



# Compound-specific Isotope Analysis (CSIA) for Source Identification

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NAVFAC EXWC

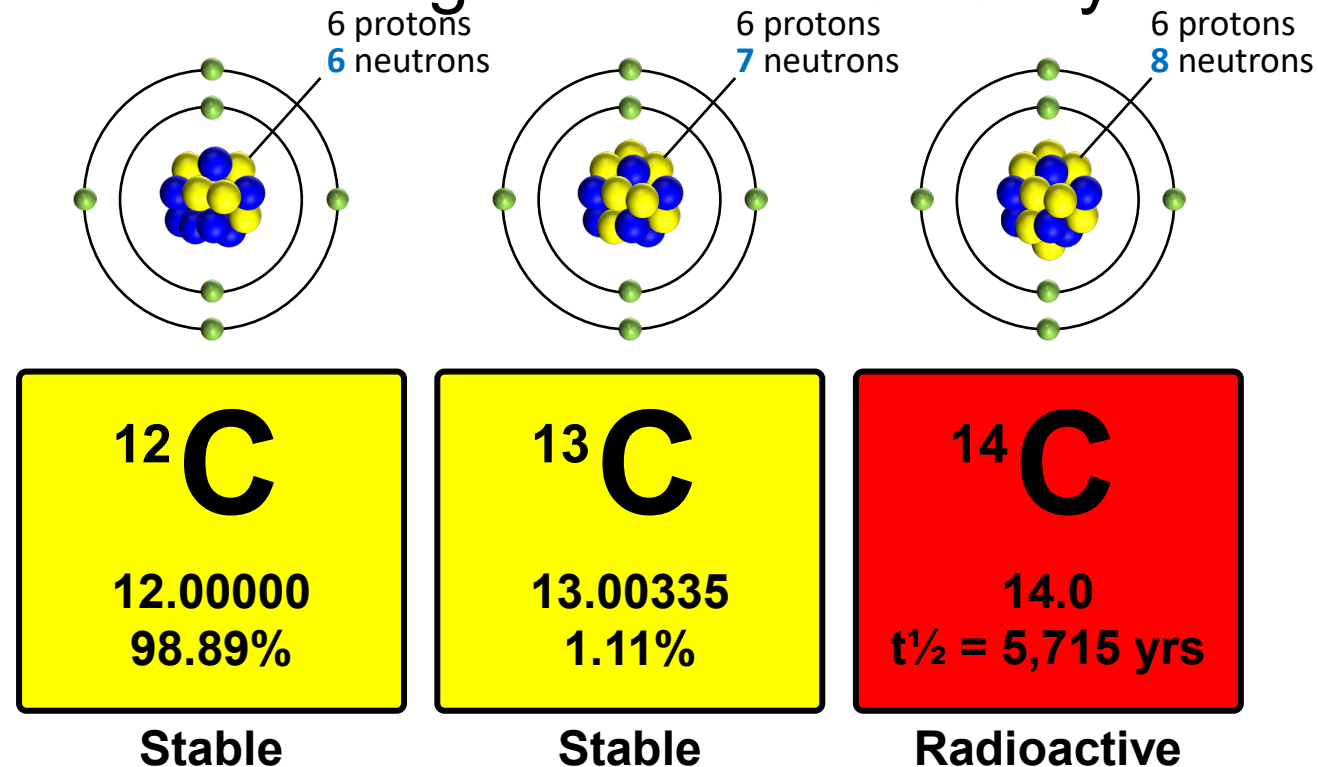
FRTR Spring 2023 General Meeting

# What Are Isotopes

The isotopes have same number of protons but different number of neutrons

Isotopes can be stable or radioactive

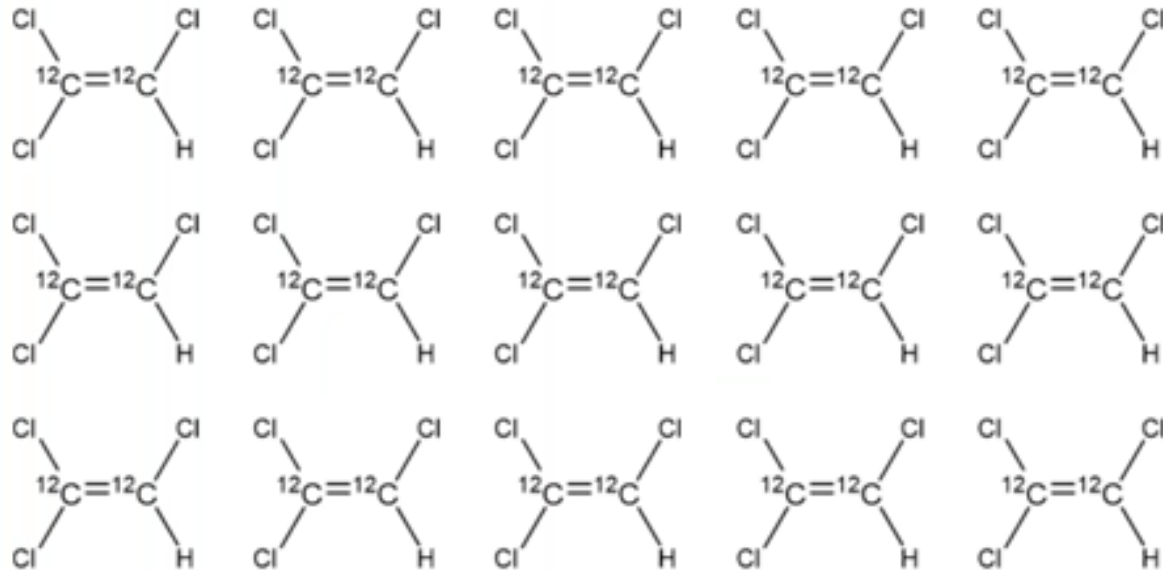
Stable isotopes do not undergo radioactive decay



# What is Compound Specific Isotope Analysis?



- Measurement of the **ratio** of **naturally** occurring stable isotopes in samples
- **Isotope ratio** - ratio of heavy to light isotopes
- Applied to chlorinated solvents, petroleum hydrocarbon, 1,4 dioxane, pesticides
- In addition to source identification can be used to determine degradation



Element	Stable Isotopes	Natural Abundance (%)
Carbon	12C, 13C	98.89, 1.11
Hydrogen	1H, 2H	99.985, 0.015
Oxygen	16O, 17O, 18O	99.76, 0.04, 0.2
Nitrogen	14N, 15N	99.6, 0.04
Chlorine	35Cl, 37Cl	76, 24
Sulfur	32S, 34S	94.99, 4.25

# Isotope ratio - how measured



- Ground water, soil or air samples
- Gas chromatography - isotope ratio mass spectrometry (GC – IRMS) or GC-MS

$$\delta^{13}\text{C} = \frac{R_x - R_{\text{std}}}{R_{\text{std}}} \times 1,000$$

- $R_x = 13\text{C}/12\text{C}$ ,  $\delta$  is negative
- Standard = Vienna Pee Dee Belemnite (VPDB) for carbon and Standard Mean Ocean Chlorine (SMOC) for chlorine
- Measured in units of = per mil = ‰ = 1/1000 OR parts per thousand

# Benefits and Limitations of CSIA

## Benefits

- Does not rely on concentration trends
- Highly sensitive revealing subtle but important differences
- Useful fingerprinting tool



