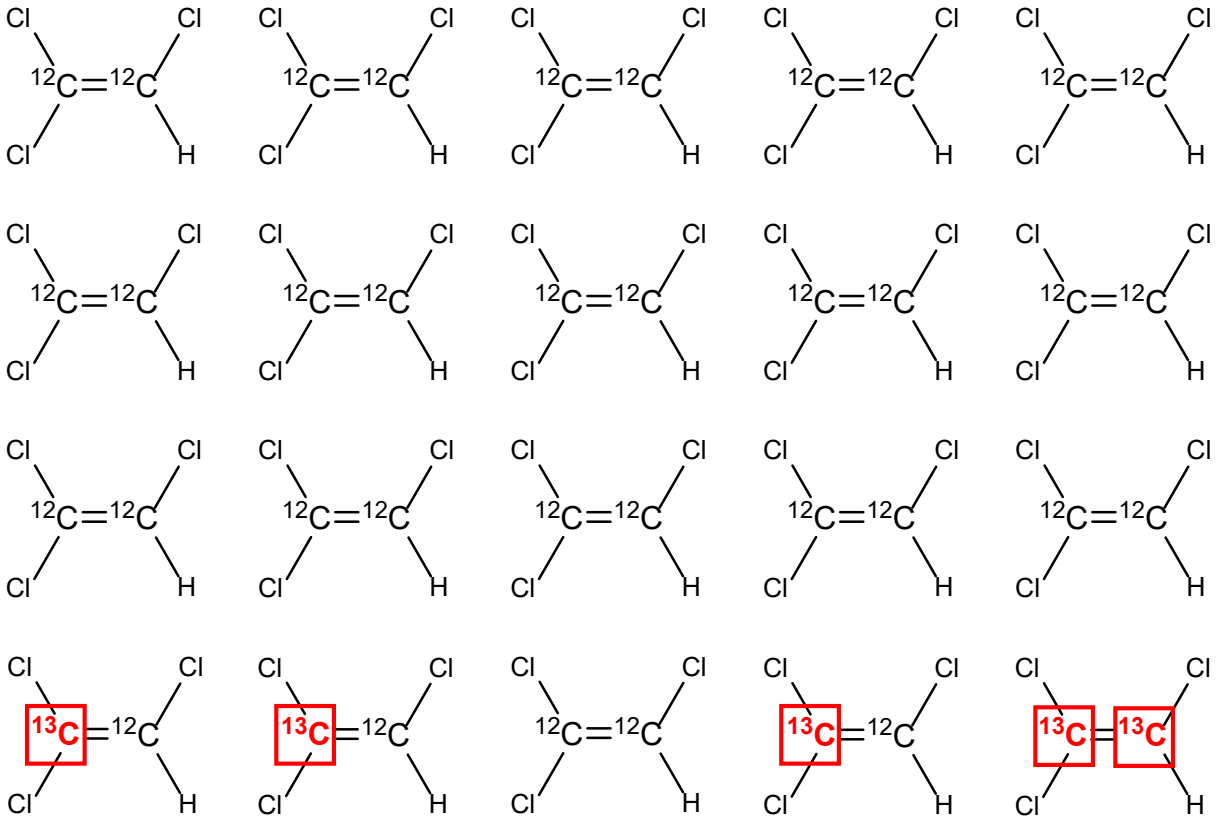
Source Delineation Using CSIA

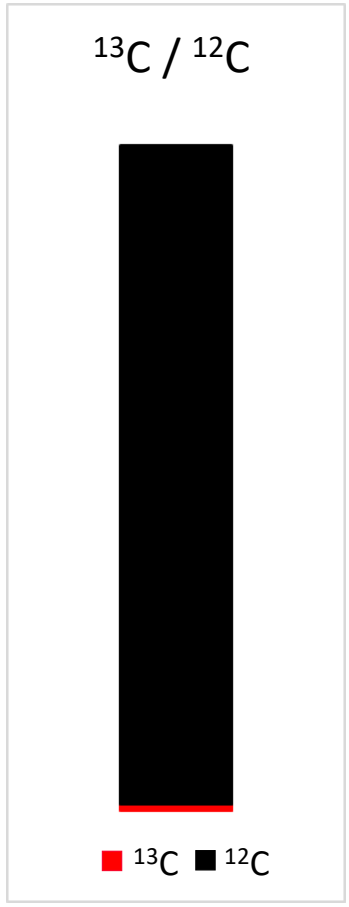
4/16/2019

Battelle Bioremediation Symposium 2019

Compound Specific Isotope Analysis (CSIA)

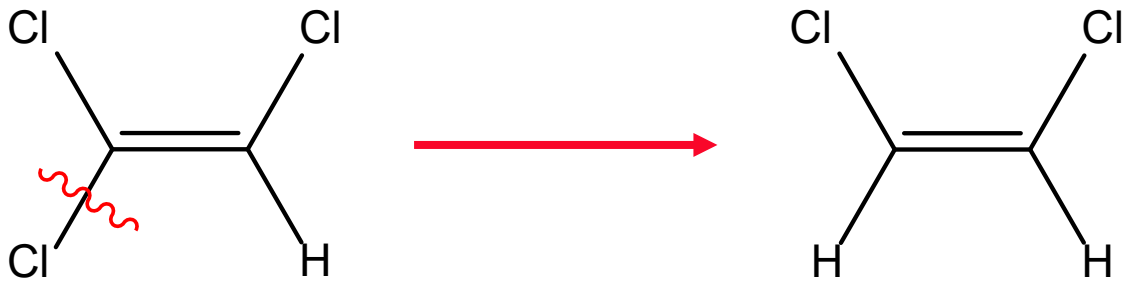
Measuring isotope ratios





Effect of Degradation

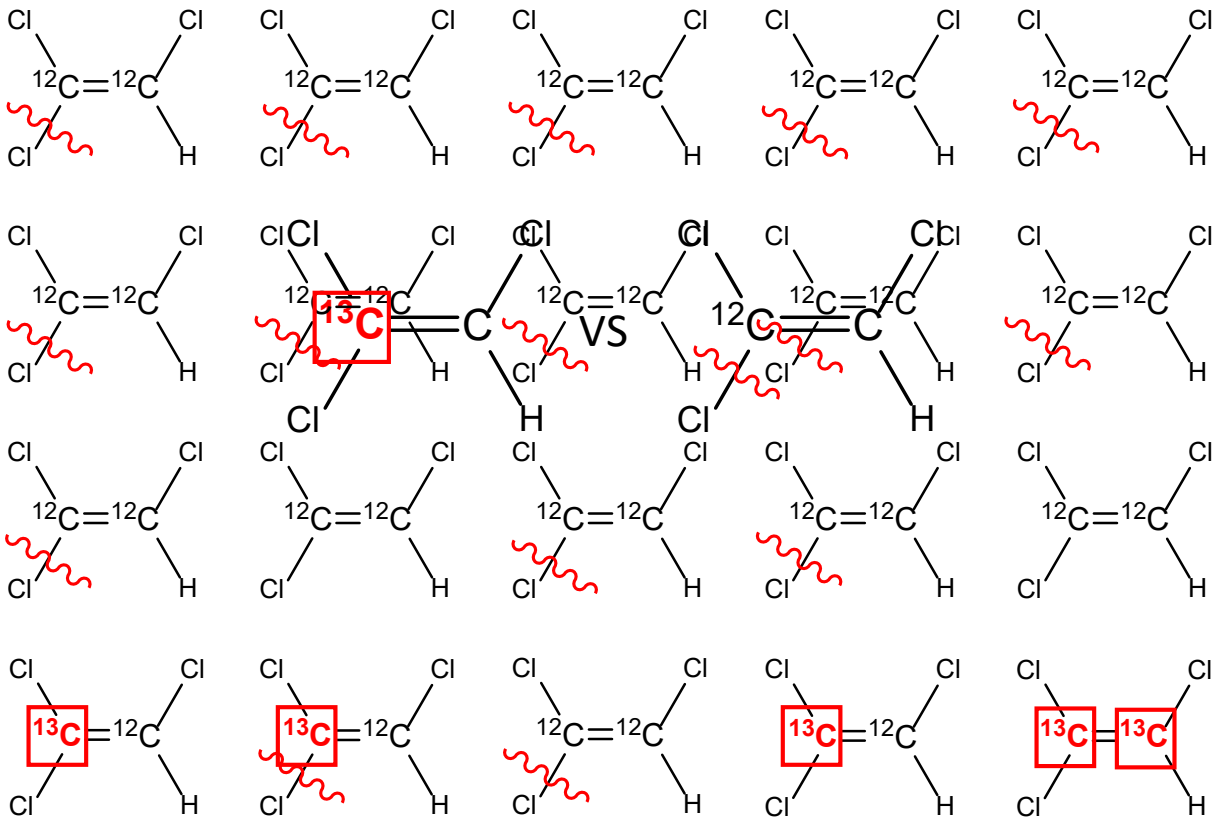
Contaminant degradation = breaking bonds

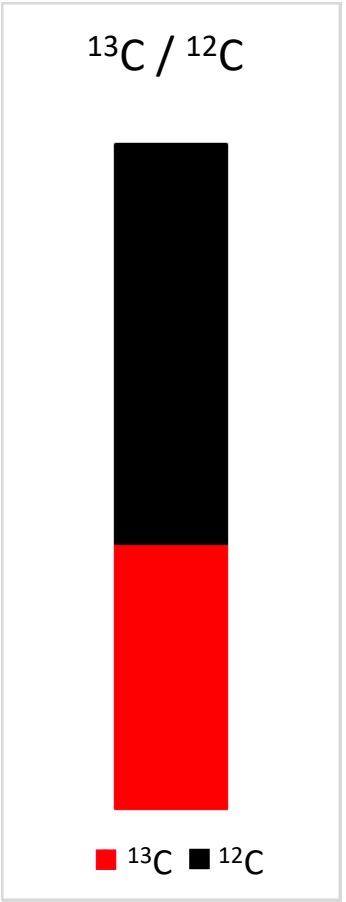


TCE c-DCE

Isotope Fractionation

^{13}C bonds are stronger than ^{12}C bonds





Terminology

1

What is a delta value ($\delta^{13}C$)?

