≋USGS
science for a changing world

Response of Selenium Concentrations in Groundwater to Seasonal Canal Leakage, Lower Gunnison River Basin, Colorado, 2013

Scientific Investigations Report 2016–5047

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

Response of Selenium Concentrations in Groundwater to Seasonal Canal Leakage, Lower Gunnison River Basin, Colorado, 2013

By J.I. Linard, P.B. McMahon, L.R. Arnold, and J.C. Thomas

Scientific Investigations Report 2016–5047

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Director

U.S. Geological Survey, Reston, Virginia: 2016

Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
micrometer (μm)	3.93701e-5	inch (in.)
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
Area		
square kilometer (km^2)	247.1	acre
square centimeter (cm^2)	0.001076	square foot (ft^2)
Volume		
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
milliliter (mL)	0.033814	ounce, fluid (fl. oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32

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).

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

*Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [(ft^3/d)/ft^2]ft. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

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

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

Response of Selenium Concentrations in Groundwater to Seasonal Canal Leakage, Lower Gunnison River Basin, Colorado, 2013

By J.I. Linard, P.B. McMahon, L.R. Arnold, and J.C. Thomas

Abstract

Selenium is a water-quality concern in the lower Gunnison River Basin because irrigation water interacting with seleniferous soils derived from the Mancos Shale Formation has mobilized selenium and increased its concentrations in surface water. Understanding the occurrence of elevated selenium concentrations in groundwater is necessary because groundwater discharge is an important source of selenium in surface water in the basin. In 2013, the U.S. Geological Survey, in cooperation with the Bureau of Reclamation and the Colorado Water Conservation Board, began a study to understand how changes in groundwater levels attributed to canal leakage affected the concentrations and speciation of dissolved selenium in groundwater. The purpose of this report is to characterize the groundwater adjacent to an unlined leaky canal. Two locations, near the East Canal (W-N1 and W-N2) and farther from the East Canal (W-M1 and W-M2), were selected for nested monitoring well installations. The pressure exerted by changes in canal stage was more readily transferred to the deep groundwater measured in the W-N1 near the canal than the shallow groundwater at the W-N2 well. No definitive relation could be made between canal water-level elevation and water-level elevations in monitoring wells farther from the canal (W-M1 and W-M2).

Water flowing through the East Canal before the irrigation season had much higher selenium concentrations (140 micrograms per liter) than water in the canal during the irrigation season (3.02 micrograms per liter). Total selenium concentrations in the monitoring wells near the canal initially increased to 51.8 micrograms per liter in W-N1 and 1.66 micrograms per liter in W-N2. The initial increase in groundwater selenium concentrations presumably resulted from the dissolution of salts in the unsaturated zone by rising groundwater levels associated with canal leakage. The subsequent decrease in total selenium concentrations resulted from a combination of dilution by canal leakage and selenium reduction processes. Total selenium concentrations in monitoring wells located farther from the canal were not directly affected by canal leakage.

Selenite/total selenium mass ratios in the East Canal samples ranged from about 0.02 to 0.13, indicating that about 2 to 13 percent of the total selenium in canal samples was composed of selenite. The increase in total selenium at W-N1 from before the irrigation season to the early irrigation season was accompanied by a decrease in the percentage of selenite from about 10 to 1 percent, indicating that selenate was added to the groundwater. A nitrate pulse occurred with the selenate pulse in W-N1 at the beginning of the irrigation season but apparently dissipated to a low enough concentration during the irrigation season to allow for selenate reduction to occur, as indicated by the relatively high percentages of selenite in W-N1 during the late irrigation season. W-N2 generally contained higher percentages of selenite than W-N1.

Percentages of selenite in W-M1 did not change in response to filling the canal and generally composed less than 1 percent of the total selenium in that well. The predominance of selenate in W-M1, and apparent lack of selenate reduction, cannot be explained by a lack of anoxic conditions in the groundwater because all the available dissolved-oxygen data indicate that concentrations were less than 0.5 milligrams per liter. The most likely explanation for the lack of selenate reduction in W-M1 is that the exceptionally high concentrations of nitrate in the groundwater (about 340 to 390 milligrams per liter as nitrogen) inhibited selenate reduction. These high nitrate concentrations presumably come from the Mancos Shale and its weathering products because there was no evidence for a human source of nitrate at the lower Gunnison River Basin wetland. The high concentrations of selenate in W-M1 may persist and eventually discharge to surface water unless nitrate concentrations are reduced to low enough levels to permit substantial selenate reduction to occur. Well W-M2 contained relatively low concentrations of total selenium and high percentages of selenite before and at the onset of the irrigation season. An increase in total selenium concentration associated with a drying and wetting period later in the summer was accompanied by a decrease in the percentage of selenite to near 0 percent, indicating that selenate was added to the groundwater. This pattern is consistent with the examples of increasing concentrations of total selenium in the other wells and presumably resulted from the dissolution of selenate-bearing salts in the unsaturated zone by rising water levels in W-M2.

Introduction

Selenium is a water-quality concern in the lower Gunnison River Basin (LGRB) because irrigation water interacting with seleniferous soils derived from the Mancos Shale Formation has mobilized selenium and increased its concentrations in surface water (Butler, 1996). As part of the National Irrigation Water Quality Program (NIQWP), the U.S. Fish and Wildlife Service and the U.S. Geological Survey found that selenium concentrations in groundwater and surface water were greater in irrigated regions overlying the Mancos Shale than in other areas (Butler and others, 1996). The elevated selenium concentrations in surface water are considered to detrimentally affect the recruitment of native Colorado River Basin fish species: Razorback Sucker (*Xyrauchen texanus*), Colorado Pike Minnow (*Ptychocheilus Lucius*), Humpback Chub (*Gila cypha*), and the Bonytail Chub (*Gila elegans*) (Colorado River Endangered Fish Recovery Program, http://www.coloradoriverrecovery.org, accessed October 25, 2012). Specifically, selenite (SeIV) is the selenium species of concern because of its bioavailability and toxicity to fish (Lemly, 1993; Dhillon and Dhillon, 1999; Fernandez-Martinez and Charlet, 2009). How selenite affects fish is more complex than a matter of presence or absence or even exceedance of a specified concentration, and studies are being conducted that provide ecosystem-scale selenium modeling in support of criteria development for fish and wildlife (Presser and Luoma, 2010).

The bioavailability and toxicity of selenium in the environment is dependent on its solubility and oxidation state. The primary selenium oxidation states that exist in the environment are +VI (selenate SeO_4^{2-}), +IV (selenite SeO_3^{2-}), 0 (elemental selenium Se^0), and –II (selenide Se^{2-}). Selenate and selenite are both water soluble and although selenite is more bioavailable and toxic than selenate, selenate typically comprises more of the total selenium in water than selenite as it is more soluble (Fordyce, 2007). Elemental selenium is the least soluble and is the least toxic to organisms (Combs and others, 1996; Fernandez-Martinez and Charlet, 2009). The relatively insoluble organic selenides, however, have a high potential for bioavailability and toxicity (Lemly, 1993; Fernandez-Martinez and Charlet, 2009). Bound to suspended particulate matter, which carries about 85 percent of the total selenium in streams (Fernandez-Martinez and Charlet, 2009), selenides are potentially important to high selenium residues in the food web along stream corridors (Lemly, 1993). Generally the occurrence of the different selenium species in soils is a product of their physical and chemical environment. Selenate and selenite are prevalent in oxygen-rich aqueous solutions; whereas, elemental selenium and selenide are more common in low oxygen, acidic, and organic-rich soils (Fernandez-Martinez and Charlet, 2009).

The enrichment of selenium in groundwater of the LGRB occurs as a result of Mancos Shale weathering, efflorescent salt dissolution, and redox processes that keep selenium in solution. In unweathered Mancos Shale, pyrite is indicated as the main source of selenium (Tuttle and others, 2014). Iron

layers, formed by the oxidation of the pyrite, are enriched with selenium composed mostly of selenite (Tuttle and others, 2014). After further oxidation and evapotranspiration, efflorescent salts (such as gypsum [$CaSO_4$] and thenardite [Na_2SO_4]) form, within which selenium can be substituted for sulfur because of its similar chemical and physical properties (Tuttle and others, 2014; Presser and Ohlendorf, 1987). Upon exposure to water, the salts dissolve, and studies by Kumar and Riyazuddin (2011), Dhillon and others (2008), Fernandez-Martinez and Charlet (2009), and Zhang and Moore (1996) indicate that more selenate is mobilized than selenite. Selenite solubility is typically governed by sorption/desorption processes on mineral surfaces (Balistrieri and Chao, 1987) and organic matter (Fernandez-Martinez and Charlet, 2009) and the redox state of the groundwater (Tuttle and others, 2014). Redox processes are catalyzed by microorganisms that successively use terminal electron-accepting redox-sensitive chemicals (in order of preference: dissolved oxygen, DO; nitrate, NO_3; selenate; manganese, Mn(IV); iron, Fe(III); uranium, U(VI); and sulfate, [SO_4]) for respiration processes (McMahon and Chapelle, 2008; Gates and others, 2009). Highly soluble selenate may exist in groundwater under oxic conditions (defined by McMahon and Chapelle [2008] as groundwater with DO concentrations greater than or equal to 0.5 mg/L), whereas selenate may be reduced to less soluble selenite under anoxic conditions (DO concentrations of less than 0.5 mg/L; McMahon and Chapelle, 2008). The presence of nitrate in anoxic groundwater is known to inhibit the reduction of selenate to selenite (Gates and others, 2009; White and Benson, 1991). Groundwater in some locations of the LGRB exhibits naturally high nitrate concentrations (Holloway and Smith, 2005; Morrison and others, 2012; Mast and others, 2014) and suggest a limited potential for reduction of selenate in those locations.

Concentrations of dissolved selenium in surface water are increasing in some areas of the LGRB despite the implementation of salinity/selenium-control projects (such as improving irrigation efficiency or lining canals) in the region. Salinity/selenium-control projects aim to reduce percolation and subsequent mobilization of salt and selenium from groundwater to surface-water systems. Following the completion of a major salinity/selenium control project, which lined approximately 18 kilometers of irrigation canals in the LGRB, instream selenium concentrations during the nonirrigation season (composed of mostly groundwater) had decreased by 16 percent (Butler, 2001). As of 2010, however, these selenium concentrations had increased (Moore, 2011), which has led to local interest in more clearly understanding the effects of canal lining on selenium concentrations.

Geochemical conditions in groundwater adjacent to leaky canals are likely to fluctuate seasonally as canals fill and oxic water recharges the aquifer. The increase in groundwater levels subsequent to canal filling may act to dissolve soluble salts in the unsaturated zone which in turn could increase concentrations of soluble selenium in groundwater. At the completion of the irrigation season, it is likely that groundwater levels

would decrease and efflorescent salts would precipitate in the unsaturated zone, which would act to immobilize soluble selenium. After lining a leaky canal the water level adjacent to the canal would decrease further creating a thicker unsaturated zone and immobilizing more selenium. In an irrigated environment, like the LGRB, the postlining water level would still be subjected to seasonal fluctuations albeit at lower elevations. The iron layers identified by Tuttle and others (2014) could potentially provide a rich source of selenium if the depth of the layers coincided with the water level where the new fluctuations occurred.

In 2013, the U.S. Geological Survey (USGS), in cooperation with the Bureau of Reclamation and the Colorado Water Conservation Board, began a study to understand how changes in groundwater levels attributed to canal leakage affected the concentrations and speciation of dissolved selenium in groundwater.

Purpose and Scope

This report characterizes the groundwater adjacent to an unlined leaky canal. Nested shallow and deep groundwater monitoring wells were installed at different distances from the leaky canal (fig. 1). Continuous pressure (water-level) data were measured in the canal and monitoring wells. Discrete seasonal data consisting of concentrations of total selenium and selenium species and water levels in the canal water, field properties, concentrations of total selenium and selenium species, major ions, nutrients, and dissolved gases, and nitrogen isotopic compositions in groundwater were measured before, during, and after the 2013 irrigation season.

Description of Study Area

The field site for this study is a wetland in the LGRB (termed the LGRB wetland through the remainder of the report) that is approximately 5.5 kilometers (km) northeast of Olathe, Colo. (fig. 1). The site is bounded on the east, north, and west sides by the East Canal and an irrigation lateral fed by the East Canal. The East Canal is part of the east side of the Uncompahgre Project area and planning is underway to identify how best to pipe and line that irrigation water delivery system (Bureau of Reclamation, 2011). The mean annual air temperature (1980–2010) is 10.4 degrees Celsius at the LGRB wetland, which receives about 18.8 centimeters (cm) of precipitation per year (Daly and others, 2008). During the 2013 calendar year, 27.8 cm were recorded at a precipitation station about 1 km west of the LGRB wetland (Station CO-MT-25, http://www.cocorahs.org/Stations/Station.aspx?StationNumber=CO-MT-25; fig. 1). Although 90 percent of the precipitation infiltrates (Elliott and others, 2007), the evaporation induced by the arid climate combined with the poorly draining, silty clay soils that are moderately to strongly saline (Natural Resources Conservation Service, 2014; Map Unit Symbol 790), make poor growing conditions for even the native desert vegetation. The vegetation in the LGRB wetland, however, generally conforms to that of a persistent Palustrine emergent wetland with perennial water (Cowardin and others, 1979; Rector and others, 1979). The abrupt change in vegetation from the east side of the East Canal to the west indicates the East Canal as a principal source of water to the LGRB wetland. Freestanding water was evident throughout the study, and continuously flowing springs fed several ponds. Evaporation from ponds and freestanding water in the LGRB wetland can approach 150 cm per year, of which two-thirds can be lost during the irrigation season (determined at Montrose, Colo., 17 km southeast of Olathe, Colo.; Farnsworth and Thompson, 1982). The cumulative evapotranspiration from soils and plants determined for the irrigation season during 2010 was about 33 cm (Singh and others, 2014). The evapotranspiration yields efflorescent salts that are common throughout the LGRB wetland and are evidence of the saline soils, which can be composed of up to 15 percent calcium carbonate and 20 percent gypsum (Natural Resources Conservation Service, 2014; table 1 of this report).

Data collected by the Bureau of Reclamation (BOR) during the late 1970s and early 1980s from a well (Observation well E263133; 8 meters [m] deep) at the southern end of the LGRB wetland gives an indication of the geochemical nature of the groundwater in the LGRB wetland (John Sottilaire, Bureau of Reclamation, written commun., March 29, 2012; Appendix 1). Data were available on a bimonthly basis, generally, from September 1978 through October 1983 and are summarized in table 1. The distribution of cations (dominated by sodium) and anions (dominated by sulfate) are consistent with Mancos Shale groundwater (Morrison and others, 2012).

