

Prepared in cooperation with the Bureau of Land Management, White River Field Office

# **Groundwater Chemistry and Water-Level Elevations in Bedrock Aquifers of the Piceance and Yellow Creek Watersheds, Rio Blanco County, Colorado, 2013–16**

Scientific Investigations Report 2018–5142

**U.S. Department of the Interior  
U.S. Geological Survey**





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**U.S. Department of the Interior**  
**U.S. Geological Survey**

## **U.S. Department of the Interior**

RYAN K. ZINKE, Secretary

## **U.S. Geological Survey**

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U.S. Geological Survey, Reston, Virginia: 2018

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## Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
Volume		
gallon (gal)	3.785	liter (L)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

## Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

## Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (μg/L).

Water year is the 12-month period from October 1 through September 30. The water year is designated by the year in which it ends.

## Abbreviations

DIC dissolved inorganic carbon

USGS U.S. Geological Survey

VOC volatile organic compound





# Groundwater Chemistry and Water-Level Elevations in Bedrock Aquifers of the Piceance and Yellow Creek Watersheds, Rio Blanco County, Colorado, 2013–16

By Judith C. Thomas and Peter B. McMahon

## Abstract

The Piceance and Yellow Creek watersheds in Rio Blanco County, Colorado, are known to contain important energy resources (oil shale and natural gas) and mineral resources (nahcolite). The primary sources of fresh groundwater in the Piceance and Yellow Creek watersheds are bedrock aquifers in the Uinta and Green River Formations. The aquifers are divided into an upper and lower aquifer separated by a regionally extensive semiconfining layer. These aquifers provide water to streams and springs in the watersheds and are an important resource to people living and working in the area. Development of energy and mineral resources has the potential to affect the quality of groundwater in several ways. The Bureau of Land Management and the U.S. Geological Survey began groundwater monitoring in 2010 to characterize the groundwater quality and water-level elevations of shallow bedrock aquifers in the Piceance and Yellow Creek watersheds. The purpose of this report is to present groundwater chemistry and water-level elevations collected during 2013–16. Comparisons are made to data that were collected from the bedrock aquifers from 2010 to 2012 to identify the potential for changes in water quality and water-level elevations.

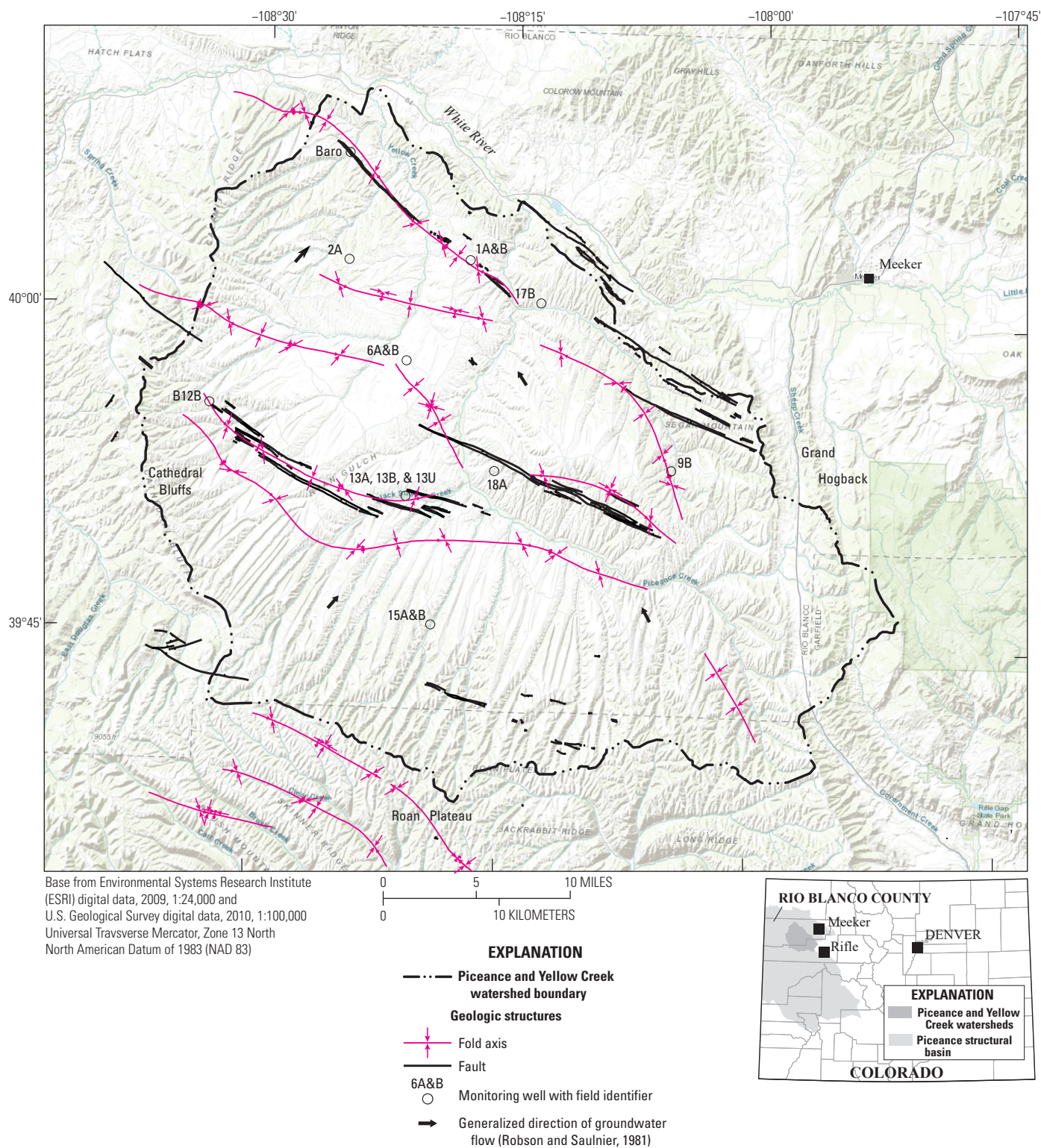
Appreciable changes in water-level elevations and hydraulic gradient were observed in early April 2015 in two wells completed in the upper and lower aquifers. The hydraulic gradient between the two wells was consistently downward from the upper aquifer to the lower aquifer during 2010–15; however, in early April 2015, the gradient changed from downward to upward between the two aquifers. Overall, water-level elevations declined by about 14 and 11 feet in the upper and lower aquifers, respectively, from 2013 to 2016. Previously published data estimated groundwater ages at 1,200 years old in the upper aquifer and 9,600 years old in the lower aquifer. These groundwater ages indicate that groundwater was recharged over thousands of years. With such long periods of time for aquifer recharge, declines in water-level elevation over short time steps (a few months) have important implications for sustainable management of this resource.

Solution mining activities or drilling for oil and natural gas in the area could be related to the changes observed in water-level elevations in these wells; however, further investigation would be needed to evaluate causation.

Changes in major-ion chemistry were evaluated in the bedrock aquifer using time series plots of select major-ion data from 2010 to 2016. Major-ion chemistry was variable for a single well from 2010 to 2016 where alkalinity and sulfate were the most variable constituents. One possible explanation for the observed changes in major-ion chemistry may be that the sample depth for that well no longer represents the most appreciable flow in the borehole. On a larger scale, potential changes in flow within the borehole may indicate changes in the regional flow system. Methane and volatile organic compound concentrations were evaluated using a similar approach to that of major ions and had similar findings. Methane concentrations in wells sampled from 2010 to 2016 were generally constant. The only exception was observed at a single well where the range of methane concentrations was from 57.4 (2010) to 4.02 milligrams per liter (2013). This is the same well where changes in water-level elevation, hydraulic gradient, and major-ion chemistry were observed, providing multiple lines of evidence to indicate change in the bedrock aquifers. Sampling of a well located in an area with little energy development but where faults or fractures could provide a path for the migration of fluids indicate mixing of groundwater between the upper and lower aquifers.

## Introduction

The Piceance and Yellow Creek watersheds in Rio Blanco County, Colorado, are known to contain important energy resources (oil shale and natural gas) and mineral resources (nahcolite) (Dubiel, 2003; Johnson and others, 2010; Brownfield and others, 2010) (fig. 1). Natural gas has been commercially produced in the study area since the 1950s and continues to the present (2018). The process of drilling for and extracting natural gas has evolved over time from a single well at a single well pad producing natural gas to multiple wells



**Figure 1.** Location of the Piceance Creek and Yellow Creek watersheds in the Piceance structural basin and the location of the monitoring-well network, Rio Blanco County, Colorado (field identifiers from table 1; geologic structure from Hail and Smith [1994, 1997]).



at a single well pad using directional drilling. In addition, conventional approaches to gas drilling have seen innovation with the use of hydraulic fracturing, which has provided the ability to liberate natural gas from previously unusable formations. Nahcolite has been mined in the study area since 1990 (Brownfield and others, 2010). The process used to extract the nahcolite is solution mining, where hot fluid is injected into the nahcolite-bearing zones to dissolve the nahcolite; then the fluid is subsequently pumped back to the surface to be processed. Primarily, one entity is mining nahcolite in the study area, and in 2013, operations were expanded to double production capacity (Natural Soda, 2017). Oil-shale deposits in the Green River Formation are estimated to contain about 1.5 trillion barrels of oil, making it the richest oil-shale deposit in the world (Johnson and others, 2010); however, there was no commercial-scale development as of 2016.

The primary sources of fresh groundwater in the Piceance and Yellow Creek watersheds are bedrock aquifers in the Uinta and Green River Formations (Weeks and others, 1974). These aquifers provide water to streams and springs in the watershed (Ortiz, 2002) and are an important resource to people living and working in the area. Development of energy and mineral resources has the potential to affect the quality of shallow groundwater in the study area in several ways. Infrastructure associated with the development of energy and mineral resources exists at the land surface throughout the study area and includes pipelines and storage ponds, which if compromised, could contaminate surface water and groundwater, incidents of which have happened in the past 10 years (Finley, 2013; Williams, 2011). Drilling operations can have a direct effect on groundwater, such as the migration of drilling fluids into permeable zones that intersect aquifers. Cement seals of gas wells have the potential to leak, allowing fluids to migrate from depth into shallow aquifers (Watson and Bachu, 2009; King and King, 2013). In addition, natural pathways along faults and fractures allow the migration of fluids from deep reservoirs into shallow aquifers (Johnson and Rice, 1990).

During the 1970s and 1980s, studies of groundwater chemistry and aquifer characterization were completed in relation to proposed oil-shale development (Welder and Saulnier, 1978; Robson and Saulnier, 1981; Slawson and others, 1982; Kimball, 1984). These studies were not meant to address the potential effects of oil and natural gas development or nahcolite mining on the bedrock aquifers. The lack of monitoring (as of 2010) of the bedrock aquifers was identified by the Bureau of Land Management as a data gap that needed to be addressed, and this data gap was formalized in a U.S. Government Accountability Report in 2010 (U.S. Government Accountability Office, 2018). The Bureau of Land Management, White River Field Office, and the U.S. Geological Survey (USGS) began a groundwater monitoring study in 2010 to characterize the groundwater quality of shallow bedrock aquifers in the Piceance and Yellow Creek watersheds. This first phase of monitoring (phase 1, 2010–12) established a monitoring-well network in the study area (McMahon and others, 2013). During phase 1, 14 monitoring wells were sampled

for field properties, major ions, nutrients, trace elements, noble gases, dissolved organic carbon, hydrocarbon molecular and isotopic compositions, volatile organic compounds (VOCs), and a broad suite of stable and radioactive isotopes. The chemical and isotopic constituents were selected to provide information on the overall groundwater quality and the occurrence and distribution of chemicals that could be related to the development of underlying reservoirs of oil and natural gas and to better understand groundwater residence times in the flow system. The second phase (phase 2, 2013–16) continues data collection from the monitoring-well network and builds on findings from phase 1. Phase 2 sampling focuses on monitoring groundwater for changes in constituent concentrations, using a smaller number of constituents selected to provide information on the overall groundwater quality, and for the occurrence of chemicals that could be related to the development of underlying oil and gas reservoirs. During phases 1 and 2, continuous water-level elevations were collected in five wells to provide information about temporal variability in water-level elevations and hydraulic gradients in the bedrock aquifers. Monitoring of groundwater from bedrock aquifers provides a tool to help differentiate natural variability in groundwater chemistry and water-level elevations from human-induced changes.

