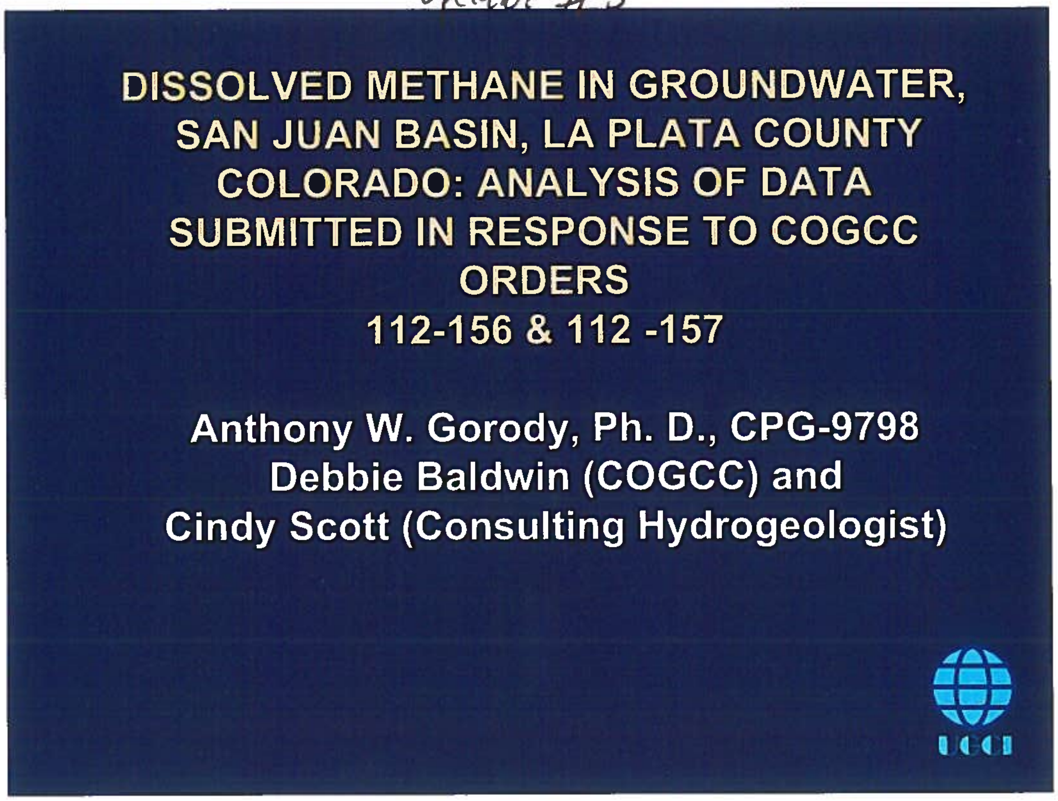
Operator #5

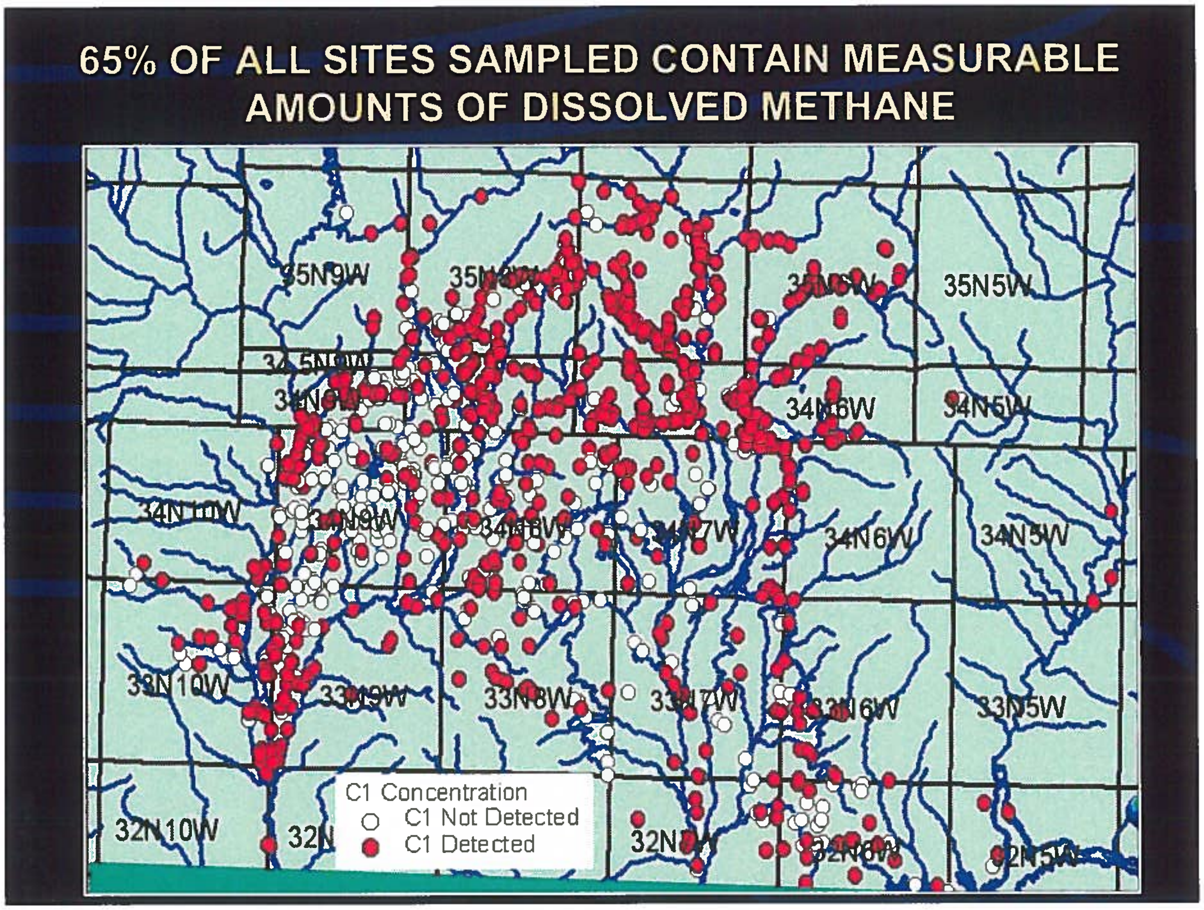


EXECUTIVE SUMMARY

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 study was to determine whether drilling optional additional wells on a 160 acre spacing has had any impact on the dissolved methane commonly found in groundwater. Field data, major ion analyses, gas chromatography, and stable isotopes of water, dissolved and produced carbon dioxide, and dissolved and produced methane, have been compiled in a COGCC database for all samples collected and analyzed. Results to date show that drilling of optional additional wells has had no detectable impact on the dissolved methane concentrations found in groundwater throughout the Colorado portion of the San Juan Basin. We demonstrate that observed short and long term changes in dissolved methane concentrations are due to a combination of sampling variability, environmental factors, mixing dilution, and methane oxidation mediated by bacteria.

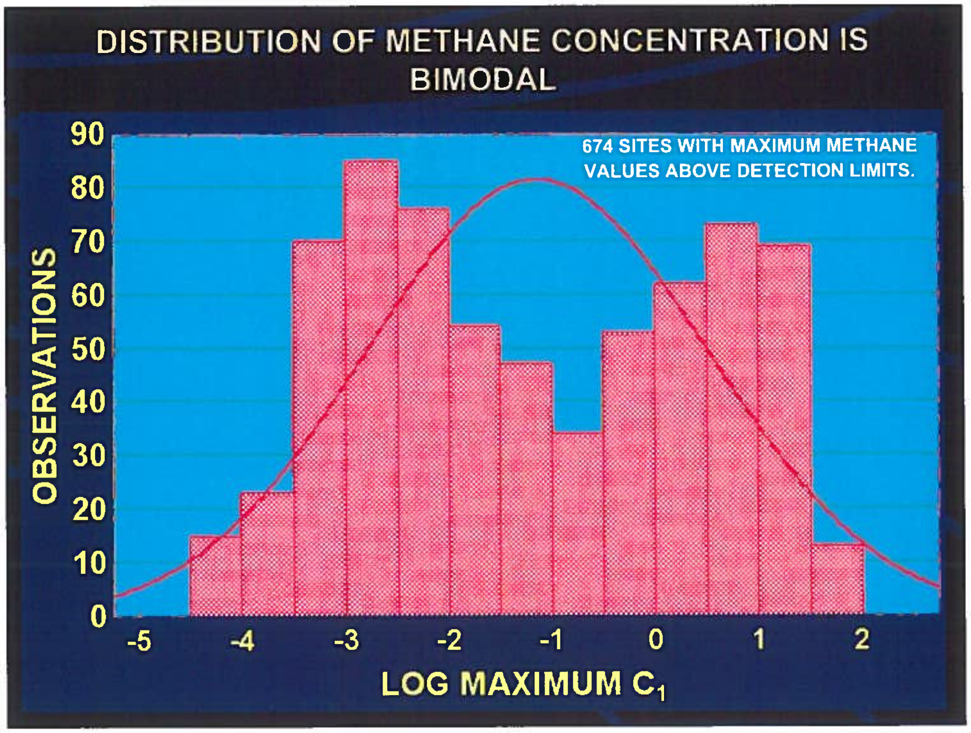
PROJECT OBJECTIVES

- DETERMINE WHETHER DRILLING OF OPTIONAL ADDITIONAL WELLS IN THE FRUITLAND FORMATION HAS HAD ANY IMPACT ON THE METHANE CONCENTRATION IN GROUNDWATER
  - COMPARE BASELINE DATA BEFORE DRILLING WITH MONITOR DATA AFTER DRILLING
  - ADDRESS CAUSES FOR OBSERVED VARIABILITY IN METHANE CONCENTRATIONS
- POST RESULTS ON THE COGCC WEB SITE
- MAKE PUBLIC PRESENTATIONS OF THE INFORMATION

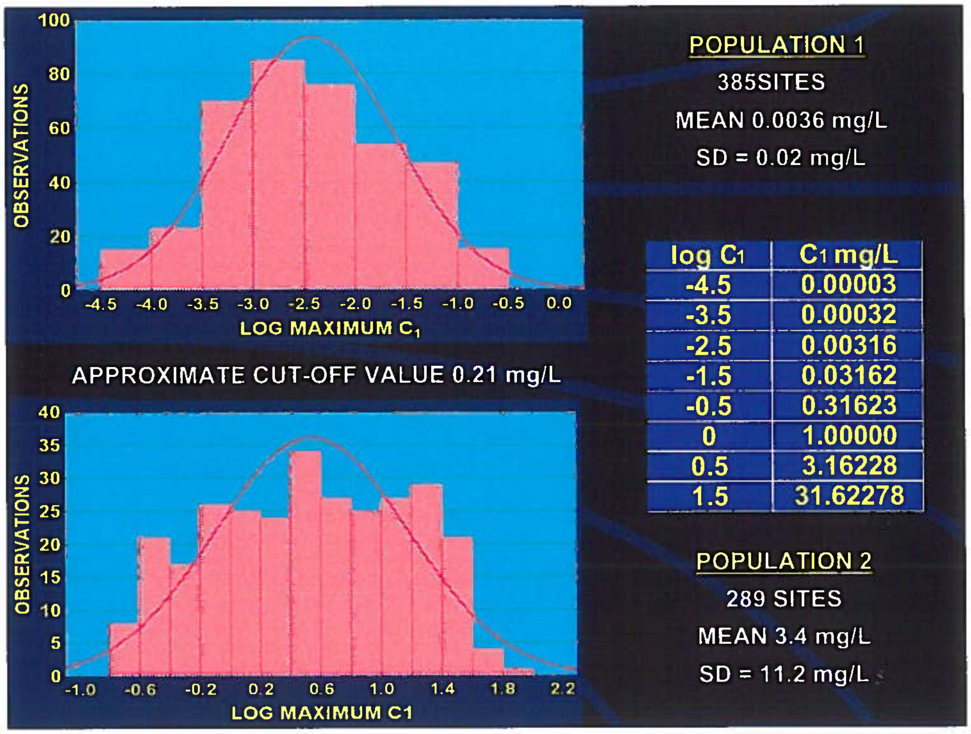


Groundwater data made available for this study are now part of the COGCC database and include samples collected and data reported since 1990 by various state and federal organizations, and industry. As of March 2004, approximately 2109 data records containing measurements of dissolved methane concentrations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

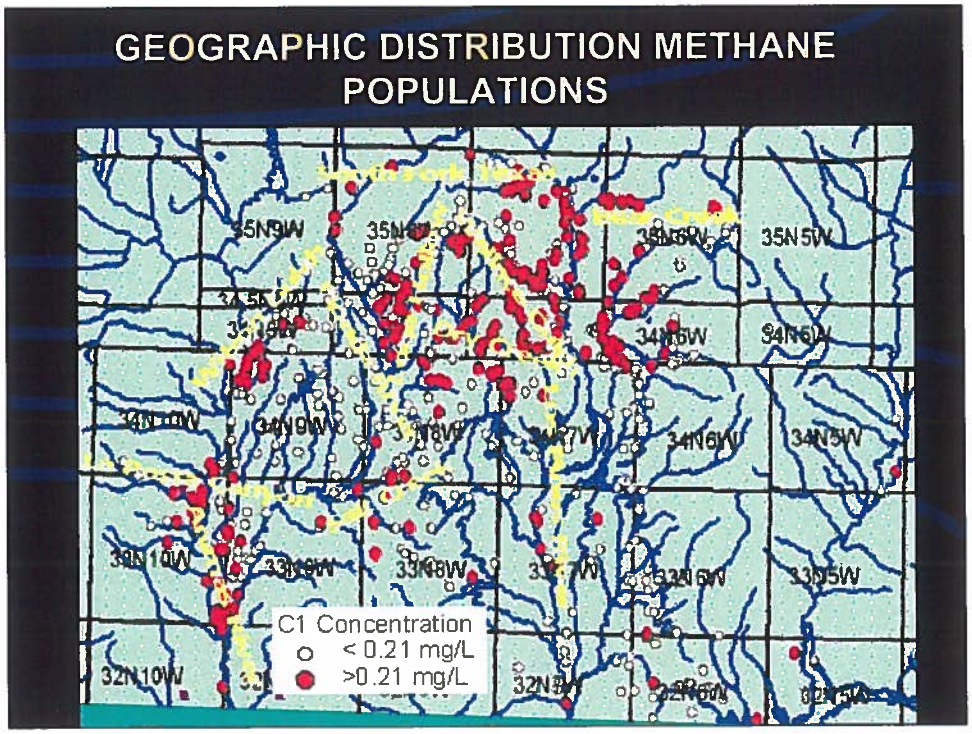
Groundwater samples have been collected from 1034 different sites. Of those, there are 445 sites with single methane analyses, and 589 sites with multiple methane analyses. Methane was detected at 674 water well sites (65% of all wells sampled).



This histogram was generated using either a single available value or the maximum value of multiple measurements at each of the 674 water wells containing methane concentrations above detection limits. Detection limits are approximately 0.00004 mg/L. Methane concentrations were converted to log-normal values because dissolved methane concentrations tend to be log-normally distributed. The results exhibit a bimodal distribution.

