Water Quality and the Presence and Origin of Methane in the Upper Pierre Aquifer in Northeastern Weld County, Morgan County and Logan County, Colorado

COGCC Project Number 2141

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COLORADO
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List of Acronyms

‰	per mil
ARP	Arapahoe-Roosevelt National Forest and Pawnee National Grassland
COENV	COGCC Environmental
COGCC	Colorado Oil and Gas Conservation Commission
DIC	dissolved inorganic carbon
DWR	Colorado Division of Water Resources
EPA	Environmental Protection Agency
mg/l	milligrams per liter
SAR	Sodium Adsorption Ratio
TDS	total dissolved solids
USFS	United States Forest Service
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
WQCC	Water Quality Control Commission

INTRODUCTION

The Colorado Oil and Gas Conservation Commission (COGCC) undertook this study to document the water quality and the presence and origin of methane in the Upper Pierre aquifer in northeastern Weld County, Morgan County and Logan County, Colorado (Figure 1). The Upper Pierre aquifer has been largely unexplored until recently, and the Colorado Division of Water Resources (DWR) has received several applications from private landowners requesting a nontributary determination for the Upper Pierre aquifer. Most applications to the DWR are for parcels of land located in northeastern Weld and Morgan Counties. Prior to this study, little public data existed to enable a characterization of water quality of the Upper Pierre aquifer. The recent increase in oil and gas exploration and production in northern Weld County, coupled with the increased interest in the Upper Pierre Aquifer as a source of water for livestock, industrial, and domestic uses, prompted COGCC to conduct this study.

Hydrogeology of the Upper Pierre Aquifer

The DWR has undertaken a regional investigation to better understand the nature and extent of the Upper Pierre aquifer, which has not been formally named. Kirkham and others (1980) may have first used the term "upper Pierre aquifer." Most recently, documents submitted with DWR (example: New Raymer water court case 12CW68) and DWR water well permits (examples: Permit Nos. 59760-F, 77932-F, 300403) refer variously to the "Upper Pierre sands," the "Pierre Shale aquifer" and the "Upper Pierre aquifer." Jehn-Dellaport and Renninger (2017) propose the name "Pawnee Aquifer". COGCC's study will refer to the Upper Pierre aquifer.

Workers identified the freshwater bearing silt and sand layers in the upper Pierre Formation as early as 1965 (Weist, Jr. 1965) and 1976 and 1977 (Kitely 1978). Water wells have long been completed in and producing from the Upper Pierre aquifer, but little study on the availability of the aquifer as a water source had been completed (DWR 2015, Jehn-Dellaport and Renninger 2017). DWR research indicates that the Upper Pierre aquifer consists of interbedded mudstone, siltstone, sandy siltstone and fine grained sandstones (DWR 2015). The aquifer is generally isolated from the overlying Laramie-Fox Hills aquifer by the 125-250 foot thick transition member of the upper Pierre Shale, except in the southeastern and eastern portion of the Cheyenne basin where the Pierre shale crops out or is overlain by Quaternary alluvium. Surface geology across the study area generally consists of the Tertiary White River Formation, which crops out in the northern part of the part of the area, the Late Cretaceous Laramie and Fox Hills Formations, which crop out along drainages incised in the area, and the transition zone of the Upper Pierre Formation, which crops out in the bottom of the most deeply incised areas and crops out more broadly across the southern portion of the area near the South Platte River (Figure 2).

DWR has initially determined the general lateral and vertical extents of the Upper Pierre aquifer based on geophysical logs of oil and gas wells throughout the region. Figures 3 and 4 are cross sections prepared by Jehn-Dellaport and Renninger (2017) that provide a general interpretation of the aquifer extent and geometry. A more comprehensive discussion of the geologic and physical characteristics of the Upper Pierre aquifer is discussed by Jehn-Dellaport and Renninger (2017). COGCC's study and this report focuses on the water quality of the aquifer.

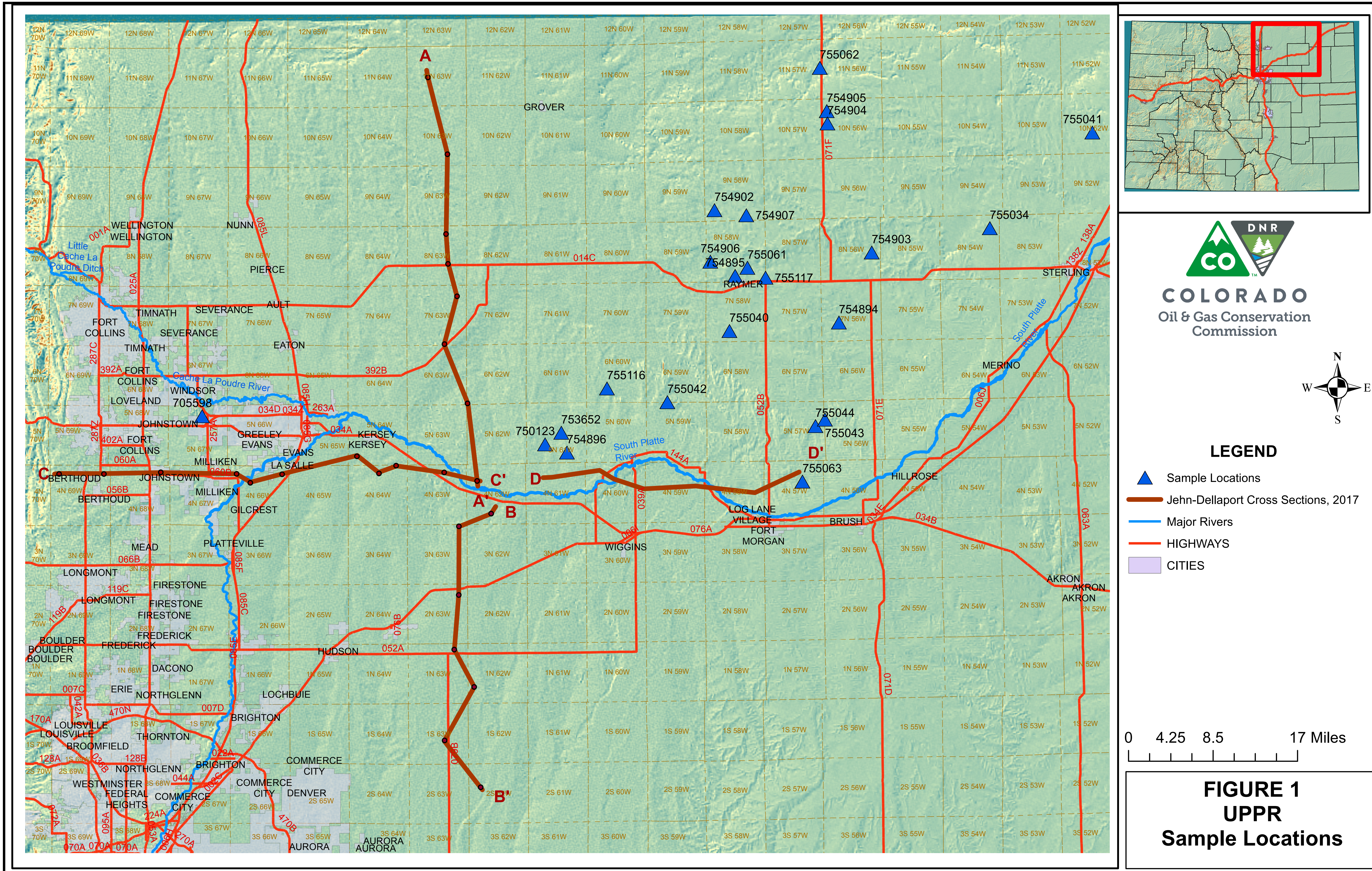

FIGURE 1
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Sample Locations

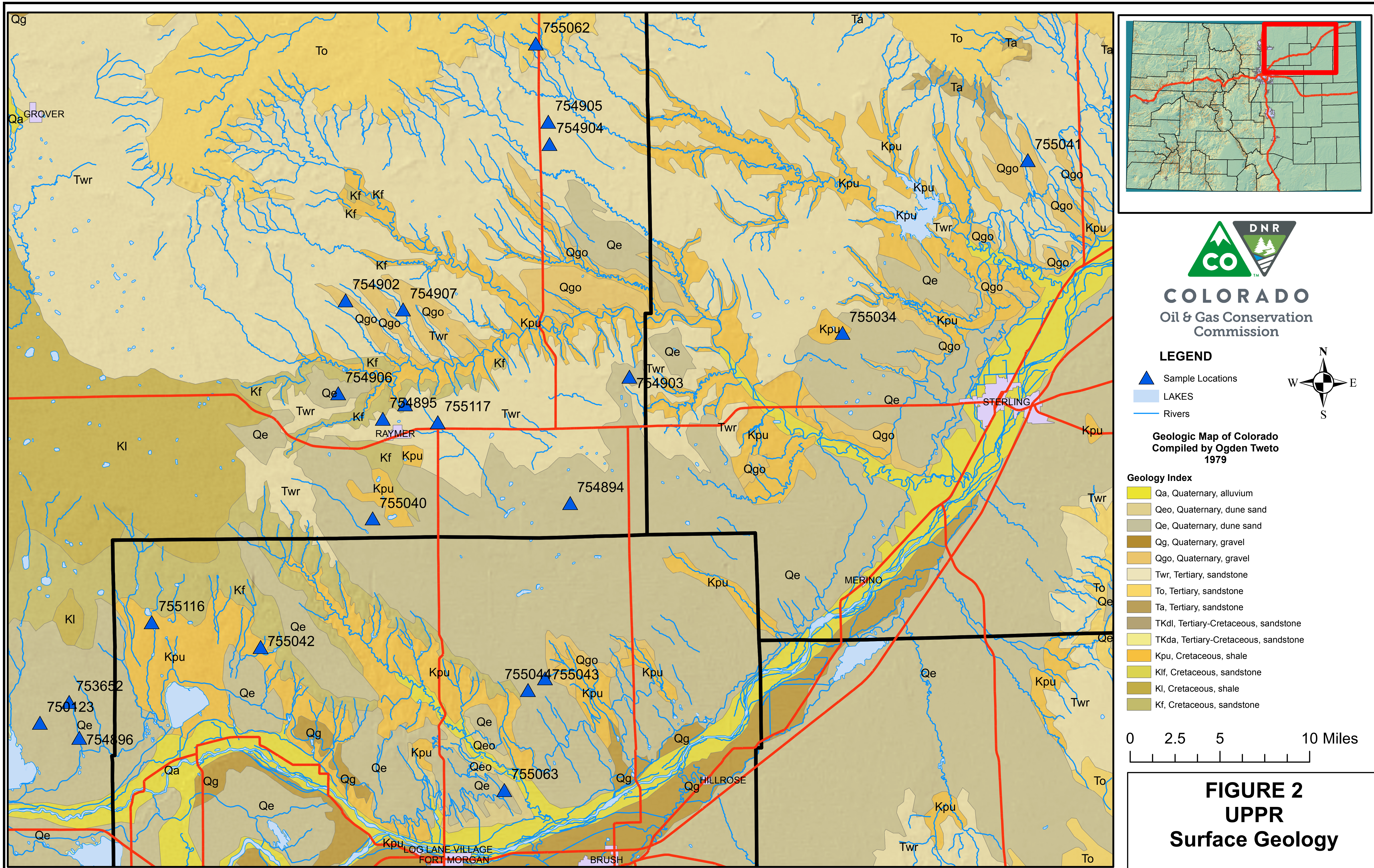

FIGURE 2
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Surface Geology

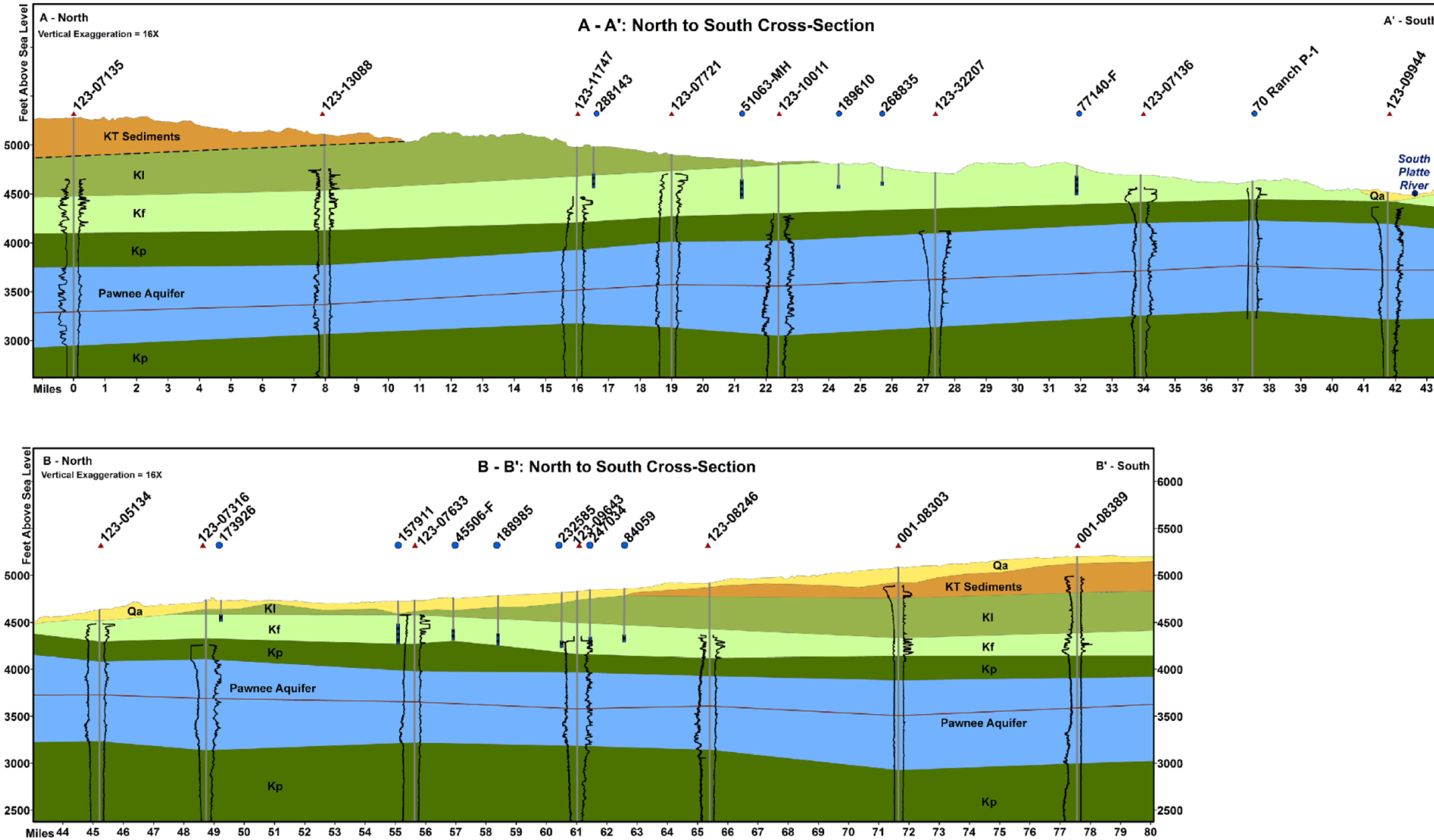

Figure 3: North-South Cross Sections through Cheyenne and Denver Basins, from Jehn-Dellaport and Renninger, 2017. Cross-section location shown on Figure 1.

