Advances in Environmental Forensic Fingerprinting Techniques: Their Use in Litigation and Determination of Responsibility for Environmental Contamination

Presented at the AEHS 2024 East Coast Meeting, Amherst, October 2024

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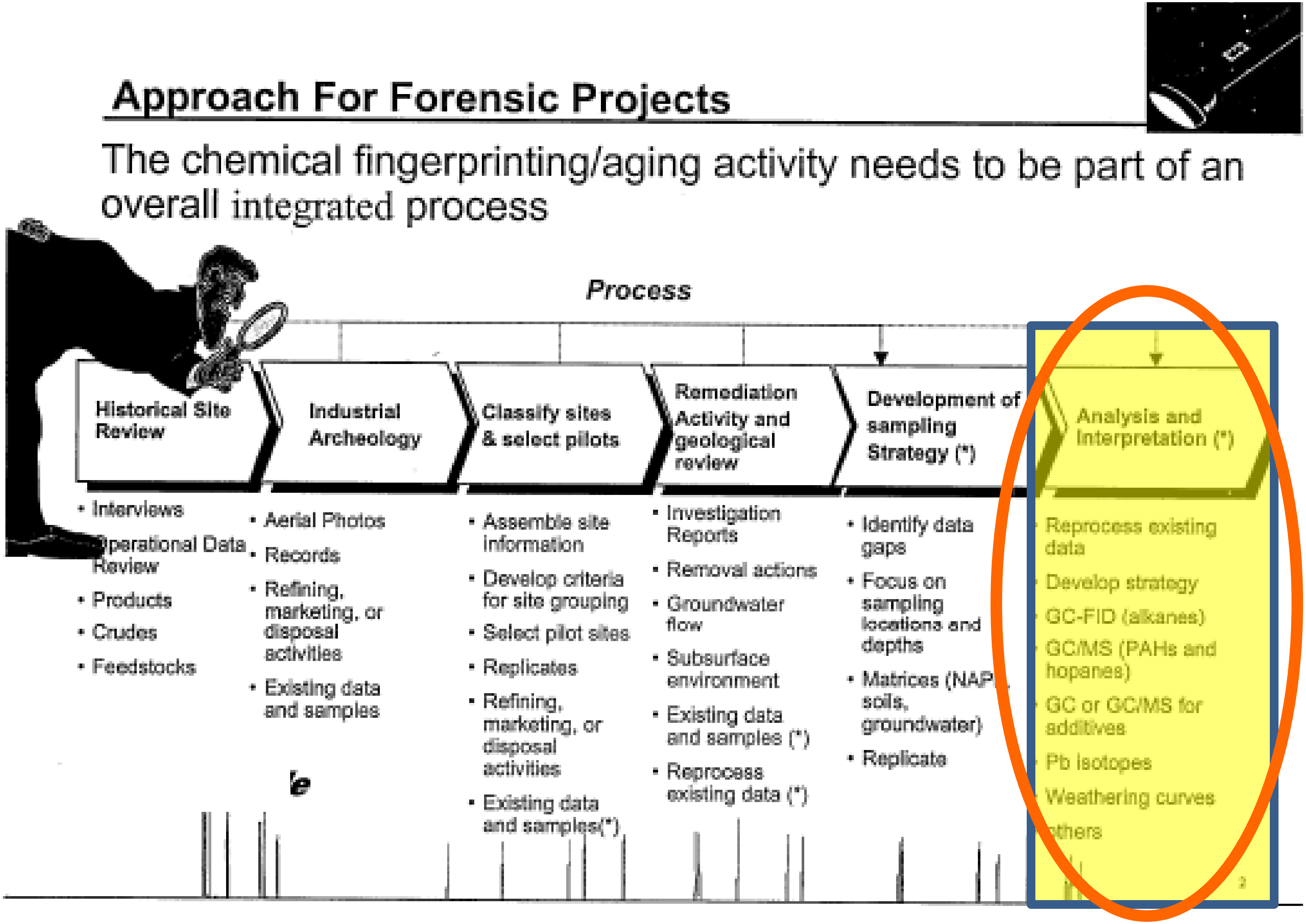
1890

Environmental Forensics

- The focus of environmental forensics is determination of responsibility for contaminants released into the environment.
- Contaminants maybe organic or inorganic-focus in this workshop is on organic contaminants.
- Wide range of compounds from volatiles (gases) to heavy nonvolatile organic residues.
- Need to determine source (responsibility) beyond reasonable doubt.
- Complicated by mixing of contaminant with natural background plus effects of weathering.

Environmental Forensics



Approach For Forensic Projects

The chemical fingerprinting/aging activity needs to be part of an overall integrated process

Process

Historical Site Review
- Interviews
- Operational Data Review
- Products
- Crudes
- Feedstocks

Industrial Archeology
- Aerial Photos
- Records
- Refining, marketing, or disposal activities
- Existing data and samples

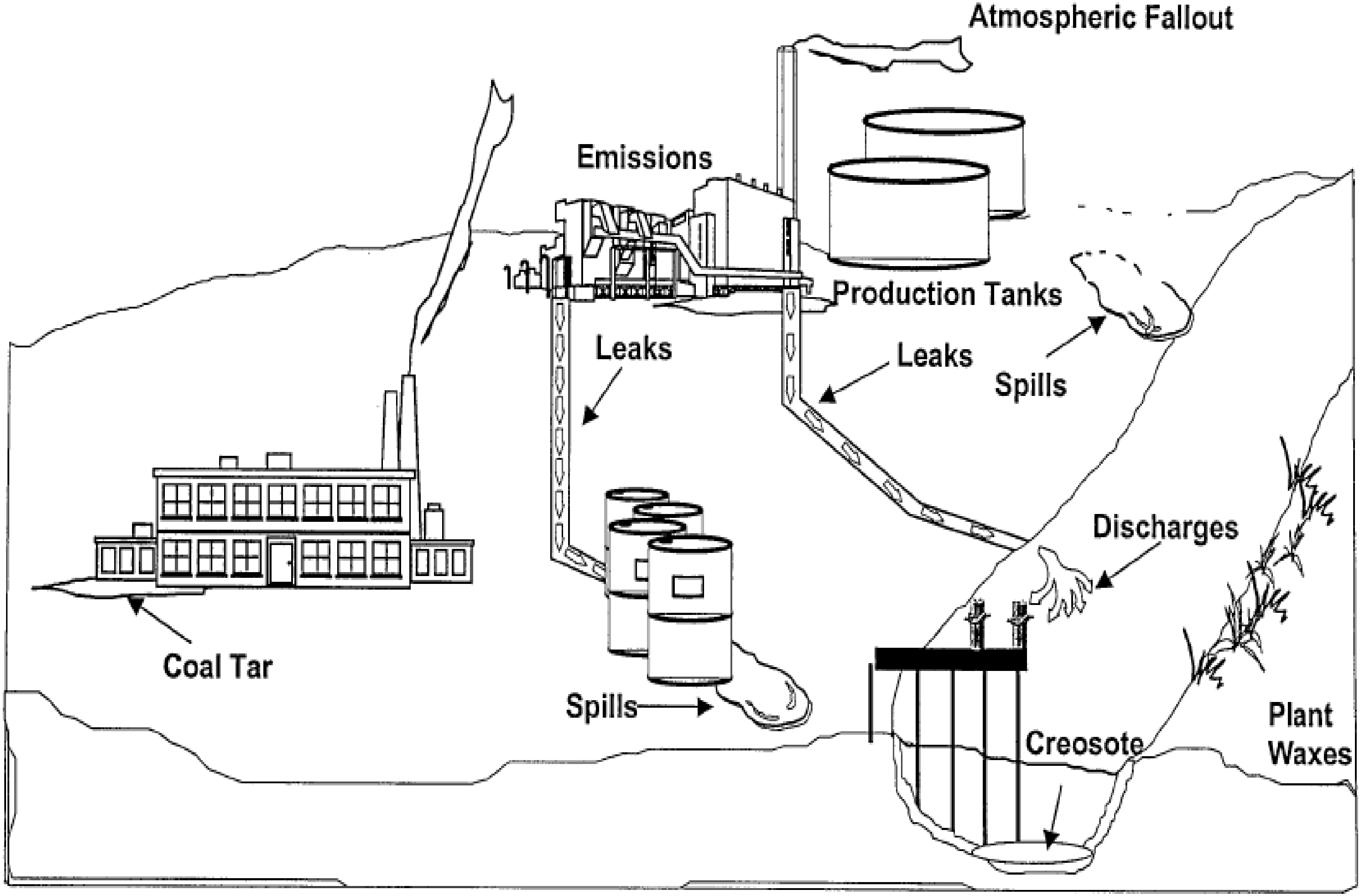
Classify sites & select pilots
- Assemble site information
- Develop criteria for site grouping
- Select pilot sites
- Replicates
- Refining, marketing, or disposal activities
- Existing data and samples(*)

Remediation Activity and geological review
- Investigation Reports
- Removal actions
- Groundwater flow
- Subsurface environment
- Existing data and samples (*)
- Reprocess existing data (*)

Development of sampling Strategy (*)
- Identify data gaps
- Focus on sampling locations and depths
- Matrices (NAPL, soils, groundwater)
- Replicate

Analysis and Interpretation (*)
- Reprocess existing data
- Develop strategy
- GC-FID (alkanes)
- GC/MS (PAHs and hopanes)
- GC or GC/MS for additives
- Pb isotopes
- Weathering curves
- others

Environmental Forensics



Environmental Forensics

- Keys to success
  - Use multiple analytical techniques to get a variety of fingerprints
  - Gather information from a wide range of sources
  - Aerial and satellite photos
  - Historical records
  - Site information
  - Information from previous employees
  - Information on nature of product and manufacturing processes. Feedstocks and methods may change over time
  - Degradation products

Satellite/Aerial Photography

Environmental Forensics

- Wide range of analytical tools available but most commonly used techniques revolve around:
  - Gas chromatography
  - Gas chromatography-mass spectrometry
  - Liquid chromatography
  - Liquid chromatography-mass spectrometry
  - Bulk stable isotopes
  - Gas chromatography-isotope ratio mass spectrometry
  - Liquid chromatography-isotope ratio mass spectrometry
  - Gas chromatography-ICPMS

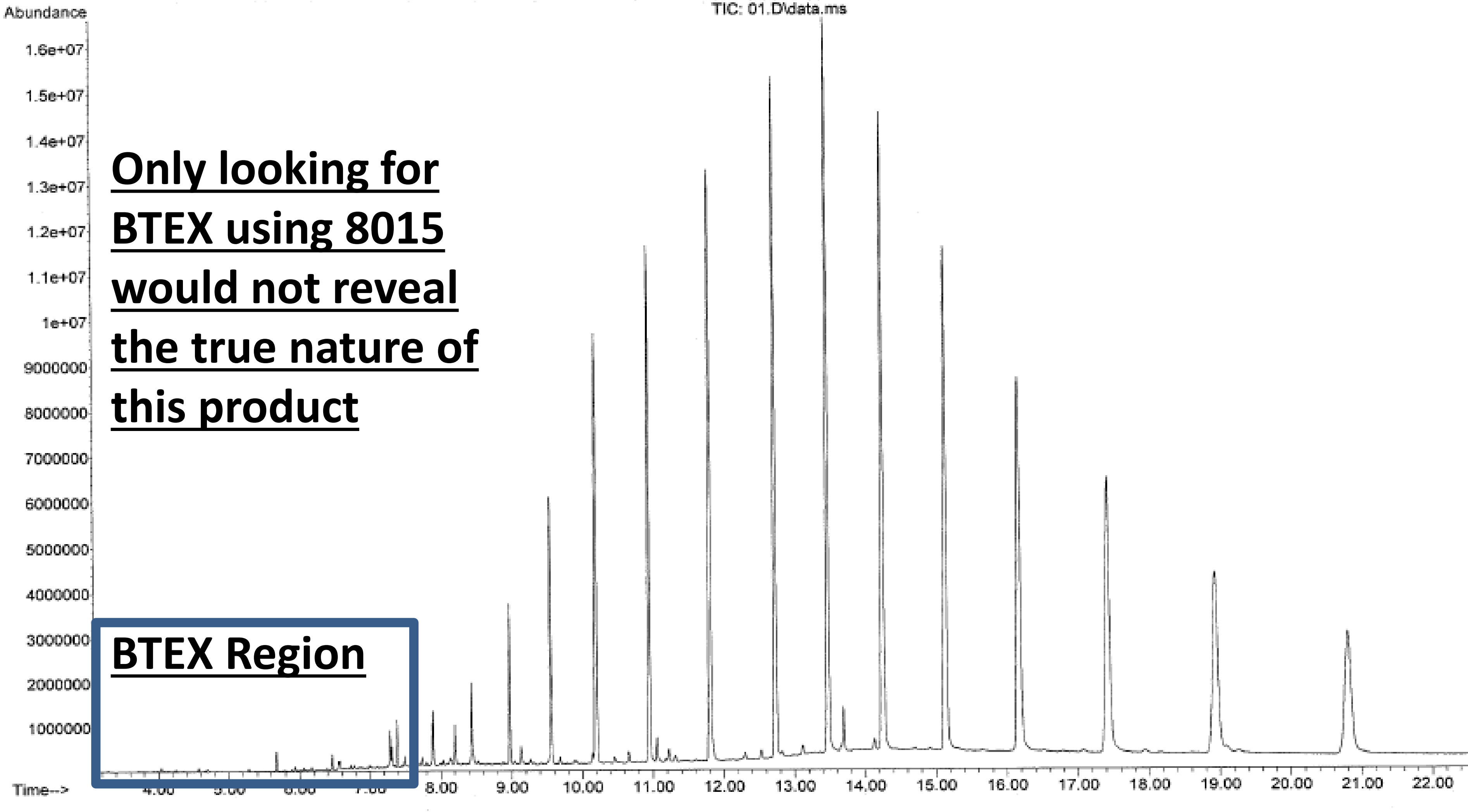
Environmental Forensics

- Major advances in all these techniques over the past several decades.
- Overall objectives remain the same. Develop a comprehensive set of fingerprints and correlate with similar fingerprints from suspected source or point of release.
- If origin unknown, interpretation of data from spilled product can be used to speculate on possible source or point of release.
- Significant differences between conventional EPA methods and the environmental forensic approach.
- Environmental forensics is more of an investigative approach.
- A good environmental forensic expert should be able to “squeeze” information from the analytical data that may be unique to the samples at hand.
- Stable isotopes now a routine fingerprinting tool complimenting more conventional fingerprinting tools.
- No EPA stable isotope method.

Environmental Forensics

- Widely used EPA methods such as 8015, 8260, and 8270 are often used, incorrectly, in forensic studies.
- Data obtained by these methods are of little use from a forensic perspective.
- These techniques are more correctly used for monitoring concentration changes of specific target compounds.
- If a compound of interest is not on the target list, it will not be reported regardless of whether it is present.
- There are also concentration limits for detection of target compounds limiting reporting.
- With environmental forensics high value compounds may be present in trace amounts but can be essential in establishing a link between source and contaminant.

EPA Methods vs. Forensic Methods



Only looking for BTEX using 8015 would not reveal the true nature of this product

BTEX Region

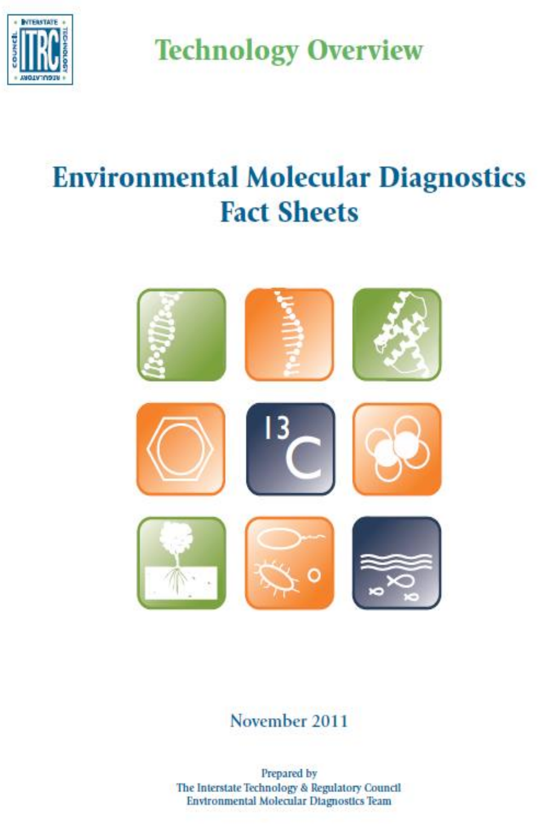
Environmental Forensics

- Petroleum geochemistry evolved in the 1970s as an exploration tool but has subsequently provided valuable information for use in forensic investigations related to oil spills or releases of refined products.

- Do not re-discover the wheel! Monitor developments in petroleum geochemistry, as well as environmental chemistry.

- A landmark paper by Kaplan and others (Organic Geochemistry, Nov. 1997) was one of the first papers that detailed the importance of understanding variations in the composition of refined products and fine details of products not commonly examined in routine monitoring studies.

Useful References

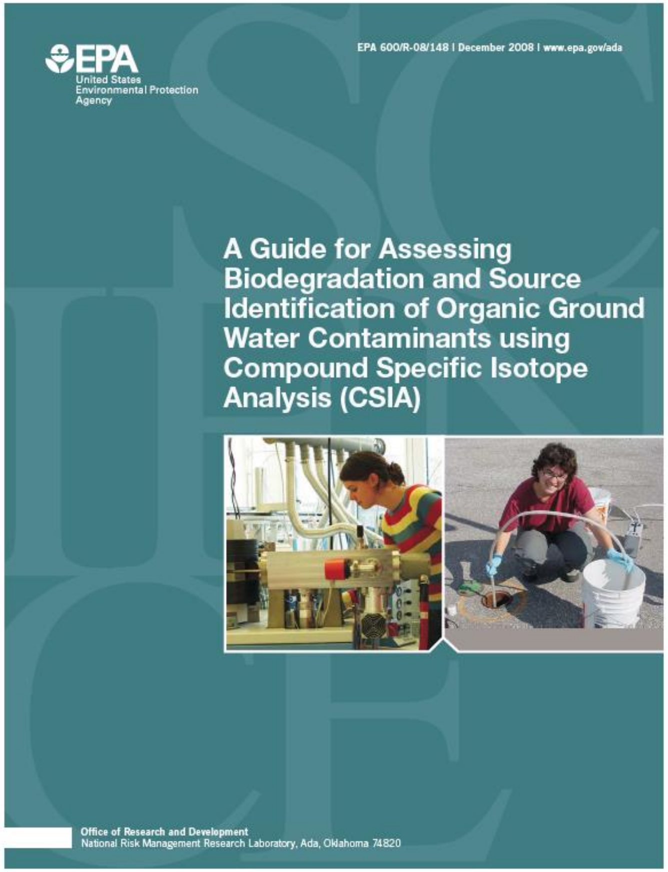


Technology Overview

Environmental Molecular Diagnostics
Fact Sheets

November 2011

Prepared by
The Interstate Technology & Regulatory Council
Environmental Molecular Diagnostics Team

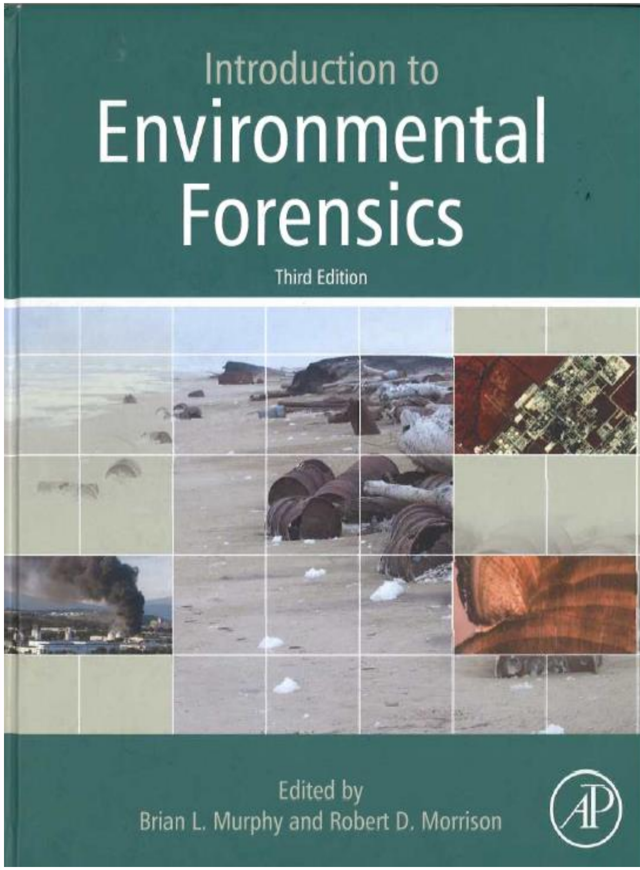


United States
Environmental Protection
Agency

EPA 600/R-08/148 I December 2008 I www.epa.gov/ada

A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820



Introduction to
Environmental
Forensics
Third Edition

Edited by
Brian L. Murphy and Robert D. Morrison

http://www.itrcweb.org/GuidanceDocuments/EMD1.pdf; EPA 600R-08/148 I December 2008 I www.epa.gov.ada

Interstate Technology & Regulatory Council (ITRC)

Analytical Techniques

- Clearly environmental forensics involves many analytical techniques.
- Many of these , particularly those involving some form of GC and/or MS will be familiar to many and will not be discussed in detail.
- Probably less familiar will be concept of stable isotopes.
- Stable isotopes have become an important and almost routine tool in environmental forensics.
- Prior to continuing with discussion of environmental forensics a brief overview of stable isotopes will be provided.

Environmental Forensics

- Stable isotopes have been around since the 1940s but a major advance occurred in the early 1980s when commercial GCIRMS systems became available permitting determination of isotope compositions of individual compounds.
- It is now possible to determine C,H,Cl,Br,S,N,O isotopes of individual compounds by various methods with detection limits for the most compounds down to 1ppb or even lower.
- The isotope approach is extremely valuable for groundwater contaminants to evaluate possible sources and monitoring attenuation.
- For semi-volatiles isotopes are important to support fingerprinting data from GC and GCMS.

Basic Environmental Forensic Questions

- What is the product? **NO**
- Is there more than one source (point of release) and, if so, which one caused the problem? **YES**
- How long has it been there? **NO**
- Is it degrading? **YES**

(Where can isotopes be of use?)

Elsner and Imfeld (2016). CSIA of micropollutants in the environment-current developments and future challenges. Current Opinions in Biotechnology., 41,60-72.

Evolution of the Isotope Approach

- For many “traditional” contaminants utilization of stable isotopes has become a routine analytical tool to monitor source and degradation.
- As novel contaminants continue to emerge it is essential the isotope approach continues to develop.
- Methods for additional elements should be developed.
- Position specific isotope analyses (PSIA) needs additional development. Currently isotope values are averages of all the individual atoms in the molecule. Two compounds could have the same average value but derived from different sources. PSIA could resolve such issues.
- Neubauer et al., (2023). Discovering nature’s fingerprints: Isotope ratio analysis on bioanalytical spectrometers. J. Am. Soc. Mass Spectrom. 34, 525-537.

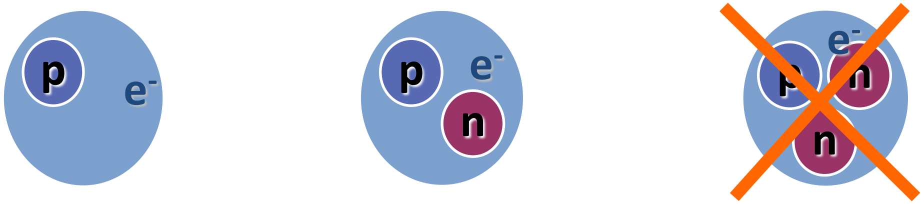
What are Stable Isotopes?

- 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 (D-deuterium) has 1 electron, 1 proton and 1 neutron.
- ^{35}Cl has 17 electrons, 17 protons and 18 neutrons; ^{37}Cl has 20 neutrons.

What are Stable Isotopes?

Isotopes of Hydrogen

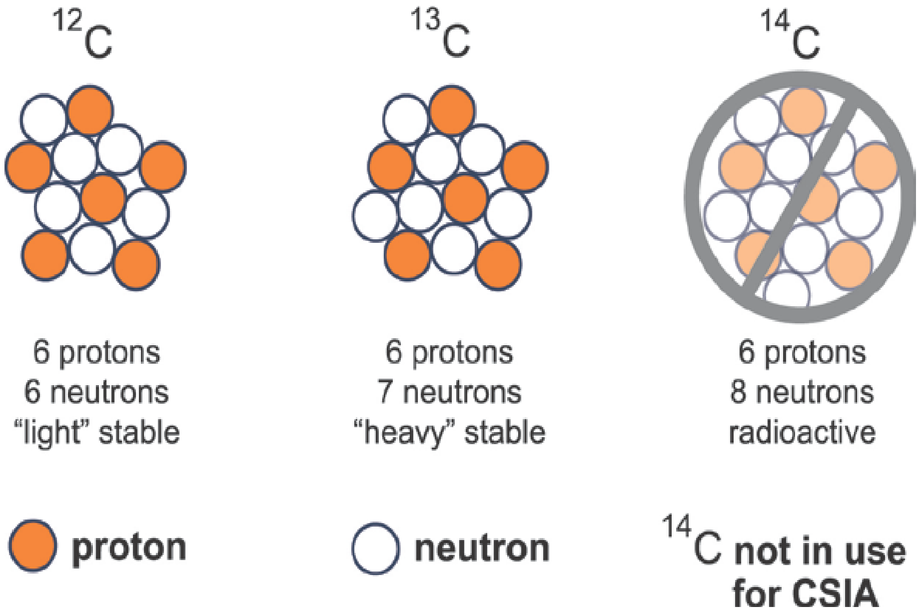
Isotopes of Carbon



Hydrogen,
^{1}H

Deuterium,
^{2}H, D

Tritium,
^{3}H, T



- Isotopes have the same number of protons – identical atomic number
- Isotopes have different number of neutrons – different atomic mass
- Stable isotopes do not undergo radioactive decay – tritium is not a stable isotope
- ^{35}Cl has 17 electrons, 17 protons and 18 neutrons; ^{37}Cl has 20 neutrons. (Cl has 25 isotopes-ranging from ^{28}Cl to ^{52}Cl-only 2 stable!)

Stable Isotopes

- **Natural isotopic abundances**

Carbon (^{12}C/ ^{13}C - ~ 99/1)

Hydrogen (^{1}H/ ^{2}H – 99.985/0.015)

Chlorine (^{35}Cl/^{37}Cl - 76/24)

Bromine (^{79}Br/^{81}Br - 51/49)

Sulfur (^{32}S/^{34}S - 94/3)

Nitrogen (^{14}N/^{15}N - 99.6/0.4)

(Mass difference for H/D is 2 thus more fractionation than C)

The Delta Notation

$$\delta^{13}\mathrm{C} = \left(\frac{\mathrm{R}_{\mathrm{sample}} - \mathrm{R}_{\mathrm{standard}}}{\mathrm{R}_{\mathrm{standard}}} \right) \times 1000$$

$R = {}^{13}C/{}^{12}C$ **(${}^{13}C/{}^{12}C$ is 0.0112372)**

${}^{13}C/{}^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is $3^{o}/_{o}$ lower than the standard. Laboratory standards must be converted to international reference standards.

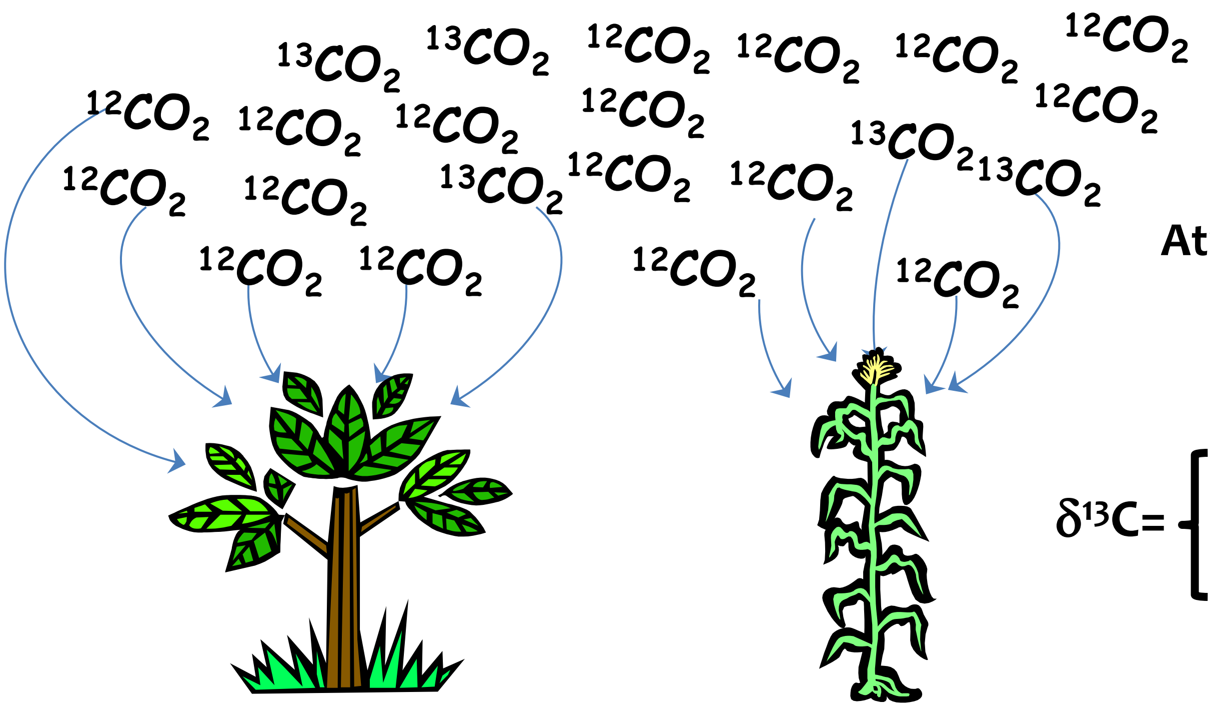
$\delta^{13}C$ of the international standard is 0 (standard = sample)

Why do Contaminants have different Stable Isotope Values

- Virtually all organic contaminants originate from a fossil fuel source (oil, gas, coal). 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.
- The extent of fractionation during photosynthesis will depend on factors such as: plant type; marine v. terrigenous; C_3 v. C_4 plant types; temperature; sunlight intensity; water depth.
- Isotopic composition of CO_2 has changed over geologic time as a result of increasing diversity of the species. Values of CO_2 have become isotopically heavier due to preferential assimilation of lighter $CO_{2,}$ hence isotopic values of crude oils have also become isotopically heavier.

Photosynthesis

Carbon isotope fractionation during photosynthesis



Atmospheric $\delta^{13}C$ ~ -8‰

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

C_3 plants : >85% of plant species
(all trees, wheat, sugar beet, tobacco, a lot of herbaceous…)

C_4 plants : <5% of plant species
(corn, sorghum, millet, sugarcane)

C3 plants $\delta^{13}C$ ~ -26‰

C4 plants $\delta^{13}C$ ~ -12‰

$$6{*}CO_2 + 12H_2O \longrightarrow {*}C_6H_{12}O_6 + 6H_2O + 6O_2$$

Presentation Overview

- Introduction
- **Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds**
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
    - Diesel, Gasoline, Motor oil
    - Groundwater contaminants
    - Chlorinated Solvents
    - PAHs
    - PCBs
    - Benzene
    - Other compounds
    - Chlorine, Bromine and Sulfur Isotopes

- Vapor Intrusion Studies
- Summary

Stable Isotope Determination

Isotopic values can be determined in two ways:

- Bulk isotopes
- Isotopic composition of individual compounds

Bulk Isotopes

- For carbon, a small volume of sample is placed in a glass tube with CuO, evacuated, sealed and heated to approx. 650^{o}C for 6 hrs. All organic matter must be totally converted to CO_2 and water.
- The tube is attached to a manifold, seal broken, and water removed. The CO_2 pulsed into mass spectrometer, interspersed with pulses of standard CO_2.
- Measure response for mass 44 and 45 ($^{12}CO_2$ and $^{13}CO_2$) and calculate $\delta^{13}C$.
- Alternatively, can be determined directly with elemental analyser interfaced to IRMS

The Delta Notation

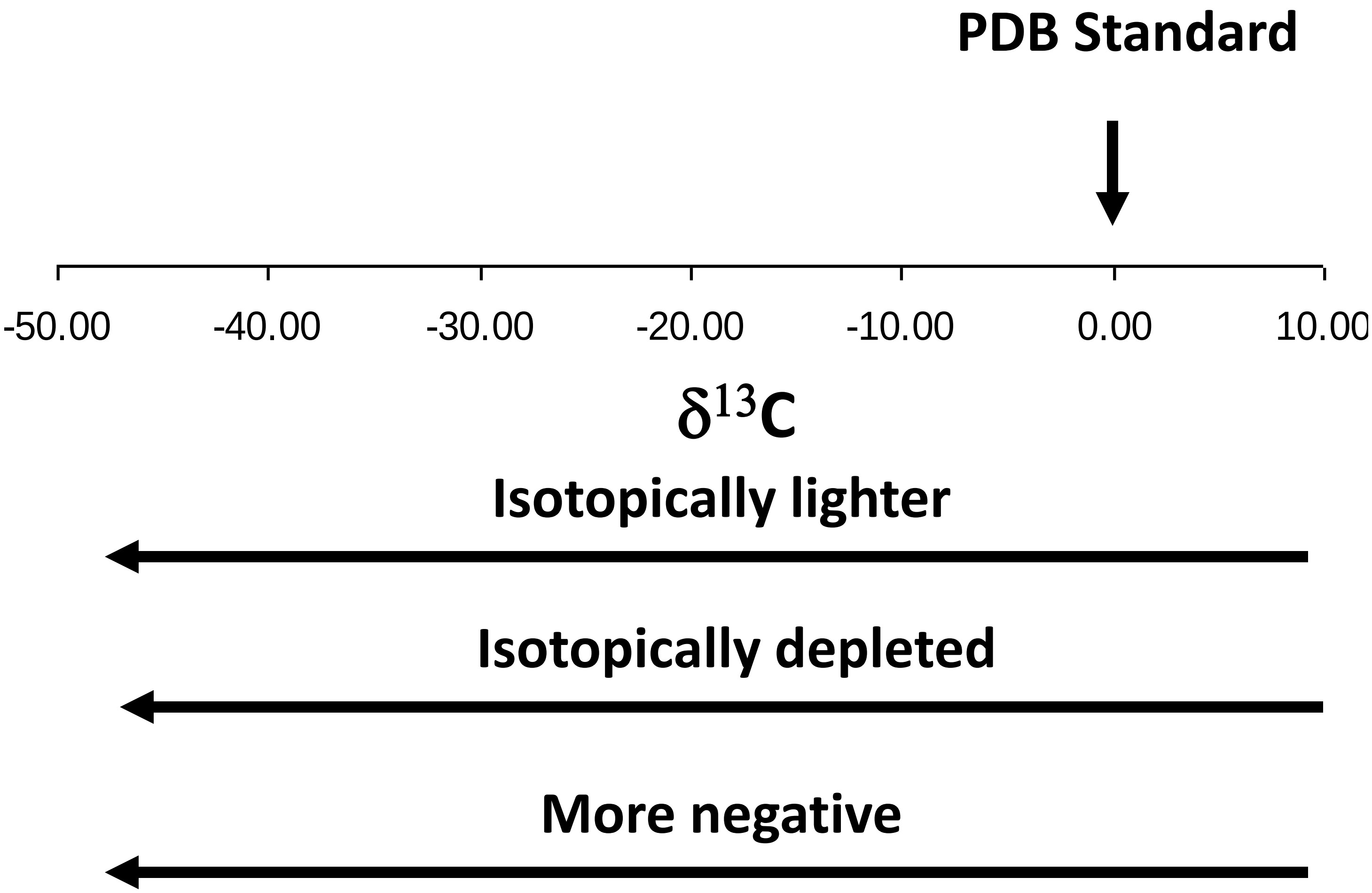
$$\delta^{13}\mathrm{C} = \left(\frac{\mathrm{R}_{\mathrm{sample}} - \mathrm{R}_{\mathrm{standard}}}{\mathrm{R}_{\mathrm{standard}}} \right) \times 1000$$

R = ^{13}C/^{12}C **(^{13}C/^{12}C is 0.0112372)**

^{13}C/^{12}C-45/44 intensity in the MS; δ^{13}C of -30 per mil means it is 3^{o}/$_{o}$ lower than the standard. Laboratory standards must be normalized to international reference standards.

δ^{13}C of the standard will be 0

Data Output-Isotope Scale



PDB Standard

δ^{13}C

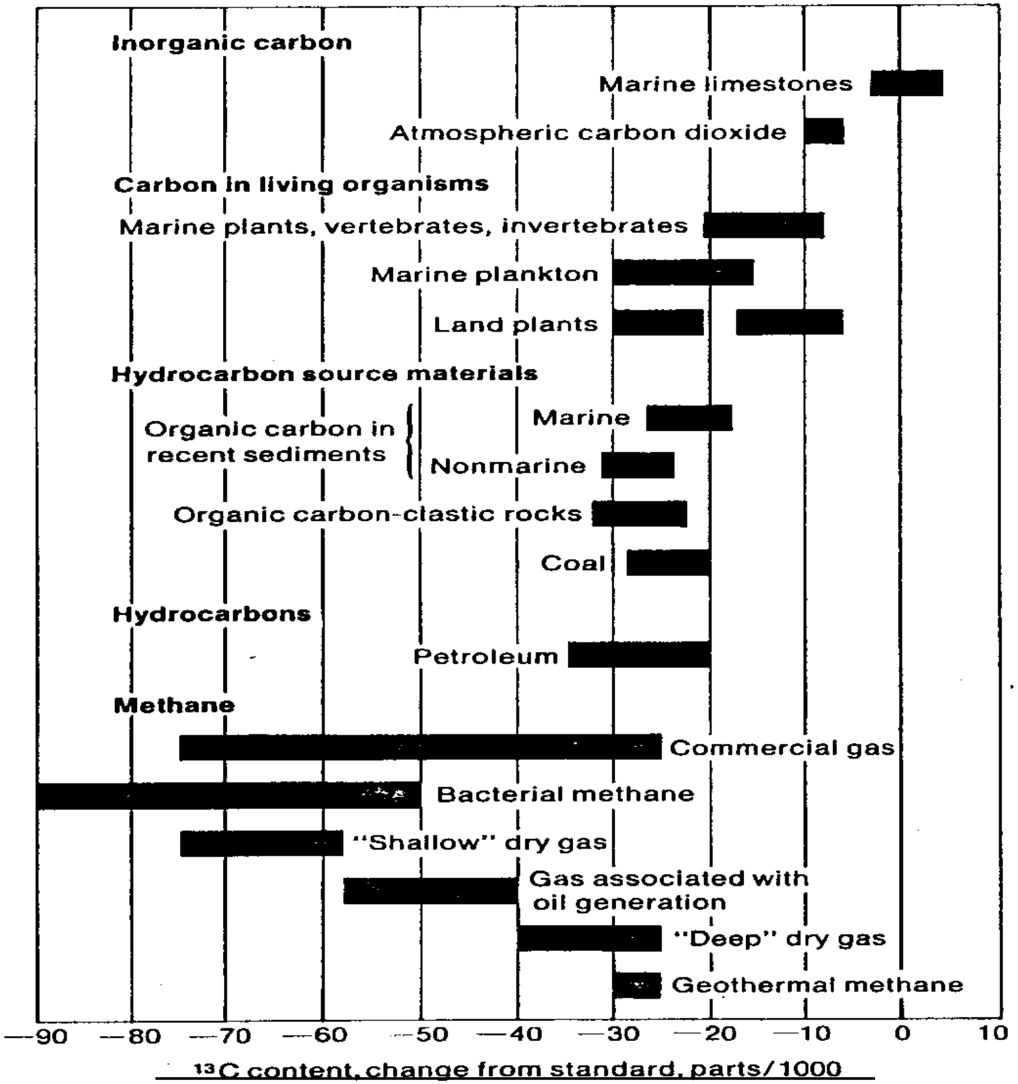
Isotopically lighter

Isotopically depleted

More negative

Variations in Bulk Isotope Values

^{13}C composition of organic matter varies depending on origin and thermal history



Source: Fuex, A. N., *J. of Geochemical Exploration*, 7, 155 (1977)

Stable Isotope Fractionation

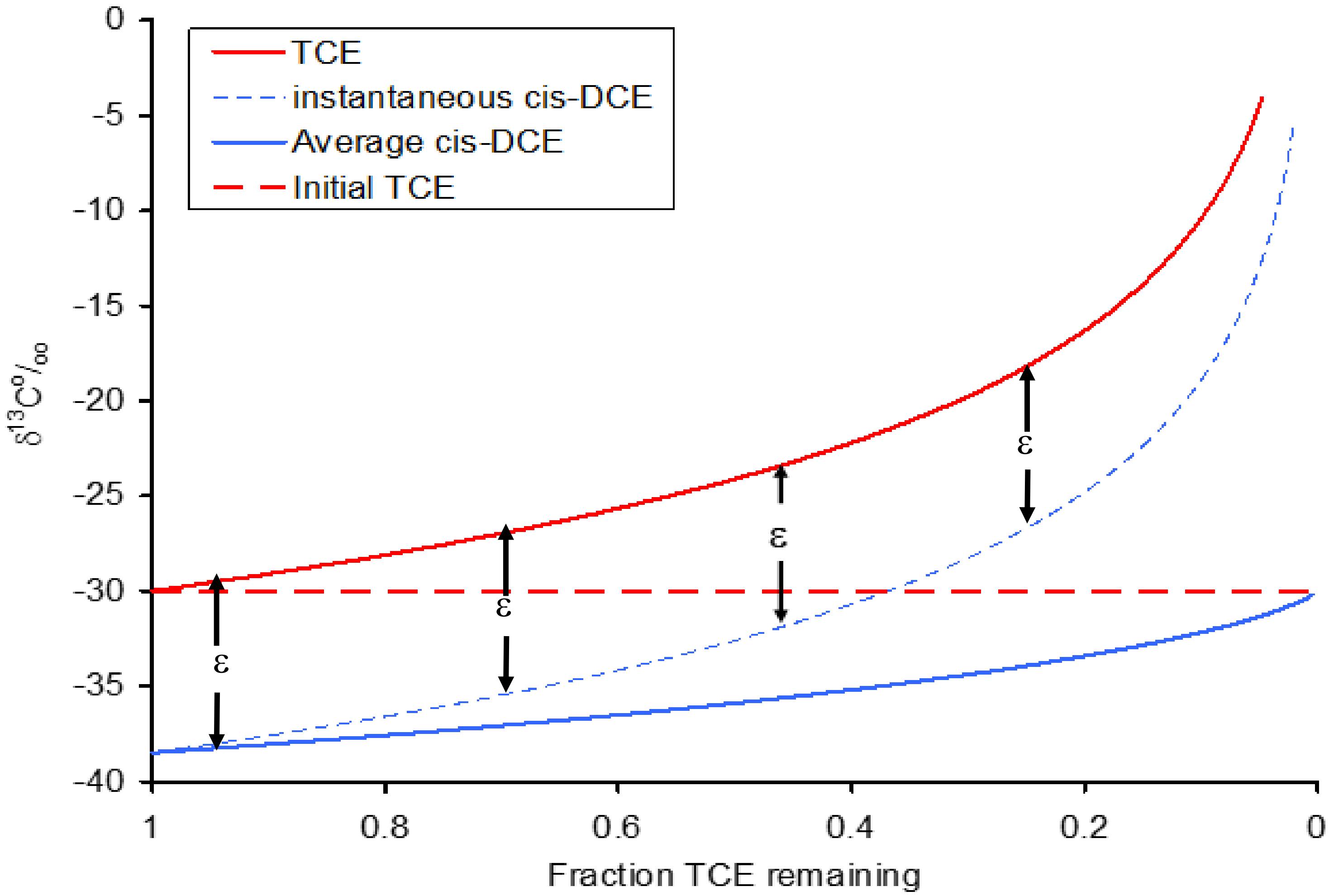
- **Preferential partitioning of isotopes between phases or between reaction and product species**
  - Function of difference in masses

- **Equilibrium isotope effect**
  - One isotope concentrates in one component of a reversible system; lighter isotopes (^{1}H, ^{16}O) partition to higher energy phase (vapor)
- **Kinetic isotope effect**
  - One isotope reacts more rapidly than the other in irreversible system

Kinetic Isotope Effect

- Hydrocarbon molecules are comprised primarily of ^{12}C-^{12}C bonds; lesser amounts of ^{12}C-^{13}C bonds and even fewer ^{13}C-^{13}C bonds. The kinetic isotope effect can be thought of as the cleavage of the weaker bonds, ^{12}C-^{12}C, which will ultimately lead to an enrichment of the residual substrate.
- Similar effects occur in chlorinated compounds where the ^{12}C-^{35}Cl bonds are preferentially cleaved.

Stable Isotopic Fractionation



Data Output

δ notation:

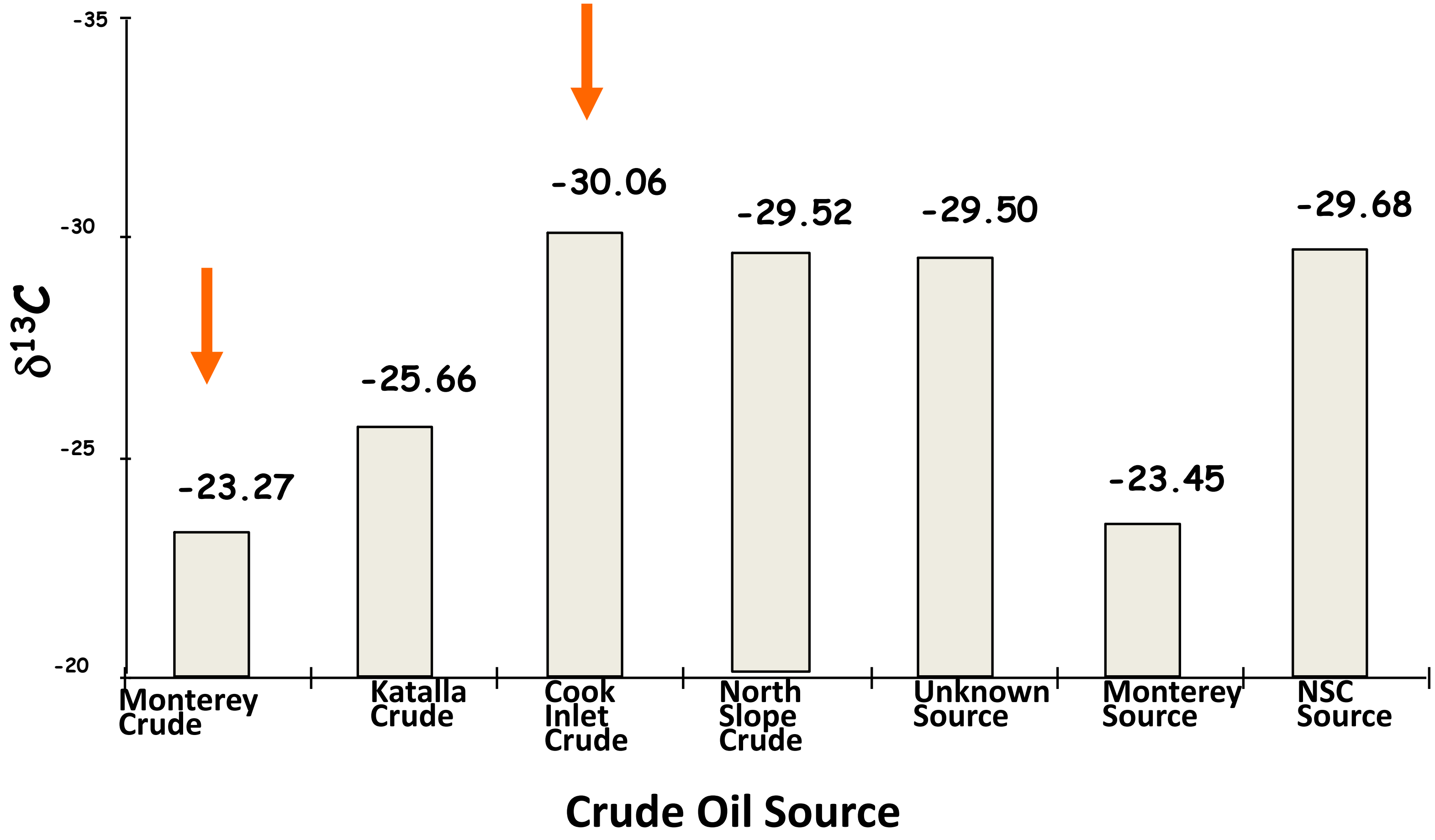
$$\delta^{13}C = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000$$

($^{13}C/^{12}C$ is 0.0112372)

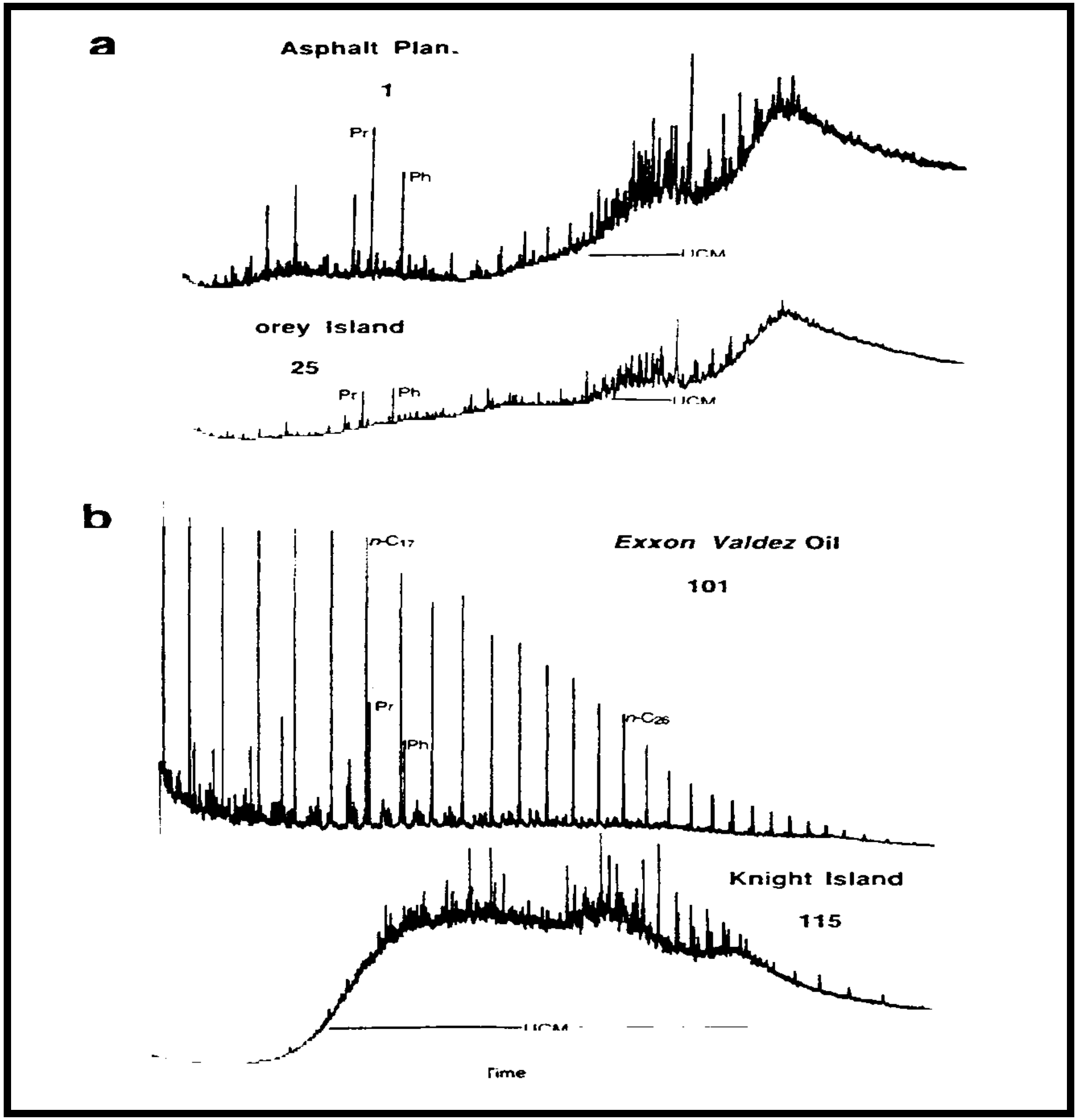
$R = {}^{13}C/{}^{12}C$

Percent MTBE remaining	$\delta^{13}C$	$^{13}C/^{12}C$
100.0	-30.0	0.010900
50.0	-24.5	0.010962
12.5	-13.4	0.011087
1.6	3.3	0.011274

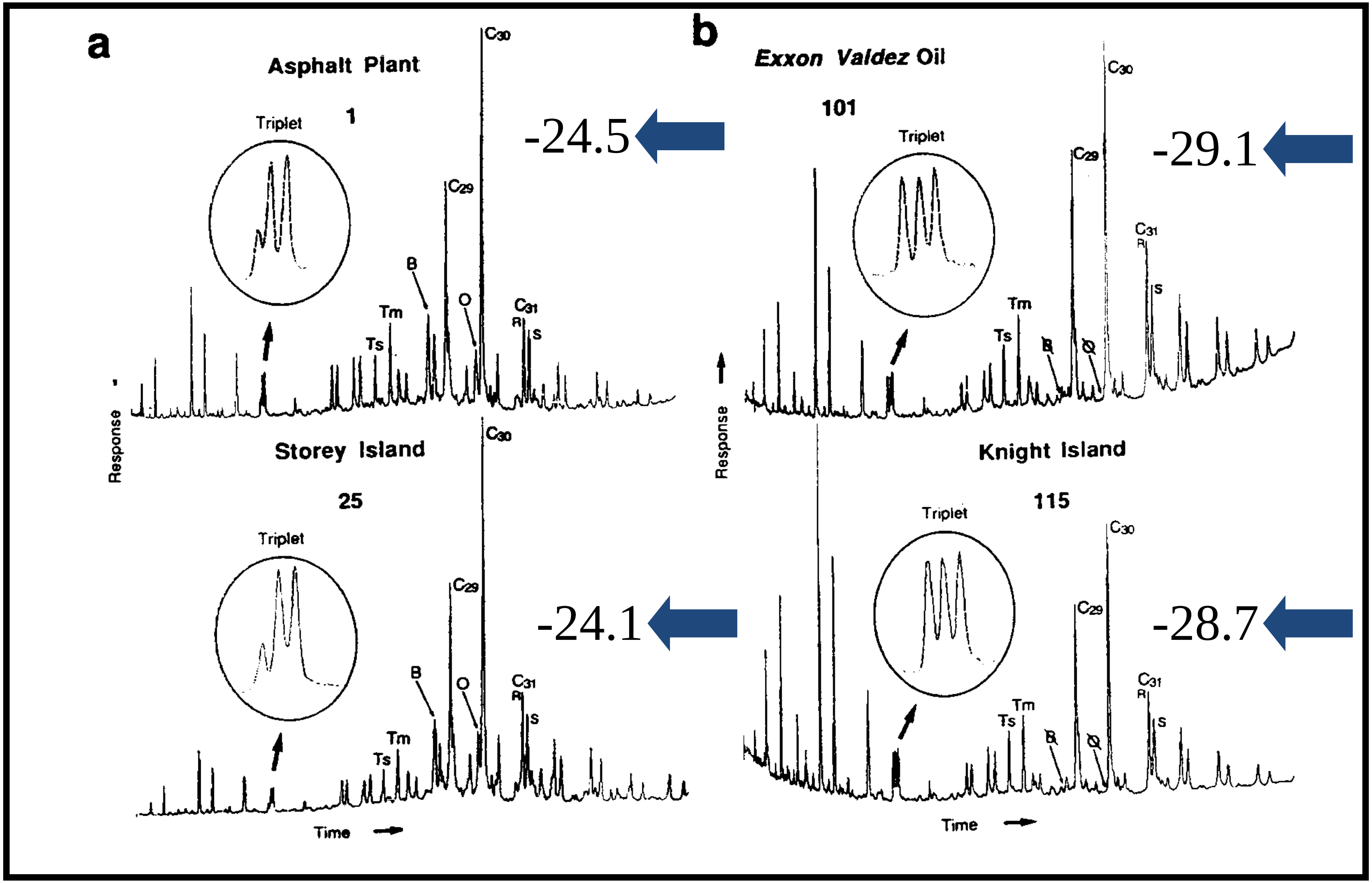
Isotope Values of Crude Oils Vary with Source



Prince William Sound Residues



Prince William Sound Residues



-24.5

-29.1

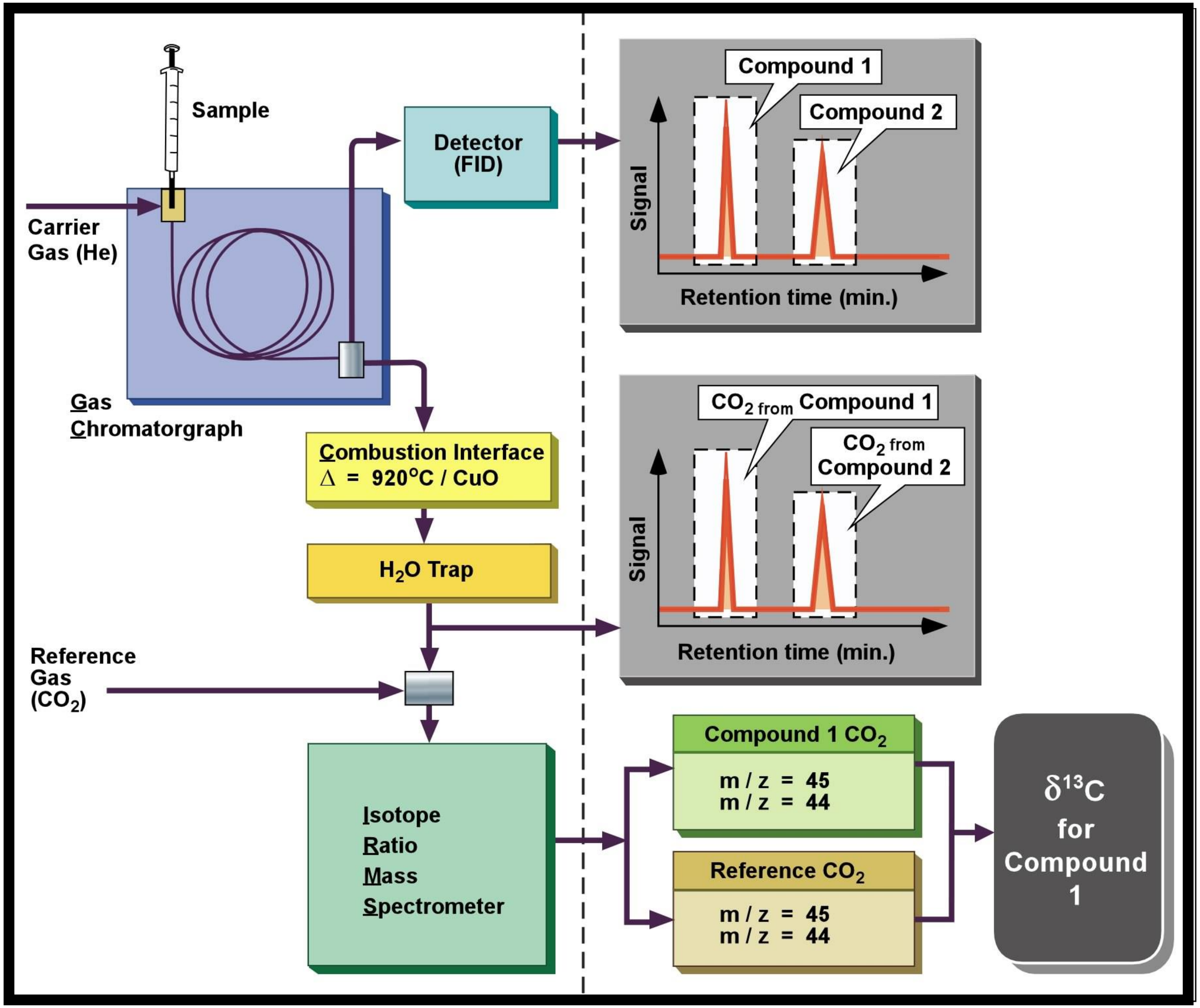
-24.1

-28.7

Compound Specific Isotope Values

- Bulk numbers represent a weighted average of the isotopic values of all the individual compounds in the sample
- The combination of gas chromatography with isotope ratio mass spectrometry (GCIRMS) permits determination of C and H isotopic composition of individual compounds in complex mixtures.
- Methods now also developed for Cl, Br, S and N discussed below.

