



Contaminant Degradation and Forensics Using Compound Specific Isotope Analysis

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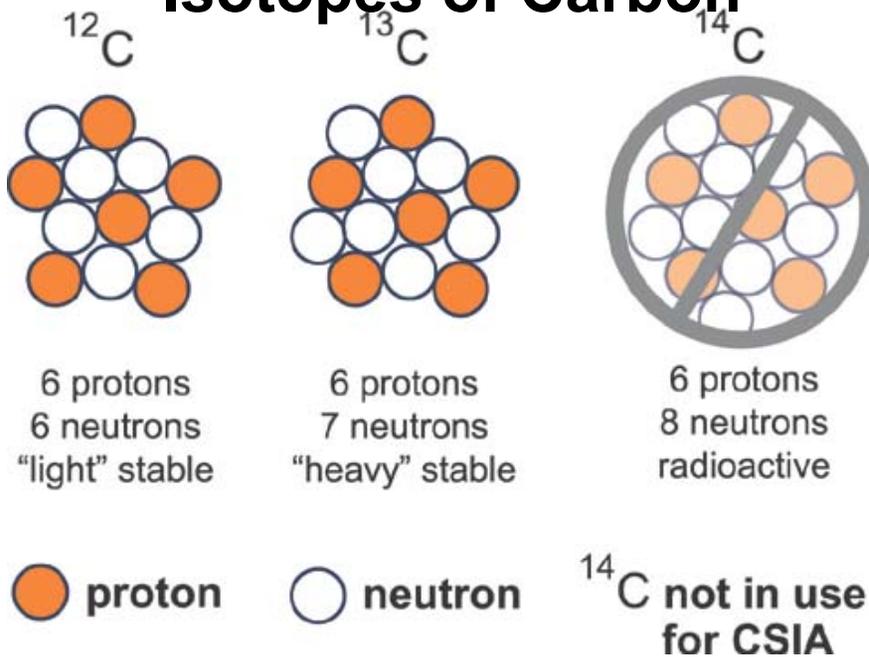


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What Is a Stable Isotope?

Isotopes: molecules of an element with same number of protons and electrons, but different number of neutrons

Isotopes of Carbon



Environmentally relevant stable isotopes

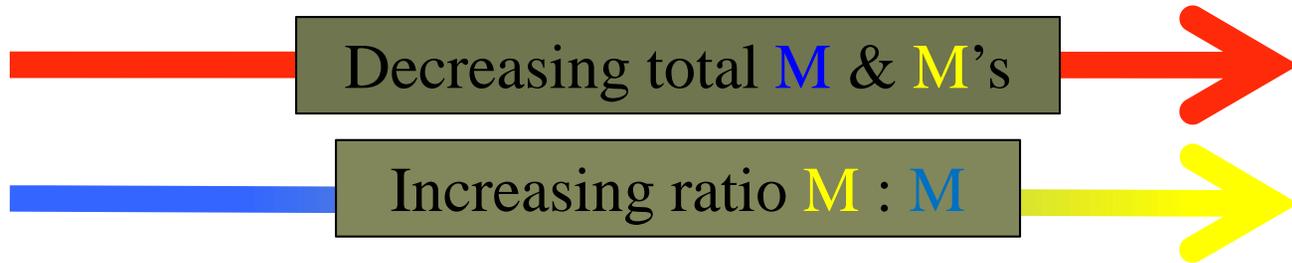
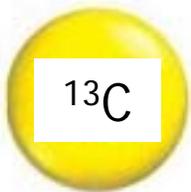
Hydrogen	^1H , ^2H
Oxygen	^{16}O , ^{17}O , ^{18}O
Carbon	^{12}C , ^{13}C
Chlorine	^{35}Cl , ^{37}Cl
Nitrogen	^{14}N , ^{15}N
Sulfur	^{32}S , ^{34}S

Stable Isotopes in In-Situ Degradation

- Compounds with Light isotopes degraded more rapidly than compounds with Heavy isotopes
- Product remaining becomes isotopically heavier
- Process of isotopic change is called fractionation



^{13}C Chocolate Fractionation



How Are Isotope Ratios Reported?

- ▶ Isotopic ratios of light elements are generally reported relative to a known standard as “delta” (δ) values and measured in parts-per-thousand (denoted “‰” = per mil)

Equation 1. δ (in ‰) = $(R_x/R_s - 1) * 1000$

R = ratio heavy/light isotope (e.g., $^{13}\text{C}/^{12}\text{C}$)

R_x = sample (e.g., $^{13}\text{C}/^{12}\text{C}$ in environmental sample)

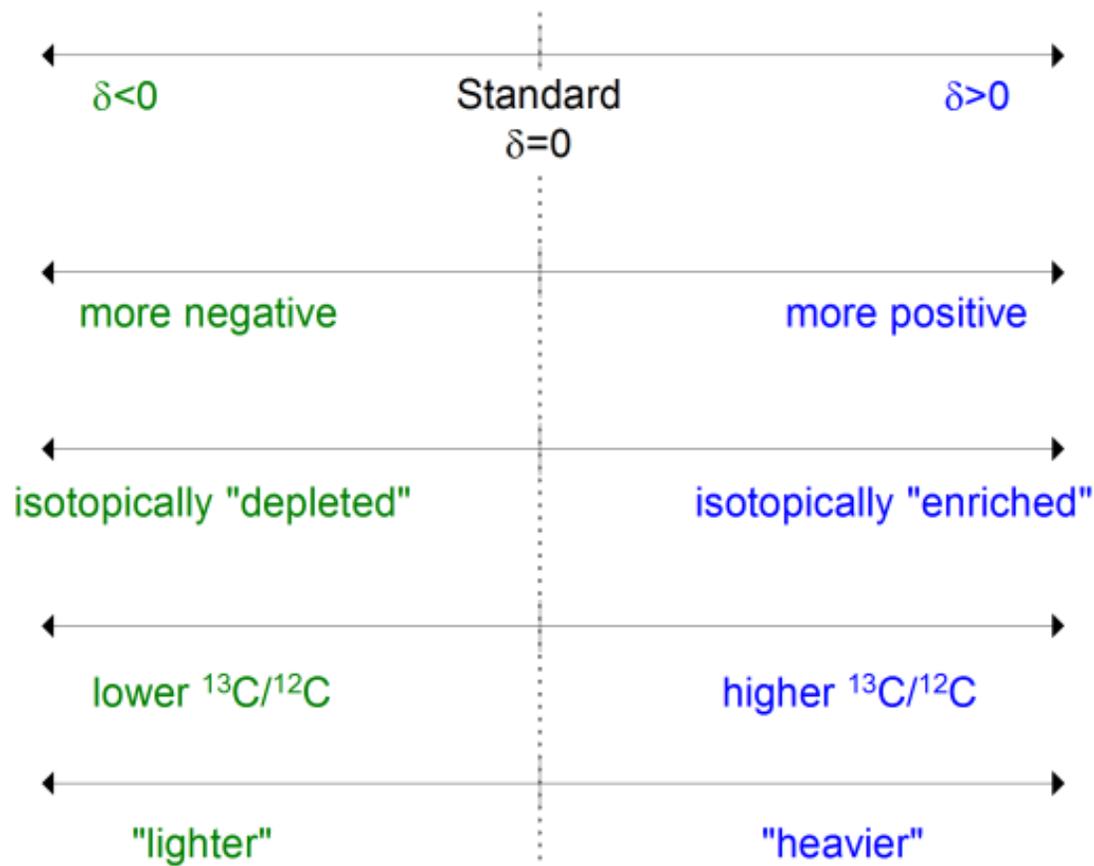
R_s = standard (e.g., $^{13}\text{C}/^{12}\text{C}$ in carbon standard “VPDB”)

