

Compound Specific Isotopic Analysis (CSIA)

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., 2000¹, as well as sources of methane and PAH compounds. 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 ²H (deuterium), ¹³C, ¹⁸O, ¹⁵N, and ³⁷Cl. The most commonly used isotopes in forensic studies include ²H, ¹³C and ³⁷Cl.

CSIA using gas chromatography-isotope ratio mass spectrometry (GC/IRMS) has developed into a mature analytical method in many application areas from the late 1990s (Schmidt, et al., 2004)². This is particularly true for carbon isotope analysis, whereas measurements of the other elements amenable to CSIA (hydrogen, nitrogen, oxygen) are much less routine.

In environmental studies, successful applications to date include (i) the allocation of contaminant sources on a local, regional, and global scale, (ii) the identification and quantification of (bio)-transformation reactions on scales ranging from batch experiments to contaminated field sites, and (iii) the characterization of reaction mechanisms that govern product formation. Items i and ii have been largely in the domain of forensic studies, while iii has been in the venue of environmental site characterization and restoration. The investigated spectrum of compounds comprises mainly *n*-alkanes, monoaromatics such as benzene and toluene, methyl *tert*-butyl ether (MTBE), polynuclear aromatic hydrocarbons (PAHs), and chlorinated hydrocarbons such as tetrachloromethane, trichloroethene, and polychlorinated biphenyls (PCBs). It should be noted however that CSIA can be applied to any compound that can be detected using a GC-MS and as a result can be applied to more families of compounds than is in the current experience base.

Fractionation

When compounds breakdown through say biodegradation or hydrolysis, chemical oxidation, etc., 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 process³. The mass difference between heavier isotope and light isotope results in a stronger bond for the heavier isotope in a molecule

CSIA for PAHs

CSIA analysis for poly-nuclear aromatic hydrocarbon (PAH) compounds has been performed for more than 10 years. Mauro (2000)⁴ presents GC/IRMS data for PAH compounds from a variety of sources

¹ 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.

² Schmidt, T.C., L. Zwank, M. Elsner, M. Berg, R.U. Meckenstock, and S.B. Haderlein (2004) *Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges*. *Analytical and Bioanalytical Chemistry*. Volume 378, Number 2. pp 283-300.

³ 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‰, with no degradation (or a mass at 100%). With, say 50% degradation, the PCE becomes heavier, at say -28‰. For the daughter product (at 50% formed from the degradation of PCE), TCE's isotope ratio would be lighter, say -32‰. Therefore, from mass balance: $-30‰ = (-30‰) \cdot 1 + (-28‰) \cdot 0.5 + (-32‰) \cdot 0.5$.

⁴ Mauro, D. (2000). *Chemical Source Attribution at Former MGP sites*, EPRI, Palo alto, CA, NYSEG, Binghampton, NY and RG&E, Rochester, NY.

(Figure 1). While not specifically labeled, the vertical axis represents $\delta^{13}\text{C}$ ratios with 13 PAH compounds identified. It is interesting to note that there is a distinct difference between the MGP sample and the creosote sample, suggesting that different sources may be identified for a given site. Sources of PAHs at MGP sites have been defined by concentration data and observations of NAPL. Unlike chlorinated solvents where the presence of daughter compounds can be detected, defining where biodegradation is in evidence in fuels, MGP wastes, and creosotes, representing mixtures of individual hydrocarbons is more difficult. These compounds show no indicators of weathering of individual compounds in preference to others, requiring mass balance calculation to evaluate concentration data (Hunkeler, et al., 2008).

DPRA's experience in CSIA for PAHs has its background in identifying and differentiating crude oils. This is a well-tested method for this purpose from both an evaluation of the crude and from a forensics perspective in identifying where the crude came from for determining cleanup responsibility in courts of law. ZymaX labs performs a comprehensive $^{13}\text{C}/^{12}\text{C}$ for the following list of common target PAH compounds:

PAH list:

Naphthalene	Beno(a)pyrene	Chrysene	Pyrene
Acenaphthene	2-Methylnaphthalene	Indeno (1,2,3-cd)pyrene	Benzo(b+k)fluoranthene
Anthracene	Fluorene	Acenaphthylene	Dibenz(a,h)anthracene
Benz(a)anthracene	Fluoranthene	Phenanthrene	Benzo(ghi)perylene

Stable isotopes of carbon will show fractionation of the individual PAH constituents over time and distance from a source. As a result, the fractionation will help define where biodegradation is occurring and where source treatment is required. Methods presented in Newell, et al., 2002⁵, one can be used with the fractionation data to project the distance or time for transformation or the extent of the release.

CSIA for Chlorinated Solvents

There are also differences 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 and trichloroethene. This shows that these two isotopic elements are different for each manufacturer, providing a fingerprint of the source manufacturer.

