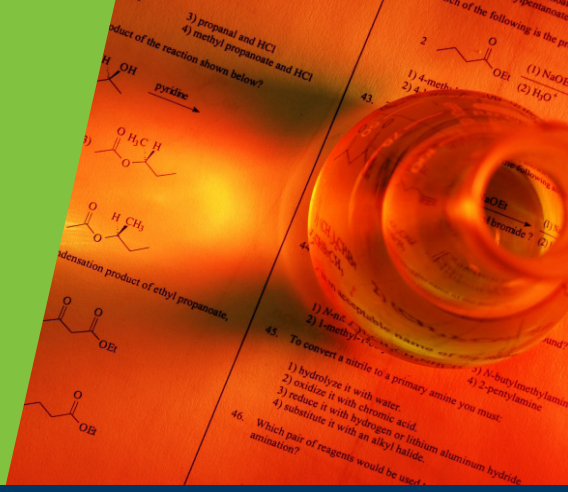
microbialinsights



CSIA and MI CSIA Database:
Multiple Sources

PROJECT SUMMARY

- During site assessment of a TCE site, compound specific isotope analysis (CSIA) conclusively demonstrated that degradation of TCE and daughter products was occurring at some locations.
- In addition to evaluating degradation, site managers also wanted to determine whether multiple TCE sources were present at the site.
- CSIA of TCE carbon ($\delta^{13}C$) and chlorine ($\delta^{37}Cl$) isotopes was conducted and a Dual Isotope Plot was constructed with the Microbial Insights CSIA Database.
- The Dual Isotope Plot suggested that two different sources of TCE may be impacting the site.

PROJECT CHALLENGE

A shallow aquifer at a manufacturing facility was impacted by historical releases of trichloroethene (TCE). Redox conditions were anaerobic and site managers wanted to conclusively determine whether contaminant degradation was occurring and whether multiple TCE sources might be present at the site.

SAMPLING AND ANALYSIS

Compound specific isotope analysis (CSIA) measures the ratio of stable isotopes (e.g. $^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$) of a contaminant. During degradation of many contaminants, the ratio of stable isotopes changes in predictable ways whereas physical processes like dilution do not appreciably impact isotope ratios. During degradation of chlorinated hydrocarbons like TCE, the chemical bonds with lighter isotopes (like ^{12}C and ^{35}Cl) are slightly weaker than those with the heavier ^{13}C or ^{37}Cl isotopes and react more readily resulting in isotopic fractionation. During degradation then the $^{13}C/^{12}C$ and $^{37}Cl/^{35}Cl$ ratios in the remaining contaminant, which has not yet degraded, increase. This isotopic fractionation (specifically significant increases in $\delta^{13}C$ and $\delta^{37}Cl$ values) **conclusively** demonstrate degradation of the contaminant.

Literature $\delta^{13}C$ values for manufactured TCE range from a minimum of -33.40‰ to a maximum of -23.20‰. Both $\delta^{13}C$ and $\delta^{37}Cl$ values for chlorinated hydrocarbons will

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Multiple Sources

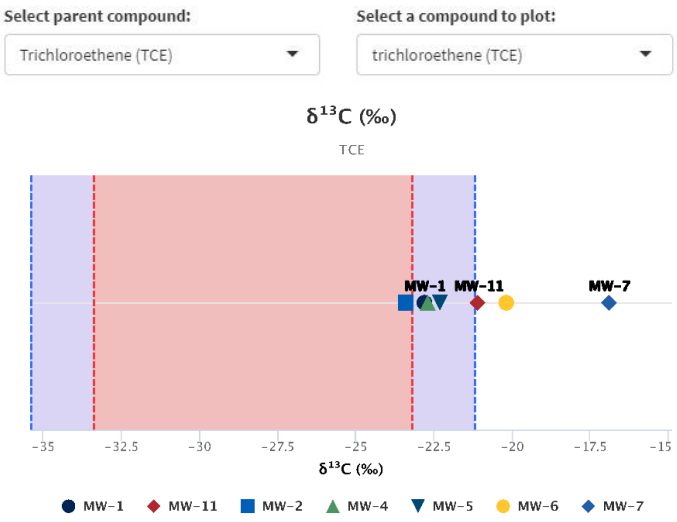
SAMPLING AND ANALYSIS (continued)

increase during degradation with increasing degradation. Therefore, at a given site, if all of the TCE parent compound is from a single source, a plot of $\delta^{37}Cl$ vs $\delta^{13}C$ values along the groundwater flow path will result in a linear trend. This plot is called a Dual Isotope Plot and can be used to determine if multiple sources of the parent compound with different initial $\delta^{13}C$ and $\delta^{37}Cl$ values exist.

HAS TCE DEGRADED?

The ideal basis for interpreting CSIA results would be the isotopic ratio ($\delta^{13}C$) of the parent contaminant of concern released at the site before it has been degraded. In practice, however, the $\delta^{13}C$ value of the original contaminant released at the site is rarely known so other approaches are used. When the original $\delta^{13}C$ value of parent compound at the site is unknown, published literature values (as noted above) of the manufactured compound can be used as an approximation.

