

**SHALLOW AQUIFER GEOCHEMISTRY IN AREAS OF INTENSE COAL BED  
METHANE RECOVERY WITHIN THE RATON BASIN, COLORADO**

A Thesis

Presented to the

Faculty of

California State Polytechnic University, Pomona

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

In

Geological Sciences

By

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2016

## **SIGNATURE PAGE**

**THESIS:** SHALLOW AQUIFER GEOCHEMISTRY  
IN AREAS OF INTENSE COAL BED  
METHANE RECOVERY WITHIN THE  
RATON BASIN, COLORADO

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## **ACKNOWLEDGEMENTS**

We thank the support of the National Science Foundation, Sustainability Research Network program (CBET-1240584). I would also like to thank my father, mother, and Stephen Osborn for all of the help and support.

## **ABSTRACT**

This thesis combines historic water quality data from the COGCC (up until 2015) with results from fieldwork conducted in 2014 to address water quality and the source of fluids (water and gas) in proximity to oil and gas production. Mixed origin (biogenic and thermogenic) Coalbed methane (CBM) is currently being heavily produced in the Basin from the Raton and Vermejo Formations at up to 1000 m. Shallow groundwater resources in the Raton Basin are to some extent comingled with the CBM producing formations possibly leaving detectable concentrations of in groundwater. Results indicate that waters are sourced from shallow meteoric recharge waters based on relatively low salinity and stable isotopes of water (O, H) and carbon (dissolved inorganic carbon). There are minor amounts of microbial methane produced in-situ in the the shallow aquifer with minor amounts of thermogenic methane. The majority of methane has been modified by mixing and oxidation. There is little evidence for impacts to shallow aquifers at the basin scale from oil/gas production based on the current dataset. Though localized impacts may be possible. More work and continues monitoring is necessary in the future.

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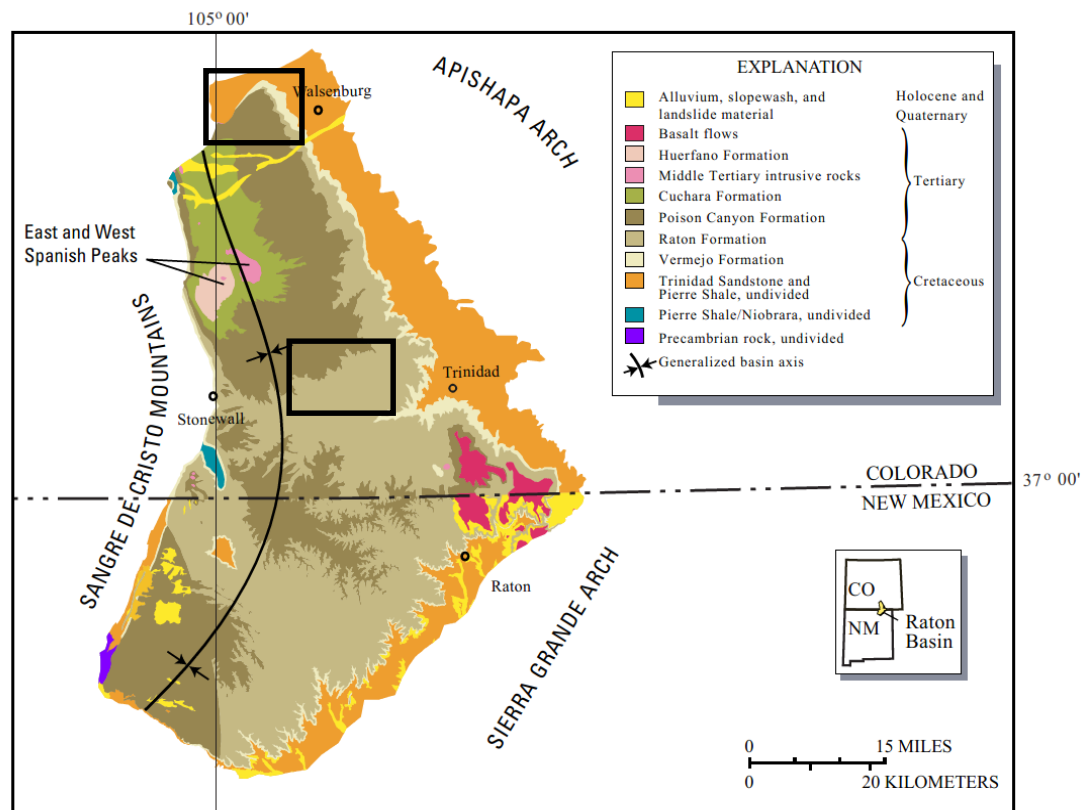
## **1.0 INTRODUCTION**

Energy production is necessary for economic growth and national security. Advances in hydraulic fracturing and horizontal drilling in unconventional oil and gas reservoirs with low permeability can now be economically developed. Public concern of water quality has increased proportionally. Specifically, the Raton Basin of southeast (SE) Colorado has unconventional gas reservoirs derived from coalbeds that have experienced increased production since 2007. The Colorado Oil and Gas Conservation Commission (COGCC) is a state agency charged with collecting water quality data in areas with extensive oil/gas production since the early 1990s. Their database of water quality data (1,458 samples) for the Raton Basin in Colorado was made publically available. However, there is limited basin wide analysis investigating possible impacts from oil/gas production. The Environmental Protection Agency (EPA) from 2011 to 2013 conducted a basin wide study (published in 2015, after fieldwork for this study) within the Raton Basin, however, only 14 domestic wells, five monitoring wells, three production wells, and three surface water bodies were sampled and limited historic data up until 2003 from the COGCC. This thesis combines historic water quality data from the COGCC (up until 2015) with results from fieldwork conducted in 2014 to address water quality and the source of fluids (water and gas) in proximity to oil and gas production.

### **1.1 Background of Study Area**

The study area of this project was located in the Raton Basin (Figure 1, Figure 2). The Raton basin covers an area of nearly 4,000 square miles and is located in southeastern Colorado and northeastern New Mexico (Flores and Bader, 1999). The

Raton Basin is bordered by the Sangre de Cristo Mountains to the west, the Apishapa arch to the northeast, and the



**Figure 1.** General geological map of the Raton Basin (Flores and Bader, 1999, Johnson and Finn, 2001, and Higley, 2007). The black box inset indicates the location of field sampling.

Sierra Grande-Las Animas arch to the southeast (Watts, 2006). The study area is considered to be semi-arid with average annual precipitations of 14 inches in Las Animas County and 15 inches in Huerfano County (Colorado Climate Center, 2015). The majority of the precipitation in these counties occurs in higher elevations as snow (Colorado Climate Center, 2015). The snowmelt from the mountains feeds into the local streams in this area.

The specific sampling locations were concentrated in southeastern Colorado in Las Animas and Huerfano counties. The Raton Basin is known to produce relatively

shallow (> 2,000 meters below ground surface) coal bed methane (CBM). With recent increases in gas production and hydraulic fracturing local citizens have become concerned with the water quality within the basin.

## **1.2 Research Questions**

The project poses several key questions of fluid migration near oil and gas production in the Raton Basin of Colorado.

### **1. What is the basic water quality of areas with intense gas production?**

Since hyper saline basin brine is strongly associated with oil/gas production, there may be some impact to basic water quality.

### **2. What is the origin of fluids found in shallow groundwater?**

Since gas producing coal seams are comingled with shallow groundwater used as a drinking water source, there is likely multiple sources of fluids (gas and water). For waters, this could be deep hyper-saline brine and/or relatively dilute shallow recharge water. The source(s) of methane could be shallow microbial and/or deep thermogenic. Thermogenic methane is produced by thermocatalytic breakdown of organic matter at temperatures between 157 to 211 °C (Stolper, 2014)

### **3. What evidence, if any, exists for possible impacts to shallow groundwater from gas production?**

There is some concern for impacts from gas production due to the close proximity of gas production and coal seams to water producing zones.

## **1.3 Review of Coal Bed Systems.**

Coal and coalbed methane (CBM) systems are considered to be a complex geologic depositional system. The information for this section was gathered from a paper

written by Tim A. Moore (2012) “Coalbed methane: A review” where the author gathered extensive information from all of the quintessential studies on coal and coalbed methane.

Coal is composed of plant remains, inorganic sediment, and water. The basic elements found in coal are C, H, O, and N. Coal can have a wide range of variations in its composition and this is due to the vast alteration of plants throughout geologic time. The process to create coal starts with a peat bog where water and plant materials form into a solid material overtime. There are 5 stages of coalification; peatification, dehydration, bituminisation, debituminisation and Graphitization. During each stage the coal will undergo chemical and physical changes, which will affect the coals grade (ratio of organic material to inorganic material), porosity, permeability, moisture content, gas origin (biogenic or thermogenic), gas holding capacity, fracture networks, and rank.

Rank has several meanings, however, it is generally defined as the level of organic metamorphism or the level of coalification. Rank is usually estimated through vitrinite reflectance ( $\%R_o$ ), which is the percentage of reflected incident light to vitrinite in sedimentary particles. It is an important factor to comprehend while analyzing a coal formation because coal rank can influence permeability, fracture networks (cleats) within the coal, gas saturation, and the types of gases that form in coals. Fracture networks, permeability, and gas saturation increase as rank increases. Furthermore, coal rank can be divided into two groups low and high. Low rank coals ( $<0.5 \%R_o$ ) usually produce dry biogenic gas. While higher ranked coal ( $>0.5 \%R_o$ ) usually produce dry or wet thermogenic gas.

Coal formations can produce both biogenic and thermogenic gases. It is possible to have a basin with a shallow coal seam producing biogenic gases, while a deeper coal seam is producing thermogenic gases at the same time. Biogenic gas production from coal, or any organic matter, begins by acetate fermentation, typically at surface environments or by CO<sub>2</sub> reduction in the subsurface (Coleman, 1984).

Many factors can increase or decrease the production of biogenic methane. First, the correct ratios of necessary microbes must be present to create the methane. Also, temperature (<80 °C), pH, and pore surface area can have a great effect on biogenic methane production.

Biogenic methane can be produced at any point during the coal's life cycle. For example over geologic time a low ranking coal producing biogenic gas can be exposed to a heat source, which will increase the rank of the coal. The heat could destroy the necessary microbes that create biogenic gases. As the coal rank increases, thermogenic gas will increase while biogenic gas will decrease. If that formation was then uplifted tectonically and recharge waters reintroduce the correct microbes the coal could then produce biogenic gases again. Though, high rank organic matter is less bioavailable to microbes and methane production is inhibited (Laughrey, 2008).

Thermogenic gas production is caused by heat, pressure and time. If a coal formation is exposed to the right temperatures and pressures for a period of time the coal will ultimately begin to devolatilize methane, other higher chained hydrocarbons, CO<sub>2</sub>, nitrogen, and hydrogen sulfide. If a coal rank increases over >0.5 vitrinite reflectance it could begin to produce thermogenic gases. Higher ranking coals usually (not always the case) are able to hold and produce more gas than lower ranking coals. Higher ranking

coals typically produces more gases than lower ranking coals because the processes of coal devitalization tends to produce more methane/natural gases than biological processes (but this is not always the case). Also, as stated before as rank increases pore surface area and fracture networks though out the coal seam increase as well. The gases produced in coals are ultimately stored by adsorption (adhesion of atoms, ions, or molecules to a surface) to the coals pore surface area. Therefore, the higher the surface area the more gas can be stored.

Coal formation properties can furthermore be influence by tectonism and overburden of sediments which can decrease the fracture networks and the pore surface area limiting the ability to hold or transmit gases. This is due to the fact that coal is considered to be compressible which makes it response to stress complex. Faults through coal formations can sometime open or close fracture networks. Also, large scale basin stresses can open or close fracture networks. The fracture networks are directly related to the permeability of the fluids in a coal formation. Also, moisture content can influence gas-holding capacity. Therefore a formation with relatively high groundwater recharge could potentially hold less gas then a formation with little recharge because the water would take up the space where gasses could be stored.

The properties of the formation can strongly influence the fracture networks, permeability, sorption, pore surface area, gas diffusion. Diffusion is proportional to the concentration gradient, pore surface area, and inversely related to distance. Therefore, methane may diffuse or move from a high concentration area to a lower concentration area, and if the coal has an extensive fracture networks the diffusion will occur more quickly.

General coal properties are an important aspect to understand when working in a coal prominent basin such as the Raton Basin while investigating the source of fluids found. Furthermore, the driving forces behind fluid migration can be heavily influence by geological and chemical factors in a coal dominated basin.

## **2.0 PREVIOUS WORK**

There is extensive literature on stable isotope geochemistry and gas composition of natural gas. The literature distinguished between different sources of natural gas, such as microbial, thermogenic, and mixed natural gases found in geologic formations. Several key concepts are reviewed below.

### **2.1 Natural Gas Geochemistry**

Natural gases have variable isotopic values, which can distinguish them into microbial methane, thermogenic methane, or mixed sources. Microbial methane is methane created by bacteria breaking down of organic matter during early diagenesis (Schoell, 1980). Microbial gases are produced by CO<sub>2</sub> reduction and acetate fermentation (schoell, 1980; Whiticar, 1986). In both of these types of reactions the hydrogen and carbon molecules are derived from either organic matter or environmental waters in-situ (Schoell, 1980; Whiticar, 1986). Thermogenic gases are generated by thermal maturation and degradation of complex organic matter in an anoxic environment and can create methane, ethane, propane, butane, and other higher chained hydrocarbon gases (Schoell, 1980).

Microbial methane can be distinguished by isotope values of <sup>13</sup>C and <sup>2</sup>H within the methane molecule (Schoell 1980; Whiticar, 1986; Jenden et al., 1993). Schoell (1980) concluded that a pure biogenic gas had  $\delta^{13}\text{C-CH}_4$  values more negative than -64 ‰ and

$\delta^2\text{H-CH}_4$  isotope values of -180 to -260‰. Whiticar et al. (1986) stated microbial gases had  $\delta^{13}\text{C-CH}_4$  isotope values from -100 to -60‰ and  $\delta^2\text{H-CH}_4$  values from -170 to -250‰. Jenden et al (1993) describes microbial gas occurring at depths less than 3 kilometers, at relatively low temperatures ( $\ll 100^\circ\text{C}$ ), and by anaerobic bacteria. The gas is characterized by low concentrations of ethane ( $\text{C}_2\text{-C}_5/\text{C}_1\text{-C}_5$  or wetness  $\ll 1\%$ ) and isotopically light methane ( $\delta^{13}\text{C-CH}_4 < -60\text{‰}$ ).

Schoell (1980) and Jenden et al. (1993) stated that thermogenic gases have  $\delta^{13}\text{C-CH}_4$  values more positive than -50‰ and the methane was associated with other higher chained hydrocarbon gases. Furthermore, thermogenic gases were considered to have  $\delta^2\text{H}$  isotopic values ranging from -260 to -150‰ for a wet gas ( $\text{C}_2\text{-C}_5/\text{C}_1\text{-C}_5 = >1\%$ ) and -180 to -130‰ for a dry ( $\text{C}_2\text{-C}_5/\text{C}_1\text{-C}_5 = \ll 1\%$ ) gas (Schoell, 1980; Jenden et al., 1993). The deuterium isotopes were much more random and the isotopic values tend to overlap. The randomness in the hydrogen isotopes were due to the thermal maturation factors such as varying temperatures, time of maturation, and different source materials (Schoell, 1980). Unlike microbial gases environmental water in-situ with the thermogenic gases had lesser influence on the hydrogen isotopes concentrations (Schoell 1980). Furthermore, Jenden et al. (1993) stated thermogenic gases occur at higher temperatures and at greater depths than biogenic gases (Jenden et al. 1993). Its chemistry is highly dependent on the type and thermal maturity of the source rocks it was produced from (Jenden et al., 1993). Therefore, isotopic values of the thermogenic methane can be highly variable and not always reliable when distinguishing a thermogenic gas.

A mixed biogenic and thermogenic gas usually occurs in an area where there are two source rocks, which produce thermogenic and biogenic gases (Jenden et al., 1993).



