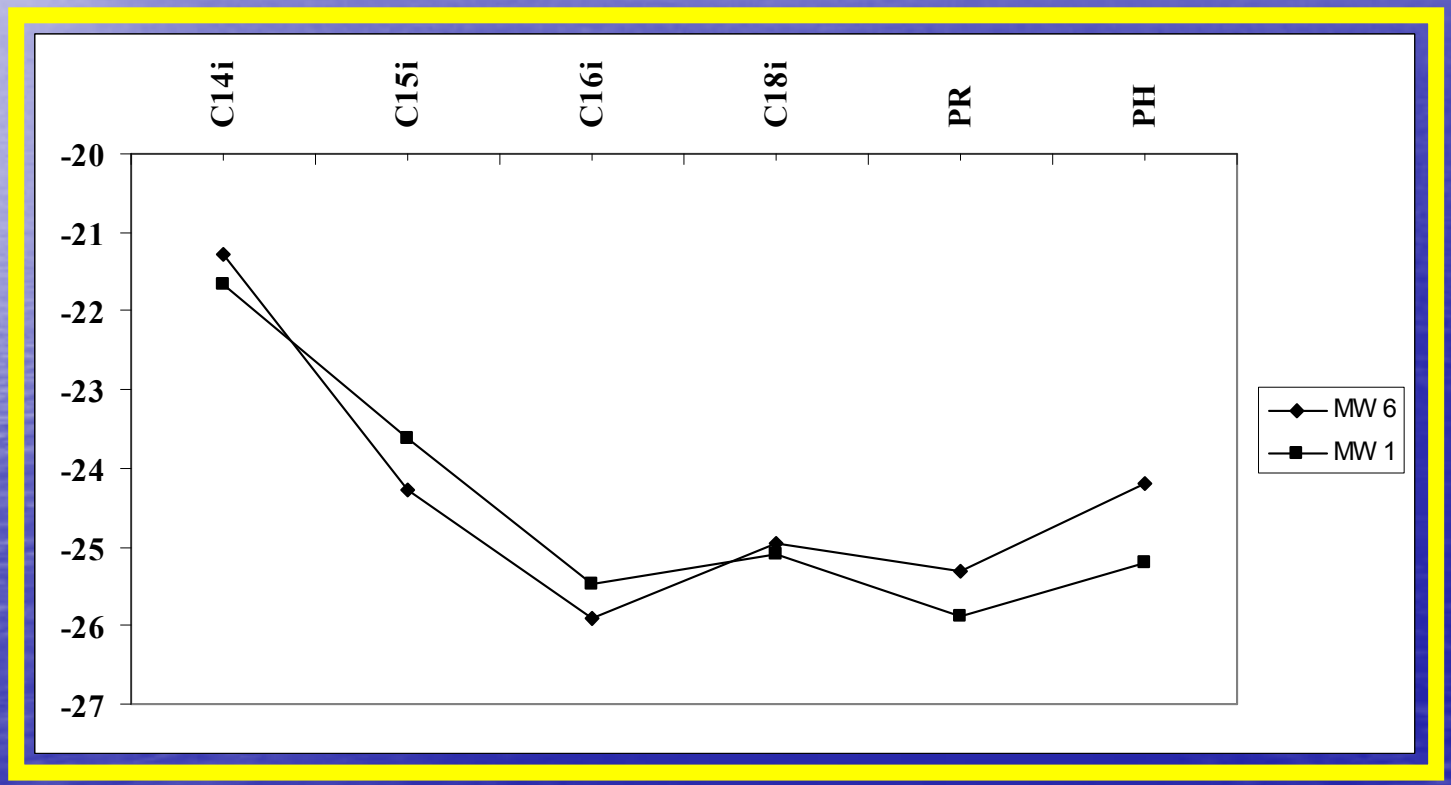
Forensic Geochemistry



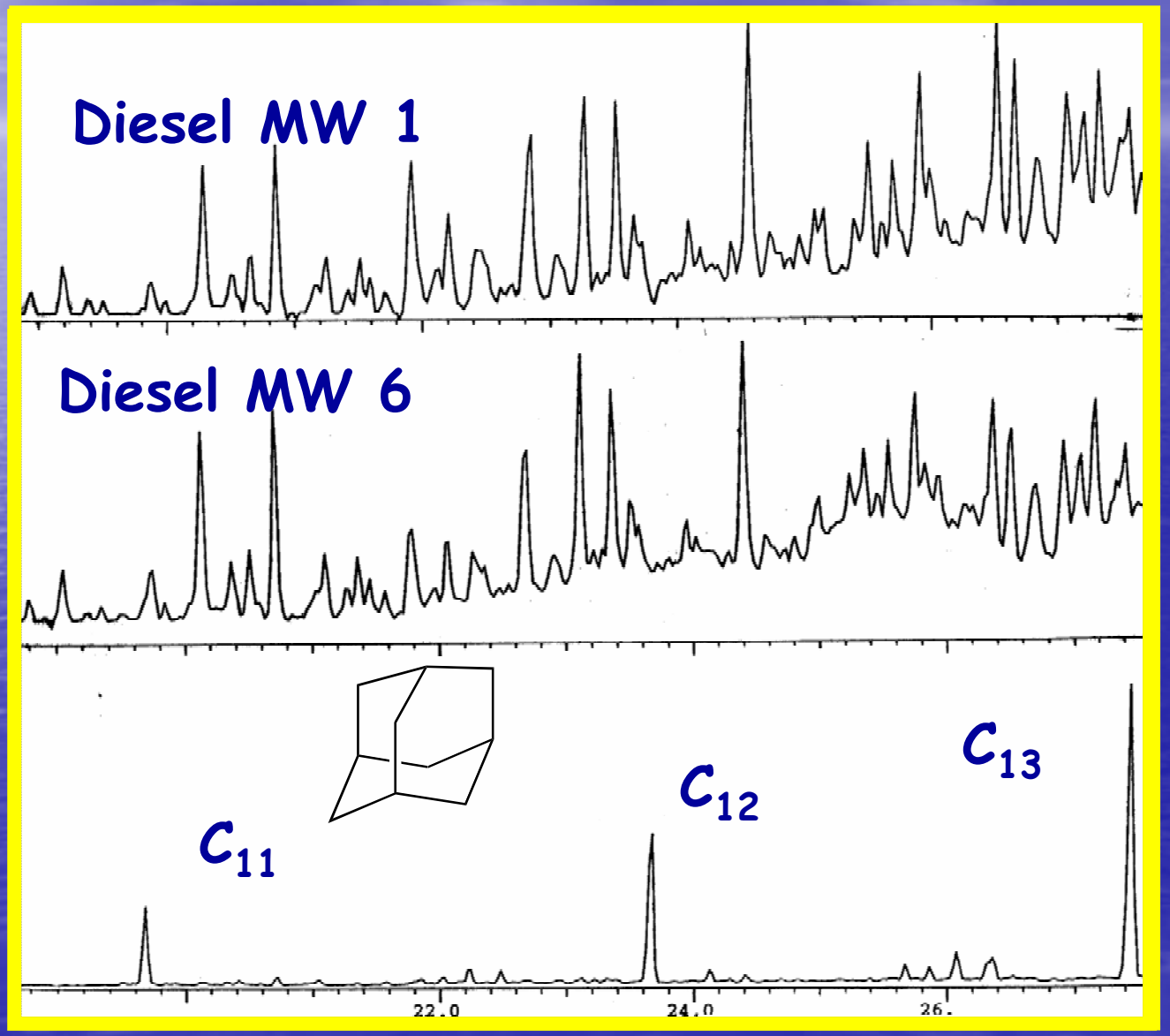
Weathered and Unweathered Diesel



Carbon Isotope Values for Isoprenoids



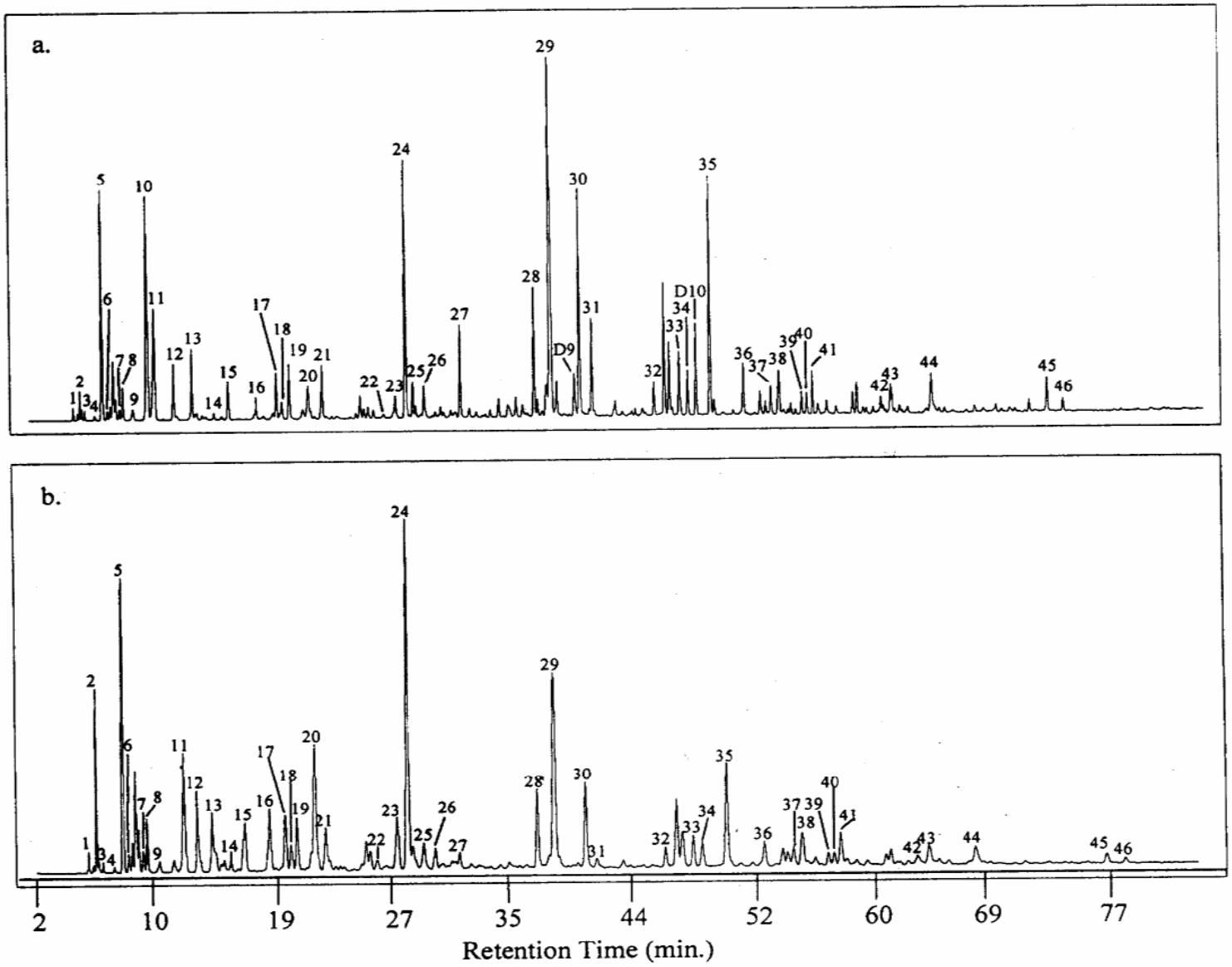
Adamantanes in Diesel Fuels



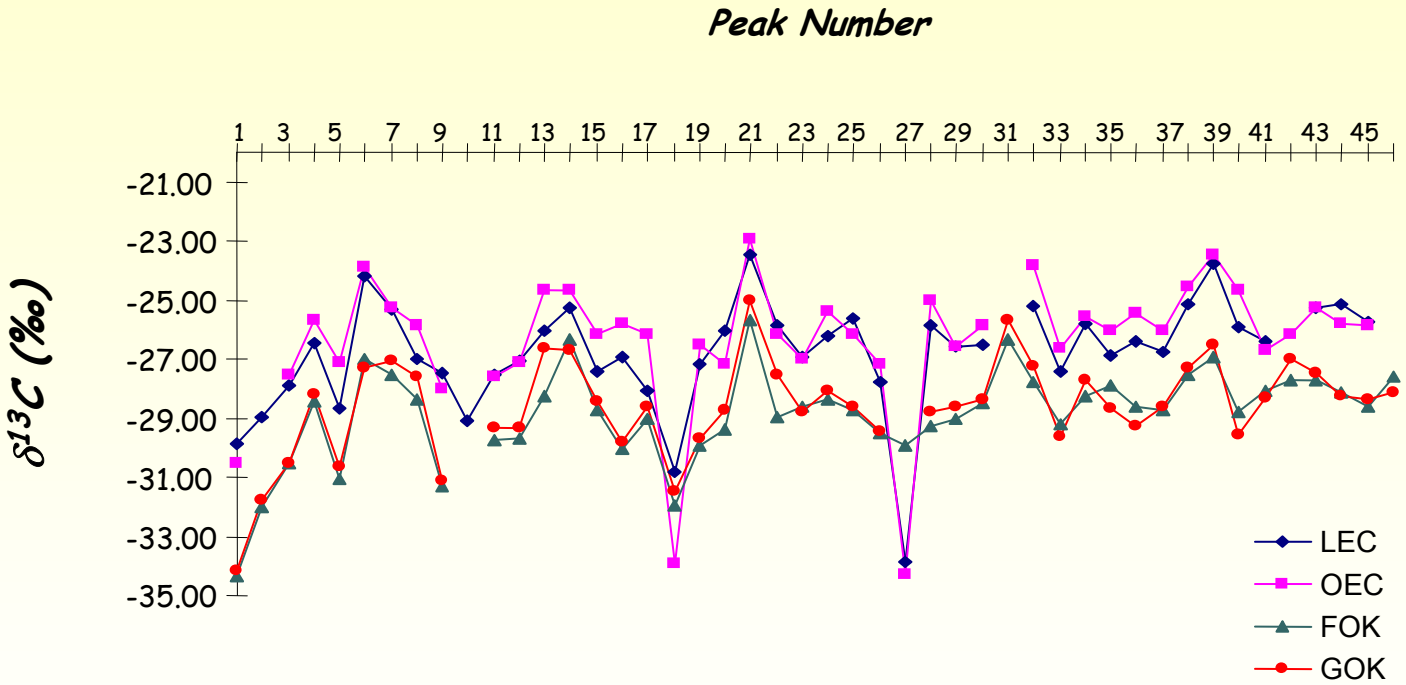
Gasolines

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

Comparison of Gasolines by GC



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



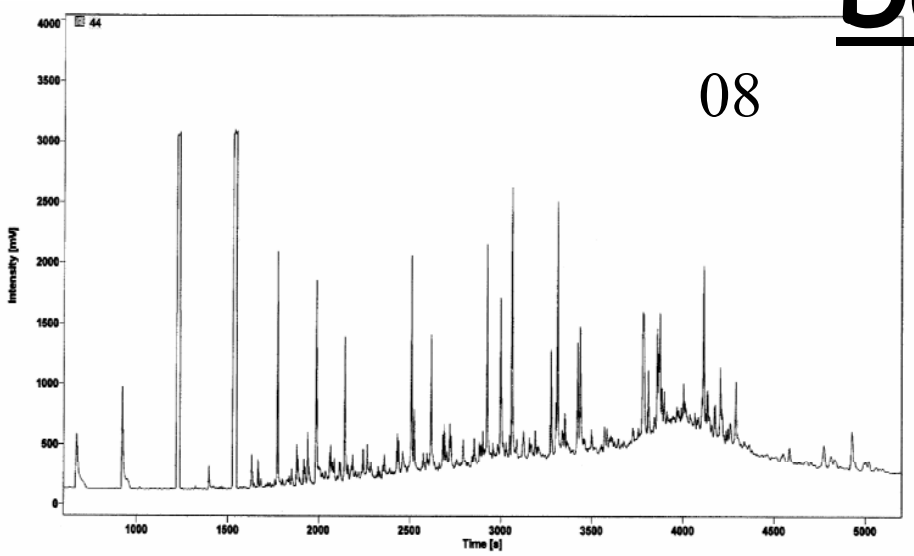
This figure shows the carbon isotopic fingerprint of gasolines sampled from Oklahoma and from the East Coast and demonstrates