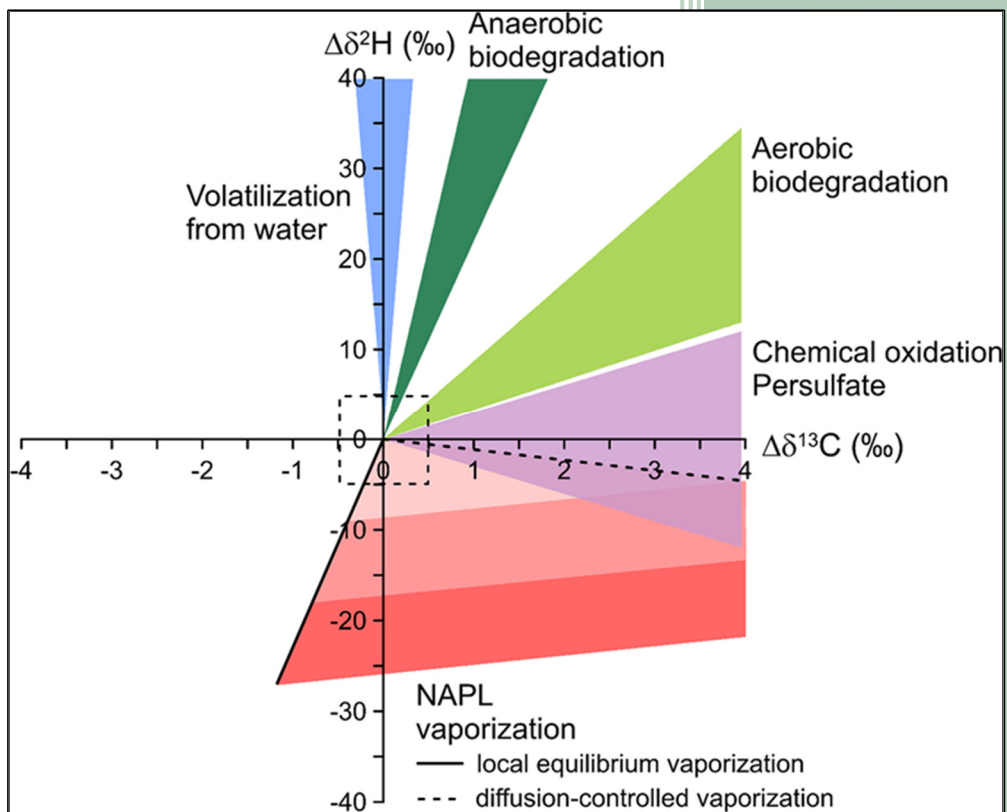


Compound-Specific Isotope Analysis (CSIA)

Environmental Forensics & Performance Monitoring



Bouchard, Daniel, Daniel Hunkeler, Eugene L. Madsen, Tim Buscheck, Eric Daniels, Ravi Kolhatkar, Christopher M. DeRito, Ramon Aravena, and Neil Thomson. "Application of Diagnostic Tools to Evaluate Remediation Performance at Petroleum Hydrocarbon-Impacted Sites." *Ground Water Monitoring & Remediation* 38, no. 4 (Fall 2018): 88–98.

