

**Dual Measurement of  $^{13}\text{C}$  and  $^{14}\text{C}$  Isotopic Composition to  
Identify Biodegradation of Fuel Hydrocarbons  
at the LLNL Gasoline Spill Site**

**M. L. Davisson  
T. P. Rose**

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## Dual Measurement of $^{13}\text{C}$ and $^{14}\text{C}$ Isotopic Composition to Identify Biodegradation of Fuel Hydrocarbons at the LLNL Gasoline Spill Site.

M. Lee Davisson and Timothy P. Rose  
Isotope Sciences Division

### Isotopic Methods

Samples of groundwater were collected in the spring of 1996 for  $^{13}\text{C}$  and  $^{14}\text{C}$  determinations of dissolved inorganic carbon (DIC). A sample of the FHC collected during steam injection was also analyzed. Groundwater was collected after appropriate pumping times in I-CHEM<sup>®</sup> 125ml amber glass bottles fitted with 1/8 inch teflon-coated rubber septa inserted into threaded caps. Bottles were filled leaving approximately a two inch head space, treated with 4 drops of saturated  $\text{HgCl}_2$  solution, and stored upside-down refrigerated until analyses. Analyses were performed within 48 hours of collection. Two duplicates were collected using evacuated glass cylinders equipped with greased stopcocks and a 1/4 inch rubber septa plug. Results of these duplicate samples were identical to those collected in the septa bottles (see Table 1).

Groundwater DIC was extracted and quantitatively measured by conversion to  $\text{CO}_2$  using orthophosphoric acid and purifying by vacuum cryogenic methods (McNichol, et al., 1994). The DIC is reported in milligrams of  $\text{HCO}_3$  per liter  $\text{H}_2\text{O}$  and has an uncertainty of ~5%. The FHC was combusted in sealed quartz tubing with  $\text{CuO}$  at  $900^\circ\text{C}$  for 3 hours. The  $\text{CO}_2$  gases were split for  $^{13}\text{C}$  and  $^{14}\text{C}$  determinations. The  $^{13}\text{C}$  was measured by a VG-Prism stable isotope ratio mass spectrometer and results are reported in  $\delta$  (del) notation,

$$\delta^{13}\text{C} = \left[ \frac{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right] 1000$$

where values are reported in per mil deviations from the standard NBS PD-Belemnite. Normally, field reproducibility of the  $\delta^{13}\text{C}$  of DIC is  $\pm 0.1$  per mil. For  $^{14}\text{C}$ , the  $\text{CO}_2$  sample was converted to graphite and analyzed on the accelerator mass spectrometer at LLNL (Vogel et al., 1987). Results are reported as percent modern carbon (pmc), where 100 pmc represents one-hundred times the  $^{14}\text{C}/^{12}\text{C}$  ratio of atmospheric  $\text{CO}_2$  in 1950 as characterized by the NBS Oxalic Acid standard. Reproducibility of the  $^{14}\text{C}$  analyses are  $\pm 1.0$  pmc.

### Isotopic Analyses

For decades  $^{14}\text{C}$  and  $^{13}\text{C}$  have been measured in natural groundwater systems for age dating purposes (Mook, 1980), but only recently have the measurement of this isotope couple been used effectively as a tracer (e.g. Rose and Davisson, 1996). Dual measurements of  $^{13}\text{C}$  and  $^{14}\text{C}$  are ideally suited for subsurface environments under the influence of biodegradation of FHCs. In particular, the absence of  $^{14}\text{C}$  in the FHCs and their low  $\delta^{13}\text{C}$  (see Deines, 1980) relative to natural groundwater DIC isotopic values provides a means to quantify the extent of biodegradation of an FHC spill independent of the DIC concentration. Previous work using only  $\delta^{13}\text{C}$  measurements of  $\text{CO}_2$  soil gas helped validate biodegradation processes in FHC spills, but suffered from large quantitative uncertainty (Aggarwal and Hinchee, 1991). The isotopic measurement of  $^{14}\text{C}$  and  $^{13}\text{C}$  in DIC of groundwater, particularly in the unsaturated zone groundwater, is superior over direct measurement of  $\text{CO}_2$  soil gas since diurnal atmospheric diffusion and mixing may disturb the latter (e.g. Severinghaus et al., 1996). The isotopic values of DIC should dampen and average any transient isotopic values in the  $\text{CO}_2$  gas since the rate of isotopic exchange between  $\text{CO}_2$  and DIC is slow (Broecker et al., 1959).

