CSIA in Site Characterization and Remediation

Introduction

Compound Specific Isotopes offer a significant cost saving over conventional concentration data in site characterization and remediation. This sounds counter-intuitive since the cost per sample is almost ten times higher than conventional EPA method analysis for say volatile organic compounds. CSIA for volatile organic compounds can involve analysis for up to 3 isotopes:

- 1D-CSIA (^{13}C) for Biodegradation analysis
- 2D-CSIA (^{13}C and ^{37}Cl) for Plume differentiation
- 3D-CSIA (^{2}H, ^{13}C and ^{37}Cl) to differentiate man made TCE from TCE produced from the reductive dehalogenation of PCE.

1D-CSIA for Biodegradation

For instances where the release to groundwater is from a known source(s) and the hydrogeology is not complex, evaluating natural attenuation or biodegradation either as part of site characterization or remediation, isotopic analysis for $\delta^{13}C$ provides a very cost effective means to evaluate a site for this purpose. The following example illustrates a site under investigation for the release of perchloroethene (PCE) and trichloroethene (TCE). Eight wells were sampled for both volatile organic compounds and $\delta^{13}C$ analysis. Distributions of concentrations of PCE and TCE are presented in Figures 1 and 2 respectively.

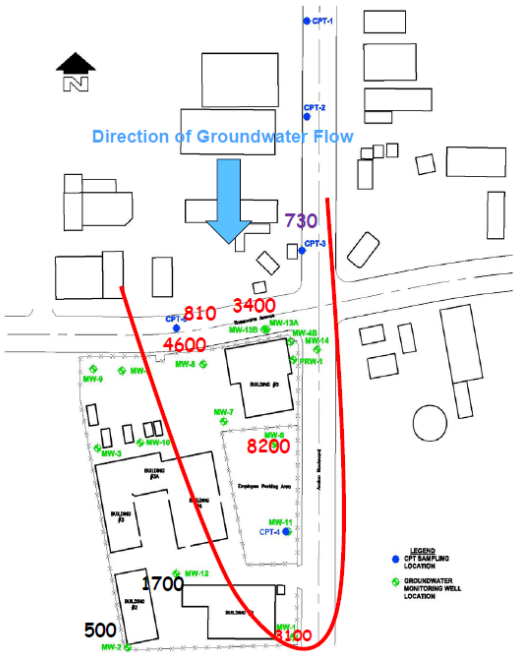

Figure 1: Site map showing concentrations of TCE (µg/l)

It can be seen that there is an upgradient source migrating onsite, a source in the middle of the site, and concentrations of PCE and TCE detected in the southwest corner of the site that appear to be inconsistent with concentration trends. Figures 3 and 4 present $\delta^{13}C$ for PCE and TCE respectively. We know from isotope research, (Hunkeler, et al., 2009)[1] that in biodegradation of chlorinated compounds that the parent compound becomes isotopically heavier, while the daughter compound is isotopically lighter.

[1] Hunkeler, D., R.U. Meckenstock, B.S. Lollar, T.C. Schmidt, and J.T. Wilson (2008). *A Guide for Assessing Biodegradation and Source Identification or Organic Groundwater Contaminants Using Compound Specific Isotope Analyses (CSIA)* EPA 600/R1481, December 2008

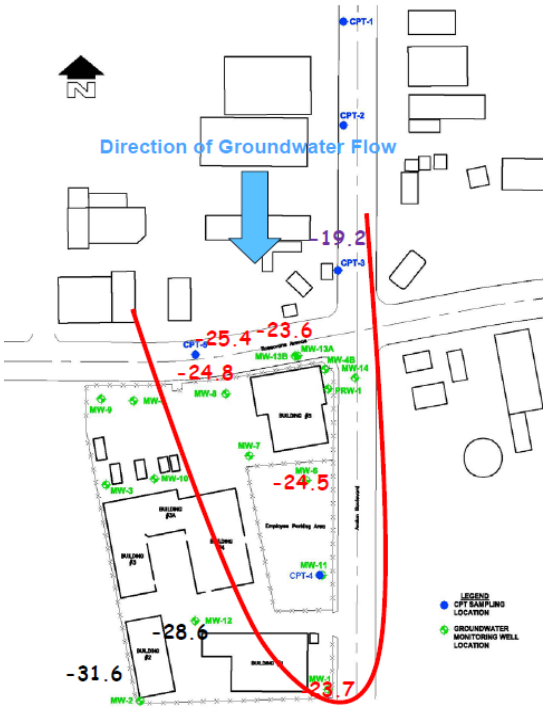

Figure 2: Distribution of $\delta^{13}C$ values for TCE presented on the site map.

