Phase II Hydrogeologic Characterization of the Mamm Creek Field Area, Garfield County, Colorado

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Prepared for:

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LIST OF ABBREVIATIONS AND ACRONYMS

‰	Per mil (parts per thousand)
^{13}C	Carbon-13, a stable isotope of carbon containing one more neutron than carbon-12, the most common isotope of carbon.
^{2}H	Hydrogen-2, or deuterium, a stable isotope of hydrogen containing one more neutron than hydrogen-1, the most common isotope of hydrogen.
$\delta^{13}C$	The ratio of carbon-13 to carbon-12 in a sample relative to the same ratio for an accepted standard material (for carbon, the standard material is the Pee Dee Belemnite). See report Section 4.1.1 for additional explanation.
δD	The ratio of hydrogen-2 to hydrogen-1 in a sample relative to the same ratio for an accepted standard material (for hydrogen, the standard material is Vienna Standard Mean Ocean Water). See report Section 4.1.1 for additional explanation.
B	Boron
Br	Bromine (used to mean bromide, the common anion in water)
C1 - C6	Hydrocarbon gases, identified based on the number of carbon atoms in the gas molecule: C1 = methane, C2 = ethane, C3 = propane, C4 = butane, C5 = pentane, C6 = hexane.
Ca	Calcium
CBGWS	Colorado Basic Ground Water Standard
Cl	Chlorine (used to mean chloride, the common anion in water)
CO_2	Carbon dioxide
CO_3	Carbonate, an anion in water
COGCC	Colorado Oil and Gas Conservation Commission
D	Deuterium, also known has hydrogen-2 (see ^{2}H, above)
EPA	United States Environmental Protection Agency
ERF	Environmental Response Fund (administered by the COGCC)
F	Fluorine (used to mean fluoride, the common ion in water)
HCO_3	Bicarbonate, an ion in water
MCL	Maximum contaminant level
meq/L	Millequivalents per liter
Mg	Magnesium
mg/L	Milligrams per liter
Na	Sodium
NO_2	Nitrite, an anion in water
NO_3	Nitrate, an anion in water
PDB	Pee Dee Belemnite
Ppmv	Parts per million on a volumetric basis

LIST OF ABBREVIATIONS AND ACRONYMS (Cont.)

QA/QC	Quality Assurance/Quality Control
Se	Selenium
SMCL	Secondary maximum contaminant level
SO_4	Sulfate, an anion in water
Sr	Strontium
TDS	Total dissolved solids
USGS	United States Geological Survey
VSMOW	Vienna Standard Mean Ocean Water

EXECUTIVE SUMMARY

The Phase II Hydrogeologic Characterization for the Mamm Creek Field Area is a continuation of the Phase I study for the same area (URS, 2006), which is located south of the Colorado River between the cities of Rifle and Silt, Colorado. The Phase II study included two field sampling tasks. In Task 1, water quality and gas composition and methane stable isotope samples were collected from domestic wells in the Mamm Creek study area that had previously had one or more compounds of concern at or above regulated concentrations, or that had sodium-chloride (Na-Cl) concentrations that suggested possible mixing with Na-Cl water with marine or brackish water characteristics. In Task 2, produced water and natural gas samples were collected from gas wells in the immediate vicinity of domestic wells whose water and gas chemistry sampling results suggested possible potential impacts from deeper formations or other external sources, whether natural or due to natural gas drilling and/or production activities.

The first three sections of this report provide: 1) a summary of existing geologic and water and gas quality information for the Mamm Creek Field area; 2) methods used to determine sampling locations; and 3) sampling methods and parameters. Sample parameters for the Task II study included:

- Standard water quality parameters for all water samples;
- Nitrate, fluoride, and selenium, which previously have been detected in wells in the study area at concentrations above Colorado Basic Ground Water Standards (CBGWS)for human health (nitrate was sampled in all wells; fluoride and selenium were sampled only in wells where previous concentrations had exceeded CBGWS);
- Methane for wells which previously had concentrations above 1 milligram/liter (mg/L);
- Tracer compounds bromide, boron, and strontium for all produced water samples and for wells that had possible impacts from Na-Cl waters; and
- Dissolved gases and methane isotopes in domestic wells that had previously had methane concentrations above 2 mg/L and in all gas well production gas samples.

Section 4 of the report discusses the results of the water quality and gas sampling conducted for the Phase II study and it relationship to previous sampling. The section also provides limited interpretation for water quality trends, water sources, and hydrocarbon gas characteristics. Sections 5 and 6 provide a summary of findings and recommendations, respectively, based on the Phase II study.

Findings from the Phase II Hydrogeologic Characterization include the following.

- Results of domestic well sampling for fluoride, nitrate, and selenium indicate that while there are wells with concentrations in excess of human health standards, the number of wells with concentrations in excess of CBGWS fell for each of these compounds relative to previous sample results. Fluoride and selenium concentrations are elevated in areas on the east side similar to other water quality parameters; however, there are no discernable trends that clearly link them to anthropogenic sources.
- The geographic distribution of bicarbonate (HCO_3) and sulfate (SO_4) water types from the Wasatch aquifer and a possible bimodal pattern for cations in the samples suggest a more complex mechanism than a simple, gradual evolution from a bicarbonate to sulfate water type. It is possible that water from depth mixing with the Wasatch aquifer may contribute to this pattern.
- Analyses of produced water samples indicate that Williams Fork Formation water is primarily brackish and of two water types. The majority of the wells sampled had Na-Cl geochemical signatures; however, $Na\text{-}HCO_3$ water was also present. The Na-Cl signature appears to be characteristic of water from Williams Fork Formation clastic sedimentary deposits, while the $Na\text{-}HCO_3$ water may indicate coalbed formation water.
- For the tracer compounds bromide (Br), boron (B), and strontium (Sr), the distinction between Ca/Sr mass ratios between the produced water and domestic water may provide sufficient information to evaluate water sources or mixing. Cl/Br and Cl/B ratios may be reasonable indicators for certain shallow anthropogenic impacts to Wasatch Formation groundwater. Additionally, sulfate and chloride major ion concentrations and ratios may serve as indicators for possible deep water impacts to the drinking water aquifer.
- Two of the domestic wells sampled for gas composition and methane stable isotopes had results indicating a possible thermogenic source for the gases in the wells. Most of the domestic wells in the field area, however, have hydrocarbon gas characteristics indicative of a biogenic source.

Based on the review of existing and new water quality and gas composition and isotope data for the Mamm Creek study area, the following are recommended for future work:

- Well 703961, located between Mamm Creek and Dry Hollow Creek in the northern portion of the study area, which has only been sampled one time for human health parameters and which had elevated concentration of nitrate, fluoride, and selenium, should be resampled. The sample should be analyzed for major ions, human health parameters, tracer compounds, dissolved methane, and gas composition and methane isotopes.

- Well 704330, which is located in the southeast corner of the study area, and which had a Na-Cl geochemical signature and dissolved methane at a concentration of 11 mg/L, should be resampled. The well is apparently a different well than was sampled in January 2003 (and that was also identified as 704330). The sample should be analyzed for major ions, human health parameters, tracer compounds, dissolved methane, and gas composition and methane isotopes. Because of the high methane concentration, an inspection of the water delivery infrastructure should also be conducted to ensure that explosive conditions do not exist.
- An examination of existing domestic wells and gas wells and their sample histories should be conducted for the southeast quarter of Township 7 South, Range 92 West (extending as far north as Sections 14 and 15). Efforts should be directed at characterizing both the general water chemistry (including the Na-Cl patterns) and the nature of the methane and other gases in the water. Sampling should include tracer analyses and gas composition and methane isotopes. Both domestic wells and gas wells should be targeted for this investigation.
- Well owners whose wells contained greater than 1 mg/L of dissolved methane (six wells for this investigation) should be encouraged to continue to have their wells sampled for dissolved methane.
- It is possible that the significance of tracer ratios for Wasatch Formation groundwater will be more likely to be discerned with additional sampling of the Tertiary aquifer and of produced water from deeper formations. Tracer compounds should be included in future sampling events, including in areas where no natural gas production has occurred in order to build a useful baseline dataset.
- The effect on groundwater due to the introduction of drilling or well completion/ hydrofracturing fluids into the shallow aquifer was not investigated for this study. A study evaluating possible local effects of drilling or hydrofracturing fluids on domestic groundwater should be considered.

1.0 INTRODUCTION

The Piceance Basin, which covers an area of approximately 7,100 square miles in western Colorado (Figure 1.1), has been the site of extensive oil and gas exploration in recent years. Currently, gas wells are being drilled and completed in the Upper Cretaceous Mesaverde Group in the eastern portion of the basin south of the Interstate 70 corridor in Garfield County.

In March 2004, a leaking natural gas well located approximately six miles south of the community of Silt released methane into Divide Creek. The Colorado Oil and Gas Conservation Commission (COGCC) directed initial response actions following the release. Garfield County subsequently undertook a hydrogeologic investigation using funds provided through the COGCC Environmental Response Fund (ERF). The initial phase of this investigation, summarized in the report "Phase I Hydrogeologic Characterization of the Mamm Creek Field" (URS, 2006), assembled a diverse set of geologic, gas and water production, and hydrologic data and provided a broad overview of conditions in the area between the towns of Rifle and Silt and south of the Colorado River that encompasses the Mamm Creek Field and the location of the release (Figure 1.2). The Phase II hydrogeologic characterization is a continuation of the Mamm Creek Field area investigation with emphasis on the collection of additional water quality and gas composition and stable isotope data from both domestic water supply wells and natural gas wells.

S. S. Papadopulos & Associates, Inc. conducted the Phase II hydrogeologic characterization under contract to the Garfield County Board of Commissioners with additional oversight provided by the COGCC. For the study, two rounds of sampling were conducted. In the initial round (Task 1), conducted in June and July 2007, samples were collected from 66 domestic water supply wells. Analyses included an extensive suite of inorganic parameters. In addition, water from 13 wells was also analyzed for dissolved methane, with gas composition and hydrogen and carbon stable isotopes of methane determined for 11 of those wells. In the second round (Task 2), produced water samples were collected from 16 active natural gas wells and production gas samples were collected from four wells. The produced water samples were analyzed for inorganic parameters and the gas samples were analyzed for gas composition and hydrogen and carbon stable isotopes of methane. This report describes the field sampling, summarizes and evaluates the analytical results, and provides recommendations for future activities.

1.1 Objectives

The objectives of the "Mamm Creek Field Area Phase II Hydrogeological Characterization" study were to:

- Identify and sample domestic water wells or springs within the study area where previous water sampling results indicated that the groundwater exceeded primary health-based drinking water standards, or had elevated dissolved methane or sodium-chloride (Na-Cl) concentrations, and where resampling was required to confirm the earlier results.
- Identify and sample up-gradient producing natural gas wells near domestic wells with elevated methane concentrations and/or Na-Cl signatures.
- Develop a database of newly acquired sample results to add to existing COGCC databases and evaluate possible connections between the water supply aquifers and natural gas exploration and production activities in the Mamm Creek study area.

