

A large, light green graphic element on the left side of the page, consisting of a thick, curved line that starts from the bottom left and curves upwards and to the right. A smaller, teal-colored line loops around a black dot at the top left, resembling a stylized orbit or a path.

*Pace Analytical*<sup>®</sup>

# *CSIA Fundamentals and Application Guide*



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# Compound Specific Isotope Analysis

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# Fundamentals of CSIA

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Several elements including carbon, hydrogen, chlorine, nitrogen, sulfur and oxygen have more than one stable isotopic form, which when incorporated into compounds of environmental interest provide a means of characterization that contains information both about the compounds source and about any degradation of that compound. It is often possible to isolate a compound (at concentrations as low as 5 PPB) and measure the abundance of those isotopes and to express that abundance as an isotopic composition. This isotopic composition has a predictable range and varies within that range as a function of its source, including raw materials and the process used to make it. Additionally, when the compound is degraded, the isotopic composition changes predictably in a process called fractionation. These two attributes of the isotopic composition provide a means to distinguish between different sources of the contaminant and to more definitively characterize the processes of remediation.

PAES has developed the capability to measure the isotopic composition of each of these elements in a variety of contaminants. CSIA provides insights for remediation and forensic investigations that were previously not available to environmental scientists. The following isotopic compositions can be determined by Pace:

## Carbon Isotopic Composition

- Establish unequivocal evidence of degradation vs. dilution
- Identify the mechanism of degradation
- Measure the fraction of compound degraded
- Calculate the first order rate of degradation

## Carbon and Chlorine Isotopic Composition

- Provide environmental forensic evidence of multiple sources of chlorinated solvents using two isotopes
- Tap the power of analytical techniques which provide information both on forensics and on degradation

## Carbon and Hydrogen Isotopic Composition

- Provides the same power to hydrocarbon forensics that chlorine CSIA provides to chlorinated solvent forensics.
- Helps track changing degradation mechanisms across a site

## Hydrogen and Oxygen Isotopic Composition

- Distinguish the origin of water from different aquifers.

## Nitrogen and Oxygen Isotopic Composition

- Discern different sources of nitrate.

## Sulfur and Oxygen Isotopic Composition

- Detect different sources of sulfate
- Identify onset of sulfate reduction



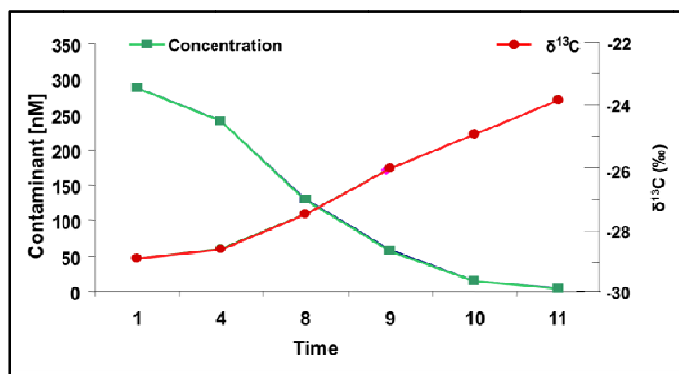
# CSIA Applications

## Contaminant Degradation (One-Dimensional CSIA)

Decreases in contaminant concentrations in groundwater may be attributed to dispersion, sorption, volatilization or degradation. Of these four natural attenuation processes, degradation is the only one that results in contaminant destruction. As contaminants degrade, their isotopic compositions change in a process known as fractionation. The result of this process is that the remaining contaminant is “enriched” in the heavier isotope. Measuring the isotopic composition of compounds of interest establishes that fractionation, and therefore degradation, has occurred.