that these gasolines are significantly different in terms of isotopic composition and can be discriminated from each other on this basis. The peak numbers are identified in the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

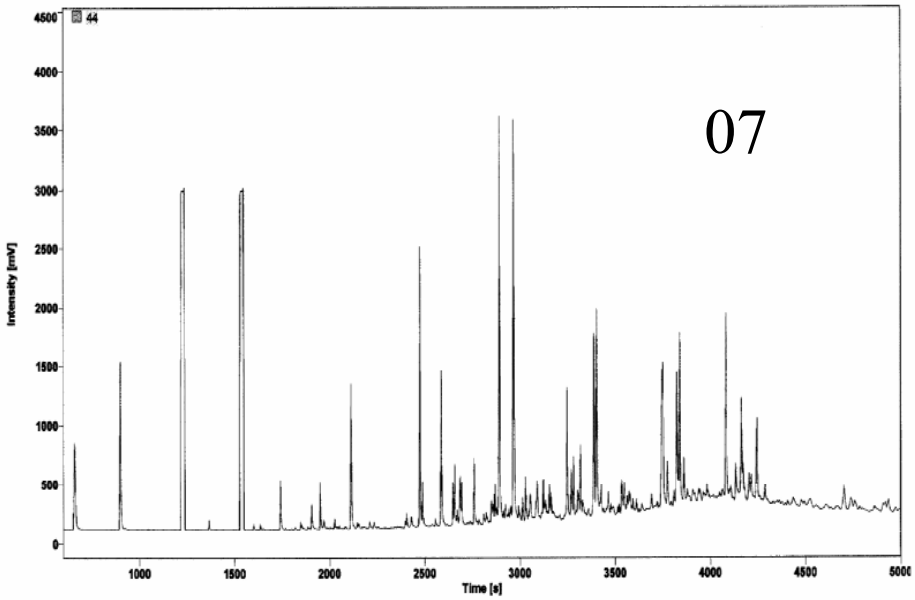
Coal Tar-PAHs

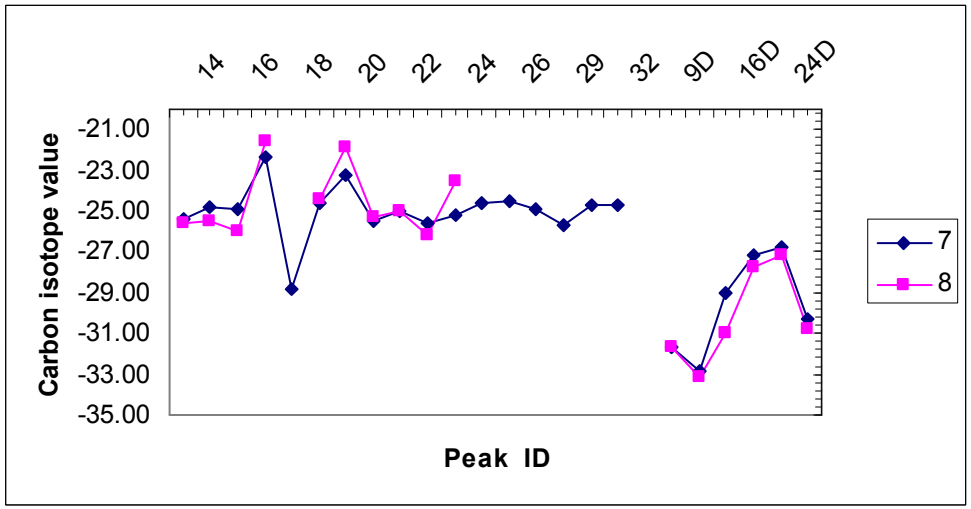
PAHs and Stable Isotopes

- Current interest is in discriminating PAHs derived from former manufactured gas plant (MGP) wastes versus those from general urban background aromatics
- Urban backgrounds have a fairly narrow range and small differences may be related to source differences

