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CSIA: For Performance Evaluation

PROJECT SUMMARY

- Stakeholders at a TCE-impacted site required conclusive evidence of degradation of TCE and daughter products. Compound specific isotope analysis (CSIA) was performed during site assessment to determine whether degradation of TCE and cis-DCE was occurring under existing site conditions.
- CSIA indicated that degradation of TCE or daughter products could not be conclusively demonstrated. Therefore, enhanced degradation through injection of an electron donor was selected as a treatment strategy.
- Comparison of CSIA results pre- and post-injection of the electron donor conclusively demonstrated TCE, cis-DCE, and vinyl chloride degradation was stimulated in response to electron donor addition.

PROJECT CHALLENGE

At a former industrial facility, groundwater was impacted by historical releases of trichloroethene (TCE). Redox conditions were anaerobic, and some daughter products were detected. Site managers wanted to (1) conclusively determine whether biodegradation of TCE and cis-DCE was occurring under existing conditions, (2) assess the need for enhanced remediation, and (3) if necessary, evaluate the effectiveness of any enhanced remediation activities.

SAMPLING AND ANALYSIS

Compound specific isotope analysis (CSIA) was performed to conclusively determine whether TCE and daughter products were degrading under existing conditions and to evaluate remedy performance. CSIA measures the ratio of stable isotopes (e.g. $^{13}C/^{12}C$) 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, 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 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 to assess CSIA results for conclusive evidence of degradation.

Time or Location Approach: If the $\delta^{13}C$ value of a contaminant increases by at least 2‰ (measurement uncertainty) over time in a given well or along the groundwater flow path, it is **conclusive** evidence that the compound has degraded.

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 in the example below for TCE.

Microbial Insights CSIA Database

Manufactured Range

Compound	Isotope	Min (‰)	Max (‰)	Mean (‰)	Range	n
Trichloroethene (TCE)	$\delta^{13}C$	-33.40	-23.20	-29.13	10.20	29

Conservative $\delta^{13}C_{source}$ based on Published Values	=	"Highest" $\delta^{13}C$ of Manufactured (non-degraded) TCE	+	Safety Factor of an Additional 2‰
-21.20‰	=	-23.20‰	+	2‰

$\delta^{13}C_{source}$ Estimation Approach: With a good knowledge of site history and hydrogeology, $\delta^{13}C$ of the parent compound can be estimated based on values measured in monitoring wells within the known source area. If the $\delta^{13}C$ value of a contaminant increases over this value by at least 2‰ along the groundwater flow path, it is significant and conclusive evidence of that the compound has degraded.

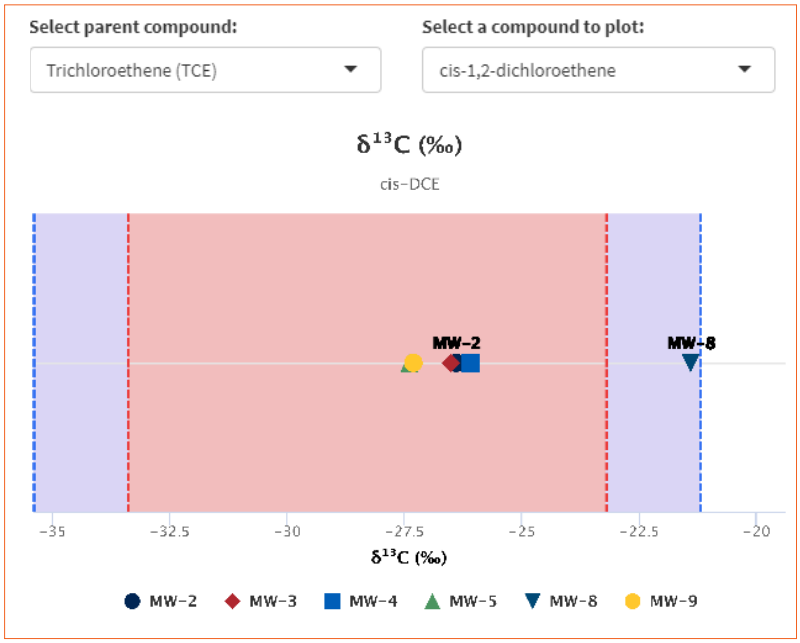
Most Negative Approach: Since degradation causes an increase in $\delta^{13}C$ values, the lowest (or most negative) $\delta^{13}C$ value detected at the site is sometimes used as an estimate of $\delta^{13}C_{source}$.

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 under existing conditions? A baseline assessment of TCE $\delta^{13}C$ values at the site showed all values to be < -21.20‰. Therefore, TCE may or may not have occurred. If TCE degradation has occurred at the site under existing conditions, degradation has not proceeded sufficiently to be detected by CSIA given the uncertainty in $\delta^{13}C_{source}$.