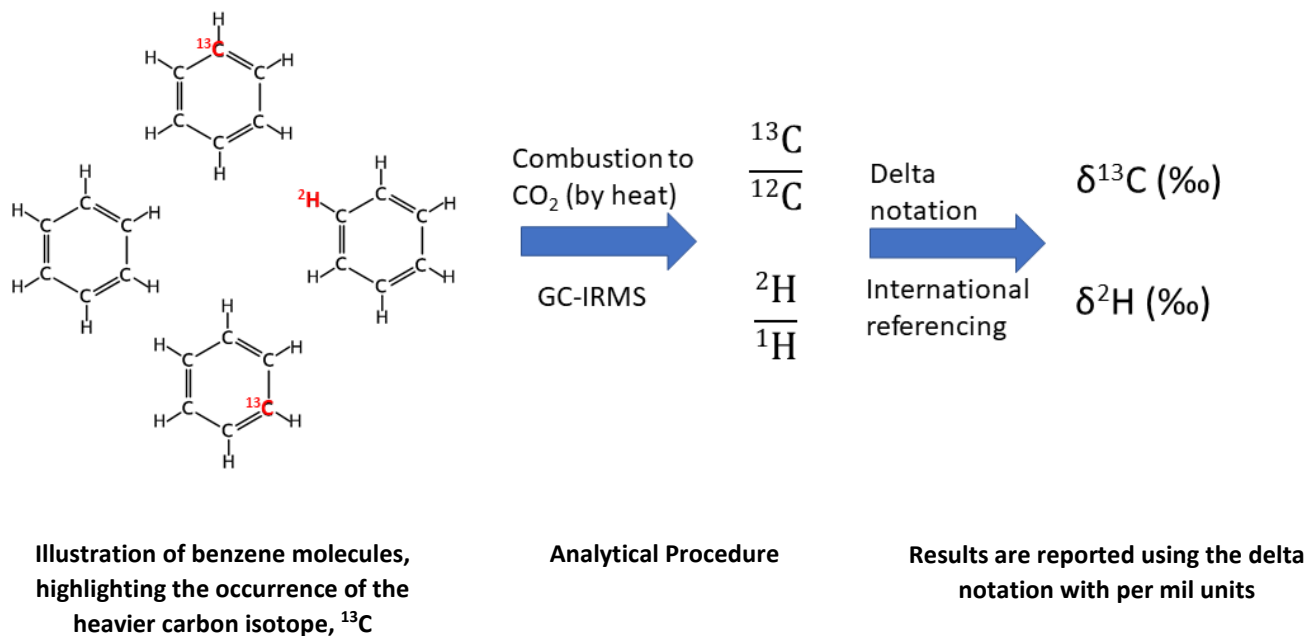
WHAT IS CSIA?

Compound-specific isotope analysis (CSIA) measures isotope ratios (e.g., $^{13}\text{C}/^{12}\text{C}$, $^2\text{H}/^1\text{H}$, $^{37}\text{Cl}/^{35}\text{Cl}$) of individual elements, typically of those in volatile and semi-volatile compounds of concern within environmental samples. This powerful tool is used to verify the in situ degradation of volatile organic compounds (VOCs), conduct forensic investigations to distinguish sources, assess the extent of degradation, track plume commingling, and determine chemical origins.

CSIA offers insights beyond concentration data. For example, CSIA can quantitatively differentiate extent of either abiotic or biotic degradation pathways. It can also provide direct evidence of biodegradation processes by tracing an element from origin to final fate. Typically, practitioners incorporate CSIA to distinguish pollutant sources, evaluate the performance of a remediation event, and support monitored natural attenuation (MNA) at contaminated sites.

HOW DOES IT WORK?

Many elements have naturally occurring stable isotopes. In nature, carbon, chlorine, and hydrogen exist in both light (^{12}C , ^{35}Cl , ^1H) and heavy (^{13}C , ^{37}Cl , ^2H) forms at specific ratios. CSIA can measure these isotope ratios for VOCs and results are reported using an international reference system. Because results are an exceedingly small number, the ratio is multiplied by one thousand and expressed in “per mil” (‰) units.



WHAT ARE THE TARGETED CONTAMINANTS?

CSIA is an ideal tool for small molecules such as:

- BTEX, MTBE
- Chlorinated solvents

Certain CSIA objectives are possible with other compounds:

- Chlorobenzenes, ETBE
- Carbon Tetrachloride, chloroform
- Naphthalene
- <8 Carbon chain Alkanes, PH Gases
- 1,4 dioxane
- Sulfate, Nitrate, Water

FOR WHICH SAMPLING MATRIX?

