

Frequently Asked Questions for CSIA

This guide is intended to be a brief overview for users of CSIA who have not worked with CSIA previously. While we have strived for technical accuracy and have tried to include all of the pros and cons of CSIA data, this is by no means an exhaustive treatise. It is also important to remember that for the sake of brevity this document focuses on CSIA of carbon. Many of the principles discussed here apply to isotopes of hydrogen and chlorine as well, but they are not the focus of this document. The interested reader is encouraged to pursue further reading. The USEPA has published "A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis" (EPA 600/R-08/148). This and several other very good resources are available at www.pacelabs.com.

What are isotopes?

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What are isotopes?

Neutrons are very important to atomic physicists, but for geochemical purposes they function mainly as spectators. They contribute mass but have no charge and have almost no effect on the chemistry of the atom. For carbon, there are three isotopes that are commonly known. These three isotopes are pictured in Figure 1.

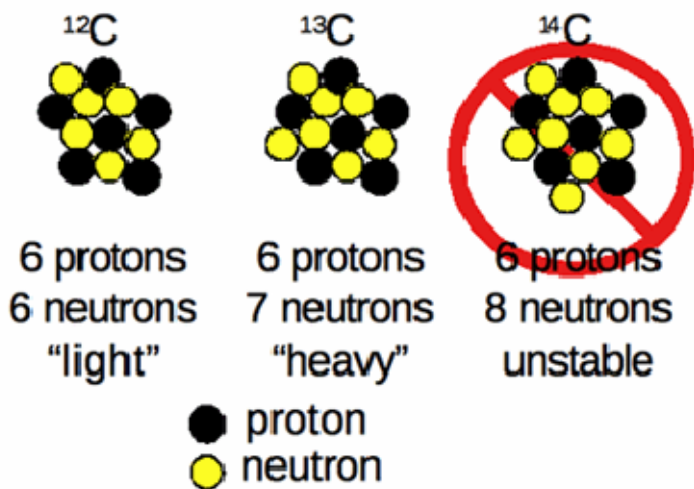


Figure 1. Isotopes of carbon

The lightest is ^{12}C , and we refer to it as the "light" isotope. This light isotope makes up over 99% of all carbon in the environment and has 6 protons (as all carbon does) and 6 neutrons. The "heavy" isotope is ^{13}C and it has 6 protons, 7 neutrons and makes up most, but not all, of the remaining carbon. There are heavier isotopes (a well known example is ^{14}C or "carbon 14") but they are unstable and subject to radioactive decay. CSIA uses only stable atoms, so we will only consider the light and heavy isotope.

Why are isotopes useful?

It takes a little less energy to break a bond between a light isotope and another atom than it takes to break a bond between a heavy isotope and that same atom. This leads to very slightly slower reaction rates for heavy isotopes compared to light isotopes, and this in turn leads to a pooling, or increased percentage of heavy isotopes in the reactants of a reaction that breaks a bond and a pooling of light isotopes in the products of that reaction. This is called isotopic fractionation. A somewhat exaggerated example of this is shown for a carbon-chlorine (C-Cl) bond in Figure 2.

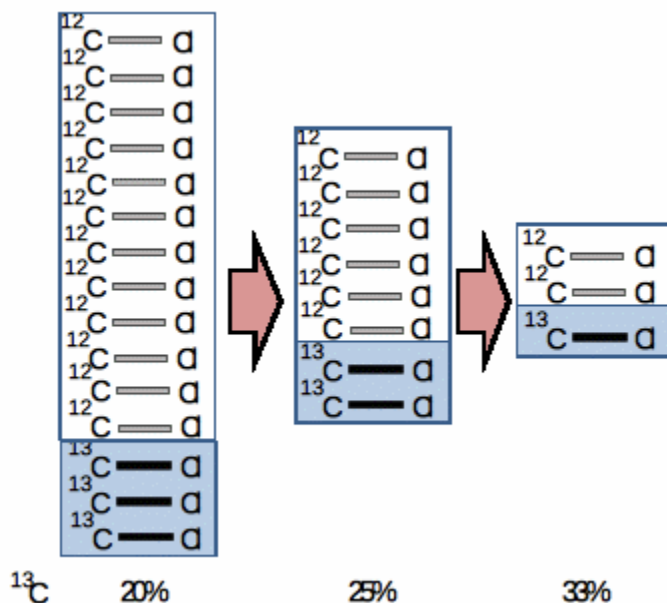


Figure 2. Pooling of heavy isotope (^{13}C) in unreacted compound

CSIA allows measurement of isotopic ratios, so by measuring the isotopic ratios in either the reactant or the product, you get an estimate of how far a particular reaction has progressed.

How are isotopes measured?