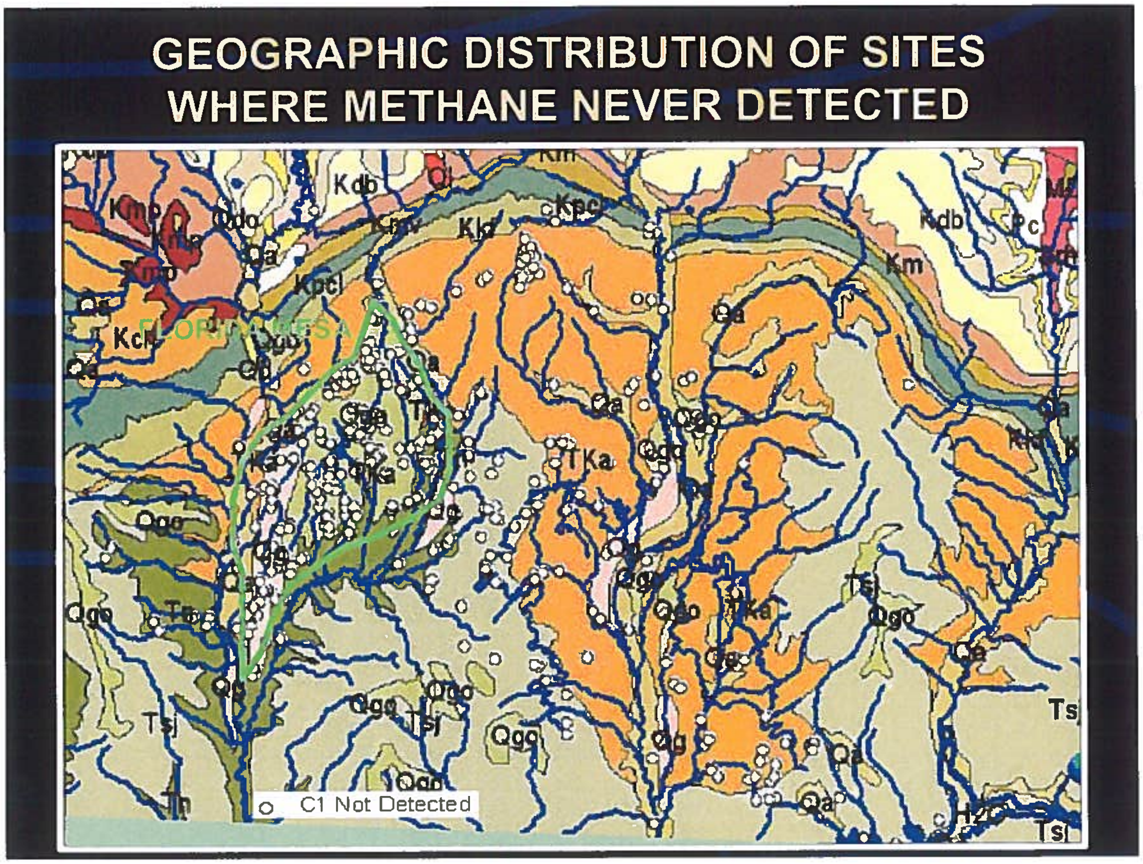


A cut off value of 0.21 mg/L (-0.678 log scale) provides a reasonably good arbitrary value for distinguishing between the two populations evident in the previous histogram. Population 1 appears to have a log-normal distribution of values with a mean value of 0.0036 mg/L and a standard deviation of 0.02 mg/L. The second population of dissolved methane concentrations is more broadly distributed with a mean of 3.4 mg/L and a standard deviation of 11.2 mg/L. Only samples containing more than 2 mg/L of dissolved methane are routinely analyzed to determine the origin of dissolved gases using chromatographic and stable isotopic analytical methods. Accordingly, the results of such analyses are entirely derived from the second population of dissolved methane concentrations.



Water wells containing methane concentrations greater than 0.21 mg/L occur along drainage valleys. In particular, clusters of water wells with high methane occur along the upper reaches of the Los Pinos River drainage valley and its tributaries north of the Ute Line (Los Pinos River, South Fork of the Texas Creek, Wallace Gulch, Bear Creek, Beaver Creek, Saul's Creek, Dry Creek, and Hartman Canyon), the upper reaches of the Florida River and its Lone Hollow tributary, and along the Animas River valley, with a large number of sites occurring just south of the Ute line at the confluence with Wilson Gulch, and further south along La Posta Canyon and the Florida River.

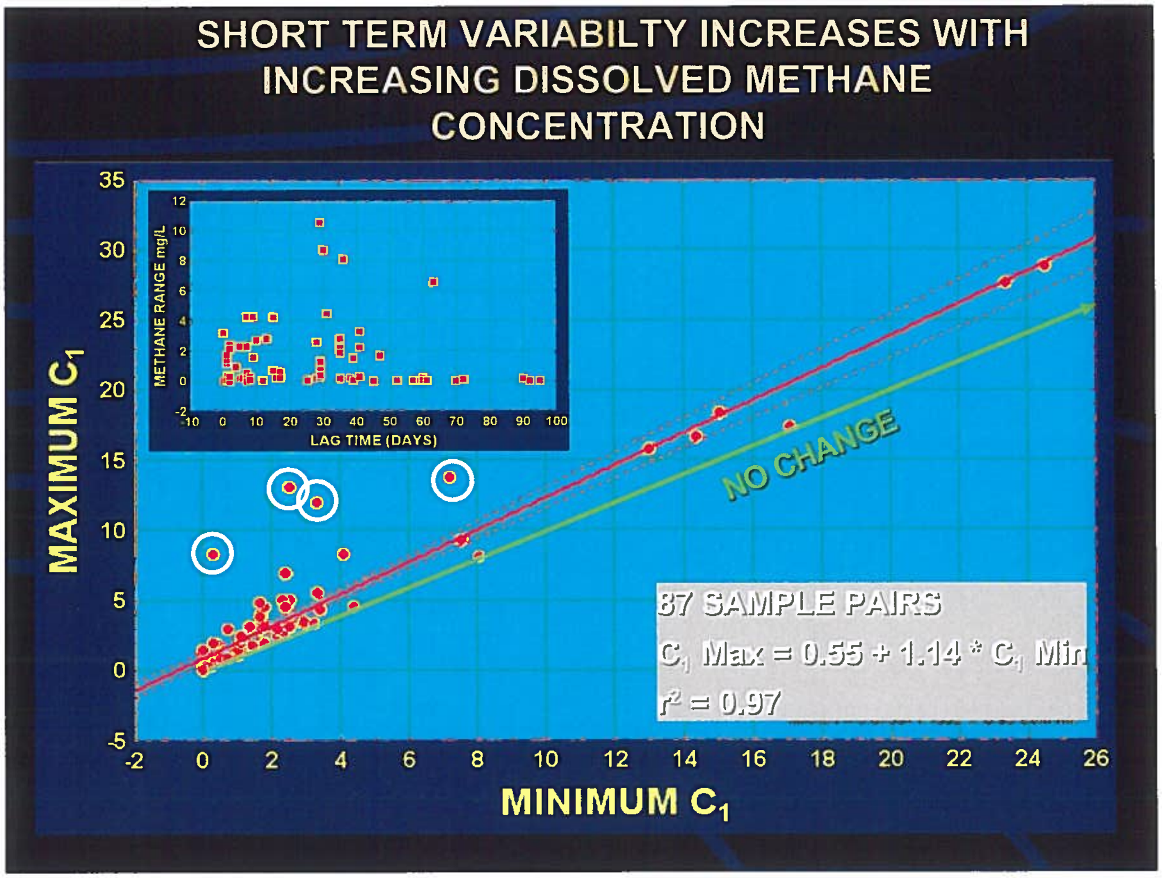
Water wells containing dissolved methane concentrations greater than 0.21 mg/L are conspicuous along the outcrop belt of the Fruitland Formation, along the South Fork of Texas Creek, and along Bear Creek which flows along the outcrop belt of the Lewis Shale.



The distribution of the 360 water wells where dissolved methane was never detected in groundwater is concentrated along the Florida Mesa. Most of the water wells there are completed in Quaternary gravels and fluvial terraces. Infiltration of irrigation water applied on top of the mesa is the primary source of recharge to groundwater in this area.

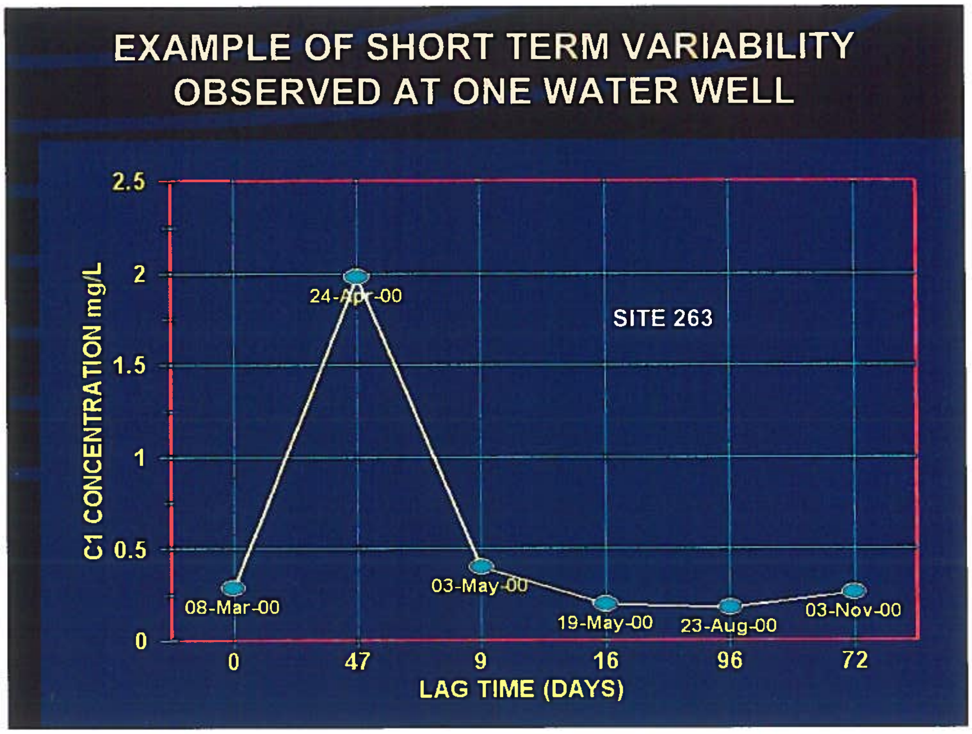
APPROACH USED TO EVALUATE THE POTENTIAL IMPACT OF ADDITIONAL DRILLING ON METHANE CONCENTRATIONS

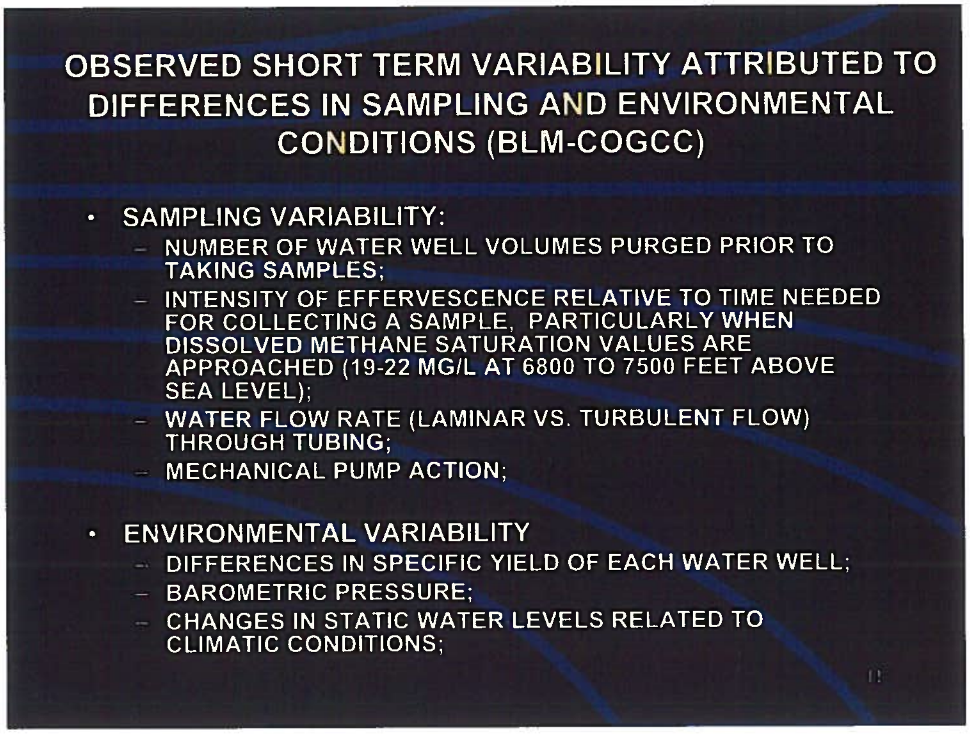
- EXAMINE SHORT TERM VARIABILITY
- EXAMINE HISTORIC VARIABILITY
- COMPARE SHORT TERM AND HISTORIC VARIABILITY WITH PRE-DRILLING VS. POST DRILLING VARIABILITY
- QUANTIFY AVERAGE EXPECTED VARIABILITY
- IDENTIFY SITES WHERE POST DRILLING DISSOLVED METHANE CONCENTRATIONS EXCEED AVERAGE EXPECTED VARIABILITY
- CHARACTERIZE THE AQUIFER AND DISSOLVED METHANE WHERE CONCENTRATIONS EXCEED AVERAGE EXPECTED VARIABILITY



87 pairs of consecutive methane concentration measurements from 43 different water wells were selected for this graph. Sample pairs with consecutive non-detect values were not included. The lag time between consecutive analyses is illustrated in the inset graph. At 32 of the water wells, there were only 2 consecutive analyses available within a period of less than 95 days (3 months). Maximum and minimum values of methane concentration for each consecutive pair of analyses are plotted in this figure. The regression equation excludes the four sample pairs which are treated here as outliers.

The majority of paired samples, or 64%, vary in concentration by less than 1 mg/L. As illustrated, the slope of a regression line between minimum and maximum paired values is greater than 1. Variability increases with an increasing amount of methane dissolved in water at any site. Such variability is far greater than the analytical detection limit of 0.00004 mg/L.


EXAMPLE OF SHORT TERM VARIABILITY
OBSERVED AT ONE WATER WELL
C1 CONCENTRATION mg/L
2.5
2
1.5
1
0.5
0
24-Apr-00
SITE 263
08-Mar-00
03-May-00
19-May-00
23-Aug-00
03-Nov-00
0
47
9
16
96
72
LAG TIME (DAYS)



The Bureau of Land Management and COGCC (BLM-COGCC, 1994) identified the following factors influencing variability in methane concentrations in the San Juan Basin water wells:

SAMPLING VARIABILITY:

- number of water well volumes purged prior to taking samples;
- intensity of effervescence relative to time needed for collecting a sample, particularly when dissolved methane saturation values are approached (19-22 mg/L at 6800 to 7500 feet above sea level);
- laminar vs. turbulent flow through tubing;
- mechanical pump action.