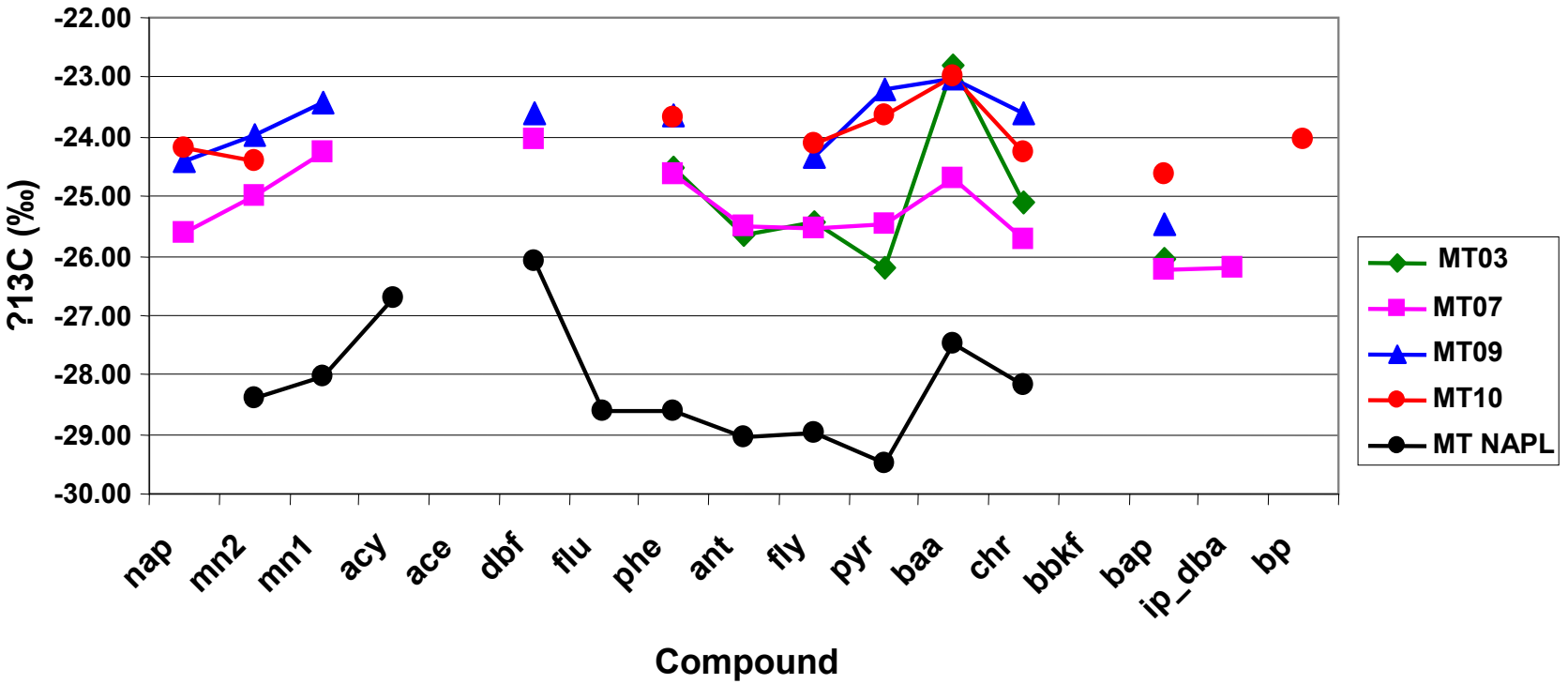
PAHs-Combined GC and GCIRMS Data



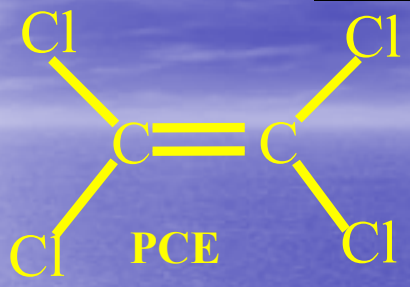




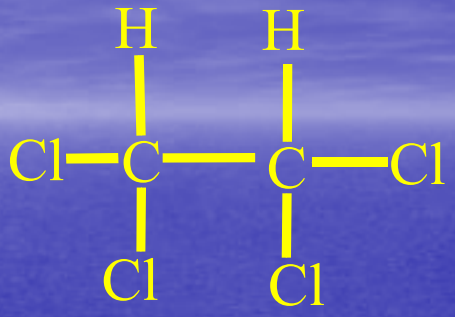
Comparison of MT Soil and NAPL CSIR Results