1.2 Project Approach

The Phase II hydrogeologic characterization was a narrowly scoped continuation of the Phase I study for the Mamm Creek Field area (URS, 2006) based on specific recommendations provided in that investigation. As described above, the objectives of the Phase II study primarily were to evaluate water quality of domestic wells and springs in areas that in the past have had elevated concentrations for heath-based parameters or conditions suggesting possible impacts from deeper sources—whether or not the impacts are natural or the result of natural gas development in the area.

To focus the investigation, the field-sampling program was divided into two tasks. For the first task, the existing database of water quality and gas composition and isotope sample results compiled for the Mamm Creek area and provided by the COGCC was thoroughly reviewed and domestic water supply wells and springs that reported only one sample exceeding one of the following criteria were identified for sampling:

- Nitrate (NO_3), fluoride (F), and/or selenium (Se) concentration above Colorado Basic Ground Water Standards (CBGWS), as specified in Colorado Water

Quality Control Commission regulation 5 CCR 1002-41 for domestic groundwater supplies;

- Dissolved methane concentration above 2 mg/L, the COGCC recommended level for resampling and collection of gas composition and methane stable isotope samples; and/or
- The presence of total dissolved solids (TDS) at a concentration of 1,500 milligrams/liter (mg/L) or greater, with sodium and chloride concentrations that could potentially indicate the mixing of Na-Cl water in the domestic water supply aquifer.

Depending on the reason(s) for sampling, the list of parameters to be analyzed was adjusted for each sample location. Specific sample parameter lists are provided in the Task 1 Field Sampling Plan included as Appendix A to this report.

At the conclusion of Task 1 sampling, the new analytical data were incorporated into the Mamm Creek area database and the database was reviewed to identify locations where probable thermogenic methane and/or Na-Cl impacts were confirmed. This evaluation included not only Task 1 sample results, but also previous sample results that met either of these criteria. Based on the results of this evaluation, natural gas well locations were tentatively identified for Task 2 sampling. In general, the Task 2 sample locations were within a mile of the potentially impacted domestic sample locations, and where possible, up-gradient (relative to estimated groundwater flow directions) of each location. Several factors (discussed in Section 3.2, below) often resulted in modifications to this approach. As with the Task 1 groundwater sampling, parameters sampled at the gas wells were dependent on factors that motivated the sampling. If the sampling was motivated by Na-Cl water signatures, then only produced water was sampled from the gas well; if sampling was driven by methane-related issues, a production gas sample was collected in addition to a sample of produced water. Specific sample parameter lists are provided in the Task 2 Field Sampling Plan included as Appendix B to this report.

The analytical data from both Task 1 and Task 2 sampling events were used to evaluate aquifer conditions in the Mamm Creek area (see Section 4, below).

2.0 STUDY AREA SETTING

2.1 Study Area Location

The Mamm Creek Field study area (Figure 1.2) extends approximately 9½ miles south of the Colorado River, between the towns of Rifle and Silt and covers an area of approximately 110 square miles. There are more than 500 known and permitted domestic and livestock water supply wells in the area. A detailed description of the geographic setting, overall land use, and development of natural gas resources in the area is reported in the Phase I Hydrogeologic Study (URS, 2006).

2.2 Natural Gas Production

Natural gas exploration and production is occurring across much of the study area, both within and outside of the extents of the Mamm Creek Field (Figure 1.2). Through August 2005, approximately 978 wells had been drilled and of that number 904 wells were reportedly producing (URS, 2006). Since that time, through August 2007, an additional 300 wells had begun producing in the study area. Natural gas in the Mamm Creek Field is produced primarily from sandstone lenses within the Williams Fork Formation of the Upper Cretaceous Mesaverde Group (Figure 2.1). Additional production occurs from lower in the Mesaverde Group, including from coalbeds of the Cameo Coal. The Mesaverde Group directly underlies the Lower Tertiary Wasatch Formation, which is the bedrock water supply aquifer for wells in the study area. Typically, several thousand feet of bedrock separate the uppermost gas-producing sandstones of the Williams Fork and the water supply aquifer in the Wasatch Formation. Above the Divide Creek Anticline in the southeast portion of the study area (see Figure 1.2), where this thickness is a minimum, there are more than 2,000 feet between the productive intervals of the Mesaverde Group and the deepest water supply wells in the Wasatch Formation.

All natural gas wells in the Mamm Creek field and throughout the study area are hydraulically fractured to stimulate gas production. Hydraulic fracturing is a process of injecting liquids containing proppants such as sand, glass beads or other solid materials into the gas-bearing formation at high pressures to facilitate fracturing the rocks, thereby providing pathways to dissipate the fracture fluids into the formation. Fracture fluids can include a wide variety of materials, including diesel fuel, gels, foams, acids or gases, and may be water-based or polymerbased (EPA, June 2004). Operators attempt to control the extent of the fractures to optimize gas production by varying fracture fluid characteristics, fracturing pressures, and injection rates. After the proppants are injected into the fractures, the pressure in the borehole is reduced and fluids used to fracture the formation are allowed to flow back into the well.

COGCC requires that all oil and gas wells have surface casings that reach below domestic water supply aquifers and that they be fully cemented into place. Further, since July 2004, for the Piceance Basin, COGCC has required that all production casing be cemented a minimum of 500 feet above the top of gas (in the Williams Fork Formation) to minimize the potential for migration of gas into the annular space of the wells. In many cases, operators choose to cement production casing from the total depth of the casing to the ground surface. While these actions should reduce the potential for migration of gas into the shallow subsurface or to the ground surface for present and future drilling and gas production activities, there are many older wells in the area that were not constructed under the new requirements or that were abandoned before modern methods were implemented and that have an increased potential to provide migration pathways for methane and/or water from sources beneath the Wasatch Formation.

2.3 Hydrogeologic Setting

Both alluvial and bedrock aquifers are utilized for fresh water supply in the study area. The alluvial aquifers are limited in extent and typically occur only locally in stream valleys. Wells that are completed in the alluvium primarily are adjacent to the Colorado River; only a few alluvial wells are present in the tributary drainages in the study area (e.g., Mamm Creek, Dry Hollow Creek, and West Divide Creek). The large majority of water supply wells are completed in the Lower Tertiary Wasatch Formation. The Wasatch Formation is present at the ground surface over the entire study area except at the southwest corner where it is overlain by the Green River Formation. The Wasatch Formation ranges between 1,200 and 6,000 feet thick, and directly overlies the Upper Cretaceous Mesaverde Group. The maximum depth reported by URS (2006) for Wasatch water supply wells is approximately 600 feet. (For wells completed in alluvium, the maximum depth is 100 feet). The Wasatch Formation is composed primarily of fine-grained siltstones and mudstones with lenses of very fine to coarse sandstones that were deposited in a non-marine coastal plain alluvial/fluvial environment. In general, groundwater produced from the Wasatch Formation is believed to come primarily from flow through fractures. Well yields vary widely, but are usually less than 10 gallons per minute (URS, 2006).

The vertical separation between the water supply wells in the Wasatch Formation and the top of the gas-producing horizons in the Mesaverde Group increases from close to 2,500 feet in the southeast corner of the study area above the axis of the Divide Creek anticline to greater than 7,000 feet along the west side of the study area (URS, 2006). The Williams Fork Formation, which is the uppermost unit within the Mesaverde Group, is the primary gas producer in the study area. The Williams Fork is characterized as a non-marine coastal plain sequence that consists primarily of shales interbedded with lenticular sandstones. The sandstone stratigraphy is complex; individual beds are generally not laterally continuous, with many of them considered to be fluvial point-bar deposits (Cumella and Ostby, 2003). The Williams Fork is approximately 3,700 to 4,300 feet thick in the study area (Johnson and Flores, 2003). The lower portion of the unit contains numerous coals of the Cameo Coal sequence. The coals are the most laterally continuous units in the Williams Fork and are also considered to be the most permeable due to the presence of cleats (i.e., regularly spaced and oriented fractures) within the beds. Permeability of the sandstones is very low and fracturing provides most of the permeability in the clastic sequence. A minor amount of coalbed methane gas production has occurred in the study area, but the primary production is from gas charged sandstones above the coal beds.

The water that is produced from Mesaverde Group gas wells normally has very high TDS concentrations relative to the water produced from alluvium and the Wasatch Formation. (The formation water is not as saline as ocean water and is considered to be brackish.) The transition in water quality from the Tertiary aquifer to the deeper hydrocarbon producing intervals in the Williams Fork Formation is not well understood in the study area because of a lack of water samples from the intervening area; but it is a potentially important factor in understanding the water quality relationship between the Wasatch and Williams Fork Formations.

While fracturing within the sandstone layers and coals is widespread, the vertical continuity of the fractures through intervening shale layers is not believed to be common within the Mesaverde Group (Lorenz, 2003), although there may be exceptions to this in areas—

possibly including the Divide Creek Anticline area—where tensional regimes exist (or may have existed) above anticlinal structures (Tyler, 1996; Kaiser and Scott, 1996).

In the alluvial aquifers, groundwater flow is generally in a downstream direction in the valleys where saturated alluvium exists. The streams in the study area are likely to be regions of groundwater discharge. Recharge in the alluvial aquifers is expected to be predominantly from infiltration of precipitation and from local shallow flow upslope of the alluvial fill. There also may be zones where water from the Wasatch Formation discharges from below into the alluvium, as suggested by the potentiometric surface map presented by URS (2006) where flow directions in the Wasatch Formation are from the topographically higher portions of the study area towards the tributary drainages and then to the Colorado River. Recharge to the Wasatch aquifer is considered to be primarily from infiltration of precipitation on the tops of mesas and from the highlands located south of the study area; although it is possible that some flow of deeper groundwater into the Wasatch aquifer may also occur. Several springs emanate from the Wasatch Formation in the vicinity of the study area. Flow from these springs may be the result of downslope flow of perched groundwater or discharge along streams that have incised into the bedrock; however, at some locations the springs may indicate that flowing artesian conditions exist. Artesian conditions could facilitate the flow of deeper bedrock-sourced groundwater into the Wasatch and alluvial aquifers and drainages in the area.

Portions of the Williams Fork Formation in the Piceance Basin, including in the area of the Divide Creek anticline, are considered to be hydrodynamically overpressured, meaning that fluids from depth potentially could flow to the ground surface if conduits exist for that flow (Kaiser and Scott, 1996). For that reason, impacts to shallower units, such as the Wasatch Formation, from Williams Fork Formation fluids (whether water or gas) could potentially occur either naturally or due to man-made conduits.

