Prepared in cooperation with the Colorado Department of Public Health and Environment

Use of Diverse Geochemical Data Sets to Determine Sources and Sinks of Nitrate and Methane in Groundwater, Garfield County, Colorado, 2009

Scientific Investigations Report 2010–5215

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

COLLAGE (LEFT TO RIGHT)

Horses near a domestic well, Garfield County, Colorado. Photograph by Peter McMahon, U.S. Geological Survey.

Livestock grazing in a pasture, Garfield County, Colorado. Photograph by Jim Collins, U.S. Geological Survey.

Drilling operation for a natural gas well, Garfield County, Colorado. Photograph by Jim Collins, U.S. Geological Survey.

FRONT COVER

Top

U.S. Geological Survey hydrologist measuring dissolved-oxygen concentrations in water from a domestic well, Garfield County, Colorado. Photograph by Peter McMahon, U.S. Geological Survey.

Bottom

U.S. Geological Survey hydrologists preparing to sample a domestic well, Garfield County, Colorado. Photograph by Jim Collins, U.S. Geological Survey.

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U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

Suggested citation:
McMahon, P.B., Thomas, J.C., and Hunt, A.G., 2011, Use of diverse geochemical data sets to determine sources and sinks of nitrate and methane in groundwater, Garfield County, Colorado, 2009: U.S. Geological Survey Scientific Investigations Report 2010–5215, 40 p.

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Volume	
liter (L)	0.2642	gallon (gal)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)

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

$$°F=(1.8×°C)+32$$

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

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

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

Abbreviations and Acronyms

‰	per mil or parts per thousand
^{14}C	carbon-14
^{3}H	tritium
^{4}He	helium-4
$^{4}He_{a}$	helium-4 in water derived from excess air
$^{4}He_{s}$	total helium-4 in a water sample
$^{4}He_{eq}$	helium-4 in water derived from air-water equilibrium
$^{4}He_{sol}$	rate at which helium-4 enters solution
$4He_{terr}$	terrigenic helium-4
cm^3 STP/g	cubic centimeters at standard temperature and pressure, per gram of water
cm^3 STP/g·yr	cubic centimeters at standard temperature and pressure, per gram of water, per year
cm^3 STP He/cm^2·yr	cubic centimeters of helium at standard temperature and pressure, per square centimeter, per year
CFC	chlorofluorocarbon
CH_4	methane
CO_2	carbon dioxide
GMWL	global meteoric water line
J	helium flux
MCL	Maximum Contaminant Level
mg/L as N	milligrams per liter as nitrogen
mm/yr	millimeters per year
n	porosity
N_2	nitrogen gas
NO_3	nitrate
O_2	dissolved oxygen
ppm	parts per million
ρ_s	rock bulk density
ρ_w	density of water
R_A	helium-3/helium-4 ratio in air
SF_6	sulfur hexafluoride
TU	tritium units
USGS	U.S. Geological Survey
VPDB	Vienna Peedee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

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Abstract

Previous water-quality assessments reported elevated concentrations of nitrate and methane in water from domestic wells screened in shallow zones of the Wasatch Formation, Garfield County, Colorado. In 2009, the U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, analyzed samples collected from 26 domestic wells for a diverse set of geochemical tracers for the purpose of determining sources and sinks of nitrate and methane in groundwater from the Wasatch Formation.

Nitrate concentrations ranged from less than 0.04 to 6.74 milligrams per liter as nitrogen (mg/L as N) and were significantly lower in water samples with dissolved-oxygen concentrations less than 0.5 mg/L than in samples with dissolved-oxygen concentrations greater than or equal to 0.5 mg/L. Chloride/bromide mass ratios and tracers of groundwater age (tritium, chlorofluorocarbons, and sulfur hexafluoride) indicate that septic-system effluent or animal waste was a source of nitrate in some young groundwater (less than 50 years), although other sources such as fertilizer also may have contributed nitrate to the groundwater. Nitrate and nitrogen gas (N_2) concentrations indicate that denitrification was the primary sink for nitrate in anoxic groundwater, removing 99 percent of the original nitrate content in some samples that had nitrate concentrations greater than 10 mg/L as N at the time of recharge.

Methane concentrations ranged from less than 0.0005 to 32.5 mg/L and were significantly higher in water samples with dissolved-oxygen concentrations less than 0.5 mg/L than in samples with dissolved-oxygen concentrations greater than or equal to 0.5 mg/L. High methane concentrations (greater than 1 mg/L) in some samples were biogenic in origin and appeared to be derived from a relatively deep source on the basis of helium concentrations and isotopic data. One such sample had water-isotopic and major-ion compositions similar to that of produced water from the underlying Mesaverde Group, which was the primary natural-gas producing interval in the study area. Methane in the Mesaverde Group was largely thermogenic in origin so biogenic methane in the sample probably was derived from deeper zones in the Wasatch Formation. The primary methane sink in the aquifer appeared to be methane oxidation on the basis of dissolved-oxygen and methane concentrations and methane isotopic data.

The diverse data sets used in this study enhance previous water-quality assessments by providing new and more complete insights into the sources and sinks of nitrate and methane in groundwater. Field measurements of dissolved oxygen in groundwater were useful indicators of the Wasatch Formation's vulnerability to nitrate and methane contamination or enrichment. Results from this study also provide new evidence for the movement of water, ions, and gases into the shallow Wasatch Formation from sources such as the Mesaverde Group and deeper Wasatch Formation.

Introduction

Nitrate, methane, and a few other chemical constituents were detected in relatively high concentrations in water from domestic wells screened in shallow zones of the Wasatch Formation, Garfield County, Colorado during previous water-quality assessments (URS Corporation, 2006; Papadopulos & Associates, Inc., 2008). In 2009, the U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, analyzed samples collected from 26 domestic wells for a diverse set of geochemical tracers for the purpose of determining sources and sinks of nitrate and methane in groundwater from the Wasatch Formation. Interpretations regarding possible sources and sinks of those constituents are important because they could help water managers understand why and where groundwater is vulnerable to certain types of contamination. Interpretations based on a relatively limited set of chemical indicators or tracers could have large uncertainties if the sources and sinks of chemicals in groundwater are complex, or if the chemical tracers on which interpretations are based have been altered by subsurface processes. Other environmental tracers that could be helpful in these circumstances include reduction/oxidation (redox) constituents (Chapelle and others, 1995; McMahon and Chapelle, 2008), stable isotopes of water (Böhlke and others, 2007; Landon and others, 2008), tracers of groundwater age (Manning and others, 2005; Rupert and Plummer, 2009), and dissolved noble gases (Zhou and others, 2005; Sherwood Lollar and Ballentine, 2009). Each of those tracers measures different processes and when used in combination, the diverse data sets can sometimes provide new and more complete insights into the sources and sinks of chemical constituents in groundwater.

Purpose and Scope

The purpose of this report was to determine sources and sinks of nitrate and methane in groundwater from the Wasatch Formation in Garfield County, Colorado, by use of diverse data sets that included concentrations of major ions, nutrients, redox constituents, and noble gases, hydrocarbon molecular and isotopic compositions, water isotopic compositions, and tracers of groundwater age. The study area is located between Silt and Rifle, Colorado (fig. 1). Twenty-six domestic wells were sampled for this broad suite of chemical and isotopic tracers (fig. 2). Ten wells were located north of the Colorado River and sampled in April 2009. Sixteen wells were located south of the river and sampled in April and October 2009.

Description of Study Area

The study area is located between Silt and Rifle, Colorado (fig. 1). The mean annual air temperature in Rifle, Colorado, was 8.7°C for the period 1910 to 2007, and mean annual precipitation was 29.4 cm (High Plains Regional Climate Center, 2010). The elevation of sampling locations ranged from 1,672 to 2,155 m. Mean annual precipitation and air temperatures at the highest-elevation sites are likely to be wetter and colder than sampling sites at lower elevations.

The primary geologic units of interest in the study were the Williams Fork and Wasatch Formations. The Williams Fork Formation, part of the Mesaverde Group, consists of mostly fluvial sedimentary rock of Late Cretaceous age (Johnson and Rice, 1990). Most natural gas wells in the study area were completed in the Williams Fork Formation at depths of about 1,830 to 3,050 m below ground surface (URS Corporation, 2006), but deeper sandstones in the Mesaverde Group and pre-Cretaceous sedimentary rock below the Mesaverde Group also produce gas (Johnson and Rice, 1990). The Wasatch Formation is the primary bedrock unit at land surface in the study area. The Wasatch Formation consists of mostly fluvial sedimentary rock of Tertiary age (Paleocene and Eocene) (Donnell, 1969). Most domestic wells in the study area were screened in the Wasatch Formation at depths generally less than 185 m below land surface. The thickness of the Wasatch Formation ranges from about 365 m near the southern end of the Divide Creek anticline to more than 1,710 m along the west side of the study area (URS Corporation, 2006). The Divide Creek anticline, located in the southeastern part of the study area, plunges into the central part of the study area (Hoak and Klawitter, 1977; Grout and Verbeek, 1992; URS Corporation, 2006). Structural features (for example, faults and fractures) associated with the anticline may be important pathways for water or gas movement, or both, from deeper to shallower zones in the area (URS Corporation, 2006).

Static water levels in the Wasatch Formation reported in drillers' logs ranged from about 0 to 105 m below land surface, with a mean of 22 m (URS Corporation, 2006). The primary sources of recharge to the Wasatch Formation were precipitation in upland areas and irrigation at lower elevations. In general, groundwater flow in the study area is probably topography controlled, moving from upland areas to local streams and springs. The Colorado River is interpreted as the regional discharge area for groundwater in the Wasatch Formation (URS Corporation, 2006).

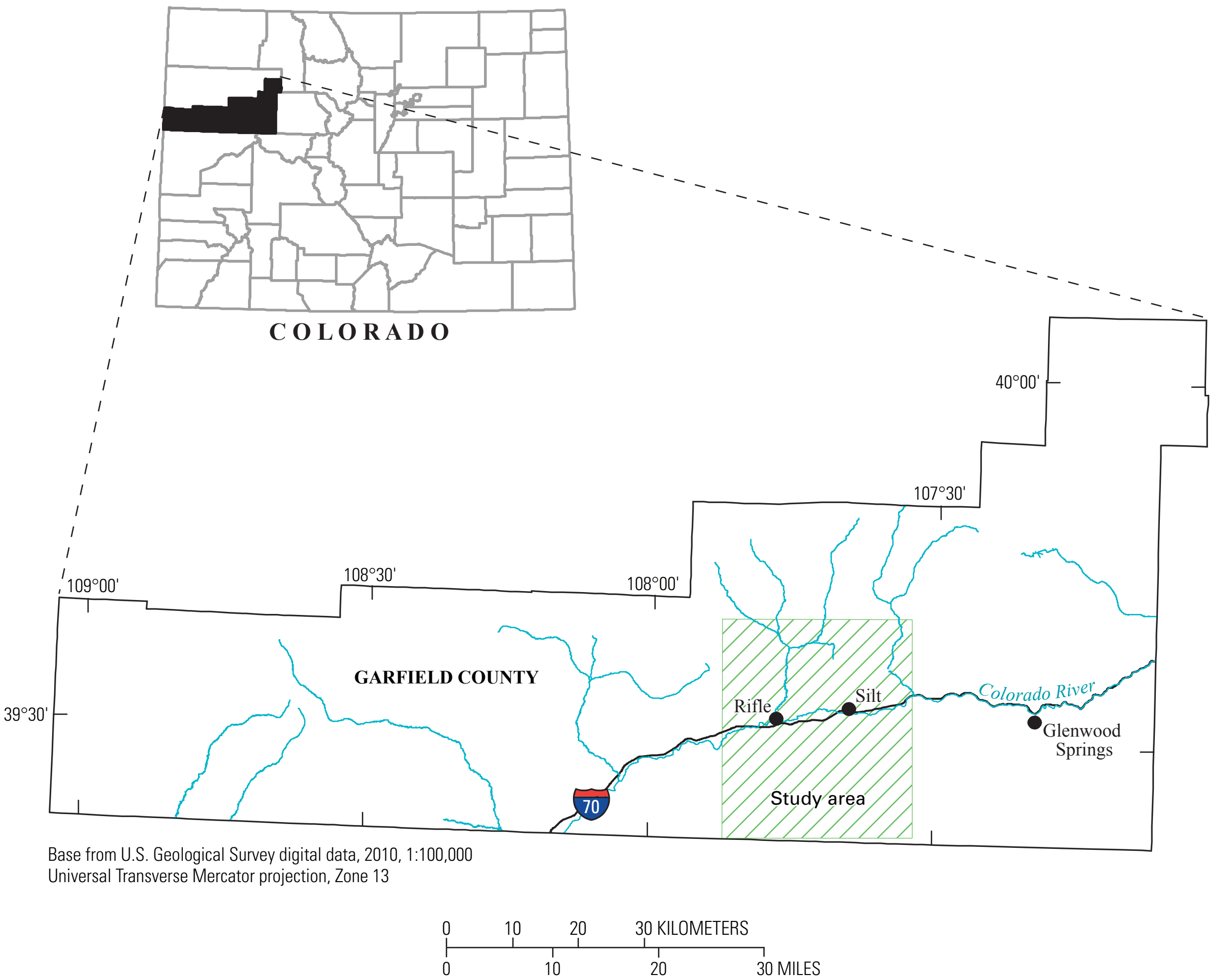
More detailed descriptions of the geology and hydrology, as well as the natural gas production history of the study area, can be found in Johnson and Rice (1990), Shroba and Scott (1997, 2001), URS Corporation (2006), and Papadopulos & Associates, Inc. (2008).

Study Methods

Water samples were collected from 26 domestic wells in April and October 2009. Wells were selected to provide relatively broad spatial coverage of the aquifer north and south of the Colorado River. Sixteen wells were located south of the river and 10 wells were located north of the river (fig. 2). Several criteria had to be met before a well was selected for sampling. The criteria included (1) well owner permission to sample, (2) availability of information on well depth, top and bottom of screened interval, and depth to water at time of drilling, (3) availability of information showing geology of the screened interval, and (4) availability of a sampling point on the well upstream from any pressure tank or treatment device.

Sample Collection

Water samples were collected from the well discharge after readings of specific conductance, pH, temperature, turbidity, and dissolved-oxygen concentration had become stable (as defined by Koterba and others, 1995). Three general groups of samples were collected: (1) inorganic ions, (2) stable isotopes and dissolved gases, and (3) environmental tracers of groundwater age. Processing chambers were used during the collection and preservation of samples to reduce airborne contamination in the samples.



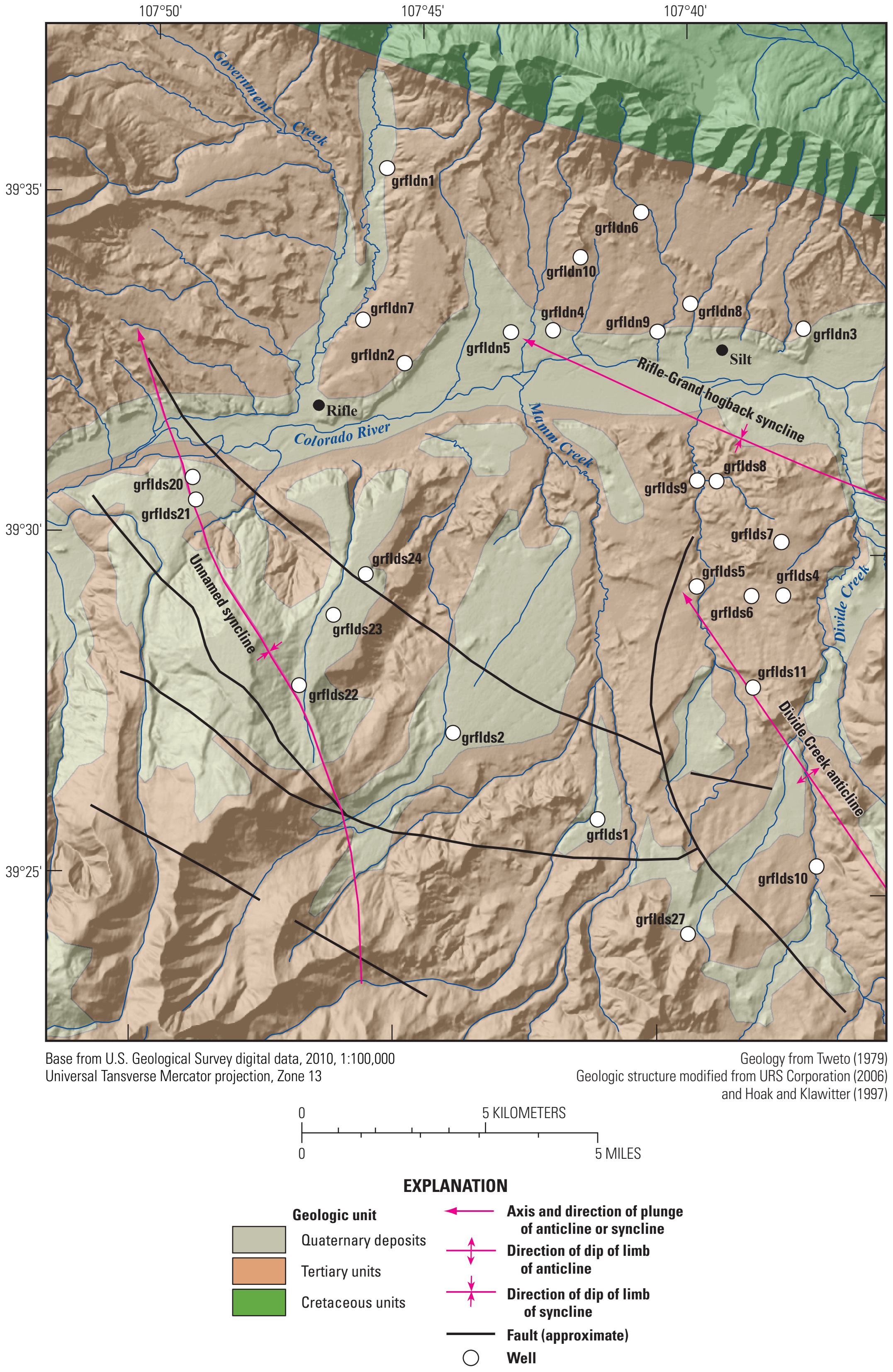
Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Transverse Mercator projection, Zone 13

Figure 1. Location of the study area.

Inorganic ions.—Samples for the analysis of alkalinity, major ions, and nutrients were filtered (0.45 micron) in the field and stored in precleaned plastic bottles. Cation samples were acidified in the field to pH less than 2 using nitric acid. Nutrient samples were kept chilled on ice until delivered to the laboratory.

Stable isotopes and dissolved gases.—Water-isotope samples ($\delta^{18}O[H_2O]$ and $\delta^{2}H[H_2O]$) were unfiltered and collected in precleaned glass bottles with polyseal caps that were secured with tape. Samples for analysis of the major gases methane, nitrogen (N_2), argon, and carbon dioxide were unfiltered and collected in precleaned glass bottles that were filled and capped with thick rubber stoppers under water to exclude headspace (atmospheric contamination). Major-gas samples were collected in duplicate at each site. Samples for analysis of the hydrocarbon gases methane, ethane, and propane and the isotopic composition of methane ($\delta^{13}C[CH_4]$ and $\delta^{2}H[CH_4]$) were unfiltered and collected in precleaned plastic bottles that were filled and capped under water. The samples were preserved in the field with a bactericide and kept chilled on ice until delivered to the laboratory. In April, unfiltered noble-gas samples were collected in precleaned glass bottles that were filled and capped with thick rubber stoppers under water to exclude headspace. These samples were analyzed for helium and neon and were used to identify helium-enriched waters that could not be age dated using the tritium/helium-3 method (Ludin and others, 1998). Wells with the greatest helium enrichment were resampled in October for analysis of the full suite of noble gases (helium, neon, argon, krypton, xenon). The October samples were unfiltered and collected in copper tubes that were sealed on both ends with pinch clamps. The copper tubes were connected in line with the pump-discharge line to prevent atmospheric contamination and slight backpressure was applied to the tubes while filling to help keep the noble gases in solution.