Natural gas in the subsurface can be highly mobile and gas mixing can be very common (Jenden et al., 1993). The natural gas moves through fracture networks and faults throughout the subsurface (Jenden et al. 1993). Jenden et al (1993) states that to distinguish mixed gas methane  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  isotope ratios,  $\delta^{13}\text{C}$  of  $\text{C}_{2+}$  hydrocarbons, and wetness must be measured. Without this information the gas could be misinterpreted (Jenden et al. 1993). Therefore, an interpreter must be familiar with the characteristic of mixed-origin gas chemistry and the source rocks, which is in question. The natural gas geochemistry in a mixed system would have  $\delta^{13}\text{C}-\text{CH}_4$  and gas wetness at an intermediate value between pure thermogenic gas and pure microbial gas end-members.

## **2.2 Natural Gas and Associated waters**

To further distinguish microbial methane from thermogenic methane associated water geochemistry was used.  $\delta^2\text{H}-\text{CH}_4$  values will vary in different types of water (deep saline or shallow fresh water) (Schoell, 1980). Precipitation water is depleted in deuterium ( $\delta^2\text{H} \sim -20$  to  $-90\text{‰}$ ), while marine/connate water is enriched with deuterium ( $\delta^2\text{H} \sim 0$  to  $-20\text{‰}$ ) (Schoell, 1980). Therefore, methane with lower deuterium concentrations would be derived from relatively shallow fresh waters, while higher enrichment of deuterium in methane was derived from deeper more saline waters (Schoell, 1980).

Furthermore, Schoel (1980) conducted an experiment that showed that environment waters were incorporated into biogenic methane molecules during the enzymatic process. The experiment incorporated different known concentrations of deuterium-enriched water into raw sewage. The methane that was produced from the

sewage had deuterium isotopes in the methane molecule. Schoell (1980) noted, as the concentration of deuterium enriched waters were increased the methane also became enriched with deuterium isotopes. The experiment discovered that hydrogen molecules from the environmental waters were being integrating into the methane. It also came to the conclusion that approximately 40% of the hydrogen associated with the methane compound was being derived from the environmental waters (Schoell, 1980).

Also, Whiticar et al. (1986) found that the waters in which the sediments the gases where generated from had an influence on the  $\delta^{13}\text{C-CH}_4$  and  $\delta^2\text{H-CH}_4$  isotopic values. Marine sediments producing microbial gases where classified as having  $\delta^{13}\text{C-CH}_4$  isotope values of -100 to -60‰ and  $\delta^2\text{H-CH}_4$  values from -250 to -170‰ (Whiticar et al. 1986). While fresh water derived biogenic gasses are classified as having methane  $\delta^{13}\text{C-CH}_4$  isotope values from -65 to -50‰ and  $\delta^2\text{H-CH}_4$  values from -400 to -250‰ (Whiticar et al. 1986). Therefore, environmental waters can have an influence on the  $^{13}\text{C}$  and  $^2\text{H}$  isotopic values within the  $\text{CH}_4$  molecule. But how is the water chemistry affected by methane production?

Specifically water isotopic composition will alter during microbial methanogenesis producing more positive carbon isotope values for dissolved inorganic carbon (DIC) and the coproduced  $\text{CO}_2$  gas (Martini et al. 2003). This is due to the fact that methanogens will be prone to use the light isotope of  $^{12}\text{C-DIC}$  during methane production thus enriching the water with  $^{13}\text{C-DIC}$  (Martini et al. 2003). Furthermore, during methanogenesis alkalinity concentration also increase. Therefore if alkalinity concentrations increase and more positive  $^{13}\text{C}$  values of DIC are notices this provides a

strong indication of microbial activity within a basin (Martini et al. 2003; Osborn and McIntosh, 2010).

### **2.3 Methane Oxidation**

Oxidation trends within a natural gas producing basin are an essential concept to understand while evaluating geochemical data of methane and formation waters.

Microbial oxidation can degrade large amounts of hydrocarbons and produce large fractionation values (Whiticar et al., 1986). Thus, without the proper evaluation oxidized methane can be interpreted as thermogenic gases as  $\delta^{13}\text{C}-\text{CH}_4$  values will shift to more positive values.

Specifically a study conducted by Martini et al. (2003) noted how microbial oxidation occurs. Martini et al. (2003) noticed that microbial activity was predominantly located on the edges of the basin while thermogenic gases were occurring in the central part of the basin. The margins of the basin had lower thermal maturity and freshwater influences. Furthermore, if the thermogenic gases migrated to the edge of the basin the microbes would oxidize the thermogenic gases. This conclusion was illustrated by using  $\text{C}_2$  and  $\text{C}_3$  cross plots. The ethane and the propane had more positive  $\delta^{13}\text{C}$  values, which occurs at higher thermal maturities, but were at low concentrations (Martini et al. 2003). The edges of the basin were thought to be shallow hydrologic systems. In a shallow hydrologic system, water with a high concentration of dissolved  $\text{O}_2$  can come into contact with stored hydrocarbon deposits. Groundwater enriched with dissolved oxygen could oxidize the hydrocarbon gases (Martini et al. 2003). Depending on which gas is oxidized ( $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$  etc.), the isotopic signatures could become thermogenic gas or a biogenic gas. In the case of Martini et al. (2003) study area the majority of the gas in the

Michigan Basin was microbial and methane made up 80 to 90% of the gas type. The little residual thermogenic gases after the oxidation were enriched in  $^{13}\text{C}$ . The ethane and propane  $^{13}\text{C}$  values were plotted against mole % to display oxidation trends. The trends showed as the  $^{13}\text{C}$  values become more positive in the  $\text{C}_2$  and  $\text{C}_3$  and the mole % decreases thus the thermogenic gas is being oxidized. They concluded that the natural gas was possibly oxidized rapidly by glacial  $\text{O}_2$  rich water and then a period of sulfate reduction occurred. The glacial loading and unloading created natural fracture networks for this melt water to percolate into the subsurface.

Therefore, oxidation trends are an important concept to understand to while classifying the natural gas geochemistry of a basin.

## **2.4 Source Rock Thermal Maturity and Natural Gas Geochemistry**

A paper written by Osborn and McIntosh (2010) conducts field sampling of natural gas and groundwater in areas of intense oil and gas production in the northern Appalachian Basin in Pennsylvania, New York, Ohio, and Kentucky. The authors used geochemical properties such as stable isotopes and water/gas chemistry, to determine the origin of the natural gas (thermogenic, biogenic, or mixed) and formation waters (deep saline or shallow fresh water) found in this area.

The rock units of interest in Appalachian Basin in this study consisted of Devonian organic rich shale and reservoir sandstones. Osborn and McIntosh (2010) discussed the significance of this study is to determine if the Appalachian basin has similar gas chemistry to the Michigan Basin. Both basins consists of age-equivalent organic rich shales with similar historical glaciation events. The Michigan basin is thermally immature and has dilute brine waters due to the infiltration of glacial water

during the melting event compared to the Appalachian basin. The Michigan Basin also consists of primarily of shallow (<550 meters) biogenic gas with relatively little thermogenic gas. Therefore, it is hypothesized that the Appalachian Basin consists of both biogenic and thermogenic gases because its rock units ages are similar to the Michigan basin. However, it is more thermally mature, and the source rocks are at greater depths than the Michigan basin.

After the field samples were collected and analyzed, the geochemical data displayed limited accumulation of biogenic gases. The Appalachian basin is comprised of primarily thermogenic gases with minor biogenic gases near Lake Erie. Dissolved gas from shallow groundwater near Lake Erie had measureable CH<sub>4</sub> (0.01-50.55 mol %), low  $\delta^{13}\text{C}$ -CH<sub>4</sub> values (-74.68 to -57.86‰), with moderate alkalinity of the groundwater (1.14 to 8.72 meq/kg), and little dissolved inorganic carbon (DIC) (-24.8 to -0.6‰) (Osborn and McIntosh, 2010). These parameters suggest that there is some degree of microbial generation present near Lake Erie. However, the bulk of the gas samples taken from the Appalachian Basin had low (C<sub>1</sub>/C<sub>2</sub>+C<sub>3</sub>) ratios (3-35 mol %) with  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of CH<sub>4</sub> at (-53.35 to -40.24‰, and -315.0 to -174‰), which suggests thermogenic gas generation. The brine waters associated with the bulk of the gas samples taken during this study had high  $\delta^{13}\text{C}$  of DIC (>+10‰), elevated alkalinity (12.01 meq/kg), and low SO<sub>4</sub> values (<1 mmole/L), which suggests microbial activity. However, some brine water samples had high concentrations of SO<sub>4</sub> (12.31 mmole/L) and low lower  $\delta^{13}\text{C}$ -DIC (<-22‰), which suggested that the microbes could be limited by SO<sub>4</sub> reduction. Therefore the majority of the gas generation in the Appalachian Basin is thermogenic with minor accumulation of biogenic gas.

This study aids in bringing more evidence to the importance of understanding the source rocks thermal maturity, the types of source rocks, the local types of reduction or oxidation trends, and gas/water geochemistry to determine the origin of natural gas. The study also gave significant evidence on how gas chemistry can change even if the basins have very similar geologic histories and characteristics.

This will be beneficial to understand that even if a basin is similar to another basin the gas/water chemistry can be significantly different from one another. This study also displays how significant isotopic/elemental data is when identifying the origin of natural gas and groundwater samples.

The studies discussed previously have been primarily about identifying the origin of the natural gases and groundwater. This is great information for understanding a petroleum deposit, but it can also be used for environmental purposes. If dissolved gases from petroleum deposits can be identified in shallow aquifers by using such chemical analysis then this would show evidence that deep thermogenic gases are comingling in shallow groundwater aquifers. But how did they get there and why?

## **2.5 Potential Impacts from Natural Gas Production**

A study written by Osborn et al., (2011) explains the possible mechanism of petroleum fluids mixing with groundwater resources and the significance of studying shallow groundwater resources near intense oil and gas production. The authors conducted a study in the Appalachian Basin, in northern Pennsylvania and upstate New York to study how shallow drinking water resources are affected by oil and gas production/hydraulic fracturing. The authors analyzed groundwater samples to determine

if hydraulic fracturing and petroleum production are influencing gas migration into shallow groundwater resources.

Osborn et al., (2011) measures dissolved salts, oxygen and hydrogen water isotopes, isotopic values of dissolved carbon, boron, and radium in the groundwater samples to determine if gases from the Marcellus and Utica shale formations are present in the drinking water. They also look at the proximity of an oil and gas well to shallow drinking water wells to determine if the oil/gas well casing is leaking and potentially causing the mixing of the fluids.

By identifying the salinity of the water this will give an indication that deep waters have mixed with shallow groundwater. Oxygen and hydrogen isotopes will depict the origin of the dissolved gases in the water samples. Dissolved organic carbon isotopic values also add in classifying the gas type.

There results concluded that 51 of the 60 wells sampled had detectable methane concentrations. Groundwater in the study area has been contaminated with methane (Osborn et al., 2001). Osborn et al, (2011) also noted that groundwater wells were closer (<1 km) to natural gas wells had considerably higher concentrations of methane than wells further away (>1 km) from the gas wells. This supports the idea that gas wells have to potential to leak out of the casing. Osborn et al, (2011) explained that areas of active drilling and gas extraction had 17-times more methane in the drinking water. The study also concluded that no deep brine waters and fracture fluids were not identified in the shallow drinking water samples.

This study shows the significance in studying shallow groundwater quality near areas of oil and gas production. It uses techniques derived by other scientist to discover the origins of the natural gas in a qualitative and quantitative manner.

All of the information discussed above will aid in the study conducted in Colorado. It is essential in understanding the significance of this information listed above to understand shallow groundwater chemistry, petroleum geochemistry, and the geology of the study area.

## **2.6 EPA Study in the Raton Basin**

To further investigate water quality within the Raton basin a recent EPA basin wide study was published May 2015. This study was preformed because in 2009, U.S. Congress encouraged the EPA to study the relationship between hydraulic fracturing and drinking water resources (EPA, 2015). The report focuses on possible contamination of drinking water where hydraulic fracturing has already been used.

This study was conducted with in the Raton Basin in Las Animas and Huerfano counties. “Water quality samples were collected from 14 domestic wells, five monitoring wells, three production wells, and three surface water bodies during four sampling rounds in October 2011, May 2012, November 2012, and April/May 2013” (EPA, 2015). The monitoring and production wells that we sampled are operated and maintained by Pioneer Natural Resources (Las Animas County) and Petroglyph Energy, Inc. (Herfano County) (EPA, 2015). The domestic wells in this study were sampled because local homeowners were concerned with their well water quality and potential impacted from drilling, hydraulic fracturing, and/or CBM production. The sample locations were also selected based upon criteria such as well depth, geologic and hydrologic, characteristics, and the



proximity to nearby gas wells (EPA, 2015). The sampling locations were in western Las Animas County and south central Huerfano County. Water samples in this study were analyzed for metals, anions, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), dissolved gases (e.g., methane and ethane), volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), low-molecular-weight acids (LMWAs), glycol ethers, gasoline-range organics (GRO), diesel-range organics (DRO), dissolved strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), and stable isotopes of oxygen and hydrogen in water ( $\delta^{18}\text{O}\text{-H}_2\text{O}$ ,  $\delta^2\text{H}\text{-H}_2\text{O}$ ), carbon and hydrogen in methane ( $\delta^{13}\text{C}\text{-CH}_4$ ,  $\delta^2\text{H}\text{-CH}_4$ ), carbon in dissolved inorganic carbon (DIC;  $\delta^{13}\text{C}\text{-DIC}$ ), sulfur and oxygen in sulfate ( $\delta^{34}\text{S}\text{-SO}_4$ ,  $\delta^{18}\text{O}\text{-SO}_4$ ), and sulfur in hydrogen sulfide ( $\delta^{34}\text{S}\text{-H}_2\text{S}$ ) (EPA, 2015). The parameters listed above were used to assess several scenarios where CBM development could be impacting drinking water in the basin. The scenarios proposed by the EPA were: “(i) potential interactions between produced water and shallow ground water via fluid migration, spills, and/or infiltration; (ii) potential for migration of chemicals used in hydraulic fracturing formulations into shallow ground water; (iii) potential gas migration from hydraulically fractured zones in the Raton and Vermejo formations into shallow ground water aquifers, including the Poison Canyon Formation and alluvial fill deposits; and (iv) secondary biogeochemical effects related to the migration and reaction of methane in shallow aquifers used for drinking water” (EPA, 2015).

Historical data from a literature review and various database (Colorado Oil and Gas Conservation Commission (COGCC), the U.S. Geological Survey (USGS), National Water Information System (NWIS), and the USGS National Uranium Resource Evaluation (NURE) database) were also compared to the data collected in this study. One

common problem that this study noted is that the majority of the data from the various databases had minimal isotopic analysis relative to other more basic water quality parameters such as specific conductivity and pH. None the less the database review proved useful in establishing baseline water quality conditions dating to the 1990s, which is before significant CBM development occurred.

The data indicated that co-produced waters with natural gas compared to shallow aquifers such as the Poison Canyon and alluvial aquifers differed in ionic chemistry. The co-produced water (water being produced in a natural gas well during natural gas production) had a distinctive chemical signature of: “sodium-bicarbonate type water with moderate concentrations of total dissolved solids (TDS); low concentrations of sulfate, calcium, and magnesium; variable chloride concentrations; enriched  $^{13}\text{C}$ -DIC; low oxidation-reduction potential (ORP); and elevated concentrations of dissolved methane and ferrous iron” (EPA, 2015). The chemical composition of the shallow aquifers where described by the EPA as being: “more variable major ion compositions (calcium-bicarbonate, sodium-bicarbonate, and sodium-sulfate water types); lower specific conductance (SPC); generally lower chloride and higher sulfate concentrations; depleted  $^{13}\text{C}$ -DIC; and variable redox conditions” (EPA, 2015). The EPA’s logic behind their observations/conclusions was that if the fluids (produced water and shallow groundwater) were mixing then the geochemical signatures would be similar. The geochemical signatures between the fluids were not identical to each other. Also, water quality data predating extensive CBM production in the Raton basin has similar ranges of specific conductance and ion chemistry to the present data. Therefore, the EPA decided that the

gas producing zones and shallow groundwater within the Raton Basin where not interacting with each other.