## Limitations

- Cannot be used for age dating
- Cannot tell % of each source
- If sources are similar may not be able to differentiate



Key  
Point

*CSIA determines if two samples are isotopically similar or not*

# What practitioners need to know about CSIA



- Can be used on all types of COCs that contain stable isotopes
- Allows differentiation between degradation of COCs and processes that do not reduce COC mass (e.g., dilution)
- Use in a multi line of evidence approach i.e. combine with chemical and geochemical analysis
- Can differentiate between COC sources

## Key Point

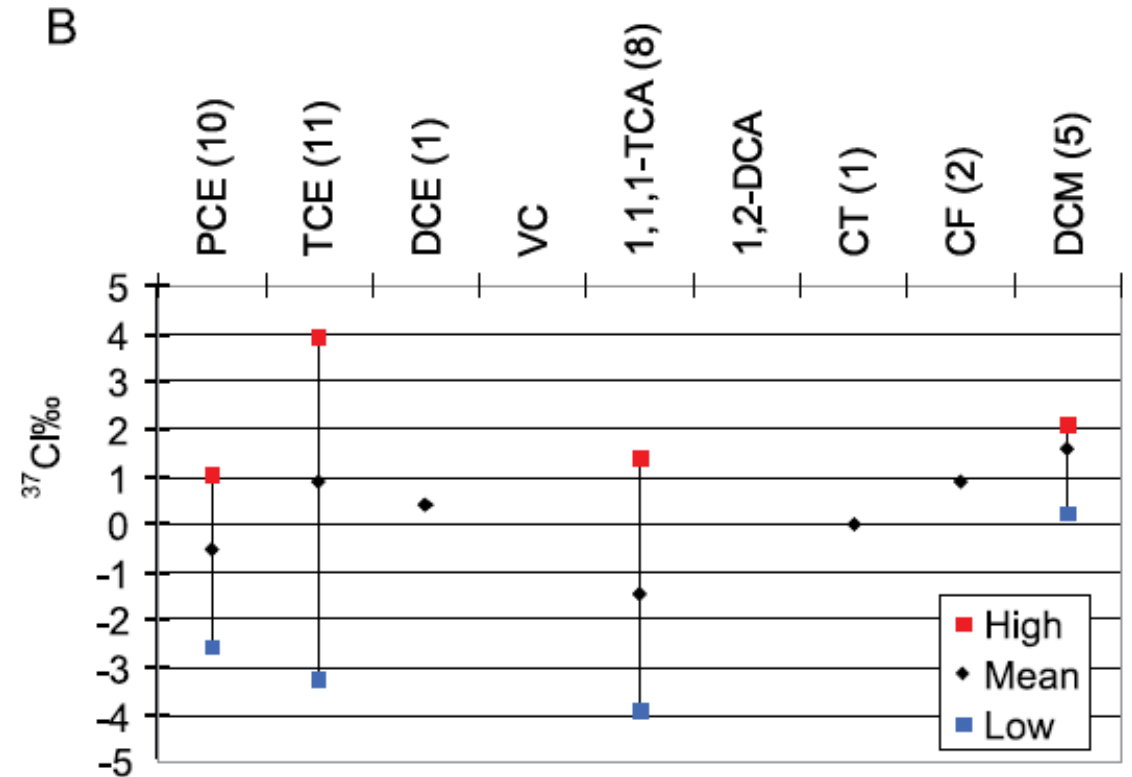
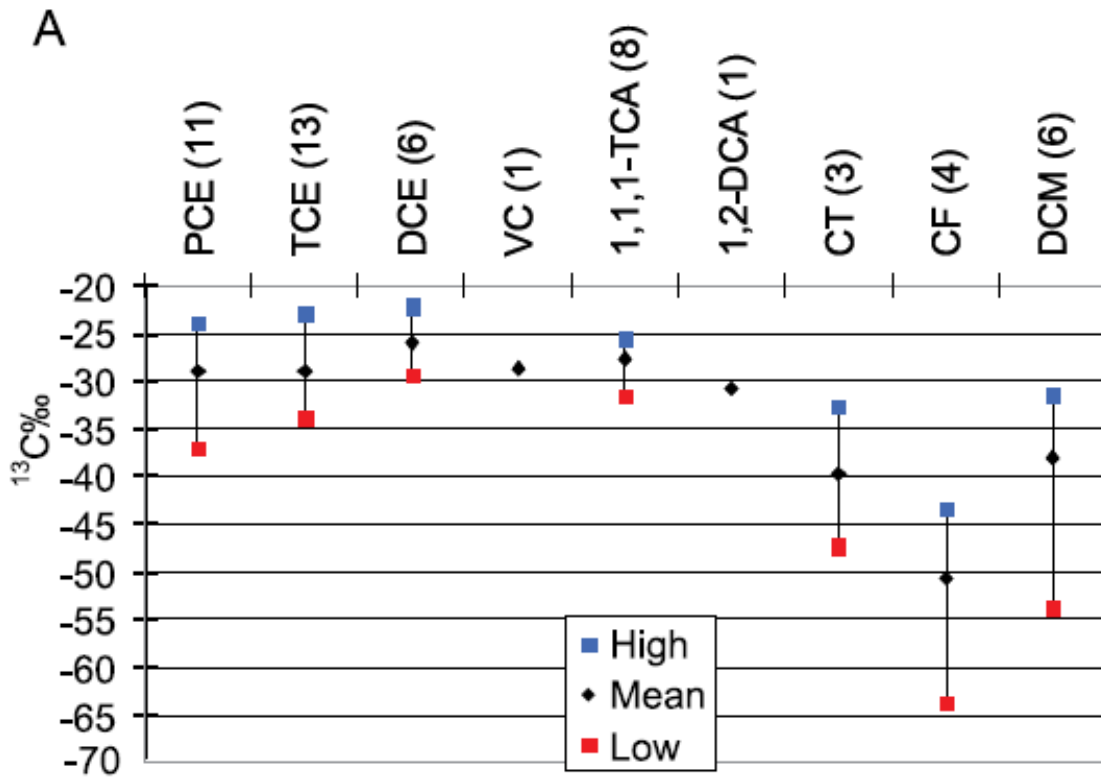
*The same compound (TCE) from two different manufacturers can have distinct isotopic ratios. This is due to differences in the raw materials and isotope fractionation during the manufacturing process and even differ between batches.*



# Variability in isotopes in chemicals



Isotope varies between manufactures and even batches – due to isotope ratio of the “ingredients”





# Is isotopic composition of source material need to be known?



- If manufacturer and batch # etc. known – Great!
- If not known – compare isotopic data from one or multiple elements
  - C and Cl for chlorinated solvents
  - C and H for hydrocarbons

