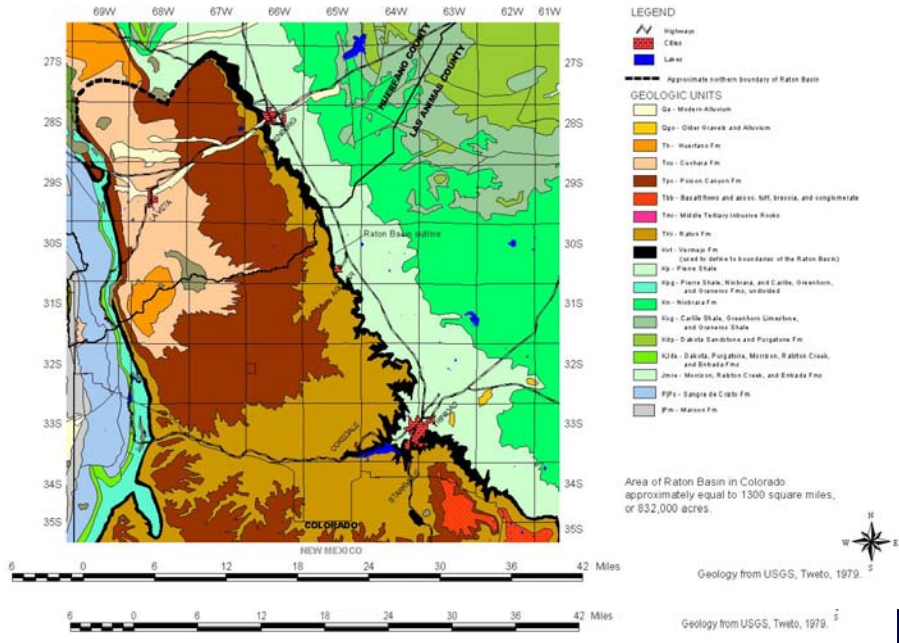


**RATON BASIN PROJECT**  
**2000-2003**

Rich Griebing –Director  
Study Funded by Severance Tax

# Raton Basin Project 2000-2003



## Raton Basin Project 2000-2003 Baseline Data Objectives

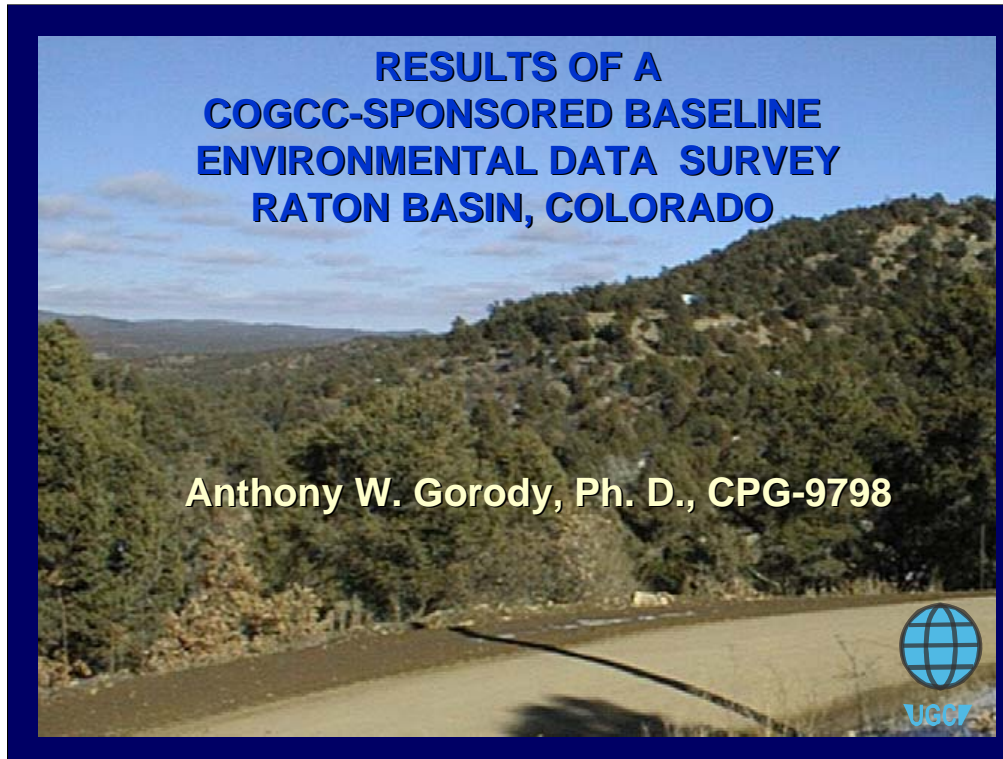
- Identify Existing Methane Seeps
- Compile Existing Water Data
- Collect New Gas and Water Samples
- Map Subsurface Coal Mines
- Prepare Data for Distribution Via Internet
- Present Results in Meetings and Papers

## Raton Basin Project 2000-2003 Acknowledgements

- Rich Griebing – COGCC Director
- Debbie Baldwin – Environmental Supervisor
- Jim Milne – GIS Administrator
- Industry Contributors - Cedar Ridge LLC, Evergreen Resources, KLT, Petroglyph Energy Inc., Paul Oldaker (AMOCO)

## Raton Basin Project 2000-2003 Contractors

- Apogee Scientific - IR Gas Survey
- Greg Lewicki Associates – Mine Mapping
- ESN - Gas Well Samples and Produced Water Samples
- Seacrest – Water Well Gas Samples and Water Samples
- Isotech Laboratory – Gas & Water Isotopes
- Anthony Gorody Ph. D.- UGCI



## Abstract

Continuing development of coal bed gas (CBG) resources has prompted concerns from local government and the public about the potential impacts to ground water in the Raton Basin. There is a concern of possible de-watering of shallow aquifers due to water being pumped from CBG wells. Some people see the CBG waste water as a valuable resource that is being lost in an arid basin. There is also a safety concern that continued development of CBG may cause gas seepage from coal seams and coal sub-crops. The COGCC conducted a baseline study to document existing conditions and provide data for addressing these concerns. This presentation summarizes the methods and results of the study with respect to the chemical and isotopic data.

A total of 2,749 linear miles were surveyed for hydrocarbon seeps using a truck-mounted infrared spectroscopy detection device. Sixty seven (67) separate seeps were found, and these were confined to an area within the Raton Formation coal outcrop and shallow subcrop. Additional investigations would be required to identify the actual source of each seep. Water wells containing measurable amounts of dissolved methane are geographically distributed in a pattern similar to that observed for methane seeps. Of 240 water well samples analyzed, 47% contain measurable amounts of dissolved methane. The source of methane can be determined by analyzing its stable carbon and deuterium isotope values. Because the range of stable isotopic values found is large, methane in groundwater and shallow seeps can be differentiated from produced methane.

Four hundred and sixty five (465) active and abandoned coal mines were identified, three hundred and twenty eight (328) were digitized, and the location of one thousand one hundred and forty one (1141) core holes were digitized, to provide spatial data of potential methane sources.

The quality of surface water, domestic well water, and springs is variable throughout the basin and composed of mixed water types. These types include calcium-magnesium bicarbonate (dissolved limestone), calcium and sodium sulfate (dissolved gypsum and thenardite), and minor amounts of sodium bicarbonate (dissolved baking soda). Water quality and water well yield are typically affected by fecal coliform bacteria and naturally-occurring coliform, sulfate-reducing, and iron-related bacteria.

Produced waters contain more total dissolved solids than shallow groundwater, and are composed principally of two mixed water types: sodium bicarbonate (dissolved baking soda) and sodium chloride (dissolved table salt), in general produced waters contained little or no sulfate. **A few CBG well areas contained elevated dissolved sulfate concentrations. These areas would require further investment to identify the source.** The stable isotopic composition of carbon in dissolved inorganic carbon is also a useful indicator for detecting the presence of shallow groundwater in producing wells.

**THIS PRESENTATION ADDRESSES  
3 WATER & GAS-RELATED  
ENVIRONMENTAL ISSUES  
ASSOCIATED WITH  
COALBED GAS DEVELOPMENT**

- **COAL MINE AND CORE HOLE INVENTORY**
- **METHANE SEEPS**
- **DISSOLVED METHANE IN GROUNDWATER**
- **TOOLS FOR ASSESING POTENTIAL IMPACT TO SHALLOW AQUIFERS**

## MULTIPLE DATA SETS USED IN STUDY

### PRODUCED WATER DATA

- COGCC Survey
  - SeaCrest
  - ESN Rocky Mtn.
  - Isotech
- KLT
- PETROGLYPH

### COAL MINE INVENTORY

- COGCC Survey

### SEEP & GROUNDWATER DATA

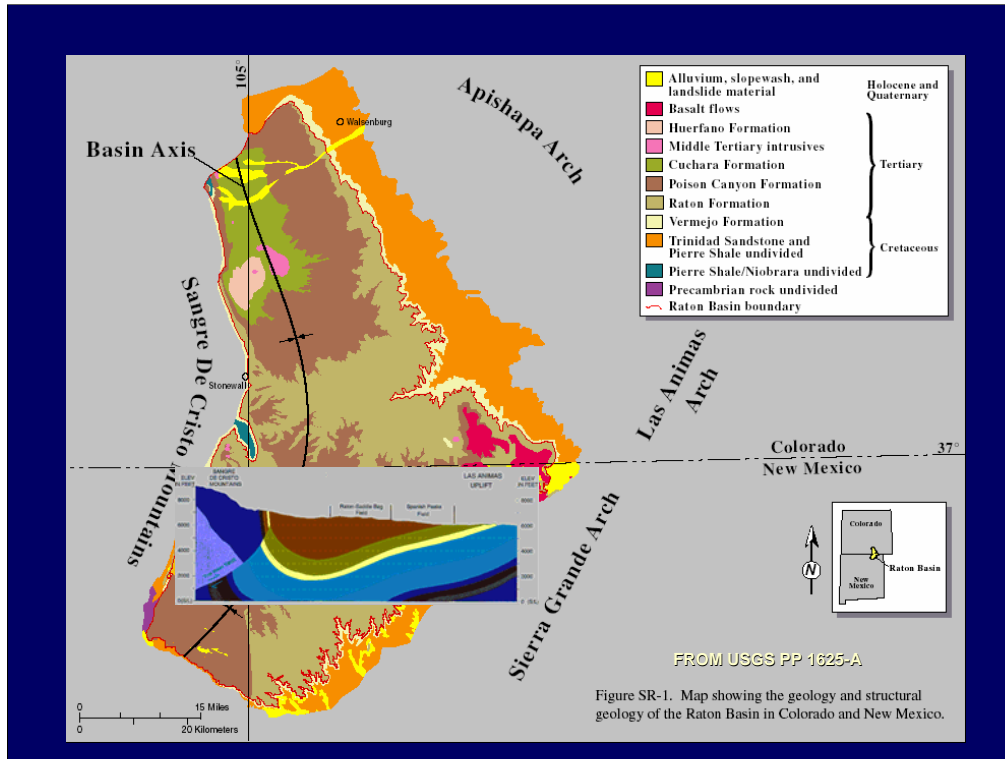
- COGCC Survey
  - Seacrest
  - ESN Rocky Mtn.
  - Apogee Scientific
- USGS WSP 2288
- APPLIED ECO.
- CEDAR RIDGE
- AMOCO
- EVERGREEN



## **OBJECTIVES OF COGCC BASELINE STUDY**

- **COLLECT, COMPILE, AND ANALYZE A VARIETY OF ENVIRONMENTAL BASELINE INFORMATION**
- **MAKE DATA AVAILABLE TO STAFF, INDUSTRY & PUBLIC**
- **DESCRIBE USEFUL METHODS FOR ADDRESSING COMPLAINTS RELATED TO GROUNDWATER ISSUES**
- **RECOMMEND PROTOCOLS FOR FUTURE MONITORING, SAMPLING, AND ANALYSIS**

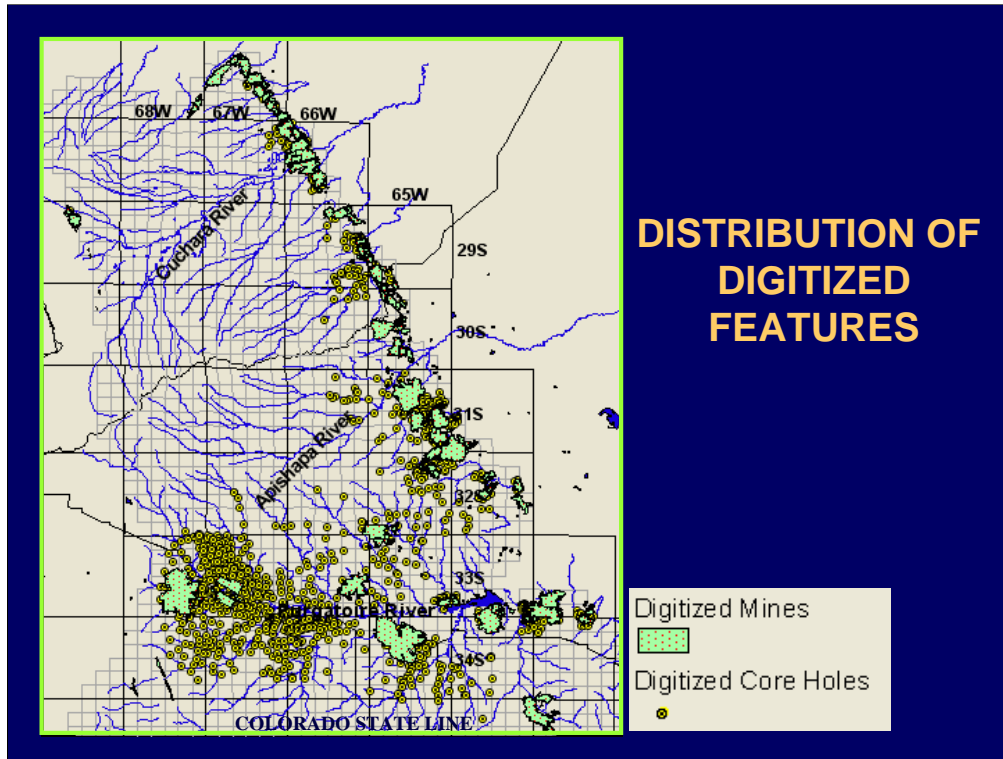
This baseline study emphasizes tools and techniques that are useful for addressing complaints and for evaluating the potential environmental impact of coalbed gas production operations on groundwater resources. No attempt is made to either define risk, rank risk, or to list and rank the potential consequences should any risks be realized. Risk, as defined here, is neutral term used for evaluating the uncertainty of an outcome having an undesired effect.



The Raton Basin is a structurally asymmetric synclinal basin, with coal outcrops along the eastern and western margins.