## Purpose and Scope

The purpose of this report is to present groundwater chemistry and water-level elevation data collected from bedrock aquifers in the Piceance and Yellow Creek watersheds during phase 2 (2013–16) of the groundwater monitoring study. Data were compared to previously published data from phase 1 (2010–12) of the study to identify changes in groundwater quality and water-level elevation (McMahon and others, 2013). Monitoring wells completed in the bedrock aquifers were sampled for select chemical constituents to provide information on the overall groundwater quality and to monitor for the occurrence of chemicals that could be related to the development of underlying oil and gas reservoirs. The Baro well was added to the monitoring-well network to evaluate sources and migration pathways of methane and VOCs where faults or fractures could provide a path for the migration of fluids from deep reservoirs to the shallow bedrock aquifers. Continuous water-level elevations were collected at a subset of wells within the monitoring-well network to understand the variability of water-level elevations and hydraulic gradients among bedrock aquifers.

## Description of the Study Area

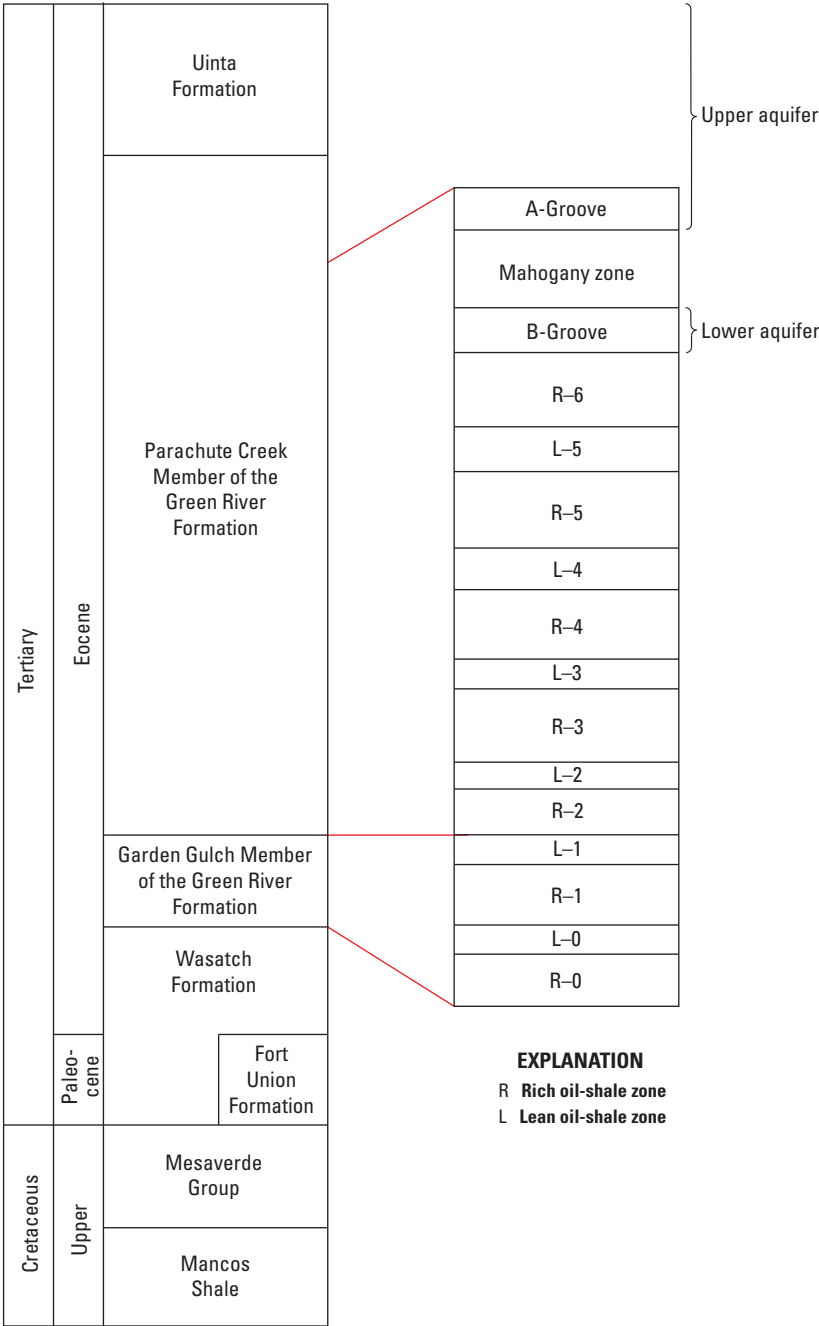
The study area is the Piceance and Yellow Creek watersheds within the Piceance structural basin in Rio Blanco County, Colo. (fig. 1). The watersheds have a combined area of about 900 square miles and are bounded by the White River to the north and by upland areas to the east (Grand Hogback),

south (Roan Plateau), and west (Cathedral Bluffs) (fig. 1). Elevations range from about 5,700 feet (ft) at the White River to more than 8,000 ft on the Roan Plateau and Cathedral Bluffs.

The primary bedrock units bearing fresh groundwater are the Uinta Formation and underlying Parachute Creek Member of the Green River Formation. Natural gas is produced primarily below these formations in the Wasatch Formation, Mesaverde Group, and other deeper geologic units (Johnson and Rice, 1990) (fig. 2). The depth of gas wells ranges from

2,500 to 8,000 ft below land surface depending on the geologic unit being targeted (Colorado Oil and Gas Conservation Commission, 2017). For comparison, the depth to the base of the deepest aquifer in the Parachute Creek Member generally is less than about 2,500 ft below land surface.

The geology of the Green River and Uinta Formations has been described in detail in Cashion and Donnell (1974), Hail (1990), Donnell (2009), Brownfield and others (2010), and Johnson and others (2010). Sedimentary strata of the



**Figure 2.** Generalized stratigraphic column for the Piceance and Yellow Creek watersheds within the Piceance structural basin, Rio Blanco County, Colorado (fig. 2 from McMahon and others [2013], modified from Johnson and Rice [1990] and Johnson and others [2010]).

Parachute Creek Member of the Green River Formation consist of calcareous and dolomitic marlstone, limestone, calcareous sandstone, siltstone, and mudstone with alternating lean and rich oil-shale zones (fig. 2). In the lower parts (L–5 and deeper zones) of the Parachute Creek Member is the saline zone, which contains nahcolite nodules and thin beds that also contain halite (Brownfield and others, 2010). The Uinta Formation overlies the Parachute Creek; however, lower parts of the formation are complexly intertongued with upper parts of the Parachute Creek (Donnell, 2009) (fig. 2). The Uinta Formation is a mix of sandstone, siltstone, mudstone, and marlstone (Johnson, 1981).

The primary sources of porosity and permeability in the Parachute Creek are fractures in the lean zones as well as vugs and breccias from the dissolution of nahcolite (Coffin and others, 1971). The rich oil-shale zones have high kerogen content and thus are more resistant to fracturing than the lean zones (Weeks and others, 1974; Robson and Saulnier, 1981).

A conceptual hydrogeologic model was proposed by USGS in the 1970s that divided the water-bearing zones in the Uinta and Parachute Creek into an upper and lower aquifer system separated by the Mahogany zone in the Parachute Creek Member of the Green River Formation (fig. 2). The Mahogany zone is a regionally extensive semiconfining layer (Coffin and others, 1971; Weeks and others, 1974; Robson and Saulnier, 1981). The upper bedrock aquifer system, consisting of water-bearing rocks of the Uinta and Parachute Creek above the Mahogany zone, has unconfined and confined zones. The lower, mostly confined aquifer system consists of water-bearing rocks of the Parachute Creek below the Mahogany zone and above the saline zone. Permeability of the saline zone and the underlying Garden Gulch Member of the Green River Formation is low, so they form the base of the freshwater-bearing aquifer system.

## Methods

Wells sampled during this study were selected from the monitoring-well network established during phase 1 (McMahon and others, 2013) plus an additional well (Baro well) (table 1). A total of 5 wells were sampled each year of the study, rotating among wells within the monitoring-well network in order to sample all 15 wells at least once during a 3-year period (table 1). Continuous water-level elevations were collected during phase 2 from the same subset of five wells as phase 1 (2013–16; table 1). The following sections provide details on the methods used for well selection, water-quality sample collection, laboratory analysis, quality control, and measurement of water-level elevations.

## Monitoring-Well Selection

Water-quality samples were collected from 5 of the monitoring wells in the monitoring-well network in August 2013, 2015, and 2016 and 2 monitoring wells in 2014, resulting in a total of 17 samples collected from 12 of the wells in the monitoring-well network (table 1). Because of site conditions at the time of sampling and changing data priorities, only 12 of the 15 wells were sampled during phase 2 (table 1). Well B12B was not sampled (table 1) because of changes in the study priorities to resample certain wells to clarify and further investigate findings of previous sample collection. Wells 1A and 1B were not sampled because road conditions prohibited access. The Baro well was initially supposed to be sampled in 2014; however, road conditions prevented access at that time (table 1).

## Sample Collection and Laboratory Analysis

Samples were collected during phase 2 from wells using either a submersible pump (wells 13A, 13B, and 13U) or a Kemmerer sampler (all other wells) (table 1) using procedures documented in the National Field Manual for the Collection of Water-Quality Data (USGS, 2006). The submersible pumps were made of stainless steel. The Kemmerer sampler is made of stainless steel with silicone seals, has a volume of 1.6 gallons, and was deployed using an electric wireline system and tripod. The Kemmerer sampler was lowered to a specified depth below land surface and then closed. The sample depth was selected using down hole geophysical data collected by USGS in 2011 (McMahon and others, 2013) to identify the depths where water entered and exited the open borehole during nonpumping conditions (Hess, 1986; Molz and others, 1994) (table 1). For wells sampled using a submersible pump, water-quality samples were collected from wells after field properties stabilized (water temperature, pH, dissolved oxygen, and specific conductance), as documented in the National Field Manual for the Collection of Water-Quality Data (USGS, 2006). For samples collected using the Kemmerer sampler, an aliquot of sample water was used to measure field properties. For all samples collected, concentrations of dissolved sulfide and alkalinity were measured in the field. Dissolved sulfide was measured in the field using the methylene blue method (Hach, 2018). Alkalinity was measured in the field by incremental titration using 1.6 normal sulfuric acid (Rounds, 2006).