Study Methods

Well Installation

Two locations, near the East Canal and farther from the East Canal, were selected for nested monitoring well installations (fig. 1). The wells near the canal (W-N1 and W-N2) were installed 24 meters (m) from the canal, and the wells farther from the canal (W-M1 and W-M2) were an additional 277 m from the near wells (301 m from the canal). Land-surface elevation at the location near the canal was 1,628.75 m and 1,625.04 m at the farther location. Drilling services, supplies, and materials were provided by the BOR. A CME75 drilling rig was used to drive hollow-stem-augers and a split spoon sampler that collected geologic material for lithologic descriptions. Borehole drilling and well installation were overseen by an onsite USGS geologist responsible for documenting daily drilling operations, logging and packaging geologic materials encountered while drilling, overseeing well installation, and preparing well-construction reports. Lithologic logs (Appendix 2) were developed from the collected geologic material and auger cuttings through visual inspection and were completed using the Wentworth
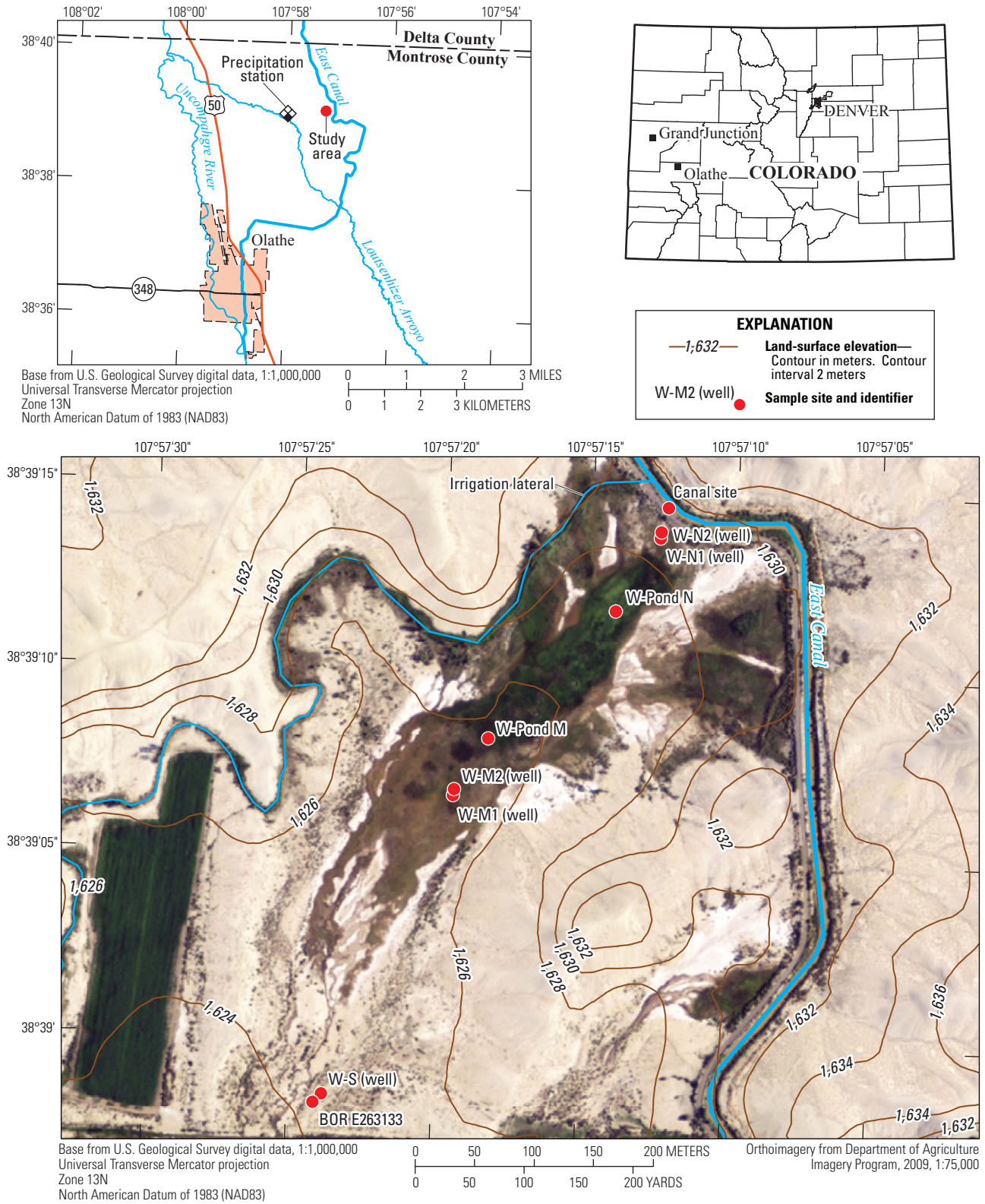
Figure 1.   Location of field site, lower Gunnison River Basin, Montrose County, Colorado.

Table 1. Physical and chemical data for soils and groundwater geochemistry data from previous studies.

[cm, centimeter; g/cm³, grams per cubic centimeter; μm/s, micrometers/second; cm/cm, centimeter per centimeter; meq/100 g, milliequivalents per 100 grams; μmhos/cm, micromhos per centimeter; mg/L, milligrams per liter]

Physical and chemical properties of the lower Gunnison River Basin wetland soils (Natural Resources Conservation Service, 2014)												
Physical soil properties							Chemical soil properties					
Map unit symbol and soil name	Depth, cm	Clay, percent	Moist bulk sensity, g/cm³	Saturated hydraulic conductivity, μm/s	Available water content, cm/cm	Organic matter, percent	Cation exchange capacity, meq/100 g	Soil reaction, pH	Calcium carbonate, percent	Gypsum, percent	Salinity, μmhos/cm	Sodium absorption ratio
	0–5.1	0–5	--	42–705	0.2–0.3	--	--	6.1–7.3	--	--	--	--
790: Aquisalids	5.1–61	25–50	1.15–1.3	0.28–2.8	0.01–0.16	0.5–5.0	10–40	8.0–9.6	0–10	0–20	8–50	8–30
	61–155	25–50	1.15–1.3	0.42–2.8	0.01–0.12	0.0–3.0	10–35	8.0–9.6	0–15	0–20	16–50	16–50

Geochemical summary of Bureau of Reclamation data collected between September 1978 and October 1983 at observation well E263133 (John Sottilaire, written commun., March 29, 2012)

Statistic	pH	Temperature, degrees Celsius	Total dissolved solids, mg/L	Electrical conductivity, μmhos/cm	Calcium, mg/L	Magnesium, mg/L	Sodium, mg/L	Potassium, mg/L	Bicarbonate, mg/L	Chloride, mg/L	Sulfate, mg/L
Minimum	7.5	9.4	16,900	16,600	441	331	4,280	39.1	312	668	9,990
Maximum	8.1	15.4	44,100	43,100	517	1,110	11,100	78.2	785	1,600	24,400
Mean	7.7	12.1	33,300	30,400	465	714	7,980	60.6	580	1,120	17,700
Standard deviation			8,700	7,760	27.7	232	2,090	15.0	142	290	792

classification system (Wentworth, 1922) and Munsell color system (Geological Society of America, 1995). Geochemical analyses of select core material were performed to determine the total selenium, organic matter, and pyrite contents and are described in detail by Mast and others (2014). For all wells, interpretation of the auger cuttings during drilling indicated a decrease in moisture content with depth through weathered Mancos Shale. Unweathered Mancos Shale with water-bearing bedding planes was encountered below weathered Mancos Shale at both locations. Consequently, groundwater monitoring wells were installed in the shallow and deep water-bearing bedding plane systems at both the near and farther locations. Based on the lithologic logs, the shallow system has minor, if any, hydraulic connection with the deep system.

The four wells installed for this study are W-N1 well (deep, near the East Canal), W-N2 (shallow, near the East Canal), W-M1 (deep, farther from the canal), and W-M2 (shallow, farther from the canal) (fig. 1). Wells were constructed using 5.08-cm diameter, Schedule 40 polyvinyl chloride (PVC) casing (Appendix 3) and equipped with 1.5-m screens using 10-slot PVC. Annular space adjacent to the screened interval was backfilled with a 20–40 graded silica sand pack, and the annular space above the sand pack was sealed with at least a one-foot thick layer of 0.95-cm diameter bentonite pellets topped by concrete to the land surface. A concrete pad and locking protective steel casing were installed at the surface. Once sites were installed, the surrounding area, well head, and measuring point were photographed for the well record, and the well location and elevation of the well head were measured to within 20 cm using a high precision Global Positioning System (GPS) unit.

Wells were developed following USGS protocols (Lapham and others, 1997) to ensure hydraulic connection with the water-bearing geologic material. A combination of a peristaltic pump and bailer were used to develop the shallow wells. While a sustainable flow rate was achieved at W-M2 with the peristaltic pump, the water level in the W-N2 well failed to recover after 24 hours when bailed dry. A Waterra Hydrolift 2 inertial pump with high-density polyethylene tubing and surge block was used to develop the deeper wells.

Continuous Data Collection

Continuous pressure (water-level) data were measured at each of the four wells and the East Canal site. The time period for which data were recorded at each site varied depending on availability of the vented YSI 600LS Sondes and battery life, although generally data were collected from March 20, 2013, to December 9, 2013. Data were recorded every 15 minutes except at W-N1, which recorded data every 2 hours. A staff plate was installed at the East Canal site to periodically measure the water level and for the correction of continuous pressure data. An electronic water-level tape was used at the monitoring wells to manually measure depth to groundwater (Cunningham and Schalk, 2011). All site information and data were entered into the USGS National Water Information System (NWIS) database (http://waterdata.usgs.gov/co/nwis/; U.S. Geological Survey, 1998).

Sample Collection and Analysis

Water-quality samples were collected at the East Canal (the above 6125 Road site), two ponds (W-Pond M and W-Pond N), and the monitoring wells (fig. 1). Depth integrated canal samples were collected before (March), during (July), and after (December) the irrigation season and analyzed for total selenium and selenite concentrations (table 2). Depth integrated samples were collected from the ponds during (April, May, August, and October) and after (December) the irrigation season. The W-Pond N was sampled because of its size (about 10 m in diameter and 1 m deep) and close proximity to the wells and springs near the East Canal. The W-Pond M was sampled because of the odor of hydrogen sulfide observed and its proximity to the wells farther from the East Canal.

Water samples were collected before (March), during (April, May, August, and October), and after (December) the irrigation season from the monitoring wells (tables 2 and 3). In the deeper wells (W-N1 and W-M1), samples were collected by using a peristaltic pump after the removal of at least three casing volumes and well discharge data for water temperature, specific conductance, pH, and dissolved-oxygen concentration had become stable (Koterba and others, 1995). Field properties were measured using a calibrated field meter, which was calibrated according to standard protocols described in the National Field Manual (U.S. Geological Survey, variously dated). Procedures for sampling the shallow wells differed in that water was purged with a peristaltic pump from the shallow wells 2 to 3 days prior to sampling to allow for adequate recovery. To preserve the redox state, water levels were constantly monitored during purging to ensure they stayed above the top of the well screen. For quality assurance and control purposes, a blank sample was collected before any sampling occurred and again at the middle of the irrigation season. Replicate samples were collected at W-M1 both early and late in the irrigation season.

Samples were collected in processing chambers to reduce the potential for airborne contamination (U.S. Geological Survey, variously dated). Samples collected for total selenium, selenite, major ions, nutrients, and dissolved organic carbon were filtered through a 0.45-micrometer (μm) capsule filter into precleaned plastic bottles (amber glass bottle for dissolved organic carbon). Major ions refers to the following dissolved constituents: calcium, magnesium, sodium, potassium, chloride, sulfate, fluoride, manganese, and iron. Dissolved concentration data for oxygen, nitrate as nitrogen, manganese, iron, and sulfate (table 3) are used to identify redox processes (McMahon and Chapelle, 2008). Total selenium and selenite samples were preserved with hydrochloric acid to pH less than 2 and analyzed to a detection limit of 0.2 micrograms per liter (μg/L) using hydride

Table 2. Total selenium, selenate, and selenite concentrations, in micrograms per liter, and selenite/total selenium mass ratios measured at the lower Gunnison River Basin wetland during 2013.

[--, no data; <, less than; selenite/total selenium mass ratio; concentration of selenite divided by concentration of total selenium]

Location	March	April	May	August	October	December
			Total selenium			
East Canal	140	--	--	[1]3.02	--	50.96
W-Pond N	--	30.0	15.3	1.30	1.20	3.83
W-Pond M	--	2.38	1.40	0.90	<0.2	0.21
W-N1	8.76	51.8	33.6	2.10	0.70	0.84
W-N2	0.79	1.66	1.2	0.90	0.40	0.66
W-M1	3,220	2,690	2,780	2,740	2,520	3,010
W-M2	1.30	1.35	1.40	10.9	6.00	2.98
W-S	--	--	--	4,100	--	--
			Selenate			
East Canal	136	--	--	[1]2.64	--	50.2
W-Pond N	--	29.4	14.4	0.90	0.90	3.51
W-Pond M	--	1.87	0.80	0.90	<0.2	<0.2
W-N1	7.89	51.4	32.0	1.50	0.4	0.44
W-N2	0.3	1.44	0.6	0.6	0.4	0.48
W-M1	3,220	2,690	2,760	2,740	2,510	2,300
W-M2	0.93	0.95	0.92	10.8	5.80	2.94
W-S	--	--	--	4,100	--	--
			Selenite			
East Canal	4.28	--	--	[1]0.38	--	0.80
W-Pond N	--	0.64	0.90	0.40	0.30	0.32
W-Pond M	--	0.51	0.60	<0.2	<0.2	<0.2
W-N1	0.87	0.39	1.60	0.60	0.30	0.40
W-N2	0.49	0.22	0.60	0.3	<0.2	<0.2
W-M1	5.37	7.00	12.9	7.40	11.5	9.95
W-M2	0.37	0.40	0.48	<0.2	0.20	<0.2
W-S	--	--	--	4	--	--
			Selenite/total selenium mass ratio			
East Canal	0.03	--	--	0.13	--	0.02
W-Pond N	--	0.02	0.06	0.31	0.25	0.08
W-Pond M	--	0.21	0.43	0.22	--	0.95
W-N1	0.10	0.01	0.05	0.29	0.43	0.48
W-N2	0.62	0.13	0.50	0.33	0.50	0.30
W-M1	0.002	0.003	0.005	0.003	0.005	0.003
W-M2	0.28	0.30	0.34	0.02	0.03	0.07
W-S	--	--	--	0.001	--	--

[1]The irrigation season East Canal sample was collected on July 1, 2013.

Table 3. Concentration data for dissolved oxygen, nitrate as nitrogen, manganese, iron, and sulfate, in milligrams per liter, in groundwater sampled at the lower Gunnison River Basin wetland monitoring wells during 2013.

[<, less than; --, no data]

Site	March	April	May	August	October	December
Dissolved oxygen (DO)						
W-N1	0.1	0.1	0.2	0.1	0.4	0.2
W-N2	3.9	2.2	3	0.3	1.9	2.7
W-M1	0.1	0.1	<0.1	<0.1	0.3	0.1
W-M2	0.1	0.1	0.1	0.1	0.3	<0.1
Nitrate as nitrogen (NO_3–N)						
W-N1	1.48	6.41	5.49	0.63	0.27	0.27
W-N2	0.20	1.08	2.13	0.32	0.1	0.11
W-M1	393	340	340	364	342	364
W-M2	<0.039	<0.120	<0.040	0.057	<0.033	<0.039
W-S	--	--	--	823	--	--
Manganese (Mn^{2+})						
W-N1	0.26	0.17	0.14	0.13	0.17	0.25
W-N2	0.23	0.29	0.72	0.28	0.45	0.024
W-M1	0.17	0.32	0.30	0.20	0.24	0.20
W-M2	1.51	1.14	0.92	1.53	1.56	1.38
W-S	--	--	--	0.85	--	--
Iron (Fe^{2+})						
W-N1	<0.012	<0.012	<0.012	<0.008	33.4	15.5
W-N2	<0.004	0.005	<0.004	0.104	0.326	<0.008
W-M1	<0.1	0.286	<0.080	<0.1	<0.080	<0.080
W-M2	0.90	3.57	1.18	7.58	25.4	13.2
W-S	--	--	--	<0.1	--	--
Sulfate (SO_4^{2-})						
W-N1	2,480	2,440	2,500	2,000	1,990	2,080
W-N2	610	841	901	1,310	1,060	1,080
W-M1	25,700	28,400	28,600	29,600	30,000	28,300
W-M2	12,100	11,900	11,900	10,300	9,370	7,870
W-S	--	--	--	14,000	--	--

generation/atomic fluorescence spectroscopy (HG-AFS) (Briggs and Crock, 1986) at the USGS Crustal Geophysics and Geochemistry Science Center, in Lakewood, Colo. Selenite was analyzed prior to digesting a mixture of sample water with nitric, hydrochloric, and perchloric acid to convert all forms of selenium to selenite. This mixture was then analyzed and used for total selenium. Using the same methodology as White and Benson (1991), selenate was determined as the difference between total selenium and selenite. Major ion samples were acidified in the field to pH less than 2 using nitric acid. Dissolved organic carbon samples were acidified in the field to pH less than 2 using sulfuric acid and chilled. Nutrient samples were chilled. Major ions, nutrients, and dissolved organic carbon were analyzed at the USGS National Water-Quality Laboratory, in Lakewood, Colo., using

methods defined by Garbarino and Struzeski (1998), Fishman and Friedman (1989), and Fishman (1993), and the results were entered into the USGS NWIS database (U.S. Geological Survey, 1998). Alkalinity was measured in the field by inflection point titration (U.S. Geological Survey, variously dated) using 0.16 or 1.6 normal sulfuric acid.