Furthermore, the EPA analyzed a total of 133 organic chemicals to determine if hydraulic fracturing fluids were interacting with shallow groundwater and surface water resources. The reasoning behind the chemical analysis was that hydraulic fracturing fluids tend to use a variety of chemicals such as glycol, ethers, ethanol, isopropanol, 2-butoxyethanol, petroleum distillates, and acetic acid, which are not generally found in clean drinking water. The data/lab analysis of the water samples indicated that “glycol ethers were not detected in groundwater samples from domestic or monitoring wells; low levels of diethylene glycol and triethylene glycol were detected in one of the production wells during the last sampling event (April/May 2013)” (EPA, 2015).

Tert-butyl alcohol (TBA), diesel-range, and gasoline-range organics were detected in some domestic well, monitoring wells and production wells above quantitation limits (QL). TBA detections were considered unique because their concentration and geographic distribution was wide spread within the study area but there were no documented releases of this chemical. TBA was detected at concentrations ranging from 6.9 to 1,310 micrograms per liter ( $\mu\text{g/L}$ ) in domestic, monitoring, and production wells (EPA, 2015). The most likely source of TBA in groundwater is the degradation of fuel oxygenate compounds such as methyl tert-butyl ether (MTBE) and/or ethyl tert-butyl ether (ETBE). As there is no documented gasoline spills which could cause TBA or MTBE to impact groundwater within the EPAs study area there are several non-gasoline related sources of TBA such as; a biochemical and/or chemical breakdown product of tert-butyl acetate (TBAc); a chemical decomposition of tert-butyl hydroperoxide (TBHP);

microbial generation from isobutene; the reaction of isobutylene and water in the presence of a catalyst (EPA, 2015). There were many different hypothesis presented by the EPA on the reasoning behind the TBA contamination, however, they could not come to a conclusion on the source being natural or anthropogenic. Prior to April 1, 2012, operators within the state of Colorado were not required to publically disclose information regarding hydraulic fracturing treatments (COGCC, 2011). Thus, making it difficult to say if the contamination was from the fracking fluids.

Furthermore, volatile organic carbon (VOCs) was detected in produced wells (natural gas wells that were permitted for surface discharge) at 0.3 to 5.1 orders of magnitude below EPA's drinking water standards (MCLs where available for benzene, toluene, ethylbenzene, xylenes, methylene chloride, and chloroform) (EPA, 2015). Almost half (46%) of the organic compounds detected were most likely associated with petroleum fuel release (EPA, 2015). There were no documented fuel releases in the area and no documented uses of these chemicals in hydraulic fracturing fluids; therefore, the EPA assumes that the organic chemicals are associated with interaction of organic matter and groundwater. Furthermore, "the presence of BTEX (benzene, toluene, ethylbenzenes, and xylenes) compounds and benzene derivatives is consistent with results reported for other areas developing CBM resources and may reflect solubilization of coal material, as a by-product of natural water-rock interactions or enhanced solubilization due to injecting fluid with solvent-like properties into coal seams" (EPA, 2015).

Furthermore, with the Cretaceous and Tertiary-age coal seams in constant contact with groundwater within the Raton Basin naturally occurring methane dissolves into the groundwater resources (EPA, 2015). The dissolved methane was found in every sample

collected during the EPA's study of the Raton Basin (EPA, 2015). Dissolved methane in high concentrations can create an explosive hazard within confined spaces. The concentrations from the samples collected ranged widely from 0.003 to 12.4 mg/L with a median value of 0.46 (mg/L) (EPA, 2015). The COGCC cautionary level at which methane can become explosive in confined spaces is 1.1 mg/L and six domestic wells sampled in this study were above this level. Carbon ( $\delta^{13}\text{C-CH}_4$ ) and hydrogen ( $\delta^2\text{H-CH}_4$ ) isotope values of methane were measured where methane concentrations to determine the origin of the gases found from each sample location. The isotopic patterns suggested biogenic and thermogenic gases were present in groundwater samples in the Raton Basin. The monitoring wells in the North Fork Ranch study area had a biogenic origin. An interesting observation by the EPA was in one domestic well in the Arrowhead Ranchettes study area where over four sampling event the gas isotopic signatures began as thermogenic and altered to a mixed (biogenic/thermogenic intermediate) signature. The EPA explained the isotopic change was most likely due to gas migration. "Finally, domestic wells in the Little Creek Field area contained methane with a thermogenic signature, similar to gas from deeper CBM-producing coal beds, but with a distinct trend indicative of methane oxidation" (EPA, 2015).

A methane oxidation trend was indicated at the Little Creek Field sampling area within Huerfano County (EPA, 2015). In 2005 a series of hydraulic fracturing applications were conducted within this study area, which increase the methane and water production till 2007. Also in 2007, it was discovered that methane was leaking into domestic water wells situated in the poison canyon aquifer system. Drinking water was impacted with free phase and dissolved methane. A remediation system (a full

description of the remediation system is given in the Retrospective Case Study in the Raton Basin, Colorado May 2015) was put in place to reduce this contamination. However, the remediation system in the Little Creek Field sampling area proved to be effective in reducing the free face methane but the dissolved methane concentrations had a variable response to the treatment system. The EPA monitored this area using stable isotopes of carbon and hydrogen in methane ( $\delta^{13}\text{C-CH}_4$ ,  $\delta^2\text{H-CH}_4$ ), DIC ( $\delta^{13}\text{C-DIC}$ ), and sulfur in sulfate ( $\delta^{34}\text{S-SO}_4$ ) and hydrogen sulfide ( $\delta^{34}\text{S-H}_2\text{S}$ ), which indicate that methane had undergone dissimilatory bacterial sulfate reduction under anaerobic conditions within the aquifer system. (EPA, 2015). Overall there were several key findings from this study, which will add in clarifying questions from the data collected in this study. The EPA's key observations were:

- CBM recovery occurs within close proximity to drinking water sources. The vertical separation from the CBM producing intervals and drinking water wells has vertical separation of <100 to more than 2,000 feet
- Ion patterns over a 1 and a half-year period indicated that there was limited water migration from the gas producing zones to the shallow aquifers used for drinking water.
- With limited levels of diethylene glycol and triethylene glycol in one production well and no glycol ethers were detected in domestic wells, monitoring wells, and surface water it is unlikely that hydraulic fracturing fluid have interacted with homeowner's wells.
- BTEX concentrations found in the groundwater are currently at low enough levels to assume water rock interaction within a coal bed methane producing basin.

- The cause of the TBA concentrations detected in this basin is currently unknown. It could be anthropogenic or naturally occurring.
- Methane was found in every groundwater sample during this study. Isotopic analysis of the methane samples in the North Fork Ranch study area indicated that the methane was microbial in origin. These samples were distinctively different from the thermogenic gas of the Vermejo formation.
- And, the Little Creek study area was hydraulically fractured and after two years methane concentration began to increase in drinking water wells. This documented that gas had migrated from the Vermejo formation into the shallow Poison Canyon aquifer. “Analysis indicates that sulfate-dependent anaerobic oxidation of methane was occurring, and elevated dissolved sulfide concentrations in ground water reflected secondary biogeochemical changes related to the migration and reaction of methane within a shallow aquifer used for drinking water” (EPA, 2015).

This study gives a strong indication of the affect that shallow groundwater resources are being affected by petroleum production within the Raton basin. It is paramount to use the EPAs observations to strengthen and support the observations made in this paper.

### **3.0 GEOLOGY AND HYDROLOGY**

The geology, structural geology, stratigraphy, and hydrogeology are described in the sections bellow. A geological map is provided in Figure 1 to indicate the different rock types found in the Raton Basin.

#### **3.1 Geology/Structure of the Raton Basin**

The Raton Basin is an asymmetrical synclinal basin with the axis near the western margin (Johnson and Finn, 2011) (Figure 1). The sediments along western edge of the basin near the Sangre de Cristo Mountains are steeply dipping to the east, overturned, highly deformed and/or faulted (Baltz, 1965; Flores and Bader, 1999; Higley, 2007). The western edge of the basin is broken up by western dipping reverse faults (Higley, 2007).

These structures are Pennsylvanian in age and were revitalized by Cretaceous and Tertiary tectonic activities caused by the Laramide orogeny, which occurred near the southern Rocky Mountains. This orogeny event began about 67.5 MA and ended around 50 Ma. (Higley, 2007). While the western edge of the basin is more influenced by tectonism the eastern sediments of the Raton are generally un-deformed and gently dipping to the west (Flores and Bader, 1999). Therefore, the western edges of the basin is more likely to have more fluid pathways due to the deformation in that area of the basin.

Also, Tertiary aged igneous dikes, sills, and stocks of the Spanish Peaks are common throughout the Raton Basin (Flores and Bader, 1999). Miocene and Pliocene dikes, sills, stocks, plugs, and laccoliths have been observed intruding through coal-bearing units such as the Vermejo and Raton Formations throughout the Raton Basin (Flores and Bader, 1999). Igneous intrusions such as dikes have been documented as destroying or thermally maturing coal reserves (Copper et al., 2007; Flores and Bader, 1999). The thickness of the dikes varies from a few centimeters (cm) to 30 meters (m) in some locations (Flores and Bader, 1999).



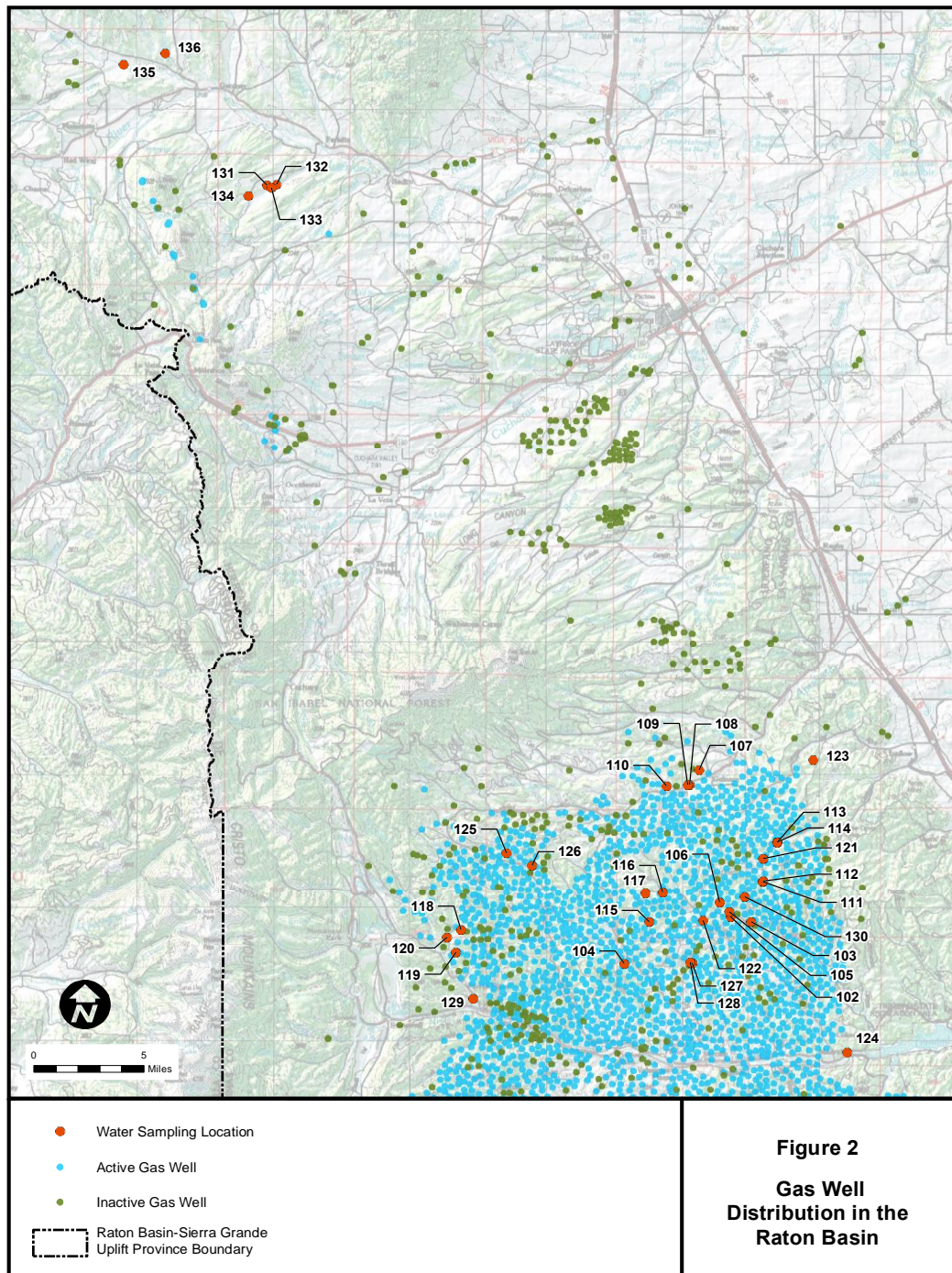
### **3.3 Stratigraphy/Coal geology of the Raton Basin**

The sedimentary units in the Raton Basin range from Devonian to Plio-Pleistocene rocks with Precambrian basement rocks underlining the sediments and as much as 6100 meters of sedimentary rocks is preserved along the basin axis (Johnson and Finn, 2001; Higley, 2007). The units/formations of interest of producing petroleum from coal bed methane in this basin are upper Cretaceous to Paleocene in age (Flores and Bader, 1999; Higley, 2007). The formations of interest are written in descending order: the Poison Canyon Formation, Raton Formation, Vermejo Formation, Trinidad Sandstone, and Pierre Shale (Figure 3 and Figure 4).

The Pierre shale is late Cretaceous in age and underlies the Trinidad Sandstone (Flores and Bader, 1999; Johnson and Finn, 2001). It is roughly 400 to 885 meters thick in the Raton Basin (Flores and Bader, 1999; Johnson and Finn, 2001). The Pierre Shale is a petroleum source rock it is not being produced in the Raton Basin (Higley, 2007; Nuccio et al., 2000).

The Trinidad Sandstone was deposited as a result of the retreat of the Cretaceous Seaway from northern New Mexico to southern Colorado (Johnson and Finn, 2001). The Trinidad Sandstone overlies the Pierre Shale. It varies in thickness from 0 to 91 m thick. (Johnson and Finn, 2001).

The Vermejo Formation overlies the Trinidad Sandstone and ranges from 0 to 116 m thick (Johnson and Finn, 2001). The depositional environment of the Vermejo ranged from fluvial channels, overbank-levees, crevasse splay, flood-plain lakes, and low-lying and raised mire environments (Johnson and Finn, 2001). The coal layer in the Vermejo is about 9 m thick.




**Figure 2.** Gas well distribution relative to sampling locations.

The Raton formation unconformably overlies the Vermejo Formation and ranges from 0 to 610 meters thick (Johnson and Finn, 2001). The Raton formation is a coal-bearing unit. It can be broken into four distinct sections. The units are basal conglomeratic interval (15 m thick), a lower coal-rich interval (30-76 m thick), a sandstone-dominated interval with little to no coal (54-183 m thick), and an upper coal rich layer (183-335 m thick) (Flores and Bader, 1999; Johnson and Finn, 2001). The lower coal rich zone of the Raton formation is composed of interbedded coal, carbonaceous shale, siltstone, mudstone, and sandstone (Flores and Bader, 1999). The upper coal rich layer is comprised of interbedded sandstone, siltstone, mudstone, coal, and carbonaceous shale. The intervals rich in coal resources are deposited in a lenticular coal bed as much as 4 m thick. Sandstone is the most abundant rock associated with the coal intervals. Therefore, coal beds in the Raton Formation can be variable in their thickness and location throughout the basin. Erosion from a fluvial system was deposited with the organic material that would later produce the coal, which created a discontinuous coal deposit (Flores and Bader, 1999).

The Poison Canyon Formation conformably overlies and intertongues the Raton Formation. It can range from 0 to 760 m thick (Johnson and Finn, 2001).

### **3.4 Gas Accumulation in the Raton Basin**

The Raton Basin is known to be a gas prone province with minor oil production or potential (Higley, 2007). The units that are considered to be gas reservoirs in the Raton Basin are the upper Cretaceous Trinidad Sandstone and Vermejo Formation, Upper Cretaceous and Paleocene Raton Formation, and the Paleocene Poison Canyon Formation (Johnson and Finn, 2001).

