

The Added Value of Stable Isotopes in Environmental Forensic Investigations.

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Introduction and Overview

- Introduction
- Environmental Forensics
- Stable Isotopes
- Vapor Intrusion
- Fate and transport modeling
- Summary

Environmental Forensics

- The basic questions:
 - What is it?
 - Where did it come from-point of release?
 - When was it released?
 - Is it degrading and/or how quickly is it degrading?

Environmental Forensics

- **Two basic schools of thought:**
 - EPA methods. However these methods are for the most part useless in terms of forensic investigations.
 - For environmental forensic investigations a far more detailed and comprehensive approach is necessary than simply determining concentrations of target compounds. The approach involves using a variety of techniques and very detailed fingerprinting of compounds or compound classes, many of which are not even on the list of EPA target compounds.

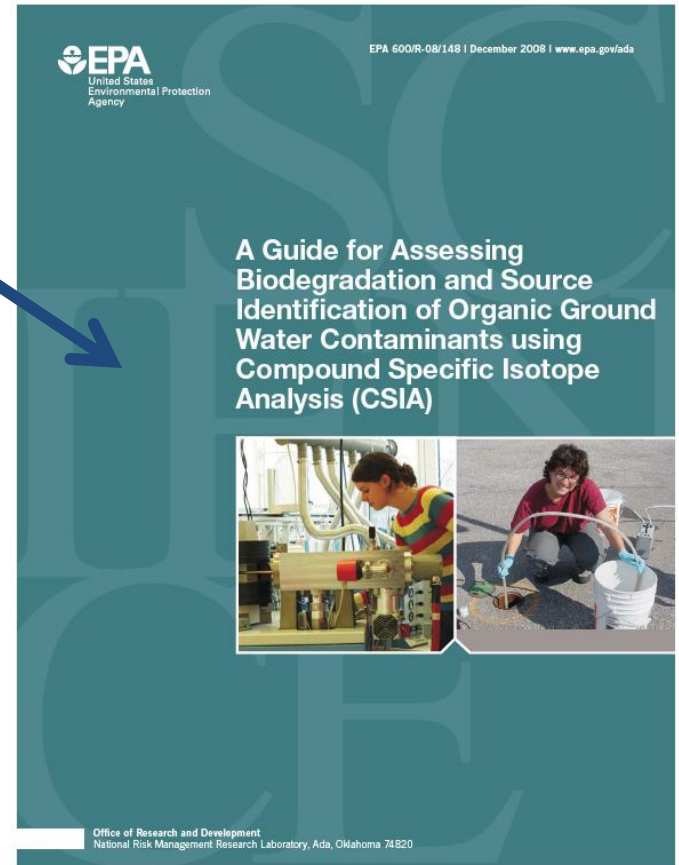
Environmental Forensics

- Important analytical techniques for organics:
 - Gas chromatography (GC)
 - Gas chromatography-Mass Spectrometry (GCMS)
 - GCGCTOFMS;GCMSMS;
 - Gas chromatography-isotope ratio mass spectrometry (GCIRMS-C;H;Cl;N;S).

CSIA in Ground Water Contaminant Studies

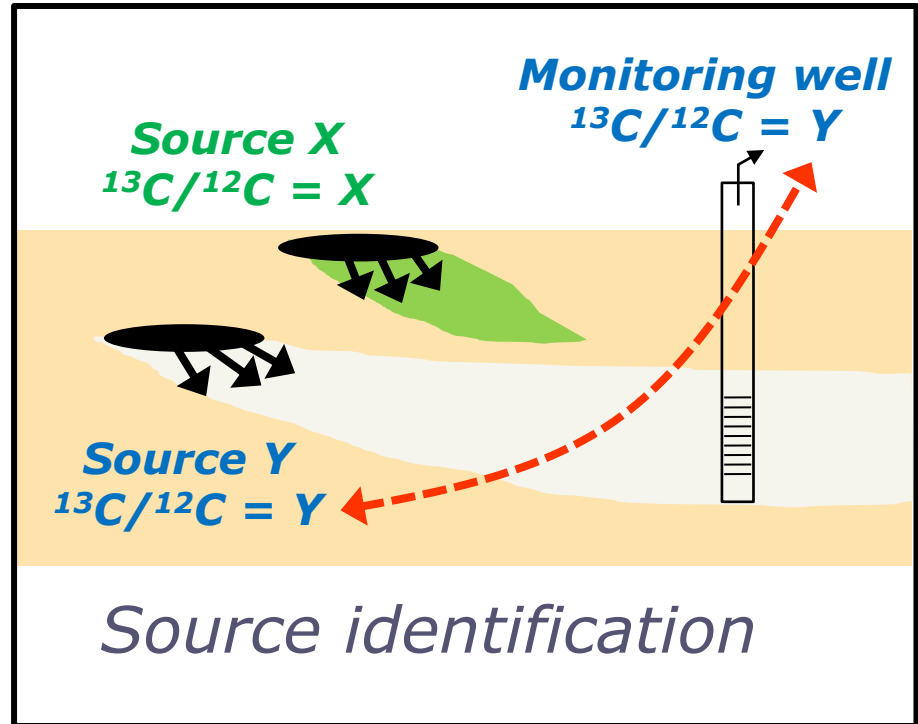
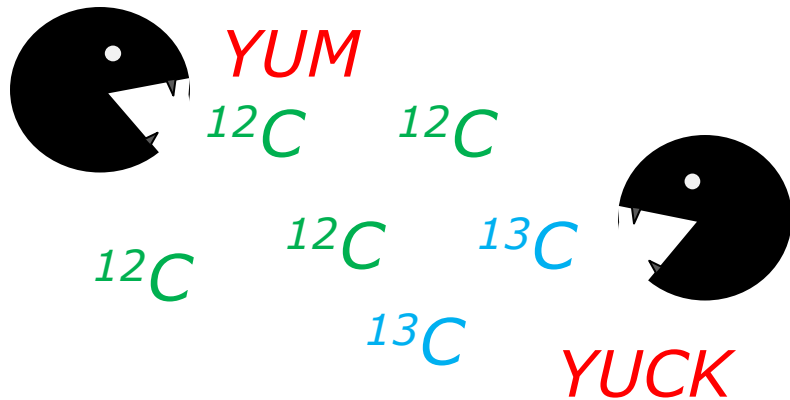
CSIA is established in ground water contaminant work, with large number of peer-reviewed publications and industry applications.

CSIA applications fairly novel in vadose zone and vapor phase contaminant studies: several peer-reviewed papers to date