Unfiltered sample water was analyzed for dissolved gases (argon, carbon dioxide, dinitrogen (N_2), and methane) and the isotopic composition of N_2 gas. Dissolved-gas samples were collected from the canal site and wells before, during, and after the irrigation season (table 2). Isotopic samples were collected from the wells during and after the irrigation season. Samples for dissolved gas and N_2 isotopes were collected in 125-milliliter glass serum bottles by filling from the bottom and allowing water to overflow to ensure

no air bubbles were trapped inside (U.S. Geological Survey, 2015a). Pellets of potassium hydroxide were added to raise the pH to greater than 11, and the bottles were sealed with no headspace and stored on ice. Samples for nitrogen and oxygen isotope analysis of nitrate were collected by successively filtering sample water through a 0.45-µm filter and 0.2-µm filter into untreated, brown polyethylene bottles and preserved with pellets of potassium hydroxide (U.S. Geological Survey, 2015b). The sample water was collected immediately after the collection of redox sensitive analytes when sampling the shallow wells. This approach provided the most representative sample possible for these wells because of their slow recovery characteristics.

Dissolved gases were analyzed using gas chromatography with thermal conductivity or flame ionization detection at the USGS Chlorofluorocarbon Laboratory in Reston, Va. (Busenberg and others, 1993; http://water.usgs.gov/lab/dissolved-gas/). The isotopic composition of N_2 was measured on an isotope ratio mass spectrometer at the USGS Stable Isotope Laboratory in Reston, Va. (Böhlke and Denver, 1995). The isotopic composition of nitrate was analyzed by bacterial conversion of nitrate to nitrous oxide and subsequent measurement on a continuous flow isotope ratio mass spectrometer at the USGS Stable Isotope Laboratory in Reston, Va. (Sigman and others, 2001; Casciotti and others, 2002; Coplen and others, 2004; and Coplen and others, 2012).

Seasonality of Water Levels

This section describes the changes in water levels in the East Canal, groundwater near the canal, and groundwater farther from the canal that occurred during the study period. Additionally, the physical processes associated with these changes are discussed.

Canal Operation

Understanding when canals are filled and drained is necessary to relate the canal leakage to changes in groundwater elevation. The elevation of water in the canal increases at the beginning of the irrigation season (on or about April 1) and correspondingly decreases at the end of the irrigation season (on or about November 1). Standing water was observed during the nonirrigation season (fig. 2) in canal bed depressions. The elevation of the nonirrigation season water level in the canal was about 1,629.60 m (fig. 3). On a weekly basis starting April 1, 2013, the canal was partially filled and drained to flush aggraded sediment and debris, and to saturate and stabilize canal banks. By the third week in April, the canal was filled to an elevation of 1,630.55 m and remained steady until August 18, 2013, after which the water-level elevation gradually decreased to 1,630.20 by the end of October when the canal was drained back to its nonirrigation season elevation.

Figure 2. Water level in the East Canal during nonirrigation, March 29, 2013. Photograph by Joshua Linard, U.S. Geological Survey.
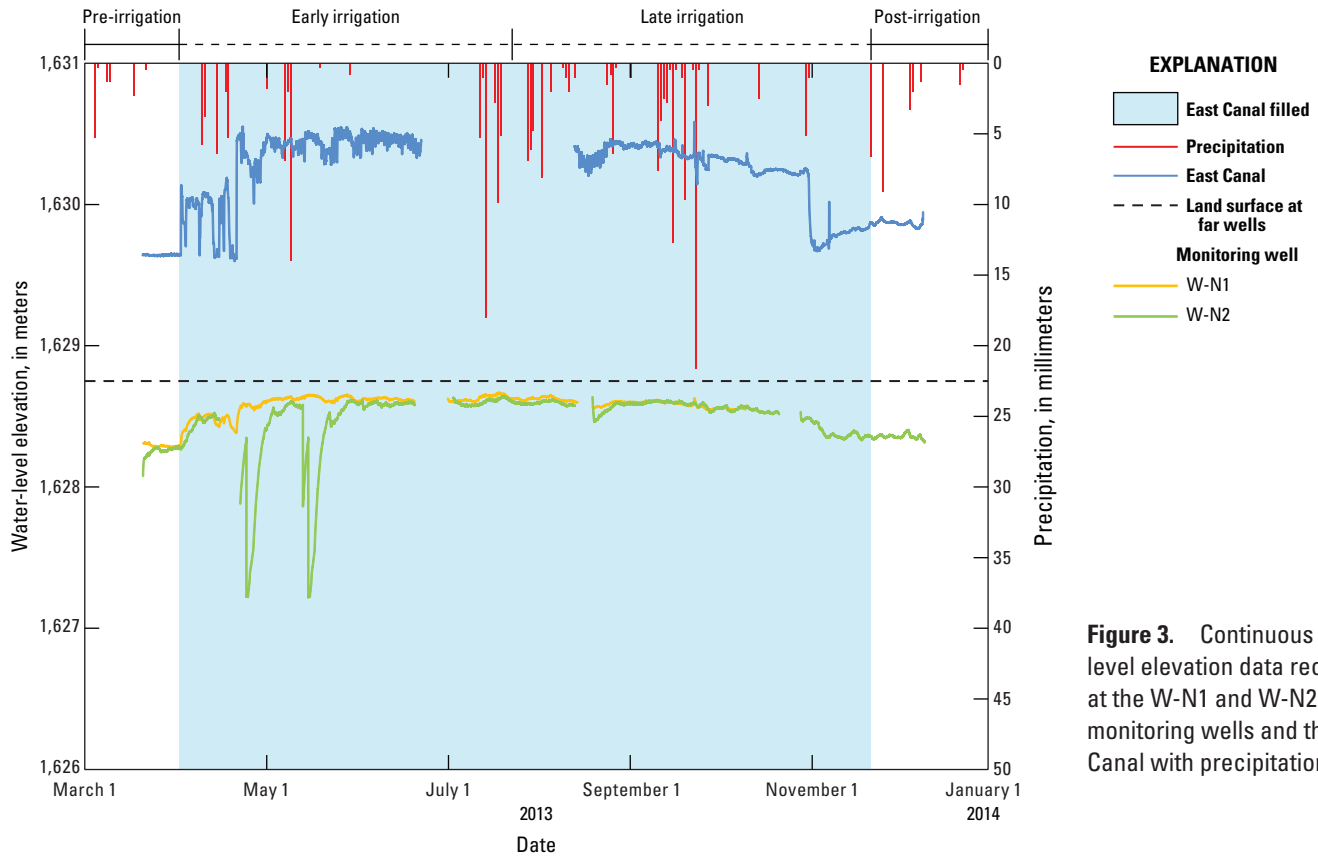
Figure 3. Continuous water-level elevation data recorded at the W-N1 and W-N2 monitoring wells and the East Canal with precipitation.
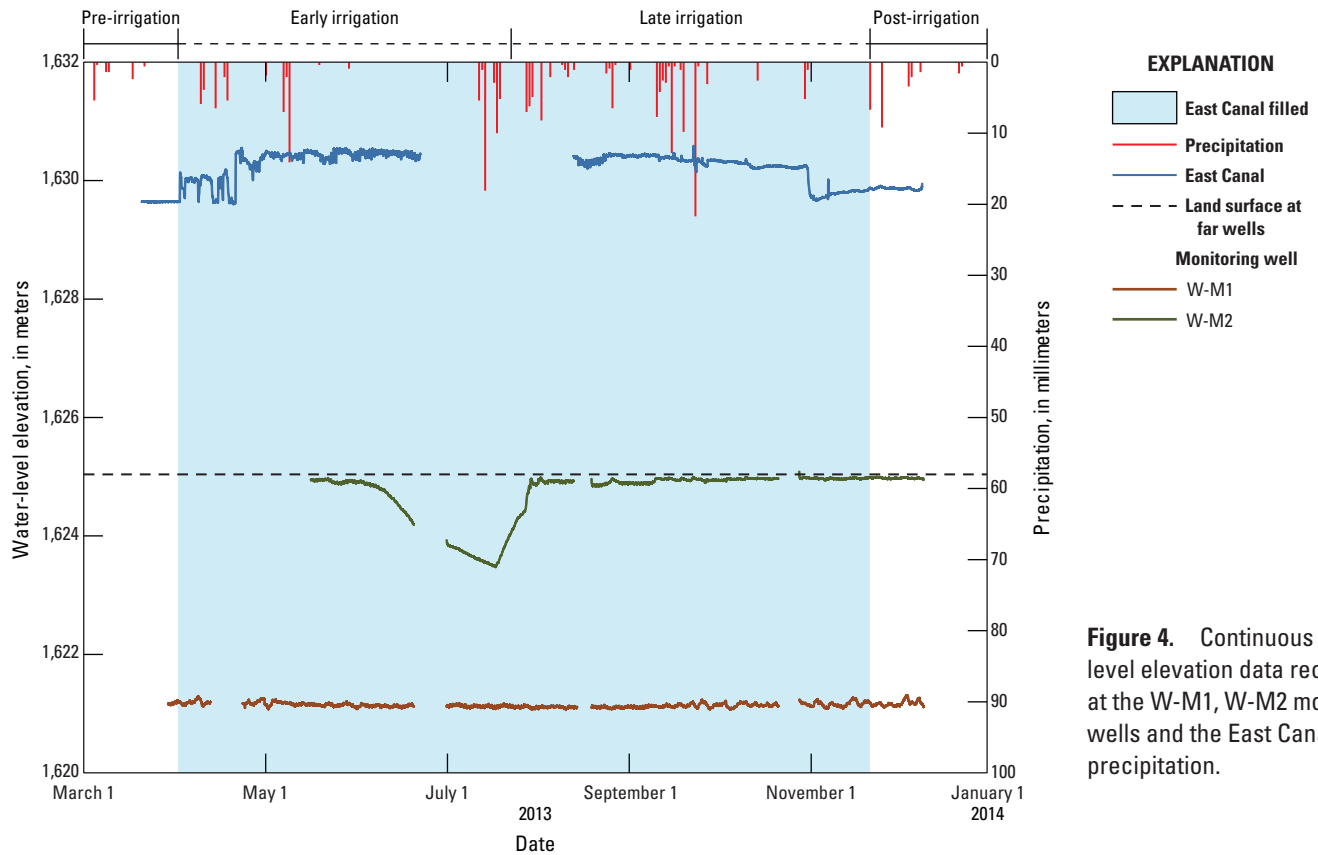

Figure 4. Continuous water-level elevation data recorded at the W-M1, W-M2 monitoring wells and the East Canal with precipitation.

Groundwater Near the Canal

Water-level elevations in the wells near the canal (W-N1 and W-N2) were affected by canal leakage during the irrigation season. Water levels in W-N1 before the irrigation season were at 1,628.31 m and increased to 1,628.55 m (0.2 m below land surface) three weeks after the canal was filled (fig. 3). The water level increased to a maximum of 1,628.65 m by the early irrigation season before it gradually decreased to 1,628.53 m near the end of the irrigation season when the canal was drained. Discrete water-level measurements after the end of the irrigation season indicated water-level elevation had returned to the nonirrigation season levels (1,628.34 m). The water level in W-N2 was at 1,628.30 m before the irrigation season and increased to 1,628.45 m after three weeks (fig. 3). Water-level elevation increased to 1,628.64 m below land surface and steadily decreased to 1,628.53 m at the end of the irrigation season. The water-level elevation had decreased to 1,628.32 m within a week of the canal being drained. After the week following the canal draining the water level had decreased to 0.41 m below land surface. The slow recovery of the W-N2 well is evidenced in the April and May continuous data and coincides with sampling period during which the continuous monitor remained in the well (fig. 3). The continuous monitors were removed prior to the successive sampling period.

The response of the water level in W-N1 to stage changes in the canal was quicker than at W-N2. Consistently, the water levels in W-N1 changed about 2 hours after changes were recorded in the canal, whereas water levels in W-N2 required about 2 days to respond. Most likely this is because of the greater hydraulic connectivity of the canal to more conductive bedding planes than to poorly draining soils of the canal bank. The bottom of the canal is at the unweathered Mancos Shale interface and fractures (created through natural processes or the periodic cleaning of canal sediment and debris with heavy construction equipment) are evident. The pressure exerted by changes in canal stage is, consequently, more readily transferred to the deep groundwater measured in W-N1 than the shallow groundwater at W-N2. The presumed relatively low-permeability sediments in which W-N2 was completed, as demonstrated by the slow recovery of water levels in the well following sampling, suggest the amount of canal leakage reaching W-N2 would be limited.

Groundwater Farther from the Canal

No definitive relation could be made between canal water-level elevation and water-level elevations in monitoring wells farther from the East Canal (W-M1 and W-M2). Water-level elevations at W-M1 averaged 1,621.14 m throughout the study period and ranged from 1,621.06 to 1,621.31 m (fig. 4). In contrast to the other wells, water levels in W-M1 were lowest during the irrigation season and highest during the nonirrigation season. The processes governing the decrease and increase are unclear, but it is evident that leakage from the East Canal did not directly affect water-level elevation at W-M1. The water-level elevations in W-M2, in contrast, remained within 0.15 m of land surface throughout the study period except for a dry period in June and July during which the water level decreased by about 1.5 m, to 1,623.48 m (fig. 4). The decrease in water level at W-M2 during the dry period suggests that the rate of evapotranspiration can exceed the rate at which water moves through the LGRB wetland soils. Although the July precipitation was sufficient to raise the water level at W-M2, it is unreasonable to suggest precipitation is the perennially sustaining source of water because wetlands are uncommon in the LGRB.

Although canal leakage seasonally affects water levels at W-N1, ancillary data and positive pressures recorded at both W-N1 and W-M1 throughout the study period suggest a source of water, supplementing that from the East Canal, affects water levels. The fact that small amounts of water move through the East Canal continually during the nonirrigation season suggests the groundwater system tapped by W-N1 and W-M1 intercepts the canal, and possibly contains seepage from higher in the system. That supplemental water source also explains why positive pressures exist in both deep wells throughout the study period rather than only during the irrigation season. The elevations of the water-bearing bedding planes were at 1,625.75 m at W-N1 and 1,617.44 m at W-M1 and nonirrigation season water-level elevations recorded at those wells were 2.54 m and 4.7 m, respectively, above those elevations. The positive pressures in the deep monitoring wells and the existence of the consistently flowing spring and free-standing water, moreover, suggest that the deep groundwater system affects water levels in the shallow groundwater system.

Seasonality of Total Selenium Concentrations

This section describes total selenium concentrations in the East Canal, ponds, groundwater near the canal, and groundwater farther away from the canal. Conceptually, an increase in total selenium concentrations is expected as rising groundwater levels dissolve soluble salts in the unsaturated zone. The major-ion chemistry of the groundwater is characteristic of calcium-sodium-sulfate to sodium-sulfate type waters (fig. 5) and is consistent with the conceptual model of soluble salts such as gypsum ($CaSO_4$) and thenardite (Na_2SO_4) controlling the water chemistry. Overall, groundwater chemistry in the LGRB wetland is similar to regional groundwater chemistry in the Mancos Shale (Morrison and others, 2012).