The $^{13}C/^{12}C$ ratio compared to a standard

- As bonds break (degradation), a delta value will increase – isotopic fractionation

-32.3 ‰ ⟶ -25.1 ‰

2

What is "per mill" (‰)?

Literally means 1/1000

- In reality, the changes in $^{13}C/^{12}C$ are very small (fractions of a percent)…

  "-0.0008"

- Multiply our delta value by one thousand…
  "-0.8 ‰"

Source Delineation through CSIA

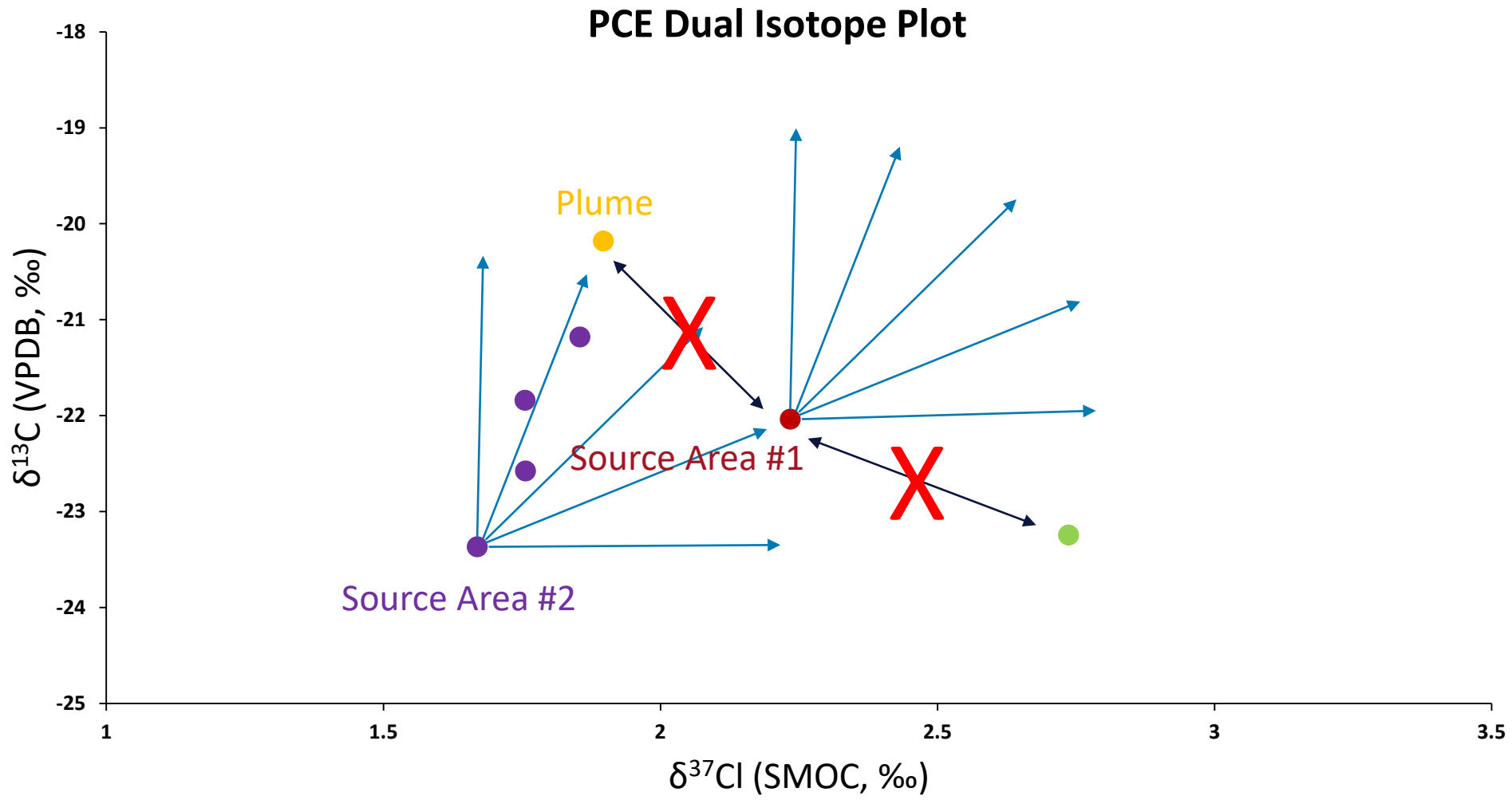
What can it provide?

- ✓ It can determine if two samples are isotopically similar or dissimilar

Some Limitations

- × It cannot *prove* that two samples are from the same source
- × It cannot age date a contaminant
- × It cannot determine what percentage a source has contributed to a plume

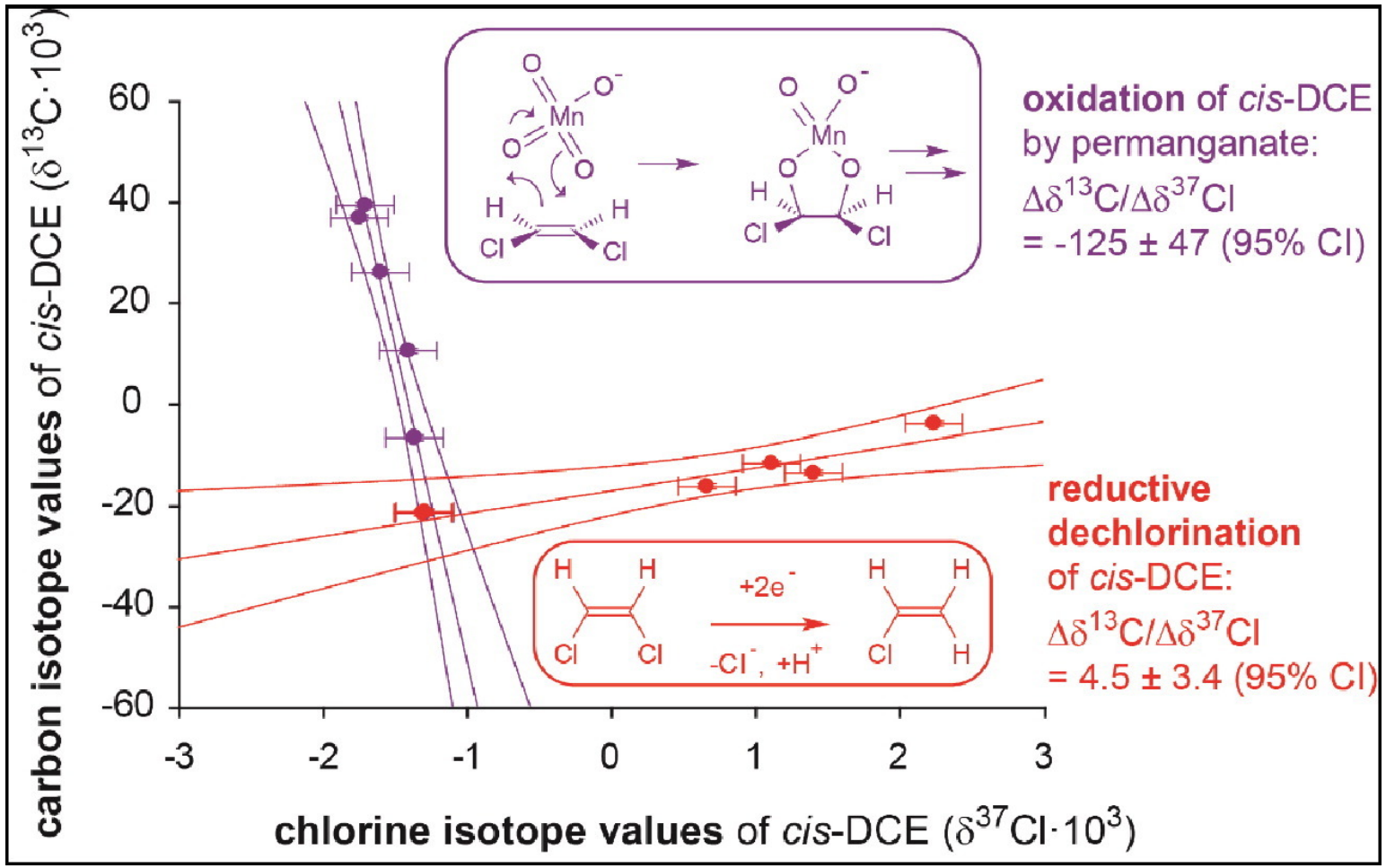
Linear Trends Are Key



CSIA Source Delineation

- CSIA data should never stand on its own
  - Multiple lines of evidence should be used
  - Isotopic data should be treated at supporting/refuting evidence
- Site/treatment history is important
  - Groundwater flow and contour maps are essential
  - Recirculation systems can confuse spatial trend models
  - Treatments applied to specific site areas can confuse the interpretation
  - Specific treatments can result in very different fractionation patterns