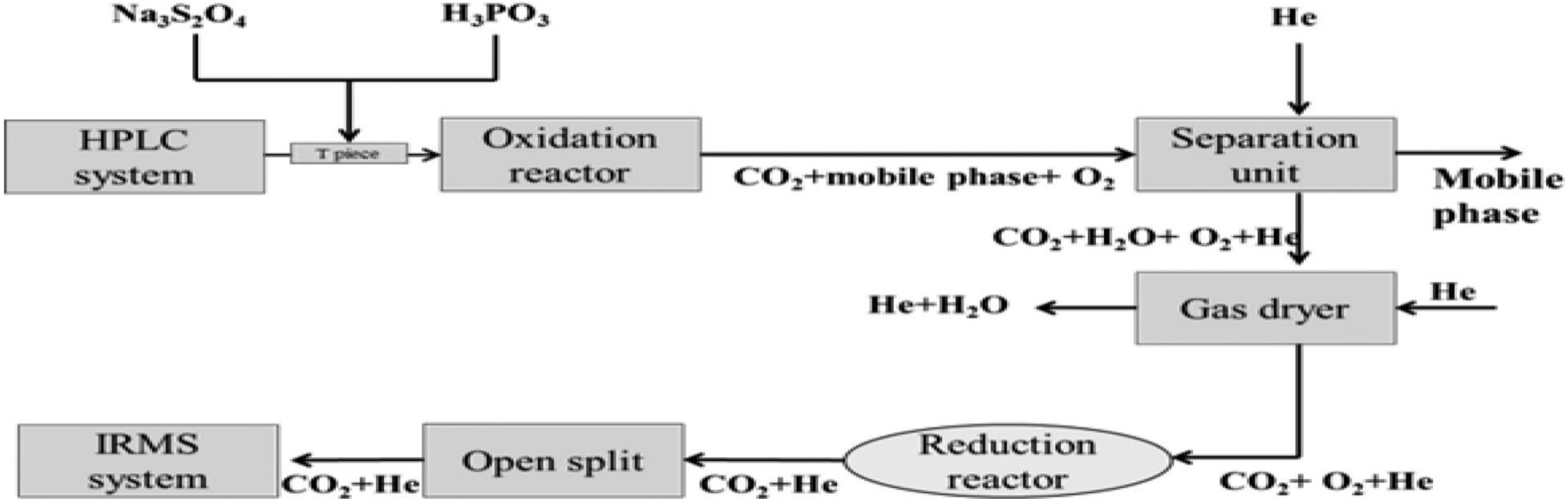
GCIRMS System



Precision for carbon +/- 0.3 per mil.
Cl/Br +/- 0.1 per mil.
H is +/- 5 per mil.
Detection limits generally around 1ppb

LC-IRMS

1. Wet oxidation following HPLC separation of CO_2



Tetyana Gilevska, Matthias Gehre,* and Hans Hermann Richnow (2014)-dx.doi.org/10.1021/ac501174d
| Anal. Chem. 2014, 86, 7252−7257

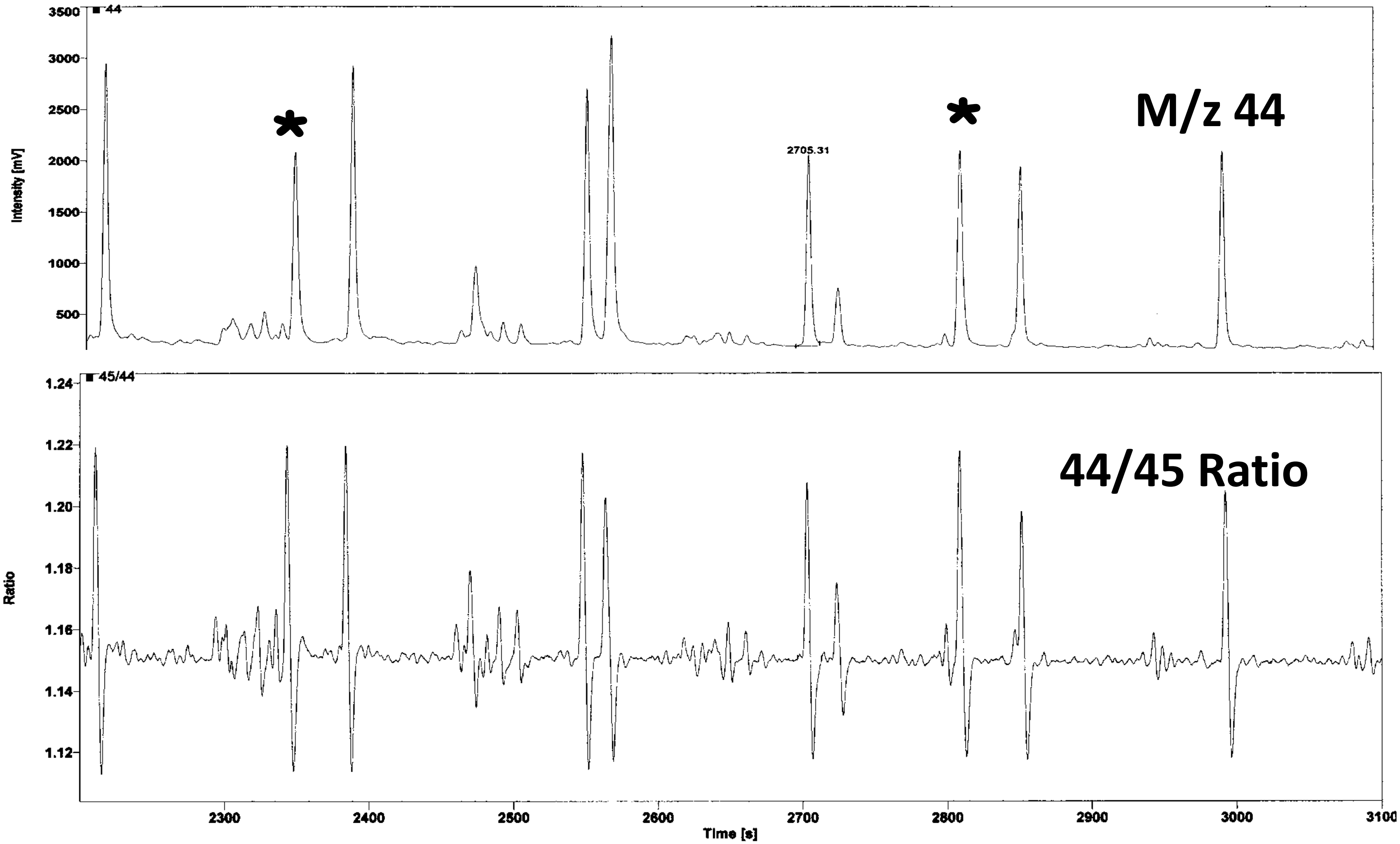
2. High temperature oxidation of non-volatile compounds followed by reduction permits both C and N isotopes to be determined.

E. Federherr, S. Willach, N. Roos, L. Lange, K. Molt, T.C. Schmidt (2016). Rapid Comm in Mass Spec., 30, 944-952. 2016.
A novel high-temperature combustion interface for compound-specific stable isotope analysis of carbon and nitrogen
via high-performance liquid chromatography/isotope ratio mass spectrometry

On-Line Determination

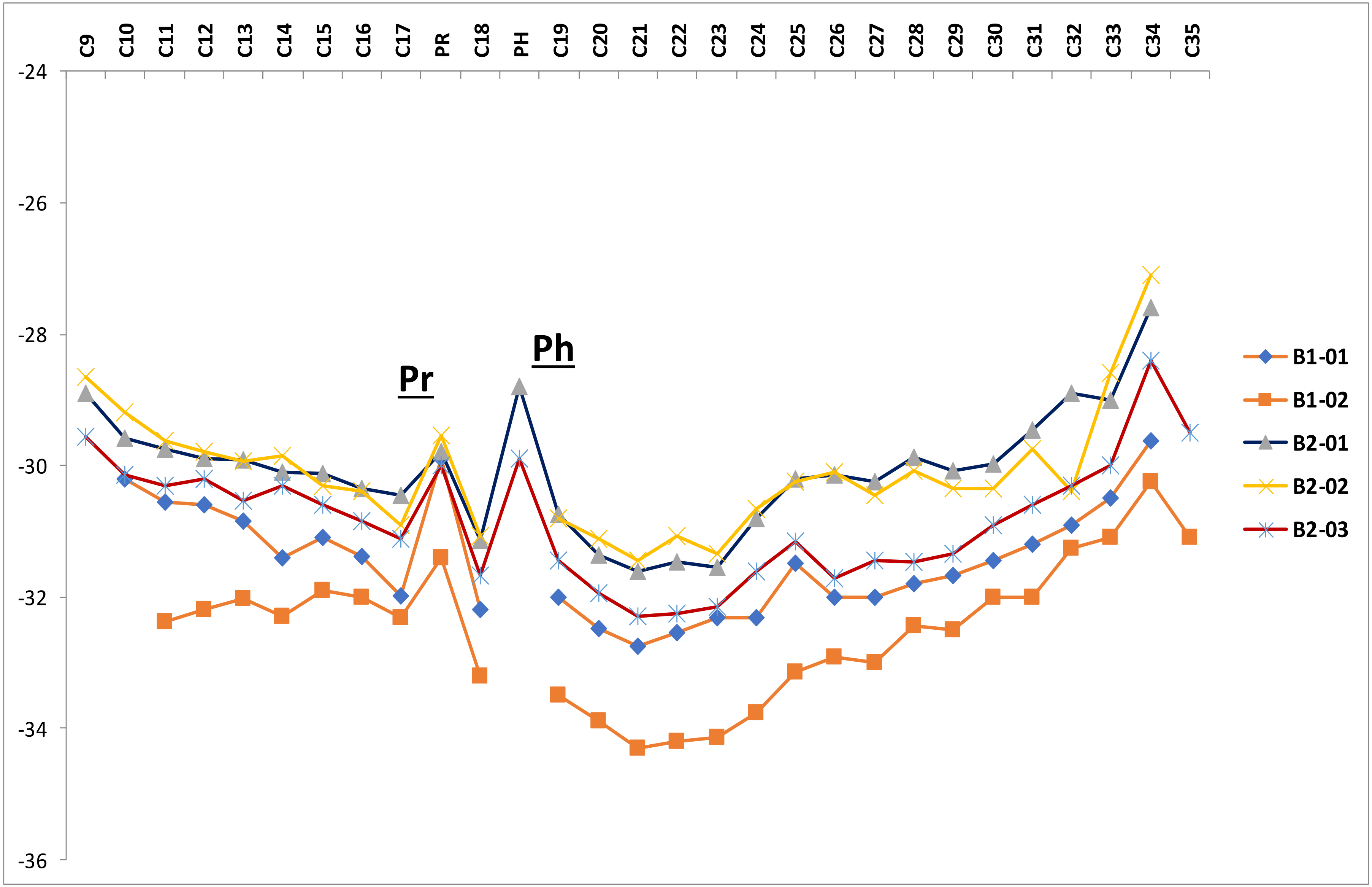
- QA/QC is critical in CSIA determinations.
- Standards of known isotopic compositions must be run at regular intervals and values obtained must be within +/- 0.5 per mil, or better, of known value prior to analyzing any samples.
- If possible internal standards of known isotopic composition should be used with the samples.
- Internal standards are often a problem because of co-elution problems.

Output from GCIRMS

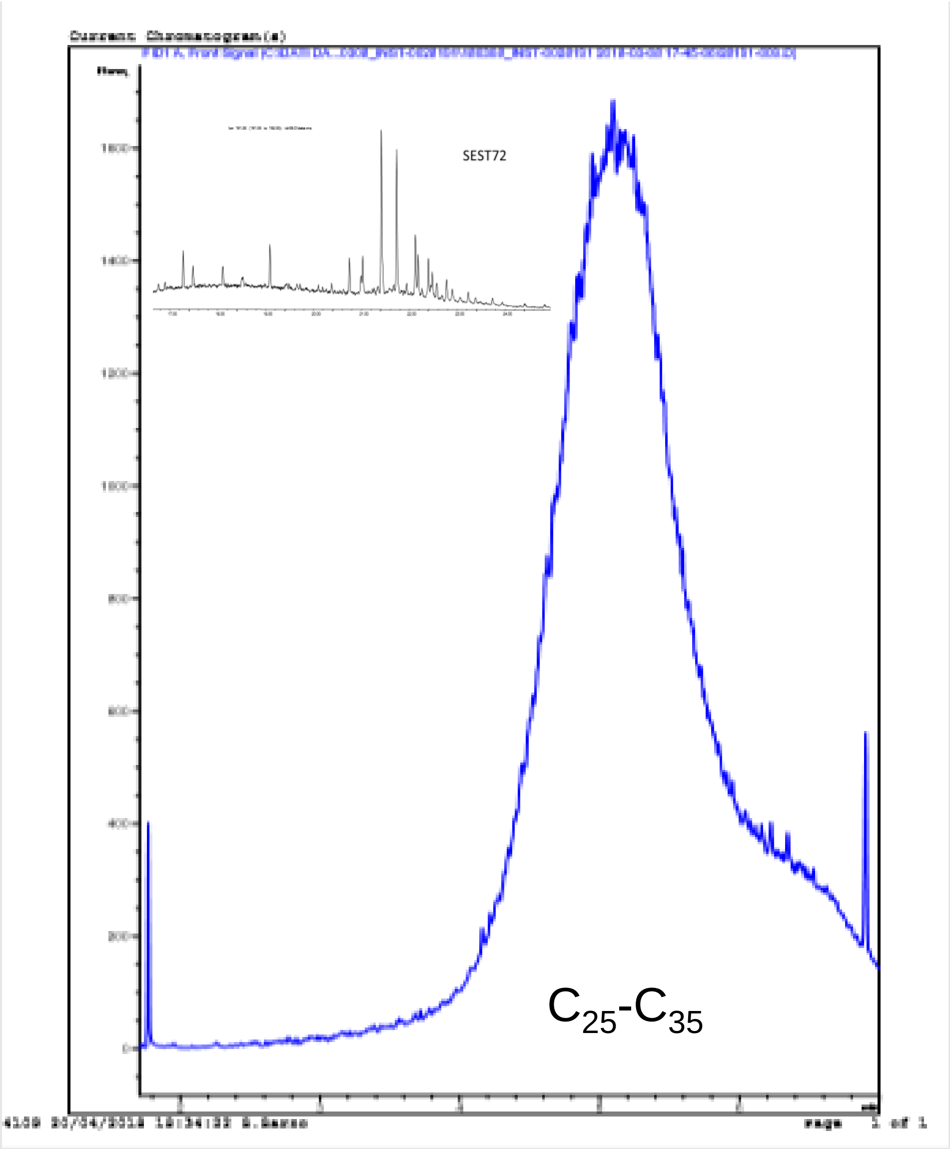


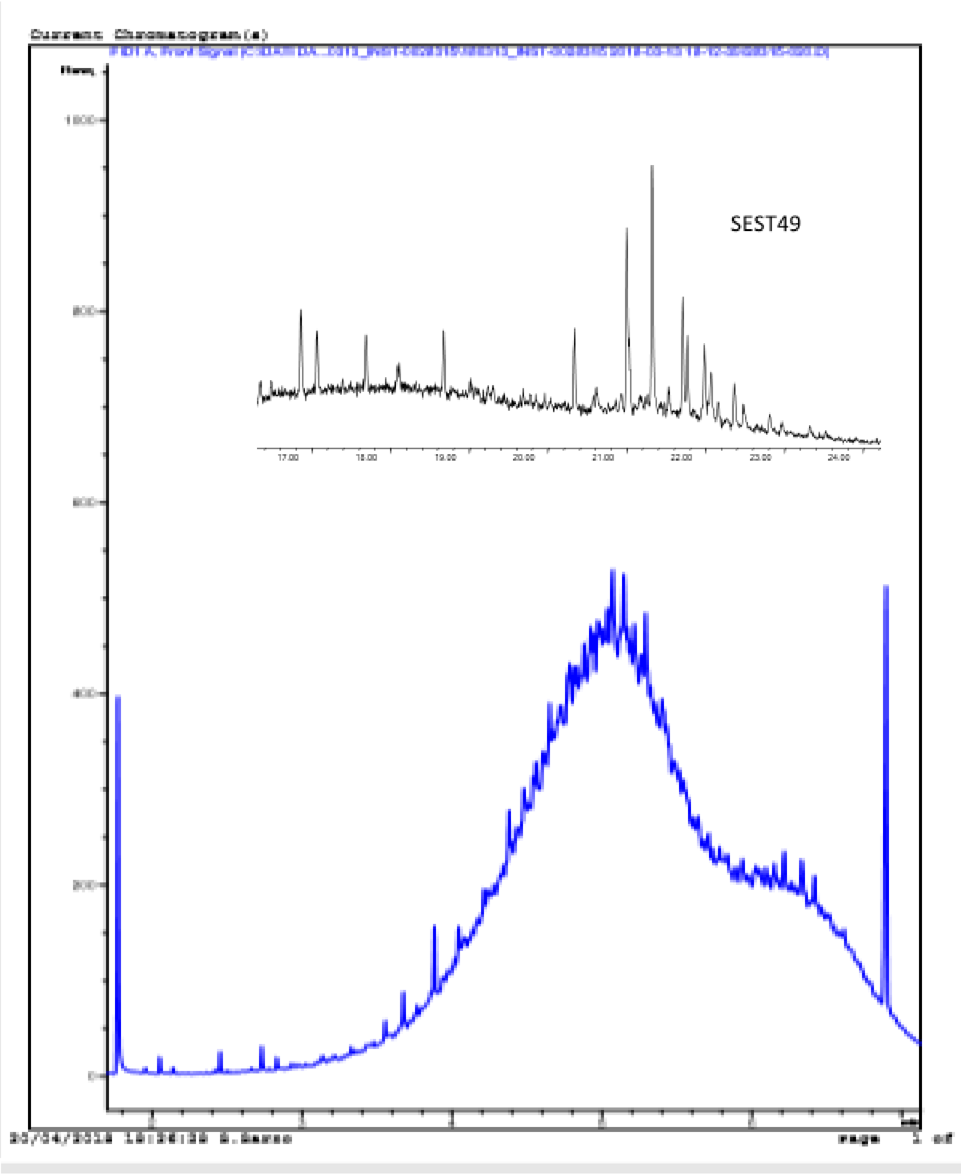
* Internal standard

GCIRMS C Data for Selected Oils



Motor Oils-Related or not?

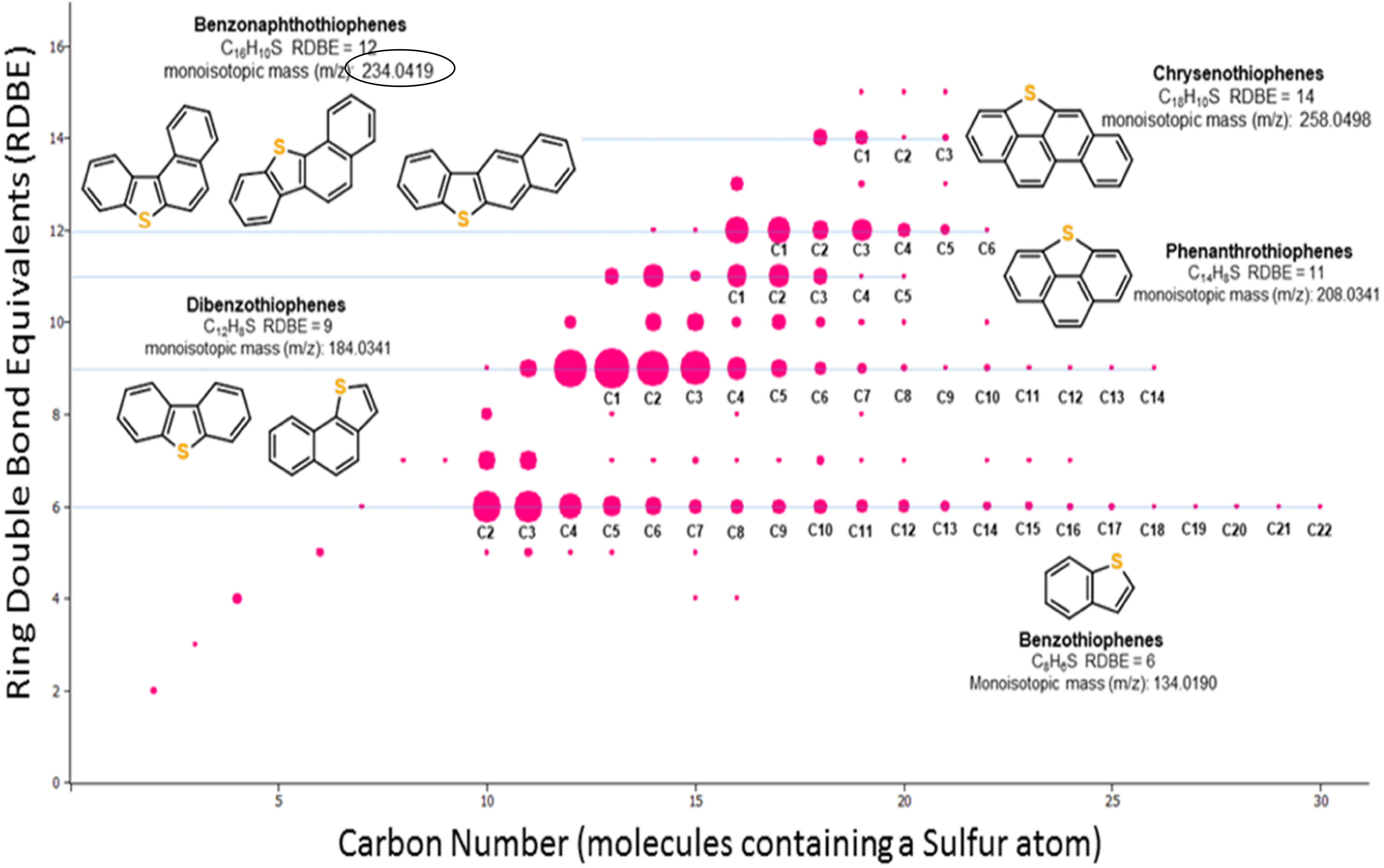




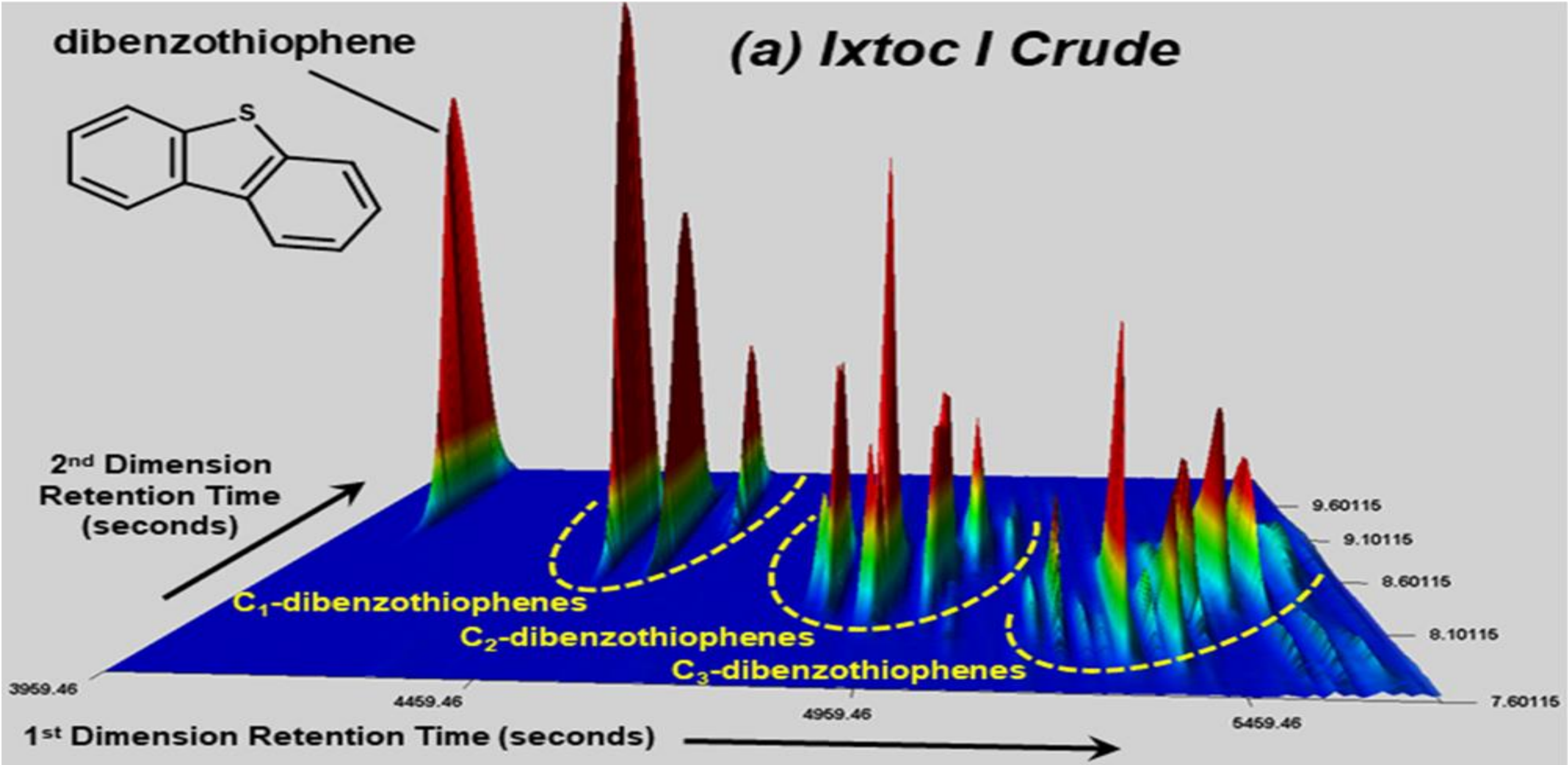
GCxGC-TOFMS

- 2D GC-TOF has greatly increased the ability to identify a far greater range of compounds than previously available with 1D GCMS.
- Does not necessarily extend the C number range of identified compounds (C_1-C_{40}).
- Despite that limitation, many previously unidentified compounds, particularly photo-oxidation products, have been identified.
- This is extremely important since many photooxidation products are toxic and may have a more significant impact on the environment than the original oil.

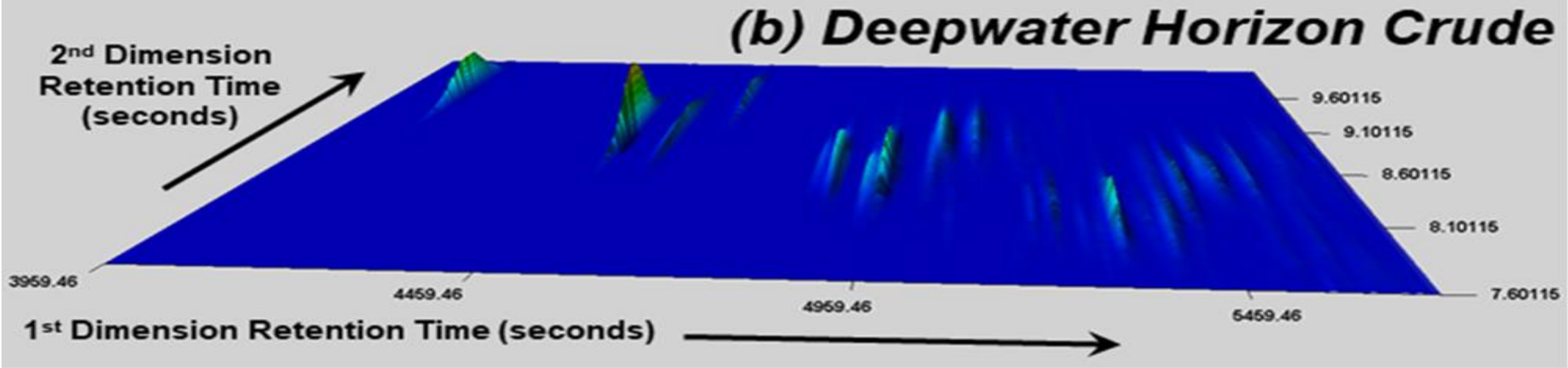
GCxGC-TOFMS


Benzonaphthothiophenes
$C_{16}H_{10}S$ RDBE = 12
monoisotopic mass (m/z): 234.0419
Chrysenothiophenes
$C_{18}H_{10}S$ RDBE = 14
monoisotopic mass (m/z): 258.0498
Phenanthrothiophenes
$C_{14}H_{8}S$ RDBE = 11
monoisotopic mass (m/z): 208.0341
Dibenzothiophenes
$C_{12}H_{8}S$ RDBE = 9
monoisotopic mass (m/z): 184.0341
Benzothiophenes
$C_{8}H_{6}S$ RDBE = 6
Monoisotopic mass (m/z): 134.0190
S
C1 C2 C3
C1 C2 C3 C4 C5 C6
C1 C2 C3 C4 C5
C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14
C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22
Ring Double Bond Equivalents (RDBE)
0
2
4
6
8
10
12
14
16
5
10
15
20
25
30
Carbon Number (molecules containing a Sulfur atom)

GCxGC-TOFMS



(a) Ixtoc I Crude



(b) Deepwater Horizon Crude

Oil Spills and Photo-oxidation

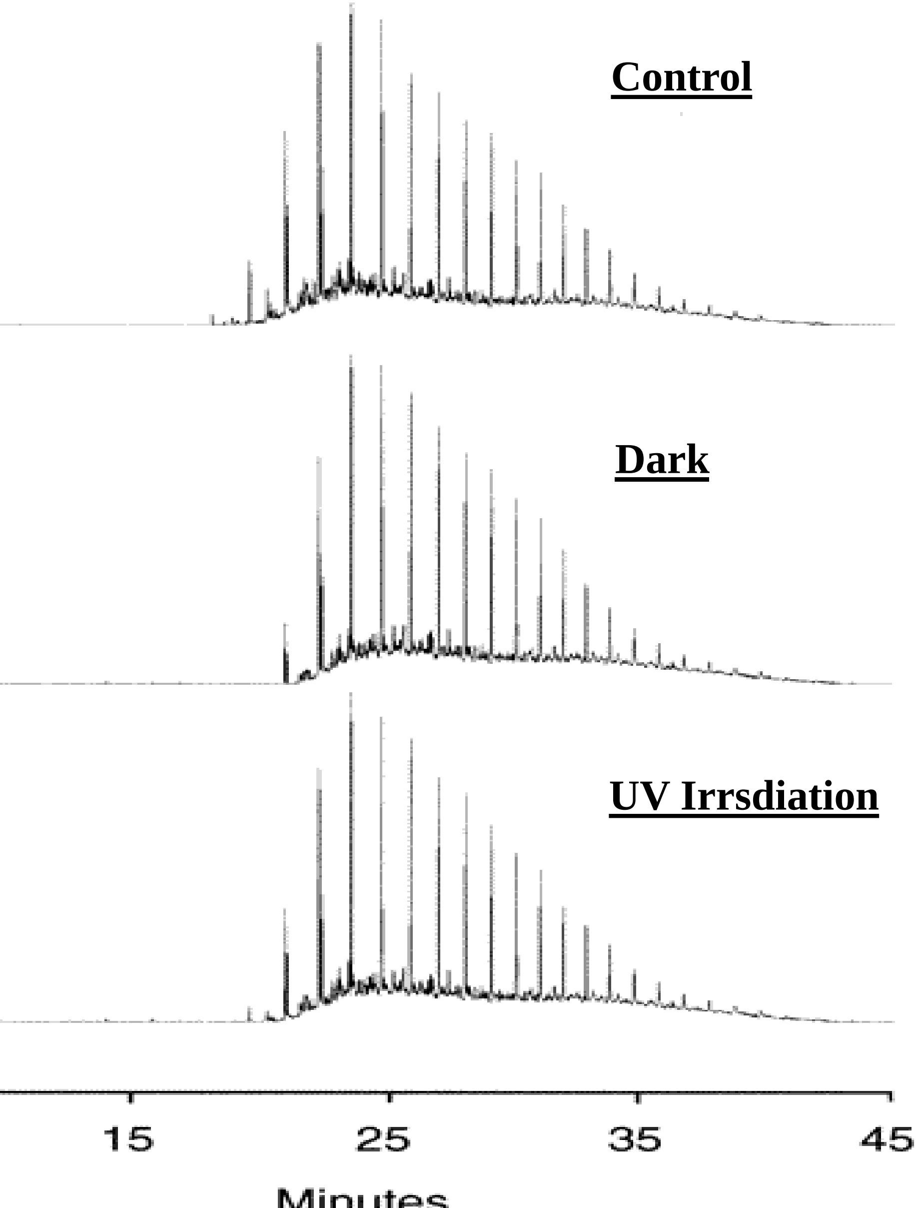
- In recent years photo-oxidation has been recognized as an important feature of crude oil weathering in addition to evaporation, water-washing and biodegradation.
- Photo-oxidation forms wide variety of acids, alcohols, peracids, epoxides and many other functionalized compounds many of which may be more toxic than the original compounds.

Photo-oxidation

Major observations:

- Saturates more resistance than aromatics
- Larger, more substituted aromatics-more susceptible
- Oxidation products typically polar
- Opposite to biodegradation-two effects may apparently cancel out in fingerprint
- Aliphatic S compounds more susceptible than thiopenic compounds

Photo-oxidation Simulation



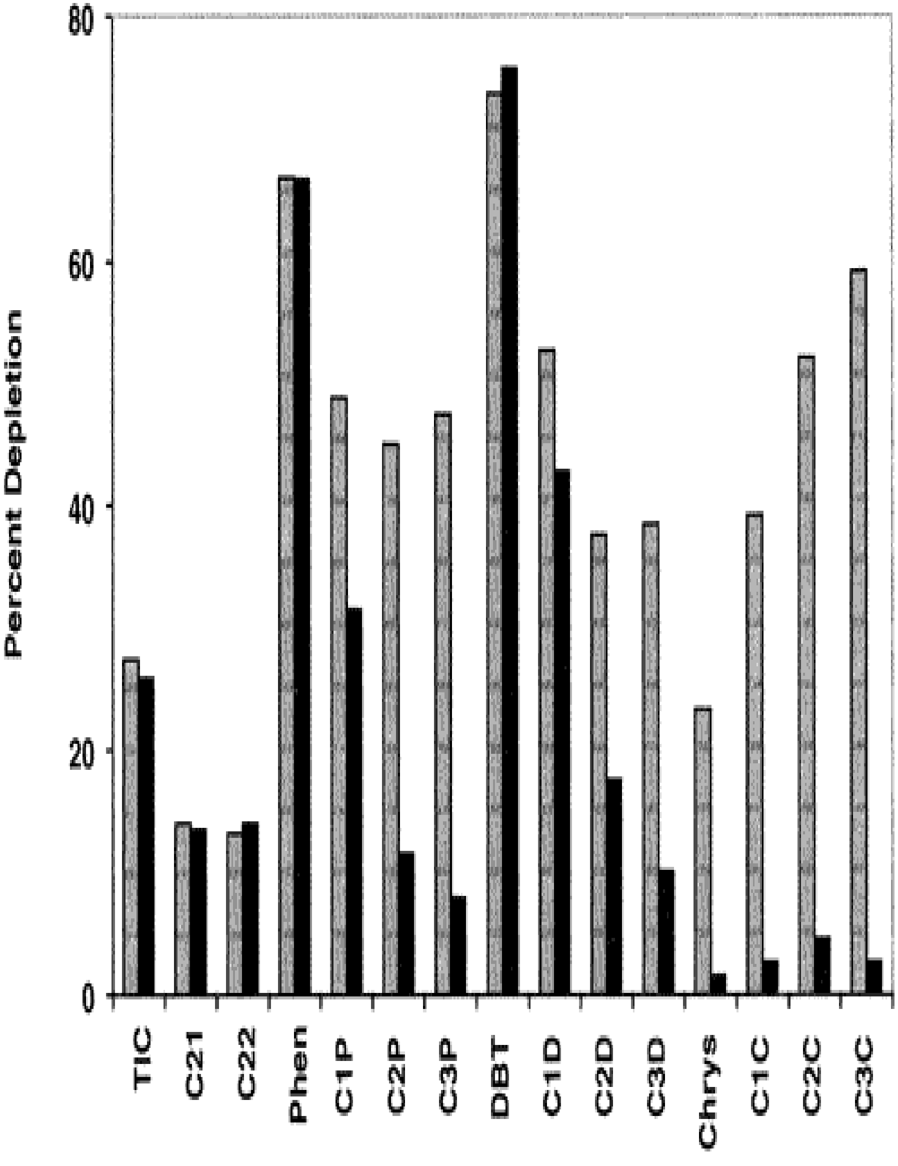
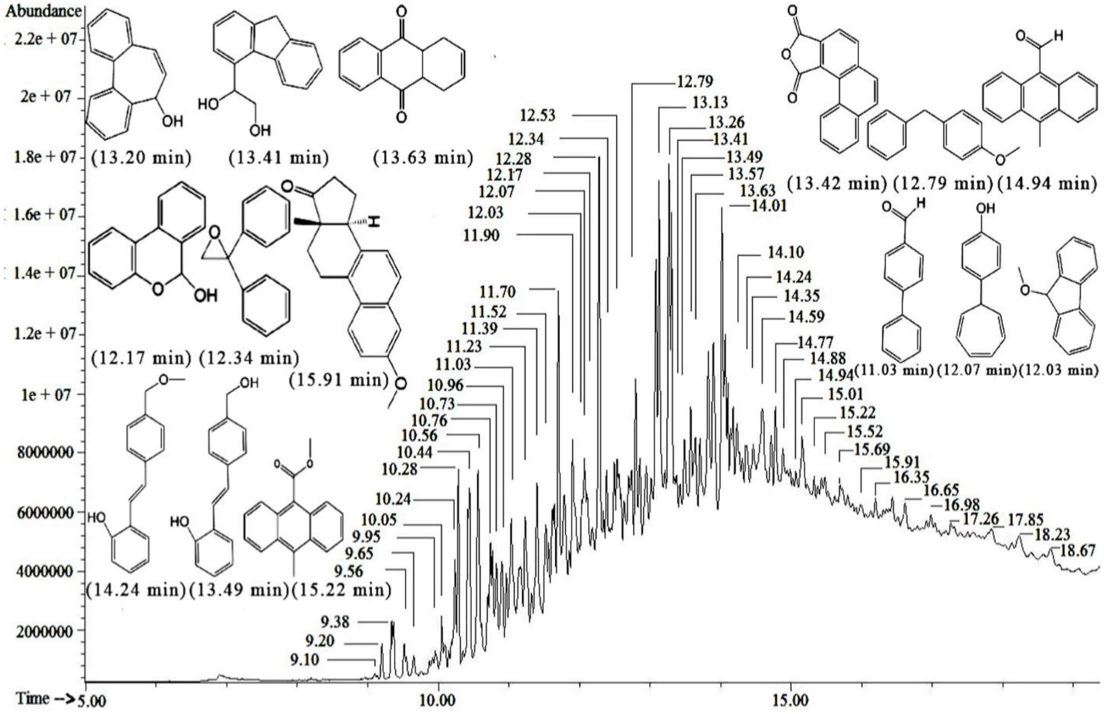
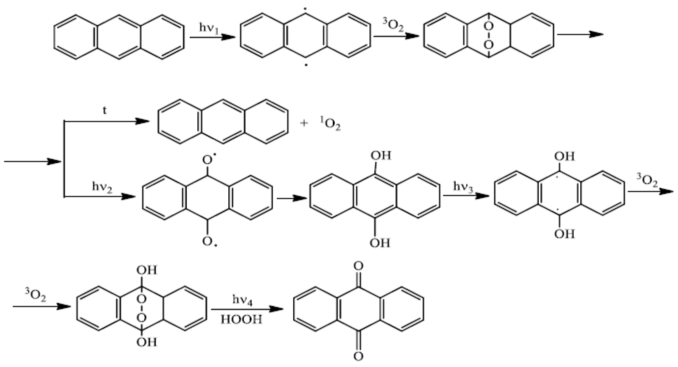
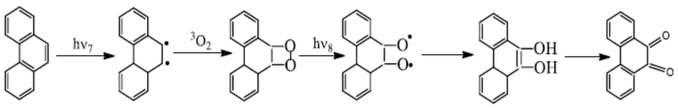


Photo-oxidation and GCxGC-TOFMS





Scheme 1. Photoradiation of linear polycyclic aromatics (anthracene type) in the oxygen medium.



Scheme 2. Photoradiation of phenes in the presence of oxygen.

Endoperoxides, hydroquinones, quinones, alcohols, aldehydes, ketones and cyclic peroxides are formed after photooxidation.

Yolchuyeva et al. (2021). Investigation of photochemical conversion processes in aromatic hydrocarbons of Balakhani oil. Journal of Petroleum Science and Engineering 196, 108089.

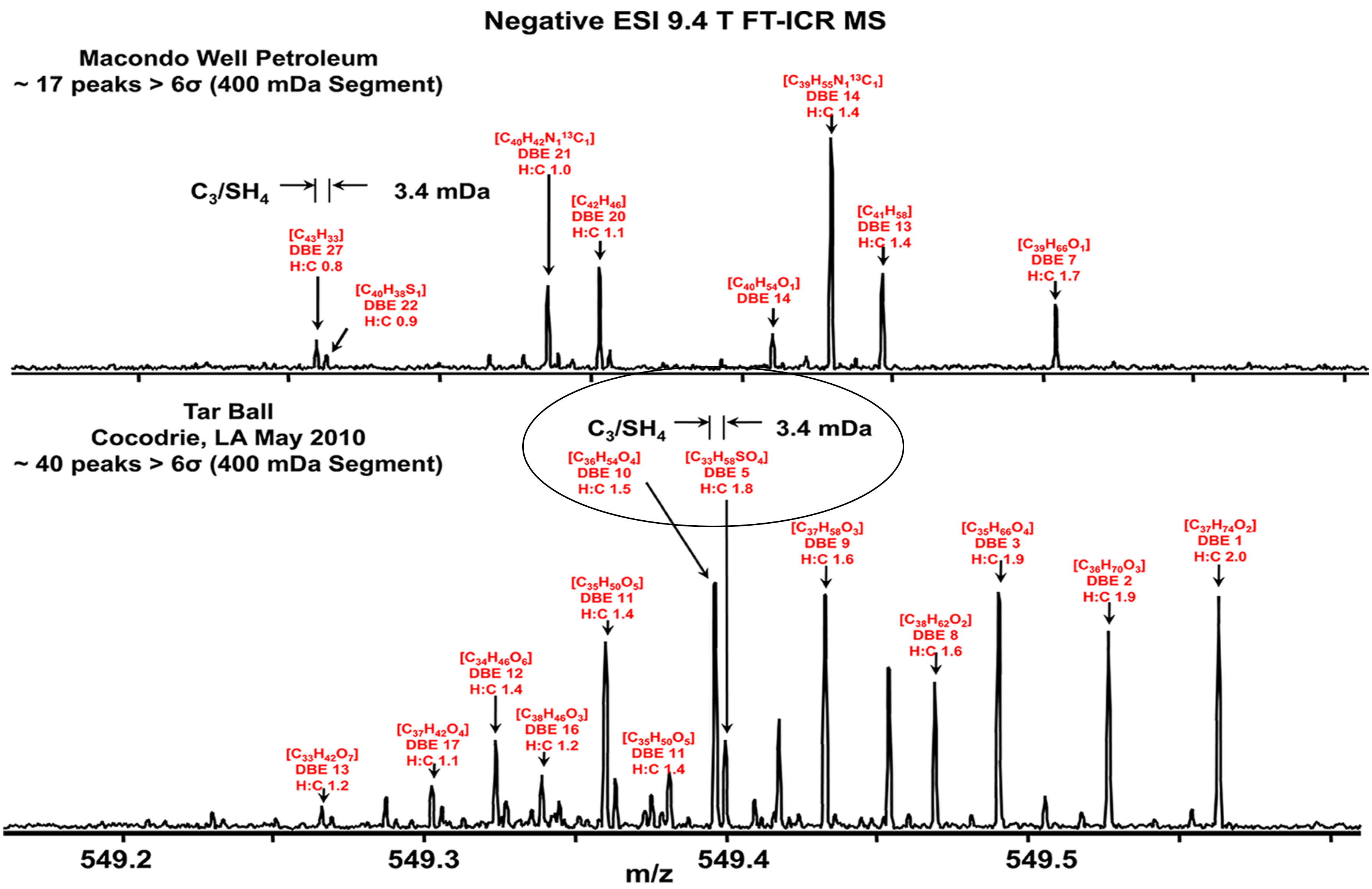
MS Resolution

- MS Resolution=Mass/ΔMass so resolution of 10,000 could separate mass 500 from mass 500.05 daltons.
- C_4H_4S and C_6H_{12} both have nominal masses of 84. However accurate masses are 84.140791 and 84.159704 respectively.
- Permits unique molecular formulae to be proposed.
- Greater the resolution smaller the mass differences determined.

Petroleomics

- Highest resolution of FT-ICR MS is currently 10,000,000 giving a Δ mass of 0.00005 daltons. Assign formulae to over 49,000 components in a single analysis.
- Parent ions generated using electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) or laser desorption.
- Output is series of parent ions with very accurate mass measurements that are converted into a unique formula and number of double bond equivalents. No structures since no fragmentation patterns available.
- Diagrams produced provide for qualitative comparison between samples.
- The actual number of compounds present in petroleum is not known and, in theory, could be many, many orders of magnitude greater than ~100,000 partially characterized.

Petroleomics



Negative ESI 9.4 T FT-ICR MS

Macondo Well Petroleum
~ 17 peaks > 6σ (400 mDa Segment)

Tar Ball
Cocodrie, LA May 2010
~ 40 peaks > 6σ (400 mDa Segment)

McKenna et al., dx.doi.org/10.1021/es305284t | Environ. Sci. Technol. 2013, 47, 7530−7539

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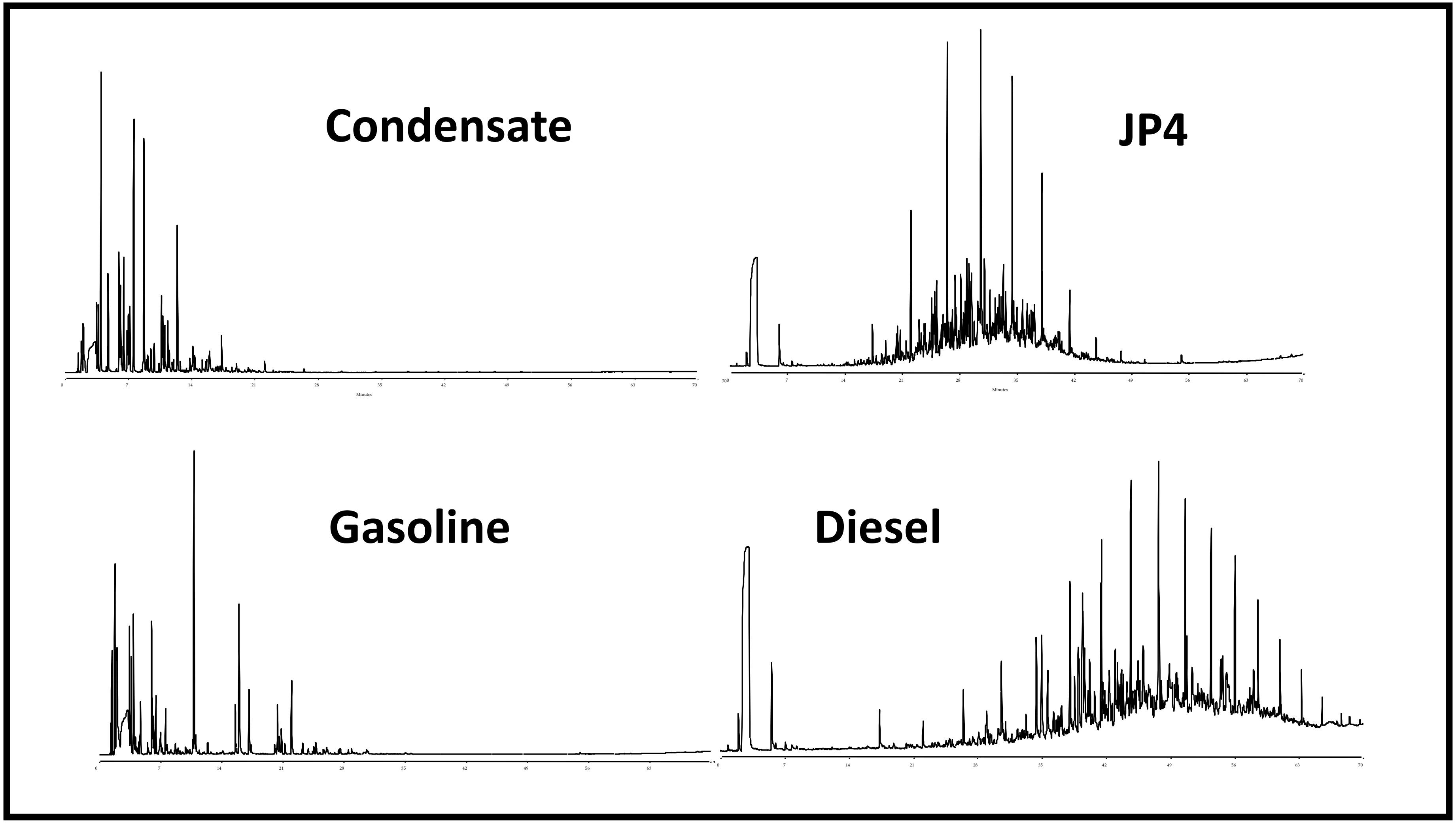
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
    - Diesel, Gasoline, Motor oil
    - Groundwater contaminants
    - Chlorinated Solvents
    - PAHs
    - PCBs
    - Benzene
    - Other compounds
    - Chlorine, Bromine and Sulfur Isotopes

- Vapor Intrusion Studies
- Summary

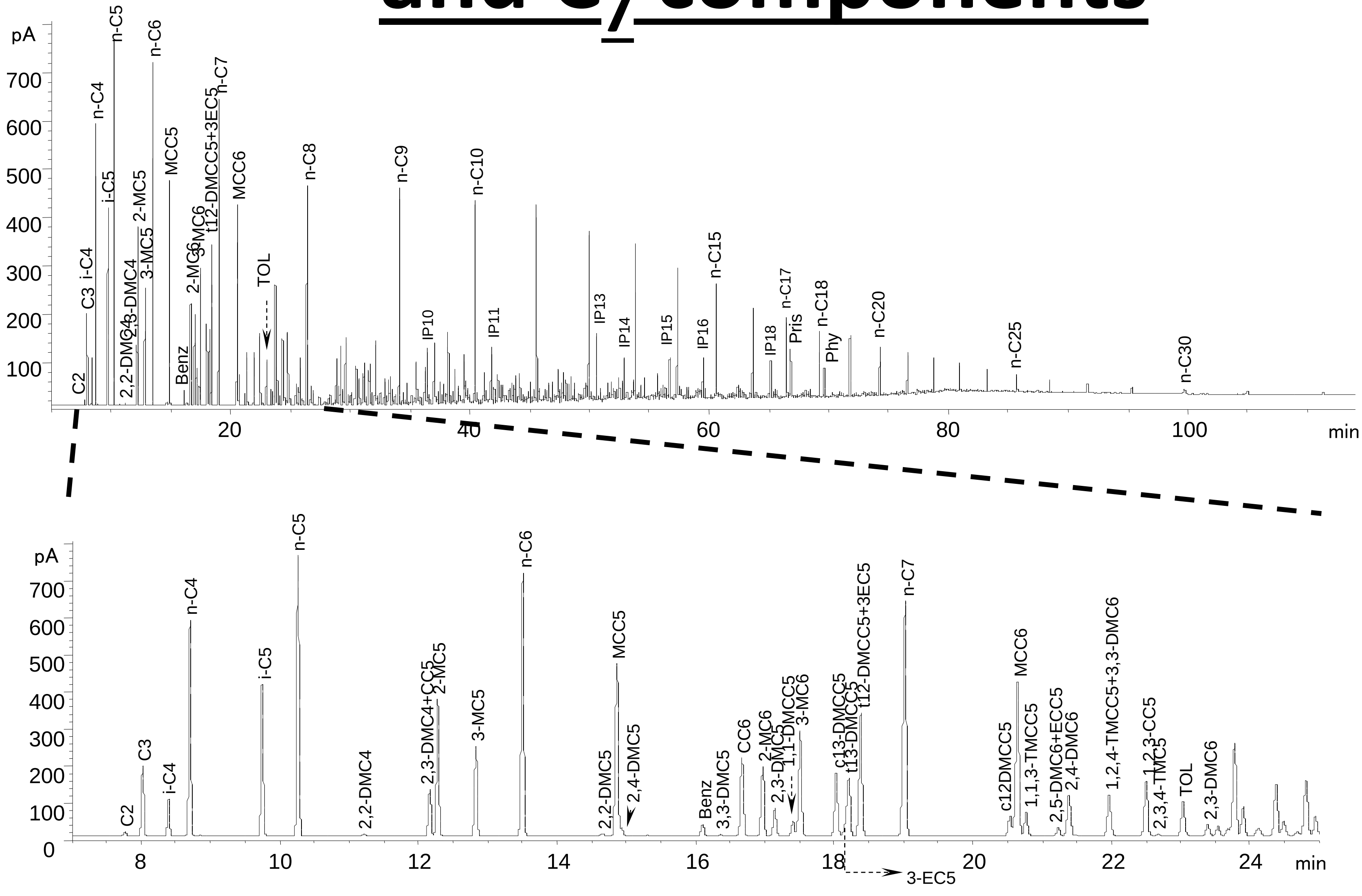
Environmental Forensics

- Hydrocarbons
  - Wide variety of sources and products
    - Tankers, pipelines, trains, wells, underground and above ground storage tanks, refineries.
    - Released products may be wide variety of crude oils; refined products; coal tars of various origins and ages; refinery streams or additives; asphalt; and many others.
  - Environmental conditions may vary significantly
    - Environmental impacts may include temperature; fresh vs. saline water; redox potential; surface release vs subsurface release; time since release occurred; environmental energy; and many others.
  - Main analytical techniques
    - GC and GCMS

Fingerprinting by Gas Chromatography



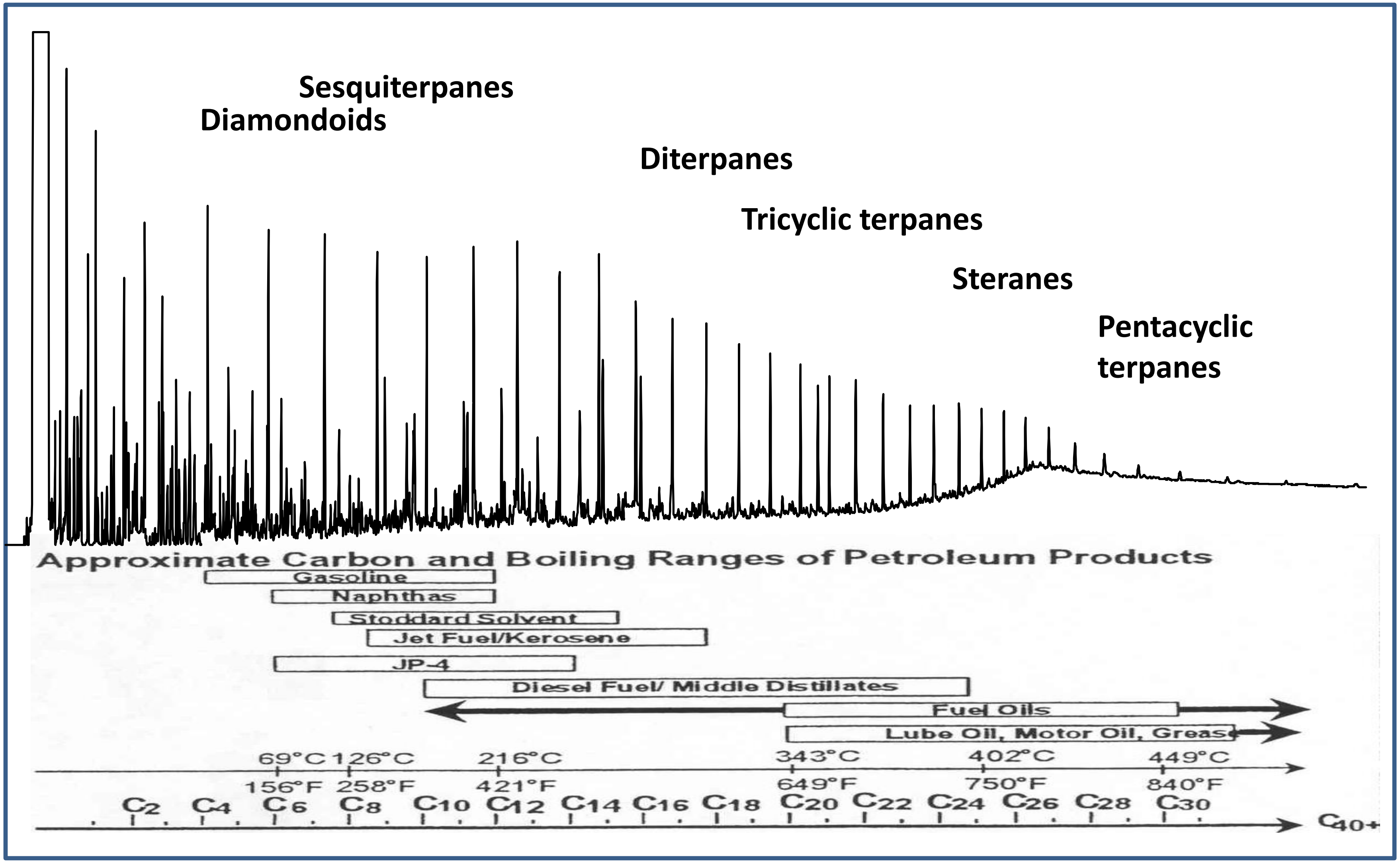
Whole oil chromatogram and C_7 components



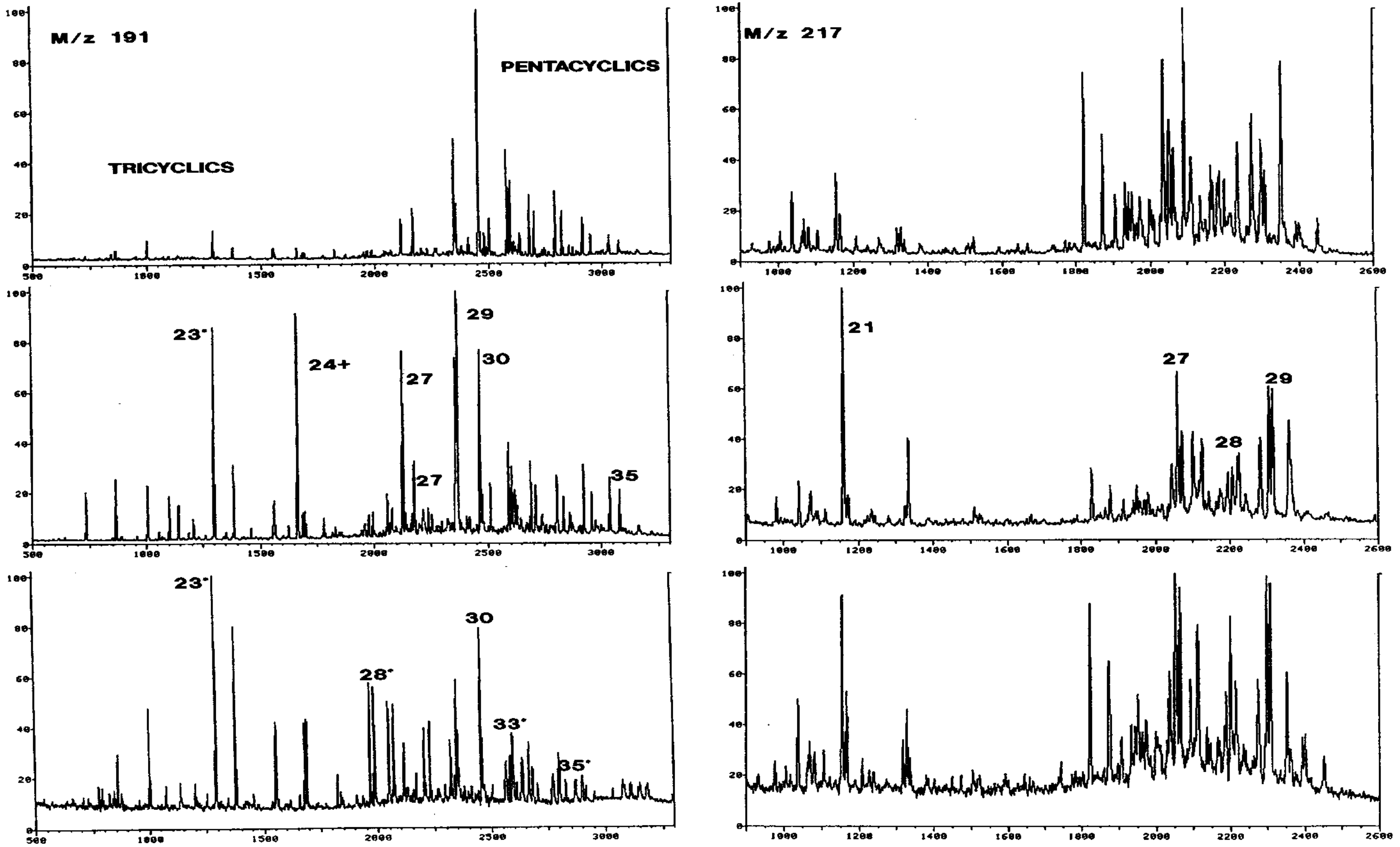
GCMS-Biomarkers

- Biomarkers have long been used in the field of petroleum exploration for characterizing and understanding the origin and history of crude oils.
- Whilst in an exploration context applications are related to understanding features such as nature of source material deposited millions of years ago; maturity; depositional environments etc., environmental applications are typically related to fingerprinting and establishing relationships between samples based on similarities or differences in their fingerprints.
- One of the significant advantages of biomarkers is that in the short term-weeks, months, or a few years, these compounds are relatively resistant to biodegradation.