Canal

Water flowing through the East Canal before the irrigation season had different selenium concentrations than water in the canal during the irrigation season. Before the irrigation season, concentrations of total selenium in the canal were 140 µg/L (table 2). The concentrations declined to 3.02 µg/L

EXPLANATION

Monitoring well
- W-N2
- W-M2
- W-N1
- W-M1

Figure 5.   Major-ion chemistry of groundwater sampled in the lower Gunnison River Basin wetland, 2013.

in soils adjacent to the ponds. Although pond-surface elevations were not surveyed at the time of each sampling period, visual reconnaissance indicated soils adjacent to the ponds wetted and dried in response to the onset and conclusion of the irrigation season. Concentrations increased after the irrigation season to 3.83 µg/L at W-Pond N, but remained relatively low (0.21 µg/L) at W-Pond M (table 2). The evaporative processes that formed salts during the drying period concentrated selenium in the groundwater (Tuttle and others, 2014) and could explain observed increases in concentrations in W-Pond N following the irrigation season.

The decrease in selenium concentration with increasing distance from the canal and through the irrigation season may be a result of selenium reduction and immobilization. The strong odor of hydrogen sulfide at W-Pond M indicates that sulfate-reducing conditions existed in that area. The odor was not detected at W-Pond N, but that does not mean sulfate reduction was not occurring; perhaps sulfate reduction occurred at a lesser rate than at W-Pond M. By the time sulfate-reducing conditions predominate in aquatic systems, selenate would be expected to be reduced to selenite and elemental selenium (Oremland and others, 1989), both of which are less mobile than selenate. Selenite/total selenium mass ratios for W-Pond N and W-Pond M (fig. 6), discussed in the section Seasonality of Selenium Species, support the hypothesis that selenate reduction occurred to a greater extent at W-Pond M than at W-Pond N, and that more selenate reduction occurred during the irrigation season than during the nonirrigation season in both ponds.

Groundwater Near the Canal

Total selenium concentrations in the monitoring wells near the canal increased as groundwater levels increased. At W-N1, total selenium concentrations increased at onset of the irrigation season to 51.8 from 8.76 µg/L (table 2, fig. 6). Concentrations decreased through the irrigation season to 0.70 µg/L before increasing to 0.84 µg/L after the irrigation season (table 2, fig. 6). Although selenium is diluted and flushed from the canal as it is filled, the flux of water into the deep groundwater from the canal would increase as the hydraulic gradient increases, which would subsequently transport selenium toward W-N1. The process of priming the canal (Kenneth Leib, U.S. Geological Survey, oral commun., October, 2011) to flush debris and saturate canal banks solubilizes efflorescent salts and, in addition to the relatively high total selenium concentrations in the canal before the irrigation season, is a potential source of selenium to nearby groundwater during the early irrigation season. The increase in specific conductance at W-N1 at the start of the irrigation season and subsequent decrease through the rest of the season support the concept of a pulse of more saline water followed by the influx of more dilute canal water (fig. 7). At W-N2, total selenium concentrations increased from 0.79 µg/L before the irrigation season to 1.66 µg/L at the onset of irrigation season (table 2, fig. 6). Concentrations decreased through the irrigation season

during the irrigation season likely because of dilution with water diverted into the canal from the Gunnison River, before increasing to almost 51.0 µg/L after the irrigation season (fig. 6). Changes in specific conductance measured in the canal were similar, exceeding 8 millisiemens per centimeter (mS/cm) before the irrigation season and then decreasing to less than 1 mS/cm at the onset of the irrigation season (fig. 7). Specific conductance stayed at this lower value until after the irrigation season when it increased to more than 7 mS/cm. Similar seasonal patterns of selenium concentrations and specific conductance in streams of the LGRB are common (Butler and others, 1996), because snowmelt runoff in the early summer dilutes surface-water selenium concentrations that are otherwise higher during the nonirrigation season because of base-flow contributions to streamflow.

Wetland Ponds

Selenium concentrations in the ponds decreased with distance from the canal and decreased throughout the irrigation season (fig. 6). Total selenium concentrations at W-Pond N decreased from 30.0 to 1.20 µg/L and from 2.38 to less than 0.20 µg/L at W-Pond M (table 2). The higher concentrations potentially result from the first canal leakage at the start of the irrigation season or from the solubilization of efflorescent salts
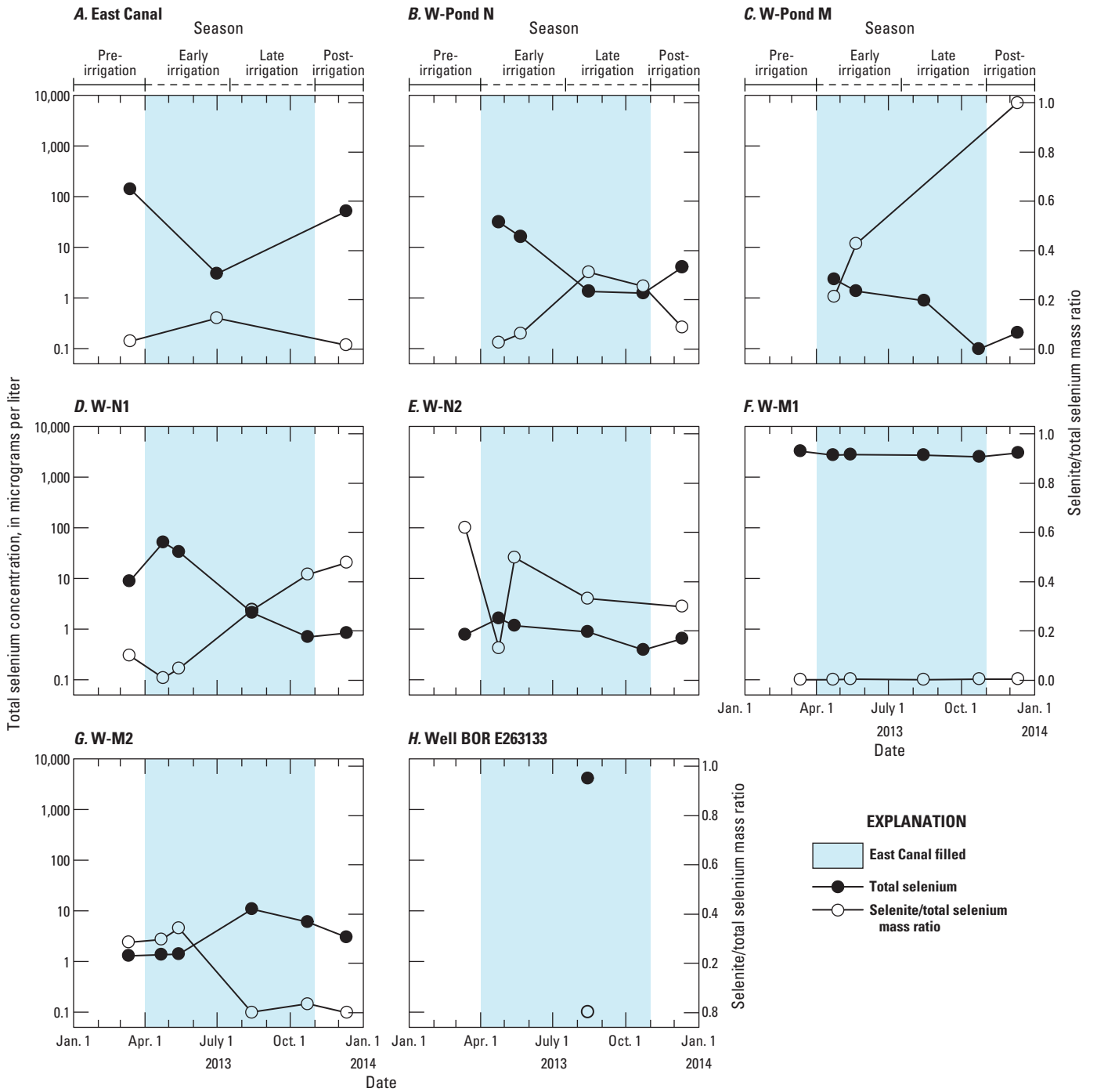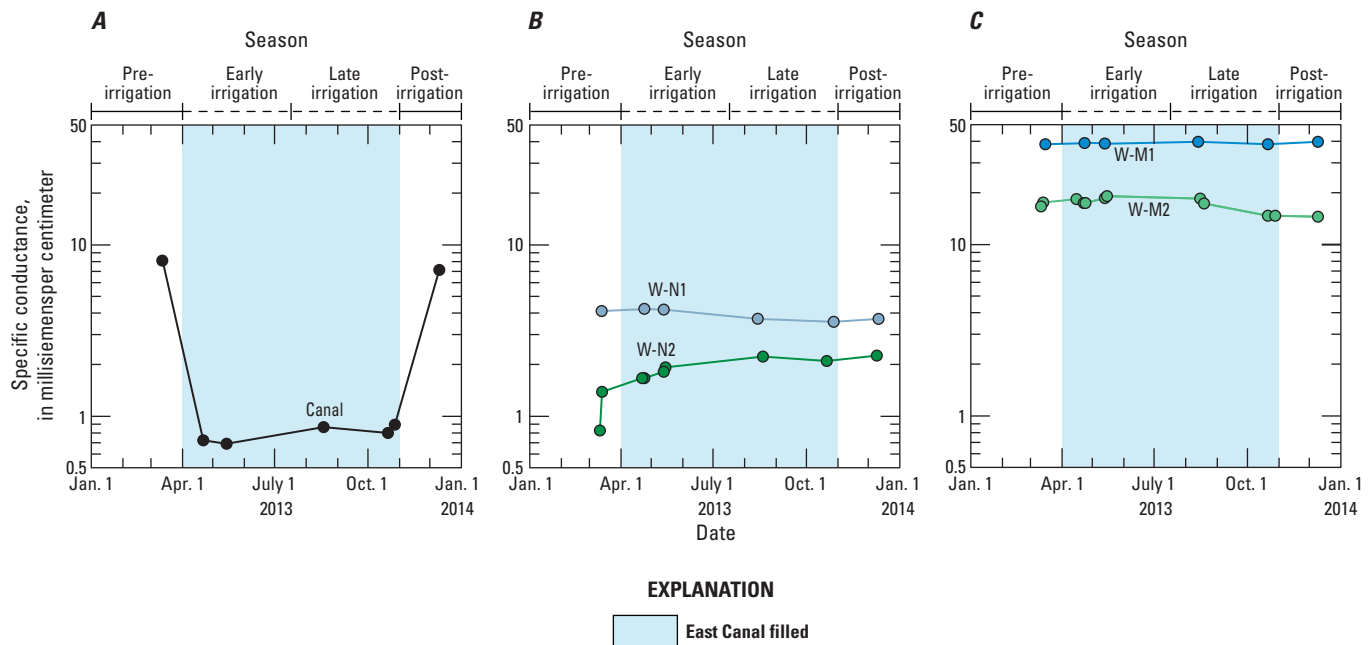
Figure 6.   Concentrations of total selenium and selenite/total selenium mass ratios in surface water and groundwater in the study area.

Figure 7.   Discrete specific conductance measured in the *A*, East Canal; *B*, W-N1, W-N2; and *C*, W-M1, and W-M2 at the lower Gunnison River Basin wetland during 2013.

to 0.40 µg/L before increasing to 0.66 µg/L after the irrigation season (table 2, fig. 6). In addition, specific conductance in W-N2 also showed a small increase during the early irriga-tion season as opposed to the decrease that would be expected if the canal leakage reaching W-N2 was composed of only dilute irrigation water (fig. 7). The increase in total selenium concentrations in W-N2 could be a result of both direct con-tributions of selenium from canal leakage through the canal banks and solubilization of efflorescent salts in the unsaturated zone as water levels increased. The quick response of water levels in monitoring wells near the canal to the beginning of the irrigation season and the relatively high selenium concen-trations measured at those wells at the onset of the irrigation season indicate canal leakage affects selenium concentrations in groundwater near the canal.

Groundwater Farther from the Canal

Total selenium concentrations in monitoring wells far-ther from the East Canal were not directly affected by canal leakage. Total selenium concentrations at W-M1were higher than concentrations at either of the near canal wells or W-M2 and ranged from 3,220 µg/L before the irrigation season to 2,520 µg/L late in the irrigation season (table 2). The replicate sample collected at W-M1 late in the irrigation season yielded a total selenium concentration of 2,960 µg/L. Although this difference was about 15 percent, the difference in the early irrigation season replicate sample was less than 2 percent and the blank samples had total selenium concentrations less than the detection limit of 0.20 µg/L. Considering the replicate

concentration, total selenium at W-M1, like water-level eleva-tion at this well, generally decreased until the middle of the irrigation season and increased thereafter. The processes gov-erning the decrease and increase are unclear, but it is evident that the transition from irrigation to nonirrigation season does not substantially affect total selenium at W-M1.

Climatology affected total selenium concentrations at W-M2. The total selenium concentrations increased after the midsummer drying and wetting periods from 1.40 to 10.9 µg/L (table 2). Solubilization of efflorescent salts in the unsaturated zone as water levels increased is the most likely explanation for the increased selenium concentrations in W-M2. Salts could have formed in the unsaturated zone as water levels declined during the drying period. When water levels started to recover in late July because of precipitation, the salts could have been redissolved, thus increasing the selenium concentration in groundwater, as was observed in the middle of the irrigation season. The drying and wetting periods, while not related to the irrigation season, are related to climatological seasons. There is potential, consequently, that large increases in total selenium concentrations may occur in shallow groundwater on an annual basis if similar drying and wetting periods occur.

Without the evident effect of canal leakage, the processes governing the seasonality of total selenium concentrations in groundwater farther from the East Canal are less clear. Any effects of canal leakage on total selenium concentrations in W-M1 and W-M2 are likely to be muted and offset by some lag time greater than that observed at wells W-N1 and W-N2 because of the distance between the East Canal and wells farther from the canal. In that case, more than one season of data col-lection may be required to identify any relations that might exist

between water levels in the canal and wells farther from the canal. What does appear to be important with respect to total selenium concentrations in deep groundwater is distance from the canal: separated by 277 m, concentrations at W-M1 were greater than those at W-N1 by at least 2,600 µg/L. Similarly, deep groundwater selenium concentrations at well W-S (roughly 275 m farther from W-M1 and 28 feet deep; fig. 1) in the middle of the irrigation season were about 1,400 µg/L greater than the W-M1 concentration measured at the same time (Mast and others, 2014). These data indicate that the deep groundwater accumulates selenium as it moves through the wetland system. This finding is important because groundwater in the deep part of the flow system may eventually discharge to surface water.

Seasonality of Selenium Species

This section describes seasonal variations in selenate and selenite concentrations in the East Canal, ponds, and groundwater relative to total selenium concentrations. The contributions of selenate and selenite to total selenium concentrations are evaluated in the context of water levels and redox conditions.

Canal

Selenite/total selenium mass ratios in the East Canal samples ranged from about 0.02 to 0.13 (fig. 6*A*, table 2), indicating that about 2 to 13 percent of the total selenium in canal samples was selenite. The smallest percentages occurred before and after the irrigation season and the largest percentage occurred during the irrigation season. Dissolved-oxygen concentrations in the canal water were not measured in this study, but the predominance of selenate in canal water throughout the year implies that the water was largely oxic (Oremland and others, 1989; Butler and others, 1996).

