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Applications of Stable Isotope Analyses to Environmental Forensics (Part 3), and to Understand the Degradation of Chlorinated Organic Contaminants (Part 4)

Sponsored by: U.S. EPA Technology Innovation and Field Services Division

Delivered: October 27, 2010, 2:00 PM - 3:30 PM, EDT (18:00-19:30 GMT)

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Michael Adam, U.S. EPA, Technology Innovation and Field Services Division (adam.michael@epa.gov)

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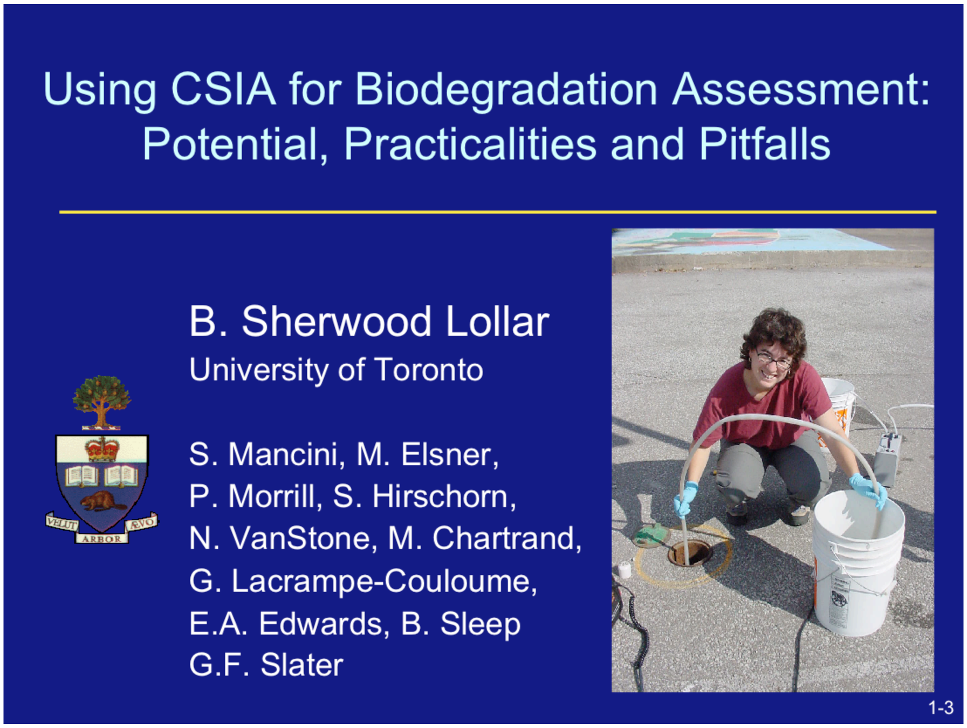
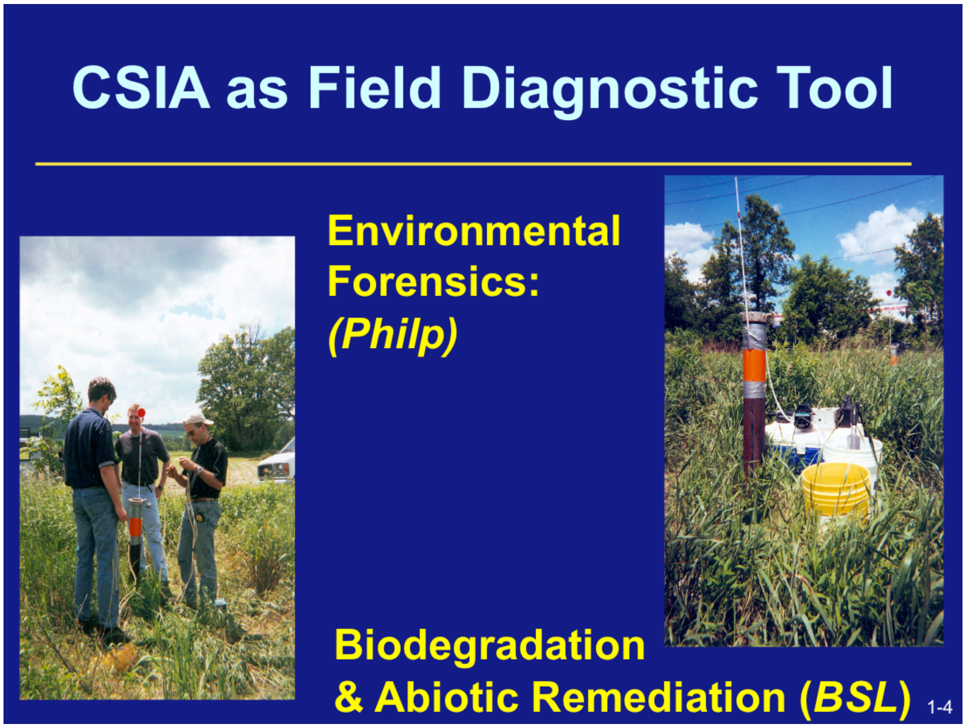


Using CSIA for Biodegradation Assessment: Potential, Practicalities and Pitfalls

B. Sherwood Lollar
University of Toronto

S. Mancini, M. Elsner,
P. Morrill, S. Hirschorn,
N. VanStone, M. Chartrand,
G. Lacrampe-Couloume,
E.A. Edwards, B. Sleep
G.F. Slater



CSIA as Field Diagnostic Tool

Environmental Forensics:
(Philp)

Biodegradation
& Abiotic Remediation (*BSL*)

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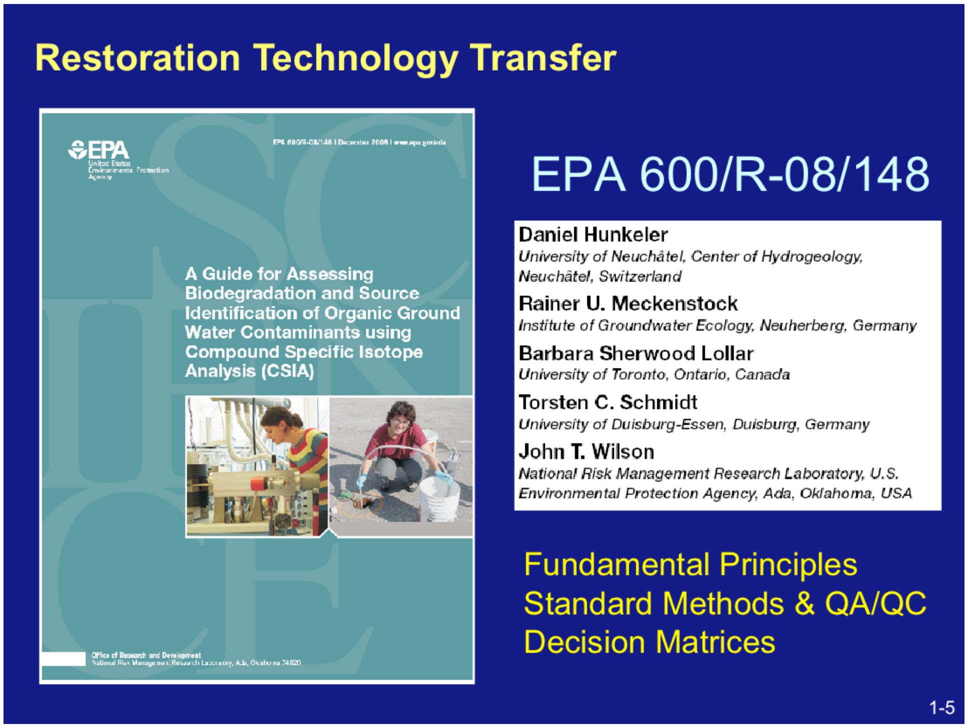

Restoration Technology Transfer

EPA
United States
Environmental Protection
Agency

EPA 600/R-08/148 | December 2008 | 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

EPA 600/R-08/148

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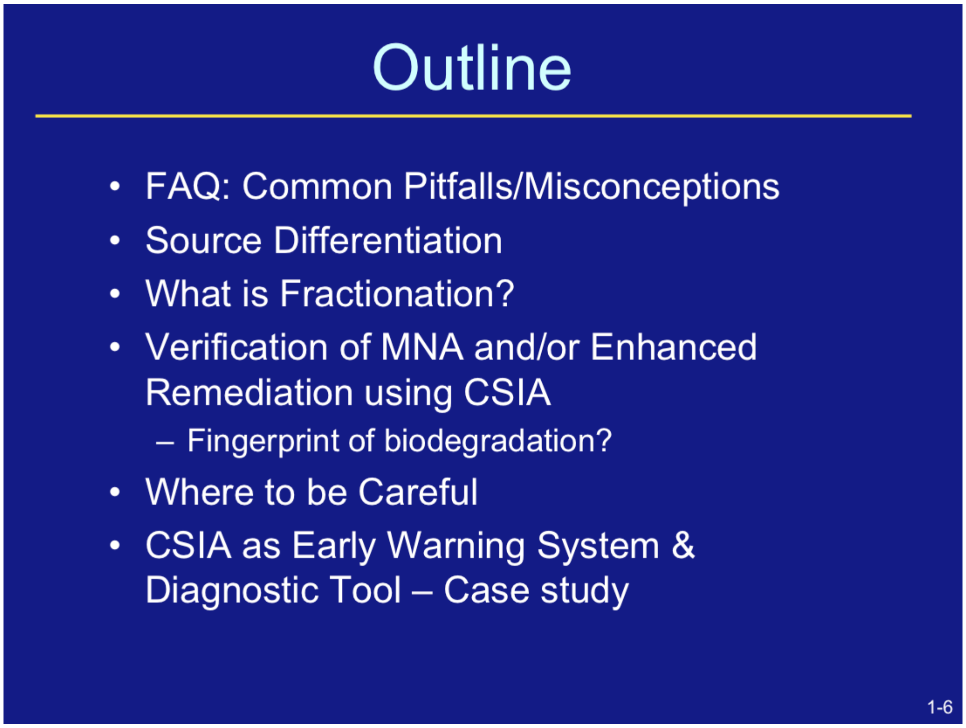
National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Ada, Oklahoma, USA

Fundamental Principles
Standard Methods & QA/QC
Decision Matrices

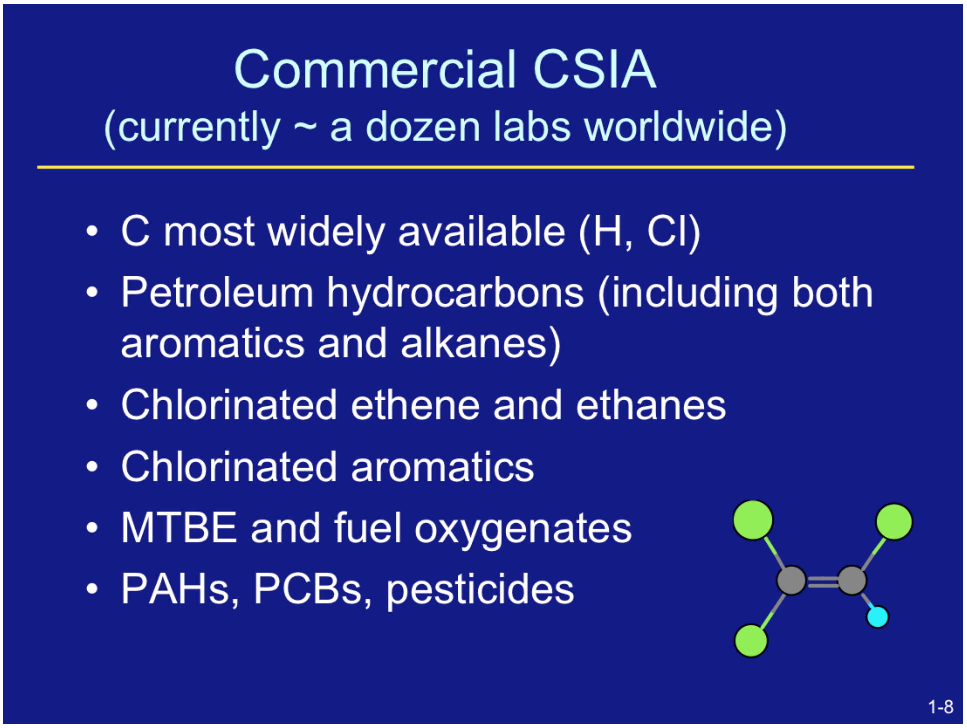


Outline

- FAQ: Common Pitfalls/Misconceptions
- Source Differentiation
- What is Fractionation?
- Verification of MNA and/or Enhanced Remediation using CSIA
  - Fingerprint of biodegradation?
- Where to be Careful
- CSIA as Early Warning System & Diagnostic Tool – Case study

FAQ Sheet

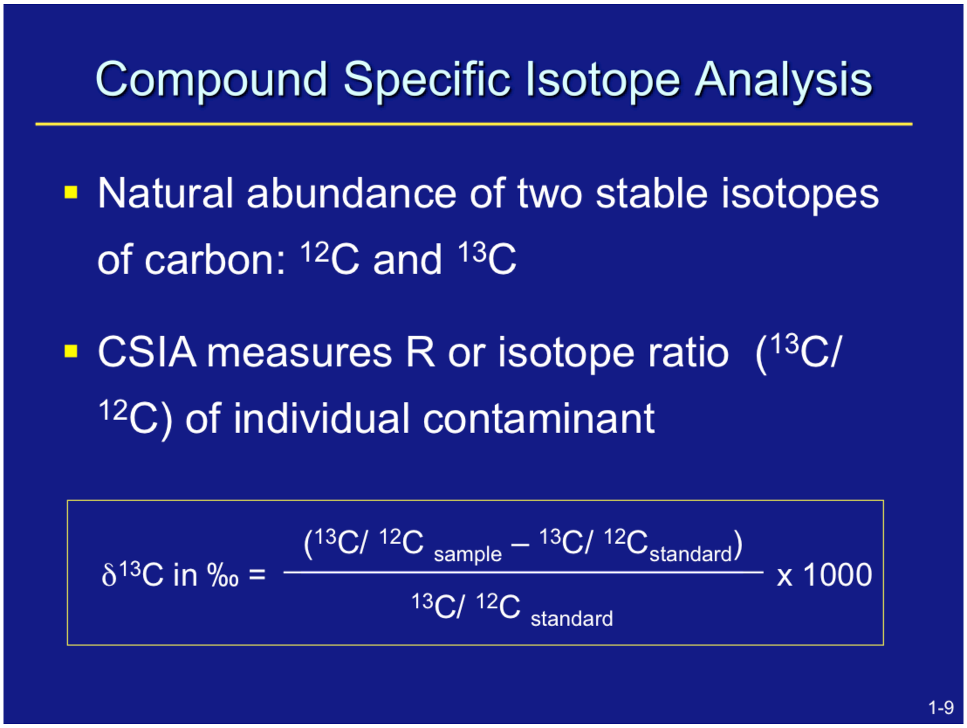
- Sample collection: adaptation of standard 40 mL VOA vial
- Turnaround: approximately 4 weeks
- Cost: less than cost of one additional monitoring well - can reduce uncertainty & risk, and drive decision making
- QA/QC: more than 50 year history of standardization and cross-calibration
- Tracer: but naturally occurring



Commercial CSIA

(currently ~ a dozen labs worldwide)

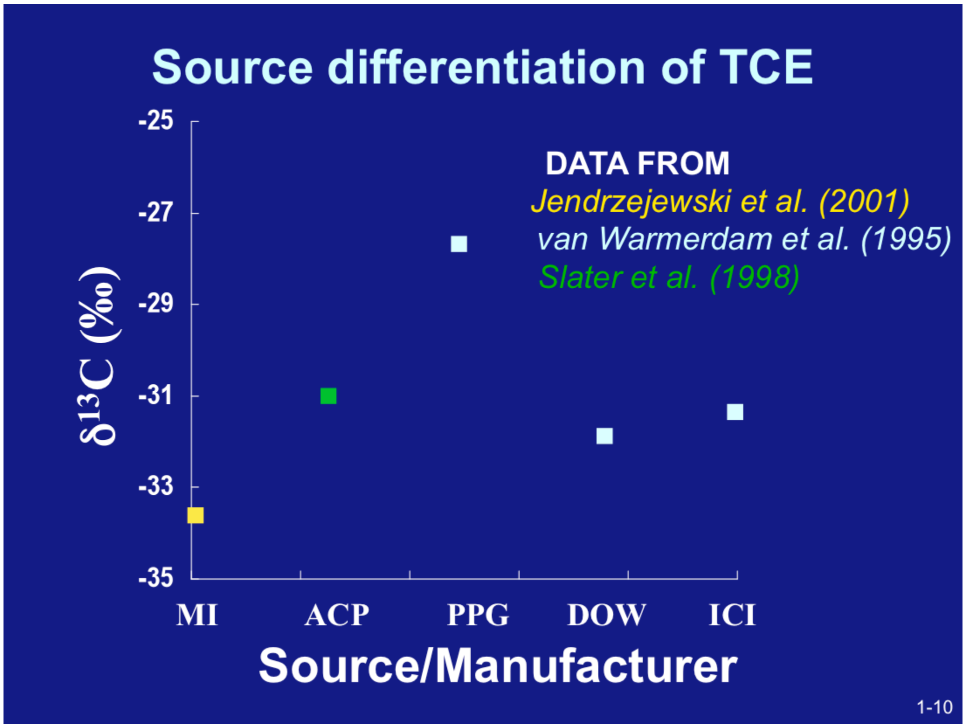
- C most widely available (H, Cl)
- Petroleum hydrocarbons (including both aromatics and alkanes)
- Chlorinated ethene and ethanes
- Chlorinated aromatics
- MTBE and fuel oxygenates
- PAHs, PCBs, pesticides