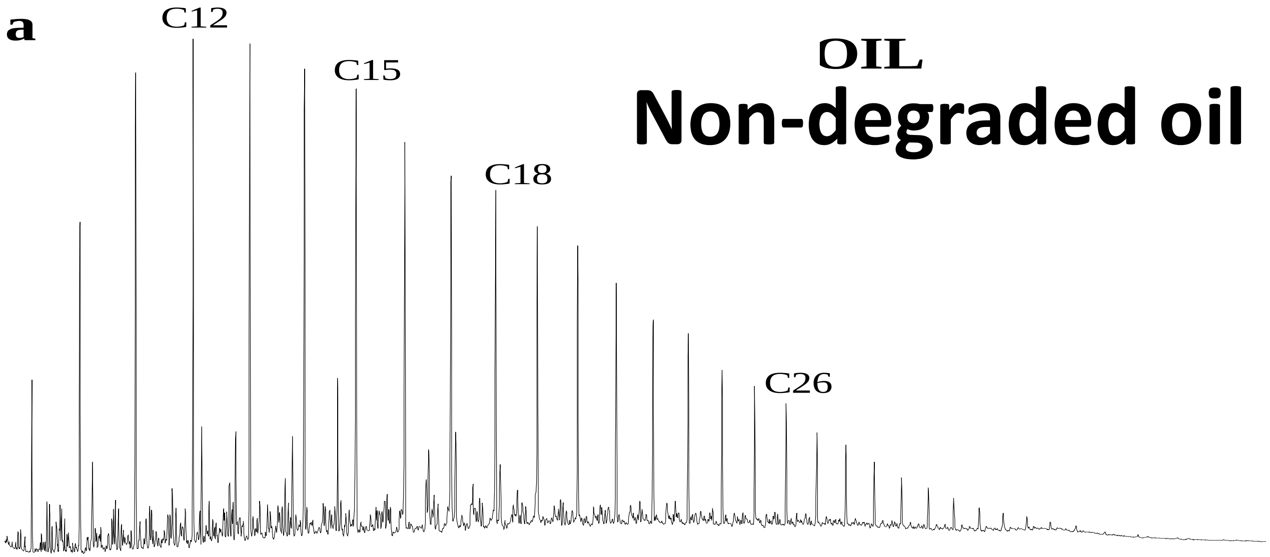
Components of a Crude Oil



Biomarker Distributions

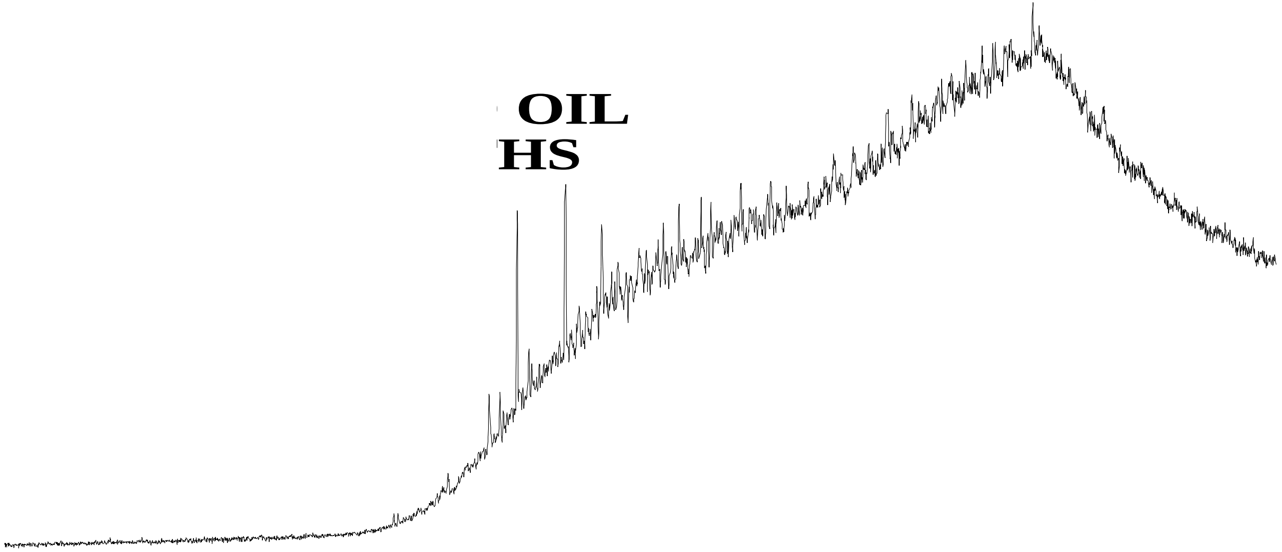


Weathering Effects on Crude Oils

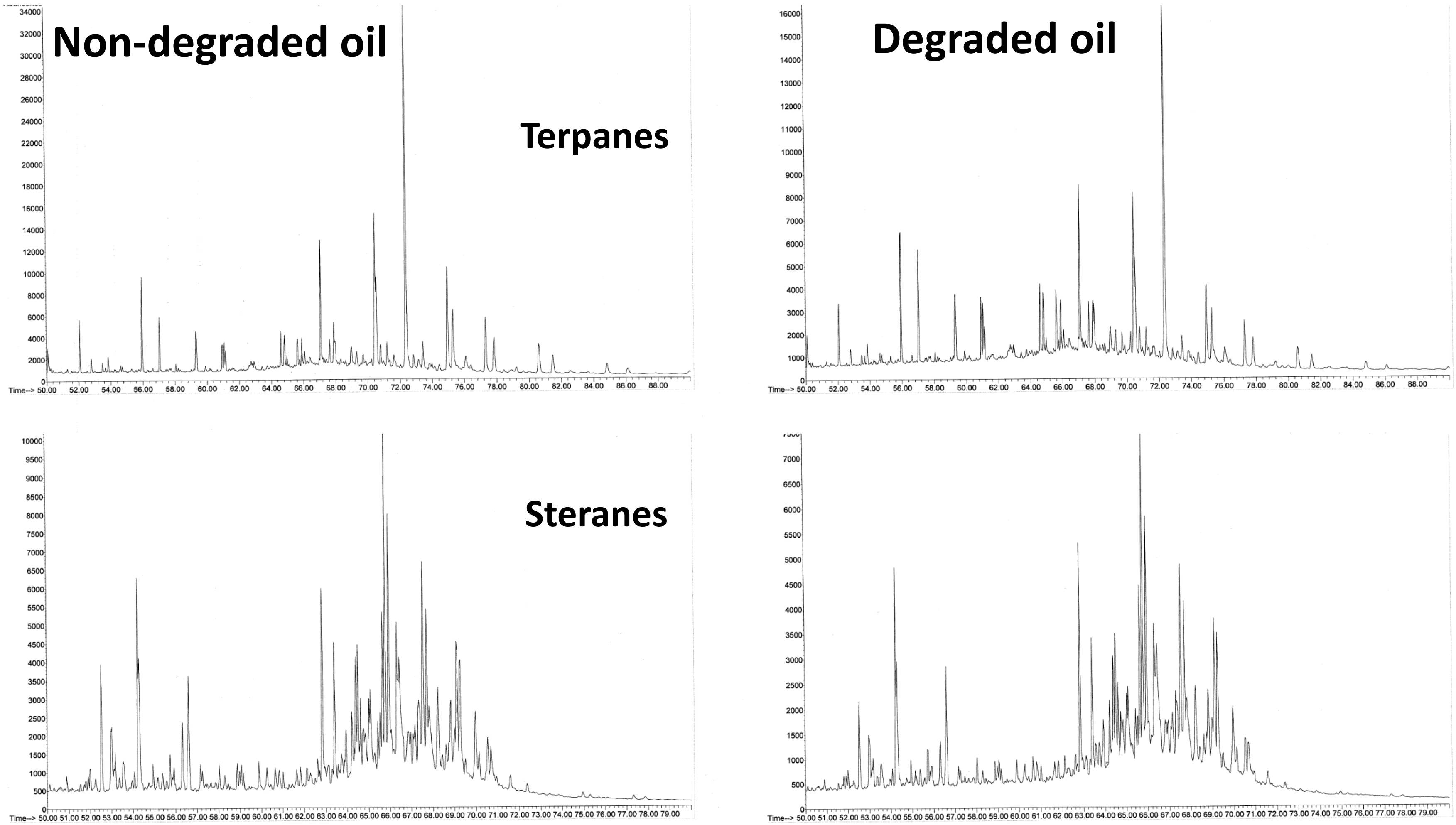


Non-degraded oil

Heavily degraded oil

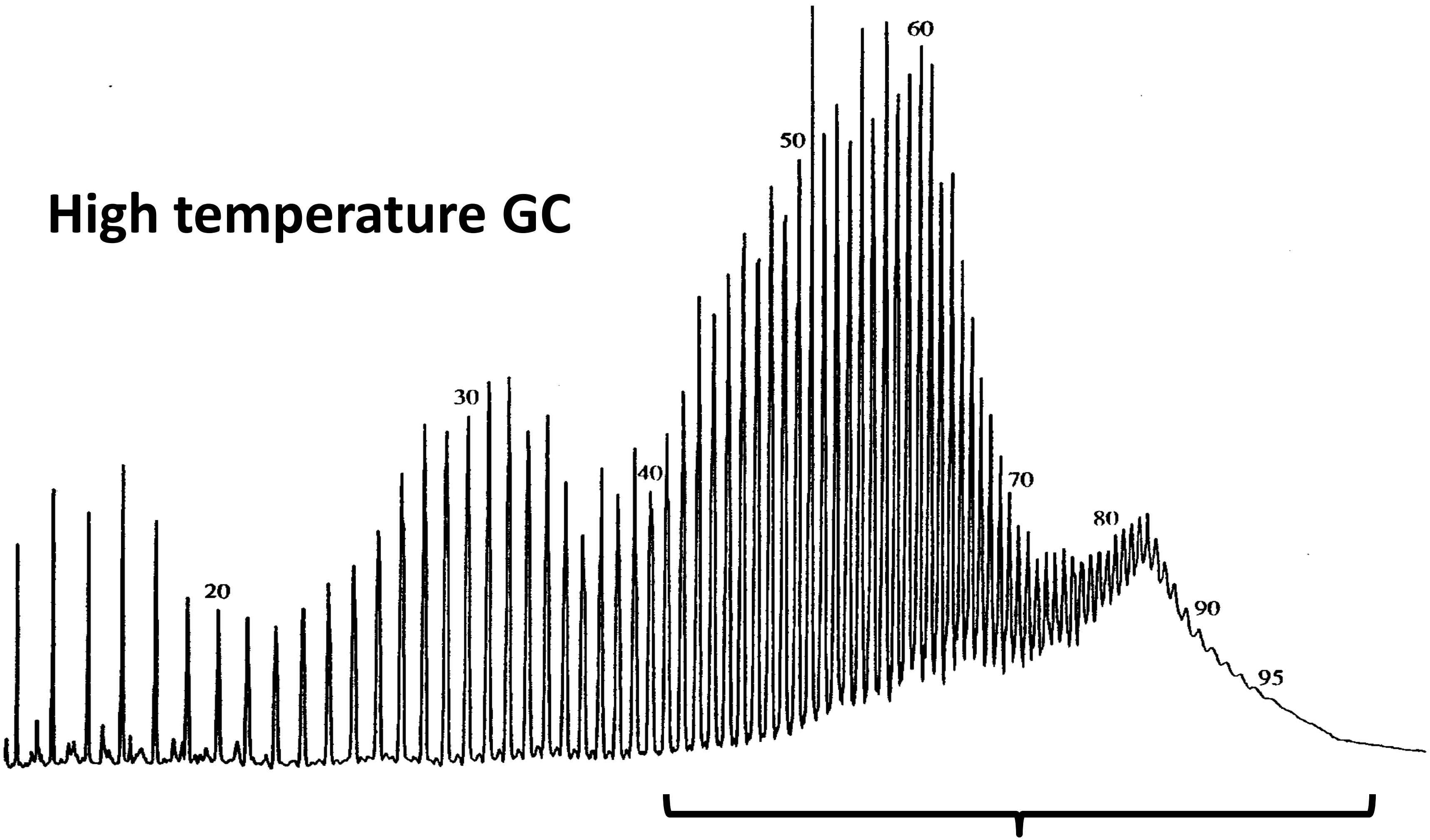


Degraded and Non-degraded Oils



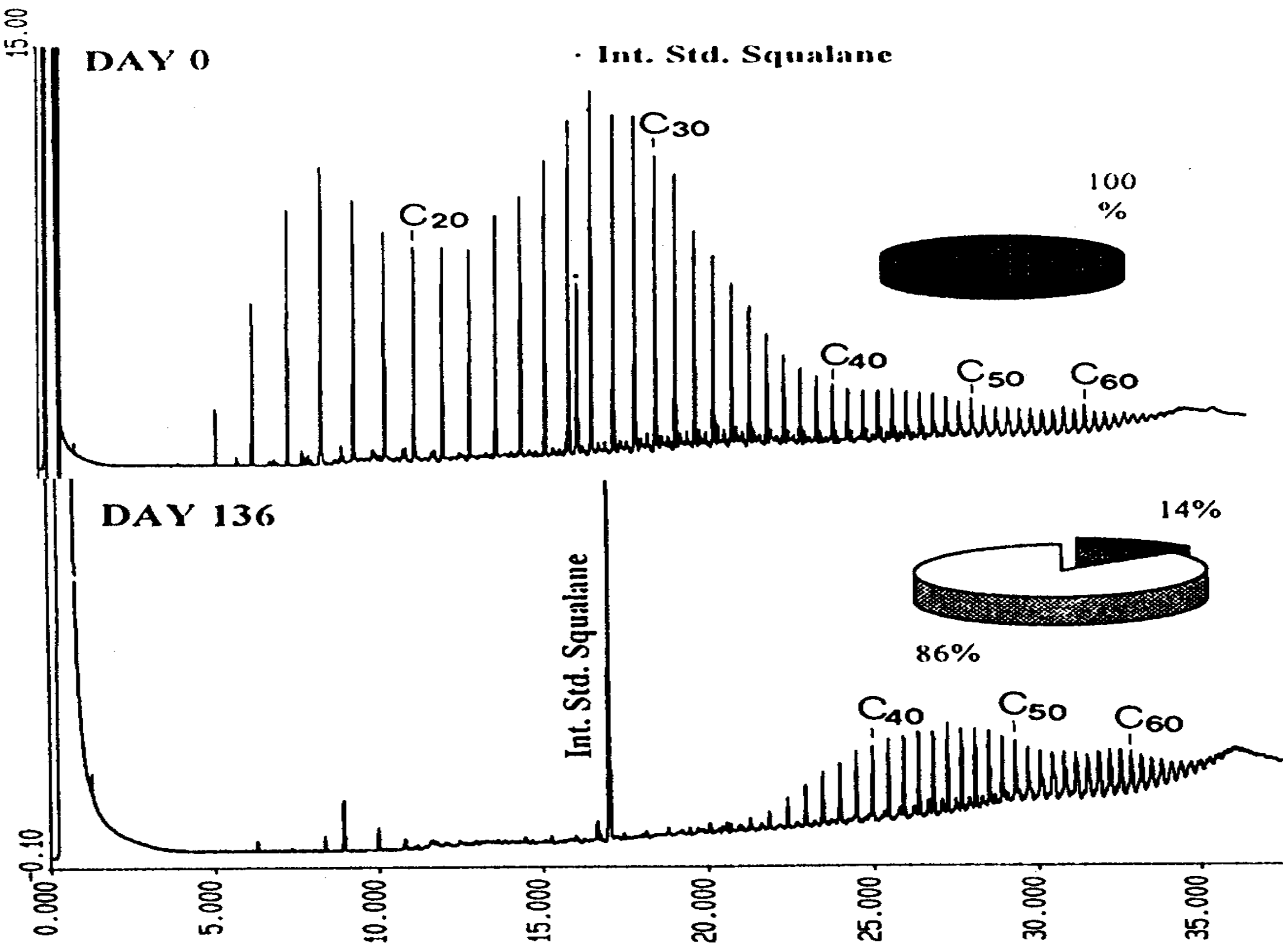
HMWHCs in Crude Oils

High temperature GC



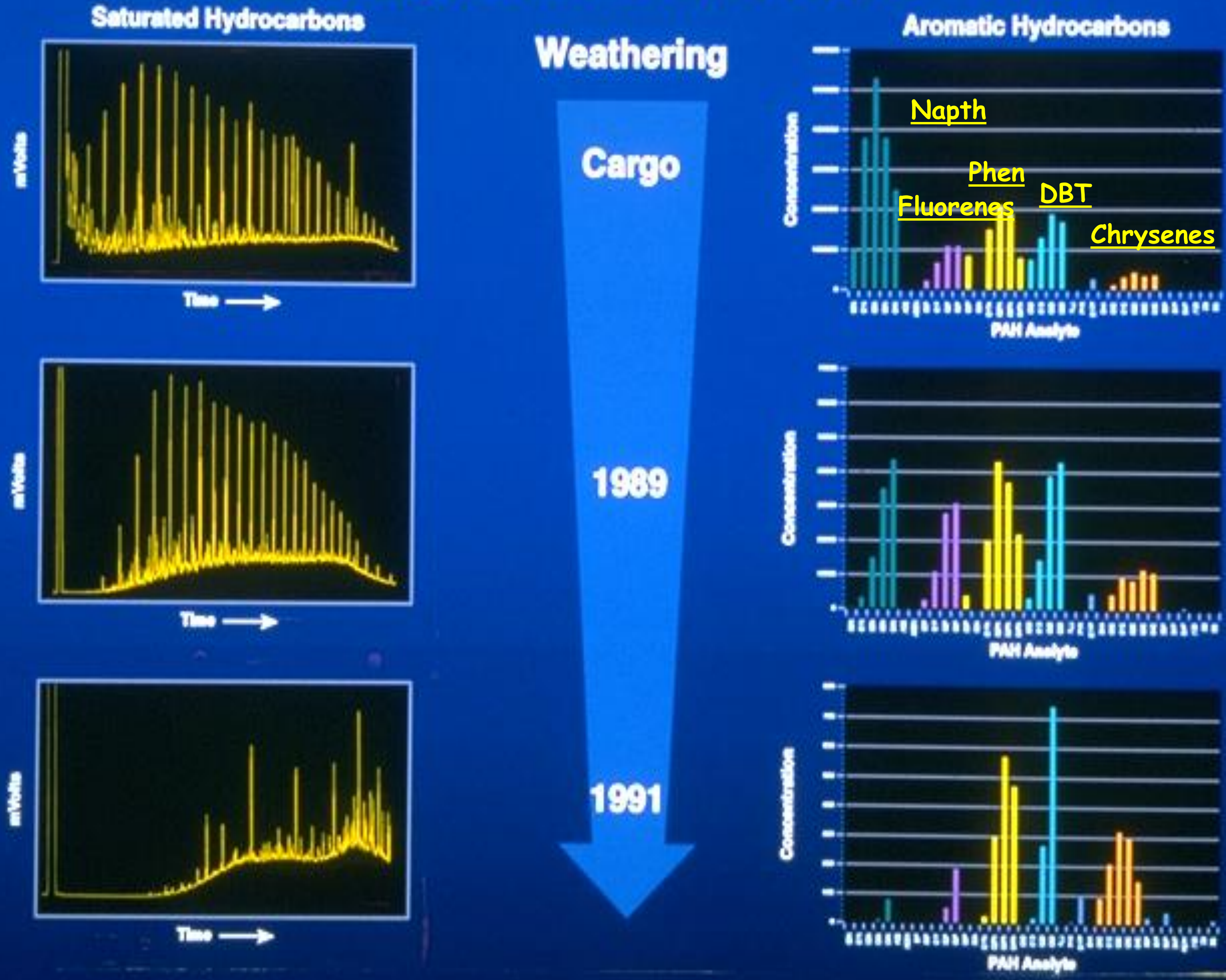
Recalcitrant and generally overlooked

Crude Oil Biodegradation



Heath DJ, Lewis CA, Rowland SJ (1997) Org Geochem 26:769–785

Weathering of EVC Oil Over 2 Years



Saturated Hydrocarbons

Weathering

Cargo

1989

1991

Aromatic Hydrocarbons

Napth

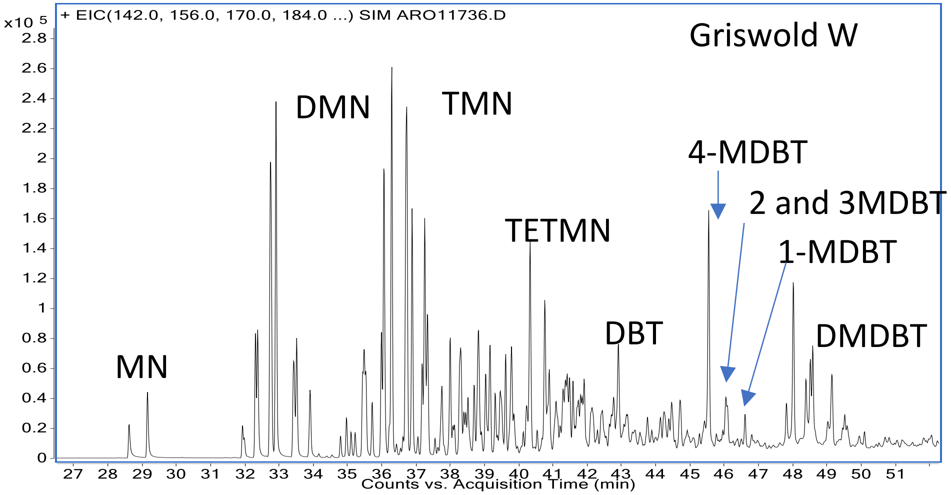
Phen

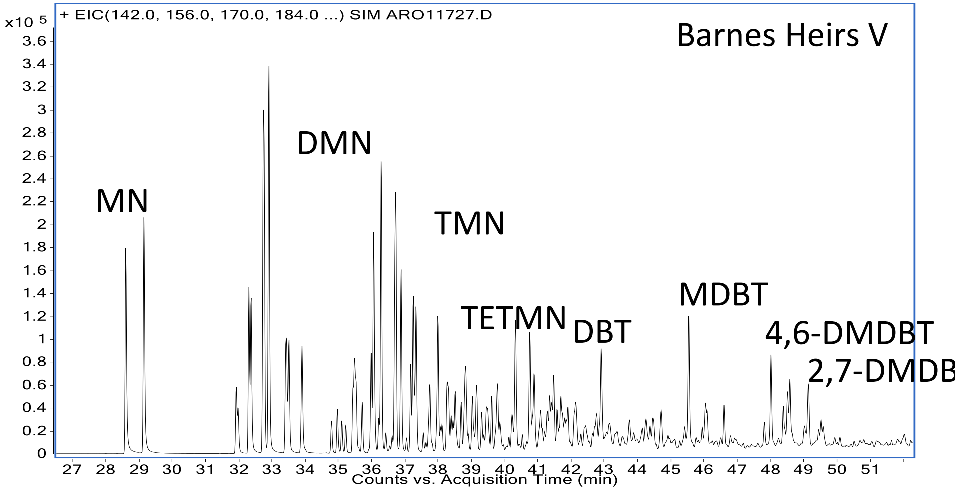
Fluorenes

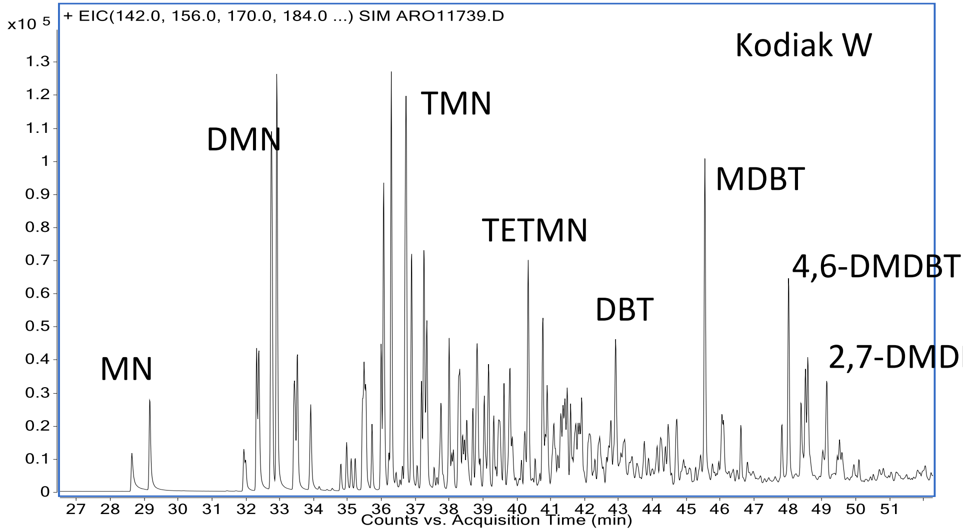
DBT

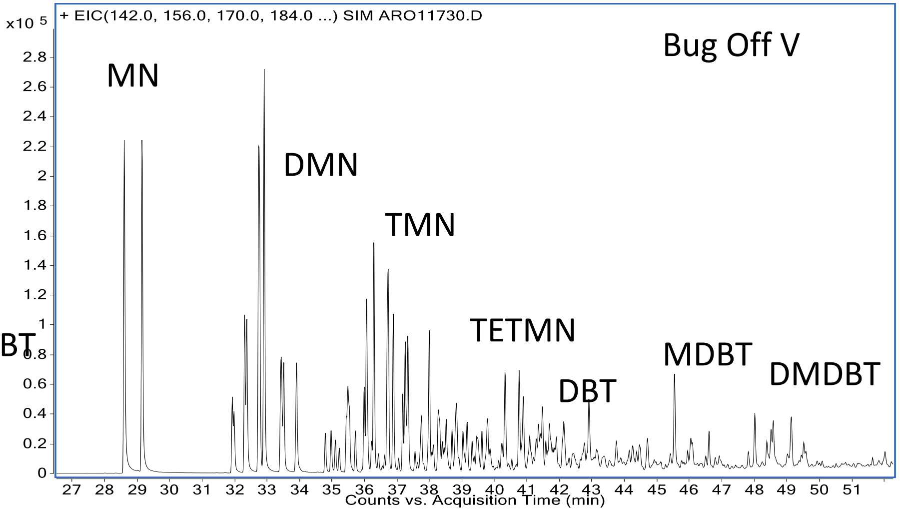
Chrysenes

Alkylnaphthalenes

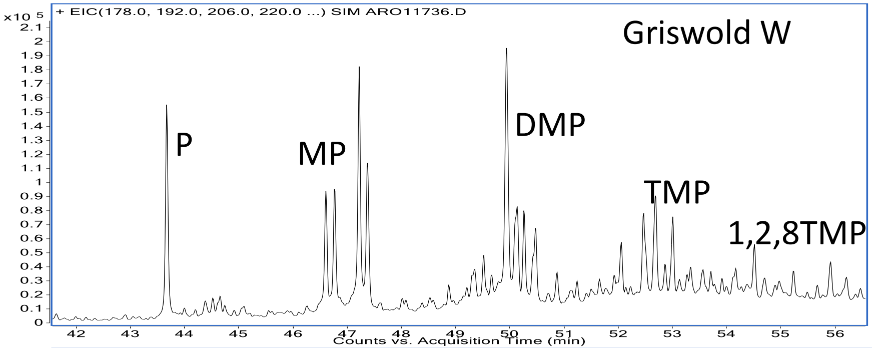


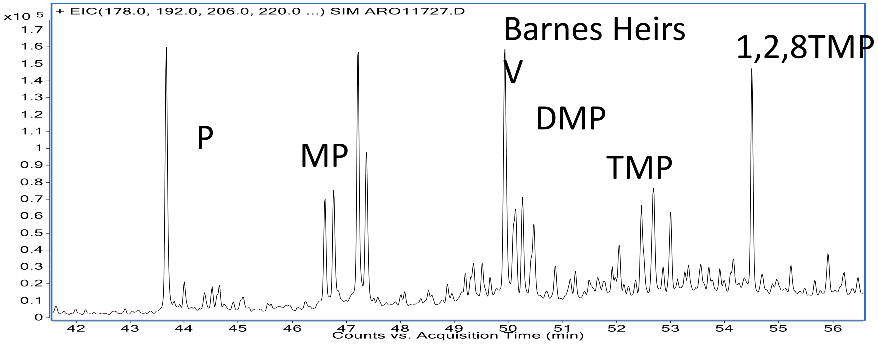


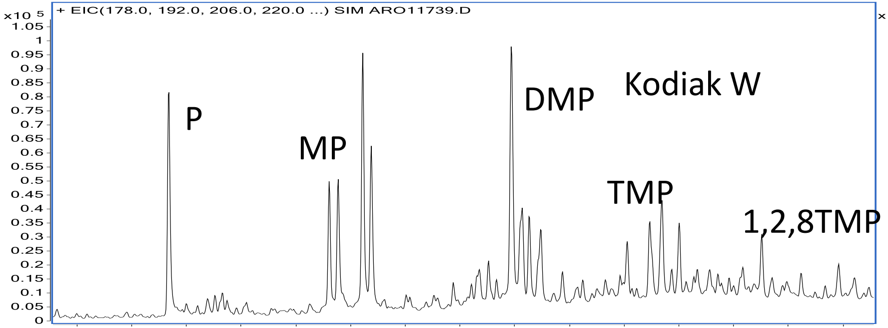


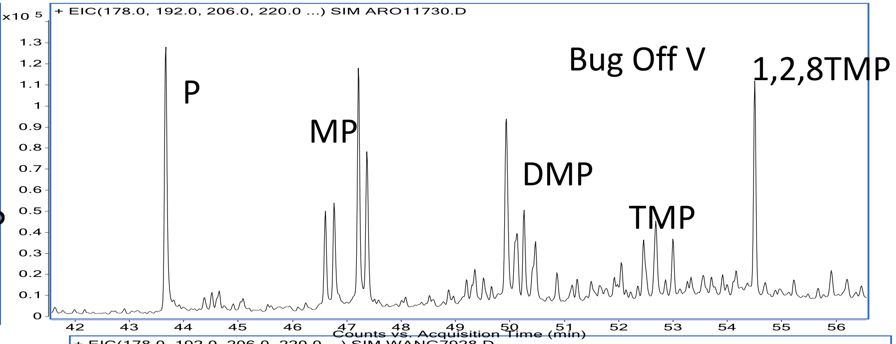


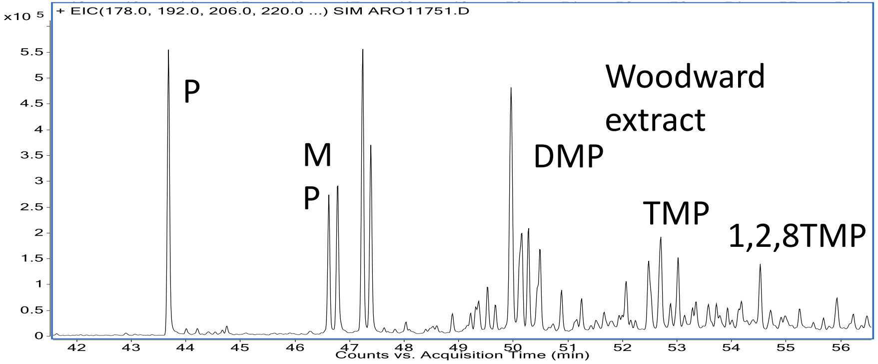
Alkylphenanthrenes

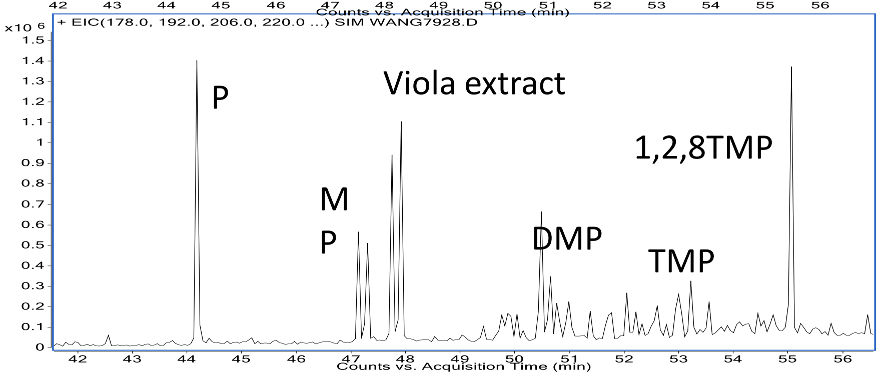




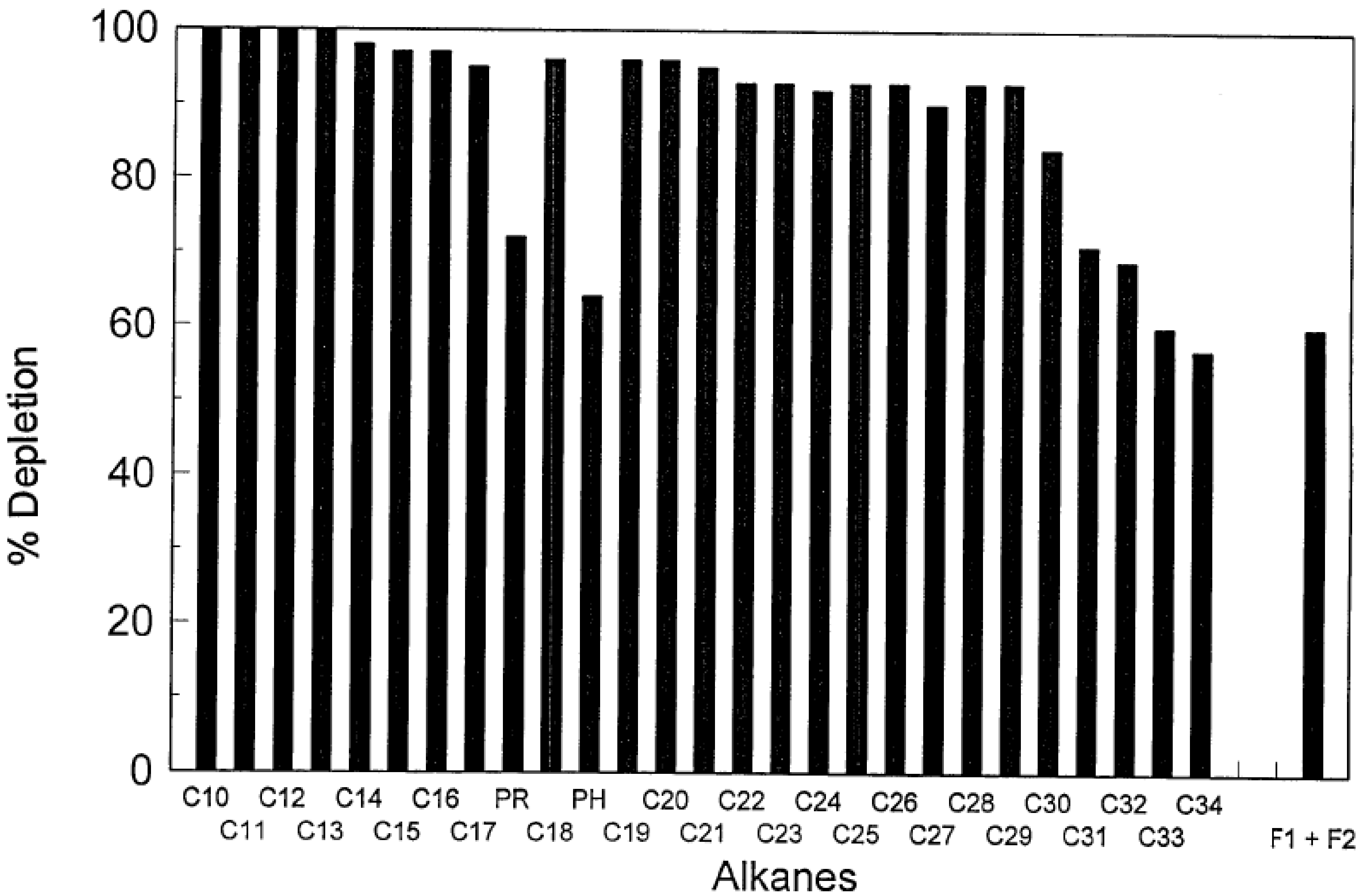






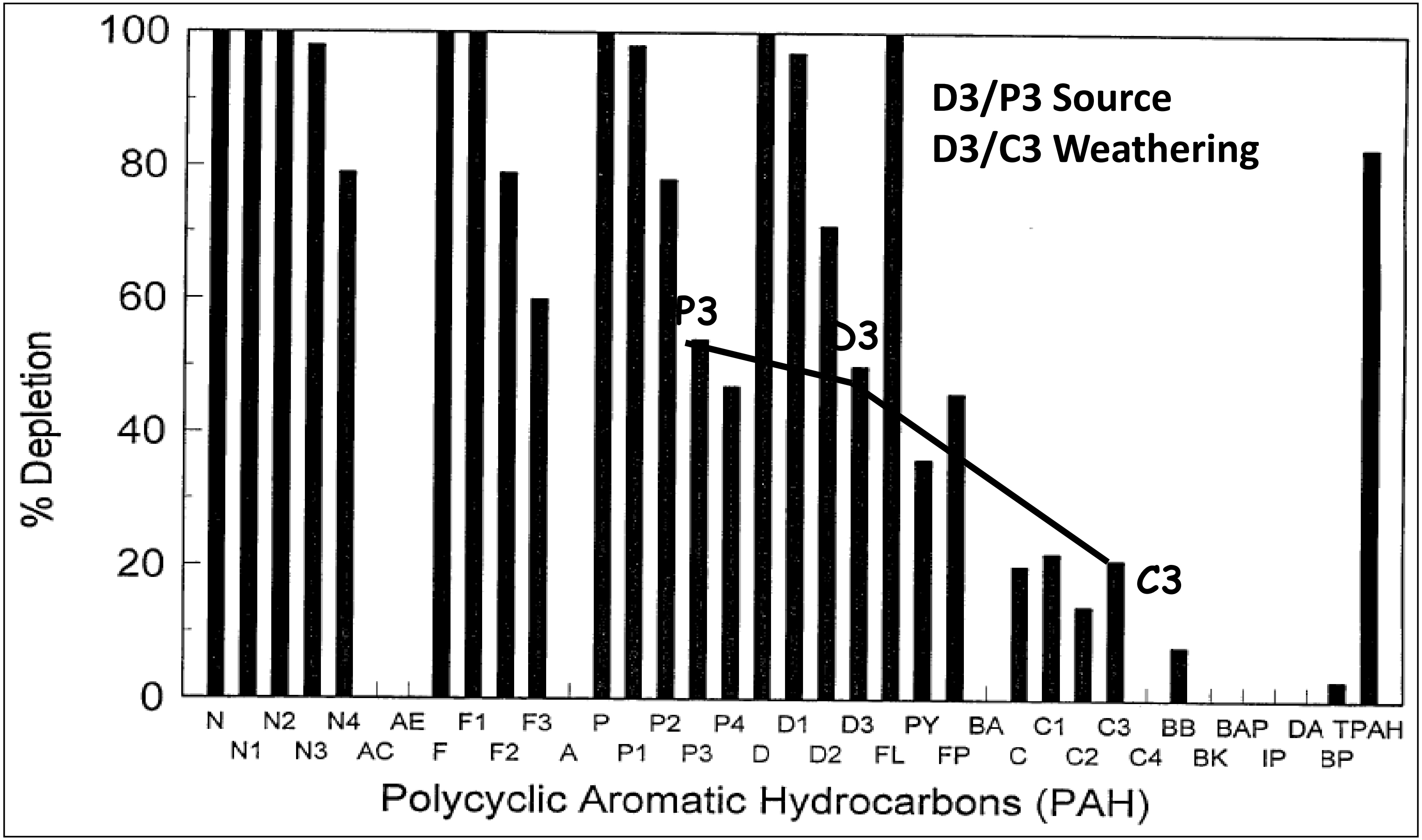


Crude oil alteration



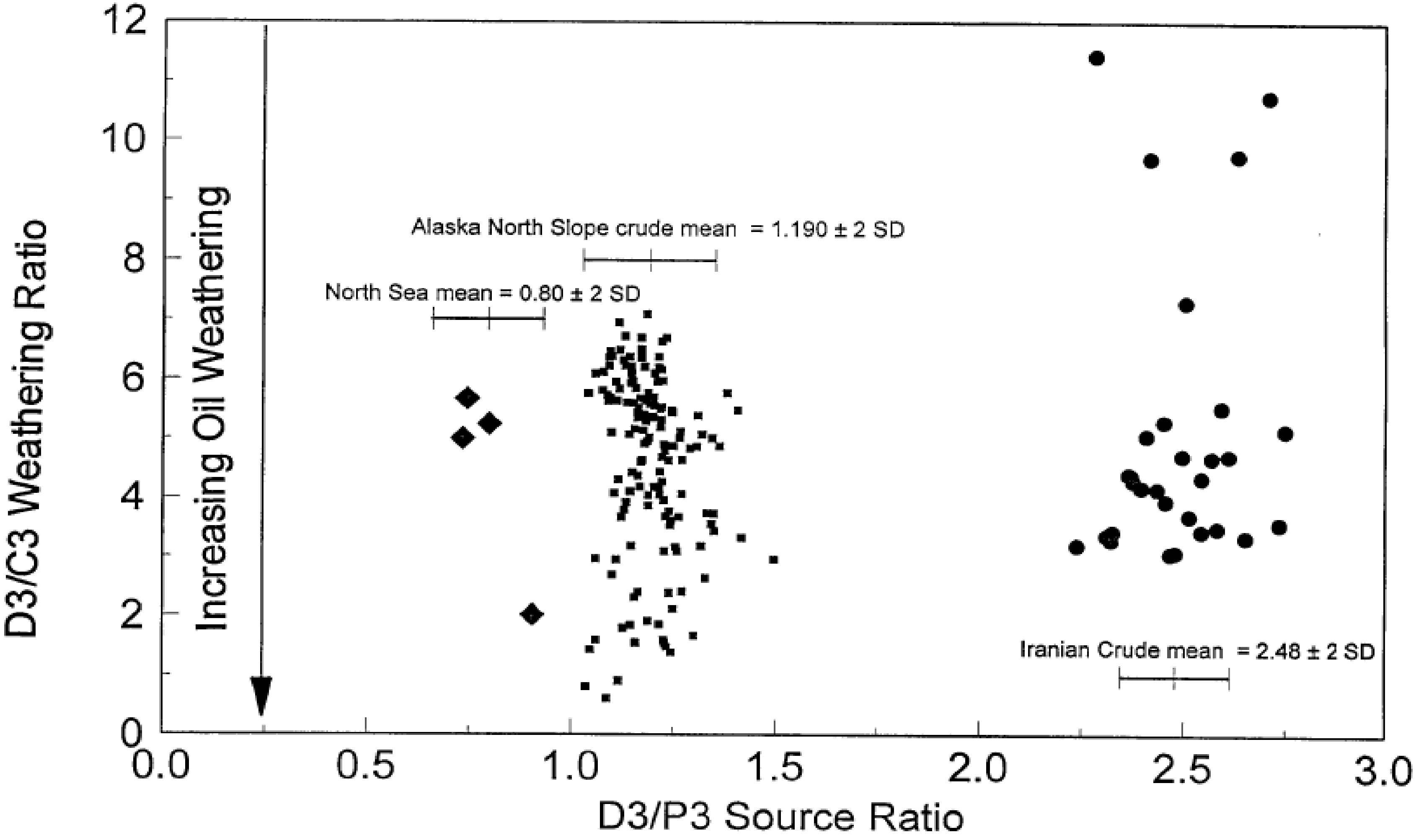
Natural degradation rates for Exxon Valdez hydrocarbons after 16 months

Crude Oil Alteration



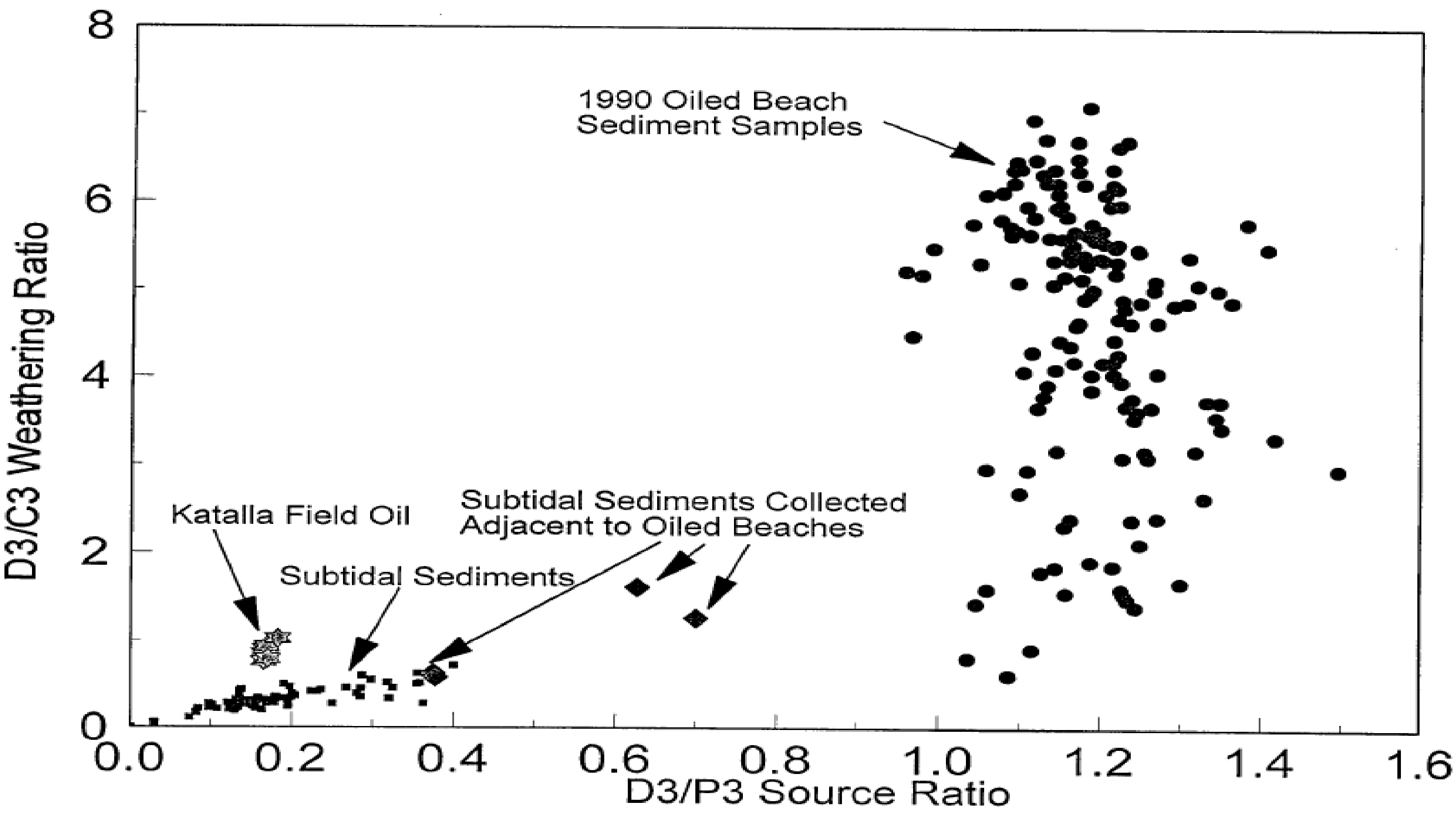
Natural degradation rates for Exxon Valdez PAH hydrocarbons after 16 months

Crude oil alteration



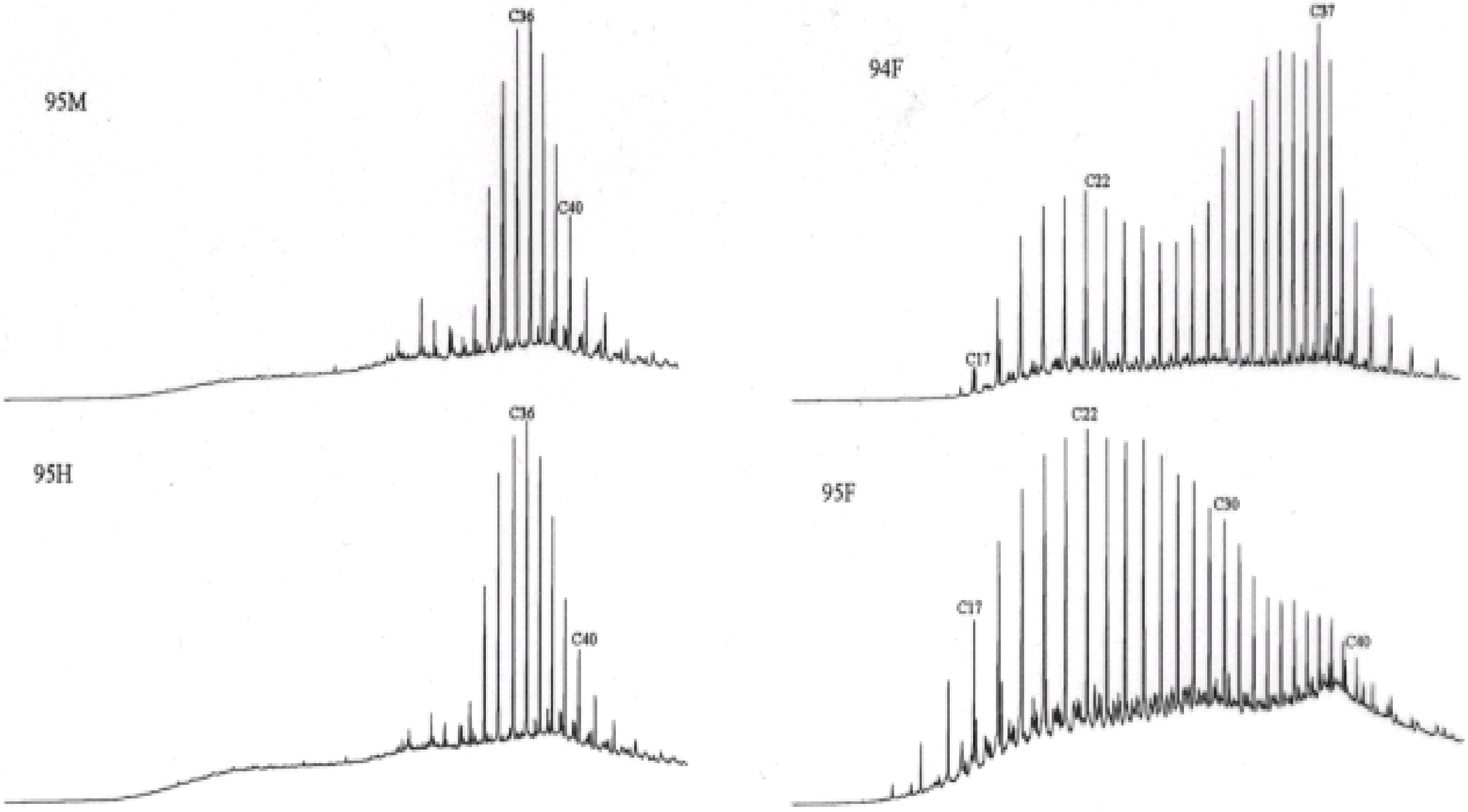
Utilization of weathering and source ratios as a means of distinguishing weathered and unweathered oils.

Crude oil alteration

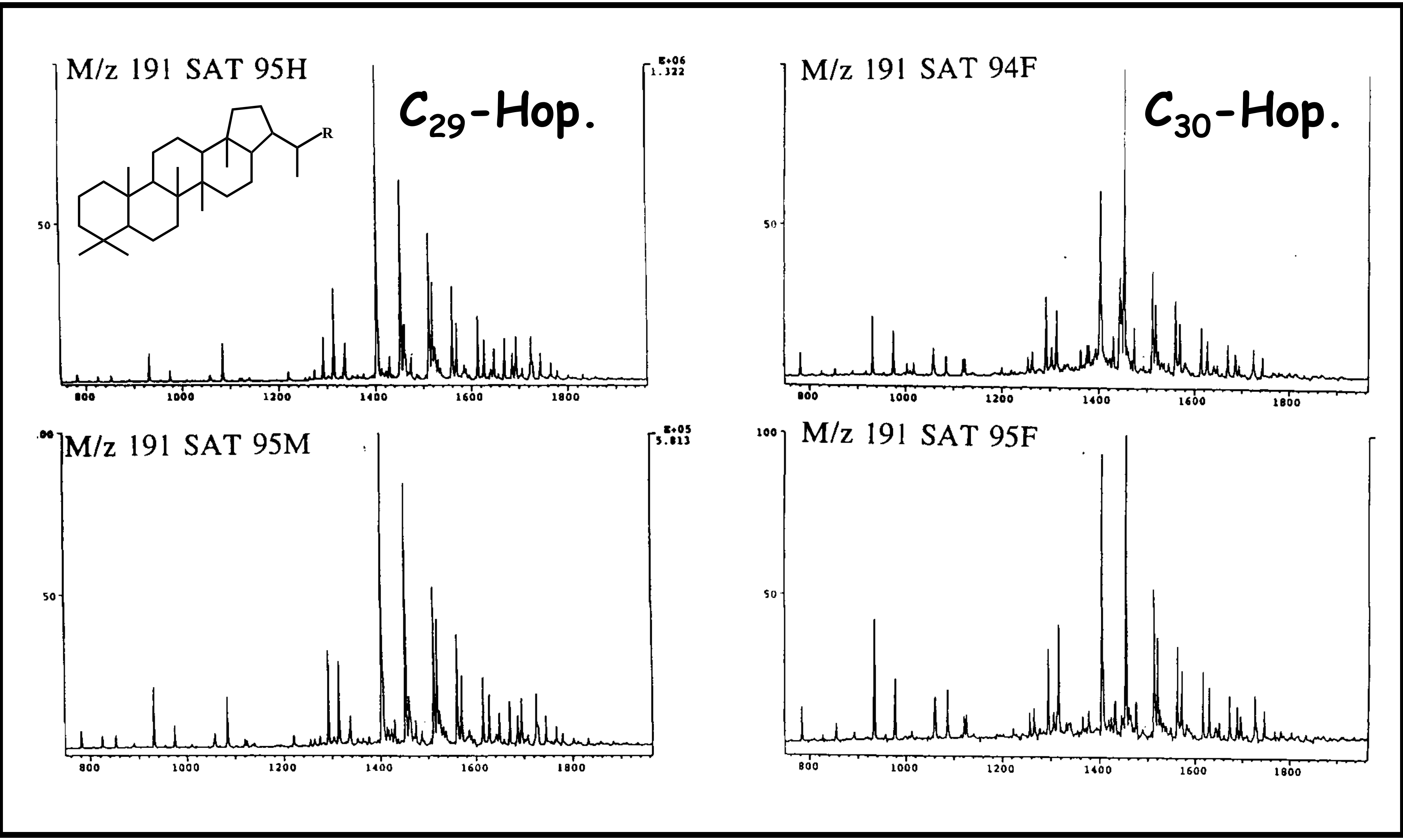


Utilization of weathering and source ratios as a means of distinguishing weathered and unweathered oils.

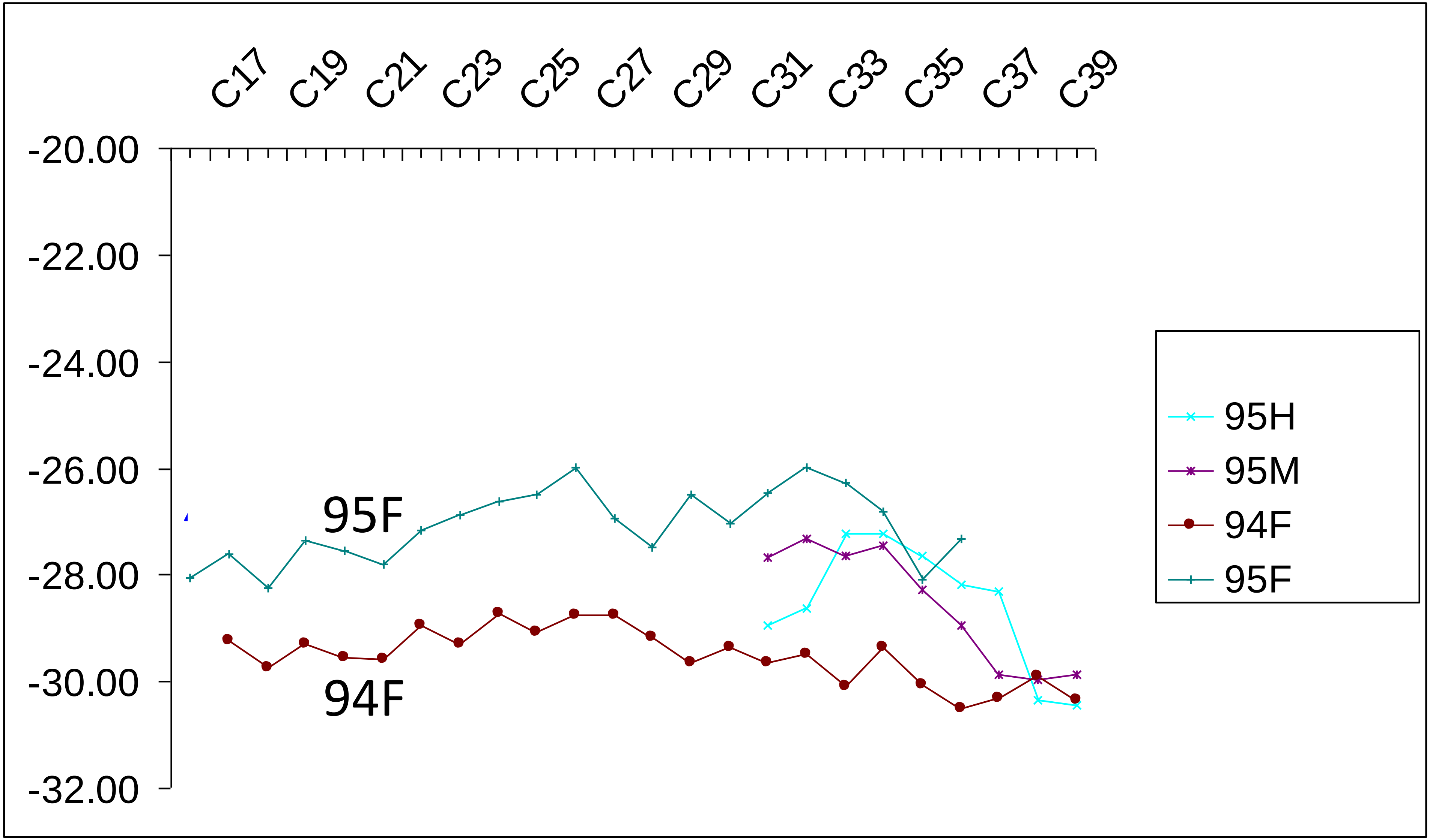
Tar Ball Chromatograms



Terpanes in Tar Ball Samples



GCIRMS – Tar Balls



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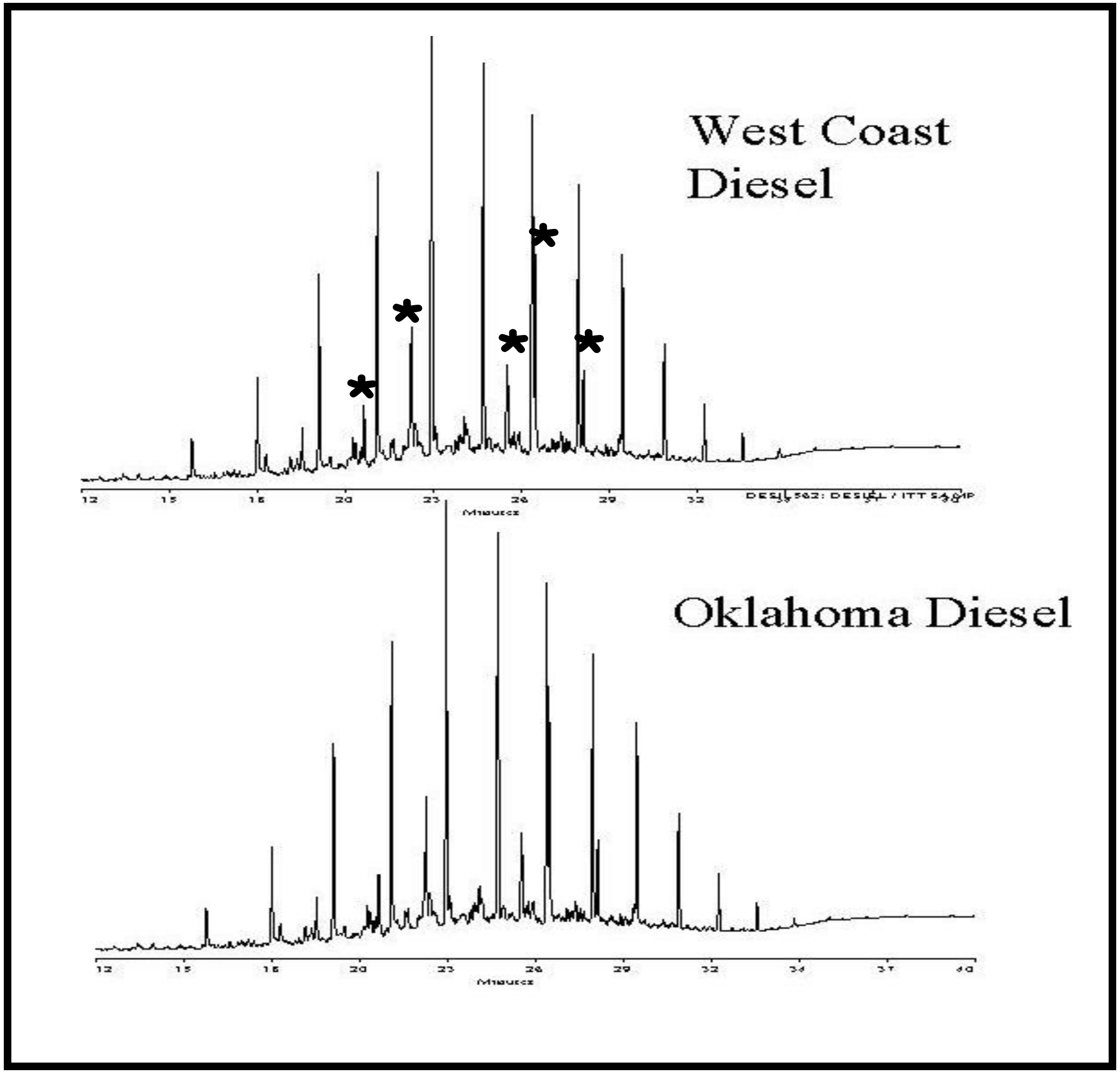
Diesel

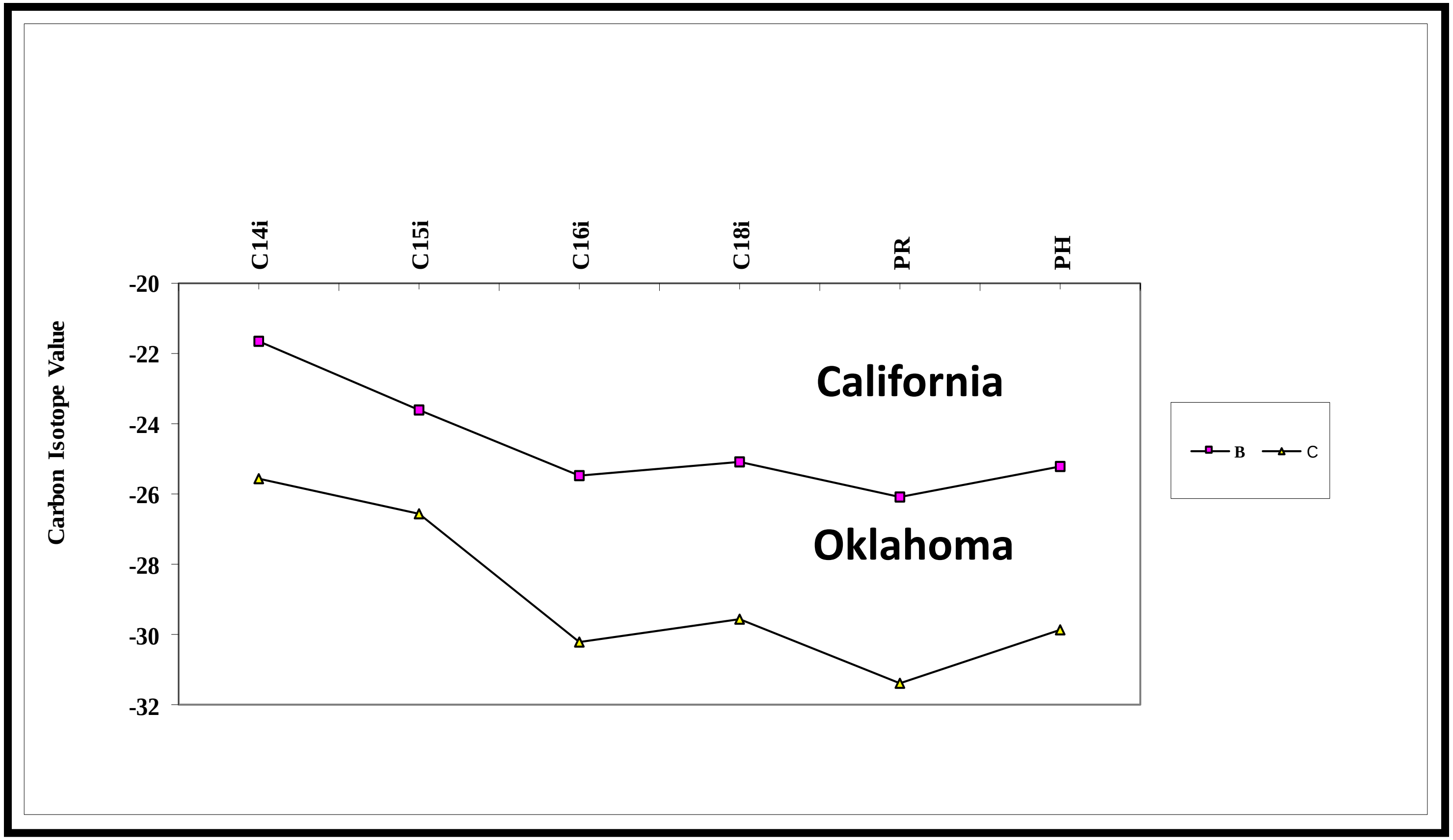
- Unlike gasolines, diesel will contain biomarkers. Diesel is typically more of a straight distillation cut with certain compounds, particularly S containing compounds removed.
- This is due to changes in regulations related to S content.
- It also means desulfurized diesel will have a higher content of decalins formed during the desulfurization process.
- Diesel typically dominated by n-alkanes in range nC_{10} to nC_{24} that are readily removed by attenuation as shown below
- Composition will vary with season and location. Colder regions will contain lower amounts of higher C-numbered alkanes since they will solidify at colder temperatures.