The decrease in total selenium concentrations in canal water during the irrigation season is considered to be mostly a result of dilution by river water diverted into the East Canal, but the increase in the percentage of selenite in the water during the irrigation season indicates that some of the concentration decrease could be because of selenate reduction to less soluble forms of selenium such as selenite. If selenate reduction did occur in the canal during the irrigation season, it was probably focused at the sediment-water interface and catalyzed by microorganisms. Selenite generated by selenate reduction at the sediment-water interface could be reoxidized to selenate once the diversion of river water into the canal stops at the end of the irrigation season and the sediment is re-exposed to the atmosphere. At the same time, dissolved selenate that was in canal water during the irrigation season could precipitate from solution (or be evaporatively concentrated) as the canal drains. The relatively large concentrations of total selenium and percentages of selenate measured in canal water during the nonirrigation season could be because of dissolution of selenate from both those sources by periodic small flows in the canal.

Wetland Ponds

About 2 to 30 percent of the total selenium in W-Pond N was selenite, whereas about 20 to almost 100 percent of the total selenium in W-Pond M was selenite (figs. 6*B* and 6*C*). The percentages of selenite in both ponds increased during the irrigation season as total selenium concentrations decreased. One mechanism that could explain the increase in selenite would be the conversion of selenate in pond water to selenite, which can occur in anoxic conditions. These percentages indicate that much less of the total selenium in pond water was selenate than was observed in canal water. A strong odor of hydrogen sulfide in W-Pond M is indicative of highly reducing conditions, which is consistent with the relatively high percentages of selenite in that pond compared to W-Pond N or the canal (figs. 6*B*–6*C*). By the late irrigation season, the total selenium concentration in W-Pond M was less than 0.20 µg/L, and after the irrigation season almost 100 percent of the total selenium concentration was selenite (table 2).

The percentage of selenite in W-Pond N decreased after the end of the irrigation season and the total selenium concentration increased (fig. 6*B*), indicating that selenate was added back into solution during that period. That pattern is similar to the pattern observed in the canal (fig. 6*A*). Like the East Canal, the banks of the ponds partially dried out during the nonirrigation season. Given the similarities between W-Pond N and the East Canal with respect to these characteristics, it is possible that the small increase in total selenium and selenate concentrations measured in the pond after the irrigation season could be a result of evaporative concentration, similar to that observed by Tuttle and others (2014).

Groundwater Near the Canal

Water samples from wells W-N1 and W-N2 were used to describe the chemistry of selenium species in groundwater near the canal (fig. 1). The increase in total selenium from before the irrigation season to the onset of the irrigation season was accompanied by a decrease in the percentage of selenite from about 10 percent to 1 percent at well W-N1 (fig. 6*D*). The data indicate that selenate was added to the groundwater at W-N1 during that period. The change in selenium chemistry and water-level rise in W-N1 corresponded closely in time to the filling of the canal. Thus, the added selenate could have come directly from the canal if the first flush of water through the canal had a similarly high total selenium concentration and small percentage of selenite as was measured in the canal before the irrigation season (fig 6*A*). Alternatively, or in addition to that scenario, the added selenate could have come from selenate-bearing salts in the unsaturated zone if they were mobilized when groundwater levels started to rise following the filling of the canal. The pulse of selenate that was present in W-N1 during the early irrigation season was dissipated through the course of the irrigation season and the fraction of selenite increased to about 43 percent (fig. 6*D*). The corresponding decrease in selenate is due at least in part to selenate reduction to less soluble forms of selenium such as selenite.

Redox data were collected from the wells to determine whether redox conditions in the aquifer were conducive to selenate reduction. Groundwater systems need to be anoxic and contain little or no nitrate for substantial selenate reduction to occur (Oremland and others, 1989). Groundwater in W-N1 was anoxic throughout the study, but nitrate concentrations were variable (fig. 8A). Nitrate concentrations in W-N1 ranged from about 0.27 to 6.41 mg/L as N (table 3), with the largest concentrations coinciding with the selenate pulse in the early irrigation season (table 2). Generally speaking, anoxic groundwater that contains more than about 0.50 mg/L of nitrate N is conducive to nitrate reduction, or denitrification (McMahon and Chapelle, 2008), the process of microbial reduction of nitrate to nitrogen gas (N_2), but not necessarily to selenate reduction because of the inhibitory effect of nitrate on the selenate-reduction process (Oremland and others, 1989). The threshold nitrate concentration above which selenate reduction is not likely to occur could be higher or lower than 0.50 mg/L as N in a particular aquifer system, but it is unlikely that selenate would have been reduced during the early irrigation season when nitrate concentrations were greater than 0.50 mg/L as N (fig. 8A).

The dissipation of nitrate concentrations in W-N1 in the later part of the irrigation season coincided with relatively high percentages of selenite and could indicate that selenate reduction had occurred. The dissipation of nitrate in W-N1 could have resulted from dilution by canal leakage and (or) denitrification in the anoxic groundwater. Nitrate concentrations in the canal were not measured in this study so the dilution process cannot be fully evaluated. Nevertheless, the specific conductance of water in W-N1 decreased through the irrigation season (fig. 7), indicating that canal water was moving through the aquifer sediments at W-N1 during the irrigation season.

The nitrogen isotopic composition of nitrate ($\delta^{15}N$) in samples collected from W-N1 in August and December were about 58 to 66 per mil (table 4) and could be evidence for denitrification (Böhlke and Denver, 1995). The oxygen isotopic composition of the nitrate ($\delta^{18}O$) was not particularly elevated (0.08 to 4.21 per mil) for samples that could be highly denitrified (Böttcher and others, 1990; McMahon and Böhlke, 2006). For example, the nitrate in highly denitrified groundwater in York, Nebraska, had $\delta^{15}N$ values of 30 to 40 per mil and $\delta^{18}O$ values of 15 to 20 per mil (McMahon and
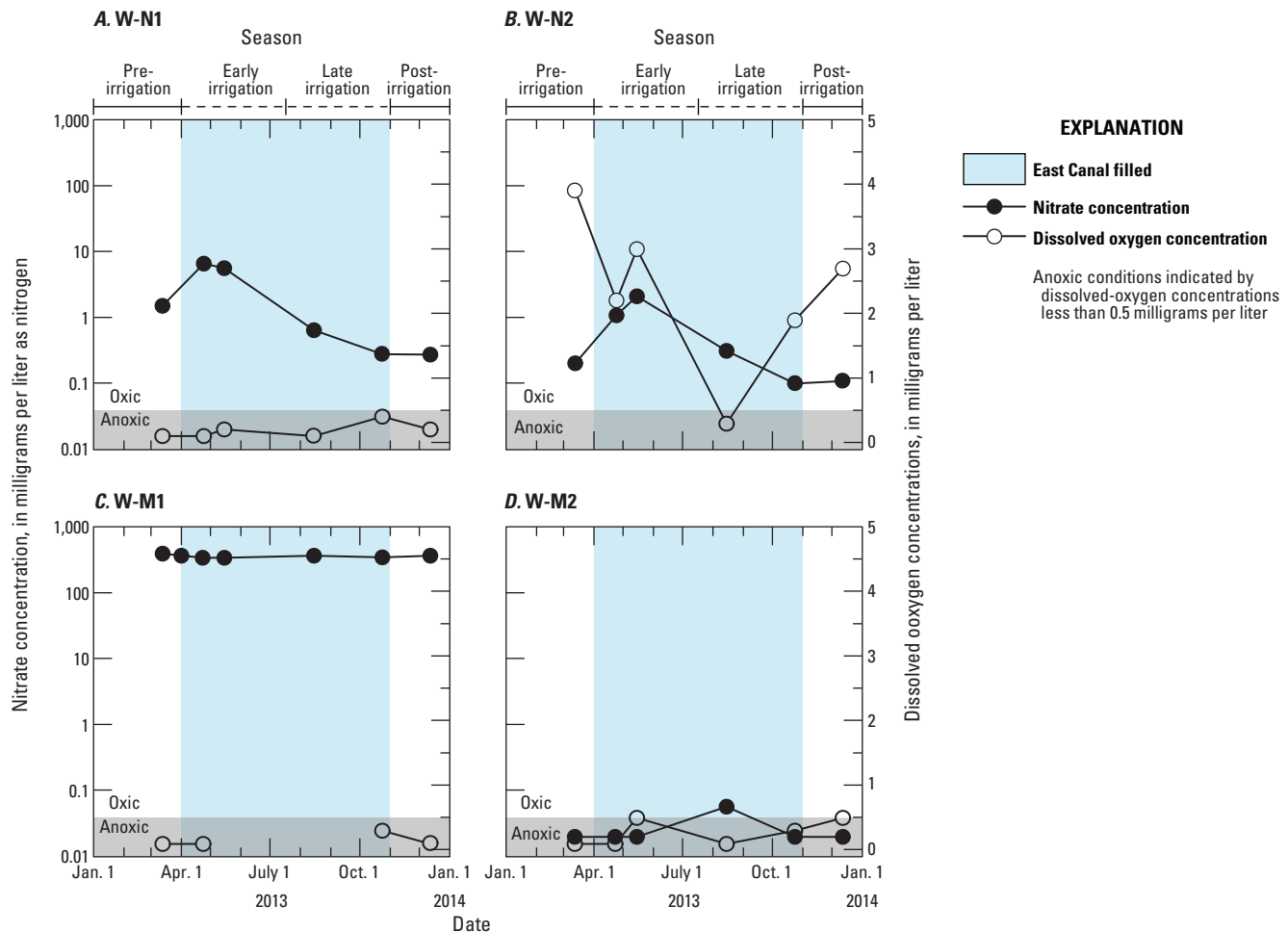
Figure 8.   Concentrations of dissolved nitrate and oxygen in groundwater in the study area.

Table 4. Measured concentrations and isotopic compositions for nitrate and nitrogen gas, and calculated initial nitrate concentrations in solution, isotopic composition of initial nitrate, and the ratio of measured to initial nitrate concentration.

[mg/L, milligrams per liter; μmol/L, micromoles per liter; N_2, nitrogen gas; $\delta^{15}N$, stable isotope composition; $\delta^{18}O$, stable isotope composition; °C, degrees Celsius; cm³/L, cubic centimeters per liter; --, no data]

Well name	Sample date	Measured							Calculated										
		Dissolved oxygen, mg/L	Dissolved nitrate, μmol/L	Dissolved N_2, μmol/L	Dissolved argon, μmol/L	$\delta^{15}N$-nitrate, per mil	$\delta^{18}O$-nitrate, per mil	$\delta^{15}N$-N_2, per mil	Scenario	Recharge temperature, °C	N_2 in air-saturated water, μmol/L	$\delta^{15}N$, N_2 in air-saturated water, per mil	Excess air, cm³/L	N_2 in excess air, μmol/L	N_2 from denitrification, μmol/L	$\delta^{15}N$, N_2 from denitrification, per mil	Initial nitrate in solution, μmol/L	$\delta^{15}N$ of initial nitrate, per mil	Measured nitrate/Initial nitrate ratio
W-N1	8/14/2013	0.1	20	604	13.5	58.45	4.21	0.77	--	--	--	--	--	--	--	--	--		--
W-N1	12/11/2013	0.2	19	606	13.3	66.38	0.08	1.25	--	--	--	--	--	--	--	--	--		--
W-N2	12/12/2013	2.7	8	688	16.3	--[1]	--[1]	1.21	--	--	--	--	--	--	--	--	--		--
W-M1	8/14/2013	--	25,993	772	13.4	12.76	7.88	−12.36	[2]1	5.4	459	0.79	2.0	70	243	−40.8	26,479	11.8	0.98
W-M1	8/14/2013	--	25,993	772	13.4	12.76	7.88	−12.36	[3]2	9.5	421	0.76	4.8	167	184	−53.6	26,361	11.8	0.99
W-M1	12/11/2013	0.1	25,993	720	12.6	13.55	8.38	−10.74	[2]1	4.9	429	0.79	2.0	70	221	−36.5	26,435	12.7	0.98
W-M1	12/11/2013	0.1	25,993	720	12.6	13.55	8.38	−10.74	[3]2	9.5	391	0.76	4.7	164	165	−48.7	26,323	12.8	0.99
W-M2	12/12/2013	0.5	1	659	15.8	--[1]	--[1]	1.46	--	--	--	--	--	--	--	--	--		--

[1] Sample could not be accurately analyzed because of matrix interferences.

[2] Assumes 2 cm³/L of excess air.

[3] Assumes recharge temperature of 9.5 °C, which is the mean annual air temperature in Montrose, Colorado (Daly and others, 2008), and an elevation of 5,326 ft above the North American Vertical Datum of 1988.

others, 2008). Thus, it is not entirely clear from the isotopic compositions of nitrate that denitrification occurred in W-N1. Data for dissolved nitrogen gas (N_2) and argon concentrations, and the nitrogen isotopic composition of the nitrogen gas, also provide no clear evidence for denitrification in W-N1 (table 4 and fig. 9). The data indicate that W-N1 mostly contained N_2 of atmospheric origin consisting of two main components: a major component of dissolved N_2 in equilibrium with air and a minor component of excess air (fig. 9). Given that the isotope samples were collected late in the year when nitrate concentrations in W-N1 were already low, it may be necessary to collect isotope samples from W-N1 during the early irrigation season when the nitrate pulse first begins to dissipate in order to better understand the role of denitrification in that area.
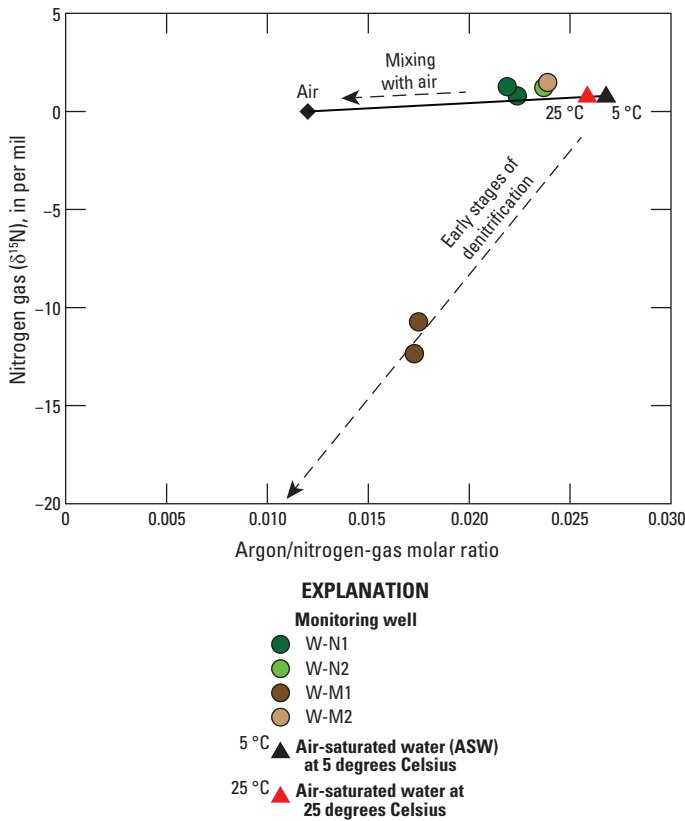
Figure 9. Argon/nitrogen gas molar ratios compared to the nitrogen isotopic composition ($\delta^{15}N$) of nitrogen gas in groundwater in the study area. Water samples from W-M1 contained a component of nonatmospheric nitrogen gas interpreted as the product of denitrification. Water samples from the other wells appeared to contain nitrogen gas from equilibration with the atmosphere as well as small amounts of trapped (excess) air that was either acquired at the time of recharge or during sampling.