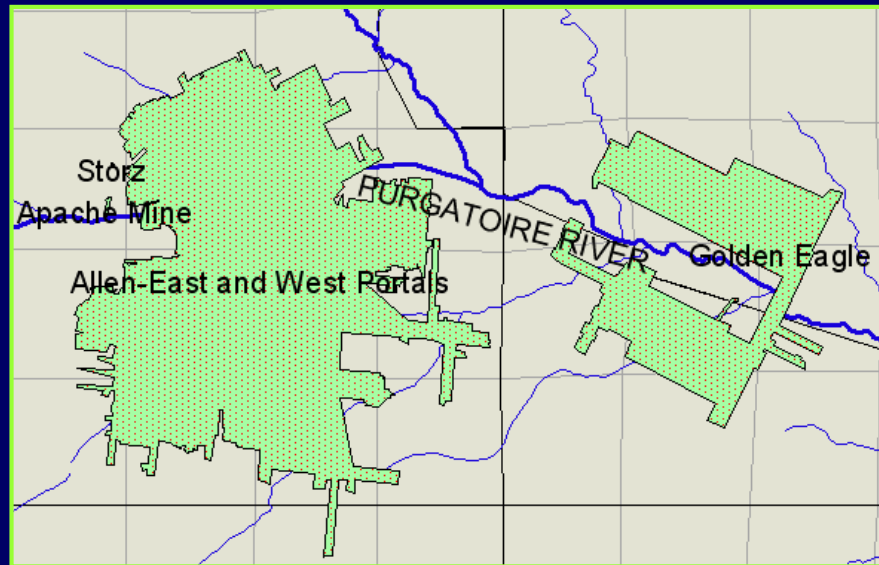
## **COAL MINE INVENTORY DIGITIZED: Lewicki & Associates**

- 465 MINES IDENTIFIED
- 328 MINE BOUNDARIES DIGITIZED
- MINE PORTALS AND OTHER FEATURES  
THAT MAY EMIT METHANE DIGITIZED
- LOCATION OF 1411 CORE HOLES DIGITIZED



The core hole data base marks locations only. Lithologic data have not been digitized.

## EXAMPLE DEGREE OF DETAIL DIGITIZED



Detailed mapping of mines helps as follows:

- Provides guide for placement of water wells and producing wells
- Identifies mine portals which may be source of methane mine emissions.

## **METHANE SEEPS & DISSOLVED METHANE**

### **DOCUMENTING BASELINE CONDITIONS**

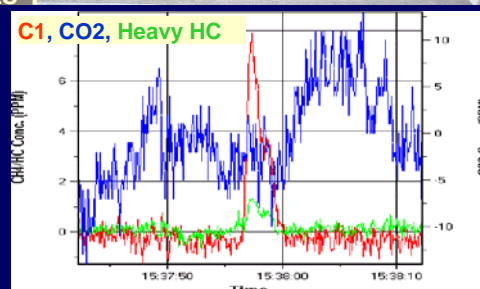
**APOGEE SCIENTIFIC**

- **METHOD USED FOR DETECTING SEEPS**
- **SEEP DISTRIBUTION AND MAGNITUDE**
- **RECOMMENDATIONS FOR ADDITIONAL SURVEYS**
- **DISTRIBUTION OF DISSOLVED METHANE**
- **USEFUL METHOD FOR IDENTIFYING METHANE SOURCES**

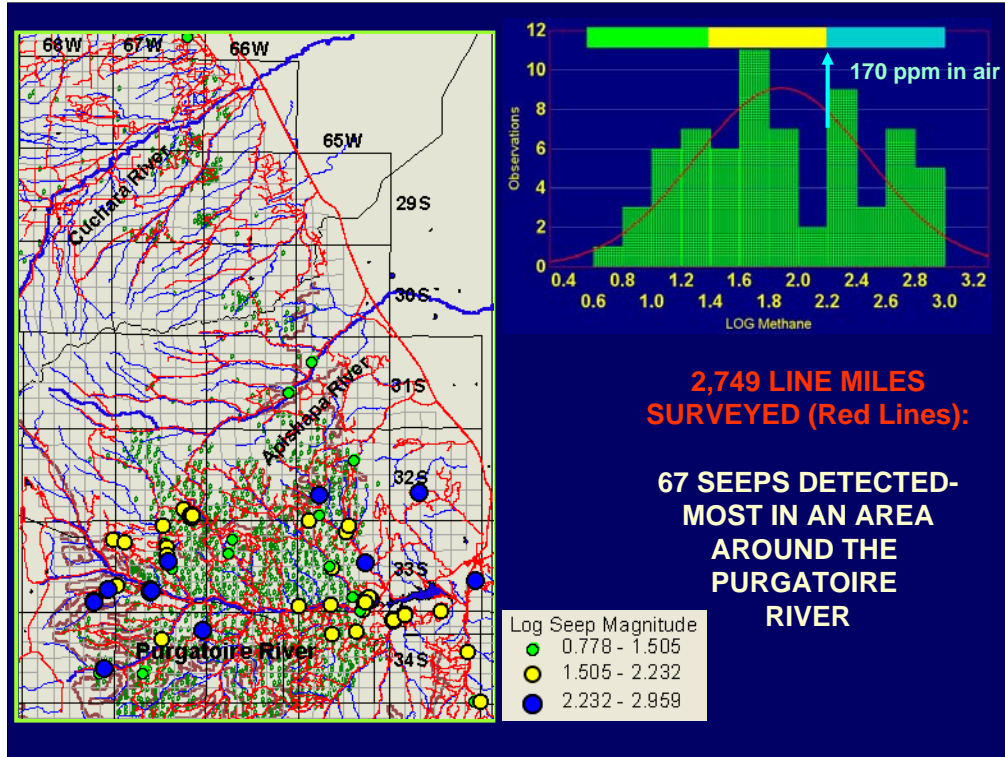
## METHANE SEEPS QUANTIFIED



**APOGEE SCIENTIFIC  
GAS SEEP DATA  
ACQUISITION  
EQUIPMENT**



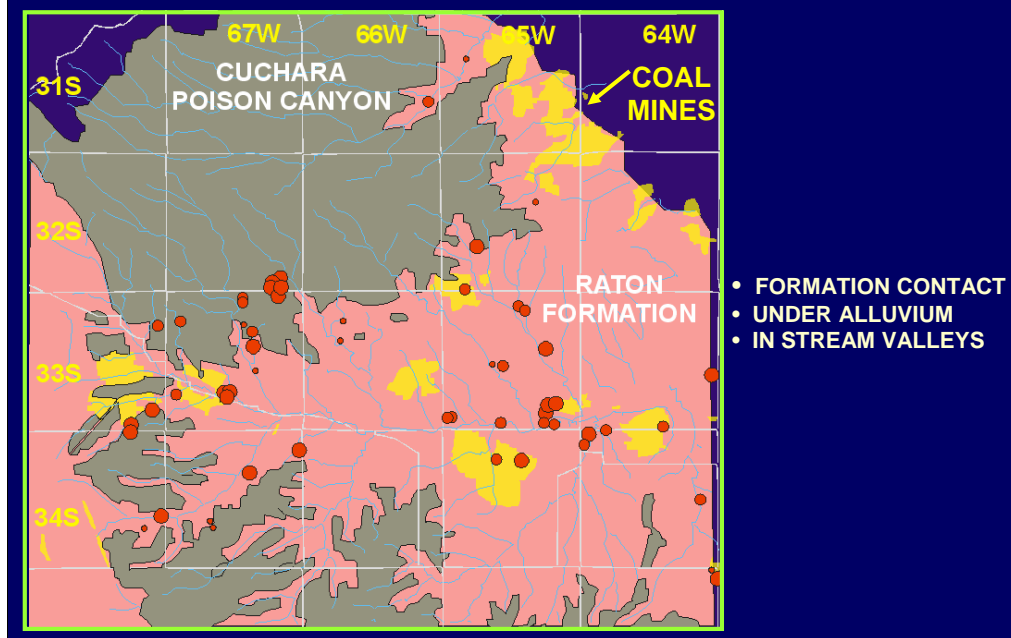
The gas detection system is based on infrared spectroscopy which differentiates methane, carbon dioxide, and heavy hydrocarbons. Air scoops, located at the front of the vehicle, continuously sample air which is analyzed at a maximum rate of 100 Hz. Normal sampling rates are on the order of 50 Hz at average ground speeds of 20-40 mph. Sensitivity to hydrocarbons of the IRS device is on the order of a few ppm by volume in air. Proximity to seeps is estimated by examining peak heights and widths. The sharper the peak, the closer the seep. Once detected, seeps can be pinpointed by driving in circles.



Methane seeps detected in this baseline study are clustered within the Purgatoire River drainage basin. Red lines indicate the 2749 mile route taken for the survey. The northernmost seep occurs at the mouth of a mine. A histogram of the logarithm of seep concentrations (in ppm) shows there are two seep populations: one less than approximately 170 ppm; the other greater than 170 ppm. For reference, the lower explosive limit (LEL) for methane in air is 5% by volume, or 50,000 ppm (log value 4.69). Safety levels of concern are usually set at 20% of the LEL, or 10,000 ppm (log value 4). There does not appear to be a spatial correlation between the distribution of seeps and the distribution of producing gas wells.



## SEEPS OCCUR WITHIN AND AROUND THE OUTCROP LIMITS OF THE COAL-BEARING RATON FORMATION



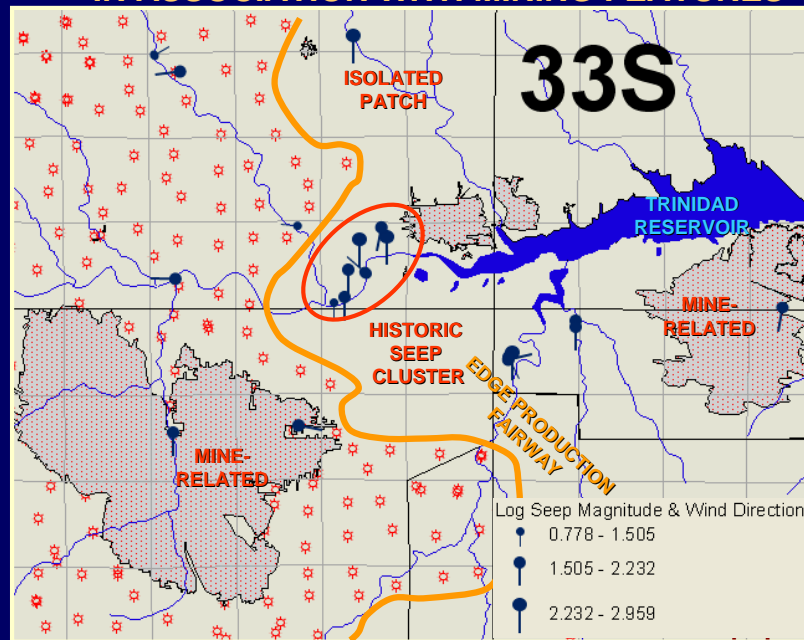
Geologic mapping shows that seeps occur exclusively within the area defined by the outcrop and shallow subcrop of the coal-bearing Raton Formation. 67 seep locations were detected. Seeps emanating from the coal-bearing subcrop are buried at depths less than 50 feet below either alluvium, or the Poison Canyon Formation. There is no apparent correlation between seep locations, coalbed gas wells, mapped dikes, or mapped faults. The majority of natural seeps occur within and along stream valleys and along road cuts where coal seams are exposed.

**SEEPS ASSOCIATED WITH COAL SEAM  
OUTCROPS**



Example of a seep emanating from exposed outcrops.

## SEEPS OCCUR IN ISOLATED PATCHES, CLUSTERS, & IN ASSOCIATION WITH MINING FEATURES



These tadpole plots show relative seep magnitudes as well as wind direction monitored at the time of the survey. Historic seeps occur outside of the updip limit of coalbed gas production activities. Coalbed gas wells are marked in red. Seeps occurring within the production trend are located in stream valleys, and may be good markers for defining areas where groundwater is discharging. Pinpointing seeps would be best accomplished by walking around a detected gas source using a hand-held flame ionization detection device.

## SEEPS RELATED TO MINES



Approximately 1/3 of the seeps detected appear to be emanating from mine-related features.

## SUMMARY OF SEEP CHARACTERISTICS

### ANTHROPOGENIC ORIGIN

- Mine-related features
- Water wells
- Pipeline right-of-ways
- Other utility Infrastructures
- Gas production?

### NATURAL ORIGIN

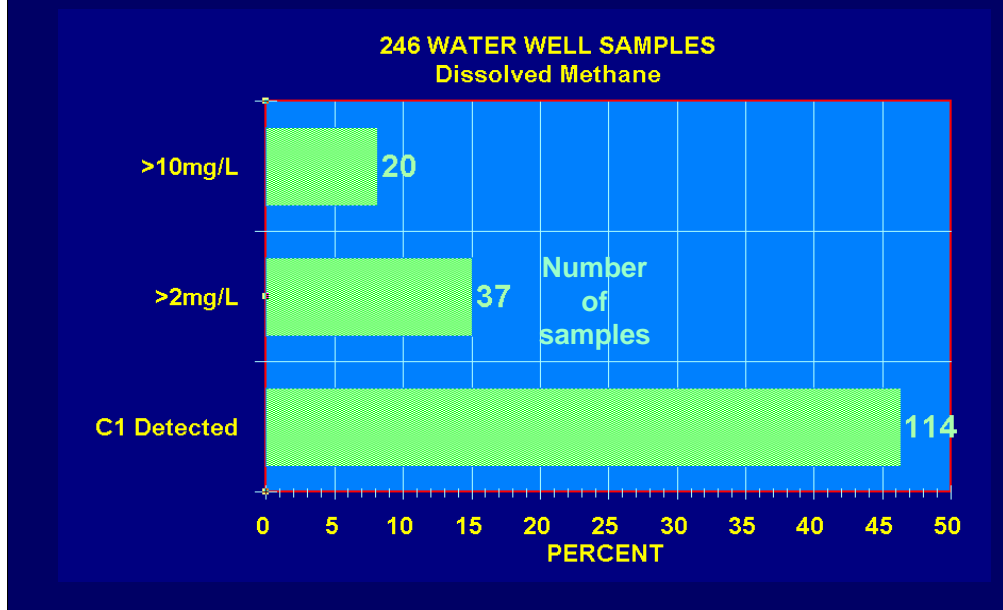
- Within outcrop trace of coal-bearing formation
- Formation contacts
- Dominant in NW & NE-trending linear stream valley traces
- Outcrop buried under shallow alluvial fill
- Historic

## **IRS IS A GOOD SCREENING TOOL**

**COVER A LOT OF AREA IN SHORT TIME**

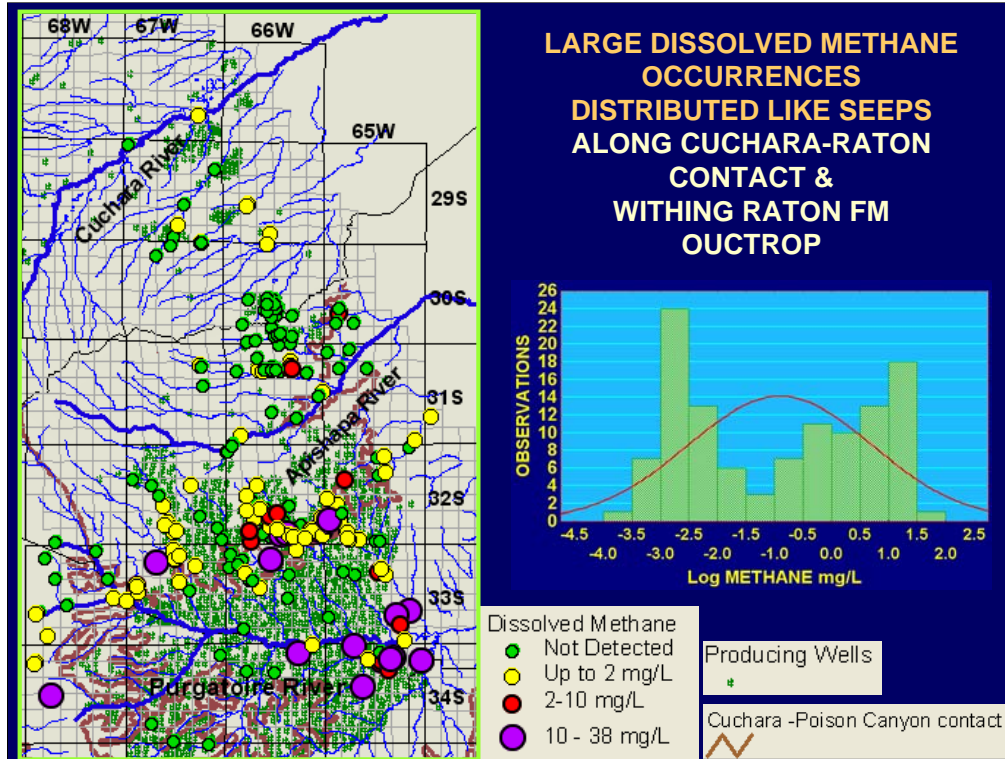
- **RECOMMENDATIONS**
  - FOLLOW UP VAN-BASED SCREENING SURVEY WITH WALKING SURVEY USING PORTABLE FID WHERE NEEDED
  - LOCATE AND ACCURATELY DESCRIBE SOURCE CHARACTERISTICS OF SELECTED SITES
  - SAMPLE GAS FROM LARGER SEEPS FOR LABORATORY ANALYSIS & COMPARE TO PRODUCTION WHERE NEEDED
  - DETERMINE NEED FOR LONG TERM SOIL GAS FLUX MONITORING

## DISSOLVED METHANE IN GROUNDWATER QUANTIFIED



Nearly half of all water wells tested for methane contain detectable concentrations. This result is normal for foreland basins along the Rocky Mountains. 15% of the wells tested contain concentrations exceeding 2 mg/L. Such concentrations define an arbitrary threshold where methane could exsolve in enclosed spaces and accumulate to explosive levels. 8% of the wells tested contain concentrations exceeding 10 mg/L. For comparison, the saturated dissolved methane concentration at atmospheric pressures typical for the high elevations in this basin is approximately 24 mg/L. Wells containing more than 10 mg/L of dissolved methane should be treated to safely remove exsolving methane.