2.4 Water Quality Characteristics Based on Previous Sampling

The quality of the surface water and groundwater used for domestic and related water supply purposes in the Mamm Creek area was summarized in the Phase I Hydrogeologic Characterization Study (URS, 2006) based on evaluation of the water quality databases obtained primarily from the COGCC and the United States Geological Survey (USGS). The Phase I study provided a general overview of the water classification based on the distribution and concentrations of the major anions and cations present, identified characteristics related to the concentrations of specific health-based and aesthetic water quality constituents with regulatory standards, and evaluated the presence of methane in the water, both in terms of concentrations and isotopic signatures. The study looked at groundwater produced from unconsolidated alluvium and from the Wasatch Formation. Pertinent findings from the Phase I study are summarized below.

2.4.1 Water Type Classification

Both surface water and groundwater are often classified based on the predominant cations and anions dissolved in the water. The evaluation of water using these characteristics can be very valuable in helping to differentiate water from different sources or to identify how far and from where it may have traveled or to determine what chemical/biological processes may have affected it in the subsurface. For the Mamm Creek study area, the Phase I hydrogeologic characterization included the following observations regarding water type classification (additional explanation, maps, and graphic plots illustrating these characteristics can be found in URS, 2006):

- In the groundwater, sodium (Na) is the dominant cation in the majority of the wells. Bicarbonate (HCO_3) is likewise the dominant anion in the majority of the wells and 49 (about 23%) of the 220 groundwater sample locations suitable for major ion evaluation had a Na-HCO_3 water type (also known as a geochemical signature). [1]
- In wells where calcium (Ca) and/or magnesium (Mg) are the dominant cations, bicarbonate is almost always the dominant anion, and the TDS levels generally are around 500 mg/L or lower.
- In the few instances where magnesium and/or calcium are present in sulfate (SO_4)-rich waters, TDS is very high, approximately 2,000 mg/L and higher.
- Sulfate-rich waters are concentrated in wells north of where Dry Hollow Creek cuts through the high-standing bench near the boundary between Townships 6 and

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[1] The geochemical signature of water is determined from the relative reactive concentrations (measured in milliequivalents/liter [meq/L]) of the specific cations and anions present in the water. Any cation or anion making up 50 percent or more of that ionic species is identified alone in the geochemical signature. If a single cation or anion does not exceed 50 percent, the geochemical signature lists, in diminishing order, the two cations or anions that are required to bring the species to greater than 50 percent. By convention, cations are listed first in geochemical signatures. For example if calcium made of 40 percent and sodium made up 35 percent of the cations in a sample, and bicarbonate made up 70 percent of the anions, the geochemical signature would be calcium-sodium-bicarbonate (Ca-Na-HCO_3).

7 South (Figure 1.2). Na-SO_4 water, which was the second most common water type (10 percent of the samples), is common in this area, which corresponds generally with the axis and the northeast limb of the Divide Creek Anticline.

- Groundwater with a Na-Cl signature is present in three areas. In the area northwest of the 2004 methane leak at Divide Creek; in a relatively sparsely sampled area near the southeast boundary of the study area; and in a few wells off the east and west flanks of Grass Mesa.
- All spring samples have bicarbonate signatures; none have chloride at anionic proportions above 20 percent and only two have sulfate at anionic proportions above 30 percent. This suggests that the sampled springs probably do not have a deep groundwater source.
- Produced water samples have very high TDS and predominantly Na-Cl geochemical signatures. No sulfate, or only insignificant amounts of sulfate, is present in any of these waters.

2.4.2 Human Health and Water Quality Parameters

The State of Colorado has established limits for constituents in groundwater in 5 CCR 1002-41, The Basic Standards for Ground Water. The CBGWS apply to wells used for domestic water supply purposes. The standards are established both for compounds that have known or suspected health effects, and for compounds that have aesthetic (e.g., taste, odor, color, etc.) effects. For the domestic wells that have been sampled in the Mamm Creek study area, health-based standards have been exceeded for nitrate, fluoride, selenium, and in two instances for arsenic (As); while aesthetic (or water quality) standards have been exceeded for chloride, iron (Fe), manganese (Mn), sulfate, and TDS. Additionally, while there is no standard established for hardness, the majority of the groundwater used for domestic supplies that has been sampled in the study area is classified as hard to very hard.

The CBGWS for nitrate is 10 mg/L. The primary concern for nitrate in groundwater is for consumption by infants under six months of age who can suffer respiratory distress or death from consuming water with high concentrations of nitrate. Elevated nitrate concentrations are usually associated with contamination from agricultural fertilizers or sewage (septic systems) or livestock wastes. In the study area approximately 15 percent of the wells sampled have been measured with nitrate concentrations exceeding 10 mg/L including approximately half of the wells sampled on Grass Mesa. Other areas where nitrate commonly exceeds 10 mg/L are the area along Dry Creek off the southeast flank of Grass Mesa, Dry Hollow Creek south of where it opens up along the north edge of Township 7 South, and along East Divide Creek southeast of the West Divide Creek methane release location. All areas where elevated nitrate concentrations are common are under cultivation, or have been within the last few years.

Fluoride is a naturally occurring compound that has a CBGWS of 4 mg/L. The primary concern for fluoride is its potential to cause tooth and bone damage at elevated concentrations (even though moderate levels can prevent dental cavities). Fluoride in excess of 4 mg/L has been detected in more than 30 wells in previous sampling in the Mamm Creek study area. All of the wells with elevated fluoride are located in the east-central and southeast portions of the study area, relatively evenly distributed above the axis of the Divide Creek Anticline from Dry Hollow Creek south-southeast towards the southeast corner of the study area. Wells with concentrations above 4 mg/L are interspersed with wells having fluoride concentrations between 1 and 4 mg/L. This contrasts with the west half of the study area, where most of the wells had concentrations less than 1 mg/L.

Selenium is a naturally occurring metal that can cause a variety of health problems ranging from hair and fingernail loss to internal tissue damage and nervous and circulatory system problems. More than 40 wells have been sampled with selenium concentrations above 0.05 mg/L, the CBGWS for the compound. As with fluoride, elevated selenium concentrations occur almost exclusively in the eastern half of the study area, although the wells with highest selenium concentration do not commonly correlate with the wells with highest fluoride concentration.

Water quality standards that are based on the aesthetic characteristics of groundwater are frequently exceeded in domestic wells in the Mamm Creek study area. The most common constituent above CBGWS is TDS, which is above the applicable concentration standard of 500 mg/L in over 80 percent of the wells sampled. In general TDS is higher in the wells on the east side of the study area and off of the top of Grass Mesa on the west side of the study area. Chloride and sulfate exceeded the CBGWS of 250 mg/L in approximately 15 and 30 percent, respectively, of the domestic wells sampled. The distribution of wells with chloride in excess of 250 mg/L was not mapped in URS (2006); as explained above, the wells with high levels of sulfate are concentrated in the Dry Hollow Gulch area. Moderately high sulfate levels are also present on the west side of the study area east of Grass Mesa. Both the wells on top of Grass Mesa and the wells installed in alluvium have low levels of sulfate.

Iron and manganese, which can impart a metallic taste to water at relatively low concentrations, exceeded CBGWS (0.3 mg/L for iron and 0.05 mg/L for manganese) in approximately 25 percent of the domestic wells sampled.

2.4.3 Methane in Groundwater

The presence of methane in groundwater can occur due to biogenic degradation of organic matter, frequently generated in close proximity to where the methane is detected, or due to thermogenic formation by intense heating of organic matter. Methane formed in the latter manner, usually forms relatively distant from the groundwater where it is detected and migrates along either natural or anthropogenic pathways into the water supply aquifer. In the San Juan Basin in southwest Colorado, the migration of thermogenic methane into shallow aquifers near the northern edge of the basin is widespread; it is not known if this is the case in the Mamm Creek study area. To determine the origin of methane in groundwater, the relative concentrations of the carbon and hydrogen stable isotopes in the methane in the water are measured and evaluated.

The majority of domestic wells containing methane above a concentration of 0.5 mg/L (well below the COGCC advisory level of 2 mg/L) are located in the east half of the study area. The exception to this is along Mamm Creek (sections 20 and 29 of Township 6S, Range 92W) where methane above 0.5 mg/L has been detected in four domestic wells.

The Phase I Hydrogeologic Characterization Study (URS, 2006) indicated that the number of groundwater and surface water locations that contained methane has increased over time. It is not clear, however, that there is a widespread trend of increasing methane detections and concentrations from the data provided in the report since the number of sampled locations also increased over time. Further, for wells with multiple methane results where at least one result is greater than 1 mg/L, seven of the wells show generally decreasing trends in methane concentrations while three have generally increasing trends.

Review of isotope data from URS (2006) for nine domestic wells indicated that one well, located south of the narrow section of Dry Hollow Gulch (Section 3, Township 7S, Range 92W) had methane with a thermogenic signature. The well is approximately 1 mile west of the Schwartz 2-15B natural gas well that leaked methane to West Divide Creek. Two wells located along East Divide Creek approximately 1 mile northeast and 1 mile southeast of the location of the methane release in West Divide Creek contained methane with a mixed isotopic signature that was neither clearly of a thermogenic or a biogenic source. A third well with a mixed isotopic signature is located approximately 1 mile west of West Divide Creek and slightly more than 2 miles south of the Schwartz 2-15B gas well. Five domestic wells contained methane that had a clear biogenic signature, including three wells located along Dry Hollow Gulch just north and west of the domestic well with thermogenic methane and one well located very close to the Schwartz 2-15B gas well.

3.0 PHASE II WATER QUALITY SAMPLING PROGRAM

As explained above, the Mamm Creek Phase II water quality sampling program was a phased effort. Task 1 drinking water well and spring sample locations were determined from existing water quality sampling results and Task 2 gas well produced water and gas sample locations were determined based on both the Task 1 and previously existing sample results. A primary goal of this phased approach was to address both drinking water health concerns and to begin to evaluate the nature of the relationships, or lack thereof, between the alluvial and Tertiary drinking water aquifers and deeper natural gas producing horizons.

3.1 Task 1 Sampling Locations and Parameters

To establish the Task 1 sampling locations, the existing water quality database was reviewed and wells, springs, and surface water locations with one known previous sampling event that met one or more of the following criteria were tentatively identified for sampling: 1) the previous sample had concentrations in excess of CBGWS for fluoride, selenium, and/or nitrate; 2) the sample had an elevated TDS concentration (1,500 mg/L or greater) and a geochemical signature indicating a significant amount of both sodium and chloride in the water; and/or 3) methane had previously been detected at a concentration of 1 mg/L or greater. A total of 98 wells and springs were identified for Task 1 sampling in this data search. Of these locations, 66 were ultimately sampled. In several instances, permission to sample was refused; at other locations, wells had been abandoned or could not be sampled for a variety of reasons (e.g., well was dry, pump in well was inoperable, etc.). No spring locations were sampled because all locations identified were part of irrigation works and agricultural return flows consisting primarily of diverted surface irrigation water were included in the water at the sample location.