Fractionation Trends



CI = confidence interval

Doğan-Subaşı et al. (2017)

CSIA Source Delineation

- Sampling strategies are important for CSIA
  - Sample the plume in question
  - Sample each possible source area
  - Collect multiple samples along the flow path between each source area and the plume
  - Take advantage of historical data and narratives
  - Be aware of any preferential pathways

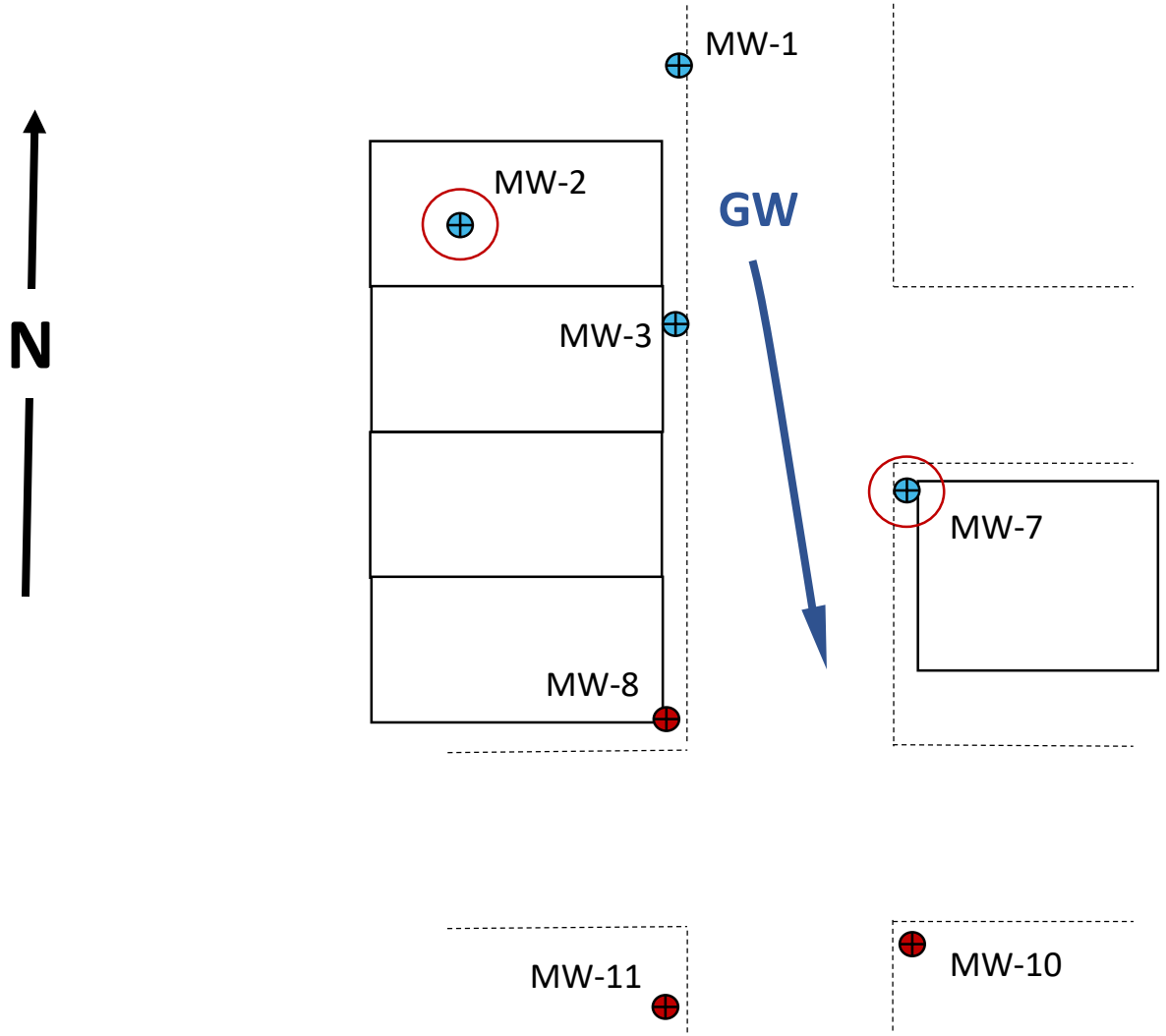
Sampling strategy

Example #1: PCE Site

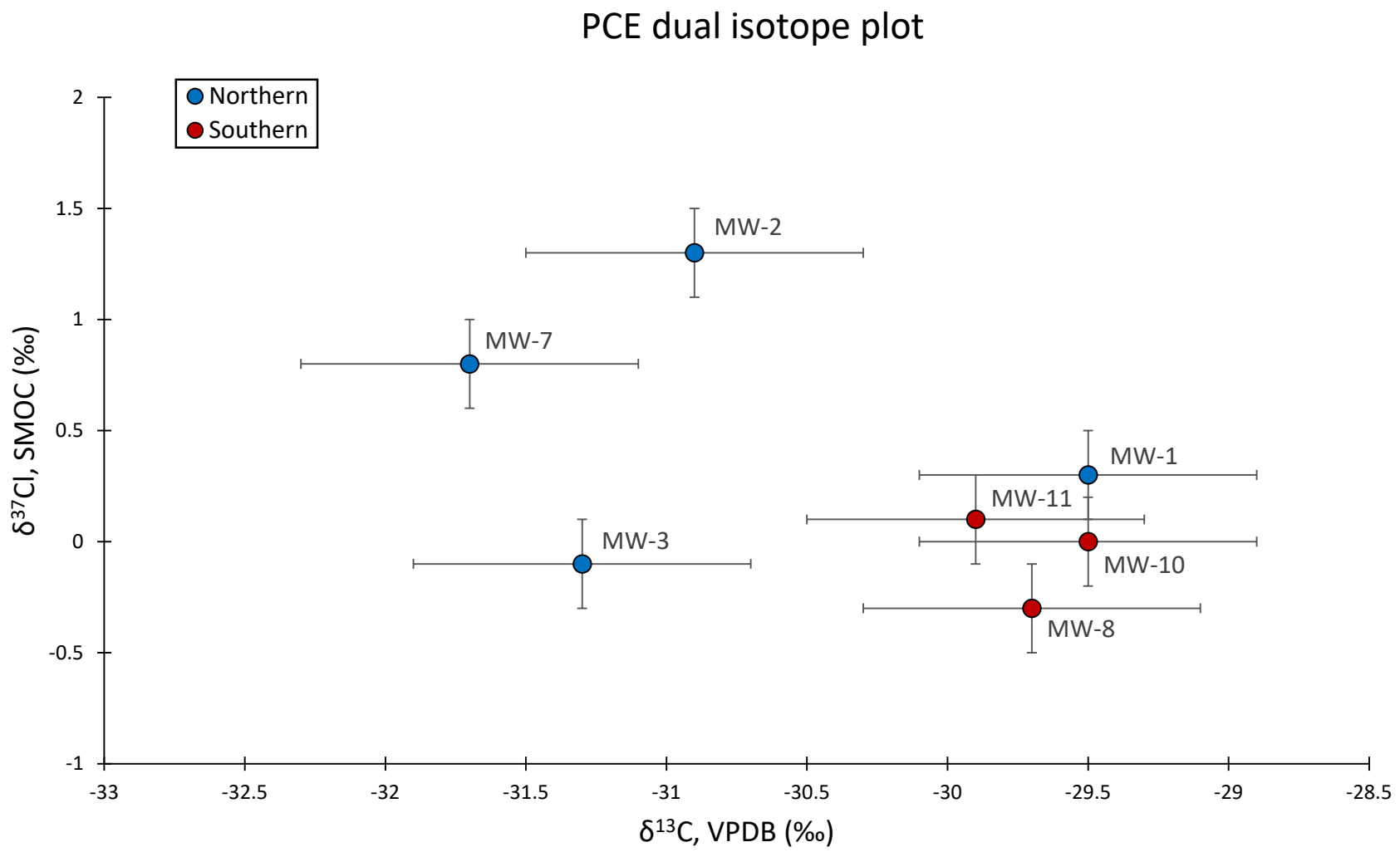
Example 1: Site Info

- Former dry cleaners
- PCE storage tank leak
  - Soil dug out, SVE system put into place
- Downgradient plume, especially concentrated near 4-way intersection
- Other possible source, old machine shop laterally across the street
  - PCE concentrations above 11 mg/L indicate local DNAPL based on relative solubility rule of thumb
  - Also more than half a dozen other potential sources within 0.5 square mile
- No reductive dechlorination daughter products – very little degradation
- Sampling: two main source areas and down the plume

