Piceance Basin Phase IV Baseline Water Quality Study – Garfield County, Colorado

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1.0 INTRODUCTION

The Piceance Basin covers an area of approximately 7,100 square miles in western Colorado (Figure 1.1). Currently, gas wells are being drilled and completed in the Upper Cretaceous Williams Fork and the Tertiary Wasatch formations in the eastern portion of the basin along the I-70 corridor in Garfield County. The Colorado Oil and Gas Conservation Commission (COGCC) is conducting the Piceance Basin Phase IV Baseline Water Quality Study to characterize baseline water quality conditions in an area that has historically had little previous drilling activity and no producing oil and gas wells, but that is expected to be the site of future natural gas exploration and production activity. This study involves sampling water wells in Garfield County between the towns of New Castle and Rifle north of the Colorado River in the area shown in Figure 1.2.

Under contract to the COGCC, S. S. Papadopulos & Associates, Inc. (SSPA) conducted the water quality field sampling for this study in July and August, 2006. Groundwater samples were collected from 70 water supply wells and analyzed for an extensive suite of inorganic and organic parameters. In addition, water from 29 wells was sampled for gas composition and for stable isotopes. This report describes the field sampling, summarizes and briefly evaluates the analytical results, and provides recommendations for future activities.

1.1 Objectives

The objectives of the Piceance Basin Phase IV Baseline Water Quality Study are to:

- Develop an electronic project database of geographic data obtained from the wells sampled and incorporate it into the existing COGCC geographic database of the project area.
- Develop an electronic environmental database that conforms to COGCC requirements for the wells sampled, including both field and laboratory analytical data.
- Prepare succinct summary tables and figures that illustrate the sample analytical results.
- Provide recommendations for possible future sampling and evaluation activities for the study area.

1.2 Hydrogeologic Setting

The study area is located in western Colorado at the eastern edge of the Piceance Basin. Oil and gas reserves in the eastern portion of the basin are found within the Upper Cretaceous Williams Fork Formation and the Lower Tertiary Wasatch Formation (USGS, 2003). The Wasatch Formation is also the primary bedrock aquifer in the study area. The Wasatch Formation consists of mudstone with intervening lenses of sandstone. Donnell (1969) has described the Wasatch Formation in detail at the "Hogback" outcrop that traverses the northeast portion of the study area. Porosity and hydraulic conductivity are low in the Wasatch and much of the groundwater produced from Wasatch wells is likely from flow through open fractures. Wasatch wells in the study area are up to 600 feet deep; well yield varies widely, but often is 5 gallons per minute (gpm) or less. Depth to water in the wells may exceed 100 feet.

Near the Colorado River, groundwater is commonly pumped from the saturated alluvium that is present adjacent to and beneath the River where it has sufficient transmissivity to produce water for domestic, industrial and/or agricultural uses. In the study area, at least two wells located on the terraced surfaces north of the Colorado River are also screened in unconsolidated alluvial deposits. Most alluvial wells do not exceed 100 to 150 feet deep. Wells completed in alluvium produce primarily from unconsolidated sandy or gravelly units. Water levels are normally within a few tens of feet of the ground surface and well yield is often above 10 gpm. Geologic maps and driller's logs indicate the presence of unconsolidated alluvial and colluvial deposits outcropping in the northern and central portions of the study area. Driller's logs indicate these deposits are greater than 60 to 80 feet thick in places.

1.3 Previous Water Quality Studies

The water quality database maintained by the COGCC was obtained by SSPA in July 2006. In the study area results are reported for 25 wells over the period from 1996 to 2005. Three wells have data for multiple sampling events. Sources of data include the COGCC, oil and gas operators, and samples collected and submitted to laboratories by local well owners. Reported analytes vary by sample location and typically include major cations and anions, metals, benzene, toluene, ethylbenzene, and xylenes (BTEX), methane, and basic water quality parameters. Sample locations are shown in Figure 1.3.

Analytical results for groundwater, spring, and stream samples collected by the U. S. Geological Survey (USGS) in the study area were obtained from the USGS website (http://waterdata.usgs.gov/nwis/nwis). This dataset includes results from one well, four springs, and 15 nearby surface water locations from 1977 to 2003. Temperature and specific conductance were measured at all sites. Samples from two of the springs and the well were analyzed for major cations and anions. The well sample was additionally analyzed for metals, volatile and semi volatile organic compounds (VOCs and SVOCs), and agricultural chemicals. Surface water locations include the Colorado River and contributing drainages as well as streams draining the study area. Surface water samples were analyzed for most major cations and anions. Sample locations are indicated in Figure 1.3.

