Protocol for Using Compound Specific Isotope Analysis (CSIA) in Environmental Forensics

Patrick W. McLoughlin

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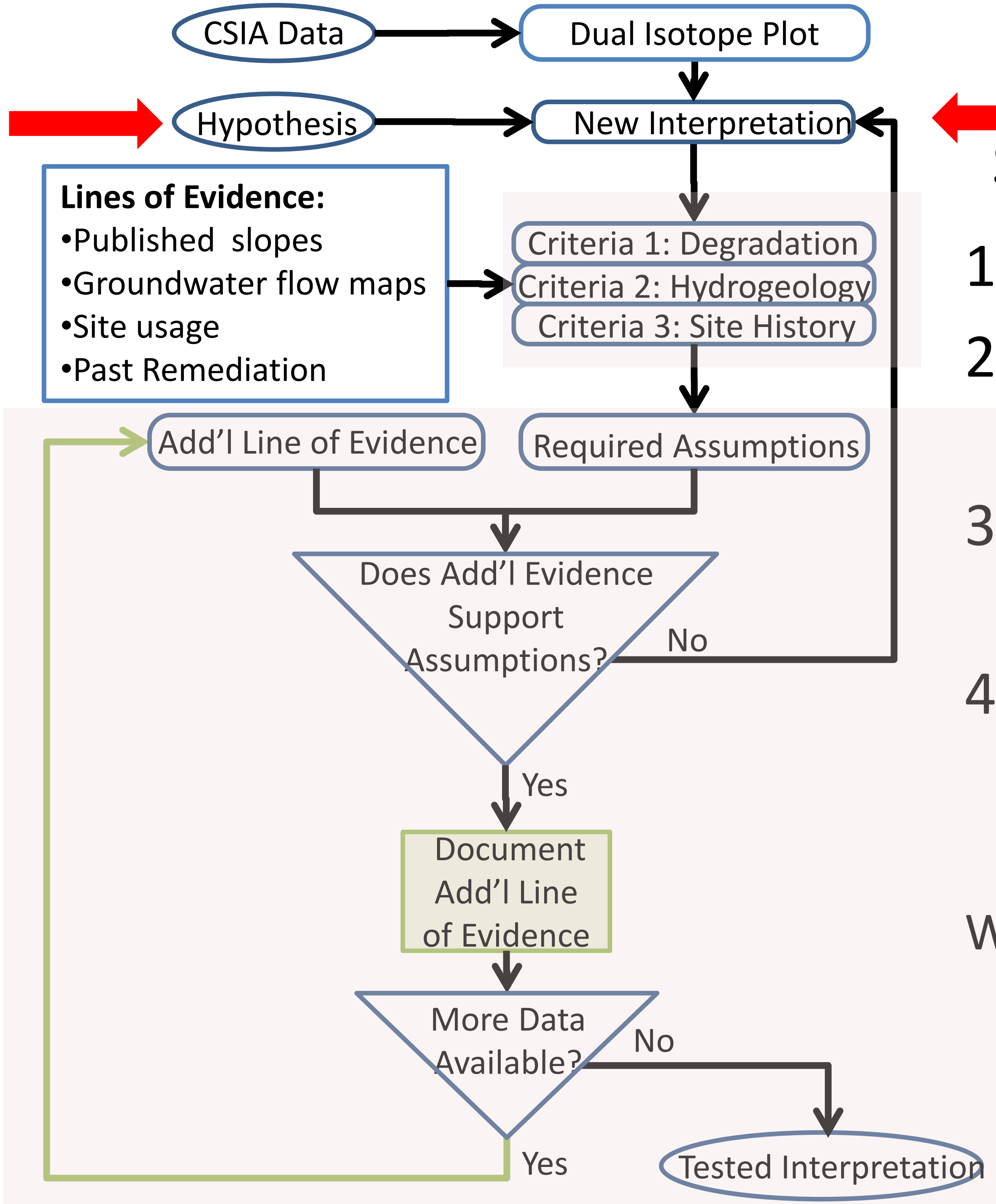
Protocol …

- Need:
  - Consistent way to evaluate CSIA groundwater forensic arguments
  - Process for using multiple lines of evidence to test/improve forensic models
- Tools:
  - Scientific method
  - Lines of Evidence
- Experience:
  - Forensic arguments are developed through a reiterative approach
  - Trivial observations may become important lines of evidence.