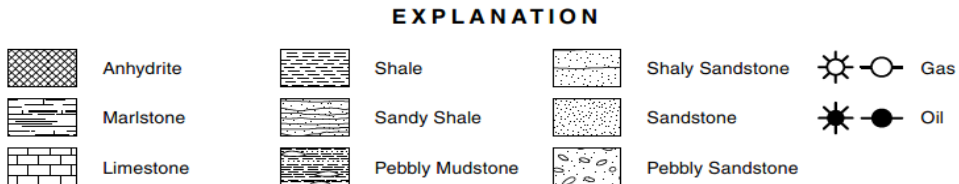
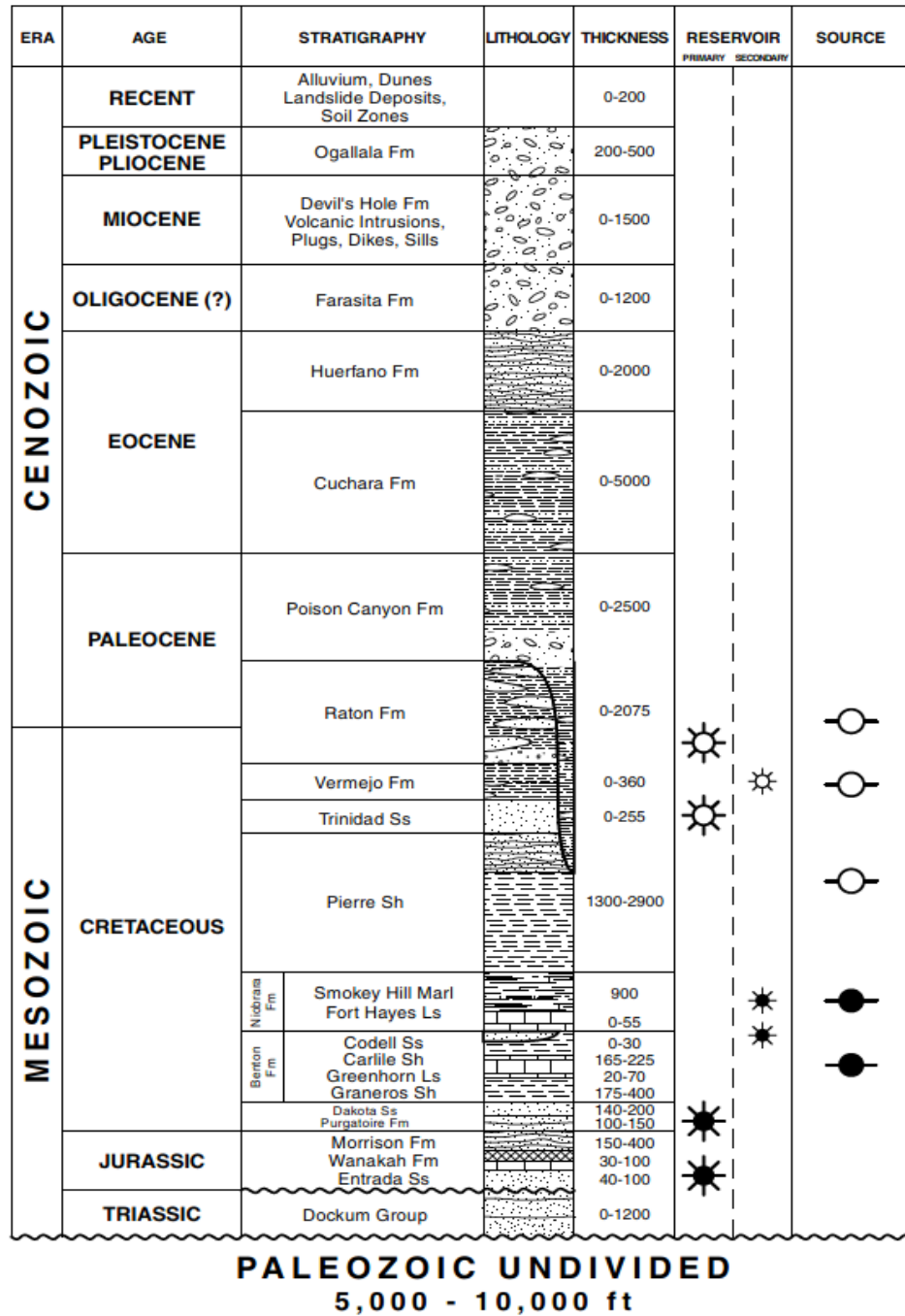
| AGE      |                  | FORMATION NAME          | GENERAL DESCRIPTION  | LITH-<br>OLOGY  | APPROX.<br>THICKNESS<br>IN FEET  |
|----------|------------------|-------------------------|--|---|----------------------------------|
| TERTIARY | PALEOCENE        | POISON CANYON FORMATION | SANDSTONE--Coarse to conglomeratic beds 13–50 feet thick. Interbeds of soft, yellow-weathering clayey sandstone. Thickens to the west at expense of underlying Raton Formation   |  | 500+                             |
|          |                  | RATON FORMATION         | Formation intertongues with Poison Canyon Formation to the west<br><br>UPPER COAL ZONE--Very fine grained sandstone, siltstone, and mudstone with carbonaceous shale and thick coal beds<br><br>BARREN SERIES--Mostly very fine to fine-grained sandstone with minor mudstone, siltstone, with carbonaceous shale and thin coal beds<br><br>LOWER COAL ZONE--Same as upper coal zone; coal beds mostly thin and discontinuous. Conglomeratic sandstone at base; locally absent |   | 0(?)–2,100<br><br>← K/T boundary |
| MESOZOIC | UPPER CRETACEOUS | VERMEJO FORMATION       | SANDSTONE--Fine to medium grained with mudstone, carbonaceous shale, and extensive, thick coal beds. Local sills   |   | 0–380                            |
|          |                  | TRINIDAD SANDSTONE      | SANDSTONE--Fine to medium grained; contains casts of <i>Ophiomorpha</i>  |   | 0–300                            |
|          |                  | PIERRE SHALE            | SHALE--Silty in upper 300 ft. Grades upward to fine-grained sandstone. Contains limestone concretions  |   | 1800-1900                        |

**Figure 3.** Generalized stratigraphic column of the Raton Basins formations of interest.

Johnson and Finn (2001) also stated “that minor amounts of hydrocarbons have been produced on structures at shallow depths (< 915 m) from fractured reservoirs in the Cretaceous Niobrara, Carlile, the Greenhorn Formations, and the Cretaceous Pierre Shale in the Raton Basin since 1892.” Therefore, due to these deeper formations relative to the coal producing formations it is possible for gases to accumulate at greater depths in the Raton Basin (Johnson and Finn, 2001).

### 3.5 Coal production and Coal-Bed Methane in the Raton Basin

It was estimated that there are 1.36 to 15.4 billion metric tons of coal in the Raton Basin (Flores and Bader, 1999). Peak production of the coal in the Raton Basin was from 1911 to 1920 where 64.4 million metric tons of coal was mined.



**Figure 4.** Stratigraphic column of post Paleozoic rocks of the Raton Basin displaying key gas producing formations. (Rose Et al.1986, and Dolly and Meissner, 1977)



Coals throughout the Raton Basin have been documented to release methane gases (Johnson and Finn, 2001). The natural gases from the Cretaceous and Tertiary coal formations in the Raton Basin have been documented as very dry biogenic and thermogenic gases (Higley, 2007). Shallow lower ranked coal from the Raton Formation exhibits a greater biogenic signature than the deeper higher ranked coals from the Vermejo Formation (Higley, 2007). The Raton Basin is a profitable producer of natural gas. In 2003 it was recorded that 287 billion cubic feet of natural gas (BCFG) and 387 million barrels of water (MMBW) have been produced from the coal bearing Upper Cretaceous Vermejo Formation and Upper Cretaceous-Tertiary Raton Formation (Higley, 2007). It was estimated that the ultimate recovery of coal bed methane in the Raton Basin from 1,621 gas wells is 1.087 trillion cubic feet of natural gas (TCFG) (Higley, 2007). The Vermejo Formation contains gas contents that range from 115 to 492 ft<sup>3</sup>/short ton of coal, while the Raton Formations gas content in coal only ranges from 23 to 193 ft<sup>3</sup>/ short ton of coal (Johnson and Finn, 2001). The gas wells in the Raton Basin are mainly targeting the Vermejo Formation (Johnson and Finn, 2001). This is mainly due to the fact that about 80% of the revocable gas in the Raton Basin is found in the Vermejo Formation (Higley, 2007). The coal bearing Vermejo Formation has a vitrinite reflectance of 0.57 percent in the northern sections of the basin and 1.58 percent in the central parts of the basin (Johnson and Finn, 2001). Furthermore, the Raton Formation has a vitrinite reflectance of 0.40 to 1.35. Vitrinite reflectance has been used as an indicator of thermal maturity of organic materials found in basins which produce oil or gas (Sweeney and Burnham, 1990). Coals in the Raton Formation are thinner and not as continuous compared to the Vermejo Formation (Higley, 2007).

The Production of coal bed methane (at depths of < 915 m) is highly concentrated near the Purgatoire River west of Trinidad Colorado where high ranked coals reside (Higley, 2007). The wells drilled in this area have encountered sills, which could explain the increase of coal rank (Higley, 2007). Heat from igneous intrusions such as dikes or sills can increase the vitrinite reflectance values and the coals rank (Higley, 2007). This can increase the gas production of a coal seam, or it can destroy the coals and decrease the gas production if the heating becomes too extreme.

The maximum depth of the coal bed methane wells is 730 m (Johnson and Finn, 2001). Some of the best gas wells yielded 16,700 cubic m of gas per day (Johnson and Finn, 2001).

The gas accumulation is much less and at a shallower depth in the Raton Basin in comparison to the Denver Julesburg Basin. Over all geologic sedimentation thicknesses separating shallow groundwater from oil/gas formations may be a substantial control on petroleum fluid migration into shallow groundwater resources.

### **3.6 Hydrogeology of the Raton Basin**

The Raton Basin in Colorado is a highly rural area with 3 to 5 people per square mile (Topper and Wilson, 2003). Most homeowners rely heavily on private groundwater wells as their only source of water. The annual precipitation in the Raton Basin is 15 to 16 inches per year on the eastern portion and 40 inches per year on the western portion.

The three main aquifers in the Raton Basin are the river valley alluvium, sandstones and siltstones of the Raton, Vermejo, and Trinidad Formations (classified as a single aquifer), and the sandstones and siltstones of the Cuchara and Poison Canyon Formation (also classified as a single aquifer) (Topper and Wilson, 2003).

The Cuchara and Poison Canyon Formations are considered to hydrogeological connected and overlie the Raton-Vermejo-Trinidad Aquifer system. The Poison Canyon formation is considered to be a more productive hydrologic unit and consists of thick permeable sandstone layers. However, the Cuchara formation does have more springs and seeps. The thickness of the saturated sandstones and siltstones in the aquifer system is considerably less than the total thickness of the formations (Topper and Wilson, 2003). This aquifer is much thicker in the northern area of the Raton Basin. Also, these formations are interbedded and therefore are considered to be a confined aquifer system.

The Raton-Vermejo-Trinidad aquifer system primarily consist of sandstones and coals from each of the formations. This aquifer system is recharged by infiltration from precipitation, run off from the Sangre de Cristo Mountains, streams, and lakes. The water in this aquifer is known to move laterally and vertically through pore spaces, along bedding planes and through fracture networks in impermeable rock units (Topper and Wilson, 2003). This aquifer will be sampled during this study.

The Alluvium aquifer is a water table aquifer and limited in extent and consists of silt, sand, and gravels (Topper and Wilson, 2003). The Dakota is a deep aquifer in this basin. It is rarely utilized for drinking water resources due to the cost of drilling to reach this aquifer.

The water quality is variable for each aquifer. The Trinidad sandstone has been documented as potable calcium-sodium-bicarbonate type water (Topper and Wilson, 2003). The Raton and Vermejo aquifers contain sodium bicarbonate or bicarbonate-sulfate type waters (Topper and Wilson, 2003). The Cuchara-Poison Canyon aquifer is heavily mineralized in the axial region of the basin and is a calcium-bicarbonate type



with minimal dissolved solids (Topper and Wilson, 2003). The deeper sections of the aquifer hold a higher concentration of total dissolved solids (TDS). The Raton-Vermejo-Trinidad aquifer has higher concentrations of TDS along flow paths.

#### **4.0 METHODS**

To address basin fluid origin and migration through the Raton Basin, elemental, stable isotope, and dissolved gas analyses were conducted on shallow groundwater samples. Geospatial relationships such as, proximity of an oil and gas well to a groundwater well was evaluated to determine if distance to the nearest oil and gas well influences the types of fluids and concentrations of dissolved constituents in shallow groundwater. Furthermore, historical groundwater geochemistry data from the COGCC, and data collected in the summer of 2014 from each of the basins, was used to see how consistent historical data was to data collected for this study.

A total of 35 water samples were collected during this study (Figure 2, Table 1 Appendix A). Thirty-one groundwater samples from private production wells, 3 stream samples, and 2 precipitation samples were analyzed for stable isotopes, elemental parameters, and dissolved gas composition (Table 1 Appendix A). Twenty of the groundwater samples were analyzed for dissolved gases. Of the twenty-dissolved gas samples, 11 samples were high enough in concentration ( $\sim >1$  mg/L) that isotopic data was analyzed. This included carbon isotopes of methane and hydrogen isotopes of methane (i.e.,  $\delta^{13}\text{C-CH}_4$ ,  $\delta^2\text{H-CH}_4$ ) (Table 1 Appendix A). Thirty-three of the thirty-five samples have isotopic data for water. This includes oxygen and hydrogen isotopes of water and carbon isotopes of dissolved inorganic carbon (i.e.  $\delta^{18}\text{O-H}_2\text{O}$ ,  $\delta\text{D-H}_2\text{O}$ , and  $\delta^{13}\text{C-DIC}$ ). Field parameters such as Temperature, pH, Conductivity, Dissolved Oxygen,

and Alkalinity are reported (Table 1 Appendix A). Elemental analyses (cations and anions) are reported in (Table 1 Appendix A). Sample type, sequence, location, and date is located on Table 1 (Appendix A).

Historical groundwater data was down loaded on September 24, 2015 from the COGCC website ([www.cogcc.state.co.gov](http://www.cogcc.state.co.gov)) of the Raton basin and is presented in (Table 2 Appendix A). Data from the COGCC website is reported to not be validated, meaning there has been limited quality control done to this data set. The data was collected from various sources (i.e. EPA, local state agencies, and private companies) and uploaded to the website for public use. The sample techniques and lab procedures used to collect and process these samples is unknown. This data was used to add to the data set collected during the 2014 field work.

#### **4.1 Field Sampling location**

Prior to field sampling water well owners were identified from publically available water well databases provided by the Colorado Division of Water Resources. Approximately five hundred letters were prepared and sent to local to home owners in areas targeted for sampling with intense gas production. The letters requested access to water wells for testing in exchange for water quality data. Approximately 20 homeowners responded with fewer that agreed to participate. The remaining sample locations were collected by word of mouth and knocking on doors.

#### **4.2 Field Sampling**

Water samples were collected from the Raton Basin in Colorado from domestic water production wells. The sampling event took approximately two weeks. When the well location was identified it was also assessed to make sure the sample was collected

before any type of treatment system or cistern to ensure the groundwater was unaltered. Water wells that had chemicals (Clorox or anti-microbial agents) injected to prevent scaling or microbial activity within 6 months prior to sampling were discounted from this study. Samples were collected first from a spigot directly from the water well when possible or the closest spigot to the water well. All water wells sampled for this study were used daily for household use or for range animals. A GPS reading was recorded for each well location.

