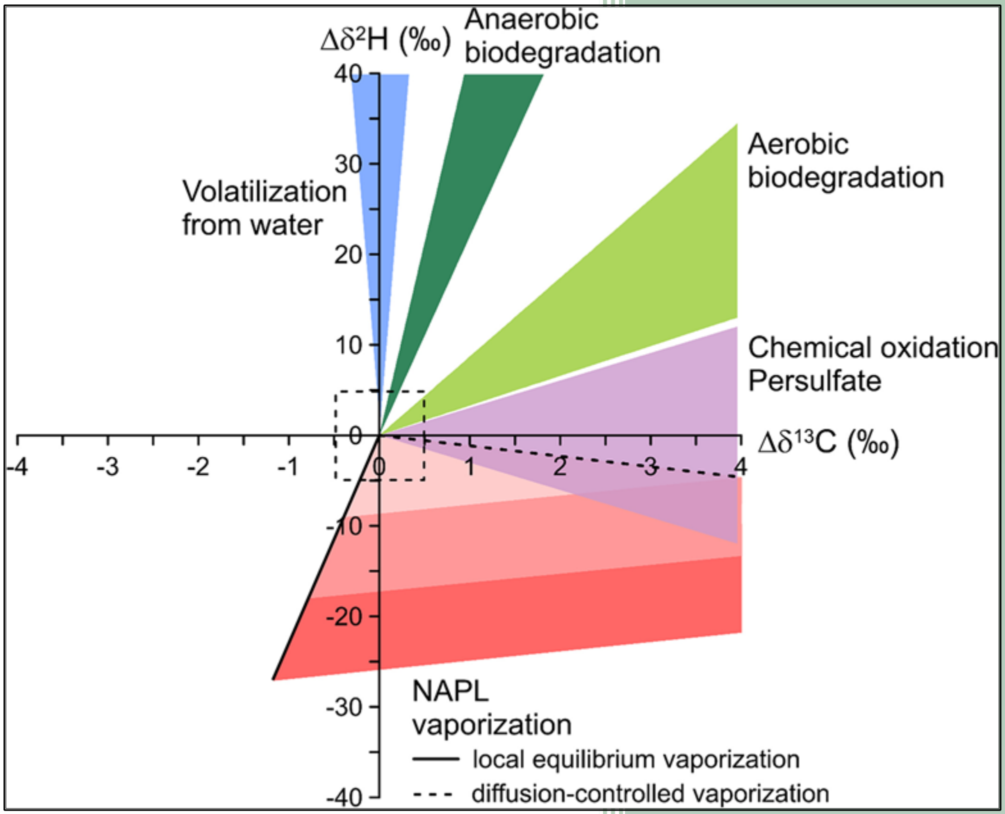
Environmental Forensics & Performance Monitoring



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Tersus Environmental
919.453.5577 • info@tersusenv.com
tersusenv.com

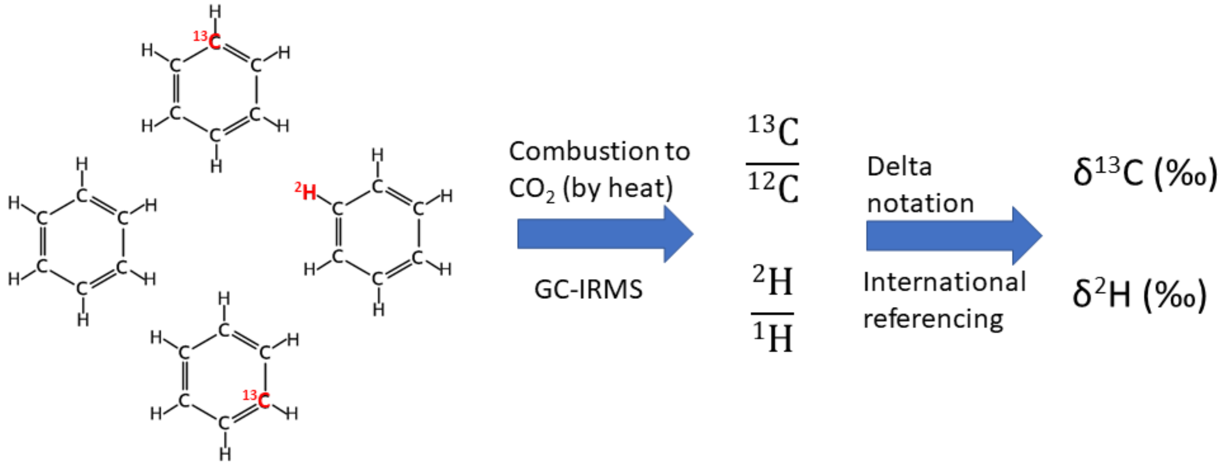
WHAT IS CSIA?