Wells should be screened for methane by filling a clean 5 gallon bucket with water and testing the air above the water with a hand-held flame ionization detector. If methane is detected, a water sample can be collected by filling a 40 ml. VOA vial under water, and ensuring that there are no bubbles present when the vial is sealed. Such samples are then sent to a laboratory for analyses defined by the USGS Kampbell protocol. Samples collected for chromatographic and stable isotopic analyses are collected by filling a 1L glass amber bottle under water. All efforts should be taken to insure that the bottle does not contain any air bubbles when sealed with a Teflon-coated rubber seal cap. If the water effervesces, then a sample should be collected in the 1L amber bottle by filling the bottle with water under water, using an inverted funnel to allow gas to displace water, and creating a headspace that fills at least  $\frac{1}{4}$  of the bottle volume. Samples are sent to the laboratory for analysis after sealing the Teflon-lined cap with tape and shipping bottles chilled and safely packed in an ice-filled chest.



Like methane seeps, the distribution of dissolved methane concentrations is bimodal. The distribution of larger dissolved methane concentrations is confined to the area bounded by the Raton and Cuchara-Poison Canyon contact. Statistical analysis of the data in the second population of values indicates a mean value of 3 mg/L and a standard deviation of 5 mg/L.

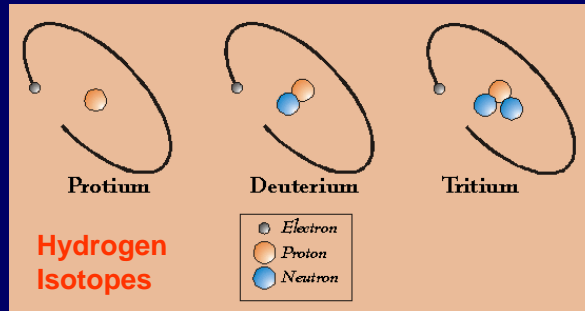




## WHAT IS A STABLE ISOTOPE?

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.

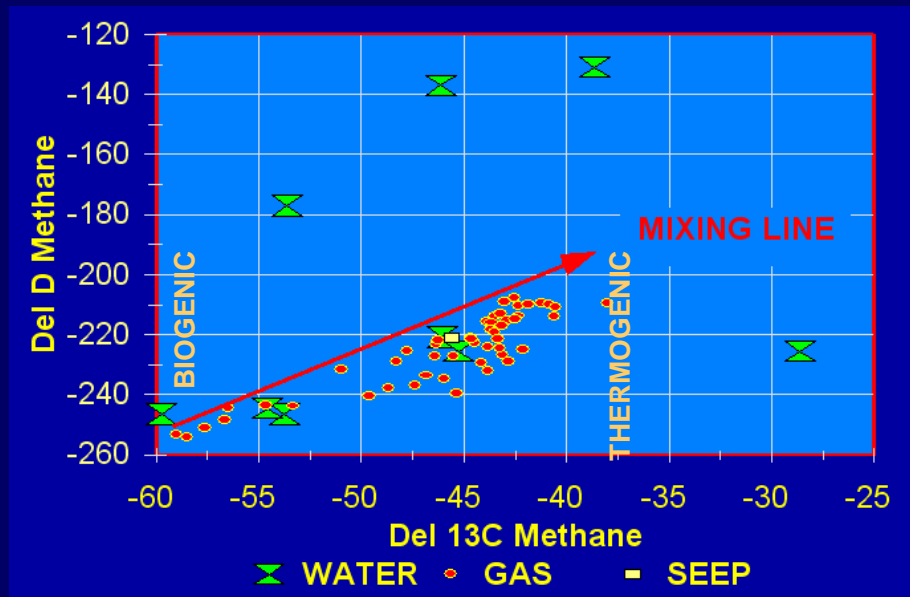


### Carbon Isotopes:

<u>Isotope</u>	<u>Protons</u>	<u>Neutrons</u>	<u>Abundance</u>	<u>Type</u>
<sup>12</sup> C	6	6	98.98%	Stable
<sup>13</sup> C	6	7	1.11%	Stable
<sup>14</sup> C	6	8	trace	Unstable

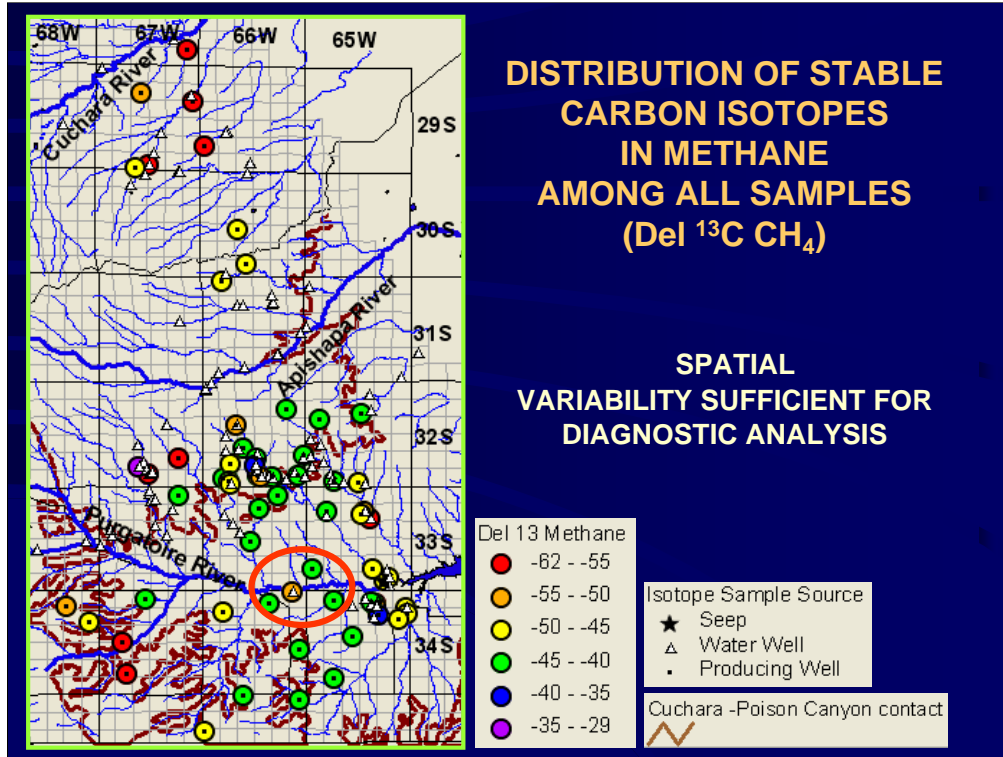
The stable carbon and deuterium isotopes of methane (CH<sub>4</sub>) are used in the oil and gas industry as a diagnostic tool to determine methane origin. Methane originating from the burial of organic sedimentary matter at high temperatures and pressures is defined as thermogenic. Methane originating 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.

**LARGE RANGE IN STABLE C AND H ISOTOPES IN PRODUCED METHANE IS DIAGNOSTIC OF MIXED BIOGENIC AND THERMOGENIC SOURCES**

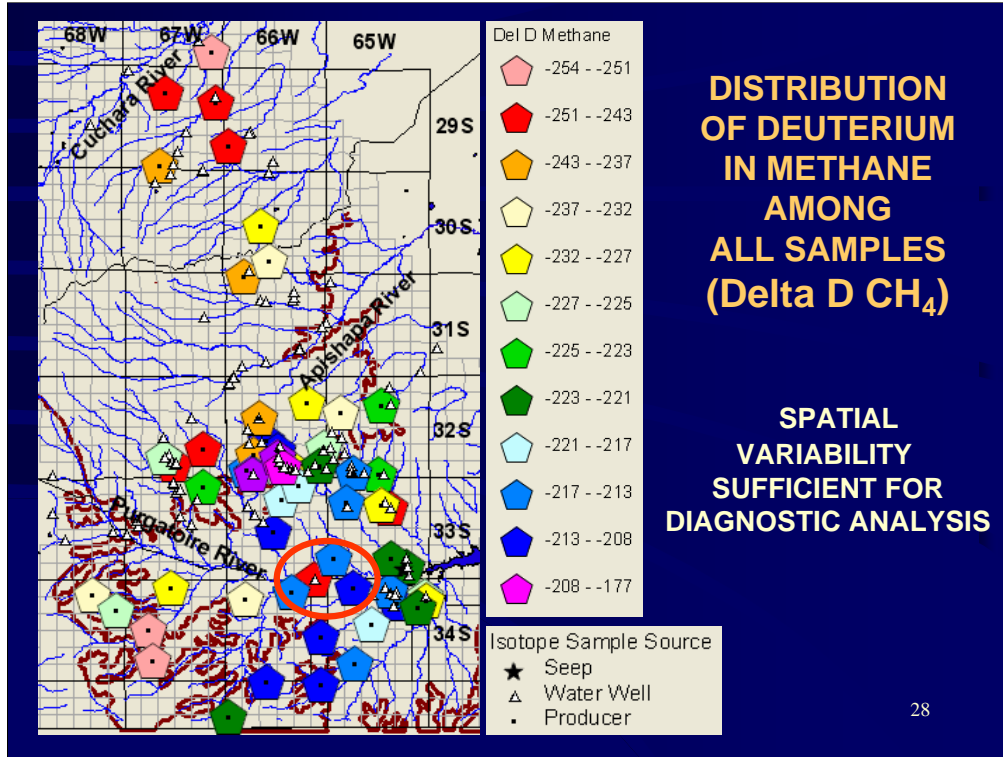


The isotopic pattern evident among samples collected from coalbed gas wells in the Raton Basin is one that is characteristic of mixed biogenic and thermogenic sources. The composition of produced gas samples with isotopic signatures characteristic of thermogenic methane generally contains higher hydrocarbons such as ethane, propane, butane, and in some cases, pentane. The composition of produced gas samples with isotopic signatures characteristic of biogenic methane generally contain only methane and minor amounts of ethane. Stable isotopic analysis of carbon in produced CO<sub>2</sub> yields very positive values, indicating that bacteria have converted CO<sub>2</sub> into methane. There is little apparent correlation between the isotopic composition of methane and the vitrinite reflectance in coals. This indicates that the gas composition has been altered by bacteria which may have been introduced along basin margins during uplift and fresh water intrusion into the basin. In general, wells producing gas with a thermogenic signature produce less water and more gas than wells producing gas with a biogenic signature. Water from wells producing thermogenic gas also tends to be more saline and enriched in chlorides.

There are only a few complete stable isotopic measurements available for methane in domestic water wells, springs, and seeps. Those available are plotted above. In some cases, the isotopic composition is similar to that observed among producing wells. In other cases, the signatures are very different. Because of the large range in isotopic values, stable isotopic analysis can be a very useful forensic tool to determine the origin of methane in domestic water wells, springs, and seeps.

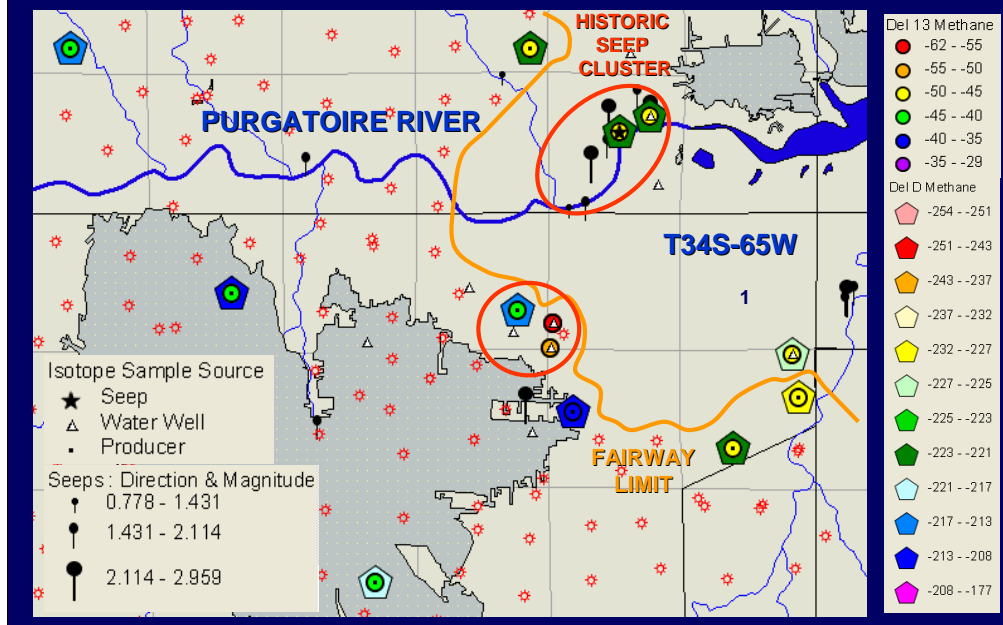


The stable isotopic composition of carbon in methane from shallow water wells is distinctly different from that found in many nearby producing wells. This can be used as a forensic tool.



The spatial distribution of deuterium values in methane from produced wells is more variable than the distribution of stable carbon values. This probably reflects a more heterogeneous distribution of the deuterium in water from which the methane was derived.