In addition to sampling actively used water wells, the wells were purged to evacuate any stagnant water in the well and sample formation water. As part of the purging process, a non-reactive hose was connected to the spigot and placed into a rinsed non-reactive bucket, which acts as a flow through cell. The field parameters pH, electrical conductivity, and temperature were monitored until readings were stable for ten minutes as an indicator of formation waters. Once the parameters became stable the readings were recorded. A non-reactive plastic bucket was filled with formation water and was used to collect elemental and isotope samples into pre-cleaned and labeled 30 ml HDPE bottles. A syringe and filter assembly was used to extract water out of the non-reactive plastic bucket and filtered directly into sample bottles. Five bottles, representing different water analyses were filled to the brim, leaving no air bubbles in the sample bottle. Air could oxidize the sample and break down different types of compounds. Therefore, it was important to eliminate any air bubbles to ensure that the sample water remained unchanged before lab testing could take place. Each of the five bottles were specifically labeled to indicate the lab test (anions, cations, water isotopes, carbon isotopes of DIC, and Alkalinity) and sample identification number. One of the five

bottles contained 2% optima grade nitric acid which was used as a preservative for the cation and metals sample. All water samples were placed immediately on ice during transit and kept in a refrigerator until analyses could be performed. Dissolved gas samples were also collected at the spigot using sampling equipment provided by Isotech Laboratory and as per industry accepted instructions provided by the laboratory. A smaller diameter tube was connected to the spigot. The smaller diameter tube was fully pressurized before it was connected to a dissolved gas sample bag to limit any atmospheric contamination. Dissolved gas sample containers had a bactericide to prevent bacterial modification of dissolved gas chemistry. Samples were also kept out of direct sunlight until shipped to Isotech Laboratories for analyses. The isotope and cation samples were dropped off at University of Arizona by Dr. Stephen Osborn directly following fieldwork. The anion samples were brought back to California Polytechnic University of Pomona and analyzed using a Dionex ICS 1100 Ion Chromatograph.

#### **4.3 Titration**

Titration for alkalinity will be conducted after each day of sampling using the methods described in Geiskes, 1984 paper. To titrate the samples a PH probe was calibrated using known PH 7 Buffer Solution. The PH probe was lowered into PH 7 and PH 4 solutions and each of the values were recorded on a work sheet. After the calibration was completed, 12 to 15 grams of a water sample was weighed in a clean beaker. A stir bar was placed in the beaker and then positioned on a stirring plate. The calibrated PH probe was cleaned with deionized (DI) water, dried with a lab tissue, secured to a stand and lowered in to the beaker of water making sure it was not in contact with the stir bar. Acid was added to the solution slowly until the pH probe was reading

220 MV. A drop of acid was then added 5 to 7 times or more. The change in PH was recorded after each drop. When the pH reading was at or over 240 MV no more reading were collected. The pH data was entered on a spreadsheet and alkalinity values were generated.

#### **4.4 Lab Work**

The anions were analyzed at California Polytechnic University of Pomona's hydrogeology and water quality laboratory. A Dionex ICS 1100 Ion Chromatograph (AS22 Column; precision  $\pm 1\%$ ) was used to measure the anions (Fluoride, chloride, bromide, nitrate, and sulfate) concentrations in the water samples. All samples were run with Calibrated standards, analytical blanks, and known checks. Samples were diluted and rerun if when original analytical run was out of range. Cations were analyzed at the University of California Riverside Environmental chemistry laboratory using a Perkin Elmer Inductively Coupled Plasma Optical Emission spectrometer (precision  $\pm 2\%$ ). Stable isotopes of O, H, and C were measured at the Environmental Isotope Laboratory at the University of Arizona. The oxygen and hydrogen isotopes were analyzed on a Finnigan Delta S gas-source isotope ratio mass spectrometer (precision  $\pm 0.9\%$  or better for H and  $\pm 0.08\%$  or better for O. The stable isotopes of carbon in DIC were measured on a Thermoquest Finnigan Delta Plus XL continuous flow gas ratio mass spectrometer (precision  $\pm 0.30\%$  or better).

#### **4.5 Data Analysis**

Historical and data collected during the field work will be analyzed to address research questions stated above. Groundwater data was down loaded from the Colorado Oil and Gas Conservation Commission (COGCC) website on October 22<sup>nd</sup> 2015. The

data was in a Windows Access Data Base format. A query was developed to pull the necessary information and the file was exported into a Windows Excel file format. The data was then formatted using pivot tables to create a table that was easier to work with the data. In some of the data columns the data had inconsistent units (i.e. the calcium data used  $\mu\text{g/L}$  and  $\text{mg/L}$ ). If this was encountered the units were converted into a standard unit. Every single data point on the formatted COGCC Table 2 was checked and converted as needed (Appendix A). This data was then incorporated with the data collected from the 2014 field sampling event to broaden the groundwater data set for the study area.

## **5.0 RESULTS**

Data collected for this study is presented in measurements, anion and cation values, dissolved gas geochemistry, isotope data, and geospatial data is presented on Table (Appendix A). The COGCC Data is presented on Table 2 (Appendix A).

### **5.1 molecular and isotopic composition of dissolved gases from shallow groundwater**

Measured  $\text{N}_2$  concentrations ranged from 5.45 to 86.18 mol%, with an average value of 58.43 mol%, and a standard deviation (S.D.) of 25.17 mol% (Table 1 Appendix A). Dissolved methane found in the groundwater samples ranged from non-detect to 86.89 mol%, with an average value of 24.51 mol%, and S.D. of 32.18 mol% (Table 1 Appendix A). Measured dissolved ethane ( $\text{C}_2$ ) concentrations ranged from non-detect to 0.978 mol%, with an average value of 0.10 mol%, and S.D. of 0.29 mol% (Table 1 Appendix A). Propane ( $\text{C}_3$ ) concentration ranged from non-detect to 0.383 mol%, with an average value of 0.06 mol%, and S.D. of 0.16 mol% (Table 1 Appendix A).

Only samples with >1 mg/L dissolved methane had isotope analysis. Ethane and propane concentrations were too low (< 1 mg/L) to run isotope analysis. The  $\delta^{13}\text{C}\text{-CH}_4$  values ranged from -42.97 to -67.03 ‰, with an average value of -55.29 ‰, and a S.D. of 6.46 ‰ (VPDB) (Table 1 Appendix A). The  $\delta^2\text{H}\text{-CH}_4$  values ranged from -132.2 to -269.0 ‰, with an average value of -212.72 ‰, and a S.D. of 45.24 ‰ (VSMOW) (Table 1 Appendix A). Gas wetness ( $\text{C}_1/\text{C}_2+\text{C}_3$ ) ranged from 29 to 5700, with an average value of 1945, and a S.D. of 1966 (Table 1 Appendix A). Other dissolved gas data can be found on Table 1 (Appendix A).

## **5.2 Groundwater Geochemistry**

Field parameters of temperatures, pH, conductivity and dissolved oxygen were measured at the time of sampling. Temperature readings of water samples ranged from 10.0 to 22.0 °C, with an average value of 16.6 °C, and a S.D. of 4.0 °C (Table 1 Appendix A). PH reading ranged from 5.90 to 8.41, with an average value of 7.01, and a S.D. of 0.64 (Table 1 Appendix A). Conductivity values ranged from 0.050 to 13.950 (mS/cm), with an average value of 1.08, and a S.D. of 2.38 (Table 1 Appendix A). Dissolved oxygen readings ranged from 0.10 to 10.87 mg/L, with an average value of 3.98 mg/L, and a S.D. of 8.67 mg/L (Table 1 Appendix A). One dissolved oxygen reading was 50.20 mg/L but is most likely an error with the probe. Alkalinity values ranged from 2.69 to 26.26 meq/Kg, with an average value of 7.49 meq/Kg, and a S.D. of 4.82 meq/Kg (Table 1 Appendix A). Groundwater samples had anion analysis of fluoride, chloride, nitrate, bromide, and sulfate. Cation analysis of calcium, magnesium, sodium, potassium, strontium, and silicon/silica. Anions and cation results are listed on (Table 1 Appendix A).

Also, groundwater isotopic delta values of Oxygen eighteen ( $\delta^{18}\text{O}-\text{H}_2\text{O}$ ), deuterium ( $\delta^2\text{H}-\text{H}_2\text{O}$ ), and carbon thirteen of dissolved inorganic carbon ( $\delta^{13}\text{C}-\text{DIC}$ ) were examined. Groundwater samples had  $\delta^{18}\text{O}-\text{H}_2\text{O}$  values ranged from -13.9 to -7.2 ‰ (VSMOW), with an average value of -11.6 ‰ (VSMOW), and a S.D. of 1.59 (VSMOW) (Table 1 Appendix A). The  $\delta\text{D}-\text{H}_2\text{O}$  values ranged from -100 to -54 ‰ (VSMOW), with an average value of -86.5 ‰ (VSMOW), and a S.D. of 10.8 ‰ (VSMOW) (Table 1 Appendix A). The  $\delta^{13}\text{C}-\text{DIC}$  values ranged from -21.1 to 21.9 ‰ (VPDB), with an average value of -5.82 ‰ (VPDB), and a S.D. of 10.1 ‰ (VPDB) (Table 1 Appendix A).

## **6.0 DISCUSSION**

The groundwater sample data from the Raton Basin investigated the source(s) fluids found in the subsurface. The possible sources of waters in shallow aquifers are: 1) shallow dilute recharge waters, 2) deep hyper saline basin brine, and 3) intermediate depth waters. The different sources of methane are 1) shallow microbial methane, 2) deep thermogenic methane.

### **6.1 Basic Water Quality**

The pH levels of the samples taken in 2014 were on average were measured to be near neutral, which is consistent with most natural waters (Table 1 Appendix A). Nitrate levels were well below the Colorado drinking water standards of 45 mg/L (Table 1 Appendix A). Conductivity values were relatively minimal (1.08 mS/cm average values) suggesting little dissolved materials in water (Todd and Mayes 1980) (Table 1 Appendix A). Alkalinity values were relatively moderate (average value 7.49 meq/Kg) with some high concentrations of 17.46 and 26.26 meq/Kg suggesting possible microbial activity (Whiticar, Faber, Schoell 1986).

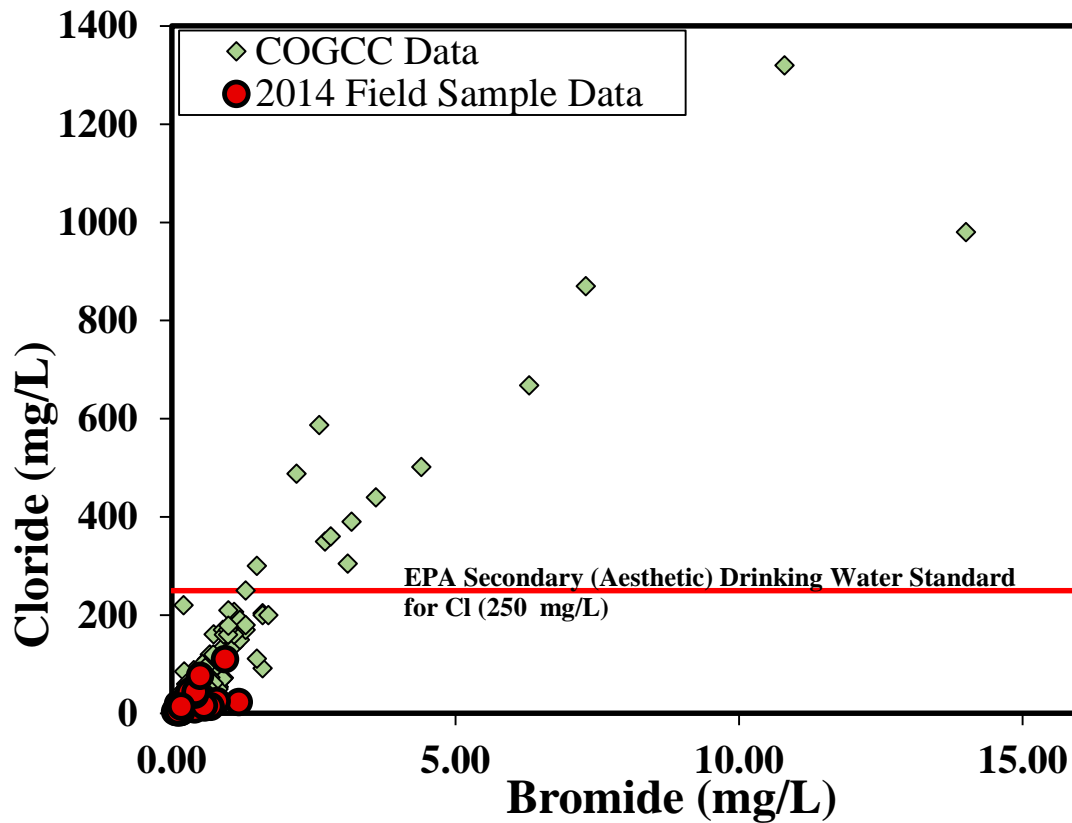


## 6.1 Source(s) of Water and Salinity

Shallow groundwater samples collected for this study appear to be relatively fresh water with little to no interaction with deep saline brines (Figure 5). The highest chloride concentration of the samples collected during the 2014 fieldwork was 109.4 mg/L, which is well below the drinking water standard of 250 mg/L by the EPA (2016) (Figure 5). Historical sample data from the Raton Basin (COGCC) has a wider range of chloride concentrations in comparison to field data collected in 2014 and only 14 out of 194 samples were above the EPA standard. The highest concentration of chloride recorded in the basin was roughly 1,320 mg/L (Figure 5). Chloride concentrations measured for this study are well below values typical of hyper-saline brine (~20,000 mg/L; Osborn and McIntosh, 2010). This indicates that at a first approximation, there is little evidence for wide spread mixing of hyper-saline brines in shallow aquifers of the Raton basin. Though localized mixing may still be possible in shallow aquifer samples with the highest salinities, it would most likely be at very small percentages given current dataset.

Furthermore, Cl/Br ratios are a common way to distinguish the source of salinity in shallow groundwater. The source of salinity may be significant as basin brines is hypothesized to possibly be sourced from evaporated seawater from the Cretaceous intercratonic seaway. The Cl/Br ratios from the 2014 sampling event had a range from 8.0 to 156.9, which is also well below the Cl/Br ratio found in ocean water of 290 (Davis et al., 1998). This is consistent with shallow groundwater with low chloride Concentration ( $t \sim < 100$  mg/L). The combined low chloride and low ratio indicates that salinity is likely not from a marine source. High salinity and low ratio values might be expected with deep hyper saline brine that was buried during the Cretaceous when the

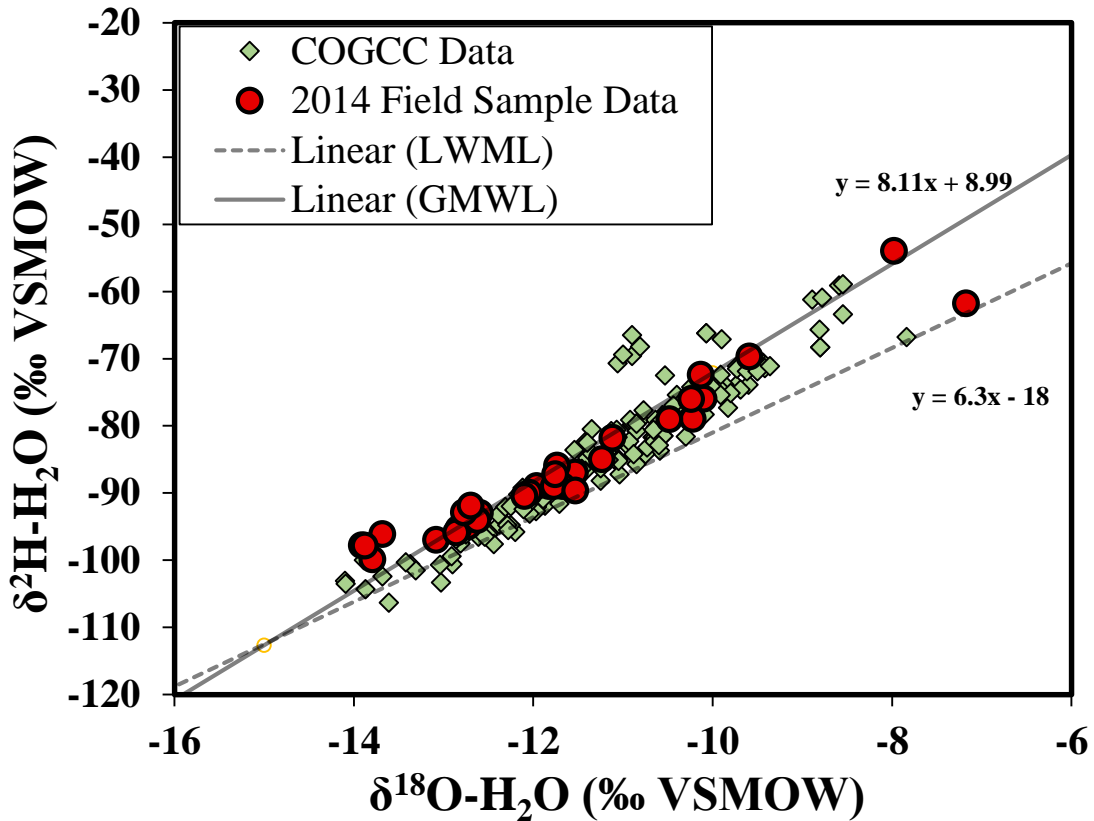
study location was under an intercratonic seaway (Davis et al., 1998; Hiling, 2007). The Historical groundwater data had Cl/Br ratios that were also largely below the ocean water Cl/Br ratio. However, there were 3 of the 194 total samples, which had Cl/Br ratios of 386, 413, and 1047 that are more consistent with halite dissolution, but are not significant at the basin scale. This suggest slightly saline to brine values, but the majority of



**Figure 5.** Chloride and bromide concentrations plotted together to indicate if the water is mixing with deep saline brines.

groundwater samples were relatively fresh water. These elevated concentrations could be remnant fluids from the Cretaceous sea way (Flores 1984; 1987), but not a significant problem at the basin scale. Therefore, shallow groundwater measured in the Raton basin appears to be relatively dilute and consistent with shallow recharge waters. The source of waters is investigated by using stable isotopes of water ( $\delta^2\text{H-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$ ).