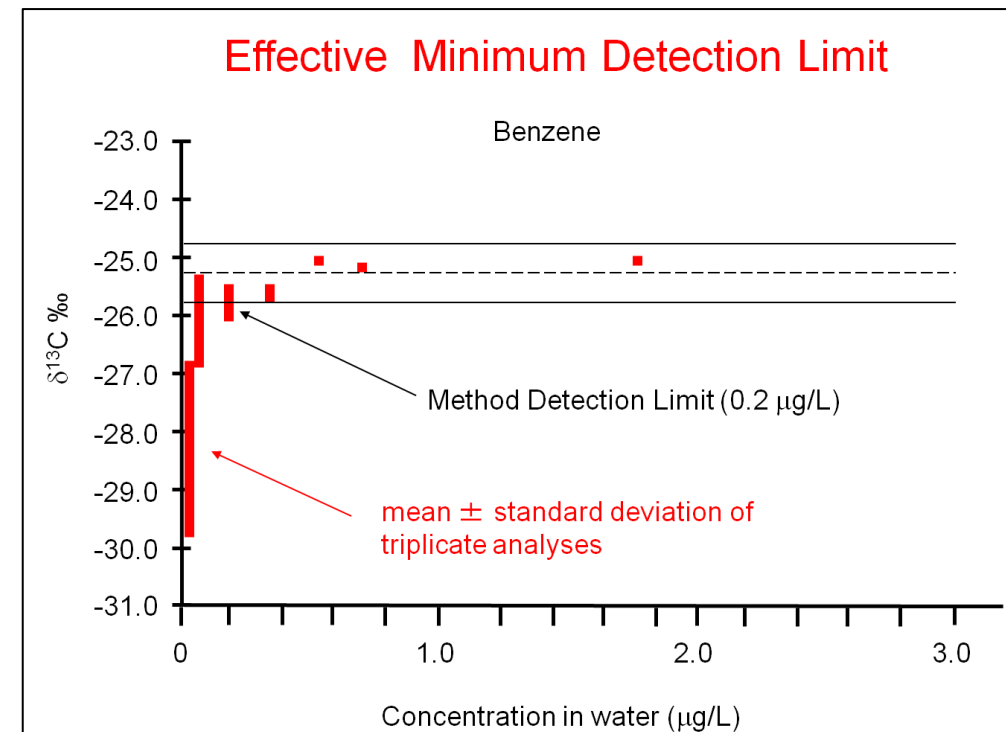
## Key Point

*Use isotope of two different elements increases data validity*

# Sampling for CSIA Source Identification



- Know site history – any remediation done? Any injections/ extractions ?
- Design sampling strategy based on CSM and potential location of sources
- Take at least three groundwater samples (within source) for each presumed source
- If NAPL is present take samples of NAPL for CSIA
- For plume characterization – take at least three samples in each plume.
- Data more reliable at higher conc.

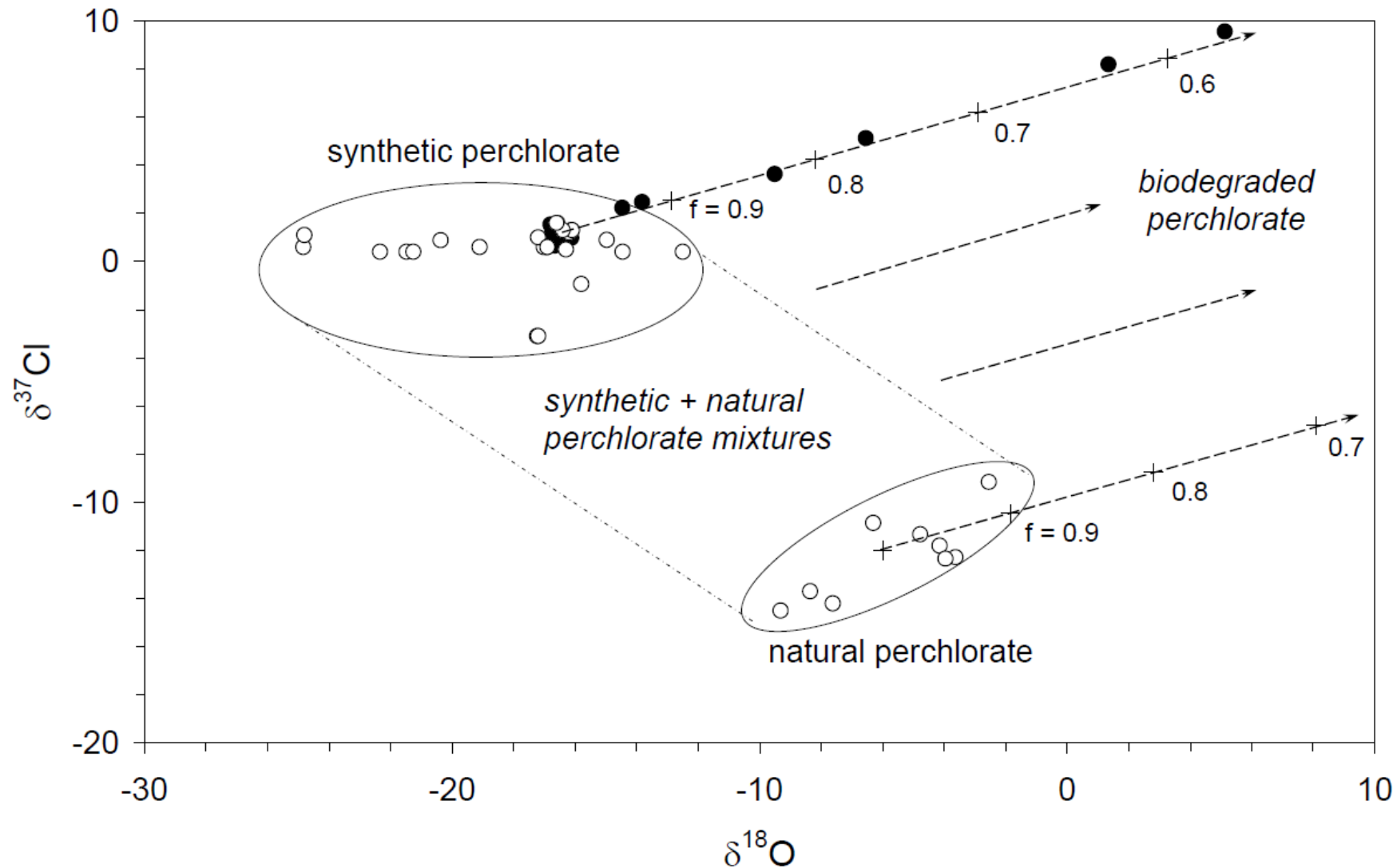


# Examples of CSIA use in forensics



- Methane source – biodegradation or pipeline gas
- Perchlorate – Is it natural or synthetic?
- VOCs – Originates from one source or multiple sources
- Nitrate - Is it run off or naturally occurring?

# Differentiating Perchlorate Sources



# Evaluating TCE Source – one element



- Two hot spots
- TCE present at concentrations  $>1\%$  solubility
- DNAPL present
- Daughter products in low concentrations
- Two vertical zones

## Questions

- Heterogeneous contaminant dissolution/flow?
- Contamination in lower zone from upper zone?