No water quality data were obtained directly from oil and gas operators. Interviews with water well owners in the study area indicate that the oil and gas operators active in the area are conducting sampling of some lease owner's wells.

2.0 WATER QUALITY SAMPLING PROGRAM

Previous water quality sampling in the study area has been conducted by several different entities, with samples analyzed for different sets of constituents, and with different end goals of water quality characterization. This sampling program represents a first attempt in the area at characterizing water quality utilizing a standard set of parameters and field and analytical methods at a scale adequate to establish general baseline water quality characteristics.

2.1 Sampling Locations

The project area encompasses approximately 31 square miles just north of the Colorado River and south of the upland "Hogback," between the communities of Rifle and Newcastle (Figure 1.2). A total of 70 wells were sampled for this project. Most of the wells were domestic water supply wells; a few provide water to more than one residence, to unincorporated subdivisions, or to businesses. Sampling locations (Figure 1.4) were based on criteria of geographic distribution, owner permission, water distribution system construction, and sample point access. Attempts were made to sample all wells that the COGCC database listed as having previously been sampled unless those wells were sampled in 2005 or 2006. Table 2.1 provides well owner and basic geographic information. Additional well information, including photographs for each location sampled, is contained in Appendix A. Detailed well information, including global positioning system (GPS) coordinates, is tabulated in Appendix B.

Prior to field sampling, SSPA obtained water well permit information from the Division of Water Resources, Office of the State Engineer (DWR-OSE) database to assist in identifying target wells for sampling. Well permit numbers were matched for 32 of the wells sampled, and of these, well construction reports were located for 29 wells. Well construction reports are contained in the well information provided in Appendix A.

2.2 Sampling Parameters

Field sampling was conducted between July 31 and August 16, 2006. Field water quality parameters and visual characteristics recorded during sampling included:

- Temperature (°C)
- Specific conductance (mS/cm)

- pH
- Dissolved oxygen (mg/L)
- Water color/clarity/odors/effervescence/sediment/bacterial fouling

Water samples were analyzed at STL Laboratories in Arvada, Colorado, for the following water quality parameters:

- Anions: chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), and nitrite (NO_2^-)
- Cations: sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+)
- Total (unfiltered) metals: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), lead (Pb), and selenium (Se)
- Halides: fluoride (F^-) and bromide (Br^-)
- pH
- Total dissolved solids (TDS)
- BTEX plus MTBE
- Dissolved methane

In addition to the water quality parameters listed above, 29 wells were sampled for dissolved gas composition and stable isotopes. These samples were analyzed at the Isotech, Inc., laboratory in Champaign, Illinois, for the following parameters:

- Fixed Gas Chromatography: hydrogen (H_2), argon (Ar), nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO)
- Hydrocarbon Gas Chromatography: C1 (methane), C2 (ethane, ethene), C3 (propane, propene), iC4 (isobutane), nC4 (normal butane), iC5 (isopentane), nC5 (normal pentane), and C6+ (hexane plus)
- Stable Isotopic Analysis: $\delta^{13}C$ of C1 (carbon-13 of methane), δD of C1 (deuterium of methane) , $\delta^{13}C$ of CO_2 (carbon-13 of carbon dioxide), $\delta^{13}C$ of C2 and C3 (carbon-13 of ethane, -ene and propane, -ene)[1]

2.3 Sample Collection Procedures

Water quality sampling was conducted in general accordance with procedures presented in the Field Sampling Plan (SSPA, 2006).

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[1] Because of the absence of sufficient hydrocarbon gases in all samples analyzed for stable isotopes, only $\delta^{13}C$ of CO_2 could be analyzed in the samples.

2.3.1 Well and Sample Identification

Well and sample identification provides a unique identifier for each location sampled. During field sampling all field forms, sample bottles, laboratory chain-of-custody forms included well and sample identifiers. In this report and in electronic databases prepared for this project all wells and samples collected are referenced by the same identifiers. The format utilized for well and sample identification is provided below:

Last Name (or Abbreviation)-*Township Identifier* S *Range Identifier* W- *Section Number*.

Samples collected and submitted for laboratory analysis were identified in the field in field notes, on sample bottles, and on sampling chain-of-custody forms using the well identifier. Duplicate samples were collected for BTEX plus MTBE and for dissolved methane. For a duplicate sample, the identifier "-D" was appended to the end of the well identifier.

