

# **DISSOLVED METHANE IN GROUNDWATER, SAN JUAN BASIN, LA PLATA COUNTY COLORADO: ANALYSIS OF DATA SUBMITTED IN RESPONSE TO COGCC ORDERS 112-156 & 112 -157**

Anthony W. Gorody, Ph. D., CPG-9798 (Universal Geoscience Consulting, Inc.)  
Debbie Baldwin (COGCC) and  
Cindy Scott (Consulting Hydrogeologist)

## **ABSTRACT**

Since the Colorado Oil and Gas Conservation Commission (COGCC) approved orders 112-156 and 112-157 issued on July 11, 2000, operators in the Ignacio Blanco Field of the San Juan Basin have been sampling domestic groundwater wells prior to and following drilling additional optional wells in the Fruitland Formation. The objective of this independent study was to determine whether infill drilling has had any impact on methane concentrations dissolved in groundwater.

The COGCC data base of water samples from the San Juan Basin contained data from 2109 groundwater samples that were collected from 1034 different water wells in the San Juan Basin. There were 292 water well sites with data from samples collected both prior to and after drilling additional optional Fruitland wells. We compared the statistical variance in dissolved methane concentrations prior to and after drilling Fruitland wells with the short term variance observed among 87 paired samples collected from individual sites within sampling lag times of up to 3 months. Results show that 61% of the 292 sites sampled did not contain any dissolved methane. Of the remaining 39% of samples, 21% had pre-drilling concentrations that were greater than post-drilling concentrations; 18% had higher post-drilling concentrations. Only 14 sites contained post-drilling methane concentrations exceeding the calculated maximum value predicted from the short term variability regression analysis. Chromatography and stable carbon and deuterium analyses of dissolved gas from 10 of those samples establish that dissolved methane in groundwater did not originate from the underlying Fruitland Formation. Methane concentrations in the other 4 samples were too small to be characterized.

Infill drilling has had no detectable impact on dissolved methane concentrations found in groundwater throughout the Colorado portion of the San Juan Basin. Observed short and long term changes in dissolved methane concentrations are due to a combination of sampling error, environmental variability, aquifer mixing dilution, mixed biogenic and migrated thermogenic gas sources, and bacterially-mediated methane oxidation.

# INTRODUCTION

The Colorado Oil and Gas Conservation Commission (COGCC) orders 112-156 and 112-157 issued on July 11, 2000, require operators in the Ignacio Blanco Field of the San Juan basin to sample the 2 closest domestic groundwater wells within a ½ mile radius of each planned additional optional well in the Fruitland Formation. The results are treated as “baseline” data used to evaluate potential future impacts on shallow groundwater resources that may result from drilling operations. Each water well then becomes a “monitor” well which is subsequently sampled within one year, three years, and six years after the additional Fruitland well has been drilled.

Several types of analyses are routinely run for each sample collected at a water well site. These include standard field parameters, dissolved major ion concentrations, dissolved methane concentrations, stable carbon and deuterium isotopic analyses of dissolved methane when exceeding concentrations of 2 mg/L, and fixed gas and hydrocarbon chromatography of samples sent for stable isotopic analysis. Some operators, such as BP, supplement the data required by the COGCC with stable isotopic analyses of oxygen and deuterium in water, and stable isotopic analyses of dissolved inorganic carbon. When measured methane concentrations exceed 10 mg/L or increase by 5 mg/L in successive samples, operators are required to determine if the dissolved methane is of thermogenic or biogenic origin. If the stable isotopic values appear thermogenic, then the produced gas from the additional optional Fruitland Formation well is sampled and compared with the dissolved gas composition extracted from the water well sample.

The COGCC’s objectives for this commissioned study were as follows:

1. Determine whether drilling of optional additional wells in the Fruitland formation has had any impact so far on the methane concentration in groundwater;
2. Compare baseline data before drilling with monitor data after drilling;
3. Address causes for observed variability in methane concentrations;
4. Post results on the COGCC web site;
5. Make public presentations of the information.

Groundwater data made available for this study are now part of the COGCC database and include samples collected and data reported since 1990 by various state and federal organizations, and industry. These data are available on line through the COGCC web site. The analyses reported here are based on the data available through March 2004. Up to that time, approximately 2109 data records containing measurements of dissolved methane concentrations in groundwater were available in the COGCC database.

The data used for this study was compiled by various sources including industry operators, the Bureau of Land Management, the United States Geological Survey, and the COGCC (1,2,3). Groundwater samples were collected from 1034 different sites. Of those, there were 445 sites with single methane analyses, and 589 sites with multiple methane analyses. Methane was detected at 674 water well sites (65% of all wells sampled). Detection limits are approximately 0.004 mg/L.

## SHORT TERM VARIABILITY

To evaluate the significance of long term changes in methane concentrations, we first evaluated changes typically observed in water well samples over the short term. The COGCC data base contained 87 pairs of multiple methane concentration measurements from 43 different water wells. The sample data shown in Figure 1 were collected within a maximum period of 95 days. At 32 of the water wells, there were only 2 consecutive analyses available within that period. Each data point represents the lag time between consecutive measurements, and the difference between the maximum and minimum methane concentration values between consecutive samples. Results indicate that short term variability between consecutive samples is large.

Figure 2 shows the results of a least squares regression analysis of the minimum and maximum methane concentration values observed between consecutive sample pairs. The majority, or 64%, of paired samples vary in concentration by less than 1 mg/L, and the short variability in methane concentration increases with increasing methane concentration. This variability is far greater than the analytical detection limit of 0.004 mg/L. On average, we can predict the minimum and maximum methane concentration at any give water well as:

$$\text{EQ.1: Maximum Methane Concentration} = 0.55 * 1.14 \text{ Minimum Methane Concentration}$$

Although there are many data points outside of the 95% confidence level for the regression shown in Figure 2, the mean regression value provides a reasonable estimate for short term variability. We use the regression result to address changes in pre-drilling and post-drilling methane concentrations among water well sites sampled within a period of one year or more.