Stable Isotopes-Major Applications

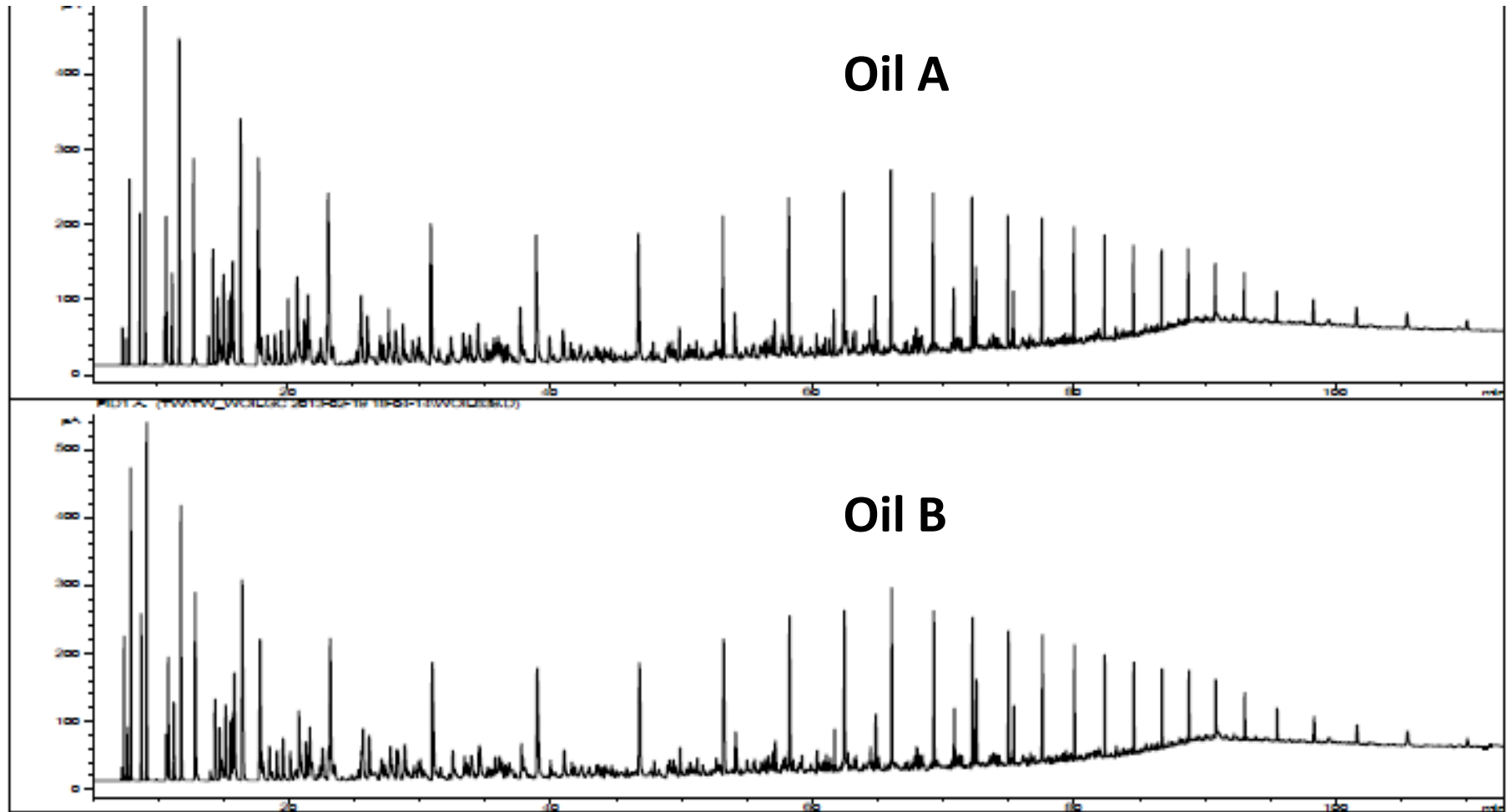
*Assessment of
in-situ degradation*



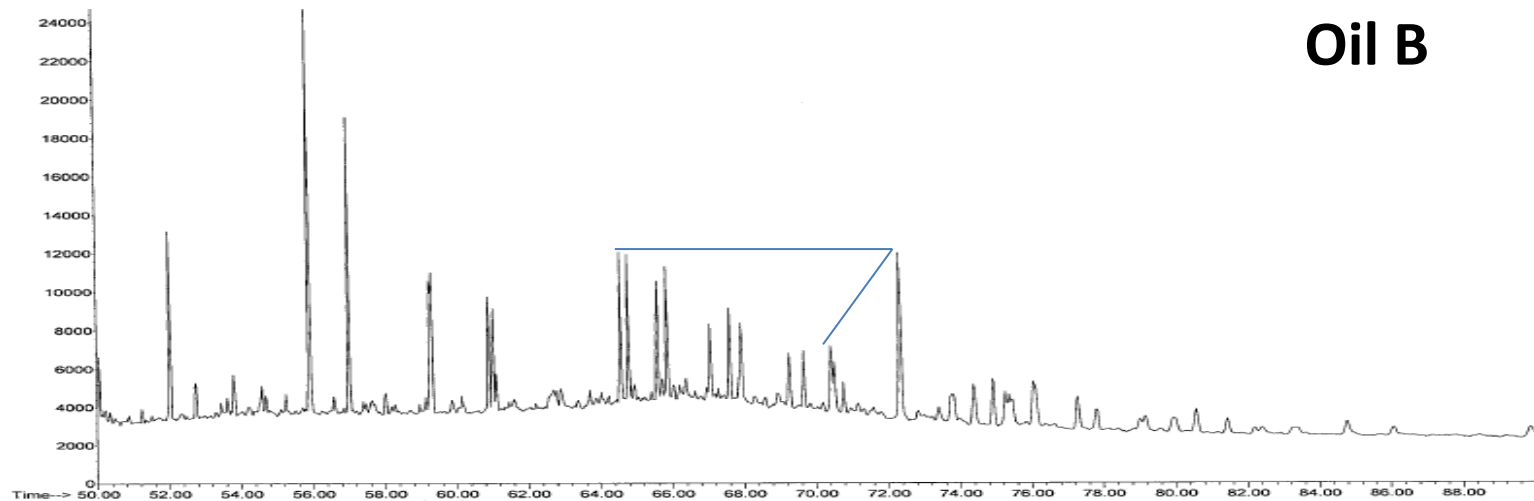
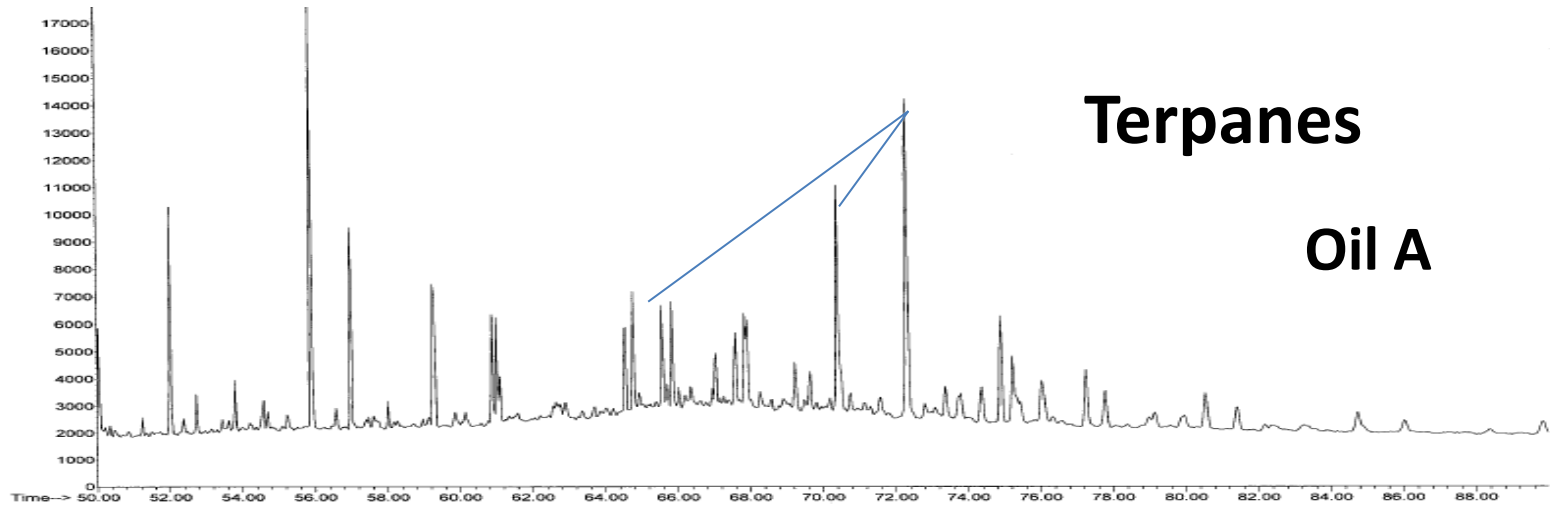
Environmental Forensics

- **Biomarkers**-a detailed understand of these compounds can provide significant information that may not be obvious to the in-experienced investigator.
- Many people have heard enough about steranes, terpanes and isoprenoids to be dangerous.
- Not possible to routinely determine stable isotope values of individual biomarkers.