Diesel Fingerprints

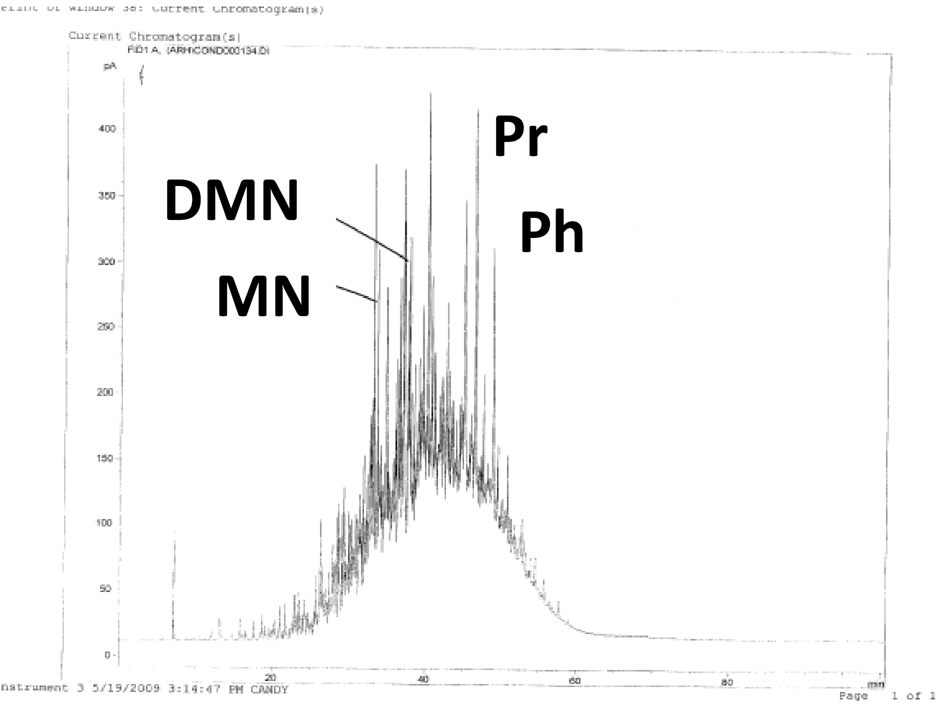


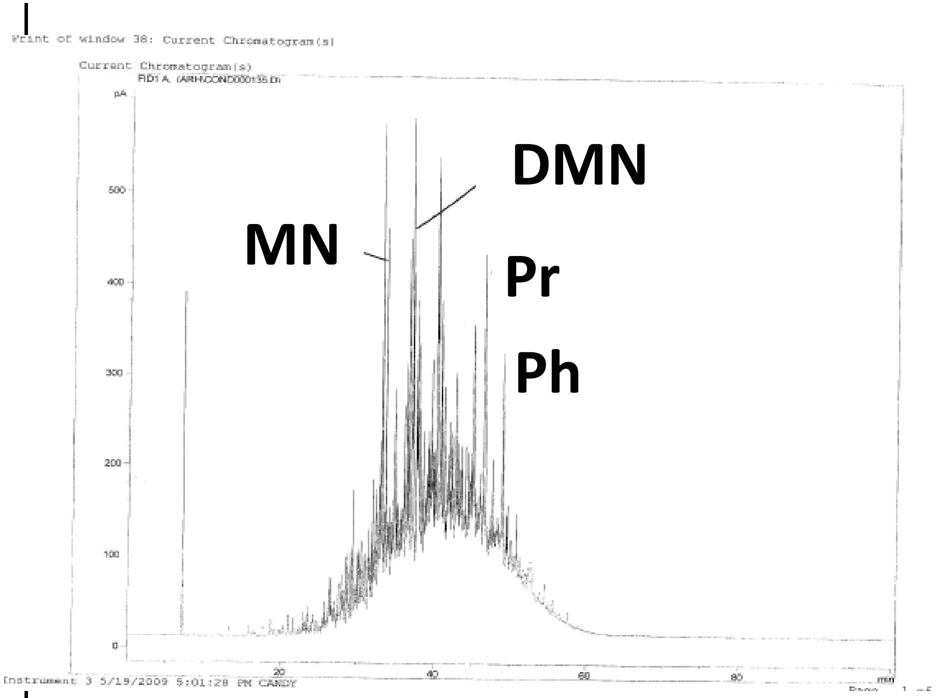
West Coast	**-24.72**
Oklahoma	**-27.86**

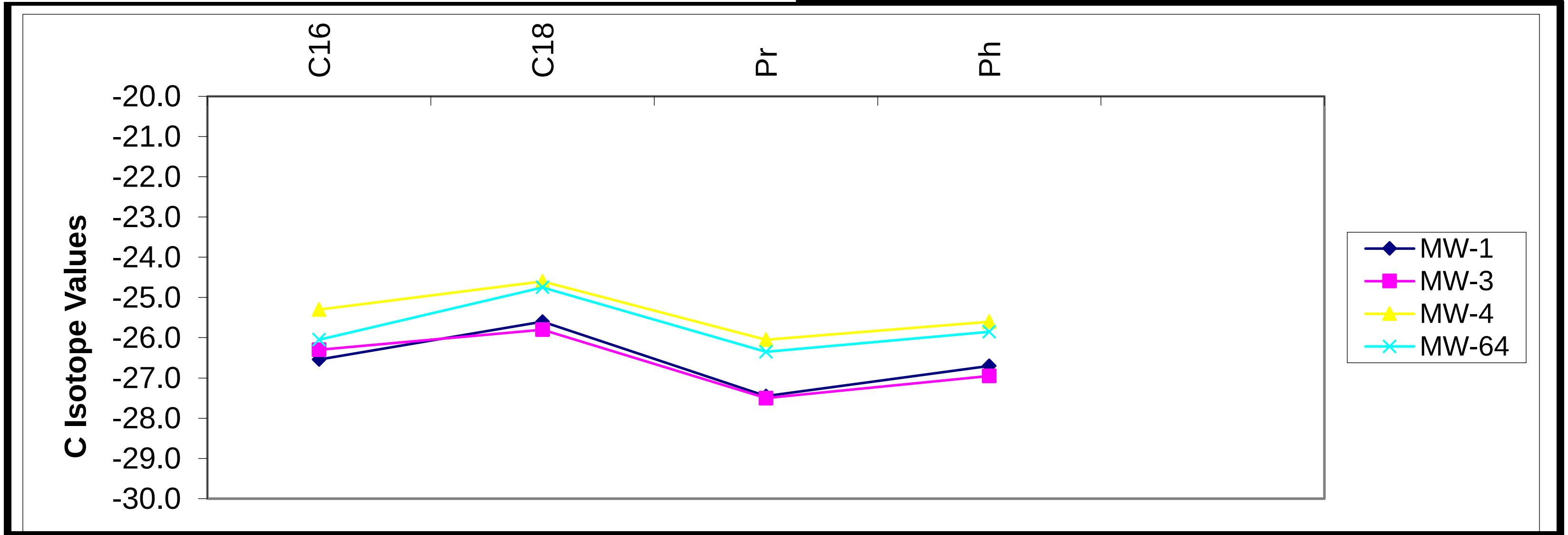
Isoprenoid Isotope Fingerprints



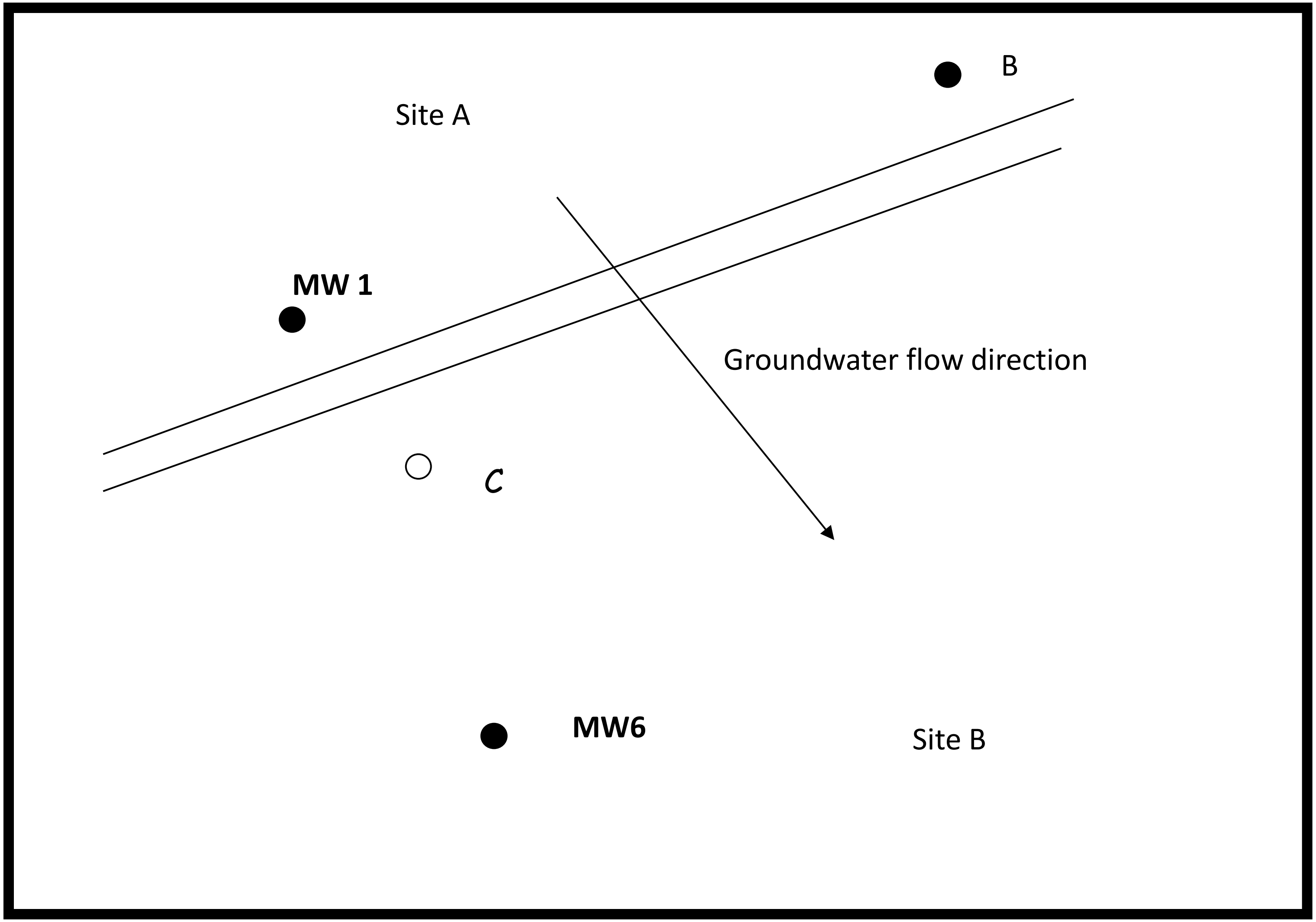
Diesel –Source Differentiation



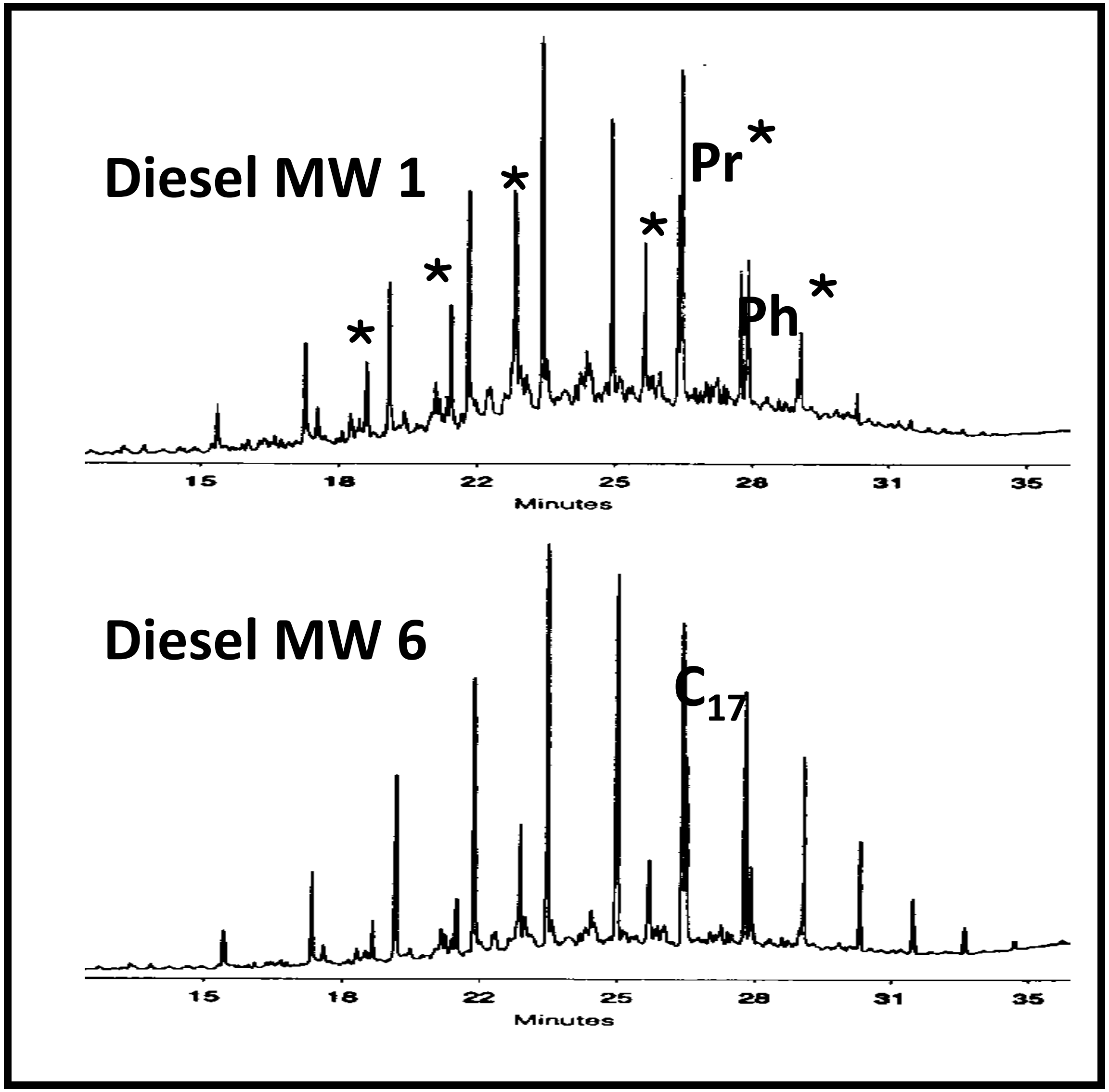




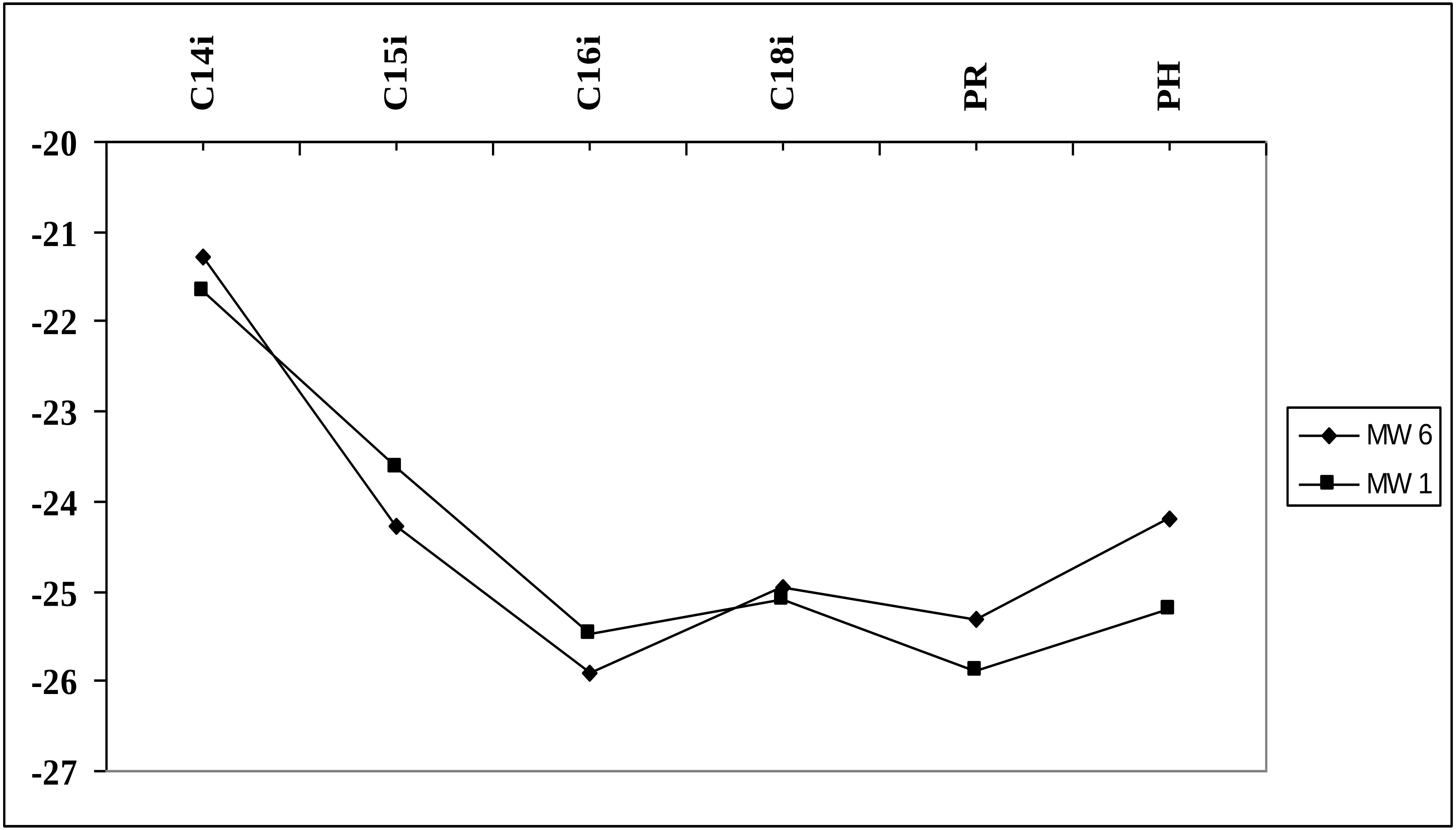
Homogenous or Heterogenous Plume?



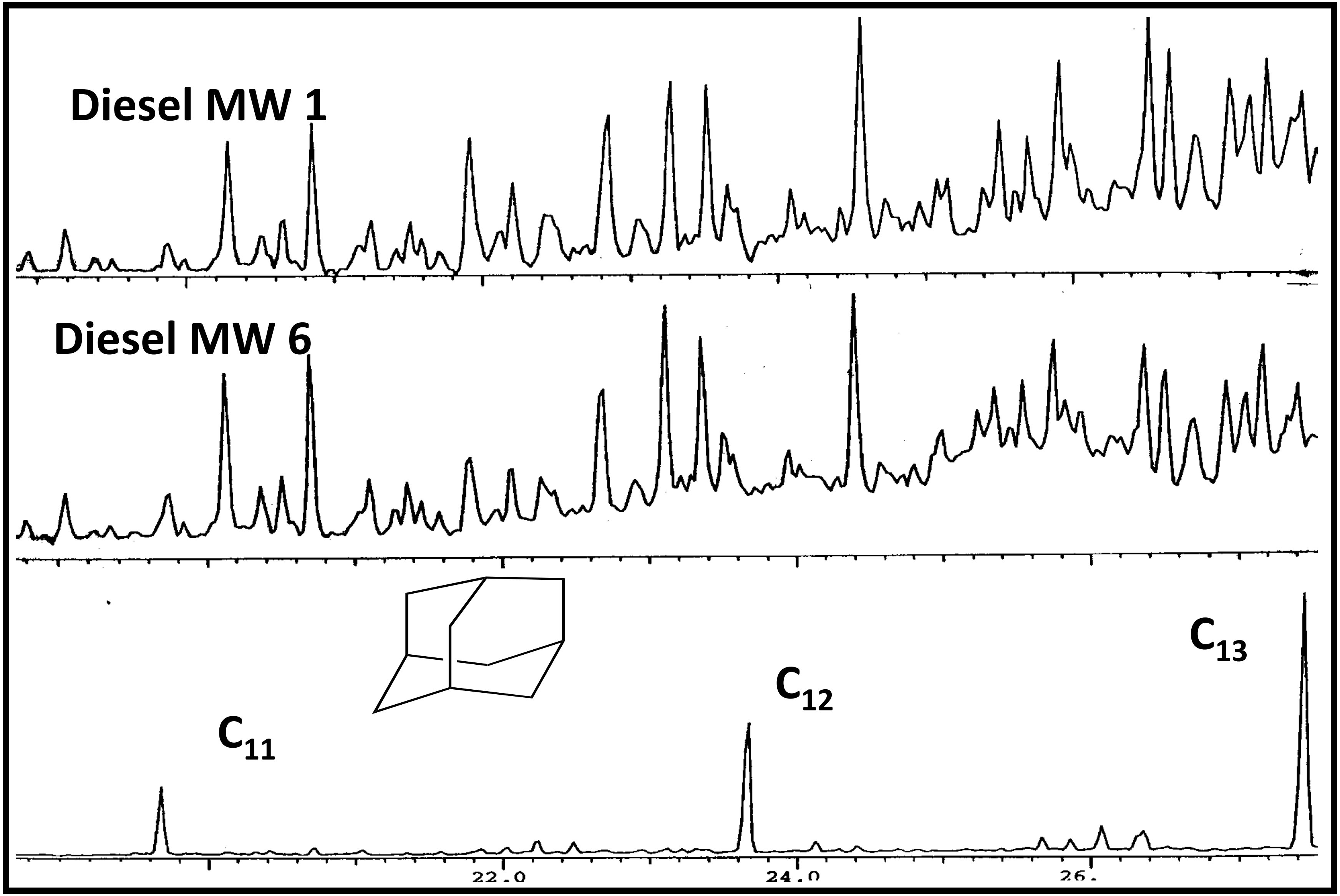
Weathered and Unweathered Diesel



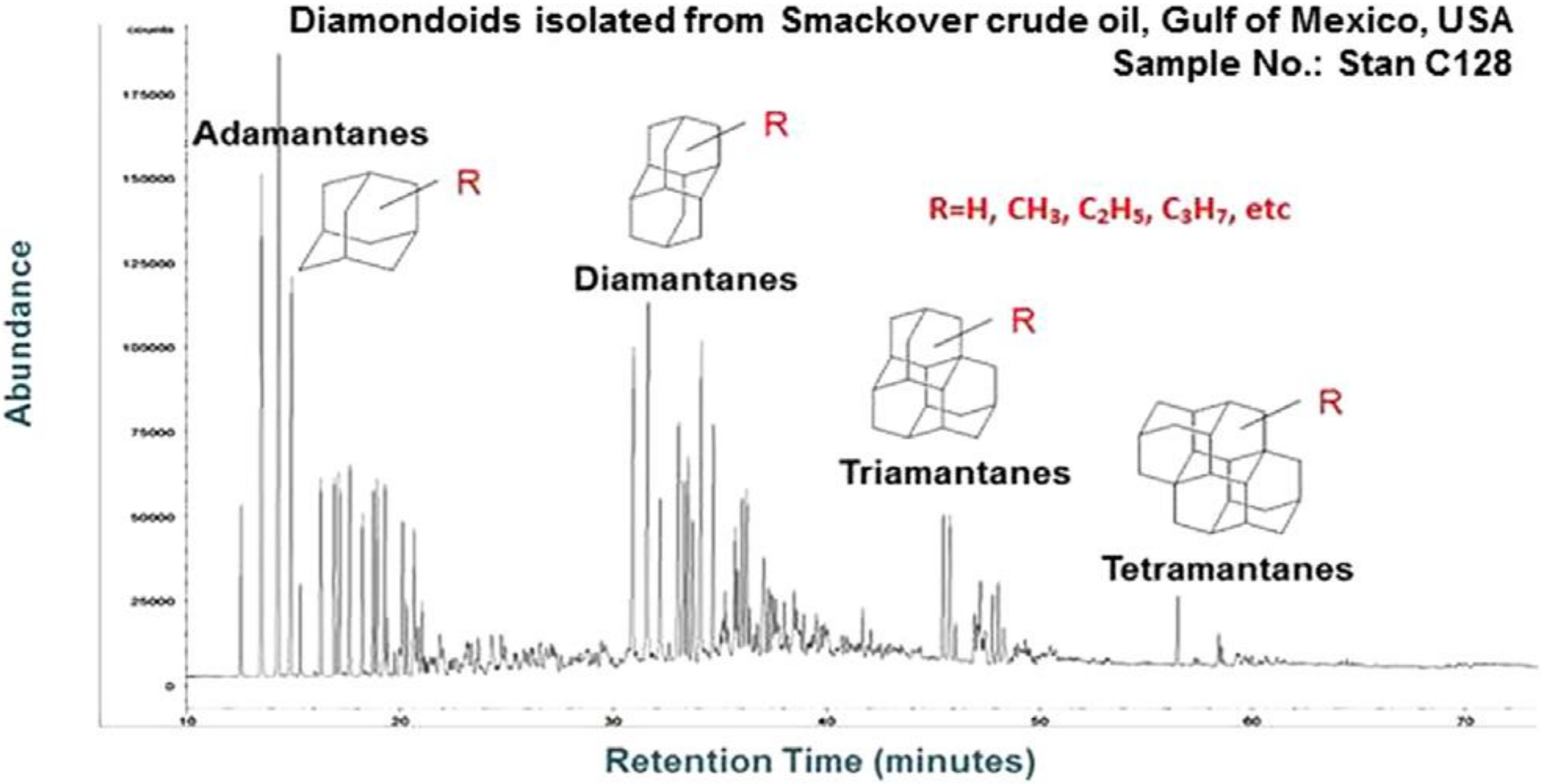
Carbon Isotope Values for Isoprenoids



Diamondoids in Diesel Fuels



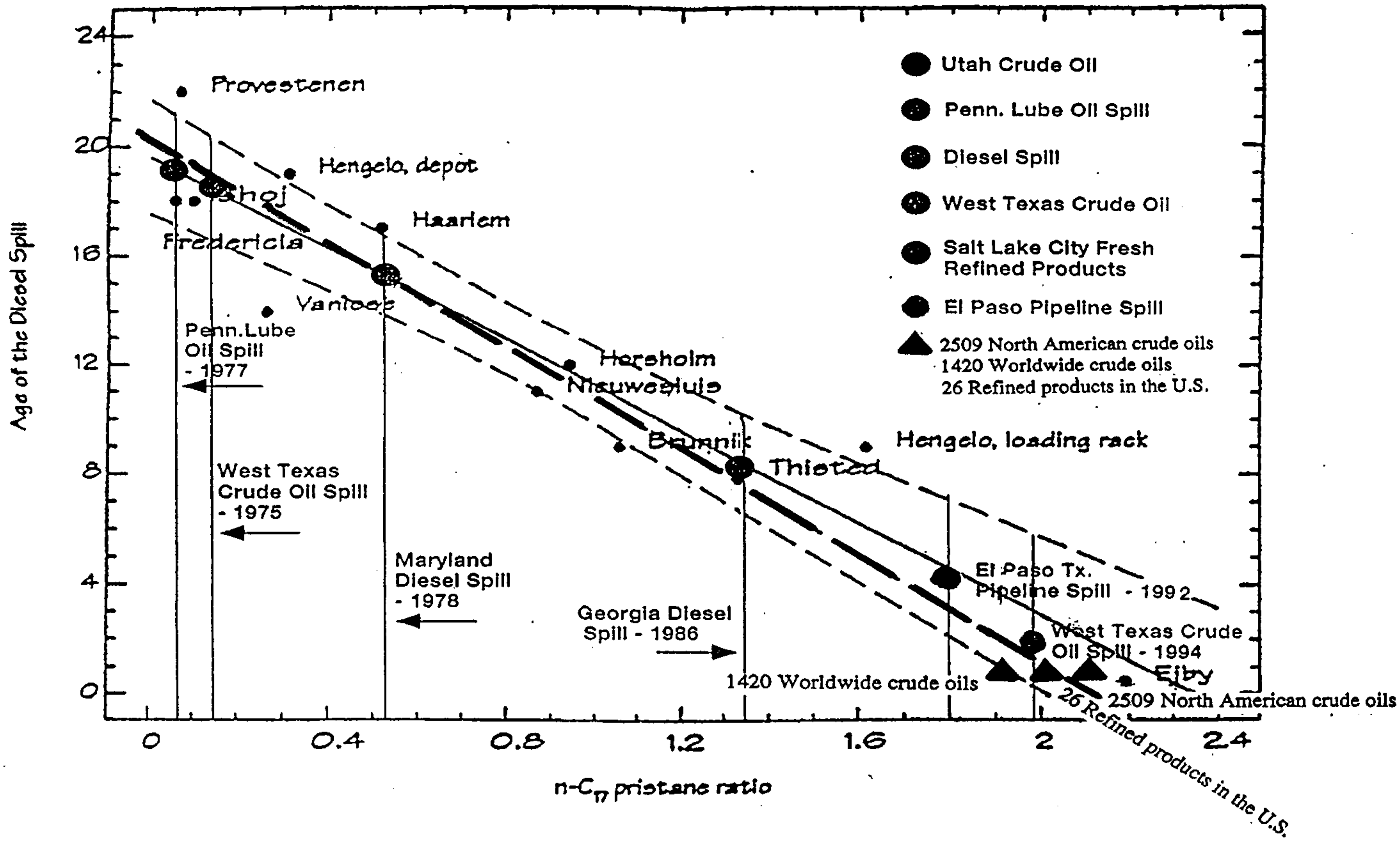
Diamondoid distribution


Diamondoids isolated from Smackover crude oil, Gulf of Mexico, USA
Sample No.: Stan C128

Sulfur in diesel and gasoline

- Limits for gasoline: 120ppm - 2004; 30ppm - 2006; and 15ppm by 2007 for diesel (ultra-low S diesel-ULSD).
- After 2010 all highway diesel fuel supplied to the market was ULSD; and all highway diesel vehicles must use ULSD.
- EU limits: Refiners needed to phase in gasoline and diesel with less than 10ppm of sulfur by 2005-fully available by 2009.
- Limits previously set 150ppm for diesel and gasoline by 2005; present EU limits 350ppm for diesel and 150ppm for gasoline.
- (Source EST March 1st, 2003, p85A and recent EPA web sites)

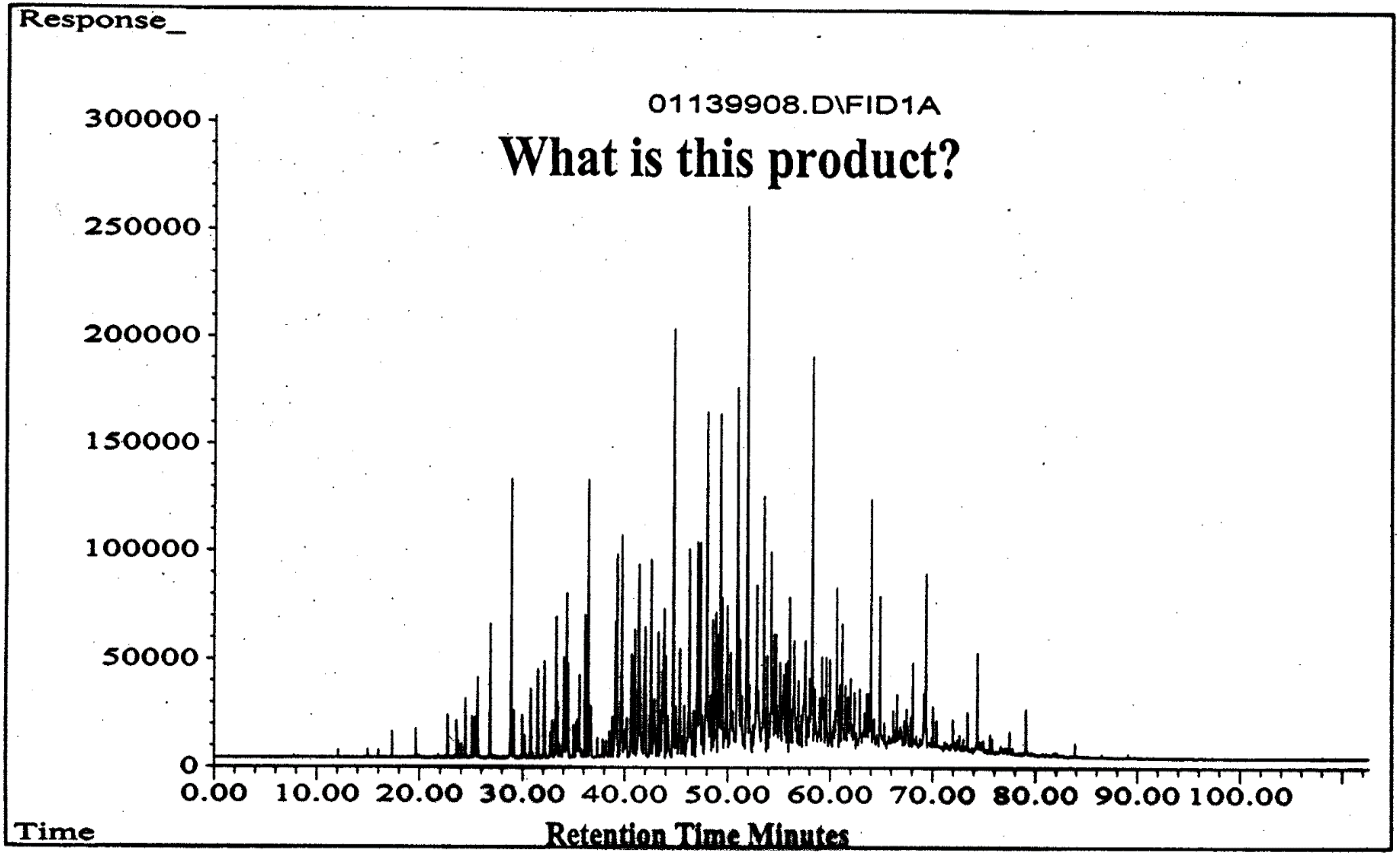
Age dating diesel



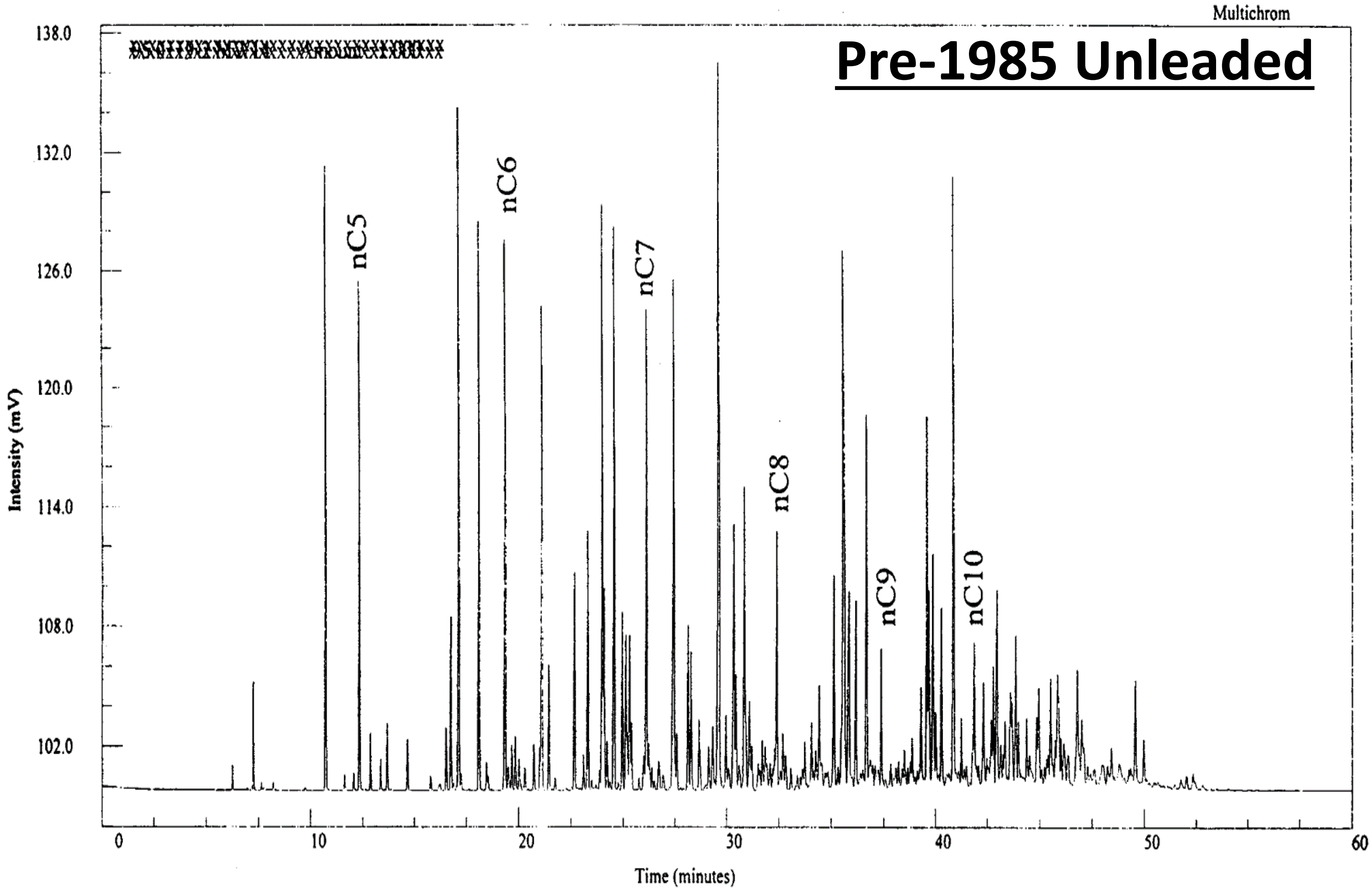
Gasolines

- 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.
- Gasolines have no biomarkers.
- Various ratios may be useful in distinguishing gasolines, particularly if produced via different refinery processes.
- An additional tool here would be GCIRMS for both the hydrocarbons and additives.

Gasoline composition has changed with time

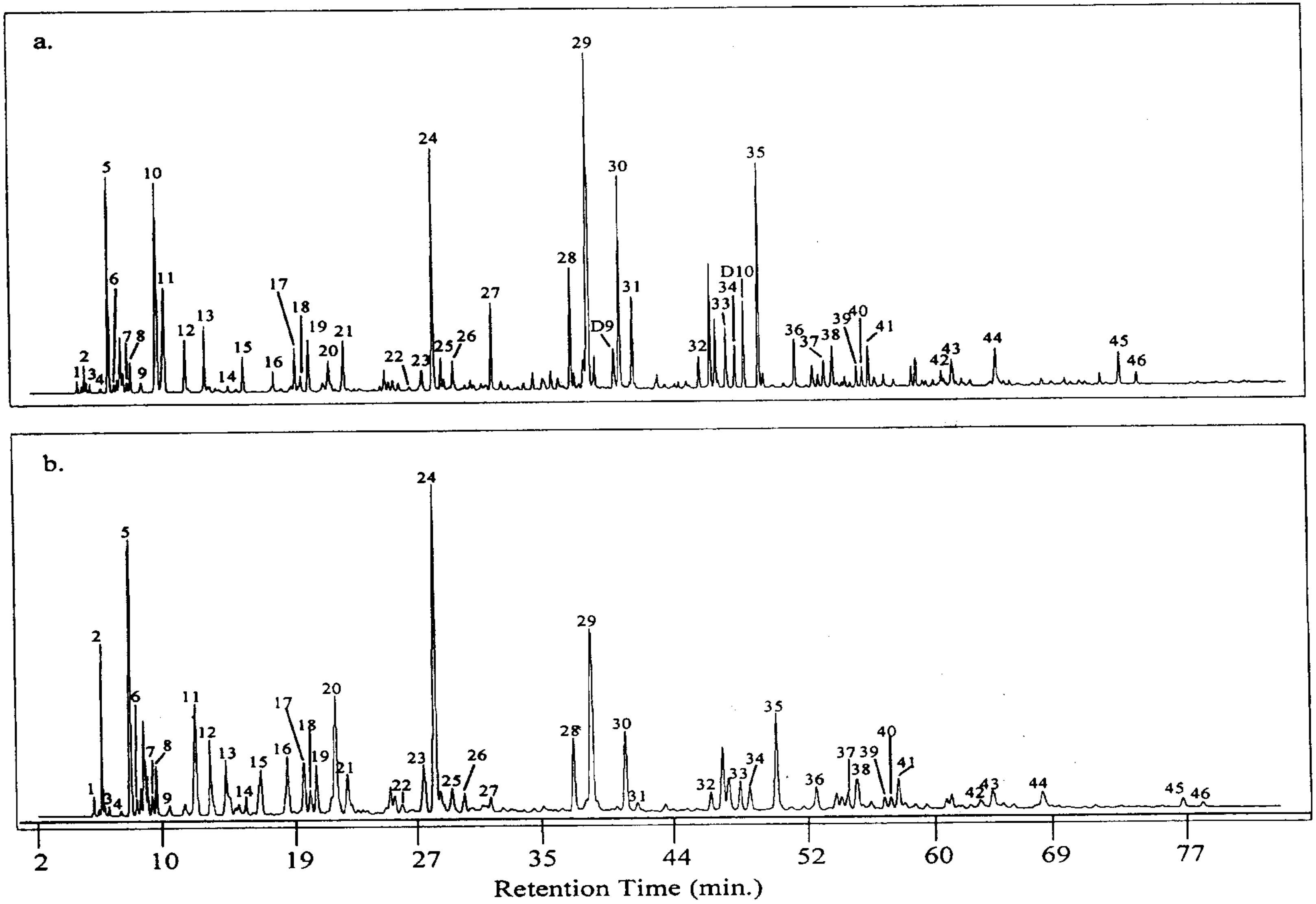


Gasoline composition has changed with time

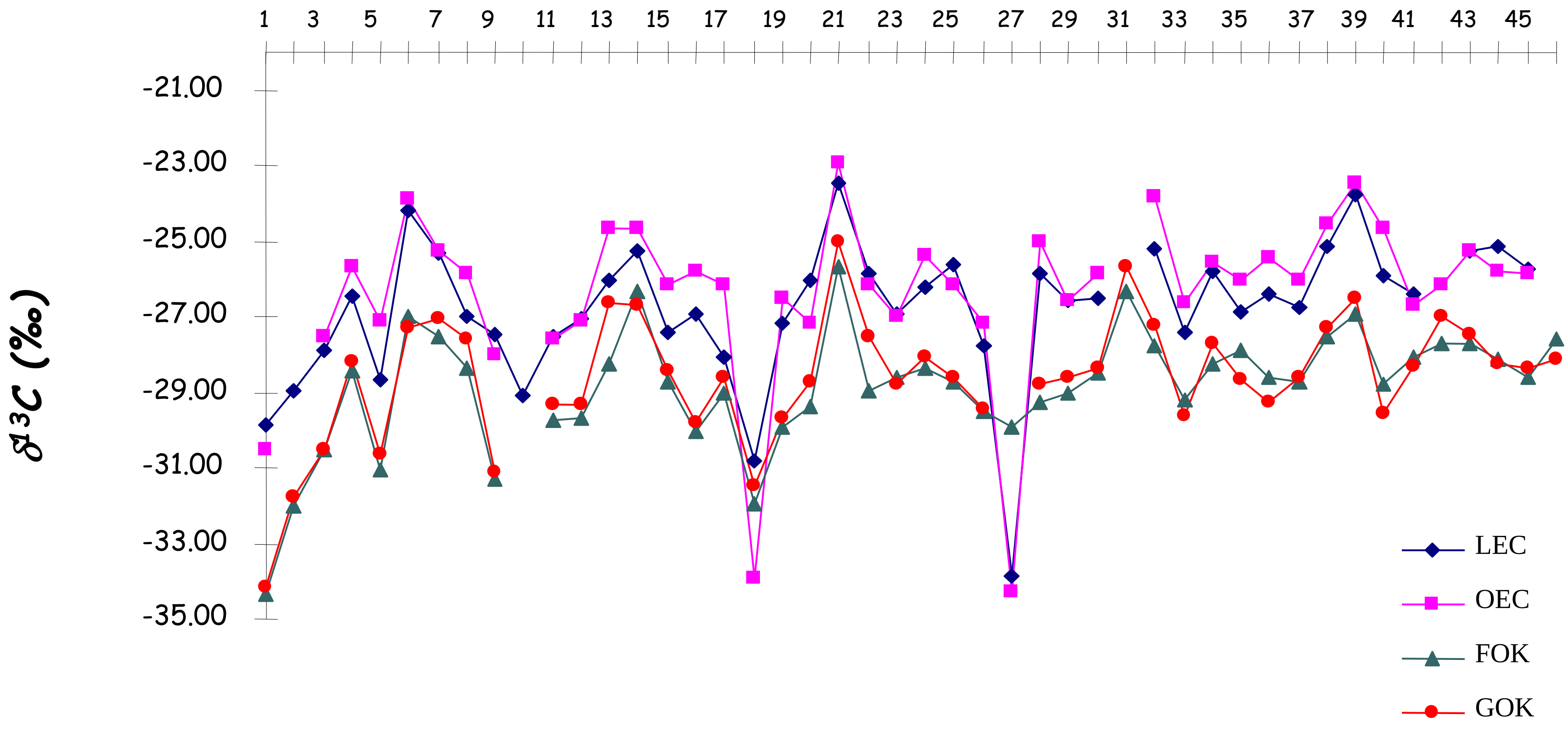


Pre-1985 Unleaded

Gasoline composition has changed with time

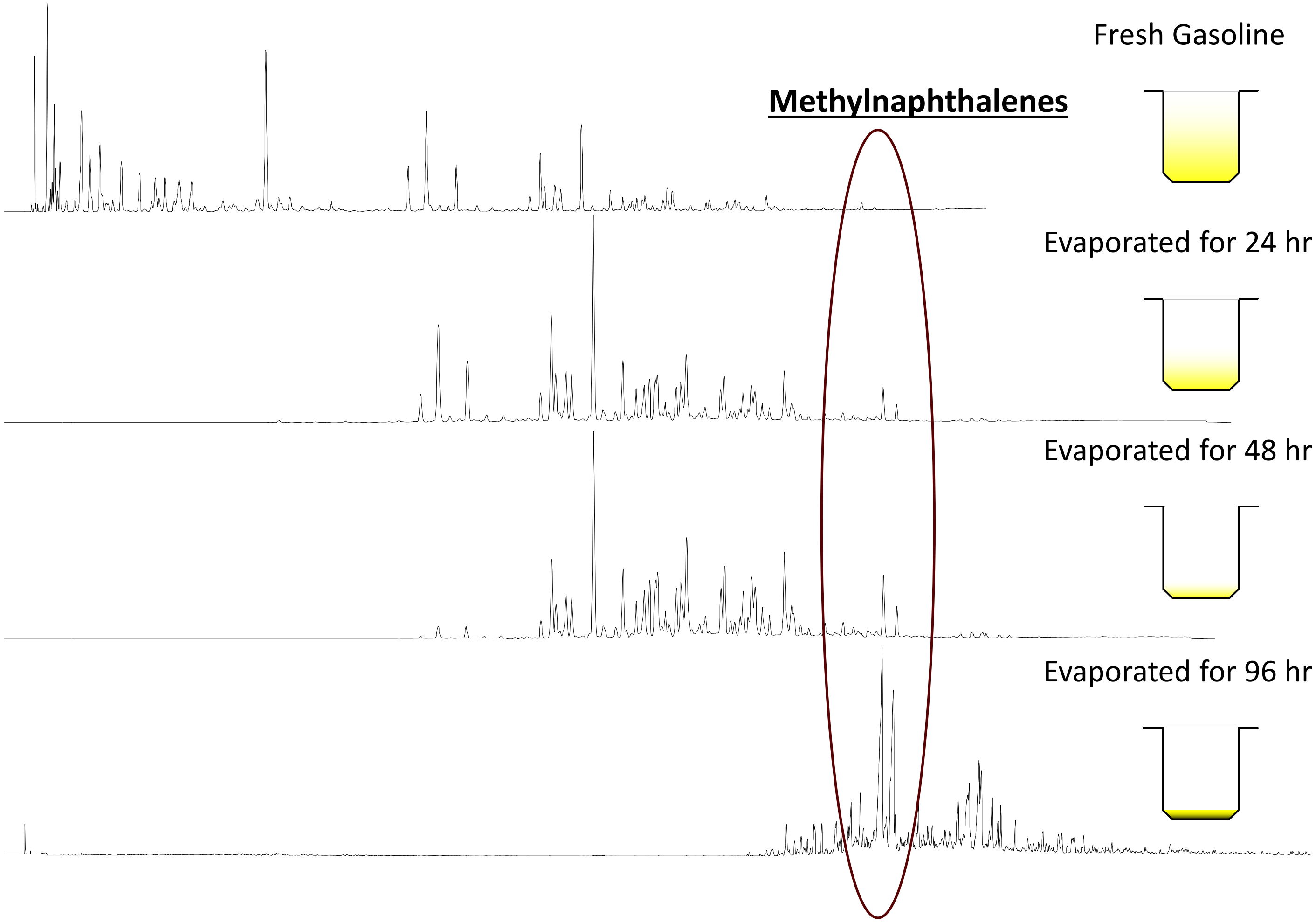


Carbon Isotopic Composition of Gasolines

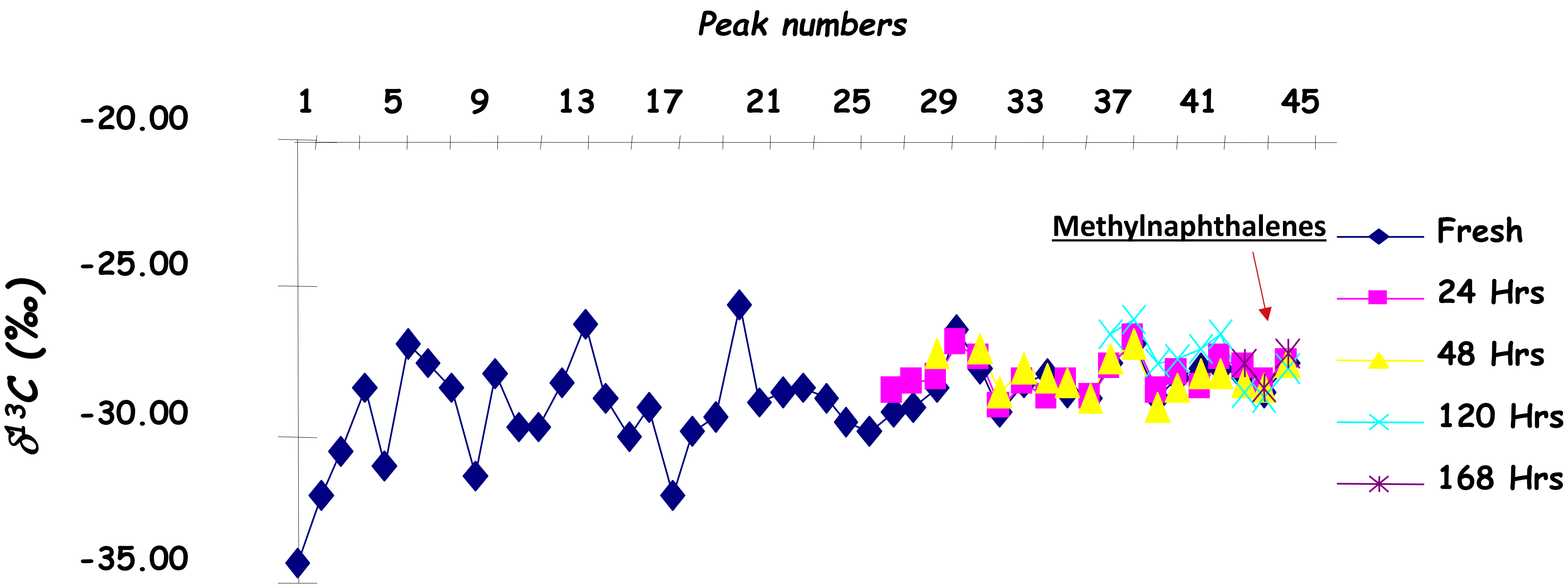


This figure shows the carbon isotopic fingerprint of gasolines sampled from Oklahoma and from the East Coast and demonstrates that these gasolines are significantly different in terms of isotopic composition and can be discriminated from each other on this basis. The peak numbers are identified in the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

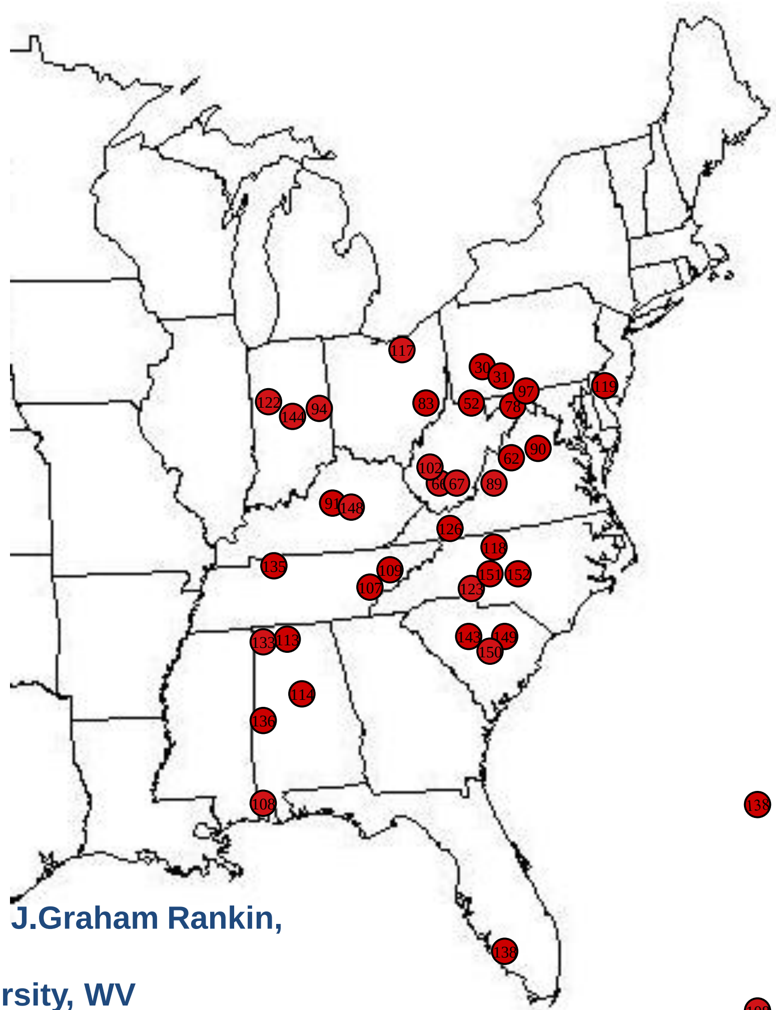
Gasoline evaporation



Stability of isotope values with evaporation



Gasoline database



Retail stations locations

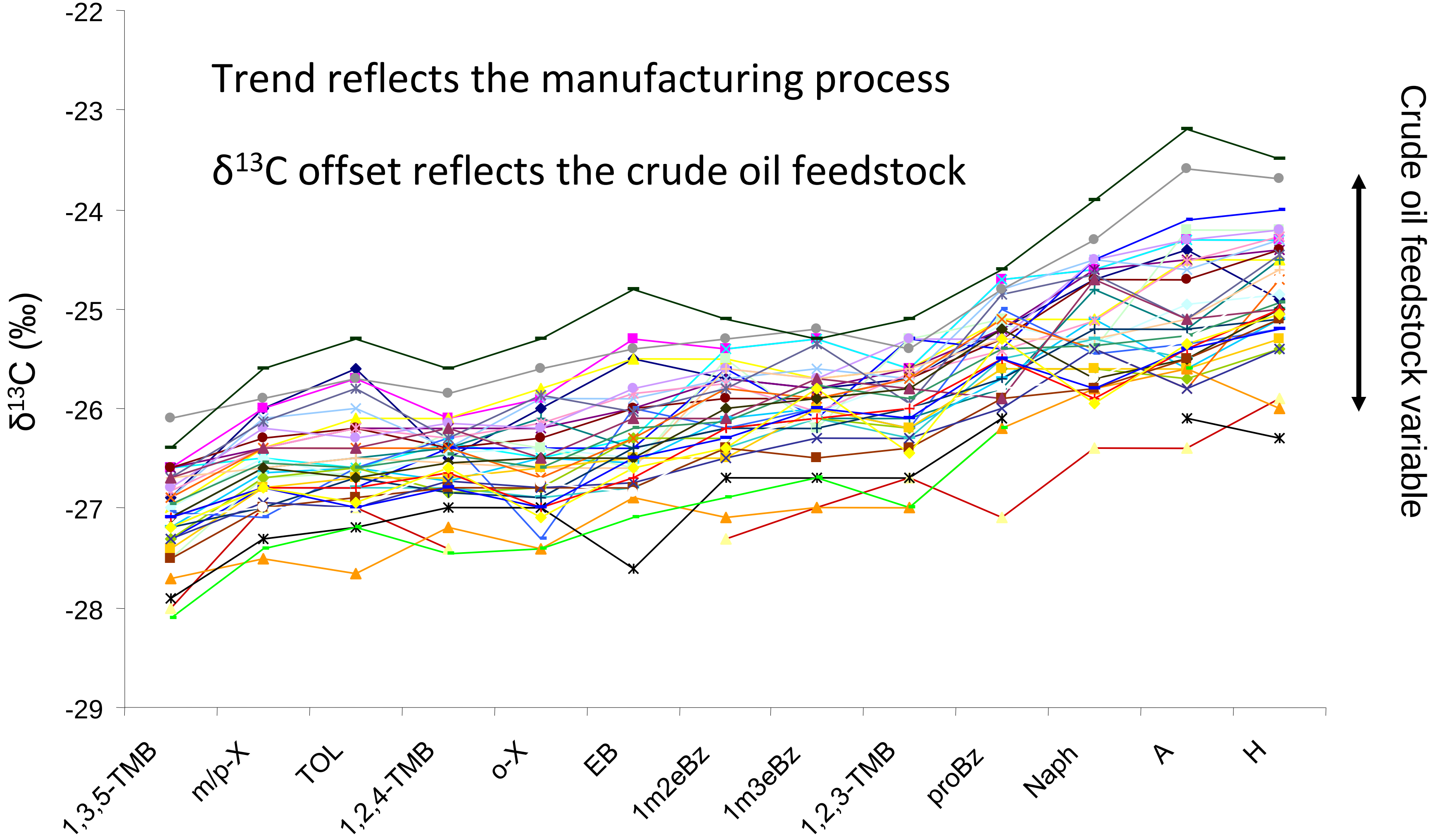
138 Aromatics $\delta^{13}C$ + δD, oxygenates (MTBE, TBA)

