Prepared in cooperation with Upper Black Squirrel Creek Ground Water Management District

Characterization of and Temporal Changes in Groundwater Quality of the Upper Black Squirrel Creek Basin, El Paso County, Colorado, 2018–20

Scientific Investigations Report 2022–5061

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

Cover. Water-quality sampling from a monitoring well in the Upper Black Squirrel Creek Basin, Colorado.

Characterization of and Temporal Changes in Groundwater Quality of the Upper Black Squirrel Creek Basin, El Paso County, Colorado, 2018–20

By Zachary D. Kisfalusi, Nancy J. Bauch, and Carleton R. Bern

Prepared in cooperation with Upper Black Squirrel Creek Ground Water
Management District

Scientific Investigations Report 2022–5061

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

U.S. Geological Survey, Reston, Virginia: 2022

Suggested citation:
Kisfalusi, Z.D., Bauch, N.J., and Bern, C.R., 2022, Characterization of and temporal changes in groundwater quality of the Upper Black Squirrel Creek Basin, El Paso County, Colorado, 2018–20: U.S. Geological Survey Scientific Investigations Report 2022–5061, 43 p., https://doi.org/10.3133/sir20225061.

Associated data for this publication:
U.S. Geological Survey [USGS], 2021, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed March 10, 2021, at https://doi.org/10.5066/F7P55KJN.

ISSN 2328-031X (print)
ISSN 2328-0328 (online)

ISBN 978-1-4113-4474-7

Acknowledgments

Thank you to Upper Black Squirrel Creek Ground Water Management District, El Paso County Public Health, and all other collaborating parties that allowed for this project to take place. The study benefited from the many landowners who permitted the use of their wells for collection of groundwater-quality samples. Thank you to Evan Gohring and Elsie McBride for their assistance in sampling many of the wells throughout the several years of data collection. Thank you to Suzanne Paschke for establishing the sampling network and organizing this project with the cooperator. Thank you to Laura Bexfield and Connor Newman for their thorough reviews.

Contents

Figures

Tables

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km^2)

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

$$°F = (1.8 \times °C) + 32.$$

Datum

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

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

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

Supplemental Information

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

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

Results for measurements of stable isotopes of an element (with symbol E) in water, solids, and dissolved constituents commonly are expressed as the relative difference in the ratio of the number of the less abundant isotope (iE) to the number of the more abundant isotope of a sample with respect to a measurement standard in per mil (‰).

Abbreviations and Acronyms

$\delta^{15}N$	ratio of the two stable isotopes of nitrogen, nitrogen-15 and nitrogen-14
$\delta^{18}O$	ratio of the two stable isotopes of oxygen, oxygen-18 and oxygen-16
δD	ratio of the two stable isotopes of hydrogen, deuterium (hydrogen-2) and hydrogen-1
EPA	U.S. Environmental Protection Agency
$<$	less than
$\leq$	less than or equal to
in.	inch
LSD	Land Surface Datum
MCL	maximum contaminant level
meq/L	milliequivalents per liter
µg/L	micrograms per liter
µm	micrometers
µS/cm	microsiemens per centimeter
mg/L	milligrams per liter
NFM	National Field Manual
NTU	nephelometric turbidity units
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OIPC	Online Isotope Precipitation Calculator
‰	per mil
RPD	relative percent difference
SMCL	secondary maximum contaminant level
UBSB	Upper Black Squirrel Creek Basin
UBSCDGWB	Upper Black Squirrel Creek Designated Ground Water Basin
USGS	U.S. Geological Survey
WWTP	wastewater treatment plant

Characterization of and Temporal Changes in Groundwater Quality of the Upper Black Squirrel Creek Basin, El Paso County, Colorado, 2018–20

By Zachary D. Kisfalusi, Nancy J. Bauch, and Carleton R. Bern

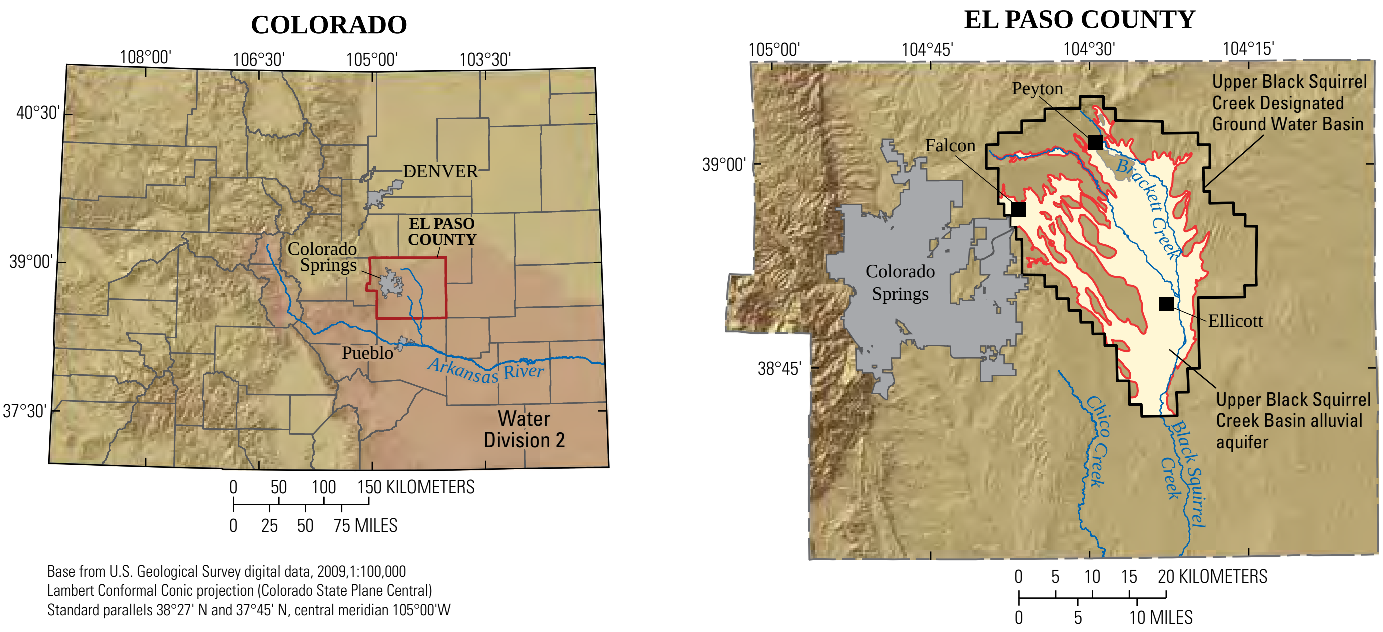
Abstract

In 2018–20, the U.S. Geological Survey, in cooperation with Upper Black Squirrel Creek Ground Water Management District, sampled 48 wells for Phase III of a multiphase plan investigating groundwater quality in the alluvial aquifer of the Upper Black Squirrel Creek Basin (UBSB), El Paso County, Colorado. Results for samples collected from October to December each year were used to assess spatial and temporal changes in groundwater quality and to differentiate sources of nitrate. Groundwater was predominantly classified as mixed-cation and mixed-anion water type in the aquifer, with variable chemistry along the periphery. Concentrations of constituents in groundwater were generally less than regulatory standards, except for nitrate in four wells. Isotopes of nitrogen and oxygen in nitrate identified four different potential sources or processes affecting nitrate in the alluvial aquifer: naturally occurring nitrate from soils, nitrate from animal and (or) human waste, and an unknown source, along with evidence of denitrification. Pharmaceutical compounds and personal-care products were detected in seven wells, with three wells having multiple detections. Stable isotopes of water indicated variability in seasonality of recharge throughout the UBSB alluvial aquifer. Nitrate concentrations from the 1984 study and the 1996 study were compared to the more recent concentrations in the 2013 study and the 2018–20 study. The northern one-third of the UBSB alluvial aquifer had a statistically significant increase in nitrate concentration from the 2013 study to the 2018–20 study, but no change was shown from the 1984 study to the 1996 study. The opposite was found true for the southern two-thirds of the UBSB alluvial aquifer with no statistically significant difference in nitrate concentration from the 2013 study to the 2018–20 study. Analysis of temporal changes indicated an increase in median and maximum nitrate concentrations from the 2013 study to the 2018–20 study throughout the UBSB alluvial aquifer. Continued sampling of wells in the UBSB would be beneficial to better determine temporal changes in groundwater quality, characterize human effects on water quality, and understand characteristics of the alluvial aquifer pertaining to sustainability of the resource.

Introduction

Human activities related to agriculture and urbanization have a continued and growing effect on the groundwater quality throughout the United States (DeSimone and others, 2015). Effects of human activities on groundwater quality are of particular concern for alluvial aquifers, where proximity to the land surface, shallow depth to the groundwater, and unconfined conditions create a favorable environment for chemicals to migrate to the water table (Winter and others, 1998). Nutrients in drinking water, in particular nitrate, are a major concern in both agricultural and urbanized areas. Excess nitrate concentrations can be harmful to human health, particularly that of infants (Brendle, 1997). Human sources of nitrate to groundwater include long-term agricultural land use (fertilizer application), septic system use in rural residential areas, animal feedlots, or wastewater (Kendall, 1998; Gurdak and others, 2009). Nitrate contamination may persist for decades in groundwater and can travel from its source for miles through an aquifer (LeBlanc, 2006; Topper and Horn, 2011). In Colorado, one area with several potential sources of nitrate to groundwater and associated concern for groundwater quality is the Upper Black Squirrel Creek Designated Ground Water Basin (UBSCDGWB), located about 15 miles east of Colorado Springs in El Paso County, Colorado (fig. 1). A designated groundwater basin is identified by the state of Colorado as an area in the eastern plains of Colorado with little surface water where users rely primarily on groundwater as their source of water supply (Upper Black Squirrel Creek Ground Water Management District, 2021). High concentrations of nitrate in the alluvial aquifer of the Upper Black Squirrel Creek Basin (UBSB) and increased urbanization and development within the basin have led to a greater need to understand the changes to groundwater quality in the alluvial aquifer through time (Wellman and Rupert, 2016).

The alluvial aquifer of the UBSB supplies most of the water for irrigation and domestic use in the basin, and, since 1964, supplies water for export to the Colorado Springs area (Buckles and Watts, 1988; Wellman and Rupert, 2016).



Base from U.S. Geological Survey digital data, 2009,1:100,000
Lambert Conformal Conic projection (Colorado State Plane Central)
Standard parallels 38°27' N and 37°45' N, central meridian 105°00'W

Figure 1. Site location of alluvial aquifer in the Upper Black Squirrel Creek Designated Ground Water Basin in Colorado Division of Water Resources Water Division 2 east of Colorado Springs, El Paso County, Colorado, 2018–20 (modified from Wellman and Rupert, 2016).

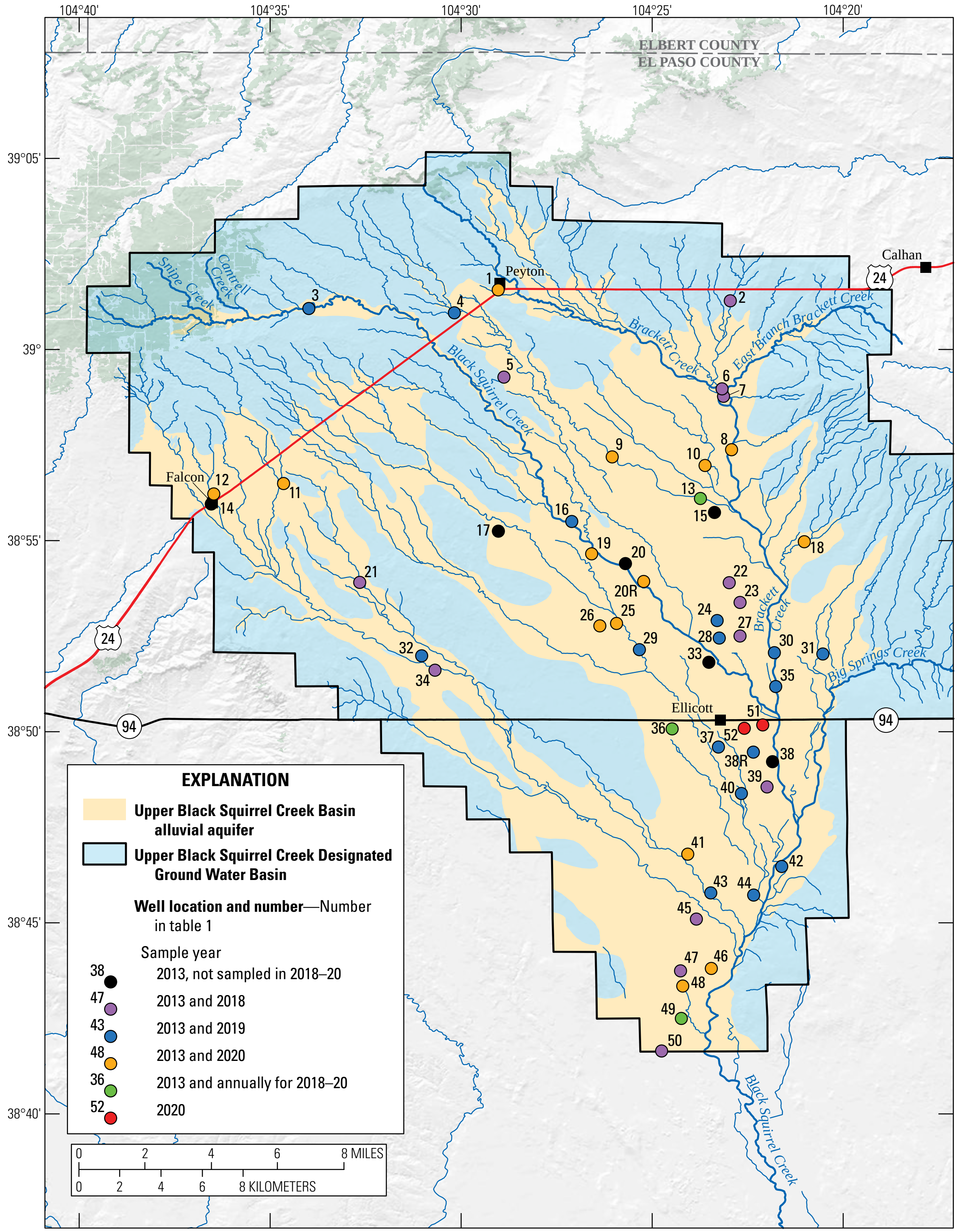
Water availability for irrigation and livestock is an important economic driver in the UBSCDGWB. Agriculture in this area requires substantial water and has enabled sod growing and grazing operations (Wellman and Rupert, 2016). El Paso County and the UBSCDGWB experienced substantial (10 to 20 percent) residential growth from 2010 to 2020 (U.S. Census Bureau, 2021), creating a greater need for a detailed understanding of groundwater availability and quality in the area. Additionally, information on changes in nutrient concentrations through time, and sources of nitrate to the groundwater in the basin are important to help guide county managers as they make decisions affecting land use related to increased urbanization in the UBSCDGWB.

Previous studies have investigated ways to increase groundwater availability and assess groundwater quality in the UBSCDGWB. Colorado Water Conservation Board (2007) identified potential alluvial storage areas throughout Colorado including the UBSCDGWB. A study by Topper (2008) investigated the potential to use alluvial storage as a means for future storage and augmentation of existing groundwater resources in the UBSCDGWB. Wellman and Rupert (2016) summarized a study completed in 2013 that assessed groundwater quality and groundwater age in the basin with an emphasis on characterizing nitrate in the groundwater.

During 2018–20, the U.S. Geological Survey (USGS), in cooperation with the Upper Black Squirrel Creek Ground Water Management District, sampled 48 wells for Phase III of a multiphase plan investigating the groundwater quality in the alluvial aquifer of the UBSB (fig. 2). The main objectives of the study were to assess potential changes in groundwater quality since 2013 and to better understand sources of nitrate and water in the UBSB alluvial aquifer. An additional objective was to compare temporal changes in groundwater-quality results from Phases II and III, in 2013 (Wellman and Rupert, 2016) and 2018–20, respectively, to results from studies in 1984 (Buckles and Watts, 1988) and 1996 (Brendle, 1997).

Multiphase Plan

The El Paso County Board of County Commissioners has been investigating groundwater quality in the UBSB alluvial aquifer under a multiphase plan. Phase I of the study, completed by the Colorado Geological Survey in April 2011, included a compilation and summary of historical water-quality data collected prior to 2009 (Topper and Horn, 2011). Topper and Horn (2011) found 141 detections of nitrate in 148 samples collected from 72 wells between 1971 and 2009. The mean concentration was 6.8 milligrams per liter (mg/L), and 9 of the 141 detections exceeded the primary drinking water standard maximum contaminant level (MCL) of 10 mg/L for nitrate (U.S. Environmental Protection Agency [EPA], 2020a). The majority (50 wells) of nitrate concentrations ranged between 2.5 and 7.5 mg/L. Based on these data, Topper and Horn (2011) concluded nitrate values greater than 5.0 mg/L were common in the UBSCDGWB and suggested the alluvial aquifer water quality has been affected by nutrient loading. Analysis of changes in nitrate concentrations through time was limited because only four wells from the dataset were sampled on more than three occasions, yet the conclusions from Topper and Horn (2011) helped guide future sampling in Phase II of the study.



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 2. Locations of wells sampled within the Upper Black Squirrel Creek Designated Ground Water Basin, El Paso, County, Colorado, 2018–20.

Phase II of the study was conducted by the USGS in 2013, in cooperation with the Cherokee Metropolitan District, El Paso County, Meridian Service Metropolitan District, Mountain View Electric Association, Upper Black Squirrel Creek Ground Water Management District, Woodmen Hills Metropolitan District, Colorado State Land Board, Colorado Water Conservation Board, and the stakeholders represented in the Groundwater Quality Study Committee of El Paso County. Groundwater quality and age were assessed, with an emphasis on characterizing groundwater nitrate concentrations. Historical data were examined, and 50 randomly selected alluvial wells were sampled (Wellman and Rupert, 2016). Statistical analysis demonstrated nitrate concentrations were correlated to land use—both agriculture and, in residential areas, septic use—and the study concluded future development of agriculture and (or) septic use had the greatest potential to affect nitrate levels on a per area basis (Wellman and Rupert, 2016).

Purpose and Scope

The primary purpose of this report is to describe groundwater quality in 48 wells sampled in the UBSB alluvial aquifer in 2018–20 and to discuss changes in groundwater quality since 2013. Table 1 and figure 2 display wells sampled in Phase II to show consistency between sampling efforts in 2013 and those conducted in Phase III. A secondary purpose of this report is to expand the discussion of temporal changes in groundwater quality to include data collected in 1984 (Buckles and Watts, 1988) and 1996 (Brendle, 1997). Field properties of groundwater, measurements of water temperature, pH, specific conductance, dissolved oxygen, alkalinity, and turbidity measured in 2018–20, are described, as are analytical results for major ions, the positively and negatively charged ions present in natural waters at levels in the parts per million and higher range (for example, chloride, bromide, and sulfate anions). Major ions are the constituents that contribute to the amount of total and dissolved solids and specific conductance in waters. Nutrients (species of nitrogen and phosphorus found in natural waters) and nitrate isotopes, pharmaceutical compounds and personal-care products, selenium and uranium, and water isotopes are also analyzed. Temporal changes in groundwater quality using paired t-tests from earlier studies, the 2013 study, and the 2018–20 study are discussed.

Description of Study Area

The principal land use in the UBSCDGWB, El Paso County, Colorado, is grazing (Wellman and Rupert, 2016) and depicted as herbaceous and shrub and scrub in figure 3. Cultivated cropland, historically for field corn and currently (2022) turf grass for sod production (hay and pasture), is also prevalent along the main corridor in a north−south direction in the central and eastern parts of the UBSB (fig. 3). Clusters of residential land parcels, represented by different levels of developed intensity, are located in the northwest part of the UBSB (fig. 3). Increased urbanization occurred in the UBSB since the 1990s (Watts, 1995) with growth focused around Falcon, Colo. Impervious surfaces from the National Land Cover Dataset, based on satellite imagery, increased in this area as well (Homer and others, 2020). U.S. Census Bureau (2021) data estimate a population growth of 15 percent in this area since 2010. The majority of the basin and the area underlain by the alluvial aquifer has not had any substantial changes in land use or increase in impervious surfaces from 2011 to 2016, except around the areas of growth previously mentioned (Homer and others, 2020).

The climate of the UBSB is semiarid and mean annual precipitation ranges from 15 to 22 inches (in.) per year from 1981 to 2010 (Wellman and Rupert, 2016). Climate data were extracted from the Climate Engine online tool (Huntington and others, 2017) for three locations in the study area: Peyton, Falcon, and Ellicott, Colo. (fig. 1). Mean annual precipitation for these three locations is 19, 19, and 16 in., respectively, from 1979 to 2021, reflecting orographic effects on precipitation, which generally decreases in a northwest to southeast direction. Infiltration of precipitation and surface water is the main source of groundwater recharge, estimated at 0−8 in. per year, representing about 93 percent of total recharge to the alluvial aquifer, although upwelling from bedrock is about 7 percent of total recharge (Watts, 1995). Mean annual potential evaporation estimates range from 50 to 70 in. (Hansen and others, 1978; Watts, 1995).

All streams in the UBSB are ephemeral, and episodic streamflow occurs during periods of spring snowmelt runoff and major storms (Buckles and Watts, 1988). The streambeds have sandy bottoms, and runoff generally infiltrates the streambeds within the UBSB instead of remaining as surface-water flow (Watts, 1995). Segments of the streams were historically intermittent—with flow being somewhat persistent rather than ephemeral—prior to large groundwater-level declines caused by increases in groundwater pumpage beginning in the 1950s and 1960s (Buckles and Watts, 1988). With the drop in the water table, there is no perennial surface-water flow within the UBSB. Black Squirrel Creek is a tributary of Chico Creek before the latter flows south until its mouth at the Arkansas River east of Pueblo, Colo. (fig. 1).

The alluvial aquifer underlying about 90 square miles of the UBSCDGWB is composed of permeable unconsolidated deposits of floodplain alluvium, Piney Creek Alluvium, Rocky Flats Alluvium, Slocum Alluvium, and aeolian sediment of Quaternary age (Watts, 1995; Wellman and Rupert, 2016) and is the primary source of groundwater in the area (Watts, 1995). The Quaternary deposits were mapped by Tweto (1979; fig. 4) and updated by Topper (2008).

Prior to development and use of irrigation wells in the UBSB during the 1950s and 1960s, the saturated thickness of the alluvium was more than 98 feet (ft) (McGovern and Jenkins, 1966). Since 1964, the alluvial aquifer has supplied

Table 1. Well identification and site information, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2013 (Wellman and Rupert, 2016) and 2018–20 (current study).