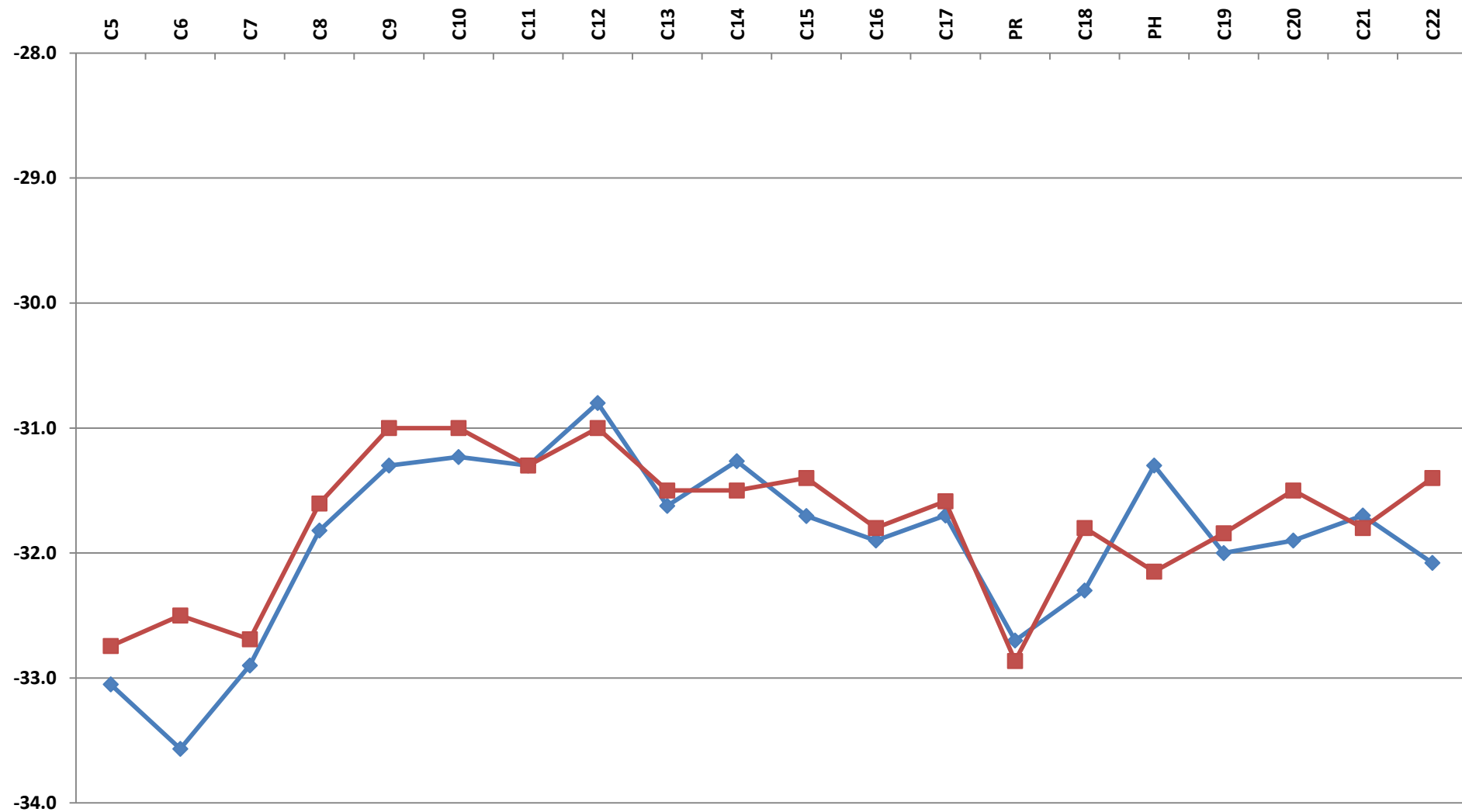
Oil/Oil Correlations



Biomarker Fingerprints

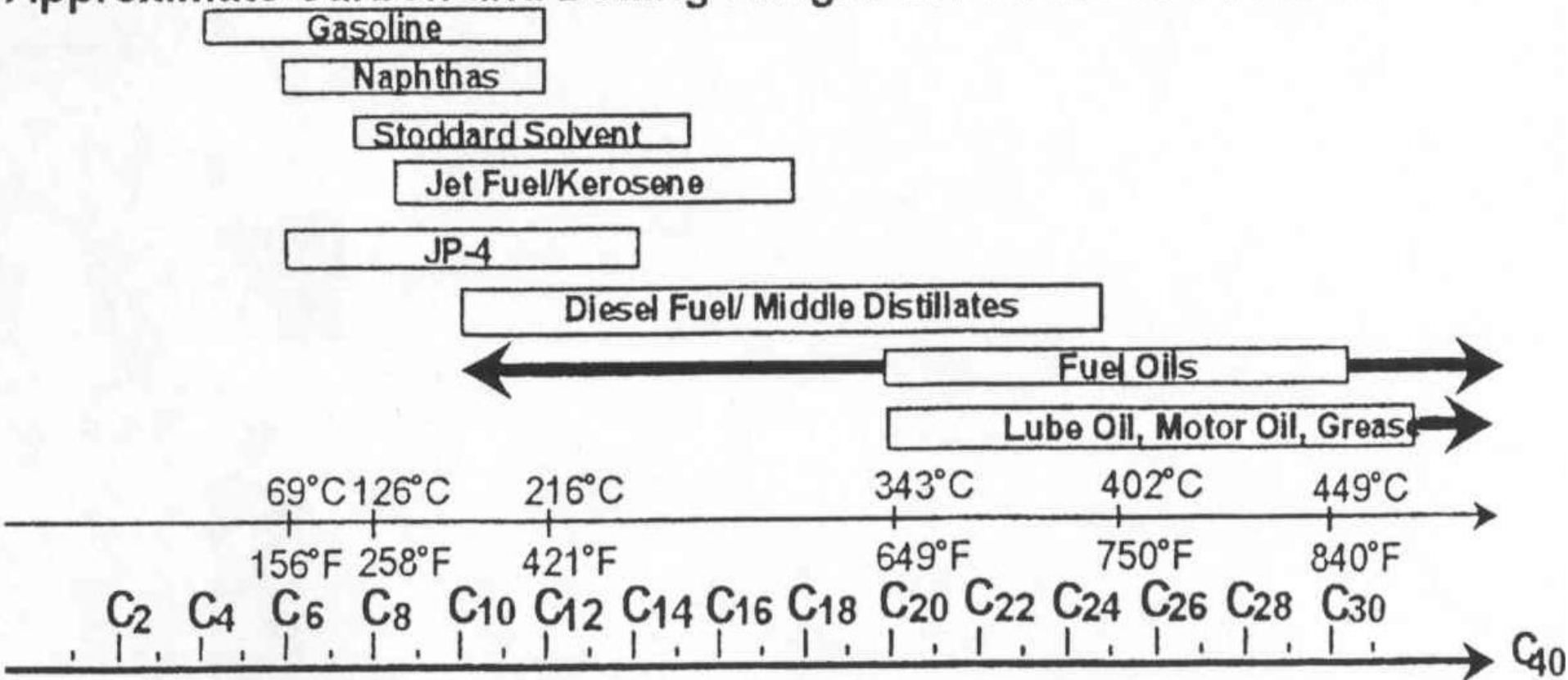


CSIA Oil/Oil Correlations

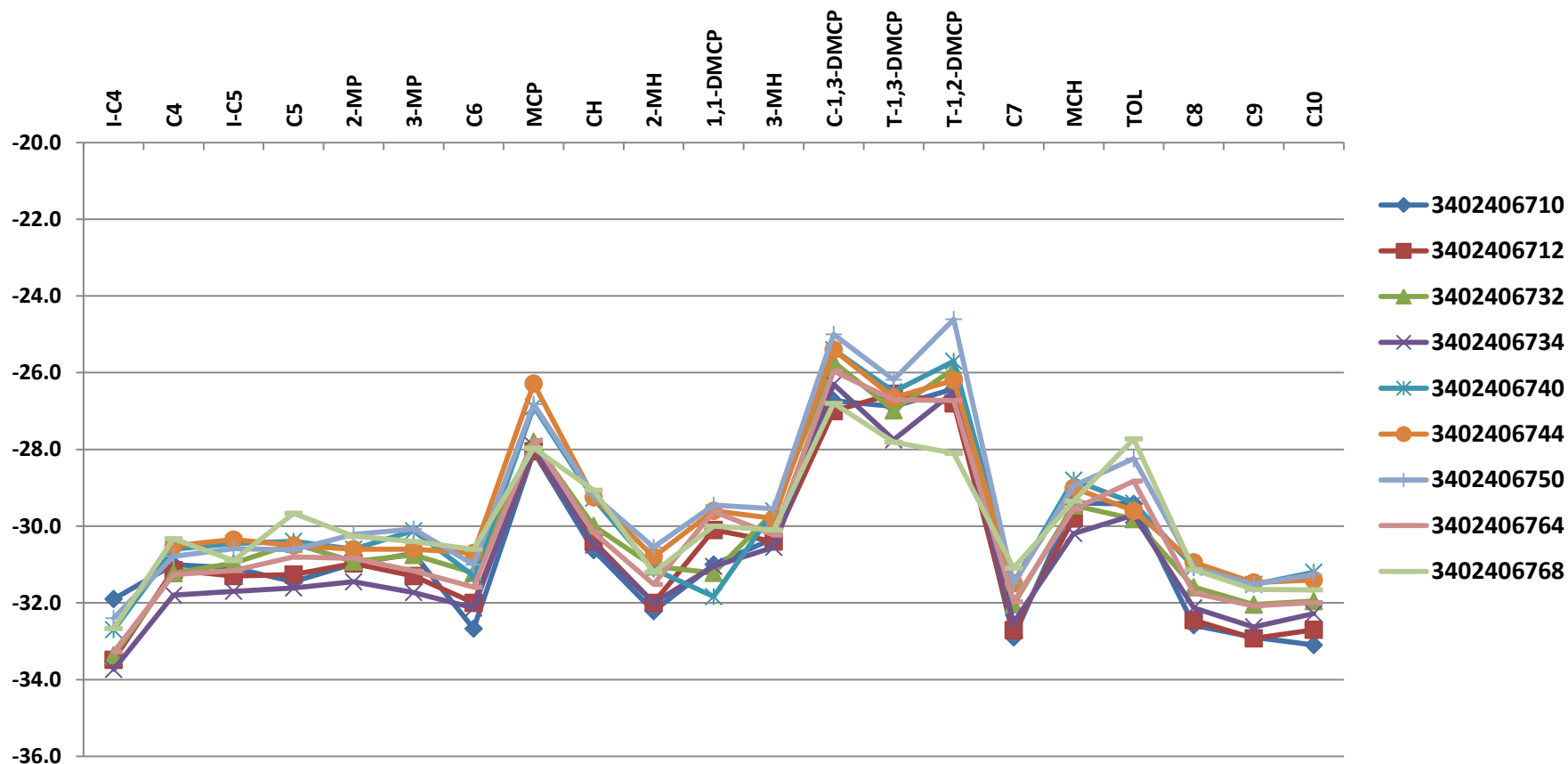


Carbon Number Distribution of Hydrocarbon Products

Approximate Carbon and Boiling Ranges of Petroleum Products



Correlations using C₇ Components

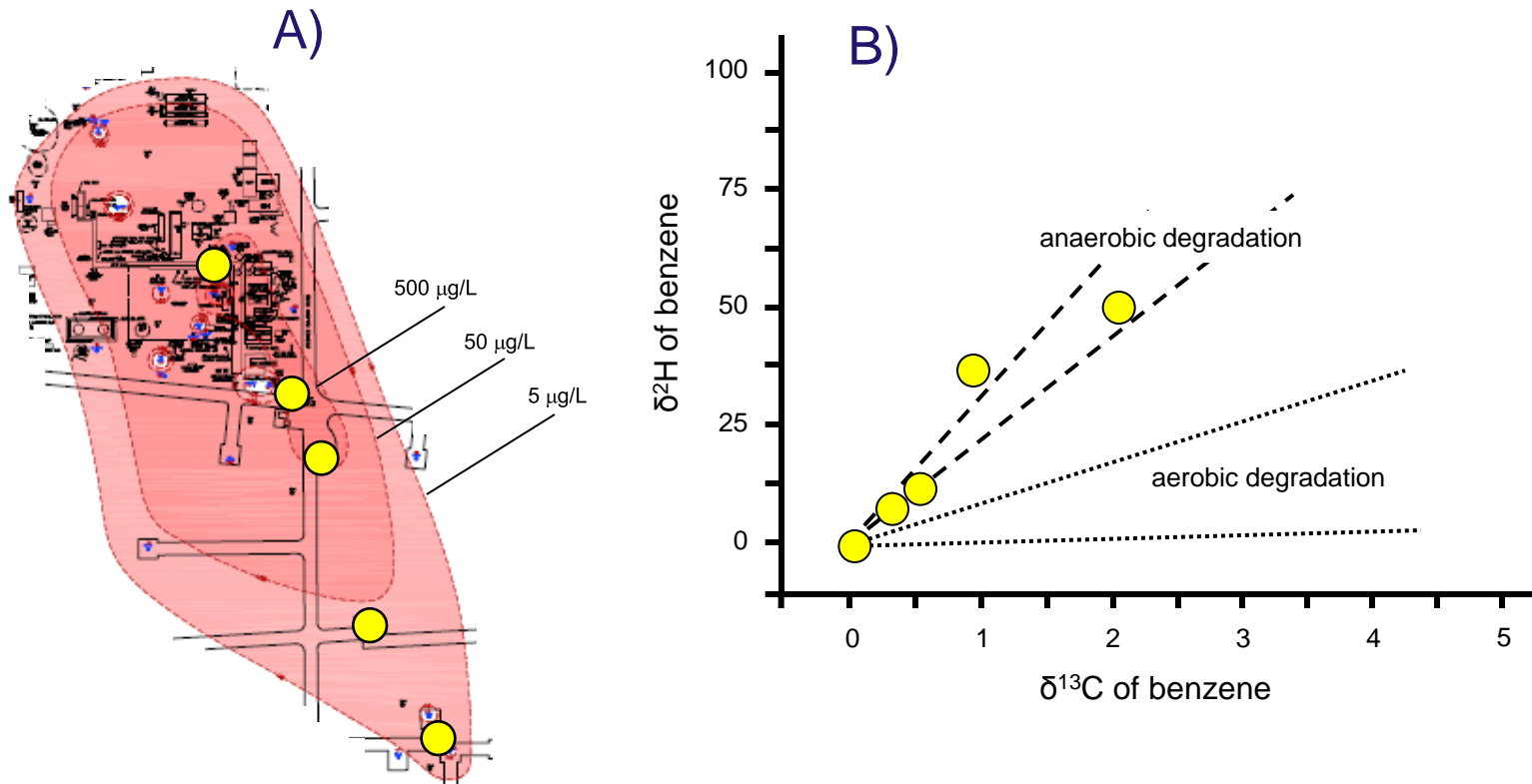


Stable Isotopes

- **Where they will not work at this time:**
 - If you cannot see the compound on the GC trace cannot get an isotope number.
 - Age dating.
 - Identifying manufacturers of spilled products.
 - Spilled product and source may be isotopically similar but that does not necessarily prove they are related. If isotopically different, and not biodegraded, then probably not related.
 - Isotopically light TCE not necessarily produced in environment by reductive dechlorination

2D-CSIA Discrimination of Benzene

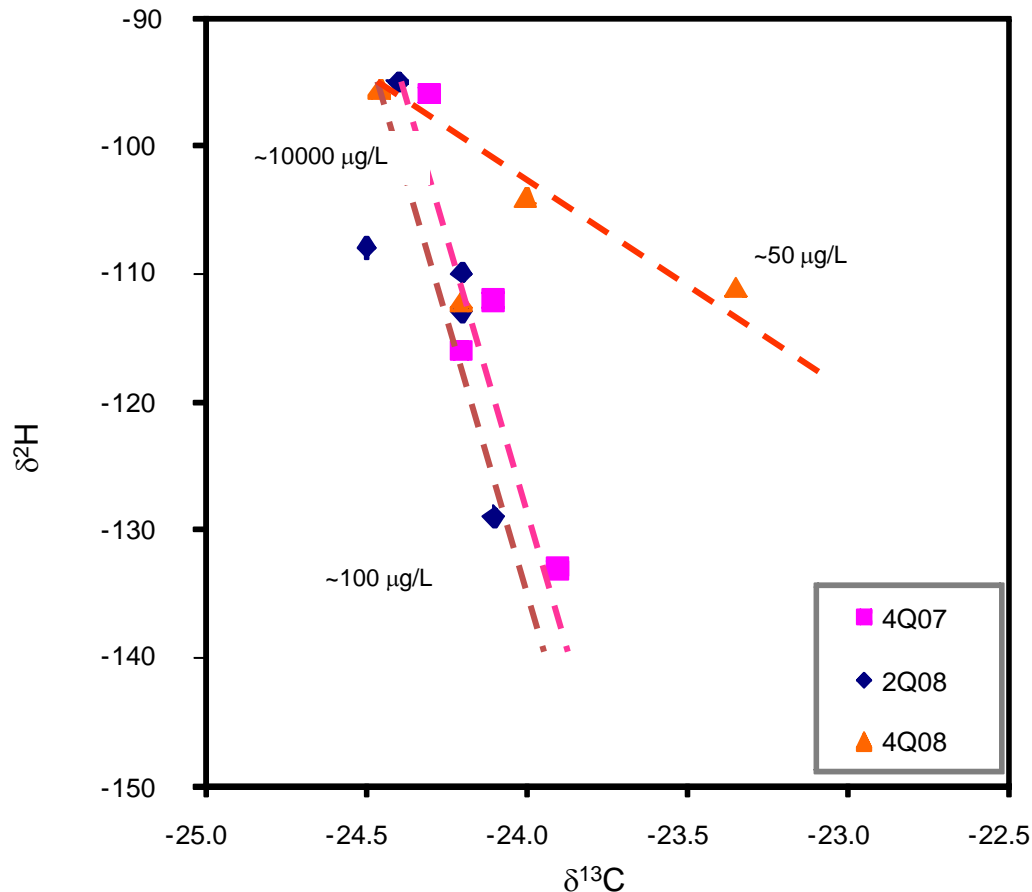
Degradation Pathways



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.