Oxygen and hydrogen isotopic data indicate that waters in the shallow aquifer are largely sourced from meteoric waters recharged in the basin (Figure 6). This is consistent with the source of salinity not being from brine. Isotopes values of



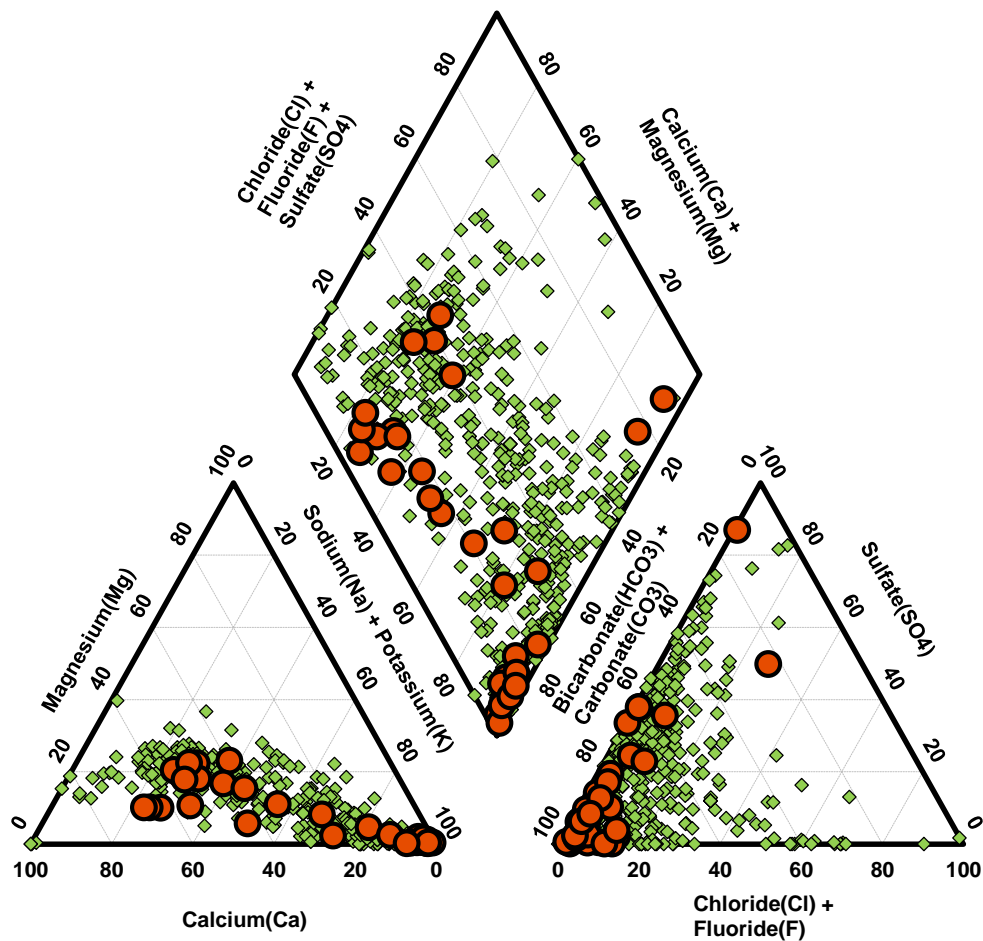
**Figure 6.**  $\delta^{18}\text{O-H}_2\text{O}$  and  $\delta^2\text{H-H}_2\text{O}$  of water samples collected in the Raton Basin where plotted with global (Craig, 1961) and local meteoric water lines (Kendall and Coplen, 2001) to better understand the origins of the water samples.

$\delta^{18}\text{O}$  and  $\delta^2\text{H}$  from one precipitation sample (-8 and -54 ‰ VSMOW, respectively) and three surface water samples (-12.8 and -93 (Sample #124), -10.2 -79 (Sample #112) and -7.2 and -62 (Sample #127) ‰ VSMOW) indicate that there is a variation in water origin, which possibly could come from mixing between different age waters. If the surface water was purely from rain fall it would resemble the precipitation isotopic  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signature. One surface water sample (#127) is fairly similar while the other two are more

negative in their  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values. This difference in surface water isotopic values indicate that there is another source of water influencing the streams in this area. The Spanish Peaks and Sangre De Cristo Mountains are west of the study area and these mountains most likely have snowmelt water. Alpine waters are usually depleted in  $^{18}\text{O}$  and  $^2\text{H}$ , which would produce more negative delta values (Bassett et al., 2004). This is due to the fact that seasonal (temperature change) and topographic variations can alter the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values. It is possible that some of the surface waters within the study area have not yet been influenced by summer rains (more positive isotope values) as much as other rivers and stream.

Groundwater samples appear to plot between the local meteoric water line for Colorado (Kendall and Copeland, 2001) and the global meteoric water line (Craig, 1961). This may be due to the fact that the local meteoric water line is not well constrained for southern Colorado, or that there are possibly two sources of meteoric water converging locally and groundwater represent the mixed average between the two end-member water lines. Since the one precipitation sample collected for this study plot on top of the local meteoric water line and that both meteoric water lines constrain the majority of samples (this study and COGCC), we favor a mixed meteoric source for groundwater. There is little evidence for mixing between shallow meteoric groundwater and evaporated deep basin brine. The brine would be expected to plot well below the local meteoric water (LMWL) line with a mixing trend back to the LMWL. This trend is not apparent and is consistent with the discussion of the sources of salinity being consistent with shallow recharge waters and not brine as a whole. This conclusion is also consistent with the EPA study (2015) that was conducted in the Raton basin.

A piper plot of data from this study and COGCC data was used to further constrain the evolution of groundwater and sources of water (Figure 7). Groundwater appears to be a mixture of sodium bicarbonate type waters and calcium type waters. Most of the groundwater data indicates that there is a mixing trend between sodium bicarbonate and calcium bicarbonate water. Though, there are some minor amounts of chloride and sulfate as secondary anions that may be slightly significant (Figure 7).



**Figure 7.** Piper Plot displaying the anions and cations with the shallow groundwater in the Raton Basin.

The calcium bicarbonate water is most likely meteoric recharge water that transitioned to a sodium bicarbonate type groundwater that is most likely older/intermediate evolved groundwater. This shows mixing from most likely recharge water and groundwater, but does not suggest deep basin brines as concentrations of chloride are relatively low. Therefore, there are two broad types of groundwater found in the Raton Basin. Again, this conclusion is consistent with the discussion above from sources of salinity and stable isotopes of water.

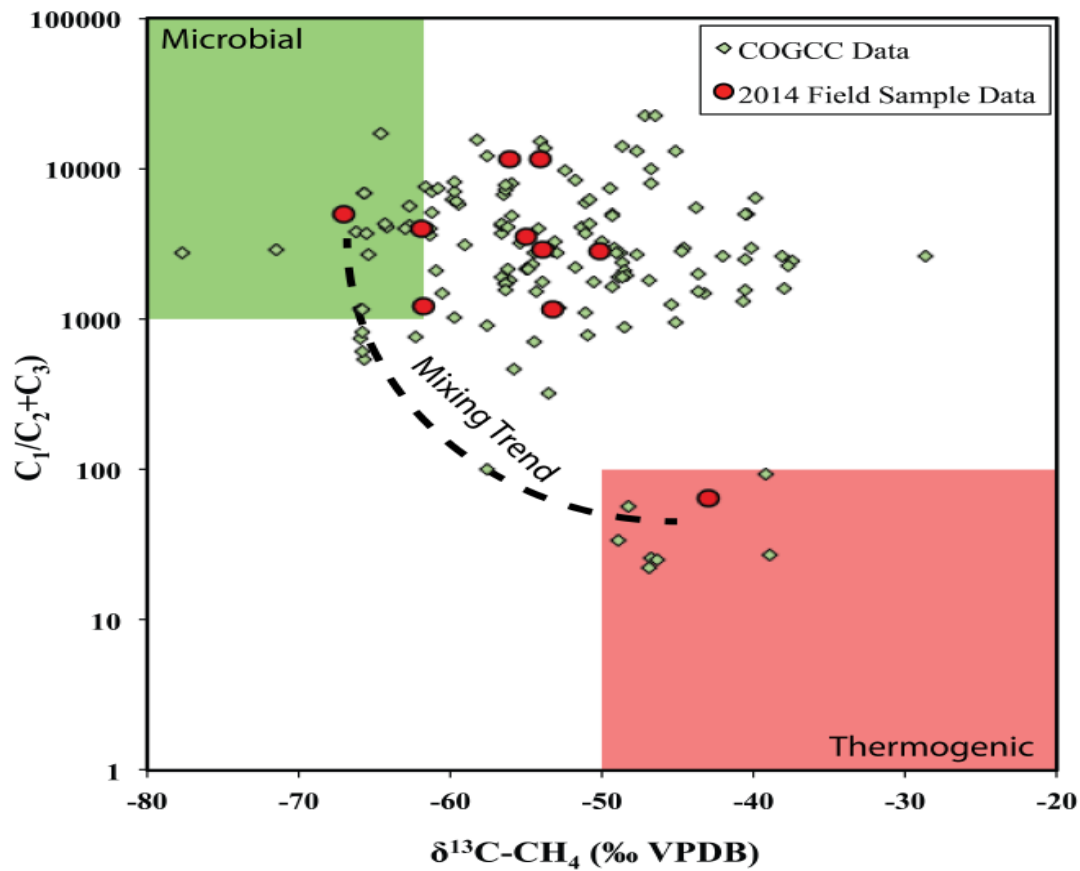
## **6.2 Source(s) of Methane**

The dissolved gas geochemistry found in shallow groundwater samples indicates that there is microbial methane, thermogenic methane, and mixture of these two end-members. Isotopic signatures of  $^{13}\text{C-CH}_4$  and gas wetness (methane/higher chain hydrocarbons;  $\text{C}_1/\text{C}_2+\text{C}_3$ ) plotted on Figure 8 (known as a Bernard plot) were used to indicate the types of gasses (Biogenic or Thermogenic) found in the Raton Basin (Osborn and McIntosh 2010; Schoell, 1980). A minority of shallow dissolved samples plots as pure microbial methane and even fewer samples as pure thermogenic methane with mixing between the two end-members.

Two samples from the 2014 field sample data plot at each end of the spectrum of pure biogenic or pure thermogenic gas (Figure 8). However, the majority of dissolved gas samples indicate post origin modification of the carbon isotope value of methane. The dissolved gas found in the groundwater of the Raton Basin are relatively dry ( $\text{C}_1/\text{C}_2+\text{C}_3 > 1,000$ ) and with a positive shift in  $\delta^{13}\text{C-CH}_4$  isotopic values moving them away from pure biogenic gases end-member due to mixing and/or it is also consistent with mixing of oxidized methane (Schoell, 1980; Jenden et al., 1993; Whitcar et al., 1986). This result is

perhaps a reflection of the complexity of coal seam geology, and comingling of water producing and methane producing zones in the study area.

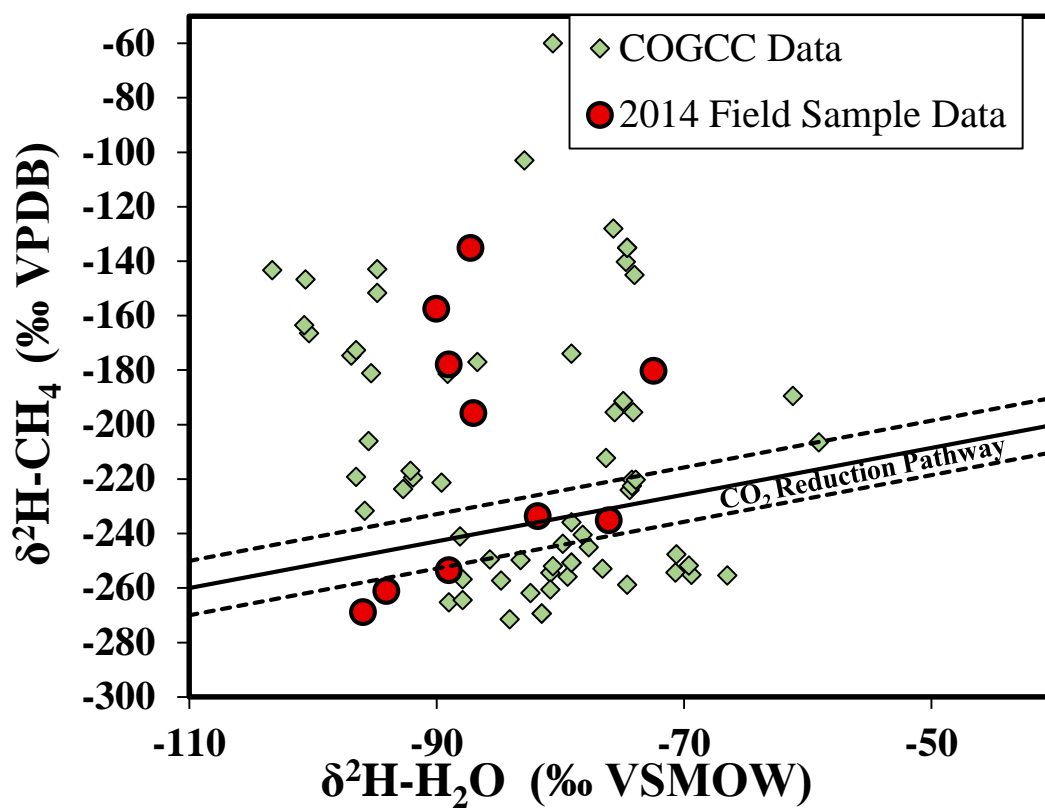
In Figure 9 the CO<sub>2</sub> reduction methanogenic pathway is plotted using  $\delta D-H_2O$  and  $\delta D-CH_4$  (Schoell, 1980; McIntosh and Martini, 2008). Since microbes that hydrogen from the source organic matter and from water, a correlation between the two isotopic values would be predicted for a given microbial metabolism (CO<sub>2</sub> reduction or acetate fermentation; Schell, 1980). This is true for in-situ production of methane with formation waters. A few samples plot along the CO<sub>2</sub> reduction metabolic pathway, while the other samples are scattered above and below the line (Figure 9). This result indicates that minor amounts of microbial methane are being produced in-situ in the shallow aquifer, though the majority of samples have been either produced elsewhere or have been subsequently modified by mixing or oxidation. This result is also consistent with the Bernard plot above (Figure 8). Furthermore, no samples indicated acetate fermentation which would be more indicative of surface water environments (Schoell, 1980; Osborn and McIntosh, 2010). Interestingly, thermogenic methane tends to be in highest concentration, based on current data (Figure 10). The carbon isotope value of dissolved inorganic carbon ( $\delta^{13}C-DIC$ ) and Alkalinity support the in-situ production of minor amounts of microbial methane. Methanogens producing methane by CO<sub>2</sub> reduction will fractionate carbon isotopic values of DIC to more positive values and produce alkalinity in doing so (Figure 11). A minor amount of water samples collected for this study and from the COGCC database exhibit elevated alkalinity and stable carbon isotope values that are more positive than +10‰ (VPDB) consistent with in-situ production of microbial methane.