Scientific Method

1. Hypothesis
2. Prediction

   "New Interpretation"
3. Testing

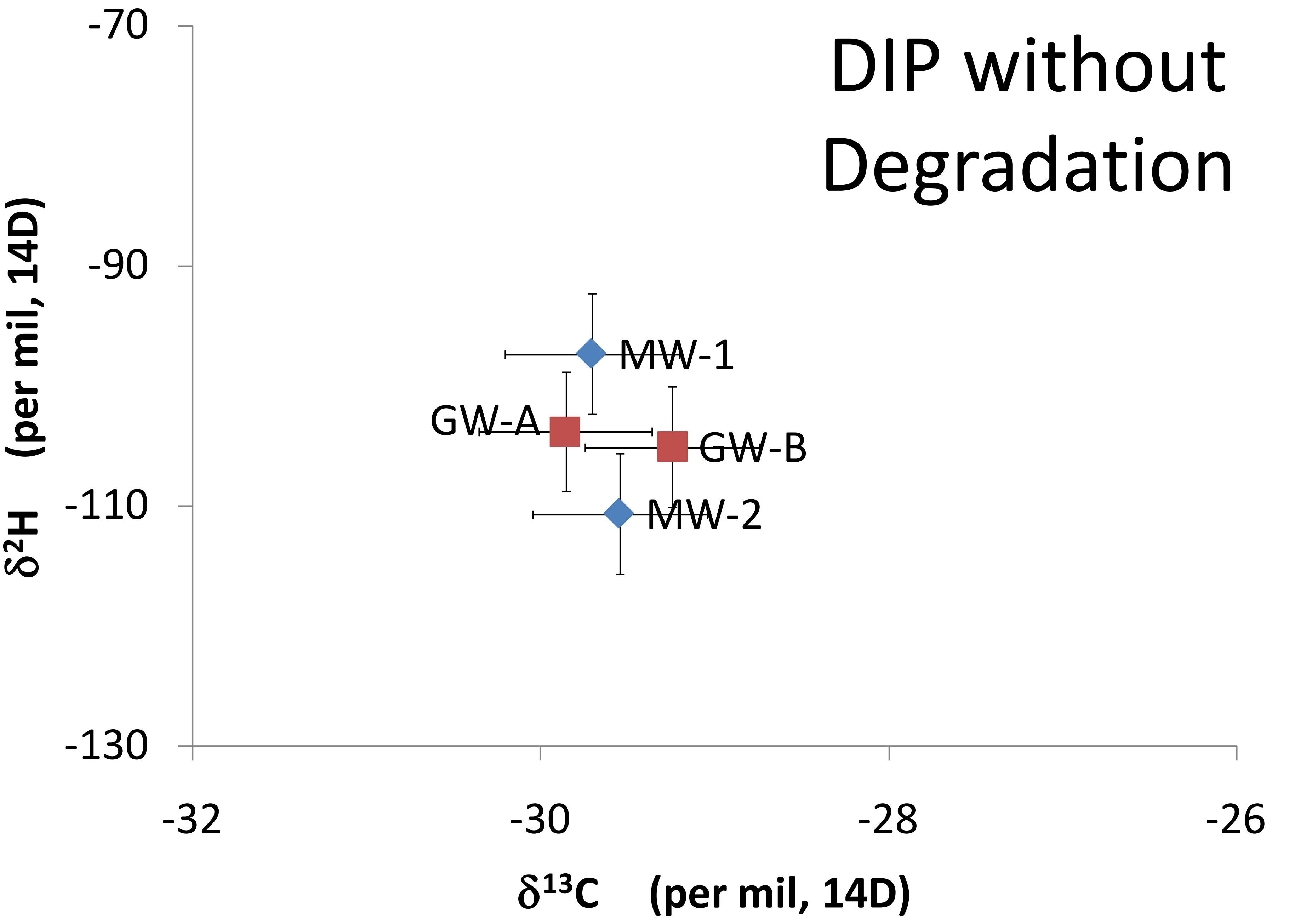
   Applying Criteria
4. Analysis

   Bottom 2/3

We will focus on Criteria

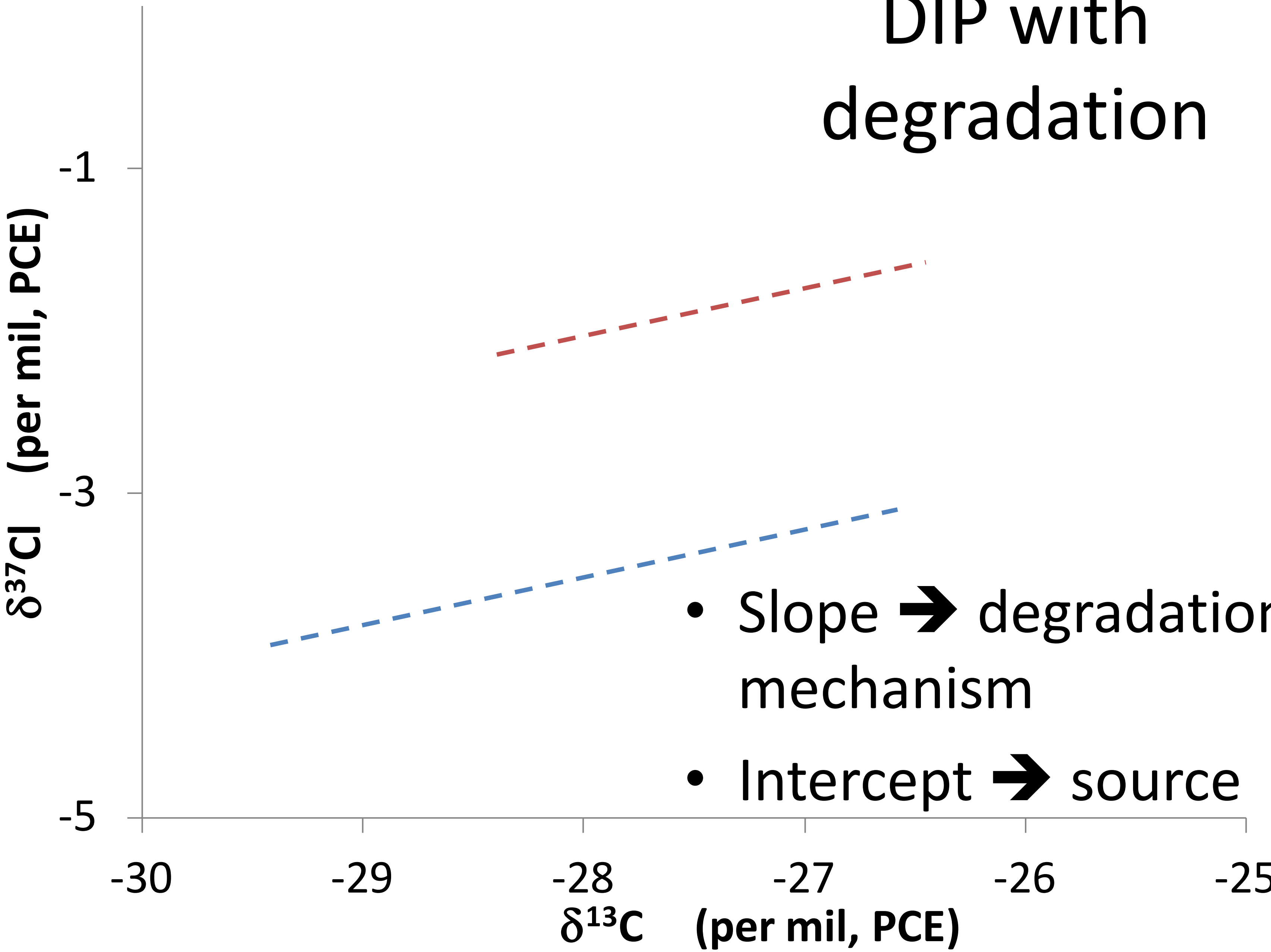
DIP and Source Differences

- Start with a dual isotope plot (DIP)
  - Chlorine δ vs. carbon δ for TCE or PCE
  - Hydrogen δ vs. carbon δ for BTEX or 14D
  - Based on simplified Rayleigh: $\delta = \delta_0 + \varepsilon * \ln(F)$
    - δ_0 is the δ of the undegraded compound
