Compound-Specific Isotope Analysis as a Forensic Tool to Distinguish Sources

AEHS Foundation®

32nd Annual International Conference on Soil, Water, Energy, and Air

Wednesday, March 22 , 2023
11:00 AM – 11:30 AM

tersus environmental

Agenda

What is CSIA

01

02 How Does it Work

Why Use CSIA

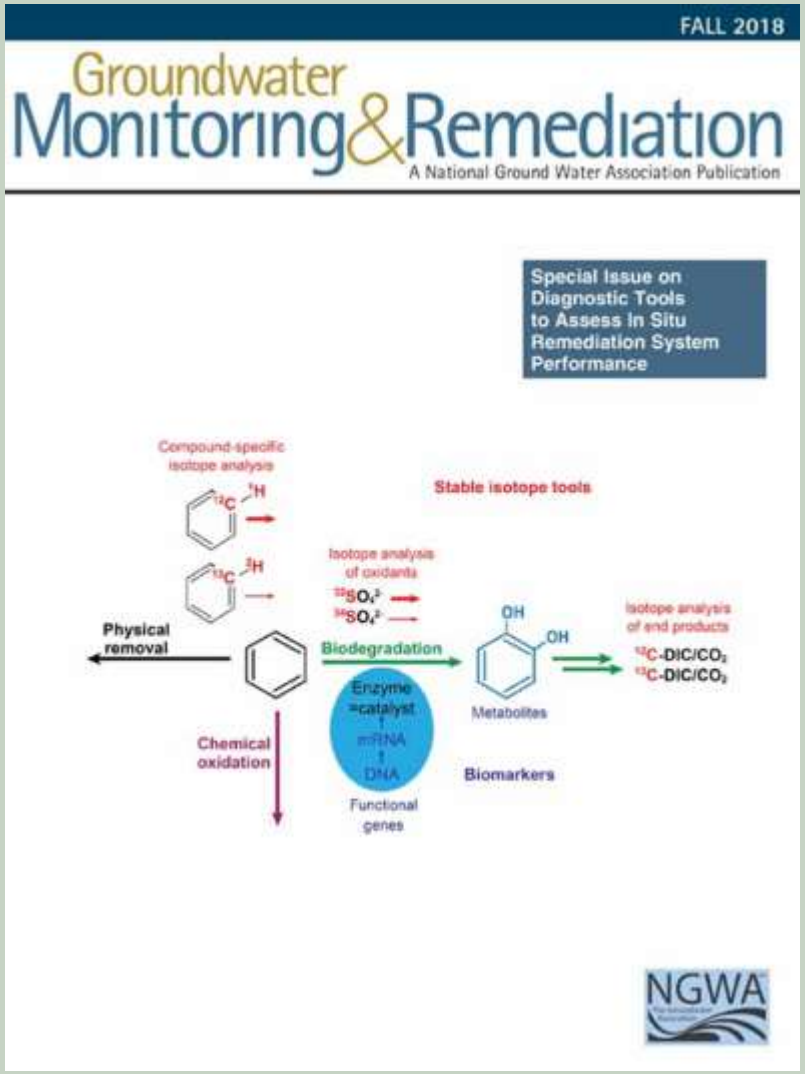
Origin and Fate

03

04 Example Project

List of Notations

$\delta\,^{13}C$	Carbon 13 to carbon 12 isotopic ratio (expressed in delta notation)
$\delta\,^{37}Cl$	Chlorine 37 to chlorine 35 isotopic ratio (expressed in delta notation)
Δ	Isotopic shift between two measured samples
$\Delta\,\delta^{13}C$	Carbon isotope shift between two measured samples



Groundwater Monitoring&Remediation

FALL, VOLUME 38, ISSUE 4

Cutting-Edge Technical Papers

Technical Note

Columns

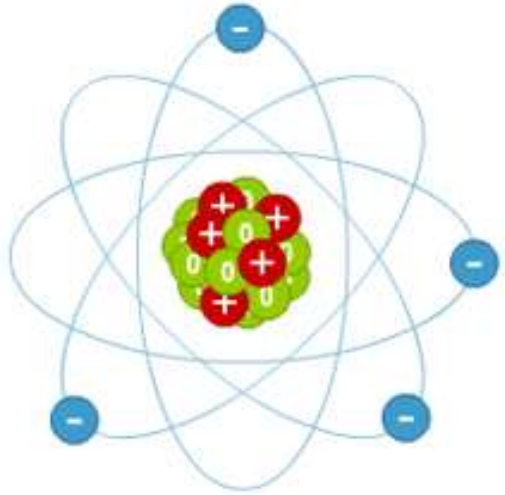
This publication is created in association with:

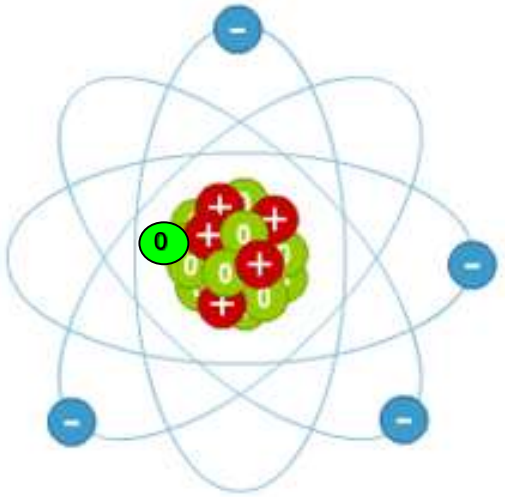
NGWA Groundwater

Compound-Specific Isotope Analysis (CSIA)

- What is CSIA?
  - Measurement of the isotope ratios of individual volatile and semi-volatile compounds extracted from in environmental samples
    - (e.g., $^{13}C/^{12}C$, $^{2}H/^{1}H$, or $^{37}Cl/^{35}Cl$)
  - Provides information that cannot be gained from evaluation of concentration data
  - Isotope composition = isotope signature = isotope fingerprint
  - Isotope fractionation over time: proof of biotic and biotic degradation