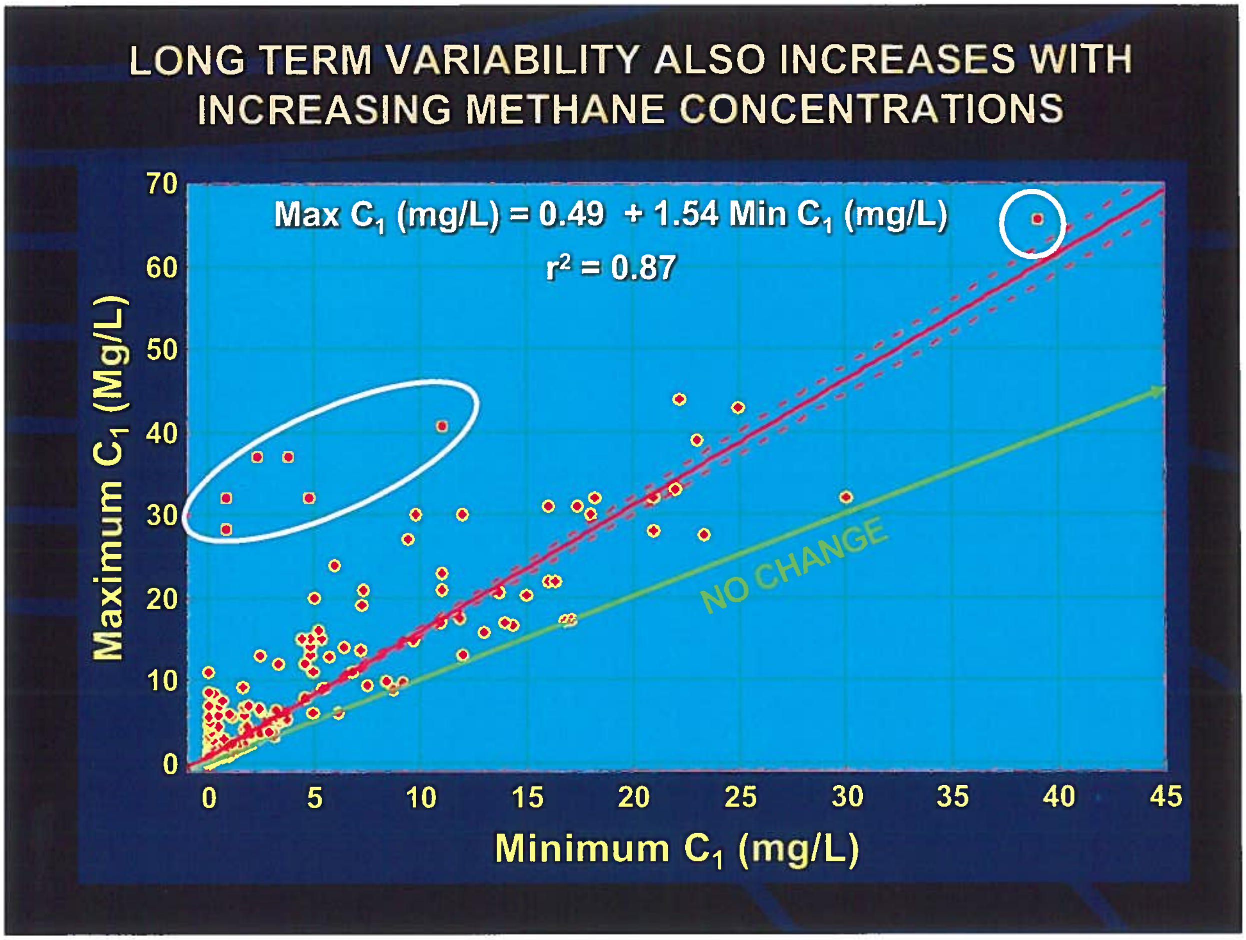
ENVIRONMENTAL VARIABILITY

- differences in specific yield of each water well;
- barometric pressure
- changes in static water levels related to climatic conditions;

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 significant.

Sampling variability can be reduced by following specific protocols as follows:

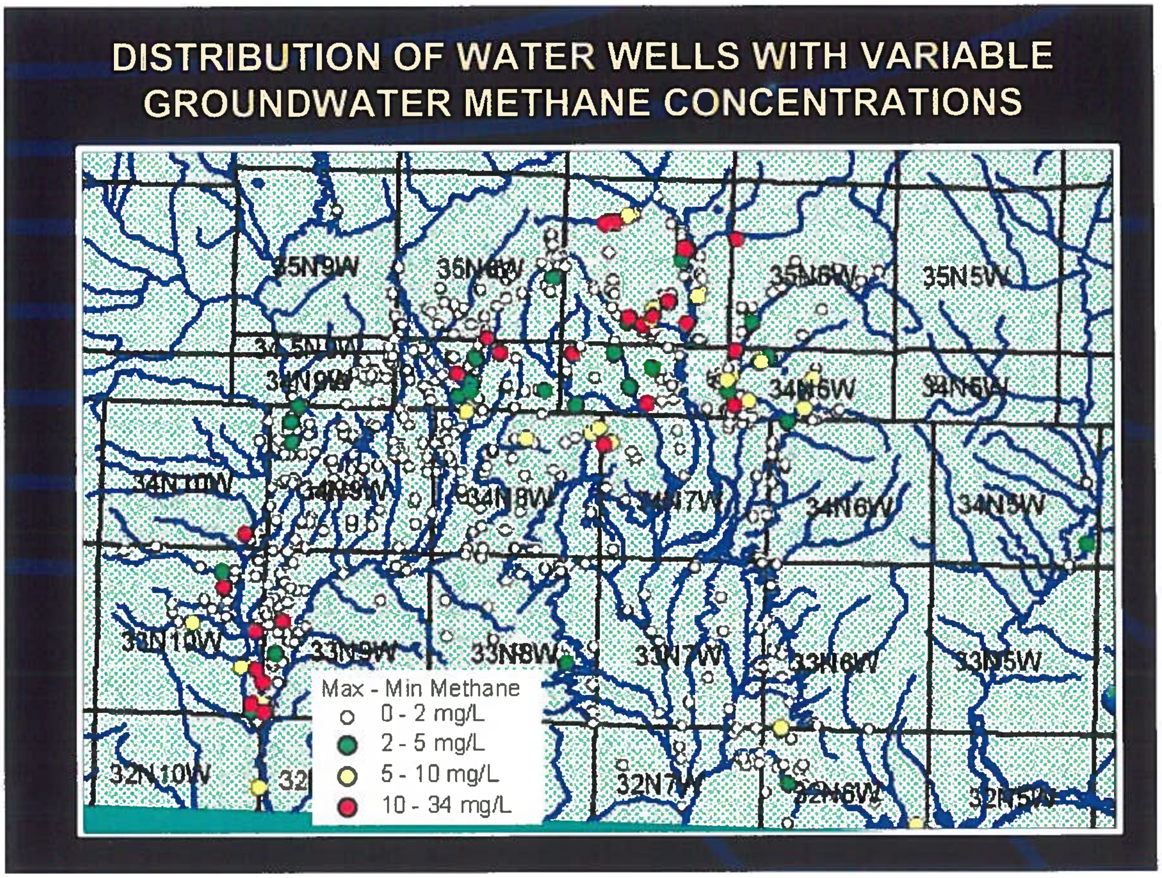
1. Purge water wells by three well bore volumes, or until field parameters such as temperature, pH, and conductivity reach equilibrium (in some cases, well yield may be insufficient to allow purging);
2. Reduce water flow to between 0.1 to 0.5 gallons per minute for at least 15 minutes before collecting a sample. In some cases, well design and pump types used in the well will determine minimum sustainable flow rates achievable without surging the pump;
3. Collect samples under a head of water in a 5 gallon bucket to limit the rate of effervescence or potential exsolution.
4. Collect and analyze duplicate (consecutive) samples for at least 1 out of every ten samples collected



All water wells that were sampled at least twice and analyzed to determine dissolved methane concentrations were considered for this analysis. This includes sample pairs collected prior to and after drilling additional optional wells in the Fruitland Formation. If more than two samples were collected and sampled at any given water well, then the values chosen for this plot only include the maximum and minimum methane concentrations measured at a given water well. Water wells with single sample measurements or with maximum non-detect values were not included in this analysis. A value of 0.00001 mg/L was assigned to the minimum concentration among measurements where methane was not detected.

There are 397 sites at which methane concentrations were analyzed more than once since 1994, and where maximum values were above detection limits. Eight pairs of measurements, as indicated in the graph, were treated as outliers and were removed from the regression analysis.

These long term, historical data show that the average difference in methane concentration between maximum and minimum values increases with increasing minimum methane concentration. The slope of the regression line for historic data is higher than the slope determined from short term samples. On average, the difference between minimum and maximum dissolved methane concentrations over the short term is 14%, whereas concentrations over the long term vary on average by 54%. These results are consistent with the results reported by the BLM (BLM-COGCC, 1994).



The difference in maximum minus minimum methane concentrations measured at all 397 water wells with multiple analyses is illustrated on this map.

SUMMARY

- SHORT AND LONG TERM TEMPORAL VARIABILITY IS SIGNIFICANT
  - MAXIMUM AND MINIMUM DISSOLVED METHANE CONCENTRATIONS VARY BY AN AVERAGE FACTOR OF 14% PLUS 0.55 mg/L OVER THE SHORT TERM
  - MAXIMUM AND MINIMUM DISSOLVED METHANE CONCENTRATIONS VARY BY AN AVERAGE FACTOR OF 54% PLUS 0.49 mg/L OVER THE LONG TERM
- SITES WITH THE HIGHEST METHANE VALUES ARE LOCALIZED
  - ALONG DRAINAGE VALLEYS NORTH OF THE UTE LINE
  - AT THE CONFLUENCE OF THE FLORIDA AND ANIMAS RIVERS

APPROACH USED TO EVALUATE DIFFERENCES IN GROUNDWATER METHANE CONCENTRATION PRIOR TO AND AFTER DRILLING ADDITIONAL FRUITLAND WELLS:

- COMPARE DIFFERENCES IN MAXIMUM AND MINIMUM VALUES OF CONSECUTIVE SAMPLE PAIRS TO AVERAGE DIFFERENCES OBSERVED OVER THE SHORT TERM
- DETERMINE AT WHICH SITES POST DRILLING METHANE VALUES ARE GREATER THAN PRE DRILLING METHANE VALUES
- CHARACTERIZE WATER QUALITY AND METHANE CONCENTRATIONS IN GROUNDWATER FROM WELLS WHERE POST DRILLING METHANE VALUES ARE AT LEAST 14% PLUS 0.55 mg/L HIGHER THAN PRE DRILLING VALUES
- DETERMINE WHETHER DISSOLVED METHANE FOUND IN THESE WATER WELLS ORIGINATES FROM THE FRUITLAND FORMATION

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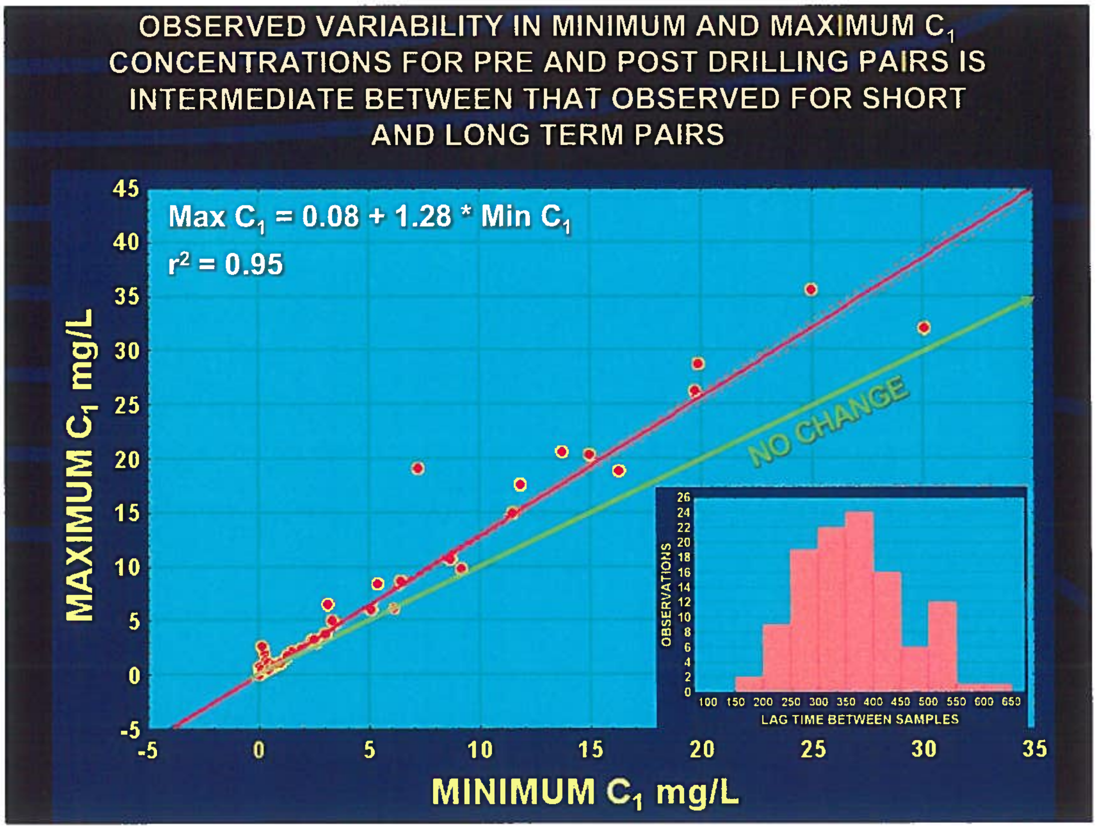
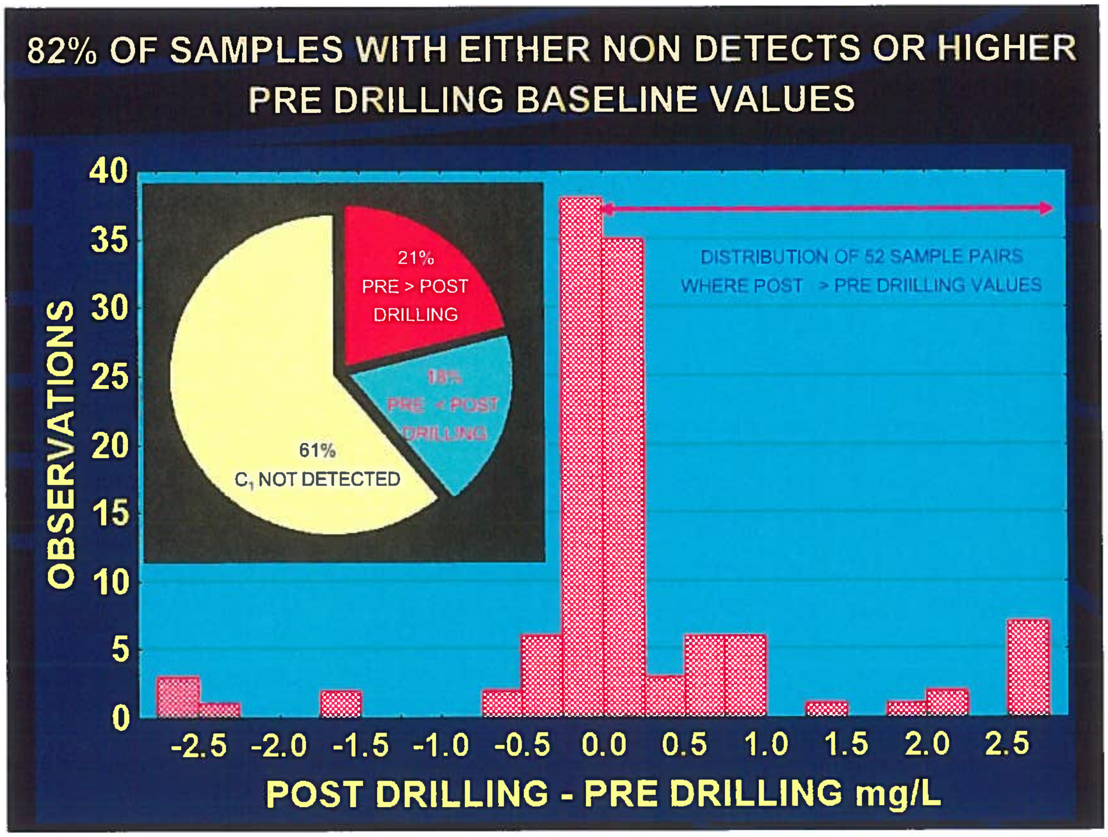