# Evaluating TCE Source – one element

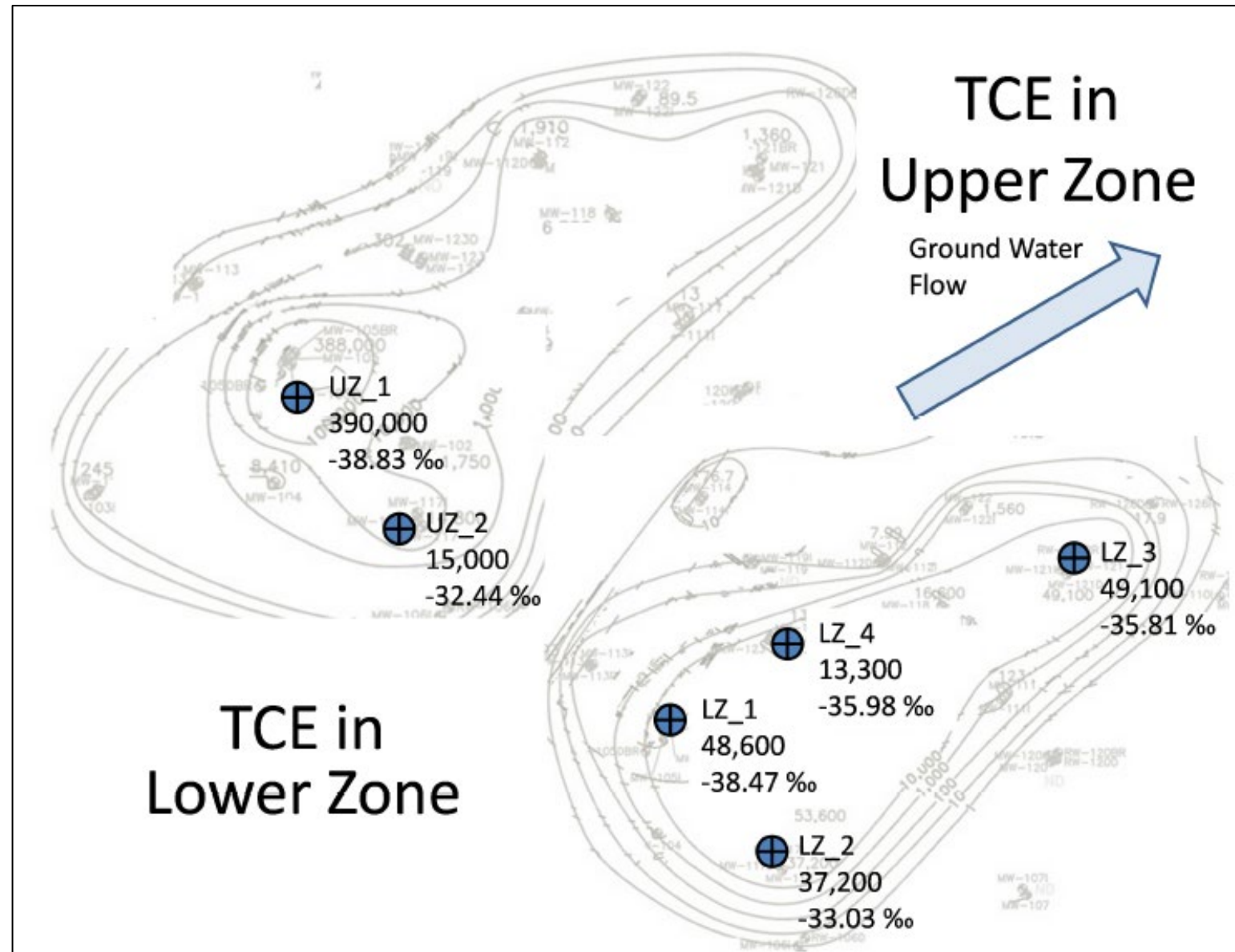


## Approach

- 6 GW wells
- TCE concentration measured
- Carbon isotope ratio measured
- Along flow path

## Outcome

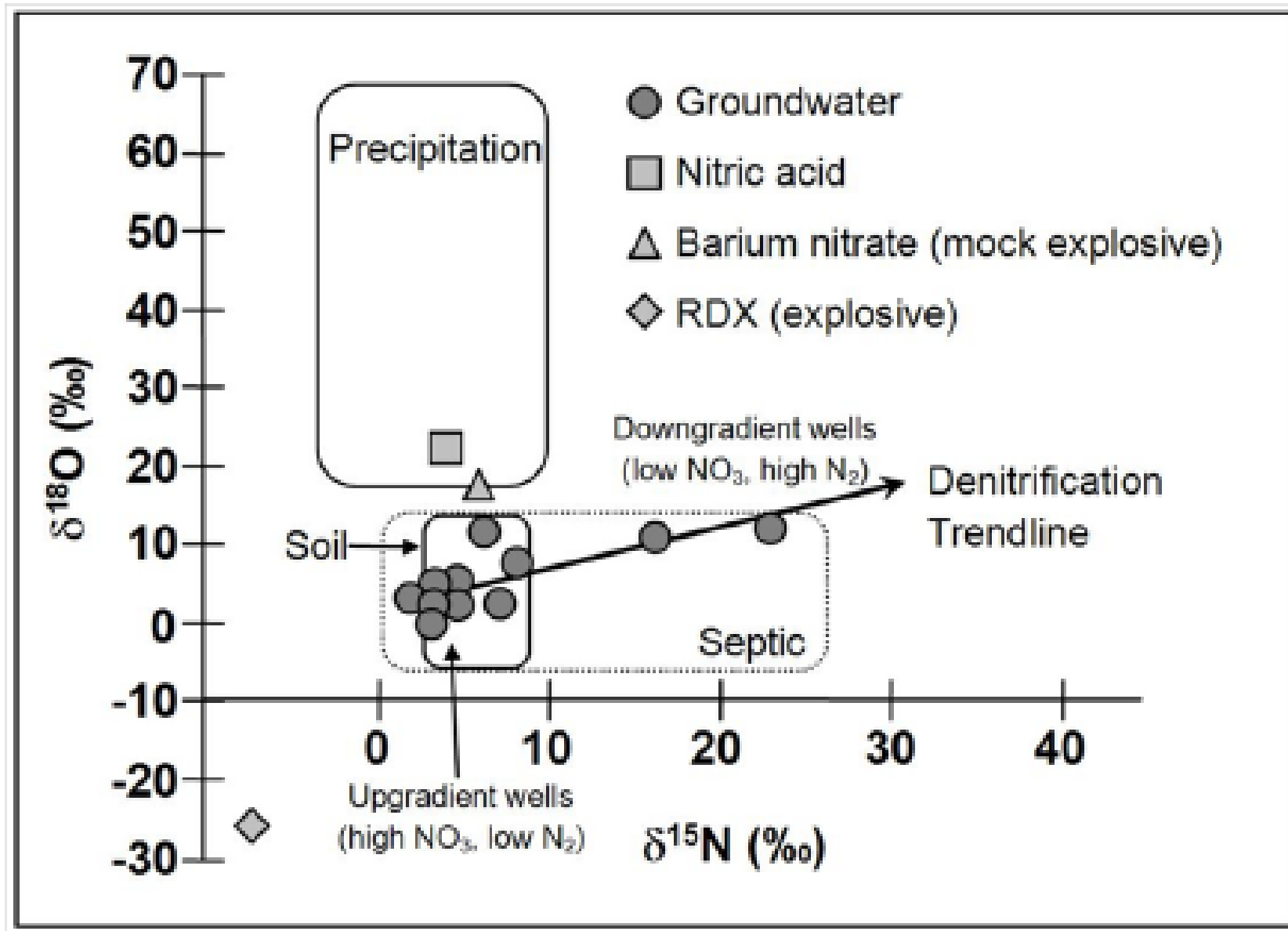
- $\delta^{13}C$  UZ-1 and LZ-1 similar
- $\delta^{13}C$  UZ-2 and LZ-2 similar



## Conclusion

- Significant difference in  $\delta^{13}\text{C}$  of TCE in the two hot spots
- Carbon only CSIA provided sufficient information
- Down gradient wells may be influenced by both hot spots
- Upper and lower zone contamination from same source