Measurement of Isotope Ratios





Carbon 12

Stable atom

6 neutron

6 proton

electron

Carbon 13

Stable atom

7 neutron

6 proton

electron

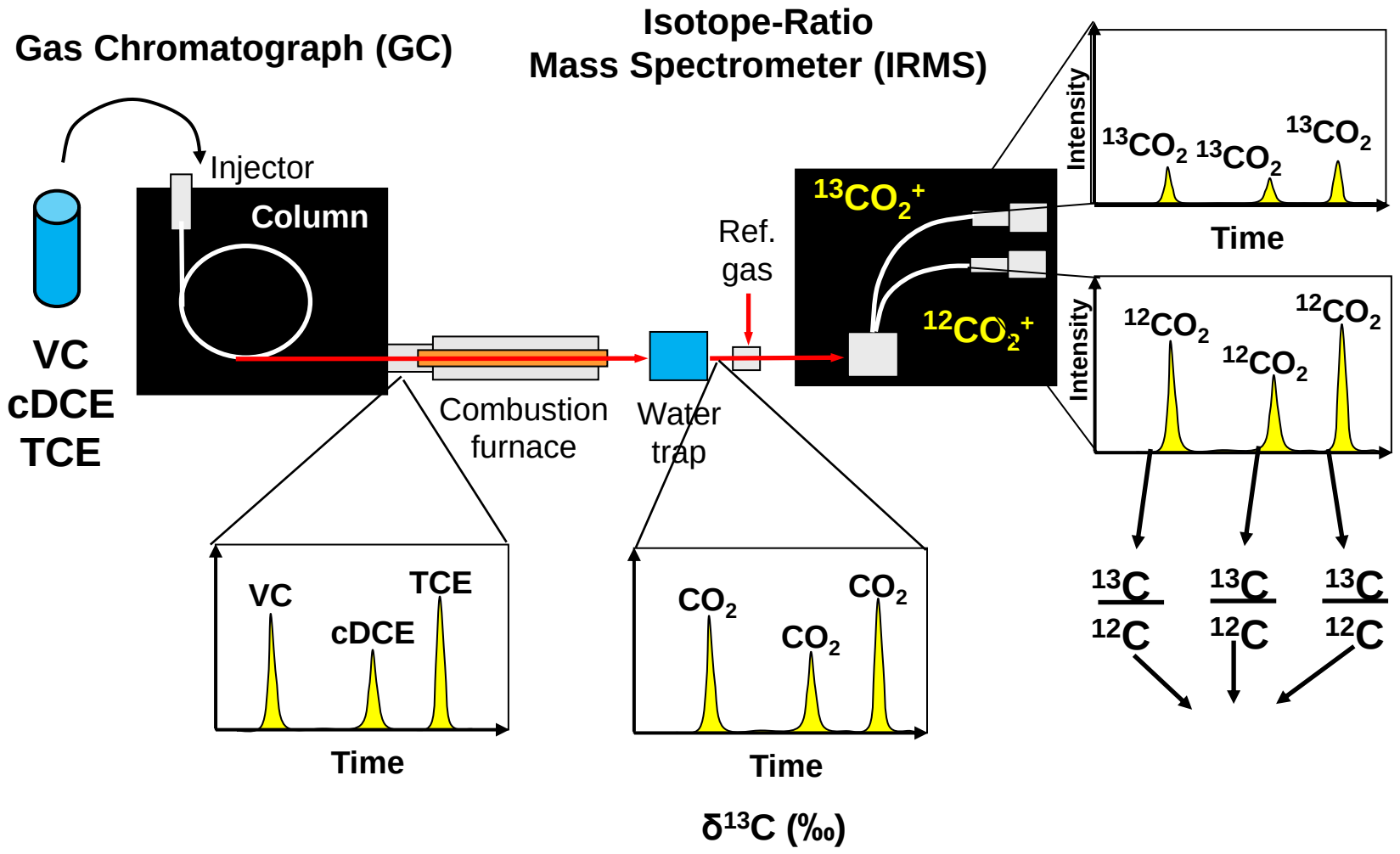
Relative Abundances

- **Carbon**
  - ^{12}C: 98.89 %
  - ^{13}C: 1.11 %
- **Hydrogen**
  - ^{1}H: 99.985 %
  - ^{2}H : 0.0155 %
- **Chlorine**
  - ^{35}Cl: 75.7 %
  - ^{37}Cl : 24.3 %
- **Oxygen***
  - ^{16}O: 99.72%
  - ^{17}O: 0.037%
  - ^{18}O: 0.204%
- **Nitrogen**
  - ^{14}N: 99.6%
  - ^{15}N: 0.4%

***Earth's atmosphere**

- **Sulfur**
  - ^{32}S: 95.02%
  - ^{33}S: 0.75%
  - ^{34}S: 4.21%
  - ^{36}S: 0.02%
- **Lead**
  - ^{204}Pb: 1.5%
  - ^{206}Pb: 24%
  - ^{207}Pb: 22%
  - ^{208}Pb: 52.5%

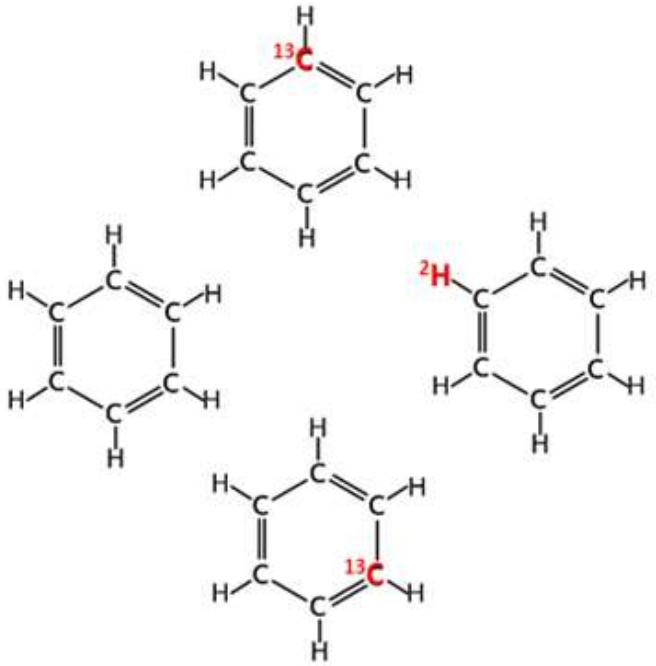
Compound-Specific Isotope Analysis (CSIA)



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

How Does It Work?