    - ε is the enrichment factor
    - *F* is the fraction remaining (1 ➔ 0)
- Points lie in groups for each source, if no degradation
- Points on a DIP lie on a line if there is degradation AND they have the same:
  - Source
  - Degradation mechanism


DIP without Degradation
-70
-90
-110
-130
-32
-30
-28
-26
MW-1
GW-A
GW-B
MW-2
δ²H (per mil, 14D)
δ¹³C (per mil, 14D)

Criteria 1: Degradation

DIP with degradation



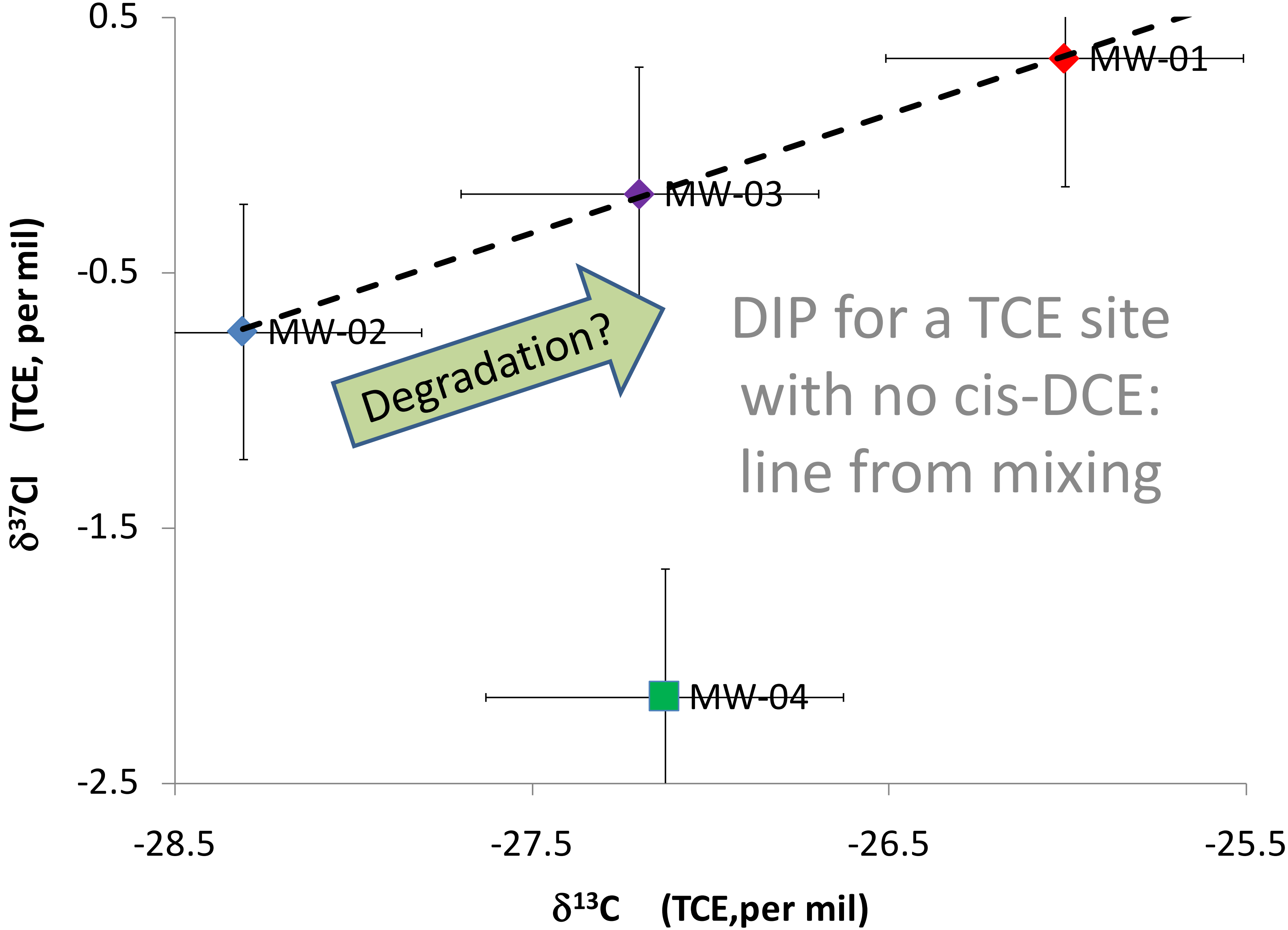
- Slope ➔ degradation mechanism
- Intercept ➔ source