Sample parameters were determined based on the initial sample results from each well. Three individual programs were designed depending on whether sampling was motivated by 1) exceedances of CBGWS for the drinking water health parameters nitrate, fluoride, and/or selenium; 2) the presence of methane in the well; and/or 3) elevated TDS with significant concentrations of sodium and chloride. Analytical parameters included major ions and cations; regulated inorganic compounds, inorganic tracers, dissolved methane, and gas composition and stable carbon and hydrogen isotopes of methane. The specific parameter list for each situation is provided in the Task 1 Field Sampling Plan in Appendix A. Sampling methods used in the field are also provided in the Task 1 Field Sampling Plan.

3.2 Task 2 Sampling Locations and Parameters

Following completion of Task 1 sampling and validation of results, the new analytical data was added to the water quality database for the Mamm Creek study area and initial evaluation of the data was conducted to identify the location of areas for Task 2 sampling. By design of the Scope of Work for the Phase II study, Task 2 sampling was directed at the collection of natural gas and produced water samples from gas wells in areas where specific criteria were met for Task 1 and earlier water quality sampling. Two criteria were used to establish Task 2 sampling points: 1) presence of possible thermogenic methane in wells or springs based on examination of carbon-13 (^{13}C) and deuterium (^{2}H) isotopes of methane, and 2) on the presence of high TDS groundwater that indicated possible influence or mixing with Na-Cl water.

For locations flagged for either of the criteria, gas wells located within approximately one mile of the flagged location were identified for possible Task 2 sampling. By the Scope of Work for the project, the nearest two up-gradient gas wells were to be sampled for the water wells/springs targeted for further investigation. However, several factors made the selection of gas wells for sampling very challenging. Initially, gas wells in the direction most likely to be up-gradient of the previously sampled wells were targeted, however, in some cases the nearest gas wells were downgradient of the previously sampled wells. In some cases, there were no active gas wells within one mile of the water sampling points. Gas well selection was further complicated by the methods involved in developing the natural gas resource in the area. Complicating factors included:

- Installation of multiple wells within a few feet of each other at a single well pad;
- Significant deviation from vertical at depth for most wells at a well pad;
- Presence of wells that were shut-in and not able to be sampled; and
- Commingling of produced water with other wells at a well pad prior to any sampling point.

After factoring in the above criteria, of the 28 gas well locations initially identified for sampling, samples were collected at 18 locations. Produced water samples were collected at 16 locations and production gas samples were collected at four locations (at two of these locations, water was not being produced and so no water samples were collected). The produced water samples were analyzed for major ions and for tracer compounds and the production gas samples were analyzed for gas composition and for methane isotopes. Specific parameter lists for both sets of samples are provided in Task 2 Field Sampling Plan, which is included in Appendix B of this report.

The gas well sampling was conducted with the assistance of personnel from the operator's whose wells were sampled, either Encana Oil and Gas (USA), Inc., or Bill Barrett Corporation. Sampling methods were approximately as described in the Task 2 Field Sampling Plan (Appendix B).

4.0 SUMMARY OF GROUNDWATER QUALITY CONDITIONS

This section summarizes analytical results for water quality parameters and for gas composition and methane stable isotopes for groundwater samples collected for Task 1 of the Mamm Creek Phase II hydrogeologic investigation and for produced water and natural gas samples collected for Task 2 of the investigation.

Task 1 water quality and dissolved gas/isotope samples were collected between June 8 and July 14, 2007, with Quality Assurance/Quality Control (QA/QC) samples collected on September 5 and 6, 2007. Where applicable, the results are compared to CBGWS for domestic groundwater supply systems as specified in Colorado Water Quality Control Commission regulation 5 CCR 1002-41. These results and results from previous sampling in the Mamm Creek study area were evaluated with respect to overall hydrologic setting and for potential effects from shallow contaminant sources or from deeper sources of groundwater or natural gas. The gas composition and stable isotope analyses provide insights into the origins of gases present in the groundwater.

Task 2 produced water and production gas sampling was conducted on December 5 and 6, 2007, with the cooperation and assistance of personnel from EnCana Oil and Gas (USA), Inc., and Bill Barrett Corporation, whose wells were being sampled. Sampling locations were selected on the basis of results from the Task 1 sampling, as well as on the review of domestic well analytical results from previous sampling in the Mamm Creek study area.

4.1 Analytical Results

4.1.1 Task 1 Analyses

ACZ Laboratories in Steamboat Springs, Colorado, analyzed groundwater samples from 66 domestic water wells for major anions and cations, metals, halides, and dissolved methane. Locations of the wells sampled are shown on Figure 4.1. Electronic results were incorporated into the geochemistry database provided by the COGCC for Garfield County Townships 6S and 7S and Ranges 92W and 93W that was used initially to establish Task 1 sampling points. Laboratory reports for the Task 1 groundwater analyses are provided in Appendix C and summarized in Table 4.1.

Isotech Laboratories in Champaign, Illinois, analyzed water or headspace gas samples from 11 domestic wells (shown on Figure 4.1) for chromatographic gas composition and stable isotopes of methane. Electronic results were added to the COGCC Mamm Creek area geochemistry database. The laboratory reports for the samples are provided in Appendix D and summaries of results are presented in Table 4.2. Gas composition was measured for the common atmospheric gases helium (He), hydrogen (H_2), argon (Ar), nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO), and for C1 through C6 hydrocarbon gases (methane, ethane, propane, isobutane, n-butane, isopentane, n-pentane, and hexane). Results are reported as the molar percentage of each gas (where total gases equal 100 percent). The detection limits for the gases ranged from 10 to 50 parts per million by volume (ppmv) in undiluted samples of headspace gas. Where no headspace gas accumulates during sampling (see Appendix A for sampling methods), dissolved gases were stripped from the water samples in the laboratory using helium as a carrier gas and resultant quantitation limits were 3-4 times higher.

For the gas isotope analyses, both carbon and hydrogen stable isotopes of methane (^{13}C for carbon and ^{2}H, or D, for hydrogen) were analyzed. The results are reported in standard delta (δ) notation in units of per mil or parts per thousand (‰) which scales the isotope ratio ($^{13}C/^{12}C$ for carbon and $^{2}H/^{1}H$ for hydrogen) of the sample to that of universally accepted standard reference materials. For carbon isotope analysis, $\delta^{13}C$ is defined as

$$\delta^{13}\mathrm{C} = \frac{R_S - R_{PDB}}{R_{PDB}} \times 1000$$

where R denotes the ratio of the heavy to light isotope ($^{13}C/^{12}C$), and R_S and R_{PDB} are the ratios in the sample and standard, respectively. The reference standard for ^{13}C is the Pee Dee Belemnite (PDB), a calcite ($CaCO_3$), which by definition has a $\delta^{13}C$ value of 0. A positive δ value means that the isotopic ratio of the sample is higher (i.e. has more of the heavy isotope) than the standard; a negative δ value means that the isotopic ratio of the sample is lower (i.e. has less of the heavy isotope) than the standard. For example, a $\delta^{13}C$ value of -20 per mil ($\delta^{13}C$ = -20 ‰) means that the $^{13}C/^{12}C$ ratio of the sample is 20 parts per thousand or 2.0 percent lower than that of the PDB standard.

The heavy stable hydrogen isotope, ^{2}H, is also commonly referred to as deuterium (D). Similar to δ^{13}C, δD is defined as

$$\delta\mathrm{D} = \frac{R_S - R_{VSMOW}}{R_{VSMOW}} \times 1000$$

where R denotes the ratio of the heavy to light isotope (D/^{1}H), and R_S and R_{VSMOW} are the ratios in the sample and standard, respectively. The reference standard for D is Vienna Standard Mean Ocean Water (VSMOW), which by definition has a δD value of 0. A positive δ value means that the isotopic ratio of the sample is higher (i.e. has more of the heavy isotope) than the standard; a negative δ value means that the isotopic ratio of the sample is lower (i.e. has less of the heavy isotope) than the standard.

Both δ^{13}C and δD in methane tend to be depleted relative to their respective standards; δ^{13}C generally ranges between -100 to -20 ‰ while δD varies from about -400 to -100 ‰. In samples measured for gas composition and isotopes, the relationship between the two values can be used to provide insight as to the source of the gas.

4.1.2 Task 2 Analyses

Twenty-eight produced water sampling locations were identified for the Task 2 event and 16 produced water samples were collected. At nine locations, the wells were shut-in or water was not being produced. Of the 16 samples, 12 were collected from pads containing multiple wells. Where possible, the produced water sample streams were isolated to particular wells of interest; however, at a few locations it was necessary to sample from holding tanks or piping that potentially had mixed water from multiple wells. The produced water samples were analyzed by ACZ Laboratories for major anions and cations, metals, and halides. The produced water sample locations are shown on Figure 4.2. Laboratory reports for the Task 2 analyses are contained in Appendix C and the water quality results are summarized in Table 4.3.

Production gas samples were collected from specific wells at a subset of the locations where produced water samples were collected. The decision to collect gas samples was based on proximity to domestic wells where elevated concentrations of methane had been detected and/or where gas composition and stable isotope analysis indicated a possible thermogenic source for methane present in the groundwater. Nine wells were proposed for gas composition and stable isotope sampling, however, only four samples could be collected because several wells of interest were shut-in and fresh flowing gas could not be obtained. The produced gas samples were analyzed by Isotech Laboratories. The wells where gas samples were collected are shown on Figure 4.2. Gas composition and stable isotope laboratory reports are provided in Appendix D and results are summarized in Table 4.2.

4.2 Human Health and Drinking Water Standards

Task 1 analytical results were screened for exceedances of CBGWS for human health and drinking water quality parameters as established in 5 CCR 1002-41 for domestic groundwater supply systems. The *human health standards* (which are equivalent for most compounds to federal maximum contaminant levels, or MCLs) are established based on potential health effects resulting from exposure to drinking water containing a regulated compound. In the Mamm Creek study area, three compounds with potential health effects—nitrate, fluoride, and selenium—have been detected above CBGWS. In contrast to the human health standards, *water quality standards* (which are generally equivalent to federal secondary MCLs, or SMCLs) are related to the aesthetic qualities of water, such as odor and taste. In the Mamm Creek study area, analyzed compounds that have water quality standards are chloride, sulfate, iron, and TDS, all of which have been detected at concentrations above their respective standards.