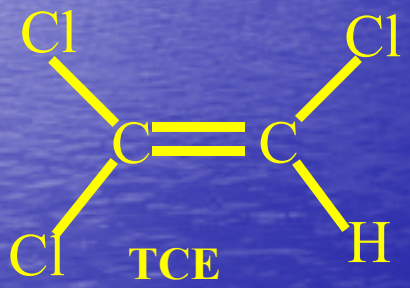
Chlorinated Solvents-Source Structures



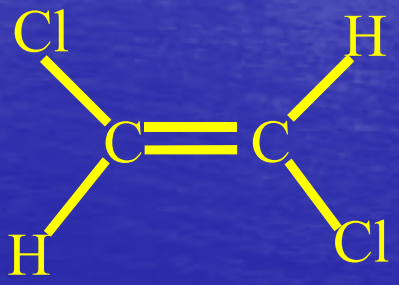
PCE



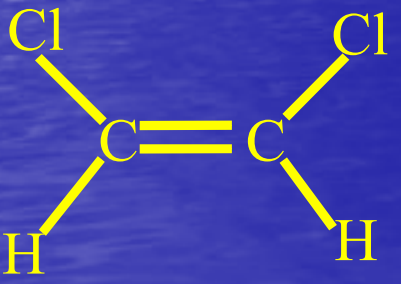
1,1,2,2-PCA



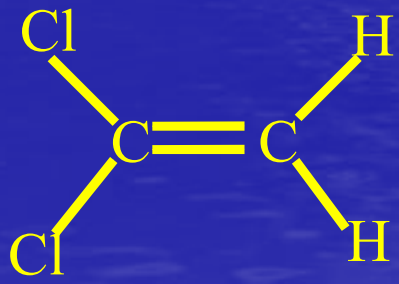
TCE



trans-1,2-DCE

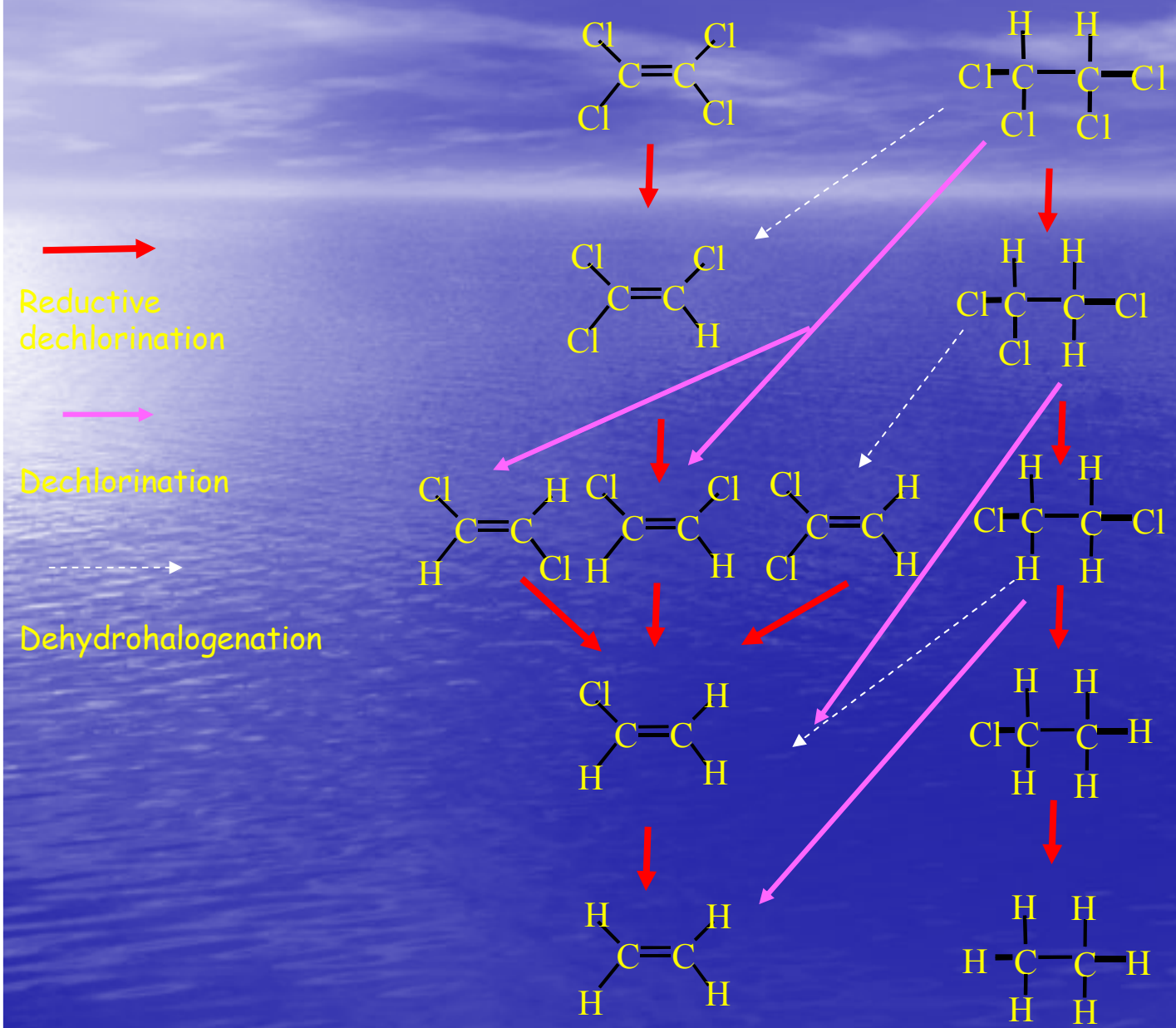


cis-1,2-DCE



1,1-DCE

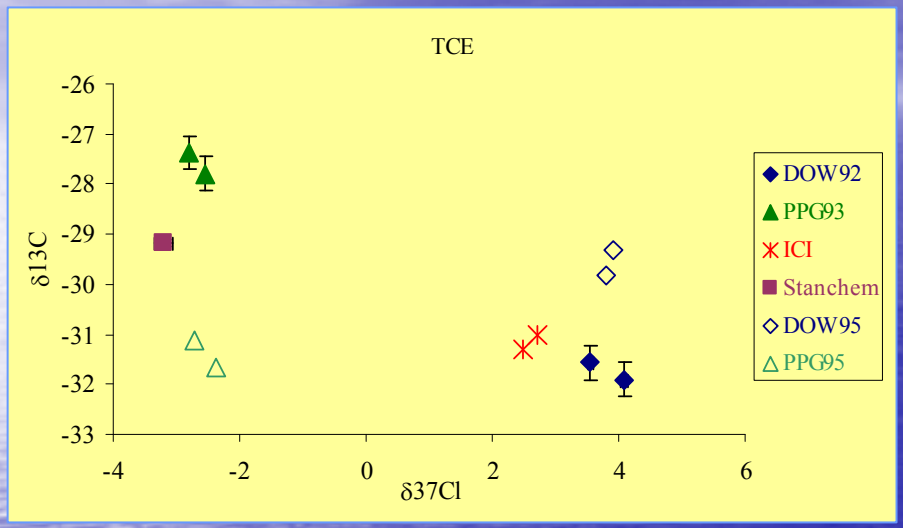
Degradation of Chlorinated Solvents



Chlorinated Solvents

- Source differentiation of chlorinated solvents-limited success due to small range of source values.
- Monitoring natural attentuation - significant success-isotopic enrichment
- Differentiation of abiotic v. biotic transformation-promising laboratory results now being applied to field studies

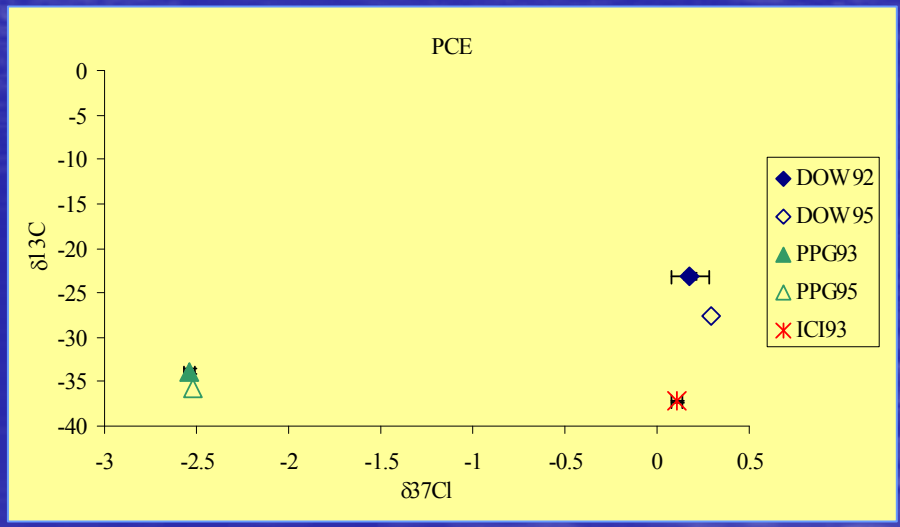
C-Cl information



Each compound from each manufacturer show a specific isotopic composition on C and Cl.

The variations between years are due to changes in the isotopic composition of products used in the synthesis of PCE and TCE.

The idea was to conduct this kind of survey study with TCE and PCE coming from different manufacturers (DOW, PPG, ICI)…



From Beneteau et al., 1999; Warmerdarm et al., 1995

TCE Degradation Site Study

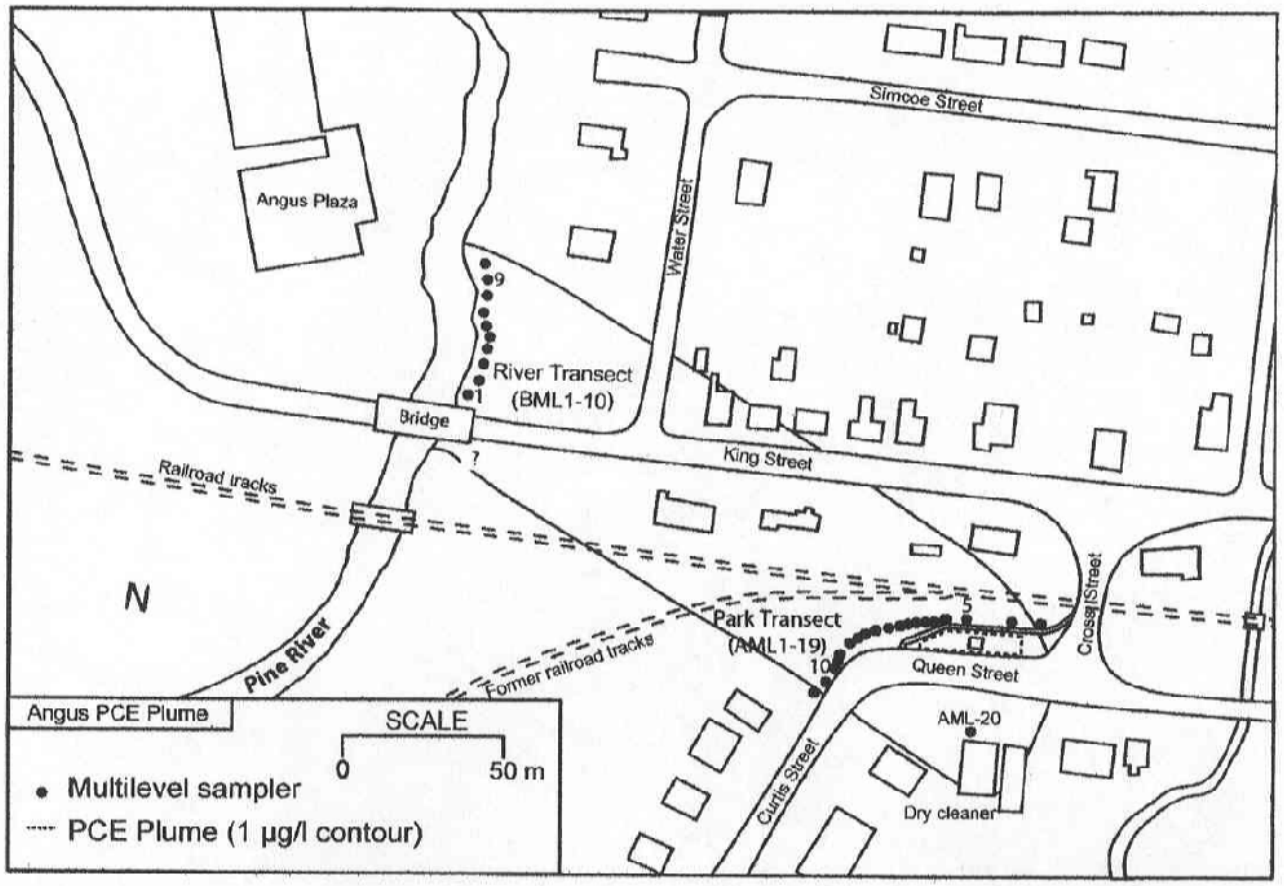
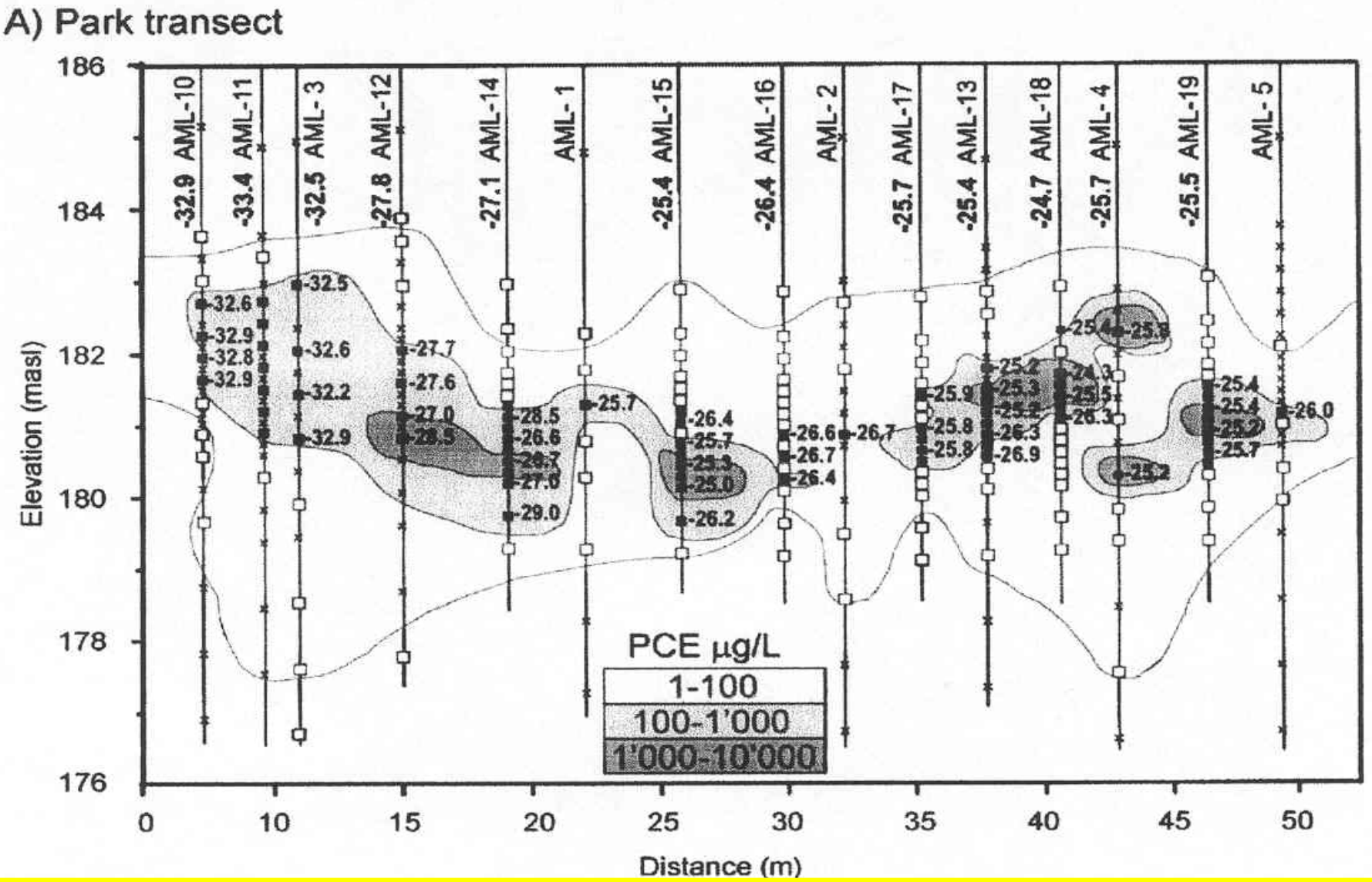