- Slope function of degradation mechanism

Compound	Slope	Mechanism	Reference
TCE	0.37 ± 0.11	reductive de-chlorination	Wiegert et al. 2013
PCE	0.35 ± 0.11	reductive de-chlorination	Wiegert et al. 2013
14D	7.5 ± 1.1	Co-metabolic MMO, propane grown	Bennett et al. 2018
14D	37.2 ± 2.6	co-metabolic MMO, THF° grown	Bennett et al. 2018
Benzene	14.9 ± 9.6	nitrate reduction	Mancini et al. (2003)
Benzene	24.7 ± 6.7	sulfate reduction	Mancini et al. (2003)
Benzene	30.6 ± 3.5	methanogenesis	Mancini et al. (2003)

- Without specific geochemical or microbiology evidence, must assume degradation mechanism is the same across the site.

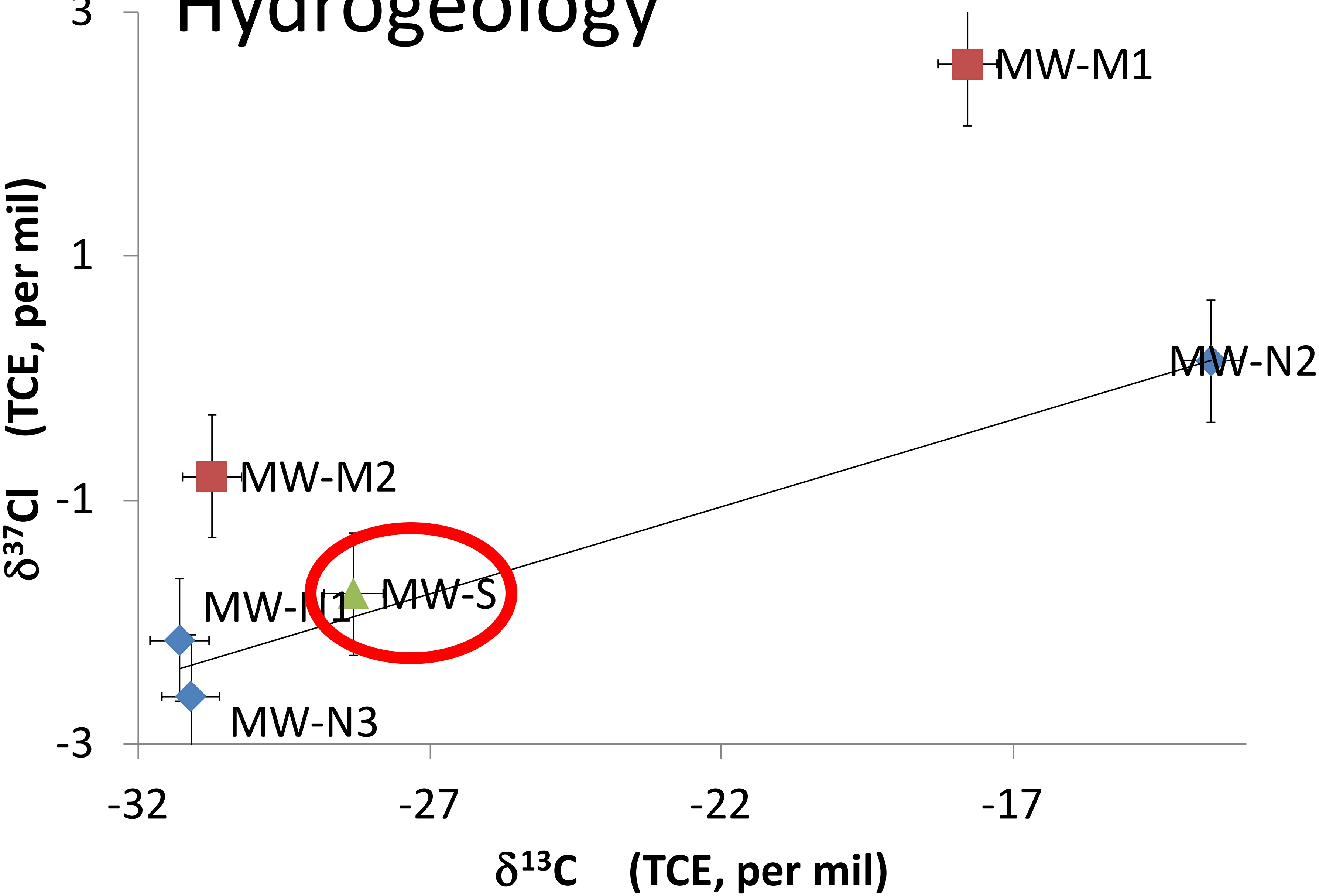
Need for Multiple Lines of Evidence



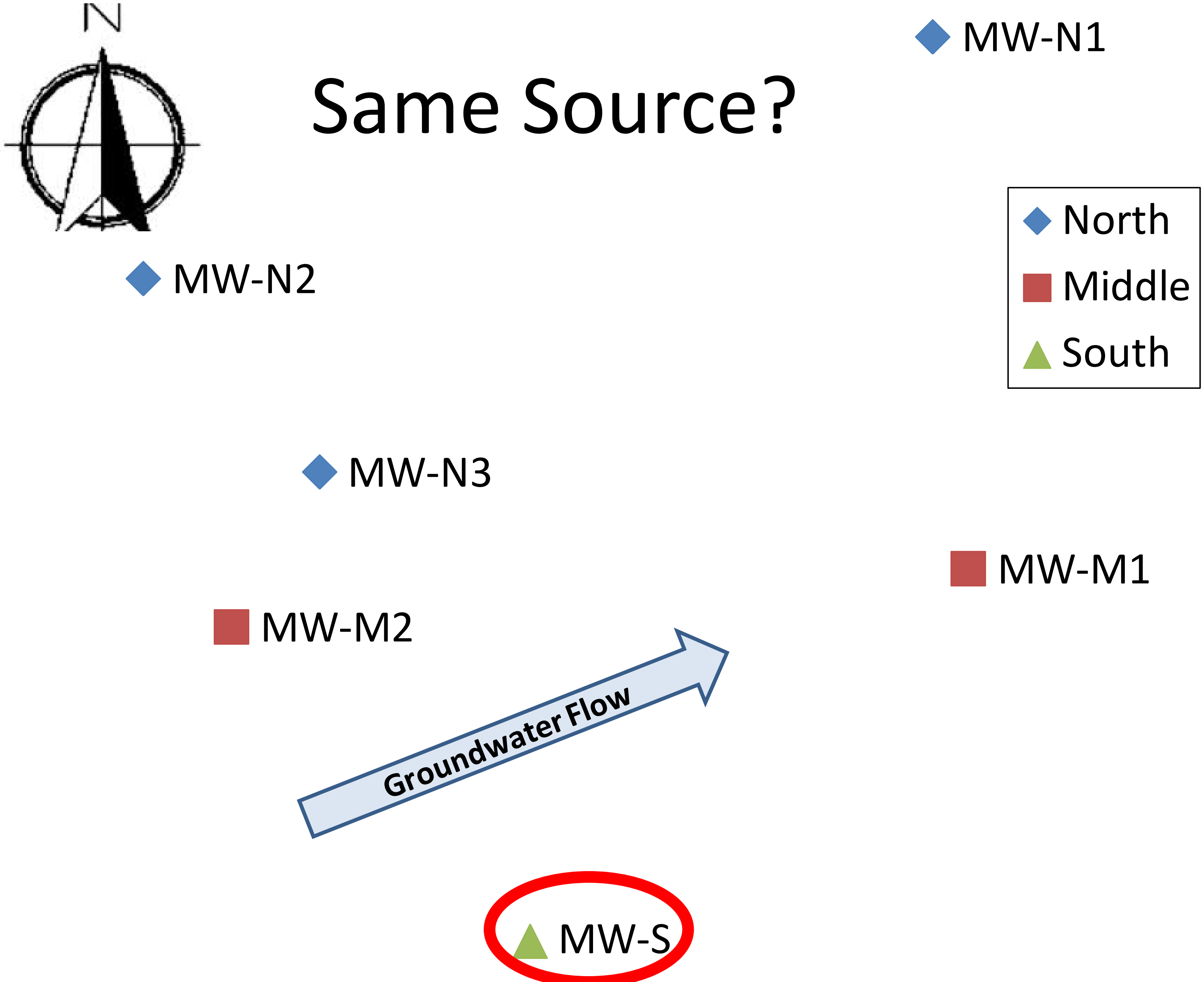
Criteria 2: Hydrogeology

Step 1 - Always Look at the Map

Hydrogeology



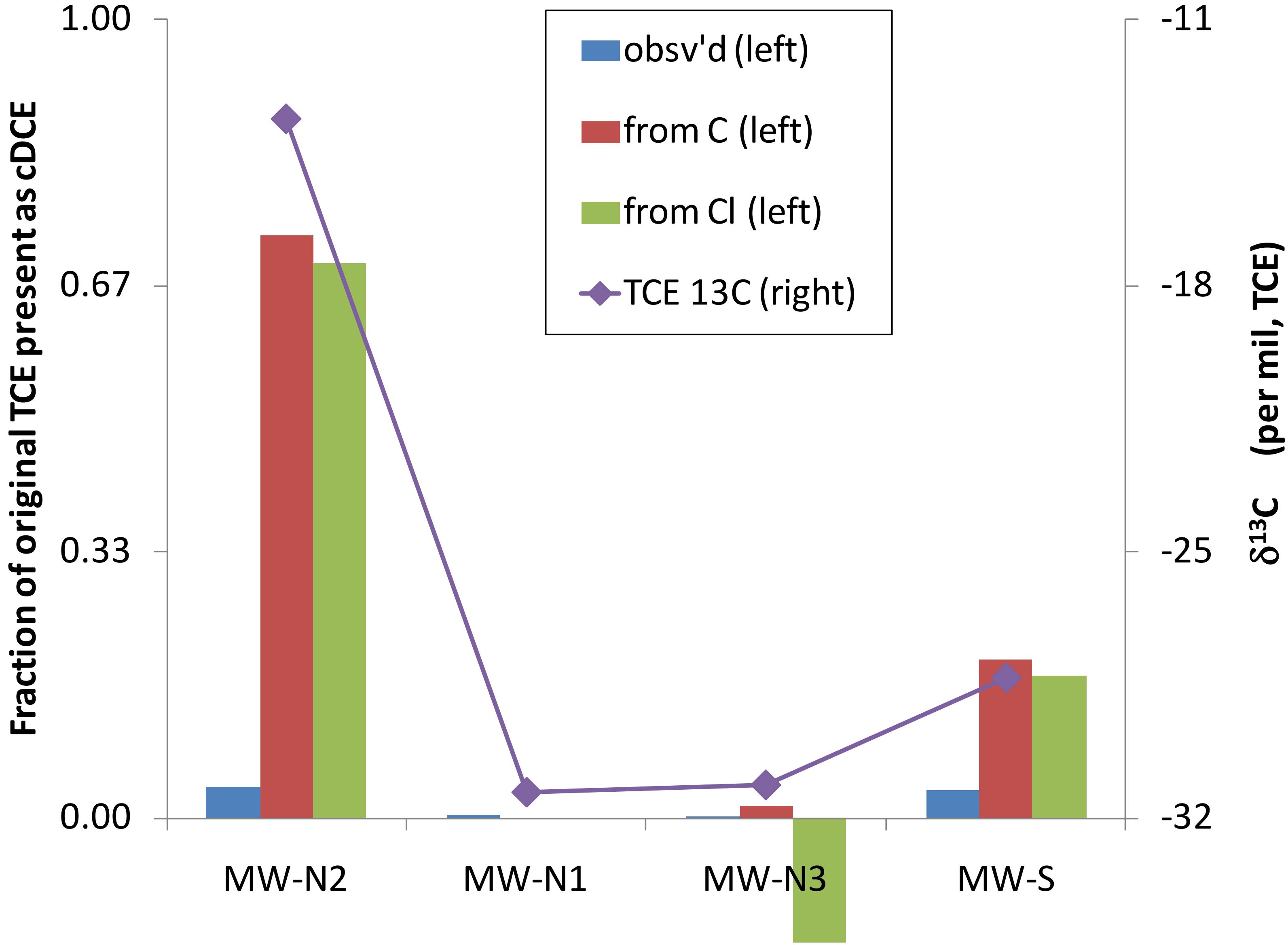
Same Source?