Example: $\delta^{13}\text{C} = + 30 \text{ ‰}$

30 parts-per-thousand (3 %) higher ratio of $^{13}\text{C}/^{12}\text{C}$ in sample relative to a known isotopic standard

Stable Isotope Ratios as Delta Notation (δ)

δ scale



Isotope ratios use a sliding scale - everything is relative to a standard

Stable Isotopes in In-Situ Degradation

Significant Fractionation Occurs in:

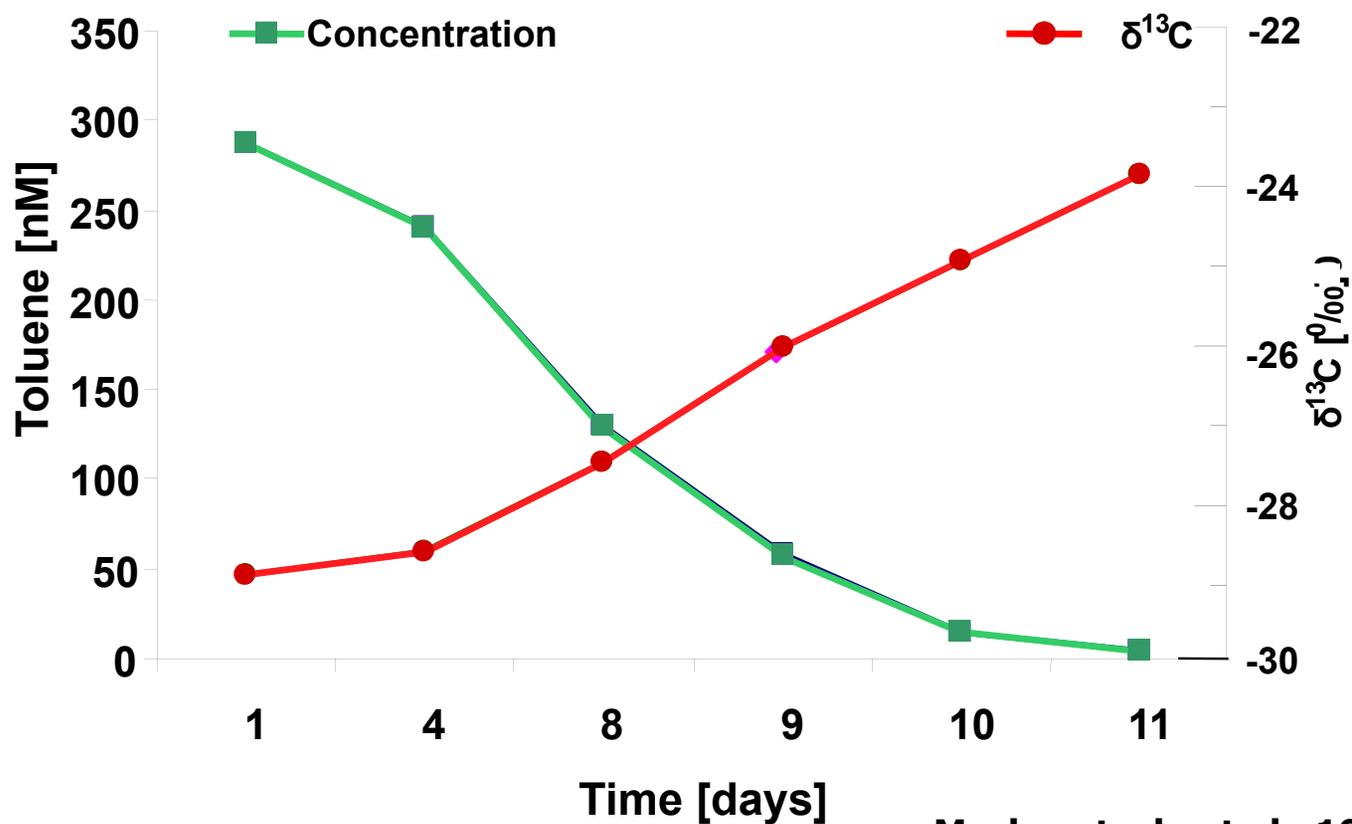
- ❑ Biological Oxidation
- ❑ Biological Reduction
- ❑ Abiotic Degradation
- ❑ In-Situ Chemical Oxidation
- ❑ In-Situ Chemical Reduction

Stable Isotopes in In-Situ Degradation

Little or No Fractionation Occurs in:

- Dilution
- Volatilization
- Sorption

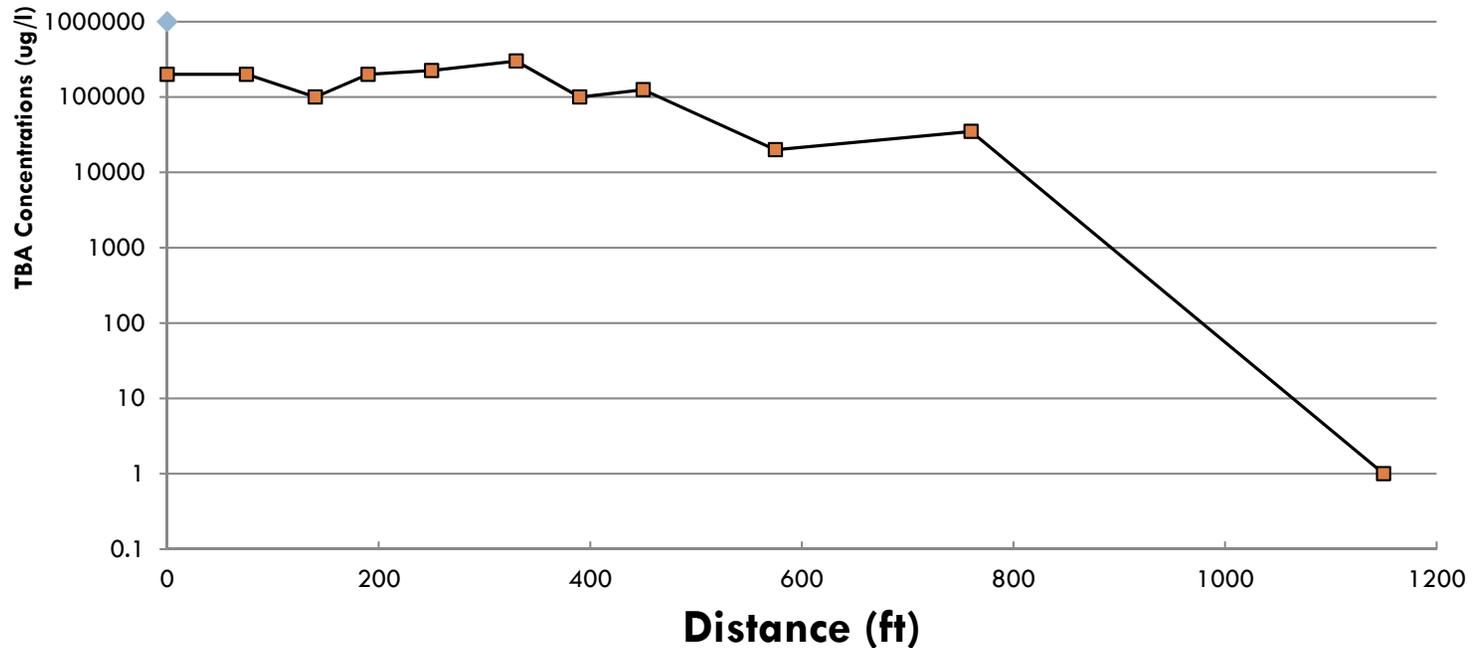
Degradation of Toluene under Sulfate Reducing Conditions



Meckenstock, et al., 1999.