Different constituents were sampled at different wells based on study priorities. Water samples collected from all wells were analyzed for major ions, dissolved gases (methane, nitrogen, argon, and carbon dioxide), and VOCs. The Baro well was sampled for additional constituents including trace



**Table 1.** Location, construction, geologic information, and year sampled during phase 2 (2013–16) for wells in the monitoring-well network, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[Coordinate datum World Geodetic System 1984; gray shading indicates continuous water-level elevation monitoring; USGS, U.S. Geological Survey; NAVD88, North American Vertical Datum of 1988; --, not sampled; x, sampled; note, unable to access site in 2014 because of road conditions]

USGS site number	Station name	Field identifier	Latitude	Longitude	Year drilled	Land- surface elevation, in feet above NAVD88	Sample interval, in feet below land surface	Sampling device	Aquifer assignment for sample interval	Wells sampled, by year			
										2013	2014	2015	2016
395458108325002 <sup>1</sup>	SC00109931CD2 B12-31-199-B	B12B	39.916	-108.547	2002	7,458	407–491	submersible pump	lower aquifer	--	--	--	--
400218108170600 <sup>1</sup>	SB00109721CAD2 TH 75-1A (B1-97-21 CAD1)	1A	40.038	-108.286	1975	6143	550	Kemmerer	upper aquifer	--	--	--	--
400218108170601 <sup>1</sup>	SB00109721CAD TH 75-1B	1B	40.038	-108.285	1975	6,146	1,300	Kemmerer	lower aquifer	--	--	--	--
400228108245400	SB00109820BD TH 75-2A	2A	40.041	-108.415	1975	6,719	761	Kemmerer	upper aquifer	--	--	x	--
395755108211400	SC00109814ADC1 TH 75-6A	6A	39.964	-108.354	1975	6,439	400	Kemmerer	upper aquifer	--	--	--	x
395755108211401	SC00109814ADC2 TH 75-6B (C1-98-14 ADC2)	6B	39.965	-108.354	1975	6,438	1,440	Kemmerer	lower aquifer	x	--	--	x
395310108050401	SC00209508CCA TH 75-9B	9B	39.886	-108.085	1975	7,350	1,325	Kemmerer	lower aquifer	--	--	x	--
395136108210000	SC00209824CBB TH 75-13A (C2-98-24 CBB2)	13A	39.860	-108.350	1975	6,400	557–640	submersible pump	upper aquifer	x	--	--	x
395136108210001	SC00209824CBB TH 75-13B	13B	39.860	-108.351	1976	6,399	776–870	submersible pump	lower aquifer	x	--	--	x
395136108210004	SC00209824CBB4 TH75-13U	13U	39.860	-108.351	2010	6,400	159–239	submersible pump	upper aquifer	x	--	--	x
394540108191201	SC00309730AC TH 75-15A (C3-97-30 ACC1)	15A	39.761	-108.320	1975	6,816	525	Kemmerer	upper aquifer	--	x	--	--
394540108191202	SC00309730ACC2 TH 75-15B	15B	39.761	-108.320	1975	6,816	775	Kemmerer	lower aquifer	--	x	--	--
400045108131401	SB00109736ADC3 TH 75-17B, CR2, (B1-97-36 ADC3)	17B	40.012	-108.222	1975	6,100	1,050	Kemmerer	lower aquifer	--	--	x	--
395255108154200	SC00209715ACC2 TH 75-18A (C2-97-15 AAC1)	18A	39.882	-108.263	1975	6,740	600	Kemmerer	upper aquifer	x	--	x	--
400725108250400	BARODYANAM 72-1 B2- 98-20CDBA	Baro	40.124	-108.418	1972	5,966	610	Kemmerer	upper aquifer	--	note	x	--

<sup>1</sup>Wells not sampled during 2013–16.

elements, nutrients, dissolved organic carbon, stable isotopes of water ( $\delta^2\text{H-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$ ), stable carbon isotopes of dissolved inorganic carbon (DIC) ( $\delta^{13}\text{C-DIC}$ ), carbon-14 of DIC, and tritium. A total of four wells (13A, 13B, 13U, and Baro well) also were sampled for stable carbon isotope composition ( $\delta^{13}\text{C}$ ) of methane (methane isotope), hydrocarbon gas composition, and methane concentrations.

Samples were processed in the field using filtration, acidification, and refrigeration as appropriate based on the constituent and following USGS sample processing procedures (Wilde and others, 2004). Constituents are grouped by preservations (filtration, acidification, and refrigeration) and sampling techniques used. Samples for the analysis of alkalinity, major ions, trace elements, nutrients, dissolved organic carbon,  $\delta^{13}\text{C-DIC}$ , and carbon-14 of DIC were filtered at the time of collection using a disposable, one-time use, 0.45-micron capsule filter. All samples were collected in prerinsed, plastic bottles except for VOCs, dissolved organic carbon,  $\delta^{13}\text{C-DIC}$ , and carbon-14 of DIC, which were collected in baked amber glass bottles. Samples for cation and trace-element analysis were acidified in the field to a pH of less than 2 using nitric acid. VOC samples were unfiltered and acidified in the field with 1:1 hydrochloric acid. Samples for dissolved organic carbon analysis were acidified in the field using sulfuric acid. Samples for dissolved gases, VOCs, nutrients, and dissolved organic carbon were kept chilled on ice until delivered to the laboratory. Samples for analysis of dissolved gases were unfiltered and collected in glass bottles that were filled and capped with thick rubber stoppers under water to exclude headspace (atmospheric contamination) (USGS, 2017a). Samples for dissolved-gas analysis were collected in duplicate at each well. Samples analyzed for stable isotopes of water ( $\delta^2\text{H-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$ ) were unfiltered and collected in glass bottles with polyseal caps secured with electrical tape (USGS, 2017b). Samples for tritium analysis were unfiltered and collected in plastic bottles with polyseal caps and secured with electrical tape. All data collected are stored in the USGS National Water Information System and available to the public (USGS, 2018).

In presenting constituent analysis, constituents were grouped according to the laboratory completing the analysis. Major ions, VOCs, trace elements, nutrients, and dissolved organic carbon were analyzed using standard methods at the USGS National Water Quality Laboratory in Lakewood, Colo. (Brenton and Arnett, 1993; Fishman, 1993; Fishman and Friedman, 1989; Garbarino and others, 2006; Rose and others, 2016). Concentrations of dissolved gases were measured by the USGS Groundwater Dating Laboratory in Reston, Virginia, using gas chromatography (Busenberg and others, 1993). The USGS Reston Stable Isotope Laboratory in Reston, Va., analyzed samples for  $\delta^2\text{H-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$  (Révész and Coplen, 2008a and 2008b). Hydrogen and oxygen isotopes in water were reported relative to Vienna Standard Mean Ocean Water. All isotope results were reported using the standard delta notation ( $\delta$ ), in per mil (o/oo, parts per thousand); for example,  $\delta^{18}\text{O-H}_2\text{O}$  is defined as the following:

$$\delta^{18}\text{O-H}_2\text{O} = ([^{18}\text{O}/^{16}\text{O}]_{\text{sample}} / [^{18}\text{O}/^{16}\text{O}]_{\text{ref}} - 1) \times 1,000 \quad (1)$$

where

$^{18}\text{O}/^{16}\text{O}$  is the ratio of oxygen-18 to oxygen-16 in the *sample* and reference (*ref*) material (Vienna Standard Mean Ocean Water in this example).

The  $\delta^{13}\text{C-DIC}$  and carbon-14 of DIC samples were measured at the Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry facility (Woods Hole Oceanographic Institution, 2018). The  $\delta^{13}\text{C-DIC}$  results are reported relative to Vienna Pee Dee belemnite, and the carbon-14 of DIC results are reported in percent modern carbon. Radiocarbon age was calculated from the  $\delta^{13}\text{C}$  corrected fraction modern according to the following formula:

$$\text{Age} = -8,033 \ln(Fm) \quad (2)$$

where

$\ln$  is the natural log and  
 $Fm$  is the  $\delta^{13}\text{C}$  fraction modern.

The reporting of ages and activities follows the conventions outlined by Stuiver and Polach (1977) and Stuiver (1980). Tritium analyses were completed at USGS Noble Gas Laboratory in Denver, Colo., and reported in tritium units (TU) (Bayer and others, 1989).

A total of four wells were sampled for stable carbon isotope composition ( $\delta^{13}\text{C}$ ) of methane (methane isotope), hydrocarbon gas composition, and methane concentrations. These samples were collected using an IsoFlask® obtained from Isotech Laboratories, Inc., Champaign, Illinois (Isotech Laboratories, Inc., 2018a). Instructions for filling IsoFlasks® are provided by Isotech Laboratories, Inc. Filled IsoFlasks® were placed in a protective box lying flat and shipped overnight to Isotech Laboratories for analysis. Stable carbon isotope compositions of gas components were determined by chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry (Isotech Laboratories, Inc., 2018b). Chromatographic determination was used to determine hydrocarbons, and dissolved methane concentration was calculated using a head-space equilibration method (Isotech Laboratories, Inc., 2018c).

## Quality Control

Quality-control data were collected during each sampling event and included a field blank and a sequential replicate, except during 2013 where only a replicate sample was collected (tables 2 and 3), following USGS procedures (USGS, 2006). Field blanks were collected to evaluate potential sample contamination related to sample collection, handling, and equipment cleaning under field conditions and

**Table 2.** Results of sample blank analysis for study period, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.[mg/L, milligram per liter; SiO<sub>2</sub>, silicon dioxide; µg/L, microgram per liter; <, less than; --, no data]

Field identifier	Date	Time	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Bromide (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Silica (mg/L) as SiO <sub>2</sub>	Sulfate (mg/L)
15B	7/30/2014	1359	<0.022	<0.011	<0.03	<0.06	<0.030	<0.04	<0.02	0.042	<0.04
18A	8/19/2015	1259	<0.022	<0.011	<0.03	<0.06	<0.030	<0.02	<0.01	<0.018	<0.02
13A	8/25/2016	0859	0.093	0.061	<0.06	<0.10	<0.010	<0.02	<0.01	0.032	0.03
Reporting level(s)	--	--	0.022	0.011	0.03, 0.06	0.06, 0.10	0.010, 0.030	0.02, 0.04	0.01, 0.02	0.018	0.02, 0.04
Minimum blank concentration	--	--	<0.022	<0.011	<0.03	<0.06	<0.030	<0.02	<0.01	<0.018	<0.02
Maximum blank concentration	--	--	0.093	0.061	<0.03	<0.06	<0.030	<0.02	<0.01	0.042	0.03
Minimum environmental sample concentration	--	--	3.73	3.05	0.23	191	0.050	5.3	0.11	10.0	0.08
Maximum environmental sample concentration	--	--	79.8	104	13.3	6,570	0.388	1,240	26.4	41.4	525

Field identifier	Date	Time	Iron (µg/L)	Manganese (µg/L)	Benzene (µg/L)	Ethyl- benzene (µg/L)	Methyl tert-butyl ether (µg/L)	m-Xylene plus p-xylene (µg/L)	o-Xylene (µg/L)	Toluene (µg/L)
15B	7/30/2014	1359	<4.0	<0.20	<0.1	<0.1	<0.2	<0.2	<0.1	<0.1
18A	8/19/2015	1259	<4.0	<0.20	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
13A	8/25/2016	0859	<5.0	<0.20	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
Reporting level(s)	--	--	4.0, 5.0	0.20	0.026, 0.1	0.1, 0.036	0.2, 0.1	0.2, 0.08	0.1, 0.032	0.1, 0.02
Minimum blank concentration	--	--	<4.0	<0.20	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
Maximum blank concentration	--	--	<4.0	<0.20	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
Minimum environmental sample concentration	--	--	5.1	0.96	<0.026	<0.036	<0.10	<0.08	<0.032	0.03
Maximum environmental sample concentration	--	--	306	14.5	0.3	<0.036	<0.10	0.05	<0.032	2.6



**Table 3.** Results of sample replicate analysis for study period, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[mg/L, milligram per liter; SiO<sub>2</sub>, silicon dioxide; µg/L, microgram per liter; relative percent difference, the absolute difference between replicate analyses divided by the average of the analyses and expressed as percent; <, less than; --, no data]

Field identifier	Date	Time	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Bromide (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Silica (mg/L as SiO <sub>2</sub> )	Sulfate (mg/L)
13U	8/20/2013	1130	72.2	88.9	0.47	203	0.074	8.57	0.32	35.8	525
13U - replicate	8/20/2013	1131	71.3	88.3	0.49	199	0.079	8.52	0.31	35.9	519
Relative percent difference			1.25	0.677	4.17	1.99	6.54	0.585	3.17	0.279	1.15
15A	7/30/2014	1200	7.57	4.92	1.54	501	0.264	118	16.9	10.5	27.3
15A - replicate	7/30/2014	1201	7.78	4.97	1.53	522	0.266	119	17.1	10.6	26.4
Relative percent difference			2.74	1.01	0.651	4.11	0.755	0.844	1.18	0.948	3.35
18A	8/20/2015	1500	42.2	98.2	0.31	209	<0.060	6.05	1.59	30.9	449
18A - replicate	8/20/2015	1501	43	98.7	0.31	214	<0.060	5.82	1.49	31.3	432
Relative percent difference			1.88	0.508	0	2.36	0	3.87	6.49	1.29	3.86
6A	8/25/2016	1400	8.55	13	0.65	329	0.086	10.7	0.2	13	451
6A - replicate	8/25/2016	1401	8.59	13.1	0.64	320	0.087	10.9	0.2	12.9	461
Relative percent difference			0.467	0.766	1.55	2.77	1.16	1.85	0	0.772	2.19
Minimum relative percent difference			0.47	0.51	0	1.99	0	0.59	0	0.28	1.15
Maximum relative percent difference			2.74	1.01	4.17	4.11	6.54	3.87	6.49	1.29	3.86