- **Groundwater:** CSIA assessments are commonly carried out for VOCs dissolved in groundwater.
- **Gaseous phase:** With the advent of reliable gas-phase sampling devices, CSIA assessments can now be conducted for gas-phase VOCs, including soil gas, atmospheric air, and indoor air.
- **Soil:** Application of CSIA on soil cores remains less frequent for the moment.

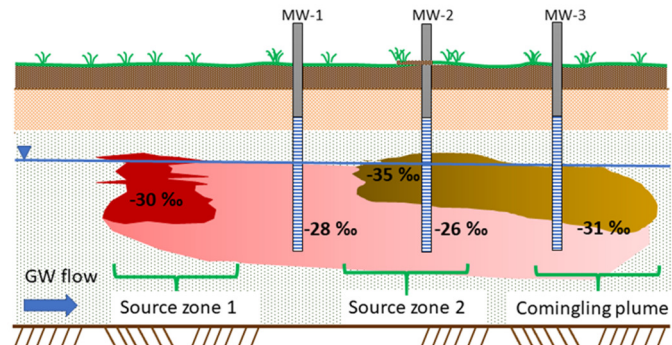
WHY USE CSIA?

Field practitioners leverage the naturally occurring isotopic signature to gain insights into the **origin** and **fate** of targeted organic contaminants.

Origin

Because diverse factors govern the synthesis of petroleum hydrocarbons or the manufacturing of chlorinated solvents, different $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$ and $\delta^2\text{H}$ distinguish a VOC. The isotopic ratio is thus the fingerprint of the contaminant. CSIA becomes a tool that can:

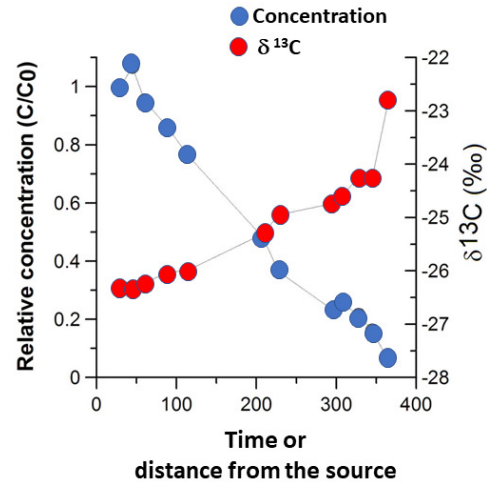
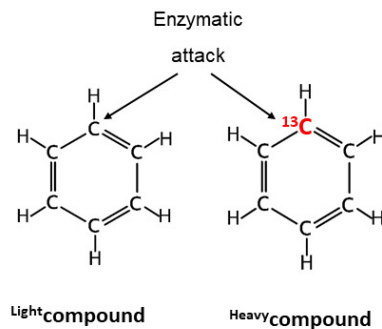
- Distinguish two sources of the same contaminant on a given site.
- Identify a contaminant coming from an off-site source located upgradient.
- Establish a link between an observed compound and its potential emitting source



Users should recognize that biological, chemical, and certain physical processes can alter isotope ratios over time and space. Interpreting CSIA data necessitates understanding how each process impacts the results and how the data can serve as evidence of biodegradation.