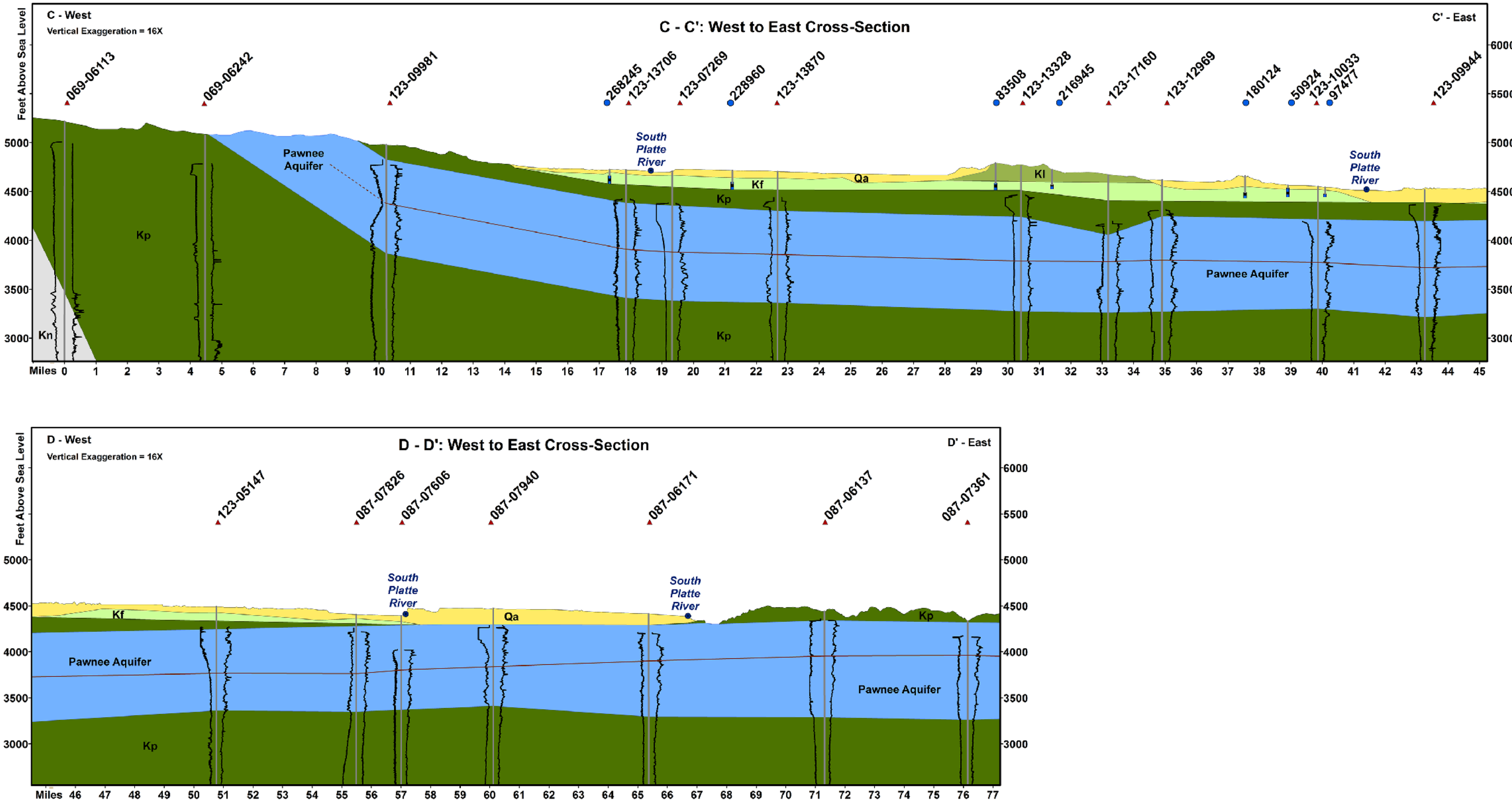

Figure 4: West-East Cross Sections through Cheyenne and Denver Basins, from Jehn-Dellaport and Renninger, 2017. Cross-section location shown on Figure 1.

FIELD ACTIVITIES

Well Selection

COGCC used a query conducted by the DWR of their water resource database Hydrobase to identify water wells as potential sample candidates. The Hydrobase query returned records of 134 water supply wells that were partially or wholly completed in the Upper Pierre aquifer. Using the results of this query, COGCC filtered the list to only those water wells located in northeastern Weld County, and then reviewed those water well records to identify those water wells most likely to be wholly completed in the Upper Pierre aquifer. This filter process returned 25 water wells in Weld County thought to be completed in the Upper Pierre aquifer. COGCC hired Pinyon Environmental to contact landowners, obtain permission to access the property and to collect water well samples.

Due to a lack of a response from landowners, denial of access, or determination that an identified water well was abandoned or not operable, COGCC expanded the potential sampling list of water wells to include water wells in Morgan and Logan Counties. In addition, through conversations with the United States Forest Service (USFS) Arapahoe-Roosevelt National Forest and Pawnee National Grassland (ARP), and conversations with landowners or consultants in the area, COGCC identified potential water wells not included in the DWR query as candidates for sampling. These additional water wells may have characteristics that excluded them from the original query. Such characteristics may include perforations in the Upper Pierre Aquifer but insufficient information regarding the grout seal, or a grout seal that protects surface infiltration (the upper 40 feet of the wellbore is grouted) but allows potential mixing within the wellbore of water from shallower sources such as the Fox Hills Sandstone or White River Formation.

Table 1a summarizes all water wells sampled by Pinyon Environmental on behalf of COGCC as part of this project. Pinyon Environmental collected samples from a total of 20 water wells between May 2016 and September 2016. Of those 20 water wells, COGCC determined that one water well, sample ID 755062, was likely not completed in the Upper Pierre aquifer, but likely completed in the White River Formation or Fox Hills Formation. COGCC did not include data collected from water well sample ID 755062 in the discussions of sampling results presented in Section 3 of this report. The remaining water wells are either fully or partially screened within the Upper Pierre aquifer. Some water wells are completed in the Upper Pierre aquifer, but shallower rocks are not isolated with grout except at the surface in the upper 40 feet of the water well. However, these water wells likely largely produce from the Upper Pierre aquifer and meet the goals of this study by providing an initial data set to characterize the water quality of the aquifer.

COGCC queried the COGCC Environmental (COENV) Sample Database for water wells that had been sampled prior to this study and may be completed in the Upper Pierre aquifer. COGCC queried the database for water well samples with well depths greater than 500 feet and located in Township 5 North through Township 12 North of Weld County. The initial query returned 58 records of samples from wells greater than 500 feet, which COGCC reviewed in greater detail. Most of the water wells appear to be completed in the Laramie-Fox Hills Aquifer or were dually completed in the Laramie-Fox Hills Aquifer and Upper Pierre Aquifer. Some water wells had been impacted by thermogenic gas and were unsuitable for use in this study. COGCC ultimately identified four candidates for inclusion in the study, and three of those candidate sample IDs contain sample results. Table 1b summarizes the three water wells from the query that are completed in the Upper Pierre aquifer and contain sample results. Although not sampled by COGCC specifically for this study, these three water well samples are included in the discussion below, but the analyte lists may not be as comprehensive as the analyte lists for the 20 water wells listed on Table 1a.

Sample Locations

Pinyon Environmental collected samples from 20 water wells located in eastern Weld County, Morgan County and Logan County, Colorado. Fourteen water wells are located in eastern Weld County, five water wells are located in Morgan County, and one water well is located in Logan County (Figure 1). Fourteen of the water wells are at least 800 feet deep and completed in an area where the Upper Pierre aquifer is confined by the overlying Pierre Shale transition zone. Four of the water wells are shallower, ranging in depths between 480 and 740 feet, and are located closer to the South Platte River where the Upper Pierre aquifer may lie in outcrop or in subcrop beneath the Quaternary alluvium. One water well, sample ID 755062, is located in far northeastern Weld County where the Ogallala Formation is present in outcrop. The high surface elevation (approximately 4,960 feet above mean sea level) , the presence of the Ogallala Formation at the surface, and the relatively shallow depth (420 feet) of this water well suggest it is completed in either the lower White River Formation or in the Laramie or Fox Hills Formation. As stated earlier, sample ID 755062, while sampled as part of this study, is not included as a data point in the characterization of the Upper Pierre aquifer.

Two of the three water wells listed in Table 1b are located in Weld County (Figure 1) and appear to be completed in the Upper Pierre aquifer where it is confined by the overlying Pierre transition zone with the Foxhills Formation or Laramie Formation either in outcrop or in subcrop. The third water well is located in Logan County (Figure 1) and is located in an area where the Upper Pierre Formation crops out at surface or is overlain by eolian deposits. These three water wells range in depth from 600 feet to 1,170 feet.

Field Effort and Sampling Parameters

Pinyon Environmental collected samples from all 20 water wells included in the study between May 25, 2016 and September 28, 2016. Pinyon attempted to consolidate sampling events to maximize efficiency. COGCC directed Pinyon Environmental to generally follow the sampling procedures described in the COGCC Model Sampling Analysis Plan, Version 1, dated May 1, 2013.

Pinyon Environmental collected the geographic coordinates of each water well location and took digital photographs to document the water well locations. The exceptions are two water wells owned by the United States Air Force who did not allow the collection of geographic coordinates or photography due to security restrictions. COGCC used the geographic coordinates collected by Pinyon Environmental to create a unique Facility ID in the COENV Sample Database from each set of water well coordinates. All data collected for this study are stored in the COENV Sample Database, and can be accessed via the hyperlinks for each Facility in Table 1.

At each sampling site, Pinyon Environmental collected field data including volume of well water purged, pH, specific conductivity, dissolved oxygen, temperature, and clarity, and noted additional observations such as odor, effervescence and oxidation-reduction potential. Pinyon Environmental purged the water wells until pH, temperature and specific conductivity readings stabilized. Field data sheets prepared by Pinyon Environmental are stored in the COENV Sample Database. Site photographs are also included with the field data sheets stored in the COENV Sample Database and can be accessed from the "Docs" tab for each respective COGCC facility.

After purging, Pinyon Environmental collected samples for laboratory analysis and delivered the samples to COGCC's contract laboratories: ALS Environmental in Fort Collins, Colorado for general environmental chemistry analysis and Dolan Integration Group in Westminster, Colorado for analysis of gas composition and stable isotope ratios. All laboratory analytical reports are stored in the COENV Sample Database and can be accessed through the hyperlinks in Table 1a.

COGCC requested ALS Environmental to analyze all water samples for the following analytes:

- General water chemistry: pH, specific conductivity, total dissolved solids (TDS), carbonate, bicarbonate and total alkalinity
- Dissolved metals: barium, boron, calcium, chromium, iron, lead, magnesium, manganese, potassium, selenium, sodium, strontium
- Anions: bromide, chloride, fluoride, nitrite, nitrate, phosphate, sulfate
- Dissolved gases: methane, ethane, propane
- Volatile organic compounds

COGCC requested Dolan Integration Group to analyze all water samples for the following:

- Gas composition
- Stable isotope ratios of carbon and hydrogen of methane, if present
- Stable isotope ratios of hydrogen and oxygen contained in sample water
- Stable isotope ratio of carbon present in dissolved inorganic carbon

The three water well samples listed on Table 1b have analyte lists similar to that listed above, but may not include as comprehensive of a list of metals, volatile organic compounds or stable isotopes of water.

RESULTS

This section describes the chemical characteristics of the groundwater samples collected from the Upper Pierre aquifer. It also discusses comparisons of the stable isotope ratios of gases detected in the samples to determine the origin of those gases, as well as the stable isotope ratios of water compared to other bedrock aquifers of the Denver Basin. The sample ID 753652 has two sets of sample results because an oil and gas Operator sampled the 753652 water well for compliance with COGCC Rule 318A. The second 753652 sample was collected after the water well owner had performed well maintenance, and the results of the second sample are markedly different than the results from the COGCC sample.

This section also compares the major cations, anions, dissolved metals and volatile organic compounds results to the Colorado Department of Health and Environment, Water Quality Control Commission Regulation 41 Basic Standards for Groundwater (Regulation 41).

General Water Chemistry Major Cations and Anions

The water chemistry profile of the samples collected is dominated by sodium-bicarbonate and sodium-sulfate type waters, although the 755116 and 755040 water samples also contain higher concentrations of chloride. The concentration of bicarbonate and sulfate varies depending on well construction and location of the water well. Table 2 is a summary of inorganic water quality parameters and anions, and Table 3 is a summary of dissolved metals including major cations.

COGCC calculated the major cation-anion balance using Rockworks v.15 for each water well sample collected. All samples were within a 10 percent difference cation-anion balance except for sample ID 755116 with a -37.6 balance and sample ID 754902 with a +11.5 balance. Although these samples did not stand out individually in the results discussed below, their results should be used with caution.

The TDS concentration averages 1,468 milligrams per liter (mg/l) with a minimum concentration of 560 mg/l in the 755041 sample to a maximum of 2,700 mg/l in the COGCC 753652 water well sample. The second 753652 water well sample contained a TDS concentration of 1,800 mg/l. TDS concentration generally increases from north to south across the study area with water well samples containing the highest TDS collected in Townships 4, 5 and 6 North (Figure 5).

The geochemical composition of water samples can be interpreted and compared using a trilinear diagram (Hem 1989). Sample populations can be compared to identify high level trends or mixtures of water types. Figure 6 is a trilinear (Piper) diagram that plots all samples collected from the Upper Pierre aquifer for this study. Stiff diagrams, presented in Figure 7, are useful diagrams to show and compare the geochemical composition of individual samples, and can be used on maps to show spatial distributions of geochemical signatures (Hem 1989) (Figure 5).