Pulses of selenium and nitrate also appeared in W-N2 at the onset of the irrigation season, but they were much smaller than the pulses in W-N1 (figs. 6E and 8B). The maximum total selenium concentration in W-N2 was about 1.66 μg/L (table 2), and the maximum nitrate concentration was about 2.13 mg/L as N (table 3). As at W-N1, the increased concentration of total selenium in W-N2 was accompanied by a decrease in the percentage of selenite in the water (from about 62 to 13 percent), indicating that selenate also was added to groundwater at W-N2 (fig. 6). Field observations and specific-conductance data indicate that the small additions of selenate and nitrate in W-N2 probably came mostly from salts in the unsaturated zone and less so from the canal.

Well W-N2 generally contained higher percentages of selenite than W-N1 (figs. 6D and 6E), even though W-N2 contained more dissolved oxygen than W-N1 (fig. 8A and 8B). The apparent occurrence of selenate reduction in oxic groundwater could be an artifact of how the well was sampled. Because W-N2 had such poor water-bearing properties, it had to be purged a day or two before sampling to give it time to recover. Water in the well potentially became oxygenated from exposure to the atmosphere during the recovery period. Exposure of well water to atmospheric oxygen would not have artificially increased the percentage of selenite in the water (Fernandez-Martinez and Charlet, 2009), so the high levels of selenite measured in the well are presumed to be representative of the aquifer.

Denitrification might be expected to be more important at W-N2 than W-N1 because of the slow movement of water through the relatively low-permeability sediments at W-N2. However, there was no evidence that denitrification occurred at W-N2 on the basis of N_2 and argon concentrations and the nitrogen isotopic composition of N_2 (fig. 9). The sample from W-N2 appeared to contain mostly N_2 from atmospheric sources (fig. 9). As with the dissolved-oxygen data, possibly the N_2 and argon data were affected by exposure of the well water to the atmosphere during recovery of the water level in the well prior to sampling. The isotopic composition of nitrate in W-N2 could not be determined because of matrix interference with the sample during the analysis (table 4).

Concentrations of selenate and nitrate in groundwater near the canal increased shortly after the canal was filled with water at the onset of the irrigation season. The increases in concentrations were larger in W-N1 than W-N2. The two likely sources of selenate and nitrate were canal leakage into the aquifer and soluble salts in the unsaturated zone that were mobilized when groundwater levels increased in response to the canal being filled. Selenate and nitrate concentrations in groundwater decreased through the irrigation season in both wells. Decreases in selenate concentrations were because of selenate reduction to selenite and dilution by canal leakage. Decreases in nitrate concentrations in W-N1 appeared to result mostly from dilution by canal leakage. The processes responsible for decreases in nitrate concentrations in W-N2 are not well characterized in part because of the poor water-yielding characteristics of the well that may have affected the integrity of dissolved-gas samples.

Groundwater Farther from the Canal

Water samples from wells W-M1 and W-M2 were used to describe the chemistry of selenium species in groundwater farther from the canal (fig. 1). Unlike at wells W-N1 and W-N2, concentrations of total selenium and percentages of selenite in W-M1 did not change in response to filling the canal (figs. 6F and 6G). The fraction of selenite in W-M1 remained close to 0 percent throughout the study. The predominance of selenate in W-M1, and apparent lack of selenate reduction, cannot be explained by a lack of anoxic conditions in the groundwater because all the available dissolved-oxygen data indicate that concentrations were less than 0.50 mg/L (fig. 8C). The most likely explanation for the lack of selenate reduction in W-M1 is that the high concentrations of nitrate in the groundwater (about 340 to 390 mg/L as N, table 3) inhibited selenate reduction (Oremland and others, 1989). The high concentrations of selenate in W-M1 (about 2,500 to 3,200 µg/L; table 2) may persist and eventually discharge to surface water unless nitrate concentrations are reduced to low enough levels to permit substantial selenate reduction to occur.

Dilution by canal leakage is not a viable process for lowering nitrate concentrations in W-M1 because the canal is located too far from the well to affect groundwater chemistry. Denitrification is the only process that might be capable of lowering nitrate concentrations in groundwater at W-M1. There is evidence that denitrification occurred at W-M1 on the basis of N_2 and argon concentrations and the nitrogen isotopic composition of N_2 (fig. 9). The data indicate that W-M1 contained an additional N_2 component of nonatmospheric origin (referred to as excess N_2). Both samples from W-M1 plotted below the mixing line between air-saturated water and air and had $\delta^{15}N$ values for excess N_2 (defined at $Ar/N_2 = 0$ in fig. 9) less negative than -20 per mil, which is consistent with isotope fractionation in the early stages of denitrification. However, the denitrification process appears to have removed no more than about 1 to 2 percent of the nitrate (table 4, Appendix 4). (Appendix 4 describes the method used to calculate the ratio of measured to initial nitrate in solution, as well as the initial nitrate concentration in solution and the initial isotopic composition of the nitrate.)

If groundwater velocities were slow enough and distances to discharge areas were far enough, it might be possible that the rate of denitrification in the deep groundwater could outpace the rate of nitrate transport, thereby allowing substantial selenate reduction to occur before the groundwater discharged to surface water. However, concentrations of selenate and nitrate in groundwater actually increased from W-N1 to W-M1 to W-S (fig. 1, tables 2 and 3), indicating that selenium and nitrate were added to groundwater as it moved through the LGRB wetland. If the added nitrate was from human sources such as fertilizer or manure associated with agricultural activities, then removing those sources would help reduce the inhibitory effect of nitrate on selenate reduction. However, there was no evidence for a human source of nitrate at the LGRB wetland to account for those increasing concentrations, so the large nitrate concentrations in W-M1 are presumed to come from the Mancos Shale and its weathering products. This interpretation is consistent with the results from Mast and others (2014) showing that some sediments derived from the Mancos Shale contain naturally high concentrations of selenium and nitrate.

Mast and others (2014) reported nitrogen isotopic compositions for nitrate and total nitrogen in Mancos Shale sediments at W-M1 as 1.86 per mil and at W-S as 2.5 per mil. The nitrogen isotopic composition of nitrate in W-M1 water, corrected for denitrification effects (Böhlke and Denver, 1995; Böhlke and others, 2002), was about 12 per mil (table 4, Appendix 4). The reason for the discrepancy in isotopic values for nitrogen in sediment and nitrate in groundwater is unknown but warrants further study because of the importance of nitrate in inhibiting selenate reduction.

Well W-M2 contained relatively low concentrations of total selenium and high percentages of selenite before and at the onset of the irrigation season (fig. 6G). During that period, concentrations of dissolved oxygen and nitrate in W-M2 also were low (fig. 8), consistent with the idea that selenate-reducing conditions were present in the aquifer at that location. The increase in total selenium concentration associated with the drying and wetting period was accompanied by a decrease in the percentage of selenite to near 0 percent (fig. 6G), indicating that selenate was added to the groundwater. This pattern is consistent with the examples of increasing concentrations of total selenium in the other wells and W-Pond N and presumably resulted from the dissolution of selenate-bearing salts in the unsaturated zone by rising water levels in W-M2.

Nitrate concentrations in W-M2 generally were less than 0.1 mg/L as N throughout the study (table 3). There is no evidence on the basis of N_2 and argon concentrations and the nitrogen isotopic composition of N_2 that denitrification was responsible for the low nitrate concentrations (fig. 9). The water possibly never contained high nitrate concentrations or other processes, such as plant uptake, kept the concentrations at low levels.

Summary

Selenium is a water-quality concern in the lower Gunnison River Basin (LGRB) because irrigation water interacting with seleniferous soils derived from the Mancos Shale Formation has mobilized selenium and increased its concentrations in surface water. The elevated selenium concentrations in surface water are considered to detrimentally affect the recruitment of native Colorado River Basin fish species: Razorback Sucker (*Xyrauchen texanus*), Colorado Pike Minnow (*Ptychocheilus Lucius*), Humpback Chub (*Gila cypha*), and the Bonytail Chub (*Gila elegans*). The bioavailability and toxicity of selenium in the environment is dependent on its solubility and oxidation state. Selenate and selenite are both water soluble and although selenite is more bioavailable and toxic than selenate, selenate typically comprises more of the total selenium in water than selenite as it is more soluble.

The enrichment of selenium in groundwater of the LGRB occurs as a result of Mancos Shale weathering, efflorescent salt

dissolution, and redox processes. Total selenium concentrations in surface water are increasing in some areas of the LGRB despite the implementation of salinity/selenium-control projects (such as improving irrigation efficiency or lining canals) in the region that aim to reduce percolation and subsequent mobilization of salt and selenium from groundwater to surface-water systems. Geochemical conditions in groundwater adjacent to leaky canals fluctuate seasonally as canals fill and oxic water recharges the aquifer. In 2013, the U.S. Geological Survey, in cooperation with the Bureau of Reclamation and the Colorado Water Conservation Board, began a study to understand how changes in groundwater levels attributed to canal leakage may affect concentrations and speciation of dissolved selenium in groundwater. The purpose of this report is to characterize the groundwater adjacent to an unlined leaky canal.

Two locations, near the East Canal and farther from the East Canal, were selected for nested monitoring well installations. The four wells installed for this study are the W-N1 well (deep, near the East Canal), W-N2 (shallow, near the East Canal), W-M1 (deep, farther from the canal), and W-M2 (shallow, farther from the canal). Continuous pressure (water level) data were measured at each of the four wells and the East Canal site. Water-quality samples were collected at the canal, two ponds, and the monitoring wells. Samples were collected in processing chambers to reduce potential for airborne contamination and filtered samples were analyzed for total selenium, selenite, major ions, nutrients, and dissolved organic carbon. Unfiltered sample water was analyzed for dissolved gases (argon, carbon dioxide, dinitrogen [N_2], and methane) and the isotopic composition of N_2 gas.

Understanding when canals are filled and drained is necessary to relate canal leakage to changes in groundwater elevation. The elevation of water in the canal increases at the beginning of the irrigation season (on or about April 1) and correspondingly decreases at the end of the irrigation season (on or about November 1). The pressure exerted by changes in canal stage was more readily transferred to the deep groundwater measured in W-N1 than the shallow groundwater at W-N2. The relatively low-permeability sediments in which W-N2 was completed and the slow recovery of water levels in that well following sampling suggest the amount of canal leakage reaching W-N2 would be limited. No definitive relation could be made between canal water-level elevation and water-level elevations in monitoring wells farther from the canal (W-M1 and W-M2). Although the canal leakage seasonally affects water levels at W-N1, ancillary data and positive pressures recorded at both W-N1 and W-M1 throughout the study period suggest a source of water, in addition to that of the canal, affects water levels.

Conceptually, an increase in total selenium concentrations is expected as rising groundwater levels dissolve soluble salts in the unsaturated zone. Water flowing through the East Canal before the irrigation season had different selenium concentrations (140 micrograms per liter) than water in the canal during the irrigation season (3.02 micrograms per liter). Selenium concentrations in the ponds decreased with distance from the canal and decreased throughout the irrigation season.

Total selenium concentrations in the monitoring wells near the canal increased to 51.8 micrograms per liter in W-N1 and 1.66 micrograms per liter in W-N2 in response to increases in water level related to canal leakage. Total selenium concentrations in monitoring wells farther from the canal were not directly affected by canal leakage. Climatology affected total selenium concentrations at W-M2 where the total selenium concentrations increased after the midsummer drying and wetting events from 1.40 to 10.9 µg/L.

The contributions of selenate and selenite to total selenium concentrations were evaluated in the context of water levels and redox conditions. Selenite/total selenium mass ratios in the East Canal samples ranged from about 0.02 to 0.13, indicating that about 2 to 13 percent of the total selenium in canal samples was selenite. The decrease in total selenium concentrations in canal water during the irrigation season is considered to be mostly a result of dilution by river water diverted into the East Canal, but the increase in the percentage of selenite in the water during the irrigation season indicates that some of the concentration decrease could be because of selenate reduction to less soluble forms of selenium such as selenite. About 2 to 30 percent of the total selenium in W-Pond N was selenite, whereas about 20 to almost 100 percent of the total selenium in W-Pond M was selenite. The percentage of selenite in W-Pond N decreased after the end of the irrigation season, and the total selenium concentration increased, indicating that selenate was added back into solution during that period.

Water samples from wells W-N1 and W-N2 were used to describe the chemistry of selenium species in groundwater near the canal. The increase in total selenium in W-N1 from before the irrigation season to the early irrigation season was accompanied by a decrease in the percentage of selenite from about 10 percent to 1 percent, indicating that selenate was added to the groundwater. Redox data were collected from the wells to determine whether redox conditions in the aquifer were conducive to selenate reduction. Even though concentrations of dissolved oxygen in W-N1 were low, a pulse of relatively high nitrate concentrations occurred in the groundwater in the early irrigation season that appeared to inhibit selenate reduction. The nitrate pulse in W-N1 apparently dissipated to a low enough concentration during the irrigation season to allow for selenate reduction to occur later in the season, as indicated by the relatively high percentages of selenite in W-N1 during the late irrigation season. Pulses of selenium and nitrate also appeared in W-N2 during the early irrigation season, but they were much smaller than the pulses in W-N1. There was no clear evidence for denitrification at W-N1 based on dissolved-gas and nitrogen isotopic data; therefore, dissipation of the nitrate pulse in W-N1 is attributed mostly to dilution by canal leakage. W-N2 generally contained higher percentages of selenite than W-N1, even though W-N2 contained more dissolved oxygen than W-N1. Denitrification might be expected to be more important at W-N2 than W-N1 because of the slow movement of water through the relatively low-permeability sediments at W-N2. However, denitrification could not be accurately assessed because the poor water-yielding characteristics of that well may have affected the

integrity of gas samples collected from the well. High nitrate concentrations presumably come from the Mancos Shale and its weathering products because there was no evidence for a human source of nitrate at the lower Gunnison River Basin wetland.

Unlike at wells W-N1 and W-N2, concentrations of total selenium and percentages of selenite in W-M1 did not change in response to filling the canal. The fraction of selenite in W-M1 remained close to 0 percent throughout the study. The predominance of selenate in W-M1, and apparent lack of selenate reduction, cannot be explained by a lack of anoxic conditions in the groundwater because all the available dissolved-oxygen data indicate that concentrations were less than 0.50 milligrams per liter. The most likely explanation for the lack of selenate reduction in W-M1 is that the exceptionally high concentrations of nitrate in the groundwater (about 340 to 390 milligrams per liter as N) inhibited selenate reduction. The high concentrations of selenate in W-M1 (about 2,500 to 3,200 micrograms per liter) may persist and eventually discharge to surface water unless nitrate concentrations are reduced to low enough levels to permit substantial selenate reduction to occur. Dilution by canal leakage is not a viable process for lowering nitrate concentrations in W-M1 because the canal is located too far from the well to have such a direct effect on groundwater chemistry. There is evidence for denitrification at W-M1, but it removed less than 2 percent of the nitrate. If groundwater velocities were slow enough and distances to discharge areas were far enough, it might be possible that the rate of denitrification in the deep groundwater could outpace the rate of nitrate transport, thereby allowing selenate reduction to occur before the groundwater discharged to surface water. However, concentrations of selenium and nitrate in groundwater increased from W-N1 to W-M1 to W-S, indicating that selenium and nitrate were actually added to groundwater as it moved through the LGRB wetland. Well W-M2 contained relatively low concentrations of total selenium and high percentages of selenite before and at the onset of the irrigation season. The increase in total selenium concentration associated with the drying and wetting period was accompanied by a decrease in the percentage of selenite to near 0 percent, indicating that selenate was added to the groundwater. Presumably this resulted from the dissolution of selenate-bearing salts in the unsaturated zone by rising water levels in W-M2.

References

Balistrieri, L.S., and Chao, T.T., 1987, Selenium adsorption by goethite: Soil Science Society of America Journal, v. 51, p. 1145–1151.

Böhlke, J.K., and Denver, J.M., 1995, Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland: Water Resources Research, v. 31, p. 2319–2339.