Field identifier	Date	Time	Iron (µg/L)	Manganese (µg/L)	Benzene (µg/L)	Ethyl-benzene (µg/L)	Methyl tert-butyl ether (µg/L)	m-Xylene plus p-xylene (µg/L)	o-Xylene (µg/L)	Toluene (µg/L)
13U	8/20/2013	1130	21.7	10.8	0.2	<0.1	<0.2	<0.2	<0.1	<0.1
13U - replicate	8/20/2013	1131	22.1	10.8	0.2	<0.1	<0.2	<0.2	<0.1	<0.1
Relative percent difference			1.83	0	0	0	0	0	0	0
15A	7/30/2014	1200	30.9	2.46	0.3	<0.1	<0.2	<0.2	<0.1	<0.1
15A - replicate	7/30/2014	1201	28.2	2.49	0.3	0.1	<0.2	<0.2	<0.1	<0.1
Relative percent difference			9.14	1.21	0	--	0	0	0	0
18A	8/20/2015	1500	36.2	3.51	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
18A - replicate	8/20/2015	1501	34.2	3.53	<0.026	<0.036	<0.10	<0.08	<0.032	<0.02
Relative percent difference			5.62	0.568	0	0	0	0	0	0
6A	8/25/2016	1400	11.1	14.5	<0.026	<0.036	<0.10	<0.08	<0.032	0.05
6A - replicate	8/25/2016	1401	10.8	14.3	<0.026	<0.036	<0.10	<0.08	<0.032	0.05
Relative percent difference			2.74	1.39	0	0	0	0	0	0
Minimum relative percent difference			1.83	0	0	0	0	0	0	0
Maximum relative percent difference			9.14	1.39	0	0	0	0	0	0

were analyzed for major ions and VOCs. Few constituents were detected in field blanks, and detections were less than minimum environmental sample concentrations except for *m*-xylene plus *p*-xylene where the maximum environmental sample concentration was 0.05 micrograms per liter ( $\mu\text{g/L}$ ), which is below the laboratory reporting level but above the long-term method detection level (table 2). Sequential replicate samples were collected for major ions and VOC's immediately after environmental samples to assess analytical variability and variability resulting from sample collection. Analysis of replicate samples indicated that most constituents had relative percent differences of less than 5 percent, and all constituents had relative percent differences below 10 percent (table 3).

Charge balance was used to evaluate sample quality by determining the difference in milliequivalents between the cations and anions for each environmental sample. Milliequivalent balances were calculated according to methods described by Hem (1985). Charge balances for all but one sample were between 5 and 10 percent, indicating generally good analytical results for major ions.

## Measurement of Water-Level Elevations

A discrete water level (depth to water in ft below land surface) was measured in wells at the time of sample collection using either a steel tape or an electric tape, following USGS procedures (Cunningham and Schalk, 2011). The water-level elevation was determined by subtracting the measured depth to water in ft below land surface (table 4) from the land-surface elevation above North American Vertical Datum of 1988 at each well location (table 1). Continuous water-level elevations were collected at five wells in the monitoring-well network to provide information on changes in water-level elevations and hydraulic gradients between the upper and lower aquifers (table 1). Continuous water-level elevations were measured using nonvented pressure transducers. Pressure readings were corrected for fluctuations in barometric pressure using data from a barometric pressure sensor (Cunningham and Schalk, 2011). Continuous water-level elevations in this report are presented as daily mean values by water year (a water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends) and processing of the measured data followed USGS guidelines (Freeman and others, 2004). All water-level elevations (discrete and continuous) are available from the National Water Information System (USGS, 2018).

## Groundwater Chemistry and Water-Level Elevations in Bedrock Aquifers

The following sections of the report describe the results of groundwater monitoring. The sections on reduction-oxidation (redox) processes, major-ion chemistry, and methane and VOCs describe the conditions observed during phase 2 (2013–16) and comparison to observations and data presented from phase 1 (McMahon and others, 2013). Within the section on redox, concentrations of dissolved oxygen, methane, dissolved sulfide, sulfate, and methane isotopes are discussed as they pertain to redox. The section on the Baro well describes the reasons for the addition of this well into the monitoring-well network and the results and implications from this well. Continuous water-level elevations were used to identify appreciable changes in water-level elevation and to understand hydraulic gradients between the upper and lower aquifers.

## Reduction-Oxidation Processes

Reduction-oxidation (redox) processes involve the transfer of electrons from one chemical species to another. Electron acceptors are reduced, and electron donors are oxidized. Dissolved oxygen, when present, is the preferred electron acceptor because the reduction of oxygen produces more energy than any other common electron acceptor (McMahon and Chapelle, 2008). Groundwater containing at least 0.5 milligrams per liter ( $\text{mg/L}$ ) of dissolved oxygen is considered to be oxic, whereas anoxic groundwater contains less than 0.5  $\text{mg/L}$  of dissolved oxygen. Anoxic conditions existed for all samples collected during phase 2, as evidenced by dissolved oxygen concentrations less than 0.5  $\text{mg/L}$  (table 4).

Sulfate reduction and methanogenesis were important redox processes in anoxic groundwater in the study area based on the presence of dissolved sulfide (table 4) and methane (table 5) in water from several wells. The inverse relation observed between methane and sulfate (fig. 3) likely results from sulfate-reducing microbes outcompeting methanogens for electron donors needed to support their metabolism (Lovley and Klug, 1986). This relation appears in all samples except samples from well 13U, where high sulfate concentrations were present with high methane concentrations (fig. 3). As McMahon and others (2013) observed during phase 1, samples from well 13U consisted almost entirely of thermogenic methane. Methane isotope data collected during phase 2

**Table 4.** Field properties and major-ion data for water collected from monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[mg/L, milligram per liter;  $\mu\text{S}/\text{cm}$  at 25 °C, microsiemen per centimeter at 25 degrees Celsius ; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L as  $\text{CaCO}_3$ , milligram per liter as calcium carbonate;  $\mu\text{g}/\text{L}$ , microgram per liter; <, less than; --, not analyzed]

Field identifier	Date	Time	Depth to water, in feet below land surface	Dissolved oxygen (mg/L)	pH (standard unit)	Specific conductance ( $\mu\text{S}/\text{cm}$ at 25 °C)	Temperature (°C)	Turbidity (NTRU)	Dissolved solids (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)
13A	8/20/2013	1230	58.4	<0.5	7.6	1,400	16.2	1	932	24.2	50.6	0.23	203
13A	8/24/2016	1530	56.3	<0.5	7.7	1,390	16.3	--	925	26.1	57.0	0.35	231
13B	8/20/2013	1500	80.7	<0.5	7.8	1,360	18.0	64	845	15.7	17.6	0.52	268
13B	8/24/2016	1400	78.3	<0.5	7.8	1,300	16.6	--	854	12.6	18.4	0.64	306
13U	8/20/2013	1130	60.9	<0.5	7.1	1,790	14.7	1.3	1,270	72.2	88.9	0.47	203
13U	8/24/2016	1300	58.8	<0.5	7.1	1,790	13.8	--	1,260	79.8	97.6	0.64	233
15A	7/30/2014	1200	48.6	<0.5	7.0	2,190	14.8	13	1,370	7.57	4.92	1.54	501
15B	7/30/2014	1400	31.3	<0.5	7.7	2,370	15.6	9.8	1,480	4.09	4.34	1.28	540
17B	8/19/2015	1530	67.1	<0.5	7.4	6,590	21.1	1.9	4,320	5.93	5.47	6.36	1,600
18A	8/21/2013	1330	412.9	<0.5	7.6	1,560	15.8	0.9	1,070	36.2	81.3	0.29	191
18A	8/20/2015	1500	415.5	<0.5	7.5	1,690	--	2.1	1,090	42.2	98.2	0.31	209
2A	8/19/2015	1200	589.3	<0.5	7.4	1,830	16.1	1.9	1,280	67.5	104.0	0.5	230
6A	8/25/2016	1400	--	<0.5	8.1	1,510	17.9	1.8	994	8.55	13.0	0.65	329
6B	8/22/2013	1300	284.7	<0.5	8.6	1,390	14.5	--	882	4.42	3.5	0.39	274
6B	8/25/2016	1200	294.6	<0.5	8.1	1,510	14.3	2.4	1,000	3.73	3.05	0.91	370
9B	8/20/2015	1100	458.5	<0.5	7.9	1,610	17.5	7.5	973	7.66	3.88	0.84	386
Baro	8/18/2015	1200	39.0	<0.5	7.7	23,000	--	20	17,400	7.71	26.9	13.3	6,570

**Table 4.** Field properties and major-ion data for water collected from monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.—Continued.

[mg/L, milligram per liter;  $\mu\text{S}/\text{cm}$  at 25 °C, microsiemen per centimeter at 25 degrees Celsius ; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L as  $\text{CaCO}_3$ , milligram per liter as calcium carbonate;  $\mu\text{g}/\text{L}$ , microgram per liter; <, less than; --, not analyzed]

Field identifier	Date	Time	Alkalinity (mg/L as $\text{CaCO}_3$ )	Bicarbonate (mg/L)	Bromide (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Sulfate (mg/L)	Dissolved sulfide (mg/L)	Iron ( $\mu\text{g}/\text{L}$ )	Manganese ( $\mu\text{g}/\text{L}$ )
13A	8/20/2013	1230	445	542	0.062	--	6.83	2.93	342	0.54	5.1	0.97
13A	8/24/2016	1530	436	528	0.054	1.7	6.28	2.61	321	0.4	10.9	1.22
13B	8/20/2013	1500	758	924	0.087	--	9.13	4.77	97.6	74	47.2	5.24
13B	8/24/2016	1400	735	888	0.059	3.8	9.04	4.31	35.5	--	19.2	5.63
13U	8/20/2013	1130	539	657	0.074	--	8.57	0.32	525	4.4	21.7	10.8
13U	8/24/2016	1300	538	654	0.067	0.7	7.66	0.28	499	5.7	7.9	7.63
15A	7/30/2014	1200	1,020	1,240	0.26	--	118	16.9	27.3	12.3	30.9	2.46
15B	7/30/2014	1400	1,140	1,400	<0.150	--	113	22.6	0.08	0.01	183	0.96
17B	8/19/2015	1530	3,400	4,150	0.39	--	304	26.4	0.17	0.036	306	2.19
18A	8/21/2013	1330	541	659	0.05	--	6.86	2.35	444	44	12	2.36
18A	8/20/2015	1500	487	594	<0.060	--	6.05	1.59	449	14.7	36.2	3.51
2A	8/19/2015	1200	673	821	<0.060	--	5.3	0.11	361	0.054	192	7.87
6A	8/25/2016	1400	292	346	0.086	5.1	10.7	0.2	451	0.01	11.1	14.5
6B	8/22/2013	1300	351	381	0.091	23	12	1.69	367	1.5	71.6	10.8
6B	8/25/2016	1200	723	860	0.088	10.6	23.1	9.32	113	37	17.8	5.17
9B	8/20/2015	1100	834	1,020	<0.060	--	14.2	14.5	0.59	0.182	119	2.48
Baro	8/18/2015	1200	13,400	16,300	<1.50	--	1,240	21.6	42.5	8.0	<100	8.18