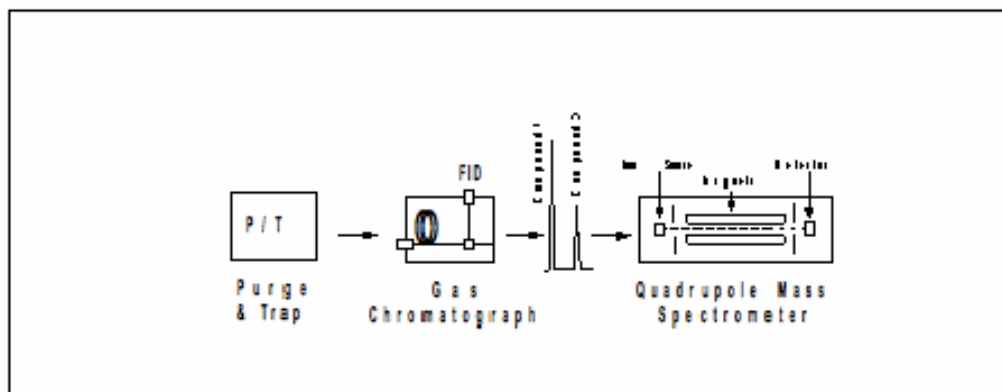


Figure 3. Instrumentation for a GCMS concentration analysis (for example, SW846-5030/8260)

In the most useful application of CSIA for VOC's of interest in environmental remediation, the instrumentation is formally similar to that for SW846-8260. The instrumentation, shown in Figure 4, is a GC/C/IRMS where "IRMS" stands for Isotope Ratio Mass Spectrometer and "C" stands for a combustion (oxidation) chamber which has been positioned between the GC and the IRMS.

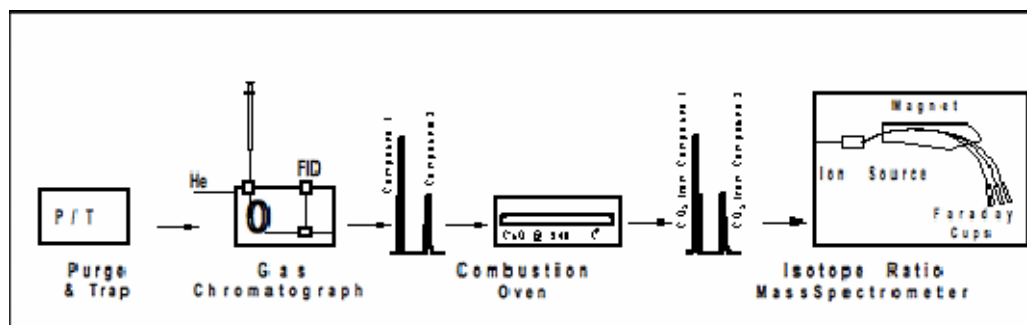


Figure 4. Instrumentation for CSIA

Ground water samples are purged, trapped and desorbed onto a modern GC analytical column where they are separated into discrete packets before exiting the column. At this point instead of directly entering a mass spectrometer to be broken into molecular ion fragments for analysis as in SW846-8260, each packet is passed through a chamber where the compound is thermally converted to carbon dioxide. Upon exiting that chamber, the carbon dioxide enters the IRMS for isotope analysis. Although the mass spectrometer for isotope measurements differs from the one used in SW846-8260, the process is formally similar.

CSIA is a very sensitive technique. Much is learned through the observation of small changes in the isotopic ratio. The isotopic ratio of carbon, that is $^{13}\text{C}/^{12}\text{C}$, is approximately 0.112. Rather than have to talk about important differences between 0.1127 and 0.1122, it is more convenient to express the ratios relative to some standard and in "per mil" notation. The standard is some isotopic ratio of an internationally agreed upon ratio, $R_{\text{std}} = 0.11292$. The formula, in "per mil" is: $\delta(^{13}\text{C})_x = 1000 \times R_x -$



RStdRStd where the Rx refers to the isotopic ratio of the sample and (^{13}C) is called "del" and is linearly related to the isotopic ratio. It is also important to note that for the purposes of VOC's there is no significance to the identity of the standard; "-24 per mil" means that in the sample the $^{13}\text{C}/^{12}\text{C}$ is 24 per mil, or 2.4 per cent, lower than in the standard.

What changes the isotopic ratio?

As we described above, changes in isotopic ratio are caused by the breaking of bonds. Dilution, diffusion and volatilization don't measurably change the isotopic ratio of VOC's in ground water. For an isotopic ratio to measurably change, a bond must be broken. For VOC's in ground water, that means degradation of a compound is the only significant cause of increasing dels for that compound.

What are some typical dels?