Environmental tracers of groundwater age.—Tritium samples were unfiltered and collected in precleaned plastic bottles with polyseal caps that were secured with tape. Samples for analysis of chlorofluorocarbon-11, chlorofluorocarbon-12, and chlorofluorocarbon-113 were unfiltered and collected in precleaned glass bottles that were filled and capped under water to exclude headspace. The caps were secured with tape and the bottles were kept chilled on ice until delivered to the



Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Tansverse Mercator projection, Zone 13

Geology from Tweto (1979)
Geologic structure modified from URS Corporation (2006)
and Hoak and Klawitter (1997)

Figure 2. Location of the domestic wells sampled for this study.

laboratory. Sulfur hexafluoride samples were collected and preserved in the same way as chlorofluorocarbon samples. Samples for tritium/helium-3 dating were collected in copper tubes as described above.

Sample Analysis

Inorganic ions.—Alkalinity was measured in the field by incremental titration using 0.16 normal sulfuric acid. Major ions and nutrients were measured by standard methods of the U.S. Geological Survey (USGS) National Water Quality Laboratory in Lakewood, Colorado (Fishman and Friedman, 1989), with a reproducibility of about ±1 percent.

Stable isotopes and dissolved gases.—The water-isotope samples were analyzed at the USGS Stable Isotope Laboratory in Reston, Virginia, by hydrogen- and carbon dioxide-gas equilibration and mass spectrometry (U.S. Geological Survey, 2008a). Stable-isotope results are reported using the standard delta (δ) notation, in per mil (‰, parts per thousand). For example, the stable oxygen-isotopic composition of a water sample ($\delta^{18}O[H_2O]_{sample}$) is equal to

$$\delta^{18}O[H_2O]_{sample} = ((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{ref} - 1)\cdot 1000 \qquad (1)$$

where

$^{18}O/^{16}O$ is the ratio of the oxygen-18 to oxygen-16 isotopes in the sample and a reference (ref) material.

The $\delta^2H[H_2O]$ and $\delta^{18}O[H_2O]$ values were referenced to the VSMOW scale (Vienna Standard Mean Ocean Water) (Coplen, 1988), with reproducibility of about ±1‰ and ±0.1‰, respectively. Major gases were measured at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia (U.S. Geological Survey, 2008b), by gas chromatography with reproducibility of about ±2 to 4 percent. Major gases were measured in duplicate and average values were reported in table 1. Hydrocarbon molecular and isotopic compositions were measured at the Isotech Laboratory, Champaign, Illinois, by gas chromatography and mass spectrometry, respectively. Concentrations of methane, ethane, and propane were reported in mole percent with a reproducibility of about ±2 percent. The $\delta^{13}C[CH_4]$ values were reported relative to Vienna Peedee Belemnite (VPDB) with a reproducibility of ±0.3‰. The $\delta^2H[CH_4]$ values were reported relative to VSMOW with a reproducibility of ±2‰. Noble-gas samples (helium and neon) collected in April were analyzed at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia (U.S. Geological Survey, 2008b), using gas chromatography, with a reproducibility of about ±10 to 20 percent. Noble-gas samples collected in October were analyzed at the USGS Noble Gas Laboratory in Denver, Colorado (Hunt and others, 2010), using mass spectrometry. Reproducibilities for helium, neon, argon, krypton, and xenon were about ±1, 3, 2, 3, and 3 percent, respectively.

Environmental tracers of groundwater age.—Tritium was analyzed at the USGS Tritium Laboratory in Menlo Park, California, using electrolytic enrichment and gas counting (Thatcher and others, 1977). Reproducibility of the tritium analyses generally was better than ±5 percent. Chlorofluorocarbons and sulfur hexafluoride were analyzed at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia, using gas chromatography (Plummer and Busenberg, 2000; Busenberg and Plummer, 2000). The reproducibility of chlorofluorocarbon and sulfur hexafluoride measurements was about ±3 percent. Samples for tritium/helium-3 dating were analyzed at the Lamont-Doherty Earth Observatory Noble Gas Laboratory in Palisades, New York (Schlosser and others, 1989; Ludin and others, 1998). These samples were analyzed for helium-4, neon, and helium-3/helium-4 ratios using mass spectrometry, with reproducibilities of about ±1, 3, and 1 percent, respectively.

Determination of recharge temperature, excess air, excess nitrogen gas, and initial nitrate concentration in recharge.—Recharge temperature refers to the temperature of water at the time it recharged the aquifer and excess air refers to air bubbles that get trapped in groundwater at the time of recharge (Andrews and Lee, 1979; Heaton and Vogel, 1981). Recharge temperatures and concentrations of excess air were calculated using measured concentrations of nitrogen gas and argon (Herzberg and Mazor, 1979; Heaton and Vogel, 1981; Böhlke and others, 2002). In the calculations, recharge elevation was assumed to be the elevation of the water table in the sampled well and salinity was assumed to equal the concentration of dissolved solids in the sample (table 1). Generally, this method for determining recharge temperature and excess air is suitable for samples containing more than 2 mg/L dissolved oxygen because they are not likely to contain excess nitrogen gas from denitrification. In other words, the only source of nitrogen gas in those samples would be the atmosphere. Excess nitrogen gas from denitrification is more likely to occur in groundwater containing less than 2 mg/L dissolved oxygen because denitrification is a microbial process that occurs in the absence of dissolved oxygen. McMahon and Chapelle (2008) proposed a dissolved-oxygen concentration threshold of 0.5 mg/L for the onset of denitrification in groundwater, but because of mixing between oxic and anoxic waters in some well screens, the effects of denitrification sometimes can be observed in samples containing more than 0.5 mg/L dissolved oxygen (Böhlke and others, 2002, 2007; McMahon and others, 2004). In this study, for samples with dissolved-oxygen concentrations less than or equal to 2 mg/L, it was assumed that recharge temperatures and concentrations of excess air were equal to the median recharge temperature and excess-air concentration in samples with dissolved-oxygen concentrations greater than 2 mg/L (7.9°C and 1.9 cubic centimeters at standard temperature and pressure, per liter of water (cm^3 STP/L), respectively).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Land surface elevation (m above NGVD 29)	Well depth (m below land surface)	Depth to top of screened interval (m below land surface)	Depth to bottom of screened interval (m below land surface)	Screen length (m)	Formation/ aquifer name
grfldn1	393528107453601	1,730	30.5	6.1	30.5	24.4	Wasatch
grfldn2	393237107450901	1,711	70.1	61.0	70.1	9.1	Wasatch
grfldn3	393318107373601	1,750	30.5	12.2	24.4	12.2	Wasatch
grfldn4	393310107422101	1,672	24.4	12.2	18.3	6.1	Wasatch
grfldn5	393407107430901	1,718	37.5	18.3	30.5	12.2	Wasatch
grfldn6	393456107404501	1,814	61.0	24.4	61.0	36.6	Wasatch
grfldn7	393314107455801	1,708	33.5	28.0	33.5	5.5	Wasatch
grfldn8	393337107394601	1,719	36.6	36.6	44.2	7.6	Wasatch
grfldn9	393311107402201	1,693	21.9	9.8	15.8	6.1	Wasatch
grfldn10	393415107415201	1,742	45.1	21.3	42.1	20.7	Wasatch
grfldn10-rep	393415107415201	1,742	45.1	21.3	42.1	20.7	Wasatch
grflds1	392631107411401	1,903	36.6	24.4	36.6	12.2	Wasatch
grflds2	392712107440101	1,951	30.2	23.8	30.2	6.4	Wasatch
grflds4	392922107375001	1,811	150.9	120.4	150.9	30.5	Wasatch
grflds4	392922107375001	1,811	150.9	120.4	150.9	30.5	Wasatch
grflds5	392928107392901	1,775	43.6	18.3	43.6	25.3	Wasatch
grflds6	392921107382601	1,779	61.0	54.9	61.0	6.1	Wasatch
grflds7	393009107375401	1,821	42.7	27.4	42.7	15.2	Wasatch
grflds8	393101107391001	1,708	45.7	29.0	45.7	16.8	Wasatch
grflds9	393101107393201	1,722	137.2	120.4	134.1	13.7	Wasatch
grflds9	393101107393201	1,722	137.2	120.4	134.1	13.7	Wasatch
grflds10	392524107370301	1,934	45.7	24.4	45.7	21.3	Wasatch
grflds11	392800107382101	1,868	52.7	18.3	30.5	12.2	Wasatch
grflds20	393051107490601	1,724	48.8	36.6	48.8	12.2	Wasatch/ colluvium
grflds21	393031107490201	1,756	73.2	57.9	72.2	14.3	Colluvium
grflds22	392750107465801	2,155	50.3	30.5	48.8	18.3	Wasatch
grflds22-rep	392750107465801	2,155	50.3	30.5	48.8	18.3	Wasatch
grflds23	392853107462101	2,045	54.9	42.7	54.9	12.2	Wasatch/ colluvium
grflds24	392930107454601	1,971	61.0	54.9	61.0	6.1	Wasatch
grflds27	392421107392701	1,993	53.3	44.2	53.3	9.1	Wasatch

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Collection date	Depth to water (m below land surface)	Source of water level data	Depth below water to screen midpoint (m)	Specific conductance (µS/cm at 25°C)	pH	Water temperature (°C)
grfldn1	393528107453601	4/26/2009	11.9	driller log	6.4	2,765	7.75	10.6
grfldn2	393237107450901	4/24/2009	53.3	driller log	12.2	1,983	7.10	11.5
grfldn3	393318107373601	4/20/2009	5.2	driller log	13.1	1,895	7.02	10.8
grfldn4	393310107422101	4/21/2009	5.5	driller log	9.8	1,672	7.20	10.4
grfldn5	393407107430901	4/24/2009	7.6	driller log	16.8	1,150	7.30	11.8
grfldn6	393456107404501	4/22/2009	18.3	driller log	24.4	813	7.55	13.3
grfldn7	393314107455801	4/26/2009	29.0	driller log	1.8	2,866	6.85	12.4
grfldn8	393337107394601	4/24/2009	30.5	driller log	9.9	1,580	7.24	12.7
grfldn9	393311107402201	4/22/2009	6.4	driller log	6.4	1,415	7.33	10.6
grfldn10	393415107415201	4/22/2009	6.1	driller log	25.6	1,510	8.20	10.5
grfldn10-rep	393415107415201	4/22/2009	6.1	driller log	25.6	1,510	8.20	10.5
grflds1	392631107411401	4/21/2009	19.8	driller log	10.7	1,310	7.20	10.8
grflds2	392712107440101	4/25/2009	21.3	driller log	5.6	1,190	7.25	11.9
grflds4	392922107375001	4/26/2009	13.1	driller log	122.5	1,834	7.45	12.0
grflds4	392922107375001	10/26/2009	13.1	driller log	122.5	1,814	7.75	13.6
grflds5	392928107392901	4/27/2009	6.4	driller log	24.5	1,232	7.51	11.1
grflds6	392921107382601	4/23/2009	48.8	driller log	9.1	2,460	7.90	9.1
grflds7	393009107375401	4/23/2009	21.3	driller log	13.7	2,130	7.10	12.0
grflds8	393101107391001	4/25/2009	19.5	driller log	17.8	6,622	7.55	10.1
grflds9	393101107393201	4/25/2009	25.3	driller log	102.0	3,530	8.36	15.3
grflds9	393101107393201	10/28/2009	25.3	driller log	102.0	5,320	8.10	16.0
grflds10	392524107370301	4/21/2009	13.7	driller log	21.3	1,640	7.20	11.7
grflds11	392800107382101	4/23/2009	3.0	driller log	21.3	1,430	8.30	11.0
grflds20	393051107490601	10/27/2009	35.1	driller log	7.6	962	7.97	12.6
grflds21	393031107490201	10/27/2009	56.4	driller log	8.7	719	8.10	13.1
grflds22	392750107465801	10/27/2009	25.3	driller log	14.3	592	7.55	10.4
grflds22-rep	392750107465801	10/27/2009	25.3	driller log	14.3	592	7.55	10.4
grflds23	392853107462101	10/28/2009	35.1	driller log	13.7	711	7.64	11.4
grflds24	392930107454601	10/28/2009	21.0	driller log	36.9	585	8.21	12.0
grflds27	392421107392701	10/26/2009	6.4	driller log	42.4	1,440	7.90	11.0

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Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Turbidity (NTU)	Dissolved oxygen (mg/L)	Redox state	Alkalinity (mg/L as $CaCO_3$)	Dissolved solids, residue on evaporation at 180°C (mg/L)	Calcium, dissolved (mg/L)
grfldn1	393528107453601	0.6	0.7	oxygen reducing	475	1,954	53.2
grfldn2	393237107450901	--	2.4	oxygen reducing	481	1,614	157
grfldn3	393318107373601	--	0.5	oxygen reducing	604	1,518	151
grfldn4	393310107422101	0.2	5.5	oxygen reducing	456	1,102	87.0
grfldn5	393407107430901	0.4	8.6	oxygen reducing	364	773	94.5
grfldn6	393456107404501	0.9	7.7	oxygen reducing	257	558	51.3
grfldn7	393314107455801	0.2	0.7	oxygen reducing	352	2,760	384
grfldn8	393337107394601	--	4.2	oxygen reducing	460	1,086	114
grfldn9	393311107402201	0.2	5.5	oxygen reducing	394	1,003	95.5
grfldn10	393415107415201	2.5	3.7	oxygen reducing	374	1,001	11.4
grfldn10-rep	393415107415201	2.5	3.7	--	374	1,006	10.9
grflds1	392631107411401	1.6	2.0	oxygen reducing	645	863	83.5
grflds2	392712107440101	--	1.5	oxygen reducing	488	782	90.0
grflds4	392922107375001	2.2	1.0	mixed oxygen-manganese reducing	594	1,170	16.6
grflds4	392922107375001	--	2.9	--	--	--	--
grflds5	392928107392901	0.2	8.6	oxygen reducing	505	796	52.4
grflds6	392921107382601	2.0	0.2	suboxic	402	1,667	21.1
grflds7	393009107375401	0.2	0.2	denitrifying	551	1,491	87.4
grflds8	393101107391001	0.2	0.2	manganese reducing	249	5,280	258
grflds9	393101107393201	0.6	0.2	suboxic	113	1,960	29.4
grflds9	393101107393201	--	0.6	--	--	--	--
grflds10	392524107370301	0.2	2.8	oxygen reducing	445	1,184	133
grflds11	392800107382101	0.3	0.1	suboxic	354	922	8.33
grflds20	393051107490601	0.2	8.3	oxygen reducing	334	630	31.6
grflds21	393031107490201	0.1	8.2	oxygen reducing	348	461	22.8
grflds22	392750107465801	0.1	6.8	oxygen reducing	291	373	70.2
grflds22-rep	392750107465801	0.1	6.8	--	291	378	70.1
grflds23	392853107462101	0.2	3.5	oxygen reducing	296	434	58.1
grflds24	392930107454601	0.2	0.8	oxygen reducing	303	372	26.9
grflds27	392421107392701	0.5	0.1	suboxic	580	943	11.2

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Bromide, dissolved (mg/L)
grfldn1	393528107453601	19.7	567	4.28	860	82.6	1.27	0.10
grfldn2	393237107450901	111	166	6.42	713	14.2	0.327	0.120
grfldn3	393318107373601	153	100	2.98	603	4.42	0.680	0.06
grfldn4	393310107422101	83.4	165	3.46	244	152	0.974	0.12
grfldn5	393407107430901	73.3	65.8	2.01	248	31.5	0.512	0.07
grfldn6	393456107404501	53.0	45.4	5.25	187	9.38	0.686	0.05
grfldn7	393314107455801	159	174	4.47	1,590	13.4	0.350	0.08
grfldn8	393337107394601	67.9	157	2.90	396	27.6	0.534	0.12
grfldn9	393311107402201	62.2	159	3.17	354	39.9	0.741	0.14
grfldn10	393415107415201	3.56	343	1.84	357	23.3	1.01	0.06
grfldn10-rep	393415107415201	3.47	348	1.81	358	23.6	1.02	0.066
grflds1	392631107411401	53.2	150	3.17	106	5.71	0.353	0.05
grflds2	392712107440101	59.9	105	3.40	180	9.59	0.378	0.09
grflds4	392922107375001	4.65	395	1.53	176	126	4.07	0.90
grflds4	392922107375001	--	--	--	--	--	--	--
grflds5	392928107392901	51.6	164	1.64	140	24.4	1.96	0.19
grflds6	392921107382601	4.87	538	1.70	748	70.9	2.52	0.79
grflds7	393009107375401	41.3	367	2.72	568	43.3	0.784	0.49
grflds8	393101107391001	62.1	1,340	5.05	2,880	391	1.30	1.63
grflds9	393101107393201	1.29	682	1.61	15.7	1,120	3.76	4.75
grflds9	393101107393201	--	--	--	--	--	--	--
grflds10	392524107370301	114	75.5	8.99	362	108	0.929	0.24
grflds11	392800107382101	0.248	305	0.548	302	43.4	2.37	0.36
grflds20	393051107490601	59.0	101	11.7	167	15.1	0.451	0.210
grflds21	393031107490201	25.5	111	6.19	42.0	3.68	0.650	0.049
grflds22	392750107465801	29.9	20.5	3.03	19.1	13.5	0.280	0.152
grflds22-rep	392750107465801	29.6	20.4	2.99	19.1	13.5	0.274	0.154
grflds23	392853107462101	48.0	27.3	3.52	21.8	41.8	0.290	0.281
grflds24	392930107454601	30.8	67.3	2.61	21.4	7.65	0.382	0.109
grflds27	392421107392701	0.755	352	0.989	55.7	128	1.63	0.903

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Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; CaCO$_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R$_a$, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Chloride/ bromide mass ratio	Silica, dissolved (mg/L)	Nitrite, dissolved (mg/L as N)	Nitrite+Nitrate, dissolved (mg/L as N)	Ammonia, dissolved (mg/L as N)	Orthophosphate, dissolved (mg/L as P)
grfldn1	393528107453601	826	5.51	<0.002	4.03	<0.02	0.008
grfldn2	393237107450901	118	17.9	<0.002	1.51	<0.02	0.010
grfldn3	393318107373601	74	15.7	0.002	0.18	<0.02	0.014
grfldn4	393310107422101	1269	18.6	<0.002	2.24	<0.02	0.014
grfldn5	393407107430901	450	23.6	<0.002	1.61	<0.02	0.013
grfldn6	393456107404501	188	23.2	<0.002	0.62	<0.02	0.017
grfldn7	393314107455801	168	14.6	<0.002	0.08	0.025	0.009
grfldn8	393337107394601	230	14.8	<0.002	1.14	<0.02	0.011
grfldn9	393311107402201	285	15.8	<0.002	0.79	<0.02	0.013
grfldn10	393415107415201	388	6.97	<0.002	0.67	<0.02	E0.00441
grfldn10-rep	393415107415201	360	7.01	<0.002	0.67	<0.02	E0.00473
grflds1	392631107411401	114	29.7	0.013	6.74	<0.02	0.021
grflds2	392712107440101	107	32.7	<0.002	3.03	0.033	0.026
grflds4	392922107375001	140	9.17	<0.002	<0.04	0.087	0.011
grflds4	392922107375001		--	--	--	--	--
grflds5	392928107392901	128	36.2	<0.002	0.25	<0.02	0.023
grflds6	392921107382601	90	7.18	<0.002	0.17	E0.01358	E0.00652
grflds7	393009107375401	88	8.99	<0.002	0.94	<0.02	E0.00626
grflds8	393101107391001	240	7.23	E 0.001	0.40	0.068	E0.00516
grflds9	393101107393201	236	8.32	<0.002	<0.04	0.171	E0.00428
grflds9	393101107393201		--	--	--	--	--
grflds10	392524107370301	449	32.1	<0.002	1.20	<0.02	0.023
grflds11	392800107382101	121	9.22	0.013	0.21	0.028	0.009
grflds20	393051107490601	72	31.5	<0.002	3.26	<0.02	0.039
grflds21	393031107490201	75	30.6	<0.002	1.54	<0.02	0.056
grflds22	392750107465801	89	32.2	<0.002	0.72	<0.02	0.033
grflds22-rep	392750107465801	88	32.2	<0.002	0.72	<0.02	0.033
grflds23	392853107462101	149	35.0	<0.002	3.37	<0.02	0.040
grflds24	392930107454601	70	26.3	<0.002	0.11	0.09	0.069
grflds27	392421107392701	142	7.19	0.012	0.16	0.07	E0.0068