Fig. 2. Map of Angus field site with locations of multilevel samplers (circles) at park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

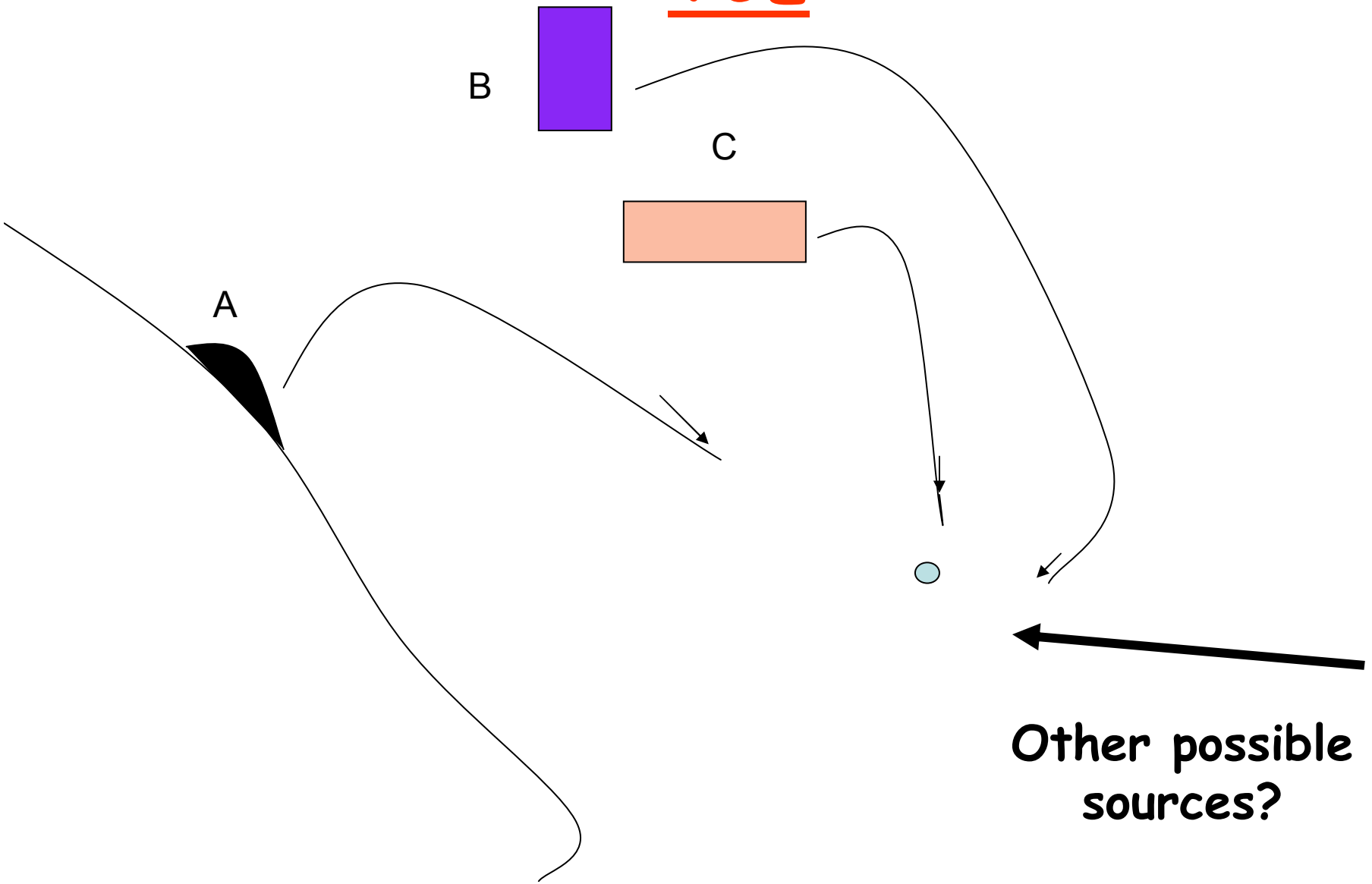
Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.

TCE Degradation Site Study

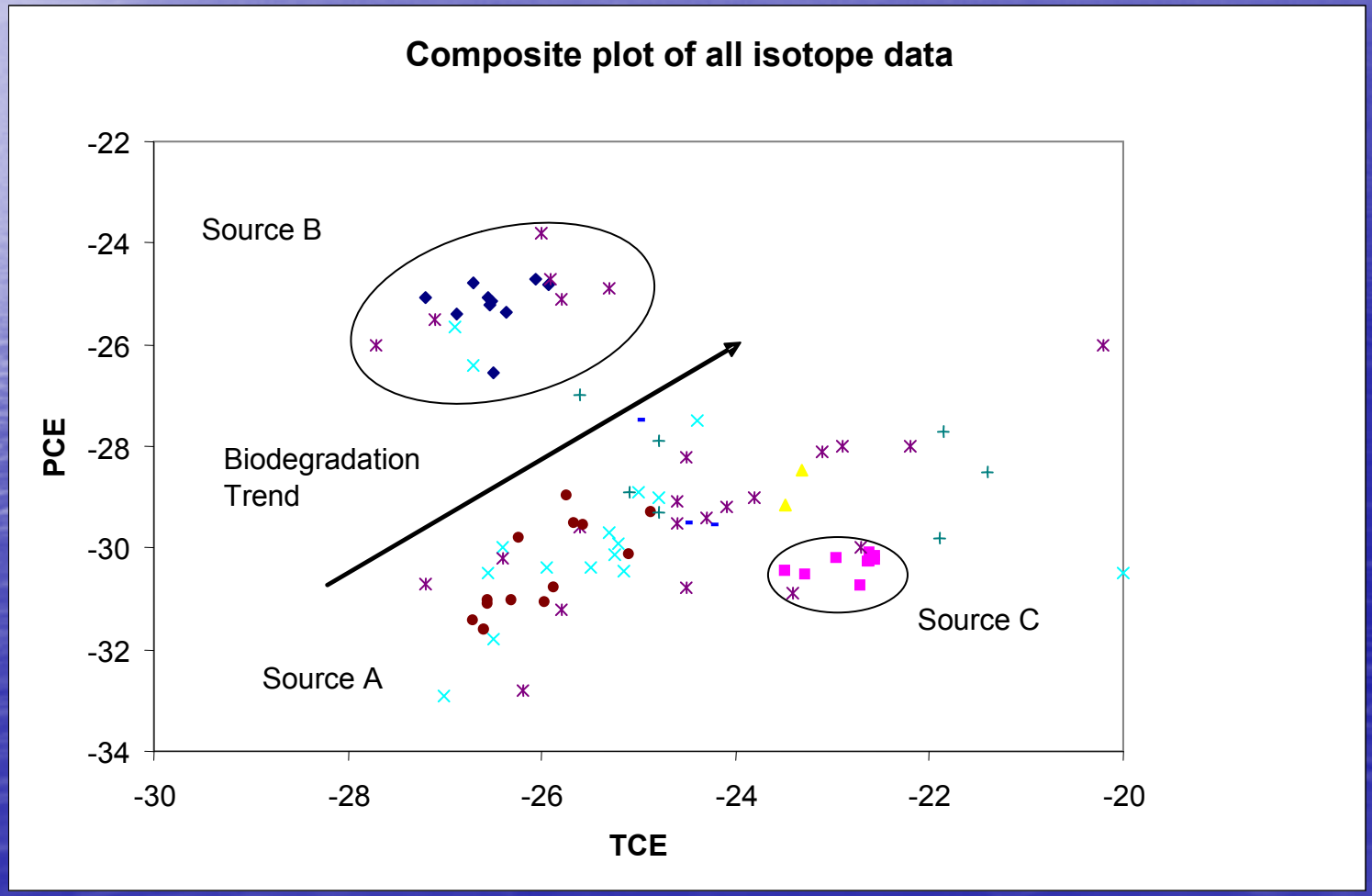


Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.