Benzene



Combustion to CO_2 (by heat)

GC-IRMS

$$\frac{^{13}C}{^{12}C}$$

$$\frac{^{2}H}{^{1}H}$$

Delta notation

International referencing

$\delta^{13}C$ (‰)

$\delta^{2}H$ (‰)

Targeted Contaminants

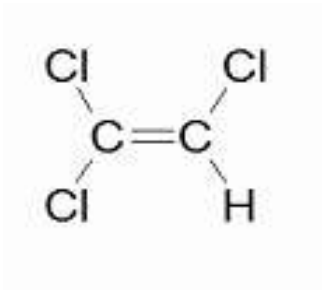
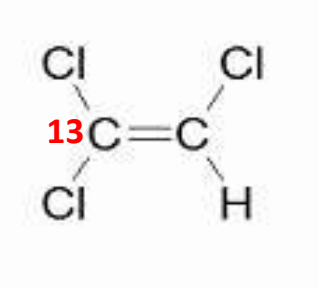
Small molecular size VOCs such as:

- BTEX
- MTBE
- Chlorinated solvents

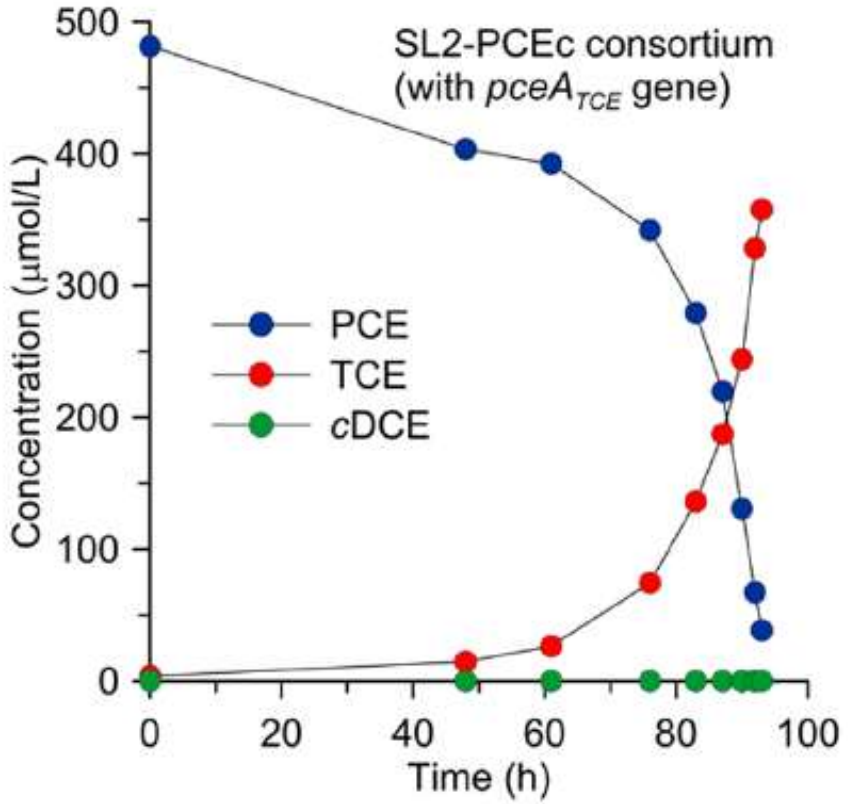
Additional VOCs

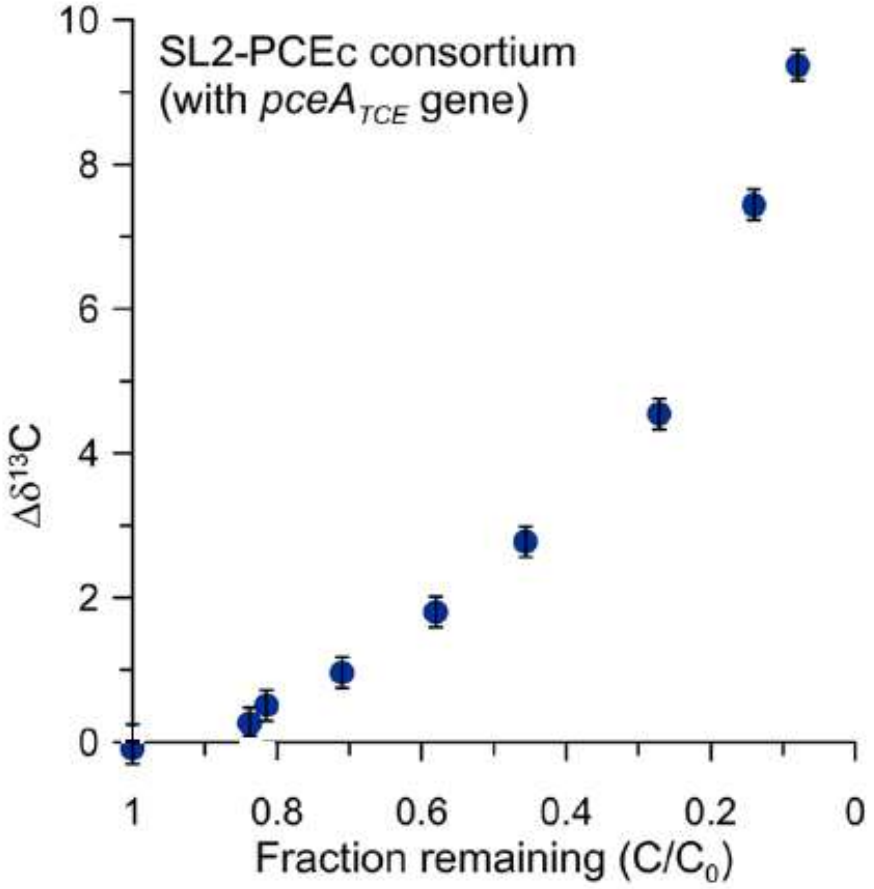
- Chlorobenzene
- Naphthalene
- ETBE
- 1,4 dioxane
- Alkanes < C8 for biodegradation
- All alkanes for forensics

Implication of Heavy Isotopes

	light TCE	heavy TCE	heavy TCE
			
Biodegradation Rate	Normal	Slower	Slower
Chemical Oxidation Rate	Normal	Slower	Slower