Böhlke, J.K., Wanty, R., Tuttle, M., Delin, G., and Landon, M., 2002, Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota: Water Resources Research, v. 38, doi: 10.1029/2001WR000663.

Böttcher, J., Strebel, O., Voerkelius, S., and Schmidt, H.L., 1990, Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer: Journal of Hydrology, v. 114, p. 413–424.

Briggs, P.H., and Crock, J.G., 1986, Automated determination of total selenium in rocks, soils, and plants: U.S. Geological Survey Open-File Report 86–40, 20 p.

Bureau of Reclamation, 2011, Selenium Management Program—Program formulation document Gunnison River Basin, Colorado: accessed April 14, 2014, at: http://www.usbr.gov/uc/wcao/progact/smp/docs.html.

Busenberg, Eurybiades, Weeks, E.P., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating ground water by use of chlorofluorocarbons (CCl_3F and CCl_2F_2) and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho, USA: U.S. Geological Survey Water-Resources Investigations Report 93–4054, 47 p.

Butler, D.L., 1996, Trend analysis of selected water-quality data associated with salinity-control projects in the Grand Valley, in the lower Gunnison River Basin, and at Meeker Dome, western Colorado: U.S. Geological Survey Water-Resources Investigations Report 95–4274, 38 p.

Butler, D.L., 2001, Effects of piping irrigation laterals on selenium and salt loads, Montrose Arroyo Basin, western Colorado: U.S. Geological Survey Water-Resources Investigations Report 01–4204, 18 p.

Butler, D.L., Wright, W.G., Stewart, K.C., Osmundson, B.C., Krueger, R.P., and Crabtree, D.W., 1996, Detailed study of selenium and other constituents in water, bottom sediment, soil, alfalfa, and biota associated with irrigation drainage in the Uncompahgre area and in the Grand Valley, west-central Colorado, 1991–1993: U.S. Geological Survey Water-Resources Investigations Report 96–4138, 136 p.

Casciotti, K.L., Sigman, D.M., Galanter Hastings, M., Böhlke, J.K., and Hilkert, A., 2002, Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method: Analytical Chemistry, v. 74, p. 4905–4912.

Combs, G.F., Garbisu, C., Yee, B.C., Yee, A., Carlson, D.E., Smith, N.R., Magyarosy, A.C., Leighton, T., and Buchanan, B.B., 1996, Bioavailability of selenium accumulated by selenite-reducing bacteria: Biological Trace Element Research, v. 52, p. 209–225.

Coplen, T.B., Böhlke, J.K., and Casciotti, K.L., 2004, Using dual-bacterial denitrification to improve delta 15N determinations of nitrates containing mass-independent 17O: Rapid Communications in Mass Spectrometry, v. 18, p. 245–250.

Coplen, T.B., Qi, Haiping, Révész, Kinga, Casciotti, Karen, and Hannon, J.E., 2012, Determination of the δ15N and δ18O of nitrate in water; RSIL lab code 2900, chap. 17 of Stable isotope-ratio methods, sec. C of Révész, Kinga, and Coplen, T.B., eds., Methods of the Reston Stable Isotope Laboratory (slightly revised from version 1.0 released in 2007): U.S. Geological Survey Techniques and Methods, book 10, 35 p., available at http://pubs.usgs.gov/tm/2006/tm10c17/. (Supersedes version 1.0 released in 2007.)

Cowardin, L.M., Carter, V., Golet, F.C., LaRoe, E.T., 1979, Classification of wetlands and deepwater habitats of the United States: U.S. Department of the Interior, Fish and Wildlife Service, version 04DEC1998.

Cunningham, W.L., and Schalk, C.W., comps., 2011, Ground-water technical procedures of the U.S. Geological Survey: U.S. Geological Survey Techniques and Methods 1–A1, 151 p., available at http://pubs.usgs.gov/tm/1a1/.

Daly, Christopher, Halbleib, M., Smith, J.I., Gibson, W.P., Doggett, M.K., Taylor, G.H., Curtis, J., and Pasteris, P.P., 2008, Physiographically sensitive mapping of climatological temperature and precipitation across the conterminous United States: International Journal of Climatology, v. 28, p. 2031–2064.

Dhillon, K.S., and Dhillon, S.K., 1999, Adsorption-desorption reaction of selenium in some soils of India: Geoderma, v. 93, p. 19–31.

Dhillon, S.K., Dhillon, K.S., Kohli, A., and Khera, K.L., 2008, Evaluation of leaching and runoff losses of selenium from seleniferous soils through simulated rainfall: Journal of Plant Nutrition and Soil Science, v. 171, p. 181–192.

Elliott, J.E., Herring, J.R., Ingersoll, G.P., Kosovick, J.J., and Fahy, J., 2007, Rainfall-runoff and erosion data from the Mancos Shale Formation in the Gunnison Gorge National Conservation Area, southwestern Colorado, 2003–2006: U.S. Geological Survey Open-File Report 2007–1002G, 67 p.

Farnsworth, R.K., and Thompson, E.S., 1982, Mean monthly, seasonal, and annual pan evaporation for the United States: National Oceanic and Atmospheric Administration Technical Report NWS 34, 91 p.

Fernandez-Martinez, Alejandro, and Charlet, L., 2009, Selenium environmental cycling and bioavailability—A structural chemist point of view: Reviews of Environmental Science and Bio/Technology, v. 8, p. 81–110.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 54 p.

Fordyce, Fiona, 2007, Selenium geochemistry and health: Ambio, v. 36, p. 94–97.

Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 98–165, 101 p.

Gates, T.K., Cody, B.M., Donnelly, J.P., Herting, A.W., Bailey, R.T., and Price, J.M., 2009, Assessing selenium contamination in the irrigated stream-aquifer system of the Arkansas River, Colorado: Journal of Environmental Quality, v. 38, p. 2344–2356.

Geological Society of America, 1995, Rock color chart with genuine Munsell color chips (8th printing): Boulder, Colo., Munsell Color, 10 p.

Holloway, J.M., and Smith, R.L., 2005, Nitrogen and carbon flow from rock to water—Regulation through soil biogeochemical processes, Mokelumne River watershed, California, and Grand Valley, Colorado: Journal of Geophysical Research, v. 110, F01010, doi: 10.1029/2004JF000124.

Klots, C.E., and Benson, B.B., 1963, Isotope effect in the solution of oxygen and nitrogen in distilled water: Journal of Chemical Physics, v. 38, p. 890-892.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399, 113 p.

Kumar, A.R., and Riyazuddin, P., 2011, Speciation of selenium in groundwater—Seasonal variations and redox transformations: Journal of Hazardous Materials, v. 192, p. 263–269.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1997, Guidelines and standard procedures for studies of ground-water quality—Selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96–4233, 110 p.

Lemly, A.D., 1993, Guidelines for evaluating selenium data from aquatic monitoring and assessment studies: Environmental Monitoring and Assessment, v. 28, p. 83–100.

Mast, M.A., Mills, T.J., Paschke, S.P., Keith, G., and Linard, J.I., 2014, Release and transport of selenium from the Mancos Shale and associated soils in the lower Uncompahgre River Basin, Colorado: Applied Geochemistry, v. 48, p. 16–27.

McMahon, P.B., and Böhlke, J.K., 2006, Regional patterns in the isotopic composition of natural and anthropogenic nitrate in groundwater, High Plains, USA: Environmental Science & Technology, v. 40, p. 2965–2970.

McMahon, P.B., Böhlke, J.K., Kauffman, L.J., Kipp, K.L., Landon, M.K., Crandall, C.A., Burow, K.R., and Brown, C.J., 2008, Source and transport controls on the movement of nitrate to public supply wells in selected principal aquifers of the United States: Water Resources Research, v. 44, doi:10.1029/2007WR006252.

McMahon, P.B., and Chapelle, F.H., 2008, Redox processes and water quality of selected principal aquifer systems: Ground Water, v. 46, p. 259–271.

Moore, J.L., 2011, Characterization of salinity and selenium loading and land-use change in Montrose Arroyo, Western Colorado, from 1992 to 2010: U.S. Geological Survey Scientific Investigations Report 2011–5106, 23 p.

Morrison, S.J., Goodknight, C.S., Tigar, A.D., Bush, R.P., and Gil, A., 2012, Naturally occurring contamination in the Mancos Shale: Environmental Science and Technology, v. 46, p. 1379–1387.

Natural Resources Conservation Service, 2014, Web soil survey: accessed March 24, 2014, at http://websoilsurvey.nrcs.usda.gov/.

Oremland, R.S., Hollibaugh, J.T., Maest, A.S., Presser, T.S., Miller, L.G., and Culbertson, C.W., 1989, Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture—Biogeochemical significance of a novel sulfate-independent respiration: Applied and Environmental Microbiology, v. 55, p. 2333–2343.

Presser, T.S., and Luoma, S.N., 2010, Ecosystem-scale selenium modeling in support of fish and wildlife selenium criteria development for the San Francisco Bay—Delta Estuary, California: U.S. Geological Survey Administrative Report for (2010) and released by the U.S. Environmental Protection Agency (2011), Region 9, San Francisco, Calif., 101 p., and appendixes A–D, accessed June 12, 2012, at http://www.epa.gov/region9/water/ctr.

Presser, T.S., and Ohlendorf, H.M., 1987, Biogeochemical cycling of selenium in the San Joaquin Valley, California, USA: Environmental Management, v. 11, no. 6, p. 805–822.

Rector, C.D., Mustard, E.W., and Windell, J.T., 1979, Lower Gunnison River wetland inventory and evaluation: U.S. Department of Agriculture, Soil Conservation Service, 90 p.

Singh, R.K., Senay, G.B., Velpuri, N.M., Bohms, S., Scott, R.L., and Verdin, J.P., 2014, Actual evapotranspiration (water use) assessment of the Colorado River Basin at the Landsat resolution using the Operational Simplified Surface Energy Balance Model: Remote Sensing, v. 6, p. 233–256.

Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, M., and Böhlke, J.K., 2001, A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater: Analytical Chemistry, v. 73, p. 4145–4153.

Tuttle, M.L.W., Fahy, J.W., Elliott, J.G., Grauch, R.I., and Stillings, L.L., 2014, Contaminants from Cretaceous black shale—I. Natural weathering processes controlling contaminant cycling in Mancos Shale, southwestern United States, with emphasis on salinity and selenium: Applied Geochemistry, http://dx.doi.org/10.1016/j.apgeochem.2013.12.010.

U.S. Geological Survey, 2015a, The Reston Groundwater Dating Laboratory, dissolved gases N2/Ar, sampling: accessed July 21, 2015, at http://water.usgs.gov/lab/dissolved-gas/sampling/.

U.S. Geological Survey, 2015b, Reston Stable Isotope Laboratory, Instructions for collecting samples: accessed July 21, 2015, at http://isotopes.usgs.gov/lab/instructions.html.

U.S. Geological Survey, 1998, National Water Information System (NWIS): U.S. Geological Survey Fact Sheet 027–98, 2 p., accessed February 21, 2013, at http://pubs.usgs.gov/fs/FS-027-98/index.html.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, available online at http://pubs.water.usgs.gov/twri9A.

Weiss, R.F., 1970, The solubility of nitrogen, oxygen, and argon in water and seawater: Deep-Sea Research, v. 17, p. 721–735.

Wentworth, C.K., 1922, A scale of grade and class terms for clastic sediments: Journal of Geology, v. 30, p. 377–392.

White, A.F., and Benson, S.M., 1991, Groundwater contamination at the Kesterson Reservoir, California 1. Hydrogeologic setting and conservative solute transport: Water Resources Research, v. 27, no. 6, p. 1071–1084.

Zhang, Yiqiang, and Moore, J.N., 1996, Selenium fractionation and speciation in a wetland system: Environmental Science and Technology, v. 30, p. 2613–2619.

Appendixes

Appendix 1.   Water-quality data (raw) collected between September 1978 and October 1983 at Bureau of Reclamation observation well E263133, Montrose County, Colorado.

[Data from John Sottilaire, Bureau of Reclamation, written commun., March 29, 2012; µmhos/cm, micromhos per centimeter; mg/L, milligrams per liter; --, no data; DRY, no water in observation well at time of site visit]

Date	Water level in feet below ground surface	pH	Temperature, degrees Celsius	Electrical conductivity, µmhos/cm	Total dissolved solids, mg/L	Calcium, mg/L	Magnesium, mg/L	Sodium, mg/L	Potassium, mg/L	Bicarbonate, mg/L	Chloride, mg/L	Sulfate, mg/L
9/20/1978	19.9	7.9	11.7	16,559	16,900	517	331	4,280	46.9	312	668	9,990
5/2/1979	21.4	7.5	11.7	23,538	23,250	--	--	--	--	--	--	--
6/21/1979	22.1	7.5	12.2	28,115	27,500	441	626	7,360	68.4	519	1,030	17,200
8/7/1979	22.8	7.5	13.9	30,671	30,000	441	669	8,120	78.2	549	1,130	17,100
9/25/1979	23.2	7.7	12.2	30,012	32,200	451	754	8,620	58.6	604	1,150	18,700
11/14/1979	23.9	7.6	10.5	31,490	34,500	451	796	9,010	46.9	625	1,230	19,600
1/21/1980	24.2	7.5	11.1	31,328	36,600	451	882	9,310	68.4	714	1,350	21,200
3/10/1980	24.8	--	--	--	--	--	--	--	--	--	--	--
5/14/1980	24.6	7.5	12.2	33,739	42,173	--	--	--	--	--	--	--
7/16/1980	24.9	--	--	--	--	--	--	--	--	--	--	--
9/15/1980	24.9	7.8	12.2	28,571	39,830	--	--	--	--	--	--	--
11/17/1980	24.6	7.6	10.0	37,500	41,900	481	1,110	11,100	78.2	785	1,600	24,400
1/22/1981	25.2	--	--	--	--	--	--	--	--	--	--	--
3/23/1981	25.1	7.7	13.3	43,134	44,130	--	--	--	--	--	--	--
5/15/1981	25.1	7.7	12.2	38,340	39,106	--	--	--	--	--	--	--
7/23/1981	21.7	7.9	15.5	22,228	23,330	491	547	6,070	39.1	530	840	13,600
9/28/1981	23	--	--	--	--	--	--	--	--	--	--	--
1/22/1982	23.3	7.8	9.4	17,085	21,356	--	--	--	--	--	--	--
3/10/1982	23.9	--	--	--	--	--	--	--	--	--	--	--
5/17/1982	23.6	8.1	13.3	41,407	36,865	--	--	--	--	--	--	--
7/22/1982	DRY	--	--	--	--	--	--	--	--	--	--	--
11/17/1982	DRY	--	--	--	--	--	--	--	--	--	--	--
1/21/1983	23.9	--	--	--	--	--	--	--	--	--	--	--
3/31/1983	DRY	--	--	--	--	--	--	--	--	--	--	--
5/20/1983	DRY	--	--	--	--	--	--	--	--	--	--	--
7/12/1983	23.7	8	12.8	31,953	43,568	--	--	--	--	--	--	--
10/18/1983	DRY	--	--	--	--	--	--	--	--	--	--	--

Appendix 2

Lithologic Logs

Wells W-N1 and W-N2
Date wells completed: 11/13/2012
Log prepared by L.R. Arnold

[Depth intervals in feet below land surface; mm, millimeters; ft, feet; HCl, hydrochloric acid; 1 ft=30.48 centimeters]

Depth	Sample type	Description[1]
0–3	surface and core	Deeply weathered Mancos Shale—Clay, olive gray (5Y4/1), little very fine sand and trace fine-medium sand, soft–firm, wet 0–2 ft, moist 2–3 ft, some small gypsum crystals 0–0.5 ft, some organic material 0–1.5 ft, reacts to HCl.
12–14.8	core	Weathered Mancos Shale—Clay, olive gray (5Y3/2) to dark gray (N3), trace very fine sand, nonfissile, hard, damp, water-bearing fractures below about 10 ft, small gypsum crystals and iron staining, reacts to HCl, drilling refusal at 14.8 ft.