Source Discrimination of PCE and TCE



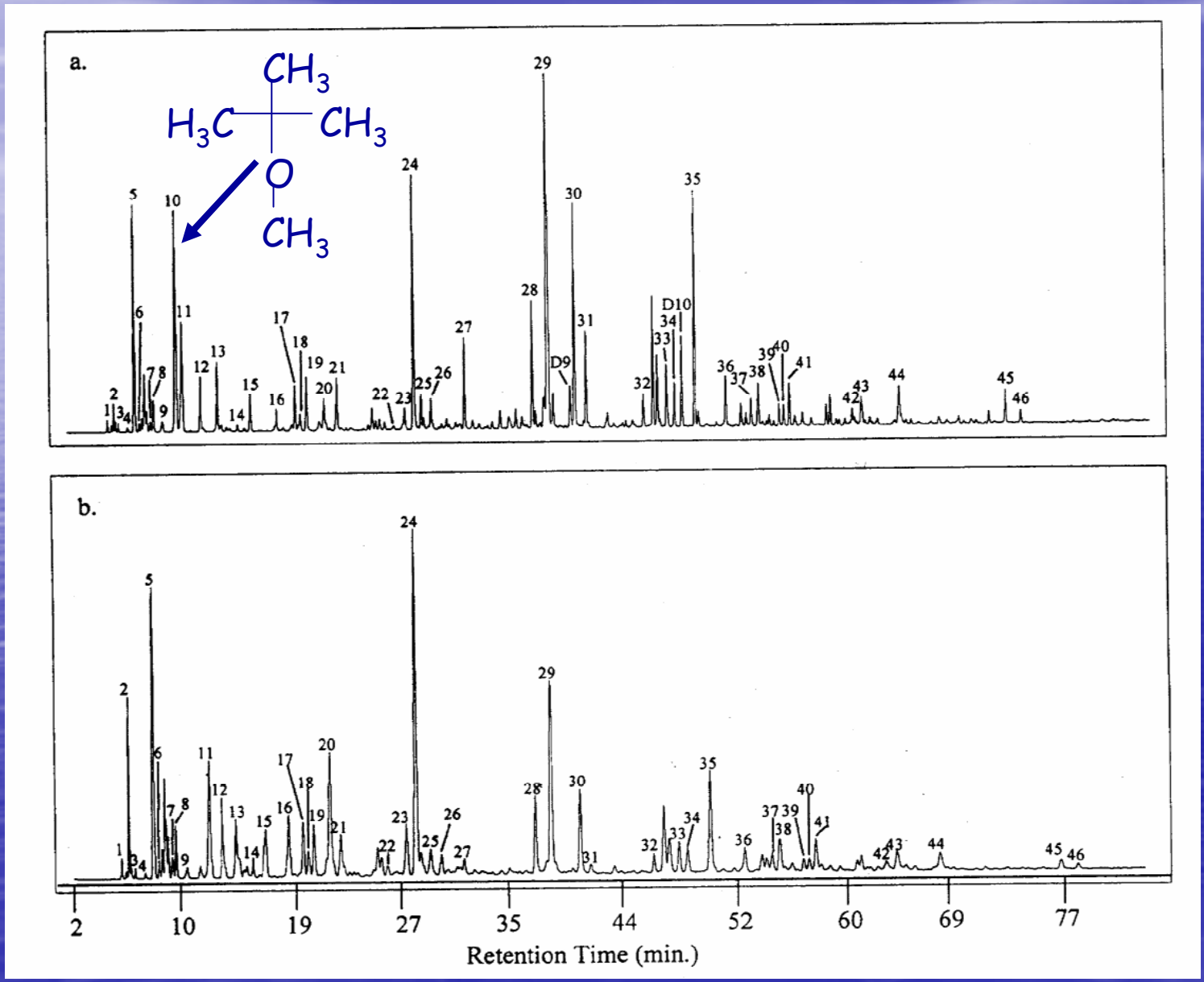
Source Discrimination of PCE and TCE



MTBE

- MTBE-octane enhancer and oxygenate
- MTBE may represent 11-15% of gasoline volume in some cases
- MTBE relatively calcitrant and very water soluble
- Isotopes utilized for monitoring natural attenuation

Comparison of Gasolines by GC



Monitored Natural Attenuation

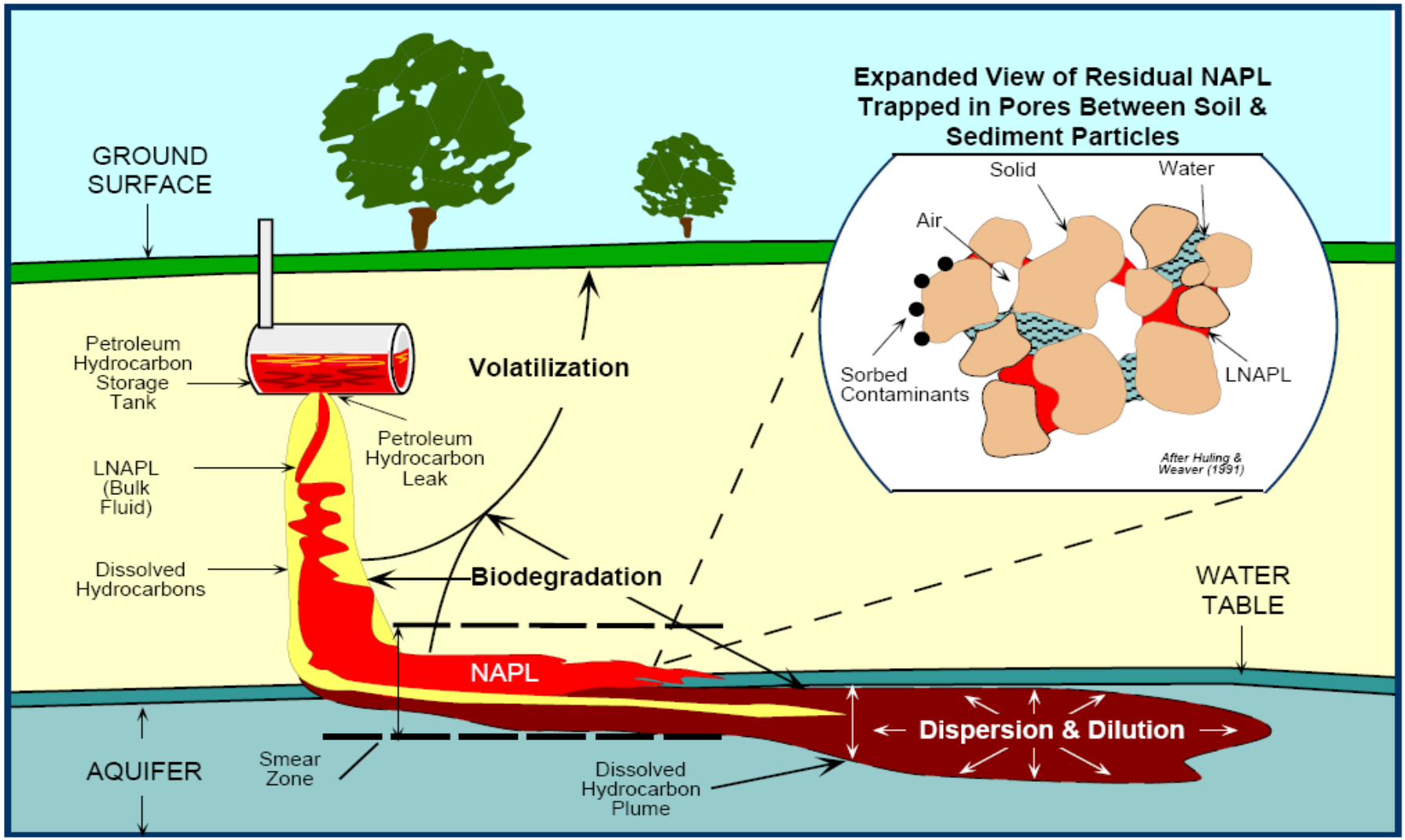
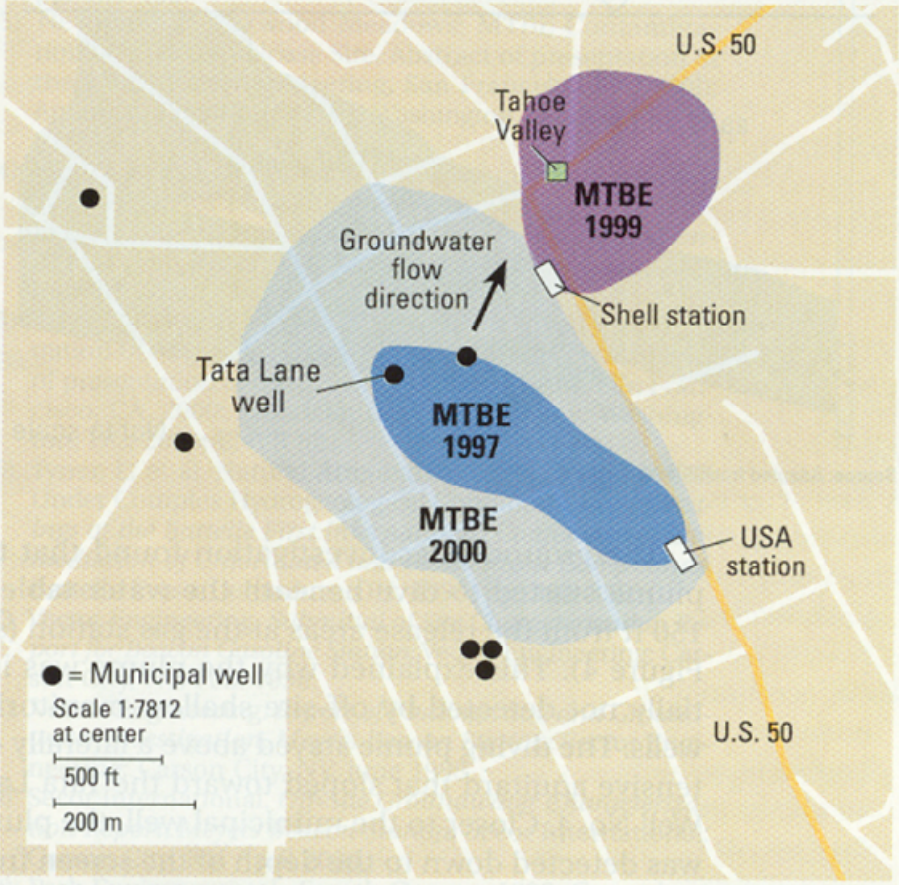