Application to Recalcitrant Compounds

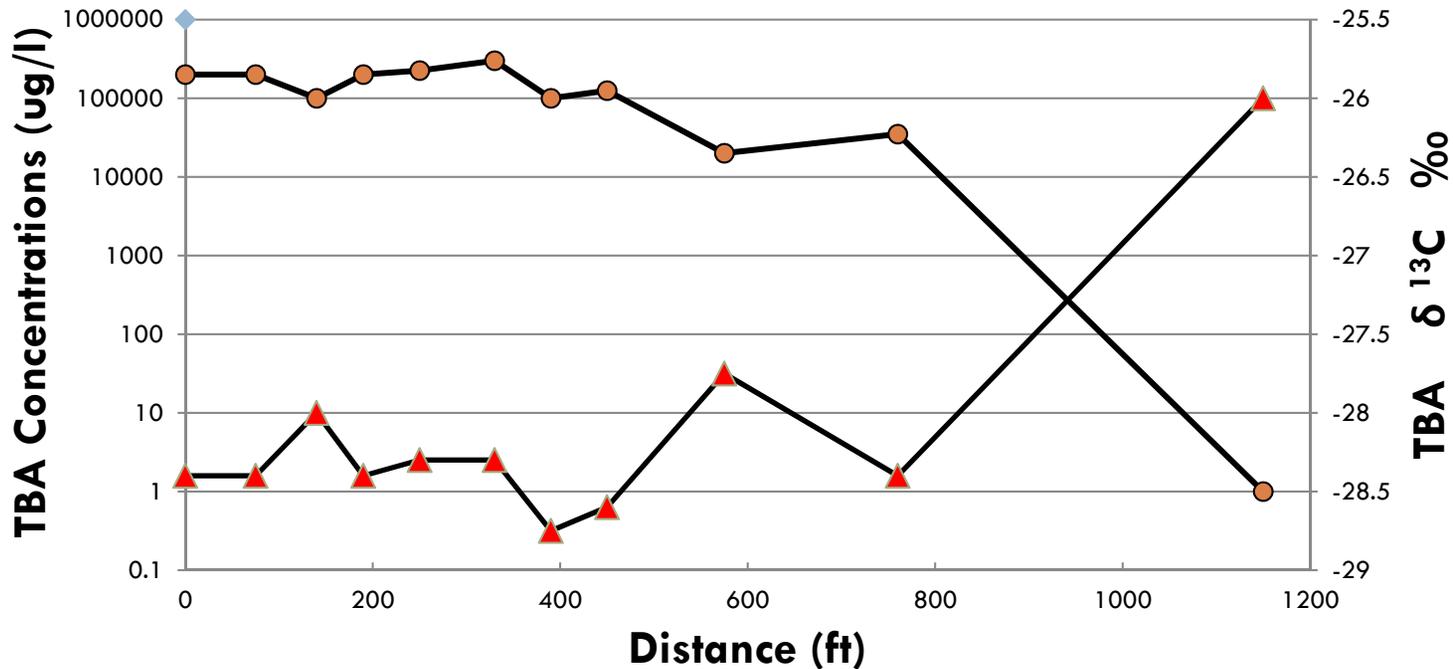
tert-butyl Alcohol (TBA) Concentration



Day, et.al. (2003); Gulliver (2003)

Application to Recalcitrant Compounds

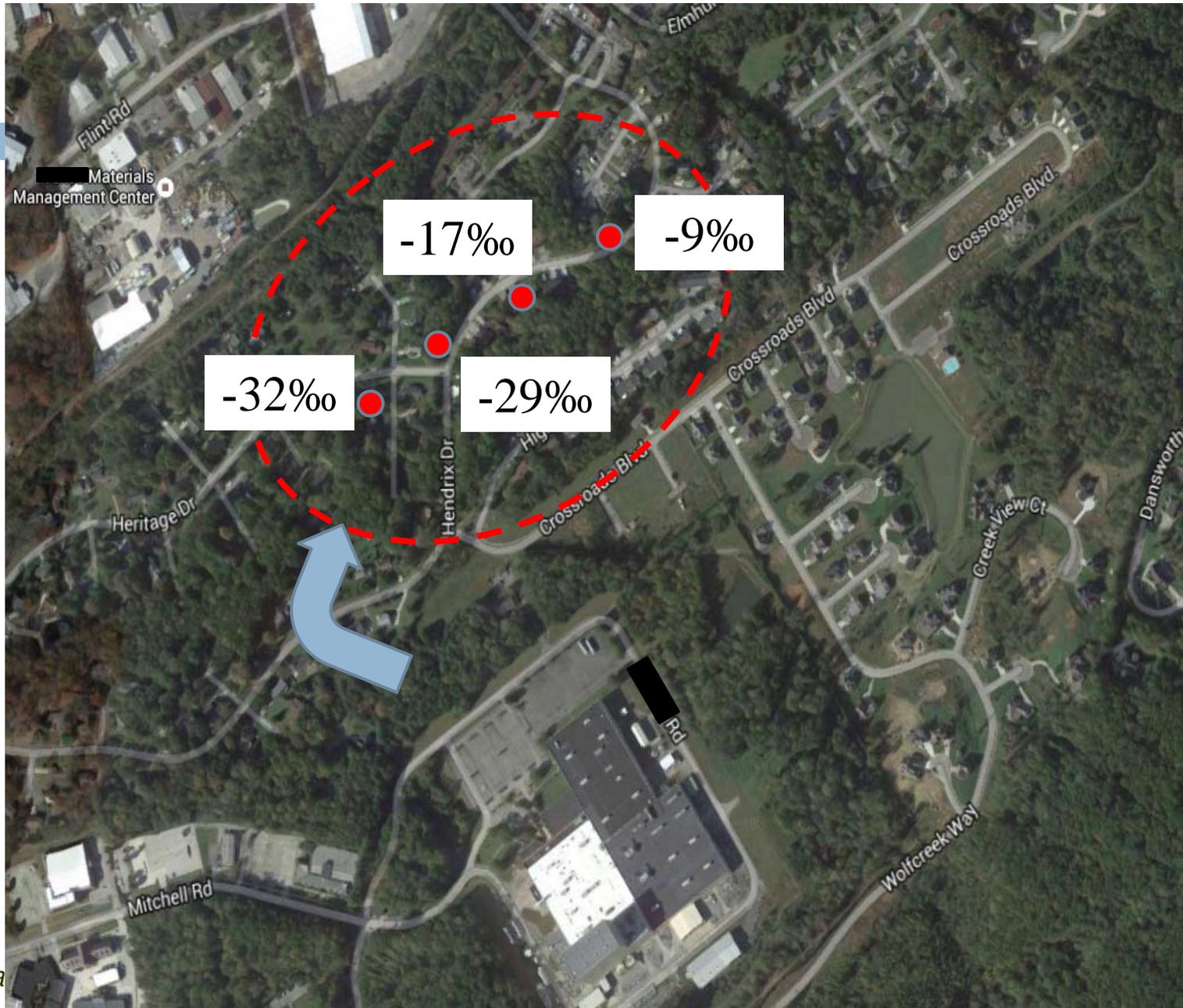
tert-butyl alcohol (TBA) Concentration and Isotopic Composition



Day, et.al. (2003); Gulliver (2003)

TCE Degradation?