2.3.2 Sample Point Selection

Efforts were taken to collect water samples from locations that were as close as possible to the well on the well discharge line. Before sampling, the operations of the well and details of the water supply system were discussed with the well owner, and where possible the plumbing system was inspected. Sampling points were preferentially chosen before the pressure tank on the well where possible. Otherwise sampling points on or after the pressure tank were deemed acceptable as long as the sample point was not located downstream of an non-pressurized water storage tank, water softener or other water treatment or purifying device and as long as no aerator was installed on the sample point. Samples were not collected from points on hot water lines. Except as noted below, if a sample of unheated, untreated, and/or non-aerated water could not be collected, the well was not sampled. In one case (Blair-5S92W-36), samples were collected downstream of a non-pressurized storage tank. While these samples could provide only minimum concentrations for the volatile compounds analyzed (BTEX plus MTBE and methane) and allowed for some re-equilibration of dissolved gases, the concentrations of the other constituents should not have been affected significantly.

2.3.3 Groundwater Purging Procedures

Most standard environmental water well sampling protocols require purging a minimum of three well bore volumes of water prior to collecting water samples. When sampling water supply wells in areas where low yields are common, this methodology must be modified to prevent a well from being pumped dry prior to sample collection. In the project study area, wells drilled into the Wasatch Formation frequently have low yields; therefore, an alternative sampling technique that is utilized by the COGCC and based on low flow-rate sampling techniques used in the environmental industry (Puls and Barcelona, 1996; ASTM, 2002; etc.) was employed. As with other low flow techniques, determining when a sample should be collected was based on field measurement of basic water quality parameters. Stabilization of those parameters, collected over a several minute period with continuous flow at a relatively low and sustainable rate allowed efficient and consistent sampling and avoided over-pumping low yield wells.

For this study, SSPA field personnel used the following groundwater purging protocols:

1. The well owner was questioned about well yield prior to purging the well. If well yields were estimated to be less than 5 gpm, then the maximum flow rate for purging was set to be 2 to 3 gpm or less based on well owner information. A 5-gallon bucket was used to allow flow rates during purging to be estimated. The following method was used to establish the flow rate for purging each well:
    - All wells were purged slowly at first and visual water characteristics (color, turbidity, etc.) were observed.
    - If the water was clear and remained clear, the flow rate was increased gradually to a maximum of 3 to 5 gpm—or to a lower flow rate if the well was considered to be low yield—as long as no increase in entrained sediment or other changes in appearance were observed.
    - Throughout the purging period the approximate cumulative quantity of water produced was tracked informally.
2. The well was allowed to purge for approximately 10 minutes. During that time the sampling personnel would listen at the wellhead or the pressure tank to ensure that the pump cycled on at least one time and would record the following visual field observations of the water quality:
    - Water color
    - Water clarity
    - Odors (if any)
    - Effervescence (if any)
    - Produced sediment (if any)
    - Evidence of bacterial fouling (bioslimes or biofilms)
3. After the water had run for approximately 10 minutes and the pump had cycled on at least once, sampling personnel would begin measuring field water quality

parameters using a calibrated YSI 556 MPS multi-parameter water quality meter with probes connected to a flow-through cell. The parameters measured were pH, specific conductance (SC), temperature (T), and dissolved oxygen (DO).

4. Field water quality parameter measurements were recorded at approximately 5-minute intervals until three consecutive measurements indicated that stabilization of all field parameters had occurred. Stabilization for each parameter was determined as follows:
   - pH varied by less than 0.1 units between measurements,
   - Temperature varied by less than 0.2°C,
   - Specific conductance varied by less than 5 percent for values < 0.1 millisiemens/centimeter (mS/cm) and by less than 3 percent for values > 0.1 mS/cm, and
   - Dissolved oxygen varied by less than 0.3 mg/L.
5. If a well did not stabilize after 6 field measurements, the water flow rate was adjusted for sampling and in most cases two more sets of field parameter measurements were collected. If stabilization did not occur, the sampling personnel recorded that sampling was conducted although the stabilization of parameters was not achieved. Final field parameters values, measured prior to sampling, are summarized in Table 2.2.

2.3.4 Water Quality Sampling Procedures

Samples collected for analysis of anions and cations, metals, halides, pH, and BTEX plus MTBE were placed into new sample containers provided by STL Laboratories as listed below:

Analysis	Container	Preservative	Containers per well
Anions, halides, pH, TDS	1 L polyethylene	None	1
Cations, Metals	500 mL polyethylene	Nitric acid (HNO_3)	1
BTEX plus MTBE	40 mL VOA	Hydrochloric acid (HCl)	3

The polyethylene containers were filled to the neck with water and capped securely. The 40 mL VOA vials were carefully and completely filled at a low flow rate. For the BTEX plus MTBE samples, a positive meniscus was present on the top of the vial to exclude entrapment of air bubbles. All containers were labeled with sample identification number, sample date and time, preservative (if appropriate), and project and sampling personnel identification. After collection and prior to shipping, all samples were stored securely in a cooler on ice.