2D-CSIA Discrimination of Benzene

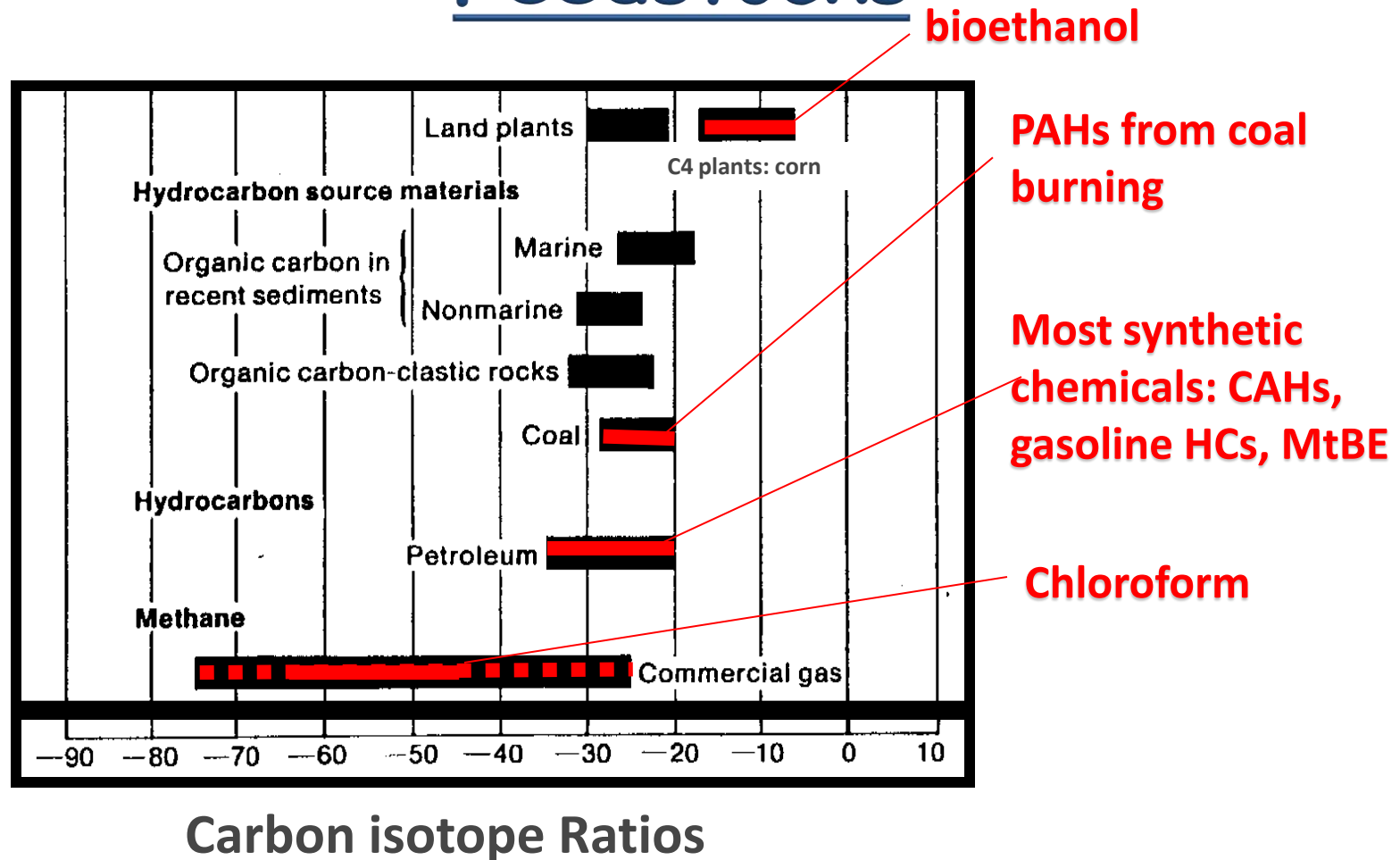
Degradation Pathways



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

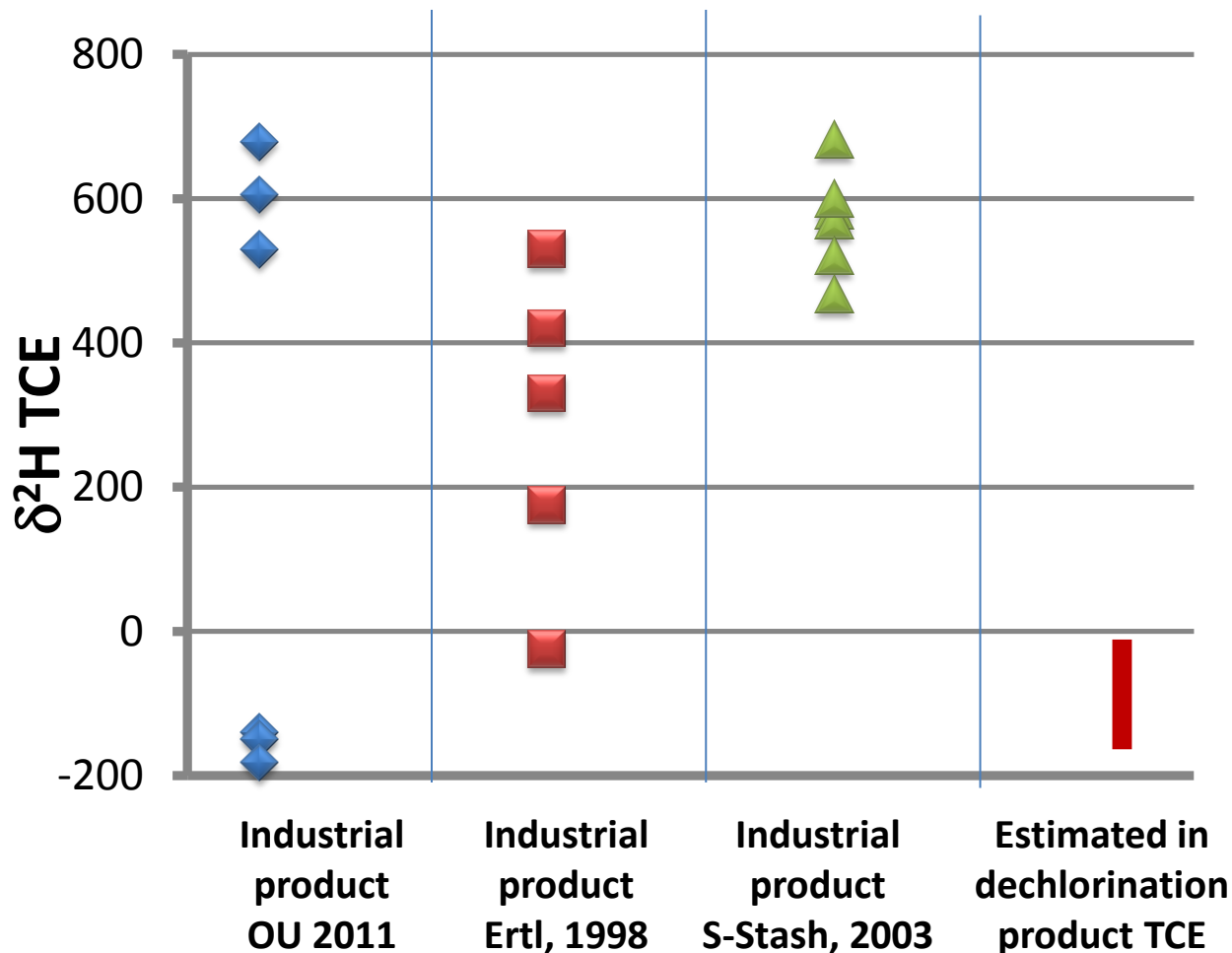
Vapor Intrusion

The Isotopes in Manufactured Chemicals are Inherited from Synthetic Feedstocks

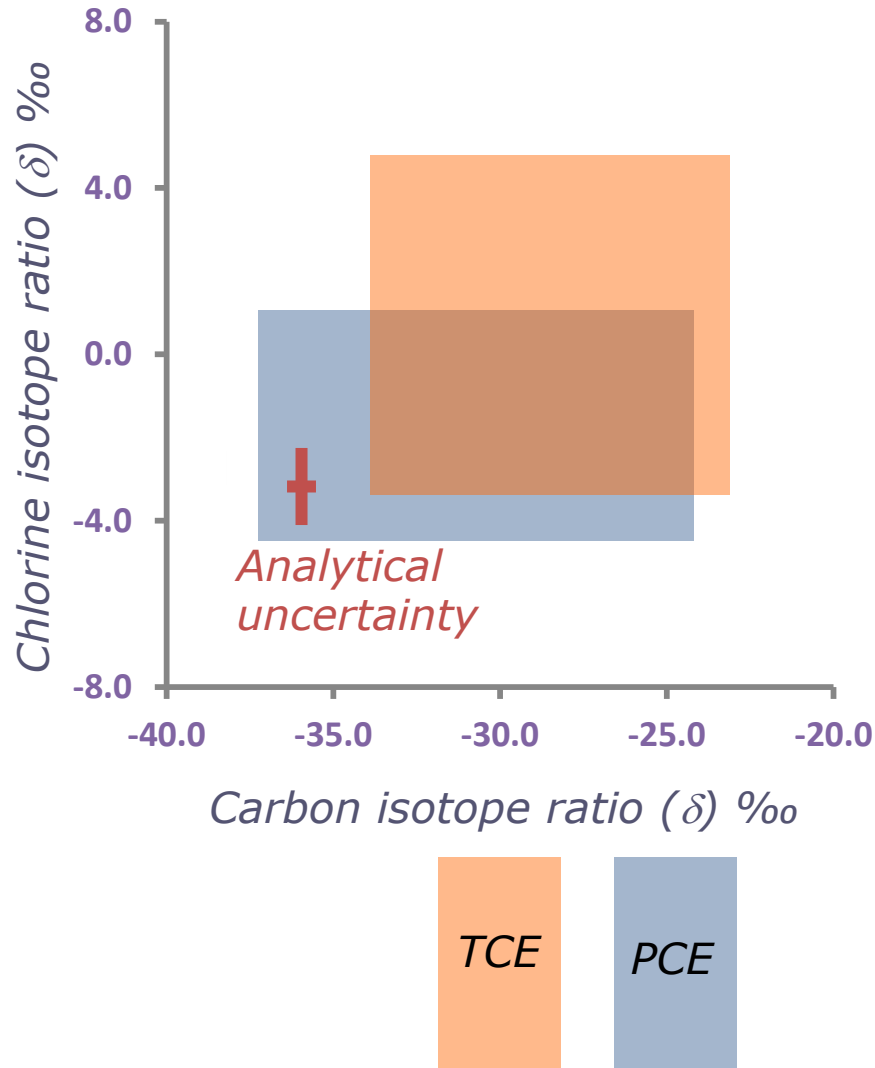


H Isotope Ratios of Manufactured TCE

(Source or PCE Degradation)



Indoor Sources: Narrow Range of Isotope Ratios



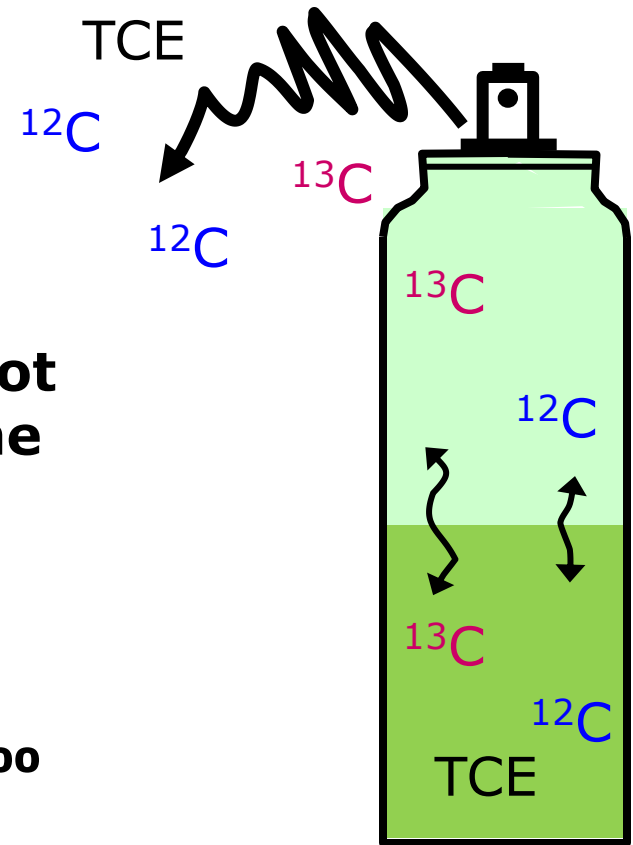
Isotope ratios of undegraded VOCs tend fall within a relatively narrow range of values.