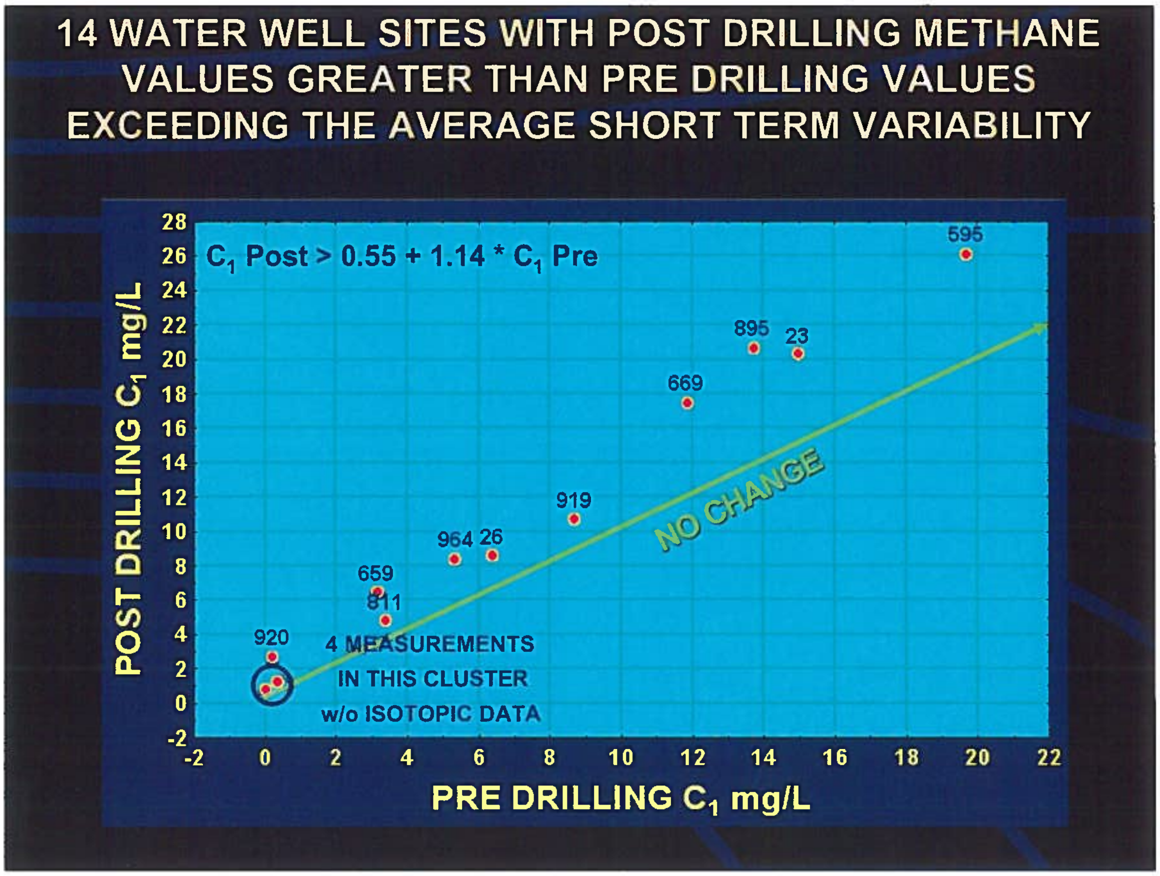
There were 292 sample pairs used for this analysis representing methane concentrations measured prior to and after drilling optional additional Fruitland wells. 179 of those sample pairs of those water wells (61%) had consecutive measurements below detection limits. There were 113 sample pairs for which there were detectable amounts of methane measured at least once.

The average difference between maximum and minimum values of dissolved methane among pre and post drilling sample pairs containing measurable amounts of methane increases with increasing amounts minimum values. The rate of this increase is intermediate (28%) between that observed among short term samples (14%) and historic data (54%).

25 sites have maximum values that are higher than expected based on the variability between maximum and minimum values observed among samples taken over the short term. Maximum values occur in post-drilling samples in 14 of the 25 sites, whereas maximum values occur in pre-drilling samples in 11 of the sites.

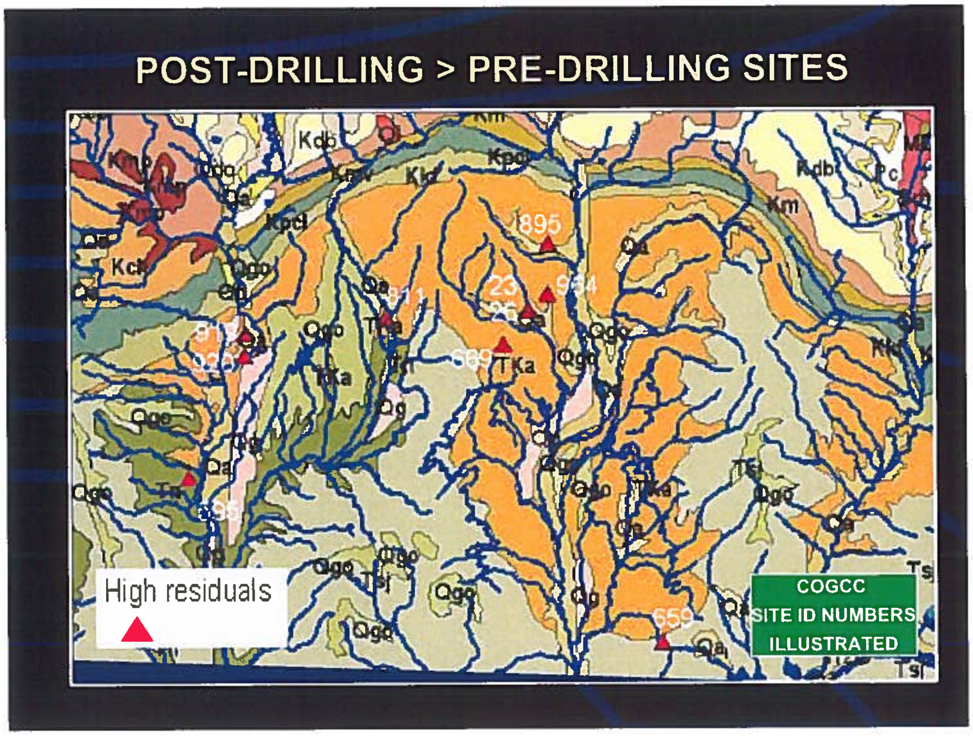


Of the 113 sample pairs with at least one measurement detecting dissolved methane, 61 (or 54%) had pre drilling values that were higher than post drilling values. Thus 82 % of sample pairs either did not contain dissolved methane, or contained more dissolved methane prior to drilling.



Based on the average variability in methane concentrations established using short term sample pairs, 14 sites have higher than expected post drilling values. The expectations are based on the regression line used to establish variability for short term sampling (C_1 Max > 0.55 + 1.14 * C_1 Min).

10 water well sites, where at least one sample was found to contain a dissolved methane concentration of 2 mg/L, will now be characterized to determine whether the gas originates from Fruitland production. The COGCC orders 112-156 and 112-157 do not require either chromatographic analysis of dissolved gas or isotopic analysis of methane if concentrations are below 2 mg/L.



The geographic distribution of 10 sites with higher than expected post-drilling values.

APPROACH USED TO CHARACTERIZE SITES WITH LARGER THAN EXPECTED POST DRILLING VALUES

- STABLE ISOTOPES
  - CARBON 13 METHANE: GROUNDWATER VS. PRODUCED
  - DEUTERIUM METHANE: GROUNDWATER VS. PRODUCED
  - CARBON 13 DISSOLVED INORGANIC CARBON
  - CARBON 13 PRODUCED CO_2
- GAS CHROMATOGRAPHY
  - DISSOLVED ATMOSPHERIC GASES IN GROUNDWATER
  - DISSOLVED HYDROCARBONS $C_1 - C_6$ IN GROUNDWATER
  - HYDROCARBONS $C_1 - C_6$ IN PRODUCED GAS
- AQUIFER CHEMISTRY
  - STABLE OXYGEN AND DEUTERIUM VALUES OF WATER
  - MAJOR ION ANALYSIS

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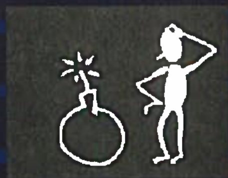
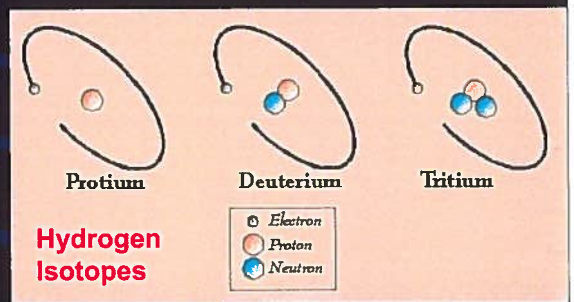


WHAT IS A STABLE ISOTOPE?

STABLE ISOTOPES ARE USEFUL TOOLS USED TO DETERMINE THE ORIGIN OF FLUIDS AND GASES.

Many elements can exist in different forms known as isotopes. They differ in the number of neutrons in the nucleus but do not differ in the number of protons. Stable isotopes are not radioactive.

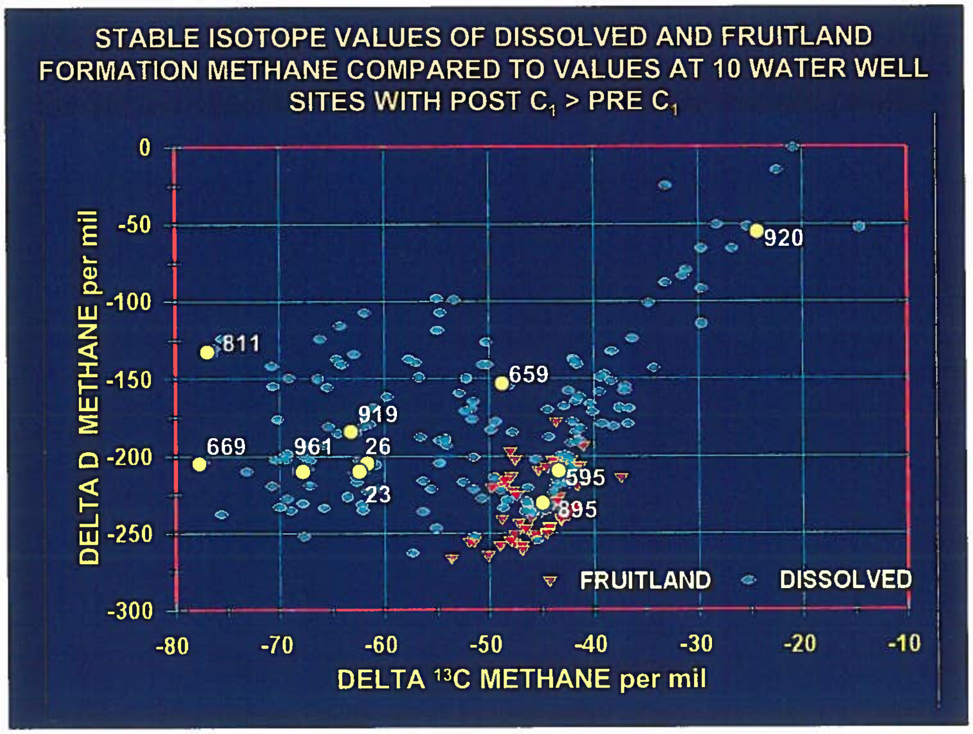


Carbon Isotopes:

Isotope	Protons	Neutrons	Abundance	Type
^{12}C	6	6	98.98%	Stable
^{13}C	6	7	1.11%	Stable
^{14}C	6	8	trace	Unstable

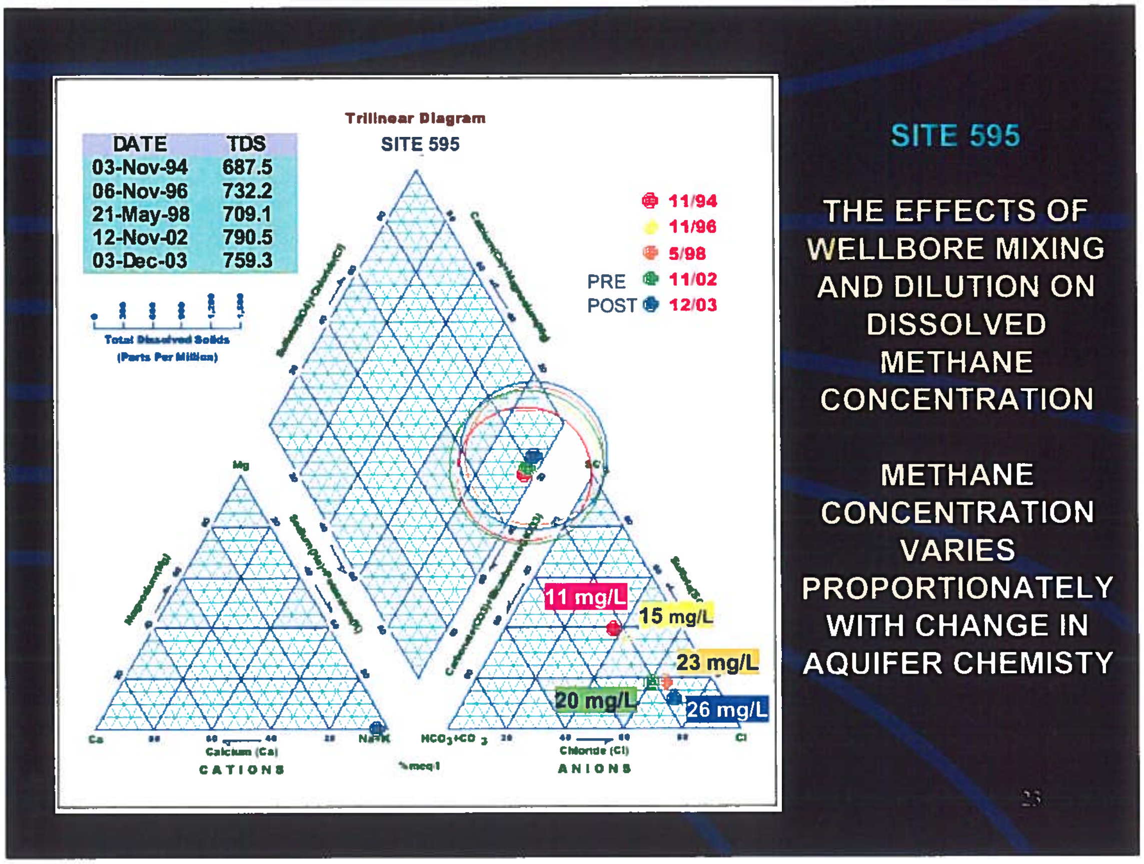
Stable carbon and deuterium isotopes of methane (CH_4) are used in the oil and gas industry as a diagnostic tool to determine methane origin. Methane originating from the burial of organic sedimentary matter at high temperatures and pressures is defined as thermogenic. Methane originating from bacterial 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.