Compound Specific Isotope Analysis

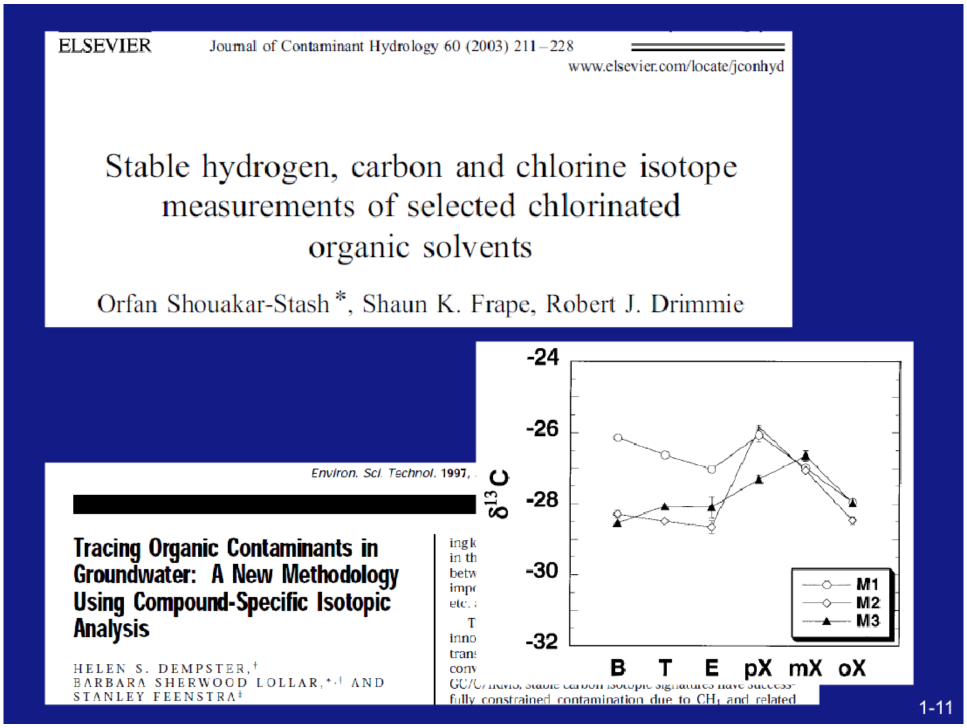
- Natural abundance of two stable isotopes of carbon: ^{12}C and ^{13}C
- CSIA measures R or isotope ratio ($^{13}C/^{12}C$) of individual contaminant

$$\delta^{13}C \text{ in ‰} = \frac{(^{13}C/\,^{12}C_{\text{sample}} - {}^{13}C/\,^{12}C_{\text{standard}})}{^{13}C/\,^{12}C_{\text{standard}}} \text{ x } 1000$$



Source differentiation of TCE

DATA FROM
Jendrzejewski et al. (2001)
van Warmerdam et al. (1995)
Slater et al. (1998)



ELSEVIER Journal of Contaminant Hydrology 60 (2003) 211–228
www.elsevier.com/locate/jconhyd

Stable hydrogen, carbon and chlorine isotope measurements of selected chlorinated organic solvents

Orfan Shouakar-Stash*, Shaun K. Frape, Robert J. Drimmie

Environ. Sci. Technol. **1997**,

Tracing Organic Contaminants in Groundwater: A New Methodology Using Compound-Specific Isotopic Analysis

HELEN S. DEMPSTER,[†]
BARBARA SHERWOOD LOLLAR,[*,‡] AND
STANLEY FEENSTRA[‡]

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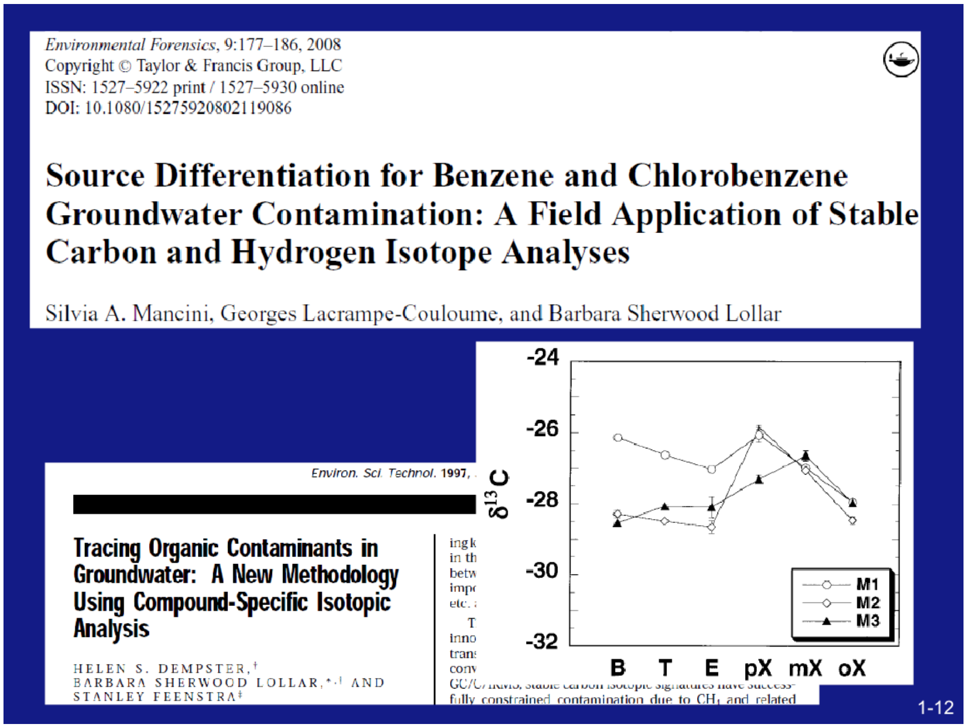

Environmental Forensics, 9:177–186, 2008
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DOI: 10.1080/15275920802119086

Source Differentiation for Benzene and Chlorobenzene Groundwater Contamination: A Field Application of Stable Carbon and Hydrogen Isotope Analyses

Silvia A. Mancini, Georges Lacrampe-Couloume, and Barbara Sherwood Lollar

Environ. Sci. Technol. **1997**,

Tracing Organic Contaminants in Groundwater: A New Methodology Using Compound-Specific Isotopic Analysis

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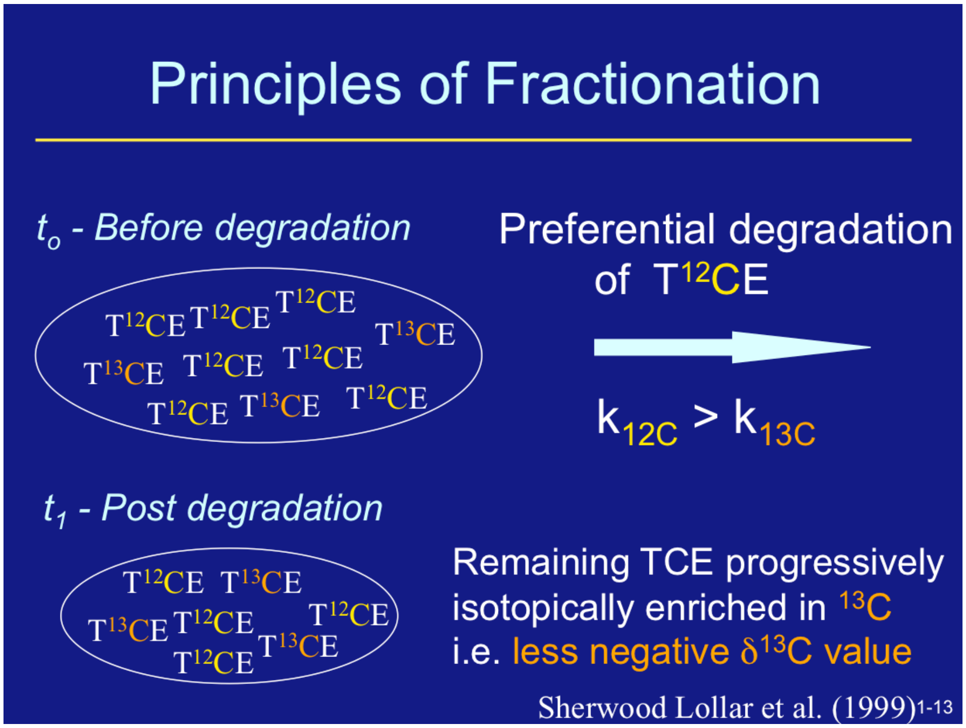


Principles of Fractionation

t_o - Before degradation

T^{12}CE T^{12}CE T^{12}CE T^{13}CE
T^{13}CE T^{12}CE T^{12}CE
T^{12}CE T^{13}CE T^{12}CE

Preferential degradation of T^{12}CE

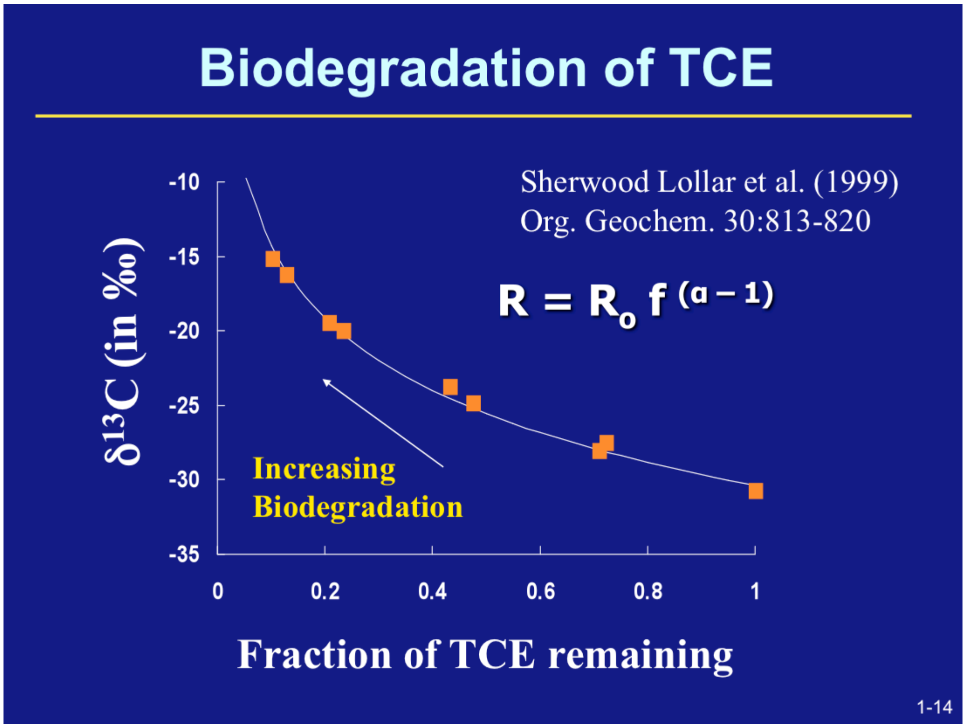
$k_{12C} > k_{13C}$

t_1 - Post degradation

T^{12}CE T^{13}CE
T^{13}CE T^{12}CE T^{12}CE
T^{12}CE T^{13}CE

Remaining TCE progressively isotopically enriched in ^{13}C i.e. less negative δ^{13}C value