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Stable Isotopes in In-Situ Degradation

- ❑ Fractionation is unequivocal proof of in-situ degradation
- ❑ Related to the mechanism of degradation
- ❑ Related to the fraction of component degraded
- ❑ Related to the rate of degradation
- ❑ Used in groundwater modeling



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What questions can be asked and answered?

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- Is there more than one source?
- Who is responsible?
- When did it happen?
- Who will pay for the cleanup?

Typical environmental contaminants where forensics can be applied

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- Petroleum Hydrocarbons
- Chlorinated Solvents
- Methane Gas
- Nitrate contamination

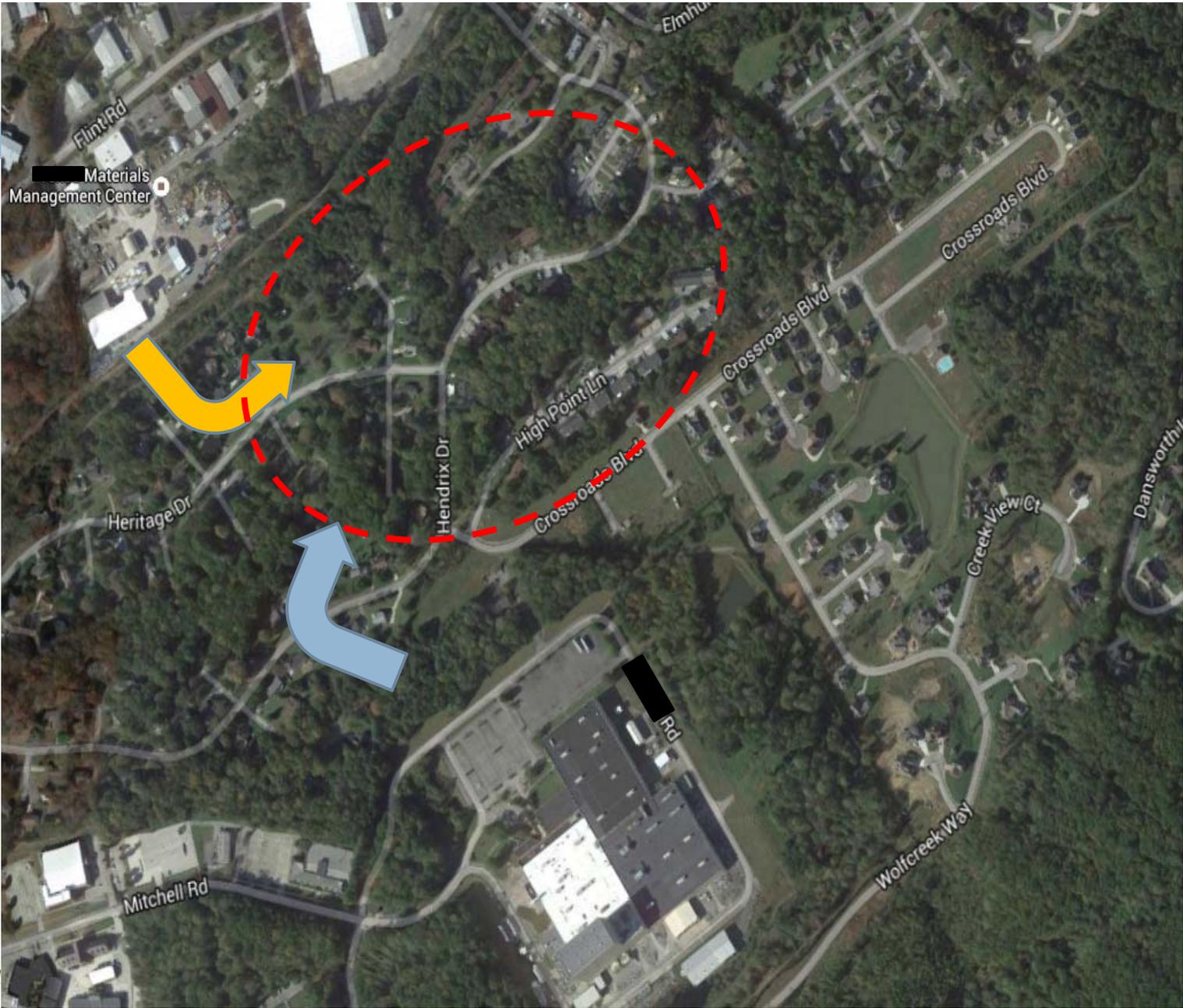
Typical Forensic Applications

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- Petroleum
 - ▣ Gas stations, refineries, industrial areas, any USTs.
- Chlorinated Plumes
 - ▣ Dry cleaners, industrial areas.
- Shale Oil/Gas production
- Confined animal feeding operations
- Combined sewer overflow
- Vapor intrusion

Chlorinated Plumes: Who is responsible?

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Corner Gas Station(s)

18



Second Street

Main Street

Gasoline LNAPL



Shale Oil/Gas

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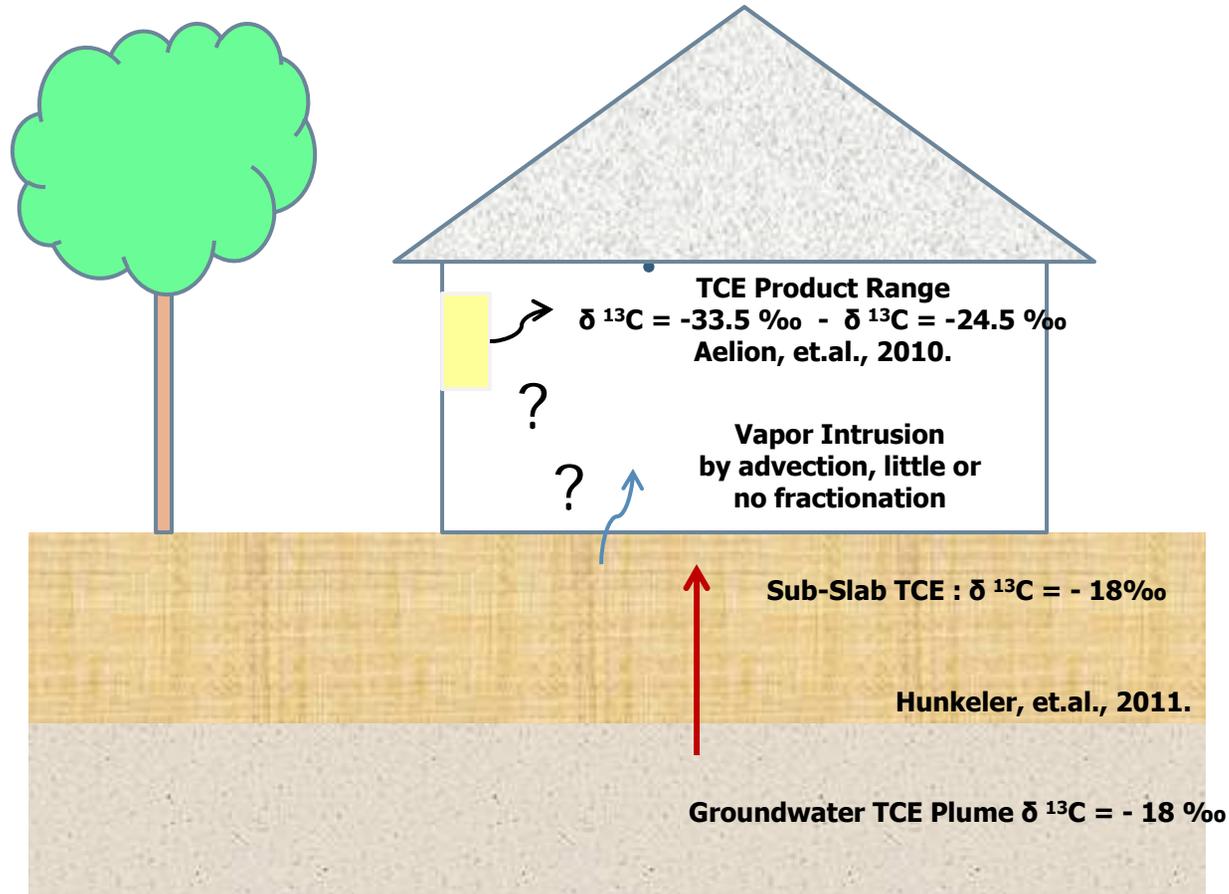
I
smell
gas!