By convention, isotope ratios are expressed in delta notation (d) 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 in a standard. 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.



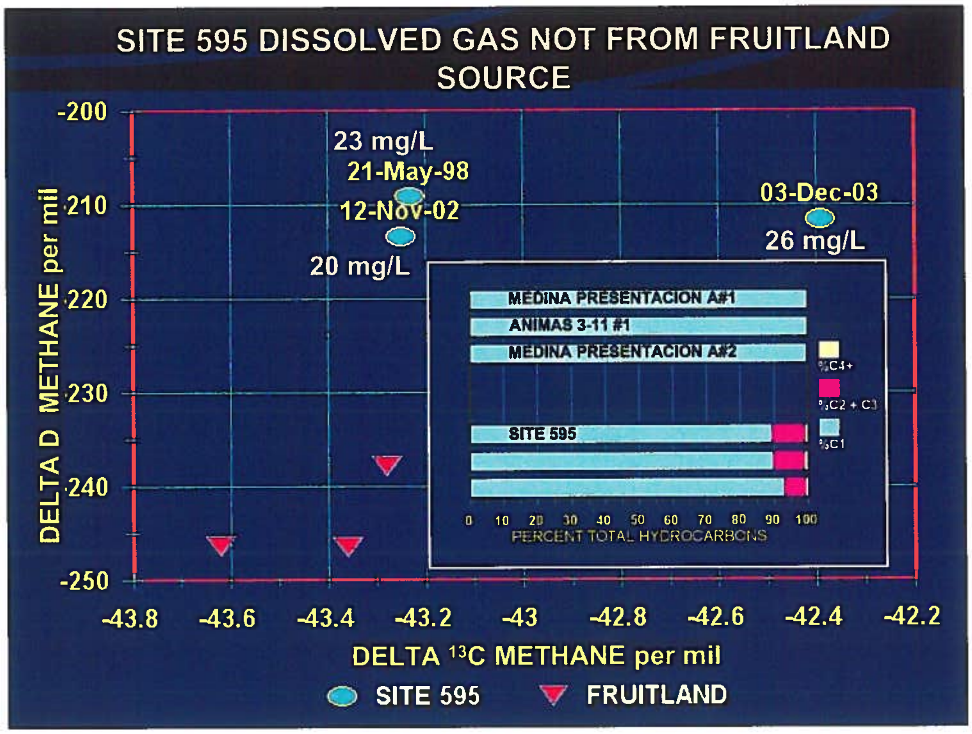
The range in stable isotope ratios for dissolved methane in water wells far exceeds the range in values reported from producing Fruitland Formation gas wells. The range in carbon isotope ratios for produced Fruitland Formation gases is between -53.63 and -37.31 per mil, and the range in deuterium isotope ratios is between -266.9 and – 179 per mil.

Among the 10 sites with significant methane concentrations above predicted averages, only 2 (595 and 895) have carbon and deuterium isotope ratios that are in the range of produced Fruitland Formation gas samples.



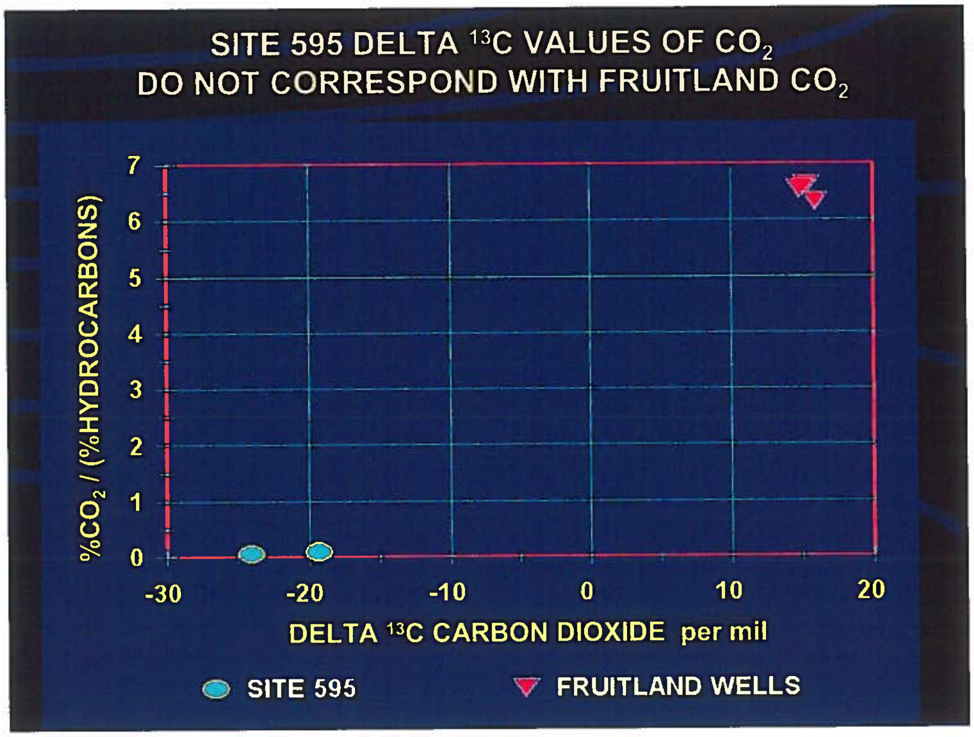
Samples collected and analyzed from water well site #595 provide an excellent example of the influence that fluid mixing and dilution have on dissolved methane concentrations. There are 5 sets of available historic data for this site that include both measured dissolved methane concentrations and water chemistry. The water well now contains high methane concentrations, and since 1994 the concentrations have increased consistently.

The trilinear diagram shows that since 1994, the water chemistry has been composed of variable mixtures of $NaHCO_3$ (sodium bicarbonate), Na_2SO_4 (sodium sulfate), and NaCl (sodium chloride). Sodium is the common cation and its relative concentration remains at near 100%. Through time, the relative amount of sodium bicarbonate has stayed approximately constant at 20%. In contrast, 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 the sulfate, the sodium chloride concentration has increased by 175% since 1994. Over the same period, the measured dissolved methane concentration 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 NaCl type waters entering this well carry dissolved methane, whereas the $NaHCO_3$ and Na_2SO_4 type waters do not. This domestic water well, 327 feet deep, provides a mixing environment for different water types that originate from different sources or aquifers. Since 1994, the amount of Na_2SO_4 type fluids available to dilute the methane-bearing NaCl type waters has systematically decreased.

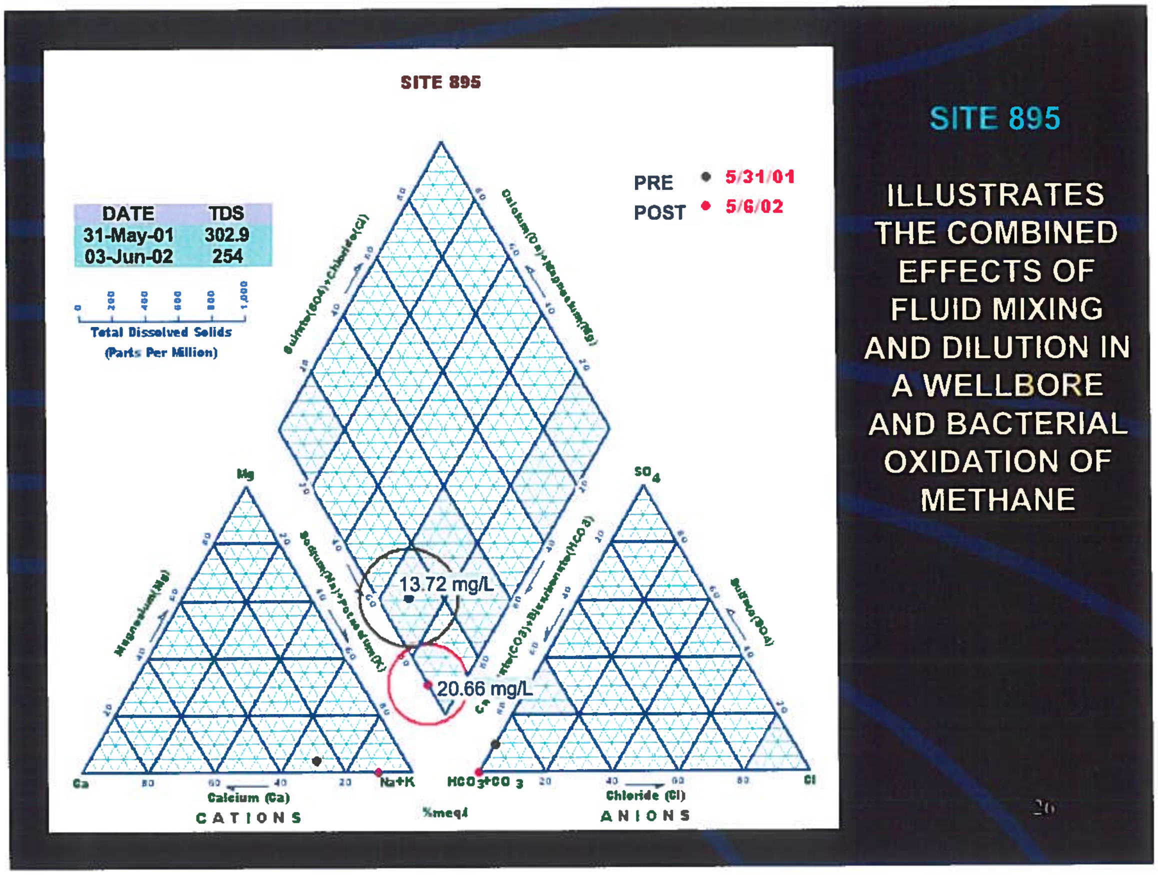


Site #595 is one of the water wells monitored for the Medina Presentacion A#2 Fruitland Formation gas well. High methane concentrations were present in this well prior to drilling the additional well. Chromatographic and isotopic data are used to show that the dissolved gases in the domestic water well are not derived from the underlying Fruitland Formation.

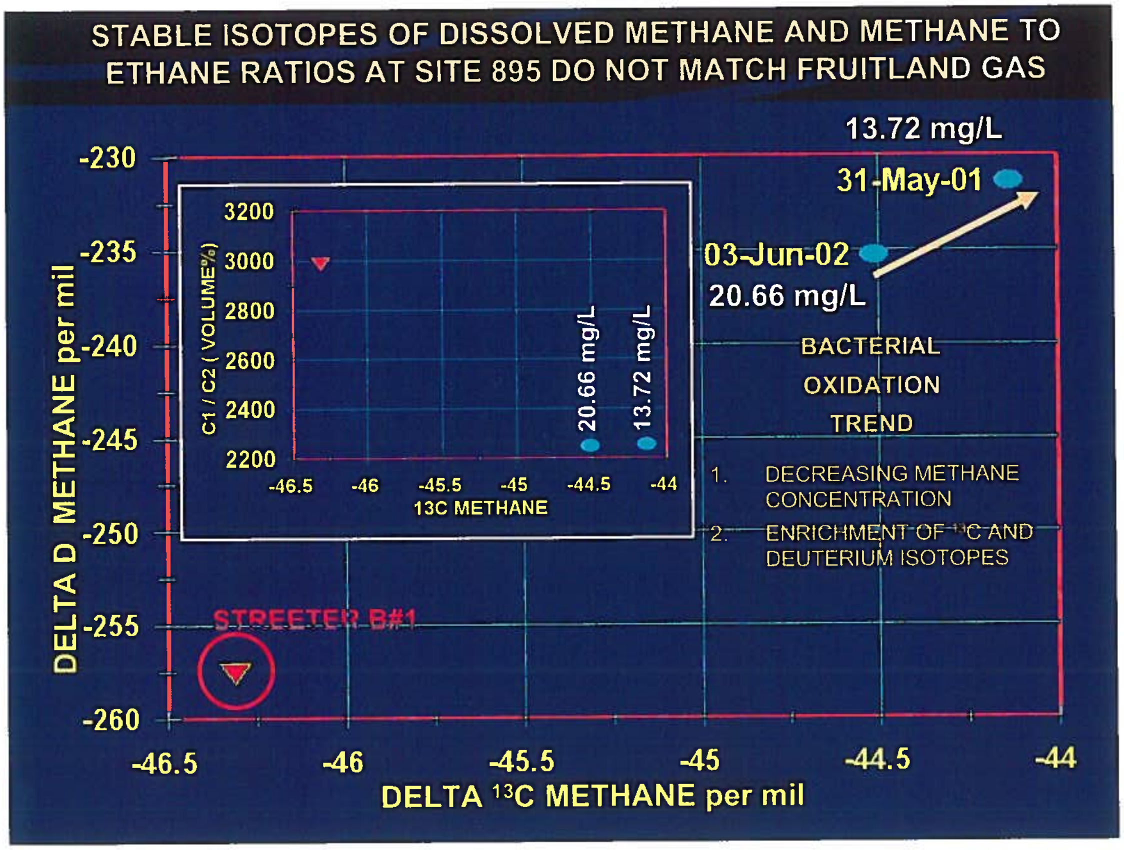
Fruitland Formation gas, sampled from three producing wells in the area is entirely composed of methane, whereas the dissolved gases sampled from the monitor well contain ethane, propane, butane, and pentane. The isotopic composition of the methane in the monitor well is also different from that in the 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.



On average, Fruitland gas in this area contains high CO_2 concentrations with positive carbon isotope values. The high proportion of CO_2 relative to the total hydrocarbon volume is not reflected in the dissolved gas found in the water well. The stable carbon isotope ratio of carbon in CO_2 is also vastly different between that found dissolved in water and the CO_2 produced from the Fruitland Formation



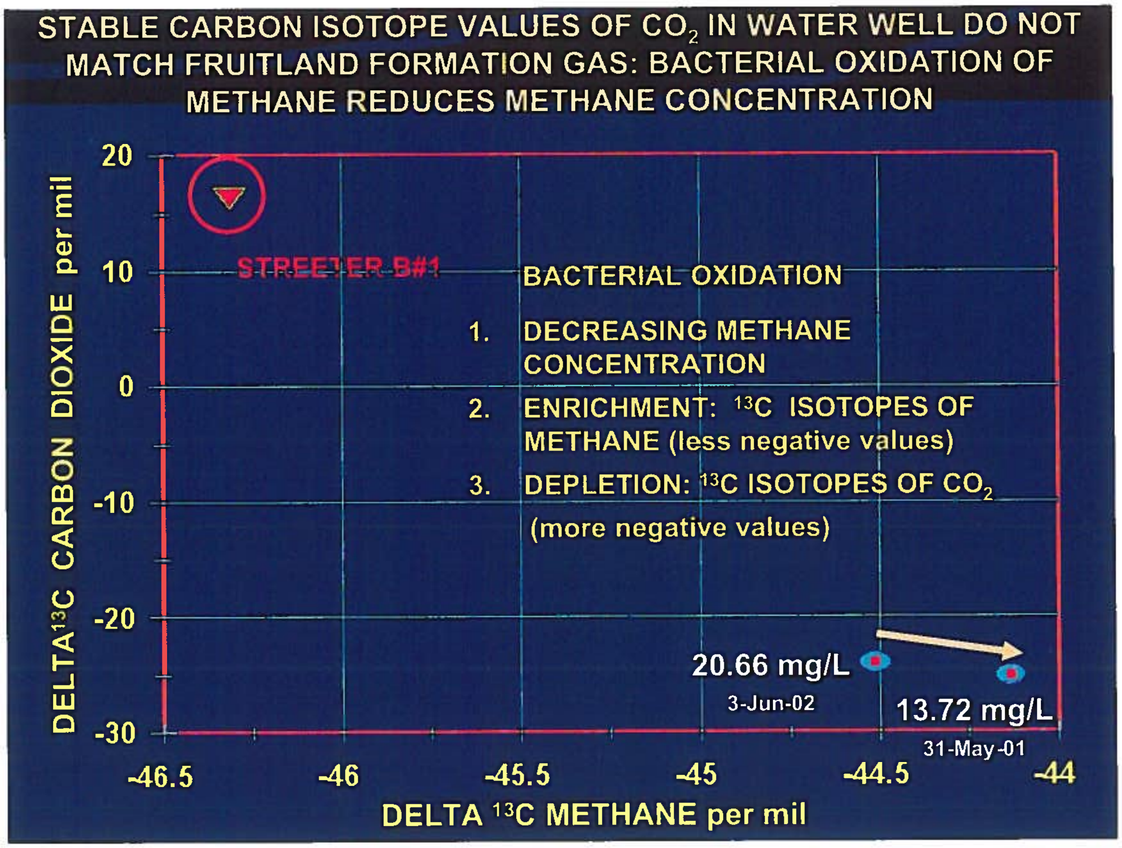
Major ion data for water well #895 show the effects of mixing. In this example, differences in water composition are principally due to differences in the relative concentrations of sulfate anions and calcium cations. Among the anions, the change in composition is on the order of 10% (from 10% of the total milliequivalents as sulfate to 0% as sulfate). Among the cations, the change in composition is on the order of 20% (from a relative 30% concentration of calcium milliequivalents to a relative concentration of 10%). Methane appears to be carried by the less saline fluid depleted in calcium bicarbonate and sodium sulfate, and relatively enriched in sodium bicarbonate. Salinity also decreases 13% from a value of 302 mg/L to a value of 264 mg/L. However, methane concentration in the less saline water increases approximately 7 mg/L, from 13.72 mg/L to 20.66 mg/L. Such an increase by a factor of 50%, is too large to be accounted for by mixing dilution. Accordingly, some other factor must account for the difference.