[ID, identification; USGS, U.S. Geological Survey; NAD 83, North American Datum of 1983; ft, feet; LSD, land surface datum relative to North American Vertical Datum of 1988; >, greater than; R, replacement]

Well ID	USGS station ID	Latitude, in decimal degrees (NAD 83)	Longitude, in decimal degrees (NAD 83)	Well depth, in ft from LSD	Land use (Wellman and Rupert, 2016)
[1]1	390134104290201	39.026672	−104.482643	25	County land
[2]2	390116104225701	39.021250	−104.382561	179	Residential 2.5−5 acres
[3]3	390104104335901	39.017889	−104.566450	25	County land
[3]4	390058104301101	39.015904	−104.497096	31	County land
[2]5	385917104285301	38.987890	−104.481437	95	Grazing land
[2]6	385858104231001	38.982928	−104.386154	118	Grazing land
[2]7	385848104230801	38.979600	−104.385519	113	Grazing land
[1]8	385727104225101	38.956494	−104.381544	57	Irrigated land
[1]9	385712104260201	38.953180	−104.434084	36	Grazing land
[1]10	385658104233501	38.949436	−104.393578	96	Residential >5 acres
[1]11	385630104343901	38.941561	−104.577481	25	County land
[1]12	385613104362801	38.937031	−104.607931	25	County land
[4]13	385608104233702	38.935532	−104.394909	159	Grazing land
[5]14	385558104363201	38.932639	−104.609019	50	Commercial
[5]15	385546104232201	38.928956	−104.389444	171	Residential >5 acres
[3]16	385530104270601	38.925011	−104.451731	35	Grazing land
[5]17	385515104290201	38.920789	−104.483750	90	Grazing land
[1]18	385458104210101	38.916344	−104.350042	71	Grazing land
[1]19	385439104263501	38.910911	−104.443050	40	Grazing land
[5]20	385424104254001	38.906661	−104.428300	90	Grazing land
[6]20R	385356104251301	38.898855	−104.420346	140	Residential >5 acres
[2]21	385354104323901	38.898441	−104.544215	84	Irrigated land
[2]22	385354104225701	38.897980	−104.385395	196	Grazing land
[2]23	385323104224001	38.888985	−104.378439	176	Grazing land
[3]24	385254104231801	38.881819	−104.388300	107	Residential >5 acres
[1]25	385250104255401	38.881214	−104.432594	110	Grazing land
[1]26	385246104262201	38.879500	−104.439481	110	Grazing land
[2]27	385229104223601	38.874990	−104.377655	170	Grazing land
[3]28	385227104231402	38.874181	−104.387369	69	Grazing land
[3]29	385209104252001	38.869971	−104.420883	111	Residential >5 acres
[3]30	385204104214801	38.867811	−104.363331	100	Grazing land
[3]31	385202104203201	38.867239	−104.342181	42	Grazing land
[3]32	385159104310201	38.866439	−104.517219	95	Residential 2.5−5 acres
[5]33	385148104233101	38.863622	−104.391911	120	Grazing land
[2]34	385136104303801	38.860165	−104.511404	96	Grazing land
[3]35	385111104214401	38.852696	−104.361619	128	Grazing land
[4]36	385004104242901	38.837263	−104.406490	200	Grazing land
[2]37	384936104231401	38.826691	−104.387272	183	County land
[5]38	384913104214901	38.820273	−104.364131	120	Irrigated land
[6]38R	384928104221001	38.824444	−104.372500	120	Residential >5 acres

Table 1. Well identification and site information, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2013 (Wellman and Rupert, 2016) and 2018–20 (current study).—Continued

[ID, identification; USGS, U.S. Geological Survey; NAD 83, North American Datum of 1983; ft, feet; LSD, land surface datum relative to North American Vertical Datum of 1988; >, greater than; R, replacement]

Well ID	USGS station ID	Latitude, in decimal degrees (NAD 83)	Longitude, in decimal degrees (NAD 83)	Well depth, in ft from LSD	Land use (Wellman and Rupert, 2016)
[2]39	384834104215704	38.809391	−104.366627	120	Grazing land
[3]40	384823104224001	38.806400	−104.377719	155	Residential 2.5−5 acres
[1]41	384648104240401	38.779950	−104.401119	215	Residential > 5 acres
[3]42	384628104213601	38.774581	−104.360120	93	Grazing land
[3]43	384547104232601	38.762725	−104.390861	161	Grazing land
[3]44	384544104222001	38.762110	−104.372369	77	Grazing land
[2]45	384506104235001	38.751639	−104.397361	163	Grazing land
[1]46	384348104232201	38.730111	−104.390833	60	County land
[2]47	384345104241401	37.729165	−104.403716	152	Irrigated land
[1]48	384333104241301	38.722439	−104.403311	146	Irrigated land
[4]49	384230104241401	38.708311	−104.403919	113	Grazing land
[2]50	384139104244501	38.694237	−104.412554	129	Grazing land
[6]51	385011104220601	38.836308	−104.368406	130	Irrigated land
[6]52	385005104223501	38.834833	−104.376447	134	Irrigated land

[1] Well sampled in 2013 and 2020.

[2] Well sampled in 2013 and 2018.

[3] Well sampled in 2013 and 2019.

[4] Well sampled in 2013 and each year 2018–20.

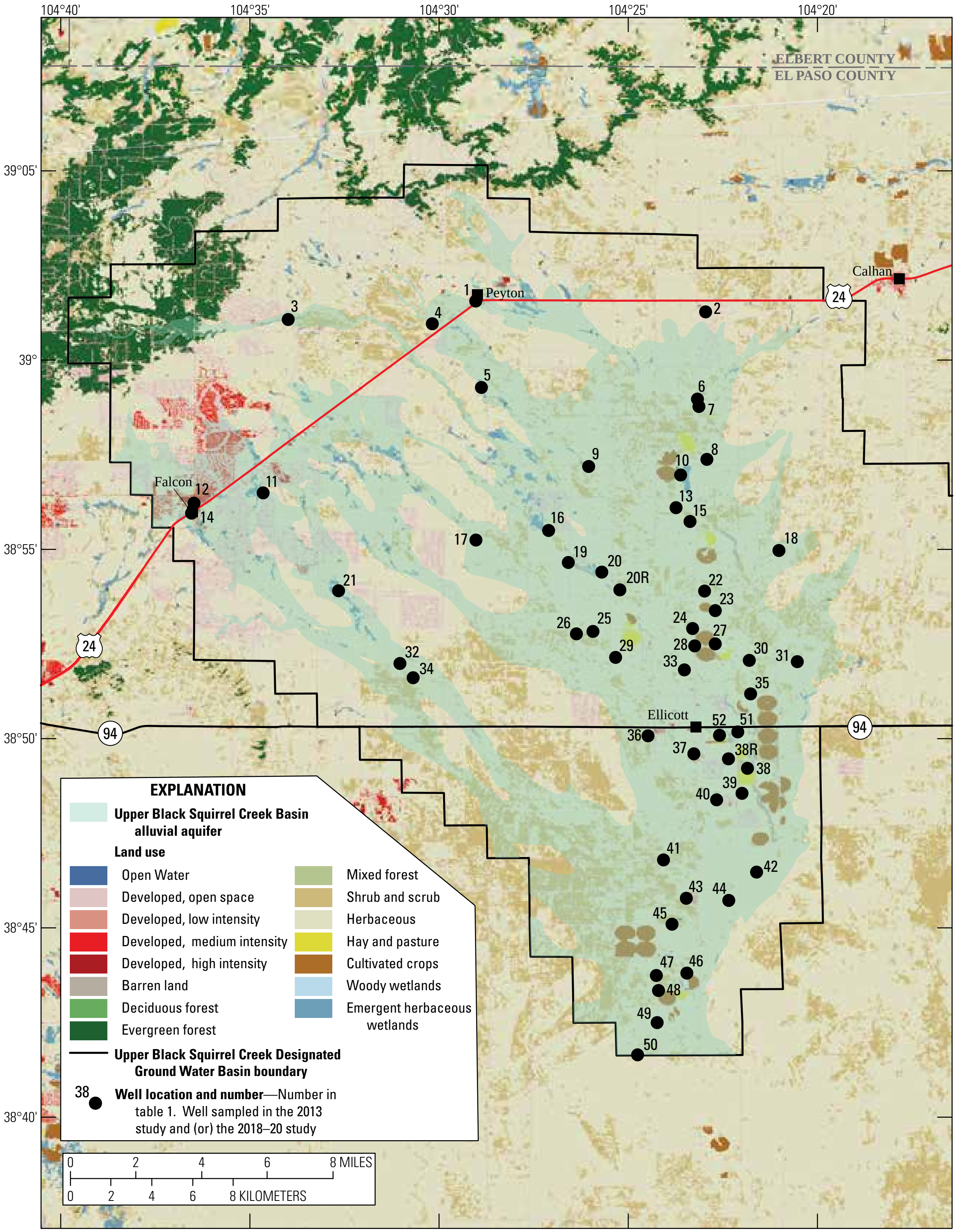
[5] Well sampled in 2013, unable to sample in 2018–20.

[6] Well sampled only in 2019 or 2020.

water for export to the Colorado Springs, Colo., area for municipal use (Buckles and Watts, 1988; Wellman and Rupert, 2016). Sprinkler (center pivot) irrigation has increased since 1970 and has become the predominant method of irrigation in the UBSB in the following decades (Watts, 1995). Buckles and Watts (1988) found the saturated thickness of the alluvium had declined by the mid-1980s by 10−30 ft.

Topper (2008) evaluated the hydrogeology in the alluvial aquifer, and Watts (1995) approximated the thickness at 0−120 ft throughout the UBSB. Regional flow paths in the alluvial aquifer generally are from the north-northwest to the south-southeast, and groundwater continues as underflow at the southern end of the basin (Buckles and Watts, 1988; Watts, 1995; Wellman and Rupert, 2016). Watts (1995) performed aquifer tests and compiled estimated hydraulic conductivity values from previous tests (McGovern and Jenkins, 1966) and numerical model outputs (Buckles and Watts, 1988). Wellman and Rupert (2016) found the median groundwater age in the alluvial aquifer to be about 30 years with a standard deviation of 6 years, indicating most groundwater analyzed in the study to be from recharge in the last few decades. Thus, land-use practices during the investigation of Wellman and Rupert (2016) and those during this study, 2018−20, could affect stable constituents in the groundwater for decades to come.

The UBSB alluvial aquifer overlies the Denver Basin aquifer system. Consolidated geologic units in the UBSB in descending stratigraphic order include the Late Cretaceous to early Tertiary Dawson Arkose, the Late Cretaceous and early Tertiary Denver Formation, and the Late Cretaceous Arapahoe Formation, Fox Hills Sandstone, Laramie Formation, and Pierre Shale (Buckles and Watts, 1988). These geologic units are important water-bearing aquifers as secondary sources of domestic and irrigation water in the UBSB (Watts, 1995). Development in these underlying bedrock aquifers, which are thought to be hydraulically connected to the alluvial aquifer, has increased since the 1990s and could have adverse effects on water supplies and quality within the alluvial aquifer of the UBSB (Buckles and Watts, 1988; Watts, 1995; Wellman and Rupert, 2016).



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 3. Land use from National Land Cover Dataset, 2016 (Homer and others, 2020), in Upper Black Squirrel Creek Designated Ground Water Basin, El Paso, County, Colorado.

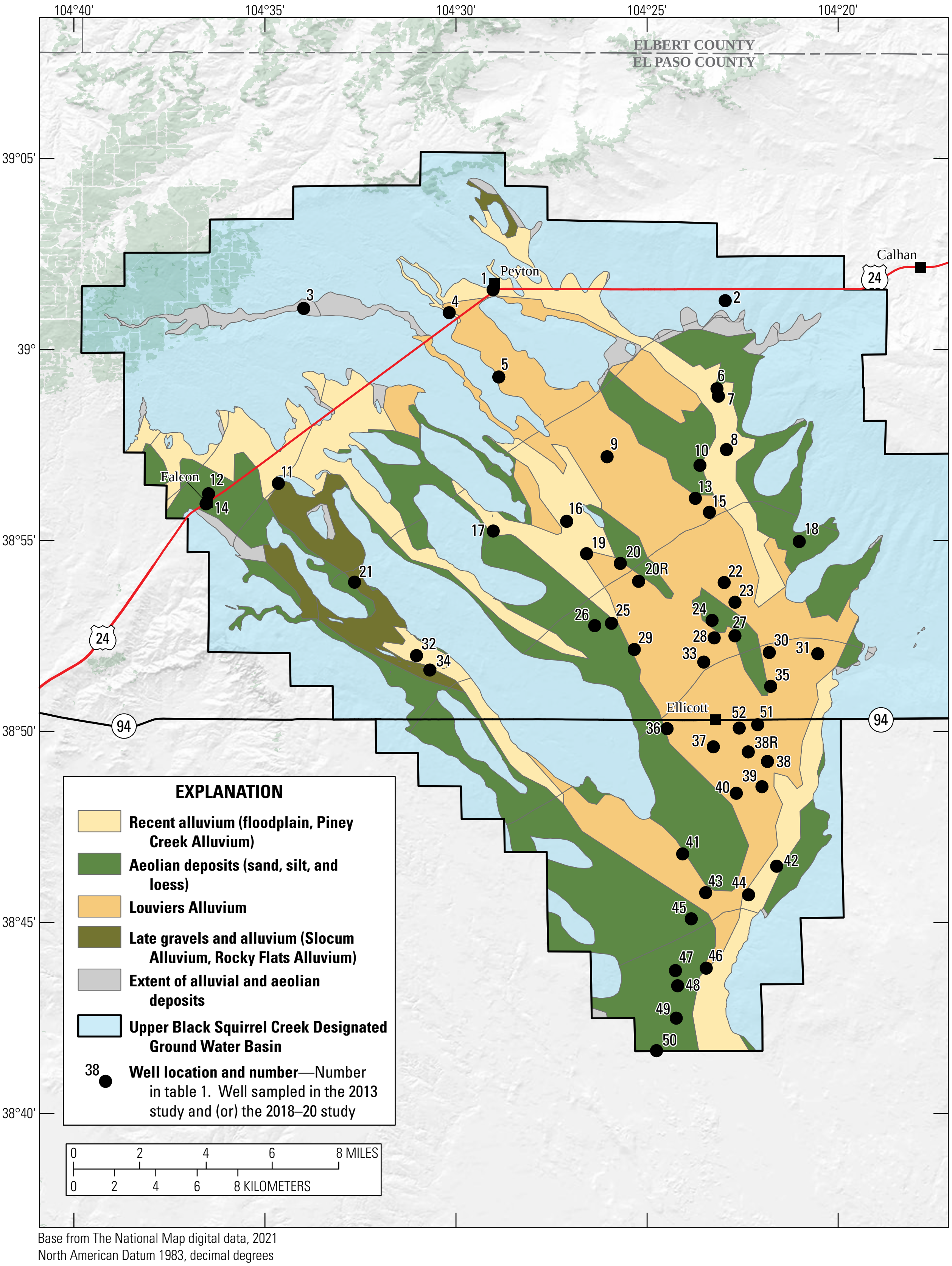


Figure 4. Unconsolidated Quaternary deposits mapped from Tweto (1979) and locations of sampled wells in the Upper Black Squirrel Creek Designated Ground Water Basin, El Paso, County, Colorado, 2018–20.

Methods

Groundwater sampling occurred between October and December each year (2018–20) following the summer irrigation season in contrast to the 2013 study, which collected samples during the summer. A repeat sampling of 44 of the 50 wells from the 2013 study (Wellman and Rupert, 2016) was conducted, along with sampling of 4 substitute wells. Wells 14, 15, 17, and 33 were not able to be sampled or replaced in Phase III (fig. 2). Two of the wells not resampled (wells 20 and 38) were replaced with wells of similar depth, construction, and location (wells 20R and 38R), and two wells (wells 51 and 52) were added in an area of the UBSB without any previous data (fig. 2, table 1). Three wells (13, 36, and 49) were sampled annually in 2018−20. Median concentrations and water classifications for the annually sampled wells are shown in figures 6, 7, 9, 12, 13, 15, and 18. The 48 sampled wells are used for production, monitoring, irrigation, livestock, and some serve multiple purposes. Site information for the sampled wells is provided in table 1. Water levels were measured, and samples were analyzed for a broad suite of natural and human compounds, stable isotopes of water, and for the nitrogen and oxygen isotopic composition of nitrate, when present in the groundwater.

Groundwater-Quality Sampling

Groundwater samples were collected, processed, and preserved using procedures described by the USGS National Field Manual (NFM; USGS, variously dated) and the USGS Reston Stable Isotope Laboratory (RSIL) in Reston, Va. (https://isotopes.usgs.gov/lab/instructions.html, accessed June 14, 2018). Water was pumped from production wells using existing pumps, and samples were collected between the wellhead and any pressure tanks, filtering, or treatment devices. Water was pumped from monitoring wells with a submersible electric pump constructed of stainless steel and Teflon. For the majority of constituents, the groundwater was passed through a filter—either 0.2 micrometers (µm) (nitrate isotope after passing through 0.45 µm), 0.45 µm (major ions, nutrients, nitrate isotope, selenium, and uranium), or 0.7 µm (pharmaceutical compounds and personal-care products)—during collection. Sampling equipment was cleaned before sample collection at each well, also using procedures in the USGS NFM (USGS, variously dated). Groundwater wells were purged prior to sample collection according to procedures in the USGS NFM (USGS, variously dated).

Field properties were measured until stabilization while purging the well before sample collection and after were remeasured as a quality assurance check, and groundwater samples were submitted for laboratory analysis of major ions, nutrients, the trace elements selenium and uranium, pharmaceutical compounds and personal-care products, nitrogen and oxygen isotopes of detected nitrate, and hydrogen and oxygen isotopes of water. Field properties were measured with a YSI multiparameter instrument and included specific conductance, pH, water temperature, and dissolved oxygen. Turbidity was measured using a Hach benchtop meter dedicated to the parameter only. Alkalinity for each sample was measured by incremental titration at the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo., using a titration method in the NFM (USGS, variously dated). Samples for major ions, nutrients, selenium, uranium, pharmaceutical compounds, and personal-care products were analyzed by the NWQL (Fishman and Friedman, 1989; Fishman, 1993; Garbarino, 1999; Patton and Kryskalla, 2003; Garbarino, and others, 2006; Patton and Kryskalla, 2011; Furlong and others, 2014). The NWQL applied detection limit procedures and primary laboratory reporting level conventions are available in Foreman and others (2021). Stable isotopes of nitrate ($\delta^{15}N$, $\delta^{18}O$) were analyzed by continuous-flow isotope-ratio mass spectrometry (IRMS) (Coplen and others, 2012) at the RSIL and are reported in standard stable-isotopic units of per mil (‰) with uncertainties of +/−0.5‰. Stable isotopes of water (δD, $\delta^{18}O$) were analyzed by dual-inlet IRMS (Révész and others, 1997; Révész and Copen, 2008a; 2008b) at the RSIL with uncertainties of +/−2‰ and +/−0.2‰, respectively. Isotope ratios for nitrate were only measured if the concentration of nitrate was at least 0.06 mg/L as nitrogen (N). Data for field properties and laboratory analytical results for the 2018–20 study, along with that of the 2013 study, are available from the USGS National Water Information System (NWIS) database (USGS, 2021; https://doi.org/10.5066/F7P55KJN) using USGS station identification numbers provided in table 1.

Data Compilation and Analysis

The data compilation and analyses included uploading the data to NWIS, conducting quality-assurance examinations, and performing statistical analyses. Specifically, after sampling, field measurements and ancillary information about the well and sample were checked for accuracy and then uploaded to NWIS. When analytical results were received from the laboratories, the data were checked, and analytical reruns or verifications of results were requested as needed. Inconsistent detections of pharmaceutical compounds and personal-care products can be an important indicator of data quality at small concentrations. Only one analytical result, for the wastewater-indicator compound nicotine, was excluded from the study after these checks. The nicotine detected for well 9 sampled on October 20, 2020, was determined to be unreliable. The well is isolated in grazing land with no nearby sources of nicotine. In addition, no nicotine sources associated with field samplers, equipment, or supplies were identified, and nicotine has been previously documented as questionable in a national groundwater study (Bexfield and others, 2019). Temporal analysis was conducted using paired t-tests (Helsel and others, 2020) when comparing nitrate concentrations from different studies.

Quality Assurance and Quality Control

In accordance with USGS protocols, source solution blanks, equipment blanks, and field blanks were collected during the study to identify potential sample bias caused by contamination, and sequential replicate samples were collected to evaluate sample variability (Mueller and others, 2015). Source solution blanks are used to assess blank water as a potential source of contamination and were collected directly from the blank water bottle into sample bottles. Whereas equipment blanks are used to evaluate the equipment and equipment-cleaning procedures and were collected prior to each year of sampling in the local laboratory using the electric pump and designated clean standpipe. Field blanks are used to evaluate the adequacy of field and laboratory protocols to prevent contamination bias (Mueller and others, 2015). All blank samples were collected using certified inorganic and organic blank water prepared at the NWQL. The blank water is certified to be free of environmental sample analytes at concentrations greater than reporting levels, and field blanks were collected using the same procedures as those used for environmental samples (USGS, variously dated).

For each year of sampling, the source solution and equipment blanks were collected before the beginning of sampling activities, whereas two field blanks were collected during sampling at randomly selected wells. The blank samples were collected for analysis of major ions, nutrients, selenium, uranium (table 2), pharmaceutical compounds, and personal-care products. The blank samples composed 22 percent (12 of 54) of the total number of samples collected in 2018–20.

Most (8 of 12) blank samples had a constituent detected at a concentration greater than a laboratory reporting level (Foreman and others, 2021), which included about 15 percent (32 of 224) of individual analytical results shown in table 2. All or most detections of magnesium, chloride, sulfate, fluoride, ammonia, and total nitrogen were at or near the respective laboratory reporting level for each constituent. All results for pharmaceutical compounds and personal-care products (not shown in table 2) were nondetections, values less than laboratory reporting levels. Only calcium and manganese had three or more detected concentrations two times greater than their reporting levels. All detections of constituents in blank samples, especially those of calcium and manganese, were taken into consideration in the interpretation of the environmental data, because the potential for substantial bias is low. However, for most constituents, including calcium, concentrations in blank samples typically were much lower than concentrations in the environmental samples, and the detections in the blank samples would not affect the interpretation of the environmental data. The maximum calcium concentration in a blank sample, for example was 0.107 mg/L, whereas the minimum concentration in an environmental sample was 12.5 mg/L. Detection of manganese (maximum 6 micrograms per liter [µg/L] in an equipment blank) at similarly low concentrations in environmental samples could introduce bias in the evaluation of manganese detections for environmental samples at low concentrations.

Replicate samples were collected to assess variability caused by the collection and analysis of samples (Mueller and others, 2015). All replicates collected were sequential; the replicate sample was collected after the environmental sample using the same sampling methods (USGS, variously dated). The relative percent difference (RPD) in concentrations between the environmental and replicate sample for each replicate pair was determined by calculating the difference in concentrations divided by their average, expressed as a percentage of the average. If one or both concentrations were less than the laboratory reporting level, no RPD was calculated.

Seven replicate samples were collected in 2018–20, which included 166 individual constituent replicate pairs shown in table 3. About 83 percent (137 of 166) of the replicate pairs had concentrations greater than the laboratory reporting level (Foreman and others, 2021) reported for both samples and thus could be evaluated for variability in constituent concentrations. The RPD of replicate concentrations was small (less than [<] 10 percent) for most replicate pairs; only a total of 13 replicate pairs for 5 constituents had an RPD greater than 10 percent. For most (12 of 13) of these replicate pairs, the environmental and replicate samples had low concentrations, and there was little absolute difference between the sample concentrations including iron, manganese, selenium, and the $\delta^{18}O$ of nitrate. Only the first replicate pair (sampled October 22, 2018) for manganese had a RPD greater than 50 percent, yet the low concentrations of both the environmental and replicate samples indicated minimal effect on the reproducibility and bias on sampling. Except for sulfamethoxazole (table 3), all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection.