The Piper diagram in Figure 6 shows that sodium is the dominant cation in all samples collected, with the exception of the 755041 sample. The 755041 sample has a balanced water profile with a lower overall TDS (560 mg/l) than other samples in the study. Calcium is present at concentrations greater than 10 mg/l in an additional five water well samples. The molar ratio of sodium to calcium plus magnesium (termed sodium excess in Musgrove et al. 2014) generally increases with well depth (Figure 8), which is likely a result of longer residence time and interaction with the aquifer rocks. Robson (1987) and Musgrove et al. (2014) both document a transition from calcium composition waters to sodium composition in the Denver Basin bedrock aquifers dependent on depth of aquifer and presumably time since recharge occurred.

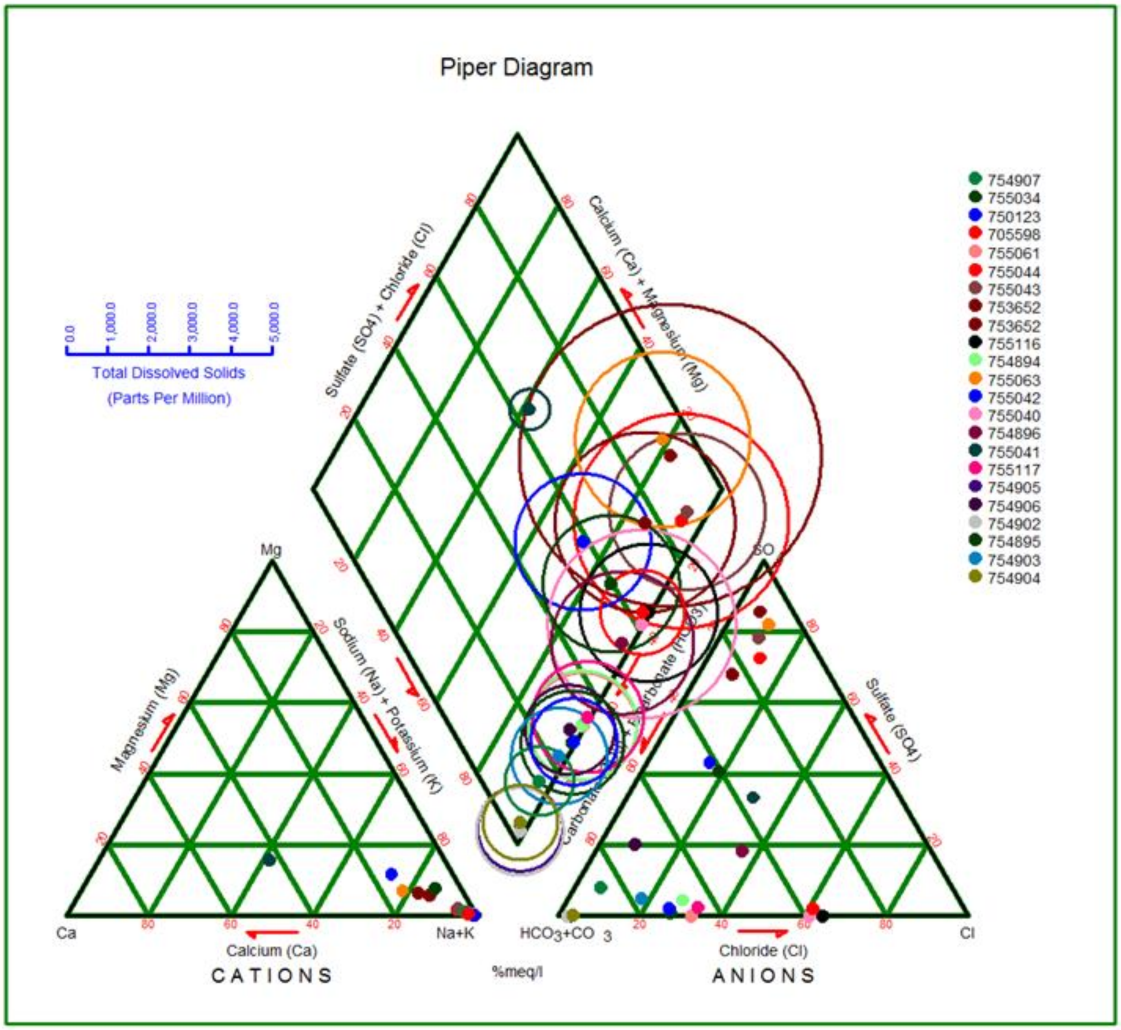

Figure 6: Trilinear diagram showing each water well sample with total dissolved solids scaled circles.

ALS Environmental calculated the Sodium Adsorption Ratio (SAR) for the water well samples analyzed for this study. Most water well samples had an SAR greater than 20, except sample ID 755041, which is a domestic water well with a balanced water profile and low TDS (TDS = 560 mg/l) located in the eastern portion of the study area. Sample Facility ID 755042 is the second sample with a relatively low SAR (9.9), and while this sample has a TDS and sodium concentration similar to most of the sample population, the sample has relatively high concentrations of calcium and magnesium.

Bicarbonate alkalinity dominates the water profile in most samples, with results ranging from 520 mg/l to 770 mg/l. Sulfate anions dominate the water profile in four water well samples with sulfate concentrations ranging from 1,000 to 2,200 mg/l (Figures 6 and 7). Figure 6 shows that two populations of data exist. One population ranges between a bicarbonate and sulfate dominated profile, while the other population ranges between a bicarbonate and chloride dominated profile.

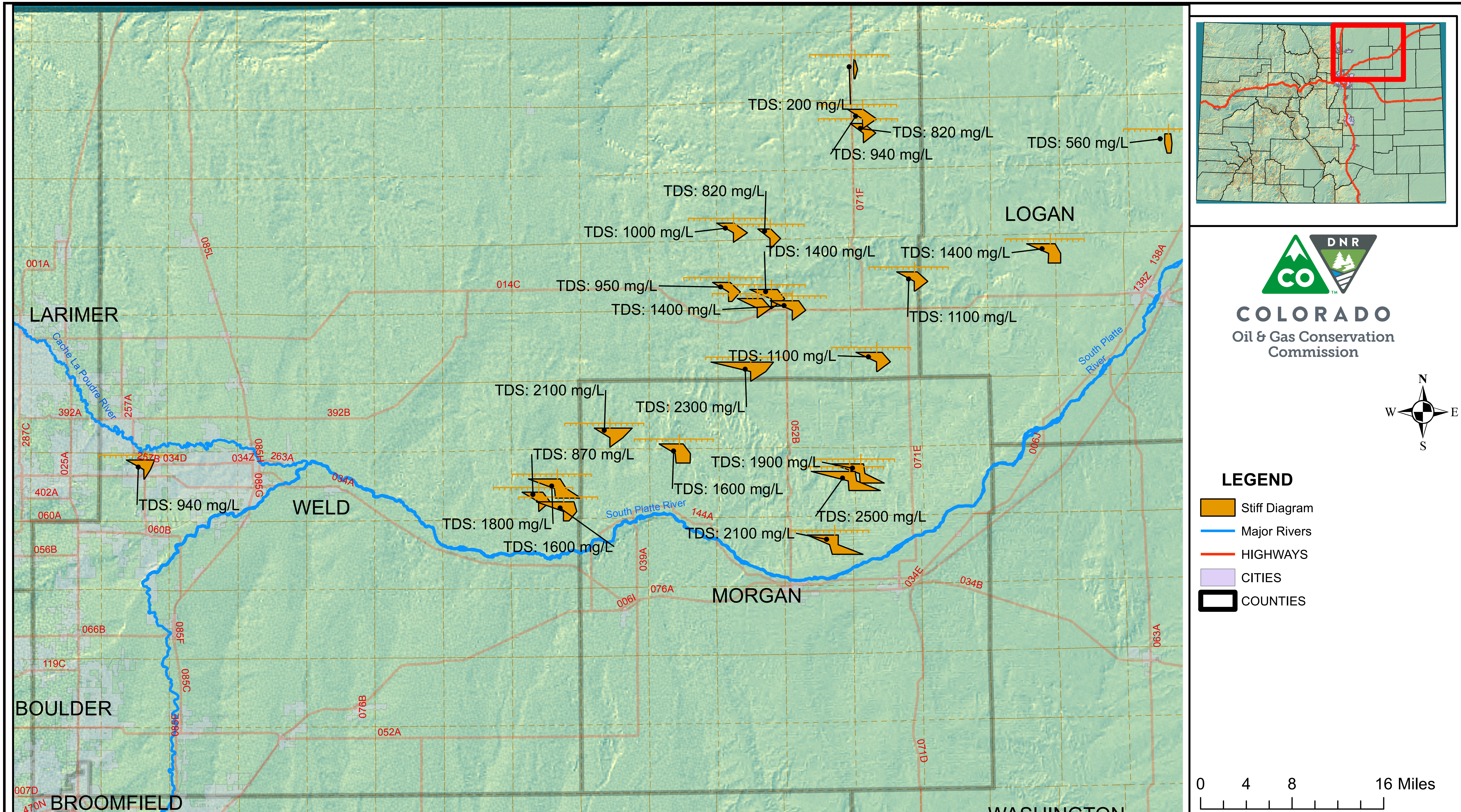

FIGURE 5
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Stiff Diagram Map

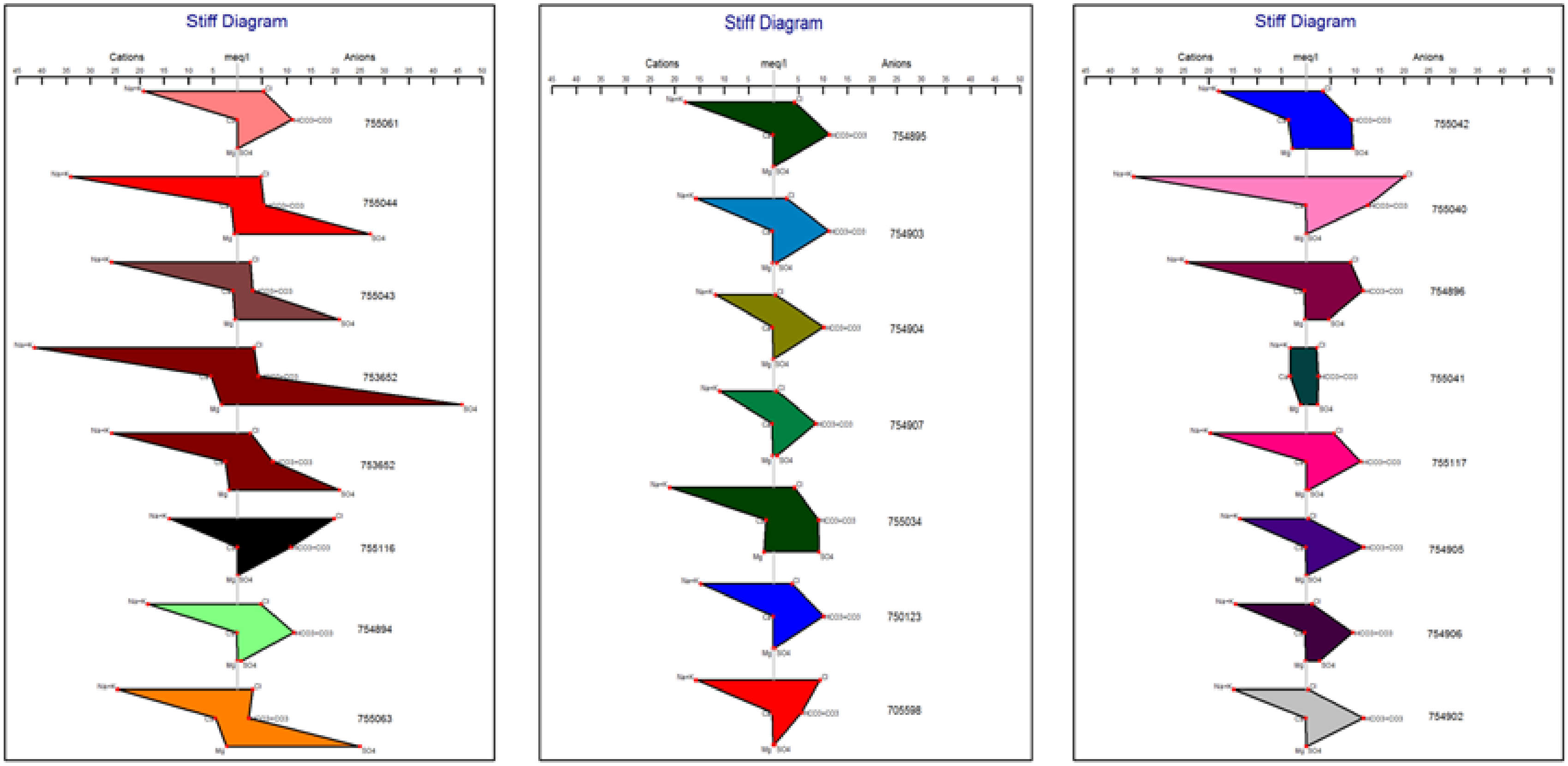


Figure 7: Stiff diagram of all water well samples.