Table 1 presents the isotope fraction factor (α_{PR}; >1, fractionation is occurring), the isotopic enrichment factor (ε_{PR}), the fraction of TCE remaining (f), the first order degradation constant (λ), and the resultant half-life for TCE fro this site. The same analyses were performed for PCE and cis-1,2-dichloroethene as well. The enrichment factor can be used to determine the oxidation/reducing conditions in groundwater from data supplied in Hunkeler, et al., (2009). The fraction remaining values can only be determined using isotopic analyses and is especially useful in evaluating the effectiveness of mass removal/destruction under natural and remediation conditions.

Table 1: Biodegradation Summary from $\delta^{13}C$ Analyses

Flow Path	α_{PR}	ε_{PR}	f	λ (day^{-1})	$t_{1/2}$ (days)
CPT5 - MW-8	1.001	-23.6	0.97	0.002	452.2
MW-8 - MW-6	1.0003	-12.1	0.97	0.0006	1090.2
MW-6 - MW-1	1.00082	-32.7	0.98	0.0003	2015.1

The above data interpretation was performed for PCE and DCE as well and for various groundwater migration pathways for $2,400 over conventional concentration data. This compares to an average of $125,000 for natural attenuation studies to obtain the same information that are incapable of determining *f* (Parsons Engineering, 1999)[2].

2D-CSIA for Plume Differentiation

2D-CSIA involves the analyses for $\delta^{13}C$ and $\delta^{37}Cl$, which as its name suggests provides another dimension in data interpretation. With this technique we are able to differentiate sources as well as fate and transport mechanisms, as illustrate in Figures 3 and 4.

Adding this dimension of analysis to the data for the site described above would have added $2,400 to the analyses and provided greater differentiation of the plumes, and would have determined at a given location the relative contribution from the individual sources. 2D-CSIA provides the only means to provide this data.

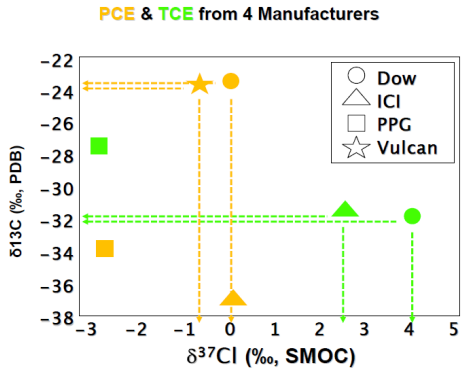

Figure 3: Differentiation of Sources of PCE and TCE

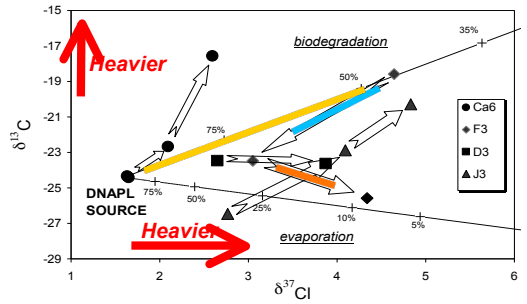

Figure 4: Differentiation of Fate Mechanisms

3D-CSIA for Differentiating Sources of Daughter Compounds

For the site described above, if there was concern over differentiating released TCE from that resulting from the biodegradation of PCE, the addition of $\delta^{2}H$ as part of the analytical suite provides this capability. Manufactured TCE derives its hydrogen from hydrochloric acid, while that form through biodegradation derives hydrogen from its aqueous environment, and the difference is significant, as illustrated in Figure 5.

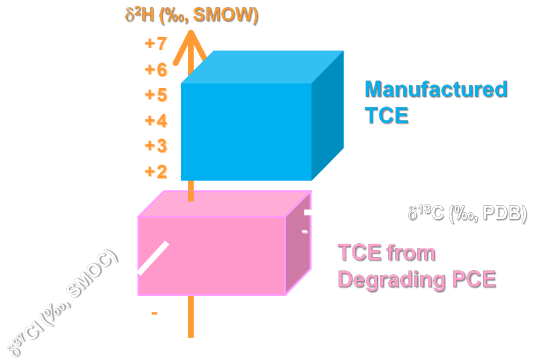

Figure 5: Clustering of isotopic data to illustrate the difference between manufactured TCE and TCE resulting from biodegradation.

Summary

CSIA analysis, while more expensive than conventional EPA methods for obtaining concentration provides a greater degree of understanding of site conditions, and with this a lower overall cost to obtain the same information. Further, CSIA provides the opportunity to differentiate co-mingle plumes that no other technique provides. Natural attenuation studies can be completed at a fraction of the cost of conventional studies of this nature, without the need to install additional monitoring points to more optimally locate wells within complex hydrogeologic settings. CSIA studies can be tailored to a variety of contaminants (e.g., fuels, PAHs, PCBs) site needs, to perform biodegradation evaluations, differentiation of co-mingled plumes, and source differentiation.

For more information, contact: Greg Smith, 630-696-2387

[2] Parsons Engineering, Inc. (1999). Natural Attenuation of Fuel Hydrocarbons Performance and cost Results from Multiple Air Force Demonstration Sites. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas 78235