CSIA is especially useful in tracking the transformation of chlorinated solvents and interpreting transformation with distance since fractionation is not sensitive to concentration

CSIA During Remediation

During remediation, it is important to track the fate of the contaminants in groundwater to 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 determined that natural attenuation is taking place, conventional natural attenuation evaluations can be used to determine if active remediation can be discontinued.

A former electronics manufacturing plant in the Chicago area was investigated with five separate sampling trips in January, April, August, and December, 1998, and January 1999. Carbon and chlorine isotope data for bulk chlorinated aliphatic hydrocarbon (CAH) extracted from groundwater from four wells at the Chicago area site are shown in Figure 7. The isotopic compositions of d^{13}C and d^{37}Cl in the bulk CAH varied significantly over this time period. The details of the variations within each well yield information on the identity and the extent of the CAH attenuation processes that were occurring.

⁵ Newell, C.J., H.S. Rifai, J.T. Wilson, J.A. Connor, and J.J. Aziz, M.P. Suarez, 2002. *Calculation and Use of First-Order Rate Constants For Monitored Natural Attenuation Studies*, U.S. EPA Remedial Technology Fact Sheet, U.S. Environmental Protection Agency. EPA/540/S-02/500, November 2002.

Figure 3 shows the changes in isotopic ratios with time reflecting the various fate mechanisms that were occurring; e.g., biodegradation, evaporation and a combination of both. Therefore, as the remediation progressed, we were able to observe in the monitored locations whether heating could be terminated, without concern over the uncertainty of evaporative losses of the more volatile compounds during sampling.

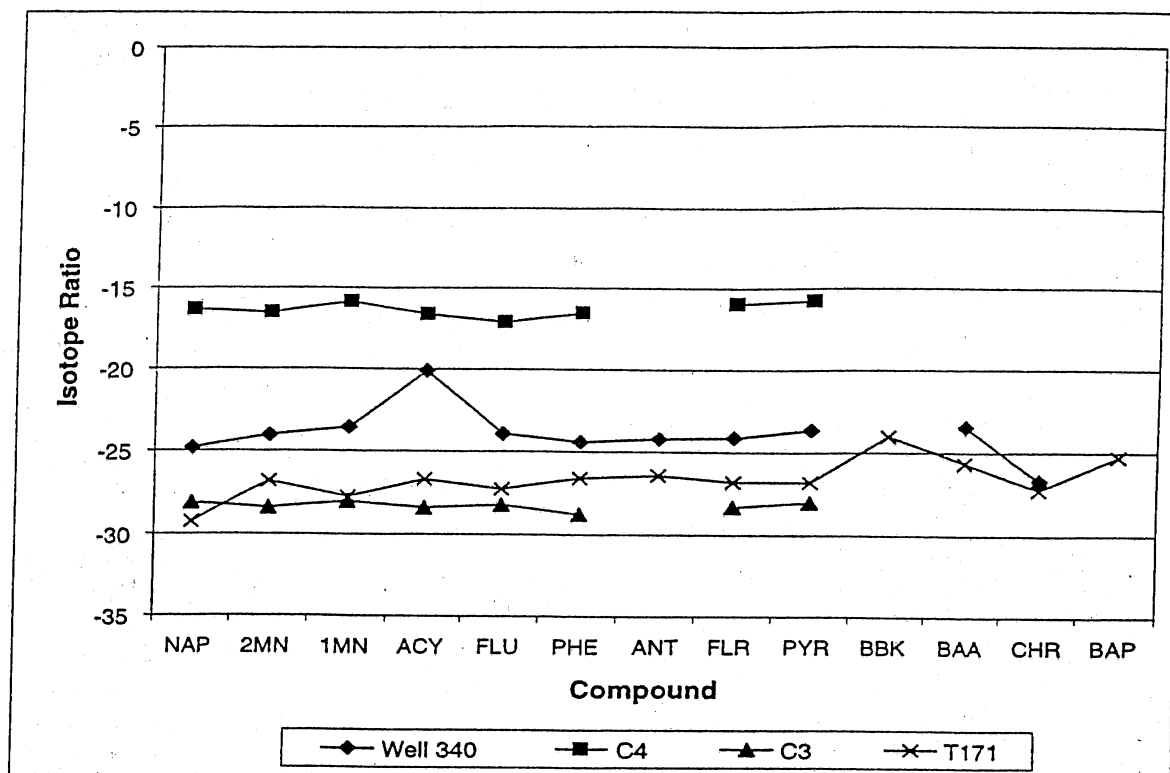


Figure 1: GC/IRMS Analysis of Creosote (Well 340), Combustion Byproducts (C4 Grass Species and C3 Plant Species), and MGP Tar (T171).