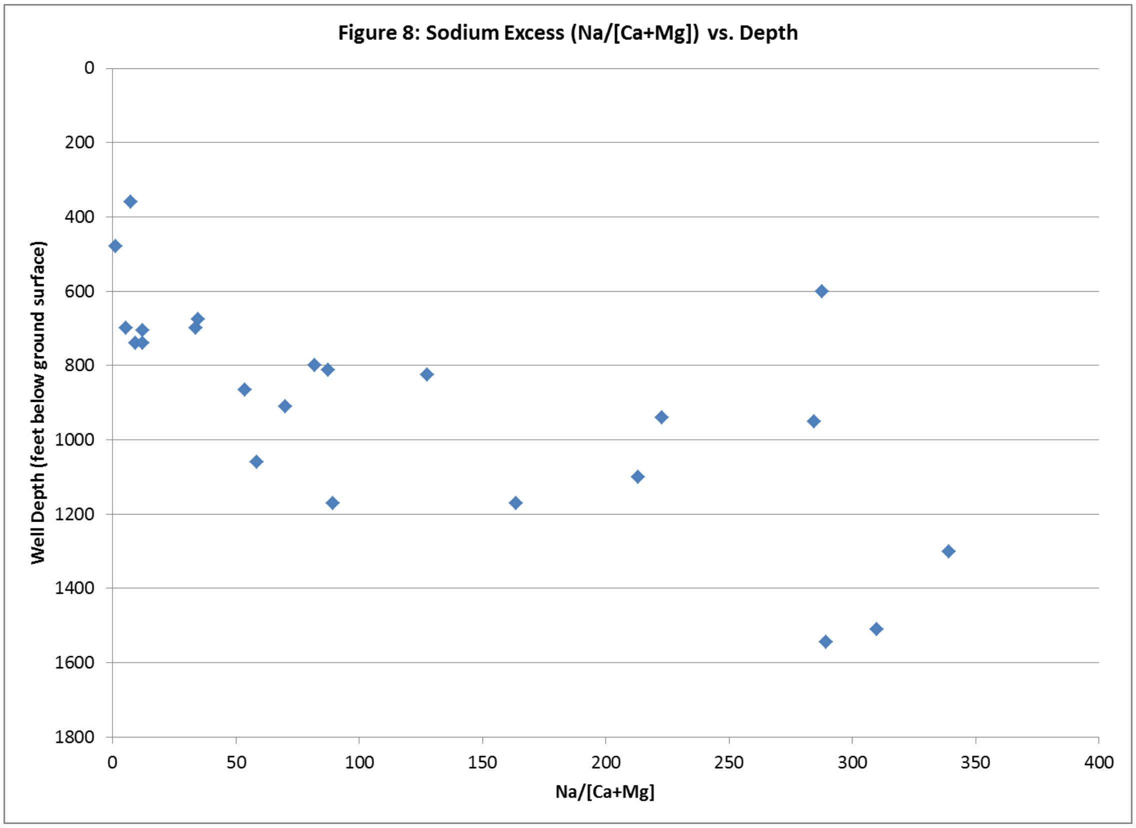


Figure 8: Sodium Excess (Na/[Ca+Mg]) vs. Depth
Well Depth (feet below ground surface)
Na/[Ca+Mg]
0
200
400
600
800
1000
1200
1400
1600
1800
0
50
100
150
200
250
300
350
400

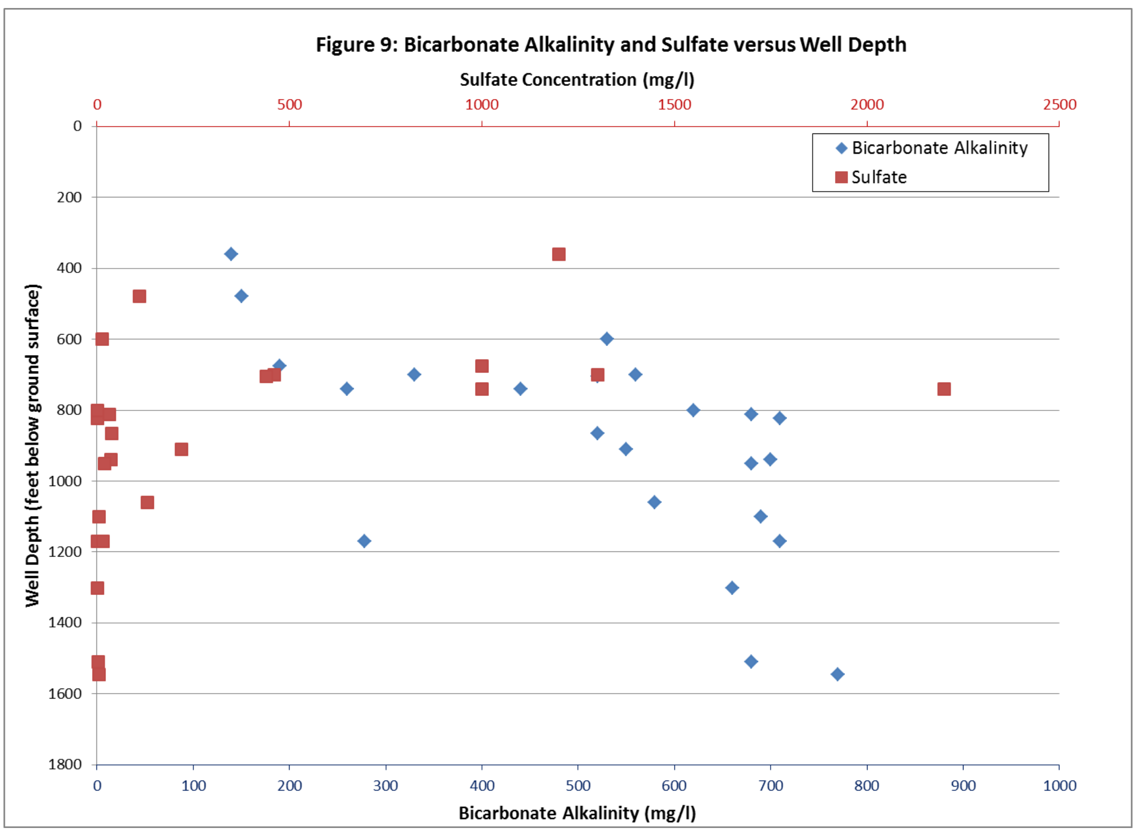
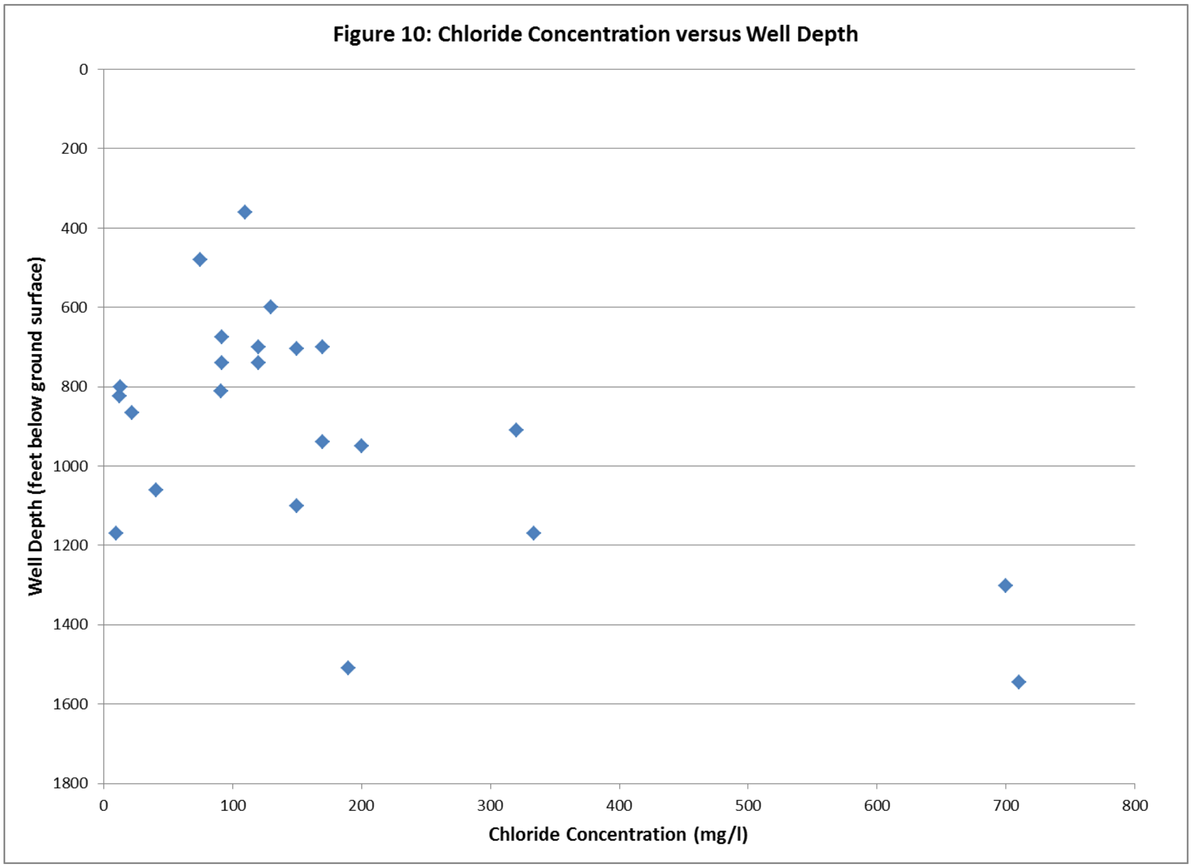


Figure 9: Bicarbonate Alkalinity and Sulfate versus Well Depth
Sulfate Concentration (mg/l)
0
500
1000
1500
2000
2500
Bicarbonate Alkalinity
Sulfate
Well Depth (feet below ground surface)
0
200
400
600
800
1000
1200
1400
1600
1800
0
100
200
300
400
500
600
700
800
900
1000
Bicarbonate Alkalinity (mg/l)

The wells with the shallowest completion depths have the highest sulfate concentrations. Some deeper completed wells (700 feet to 1,060 feet) with a bicarbonate dominated profile have sulfate concentrations in the hundreds of mg/l range, but the deepest water well samples contain little to no sulfate (Figure 9). Bicarbonate and chloride both generally decrease with well depth (Figures 9 and 10), and the relationship between well depth and chloride is more pronounced (Figure 10). Three of the water well samples have a chloride dominated anion profile, with no to little sulfate (Figures 6 and 7).



There are no human health standards for the major cations and anions discussed above. However the Water Quality Control Commission (WQCC) and the Environmental Protection Agency (EPA) have established aesthetic standards for certain analytes as guidance for maintaining public water supplies in regard to taste, odor and appearance. Regulation 41 specifies the maximum allowable TDS concentration to be 1.25 times the background value. As such, there is no standard for TDS in Regulation 41 with which the results of this study can be compared. However, the EPA has set the secondary maximum contaminant level (SMCL) for TDS at 500 mg/l. This is not an enforceable standard and is established as guidance to public water systems for maintaining the aesthetic quality of drinking water.

The WQCC Regulation 41 standard for sulfate is 250 mg/l, and several water wells contained concentrations of sulfate in excess of this standard.

Secondary Dissolved Metals

In addition to the major cations calcium, magnesium, potassium and sodium, COGCC also analyzed the water samples for the following dissolved metals: boron, barium, chromium, iron, lead, manganese, selenium and strontium (Table 3). All concentrations discussed in this section are from dissolved phase metals.

Boron was detected at a concentration that exceeds the WQCC Regulation 41 Agricultural Standard for boron in groundwater of 0.75 mg/l in 15 of the water well samples collected. Boron is an essential plant nutrient, but can be toxic to plants at concentrations exceeding the agricultural standard. Boron concentrations in the water well samples collected average 1.2 mg/l and range from 0.33 to 3.3 mg/l. By comparison, Musgrove et al. (2014) reported boron concentrations in the Denver Basin bedrock aquifers that average from 0.026 mg/l in the Dawson aquifer to 0.174 mg/l in the Laramie-Fox Hills aquifer.

Barium was detected in all of the groundwater samples collected, but at concentrations one to two orders of magnitude less than the Regulation 41 Human Health Standard of 2.0 mg/l.

Chromium was the only dissolved metal not detected in any of the water well samples analyzed.

Dissolved iron was detected in five of the water well samples, but at concentrations below the Regulation 41 Domestic Water Supply Drinking Water Standard of 0.3 mg/l.

Lead was detected at concentrations ranging from 0.0007 mg/l to 0.0037 mg/l in five of the water samples collected. These concentrations are below the Regulation 41Human Health Standard for lead of 0.05 mg/l.

Manganese was detected in all but one water well sample. Concentrations of manganese detected range from 0.0021 mg/l to 0.11 mg/l and average 0.016 mg/l. One sample contained manganese at a concentration exceeding the Regulation 41Domestic Water Supply Drinking Water Standard, which is an aesthetic standard, of 0.05 mg/l.

Selenium was detected in one water well sample collected, but at a concentration below the Regulation 41 Human Health Standard of 0.05 mg/l.

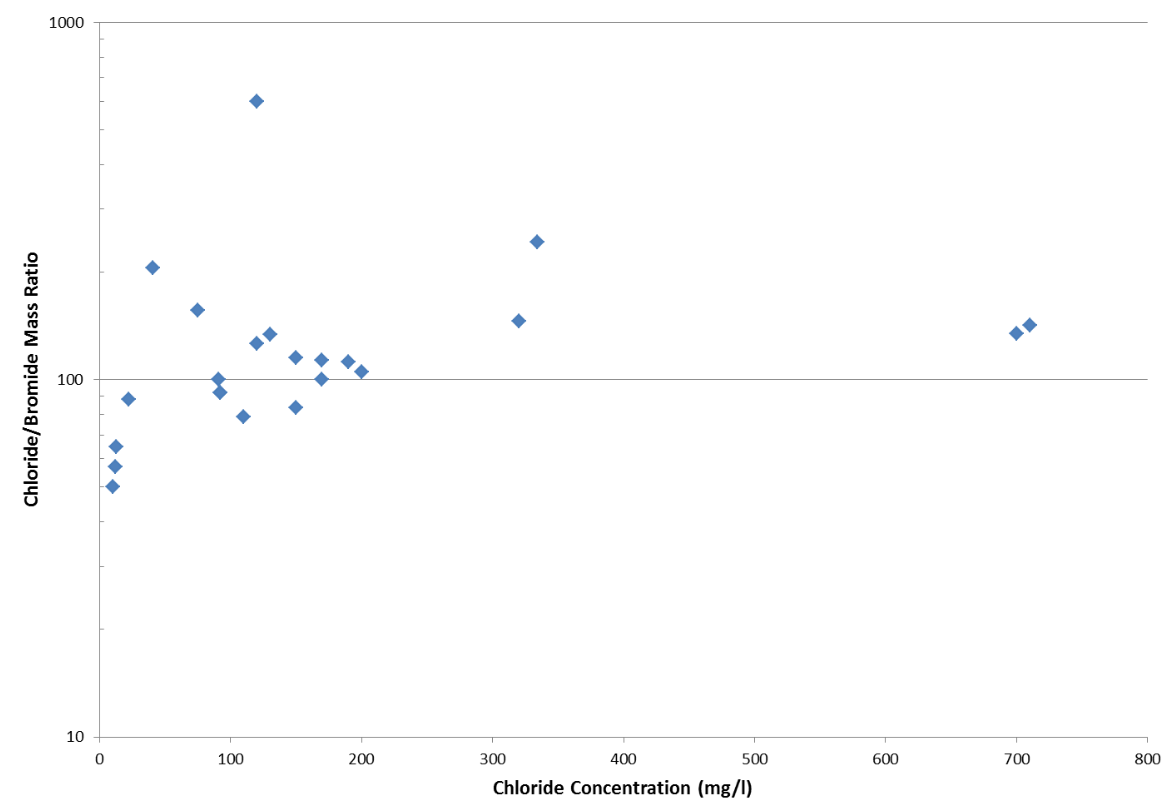
Strontium was detected in all the water well samples at concentrations ranging from 0.08 mg/l to 4.5 mg/l, with an average concentration of 0.76 mg/l. There are no Human Health or Drinking Water Standards for strontium in Regulation 41. EPA has published a Lifetime Health Advisory of 4 mg/l in the 2012 Edition of the Drinking Water Standards and Health Advisories. The EPA has delayed the final regulatory determination on strontium (EPA 2016), and as such there is no enforceable drinking water standard for strontium.