Example 1: Site Map



CSIA: Dual Isotope Plot



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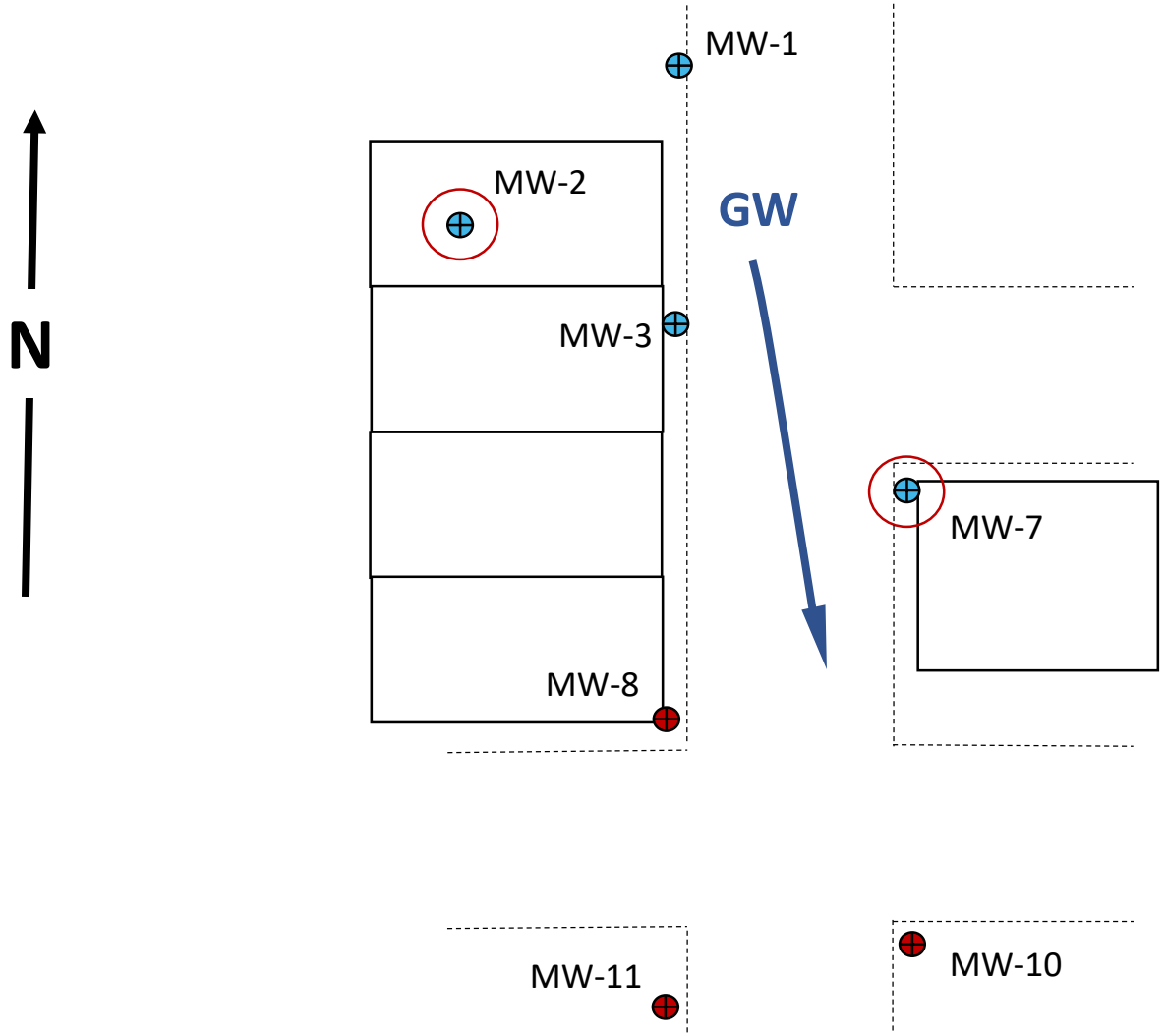
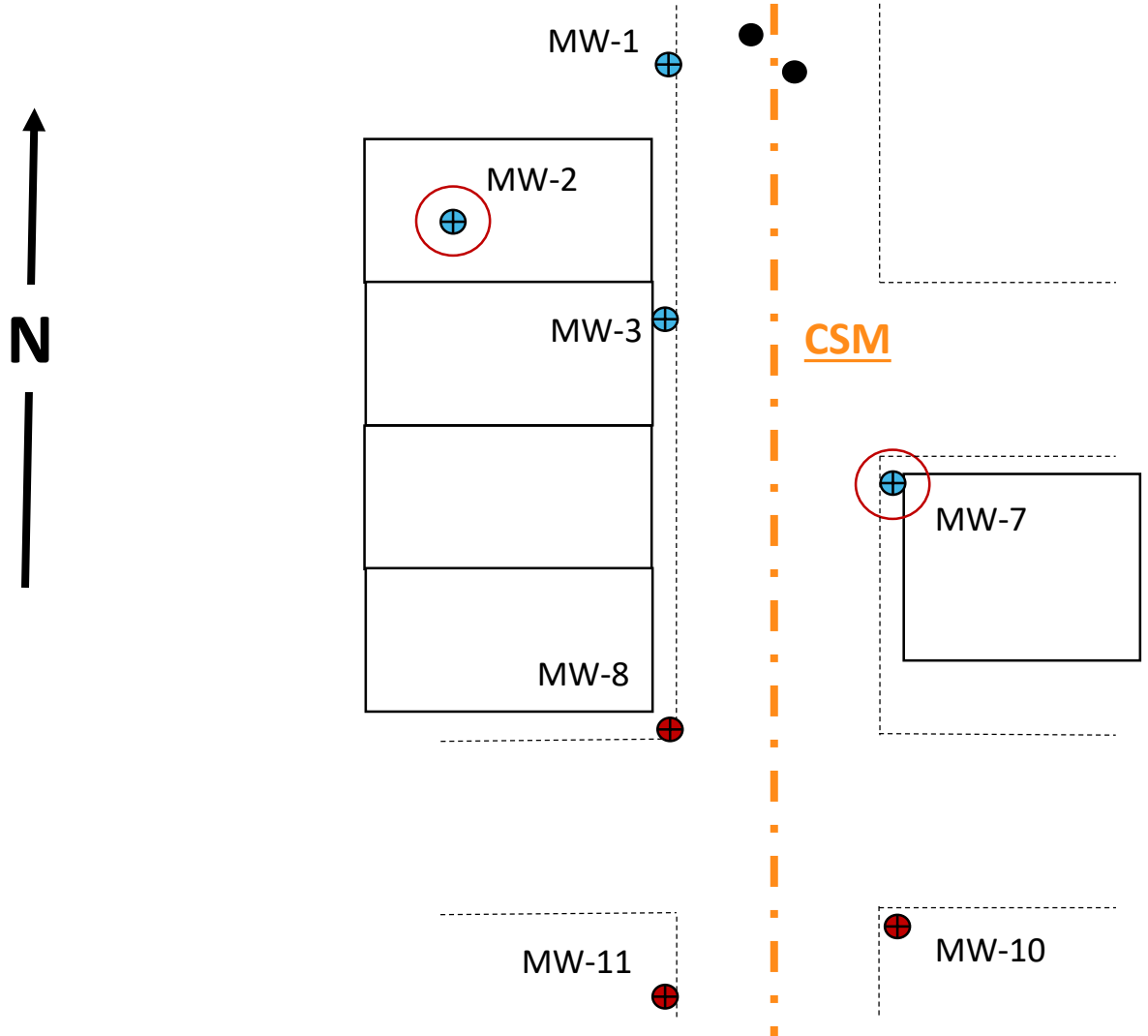