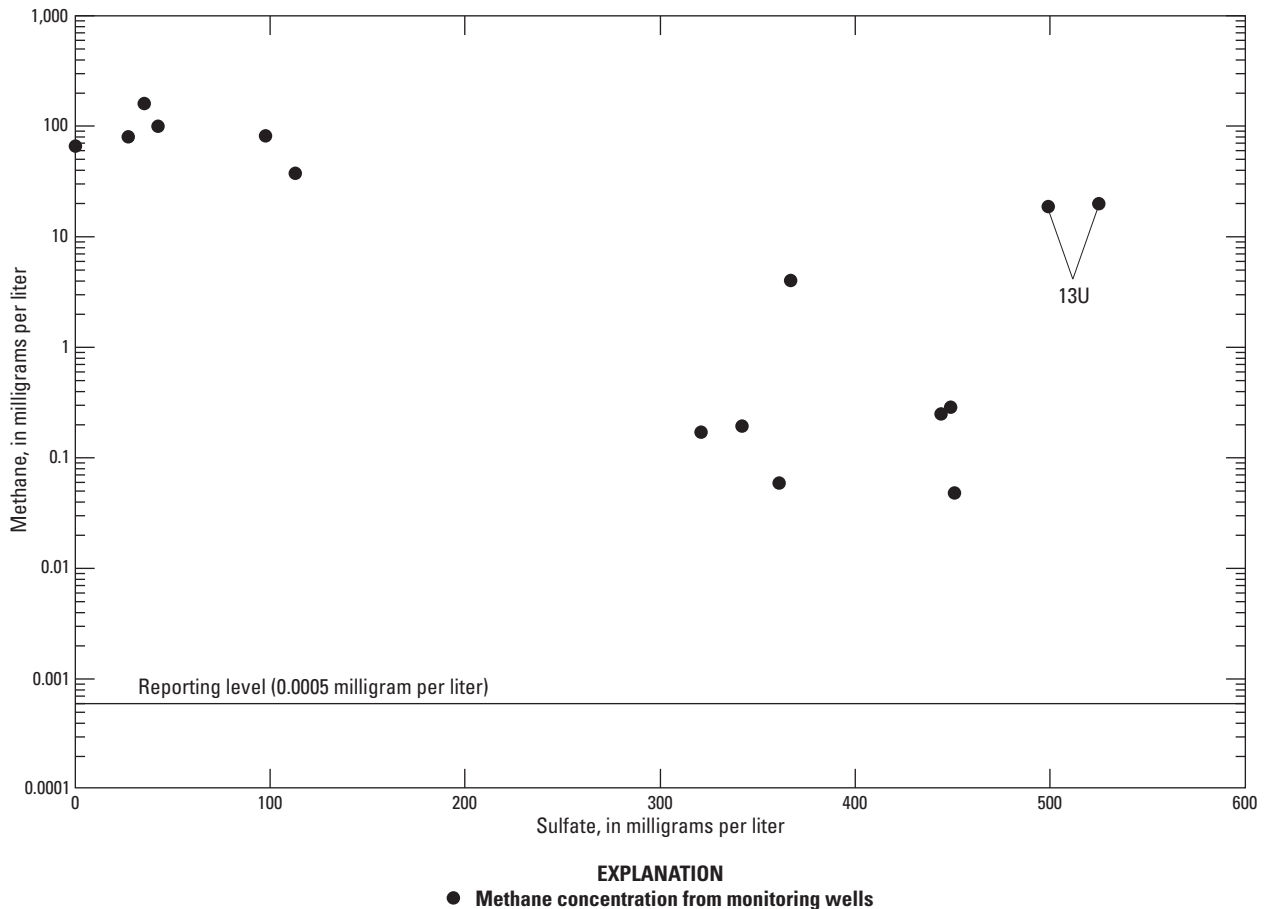
**Table 5.** Methane and volatile organic compound concentration data for water collected from monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[Methane concentration was determined by U.S. Geological Survey Reston Groundwater Dating Laboratory unless otherwise indicated; µg/L, microgram per liter; mg/L, milligram per liter; E, signifies that the measured concentration was estimated by the National Water Quality Laboratory because of the high degree of variability in this constituent (Childress and others, 1999); --, not analyzed; <, less than]

Field identifier	Date	Time	Methane (mg/L)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	<i>m</i> -Xylene plus <i>p</i> -xylene (µg/L)	<i>o</i> -Xylene (µg/L)	Methyl <i>tert</i> -butyl ether (µg/L)	Carbon disulfide (µg/L)	Butane (µg/L)	Hexane (µg/L)	<i>n</i> -Pentane (µg/L)	Trichloro-methane (µg/L)
13A	8/20/2013	1230	0.194	<0.1	0.9	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
13A	8/24/2016	1530	0.171	<0.026	2.6	<0.036	<0.08	<0.032	<0.10	<0.1	<0.038	<0.024	<0.022	<0.03
13B	8/20/2013	1500	81.5	<0.1	0.9	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
13B	8/24/2016	1400	160 <sup>1</sup>	<0.026	0.53	<0.036	<0.08	<0.032	<0.10	<0.1	4.06	E0.023	0.37	<0.03
13U	8/20/2013	1130	19.9	0.2	<0.1	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
13U	8/24/2016	1300	18.7	0.136	<0.02	<0.036	<0.08	<0.032	<0.10	<0.1	0.094	<0.024	<0.022	0.03
15A	7/30/2014	1200	80.0	0.3	<0.1	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
15B	7/30/2014	1400	--	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
17B	8/19/2015	1530	66.1	0.015	E0.02	<0.036	0.05	<0.032	<0.10	--	--	--	--	--
18A	8/21/2013	1330	0.25	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
18A	8/20/2015	1500	0.287	<0.026	<0.02	<0.036	<0.08	<0.032	<0.10	--	--	--	--	--
2A	8/19/2015	1200	0.059	<0.026	E0.02	<0.036	<0.08	<0.032	<0.10	--	--	--	--	--
6A	8/25/2016	1400	0.048	<0.026	0.05	<0.036	<0.08	<0.032	<0.10	<0.1	<0.038	<0.024	<0.022	<0.03
6B	8/22/2013	1300	4.02	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	--	--	--	--	--
6B	8/25/2016	1200	37.4	<0.026	<0.02	<0.036	<0.08	<0.032	<0.10	E0.2	<0.038	<0.024	<0.022	<0.03
9B	8/20/2015	1100	--	<0.026	0.03	<0.036	0.03	<0.032	<0.10	--	--	--	--	--
Baro	8/18/2015	1200	100 <sup>1</sup>	<0.026	0.04	<0.036	<0.08	<0.032	<0.10	--	--	--	--	--

<sup>1</sup>Methane concentration from table 6.





**Figure 3.** Methane concentrations in relation to sulfate concentrations for water samples collected from monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

(table 6) are consistent with phase 1 findings (fig. 6 of McMahon and others, 2013). The combination of isotope data and sulfate and methane concentration data indicate that biogenic processes are not a primary control on methane concentrations in well 13U.

## Major-Ion Chemistry

Major-ion chemistry is the principal contributor of electrical charge for dissolved constituents in water and is used to define water types (Hem, 1985). Concentrations of dissolved solids in water samples ranged from 845 to 17,400 mg/L (table 4). The highest concentrations were in samples from well 17B (4,320 mg/L) and the Baro well (17,400 mg/L), which were in the regional discharge area at the northern end of the study area (fig. 1). Based on sample composition in percentage of milliequivalents per liter, water types for all samples were generally mixed cation-bicarbonate-sulfate and sodium-bicarbonate water types (fig. 4). McMahon and others (2013) observed that these two water types indicate the evolution of groundwater along its flow path where the

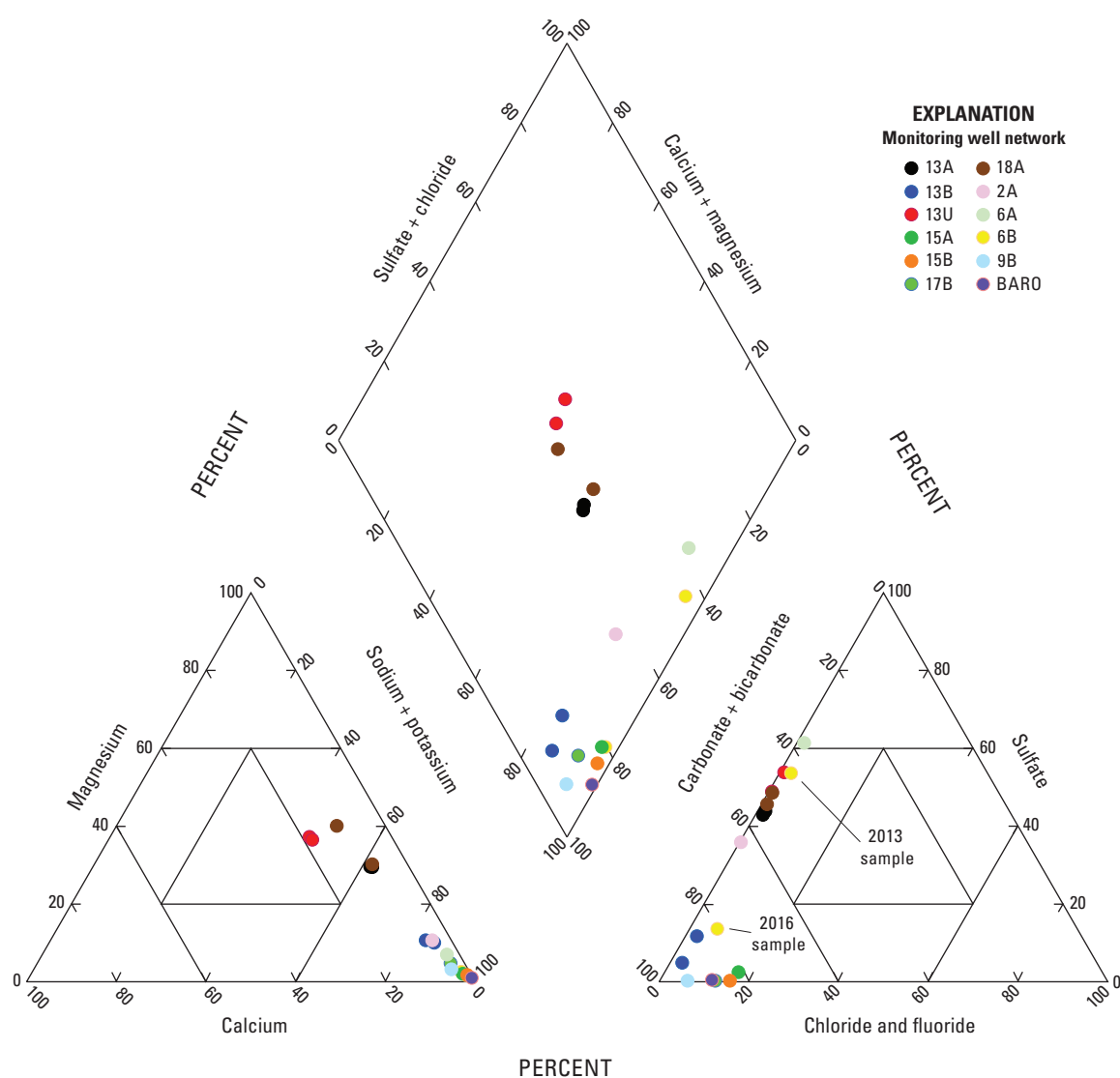
mixed cation-bicarbonate-sulfate water type represents water closer to its recharge areas in higher topographic locations in the study area. The sodium-bicarbonate water type represents water that has traveled farther along its flow path toward the regional groundwater discharge area in the northern part of the study area (McMahon and others, 2013). Wells 13A, 13B, 13U, 18A, and 6B were sampled twice during phase 2, where the two samples from each well plot relatively close to one another on the trilinear diagram except for 6B. Well 6B cations did not change for the two samples collected during phase 2, but anions were a mix of bicarbonate and sulfate during the 2013 sample and almost entirely bicarbonate during the 2016 sample (table 4, fig. 4).