In addition to providing unambiguous proof of contaminant degradation, CSIA can be a powerful tool for other remediation applications including:

- Identification of degradation mechanisms
- Determination of degradation rates
- Determination of the extent of degradation



**According to the USEPA, “isotopic fractionation unequivocally proves that contaminant degradation is occurring.”**

**CSIA determines the isotopic composition of compounds of concern to demonstrate isotopic fractionation.**

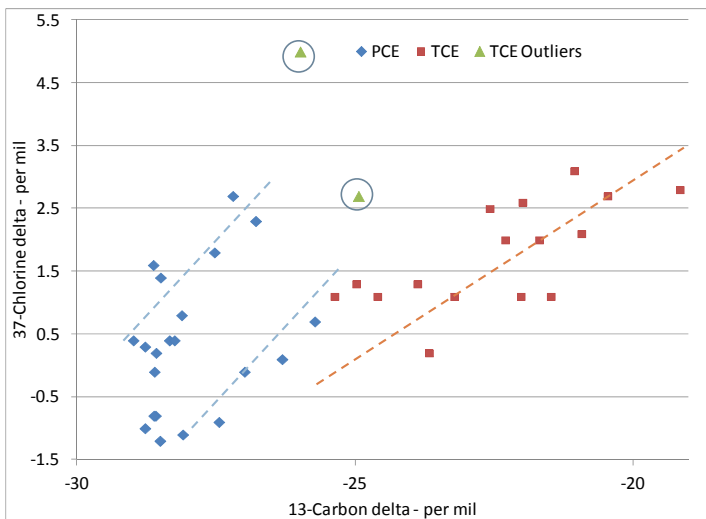
When CSIA data is integrated into reactive transport models, it can be a powerful tool for forecasting the extent and duration of contaminant plumes. Obtaining this information regarding the projected size and scope of the contaminant plume can significantly decrease monitoring and remediation costs.

This figure illustrates isotopic fractionation of a contaminant during degradation. Notice how the measure of the isotopic composition,  $\delta^{13}\text{C}$ , increases as the contaminant concentration decreases.

# CSIA Applications

## Establishing Multiple Sources (Multi-Dimensional CSIA)

The isotopic compositions of contaminants which are identical on a molecular basis, are often sufficiently unique to differentiate between them. When attempting to establish multiple sources of contamination, isotopic compositions for multiple elements (carbon and chlorine, for example) are plotted on a two dimensional graph. Generally, the isotopic compositions from the same source will cluster in a recognizable way. As you collect samples away from the suspected source area, the isotopic data from a single source will plot linearly.



The figure above is a graphical representation of carbon and chlorine isotopic compositions. The data suggests there are at least two distinct sources of PCE and one source for TCE.

Establishing multiple sources is invaluable for managing complex sites and determining financial responsibility for remediation. CSIA can be extremely useful for establishing multiple sources of:

- Chlorinated Solvents  
Carbon, Chlorine, & Hydrogen Isotopes
- Petroleum Hydrocarbons  
Carbon and Hydrogen Isotopes
- 1,4-Dioxane  
Carbon and Hydrogen Isotopes
- MTBE & Fuel Oxygenates  
Carbon and Hydrogen Isotopes

Other potential source evaluations using CSIA may include:

- Water
- Nitrate, Sulfate and other In-organics
- Select Semi-Volatile Organic Compounds



# CSIA Applications

## Vapor Intrusion Pathway Confirmation

Contaminants in groundwater plumes often enter the vadose zone and migrate to the surface. If at the surface these vadose zone vapors a slab on the underside of a building they may accumulate there. If the slab has permeability such as cracks or openings around plumbing, these vapors may “intrude” through the slab into the building where they may represent health and or safety issues to the occupants of the building. Many of these contaminants may also have potential indoor sources and thus it is often required to distinguish their origin to establish remedial responsibility.