2.3.5 Dissolved Methane Sampling

Samples were collected into unpreserved 40 mL VOA vials for dissolved methane analysis. Because dissolved methane gas concentrations in well water can vary significantly over a very short period of time, it was important to maintain a consistent sampling protocol when collecting samples for dissolved methane analysis. Depending on whether or not the well water effervesced, two methods were employed for collecting samples for dissolved methane analysis.

Non-Effervescent Water: The following procedure was used to collect dissolved methane samples from wells with water that did not effervesce.

1. A flow of water sufficiently low to ensure that laminar conditions were maintained was established though the clear 3/8-inch outside diameter polyvinyl sample discharge tubing.
2. The end of the sample discharge tubing was placed into the bottom of a clean white 5-gallon bucket filled most of the way with purge water The tubing was kept submerged in water to minimize the free gas space in the line.
3. Using gloved hands, a sealed Teflon-capped VOA vial with no preservative was lowered to near the bottom of the bucket, uncapped, and allowed to fill completely with water.
4. The VOA vial was then inverted and the discharge tubing inserted into the vial to flush it with sample water. Sufficient water was allowed to flow through the vial to displace twice its volume. While keeping the VOA vial inverted and as near as possible to the bottom of the bucket, the tubing was slowly removed and the vial was capped securely.
5. After the vial was capped and removed from the bucket, it was inspected to insure that there were no gas bubbles trapped in it. If bubbles were visible, the water in the vial was discarded and the sampling process was repeated.

Effervescent Water: If the water discharging from the sample line at the bottom of the 5-gallon bucket effervesced, then the following modified sampling process was used.

1. Steps 1 through 3, above, were followed.
2. After filling the inverted VOA vial with water, the discharge tubing was removed from the vial and, with the flow from the tubing directed over the open end of the VOA vial, the vial was slowly tilted upward until the gas bubbles were released. The vial was then capped, removed from the water, and inspected to ensure that no gas bubbles were present. If bubbles were present, the water in the vial was discarded and the sampling process was repeated.

3. If it was not possible to remove all the gas bubbles after repeated attempts, the sample bottle(s) with bubbles were retained for shipment to the analytical laboratory and the presence of the bubbles was noted on the field sampling form.

2.3.6 Chromatographic Gas Composition and Stable Isotope Sampling

As with the collection of samples for dissolved methane, the method used to collect samples for chromatographic gas composition and stable isotopes depended on whether or not the well water effervesced when it was discharged at the ground surface. For determining gas composition and stable isotopes, if dissolved gases were exsolving at a high rate and the water effervesced vigorously, a sample of gas was collected by displacing well water from a sample bottle with a gas headspace. Collection methods for the two situations are described below.

Non-Effervescent Water: If the water being sampled was not effervescent or produced only a small amount of gas when it discharged then the following sampling procedure was used.

1. A flow of water sufficiently low to ensure that laminar conditions were maintained was established though the clear 3/8-inch outside diameter polyvinyl sample discharge tubing and a clean 5-gallon bucket was filled most of the way full of water.
2. Using gloved hands, a new clear plastic 1-liter sample bottle provided by Isotech Laboratories was opened and with the discharge tubing placed at the bottom of the bottle, and it was filled with water.[2]
3. Once the bottle was filled it was immersed in the bucket full of water, keeping the tubing at the bottom of the bottle. With the bottle at the bottom of the bucket under a head of water flow was maintained until a minimum of two volumes of water had been displaced from the bottle. The tubing was then slowly lifted out of the bottle and it was immediately capped while still under water.
4. After the bottle was capped and removed from the bucket, it was turned upside down and inspected to insure that there were no bubbles present. If bubbles were visible, the water was discarded and another sample was collected using the same procedure.
5. After an acceptable sample was collected, the outside of the bottle was dried and the cap was secured to the bottle with airproof and waterproof tape. To ensure that the bactericide capsule in the cap remained in contact with the water, the sample bottle was packed upside down in a cooler containing ice.

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[2] Each 1-liter bottles provided by Isotech Laboratories contained a bactericide capsule attached to the cap. To ensure proper sample preservation it was necessary that the capsule remained in the cap and was sealed in the bottle after the sample was collected.

Effervescent Water: If the water being sampled effervesced strongly or a gas-free water sample was not able to be collected using the method described immediately above, the following procedure was used to collect a sample of gas from the water.