Confined Animal Feeding Operations



Vapor Intrusion



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Case Study: Comingled Chlorinated Solvent Plume

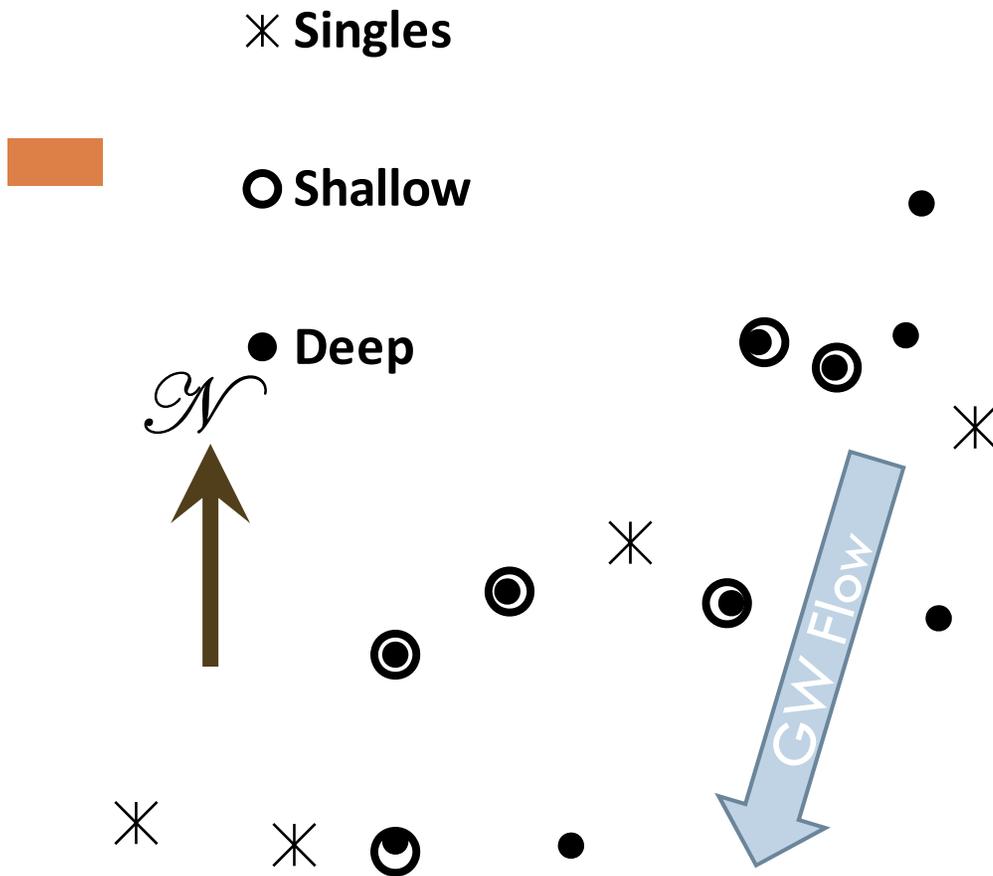
Site Introduction

Background

- Groundwater impacted with PCE and TCE, but very little cis-DCE is present.
- Impact has led to a vapor intrusion concern, and indoor air contains PCE and TCE.
- Site is in an industrial area.
- Site geology is very complex:
 - ▣ Apparent deep and shallow aquifers in some areas
 - ▣ Deep and Shallow are not distinct in other areas

Questions

- Was TCE from degradation or original release?
- Variable ratios of PCE/TCE.
 - ▣ Is this the result of degradation or indicative of multiple sources?
- Concentrations increase with groundwater flow.
 - ▣ Suggests multiple sources, but how many and where?