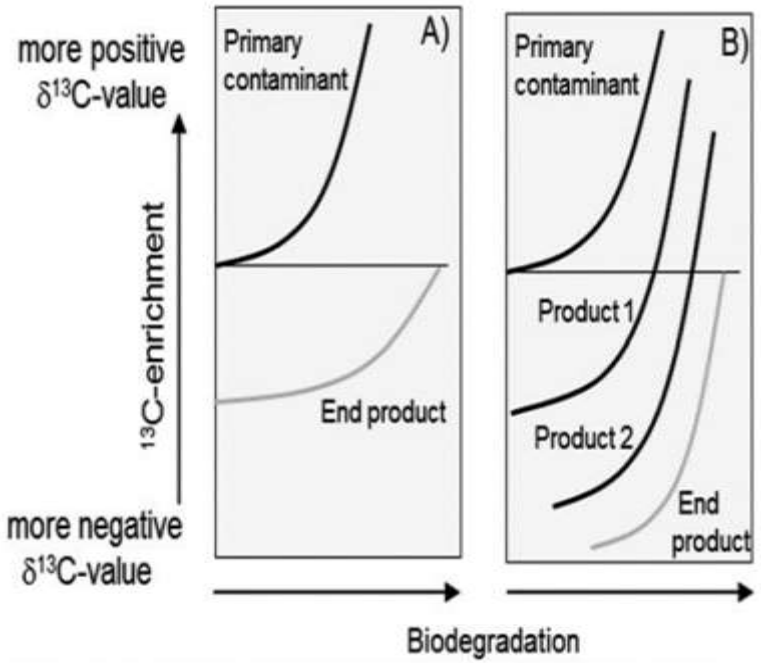
Implication of Heavy Isotopes



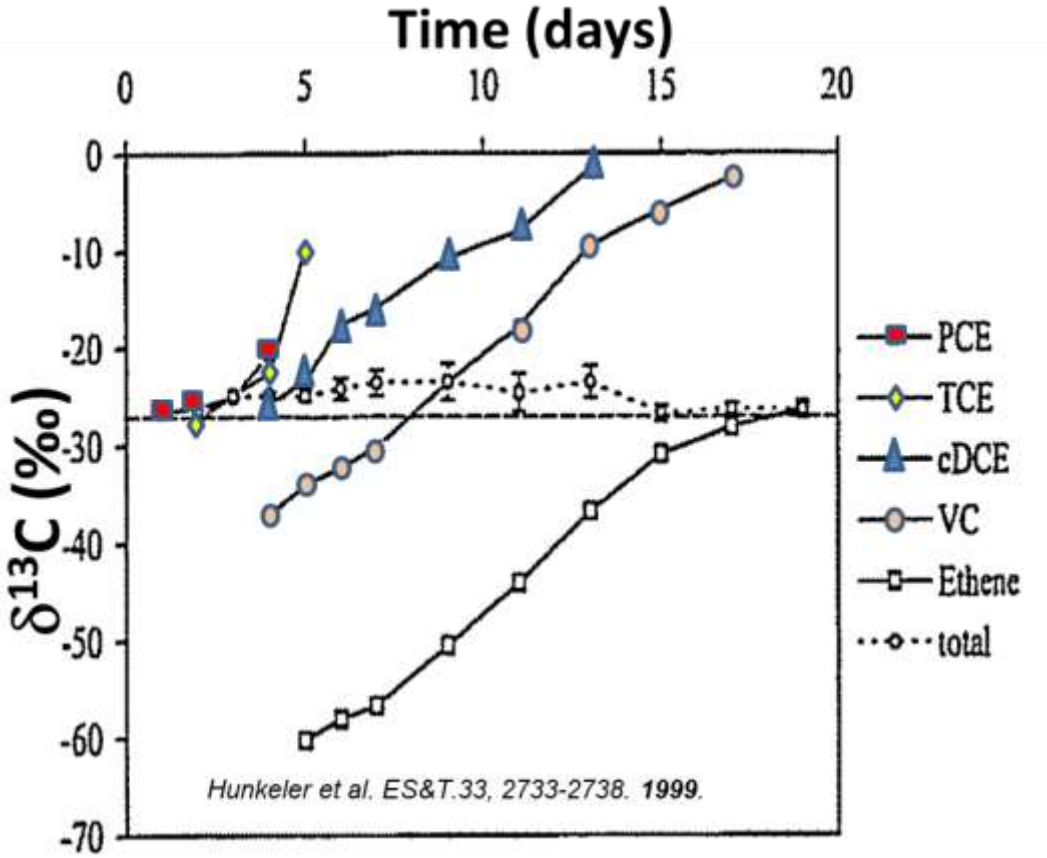


Badin, et al, ES&T, 48, 9179-9186 ,2014

Isotopic Mass Balance

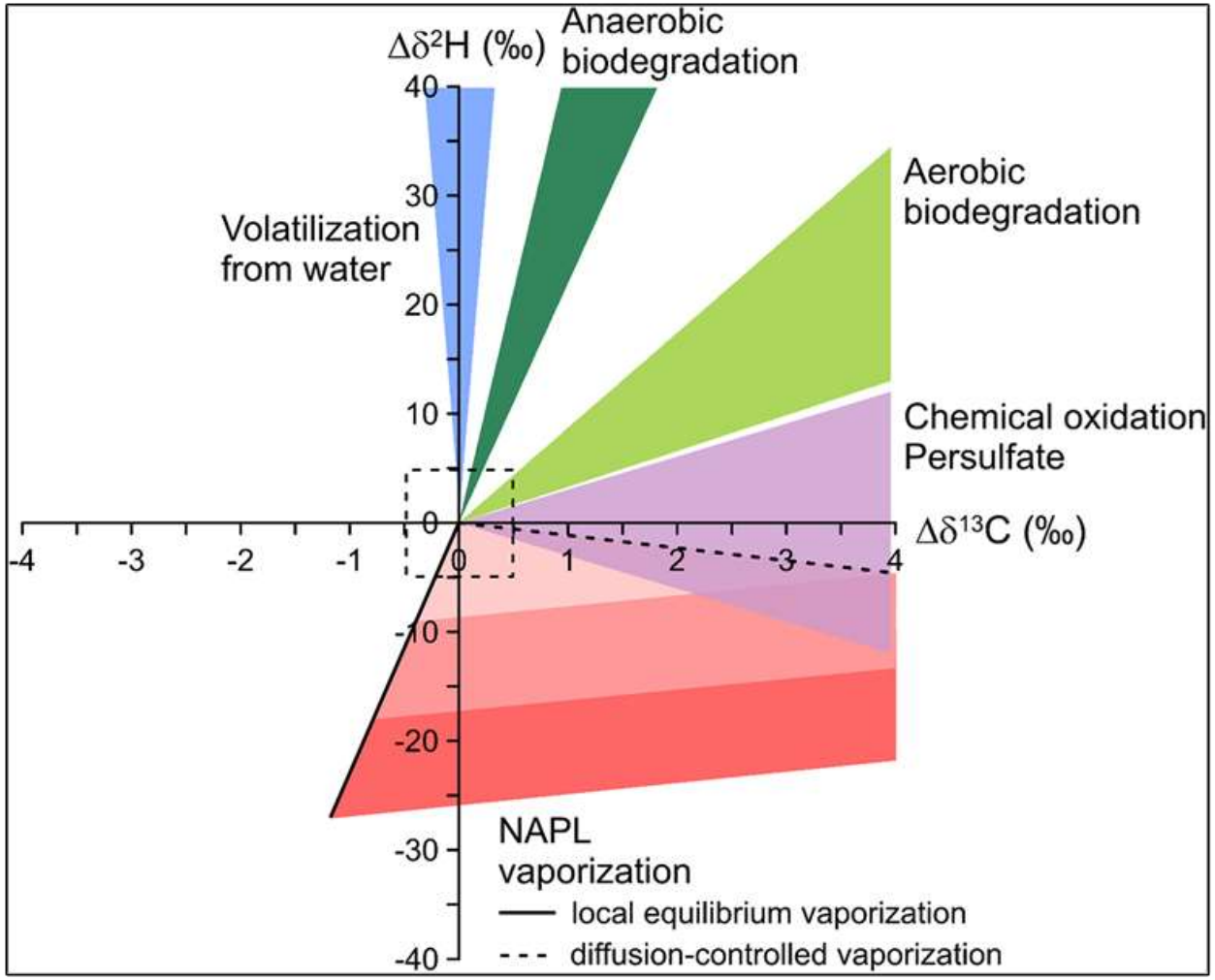


Kuntze, et al, Handbook of Hydrocarbon and Lipid Microbiology. Springer. 2019



Application During *In Situ* Remediation

Applying a dual isotope plot to
destructive and non-destructive processes



Groundwater Monitoring Rem, Volume: 38, Issue: 4, Pages: 88-98, First published: 04 September 2018, DOI: (10.1111/gwmr.12300)

Sample Matrix

- Groundwater
- Soil
