

## Stable Isotopes in Environmental Forensics and Remediation

### Introduction

Stable isotopes have been used in what has become known as environmental forensics since the 1990s to define sources of petroleum from spills, and the fate of chlorinated solvents in groundwater (Sturchio, et al., 2000<sup>1</sup>). Stable isotopes are naturally occurring elements that do not break down (i.e., are not radioactive) or have extremely long half lives. Examples of stable isotopes are <sup>2</sup>H (deuterium), <sup>13</sup>C, <sup>18</sup>O, <sup>15</sup>N, and <sup>37</sup>Cl.

Isotopes are expressed as ratios, where the two most abundant isotopes in a sample are compared to the same ratio in an international standard, using the 'delta' (δ) notation. Because the differences in ratios between the sample and standard are very small, they are expressed as parts per thousand or per mil (‰) deviation from the standard. The most commonly used isotopes in forensic studies include <sup>2</sup>H, <sup>13</sup>C and <sup>37</sup>Cl.

Presented below in Figure 1 is the range of <sup>13</sup>C values from natural sources. This can be used to differentiate organic carbon from multiple sources.

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<sup>1</sup> Sturchio, N. C., L. Heraty, B. D. Holt, L. Huang, T. Abrajano, and G. Smith (2000) *Stable Isotope Diagnostics of Chlorinated Solvent Behavior in Contaminated Aquifers*. Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 22-25, 2000, Monterey, CA.

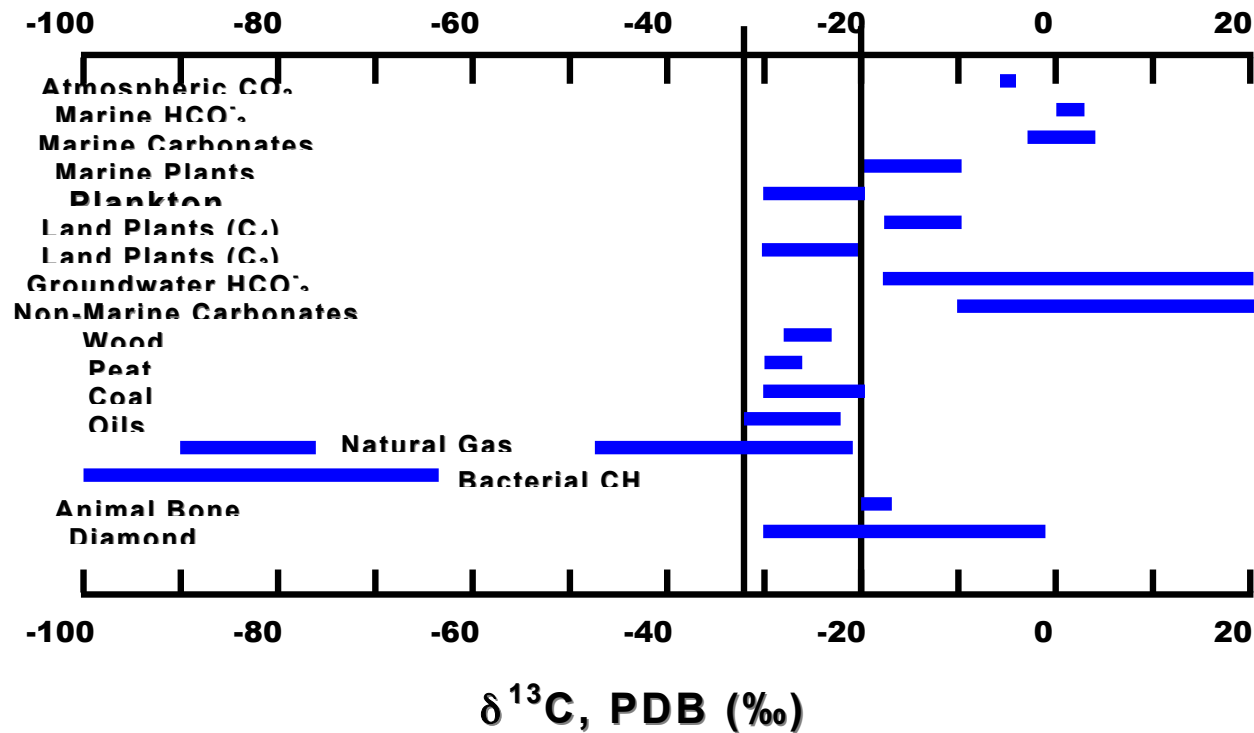
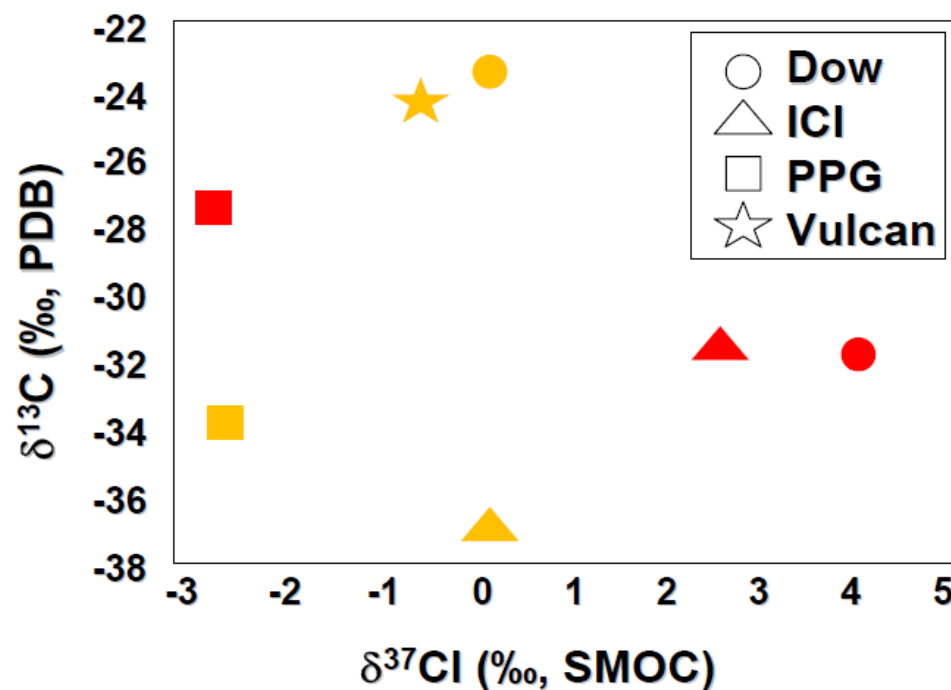