The Bureau of Land Management and COGCC (2) recognized that measured methane concentrations in samples from a single water well can vary significantly. The authors of the San Juan basin water study (2) attributed such variability to a combination of sampling error, and environmental factors. Sampling variability was attributed to the following factors:

- Differences in the number of water well volumes purged prior to taking samples;
- Intensity of methane effervescence relative to time required to collect a sample
- Laminar vs. turbulent flow through tubing when collecting samples;
- Intensity and timing of mechanical pump action.

Environmental variability was attributed to the following factors:

- Changes in specific yield;
- Changes in barometric pressure;
- And seasonal changes in static water levels;

The BLM-COGCC report concluded that variations of between 50 and 100% should be considered “normal”, whereas changes of an order of magnitude or more should be considered to be outside the “normal” range.

## **METHANE CONCENTRATIONS BEFORE DRILLING AND AFTER DRILLING**

There were 292 sample pairs used for this analysis representing methane concentrations measured prior to and after drilling optional additional Fruitland wells. The average time lag between paired sample measurements was 378 days. 179 of those sample pairs (61%) had consecutive measurements below detection limits. There were 113 sample pairs for which there were detectable amounts of methane measured at least once. Of those, 21% of the samples had methane concentrations that were higher in wells sampled before drilling than after drilling; 18% of the samples had higher methane concentrations after drilling (pie chart inset Figure 3). The approximately equal partitioning of sample pairs with either increasing or decreasing methane concentrations suggests that the observed changes are random.

Using equation 1, we can calculate an expected maximum methane value based on the minimum value of a sample pair. Figure 3 shows that 14 sample pairs with higher post-drilling dissolved methane concentrations exceeded the predicted maximum methane concentration calculated on the basis of the regression equation 1.

There were 16 water wells which were tested a second time after the pre drilling baseline measurement (usually during the second year after new well was drilled). Of these, 10 (63%) did not contain detectable amounts of dissolved methane. Of the 6 water wells with detectable methane, only three had methane concentrations higher than that measured the previous year. Of those, none had maximum methane concentrations above that predicted using the short term regression equation. Of those 6 sites, only site #811 contained more than 2 mg/L of dissolved methane (Figure 4).

## **ADDRESSING THE ORIGIN OF DISSOLVED GAS**

COGCC orders 112-156 and 112-157 do not require either chromatographic analysis of dissolved gas or stable isotopic analysis of methane if concentrations are below 2 mg/L. Of the 14 sample pairs found to exceed the average predicted maximum methane concentration after drilling, only 10 contained at least one sample with 2 mg/L or more of methane. These samples were analyzed using GC chromatography, mass spectrometric analysis of stable carbon isotope ratios in methane and carbon dioxide, and mass spectrometric analysis stable deuterium isotopes in methane.

Stable carbon and deuterium isotopes of methane ( $\text{CH}_4$ ) are used in the oil and gas industry as a diagnostic tool to determine methane origin (5,6,7). Methane originating from the burial of organic sedimentary matter at high temperatures and pressures is defined as thermogenic. Methane originating from bacterial fermentation or from the bacterially-mediated reduction of carbon dioxide is defined as biogenic. Biogenic methane is a common constituent of groundwaters around the world. Approximately 20% of the world's commercial natural gas reserves is biogenic (4).

By convention, isotope ratios are expressed in delta ( $\delta$ ) notation indicating the difference in the molar ratio of the heavy to light isotope of a sample relative to the molar ratio of the heavy to light isotope of an National Bureau of Standards standard (5). In natural gases such as methane

and carbon dioxide, this difference between samples and a standard, for both deuterium and carbon isotopes, is very small and expressed in per mil or parts per thousand. Also by convention, negative values indicate that samples are less heavy than the standard. When comparing samples, differences are expressed as being either relatively enriched or relatively depleted in the heavier isotope.

The range in stable isotope ratios for dissolved methane in water wells far exceeds the range in values reported from producing Fruitland Formation gas wells (Figure 4). The range in carbon isotope ratios for produced Fruitland Formation gases is between delta -53 and -37 per mil, and the range in deuterium isotope ratios is between delta -266 and -179 per mil (as indicated with the shaded ellipse). Among the 10 sites with significant methane concentrations above predicted averages, only two (site 595 and site 895) have carbon and deuterium isotope ratios that are in the measured range of produced Fruitland Formation gas samples throughout the Ignacio Blanco gas field. Stable carbon isotope values of delta -55 per mil have historically been used in this basin as an arbitrary cut off value used to differentiate between more thermogenic and biogenic gas (1,2).

Site #595 is one of the water wells monitored for the optional additional Medina Presentacion A#2 Fruitland Formation gas well. High methane concentrations were present in this well prior to drilling the additional well. Chromatographic and isotopic data are used to show that the dissolved gases in the domestic water well are not derived from the underlying Fruitland Formation (Figure 5). Fruitland Formation gas, sampled from three closest surrounding producing wells in the area, is composed of methane (C<sub>1</sub>) with trace quantities of ethane (C<sub>2</sub>); dissolved gases sampled from the monitor well contain C<sub>1</sub>, C<sub>2</sub>, propane (C<sub>3</sub>), butane (C<sub>4</sub>), and pentane (C<sub>5</sub>). The isotopic composition of the methane in the monitor well is also different from that in the Fruitland Formation. Although the stable carbon isotope ratios are similar to those measured in methane produced from the Fruitland Formation, the stable deuterium isotope ratios differ by more than 22 per mil. Accordingly, the dissolved hydrocarbons found in water well site 595 do not originate from the underlying Fruitland Formation.

Site #895 is one of the monitor water wells for the optional additional Streeter Gas Unit B#1 Fruitland Formation producing gas well. Variably high dissolved methane concentrations were present in this water well prior to drilling the new Fruitland Formation well. In this area of the San Juan Basin, both methane and ethane are present in produced Fruitland Formation gas. Both dissolved methane and ethane are also present in the water well. However, the C<sub>1</sub>/C<sub>2</sub> ratio is significantly different between the two types of samples. The stable isotopes of methane are also significantly different. Thus the dissolved hydrocarbons in the water well do not originate from the underlying Fruitland Formation.

