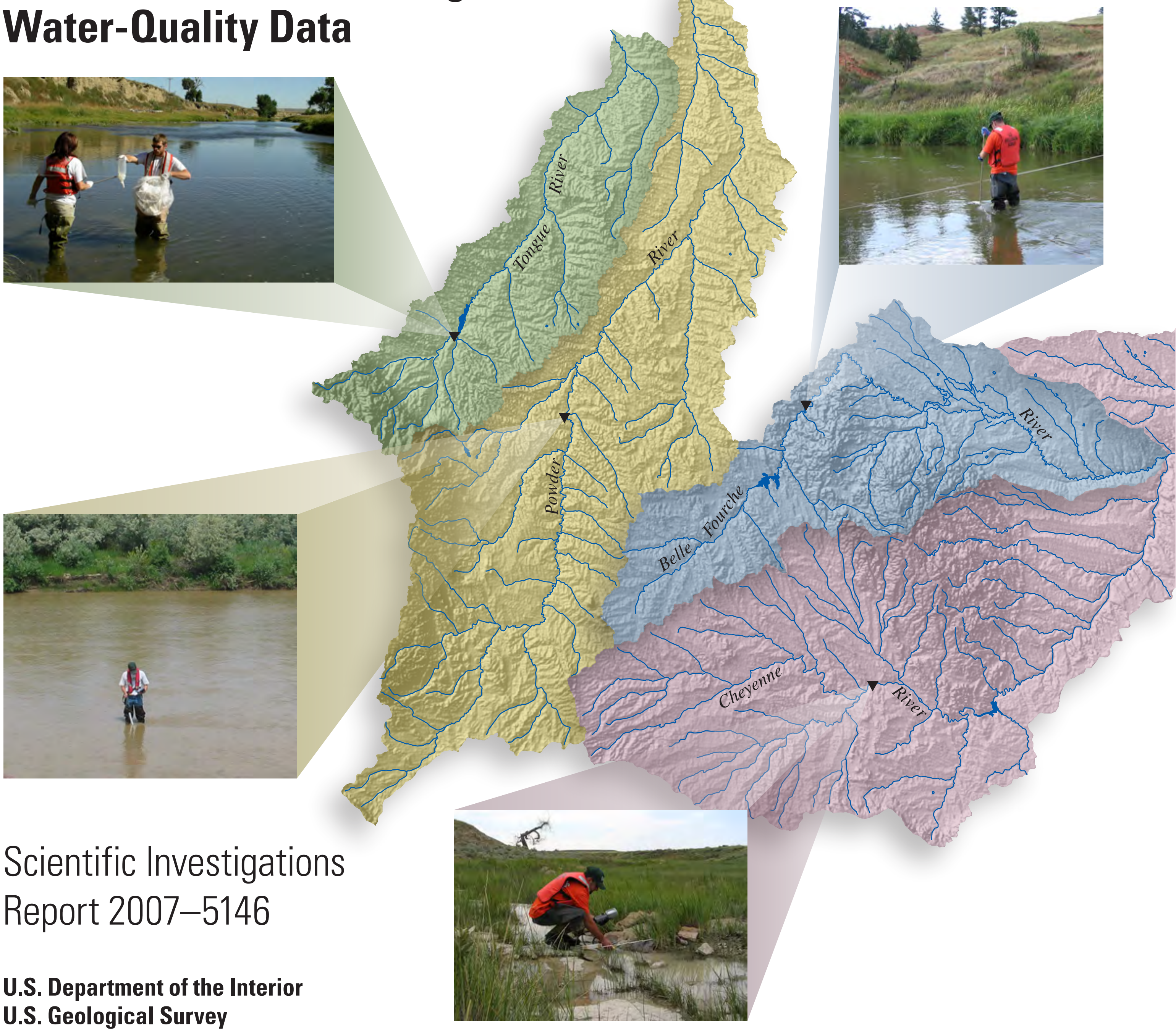
Prepared in cooperation with the Wyoming Department of Environmental Quality

Water-Quality Characteristics for Sites in the Tongue, Powder, Cheyenne, and Belle Fourche River Drainage Basins, Wyoming and Montana, Water Years 2001–05, with Temporal Patterns of Selected Long-Term Water-Quality Data



Scientific Investigations
Report 2007–5146

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

Cover photographs Clockwise from upper left: Site T4, Tongue River near Decker, Montana (photo by David Nimick); Site B5, Belle Fourche River below Hulett, Wyoming (photo by Jason Swanson); Site C3, Cheyenne River near Spencer, Wyoming (photo by Jason Swanson); and Site P5, Powder River at Arvada, Wyoming (photo by Melanie Clark).

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By Melanie L. Clark and Jon P. Mason

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U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
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Conversion Factors and Datums

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch	2.54	centimeter (cm)
inch	25.4	millimeter (mm)
foot (ft)	.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
cubic foot (ft^3)	0.02832	cubic meter (m^3)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
acre-foot (acre-ft)	.001233	cubic hectometer (hm^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

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

$$°F=(1.8\times°C)+32$$

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

$$°C=(°F-32)/1.8$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

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

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

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

Water year is the 12-month period from October 1 through September 30 and is designated by the year in which it ends. For example, the water year ending September 30, 2001 is called water year 2001.

Abbreviated Water-Quality Units

mg/L	milligrams per liter
µg/L	micrograms per liter
µm	micrometer
µS/cm at 25°C	microsiemens per centimeter at 25 degrees Celsius

Abbreviations

BLM	Bureau of Land Management
CBNG	coalbed natural gas
ESTREND	estimate trend
LOWESS	locally weighted, scatterplot smoothing
NWIS	National Water Information System
RPD	relative percent difference
SAR	sodium-adsorption ratio
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WDEQ	Wyoming Department of Environmental Quality

Water-Quality Characteristics for Sites in the Tongue, Powder, Cheyenne, and Belle Fourche River Drainage Basins, Wyoming and Montana, Water Years 2001–05, with Temporal Patterns of Selected Long-Term Water-Quality Data

By Melanie L. Clark and Jon P. Mason

Abstract

Water-quality sampling was conducted regularly at stream sites within or near the Powder River structural basin in northeastern Wyoming and southeastern Montana during water years 2001–05 (October 1, 2000, to September 30, 2005) to characterize water quality in an area of coalbed natural gas development. The U.S. Geological Survey, in cooperation with the Wyoming Department of Environmental Quality, characterized the water quality at 22 sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins. Data for general hydrology, field measurements, major-ion chemistry, and selected trace elements were summarized, and specific conductance and sodium-adsorption ratios were evaluated for relations with streamflow and seasonal variability. Trend analysis for water years 1991–2005 was conducted for selected sites and constituents to assess change through time.

Average annual runoff was highly variable among the stream sites. Generally, streams that have headwaters in the Bighorn Mountains had more runoff as a result of higher average annual precipitation than streams that have headwaters in the plains. The Powder River at Moorhead, Mont., had the largest average annual runoff (319,000 acre-feet) of all the sites; however, streams in the Tongue River drainage basin had the highest runoff per unit area of the four major drainage basins. Annual runoff in all major drainage basins was less than average during 2001–05 because of drought conditions. Consequently, water-quality samples collected during the study period may not represent long-term water-quality conditions for all sites.

Water-quality characteristics were highly variable generally because of streamflow variability, geologic controls, and potential land-use effects. The range of median specific-conductance values among sites was smallest in the Tongue River drainage basin. Median values in that basin ranged from 643 microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C) on the Tongue River to 1,460 μS/cm at 25°C on Prairie Dog Creek. The Tongue River drainage basin has the largest percentage of area underlain by Mesozoic-age and older rocks and by more resistant rocks. In addition, the higher annual precipitation and a steeper gradient in this basin compared to basins in the plains produce relatively fast stream velocities, which result in a short contact time between stream waters and basin materials. The Powder River drainage basin, which has the largest drainage area and most diverse site conditions, had the largest range of median specific-conductance values among the four major drainage basins. Median values in that basin ranged from 680 μS/cm at 25°C on Clear Creek to 5,950 μS/cm at 25°C on Salt Creek. Median specific-conductance values among sites in the Cheyenne River drainage basin ranged from 1,850 μS/cm at 25°C on Black Thunder Creek to 4,680 μS/cm at 25°C on the Cheyenne River. The entire Cheyenne River drainage basin is in the plains, which have low precipitation, soluble geologic materials, and relatively low gradients that produce slow stream velocities and long contact times. Median specific-conductance values among sites in the Belle Fourche River drainage basin ranged from 1,740 μS/cm at 25°C on Caballo Creek to 2,800 μS/cm at 25°C on Donkey Creek.

Water in the study area ranged from a magnesium-calcium-bicarbonate type for some sites in the Tongue River drainage basin to a sodium-sulfate type at many sites in the Powder, Cheyenne, and Belle Fourche River drainage basins. Little Goose Creek, Goose Creek, and the Tongue River in the Tongue River drainage basin, and Clear Creek in the Powder River drainage basin, which have headwaters in the Bighorn Mountains, consistently had the smallest median dissolved-sodium concentrations, sodium-adsorption ratios, dissolved-sulfate concentrations, and dissolved-solids concentrations. Salt Creek, Wild Horse Creek, Little Powder River, and the Cheyenne River, which have headwaters in the plains, tended to have the largest median concentrations of these constituents. Salt Creek had large concentrations of several constituents, including dissolved chloride, as a result of saline ground waters discharged to Salt Creek or its tributaries from conventional oil and gas production. Dissolved-chloride concentrations frequently were greater than State of Wyoming water-quality criteria in samples from Salt Creek and on the Powder River at sites downstream from Salt Creek.

Total-aluminum, dissolved-arsenic, total-barium, total-beryllium, dissolved-iron, dissolved-manganese, and total-selenium concentrations were variable across the drainage basins. Median total-aluminum concentrations were greater than 100 micrograms per liter at most sites. In contrast, concentrations of other constituents, such as total beryllium, generally were small; median concentrations for beryllium were less than 0.1 microgram per liter at many sites. Total aluminum and dissolved manganese were the trace elements that most frequently occurred in concentrations greater than established water-quality criteria for Wyoming.

An analysis of specific conductance and sodium-adsorption ratios indicated both constituents generally had an inverse relation with streamflow. Land-use activities that may modify natural stream characteristics may have weakened the constituent and streamflow relations at some sites. Seasonal variability in specific conductance and sodium-adsorption ratios generally was significant (*p*-values less than 0.10) for streams that have headwaters in mountainous areas. Seasonal variability in specific conductance generally was not significant (*p*-values greater than 0.10) for streams that have headwaters in the plains; however, seasonal variability generally was observed for sodium-adsorption ratios at these sites.

Eight sites in the Tongue, Powder, and Belle Fourche River drainage basins having sufficient long-term data were evaluated for trends in specific conductance during water years 1991–2005. Trends in specific conductance were not significant (*p*-values greater than 0.10) at the eight sites when values were flow-adjusted for streamflow variability. Four sites in the Powder River drainage basin also were evaluated for trends in sodium-adsorption ratios. Upward trends in flow-adjusted sodium-adsorption ratios were significant (*p*-values less than 0.10) for a site on Salt Creek and two sites on the Powder River. A downward trend in flow-adjusted values for sodium-adsorption ratios was significant for a site on the Little Powder River. The causes of the trends were not determined.

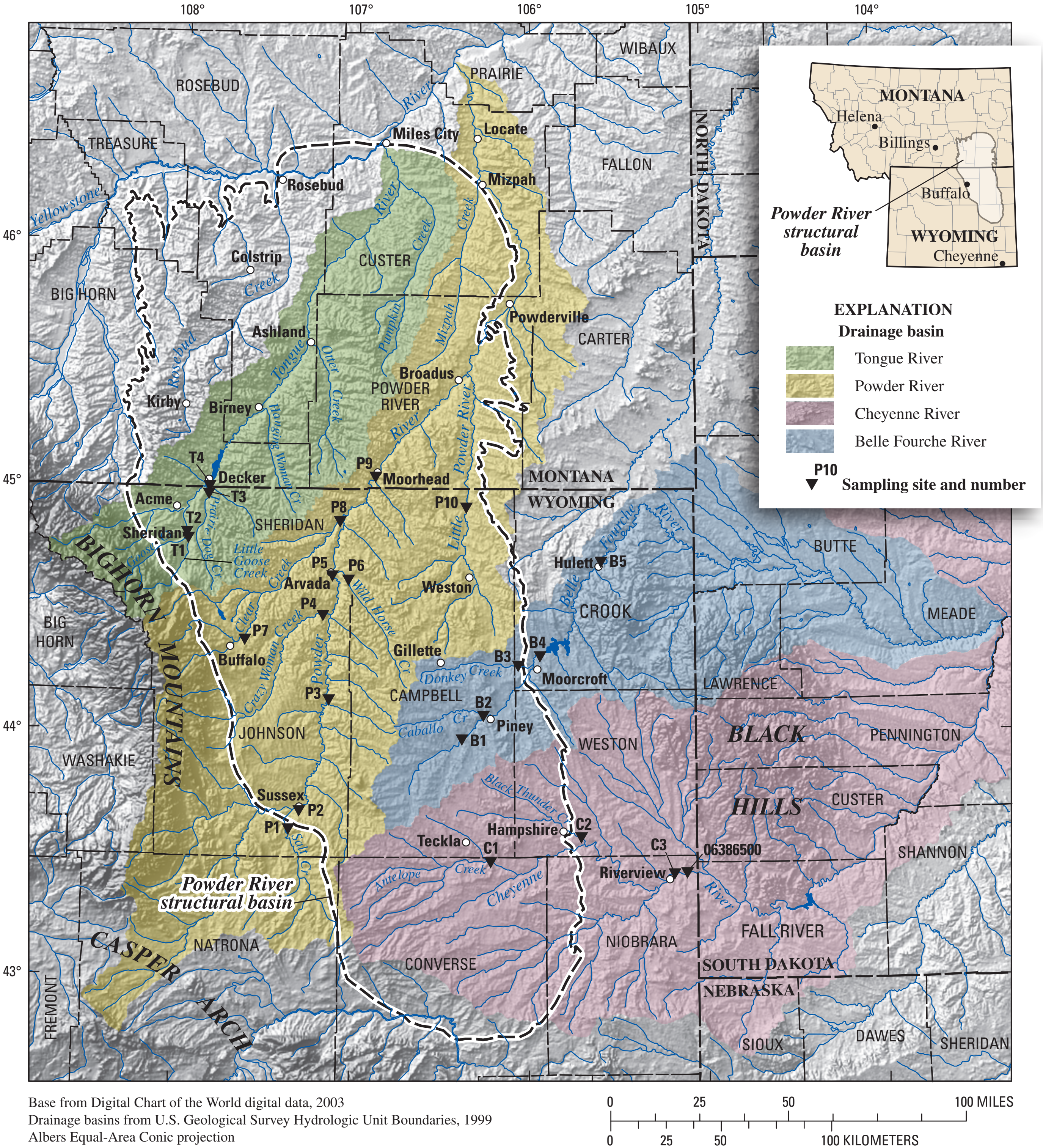
Introduction

In recent years, coalbed natural gas (CBNG) has become an important resource for the United States. The Powder River structural basin (fig. 1) in northeastern Wyoming and southeastern Montana contains large amounts of coal and was estimated to contain nearly 14.3 trillion cubic feet (mean estimate) of undiscovered CBNG when last assessed by the U.S. Geological Survey (USGS) in 2001 (U.S. Geological Survey, 2002). CBNG development, which began in the 1980s, became widespread in the late 1990s. During CBNG development, water is pumped from wells drilled into coalbeds, thus lowering the hydrostatic pressure in the coalbeds and allowing the natural gas that was confined and stored within the internal surfaces and voids of the coal to flow and be captured for use (DeBruin and others, 2000; Bryner, 2002). The amount of water produced during CBNG development in the Powder River structural basin in Wyoming (fig. 2) ranged from about 66,000 to 73,000 acre-feet (acre-ft) per year from 2001 to 2005 (Wyoming Oil and Gas Conservation Commission, 2006). Currently (2007), most water produced during CBNG development in Wyoming is discharged into constructed reservoirs or into surface drainages where the water may infiltrate into the ground, become part of the streamflow, or evaporate. Montana has much less CBNG development than Wyoming, and development in Montana is limited to areas near Decker (Wheaton and Donato, 2004).

Concerns have been expressed regarding the quality of some waters produced during CBNG development and the effect produced waters may have on the water quality of streams that drain the CBNG-development area. The quantity and quality of the produced waters vary depending on the coalbed source (Rice and others, 2000; Bartos and Ogle, 2002). Specific conductance and sodium-adsorption ratios (SARs) of the produced waters have been of particular concern because the amounts of those constituents may be larger in produced waters than those in the receiving streams. An increase of specific conductance and SARs in streams has the potential to affect the use of the streams for irrigation (Hanson and others, 1999). Specific conductance and SARs in coalbed waters of the Powder River structural basin increase to the north and west in the development area (Rice and others, 2002). To help address stream-water-quality concerns, the USGS, in cooperation with the Wyoming Department of Environmental Quality (WDEQ) and the Bureau of Land Management (BLM), began monitoring water quality in areas of CBNG development at sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins during water year 2001. Currently (2007), the water-quality monitoring continues on streams in those drainage basins. A study was done by the USGS, in cooperation with the WDEQ, to characterize the water quality at 22 sites in Wyoming or near the Wyoming-Montana State line.

Purpose and Scope

The purpose of this report is to characterize the water quality at 22 sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins. Specifically, this report presents (1) a description of general hydrology; (2) summaries of water-quality characteristics for water years 2001–05; (3) an analysis of specific conductance and SAR for water years 2001–05 that includes relations with streamflow and seasonal variability; and (4) temporal patterns in selected long-term water-quality data, including a trend analysis of selected sites and constituents for water years 1991–2005.



Base from Digital Chart of the World digital data, 2003
Drainage basins from U.S. Geological Survey Hydrologic Unit Boundaries, 1999
Albers Equal-Area Conic projection
Standard parallels 41°00′N and 45°00′N, central meridian 105°00′W

Figure 1. Location of sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

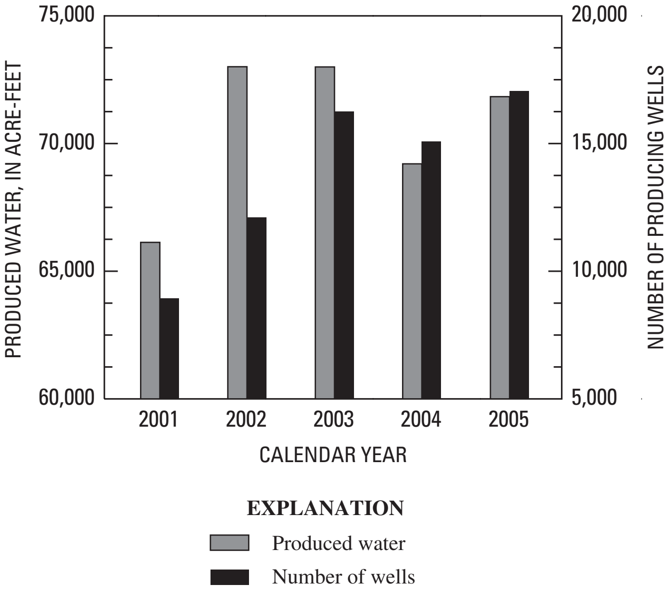


Figure 2. Amount of produced water and number of producing coalbed-natural-gas wells, Powder River structural basin, Wyoming, calendar years 2001–05. (Wyoming Oil and Gas Conservation Commission, 2006)

The sites were on main stems, on tributaries that have headwaters in mountainous areas, and on tributaries that have headwaters in the plains (table 1). Drainage areas (where determined) varied widely among the sites and ranged from 159 square miles (mi^2) at site T1 on Little Goose Creek to 8,088 mi^2 at site P9 on the Powder River. The site numbers given in table 1 and on figure 1 are used throughout the report for site identification; the formal USGS station numbers and station names are given in table 1. The site numbers are composed of a letter followed by a number. The letter denotes the major drainage basin in which the site is located: T, Tongue River; P, Powder River; C, Cheyenne River; and B, Belle Fourche River. The number denotes the downstream order of the site or the downstream order in which streamflow from a tributary enters the main stem of the drainage. For example, site P1 is the farthest upstream site in the Powder River drainage basin, site P2 is the second farthest upstream site, and so on.

Previous Investigations

The water resources of the Powder River structural basin have been the subject of many previous studies in which stream-water quality, stream-water quantity, ground-water quality, and ground-water quantity have been investigated. This section describes only selected investigations that include characterizations of stream-water quality in the study area and is not intended to be a comprehensive summary of all the available literature.

An early report by Hembree and others (1952) describes sedimentation and chemical quality of streams in the Powder River drainage basin. The hydrologic investigations atlas by Hodson and others (1973) includes descriptions of stream-water quality and streamflow statistics for selected sites in and adjacent to the Powder River structural basin. In a report by Druse and others (1981), results are presented for base-flow streamflow measurements and water-quality measurements made in the fall of 1977 and 1978 at sites in the northern Great Plains of Montana and Wyoming. Water resources and coal-mining issues in several drainages, including the Tongue River and Goose Creek drainages, are described in a report by Slagle and others (1983). In the same report series, Lowry and others (1986) described the effects of coal mining on water resources in parts of the Powder River structural basin, including the Cheyenne and Belle Fourche River drainage basins. Their report includes sections on streamflow statistics and stream-water quality. Peterson (1988) statistically summarized stream-water-quality data collected at sites in coal regions of Wyoming, including the Powder River coal basin, for water years 1975–81. Many of the sites are the same as the sampling sites used in this report. Although other land uses may have affected water quality for that time period, the report does provide a summary of water-quality conditions prior to CBNG development. Martin and others (1988) described the potential cumulative effects of existing and anticipated surface-coal mining on the hydrologic system of the eastern Powder River structural basin. Trends in water-quality constituents for stream sites in the Powder River drainage basin are discussed in reports by Cary (1989, 1991). The geohydrology and potential effects of coal mining in coal-lease areas in the Powder River structural basin are described in a report by Fogg and others (1991). Although the focus of the report by Fogg and others (1991) is on ground water, the report also discusses some of the implications of ground-water movement on surface-water drainage systems. The chemical quality of the Powder River and its principal tributaries are described in a report by Lindner-Lunsford and others (1992). The report also describes a monthly mass-balance model, along with several simulations employing the model, of the surface-water system in the Powder River drainage basin, emphasizing the hydrologic processes that affect streamflow and the chemical quality of water. Lindner-Lunsford and Wilson (1992) provided a comprehensive bibliographic summary of publications for the Powder River structural basin for 1950–91. Miller and others (2005) described water-quality characteristics for three sites in the Powder River structural basin that were sampled as part of the USGS National Water-Quality Assessment Program.

Recent publications have addressed issues specifically related to CBNG development in the Powder River structural basin. Clark and others (2001) summarized USGS historical data-collection efforts at sites in the Powder River drainage basin. McBeth and others (2003) described CBNG water chemistry in the Cheyenne, Belle Fourche, and Little Powder

Table 1. Selected characteristics for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana.

[TM, tributary that has headwaters in a mountainous area; TP, tributary that has headwaters in the plains; M, main stem; --, not determined]

Site number (fig. 1)	U.S. Geological Survey station number	U.S. Geological Survey station name	Stream type	Stream class	Drainage area (square miles)
T1	06304500	Little Goose Creek at Sheridan, Wyo.	TM	2AB[1]	159
T2	06305500	Goose Creek below Sheridan, Wyo.	TM	2AB[1]	392
T3	06306250	Prairie Dog Creek near Acme, Wyo.	TP	2AB[1]	358
T4	06306300	Tongue River at Stateline near Decker, Mont.	M	B–2[2]	1,453
P1	06313400	Salt Creek near Sussex, Wyo.	TP	2C[1]	769
P2	06313500	Powder River at Sussex, Wyo.	M	2ABWW[1]	3,090
P3	06313605	Powder River below Burger Draw near Buffalo, Wyo.	M	2ABWW[1]	--
P4	06316400	Crazy Woman Creek at upper station near Arvada, Wyo.	TM	2ABWW[1]	937
P5	06317000	Powder River at Arvada, Wyo.	M	2ABWW[1]	6,050
P6	06317020	Wild Horse Creek near Arvada, Wyo.	TP	3B[1]	250
P7	06320210	Clear Creek above Kumor Draw near Buffalo, Wyo.	TM	2AB[1]	--
P8	06324000	Clear Creek near Arvada, Wyo.	TM	2AB[1]	1,110
P9	06324500	Powder River at Moorhead, Mont.	M	C–3[2]	8,088
P10	06324970	Little Powder River above Dry Creek near Weston, Wyo.	TP	2AB[1]	1,237
C1	06364700	Antelope Creek near Teckla, Wyo.	TP	3B[1]	959
C2	06376300	Black Thunder Creek near Hampshire, Wyo.	TP	3B[1]	535
C3	06386400	Cheyenne River at Riverview, Wyo.	M	2ABWW[1]	5,160
B1	06425720	Belle Fourche River below Rattlesnake Creek near Piney, Wyo.	M	2ABWW[1]	495
B2	06425900	Caballo Creek at mouth near Piney, Wyo.	TP	3B[1]	260
B3	06426400	Donkey Creek near Moorcroft, Wyo.	TP	3B[1]	246
B4	06426500	Belle Fourche River below Moorcroft, Wyo.	M	2ABWW[1]	1,690
B5	06428050	Belle Fourche River below Hulett, Wyo.	M	2ABWW[1]	--

[1] Stream class determined by Wyoming Department of Environmental Quality (2001a).

[2] Stream class determined by Montana Department of Environmental Quality (2002).

River drainage basins. A USGS water-quality monitoring program that was developed to evaluate water quality and possible effects from CBNG development in the Tongue River drainage basin is described in a report by Nimick (2004). Patz and others (2004) described changes in major-ion chemistry, including SAR values, of waters produced in ephemeral drainages during CBNG development. Patz and others (2006) described changes in trace elements in ephemeral drainages that receive waters produced during CBNG development. A watershed monitoring plan developed by the Powder River Basin Interagency Working Group is described in a report by Clark and others (2005). The BLM compiled summaries of monitoring data for specific conductance and SAR for sites included in the monitoring plan (*http://www.wy.blm.gov/prbgroup/monitoring.htm*). A publication by Wright and others (2006) also was prepared as part of the Interagency Working Group efforts and addresses data-collection activities related to aquatic communities; otherwise, a summary of publications that address aquatic communities is outside the scope of this report. Clark and Mason (2006) presented regression equations for estimating SAR from specific conductance and determined dissolved-solids loads for four sites in the Powder River drainage basin.

Several reports and sources that include CBNG-related work from multiple researchers also have been compiled. The Wyoming Geological Association (Miller, 1999) compiled a conference guidebook that includes several papers on the topic of CBNG development in the Powder River structural basin. Although the focus of the guidebook primarily is on ground water, some of the research has implications for stream-water quality. Flores and others (2001) compiled research for a field conference on effects of CBNG in the Powder River structural basin. A public information circular compiled by Stine (2005) presents information from several research projects that addressed stream-water quality and quantity. Zoback (2005) compiled research that focused primarily on ground water, but some of the research has implications for stream-water quality. The Wyoming CBM (coalbed methane) Clearinghouse (*http://www.cbmclearinghouse.info/*) and Montana State University (*http://waterquality.montana.edu/docs/methane/cbmlinks.shtml*) have compiled electronically available references related to CBNG.

Study Area Description

The study area for this report includes those parts of the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins within or near the southern two-thirds of the Powder River structural basin (fig. 1). All sampling sites are in Wyoming, with the exception of two sites in Montana (site T4 on the Tongue River and site P9 on the Powder River) near the Wyoming-Montana border.

Altitudes in the study area range from about 3,350 feet (ft) above the National Geodetic Vertical Datum of 1929 (NGVD 29) at the streamflow-gaging station at Moorhead, Mont. (site P9), to more than 13,100 ft above NGVD 29 in the Bighorn Mountains. The study area includes parts of the Middle Rocky Mountains and Northwestern Great Plains ecoregions (Omernik, 1987). The dominant land cover upstream from the sites on plains streams is shrubland and herbaceous grassland. Streams that have drainage areas in the Bighorn Mountains or the Black Hills have evergreen forest and hay pasture land covers in addition to shrubland and herbaceous grassland (U.S. Geological Survey, 1992).

Mean annual precipitation in the study area ranges from 10 to 15 inches (in.) in the plains and is as much as 40 in. in the Bighorn Mountains (Daly and others, 1994). At a climate station at Arvada, Wyo., average annual precipitation is about 13 in. and average monthly temperature ranges from less than –15 degrees Celsius (°C) in the winter to more than 21°C during the summer for 1971 to 2000 (Western Regional Climate Center, 2005).

Overall, the bedrock geology of the Powder River structural basin is dominated by terrestrial sedimentary rocks of the Wasatch and Fort Union Formations from the Tertiary period (Love and Christiansen, 1985). Most of the CBNG is associated with shallow Tertiary-period coalbeds (DeBruin and Lyman, 1999). Clinker areas, which are areas of thermally altered rocks from the natural burning of coalbeds, are dispersed throughout the study area (Heffern and Coates, 1999). The margins of the study area have been uplifted and contain varied bedrock geology from different eras. The western margin of the structural basin mainly is formed by the Bighorn Mountains. Several uplifted areas, including the Casper Arch, form the southern margin. The Black Hills form part of the eastern margin.

The bedrock geology of the four major drainage basins is diverse. The bedrock of the western part of the Tongue River drainage basin includes rocks from the Precambrian, Paleozoic, and Mesozoic eras that compose the Bighorn Mountains (Love and Christiansen, 1985). Precambrian-era rocks include metamorphic gneiss and plutonic igneous rocks. Paleozoic- and Mesozoic-era rocks primarily are sedimentary rocks of marine origin. The Fort Union Formation occurs at low altitudes in the drainage basin. The bedrock of the eastern part of the Tongue River drainage basin, which includes the Prairie Dog Creek drainage basin, primarily is the Wasatch Formation.