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Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

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Site name	Site identifier	Iron, dissolved (µg/L)	Manganese, dissolved (µg/L)	Carbon dioxide (mg/L)	Nitrogen gas (N2) (mg/L)	Methane (mg/L)	Methane (mol %)	Ethane (mol %)	Propane (mol %)
grfldn1	393528107453601	<8	0.44	21.57	20.51	<0.0005	--	--	--
grfldn2	393237107450901	11	E0.236	72.91	19.43	<0.0005	--	--	--
grfldn3	393318107373601	31	2.12	109.4	19.63	<0.0005	--	--	--
grfldn4	393310107422101	4.4	E0.182	51.14	17.23	<0.0005	--	--	--
grfldn5	393407107430901	8.4	0.82	35.56	19.96	<0.0005	--	--	--
grfldn6	393456107404501	13	0.59	14.85	16.04	<0.0005	--	--	--
grfldn7	393314107455801	E4.6	10.1	93.76	20.65	0.001	--	--	--
grfldn8	393337107394601	20	0.88	53.09	16.17	<0.0005	--	--	--
grfldn9	393311107402201	13	2.12	33.80	17.12	<0.0005	--	--	--
grfldn10	393415107415201	5.1	1.62	5.675	23.14	<0.0005	--	--	--
grfldn10-rep	393415107415201	8.9	1.60		--	--	--	--	--
grflds1	392631107411401	16	35.0	90.25	20.81	<0.0005	--	--	--
grflds2	392712107440101	5.6	<0.2	55.21	20.07	<0.0005	--	--	--
grflds4	392922107375001	92	73.5	52.24	9.197	27.6	--	--	--
grflds4	392922107375001	--	--	23.49	18.05	0.072	6.59	0.028	0.001
grflds5	392928107392901	9.2	<0.2	41.69	15.78	<0.0005	--	--	--
grflds6	392921107382601	39	12.4	4.351	34.68	0.004	--	--	--
grflds7	393009107375401	<8	1.70	46.46	23.77	<0.0005	--	--	--
grflds8	393101107391001	23	220	13.90	28.21	0.005	--	--	--
grflds9	393101107393201	E 7.5	16.7	1.485	5.554	32.5	--	--	--
grflds9	393101107393201	--	--	0.535	5.378	29.5	81.0	0.091	<0.0001
grflds10	392524107370301	9.1	2.12	58.00	20.10	0.002	--	--	--
grflds11	392800107382101	E3.0	8.79	3.547	28.42	0.197	--	--	--
grflds20	393051107490601	7.6	0.35	10.440	14.21	<0.0005	--	--	--
grflds21	393031107490201	<6.0	<0.20	9.125	14.92	<0.0005	--	--	--
grflds22	392750107465801	<6.0	<0.20	4.010	16.16	<0.0005	--	--	--
grflds22-rep	392750107465801	<6.0	<0.20	3.69	16.15	<0.0005	--	--	--
grflds23	392853107462101	10	1.67	18.025	19.19	<0.0005	--	--	--
grflds24	392930107454601	6.1	10.5	5.310	18.13	0.001	--	--	--
grflds27	392421107392701	20	14.9	12.710	27.68	2.87	5.22	0.001	<0.0001

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Methane/ (ethane+propane)	Helium-4 (10^{-8} cm^3 STP/g)	Neon (10^{-7} cm^3 STP/g)	Argon (10^{-4} cm^3 STP/g)	Krypton (10^{-8} cm^3 STP/g)
grfldn1	393528107453601	--	8.77	2.19	3.623	--
grfldn2	393237107450901	--	5.56	2.31	3.665	--
grfldn3	393318107373601	--	9.56	2.35	3.700	--
grfldn4	393310107422101	--	191	--	3.420	--
grfldn5	393407107430901	--	6.03	2.49	3.833	--
grfldn6	393456107404501	--	4.85	2.03	3.049	--
grfldn7	393314107455801	--	5.69	2.31	3.478	--
grfldn8	393337107394601	--	8.09	2.02	3.282	--
grfldn9	393311107402201	--	4.65	1.93	3.515	--
grfldn10	393415107415201	--	7.21	2.97	4.076	--
grfldn10-rep	393415107415201	--	--	--	--	--
grflds1	392631107411401	--	5.76	2.41	3.802	--
grflds2	392712107440101	--	5.87	2.40	3.705	--
grflds4	392922107375001	--	1,100	--	2.128	--
grflds4	392922107375001	226	729	1.68	3.432	8.18
grflds5	392928107392901	--	31.3	2.33	3.330	--
grflds6	392921107382601	--	145	--	3.710	--
grflds7	393009107375401	--	61.9	2.80	4.056	--
grflds8	393101107391001	--	1,960	--	3.599	--
grflds9	393101107393201	--	4,900	--	0.488	--
grflds9	393101107393201	888	4,250	0.206	0.433	1.32
grflds10	392524107370301	--	6.30	2.44	3.703	--
grflds11	392800107382101	--	104	--	4.238	--
grflds20	393051107490601	--	--	--	3.164	--
grflds21	393031107490201	--	149	1.57	3.136	7.33
grflds22	392750107465801	--	--	--	3.254	--
grflds22-rep	392750107465801	--	--	--	3.248	--
grflds23	392853107462101	--	--	--	3.513	--
grflds24	392930107454601	--	--	--	3.340	--
grflds27	392421107392701	3,729	--	--	4.014	--

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Xenon (10^{-8} cm^3 STP/g)	R/R_a	Recharge temperature (°C)	Excess air (cm^3 STP/L)	Excess nitrogen gas (mg/L as N)	Nitrate concentration at the time of recharge (mg/L as N)
grfldn1	393528107453601	--	0.67	7.9	4.0	1.4	5.4
grfldn2	393237107450901	--	1.02	7.9	4.2	<1	1.51
grfldn3	393318107373601	--	0.64	7.4	4.3	<1	0.18
grfldn4	393310107422101	--		9.0	2.2	<1	2.24
grfldn5	393407107430901	--	0.99	5.6	3.8	<1	1.61
grfldn6	393456107404501	--	0.98	14.8	3.0	<1	0.62
grfldn7	393314107455801	--	1.15	7.9	2.4	3.1	3.2
grfldn8	393337107394601	--	0.63	9.5	1.4	<1	1.14
grfldn9	393311107402201	--	0.95	6.5	1.3	<1	0.79
grfldn10	393415107415201	--	1.07	6.6	7.6	<1	0.67
grfldn10-rep	393415107415201	--	--	--	--	--	--
grflds1	392631107411401	--	1.15	7.0	5.6	<1	6.74
grflds2	392712107440101	--	1.15	7.2	5.1	<1	3.03
grflds4	392922107375001	--		--	--	--	--
grflds4	392922107375001	1.13	0.017	7.9	2.2	0.8	--
grflds5	392928107392901	--	--	7.4	0.4	<1	0.25
grflds6	392921107382601	--	--	8.8	1.9	14.0	14.2
grflds7	393009107375401	--	--	7.8	8.8	<1	0.94
grflds8	393101107391001	--	--	7.9	4.0	9.2	9.6
grflds9	393101107393201	--	--	--	--	--	--
grflds9	393101107393201	0.112	0.009	--	--	--	--
grflds10	392524107370301	--	1.11	7.4	5.2	<1	1.20
grflds11	392800107382101	--	--	7.9	11.0	2.6	2.8
grflds20	393051107490601	--	--	8.0	–1.1	<1	3.26
grflds21	393031107490201	1.04	0.174	10.1	0.4	<1	1.54
grflds22	392750107465801	--	--	8.2	1.7	<1	0.72
grflds22-rep	392750107465801	--	--	--	--	--	--
grflds23	392853107462101	--	--	7.9	4.0	<1	3.37
grflds24	392930107454601	--	--	8.2	1.9	1.5	1.6
grflds27	392421107392701	--	--	7.9	9.2	3.9	4.1

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; CaCO$_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R$_a$, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Denitrification reaction progress	Sulfur hexafluoride, mean concentration in solution (fmol/L)	Sulfur hexafluoride, calculated atmospheric concentration (pptv)	Chlorofluorocarbon-11, mean concentration in solution (pg/kg)
grfldn1	393528107453601	0.25	--	--	--
grfldn2	393237107450901	0.00	--	--	--
grfldn3	393318107373601	0.00	--	--	--
grfldn4	393310107422101	0.00	6.92	16.14	456
grfldn5	393407107430901	0.00	--	--	--
grfldn6	393456107404501	0.00	--	--	--
grfldn7	393314107455801	0.98	--	--	--
grfldn8	393337107394601	0.00	--	--	--
grfldn9	393311107402201	0.00	--	--	538
grfldn10	393415107415201	0.00	--	--	--
grfldn10-rep	393415107415201	--	--	--	--
grflds1	392631107411401	0.00	--	--	21
grflds2	392712107440101	0.00	--	--	30
grflds4	392922107375001	--	--	--	--
grflds4	392922107375001	--	--	--	--
grflds5	392928107392901	0.00	2.35	6.38	554
grflds6	392921107382601	0.99	0.29	0.69	30
grflds7	393009107375401	0.00	--	--	31
grflds8	393101107391001	0.96	0.28	0.53	20
grflds9	393101107393201	--	--	--	--
grflds9	393101107393201	--	--	--	--
grflds10	392524107370301	0.00	--	--	374
grflds11	392800107382101	0.92	0.76	0.92	16
grflds20	393051107490601	0.00	0.95	2.77	200
grflds21	393031107490201	0.00	0.48	1.46	189
grflds22	392750107465801	0.00	0.90	2.23	45
grflds22-rep	392750107465801	--	--	--	--
grflds23	392853107462101	0.00	0.63	1.23	76
grflds24	392930107454601	0.93	0.07	0.16	19
grflds27	392421107392701	0.96	1.26	1.70	17

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Chlorofluorocarbon-11, calculated atmospheric concentration (pptv)	Chlorofluorocarbon-12, mean concentration in solution (pg/kg)	Chlorofluorocarbon-12, calculated atmospheric concentration (pptv)	Chlorofluorocarbon-113, mean concentration in solution (pg/kg)
grfldn1	393528107453601	--	--	--	--
grfldn2	393237107450901	--	--	--	--
grfldn3	393318107373601	--	--	--	--
grfldn4	393310107422101	186	272	478	62
grfldn5	393407107430901	--	--	--	--
grfldn6	393456107404501	--	--	--	--
grfldn7	393314107455801	--	--	--	--
grfldn8	393337107394601	--	--	--	--
grfldn9	393311107402201	191	352	554	74
grfldn10	393415107415201	--	--	--	--
grfldn10-rep	393415107415201	--	--	--	--
grflds1	392631107411401	7.8	219	347	2.66
grflds2	392712107440101	11	84	135	5
grflds4	392922107375001	--	--	--	--
grflds4	392922107375001	--	--	--	--
grflds5	392928107392901	208	325	541	68
grflds6	392921107382601	12	28	50	10
grflds7	393009107375401	12	104	166	3.6
grflds8	393101107391001	8	68	115	4
grflds9	393101107393201	--	--	--	--
grflds9	393101107393201	--	--	--	--
grflds10	392524107370301	142	258	420	56
grflds11	392800107382101	6.3	46	73	1.8
grflds20	393051107490601	77	222	379	43
grflds21	393031107490201	82	222	423	28
grflds22	392750107465801	18	104	186	5.6
grflds22-rep	392750107465801	--	--	--	--
grflds23	392853107462101	34	72	126	14
grflds24	392930107454601	7.4	6	10	3
grflds27	392421107392701	7	30	49	5

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Chlorofluorocarbon-113, calculated atmospheric concentration (pptv)	Apparent age of young fraction (years)	Percent young water	Tracers used to determine age
grfldn1	393528107453601	--	8	100	tritium/helium-3
grfldn2	393237107450901	--	3	100	tritium/helium-3
grfldn3	393318107373601	--	6	100	tritium/helium-3
grfldn4	393310107422101	59	20	100	tritium, chlorofluorocarbon-12 and -113
grfldn5	393407107430901	--	<1	--	tritium/helium-3
grfldn6	393456107404501	--	<1	--	tritium/helium-3
grfldn7	393314107455801	--	12	--	tritium/helium-3
grfldn8	393337107394601	--	3	100	tritium/helium-3
grfldn9	393311107402201	62	21	100	tritium, chlorofluorocarbon-113
grfldn10	393415107415201	--	5	--	tritium/helium-3
grfldn10-rep	393415107415201	--	--	--	
grflds1	392631107411401	2.2	30	100	tritium, chlorofluorocarbon-12
grflds2	392712107440101	4.3	39	100	chlorofluorocarbon-12 and -113
grflds4	392922107375001	--	--	--	--
grflds4	392922107375001	--	--	--	--
grflds5	392928107392901	60	21	100	tritium, chlorofluorocarbon-113
grflds6	392921107382601	10	31	100	tritium and sulfur hexafluoride
grflds7	393009107375401	3.1	37	100	tritium, chlorofluorocarbon-12
grflds8	393101107391001	3.6	27	50	tritium and sulfur hexafluoride
grflds9	393101107393201	--	>50	0	tritium
grflds9	393101107393201	--	--	--	--
grflds10	392524107370301	49	23	100	tritium, chlorofluorocarbon-12 and -113
grflds11	392800107382101	1.5	28	100	tritium and sulfur hexafluoride
grflds20	393051107490601	39	25	100	tritium, chlorofluorocarbon-12 and -113
grflds21	393031107490201	28	28	100	tritium, chlorofluorocarbon-113
grflds22	392750107465801	5.4	25	13	tritium, chlorofluorocarbon-113
grflds22-rep	392750107465801	--	--	--	
grflds23	392853107462101	12	25	30	chlorofluorocarbon-12 and -113
grflds24	392930107454601	3	>50	0	tritium
grflds27	392421107392701	4	23	100	tritium and sulfur hexafluoride

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	Model used to determine age	Age comment
grfldn1	393528107453601	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn2	393237107450901	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn3	393318107373601	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn4	393310107422101	piston-flow model	
grfldn5	393407107430901	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn6	393456107404501	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn7	393314107455801	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn8	393337107394601	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn9	393311107402201	piston-flow model	
grfldn10	393415107415201	piston-flow model	minimum age, tritiogenic helium-3 degassing likely
grfldn10-rep	393415107415201		
grflds1	392631107411401	exponential mixing model	
grflds2	392712107440101	piston-flow model	
grflds4	392922107375001	--	high methane, gas stripped
grflds4	392922107375001	--	high methane, gas stripped
grflds5	392928107392901	piston-flow model	
grflds6	392921107382601	piston-flow model	
grflds7	393009107375401	piston-flow model	low dissolved oxygen, chlorofluorocarbon-12 could be degraded
grflds8	393101107391001	binary-mixing model	
grflds9	393101107393201	--	
grflds9	393101107393201	--	
grflds10	392524107370301	piston-flow model	
grflds11	392800107382101	piston-flow model	
grflds20	393051107490601	piston-flow model	
grflds21	393031107490201	piston-flow model	
grflds22	392750107465801	binary-mixing model	
grflds22-rep	392750107465801		
grflds23	392853107462101	binary-mixing model	
grflds24	392930107454601	--	
grflds27	392421107392701	piston-flow model	

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

Table 1. Chemical data for water collected from domestic wells in Garfield County, Colorado.—Continued

[NGVD29, North American Vertical Datum of 1929; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; NTU, nephelometric turbidity units; <, less than; --, no data; E, estimated[1]; N, nitrogen; P, phosphorus; µg/L, micrograms per liter; ‰, per mil; VSMOW, Vienna Standard Mean Ocean Water; TU, tritium units; VPDB, Vienna PeeDee Belemnite; mol %, mole percent; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; R/R_a, helium-3/helium-4 ratio in the sample divided by the helium-3/helium-4 ratio in air; cm^3 STP/L, cubic centimeters at standard temperature and pressure, per liter of water; g, gram; fmol/L, femtomole per liter; pptv, parts per trillion by volume; pg/kg, picogram per kilogram]

Site name	Site identifier	δ^2H, water (‰, VSMOW)	$\delta^{18}O$, water (‰, VSMOW)	Tritium (TU)	δ^2H, methane (‰, VSMOW)	$\delta^{13}C$, methane (‰, VPDB)
grfldn1	393528107453601	–115.7	–15.18	5.5	--	--
grfldn2	393237107450901	–118.03	–15.44	5.4	--	--
grfldn3	393318107373601	–116.12	–15.05	5.6	--	--
grfldn4	393310107422101	–121.75	–16.25	6.6	--	--
grfldn5	393407107430901	–119.57	–15.7	5.5	--	--
grfldn6	393456107404501	–121.58	–16.02	5.0	--	--
grfldn7	393314107455801	–120.63	–15.75	5.5	--	--
grfldn8	393337107394601	–119.64	–15.74	6.0	--	--
grfldn9	393311107402201	–120.56	–15.68	5.9	--	--
grfldn10	393415107415201	–120.8	–15.93	6.0	--	--
grfldn10-rep	393415107415201	--	--	--	--	--
grflds1	392631107411401	–113.32	–15.22	11.5	--	--
grflds2	392712107440101	–119.07	–15.99	13.1	--	--
grflds4	392922107375001	–100.25	–13.7	6.2	--	--
grflds4	392922107375001	--	--	--	–152.1	–41.76
grflds5	392928107392901	–113.4	–15.15	8.2	--	--
grflds6	392921107382601	–121.23	–15.48	8.6	--	--
grflds7	393009107375401	–112.51	–15.02	8.3	--	--
grflds8	393101107391001	–115.03	–14.98	2.1	--	--
grflds9	393101107393201	–58.28	–8.9	<0.3	--	--
grflds9	393101107393201	--	--	--	–192.4	–65.75
grflds10	392524107370301	–114.46	–15.33	7.4	--	--
grflds11	392800107382101	–120.63	–15.77	10.5	--	--
grflds20	393051107490601	–119.35	–16.02	7.1	--	--
grflds21	393031107490201	–117.99	–15.94	9.5	--	--
grflds22	392750107465801	–123.35	–16.29	0.9	--	--
grflds22-rep	392750107465801	--	--	--	--	--
grflds23	392853107462101	–122.96	–16.17	0.3	--	--
grflds24	392930107454601	–124.82	–16.25	<0.5	--	--
grflds27	392421107392701	–116.84	–15.59	6.3	–146.3	–50.37

[1] Estimated (E) concentrations are those concentrations that are greater than or equal to the long-term method detection limit but less than the laboratory reporting level or lowest calibration standard, whichever is greater (Childress and others, 1999).

