Use of Compound Specific Isotope Analysis to Enhance *In Situ* Chemical Oxidation Performance Monitoring and Project Management

In this edition of Peroxygen Talk, guest authors Matt Burns and Bob Pirkle discuss the benefits of compound specific isotope analysis (CSIA) to optimize delivery and monitor performance of ISCO applications. Mr. Burns is a Senior Project Director at WSP Environment & Energy, a leading environmental, energy and sustainability consultancy with over 1,000 people in 65 global locations. He has more than 15 years of professional chemistry and engineering experience, a Master of Science Degree in Civil/Environmental Engineering from the University of Maryland, and he co-developed and co-manages WSP's Advanced Site Closure Program, a specialty services area involving the use of innovative advanced characterization technologies for optimizing the design, management and closure of sites. Dr. Pirkle is the President and cofounder of Microseeps, Inc., a niche environmental laboratory and recognized leader in the development of specialized analytical methods to support Monitored Natural Attenuation and other in-situ remediation techniques. He received his PhD in Chemistry from The University of Western Ontario has over twenty-five years of experience in geotechnical and geochemical research and development. Both Mr. Burns and Dr. Pirkle have been featured speakers at numerous technical symposia and have published extensively in technical publications.   They can be contacted at matt.burns@wspgroup.com and rpirkle@microseeps.com, respectively.

Traditional performance monitoring techniques for *in situ* chemical oxidation (ISCO) applications rely on layers of costly and often misleading performance data to demonstrate contaminant destruction.   This is because definitively attributing contaminant concentration decreases to oxidant application can not be efficiently performed using concentration data alone.   Compound-specific isotope analysis (CSIA), which has recently become commercially available (Microseeps, Inc., Pittsburgh Pennsylvania), when combined with concentration data can provide an almost definitive indication discerning contaminant destruction from non-destructive physical processes such as dilution and displacement that can be associated with ISCO.

CSIA distinguishes destructive reactions from non-destructive processes by tracking the naturally occurring stable carbon isotopes ^{13}C and ^{12}C in organic chemicals (e.g., common petroleum constituents and chlorinated solvents) present in groundwater.   The majority of all carbon is present as the ^{12}C isotope but a small percentage of carbon is naturally present as the stable (i.e., not radioactive) ^{13}C isotope (natural abundance approximately 1 percent of all carbon). Chemical bonds involving the ^{13}C isotope are slightly stronger than those of the ^{12}C isotope and as a result react slower in bond breaking reactions including chemical oxidation and biodegradation. The slower reaction rate leads to an accumulation of the ^{13}C isotope in the residual contaminant.   The physical mechanisms of natural attenuation (e.g., dilution and sorption) and mechanisms associated with amendment fluid application (e.g., displacement) do not significantly affect the isotopic signature of residual contaminant as they can with simple chemical concentration data.

Following isotopic analysis of a chemical of interest "x", the data is reported in terms of R_x (= $^{13}C_x$ /$^{12}C_x$) relative to the ratio in an international standard, R_{std} (= $^{13}C_{std}$ /$^{12}C_{std}$) as defined by the parameter δ_x for carbon in compound x,

$$\delta_x\ ^{13}C\ =\ \{(R_x - R_{std}) / R_{std}\}\ x\ 1000$$

and the units are parts per thousand or "per mil" usually denoted with the symbol $°/_{oo}$.

A broad range of recommendations for CSIA sampling, data evaluation, and interpretation are presented in the US Environmental Protection Agency's document, *A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)* (December 2008).