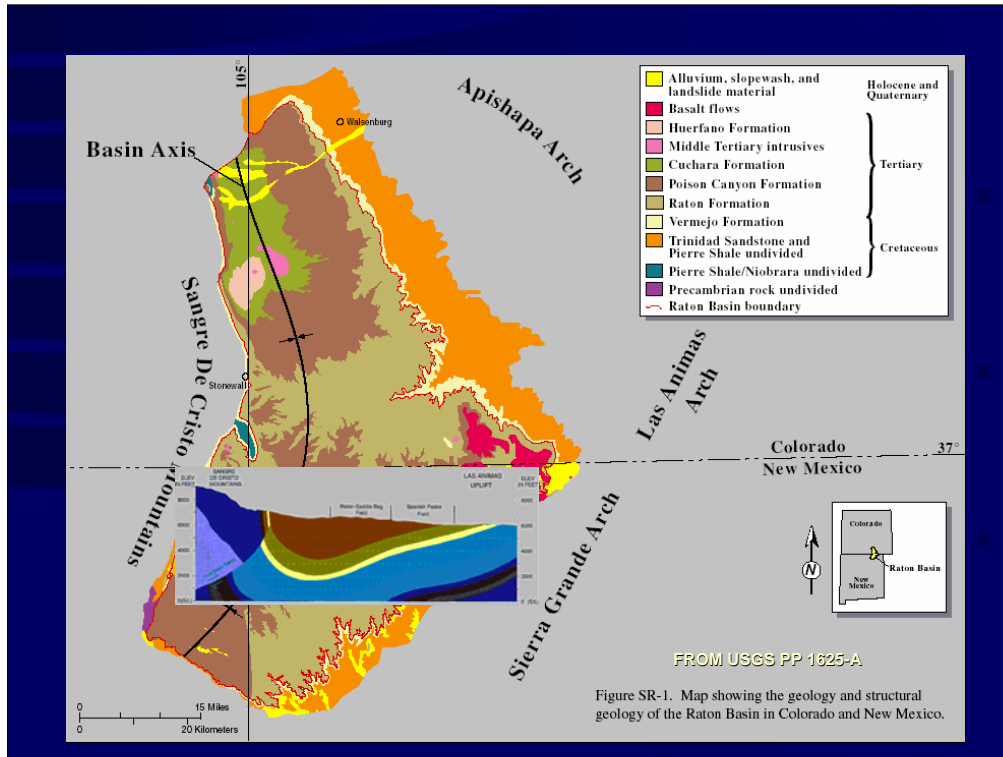
## COMBINED, STABLE ISOTOPES OF METHANE PROVIDE EXCELLENT FORENSIC TOOL



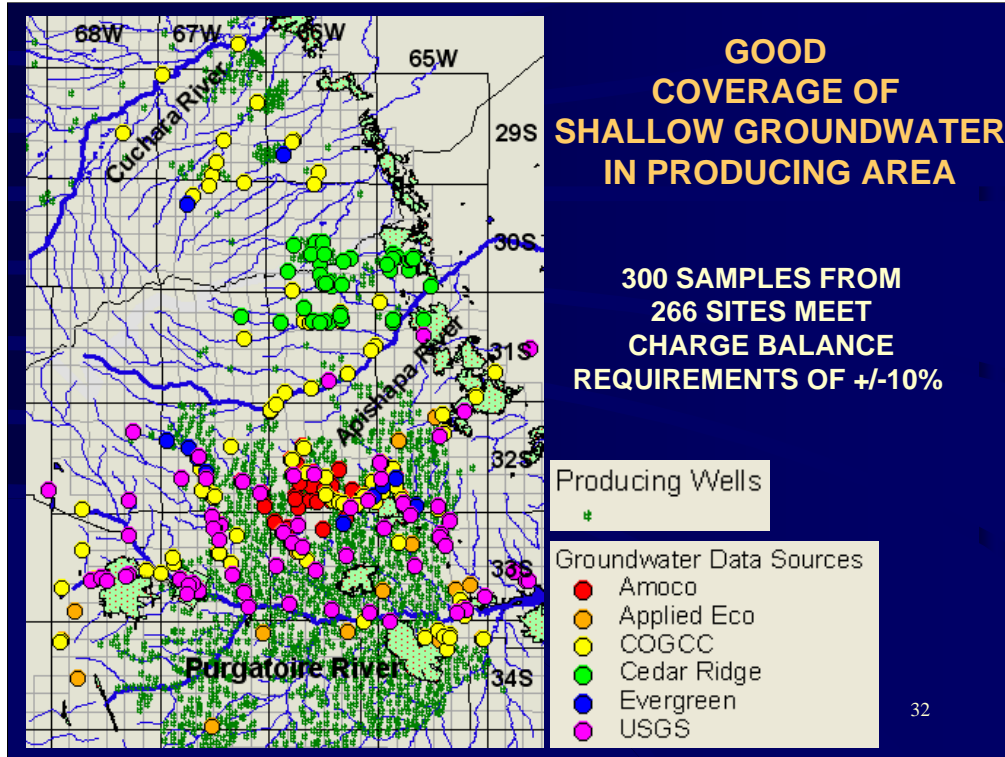
Combined, the stable carbon and deuterium isotopes of methane can be used to determine the origin of methane in seeps and domestic water wells. For example, the historic seeps at the mouth of the Trinidad Reservoir and dissolved methane in a nearby domestic water well have a composition that is nearly identical to the composition of gas from the producing well in section 28, T33S-R65W. This suggests that historic seeps may delineate in areas where groundwater is discharging. In the SW corner of section 2 in T34S-R65W, the stable isotopic signature of carbon in domestic water wells is very different from that in a nearby producing well in section 3. Methane in the domestic water wells here probably originates from shallow biogenic sources.

## **SUMMARY DISSOLVED METHANE**

- **DISSOLVED METHANE OCCURS WITHIN OUTCROP BOUNDARY OF RATON FORMATION**
- **REGULAR MEASUREMENT OF DISSOLVED METHANE IN WATER WELLS IS RECOMMENDED AS A SAFETY PRECAUTION**
- **STABLE ISOTOPES USEFUL FOR DETERMINING METHANE SOURCE AND FOR COMPARISON WITH GAS FROM PRODUCING WELLS**

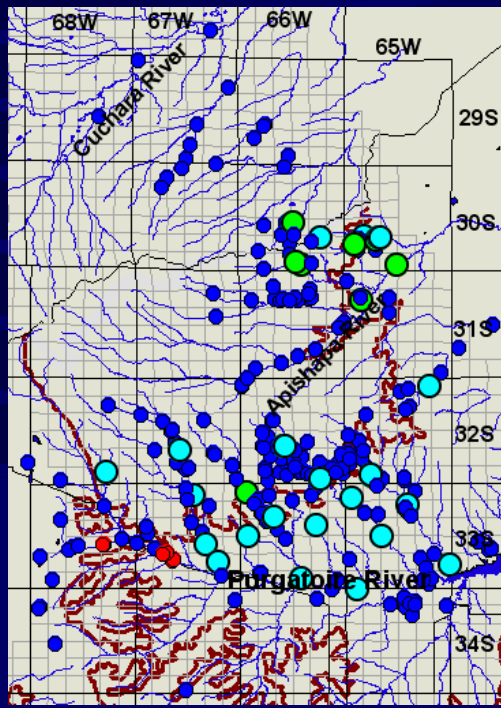


Available data indicate that the predominant area of groundwater recharge occurs along the western margin where elevations are highest and precipitation is most abundant. Because the overall topographic slope in the basin tilts towards the east, recharging fluids move generally eastward in the subsurface. Along the flowpath, groundwaters discharge into tributary stream valleys. The principal rivers of the area, the Purgatoire, the Apishapa, and the Cuchara, are “gaining” rivers, meaning that flow is enhanced by groundwater baseflow discharge. Thus the chemical composition of water in rivers at any given time results from the mixing of surface runoff and baseflow. At times of low annual precipitation rates, a larger component of the fluid chemistry is due to groundwater discharge; at times of high annual precipitation rates, the fluid chemistry is fresher and contains higher relative concentrations of calcium, magnesium, and sulfate.

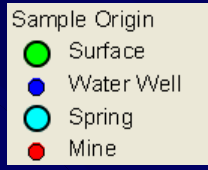


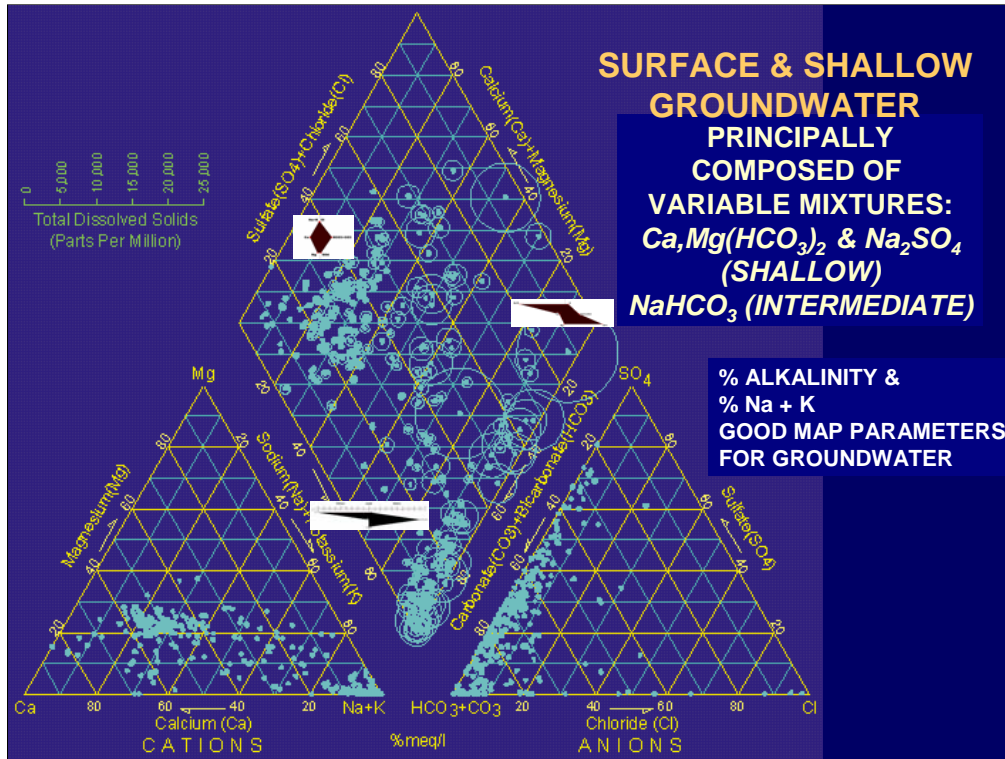
The quality of water analyses has been checked by comparing the sum of the concentrations of negatively charged dissolved anions against the sum of the concentrations of positively charged dissolved cations. Theoretically, the sum of positive and negative charges should be zero. However, due to the different analytical methods used to analyze positive ions and negative ions, it is customary to accept analyses that are within a charge balance of +/- 5%. Because of differences in analytical methods applied to obtain values used for this study, the use of different laboratories, and systematic sampling errors found in the data analyzed in this study, we chose to accept analyses that had a charge balance of +/- 10%. The largest source of errors detected in this study originate from the titration methods used to measure alkalinity. Ideally, samples should be titrated in the field because the loss of dissolved CO<sub>2</sub> during transport and protracted sample storage reduces *in-situ* values by as much as 10%. If samples are not titrated in the field, they should be titrated within one or two days after arriving at the analytical laboratory.



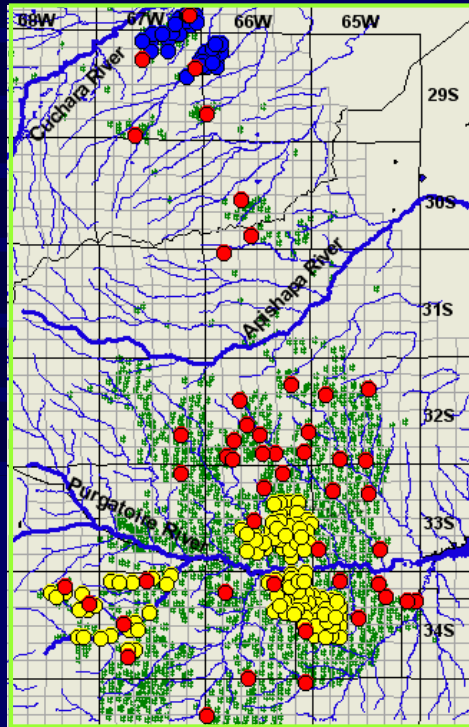


## SAMPLES COLLECTED FROM A VARIETY OF SOURCES





A trilinear diagram is used to illustrate the relative composition of the major dissolved constituents in surface and shallow groundwater. Among the positively charged dissolved cations, the distribution of points indicates variable mixtures of two principal endpoint members. End member compositions consist of 80% & 20% calcium and magnesium respectively, and 100% sodium. Among the negatively charged dissolved anions, the distribution of points indicates variable mixtures of two principal endpoint members. End member compositions consist of 80% sulfate and 100% bicarbonate. Calcium-magnesium bicarbonate type fluids contain the lowest amounts of total dissolved solids. Sodium chloride-bearing fluids occur in the most saline domestic water well aquifers, principally located along the southeastern half of the Purgatoire River groundwater flow system.