Time series plots of select major-ion data were evaluated from phase 1 (table 2 of McMahon and others [2013]) and phase 2 (table 4) to further understand potential changes in major-ion chemistry. Well 6B was the only site with variable major-ion chemistry where alkalinity and sulfate were the most variable constituents, and these changes in chemistry do not seem to correspond to appreciable changes in water-level elevations (fig. 5). Well 6B was sampled using the Kemmerer

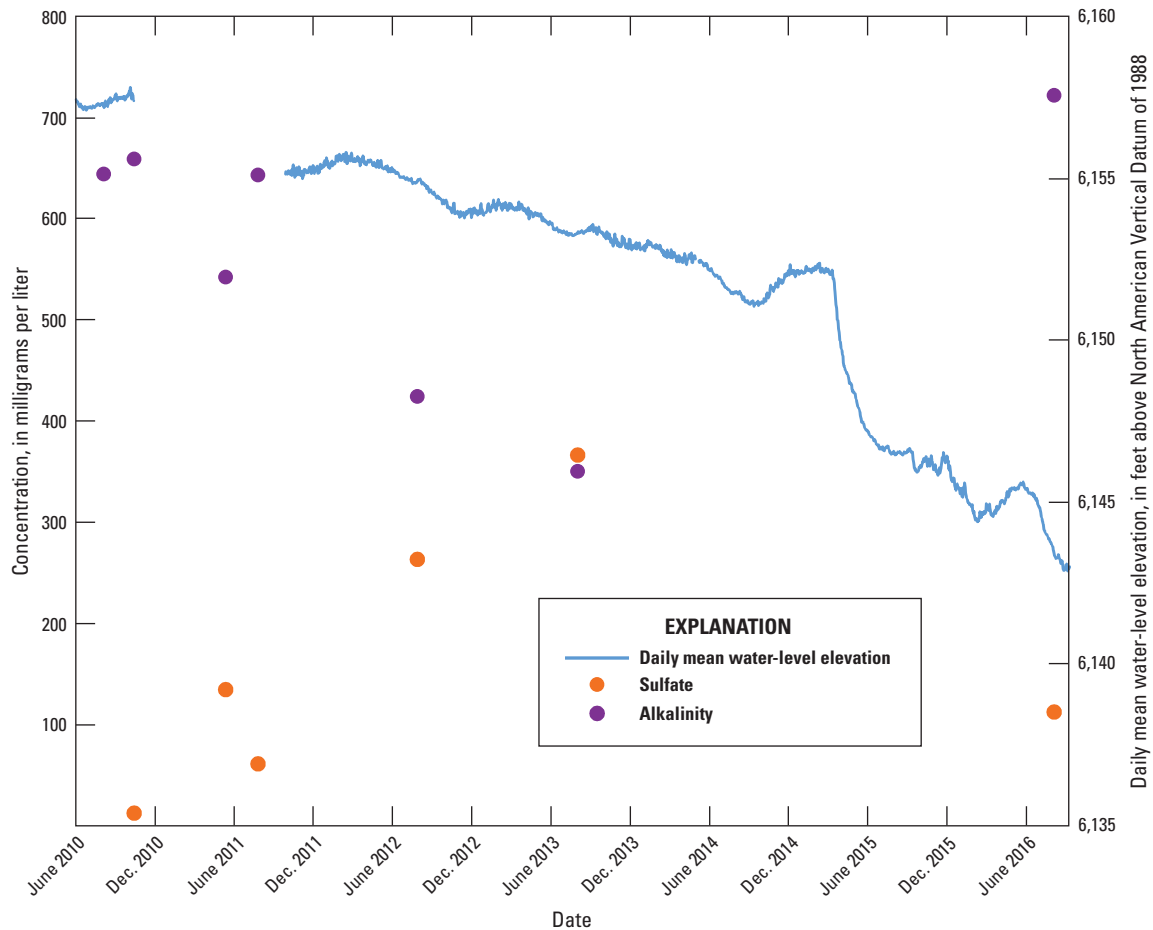
**Table 6.** Hydrocarbon composition, methane isotope, and dissolved methane concentration data for water collected from four monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[All results were determined by Isotech Laboratories Inc.;  $\delta^{13}\text{C}$ , stable carbon isotope composition; per mil, part per thousand; mg/L, milligram per liter; --, not analyzed]

Field identifier	Date	Time	Methane/ (ethane + propane)	$\delta^{13}\text{C}$ of methane, in per mil	Dissolved methane (mg/L)
Baro	8/18/2015	1200	1,267	-67.17	100
13A	8/24/2016	1530	175.4	--	0.13
13U	8/24/2016	1300	29.01	-34.06	17
13B	8/24/2016	1400	929.6	-62.38	160



**Figure 4.** Trilinear diagram showing water composition, in percent of constituents, collected from monitoring wells, 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.



**Figure 5.** Time series plot of alkalinity and sulfate concentration data collected during phase 1 and phase 2 with daily mean water-level elevation for well 6B, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

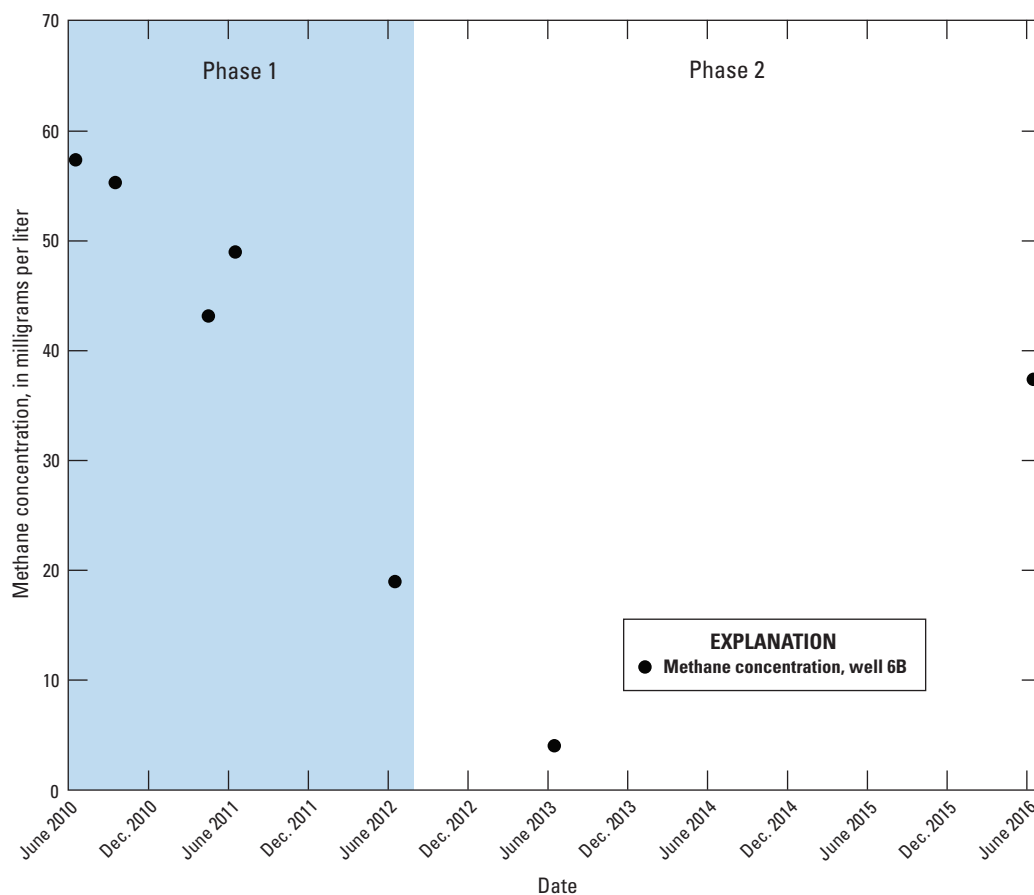
sampler for all sampling events where the sampler was lowered to a depth of 1,440 ft below land surface for sample collection (table 1). One possible explanation for the observed changes in major-ion chemistry may be that the sample depth used for well 6B no longer represents the most appreciable flow in the borehole. On a larger scale, these changes in flow within the borehole may indicate changes in the regional flow system.

## Methane and Volatile Organic Compounds

Methane concentrations in groundwater collected during phase 2 ranged from 0.048 to 160 mg/L (table 5). Although there is no Federal drinking-water standard for methane, methane concentrations greater than 28 mg/L could result in an immediate explosive hazard if methane degassed from pumped groundwater in a confined space such as a well bore, well house, or basement (Eltschlager and others, 2001). A total of five wells sampled during phase 2 had methane concentrations greater than 28 mg/L (table 5). Well 13B was sampled twice during phase 2, and both samples had methane

concentrations greater than 28 mg/L. Methane concentrations in wells sampled during phases 1 (table 4 of McMahon and others [2013]) and 2 (table 5) were generally consistent with the exception of well 6B, where methane concentrations were 57.4 mg/L in 2010 and 4.02 mg/L in 2013 (fig. 6). Like the variability observed in major-ion chemistry, variability in methane concentrations in well 6B may be the result of changes to flow in the borehole, which imply changes in the regional flow system.

During 2016, laboratory detection levels were lowered and analyses were expanded to increase the number of VOCs that were analyzed, which resulted in an increased frequency of VOC detections (table 5). Compared to results from phase 1 (table 4 of McMahon and others [2013]), toluene was detected more often during phase 2 and in more wells (table 5). Benzene was detected in samples from 3 wells during phase 2 (13U, 15A, and 17B) (table 5), 2 of which had benzene detections during phase 1 (15A and 13U) (table 4 of McMahon and others [2013]) and 1 new detection (17B), owing to the change in detection limit. Xylene (meta [*m*] and para [*p*] isomers) was not detected in any well during phase 1, but it was detected



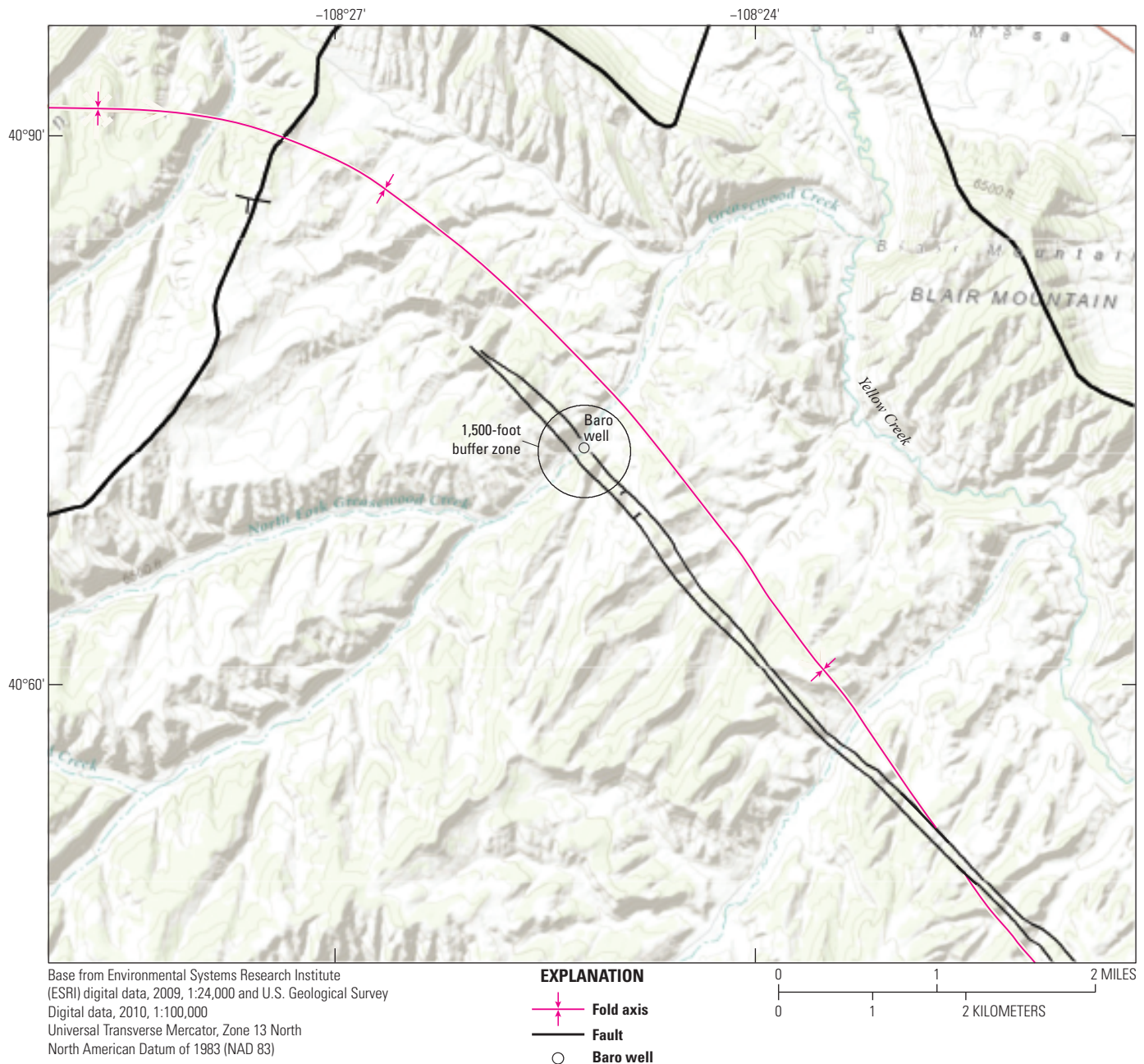
**Figure 6.** Methane concentrations in well 6B during phase 1 (2010–12) and phase 2 (2013–16), Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