The western tributaries of the Powder River have headwaters in the Bighorn Mountains. Bedrock in the upper part of the tributary drainage basins includes rocks from the Precambrian, Paleozoic, and Mesozoic eras, and bedrock in the lower part of the drainage basins is dominated by the Wasatch Formation. Sedimentary rocks of terrestrial and marine origin from the Cretaceous period occur in the southern part of the Powder River drainage basin, which includes the Salt Creek drainage basin. A large part of the central Powder River drainage basin, including the tributary drainage basins on the east, is underlain by the Wasatch Formation. The Fort Union Formation is prevalent in the lower drainage basins of Clear Creek, the Powder River, and the Little Powder River.

The upper parts of the Cheyenne and Belle Fourche River drainage basins are underlain by the Wasatch Formation. The lower reaches of those drainage basins are dominated by the Fort Union Formation and Cretaceous-period sedimentary rocks of terrestrial and marine origin. In addition, the lower part of the Belle Fourche drainage basin (south and east of site B5) is underlain by rocks from the Paleozoic and Mesozoic era that compose part of the Black Hills.

Because of the physical diversity of the study area, streams in the study area are classified differently (table 1). Stream classes for the 20 Wyoming sites were determined from the Wyoming Surface Water Classification List (Wyoming Department of Environmental Quality, 2001a). Reaches of Little Goose Creek (site T1), Goose Creek (site T2), Prairie Dog Creek (site T3), Clear Creek (sites P7 and P8), and Little Powder River (site P10) are classified as 2AB waters. Class 2AB waters are designated as cold-water game and nongame fisheries and are protected for fish consumption, aquatic life other than fish, primary contact recreation, wildlife, industry, agriculture, drinking-water supplies, and scenic value uses. Reaches of the Powder River (sites P2, P3, and P5), Crazy Woman Creek (site P4), Cheyenne River (site C3), and the Belle Fourche River (sites B1, B4, and B5) are classified as 2ABWW waters, which have the same protection and uses as class 2AB waters, except that they are warm-water fisheries. Salt Creek (site P1) is classified as a 2C water, which is protected for nongame fisheries, fish consumption, aquatic life other than fish, primary contact recreation, wildlife, industry, agriculture, and scenic value uses. The plains tributaries of Wild Horse Creek (site P6), Antelope Creek (site C1), Black Thunder Creek (site C2), Caballo Creek (site B2), and Donkey Creek (site B3) are classified as 3B waters, which are intermittent and ephemeral streams not known to support fish populations or drinking-water supplies. Those uses are not attainable in class 3B streams.

Stream classes for the two Montana sites (sites T4 and P9) were determined from Montana's surface-water-quality standards (Montana Department of Environmental Quality, 2002). The Tongue River near site T4 is classified as a B–2 water, which is to be maintained for drinking, culinary, and food processing purposes, after conventional treatment; bathing, swimming, and recreation; growth and marginal propagation of salmonid fishes and associated aquatic life, waterfowl and furbearers; and agricultural and industrial water supply. The Powder River near site P9 is classified as a C–3 water, which is to be maintained for bathing, swimming, and recreation; growth and propagation of non-salmonid fishes and associated aquatic life; and waterfowl and furbearers. The quality of class C–3 waters is naturally marginal for drinking, culinary, and food processing purposes; agriculture; and industrial water supply.

Acknowledgments

Thanks are extended to USGS colleagues in the Casper, Wyo., Field Office and the Billings, Mont., Field Office for collecting data used in this report. Thanks also are extended to Kathy Shreve of the WDEQ; Andy Bobst of the BLM; and Janet Carter, John Lambing, Keith Lucey, Cathy Martin, and Peter Wright of the USGS for providing reviews of the manuscript. Suzanne Roberts assisted in the preparation of illustrations and the layout of the report.

Data Collection and Analysis

Stream-water-quality data for 22 sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins for water years 2001–05 were compiled for this report. In addition to environmental water-quality samples, quality-control samples were collected to estimate the bias and variability that result from sample collection, processing, and analysis. Sampling methods, data-analysis methods, and quality-control data are described in this section of the report.

Stream-monitoring objectives for sites changed during the study period as a result of CBNG development in the Powder River structural basin. The sampling frequency varied at the 22 sites during water years 2001–05. Samples generally were collected on a monthly basis; however, the frequency may have been less often, particularly in the early part of the study period, or more often for some sites. Data collection in response to CBNG development did not begin until water year 2002 at five sites (sites T1, T2, P7, C3, and B5). The sampling frequency was substantially less for a few sites because some of the sites in the plains often were not flowing at the time of the site visit. Because constituents for which the samples were analyzed also varied among sites, a subset of stream properties and constituents common to all 22 sites was selected for the data analysis of field measurements, major-ion chemistry, and trace elements (table 2). Laboratory reporting levels for trace elements varied for some samples because of instrument variability and matrix effects in samples that had large dissolved-solids concentrations (table 2). Water-quality analyses are electronically stored in the USGS's National Water Information System (NWIS) and are available to the public from NWISWeb at *http://waterdata.usgs.gov/nwis/*.

Sampling Methods

Field measurements were made and samples were collected in accordance with methods established by the USGS (U.S. Geological Survey, 1997–2007). Instantaneous streamflow typically was measured using a current meter.

Table 2. Stream properties measured in the field and constituents for which water-quality samples were analyzed.

[--, not applicable]

Stream property or constituent	Unit of measure	Laboratory reporting level for samples, in unit of measure
Field measurements		
Instantaneous streamflow	Cubic feet per second	--
Water temperature	Degrees Celsius	--
Specific conductance	Microsiemens per centimeter at 25 degrees Celsius	--
pH	Standard units	--
Dissolved oxygen	Milligrams per liter	--
Major-ion chemistry		
Calcium, dissolved	Milligrams per liter	0.02
Magnesium, dissolved	Milligrams per liter	.008
Sodium, dissolved	Milligrams per liter	.20
Sodium-adsorption ratio (calculated)	--	--
Potassium, dissolved	Milligrams per liter	.16
Alkalinity	Milligrams per liter as calcium carbonate	5.0
Sulfate, dissolved	Milligrams per liter	.18
Chloride, dissolved	Milligrams per liter	.20
Fluoride, dissolved	Milligrams per liter	.1
Silica, dissolved	Milligrams per liter	.04
Dissolved solids, sum of constituents (calculated)	Milligrams per liter	--
Trace elements		
Aluminum, total	Micrograms per liter	2
Arsenic, dissolved	Micrograms per liter	Variable; ranged from 0.12 to 4
Barium, total	Micrograms per liter	0.2
Beryllium, total	Micrograms per liter	Variable; ranged from 0.06 to 2
Iron, dissolved	Micrograms per liter	Variable; ranged from 6 to 64
Manganese, dissolved	Micrograms per liter	0.2 and 0.6
Selenium, total	Micrograms per liter	Variable; ranged from 0.08 to 0.8

For sampling sites where streamflow-gaging stations operate, some instantaneous-streamflow measurements were obtained by recording gage heights and determining the streamflow using the most current streamflow rating curve. Water temperature, specific conductance, pH, and dissolved oxygen generally were measured instream using a multi-parameter water-quality probe.

During normal streamflow conditions, samples to be analyzed for major-ion chemistry and trace elements generally were collected using depth-integrated samplers and applying the equal-width-increment method described by Ward and Harr (1990). When samples were collected during extreme conditions, such as hazardous ice conditions and very low flows of shallow depth, traditional depth- and width-integrating techniques may not have been possible and multiple-vertical or dip-sampling techniques were used.

Samples were composited in a polyethylene churn splitter and processed onsite using standard methods and equipment described by Horowitz and others (1994) and the U.S. Geological Survey (1997–2007). Subsamples to be analyzed for whole-water (unfiltered) concentrations of selected trace elements (aluminum, barium, beryllium, and selenium) were collected directly from the churn. Subsamples to be analyzed for concentrations of major ions and other selected trace elements (arsenic, iron, and manganese) were filtered from the churn with a disposable filter that had a pore size of 0.45 micrometer (µm). Subsamples to be analyzed for concentrations of major cations (calcium, magnesium, potassium, and sodium) and trace elements were acidified onsite with nitric acid.

Samples were sent to the USGS National Water Quality Laboratory in Lakewood, Colo., for analysis using standard USGS methods (Fishman and Friedman, 1989; Fishman, 1993; Garbarino and Struzeski, 1998). Constituent concentrations detected in whole-water samples were reported as total. Constituent concentrations detected in filtered samples were reported as dissolved. Alkalinity was reported as an equivalent amount of calcium carbonate. SAR values and dissolved-solids concentrations are calculated on the basis of laboratory results for discrete samples. SAR values were calculated using the analytical results for dissolved calcium, dissolved magnesium, and dissolved sodium obtained for a discrete sample using the following equation:

$$SAR = \frac{\left(Na^{+}\right)}{\sqrt{\frac{1}{2}\left[\left(Ca^{2+}\right)+\left(Mg^{2+}\right)\right]}} \qquad (1)$$

where

Na^{+}, Ca^{2+}, and Mg^{2+} represent concentrations expressed in milliequivalents per liter for each constituent.

Dissolved-solids concentrations were calculated as the combined sum of dissolved constituents detected in a water sample, where the major ions and nonionic silica are the primary contributors (Hem, 1985).

Data-Analysis Methods

Data for this report were summarized using several statistical techniques. Descriptive summary statistics were computed for field measurements, major-ion chemistry, and trace elements and are displayed using box plots. The lower and upper edges of the box indicate the 25th and 75th percentiles, respectively, and the median is a line within the box. The whiskers extend beyond the 25th and 75th percentiles to 1.5 times the interquartile range. If the smallest or largest value in the data set is less than 1.5 times the interquartile range, the whisker extends to the smallest or largest value. Otherwise, values outside the whiskers are shown as individual points.

Data sets for dissolved arsenic, total beryllium, dissolved iron, and total selenium had many concentrations that were censored (less than the respective laboratory reporting level). Summary statistics for data sets that include censored concentrations were estimated using a log-probability regression method that combines the distribution of uncensored (measurable) concentrations with censored concentrations (Helsel and Cohn, 1988; Helsel and Hirsch, 1992). Summary statistics were estimated for arsenic, beryllium, iron, and selenium. For this report, presentation of summary statistics required that at least six samples have uncensored concentrations.

Additional statistical analyses were conducted for specific conductance and SAR, which are of particular concern in the CBNG-development area. A nonparametric correlation coefficient called Spearman's rho was used to measure the strength and direction of relation between each of those water-quality variables and streamflow. Spearman's rho uses rank-based procedures rather than actual data values to reduce the effect of outliers (Helsel and Hirsch, 1992). Using data collected at the 22 sampling sites, correlations were determined between specific conductance and streamflow and between SAR and streamflow. Spearman's rho values are presented with *p*-values, which indicate the probability of determining the correlation strength by chance alone.

The nonparametric Kruskal-Wallis test was used to compare whether specific conductance and SAR values varied seasonally. The Kruskal-Wallis test also uses data ranks rather than actual data values to reduce the effect of outliers. In the most general form, the Kruskal-Wallis test determines whether three or more groups of ranked data have similar distributions or whether at least one group differs in its distribution (Helsel and Hirsch, 1992). Statistical significance for Kruskal-Wallis tests was determined using a 90-percent confidence level (*p*-values less than 0.10).

A trend analysis was conducted for eight sites that have a sufficient amount of long-term data to help determine if specific conductance and SAR values have changed through time at sites in the Powder River structural basin. Trend-analysis techniques that account for the inherent variability of water-quality data have been developed by the USGS and include a program called Estimate Trend (ESTREND). The ESTREND statistical trend procedure used for this study was the seasonal Kendall test, a nonparametric test to determine monotonic (single direction) trends in water quality that may occur gradually with time or as abrupt changes (Schertz and others, 1991).

The seasonal Kendall test accounts for the effect of seasonal variability by computing the Mann-Kendall test statistic for each of the seasons separately and then summing the seasonal test statistics to form an overall test statistic (Helsel and Hirsch, 1992). The test makes all possible pairwise comparisons of time-ordered water-quality values and assigns a large value that is later in time a “plus” and a small value that is later in time a “minus.” The test statistic is computed as the difference between the total number of pluses and the total number of minuses. The null hypothesis (no trend) has a test statistic of zero; therefore, the more the test statistic deviates from zero, the more likely a trend exists in the data. If the sampling frequency is variable, the test requires the seasons to be defined on the basis of the most restrictive sampling frequency. For this analysis, the seasonal periods were defined as October through December, January through March, April through June, and July through September, coinciding with historical quarterly sampling frequencies.

The ESTREND program will compute trend results on either unadjusted concentrations or flow-adjusted concentrations. Trend results for unadjusted concentrations may be useful to water managers because unadjusted concentrations frequently are used for making water-quality assessments, such as comparisons to water-quality criteria. Otherwise, the usefulness of trend results for unadjusted concentrations is limited because concentrations of water-quality constituents frequently are correlated with streamflow, which may change in response to seasonal and annual climatic variability. An apparent trend in unadjusted concentrations may be an artifact of streamflow conditions at the time of sampling. Changes in concentrations as a result of changes in land-use activities that affect either constituent supply or delivery to a stream may be difficult to discern for a short-term period because of inherent variability in concentrations as a result of variability in streamflow.

Statistical techniques, such as regression models, exist for filtering out streamflow-related variability before analyzing for constituent trends. The ESTREND program selects the “best fit” regression model for streamflow and a water-quality constituent from several predefined regression models and then uses the residuals (estimated values minus measured values), which are called flow-adjusted concentrations, for the seasonal Kendall trend test (Schertz and others, 1991). Flow-adjusting techniques increase the likelihood that a resulting trend is real and not an artifact of streamflow variability. For some trend tests, the streamflow-constituent regression relation was not significant. In those cases, trends in flow-adjusted concentrations were not computed.

The seasonal Kendall test statistic, *p*-values, and direction of the trend are presented in this report for significant trends. The statistical significance for regression relations and the trend tests were determined using a 90-percent confidence level (*p*-values less than 0.10). For unadjusted concentrations, the slopes of the trends, which are represented by the change per year in the constituent in original measurement units, also are presented. Time-series plots for sites that had significant trends in unadjusted concentrations are shown with a locally weighted, scatterplot smoothing (LOWESS) technique, which graphically smoothes the pattern of the data with time. Time-series plots and the slopes of the trends are not presented for flow-adjusted concentrations because the trend data are referenced to the residuals and not to the original data values.

Quality Control

Quality-control samples, including equipment blanks and replicates, were collected to help estimate the bias and variability resulting from sample collection, processing, and chemical analysis. Equipment blanks typically are collected and processed to demonstrate that field methods and laboratory analysis have not introduced contamination to the sample, thus providing a measure of bias (Mueller and others, 1997). Laboratory analyses of replicate water samples provide a measure of variability.

Equipment blanks are prepared in the field by processing certified inorganic-grade deionized water through the sampling equipment immediately before collecting an environmental water-quality sample. Summary statistics (table 3) for selected constituents in the blank samples (dissolved calcium, dissolved magnesium, dissolved sodium, dissolved chloride, dissolved silica, total aluminum, total barium, and dissolved manganese) were calculated using log-probability methods for censored concentrations (Helsel and Cohn, 1988). Summary statistics could not be calculated for dissolved potassium, dissolved fluoride, dissolved sulfate, dissolved arsenic, total beryllium, dissolved iron, and total selenium because fewer than six of the blank samples had measurable concentrations for those constituents.

Concentrations for major ions and trace elements in the field equipment blanks generally were small relative to concentrations in the associated environmental samples (table 3). Maximum concentrations in the blank samples were less than minimum concentrations in the associated environmental samples for all constituents except dissolved fluoride, dissolved silica, total aluminum, dissolved manganese, and total selenium. For dissolved fluoride, dissolved silica, dissolved manganese, and total selenium, concentrations in blank samples were small and near laboratory reporting levels. For total aluminum, the 75th percentile of the concentrations in blank samples was 3 micrograms per liter (μg/L) and the maximum concentration was 36 μg/L, indicating a small positive bias may exist for some environmental concentrations. The total aluminum in the blank samples may have been from clay particles that may have adhered to sampling equipment during cleaning or from deionized water (or both). Because total-aluminum concentrations in the environmental samples generally were large (the interquartile range was

Table 3. Statistical summary for concentrations of selected constituents in field equipment blanks and environmental water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

[Summary statistics for all constituents in blank samples and for arsenic, beryllium, and iron in environmental samples were determined using log-probability methods for censored concentrations; <, less than; --, distribution for censored concentrations could not be determined because measurable concentrations occurred in fewer than six blank samples]

Constituent	Blank samples						Environmental samples					
	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum
Major-ion concentrations, in milligrams per liter												
Calcium, dissolved	46	<0.006	0.008	0.01	0.02	0.07	1,263	16.2	81.6	127	160	418
Magnesium, dissolved	46	<.002	.004	.006	.009	.037	1,263	6.3	44.3	61.5	93.4	300
Potassium, dissolved	[1]44	--	--	--	--	--	1,257	.93	4.60	8.30	13.7	76.5
Sodium, dissolved	46	<.03	.04	.06	.08	.17	1,263	5.74	66.5	222	337	1,490
Chloride, dissolved	46	<.04	.06	.10	.14	.32	1,256	.83	5.35	25.2	153	1,530
Fluoride, dissolved	[2]45	--	--	--	--	--	1,257	.06	.3	.5	.8	3.3
Silica, dissolved	45	<.007	.02	.04	.06	2.50	1,257	.02	5.07	7.95	10.9	98.5
Sulfate, dissolved	46	--	--	--	--	--	1,256	20.5	387	666	1,050	4,550
Trace-element concentrations, in micrograms per liter												
Aluminum, total	31	<0.6	1	2	3	36	935	2	106	329	1,310	142,000
Arsenic, dissolved	49	--	--	--	--	--	1,208	<.2	.7	.9	1.3	10
Barium, total	43	<.06	.09	.1	.2	.6	1,214	14	39	56	82	5,810
Beryllium, total	31	--	--	--	--	--	868	<.008	.03	.06	.13	17.1
Iron, dissolved	[3]44	--	--	--	--	--	1,184	<3	7	12	23	1,810
Manganese, dissolved	49	<.02	.05	.09	.2	2.1	1,217	.59	10.1	32.1	92.5	3,380
Selenium, total	[4]32	--	--	--	--	--	916	.2	.9	1.6	2.8	13

[1] Dissolved-potassium concentration was detected in three blank samples at concentrations of 0.07, 0.14, and 0.18 milligram per liter.

[2] Dissolved-fluoride concentration was detected in four blank samples at concentrations of 0.01, 0.01, 0.02, and 0.1 milligram per liter.

[3] Dissolved-iron concentration was detected in two blank samples at concentrations of 0.4 and 0.6 microgram per liter.

[4] Total-selenium concentration was detected in four blank samples at concentrations of 0.3, 0.4, 0.5, and 0.5 microgram per liter.

106 to 1,310 µg/L), a small positive bias in some concentrations should not substantially affect the interpretation of the environmental data.

Replicate samples were prepared by splitting the routine environmental sample into duplicate subsamples, which are considered to be identical in composition. Differences in analytical results for paired replicate samples provide a measure of the variability introduced during sample processing and laboratory analysis. Measurement variability was determined for constituents by calculating a relative percent difference (RPD) between concentrations in the paired replicate samples when the constituent was detected in both samples or when the concentrations were censored at a common level in both samples. The RPD was calculated using the following equation:

$$\text{RPD}=100\text{x}\,\frac{\left|\begin{array}{c}\text{routine environmental sample concentration}-\\ \text{replicate sample concentration}\end{array}\right|}{\begin{array}{c}\text{(routine environmental sample concentration}+\\ \text{replicate sample concentration)/2}\end{array}} \qquad (2)$$

Summary statistics for the RPDs for major ions and trace elements indicate measurement variability was small for most constituents (table 4). The median RPDs were smaller for major-ion constituents (less than 1.7 percent) than the median RPDs for trace-element constituents (less than 10.0 percent). A few constituents had an occasional large RPD for some paired replicate samples; however, this generally occurred when concentrations were small and near the reporting level. For example, the maximum RPD for dissolved arsenic was 101 percent when the routine environmental sample had a concentration of 1.67 µg/L and the replicate sample had a concentration of 0.55 µg/L. Overall, most RPDs indicate the methods for sample processing and laboratory analysis generally produced data that were not highly variable and had good reproducibility. Although large RPDs may be artifacts of small concentrations or isolated occurrences of poor precision resulting from random error, caution should be used in interpreting environmental sample concentrations for constituents that consistently had large RPDs.

General Hydrology

Hydrologic conditions are an important factor in water-quality variability and are described to provide perspective on differences in water quality that can occur seasonally and annually. Annual hydrographs for selected sampling sites in the Tongue, Powder, and Belle Fourche River drainage basins during water years 2001–05 are presented in figure 3. Continuous streamflow data are not available for the sampling site on the Cheyenne River (site C3). Therefore, the general hydrology of the Cheyenne River was assessed using streamflow data from a nearby site downstream on the Cheyenne River (USGS station 06386500; fig. 1). The drainage area of USGS station 06386500 (5,270 mi^2) was comparable to that of the sampling site (5,160 mi^2).

The Tongue River typically is dominated by a single snowmelt peak of moderate duration during late spring through early summer and has relatively low variability in streamflow throughout the remainder of the year. Snowmelt peaks for some years during water years 2001–05 (fig. 3) were smaller than typical snowmelt peaks for the Tongue River. In comparison to the Tongue River, annual streamflows of the Powder, Cheyenne, and Belle Fourche Rivers are more variable. The Powder River generally has an early spring peak in response to lowland snowmelt followed by a mid- to high-altitude snowmelt peak; short duration peaks occur in response to rainfall, and periods of low flow or no flow are common in late summer (fig. 3). The Cheyenne and Belle Fourche Rivers generally have an increase in streamflow during spring in response to lowland snowmelt, intermittent peaks in response to rainstorms, and extended periods of low flow. For the Cheyenne River, extended periods of no flow are common.

Continuous streamflow records are available for 17 of the 22 sites for 1 or more years of the study period; only 8 sites have continuous streamflow records for all 5 years (table 5). The period of record available for the sites ranged from 5 to 74 years. A longer period of record provides a more accurate measure of the average annual runoff for a site. Because of the few sites that have a continuous streamflow record for the entire study period, long-term average annual runoff for the period of record was used to indicate relative differences in annual runoff among sites.

Long-term average annual runoff was highly variable among the 17 sites (table 5), and ranged from 253 acre-ft for Wild Horse Creek (site P6) to 319,000 acre-ft for the Powder River (site P9). Although the Powder River at site P9 had the largest average annual-runoff value, the annual-runoff value for the Tongue River at site T4 exceeded that for the Powder River at site P9 during 4 of the 5 years during water years 2001–05 (table 5). The average annual-runoff value for the Tongue River at site T4 (315,800 acre-ft) was similar to the average annual-runoff value for the Powder River at site 9 (319,000 acre-ft); however, the drainage area of the Tongue River at site T4 (1,453 mi^2; table 1) is substantially less than that of the Powder River at site P9 (8,088 mi^2), indicating the Tongue River drainage basin had more annual runoff per unit area than the Powder River drainage basin. The average annual-runoff value for USGS streamflow-gaging station 06386500 on the Cheyenne River was 39,240 acre-ft for the period of record for that station (Watson and others, 2006). Although the average annual-runoff value for the Belle Fourche River at site B4 (16,550 acre-ft) was less than that for the Cheyenne River, the Cheyenne River drainage basin had the least runoff per unit area of the downstream main-stem sites because of its large size.

Goose Creek (site T2) in the Tongue River drainage basin had the largest average annual-runoff value (132,600 acre-ft) of the tributary streams (table 5) and the most runoff per unit area of all 17 sites for which continuous streamflow data

Table 4. Statistical summary for relative percent difference between concentrations of selected constituents in paired replicate samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

Constituent	Number of paired replicate samples	Minimum	25th percentile	Median	75th percentile	Maximum
			Relative percent difference			
Calcium, dissolved	47	0.00	0.504	1.40	2.00	6.80
Magnesium, dissolved	47	.00	.337	.971	1.60	7.78
Potassium, dissolved	47	.00	.700	1.61	3.37	8.42
Sodium, dissolved	47	.00	.702	1.45	2.49	9.61
Chloride, dissolved	47	.00	.324	1.11	2.32	9.30
Fluoride, dissolved	47	.00	.858	1.69	3.96	17.3
Silica, dissolved	47	.017	.453	1.13	2.14	25.4
Sulfate, dissolved	47	.009	.109	.317	.533	12.1
			Relative percent difference			
Aluminum, total	32	0.146	1.77	5.81	9.86	29.3
Arsenic, dissolved	44	0	.565	4.14	10.4	101
Barium, total	46	.023	.401	.906	1.63	14.1
Beryllium, total	26	0	0	0	7.43	37.8
Iron, dissolved	42	0	.086	4.49	15.7	51.3
Manganese, dissolved	47	0	.635	1.27	2.94	52.9
Selenium, total	28	.442	5.37	9.99	14.3	65.0

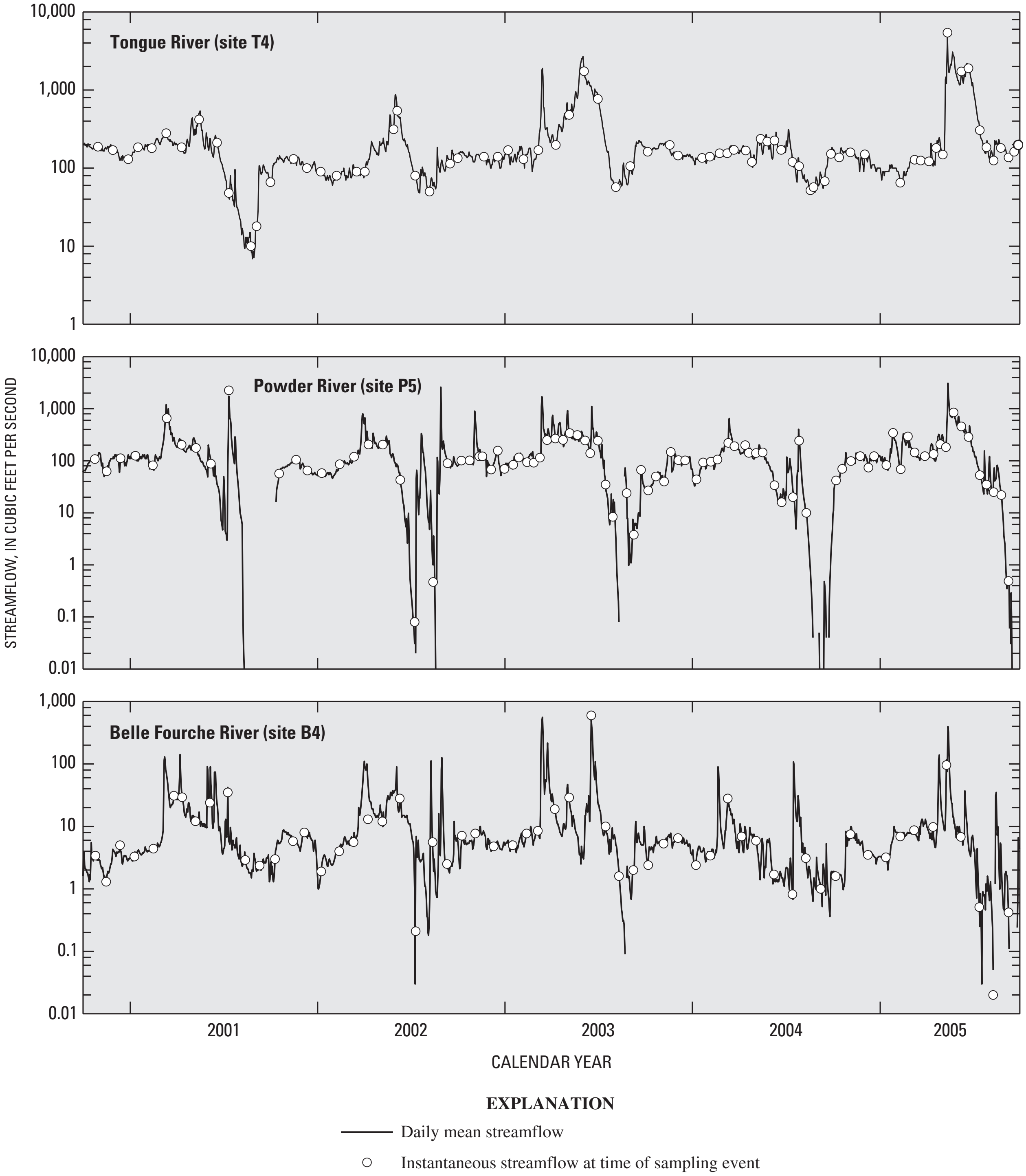


Figure 3. Streamflow and distribution of sampling events for selected main-stem sampling sites in the Tongue, Powder, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

Table 5. Annual-runoff values for selected sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

[--, not available]

Site number (fig. 1)	Period of record, with complete water years	Average annual runoff for period of record (acre-feet)	Annual runoff (acre-feet)				
			Water year 2001	Water year 2002	Water year 2003	Water year 2004	Water year 2005
T2	1942–84	132,600	--	--	--	--	--
T3	1971–79; 2001–05	26,900	12,830	13,520	18,590	10,910	19,820
T4	1961–2005	315,800	118,000	99,860	253,900	108,600	292,500
P1	1977–81; 1983–93	32,640	--	--	--	--	--
P2	1939; 1951–57; 1978–84; 1986–98; 2004–05	143,600	--	--	--	62,460	87,930
P4	1964–70; 1978–81; 2001–05	29,810	12,350	5,820	23,030	6,910	28,840
P5	1931–33; 1935–2005	194,900	93,730	80,390	125,100	63,360	127,800
P6	2001–05	253	45	8.6	509	139	562
P8	1916–17; 1940–82; 2004–05	129,200	--	--	--	33,070	119,200
P9	1930–72; 1975–2005	319,000	108,900	119,100	210,300	85,200	245,100
P10	1973–2005	14,310	5,730	1,210	5,950	1,430	5,900
C1	1978–81	7,170	--	--	--	--	--
C2	1973–90	4,900	--	--	--	--	--
B1	1976–82; 2002–05	1,750	--	1,590	1,930	2,640	1,210
B2	1978–83	1,880	--	--	--	--	--
B3	1978–81	7,540	--	--	--	--	--
B4	1944–70; 1976–83; 1986–87; 1991–2005	16,550	8,410	9,010	15,390	4,680	7,460

are available. Goose Creek has its headwaters in the Bighorn Mountains and receives snowmelt runoff, which composes a large part of the annual runoff at this site. Clear Creek (site P8) in the Powder River drainage basin also has its headwaters in the mountains and had the second largest average annual-runoff value of the tributary streams. Prairie Dog Creek (site T3) and Salt Creek (site P1) had the largest average annual-runoff values of tributaries that have headwaters in the plains (tables 1 and 5). Some of the streamflow in Salt Creek is contributed from discharge waters associated with conventional oil and gas production (RETEC Group, Inc., 2004). The streamflow-gaging station on Salt Creek was discontinued shortly after a change to subsurface injection of some discharge waters; thus, average annual runoff for water years 2001–05 may be less than that for the period of record. Wild Horse Creek (site P6), which had the smallest average annual-runoff value of all 17 sites, is a plains tributary.