108 Aromatics $\delta^{13}C$ only

Samples provided by Dr. J.Graham Rankin,

Marshall University, WV

$\delta^{13}C$ Fingerprints of 39 gasolines



Trend reflects the manufacturing process

$\delta^{13}C$ offset reflects the crude oil feedstock

Crude oil feedstock variable

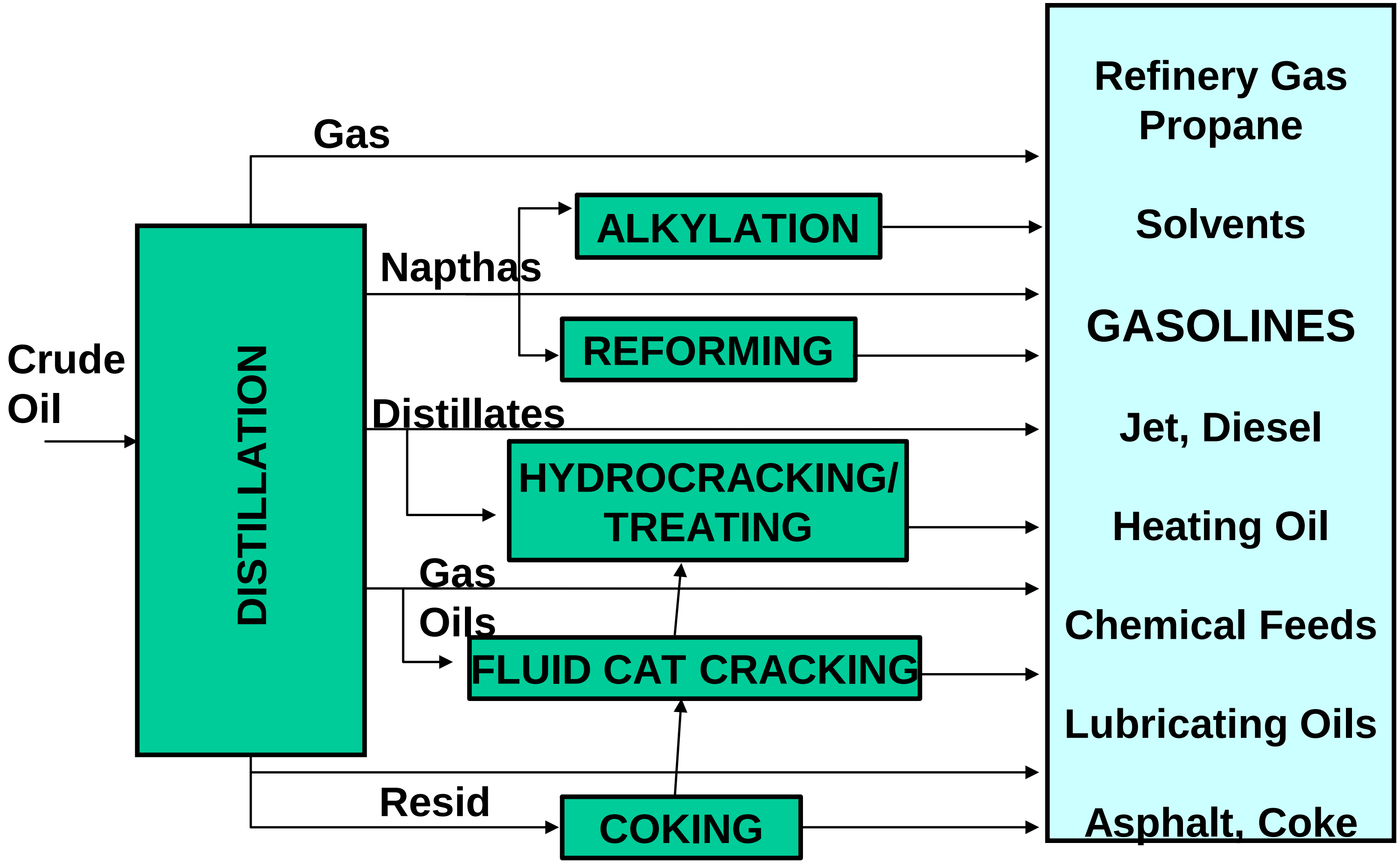
Gasoline production

- Gasoline production is complex process
- Years ago, gasoline was a straight run distillate and often confused with condensate
- Contemporary gasolines have also been confused with condensates in some cases
- Gasolines with same octane rating may have totally different compositions
- Complexity of refinery may determine gasoline composition
- Important to understand processes involved in gasoline production

Complex Refinery Flow Chart

Refinery processes include:

- Cracking big hydrocarbons ---> Increase gasoline yield/volume
- Rearranging the structure of hydrocarbons ---> Increase gasoline “octane”



Crude Oil

DISTILLATION

Gas

Napthas

ALKYLATION

REFORMING

Distillates

HYDROCRACKING/ TREATING

Gas Oils

FLUID CAT CRACKING

Resid

COKING

Refinery Gas
Propane

Solvents

GASOLINES

Jet, Diesel

Heating Oil

Chemical Feeds

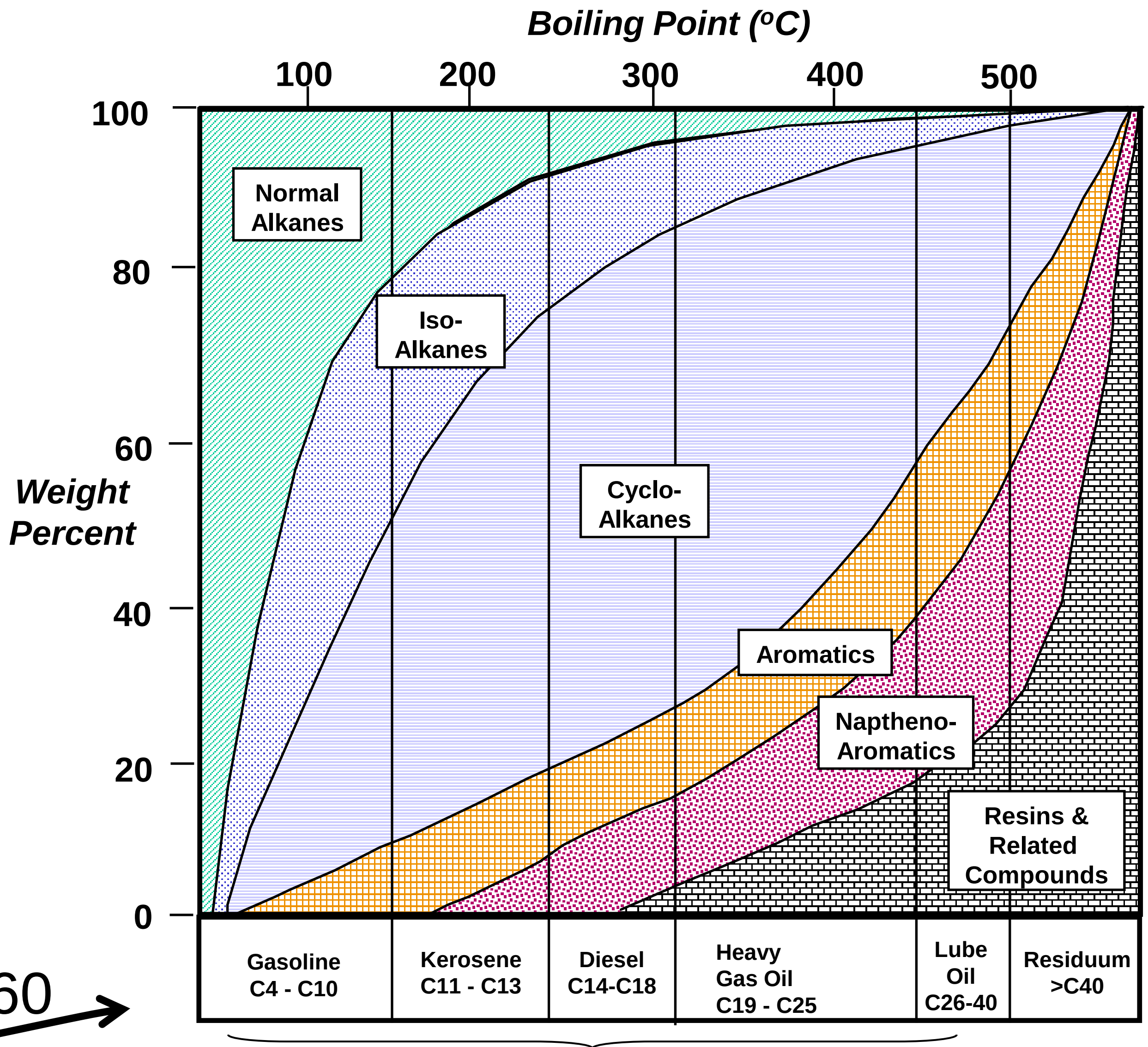
Lubricating Oils

Asphalt, Coke

Hydrocarbon types in crude oils

What portion of the crude oil can go directly into gasoline???

Octane 40-60



How do we get octane up & get the heavier hydrocarbons into the gasoline pool???

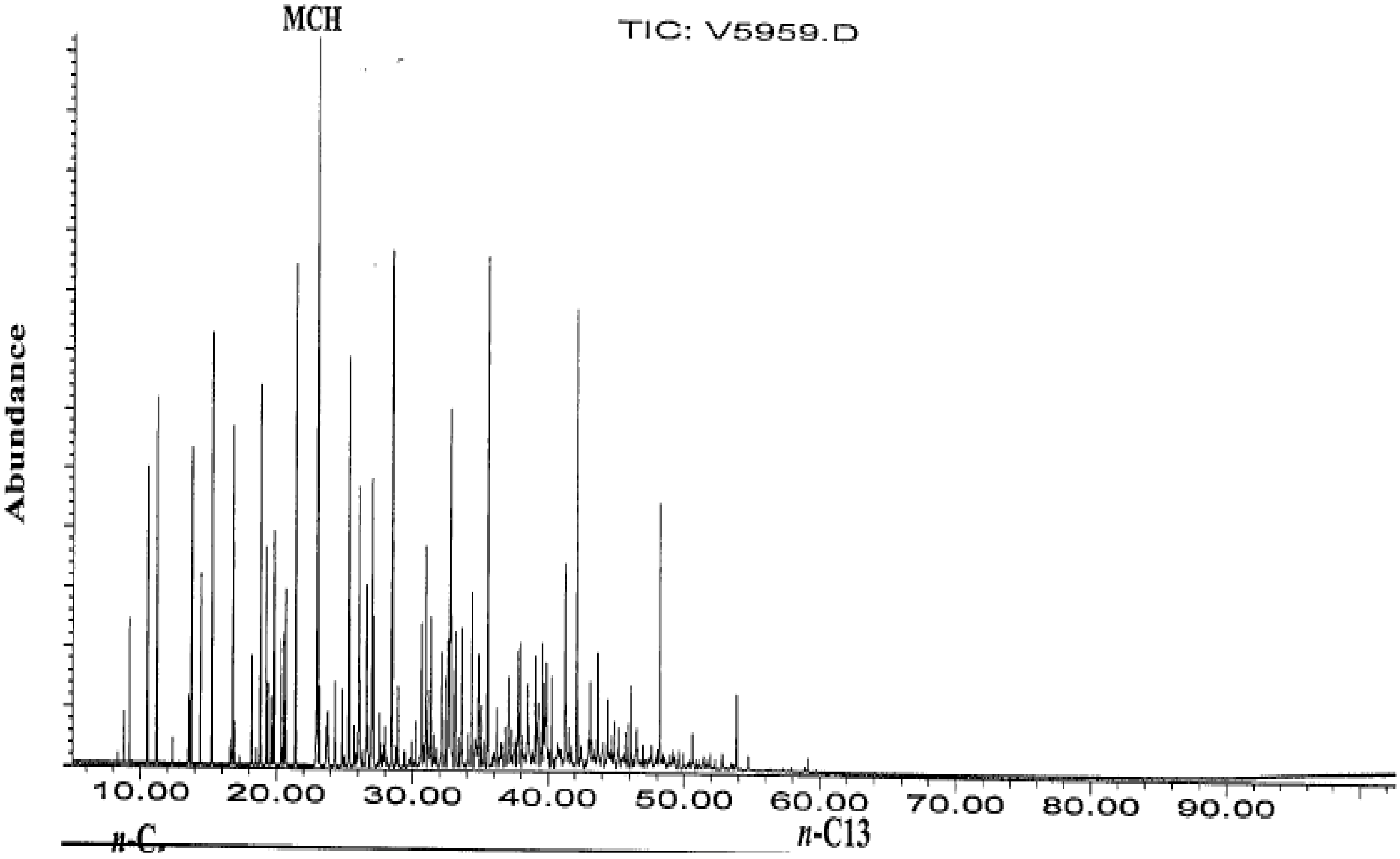
Octane number

- In a normal spark-ignition engine, the air-fuel mixture is heated due to compression and triggered to burn rapidly by the spark plug. Too much compression leads to self ignition before the spark, causing high pressures and knocking.
- 2,2,4-Trimethylpentane (iso-octane) has an octane rating of 100 whereas n-heptane has an octane rating of 0.
- The octane rating of gasoline is measured in a test engine and is defined by comparison with the mixture of 2,2,4-trimethylpentane and n-heptane that would have the same anti-knocking capacity as the fuel under test.
- The percentage, by volume, of 2,2,4-trimethylpentane in that mixture is the octane number of the fuel.
- Similar octane numbers can be obtained by different combinations of compounds.
- A mixture of 90% iso-octane and 10% heptane would have an octane rating of 90.

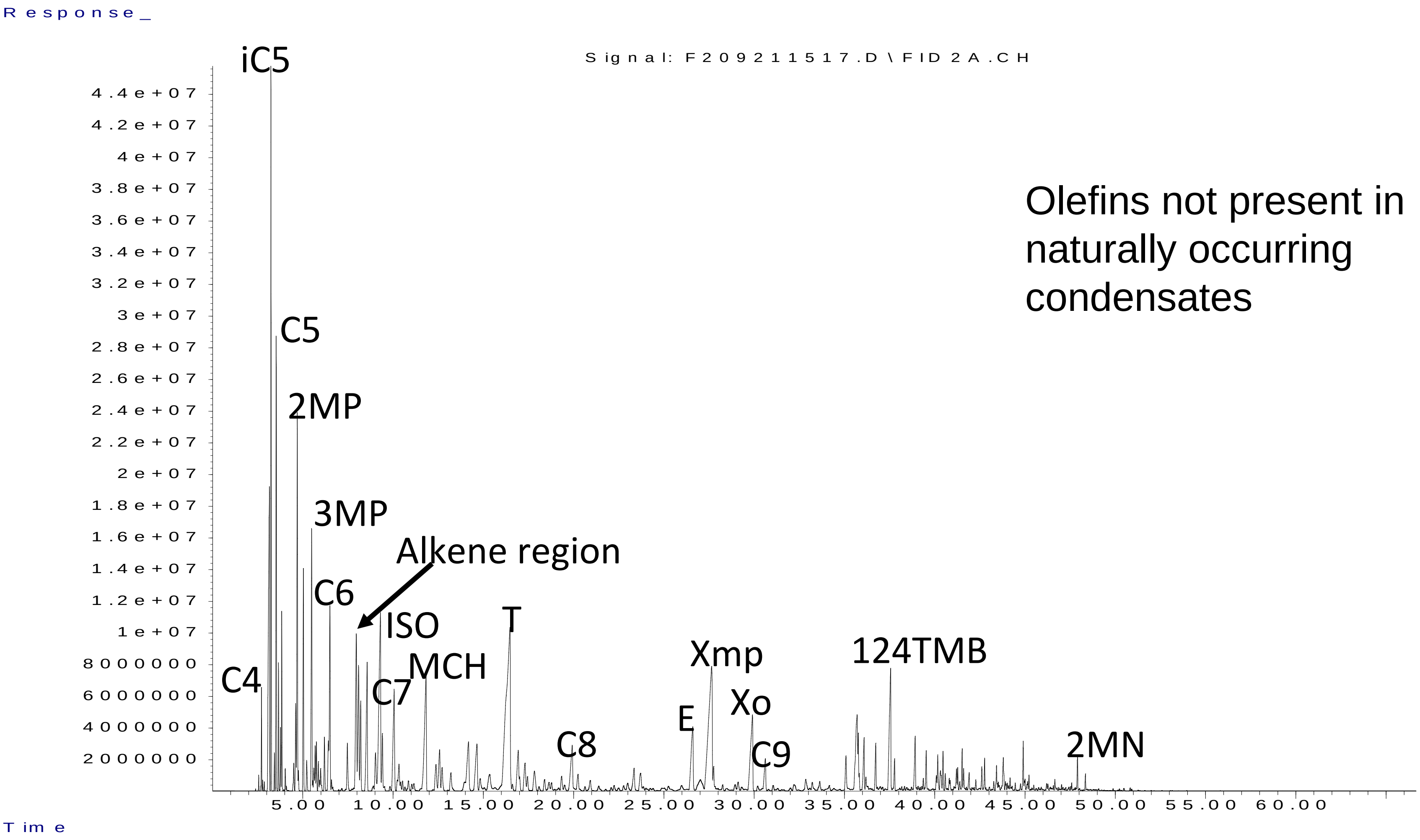
Gasoline Chemistry

- Automotive Gasoline
  - Complex mixture of hydrocarbon compounds predominantly in the C_3-C_{13} range, with a boiling point distribution between 120^{o}F and 400^{o}F
  - Manufactured by blending different refinery streams
    - Light straight run naphtha (base)
    - Alkylate-paraffinic branched chain (increase octane rating)
    - Reformate –aromatics (increase octane rating)
    - Catalytic cracking produces olefins and aromatic hydrocarbons from crude oil chromatograms

Naphtha

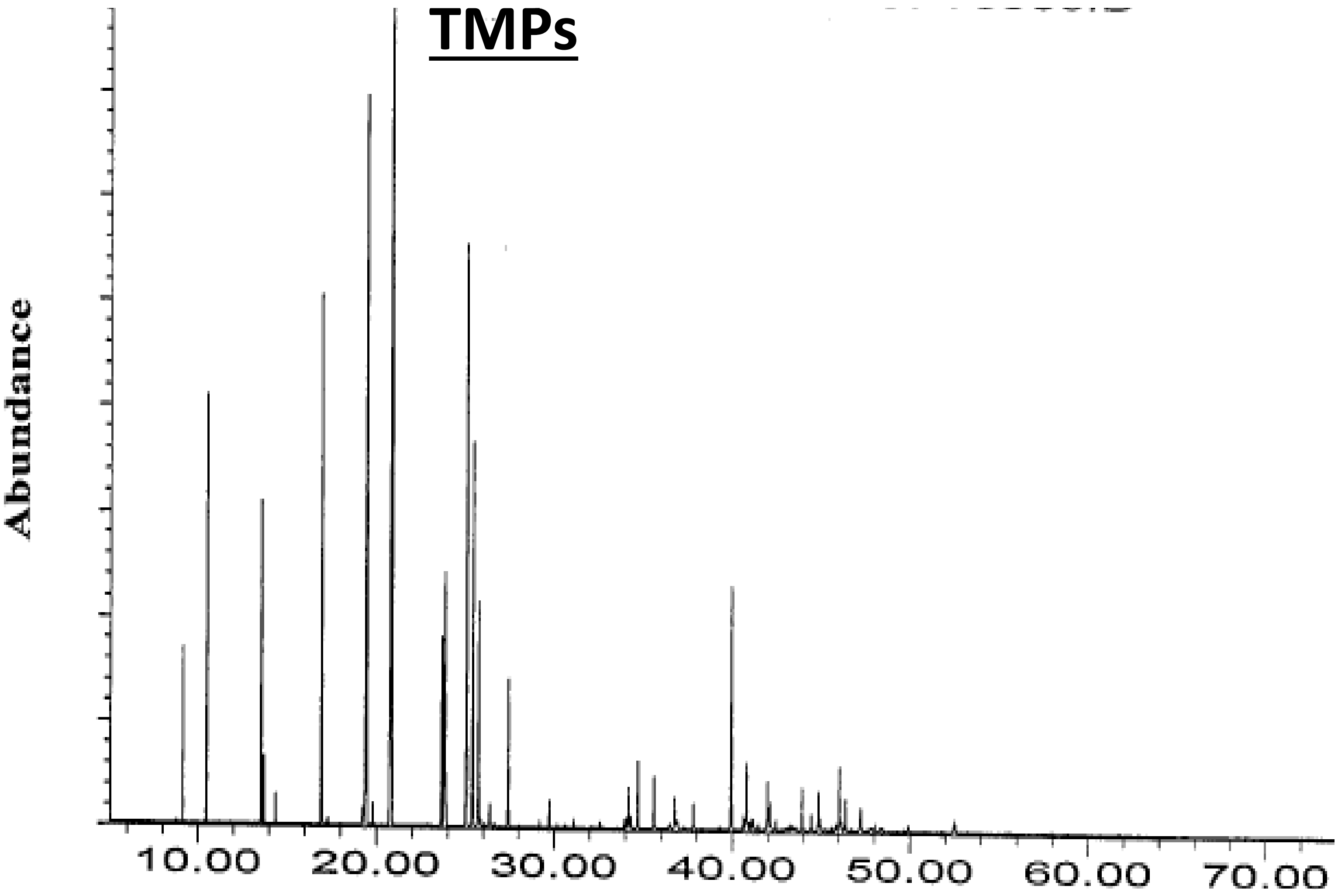

MCH
TIC: V5959.D
Abundance
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
n-C
n-C13

Olefins in Gasolines



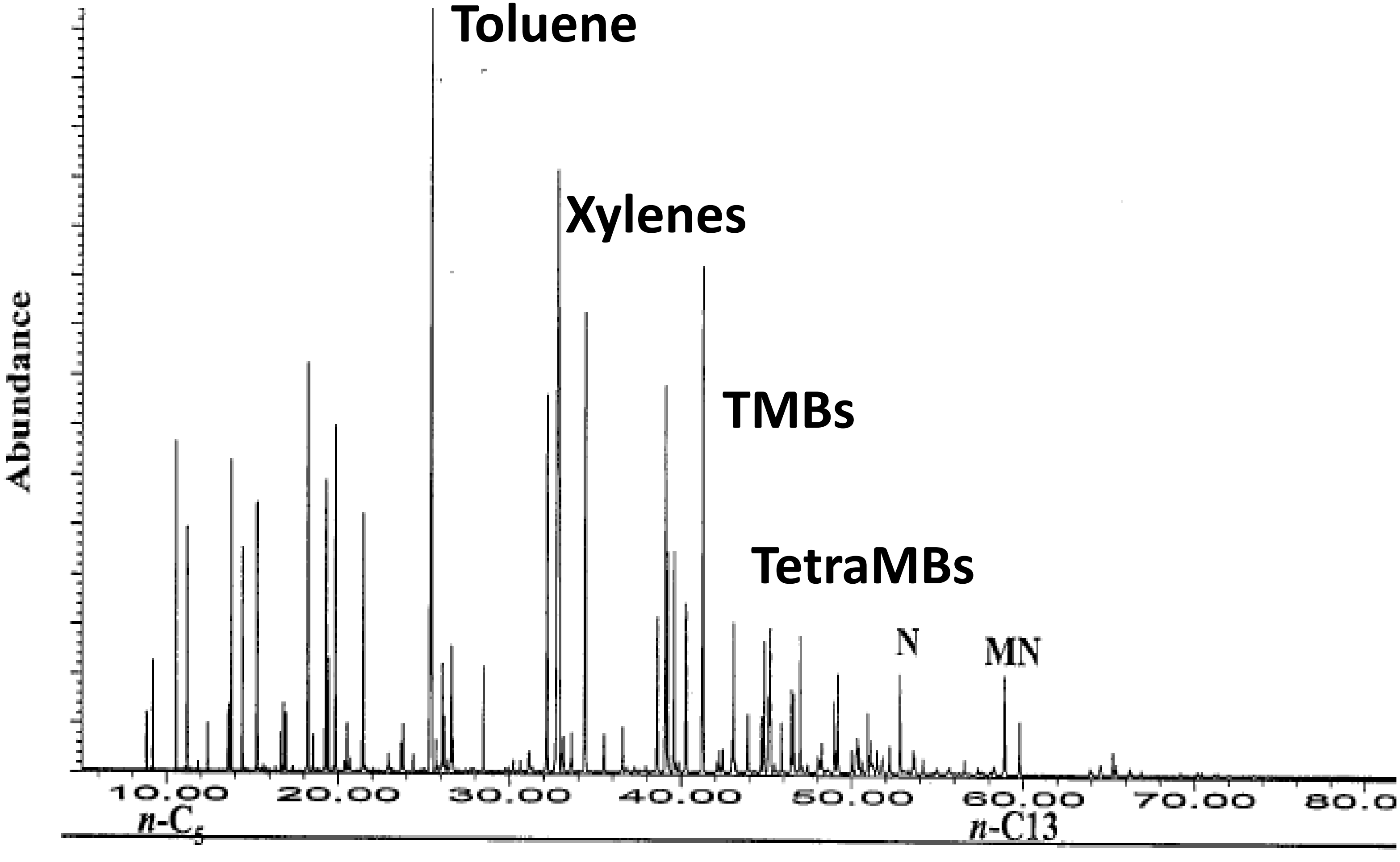
Olefins not present in naturally occurring condensates

Refinery Alkylate

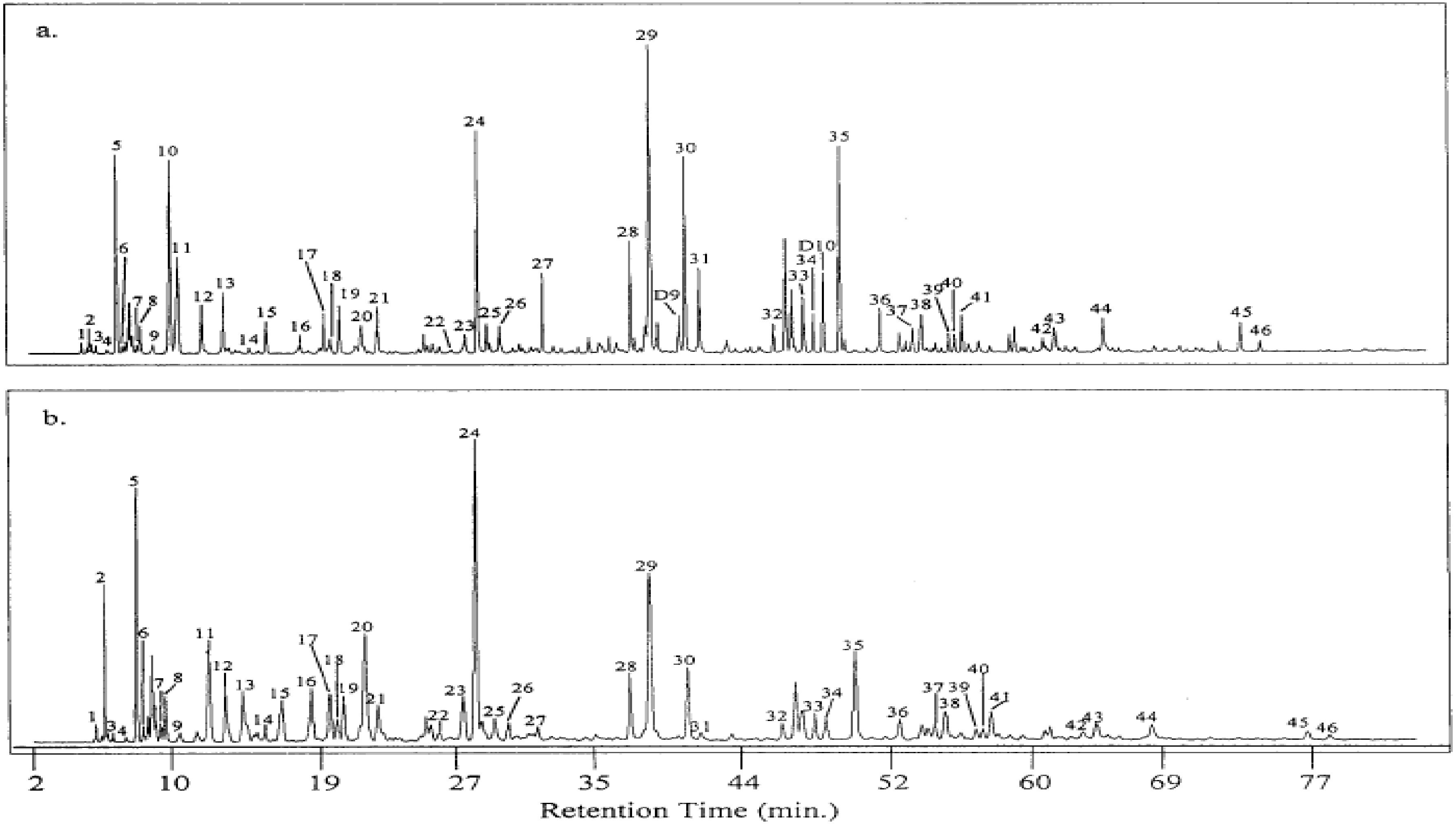


TMPs

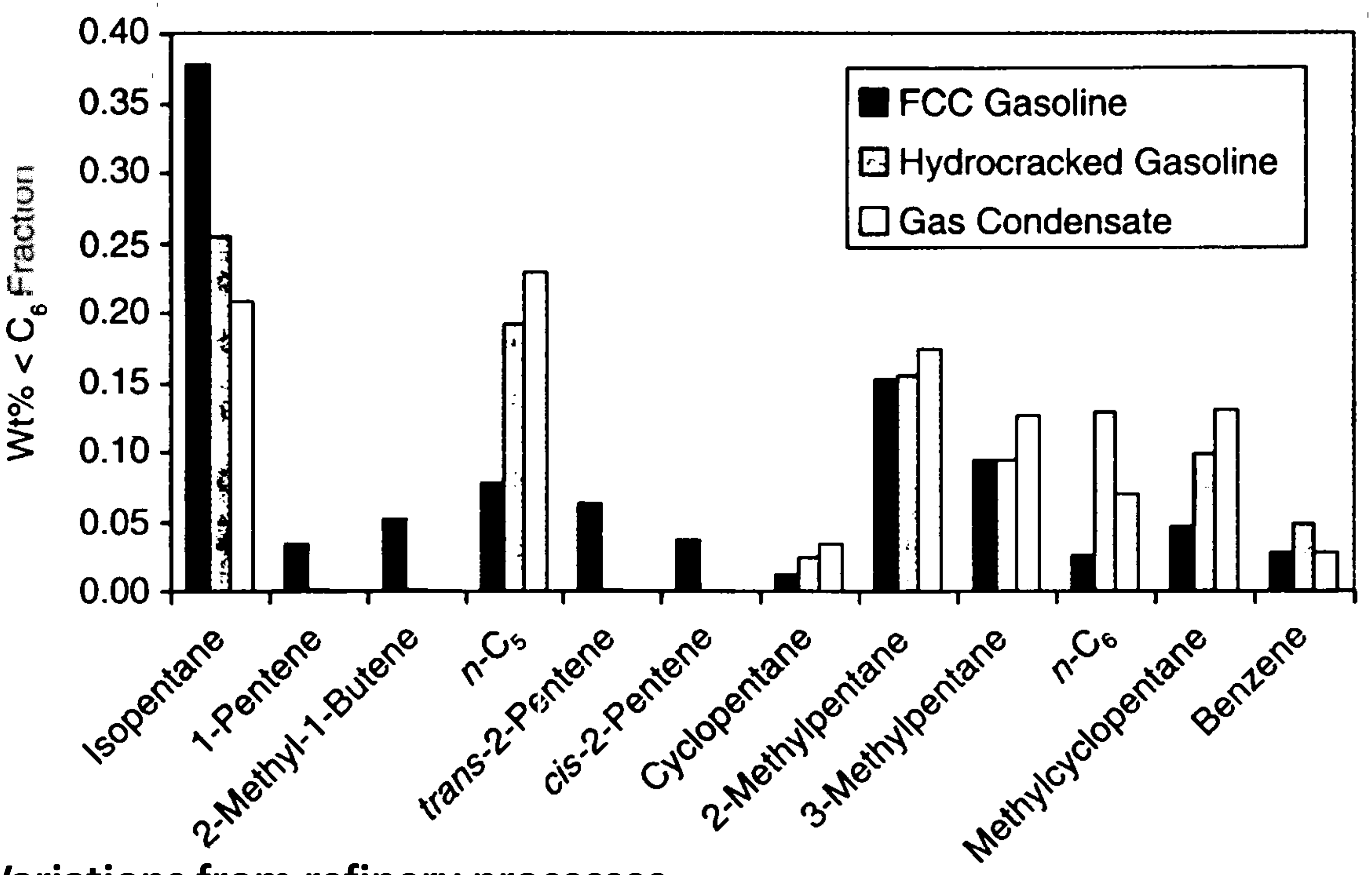
Reformate


Toluene
Xylenes
TMBs
TetraMBs
N
MN
Abundance
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.0
n-C$_5$
n-C13

Typical contemporary gasolines



Refinery-related differences

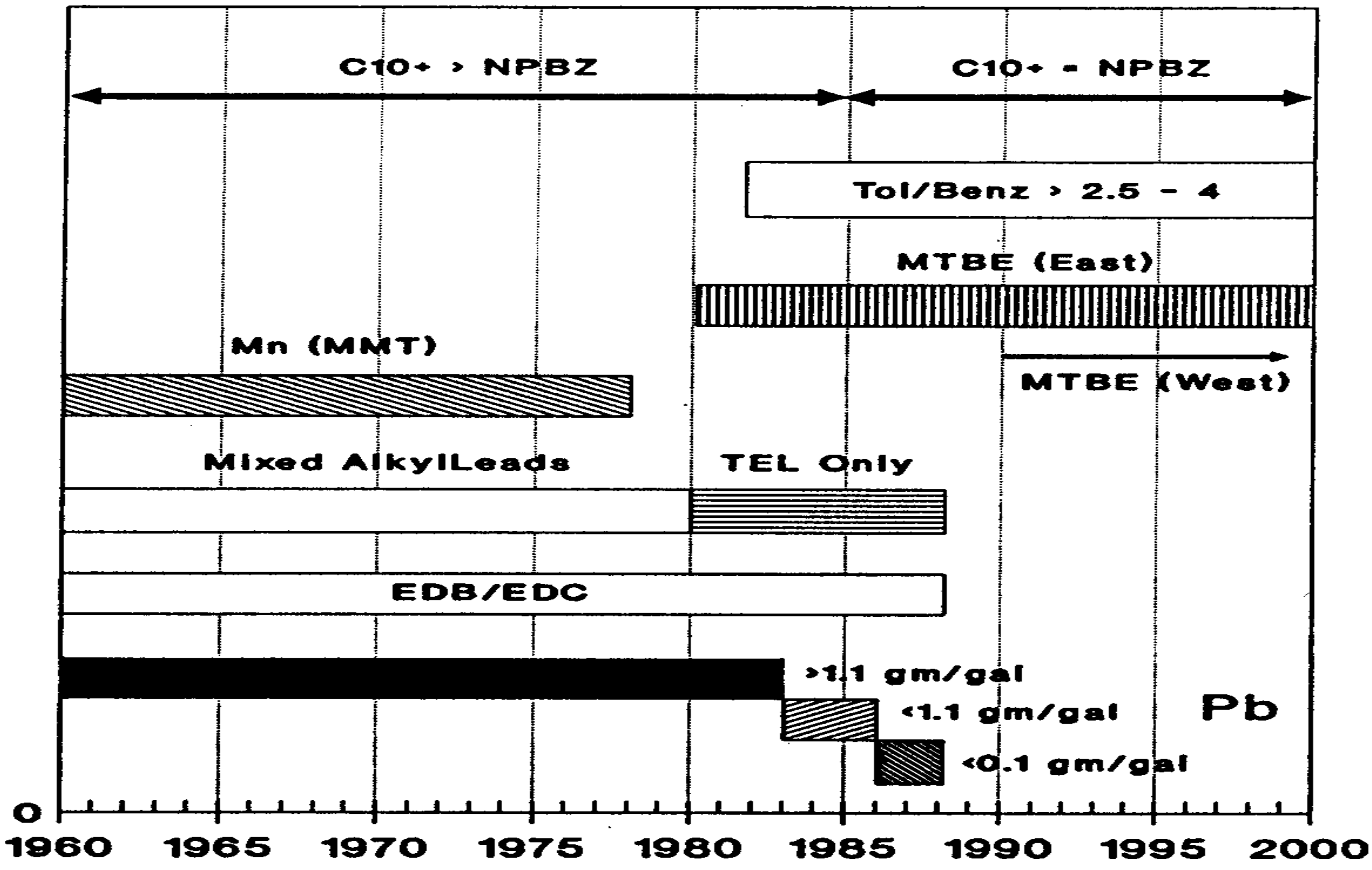


Variations from refinery processes

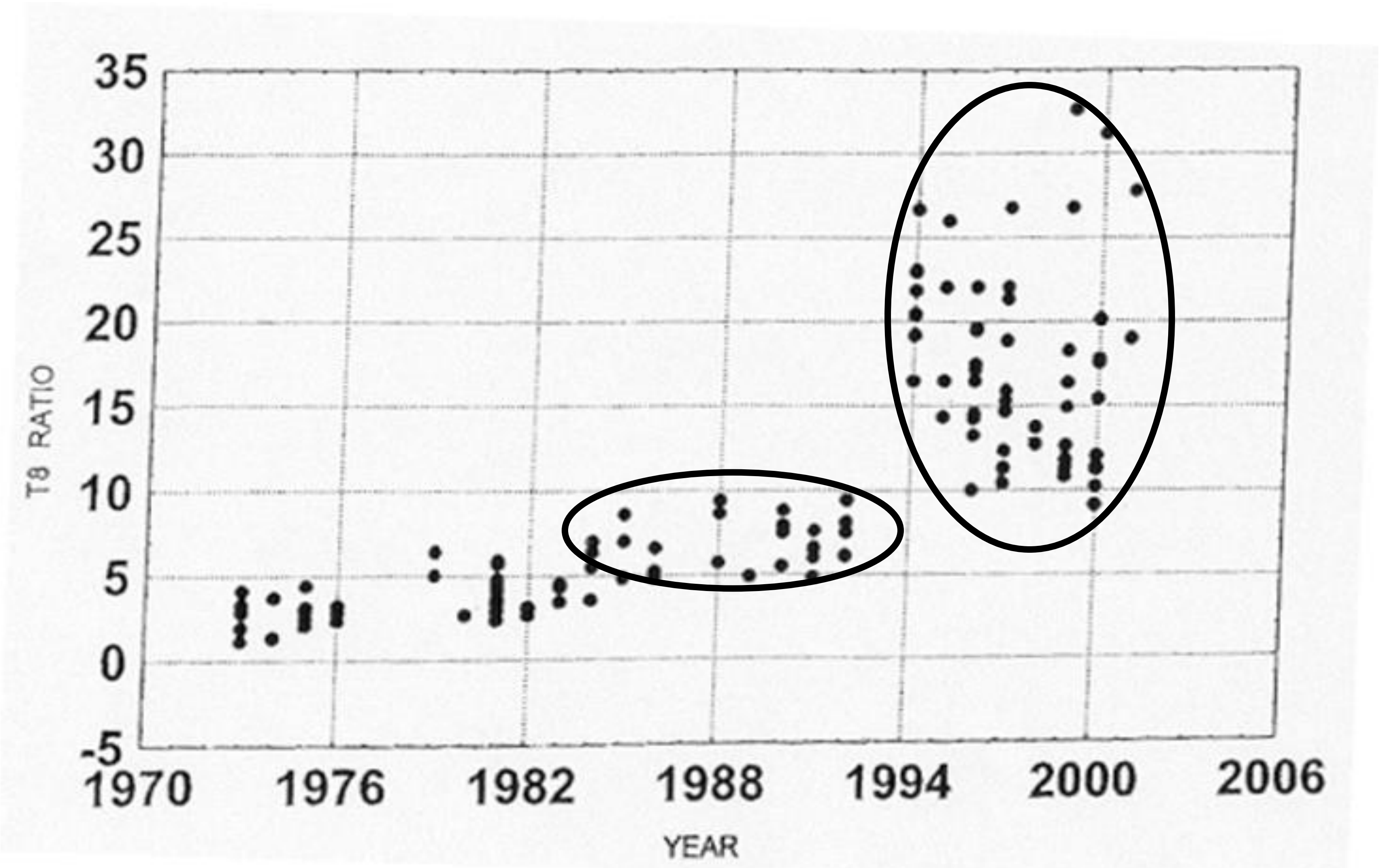
Additives

- Various additives have been used in gasoline over time:
  - Lead alkyls-anti knock
  - Lead scavengers-EDB and EDC
  - MMT Anti knock
  - Oxygenates-MTBE, EtOH.
  - Detergents to remove gums and residues
  - Anti-oxidants
  - Dyes-differentiate grades and manufacturer
- These can be extremely important for age-dating

Chronology of additives



Age dating gasolines



(Toluene + 2,2,4-TMP/nC_7 + nC_8)

Olefins

- In the US, FCC produces 4x more gasoline than hydrocracking.
- Gasolines still contain olefins although RFG must be <10% olefins by volume.
- Presence/absence/amounts of olefins can be used to discriminate gasolines, particularly if coming from a local refinery.

Reformates

- % of ethylbenzene in total C_2-aromatics is typically 10-20% in fresh gasolines; total xylenes are about 50% .
- If amounts are lower, this would suggest removal for special purpose such as manufacturing of styrene.
- Relationships between various aromatics could be used to distinguish gasolines containing different reformate blends under different conditions.

Isomerization

- Conversion of n-alkanes into branched hydrocarbons to improve octane rating.
- Specific reaction conditions produce specific isomerates.
- Differentiation of these isomerates can be used to distinguish gasolines containing different isomerate blends.

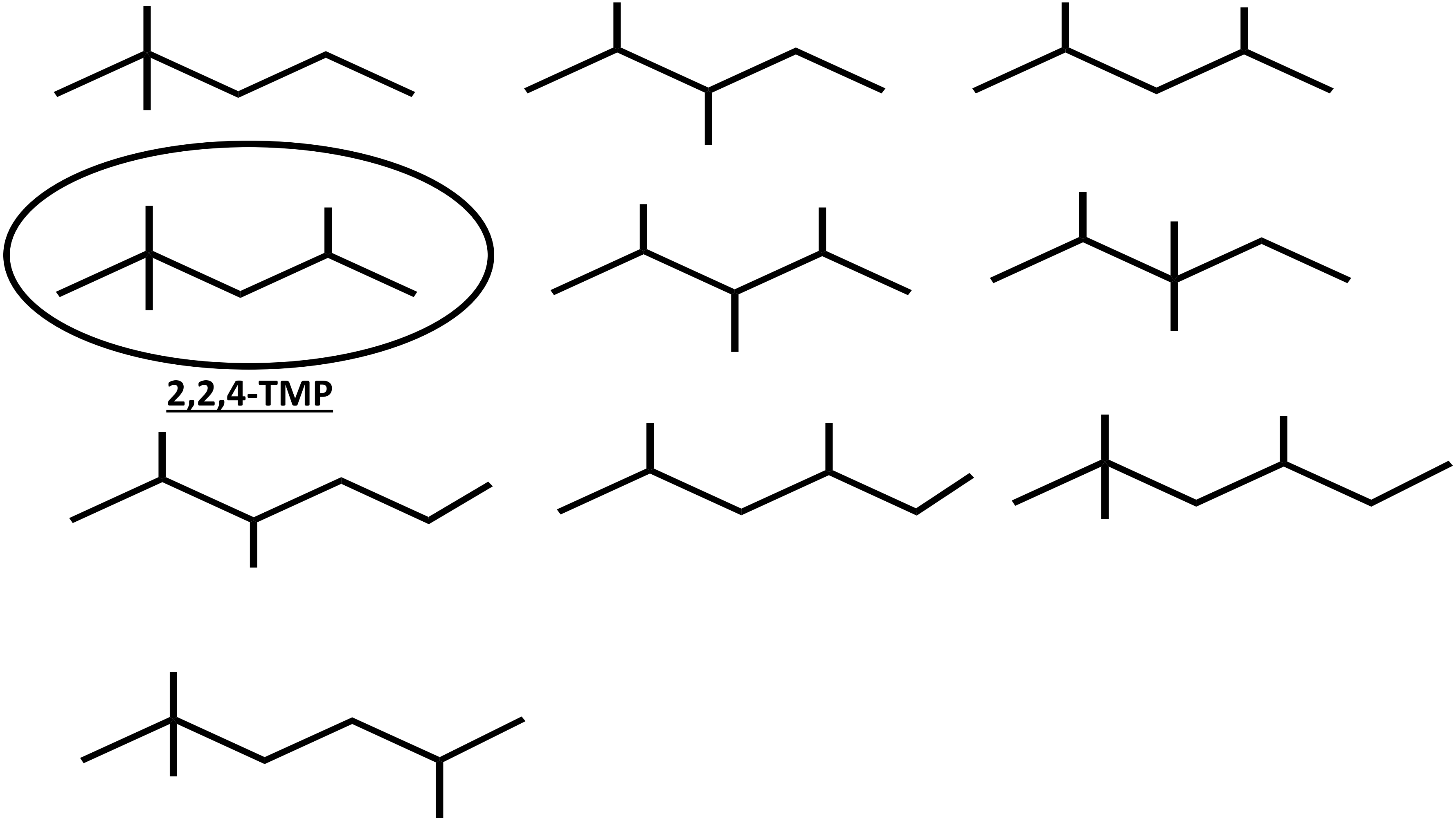
Isomerization

- Ratio between *iso*- and n-pentane and 2-Me and 3-Me-pentane will vary significantly depending on reaction conditions.
- Reaction of *iso*-butane and olefin streams in presence of acid will produce *iso*-alkanes (C_3/C_4). Proportions depends on catalyst and nature of stream.

Alkylates

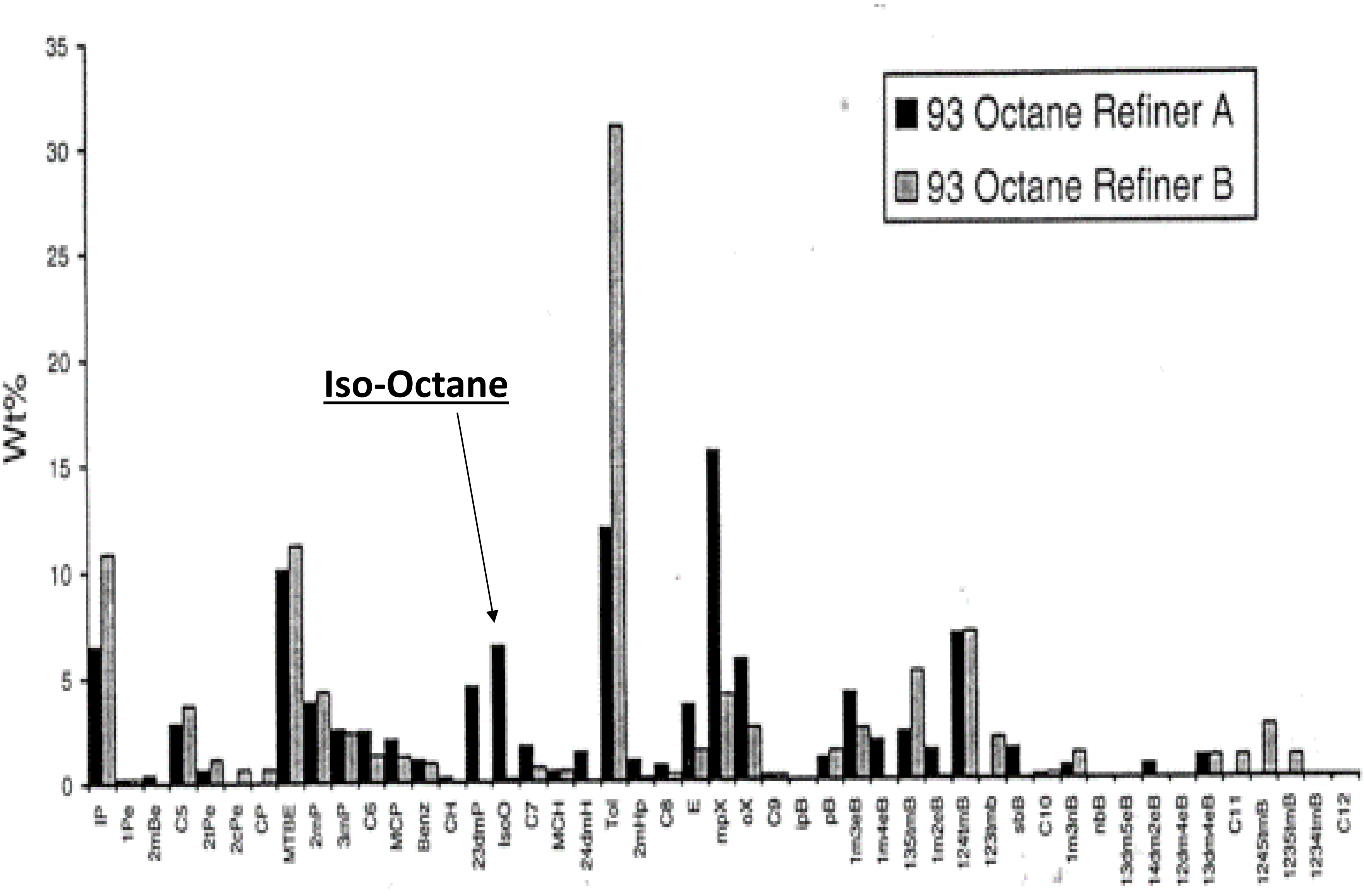
- Branched hydrocarbons produced by heating olefins with HF or H_2SO_4
- Iso-octane (2,2,4-Trimethylpentane)
- Low octane TMP/MCH<2.5
- High octane TMP/MCH >5
- Intermediate octane TMP/MCH 2.5-5
- Ratios from groundwater may vary due to purging efficiency
- No natural source of TMP

Alkylates in gasoline



2,2,4-TMP

Same octane different composition



Iso-Octane

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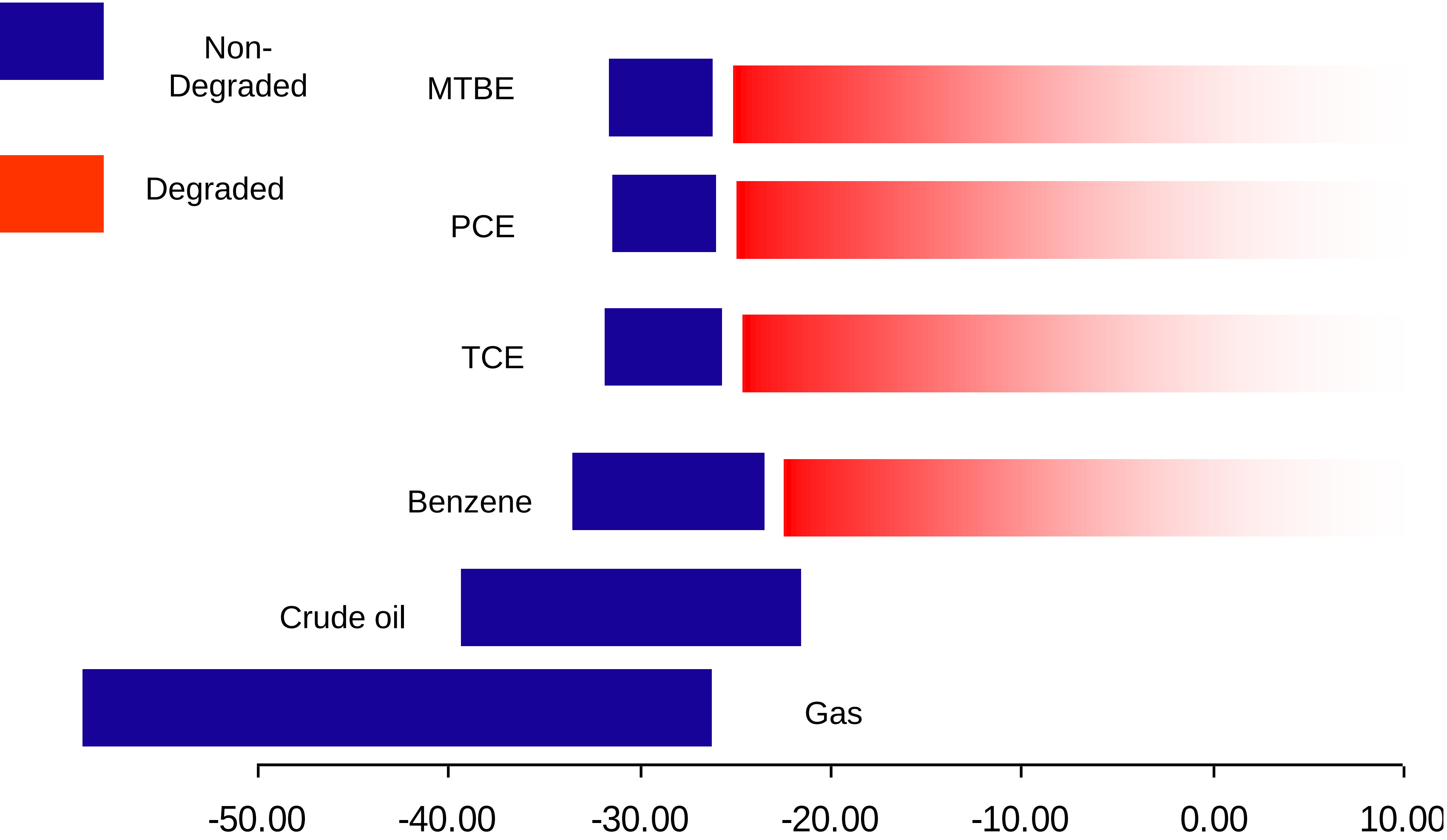
- Summary

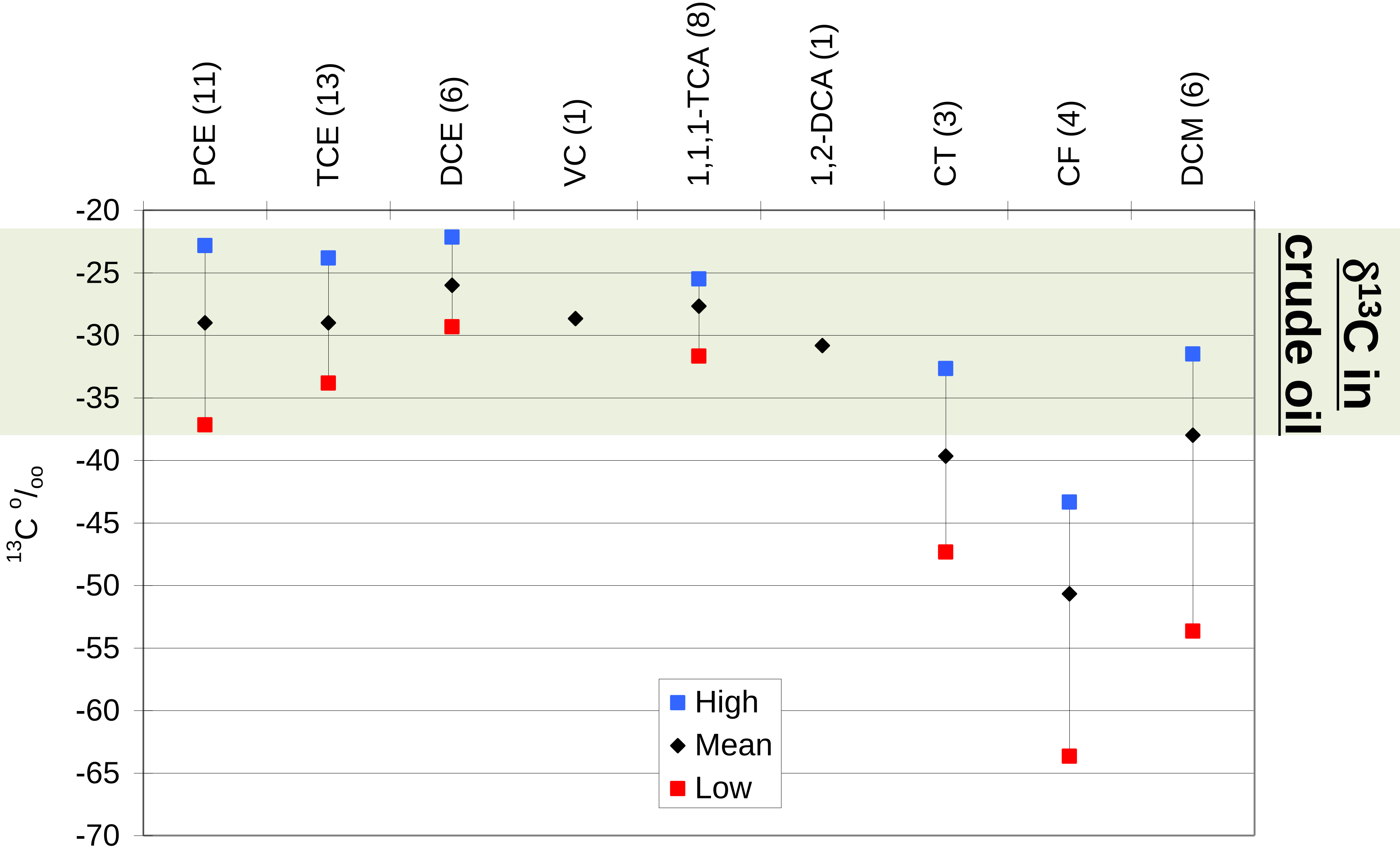
Source Discrimination-Groundwater Problems

- **Source discrimination**
  - Stable isotopes provide a tool that can be used to discriminate sources of common ground water and sediment contaminants.
  - Particularly valuable for single component contaminants
  - Volatile compound source signatures may be affected by “weathering”
  - Relatively narrow range of signatures

Non-degraded v. Degraded Components



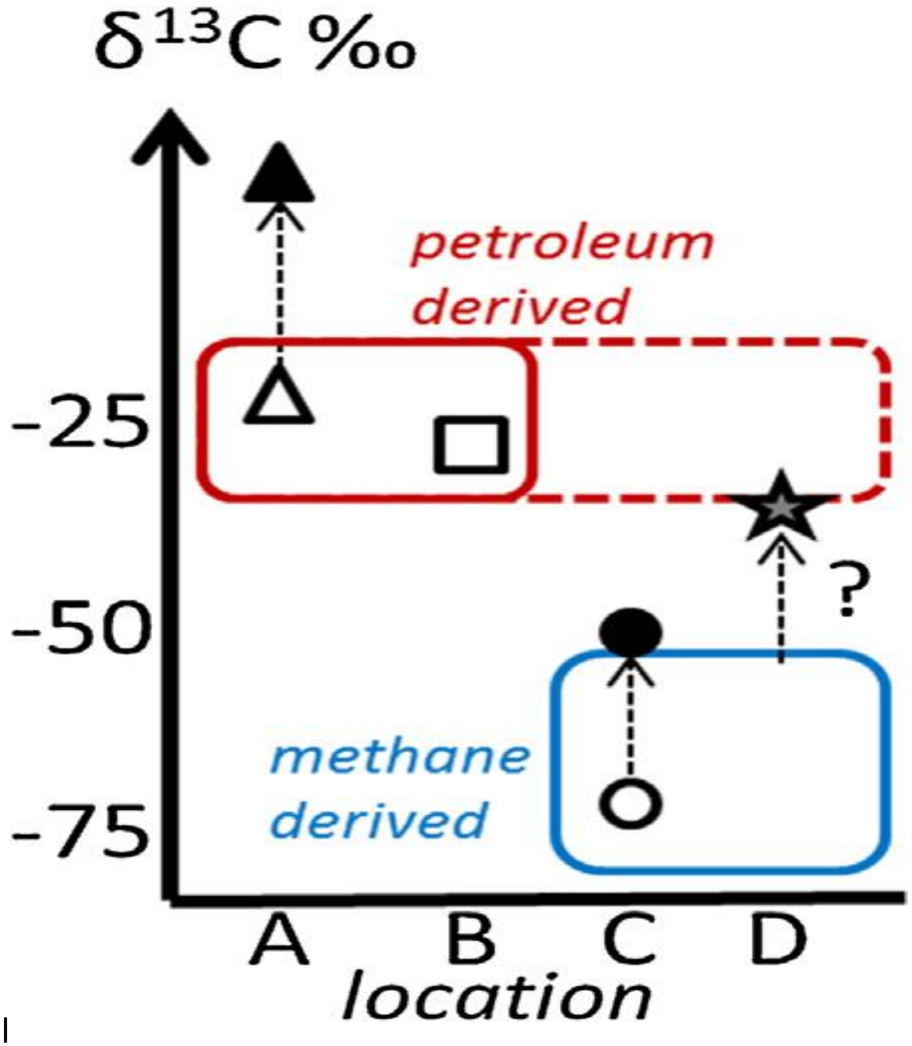
C Isotope Ratios of Misc. CAHs



after USEPA 2008

Data Interpretation

Differentiation of PCE sources dependent on feedstocks.
Possible origin(s) of sample D?