For samples with dissolved-oxygen concentrations less than or equal to 2 mg/L, excess nitrogen gas from denitrification was calculated according to equation 2:

$$\text{Excess } N_2 = N_2(\text{measured}) - N_2(\text{equilibrium}) - N_2(\text{excess air}) \qquad (2)$$

where

Excess N_2 is the concentration of excess nitrogen gas from denitrification in the sample,

N_2(measured) is the measured concentration of nitrogen gas in the sample,

N_2(equilibrium) is the concentration of nitrogen gas from equilibration with the atmosphere in the sample (calculated for each sample on the basis of its recharge temperature and elevation, and salinity),

and

N_2(excess air) is the concentration of nitrogen gas from excess air in the sample.

The initial nitrate concentration (Initial nitrate) in the sample at the time it recharged the aquifer was calculated according to equation 3:

$$\text{Initial nitrate} = \text{Measured nitrate} + \text{Excess } N_2 \qquad (3)$$

Measured nitrate is the measured concentration of nitrate in the sample. If the sample was not affected by denitrification then Excess N_2 equals zero, and Initial nitrate equals Measured nitrate. An estimate of the extent to which nitrate was removed from groundwater by denitrification was calculated according to equation 4:

$$\text{Denitrification reaction progress} = 1 - (\text{Measured nitrate}/\text{Initial nitrate}) \qquad (4)$$

Denitrification reaction progress would equal zero if no nitrate was removed by denitrification, and it would equal one if all the nitrate was removed by denitrification.

Groundwater Age

Groundwater ages calculated from environmental tracers like tritium, chlorofluorocarbons, sulfur hexafluoride, and tritium/helium-3 are referred to as "apparent ages" because they are based on simplifying assumptions regarding transport processes that may affect tracer concentrations in groundwater (Plummer and Busenberg, 2000; Rupert and Plummer, 2009). The most straightforward assumption is that transport processes (for example, mixing or dispersion) have no effect on the concentration of tracers as they move in an aquifer. Thus the tracer concentration in water at the sampling point (such as a well) is the same as the concentration at the time the water recharged the aquifer. This model is referred to as the "piston-flow model." The piston-flow model appears to be a reasonable representation of groundwater age in some instances, such as in shallow, short-screened wells. In other instances, mixing or dispersion affect measured tracer concentrations, particularly for wells with long-screened intervals. The simplest model describing the effect of mixing on tracer concentrations is the binary-mixing model, which assumes the water is a mixture of old (pretracer or pre 1950s) water and young water (containing tracer or post 1950s). More complicated models of mixing assume the sampled water represents a distribution of ages. These models, called lumped-parameter models, yield a mean age of the water sample. Perhaps the most common lumped-parameter model is the exponential model (Maloszewski and Zuber, 1982, 1996; Cook and Böhlke, 2000). The exponential model could describe the mean age of water discharged from a long-screened well in an unconfined aquifer receiving distributed recharge, for example.

The following sections discuss in more specific terms the application of tritium, chlorofluorocarbons, sulfur hexafluoride, and tritium/helium-3 tracers to groundwater dating. These tracers were used to determine apparent ages of young (generally, post 1950s) groundwater and the dilution of young groundwater with old (pre 1950s) groundwater.

Tritium.—Tritium is a radioactive isotope of hydrogen with a half-life of 12.32 years (Lucas and Unterweger, 2000). Small concentrations of tritium are produced naturally by interactions between the atmosphere and cosmic rays. It is an excellent tracer of water movement because it is part of the water molecule. In general, tritium in groundwater originates from precipitation. Because tritium is radioactive, its concentration in groundwater decreases over time because of radioactive decay. Before the onset of atmospheric testing of nuclear weapons in 1953 (prebomb), the tritium content of precipitation in the central United States probably ranged from about 3 to 8 tritium units (TU) (Kaufman and Libby, 1954; Thatcher, 1962). As a result of radioactive decay, groundwater derived from precipitation that fell before 1953 would have contained less than 0.5 TU tritium in 2010. The tritium content of precipitation increased substantially after the onset of atmospheric nuclear weapons testing with the addition of bomb tritium but has slowly decreased from its peak in the early 1960s (fig. 3). Even with the variability in tritium content of precipitation over time, groundwater totally derived from precipitation that fell since 1953 (postbomb) contained more than 0.5 TU in 2010.

Chlorofluorocarbons.—Chlorofluorocarbons are stable synthetic organic compounds that were used as refrigerants and in other industrial applications beginning in the 1930s (Plummer and Busenberg, 2000). Concentrations of chlorofluorocarbons in the atmosphere rose sharply in the 1960s and peaked in the early 1990s (Plummer and Busenberg, 2000; Plummer and others, 2006) (fig. 3). The use of

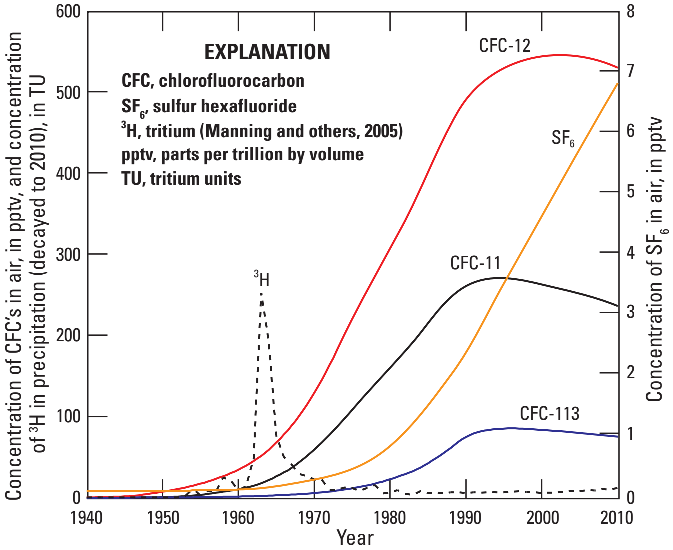


Figure 3. Concentrations of chlorofluorocarbons and sulfur hexafluoride in North American air, and concentrations of tritium in precipitation at Salt Lake City, Utah, decayed to 2010.

chlorofluorocarbons to determine groundwater age depends on relating their concentrations in groundwater to atmospheric concentrations in the recharge area at the time of recharge.

The concentration of chlorofluorocarbons in the atmosphere at the time a sample recharged the aquifer can be back calculated using the measured chlorofluorocarbon concentrations in the sample; the recharge temperature and excess-air concentration determined from the nitrogen-gas and argon concentrations, as discussed in the Sample Analysis section; salinity; recharge elevation; and Henry's Law. The year of recharge is determined by referring the back-calculated atmospheric concentration to a curve of the atmospheric-concentration history and picking the year corresponding to the back-calculated concentration (fig. 3). Apparent age simply is the sample date minus the recharge date. Since the early to mid 1990s, atmospheric concentrations of chlorofluorocarbons have begun to level off or decline (fig. 3), greatly limiting their use as age tracers for water recharged during that period. Details of the chlorofluorocarbon-dating method, including a discussion of subsurface processes that could produce erroneous apparent ages, can be found in Plummer and Busenberg (2000) and Plummer and others (2006). One such process relevant to the current study is chlorofluorocarbon biodegradation in anoxic groundwater. Biodegradation would reduce chlorofluorocarbon concentrations in groundwater and result in the calculated ages being biased old.

Sulfur Hexafluoride.—Sulfur hexafluoride is a stable gas that mainly has been used as an electrical insulator in high-voltage switches and transformers. It was produced in significant quantities beginning in the 1950s (Busenberg and Plummer, 2000). Release of sulfur hexafluoride to the atmosphere rose sharply in the 1980s and is ongoing (fig. 3). Dating groundwater with sulfur hexafluoride essentially follows the same principals as chlorofluorocarbon dating. Two advantages of sulfur hexafluoride over chlorofluorocarbons are that sulfur hexafluoride does not degrade under anoxic conditions and it can be used as a tracer of groundwater age for water recharged since the 1990s because of its continued increase in the atmosphere during that period. Details of the sulfur-hexafluoride dating method, including a discussion of subsurface processes that could produce erroneous apparent ages, can be found in Busenberg and Plummer (2000).

Tritium/Helium-3.—Helium-3 is produced from the radioactive decay of tritium. As discussed previously, tritium in groundwater recharged since the early 1950s is dominated by bomb tritium. Helium-3 derived from the decay of bomb tritium is referred to as "tritiogenic helium-3". Given that the half-life of tritium is well known (12.32 years), if the amount of bomb tritium and tritiogenic helium-3 in a sample can be measured then the apparent age of that sample can be calculated using a form of the radioactive-decay equation (Solomon and Cook, 2000). Whereas the tritium concentration in a sample can be measured directly, the tritiogenic helium-3 concentration in a sample must be calculated from mass balances on helium-3 and helium-4 concentrations, and the helium-3/helium-4 ratios of the predominant helium sources in the system. Typically, these helium sources include the atmosphere (helium-3/helium-4 = 1.384×10^{-6}; Clarke and others, 1976) and the decay of uranium and thorium in rocks and minerals in the earth's crust (helium-3/helium-4 = 2×10^{-8}; Mamyrin and Tolstikhin, 1984). In some instances, mantle helium also is important (helium-3/helium-4 = $\sim 1 \times 10^{-5}$; Ozima and Podosek, 1983). Helium mass balance is necessary because the vast majority (usually greater than 99.9 percent) of the measured helium in a groundwater sample is helium-4. Moreover, the helium-4 content of groundwater typically increases over time because of helium-4 production in the sediment from uranium and thorium decay. For tritium/helium-3 dating in this study, it was assumed that the earth's crust was the only subsurface source of helium (in other words, no mantle helium), with a helium-3/helium-4 ratio of 2×10^{-8}. The basis for this assumption is discussed in more detail in the Helium Concentrations and Isotopes section of this report. Details of the tritium/helium-3 dating method, including a discussion of subsurface processes that could produce erroneous apparent ages, can be found in Schlosser and others (1988, 1989), Solomon and Cook (2000), Böhlke and others (2007), and McMahon and others (2010). One such process relevant to the current study is incomplete tritiogenic helium-3 confinement in the aquifer because of low recharge rates. Tritiogenic helium-3 could diffuse across the water table and exit the system if recharge rates were too low to trap it below the water table. Incomplete tritiogenic helium-3 confinement would result in the calculated ages being biased young.

Geochemical Data Sets

This section describes and compares the spatial distributions of oxygen, nitrate, methane, and geochemical water types (based on major-ion data) in the Wasatch Formation.

Distributions of Oxygen, Nitrate, and Methane in Groundwater

Concentrations of dissolved oxygen in water from the sampled wells ranged from 0.1 to 8.6 mg/L (table 1), with the lowest concentrations occurring in a north-south trending zone located south of Silt (fig. 4). All the samples collected north of the Colorado River and 9 of 16 samples collected south of the river were considered to be oxygen reducing, or oxic (dissolved oxygen concentration greater than or equal to 0.5 mg/L), on the basis of the redox classification scheme of McMahon and Chapelle (2008) (table 1). Of the remaining 7 samples collected south of the river, 4 were classified as suboxic, 1 was manganese reducing, 1 was a mixture of oxygen and manganese reducing, and 1 was denitrifying (table 1).

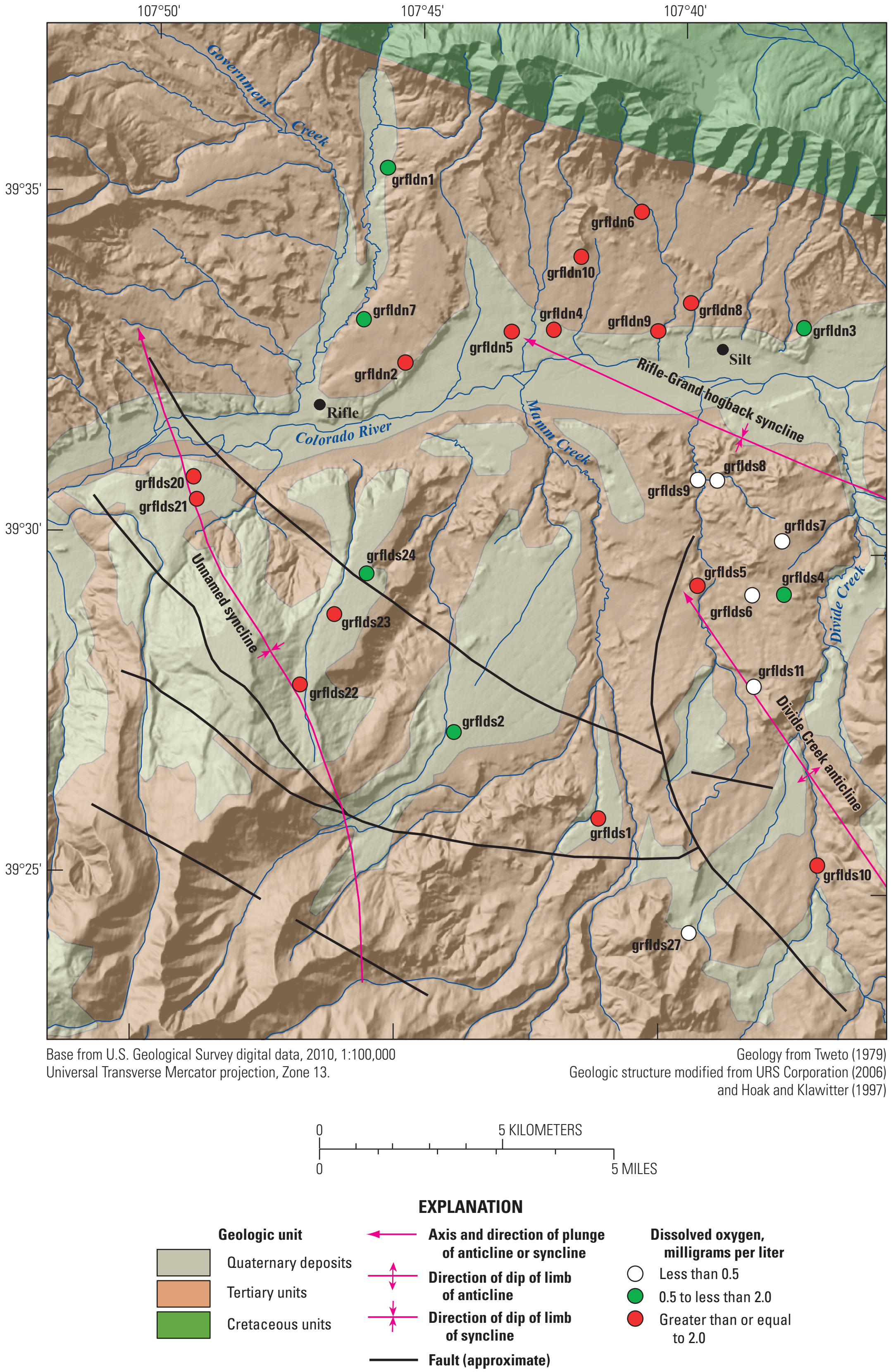
Concentrations of nitrite in most of the samples were less than the reporting level of 0.002 mg/L as N (table 1); therefore, concentrations of nitrite plus nitrate consisted almost entirely of nitrate and will be referred to as such for the remainder of this report. Concentrations of nitrate ranged from less than 0.04 to 6.74 mg/L as N (table 1). Nitrate concentrations in water samples with dissolved-oxygen concentrations less than 0.5 mg/L were significantly ($p = 0.03$) lower than nitrate concentrations in water samples with dissolved-oxygen concentrations greater than or equal to 0.5 mg/L on the basis of the nonparametric Wilcoxon rank sum test (Helsel and Hirsch, 1992). Some of the lowest nitrate concentrations occurred in the north-south trending zone of low dissolved-oxygen concentrations located south of Silt (fig. 5). In contrast, that zone hosted the highest methane concentrations (fig. 6). Overall, methane concentrations ranged from less than 0.0005 to 32.5 mg/L (table 1) and were significantly ($p = 0.007$) higher in water samples with dissolved-oxygen concentrations less than 0.5 mg/L than in samples with dissolved-oxygen concentrations greater than or equal to 0.5 mg/L. This pattern of low nitrate and high methane concentrations in groundwater containing little or no dissolved oxygen can be explained by the general principals of redox chemistry. Nitrate, presumably from anthropogenic or natural sources at the land surface, is likely to be degraded by denitrifying bacteria in anoxic groundwater (Chapelle and others, 1995; McMahon and Chapelle, 2008). In contrast, the potential for local biogenic methane production is greater in anoxic groundwater than in oxic groundwater. Methane produced externally by biogenic or thermogenic processes, and subsequently transported to the aquifer by natural or anthropogenic processes, also would be more likely to persist in anoxic groundwater than in oxic groundwater because of the possibility of methane degradation (oxidation) by methanotrophic bacteria in oxic groundwater (Barker and Fritz, 1981; Whiticar, 1999). Anoxic methane oxidation also may occur in aquifers, but generally that process is more common in marine sediments (Smith and others, 1991; Zhang and others, 1998; Whiticar, 1999; Grossman and others, 2002; Van Stempvoort and others, 2005). The processes of denitrification and methane oxidation are discussed in more detail in the Sources and Sinks of Nitrate in Groundwater and the Sources and Sinks of Methane in Groundwater sections of this report.

In general, the data in figures 4–6 indicate that field measurements of dissolved oxygen in groundwater could be useful indicators of the Wasatch Formation's vulnerability to nitrate and methane contamination, or enrichment in the case of naturally derived constituents. Oxic parts of the aquifer would be relatively more vulnerable to nitrate contamination and less vulnerable to methane contamination. Anoxic parts of the aquifer would be relatively less vulnerable to nitrate contamination and more vulnerable to methane contamination.

Major-Ion Chemistry

Water samples containing less than 1 mg/L methane and collected north of the Colorado River generally were mixed-cation-sulfate-bicarbonate waters, whereas low-methane samples collected south of the river mostly were mixed-cation-bicarbonate-sulfate waters (fig. 7). Three wells located south of the river (grflds4, grflds9, and grflds27) produced water with more than 1 mg/L methane, and they were sodium-bicarbonate to sodium-chloride waters (fig. 7). Of those samples, the one from grflds9 appeared to be closest in major-ion composition to produced water from the Mesaverde Group (fig. 7). Well grflds9 was screened from 120 to 134 m below land surface, which is considerably deeper than all the other wells except grflds4 (screened from 120 to 151 m below land surface) (table 1). Samples from two wells located north of the river (grfldn1 and grfldn10) and three wells located south of the river (grflds6, grflds8, and grflds11) also were relatively enriched in sodium but did not have methane concentrations greater than 1 mg/L (fig. 7).