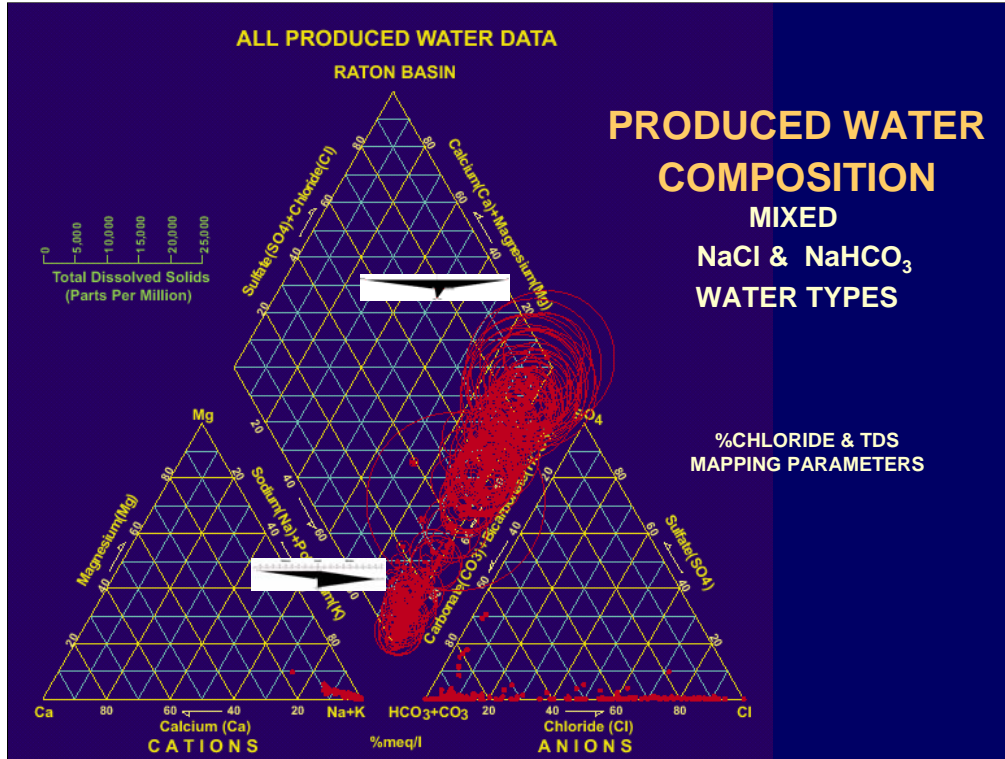
## SOURCE AND DISTRIBUTION OF PRODUCING WELLS SAMPLED

- COGCC
- KLT PRODUCTION
- PETROGLYPH

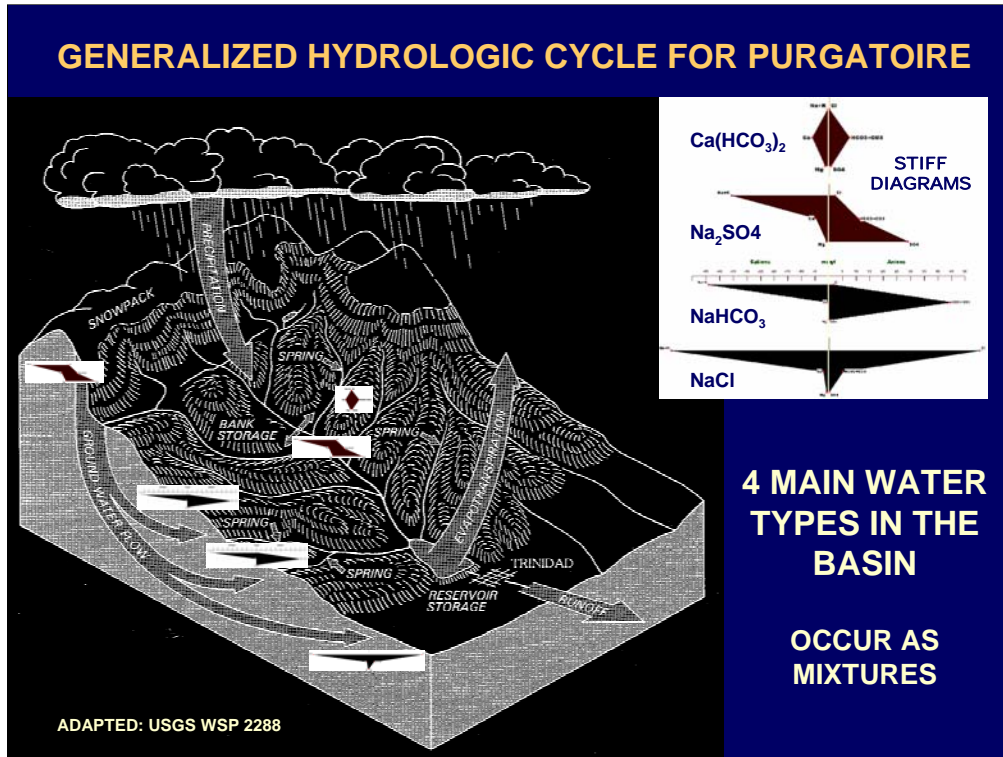
REASONABLY REPRESENTATIVE SAMPLE SET

Producing Wells





The composition of produced fluids is markedly different from that of surface and shallow groundwaters. Dissolved cations are composed almost entirely of sodium, whereas the dissolved anions are composed of two principal end point members consisting of 100% bicarbonate and 100% chloride.



There are four principal water composition types in the basin. These are as follows:

- Dissolved limestone (calcium and magnesium bicarbonate);
- Dissolved thenardite and glauber salt (sodium sulfates) with minor amounts of dissolved gypsum (calcium sulfate);
- Dissolved baking soda (sodium bicarbonate) and;
- Dissolved table salt (sodium chloride).

Calcium bicarbonate and sodium sulfate water types form the principal shallow groundwater types, whereas sodium bicarbonate and sodium chloride form the principal intermediate and deep water types. Within the coal-bearing formations, sodium bicarbonate dominates the water composition. Such compositions are typical among coal seams around the world. Sodium chloride forms a significant component of produced waters in the eastern half of the Purgatoire River groundwater flow system. These fluids are most likely present in both coal seams and permeable sandstone aquifers.

**ADDRESSING COMMUNICATION BETWEEN  
SHALLOW AQUIFERS AND GAS  
PRODUCING ZONES**

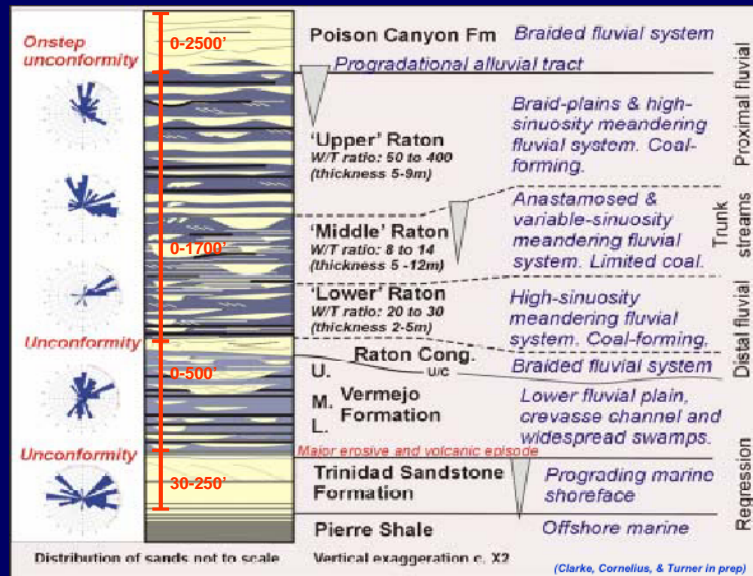
- **PUBLIC CONCERN THAT PRODUCING WATER FROM COAL IS IMPACTING AVAILABILITY OF WATER FROM SHALLOW AQUIFERS**
- **NO REGIONAL, SYSTEMATIC MONITORING OF SHALLOW GROUNDWATER LEVELS ESTABLISHED IN THE BASIN**
- **NEED TO DEVELOP SCREENING METHODS USING AVAILABLE DATA THAT IDENTIFY AREAS WHICH MAY BE AT RISK OF CROSS-AQUIFER COMMUNICATION**

## **APPROACH FOR IDENTIFYING SCREENING TOOLS**

- **MAP AREAS WHERE WATER WELLS AND PRODUCING WELL COMPLETIONS ARE IN CLOSE VERTICAL AND LATERAL PROXIMITY**
- **IDENTIFY DIAGNOSTIC PARAMETERS THAT DIFFERENTIATE SHALLOW GROUNDWATER AND PRODUCED WATER**
- **MAP DIAGNOSTIC PARAMETERS**
  - **IDENTIFY HOW THEY VARY ACROSS THE BASIN**
  - **IDENTIFY HOW THEY CHANGE WITH TIME**
- **DETERMINE WHICH PARAMETERS IN PRODUCED WATER MAY INDICATE POSSIBLE CONNECTION WITH SHALLOW AQUIFERS**



## EXTREME HETEROGENEITY IN SEDIMENTS OF GEOLOGIC COLUMN



From: Cornelius, C., 2002, 4th Unconventional Gas Symposium, Calgary

Groundwater flow rates in confined in coal seam aquifers of the Raton and Vermejo Formations are highly variable. Regionally, water pressure measurements indicate that fluid pressure gradients in coal aquifers are below hydrostatic gradients. This is principally due to generally poor vertical and lateral communication between aquifers. The existence of such poor communication is supported by the highly variable aquifer fluid chemistries that will be shown in the next few slides.

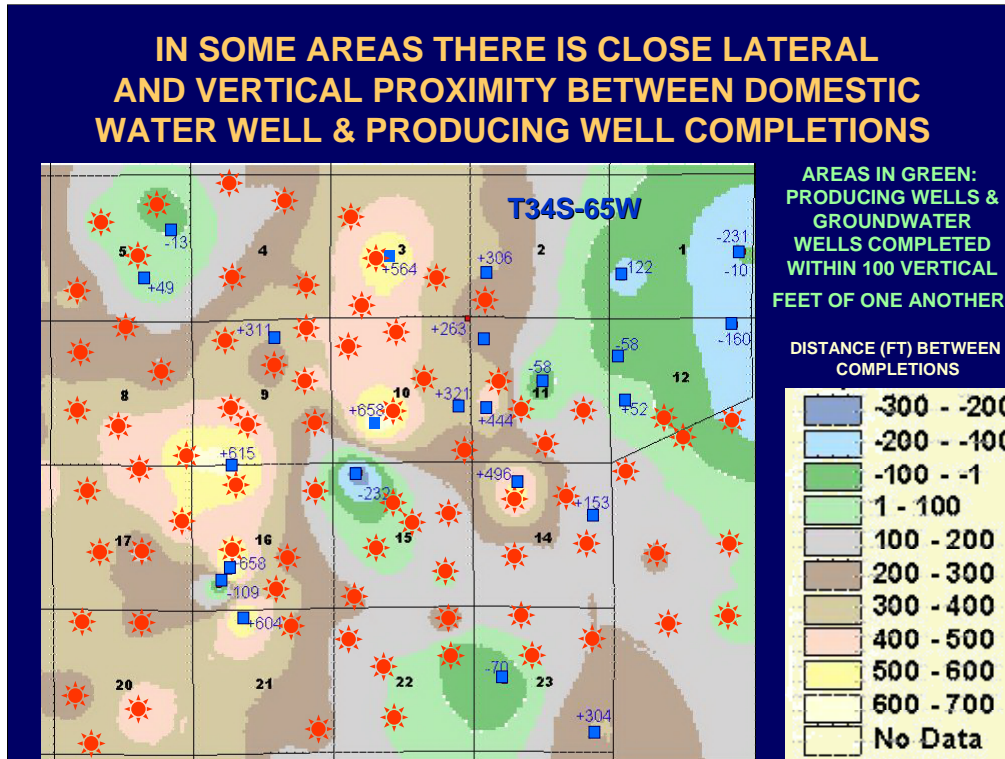
The observed poor lateral and vertical communication between aquifers is caused by a variety of factors. Based on detailed outcrop, core, and well log observations made during the past decade, the vertical and spatial distribution of permeable aquifers is highly irregular. As illustrated above, the distribution of coal and sand layers in the Poison Canyon, Raton, and Vermejo Formations is extremely heterogeneous. This has important ramifications:

- Permeable matrix will not be continuous over large areas;
- Natural and induced vertical fractures are not likely to propagate large vertical distances because of the predominance of multiple shale barriers;
- We can expect significant regional and local dispersion of fluids flowing through the matrix;
- Aquifers and producing horizons will be compartmented and discontinuous.

Additional flow barriers are present in the form of intrusive igneous dikes, syn-depositional faults accompanying basin filling coincident with Laramide-age thrusting along the western margin, and small post-depositional faults. Flow rates in sandstones is also very limited by extensive cementation of the available pore space. Coalbed gas production also seals off fluid communication between adjacent aquifers because gas evolving from coal seams significantly reduces the relative permeability of water to negligible rates. This important relative permeability phenomenon is widely overlooked in most assessments of lateral and vertical communication between aquifers. Accordingly, there is little reason to suspect that shallow aquifers will be in natural communication with water produced from deeper horizons in most areas.

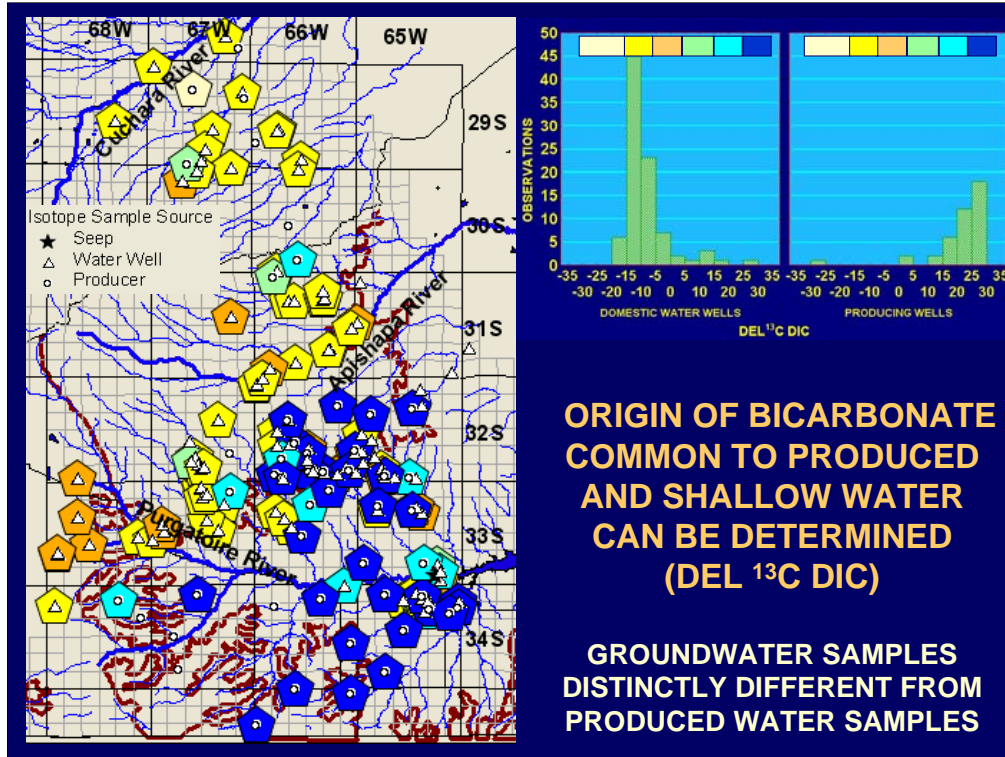






This area of the Raton Basin is one where the depth of water well completions is in relatively close lateral and vertical proximity to the top perforations in producing wells. Domestic water wells tend to be relatively deep in this area, and water quality tends to be quite poor.

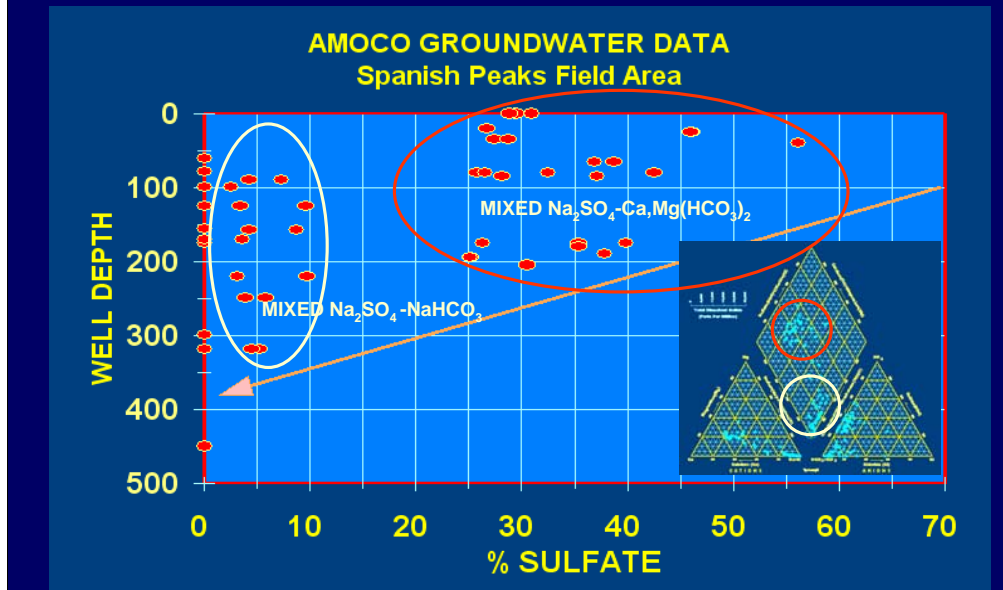
Methane isotopes can be used to determine whether the dissolved gas in domestic water wells is the same as the methane in produced gas from nearby wells. Because this area is also one where natural gas seeps have been known to occur and persist long before the advent of coalbed gas operations, it is important to collect and monitor baseline conditions. Only a few number of water level measurements are available in this area. However, the limited data available from areas contoured within the light blue and green range so far do not indicate that there is communication between producing zones and shallow aquifers. The COGCC will be monitoring 7 to 8 water wells in this area twice a year for the next three years to determine whether shallow aquifers are being impacted by coalbed methane operations.