**Figure 8.** Bernard plot indicating the origin of the dissolved gasses found in groundwater samples in the Raton Basin of Colorado.

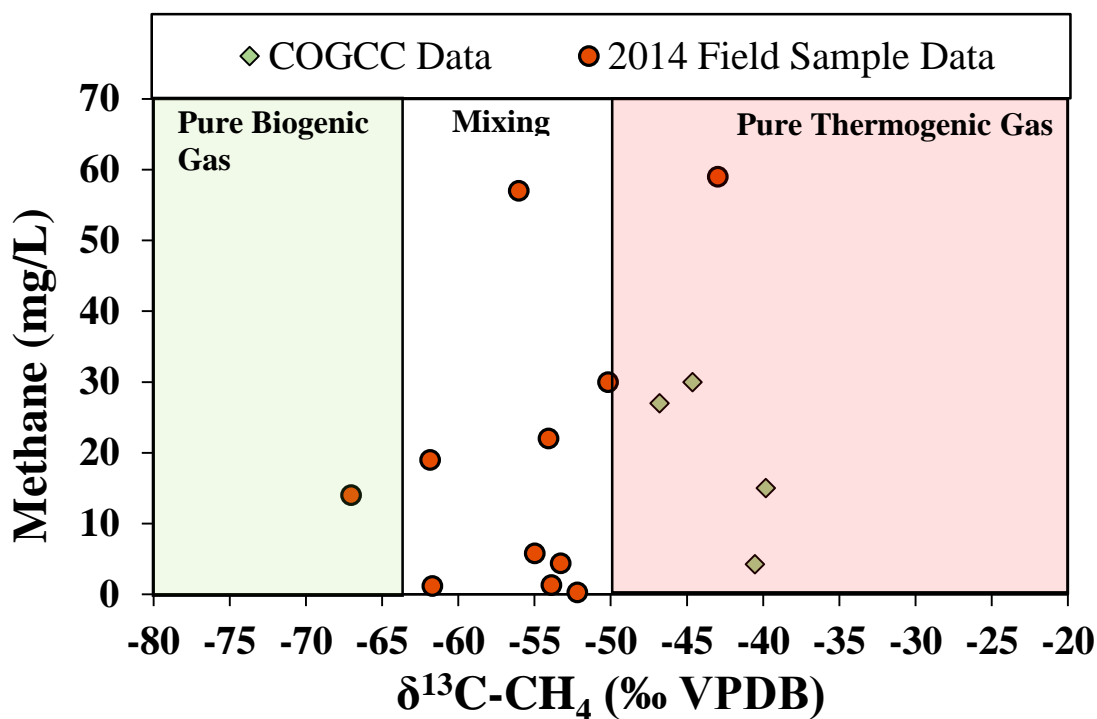
The majority of samples, however, have  $\delta^{13}\text{C-DIC}$  values ( $\sim -10\text{‰}$  to  $-17\text{‰}$ ) that are consistent with soil  $\text{CO}_2$  of shallow basin recharge waters. This is also consistent with interpretations from salinity and stable isotopes of water results. During methanogenesis, microbes will produce alkalinity and fractionate the carbon isotopes of DIC toward more positive values ( $\delta^{13}\text{C-DIC}$  values; Whitcar et al., 1986). However, a few samples do indicate that methanogens are generating biogenic gases, which are dissolved in groundwater.



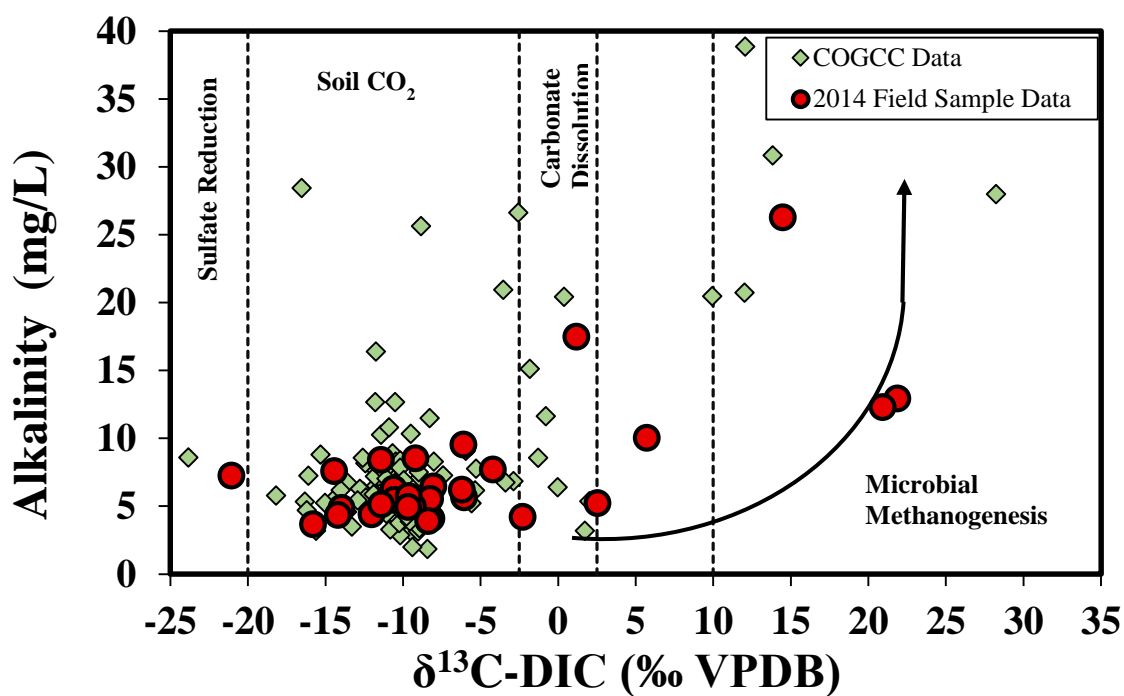


**Figure 9.** Raton Basin Colorado  $\delta^2\text{H-CH}_4$  (‰ VPDB) Vs  $\delta^2\text{H-H}_2\text{O}$  ‰ (VSMOW).  $\delta^2\text{H-CH}_4$  and  $\delta^2\text{H-H}_2\text{O}$  values were used to indicate the possible pathways of methanogenesis (Schoell, 1980).

Furthermore, alkalinity values are moderately high ( $>10$  meq/Kg) as well which could indicate some microbial activity, but not widespread through the basin. This observation is consistent with the results from the Bernard Plot above (Figure 8). Most of the data on Figure 11 indicated soil  $\delta^{13}\text{C-DIC}$  values indicative of meteoric recharge waters (-5 to -15 ‰ VPDB) that have been modified by soil zone  $\text{CO}_2$  and is consistent with the interpretation of waters from a meteoric origin (Figure 6). Therefore, on a basin wide scale the petroleum-dissolved gases found in the Raton Basin have originated from biogenic and thermogenic sources with mixing and altered by oxidation.



**Figure 10.**  $\delta^{13}\text{C-CH}_4$  (‰ VPDB) Vs Methane concentration, which was used to better understand the origin of the gas in the Raton Basin.



**Figure 11.**  $\delta^{13}\text{C-DIC}$  (‰ VPDB) Vs Alkalinity, which was used to better understand the origin on the groundwater and gases found in the Raton Basin.

Therefore, on a basin wide scale the petroleum-dissolved gases found in the Raton Basin have originated from biogenic and thermogenic sources with mixing and altered by oxidation. The geology of the area might be a key factor in explaining why such diverse gases geochemistry is present in this basin.

### **6.3 Coal Alteration**

The Raton and Vermejo Formations in the Raton Basin are the major producers of gas. The coal gas is produced at shallow depths (<1,000 meters below ground surface) and appears to be the gas found in shallow groundwater resources. The generation of biogenic and thermogenic gases are most likely a complex array of steps. A hypothesis was constructed to explain the differences in gas type and why these gases are coming into contact with shallow groundwater.

Speculation of coalbed gas origination and transformation may have occurred as follows; the coal from the Vermejo and Raton formation first produced biogenic gases. This is because without the coal interacting with a thermal source the coal would only produce biogenic gas. As geologic time progressed the coal began to be exposed to a heat source by burial or tectonic activity during the tertiary. Pressure and heat from sedimentary overburden and tectonism could have caused the thermal maturation of the Vermejo and Raton Formations (Baltz, 1965). Therefore, the coal increased in rank overtime, which limits biogenic gas production. The Vermejo underlying the Raton was most likely exposed longer and at slightly higher temperatures to a heat source, which explains the reason why it is higher in rank relative to the Raton Formation (Higly, 2007). As rank increased in the coal there is a switch from biogenic to thermogenic gas production. However, the transition was most likely not instantaneous (Higly, 2007).

While the thermal maturation occurred to the coal formations tectonic activities also progressed in the tertiary in southeastern Colorado, which slightly altered the basin with dike swarms and basin uplifted (Baltz, 1965). The dike swarms caused more localized thermal alteration or even destruction of the coal formations in the Raton Basin (Higly, 2007). It is possible the uplift of the basin in the Tertiary moved the basin slightly away from deep thermal sources and sediments were eroded away (Baltz, 1965). Even though the coals have been thermally altered, if the heat source was slightly decreased it would be possible for the microbes to be reintroduced to the formations by a shallow hydrologic flow system and continue producing biogenic gases (Moore, 2012). For the bacteria to be introduced to a coal seam groundwater recharge needs to be possible (Moore, 2012). The basin geochemistry,  $\delta^{18}\text{O-H}_2\text{O}$  (‰ VSMOW),  $\delta^2\text{H-H}_2\text{O}$  (‰ VSMOW),  $\delta^{13}\text{C-DIC}$  (‰ VPDB) values all indicated that groundwater in the shallow aquifers for this study are being recharged with relatively fresh meteoric water. The recharge waters could have reintroduce the necessary microbes to produce biogenic gases again (Moore, 2012).

The collective coal formations has the potential to store and preserve these events. As coal is compressible, it has the ability to seal or leak gases (Moore, 2012). Simply, gas adsorption or storage with subsequent release could explain the differences in the gas geochemistry. The different isotopic signatures could simply be different ages of the gases that were generated throughout the varying history of the basin. These gases could have been in storage for millions of years and recent human activities released such gases from the locked systems through hydraulic fracturing. The shift of isotopic values to the right (see Figure 8) could alternatively be explained by Raleigh fractionation as the coal begins to produce gases instead of the more common conclusion of modification by

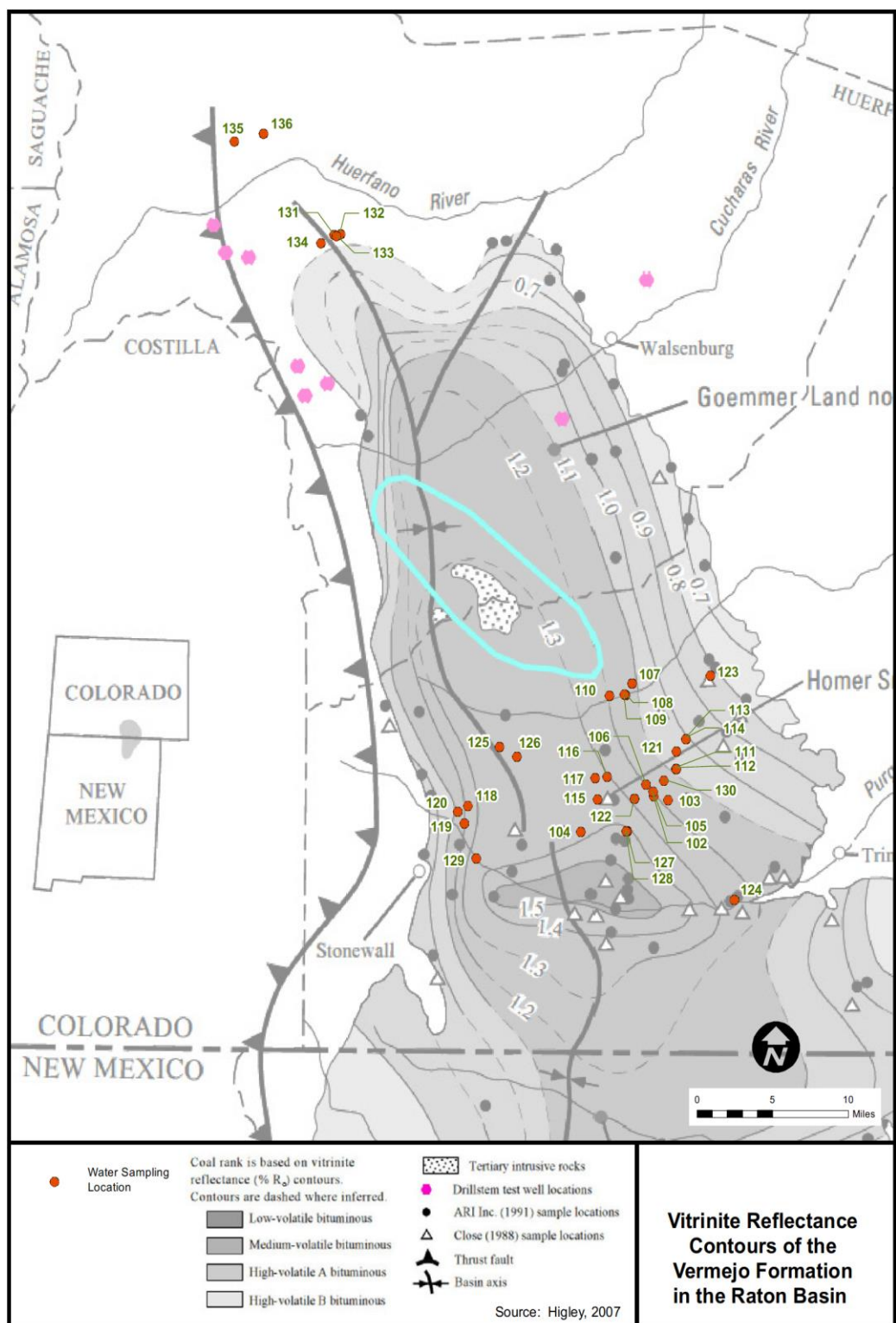
oxidation. The ratio of  $^{12}\text{C}$  to  $^{13}\text{C}$  progressively increases and the microbes are forced to start using the  $^{13}\text{C}$ . Therefore, younger gases would be depleted in  $^{13}\text{C}$  while older gases would be enriched.

Another possible way to understand the isotopic signatures of the dissolved gases found in shallow groundwater samples could be a stratified system. The Raton Formation overlies the Vermejo Formation and both formations produce natural gases. In some instances the coal seams have 185 m of vertical separation and each formation has coal seams with various thicknesses and depths (Johnson and Finn, 2001). The Raton Formation is shallower, lower in rank, and produces significantly less gas relative to the Vermejo Formation, which is deeper, higher in rank, and produces more gas relative to the Raton Formation (Higley, 2007). The Thermal maturity of the Vermejo Formation is mapped on Figure 12. Moore (2012) indicated that coal gas formations that produce thermogenic gases are most likely; high rank (thermally mature), produce more gas, and are generally located deeper in a basin relative to biogenic gas prone formations, which are usually shallow, lower in rank, and produce less gases. Therefore, the Raton most likely produces more biogenic gases and the deeper Vermejo formation produces more thermogenic gases. If The Vermejo was producing primarily thermogenic gases then the gases should be considerably wet (elevated ethane and propane concentrations) (Schoel, 1980). However, Higley (2007) gives the explanation that the gases found in the Cretaceous and Tertiary coal formations of the Raton Basin generally produces dry gases. The coal in the Vermejo most likely produces dry gas due to the original materials from which the coal was created from. Moore (2012) stated that the materials from which coal is originally derived from will have a strong influence on the types of gasses it will

generate. The coal formations with  $>0.5 R_0$  (vitrinite reflectance) values should start producing thermogenic gases (Moore, 2012). This would explain the shift in Figure 8 that the  $\delta^{13}\text{C-CH}_4$  become more positive since thermogenic gases produce more positive  $\delta^{13}\text{C-CH}_4$  values (Schoel, 1980). There is still an indication that wet thermogenic gas is present in shallow groundwater resources (Figure 8). The wet thermogenic gas could still be from the Vermejo Formation or even from deeper shale gas of the Pierre Shale or the Niobrara Formation.