- Gaseous phase
  - Soil-gas
  - Atmospheric air
  - Indoor air

Why Use CSIA?

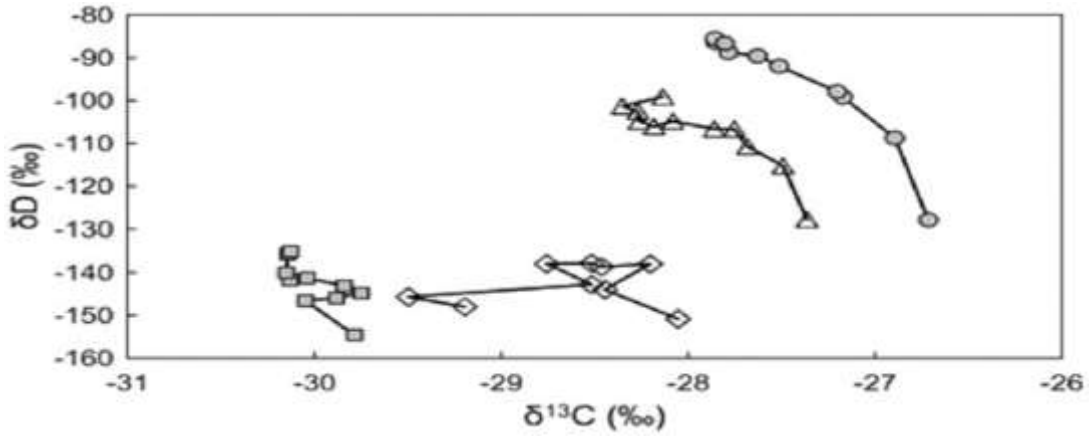
- Origin
- Fate

Origin

- Distinguish two sources of the same contaminant on a given site.
  - Different $\delta^{13}C$, $\delta^{37}Cl$, and $\delta^{2}H$ signature for the same VOC
- Identify a contaminant coming from an off-site source located upgradient.
- Establish a link between an observed compound and its potential emitting source

Isotopic Signature

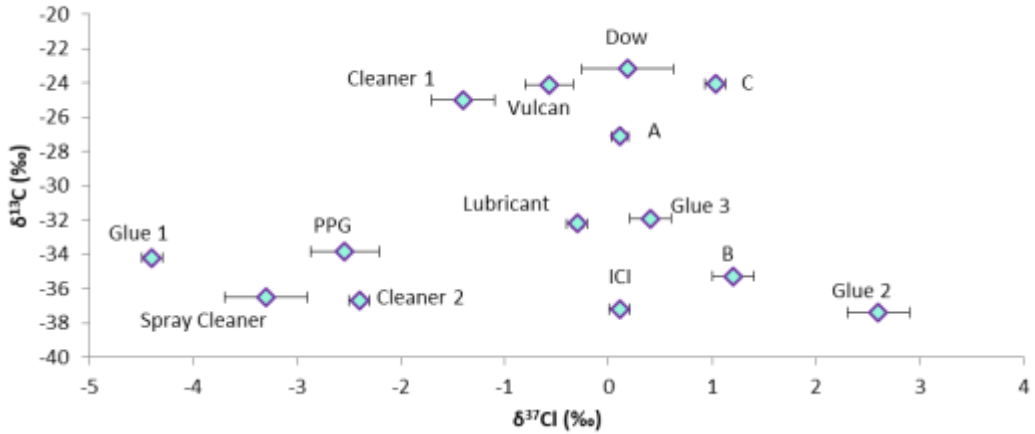
Diesel: C10 to C22 n-Alkane Samples



Isotope ratios vary according to:

- Temperature/pressure of reservoir origin
- Organic matter origin

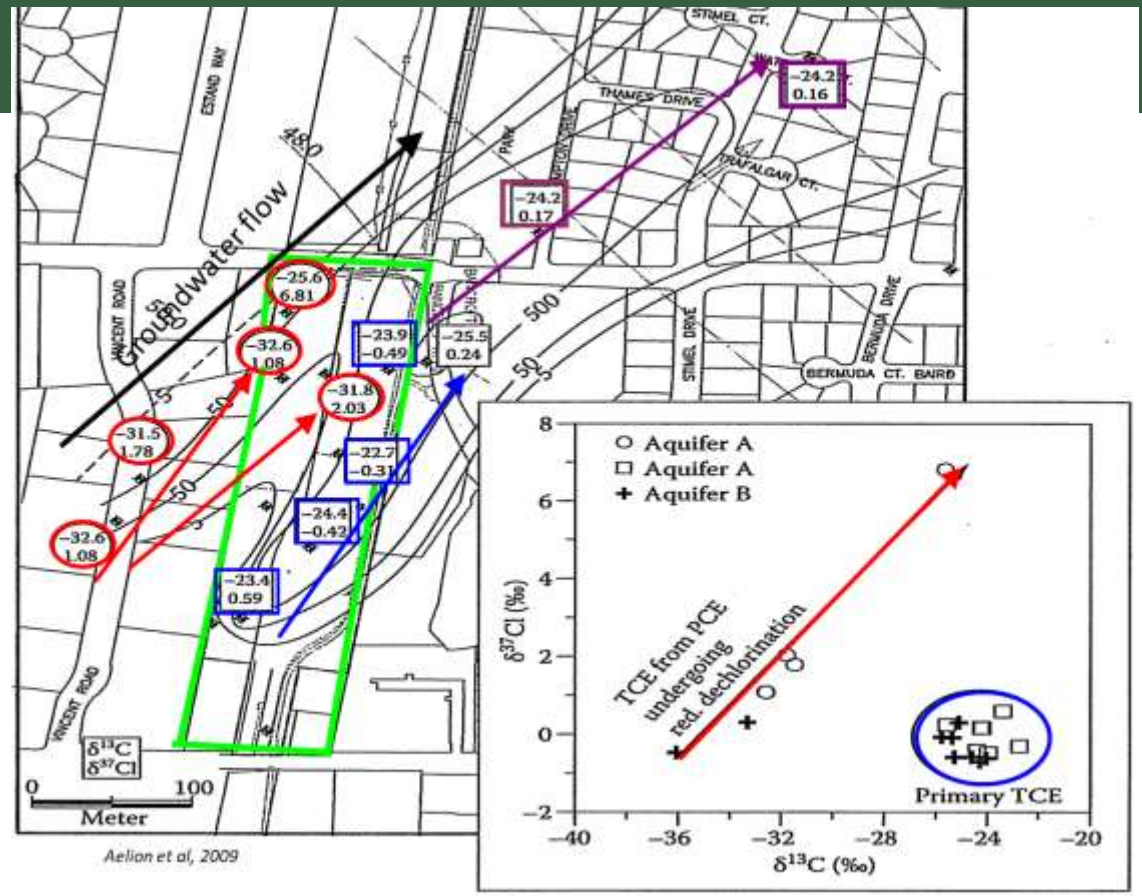
Perchloroethylene (PCE)



Isotope ratios vary according to:

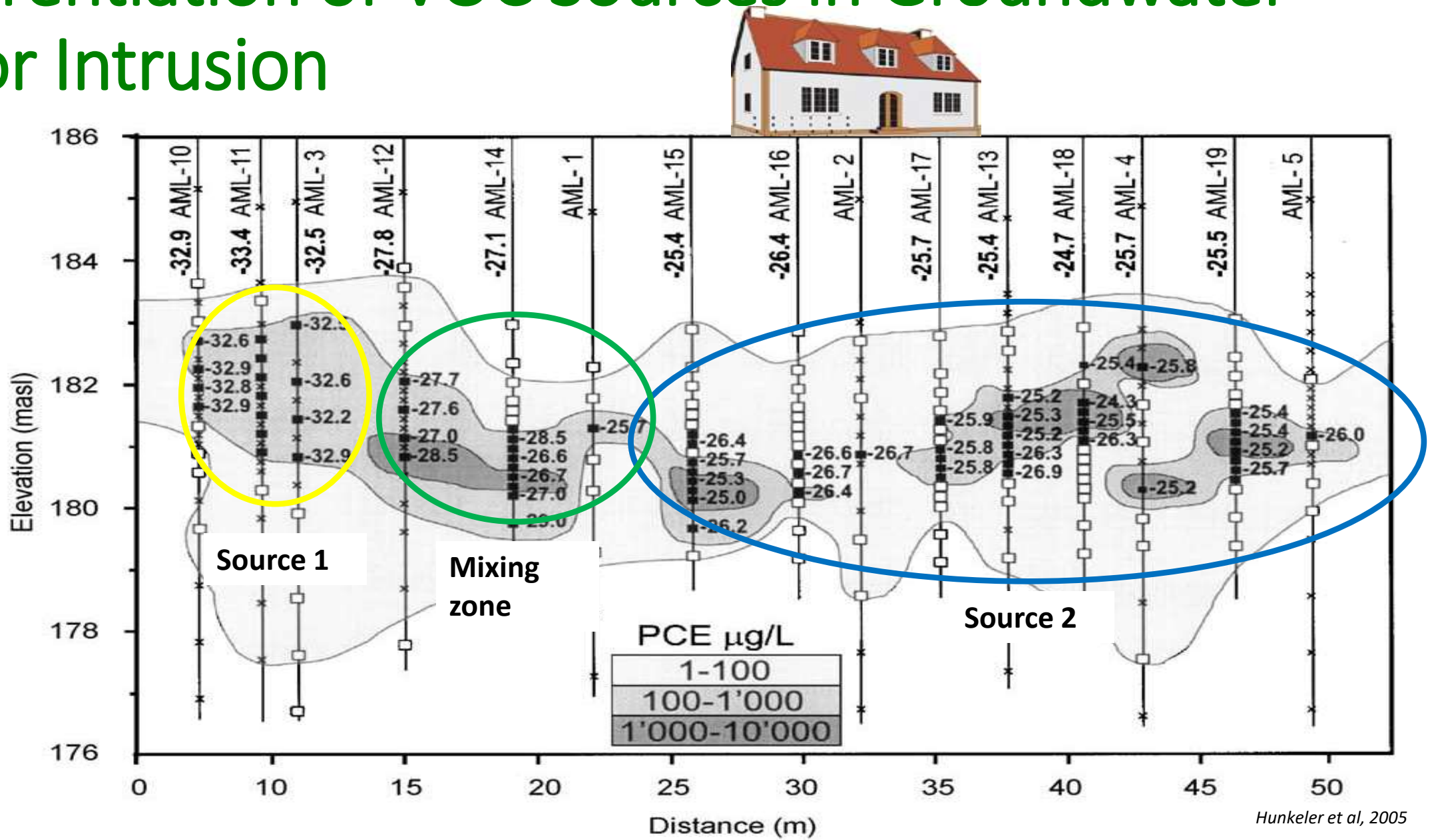
- C and Cl source
- Manufacturing process

Differentiation of TCE Source Areas in Groundwater



- Field Application Example
  - $\delta^{13}C$
  - $\delta^{37}Cl$

Differentiation of VOC Sources in Groundwater Vapor Intrusion



Hunkeler et al, 2005

Fate

- How do we know if treatment is proceeding as intended?

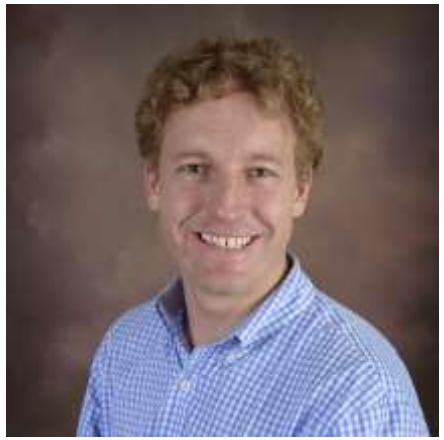
- Are the compounds degraded or diluted?