Isotope ratios of vapor emanating from an indoor source are near-identical to those of the source (\pm phase change effects).



VOCs Isotope Ratios in Vapor Emitted from Consumer Products: Minor Depletion of ^{13}C , Moderate depletion of ^{37}Cl

- ★ Molecules with different isotope substitution differ in their partitioning and diffusion coefficients
- ★ Vapor escaping from a closed product can will be similar but not identical to the product inside the can.
- ★ Expect that vapor evolving from an indoor source will show a $< 1\text{‰}$ depletion of $\delta^{13}\text{C}$ and 1-2 ‰ depletion of $\delta^{37}\text{C}$

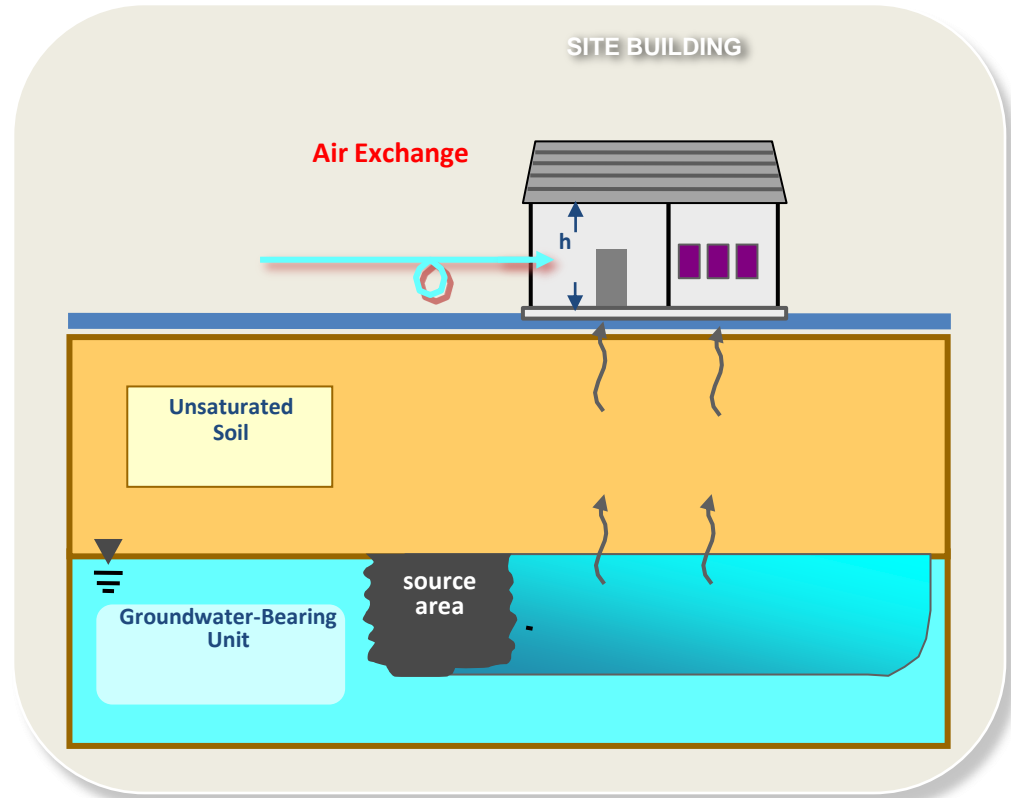


Problem Statement

In vapor intrusion (VI) management, VOCs of interest may also originate from household products (solvents, glues etc.)

VI assessment is complicated by the indoor sources of VOCs

Can we use stable isotopes to distinguish the indoor and subsurface sources?



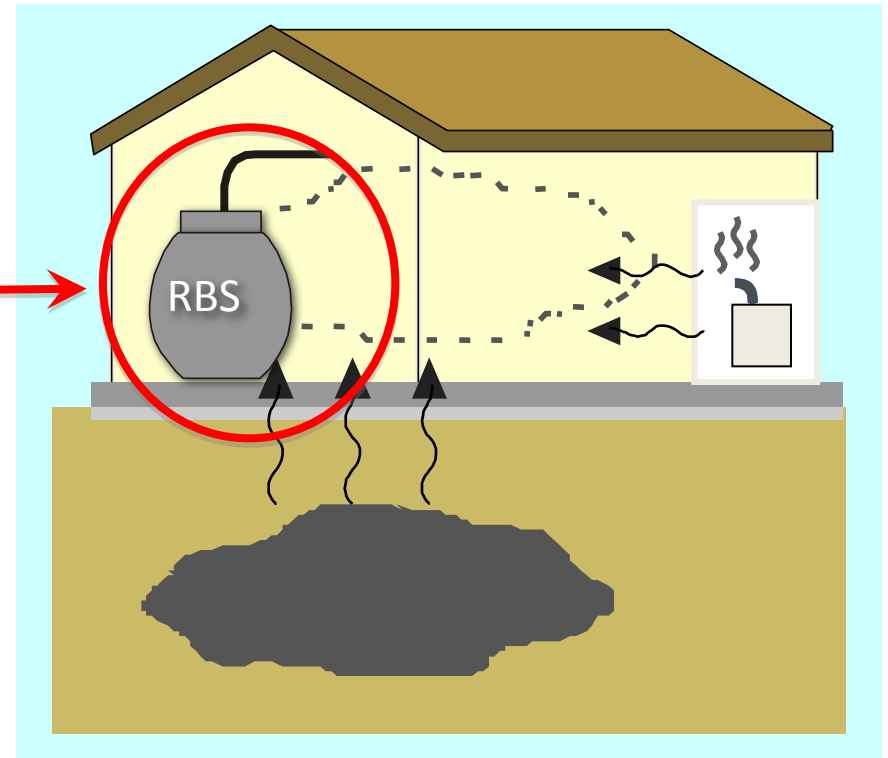
Technical Challenge of CSIA Application to VI Sites

Need >75 ng of TCE or PCE to get accurate C stable isotope ratio measurement.

Need 75 L sample at 1 $\mu\text{g}/\text{m}^3$ conc.

*Really
Big
Summa*

*Sampling challenge met by application of **active sorbent samplers**.*

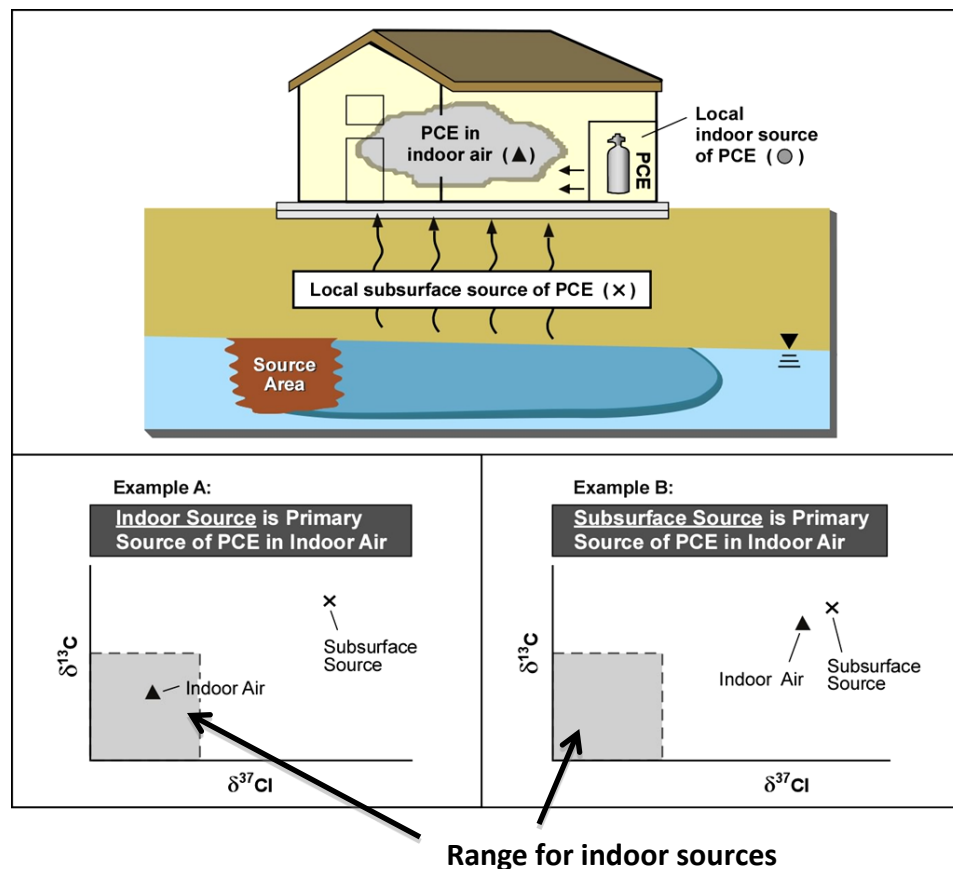


The Rationale of Using Isotope Ratios of VOCs in VI Source Discrimination

CSIA permits determination of isotope ratios (C, Cl, H) in target VOCs

Isotope ratios compared between indoor and subsurface sources and indoor air.

Predominant VOCs sources identified by their difference/similarity to the indoor air VOCs.



Isotope Ratio Analysis: Detection Limits

(Based on recent OU methodology for adsorbent tube samples)

Carbon and/or Chlorine CSIA

TCE, PCE ~75 ng

Benzene ~15 ng

Hydrogen CSIA

TCE ~ 2.5 µg

Benzene ~ 1 µg



CSIA detection limits require preconcentration of the target VOCs from relatively large volume of air (esp. indoor or ambient air)

CSIA of Chlorinated Ethenes: Detection Limits for High-Precision CSIA

(based on recent OU methodology for aqueous samples)

Carbon and Chlorine CSIA

VC 1 ug/L

DCE, TCE, PCE 1 ug/L*

Hydrogen CSIA

VC, DCE 10 ug/L

TCE 30 ug/L

* 0.5 ug/L if larger volume of sample is available

Technical Challenges of CSIA

Application to VI Sites

★ Very complex mixtures: 2D-GC is required (C CSIA)

★ Vapor samples have to meet the method detection limits. VOCs have to be recovered from large air volume (logistics!)