Table 2. Concentrations of alkalinity, major ions, nutrients, selenium, and uranium in blank samples, Upper Black Squirrel Creek Basin, El Paso County, Colorado, 2018–20.

[Gray shaded cells indicate detections in blank samples. mm, month; dd, day; yyyy, year; —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter]

Constituent	Well 50		Well 22	Well 49	Well 49		Well 40	Well 24	Well 49		Well 36	Well 12
	Sampled 10/17/2018		Sampled 10/23/2018	Sampled 11/09/2018	Sampled 10/09/2019		Sampled 10/16/2019	Sampled 11/05/2019	Sampled 10/06/2020		Sampled 10/14/2020	Sampled 10/19/2020
	Source solution blank sample	Equipment blank sample	Field blank sample	Field blank sample	Source solution blank sample	Equipment blank sample	Field blank sample	Field blank sample	Source solution blank sample	Equipment blank sample	Field blank sample	Field blank sample
Alkalinity, water, filtered, fixed endpoint, lab (mg/L as $CaCO_3$)	—	—	—	—	<4	<4	<4	<4	<4	<4	<4	<4
Calcium, filtered (mg/L)	<0.022	0.107	<0.022	<0.022	<0.022	0.072	0.033	0.047	<0.020	0.063	0.062	0.028
Magnesium, filtered (mg/L)	<0.011	0.012	<0.011	<0.011	<0.010	0.011	<0.010	<0.010	<0.010	0.011	0.011	<0.010
Sodium, filtered (mg/L)	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Iron, filtered (µg/L)	<10	<10	<10	<10	<10	<10	<10	<10	<5	<5	11	<5
Manganese, filtered (µg/L)	<0.2	1.7	<0.2	<0.2	<0.2	6.0	0.40	<0.2	<0.2	1.8	0.78	0.32
Potassium, filtered (mg/L)	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Chloride, filtered (mg/L)	<0.02	0.16	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Sulfate, dissolved (mg/L)	<0.02	0.06	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.02	<0.02
Fluoride, filtered (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
Silica, filtered (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Bromide, filtered (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ammonia, filtered (mg/L as N)	0.01	0.02	0.01	0.01	0.02	0.01	< 0.01	< 0.01	<0.02	<0.02	<0.02	<0.02
Nitrite, filtered (mg/L as N)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Nitrite plus nitrate, filtered (mg/L as N)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Total nitrogen (mg/L as N)	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Orthophosphate, filtered (mg/L as P)	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Selenium, filtered (µg/L)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Uranium, filtered (µg/L)	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03

Table 3. Concentrations of alkalinity, major ions, nutrients, selenium, uranium, sulfamethoxazole, water isotopes, and nitrate isotopes in environmental and replicate samples, and calculated relative percent difference, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

[Gray shaded cells indicate a relative percent difference greater than 10 percent for a replicate pair. Except for sulfamethoxazole, all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection; these data are not shown in the table. —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; *, unable to calculate relative percent difference; δ, delta; O, oxygen; ‰, per mil; D, deuterium]

Constituent	Environmental samples	Replicate samples	Relative percent difference
Well 39 sampled October 22, 2018			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	—	—	—
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	89	87	2.3
Calcium, filtered (mg/L)	29.2	29.5	1
Magnesium, filtered (mg/L)	3.23	3.29	1.8
Sodium, filtered (mg/L)	41.3	41.8	1.2
Potassium, filtered (mg/L)	1.9	2.01	5.6
Iron, filtered (µg/L)	<10	<10	*
Manganese, filtered (µg/L)	0.63	0.3	71
Chloride, filtered (mg/L)	10.7	10.6	0.9
Sulfate, dissolved (mg/L)	36.8	36.7	0.3
Fluoride, filtered (mg/L)	0.41	0.41	1.2
Silica, filtered (mg/L)	29.5	29.8	1
Bromide, filtered (mg/L)	0.16	0.16	0
Ammonia, filtered (mg/L as N)	<0.01	<0.01	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	7.13	7.68	7.4
Total nitrogen (mg/L as N)	7.47	7.38	1.2
Orthophosphate, filtered (mg/L as P)	0.054	0.054	0
Sulfamethoxazole, filtered (µg/L)	5	5	0
Selenium, filtered (µg/L)	5.4	5.5	1.8
Uranium, filtered (µg/L)	1.19	1.19	0
$\delta^{18}O$ of nitrate, filtered (‰)	0.25	0.26	3.9
$\delta^{15}N$ of nitrate, filtered (‰)	7.6	7.59	0.1
$\delta^{18}O$ of water, unfiltered (‰)	−10.7	−10.8	0.5
δD of water, unfiltered (‰)	−80	−80.7	0.9
Well 21 sampled October 30, 2018			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	—	—	—
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	174	162	7.1
Calcium, filtered (mg/L)	105	105	0
Magnesium, filtered (mg/L)	12.3	12.2	0.8
Sodium, filtered (mg/L)	91.4	91.7	0.3
Potassium, filtered (mg/L)	6.85	6.8	0.7
Iron, filtered (µg/L)	22.3	18.2	20
Manganese, filtered (µg/L)	1	0.8	22
Chloride, filtered (mg/L)	148	155	4.6
Sulfate, dissolved (mg/L)	96.8	100	3.3

Table 3. Concentrations of alkalinity, major ions, nutrients, selenium, uranium, sulfamethoxazole, water isotopes, and nitrate isotopes in environmental and replicate samples, and calculated relative percent difference, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.—Continued

[Gray shaded cells indicate a relative percent difference greater than 10 percent for a replicate pair. Except for sulfamethoxazole, all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection; these data are not shown in the table. —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; *, unable to calculate relative percent difference; δ, delta; O, oxygen; ‰, per mil; D, deuterium]

Constituent	Environmental samples	Replicate samples	Relative percent difference
Well 21 sampled October 30, 2018—Continued			
Fluoride, filtered (mg/L)	0.3	0.32	4.5
Silica, filtered (mg/L)	34.6	34.6	0
Bromide, filtered (mg/L)	0.25	0.25	0
Ammonia, filtered (mg/L as N)	<0.01	<0.01	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	3.75	3.58	4.6
Total nitrogen (mg/L as N)	4.09	4.13	1
Orthophosphate, filtered (mg/L as P)	0.039	0.035	11
Sulfamethoxazole, filtered (µg/L)	<26	<26	*
Selenium, filtered (µg/L)	2.7	2.9	7.1
Uranium, filtered (µg/L)	17.6	17.4	1.1
$\delta^{18}O$ of nitrate, filtered (‰)	1.76	1.65	6.5
$\delta^{15}N$ of nitrate, filtered (‰)	9	8.9	1.3
$\delta^{18}O$ of water, unfiltered (‰)	−9.33	−9.34	0.1
δD of water, unfiltered (‰)	−70.9	−71.2	0.4
Well 43 sampled October 15, 2019			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	100	100	0
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	—	—	—
Calcium, filtered (mg/L)	30.4	30.4	0
Magnesium, filtered (mg/L)	2.93	2.92	0.3
Sodium, filtered (mg/L)	34.8	34.6	0.6
Potassium, filtered (mg/L)	2.27	2.26	0.1
Iron, filtered (µg/L)	<10	<10	*
Manganese, filtered (µg/L)	0.2	<0.2	*
Chloride, filtered (mg/L)	6.84	6.85	0.3
Sulfate, dissolved (mg/L)	33.5	33.5	0
Fluoride, filtered (mg/L)	0.47	0.47	0.2
Silica, filtered (mg/L)	30.1	30	0.3
Bromide, filtered (mg/L)	0.14	0.15	6.9
Ammonia, filtered (mg/L as N)	<0.01	0.04	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	6.15	6.38	3.7
Total nitrogen (mg/L as N)	6.33	6.64	4.8
Orthophosphate, filtered (mg/L as P)	0.055	0.056	1.8
Sulfamethoxazole, filtered (µg/L)	<20	<20	*
Selenium, filtered (µg/L)	4.2	4.3	2.4

Table 3. Concentrations of alkalinity, major ions, nutrients, selenium, uranium, sulfamethoxazole, water isotopes, and nitrate isotopes in environmental and replicate samples, and calculated relative percent difference, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.—Continued

[Gray shaded cells indicate a relative percent difference greater than 10 percent for a replicate pair. Except for sulfamethoxazole, all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection; these data are not shown in the table. —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; *, unable to calculate relative percent difference; δ, delta; O, oxygen; ‰, per mil; D, deuterium]

Constituent	Environmental samples	Replicate samples	Relative percent difference
Well 43 sampled October 15, 2019—Continued			
Uranium, filtered (µg/L)	1.06	1.07	0.9
$\delta^{18}O$ of nitrate, filtered (‰)	−0.75	−0.63	17
$\delta^{15}N$ of nitrate, filtered (‰)	6.76	6.8	0.6
$\delta^{18}O$ of water, unfiltered (‰)	−10.3	−10.3	0
δD of water, unfiltered (‰)	−77	−77.3	0.4
Well 3 sampled December 4, 2019			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	191	183	4.3
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	—	—	—
Calcium, filtered (mg/L)	73.7	72.9	1.1
Magnesium, filtered (mg/L)	5.77	5.77	0
Sodium, filtered (mg/L)	10.4	10.5	1
Potassium, filtered (mg/L)	<0.3	<0.3	*
Iron, filtered (µg/L)	1,250	1,170	6.6
Manganese, filtered (µg/L)	520	490	6
Chloride, filtered (mg/L)	6.59	6.66	1.1
Sulfate, dissolved (mg/L)	20.6	20.5	0.5
Fluoride, filtered (mg/L)	0.52	0.53	1.7
Silica, filtered (mg/L)	69	68	1.5
Bromide, filtered (mg/L)	0.13	0.12	8
Ammonia, filtered (mg/L as N)	0.02	<0.01	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	<0.04	<0.04	*
Total nitrogen (mg/L as N)	0.26	0.24	8
Orthophosphate, filtered (mg/L as P)	0.024	0.025	4.1
Sulfamethoxazole, filtered (µg/L)	<20	<20	*
Selenium, filtered (µg/L)	0.26	0.23	12
Uranium, filtered (µg/L)	2.78	2.59	7.1
$\delta^{18}O$ of nitrate, filtered (‰)	—	—	—
$\delta^{15}N$ of nitrate, filtered (‰)	—	—	—
$\delta^{18}O$ of water, unfiltered (‰)	−11.5	−11.5	0
δD of water, unfiltered (‰)	−85.1	−85.5	0.5
Well 19 sampled October 16, 2020			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	173	173	0
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	—	—	—
Calcium, filtered (mg/L)	55.8	55.6	0.4
Magnesium, filtered (mg/L)	5	4.99	0.2

Table 3. Concentrations of alkalinity, major ions, nutrients, selenium, uranium, sulfamethoxazole, water isotopes, and nitrate isotopes in environmental and replicate samples, and calculated relative percent difference, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.—Continued

[Gray shaded cells indicate a relative percent difference greater than 10 percent for a replicate pair. Except for sulfamethoxazole, all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection; these data are not shown in the table. —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; *, unable to calculate relative percent difference; δ, delta; O, oxygen; ‰, per mil; D, deuterium]

Constituent	Environmental samples	Replicate samples	Relative percent difference
Well 19 sampled October 16, 2020—Continued			
Sodium, filtered (mg/L)	75.7	75.5	0.3
Potassium, filtered (mg/L)	4	4	0
Iron, filtered (µg/L)	11.5	<5	*
Manganese, filtered (µg/L)	0.46	0.33	33
Chloride, filtered (mg/L)	33.6	33.7	0.3
Sulfate, dissolved (mg/L)	106	106	0
Fluoride, filtered (mg/L)	0.67	0.66	0.9
Silica, filtered (mg/L)	31.8	31.8	0
Bromide, filtered (mg/L)	0.28	0.28	0
Ammonia, filtered (mg/L as N)	<0.02	<0.02	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	0.97	0.96	1
Total nitrogen (mg/L as N)	1.27	1.25	1.6
Orthophosphate, filtered (mg/L as P)	0.029	0.029	0
Sulfamethoxazole, filtered (µg/L)	<20	<20	*
Selenium, filtered (µg/L)	2	1.8	11
Uranium, filtered (µg/L)	10.3	10.4	1
$\delta^{18}O$ of nitrate, filtered (‰)	−1.1	−1.37	22
$\delta^{15}N$ of nitrate, filtered (‰)	6.73	6.76	0.4
$\delta^{18}O$ of water, unfiltered (‰)	−9.81	−9.82	0.1
δD of water, unfiltered (‰)	−75.1	−75.9	1.1
Well 51 sampled November 18, 2020			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	95	95	0
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	—	—	—
Calcium, filtered (mg/L)	24	23.8	0.8
Magnesium, filtered (mg/L)	2.61	2.59	0.8
Sodium, filtered (mg/L)	36.1	35.9	0.6
Potassium, filtered (mg/L)	1.71	1.69	1.2
Iron, filtered (µg/L)	<5	<5	*
Manganese, filtered (µg/L)	<0.2	<0.2	*
Chloride, filtered (mg/L)	8.64	8.71	0.8
Sulfate, dissolved (mg/L)	27.6	27.8	0.7
Fluoride, filtered (mg/L)	0.5	0.51	2
Silica, filtered (mg/L)	29.1	29.8	2.4
Bromide, filtered (mg/L)	0.11	0.12	8.7
Ammonia, filtered (mg/L as N)	<0.02	<0.02	*

Table 3. Concentrations of alkalinity, major ions, nutrients, selenium, uranium, sulfamethoxazole, water isotopes, and nitrate isotopes in environmental and replicate samples, and calculated relative percent difference, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.—Continued

[Gray shaded cells indicate a relative percent difference greater than 10 percent for a replicate pair. Except for sulfamethoxazole, all replicate pairs for pharmaceutical compounds and personal-care products had both results reported as nondetections (less than laboratory reporting levels) or had one detected concentration and one nondetection; these data are not shown in the table. —, no data; <, less than laboratory reporting level (Foreman and others, 2021); mg/L, milligrams per liter; $CaCO_3$; calcium carbonate; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; *, unable to calculate relative percent difference; δ, delta; O, oxygen; ‰, per mil; D, deuterium]

Constituent	Environmental samples	Replicate samples	Relative percent difference
Well 51 sampled November 18, 2020—Continued			
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	3.27	3.23	1.2
Total nitrogen (mg/L as N)	3.41	3.4	0.3
Orthophosphate, filtered (mg/L as P)	0.055	0.053	3.7
Sulfamethoxazole, filtered (µg/L)	<20	<20	*
Selenium, filtered (µg/L)	2.7	2.7	0
Uranium, filtered (µg/L)	1.36	1.39	2.2
$\delta^{18}O$ of nitrate, filtered (‰)	−1.51	−1.17	25
$\delta^{15}N$ of nitrate, filtered (‰)	7.06	7.19	1.8
$\delta^{18}O$ of water, unfiltered (‰)	−11.2	−11.2	0
δD of water, unfiltered (‰)	−84.5	−84.2	0.4
Well 1 sampled November 20, 2020			
Alkalinity, water, filtered, fixed endpoint, laboratory (mg/L as $CaCO^3$)	80	80	0
Alkalinity, water, filtered, inflection point, field (mg/L as $CaCO^3$)	—	—	—
Calcium, filtered (mg/L)	176	181	2.8
Magnesium, filtered (mg/L)	26.6	27.1	1.9
Sodium, filtered (mg/L)	386	400	3.6
Potassium, filtered (mg/L)	16.9	17.4	2.9
Iron, filtered (µg/L)	<10	<10	*
Manganese, filtered (µg/L)	1.02	0.68	40
Chloride, filtered (mg/L)	900	900	0
Sulfate, dissolved (mg/L)	59.4	59.6	0.3
Fluoride, filtered (mg/L)	0.12	0.12	0
Silica, filtered (mg/L)	22.8	23.1	1.3
Bromide, filtered (mg/L)	0.05	0.05	0
Ammonia, filtered (mg/L as N)	<0.02	<0.02	*
Nitrite, filtered (mg/L as N)	<0.001	<0.001	*
Nitrite plus nitrate, filtered (mg/L as N)	15.6	15.5	0.6
Total nitrogen (mg/L as N)	16.4	16.4	0
Orthophosphate, filtered (mg/L as P)	0.611	0.596	2.5
Sulfamethoxazole, filtered (µg/L)	<20	<20	*
Selenium, filtered (µg/L)	2.3	2	14
Uranium, filtered (µg/L)	0.84	0.83	1.2
$\delta^{18}O$ of nitrate, filtered (‰)	−2.83	−3.2	12
$\delta^{15}N$ of nitrate, filtered (‰)	8.9	8.95	0.6
$\delta^{18}O$ of water, unfiltered (‰)	−11.7	−11.7	0
δD of water, unfiltered (‰)	−86.5	-86.6	0.1

Analysis of the replicate data for the sample pair collected from well 19 on October 16, 2020, indicated a large difference in iron concentration for the environmental and replicate samples. Iron concentrations were 11.5 and less than 5 µg/L (table 3), respectively. These differences were likely because of changes in water quality observed during well purging and sampling. Water withdrawn from the well ranged from brown to clear to orange for more than 45 minutes. Purged water began to clear up before sampling commenced, at which time field properties stabilized at a median turbidity measurement of 16.9 nephelometric turbidity units (NTU). After collection of the environmental samples, field properties were remeasured, and the sequential replicate was collected. The remeasured turbidity of the water from the well was 5 NTU. Remnants of iron-rich and turbid water likely were collected in the environmental sample, whereas the groundwater cleared prior to collection of the replicate sample. Iron associated with the particles that imparted color to the water likely collected in the sampling tube and (or) filter, contributing to a higher concentration in the environmental sample relative to the replicate sample. Because of the large differences in values between the two sample types and the appearance that the environmental results might reflect conditions prior to sufficient purging of the well, the iron and turbidity results for each sample have been excluded from the UBSB dataset and further analysis for this report. No other constituent concentrations were affected by the conditions noted at well 19.

Generally, in a water-quality sampling project, quality-control samples can identify whether bias or variability associated with equipment, equipment cleaning procedures, and collection and analysis of samples might affect interpretation of the environmental data. As discussed for the UBSB, detections of constituents in blank samples, especially those of calcium and manganese, were considered in the interpretation of the environmental data. Manganese was the only constituent with detections in blank samples that could indicate bias in the environmental sample data at low concentrations. The data for replicate pairs indicated low variability (high precision) in concentrations for most constituents. The only variability of concern identified was for iron, manganese, selenium, and the $\delta^{18}O$ of nitrate, which were considered in the interpretation of environmental data. Overall, the quality-assurance and quality-control samples confirmed the data were suitable for the objectives of the study.

Water-Quality Standards

The EPA established primary (regulatory) drinking-water standards (MCLs) for nearly 100 chemical constituents to protect human health (EPA, 2020a) and 15 secondary drinking-water guidelines (secondary maximum contaminant levels, SMCLs) for aesthetic qualities of water (EPA, 2020b), and the SMCLs are set for constituents that can affect the taste, color, odor, and (or) corrosivity of water (EPA, 2020b). Regulatory standards (primary) compared to guidelines (secondary) apply to public water suppliers. Although many of the wells sampled were domestic wells for which the standards are not enforced, data for all well types were compared to the standards to provide context for understanding the results and how groundwater could be used for drinking-water supplies in the study area. For private self-supplied drinking water systems such as domestic wells, it is the responsibility of the well owner to test for water quality and treat, if necessary.

The MCL for nitrate in public drinking-water supplies is 10 mg/L as N to protect against infant methemoglobinemia (Ward and others, 2018), and the MCL for nitrite is 1 mg/L as N because of similar health effects to nitrate. Other MCLs used in this report include fluoride MCL of 4 mg/L, created to prevent bone disease; selenium MCL of 0.05 mg/L, created because of potential circulatory problems and hair loss, among other health effects; and uranium MCL of 0.03 mg/L, created to prevent increased risk of cancer and kidney toxicity (EPA, 2020a). The SMCLs include chloride, 250 mg/L; fluoride, 2 mg/L; iron, 0.3 mg/L; manganese, 0.05 mg/L; pH, 6.5−8.5; sulfate, 250 mg/L; and dissolved solids, 500 mg/L (EPA, 2020b).

Groundwater Quality 2018–20

Results for field properties, major ions, nutrients, nitrate isotopes, pharmaceutical compounds, personal-care products, selenium, uranium, and water isotopes for groundwater samples collected from the alluvial aquifer of the UBSB in 2018−20 are discussed in this report. As appropriate, results are compared to drinking-water standards and (or) used to help identify potential sources of nitrate and recharge to the aquifer. All data are available in USGS NWIS database (USGS, 2021), but only data used to make the figures in this report are also called in either table 4 or 5.

Field Properties

Field properties measured in 2018–20 included specific conductance, pH, water temperature, turbidity, and dissolved oxygen. Specific conductance is the ability of a substance to conduct an electric current (Hem, 1992). In water, it is generally proportional to the concentration of major ions and other dissolved constituents (for example, bicarbonate, calcium, chloride, fluoride, magnesium, potassium, silica, sodium, and sulfate). The weathering of minerals in soil and bedrock is a primary source of major dissolved constituents to water (Hem, 1992). Specific conductance ranged from 222 to 1,019 microsiemens per centimeter (µS/cm), with a median of 385 µS/cm for samples collected from the UBSB alluvial aquifer during 2018–20.

