microbialinsights

CSIA and MI CSIA Database:
Are TCE and Daughter Products Degrading

PROJECT SUMMARY

- Stakeholders at a TCE-impacted site were concerned about elevated cis-DCE and vinyl chloride concentrations relative to ethene.
- Site managers needed to conclusively determine whether these daughter products were degrading.
- Compound specific isotope analysis (CSIA) was able to prove that degradation of TCE, cis-DCE, and vinyl chloride had occurred at several locations.
- With evidence of daughter product degradation, stakeholders were more confident with the current treatment strategy and site managers continued groundwater monitoring. CSIA and QuantArray®-Chlor were included in subsequent sampling events for multiple lines of evidence.

PROJECT CHALLENGE

At a trichloroethene (TCE) impacted site which had undergone enhanced bioremediation, stakeholders were concerned about high concentrations of daughter products cis-DCE and vinyl chloride compared to ethene production. Therefore, site managers needed to confirm TCE degradation and conclusively determine whether degradation of its daughter products, cis-DCE, and vinyl chloride, had also occurred at the site.

SAMPLING AND ANALYSIS

Compound specific isotope analysis (CSIA) was performed to conclusively determine whether TCE and daughter products were biodegrading. CSIA measures the ratio of stable isotopes (e.g. $^{13}C/^{12}C$) of a contaminant. During degradation of many contaminants, the ratio of these stable isotopes changes in predictable ways, whereas physical processes like dilution do not appreciably impact isotope ratios. During degradation, the chemical bonds with the lighter ^{12}C isotope are slightly weaker than those with the heavier ^{13}C isotope and react more readily resulting in isotopic fractionation. Therefore, during degradation the $^{13}C/^{12}C$ of the remaining contaminant which has not yet degraded increases. This isotopic fractionation (specifically significant increases in $\delta^{13}C$ values) conclusively demonstrates degradation of the contaminant.

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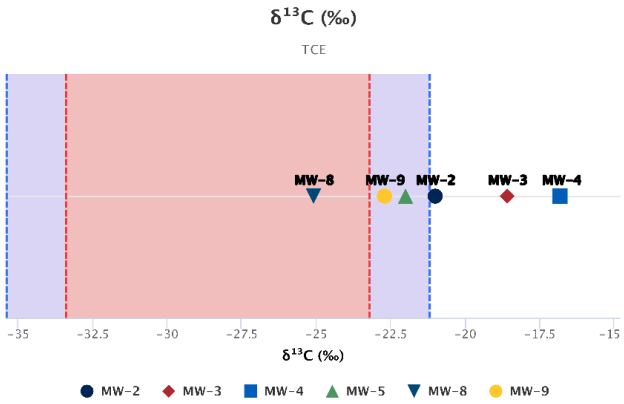
HAS TCE DEGRADED?

The ideal basis for interpreting CSIA results would be a comparison to the $\delta^{13}C$ value of the parent compound 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.

Time or Location Approach: If the $\delta^{13}C$ value of a contaminant increases by at least 2‰ over time in a given well or along the groundwater flow path, it is conclusive evidence that the compound has degraded. For an example of monitoring $\delta^{13}C$ values over time, see the case study: CSIA for Performance Evaluation.

Literature Value Approach: Published literature values of the $\delta^{13}C$ of manufactured compound can be used as a benchmark to evaluate degradation. Any time that a compound's $\delta^{13}C$ value is more than 2‰ greater than manufactured range, it is **conclusive** evidence of degradation. 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 for the site discussed here.



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. 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.

So has TCE degraded at this site?: The $\delta^{13}C$ values for TCE at MW-2 (-21.0‰), MW-3 (-18.6‰), and MW-4D (-16.8‰) **conclusively** demonstrate that TCE degradation has occurred. For the other monitoring wells (within the shaded regions), TCE degradation may or may not have occurred. CSIA cannot prove a negative. Remember we do not know the $\delta^{13}C$ value of the manufactured TCE released at this site. So we use the highest reported manufactured value + uncertainty to be conservative in our assessment.

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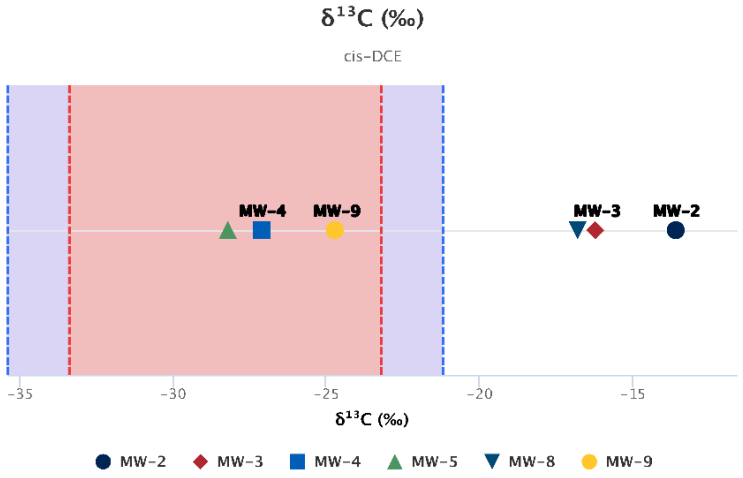
HAS CIS-DCE DEGRADED?