C and/or Cl CSIA

TCE, PCE ~ 50 ng

Benzene ~ 20 ng

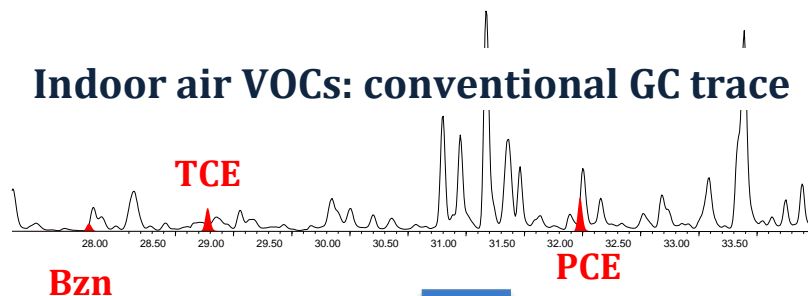
Hydrogen CSIA

TCE ~ 2500 ng

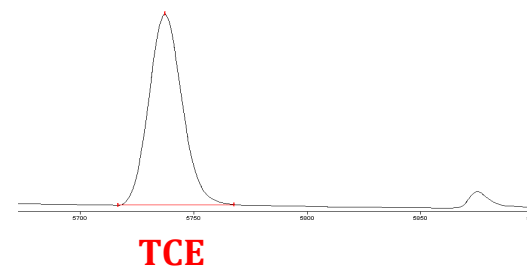
Benzene ~ 500 ng

(based on recent OU methodology)

Indoor air VOCs: conventional GC trace



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



Technical Challenge: The Need for Validation of Adsorbent Performance for CSIA

Adsorbent tubes for thermal desorption can be used to extract VOCs from air. Relatively easy to implement in routine sampling.



If target analyte breaks through in sampling or is not completely desorbed, there is a possibility of isotope fractionation.

Total sample volume; Pump flow rate; Adsorbent tube storage; Humidity; Non-target VOCs can affect target retention and recovery.

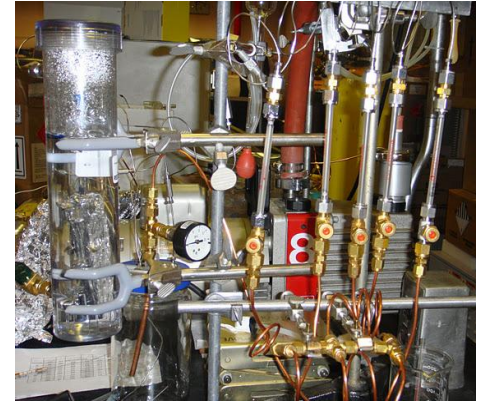
Adsorbent Testing Approach: Simulate Worst-Case Sampling Scenarios

Performance Objectives

Fractionation-free recovery of TCE, PCE and benzene from up to 100 L of air.

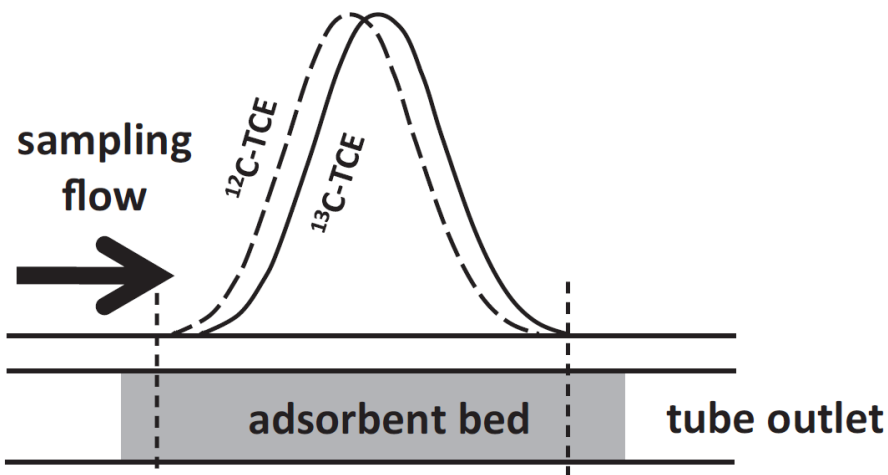
Good performance for “difficult” sampling conditions, including maximum air volume and competitive adsorption. All analyte added at T=0 and subject to maximum air volume flushing.

Good performance for different combinations of air volume/water vapor/non-target VOCs/target VOCs loading.

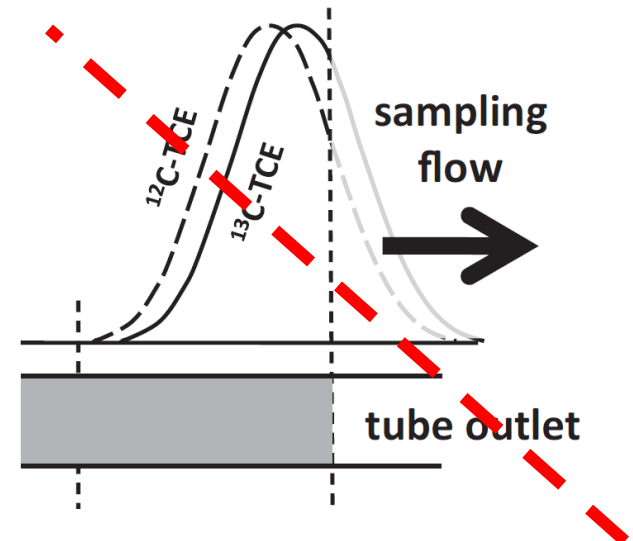


Conceptual Model of Fractionation in Adsorbent Sampling: Analyte Breakthrough

★ ^{12}C -TCE appears to have greater affinity to carbonaceous adsorbent. ^{13}C -TCE breaks through preferentially. Caused by Dispersion Force?



Complete retention = no fractionation



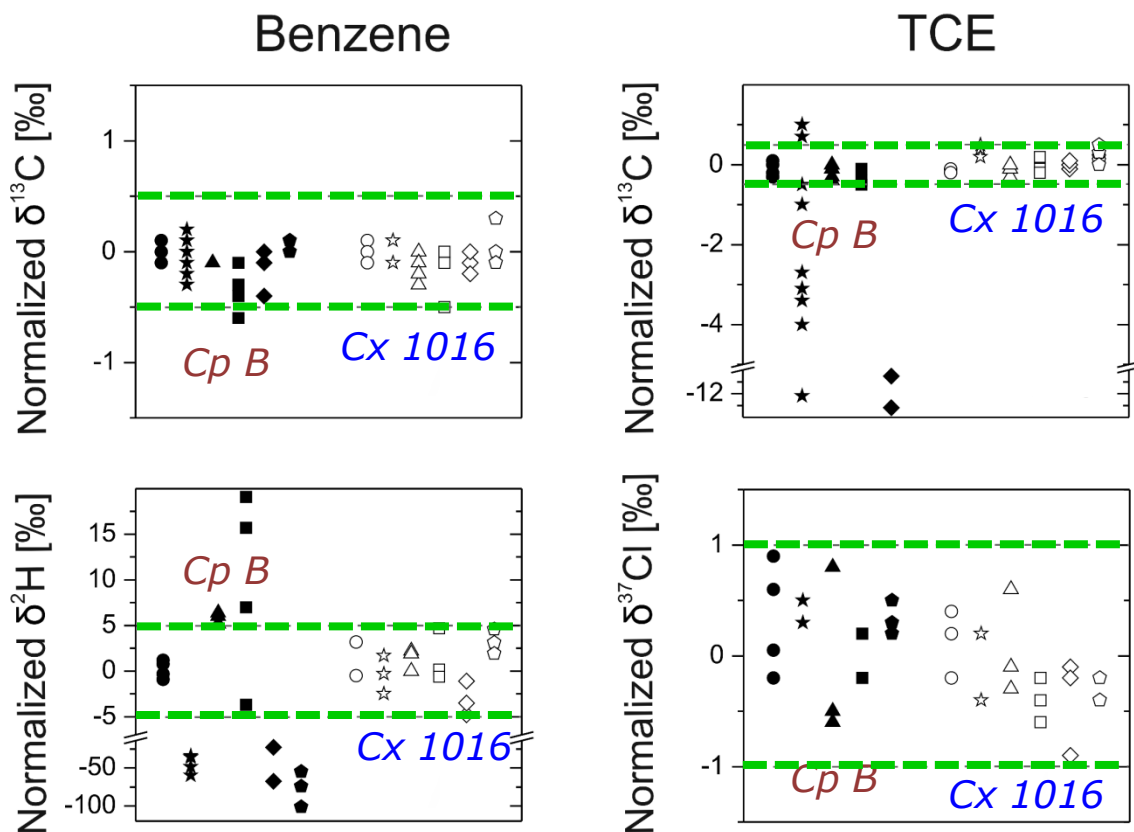
Partial breakthrough = ^{13}C -TCE lost preferentially;
Analyte fractionation.

Validation of Active Adsorbent Samplers

★ *CARBOXEN 1016 and CARBOPACK B selected for full evaluation*

★ *Tested at 6 different air volume/humidity/VOCs loadings combinations*

★ *Performance for Cx 1016 good in all treatments.
Recommended max sample volume 100 L*



Acceptable error limit

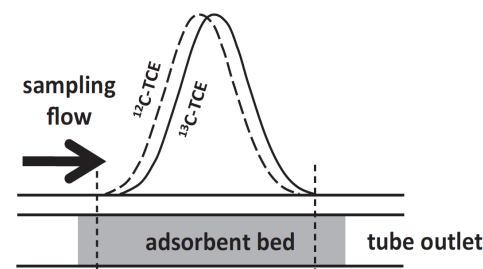
Interim Conclusions: Adsorbent Samplers Validation

CX 1016 offers good performance for all tested treatments and analytes.

CX 1016 is a recommended choice for sampling TCE, PCE or benzene from air, up to 100 L.


These results should not be extrapolated to different analytes, isotope ratios, or adsorbents. Actual performance validation is required.

These results should not be extrapolated to more challenging sampling conditions (larger air volume etc.) Actual performance validation is required.