In this particular study, only saturated zone groundwaters were measured for  $^{14}\text{C}$  and  $^{13}\text{C}$ . These groundwaters were collected after the dynamic stripping experiment located

on the south side of LLNL. No isotopic information was generated prior to steam injection. Figure 1 defines a near linear trend between the  $^{14}\text{C}$  and  $^{13}\text{C}$  of the DIC in these groundwaters. Direct measurement of the  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  in the FHC yielded -25.8 per mil and <1 pmc, respectively. DIC concentrations show a proportional increase toward the low isotopic end member (see Table 1). Note that the three samples with isotopic values closest to the FHC also have elevated temperatures. The highest  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  groundwater (GSW-326) was sampled upgradient from the spill site (Fig. 1) and is consistent with young (between 50 and 1500 yrs) natural groundwater in California (Davisson and Criss, 1995).

A linear extrapolation from the FHC to the three samples with ambient temperatures should delineate a mixing line between natural DIC and the DIC derived from biodegradation, that is the  $\text{CO}_2$  derived from the break down of the FHC that is assumed to completely dissolve in these saturated zone conditions. The three high temperature samples lie below this mixing line. Their positions can be explained by a shift in  $\delta^{13}\text{C}$  resulting from closed-system precipitation of  $\text{CaCO}_3$  during the steam injection. With increased temperature during steam injection the  $\text{CaCO}_3$  solubility decreases and precipitation results. There is a net isotopic fractionation with respect to  $^{13}\text{C}$  between DIC and the  $\text{CaCO}_3$  precipitate, where the  $^{13}\text{C}$  is isotopically enriched in the solid phase. Therefore it is assumed that before the steam injection these three groundwater sampling points had higher DIC concentrations and  $\delta^{13}\text{C}$  values. We can predict the change in  $\delta^{13}\text{C}$  of the DIC during a close-system precipitation of  $\text{CaCO}_3$  using a simple Raleigh model

$$\delta^{13}\text{C} = \left[ \left( 1000 - \delta^{13}\text{C}_o \right) f^{(\alpha-1)} \right] - 1000$$

where  $\delta^{13}C_o$  is the initial isotopic value of the DIC before  $CaCO_3$  precipitation,  $\alpha$  is the isotopic fractionation factor between DIC and  $CaCO_3$ , and  $f$  varies from 0 to 1. The fractionation factor  $\alpha$  will depend on the pH and the resulting speciation of the DIC, and in this case those values provided by Mook et al. (1974) were used. Under these model conditions, the total  $\delta^{13}C$  shift from the mixing line for samples HW-GP-104 and W-1115 (approximately 1.2 per mil) can be explained by precipitation of 10-15% of the DIC into  $CaCO_3$  at a pH range between ~6.0 and 7.0. For sample HW-GP-105, the ~2.0 per mil shift from the mixing line would require 30-50% precipitation of the DIC into  $CaCO_3$  for the same pH range.

Assuming that the isotopic values of the natural DIC has been adequately defined by sample GSW-326, the contribution of biodegraded DIC to each sample can be calculated by a simple mass balance using the  $^{14}C$  results, which is independent of the DIC concentration:

$$\frac{C_{FHC}}{C_M} = 100 - \frac{^{14}C_M}{^{14}C_N}$$

where  $C_{FHC}/C_M$  ratio is the percent FHC contribution to the DIC of the sample, and the subscripts  $M$  and  $N$  designate "measured" and "natural" abundances, respectively. The results from the six samples in this study are tabulated in Table 1. The FHC component contributed to the DIC ranges from 12 to 79%. Because only a small set of analyses are completed at this time, an inventory of total FHC degradation from these isotopic results would be premature. Generation of a statistically significant isotopic data base over the entire effected area could provide a means to calculate the total mineralized FHC in the groundwater, that is a total extent of biodegradation.