1. Steps 1 and 2, above, were followed.
2. The discharge tubing was removed from the sample bottle, and using gloved hands, the bottle was submerged in the 5 gallon bucket full of water and inverted.
3. The discharge tubing was inserted into the inverted bottle and water flow rate was increased to 2 to 3 gpm. The flow of water into the sample bottle was continued until the gases bubbling from the discharged water had displaced 1/3 to 1/2 of the water in the bottle.
4. The discharge tubing was carefully removed from the inverted bottle and the bottle was sealed under water with the screw cap containing the bactericide capsule.
5. The sealed bottle was removed from the water, dried, and the cap was secured with airproof and waterproof tape. To ensure that the bactericide capsule in the cap remained in contact with the water, the sample bottle was packed upside down in a cooler containing ice.

2.3.7 Sample Handling, Shipping, and Hold Times

Prior to final packing and shipping of samples to the analytical laboratory, required chain-of-custody forms were completed and shipped with the samples (copies of chain-of-custody forms are included with the laboratory reports in Appendix C). Both the numbers and types of bottles were double checked against the chain-of-custody forms to ensure consistency in both quantities and labeling. Chain-of-custody forms were signed prior to sealing them in ziplock bags and placing the bags in the coolers for shipment. Every cooler containing samples for analysis contained one chain-of-custody form.

Sample bottles were packed upright (or inverted for sample bottles containing bactericide capsules in the lid) in the cooler with adequate ice (approximately 1-2 times sample volume) to maintain temperature requirements for shipping times. Glass containers were separated with padding to minimize the potential for breakage during transport. Prior to sealing the sample coolers, it was confirmed that fully completed and signed chain-of-custody forms (and other laboratory-required forms) were included and stored in sealed ziplock bags. Coolers were shut securely with shipping tape and sealed with laboratory-supplied custody seals, if appropriate. When possible, courier services (e.g., Federal Express) were used to ship samples so that they were received by the laboratory within 24 hours of shipment. All holding times specified by the analytical laboratories were met with the exception of some 24-hour hold times for pH, nitrate and nitrite, as indicated in laboratory reports (Appendix C).

2.3.8 Well Location Documentation and Determination

At each location sampled, a well information form was completed. In addition to well owner and well construction information, the form contains an area for description of the location and area around the well. The description includes location relative to the nearest roads and buildings and any features or structures that may be housing or obscuring the well. In addition, the description includes where the well was sampled and how that point is located relative to the well and/or the pressure tank or other significant features on the water supply system. Photographs were taken to document sampling including the following where feasible:

- Site locator photograph showing enough information for future sampling teams to positively identify the property being sampled;
- Well head photograph; and
- Sampling location photograph.

Each photograph taken was documented on the well information form or in the sampler's field notebook.

In accordance with COGCC *Rule 215*, the locations of all water wells sampled were mapped using a differential GPS instrument. Field personnel collected GPS measurements and differential corrections were applied at the end of sampling activities. Raw positional data was recorded on field forms for security purposes. In some cases it was not possible to achieve all aspects of *Rule 215* due to interference from vegetation, lack of access to well head, poor satellite communication, or differential GPS instrument unavailability. In these cases attempts were made to best accommodate the rule using coordinates from the nearest accessible location or from a less precise GPS instrument.

3.0 SUMMARY OF WATER QUALITY CONDITIONS

This section summarizes analytical results for both water quality parameters (major anions and cations, metals, BTEX, MTBE, and dissolved methane) and for gas composition and gas isotopes. The results are considered in relation to state and federal health and water quality standards and are further evaluated with respect to overall hydrologic setting and for potential effects from activities that are normally associated with oil and natural gas production.

3.1 Analytical Results

STL Laboratories, Arvada, Colorado, analyzed the groundwater samples for major anions and cations, metals, BTEX, MTBE, and dissolved methane. An electronic database was developed from analytical results. Laboratory reports for those analyses are provided in Appendix C and summaries of results are presented in Tables 3.1 and 3.2. Table 3.1 presents major ion chemistry, pH and total dissolved solids (TDS). Table 3.2 presents metals and halides. No measurable concentrations of BTEX, MTBE, or methane were detected in any of the samples.

Concentration distribution maps and Piper diagrams were developed to illustrate the sample analytical results and are referenced in the following discussion sections. The Piper diagrams (also called trilinear plots), use major cation and anion concentrations to demonstrate relationships among multiple samples or sample groups (Hem, 1985). Note that in these diagrams the reactive quantities of the ions (measured in milliequivalents per liter; meq/L) are the basis for the plots rather than the mass quantities (mg/L) presented in Table 3.1.[3]

Isotech Laboratories in Champaign, Illinois, analyzed water or headspace gas samples from 29 wells (shown in Figure 1.4) for chromatographic gas composition and stable isotopes. An electronic database was developed from analytical results. The laboratory reports for those samples are provided in Appendix C and summaries of results are presented in Table 3.3. Gas