Anions

In addition to major anions, COGCC also analyzed the water well samples for bromide, fluoride and nitrite/nitrate (Table 2).

Bromide was detected in at concentrations above the laboratory reporting limit in all but six of the water well samples. There is no drinking water standard for bromide, but it is a useful halide for determining the comparison of waters when compared to the chloride concentrations. Chloride-bromide mass ratios have been used to determine the source of brine contaminations in groundwaters (Davis et al 1998). Chloride-bromide mass ratios of groundwater are generally between 100 and 200 (Davis et al 1998), and most samples in this study compare to that ratio (Figure 11). However, the COGCC 753652 sample has a bromide-chloride mass ratio of 600, where the second 753652 sample has a Cl-Br mass ratio of 92. This illustrates the difference in the two samples and may be related to well maintenance performed during the June 2016 sampling event when COGCC collected its sample. The second sample was collected in September 2017 after a season of stock watering and is likely more representative of Upper Pierre aquifer groundwater.

Figure 11: Chloride/Bromide Mass Ratio versus Chloride Concentration



Fluoride was detected in all water well samples collected at concentrations ranging from 0.5 mg/l to 3.4 mg/l with an average of 2.1 mg/l. The Regulation 41 Human Health Standard for fluoride is 4.0 mg/l.

Nitrite and nitrate were analyzed to determine if any of the water wells were susceptible to contamination from surface water or shallow groundwater. Nitrite and nitrate are generally present in groundwater as a result of fertilizer applications, livestock manure application or treatment, or inadequately operating septic systems. Three of the water well samples contained nitrate: The first COGCC 753652 sample (0.52 mg/l; the second 753652 sample did not contain nitrate), the 755041 sample (5.9 mg/l), and the 755062 sample (1.0 mg/l), which is not completed in the Upper Pierre aquifer.

Volatile Organic Compounds

COGCC analyzed all samples collected during the project for a list of 69 volatile organic compounds, including the petroleum volatile organic compounds: benzene, toluene, ethylbenzene and total xylenes. One sample, collected from the NGL396759 well, contained detections of volatile organic compounds, and those compounds were below the CDPHE WQCC Regulation 41 standard for organics in groundwater.

Dissolved Gases

Dissolved methane was detected at a concentration great enough to obtain stable isotope ratios in 19 of the 24 water well samples collected (Table 4). Dissolved methane was detected in an additional two water well samples, but was not present at a concentration high enough to enable stable isotope analysis. Two other samples did not contain a detectable concentration of methane. The COGCC 753652 sample did not contain sufficient methane to obtain stable isotope analysis, but the second 753652 contained methane at a concentration of 4.1 mg/l, and the Operator had stable isotope analysis performed on that sample.

Dissolved methane concentrations in 16 samples ranged from 1.9 mg/l to 33 mg/l and averaged 11.3 mg/l. These same 16 samples also contained ethane concentrations that ranged from 0.0067 mg/l to 0.065 mg/l with an average concentration of 0.022 mg/l. Five water wells samples did not contain ethane at a detectable concentration, and two water well samples were not analyzed for ethane.

Propane was not reported above the laboratories' established limit of detection in any of the water well samples collected and analyzed at both ALS Environmental (analyzed for dissolved gases) and Dolan Integration Group (analyzed for gas composition).

Stable Isotope Ratios of Methane

Nineteen water well samples contained methane at a concentration great enough to perform stable isotope analysis to determine the Carbon-13 (^{13}C) and Deuterium (D or ^{2}H) ratios for methane (Table 4). The stable carbon isotope ratios, expressed as $\delta^{13}C$, ranged from -75.3 per mil (‰) to -67.5 ‰ VPDB (Vienna Pee Dee Belemnite). The stable hydrogen isotope ratios, expressed as δD, ranged from -270 ‰ to -218 ‰ VSMOW (Vienna Standard Mean Ocean Water). Figure 12 is a crossplot that compares the stable isotope ratios of methane in the water well samples collected from the Upper Pierre aquifer to the compositions of general biogenic and thermogenic gases. These data are also presented on a natural gas plot (Whiticar 1999) (Figure 13) and compared to select production gas samples from various producing strata in the Denver Basin (Figure 14). The samples collected from water wells in the Upper Pierre aquifer plot near or within the carbonate reduction zone for microbial methanogenesis on the Whiticar plots.

The stable isotope ratios of methane in the water well samples indicate that the methane present in the samples is microbial in origin and generated through the reduction of carbon dioxide present in the aquifer. The microbial origin of the methane is further indicated by the lack of heavier gases, since no propane, butane, pentane or hexanes were detected in the samples.

Figure 12: Methane (CH_4) Isotopic Ratios - Water Wells in the Upper Pierre Aquifer

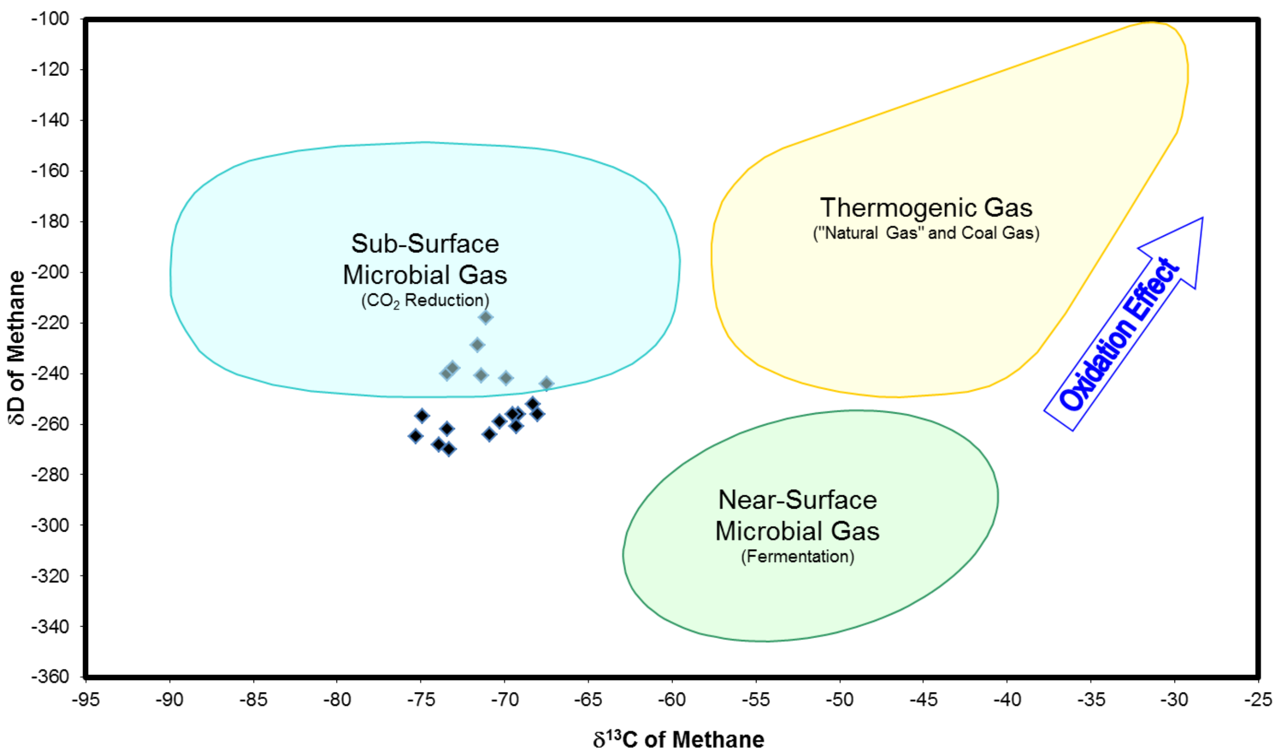


Figure 13: Natural Gas Plot Methane $\delta^{13}C$ vs δD Genetic Classification Plot

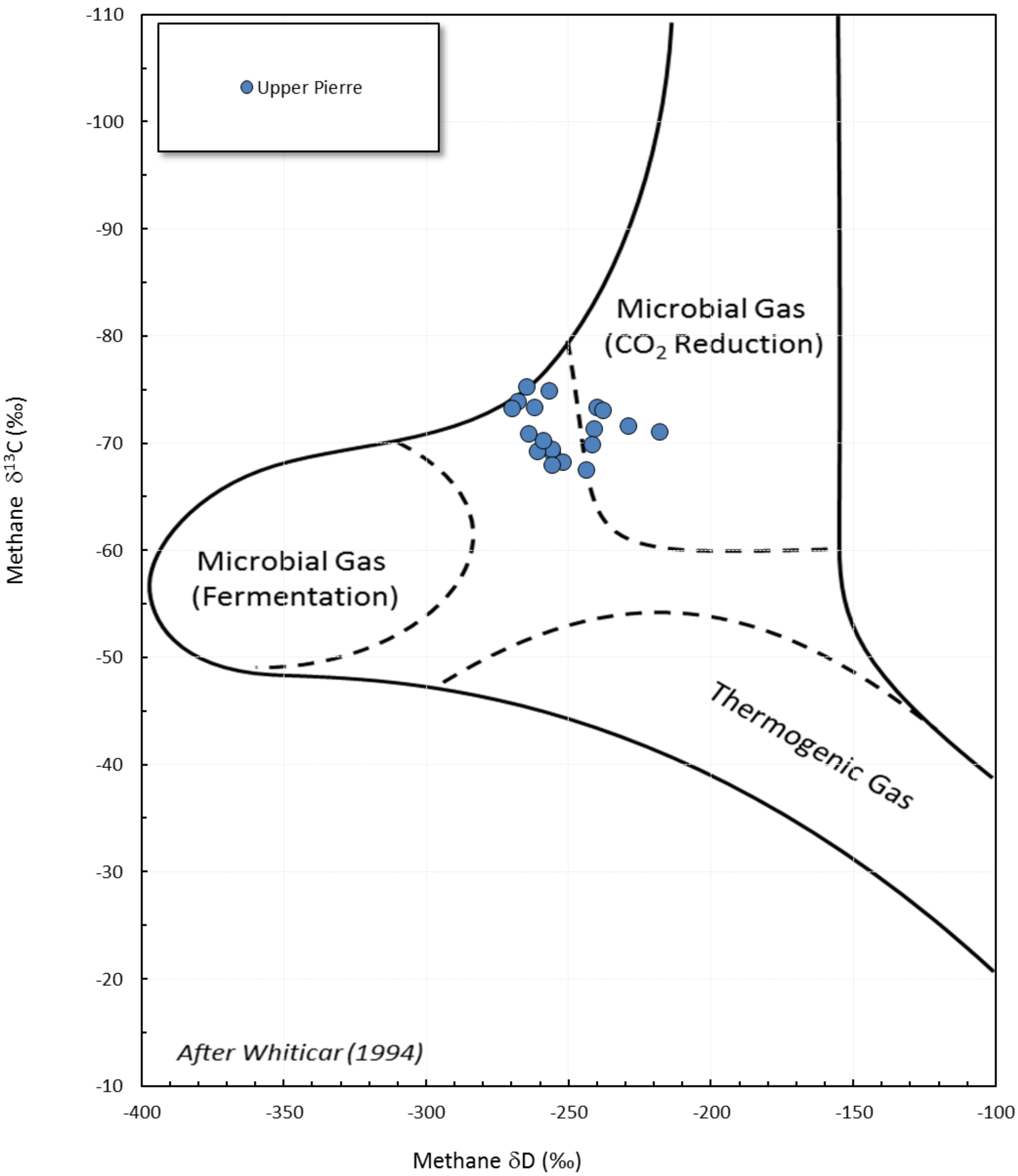
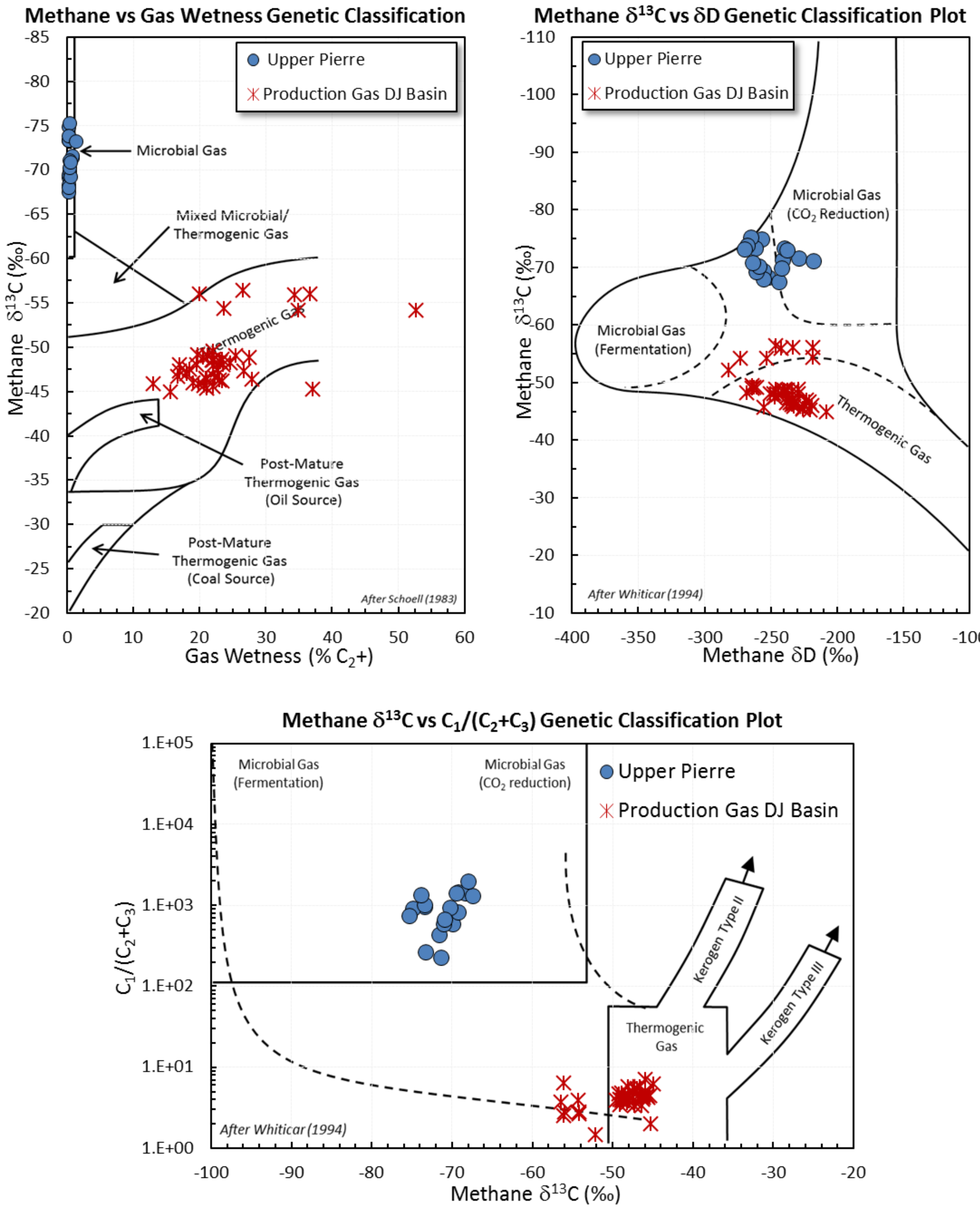