While there is no regulated standard for methane in groundwater, it is also discussed in this section because excessively high concentrations of methane in water can lead to potentially explosive conditions in holding tanks or other confined spaces such as well pits or basements.

There are several readily available sources that examine the potential effects of drinking water containing compounds at concentrations above CBGWS. A pamphlet providing information about these and other compounds was prepared for well owners whose wells were sampled for this study. A copy of the pamphlet is provided in Appendix E.

4.2.1 Results of Human Health Standards Analyses

For the Task 1 sampling event, nitrate, fluoride, and selenium were the compounds analyzed for which human health standards exist. Nitrate was detected in 56 of the 66 wells sampled and nitrate concentrations exceeded the CBGWS of 10 mg/L of nitrate as nitrogen

(NO_3-N) in three wells (see Table 4.1 and Figure 4.3). Additionally, one well had a concentration of 9.9 mg/L, just below the standard. Fluoride was detected in 53 of 61 wells sampled and equaled or exceeded the CBGWS of 4 mg/L in four wells (see Table 4.1 and Figure 4.4). Selenium was detected in all of the 50 wells where it was sampled and selenium concentrations were above the CBGWS of 0.05 mg/L in 10 wells (see Table 4.1 and Figure 4.5). No other parameters with CBGWS for human health were analyzed in the Task 1 sampling. The review of previous sample results for the Mamm Creek area (URS, 2006) indicated that the only other compound detected above human health standards in any domestic water supply wells has been arsenic in a very limited number of samples. None of wells selected for Task 1 sampling had previous arsenic concentrations above the CBGWS of 0.01 mg/L and so the compound was not included in the sampling.

4.2.2 Results of Water Quality Standards Analyses

CBGWS for drinking water quality are established as guidelines for domestic water supply aesthetics and are not enforced standards. Concentrations of sulfate, chloride, iron, and TDS exceeded CBGWS drinking water limits for several of the wells sampled during the Task 1 sampling event (Table 4.1). Additionally, the hardness of water—which is caused primarily by dissolved minerals such as calcium and magnesium—while not regulated, also affects the taste and usefulness of the water. In general, the harder the water, the more it causes deposits of calcium carbonate to build up on plumbing and on certain appliances and the more it affects the effectiveness of soaps and detergents. In the Mamm Creek study area very hard water is a common occurrence. The results of the Task 1 analyses for the water quality standards compounds and for hardness are summarized below. (Appendix E provides information about the specific effects of each of the compounds.)

- Sulfate was detected in all 66 wells sampled and exceeded the standard of 250 mg/L in 31 of the wells (see Figure 4.6). Its maximum concentration was 4,590 mg/L in well 704479; the next highest concentration was 2,500 mg/L in well 704053.
- Chloride was detected in all 66 wells sampled and exceeded the standard of 250 mg/L in 11 wells (see Figure 4.7). Its maximum concentration, detected in wells 704479 and 704330, was 1,790 mg/L.

- Iron was analyzed for in all wells and was detected in 18. Its concentration exceeded the standard of 0.3 mg/L in 4 wells; its maximum concentration was 1.92 mg/L in well 704322.
- TDS were present at detectable concentrations in all 66 wells sampled (Figure 4.8). In the Mamm Creek area, TDS has an effective CBGWS of 500 mg/L. This standard was exceeded in 56 wells. The maximum TDS was 10,100 mg/L in well 704479; the next highest concentration was 4,290 mg/L in well 704053.
- Hardness in the wells sampled during the Task 1 sampling even ranged from 22 mg/L to 2,370 mg/L (or 1.3 to 140 grains per gallon using units common in the water treatment industry). Water with hardness above 120 mg/L (7 grains per gallon) is considered to be hard or very hard; 50 of the 66 wells sampled had hardness values that exceeded 120 mg/L.

4.2.3 Dissolved Methane Analyses

Methane does not have a human health or water quality standard, but its presence in groundwater can be a concern because of the explosive characteristics of the compound. While it may occur from decomposition of organic matter in relatively shallow water supply aquifers, it is also considered to be an early indicator of possible impacts to drinking water aquifers from deeper gas-bearing formations. As such, it is tracked by the COGCC where it occurs in groundwater in areas of oil and gas exploration and production. The COGCC normally recommends resampling for wells where methane in the water exceeds 1 mg/L; where concentrations exceed 2 mg/L, COGCC recommends that follow up sampling be conducted and that the sampling include gas composition and stable isotope analysis in order to evaluate whether the gas in the water is of thermogenic origin, which may indicate impacts from deeper formations.

For the Mamm Creek Phase II investigation, dissolved methane was sampled in 13 wells during the Task 1 sampling event at locations where it had been identified previously at concentrations above 1 mg/L. As shown in Table 4.1 and on Figure 4.9, dissolved methane was detected in 12 of the samples, and exceeded the COGCC recommended gas composition and isotope analysis sampling concentration of 2 mg/L at four of the locations. Additionally, it was just below that limit at 1.9 mg/L in one other well. The maximum dissolved methane concentration detected during Task 1 sampling was 11 mg/L in well 704330, a well that had a previous dissolved methane concentration of 3.62 mg/L when sampled in January 2003. Because of the nature of the Task 1 sampling event, gas composition and stable isotope sampling was conducted concurrently with the water sampling. Ultimately, for 11 of the 13 Task 1 samples where dissolved methane was analyzed, analyses were also conducted for gas composition and stable isotopes; in wells 704010 and 704534 there was insufficient gas in the samples to allow analysis. Gas composition and stable isotope analyses are discussed in Section 4.4, below.

4.3 Groundwater Chemistry Characteristics

The geochemical nature of the groundwater used by residents in the Mamm Creek study area and recovered in conjunction with natural gas production was evaluated based on water chemistry analyses for wells sampled during the Task 1 and Task 2 sampling events, with reference back to previous sampling conducted in the study area.

4.3.1 Task 1 Domestic Water Major Ion Chemistry

Concentration distribution maps, Piper trilinear diagrams, and Stiff plots are three tools that can be applied to illustrate the different geographic and geochemical characteristics of the analytical results for the study area. Piper diagrams use major cation and anion concentrations to demonstrate relationships in a sample or among multiple samples or sample groups (Hem, 1985) while Stiff plots and concentration distribution maps assist in evaluating geochemical characteristics in an areal sense. Stiff plots can be used to evaluate individual water sample characteristics among a group either with or without an emphasis on geographic distribution.[2]

Piper diagrams, which plot relative proportions of major cations and anions in water samples, can be used to evaluate the overall chemical characteristics of the groundwater present over large areas for one or more aquifers. Specifically, the evolution of the groundwater as it travels in the subsurface can often be extrapolated from Piper diagrams that incorporate analytical results from a sufficiently large number of samples for a given area and/or period of time. Piper diagrams for the wells sampled for Task 1 are shown in Figures 4.10 and 4.11. These plots illustrate the trends in groundwater chemistry across the study area primarily for the Wasatch Formation aquifer (only two of the wells sampled for Task 1, 703266 and 704479, are known to be completed in alluvium). In the Piper diagram shown in Figure 4.10, the TDS ranges for the samples are distinguished from each other by symbol shape and color; in Figure 4.11, the sample results are differentiated as a function of well depth.

For Figure 4.10, where TDS ranges are differentiated, the cation base triangle on the lower left portion of the diagram shows that the groundwater in the study area tends either to have a relatively even mix of all three major cation groups (calcium, magnesium, and sodium plus potassium) or, with increased TDS, to trend towards a system strongly dominated by sodium. This is a common trend for groundwater, where as subsurface flowpaths increase in length and the residence time of the water grows longer, TDS increases as sodium in the aquifer host rocks is released into the water as a soluble cation. Calcium, which will precipitate out of the water as calcium carbonate ($CaCO_3$) in the presence of carbonate (CO_3) or bicarbonate (HCO_3) anions, is less likely to increase in concentration and in many cases may decrease across some ranges of TDS. For the Task 1 samples, there are relatively few samples that plot midway between the mixed cation and the sodium-dominated groups. Conditions that could be responsible for this pattern include: 1) the flow of groundwater along distinctly different shallow pathways; and/or 2) localized vertical upward flow of sodium-rich water from deeper in the Wasatch Formation or the Williams Fork Formation along natural open-fracture pathways or pathways such as well bores or hydraulically opened fractures. While considered unlikely over most of the Piceance Basin, fractures or faults accommodating flow from the Cretaceous Williams Fork Formation to the overlying Tertiary rocks are plausible in the vicinity of the Divide Creek Anticline (Tyler, 1996; Kaiser and Scott, 1996).

The anion base triangle on the lower right portion of the Piper diagram demonstrates the evolution from bicarbonate to sulfate domination as TDS increases. The spread of the data towards chloride for moderate and high TDS waters could result simply from heterogeneities arising from differing geology within the Wasatch aquifer for various shallow recharge areas and subsurface flowpaths or it could indicate mixing of deeper groundwater with water from the Wasatch aquifer.

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[2] While most concentration distribution maps are based on mass quantities of constituents, usually reported in mg/L, for both Piper diagrams and Stiff plots the reactive quantities of the ions, measured in meq/L, are the basis for the plots.

The central diamond portion of the Piper diagram compares both anion and cation characteristics for the water samples and illustrates the geochemical signature of the water. For example, water that would be considered to have a Ca-HCO_3 signature would plot within the left quarter-diamond of the central diamond. The farther to the left, the more strongly the water would have that signature. For the Task 1 sampling, the central diamond of the Piper diagram clearly shows the trend towards increasing sulfate and the dominance of sodium with increasing TDS. The diagram also illustrates the bimodal distribution between these waters and the waters with lower TDS that have Ca-Mg-Cl geochemical signatures.

Well depth information was provided by approximately two-thirds of the well owners during Task 1 sampling. The Piper diagram in Figure 4.11 includes only those wells where well depth information was obtained from the owners. While Figure 4.10 shows a general progression in the geochemical nature of the water in the Mamm Creek study area by TDS levels, it is harder to discern a similar pattern related to depth. This uncertainty highlights a complexity of the Wasatch aquifer that may be the result of the existence of vertical flowpaths in the subsurface between not only the surface and the aquifer (resulting in the influx of relatively low TDS water from precipitation), but also between the Wasatch aquifer and deeper sections of the Wasatch Formation or the Williams Fork Formation.

As can be seen in Figures 4.10 and 4.11, only one sample (from well 704330) has a strong Na-Cl signature that clearly suggests significant impacts from a brine or salt water source. The well is located in the southeast corner of the study area (see Figure 4.1). It is within 1 to 2 miles of two other wells which had Na-Cl signatures from previous sampling events (see Figure 5-6 in URS, 2006) and in an area of relatively minor oil and gas activity to date.