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[3] Note also that the following changes were made to the layout of a standard piper diagram for use in this report: Potassium (K) was removed from the cation group because it constituted very little of the total cation balance. The chloride (Cl) and bicarbonate (HCO_3) axes of the anion base triangle were shifted from the standard layout. This allows the differentiation between sulfate (SO_4) and chloride in the diamond portion of the piper diagram. Differentiation is important because the magnitudes of concentrations of these anions vary much more than those of HCO_3.

composition results are reported as the molar percentage of each gas (where total gases equal 100 percent). The detection limits for common gases nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2) and argon (Ar) are 30-50 ppm in undiluted samples of headspace gas. Where no headspace was created during sampling (see Section 2.3.6 above), dissolved gases were stripped from the water samples in the laboratory using a carrier gas and resultant quantitation limits are 3-4 times higher.

For the carbon stable isotopes analyses, the results are given as the parts per thousand (permil or ‰; 1 permil = 1/1000) ratio of the stable carbon isotopes ($^{13}C/^{12}C$) from the sample compared to the ratio in an industry-accepted marine carbonate standard. (This value is indicated in literature using the abbreviation $\delta^{13}C$.) Specifically, $\delta^{13}C$ 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 carbon (*PDB*) is 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 means that the $^{13}C/^{12}C$ ratio of the sample is 20 parts per thousand or 2.0 % lower than that of the *PDB* standard.

The absence of significant methane (CH_4) in dissolved gas samples precluded quantification of the carbon isotope ratios for this compound.

3.2 Health and Drinking Water Standards

Analytical results were screened for exceedance of Colorado Basic Groundwater Standards (CBGWS) which are regulatory human health and drinking water quality standards for groundwater supplies (see Tables 3.1 and 3.2). The primary or human health standards (same as federal maximum contaminant levels; MCLs) are established based on potential health effects resulting from exposure to drinking water containing a given compound while water quality standards are related to the aesthetic qualities of water, such as odor and taste.

Regulatory limits for human health were exceeded for nitrate (NO_3), selenium (Se), and arsenic (As) in samples from the study area. Nitrate was detected in 47 of 70 wells and nitrate concentrations exceeded the CBGWS of 10 mg/L in 5 wells (see Table 3.1 and Figure 3.1). Selenium was detected in 49 of 70 wells and selenium concentrations were above the CBGWS of 0.05 mg/L in 8 wells (see Table 3.2 and Figure 3.2). Arsenic was detected in 6 wells and exceeded the CBGWS of 0.01 mg/L in 2 wells (Table 3.2). No other parameters exceeded the CBGWS human health limits.

CBGWS for drinking water quality (same as federal secondary MCLs or SMCLs) are established as guidelines for water aesthetics and are not enforced standards. Concentrations of sulfate (SO_4), chloride, and iron (Fe) exceeded CBGWS drinking water limits on several of the wells sampled:

- Sulfate was detected in every well sampled and exceeded the standard of 250 mg/L in 51 of 70 wells;
- Chloride was detected in greater than 95 percent of the wells sampled and exceeded the standard of 250 mg/L in 7 wells; and
- Iron was detected in 13 wells and exceeds the standard of 0.3 mg/L in 3 wells.

Methane was not detected in any of the groundwater samples above the laboratory reporting limit of 0.005 mg/L. This is significantly below the concentration threshold of 2.0 mg/L used by the COGCC to identify water wells requiring further investigation of the origin of the methane in the well.

3.3 Groundwater Chemistry Evaluation

3.3.1 Major Ion Chemistry

A Piper diagram of the major water quality ion data for all wells sampled (Figure 3.3) illustrates the trends in groundwater chemistry across the study area for both the alluvial and Wasatch Formation bedrock aquifers utilized locally for water supply purposes. The cation base triangle demonstrates a trend from calcium magnesium (Ca-Mg) to sodium (Na) dominated water. The more positive relationship between Na concentration and total dissolved solids (TDS) than between Ca-Mg concentration and TDS indicates that groundwater evolves from Ca-Mg to Na dominated as the ionic species in the water increase in total concentrations (Figure 3.4). The anion base triangle demonstrates domination of sulfate (SO_4) and bicarbonate (HCO_3)

anions relative to chloride (Cl). The lack of definable trend in the anions suggests mixing of more than two water types with different anion signatures. In the central diamond portion of the Piper diagram, symbol size is scaled to TDS. Samples with highest TDS are Na-SO_4 and Na-SO_4-Cl type (bicarbonate is less than 10 percent of the total anions in these samples). No Na-Cl waters, which can be indicative of contamination by brines, are encountered in the wells sampled.