We can also compare the stable isotopic ratio of  $\delta^{13}\text{C}$  in CO<sub>2</sub> in water samples and produced gas samples to evaluate gas origins. Stable isotope values for dissolved gaseous CO<sub>2</sub> used in this study were calculated on the basis of the measured stable carbon isotopic composition of dissolved inorganic carbon (DIC) precipitated from water samples. The  $\delta^{13}\text{C}_{\text{DIC}}$  data were converted to a  $\delta^{13}\text{C}_{\text{CO}_2}$  ratio by using known fractionation factors that account for the partitioning of stable isotopes between the gaseous and dissolved phases of CO<sub>2</sub> (5). Such a conversion allows direct comparison with the  $\delta^{13}\text{C}_{\text{CO}_2}$  ratios obtained when analyzing gaseous CO<sub>2</sub> in produced Fruitland Formation gases.

Gas produced from the Streeter Gas Unit B#1 Fruitland Formation well contains small amounts of CO<sub>2</sub> (0.93% by volume). Here again we can observe that  $\delta^{13}\text{C}$  in CO<sub>2</sub> found dissolved in water well site #895 is typical of soil gas values of the basin, in the range of delta -25

to -27 per mil, and unlike that which is produced from the Fruitland Formation. Accordingly, we can conclude that the dissolved gas found in water well site #895 does not originate from the Fruitland Formation.

## **FACTORS AFFECTING DISSOLVED METHANE CONCENTRATION**

### **Dilution**

Having established that the dissolved gases in site #595 are not derived from the underlying Fruitland Formation, we can use the dissolved major ion data to determine why dissolved methane concentrations appear to have increased systematically at this site since 1994. Samples collected and analyzed from water well site #595 provide an excellent example of the influence that fluid mixing and dilution have on dissolved methane concentrations.

There are 5 sets of available historic data for site #595 that include both measured dissolved methane concentrations and major ion chemistry. The water well now contains high dissolved methane concentrations, and since 1994 the concentrations have steadily increased (Figure 7). Figure 7 also shows how the normalized relative concentration of total alkalinity (%  $\text{HCO}_3^-$ ), dissolved sulfate (%  $\text{SO}_4^{2-}$ ), and dissolved chloride (Cl) ions have varied with time. The change in the relative concentration of dissolved sulfate is inversely proportional to the change in methane concentration.

Shallow aquifers in this area of the San Juan Basin have a vertical distribution of water types. In order of increasing depth, water composition changes from being predominantly composed of  $\text{Na}_2\text{SO}_4$  (dissolved thenardite), to dissolved  $\text{NaHCO}_3$  (dissolved bicarbonate), and finally to dissolved  $\text{NaCl}$  (table salt). Such changes in dominant water types are typically observed over a depth range of 50-300 feet. Accordingly, the aquifers in this area are layered, confined, and not well vertically mixed.

Although most water wells are only screened at the bottom of the well, the permeable gravel pack in a well bore annulus can allow water to enter the screened interval from multiple water-bearing zones. The domestic water well at site #595, 327 feet deep, is among the deeper water wells in the area. Since 1994, the relative amount of sodium sulfate has continually decreased from a value of 40% of the total dissolved anion milliequivalents to 10% of the total dissolved anion milliequivalents. Conversely the relative amount of sodium chloride has increased proportionately from 40% to 70% of the total dissolved anion milliequivalents. Thus relative to sulfate, the sodium chloride concentration has increased by 175% since 1994. Over the same period, the measured dissolved methane concentration has increased by 177% from an average value of 13 mg/L to an average value of 23 mg/L. This proportionate relationship clearly shows that the more saline  $\text{NaCl}$  type waters entering this well carry dissolved methane, whereas the  $\text{NaHCO}_3$  and  $\text{Na}_2\text{SO}_4$  type waters do not. Chemical analysis of the water allows us to conclude that since 1994, the amount of  $\text{Na}_2\text{SO}_4$  type fluids available to dilute the methane-bearing  $\text{NaCl}$  type waters has systematically decreased. Mixing of fluids, sourced from different water-bearing layers in a well bore, can therefore significantly affect methane concentrations.

### **Methane Oxidation**



Bacterially-mediated methane oxidation is a common phenomenon observed in oceans, shallow surface waters, and aquifers throughout the world (7,8,9). Different bacterial groups oxidize methane via different biochemical pathways depending on whether dissolved oxygen, or bound oxygen in sulfate is used for their metabolism. It is beyond the scope of this paper to discuss the source of oxygen used by subsurface bacteria to oxidize methane. However, available data indicate that anaerobic methane oxidation in the presence of dissolved sulfate ions is the dominant metabolic mechanism in water well environments throughout the San Juan basin. Ratios of dissolved O<sub>2</sub>/Ar in most domestic water well samples from this area tend to be extremely low, indicating that the domestic wellbore environment tends to be stagnant.

Bacterially-mediated methane oxidation is recognized on the basis of a direct relationship between decreasing methane concentrations, enrichment of heavy stable carbon and deuterium isotope ratios in residual methane, and a corresponding depletion of heavy stable carbon isotope ratios of carbon dioxide (CO<sub>2</sub>) (7,8,9). Bacterial consumption rates are greater for molecules of methane containing lighter isotopes than for those containing heavier isotopes. This phenomenon, referred to as a kinetic fractionation process, occurs because the chemical bond between atoms containing heavy isotopes is stronger and requires more energy to break than the bond between atoms containing lighter isotopes. Methanotrophic bacteria generate CO<sub>2</sub> as part of their metabolic process. Because such bacteria preferentially consume the light isotopes of methane, the carbon dioxide they produce becomes progressively depleted in heavy isotopes.

At site 895, the chemical composition of water containing the lowest concentration of dissolved methane, contains sulfate ions, whereas the composition of water containing the highest concentration of dissolved methane does not contain sulfate. Figure 6 shows a trend of decreasing methane concentration, increasing  $\delta^{13}\text{C}_{\text{Methane}}$  and  $\delta\text{D}_{\text{Methane}}$  ratios, and decreasing  $\delta^{13}\text{C}_{\text{CO}_2}$  ratios (inset graph B). Thus methane oxidation by methanotropic bacteria accounts for the additional loss of methane that cannot be explained by mixing alone.

