

Assessing the Potential and the Limitations of the Current “State of the Art” of CSIA Based Forensics

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Initial Isotopic Signatures

- Set initially by raw material of manufacturing.
- Modified by:
 - Manufacturing process type
 - Manufacturing conditions
 - Post manufacturing purification conditions
- This is not changed by
 - Transportation
 - Storage
 - Non-destructive use

Product release and Isotopic Signature

There is no change in the isotopic signature of PCE or TCE because of migration

- Down to
- Into
- Within

the groundwater.

Forensic Case Study 1: Undegraded PCE

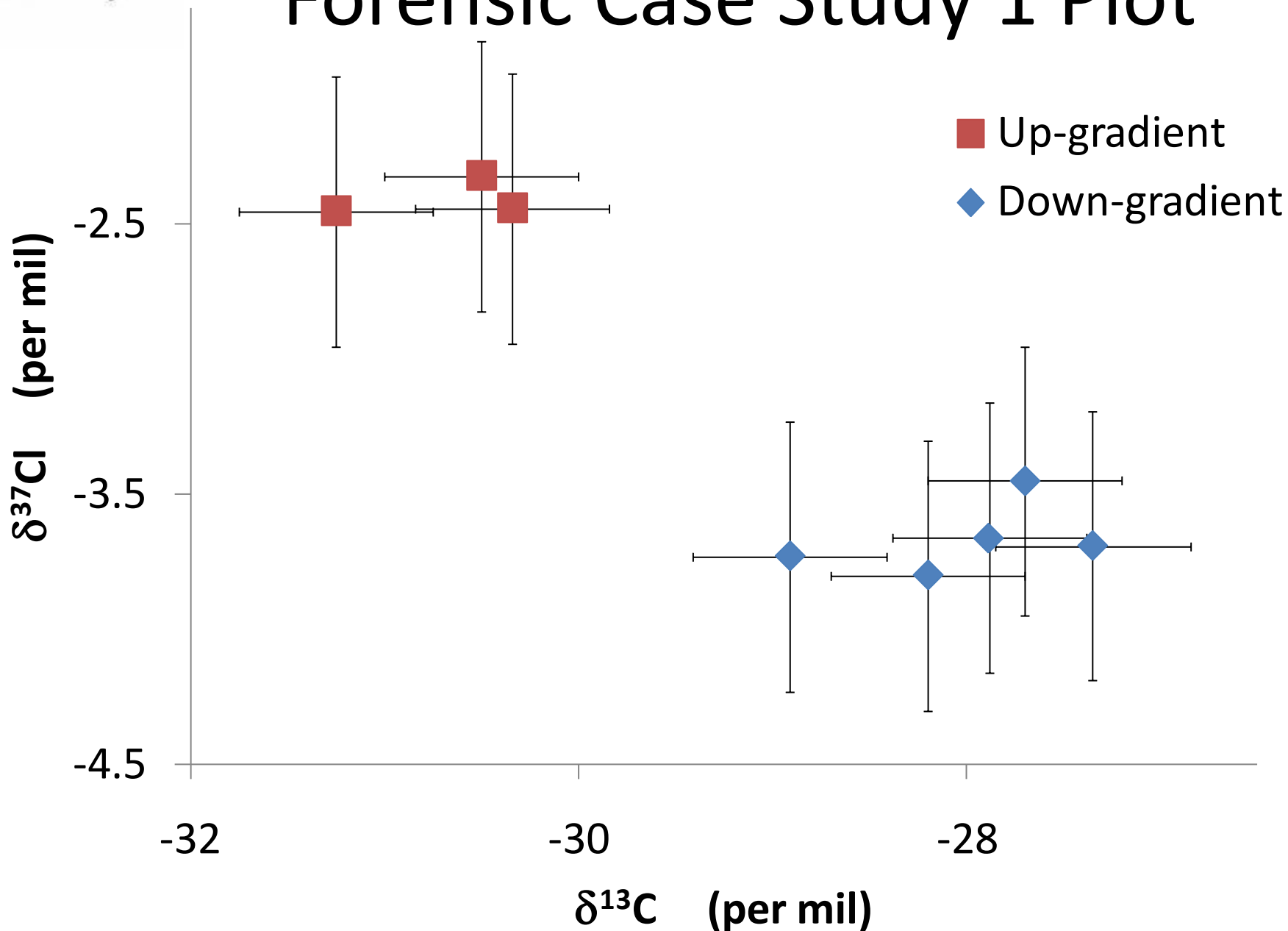
Background:

- PCE impacts were detected in the groundwater.
- PCE found both up-gradient and down-gradient of former dry cleaner.
- Concentration did increase under former dry cleaner, but it was suspected they were not sole source.

Question:

- Was there any evidence of the plume having multiple sources?

Forensic Case Study 1 Plot



Isotopic effects of Degradation

- Degradation tends to consume the lightest stuff first.
- Product is lighter than reactant.
- Undegraded reactant gets heavier than degraded reactant.
- This means as the extent of degradation increases $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ increase.
- $\delta^{37}\text{Cl}$ is a linear function of $\delta^{13}\text{C}$
 - A result of the Rayleigh Equation.
 - for PCE slope of $\delta^{37}\text{Cl}$ vs. $\delta^{13}\text{C}$ line is 0.35 ± 0.11 (for TCE it is 0.37 ± 0.11).

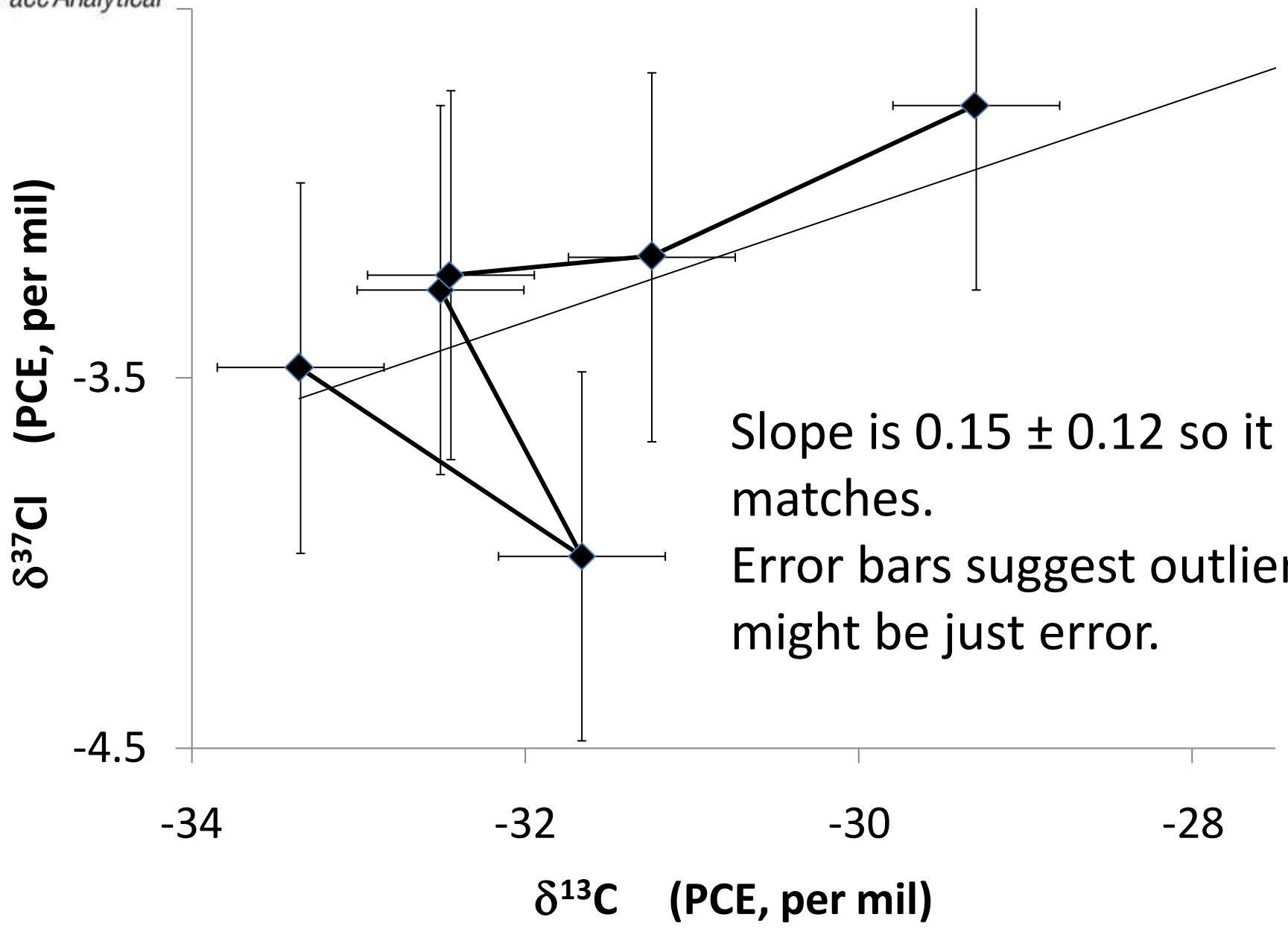
Forensic Case Study 2: Degrading PCE

Background:

- A long plume extended under multiple properties.
- The plume was originally all PCE but was now a mixture of cis-DCE and VC at its toe.
- Six wells still had measurable PCE in them.

Question:

- Since degradation was fractionating the plume, was there still any evidence that it was a single source?



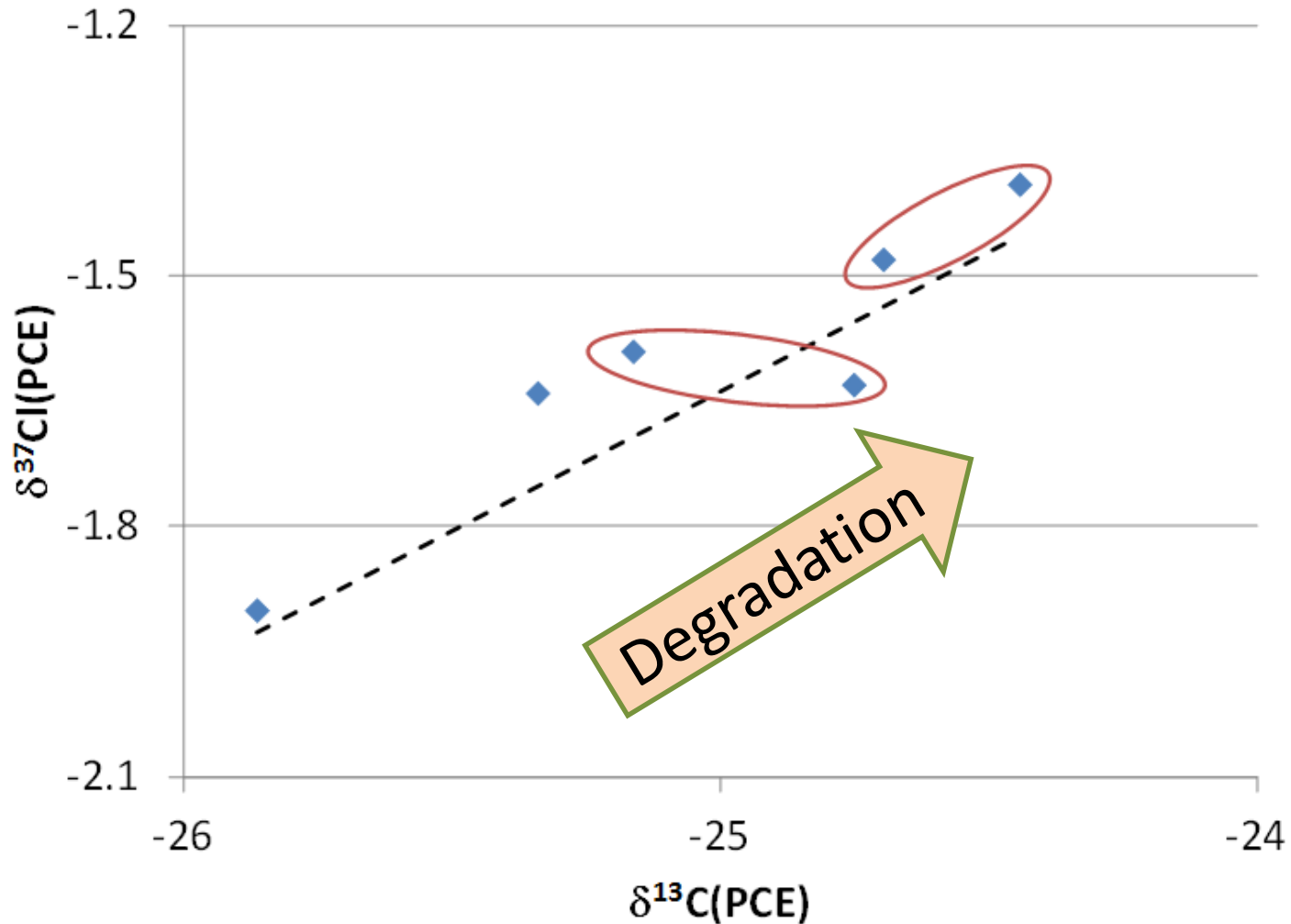
Slope is 0.15 ± 0.12 so it matches.
Error bars suggest outlier might be just error.

