

Making Sense of CSIA

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CSIA and keeping it simple

Compound Specific Isotope Analysis can seem complicated, but it doesn't have to be. This tool can help us build lines of evidence to prove that a compound of interest is degrading. CSIA uses a ratio of two forms of the same compound which are naturally occurring. Small changes in these forms indicates change in the compound of interest. With added lines of evidence, we can use CSIA to verify that certain processes are occurring, and we can also ascertain the source of a contaminant with confidence.

Determining Degradation

- Prioritize isotope selection and save money: *carbon is most important*
 - Analyze all compounds of interest, not just parent compounds

Sampling for Spatial Comparison

1. Sample source area
2. Sample down the center of the plume following the flow path to the distal plume (toe)

Sampling for Temporal Comparison

1. Start with baseline sampling strategy
2. Monitor locations of interest every 6 months
3. Be consistent, monitor the same wells regularly

Data interpretation

- Determine most negative $\delta^{13}\text{C}$ value of the parent compound at the site (most likely at the source area) - this is your baseline value
 - For temporal studies, compare all historical CSIA data, the most negative $\delta^{13}\text{C}$ value of the parent compound is the baseline value (most likely at the source area from the earliest sampling events)
- Compare $\delta^{13}\text{C}$ values of all compounds (including daughter products) to the parent compound baseline – if they are more than 2 ‰ greater than the baseline, you have proof of compound degradation in that location
 - For temporal, you have the data to monitor the $\delta^{13}\text{C}$ value changes in the same sampling location over time, as well as spatial comparisons
- To prove biodegradation of petroleum hydrocarbons, use Stable Isotope Probing.
- Limitations:
 - Can't be used to determine if a compound is *not* degrading
 - Sometimes continued monitoring is required to see if the $\delta^{13}\text{C}$ value increases

Source Distinction

Always need two isotopes

- C and Cl for chlorinated solvents
 - H analysis can confuse the issue, $^2\text{H}/^1\text{H}$ fractionation has been shown to be inconsistent
- C and H for petroleum hydrocarbons

No need to analyze daughter products

- Fractionation trends of daughter products will be inconsistent as they are produced and degraded at the same time

Sampling strategies

- Sample the plume in question (multiple locations)
- Sample every possible source area.
 - If this isn't possible, sample as close as possible to every possible source area
- Collect at least three samples along the flow path between each source area and the plume in question

Data interpretation in dual-isotope plots

- Understand fractionation trends
 - During degradation, delta values will only increase under normal environmental circumstances
 - If a contaminant in a plume originated from an upgradient source, data points should follow a linear trend between the source and the plume, sample on the dual isotope plot

Know the History of Your Site!



CSIA data and the spatial understanding of the site can be affected by many things – know when and where previous remediation treatments occurred

1. In-situ thermal
2. Recirculating pumps
3. Injections and extractions
4. Certain chemical oxidations

Understanding your QA/QC

- Negative control = method blank
- If a negative control has “Passed”, it means that none of the target compounds showed up in the blank – no contamination from the vial or the instrument
- Positive control = isotopic laboratory standard
- Standardized against an internationally recognized isotopic reference material

Precision should be within agreed upon acceptable range

- $\delta^{13}\text{C}$ should be within +/- 0.5 ‰ (standardized against VPDB)
- $\delta^{37}\text{Cl}$ should be within +/- 1.0 ‰ (against SMOC)
- $\delta^2\text{H}$ should be within +/- 10 ‰ (against VSMOW)