The effects of bacterially-mediated methane oxidation are evident in most water well sample data for which there are one or more pairs of samples with stable isotopic analyses. Figure 8 shows a reduced three dimensional plot of stable isotope ratios in methane, and methane concentration. The vertical z axis of dissolved methane concentration is represented with contour lines generated by fitting a quadratic surface through the available methane concentration data for each sample point. Also shown on Figure 8, are white arrows connecting one or more sample points obtained at various times from a unique water well sample site. Figure 8 allows us to observe that the shift towards lighter stable isotope ratios in all white arrow sample pairs occurs in the direction of decreasing methane concentration.

Figure 9 shows that the characteristic enrichment in stable carbon and deuterium ratios resulting from bacterially-mediated methane oxidation can be approximated as follows:

$$\text{EQ 2: Change in } \delta\text{D}_{\text{Methane}} = 7.4 * \text{Change in } \delta^{13}\text{C}_{\text{Methane}} + 2 \text{ per mil}$$

Although there is scatter in the data, the Pearson's correlation coefficient for this regression is significantly high. The regression value compares well with other published empirical and laboratory data (8,9).

The observed scatter in data shown in Figure 9 is surprisingly low considering the dynamic well bore environmental conditions affecting dissolved methane concentrations. A permeable, uncemented water well annulus provides the cross flow environment needed to allow reduced fluids carrying methane to mix with fluids carrying either the free or bound oxygen that

methanogens need to oxidize methane. The amount of residual, oxidized methane present at any given time can be expected to vary significantly. For example, when the rate of methane oxidation is greater than the rate of fresh methane influx, then dissolved methane concentrations will decrease and the effects of kinetic fractionation will be most evident. On the other hand, when the rate of fresh methane influx is greater than the rate of oxidation, then methane concentrations will appear to increase and the effects of kinetic fractionation will be less evident. Mixtures of oxidized and fresh aquifer methane account for much of the scatter of stable isotopic data observed among water sample pairs.

## **Mixed Methane Sources**

There is third source of variability in methane stable isotope ratios observed among water sample pairs. Up to this point, our discussion has been predicated on the assumption that a single water-bearing interval provides a source of methane in a water well. However, there are areas in the basin where both thermogenic and biogenic methane sources are present. Figure 8 shows a black arrow connecting the stable isotope ratios from consecutive samples collected from one water well. This arrow clearly shows the influence of mixing between thermogenic (more positive stable isotope ratios) and biogenic (more negative stable isotope ratios) methane sources. It is likely that such a trend in sample pairs is indicative mixing between water containing dissolved biogenic methane and water containing dissolved thermogenic methane.

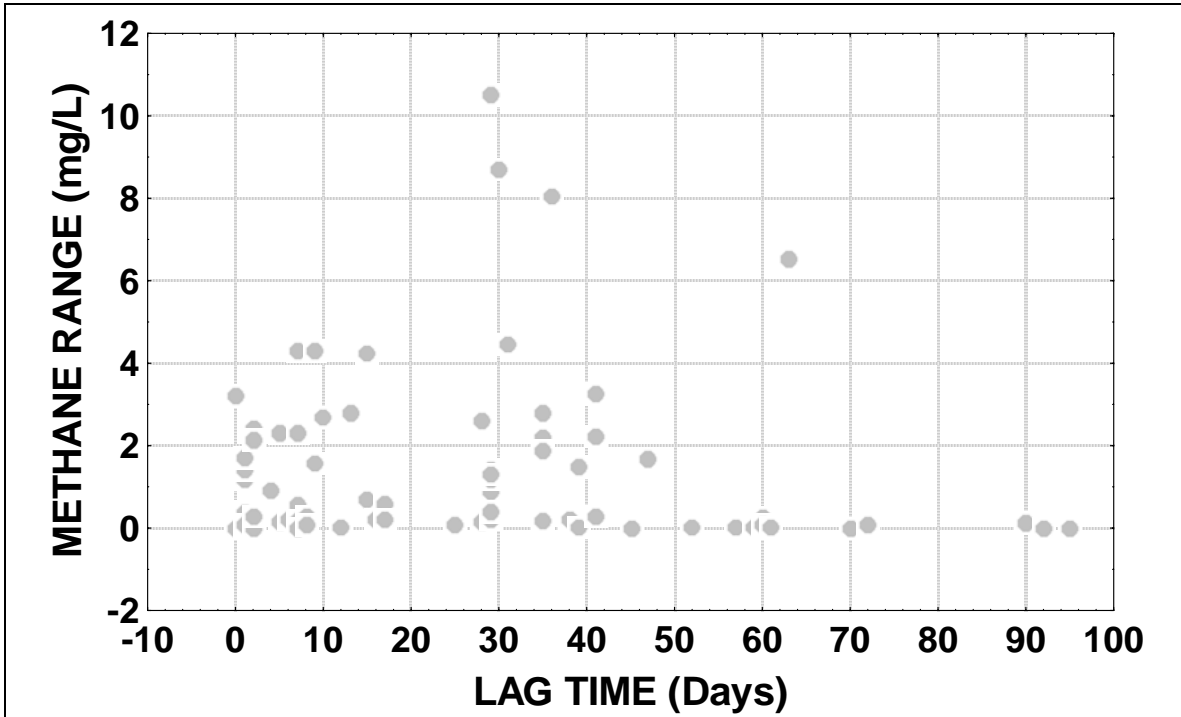
## **CONCLUSIONS**

The results of this study demonstrate that multiple types of analyses are required to address whether domestic water wells are being impacted by drilling operations in the San Juan basin. At a minimum, these include field parameters measured on site, (e.g. water temperature), analysis of the dissolved major ion concentration in water samples, analysis of dissolved methane concentrations, stable isotopic analyses of dissolved methane and carbon dioxide in water samples, and stable isotopic analysis of methane and carbon dioxide produced from producing Fruitland Formation gas wells. Together, such analyses can be effectively used to determine whether drilling additional optional Fruitland Formation wells has impacted water quality in shallow aquifers. As demonstrated here, the same methods could be used in any basin to evaluate the potential impact of oil and gas operations on shallow groundwater resources.