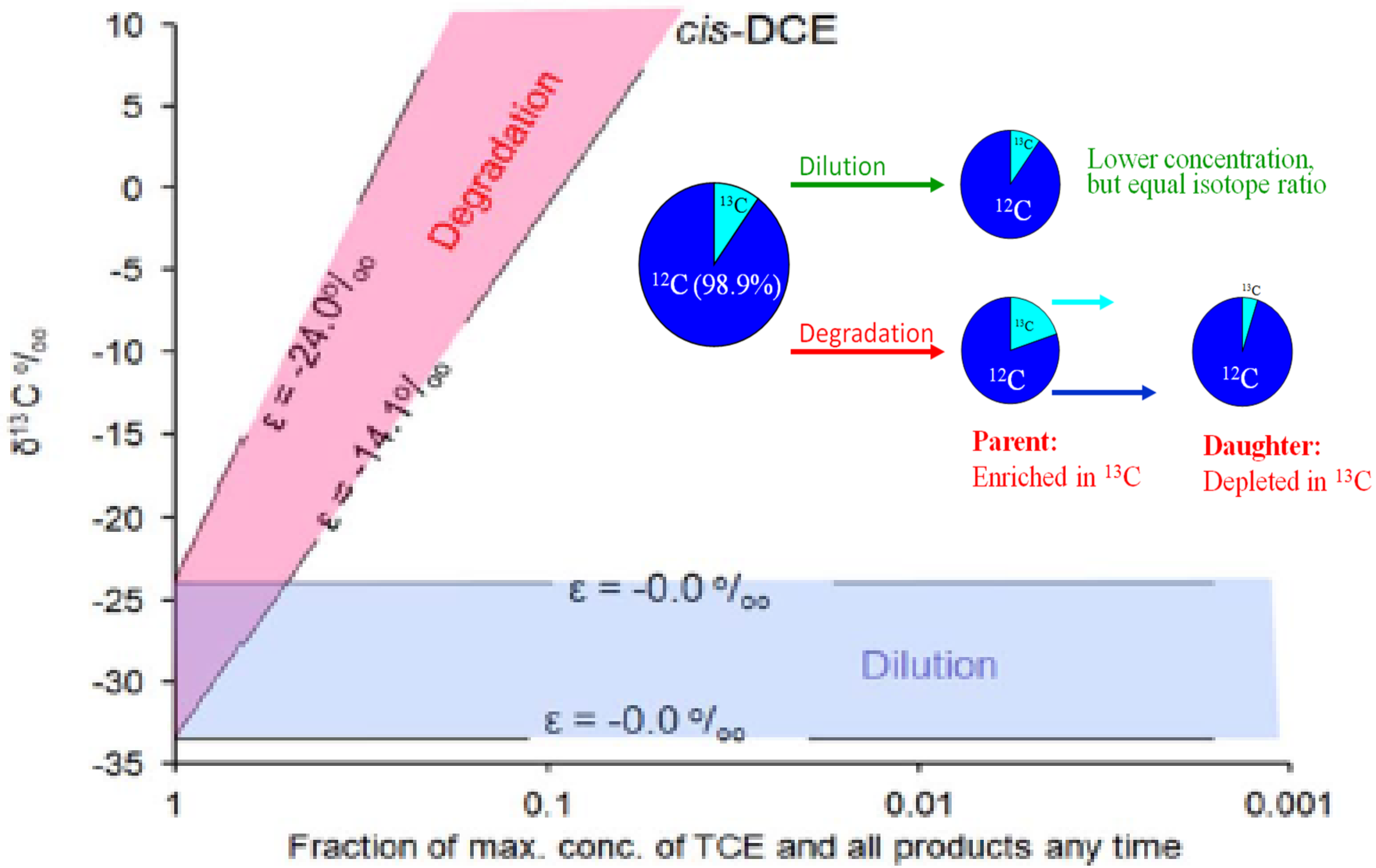
Nijenhuis et al. / Trends in Environmental Analytical Chemistry 11 (2016) 1–8

Remediation Studies

- **How can isotopes assist in remediation studies?**

- Provide independent verification that attenuation is taking place
- Provide estimates of extent of attenuation
- Distinguish mechanisms of degradation
- Distinguish non-degradative processes that may be taking place

Dilution vs. Dispersion for Chlorinated Ethenes



Remediation - Summary

- **Provide estimates of extent of attenuation**

- Conservative estimates of the extent of degradation can be obtained from the Rayleigh equation
- Information can also be incorporated into transport flow models

Use of CSIA data to determine progress of in-situ degradation (anaerobic)

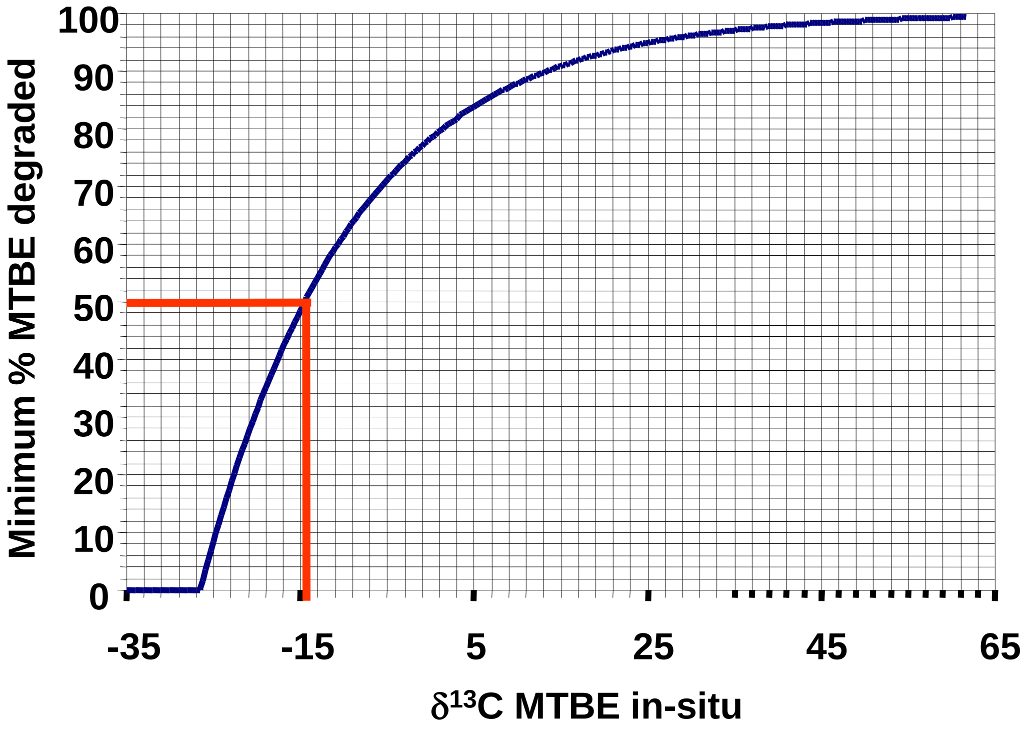
Simplified Rayleigh equation:

$$\delta^{13}C_{insitu} = \delta^{13}C_{initial} + \varepsilon * \ln F$$

Mixing with less degraded MTBE will lower the degradation estimate

Calculation is made using a conservative value of $\delta^{13}C_{initial}$

This is a conservative approach



Data Interpretation

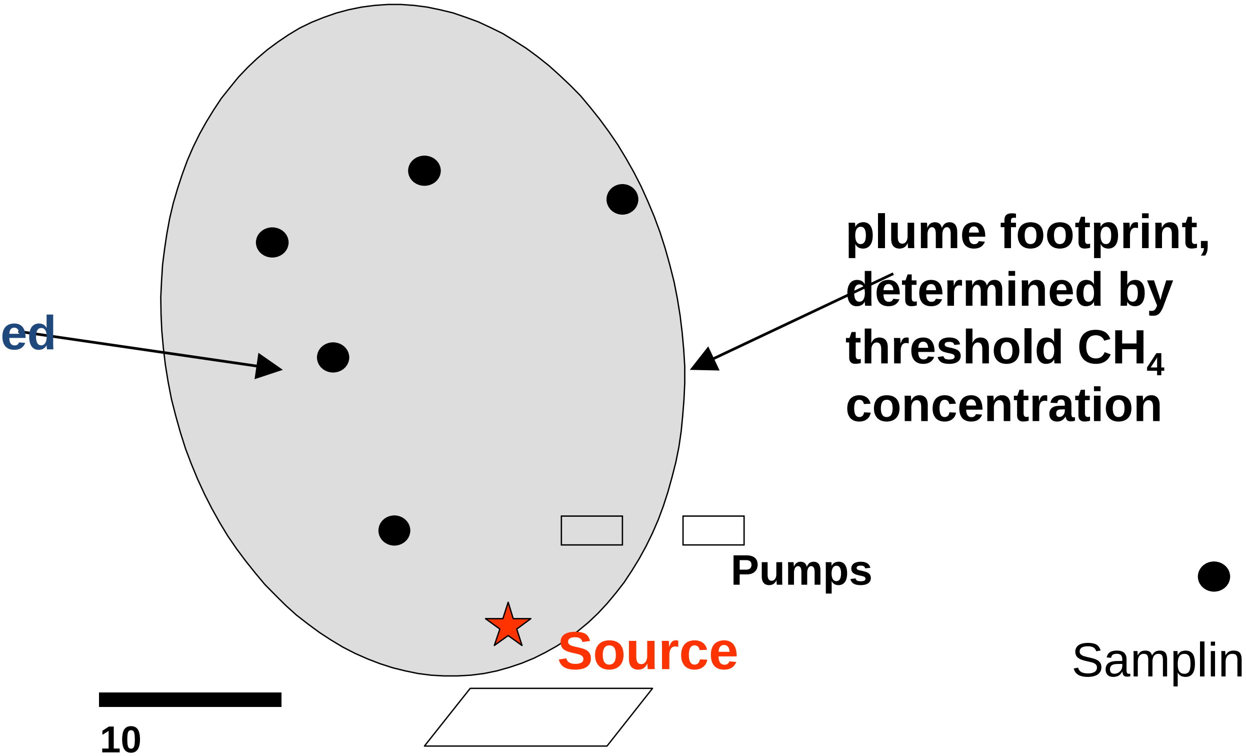
Qualitative – if MTBE composition is “heavier” than the reference commercial MTBE, degradation may be inferred

Composition range of undegraded MTBE:

Carbon: –33 to –27.5 per mil $\delta^{13}C$
Hydrogen: –125 to –80 per mil δD

Also need to consider the presence of degradation products.

Anaerobic Plume New Jersey, BP Site



Material for microcosms collected

plume footprint, determined by threshold CH_4 concentration

Pumps

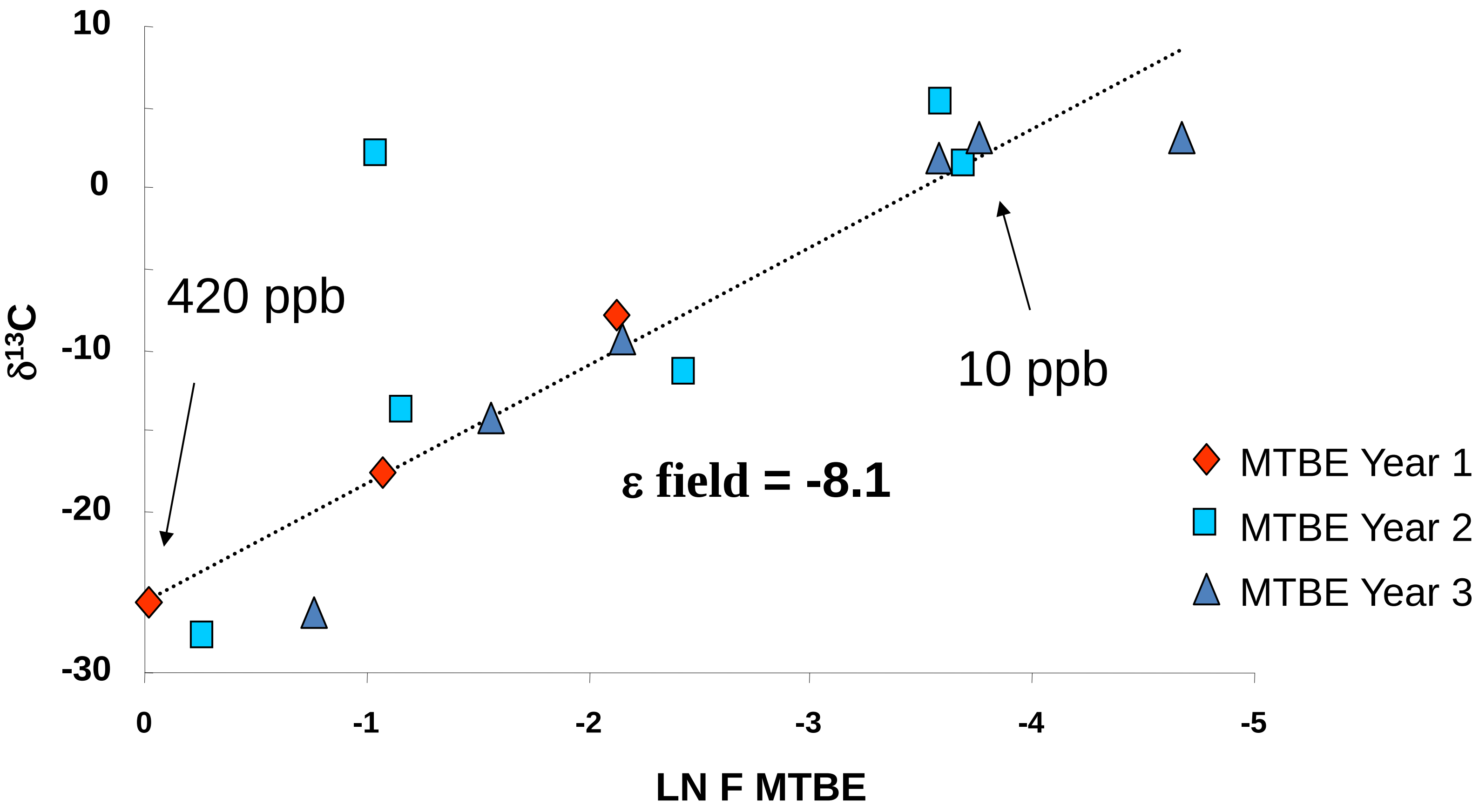
Source

● Sampling well

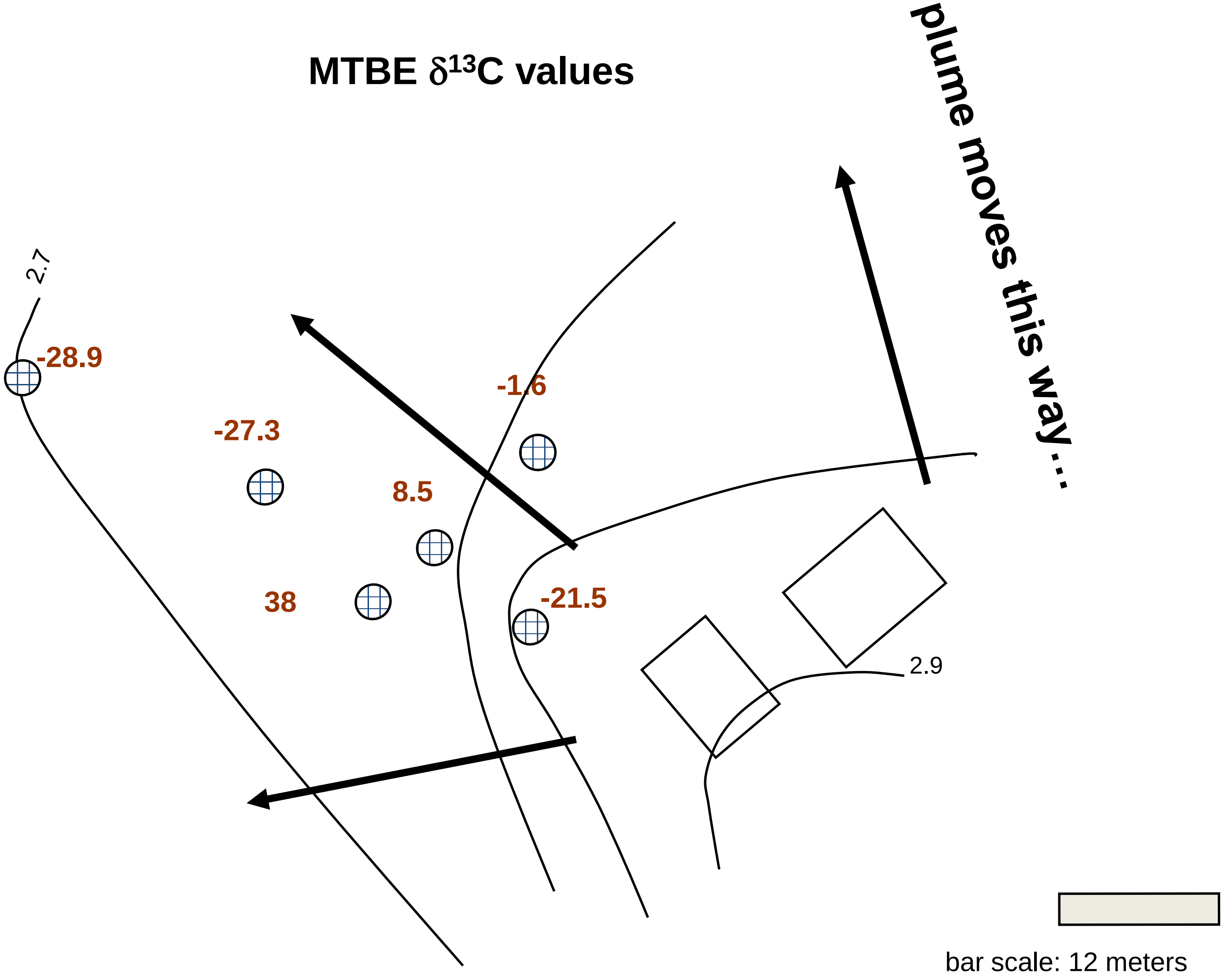
10 Meters

Station

Anaerobic Plume New Jersey



Dana Point, Orange County, CA



bar scale: 12 meters

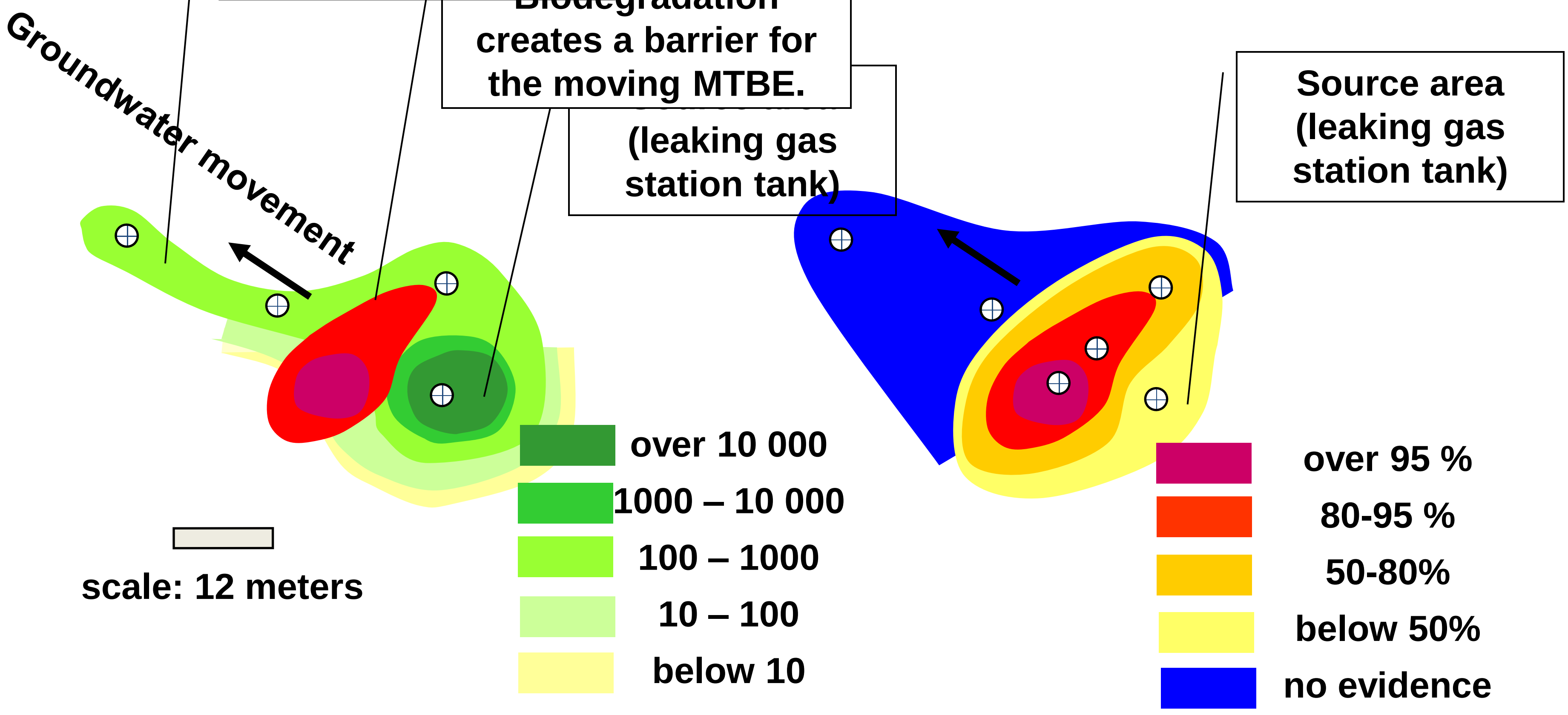
Gas st Orange County, CA, USA

This part of the plume represents MTBE avoiding the active zone

Biodegradation creates a barrier for the moving MTBE.

(leaking gas station tank)

Source area (leaking gas station tank)



MTBE concentrations (µg/L)

Conservative extent of MTBE biodegradation calculated from CSIA data

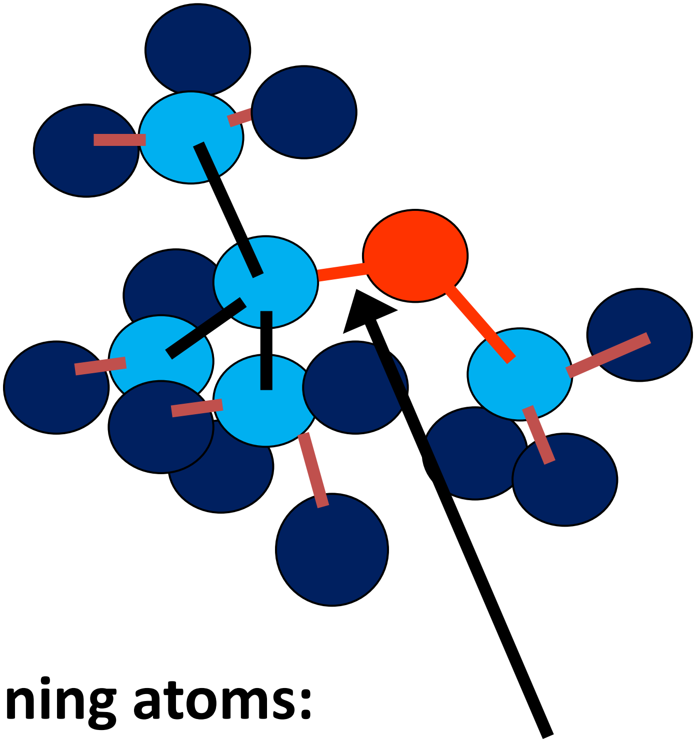
Degradation Mechanisms via Isotopes

- Kuder et al., (2005) first used C and H isotope data from both microcosm and field data to demonstrate anaerobic degradation of MTBE.
- Showed similar enrichment factors for both C and H.
- Common degradation pathway at several sites
- First step under anaerobic conditions is cleavage of -OCH_3 bond.

Kuder et al., 2005

Isotope Effects Reflect Reaction Mechanisms

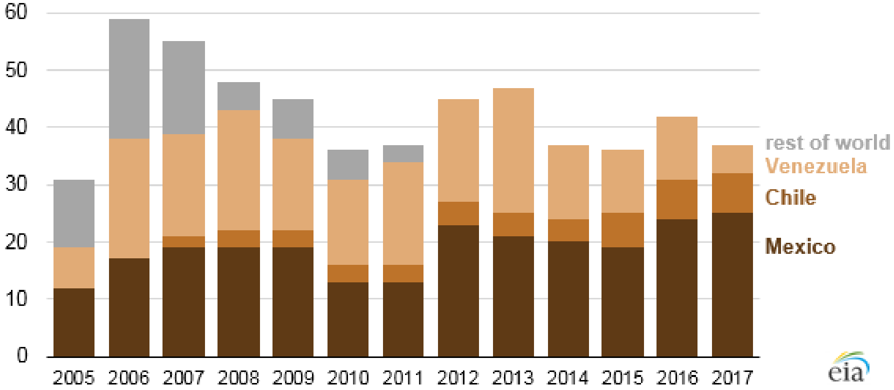
Strong isotope fractionation affects atoms of the reacting bond



Atoms at the reacting bond:

- “primary effects”
- strong for $^{13}C/^{12}C$

U.S. exports of methyl tert-butyl ether (2005-2017)
thousand barrels per day



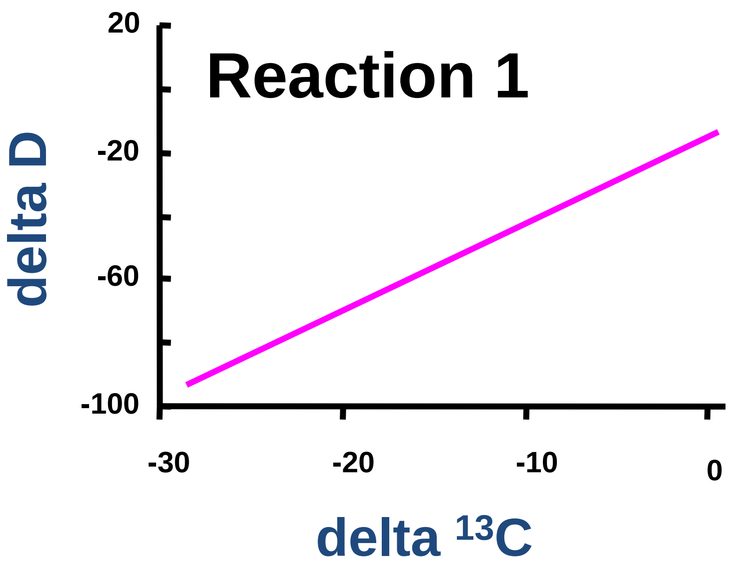
Remaining atoms:

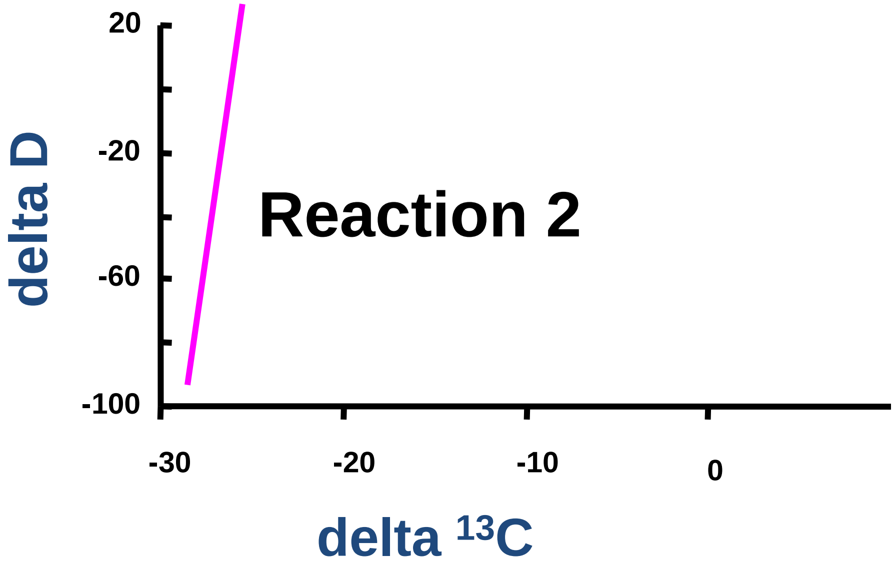
- “secondary effects”
- negligible for $^{13}C/^{12}C$

Bond cleavage

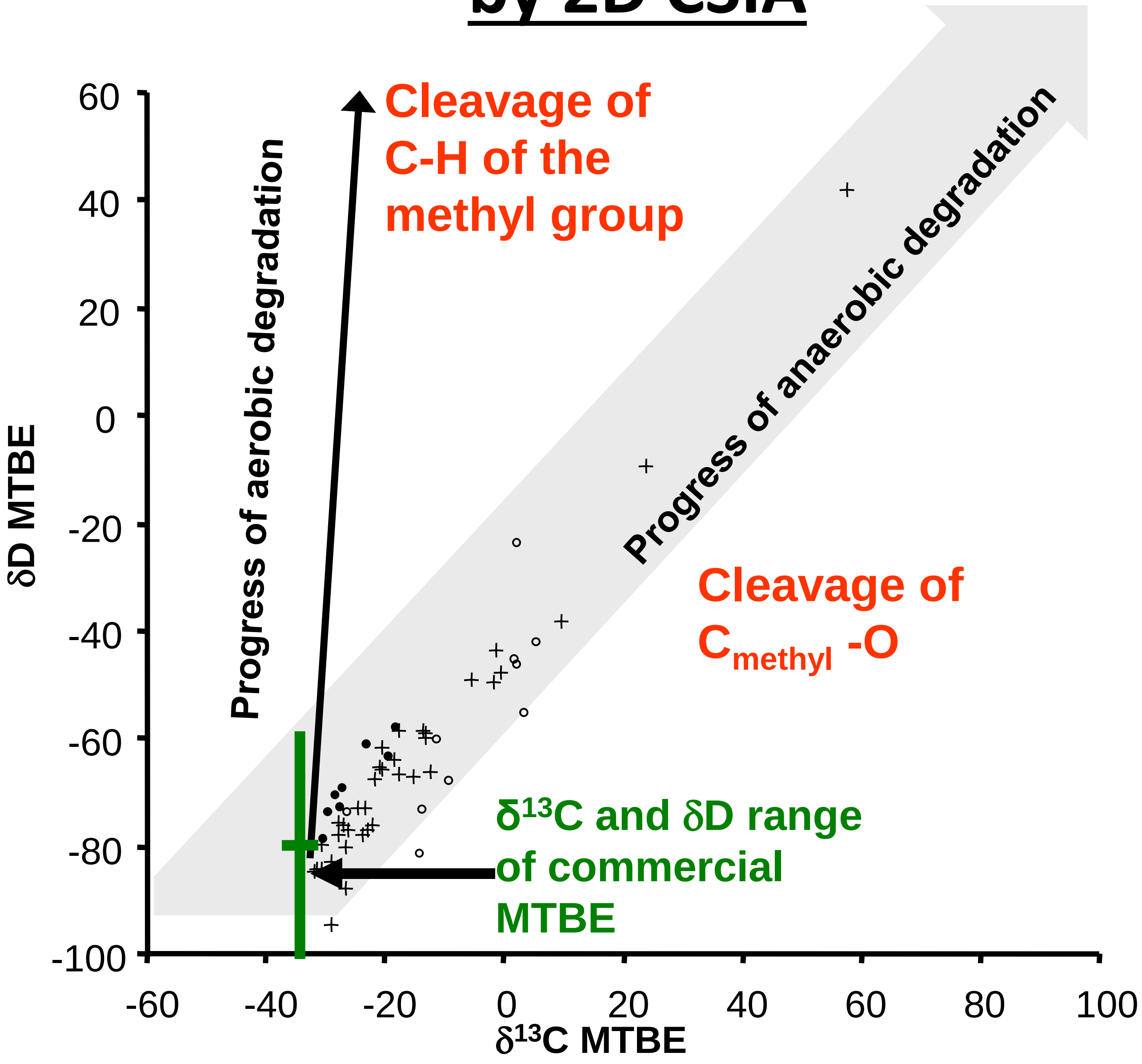
Isotopic Fractionation During MTBE – TBA Conversion

- **Reaction 1**: Ether bond hydrolysis: primary isotopic effect on carbon, secondary effect of hydrogen
- **Reaction 2**: Terminal methyl group oxidation: primary isotopic effect both on carbon and hydrogen-but stronger for hydrogen

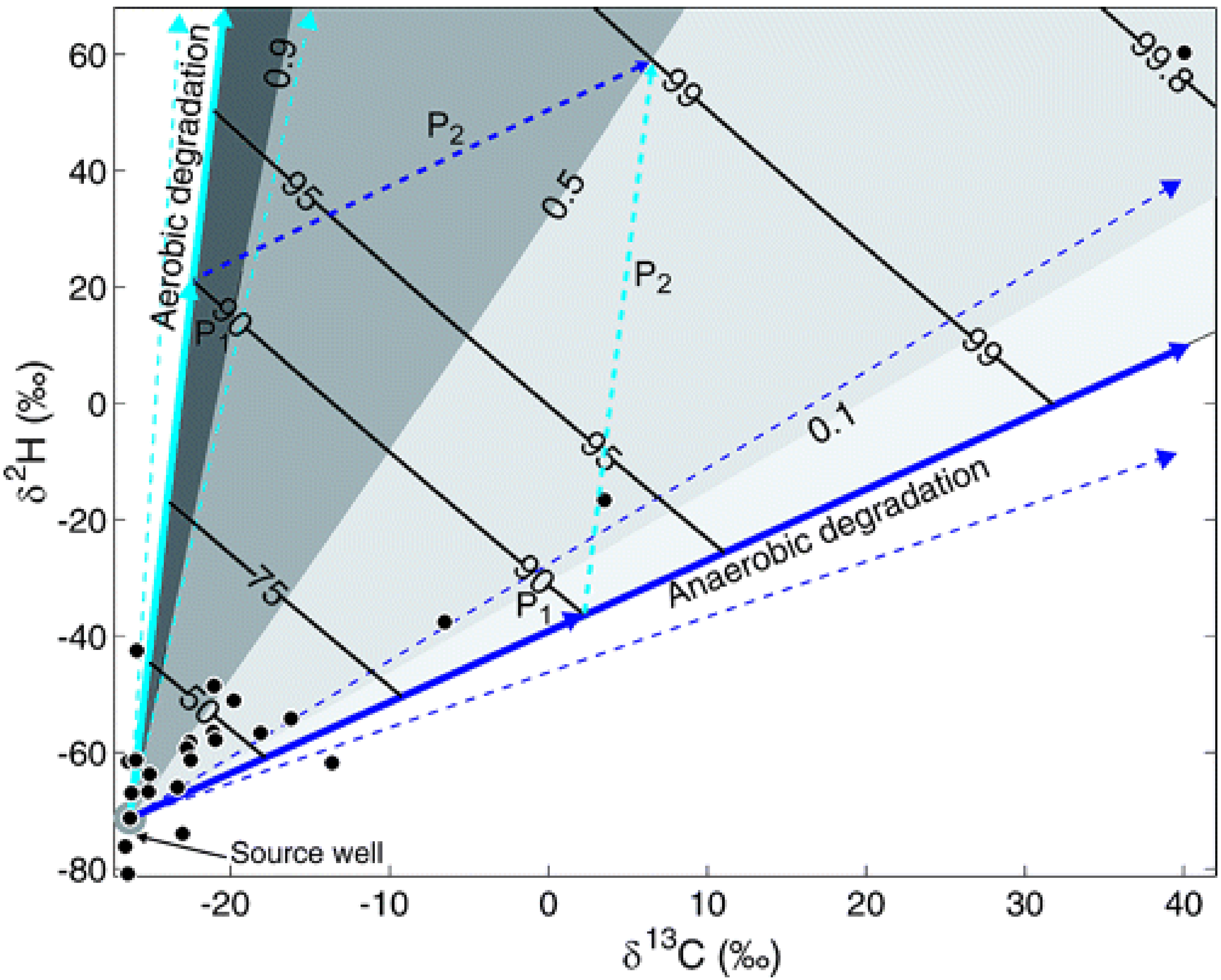




Discrimination of Aerobic vs. Anaerobic Degradation by 2D CSIA



2D-Isotope Analyses of MTBE at Industrial Site



After van Breukelen; Env. Sci. Tech.,41,4004, 2007

ETBE Replacement for MTBE

- Article noted ETBE had replaced MTBE in a number of areas.
- Discussed various ways isotopes could be used to determine whether any anaerobic degradation. Aerobic degradation quite common.
- Evidence showed at this time extent of anaerobic degradation of ETBE and TBA was very uncommon.

Van der Waals et al. (2024). Potential of stable isotope analysis to deduce anaerobic biodegradation of ethyl tert-butyl ether (ETBE) and t-butyl alcohol in groundwater a review. Environmental Science and Pollution Research. http//doi.org/10.1007/s11356-024-32109-3.

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  - **PAHs**
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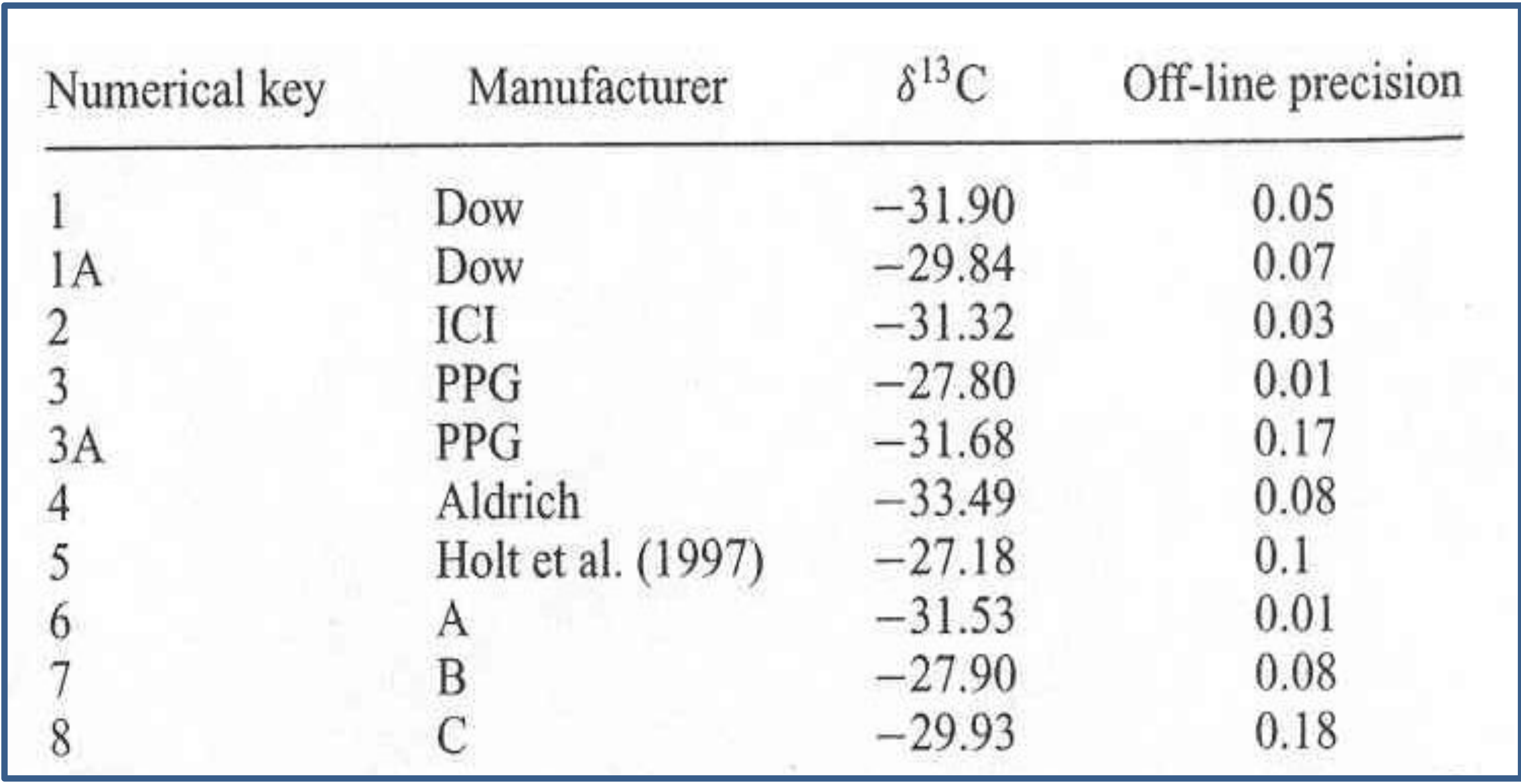
- **Summary**

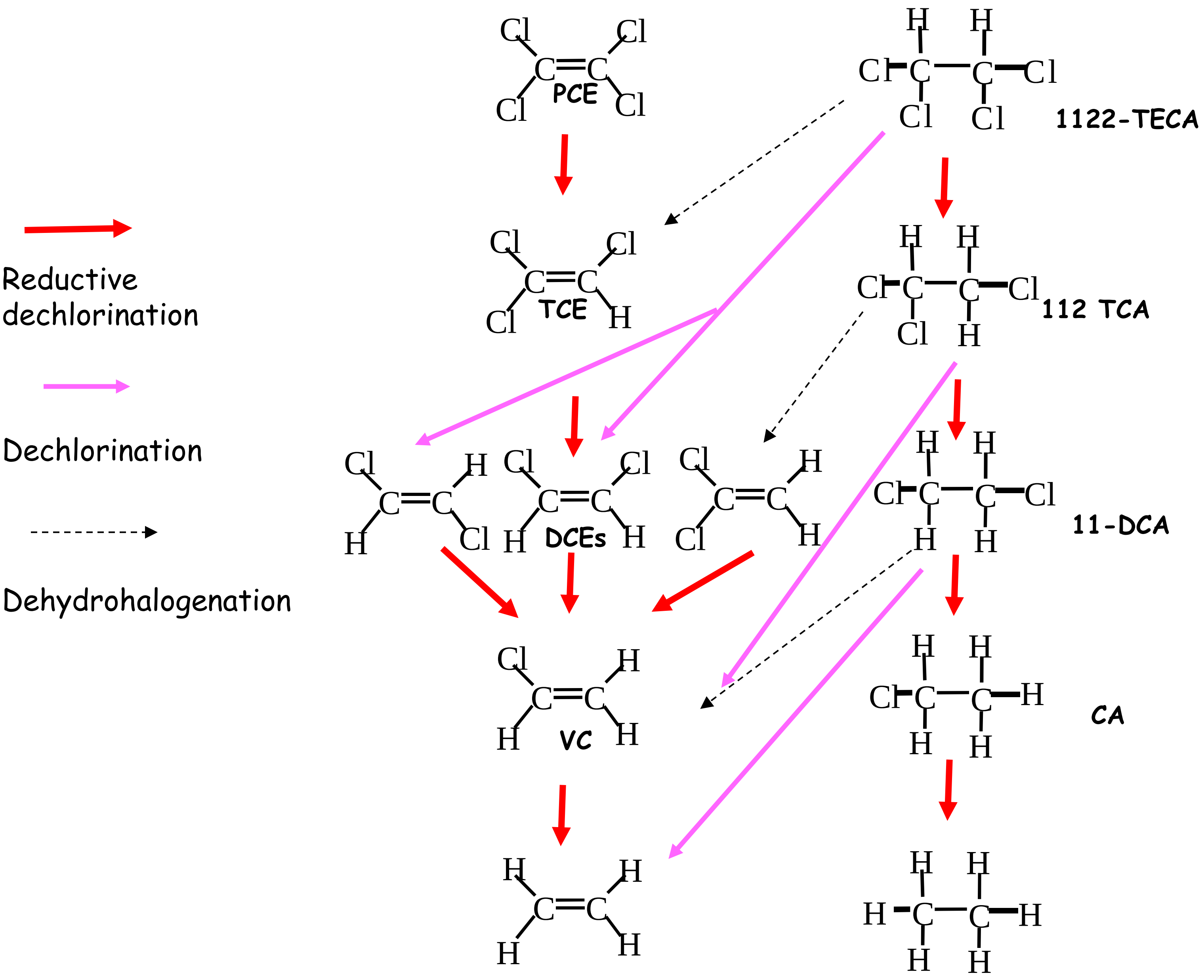
δ^{13}C Values for TCE from Several Manufacturers



Numerical key	Manufacturer	δ^{13}C	Off-line precision
1	Dow	−31.90	0.05
1A	Dow	−29.84	0.07
2	ICI	−31.32	0.03
3	PPG	−27.80	0.01
3A	PPG	−31.68	0.17
4	Aldrich	−33.49	0.08
5	Holt et al. (1997)	−27.18	0.1
6	A	−31.53	0.01
7	B	−27.90	0.08
8	C	−29.93	0.18

(Do not use isotopes to differentiate manufacturers)

Degradation of Chlorinated Solvents



Reductive dechlorination

Dechlorination

Dehydrohalogenation

Degradation of Chlorinated Solvents

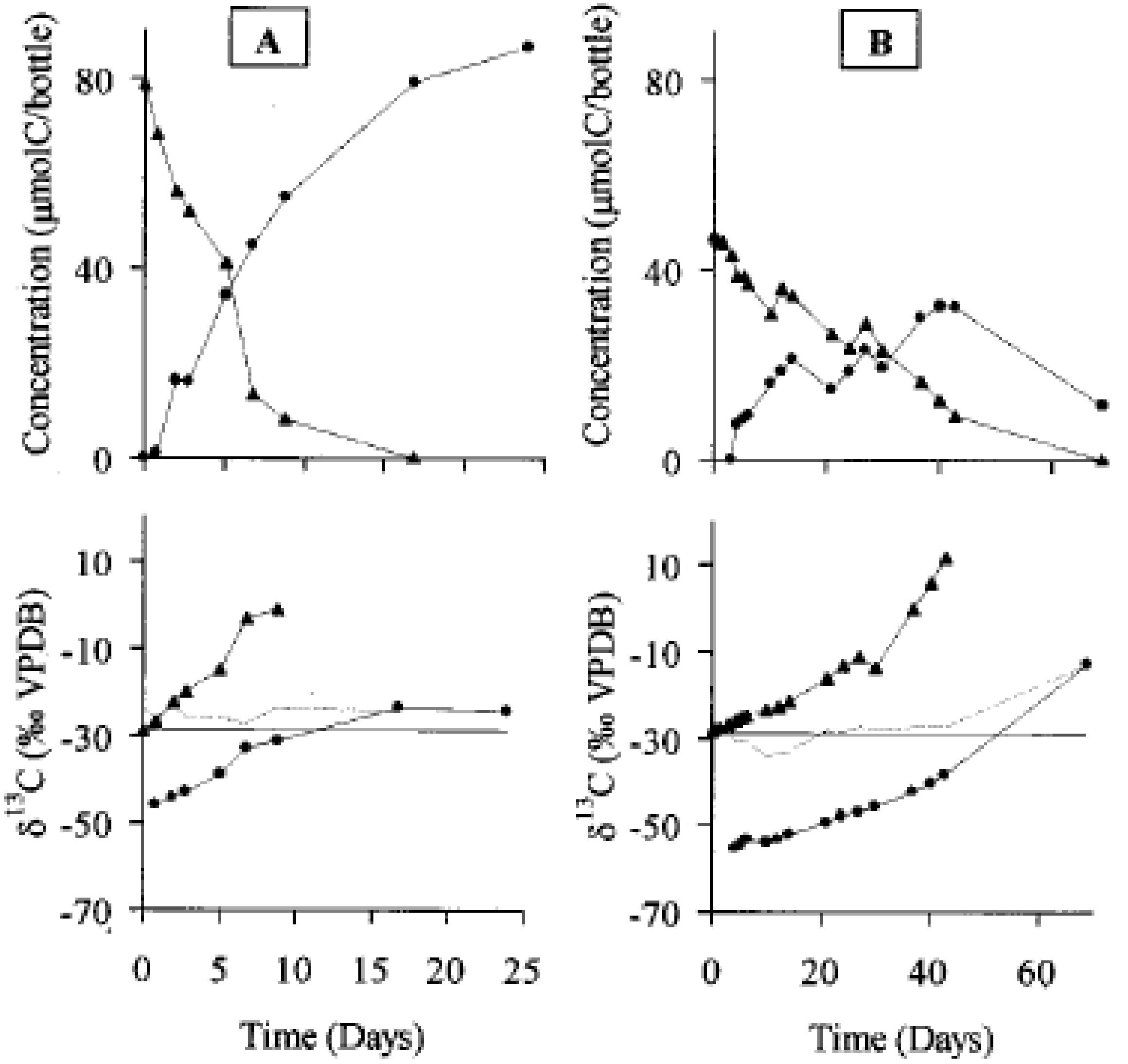
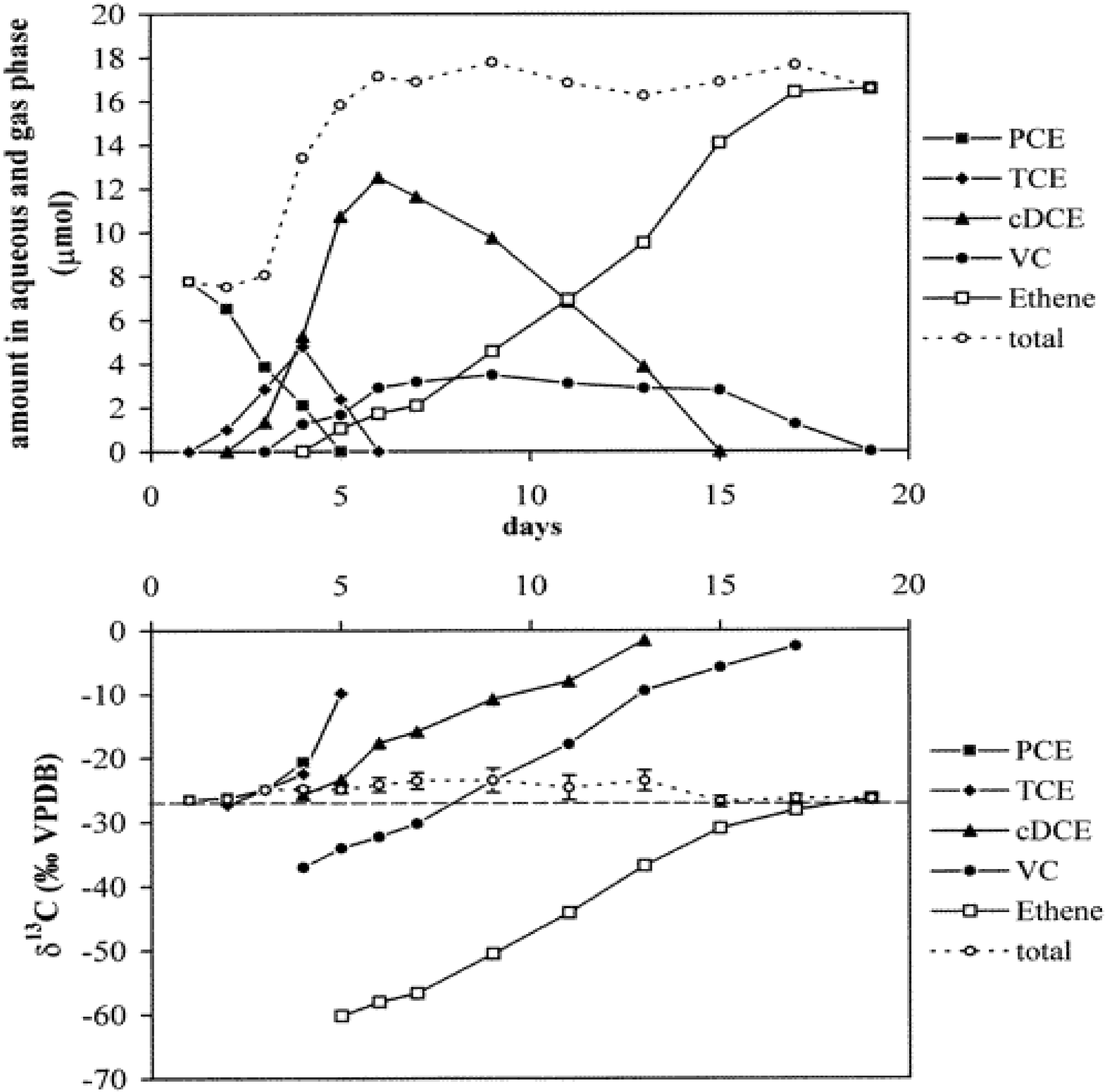


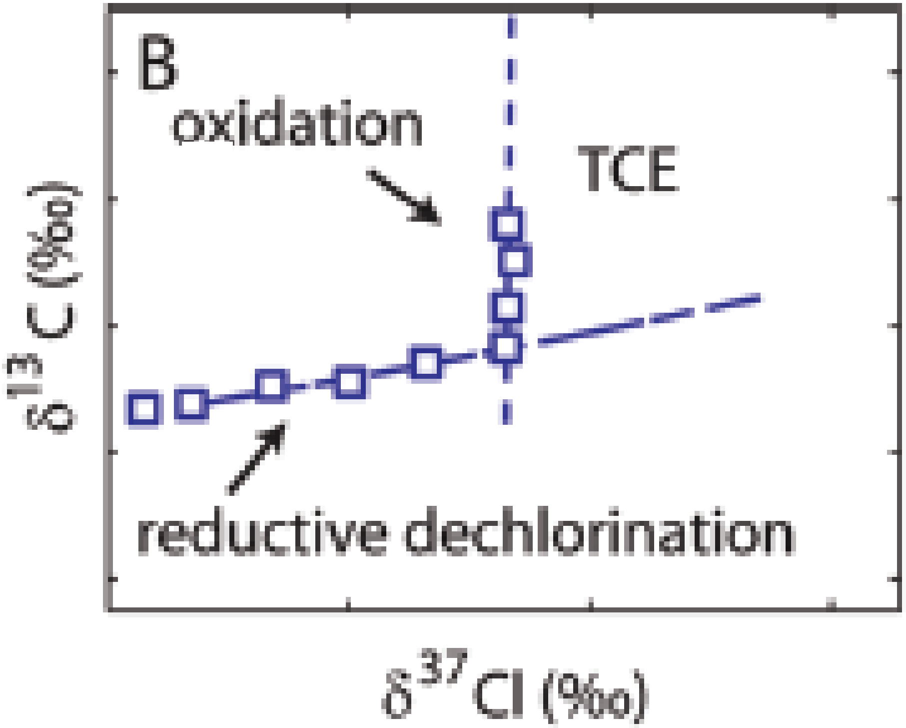
FIGURE 3. Concentration and stable carbon isotope data fo experiment A and B, VC culture (VC —▲—, ETH —●—, initial valu —, isotope balance ···).

Bloom et al., Environ. Sci. Technol., **34** (13), 2768 -2772, 2000.

Degradation of Chlorinated Solvents



Discrimination of Reaction Mechanisms by Isotope Effects



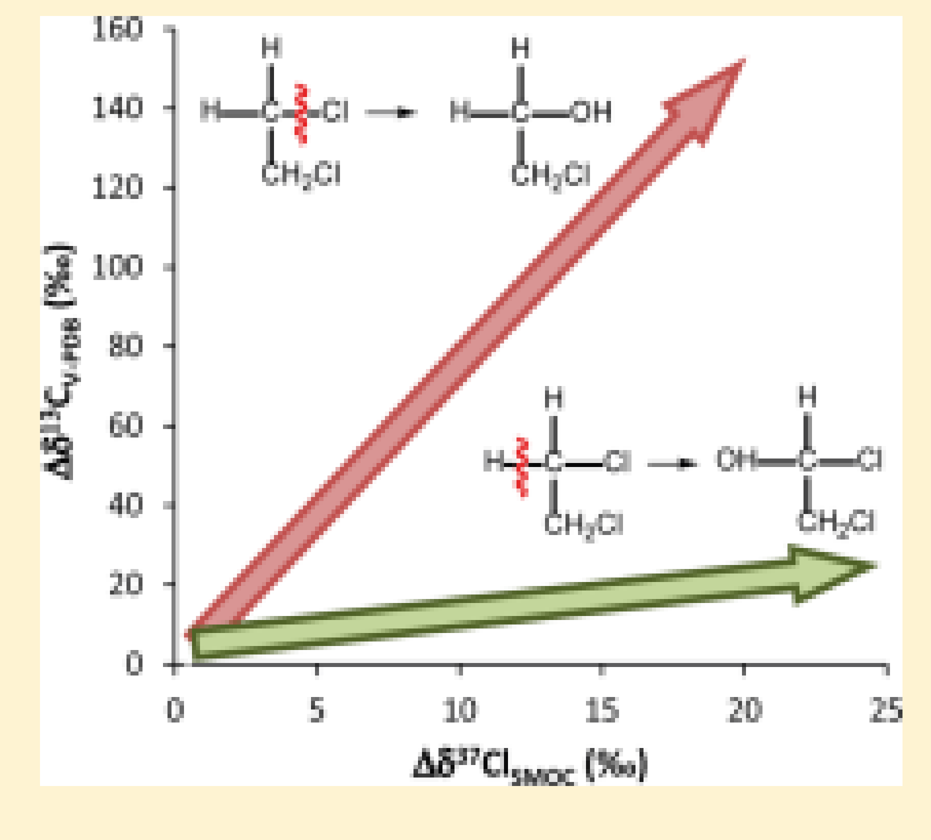
After Hunkeler et al., 2009

In different reaction types, the proportions between C, Cl and H isotope effects vary. These differences can be visualized by collecting data on 2 or 3 isotopes (e.g., C, H, and Cl).

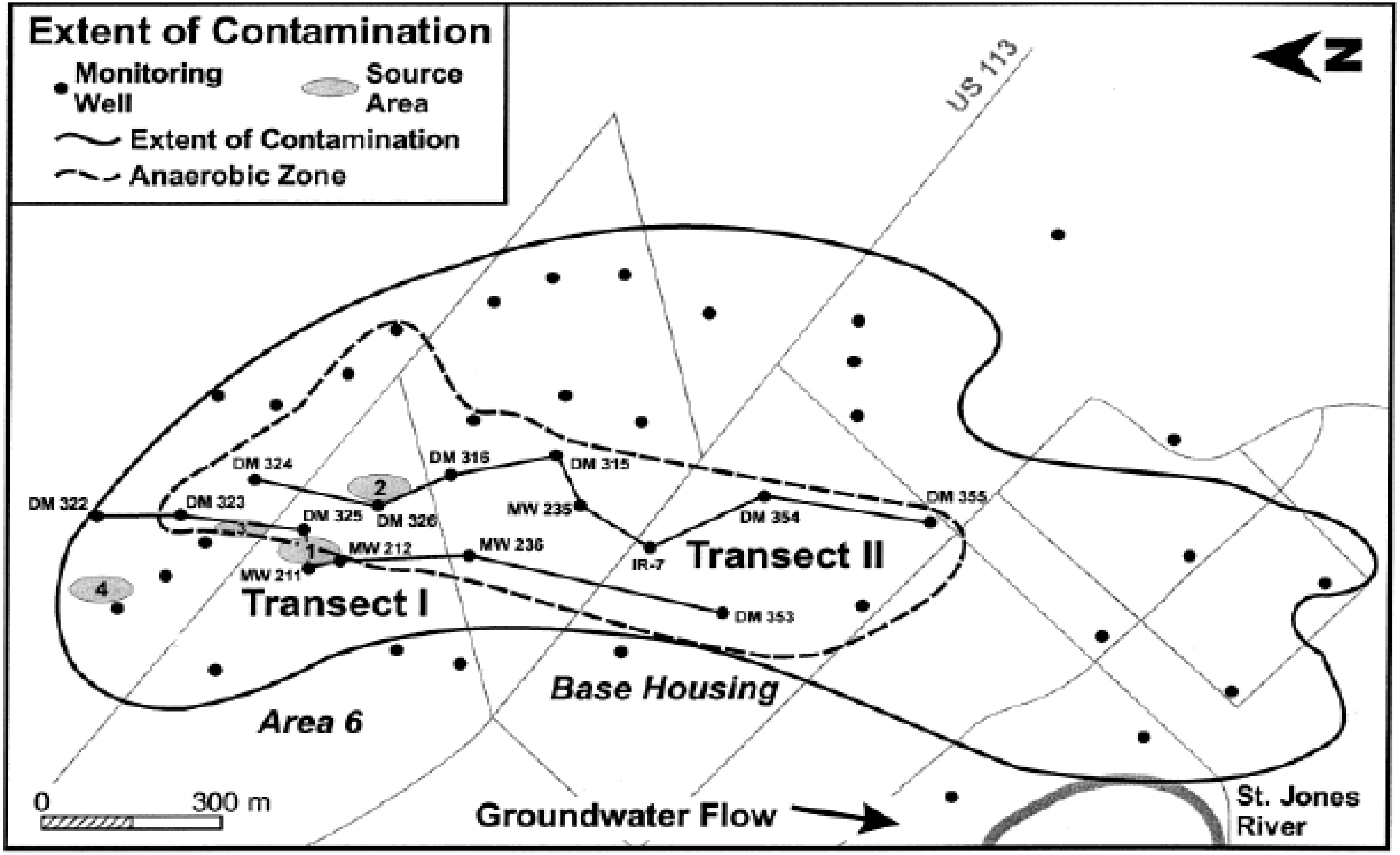
The same principles apply to biodegradation, chemical degradation and physical mass remediation.