Forensics Case Study 3: Down-gradient “hot-spot”

- Question: Plume presumed to have single source, but did it originate up-gradient?
 - Hot spot is on down-gradient site
 - Contamination of similar composition found in up-gradient well
- Primary COC's were PCE, TCE and cis-DCE
- Had been some biodegradation, but mild
- Source had long since been depleted

Forensics Case Study 3

- Circled points are duplicates
- Degradation fueled by co-contaminants.
- Expect degradation most extensive at source.



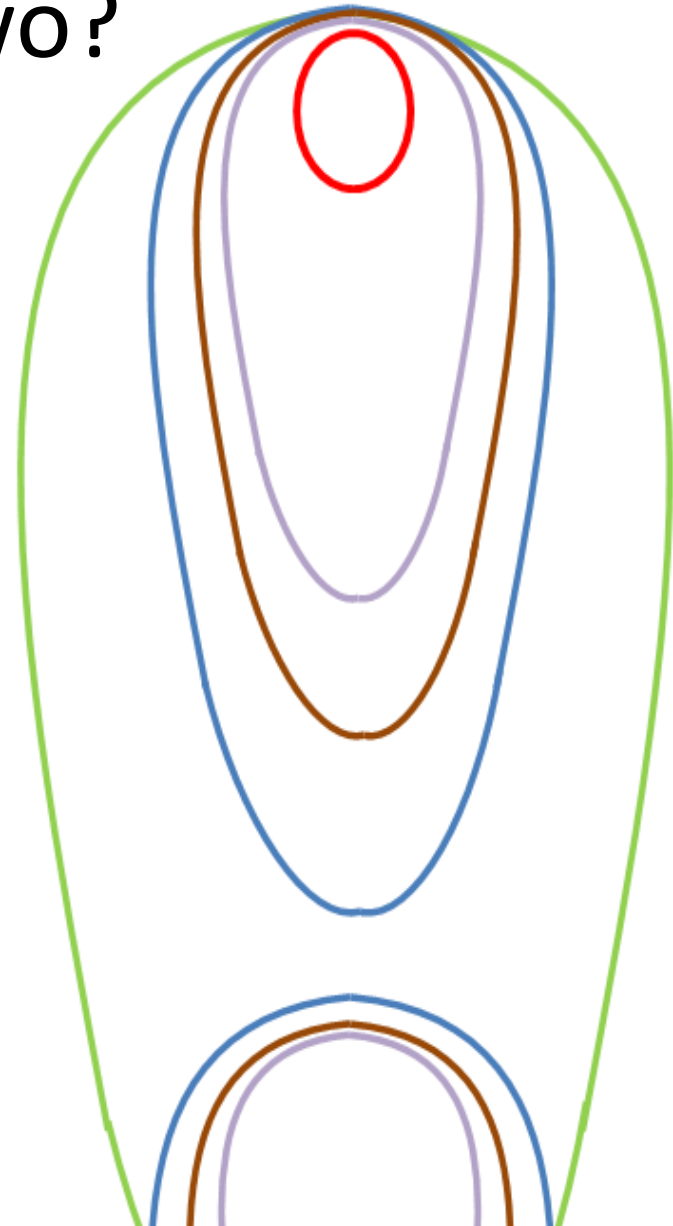
- Most degraded point is the up-gradient sample.