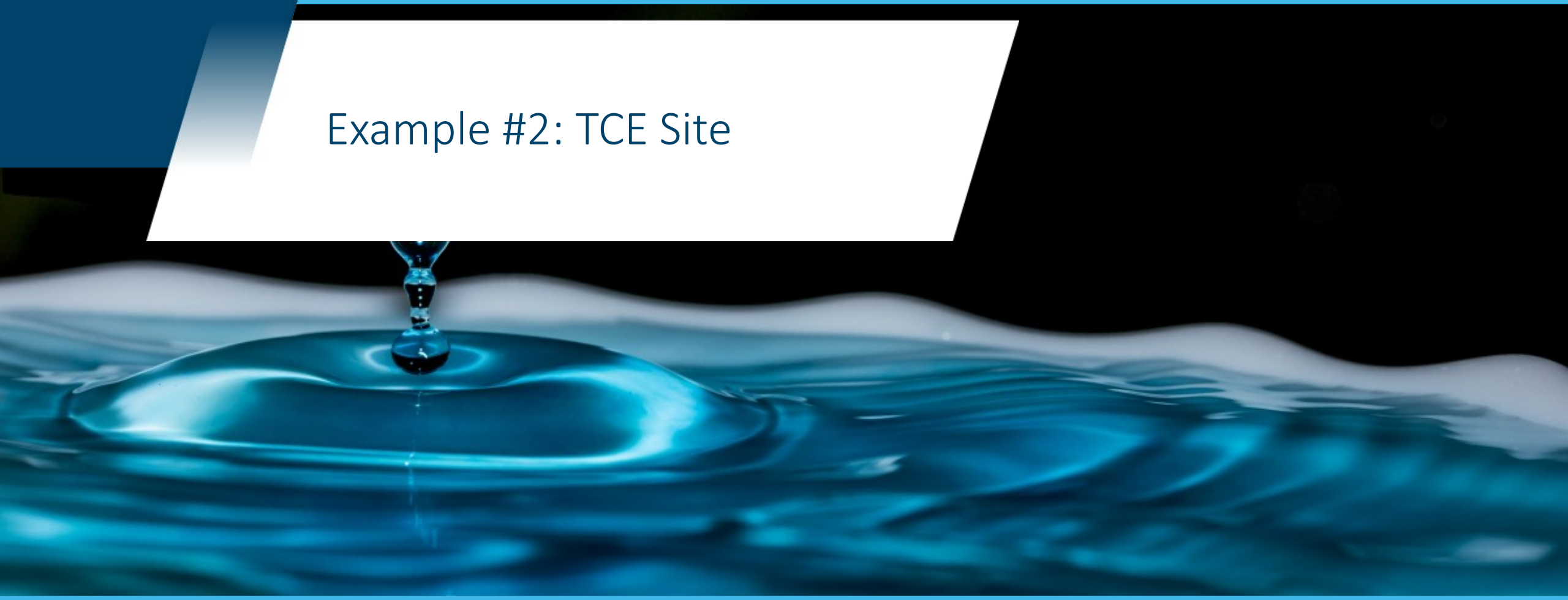
Example 1: Site Map



Example 1: Conclusions

- The more possible source areas, the trickier source delineation can be
- CSIA does not indicate that either party is a primary contributor to PCE plume
- Upgradient sampling provided PCE that isotopically matched the PCE in the plume
- Previous investigation detected high concentrations of PCE in soil upgradient of the site, directly adjacent to combined sewer main buried under the street centerline
  - Porous backfill surrounding buried utility lines can act as a preferential flowpath, greatly impacting the mas transport of contaminants
  - More sampling required to better understand source(s)