Sherwood Lollar et al. (1999)1-13



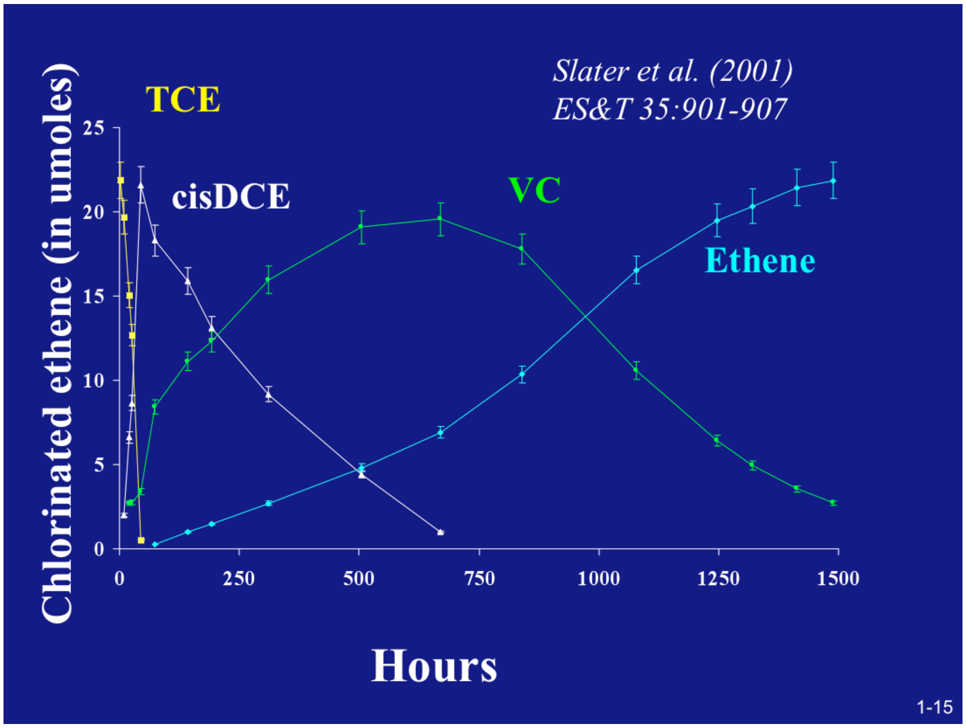
Biodegradation of TCE

Sherwood Lollar et al. (1999)
Org. Geochem. 30:813-820

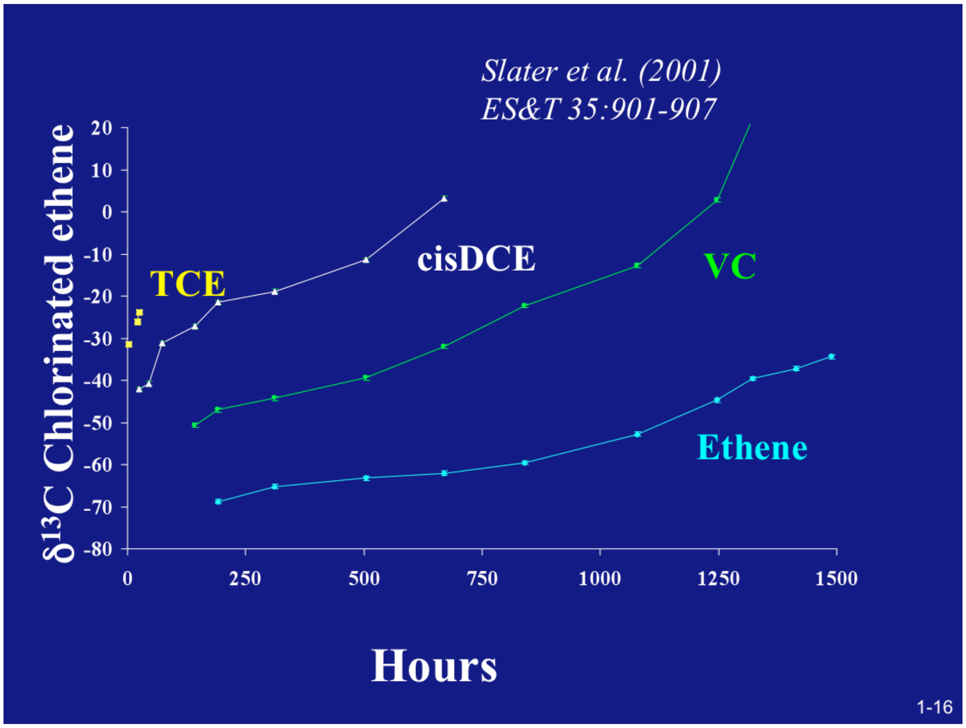
$$R = R_o f^{(\alpha - 1)}$$

Increasing
Biodegradation

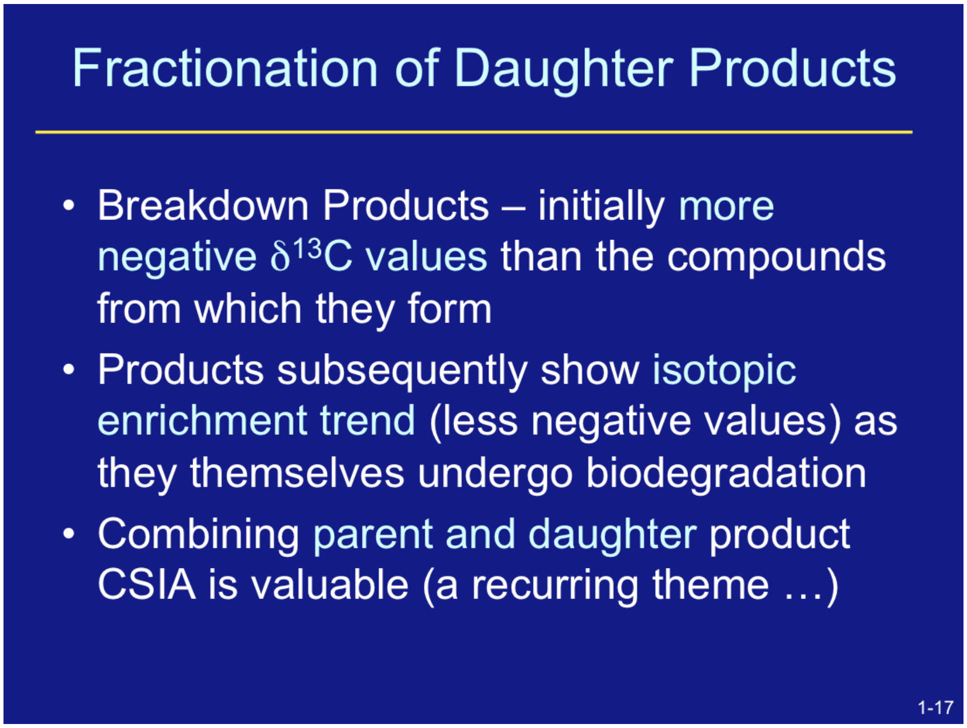
1-14



Slater et al. (2001)
ES&T 35:901-907

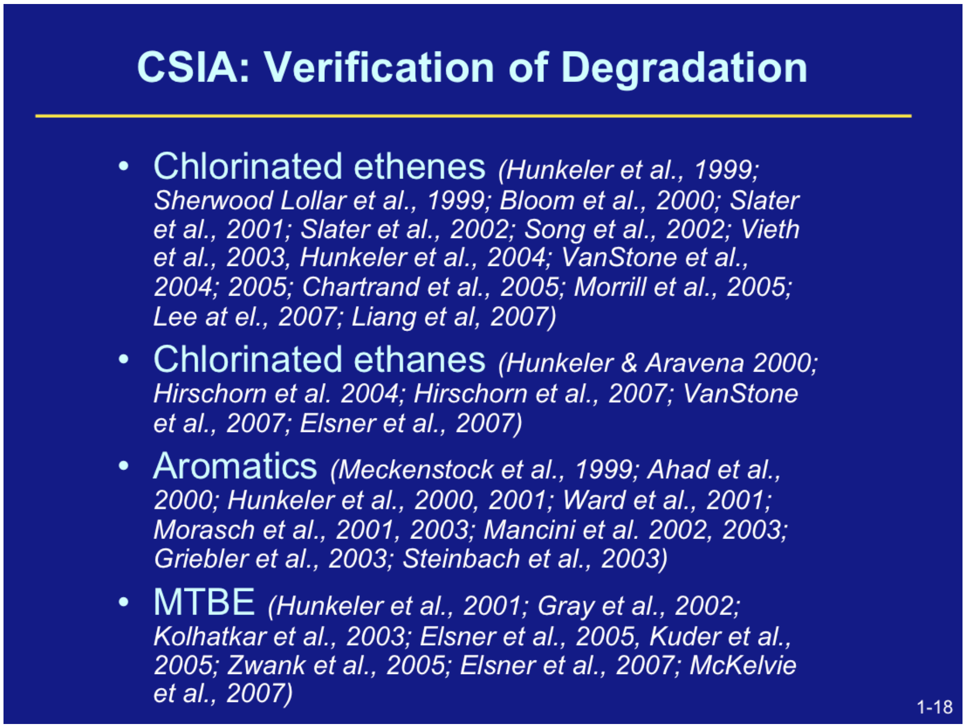


Slater et al. (2001)
ES&T 35:901-907



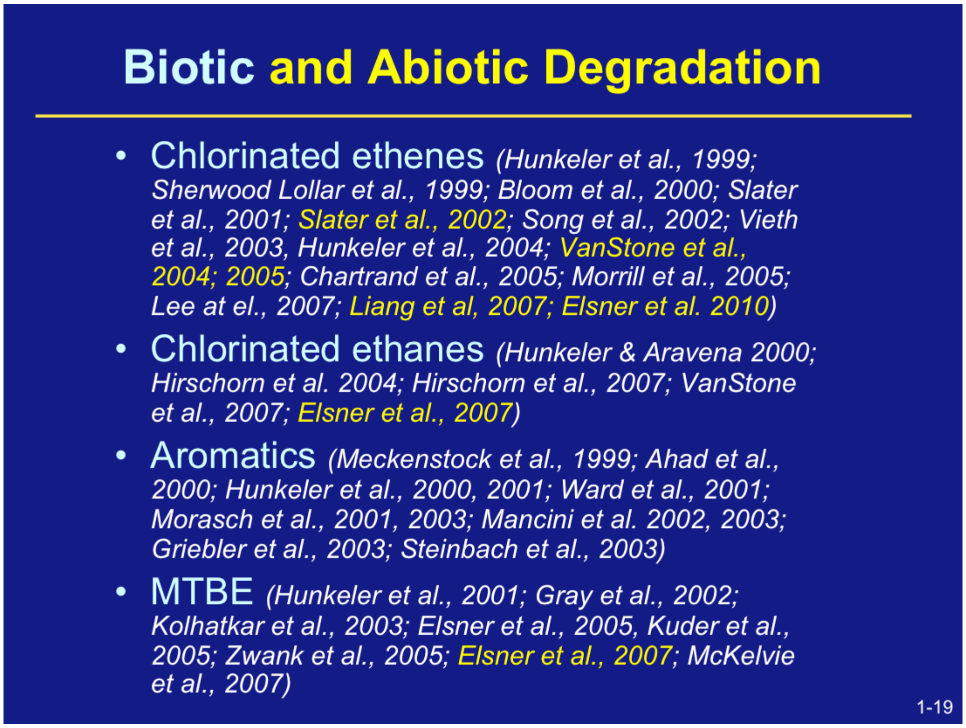
Fractionation of Daughter Products

- Breakdown Products – initially more negative $\delta^{13}C$ values than the compounds from which they form
- Products subsequently show isotopic enrichment trend (less negative values) as they themselves undergo biodegradation
- Combining parent and daughter product CSIA is valuable (a recurring theme …)



CSIA: Verification of Degradation

- Chlorinated ethenes *(Hunkeler et al., 1999; Sherwood Lollar et al., 1999; Bloom et al., 2000; Slater et al., 2001; Slater et al., 2002; Song et al., 2002; Vieth et al., 2003, Hunkeler et al., 2004; VanStone et al., 2004; 2005; Chartrand et al., 2005; Morrill et al., 2005; Lee at el., 2007; Liang et al, 2007)*
- Chlorinated ethanes *(Hunkeler & Aravena 2000; Hirschorn et al. 2004; Hirschorn et al., 2007; VanStone et al., 2007; Elsner et al., 2007)*
- Aromatics *(Meckenstock et al., 1999; Ahad et al., 2000; Hunkeler et al., 2000, 2001; Ward et al., 2001; Morasch et al., 2001, 2003; Mancini et al. 2002, 2003; Griebler et al., 2003; Steinbach et al., 2003)*
- MTBE *(Hunkeler et al., 2001; Gray et al., 2002; Kolhatkar et al., 2003; Elsner et al., 2005, Kuder et al., 2005; Zwank et al., 2005; Elsner et al., 2007; McKelvie et al., 2007)*



Biotic and Abiotic Degradation

- Chlorinated ethenes *(Hunkeler et al., 1999; Sherwood Lollar et al., 1999; Bloom et al., 2000; Slater et al., 2001; Slater et al., 2002; Song et al., 2002; Vieth et al., 2003, Hunkeler et al., 2004; VanStone et al., 2004; 2005; Chartrand et al., 2005; Morrill et al., 2005; Lee at el., 2007; Liang et al, 2007; Elsner et al. 2010)*
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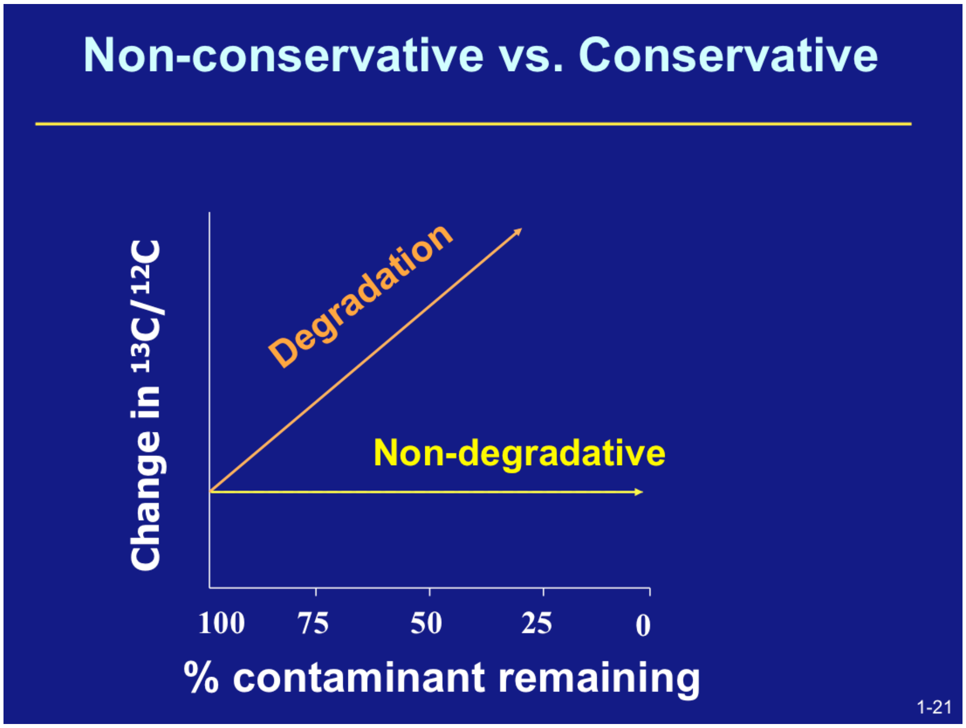
- MTBE *(Hunkeler et al., 2001; Gray et al., 2002; Kolhatkar et al., 2003; Elsner et al., 2005, Kuder et al., 2005; Zwank et al., 2005; Elsner et al., 2007; McKelvie et al., 2007)*

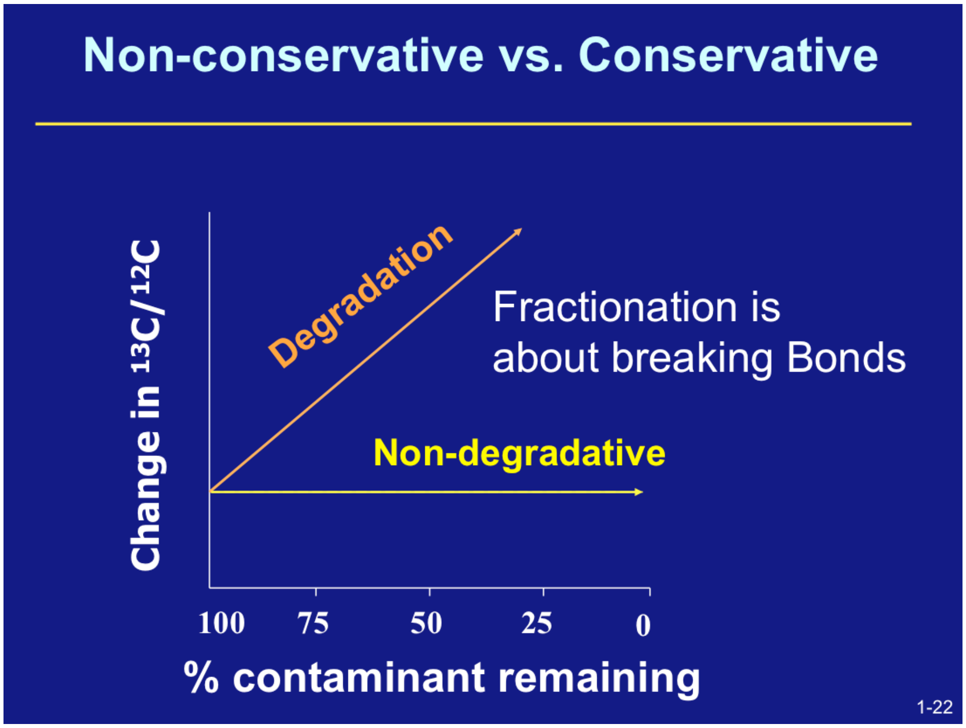
CSIA as Restoration Tool

- Isotopic enrichment in ^{13}C in remaining contaminant (less negative $\delta^{13}C$ values) a dramatic indicator of biodegradation
- Extent of fractionation predictable and reproducible – Quantification (rates) possible in many cases
- CSIA can distinguish mass loss due to the strong fractionation in degradation (biotic and abiotic)
- versus small- or non-fractionating processes such as volatilization, diffusion, dissolution, sorption, etc.