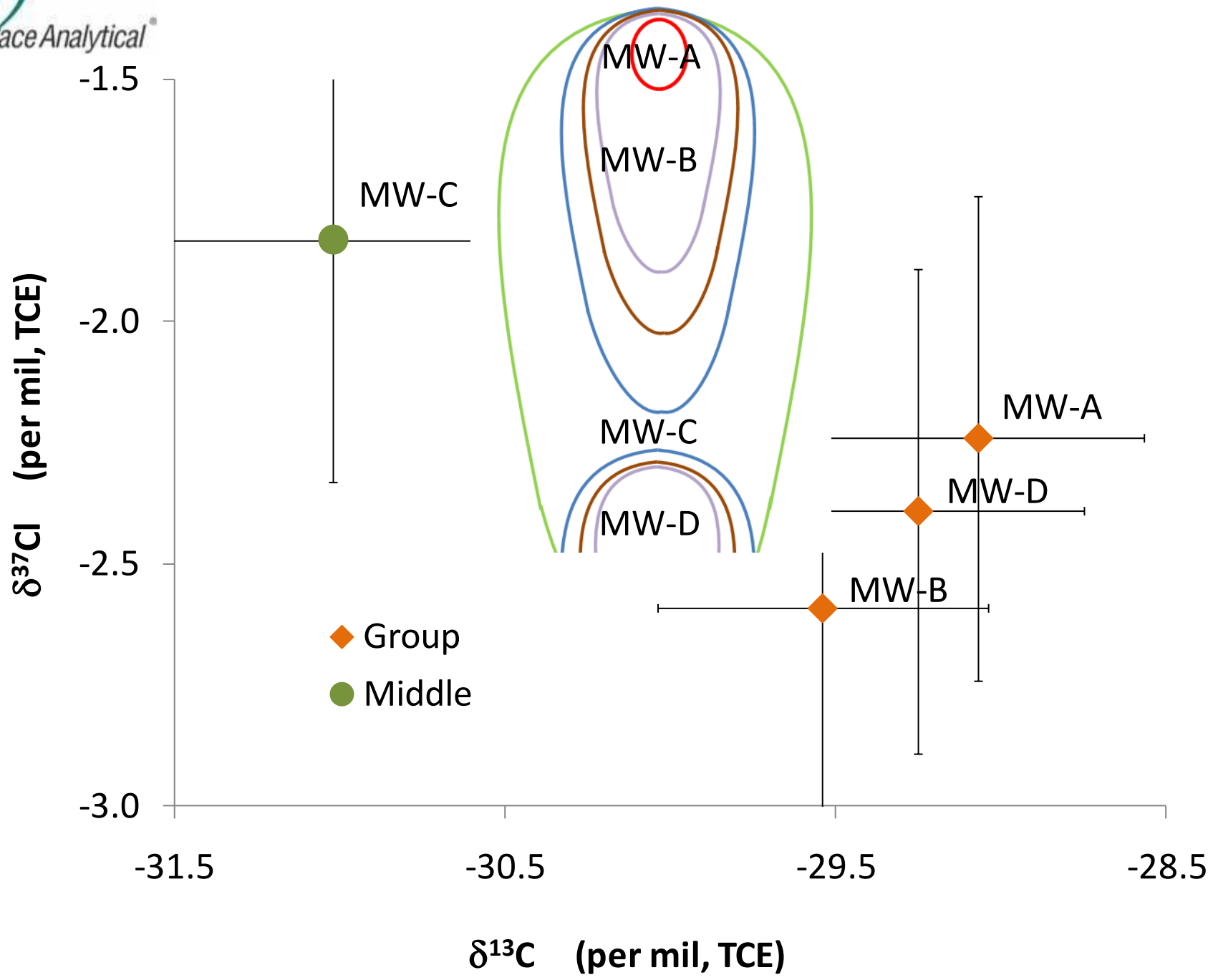
Forensic Case Study 3 – *Concl.*

- Additional observations show most degraded TCE and cis-DCE at same location
- All evidence points to a single, off-site PCE source located closest to the up-gradient (and off-site) well.

Forensics Case Study 4: One plume or two?

- TCE plume concentrations went to mostly “non-detect” then started to increase sharply along plume centerline.
- No other PRP’s in area of concentration increase.
- Question: was down-gradient impacts related to up-gradient impacts?