Figure 14: Stable Isotope Interpretive Plots UPWQ water well samples vs. DJ Basin Production Gas



Stable Carbon Isotope Ratio of Dissolved Inorganic Carbon

The stable isotope ratio of ^{13}C in dissolved inorganic carbon (DIC) can be used to provide insight into the nature of carbon dioxide, carbonate, and methane in the aquifer. All of the water samples collected for this study were analyzed for stable carbon isotope ratio of DIC and compared to the concentrations of methane, sulfate and bicarbonate in the aquifer. In general, water samples with the highest sulfate concentrations had little to no methane present and were least enriched in ^{13}C (Figure 15). Inversely, samples with higher bicarbonate alkalinity contained higher methane concentrations and low sulfate concentrations. These same samples also had more enriched values of ^{13}C (Figure 15 and Figure 16). This is indicative of microbial reduction of carbon dioxide (CO_2) to produce methane because the ^{12}C bonds are preferentially broken during microbial methanogenesis thereby enriching the resultant methane in ^{12}C relative to ^{13}C and depleting the remaining DIC in ^{12}C relative to ^{13}C (Whiticar 1999). Figure 17 compares the $\delta^{13}C$ of DIC with the $\delta^{13}C$ of methane and further illustrates the relationship between various microbial methane generation pathways and carbon stable isotope ratios.

Figure 15: δ ¹³C of Dissolved Inorganic Carbon versus Methane Concentration

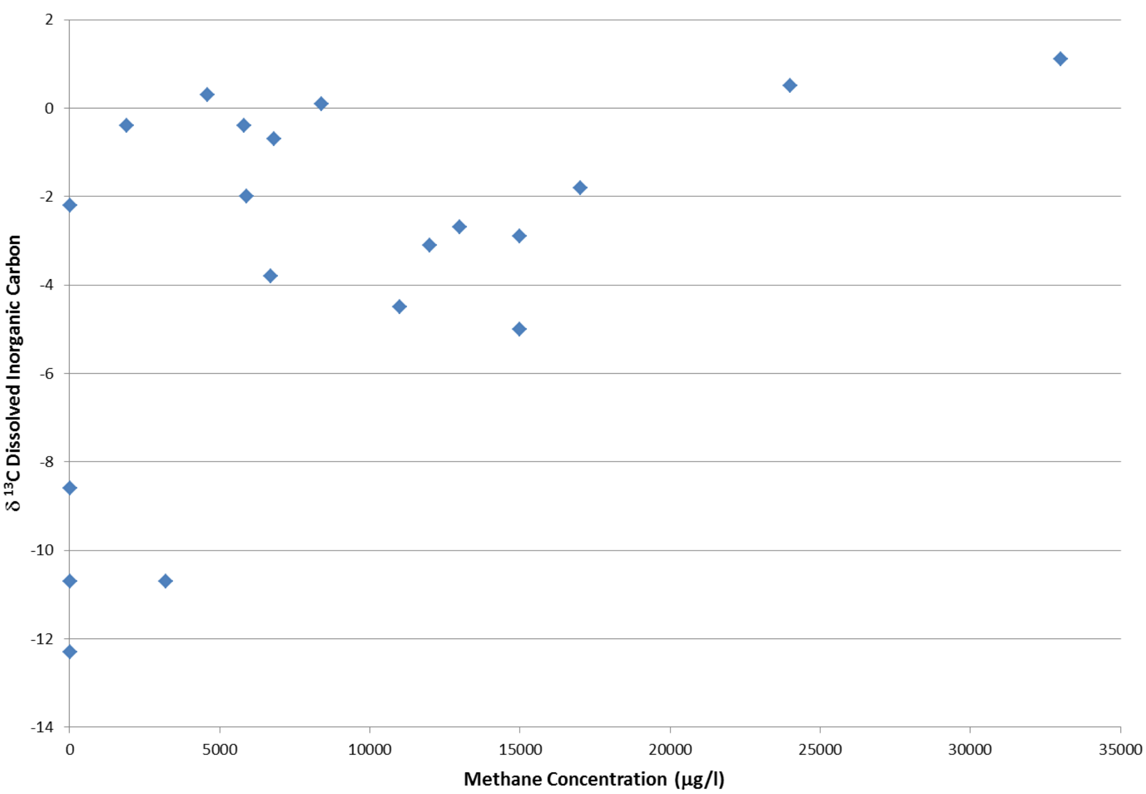


Figure 16: δ [13]C DIC vs. Sulfate Concentration and Bicarbonate Alkalinity

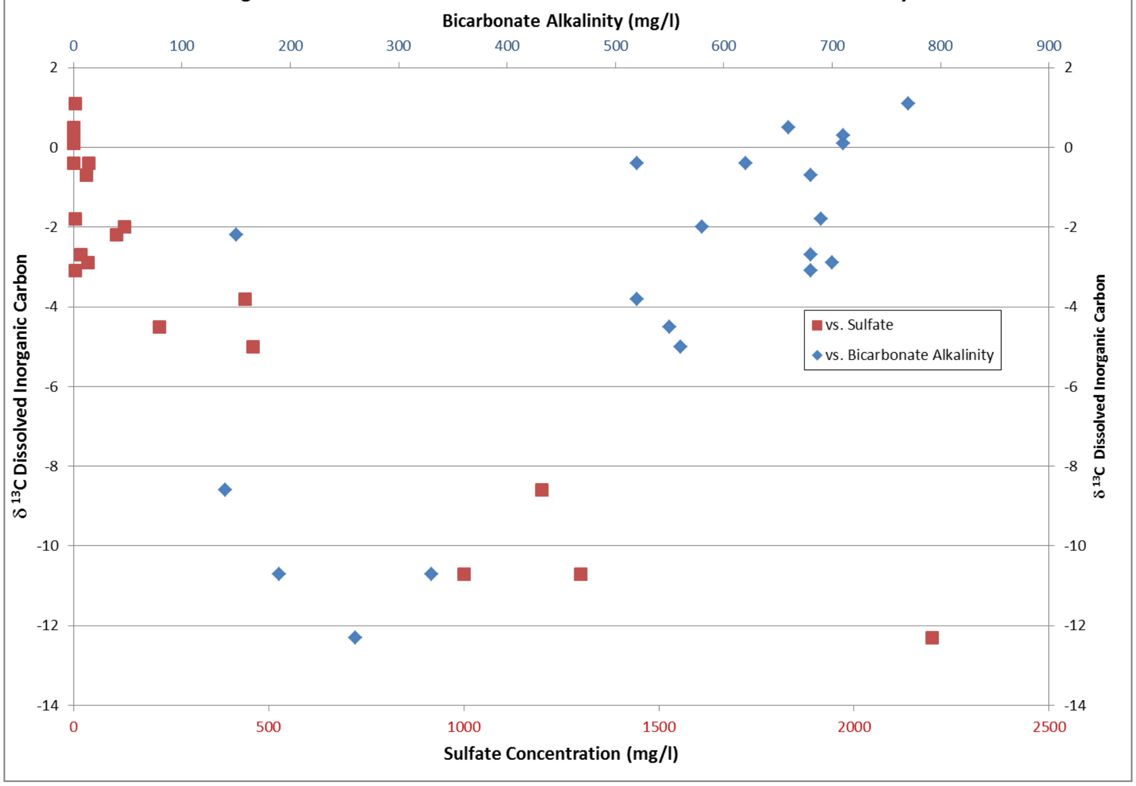
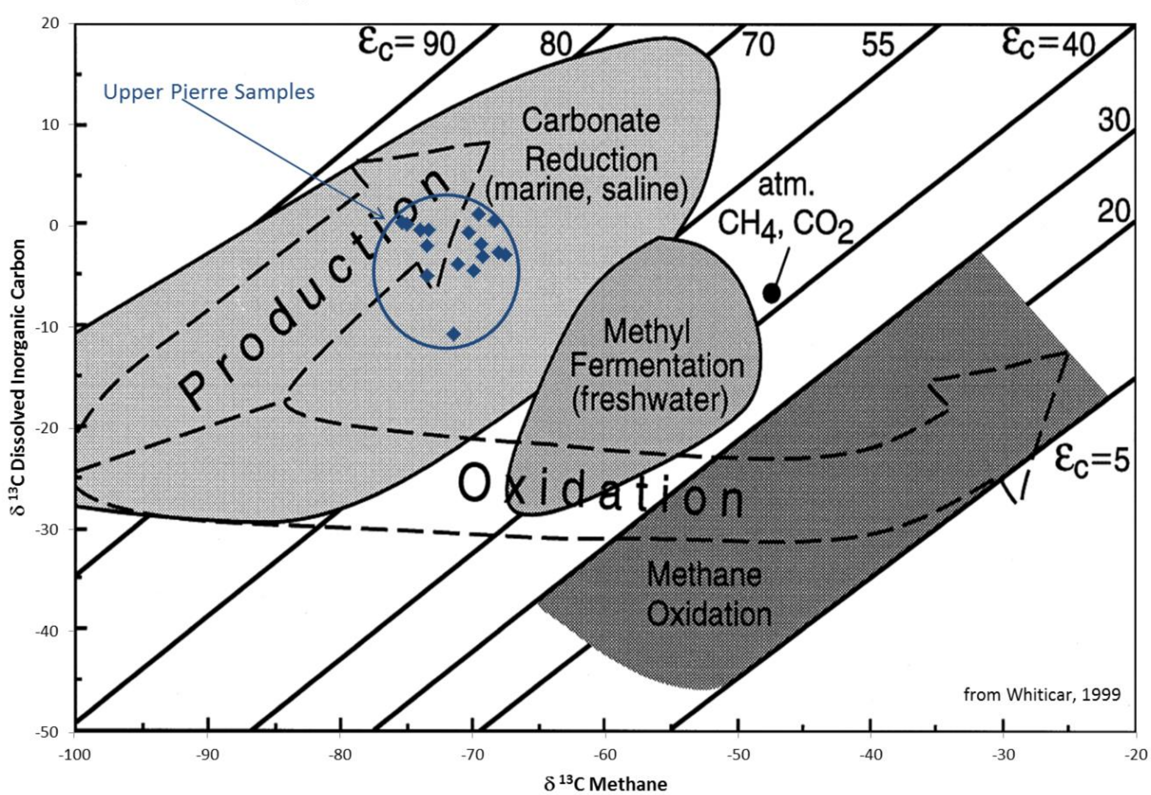


Figure 17: Combination Plot of δ [13]C DIC and δ [13]C Methane

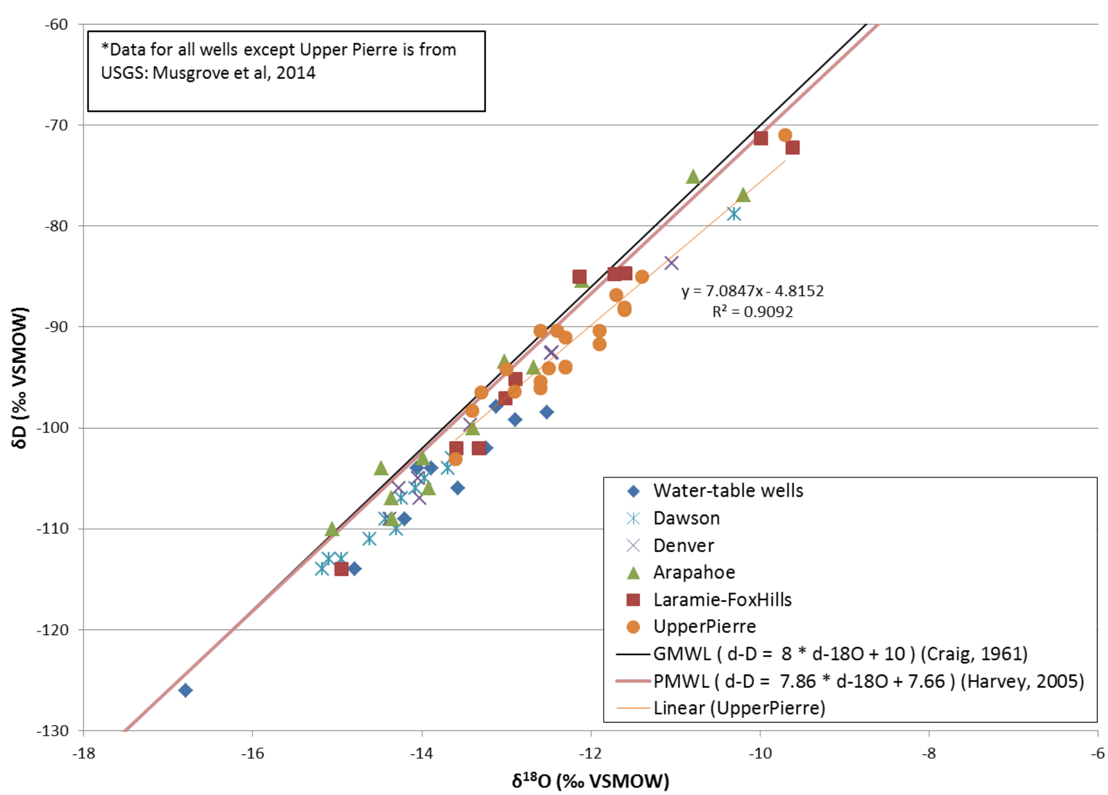


The samples with the least enrichment of ^{13}C were collected from water wells located in the south and east portions of the area, closest to the South Platte River (Figure 18), showing that reduction of CO_2 and methanogenesis does not appear to be occurring in areas closer to the river, where the Upper Pierre Formation appears to be closer to the surface and in some places in contact with the surface or Quaternary alluvium.