Overall, the study area experienced prolonged drought during water years 2001–05. Annual runoff at main-stem sites on the Tongue River (site T4), Powder River (sites P5 and P9), and Belle Fourche River (site B4), which have some of the longest periods of record, was less than average during water years 2001–05. The first, second, and third smallest average annual-runoff values for the Tongue River (site T4) for 45 years of record were in water years 2002, 2004, and 2001, respectively. The second smallest average annual-runoff values for 74 years of record for the Powder River (sites P5 and P9) and the sixth smallest average annual-runoff value for 52 years of record for the Belle Fourche River (site B4) occurred during water year 2004. Clear Creek (site P8), a mountain tributary that contributes substantial flow to the Powder River, had its smallest average annual-runoff value in water year 2004. Annual runoff at USGS streamflow-gaging station 06386500 on the Cheyenne River was 62 acre-ft in 2004 and 3,020 acre-ft in 2005 (Watson and others, 2006). For water year 2002, annual runoff for the Little Powder River (site P10) was only 8 percent of average (based on 33 years of record). Because annual runoff was less than average for water years 2001–05, samples collected during the study period may not represent long-term water-quality conditions for all sites.

Water-Quality Characteristics for Water Years 2001–05

This section of the report describes the water-quality characteristics represented by samples collected during water years 2001–05 at 22 sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins. The descriptions include statistical summaries for field measurements, major-ion chemistry, and trace elements as well as comparisons to water-quality standards and criteria.

Field Measurements

Field measurements were made at the time of sampling to accurately reflect the ambient physical properties of the stream when the sample was collected. Field measurements at the 22 sampling sites for water years 2001–05 included instantaneous streamflow, water temperature, specific conductance, pH, and dissolved oxygen.

Summaries for Water Years 2001–05

The magnitude of instantaneous streamflow during a sampling event can affect stream-water quality in several ways. For example, large magnitude streamflows tend to have small concentrations of dissolved constituents but often have large concentrations of suspended constituents. Instantaneous streamflow can vary by orders of magnitude during the year; thus, it is important to collect water-quality samples throughout the entire range of streamflows for a water year to adequately characterize extremes, seasonal differences, and average conditions. Instantaneous streamflows during sampling events were compared with daily mean streamflow for selected sampling sites to illustrate the range of hydrologic conditions during water years 2001–05 (fig. 3).

Instantaneous streamflows measured during sampling events were highly variable and ranged from 0.01 cubic feet per second (ft^3/s) at several plains sites (sites P6, P10, C1, C2, and C3) to 5,430 ft^3/s at site T4 on the Tongue River (fig. 4). For the main-stem sites, median instantaneous streamflows were substantially larger at site T4 on the Tongue River and at site P9 on the Powder River than at sites on the Cheyenne and Belle Fourche Rivers (fig. 4). Median instantaneous streamflows generally were larger for tributaries that have headwaters in mountainous areas than for tributaries that have headwaters in the plains (fig. 4, table 1). Prairie Dog Creek (site T3) and Salt Creek (site P1) had the largest median instantaneous streamflows of the plains tributaries. Variability in instantaneous streamflow results from variability in the distribution of precipitation. Mean annual precipitation for much of the plains area in the Powder River structural basin is low (10 to 15 in. per year), but mean annual precipitation in the Bighorn Mountains ranges from more than 20 in. at low altitudes to nearly 40 in. at high altitudes (Daly and others, 1994). The small instantaneous streamflows that were measured regularly during sampling events at site C1 on Antelope Creek indicate that very little surface runoff occurred during the study period and that a predominant contribution from ground water is possible.

Several of the streams that have headwaters in the plains (sites P6, C1, C2, C3, B1, and B2) had no streamflow during several site visits; therefore, some of these sites have a substantially smaller number of streamflow measurements and samples than other sites. Site P6 on Wild Horse Creek and site C2 on Black Thunder Creek were dry during more than 60 percent of the sampling events. Sites C1, C3, B1, and B2 were dry during 10 to 30 percent of the sampling events. The Powder River at site P5 was dry during 8 percent of the sampling events. The Powder River loses streamflow to alluvium in this reach (Ringen and Daddow, 1990).

Instream water temperatures are affected by solar radiation, precipitation, air and ground temperature, stream depth, and the temperature of tributary and ground-water inflows. Physical, chemical, and biological processes are directly affected by water temperature. Physical properties that are affected by water temperature include density, surface tension, gas solubility, and diffusibility (Stevens and others, 1975). These physical properties, in part, control the gain and loss of dissolved gases such as oxygen and nitrogen in stream water. Water temperature also affects the rates of chemical reactions in streams; high temperatures generally increase chemical reaction rates. Biological processes that are affected by water temperature include the metabolism of aquatic organisms and their ability to survive.

The ranges of stream temperatures measured during sampling events generally were similar among sites (fig. 4). The minimum water temperature at most of the 22 sites was zero, and the maximum water temperature was 33.5°C. The maximum was measured at site C2 on Black Thunder Creek. Median water temperatures ranged from 4.5°C at site C1 on Antelope Creek to 14.0°C at site P3 on the Powder River. Site C1 on Antelope Creek often had no streamflow during summer sampling events so the recorded water temperatures are skewed towards temperatures measured during cool months. Concerns have been expressed about changes in stream temperature and the effect on biota as a result of CBNG-produced waters; however, the measurement frequency of discrete sampling events probably is insufficient for detecting these changes.

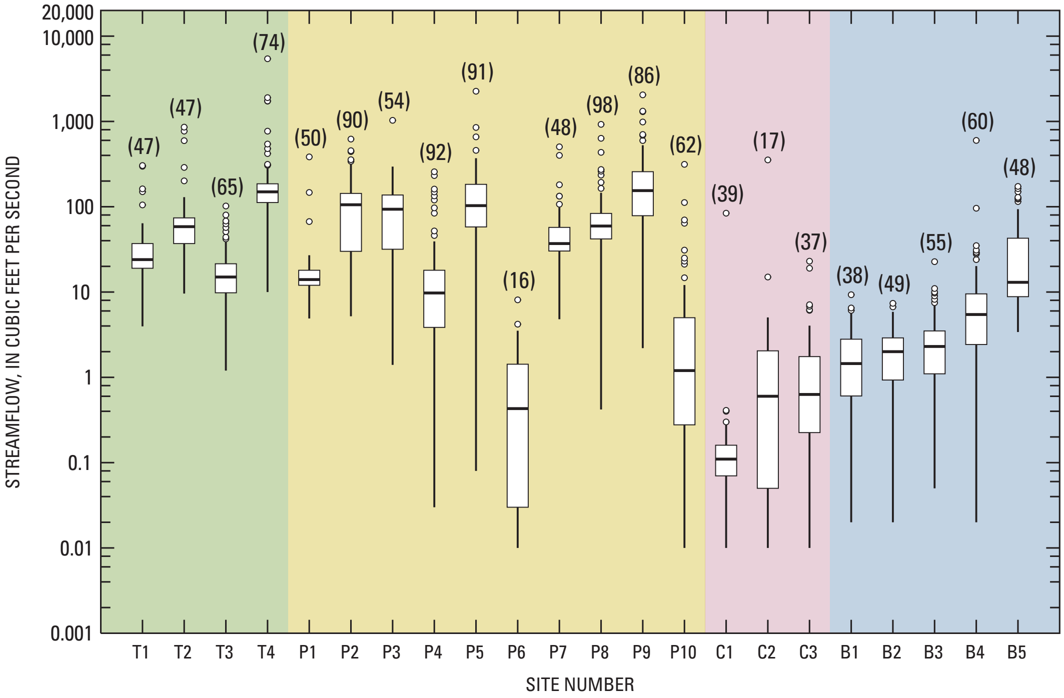
Specific conductance is a measure of a substance's ability to conduct an electrical current at a specified temperature (typically 25.0°C). Instream specific conductance is controlled mainly by the ionic charge of the predominant dissolved solids in the water; for this reason, specific conductance is a general overall indicator of a stream's major-ion chemistry. Specific conductance can directly affect a stream's ability to sustain aquatic life and suitability as a supply for municipal, industrial, and agricultural uses. Specific conductance of waters used for irrigation has an effect on soil infiltration rates. Irrigation waters that have large specific-conductance values can have a positive effect on soil properties, causing flocculation and aeration of the soil; however, irrigation waters that have excessive dissolved solids can have a negative effect on plant health (Hanson and others, 1999). In a study on the quality of coalbed waters in the Powder River structural basin, Rice and others (2000) reported that specific-conductance values ranged from 630 to 3,020 microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C). Measurements from continuous monitors (sites P2, P4, P8, and P9) provide a more accurate characterization of the fluctuations in specific conductance in the Powder River drainage basin (Clark and Mason, 2006) than the discrete measurements made for this study.

Field measurements of specific conductance in streams varied among the four major drainage basins and among sites within a given drainage basin. The range of median specific-conductance values was smallest among sites in the Tongue River drainage basin (fig. 4). Median values in that basin ranged from 643 µS/cm at 25°C at site T4 on the Tongue River to 1,460 µS/cm at 25°C at site T3 on Prairie Dog Creek (fig. 4). The Tongue River drainage basin has the largest percentage of area underlain by Mesozoic-age and older rocks and by more resistant rocks. In addition, higher annual precipitation and a steeper gradient in this basin compared to basins in the plains produce relatively fast stream velocities, resulting in a short contact time between stream waters and basin materials. The Powder River drainage basin, which has the largest drainage area and most diverse site conditions among the four major drainage basins, had the largest range of median specific-conductance values. Median values in that basin ranged from 680 µS/cm at 25°C at site P7 on Clear Creek to 5,950 µS/cm at 25°C at site P1 on Salt Creek. Discharges of saline ground waters that are associated with conventional gas and oil production in the Salt Creek drainage basin contribute to the large values at site P1 (RETEC Group, Inc., 2004).

Median specific-conductance values among sites in the Cheyenne River drainage basin ranged from 1,850 µS/cm at 25°C at site C2 on Black Thunder Creek to 4,680 µS/cm at 25°C at site C3 on the Cheyenne River (fig. 4). Unlike the Tongue and Powder River drainage basins, the entire Cheyenne River drainage basin is in the plains; the low precipitation and relatively low gradients in the plains produce slow stream velocities and long contact times with soluble geologic materials. The small range of specific-conductance values in samples collected from Antelope Creek (site C1) compared to the range in samples collected from other plains streams is consistent with ground water being the predominant source of streamflow.

Median specific-conductance values in the Belle Fourche River drainage basin ranged from 1,740 µS/cm at 25°C at site B2 on Caballo Creek to 2,800 µS/cm at 25°C at site B3 on Donkey Creek. The drainage basins for Caballo Creek and Donkey Creek are geographically close, similar in size, and have origins in the plains; however, municipal sewage effluent from the city of Gillette, Wyo. (Peterson, 1988), may affect the specific-conductance values in Donkey Creek.

Hydrogen-ion activity is a measure of a stream's acidic or alkaline character and is expressed in terms of pH, which is the negative base-10 logarithm of the hydrogen-ion activity. Streams that have pH values near 7 (in standard units) are considered neutral, streams that have pH values greater than 7 are considered alkaline, and streams that have pH values less than 7 are considered acidic. As with specific conductance, pH also can affect a stream's suitability for various uses.



EXPLANATION

🟩 Tongue River sampling sites (see table 1 for names)

🟨 Powder River sampling sites (see table 1 for names)

🟪 Cheyenne River sampling sites (see table 1 for names)

🟦 Belle Fourche River sampling sites (see table 1 for names)

MTNIST State of Montana nonirrigation season (November 1–March 1) standard for the Tongue River (Montana Department of Environmental Quality, 2002)

MTIST State of Montana irrigation season (March 2–October 31) standard for the Tongue River (Montana Department of Environmental Quality, 2002)

MTYRP State of Montana year-round standard for the Powder River (Montana Department of Environmental Quality, 2002)

WYS State of Wyoming standard (Wyoming Department of Environmental Quality, 2001b)

WYOLS State of Wyoming criterion for other life stages for 2ABWW class waters (Wyoming Department of Environmental Quality, 2001b)

WMELS State of Wyoming criterion and State of Montana standard for early life stages (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006)

(48) Number of samples

1.5 times interquartile range (IQR) or largest value

75th percentile

Median (50th percentile)

25th percentile

-1.5 times IQR or smallest value

○ Value greater than 1.5 times IQR or less than -1.5 times IQR

Figure 4. Statistical summary of instantaneous streamflow, water temperature, specific conductance, pH, and dissolved-oxygen concentrations for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

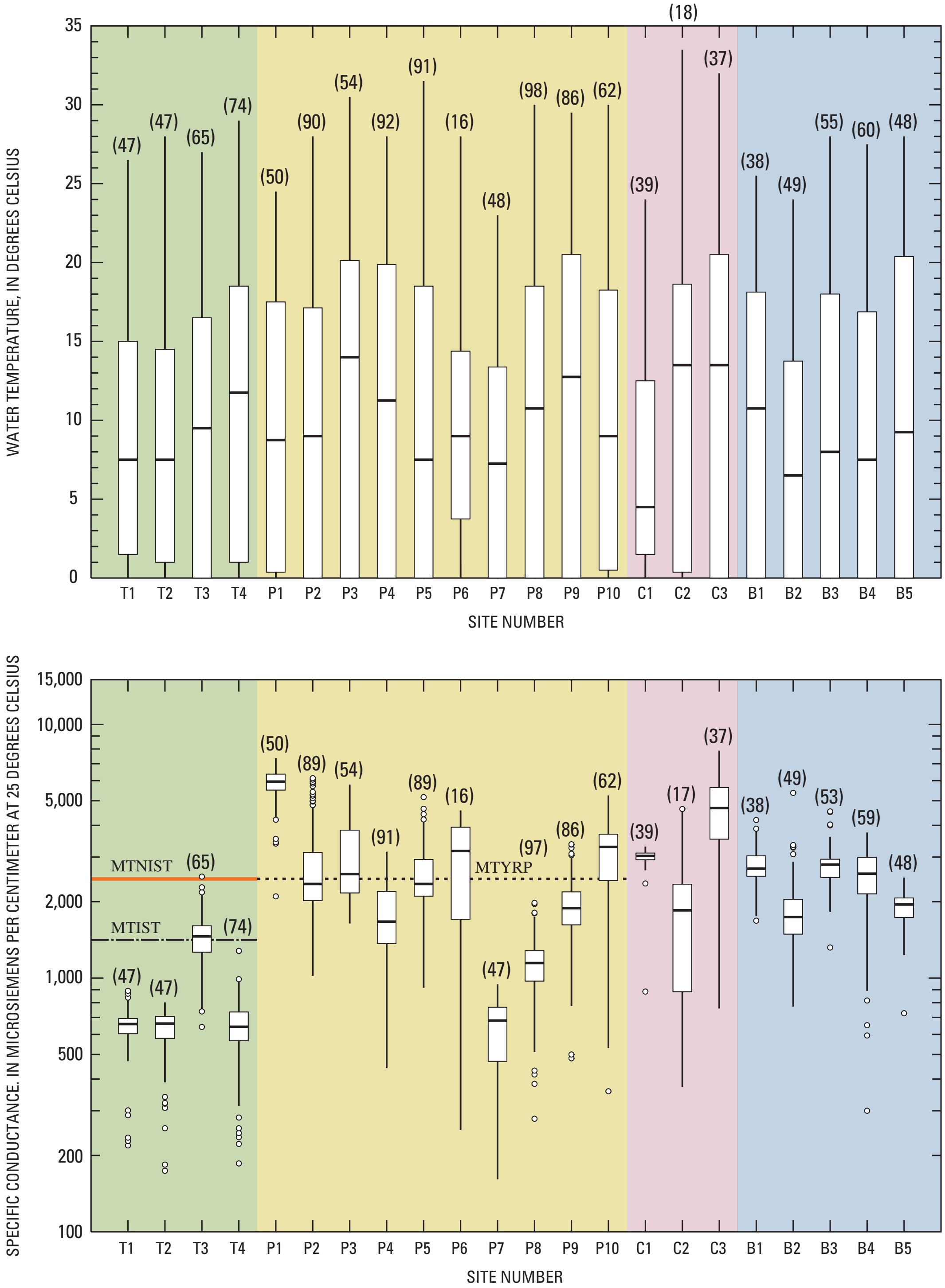
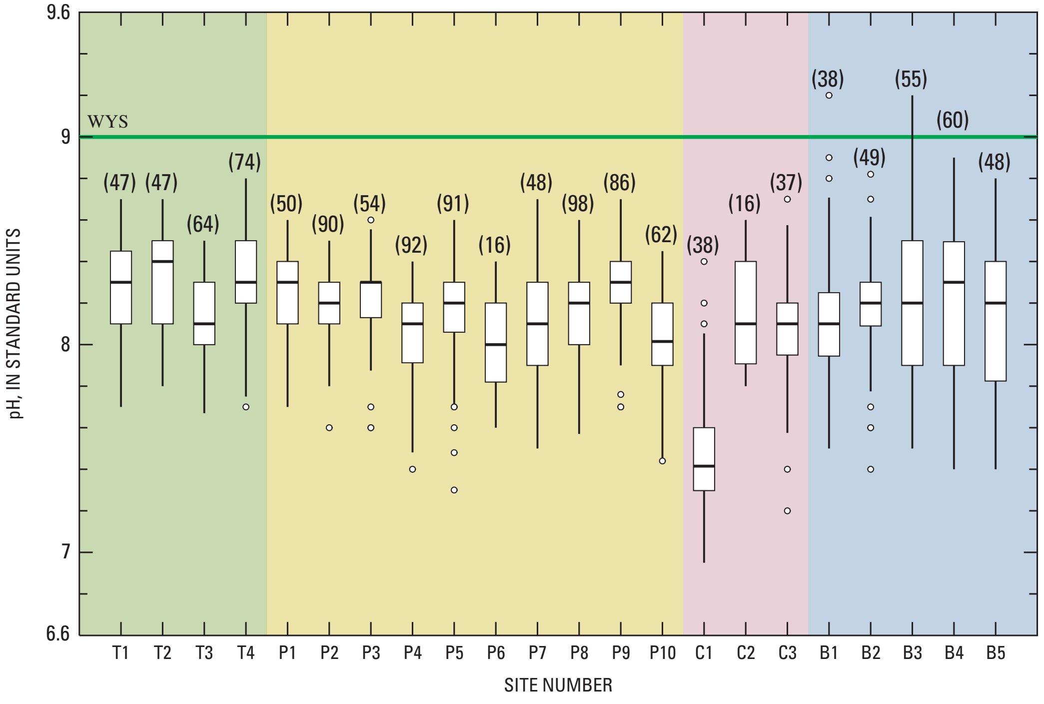


Figure 4. Statistical summary of instantaneous streamflow, water temperature, specific conductance, pH, and dissolved-oxygen concentrations for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued



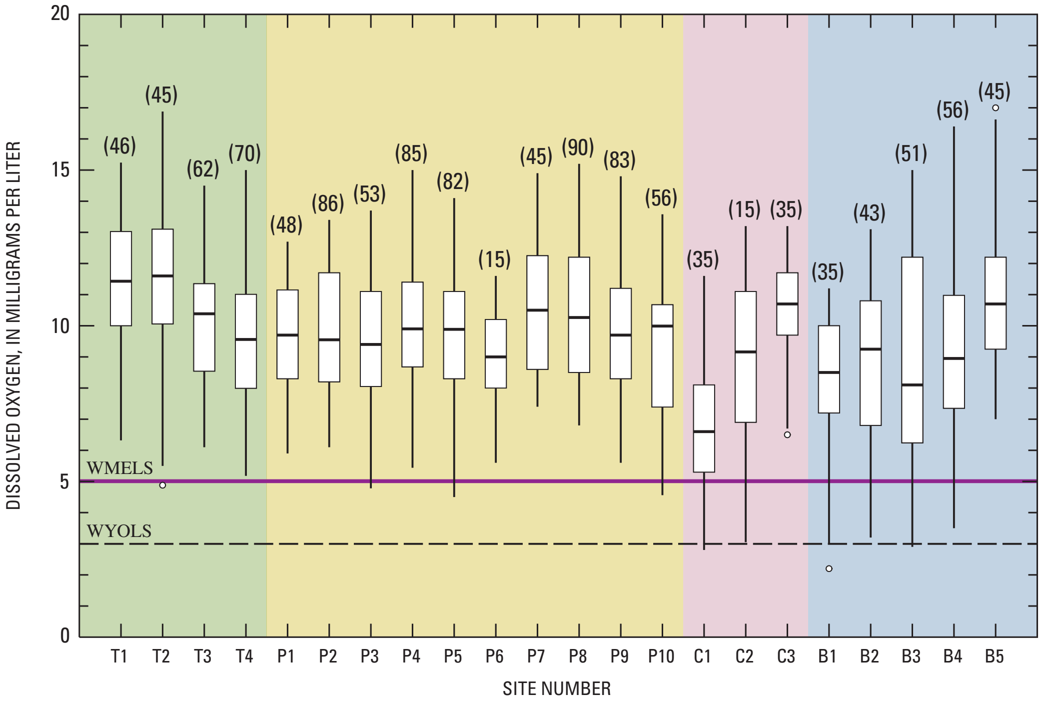


Figure 4. Statistical summary of instantaneous streamflow, water temperature, specific conductance, pH, and dissolved-oxygen concentrations for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

Field measurements of pH indicated all streams in the four major drainage basins were neutral to alkaline; pH values ranged from 7.0 at site C1 on Antelope Creek to 9.2 at site B1 on the Belle Fourche River and site B3 on Donkey Creek (fig. 4). Median pH values generally were similar among sites and ranged from about 8.0 to 8.4 for 21 of the 22 sites. On Antelope Creek (site C1), the median pH (7.4) was substantially smaller than the median pH for other sites, indicating a ground-water source for streamflow. Shallow ground water moves toward Antelope Creek from both the north and the south through mining overburden and coalbeds (Fogg and others, 1991).

Dissolved-oxygen concentrations are a measure of gaseous oxygen dissolved in streams; the solubility of oxygen in stream water is controlled by water temperature, and cool water is able to hold more oxygen than warm water. Gaseous oxygen in stream water originates from atmospheric exchange and daytime photosynthesis of aquatic plants. It is depleted in streams through respiratory uptake by organisms and by decay of organic matter in the stream water (Hem, 1985). The dissolved-oxygen concentration of stream water can vary widely on a 24-hour basis in response to the amount of photosynthetic production during daytime hours and consumption of oxygen by respiration and decay. Dissolved-oxygen concentrations and the extent of diurnal variability affect a stream's suitability to support aquatic life and affect the rate and direction of chemical oxidation and reduction reactions within the water.

Field measurements of dissolved-oxygen concentrations varied among sites. The concentrations ranged from 2.2 milligrams per liter (mg/L) at site B1 on the Belle Fourche River to 17 mg/L at site B5 on the Belle Fourche River (fig. 4). The largest median concentration for all sites was 11.6 mg/L at site T2 on Goose Creek (fig. 4). More than 75 percent of the concentrations at 21 of the 22 sites ranged from about 7.0 to 13 mg/L. In contrast, more than 50 percent of the concentrations at site C1 on Antelope Creek were less than 6.6 mg/L (fig. 4). Similar to the small pH values, the small dissolved-oxygen concentrations at site C1 indicate a ground-water source for streamflow.

Comparisons to Water-Quality Standards and Criteria

The States of Wyoming and Montana have established water-quality standards and criteria for some of the water-quality properties included in this report. In some cases, the two States may have established different values. For this report, sampling site data are compared to the standards and criteria for the State in which the site is physically located. Field measurements of water temperature were not compared to water-quality standards for stream temperatures in Wyoming and Montana because the State's water-quality standards are related to allowable increases in stream temperatures resulting from anthropogenic inputs, such as wastewater-treatment-plant effluent (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2002).

Numeric water-quality standards for specific conductance have been established in Montana, but not Wyoming (Wyoming Department of Environmental Quality, 2001b). For the two Montana sites (sites T4 and P9), the State of Montana has established seasonal water-quality standards for discrete values (samples) and monthly averages of specific conductance for the Tongue River and Powder River to address concerns about irrigation water quality (Montana Department of Environmental Quality, 2002). For this report, site data are compared to the standards established for discrete samples: (1) from November 1 through March 1, no sample from the Tongue River or the Powder River may have a specific-conductance value greater than 2,500 µS/cm at 25°C; and (2) from March 2 through October 31 (irrigation season), no sample from the Tongue River may have a specific-conductance value greater than 1,500 µS/cm at 25°C and no sample from the Powder River may have a specific-conductance value greater than 2,500 µS/cm at 25°C. At site T4 on the Tongue River, no samples had specific-conductance values that were larger than the water-quality standard (fig. 4). At site P9 on the Powder River, 8 of the 86 samples had specific-conductance values that were greater than 2,500 µS/cm at 25°C. Of these eight samples, four were collected during water year 2004, when annual runoff was only about 27 percent of average.

Water-quality standards for pH are not given as a single number. In Wyoming, pH values in the range of 6.5 to 9.0 are allowed (Wyoming Department of Environmental Quality, 2001b). Values of pH that are outside of this range are considered harmful to aquatic life. The pH values measured during one sampling event on the Belle Fourche River (site B1) and one sampling event on Donkey Creek (site B3) were greater than 9.0 (fig. 4). These large pH values were associated with large dissolved-oxygen concentrations and may have resulted from photosynthetic processes. In Montana, criteria for pH for class B–1 (Tongue River) and class C–1 (Powder River) waters are based on levels of induced change in pH of less than 0.5 standard unit, within the range of 6.5 to 8.5 (Montana Department of Environmental Quality, 2002). For this report, the induced change in pH could not be established for the Montana sites (sites T4 and P9).

Water-quality criteria for dissolved oxygen have been established in Wyoming and water-quality standards for dissolved oxygen have been established in Montana. The criteria and standards are not given as a single number and depend on aquatic life stages present in a stream and on stream class and are applicable for a given time period (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006). For this report, only values for the water column were used for comparison because measurements of intergravel dissolved-oxygen concentrations were not made. For Wyoming sites on streams with a 2AB classification, the dissolved-oxygen concentration

(4.9 mg/L) at site T2 on Goose Creek and two concentrations (4.6 mg/L and 4.8 mg/L) at site P10 on the Little Powder River were less than the water-column criterion of 5.0 mg/L for early life stages. For Wyoming sites on streams that have a 2ABWW classification, the dissolved-oxygen concentrations at sites P3 (one value) and P5 (one value) on the Powder River and at sites B1 (three values) and B4 (four values) on the Belle Fourche River were less than the criterion of 5.0 mg/L for early life stages. One dissolved-oxygen concentration at site B1 on the Belle Fourche River was less than the criterion of 3.0 mg/L for other life stages. For the Montana sites (sites T4 and P9), none of the dissolved-oxygen concentrations were less than the standard established for early life stages of 5.0 mg/L.

Major-Ion Chemistry

The general quality of stream waters often is described on the basis of the major-ion chemistry. Major ions are electronically charged dissolved constituents commonly present in natural waters at concentrations typically greater than 1.0 mg/L (Hem, 1985). This section describes the water types of the four major drainage basins and summarizes major-ion concentrations of dissolved calcium, dissolved magnesium, dissolved potassium, dissolved sodium, dissolved chloride, dissolved fluoride, and dissolved sulfate in samples collected at the 22 sampling sites during water years 2001–05. SAR, alkalinity, dissolved silica, and dissolved solids are described with the major-ion chemistry. Comparisons to water-quality standards and criteria also are presented.

In a natural drainage basin, dissolved constituents primarily are controlled by the weathering of rocks and soils near the surface. Precipitation may weather soil and rocks at the surface and carry dissolved solids directly into streams, or precipitation can infiltrate into the shallow ground-water system, weathering soil and rocks as it percolates, before discharging into a nearby stream. The Powder River structural basin is no longer in a natural state, and land uses, including urban development, irrigation, grazing, conventional oil and gas production, CBNG development, and coal mining, affect the composition and concentrations of dissolved constituents in streams.