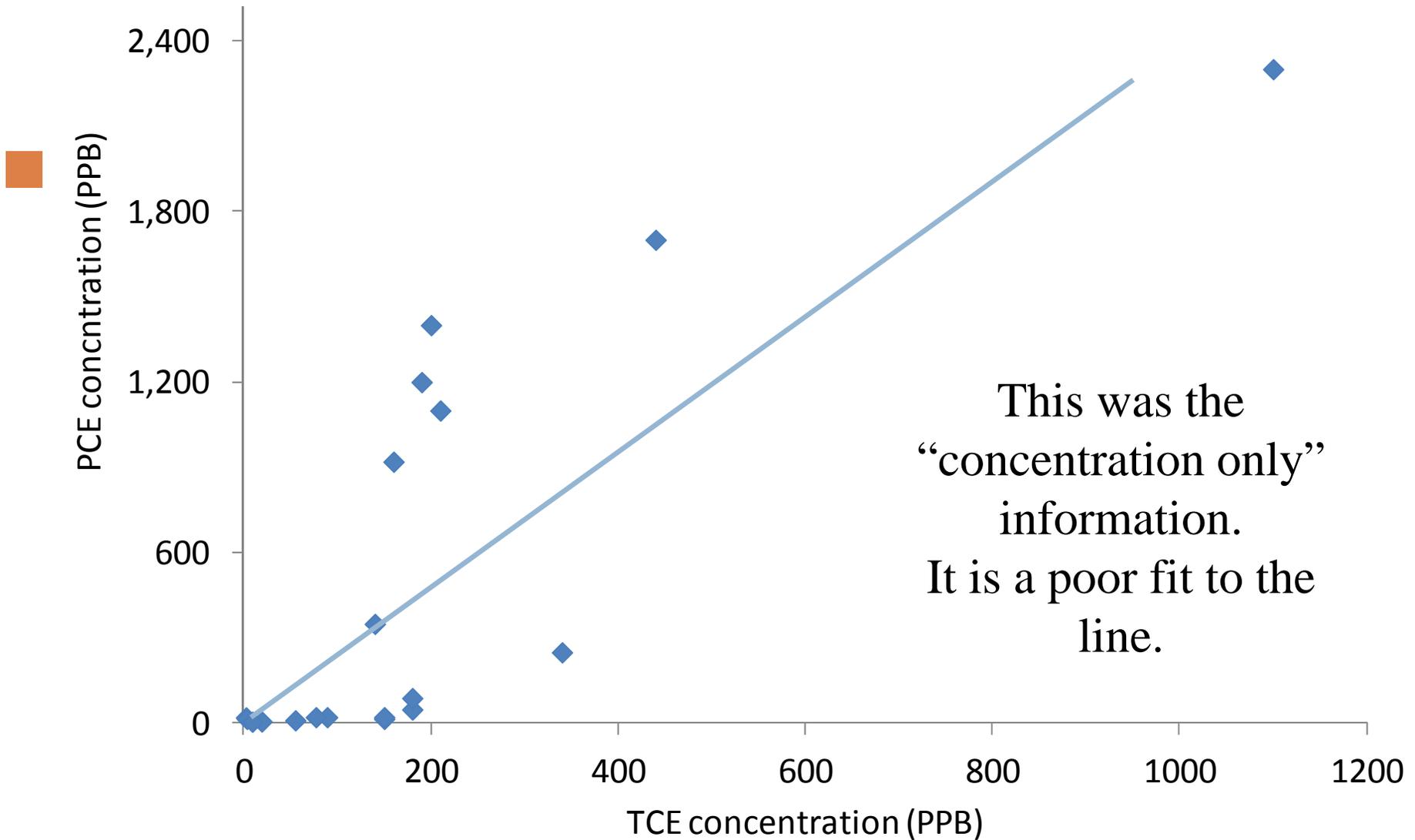
Map Showing

Inconsistent

3-D Nature of Site

“Singles” were placed in areas where “shallow” and “deep” aquifers could not be delineated.

Note: Only the wells are shown where CSIA could produce a result for PCE or TCE.



This was the
“concentration only”
information.
It is a poor fit to the
line.

In an undegraded PCE/TCE release, the ratio of the concentrations is constant.

This requires the points from a single source
to lie along a line passing through the origin.



Why Carbon and Chlorine CSIA?

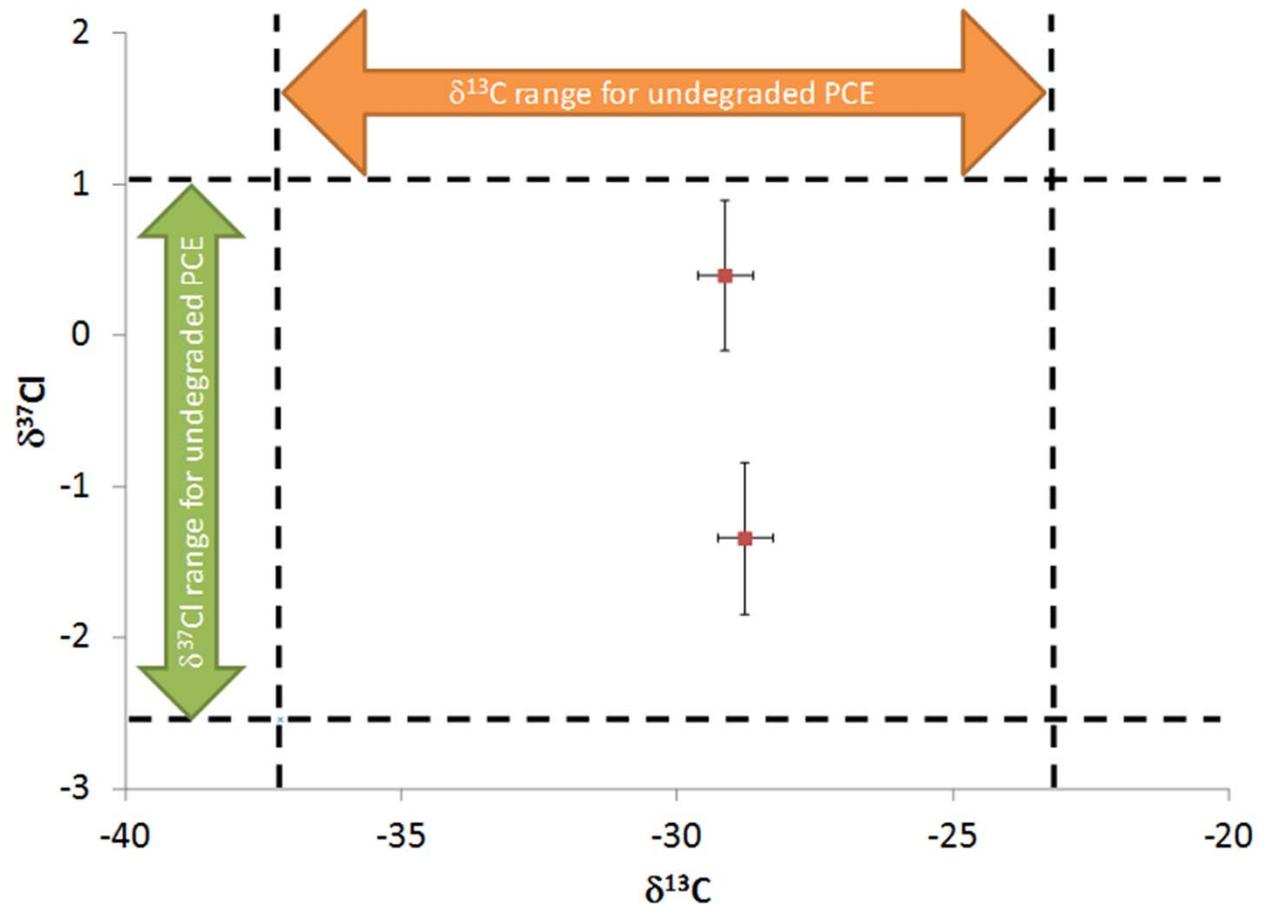
□ Increases Resolving Power

□ Chances 2 PCE sources have overlapping

- carbon CSIA 1:14
- Carbon and chlorine CSIA 1:49

□ Helps discern if differences are

- Source
- Degradation

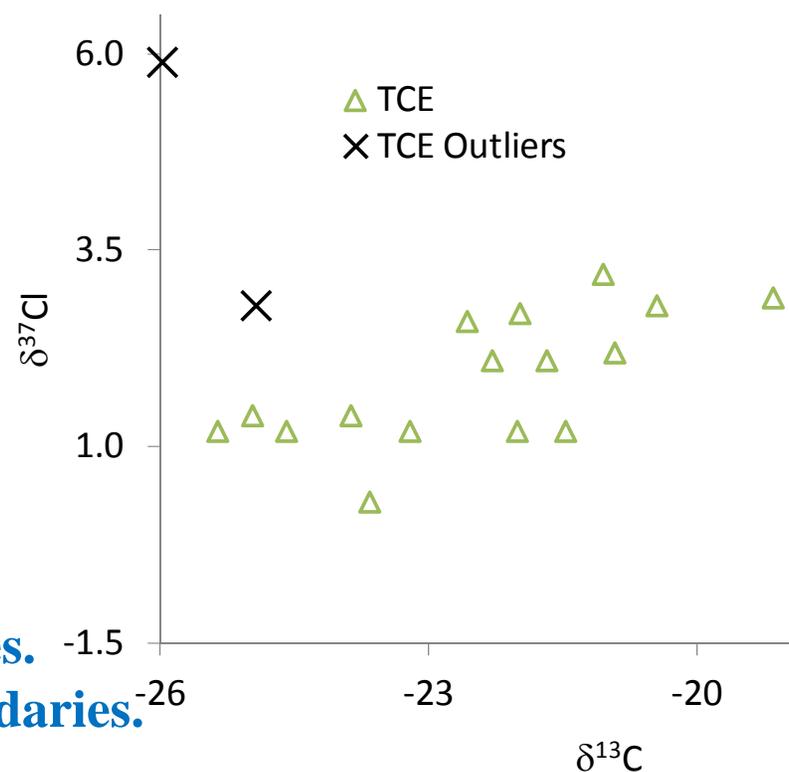


Procedure

- Analyze both carbon and chlorine CSIA of PCE and TCE
- Use results to present a simplified model that:
 - ▣ accounts for degradation (minimal)
 - ▣ does not depend on a detailed understanding of flow (groundwater flow is very important but that is an independent line of evidence)
 - ▣ Indicates similarities and differences useful in discerning sources

Conclusions 1

- All TCE points lie in a group EXCEPT for two obvious outliers.
 - ▣ Rayleigh kinetics tells us the points lie along a line with positive slope if they share the same source.
- These outliers could not lie along a single line that:
 - has a positive slope
 - Includes rest of TCE data



There are at least 3 TCE sources.