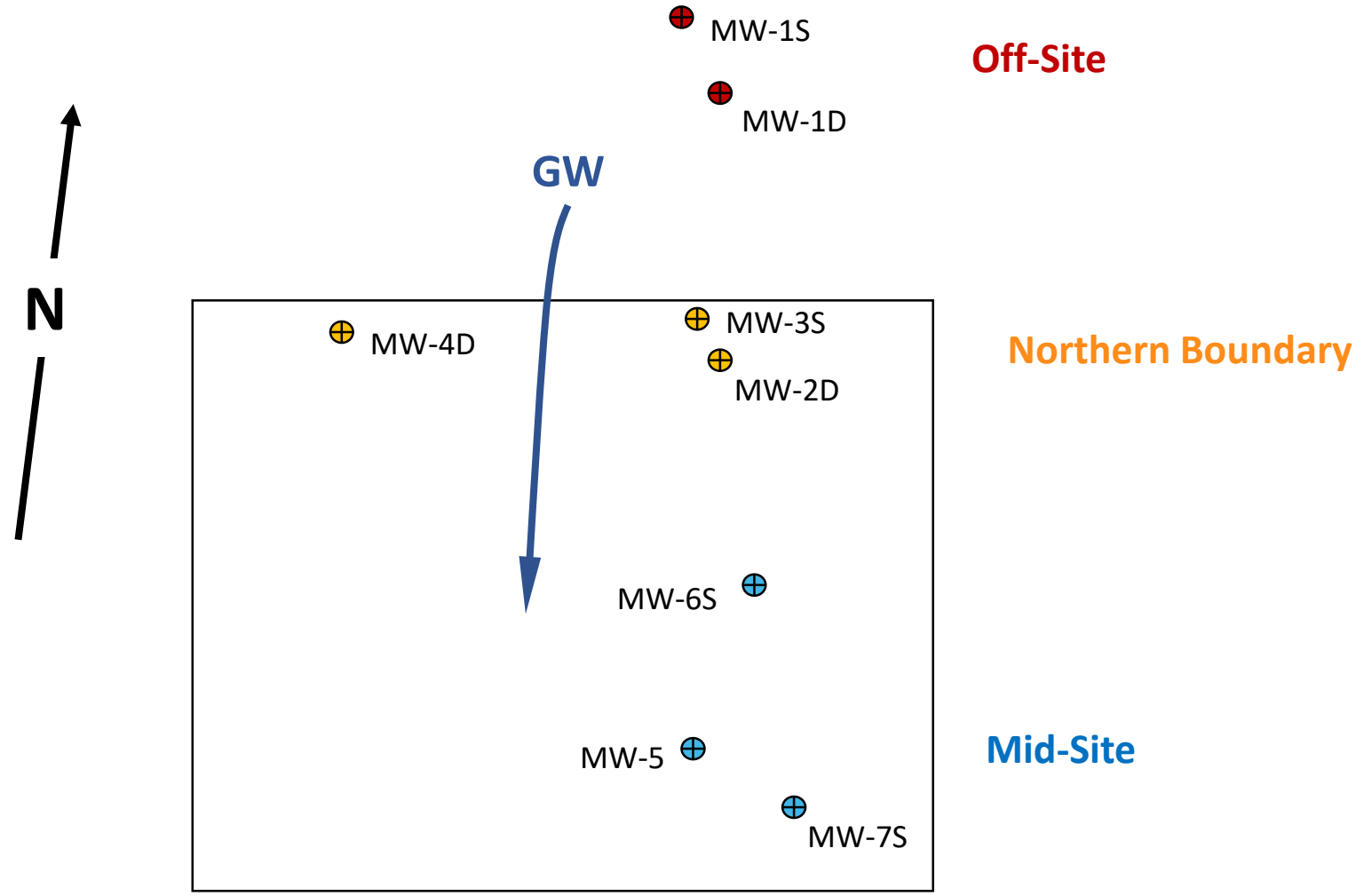
Example #2: TCE Site

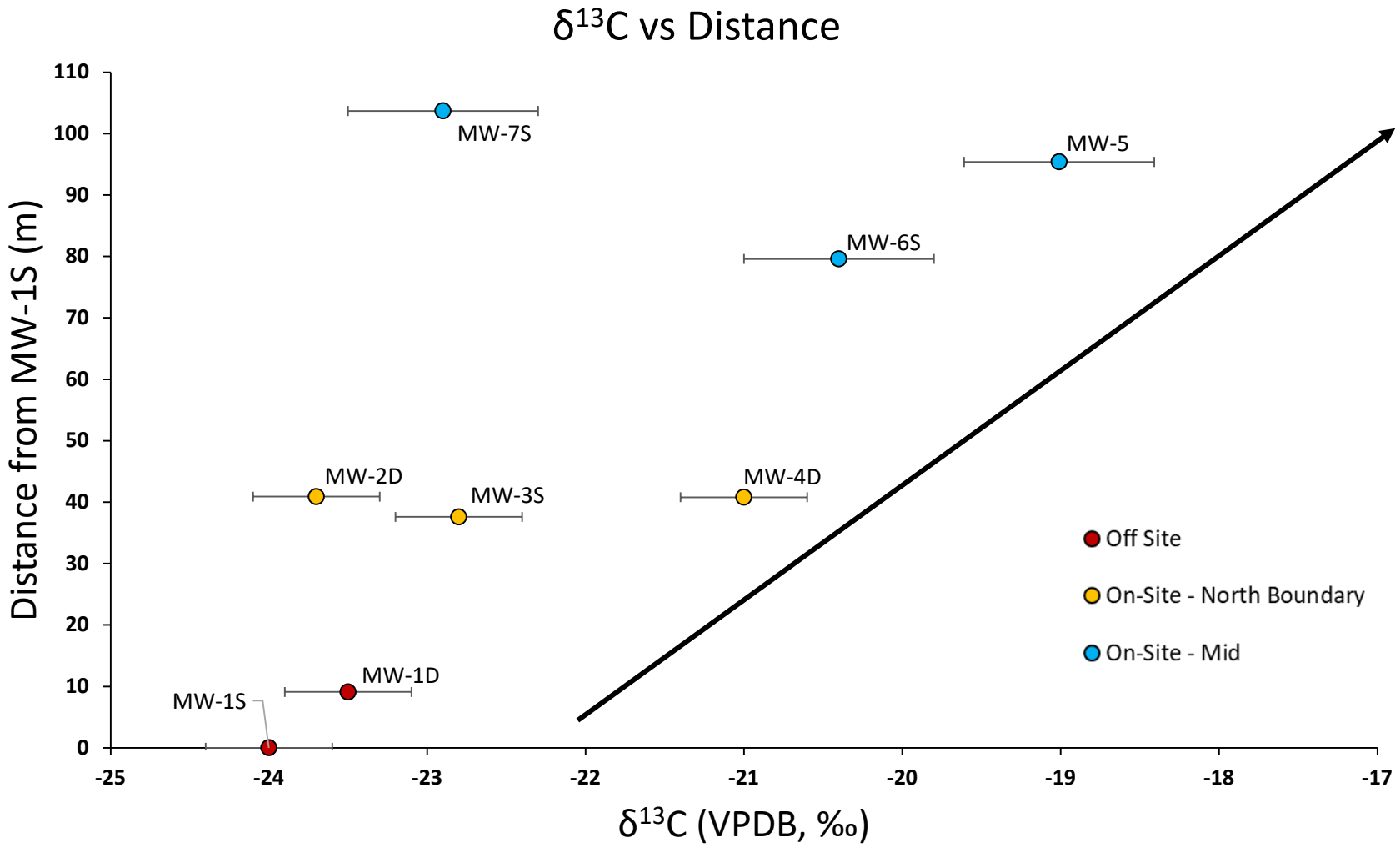


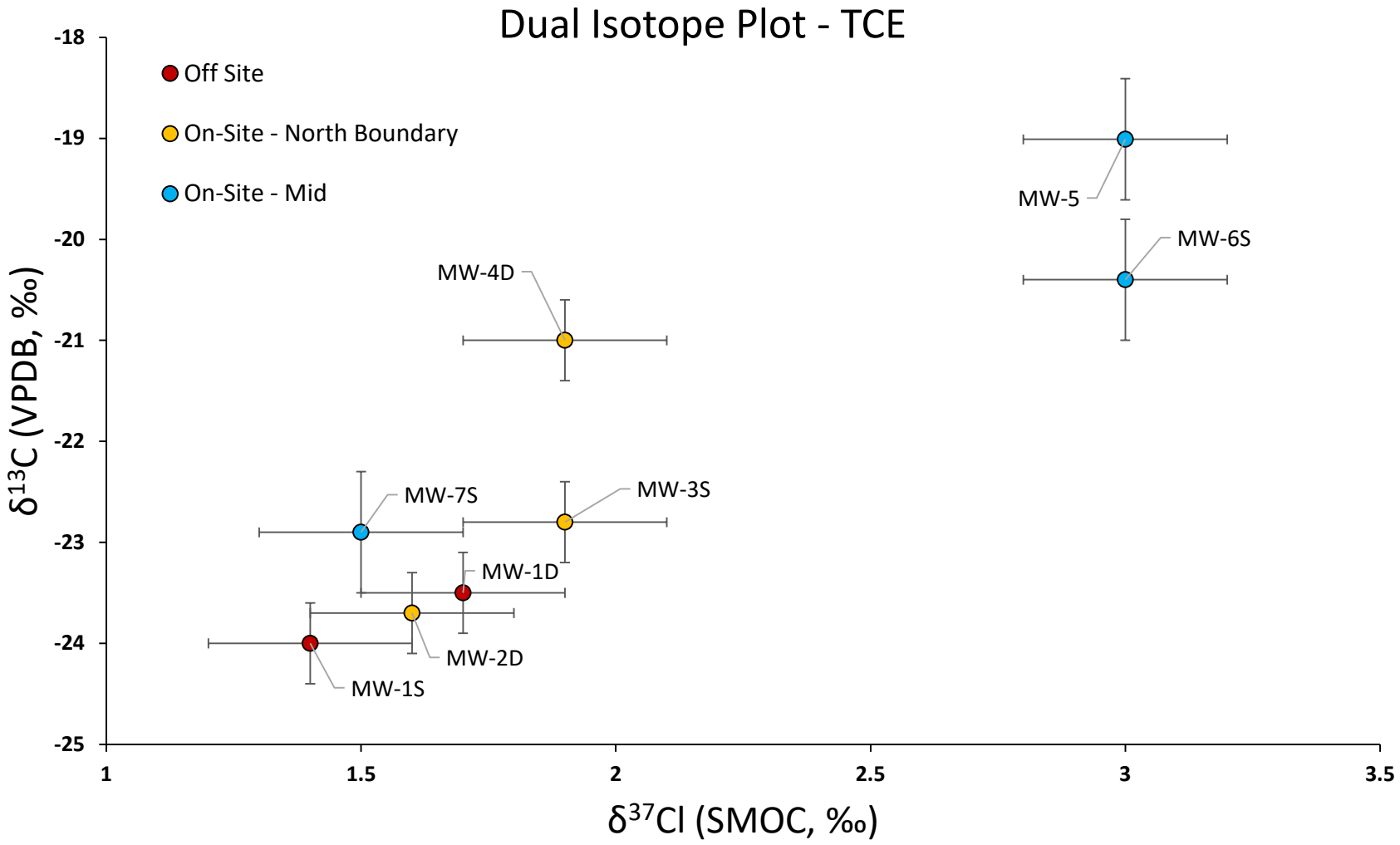
Example 2: Site Info

- Current empty lot with no known chlorinated solvent releases in the past, now contaminated with TCE (3 – 20,000 µg/L)
- One known release upgradient (north) of site
  - Pump and Treat systems implemented on the source property
- Sampling:
  - Off-site, upgradient
  - On-site at the northern boundary
  - On-site, mid
- RD daughter products indicate TCE degradation