Often, the most important question at a site impacted by TCE is whether the daughter products like cis-DCE and vinyl chloride have also degrading. The carbon and chlorine atoms that make up these daughter products come from the original parent contaminant on the site. Remember that during degradation of TCE, the chemical bonds with the lighter ^{12}C isotope are slightly weaker than those with the heavier ^{13}C isotope and react more readily resulting in isotopic fractionation. Therefore, as discussed above, the $^{13}C/^{12}C$ ratio and $\delta^{13}C$ value for remaining contaminant TCE increase as degradation proceeds. But the $^{13}C/^{12}C$ ratio and $\delta^{13}C$ value for the daughter product cis-DCE are initially lower that the TCE parent since more ^{12}C bonds are cleaved that ^{13}C bonds. If the cis-DCE is also degrading its $^{13}C/^{12}C$ ratio and $\delta^{13}C$ value will then start to increase. This confuses interpretation until the $^{13}C/^{12}C$ ratio and $\delta^{13}C$ values for cis-DCE exceed those of the conservative estimate of the $\delta^{13}C$ value of the TCE parent compound. When this is observed we can conclusively demonstrate cis-DCE degradation. Since TCE was the parent compound released at this site, the $\delta^{13}C$ of manufactured TCE is the benchmark. As detailed previously, the highest $\delta^{13}C$ value for manufactured TCE is -23.20‰. Thus, with a safety factor of an additional 2‰, any cis-DCE $\delta^{13}C$ values greater than -21.20‰ are **conclusive** evidence of degradation of cis-DCE.



So has cis-DCE been degraded?: The $\delta^{13}C$ values for cis-DCE at MW-2 (-13.6‰), MW-8 (-16.8‰), and MW-3 (-16.2‰) are **conclusive** evidence of degradation. Although significant isotopic fractionation was not observed for cis-DCE at the other monitoring wells, it is important to remember that cis-DCE degradation may well be occurring. The cis-DCE $\delta^{13}C$ may still be low at these locations due to continued cis-DCE production from reductive dechlorination of TCE. Remember the cis-DCE produced from dechlorination of TCE is "lighter" (lower $\delta^{13}C$) than the parent but then gets "heavier" (higher $\delta^{13}C$) when it degrades eventually getting heavier (higher $\delta^{13}C$) than the original parent compound if degradation proceeds sufficiently.

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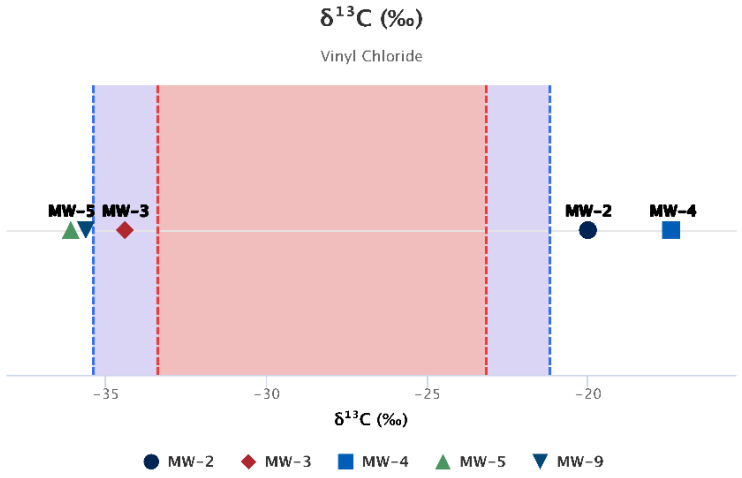
HAS VINYL CHLORIDE DEGRADED?

Like cis-DCE, vinyl chloride will initially be lighter than its parent compound (cis-DCE) then get heavier as it degrades. Once again though we can only conclusively say vinyl chloride was degraded when its $\delta^{13}C$ exceeds a conservative estimate of the original parent compound (TCE) at the site + uncertainty. As shown below, the $\delta^{13}C$ of vinyl chloride at MW-2 (-20.0‰) and MW-4 (-17.4‰) were more than 2‰ greater than the highest published $\delta^{13}C$ value for manufactured TCE (-23.20‰) demonstrating that vinyl chloride degradation has occurred. For the other monitoring wells, vinyl chloride may or may not be degrading.



Why are the $\delta^{13}C$ values for vinyl chloride at MW-5, MW-9, and MW-3 so low? Remember, TCE becomes enriched in ^{13}C (increasing $\delta^{13}C$) as it degrades while its daughter product cis-DCE is initially very depleted in the heavy isotope (has very low $\delta^{13}C$). Likewise, as cis-DCE degrades, its $\delta^{13}C$ will increase and its daughter product vinyl chloride will initially have a very low $\delta^{13}C$ value. Degradation of the ^{13}C depleted pool of cis-DCE results in an even more ^{13}C depleted pool of vinyl chloride. Thus very low $\delta^{13}C$ values for vinyl chloride are possible. As we have noted though the $\delta^{13}C$ of vinyl chloride will eventually increase as it in turn degrades.

So has vinyl chloride been degraded?: Vinyl chloride detected at MW-2 and MW-4D has degraded. For monitoring wells MW-3, MW-5, and MW-9, vinyl chloride may or may not be degrading. For subsequent sampling events, site managers decided to also submit samples for QuantArray-Chlor quantification of *Dehalococcoides* and functional genes such as vinyl chloride reductase (VCR) as an additional line of evidence to assess the potential for vinyl chloride degradation.

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KEY BENEFITS

- **Conclusive:** CSIA results **conclusively** demonstrated that TCE, cis-DCE, and vinyl chloride degradation had occurred at several locations.
- **Saved Money:** Based in part on CSIA results, site managers decided to continue monitoring rather than initiate additional injection of electron donor. QuantArray-Chlor quantification of *Dehalococcoides* and functional genes such as vinyl chloride reductase (VCR) was added to provide multiple lines of evidence for degradation of the daughter products cis-DCE and vinyl chloride.

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