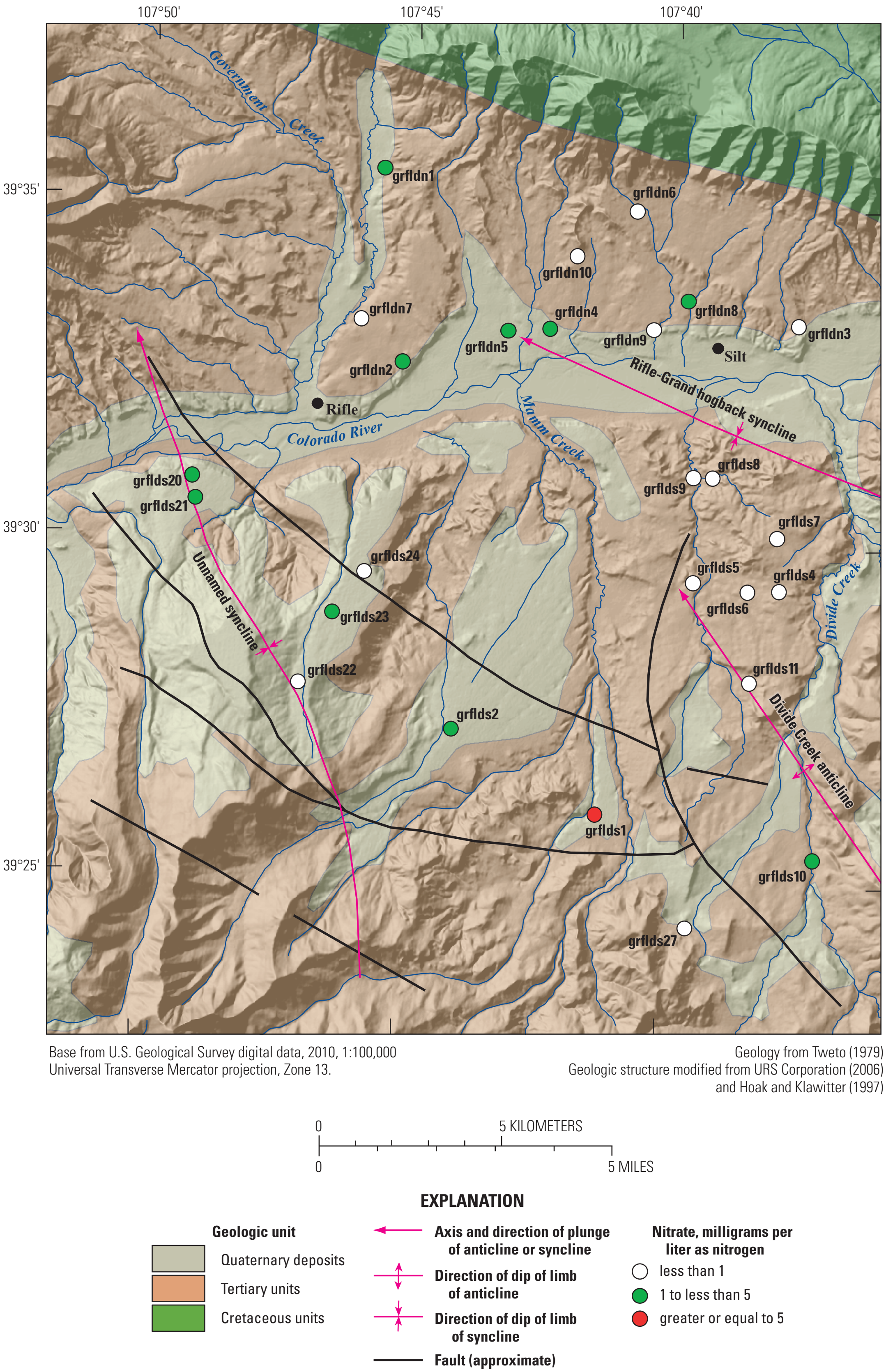
The major-ion chemistry of water collected for this study showed similar overall patterns to the chemistry of water collected from domestic wells during previous studies (fig. 8). The data in figure 8 were retrieved from the U.S. Geological Survey Piceance Basin common data repository (U.S. Geological Survey, 2010b). Many of the wells in the data repository were sampled on more than one date so only the most recent sample with complete data was used in figure 8. This same approach was used for other figures in the report in which data from the common data repository were displayed. Many of the previously collected samples containing less than 1 mg/L methane were mixed-cation-bicarbonate-sulfate waters, but several low-methane waters also were relatively enriched in sodium. Most of the high-methane waters were relatively enriched in sodium as well.



Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Transverse Mercator projection, Zone 13.

Geology from Tweto (1979)
Geologic structure modified from URS Corporation (2006)
and Hoak and Klawitter (1997)

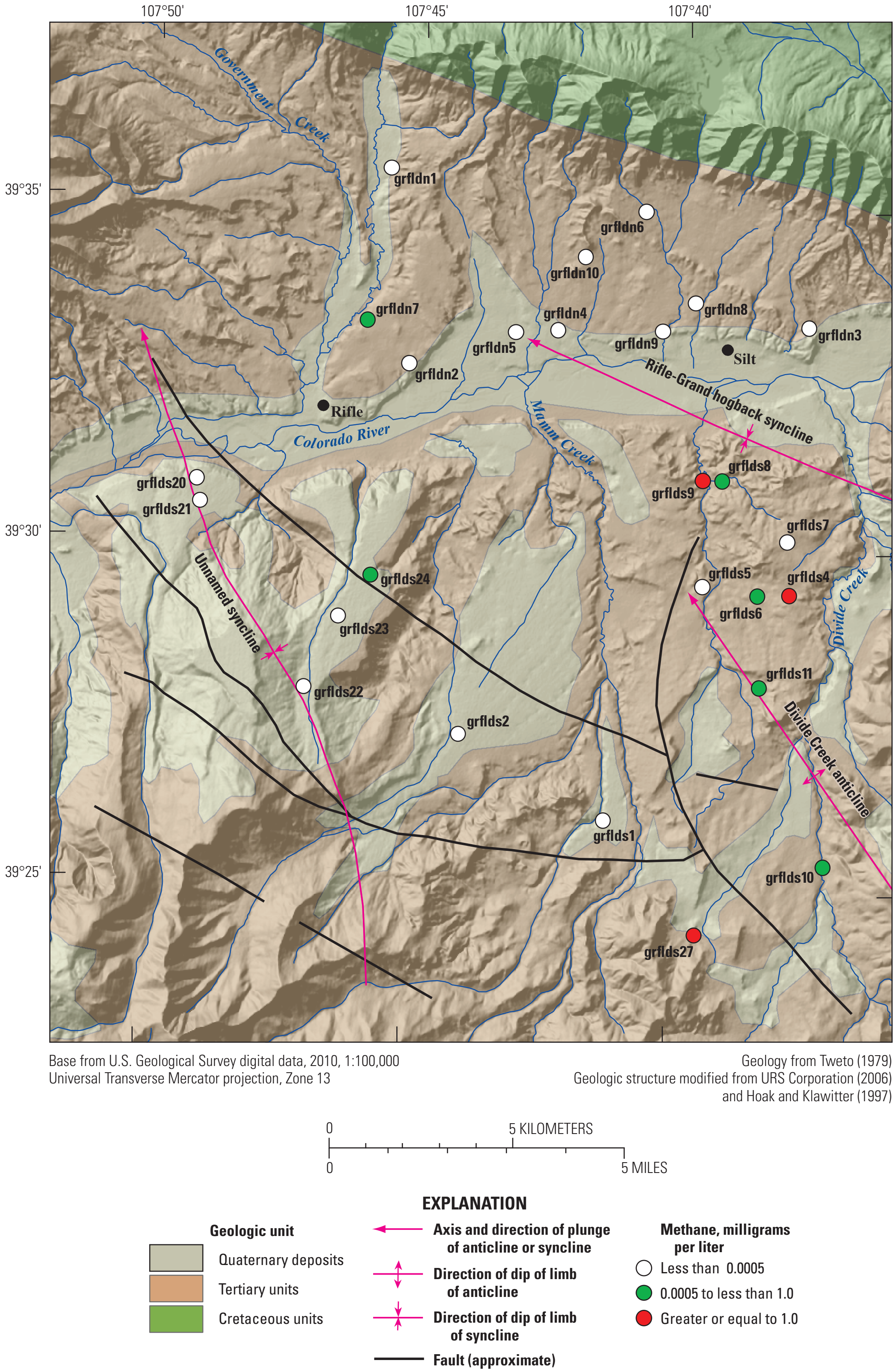
Figure 4. Concentrations of dissolved oxygen in water from domestic wells sampled for this study.



Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Transverse Mercator projection, Zone 13.

Geology from Tweto (1979)
Geologic structure modified from URS Corporation (2006)
and Hoak and Klawitter (1997)

Figure 5. Concentrations of nitrate in water from domestic wells sampled for this study.



Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Transverse Mercator projection, Zone 13

Geology from Tweto (1979)
Geologic structure modified from URS Corporation (2006)
and Hoak and Klawitter (1997)

Figure 6. Concentrations of methane in water from domestic wells sampled for this study.

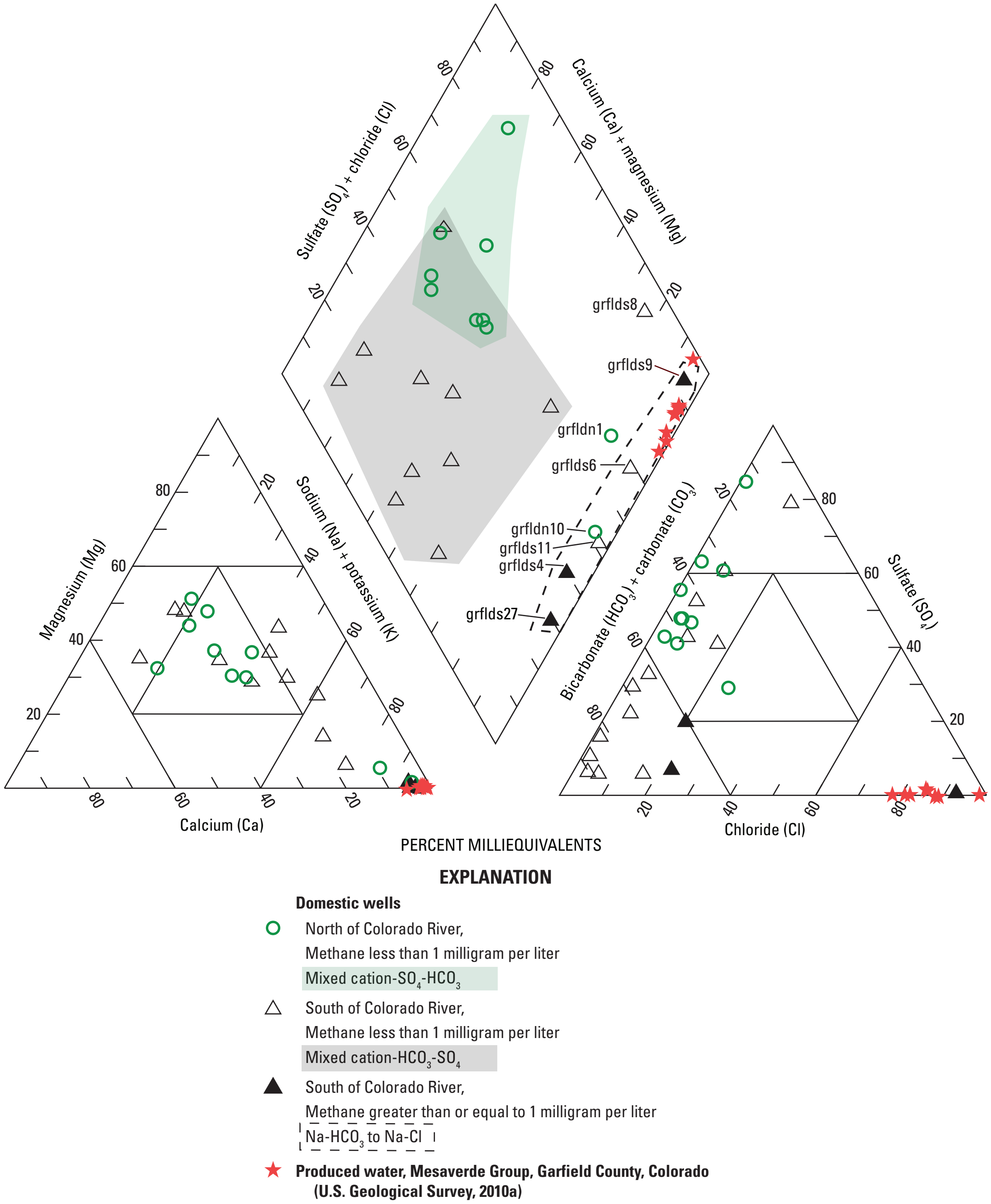


Figure 7. Major-ion chemistry of water from domestic wells sampled for this study, and major-ion chemistry of produced water from the Mesaverde Group.

Groundwater Mixing

Mixing groundwater from different sources could have important implications for the quality of groundwater in the Wasatch Formation. For example, when young, nitrate-contaminated groundwater is mixed with old, nitrate-free groundwater or when young, dilute groundwater is mixed with old, saline groundwater or old, methane-enriched groundwater the quality of the resulting mixture could be better or worse than the end-member waters. Sorting out mixing processes that could involve water, ions, and gases requires multiple tracers because those constituents may not all be derived from the same sources. This section of the report examines mixing processes in the Wasatch Formation using stable isotopes of water ($\delta^2H[H_2O]$ and $\delta^{18}O[H_2O]$), groundwater apparent ages, and chloride/bromide mass ratios.

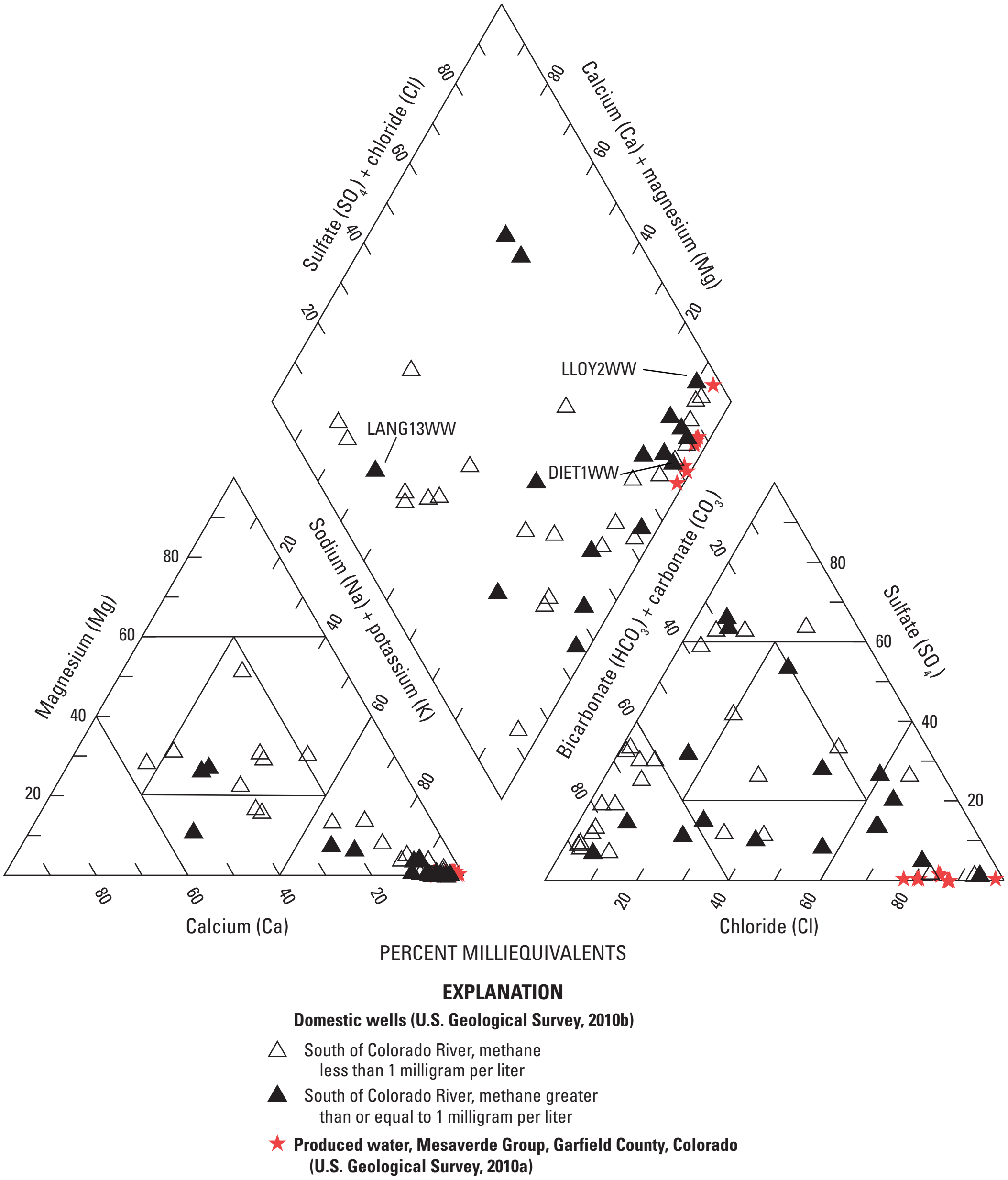


Figure 8. Major-ion chemistry of water from previously sampled domestic wells in the study area, and major-ion chemistry of produced water from the Mesaverde Group.

Stable Isotopes of Water

$\delta^{2}H$ [H_2O] and $\delta^{18}O[H_2O]$ values for samples collected for this study plotted near the Global Meteoric Water Line (Craig, 1961), indicating the water was derived from precipitation (fig. 9*A*). The samples plotted between the isotopic values for snow from Grand Mesa (located about 60 km southwest of the study area) and water from the Mesaverde Group. All but two of the samples (from grflds4, grflds9) plotted near the snow values, although shifted toward slightly more positive values, indicating they probably were derived from lower elevation precipitation than what was represented by the Grand Mesa snow samples. The Grand Mesa snow samples were collected at an elevation of 3,230 m, whereas the land-surface elevations of the sampled wells ranged from 1,672 to 2,155 m (table 1). The samples also could have contained small fractions of water from the Mesaverde Group, but that is difficult to determine from the isotopic values alone. The samples from grflds4 and grflds9 appeared to contain much larger fractions of water from the Mesaverde Group than the other samples (fig. 9*A*). All the water from grflds9 could have been from the Mesaverde Group on the basis of the $\delta^{2}H[H_2O]$ and $\delta^{18}O[H_2O]$ values and major-ion data (fig. 7).

A similar pattern in the water isotopic values was observed for samples collected from domestic wells during previous studies (fig. 9*B*). All but two of those samples (LLOY2WW, SCHW1WW) consisted mostly of snowmelt recharge. LLOY2WW and SCHW1WW apparently contained relatively large fractions of water from the Mesaverde Group. Previously collected major-ion data for LLOY2WW also indicated a similar composition to that of water from the Mesaverde Group (fig. 8). All four wells in figure 9 that contained relatively large fractions of water from the Mesaverde Group were located south of Silt in the zone that had groundwater with low concentrations of dissolved oxygen and nitrate and high concentrations of methane (figs. 4–6).

Apparent Groundwater Ages

All but two of the dated water samples collected for this study contained a component of young (less than 50 years) groundwater on the basis of tritium, chlorofluorocarbon, and sulfur hexafluoride data (table 1). Two samples (from grflds9 and grflds24) consisted entirely of old groundwater (greater than 50 years), 3 samples were mixtures of old and young groundwater (from grflds8, grflds22, and grflds23), and 12 samples consisted entirely of young groundwater (table 1). Fractions of old and young groundwater in the samples were estimated from tracer-tracer plots like the one shown in figure 10. Samples consisting entirely of young groundwater plotted along the piston-flow line, whereas samples that were mixtures of old and young groundwater plotted below the piston-flow line. For the example shown by the dashed line in figure 10, the percentages refer to the fraction of young groundwater in a mixture of old water and water recharged in 1985. Some of the data points that plotted below the piston-flow line were not necessarily mixtures of young and old water, but rather had apparently undergone some chlorofluorocarbon-113 loss, possibly because of biodegradation under anoxic conditions (Plummer and others, 2006).