Wells and samples were also grouped by total well depth and groundwater production interval to evaluate potential relationships between groundwater chemistry and well construction or production interval. To evaluate groundwater chemistry according to depth, wells were divided into shallow (less than 100 ft), intermediate (100-200 ft) and deep (greater than 200 ft) groups. For more than half of the wells sampled, no well construction information was available and these were designated as unknown. Groupings of production interval geology are Wasatch Formation and alluvium. Wasatch Formation was also assigned where well construction indicated undifferentiated bedrock since geologic maps indicate that the Wasatch is the outcropping and shallow subcropping bedrock formation in the portion of the study area where wells were sampled (Green, 1992).

As expected, the deeper wells generally are located in the northern portion of the study area, towards the “Hogback” and shallow wells are more prevalent in the south, towards the Colorado River (Figure 3.5). Alluvial wells are more prevalent near the Colorado River, though at least two alluvial wells are also present further north (Figure 3.6) where detailed geologic mapping indicates river terrace and/or alluvial deposits (USGS, 2001). Piper diagrams were generated using these groupings. No clustering of any group data is observed in either of the diagrams (Figures 3.7 and 3.8). This suggests that among the population of sampled wells with construction information there is no relationship between the major ion concentrations and the production interval or well depth.

Groundwater chemistry may be significantly affected by recharge of surface water from streams and irrigation ditches. Surface water quality data obtained from the USGS were used to examine differences and similarities between surface and ground waters. Water samples were consistently collected in late summer to fall when flow in natural drainages is most likely to represent baseflow. In some samples, where bicarbonate was not measured, this parameter was estimated assuming a neutral charge balance. This approach is reasonable for waters with near neutral pH values. TDS was estimated for these samples as the sum of major cations and anions. Streams and irrigation ditches identified in the study area are shown in Figure 3.9. The ditches carry water during the agricultural growing season imported from the Rifle Gap Reservoir, East Rifle Creek, Elk Creek and Colorado River drainages that lie outside of the study area. Ditches are generally elevated above the water table and provide seepage to the shallow groundwater system. A pumping plant at the Colorado River east of Silt supplements ditches in some parts of the south-central study area though details were not obtained (USBR, 2006). Except for short-reach spring-fed streams located in the southern portion of the study area adjacent to the Colorado River, most of the streams in the study area are intermittent and provide little recharge potential.

A Piper diagram generated from the surface water quality data is shown in Figure 3.10. The diagram, in which data were divided among drainages that lie within the study area, drainages that are outside the study area but contribute to ditches in the study area, and the Colorado River, indicates the following:

- Water quality in contributing drainages of the study area is generally calcium-magnesium-sulfate-bicarbonate (Ca-Mg-SO_4-HCO_3) type;
- Drainages within the study area are more enriched in sodium and chloride than the contributing drainages;
- Both of these groups have major ion chemistry that is similar to the groundwater samples; and
- The Colorado River is enriched in sodium and chloride and depleted in magnesium relative to the other contributing drainages. Colorado River water is chemically distinct from both the groundwater and contributing drainage samples.

The study area is situated between the “Hogback” near the edge of the Piceance Basin and the Colorado River in an area underlain by predominantly southwest dipping strata of the Wasatch Formation. The hydrogeologic setting suggests that under natural conditions a portion of shallow groundwater in the study area discharges to the Colorado River and tributaries and a portion recharges the Wasatch Formation regional groundwater system. Comparisons of well and ditch water chemistry also suggest that seepage from irrigation may have a local effect on the quality and quantity of recharging water.

As water flows through the alluvial and bedrock aquifers, it evolves chemically, dissolving minerals and exchanging dissolved ions with silicate minerals such as feldspars and weathering products such as clays. Sodium concentration appears to be a potentially useful indicator of the degree of groundwater evolution in samples. Areas of lower sodium concentrations seen in the eastern portion of the study area (Figure 3.11) suggest a close proximity to regional recharge areas of the groundwater system while clusters of groundwater samples with high sodium concentrations likely are well away from recharge zones, especially for wells which produce from the bedrock of the Wasatch Formation. Enriched chloride concentrations in the Piceance Basin may be used to identify possible discharge of deeper saline waters into the shallow groundwater system (URS, 2006). Graduated symbol maps of chloride concentrations suggest possible discharge of deeper saline waters in the study area (Figure 3.12). The chloride distribution is not dissimilar from that of sodium; however, because potential sources for chloride enrichment are more limited than for sodium, the chloride enrichment more strongly suggests a mixing of water from a source deeper than the portion of the Wasatch Formation normally exploited as a groundwater source in the study area.