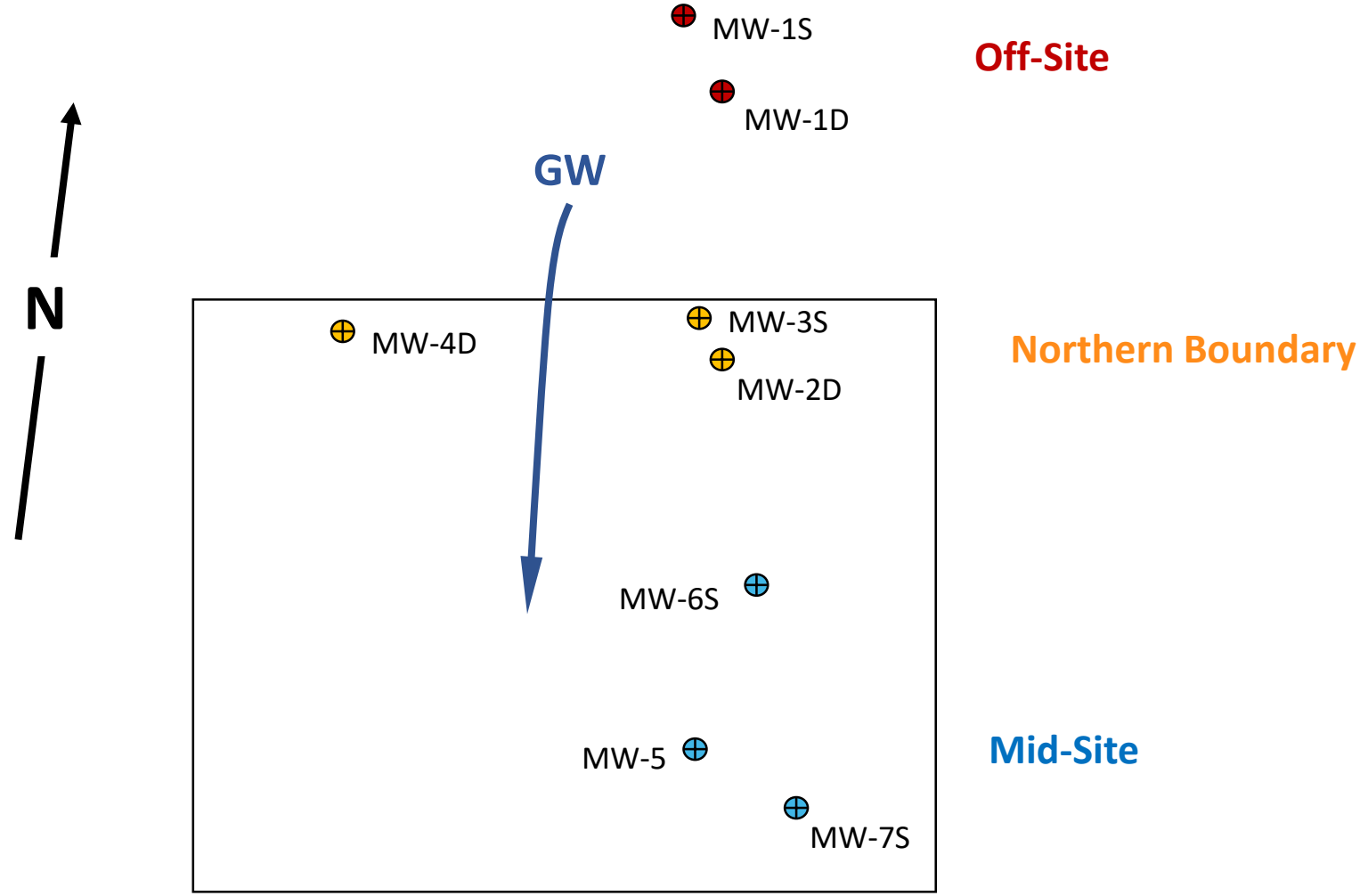
Example 2: Site Map



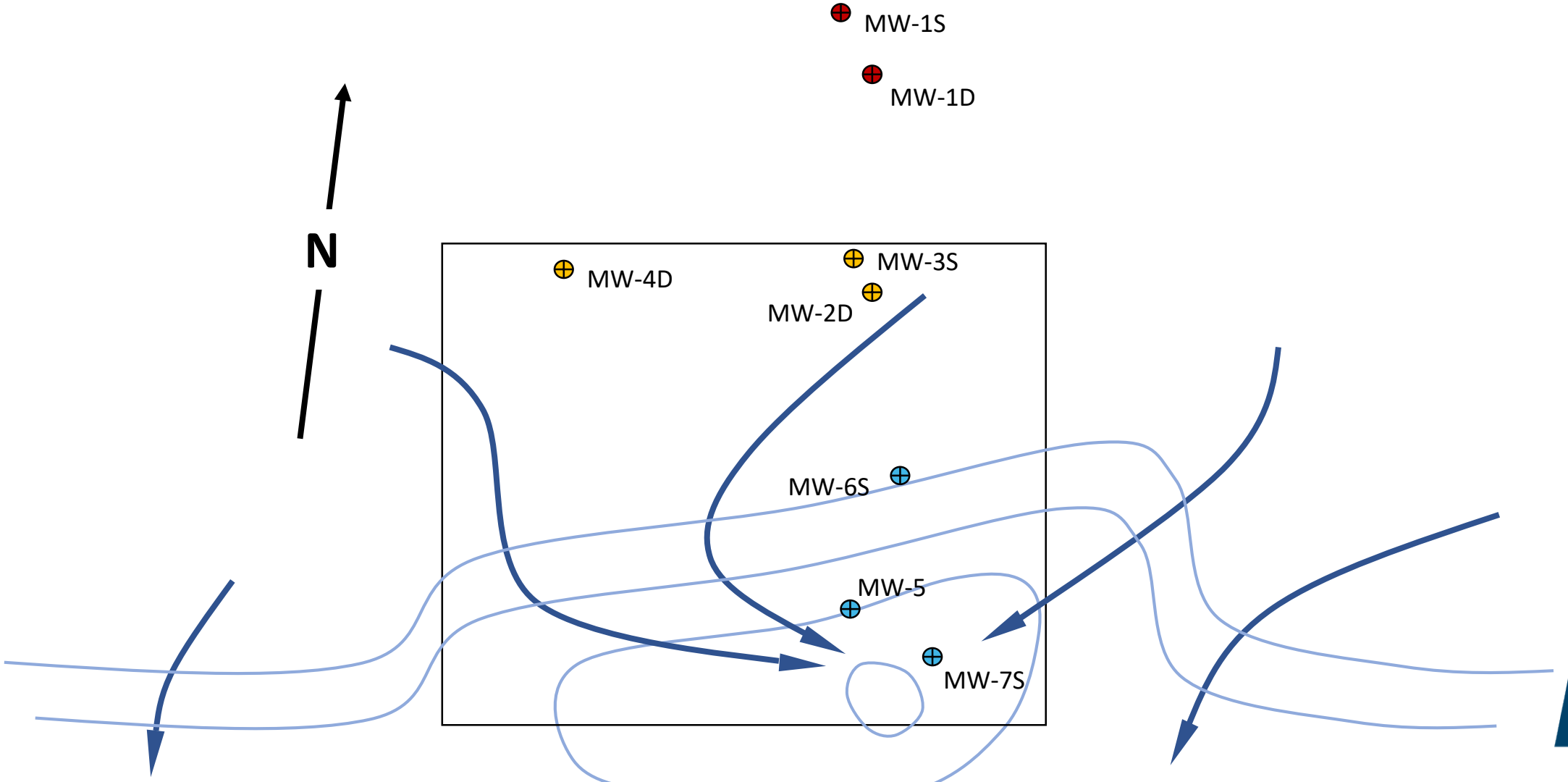

δ13C vs Distance
Distance from MW-1S (m)
δ13C (VPDB, ‰)
110
100
90
80
70
60
50
40
30
20
10
0
-25
-24
-23
-22
-21
-20
-19
-18
-17
MW-7S
MW-5
MW-6S
MW-2D
MW-3S
MW-4D
MW-1D
MW-1S
Off Site
On-Site - North Boundary
On-Site - Mid


Dual Isotope Plot - TCE
Off Site
On-Site - North Boundary
On-Site - Mid
MW-5
MW-6S
MW-4D
MW-7S
MW-3S
MW-1D
MW-2D
MW-1S
-18
-19
-20
-21
-22
-23
-24
-25
1
1.5
2
2.5
3
3.5
δ13C (VPDB, ‰)
δ37Cl (SMOC, ‰)