The relatively old age of water from grflds9, as indicated by its tritium concentration being less than 0.5 TU, is consistent with the water isotopic data for that sample (fig. 9*A*), which indicate it contained a large fraction of water from the Mesaverde Group. The tritium and isotopic data for water from grflds4 indicate that sample contained a larger fraction of young groundwater than did water from grflds9 (table 1 and fig. 9*A*). The other sample consisting entirely of old groundwater (from grflds24, with a tritium concentration less than 0.5 TU) had water isotopic values similar to snowmelt (table 1), indicating that not all the old groundwater in the study area was derived from the Mesaverde Group. Grflds24 was located west of the zone with low dissolved-oxygen concentrations (fig. 4).

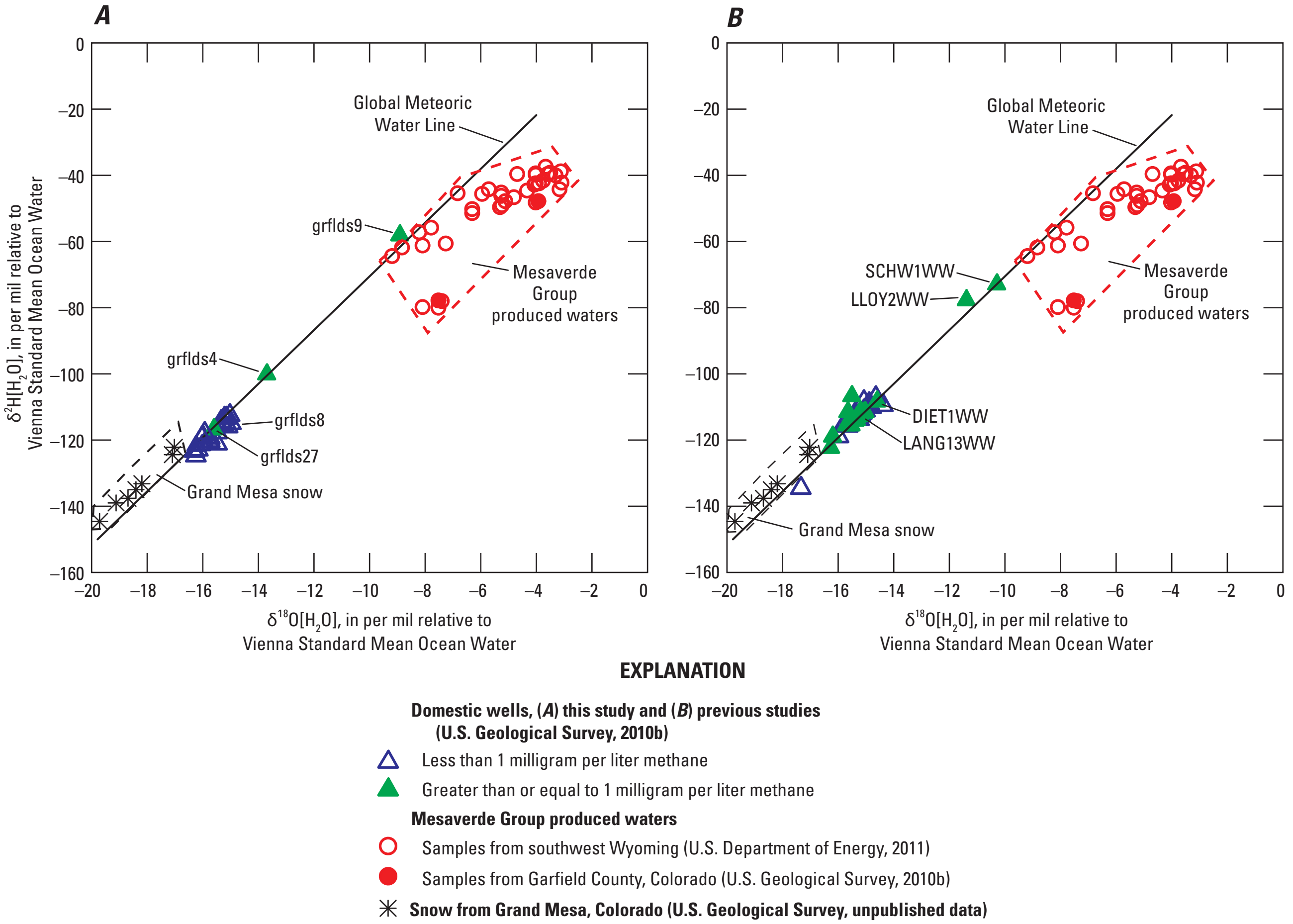


Figure 9. Stable isotopic compositions of water from domesitic wells (*A*) sampled for this study and (*B*) sampled during previous studies, compared to the stable isotopic compositions of snow from Grand Mesa, Colorado and produced waters from the Mesaverde Group.

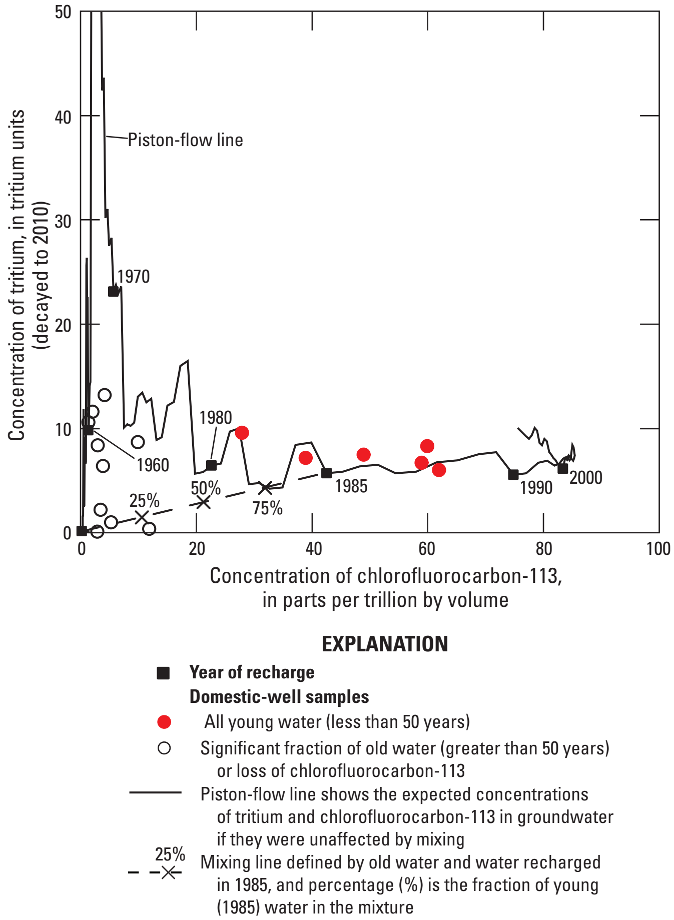


Figure 10. Concentrations of tritium and chlorofluorocarbon-113 in water from domestic wells sampled for this study.

The apparent ages of the young fraction of groundwater ranged from 20 to 39 years on the basis of tritium, chlorofluorocarbon, and sulfur hexafluoride data (table 1), and generally exhibited a positive relation with depth of the well screen below the water table (fig. 11), although the pattern contained considerable scatter. The two samples containing the oldest water (from grflds9 and grflds24) were among the deepest samples collected for this study. The age-depth patterns in figure 11 correspond to apparent vertical groundwater velocities on the order of 75 to 2,000 millimeters per year (mm/yr), or recharge rates on the order of 15 to 400 mm/yr, assuming an aquifer porosity of 20 percent. Such variability in recharge could be expected in the study area because of its diverse land use and topographic settings. Higher recharge might occur in the vicinity of ponds, irrigation ditches, or intermittent stream channels compared to natural settings or interchannel areas. Higher recharge also might be expected at higher elevations as annual precipitation is generally greater there than at lower elevations. Aquifer zones with high recharge and relatively large nitrogen inputs at the land surface could be particularly vulnerable to nitrate contamination if the groundwater is oxic. The age of the younger fraction in a mixture of two young waters cannot be resolved with existing groundwater-age tracers. Therefore, the possibility exists that the young fractions themselves were mixtures containing some groundwater that was even younger than what is reported here. Generally, the effects of mixing on groundwater ages are reduced as the length of the screened interval of the sampled well decreases.

Apparent ages based on the tritium and helium-3 data were noticeably younger than the ages based on chlorofluorocarbon and sulfur hexafluoride data (table 1 and fig. 11). This could result from incomplete confinement of tritiogenic helium-3 in the aquifer, as discussed in the Groundwater Age section. For example, four of the samples dated with the tritium/helium-3 method (from grfldn9, grflds1, grflds2, and grflds10) also were dated with the chlorofluorocarbon method. The median tritium/helium-3 apparent age for those four samples was 6 years and the median chlorofluorocarbon apparent age was 26 years, supporting the notion that incomplete confinement of tritiogenic helium-3 biased the tritium/helium-3 ages young. Thus, the tritium/helium-3 apparent ages are considered minimum ages.

Chloride/Bromide Mass Ratios

Chloride/bromide mass ratios can provide information on fractions of water and chloride contributed to the samples from different sources. Potential sources examined here included young, dilute groundwater recharge, water from the Mesaverde Group, and leachate from sewage and/or animal-waste sources

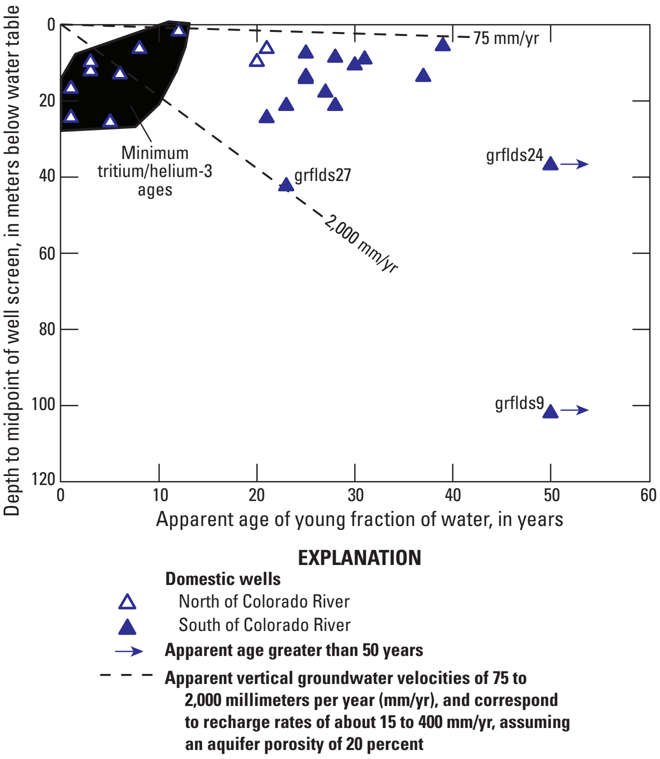


Figure 11. Apparent ages of the young fraction of water from domestic wells sampled for this study, based on tritium, chlorofluorocarbon, and/or sulfur hexafluoride measurements, except for the samples that plot in the field labeled "minimum tritium/helium-3 ages," whose ages were based on tritium and helium-3 measurements and may be biased young because of incomplete confinement of tritiogenic helium-3.

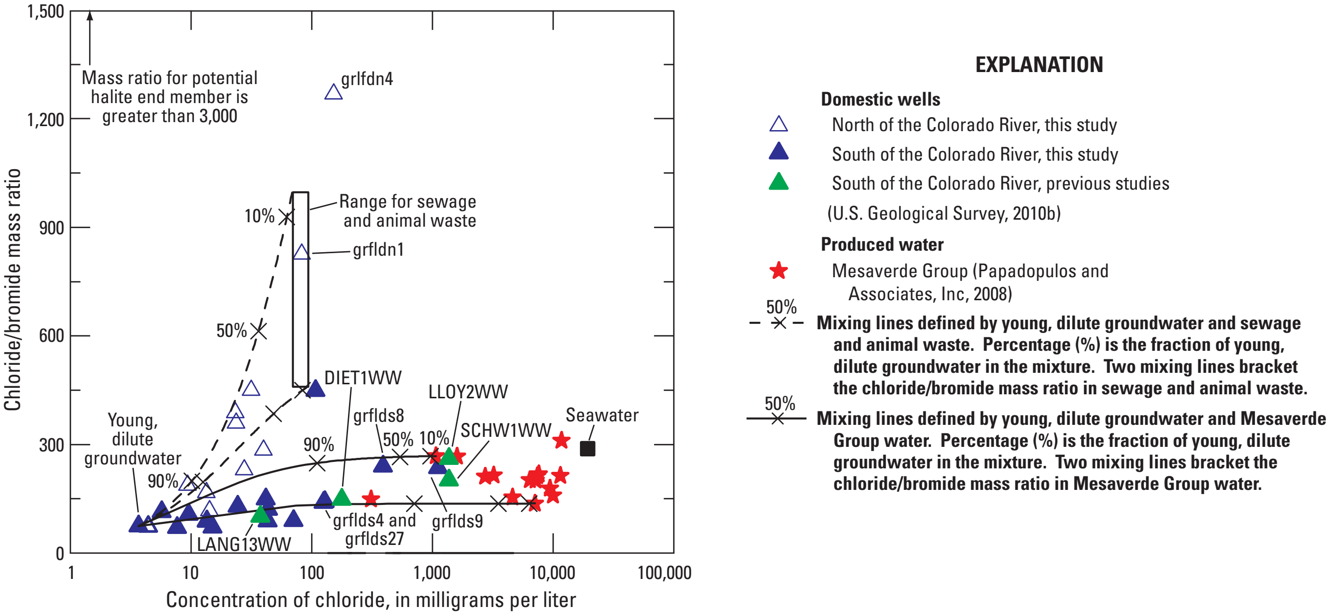


Figure 12. Chloride/bromide mass ratios in water from domestic wells sampled for this study and during previous studies. Ratios for seawater, halite, and sewage and animal waste are from Mullaney and others (2009).

(fig. 12). The most likely sources of sewage and animal waste in the vicinity of the sampled wells were septic systems and livestock/pets, respectively. Halite may have been an additional source of chloride in at least one of the samples, but halite was not used in the source analysis.

The source analysis examined two scenarios: mixing between (1) young, dilute groundwater and sewage and/or animal waste and (2) young, dilute groundwater and water from the Mesaverde Group. Two mixing lines were used to bracket the range of chloride/bromide ratios in the end-member waters (fig. 12). The fraction of water contributed to the mixture by each end member was calculated according to equations 5 and 6:

$$Cl_s = (Cl_{EM1})(f) + (Cl_{EM2})(1\text{-}f) \qquad (5)$$

$$(Cl/Br)_s = Cl_s/[(Br_{EM1})(f) + (Br_{EM2})(1\text{-}f)] \qquad (6)$$

where

Cl_s is the chloride concentration in the sample,

Cl_{EM1} and Cl_{EM2} are the chloride concentrations in end members 1 and 2, respectively,

f is the fraction of end member 1 in the mixture,

$(Cl/Br)_s$ is the chloride/bromide ratio in the sample,

and

Br_{EM1} and Br_{EM2} are the bromide concentrations in end members 1 and 2, respectively.

The fraction of chloride contributed to the mixture by each end member was calculated according to equations 7 and 8:

$$\text{Chloride from end member 1} = (Cl_{EM1})(f)/\ Cl_s \qquad (7)$$

$$\text{Chloride from end member 2} = (Cl_{EM2})(1\text{-}f)/\ Cl_s \qquad (8)$$

Most of the samples consisted of more than 90 percent young, dilute groundwater. But relatively large contributions of water and chloride from sewage and/or animal-waste sources were apparent in some samples collected north of the Colorado River and large contributions of water and chloride from the Mesaverde Group were apparent in some samples collected south of the river (fig. 12). Some samples may have contained water and chloride from more than two sources.

Samples from grflds9 (this study) and LLOY2WW and SCHW1WW (U.S. Geological Survey, 2010b) may have derived more than 90 percent of their water and chloride from the Mesaverde Group, based on the mixing scenarios shown in figure 12, whereas the sample from grfldn1 may have derived more than 90 percent of its water and chloride from sewage and/or animal-waste sources. Some samples (from grflds4, grflds27, DIET1WW, and LANG13WW) appeared to derive a large fraction of their water from dilute recharge but only a small fraction of their chloride content. The samples from grflds4 and grflds27, for example, derived about 98 percent of their water and only 3 percent of their chloride from dilute recharge, based on the mixing scenarios illustrated in figure 12. The sample from grflds8 derived about 64 percent of its water and less than 1 percent of its chloride from young, dilute recharge. The young fraction of water in grflds8 was estimated to be about 50 percent on the basis of age tracers (table 1). These results indicate the Mesaverde Group was an important source of chloride (and possibly other constituents as well) in several of the samples collected south of the river, even when the actual fraction of water from the Mesaverde Group in the sample was small. This is because of the large effect that elevated chloride concentrations in water from the Mesaverde Group have on the mixing calculations. These interpreted mixing fractions could vary if the actual end-member compositions differed from what is shown in figure 12, or if other end members not identified here contributed water and chloride to the samples.

Summary of Mixing Results

The water-isotopic, age-tracer, and chloride/bromide data indicate most of the sampled groundwater consisted of snowmelt recharge with apparent ages less than 50 years old. Some samples also contained fractions of water from sewage and/or animal-waste sources, and this was most apparent north of the Colorado River. A few samples collected south of the river contained large fractions of water from the Mesaverde Group. The samples with large fractions of water from the Mesaverde Group also contained a component of old (greater than 50 years) water based on the age tracers, but not all the old groundwater contained water from the Mesaverde Group. The Mesaverde Group appeared to be an important source of chloride in several of the samples collected south of the river, even when the actual fraction of water from the Mesaverde Group in the sample was small.

Sources and Sinks of Nitrate in Groundwater

All but two of the samples contained at least a fraction of young water, indicating the wells from which those samples were collected could have been vulnerable to nitrate contamination from surface sources. Figure 13*A* shows samples with the highest measured nitrate concentrations also contained at least a fraction of young groundwater. The most likely sources of high-nitrate groundwater in the study area included septic systems, animal manure, and fertilizer applied to lawns and crops. Several samples appeared to contain a component of water from sewage (septic-system effluent) or animal-waste sources on the basis of chloride/bromide mass ratios (fig. 12), and one of them (from grfldn1) had the second highest measured nitrate concentration (fig. 13*A*). A more precise characterization of nitrate sources was beyond the scope of this project, but well established geochemical and isotopic tracer techniques are available for such purposes (Böhlke and others, 2002; McMahon and others, 2008).

Samples with some of the lowest measured nitrate concentrations were anoxic or contained old groundwater. The low nitrate concentrations could reflect denitrification processes in the aquifer or low nitrate concentrations in the water at the time it recharged the aquifer, or both. The measured nitrate concentrations in anoxic samples where corrected for denitrification affects in the aquifer by adding back excess nitrogen gas from denitrification, thus providing an estimate of the nitrate concentration in the water at the time it recharged the aquifer. Several of the samples with low dissolved-oxygen concentrations, such as the samples from grflds6 and grflds8, had substantially larger nitrate concentrations at the time of recharge than at the time of sampling (table 1, figs. 13*A* and 13*C*). The nitrate concentration in water from grflds6 at the time of recharge was about 14 mg/L as N, which would have exceeded the federal drinking-water standard for nitrate (fig. 13*C*) (U.S. Environmental Protection Agency, 2010), but denitrification in the aquifer removed 99 percent of that nitrate during its 31-year residence time in the aquifer (table 1). These data indicate denitrification was an important sink for nitrate in parts of the aquifer containing groundwater with low concentrations of dissolved oxygen, particularly in the zone located south of Silt (figs. 4 and 5). In contrast to the samples containing young groundwater, the one sample (from grflds24) that contained 100 percent old groundwater and had sufficient gas data to make denitrification corrections was recharged with a nitrate concentration of about 1.6 mg/L as N (fig. 13), indicating nitrate concentrations in that water were low at the time it recharged the aquifer prior to the 1950s.