Water Types

The relative proportions of the major cations (calcium, magnesium, potassium, and sodium) and the major anions [bicarbonate and carbonate (based on alkalinity), chloride, fluoride, and sulfate] were used to describe the water type at the 22 sampling sites. The nitrite and nitrate anions also are used in describing water type, but these constituent concentrations typically were not provided for samples in this study, and their contribution generally is small compared to bicarbonate, chloride, and sulfate ions. Trilinear diagrams illustrate the relative percentage of the major cations (positively charged) and anions (negatively charged) on two trilinear plots and a diamond-shaped plot that combines the cation and anion information (Piper, 1944). A sample that had a dissolved-solids concentration equal to or near the median value was selected to represent the major-ion composition for each site in the Piper diagram (fig. 5). These samples were used to represent the typical major-ion composition of stream water at the sites; however, temporal variability in the composition of the stream waters may exist, and the predominant cation and anion may vary depending on the source of the waters that are contributing to flow at a given time. Concentrations and compositions of dissolved solids in study streams are affected by streamflow. Large streamflows generally dominated by snowmelt or rainfall runoff, and small streamflows often are dominated by ground-water inputs. These separate water sources can cause dissolved-solids composition to vary with streamflow.

Water types varied among the four major drainage basins and among sites within a given drainage basin (fig. 5). In general, water in Little Goose Creek (site T1), Goose Creek (site T2), and the Tongue River (site T4) was a mixed magnesium-calcium-bicarbonate type (fig. 5*A*). The headwaters for these sites in the Tongue River drainage basin are in the Bighorn Mountains, where the geology consists of resistant Precambrian-era igneous and metamorphic rocks and Paleozoic-era sedimentary rocks, including carbonate rocks. In contrast, water in Prairie Dog Creek (site T3), a plains tributary, was a mixed magnesium-calcium-sulfate type, reflecting the different bedrock geology of the Wasatch Formation.

Water types in the Powder River drainage basin were mixed (fig. 5*B*). Generally, the dominant ions in the basin were sodium and sulfate, which are common constituents in the soluble Tertiary-age sedimentary rocks. Water at upstream sites (sites P2, P3, and P5) in the Powder River was a sodium-sulfate type. Water in the western tributaries of Crazy Woman Creek (site P4) and Clear Creek (sites P7 and P8), which originate in the Bighorn Mountains, was a calcium-magnesium-sodium-sulfate type. Water in the Powder River changed to a mixed sodium-calcium-magnesium-sulfate type at site P9, reflecting the inputs from the western tributaries. Tributaries to the Powder River in the eastern part of the basin had sodium as the dominant cation. Water in Wild Horse Creek (site P6) was a sodium-magnesium-calcium-sulfate type, and water in the Little Powder River (site P10) was a sodium-sulfate type. Salt Creek (site P1) is the only site in the basin where chloride typically was the dominant anion. The predominance of sodium and chloride in samples from Salt Creek is the result of saline ground waters discharged to Salt Creek or its tributaries from conventional oil and gas production (RETEC Group, Inc., 2004).

Water types in the Cheyenne River drainage basin were mixed (fig. 5*C*). Water at site C1 on Antelope Creek was a calcium-sodium-magnesium-sulfate type, whereas water at site C2 on Black Thunder Creek and site C3 on the Cheyenne River was a sodium-sulfate type. The larger percentage of calcium at site C1 on Antelope Creek compared to that at the

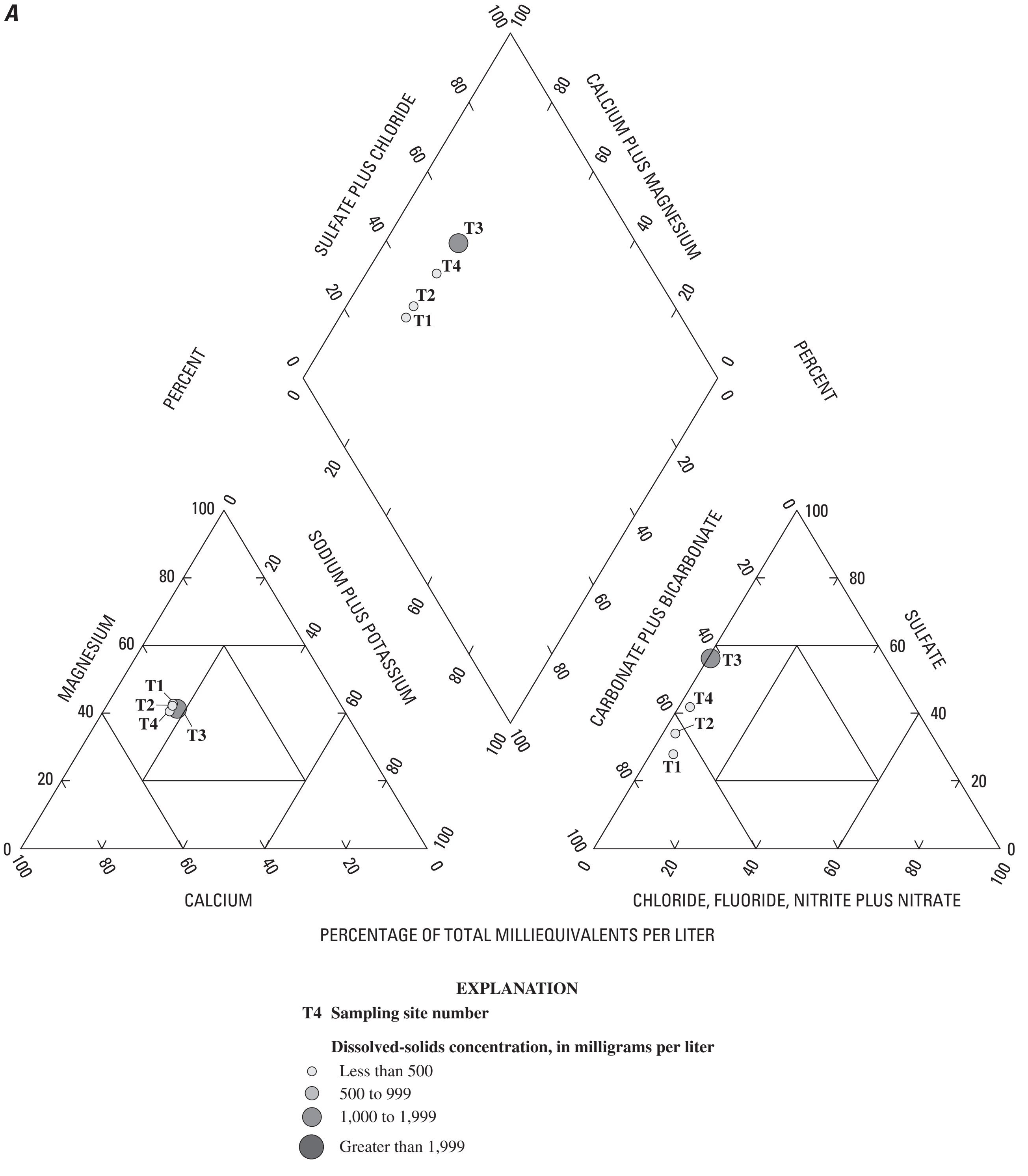


Figure 5. Major-ion composition and dissolved-solids concentrations in water-quality samples collected at sampling sites in the *A*, Tongue River drainage basin; *B*, Powder River drainage basin; *C*, Cheyenne River drainage basin; and *D*, Belle Fourche River drainage basin, Wyoming and Montana, water years 2001–05.

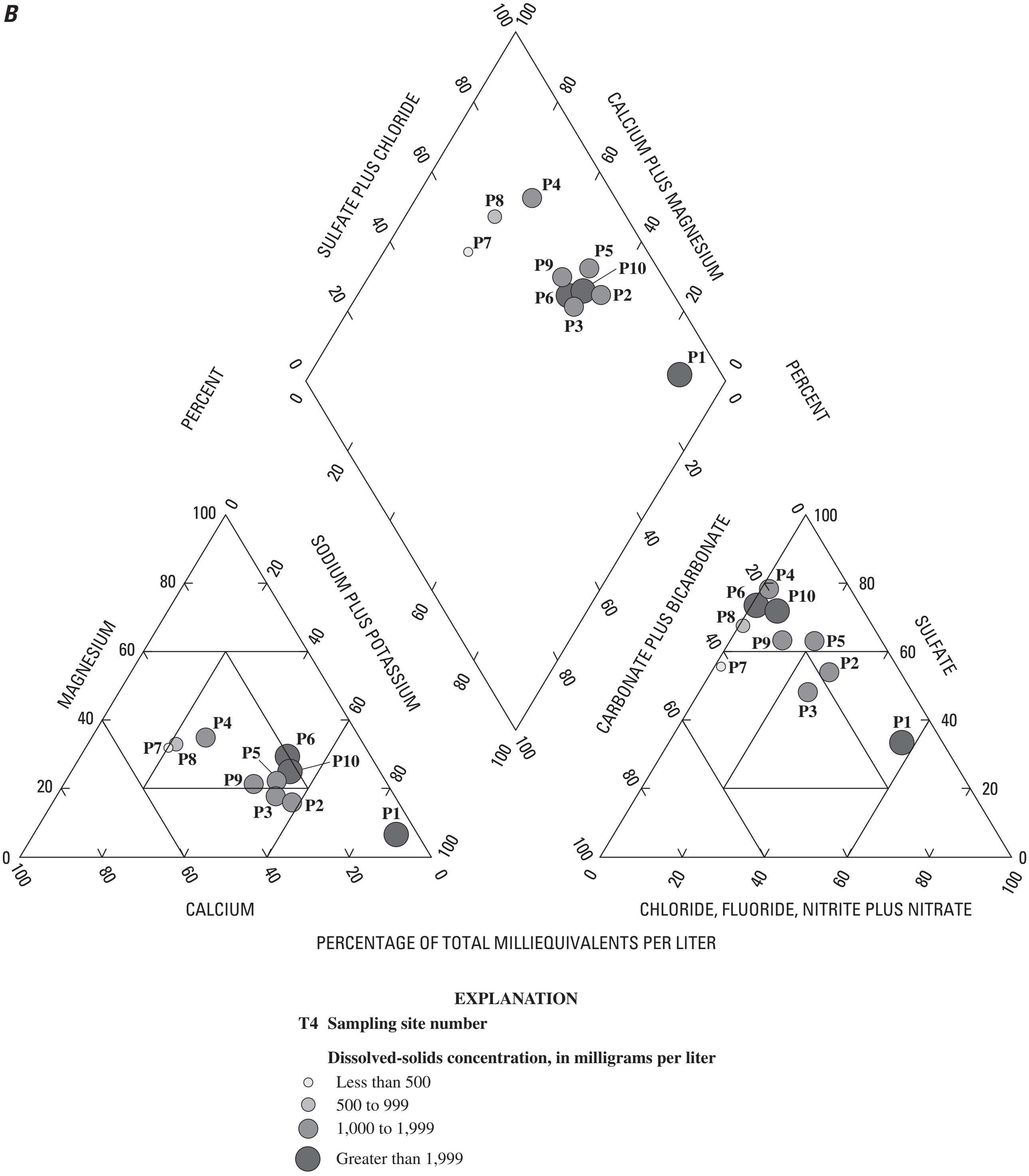


Figure 5. Major-ion composition and dissolved-solids concentrations in water-quality samples collected at sampling sites in the *A*, Tongue River drainage basin; *B*, Powder River drainage basin; *C*, Cheyenne River drainage basin; and *D*, Belle Fourche River drainage basin, Wyoming and Montana, water years 2001–05.—Continued

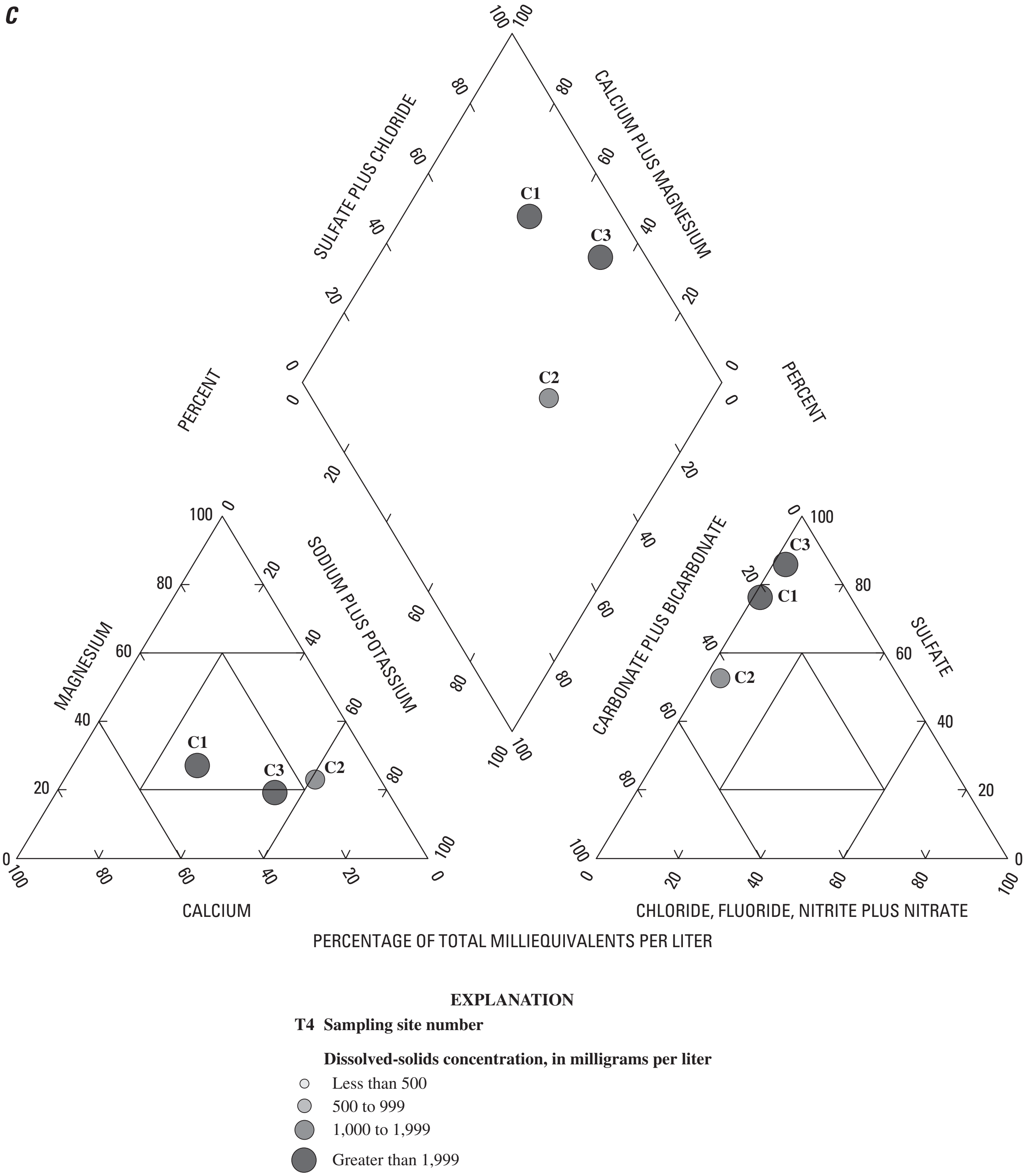


Figure 5. Major-ion composition and dissolved-solids concentrations in water-quality samples collected at sampling sites in the *A*, Tongue River drainage basin; *B*, Powder River drainage basin; *C*, Cheyenne River drainage basin; and *D*, Belle Fourche River drainage basin, Wyoming and Montana, water years 2001–05.—Continued

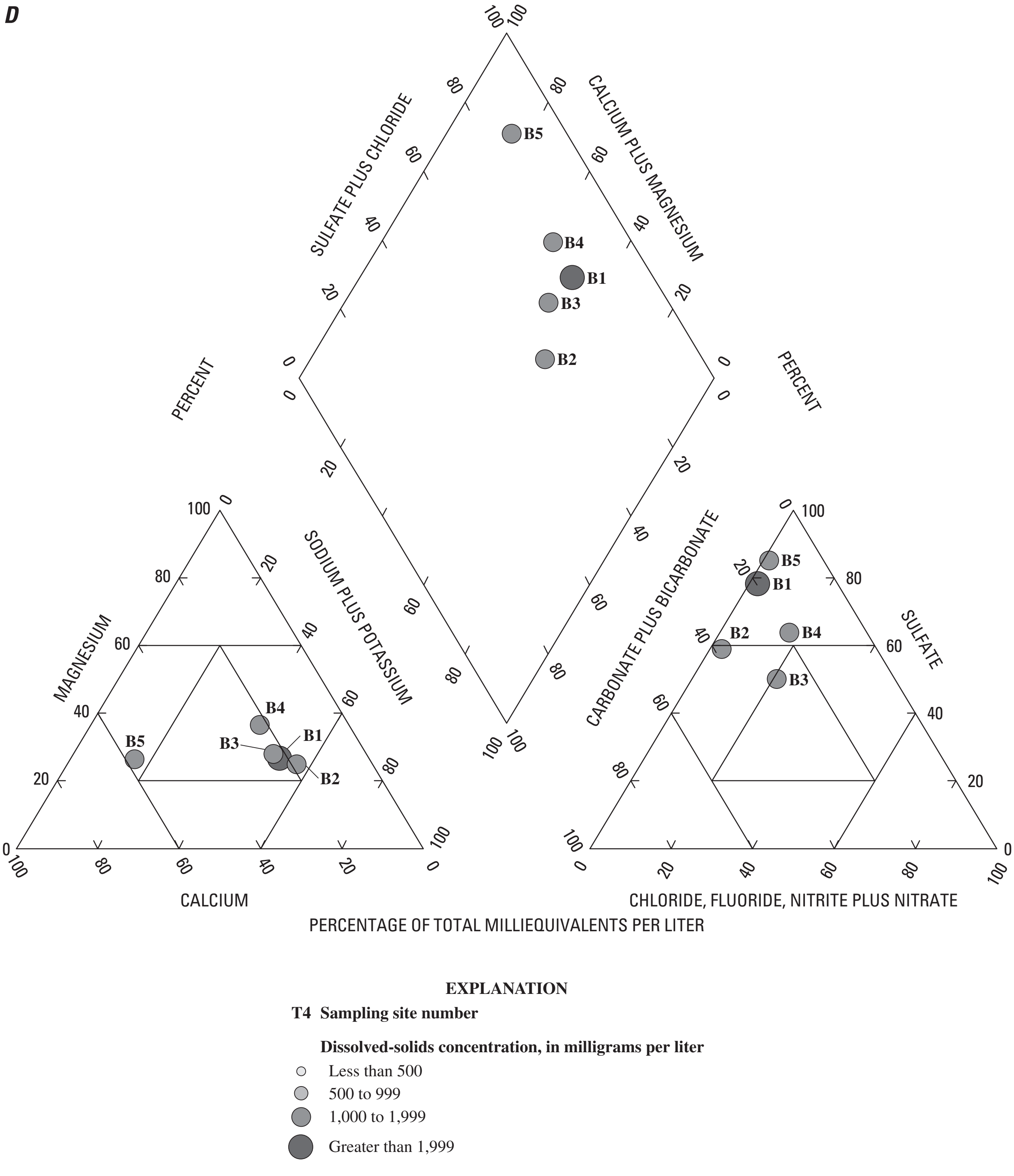


Figure 5. Major-ion composition and dissolved-solids concentrations in water-quality samples collected at sampling sites in the *A*, Tongue River drainage basin; *B*, Powder River drainage basin; *C*, Cheyenne River drainage basin; and *D*, Belle Fourche River drainage basin, Wyoming and Montana, water years 2001–05.—Continued

other two sites in Cheyenne River drainage basin may reflect shallow ground-water inputs to Antelope Creek. The quality of shallow ground water (including that associated with the spoil material from coal mining) in the Antelope Creek drainage basin is highly variable; however, ground water is sometimes a calcium-sodium-sulfate type (Fogg and others, 1991). Water at site C2 on Black Thunder Creek and at site C3 on the Cheyenne River was a sodium-sulfate type, although bicarbonate composed about 40 percent of the anions at site C2. Bicarbonate typically is associated with deep ground water, including coalbeds, although historical water-quality analyses indicate bicarbonate also is a common anion in the water associated with the spoil material from coal mining in the Black Thunder mining area (Fogg and others, 1991).

As in the plains waters in the Powder and Cheyenne River drainage basins, water types in the Belle Fourche River drainage basin generally were dominated by sodium and sulfate (fig. 5*D*). Water in the Belle Fourche River changed from a sodium-sulfate type at site B1 to a sodium-magnesium-calcium- sulfate type at site B4 to a calcium-sulfate type at site B5. Changes in geology in the lower Belle Fourche River drainage basin, including calcium-carbonate rocks associated with the Black Hills, and a reservoir between sites B4 and B5 likely affect the water type at site B5. Water at site B2 on Caballo Creek was a sodium-sulfate type; however, bicarbonate composed a larger percentage of the anions than at the other sites in the Belle Fourche River drainage basin. Water at site B3 on Donkey Creek was a mixed sodium-magnesium-calcium-sulfate type.

Summaries for Water Years 2001–05

Concentrations of major-ion constituents (fig. 6) varied among the four major drainage basins and among sampling sites within a given drainage basin during the study period. Many of the constituents showed a spatial pattern similar to the pattern for specific conductance.

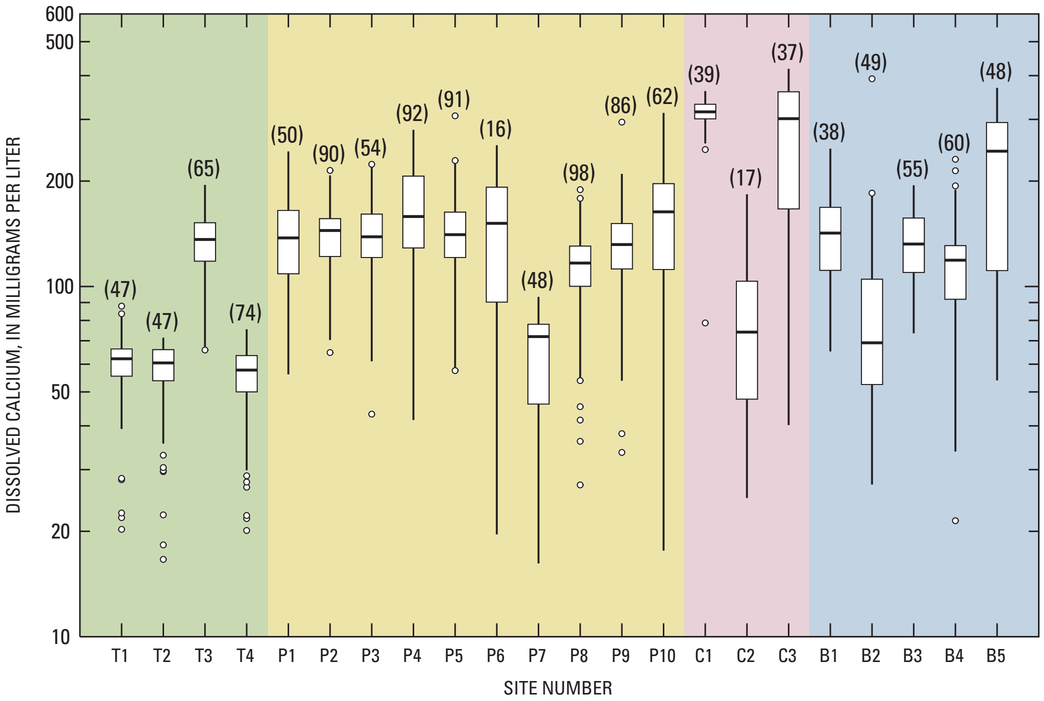
Calcium, an alkaline earth metal, can be contributed to water from sulfate- and carbonate-based rocks and minerals. Gypsum (sulfate based), anhydrite (carbonate based), and calcite (carbonate based) are minerals that commonly occur in the Tertiary-age rocks that underlie the plains of the Powder River structural basin. In addition, limestone and other calcium-carbonate rocks from the Paleozoic era also may be a calcium source in streams draining mountainous areas. Dissolved-calcium concentrations varied among the sites and ranged from 16.2 mg/L at site P7 on Clear Creek to 418 mg/L at site C3 on the Cheyenne River (fig. 6). Sites that had the largest median dissolved-calcium concentrations in each major drainage basin were site T3 on Prairie Dog Creek (136 mg/L), site P10 on the Little Powder River (163 mg/L), site C1 on Antelope Creek (315 mg/L), and site B5 on the Belle Fourche River (243 mg/L). Sites in the plains generally had large dissolved-calcium concentrations except for site C2 on Black Thunder Creek and site B2 on Caballo Creek, which had comparatively small median concentrations (74 and 69 mg/L, respectively). On the Belle Fourche River, the median dissolved-calcium concentration increased by a factor of 2 from site B4 to site B5. Changes in geology in the lower Belle Fourche River drainage basin, including calcium-carbonate rocks associated with the Black Hills, and a reservoir between sites B4 and B5 likely affect dissolved-calcium concentrations at site B5.

Magnesium, an alkaline earth metal, commonly occurs with calcium in sulfate- and carbonate-based rocks and minerals. Relative dissolved-magnesium concentrations had a spatial pattern similar to that for dissolved-calcium concentrations; however, the magnitudes of the dissolved-magnesium concentrations generally were smaller than the magnitudes of the dissolved-calcium concentrations (fig. 6). Dissolved-magnesium concentrations ranged from about 6.3 mg/L at site P7 on Clear Creek to 300 mg/L at site B2 on Caballo Creek. The large dissolved-magnesium concentration at site B2 on Caballo Creek was an outlier value for this site, which had the smallest median concentration in the Belle Fourche drainage basin. Sites that had the largest median dissolved-magnesium concentrations in each major drainage basin were site T3 on Prairie Dog Creek (87.6 mg/L), site P6 on Wild Horse Creek (121 mg/L), site C1 on Antelope Creek (127 mg/L), and site B1 on the Belle Fourche River (120 mg/L).

Potassium, an alkali metal, commonly occurs in clay minerals. Dissolved-potassium concentrations ranged from about 1 mg/L at several sites (T1, T2, T4, and P7) to 76.5 mg/L at site P2 on the Powder River (fig. 6). Sites that had the largest median dissolved-potassium concentrations in each major drainage basin were site T3 on Prairie Dog Creek (7.4 mg/L), site P1 on Salt Creek (32 mg/L), site C1 on Antelope Creek (18 mg/L), and site B3 on Donkey Creek (15 mg/L).

Sodium, an alkali metal, is associated with soluble rocks and minerals in the plains of the Powder River structural basin. Sodium concentrations can have a large range of values in natural waters because large concentrations can be reached before precipitates form (Hem, 1985, p. 101). Sodium concentrations may be larger in coalbed waters than in some of the streams receiving CBNG-produced waters; thus, sodium is one of the primary constituents of concern during CBNG development. Rice and others (2000) reported sodium concentrations ranging from 110 to 800 mg/L in coalbed waters from the Powder River structural basin. Sodium is a concern for irrigation water use; large concentrations can have a negative effect on soils by causing dispersion and swelling of montmorillonite soils. Soil dispersion and swelling can reduce infiltration rates, hydraulic conductivity, and aeration of the soil, resulting in a negative effect on plant health (Hanson and others, 1999).