Both shallow groundwaters and produced fluids contain a high relative percentage of dissolved bicarbonate anions. However, bicarbonate can be differentiated on the basis of stable carbon isotopes. The stable isotopic composition of carbon in dissolved inorganic carbon (DIC) among shallow groundwaters is distinctly different from that found in produced fluids. The stable carbon isotope ratios of DIC in shallow groundwater are predominantly in the range between -10 to -15 per mil. This is a characteristic of bicarbonates formed in soils.

The stable carbon isotope ratios of DIC in produced fluids are predominantly in the range of +20 to +30 per mil. These values were derived on the basis of the isotopic composition carbon in the CO<sub>2</sub> analyzed from the gas stream of producing wells. This conversion assumes that gaseous CO<sub>2</sub> has equilibrated with the CO<sub>2</sub> dissolved in water as DIC at an average formation temperature of 95°F. Positive values indicate that a significant amount of methane originated from bacteria that convert CO<sub>2</sub> to methane. Bacteria selectively use the lighter carbon isotope in CO<sub>2</sub> for their metabolism (kinetic fractionation), leaving the remaining CO<sub>2</sub> pool enriched in the heavier carbon. Regardless of the origin of such positive values, the large differences observed in the stable carbon isotope values of bicarbonate indicate that this parameter can be used to detect the presence of shallow groundwater in produced fluids.

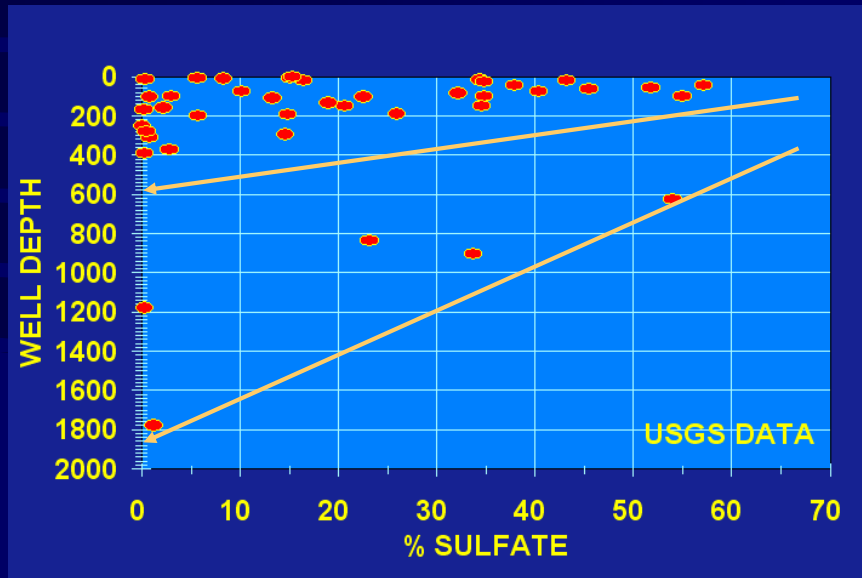
## SULFATE DECREASES WITH DEPTH



Elevated shallow groundwater sulfate concentrations originate from the near-surface oxidation of sulfide-bearing minerals such as pyrite. Such minerals are common in organic-rich shales and in coal seams where they outcrop. Sulfate concentrations tend to decrease with depth (Geldon, 1989 and this study) principally as the result of sulfate-reducing bacteria. Concentrations also decrease as a result of mixing with discharging intermediate water types of different composition. Similar patterns of decreasing sulfate concentrations with depth have been observed by the author in both the San Juan and Powder River Basins.

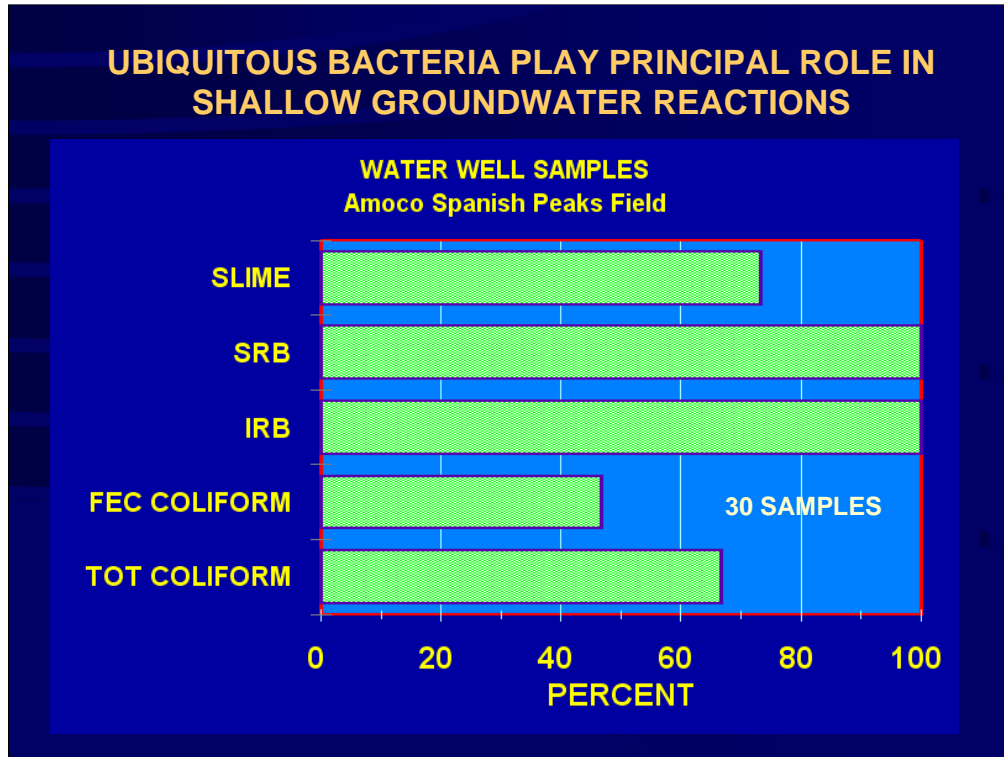
Values for % sulfate shown on the x-axis are calculated as the concentration of sulfate in milliequivalents per liter divided by the sum total of all dissolved anions in milliequivalents per liter ( $\text{Cl}^- + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{SO}_4^{2-}$ ). This is the same calculation used to create tri-linear diagrams. Note how the highest sulfate values are associated with calcium-magnesium bicarbonate waters that occur in shallow aquifers and surface waters. The lowest sulfate values are associated with sodium bicarbonate waters of intermediate aquifer depth.

**USGS DATA ALSO INDICATE A  
SULFATE DECREASES WITH DEPTH  
DUE TO BACTERIAL REDUCTION AND DILUTION**



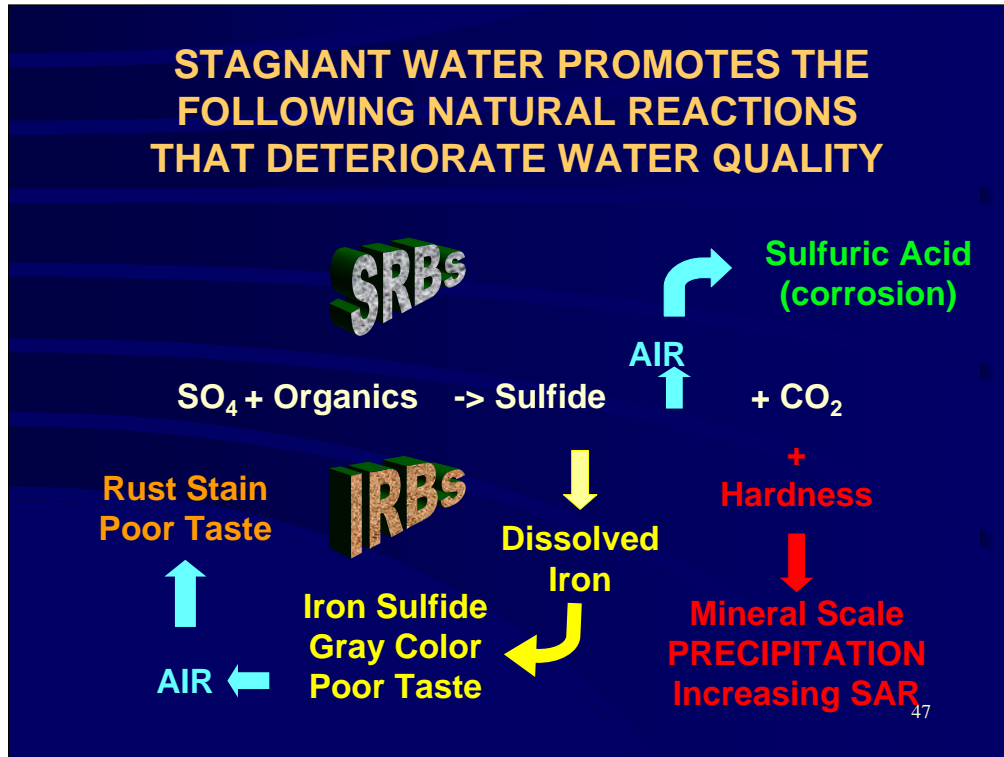
Data published by the USGS in their Water Supply Paper for the basin (Geldon, 1989, WSP # 2288) show similar results to those found using Amoco's Spanish Peaks field data illustrated in the previous slide. Both data sources provide evidence of decreasing sulfate concentrations with depth.

## UBIQUITOUS BACTERIA PLAY PRINCIPAL ROLE IN SHALLOW GROUNDWATER REACTIONS



The data shown above are derived from a limited set of Biologic Activity Reaction Tests (BART) performed on domestic water well samples. Because BART samples are easy to collect and analyze, they should become a standard part of domestic water well sampling protocols. Water wells in most western basins contain bacterial consortia that can significantly alter water quality and water well yield.

## STAGNANT WATER PROMOTES THE FOLLOWING NATURAL REACTIONS THAT DETERIORATE WATER QUALITY



The principal reported cause of poor domestic water quality and low water well yields in western basins is bacterial fouling and mechanical problems. There are established methods available to determine whether problems with water quality and well yield are related to bacteria. Analytical methods which can be used to sample wells in the field include BART (Biologic Activity Reaction Tests), analysis of fixed gases, and analyses of chemical composition. Results are used to determine the relative impact of scaling and bio-fouling. Chemical analysis is used to determine the scaling or corrosion potential of water (e.g. Langelier Saturation Index and Ryznar Stability Index). Such tests should be conducted and analyzed routinely before attempting to determine whether changes in water quality and yield are due to coalbed gas or other oil and gas production activities.

The ubiquitous presence of SRB's in the Amoco sample set explains why sulfate concentrations decrease with depth. Sulfate is converted to sulfide in the presence of organic matter. These bacterially-mediated reactions occur under stagnant conditions when dissolved oxygen concentrations in aquifers are very low or absent.