Fate

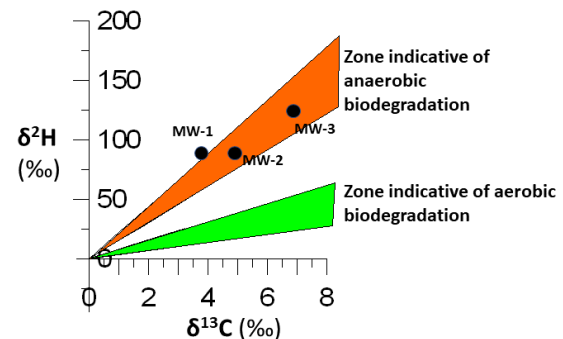
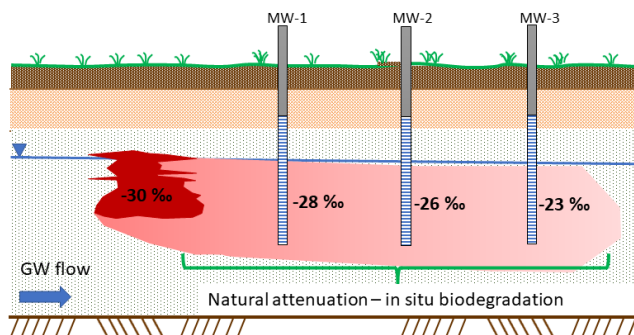
The most common use of CSIA is to demonstrate the presence of an active microbial population biodegrading organic contaminants dissolved in groundwater. The relative abundance of heavy isotopes in certain molecules (which we can simply refer to as heavy molecules) degrade more slowly compared to light molecules. Consequently, the remaining pool of contaminants becomes progressively enriched in heavy compounds, which is reflected by monitoring the relative abundance of ^{13}C and ^2H . The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values thus tend to shift toward more positive values.



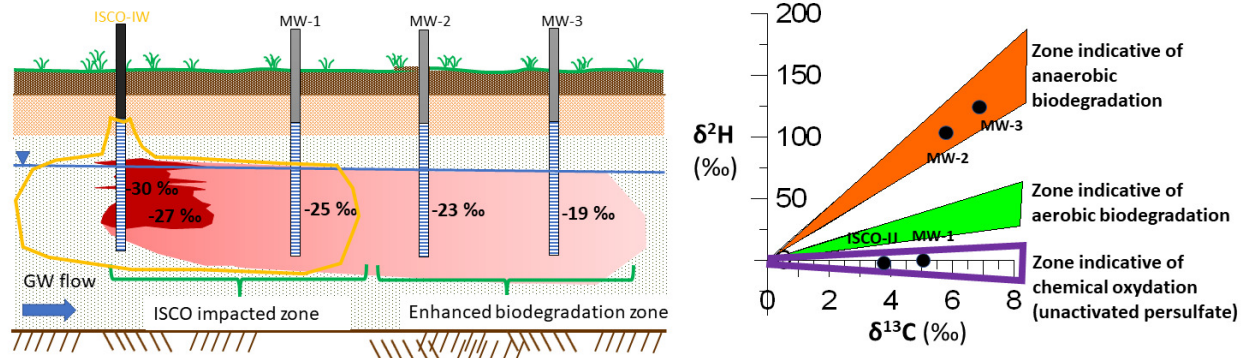
In a dynamic environment such as aquifers, isotope ratio evolution over time can be monitored to gain information on the processes affecting the fate of targeted VOCs. This assessment can be framed in the context of a monitored natural attenuation (MNA) program, or to evaluate the performance of a remediation treatment.

During MNA, CSIA can present three types of lines of evidence:

1. Demonstrating contaminant mass destruction (versus dilution)
2. Direct evidence of type of microbial activity on the contaminant
3. Evaluate biodegradation rates (independent of concentration data)



In addition to the impacts on isotope ratios due to biodegradation, recent studies have shown that positive and negative shifts in $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$, and $\delta^2\text{H}$ values can occur due to certain physical and chemical processes induced during remediation. By analyzing the observed isotopic signature trends, a dominant physical or chemical removal process can be distinguished from other processes affecting the compound.