Table 4. Selected water-level, nutrient, selenium, uranium, nitrate isotope, and water isotope results for groundwater, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

[ID, identification; mm, month; dd, day; yyyy, year; ft, feet; LSD, land-surface datum relative to North American Vertical Datum of 1988; mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; δ, delta; O, oxygen; ‰, per mil; D, deuterium; —, no data; <, less than laboratory reporting level (Foreman and others, 2021); R, replacement]

Well ID	Sample date (mm/dd/yyyy)	Measured depth to groundwater, in ft below LSD	Nitrate plus nitrite, filtered (mg/L as N)	Dissolved oxygen (mg/L)	Selenium, filtered (µg/L)	Uranium, filtered (µg/L)	$\delta^{18}O$ of nitrate, filtered (‰)	$\delta^{15}N$ of nitrate, filtered (‰)	$\delta^{18}O$ of water, unfiltered (‰)	δD of water, unfiltered (‰)
1	11/20/2020	9.64	15.6	4.89	2.27	0.80	−2.8	8.9	−11.7	−86.5
2	10/25/2018	78.15	8.94	6.08	3.58	1.85	−1.5	8.2	−13.1	−99.0
3	12/04/2019	3.14	< 0.04	3.82	0.261	2.78	—	—	−11.5	−85.1
4	12/04/2019	6.56	0.151	3.17	1.05	1.14	−1.6	8.0	−8.5	−72.4
5	10/25/2018	31.29	3.61	3.85	0.750	0.636	−0.5	8.8	−11.0	−82.7
6	10/24/2018	55.75	10.3	6.86	4.69	1.18	−0.4	9.2	−12.3	−93.2
7	10/24/2018	59.00	7.65	7.79	4.64	2.13	−1.1	8.3	−12.4	−93.1
8	10/20/2020	—	1.45	0.27	0.624	0.215	2.4	10.3	−11.5	−84.5
9	10/20/2020	10.92	1.41	5.61	1.44	1.90	−0.9	6.7	−9.9	−72.9
10	10/20/2020	—	7.34	7.36	2.16	1.45	−0.9	6.9	−11.3	−85.3
11	10/15/2020	6.77	0.054	0.91	2.40	0.646	12.1	19.4	−12.5	−93.3
12	10/19/2020	5.05	< 0.04	0.54	0.15	1.21	—	—	−10.4	−77.3
13	10/23/2018	100.24	5.40	4.31	11.7	1.62	0.2	7.5	−11.3	−86.0
13	10/15/2019	106.74	5.88	4.95	10.7	2.05	0.0	7.4	−11.4	−84.7
13	10/13/2020	103.10	6.41	3.02	12.6	1.81	0.1	8.0	−11.3	−85.0
16	12/05/2019	10.28	1.44	1.22	0.910	11.4	1.4	11.3	−9.1	−72.1
18	10/19/2020	47.62	7.96	8	1.62	1.37	−1.9	5.9	−11.5	−82.9
19	10/16/2020	13.30	0.970	7.07	1.95	10.3	−1.1	6.7	−9.8	−75.1
20R	11/19/2020	82.99	4.89	4.06	2.29	9.05	3.5	12.6	−10.5	−80.3
21	10/30/2018	—	3.75	3.19	2.74	17.6	1.8	9.0	−9.3	−70.9
22	10/23/2018	159.91	5.46	5.82	4.88	1.27	0.0	8.0	−11.5	−87.0
23	10/23/2018	107.93	8.45	8.02	5.86	1.12	−0.3	6.9	−11.2	−85.2
24	11/05/2019	—	5.54	5.71	3.21	0.090	−0.2	6.9	−10.7	−79.9
25	10/15/2020	37.98	7.93	6.36	3.11	3.29	−0.1	7.3	−10.2	−76.7
26	10/15/2020	60.14	6.16	7.19	3.38	4.23	−0.7	6.7	−10.2	−77.2
27	10/23/2018	97.88	10.3	9.45	4.49	1.89	0.0	6.7	−10.8	−82.0
28	11/05/2019	49.47	2.16	6.81	5.87	2.94	2.8	9.8	−10.7	−78.4
29	12/05/2019	35.76	6.94	5.63	3.87	2.23	0.3	7.8	−10.7	−79.4
30	11/04/2019	72.90	6.63	10.58	8.93	2.98	−0.3	8.3	−11.3	−82.8
31	11/04/2019	32.25	1.09	7.23	1.52	1.72	4.0	9.0	−9.6	−68.1
32	12/04/2019	20.55	2.58	7.71	4.04	5.35	−0.3	7.1	−9.6	−71.8
34	10/24/2018	35.09	3.73	5.74	3.21	10.2	0.4	10.3	−9.2	−69.4
35	10/15/2019	87.58	6.78	8.64	8.42	1.21	−0.7	8.0	−10.9	−79.1
36	10/25/2018	—	7.05	6.95	3.68	1.29	−0.6	6.7	−10.2	−77.1
36	10/17/2019	—	7.60	8.53	3.51	1.60	−0.5	6.6	−10.3	−77.6
36	10/14/2020	—	7.38	6.72	3.46	1.51	−0.5	6.8	−10.3	−76.7
37	10/17/2019	—	4.90	7.13	2.85	1.12	0.2	7.9	−10.9	−82.5
38R	11/05/2019	83.20	8.78	5.73	4.34	1.29	0.5	8.2	−10.4	−78.6

Table 4. Selected water-level, nutrient, selenium, uranium, nitrate isotope, and water isotope results for groundwater, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.—Continued

[ID, identification; mm, month; dd, day; yyyy, year; ft, feet; LSD, land-surface datum relative to North American Vertical Datum of 1988; mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; δ, delta; O, oxygen; ‰, per mil; D, deuterium; —, no data; <, less than laboratory reporting level (Foreman and others, 2021); R, replacement]

Well ID	Sample date (mm/dd/yyyy)	Measured depth to groundwater, in ft below LSD	Nitrate plus nitrite, filtered (mg/L as N)	Dissolved oxygen (mg/L)	Selenium, filtered (µg/L)	Uranium, filtered (µg/L)	$\delta^{18}O$ of nitrate, filtered (‰)	$\delta^{15}N$ of nitrate, filtered (‰)	$\delta^{18}O$ of water, unfiltered (‰)	δD of water, unfiltered (‰)
39	10/22/2018	87.21	7.13	6.57	5.41	1.19	0.3	7.6	−10.7	−80.0
40	10/16/2019	89.66	10.1	6.2	3.01	1.21	−1.1	7.7	−10.2	−76.8
41	10/14/2020	108.45	6.58	10.62	4.66	1.02	−1.6	7.2	−9.5	−69.6
42	10/16/2019	—	9.10	8.77	8.75	10.6	−0.2	6.2	−9.6	−71.1
43	10/15/2019	102.30	6.15	6.42	4.22	1.06	−0.8	6.8	−10.3	−77.0
44	10/16/2019	38.51	7.21	8.41	7.86	2.22	0.5	6.3	−9.4	−68.8
45	10/22/2018	102.04	5.27	6.07	4.48	0.856	−0.6	6.7	−10.2	−77.2
46	11/18/2020	29.90	6.42	7.38	9.14	2.13	−0.2	7.5	−10.8	−79.5
47	10/22/2018	83.49	4.84	5.09	1.40	11.0	1.9	20.0	−10.1	−78.0
48	10/13/2020	55.74	4.77	4.33	2.38	9.80	1.2	20.0	−10.0	−77.6
49	11/09/2018	47.37	8.07	8.97	9.09	3.92	1.4	12.2	−10.5	−79.6
49	10/15/2019	—	7.48	7.57	7.78	5.17	1.6	12.8	−10.4	−78.2
49	10/13/2020	53.80	6.48	7.74	6.94	5.76	1.1	13.6	−10.3	−78.5
50	10/22/2018	80.14	7.47	7.69	8.53	1.76	1.4	9.3	−10.1	−75.1
51	11/18/2020	—	3.27	6.26	2.67	1.36	−1.5	7.1	−11.2	−84.5
52	11/19/2020	—	7.81	7.32	2.75	1.05	−1.0	7.4	−10.6	−80.2

Table 5. Detections of pharmaceutical compounds and personal-care products in groundwater, Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

[ID, identification; mm, month; dd, day; yyyy, year; µg/L, micrograms per liter; —, not detected; E, estimated concentration (Furlong and others, 2014)]

Well ID	Sample date (mm/dd/yyyy)	Carbamazepine (µg/L)	Sulfamethoxazole (µg/L)	Fluconazole (µg/L)	Carisoprodol (µg/L)	Metaxalone (µg/L)	Methylbenzotriazole (µg/L)	Famotidine (µg/L)
5	10/25/2018	235	—	—	—	—	—	—
32	12/04/2019	—	40.1	—	—	—	—	—
34	10/24/2018	17.3	—	—	—	—	—	—
45	10/22/2018	—	—	—	—	—	—	E 52.1
47	10/22/2018	290	23.4	115	23.8	63.5	344	—
48	10/13/2020	351	E 30.3	159	—	61.9	E 636	—
49	11/09/2018	19.1	—	—	—	—	—	—
49	10/15/2019	99.5	33.9	—	—	—	94.7	—
49	10/13/2020	132	E 24.5	—	—	—	E 145	—

The pH represents the effective concentration (activity) of hydrogen ions in water and is measured as the negative logarithm of the hydrogen ion activity (Hem, 1992). Neutral water has a pH of 7. A pH lower than 7 is considered acidic, and a pH higher than 7 is considered alkaline or basic. The pH of a water-quality sample can be affected by biological activity, geology, mineral precipitation or dissolution, and human activities (Hem, 1992). The pH ranged from 6.5 to 7.8 for samples collected from the UBSB alluvial aquifer during 2018–20.

Water temperature controls biological and chemical reaction rates. Water temperature ranged from 10.2 to 15.7 degrees Celsius (°C), with a median of 13.1 °C for samples collected from the UBSB alluvial aquifer during 2018–20.

Turbidity is the measure of relative clarity of a liquid, an optical characteristic of water, and is a measurement of the amount of light scattered by material in the water when a light is shined through the water sample (Swenson and Baldwin, 1965). In sampling for groundwater, the lower the turbidity value, the clearer the water; lower turbidity often is considered an indicator of water flowing directly from the aquifer through the casing opening(s), in contrast to static water in the casing prior to pumping. Values ranged from 0.16 to 95 NTU for samples collected from the UBSB alluvial aquifer during 2018–20.

The amount of dissolved oxygen in surface water, which can be a source of groundwater recharge, varies with water temperature, elevation, and water depth. The amount of dissolved oxygen retained after surface water or precipitation recharges the groundwater is affected by many factors, such as biological activity and inputs from point and nonpoint sources. Dissolved-oxygen concentrations for samples collected from the UBSB alluvial aquifer during 2018–20 ranged from 0.3 to 10.6 mg/L (table 4). Anoxic conditions (< 0.5 mg/L dissolved oxygen; McMahon and Chapelle, 2008) at well 8 or nearly anoxic conditions (0.5−1.2 mg/L) were present at wells 11, 12, and 16 (table 4).

Major-Ion Chemistry

Major-ion chemistry was represented and categorized using a Piper diagram (Piper, 1944; Freeze and Cherry, 1979). The Piper diagram is used to analyze major-ion chemistry by illustrating relative proportions of individual cations and anions (from 0 to 100 percent) in a water sample in milliequivalents per liter (meq/L). Major-ion chemistry data indicated groundwater from most wells sampled in the alluvial aquifer can be classified as a mixed water with the dominant categorization of a mixed-cation, mixed-anion water (fig. 5). Cation data showed a linear pattern between two end members: sodium and calcium (fig. 5), whereas no such pattern is evident in the anion data. However, groundwater samples from wells 1, 3, 4, 18, 28, 44, and 52, located mainly along the periphery of the alluvial aquifer, had cation and (or) anion compositions greater than 60 percent and were categorized based on their dominant species (sodium, calcium, and (or) chloride) (figs. 5 and 6).

Sodium-rich, bicarbonate waters identified in wells 4, 28, and 44 (fig. 5) and sodium, mixed-anion waters in wells 5, 8, 13, 31, and 32, were consistent with water sourced mainly from the underlying bedrock aquifers, which tend to have relatively high proportions of sodium (Watts, 1995; Wellman and Rupert, 2016). Calcium-rich, bicarbonate waters identified in wells 3, 18, 52 (fig. 5) and calcium, mixed-anion waters in wells 2, 7, and 12 had major-ion proportions consistent with fresh, shallow groundwater mixing with some bedrock water (Watts, 1995; Wellman and Rupert, 2016). The major-ion composition reported for well 1 (fig. 5) appears to be unique from all other wells, which could be related to effects of land use or to a contribution from an unknown source of sodium-chloride water.

Overall, groundwater from the UBSB alluvial aquifer was classified as a mixture of waters from multiple sources and could represent any of several different scenarios of mixing in the aquifer. The alluvial aquifer receives groundwater inflow from areas near the aquifer periphery, as well as inputs from precipitation, infiltration of excess agricultural irrigation water, treated septic water, and domestic water applied to yards and gardens (Buckles and Watts, 1988). In general, sodium-calcium, bicarbonate-mixed anion water was prominent across broad areas along the main north−south axis of the alluvial aquifer and may represent more thorough mixing among multiple groundwater sources than in other areas of the alluvial aquifer. These data were consistent with the findings from Watts (1995) and Wellman and Rupert (2016). The latter summarized the more variable water types along the periphery fingers of the aquifer (fig. 6), where the alluvial deposits are thin and depth to bedrock aquifers is relatively shallow, was because of localized sources of surface recharge mixing with inputs of water from other sources in the alluvial aquifer and become altered geochemically by the in-situ conditions.

Dissolved solids can be used as proxy for salt loading and potential mobilization of trace elements (Bern and others, 2020a). Observed dissolved solids values were less than the SMCL of 500 mg/L for samples from all except six wells, ranging from 512 to 1,762 mg/L (USGS, 2021). Concentrations of chloride, iron, and manganese each exceeded their SMCLs in samples from wells 1 (chloride), 3 (iron), 4 (iron and manganese), and 12 (manganese) (USGS, 2021). Sulfate and fluoride concentrations did not exceed their respective SMCLs.

Nutrients

Samples collected from the UBSB alluvial aquifer during 2018–20 were analyzed for nutrients, including ammonia, nitrite, nitrate, and orthophosphate. All concentrations of ammonia and nitrite, as well as most concentrations of orthophosphate, were less than 0.1 mg/L (USGS, 2021). The maximum orthophosphate concentration of 0.611 mg/L was detected in the sample from well 1, which also had unique major-ion chemistry and a high nitrate concentration (15.6 mg/L) compared with the other UBSB wells

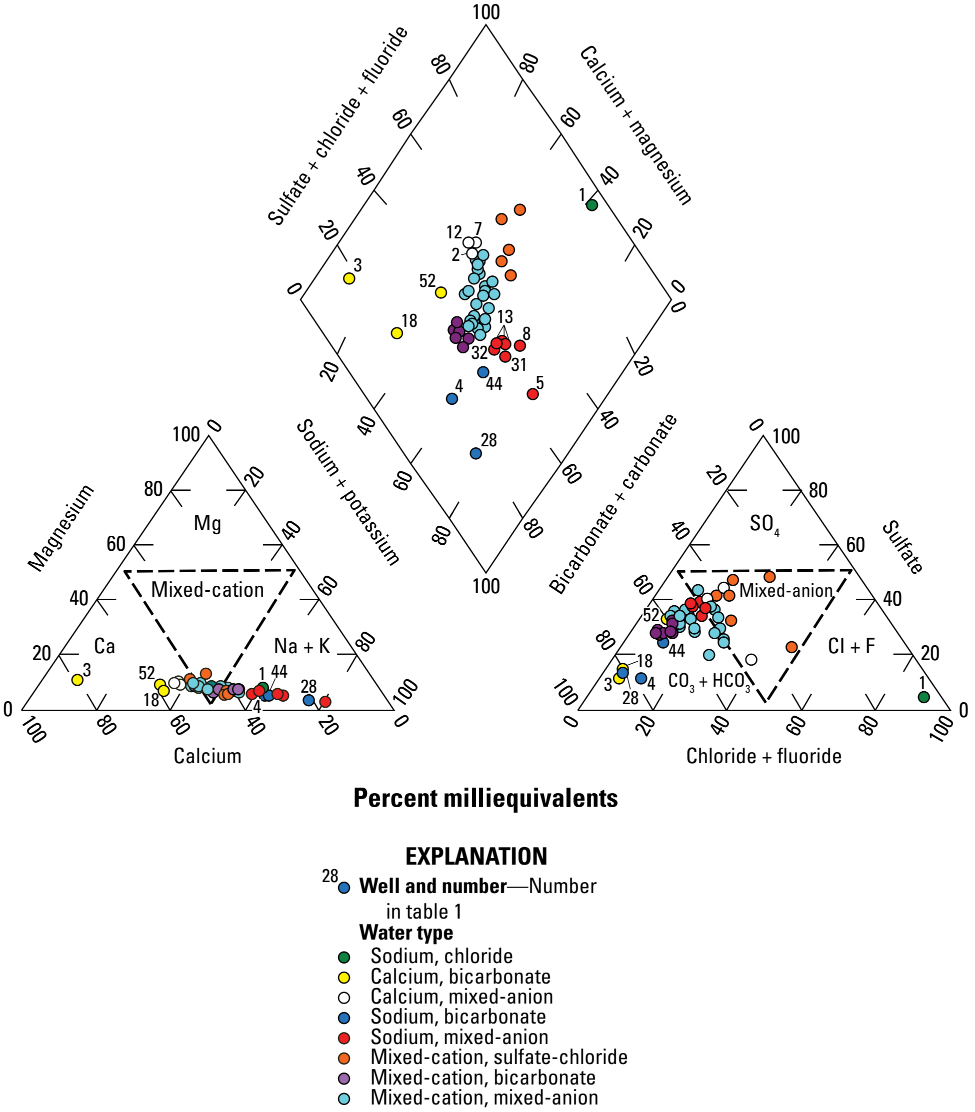
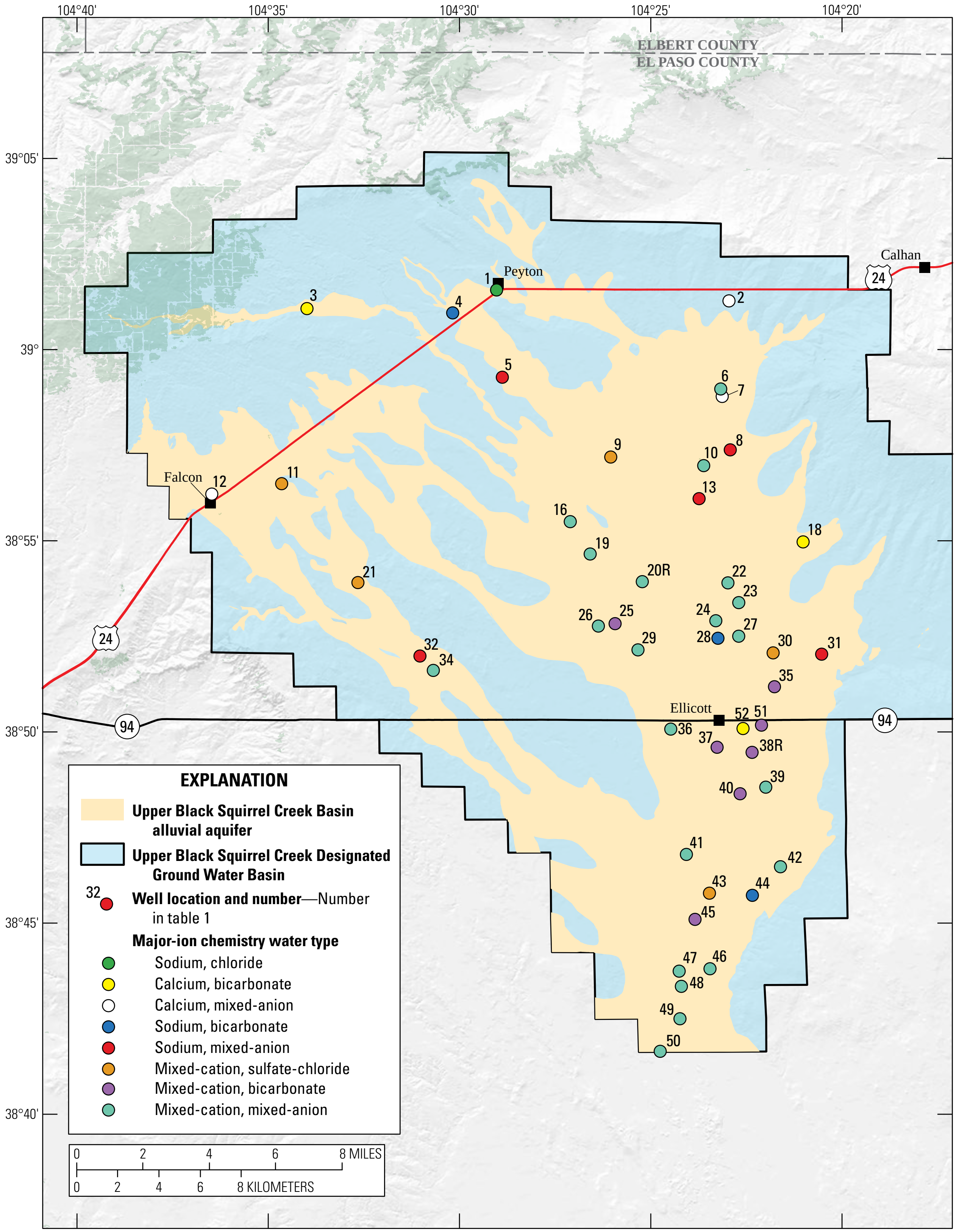


Figure 5. Major-ion chemistry of groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

(USGS, 2021). Minimal concentrations of nitrite, ammonia, and orthophosphate indicated these three nutrients are not of water-quality concern for the UBSB. Concentrations of nitrite were observed to be negligible in the generally oxic groundwaters of the UBSB alluvial aquifer; nitrate plus nitrite is hereinafter referred to as "nitrate."

Nitrate is the primary constituent of interest in managing groundwater quality in the UBSB (Wellman and Rupert, 2016). Historically, concentrations of nitrate in samples from some wells completed in the UBSB alluvial aquifer exceeded the MCL of 10 mg/L as N (Brendle, 1997; Wellman and Rupert, 2016) and were greater than or equal to the MCL of 10 mg/L as N in 10 percent of the samples. Overall, nitrate concentrations for samples collected during 2018–20 ranged from <0.04 to 15.6 mg/L as N (fig. 7), with a median concentration of 6.4 mg/L. Samples collected from about 8 percent (4 of 48) of wells during 2018–20 had nitrate concentrations that exceeded the MCL (fig. 7). Of the four wells with exceedances, only well 13 was sampled every year of the study. The concentration exceeded the MCL only once in the three years and is graphically represented as the median concentration (fig. 7). About 67 percent (32 of 48) of wells had a sample with a nitrate concentration greater than 5 mg/L as N, and about 90 percent (43 of 48) of wells had a concentration greater than 1 mg/L as N, the estimated national background concentration of nitrate in groundwater (Dubrovsky and others, 2010). Samples from only two wells (wells 3 and 12) had concentrations of nitrate below the reporting level (<0.04 mg/L as N) (table 4).



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 6. Location of wells with major-ion chemistry water types determined for samples collected from the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

Low or undetected concentrations of nitrate in samples from wells 3, 4, 11, and 12, nearest to urbanization in the northwest part of the study area in the vicinity of Falcon and Peyton (fig. 1), imply urbanization in those areas currently (2022) has not substantially affected water quality in the alluvial aquifer. However, urbanization can affect some aspects of groundwater quality (such as dissolved solids concentrations or the presence of human-made organic compounds) without affecting nitrate concentrations, particularly where the groundwater is suboxic or anoxic, indicating the potential for denitrification (McMahon and Chapelle, 2008). Wells 11 and 12 both had dissolved-oxygen concentrations below 1 mg/L, which could indicate the potential for denitrification to occur. Also, based on samples collected during 2013, the apparent groundwater age in the north and northwest parts of the alluvial aquifer was often older than 30 years (Wellman and Rupert, 2016). This could indicate recharge associated with recent urbanization (within the past 30 years) has not yet reached the depth of the well screens in the sampled wells, and thus nitrate concentrations in sampled groundwater in the northwest part of the UBSB may not reflect the effects of recent urbanization. Concentrations of nitrate varied spatially throughout the UBSB. The lowest concentrations were commonly detected in the northern half of the UBSB, but that is also where three of the four wells with nitrate concentrations greater than the MCL of 10 mg/L are located (fig. 7).