Sodium was the dominant cation in samples collected from many of the streams in the study area. Dissolved-sodium concentrations ranged from 5.7 mg/L at site T4 on the Tongue River to 1,490 mg/L at site P1 on Salt Creek (fig. 6). Sites that had the largest median dissolved-sodium concentrations



EXPLANATION

🟩	Tongue River sampling sites (see table 1 for names)
🟨	Powder River sampling sites (see table 1 for names)
🟪	Cheyenne River sampling sites (see table 1 for names)
🟦	Belle Fourche River sampling sites (see table 1 for names)
MTNIST	State of Montana non-irrigation season (November 1–March 1) standard for the Tongue River (Montana Department of Environmental Quality, 2002)
MTIST	State of Montana irrigation season (March 2–October 31) standard for the Tongue River (Montana Department of Environmental Quality, 2002)
MTNISP	State of Montana non-irrigation season (November 1–March 1) standard for the Powder River (Montana Department of Environmental Quality, 2002)
MTISP	State of Montana irrigation season (March 2–October 31) standard for the Powder River (Montana Department of Environmental Quality, 2002)
WYAAC	State of Wyoming acute aquatic-life criterion (Wyoming Department of Environmental Quality, 2001b)
WYCAC	State of Wyoming chronic aquatic-life criterion (Wyoming Department of Environmental Quality, 2001b)
WMHHC	State of Wyoming and State of Montana human-health criteria (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006)
(47)	Number of samples

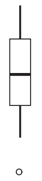

1.5 times interquartile range (IQR) or largest value
75th percentile
Median (50th percentile)
25th percentile
-1.5 times IQR or smallest value
Value greater than 1.5 times IQR or less than -1.5 times IQR

Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

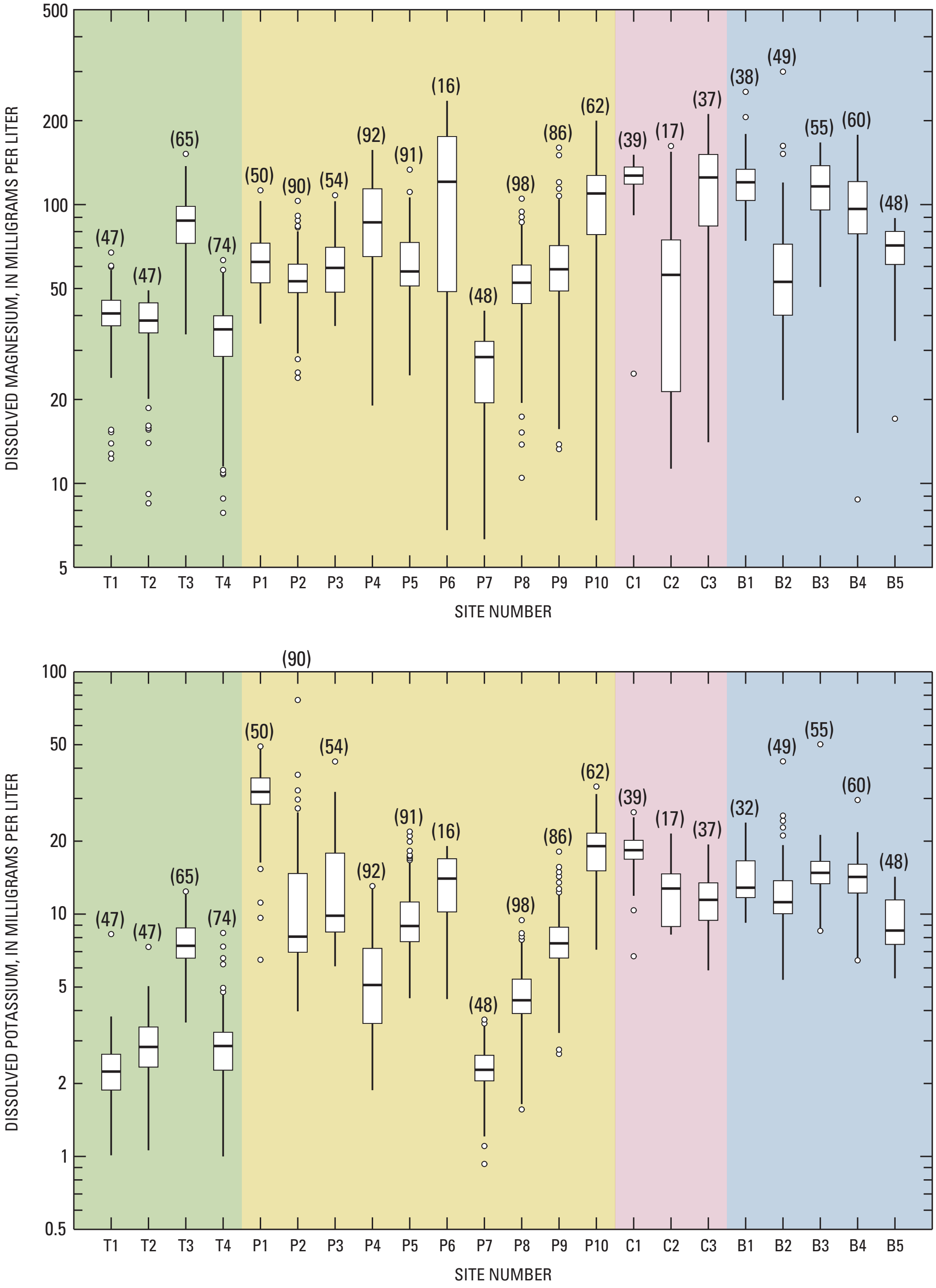


Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

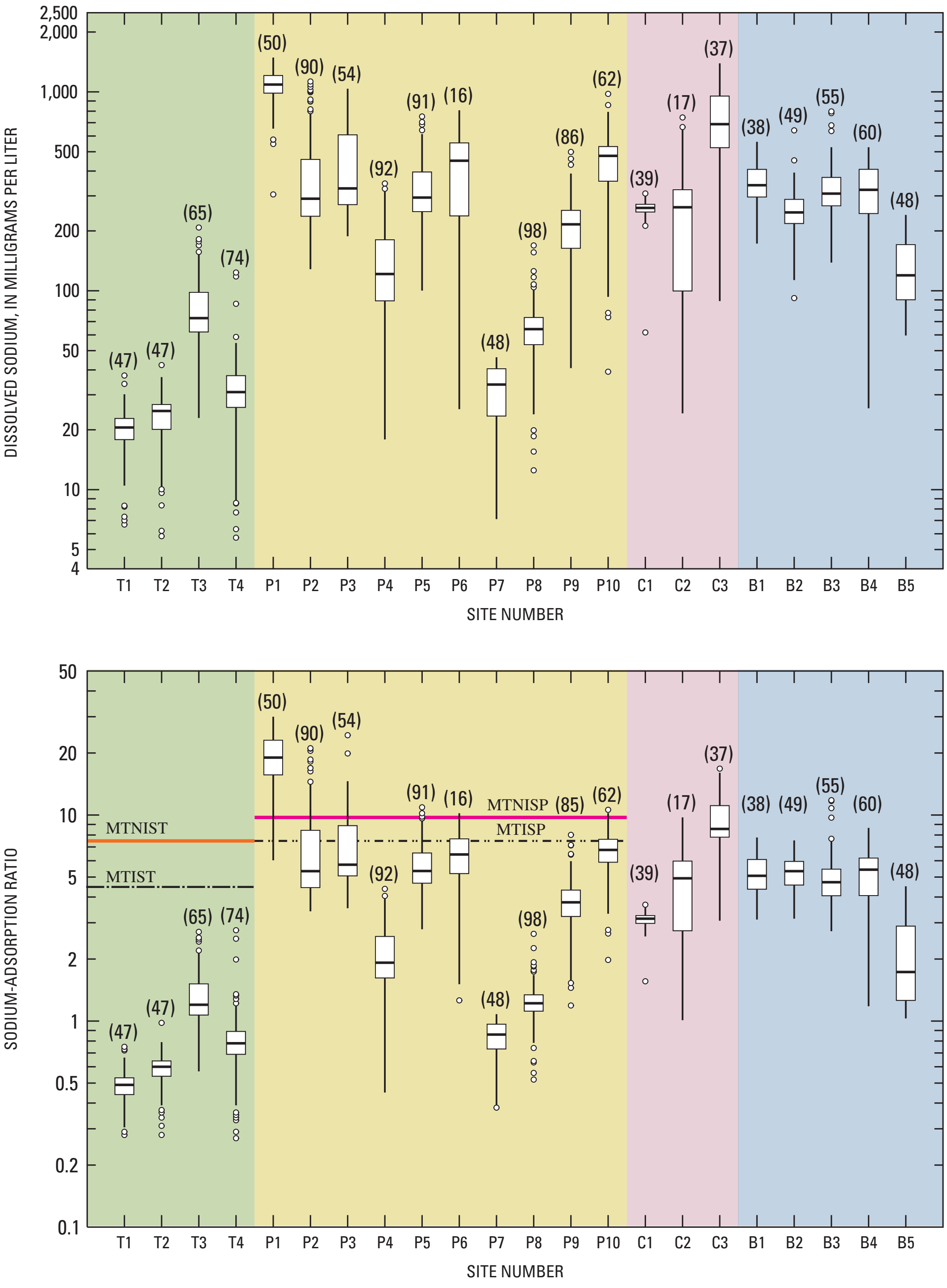


Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

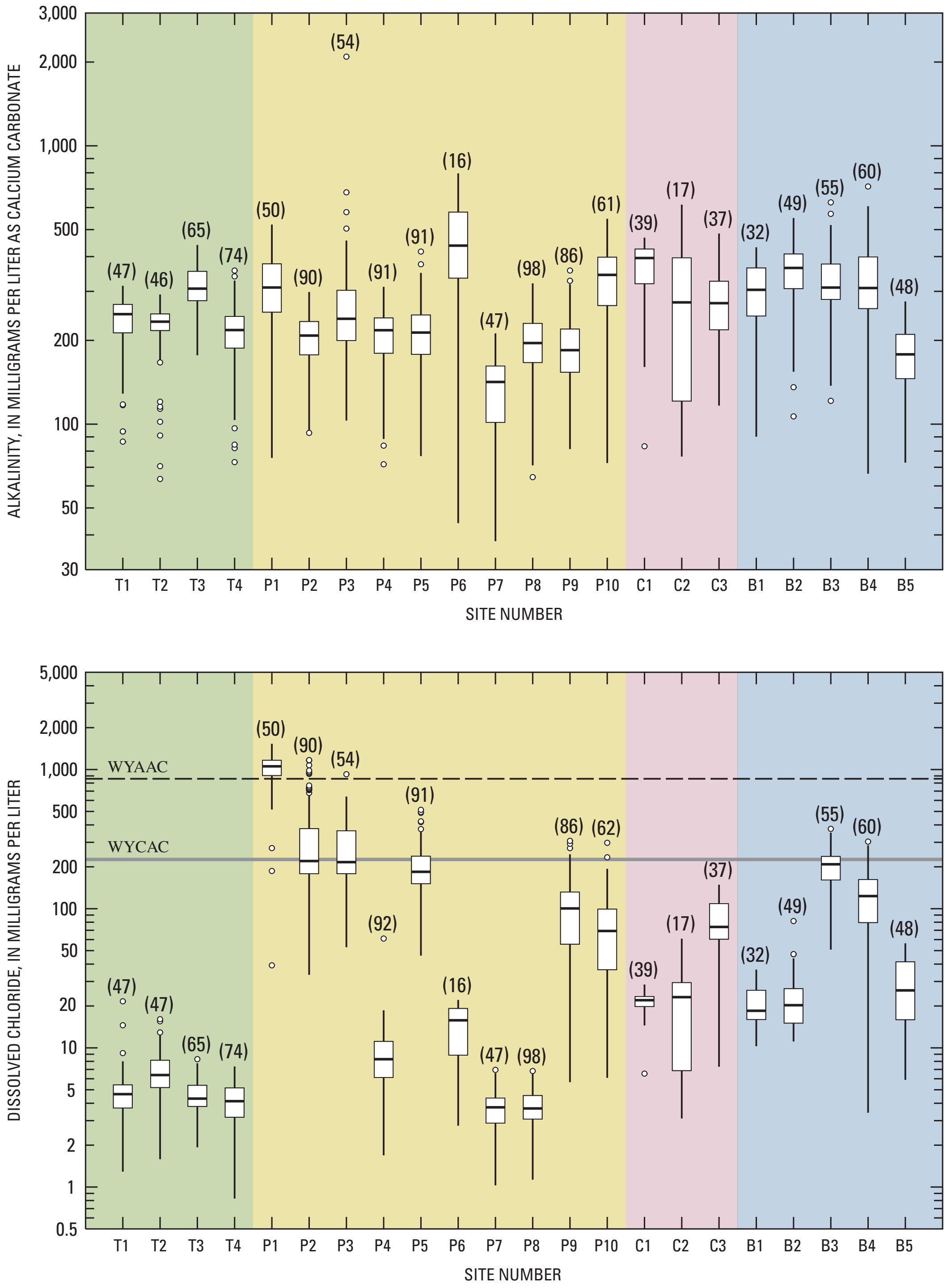


Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

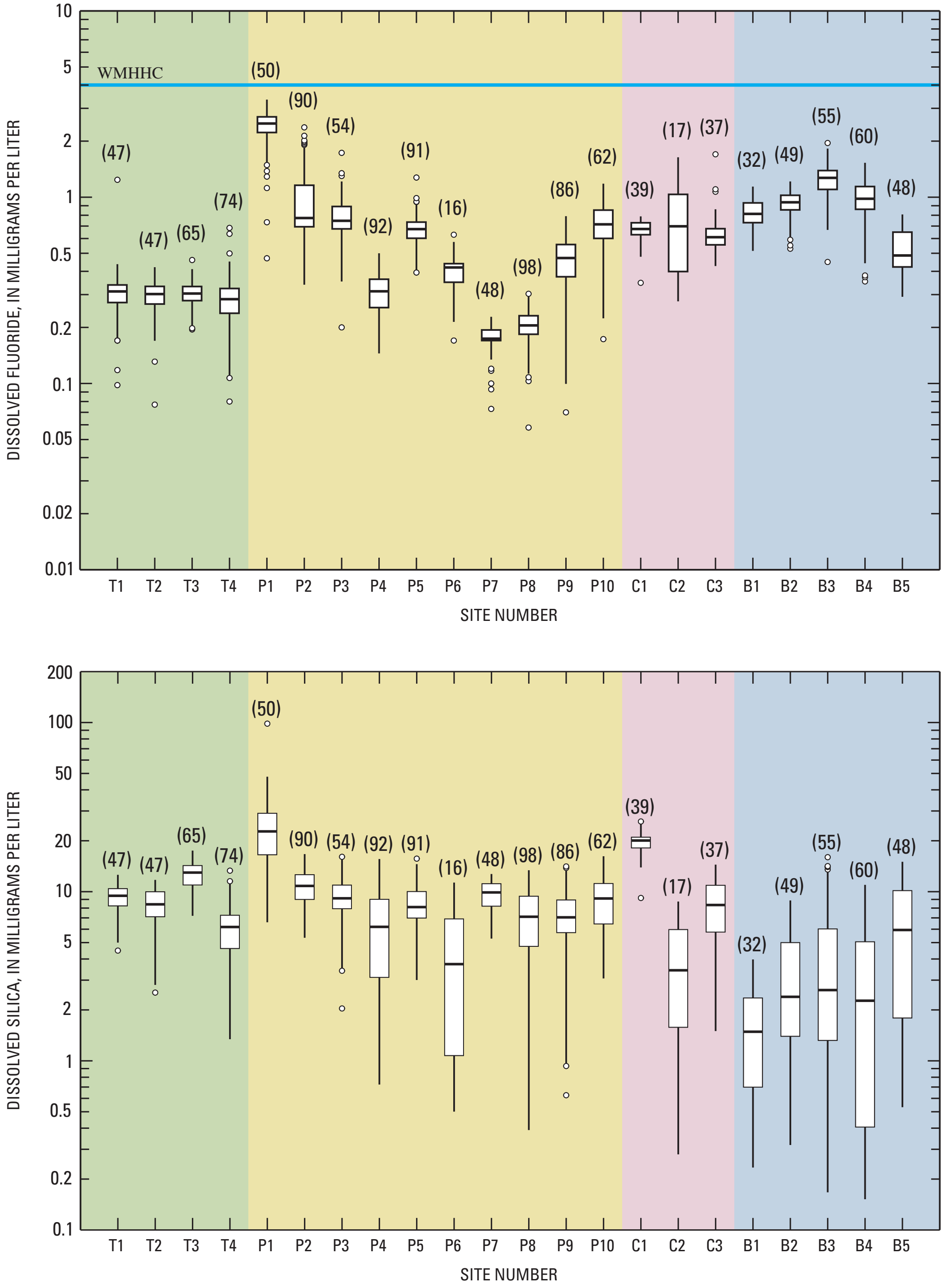
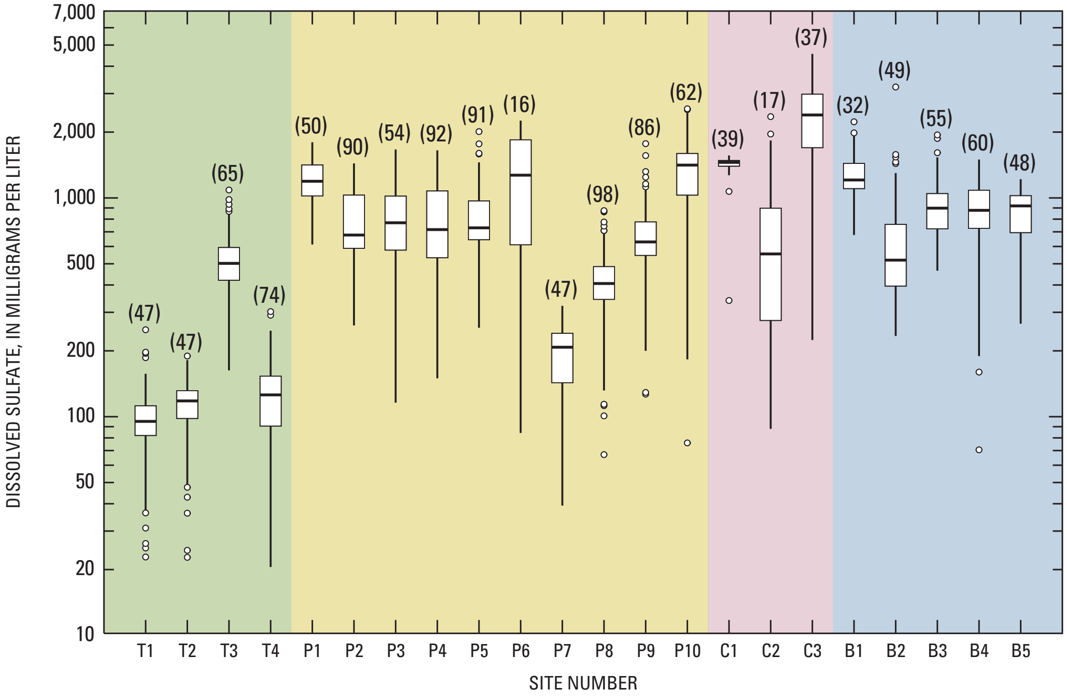


Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued



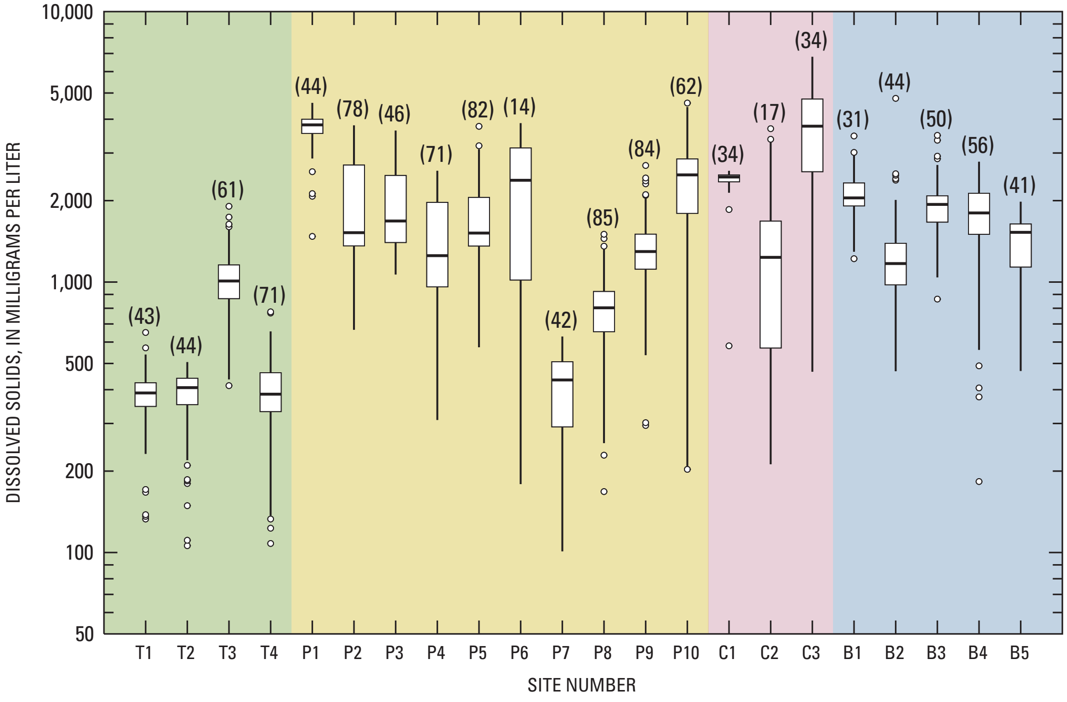


Figure 6. Statistical summary of major-ion chemistry in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

in each major drainage basin were site T3 on Prairie Dog Creek (73 mg/L), site P1 on Salt Creek (1,090 mg/L), site C3 on the Cheyenne River (688 mg/L), and site B1 on the Belle Fourche River (339 mg/L). On the main stem of the Powder River, median dissolved-sodium concentrations at sites P2, P3, and P5 were about 300 mg/L. The median dissolved-sodium concentration decreased to about 216 mg/L at site P9 on the Powder River as a result of diluting flows from Clear Creek (sites P7 and P8).

SAR, a calculated constituent, is the ratio of the concentrations (expressed in milliequivalents per liter) of sodium ions to calcium and magnesium ions (eq. 1); the larger the proportion of sodium, the larger the SAR value. SAR can be used to estimate the degree to which irrigation water enters into cation-exchange reactions in soil and is used to determine the sodium hazard for irrigation waters (U.S. Salinity Laboratory Staff, 1954). The suitability of water for irrigation decreases as SAR increases. Rice and others (2000) indicated SAR values in coalbed waters typically are greater than values in streams receiving CBNG-produced waters. SAR values reported by Rice and others (2000) ranged from 5.7 to 29 in coalbed waters from the Powder River structural basin. A reconnaissance sampling by the USGS during September 2005 (*http://tonguerivermonitoring.cr.usgs.gov/SC_Synoptic_2005.htm*) of the Tongue River and CBNG-produced waters discharging directly to the stream indicated CBNG-produced waters in the reach upstream from site T4 had SAR values greater than 50. SAR values have been estimated in real time using specific conductance from continuous monitors to assist irrigators and water managers in evaluating the suitability of water for irrigation (Nimick, 2004; Clark and Mason, 2006).

SAR values generally had the same spatial distribution as dissolved-sodium concentrations (fig. 6). Samples that had the smallest SAR values were collected at sites T1, T2, and T4 in the Tongue River drainage basin and at sites P7 and P8 on Clear Creek. SAR values also generally were smaller at site T3 on Prairie Dog Creek, site P4 on Crazy Woman Creek, and site B5 on the Belle Fourche River than at most other sites. Calcium and magnesium are large contributors to the cation composition of these streams, thus lowering the SAR values in the streams. Sites that had the largest median SAR values in each major drainage basin were site T3 on Prairie Dog Creek (1.2), site P1 on Salt Creek (19), site C3 on the Cheyenne River (8.6), and site B4 on the Belle Fourche River (5.4). The large SAR values for Salt Creek (site P1) contribute to increases in the SAR values at downstream sites (sites P2, P3, and P5) on the Powder River. A decrease in the median SAR value on the Powder River at site P9 results from diluting flows from Clear Creek, which contain proportionally more calcium and magnesium compared to sodium.

Small SAR values for streams in the Tongue River drainage basin (sites T1, T2, and T4) and for Clear Creek (site P7) make these waters particularly desirable for irrigation use. A potential increase in SAR values of the streams from inputs of CBNG-produced waters in the area has been a concern in these basins because these streams also have relatively small specific-conductance values. As specific conductance decreases, increasing SAR values may result in a large reduction in the rate of infiltration, which is affected by both SAR and specific conductance of the irrigation water.

Alkalinity generally is attributable to bicarbonate ions, and to a lesser extent carbonate ions, in stream waters. In the Powder River structural basin, sulfate generally is the dominant anion in oxygenated streams and bicarbonate is the second most dominant anion. In contrast, reduced-state coalbed waters have bicarbonate as the dominant anion (Rice and others, 2002; Bartos and Ogle, 2002). Rice and others (2000) reported alkalinity concentrations in coalbed waters ranged from 290 to 2,320 mg/L.

Alkalinity concentrations (expressed as calcium carbonate) ranged from about 38 mg/L at site P7 on Clear Creek to about 2,090 mg/L at site P3 on the Powder River (fig. 6). Occasional large alkalinity concentrations and a larger median concentration at site P3 than at site P2 on the Powder River likely are a result of CBNG-produced waters. Site P3 is located downstream from a tributary drainage that has CBNG development (Patz and others, 2004). Sites that had the largest median alkalinity concentrations in each major drainage basin were site T3 on Prairie Dog Creek (307 mg/L), site P6 on Wild Horse Creek (438 mg/L), site C1 on Antelope Creek (395 mg/L), and site B2 on Caballo Creek (364 mg/L). These sites are in tributary basins that receive CBNG-produced waters.

Chloride is present in most streams at concentrations that are smaller than bicarbonate or sulfate concentrations. In the Powder River structural basin, chloride generally occurs in the soluble sedimentary rocks in the plains. Dissolved-chloride concentrations ranged from 0.83 mg/L at site T4 on the Tongue River to 1,530 mg/L at site P1 on Salt Creek (fig. 6). Sites that had the largest median dissolved-chloride concentrations in each major drainage basin were site T2 on Goose Creek (6.4 mg/L), site P1 on Salt Creek (1,050 mg/L), site C3 on the Cheyenne River (74 mg/L), and site B3 on Donkey Creek (209 mg/L). The effect of the saline ground waters discharged from conventional oil and gas production on Salt Creek or its tributaries is particularly apparent when dissolved-chloride concentrations at site P1 are compared to concentrations at the other sites. The effect of Salt Creek on the Powder River is shown by the dissolved-chloride concentrations at sites P2, P3, P5, and P9 on the Powder River. The larger dissolved-chloride concentrations at site B3 on Donkey Creek compared to those at sites B1 and B2 in the Belle Fourche drainage basin likely are from municipal sewage effluent. The effect of Donkey Creek on dissolved-chloride concentrations in the Belle Fourche River is shown by the concentrations at site B4.

Fluoride typically is grouped and analyzed with the other major ions; however, it generally occurs at concentrations less than 1.0 mg/L (Hem, 1985). The solubility of common fluoride minerals, such as fluorite, is low, resulting in small concentrations in natural waters. Dissolved-fluoride concentrations ranged from 0.06 mg/L at site P8 on Clear Creek to about 3.3 mg/L at site P1 on Salt Creek (fig. 6). The larger dissolved-fluoride concentrations at site P1 relative to those at the other sites probably are a result of saline ground waters discharged to Salt Creek.

After oxygen, silicon is the most abundant element in the Earth’s crust. Silicon combines with oxygen to form the basis of the silicate minerals. Silica, which is the oxide SiO_2, generally is used for representing silicon in natural waters. Most of the dissolved silica in natural waters results from chemical breakdown of silicate minerals during weathering (Hem, 1985, p. 70). Although silica is relatively abundant in rocks and minerals, dissolved-silica concentrations were smaller than concentrations of many of the major ions (fig. 6). Dissolved-silica concentrations ranged from less than 0.2 mg/L at several sites to about 98 mg/L at site P1 on Salt Creek. The concentration range commonly observed in natural waters is from about 1 to 30 mg/L (Hem, 1985, p. 73). Median dissolved-silica concentrations at all sites were within this range. The larger median dissolved-silica concentrations at site P1 on Salt Creek and at site C1 on Antelope Creek compared to those at the other sites likely reflect ground-water contributions.

Sulfate-based minerals, such as gypsum, commonly occur in the sediments of the plains in the Powder River structural basin. Because some of these minerals are readily dissolved, sulfate was the most dominant anion in samples collected from most streams in the study area. Dissolved sulfate had the largest range of concentrations as compared to the ranges for the other major ions. Dissolved-sulfate concentrations ranged from 20.5 mg/L at site T4 on the Tongue River to 4,550 mg/L at site C3 on the Cheyenne River (fig. 6). Sites that had the largest median dissolved-sulfate concentrations in each major drainage basin were site T3 on Prairie Dog Creek (502 mg/L), site P10 on the Little Powder River (1,410 mg/L), site C3 on the Cheyenne River (2,390 mg/L), and site B1 on the Belle Fourche River (1,210 mg/L). Sites on Little Goose Creek (site T1), Goose Creek (site T2), the Tongue River (site T4), and Clear Creek (site P7), which have a large part of their drainage basins underlain by more resistant rock types, had small median dissolved-sulfate concentrations.

Dissolved solids represent the combined sum of all the dissolved constituents in a water sample. Dissolved-solids concentrations are closely correlated with specific conductance, and the patterns observed in dissolved-solids concentrations (fig. 6) are the same as the patterns observed in specific conductance (fig. 4). For natural waters, the conversion factor from specific conductance to dissolved solids ranges from about 0.54 to about 0.97 (Hem, 1985). The median conversion factor for the 22 sites ranged from 0.65 at site T1 on Little Goose Creek to 0.91 at site C1 on Antelope Creek. Conversion factors tend to be large when large dissolved-sulfate concentrations are present.

Dissolved-solids concentrations in samples collected from the 22 sampling sites ranged from 101 mg/L at site P7 on Clear Creek to 6,810 mg/L at site C3 on the Cheyenne River. The Tongue River and its tributary streams generally had the smallest dissolved-solids concentrations of the four major drainage basins. Dissolved-solids concentrations at sites in the Powder, Cheyenne, and Belle Fourche River drainage basins generally were larger and much more variable than dissolved-solids concentrations at sites in the Tongue River drainage basin. Sites T1, T2, and T4 in the Tongue River drainage basin and site P7 on Clear Creek in the Powder River drainage basin had the smallest median dissolved-solids concentrations. These sites share the common characteristic of being in proximity to their headwaters in the Bighorn Mountains, which receive higher precipitation, have more resistant geology, and have steeper gradients than the plains. Streams that have headwaters in the plains, such as Wild Horse Creek (site P6), Little Powder River (site P10), and Cheyenne River (site C3), tended to have large dissolved-solids concentrations because of abundant geologic sources of salts and the accumulation of soluble salts on or near the surface as a result of low precipitation and high rates of evaporation. Sites that have the largest median dissolved-solids concentrations in each major drainage basin were site T3 on Prairie Dog Creek (1,010 mg/L), site P1 on Salt Creek (3,810 mg/L), site C3 on the Cheyenne River (3,770 mg/L), and site B1 on the Belle Fourche River (2,050 mg/L).

Generally, dissolved constituents in streams tend to become more concentrated as the streams flow downstream and across the plains. Typical changes that occur in dissolved-solids concentrations as a stream flows from the mountains to the plains are observed in samples from sites P7 and P8 on Clear Creek. An increase in the median dissolved-solids concentration, as well as in the individual major-ion constituents (except chloride and silica) and SAR, is observed between sites P7 and P8. In contrast, median dissolved-solids concentrations in samples collected from the Powder River are larger at the upstream sites (P2, P3, and P5) than at the downstream site (P9). In this case, diluting flows from Clear Creek decrease the dissolved-solids concentrations in the Powder River. Likewise, median dissolved-solids concentrations for samples collected from the Belle Fourche River also show a pattern of larger concentrations at the upstream sites (B1 and B4) than at the downstream site (B5). The geology in the lower Belle Fourche River drainage basin, which includes more resistant rock types, and a reservoir between sites B4 and B5 likely affect the dissolved-solids concentrations at site B5.