# Evaluating Nitrate Sources – two elements





# CSIA and Vapor Intrusion

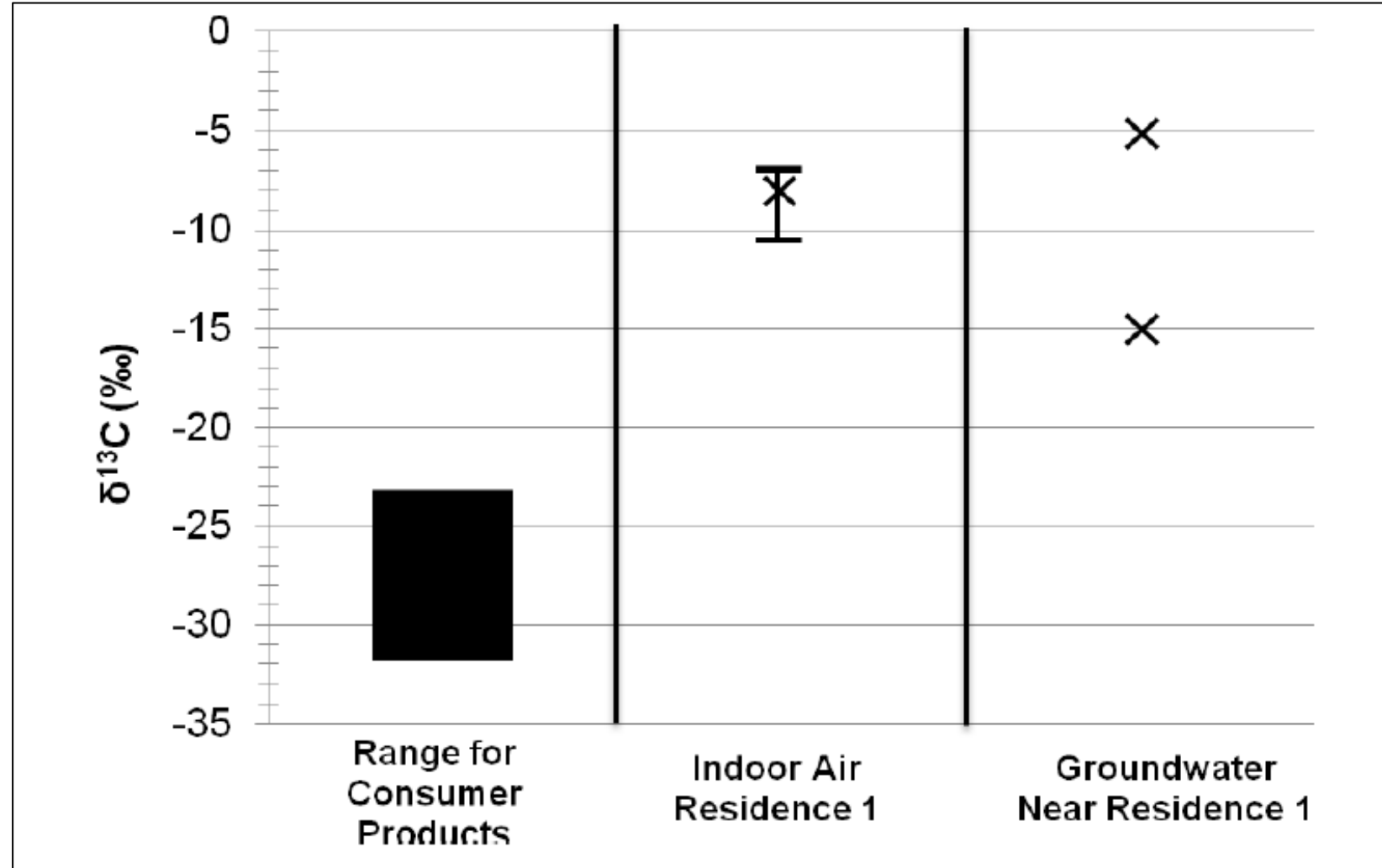


- Goal – differentiate VOC vapor intrusion from indoor sources
- Carbon and chlorine isotope ratio for PCE and TCE
- Indoor air, GW and soil gas samples, commercial products containing TCE or PCE
- Compare ratios to commercial products and GW
- Approach taken at 5 residence

# CSIA and VI Residence 1



- $\delta^{13}\text{C}$  indoor air similar to GW values for TCE
- CSIA alone provided conclusive results
- Source TCE from GW



# CSIA and VI Residence 2 and 3



Two element approach

**Residence 2** -  $\delta^{37}\text{Cl}$  for GW and indoor air similar (from GW?) BUT

- $\delta^{13}\text{C}$  for soil gas and indoor air in range of commercial products
- Further investigation

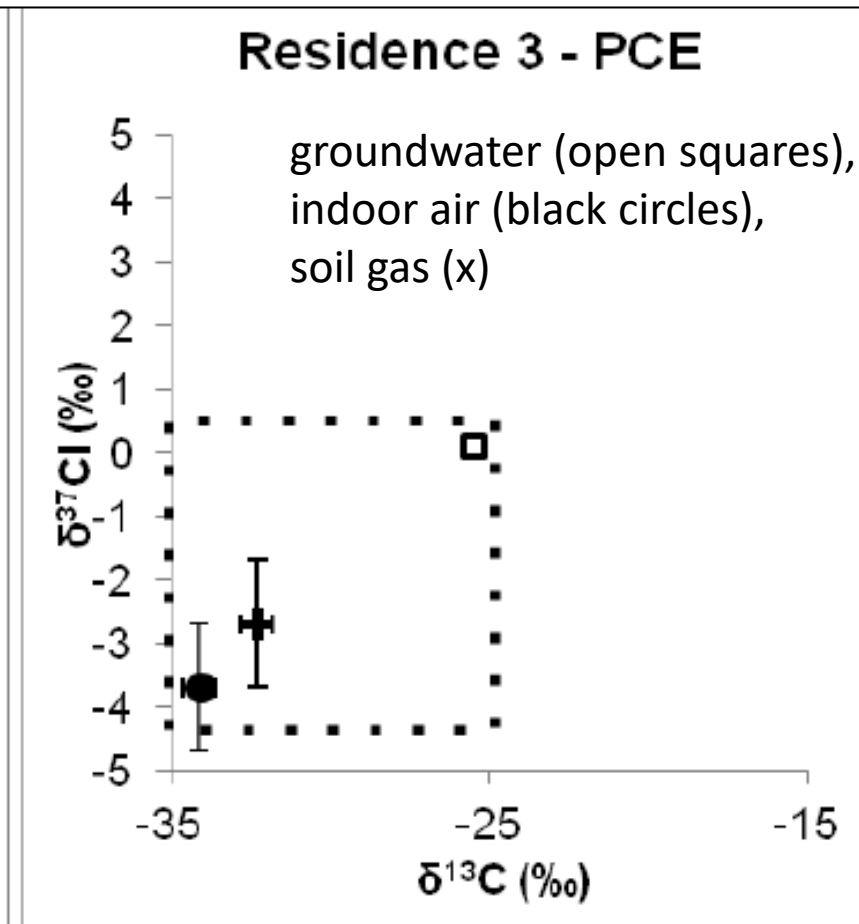
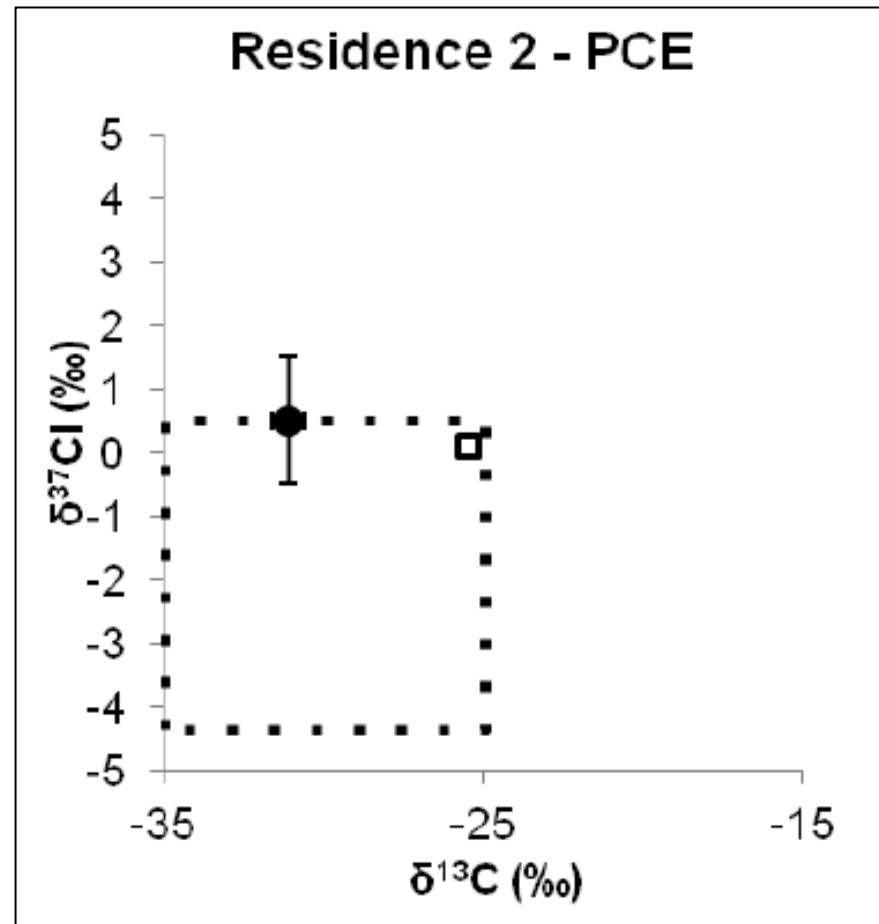
indicated Indoor air