Site #895 is one of the monitor water wells for the additional Streeter Gas Unit B#1 Fruitland Formation producing gas well. 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, methane and ethane are present in both the produced Fruitland Formation gas and in the hydrocarbon gas dissolved in groundwater. However, the C_1/C_2 ratio is significantly different between the two types of samples. The stable isotopes of methane are also significantly different.

The trend of decreasing methane concentration and enrichment in the heavy isotopes is characteristic of methane oxidation by methanotrophic (methane-consuming) bacteria. Bacterial consumption rates are greater for molecules of methane containing the 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. Thus residual methane left in solution will contain a greater proportion of heavy isotopes, driving the isotopic values towards heavier (more positive) values.

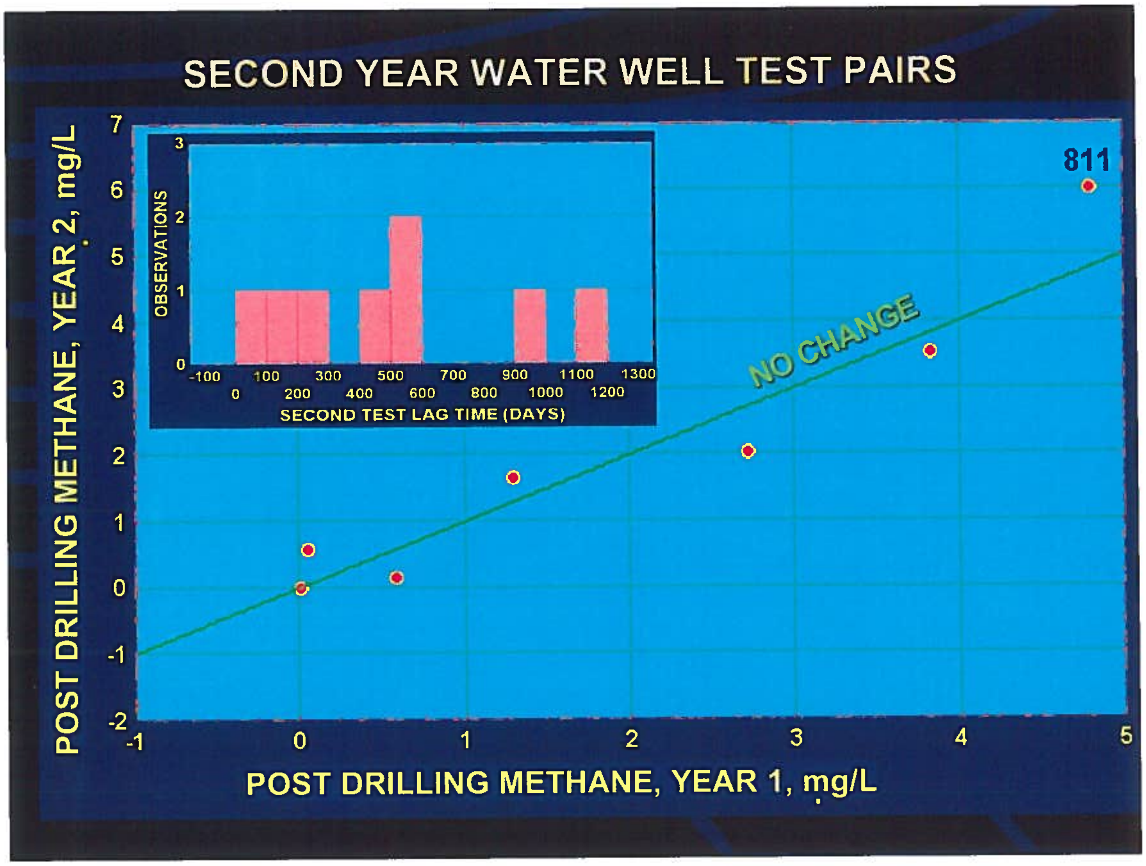
The source of oxygen used by methane-oxidizing bacteria to generate CO_2 in shallow San Juan Basin aquifers is likely to be the oxygen in sulfate. Almost all the analyses of water samples from domestic water wells show that the domestic wellbore environment is strongly stagnant, with very little free dissolved oxygen. At site 895, the chemical composition of water containing the lowest concentration of dissolved methane also contains sulfate ions, whereas the composition of water containing the highest concentration of dissolved methane does not contain sulfate. Thus, the rate of methane oxidation in well water is likely to depend on the amount of mixing that takes place between bicarbonate type waters and sulfate type waters.



Methanotrophic bacteria generate carbon dioxide as part of their metabolic process. Because such bacteria preferentially consume the light isotopes of methane, the carbon dioxide they produce is isotopically light. Accordingly, evidence for bacterial oxidation includes decreasing dissolved methane concentrations, enrichment of heavy ^{13}C isotopes in residual methane, and depletion of heavy ^{13}C isotopes in carbon dioxide.

The trend of decreasing methane concentration, increasing stable carbon isotope values for methane, and decreasing delta ^{13}C CO_2 values are exactly what is observed at site 895. Thus methane oxidation by methanotropic bacteria accounts for the additional loss of methane that cannot be explained by mixing alone.

Dissolved methane that is transported through a reduced aquifer to the well bore is not likely to become oxidized until it mixes with water containing oxygen. Methanotrophic bacteria can use either dissolved free oxygen or oxygen bound in sulfate to convert methane to CO_2. 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 methane sampled at any given time will vary greatly depending on dynamic conditions in each water well and on seasonal conditions. 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; when the rate of 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. Such dynamics can be substantially different at different times within a single well. To determine whether dissolved methane concentrations are systematically increasing in this well requires more frequent sampling. The latest samples collected on 6/8/04 show dissolved methane concentrations 14.78 mg/L. We are still waiting for the isotope data.



There are 16 water wells which have been 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 have methane concentrations that are higher than that measured the prior year. Of those, none have maximum values above that predicted using short term results. Site 811 is the only site of the three with sufficient dissolved methane to warrant isotopic analysis. As shown in the previous slide on page 22, dissolved methane at site 811 is of biogenic origin.

OPTIONAL ADDITIONAL DRILLING OF FRUITLAND GAS WELLS HAS NOT HAD ANY DISCERNIBLE IMPACT ON DISSOLVED METHANE CONCENTRATONS IN GROUNDWATER

- 179 OF 292 OR 61% OF WATER WELLS SAMPLED WITH POST DRILLING TEST RESULTS DO NOT CONTAIN DETECTABLE AMOUNTS OF DISSOLVED METHANE
- 61 OF THE 113 WATER WELLS (54%) CONTAINING DISSOLVED METHANE HAD LARGER MEASURED METHANE CONCENTRATIONS PRIOR TO DRILLING AN ADDITIONAL FRUITLAND GAS WELL
- OF THE REMAINING 52 SITES, 9 HAD POST DRILLING METHANE CONCENTRATIONS THAT WERE HIGHER BY MORE THAN 1.2 mg/L (STANDARD DEVIATION OF BASELINE VALUES) AND 14 HAD VALUES ABOVE THE AVERAGE EXPECTED VARIANCE OBSERVED WITH SHORT TERM SAMPLING
- ONLY 10 OF THE 14 SITES COULD BE CHARACTERIZED USING STABLE ISOTOPES: OF THOSE, ONLY 2 CONTAINED METHANE WITH STABLE ISOTOPE VALUES IN THE RANGE FOUND FOR PRODUCING FRUITLAND GAS WELLS IN THE SAN JUAN BASIN
- NEITHER OF THE 2 MONITOR WATER WELLS CONTAINED DISSOLVED HYDROCARBONS SIMILAR IN EITHER CHEMICAL OR STABLE ISOTOPE COMPOSITION TO THE NEW FRUITLAND GAS PRODUCTION WELLS MONITORED
- VARIABILITY IN METHANE CONCENTRATION IS DUE TO:
  - SAMPLING AND ENVIRONMENTAL FACTORS
  - MIXING OF WATER FROM DIFFERENT AQUIFERS WITHIN A WATER WELL
  - METHANE OXIDATION BY METHANOTROPHIC BACTERIA

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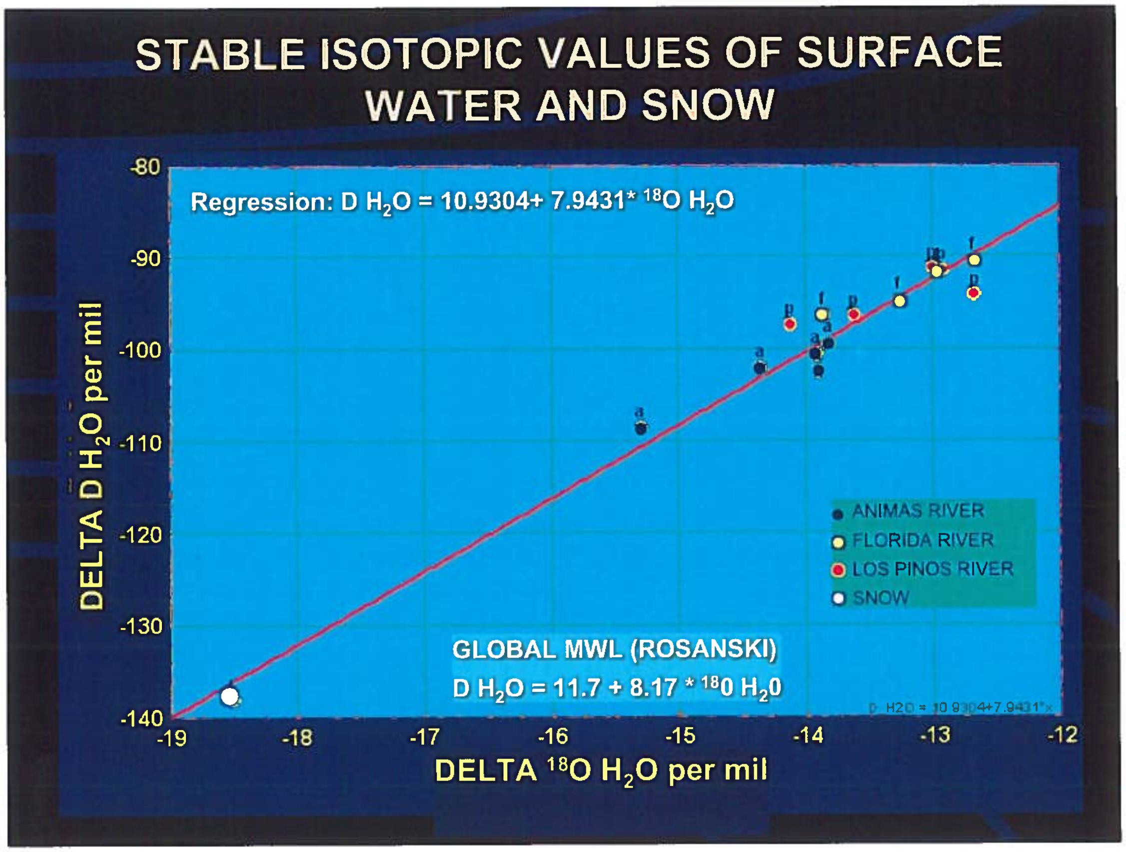
DOCUMENTING HOW MIXING AND BACTERIAL OXIDATION INFLUENCE METHANE CONCENTRATIONS

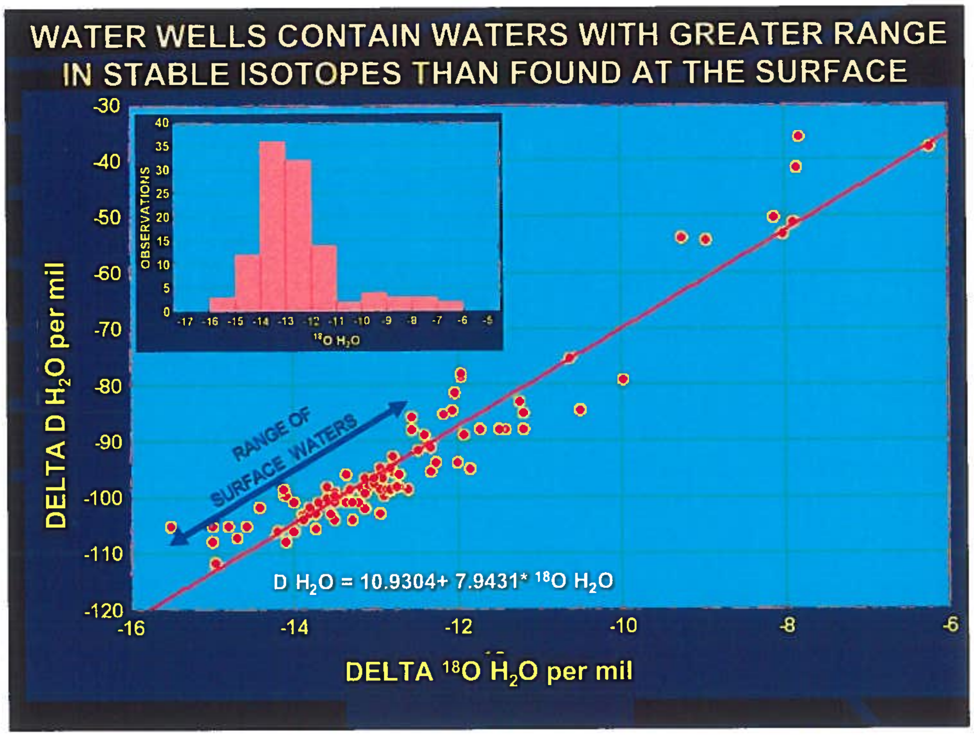
- APPROACH: OBSERVATIONS AMONG SAMPLES COLLECTED AT THE SAME SITE AT DIFFERENT TIMES
  - STABLE ISOTOPES OF WATER
    - OXYGEN AND DEUTERIUM
  - MAJOR ION CHEMISTRY
  - STABLE ISOTOPES OF DISSOLVED METHANE