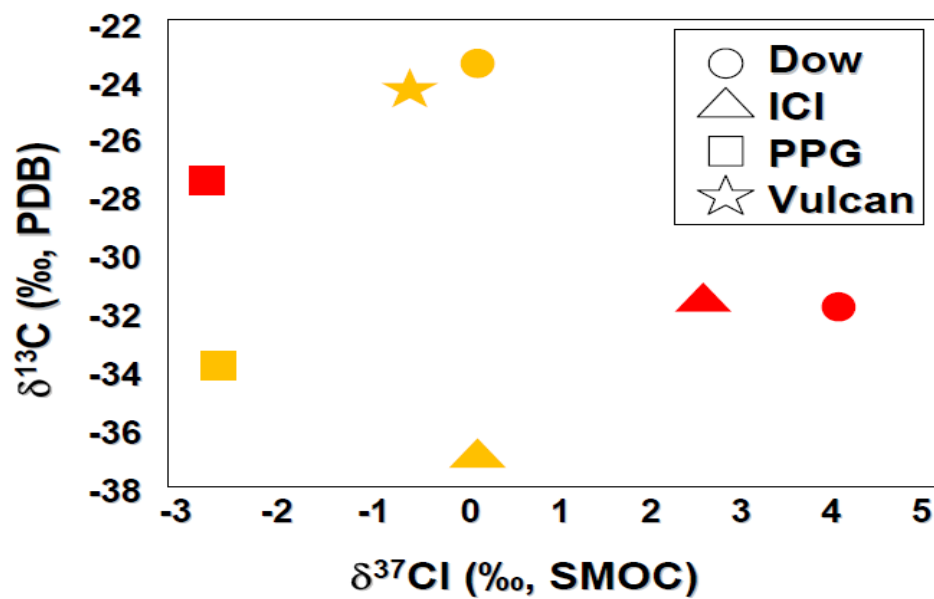


Figure 2: $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ for **PCE** and **TCE** from 4 Manufacturers⁶ van Warmerdam et al. 1995

⁶ van Warmerdam, E.M., S.K. Frapce, 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

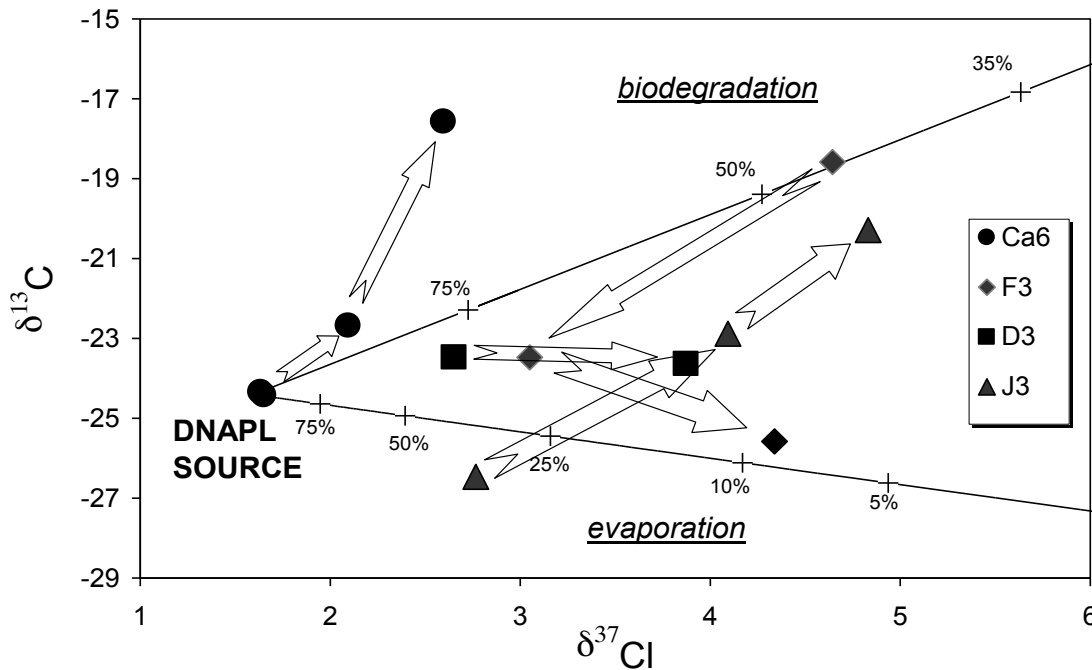


Figure 3: ^{13}C vs. ^{37}Cl isotope ratios of TCE in groundwater from 4 source location wells at a Chicago site during ERH remedial activities. Evaporation and biodegradation trends are shown, with residual TCE percentages indicated. Arrows indicate time sequence. When biodegradation was dominant fate mechanism, ERH was shut down in that particular treatment area.