Figures 4.12 and 4.13 are mass ratio distribution maps for Na/(Ca+Mg) and SO_4/HCO_3, respectively, for the Task 1 samples. These maps are provided in addition to earlier concentration distribution maps (Figures 4.6 through 4.8) to allow geographic characteristics of sampled groundwater to be evaluated for the study area. The figures provide a means to evaluate potential effects of surface recharge and trends in groundwater chemistry along subsurface flowpaths. Although most of the wells in the study area are completed in the Wasatch Formation, there is not a gradual increase in ratios from south to north in the primary flow direction as might be expected. Rather, the figures indicate that the influences of surface recharge may have an appreciable effect on water quality on Grass Mesa and in parts of the southeast portion of the study area. In contrast, many of the wells in the Dry Hollow Creek area above the north flank of Divide Creek Anticline have significantly higher ratios for both Na/(Ca+Mg) and SO_4/HCO_3, suggesting much different flow pathways for specific areas.

Figure 4.14 overlays Stiff plots for selected wells in the study area to facilitate evaluation of general groundwater geochemistry over the entire area. The Figure illustrates the differences discussed above between the northeast portion of the study area and the other regions. Further, the plot highlights both well 704330, the well with a Na-Cl geochemical signature discussed above, and well 704479. Well 704479 is an alluvial well located in the northwest portion of the study area adjacent to Last Chance Ditch. Both this sample and the previous sample from the well (collected in August 2004) had extremely high TDS concentrations (10,100 mg/L in 2007 and 8,800 mg/L in 2004) and the water from both samples is classified as Na-SO_4. As discussed below, impacts from shallow sources are suspected for this well.

4.3.2 Task 2 Produced Water Major Ion Chemistry

For the 16 Task 2 produced water samples all but one had elevated TDS concentrations (7,390 mg/L to 21,700 mg/L), as is normally the case for water produced from natural gas wells completed in the Williams Fork Formation. In contrast, the sample from well 05-045-06934 (see Figure 4.2) had a TDS concentration of 690 mg/L—more than an order of magnitude lower than any of the other produced water samples and lower than almost 75 percent of the domestic wells sampled for this study. As shown on the lower portion of Table 4.3 and on the Piper diagram in Figure 4.15, 12 of the 16 samples had very distinct Na-Cl geochemical signatures, including well 05-045-06934. Three wells had Na-HCO_3 signatures, which is a common characteristic of water produced from coalbed methane wells. It is possible that these wells are perforated in Williams Fork Formation coalbeds as well as in gas-bearing sandstones and that the majority of the water produced from them is from the coal-bearing intervals. One well, 05-045-09156, had similar reactive amounts of chloride and HCO_3 and lies on the cation mixing line between the Na-Cl and the Na-HCO3 samples. This well may produce water from both coal and sandstone perforated intervals.

Sulfate is almost completely absent from all of the produced water samples. This is likely due to the reduction of any sulfate which may have been present in the formation water as it reacted with organic compounds in the host rocks (Van Voast, 2003).

4.3.3 Geochemical Mass Ratio Analysis

Williams Fork Formation strata in the eastern Piceance Basin were deposited in marginal marine, coastal plain, and alluvial plain environments. While not truly marine, the strata were deposited in low-lying areas near the interior seaway that existed to the east and southeast during the late Cretaceous period and the streams, swamps and bays where the sediments accumulated were frequently within salt water regimes. As such, water contained within the Williams Fork Formation is normally brackish, with elevated TDS and Na-Cl concentrations. While not as saline as normal ocean water, Williams Fork Formation waters bear some geochemical similarities to ocean waters.

The ocean water influence distinguishes the Williams Fork from the overlying Wasatch Formation and may allow potential Na-Cl impacts in the Wasatch aquifer to be investigated through the use of certain compounds that are characteristic constituents of ocean waters or brines (e.g., Davis et al., 1998; Vengosh and Pankratov, 1998; Panno et al., 2006). Often these compounds are trace elements that are not major constituents of either fresh or saline water. To investigate possible characteristics that could potentially identify impacts to shallow freshwater impacts by deeper more saline water, in wells identified prior to the Task 1 sampling as having either a Na-Cl signature or elevated TDS with relatively high proportions of sodium and chloride, samples were analyzed for bromide (Br), boron (B), and strontium (Sr) in addition to the standard suite of cations and anions. To provide a comparative basis, all of the Task 2 produced water samples were also analyzed for bromide, boron, and strontium in addition to the standard cations and anions.[3] The COGCC database includes bromide, boron, and strontium analyses for several domestic wells, a subset of which were deemed useful for this study. For

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[3] The Task 2 produced water samples used for trace element evaluations included the primary analyses for 14 of the wells. Well 05-045-11402 had a cation-anion balance of -16.1 percent and so the duplicate sample for the well, which had a cation-anion balance of -1.7 percent, was used instead. The sample from well 05-045-10106 was dropped from ratio evaluation because it had a cation-anion balance of -15.1 percent, well above the standard acceptance limit of ± 10 percent.

produced water samples the database included four samples for boron, but none for either bromide or strontium.

Cl/Br is the most commonly used mass ratio for water source analysis involving potential mixing of ocean waters or subsurface brines (or anthropogenic sources) with groundwater supply aquifers. Cl/Br ratios for both the domestic water and produced water samples collected for the Mamm Creek Phase II investigation are shown plotted against chloride concentrations on Figure 4.16a. Also shown on the figure is the normal range for Cl/Br ratios for pristine groundwater with chloride concentrations less than 200 mg/L and the ocean water mean Cl/Br ratio of approximately 290 (Davis et al., 1998). Review of bromide concentrations and ratios for samples from the Mamm Creek study area indicates the following:

- The Cl/Br ratios in the produced water averaged 207 ± 49 for the 15 samples evaluated and had no discernable trend with increasing chloride concentration. Except for well 05-045-09418, which had a Cl/Br ratio of 311, all of the Cl/Br ratios were below the mean standard seawater value of 290 (Davis, et al., 1998).
- With few exceptions, samples from domestic wells in the Mamm Creek area with chloride less than 200 mg/L fall within the expected range for Cl/Br (less than 200). As shown in Figure 4.16a, where chloride concentrations are above 200 mg/L, Cl/Br ratios are usually similar to the produced water samples, whether or not the domestic water had a Na-Cl geochemical signature.
- Domestic well 704479 had the highest Cl/Br ratio (approximately 450) of all the wells sampled. The well, which had a TDS concentration of 10,100 mg/L when sampled in June 2007 and a Na-SO_4 geochemical signature, is located adjacent to Last Chance Ditch, within one-half mile of the Colorado River, and north of the natural gas development in the area. The elevated Cl/Br ratio suggests that the well is impacted by one or more common anthropogenic sources such as road salt, septic effluents, animal wastes, or agricultural return flows from the adjacent irrigation ditch and/or farm fields.
- Because of the similarity between Cl/Br ratios for domestic water and for produced water in the Mamm Creek area (except for well 704479), it is not possible to evaluate mixing of the Wasatch and Williams Fork water sources based on Cl/Br ratios.

Boron has a measurable concentration in ocean water of approximately 4.6 mg/L (Hem, 1985, after Goldberg, et al., 1971) and is often present in groundwater at concentrations within the range of measurement for standard analytical techniques. Similar to the Cl/Br mass ratios, Cl/B mass ratios for both domestic water and produced water are plotted against chloride concentration on Figures 4.16b. Evaluation of this plot indicates the following:

- There is a strong positive correlation between Cl/B and chloride concentration for the domestic well samples. (The one well that falls outside the trend is 704479, which has a low Cl/B ratio given the elevated chloride concentration for the well. Because boron is commonly added to fertilizers; the elevated boron concentration in the well suggests that agricultural return flows may impact the well.)
- Cl/B ratios in produced water have a similar, although less distinct, positive correlation with chloride concentration, except that the produced water is apparently enriched in boron relative to the domestic water. In is possible, therefore, that the enrichment of produced water from the Williams Fork Formation in boron may allow potential mixing between the Wasatch Formation aquifer and deeper groundwater to be identified. More realistically, impacts due to shallow anthropogenic sources are more likely to be identified using Cl/B ratios (e.g., as shown by domestic well 704479).

Strontium concentration in modern seawater is approximately 8 mg/L (Hem, 1985, after Goldberg, et al., 1971). Similar to bromide and boron, strontium is also commonly present at low but detectable concentrations in drinking water aquifer samples. As such, Cl/Sr mass ratios for both domestic water and produced water are plotted against chloride concentration on Figure 4.17a. Additionally, because of the geochemical similarities and affinities for strontium with calcium, Ca/Sr is plotted against chloride concentration in Figure 4.17b. Review of these plots indicates the following:

- In the produced water samples from the Williams Fork Formation in the Mamm Creek study area, strontium concentrations ranged from 4.5 to 145 mg/L and correlates directly with increasing chloride concentration. Cl/Sr ratio for all of the produced water samples is 144 ± 66, well below the expected seawater ratio of approximately 2,400, indicating that Williams Fork water is enhanced in strontium.
- Domestic water samples showed a generally increasing Cl/Sr trend with increasing chloride concentration (Figure 4.17a). Because the domestic water Cl/Sr ratios overlap the Cl/Sr ratios for the produced water samples, it is unlikely that Cl/Sr ratios can be used to discern impacts of deep formation water on domestic water in the Mamm Creek area.
- Strontium is chemically similar to calcium and frequently replaces it in geologic materials. The strontium concentrations in the produced correlated directly with increasing calcium concentrations resulting in Ca/Sr ratio in the produced water was very stable across the whole range of samples (5.5 ± 1.6). In contrast, the domestic water samples had Ca/Sr ratios that were considerably higher than the produced water samples and that did not correlate closely calcium concentrations (Figure 4.17b).
- Based on the distinct differences in Ca/Sr ratios between domestic water and produced water in the Mamm Creek area, it may be possible to tentatively identify

impacts from deeper sources for domestic wells that have anomalously low Ca/Sr ratios.

In addition to the compounds discussed above, relative concentrations and ratios of major ions may also yield insights into water sources. For the Mamm Creek area, plots of SO_4 against chloride and the ratio of SO_4/Cl against chloride illustrate distinctive characteristics between the domestic water and Williams Fork Formation produced water (see Figures 4.18a and 4.18b). The nearly complete lack of sulfate in the produced water contrasts sharply with the Wasatch and alluvial aquifers which normally have detectable sulfate concentrations even when TDS is very low. Domestic wells, such as 704330, with elevated chloride and anomalously low sulfate potentially may indicate impacts from deeper formation water mixing with Wasatch aquifer water. In contrast, well 704479, which also has a high chloride concentration, is very dissimilar when compared to the produced water, and apparently does not indicate mixing with Williams Fork Formation water.