Whether a remediation project is pilot- or full-scale, CSIA is useful to validate if the intended mass removal process has been initiated by the treatment. Here are some CSIA applications as a function of remediation treatment:

Remediation Approach	Uncertainties Addressed by CSIA
Permeable Reactive Barrier	<ul style="list-style-type: none"> • Answer if all VOCs being impacted by the PRB • Help validate if the PRB's thickness or amendment density is adequate • Identify weak points within the barrier
<i>In Situ</i> Chemical Oxidation (ISCO)	<ul style="list-style-type: none"> • If VOC are destroyed or simply diluted • If the chemical dose is sufficient • Quantify destroyed VOC mass • If biodegradation is established following oxidant injections • If anaerobic biodegradation is establishing following injections
Air Sparging/SVE	<ul style="list-style-type: none"> • What process dominates, volatilization or biodegradation • If the aquifer switches to aerobic biodegradation conditions • If the SVE system reached its efficiency limit (diffusion-limited mass removal as opposed to direct air-NAPL partitioning)
Reductive Dechlorination	<ul style="list-style-type: none"> • If PCE is entirely degrading to ethene • If DCE or VC degradation is occurring • If heterogeneity is impacting a uniform remediation

The Tersus team is available to evaluate how CSIA can be strategically implemented in your project.

EVALUATING MASS DISCHARGE AND MASS FLUX

IsoFLUX is a passive sampler device capable of measuring groundwater and contaminant mass flux, in addition to CSIA. This innovative tool verifies changes in mass flux, *in situ* degradation rate constants, and obtains essential parameters for plume modeling over time and space. It is a critical risk assessment tool that enhances predictions of groundwater pollutant impacts on drinking water wells and surface waters.

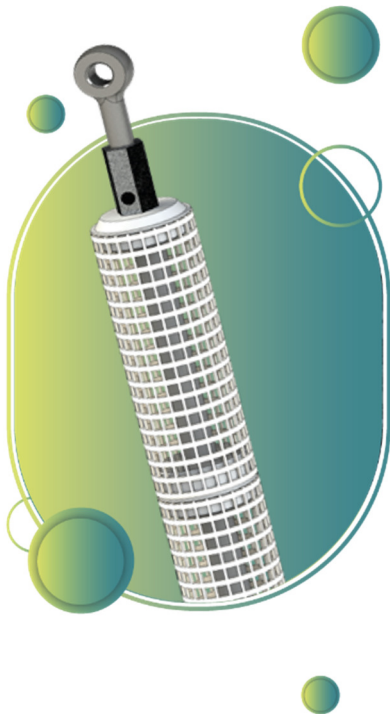
Beyond degradation evaluations, identifying contaminant contributions from different sources is crucial for cost-effective remediation. IsoFLUX assesses flux from multiple sources, serving as a forensic tool to distinguish pollutant origins and associated mass discharge towards sensitive receptors.



www.iFLUX.be/sampler

Benefits of IsoFLUX

- IsoFLUX enhances risk assessment by providing more reliable predictions of how groundwater pollutants affect receptors over time. Unlike conventional groundwater measurements, IsoFLUX offers deeper insights into pollutant migration and degradation, thereby improving the protection of our vital drinking water resources.
- IsoFLUX assesses contaminant flux from multiple sources, serving as a forensic tool to identify and differentiate pollutant origins. By quantifying mass-flux contributions, it supports informed remedial cost allocation.
- IsoFLUX samplers deliver highly sensitive and precise flux measurements incorporating CSIA of groundwater pollutants like chlorinated solvents (CVOs) and PFAS. Laboratory tests demonstrate superior isotope analysis with significantly lower detection limits compared to conventional sampling methods.



CSIA ADVANTAGES AND LIMITATIONS

CSIA is a relatively recent technique for assessing remediation performance, offering significant advantages over traditional methods:

- Provides compound-specific information
- Differentiates between dilution and contaminant mass destruction or removal. VOC concentration changes do not affect $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values, and uniform concentrations do not necessarily indicate lack of contaminant destruction.
- Applicable to both source and downgradient zones within the contaminant plume(s).
- Simple implementation—sampling requires standard groundwater or iFLUX sampler procedures.
- Enhances pilot-scale insights to improve large-scale treatment design.
- Isotope shifts over time validate remediation progress and success.
- CSIA helps remediation managers determine if treatment adjustments are needed.
- CSIA validates transitioning to MNA or site closure.