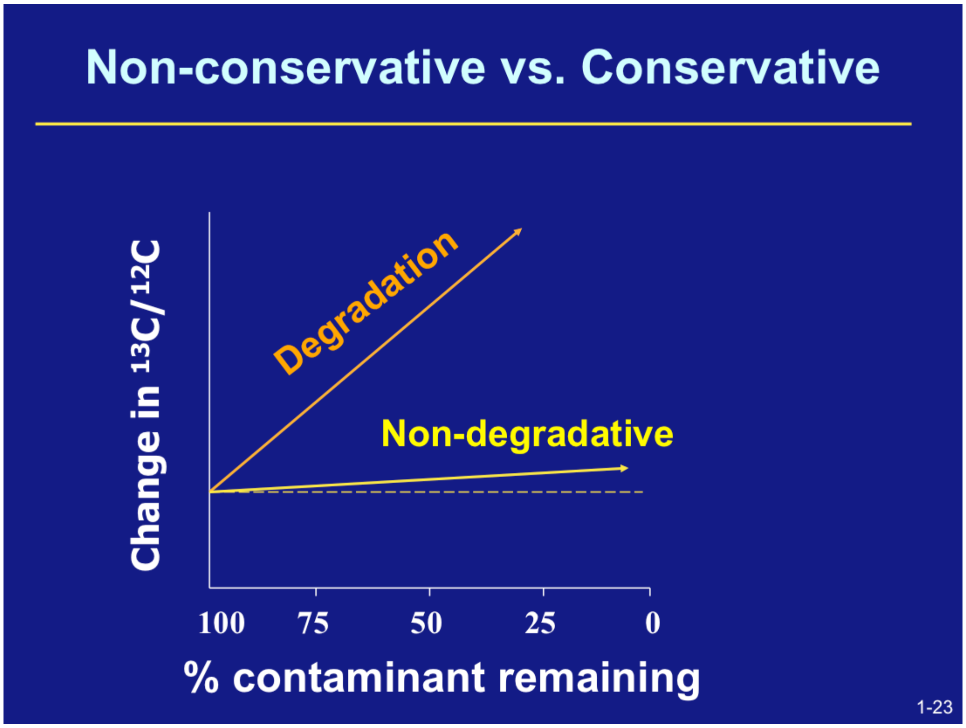
Non-conservative vs. Conservative

1-21

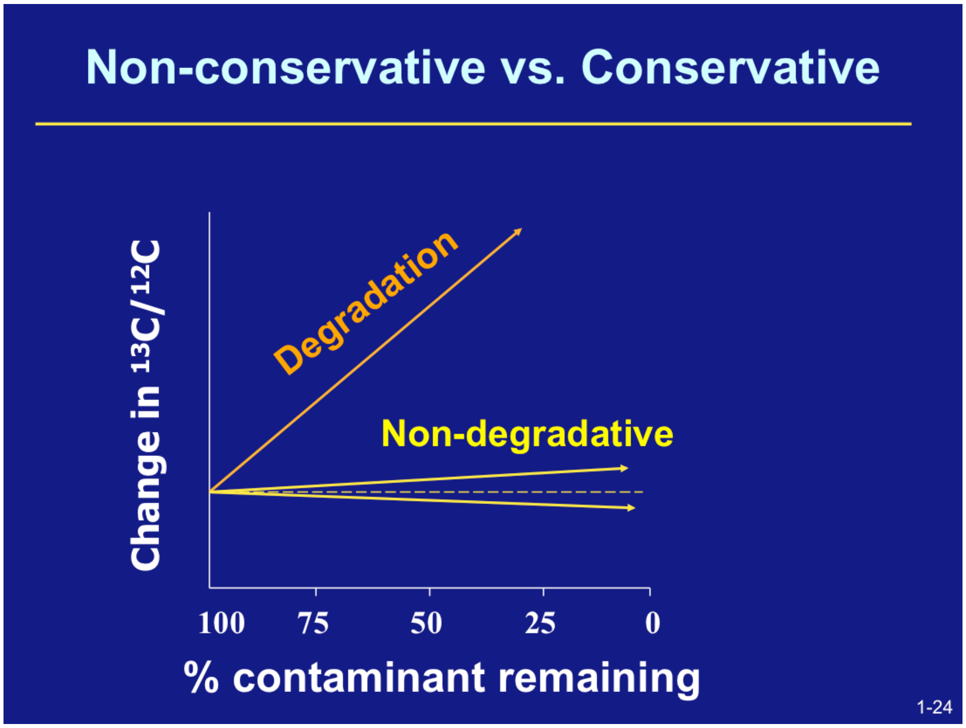


Non-conservative vs. Conservative

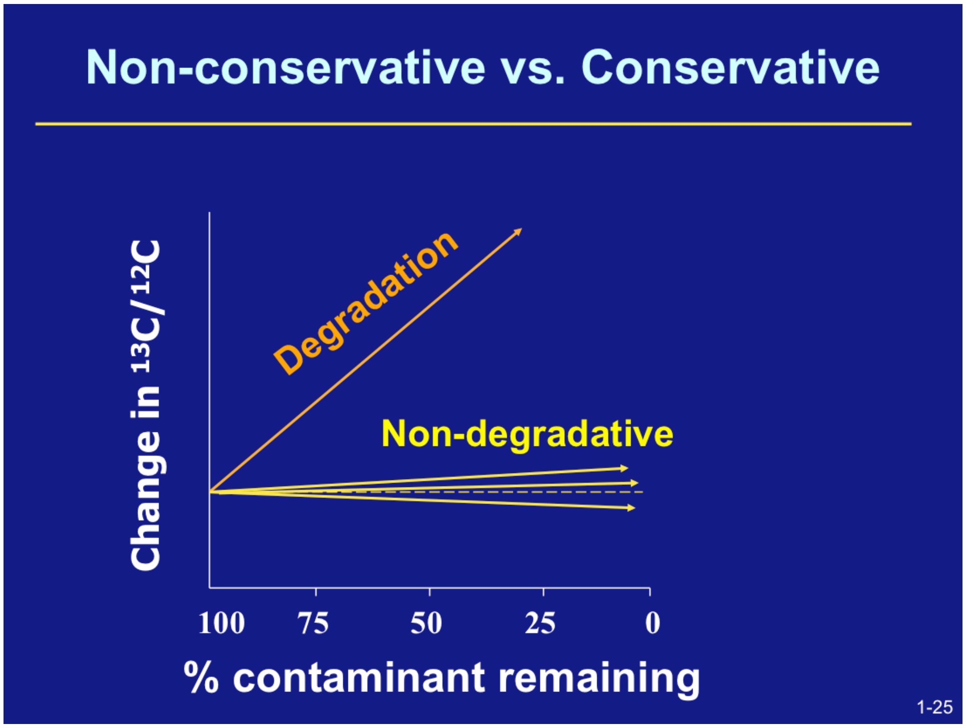
Fractionation is
about breaking Bonds



Non-conservative vs. Conservative

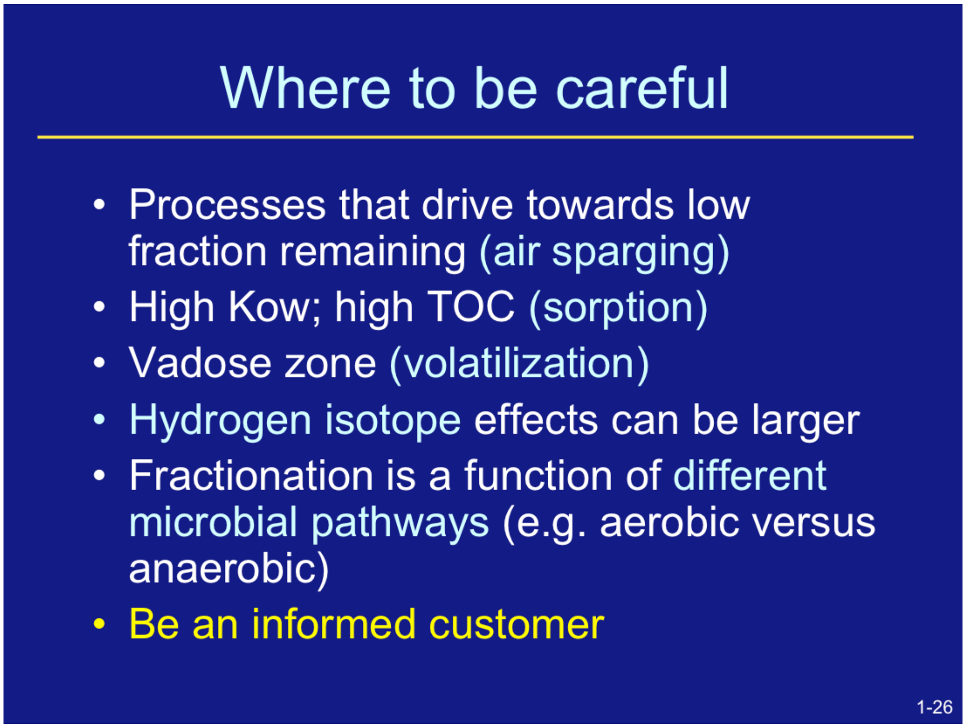


Non-conservative vs. Conservative



Non-conservative vs. Conservative

1-25



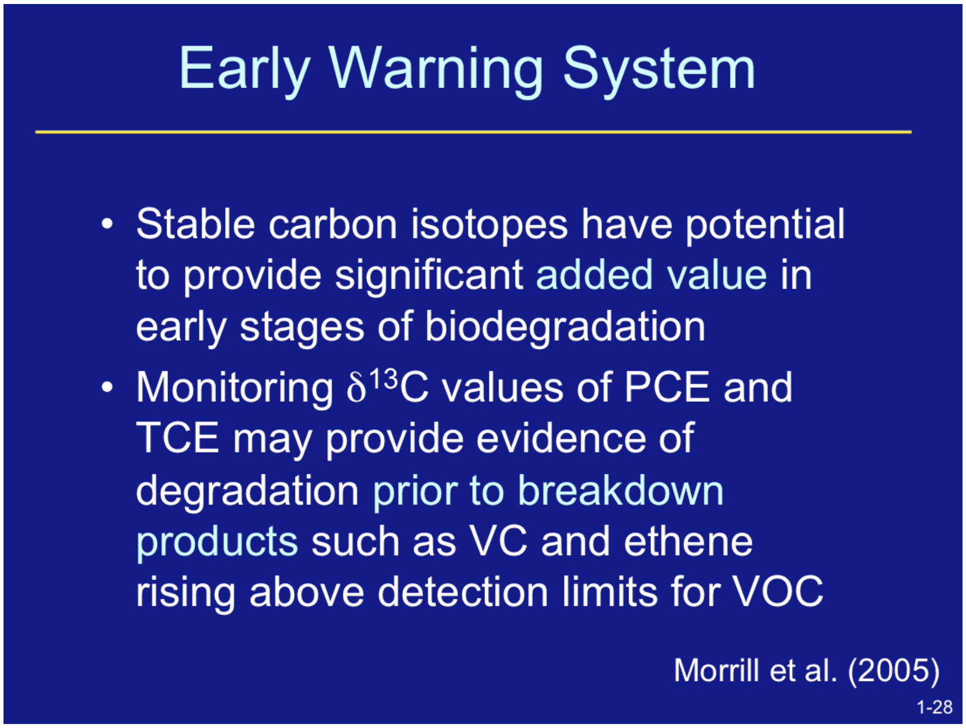
Where to be careful

- Processes that drive towards low fraction remaining (air sparging)
- High Kow; high TOC (sorption)
- Vadose zone (volatilization)
- Hydrogen isotope effects can be larger
- Fractionation is a function of different microbial pathways (e.g. aerobic versus anaerobic)
- Be an informed customer

Case Study I:
CSIA as early warning system for bioremediation: Kelly AFB

P. Morrill, G. Lacrampe-Couloume, G. Slater, E. Edwards, B. Sleep, B. Sherwood Lollar, M. McMaster and D. Major

JCH (2005) 76:279-293



Early Warning System

- Stable carbon isotopes have potential to provide significant added value in early stages of biodegradation
- Monitoring $\delta^{13}C$ values of PCE and TCE may provide evidence of degradation prior to breakdown products such as VC and ethene rising above detection limits for VOC

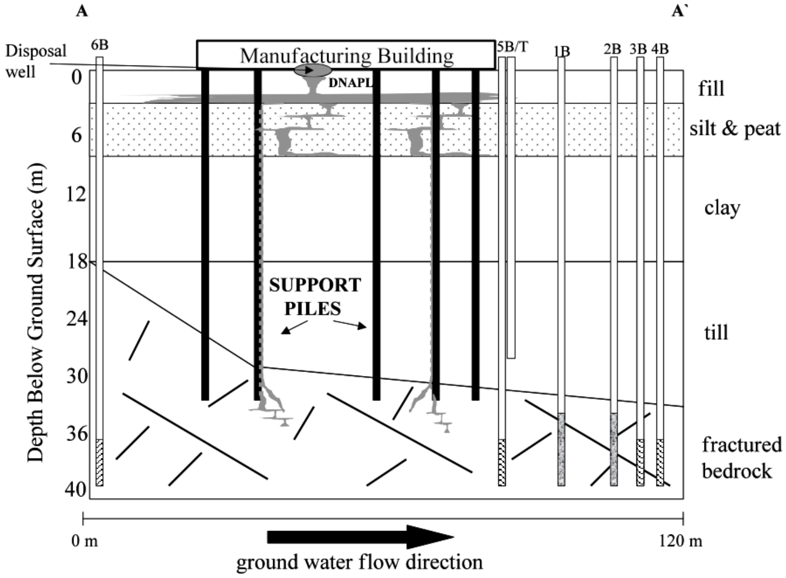
Morrill et al. (2005)

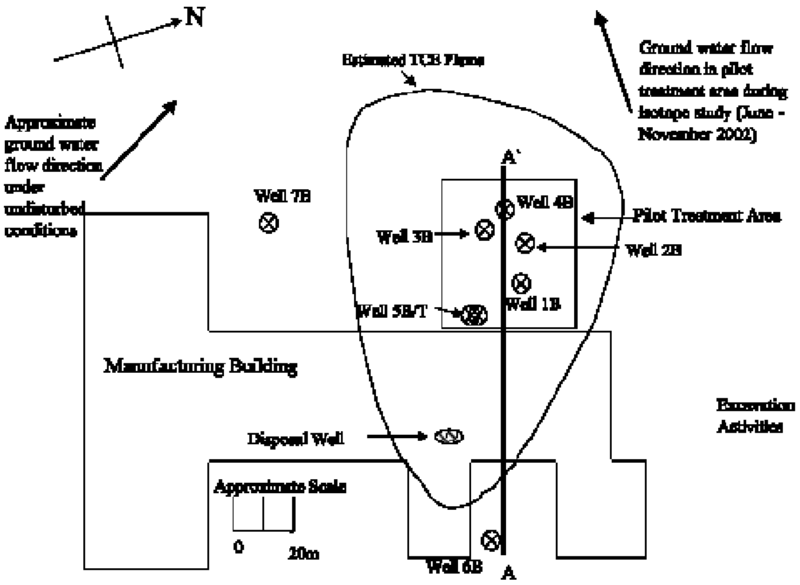
Case Study II:
CSIA to trouble-shoot potential cisDCE stall

M. Chartrand, P. Morrill, G. Lacrampe-Couloume, and
B. Sherwood Lollar

ES&T (2005) 39:4848-4856

CSIA at Fractured Rock Site





Chartrand et al. (2005) ES&T ***39:****4848-4856*

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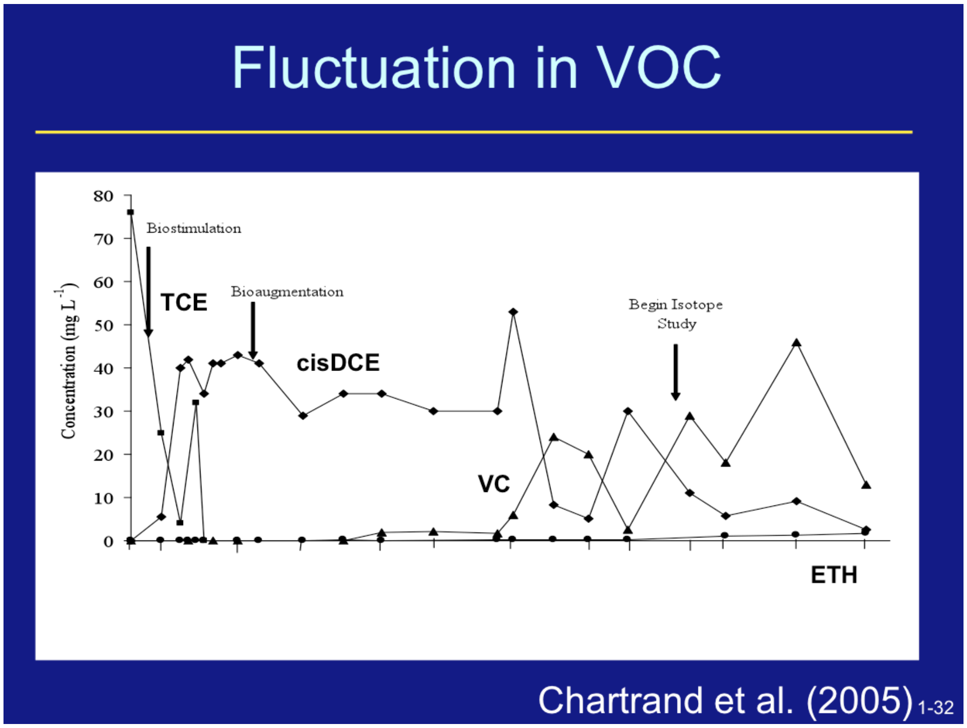
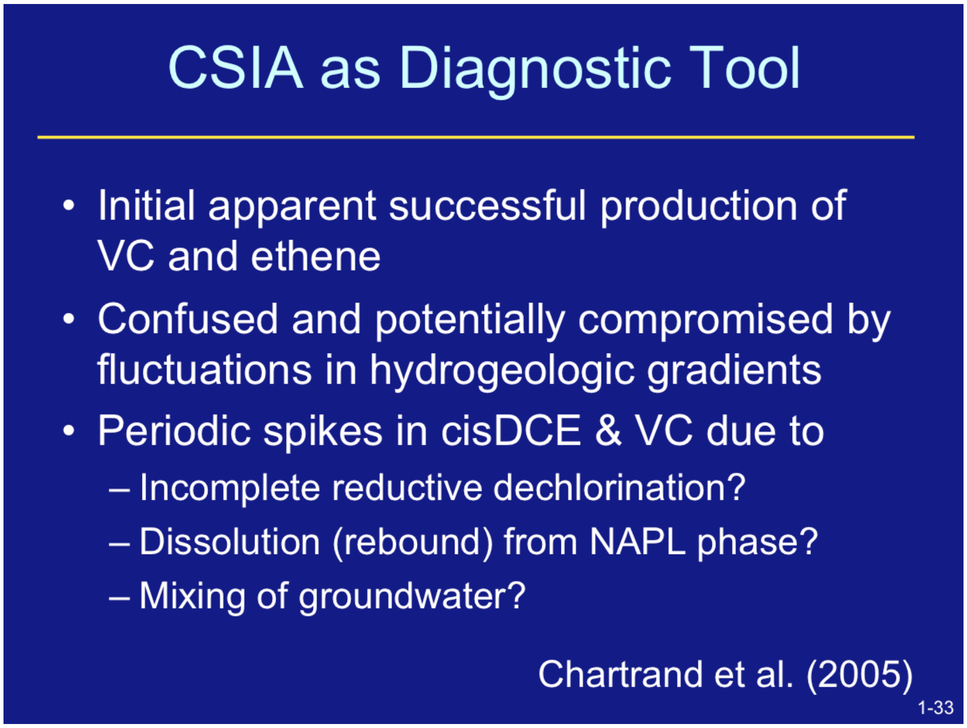


Fluctuation in VOC

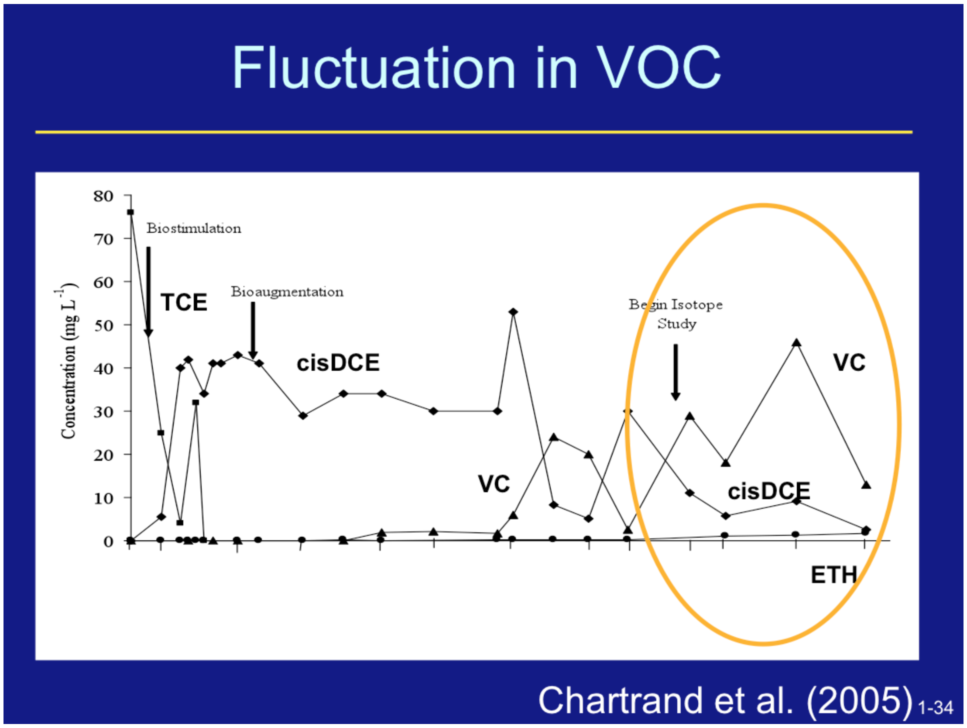
Chartrand et al. (2005)



CSIA as Diagnostic Tool

- Initial apparent successful production of VC and ethene
- Confused and potentially compromised by fluctuations in hydrogeologic gradients
- Periodic spikes in cisDCE & VC due to
  - Incomplete reductive dechlorination?
  - Dissolution (rebound) from NAPL phase?
  - Mixing of groundwater?