during phase 2 in samples from wells 17B and 9B. Ethylbenzene was detected once during phase 1 in a sample from well 15A (table 4 of McMahon and others [2013]), and had no detections during phase 2 (table 5). Additional constituents detected as part of the expanded constituent list included carbon disulfide (6B), butane (13B and 13U), hexane (13B), n-pentane (13B), and trichloromethane (13U), which is commonly known as chloroform (table 5). Butane, hexane, and n-pentane in the shallow bedrock aquifers indicate a mixing with deeper groundwater (Warner and others, 2012). Detections of these compounds were at low concentrations but provided indication of the widespread and persistent occurrence of select VOCs in the shallow bedrock aquifers.

## Baro Well

One recommendation from McMahon and others (2013) was to evaluate sources and migration pathways of methane and VOCs in the study area by sampling a well where there was little energy development but where faults or fractures could provide a path for the migration of fluids from deep

reservoirs to the shallow bedrock aquifers (fig. 7). The Baro well was selected for addition into the monitoring-well network based on these criteria. The well is in the Greasewood Creek drainage, which is tributary to Yellow Creek (fig. 7). Based on geophysical data and interpretation by Shell Exploration and Production Company, the well is completed primarily in the Uinta Formation in the upper aquifer (Day and others, 2010). The depth to water below land surface is 39.0 ft (table 4), and the well itself is in the northern part of the study area, which is considered the regional groundwater discharge area. Dissolved solids concentrations were 17,400 mg/L, the highest measured during phase 2 (table 4). Major-ion data indicate the Baro well had a sodium-bicarbonate water type similar to well 17B (fig. 4). Well 17B also is in the northern part of the study area but completed in the lower aquifer. Fluoride concentrations in the Baro well were 21.6 mg/L, and trace element concentration data indicated elevated concentrations of barium, lithium, strontium, and boron (tables 4 and 7). These results are similar to trace element results collected during phase 1 at wells completed in the lower aquifer (McMahon and others, 2013). Methane concentration was 100 mg/L, and hydrocarbon gas molecular composition and  $\delta^{13}\text{C}$  of methane



**Figure 7.** Location of geologic structures (faults and fold axes) near the Baro well (1,500-foot buffer zone around well), Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado (geologic structure from Hail and Smith [1994, 1997]).

indicate the methane is biogenic in origin (table 6) using boundary conditions for biogenic and thermogenic methane from Bernard and others (1976) and Whiticar (1999). The  $\delta^{13}\text{C}$  of methane for the Baro well is isotopically lighter than that of wells with thermogenic methane like 13U (table 6). Toluene was detected at a concentration of 0.04  $\mu\text{g/L}$ , which again illustrates the widespread occurrence of VOCs in bedrock aquifers, even in areas with little or no energy development (table 5). The radiocarbon age for the Baro well was 48,129 plus or minus ( $\pm$ ) 3,200 years (table 8). The tritium concentration for

the Baro well was 0.1 TU, which is generally considered to represent old groundwater using criteria defined in McMahon and others (2013). Overall, water chemistry and groundwater age from the Baro well were similar to those of wells completed in the lower aquifer (McMahon and others, 2013). These chemical data indicate a mixing of groundwater between the upper and lower aquifers. The mixing may be due to the well's location near the regional discharge area and the nearby faults that could serve as pathways for the upward movement of groundwater from the lower aquifer to the upper aquifer.



**Table 7.** Nutrient and trace element data for water collected from the Baro well, August 18, 2015, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

[mg/L, milligram per liter; &lt;, less than; µg/L, microgram per liter]

Field identifier	Date	Time	Ammonia (mg/L as nitrogen)	Nitrate plus nitrite (mg/L as nitrogen)	Nitrite (mg/L as nitrogen)	Orthophosphate (mg/L as phosphorus)	Total nitrogen (mg/L)
Baro well	8/18/2015	1200	0.14	<0.040	<0.002	0.037	8.11
Aluminum (µg/L)	Barium (µg/L)	Beryllium (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Lead (µg/L)
<30.0	11,600	0.764	0.839	<3.0	<0.500	<8.0	<0.400
Lithium (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Silver (µg/L)	Strontium (µg/L)	Thallium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)
1,590	1.33	<2.0	1.87	4,700	<0.300	6.9	<20.0
Antimony (µg/L)	Arsenic (µg/L)	Boron (µg/L)	Selenium (µg/L)	Organic carbon (mg/L)	Uranium (natural) (µg/L)		
<0.270	<1.0	6,650	<0.50	10	0.244		

**Table 8.** Isotopic data and calculated radiocarbon age for water collected from the Baro well, August 18, 2015, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

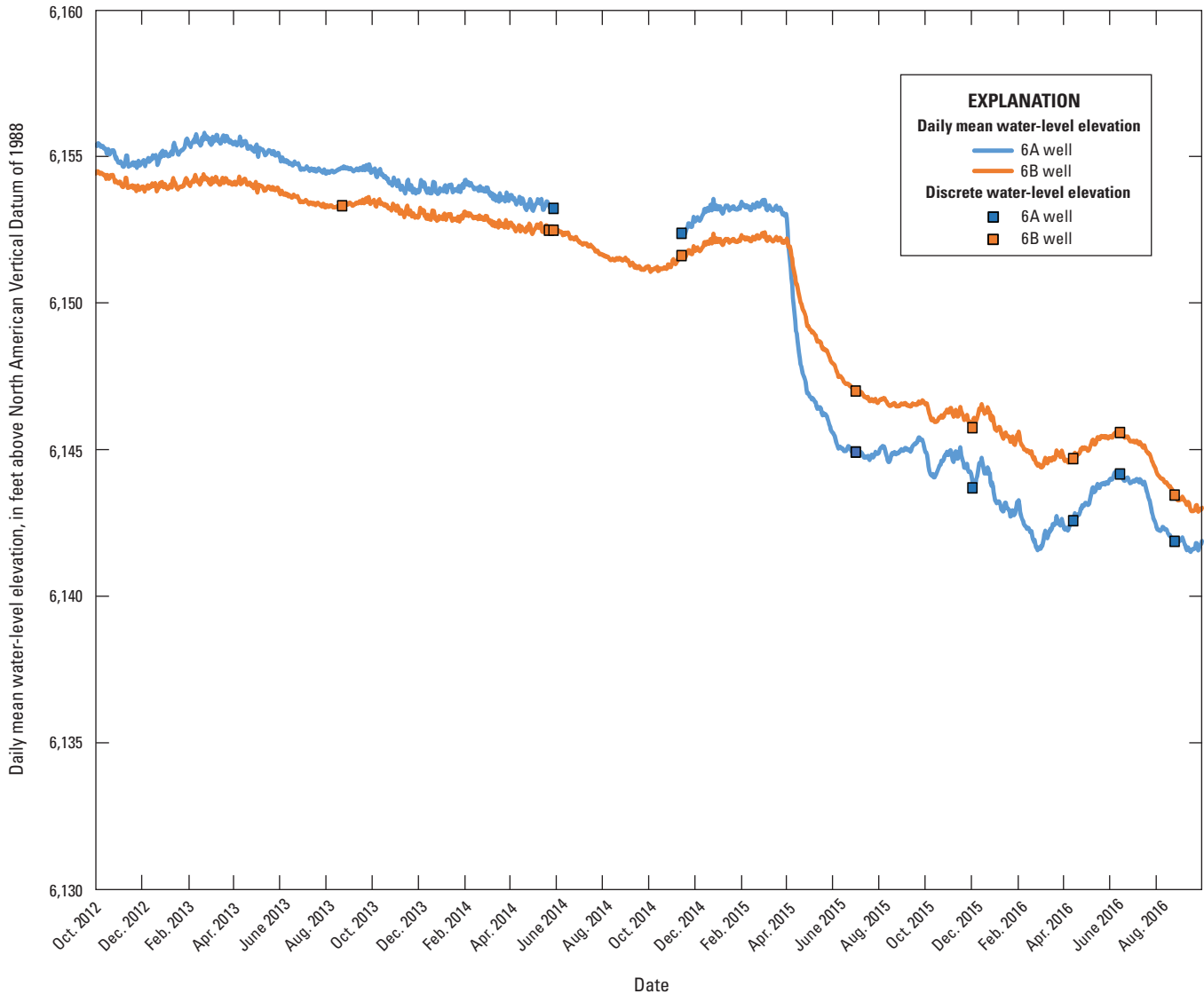
[Σ, sigma; δ, delta; per mil, part per thousand]

Constituent, in units	Value
Carbon-14 of dissolved inorganic carbon, in percent modern	0.25
Carbon-14 of dissolved inorganic carbon counting error, in percent modern	0.1
Calculated radiocarbon age (normalized), in years	48,129
Radiocarbon age error 1 Σ (normalized), in years	3,200
δ carbon-13/carbon-12, in per mil	6.66
δ hydrogen-2/hydrogen-1, in per mil	-139
δ oxygen-18/oxygen-16, in per mil	-18.2
Tritium, in tritium units	0.1

## Water-Level Elevations

Continuous water-level elevations were collected in wells 6A and 6B and wells 13U, 13A, and 13B to provide information about temporal variability in daily mean water-level elevations and hydraulic gradients in the bedrock aquifers during water years 2013–16 (figs. 8 and 9). Wells 6A and 6B were completed in the upper aquifer (Parachute Creek Member above the Mahogany zone) and the lower aquifer (Parachute Creek Member below the Mahogany zone), respectively. Water-level elevations at wells 6A and 6B generally decreased from water years 2013 to 2016 (fig. 8). During October 2012 through March 2015, the hydraulic gradient

was consistently downward from the upper aquifer (6A) to the lower aquifer (6B). In early April 2015, the hydraulic gradient changed from downward to upward between the upper and lower aquifers (fig. 8). During early April 2015 to mid-June 2015, daily mean water-level elevations decreased by about 10 ft in both wells (fig. 8), indicating some event caused this rapid decline in water-level elevations and the subsequent reversal in hydraulic gradient. Overall, daily mean water-level elevations declined by about 14 and 11 ft in wells 6A and 6B, respectively, during water years 2013–16. McMahon and others (2013) estimated groundwater ages for wells 6A and 6B to be 1,200 and 9,600 years old, respectively. These groundwater ages indicate that groundwater was