Figure 1: Range of  $\delta^{13}\text{C}$  values in nature

## CONCEPTS

### Source Identification

Differences have been noted in the isotopic composition of various chlorinated solvents by manufacturer. Figure 2 shows the  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  isotope distribution for various manufacturers of perchloroethene (PCE) and trichloroethene (TCE). This shows that these two isotopic elements are different for each manufacturer, providing a fingerprint of the source manufacturer.



van Warmerdam et al. 1995

Figure 2:  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  for PCE and TCE from 4 Manufacturers<sup>2</sup>

Isotopically, manufactured TCE is significantly heavier than TCE produced from the biodegradation of PCE, so it is relatively straightforward to differentiate. This can be a critical piece of information that could not likely have been determined from concentration data alone.

Figure 3 shows the isotopic interpretation of the differing fate mechanisms that occurred for two TCE releases at a confidential site in South Carolina: biodegradation, mixing between two sources, and evaporation. The majority of  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  ratios at the lower

<sup>2</sup> van Warmerdam, E.M., S.K. Frape, R. Aravena, R.J. Drimmie, H. Flatt and J.A. Cherry (1995). *Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents*. *Applied Geochemistry* Volume 10, Issue 5, September 1995, Pages 547-552

concentrations of TCE are heavier than the highest concentration as a result of fractionation due to biodegradation. Some  $\delta^{13}\text{C}$  isotope ratios are heavier as a result of evaporation, while mixing between Source A and Source B has resulted in an increase in  $\delta^{37}\text{Cl}$  ratios compared to Source A.