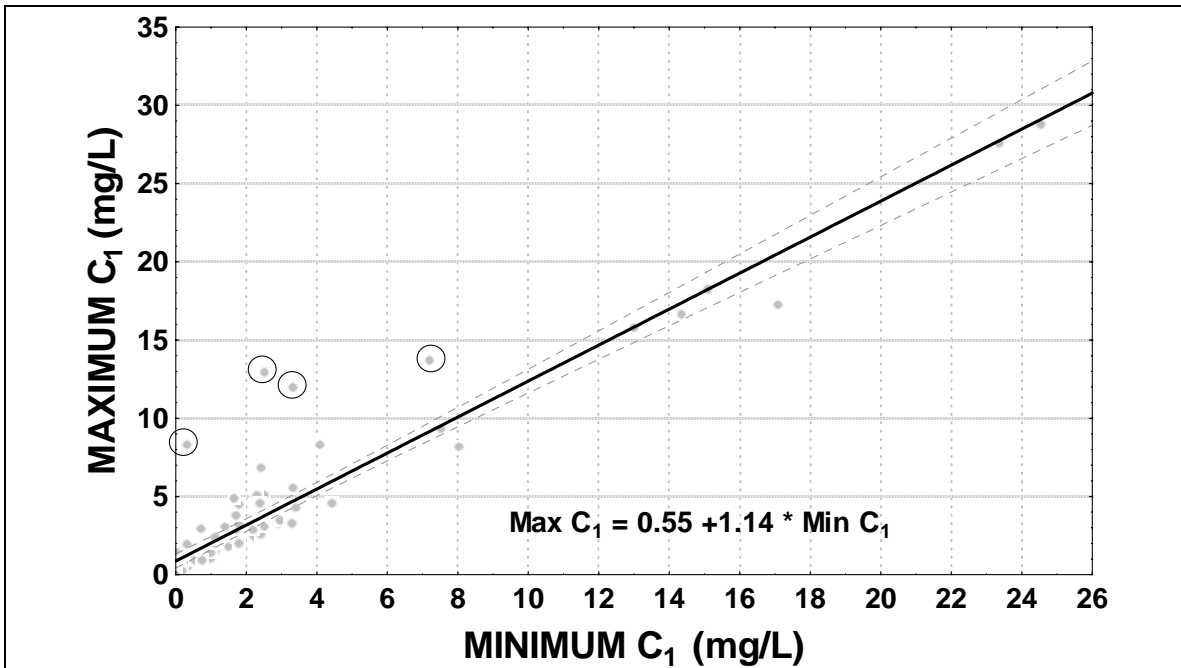
Based analyses of pre-drilling baseline and post-drilling water well samples, predominantly acquired within a year after a Fruitland well was drilled, the results of this study demonstrate that production operations have not had any detectable impact shallow groundwater resources in the Colorado portion of the San Juan Basin. Observed short and long term changes in dissolved methane concentrations are due to a combination of sampling error, environmental variability, aquifer mixing dilution, mixing of biogenic and thermogenic gas sources, and bacterially-mediated methane oxidation.