Nitrate Isotopes

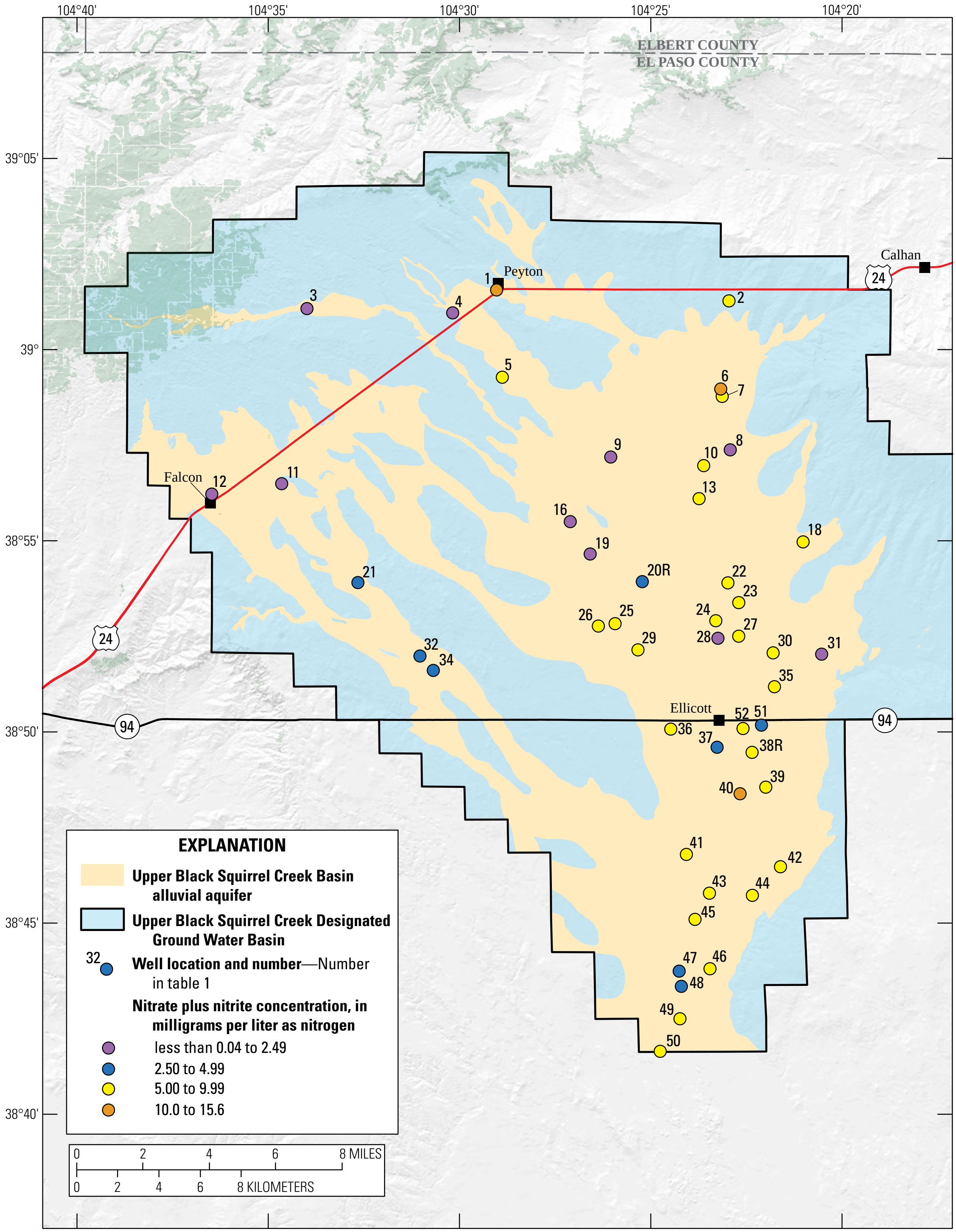
Isotope ratios of nitrogen (δ^{15}N) and oxygen (δ^{18}O) in nitrate can be used to help identify different nitrate sources and characterize nitrate reduction (Kendall, 1998). Naturally occurring nitrate can be found in the soil with likely ranges of δ^{15}N from 2 to 5‰ (per mil) (Kendall, 1998) and can accumulate because of lack of leaching under dry climates (Jackson and others, 2004). Human nitrate in the UBSB can be sourced from fertilizers, manure, sewage, and (or) septic effluent (Brendle, 1997). Synthetic fertilizers have a typical range of δ^{15}N from -2 to 2‰ (Kendall, 1998), whereas Fogg and others (1998) found the range of δ^{15}N in septic effluent and animal waste to be comparable from 8 to 20‰. Nitrate concentrations in groundwater are controlled by nitrogen inputs and redox conditions in the aquifer. Once nitrate has entered the groundwater, it can be removed naturally by denitrification, a process that converts nitrate into reduced species like nitrogen gas. Denitrification occurs when the groundwater is anoxic (generally when concentrations of dissolved oxygen are less than 0.5 mg/L) (McMahon and Chapelle, 2008; Bauch and others, 2012), whereas nitrate is stable under oxic conditions. Kendall and others (2014) explain biologically mediated reactions such as denitrification strongly control nitrogen dynamics in the soil and can affect and (or) control nitrogen dynamics in water under certain conditions. These reactions almost always result in δ^{15}N enrichment in the substrate of the remaining nitrate.

The isotopic compositions of nitrate in groundwater samples collected in the UBSB alluvial aquifer in 2018–20 were indicative of four main categories of sources or processes: soils, animal and (or) human waste, and an unknown source, along with samples showing evidence of denitrification (fig. 8). No sample displayed a composition similar to fertilizer. Most samples during 2018–20 had isotopic compositions similar to the expected naturally occurring sources in soil. Low nitrate concentration (fig. 7) combined with the isotopic composition of nitrate indicates denitrification had removed nitrate to a great degree, fractionating the isotopes in the process (fig. 8). Newman and others (2021) provide evidence of nitrate-reducing conditions in a nearby alluvial aquifer near wastewater treatment plants (WWTP) showing similar isotopic fractionation in response to denitrification. In groundwater studies, the isotopic signature of nitrate from animal or sewage waste, in contrast with fertilizer, is commonly less affected by interaction with soil nitrogen, because the distribution of waste is often localized at point sources of high concentration (Heaton, 1986). Elevated (above MCL) nitrate concentrations and the ratio of δ^{15}N and δ^{18}O of nitrate indicated a nitrogen source consistent with animal and (or) human waste at five wells (fig. 8; note results for two samples are plotted for well 49, which was sampled annually). Wellman and Rupert (2016) found nearly 25 percent of all the nitrate in the alluvial aquifer was from septic systems. The majority of the samples had δ^{18}O values range from -0.9 to 2.2‰ predicted for nitrate based on incorporation of oxygen from water with δ^{18}O like that of UBSB groundwater (table 4).

The distribution of the types of likely nitrogen sources varies spatially across the UBSB alluvial aquifer. For example, wells 47–49, where isotopes of nitrate indicate a source associated with animal and (or) human waste, are downgradient from a WWTP (figs. 9 and 10), which was noted as a factor in the detections of the pharmaceutical compounds and personal-care products (see the Pharmaceutical Compounds and Personal-Care Products section of this report). Wells 13 and 16, also having isotopes indicating a nitrate source associated with animal and (or) human waste, are both on grazing land with cattle operations (fig. 3). For well 1, the high nitrate concentration (fig. 7) and the outlier isotopic data (fig. 8) suggest an additional unknown source is present (fig. 9). This source could be human or naturally occurring, but the available data are inconclusive.

Pharmaceutical Compounds and Personal-Care Products

Pharmaceutical compounds and personal-care products, such as acetaminophen, caffeine, and lidocaine are used by many people as part of daily life and are not always completely metabolized in the body or are partially washed off after application. Hence, these substances are often a component of waste to domestic septic systems and WWTPs and



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 7. Nitrate plus nitrite concentrations for samples collected from the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

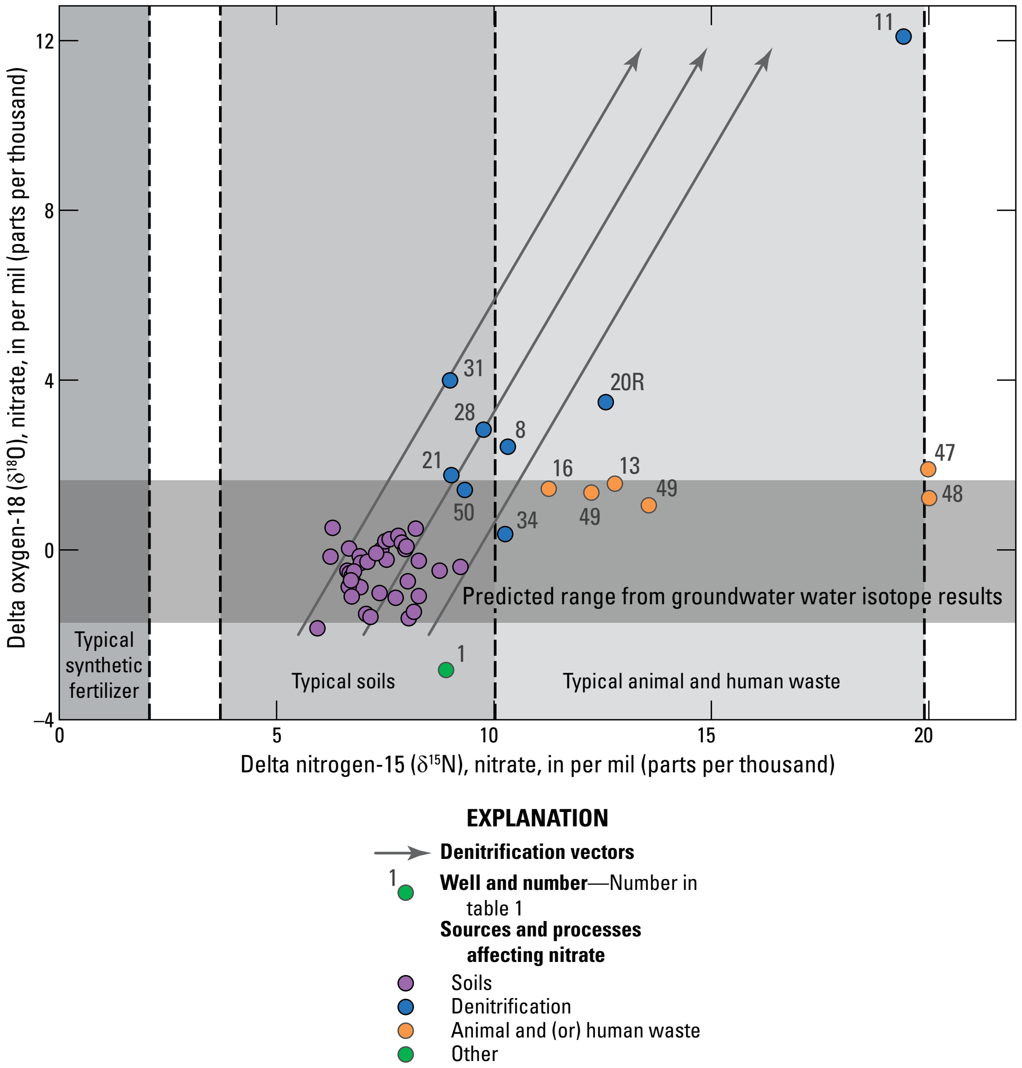
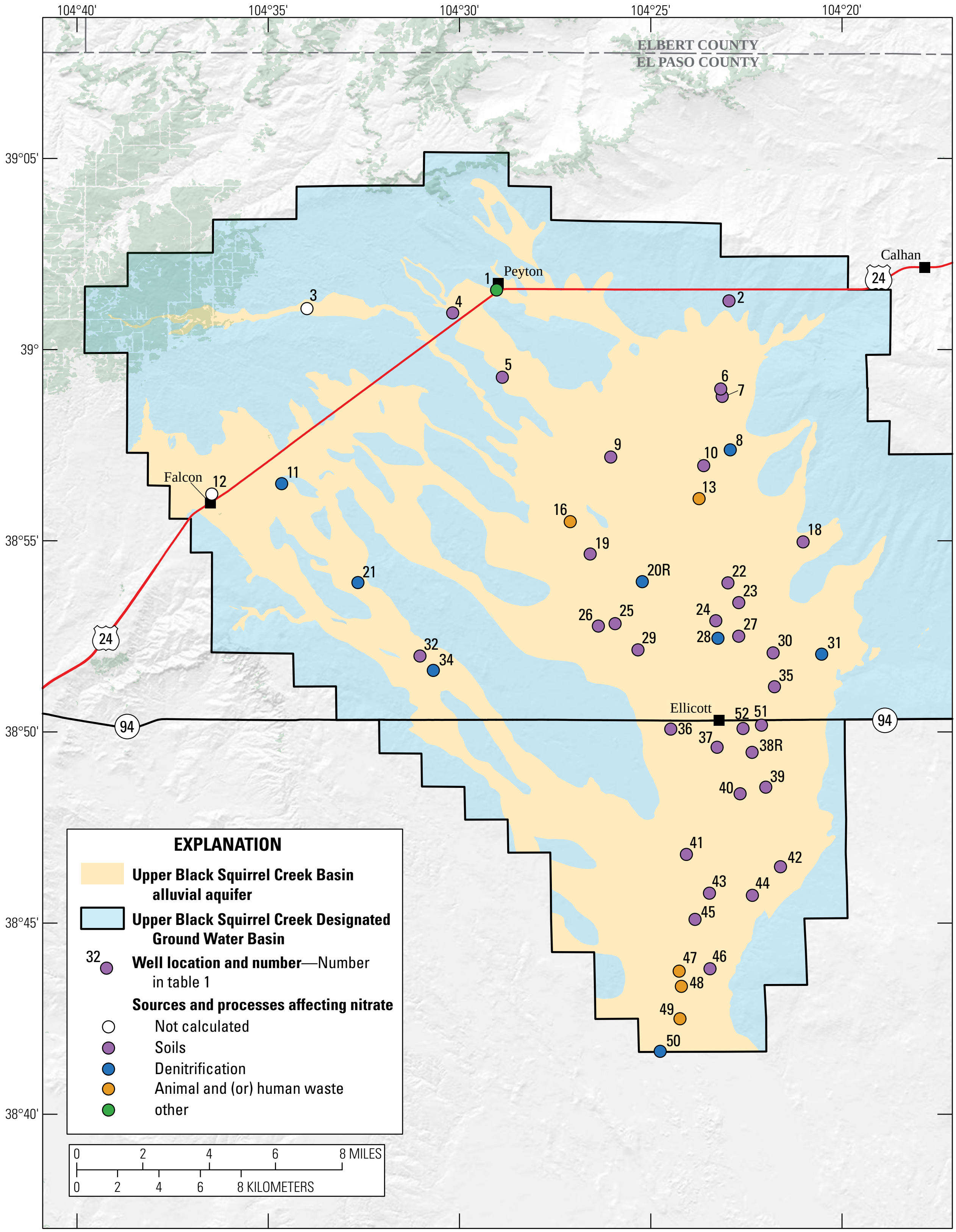


Figure 8. Relation between nitrogen and oxygen isotopes of nitrate and potential nitrate sources and processes identified from data collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

can subsequently reach groundwater as effluent. Removal of these compounds by processes at wastewater treatment plants is highly variable, depending on each compound’s degradation rate, and the wastewater treatment techniques used (Patel and others, 2019; Angeles and others, 2020). Some of these compounds have been identified as the term, “pseudo-persistent” meaning their continuous influx into the environment offsets their degradation and removal by various processes (Patel and others, 2019).

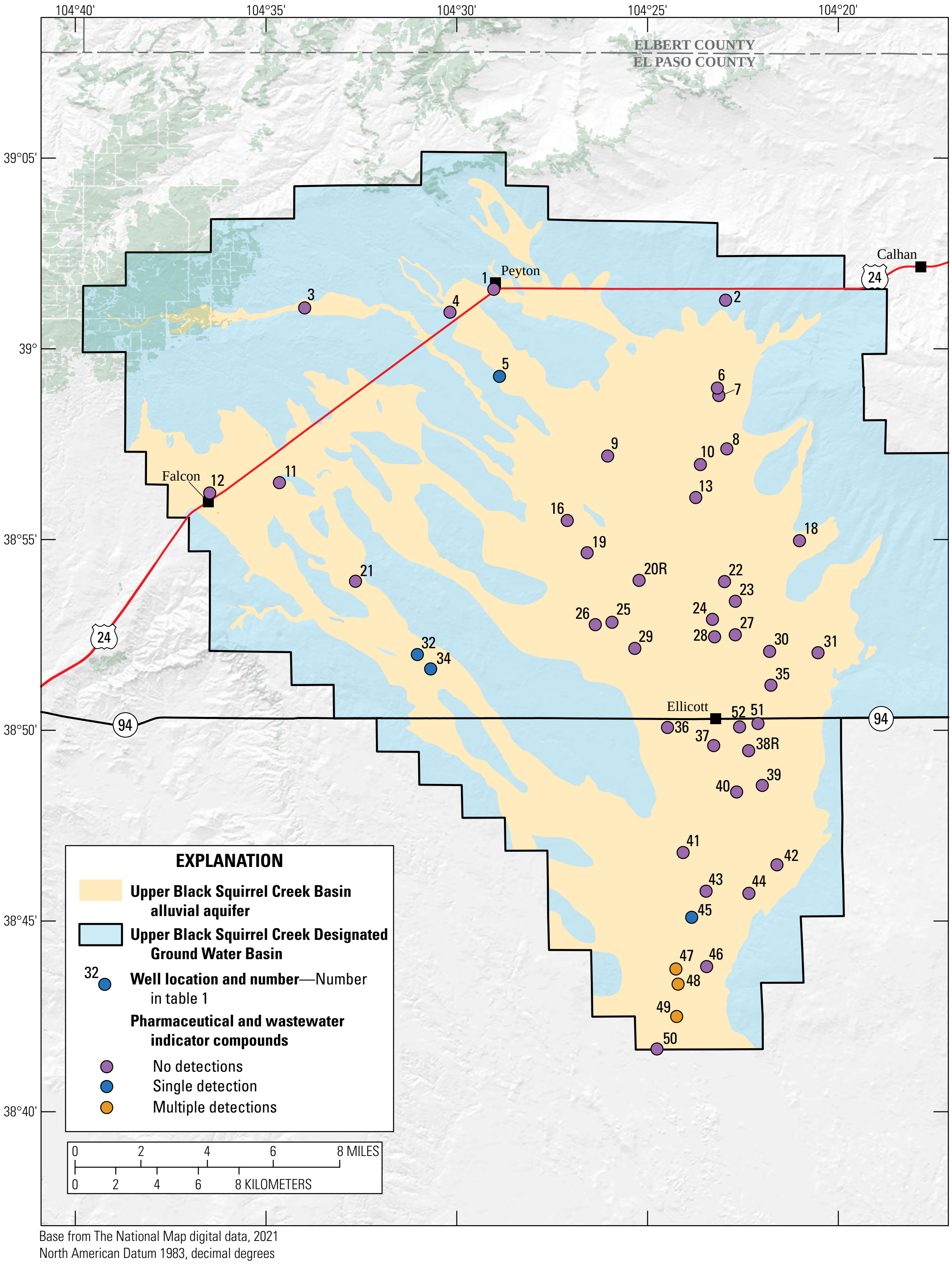
Groundwater samples from the UBSB alluvial aquifer have not previously been analyzed for pharmaceutical compounds and personal-care products. Therefore, this report provides a baseline dataset for the UBSB alluvial aquifer. Pharmaceutical compounds and personal-care products were not detected in 85 percent of wells sampled. However, seven of the compounds and products were detected in groundwater samples from seven wells (wells 5, 32, 34, 45, 47, 48, and 49) (fig. 10, table 5). At most, six compounds were detected in a single sample (well 47). Two sulfamethoxazole detections, two methylbenotriazole detections, and the famotidine detection had estimated concentrations reported by the NWQL (table 5). Potential reasons for signifying an estimated (E) value were possible matrix interference, the quality control sample results were out of range, or the sample result did not meet set laboratory reporting matrices (Furlong and others, 2014, appendix table 1–3). An estimated concentration was treated as a detection in this analysis.

Carbamazepine and sulfamethoxazole were the most commonly detected compounds, each being detected in samples from four wells. These two compounds were also among the most frequently detected compounds in studies of pharmaceutical compounds and personal-care products in other groundwater settings (Bexfield and others, 2019; Elliott and others, 2018), including the nearby Fountain Creek



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 9. Sources and processes affecting nitrate in groundwater, based on data collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 10. Detections of pharmaceutical compounds and personal-care products in groundwater from the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

alluvial aquifer (Newman and others, 2021). The pharmaceutical compounds and personal-care products detected in the UBSB wells have a variety of uses. Carbamazepine is an anti-epileptic; sulfamethoxazole is an antibiotic; fluconazole is a fungicide; carisoprodol and metaxalone are muscle relaxants; methylbenotriazole is a corrosion inhibitor, deicer, and used as a component in soaps; and famotidine is an antacid (National Center for Biotechnology Information [NCBI], 2021).

The presence of these compounds in groundwater of the UBSB alluvial aquifer indicates a likely contribution of sewage and (or) septic system water, and the compounds for this study can be considered as wastewater-indicator compounds (Glassmeyer and others, 2005). Wells 45−49 are near or downgradient from the same WWTP discussed in the “Nitrate Isotopes” section of this report (fig. 11). Detections for these wells, in addition to the isotopic composition of nitrate for wells 47−49, are consistent with a contribution from effluent seepage to groundwater. In particular, detections of carbamazepine and sulfamethoxazole at wells 47−49 are consistent with results from other studies indicated the effects of wastewater on groundwater quality (Godfrey and others, 2007; Barnes and others, 2008; Elliott and others, 2018). Continual loading of carbamazepine to the alluvial aquifer, and (or) persistence of this compound through time, is indicated by detections in each of the three annual samples collected from well 49 (table 5). The wells located downgradient from the WWTP (wells 47−49) are the only wells with multiple pharmaceutical compounds detected in a single sample. Wells 5, 32, 34, and 45 had single detections (fig. 10). The variable occurrences of the compounds could be linked to differences in individual sources, degradation of compounds, and properties of transport (Newman and others, 2021). Although pharmaceutical compounds and personal-care products were only detected in about 15 percent of wells and detected concentrations were low, the presence of these compounds in the groundwater in the alluvial aquifer supports nitrate concentrations and isotopes as indicators of the effects of human activities on groundwater quality in the UBSB alluvial aquifer.

Selenium and Uranium

Selenium and uranium are two trace elements of concern for water quality in much of Colorado because of the interaction between irrigated agriculture, a semiarid climate, and Cretaceous marine shales and limestones that weather to release these constituents to surface water and groundwater (Bern and Stogner, 2017; Bern and others, 2020a). Selenium concentrations greater than 6.0 µg/L were found at wells located along the main channel of the alluvium, most commonly at the southernmost end of the aquifer (fig. 12, table 4). None of the selenium concentrations exceeded the 50 µg/L MCL (EPA, 2020a). Uranium concentrations greater than 6.0 µg/L were found at wells in the western reaches of the alluvium, along with the downgradient part of the aquifer associated with WWTP effluent (fig. 13, table 4). The maximum concentration of uranium was 17.6 µg/L (well 21), which is roughly half of the MCL of 30 µg/L (fig. 13, table 4; EPA, 2020a). Well 44 was the only well to have both selenium and uranium concentrations exceed 6.0 µg/L (figs. 12 and 13; table 4).