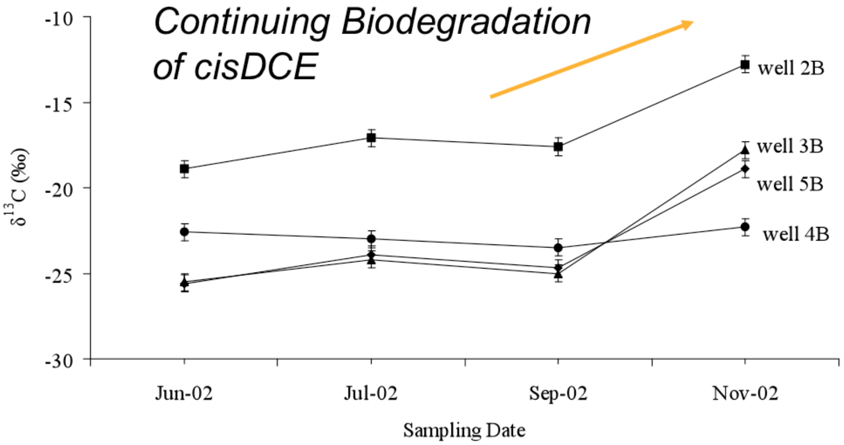
Chartrand et al. (2005)



Fluctuation in VOC

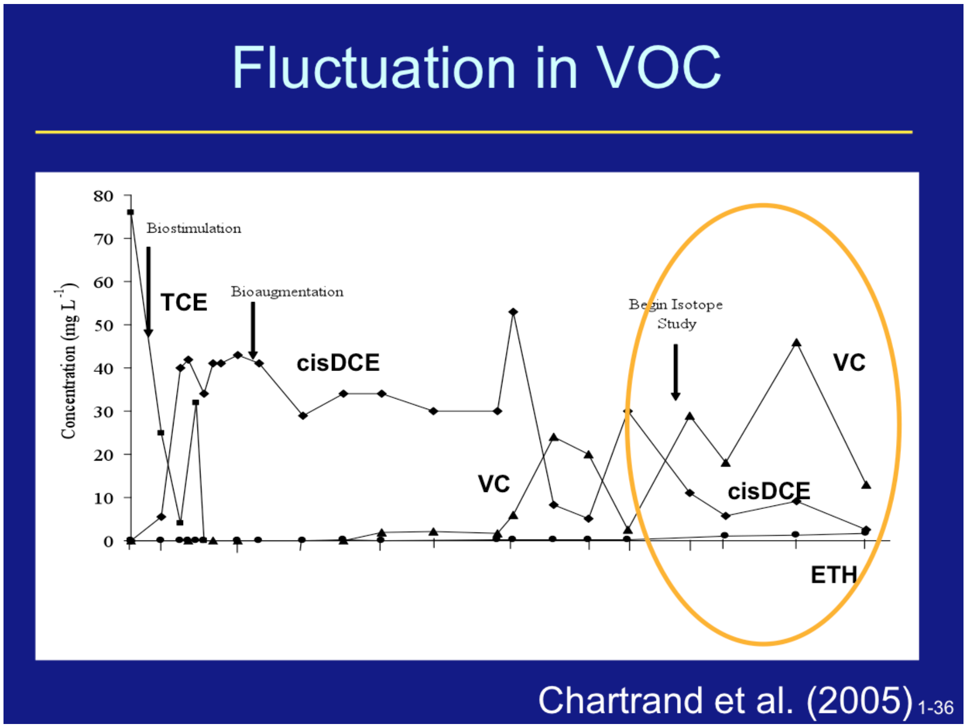
Chartrand et al. (2005)

Continued ^{13}C enrichment despite VOC fluctuations



Continuing Biodegradation of cisDCE

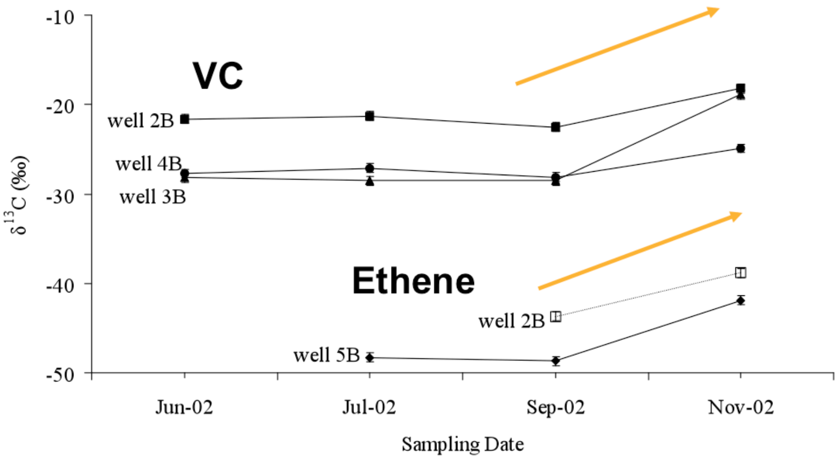
Chartrand et al. (2005)



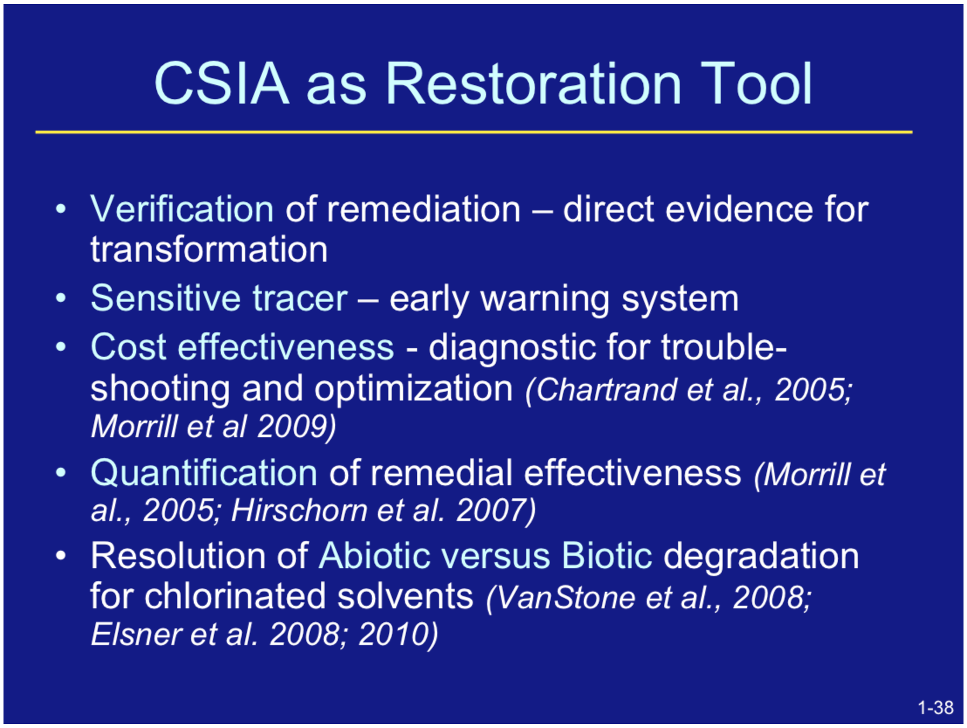
Fluctuation in VOC

Chartrand et al. (2005) 1-36

Continuing Net Biodegradation



Chartrand et al. (2005)



CSIA as Restoration Tool

- Verification of remediation – direct evidence for transformation
- Sensitive tracer – early warning system
- Cost effectiveness - diagnostic for trouble-shooting and optimization *(Chartrand et al., 2005; Morrill et al 2009)*
- Quantification of remedial effectiveness *(Morrill et al., 2005; Hirschorn et al. 2007)*
- Resolution of Abiotic versus Biotic degradation for chlorinated solvents *(VanStone et al., 2008; Elsner et al. 2008; 2010)*

More information?

- isotopes@geology.utoronto.ca

Environmental Forensics

R. Paul Philp, School of Geology
and Geophysics, University of
Oklahoma, Norman, OK. 73019

▫

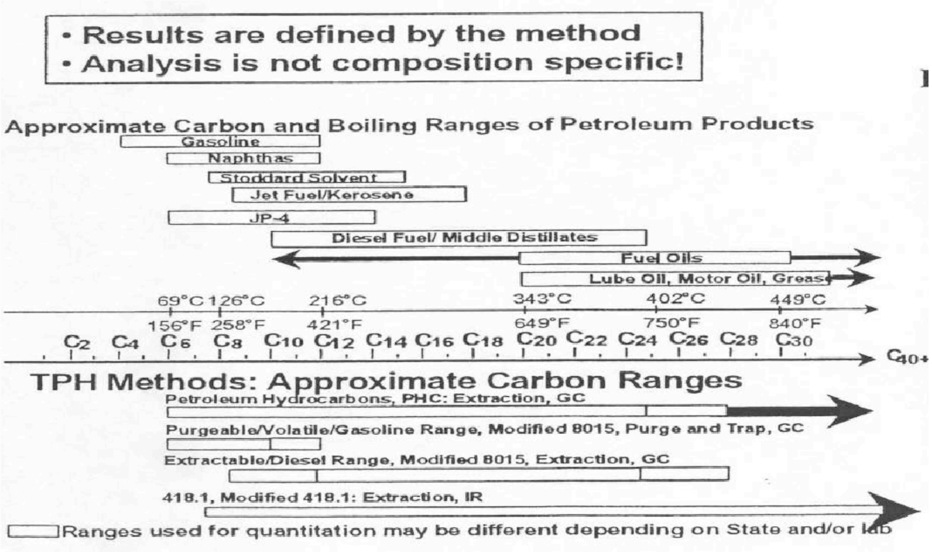
Environmental Forensics

- What is “Environmental Forensics”?

- “Environmental Forensics” can be defined as a scientific methodology developed for identifying petroleum-related and other potentially hazardous environmental contaminants and for determining their sources and time of release. It combines experimental analytical procedures with scientific principles derived from the disciplines of organic geochemistry and hydrogeology. Environmental Forensics provides a valuable tool for obtaining scientifically proven, court admissible evidence in environmental legal disputes.
- Much of the information required in this approach will not be obtained from the data obtained using the conventional EPA methods

2-2

Crude Oils and Related Products



- Results are defined by the method
- Analysis is not composition specific!

Approximate Carbon and Boiling Ranges of Petroleum Products

TPH Methods: Approximate Carbon Ranges

▭ Ranges used for quantitation may be different depending on State and/or lab

▫

Basic Environmental Forensic Questions

- What is the product?
- Is there more than one source and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?

2-4

With any forensic environmental study the basic questions that must be asked are summarized here. First what is it? A second question how many sources and if more than one which one (s) is causing the problem. Then how long has it been there-the reason for this is basically did you own the site when the spill occurred. If it can be shown the age of the spill is such that it occurred before you owned the site that is very advantageous. Finally is the product degrading? This becomes important for cleanup processes. Can you demonstrate natural attenuation is occurring-if so then that is very advantageous for clean up strategies.

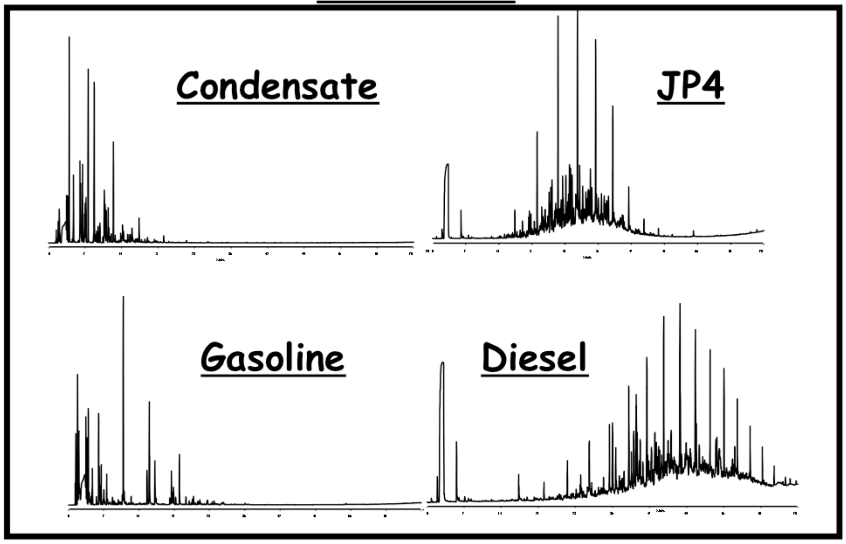
□

Fingerprinting and Correlation

- What are the most commonly used techniques for such purposes?

  Gas chromatography
  Mass Spectrometry
  Gas chromatography-Isotope Ratio Mass Spectrometry (GCIRMS)

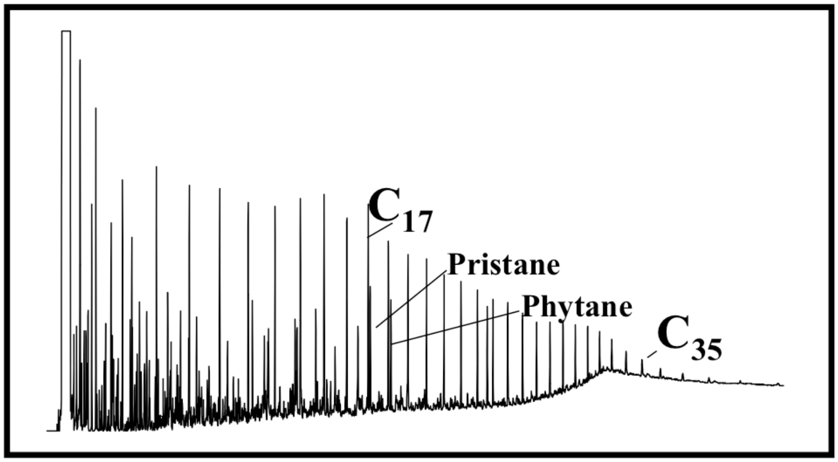
GC Fingerprints of Different Products



GC Fingerprints of different products

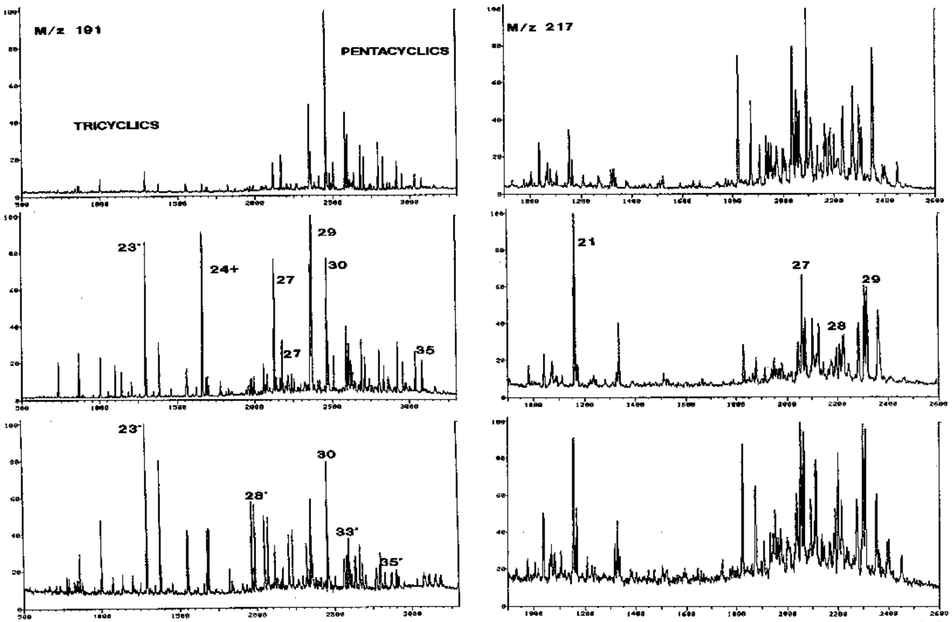
- Although GC permits product identification, many gasoline samples, for example, will be chromatographically similar, even if from different sources.
- Refined products generally do not contain biomarkers making GCMS of little consequence.
- If refined products are from different sources, stable isotopes may provide a potential solution.