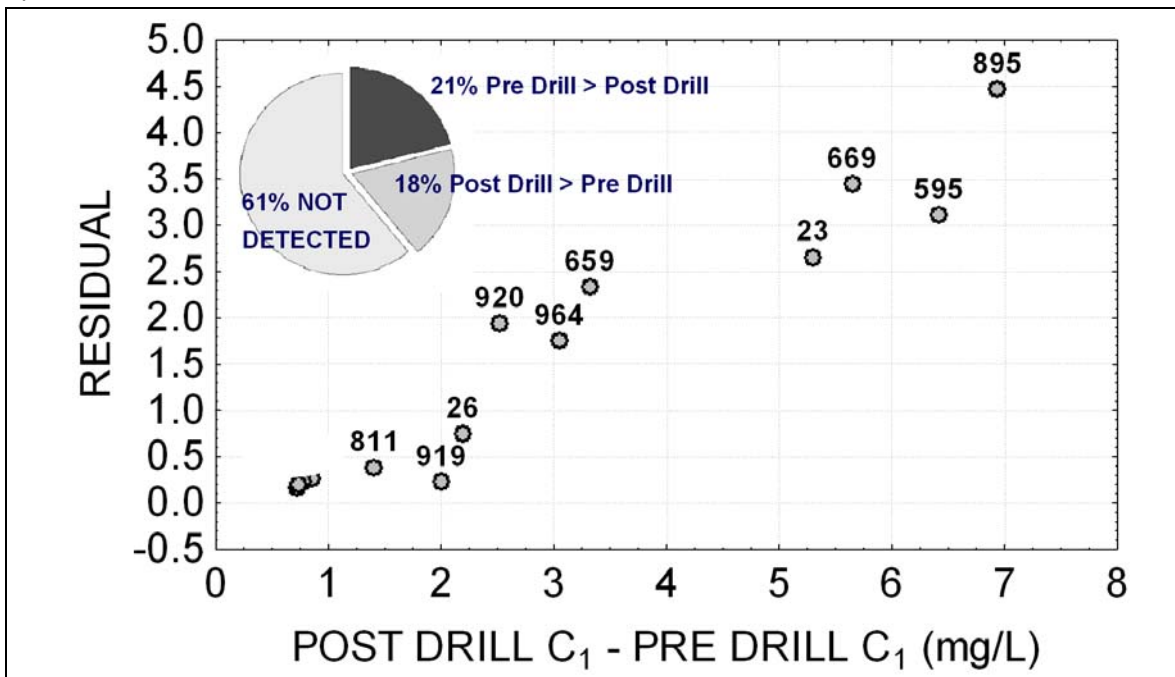
# FIGURES



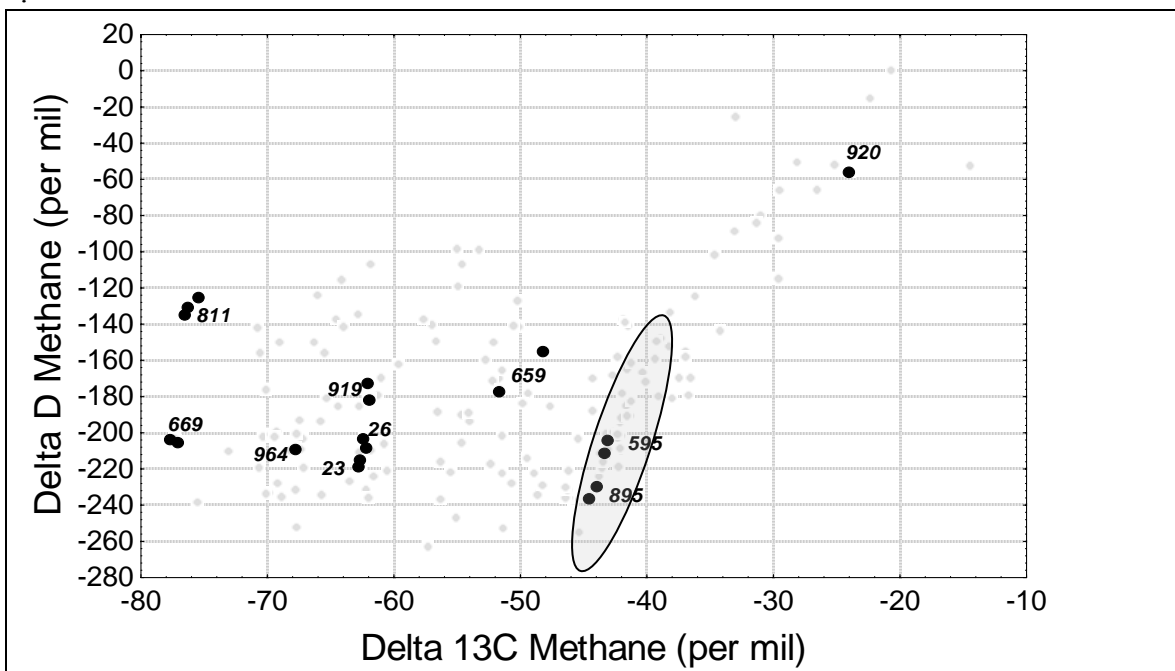
**Figure 1.** Difference between minimum and maximum methane concentration values in water well sites sampled multiple times within a period of 95 days. Sample pairs with consecutive non-detect values are not included.



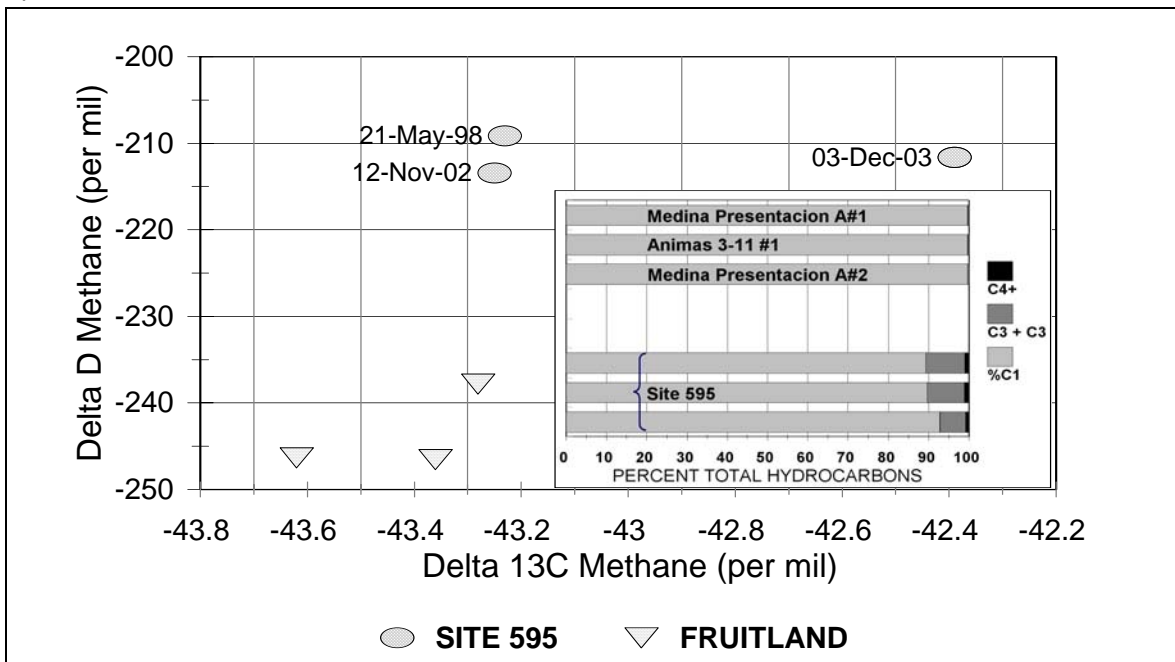
**Figure 2.** Regression analysis of the data shown in Figure 1 with 4 large outliers (circled) removed. The dotted line represents the 95% confidence level for the regression.



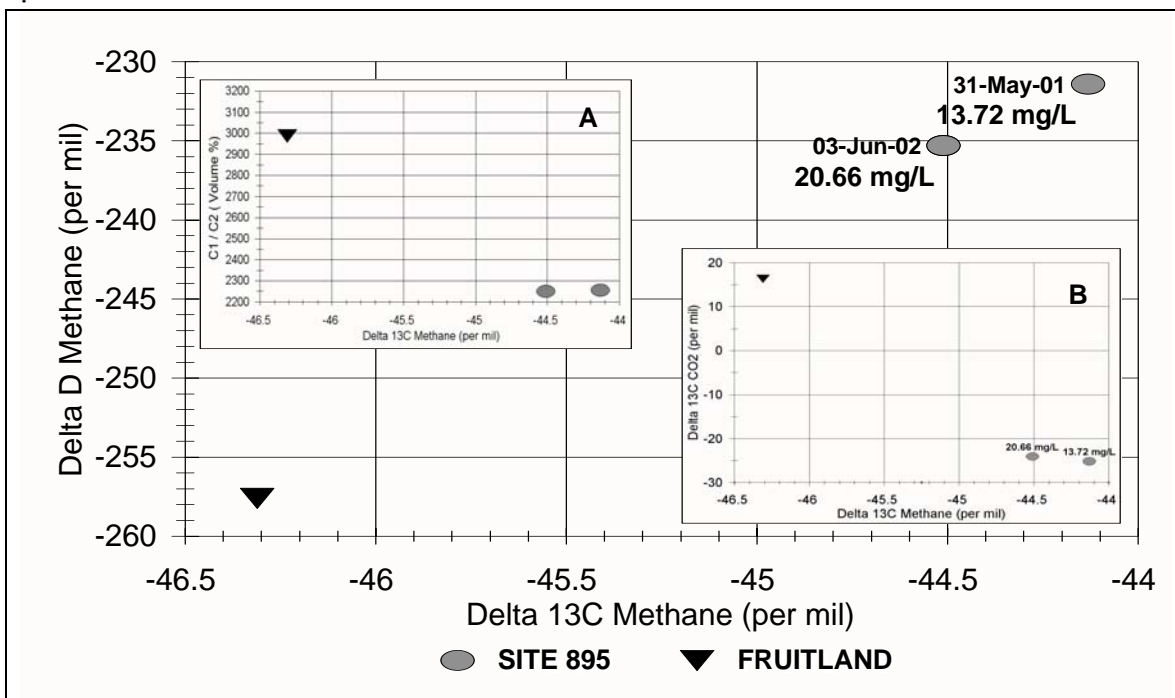
**Figure 3.** The difference in methane concentration between sample pairs from a single well site plotted against the residual value calculated on the basis of the regression equation in Figure 2. The residual value is the difference between the actual maximum methane concentration and the predicted value. Also shown is a pie chart showing the change in methane concentration observed among 292 sample pairs collected within an average period of 357 days.