FIGURE 3

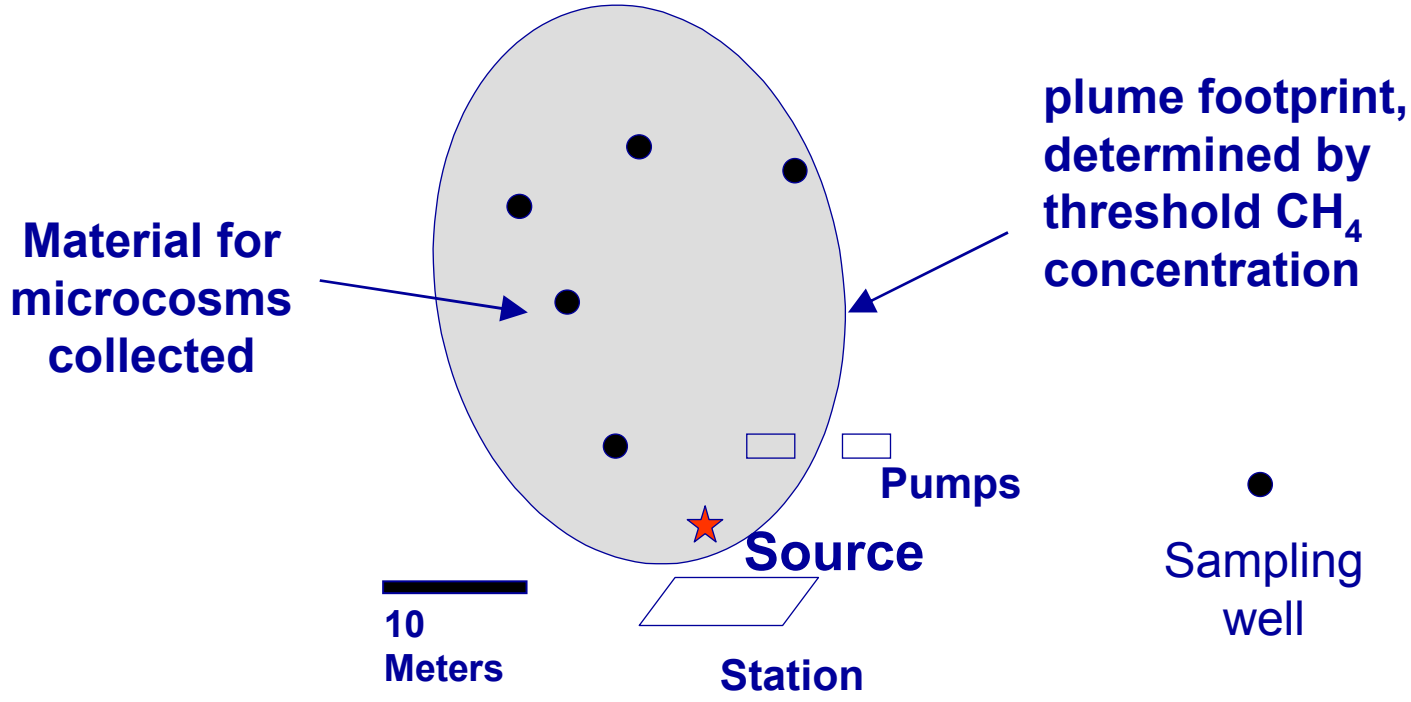
The effect of remedial extraction pumping

In 1997, the MTBE plume (dark blue) was being pulled cross-gradient to groundwater flow direction to the Tata Lane Well No. 4; the extent of the MTBE plume (light blue; as seen in 2000) is considerable after Tata Well No. 4 ceased pumping for several months and was restarted at a lower pumping rate. The plume has since commingled with an MTBE plume (purple) from another gas station acted on by natural groundwater flow.

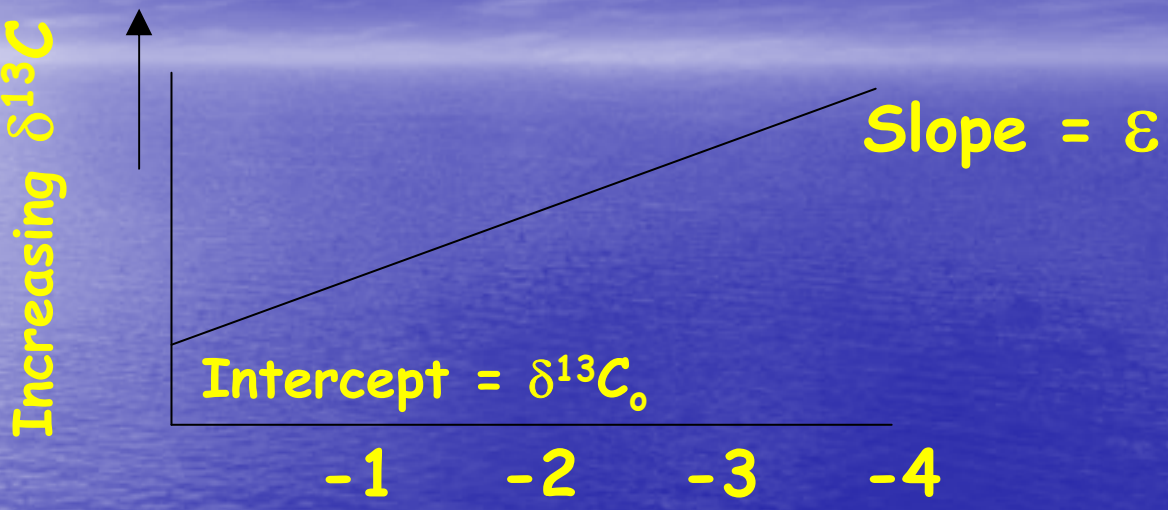


Source: Adapted from data in References (*3*) and (*6*).

Anaerobic Plume
New Jersey, BP site



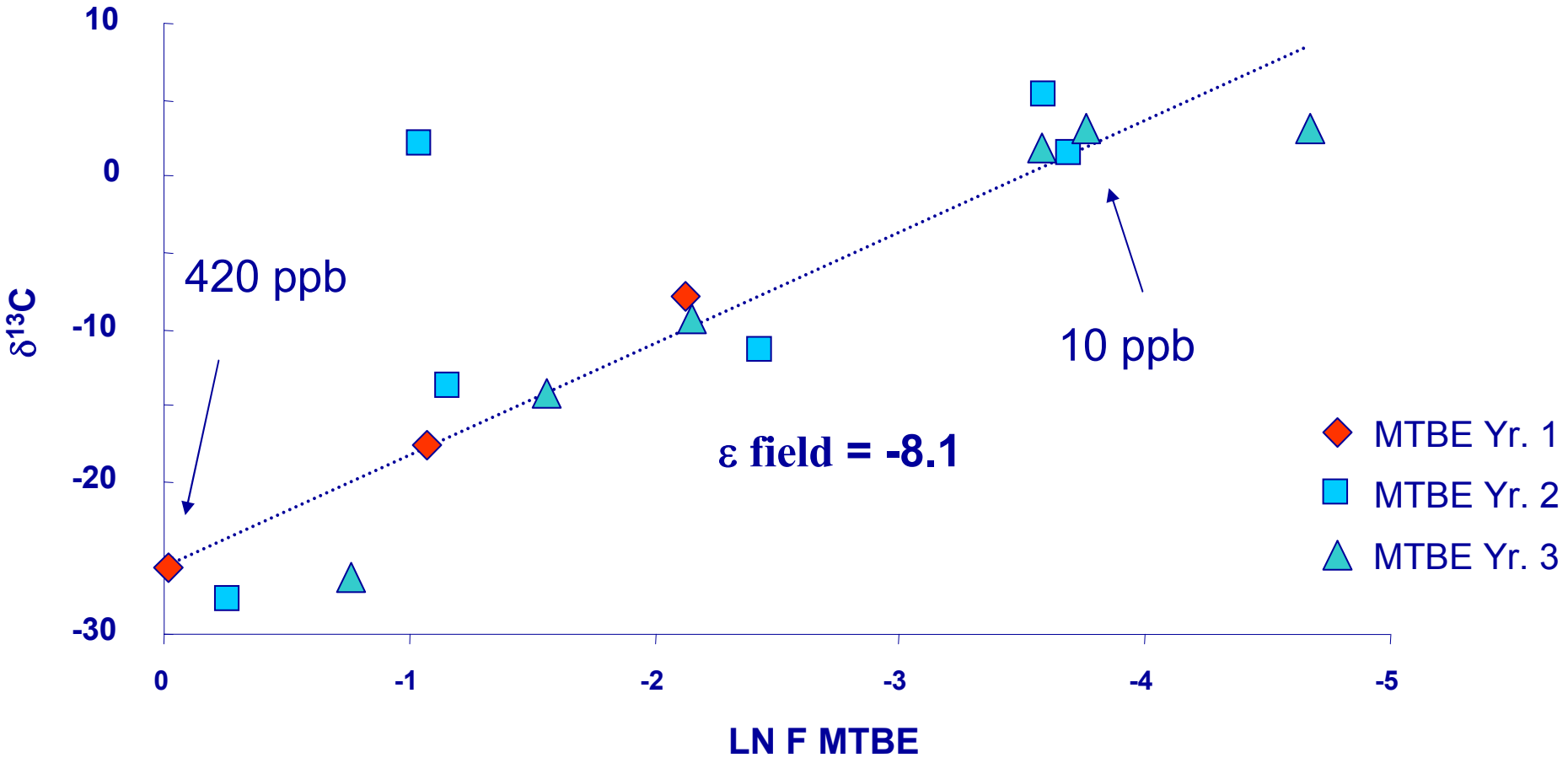
Stable Isotopic Fractionation
Rayleigh Model