Importance of Enrichment Factors

- Study by Palau et al., 2014 (Environ. Sci. Technol., 48, 9430-9437) showed two distinct pathways for degradation of 1,2-DCA.
- For oxidative cleavage of C-H the carbon enrichment factor was -3.5 whereas for the C-Cl cleavage the enrichment factor was around -32 per mil but Cl values were similar for both mechanisms.

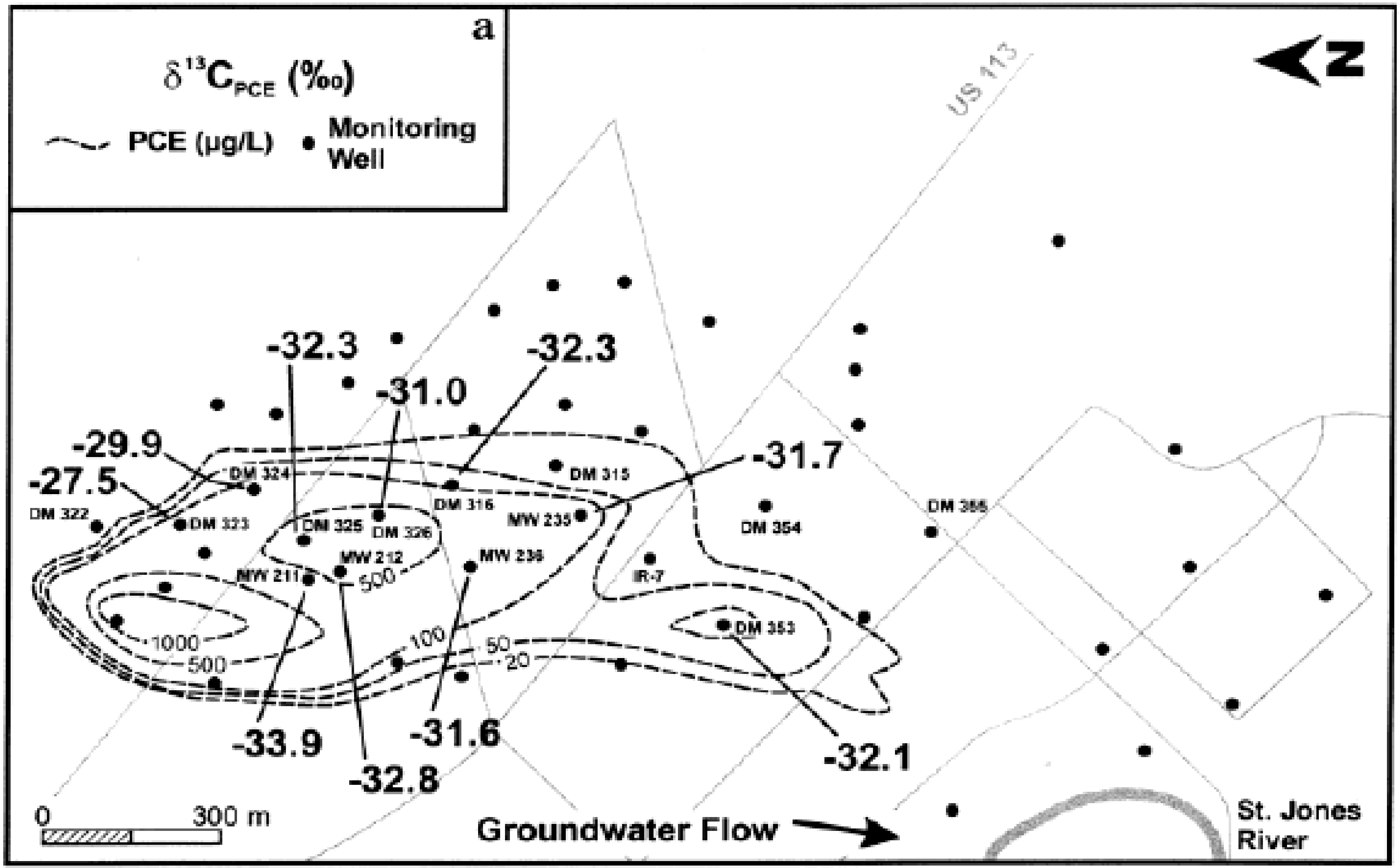


Reductive Dechlorination of PCEs

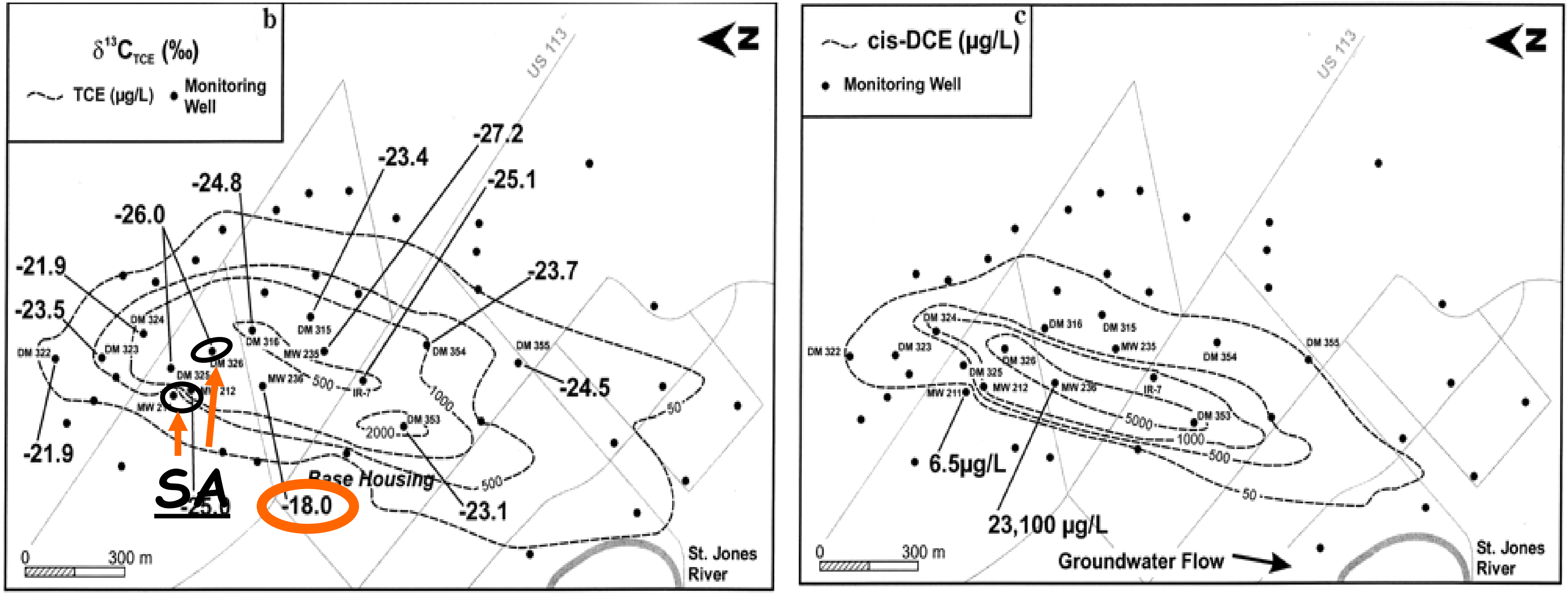


Sherwood Lollar et al., EST 2001,35,261-269-Dover AFB

Reductive Dechlorination of PCEs



Reductive Dechlorination of PCEs



PCE Degradation Site Study

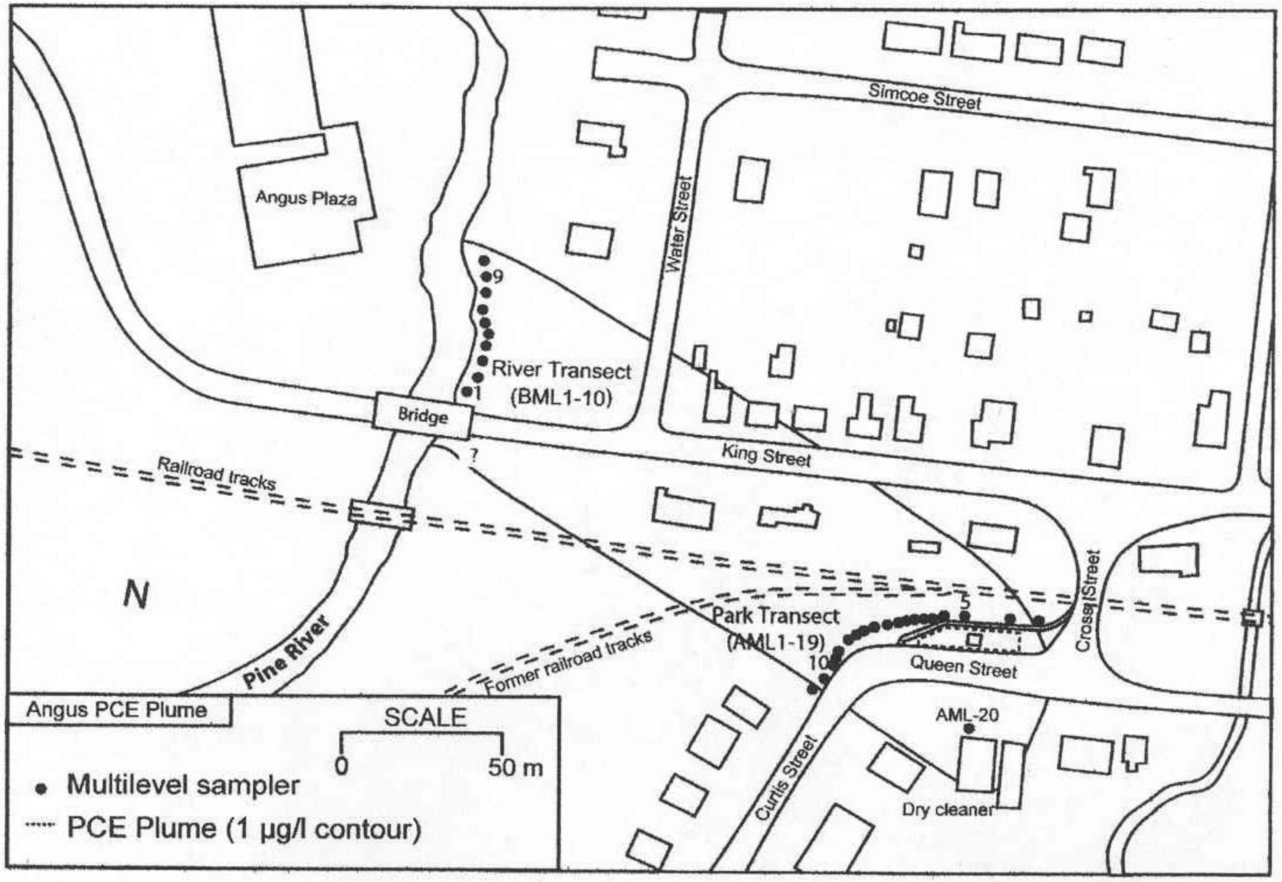
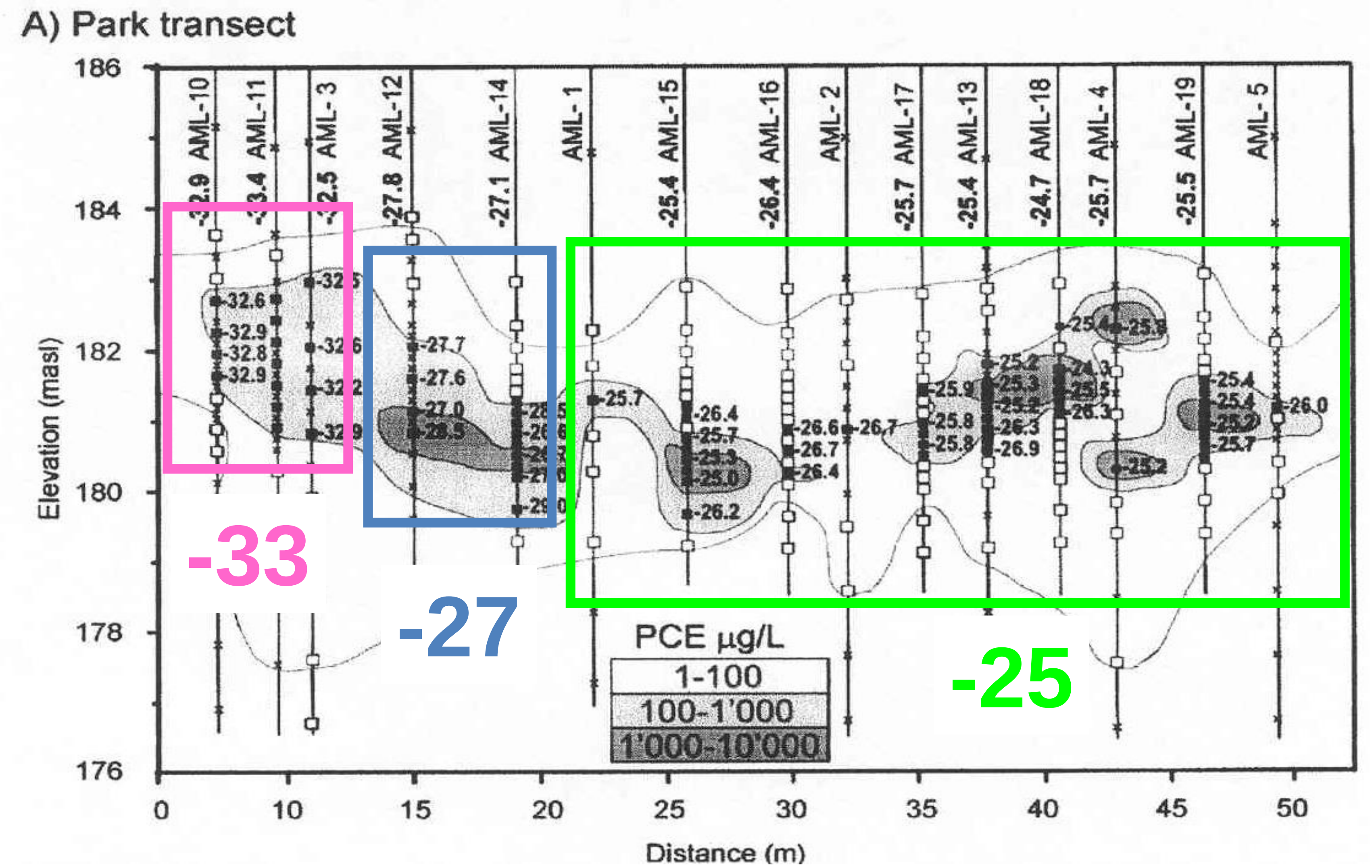


Fig. 2. Map of Angus field site with locations of multilevel samplers (circles) at park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

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

PCE Source Evaluation Study



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

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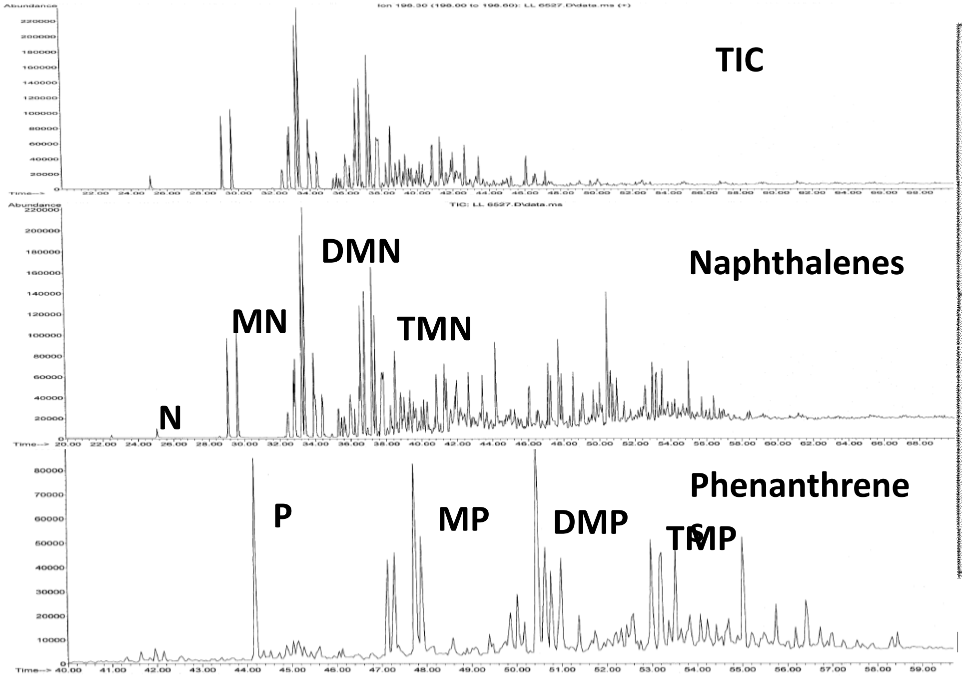
Sources of PAHs to Urban Background

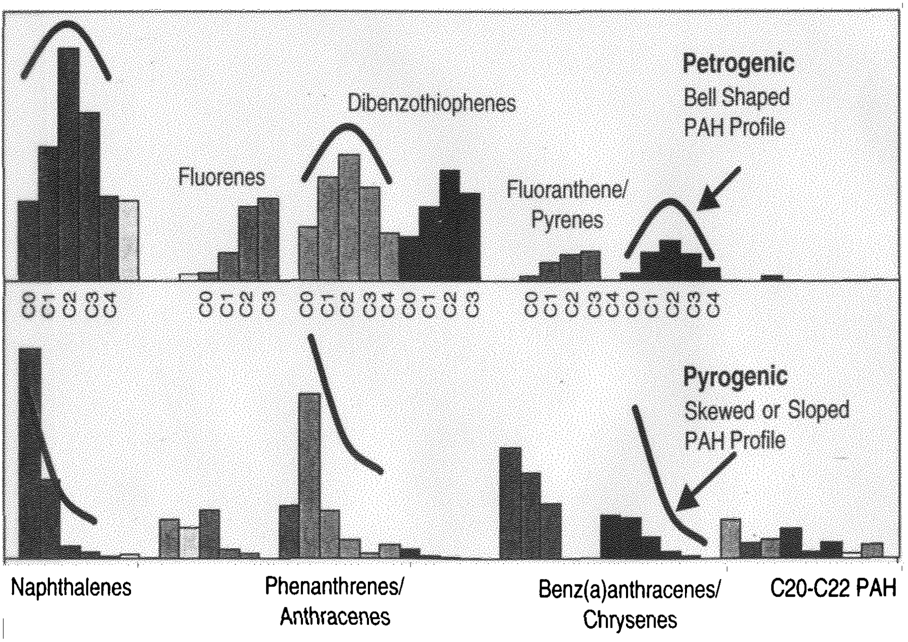
- **Natural background**
  - **Pre-existing and naturally produced**
- **Atmospheric fallout**
  - **Transportation, heating systems, power generation, industries**
- **Fill**
  - **Building materials**
  - **Debris, ash, trash**
- **Spills and sprays**

Are *the isotope ratios different for different sources? Can they be sorted out?*

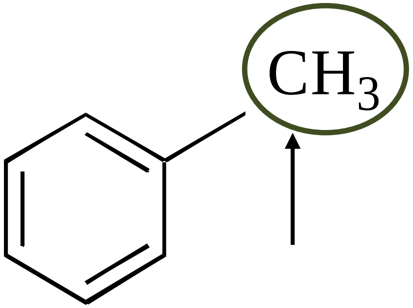
Coal Tar

PAH Distributions - Petrogenic or Pyrogenic?

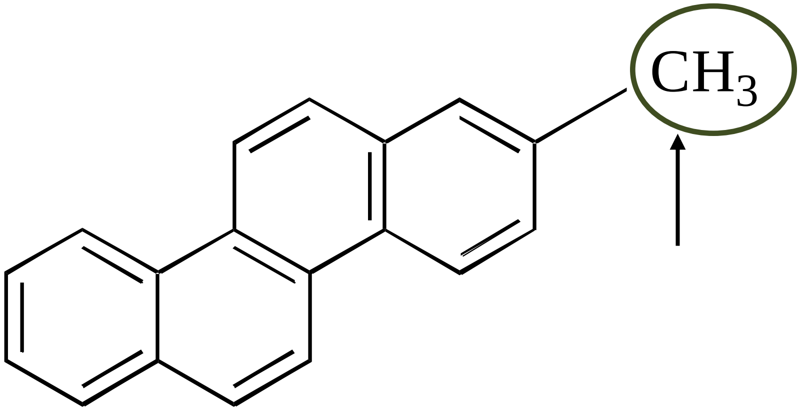




CSIRs of Coal Tar NAPL Samples



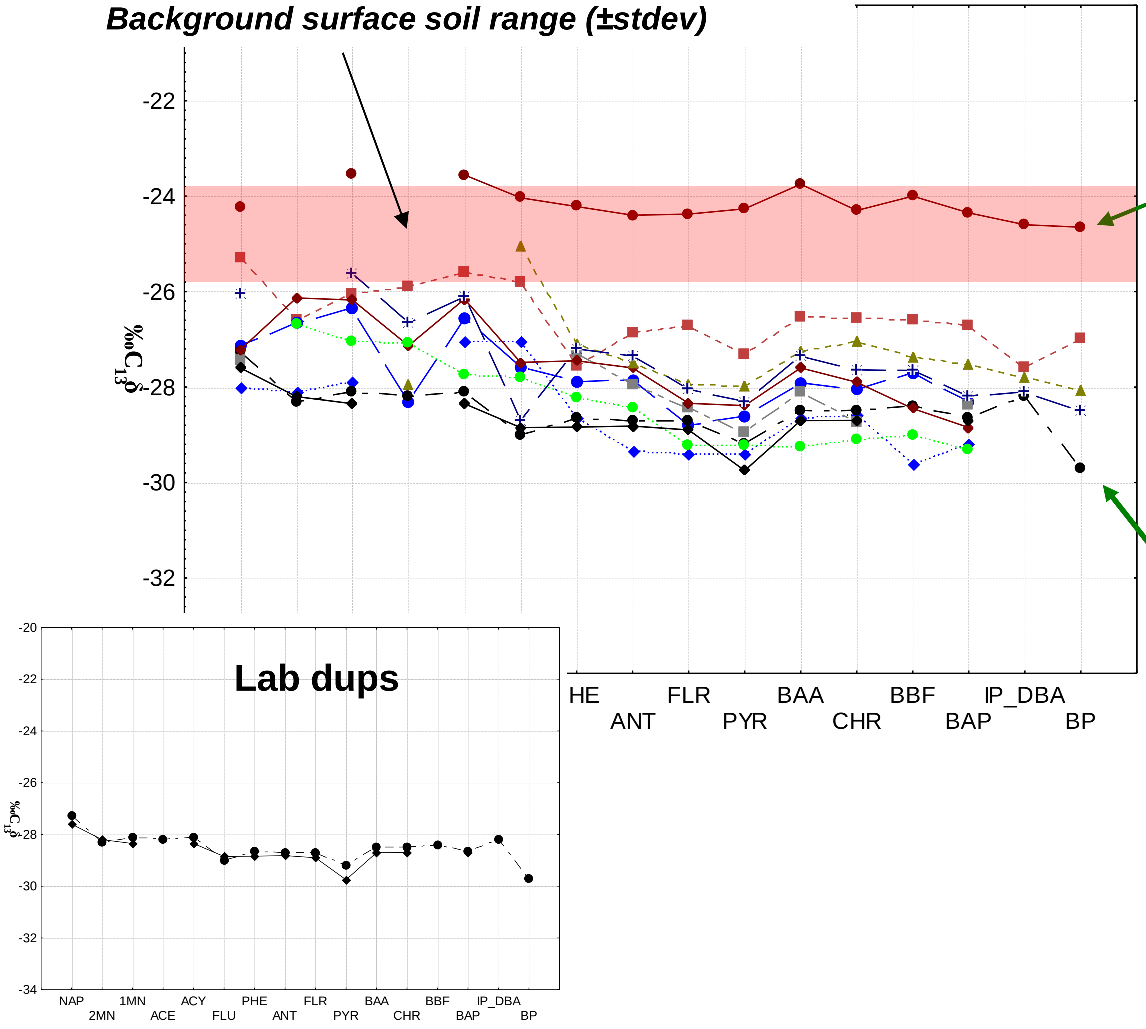
1:7

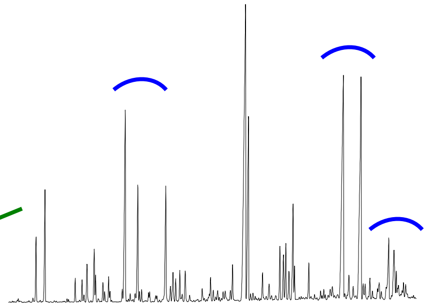


1:19

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

Combining CSIRs with GC/FID and PAH Ratios adds Confidence

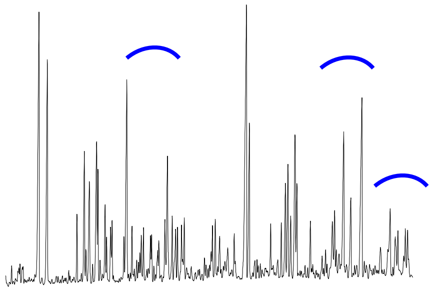




Fl/Py = 1.39

BF/MP = 1.29

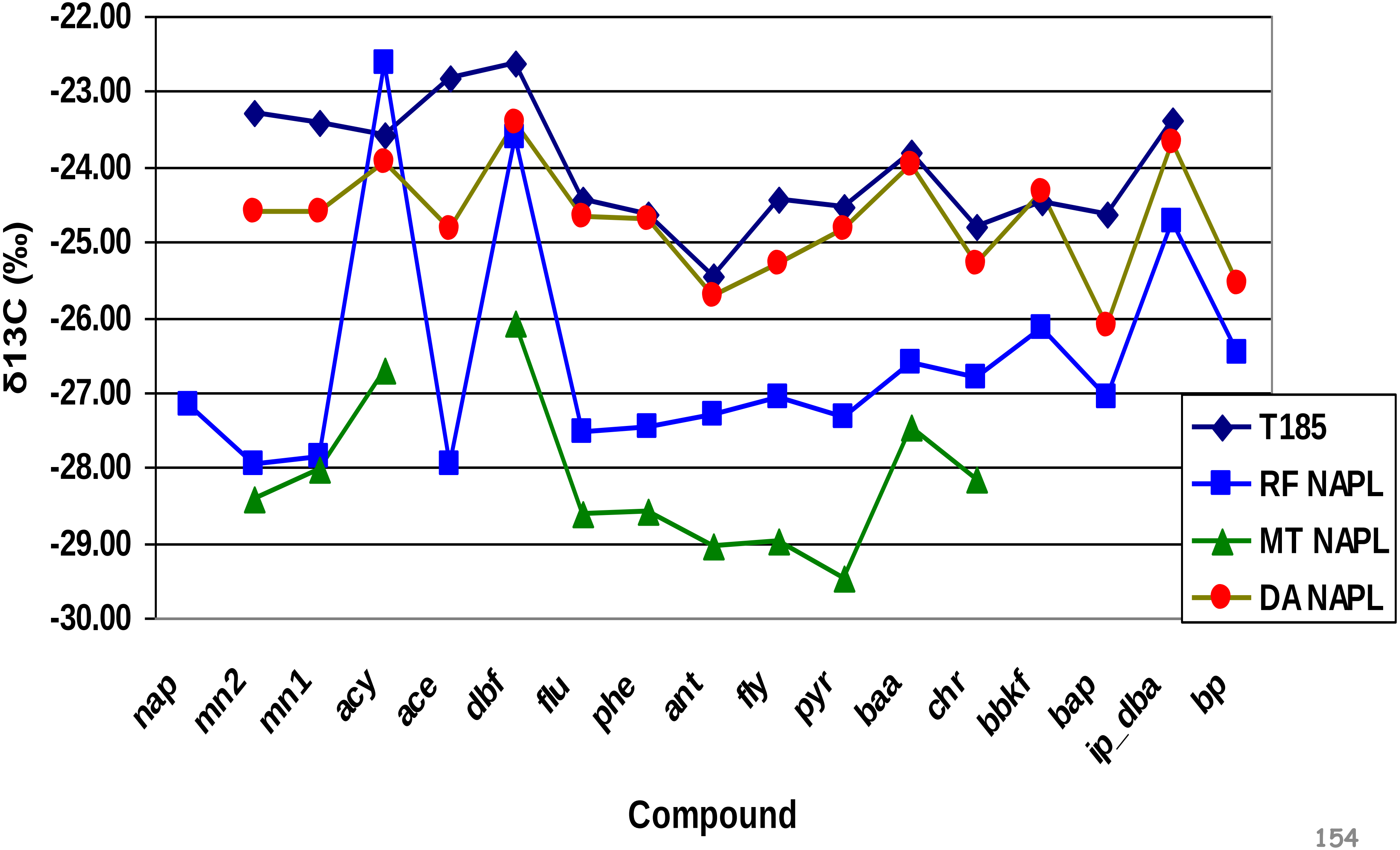
Combined GC/FID and CSIRs identify sediments contaminated from 2 or more coal tar sources



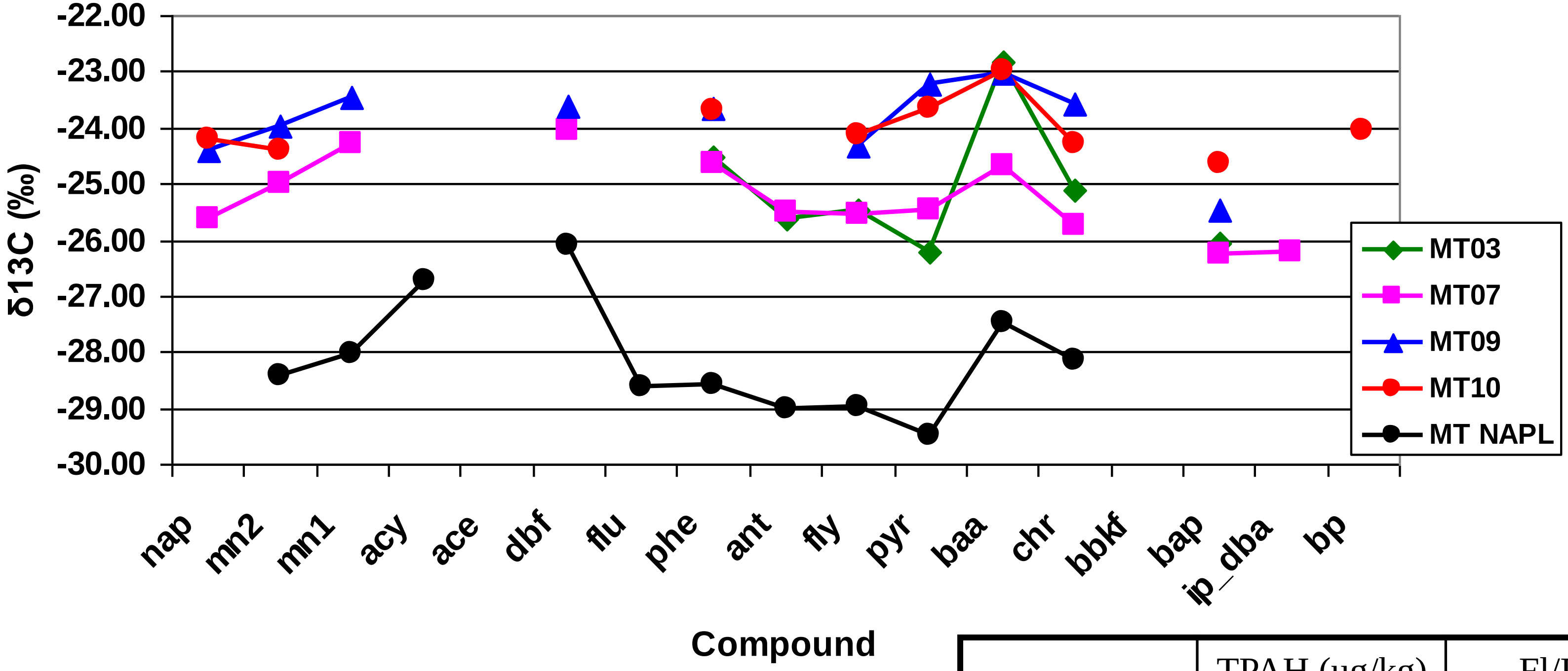
Fl/Py = 0.75

BF/MP = 0.41

CSIRs of Coal Tar NAPL Samples



PAH Fingerprints and Isotopes Show No MGP Contribution to Background



MT03, MT07, MT09, MT10 – background soil samples from town

MT NAPL – tar from MGP site in town

	TPAH (ug/kg)	Fl/Py
MT03	2,510	1.177
MT07	11,100	1.136
MT09	3,880	1.194
MT10	6,940	1.208
MT NAPL		0.64

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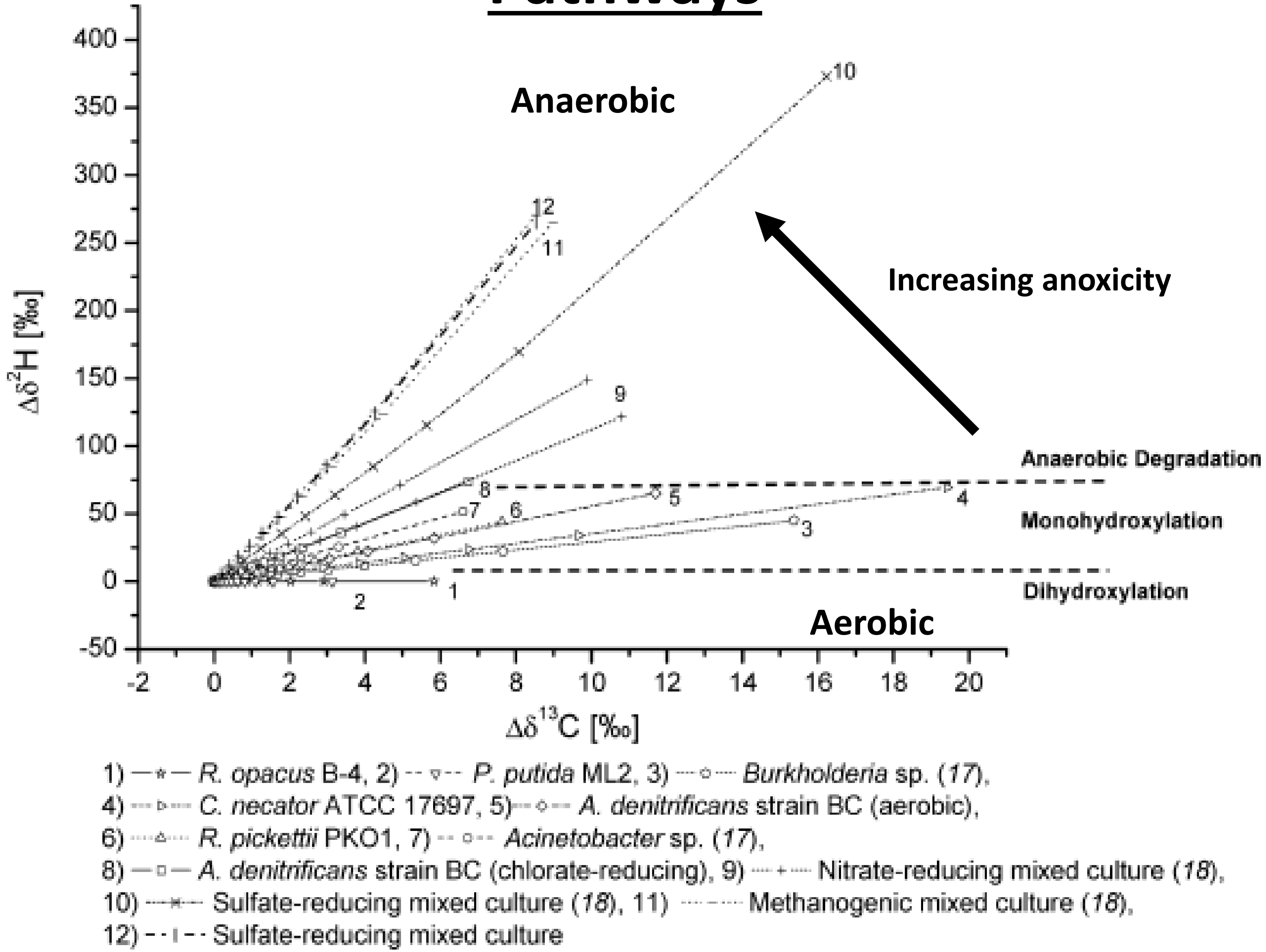
  - **Diesel, Gasoline, Motor oil**
  - **Groundwater contaminants**
  - **Chlorinated Solvents**
  - **PAHs**
  - **PCBs**
  - **Benzene**
  - **Other compounds**
  - **Chlorine, Bromine and Sulfur Isotopes**

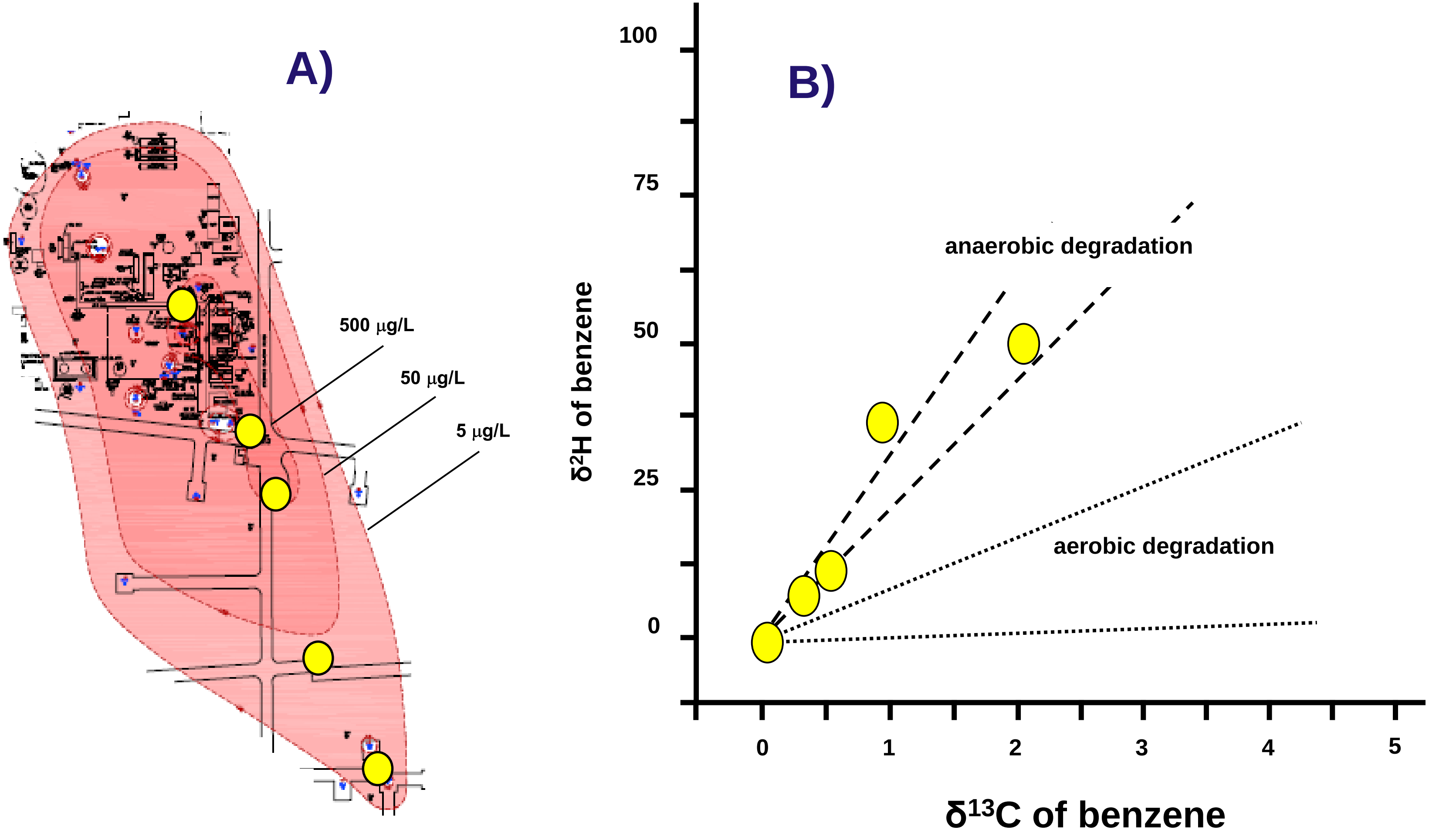
- **Vapor Intrusion Studies**
- **Summary**

2D-CSIA Discrimination of Benzene Degradation Pathways



1) —★— *R. opacus* B-4, 2) - - ▽ - - *P. putida* ML2, 3) ····○···· *Burkholderia* sp. (*17*),
4) ····▷···· *C. necator* ATCC 17697, 5)····◇···· *A. denitrificans* strain BC (aerobic),
6) ····△···· *R. pickettii* PKO1, 7) - - ○ - - *Acinetobacter* sp. (*17*),
8) —□— *A. denitrificans* strain BC (chlorate-reducing), 9) ····+···· Nitrate-reducing mixed culture (*18*),
10) ····×···· Sulfate-reducing mixed culture (*18*), 11) ····—···· Methanogenic mixed culture (*18*),
12) - · I - · Sulfate-reducing mixed culture

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).

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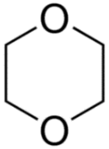
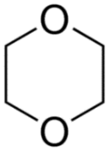


1,4-Dioxane



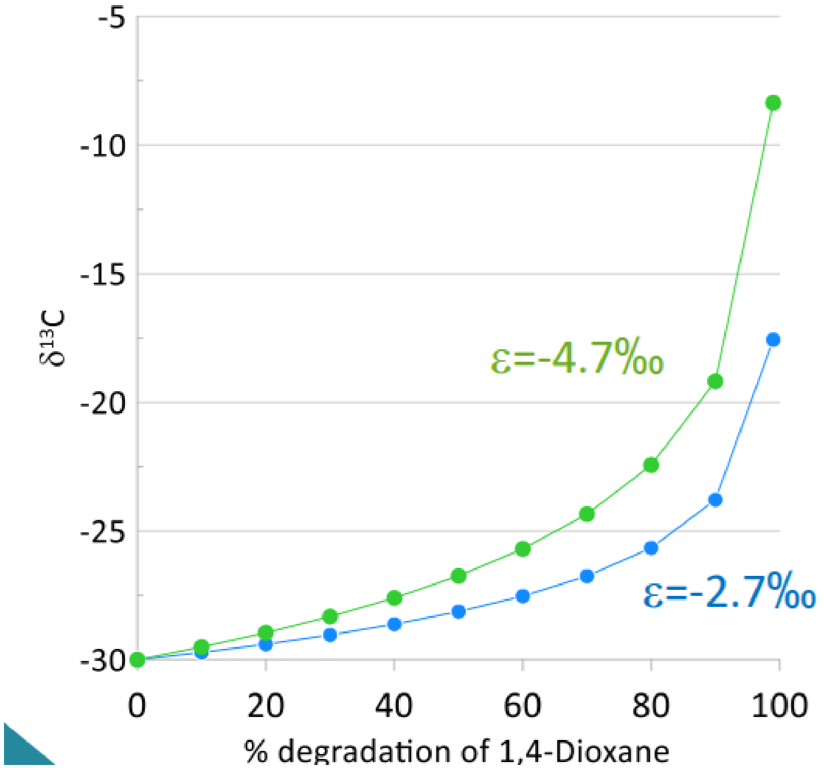
- 1,4-Dioxane used as a stabilizer for chlorinated solvents and an ingredient in personal care products and printer inks. Probable carcinogen.
- Highly water soluble, spreads more extensively than chlorinated solvents.
- Can be degraded in advance water treatment methods. Will degrade anaerobically (Pornwongthong et al., 2011); natural attenuation maybe a clean up method if time not a problem.
- Recent studies include:

  Chu and Bennett, 5th International on Bioremediation and Sustainable Environmental Technologies, Baltimore, MD, April 15-18, 2019.

  Ramalingam et al., Applied microbiology and biotechnology, 104, 4155-417, 2020.

1,4-Dioxane

Rayleigh equation used to estimate % 1,4-dioxane degradation



- Simplified form: $\delta^{13}C_t = \delta^{13}C_o + \varepsilon \ln f$
  - $\delta^{13}C_t$ = isotope ratio in sample at time t
    - this is what we measure in well samples
  - $\delta^{13}C_o$ = isotope ratio at time t=0
    - this is the isotope ratio before biodegradation begins (source term)
  - ε is the "enrichment factor"
    - Degradation reactions in laboratory
  - *f* is the "fraction remaining"
    - (1-*f*)x100 = %degradation
- % degradation can be calculated if $\delta^{13}C_o$, ε , and $\delta^{13}C_t$ are know

Chu and Bennett, 5th International on Bioremediation and Sustainable Environmental Technologies, Baltimore, MD, April 15-18, 2019.

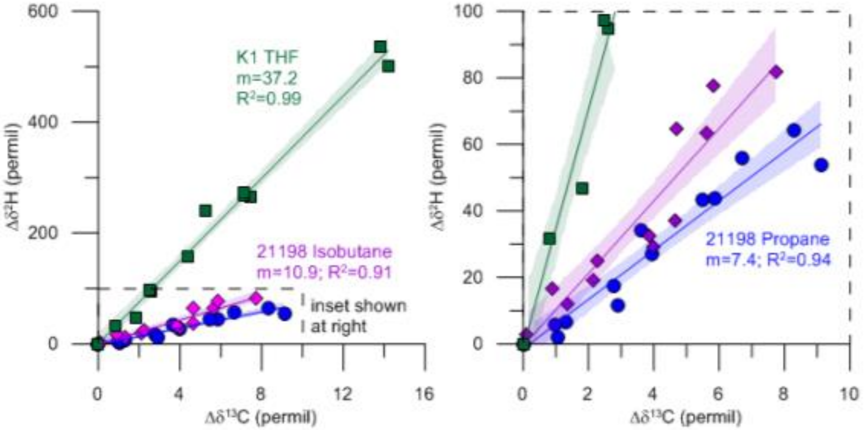
1,4-Dioxane

Enrichment trends from reactions with pure cultures

Enrichment factors (ε) are distinct for different reaction conditions:

strain	substrate	ε_C (‰)	ε_H (‰)
*Mycobacterium 1A**	propane	-2.0	-26
*R. rhodochrous** ATCC 21198*	propane	-2.7±0.3	-21±2
	isobutane	-2.5±0.3	-28±6
*P. tetrahydrofuran-oxidans K1***	THF	-4.7±0.9	-147±22

Dual-isotope plots show distinct slope for each reaction condition:



*Bennett, P. & Aravena, R. (2017). **Extending the application of compound-specific isotope analysis to low concentrations of 1,4-dioxane**. *SERDP ER-2535 Final Report.*

Bennett, P., Hyman, M., Smith, C., El Mugammar, H., Chu, M.-Y., Nickelsen, M., & Aravena, R. (2018). **Enrichment of carbon-13 and deuterium during monooxygenase-mediated biodegradation of 1,4-dioxane. *Environmental Science & Technology Letters*

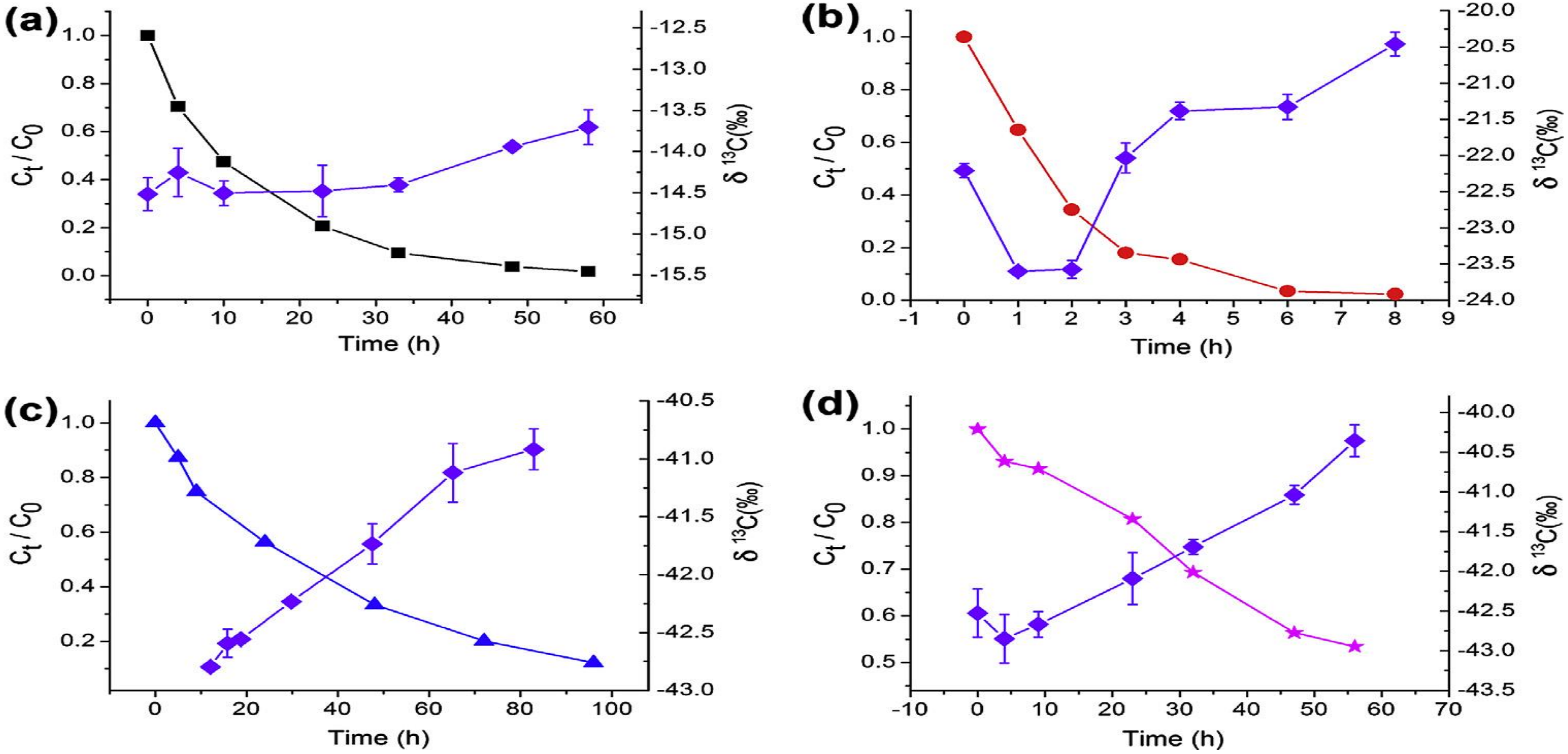
Chu and Bennett, 5th International on Bioremediation and Sustainable Environmental Technologies, Baltimore, MD, April 15-18, 2019.

Organophosphorous Pesticides

- Organic pesticides frequently detected in drinking water wells (Spliid and Køppen, 1998; Turner et al., 2006; Vorkamp et al., 2014) causing shutdown.
- Pesticides bypass wastewater treatment plants and enter natural aquatic systems risking aquatic life and human health (Schwarzenbach et al., 2010).
- Chiral compounds represent an important fraction of organic pesticides released in the environment as mixtures of two enantiomers
- Stereoisomers of one chiral compound often have different biological fate and toxic effects (Bollmann et al., 2014; Petrie et al., 2014).
- Detailed understanding of environmental distribution and degradation processes of chiral pesticides is essential for risk assessment and evaluating hazardous effects (Wong, 2006; Stenzel et al., 2013).
- Annual production of organophosphorus pesticides (OP pesticides) is more than 100,000 t in China-80% of worldwide pesticide production.

Biao Jin, Massimo Roll (2016). Joint interpretation of enantiomer and stable isotope fractionation for chiral pesticides degradation Water Research, 105, 178-186.

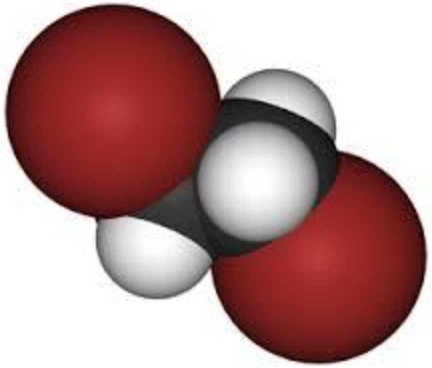
Organophosphorous Pesticides



Changes in concentrations (Ct/C0) and carbon isotope ratios (δ^{13}C) of OP pesticides during degradation. (a–c) Demonstrate the hydrolysis degradation of dichlorvos (j),omethoate (d) and dimethoate (N); (d) demonstrates the photolysis of dimethoate (H).

Langping Wua, Jun Yao, Polonca Trebse, Ning Zhang, Hans H. Richnow. Compound specific isotope analysis of organophosphorus pesticides. Chemosphere 111 (2014) 458–463

EDB as an Emerging Contaminant



1,2-Dibromoethane; ethylene dibromide; EDB

USEPA classification: probable human carcinogen; also, high toxicity

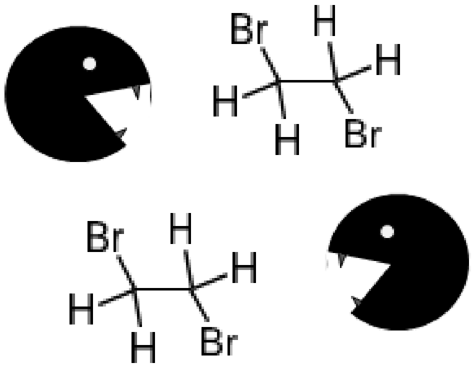
USEPA drinking water MCL: 50 ng/L (50 ppt)

Main source: spills of leaded gasolines (EDB was used as a lead scavenger compound); if sensitive methods were used, EDB was detected above MCL at about half of the older gasoline spill sites. Still present in certain aviation fuels.

NOTE: the MCL is significantly lower than the reporting limits of the standard GCMS methods (such as USEPA 8060); EDB can be easily missed in routine site assessment.

EDB Degradation

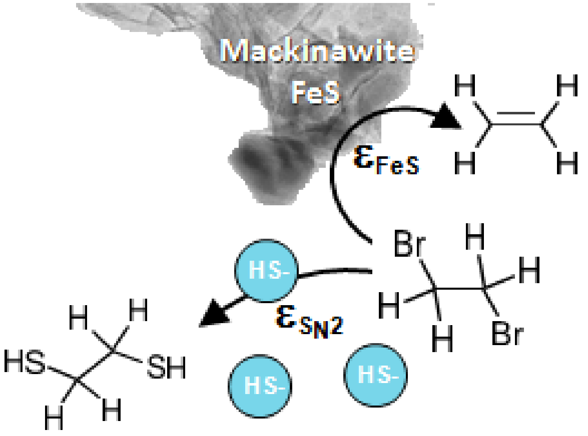
BIOTIC



Anaerobic degradation (reductive) to bromoethane, ethene and/or ethane

Aerobic/anaerobic hydrolysis (analogy with 1,2-DCA reactions)

Aerobic, cometabolic oxidation



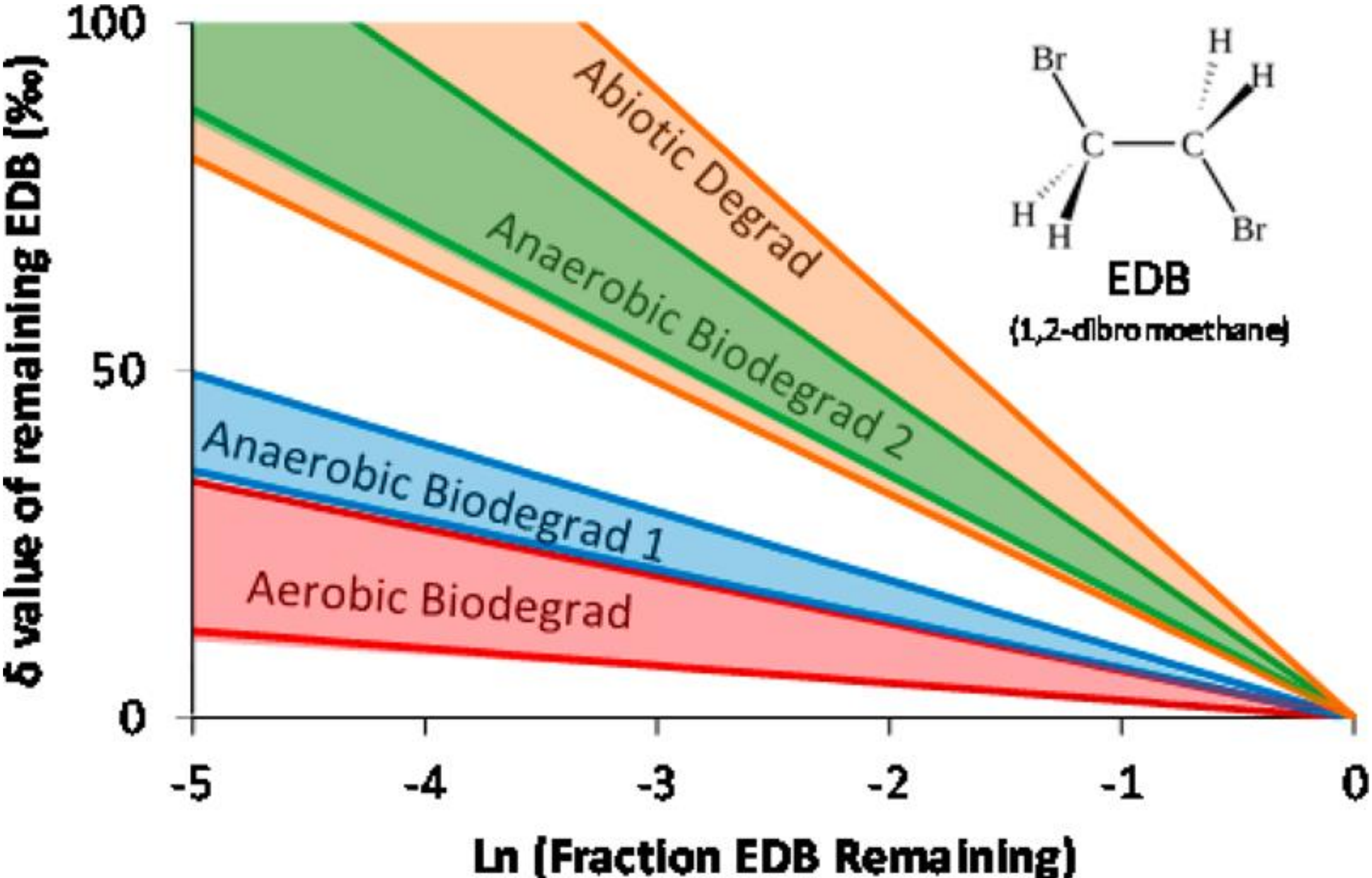
ABIOTIC

β-elimination by Fe(II) minerals and zero-valent metals to ethene

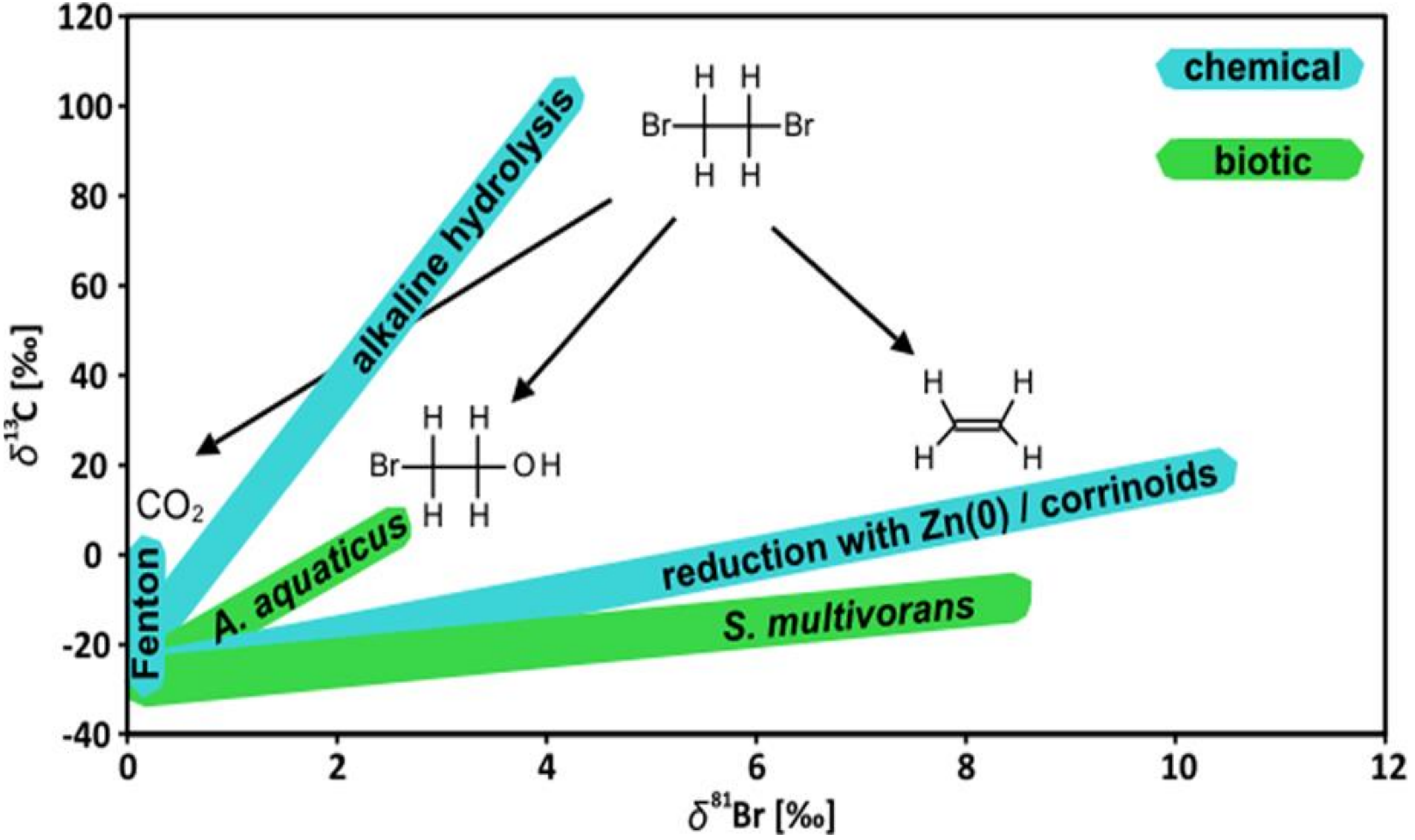
Reactions with sulfide nucleophiles

Hydrolysis (relatively slow)

EDB Degradation



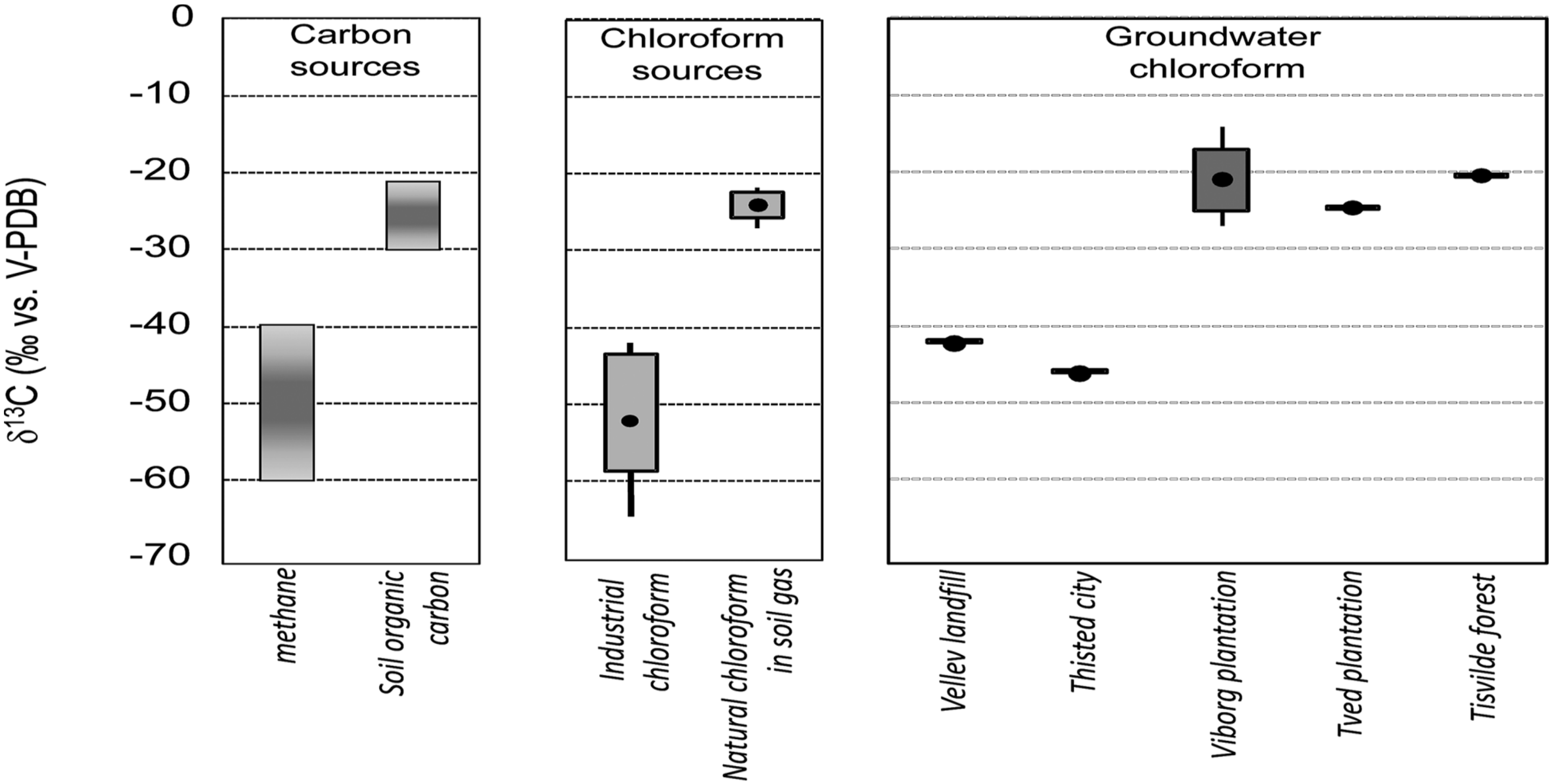
Br/C Isotopes-EDB Degradation



Chloroform

- Presence of chloroform with trihalomethanes (THMs), haloacetic acids (HAAs) and total organic halides (TOX) is evidence for chlorination of water containing natural organic matter from sewer and or water pipelines.
- Chlorination of humic acids may also produce chloroform.
- Termites may produce as much as 100,000 tons /yr and represent 15% of total global emissions.
- Chloroform produced by chlorination of methane is generally isotopically light (-43 to -64 per mil).
- Chloroform found beneath coniferous forests was found to be isotopically heavy (-13 to -27 per mil).