**Figure 4.** Stable carbon and deuterium isotope ratios for the 10 sample sites with higher post-drilling methane concentrations are highlighted within the values measured for all samples in the COGCC data base. The range in values of methane from the Fruitland Formation generally falls within the shaded ellipse.



**Figure 5.** The dissolved gas composition (inset) and the stable isotopic composition of methane at site 595 does not correspond to that in underlying Fruitland Formation gas.



**Figure 6.** The dissolved gas composition (inset) and the stable isotopic composition of methane and CO<sub>2</sub> at site 895 does not correspond to that in underlying Fruitland Formation gas. Decreasing methane concentrations correspond with more positive (enriched) stable carbon and deuterium ratios in methane, and more negative (depleted) stable carbon isotope ratios in CO<sub>2</sub>.

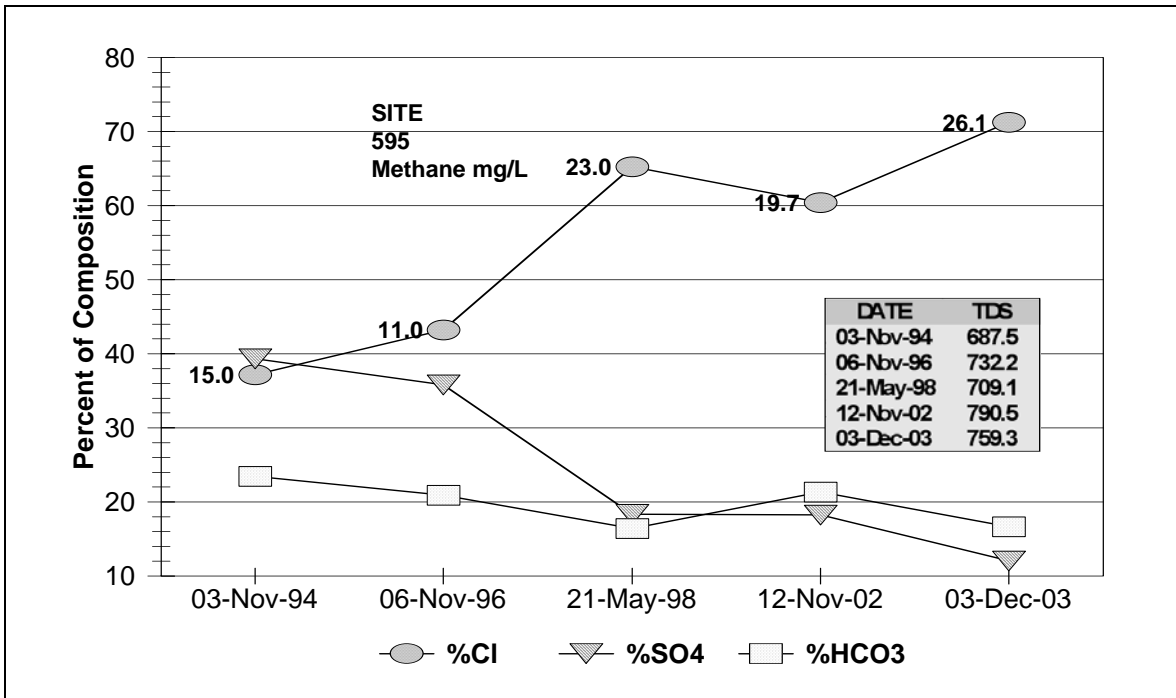


Figure 7.