Sources and Sinks of Methane in Groundwater

Sources and sinks of methane in water from the Wasatch Formation were examined using hydrocarbon and noble-gas tracers. Hydrocarbon molecular and isotopic tracers were used to determine whether the high methane concentrations in some samples were biogenic or thermogenic in origin and whether oxidation processes in the aquifer could be a sink for methane. Biogenic methane is derived from the microbial degradation of organic matter by methanogenic bacteria in the subsurface. Thermogenic methane is derived from the abiotic degradation of organic matter at high temperatures and pressures when it is deeply buried in the subsurface. Helium concentrations and isotopes were used to examine whether the high methane concentrations in some samples could have formed within or external to the sampled intervals of the Wasatch Formation and they were used to provide qualitative constraints on the age of groundwater containing the highest methane concentrations.

Hydrocarbon Molecular and Isotopic Compositions

Hydrocarbon molecular and isotopic compositions have been used in several studies to determine sources of methane in groundwater (Bernard and others, 1978; Barker and Fritz, 1981; Whiticar, 1999; URS Corporation, 2006; Papadopulos & Associates, Inc., 2008). Data from this study indicate methane in two of the three samples with high concentrations (from grflds9 and grflds27) was biogenic in origin, whereas methane in natural-gas samples from the Piceance Basin was thermogenic in origin (fig. 14*A*) (Johnson and Rice, 1990). Data for the third sample with a high methane concentration (from grflds4) plotted between the fields for thermogenic and biogenic gases in figure 14*A*, which could be interpreted as a mixture of gases from both sources. As discussed previously, water from grflds4 was a mixture of young and old waters. But water from grflds4 also contained dissolved oxygen (table 1), presumably from the young fraction of water in the sample, so the possibility that methane oxidation affected the composition of that sample cannot be ruled out. Methane oxidation would have the effect of shifting the molecular and isotopic compositions of the sample away from the biogenic field and toward

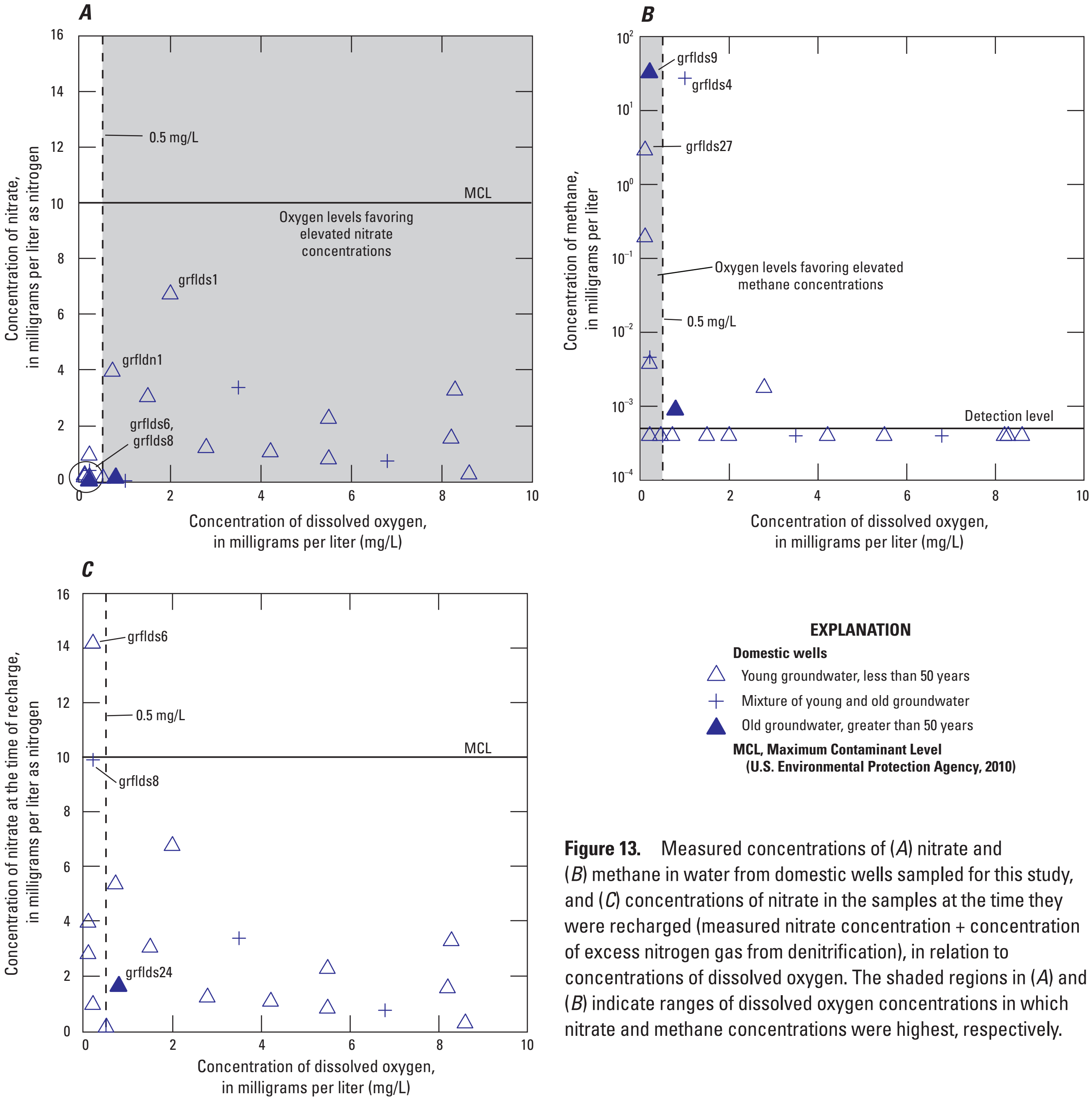


Figure 13. Measured concentrations of (*A*) nitrate and (*B*) methane in water from domestic wells sampled for this study, and (*C*) concentrations of nitrate in the samples at the time they were recharged (measured nitrate concentration + concentration of excess nitrogen gas from denitrification), in relation to concentrations of dissolved oxygen. The shaded regions in (*A*) and (*B*) indicate ranges of dissolved oxygen concentrations in which nitrate and methane concentrations were highest, respectively.

the thermogenic field of figure 14*A* (Whiticar, 1999). Based on the dissolved-oxygen data and position of the sample from grflds4 in figure 14*A* relative to the likely mixing scenarios, methane in that sample was considered to be biogenic in origin but affected by oxidation processes.

Methane oxidation also may have affected hydrocarbon molecular and isotopic compositions in samples collected during previous studies (fig. 14*B*). The median concentration of dissolved oxygen in samples with methane/(ethane + propane) ratios larger than 200 (biogenic methane) was 1.1 mg/L and it was 2.7 mg/L in samples with ratios less than 50 (thermogenic methane). In other words, the most oxic groundwater samples plotted in the thermogenic field of fig. 14*B*, indicating methane oxidation could have altered the composition of some of those samples. Methane oxidation also could be coupled with sulfate reduction in groundwater with low concentrations of dissolved oxygen (Van Stempvoort and others, 2005), but data needed to evaluate that process were not collected as part of this study. Despite the probable role of aerobic oxidation as a methane sink in the aquifer, several of the samples, such as DIET1WW and LANG13WW, were both anoxic and had molecular and isotopic compositions indicative of a thermogenic methane source (fig. 14*B*). So there is evidence for the occurrence of thermogenic methane from the Mesaverde Group, or some other deep

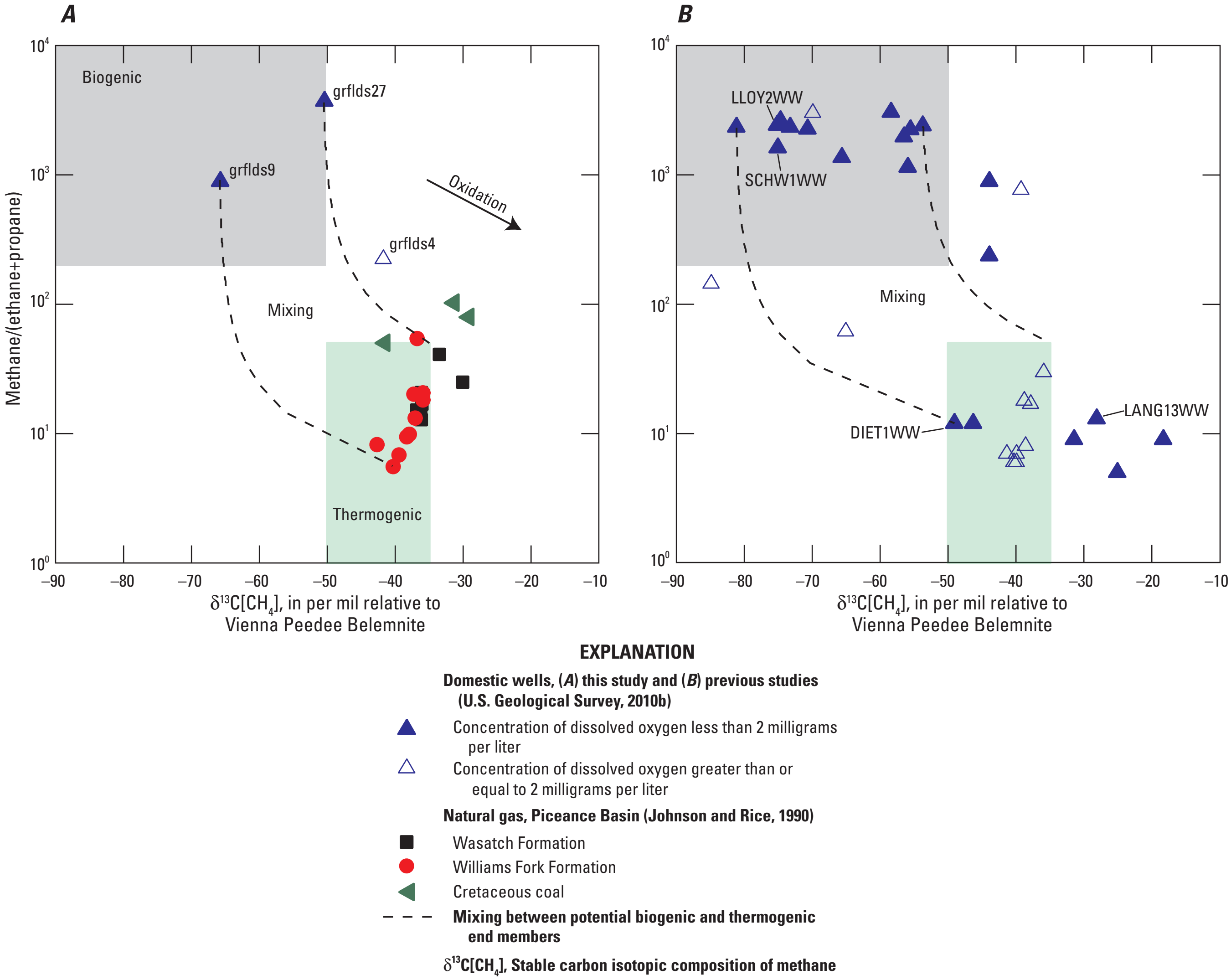


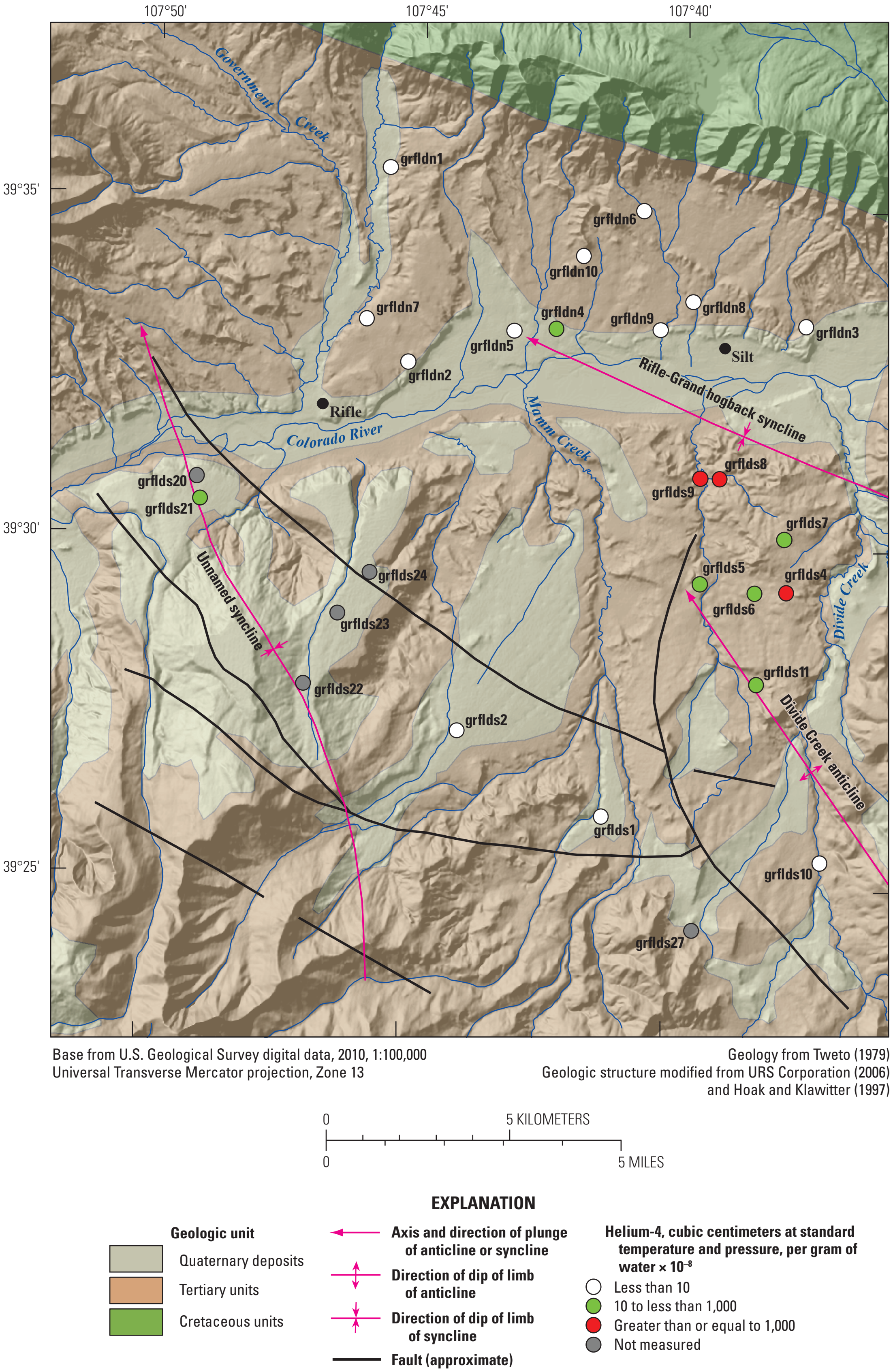
Figure 14. Molecular and isotopic composition of short-chain hydrocarbons in water from domestic wells (*A*) sampled for this study and (*B*) sampled during previous studies. Biogenic and thermogenic fields modified from Bernard and others (1978) and Whiticar (1999).

source, in the Wasatch Formation. Like the wells sampled for this study that produced high-methane water, DIET1WW and LANG13WW were located in the zone of low dissolved-oxygen and high methane concentrations south of Silt. Even though the DIET1WW and LANG13WW samples appeared to contain thermogenic methane, the water-isotopic and chloride/bromide data indicate they contained relatively little water from the Mesaverde Group.

Helium Concentrations and Isotopes

Although the high concentrations of methane in some samples collected for this study appeared to be biogenic in origin that does not necessarily mean the methane was produced in the sampled intervals of the Wasatch Formation. The major-ion, water-isotopic, and chloride/bromide data show that samples containing high concentrations of biogenic methane, like the samples from grflds9, LLOY2WW, and SCHW1WW, also appeared to contain substantial fractions of Mesaverde water and ions. Noble-gas measurements indicate the zone of low dissolved-oxygen and high methane concentrations in which those wells were located (south of Silt) also was an area of high helium-4 concentrations, with concentrations up to 4,900 × 10^{-8} cubic centimeters at standard temperature and pressure, per gram of water (cm^3 STP/g) (table 1 and fig. 15). That helium-4 concentration is about 1,000 times higher than the concentration expected in water equilibrated with air at 10ºC and 1,800 m elevation, indicating groundwater in that area contained a large component of helium-4 derived from subsurface (terrigenic) sources. Importantly, there appeared to be a positive relation between methane and helium-4 concentrations (fig. 16*A*), implying helium-4 could be a useful tracer for understanding the geologic source of the high methane concentrations.

The primary terrigenic sources of helium-4 are upward fluxes from the mantle and decay of uranium and thorium in rocks and sediment of the earth's crust. If terrigenic helium-4 in the samples was from mantle sources then the co-occurrence of high concentrations of helium-4 and biogenic methane (fig. 16*A*) may just be coincidental because biogenic



Base from U.S. Geological Survey digital data, 2010, 1:100,000
Universal Transverse Mercator projection, Zone 13

Geology from Tweto (1979)
Geologic structure modified from URS Corporation (2006)
and Hoak and Klawitter (1997)

Figure 15. Concentrations of helium-4 in water from domestic wells sampled for this study. Geology from Tweto (1979). Geologic structure modified from URS Corporation (2006) and Hoak and Klawitter (1997).