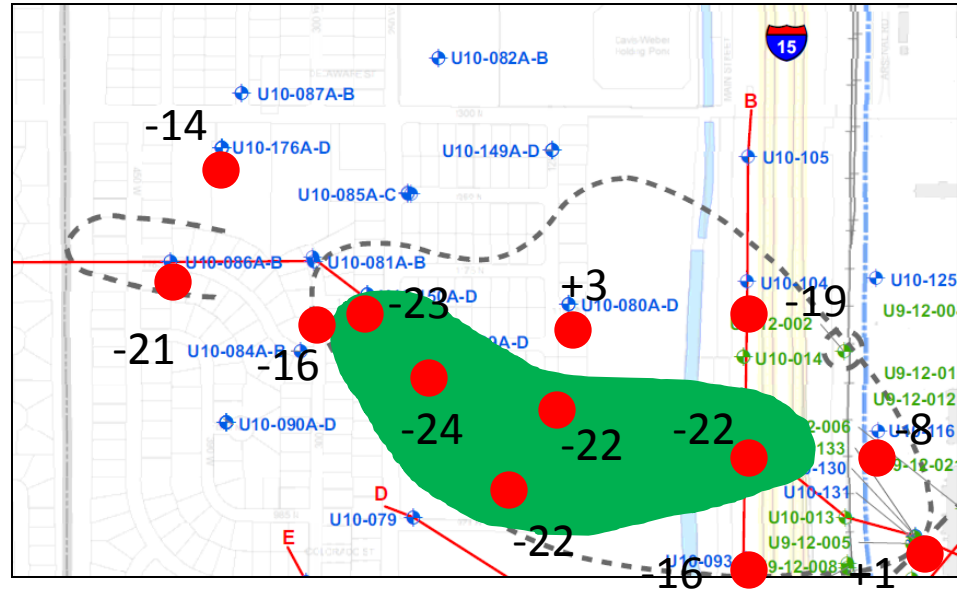


Effects of Biodegradation in Subsurface Sources

- ★ Preferential biodegradation of ^{12}C -TCE causes ^{13}C -TCE enrichments in undegraded residue. **Robust evidence of subsurface origin of the analyte.**

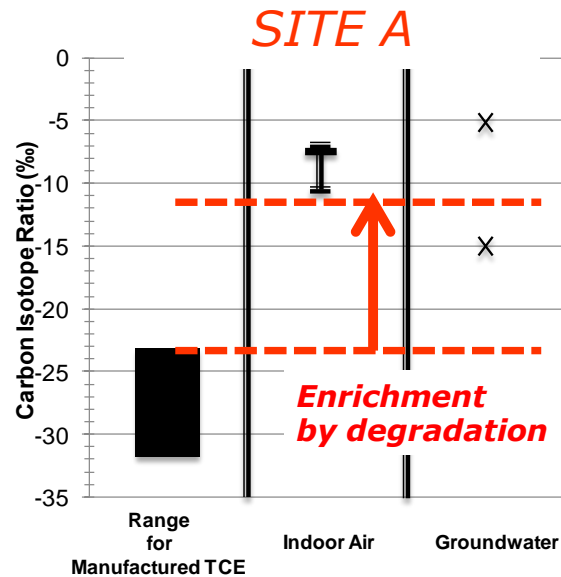
 *In part of the plume (green), TCE values are near the "heavy" end of the -23/-33 range of indoor sources*

★ *Isotope ratios are "heavier" than the range of indoor sources in the remainder of the plume footprint*



Example: Carbon isotope data from a TCE plume in UT

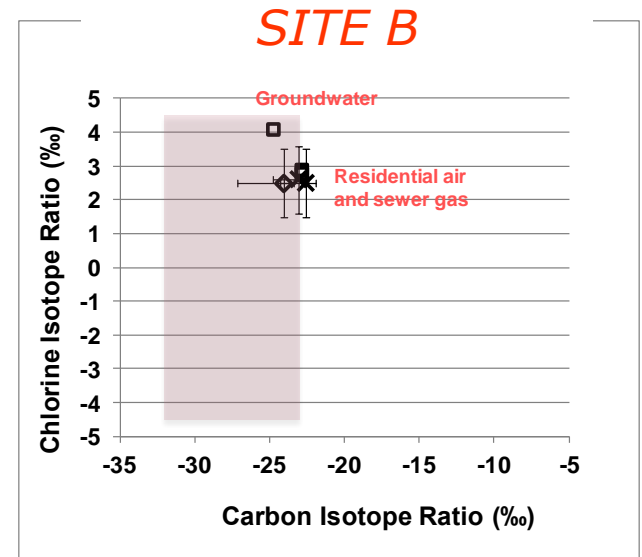
Examples: Predominant Subsurface Sources of TCE in Residential Air (True VI); Hill AFB Study



Indoor air TCE shows strong ^{13}C enrichment indicative of a biodegraded subsurface source

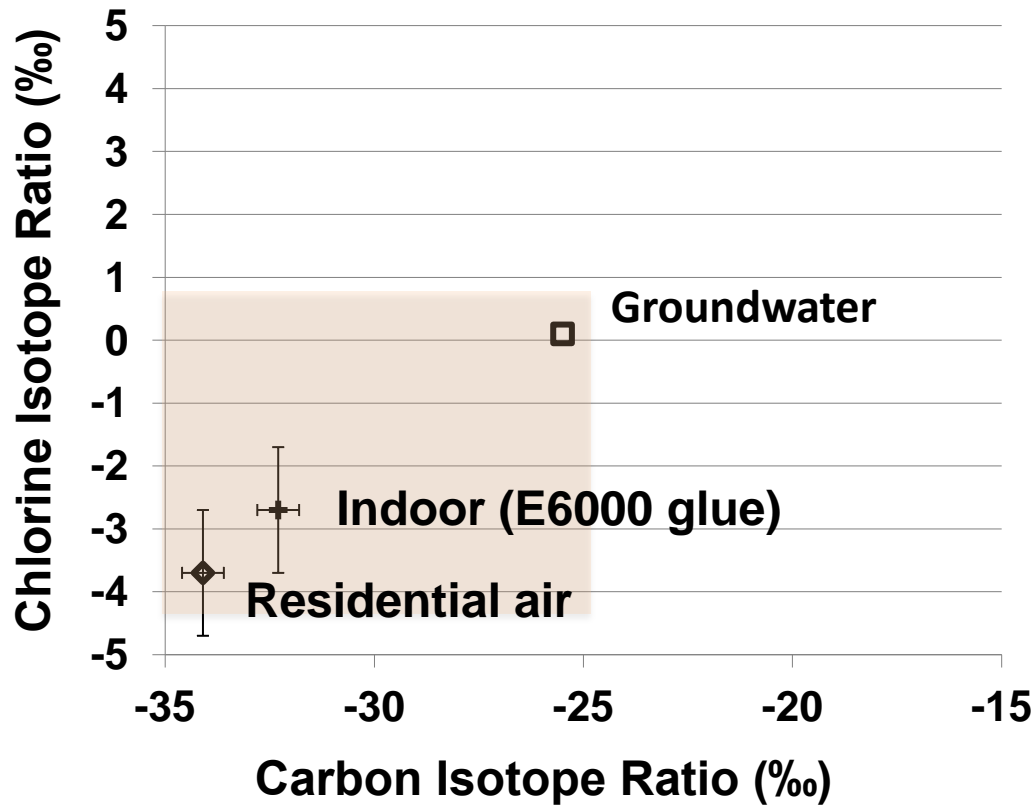
Clear case of subsurface source of TCE, evident by C CSIA data alone.

Good match of TCE isotope ratios between residential air and sewer gas supports existing conceptual model for this residence.



Predominant Indoor Source; Hill AFB Study

Residence 3 - PCE



Close match of C and Cl in indoor air PCE and a PCE-containing product identified on site (a tube of glue found on-site).

Clear case of **indoor source** of PCE.

Modeling Studies-Background

- Compound-Specific Isotope Analysis (CSIA) provides direct evidence of mass destruction of chlorinated ethenes, however, *quantitative interpretation of results is often problematic due to complex hydrogeology and/or competing reaction pathways.*
- Integration of CSIA with Reactive Transport Modeling (RTM) offers a means of accounting for the site-specific complexity.
- RTM with high-quality field data will confirm whether integration of CSIA with RTM offers a benefit versus the traditional approaches (RTM with contaminant concentrations only; interpretation of CSIA data based on Rayleigh Model).

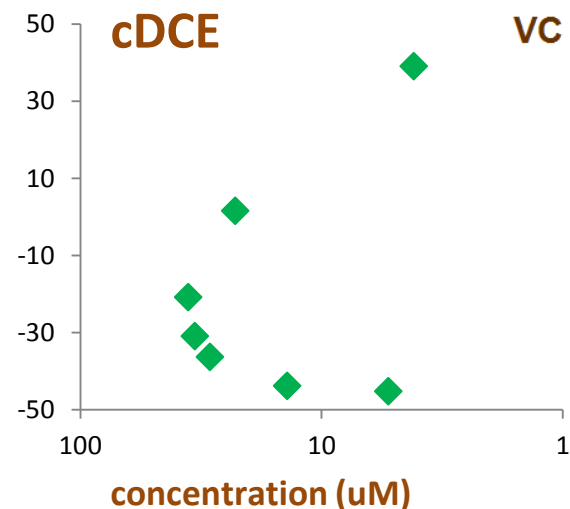
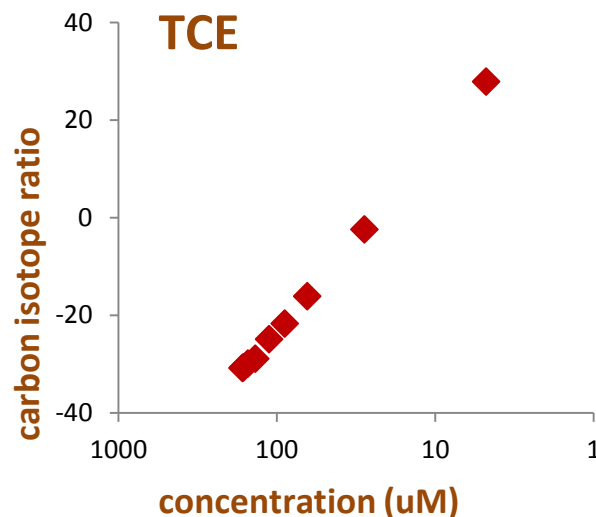
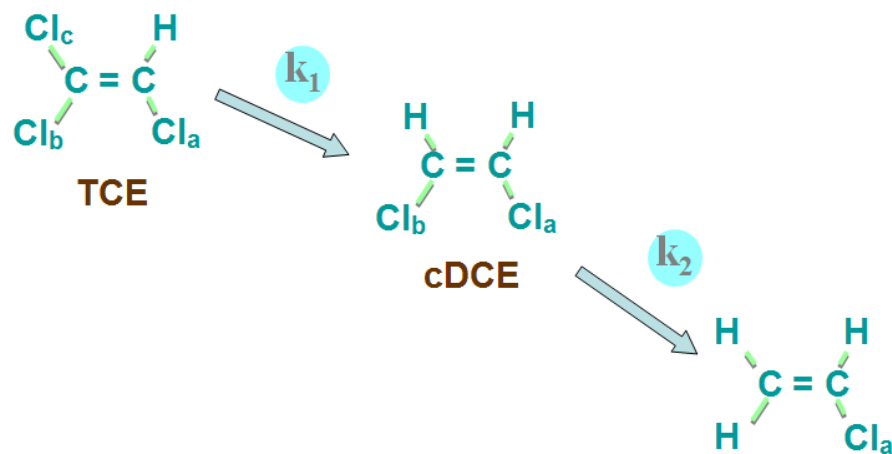
Why is Reactive Transport Modeling (RTM) needed for CSIA data?

- The analytical Rayleigh equation can only calculate the extent of mass destruction for a *parent* compound (e.g., PCE/TCE). This equation *underestimates* the true extent of degradation due to hydrodynamic dispersion attenuating the isotope signals.
- To quantitatively assess the fate of reaction products, e.g. lower chlorinated ethenes (DCE, VC) and the supposed stable ethene, a RTM approach is required.
- Furthermore, full complexity can be accounted for with RTM: hydrodynamic dispersion, effects of isotopologue-dependent diffusion and sorption, advanced degradation kinetics, etc
- RTM can be simple like any other model: a 1-D model with user adjustable parameter values (rate constants, fractionation factors, dispersivities, etc) without the need to understand the working of the “engine”.