Chloroform



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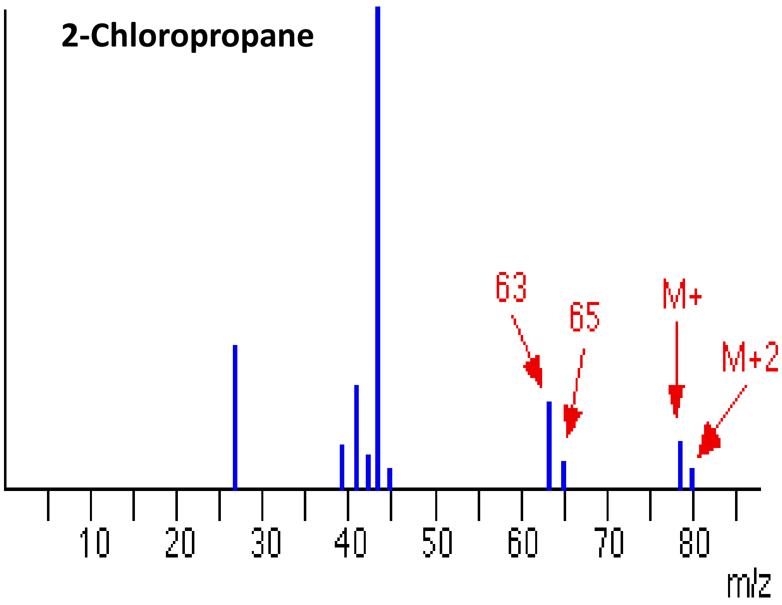
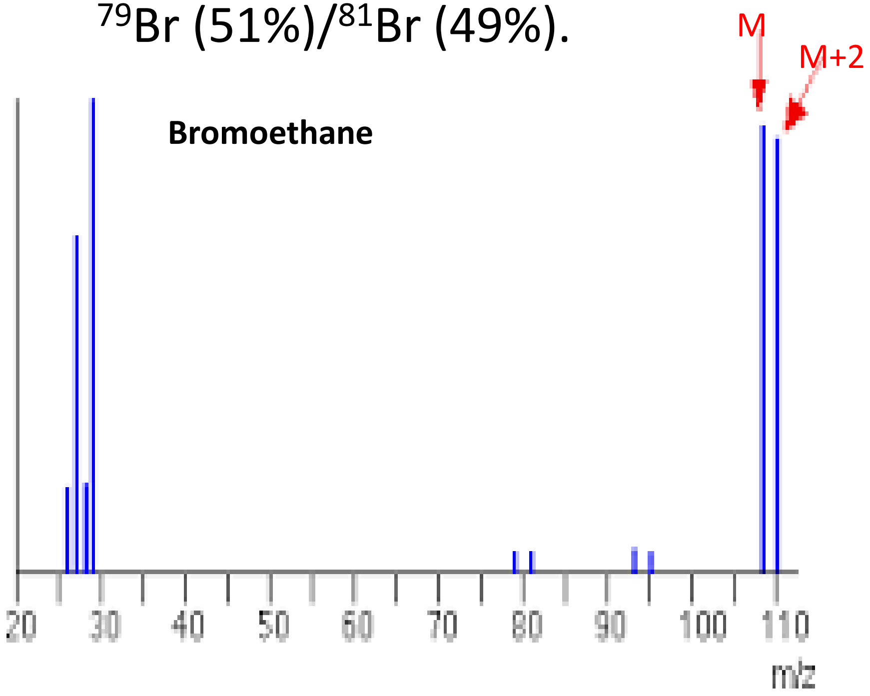
Chlorine and Bromine-containing Compounds

^{35}Cl (75.77%)/^{37}Cl (24.23%)

^{79}Br (51%)/^{81}Br (49%).



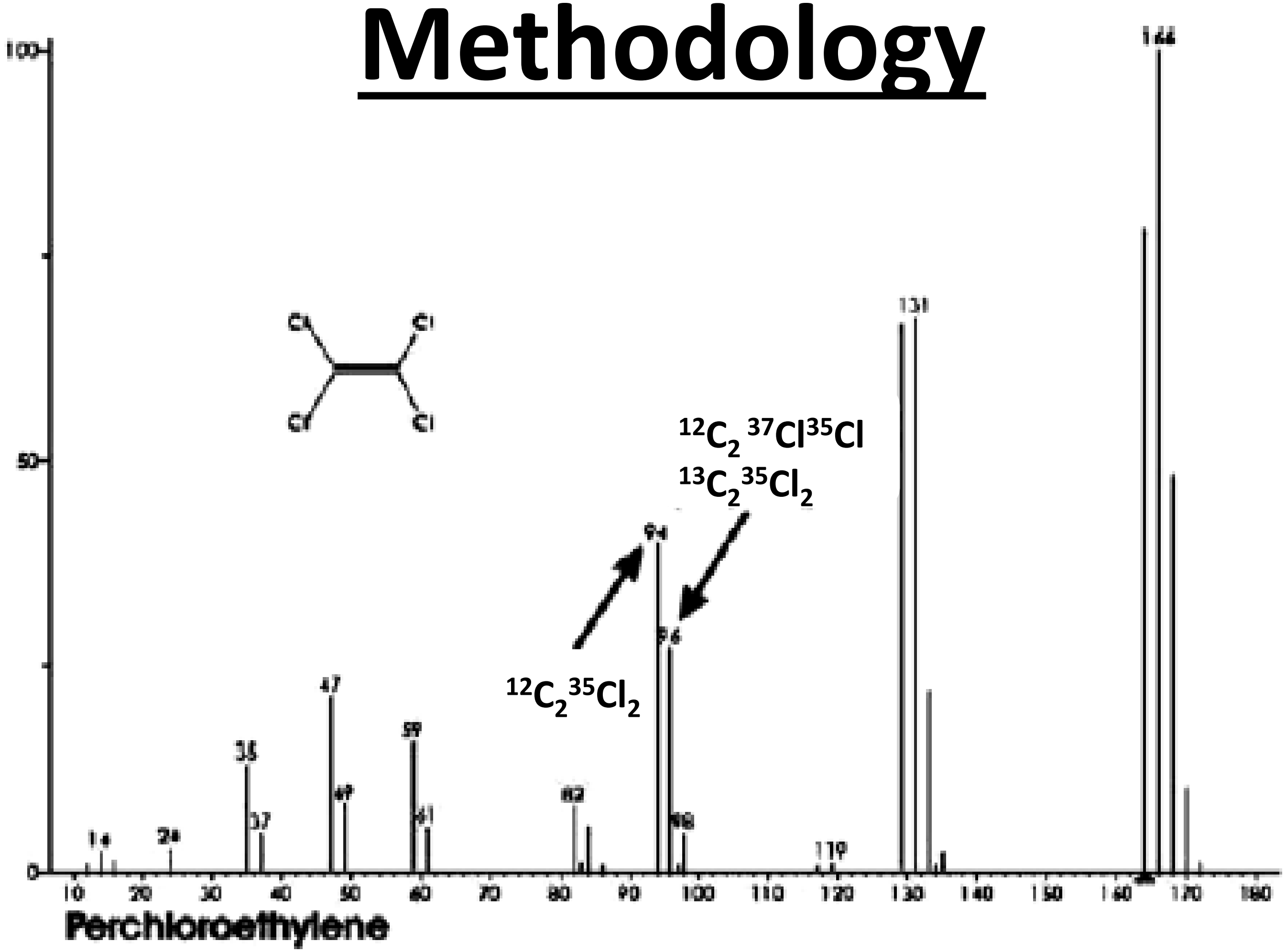


As with carbon and hydrogen the two problems that, potentially, can be investigated with chlorine are:

Source

Natural Attenuation

Methodology



$^{12}C_2\,^{37}Cl^{35}Cl$

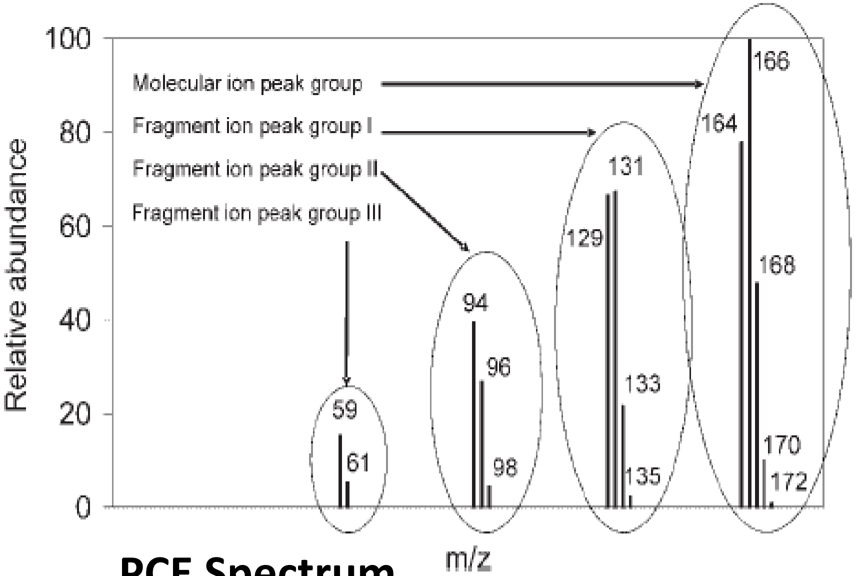
$^{13}C_2\,^{35}Cl_2$

$^{12}C_2\,^{35}Cl_2$

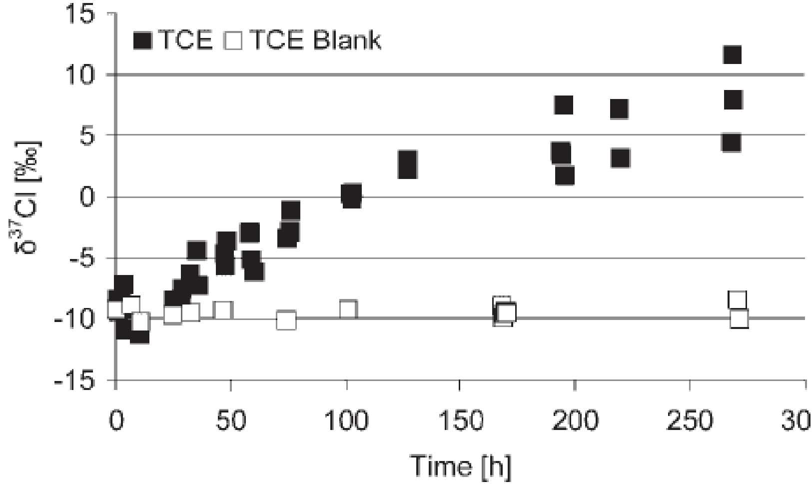
For Cl, a method was developed that utilizes regular GCMS and measures relative intensity of various fragment ions. These ions will vary depending on the specific compound being analysed. These values are then measured relative to standard samples whose Cl isotope ratios have been determined relative to the Cl standard –SMOW.

Shouakar-Stash et al., Applied Geochem. 21,766-781, (2006)

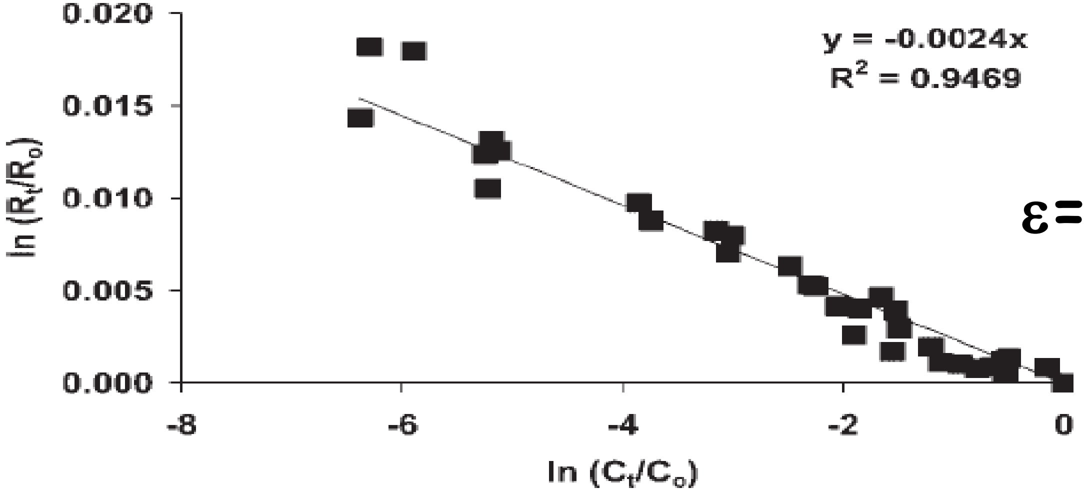
Chlorine CSIA: TCE Analysis



PCE Spectrum



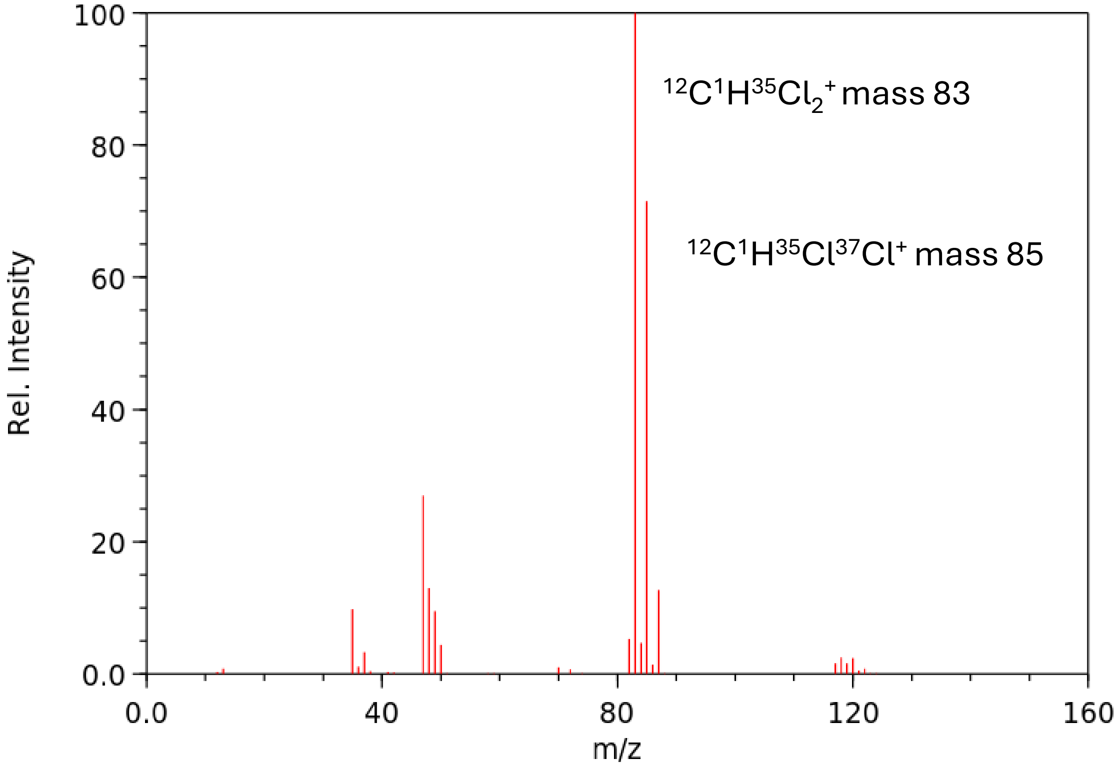
Abiotic Degradation of TCE



$\varepsilon = -2.4^{o}/_{oo}$

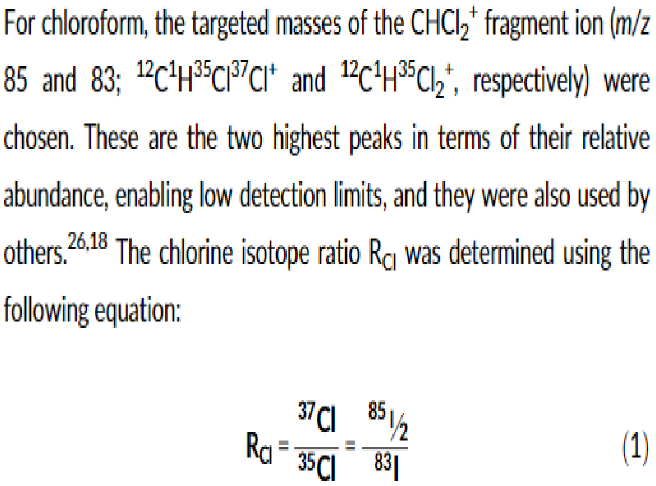
Chlorine Isotopes- Sakaguchi-Soder et al., 2007. Rapid Comm. Mass Spec., 21,3077.

Chloroform – Cl Determination



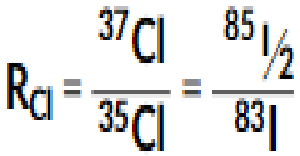
$^{12}C^{1}H^{35}Cl_2^{+}$ mass 83

$^{12}C^{1}H^{35}Cl^{37}Cl^{+}$ mass 85



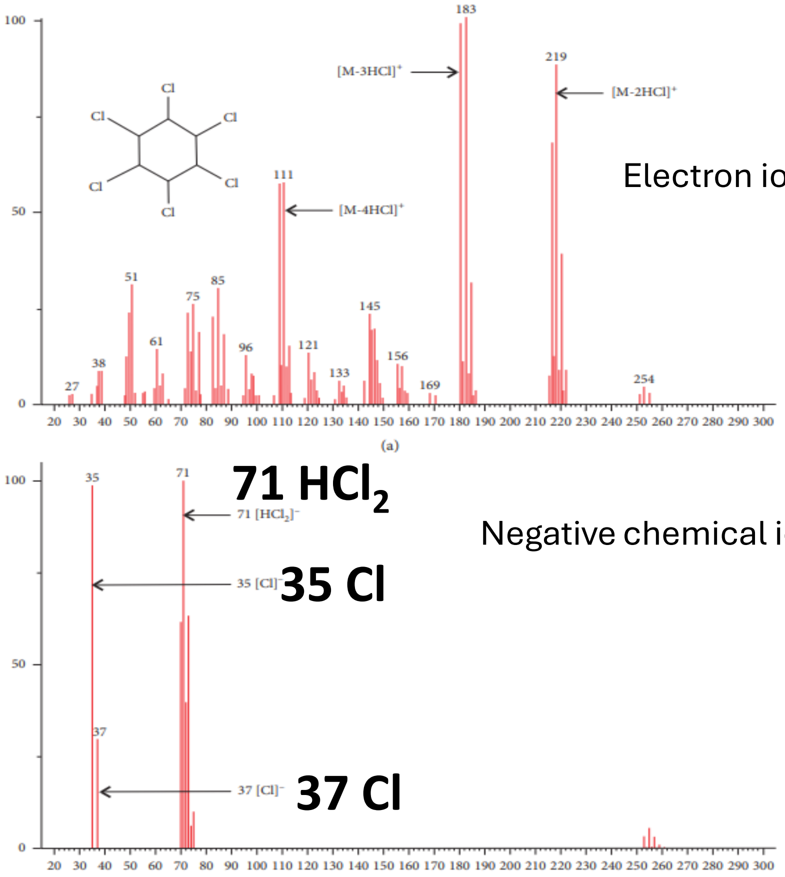
For chloroform, the targeted masses of the $CHCl_2^{+}$ fragment ion (*m/z* 85 and 83; $^{12}C^{1}H^{35}Cl^{37}Cl^{+}$ and $^{12}C^{1}H^{35}Cl_2^{+}$, respectively) were chosen. These are the two highest peaks in terms of their relative abundance, enabling low detection limits, and they were also used by others.[26,18] The chlorine isotope ratio R_{Cl} was determined using the following equation:

$$R_{Cl} = \frac{^{37}Cl}{^{35}Cl} = \frac{^{85}I/2}{^{83}I} \quad (1)$$



$$R_{Cl} = \frac{^{37}Cl}{^{35}Cl} = \frac{^{85}I/2}{^{83}I}$$

Chromatography-Negative Chemical Ionization Mass Spectrometry



Electron ionization

71 HCl_2

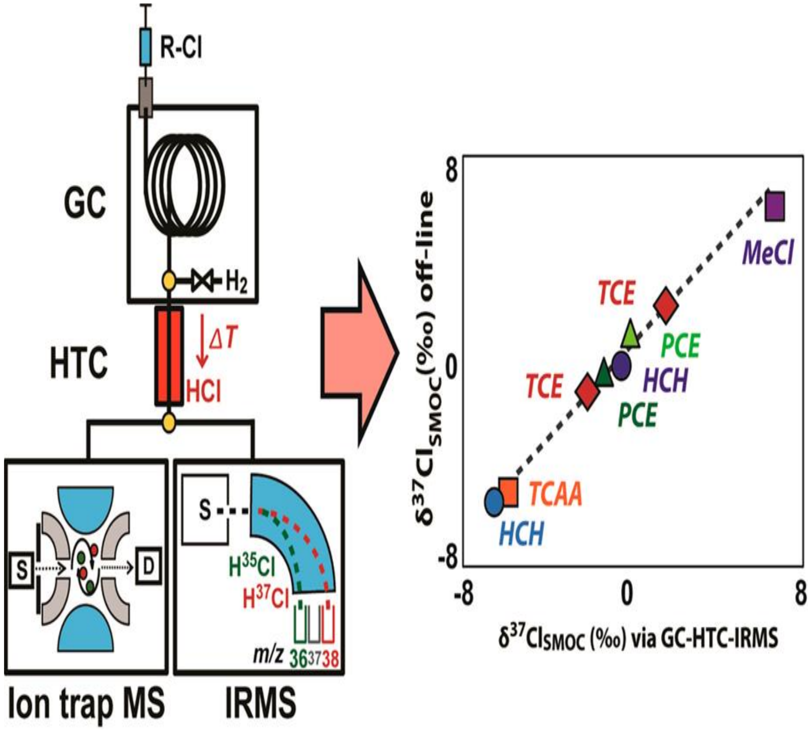
Negative chemical ionization

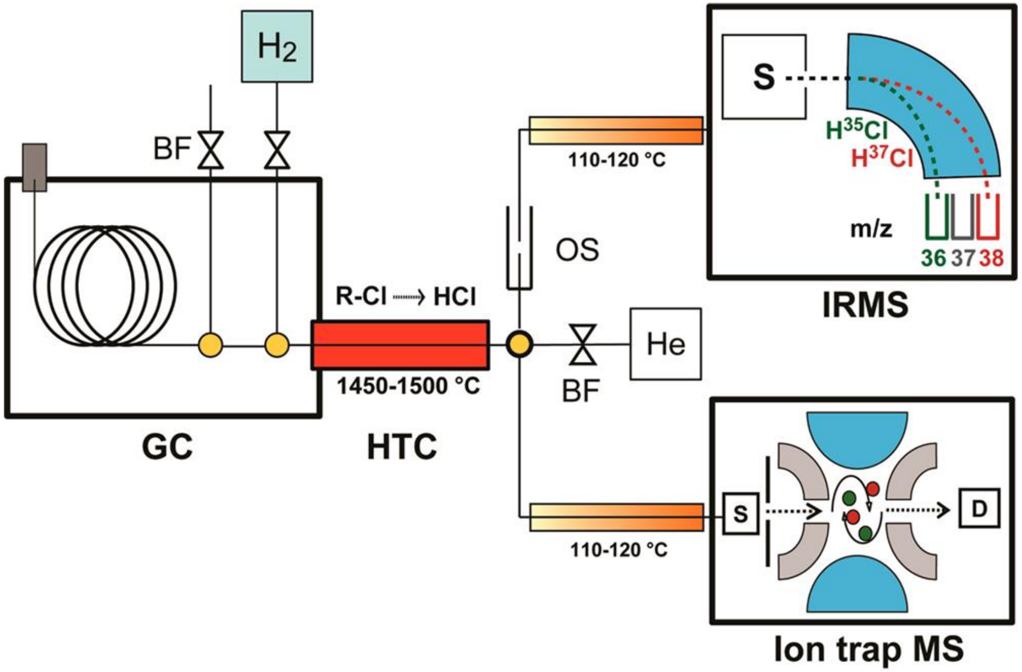
35 Cl

37 Cl

Compound-Specific Chlorine Isotope Analysis of Organochlorine Pesticides by Gas Chromatography-Negative Chemical Ionization Mass Spectrometry Jing Zhang Shenghua Liu , Jianye Gui, Xiaoya Li, and Guochen Qi . Hindawi Journal of Analytical Methods in Chemistry Volume 2021, Article ID 8874679, 10 pages

High Temperature Conversion of Cl-containing compounds to HCl.





$H^{35}Cl/H^{37}Cl$

The performance of chlorine isotope analysis was shown for chloromethanes, chloroethenes, chlorocyclohexanes, and chloroacetic acid methyl ester.

Julian Renpenning, Kristina L. Hitzfeld, Tetyana Gilevska, Ivonne Nijenhuis, Matthias Gehre,*and Hans-Hermann Richnow (2015). Development and Validation of an Universal Interface for Compound-Specific Stable Isotope Analysis of Chlorine ($_{37}$Cl/$_{35}$Cl) by GC-High-Temperature Conversion (HTC)-MS/IRMS. Anal. Chem. 87, 2832−2839

Other GCMS Methods for Cl Isotope Values using GCMS

$$\begin{aligned} R_{TCE} = {} & \frac{I_{130}}{I_{130} + I_{95} + I_{60}} \times \left(\frac{1}{3} \cdot \frac{I_{132}}{I_{130}}\right) \\ & + \frac{I_{95}}{I_{130} + I_{95} + I_{60}} \times \left(\frac{1}{2} \cdot \frac{I_{97}}{I_{95}}\right) \\ & + \frac{I_{60}}{I_{130} + I_{95} + I_{60}} \times \left(\frac{I_{62}}{I_{60}}\right) \\ = {} & \frac{1}{3} \cdot \frac{I_{132}}{I_{130} + I_{95} + I_{60}} + \frac{1}{2} \cdot \frac{I_{97}}{I_{130} + I_{95} + I_{60}} \\ & + \frac{I_{62}}{I_{130} + I_{95} + I_{60}} \end{aligned}$$

$$R_{\mathrm{TCE}} = \frac{1}{3} \cdot \frac{I_{132}}{I_{130}} = \frac{1}{2} \cdot \frac{I_{97}}{I_{95}} = \frac{I_{62}}{I_{60}}$$

$RCl={}^{37}Cl/{}^{35}Cl=85/_{I/2}83_{I}$

Raw values then converted to δ values.

Evaluating Chlorine Isotope Effects from Isotope Ratios and Mass Spectra of Polychlorinated Molecules Martin Elsner and Daniel Hunkeler*Anal. Chem.2008,80,4731–4740

Asfaw et al. (2020). Optimization of compound-specific chlorine stable isotope analysis of chloroform using the Taguchi design of experiments. Rapid Comm. Mass Spectrom. 34, 2020. https://doi.org/10.1002/rcm.8922

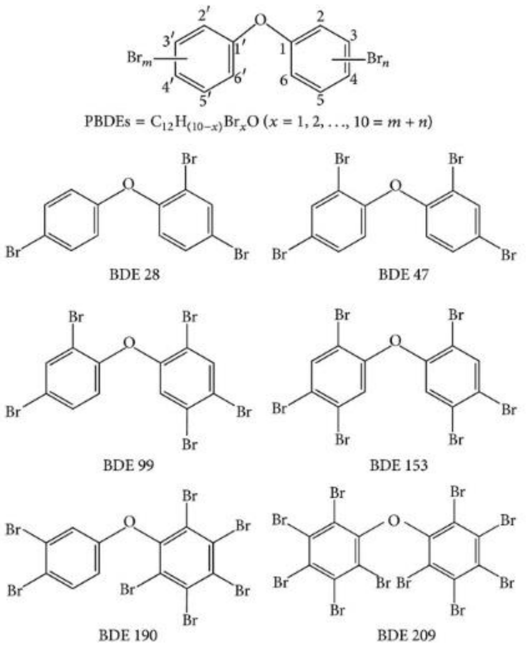
Bernstein et al., (2021). Compound-Specific Chlorine Isotope Analysis: A Comparison of Gas Chromatography/Isotope Ratio Mass Spectrometry and Chromatography/Quadrupole Mass Spectrometry Methods in an Interlaboratory Study . American Chemical Society. dx.doi.org/10.1021/ac200516c|Anal.Chem.2011, 83, 7624–7634

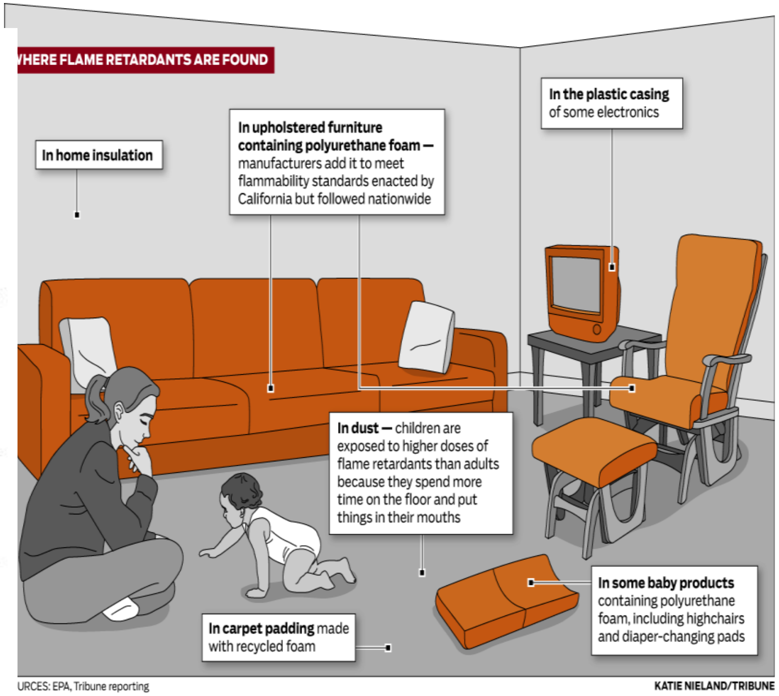
Environmental Forensics-Halogenated Compounds

- Brominated organic compounds (BOCs) have not yet received the same level of attention as their chlorinated counterparts in forensic studies.
- BOCs are widely used in many consumer products including pesticides, dyes and flame retardant additives.
- Bromine has two stable isotopes ^{81}Br and ^{79}Br. Initial attempts to determine δ^{81}Br values used ICPMS. Since relatively few laboratories working in the environmental field have access to ICP MS relatively few investigations have occurred to date.
- More recently a GCMS method, like the method successfully used for Cl isotope analyses has also been developed for Br isotope determination.
- Precisions in the range 0.2-0.3 per mil are possible via the GCMS method.
- Note there are analogous naturally occurring polycyclic brominated compounds in marine organisms. It is now possible to differentiate these naturally compounds using ^{14}C CSIA. (Expensive and not readily available).

(Gelman et al., (2016) Compound specific bromine isotope ratio analysis using gas chromatography-quadrupole mass spectrometry. Rapid Comm. in Mass Spectrometry, RCM-16-0055.R1).

Polybrominated Diphenyl Ethers (PBDEs)




HERE FLAME RETARDANTS ARE FOUND

In home insulation

In upholstered furniture containing polyurethane foam — manufacturers add it to meet flammability standards enacted by California but followed nationwide

In the plastic casing of some electronics

In dust — children are exposed to higher doses of flame retardants than adults because they spend more time on the floor and put things in their mouths

In some baby products containing polyurethane foam, including highchairs and diaper-changing pads

In carpet padding made with recycled foam

URCES: EPA, Tribune reporting

KATIE NIELAND/TRIBUNE

Wide range of isomers used as fire retardants; also produced during incineration and other process.

Can be converted into more toxic compounds during degradation.

Degrade faster than chlorinated equivalents.

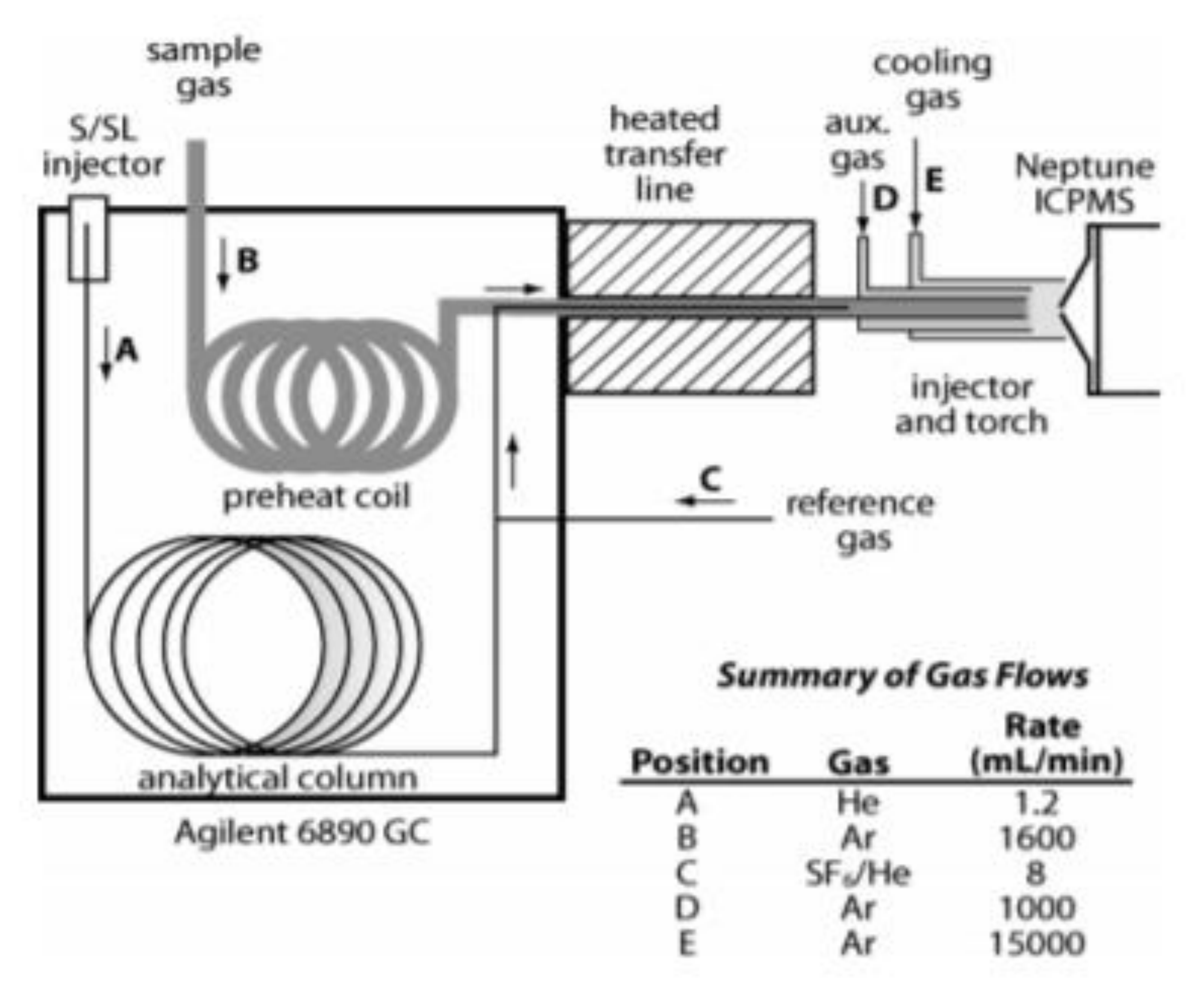
Compounds of similar Structures occur in marine sources.

S Isotopes

Environmental Forensics-Halogenated Compounds

- Inductively coupled plasma (ICP) generally used for determining isotopic compositions of metals but more recently starting to be used for C, S, N, Cl and Br isotope determinations.
- Multicollector inductively coupled plasma (ICP) mass spectrometers consist of sample inlet (GC or LC); inductively coupled argon plasma for vaporization, atomizing and ionization; interface separating plasma from mass analyzer; mass analyser with multicollector array.
- Measurement of S isotopes in this manner requires conversion into SO_2 or SF_6 and then monitoring $^{32}S^+$; $^{33}S^+$; $^{34}S^+$.

Determination of S Isotopes using GC-ICPMS

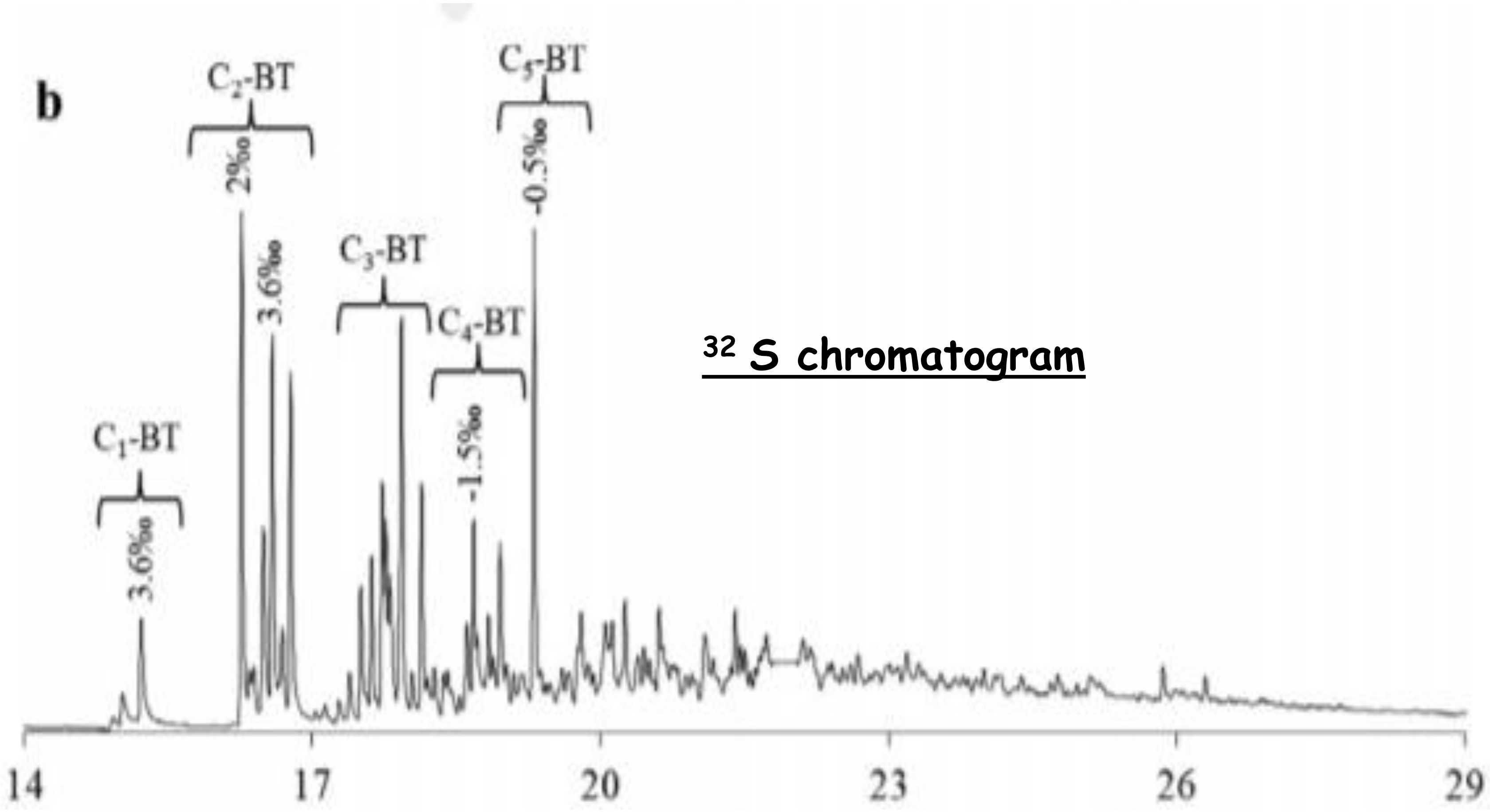


Summary of Gas Flows

Position	Gas	Rate (mL/min)
A	He	1.2
B	Ar	1600
C	SF_6/He	8
D	Ar	1000
E	Ar	15000

Simultaneously monitor ^{32}S and ^{34}S which are converted into $\delta^{34}S$ values; SF_6 used as standard.

S-Isotopes by GC-ICPMS



^{32} S chromatogram

S Isotopes of individual benzothiophenenes

Shawar et al., Sulfur isotope composition of individual compounds in immature organic-rich rocks and possible geochemical implications. Geochim. Cosmochim Acta, 274, 20-44, 2020.

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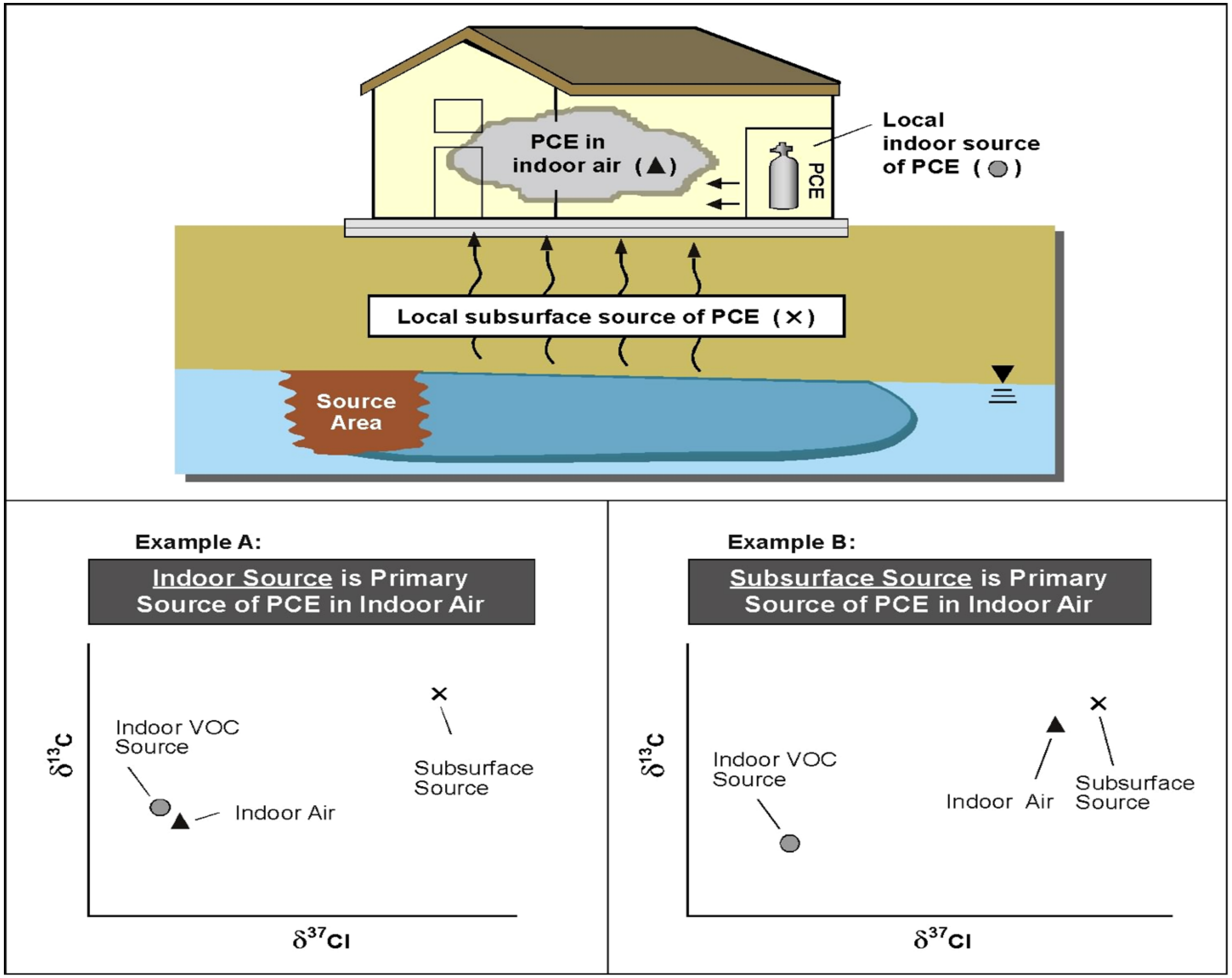
- Introduction
- Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
  - Diesel, Gasoline, Motor oil
  - Groundwater contaminants
  - Chlorinated Solvents
  - PAHs
  - PCBs
  - Benzene
  - Chlorine Isotopes

- Vapor Intrusion Studies
- Summary

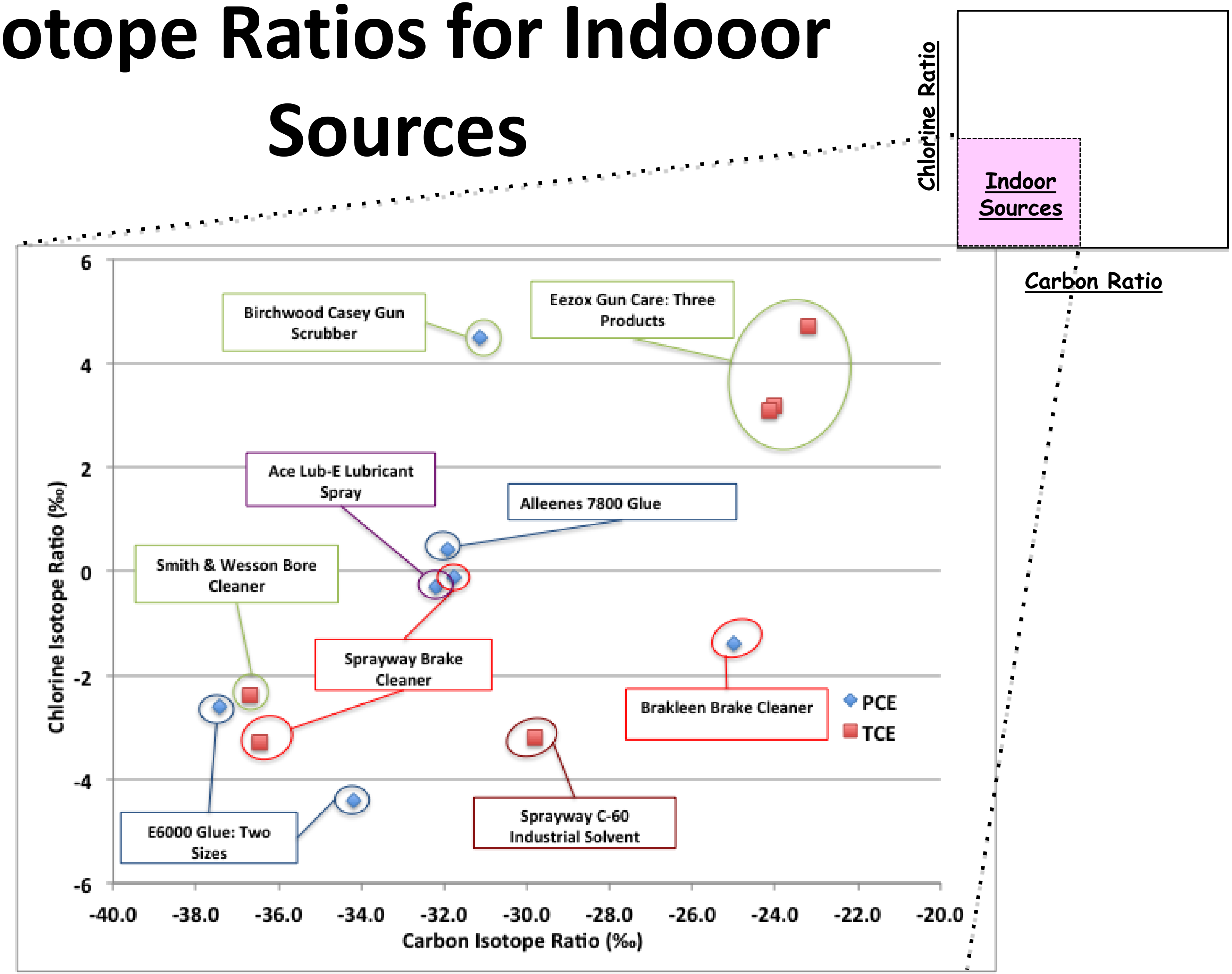
Vapor Intrusion

- **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.**

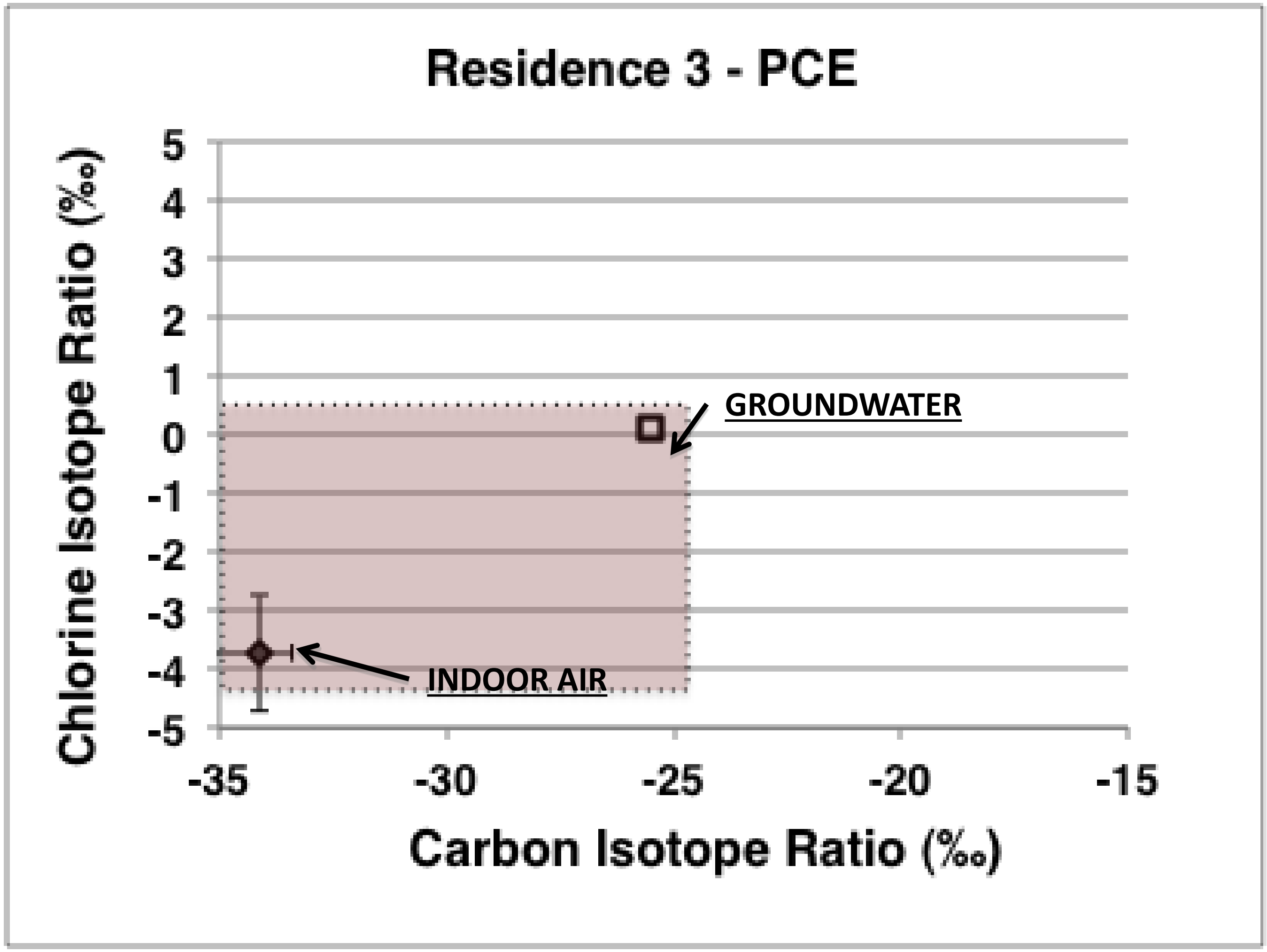


Key Point: ***Critical need for reliable methods to distinguish between vapor intrusion and indoor sources of VOCs.***

Isotope Ratios for Indooor Sources



RESULTS FOR INDOOR AIR



FINDING:

PCE in indoor air is from **indoor source.**

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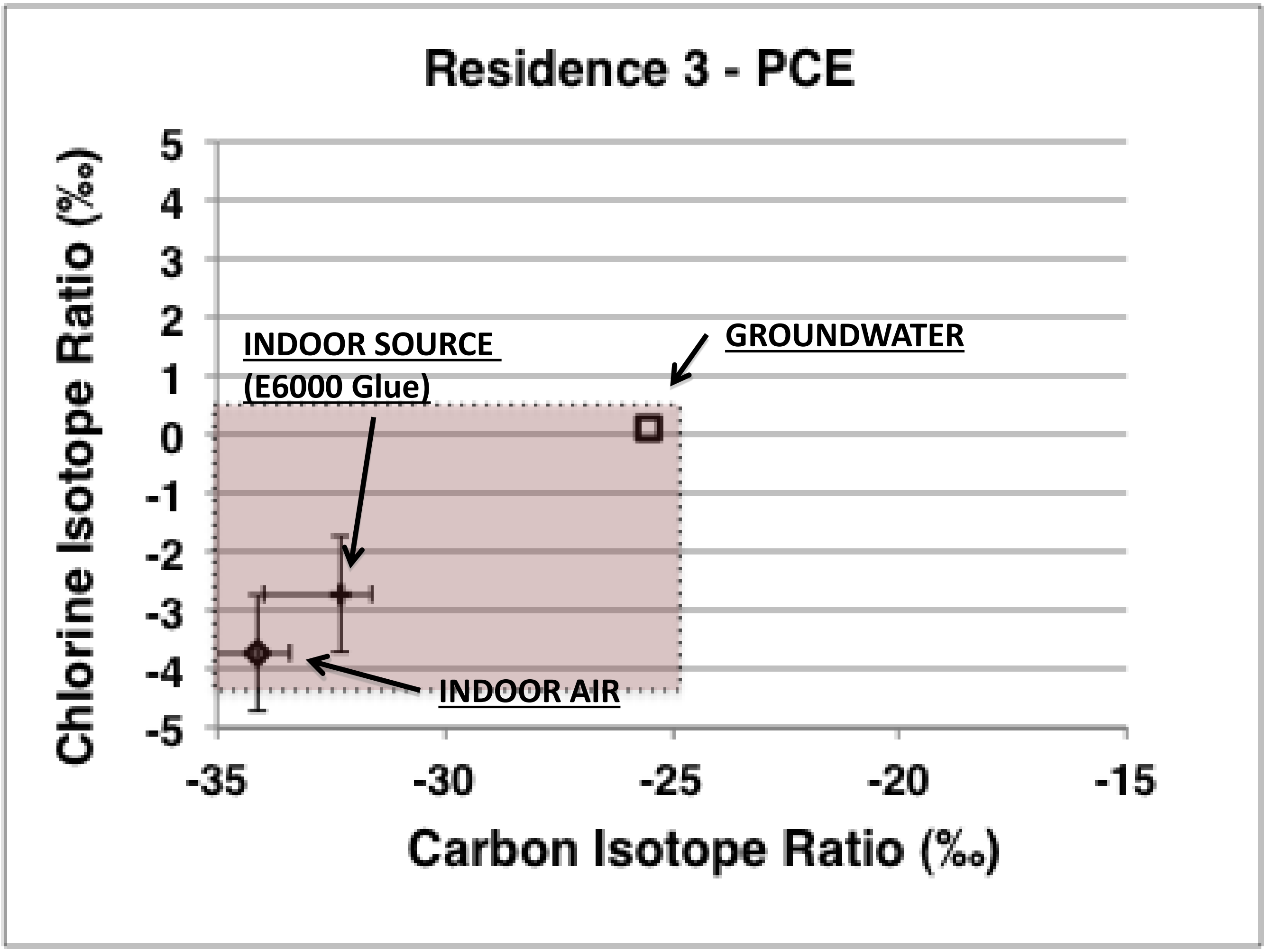

FINDING:

PCE in indoor air is from **indoor source.**

(Source later identified as E6000 glue)

SUMMARY

- Stable isotopes provide a powerful complimentary tool for the correlation of spilled products in the environment with suspected sources.
- Can be used to evaluate onset, extent, and mechanisms of degradation.
- GC and GCMS already widely used techniques in forensic geochemistry
- Stable isotopes (C,H, and Cl) of individual compounds are extremely important tools in environmental forensics. Expanded use of Br, S and N isotopes in the future.