Water Isotopes

Groundwater samples were analyzed for stable isotope ratios of hydrogen (δD) and oxygen ($\delta^{18}O$) in water to provide information about potential sources of groundwater recharge and hydrologic processes such as evaporation and mixing (Clark and Fritz, 1997). Just as stable isotope ratios for Denver Basin aquifers were not significantly correlated with age-tracer results (Musgrove and others, 2014), neither were age-tracer results from Wellman and Rupert (2016) correlated, using a Pearson correlation (p=0.21), to stable isotope ratios measured for the same wells sampled in 2018–20 for this study. The 2018–20 isotopic data for groundwater samples from the UBSB alluvial aquifer plotted between the Global Meteoric Water Line (Global MWL: $\delta D=8.0*\ \delta^{18}O+10‰$) (Craig, 1961) and the Northeastern Colorado MWL (Harvey, 2005: $\delta D=7.86*\ \delta^{18}O+7.66‰$) (fig. 14). A linear regression line calculated using the 2018–20 δD and $\delta^{18}O$ datasets has a slope comparable to the two MWLs, consistent with meteoric water with only minor evaporative concentration as the likely source of most groundwater recharge to the aquifer (fig. 14). Similarly, Musgrove and others (2014) concluded the stable isotope values for groundwater within the Denver Basin aquifers, including shallow alluvium wells, indicated meteoric water was the primary source of groundwater recharge.

The relatively slight variations in the relation between $\delta^{18}O$ and δD for most groundwater samples may reflect some degree of evaporative effect prior to recharge and (or) climatic conditions during recharge. Evaporation favors the lighter isotopes of oxygen and hydrogen in water and causes heavy isotope enrichment in the water left behind (Bern and others, 2020b). The position of the data point for well 4, enriched and rightward from the regression line for the other wells, indicates more substantial effects of evaporation (fig. 14). Groundwater sampled from well 4 either underwent more substantial evaporative concentration itself or mixed with another source of water that underwent substantial evaporative concentration that was not included in the linear regression (fig. 14).

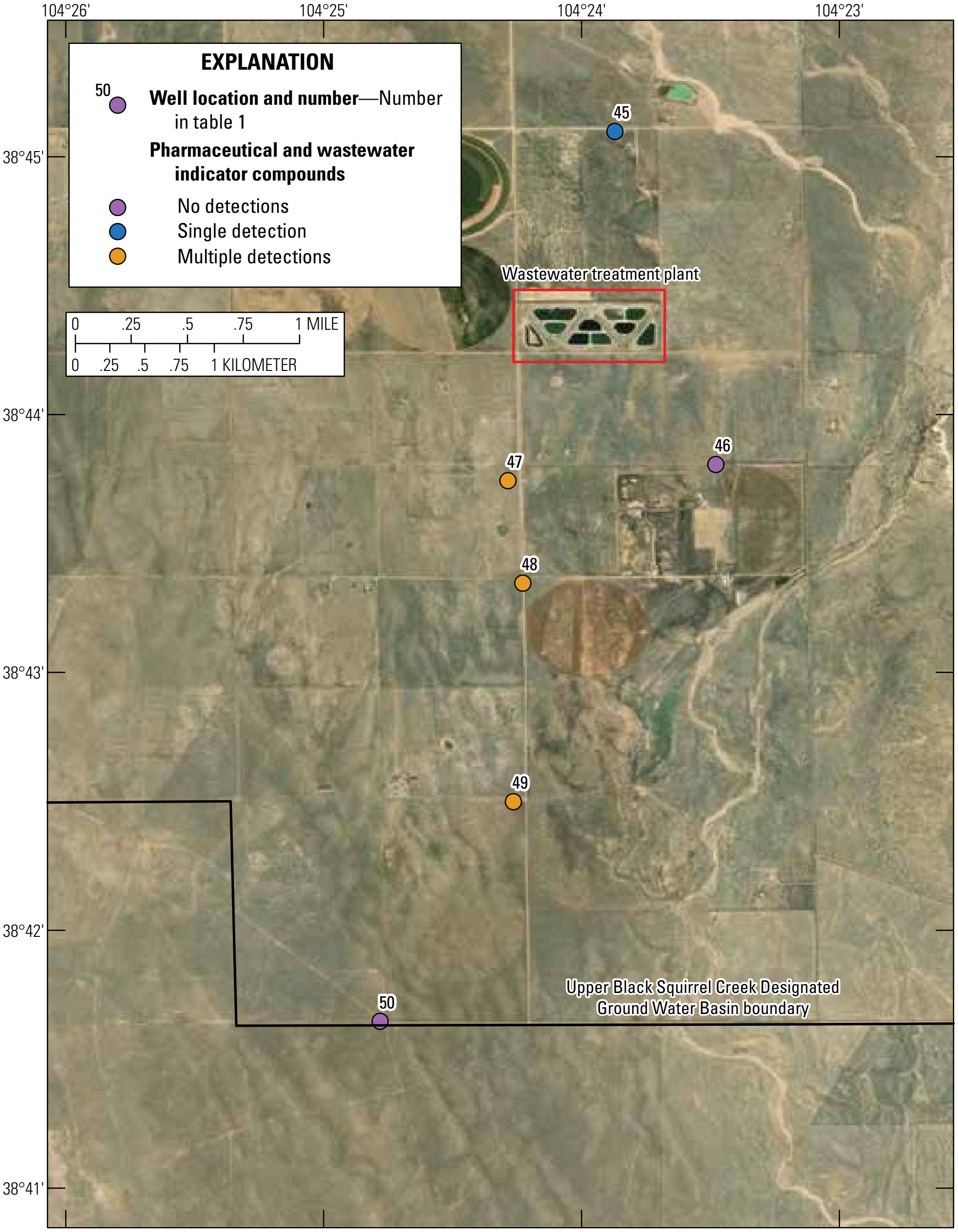


Figure 11. Proximity of wells 45–50 to a wastewater treatment plant installed during 2012, Upper Black Squirrel Creek Designated Ground Water Basin, El Paso County, Colorado.

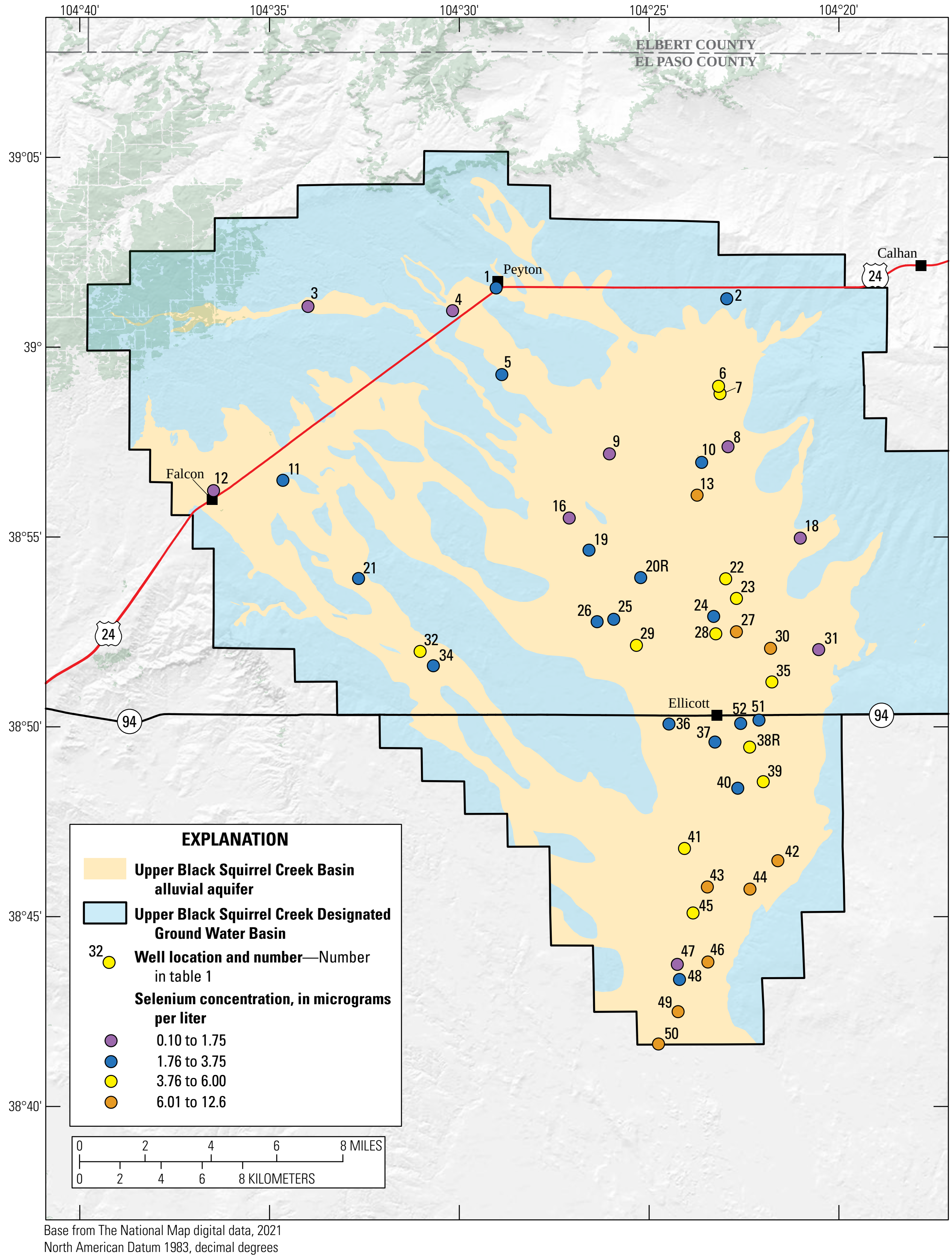
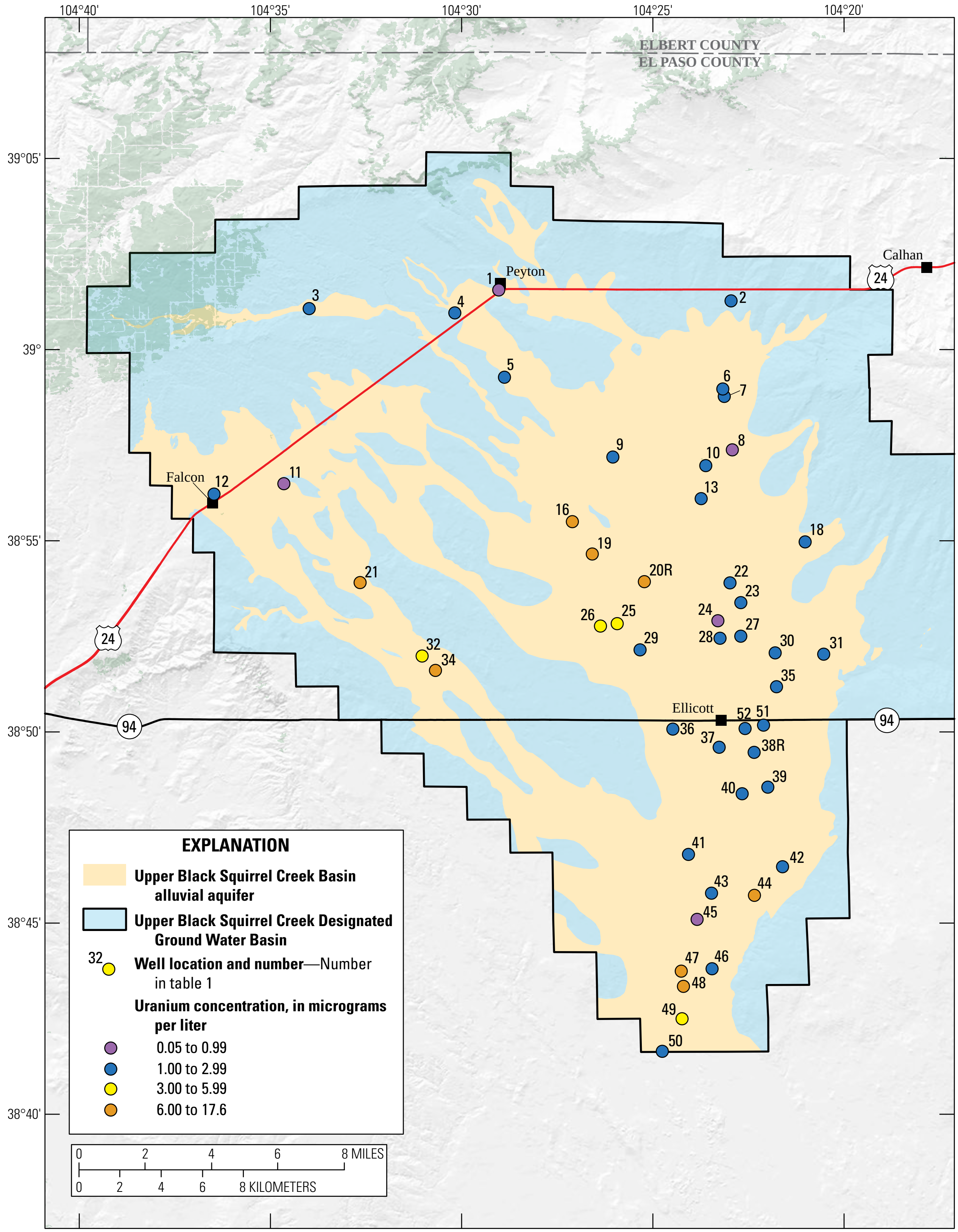


Figure 12. Selenium concentrations in groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 13. Uranium concentrations in groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

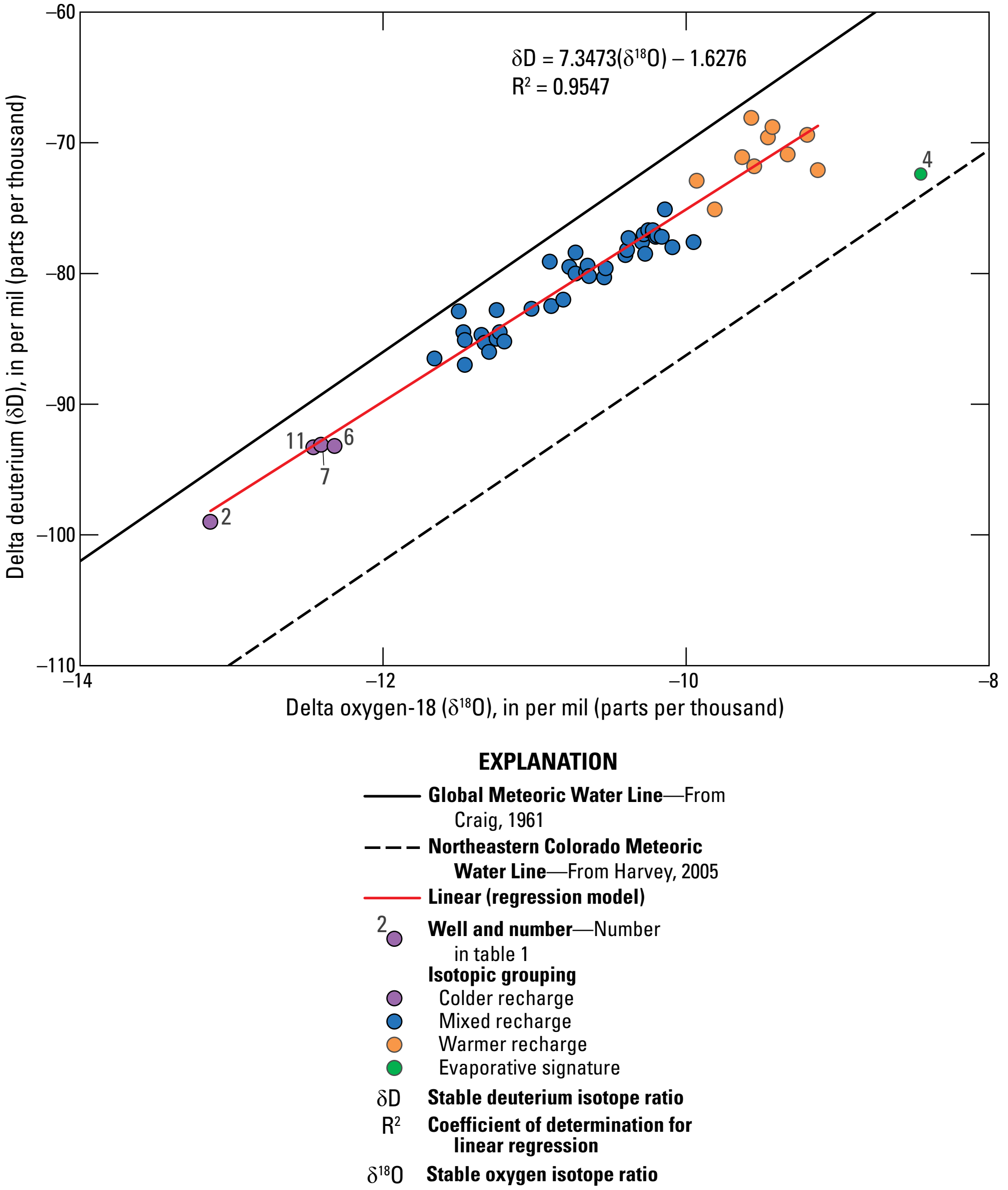
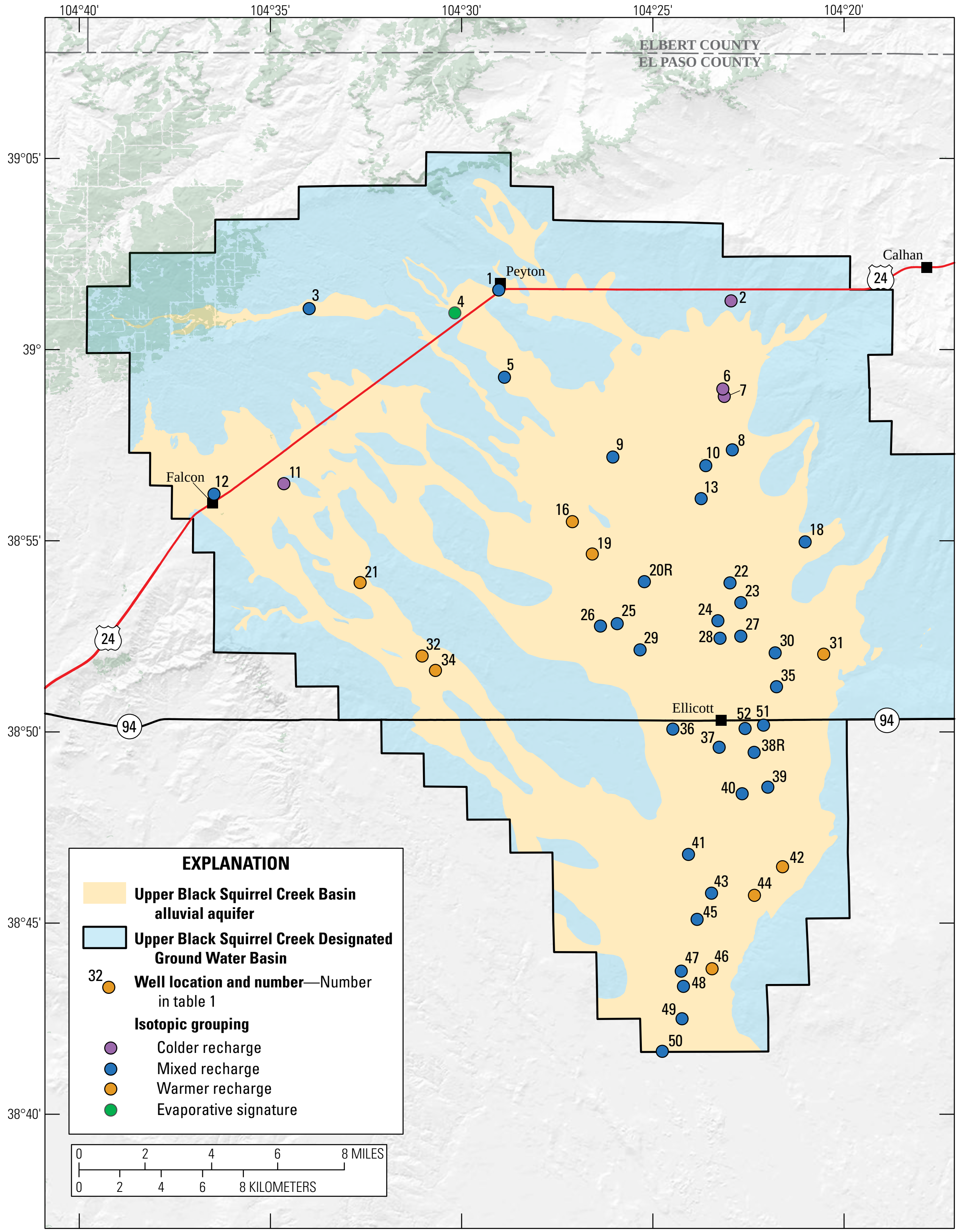


Figure 14. Relation between deuterium and oxygen isotopes for groundwater samples from the Upper Black Squirrel Creek Basin alluvial aquifer and groupings identified from the isotopic data, El Paso County, Colorado, 2018–20.

Isotopic ratios of δD and $\delta^{18}O$ in precipitation samples can be indicative of the temperature and (or) seasonal timing of recharge to an aquifer (fig. 15). More negative (depleted) isotopic ratios are associated with colder temperatures at the time precipitation falls and heavier (more enriched) isotopic ratios are associated with warmer temperatures during precipitation. This pattern can be described using lapse rates for the isotopic composition of precipitation compared to altitude that parallel those for temperature compared to altitude (Poage and Chamberlain, 2001). Using a typical $\delta^{18}O$ lapse rate of 0.85‰ per 1,000 feet altitude (Poage and Chamberlain, 2001), and an altitude range of 5,585 to 7,075 feet North American Vertical Datum of 1988 in the UBSB, $\delta^{18}O$ variation within the basin driven by altitude-associated temperature effects theoretically would have a range of approximately 1.3‰. In contrast, analytical results indicated a range of 3.4‰ for $\delta^{18}O$ in groundwater (−12.5‰ to −9.1‰), which indicates an altitude recharge range spanning approximately 4,000 feet. Because such an altitude range is not present in the basin, the isotopic range could indicate that water has entered the basin from higher altitudes, or there has been mixing with older waters from underlying Denver Basin formations.



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 15. Recharge groupings based on oxygen isotopes for groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado 2018–20.