4.4 Gas Composition and Methane Stable Isotopes in Groundwater and Natural Gas

Methane gas of both biogenic and thermogenic origin has been detected in groundwater in the Mamm Creek study area. Biogenic methane commonly forms in shallowly buried organic-rich deposits such as peat or from decaying organic matter in oxygen-deficient water bodies. Biogenic methane is produced from these deposits by microbial activity via two mechanisms: (1) fermentation reactions in anaerobic conditions or (2) carbonate reduction reactions in marine or freshwater environments. Thermogenic methane, in contrast, is produced from thermal degradation of organic matter in sedimentary deposits. Normally in this process, organic matter that has accumulated in sedimentary deposits that are deeply buried becomes hot enough that the organic matter is first converted to hydrocarbon liquids and then, with increasing heat, to hydrocarbon gases, that may include or be dominated by methane.

The isotopic signatures of carbon and hydrogen in methane reflect its source, the conditions (temperature, in particular) under which it was generated, and effects of subsequent oxidation reactions. Generally, biogenic methane will have very low $\delta^{13}C$ values (less than -50 ‰), whereas thermogenic methane is characterized by less negative $\delta^{13}C$ values (normally between -50 and -20 ‰). Biogenic methane has a wide range of δD values (from -100 to -400

‰) depending on the formation reaction, and thermogenic methane can have δD values that cover a significant portion of the biogenic methane range for δD. Oxidation reactions, which convert methane to carbon dioxide, affect isotopic ratios, shifting both $\delta^{13}C$ and δD values in a more positive direction. In other words, as methane is oxidized to carbon dioxide, molecules containing the heavier isotopes tend to be less reactive than the lighter molecules; and through this isotopic fractionation process, the remaining methane becomes progressively more enriched in the heavier isotopes as it is oxidized. This increase in $\delta^{13}C$ and δD values may result in the isotopic signatures of biogenic methane overlapping with those of thermogenic methane.

In these situations, the evaluation of heavier hydrocarbons can often provide additional insight on the source(s) of the methane. One tool used to evaluate methane source using heavier hydrocarbons is the Bernard diagram (Whiticar, 1990; based on Bernard et al., 1978), which plots $\delta^{13}C$ against the hydrocarbon gas ratio C1/(C2+C3). Because the heavier hydrocarbons, or wet gases (C2 and C3 and heavier), are not readily formed by microbial activity, the presence of heavier hydrocarbons (i.e., a lower C1/(C2+C3) ratio) suggests a thermogenic or a mixed methane source.

Gas composition and stable isotope data were collected for the Mamm Creek Phase II hydrogeologic investigation. For Task 1, dissolved gases in groundwater were analyzed from a subset of the wells for which groundwater samples were collected; for Task 2, production gas samples were collected from four natural gas wells in conjunction with collection of produced water samples. Data from the gas sampling were added to the existing COGCC database, which also included previously collected gas composition and stable isotope data for domestic and monitoring wells, surface water, produced water, and natural gas wells. For the isotope samples, all useable sampling locations from that database are included on Figure 4.19, which plots $\delta^{13}C$ against δD for methane, and on the Bernard diagram shown on Figure 4.20.[4] Regions that correspond to biogenic and thermogenic origin (as adapted from Whiticar, 1990) are highlighted on both plots.

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[4] Several locations have multiple gas composition and isotope results; in many cases results between samples are similar and so mean isotope ratios were calculated and plotted on the figures. In a few cases, trends in the data were observed; however , the $\delta^{13}C$ and δD ratios were constrained within a range that did not preclude calculation of mean values for use in the figures. In only two cases were multiple measurements from the same sample location plotted on the figures.

For the Task 2 sampling, natural gas samples were collected from four producing gas wells in order to provide baseline information on the natural gas being produced by operators in the study area. As shown on Table 4.2, the gas compositional analysis conducted on the production gas samples was similar both for the hydrocarbon and non-hydrocarbon gases. As would be expected, methane was the predominant gas in the samples and ranged from 83.1 to 84.8 molar percent of all the gases in the samples. In addition to methane, all four of the produced gas samples contained measurable concentrations of heavier C2 through C6+ hydrocarbon gases. In total, hydrocarbon gases constituted between 96.4 and 99.3 molar percent of each gas sample. The 2.9 molar percent difference in carbon dioxide between well 05-045-07155 (0.6 molar percent) and well 05-045-13527 (3.5 molar percent) was the largest difference measured between wells for any of the gases, whether hydrocarbon or non-hydrocarbon.

As for the gas composition, the ^{13}C and D methane isotopic signatures for the Task 2 production gas samples were very similar ($\delta^{13}C = -41.6 \pm 0.2$ ‰ and $\delta D = -196.0 \pm 3.3$ ‰ for the four samples). As shown in Figure 4.19, the Task 2 produced gases cluster near the center of the region that includes samples from other gas wells in the study area, and clearly in the region for gases of thermogenic origin. Further, as can be seen on Bernard diagram on Figure 4.20, the thermogenic origin for the production gases sampled during Task 2 is confirmed by the low C1/(C2+C3) gas ratios of the samples.

In contrast to the production gas samples, the composition of the most common dissolved gases in the groundwater sampled during Task 1 varied considerably (see Table 4.2). The gas compositional analysis conducted on the dissolved or headspace gases from 11 domestic wells in the study area indicates that for most of the samples the predominant non-hydrocarbon gases in the groundwater sampled were nitrogen, oxygen, carbon dioxide, and argon. Nitrogen varied from 5 to 84 percent in the samples and always had the highest concentration of the non-hydrocarbon gases. Concentrations of the other three gases were considerably lower and were variable relative to each other from sample to sample.

For hydrocarbon gases, methane was detected in 9 of the 11 samples submitted for dissolved gas analysis. Methane content in the samples ranged from 0.06 to 93.31 molar percent. Heavier hydrocarbons were also detected in some samples:

- Ethane (C2) was detected in 6 samples and ranged between 0.0085 and 0.35 molar percent;
- Propane (C3) was detected in 2 samples at 0.0014 and 0.0055 molar percent; and
- Isobutane (iC4) was detected in 1 sample at 0.0024 molar percent.

Seven of the 11 gas samples contained sufficient quantities of methane to perform stable isotope analysis. In those samples the $\delta^{13}C$ and δD of methane varied considerably; $\delta^{13}C$ ranged between -64.91 and -36.97 ‰, while the δD ranged between -236.5 and -119.6 ‰.

As can be seen in Figure 4.19, the methane $\delta^{13}C$ vs. δD points for the domestic and monitoring well and surface water samples (including the Task 1 samples) are distributed across a wide area. Some samples clearly lie in the biogenic fermentation and carbonate reduction fields, while many more are scattered across the thermogenic range. The figure also shows the normal direction of the isotopic fractionation shift caused by the oxidation of methane. The plot suggests that methane detected in many of the domestic wells is biogenic in origin, with some evidence of various degrees of methane oxidation. Similar oxidation-related trends appear to occur for samples from the monitoring wells installed in the vicinity of West Divide Creek methane release, although the methane at most of the monitoring well locations appears to have a thermogenic source.

The Bernard diagram shown on Figure 4.20 shows that in the Mamm Creek study area, production gas samples (all of which were collected from produced water streams prior to this investigation) and the four new Task 2 samples cluster around -40 ‰ for $\delta^{13}C$ and between 5 and 10 for C1/(C2+C3), with some of the gas from produced water ranging to higher values for C1/(C2+C3). The large majority of these samples are clearly of thermogenic origin. In contrast, only a few domestic wells in the Mamm Creek study area, including one well sampled during the Task 1 sampling event (704023), have isotope values and compositional gas ratios that fall into thermogenic realm. Samples with $\delta^{13}C$ values that fall into the thermogenic range, but with C1/(C2+C3) values that are above the thermogenic range could indicate a mixing process or, more likely, a biogenic methane oxidation shift. The possible exception is well 703996, which has similar isotopic and gas compositional characteristics to a few of the produced water gas samples and may indicate the presence of coalbed gas.

Figure 4.21 shows the location of domestic and monitoring wells in the study area that have gas composition and methane stable isotope analyses. The figure also highlights the five domestic well locations where gas composition and stable isotope samples probably reflect thermogenic properties based on $\delta^{13}C$ vs. δD and Bernard Diagram analysis. The figure shows that the domestic wells with potential thermogenic methane sources are geographically associated both with the development of natural gas and with the axis of the Divide Creek Anticline.

For two of the gas wells where production gas samples were collected, associated produced water samples were also collected. The water for both 05-045-07155 and for 05-045-09156 contained a significant amount of bicarbonate, suggesting a possible mixing of coalbed water in the samples. Since water could not be collected at the other two locations where production gas samples were collected, it is not known if a bicarbonate component (indicating possible coalbed water) would have been present. Because coalbed gas normally has only minimal amounts of hydrocarbon gases heavier than methane, the low C1/(C2+C3) ratios for all four Task 2 gas samples suggest only minimal mixing, if any, of coalbed gas with conventional gas.

4.5 Water Chemistry Temporal Trends

Task 1 of the Mamm Creek Phase II Hydrogeologic Investigation was directed primarily at resampling domestic wells that previously had one or more compounds with concentrations above health-based CBGWS. Wells that previously had methane concentrations above 1 mg/L but that did not have isotope or gas composition analysis conducted were also selected for sampling. The investigation was not designed to evaluate temporal changes in water quality over the long term. However, a cursory review of changes for parameters with CBGWS (fluoride, nitrate, and selenium) and for dissolved methane is provided below to provide an overall sense of change in individual wells for these constituents. (See Table 4.1 for a summary of the Task 1 water quality sample results.)

- Fluoride was present at or above its CBGWS of 4 mg/L in four wells sampled during the Task 1 sampling event. Well 703961 which had a concentration of 4.0 mg/L had never been sampled for fluoride before and the other three wells exhibited very little change in concentration from previous rounds of sampling. Overall, fluoride concentrations dropped below CBGWS in nine wells and increased from below to above the standard in one well (well 704526 increased from 3.7 mg/L in April 2005 to 4.2 mg/L in June 2007).

- Nitrate was present above its CBGWS of 10 mg/L NO_3-N in three wells sampled during Task 1 and was present at a concentration of 9.9 mg/L one other well. Well 703961 which had a concentration of 15.7 mg/L of NO_3-N had never been sampled for nitrate before. The other two wells with nitrate concentrations in excess of the CBGWS both exceeded the nitrate CBGWS for the first time. In contrast, nitrate concentrations dropped below 10 mg/L in 11 wells and in nine other wells the Task 1 sampling confirmed what had previously been significant drops in nitrate concentration from above to below 10 mg/L.
- Selenium was present at or above its CBGWS of 0.05 mg/L in 10 wells sampled during Task 1. Well 703961 which had not been sampled for selenium, had a concentration of 0.792 mg/L for the compound, well above its CBGWS. Of the other nine wells where the selenium standard was exceeded during the Task 1 sampling, eight previously had selenium above the standard; in two of those wells (703933 and 704526) concentrations dropped significantly. In eight instances, concentrations of selenium dropped below the CBGWS.
- Dissolved methane concentrations above 2 mg/L were measured in four of the 13 wells sampled for the compound during the Task 1 sampling. In all four wells, previous sample results had also had methane in excess of 2 mg/L. In the other wells sampled for methane, concentrations were either low to begin with, or dropped between sample rounds.