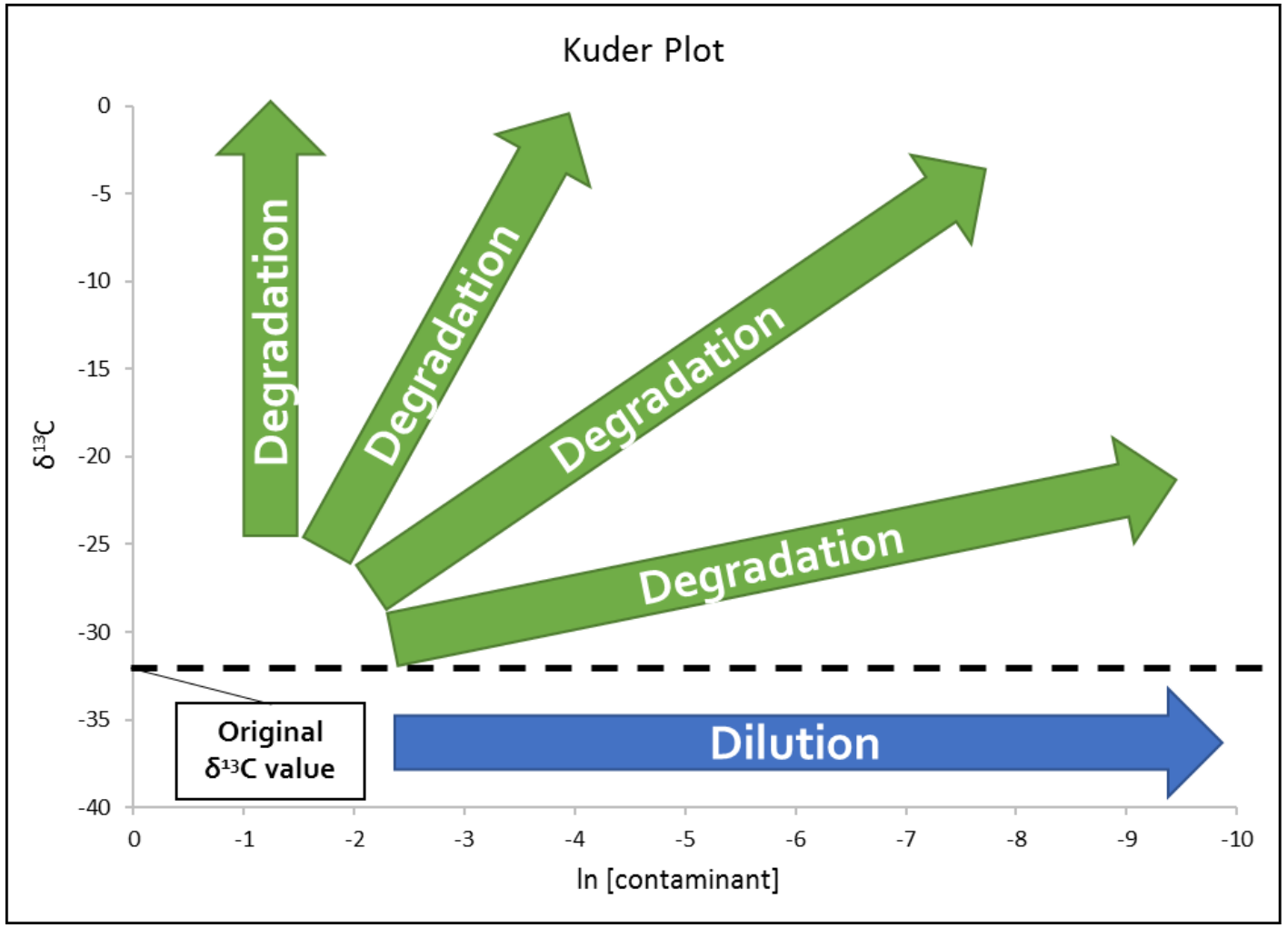
Example 1: Groundwater Flow - Bedrock



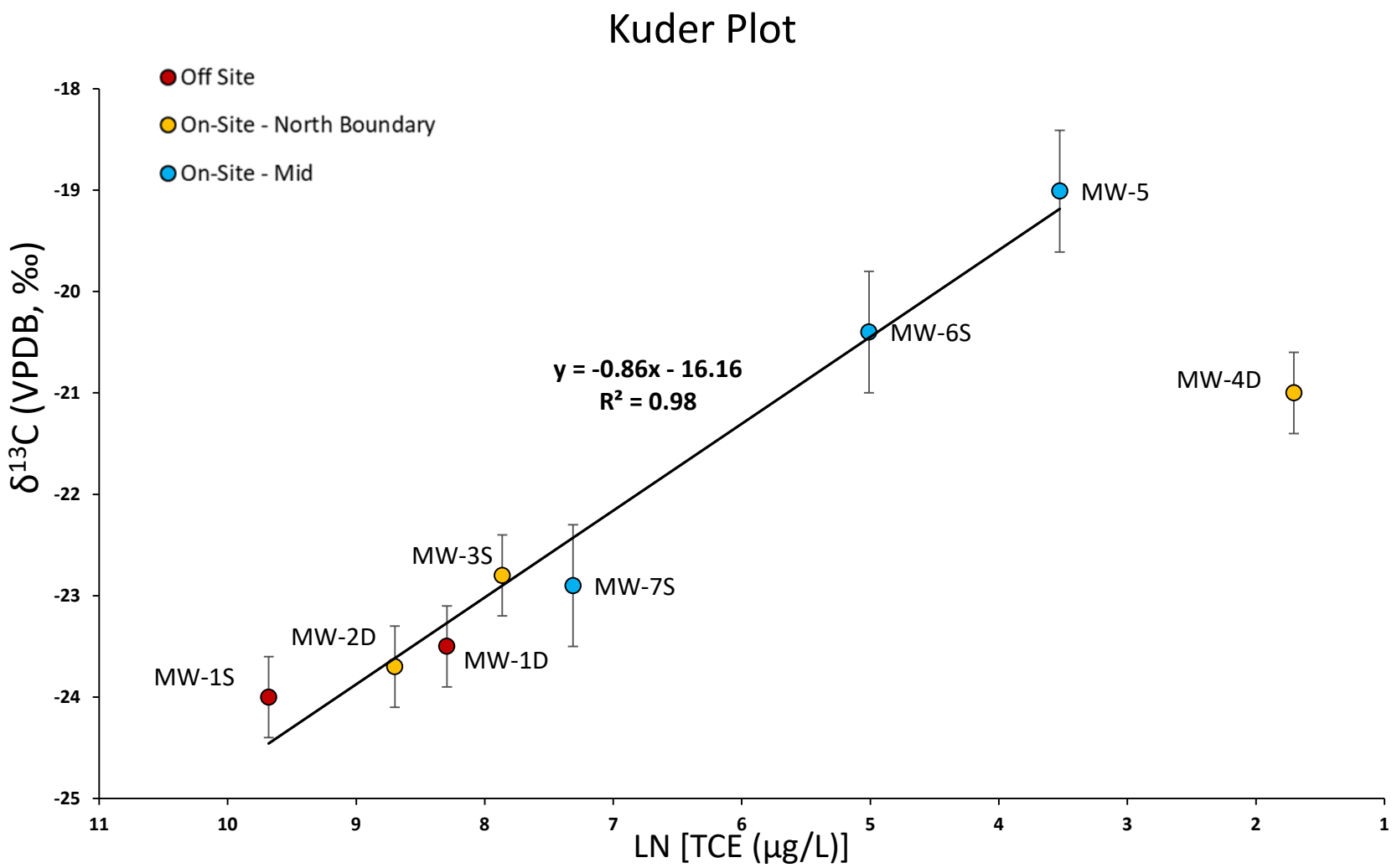
Example 1: Groundwater Flow - Overburden



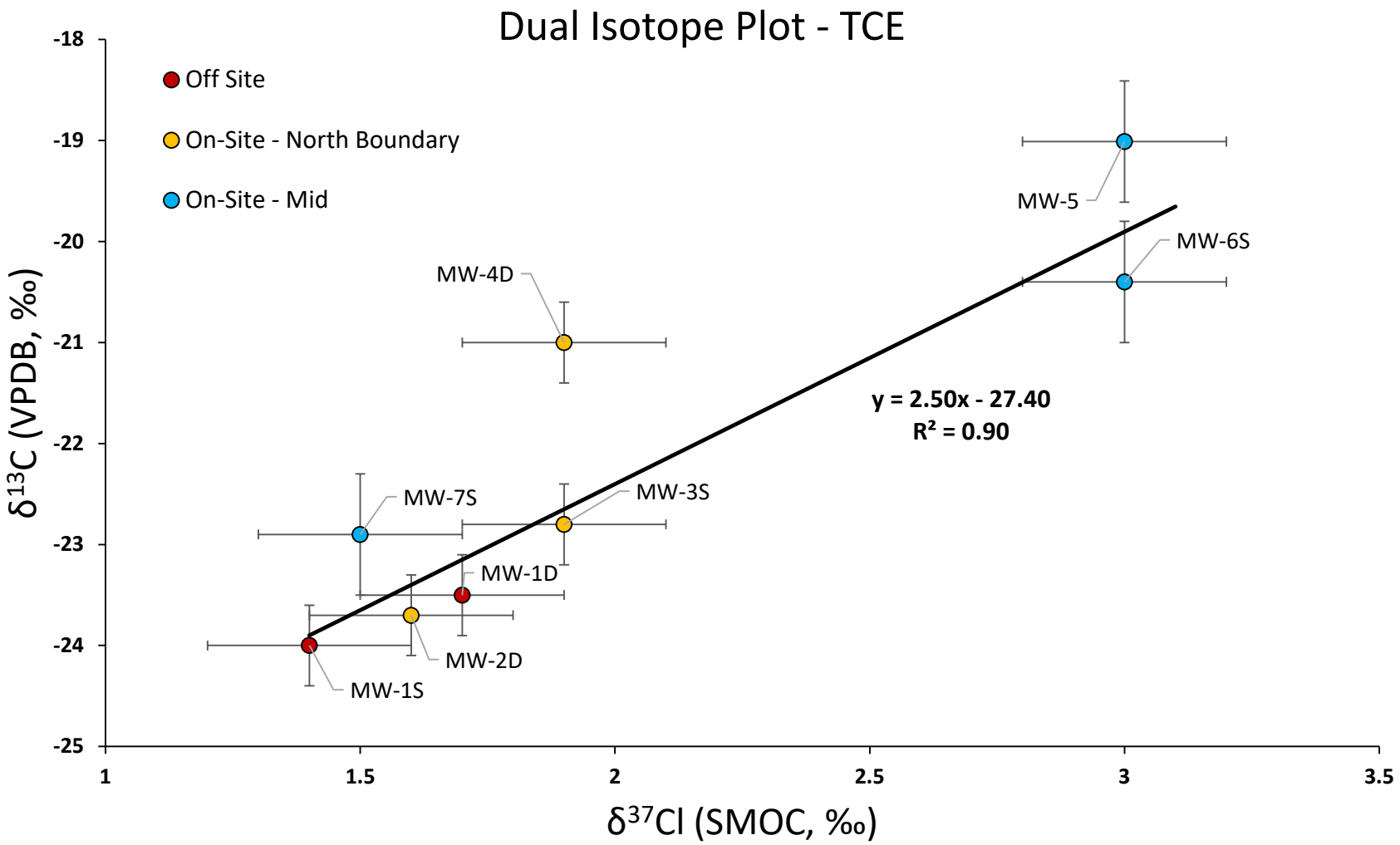
Getting More Info: Kuder Plot



Getting More Info: Kuder Plot



CSIA – Dual Isotope Plot



Example 2: Conclusions

- The TCE appears to be originating offsite
- TCE impacting MW-4D does not overlap with either the Kuder Plot or Dual Isotope trendlines
  - Site manager has said that there is another possible northwest source
  - More data needs to be collected
- Important reminders for site characterization:
  - Data in context with the QA/QC
  - Viewing the data in more than one way (Distance, Kuder Plot, Dual Isotope Plot)
  - Knowing the site hydrogeology

Final Conclusions

- CSIA for source distinction very rarely provides a clear yes/no
  - Understand the limitations
- Isotopic data must be compared to additional lines of evidence
  - Chemical
  - Geological
  - Spatial
  - Historical narrative
- Strategic sampling is very important
  - The plume in question
  - Each possible source area
  - Multiple samples along the flow path between each source area and the plume
- Data should be viewed in context of QA/QC
- Isotopic data can contribute to the model in more ways than just a Dual Isotope Plot
  - Plotting the data in different ways can help support/refute assumptions

Thank you
for your time

Are there any final questions?

microbialinsights