Comparisons to Water-Quality Standards and Criteria

Water-quality standards and criteria have been established only for the major-ion constituents of SAR, chloride, and fluoride. In some cases, the States of Wyoming and Montana have established different standards or criteria. For this report, sampling site data are compared to the standards and criteria for the State in which the site is physically located.

Numeric water-quality standards for SAR have not been established in Wyoming (Wyoming Department of Environmental Quality, 2001b). For the two Montana sites (sites T4 and P9), the State of Montana has established seasonal water-quality standards for discrete values (samples) and monthly averages of SAR for the Tongue River and Powder River to address concerns about irrigation water quality (Montana Department of Environmental Quality, 2002). Site data are compared to the standards established for discrete samples: (1) from November 1 through March 1, no sample from the Tongue River may have an SAR value greater than 7.5 and no sample from the Powder River may have an SAR value greater than 9.75; and (2) from March 2 through October 31 (irrigation season), no sample from the Tongue River may have an SAR value greater than 4.5 and no sample from the Powder River may have an SAR value greater than 7.5. At site T4 on the Tongue River, no samples had SAR values greater than the water-quality standard. At site P9 on the Powder River, one sample had an SAR value of 8.0 during June 2004, which is greater than the irrigation season standard of 7.5.

Wyoming has established both acute and chronic aquatic-life criteria for chloride (Wyoming Department of Environmental Quality, 2001b). A numeric water-quality standard for chloride has not been established in Montana (Montana Department of Environmental Quality, 2006). The Wyoming criteria are based on total concentrations, which include the dissolved and particulate phase. For this report, the dissolved-chloride concentrations are compared to the criteria and should provide a useful estimate of total chloride because most of the chloride in natural waters typically occurs in the dissolved phase (Hem, 1985).

Dissolved-chloride concentrations were greater than aquatic-life criteria at several sites (fig. 6). The largest dissolved-chloride concentrations were at site P1 on Salt Creek, where 96 percent of the samples had concentrations greater than the chronic criterion of 230 mg/L and 80 percent had concentrations greater than the acute criterion of 860 mg/L. Salt Creek has been listed for water-quality impairments because of chloride by the WDEQ (Wyoming Department of Environmental Quality, 2006). A Use Attainment Analysis conducted on Salt Creek indicates the "natural" flow in the Salt Creek drainage basin normally has chloride concentrations that range from less than 100 mg/L to as much as 235 mg/L. The chloride-rich produced waters discharged to Salt Creek increase the chloride concentrations; however, Salt Creek would have no flow during many parts of the year without these discharges (RETEC Group, Inc., 2004). The reach of the Powder River downstream from Salt Creek to the confluence with Clear Creek also has been listed for chloride-related water-quality impairments by the WDEQ (Wyoming Department of Environmental Quality, 2006). About 46 percent of the samples collected at site P2 on the Powder River had dissolved-chloride concentrations greater than the chronic criterion, and about 9 percent of the samples had concentrations greater than the acute criterion. Dissolved-chloride concentrations decrease downstream on the Powder River. About 44 percent of the samples collected at site P3 had concentrations greater than the chronic criterion. Crazy Woman Creek (site P4) had substantially smaller dissolved-chloride concentrations than the upstream Powder River sites and diluted the dissolved-chloride concentrations at site P5 on the Powder River, where about 27 percent of the samples had concentrations greater than the chronic criterion. Other Wyoming sites that had dissolved-chloride concentrations that were greater than the chronic aquatic-life criterion were site P10 on the Little Powder River (about 3 percent of the samples), site B3 on Donkey Creek (about 29 percent of the samples), and site B4 on the Belle Fourche River (about 10 percent of the samples).

The States of Wyoming and Montana have established a human-health criterion or standards of 4 mg/L for dissolved fluoride in surface waters on the basis of the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for fluoride in drinking water (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006). Small amounts of fluoride in diets have been shown to promote dental health, but large doses can cause health problems including discoloring of teeth and bone disease (U.S. Environmental Protection Agency, 2006). Dissolved-fluoride concentrations in all samples collected at sampling sties were less than 4.0 mg/L (fig. 6).

Trace Elements

Trace elements (generally metals) occur in natural waters at concentrations typically less than 1.0 mg/L (Hem, 1985, p. 129). Selected trace elements have been of interest because of their potential association with CBNG-produced waters in the Powder River structural basin. Samples from the 22 sampling sites in the Powder River structural basin were analyzed for total aluminum, dissolved arsenic, total barium, total beryllium, dissolved iron, dissolved manganese, and total selenium. Summaries of trace-element data for water years 2001–05 and comparisons to water-quality criteria are presented in the following sections.

Summaries for Water Years 2001–05

Trace-element concentrations varied (fig. 7, table 6) among the four major drainage basins and among sampling sites within a given drainage basin during the study period. For most sites, total-aluminum, total-barium, dissolved-iron, and dissolved-manganese concentrations generally were at least one order of magnitude larger than dissolved-arsenic, total-beryllium, and total-selenium concentrations. Concentration differences in trace elements generally are related to their phase and their relative abundance in the Earth's crust.

Aluminum is the third most abundant element in the Earth's crust and is the most abundant of the metal trace elements. For total-aluminum, the most variable of all the trace elements for which samples were analyzed for this study, concentrations ranged over several orders of magnitude from about 2 μg/L at site T3 on Prairie Dog Creek to 142,000 μg/L at site P1 on Salt Creek (fig. 7). Median total-aluminum concentrations were greater than 100 µg/L at most sites. The largest median total-aluminum concentrations were greater than 1,000 µg/L and occurred at sites P2, P3, P5, and P9 on the main stem of the Powder River. The large total-aluminum concentrations likely result from sediment in the whole-water samples. Much of the Powder River flows across erodable Tertiary-age formations, resulting in relatively large suspended-sediment concentrations during runoff events. Size distributions of the sediment particles in the Powder River typically are in the clay to silt range (Hembree and others, 1952), and aluminum is a common element in the mineral structure of fine-grained particles such as clays. Samples collected from Salt Creek (site P1) also had large total-aluminum concentrations; Salt Creek also carries fine-grained sediments (Hembree and others, 1952). Other streams in the study area that flow over similar sediments either flow across Tertiary-age sediments for a relatively short distance or were not sampled during the brief runoff conditions when suspended-sediment concentrations were large. The small concentrations at site B5 on the Belle Fourche River probably result from an upstream reservoir trapping suspended sediment, thereby decreasing the particulate fraction of total aluminum.

Arsenic is a nonmetallic trace element of concern because even small amounts can be toxic (Hem, 1985, p. 144). Dissolved-arsenic concentrations generally were small and frequently were reported as less than the laboratory reporting levels. Dissolved-arsenic concentrations ranged from less than 0.2 µg/L at site P7 on Clear Creek to 10 µg/L at site B3 on Donkey Creek (table 6). Median dissolved-arsenic concentrations were about 1.0 µg/L at many of the sites. Patz and others (2006) reported a mean dissolved-arsenic concentration of about 2 µg/L for selected samples of CBNG-produced waters and increasing in-channel arsenic concentrations as CBNG-produced waters flowed downstream. Median dissolved-arsenic concentrations were slightly larger (greater than 2 µg/L) at site P1 on Salt Creek and site B3 on Donkey Creek than at other sites sampled for this study. The smallest median dissolved-arsenic concentrations generally were reported for sites that have headwaters in mountainous areas, including site T1 on Little Goose Creek, site T2 on Goose Creek, and site P7 on Clear Creek.

Barium, an alkaline-earth metal (like calcium and magnesium), can enter into the structure of carbonate and sulfate minerals. The solubility of barite, a barium-sulfate mineral, is one of the common controls of the concentration of barium in natural waters (Hem, 1985, p. 136). Rice and others (2000) reported a mean dissolved-barium concentration of 620 µg/L for samples of coalbed waters in the Powder River structural basin. Total-barium concentrations varied and ranged from about 14 µg/L at site B1 on the Belle Fourche River to about 5,810 µg/L at site P9 on the Powder River (fig. 7). Median total-barium concentrations ranged from 28.7 µg/L at site B5 on the Belle Fourche River to 113 µg/L at site P3 on the Powder River. Samples that had small total-barium concentrations were collected at sites that have headwaters in mountainous areas (for example, sites T1, T2, and P7) as well as at sites that have headwaters in the plains (for example, sites C1, C3, and B3). Samples that had relatively large total-barium concentrations (greater than 200 µg/L) generally were collected at sites in the Powder River drainage basin. Total-barium concentrations were greater than 200 µg/L at site P1 on Salt Creek, sites P2, P3, P5, and P9 on the Powder River, and site P4 on Crazy Woman Creek. Total-barium concentrations were greater than 200 µg/L in a few samples from Black Thunder Creek (site C2), Caballo Creek (site B2), and the Belle Fourche River (site B4).

Like barium, beryllium also is included in the alkaline-earth metal group; however, its occurrence in natural waters is rare. Stream waters typically have beryllium concentrations that are less than 1 µg/L (Hem, 1985, p. 135). Total-beryllium concentrations ranged from less than 0.02 µg/L at several sites to 17.1 µg/L at site P2 on the Powder River (table 6); total-beryllium concentrations were less than laboratory reporting levels in about 55 percent of all samples. Median total-beryllium concentrations were less than 0.1 µg/L at many sites. Total-beryllium concentrations were 1 µg/L or larger in only about 5 percent of all samples; most of these samples were collected from sites on the Powder River.

Iron is the second most abundant metal trace element in the Earth's crust; however, dissolved-iron concentrations in surface waters commonly are small. The occurrence of dissolved iron in water is largely a function of environmental conditions, especially changes in oxidation and reduction states (Hem, 1985, p. 77). Rice and others (2000) reported a mean dissolved-iron concentration of 800 µg/L for samples of coalbed waters from the Powder River structural basin. Ground water frequently has dissolved-iron concentrations greater than 1,000 µg/L because reducing environments mobilize iron (Hem, 1985, p. 83). Most iron in CBNG-produced water precipitates near the outfalls in the form of oxides or hydroxides after initial contact with the atmosphere (Patz and others, 2006).

Dissolved-iron concentrations generally were relatively small (table 6); about 38 percent of all samples had concentrations less than laboratory reporting levels. The largest median dissolved-iron concentration was 57 µg/L at site P6 on Wild Horse Creek. The smallest median dissolved-iron concentrations (about 5 µg/L or less) were for sites P2, P3, P5, and P9 on the Powder River. The largest dissolved-iron concentration was 1,810 µg/L at site P2 on the Powder River. Filtered samples that had large dissolved-iron concentrations probably contained very small particulate material. The dissolved fraction of a sample is operationally defined by the nominal pore size of the 0.45-µm filter; however, some iron particles occur as colloids that are small enough to pass through the filter and be analyzed as part of the dissolved fraction.

Manganese is a relatively abundant metallic element commonly occurring in surface water at concentrations greater than a few hundred micrograms per liter (Hem, 1985,

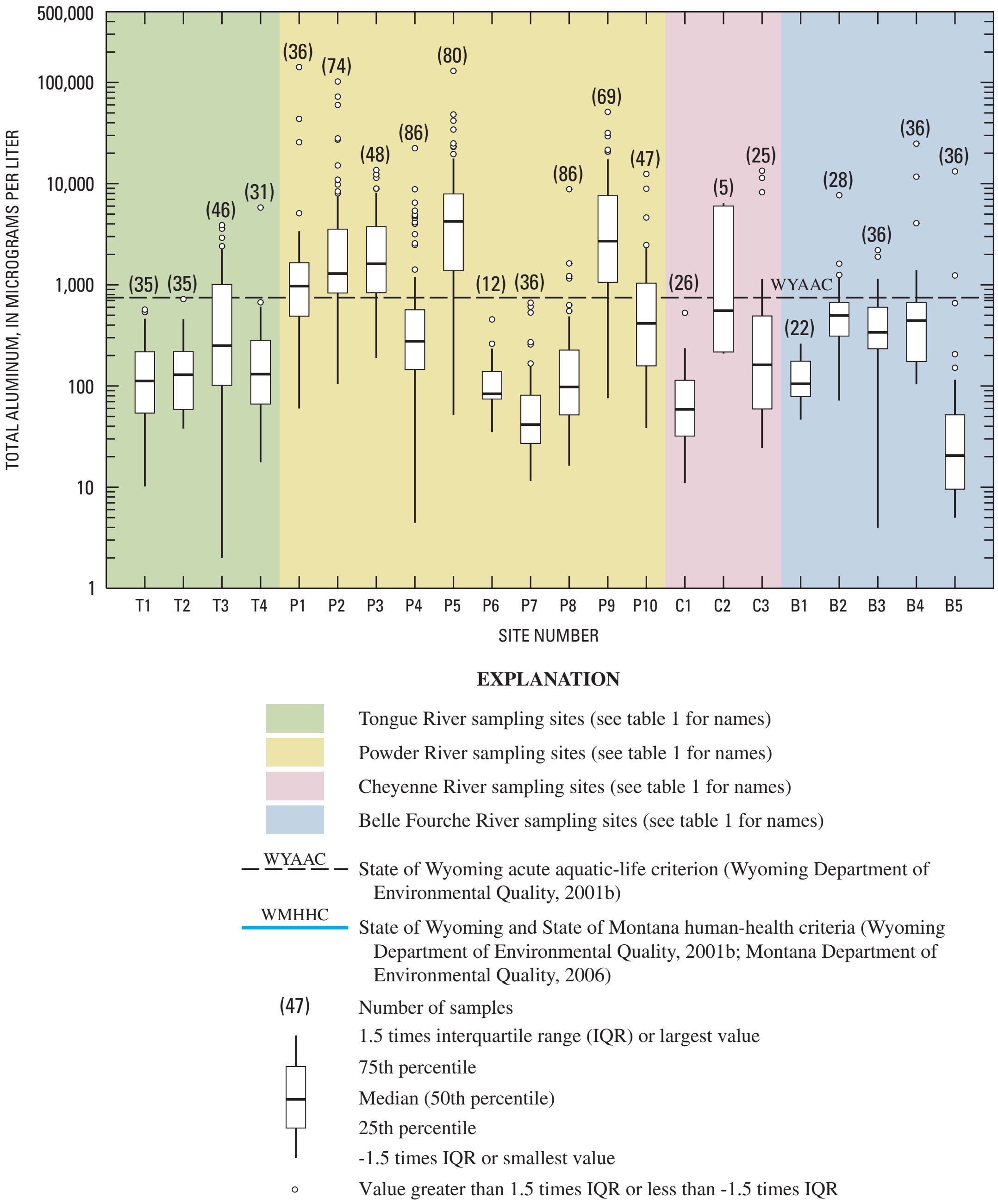


Figure 7. Statistical summary of total-aluminum, total-barium, and dissolved-manganese concentrations in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

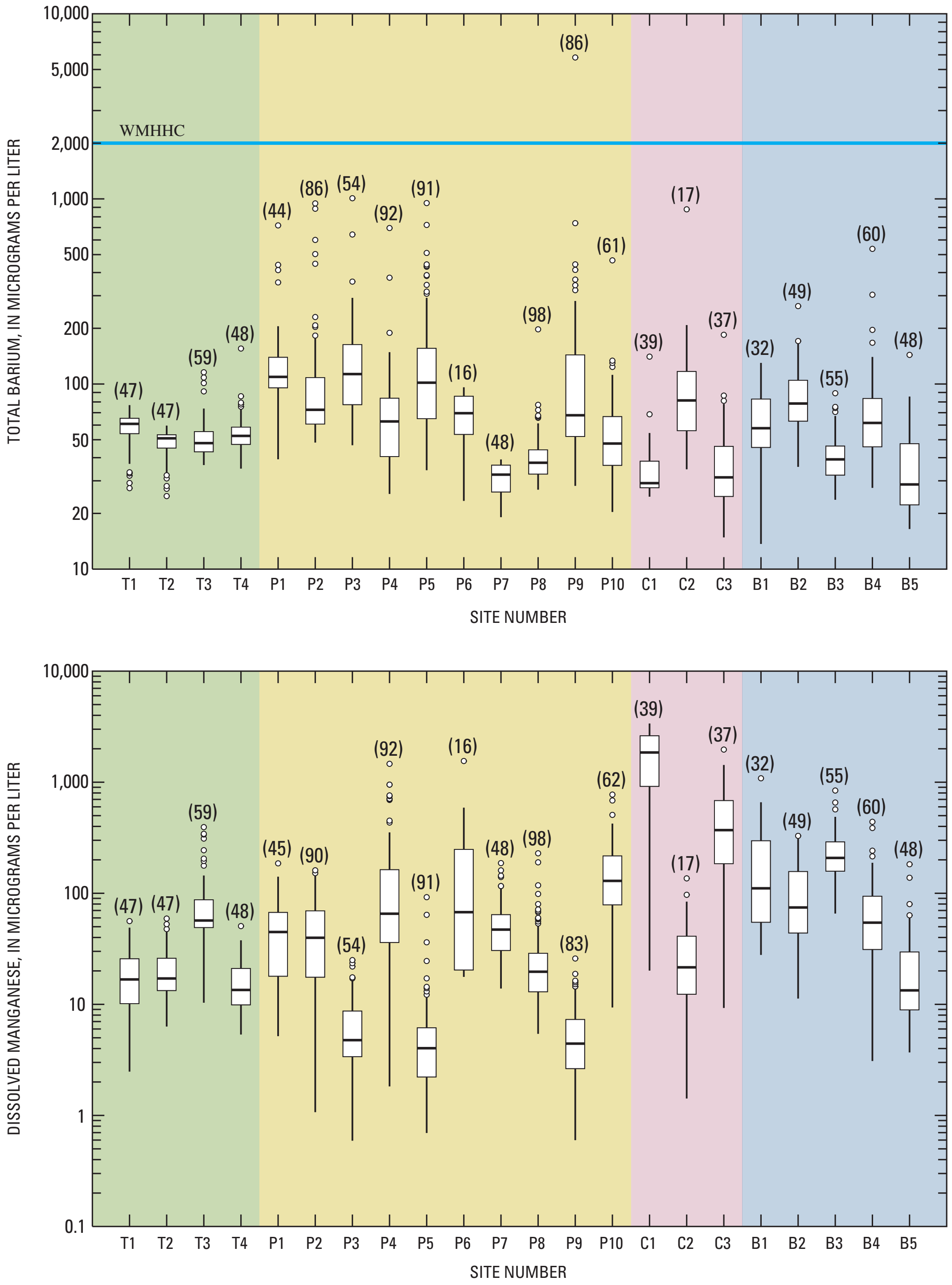


Figure 7. Statistical summary of total-aluminum, total-barium, and dissolved-manganese concentrations in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

Table 6. Statistical summary for concentrations of selected trace elements in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

[Constituent concentrations in micrograms per liter; <, less than; --, distribution for censored concentrations could not be determined because measurable concentrations occurred in fewer than six samples]

Site number (fig. 1)	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum
Arsenic, dissolved						
T1[1]	47	<0.3	0.4	0.5	0.7	1.2
T2[1]	47	<.3	.4	.5	.6	1.2
T3[1]	59	<.6	.7	.8	1.0	1.5
T4	48	.3	.4	.5	.7	1.3
P1	45	.6	2.0	2.7	3.5	5.5
P2	89	.7	1.1	1.2	1.5	2.8
P3[1]	54	<.8	1.0	1.1	1.4	2.3
P4	92	.4	.6	.8	1.0	2.0
P5[1]	91	<.7	.8	1.0	1.1	2.0
P6[1]	16	<.4	1.5	1.8	2.3	3.4
P7[1]	48	<.2	.3	.3	.4	.5
P8[1]	98	<.4	.5	.6	.8	1.3
P9	84	.2	.7	.9	1.0	2.1
P10	62	.4	.9	1.1	1.3	2.3
C1[1]	39	<.6	.6	.8	.9	1.7
C2[1]	17	<.8	.9	1.0	1.2	1.4
C3[1]	37	<.8	1.0	1.3	1.5	3.0
B1	23	.8	1.0	1.2	1.9	4.3
B2[1]	49	<.7	.9	1.2	1.5	3.3
B3	55	1.1	2.1	2.9	3.6	10
B4[1]	60	<1.1	1.4	1.6	2.0	3.5
B5[1]	48	<.6	.6	.7	.9	1.7
Beryllium, total						
T1[1]	35	<0.03	0.03	0.04	0.04	0.06
T2[1]	35	<.04	.04	.04	.04	.06
T3[1]	35	<.02	.04	.05	.12	.33
T4[1]	31	<.02	.03	.04	.06	.75
P1[1]	36	<.02	.05	.11	.22	7.8
P2[1]	74	<.04	.08	.11	.30	17.1
P3[1]	36	<.04	.07	.13	.28	1.4
P4[1]	74	<.02	.03	.06	.09	2.0
P5[1]	69	<.05	.12	.42	.68	15.8
P6	12	--	--	--	--	<.12
P7	36	--	--	--	--	<.06
P8[1]	74	<.02	.03	.05	.06	.83
P9[1]	69	<.03	.08	.19	.65	6.5
P10[1]	36	<.04	.07	.09	.13	1.0

Table 6. Statistical summary for concentrations of selected trace elements in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

[Constituent concentrations in micrograms per liter; <, less than; --, distribution for censored concentrations could not be determined because measurable concentrations occurred in fewer than six samples]

Site number (fig. 1)	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum
C1	26	--	--	--	--	<0.18
C2	5	<0.06	--	--	--	.53
C3	25	<.12	--	--	--	1.6
B1	22	--	--	--	--	<.12
B2[1]	28	<.04	0.04	0.05	0.07	1.1
B3[1]	36	<.03	.04	.06	.09	.22
B4[1]	36	<.02	.03	.07	.09	4.0
B5	38	--	--	--	--	<2.0
Iron, dissolved						
T1	47	5	14	18	28	96
T2	47	6	16	20	26	72
T3[1]	59	<4	6	8	11	50
T4[1]	31	<6	10	17	28	43
P1[1]	45	<8	11	13	19	58
P2[1]	90	<2	3	5	10	1,810
P3[1]	54	<2	3	4	7	22
P4[1]	92	<5	8	12	22	114
P5[1]	91	<1	3	5	11	1,600
P6	16	31	43	57	91	131
P7	48	14	26	37	48	124
P8[1]	98	<6	11	20	30	61
P9[1]	67	<3	4	5	7	20
P10[1]	62	<5	8	15	21	198
C1[1]	39	<10	20	45	374	1,510
C2[1]	17	<6	7	10	18	25
C3[1]	37	<6	9	13	19	64
B1[1]	32	<10	16	25	45	172
B2[1]	49	<4	6	8	12	57
B3[1]	55	<10	14	21	32	494
B4[1]	60	<6	8	11	15	29
B5[1]	48	<5	8	12	26	49
Selenium, total						
T1[1]	35	<0.3	0.4	0.5	0.7	1.1
T2[1]	35	<.4	.4	.6	.7	1.2
T3	35	.5	1.0	1.4	1.6	2.0
T4[1]	48	<.3	.3	.5	.6	1.6
P1	36	.2	2.1	4.0	6.3	9.8
P2	74	1.4	2.8	3.6	4.3	13

Table 6. Statistical summary for concentrations of selected trace elements in water-quality samples collected at sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.—Continued

[Constituent concentrations in micrograms per liter; <, less than; --, distribution for censored concentrations could not be determined because measurable concentrations occurred in fewer than six samples]

Site number (fig. 1)	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum
P3	36	0.8	3.4	3.8	4.7	8.3
P4	74	.5	1.2	1.5	1.7	3.2
P5	69	1.7	2.9	3.7	4.5	13
P6	12	.5	1.0	1.7	2.4	2.8
P7[1]	36	<.3	.3	.4	.6	1.2
P8	74	.3	.6	.8	1.0	1.4
P9	86	.4	1.8	2.5	3.1	8.2
P10	52	.5	1.1	1.4	1.7	2.9
C1	26	.4	.7	.9	1.5	2.4
C2	5	.9	--	--	--	2.1
C3	25	.7	1.5	2.0	2.5	4.7
B1	22	.4	.7	1.1	1.5	2.1
B2	28	.7	.8	1.2	2.0	12
B3	36	.7	1.7	2.0	2.8	5.4
B4	36	.9	1.4	1.7	2.2	4.3
B5	36	1.0	1.6	2.4	3.2	5.0

[1] Summary statistics for site were determined using log-probability methods for censored concentrations.

p. 89). Compared to iron, manganese ions are more stable in streams and can be transported at large concentrations without being complexed; consequently, dissolved-manganese concentrations were larger than dissolved-iron concentrations in many samples. However, as was previously described for iron, Patz and others (2006) noted that some manganese in CBNG-produced water also precipitated near the outfalls in the form of oxides or hydroxides after initial contact with the atmosphere. Dissolved-manganese concentrations ranged from about 0.6 µg/L at site P3 on the Powder River to about 3,400 µg/L at site C1 on Antelope Creek (fig. 7). The smallest median dissolved-manganese concentrations (less than 10 µg/L) were for sites P3, P5, and P9 on the Powder River. The median concentration in samples from the Powder River decreased from about 40 µg/L at site P2 to about 5 µg/L at site P3. A cause for the decrease in dissolved-manganese concentrations was not determined, but chemical precipitation may have removed some manganese from solution. The largest median dissolved-manganese concentration was about 1,900 µg/L at site C1 on Antelope Creek. Ground water is a likely source of the manganese at this site. Other sites that had large median dissolved-manganese concentrations (greater than 100 µg/L) were sites that have headwaters in the plains in the eastern part of the study area, including site P10 on the Little Powder River, site C3 on the Cheyenne River, site B1 on the Belle Fourche River, and site B3 on Donkey Creek. Miller and others (2005) reported that dissolved-manganese concentrations at site P10 on the Little Powder River show an inverse relation with streamflow, indicating the manganese probably is from ground-water sources.

Selenium is a nonmetallic trace element that naturally occurs in geologic materials in the Western United States (U.S. Department of the Interior, 1998). Selenium behaves similarly to sulfur and, in an oxidized state, may substitute for sulfate in the lattice structure of soluble sulfate salts. Although the source of selenium is natural, studies in Wyoming have reported increased concentrations as a result of land-use activities, such as coal mining and irrigation, that mobilize the selenium (See and others, 1995; U.S. Department of the Interior, 1998). Excessive selenium concentrations can be toxic to plants and animals. Alkaline soils, like those in parts of the study area, enhance the mobility of selenium. As a result, selenium is a constituent of concern with CBNG development. Patz and others (2006) reported that selenium concentrations increased in the channel as CBNG-produced waters flowed downstream.

Total-selenium concentrations ranged from less than 0.3 µg/L at several sites to 13 µg/L at sites P2 and P5 on the Powder River (table 6). Some total-selenium concentrations in samples were less than laboratory reporting levels. Total-selenium concentrations at sites that have headwaters in mountainous areas (sites T1, T2, T4, and P7) generally were smaller than concentrations at sites that have headwaters in the plains. The largest median concentration was 4.0 µg/L at site P1 on Salt Creek. The Salt Creek drainage basin has proportionally more area underlain by Cretaceous-age sedimentary rocks and materials derived from these rocks than other drainage basins. Cretaceous-age sedimentary rocks and materials derived from these rocks are known sources of selenium (U.S. Department of the Interior, 1998).

Comparisons to Water-Quality Criteria

The States of Wyoming and Montana have established one or more water-quality criteria (chronic aquatic life, acute aquatic life, and human health) for the trace elements for which samples were analyzed for this study. In some cases, the two States have established different water-quality criteria. In general, most of Wyoming's trace-element criteria are based on dissolved concentrations, whereas most of Montana's criteria are based on total-recoverable (or total) concentrations. Only criteria applying to the phases of the trace elements summarized in this report are described. For this report, sampling site data are compared to the criteria for the State in which the site is located.

The State of Wyoming has established chronic (87 µg/L) and acute (750 µg/L) aquatic-life criteria for aluminum that are based on total concentrations; however, the chronic criterion does not apply to waters that have high hardness and pH, such as those in the Powder River structural basin (Wyoming Department of Environmental Quality, 2001b). The State of Montana has established criteria for dissolved, but not total, aluminum (Montana Department of Environmental Quality, 2006). Total-aluminum concentrations in some samples collected at 14 of the Wyoming sites were greater than the acute aquatic-life criterion (fig. 7). Of the 14 sites, 8 sites are in the Powder River drainage basin. More than 75 percent of the samples collected from the Powder River at sites P2, P3, and P5 had total-aluminum concentrations that were greater than the acute aquatic-life criterion of 750 µg/L. As previously discussed, clay minerals that are prevalent throughout the study area probably are the source of the relatively large aluminum concentrations. Particulate material in stream waters typically is considered to be less biologically available than dissolved ions; however, trace elements can accumulate in the biotic and abiotic material on submerged surfaces and eventually enter into the food chain (Moore and Ramamoorthy, 1984). Because a small positive bias was detected in some blank samples for aluminum, some caution should be used in interpreting values that are at or near the criterion.

The State of Wyoming has established chronic (150 µg/L) and acute (340 µg/L) aquatic-life criteria for arsenic based on dissolved concentrations (Wyoming Department of Environmental Quality, 2001b). The State of Montana has established criteria for total, but not dissolved, arsenic (Montana Department of Environmental Quality, 2006). Dissolved-arsenic concentrations in samples collected at the 20 Wyoming sites were small compared to both the chronic and acute aquatic-life criteria.