4.6 Quality Assurance and Quality Control

At the conclusion of the Task 1 sampling, QA/QC samples were collected to provide an evaluation of the initial Task 1 sampling event. The QA/QC samples were collected from selected wells on September 5-6, 2007. Water chemistry parameters were sampled from seven wells that had been sampled in June or July 2007 (1:10 duplicate ratio), with duplicates of those samples collected in three wells. Gas composition and isotopic analysis was duplicated in one well. The results of the duplicate water quality sampling are shown in Table 4.4 and on the Piper diagram in Figure 4.22. While wells 703967 and 704050 exhibited the greatest differences in concentrations between sample events (concentration increased by up to approximately 50 percent for some compounds in the latter sample from 703967 and several decreased in 704050), the shift in overall water chemistry was very small. In well 704050, dissolved methane did increase from 0.006 mg/L to 1.7 mg/L; however, the dissolved methane concentration in the well when it was last sampled in April 2005 was 1.3 mg/L, down from 8.04 mg/L in March 2003, so the changes measured in 2007 appear to reflect normal variations in the concentration of the gas at the sample location.

Two QA/QC produced water samples were collected during the Task 2 sampling event on September 5 and 6, 2007 (see Table 4.3). For well 05-045-09158, concentration of all compounds present above 1 mg/L in the sample were well within 10 percent of each other except for iron, which was 2.5 times higher in the duplicate sample than in the primary sample (110 mg/L vs. 44 mg/L). For well 05-045-11402, results for the anions, pH, and TDS were comparable between the duplicate and primary sample; however, major cation concentrations in the duplicate sample were approximately 30 to 50 percent higher than in the primary sample. Because the cation-anion balance showed a 16.1 percent deficit of cations in the primary sample while the duplicate sample showed only a 1.7 percent deficit, all evaluations of geochemical data involving 05-045-11402, use the concentrations from the duplicate sample (05-045-11402-D).

The sample analysis for 05-045-10206 also had a large ionic balance difference (-15.6 percent); however all other produced water samples had balances within ±5.2 percent. Because of the large ionic balance difference, the sample from 05-045-10206 was not used in evaluating tracer compound (bromide, strontium, and boron) ratios for this study.

5.0 SUMMARY OF FINDINGS

The Phase II Hydrogeologic investigation included both water quality and gas composition and methane stable isotope sampling for domestic wells and natural gas wells in the Mamm Creek study area. Samples collected for Task 1 of the investigation were from previously sampled domestic wells that had one or more compounds of concern (including methane) at or above regulated concentrations in a previous sample event or that had Na-Cl or near Na-Cl geochemical signatures. Task 2 samples were collected from natural gas wells in the immediate vicinity of domestic wells that exhibited potential impacts from deeper formations or from natural gas drilling and/or production activities.

Findings from the Phase II Hydrogeologic investigation, based on the review of sample results from the Task 1 and Task 2 sampling, and considered in conjunction with previous water and gas analyses from the area, include the following.

- The domestic groundwater used in the study area normally is hard or very hard and most private well owners do not drink the water from their wells, although they use it for other household purposes and for watering livestock. The water is often treated or filtered, although in many cases the effectiveness of the filtering/treatment systems is questionable.
- Several wells were sampled because fluoride, nitrate, and/or selenium concentrations previously had been detected at or above CBGWS for human health. Results of this sampling showed that while there are wells with concentrations in excess of human health standards, the number of wells with concentrations in excess of CBGWS fell for each of these compounds relative to previous sample results. Fluoride and selenium concentrations primarily are elevated in areas on the east side of the study area; however, there are no discernable trends that clearly link them to anthropogenic sources.
- The Wasatch aquifer consists primarily of mixed cation and bicarbonate anion water where TDS is below approximately 1,500 mg/L, and Na-SO4 water where TDS is above that level. The bimodal patterns for cations in the samples (as illustrated on Figure 4.8), coupled with the geographic distribution of the bicarbonate and sulfate water types, do not indicate a simple, gradual evolution of the groundwater within the aquifer from a bicarbonate to sulfate water type. It is possible that the geochemically distinct waters reflect significantly different conditions in the shallow subsurface, or alternatively, that water from depth (either lower Wasatch or Williams Fork Formations) mixing with the Wasatch aquifer may contribute to this pattern.
- Produced water samples collected from 16 gas wells located in the vicinity of domestic wells that may be affected by water from deeper formations and/or from

gas exploration/production activities indicate that Williams Fork Formation water is primarily brackish and of two water types. In the majority of the wells sampled, the water had a Na-Cl geochemical signature; however, three wells had a Na-HCO_3 geochemical signature and two wells had mixed Na-Cl and Na-HCO_3 water. The Na-Cl signatures appear to be characteristic of water from Williams Fork Formation clastic sedimentary deposits, while the Na-HCO_3 water may indicate coalbed formation water.

- Tracer mass ratios for both Cl/Br and Cl/Sr overlapped between produced water and domestic water samples preventing positive identification of mixing between Williams Fork Formation and Wasatch Formation groundwater. The distinction in Ca/Sr and SO_4/Cl mass ratios between the produced water and domestic water, however, may provide sufficient information to evaluate mixing of water sources. Both Cl/Br and Cl/B ratios may serve as indicators for certain types of shallow anthropogenic impacts to alluvial and Wasatch Formation groundwater.
- Production gas sample result from four natural gas wells sampled during the Task 2 sampling event were similar both compositionally and for methane stable isotopes. The results indicate that the gases are from a conventional thermogenic natural gas source. Two of the four wells had associated produced water samples, both of which had Na-HCO_3 geochemical signatures. While significant portions of the water from these two wells may have been from coalbeds, it does not appear that coalbed gas is a significant proportion of the gas production from the wells.
- Domestic wells 703996 and 704023 both had methane $\delta^{13}C$ and δD stable isotope values and hydrocarbon gas compositions that indicate a possible thermogenic source for the gases in the wells, although in both cases, C1/(C2+C3) ratios are somewhat elevated. For well 703996, this may indicate oxidation of biogenic gas; however, it may also indicate the presence of thermogenic coalbed gas. For well 704023, which had enriched D, this may indicate oxidation of a conventional thermogenic gas.
- Of the five other domestic wells sampled for methane isotopes, three had $\delta^{13}C$ and δD values in the range of thermogenic gases, but had elevated C1/(C2+C3) ratios. These wells are in the vicinity of 703996 and 704023, but appear to reflect either oxidation of biogenic gases or mixing of gases, possibly including coalbed gas. The other two wells, located several miles to the north and northwest near Dry Hollow Creek and Mamm Creek, had isotopic signatures that reflect a biogenic origin for the gas.
- Two domestic wells are clear outliers among the 66 wells sampled for Task 1:
    - Well 704479, which had a TDS value of 10,100 mg/L, appears to be impacted by anthropogenic sources, based on location, elevated Cl/Br and SO_4/Cl mass ratios, and reduced Cl/B mass ratio. A probable contaminant source for the well is agricultural return flows from the adjacent farm fields and/or Last Chance irrigation ditch.

  - Well 704330 had a distinct Na-Cl geochemical signature and a dissolved methane concentration of 11 mg/L. The well was not sampled for tracer compounds and methane stable isotopes compositions suggest either mixing of methane gases or an oxidized biogenic gas. Sulfate and chloride concentrations in the well indicate a possible mixing of deeper water with the Wasatch aquifer water. The well is not in an area of extensive gas production and there are other domestic wells in the vicinity with Na-Cl signatures so it is possible that the water quality may be the result of natural deeper flow processes.

- Major ion chemistry and gas composition and methane isotope sampling results for domestic wells located along the axis of the Divide Creek Anticline in the southeast portion of the Mamm Creek study area indicate that the Wasatch aquifer potentially may be impacted by both groundwater and natural gas from beneath the Tertiary aquifer. This area, the southeast quarter of Township 7 South, Range 92 West, has experienced only modest natural gas exploration and production activity, and distinguishing impacts due to natural sources from those due to gas exploration production cannot definitively be made.

6.0 RECOMMENDATIONS

Based on the review of existing and new water quality and gas composition and isotope data for the Mamm Creek area, the following are recommended for future work:

- Well 703961, which had elevated concentrations for nitrate, fluoride, and selenium, should be resampled. The sample should be analyzed for major ions, human health parameters, tracer compounds, dissolved methane, and gas composition and methane isotopes.
- Well 704330, which had a Na-Cl geochemical signature and dissolved methane at a concentration of 11 mg/L, should be resampled. Because the well is apparently a different well than was sampled in January 2003 (and that was also identified as 704330), the sample should be analyzed for major ions, human health parameters, tracer compounds, and dissolved methane. Since the initial gas composition and methane isotope sample from the well indicated either oxidized biogenic gas or mixed gas sources, a gas composition and methane stable isotope sample should also be collected. Finally, because of the high concentration of methane in the well, an inspection of the water delivery infrastructure should also be conducted to ensure the explosive conditions do not exist.
- An examination of existing domestic wells and gas wells and their sample histories should be conducted for the southeast quarter of Township 7 South, Range 92 West (extending as far north as Sections 14 and 15). A sampling program should be designed to further examine the general water chemistry (including the Na-Cl patterns) and the nature of the methane and other gases in the water. Sampling should include tracer analyses and gas composition and methane isotopes. Both domestic wells and gas wells should be targeted for this investigation.
- Well owners whose wells contained greater than 1 mg/L of dissolved methane (six wells for this investigation) should be encouraged to continue to have their wells sampled for dissolved methane.
- The possible significance of tracer ratios for Wasatch Formation groundwater is more likely to be discerned if future domestic water and produced water sampling includes tracer compound analysis. Previous sampling, including sampling conducted for this study, focused on wells thought to be susceptible to impacts by deeper waters or by activities related to natural gas production. Expanding tracer compound sampling to areas less affected or unaffected by natural gas exploration and production will provide a valuable baseline tracer compound dataset.
- The effect on groundwater due to the introduction of drilling or well completion/ hydrofracturing fluids was not evaluated for this investigation. A study evaluating possible local effects of drilling or hydrofracturing fluids on domestic groundwater should be considered for the Mamm Creek area.

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