The Microbial Insights CSIA Database includes compilations of published $\delta^{13}C$ values for many contaminants and graphing functions for straightforward data interpretation as shown below.



Select Parent Compound: TCE was the parent compound released at this site. Literature $\delta^{13}C$ values for manufactured TCE range from a minimum of -33.40‰ to a maximum of -23.20‰ as shown in the red shaded area in the plot above. Since $\delta^{13}C$ of TCE increases as it is degraded, the "highest" published $\delta^{13}C$ for manufactured TCE (-23.20‰) is used as a conservative estimate of the $\delta^{13}C$ of the original TCE release. Applying a safety factor of an additional 2‰ to account for uncertainty (blue shading), a TCE $\delta^{13}C$ value greater than -21.20‰ (= -23.20‰ + 2‰) is conclusive evidence of degradation.

Decision: The $\delta^{13}C$ values for TCE at MW-11 (-21.1‰), MW-6 (-20.2‰), and MW-7 (-16.9‰) **conclusively** demonstrate that TCE degradation has occurred. For the other monitoring wells (within the shaded regions), TCE degradation may or may not have occurred. For a more complete discussion of how CSIA results can be used to demonstrate biodegradation of TCE and daughter products, please see the case study titled "CSIA - Are TCE and Daughter Products Degrading?".

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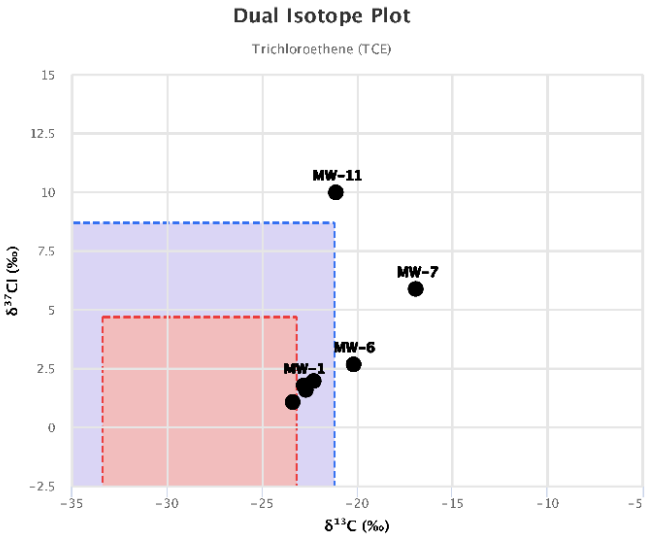
ARE THERE MULTIPLE SOURCES OF TCE?

As shown in the previous section, CSIA of one isotope (carbon) is usually sufficient to conclusively determine whether degradation has occurred. To delineate multiple contaminant sources, however, MI recommends analyzing both carbon ($\delta^{13}C$) and chlorine ($\delta^{37}Cl$) isotopes and using the **Microbial Insights CSIA Database** to construct a **Dual Isotope Plot** as shown below.



TCE was the parent compound released at this site. Therefore, the width of the red box along the x-axis of the Dual Isotope Plot represents the range of published $\delta^{13}C$ values for manufactured TCE. Similarly, the height of the red box along the y-axis represents the range of $\delta^{37}Cl$ values of manufactured TCE. The blue box adds a safety factor of 2‰ for $\delta^{13}C$ and 4‰ for $\delta^{37}Cl$ to account for uncertainty. Sample results greater than this blue box indicate degradation of the compound (MW-11, MW-6, and MW-7).

Single Source: In a Dual Isotope Plot, consistent degradation of the parent compound from a single source to downgradient wells will result in a linear trend as both $\delta^{13}C$ and $\delta^{37}Cl$ increase along the groundwater flow path. If the target compound is not degrading, the results will form a cluster.

Multiple Sources: There is a wide range of $\delta^{13}C$ and $\delta^{37}Cl$ values for pure, manufactured compounds (red box). For this reason, two different contaminant sources can have differing coordinates on a Dual Isotope Plot. If both sources are experiencing degradation over time or down gradient, this can result in two distinct linear trends.

In this case, the CSIA results appear to form a general linear trend for all monitoring wells except MW-11 which seems to be an outlier.

Decision: While multiple lines of evidence including a thorough characterization of subsurface hydrogeology are needed to conclusively demonstrate multiple contaminant sources, the CSIA results suggested that TCE at MW-11 may be from different source.

CSIA and MI CSIA Database:
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KEY BENEFITS

- **Source Delineation:** In conjunction with other lines of evidence, the CSIA results and Dual Isotope Plot suggested the presence of a second TCE source.
- **Conclusive:** CSIA results **conclusively** demonstrated that degradation of TCE had occurred.
- **Informative:** The Microbial Insights CSIA Database has custom graphing capabilities to aid interpretation and the manufactured range and enrichment factors from the literature complied into easy to use tables.

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