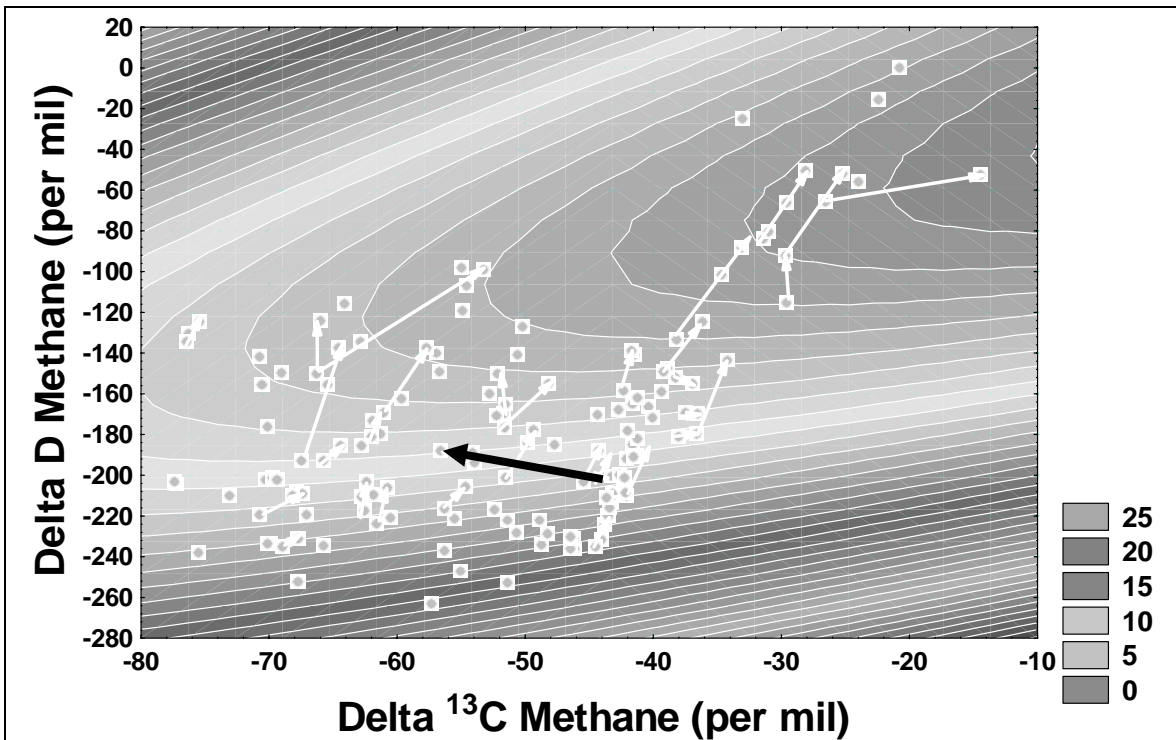
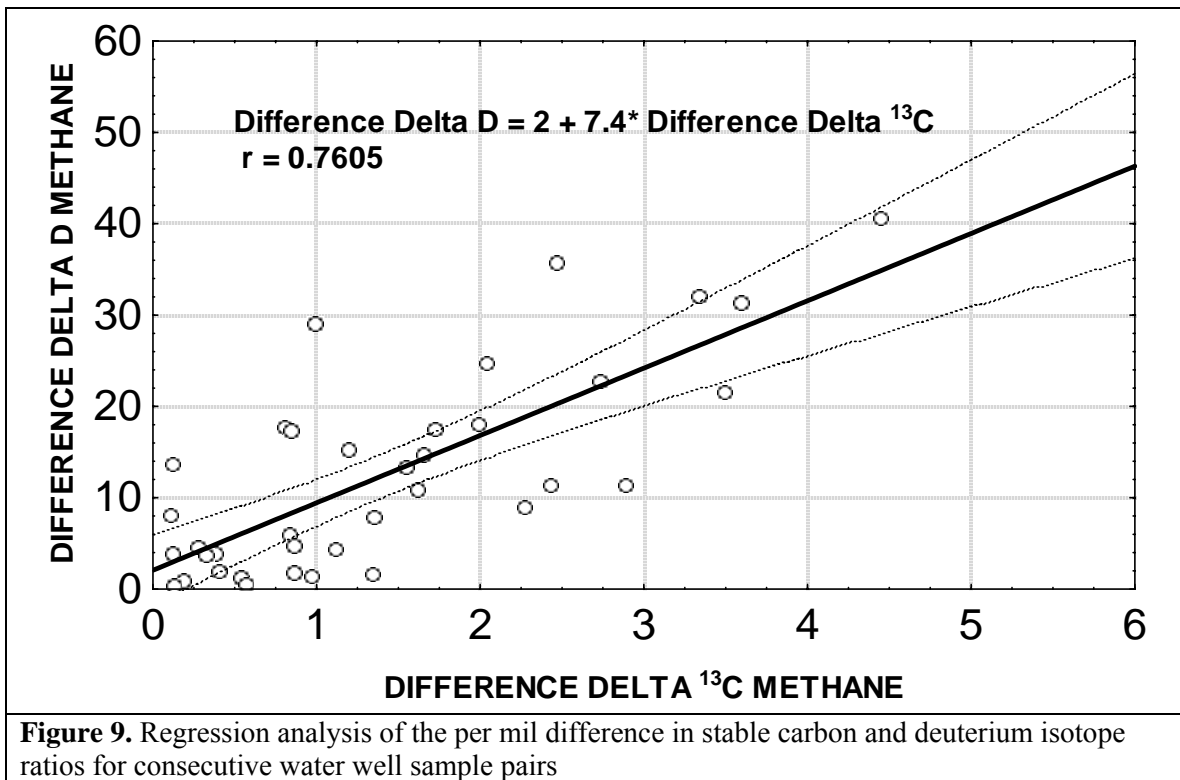


Figure 8. Quadratic surface of decreasing methane concentration. Stable isotope ratios from paired samples collected in a water well site are indicated with connecting arrows.



## REFERENCES CITED

1. Chafin, D. T., "Sources and migration pathways of natural gas in near-surface groundwater beneath the Animas River valley, Colorado and New Mexico," *USGS Water Resources Inv. Rpt. 94-4006*, 56 p. (1994).
2. Bureau of Land Management and Colorado Oil and Gas Conservation Commission, "1994 Groundwater monitoring San Juan Basin, La Plata County, Colorado: Comprehensive infill testing including data obtained in the Pine River Fruitland Coal Outcrop investigative study, Final Report with tables and appendices", (1994).
3. Robson, S. G., and Wright, W. G., "Ground-water resources of the Florida Mesa area, La Plata County, Colorado", *USGS Water-Resources Investigations Rpt. 95-4190*, (1995).
4. Rice, D. D., "Biogenic gas: controls, habitats, and resource potential", In: *The Future Of Energy Gases*, Howell, D. G. (ed.), U. S. Geol. Surv. **Prof. Paper 1570**, 583-606, (1993).
5. Clark, I. D., and Fritz, P., *Environmental Isotopes In Hydrogeology*, Lewis Pub., (1997).
6. Prinzhofer, A., Mello, M. R., and Takaki, T., "Geochemical characterization of natural gas: a physical multivariable approach and its applications in maturity and migration estimates", *AAPG Bull.*, **84**, 1152 – 1172 (2000).

7. Whiticar, M. J., "Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane," *Chem. Geol.*, **161**, 291 – 314,(1999).
8. Zyakun, A. M., "Potential of  $^{13}\text{C}/^{12}\text{C}$  variations in bacterial methane in assessing origin of environmental methane", *AAPG Mem.* **66**, 341-352, (1996).
9. Coleman, D. D., Risatti, J. B., and Schoell, M., "Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria," *Geochim. et Cosmochim. Acta*, **45**, 1033 -1037 (1981).