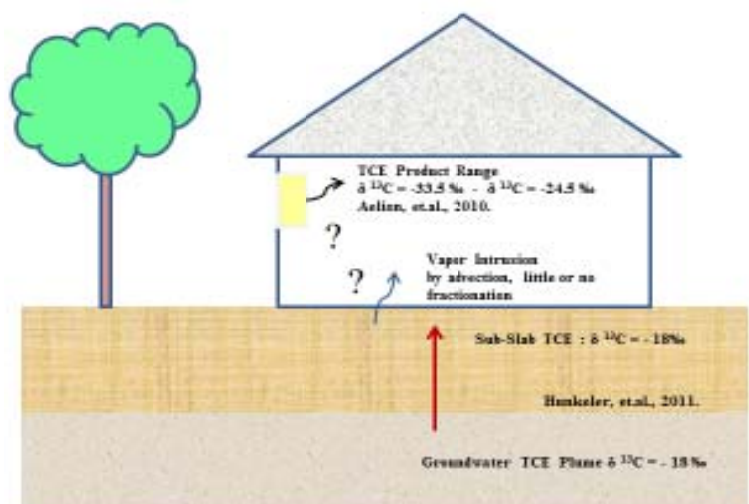
On a molecular basis TCE from vapor intrusion and an indoor source are identical and thus no source differentiation is possible. On an isotopic basis however, contaminants from a groundwater plume are often isotopically distinct from their manufactured range due to fractionation. Isotopic composition is therefore potentially indicative of vapor intrusion vs. an indoor source.

The CSIA solution for vapor intrusion may be applicable to:

- Chlorinated Solvents
- Petroleum Hydrocarbons
- 1,4-Dioxane
- MTBE

Compound Specific Isotope Analysis  
can differentiate between  
vapor intrusion and indoor sources!

The figure below represents a building above a groundwater plume of TCE which has degraded and has an isotopic composition of  $-18\text{‰}$ . It has been shown that there is no fractionation during migration through the vadose zone, therefore the subslab composition is also  $-18\text{‰}$ . If vapor intrusion occurs, the indoor air composition will be the same as subslab. The range of isotopic composition of manufactured TCE is  $-24.5\text{‰}$  to  $-33.5\text{‰}$ , and thus isotopic composition will be very capable of distinguishing VI and an indoor source.



# CSIA Applications

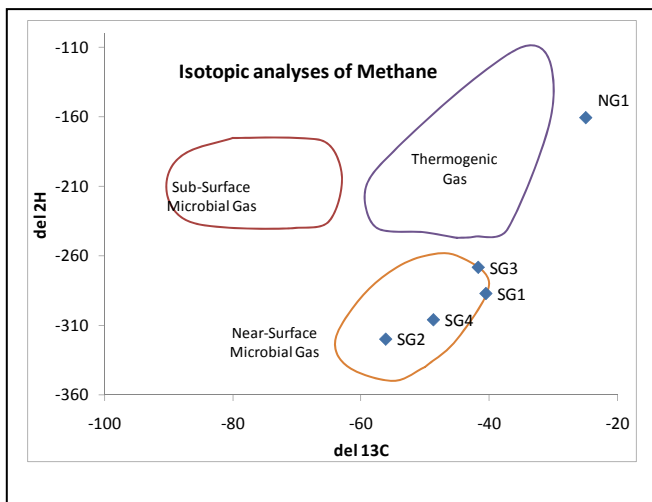
## Methane Source Identification

The origin of methane usually occurs by three different mechanisms, two of which are biogenic and one is thermogenic. The biogenic sources are acetogenesis in the near surface and reduction of carbon dioxide in the deep subsurface. The thermogenic source occurs by the thermal breakdown of organic material which experiences high temperatures at depth. Biogenic sources usually exhibit high (> 1000) methane to ethane ratios, while thermogenic sources are generally < 500. The extremes of compositional ratios often leave little doubt as to the origin, however these sources also have unique isotopic compositions which are generally viewed as the “gold standard” to resolve otherwise ambiguous cases.

**Methane source identification is a scientifically sound technique that mitigates risk for everyone.**

**CSIA identification of elevated methane is expected to become widely adopted and already required by some states.**

The figure below shows soil gas methane/ethane ratios of four biogenic soil gas samples vs. 1 thermogenic natural gas sample. This is an example where concentration ratios leave little doubt as to the origin of the methane.



Sample ID	Methane/Ethane Ratio
SG1	13,913
SG2	43,206
SG3	20,000
SG4	46,111
NG1	28

The means to evaluate the isotopic signatures of methane was developed by Schoelle, et. al. from methane compositions of known origin. The carbon and hydrogen isotopic compositions of the samples in the above example are plotted on this figure and demonstrate that the soil gas samples are of microbial origin, whereas the natural gas sample is of thermogenic origin.