Source: commercial product  
CSIA supported by other data

## Residence 3

$\delta^{37}\text{Cl}$  and  $\delta^{13}\text{C}$  similar to that of commercial product found in home

Source: commercial product  
CSIA alone



# CSIA and VI Residence 2 and 3



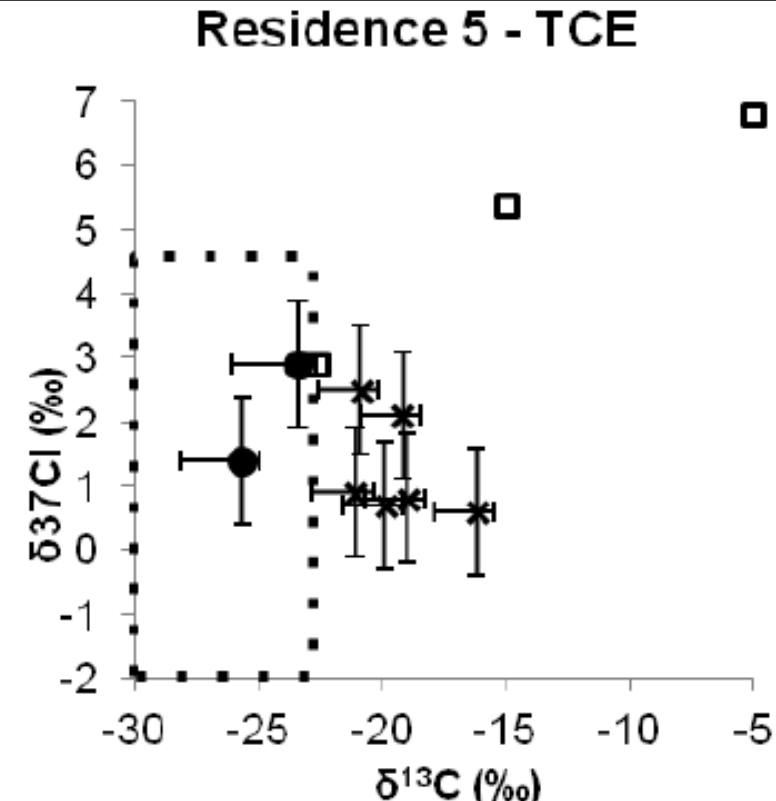
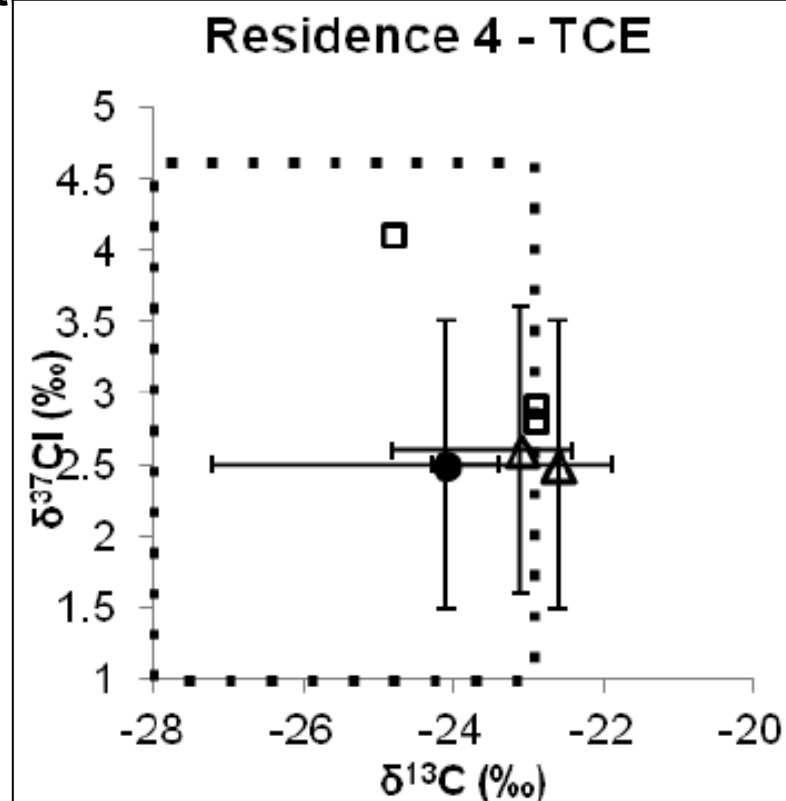
## Residence 4

- Indoor air  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  values for PCE were similar to those for TCE in the sewer headspace and groundwater.
- GW discharges to sewer lines
- CSIA supported by other data
- **Source – GW**

## Residence 5

- Wide variety of isotope ratios
- CSIA inconclusive
- **Possibly Multiple sources**

groundwater (open squares),  
indoor air (black circles),  
soil gas (x)