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**Table 1: Isotopic Analyses of Dissolved Inorganic Carbon (DIC) of Goundwater from Gas Pad.**

Sample	$\delta^{13}\text{C}$ per mil	$^{14}\text{C}$ pmc	DIC mg/L $\text{HCO}_3$	% FHC
GSW-266	-17.8	62	464	27
GSW-326	-15.5	85	190	0
HW-GP-104	-21.1	50	583	41
HW-GP-105	-20.1	64	514	24
MW-256	-16.7	74	205	12
W-1115	-25.0	18	790	79
GSW-266 duplicate	-17.8	-	*508	-
GSW-326 duplicate	-15.5	-	*212	-

\* Volume calculations in the duplicate analyses had greater uncertainties than with standard methods.



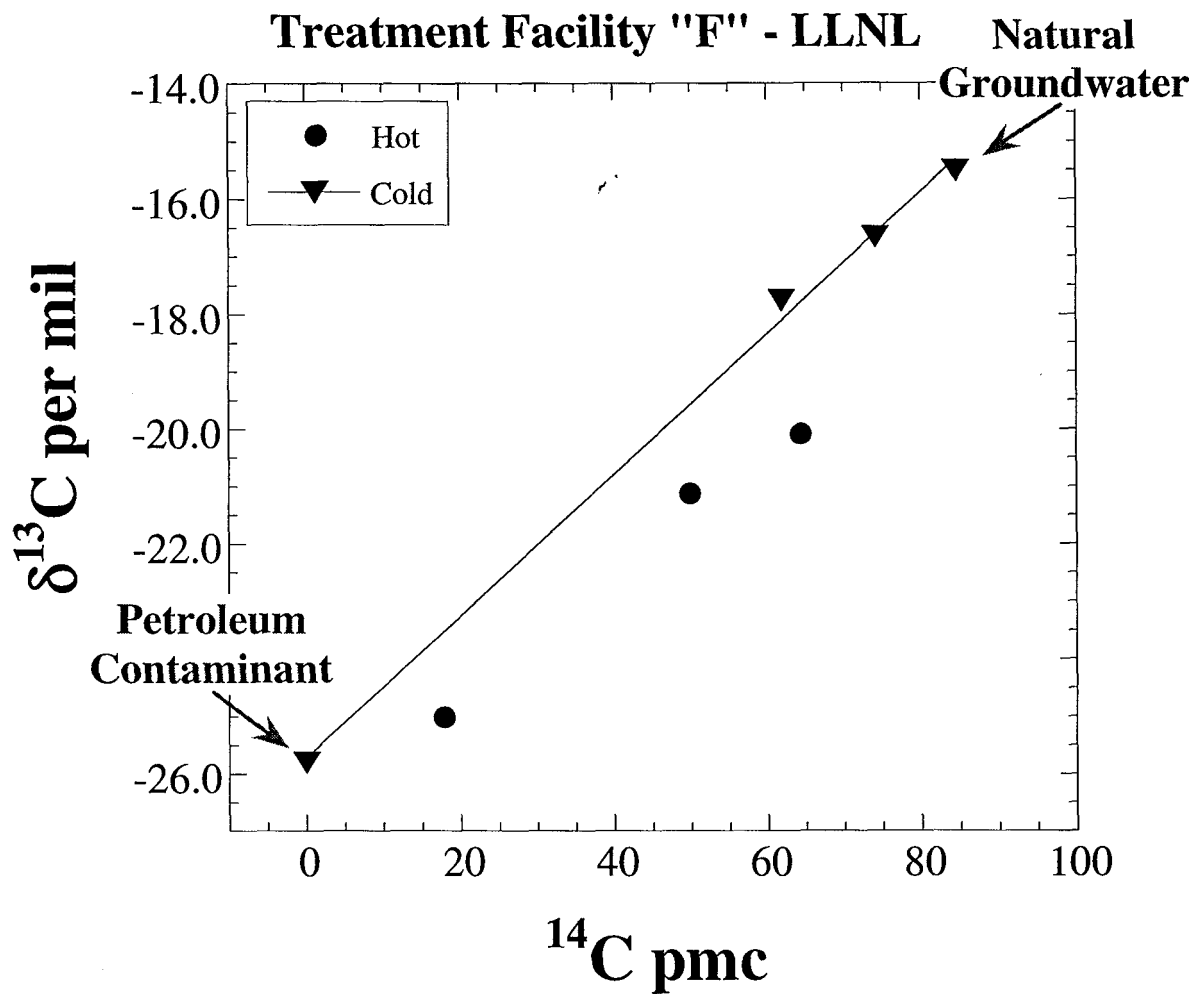


Figure 1