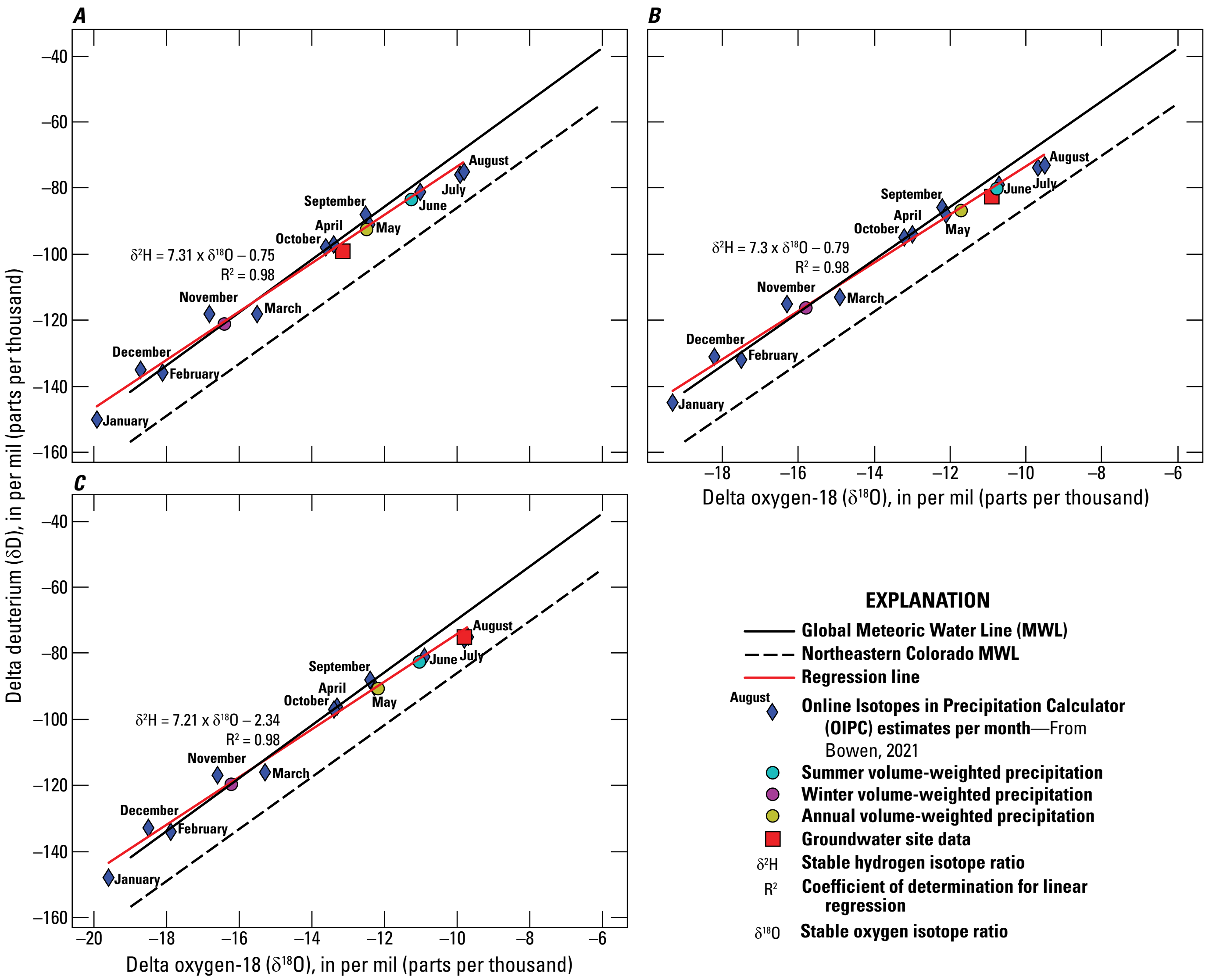


Figure 16. Stable isotopes of precipitation from the Online Isotopes in Precipitation Calculator compared to groundwater collected from (*A*) well 2, (*B*) well 37, and (*C*) well 19 (identification from table 1) during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, 2018–20.

An alternate explanation of the broad spread of the isotopic data (figs. 14 and 16) is spatial variation in seasonality, winter (October–March) compared to summer (April–September), of sources of recharge. Following the approach of Jasechko and others (2014), the seasonality of groundwater recharge was assessed by examining the isotopic composition of groundwater and precipitation throughout the year. Timing of groundwater recharge is associated predominantly with either winter or summer compared with of volume-weighted precipitation composition. Estimates of monthly isotopic composition of local precipitation were obtained from the Online Isotopes in Precipitation Calculator (OIPC) (Bowen and Revenaugh, 2003; Bowen, 2021). Three different location-based estimates were used to make precipitation estimates as comparable as possible to well location (Huntington and others, 2017). Figure 16 shows how groundwater δD and δ^{18}O compared to monthly precipitation estimated by the OIPC (Bowen and Revenaugh, 2003; Bowen, 2021). The more depleted groundwaters as represented by the sample from well 2 (categorized as colder recharge) are comparable to the annual volume-weighted precipitation average (fig. 16*A*), but the majority of the wells, as represented by wells 37 (mixed recharge) and 19 (warmer recharge), are more comparable to the summer volume-weighted precipitation average (figs. 16*B* and *C*). The wells with values more enriched than the summer-volume weighted precipitation average (warmer recharge) (figs. 14 and 15) lie along the perimeter of the aquifer where the alluvium thickness is estimated to be the thinnest in the main channel (Wellman and Rupert, 2016) and indicate a likely relation to the summer monsoon season as a predominant source of recharge (fig. 16). The overall association of most groundwater (mixed or warmer recharge) with expected isotope values for summer precipitation matches with the local climate, given the majority of precipitation falls in April through August. Figures 14 and 15 indicate groundwater throughout the majority of the alluvium (mixed recharge) reflects a mixing of the different recharge timings indicated by the values in figure 16.

Temporal Changes in Groundwater Quality

Assessing temporal changes in groundwater quality throughout the UBSB is crucial to create a better understanding of the geochemical processes and human effects on the alluvial aquifer. An earlier study by Brendle (1997) compared nitrate concentrations observed for groundwater of the UBSCDGWB in 1984 (Buckles and Watts, 1988) and 1996 (Brendle, 1997). The statistical analysis (paired t-test) of nitrate data from 28 of the 36 wells from Buckles and Watts (1988) for which there were data for both the 1984 study and the 1996 study indicated there was no significant difference in the average nitrate concentration between the 1984 study and the 1996 study data (p=0.70). However, the study area was subsequently divided into two subareas for analysis because wells in the northern one-third of the basin showed a different pattern of change in nitrate concentrations compared to wells in the southern two-thirds of the basin. The additional statistical analysis (paired t-tests) indicated nitrate concentrations in the 10 wells sampled in the northern one-third of the basin did not differ significantly between 1984 and 1996 (p= 0.16), but nitrate concentrations in the 18 wells sampled in the southern two-thirds of the basin had increased significantly between the 1984 study and the 1996 study (p<0.01) (Brendle, 1997).

Temporal changes were assessed comparing data from the 2013 study (Phase II results published by Wellman and Rupert [2016]) to the 2018–20 study using similar methods to Brendle (1997). The statistical analysis (paired t-test) of nitrate data from the 46 wells (including replacement wells for 20 and 38) for which there were data for both the 2013 study and the 2018–20 study indicated there was no significant difference in the average concentration between the 2013 study and the 2018–20 study data (p=0.37). Despite the lack of a consistent temporal change between the 2013 study and the 2018–20 study throughout the UBSB alluvial aquifer, there were some localized patterns to changes in nitrate concentrations during this period. The UBSB alluvial aquifer was divided up into the northern one-third (wells 1–19) and the southern two-thirds (wells 20−52). Yet unlike the Brendle (1997) findings, nitrate for the northern one-third of the UBSB had a significant increase in concentration (p=0.03), whereas concentrations for the southern two-thirds of the UBSB did not have a significant difference (p=0.87) between the 2013 study and the 2018–20 study. When evaluating only observations with concentrations greater than 5.0 mg/L as N, 37 samples were analyzed using a paired t-test. The results were comparable to the total dataset with no significant difference observed basinwide (p=0.45); the northern one-third of the UBSB alluvial aquifer had a significant increase in concentration (p=0.01) and no significant difference for the southern two-thirds of the UBSB (p=0.73). Wellman and Rupert (2016) found nitrate concentrations increased in the UBSB from 1985 to the 2013 study using several nonparametric correlation coefficients and the Pearson method (Helsel and others, 2020).

Only seven wells were part of the collection and analyses of Buckles and Watts (1988) from the 1984 study, Brendle (1997) from the 1996 study, Wellman and Rupert (2016) from the 2013 study, and the 2018−20 study. Each of the seven wells were in the southern two-thirds of the basin. For those seven wells (wells 20, 22, 23, 25, 27, 35, and 37), the maximum and median nitrate concentrations increased from the 1984 study to the 1996 study and from the 1996 study to the 2013 study before decreasing in the 2018–20 study. The remaining basinwide results for the 2013 study and the 2018–20 study are only vaguely comparable with the samples discussed in Brendle (1997) with similar spatial coverage of the UBSB alluvial aquifer and all wells finished in the alluvium, yet lack of consistency in the sampling season, well type, updated method of collection, or land use made a more robust statistical analysis impossible. The maximum, basinwide concentration decreased from the 1984 study to the 2013 study before increasing in the 2018−20 study; nitrate concentrations may have decreased, because these statistics are heavily affected by single wells, which could be outliers when compared to the other wells sampled. Median nitrate concentrations increased from 5.1 mg/L as N in the 1984 study to 6.41 mg/L as N in the 2018−20 study. These values are generally considered more representative of typical conditions in the aquifer, yet the variation in seasonality of collection, land-usage change, and creation of new septic fields to go with the growing development may misrepresent the small differences in concentrations observed in aquifer conditions throughout the UBSB alluvial aquifer.

When comparing nitrate concentrations for the same wells sampled in the 2013 study (Wellman and Rupert, 2016) and the 2018−20 study, concentrations in 23 wells increased by at least 0.5 mg/L as N, whereas concentrations for 13 wells decreased by at least 0.5 mg/L as N, and concentrations for 16 wells had no substantial change (less than 0.5 mg/L as N) (figs. 17 and 18). Two wells (51 and 52) sampled in the 2018–20 study were not sampled in 2013 (the Phase II study) and thus were not included in this temporal analysis. Nitrate concentrations in 88 percent of the groundwater samples from the 2013 study (Wellman and Rupert, 2016) were greater than the estimated national background concentration of 1 mg/L (Dubrovsky and others, 2010), compared with 90 percent from the 2018–20 study. There was no discernable change in proportion of nitrate concentrations exceeding this background, yet the absolute proportion remained high through time.

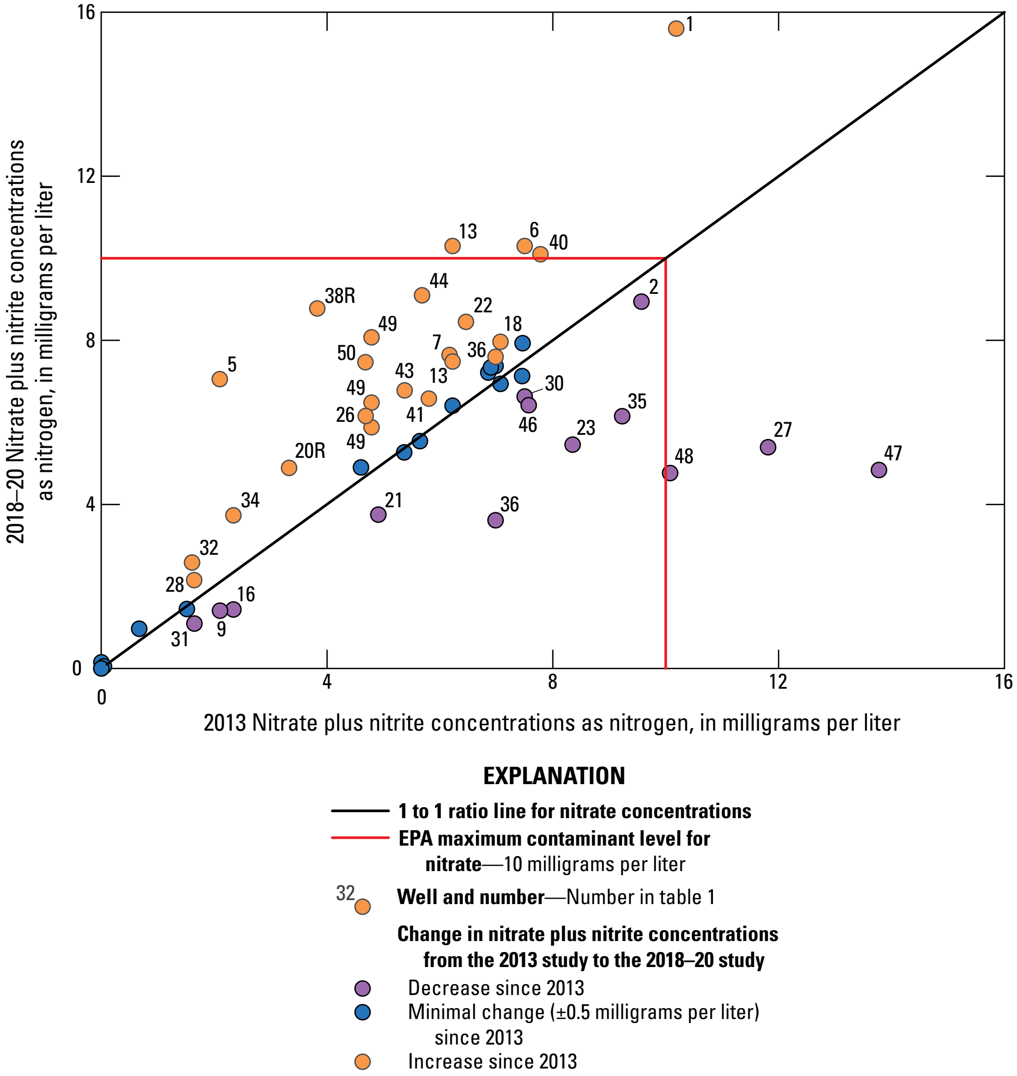
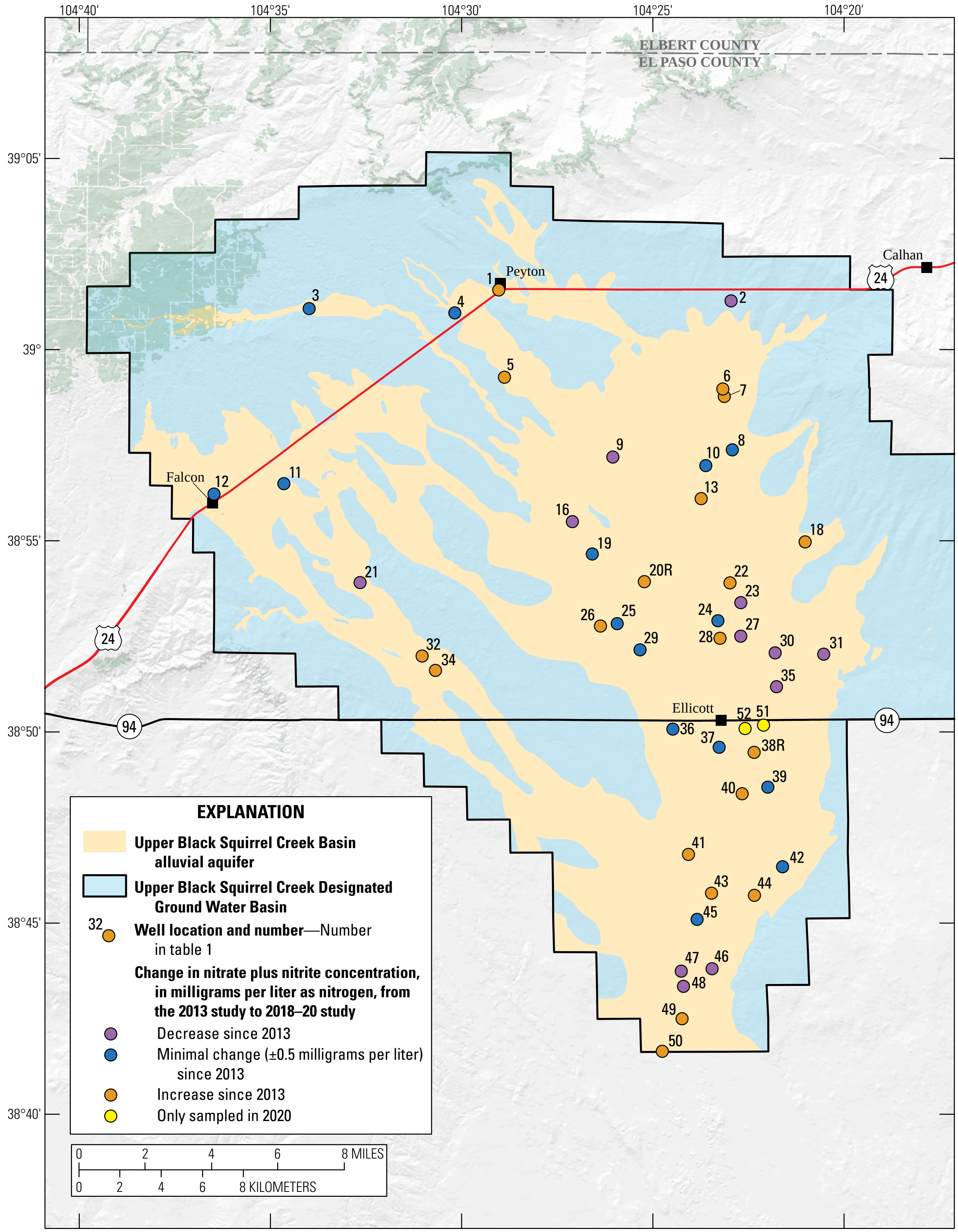


Figure 17. Relation between the 2013 study and the 2018–20 study nitrate plus nitrate concentrations in groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado and compared to U.S. Environmental Protection Agency (EPA) maximum contaminant level.

The percentage of wells with concentrations greater than 5 mg/L as N was higher in the 2018–20 study (67 percent) than in 2013 (54 percent; Wellman and Rupert, 2016). The nitrate results from the 2018–20 study support 2013 findings of a higher probability of nitrate concentrations greater than or equal to 5 mg/L on the most downgradient part of the alluvial aquifer and along the main channel (fig. 7). For example, the decrease in nitrate concentrations in samples from wells 46−48 was likely because of an improvement in processes of removing nitrate from the WWTP effluent upgradient (figs. 11 and 18). Well 1 is the only site to have nitrate concentrations greater than the MCL for the 2013 study and the 2018–20 study (fig. 17). For sites with samples collected annually for the 2018−20 study, variability in nitrate concentrations during this relatively short time period were noted and similarly showed different temporal patterns among wells. Site 13 concentrations decreased each year for 2018-20 but were still greater than concentrations in the 2013 study. Concentrations at site 36 decreased from 2013 to 2018, increased in 2019, and had minimal change in 2020. Finally, site 49 had higher nitrate concentrations in the 2018–20 study than in the 2013 study, with some variability in concentration between each year of sampling (table 4).

Brendle (1997) suggested the variation in nitrate concentrations observed in the UBSCDGWB were because of changes in amount of recharge from precipitation, amount of nitrate mobilized in the aquifer, agricultural practices like manure or fertilizers applied to fields, and (or) quantity and volume of septic effluent. Increases in nitrate concentrations in the alluvial aquifer are expected in areas where nutrient and



Base from The National Map digital data, 2021
North American Datum 1983, decimal degrees

Figure 18. Nitrate plus nitrite concentrations for groundwater collected during sampling of the Upper Black Squirrel Creek Basin alluvial aquifer, El Paso County, Colorado, the 2013 study compared to the 2018–20 study.

water-management practices result in residual nitrate in the soil and nitrate in the unsaturated zone being leached to the water table (Brendle, 1997) and is predominant in agricultural areas seconded by septic fields (Wellman and Rupert, 2016). The lack of a statistically significant trend for the southern two-thirds of the UBSCDGWB for this study contradicts the findings from Brendle (1997) but may have been caused by the increase in nitrate removal from the WWTP between sampling efforts in the 2013 study and the 2018–20 study and decrease in sod production in the area. The northern one-third of the UBSCDGWB has experienced more development since the late 1990s and is the likely cause of the statistically significant increase in nitrate concentrations from the 2013 study and the 2018–20 study. Many of the analyses for individual wells were between two, three, or four data points, and no conclusive interpretations could be identified through time without more sampling at these specific locations. As nitrate concentrations fluctuate in the UBSCDGWB, the individual changes by well could be affected by the potential changes of the sources of nitrate, changes in land use, changes in geochemical conditions that promote denitrification, declines in the water table (Watts, 1995), and increased time since septic fields were installed in new developments (Wellman and Rupert, 2016).

Overall, the continued water-quality sampling of wells in the area would be beneficial to better understand trends and changes in water quality in the UBSB, effects of human activities on groundwater quality, and to indicate the overall sustainability of the alluvial aquifer for use as a resource. Field properties and major-ion data were found to be consistent between the 2013 study (Wellman and Rupert, 2016) and the 2018–20 study throughout the UBSB. In this study, only one constituent, nitrate, had concentrations which exceeded an MCL. For new constituents analyzed in the 2018–20 study (stable isotopes of water, isotopes of nitrate, and pharmaceutical compounds and personal-care products), more data would be needed to properly interpret temporal and spatial differences. For example, variability in pharmaceutical and personal-care product detections could be controlled by the solubility and persistence in the environment of the more than 200 compounds analyzed in addition to the presence or absence of these compounds in point sources. Future interpretations of data from sampled wells would assist in informing land-use decisions that affect groundwater quality and guide long-term planning for water-resource protection, as well as use and management of the groundwater resource in the alluvial aquifer in the UBSB.

Summary

High concentrations of nitrate in the alluvial aquifer of the Upper Black Squirrel Creek Basin (UBSB), about 15 miles east of Colorado Springs, in El Paso County, Colorado, and an increase in urbanization and development within the UBSCDGWB, have led to a greater need to understand changes in groundwater quality of the UBSB alluvial aquifer. In 2018–20, the U.S. Geological Survey, in cooperation with Upper Black Squirrel Creek Ground Water Management District, conducted Phase III of a multiphase plan investigating the groundwater quality in the alluvial aquifer of the UBSB. Main objectives of the study were to assess potential changes in groundwater quality since the 2013 study and to differentiate natural and human sources of nitrate to groundwater. An additional objective was to compare temporal changes in groundwater quality in the 2013 study and the 2018–20 study to results from the 1984 study and the 1996 study. A total of 48 wells were sampled in the 2018–20 study between October and December. Field properties were measured, and samples were analyzed for natural and human source compounds and select isotopes.

The results for major-ion chemistry indicated the alluvial aquifer was predominantly made up of a mixed-cation, mixed-anion water. Along the periphery and thinner fingers of the aquifer, calcium, sodium, and (or) chloride were individually more dominant species in the groundwater, indicating possible mixing of groundwater between the alluvial aquifer and the underlying bedrock aquifers. Minimal concentrations of nitrite, ammonia, and orthophosphate indicated that these three nutrients are not of water-quality concern for the UBSB alluvial aquifer.