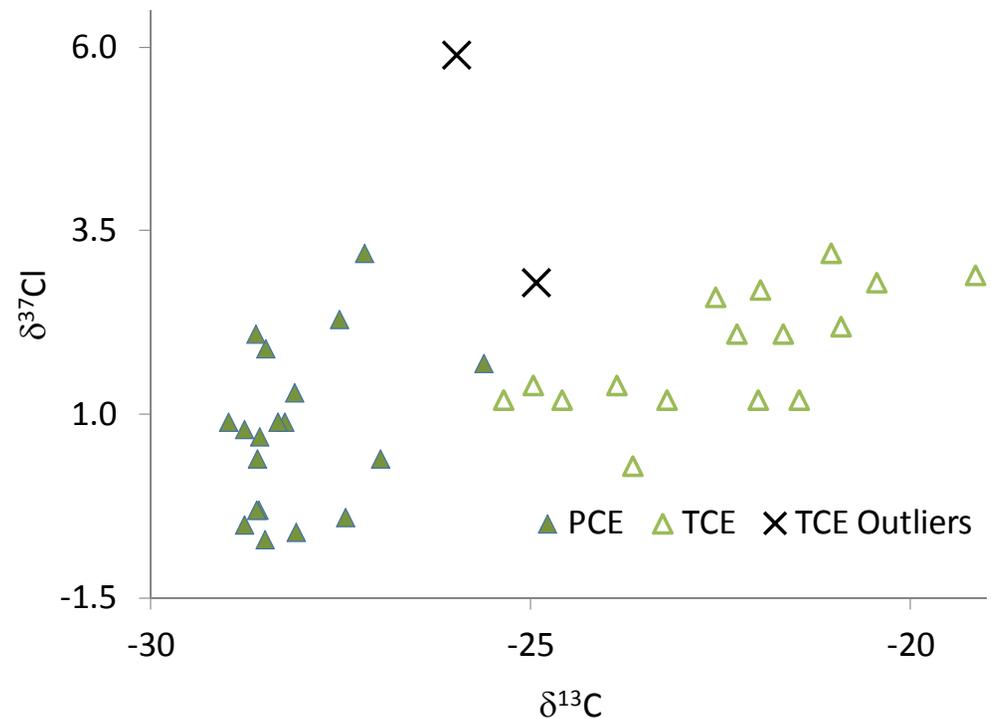
Other sources are off-site/near boundaries.



Was TCE originally PCE that has been degraded, or was it part of the original release and always distinct?

Conclusion 2

- Degradation is minimal:
 - ▣ No cis-DCE, the degradation product of TCE.
 - ▣ Heaviest observed $\delta^{13}\text{C}$ of TCE is -19.2‰ , EPA limit is -22.5‰ .
 - ▣ At least 76% of the original PCE remains (Rayleigh equation).



Conclusion 2

- Degradation is minimal:
 - No cis-DCE, the degradation product of TCE.
 - Heaviest observed $\delta^{13}\text{C}$ of TCE is -19.2 ‰, EPA limit is -22.5‰.
 - At least 76% of the original PCE remains (Rayleigh equation).
- Most observed TCE heavier than observed PCE.
- As PCE is degraded to TCE, the lightest portion of the PCE is always what is degraded. So the produced TCE is always lighter than the PCE from which it was produced.

Most observed TCE was released as TCE and is not the product of PCE degradation.

Distinguishing On-Site TCE Sources

- Step 1: Correlate map with CSIA data.
- Step 2: Using concentration data and the principle all PCE vs. TCE points from a single source lie on a straight line starting at the origin, validate/refine conclusions from step 1.

TCE

3.0

1.5

$\delta^{37}\text{Cl}$

● Singles

AB

○ Shallow

CD

● Deep

△ AB

□ CD

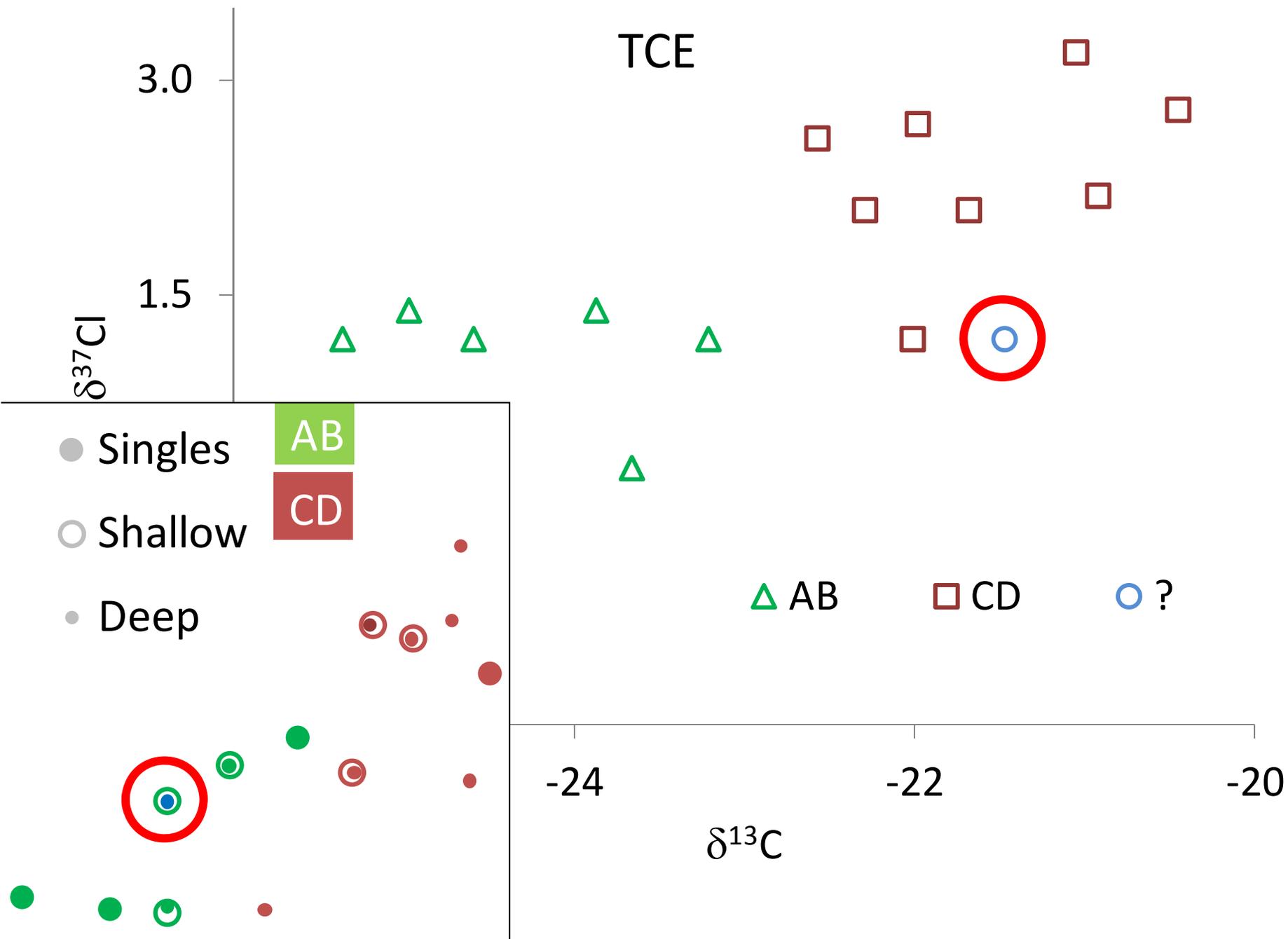
○ ?