## BACTERIAL CONSORTIA FOUL WELLS

- CONSUME OXYGEN AND TURN WATER STAGNANT
- BIOSLIME CLOGS PERFORATIONS
- MINERAL SCALING CLOGS PERFORATIONS

**RESULT:**

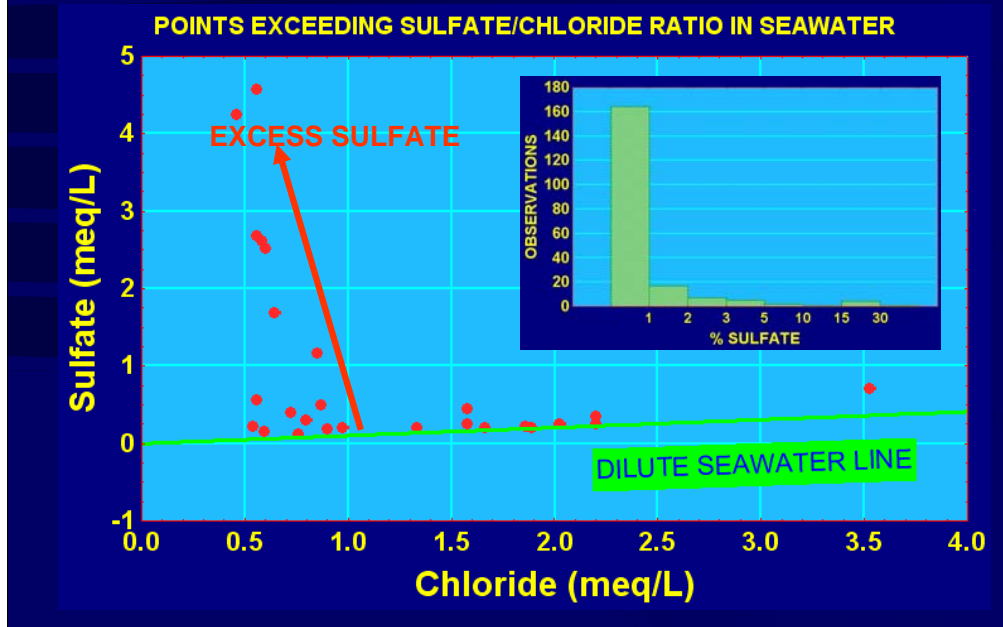


**WELL YIELD IMPAIRED**

48

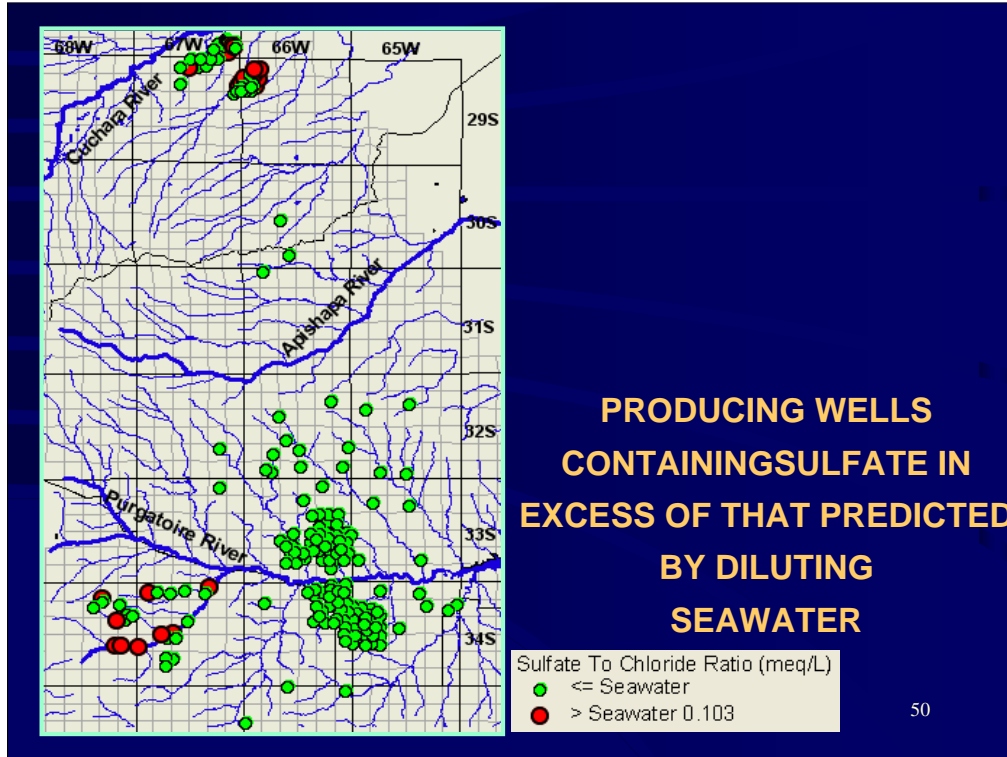


## SOME SULFATE IN PRODUCED WATERS ORIGINATES FROM DILUTE CONNATE SEAWATER

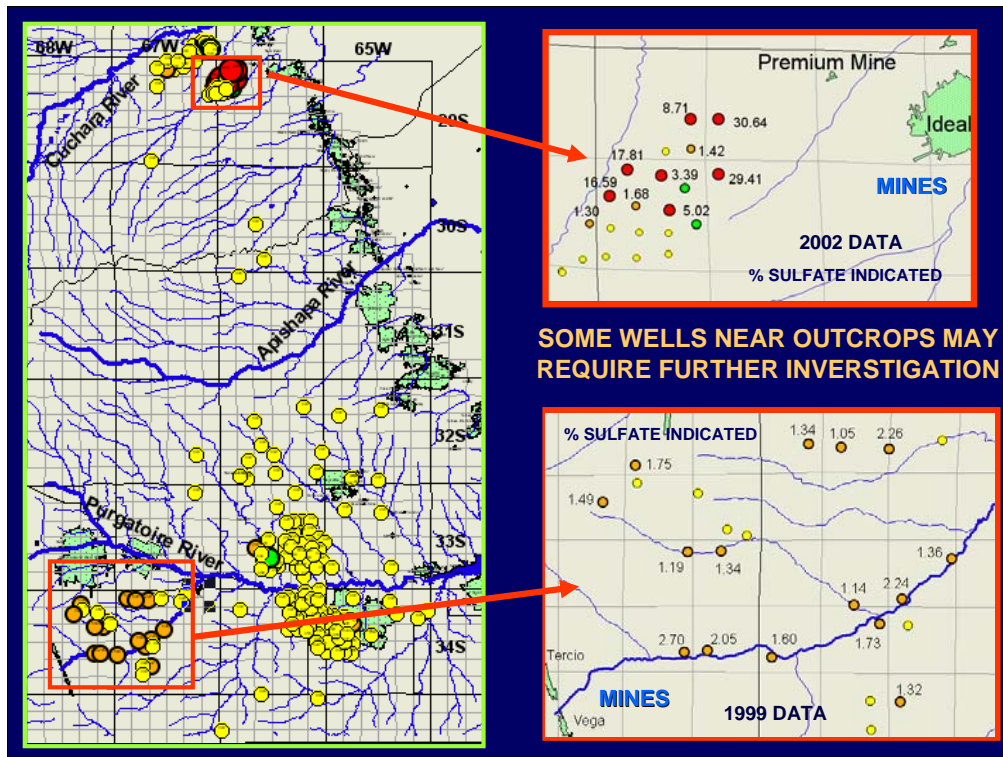


Because sulfate concentrations decrease with increasing depth, the presence of sulfate in produced fluid sulfate are present in producing fluids one should test the waters periodically to determine whether conc

Not all sulfate is derived from the surface however. Some sulfate found in produced waters may origina line shown above marks a constant ratio of sulfate to chloride equal to 0.1030. Points falling above that



CBG wells producing water with excess sulfate appear to be confined to two areas.



A cluster of northern wells on the eastern side of the basin's synclinal axis have the highest sulfate contents of any produced wells analyzed. These wells produce large volumes of water and relatively little gas. There appears to be a gradient in sulfate contents that increases towards the outcrop belt. This may be an indication that these wells could be in communication with near-surface fluids originating not from overlying aquifers, but from the outcrop belt, or perhaps from the Ideal mine. Alternatively, these wells could be tapping a deeper source of deep-seated sulfate.

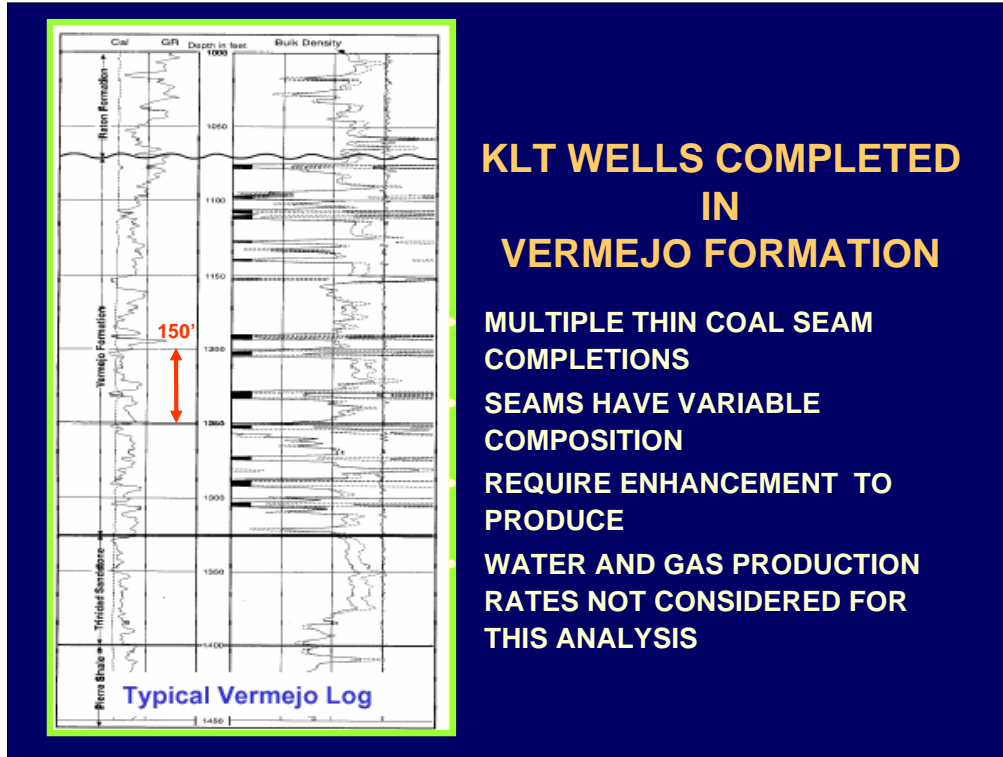
A cluster of southern wells along the South Fork of the Purgatoire River are on the west side of the basin's synclinal axis. The relative sulfate content in these wells may also be slightly elevated from recharging groundwater sources to the west. Elevated sulfate concentrations in this area are not nearly as high as those observed in northern wells. Produced fluids in this area were sampled in 1999, and could be sampled again to determine if there are systematic changes in relative sulfate content. If water production volumes have declined significantly, further sampling may not be necessary because the producing horizon may be isolated by the low permeability of gas-saturated coal.

The presence of elevated sulfate in these regions may trigger further investigations to determine the origin of sulfate at these unexpected depths. This investigation would consider, for example, background sulfate levels at depth, changes over time, and gas well completion and operations data. Periodic measurements could show if the relative amounts of sulfate are increasing, or if  $^{13}\text{C}$  DIC values are decreasing.

## **SPATIAL AND TEMPORAL STUDY OF KLT PRODUCING WELLS: VISUALIZING AQUIFER RESPONSE**

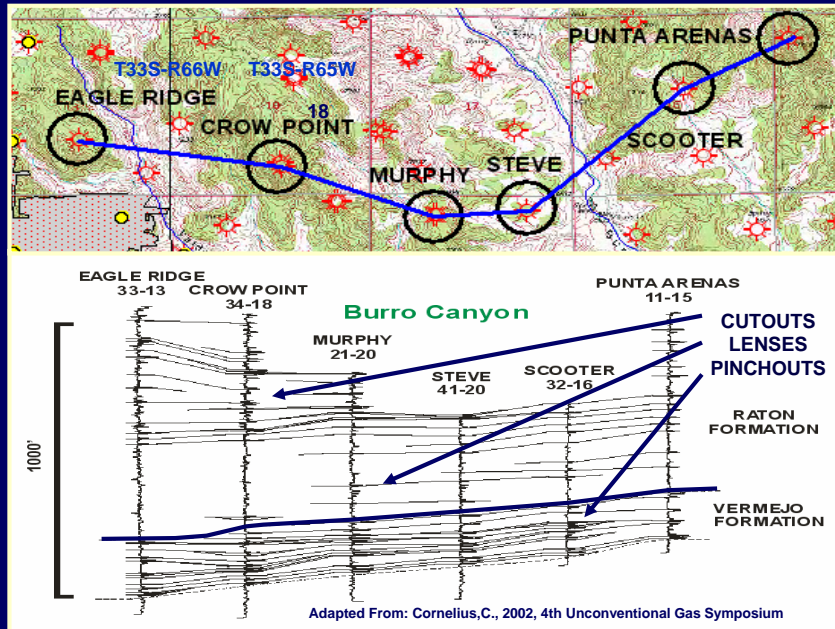
- **95 PAIRS OF SAMPLES EVALUATED**
- **AVERAGE LAG TIME BETWEEN SAMPLES 3 YRS. FROM 1999 - 2002**
- **EARLY DATA SET CONTAINS ALL MAJOR IONS**
- **LATE DATA SET CONTAINS LIMITED DATA INCLUDING DISSOLVED CHLORIDE & BICARBONATE CONTENT**
- **DATA USEFUL TO EXAMINE**
  - **POTENTIAL FOR COMMUNICATION WITH SURFACE**
  - **PRODUCTION COMPARTMENTATION**
  - **REGIONAL FLOW RATE BOUNDARIES**
  - **LOCAL FLOW RATE BOUNDARIES**

The principal objective of this study is to determine if produced water chemistry can help establish the spatial range of connectivity among the gas productive water-bearing horizons. Methods used to assess reservoir continuity using geochemical data rely on examining both spatial and temporal trends.

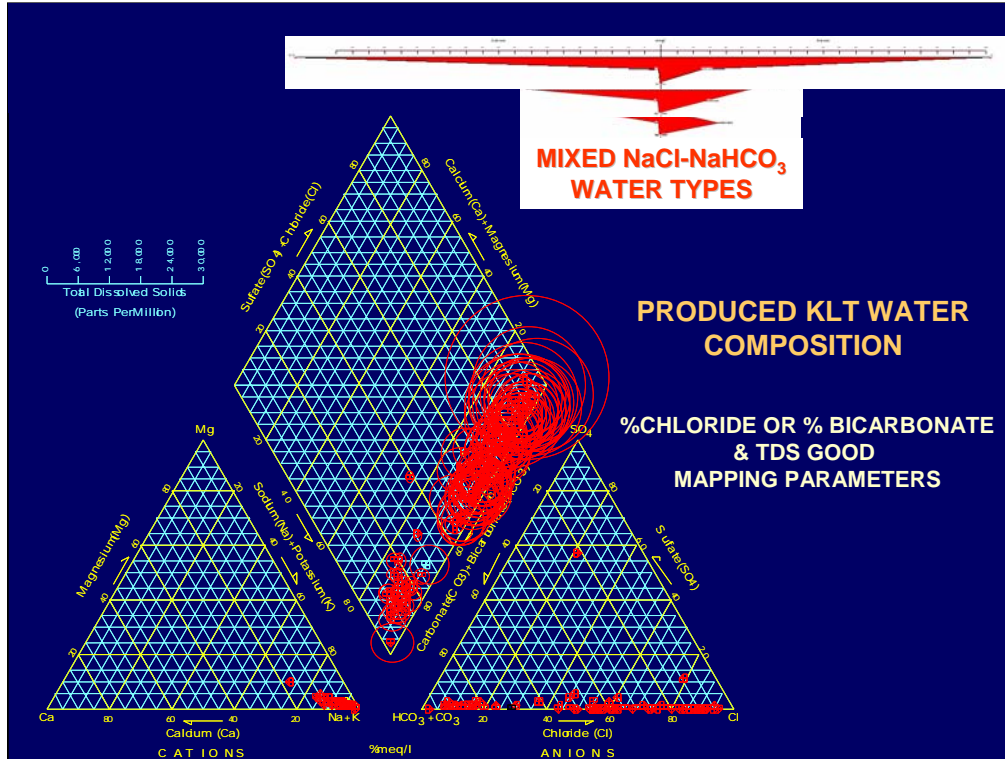


Coal seams in the Vermejo Formation are largely thin and discontinuous. Published geologic studies in the area commonly note great difficulty in correlating seams beyond distances of one to two miles. There are also other factors that isolate the production behavior of producing coalbed gas wells. Such factors include: variable formation damage due to drilling, variable effectiveness of completions in each seam, structural discontinuities along minor faults that generally offset coals across vertical distances between 25 to 50 feet, and discontinuities introduced by volcanic intrusions such as dikes and sills. Published data show that each coal seam interval must be hydraulically stimulated to produce effectively. Tracer analyses further show that induced hydraulic fractures do not extend far beyond the vertical intervals perforated. Such data provide important evidence documenting the limited extend of vertical communication between coal seam aquifers.

## NEARBY CROSS SECTION SHOWS VARIABILITY IN VERMEJO COAL CONTINUITY



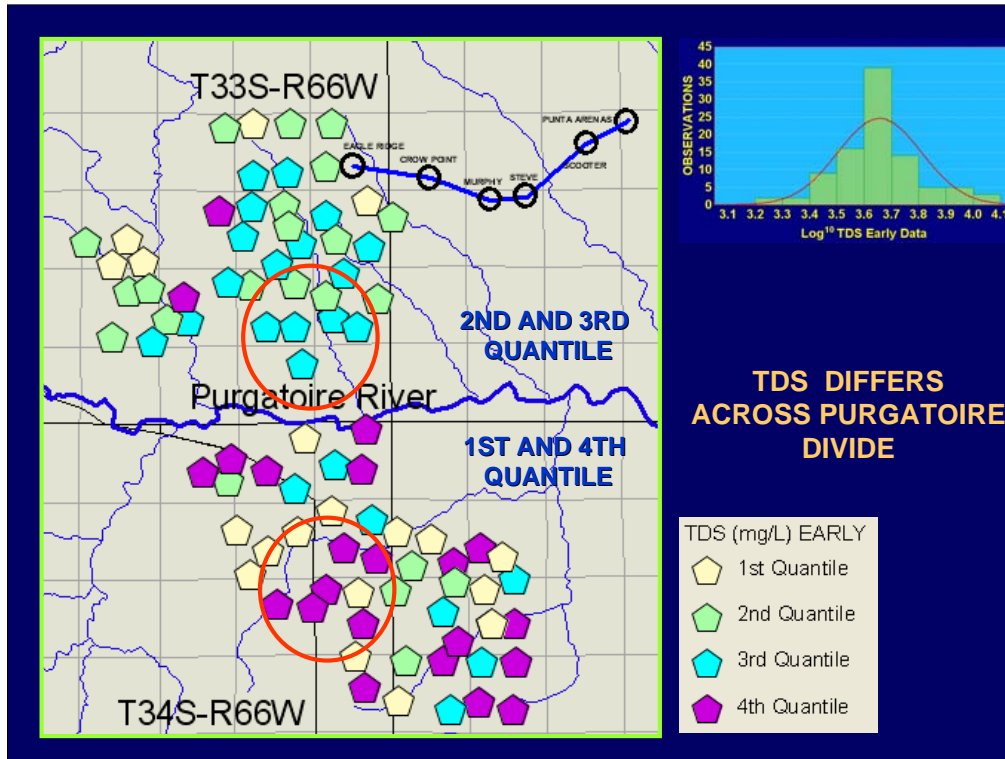
This cross-section, just to the east of the KLT wells to be illustrated next, identifies the stratigraphic variables governing the heterogeneity of coal seams and other sediments in the area. Each square in the diagram represents a section. These discontinuous coal seams are encased in impermeable shale layers and cemented sandstone layers.