The isotopic effects of chemical oxidation are apparent in Figure 1 where isotopic effects of oxidation are normalized and plotted as a function of the fraction of tetrachloroethene (PCE) remaining for a series experiments. The lower right on the graph shows the beginning of the experiments. As the PCE is destroyed, the fraction of PCE remaining decreases (the natural log of the fraction remaining also decreases). Consequently, the relative abundance of ^{13}C in the remaining PCE increases due to slower reactivity of ^{13}C chemical bonds, resulting in an increase in fractionation (which has been normalized in Figure 1 by dividing the isotopic signature of the treated PCE by the initial isotopic signature; increases in the natural log of this data reflect increased abundance of ^{13}C or fractionation)

Figure 1. Abiotic Oxidation of PCE

(Poulson and Naroaka, 2002)
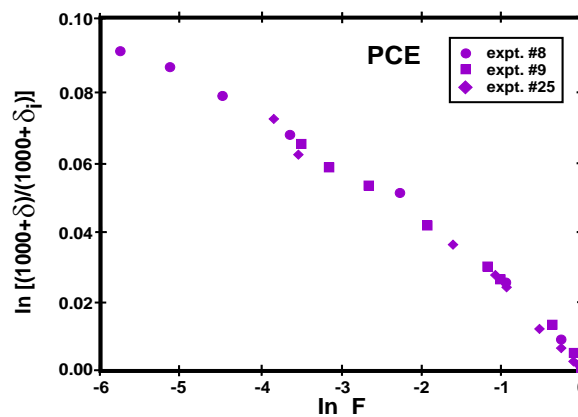
WSP has used CSIA as part of the performance monitoring of several ISCO application sites and at each site the data has provided an understanding of processes that would not have been identified using concentration data alone.

CSIA and concentration data for groundwater samples from a site in New Jersey collected immediately before and approximately 3 months following ISCO application are presented in Table 1. The data from the MW-1 sample show a significant decrease in trichloroethene (TCE) concentration which is confirmed by the isotopic fractionation data (^{13}C accumulates and the $\delta^{13}C$ increases or becomes less negative). The data for samples collected from MW-2 also show fractionation, definitively proving the occurrence of bond breaking. The data from MW-1 suggest that there has been significant degradation and little if any rebound had occurred at the time of Post-ISCO sampling. At MW-2, while the degradation and fractionation may have been similar in scope, rebound has occurred as is evident from the increase in concentration. The $\delta^{13}C$ observed, while obviously more positive at the Post-ISCO sampling time than the Pre-ISCO sampling, is the average of the TCE treated by ISCO and that which has entered the area during rebound.

Without the CSIA data, the concentration data alone may have been used to judge the ISCO application as ineffective in the MW-2 area because the concentrations increased. The ability of CSIA to demonstrate treatment within dynamic systems is directly applicable to assessing effectiveness of pilot-scale tests within larger plumes.

Table 1. New Jersey Site Initial CSIA Data				
	MW-1		MW-2	
	Pre-ISCO	Post-ISCO	Pre-ISCO	Post-ISCO
TCE: CSIA, $\delta^{13}C$ (‰)	-29.6	-3.7	-34.4	-25.7
TCE Concentration (µg/l)	3,000	80	400	500

CSIA is also effective in showing the effect of rebound following ISCO application. The isotopic effect of rebound at a site in Florida where Klozur® CR was applied is shown on Table 2. Pre-Klozur CR application data were not collected at this site, but it is assumed that fractionation has occurred since the first quarterly post-ISCO sample data are fractionated relative to typical isotopic signatures of benzene ($\delta^{13}C$: -23.5 ‰ to – 31.5‰) and MTBE ($\delta^{13}C$: -27.5 ‰ to – 33 ‰) within gasoline.

Between the T-1 and T-2 sampling events, the pool of ^{13}C comprising the MTBE and benzene decreased. A decrease in the pool of ^{13}C that comprises the benzene is explained by the subsequent flux of untreated contaminant into the sampling point (i.e., rebound). At this site, which consists of a sandy aquifer with a relatively flat gradient, the rebound is likely attributable to desorption from saturated soils or dissolution from residual product (gasoline). In addition to temporal and heterogeneity based explanations, one possibility to explain the change in the isotopic signature of MTBE between T-1 and T-2, where the MTBE concentration decreased, is that at some time between T-1 and T-2 essentially all of the MTBE originally there was degraded leaving only an extremely small concentration. The 40 µg/l concentration at T-2 with a $\delta^{13}C$ = -26.4 would then be virtually entirely due to rebounded MTBE. The important observation here is that the CSIA data from the third quarterly sample (T-3) reveals fractionation of both benzene and MTBE is continuing and is indicative of contaminant destruction.