N
MW-N1
North
Middle
South
MW-N2
MW-N3
MW-M1
MW-M2
Groundwater Flow
MW-S

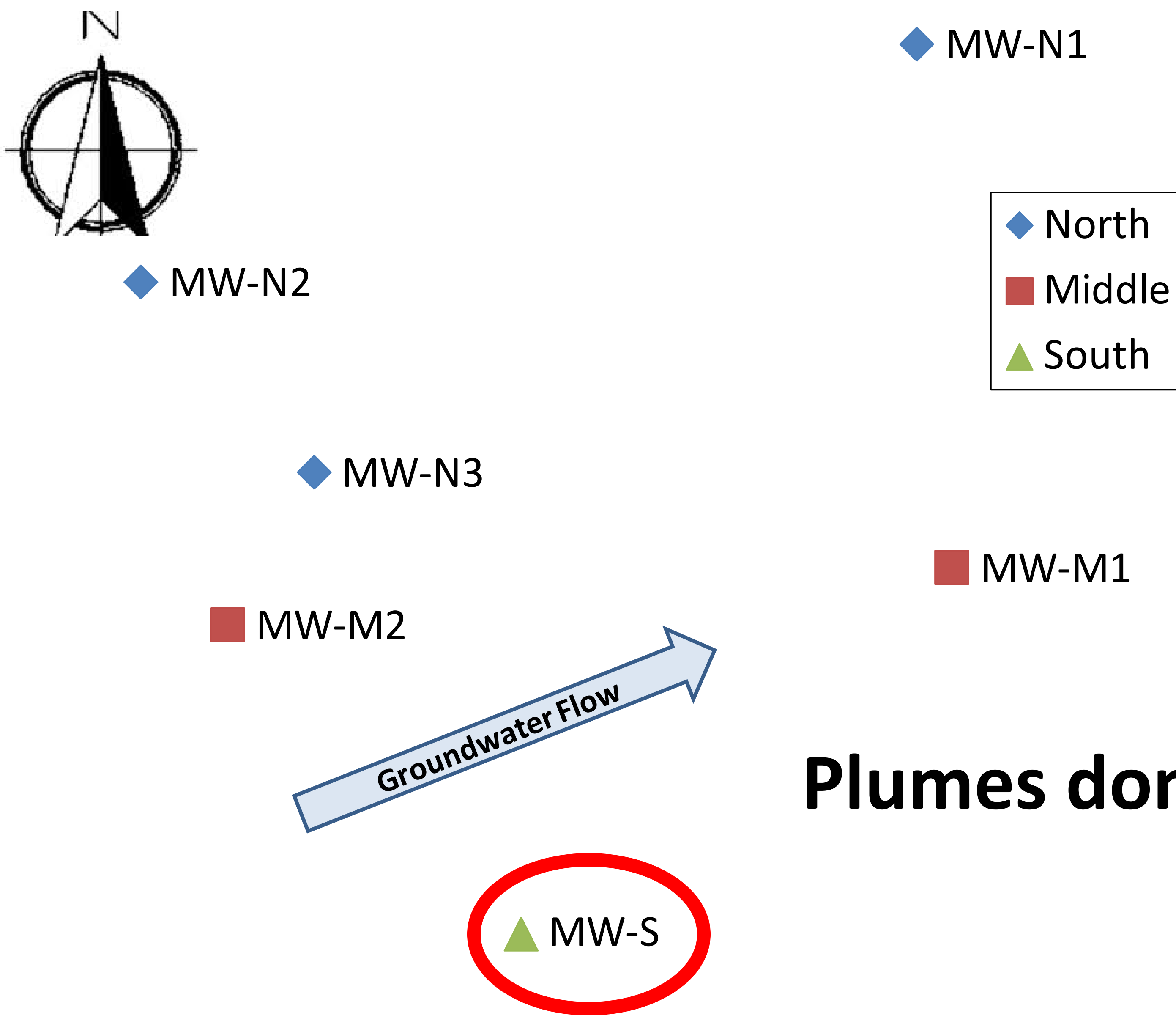
Same source? - Comparing Observed and Predicted cis-DCE Fractions

- Can use Rayleigh Equation to predict fraction of original TCE present as cis-DCE.
- To get some idea of uncertainty in calculation, do for both carbon and chlorine.
- Compare calculation to observed concentrations.