Example Project

- PCE and TCE detected in groundwater
- Owner acknowledged use of TCE on site, but not PCE
- Suspicions of in-coming PCE from the north

Acknowledgment

Tersus Environmental
Project Manager



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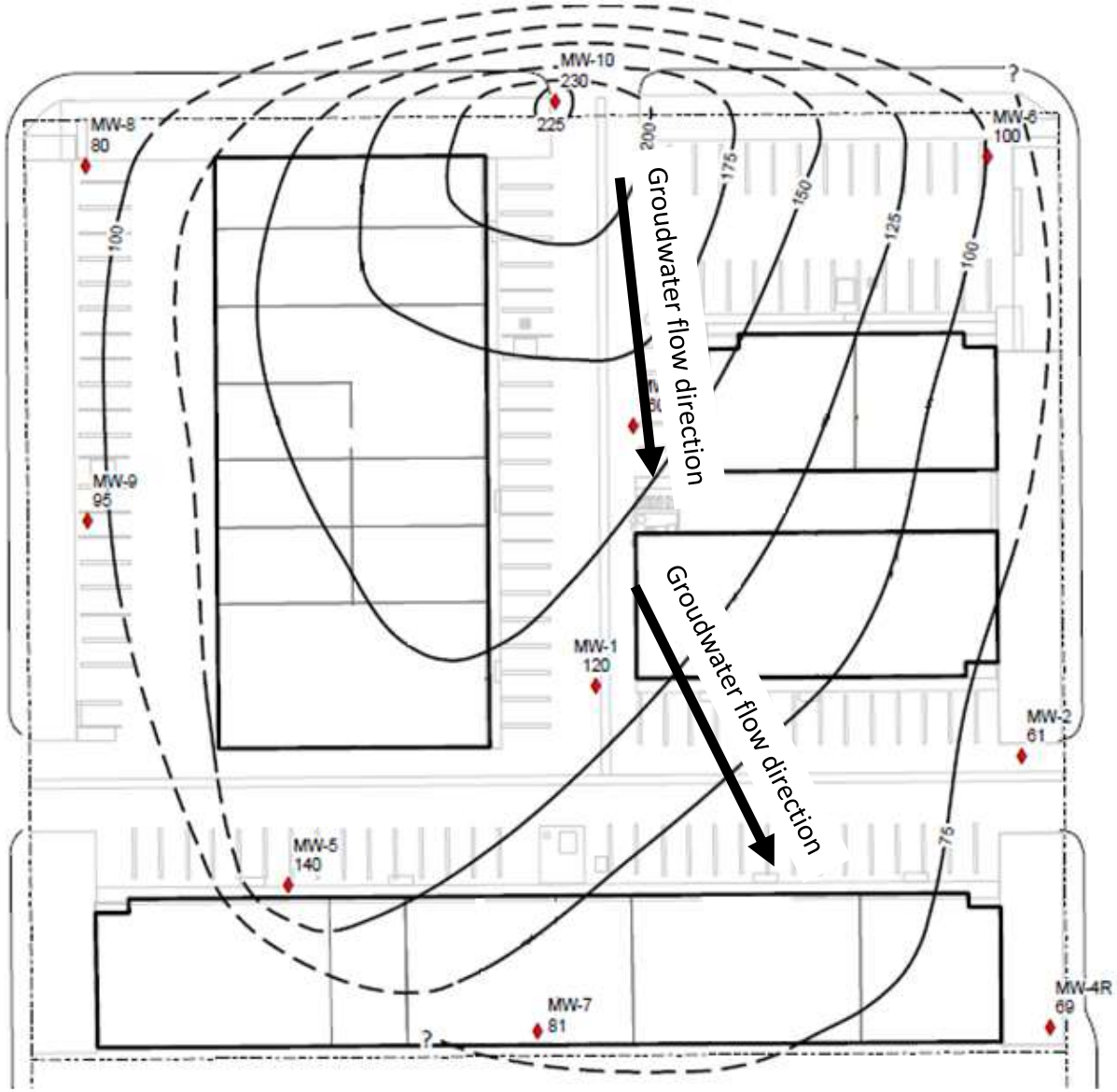
PCE Isoconcentration Map