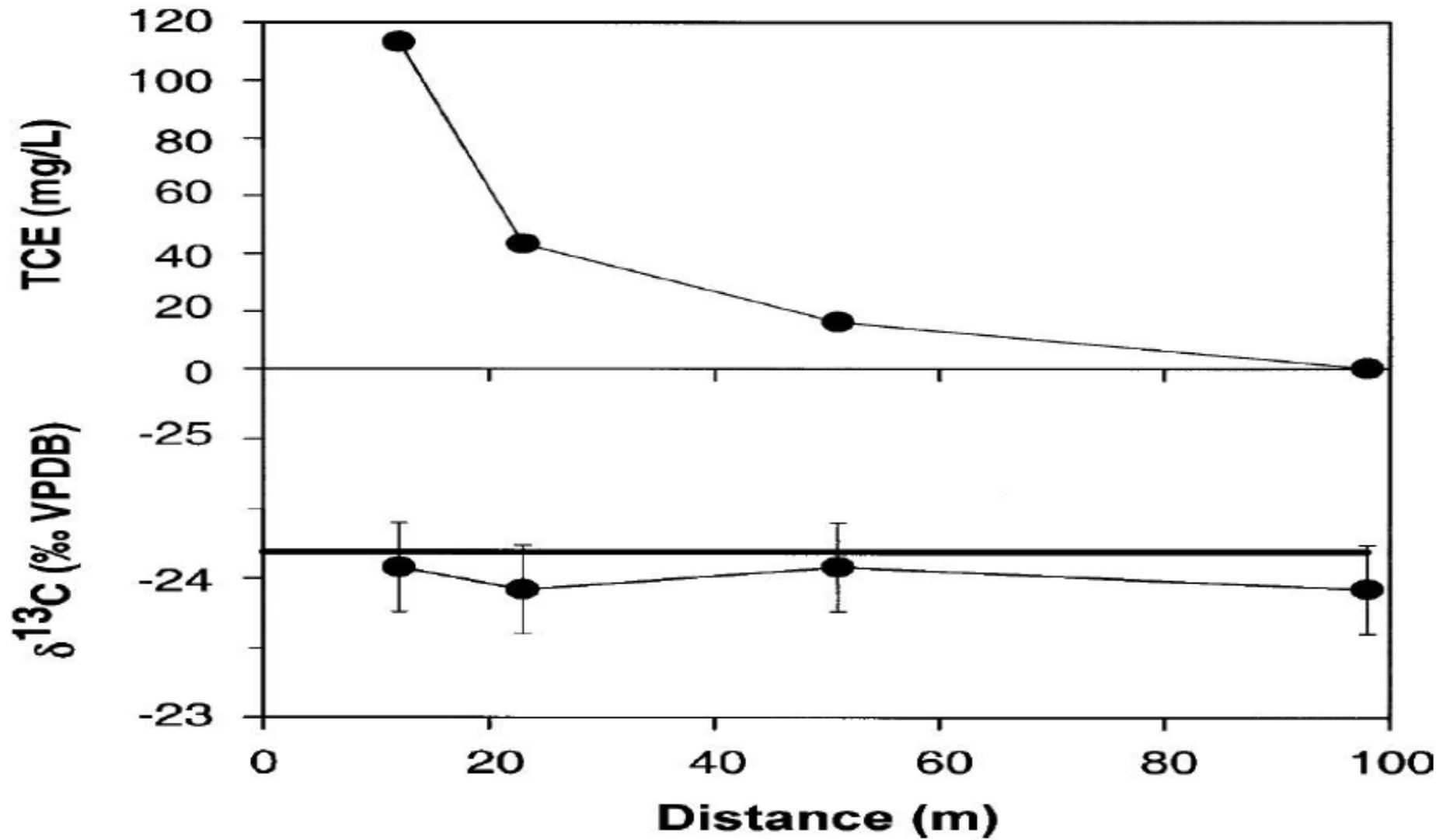


# Questions CSIA can answer in Site Characterization



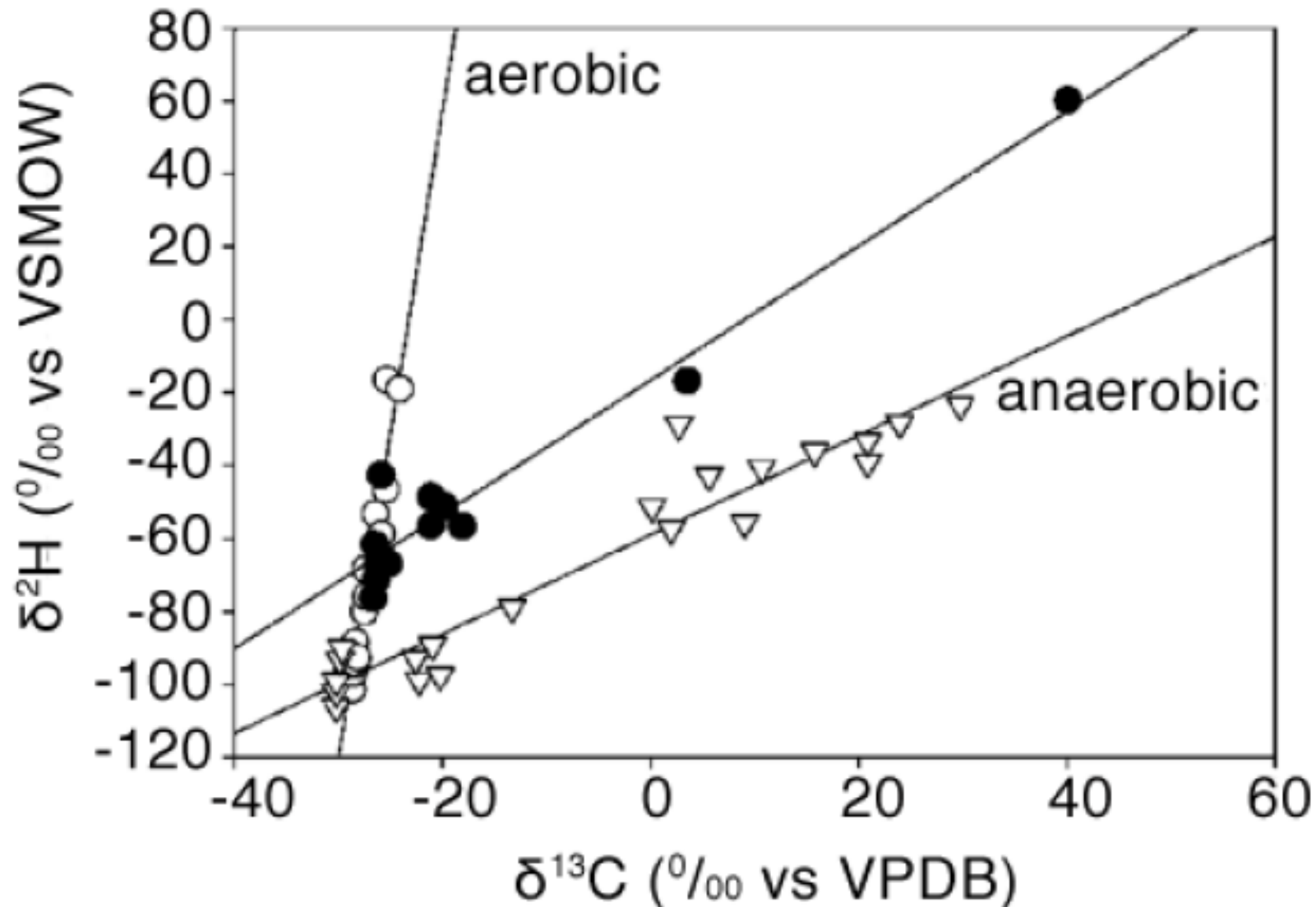
- Has biological or abiotic degradation occurred?
- If so, how much and where?
- Is methane from near-surface biodegradation or natural gas production?
- Is the TCE a parent from one source or a daughter product of perchloroethene (PCE) from another source?
- Is there evidence of multiple sources?
- Is the contaminant in the dissolved or nonaqueous phase?
- Is there evidence of a rate-limiting step (i.e., accumulation of contaminant intermediates)?