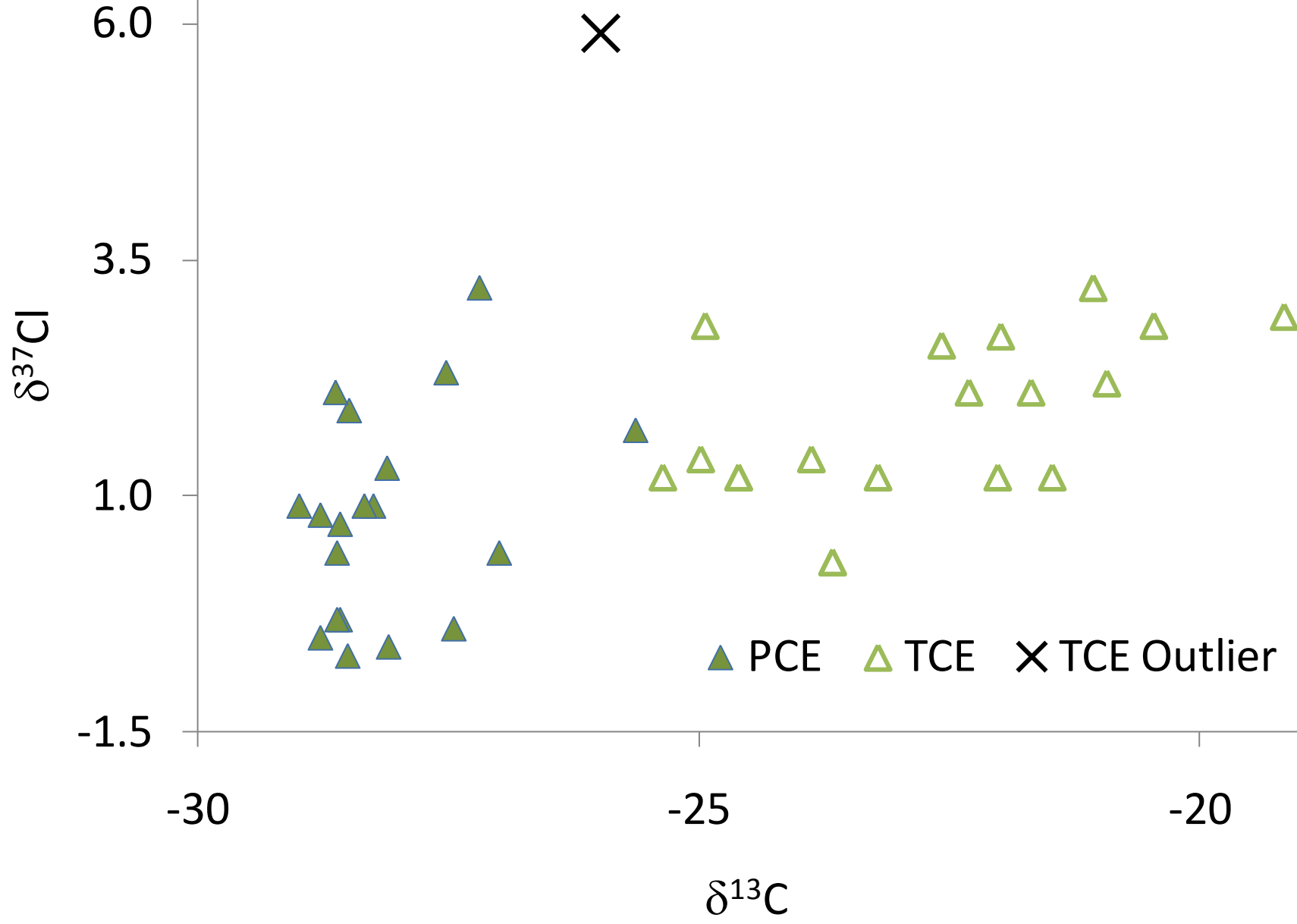


Forensic Case Study 4 – *Concl.*

- MW-A, MW-B and MW-D all isotopically indistinguishable – likely same source.
- MW-C distinct.
 - Under MNA conditions, fractionation by volatilization/evaporation is minimal for TCE (and PCE).
 - However, here the plume was treated with a combination of air sparging and soil vapor extraction, so volatilization is extensive.
 - TCE (and PCE) volatilization make $\delta^{37}\text{Cl}$ heavier but $\delta^{13}\text{C}$ lighter.
 - Likely that MW-C started with the same isotopic signature of the other wells but was fractionated by the AS/SVE.
- Ground water flow suggests:
 - MW-D was at source before system was on.
 - MW-A and MW-B were at source after system was off.
 - Only MW-C was at source while system was on.