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 degraded at the site under existing conditions? 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.

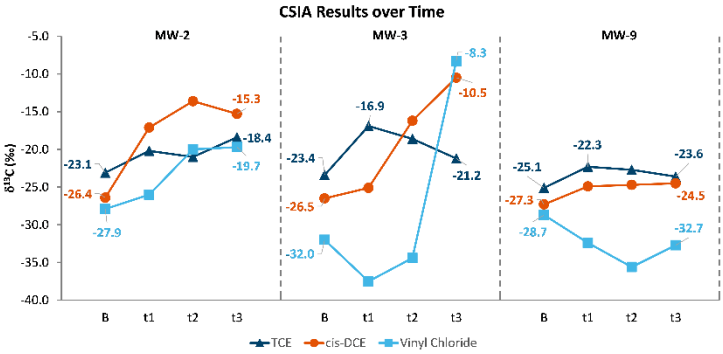
Although very close for MW-8, the $\delta^{13}C$ values for cis-DCE detected at the selected monitoring wells was not significantly greater than the range of manufactured TCE published in the literature. Although significant isotopic fractionation was not observed, it is important to remember that cis-DCE degradation may 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.

HAS CIS-DCE DEGRADED? (continued)

Decision: Without conclusive evidence of TCE or cis-DCE degradation under existing site conditions, site managers selected enhanced bioremediation as the corrective action. CSIA results from the site assessment then served as a baseline to evaluate the effectiveness of electron donor injection. Remember that a stimulation in degradation of TCE or daughter products will be indicated by an increase in the $\delta^{13}C$ values of more than 2‰.

PERFORMANCE EVALUATION

CSIA can conclusively prove whether degradation has occurred making it a powerful tool for evaluating remedy performance. The figure below shows $\delta^{13}C$ values for TCE and daughter products cis-DCE and vinyl chloride detected at three monitoring wells during site assessment/baseline sampling (B) and three sampling events (t1-t3) following injection of an electron donor.



MW-2: The $\delta^{13}C$ values for TCE (dark blue triangles), cis-DCE (orange circles), and vinyl chloride (light blue squares) all increased by more than 2‰ from the baseline sampling event and TCE benchmark (-21.20‰) demonstrating degradation of TCE and each daughter product following electron donor addition.

MW-3: For TCE, the $\delta^{13}C$ value increased by more than 2‰ from baseline (-23.4‰) and TCE benchmark (-21.20‰) demonstrating degradation had occurred. However, TCE $\delta^{13}C$ values decreased following time t1 (-16.9‰) to t3 (-21.2‰) possibly due to back diffusion of non-degraded TCE (more negative $\delta^{13}C$) from a less permeable zone. The cis-DCE $\delta^{13}C$ values increased significantly demonstrating biodegradation had occurred. For vinyl chloride, the $\delta^{13}C$ results initially decreased as would be expected. By time t3 though, the vinyl chloride $\delta^{13}C$ had increased to -8.3‰ conclusively demonstrating vinyl chloride degradation.

MW-9: The overall response to electron donor addition was less striking at MW-9 than at the other wells. After an initial increase, the TCE $\delta^{13}C$ value at t3 was not significantly greater than observed during the baseline event. However, the $\delta^{13}C$ value of cis-DCE did increase from B (-27.3‰) to t3 (-24.5‰) demonstrating degradation. For vinyl chloride, $\delta^{13}C$ values after injection were lower than baseline. While not demonstrating vinyl chloride degradation, the decrease in vinyl chloride $\delta^{13}C$ is consistent with cis-DCE degradation.

PERFORMANCE EVALUATION (continued)

Decision: Success – Electron donor addition significantly enhanced biodegradation of TCE and daughter products at monitoring wells MW-2 and MW-3. As a supporting line of evidence, site managers will incorporate QuantArray-Chlor quantification of *Dehalococcoides* and other halorespiring bacteria into future sampling events.

KEY BENEFITS

- **Actionable:** In conjunction with other lines of evidence, the CSIA results indicated that enhanced remediation was warranted.
- **Conclusive:** CSIA results conclusively demonstrated enhanced biodegradation of TCE, cis-DCE, and vinyl chloride in response to electron donor addition.
- **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.

LAB LOCATIONS

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735 Griffith Court, Burlington Ontario, L7L 5R9

Microbial Insights (Australia), c/o AGRF Ltd
Plant Genomics Centre, Hartley Grove, Urrbrae SA 5064, Australia

Microbial Insights Europe, c/o Avecom
Industrieweg 122P, B-9032 Wondelgem, Belgium

Microbial Insights Europe (Germany), c/o Sensatec
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Microbial Insights China, Xiuying Li (cell# 13204027102)
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