SERVICES OFFERED

Tersus provides CSIA support to help remediation practitioners effectively incorporate this analytical method into their projects. Whether CSIA is used to identify sources, demonstrate natural attenuation, or evaluate remediation treatment performance, the Tersus Team offers valuable assistance.

- Site data review to evaluate site-specific CSIA application
- Develop assessment strategies
- Deployment assistance (i.e., field work for sampling, etc.)
- Data interpretation & reporting
- Discussion platform and recommendations

SUGGESTED PUBLICATIONS TO LEARN MORE

Hunkeler D., Meckenstock, R.U., Lollar, B., Schmidt, T.C., Wilson, J.T.. A Guide for Assessing Biodegradation and Source Identification of Organic Groundwater Contaminants Using Compound

Specific Isotope Analysis (CSIA). U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-08/148, 2009. <https://clu-in.org/download/contaminantfocus/vi/A%20Guide%20for%20Assessing%20Biodegradation.pdf>

ITRC. Compound Specific Isotope Analysis. EMD Team Fact Sheet—November 2011 https://www.itrcweb.org/Documents/team_emd/CSIA_Fact_Sheet.pdf

Aelion, C.M., Höhener, P., Hunkeler, D., Aravena, R. Environmental Isotopes in Biodegradation and Bioremediation. 2009. CRC Press. 464 Pages, 1st Edition. ISBN 9781566706612.

Bouchard, D., Hunkeler, D., Madsen, E.L., Buscheck, T., Daniels, E., Kolhatkar, R., DeRito, C.M., Aravena, R., Thomson, N. Application of Diagnostic Tools to Evaluate Remediation Performance at Petroleum Hydrocarbon-Impacted Sites. 2018. GWMR, vol 38, issue 4, 88-98.

Products & Services for *In Situ* Remediation

For Every Zone of Your Plume, We've Got You Covered!

1

Vadose Zone

- *In-Situ* Chemical Oxidation (ISCO)
- *In Situ* Chemical Reduction (ISCR)

2

Source Zone

- Surfactant-Enhanced Aquifer Remediation (SEAR)
- *In-Situ* Chemical Oxidation (ISCO)
- *In Situ* Chemical Reduction (ISCR)

3

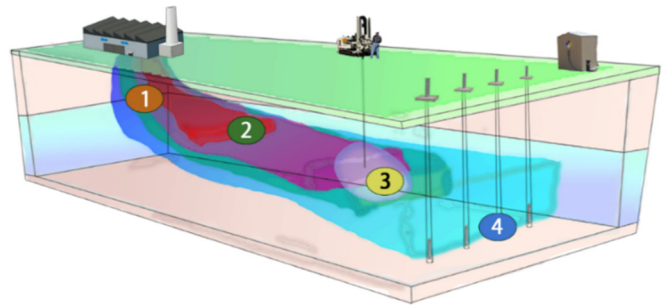
Dissolved Phase

- *In-Situ* Chemical Oxidation (ISCO)
- *In Situ* Chemical Reduction (ISCR)
- *Carbon-Based Injectates (CBI)* for *In Situ* Sorption and Bioremediation
- Anaerobic Oxidative Biostimulation
- Anaerobic Reductive Bioremediation
- Bioaugmentation

4

Leading Edge

- Aerobic Biostimulation
- Aerobic Bioaugmentation



Professional Services

- Contaminant Mass Flux Measurements
- Environmental Forensics
- Performance Monitoring Plans

Field Services

- Treatability Studies
- Deployment Assistance
- Turn-key Services

REQUEST A SITE EVALUATION AND COST ESTIMATE

If you have a project and need a remediation solution, visit tersusenv.com/support and complete the Site Evaluation Form. Our team will then reach out to offer options that best suit your goals.



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