Observations vs. Calculations

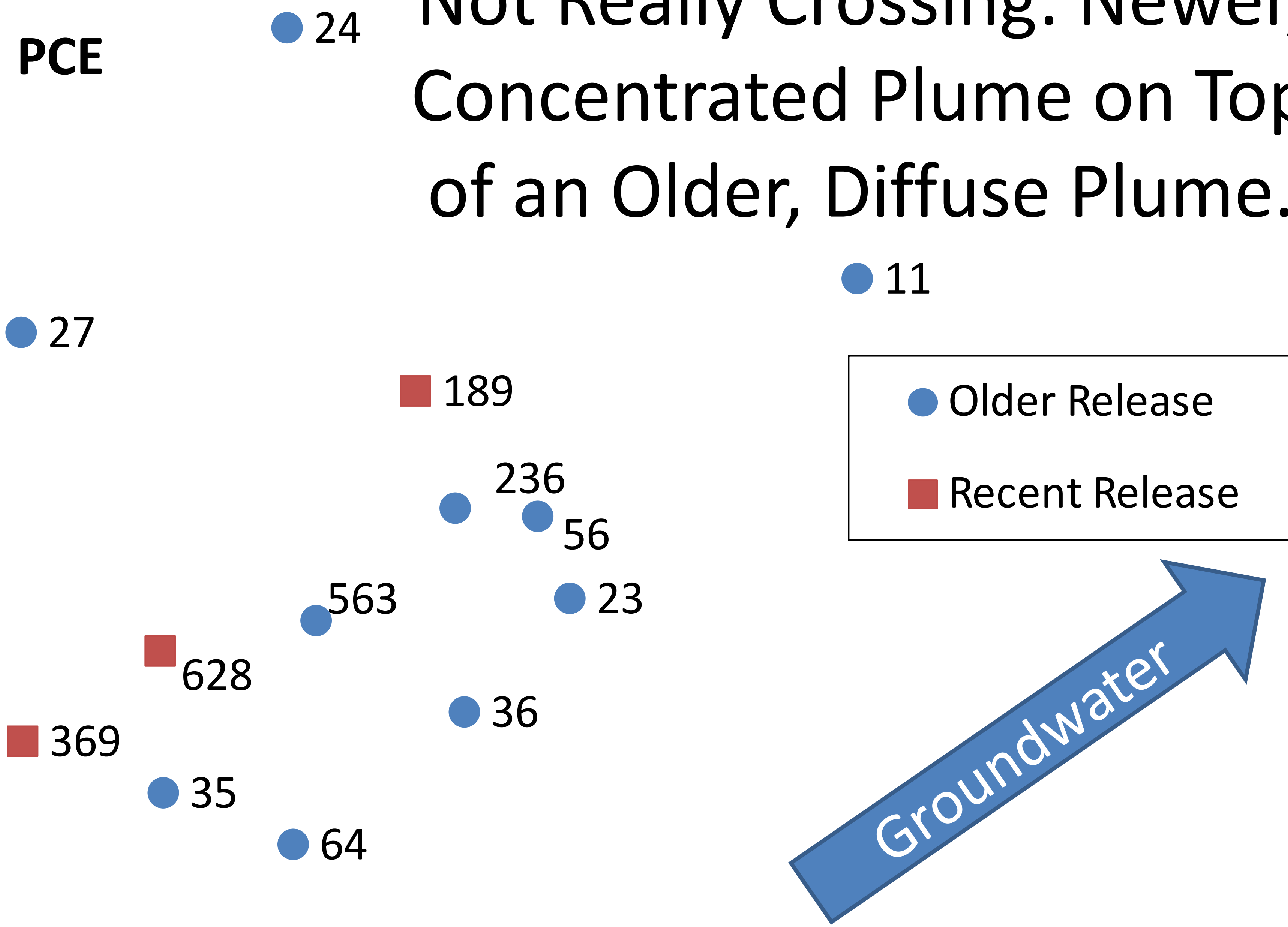


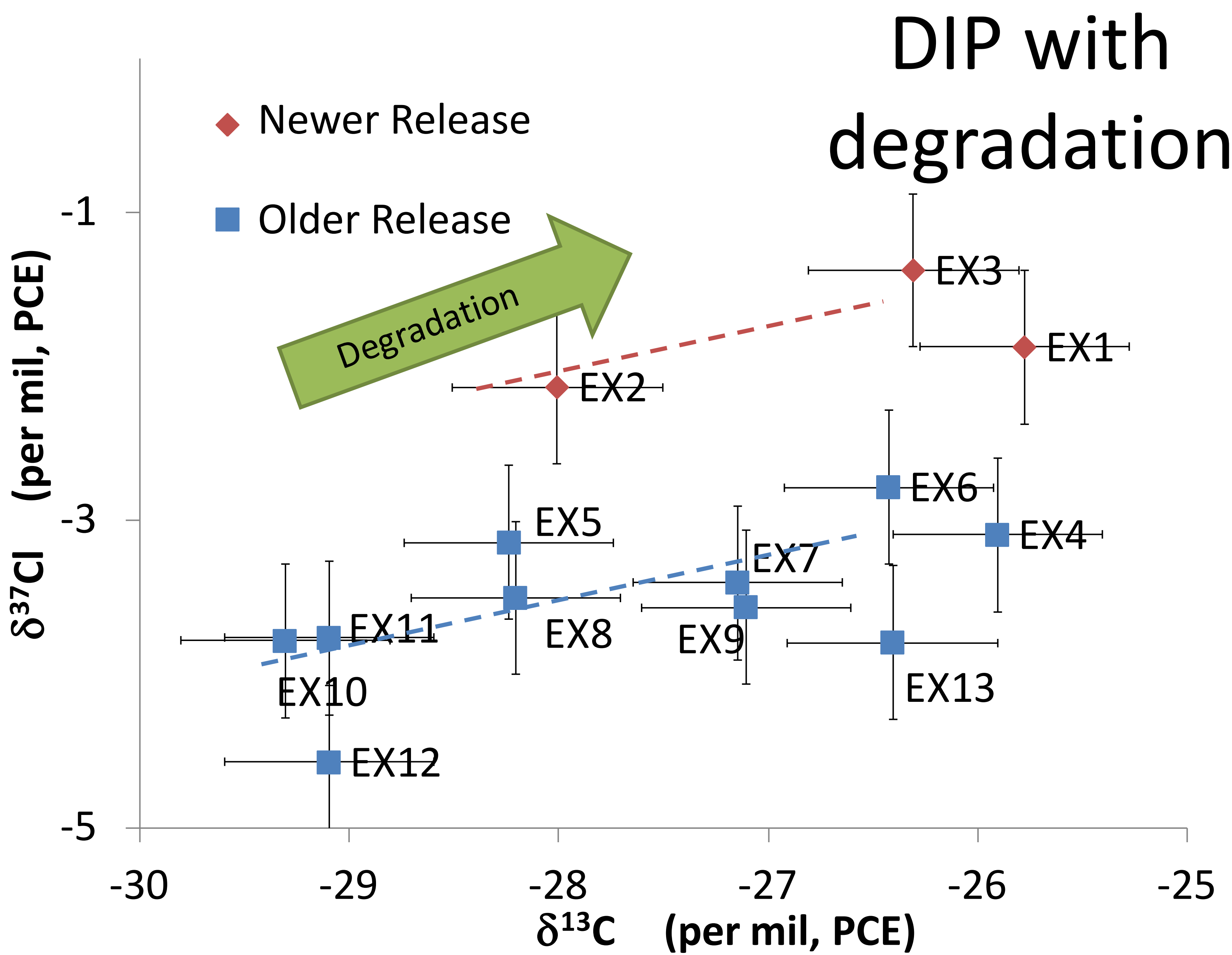
Different Sources



Plumes don’t cross!

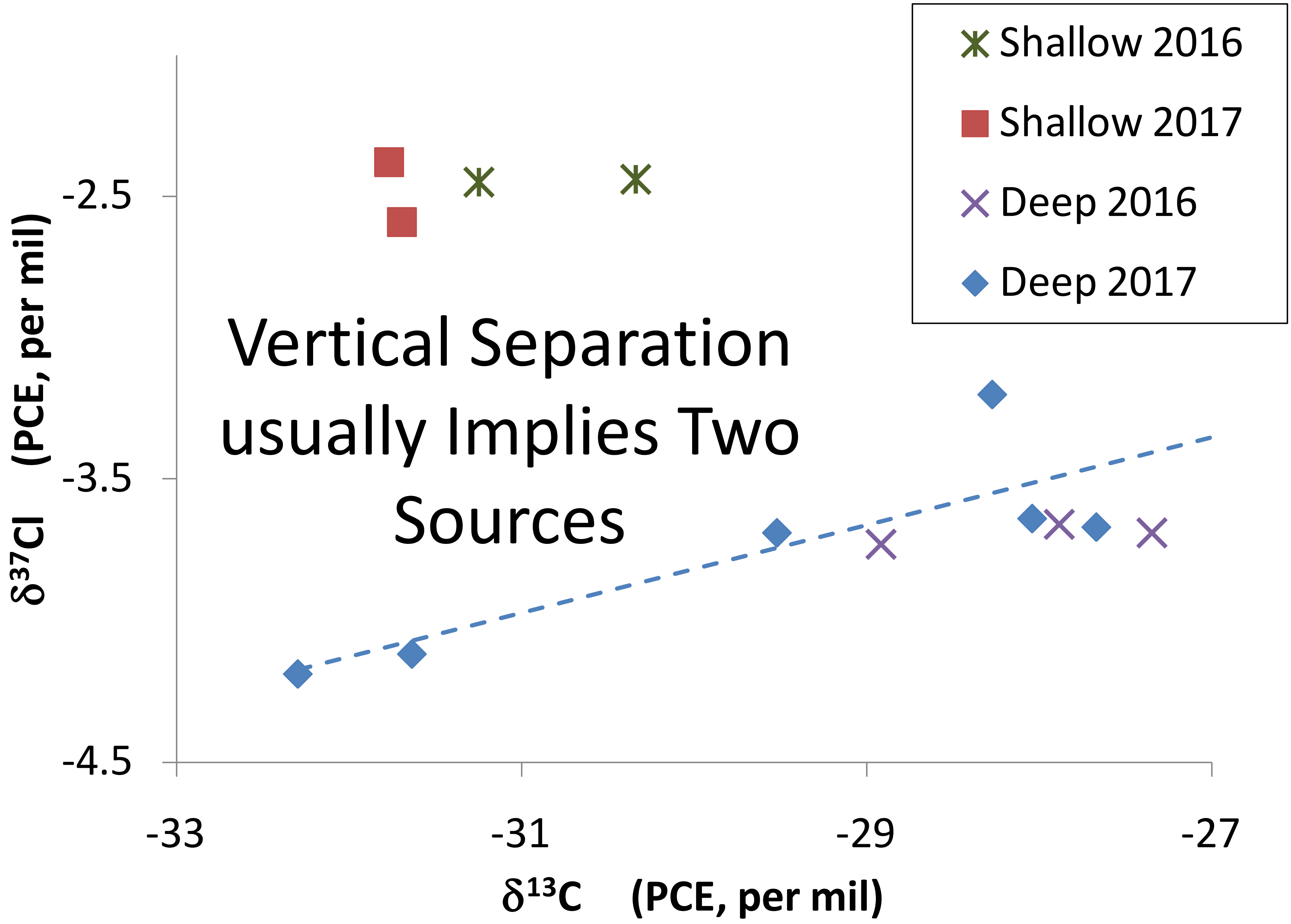
Not Really Crossing: Newer, Concentrated Plume on Top of an Older, Diffuse Plume.