Nitrate is the constituent of primary interest in the UBSCDGWB. The U.S. Environmental Protection Agency maximum contaminant level of 10 milligrams per liter (mg/L) for nitrate was exceeded in samples from four wells, and about 67 percent of wells had concentrations greater than 5 mg/L. The median nitrate concentration observed among all wells was 6.4 mg/L. Analysis of groundwater samples collected in 2018–20 for pharmaceutical compounds established a baseline for the UBSB and indicated the likely contribution of wastewater effluent and (or) septic leakage in parts of the aquifer. The isotopic composition of nitrate identified four different potential sources or processes affecting nitrate in the alluvial aquifer including naturally occurring nitrate in the soils, nitrate from animal and (or) human waste, an unknown source, and nitrate removal by denitrification.

Six pharmaceutical compounds and personal-care products were not detected in 85 percent of wells sampled. However, seven of the compounds and products were detected in samples from seven wells, with only three wells having samples with multiple detections. Each of three wells with multiple detections were in the farthest downgradient part of the alluvial aquifer, had an identified nitrate source type of animal and (or) human waste, and were downgradient from a wastewater treatment plant. The presence of these compounds in the groundwater in the alluvial aquifer supports nitrate concentrations and isotopes as indicators of the effects of human activities on groundwater quality in the UBSCDGWB.

Stable isotopes of water indicated meteoric water with a composition that falls between the Global Meteoric Water Line and the Northeastern Colorado Meteoric Water Line is the primary source of recharge to the aquifer. In the UBSB alluvial aquifer, variability in spatial variation in seasonality (winter compared to summer) of recharge sources was evident. Well 4 produced groundwater that underwent more substantial evaporative concentration itself or mixed with another source of water that underwent substantial evaporative concentration. Nine wells along the periphery of the aquifer showed an isotopic signature similar to summer precipitation in particular.

Temporal changes in groundwater quality and the spatial patterns of those changes were assessed by comparing the 2013 study and the 2018–20 study data for many of the same wells, and with earlier data from the 1984 study and the 1996 study for other sampling locations. Some spatial patterns were observed in nitrate concentrations for samples from individual wells. Across the basin, there was not a statistically significant change in nitrate concentration from the 2013 study and the 2018–20 study. The northern third of the basin showed no statistically significant change from the 1984 study and the 1996 study but an increase evident from the 2013 study and the 2018–20 study, whereas the southern two-thirds of the basin showed a statistically significant increase in nitrate concentration from the 1984 study and the 1996 study but showed no significant change from the 2013 study and the 2018–20 study. The available data indicated median nitrate concentrations likely increased from the 1984 study to the 2018−20 study, whereas the maximum concentration increased from the 2013 study and the 2018–20 study but decreased relative to historical data. Nitrate concentration did increase through time from the 1984 study to the 2018−20 study. Changes in land use, changes in geochemical conditions that promote denitrification, declines in the water-table, and increased time since septic fields were installed in new developments are likely causes for these increases or lack thereof. Well 1 was the only site with nitrate concentrations above the maximum contaminant level for the 2013 study and the 2018–20 study. Many of the analyses for individual wells were between two, three, or four data points, and no conclusive interpretations could be identified through time without more sampling at these specific locations.

Physical properties and major-ion chemistry data were similar for the 2013 study and the 2018–20 study. Continued water-quality sampling of wells would be beneficial to better understand trends and changes in water quality in the UBSB, to characterize the effects of human activities on groundwater quality, and to understand the overall sustainability of groundwater in the alluvial aquifer for the intended use as a resource.

References Cited

Angeles, L.F., Mullen, R.A., Huang, I.J., Wilson, C., Khunjar, W., Sirotkin, H.I., McElroy, A.E., and Aga, D.S., 2020, Assessing pharmaceutical removal and reduction in toxicity provided by advanced wastewater treatment systems: Environmental Science. Water Research & Technology, v. 6, no. 1, p. 62–77, accessed September 17, 2021, at https://doi.org/10.1039/C9EW00559E.

Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., and Barber, L.B., 2008, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I. Groundwater: Science of the Total Environment, v. 402, no. 2–3, p. 192–200, accessed September 17, 2021, at https://10.1016/j.scitotenv.2008.04.028.

Bauch, N.J., Moore, J.L., Schaffrath, K.R., and Dupree, J.A., 2012, Water-quality assessment and macroinvertebrate data for the Upper Yampa River watershed, Colorado, 1975 through 2009: U.S. Geological Survey Scientific Investigations Report 2012–5214, 129 p., accessed May 17, 2021, at https://doi.org/10.3133/sir20125214.

Bern, C.R., Holmberg, M.J., and Kisfalusi, Z.D., 2020a, Salt flushing, salt storage, and controls on selenium and uranium—A 31-year mass-balance analysis of an irrigated, semiarid valley: Journal of the American Water Resources Association, v. 56, no. 4, p. 647–668, accessed November 23, 2021, https://doi.org/10.1111/1752-1688.12841.

Bern, C.R., Holmberg, M.J., and Kisfalusi, Z.D., 2020b, Effects of John Martin Reservoir, Colorado on water quality and quantity—Assessment by chemical, isotopic, and mass-balance methods: Journal of Hydrology: X, v. 7, article 100051, 13 p., accessed November 23, 2021, at https://doi.org/10.1016/j.hydroa.2020.100051.

Bern, C.R., and Stogner, R.W.S., Sr., 2017, The Niobrara Formation as a challenge to water quality in the Arkansas River, Colorado, USA: Journal of Hydrology, Regional Studies, v. 12, p. 181–195, accessed November 23, 2021, https://doi.org/10.1016/j.ejrh.2017.05.001.

Bexfield, L.M., Toccalino, P.L., Belitz, K., Foreman, W.T., and Furlong, E.T., 2019, Hormones and pharmaceuticals in groundwater used as a source of drinking water across the United States: Environmental Science & Technology, v. 53, no. 6, p. 2950–2960, accessed August 23, 2021, at https://doi.org/10.1021/acs.est.8b05592.

Bowen, G.J., 2021, OIPC—Online isotopes in precipitation calculator (ver. 3.1): Salt Lake City, Utah, University of Utah, Spatio-Temporal Isotope Analytics Lab website, accessed June 20, 2021, at https://wateriso.utah.edu/waterisotopes/pages/data_access/oipc.html.

Bowen, G.J., and Revenaugh, J., 2003, Interpolating the isotopic composition of modern meteoric precipitation: Water Resources Research, v. 39, no. 10, 13 p., accessed June 20, 2021, at https://doi.org/10.1029/2003WR002086.

Brendle, D.L., 1997, Have nitrate concentrations changed in the Upper Black Squirrel Creek Basin since 1984?: U.S. Geological Survey Fact Sheet FS–072–97, 4 p., accessed February 24, 2021, at https://doi.org/10.3133/fs07297.

Buckles, D.R., and Watts, K.R., 1988, Geohydrology, water quality and preliminary simulations of ground-water flow of the alluvial aquifer in the Upper Black Squirrel Creek Basin, El Paso County, Colorado: U.S. Geological Survey Water-Resources Investigations Report 88–4017, 49 p., accessed February 24, 2021, at https://doi.org/10.3133/wri884017.

Clark, P.F., and Fritz, I.D., 1997, Environmental isotopes in hydrogeology: New York, CRC Press, 328 p., accessed April 26, 2021, at https://doi.org/10.1201/9781482242911.

Colorado Water Conservation Board, 2007, SB06–193 Underground water storage study: Denver, Colo., Colorado Water Conservation Board, 74 p., accessed May 15, 2021, at https://spl.cde.state.co.us/artemis/nrmonos/nr32un22007internet.

Coplen, T.B., Qi, H., Révész, K., Casciotti, K., and Hannon, J.E., 2012, Determination of the δ15N and δ18O of nitrate in water; RSIL lab code 2900, *in* Révész, K., and Coplen, T.B., eds., Methods of the Reston Stable Isotope Laboratory—Stable isotope-ratio methods: U.S. Geological Survey Techniques and Methods, book 10, chap. C17, 35 p., accessed April 26, 2021, at https://pubs.usgs.gov/tm/2006/tm10c17/. [Revised from version 1.0 released in 2007. Supersedes version 1.0 released in 2007.]

Craig, H., 1961, Isotopic variations in meteoric waters: Science, v. 133, no. 3465, p. 1702–1703, accessed April 26, 2021, at https://10.1126/science.133.3465.1702.

DeSimone, L.A., McMahon, P.B., and Rosen, M.R., 2015, The quality of our Nation's waters—Water quality in principal aquifers of the United States, 1991–2010: U.S. Geological Survey Circular 1360, 151 p., accessed February 26, 2021, at https://doi.org/10.3133/cir1360.

Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton, P.A., Hitt, K.J., Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr, N.E., Sprague, L.A., and Wilber, W.G., 2010, The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004: U.S. Geological Survey Circular 1350, 174 p., accessed April 26, 2021, at https://doi.org/10.3133/cir1350.

Elliott, S.M., Erickson, M.L., Krall, A.L., and Adams, B.A., 2018, Concentrations of pharmaceuticals and other micropollutants in groundwater downgradient from large on-site wastewater discharges: PLoS One, v. 13, no. 11, e0206004, accessed August 23, 2021, at https://10.1371/journal.pone.0206004.

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., accessed April 26, 2021, at https://doi.org/10.3133/ofr93125.

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, 545 p., accessed April 26, 2021, at https://doi.org/10.3133/twri05A1.

Fogg, G.E., Rolston, D.E., Decker, D.L., Louie, D.T., and Grismer, M.E., 1998, Spatial variation in nitrogen isotope values beneath nitrate contamination sources: Ground Water, v. 36, no. 3, p. 418–426, accessed June 10, 2021, at https://10.1111/j.1745-6584.1998.tb02812.x.

Foreman, W.T., Williams, T.L., Furlong, E.T., Hemmerle, D.M., Stetson, S.K., Jha, V.K., Noriega, M.C., Decess, J.A., Reed-Parker, C., and Sandstrom, M.W., 2021, Comparison of detection limits estimated using single- and multi-concentration spike-based and blank-based procedures: Talanta, v. 228, 122139, accessed August 23, 2021, at https://10.1016/j.talanta.2021.122139.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, 604 p.

Furlong, E.T., Noriega, M.C., Kanagy, C.J., Kanagy, L.K., Coffey, L.J., and Burkhardt, M.R., 2014, Determination of human-use pharmaceuticals in filtered water by direct aqueous injection–high-performance liquid chromatography/tandem mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B10, 49 p., accessed August 23, 2021, at https://doi.org/10.3133/tm5B10.

Garbarino, J.R., 1999, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99−093, 31 p., accessed February 24, 2021, at https://doi.org/10.3133/ofr9993.

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B1, 88 p., accessed February 24, 2021, at https://doi.org/10.3133/tm5B1.

Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Cahill, J.D., Zaugg, S.D., Werner, S.L., Meyer, M.T., and Kryak, D.D., 2005, Transport of chemical and microbial compounds from known wastewater discharges—Potential for use as indicators of human fecal contamination: Environmental Science & Technology, v. 39, no. 14, p. 5157–5169, accessed August 23, 2021, at https://10.1021/es048120k.

Godfrey, E., Woessner, W.W., and Benotti, M.J., 2007, Pharmaceuticals in on-site sewage effluent and ground water, Western Montana: Ground Water, v. 45, no. 3, p. 263–271, accessed August 23, 2021, at https://10.1111/j.1745-6584.2006.00288.x.

Gurdak, J.J., McMahon, P.B., Dennehy, K.F., and Qi, S.L., 2009, Water quality in the High Plains aquifer, Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming, 1999–2004: U.S. Geological Survey Circular 1337, 63 p., accessed August 23, 2021, at https://doi.org/10.3133/cir1337.

Hansen, W.R., Chronic, J., and Matelock, J., 1978, Climatography of the Front Range Urban Corridor and vicinity, Colorado: U.S. Geological Survey Professional Paper 1019, 59 p., accessed June 10, 2021, at https://doi.org/10.3133/pp1019.

Harvey, F.E., 2005, Stable hydrogen and oxygen isotope composition of precipitation in northeastern Colorado: Journal of the American Water Resources Association, v. 41, no. 2, p. 447–460, accessed June 22, 2021, at https://doi.org/10.1111/j.1752-1688.2005.tb03748.x.

Heaton, T.H.E., 1986, Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere—A review: Chemical Geology, Isotope Geoscience Section, v. 59, p. 87–102, accessed February 23, 2021, at https://10.1016/0168-9622(86)90059-X.

Helsel, D.R., Hirsch, R.M., Ryberg, K.R., Archfield, S.A., and Gilroy, E.J., 2020, Statistical methods in water resources: U.S. Geological Survey Techniques and Methods, book 4, chap. A3, 458 p., accessed October 14, 2021, at https://doi.org/10.3133/tm4A3. [Supersedes USGS Techniques of Water-Resources Investigations, book 4, chap. A3, version 1.1.

Hem, J.D., 1992, Study and interpretation of the chemical characteristics of natural water (3rd ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p., accessed June 22, 2021, at https://pubs.usgs.gov/wsp/wsp2254/html/pdf.html.

Homer, C.G., Dewitz, J.A., Jin, S., Xian, G., Costello, C., Danielson, P., Gass, L., Funk, M., Wickham, J., Stehman, S., Auch, R.F., and Riitters, K.H., 2020, Conterminous United States land cover change patterns 2001–2016 from the 2016 National Land Cover Database: ISPRS Journal of Photogrammetry and Remote Sensing, v. 162, p. 184–199, accessed January 22, 2021, at https://10.1016/j.isprsjprs.2020.02.019.

Huntington, J., Hegewisch, K., Daudert, B., Morton, C., Abatzoglou, J., McEvoy, D., and Erickson, T., 2017, Climate Engine—Cloud computing of climate and remote sensing data for advanced natural resource monitoring and process understanding: Bulletin of the American Meteorological Society, v. 98, no. 11, p. 2397–2410, accessed June 6, 2021, at https://10.1175/BAMS-D-15-00324.1.

Jackson, R.B., Berthrong, S.T., Cook, C.W., Jobbagy, E.G., and McCulley, R.L., 2004, Comment on “a reservoir of nitrate beneath desert soils”: Science, v. 304, no. 5667, p. 51, accessed January 22, 2021, at https://10.1126/science.1094294.

Jasechko, S., Birks, S.J., Gleeson, T., Wada, Y., Fawcett, P.J., Sharp, Z.D., McDonnell, J.J., and Welker, J.M., 2014, The pronounced seasonality of global groundwater recharge: Water Resources Research, v. 50, no. 11, p. 8845–8867, accessed June 6, 2021, at https://10.1002/2014WR015809.

Kendall, C., 1998, Tracing nitrogen sources and cycling in catchments, *in* Kendall, C., and McDonnell, J.J., eds., Isotope tracers in catchment hydrology: Amsterdam, Elsevier, p. 519–576, accessed June 6, 2021, at https://doi.org/10.1016/B978-0-444-81546-0.50023-9.

Kendall, C., Doctor, D.H., and Young, M.B., 2014, Environmental isotope applications in hydrologic studies: Treatise on Geochemistry, v. 7, no. 9, p. 273–327, accessed June 6, 2021, at https://10.1016/B978-0-08-095975-7.00510-6.

LeBlanc, D., 2006, Cape Cod Toxic substances hydrology research site: U.S. Geological Survey Fact Sheet 2006–3096, 2 p., accessed June 6, 2021, at https://pubs.usgs.gov/fs/2006/3096/.

McGovern, H.E., and Jenkins, E.D., 1966, Ground water in Black Squirrel Creek valley, El Paso County, Colorado: U.S. Geological Survey Hydrologic Investigations Atlas HA–236, 1 sheet, scale 1:62,500, accessed January 22, 2021, at https://doi.org/10.3133/ha236.

McMahon, P.B., and Chapelle, F.H., 2008, Redox processes and water quality of selected principal aquifer systems: Ground Water, v. 46, no. 2, p. 259–271, accessed August 16, 2021, at https://10.1111/j.1745-6584.2007.00385.x.

Mueller, D.K., Schertz, T.L., Martin, J.D., and Sandstrom, M.W., 2015, Design, analysis, and interpretation of field quality-control data for water-sampling projects: U.S. Geological Survey Techniques and Methods, book 4, chap. C4, 54 p., accessed January 22, 2021, at https://doi.org/10.3133/tm4C4.

Musgrove, M., Beck, J.A., Paschke, S.S., Bauch, N.J., and Mashburn, S.L., 2014, Quality of groundwater in the Denver Basin aquifer system, Colorado, 2003–5: U.S. Geological Survey Scientific Investigations Report 2014–5051, 107 p., accessed June 23, 2021, at https://doi.org/10.3133/sir20145051.

National Center for Biotechnology Information [NCBI], 2021, PubChem: Bethesda, Md., National Institutes of Health, National Center for Biotechnology Information online database, accessed October 12, 2021, at https://pubchem.ncbi.nlm.nih.gov/.

Newman, C.P., Paschke, S.S., and Keith, G., 2021, Natural and anthropogenic geochemical tracers to investigate residence times and groundwater–surface-water interactions in an urban alluvial aquifer: Water, v. 13, no. 6, article 871, 30 p., accessed June 23, 2021, at https://doi.org/10.3390/w13060871.

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C.U., Jr., and Mohan, D., 2019, Pharmaceuticals of emerging concern in aquatic systems—Chemistry, occurrence, effects, and removal methods: Chemical Reviews, v. 119, no. 6, p. 3510–3673, accessed August 23, 2021, at https://10.1021/acs.chemrev.8b00299.

Patton, C.J., and Kryskalla, J.R., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of alkaline persulfate digestion as an alternative to kjeldahl digestion for determination of total and dissolved nitrogen and phosphorus in water: Water-Resources Investigations Report 03–4174, 33 p., accessed August 23, 2021, at https://doi.org/10.3133/wri034174.

Patton, C.J., and Kryskalla, J.R., 2011, Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods: U.S. Geological Survey Techniques and Methods, book 5, chap. B8, 34 p., accessed June 23, 2021, at https://doi.org/10.3133/tm5B8.

Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: Transactions - American Geophysical Union, v. 25, no. 6, p. 914–923, accessed January 13, 2021, at https://10.1029/TR025i006p00914.

Poage, M.A., and Chamberlain, C.P., 2001, Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters—Considerations for studies of paleoelevation change: American Journal of Science, v. 301, no. 1, p. 1–15, accessed June 10, 2021, at https://10.2475/ajs.301.1.1.

Révész, K., Böhlke, J.K., and Yoshinari, T., 1997, Determination of δ18O and δ15N in nitrate: Analytical Chemistry, v. 69, no. 21, p. 4375–4380.

Révész, K., and Coplen, T.B., 2008a, Determination of the δ(2H/1H) of water—RSIL lab code 1574, *in* Révész, K., and Coplen, T.B., eds., Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods, book 10, chap. C1, 27 p., accessed February 24, 2021, at https://doi.org/10.3133/tm10C1.

Révész, K., and Coplen, T.B., 2008b, Determination of the δ(18O/16O) of water—RSIL lab code 489, *in* Révész, K., and Coplen, T.B., eds., Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods, book 10, chap. C2, 28 p., accessed February 24, 2021, at https://doi.org/10.3133/tm10C2.

Swenson, H.A., and Baldwin, H.L., 1965, A primer on water quality: Washington, D.C., U.S. Geological Survey General Interest Publication, 27 p., accessed February 24, 2021, at https://doi.org/10.3133/7000057.

Topper, R., 2008, Upper Black Squirrel Creek Basin aquifer recharge and storage evaluation: Colorado Geological Survey, prepared for the El Paso County Water Authority, accessed June 21, 2021, https://coloradogeologicalsurvey.org/publications/upper-black-squirrel-creak-basin-aquifer-recharge-storage-evaluation/.

Topper, R., and Horn, A., 2011, El Paso County groundwater quality study phase 1: Colorado Geological Survey, prepared for the El Paso Groundwater Quality Study Committee for presentation to the El Paso County Board of County Commissioners, accessed June 21, 2021, https://coloradogeologicalsurvey.org/publications/el-paso-groundwater-quality/.

Tweto, O., comp., 1979, Geologic map of Colorado: U.S. Geological Survey, 1 sheet, scale 1:500,000.

Upper Black Squirrel Creek Ground Water Management District, 2021, Rules and regulations and statement of policy—As amended through February 3, 2021: Colorado Department of Natural Resources, Division of Water Resources, 17 p., accessed June 9, 2021, at https://upperblacksquirrelcreekwater.com/media/documents/regulatory/rules_2009.pdf.

U.S. Census Bureau, 2021, Colorado quick facts: U.S. Census Bureau web page, accessed March 4, 2021, at https://www.census.gov/quickfacts/fact/table/CO/PST120219.

U.S. Environmental Protection Agency, [EPA], 2020a, National primary drinking water regulations: U.S. Environmental Protection Agency web page, accessed October 10, 2020, at https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.

U.S. Environmental Protection Agency, [EPA], 2020b, Secondary drinking water standards—Guidance for nuisance chemicals: U.S. Environmental Protection Agency web page, accessed October 12, 2020, at https://www.epa.gov/sdwa/secondary-drinking-water-standards-guidance-nuisance-chemicals.

U.S. Geological Survey [USGS], 2021, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed March 10, 2021, at https://doi.org/10.5066/F7P55KJN.

U.S. Geological Survey [USGS], [variously dated], National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, 10 chap. (A1–A10), accessed June 25, 2021, at https://doi.org/10.3133/twri09.

Ward, M.H., Jones, R.R., Brender, J.D., De Kok, T.M., Weyer, P.J., Nolan, B.T., Villanueva, C.M., and Van Breda, S.G., 2018, Drinking water nitrate and public health—An updated review: International Journal of Environmental Research and Public Health, v. 15, no. 7, 1,557 p., accessed October 10, 2020, at https://doi.org/10.3390/ijerph15071557.

Watts, K.R., 1995, Hydrogeology and simulation of flow between the alluvial and bedrock aquifers in the Upper Black Squirrel Creek Basin, El Paso County, Colorado: U.S. Geological Survey Water-Resources Investigations Report 94–4238, 82 p., accessed February 10, 2021, at https://doi.org/10.3133/wri944238.

Wellman, T.P., and Rupert, M.G., 2016, Groundwater quality, age, and susceptibility and vulnerability to nitrate contamination with linkages to land use and groundwater flow, Upper Black Squirrel Creek Basin, Colorado, 2013: U.S. Geological Survey Scientific Investigations Report 2016–5020, 78 p., accessed October 10, 2020, at https://doi.org/10.3133/sir20165020.

Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998, Ground water and surface water a single resource: U.S. Geological Survey Circular 1139, 79 p., accessed January 14, 2021, at https://doi.org/10.3133/cir1139.

Publishing support provided by the Science Publishing Network,
Denver Publishing Service Center

For more information concerning the research in this report, contact the
Director, USGS Colorado Water Science Center
Box 25046, Mail Stop 415
Denver, CO 80225
(303) 236-6900
Or visit the Colorado Water Science Center website at
https://www.usgs.gov/centers/co-water

Publishing support provided by the Science Publishing Network,
Denver and Lafayette Publishing Service Centers

Kisfalusi and others—**Characterization of and Temporal Changes in Groundwater Quality of the Upper Black Squirrel Creek Basin, 2018–20**—SIR 2022–5061

ISBN 978-1-4113-4474-7

ISSN 2328-031X (print)
ISSN 2328-0328 (online)
https://doi.org/10.3133/sir20225061