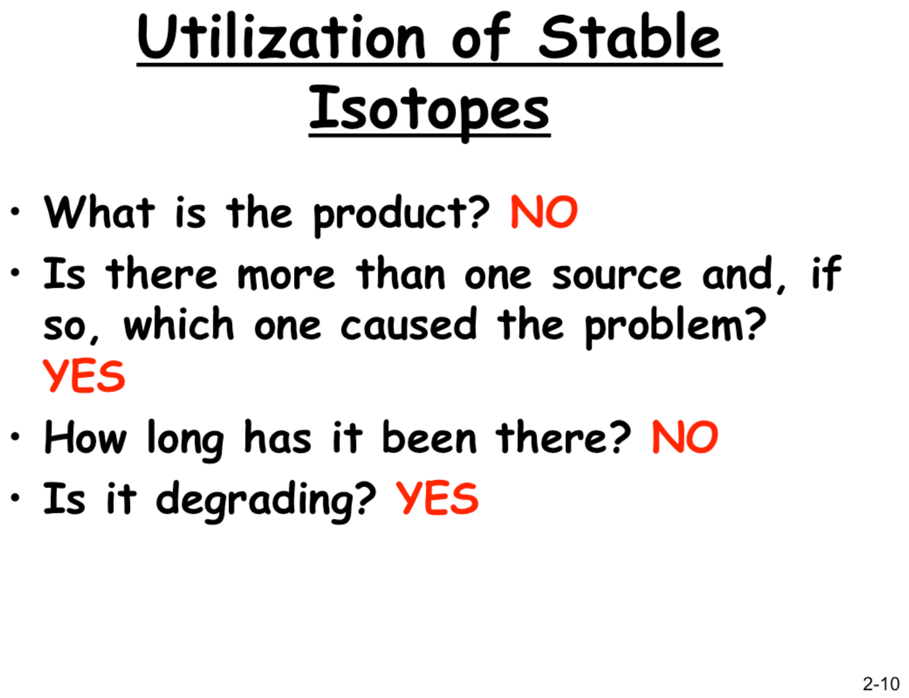
Crude Oil Chromatogram



2-8

Biomarker Distributions





Utilization of Stable Isotopes

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

2-10

This is basically indicating which questions listed in the previous slide can be addressed through the use of stable isotopes.

▫

Utilization of Stable Isotopes

Why do compounds derived from different feedstocks have different isotope values?

2-11

▫

Carbon Isotopes

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

▫

Carbon Isotopes

- Extent of fractionation during photosynthesis depends on factors such as: plant type; marine v. terrigenous; C_3 v. C_4 plant types; temperature; sunlight intensity; water depth.
- (C_3Temperate plants; trees; not grasses; 95% plant species -22 to -30; C_4 plants grasses; sugar cane; corn; higher temps and sunlight-10 to -14 per mil)

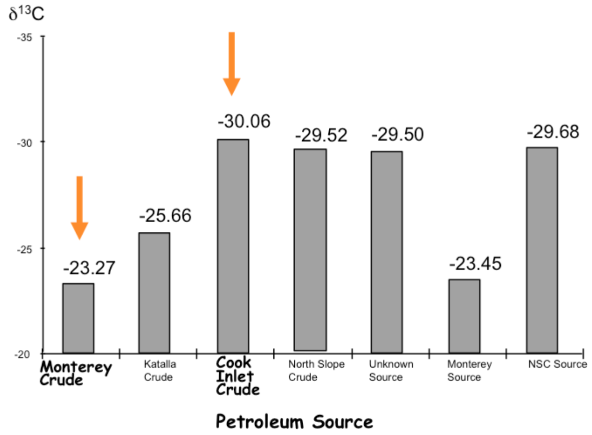
□

Stable Isotope Determinations

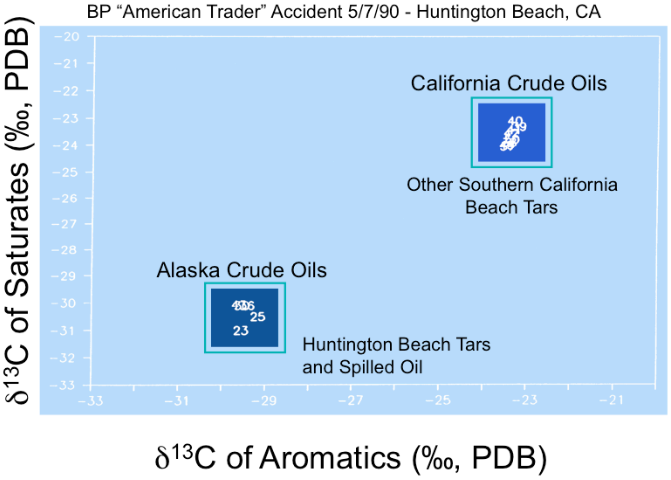
ISOTOPIC VALUES CAN BE MEASURED IN TWO WAYS:

- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS

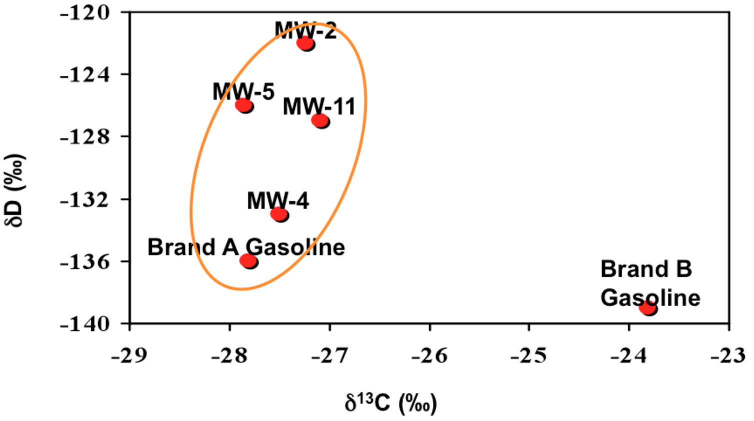
Isotope Values of Crude Oils Vary with Source



Correlations Using Carbon Isotopes



Correlation Using Bulk Isotope Ratios



Contamination in monitoring wells had two possible sources; GC fingerprints were similar since both were contemporary gasolines; isotopically distinct since derived from different crude oils

2-17

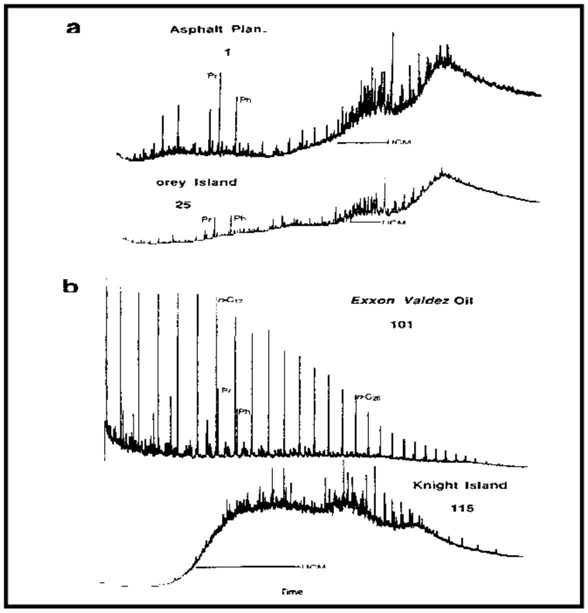
Brand A gasoline clearly different than brand B gasoline. Gasoline in groundwater degraded relative to Brand A and cannot be from Brand B. This is an example where the bulk C and H isotopes were determined on the gasoline samples and used to discriminate samples of different origins and to relate one source to the samples in the monitoring wells.

▫

EXXON VALDEZ

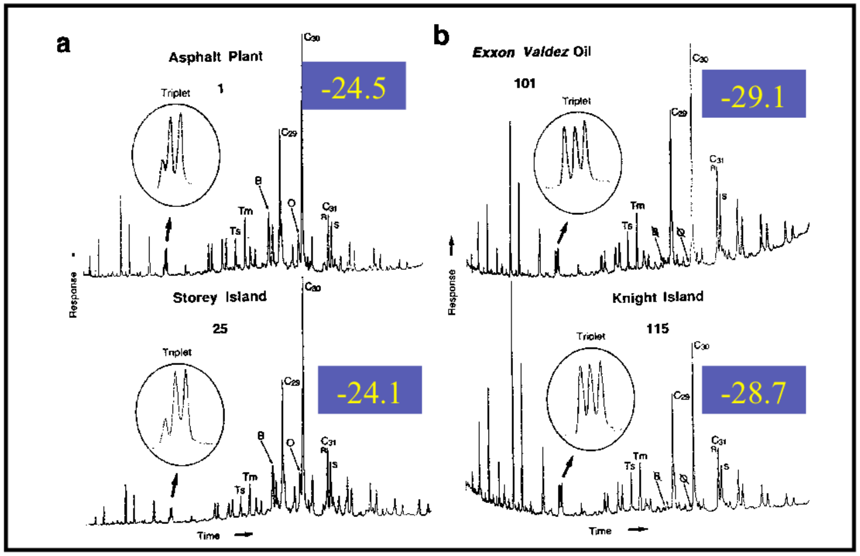
- March 24th, 1989
- 258,000 barrels of Alaskan North Slope crude oil spilled into Prince William Sound

Residues from Prince William Sound



2-19

Terpanes in Prince William Sound Residues



2-20

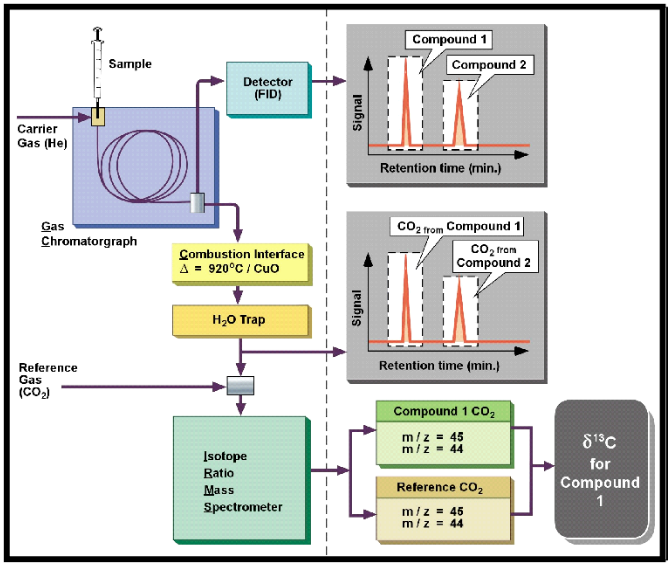
▫

Stable Isotope Determinations

ISOTOPIC VALUES CAN BE
MEASURED IN TWO WAYS:

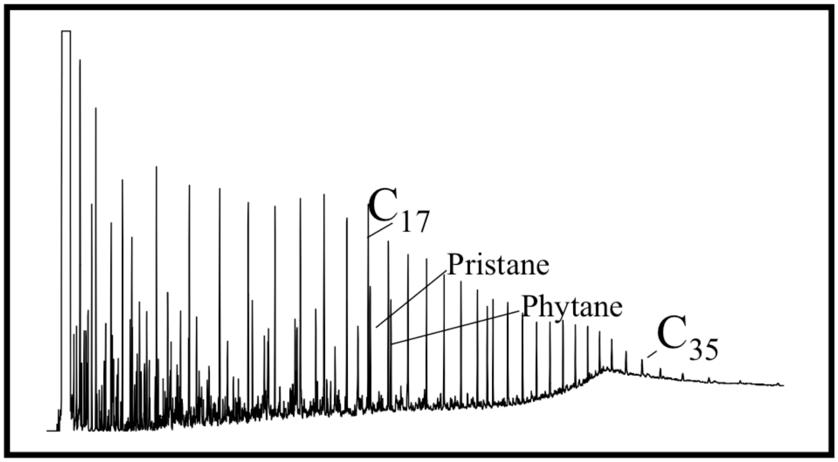
- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS

GCIRMS System



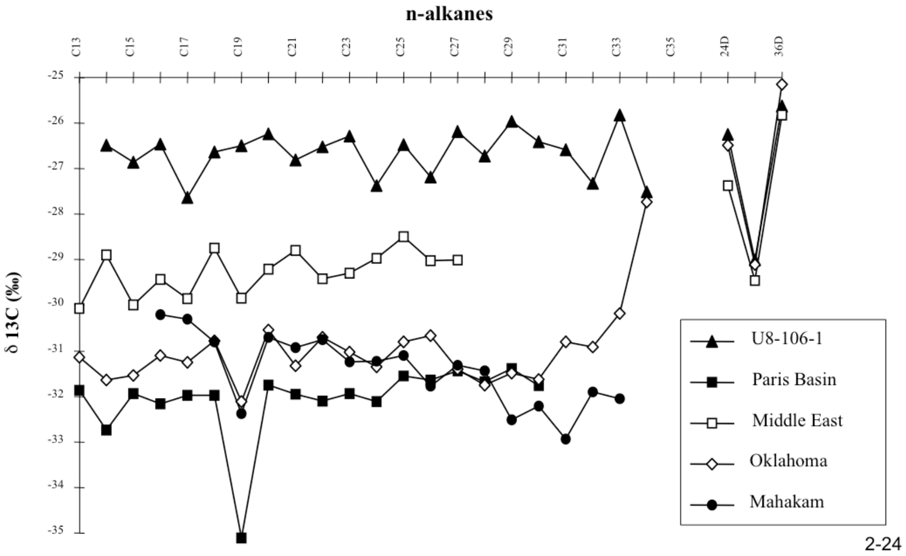
2-22

Crude Oil Chromatogram



2-23

GCIRMS DATA FOR SELECTED OILS

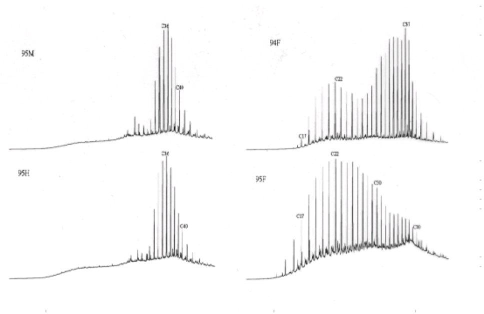


▫

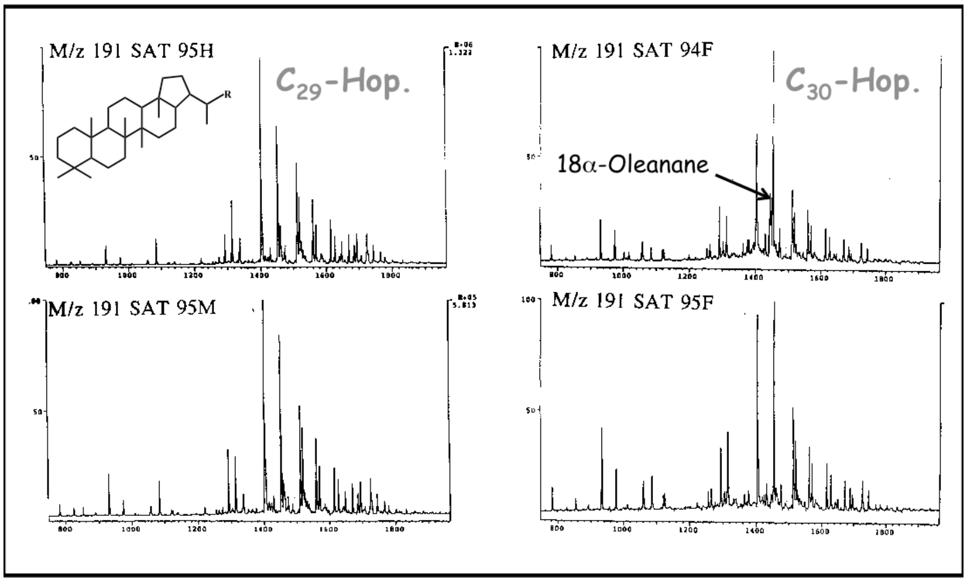
Hydrocarbon Spills and Weathering

- Major effects of weathering from a geochemical perspective are :
  - Evaporation
  - Water washing
  - Biodegradation