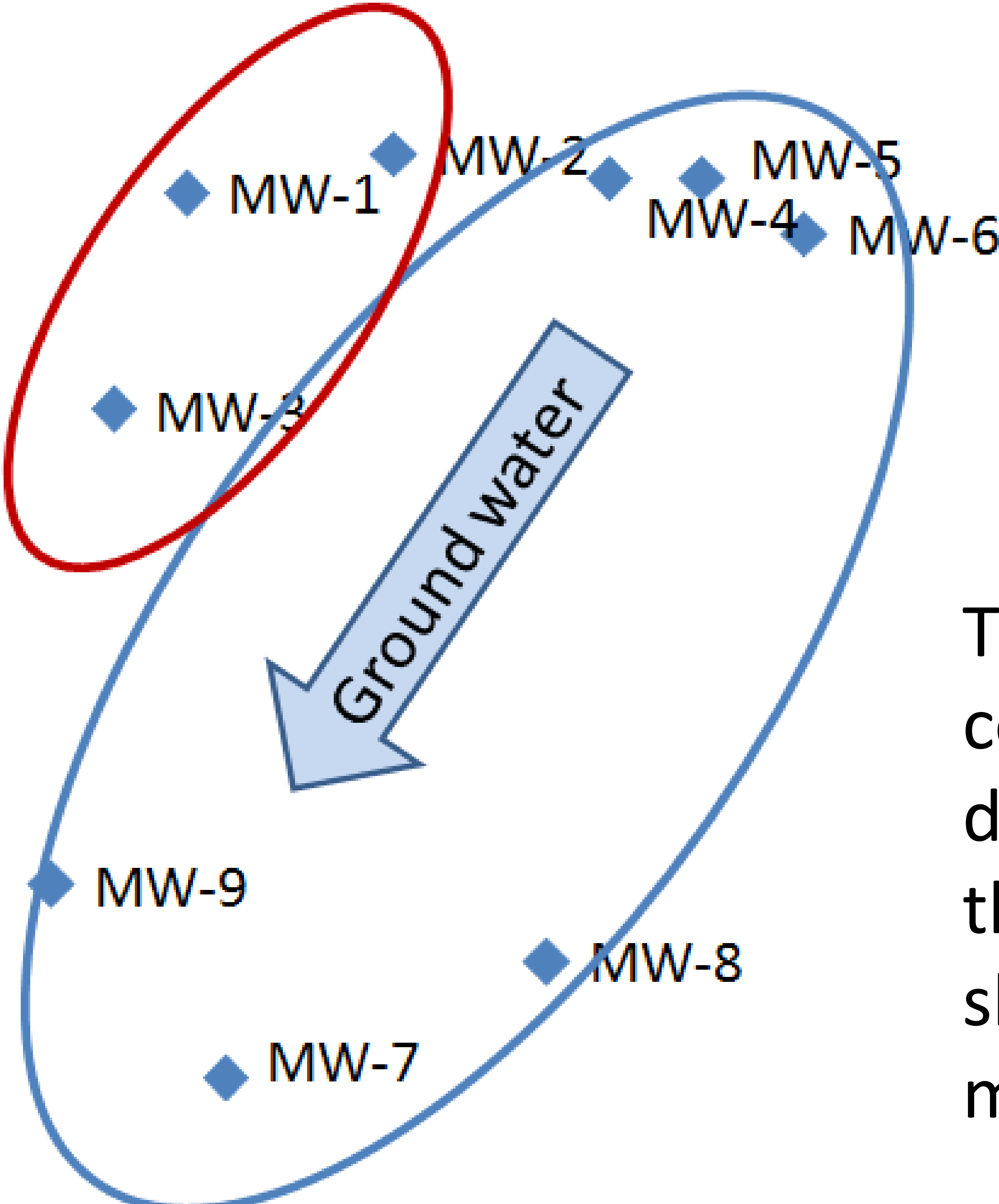

DIP with degradation
Newer Release
Older Release
Degradation
EX1
EX2
EX3
EX4
EX5
EX6
EX7
EX8
EX9
EX10
EX11
EX12
EX13
-1
-3
-5
-30
-29
-28
-27
-26
-25
δ37Cl (per mil, PCE)
δ13C (per mil, PCE)

Criteria 2: Hydrogeology

Step 2 – Don’t forget depth

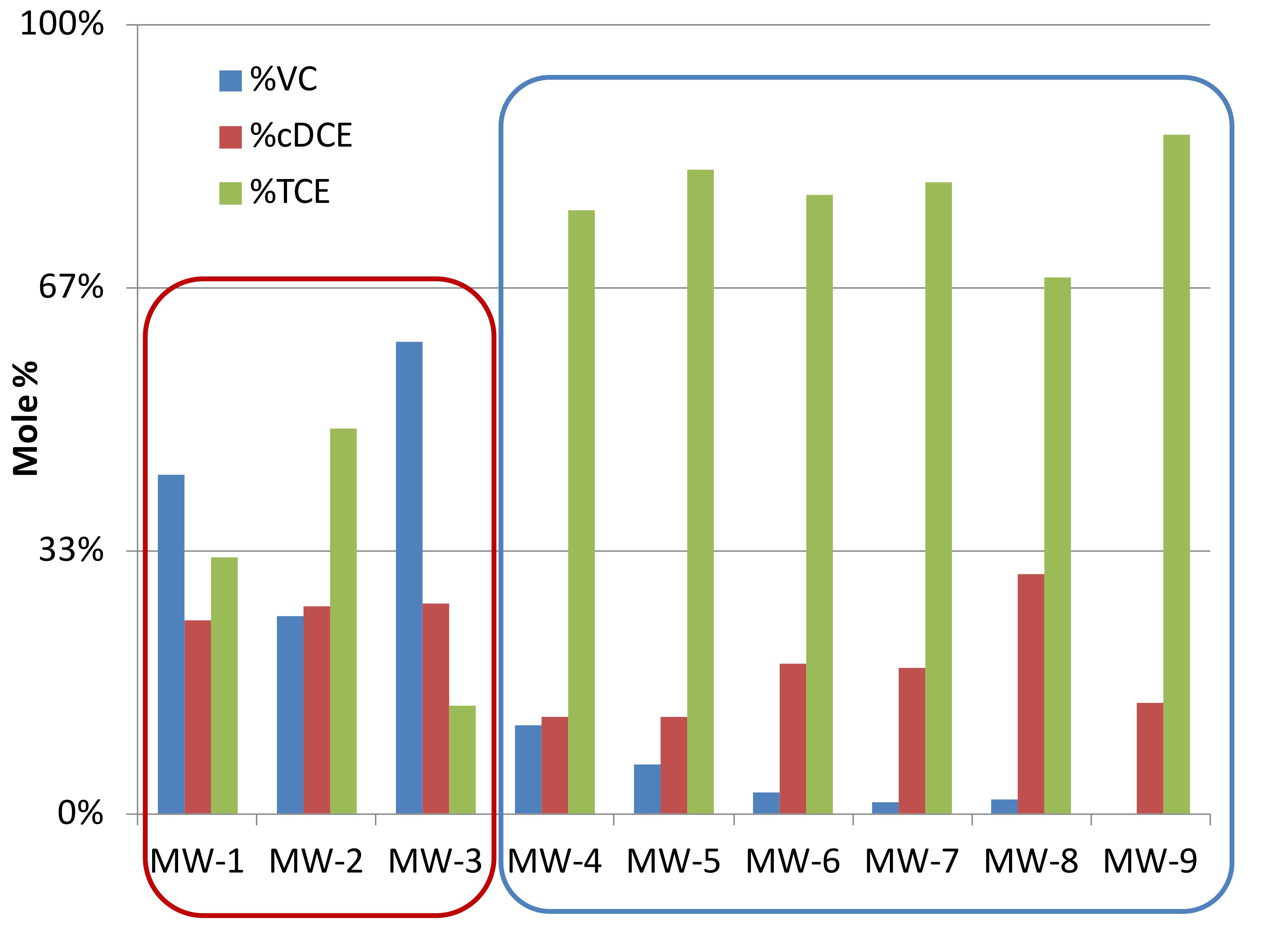

Shallow 2016
Shallow 2017
Deep 2016
Deep 2017
Vertical Separation usually Implies Two Sources
-2.5
-3.5
-4.5
δ37Cl (PCE, per mil)
-33
-31
-29
-27
δ13C (PCE, per mil)