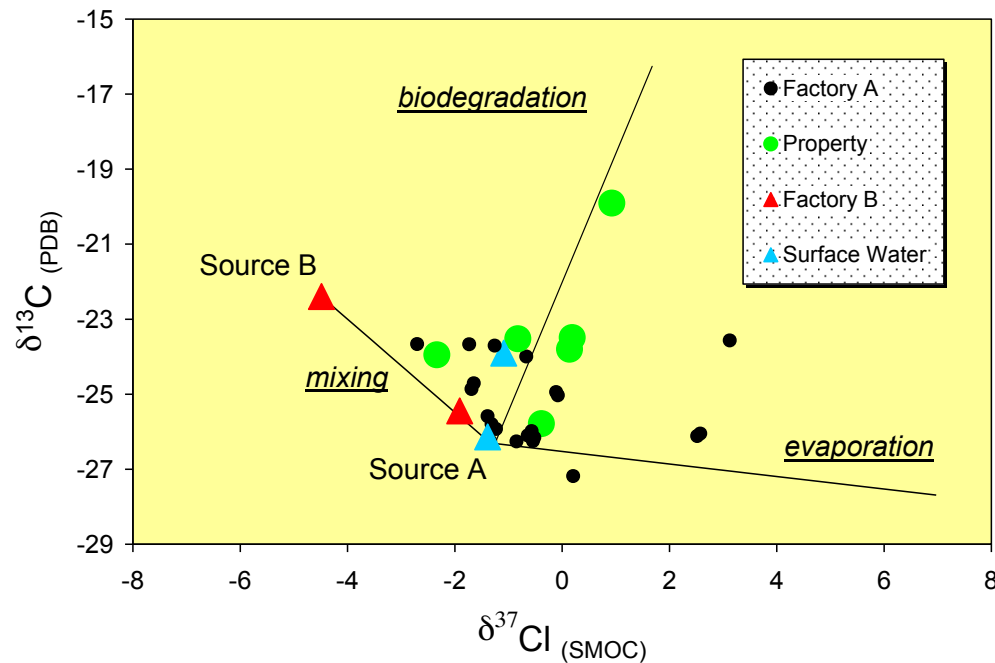


Figure 3:  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  ratios from a confidential site located in South Carolina.

Figure 4 illustrates how one can differentiate the relative contribution from two sources in a mixed plume. For each monitoring point in the mixing zone depicted in Figure 3, the relative contribution from each source (A and B) can be determined.

Figure 4: Apportionment of Sources based on Isotopic ratios

## Allocation Two Sources bv TCE $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$

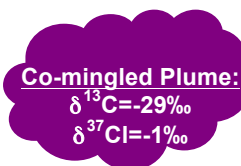
Source A:

$\delta^{13}\text{C} = -$



Source B:

$\delta^{13}\text{C} = -$



Determined by  $\delta^{13}\text{C}$ :  $-29 \times 1 = -30 \times A + (-25) \times (1-A)$

$A = 80\%$

Sueker.

## Fractionation

Chemical bonds can be likened to a gravitational attraction. The mass difference between heavier isotope and light isotope results in a stronger bond for the heavier isotope in a molecule. Therefore, when compounds breakdown through biodegradation or hydrolysis, the chemical bonds in the lighter isotopes break down in preference to the heavier isotopes. This process is called “fractionation” and is the reason why isotopes can be used to determine the fate of these compounds in the environment. Fractionation means a change to the isotope ratio during a process<sup>3</sup>.

<sup>3</sup> Fractionation occurs when isotopes are re-distributed between the reactant and the product, such as PCE and its degradation daughter product TCE. From originally one chemical (PCE) to two chemicals (PCE plus TCE), mass does not disappear, the combined or weight-averaged isotope ratio stays the same. For example, given PCE with an original  $\delta^{13}\text{C}$  isotope ratio at say  $-30\text{‰}$ , with no degradation (or a mass at 100%). With, say 50% degradation, the PCE becomes heavier, at say  $-28\text{‰}$ . For the daughter product (at 50% formed from the degradation of PCE), TCE's isotope ratio would be lighter, say  $-32\text{‰}$ . Therefore, from mass balance:  $-30\text{‰} \cdot (-30\text{‰}) \cdot 1 = (-28\text{‰}) \cdot 0.5 + (-32\text{‰}) \cdot 0.5$ .

Figure 5 presents a generalization of the trends of  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  during in situ thermal remediation that can be used to interpret the changes that occur during treatment of the groundwater. Because of the extremely low detection capability of these measurements, this can be done to a higher degree of certainty than is currently done using conventional concentration data.