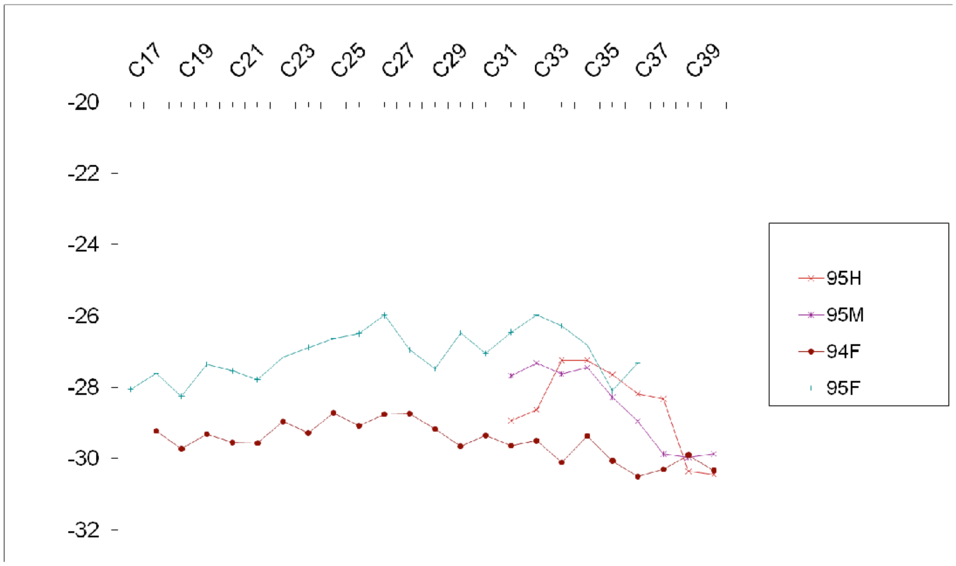
Tar Ball Chromatograms



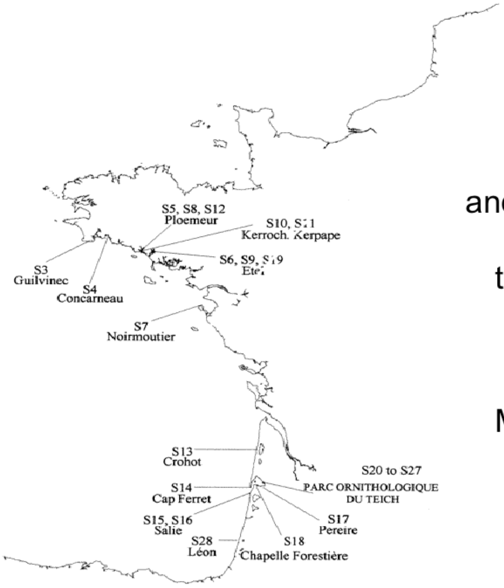
Terpanes in Tar Ball Samples



GCIRMS – Tar Balls



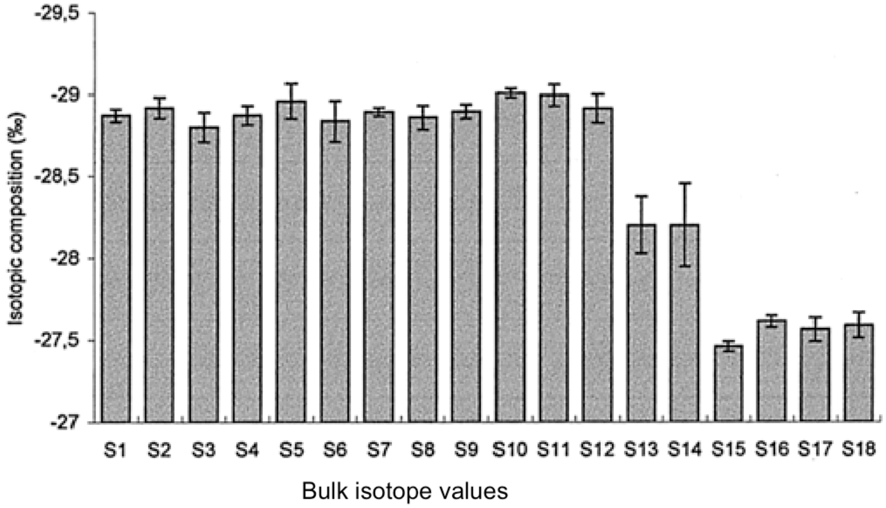
The Erika Oil Spill.



Sampling locations of oil residues and oiled bird feathers collected along the Atlantic Coast of France after the Erika oil spill.

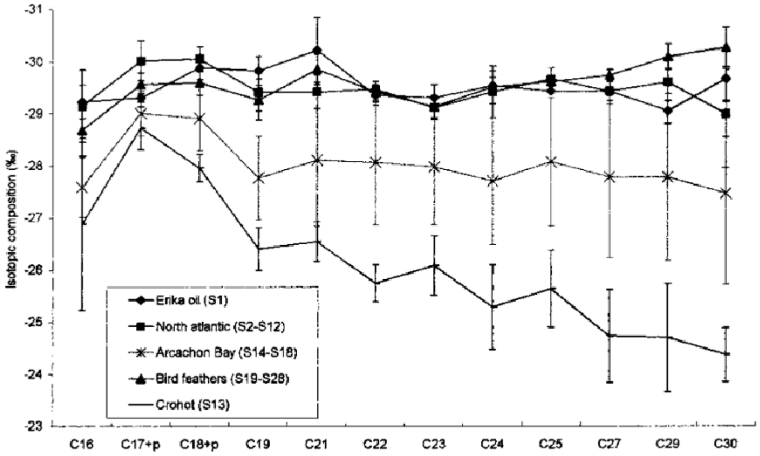
Mazeas et al., EST, 36(2), 130-137, 2002

The Erika Oil Spill.



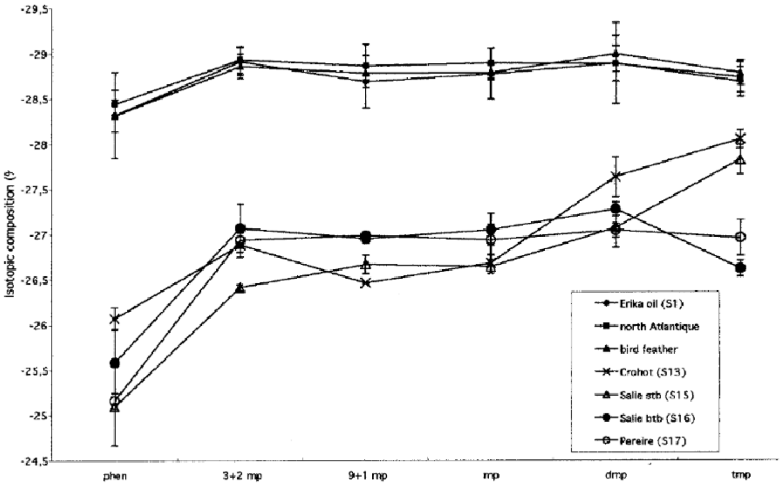
2-30

The Erika Oil Spill.



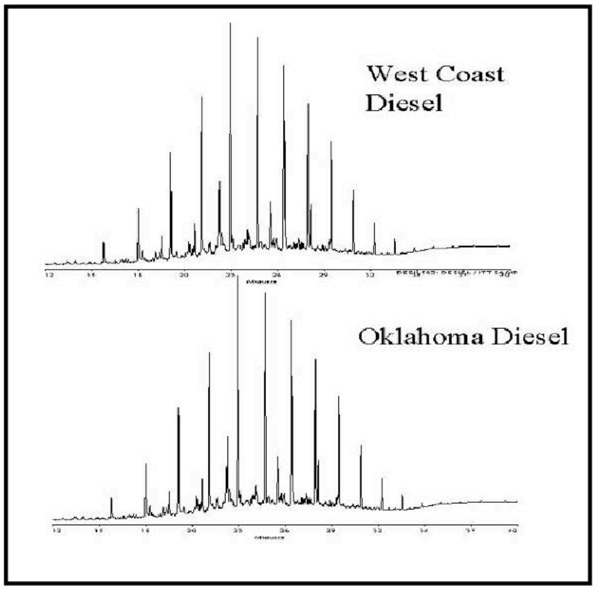
Molecular *n*-alkane isotopic compositions of the oil residues collected in the north Atlantic shoreline (mean of S2-S12), on the Crohot Beach (S13), in the Arcachon Bay area (mean of S14-S18), and of bird feathers (mean of S19-S28) are compared with Erika oil.

The Erika Oil Spill.

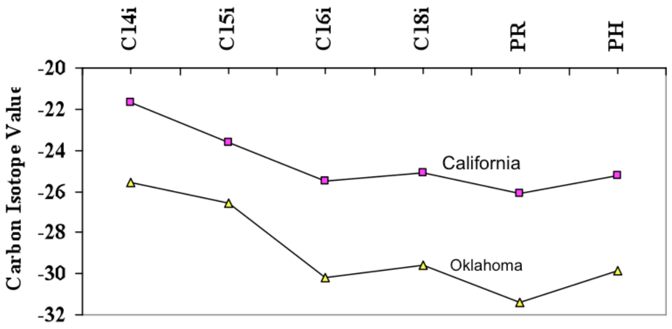


Compound specific isotopic composition of oil residues and oiled bird feathers collected along the Atlantic Coast of France compared with Erika oil isotopic composition.

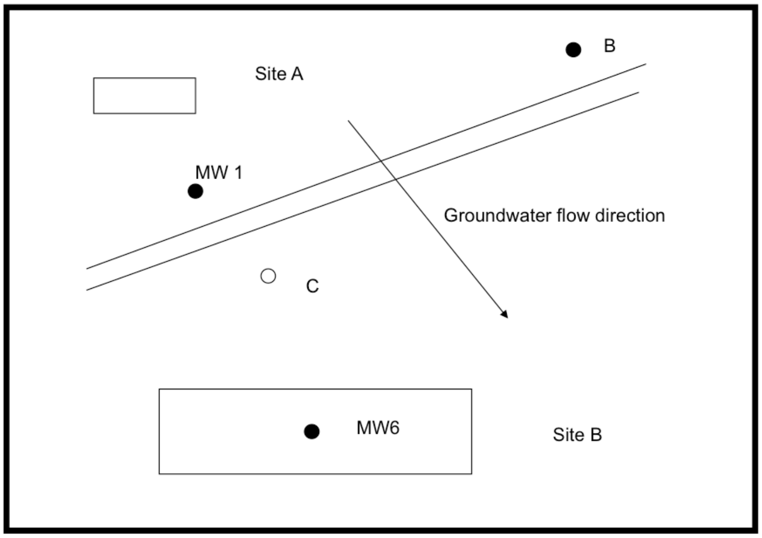
Diesel Fingerprints



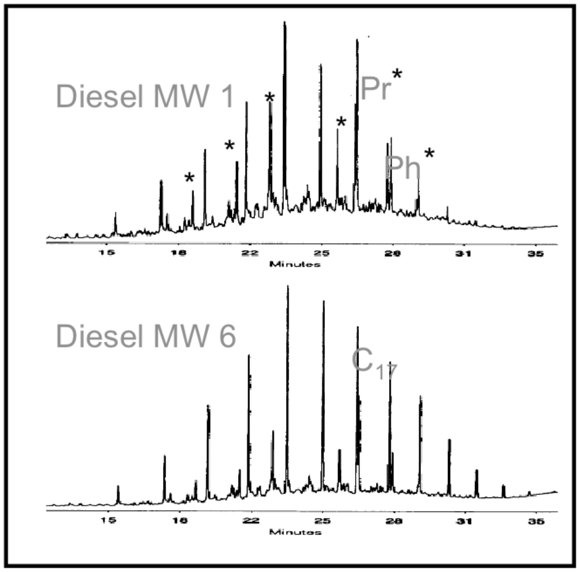
Isoprenoid Isotope Fingerprints



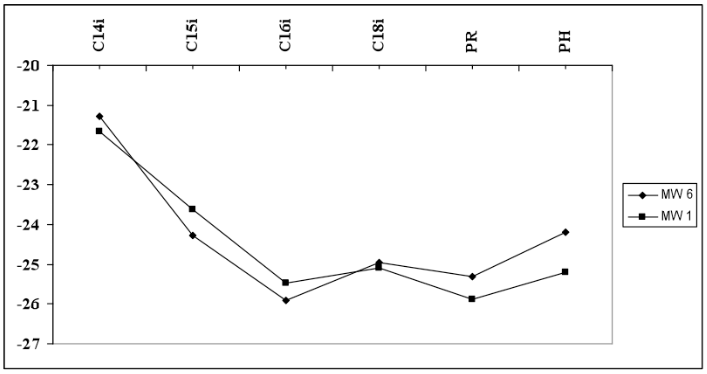
Forensic Geochemistry



Weathered and Unweathered Diesel



Carbon Isotope Values for Isoprenoids



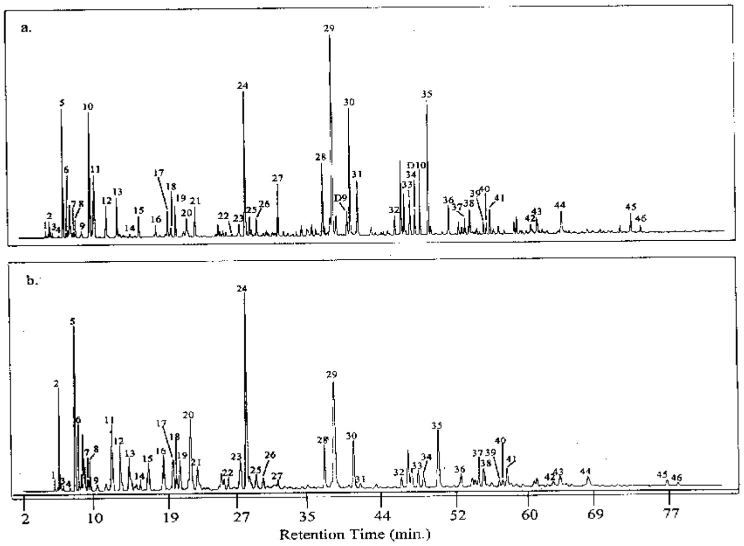
▫

Gasolines

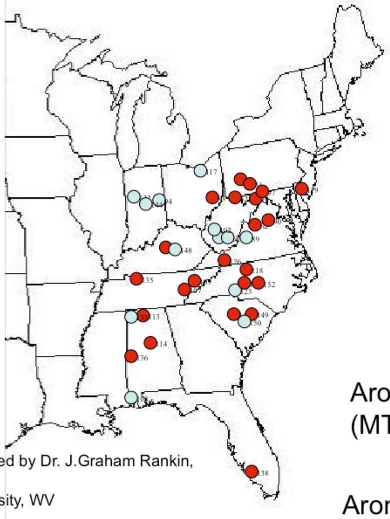
- Gasolines from different sources often have very similar chromatograms, making it difficult to distinguish such samples
- Gasolines are also devoid of biomarkers, further limiting correlation possibilities
- One solution here is to use GCIRMS for both the hydrocarbons and additives

This is another example of the advantage of using isotope compositions of individual compounds in gasolines. Again gasolines are chromatographically very similar even when coming from different sources. Hence GC and GCMS are of relatively little use in discriminating samples from different sources. However if the gasolines are derived from different crude oils it may be possible that the isotopic fingerprints can be used to differentiate the products.

Comparison of Gasolines by GC



Gasoline Database



Retail stations locations

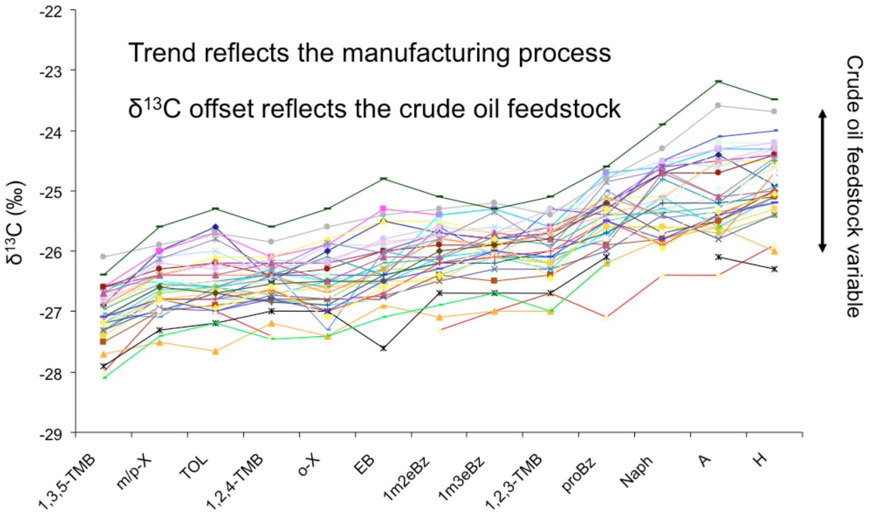
Aromatics $\delta^{13}C$ + dD, oxygenates (MTBE, TBA) ●

Aromatics $\delta^{13}C$ only ○

Samples provided by Dr. J.Graham Rankin,

Marshall University, WV

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

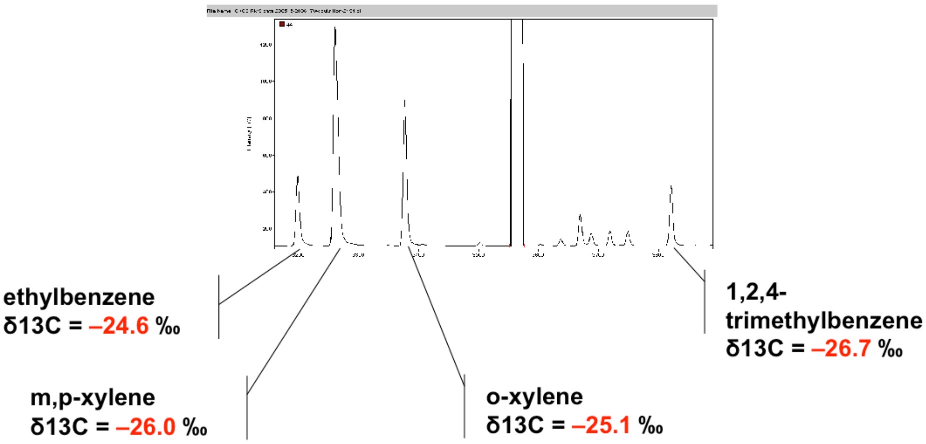


Trend reflects the manufacturing process

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

Crude oil feedstock variable

CSIA of Gasoline



ethylbenzene
δ13C = –24.6 ‰

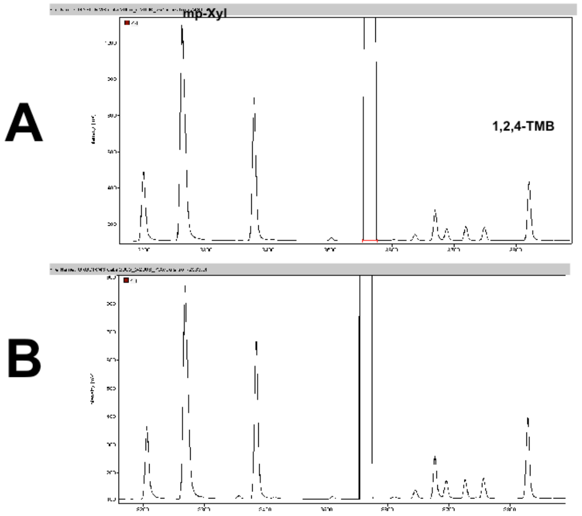
m,p-xylene
δ13C = –26.0 ‰

o-xylene
δ13C = –25.1 ‰

1,2,4-
trimethylbenzene
δ13C = –26.7 ‰

In a previous slide the bulk isotope values for a brand A and brand B gasoline were given. However these bulk values are the weighted averages of the isotopic compositions of all the individual compounds in the gasolines. Here is a portion of a gasoline chromatogram that has been analysed by GCIRMS and the isotopic compositions of several individual compounds are shown. The variations in these individual compounds highlights the fact that the isotopic fingerprint potentially provides another tool that can be used to differentiate products from different sources providing far more specificity than the bulk values alone.