# Degradation or Dilution?



Hunkeler, D.; Chollet, N.; Pittet, X.; Aravena, R.; Cherry, J.A.; and Parker, B.L.; "Effect of source variability and transport processes on carbon isotope ratios of TCE and PCE in two sandy aquifers", Journal of Contaminant Hydrology 74, 265-274, 2004.

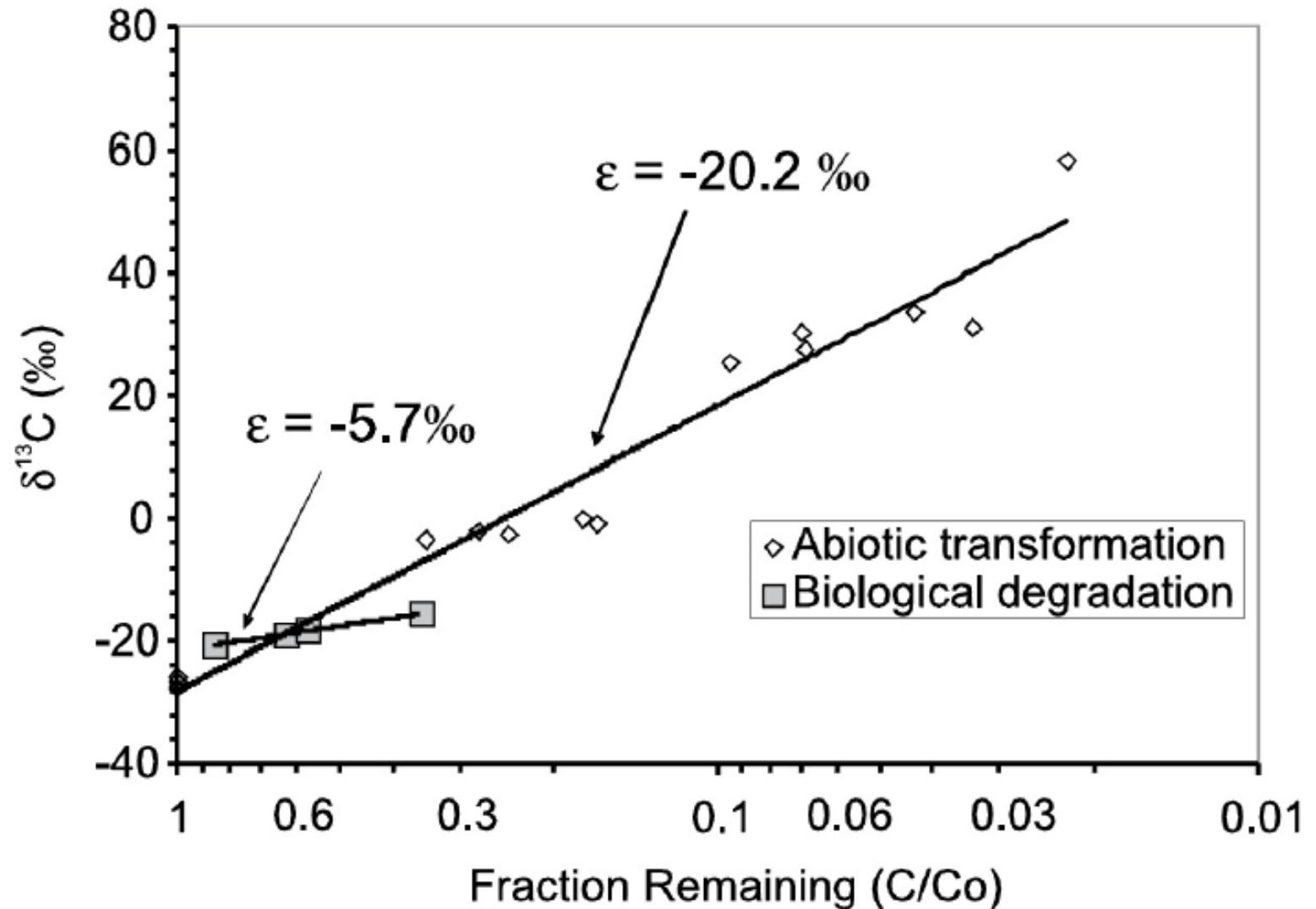
# Aerobic or Anaerobic Degradation?



# Abiotic vs Biological Degradation



- EDB concentrations decreasing over time
- Mechanism of degradation unknown
- Site conditions - anoxic
- Literature EDB can degrade both biologically and abiotically
- qPCR – no evidence of EDB degrading microbes
- Measured  $^{13}\text{C}$  with distance from source
- EDB was degrading abiotically





# General Data Interpretation



Result	Conclusion Recommendation
<ul style="list-style-type: none"><li>- No difference in the isotope ratio between different location</li></ul>	<ul style="list-style-type: none"><li>- Possibly a single source</li><li>- Multiple sources with same isotope ratio</li><li>- Review additional site data</li></ul>
<ul style="list-style-type: none"><li>- Samples from different locations with different plumes and flow paths vary in isotope ratio</li></ul>	<ul style="list-style-type: none"><li>- Most likely multiple sources</li></ul>
<ul style="list-style-type: none"><li>- Samples partition into groups that contradict the CSM</li></ul>	<ul style="list-style-type: none"><li>- Revise your CSM</li></ul>
<ul style="list-style-type: none"><li>- Most samples are isotopically different from each other</li></ul>	<ul style="list-style-type: none"><li>- Degradation may have occurred</li><li>- Review additional site data</li></ul>

# Key Points



- In site characterization CSIA can be used for source identification and to determine if degradation has taken place
- Isotope ratio of synthetic chemicals vary by manufacturer and batch
- CSIA best along side other characterization techniques
- Better to determine isotope ratio of two elements
- Collect multiple samples for CSIA along a flow path

# References



Hunkeler, D., R. U. Meckenstock, B. Lollar, T. C. Schmidt, AND J. T. WILSON. A Guide for Assessing Biodegradation and Source Identification of Organic Groundwater Contaminants Using Compound Specific Isotope Analysis (CSIA). U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-08/148, 2009.

SERDP/ESTCP EnviroWiki [Compound Specific Isotope Analysis \(CSIA\) - Enviro Wiki](#)

ITRC CSIA Overview [3 Compound specific isotope analysis \(itrcweb.org\)](#)

ITRC CSIA Case study [A 3 Application of Compound Specific Isotope Analysis CSIA for TCE in groundwater for site characterization NJ \(itrcweb.org\)](#)

NAVFAC Factsheet Environmental Molecular Diagnostics: Chemical based Tools

# Questions