Stable Isotope Ratios of Water

All of the water well samples collected were analyzed for stable isotope ratios of hydrogen, deuterium (δD) and oxygen ($\delta^{18}O$), of water. The stable isotope ratios of deuterium and oxygen can be used in hydrologic studies to compare the origin of waters. All samples in this study were analyzed for stable isotopes of water and compared to the global meteoric water line (Craig 1961), the Pawnee local meteoric water line (Harvey 2005) and the stable isotopes of water samples collected from the Denver Basin aquifers (Musgrove et al 2014) (Figure 19).

Figure 19: Stable Istopes of Hydrogen and Oxygen - Denver and Cheyenne Basin Aquifers



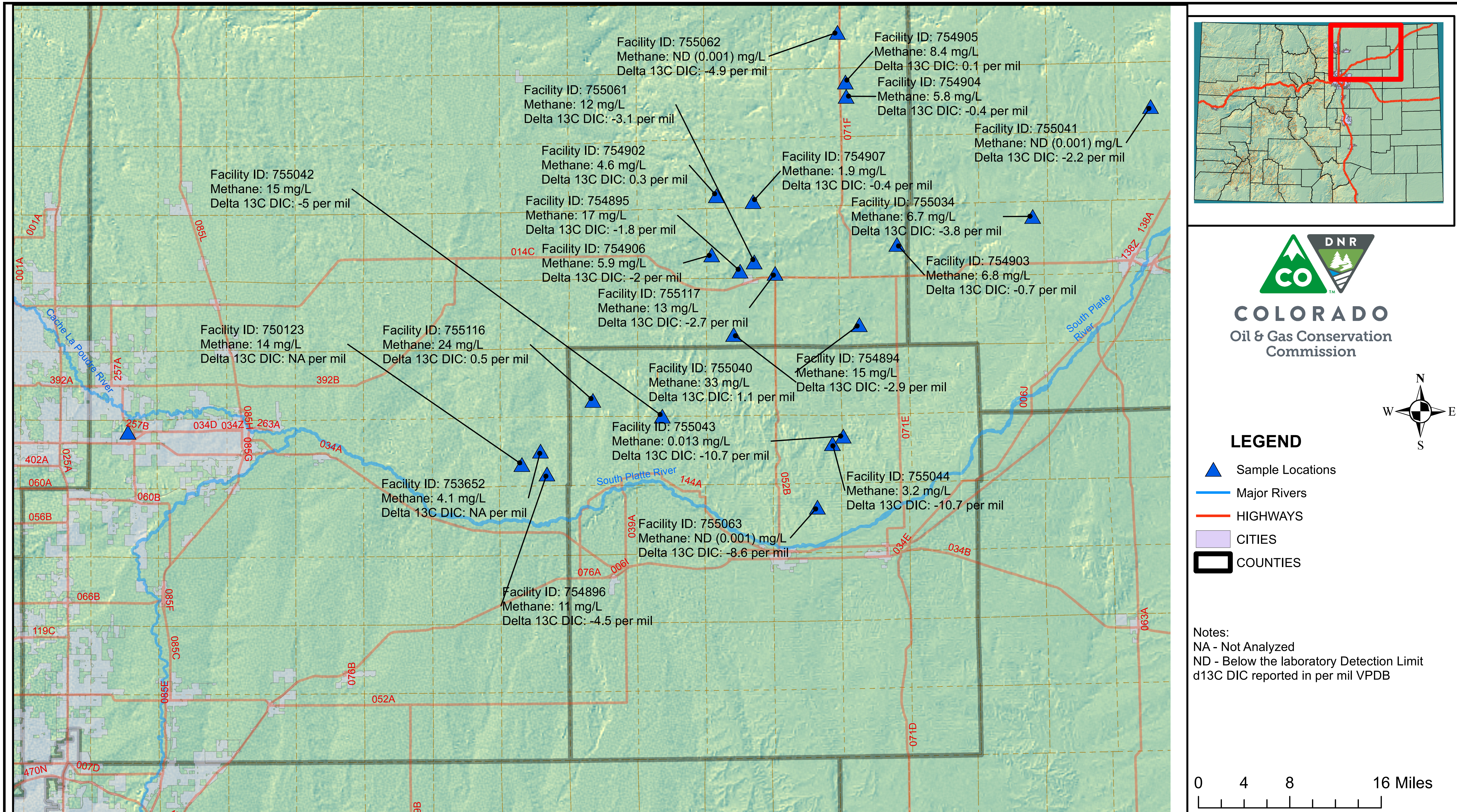


FIGURE 18
UPPR
Dissolved Methane and
d13C Dissolved Inorganic Carbon

A comparison of the isotopic data from the Upper Pierre samples to the global and local meteoric water lines indicates that the aquifer is recharged with meteoric water. The isotopic data for the water samples from the Upper Pierre aquifer plot along and below the global and local meteoric water lines, and appear slightly enriched in isotopic values of both D and ^{18}O compared to the bulk of the Denver Basin aquifer data, although a small subset of the Denver Basin aquifer data are also slightly enriched in isotopic values as discussed in Musgrove et al. (2014). This enrichment in D and ^{18}O could be the result of differences in recharge water, or residence time and bedrock interaction in the aquifer or a combination of both. One Upper Pierre sample is enriched in D and ^{18}O compared to the other Upper Pierre samples and compared to all the samples from the Musgrove et al (2014) study. This sample was collected from a water well located in Logan County, the easternmost point in the study area.

The Upper Pierre stable isotope data have a slope that is slightly smaller than the slopes of the meteoric and Denver Basin aquifers.

SUMMARY

COGCC sampled 20 water wells as part of this study, one of which was determined to be not completed in the Upper Pierre aquifer. COGCC identified two additional water wells in the COENV Database that had been sampled as a result of a complaint, and one water well in the COENV Database that was sampled by an operator for Rule 318A compliance.

The sample results show that the Upper Pierre aquifer is dominated by sodium bicarbonate water that approaches sodium bicarbonate-chloride water with depth. The water quality is likely sufficient for livestock and industrial uses, but may need treatment for irrigation use due to its TDS, sodicity (SAR) and boron content. The water is not likely useable for domestic purposes without treatment, and some water well owners have been using the water successfully for domestic purposes with treatment.

Portions of the aquifer that crop out or are in subcrop near the South Platte River contain higher concentrations of sulfate where more oxygenated water prevents the reduction of sulfate anions. Areas where the Upper Pierre aquifer is confined contain the least sulfate, and also contain methane of microbial origin. Thermogenic methane was not detected in any of the water wells sampled. The combination of gas composition (only methane and traces of ethane were detected, and no propane or heavier hydrocarbons were detected), and the stable isotope ratios of methane and DIC demonstrate that the methane is microbial in origin.

This study documents an initial characterization of the quality of the water produced from the Upper Pierre aquifer showing that the Upper Pierre aquifer is a freshwater aquifer. In addition, the study clearly shows that microbial methane is present in the aquifer, especially where the aquifer is deeper and confined. However, further sampling of a greater number of water wells is required to more fully characterize the exact line of transition from oxygen depleted and methane containing waters to more oxygenated, sulfate dominated waters with little or no methane present. Water wells that are recently completed in the Upper Pierre aquifer would be the most valuable for analysis.

ACKNOWLEDGEMENTS

COGCC thanks the Colorado Division of Water Resources for discussions in understanding the recent increase in exploration and interest in the Upper Pierre aquifer and for data to identify potential water wells for sample collection. Several COGCC staff participated in the generation of figures, internal discussion and review of this manuscript. COGCC thanks all the private water well owners who provided access to their water wells for this project. The United States Forest Service, Arapahoe-Roosevelt National Forest-Pawnee National Grassland provided access to six water wells on the Pawnee National Grassland. The United States Air Force F.E. Warren Air Force Base provided access to two water supply wells at their Missile Alert Facilities. Quantum Water Consulting provided access to a pumping test of a private water well recently completed in the Upper Pierre aquifer. This project was funded by the COGCC's Environmental Response Fund (Fund 170).

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TABLES

TABLE 1A SUMMARY OF WATER WELL CONSTRUCTION AND LOCATIONS FOR WATER WELLS SAMPLED AS PART OF THE COGCC UPWQ STUDY

COGCC Facility ID	COGCC Facility Name	Applicant_Name	Receipt	PermitNo	Latitude	Longitude	Township	Range	Section	Q160	Q40	Use1	Well Constructed	Static WL	Division of Water Resources Permit Summary	Well Depth	Top Perf Casing	Bott Perf Casing	Top Filter Pack	Bottom Filter Pack	Bottom Grout
755062	AFB L-01 11500	AFB L-01	3644914B	11500-A	40.92125	-103.69197	11N	57W	13	NW	NW	HOUSEHOLD	6/3/2011	80	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3644914B	420	250	355	50	420	50
755061	AFB N-01 11503	AFB N-01	493171	11503	40.63135	-103.83634	8N	58W	26	SW	NW	DOMESTIC	7/1/2002	559	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0493171	1510	1014	1074	930	1137	981
755044	Brown276199	Ronald Brown	3623299A	26760A	40.39925	-103.71045	5N	57W	13	SE	NE	STOCK	1/9/2008	300	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3623299A	700	600	700	600	700	600
755043	Carmin276799A	Kelly Carmin	3671038	276799A	40.40855	-103.69227	5N	56W	7	SW	SW	STOCK	9/2/2015	380	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3671038	675	475	655	80	675	80
753652 **	Daniel 3661982	Daniel John Carlyle	3661982	292812	40.39407	-104.19531	5N	61W	15	SW	SE	STOCK	12/10/2013	210	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3661982	740	540	740	40	740	40
755116	Davis255302	Chris Davis	0520255	255302	40.45788	-104.10730	6N	60W	28	SW	NW	DOMESTIC STOCK	8/20/2004	280	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0520255	1302	756	1302	700	1302	700
754894	Hoozee278872	HOOZEE FARM LLC	3632805A	278872	40.54976	-103.66284	7N	56W	29	NE	NE	STOCK	11/3/2008	445	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3632805A	940	600	940	500	940	500
755063	M&C Farms 277080A	M & C FARMS INC	3627147B	277080	40.31881	-103.73687	4N	57W	15	NE	NE	DOMESTIC STOCK	5/12/2008	112	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3627147B	360	160	360	140	360	140
755042	Madsen236228A	Hall Jay R	3630645	236228A	40.43690	-103.99242	6N	59W	33	SW	SW	DOMESTIC STOCK	9/29/2001	310	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3630645	700	520	700	300	700	300
755040	Mertens300403	James S Mertens	3673396	300403	40.53958	-103.87221	7N	58W	28	SW	SE	STOCK	9/12/2016	548	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3673396	1545	741	761	632	1545	632
754896	NGL296759	NGL Water Solutions	3667195	296759	40.36500	-104.18500	5N	61W	27	SE	SE	COMMERCIAL	4/21/2015	98	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3667195	910	810	910	NR	NR	40
755041	Ommen260312	Theresa Ommen	0530446	260312	40.81998	-103.17074	10N	52W	22	SW		DOMESTIC	1/6/2006	105	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0530446	480	360	460	320	480	320
755117	PrairieSchool25131	Prairie School	9063090	25131	40.61656	-103.80190	8N	58W	36	SE	SE	DOMESTIC	7/31/1965	400	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9063090	950	831	951	NR	NR	NR
754905	USFS10603	U.S. Forest Service	9060402	10603	40.85800	-103.68000	10N	56W	7	NW	NE	STOCK	6/21/1974	440	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9060402	824	704	824	NR	NR	10
754906	USFS115190	U.S. Forest Service	9066281	115190	40.64100	-103.90700	8N	58W	19	SW	SE	STOCK	9/3/1980	550	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9066281	1060	820	1060	none	none	10
754902	USFS226830	U.S. Forest Service	459606	226830	40.71600	-103.89800	9N	58W	30	SE	SE	STOCK	3/2/2002	603	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0459606	1170	1086	1170	none	none	1020
754895	USFS280068	US FOREST SERVICE	3637932	280068	40.62000	-103.86000	8N	58W	33	NE	SE	STOCK	5/11/2009	540	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=3637932	1100	900	1100	300	1100	300
754903	USFS37078	U.S. Forest Service	9063900	37078	40.65100	-103.59800	8N	56W	24	NW	NW	STOCK	5/8/1976	450	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9063900	812	712	812	none	none	60
754904	USFS37115A	U.S. Forest Service	51059	37115A	40.84000	-103.67900	10N	56W	18	NE	SW	STOCK	3/18/2013	350	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0051059	800	600	800	40	800	40
754907	USFS45886	U.S. Forest Service	9064474	45886	40.70800	-103.83700	9N	58W	35	NW	SW	STOCK	5/1/1971	260	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9064474	865	845	865	NR	NR	NR

*NR = No Record

The Daniel 3661982 water well has been sampled by industry for compliance with Rule 218A, in addition to the COGCC sample collected for this study.

TABLE 1B SUMMARY OF WATER WELL CONSTRUCTION AND LOCATIONS FOR WATER WELLS WITH SAMPLES IN THE COGCC ENVIRONMENTAL DATABASE

COGCC Facility ID	COGCC Facility Name	Applicant_Name	Receipt	PermitNo	Latitude	Longitude	Township	Range	Section	Q160	Q40	Use1	Well Constructed	Static WL	Division of Water Resources Permit Summary	Well Depth	Top Perf Casing	Bott Perf Casing	Top Filter Pack	Bottom Filter Pack	Bottom Grout
755034	Anderson 2646	British American Oil Produc	9042895	2646-F	40.68354	-103.37108	8N	54W	1	SW	SW	INDUSTRIAL	7/9/1960	228	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=9042895	705	225	705	NR	NR	NR
750123	Bale 221096	Sandy Hill Land LLC	451016	221096	40.37740	-104.22640	5N	61W	29	NE	NE	DOMESTIC STOCK	2/10/2000	150	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0451016	600	400	600	380	600	380
705598	Phillips water well	Phillip, Ronald L	284811	150855	40.42084	-104.88035	5N	67W	10	NW	NE	DOMESTIC STOCK	6/8/1988	235	http://www.dwr.state.co.us/WellPermitSearch/View.aspx?receipt=0284811	1170	750	1170	NR	NR	263

*NR = No Record

** The Facility ID 753652 (Daniel 36619982) water well was sampled two times during this study. One time by COGCC for this study, and again by an Operator for compliance with Rule 318A

The Anderson 2646 water well was sampled by COGCC on October 6, 2016 at request of the landowner.

The Bale 221096 water well was sampled by industry for compliance with Rule 318A.

The Phillips water well was sampled by COGCC on March 24, 2009 in response to COGCC complaint #200206882.