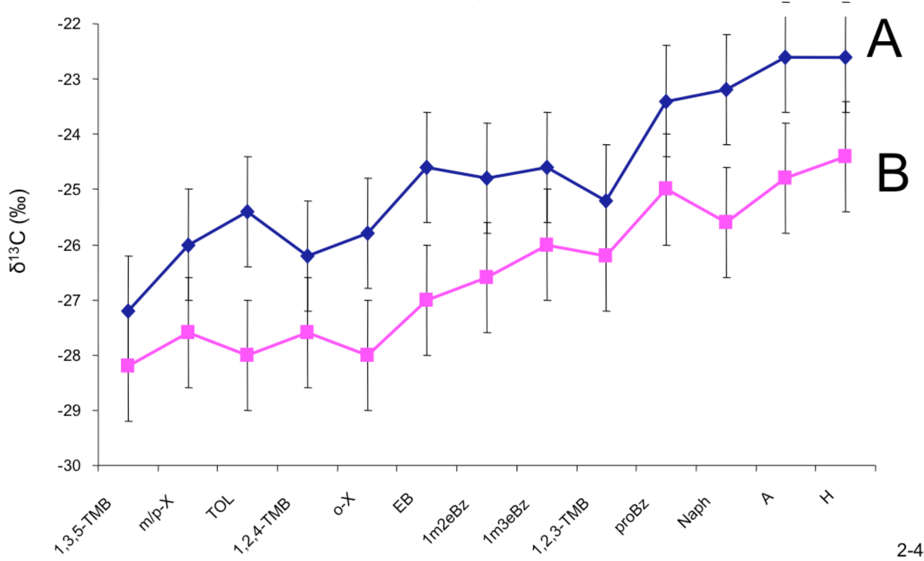
Gasolines – GC Signals



2-43

Partial chromatograms showing the similarity in these two gasoline products.

Gasolines – Different $\delta^{13}C$ Fingerprints



2-44

PCE Degradation Site Study

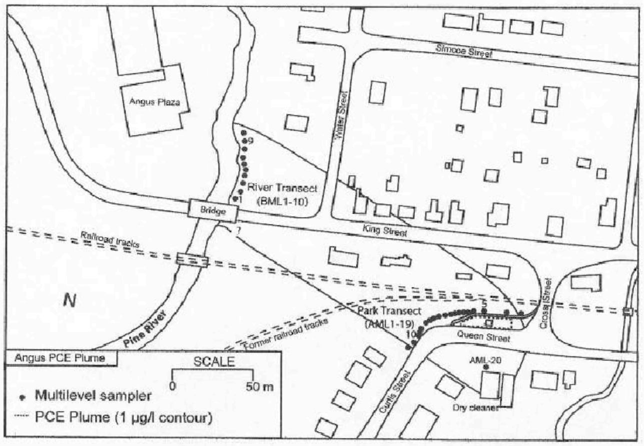
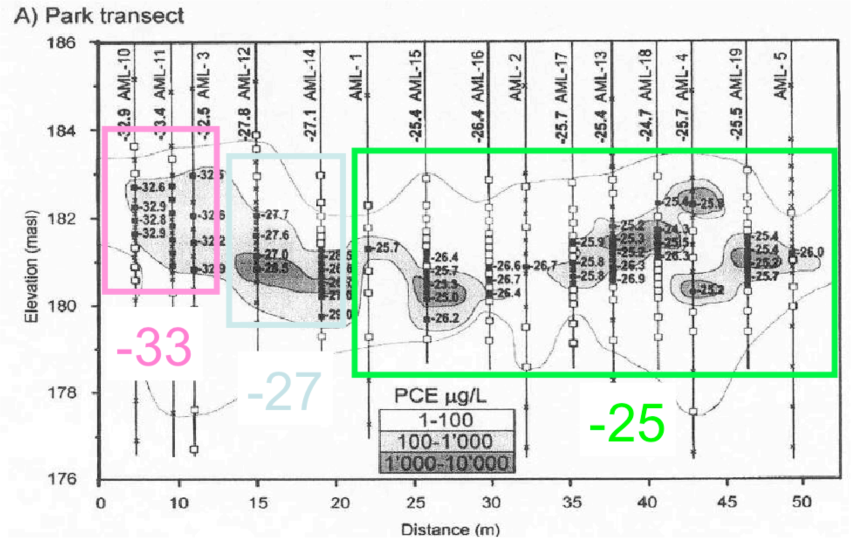


Fig. 2. Map of Angus field site with locations of multilevel samplers (circles) at park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

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

□

PCE Source Evaluation Study



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

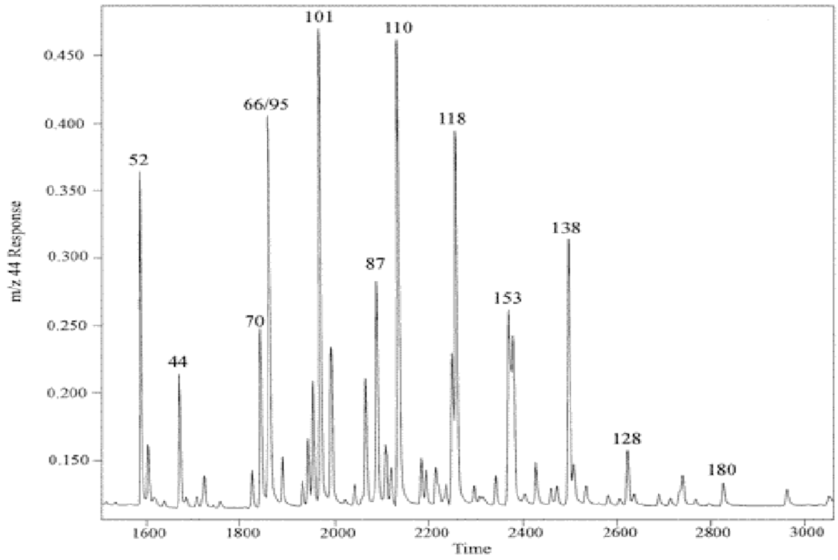
The cross section close to the source shows that now instead of one homogeneous source there are three isotopically distinct sources across the transect. These three may represent multiple sources or multiple releases from the same source. These variations did not result from biodegradation since no degradation products were observed.

▫

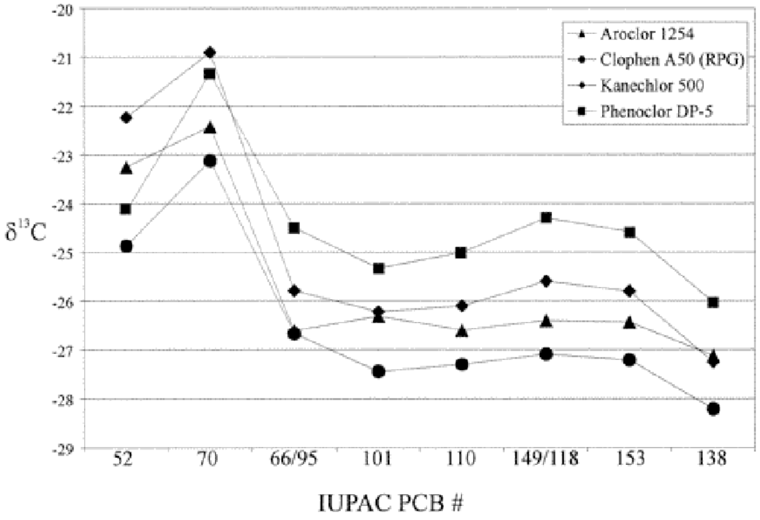
PCBs

- Study by Yanik et al., *OG*, 239-253, 34, 2003 showed that different Aroclors may be isotopically different and thus useful for source discrimination although there is some slight enrichment from degradation.

M/z 44 Chromatogram for Aroclor 1245



Variations in Isotopic Composition of Various Congeners



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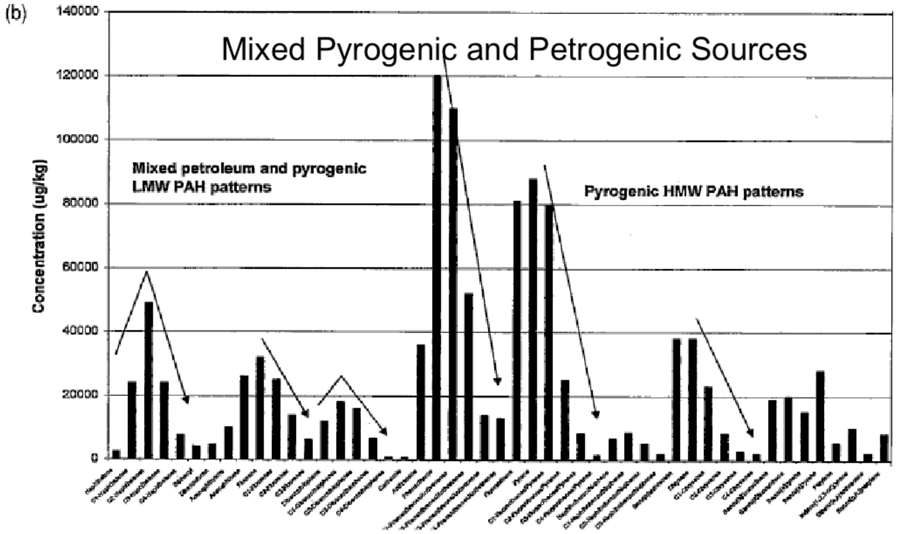
PAHs and Stable Isotopes

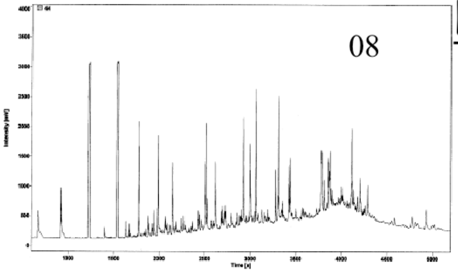
- Current interest is centered around whether carbon isotopes can be used to discriminate PAHs derived from former manufactured gas plant (MGP) wastes versus those from general urban background aromatics
- Urban backgrounds have a fairly narrow range and small differences may be related to source differences

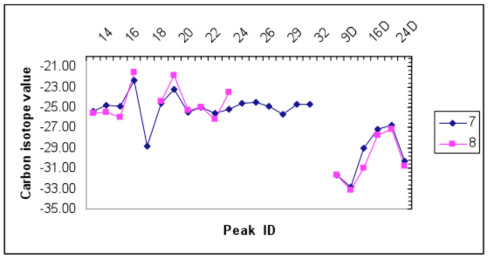
Sources of PAHs to Urban Background

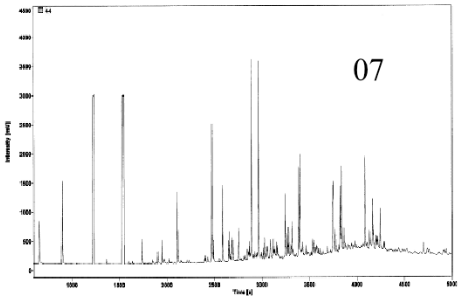


2-51

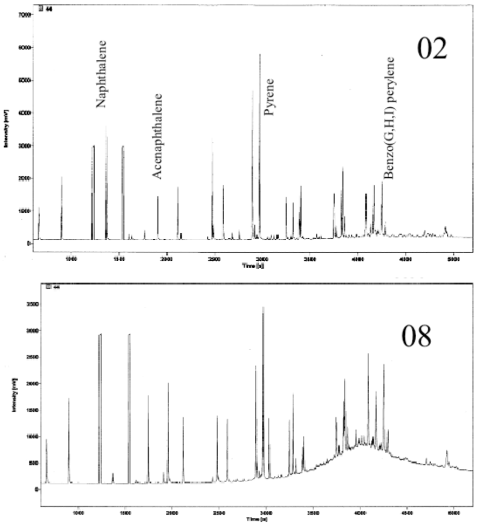
PAHs-Combined GC and GCIRMS Data

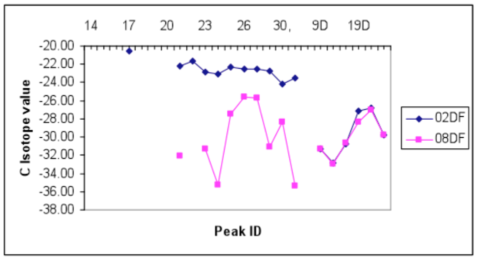




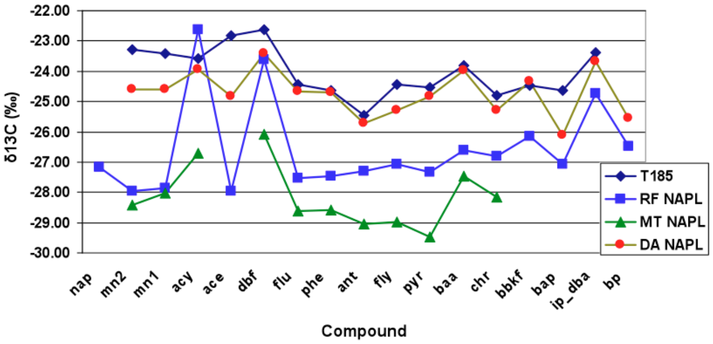


PAHs-Combined GC and GCIRMS Data

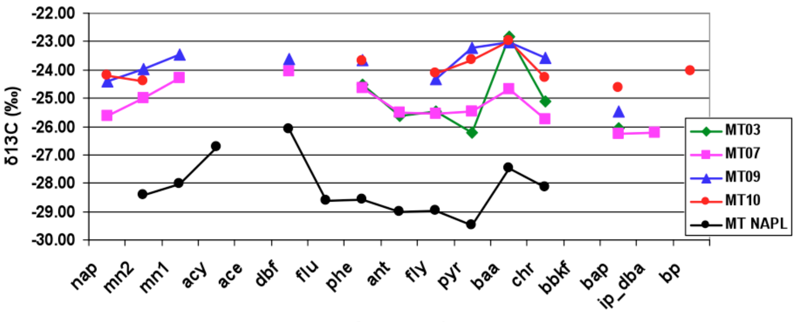




CSIRs of NAPL Samples



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

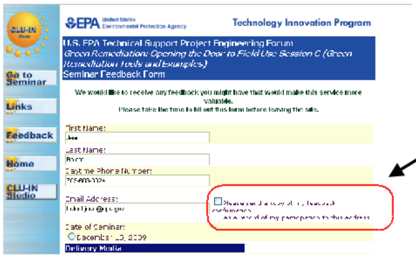
Summary

- Environmental Forensics combines a variety of analytical tools to typically provide information on origin and state of contaminants in the environment.
- One of these tools involves utilization of stable isotopes.
- In some situations stable isotope data compliments other analytical data. In other cases may be only tool available.

2-56

Resources & Feedback

- To view a complete list of resources for this seminar, please visit the **Additional Resources**
- Please complete the **Feedback Form** to help ensure events like this are offered in the future



U.S. EPA Technical Support Project Engineering Forum
Green Remediation: Opening the Door to Field Use Session C (Green Remediation Tools and Examples)
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