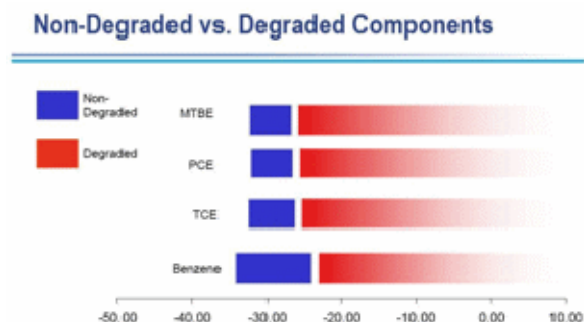


Figure 5. Some dels for typical VOC's and how those dels change with degradation

Figure 5 summarizes some typical dels and how degradation changes them. It can be seen from that figure that degradation increases the del of the unreacted fraction - the lighter fraction of it goes away first, leaving behind the heavier fraction. This increases the $^{13}\text{C}/^{12}\text{C}$ ratio, causing dels to become more positive - indeed, when the degradation is extensive, the dels can even become positive.

How do isotopic ratios compare to concentration?

Part of the power of CSIA lies in the fact that isotopic ratios are completely independent from concentration; this means that CSIA enables the practitioner to look at a site "from a new angle". This implies that by using both concentration and isotopic ratio information it is possible to answer questions that previously could not be answered about sources or fate and transport

What is the trend I might expect?

The trend really depends on the mechanism of degradation. Figure 6 presents the most typical causes for a change in the isotopic ratio, or δ , of VOC's in ground water.

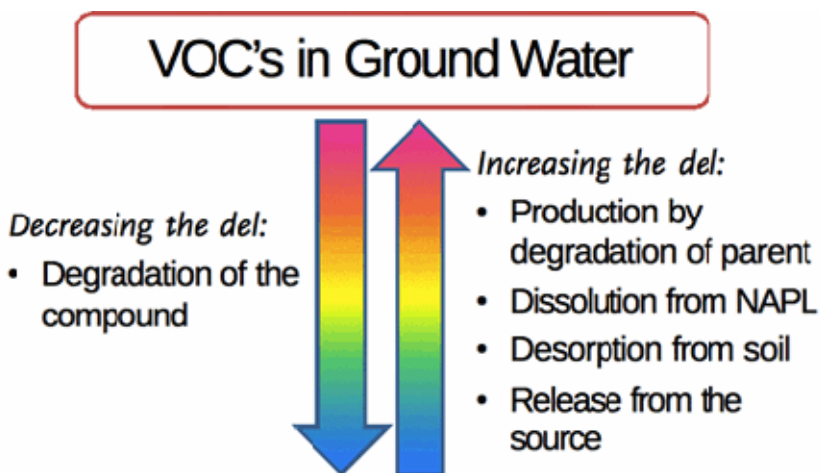


Figure 6. The most typical things to cause a change in the δ , or isotopic ratio, and the direction of that change

As we have said above, degradation causes the remaining VOC's to get heavier. So if you have a system where there is no longer a source, there is no NAPL and there is only degradation, then the situation is simple. The only thing that changes the δ is degradation and CSIA is a direct indicator of the extent of that degradation. That situation often describes MTBE releases or TCE co-metabolism. However, when there is a source, when there is NAPL, or when there is both degradation and production (as is the case with TCE at DNAPL sites where there is reductive dechlorination of both the PCE and the TCE) the situation is much more complex. At those sites CSIA can still be a very powerful tool, but qualitative interpretation is difficult (but possible and very useful) and quantitative interpretation requires sophisticated computer modeling of the fate and transport issues in models that include isotopic fractionation.

How should I interpret the data?

The qualitative trends are discussed above and are highlighted in the figures. However, the CSIA data is very powerful, so a detailed explanation of it must be done in light of the proposed fate and transport mechanisms (for example, is the degradation from reductive dechlorination or from ISCO? Was there ever a DNAPL source such that desorption could now be a major source? Is there an active pump and treat system driving the contaminant transport?). For several cases in which the proposed fate and transport mechanisms are known the use and interpretation of the CSIA data is detailed in the "Case Studies" document prepared by Microseeps, now part of Pace Analytical Energy Services. The case studies chosen for that document are intended to be a reflection of the most typically encountered problems that can be addressed with CSIA, but CSIA data can be used in many other ways as well. For questions about a particular scenario that is not covered in that document, please contact us.



Suggested Further Reading

The previously mentioned USEPA guide is an excellent source, and at 67 pages it is fairly approachable. Previous to the release of the EPA document, scientists at Microseeps produced a 36 page primer on CSIA that is available at the Pace Analytical website and is entitled "Compound Specific Isotope Analysis: the Science, Technology and Selected Examples from the Literature with Application to Fuel Oxygenates and Chlorinated Solvents". Production of that earned PAES scientists the privilege to work on the USEPA document and to be included in the acknowledgements. Another informative and very practical document is "CSIA Case Studies." The format is easy to read slides, designed for either printing or projecting, and the presentation is 26 slides long.