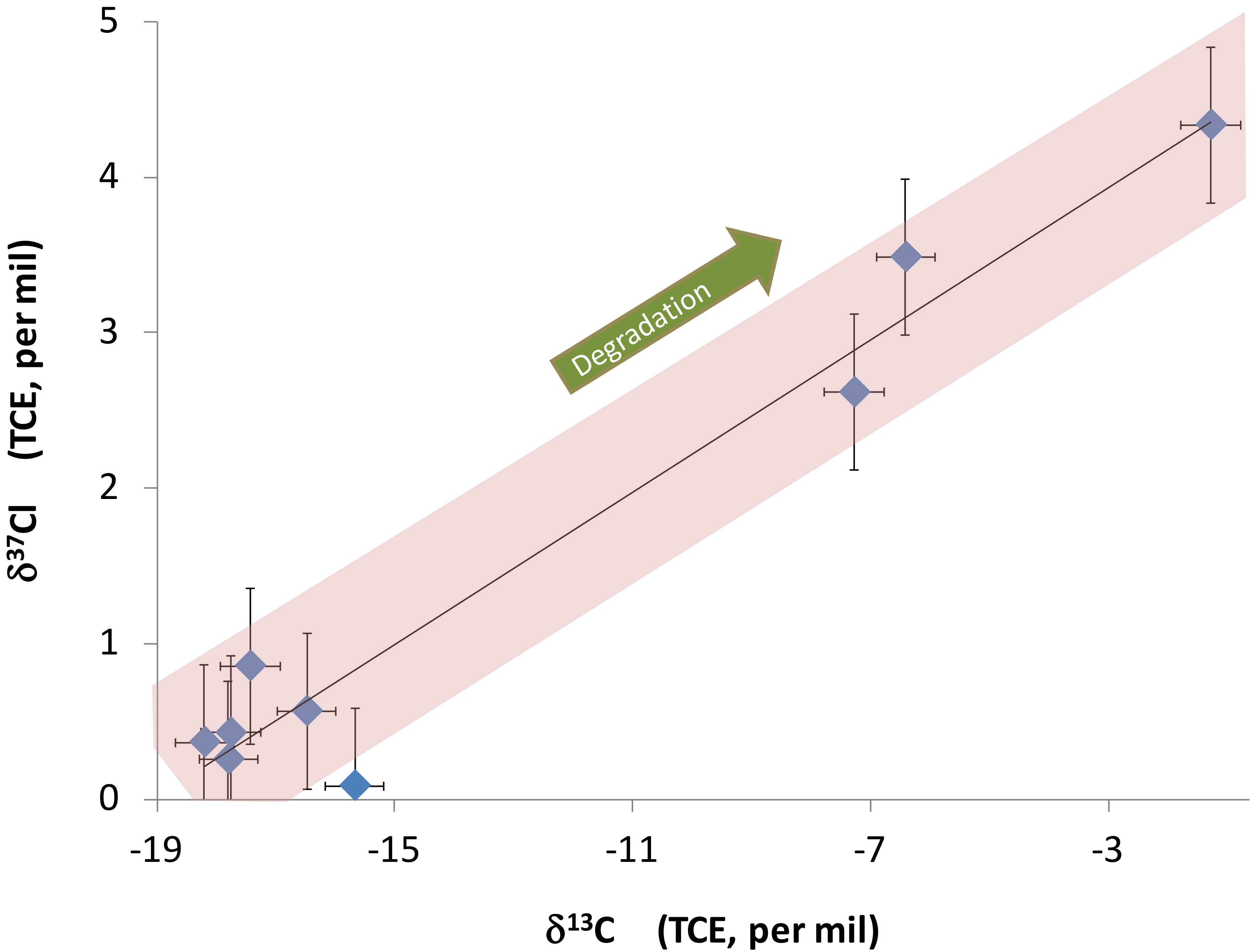
Criteria 3:



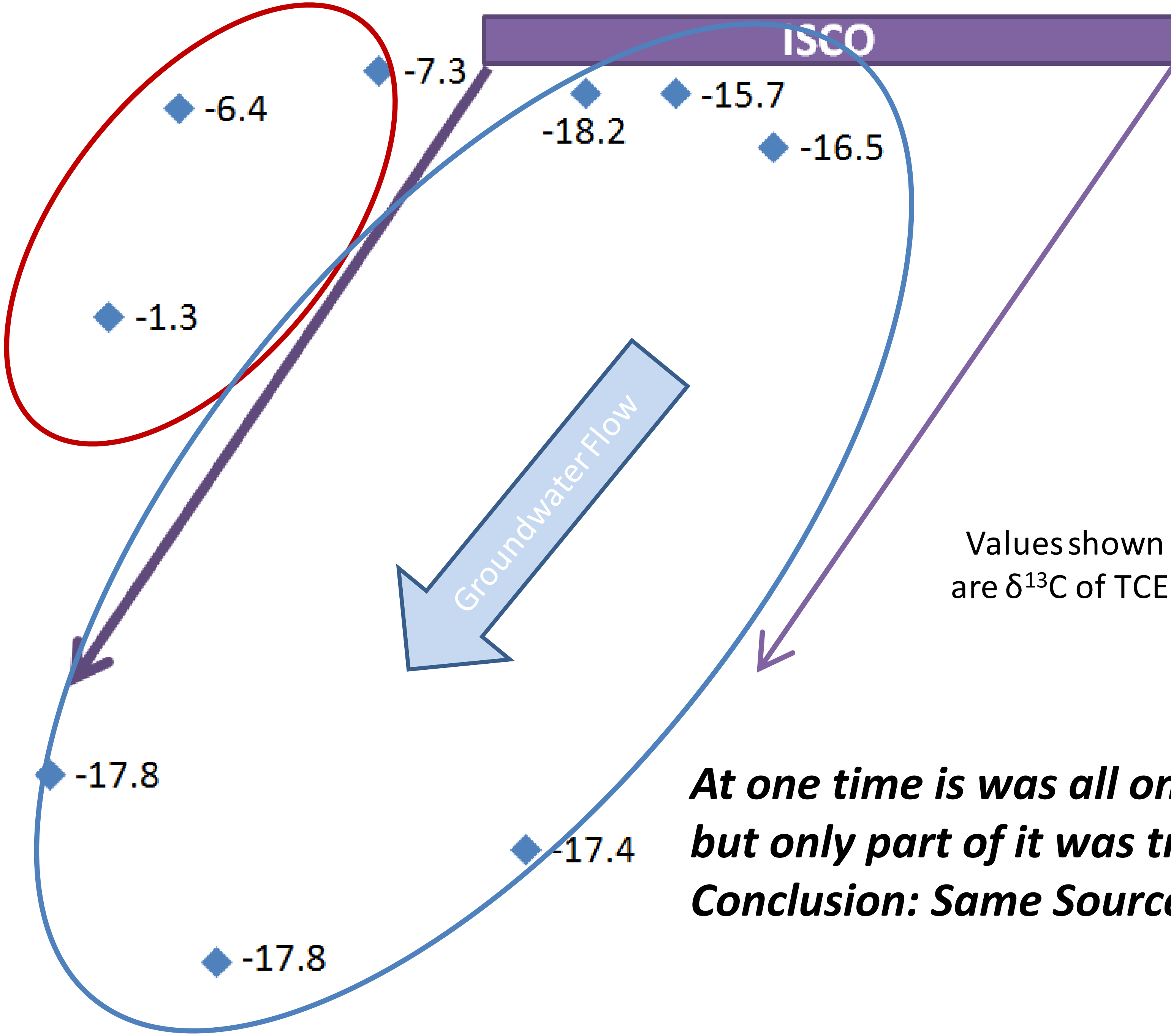
Site History

The concentration data suggested the separation shown in this map.


100%
67%
33%
0%
Mole %
%VC
%cDCE
%TCE
MW-1
MW-2
MW-3
MW-4
MW-5
MW-6
MW-7
MW-8
MW-9



5
4
3
2
1
0
-19
-15
-11
-7
-3
Degradation
δ37Cl (TCE, per mil)
δ13C (TCE, per mil)



At one time is was all one plume, but only part of it was treated.
Conclusion: Same Source

Thank You!

McLoughlin P. Protocol for using compound-specific isotope analysis in environmental forensics. Remediation. 2019;29:45–52. https://doi.org/10.1002/rem.21588