Compound-specific isotope analysis (CSIA) refers to the measurement of the isotope ratios (e.g., 13C/12C, 2H/1H, or 37Cl/35Cl) of individual volatile and semi-volatile compounds extracted from in environmental samples. This characterization tool can be used for demonstrating *in situ* destruction of selected VOC and for forensic investigations to gain information about potential contaminant sources, the extent of degradation, comingling of contaminant plumes, and the origins of some chemicals.

This powerful tool can reveal information that cannot be gained by from evaluation of concentration data. CSIA provides a quantitative means to differentiate reaction pathways for abiotic and biotic degradation. It can provide information biodegradation pathways and may serve as a basis for identification of distinct pollutant sources. CSIA can provide evidence for monitored natural attenuation of sites contaminated with a wide variety of pollutants.

HOW DOES IT WORK?

Many atoms have a heavier counter partner naturally occurring in nature. Since the C, Cl and H atoms pool in nature is composed of light isotopes (12C, 35Cl and 1H) and heavy isotopes (13C, 37Cl and 2H) in different proportions heavy to light, occurrence of one heavy isotope is hence expected within the constitution of some organic molecules. The 13C/12C and 2H/1H isotope ratios for each VOC of interest included in a mixture can be measured and reported accordingly to an international referencing system. The final ratio is finally multiplied by 1000 to avoid reporting very small fractions, hence making the units in per mil. i.e., ‰.



WHAT ARE THE TARGETED CONTAMINANTS?

For several mechanistic reasons, CSIA is a tool adapted for small molecular size VOCs such as:

- BTEX
- MTBE
- Chlorinated solvents

With some restrictions, additional VOCs can be addressed within some defined and site-specific objectives:

- Chlorobenzene
- Naphthalene
- ETBE
- 1,4 dioxane
- Alkanes < C8

FOR WHICH SAMPLING MATRIX?

- **Groundwater:** CSIA assessments are commonly carried out for VOCs dissolved in groundwater.
- **Gaseous phase:** With the recent development of reliable gas-phase sampling devices, CSIA assessments can also be performed for gas-phase VOC (such as soil-gas, atmospheric or indoor air).
- **Soil:** Application of CSIA on soil cores remains less frequent for the moment, as research studies yet remain scarce.

WHY USE CSIA?

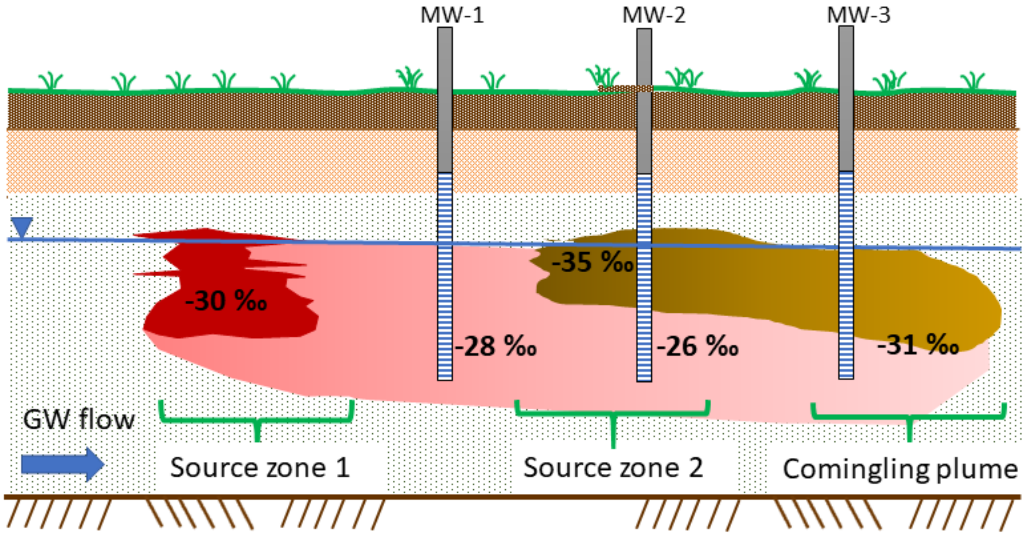
Field practitioners are taking advantage of this naturally occurring confection default of the atom to gain insight on the ***origin*** and ***fate*** of targeted organic contaminants.