-24

-22

-20

$\delta^{13}\text{C}$



Concentration ratios and Dilution

- Each release has a unique PCE/TCE concentration ratio.
- Dilution effects PCE and TCE the same, so it does not alter the PCE/TCE ratio.
- If we plot PCE concentration vs. TCE concentration, the points from each source should lie on a line that goes to the origin.
- Biodegradation would alter it, but biodegradation has been minimal at this site.

Concentration Ratios: Interpretation

- AB concentrations mostly off-scale

- CD has:

 - 2 groups

 - One outlier
(blue, on left)

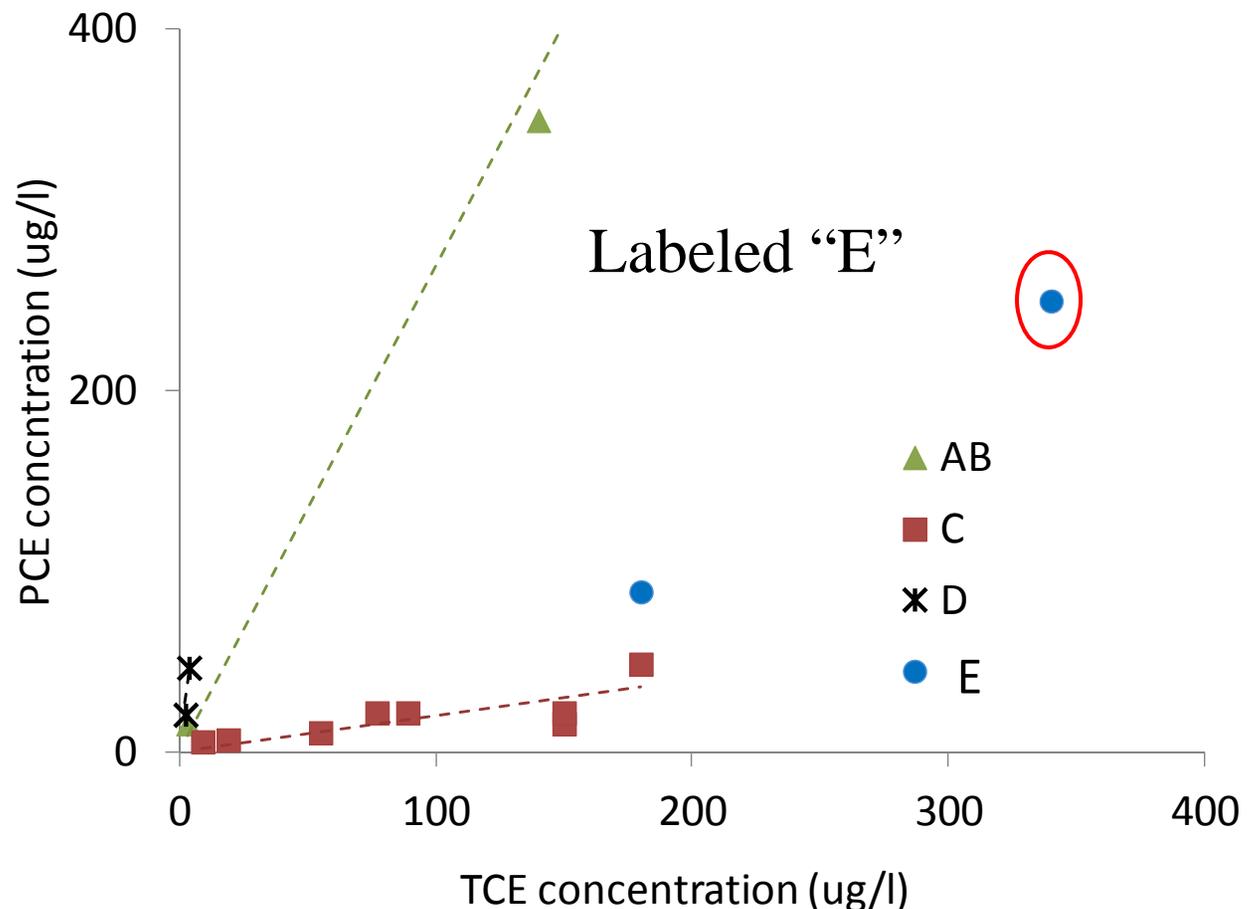
- Circled point

 - not part of AB,
C or D

 - Lines up with

 - CD outlier

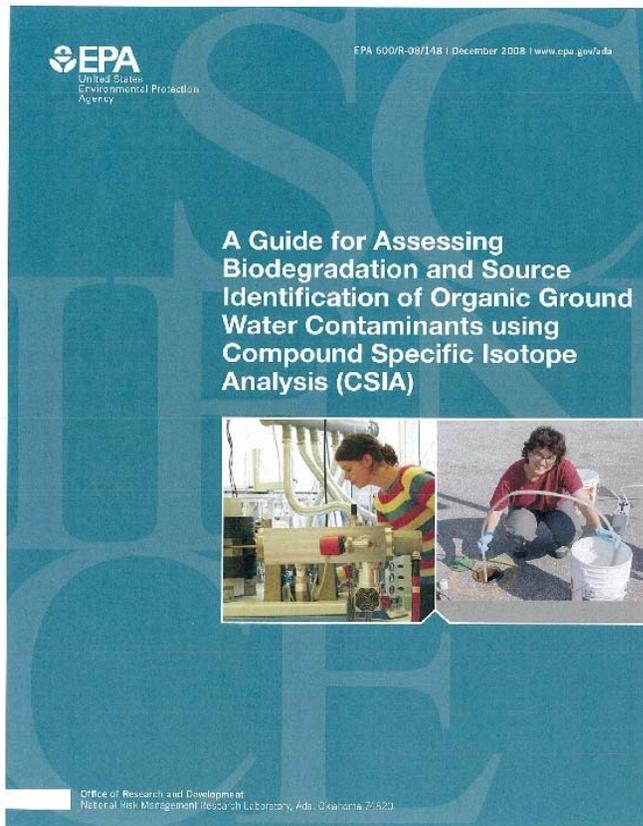
 - Origin



Summary

- Have found:
 - ▣ 4 PCE/TCE sources on-site (AB, C, D, E)
 - ▣ 2 TCE sources off-site or near boundaries.
- This much information was enough to save the client substantially.
 - ▣ Savings “had several more 0’s than analytical cost”.
 - ▣ Analytical costs were minimal compared to risk.
- Further interpretation done later:
 - separated AB into A and B.
 - didn’t change the bottom line.

USEPA Guide for CSIA



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Discussion



Questions?