31

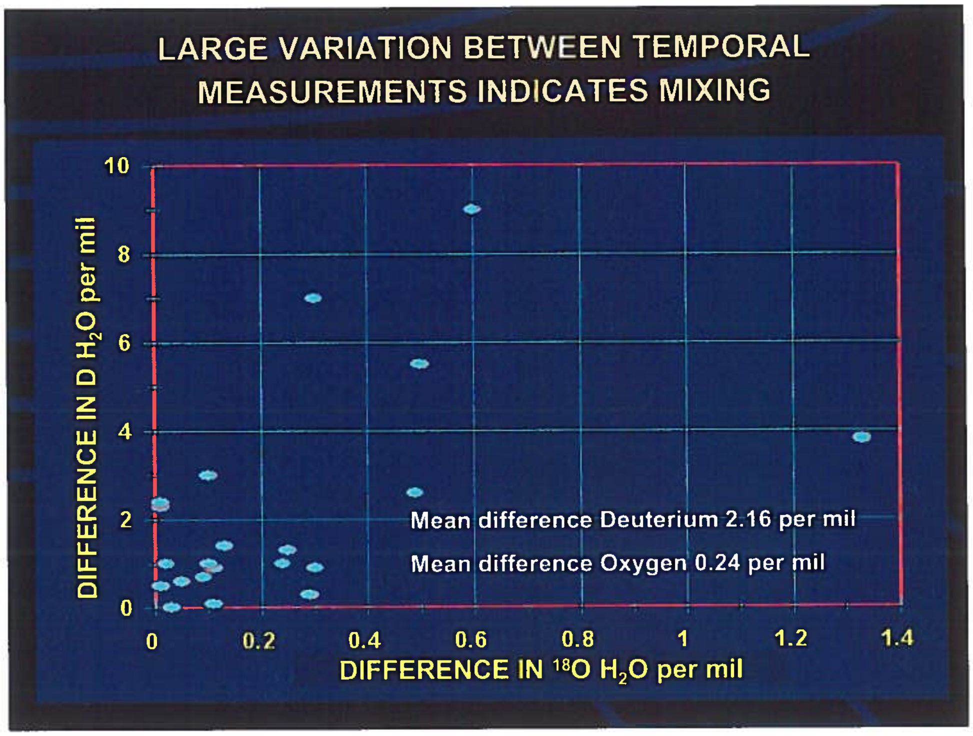


Stable deuterium and oxygen isotopes of water are useful for examining water provenance, recharge, and groundwater flow. Data used for the following graphs are derived from both proprietary databases, and from the COGCC database.

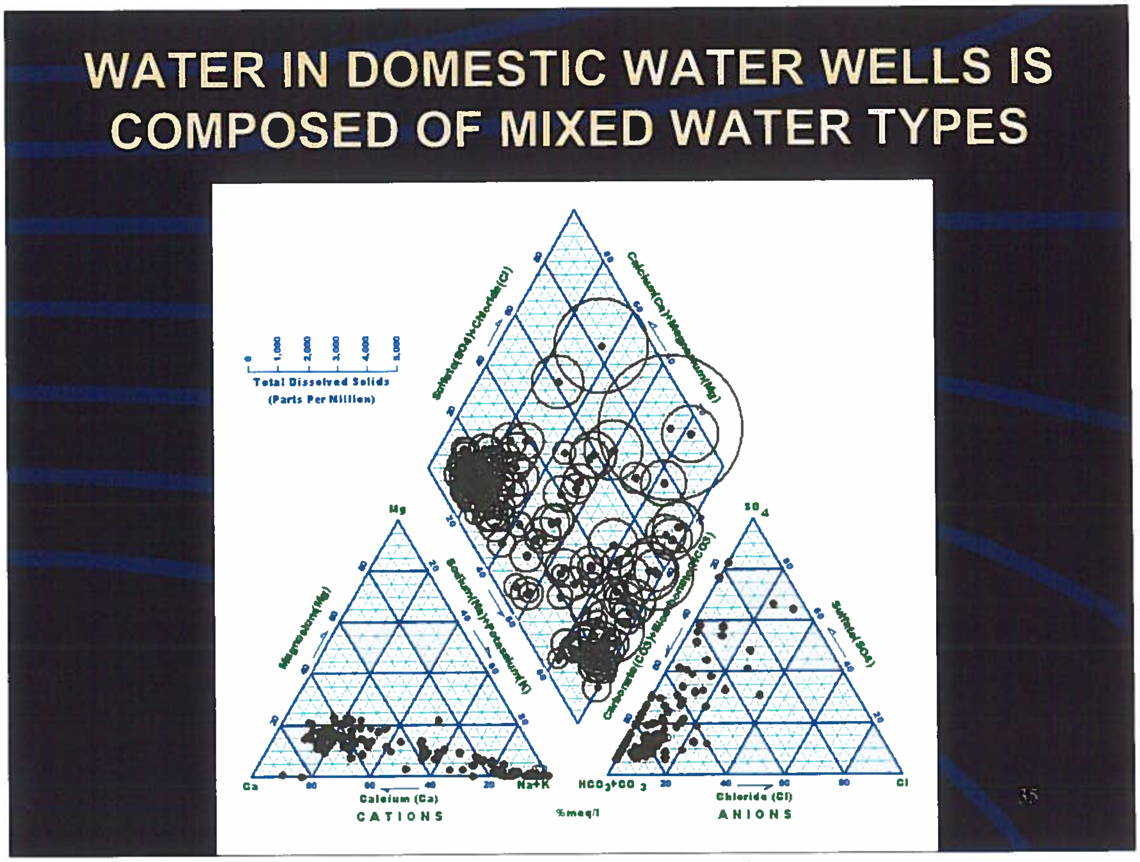
The regression line derived using samples from surface waters closely coincides with the global meteoric water line. Animas River samples are slightly more negative than those from the Los Pinos and Florida Rivers.



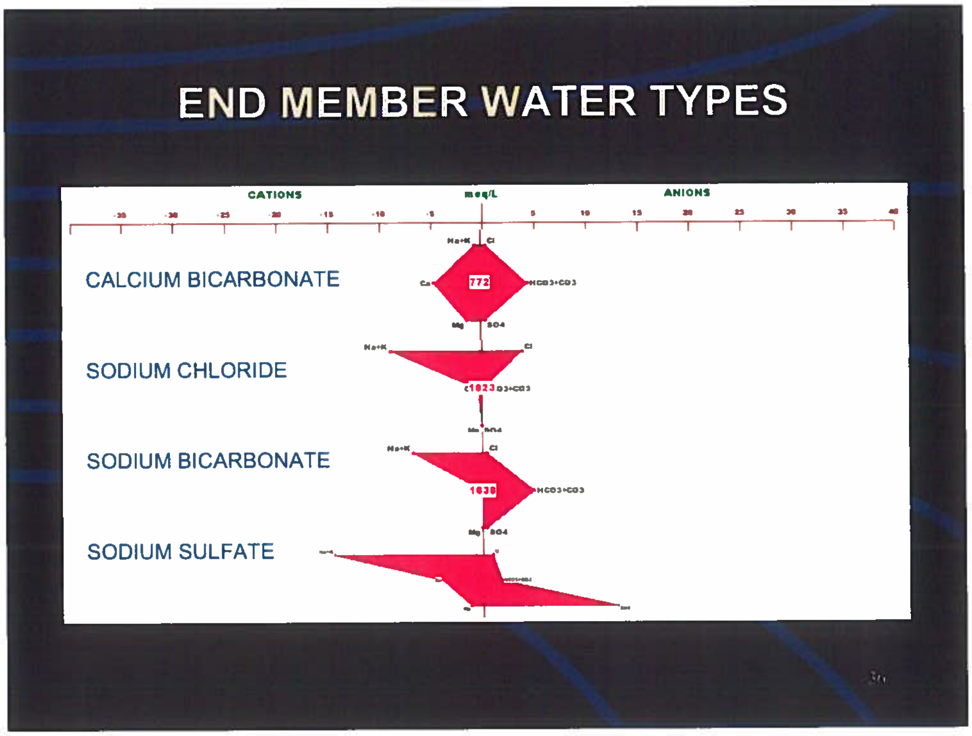
The range of stable isotope values among samples taken from domestic water wells is larger than the range observed among surface water samples. There is also a significant amount of scatter among samples.



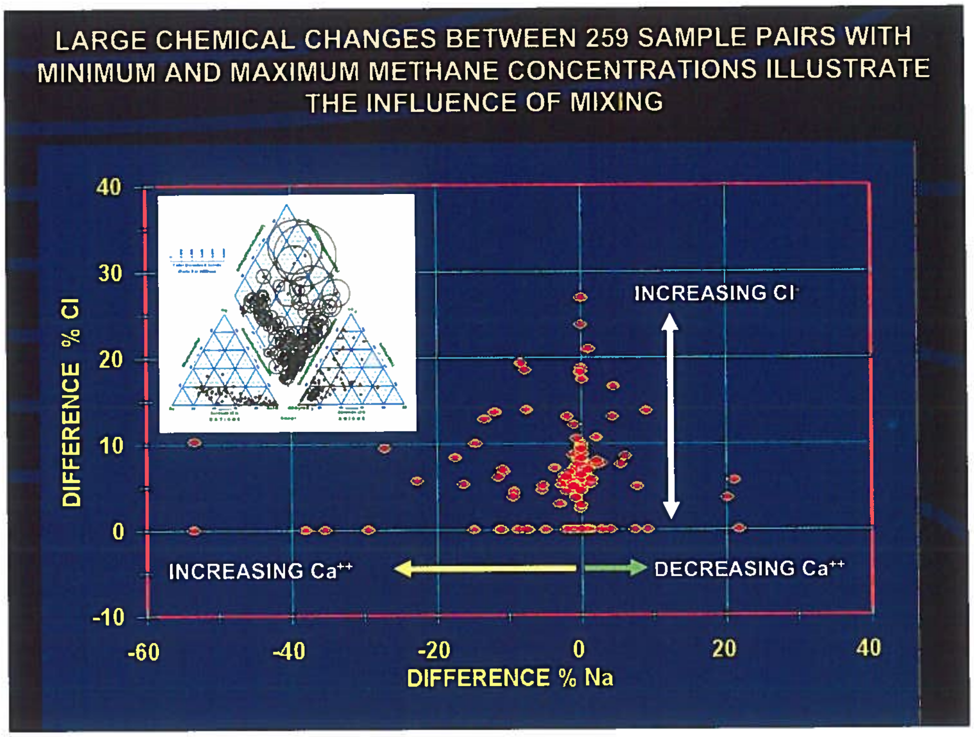
Among the 21 samples sites with more than one analysis of stable water isotopes, the range in values between consecutive measurements at any site is relatively large. Delta D H_2O values vary by as much as 9 per mil, and delta ^{18}O H_2O values vary by as much as 1.3 per mil. Such variability is large relative to all the values found for groundwater samples and indicates mixing of water from different aquifers.



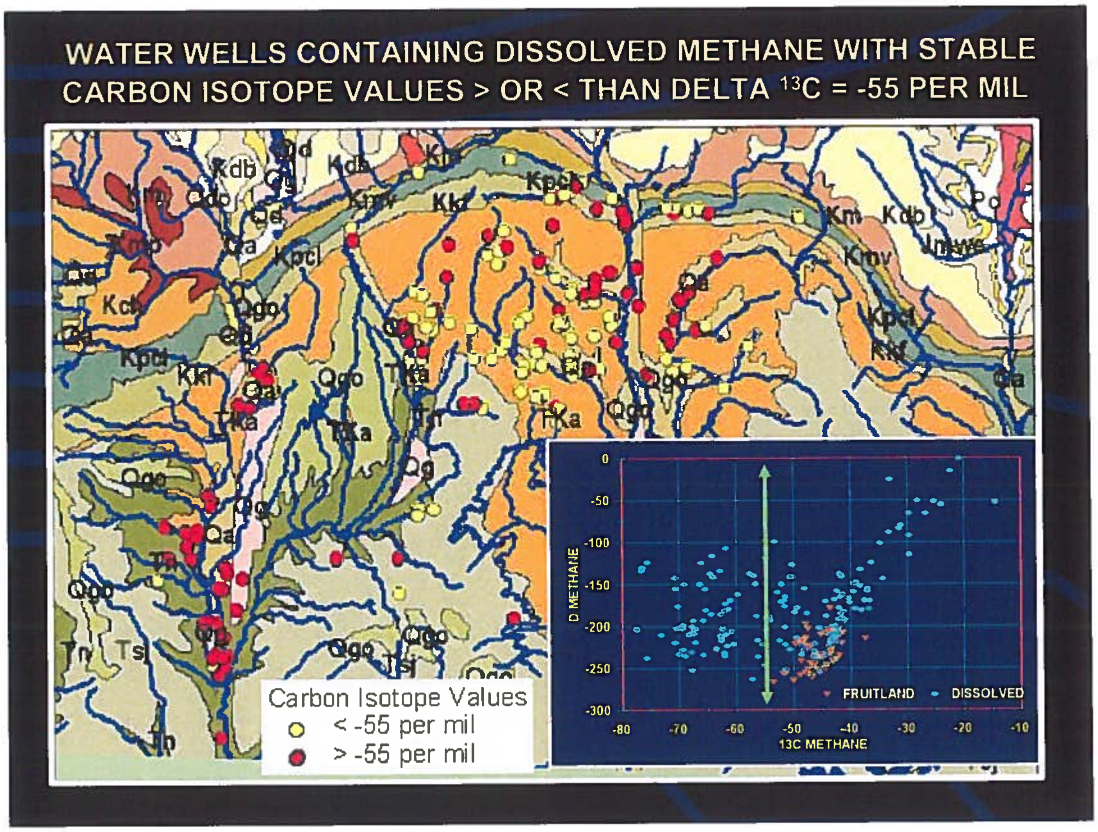
These trilinear diagrams represent the composition of domestic water well samples that have been analyzed for their dissolved major ion content. Samples shown are in charge balance within +/- 15%. The cations plot along a two end member mixing line composed principally of calcium and sodium. Accordingly, the relative concentration of sodium can be used to adequately characterize a water well's cation composition. Anions, on the other hand, are distributed along a broad mixing line that extends principally between dissolved sulfate and total carbonate anions. The width of the line is moderated by the addition of dissolved chloride ions.