ORIGIN

The isotopic ratio is the fingerprint of the contaminant. Because several diverse factors govern the synthesis of petroleum hydrocarbons or the manufacturing of chlorinated solvents, different δ13C, δ37Cl and δ2H signature for the same VOC coming from a different synthesis\manufacturing process will be obtained. A substantial advantage of this non uniformity is that the isotopic ratio can serve as a fingerprint once the product reached the commercial level. This translates into a tool that can:

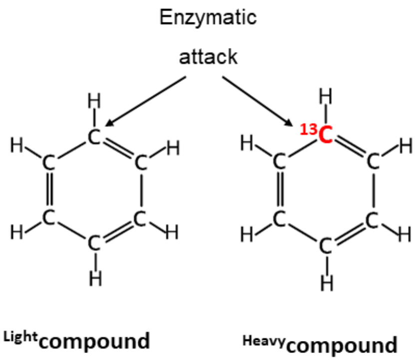
- Distinguish 2 sources of the same contaminant on a given site.
- Identify a contaminant coming from an off-site source located upgradient.
- Establish a link between an observed compound and its potential emitting source

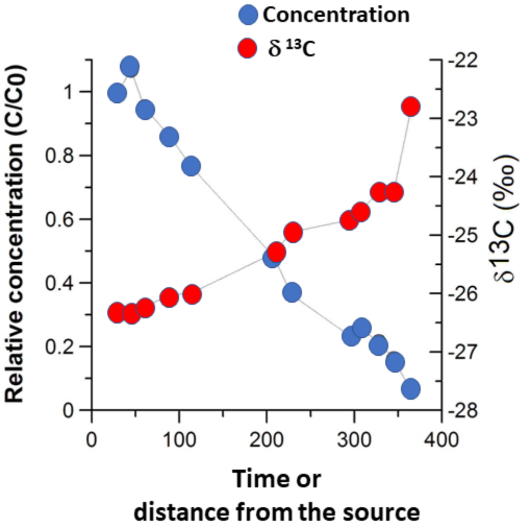
Nonetheless, the user must be aware that biological, chemical and some physical processes can change the isotope ratio. Therefore, sound, and comprehensive interpretation shall be made with the CSIA results, for which the conclusions can be considered as an additional line of evidence in the assessment.



FATE

The most common use of CSIA is to demonstrate an active microbial population biodegrading the organic contaminant dissolved in groundwater. Due to the presence of a heavy isotope in the molecules (Heavy molecules), the latter are more slowly degraded compared to Light molecules. Consequently, the remaining pool of contaminant progressively gets enriched in Heavy compounds, which is reflected by monitoring δ13C and δ2H values shifting toward more positive values.