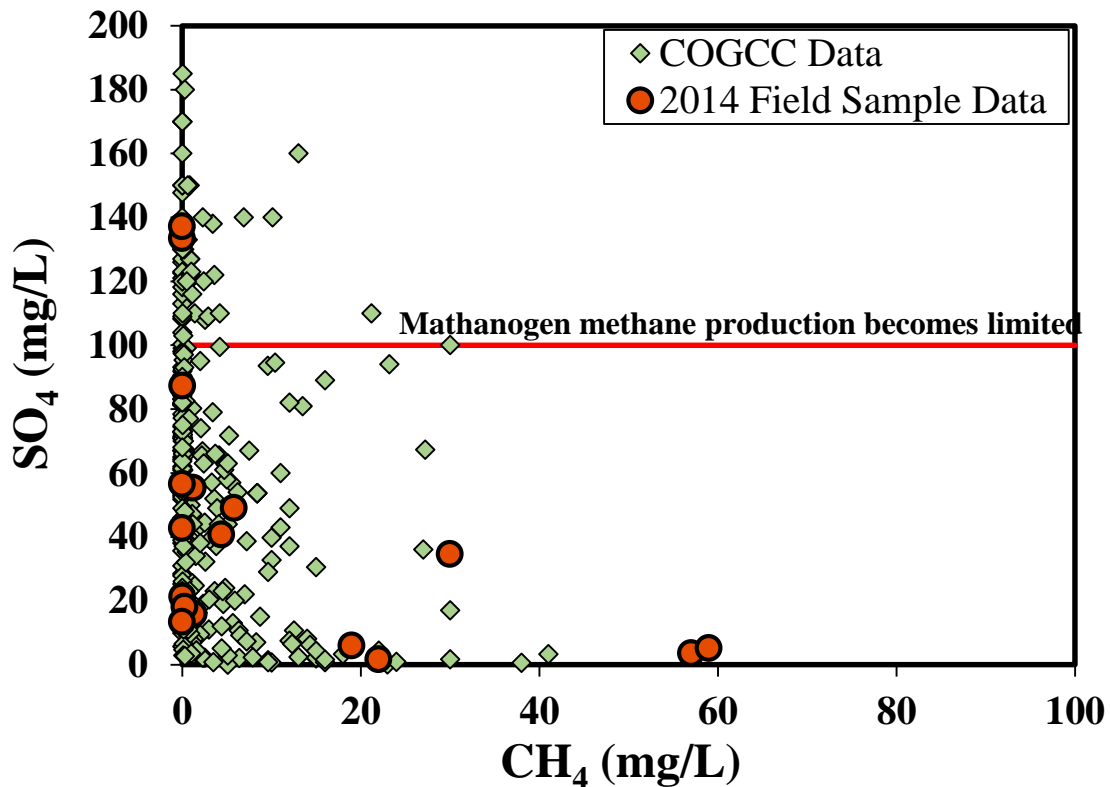
The plots indicated by past studies to better distinguish biogenic and thermogenic gases have mainly been used in shale gas systems and it is possible that coal gas systems produce similar  $^{13}\text{C-CH}_4$  isotopic gas signatures and slightly different gas wetness values. Thus explaining the shift in  $\delta^{13}\text{C-CH}_4$  and a minimal change in gas wetness values as coal bed gases can be considerably dry. However, this could be a basin specific phenomenon as this hypothesis has not been compared to other prominent coal bed methane producing basins.

Another possible way to explain the shift from pure biogenic gases to more positive  $\delta^{13}\text{C-CH}_4$  values with little change in gas wetness is that the gas was originally biogenic and was altered by REDOX (oxidation reduction) process. If sulfate reduction was prominent in the basin microbes would most likely use the lighter isotopes of carbon found in the methane molecule causing the methane to be oxidized, which will cause an enrichment (a positive shift) in  $\delta^{13}\text{C-CH}_4$  and an increase in  $\text{CO}_2$  production. Sulfate values in the basin are generally high but Figure 13 indicates that sulfate concentrations were only high enough in two samples in the 2014 data to limit methanogenesis.



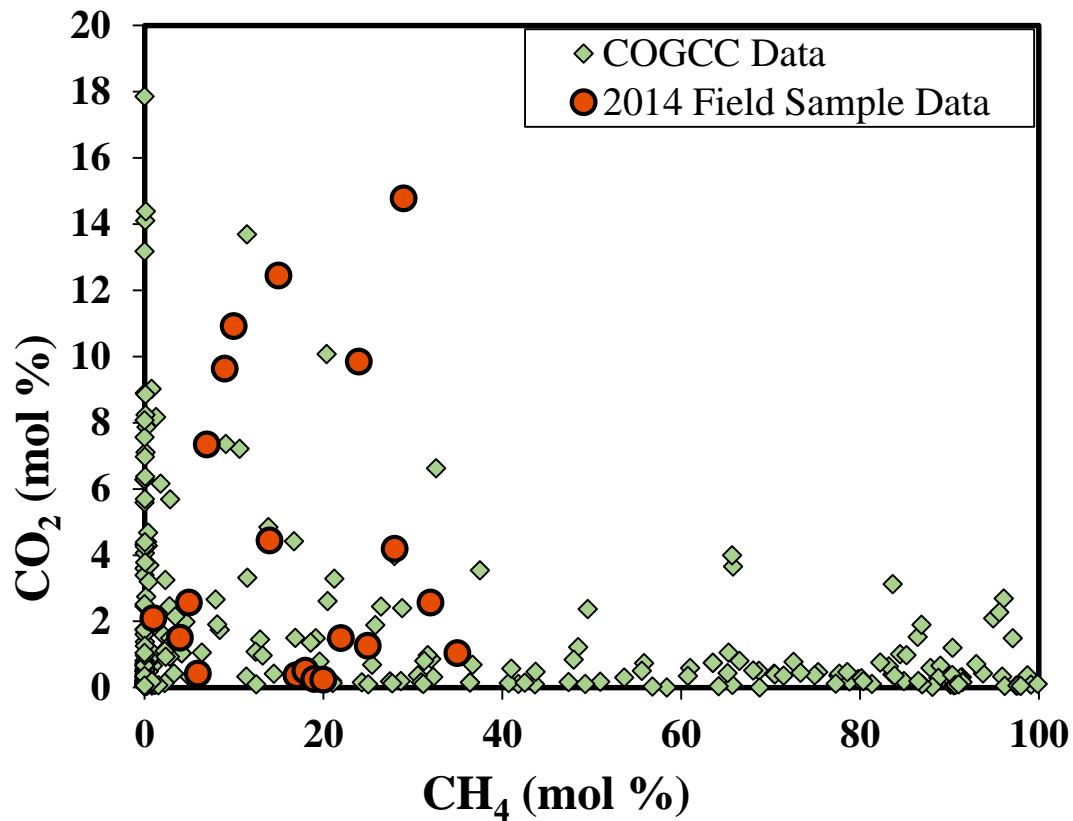
**Figure 12.** Thermal maturity map of the Vermejo Formation. The figure was modified from Higley, 2007.

Also, even if sulfate reduction was a driving force it still would not limit thermogenic gas generation and even if it altered thermogenic gases the  $\delta^{13}\text{C}\text{-CH}_4$  would only be considered more thermogenic as the  $\text{CH}_4$  molecules would be more enriched in  $^{13}\text{C}$ . The 2015 EPA study suggested methane oxidation had occurred in a select area of the basin based on sulfur isotopic analyses, which was not conducted in this study. However, sulfate concentrations are consistent with methane oxidation as a whole (Figure 13 and 14). Methane concentrations tend to be lowest where sulfate is at high concentration. As a first approximation, this is consistent with the interpretation of redox controlled methane concentrations in the basin as a whole. Since  $\text{CO}_2$  is a byproduct of methane oxidation, there should also be an inverse relationship with methane concentrations. Figure 14 depicts the relationship between methane and  $\text{CO}_2$  concentrations.



**Figure 13.** Relationship between sulfate and methane concentrations.





**Figure 14.** Relationship between methane and CO<sub>2</sub> concentrations.

#### 6.4 Fluid Migration

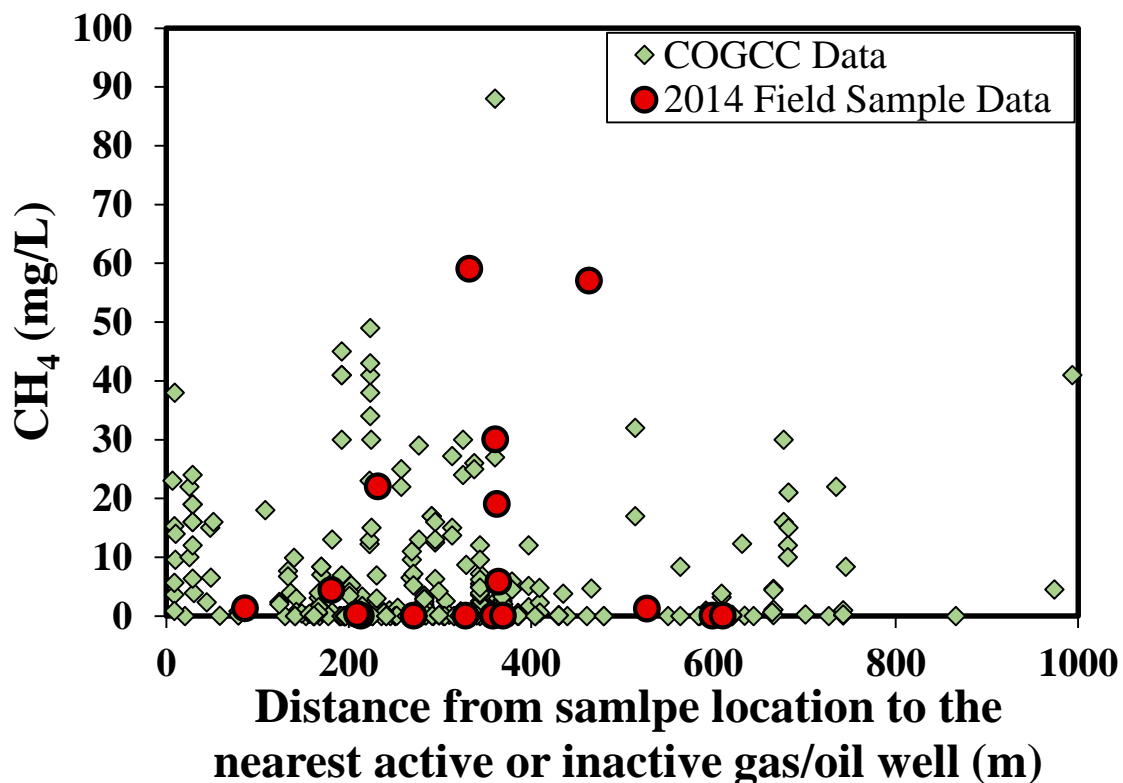
Ultimately dissolved petroleum gases were detected in shallow groundwater in the Raton Basin. The gases in the basin appear to be biogenic, thermogenic, oxidized and possibly a mixture. What is causing the gases to move into shallow groundwater resources? It has been shown that areas of intense oil and gas production cause fluids throughout the subsurface to migrate into groundwater resources (Osborn et al., 2011). Also the case study conducted by the EPA (2015) indicated that gasses fluids were migrating in some areas where hydraulic fracturing had occurred. Fluids will almost always follow the path of least resistance. For instance when a bore hole is drilled a

pathway for fluids to travel is created in and around the bore hole casing. About 10% of all petroleum wells leak (Personal communication with Osborn, 2015). If there is a high density of petroleum wells though out a basin the wells themselves may cause some fluid interaction between different layers of the basin (Figure 2). Take into consideration that a trend may exist between methane concentration and the distance to the nearest gas well (Figure 15). If the gas wells in the Raton basin are leaking or causing fluid migration then shallow groundwater samples should have higher concentration of dissolved methane if the water well is within close proximity of a petroleum well. These parameter were plotted on Figure 15 and listed on Tabel 1 and there is not a strong indication that the wells in this area are creating a conduit for fluid migration (Appendix A). The plot is rather random and not consistent. This could be due to the fact that the wells in this area were drilled and completed correctly with a high quality control factor. Or this hypothesis simply does not apply to this basin due to the fact that some other factor is dictating this fluid interaction.

Fluid migration is most likely caused by fracture networks throughout the basin. If a pathway exists then gaseous fluids will more through it. As methane is less dense than water the gases will progressively move up though the fracture networks and into shallow groundwater. Thus a highly faulted and deformed petroleum producing basin as seen in the Appellation Basin could potentially have hydrocarbon fluids from great depths interacting with shallow groundwater resources (Osborn and McIntosh, 2010). The Raton is not highly deformed except along the western edge of the basin where thrust faulting has occurred. Furthermore, the shallow groundwater aquifers are known to be in contact with the coal seams in this area. Aquifers are found in the interbedded sandstones

in the Raton and Vermejo Formations. Therefore, if methane or petroleum fluids are in the vicinity of groundwater resources it is expected that such fluids will dissolve into solution to some extent. Even if this is occurring at great depths of 1,000 mbgs the methane will always work its way up through fracture networks by concentration gradients and simply density stratification principals. Furthermore, if more pathways are artificially created by hydraulic fracturing it is only probable that more petroleum fluids will interact with shallow groundwater resources relative to the naturally occurring interaction. With the increase in hydraulic fracturing with in the basin, there most likely has been an increase in fracture networks throughout the subsurface.

If groundwater monitoring was implemented on at least an annual basis dissolved methane found in groundwater plotted vs time could indicate if this is the case.



**Figure 15.** Methane concentration vs. distance to the nearest gas well.

As coal bed gases begin to deplete overtime in turn the dissolved methane in groundwater will also diminish. This would clearly indicate where the gases were coming from but it is not providing immediate answers. It is important to start understanding what the consequences are to the technologies we are creating before we start implementing them on a large scale. The 2015 EPA study and this paper have indicated that methane is migrating into shallow groundwater most likely by natural causes and by petroleum production within this basin. It is difficult to say why some areas tend to act different to others when they are hydraulically fractured. Most likely the geology of the subsurface dictates fluid flow. A petroleum producing formation is never homogenous and the complexities and interaction between hydraulic fracturing and the geology will generate variable consequences. Therefore it is paramount to continue studying groundwater quality parameters in the vicinity of petroleum producing areas to at least mediate any possible sources of contamination before the problem becomes overwhelming to the area.

## **7.0 CONCLUSION**

The following conclusions are summarized below from results presented herein:

- 1) Pure microbial and thermogenic methane is not significant in shallow aquifers at the basin scale.
- 2) Dissolved methane in shallow aquifers have minor amounts of mixed microbial and thermogenic methane that have most likely undergone post origin oxidation and/or rayleigh fractionation of basin coal seams (methane source).
- 3) Shallow groundwaters are largely meteoric recharge waters in origin. This is based on the oxygen (water), hydrogen (water), and carbon isotopes (DIC).

- 4) There is little evidence, based on this dataset for deep basin brines mixing in shallow aquifers based on relatively low chloride concentrations ( $\sim >100$  mg/L) and low chloride to bromide ratios (8 to 156). Halite dissolution is a very minor source of salinity.
- 5) There is little evidence that natural gas production in the study area is impacting shallow groundwater resources at the basin scale based on the current data depicting no apparent correlation between the distance to the nearest gas well and methane concentrations.
- 6) More work should be done to incorporate fluids produced from gas wells (not sampled as part of this study) with existing and historic shallow aquifer geochemistry to address potential impacts more thoroughly.

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## **Appendix A**

See CD