The States of Wyoming and Montana have established a human-health criterion for barium of 2,000 µg/L based on total concentrations (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006). Total-barium concentrations in samples collected at the 20 Wyoming sites were less than the criterion. Total-barium concentrations in samples collected at the two Montana sites generally were small compared to the criterion. The concentration in one sample collected at site P9 on the Powder River was 5,810 µg/L, which is greater than the human-health criterion.

The States of Wyoming and Montana have established a human-health criterion for beryllium of 4 µg/L based on total concentrations (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006). For Wyoming sites, total-beryllium concentrations in one sample collected at site P1 on Salt Creek (7.8 µg/L), two samples collected at site P2 on the Powder River (7.5 and 17.1 µg/L), and two samples collected at site P5 on the Powder River (4.1 and 15.8 µg/L) were greater than 4 µg/L. For Montana sites, the total-beryllium concentration in one sample collected at site P9 on the Powder River (6.5 µg/L) was greater than the criterion.

The State of Wyoming has established a chronic aquatic-life criterion for iron (1,000 µg/L) and a human-health criterion (300 µg/L) that are based on dissolved concentrations (Wyoming Department of Environmental Quality, 2001b). The State of Montana has established criteria for total, but not dissolved, iron (Montana Department of Environmental Quality, 2006). Dissolved-iron concentrations in samples collected at the Wyoming sites generally were small compared to the criteria (table 6). Dissolved-iron concentrations were greater than the chronic aquatic-life criterion in one sample collected at site P2 on the Powder River, one sample collected at site P5 on the Powder River, and two samples collected at site C1 on Antelope Creek. The human-health criterion of 300 µg/L is based on a secondary drinking-water standard that is intended to prevent undesirable aesthetic effects (U.S. Environmental Protection Agency, 2006). The criterion only applies to class 2AB and 2ABWW waters that have drinking-water supply as a designated use. The dissolved-iron concentration was greater than 300 µg/L in two samples collected at site P2 on the Powder River and two samples collected at site P5 on the Powder River; however, this reach of the Powder River is not used as a drinking-water supply.

The State of Wyoming has established chronic and acute aquatic-life criteria and a human-health criterion for manganese based on dissolved concentrations (Wyoming Department of Environmental Quality, 2001b). The State of

Montana has established some standards for manganese, but none have been established for stream reaches in this study (Montana Department of Environmental Quality, 2006). The Wyoming chronic and acute aquatic-life criteria for manganese are not fixed numeric values but are dependent on water hardness at the time of sampling. Sample-specific criteria were calculated using the equations in the State surface-water-quality standards (Wyoming Department of Environmental Quality, 2001b). Dissolved-manganese concentrations were greater than calculated chronic aquatic-life criteria in three samples collected at site C1 on Antelope Creek. Dissolved-manganese concentrations were less than the calculated acute aquatic-life criterion for all of the samples collected at the 20 Wyoming sites.

The human-health criterion of 50 µg/L for dissolved manganese is based on a secondary drinking-water standard that is intended to prevent undesirable aesthetic effects (U.S. Environmental Protection Agency, 2006). The criterion applies to class 2AB and 2ABWW waters that have drinking-water supply as a designated use. Dissolved-manganese concentrations were greater than the criterion in at least one sample from all streams where the criterion applies: Little Goose Creek, Goose Creek, Prairie Dog Creek, Powder River, Crazy Woman Creek, Clear Creek, Little Powder River, Cheyenne River, and Belle Fourche River. Prairie Dog Creek (site T3), Crazy Woman Creek (site P4), the Little Powder River (site P10), the Cheyenne River (site C3), and the Belle Fourche River (site B1) had dissolved-manganese concentrations greater than 50 µg/L in more than 50 percent of the samples collected. However, the Powder River, Crazy Woman Creek, the Cheyenne River, and the Belle Fourche River are not used as drinking-water supplies within the State of Wyoming.

The States of Wyoming and Montana have established chronic (5 µg/L) and acute (20 µg/L) aquatic-life criteria and a human-health criterion (50 µg/L) for total selenium (Wyoming Department of Environmental Quality, 2001b; Montana Department of Environmental Quality, 2006). Total-selenium concentrations were less than either the acute aquatic-life criterion or the human-health criterion in all samples collected at the 20 Wyoming sites (table 6). For Wyoming, total-selenium concentrations in many samples collected at site P1 on Salt Creek and in many samples collected at sites P2, P3, and P5 on the Powder River were greater than the chronic criterion. Selenium has been listed as a water-quality impairment by the WDEQ for the reach of the Powder River downstream from Salt Creek to the confluence with Crazy Woman Creek (Wyoming Department of Environmental Quality, 2006). The total-selenium concentrations in one sample (12 µg/L) collected at site B2 on Caballo Creek and in one sample (5.4 µg/L) collected at site B3 on Donkey Creek were greater than the chronic aquatic-life criterion. For Montana, total-selenium concentrations were less than either the acute aquatic-life criterion or the human-health criterion in all samples collected at sites T4 and P9. Total-selenium concentrations were greater than the chronic aquatic-life criterion of 5 µg/L in three samples collected at site P9 on the Powder River.

Specific Conductance and Sodium-Adsorption Ratio Relations with Streamflow and Seasonal Variability for Water Years 2001–05

In some parts of the Powder River structural basin (particularly the northwestern part), waters associated with coalbeds and discharged during CBNG development have larger specific conductance and SAR values than receiving streams. Because of their potential to affect water for irrigation use, specific conductance and SAR have been two of the primary constituents of concern during CBNG development and are examined in greater detail in this section. The effect of irrigation water on soil infiltration rates is dependent upon the interaction between the flocculating effects of specific conductance and the dispersion effects of sodium. Soils are able to tolerate irrigation waters that have large SAR values if the specific-conductance values also are large (Hanson and others, 1999). Specific conductance and SAR relations with streamflow and seasonal variability in values were examined for water years 2001–05 to help describe patterns of water-quality variability in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins.

Relations with Streamflow

Water-quality constituents frequently are correlated with streamflow. Negative (or inverse) relations between water-quality constituents and streamflow indicate dilution of constituent concentrations occurs with increasing streamflow. Positive relations indicate constituent concentrations increase with increasing streamflow, commonly as a result of increased particulate content caused by erosion during runoff. The strength of the relation is indicated by the Spearman's rho value, with values closest to –1 or 1 indicating the strongest association with streamflow.

Specific conductance and streamflow for water years 2001–05 were negatively correlated at all 22 sampling sites; however, the strengths of the relations were variable (table 7, fig. 8). For most streams, the largest specific-conductance values tended to occur during low-flow conditions, when ground water composes a large part of the streamflow. Correspondingly, the smallest values tended to occur during high streamflows associated with precipitation runoff. Specific conductance and streamflow relations generally were the most consistent at sites in the Tongue River drainage basin, where rho values ranged from –0.601 (site T2) to –0.766 (site T3). The relations were highly variable in the Powder River drainage basin, where rho values ranged from –0.136 (site P1)

Table 7. Spearman correlation coefficients between specific conductance and streamflow and between sodium-adsorption ratios and streamflow for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

[<, less than]

Site number (fig. 1)	Specific conductance and streamflow		Sodium-adsorption ratio and streamflow	
	Rho value	*p*-value	Rho value	*p*-value
T1	–0.664	<0.001	–0.642	<0.001
T2	–.601	<.001	–.672	<.001
T3	–.766	<.001	–.699	<.001
T4	–.683	<.001	–.788	<.001
P1	–.136	.341	–.394	.006
P2	–.849	<.001	–.744	<.001
P3	–.800	<.001	–.685	<.001
P4	–.863	<.001	–.836	<.001
P5	–.791	<.001	–.563	<.001
P6	–.249	.332	–.732	.005
P7	–.620	<.001	–.665	<.001
P8	–.850	<.001	–.871	<.001
P9	–.477	<.001	–.112	.304
P10	–.390	.002	–.172	.179
C1	–.399	.014	–.056	.729
C2	–.326	.190	–.303	.224
C3	–.936	<.001	–.834	<.001
B1	–.613	<.001	–.855	<.001
B2	–.414	.004	–.031	.830
B3	–.571	<.001	–.728	<.001
B4	–.639	<.001	–.650	<.001
B5	–.777	<.001	.416	.004

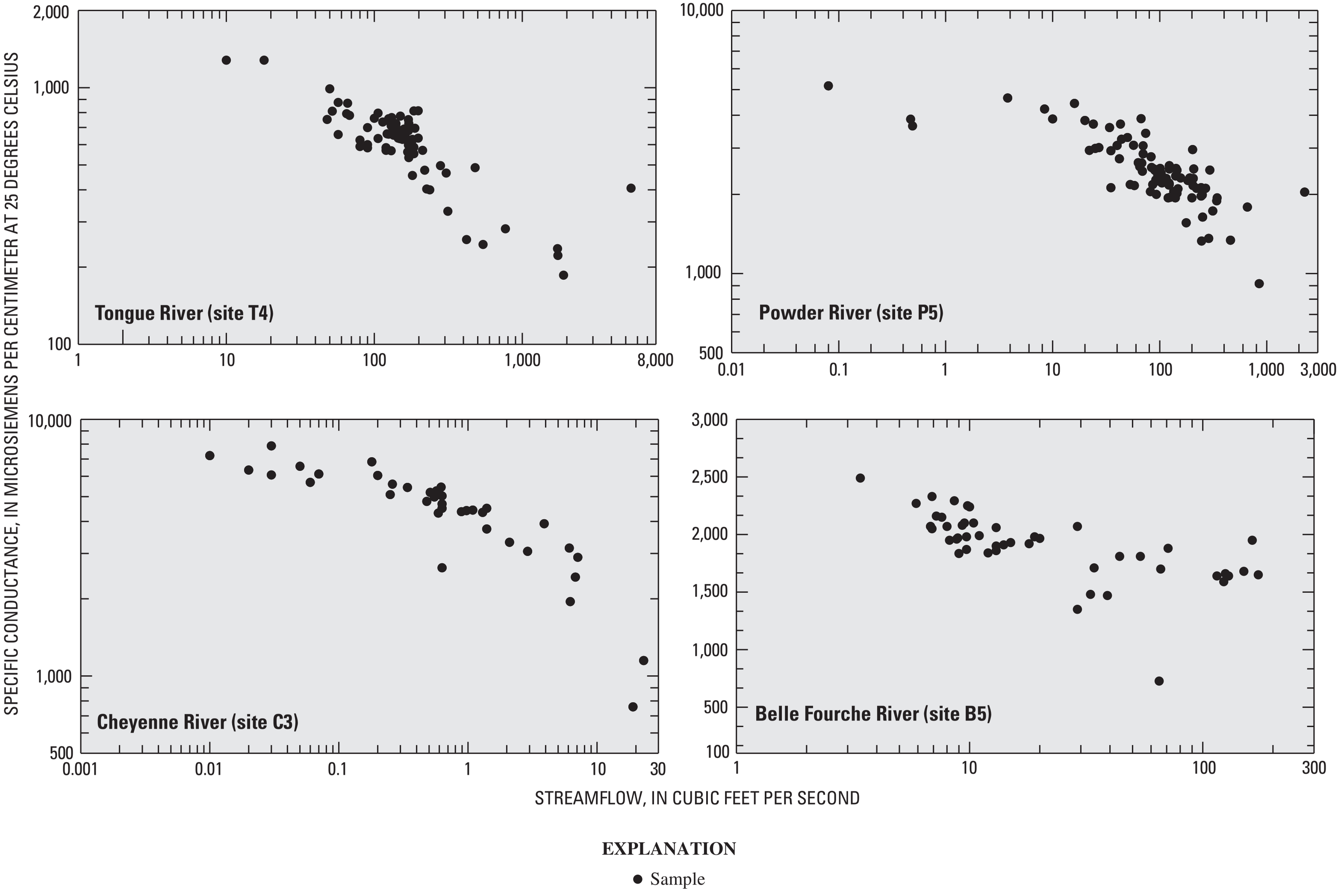


Figure 8. Specific conductance and streamflow relations for selected main-stem sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

to –0.863 (site P4), and in the Cheyenne River drainage basin, where rho values ranged from –0.326 (site C2) to –0.936 (site C3). Rho values in the Belle Fourche drainage basin were intermediate when compared to those of the other drainage basins (table 7). The relation between specific conductance and streamflow is stronger at site B5 on the Belle Fourche River (–0.777) than might be expected because reservoirs can weaken flow-dilution relations. Specific conductance and streamflow relations generally were strong for the main-stem sites in each of the drainage basins (fig. 8). The relation at site P9 on the Powder River was weaker than that at the upstream sites (P2, P3, and P5). This probably is the result of variable contributing areas at the downstream site, including the Clear Creek drainage basin, which has different geology, streamflow characteristics, and stream chemistry compared to tributaries entirely within the plains.

Land-use activities may weaken specific conductance and streamflow relations at some tributary sites by causing greater scatter through modifications to streamflow quantity or inputs of constituents. Specific conductance and streamflow were poorly correlated at site P1 on Salt Creek, site P6 on Wild Horse Creek, and site C2 on Black Thunder Creek. Ground-water discharges associated with conventional oil and gas production probably cause the poor relation at site P1 on Salt Creek. Discharge of CBNG-produced waters into Wild Horse Creek likely is the cause of the poor relation at site P6. Possible explanations for the poor relation at site C2, as well as the relatively weak relations at site P10 on the Little Powder River, site C1 on Antelope Creek, and site B2 on Caballo Creek, include the effect of coal-mine discharges or waters draining through mining overburden in the basins as well as CBNG-produced waters. In addition, evaporative accumulation of surface salts in watersheds of the plains can be flushed to streams during the initial phases of rainfall events. Such short-lived pulses of increased specific conductance during periods of increasing flow, followed by decreases in specific conductance as the supply of surface salts is depleted, can complicate the overall constituent-streamflow relation and result in a wider scatter of data for a given flow.

SAR and streamflow were negatively correlated at 21 of the 22 sites (table 7). Similar to specific conductance, the largest SAR values tended to occur during low-flow conditions, when ground water composes a large part of the streamflow. The relations between SAR and streamflow generally were the most consistent at sites in the Tongue River drainage basin, where rho values ranged from –0.642 (site T1) to –0.788 (site T4). The relations were highly variable in the Powder River (–0.112 to –0.871), Cheyenne River (–0.056 to –0.834), and Belle Fourche River (–0.855 to 0.416) drainage basins. The strongest relation for the main-stem sites (–0.834) was at site C3 on the Cheyenne River (fig. 9). The positive relation between SAR and streamflow at site B5 on the Belle Fourche River (0.416) is not typical and likely is affected by the upstream reservoir. The relation between SAR and streamflow was poor (–0.112) at site P9 on the Powder River. In general, SAR and streamflow relations weakened in the downstream direction on the Powder River. Similar to specific conductance, the variable major-ion chemistry of water from the diverse contributing areas of the Powder River drainage basin, including Crazy Woman Creek and Clear Creek, probably cause the scatter in the data. SAR and streamflow were poorly correlated at the tributary sites on the Little Powder River (site P10), Antelope Creek (site C1), Black Thunder Creek (site C2), and Caballo Creek (site B2). The drainage basins for those streams have some common characteristics, including coal mines that may have surface discharges and ground waters that have flowed through mining overburden, in addition to CBNG development.

Overall, negative relations between specific conductance and streamflow, as well as between SAR and streamflow, tended to be most consistent at main-stem sites and in tributaries that have headwaters in mountainous areas. Tributaries that have headwaters in the plains tended to have weaker relations. Streamflows during water years 2001–05 were less than average as a result of drought conditions in the study area (table 5). Because streamflow had negative relations with specific conductance and SAR, some constituent concentrations may have been more concentrated during persistent low-flow conditions of the study period than might be observed during average streamflow conditions.

Seasonal Variability

Seasonal variability of specific conductance and SAR was examined by segregating data for sampling events during water years 2001–05 into four periods, generally corresponding with the quarterly seasons—October through December (fall), January through March (winter), April through June (spring), and July through September (summer). A Kruskal-Wallis test was used to determine if seasonal differences occurred at the sampling sites.

Specific-conductance data were tested for seasonal differences at 21 of the 22 sampling sites (table 8). The small number of samples for site P6 was insufficient to meet the seasonal test requirements. Seasonal variability in specific conductance was statistically significant (*p*-values less than 0.10) at 13 of the 21 sites for which data were tested. Tests for all five of the sites on tributaries that have headwaters in mountainous areas (sites T1, T2, P4, P7, and P8) were significant. Seasonal variability in specific conductance was not statistically significant (*p*-values greater than 0.10) at 8 of the 21 sites for which data were tested. Of those sites, five (sites T3, P10, C1, C2, and B3) are on tributaries that have headwaters in the plains, and two are on main-stem streams (site C3 on the Cheyenne River and site B1 on the Belle Fourche River) that have headwaters in the plains. Seasonal variability in specific conductance also was not statistically significant at site P9 on the Powder River.

Selected sites within each major drainage basin were grouped by stream type (table 1) to illustrate seasonal variability in specific conductance (fig. 10). The smallest median

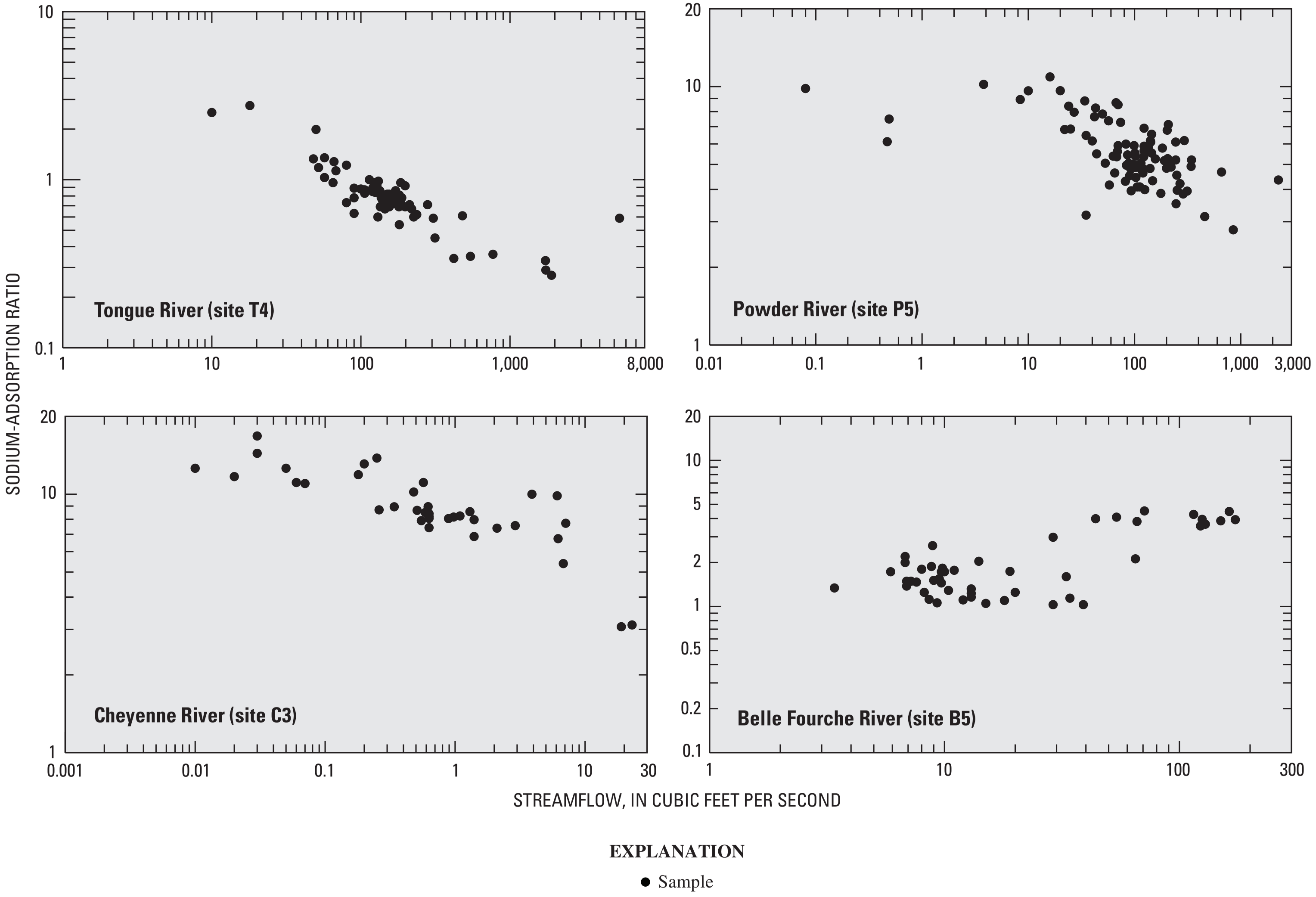


Figure 9. Sodium-adsorption ratio and streamflow relations for selected main-stem sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

Table 8. Results of Kruskal-Wallis test for seasonal variability in specific conductance and sodium-adsorption ratios for sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

[<, less than; --, not determined]

Site number (fig. 1)	Specific conductance		Sodium-adsorption ratio	
	Test statistic	*p*-value	Test statistic	*p*-value
T1	7.29	0.063	6.65	0.084
T2	19.3	<.001	15.3	.002
T3	3.66	.301	12.6	.006
T4	20.2	<.001	15.7	.001
P1	7.01	.072	7.28	.063
P2	38.8	<.001	36.8	<.001
P3	24.7	<.001	23.2	<.001
P4	12.6	.006	11.5	.009
P5	20.5	.001	13.5	.004
P6	--	--	--	--
P7	15.9	.001	17.4	.006
P8	12.2	.007	6.21	.102
P9	2.43	.487	8.75	.033
P10	5.23	.156	2.48	.479
C1	1.34	.719	15.4	.001
C2	5.77	.123	6.30	.098
C3	1.58	.664	1.44	.697
B1	4.62	.202	14.6	.002
B2	8.74	.033	6.10	.107
B3	1.09	.779	9.19	.027
B4	6.65	.084	9.70	.021
B5	13.4	.004	29.6	<.001

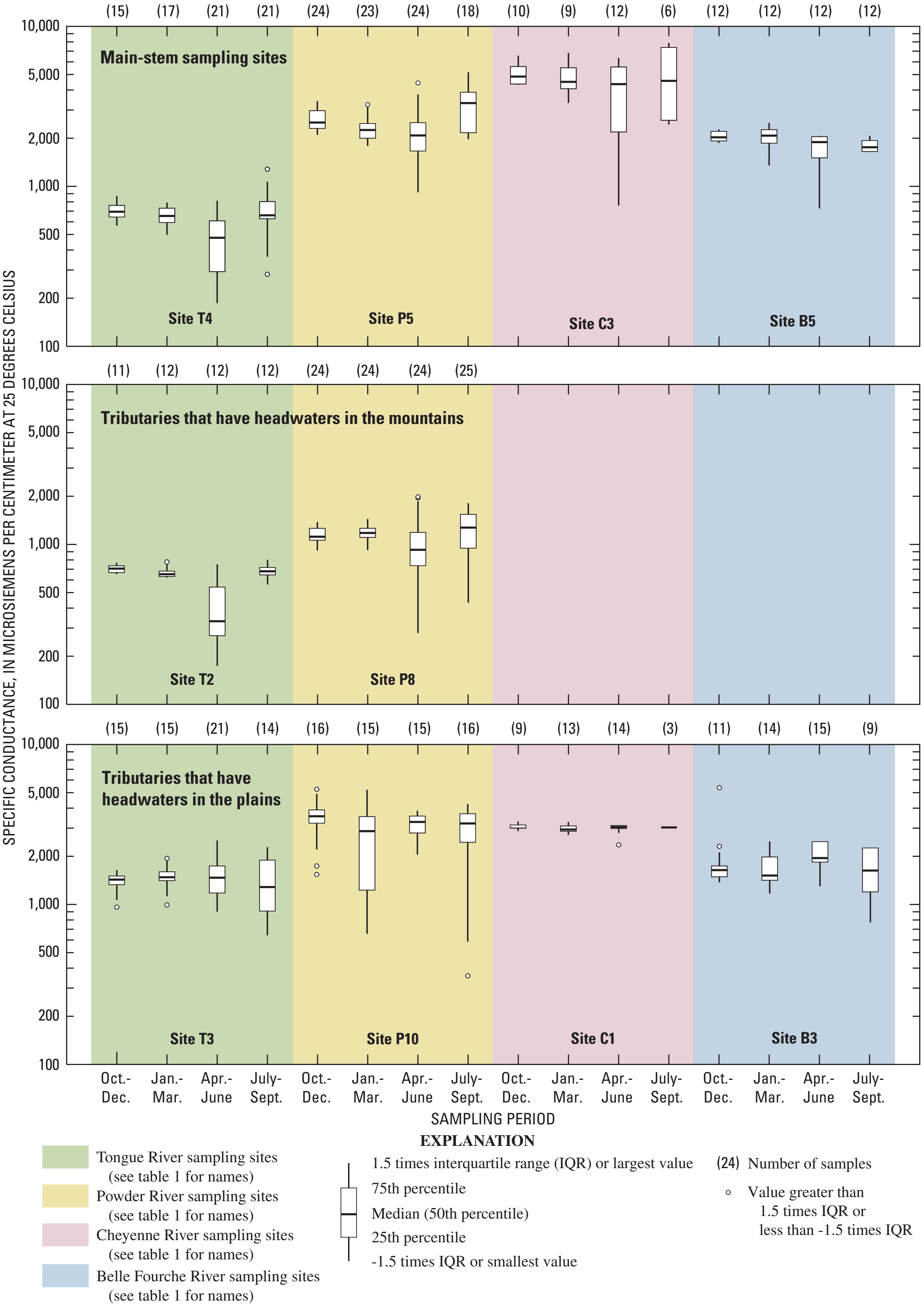


Figure 10. Statistical summary of seasonal specific conductance by stream type for selected sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

specific-conductance values for the main-stem sites on the Tongue River (site T4) and Powder River (site P5) were for April through June. High flow from snowmelt runoff typically occurs during this time period, providing dilution effects on specific conductance. The largest median values for these sites were during October through December at site T4 and during July through September at site P5, when streamflows are low. Although no significant seasonal difference was determined for specific conductance in the Cheyenne River, the smallest median value at site C3 also was for April through June. In contrast, this pattern was not observed at site B5 on the Belle Fourche River, where the smallest median value was for July through September. Median streamflows also were the largest during this period, which is consistent with the negative correlation between specific conductance and streamflow at this site. As for the Tongue River and Powder River, the smallest median specific-conductance values for Goose Creek (site T2) and Clear Creek (site P8), tributaries that have headwaters in the Bighorn Mountains, were for April through June as a result of snowmelt runoff (fig. 10).

A consistent seasonal pattern was not observed for tributaries that have headwaters in the plains. Site T3 on Prairie Dog Creek had the largest median specific-conductance value during January through March and the smallest median value during July through September (fig. 10). In contrast, site B3 on Donkey Creek had the smallest median value during January through March and the largest median value during April through June (fig. 10). The small variability of specific conductance by season at site C1 on Antelope Creek is consistent with ground-water control on water quality at that site. The amount of seasonal variability in specific conductance at all sites may not have been representative of seasonal variability during average conditions because streamflows were less than average during the study period.

SAR data were tested for seasonal differences at 21 of the 22 sites (table 8). The small number of samples for site P6 was insufficient to meet the seasonal test requirements. Seasonal variability in SAR was statistically significant (*p*-values less than 0.10) at 17 of the 21 sites. Three of the sites where no significant seasonal variability was determined for SAR (*p*-values greater than 0.10) were on streams that have headwaters in the plains (site P10 on the Little Powder River, site C3 on the Cheyenne River, and site B2 on Caballo Creek). In addition, no significant seasonal variability was determined for SAR at site P8 on Clear Creek. Site P8 on Clear Creek and site B2 on Caballo Creek were the only sites where significant seasonal variability was determined for specific conductance, but not for SAR. Several sites that did not have significant seasonal variability in specific conductance did have significant seasonal variability in SAR (sites T3, P9, C1, C2, B1, and B3).

Selected sites within each major drainage basin were grouped by stream type (table 1) to illustrate seasonal variability in SAR (fig. 11). The pattern for the main-stem sites varied slightly from the pattern for specific conductance. The smallest median SAR value at site T4 on the Tongue River was for the runoff period of April through June; however, the smallest median SAR values for site P5 on the Powder River and site C3 on the Cheyenne River were for the winter low-flow period of January through March. SAR had a different pattern compared to specific conductance at site B5 on the Belle Fourche River. The median SAR value at site B5 on the Belle Fourche River was substantially larger during July through September compared to that during the other three sampling periods, although the median specific-conductance value was smallest during July through September. Median streamflows also were largest during July through September, which is consistent with the positive correlation between SAR and streamflow at this site. The high streamflows and large SAR values during July through September may be a result of releases of water from the reservoir upstream from site B5.

Goose Creek (site T2) and Clear Creek (site P8), tributaries that have headwaters in the Bighorn Mountains, had the smallest median SAR values during the runoff period of April through June and the largest median SAR values during the low-flow period of July through September. The small range of values from October through March probably reflects the effect of ground water on stream base flow. The relatively large range of values from April through September probably is the result of dilution during snowmelt runoff, irrigation return flows, and low streamflows in summer.

Seasonal variability was significant (*p*-values less than 0.10) for tributaries that have headwaters in the plains (site T3 on Prairie Dog Creek, site C1 on Antelope Creek, and site B3 on Donkey Creek). In contrast to Goose Creek and Clear Creek, site T3 on Prairie Dog Creek had the largest median SAR value during April through June and the smallest median value during July through September (fig. 11). Site B3 on Donkey Creek had the largest median SAR value during July through September and the smallest median value during April through June. The amount of seasonal variability in SAR at all sites may not have been representative of seasonal variability during average conditions because streamflows were less than average during the study period.