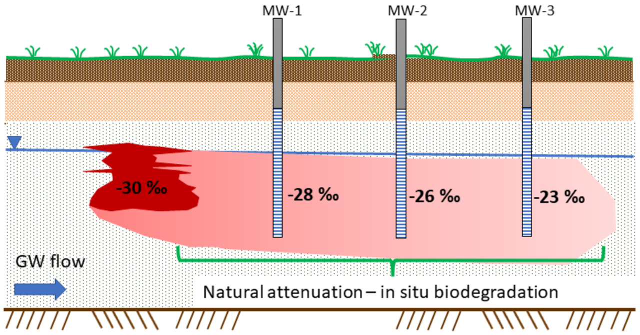


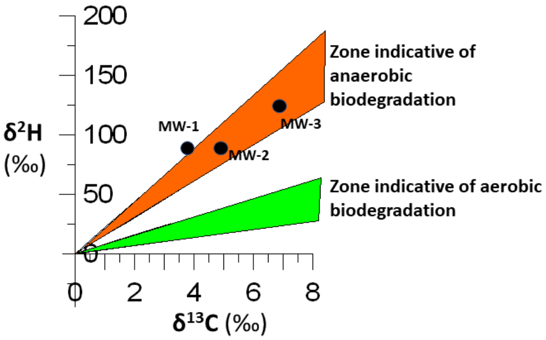


In a dynamic environment such as aquifers, isotope ratio evolution over time can be monitored to gain information on the processes affecting the fate of targeted VOC. This tracking assessment can be performed in the frame of a monitored natural attenuation (MNA) program, or during the application of a remediation treatment.

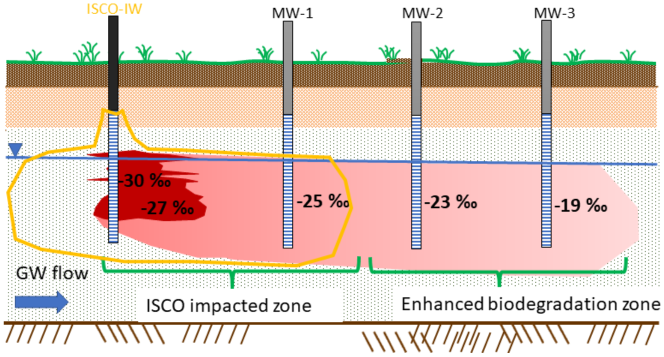
The benefits of applying CSIA in a MNA program are numerous. The tool can fulfil three lines of evidence to demonstrate natural attenuation of contaminants in the system:

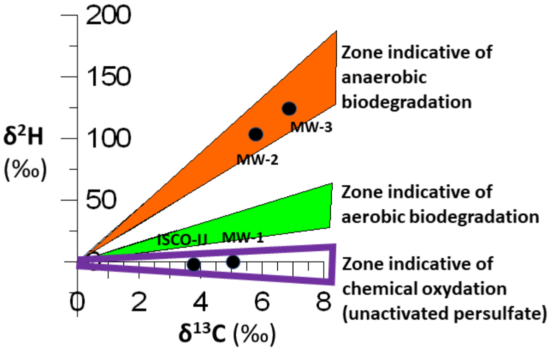
1. Demonstrate destruction of contaminant mass
2. Direct and unequivocal evidence of microbial activity
3. Evaluate the rate of biodegradation independently of concentration data





Beside biodegradation, recent studies have shown that positive and negative shifts in the δ13C, δ37Cl and δ2H values can be created by some physical and chemical removal processes induced by remediation treatments. According to the specific trend observed, a dominant physical or chemical removal process can thus be distinguished from another physical removal process or biological destruction of the compound.





Whether you are at conducting pilot scale or large-scale treatment, CSIA can be a valuable tool to validate if the intended mass removal process is initiated by the treatment. Here are some application suggestions for selected remediation treatments:

Remediation treatment	Uncertainties addressed by CSIA
Permeable reactive barrier	• Are all VOCs destroyed or going through unaffected? Confirming thickness of the wall and/or ZVI proportion • Any weak points along the barrier?
ISCO treatment	• Are VOC destroyed or just diluted due to injection volumes? • Was the chemical dosing sufficient? • How much VOC mass was destroyed by the given injected chemical? • Is aerobic biodegradation establishing following injections of H_2O_2 or persulfate? • Is anaerobic biodegradation establishing following injections persulfate (induced by produced SO_4)?
Air sparging/SVE	• Are VOCs preferentially volatilized or biodegraded? • Is the aquifer switching to aerobic biodegradation conditions? • Did the SVE system reached its limits of efficiency (diffusion-limited mass removal instead of direct air-NAPL partitioning)?
Bio-augmentation (chlorinated solvents)	• Is PCE entirely degraded to ethene? • Any DCE or VC stall? • Any local heterogeneity on the site?

We our available to assist you in evaluating how CSIA can be strategically implemented to your site-specific remediation design.