Early data collected by KLT and analyzed sometime in 1999 contain complete analyses of the major ions. Results of these analyses are illustrated above. Late data collected in 2001 and 2002 only contain quantitative analyses of chlorides, bicarbonates, and total dissolved solids.

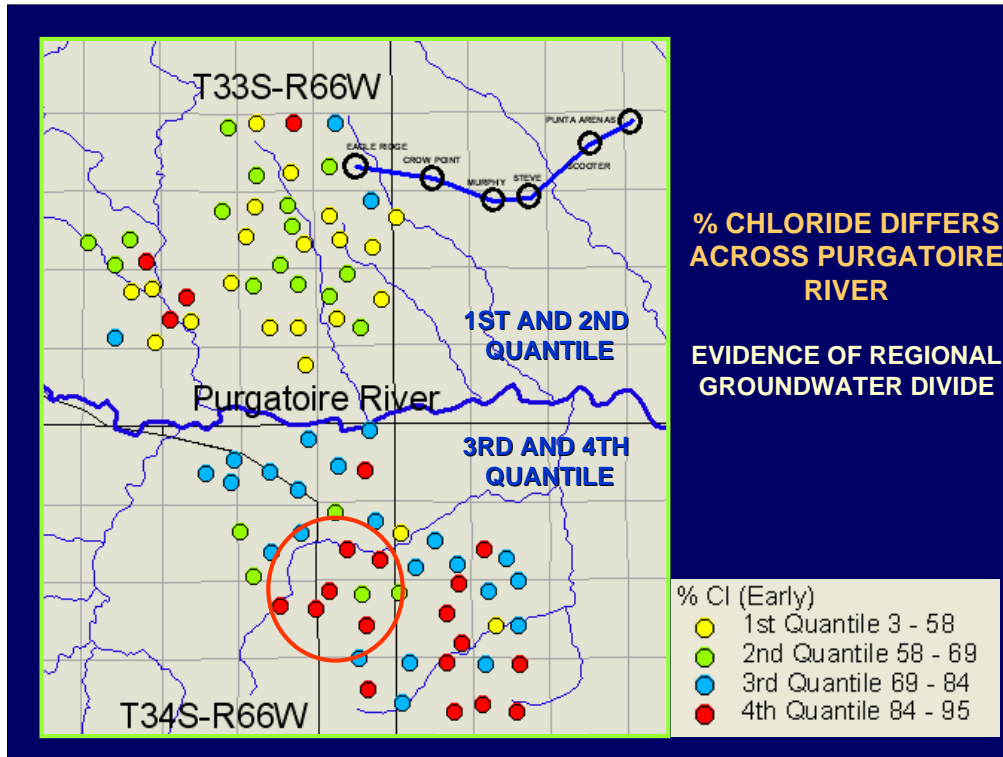
The trend observed among KLT producing wells is the same as the trend observed for all samples of produced water. Formation fluids are principally composed of mixtures of sodium bicarbonate and sodium chloride. Accordingly, by plotting either percent chloride or percent bicarbonate, one can fully represent the chemical composition of produced fluids.

Two types of compositional plots can help us understand aquifer compartmentation in the basin. The spatial distribution of values obtained early in the production history of a field is best used to observe the net result of long term mixing between aquifers. Temporal chemical changes measured over the short term during production are better suited to show both the spatial distribution of local flow units and the effectiveness of well bore completions.

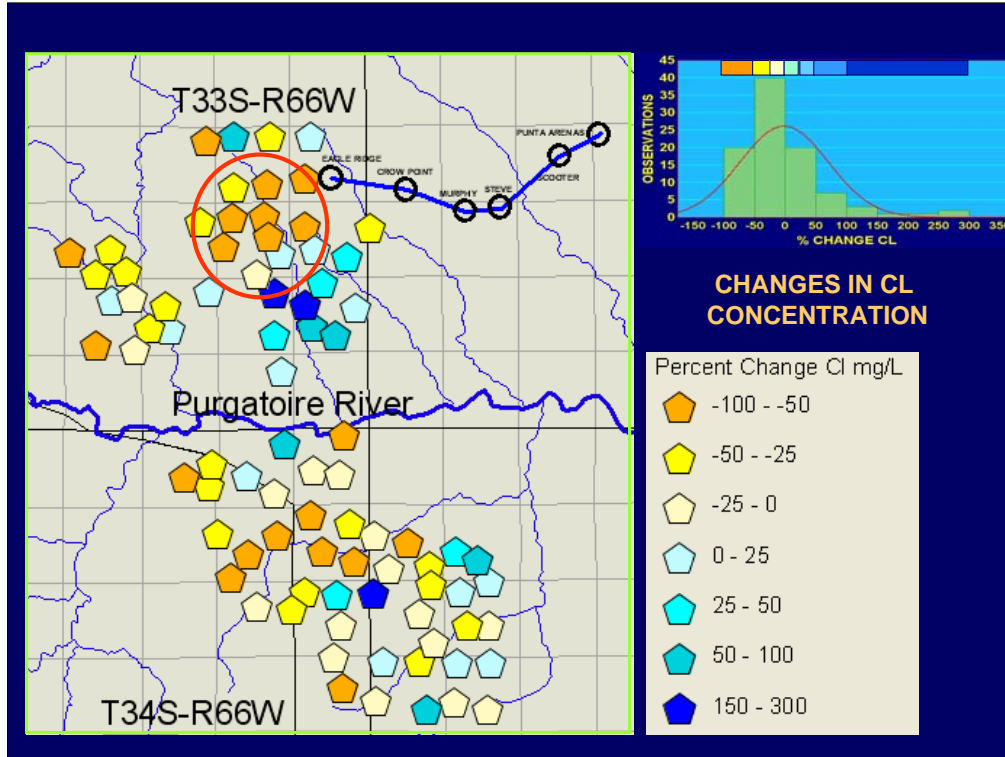


TDS values collected in 1999 have also been simplified in terms of quartiles in the above illustration. The trends observed in TDS are distinctly different than the trends observed using normalized % chloride values. North of the Purgatoire River divide, TDS is dominated by values in the 2<sup>nd</sup> and 3<sup>rd</sup> quartiles; south of the divide, TDS is dominated by values in the 1<sup>st</sup> and 4<sup>th</sup> quartiles. A large amount of local heterogeneity is also evident. Patterns of similar TDS values among adjacent wells do not extend outside a maximum radius of  $\frac{3}{4}$  miles.





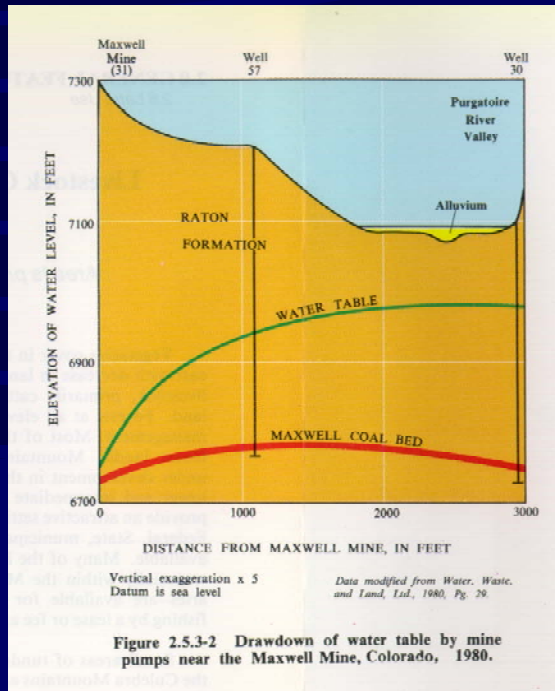
The spatial distribution of produced water chemistry evolved over geologic time is illustrated above. To simplify results, % chloride has been color coded to represent quartiles in the relative chloride content as measured among producing KLT wells in 1999. It is evident that the Purgatoire River drainage divide separates groundwaters into two distinct hydrologic regimes. Chloride values in the 1<sup>st</sup> and 2<sup>nd</sup> quartiles dominate the northern half of the divide, whereas chloride values in the 3<sup>rd</sup> and 4<sup>th</sup> quartiles dominate the southern half of the divide. There is also a fair amount of spatial discontinuity among chloride values on each side of the divide. Such data provide evidence of both regional and local aquifer discontinuities. Patterns of similar %Chloride values among adjacent wells do not extend outside a maximum radius of ¾ miles.



The percent change in chloride concentrations was calculated by subtracting early measurements from late measurements (in mg/L) and dividing them by the early measurements. As noted earlier, changes in chloride concentrations do not exhibit the same regional and local patterns as changes in bicarbonate concentrations. This supports the concept that chloride-bearing fluids may originate from different sources, such as permeable sandstones.

Maps such as these could be combined with water production data for a variety of uses. For example, they may be used to examine the effectiveness of completions in coal. For example, areas where the bicarbonate concentration decreases while the chloride concentration increases may be indicative of sandstones that are contributing significantly to water production. The highly heterogeneous response also has implications to those attempting to explore for gas accumulations in sandstone bodies. These data indicate that values of formation water resistivity are likely to be very different among individual sandstone bodies. Accurate assessment of formation water resistivity is of paramount importance when attempting to predict gas saturation in sandstones.

The main conclusion to be drawn from mapping spatial and temporal maps of dissolved constituents in produced water is that visible patterns are clustered. Clusters show a different degree of spatial coherence at both the regional and local level. At the local level, it is not possible to correlate produced water patterns beyond an area with a  $\frac{3}{4}$  mile radius. We can reasonably conclude from these data that the aquifer continuity in this portion of the Raton Basin is limited, and that production practices are not likely to influence an area larger than that confined to a  $\frac{3}{4}$  mile radius. Although results of pressure interference testing could add more information to the degree of communication between adjacent wells, such data are not available in the public domain.

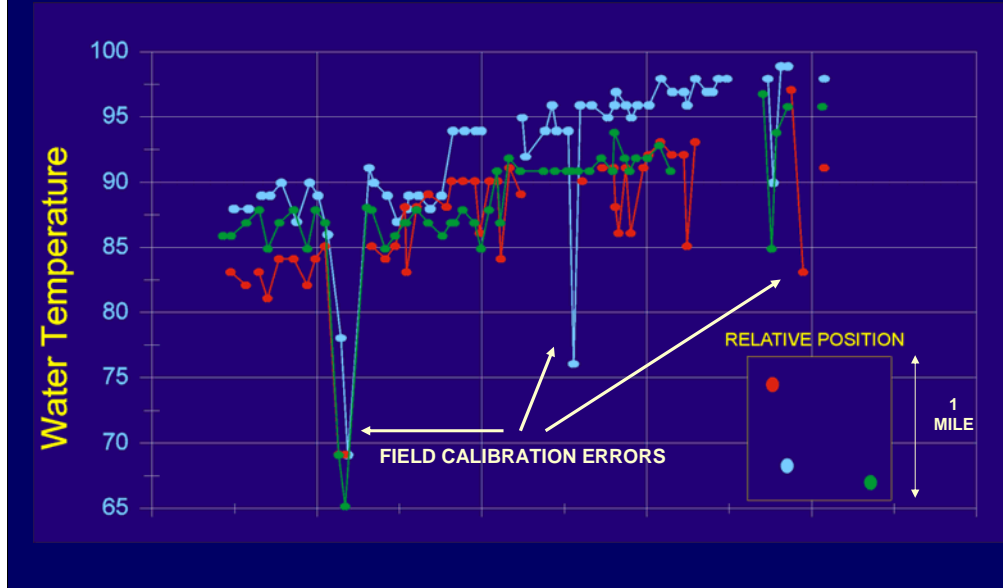


RESULTS  
CONSISTENT  
WITH  
USGS OFR-83-132

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Data published by the USGS (OFR 83-132) show that water levels in the Maxwell coal seam, declining as a result of mine pumping, can be affected to distances approaching a ½ mile radius from the mine. Such corroborating evidence confirms the relatively limited lateral extent of aquifer continuity in the basin.

## CHANGES IN PRODUCED WATER TEMPERATURE USEFUL FORENSIC TOOL TO EVALUATE CONNECTION WITH SHALLOW AQUIFERS



Water composition data are not the only types of measurements useful for examining fluid flow in producing coalbed aquifers. These monthly temperature measurements, obtained from producing wells in Huerfano County, were made using a thermistor device. Unfortunately, the thermistor was not regularly calibrated. Calibration errors are evident as strong excursions from the observed long term trends. The relative position of wells in a one square mile section is indicated in the reference box at the lower right hand side of the diagram. Regular measurements of produced water temperatures can be most useful for determining potential communication with the surface. Long term cooling trends would indicate possible communication with relatively cool near-surface waters. As evident here, the long term trends indicate admixture with warmer waters. Because topographic relief and therefore formation temperature increases to the west, this diagram would indicate a net flow of fluids from the west. Excursions from long term trends measured in real time should provide an important screening tool necessary to sample fluids for complete chemical analysis.

## **SUMMARY:**

### **USEFUL SCREENING TOOLS TO ADDRESS POTENTIAL IMPACT ON SHALLOW AQUIFERS**

- **TRILINEAR DIAGRAMS - VIEW MIXING TRENDS AND  
SELECT MAP PARAMETERS**
- **SPATIAL MAPS - LARGE SCALE HETEROGENEITY**
- **TEMPORAL MAPS - SMALL SCALE HETEROGENEITY &  
CONNECTIVITY OF AQUIFERS**
- **SULFATE CONTENT: SURFACE WATER MARKER**
- **$^{13}\text{C}$  DIC-  $\text{HCO}_3$  : SURFACE MARKER, SOURCE MARKER**
  - (SPATIAL & TEMPORAL)
- **PRODUCED WATER TEMPERATURE**
- **COMPLETION INFORMATION**
  - BASE WATER WELL PERFORATION
  - TOP PRODUCING WELL PERFORATION

## **CONCLUSIONS**

- **POTENTIAL IMPACT TO SHALLOW AQUIFERS CAN BE SCREENED AS FOLLOWS:**
  - **MAP LATERAL AND VERTICAL PROXIMITY OF GROUNDWATER AND PRODUCED WATER COMPLETIONS**
    - **MONITOR SHALLOW AQUIFER WATER LEVELS WHERE NEEDED**
  - **ANALYZE PRODUCED WATER PROPERTIES**
    - **INITIAL MAJOR ION ANALYSES**
    - **STABLE ISOTOPIC ANALYSIS OF DISSOLVED BICARBONATE**
    - **PERIODIC MONITORING DURING DRY AND WET SEASONS**
      - **MONITOR CHANGES IN TDS AND SULFATE CONTENT**
    - **REGULAR, CALIBRATED TEMPERATURE SURVEYS**
- **SCREEN FOR METHANE WITH IRS AND DISSOLVED METHANE MEASUREMENTS**
  - **THE ORIGIN OF METHANE CAN BE DETERMINED USING STABLE ISOTOPE MEASUREMENTS**

## Raton Basin Project 2000-2003 Deliverables

- Project Web Site Listing Index Page
- Digital Locations of Data on COGCC Internet Map
- Raw Chemistry Data for Download
- Contractors Reports
- Paper in Industry Journal

## Raton Basin Project 2000-2003

### Further Investigations

- Monitor Water Wells that are in Close Vertical Proximity to CBM Gas Wells
- Utilize Chemical Data to Identify Areas for Further Investigation
- Update Data in the Project Area