Forensic Case Study 5: PCE & TCE mix

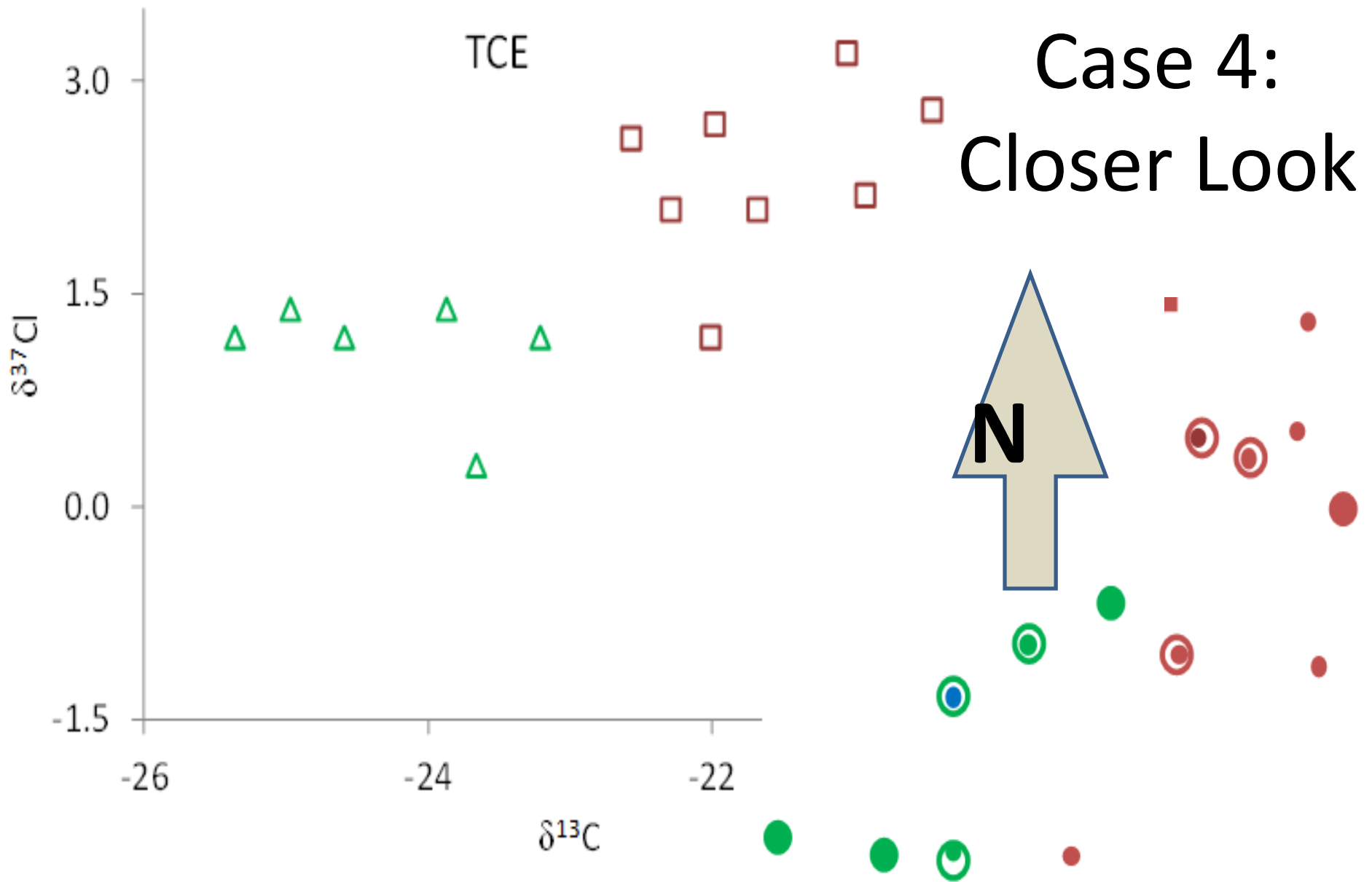
- Background:
 - PCE and TCE were impacting groundwater.
 - Area around impacts was heavily Industrialized.
 - Only small, sporadic hits of cis-DCE.
 - Just outside area of impacts was a residential area with large vapor intrusion issues.
 - The cost to remediate the vapor was a driver. The named responsible party did not think that the problem was all theirs’.
- Question
 - Since there was little, if any, degradation was it possible to do any forensics using CSIA?



Forensics Case Study 5 – *Concl.*

- Outlier from off-site – not similar to on-site TCE
- TCE produced from PCE is lighter than that PCE in carbon.
 - That TCE only gets heavier if it degrades.
 - Minimal degradation at this site, so TCE is not from PCE.

Case 4: Closer Look



Case 5: More Conclusions

- TCE to the West all lighter than TCE on the East
- 2 on-site TCE sources, at least one on-site PCE source and one off-site TCE source
- Saved client \$500,000-\$2,000,000

Limitations

- “isotopic signatures can vary by batch”
 - Above ground, that is absolutely true.
 - Once dissolved in groundwater, many identical samples suggest that variation is “smeared out”.
- Neighboring properties in operation at same time may have gotten solvents from same source.
- Extensive biodegradation convolutes the signal.
 - Complete biodegradation, no forensics!!!
 - Near complete biodeg. VERY limited forensics.

Summary

- Current CSIA techniques can distinguish otherwise identical PCE and TCE.
- While extensive biodegradation is a problem, a small extent of biodegradation is not a problem and is sometimes even helpful.
- Adding ground water flow into the mix is not a problem either.
- Savings can be $> \$1,000,000$.