CSIA ADVANTAGES AND LIMITATIONS

The use of CSIA to assess performance of remediation treatment is quite recent and offers substantial advantages compared to traditional approaches:

- Gain of information on single compound
- Distinguish dilution from contaminant mass removal process. VOC concentration dilution due to fluid addition does not affect the δ13C and δ2H values
- Can be applied on site regardless of the treated zone (source or plume zone)
- Application simplicity: CSIA sampling procedure follows the SOP for VOC concentration analysis. The only need is to sample additional 40 ml glass vials.
- Deepen the knowledge gained during pilot scale efforts to further help dimensioning large scale treatment.
- The isotope shift over time validate remediation progress and/or success.
- Support remediation manager’s decision in whether the treatment needs timely adjustment.

SERVICES OFFERED

Our goal is to provide you the CSIA expertise you need to effectively implement CSIA on your site. Whether the assessment concern forensics, natural attenuation or remediation treatment performance, our Team can offer valuable support. These services include:

- Site data review to evaluate site-specific CSIA application, combined or not with other molecular tools (such as functional gene assays)
- Establishment of the assessment strategy
- Support with sampling requirements
- Data interpretation & reporting
- Discussion platform and recommendations

Is CSIA the right solution for your project? Have questions or want to explore some ideas? Contact Us to learn how we can put together a money saving program to get your project over the finish line. If you currently have a project and need a remediation solution, scan the code to the right or visit tersusenv.com/support and supply us with the appropriate site information by selecting the option that best suits your schedule and needs. Our online form will guide you as to what sort of information we need. Don't worry if you don't have all the information we ask for. We will contact you to confirm details.

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

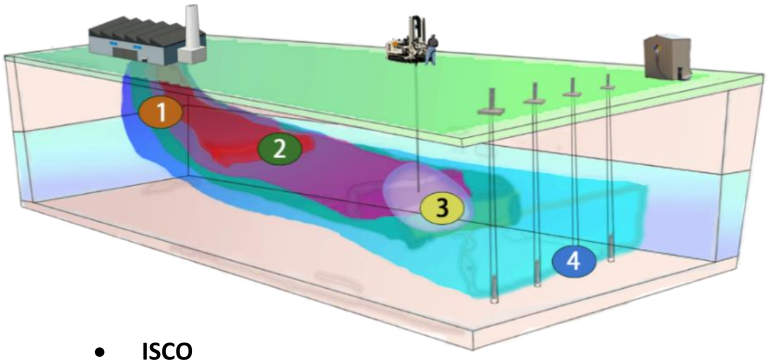
ITRC. Compound Specific Isotope Analysis. EMD Team Fact Sheet—November 2011 https://www.itrcweb.org/Documents/team_emd/CSIA_Fact_Sheet.pdf

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)**
  Modulated TersOx™ Liquid
- ***In Situ* Chemical Reduction (ISCR)**
  Microscale ZVI Suspensions

2 Source Zone

- **Surfactant-Enhanced Aquifer Remediation (SEAR)**
  TASK™ (Tersus Advanced Surface Kinetics)
- **ISCO**
  Modulated TersOx™ Liquid
- **ISCR**
  Microscale ZVI Suspensions

3 Dissolved Phase

- ***In Situ* Sorption and Biodegradation**
  NutriBind®
- **ISCR**
  Microscale ZVI Suspensions
  Iron Sulfide Reagent (ISR)
- **Anaerobic Reductive Bioremediation**
  Emulsified Vegetable Oils (EVO): *EDS-ER™* and *EDS-Advanced™*
  EVO Emulsifiers: *TASK™ MicroEVO™ Self-Emulsifier*
  Soluble electron donors: *EDS-QR™* and *Nutrimens®*
- **Anaerobic Reductive Bioremediation (Continued)**
  Nutrients: *Nutrimens®* and *TersOx™ Nutrients*
  Vitamin B_{12} supplement for *Dhc*
  Bioaugmentation: *KB-1®* culture and anoxic media *KB-1®* Primer
- **Anaerobic Oxidative Bioremediation**
  Nutrisulfate®
- **ISCO**
  Modulated TersOx™ Liquid

4 Leading Edge

- **Aerobic Bioremediation**
  Oxygen-releasing chemistries (*TersOx™*)
  TersOx™ Nutrients (Slow Release, Quit Release, and Custom Formulations)
  Oxygen delivery systems (*Waterloo Emitter™)*
  TersOx™ Microbe

Sales and Technical Support

For every zone of your plume, we've got you covered!

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