Concentration and CSIA results for PCE

MW-10

$\delta^{13}C$ (‰): -33.4±0.2

$\delta^{37}Cl$ (‰): -0.9±0.2
Conc.: 160 ug/L

MW-1

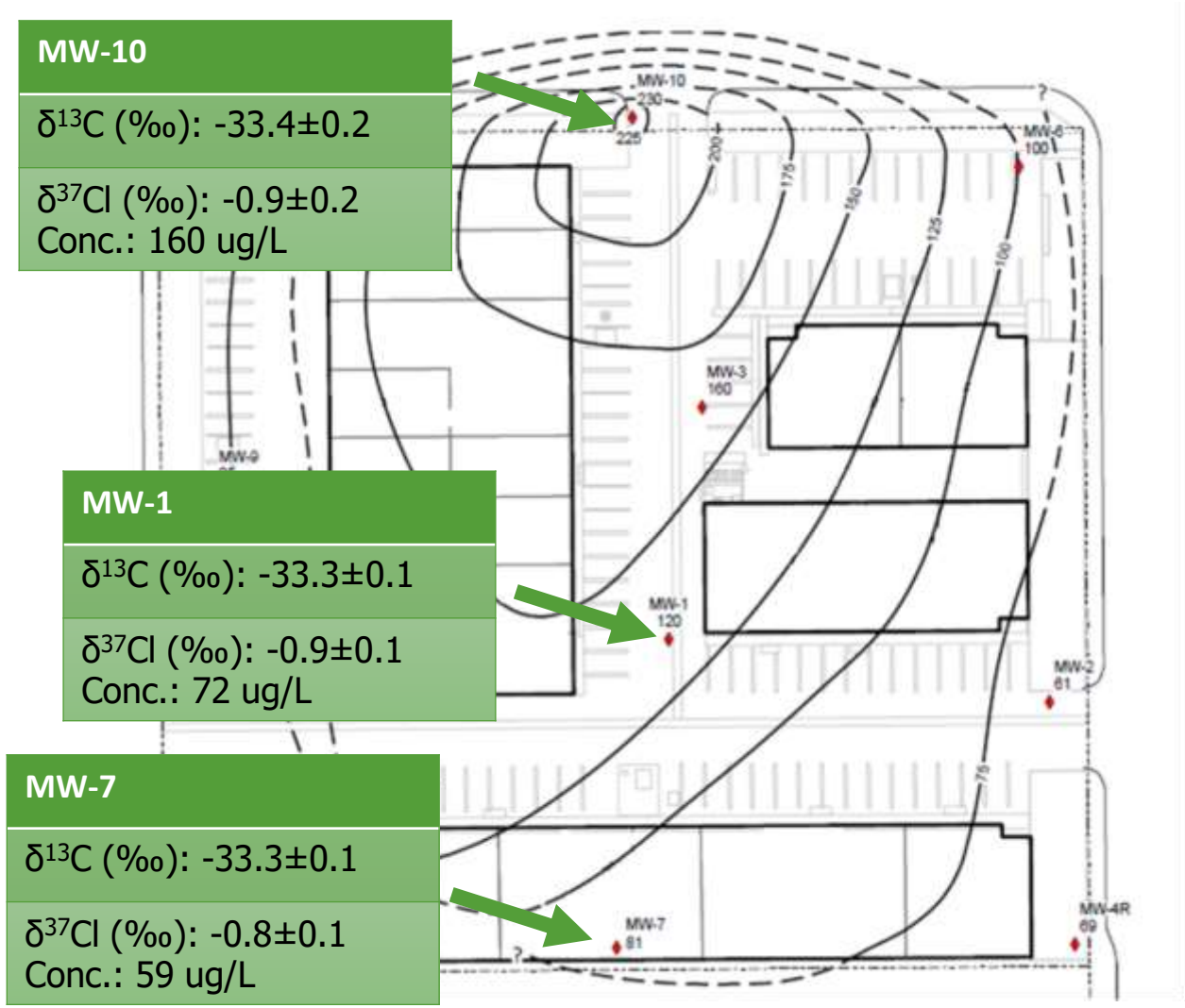
$\delta^{13}C$ (‰): -33.3±0.1

$\delta^{37}Cl$ (‰): -0.9±0.1
Conc.: 72 ug/L

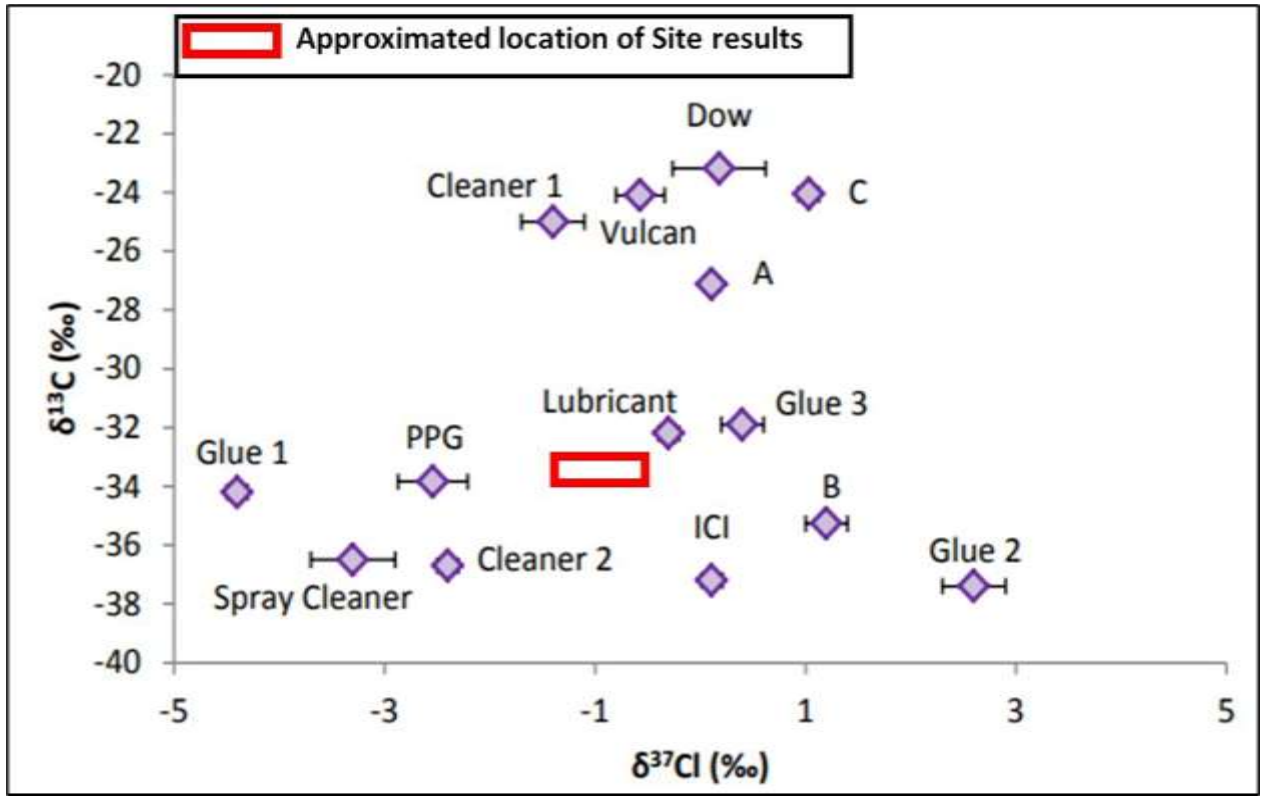
MW-7

$\delta^{13}C$ (‰): -33.3±0.1

$\delta^{37}Cl$ (‰): -0.8±0.1
Conc.: 59 ug/L



Commercial PCE Isotopic Signatures vs Site Results



Variation of δ13C and δ37Cl values for a selection of manufactured PCE and commercial PCE-based products. From Badin (2015), using data from Van Warmerdam (1995) and McHugh et al. (2011). The red box incorporates all results (2019 and 2021) measured at the Site.

Findings and Conclusion

- **PCE is unrelated with Owner's site:**
  - PCE concentration gradient from North to South, in sync with groundwater flow
  - No PCE hot spot on-site
  - Same PCE material throughout the site
  - PCE is not biodegraded, hence not at the origin of TCE in groundwater
- **Owner responsible to remove TCE in vadose zone/groundwater; but not PCE in groundwater**

CSIA Advantages

- Environmental Forensics
  - Can distinguish multiple sources of same contaminant
  - Identify if contamination is from an off-site source
  - Establishes link between observed contaminant and potential emitting source
  - Distinguish dilution from contaminant mass removal process

CSIA Advantages

- Provide conclusive proof of:
  - Contaminant degradation
  - Insight into degradation mechanisms
  - Rate estimations
  - Contaminant source distinction/delineation

Thank you

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