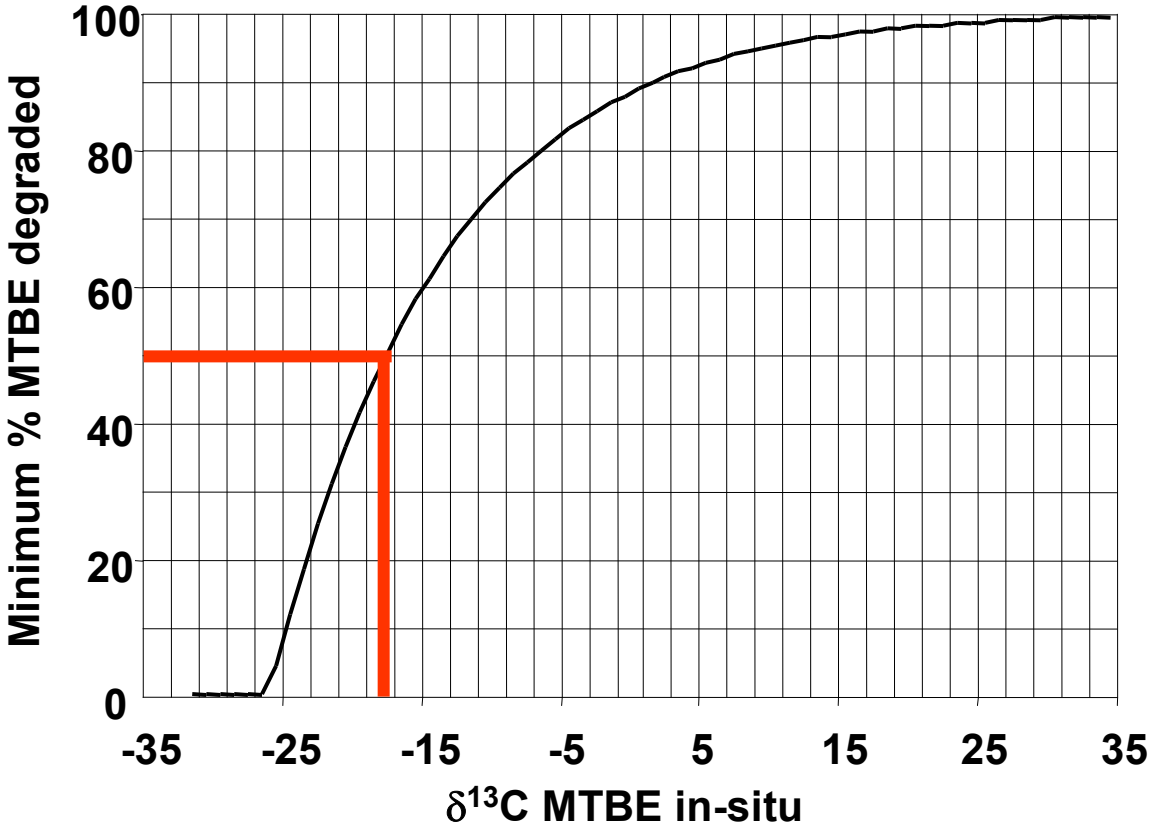
MTBE concentration decreases →

$$\delta^{13}C_t = \varepsilon^* \ln F + \delta^{13}C_o$$

Anaerobic Plume New Jersey, BP



Biodegradation Graph



If the observed $\delta^{13}C$ is –18, at least 50 % of MTBE has been degraded in the sampled volume (Rayleigh Eqn)

$$\delta^{13}C_t = \varepsilon^* \ln F + \delta^{13}C_o$$

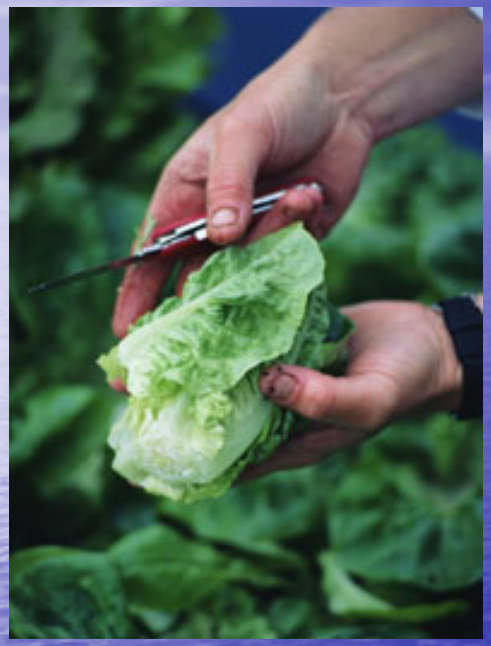
Chlorine-Perchlorate

Perchlorate

Perchlorate taints water in 22 states. Main sources: Military bases, aerospace installations, and defense contractors that build rockets.

A small amount of perchlorate pollution in the U.S. is believed to have stemmed from a sodium nitrate fertilizer made in Chile.

TOXIC ROCKET FUEL FOUND IN MILK SAMPLES FROM TEXAS SUPERMARKETS

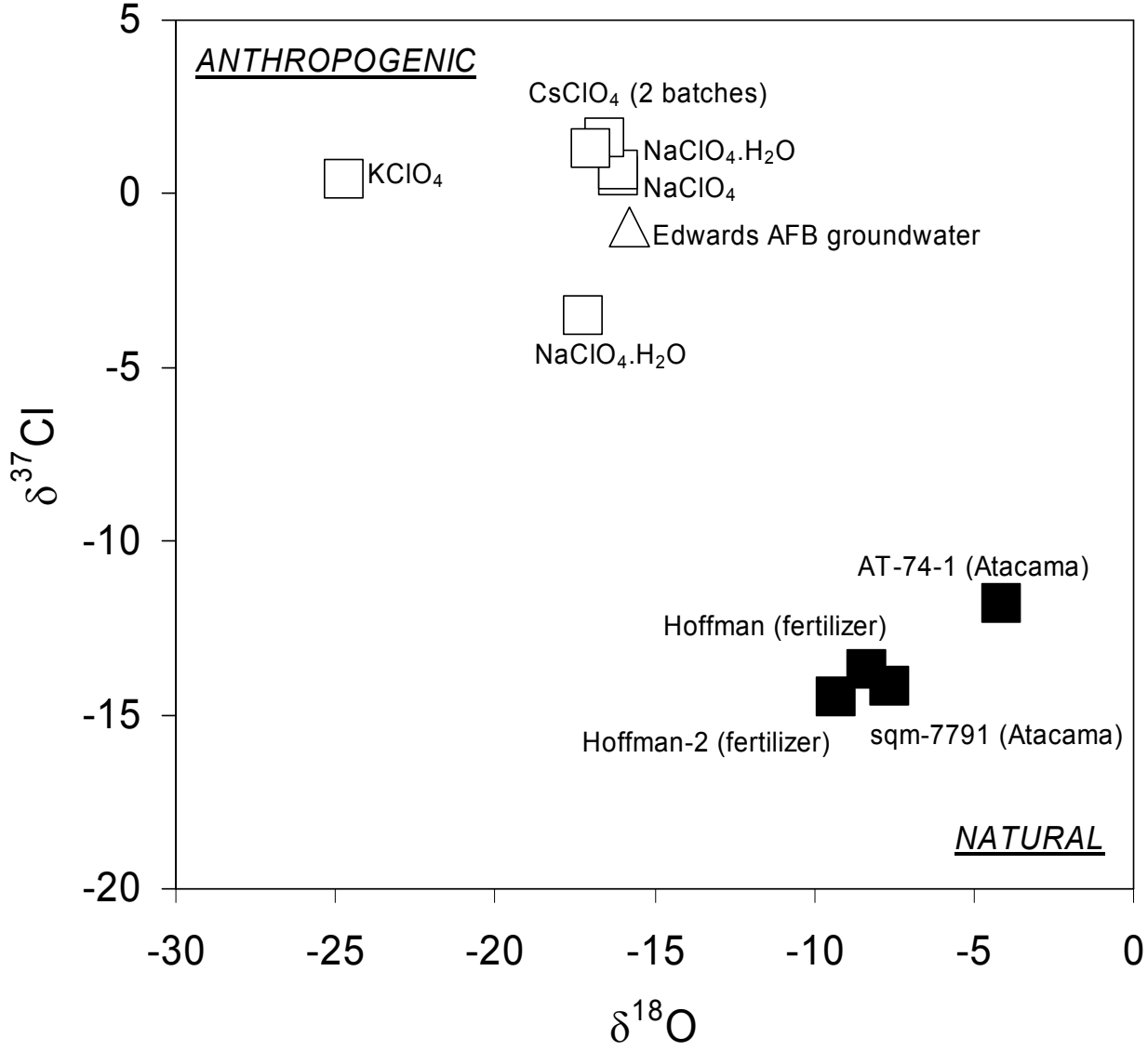


Studies released last week finding perchlorate in lettuce have focused attention on a struggle between EPA and the Pentagon over cleanup standards for the chemical.
Perchlorate—ClO_4^-, a component of solid rocket fuel—disrupts thyroid uptake of iodine and taints water supplies in 20 states.

A study sponsored by the Press Enterprise of Riverside, Calif., found perchlorate ion in all 18 samples of lettuce analyzed, and a test sponsored by the Environmental Working Group (EWG) detected the substance in four of 22 lettuce samples purchased in California. The source is thought to be irrigation water from the lower Colorado River, which carries perchlorate from a former industrial plant near Las Vegas.

LUBBOCK, TX, Sept. 19 - A toxic component of rocket fuel has been found in supermarket milk at levels exceeding the federal governments currently recommended safe dose (1ppb currently) for drinking water……..

Are Perchlorate Sources Isotopically Distinct?



Summary

- The concept of environmental forensics is a rapidly expanding.
- Conventional analytical techniques such as GC and GCMS are used extensively but in some cases provide limited useful data.
- The emergence of GCIRMS has lead to numerous applications for both source determinations and, perhaps more importantly, monitoring natural attenuation.