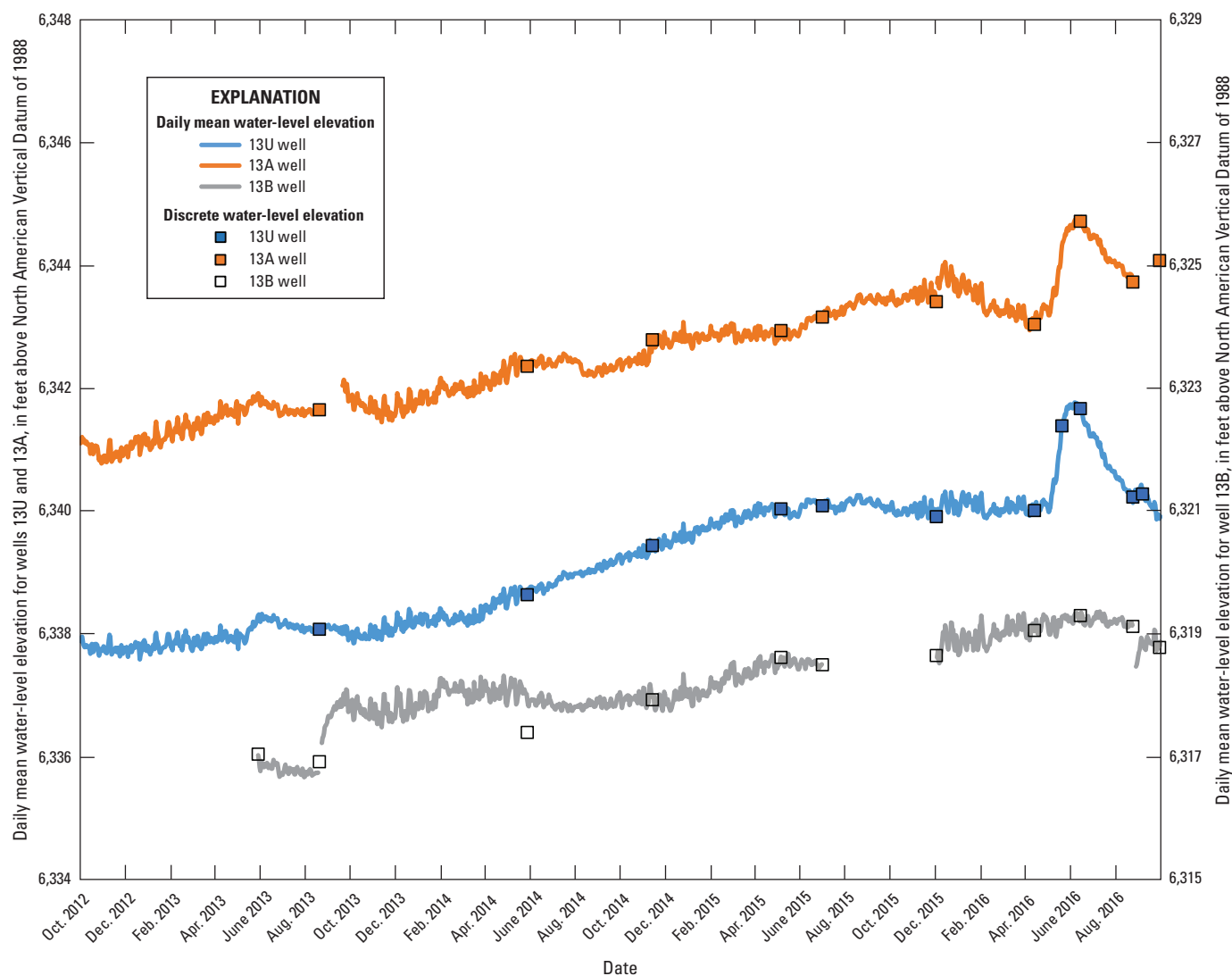


**Figure 8.** Daily mean water-level elevations in relation to time at wells 6A and 6B, water years 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

recharged over thousands of years. With such long periods of time for aquifer recharge, declines in water-level elevation over short time steps (a few months) have important implications for sustainable management of this resource. Solution mining activities or drilling for oil and natural gas in the area could be related to changes in water-level elevations in these wells. Solution mining is about 2.5 miles to the south of the wells. Several well pads are near the wells where activities include drilling, hydraulic fracturing, and well stimulation. It was not clear if these land-use activities were related to the changes in observed water-level elevations; however, further investigation would be needed to evaluate the possible causation. Changes in major-ion chemistry, methane concentrations, water-level elevation, and hydraulic gradient provide multiple lines of evidence of change in the bedrock aquifer.

Wells 13U and 13A were completed in the upper aquifer, where 13U was completed in the Uinta Formation and 13A

was completed in the Parachute Creek Member above the Mahogany zone. Well 13B was completed in the lower aquifer, which includes the Parachute Creek below the Mahogany zone. The gradient relative to the Parachute Creek above the Mahogany zone (13A) was upward into the Uinta (13U) and downward into the Parachute Creek below the Mahogany zone (13B) (fig. 9) and was consistent with the findings from phase 1 (McMahon and others, 2013). Daily mean water-level elevations at all three wells generally increased by about 2 to 2.5 ft from water year 2013 to water year 2016 (fig. 9). During spring and summer of 2016, seasonal responses in water-level elevations were observed in the upper aquifer wells (13U and 13A) (fig. 9). Water-level elevations in the lower aquifer (13B) did not demonstrate the seasonal patterns observed in the upper aquifer, which indicates the lower aquifer is not hydraulically connected with the upper aquifer and that the Mahogany zone is a confining layer in this location.



**Figure 9.** Daily mean water-level elevations in relation to time at wells 13U, 13A, and 13B, water years 2013–16, Piceance and Yellow Creek watersheds, Rio Blanco County, Colorado.

## Summary

The Piceance and Yellow Creek watersheds in Rio Blanco County, Colorado, are known to contain important energy resources (oil shale and natural gas) and mineral resources (nahcolite). The primary sources of fresh groundwater in the Piceance and Yellow Creek watersheds are bedrock aquifers in the Uinta and Green River Formations. The aquifers are divided into an upper and lower aquifer separated by a regionally extensive semiconfining layer. These aquifers provide water to streams and springs in the watersheds and are an important resource to people living and working in the area. Development of these resources has the potential to affect the quality of shallow groundwater in the study area in several ways. Studies of groundwater chemistry and aquifer characterization have been done in relation to proposed oil-shale

development. The lack of monitoring (as of 2010) of the shallow bedrock aquifers was identified by the Bureau of Land Management as a data gap that needed to be addressed. The Bureau of Land Management, White River Field Office, and the U.S. Geological Survey began groundwater monitoring in 2010 to characterize the groundwater quality of shallow bedrock aquifers in the Piceance and Yellow Creek watersheds. This first phase of monitoring (phase 1, 2010–12) established a monitoring-well network in the study area where wells were monitored for chemical constituents that could be related to the development of underlying natural-gas reservoirs. The second phase (phase 2, 2013–16) continues data collection from the monitoring-well network and builds on findings from phase 1. Phase 2 sampling focuses on monitoring groundwater for changes in constituent concentration using constituents selected to provide information on the overall groundwater quality and the occurrence of chemicals that could be related

to the development of underlying oil and gas reservoirs. During phases 1 and 2, continuous water-level elevations were collected in five wells to provide information about temporal variability in water-level elevations and hydraulic gradients in the bedrock aquifers. Long-term monitoring of bedrock aquifers provides a tool to help differentiate natural variability in groundwater chemistry and water-level elevations from human-induced changes. The purpose of this report is to present groundwater chemistry and water-level elevations collected during 2013–16. Comparisons are made to data that were collected from the bedrock aquifers from 2010 to 2012 to identify the potential for changes in water quality and water-level elevations.

Reduction-oxidation (redox) data indicate that all samples collected during phase 2 were anoxic. Sulfate reduction and methanogenesis were important redox processes in anoxic groundwater in the study area based on dissolved sulfide and methane in water from several wells. The inverse relation observed between methane and sulfate is the result of sulfate-reducing microbes outcompeting methanogens for electron donors needed to support their metabolism. Water types were generally mixed cation-bicarbonate-sulfate and sodium-bicarbonate water types. Time series plots of select major-ion data were evaluated from phase 1 and phase 2 to further understand potential changes in major-ion chemistry. Major-ion chemistry at well 6B was variable in phase 1 and in phase 2 where alkalinity and sulfate were the most variable constituents. One possible explanation for the observed changes in major-ion chemistry may be that the sample depth used at well 6B may no longer represent the most appreciable flow in the borehole. On a larger scale, these changes in flow within the borehole may indicate changes in the regional flow system.

Methane concentrations in groundwater collected during phase 2 ranged from 0.048 to 160 milligrams per liter (mg/L). Methane concentrations in wells sampled during phase 1 and phase 2 were generally similar except for 6B where methane concentrations were 57.4 mg/L in 2010 and 4.02 mg/L in 2013. During 2016, laboratory detection levels were lowered and analyses were expanded to increase the number of volatile organic compounds (VOCs) that were analyzed. These changes resulted in an increased frequency of VOC detections. Detections of these compounds were at low concentrations but indicated the widespread and persistent occurrence of select VOCs in bedrock aquifers.

One recommendation from phase 1 was to evaluate sources and migration pathways of methane and VOCs in the study area by sampling a well where there was little energy development but where faults or fractures could provide a path for the migration of fluids from deep reservoirs to the shallow

bedrock aquifers. The Baro well is in the Greasewood Creek drainage, which is tributary to Yellow Creek. The chemistry of water from the Baro well is similar to groundwater from the lower aquifer. Results from the Baro well indicate VOCs were in groundwater where there was little to no energy development. The mixing may be due to the well's location near the regional discharge area and the nearby faults that could serve as pathways for the upward movement of groundwater from the lower aquifer to the upper aquifer.

Continuous water-level elevations were collected in wells 6A and 6B and wells 13U, 13A, and 13B, providing information about temporal variability in water-level elevation and vertical hydraulic gradients in the bedrock aquifers. Wells 6A and 6B were completed in the upper aquifer (Parachute Creek Member above the Mahogany zone) and the lower aquifer (Parachute Creek below the Mahogany zone), respectively. From October 2012 through March 2015, the hydraulic gradient was consistently downward from the upper aquifer (6A) to the lower aquifer (6B). In early April 2015, the hydraulic gradient changed from downward to upward between the upper and lower aquifers. Overall, water-level elevations declined by about 14 and 11 feet in wells 6A and 6B, respectively, during water years 2013–16. Estimated groundwater ages from phase 1 for 6A and 6B were 1,200 and 9,600 years old, respectively. These groundwater ages indicate that groundwater was recharged over thousands of years. With such long periods of time for aquifer recharge, declines in water-level elevation over short time steps (a few months) have important implications to sustainable management of this resource. Solution mining activities or drilling for oil and natural gas in the area could be related to the changes in observed water-level elevations in these wells; however, further investigation would be needed to evaluate causation. Changes in major-ion chemistry, methane concentrations, water-level elevation, and hydraulic gradient provide multiple lines of evidence of change in the bedrock aquifer.

Wells 13U and 13A were completed in the upper aquifer, where 13U was completed in the Uinta Formation and 13A was completed in the Parachute Creek Member above the Mahogany zone. Well 13B was completed in the lower aquifer, which includes the Parachute Creek below the Mahogany zone. The gradient relative to the Parachute Creek above the Mahogany zone (13A) was upward into the Uinta (13U) and downward into the Parachute Creek below the Mahogany zone (13B) and was consistent with the findings from phase 1. Water-level elevations at 13B did not show the seasonal patterns observed in 13U and 13A, which indicates the lower aquifer is not hydraulically connected with the upper aquifer indicating that the Mahogany zone is a confining layer in this location.



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