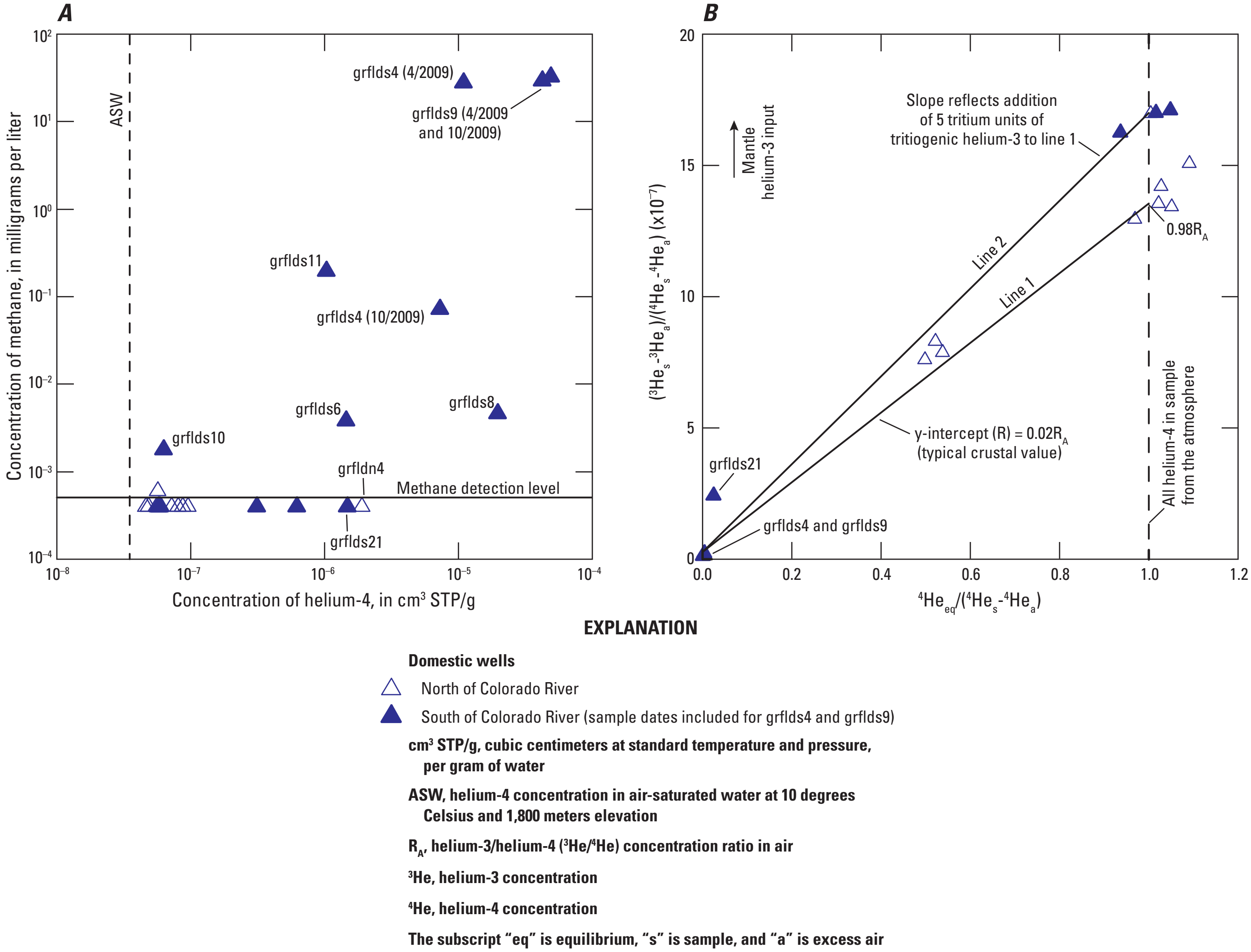


Figure 16. (*A*) Methane concentrations in relation to helium-4 concentrations in water from domestic wells sampled for this study and (*B*) measured helium-3/helium-4 ratios corrected for excess air in relation to the relative amount of helium-4 derived from air-water equilibrium with respect to total helium-4 in the sample, corrected for excess air.

methane is not likely to form under the high temperature and pressure conditions in the earth's mantle (Scott and others, 2004). Helium-3/helium-4 ratios can be used to differentiate mantle and crustal sources of ^{4}He. Crustal sources of helium typically have helium-3/helium-4 ratios about 0.02 times the ratio in air (0.02R_A), whereas mantle helium typically has ratios that are about 7R_A (Mamyrin and Tolstikhin, 1984; Ozima and Podosek, 1983). In figure 16*B*, helium-3/helium-4 ratios were plotted in relation to the relative amount of helium-4 derived from air-water equilibrium with respect to total helium-4 in the sample. An x-axis value of 0 indicates essentially all the helium-4 in the sample was from terrigenic sources. An x-axis value of 1 indicates all the helium-4 was from the atmosphere. Most of the samples had x-axis values near 1, indicating a predominantly atmospheric source for the helium (samples with x-axis values greater than 1 probably were affected by degassing at the time of recharge or during sampling). Of those samples, some had helium-3/helium-4 ratios equal to 0.98R_A, consistent with helium from water-air equilibration, and some had ratios greater than 0.98R_A. In the latter case, this is likely explained by contributions of tritiogenic helium-3 to those samples from tritium decay because all of them contained tritium (line 2 in fig. 16*B*). The data indicate essentially all the helium-4 in the high-methane samples from grflds4 and grflds9 was from crustal sources (x-axis value near 0 and helium-3/helium-4 ratio near 0.02R_A (0.009R_A to 0.017R_A)). One sample, from grflds21, that had a large component of terrigenic helium-4 (x-axis value less than 0.2) also had a helium-3/helium-4 ratio larger than 0.02R_A (0.174R_A). That sample could contain a small component of mantle helium. In general, the data in figure 16*B* indicate the primary terrigenic source of helium-4 in the samples was the crust, with a helium-3/helium-4 ratio close to 0.02R_A.

The three most likely sources of crustal helium-4 are (1) helium-4 produced within the aquifer itself from the decay of uranium and thorium, (2) helium-4 produced at depths below the aquifer and then transported into the aquifer by diffusion or advection, and (3) helium-4 stored in aquifer minerals that is released from the surfaces of relatively freshly fractured or weathered rocks (Torgersen, 1980; Kulongoski and others, 2005). Helium-4 concentrations plotted in relation to depth of the well screen below the water table indicate most of the samples plotted within an envelope of helium-4 concentration gradients ranging from about 1 × 10^{-8} to 1 × 10^{-7} cm^3 STP/g·m (fig. 17). Most of those samples were recharged in the past 50 years (fig. 11), and they contained only very small fractions of water from the Mesaverde Group on the basis of water-isotopic and chloride/bromide data (figs. 9 and 12). The data are consistent with in-situ production of small amounts of helium-4 in the Wasatch Formation from uranium and thorium decay during the short residence time of those samples in the aquifer (crustal source 1). Samples from grflds8 and grflds9, which had the highest helium-4 concentrations and largest fractions of water from the Mesaverde Group on the basis of chloride/bromide data (fig. 12), represented larger gradients ranging from about 4 × 10^{-7} to 1 × 10^{-6} cm^3 STP/g·m. The disparity in helium-4 gradients between the samples with small and large fractions of water from the Mesaverde Group could indicate high helium-4 in the latter group of samples was contained in much older groundwater, such as in the Mesaverde Group or some other relatively deep geologic unit, and subsequently transported into the Wasatch Formation (crustal source 2). The other possible source of high helium-4 in water from grflds8 and grflds9, release from relatively freshly fractured or weathered rocks in the aquifer (crustal source 3), cannot be ruled out but seems less likely because of the Mesaverde-like composition of those water samples.

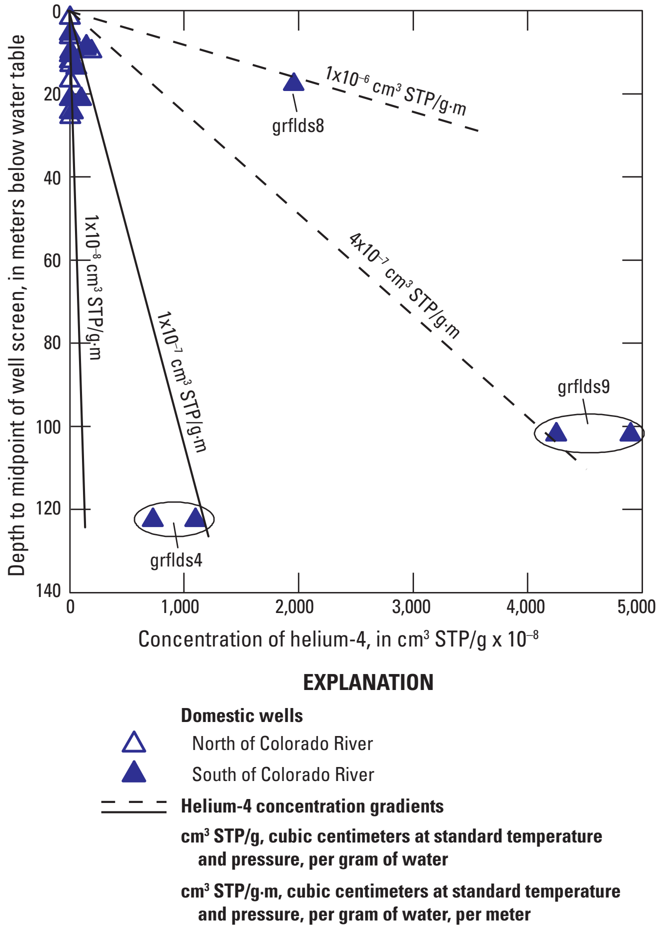


Figure 17. Concentrations of helium-4 in water from domestic wells sampled for this study in relation to depth below the water table to the midpoint of the well screen.

Concentrations of crustal helium-4 in the samples can be used to qualitatively constrain groundwater age in the flow system using the following equations (Andrews and Lee, 1979; Stute and others, 1992):

$$^4He_{sol} = \rho_s \times \Lambda \times \{1.19\times10^{-13}[U] + 2.88\times10^{-14}[Th]\} \times \frac{(1-n)}{n} \qquad (9)$$

and

$$age = \frac{^4He_{crustal}}{\dfrac{J}{100nz\rho_w} + {}^4He_{sol}} \qquad (10)$$

where

$^4He_{sol}$	is the rate at which helium-4 enters solution from uranium and thorium decay, in cubic centimeters at standard temperature and pressure, per gram, per year (cm^3 STP/g·yr);
ρ_s	is rock bulk density, in grams per cubic centimeter (g/cm^3);
Λ	is the fraction of helium-4 produced in the rock that is released into solution, unitless (Λ is assumed to equal 1 for aquifers; Andrews and Lee, 1979; Torgersen and Clarke, 1985);
$[U]$ and $[Th]$	are uranium and thorium concentrations in the aquifer material, in parts per million (ppm);
n	is porosity, unitless;
$^4He_{crustal}$	is the concentration of crustal helium-4 in the sample, in cubic centimeters at standard temperature and pressure, per gram of water (cm^3 STP/g);
J	is the helium-4 flux across the base of the aquifer, in cubic centimeters at standard temperature and pressure, per square centimeter, per year (cm^3 STP/cm^2·yr);
z	is the distance from the well screen to the base of the aquifer, in meters;

and

ρ_w	is the density of water (about 1 g/cm^3).

For the age calculations summarized in table 2, it was assumed that $\rho_s = 2.65$ g/cm^3, [U] = 2.2 ppm and [Th] = 9 ppm, and n = 0.2. Concentrations of uranium and thorium in the Wasatch outcrop area, derived from aerial gamma-ray contour maps (Phillips and others, 1993), were used as estimates of [U] and [Th]. Values for J and z in the study area are not known, so ranges of values were used based on data from the literature. Three values of J were assumed: 0 (no helium flux), 3×10^{-6} (average crustal degassing rate; O'Nions and Oxburgh, 1983), and 3×10^{-5} (a high degassing rate, such as was reported in a tectonically active area of California; Kulongoski and others, 2005) cubic centimeters of helium-4 at standard temperature and pressure, per square centimeter, per year (cm^3 STP ^{4}He/cm^2·yr,). Two values of z were assumed (670 and 1,200 meters) based on data for the Wasatch Formation reported by URS Corporation (2006).

Apparent helium-4 ages were calculated for water from grflds9 because it had the highest measured helium-4 concentrations and tritium data indicate it contained no young groundwater. The oldest calculated ages (more than 5 million years) were obtained for the zero flux condition (table 2), but that condition does not seem likely for water from grflds9 based on the helium-4 concentration gradients in figure 17. The higher-flux conditions resulted in ages from about 19,000 to 326,000 years (table 2), which were substantially older than the apparent ages for the other samples from the Wasatch Formation (fig. 11) and indicate a deep source for helium-4 in that sample. The co-occurrence of high concentrations of methane with helium-4 in that sample (fig. 16*A*) implies the biogenic methane also was derived from a deep source. Although the values of J selected for this analysis were intended to represent a range of possible flux conditions it is not possible to directly evaluate their applicability to the study area in the absence of other data such as groundwater radiocarbon ages (Kulongoski and others, 2005). Also, this age analysis did not account for the effects of diffusion and advective groundwater flow in the aquifer on the observed helium-4 distributions (Stute and others, 1992; Castro and others, 2000). Nevertheless, the apparent helium-4 ages and concentration gradients are generally consistent with the water-isotopic, major-ion, and chloride/bromide data and, together, the diverse geochemical data sets indicate that water, ions, and gases in grflds9 were derived from deep sources.

Methane Transport

The water-isotopic and major-ion data indicate the Mesaverde Group was the source of water and ions in grflds9 (figs. 7 and 9*A*). But it probably was not the source of biogenic methane in grflds9 because methane from the Mesaverde Group appeared to be thermogenic in origin (Johnson and Rice, 1990; Papadopulos and Associates, Inc., 2008) (fig. 14*B*). Deeper zones in the Wasatch Formation were a more likely source for the biogenic methane in grflds9. The Wasatch Formation extends several hundred meters below the depth of grflds9 on the basis of the isopach map of the Wasatch Formation published by URS Corporation (2006). Water from the Mesaverde Group could incorporate biogenic methane from the deep Wasatch Formation before entering the shallow Wasatch Formation if it moved through natural fractures or uncemented annular space in gas wells that intersected zones enriched in biogenic methane. The north-south trending zone where domestic wells produced water with high methane and helium-4 concentrations generally coincided with known geologic structures such as the Divide Creek anticline, Rifle-Grand Hogback syncline, and deep faults (figs. 6 and 15), and they could be pathways for water and gas migration. This convergence of chemistry and geologic structure was noted by URS Corporation (2006) and Papadopulos and Associates, Inc. (2008). A compilation of data on surface-casing depths in 924 gas wells in the study area done by URS Corporation (2006) showed a median casing depth of 260 m, which is probably several hundred meters above the base of the Wasatch Formation in the high methane zone. Presumably, the annular space in those wells was uncemented between the bottom of the surface casing in the Wasatch Formation and the top of cement used to seal the gas-producing interval in the Mesaverde Group (URS Corporation, 2006). Some of those uncemented intervals could contain high concentrations of biogenic methane and act as pathways for water and gas migration.

Well LANG13WW, in contrast to grflds9, had water-isotopic and major-ion compositions similar to that of water from the shallow Wasatch Formation (figs. 8, 9*B*, and 12), but it contained thermogenic methane (fig. 14*B*). Both wells contained more than 1 mg/L methane. The data from

Table 2. Modeled helium-4 ages, in years, of water from well grflds9, Garfield County, Colorado.

[ppm, parts per million; g/cm^3, grams per cubic centimeter; ^{4}He$_{sol}$, helium-4 solution rate; cm^3 STP/g·yr, cubic centimeters at standard temperature and pressure, per gram of water, per year; ^{4}He$_{crustal}$, concentration of crustal helium-4 in the sample; cm^3 STP/g, cubic centimeters at standard temperature and pressure, per gram of water; J, helium-4 flux across the base of the aquifer; cm^3 STP/cm^2·yr, cubic centimeters at standard temperature and pressure, per square centimeter, per year; z, distance from well screen to base of aquifer; m, meters. Fixed parameter values in the models: uranium concentration in sediment = 2.2 ppm; thorium concentration in sediment = 9.0 ppm; porosity = 0.2; sediment bulk density = 2.6 g/cm^3; ^{4}He$_{sol}$ = 5.42×10^{-12} cm^3 STP/g·yr]

Well name	Sample date	^{4}He$_{crustal}$ (10^{-8} cm^3 STP/g)[1]	J = 0 (cm^3 STP/cm^2·yr)		J = 3×10^{-6} (cm^3 STP/cm^2·yr)		J = 3×10^{-5} (cm^3 STP/cm^2·yr)	
			z = 670 m	z = 1,200 m	z = 670 m	z = 1,200 m	z = 670 m	z = 1,200 m
grflds9	10/28/2009	4,250	7,841,328 years	7,841,328 years	185,346 years	325,870 years	18,937 years	33,853 years

[1] Recharge temperature assumed to equal 7.9 degrees Celsius.

LANG13WW could be consistent with fluids containing a high ratio of gas to water leaking upward from the Mesaverde Group, whereas the data from grflds9 appear to be more consistent with the leaking fluids containing a low ratio of gas to water. Determining whether these apparent differences in ratios of gas to water are indicative of different transport pathways was beyond the scope of this investigation. To address that question it would be helpful to collect more geochemical data that could be used to trace water, ion, and gas movement in the area around those wells. Equally important would be the collection of detailed geospatial data on water-well, gas-well, and fracture locations to determine whether the thermogenic gas in water wells could be spatially related to gas wells or to fractures. More generally, it would be helpful to collect a diverse set of baseline geochemical data in areas prior to natural-gas development.

Summary

Previous water-quality assessments reported elevated concentrations of nitrate and methane in water from domestic wells screened in shallow zones of the Wasatch Formation, Garfield County, Colorado. In 2009, the U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, analyzed samples collected from 26 domestic wells for a diverse set of geochemical tracers for the purpose of determining sources and sinks of nitrate and methane in groundwater from the Wasatch Formation. The measured constituents included major ions, nutrients, hydrocarbon molecular and isotopic compositions, redox constituents, water isotopic compositions, tracers of groundwater age (tritium, chlorofluorocarbons, sulfur hexafluoride, and tritium/helium-3), and noble gases. Nitrate concentrations ranged from less than 0.04 to 6.74 milligrams per liter as nitrogen and were highest in young (less than 50 years), oxic (concentrations of dissolved oxygen greater than or equal to 0.5 milligram per liter) groundwater and lowest in anoxic groundwater, regardless of age. Methane concentrations ranged from less than 0.0005 to 32.5 milligrams per liter. High methane concentrations (greater than 1 milligram per liter) occurred in a north-south trending zone of anoxic groundwater located south of Silt, Colorado.

Chloride/bromide mass ratios and tracers of groundwater age indicate that septic-system effluent or animal waste was a source of nitrate in some young groundwater, although other sources such as fertilizer also may have contributed nitrate to the groundwater. Denitrification removed most of the nitrate in anoxic samples. The nitrate concentration in one such sample at the time it recharged the aquifer was calculated to be about 14 milligrams per liter as nitrogen, which would have exceeded the federal drinking-water standard for nitrate, but denitrification in anoxic parts of the aquifer removed 99 percent of the nitrate before it reached the sampled well.

Hydrocarbon molecular and isotopic composition data indicate that the highest concentrations of methane were biogenic in origin. The primary methane sink in the aquifer appeared to be methane oxidation on the basis of dissolved-oxygen and methane concentrations and methane stable-isotopic data. The north-south trending zone containing high methane concentrations also was characterized by high concentrations of helium-4 derived from a relatively deep crustal source on the basis of helium-3/helium-4 ratios, helium-4 concentration gradients in the aquifer, and apparent helium-4 groundwater ages (possibly greater than 19,000 years in the sample with the highest helium-4 and methane concentrations). The co-occurrence of high concentrations of methane and helium-4 implies the biogenic methane also was derived from a deep source. One sample containing high concentrations of biogenic methane and helium-4 had water-isotopic and major-ion compositions similar to that of water from the underlying Mesaverde Group, which was the primary natural-gas producing interval in the study area. Methane from the Mesaverde Group was largely thermogenic in origin so biogenic methane in the sample was more likely derived from deeper zones in the Wasatch Formation.

Water from the Mesaverde Group could incorporate biogenic methane from the deep Wasatch Formation before entering the shallow Wasatch Formation if it moved through natural fractures or uncemented annular space in gas wells that intersected zones enriched in biogenic methane. The north-south trending zone where domestic wells produced water with high methane and helium-4 concentrations generally coincided with known geologic structures such as the Divide Creek anticline, Rifle-Grand Hogback syncline, and deep faults, and they could be pathways for water and gas migration. A compilation of data on surface-casing depths in 924 gas wells done by URS Corporation (2006) showed a median casing depth of 260 m, which is probably several hundred meters above the base of the Wasatch Formation in the high methane zone. Presumably, the annular space in those wells was uncemented between the bottom of the surface casing in the Wasatch Formation and the top of cement used to seal the gas-producing interval in the Mesaverde Group (URS Corporation, 2006). Some of those uncemented intervals could contain high concentrations of biogenic methane and act as pathways for water and gas migration.

Acknowledgments

The authors wish to thank homeowners in Garfield County for allowing us to sample their wells. Bryant Jurgens and Mark Levorsen provided helpful comments on earlier versions of the manuscript.

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Publishing support provided by:
Denver Publishing Service Center, Denver, Colorado

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McMahon and ohters—**Use of Diverse Geochemical Data Sets in Groundwater, Garfield County, Colorado, 2009**—USGS/SIR 2010–5215