The contaminant destruction observed for both chemicals in the T-3 sample is likely attributable to the rate of biodegradation being greater than the rate of desorption/dissolution that was observed in earlier samples. This effect is expected as the unique "chem/bio" formulation of Klozur CR stimulates biodegradation by elution of dissolved oxygen from the engineered calcium peroxide used to activate the persulfate and direct use of residual sulfate by the attenuating microbes. Also note the reliance on CSIA data as compared to concentration data to assess remedial performance at this site.

Table 2. Isotopic Effect of Rebound at a Florida Site			
	MW-5		
	Post- ISCO T-1	Post-ISCO T-2	Post-ISCO T-3
Benzene: CSIA, $\delta^{13}C$ (‰)	-24.6	-26.4	-25.5
Benzene Concentration (µg/l)	200	800	151
MTBE: CSIA, $\delta^{13}C$ (‰)	-24.6	-26.3	-25.6
MTBE Concentration (µg/l)	70	40	10

The effects of rebound for another site located in Switzerland are shown on Table 3. At this site, both isotopic data and concentration data are consistent (i.e. increased δ13C corresponds to a decrease in PCE concentration and decreased δ13C corresponds to an increase in PCE concentration).

Table 3. Isotopic Effect of Rebound at a Switzerland Site			
	MW-4		
	Pre- ISCO	Post-ISCO T-1	Post-ISCO T-2
PCE: CSIA, δ13C (‰)	-25.8	-23.7	-24.5
PCE Concentration (µg/l)	6100.0	480.0	1700.0

The rebound shown in the examples above is likely attributable to desorption or dissolution. This effect is primarily due to oxidant reaction efficiency bias to the aqueous phase (i.e., reduced treatment efficiency of soil-sorbed chemicals) and the limited longevity of oxidants within the aquifer to oxidize chemicals as they desorb. Accordingly, oxidants with greater *in situ* longevity, such as Klozur persulfate, typically result in more effective treatment than shorter lived oxidants.

Rebound can also be attributable to delivery inefficiencies. This type of rebound occurs when preferential flow paths limit treatment to a fraction of the affected volume. After the oxidant concentration decreases, untreated groundwater migrates to treated areas causing a dramatic isotopic rebound. Characteristics of delivery rebound are wide fluctuation in chemical concentration and isotopic rebound approaching the initial isotopic signature. Rebound attributable to delivery inefficiency is shown in data from the New Jersey site on Table 4.

Table 4. Rebound Caused by Delivery Inefficiency at a New Jersey Site			
	MW-1		
	Pre- ISCO	Post-ISCO T-1	Post-ISCO T-2
TCE: CSIA, δ13C (‰)	-29.6	-3.7	-27.0
TCE Concentration (µg/l)	3,000	80	600

Although use of CSIA for ISCO performance monitoring is an emerging application of this technology, early data, as shown in some of the examples above, have provided definitive results by confirming contaminant destruction and identifying delivery limitations. The nature of the CSIA data provides more actionable data than concentration data alone which can lead to quicker site closure and cost savings. For example, at the New Jersey site, a well field wide evaluation of the combined CSIA/chemical concentration data set led to the conclusion that improved ISCO distribution through pneumatic fracturing was warranted at some locations. The conclusion was based on inconsistencies between isotopic and concentration data (e.g., MW-2 data in Table 1). Enhancing oxidant delivery within these areas has greatly increased treatment efficiency, saved the costs of ineffective treatment, and will lead to quicker site closure. Based on these results, CSIA can be a valuable tool for monitoring the performance and enabling better project management decisions at ISCO and chem/bio applied sites.

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