3.3.2 Gas Composition in Groundwater

The composition of common dissolved gases in groundwater samples varied considerably (Figure 3.13). The chromatographic gas compositional analysis conducted on the dissolved or headspace gases from 29 wells in the study area indicates that the predominant gas in the groundwater sampled was nitrogen (N_2) which was from 68.3 to 96.3 percent by volume of the total gases present in the samples. Oxygen (O_2) ranged from 1.8 to 24.0 percent and carbon dioxide (CO_2) was found in the range of 0.7 to 19.5 percent. In some samples the molar fraction of CO_2 was considerably greater than O_2. Argon (Ar) was detected in the range of 0.8 to 1.5 percent. Carbon monoxide was detected above the detection limits of 10 ppmv in 7 of 29 samples (maximum of 0.07 percent). Though methane was not detected above a reporting limit of 0.005 mg/L in water samples analyzed by STL laboratories, small quantities of methane were detected in 5 of 29 of the gas samples (maximum of 0.04 percent). No additional hydrocarbon gases were detected in any sample.

The Ar/N_2 ratio is often used in the interpretation of groundwater geochemistry. Both are inert elemental gases that do not readily participate in chemical reactions and interpretation is relatively straightforward. The Ar/N_2 ratio in dissolved gas samples is less than the ratio found in air-saturated water that is in equilibrium with the surrounding air. The lower ratio observed indicates either N_2 enrichment or Ar depletion in the water (Figure 3.14). Enrichment of N_2 in groundwater may result from denitrification, the process in which nitrate (NO_3) is reduced to N_2 under anaerobic conditions; however, the abundance of O_2 suggests that anaerobic conditions have not been met in most groundwater samples. The N_2 enrichment may also be explained by the injection of atmospheric air (excess air), as is believed to occur during some recharge events. Ar/N_2 ratios are significantly lower in the six samples where water effervesced and a headspace gas sample was collected. The cause behind the depletion of the ratio in these samples is unclear but may be related to pressure reductions that occur using the sampling methodology employed in this project. These samples have similarly depleted CO_2/N_2 ratios (Table 3.3).

3.3.3 Stable Isotopes in Groundwater

Stable isotopes of carbon in carbon dioxide (CO_2) were measured for the 29 samples in which gas composition was analyzed. Stable isotopes of methane and other hydrocarbons were not measured by the laboratory because not enough of these gases were present in the samples. The quantity of carbon isotopes in water, referred to using the symbol $\delta^{13}C$, can indicate the source of dissolved CO_2 in groundwater. Potential sources of CO_2 are the soil root zone (respiration), oxidation of methane and/or oxidation of organic carbon. In the wells sampled for this study, $\delta^{13}C$ ranges from -22.5 to -16.6 ‰ (Figure 3.15). These values fall within the normal range of soil CO_2, the CO_2 with which recharging groundwater equilibrates. A significant contribution from a deeper source with different $\delta^{13}C$, such as methane, would deplete values from the normal range (i.e., cause them to become more negative). A significant contribution to CO_2 from the oxidation of biogenic or thermogenic methane would result in the mixing of these signatures and some depletion in the values of $\delta^{13}C$. Oxidation of methane is not suggested by the $\delta^{13}C$ values of any of the samples, which is consistent with the general absence of dissolved methane in the sampled wells. A slight depletion may result from the oxidation of organic matter, potentially including coal. As shown in Figure 3.15, no clear relationship is indicated between the CO_2 content of dissolved gas and $\delta^{13}C$. The $\delta^{13}C$ signature of dissolved CO_2 may be a useful indicator parameter of potential future impacts from gas exploration and production in the study area, as the baseline data indicate it is relatively independent of concentration, and inputs from these sources would likely result in a shift to lower values.

4.0 RECOMMENDATIONS

The baseline water quality for the alluvial and Wasatch Formation bedrock aquifers in the study area was adequately characterized with regards to major ions, metals, VOCs (specifically BTEX and MTBE), methane, and carbon stable isotopes in carbon dioxide.

For the water quality sampling program for the study area, the following recommendations should be considered for future sampling:

- Institute a similar sampling program for industry for water supply wells located in the immediate vicinity of oil and gas wells as is in place in other areas of active oil and gas development in the state. In addition to this required sampling, COGCC should repeat the sampling effort implemented for this work approximately 5 years from now—or sooner if development occurs at a rapid pace in the near future.
- Since the region covered by the study area is experiencing active real estate development, with associated construction of new water supply wells and growing demands on the local aquifers, when the sampling is repeated, the network of target wells should be increased selectively to include additional wells that can be definitively linked to well permits and well construction logs.
- In preparing for, conducting, and evaluating the results from the next sampling event, specifically consider the potential timing and impact of irrigation practices on groundwater quality.

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