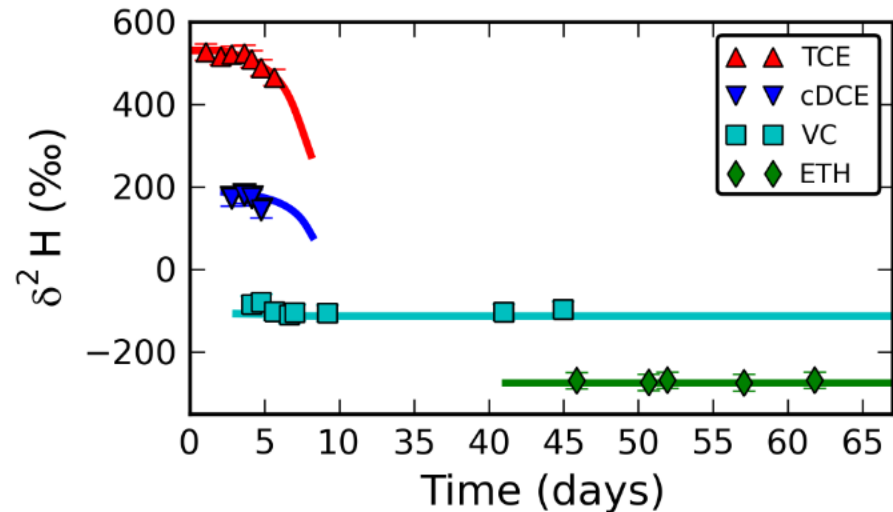
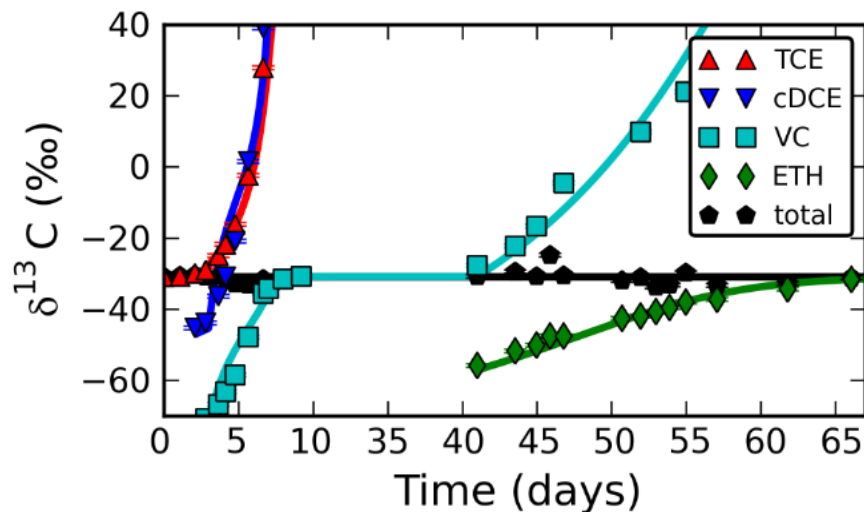
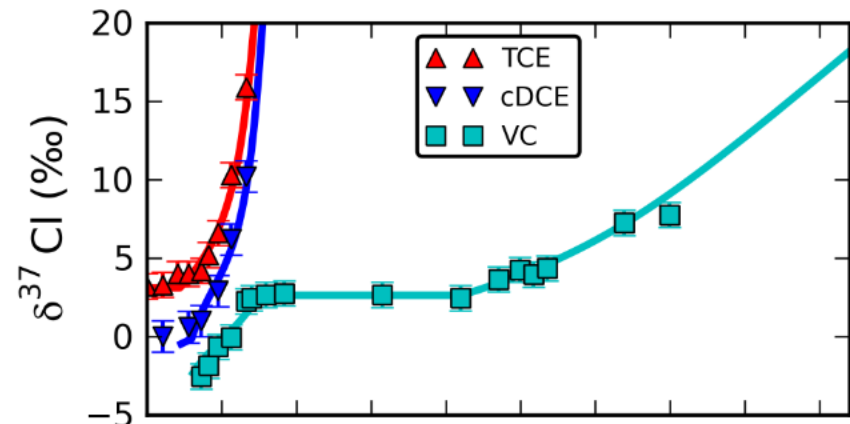
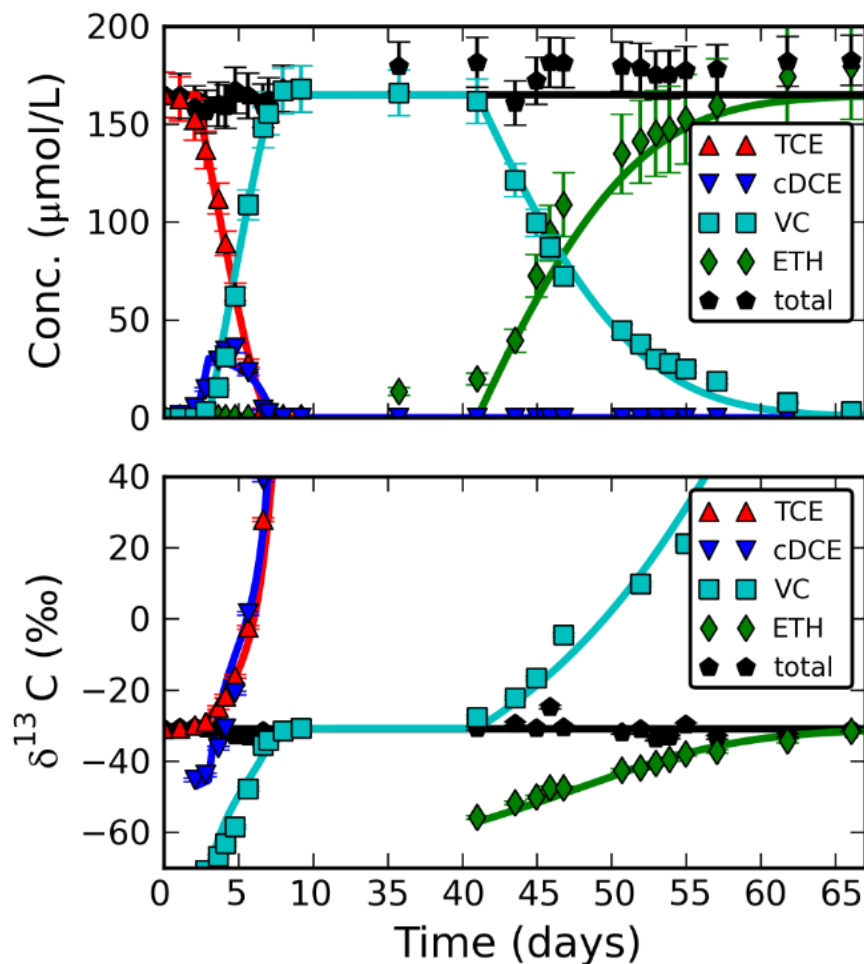
CSIA for Degradation Intermediates

- Isotope effects in the parent compound conform to the Rayleigh model.

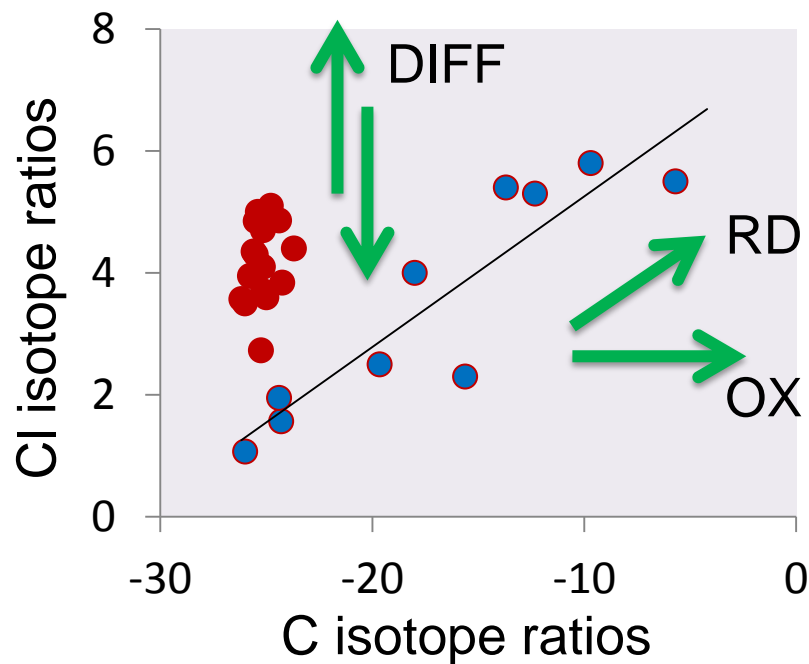
- Isotope effects in the intermediates reflect their production and degradation.



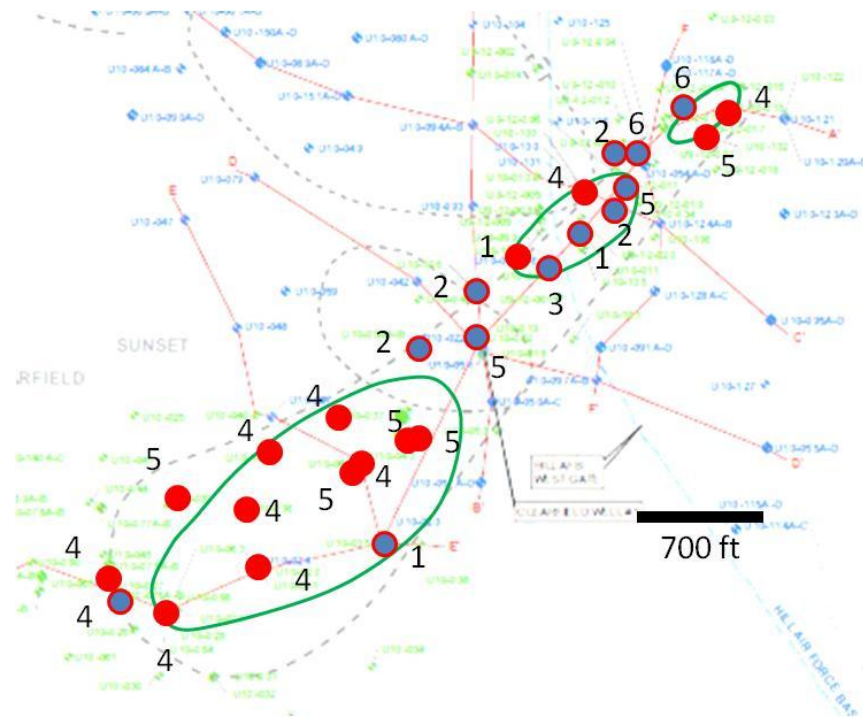
Model Calibration with the Microcosm Data



2D-CSIA Data: Consider Different Scenarios



A C-Cl trend consistent with reductive dechlorination apparent for a group of samples



Bimodal distribution of data can be rationalized by several alternative scenarios, to be tested by RTM.

Summary

- Environmental forensics utilizes a wide range of techniques and approaches which are far more flexible than the standard EPA methods.
- ^{14}C isotopes has a role to play in certain environmental applications
- Stable isotopes continue to evolve and play a role in a number of environmental forensic studies.
- Vapor intrusion studies and RTM studies are emerging applications.
- Don't rediscover the wheel!