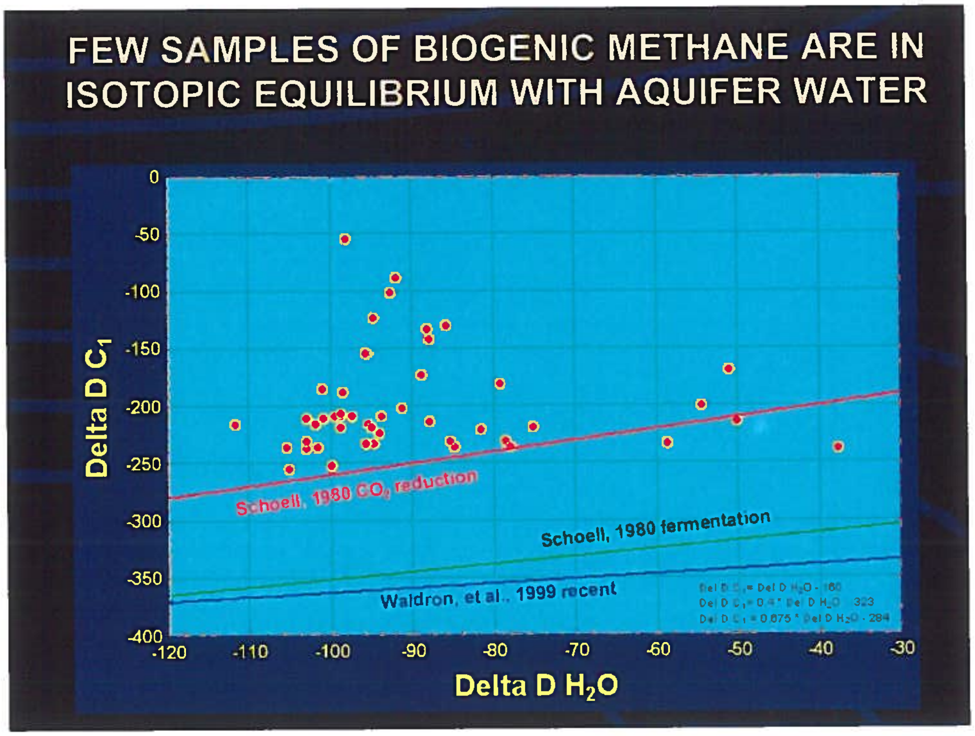
As seen in these Stiff diagrams, there are four end member water types in the aquifers of this basin. Dilute calcium-magnesium bicarbonate type waters dominate the composition of surface waters and very shallow aquifers close to recharge.



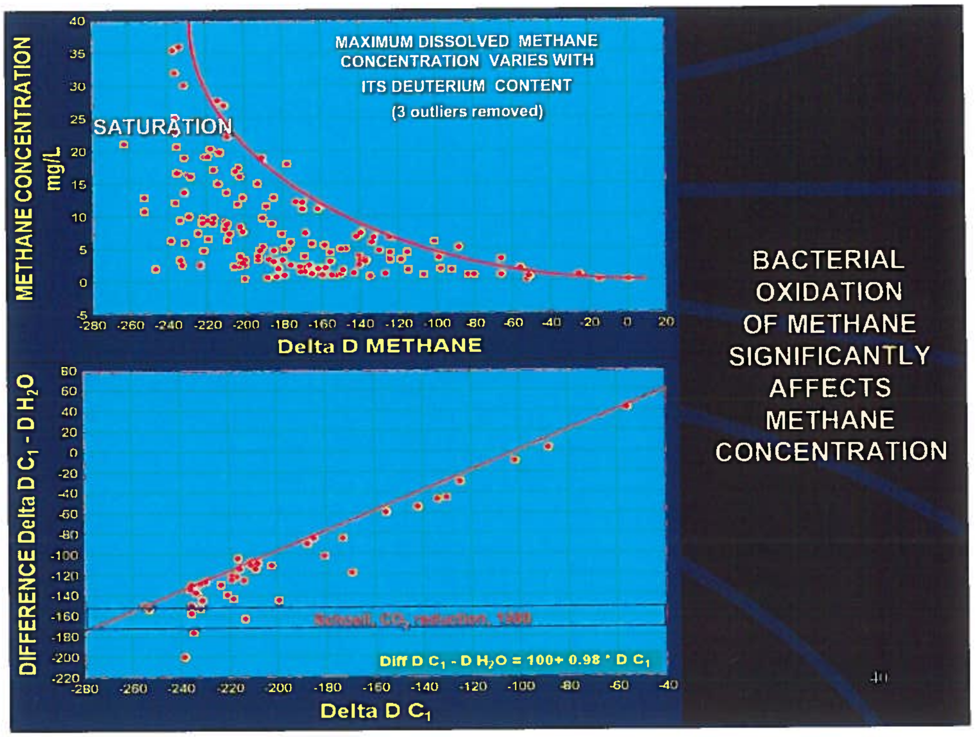
This chart shows the difference in relative sodium and chloride concentrations (milliequivalents) calculated for sample pairs with corresponding minimum and maximum dissolved methane concentrations. Chloride was selected as the anion of choice for this diagram because it is the least reactive. Chemical reactions in the wellbore environment are mediated by bacteria. For example, sulfate concentrations decrease and bicarbonate concentrations increase when sulfate-reducing bacteria consume dissolved sulfate ions. Such reactions are dominant in San Juan basin water wells. The large scatter among the 259 sample pairs used for this analysis indicates that mixing of different water types in water wells is significant. Water wells provide a mixing zone environment for different water types that infiltrate from different aquifers into the well bore.



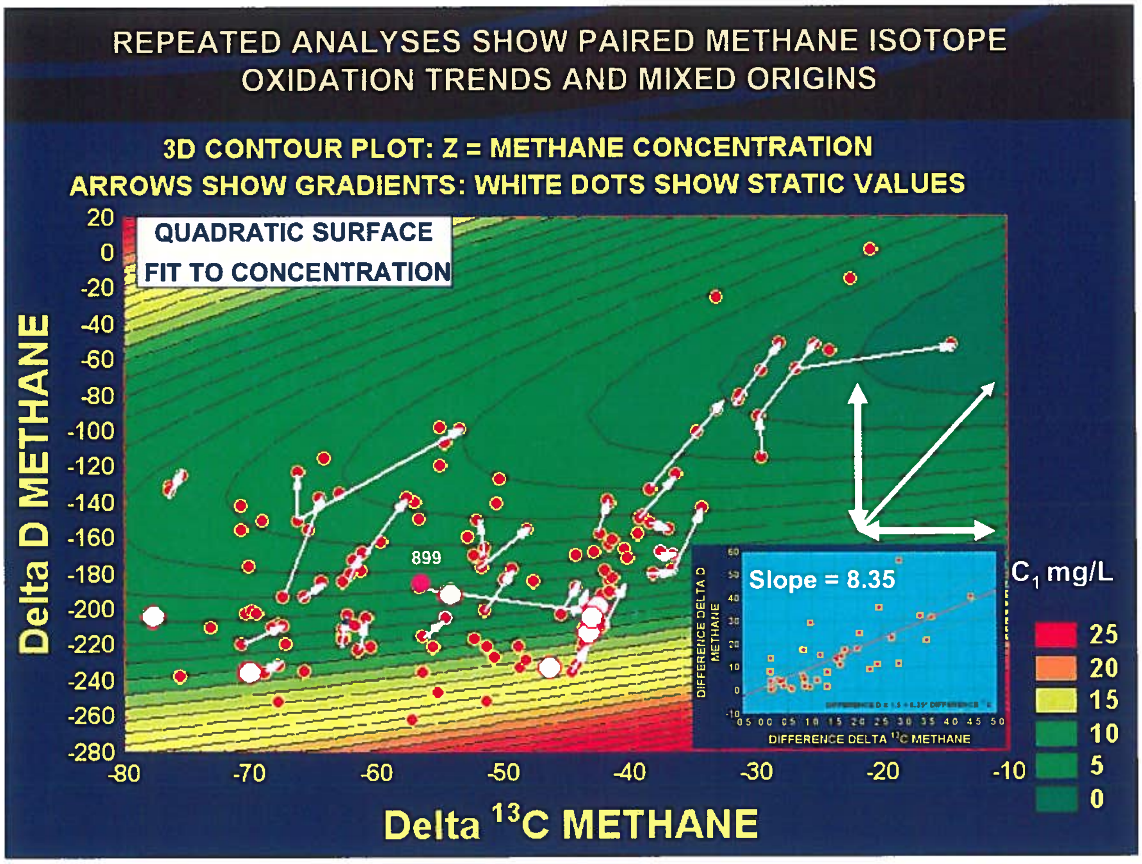
Stable carbon isotopes have been analyzed in the dissolved methane collected from 339 samples at 203 water wells. Water wells with delta ^{13}C values less – 55 per mil are predominantly located within the outcrop boundary of the Tertiary Animas Formation (TKa) and the along the outcrop belt of the Fruitland and Pictured Cliffs Formations.



Based on an empirical isotopic equilibrium relationship established between the deuterium content in biogenic methane and the deuterium of water in which it is formed (Schoell, 1980 & 1988), biogenic methane in the San Juan Basin is principally derived from the reduction of CO_2. There are only a few samples that fall close to the empirical fractionation line predicted for biogenic methane. A few points falling below the line may indicate some contribution of methane from acetate-fermenting bacteria.



Both these graphs show conclusively that bacterial methane oxidation strongly moderates the maximum methane concentrations found in water wells. The upper graph shows that the maximum methane concentration decreases systematically as the delta D ratios for methane become more positive. The shift towards more positive values results from the kinetic fractionation in deuterium induced by methanotrophs. The lower graph shows a systematic decrease in deuterium fractionation between the stable deuterium values in water and the deuterium values for methane. Because bacterial oxidation of methane does not affect the value in water, the difference between the delta D values of methane and water would increase systematically with progressive oxidation. Saturation indicates the maximum amount of methane water can hold within the range of atmospheric pressures present at elevations between 6,900 to 7,500 feet above sea level and at average water temperatures of 15°C.

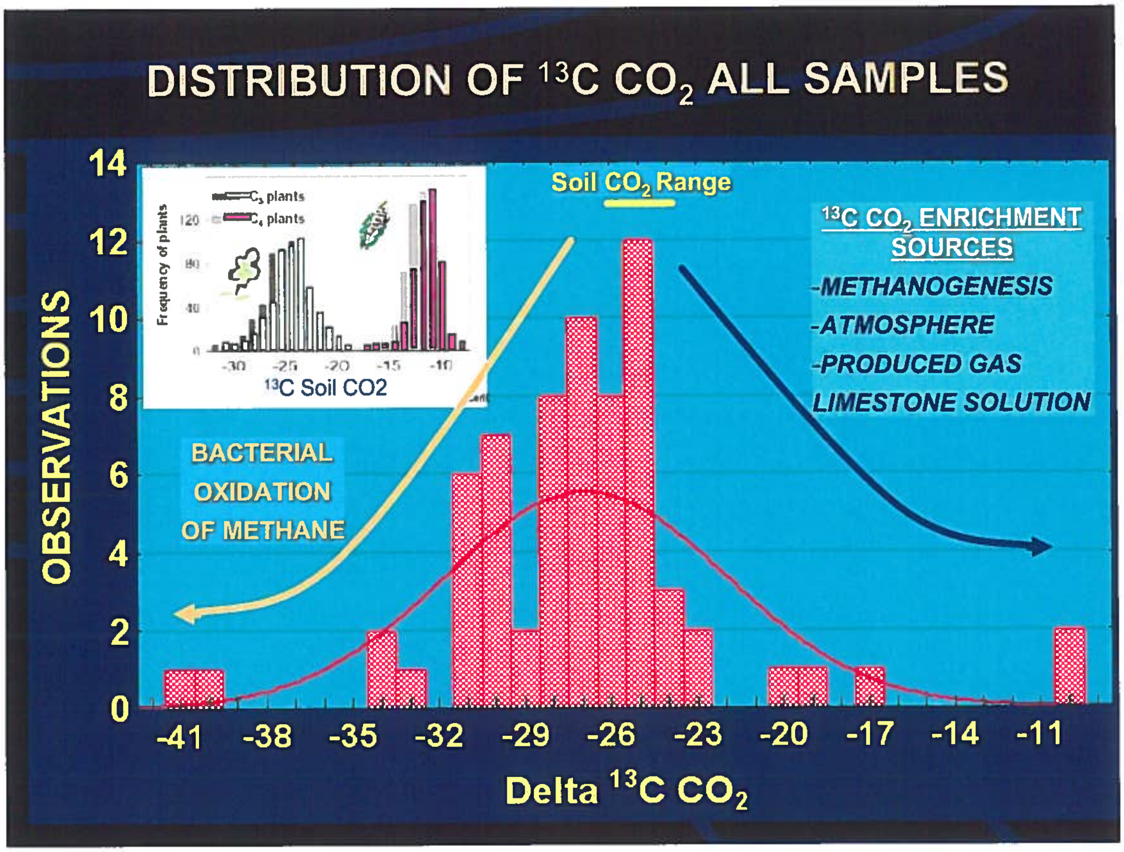


In this illustration, white vectors illustrate the difference in stable isotope values of dissolved methane between multiple samples from a given water well. The contour lines correspond to a quadratic surface used to fit points of varying methane concentrations.

Among most samples, the expected enrichment in both stable carbon and deuterium isotope ratios due to bacterial oxidation crosses contour lines of decreasing methane concentration. On average, the rate of deuterium enrichment is approximately 8 to 9 times the rate of carbon enrichment (inset) for all sample pairs where both carbon and deuterium are both enriched. This corresponds to differences reported in the literature for bacterial methane oxidation (Coleman et al, 1981).

Historical data show one sample pair (from water well # 899) projects a vector that cuts across contours towards increasing methane concentrations. Such a trend in sample pairs is indicative mixing between water containing dissolved biogenic methane and water containing dissolved thermogenic methane.

A third group of methane pairs have stable isotope values that do not significantly change. This group of samples plot along contours with relatively high methane concentrations. In these wells, it is likely that dissolved methane is being continually replenished from the aquifer at a rate that is greater than the rate at which bacteria can oxidize methane.



Delta ^{13}C CO_2 ratios shown here are obtained by either direct measurement of CO_2 gas extracted from water or calculated from the ^{13}C DIC using known fractionation equations at the measured temperature of the water sample from the water well (Clark & Fritz, 1997).

In this area of the San Juan Basin, plant photosynthesis is dominated by C_3 plants using the Calvin Cycle. In these plants, the first stable compound formed from CO_2 during photosynthesis is a three carbon compound. The vast majority of plants we usually see around us assimilate carbon dioxide via C_3 photosynthetic pathway. The delta ^{13}C CO_2 isotopic ratio of CO_2 in soils containing the organic remains of C_3 plants is in the range of –25 ± 2–3 per mil (Coleman and Fry, 1991). This average value corresponds well with the mode of values found in this area of the San Juan Basin which is in the range of -26 to -25 per mil.

The majority of samples deviating from expected soil ^{13}C CO_2 values trend toward more negative values reaching a minimum value of -41 per mil. This is another characteristic illustrating the influence of methane oxidation mediated by bacteria. Methanotrophs preferentially consume methane containing the lighter carbon isotope during oxidation. This leaves the residual pool of methane enriched in the heavy carbon isotope and creates a pool of carbon dioxide containing carbon depleted in the heavy carbon isotope.

AQUIFER MIXING AND BACTERIAL OXIDATION STRONGLY MEDIATE DISSOLVED METHANE CONCENTRATIONS

- EVIDENCE OF MIXING AND DILUTION
  - LARGE RANGE IN STABLE ISOTOPE SIGNATURES IN SAMPLES FROM ONE WELL
  - LARGE RANGE IN CHEMICAL COMPOSITION IN SAMPLES FROM ONE WELL
- EVIDENCE OF BACTERIAL OXIDATION OF METHANE
  - SYSTEMATIC ENRICHMENT OF STABLE CARBON AND DEUTERIUM ISOTOPES WITH DECREASING METHANE CONCENTRATION (1::8.3 PER MIL RESPECTIVELY)
  - SYSTEMATIC ENRICHMENT IN DELTA ^{13}C METHANE AND DEPLETION OF DELTA ^{13}C IN CO_2
  - LARGE NUMBER OF SAMPLES WITH MORE NEGATIVE THAN EXPECTED CARBON ISOTOPIC VALUES FOR CO_2

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