[1]Grain size based on the Wentworth classification system (Wentworth, 1922). Proportions defined using the following terms: "trace" (0–10 percent), "little" (10–20 percent), "some" (20–35 percent), and "and" (35–50 percent). Color codes refer to the Munsell color system (Geological Society of America, 1995).

Wells W-M1 and W-M2
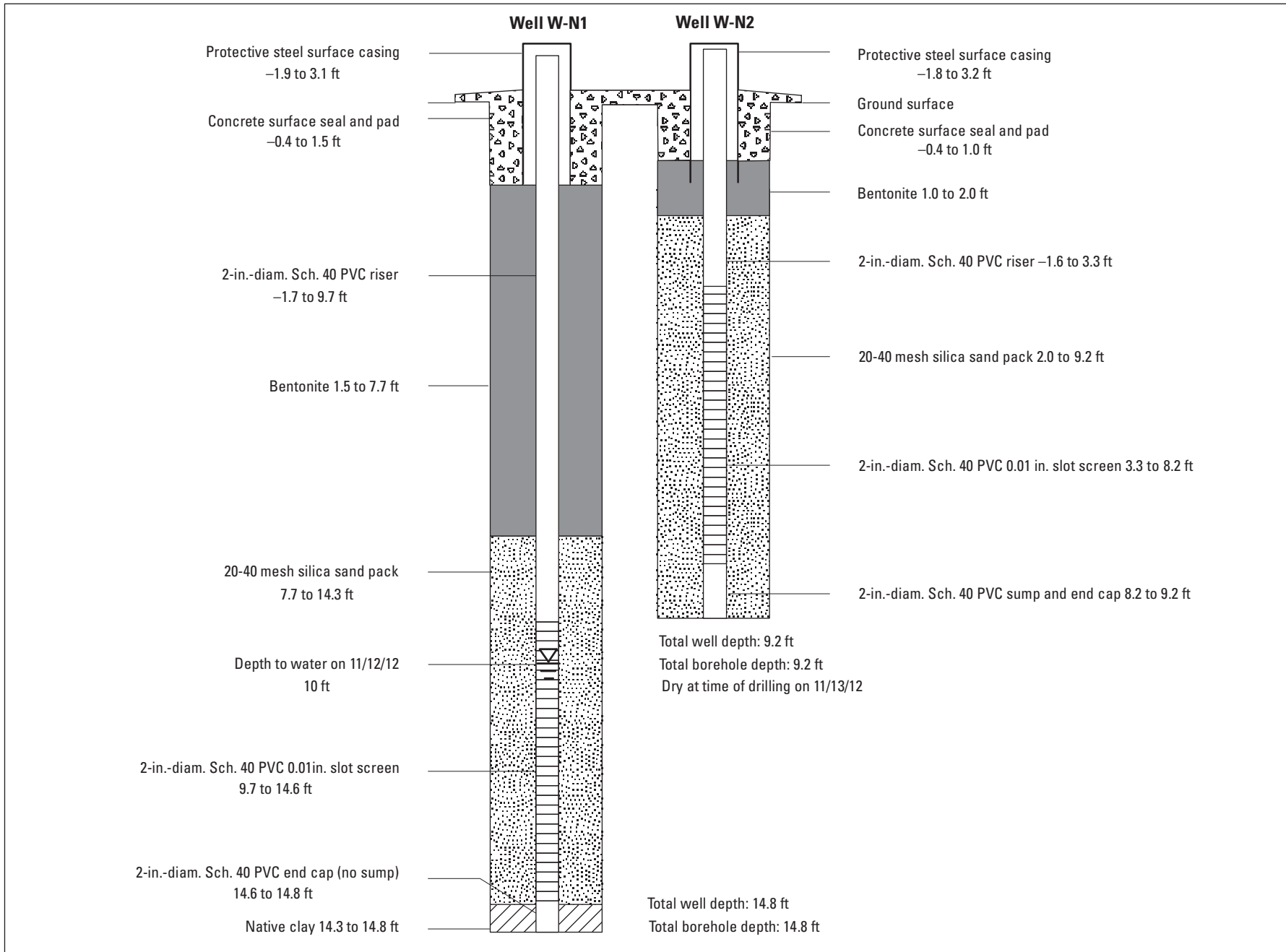### Well W-M1 completed 11/08/2012
Well W-M2 completed 11/9/2012
Log prepared by L.R. Arnold

[Depth intervals in feet below land surface; mm, millimeters; ft, feet; HCl, hydrochloric acid; 1 ft=30.48 centimeters]

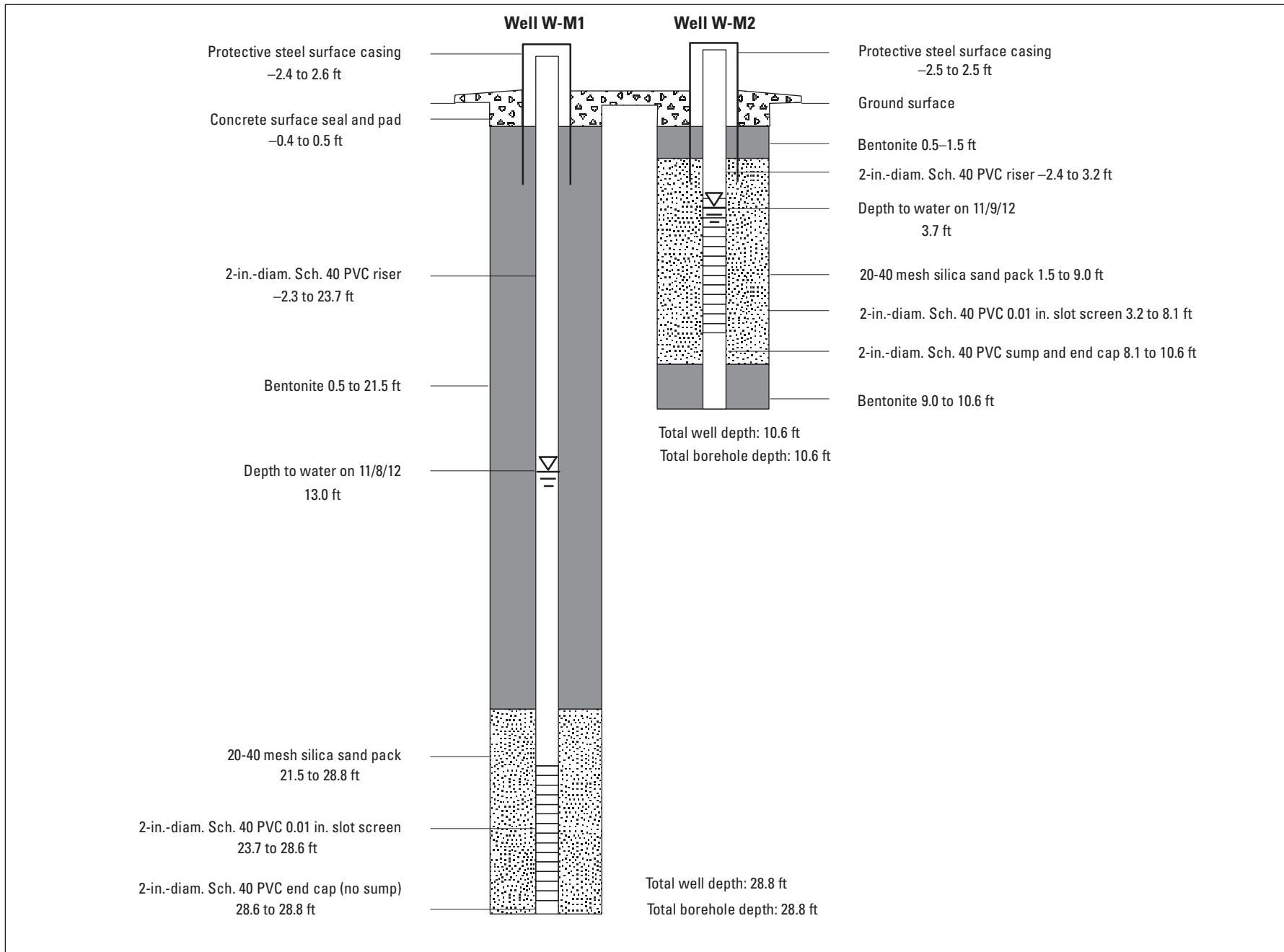| Depth	Sample type	Description[1]
0–12	surface and core	Deeply weathered Mancos Shale—Clay, dark yellowish brown (10YR4/2), little very fine sand, soft, wet-saturated, trace iron staining, some organic material from 0 to 1 ft, reacts to HCl.
12–28.8	core	Weathered Mancos Shale—Clay, light olive gray (5Y5/2) to olive gray (5Y3/2), becoming more dark gray (N3) below about 18 ft, some very fine sand, lenses of trace fine-medium sand, nonfissile, stiff–hard, damp–moist, water-bearing fractures 24.9–28.8 ft, trace calcium carbonate mottling, small gypsum crystals, and iron staining, reacts to HCl, drilling refusal at 28.8 ft.

[1]Grain size based on the Wentworth classification system (Wentworth, 1922). Proportions defined using the following terms: "trace" (0–10 percent), "little" (10–20 percent), "some" (20–35 percent), and "and" (35–50 percent). Color codes refer to the Munsell color system (Geological Society of America, 1995).

Appendix 3

Well W-N1

Well W-N2

Protective steel surface casing
−1.9 to 3.1 ft

Concrete surface seal and pad
−0.4 to 1.5 ft

2-in.-diam. Sch. 40 PVC riser
−1.7 to 9.7 ft

Bentonite 1.5 to 7.7 ft

20-40 mesh silica sand pack
7.7 to 14.3 ft

Depth to water on 11/12/12
10 ft

2-in.-diam. Sch. 40 PVC 0.01in. slot screen
9.7 to 14.6 ft

2-in.-diam. Sch. 40 PVC end cap (no sump)
14.6 to 14.8 ft

Native clay 14.3 to 14.8 ft

Protective steel surface casing
−1.8 to 3.2 ft

Ground surface

Concrete surface seal and pad
−0.4 to 1.0 ft

Bentonite 1.0 to 2.0 ft

2-in.-diam. Sch. 40 PVC riser −1.6 to 3.3 ft

20-40 mesh silica sand pack 2.0 to 9.2 ft

2-in.-diam. Sch. 40 PVC 0.01 in. slot screen 3.3 to 8.2 ft

2-in.-diam. Sch. 40 PVC sump and end cap 8.2 to 9.2 ft

Total well depth: 9.2 ft
Total borehole depth: 9.2 ft
Dry at time of drilling on 11/13/12

Total well depth: 14.8 ft
Total borehole depth: 14.8 ft

Well W-M1

Well W-M2

Protective steel surface casing
−2.4 to 2.6 ft

Protective steel surface casing
−2.5 to 2.5 ft

Concrete surface seal and pad
−0.4 to 0.5 ft

Ground surface

Bentonite 0.5–1.5 ft

2-in.-diam. Sch. 40 PVC riser −2.4 to 3.2 ft

Depth to water on 11/9/12
3.7 ft

2-in.-diam. Sch. 40 PVC riser
−2.3 to 23.7 ft

20-40 mesh silica sand pack 1.5 to 9.0 ft

2-in.-diam. Sch. 40 PVC 0.01 in. slot screen 3.2 to 8.1 ft

2-in.-diam. Sch. 40 PVC sump and end cap 8.1 to 10.6 ft

Bentonite 0.5 to 21.5 ft

Bentonite 9.0 to 10.6 ft

Total well depth: 10.6 ft
Total borehole depth: 10.6 ft

Depth to water on 11/8/12
13.0 ft

20-40 mesh silica sand pack
21.5 to 28.8 ft

2-in.-diam. Sch. 40 PVC 0.01 in. slot screen
23.7 to 28.6 ft

2-in.-diam. Sch. 40 PVC end cap (no sump)
28.6 to 28.8 ft

Total well depth: 28.8 ft
Total borehole depth: 28.8 ft

Appendix 4   Methods for Calculating Initial Nitrate Concentration, Initial Nitrogen Isotopic Composition of Nitrate, and Ratio of Measured to Initial Nitrate in W-M1

Denitrification is a microbially mediated process that reduces nitrate to nitrogen gas (N_2) in anoxic environments. One way to evaluate whether denitrification has occurred in an aquifer is to calculate the amount of N_2 in groundwater from denitrification, referred to here as "excess N_2." The concentration of excess N_2 in samples from W-M1 was estimated by assuming (1) all samples were recharged with the same amount of excess air but with varying recharge temperatures (Scenario 1 in table 4) and (2) all samples were recharged at the same temperature but with varying amounts of excess air (Scenario 2 in table 4) (Böhlke and others, 2002). Excess N_2, recharge temperatures, and excess air were then calculated using the measured N_2 and argon concentrations (Böhlke and Denver, 1995). These assumptions may not be entirely accurate, but the difference in estimated excess N_2 concentrations between assumptions 1 and 2 was small (about 55 to 60 micromoles per liter [µmol/L]) compared to the concentrations of nitrate (25,993 µmol/L) and total N_2 (720 to 772 µmol/L) in the samples (table 4). The concentration and isotopic composition of excess N_2 in the samples were calculated using equations 1 through 3 (Böhlke and others, 2002).

$$\text{excess N2} = [N_2 \text{ total}] - [N_2 \text{ air saturation}] - [N2 \text{ excess air}] \tag{1}$$

$$\text{N2 excess air} = [N_2/Ar]\text{air} \times \{[\text{Argon total}] - [\text{Argon air saturation}]\} \tag{2}$$

$$\delta15N \text{ (excess N2)} = \{\delta15N(N2 \text{ total}) \times [N2 \text{ total}] - \delta15N(N2 \text{ air saturation}) \times [N2 \text{ air saturation}]\} / [N2 \text{ excess air}] \tag{3}$$

[N_2 total] and [Argon total] are the measured concentrations of N_2 and argon in the samples, [N_2 air saturation] and [Argon air saturation] are the concentrations of N_2 and argon in the samples from air-water equilibration at 4.9 to 9.5 °C and 5,326 ft elevation (table 4) (Weiss, 1970), and [N_2 excess air] is the concentration of N_2 in the samples from unfractionated excess (trapped) air. [N_2/Ar]$_{air}$ is the molar ratio of N_2 and argon in air (83.6) (Böhlke and others, 2002). $\delta^{15}N(N_2$ total) is the measured isotopic composition of the total N_2 in the sample and $\delta^{15}N(N_2$ air saturation) is the isotopic composition of N_2 in the sample from air-water equilibration (0.76 to 0.79 per mil) (Klots and Benson, 1963).

The initial concentrations and isotopic compositions of nitrate in W-M1, corrected for denitrification effects, were estimated using equations 4 and 5 (Böhlke and others, 2002).

$$[\text{nitrate initial}] = [\text{nitrate measured}] + 2 \times [\text{excess } N_2] \tag{4}$$

$$\delta^{15}N(\text{nitrate initial}) = \{\delta^{15}N(\text{nitrate measured}) \times [\text{nitrate measured}] + 2 \times \delta^{15}N(\text{excess } N_2) \times [\text{excess } N_2]\} / [\text{nitrate initial}] \tag{5}$$

[nitrate initial] and [nitrate measured] are the initial and measured concentrations of nitrate in the sample. $\delta^{15}N$(nitrate initial) and $\delta^{15}N$ (nitrate measured) are the isotopic compositions of the initial and measured nitrate.

The ratio of measured to initial nitrate in the sample is given by equation 6.

$$\text{Ratio} = [\text{nitrate measured}]/[\text{nitrate initial}] \tag{6}$$

USGS