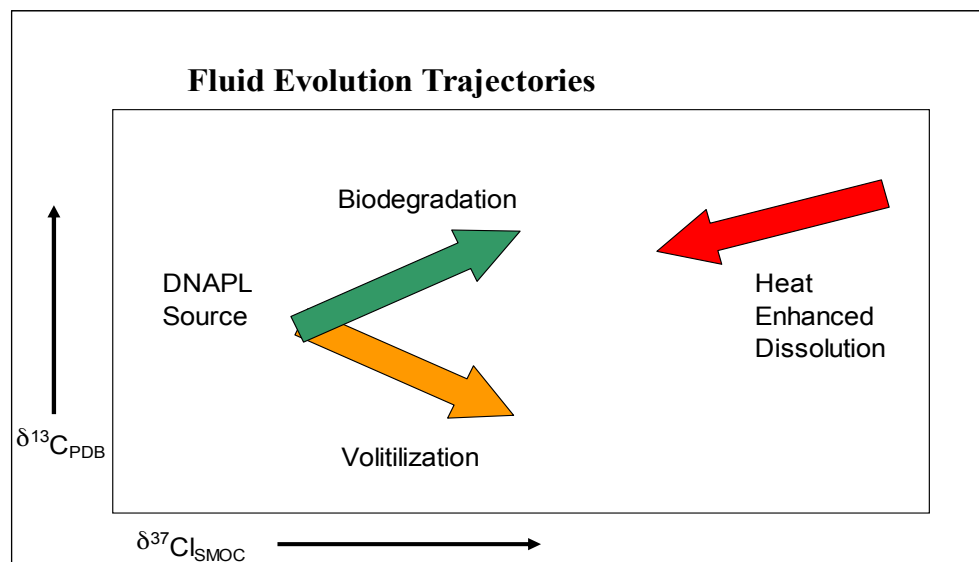


Figure 5: Trajectories of bulk isotope ratios undergoing the labeled processes (From Sturchio et al., (2000)).

During source remediation, tracking the fate of the contaminants in groundwater can determine if active treatment can be discontinued. The active remediation may involve pump and treat, in situ thermal, chemical oxidation, etc. Once it has been isotopically determined that intrinsic biodegradation is taking place, active remediation was discontinued. Conventional natural attenuation evaluations were then used to corroborate if active remediation could be discontinued.

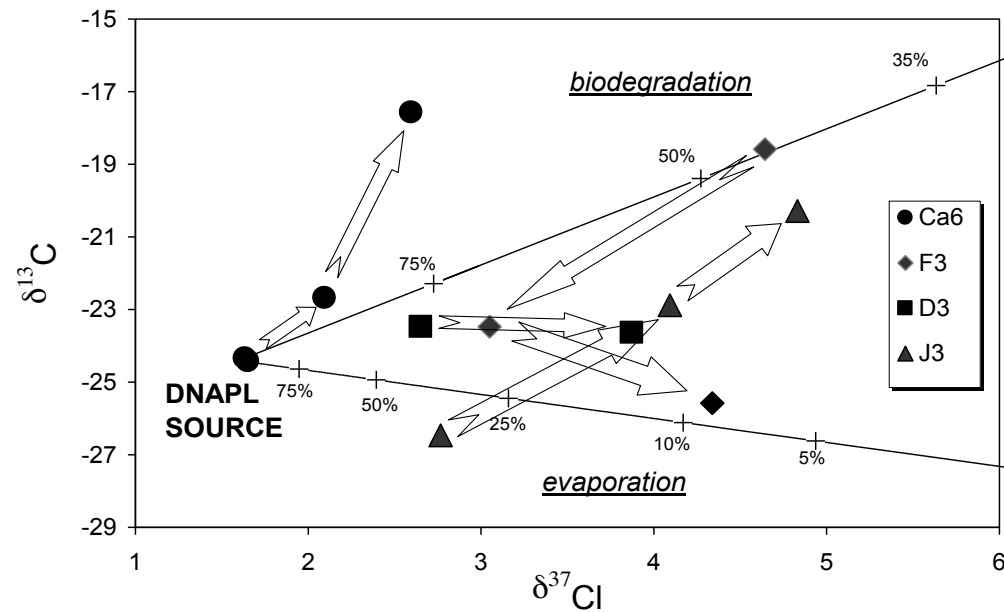


Figure 6:  $^{13}\text{C}$  vs.  $^{37}\text{Cl}$  isotope ratios of TCE in groundwater from 4 source location wells at a Chicago site during electrical resistance heating treatment. Evaporation and biodegradation trends are shown, with residual TCE percentages determined from the isotope data indicated. Arrows indicate time sequence. When biodegradation was dominant fate mechanism, ERH was shut down in that particular treatment area.