TABLE 2 SUMMARY OF INORGANIC WATER QUALITY PARAMETERS AND ANIONS

COGCC Facility ID	FACILITY NAME	INORGANIC PARAMETERS											
		BICARBONATE ALKALINITY as CACO3	CARBONATE ALKALINITY AS CACO3	TOTAL ALKALINITY AS CACO3	pH	SPECIFIC CONDUCTIVITY	TOTAL DISSOLVED SOLIDS	BROMIDE	CHLORIDE	FLUORIDE	SULFATE	NITRITE AS N	NITRATE AS N
		mg/L	mg/L	mg/L	SU	UMHOS/CM	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
755062	**AFB L-01 11500**	110	ND (20)	110	8.11	258	200	ND (0.2)	1.8	0.77	8.4	ND (0.1)	1
755061	**AFB N-01 11503**	680	ND (20)	680	8.67	1,875	1,400	1.7	190	3.2	ND (4)	ND (0.4)	ND (0.8)
755044	**Brown276199**	330	ND (20)	330	8.38	3,480	2,500	1.7	170	1.4	1,300	ND (0.5)	ND (1)
755043	**Carmin276799A**	190	ND (20)	190	8.39	2,660	1,900	ND (1)	92	0.91	1,000	ND (0.5)	ND (1)
753652	**Daniel 3661982**	260	ND (20)	260	7.67	4,690	2,700	ND (0.2)	120	0.63	2,200	0.48	0.52
753652	**Daniel 3661982***	440	ND (20)	440	8.36	2,856	1,800	1	92	1.9	1,000	NA	NA
755116	**Davis255302**	660	ND (20)	660	8.51	3,650	2,100	5.2	700	3	ND (1)	ND (0.1)	ND (0.2)
754894	**Hoozee278872**	700	ND (20)	700	8.59	1,750	1,100	1.5	170	2.5	36	ND (0.5)	ND (1)
755063	**M&C Farms 277080A**	140	ND (20)	140	7.85	3,110	2,100	1.4	110	0.5	1,200	ND (0.5)	ND (1)
755042	**Madsen236228A**	560	ND (20)	560	8.27	2,170	1,600	0.95	120	2.1	460	ND (0.4)	ND (0.8)
755040	**Mertens300403**	770	ND (20)	770	8.63	3,370	2,300	5	710	3.4	ND (5)	ND (0.5)	ND (1)
754896	**NGL296759**	550	78	620	8.82	2,490	1,600	2.2	320	2.4	220	ND (0.5)	ND (1)
755041	**Ommen260312**	150	ND (20)	150	7.92	780	560	0.48	75	0.56	110	ND (0.1)	5.9
755117	**PrairieSchool25131**	680	ND (20)	680	8.56	2,019	1,400	1.9	200	3	19	ND (0.1)	ND (0.2)
754905	**USFS10603**	710	ND (20)	710	8.63	1,235	940	0.21	12	1.9	ND (1)	ND (0.1)	ND (0.2)
754906	**USFS115190**	580	ND (20)	580	8.66	1,395	950	ND (0.2)	41	2.1	130	ND (0.1)	ND (0.2)
754902	**USFS226830**	710	ND (20)	710	8.63	1,312	1,000	ND (0.2)	10	2.2	ND (1)	ND (0.1)	ND (0.2)
754895	**USFS280068**	690	ND (20)	690	8.63	1,658	1,000	1.3	150	3	5.2	ND (0.4)	ND (0.8)
754903	**USFS37078**	680	ND (20)	680	8.67	1,517	1,100	0.91	91	2.4	33	ND (0.1)	ND (0.2)
754904	**USFS37115A**	620	ND (20)	620	8.7	1,100	820	ND (0.2)	13	2.1	1.3	ND (0.1)	ND (0.2)
754907	**USFS45886**	520	ND (20)	520	8.66	1,058	820	0.25	22	1.9	38	ND (0.1)	ND (0.2)
755034	**Anderson 2646**	520	17	540	8.3	2,000	1400	1.8	150	1.9	440	ND (0.1)	ND (0.1)
750123	**Bale 221096**	530	42	570	8.73	1,399	870	0.97	130	3	14	ND (0.1)	ND (0.2)
705598	**Phillips water well**	278	33.6	311	8.74	1,590	940	1.38	334	2.7	14.6	ND (0.61)	ND (0.045)
CDPHE-WQCC REGULATION 41 BASIC STANDARDS FOR GROUNDWATER		NS	NS	NS	6.5 - 8.5 [B]	NS	<500 or 1.25x background [D]	NS	250 [B]	4.0 [A]	250 [B]	1 [A] or 10 [C]	10 [A] or 100 [C]

NOTES:

* Sample was collected by industry for compliance with Rule 318A

ND (number) = Analyte was not detected by the laboratory above the laboratory reporting limit

NS = No Standard for the analyte in groundwater

CDPHE-WQCC = Colorado Department of Public Health and Environment - Water Quality Control Commission

[A] The standard listed is from Regulation 41 Table 1 Domestic Water Supply - Human Health Standards

[B] The standard listed is from Regulation 41 Table 2 Domestic Water Supply - Drinking Water Standards

[C] The standard listed is from Regulation 41 Table 3 Agricultural Standards

[D] The standard listed is from Regulation 41 Table 4 TDS Water Quality Standards

TABLE 3 SUMMARY OF DISSOLVED METALS CONCENTRATIONS

COGCC Facility ID	FACILITY NAME	DISSOLVED METALS BORON mg/L	BARIUM mg/L	CALCIUM mg/L	CHROMIUM mg/L	IRON mg/L	LEAD mg/L	MAGNESIUM mg/L	MANGANESE mg/L	POTASSIUM mg/L	SELENIUM mg/L	SODIUM mg/L	STRONTIUM mg/L	SODIUM ADSORPTION RATIO No Unit	Cation-Anion Balance No Unit
755062	**AFB L-01 11500**	0.058	0.085	22	ND (0.01)	ND (0.1)	ND (0.0005)	7.5	0.0029	5.5	ND (0.001)	15	0.33	0.70	--
755061	**AFB N-01 11503**	2.1	0.049	1.7	ND (0.01)	ND (0.1)	ND (0.0005)	0.47	0.0055	1.2	ND (0.001)	440	0.1	77	7.8
755044	**Brown276199**	1.3	0.016	27	ND (0.01)	ND (0.1)	ND (0.0005)	8.2	0.027	4.7	ND (0.001)	780	1.5	34	-1.6
755043	**Carmin276799A**	0.78	0.0091	19	ND (0.01)	ND (0.1)	ND (0.0005)	6.4	0.025	4.8	ND (0.001)	590	1.1	30	1.4
753652	**Daniel 3661982**	0.4	0.023	110	ND (0.01)	ND (0.1)	0.0037	40	0.015	7.3	ND (0.001)	950	4.5	20	-3.0
753652	**Daniel 3661982***	NA	NA	51	NA	NA	NA	21	NA	4.1	NA	590	NA	17	-1.0
755116	**Davis255302**	0.69	0.062	1.1	ND (0.01)	0.17	0.0034	0.33	0.0027	ND (1)	ND (0.001)	320	0.12	69	-37.2
754894	**Hoozee278872**	1.9	0.048	2.2	ND (0.01)	ND (0.1)	ND (0.0005)	0.66	0.0062	1.9	ND (0.001)	420	0.098	64	4.1
755063	**M&C Farms 277080A**	0.56	0.01	91	ND (0.01)	ND (0.1)	ND (0.0005)	27	0.11	6.7	ND (0.001)	560	4	13	1.5
755042	**Madsen236228A**	1.2	0.066	73	ND (0.01)	ND (0.1)	0.00057	35	0.0022	4.7	ND (0.001)	410	1.6	9.8	5
755040	**Mertens300403**	3.3	0.11	2.9	ND (0.01)	0.14	ND (0.0005)	1.2	0.031	2	ND (0.001)	810	0.25	101	4.2
754896	**NGL296759**	1.3	0.07	7.7	ND (0.01)	ND (0.1)	ND (0.0005)	3.8	0.013	1.6	ND (0.001)	560	0.36	41	-0.2
755041	**Ommen260312**	0.33	0.042	67	ND (0.01)	ND (0.1)	ND (0.0005)	15	ND (0.002)	7	0.015	71	0.88	2	6.7
755117	**PrairieSchool25131**	1.8	0.052	1.9	ND (0.01)	ND (0.1)	0.0012	0.52	0.0047	1.1	ND (0.001)	450	0.11	74	6.9
754905	**USFS10603**	1.2	0.037	2.9	ND (0.01)	0.15	ND (0.0005)	0.81	0.0052	2.5	ND (0.001)	310	0.12	41	6.9
754906	**USFS115190**	0.97	0.035	6.4	ND (0.01)	ND (0.1)	ND (0.0005)	2.1	0.0053	3.4	ND (0.001)	330	0.23	29	5.5
754902	**USFS226830**	1	0.037	2.5	ND (0.01)	0.11	ND (0.0005)	0.68	0.0046	1.9	ND (0.001)	340	0.12	49	11.5
754895	**USFS280068**	1.5	0.041	2.2	ND (0.01)	ND (0.1)	0.0007	0.7	0.0063	1.3	ND (0.001)	410	0.1	61	7.1
754903	**USFS37078**	1.4	0.028	4.2	ND (0.01)	ND (0.1)	ND (0.0005)	1.8	0.0033	2.5	ND (0.001)	360	0.19	37	5.5
754904	**USFS37115A**	0.93	0.046	4.1	ND (0.01)	ND (0.1)	ND (0.0005)	1	0.006	2.8	ND (0.001)	270	0.14	31	6.8
754907	**USFS45886**	0.78	0.047	5.3	ND (0.01)	ND (0.1)	ND (0.0005)	1.7	0.0041	3.6	ND (0.001)	250	0.18	24	6.7
755034	**Anderson 2646**	NA	NA	30	NA	ND (0.1)	NA	23	0.038	7	NA	480	NA	16	4.2
750123	**Bale 221096**	0.71	0.03	1.5	NA	ND (0.1)	NA	0.34	0.0021	ND (1)	ND (0.001)	340	0.08	65	2.9
705598	**Phillips water well**	NA	NA	5.2	NA	0.19	NA	1.1	0.0083	1.6	NA	360	NA	37	2.1
CDPHE-WQCC REGULATION 41 BASIC STANDARDS FOR GROUNDWATER		0.75 [C]	2.0 [A]	NS	0.1 [A]	0.3 [B] or 5.0 [C]	0.05 [A] or 0.1 [C]	NS	0.05 [B] or 2.0 [C]	NS	0.05 [A] or 0.02 [C]	NS	NS		

NOTES:

* Sample was collected by industry for compliance with Rule 318A

ND (number) = Analyte was not detected by the laboratory above the laboratory reporting limit

NA = Not Analyzed

NS = No Standard for the analyte in groundwater

CDPHE-WQCC = Colorado Department of Public Health and Environment - Water Quality Control Commission

[A] The standard listed is from Regulation 41 Table 1 Domestic Water Supply - Human Health Standards

[B] The standard listed is from Regulation 41 Table 2 Domestic Water Supply - Drinking Water Standards

[C] The standard listed is from Regulation 41 Table 3 Agricultural Standards

SODIUM ADSORPTION RATIO (SAR) from ALS Environmental Laboratory Report or calculated as SAR = Na/sqrt((Ca+Mg)/2); concentrations of Na, Ca, and Mg converted from mg/l to meq/l

Cation-Anion Balance calculated in Rockworks v15

TABLE 4 SUMMARY OF DISSOLVED GAS CONCENTRATIONS AND STABLE ISOTOPE RATIOS

COGCC Facility ID	FACILITY NAME	DISSOLVED GASES		STABLE ISOTOPE RATIOS GAS		STABLE ISOTOPE RATIOS WATER		
		METHANE	ETHANE	$\delta^{13}C$ C1 (Methane)	δD C1 (Methane)	$\delta^{13}C$ DIC (Dissolved Inorganic Carbon)	$\delta^{18}O$ H_2O (Water)	δD H_2O (Water)
		µg/L	µg/L	per mil VPDB	per mil VPDB	per mil VPDB	per mil VSMOW	per mil VSMOW
755062	**AFB L-01 11500**	ND (1)	ND (2)	NA	NA	-4.9	-11.4	-85
755061	**AFB N-01 11503**	12000	14	-69.2	-256	-3.1	-12.5	-94.1
755044	**Brown276199**	3200	ND (2)	-71.4	-241	-10.7	-11.6	-88.1
755043	**Carmin276799A**	13	ND (2)	NA	NA	-10.7	-11.6	-88.3
753652	**Daniel 3661982**	2.7	ND (2)	NA	NA	-12.3	-12.3	-93.9
753652	**Daniel 3661982***	4100	6.7	-71.6	-229	NA	NA	NA
755116	**Davis255302**	24000	33	-68.3	-252	0.5	-11.7	-86.8
754894	**Hoozee278872**	15000	20	-67.5	-244	-2.9	-12.6	-96.1
755063	**M&C Farms 277080A**	ND (1)	ND (2)	NA	NA	-8.6	-13.6	-103.1
755042	**Madsen236228A**	15000	65	-73.4	-240	-5	-11.9	-91.7
755040	**Mertens300403**	33000	24	-69.5	-256	1.1	-11.6	-88.2
754896	**NGL296759**	11000	26	-69.9	-242	-4.5	-11.9	-90.4
755041	**Ommen260312**	ND (1)	ND (2)	NA	NA	-2.2	-9.7	-71
755117	**PrairieSchool25131**	13000	15	-68	-256	-2.7	-12.6	-95.4
754905	**USFS10603**	8400	17	-74.9	-257	0.1	-13.3	-96.5
754906	**USFS115190**	5900	12	-73.4	-262	-2	-12.4	-90
754902	**USFS226830**	4600	9.1	-75.3	-265	0.3	-13.4	-98.3
754895	**USFS280068**	17000	23	-69.3	-261	-1.8	-12.3	-91
754903	**USFS37078**	6800	11	-70.3	-259	-0.7	-12.9	-96.4
754904	**USFS37115A**	5800	12	-73.9	-268	-0.4	-13	-94.2
754907	**USFS45886**	1900	6.8	-73.3	-270	-0.4	-12.6	-90.4
755034	**Anderson 2646**	6700	NA	-71.1	-218	-3.8	-12.3	-93.7
750123	**Bale 221096**	14000	50	-73.1	-238	NA	NA	NA
705598	**Phillips water well**	13000	NA	-70.9	-264.1	NA	NA	NA

NOTES:
* Sample was collected by industry for compliance with Rule 318A
ND (number) = Analyte was not detected by the laboratory above the laboratory reporting limit
NA = Not Analyzed
VPDB = Vienna Pee Dee Belemnite
VSMOW = Vienna Standard Mean Ocean Water