Temporal Patterns of Selected Long-Term Water-Quality Data

Concerns have been expressed about whether stream-water quality is changing in the Powder River structural basin as a result of CBNG development. Temporal patterns in selected long-term water-quality data were examined for this report. Specific conductance and SAR data for water years 2001–05 were compared to historical data for water years 1975–81 for selected sampling sites. Trend analysis, a statistical technique, was used for selected data to help evaluate whether changes in water quality have occurred.

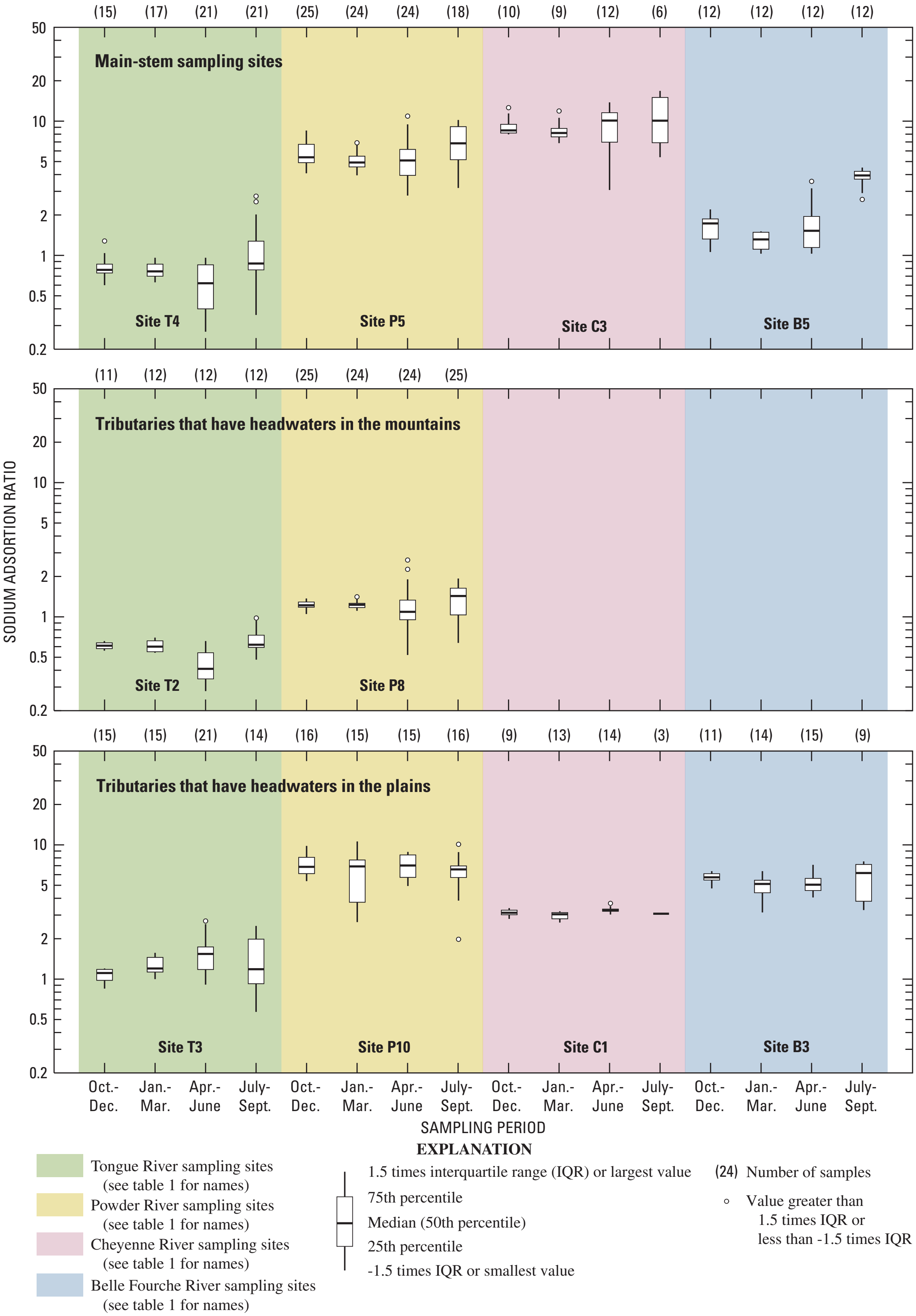


Figure 11. Statistical summary of seasonal sodium-adsorption ratios by stream type for selected sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins, Wyoming and Montana, water years 2001–05.

Comparisons to Historical Data from Water Years 1975–81

Peterson (1988) presented summary statistics for water-quality constituents at 15 of the 22 sampling sites for a period prior to CBNG development (water years 1975–81). Those statistics were used for comparison in this report. Historical data were compared for three sites in the Tongue River drainage basin (sites T1, T2, and T4); seven sites in the Powder River drainage basin (sites P1, P2, P4, P5, P8, P9, and P10); one site in the Cheyenne River drainage basin (site C1); and four sites in the Belle Fourche River drainage basin (sites B1, B2, B3, and B4). Specific-conductance and SAR data were selected for comparison with historical data; however, because those constituents generally are correlated with streamflow at most sites, streamflow data also were evaluated.

Median instantaneous streamflow was substantially less for water years 2001–05 compared to that for water years 1975–81 for sites in the Tongue River (sites T1, T2, and T4), Powder River (sites P1, P2, P4, P5, P8, P9, and P10), and Cheyenne River (site C1) drainage basins. In contrast, median instantaneous streamflow was higher for water years 2001–05 compared to that for water years 1975–81 for sites in the Belle Fourche River drainage basin (sites B1, B2, B3, and B4).

Median specific-conductance values for water years 2001–05 for site T1 on Little Goose Creek, site T2 on Goose Creek, and site T4 on the Tongue River were smaller (by about 100 µS/cm at 25°C) than median values presented by Peterson (1988) although streamflows were less for water years 2001–05 than that for water years 1975–81. The median specific-conductance value at site P1 on Salt Creek for water years 2001–05 was substantially less (by about 750 µS/cm at 25°C) than for water years 1975–81. Median specific-conductance values at sites P2, P5, and P9 on the Powder River also were less for water years 2001–05 than for water years 1975–81. For Salt Creek and Powder River sites, the decrease is likely a result of subsurface injection of some of the saline discharge waters in the Salt Creek drainage basin that began in 1990 (Lindner-Lunsford and others, 1992). Median specific-conductance values for water years 2001–05 were similar to median values presented by Peterson (1988) for site P4 on Crazy Woman Creek and site P8 on Clear Creek. The median specific-conductance value at site P10 on the Little Powder River (3,290 µS/cm at 25°C) for water years 2001–05 was slightly larger than the median value (3,000 µS/cm at 25°C) presented by Peterson (1988), possibly as a result of the lower streamflow for water years 2001–05 than for water years 1975–81. The largest increase in the median values (from 2,240 µS/cm at 25°C for water years 1975–81 to 3,030 µS/cm at 25°C for water years 2001–05) occurred at site C1 on Antelope Creek; site C1 also had a substantially lower median streamflow for water years 2001–05 than for water years 1975–81. In contrast, median values for water years 2001–05 were substantially smaller (by about 800 µS/cm at 25°C or more) at site B1 on the Belle Fourche River, site B2 on Caballo Creek, and site B3 on Donkey Creek in the Belle Fourche River drainage basin than those presented by Peterson (1988); however, the median value for the Belle Fourche River at site B4 was larger for water years 2001–05 than for water years 1975–81. Changes in specific-conductance values that may have resulted from CBNG development from water years 1975–81 to water years 2001–05 are difficult to determine because of the differences in streamflows and other land-use activities between the two time periods.

Median SAR values determined by Peterson (1988) for two sites (sites T2 and T4) in the Tongue River drainage basin for water years 1975–81 were about the same as those for water years 2001–05. The median SAR value of 19 at site P1 on Salt Creek for water years 2001–05 was substantially less than the median value of 32.5 for water years 1975–81. Correspondingly, median SAR values for sites on the Powder River (sites P2, P3, P5, and P9) for water years 2001–05 were less than median values determined by Peterson (1988) for water years 1975–81. Any potential change in SAR values in the Powder River as a result of CBNG development is difficult to determine because of the effect of Salt Creek. The median SAR value for site P10 on the Little Powder River was 5.6 for water years 1975–81 compared to 6.8 for water years 2001–05. The median SAR value of 3.1 for site C1 on Antelope Creek for water years 2001–05 was slightly larger than the median value of 2.7 for water years 1975–81. In the Belle Fourche River drainage basin, median SAR values were smaller at sites B3 and B4 and larger at sites B1 and B2 for water years 2001–05 compared to than those determined by Peterson (1988) for water years 1975–81. The median SAR value at site B2 on Caballo Creek increased from 2.4 for water years 1975–81 to 5.3 for water years 2001–05. Similar to specific conductance, changes in SAR values that may have resulted from CBNG development from water years 1975–81 to water years 2001–05 are difficult to determine because of differences in streamflows and other land-use activities between the two time periods.

Trend Analysis for Water Years 1991–2005

Trend software, ESTREND, which uses the seasonal Kendall trend test, was applied to data collected at the 22 sampling sites. However, because too few data were collected at the sites during water years 2001–05 to meet seasonal requirements in the ESTREND software, longer time periods of available water-quality data for consecutive years were examined for the trend analysis. During 1990, disposal of some of the saline ground waters associated with conventional oil and gas production in the Salt Creek drainage basin that substantially affected water quality downstream on the Powder River was modified to include subsurface injections (Lindner-Lunsford and others, 1992). As a result of this time-specific change to the water quality in the Powder River drainage basin, water years 1991–2005 were selected as the trend-analysis period to exclude the pre-1991 characteristics of the water quality of Salt Creek that are unrelated to CBNG development. The trend-analysis period selected for the Tongue River was water years 1991–2005 to be consistent with the trend-analysis period for the Powder River. Many of the 22 sites either did not have available data for water years 1991–2000, or data collection was interrupted for specific conductance or sodium-adsorption ratios, making the sites ineligible for the trend analysis.

The seasonal Kendall test was applied to specific-conductance values for 8 of the 22 sites: sites T2 and T4 in the Tongue River drainage basin; sites P1, P2, P5, P9, and P10 in the Powder River drainage basin; and site B4 in the Belle Fourche River drainage basin. Results of the seasonal Kendall test for unadjusted values (table 9, fig. 12) indicated a significant upward trend (*p*-values less than 0.10) in specific conductance at site T2 on Goose Creek, site T4 on the Tongue River, and sites P2 and P5 on the Powder River. Increases in specific conductance appear to have started around 2000 at sites T2, P2, and P5 (fig. 13) compared to site T4, which shows a steady increase through about 2001 and then a slight decrease through 2005. Because specific conductance and streamflow are negatively correlated at these sites (table 7), decreased streamflow as a result of drought during the latter part of the trend period generally could have resulted in an increase in specific conductance. Also, greater sampling frequency since about 2001 may have affected trends if the hydrologic conditions differed during the seasonal periods. No significant trends in unadjusted specific-conductance values were determined (*p*-values greater than 0.10) for site P1 on Salt Creek, site P9 on the Powder River, site P10 on the Little Powder River, and site B4 on the Belle Fourche River.

Results of the seasonal Kendall test for flow-adjusted values (table 9, fig. 12), which have been adjusted for streamflow variability, indicated no significant trend (*p*-values greater than 0.10) in specific conductance for any of the eight sites during water years 1991–2005. This indicates the decrease in streamflow probably was the cause of the upward trends in the unadjusted specific-conductance values for water years 1991–2005 at site T2 on Goose Creek, and site T4 on the Tongue River, and sites P2 and P5 on the Powder River.

Cary (1991) presented trend results for dissolved solids, which closely relate to specific conductance, for water years 1975–88 at three of the sites (sites P1, P5 and P9) in the Powder River drainage basin. Results from that study indicated no significant trend (*p*-values greater than 0.10) in flow-adjusted concentrations of dissolved solids at site P1 on Salt Creek and site P9 on the Powder River. A significant upward trend for dissolved solids was reported for site P5 on the Powder River for water years 1975–88; however, the results for the specific conductance trend test for water years 1991–2005 indicate the upward trend did not continue. The upward trend determined by Cary (1991) probably did not continue past 1990 because of the change to subsurface injection of saline waters in the Salt Creek drainage basin (Lindner-Lunsford and others, 1992).

The seasonal Kendall test was applied to SAR data for 4 of the 22 sites. All four sites were in the Powder River drainage basin (sites P1, P2, P5, and P10). Results of the seasonal Kendall test for unadjusted values indicated a significant upward trend (*p*-values less than 0.10) in SAR at site P1 on Salt Creek and at sites P2 and P5 on the Powder River for water years 1991–2005 (table 9, fig. 12). Increases in SAR appear to have started around 2000 at sites P2 and P5 (fig. 14), whereas SAR at site P1 shows a gradual increase throughout the trend period. No significant trend was determined for unadjusted SAR values at site P10 on the Little Powder River.

Results of the seasonal Kendall test for flow-adjusted values indicated a significant upward trend (*p*-values less than 0.10) in SAR values occurred at sites P1, P2, and P5 for water years 1991–2005 (table 9, fig. 12). This indicates the cause of the unadjusted trends was not necessarily streamflow variability during water years 1991–2005. The upward trends in flow-adjusted SAR values at sites P2 and P5 on the Powder River likely were caused in part by an increase in SAR in Salt Creek (site P1). The Salt Creek drainage basin is upstream from CBNG development but does have conventional oil and gas production that affects the water quality of the Powder River, although presumably to a lesser extent than before the implementation of subsurface injection in 1990. In addition, downstream sites on the Powder River receive CBNG-produced waters in the reach between Sussex, Wyo. (site P2), and Arvada, Wyo. (site P5). The Little Powder River (site 10), which also receives CBNG-produced waters, had a significant downward trend (*p*-value of 0.019) in flow-adjusted SAR values for water years 1991–2005 (table 9, fig. 12). The cause of the downward trend at site 10 was not determined because a greater sampling frequency since about 1999 may have affected the trend if hydrologic conditions differed during the seasonal periods and changes in discharge practices of the coal mines may have occurred in addition to CBNG development.

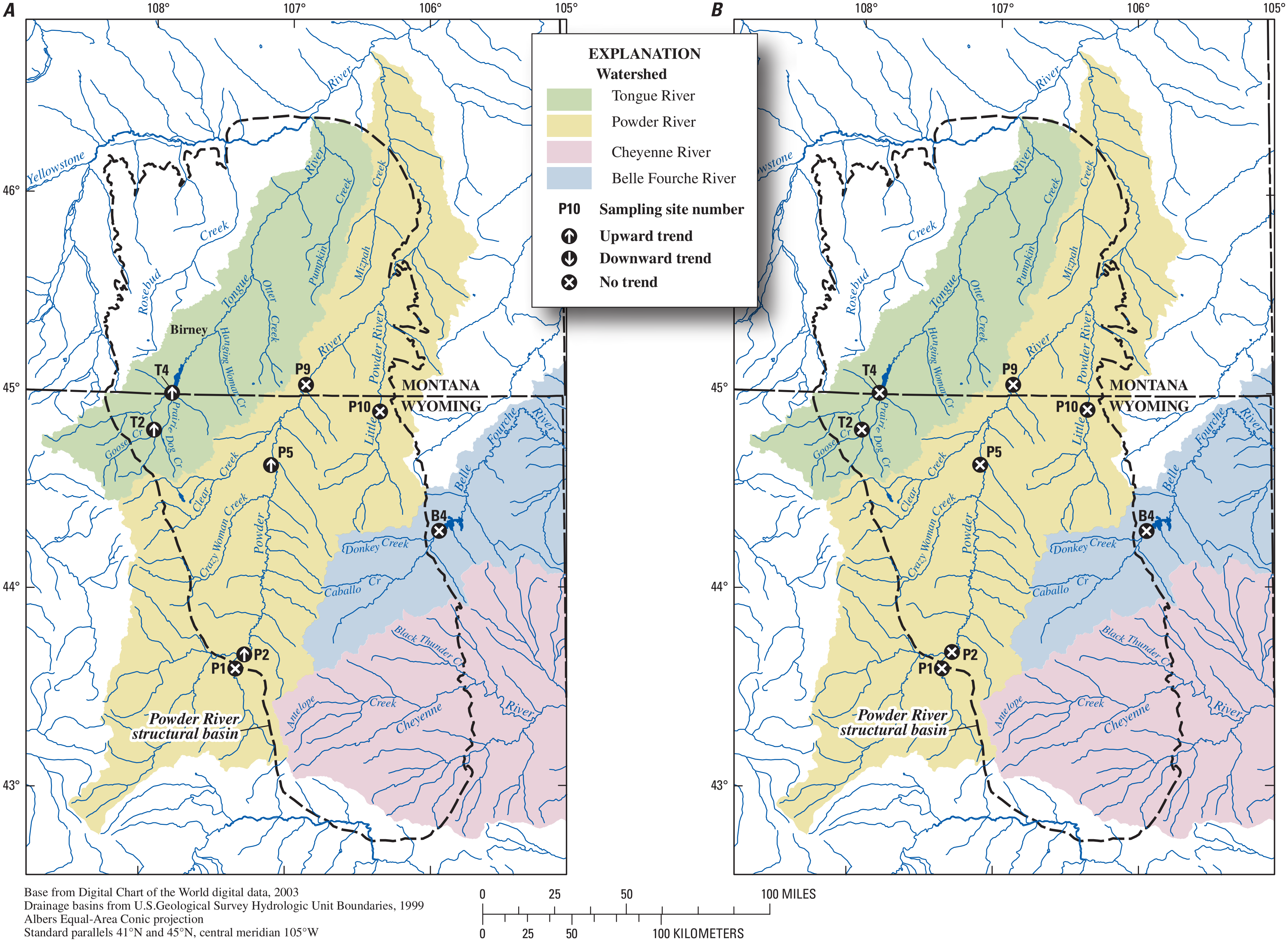
Cary (1991) presented flow-adjusted trend results for water years 1975–88 for adjusted SAR values (SAR values that are computed using adjusted calcium concentrations to account for effects of dissolution and precipitation) for two of the sites (sites P1 and P5). Cary (1991) reported significant upward trends (*p*-values less than 0.10) in adjusted SAR values at site P1 on Salt Creek and site P5 on the Powder River for water years 1975–88. Although flow-adjusted trend results for adjusted SAR values from Cary's (1991) study and SAR values from this study cannot be compared directly, the results may indicate the upward trend in SAR values for water years 1991–2005 is part of a long-term upward trend. The quantity of saline discharges in the Salt Creek drainage basin has been reduced by subsurface injection; however, the composition of discharged waters may have changed.

To further assess the flow-adjusted trend results for the SAR values for water years 1991–2005, trend tests were conducted for flow-adjusted dissolved-calcium, dissolved-magnesium, and dissolved-sodium concentrations at four sites in the Powder River drainage basin (sites P1, P2, P5, and P10;

Table 9. Trend results for specific conductance and sodium-adsorption ratios for selected sampling sites in the Tongue, Powder, and Belle Fourche River drainage basins, Wyoming and Montana, water years 1991–2005.

[--, not determined]

Site number (fig. 1)	Number of samples	Type of values used in trend test	Test statistic	*p*-value	Change per year in unadjusted concentrations, in unit of measure	Trend direction
Specific conductance						
T2	60	Unadjusted	0.340	0.007	9.7	Upward
T4	55	Unadjusted	.263	.018	9.3	Upward
P1	55	Unadjusted	.045	.756	--	No trend
P2	60	Unadjusted	.205	.096	30	Upward
P5	59	Unadjusted	.236	.037	27	Upward
P9	56	Unadjusted	.151	.249	--	No trend
P10	58	Unadjusted	.066	.579	--	No trend
B4	56	Unadjusted	.093	.429	--	No trend
T2	60	Flow-adjusted	.029	.779	--	No trend
T4	55	Flow-adjusted	–.141	.236	--	No trend
P1	55	Flow-adjusted	.025	.850	--	No trend
P2	60	Flow-adjusted	.119	.339	--	No trend
P5	59	Flow-adjusted	.069	.438	--	No trend
P9	56	Flow-adjusted	.060	.652	--	No trend
P10	58	Flow-adjusted	–.143	.233	--	No trend
B4	56	Flow-adjusted	.088	.533	--	No trend
Sodium-adsorption ratio						
P1	55	Unadjusted	0.459	0.003	0.53	Upward
P2	60	Unadjusted	.319	.030	.12	Upward
P5	59	Unadjusted	.330	.015	.13	Upward
P10	58	Unadjusted	–.015	.914	--	No trend
P1	55	Flow-adjusted	.382	.009	--	Upward
P2	60	Flow-adjusted	.252	.060	--	Upward
P5	59	Flow-adjusted	.271	.005	--	Upward
P10	58	Flow-adjusted	–.291	.019	--	Downward



Base from Digital Chart of the World digital data, 2003
Drainage basins from U.S.Geological Survey Hydrologic Unit Boundaries, 1999
Albers Equal-Area Conic projection
Standard parallels 41°N and 45°N, central meridian 105°W

Figure 12. Trend results for *A*, unadjusted specific conductance; *B*, flow-adjusted specific conductance; *C*, unadjusted sodium-adsorption ratios; and *D*, flow-adjusted sodium-adsorption ratios for selected sampling sites in the Tongue, Powder, and Belle Fourche River drainage basins, Wyoming and Montana, water years 1991–2005.

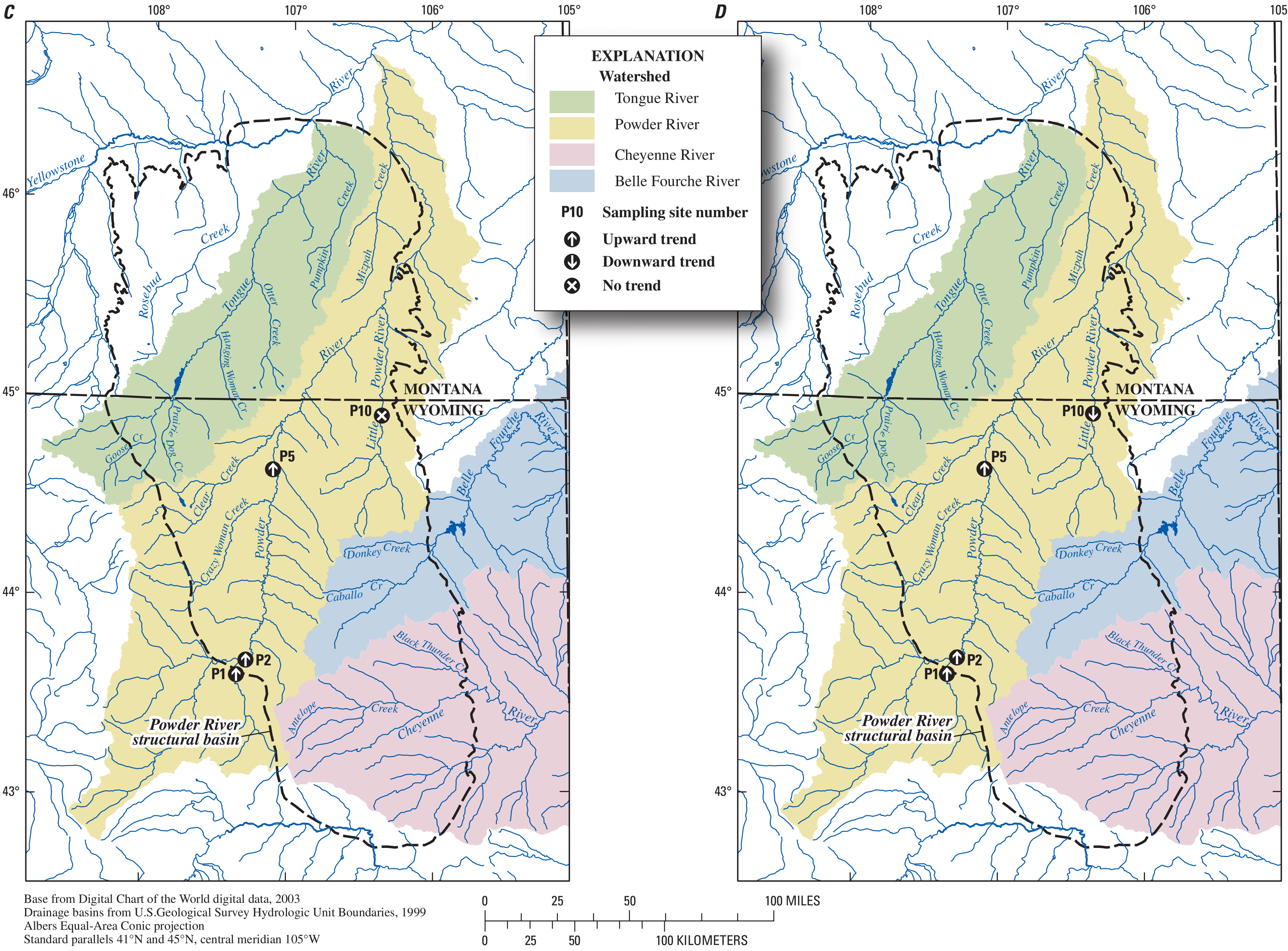


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Figure 12. Trend results for *A*, unadjusted specific conductance; *B*, flow-adjusted specific conductance; *C*, unadjusted sodium-adsorption ratios; and *D*, flow-adjusted sodium-adsorption ratios for selected sampling sites in the Tongue, Powder, and Belle Fourche River drainage basins, Wyoming and Montana, water years 1991–2005.—Continued

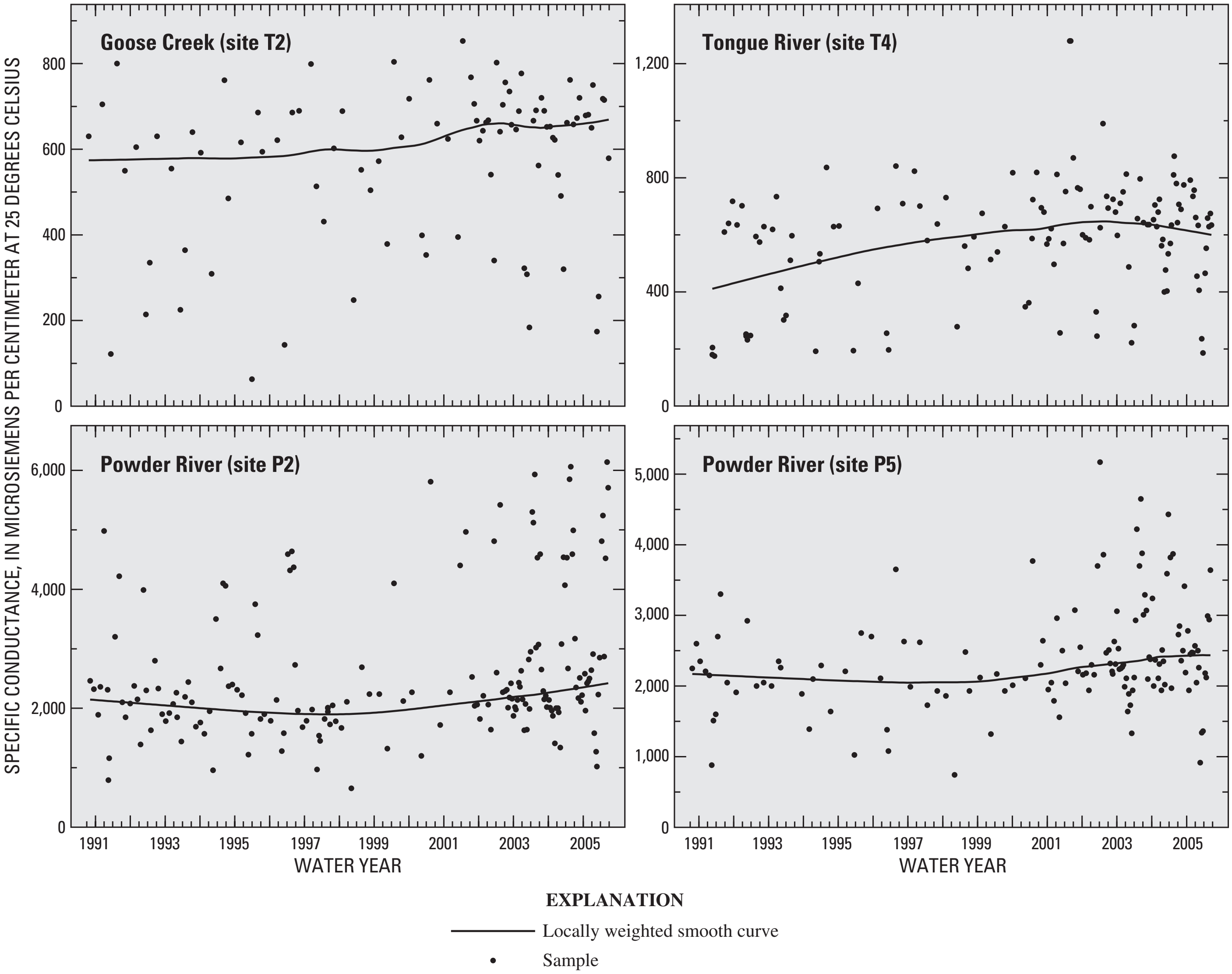

Figure 13. Time-series distribution of specific conductance for selected sampling sites in the Tongue and Powder River drainage basins, Wyoming and Montana, water years 1991–2005.

table 10). A significant relation did not exist between dissolved calcium and streamflow or between dissolved magnesium and streamflow at site P1 on Salt Creek; thus, the flow-adjusted trend test was not conducted for these constituents at this site. No significant trend was determined for flow-adjusted dissolved-sodium concentrations at site P1 for water years 1991–2005. Trend results did not show a consistent spatial pattern for sites P2 and P5 on the Powder River (table 10). No significant trends were determined for flow-adjusted dissolved-calcium, dissolved-magnesium, and dissolved-sodium concentrations at site P2. At site P5, downward trends in flow-adjusted dissolved-calcium and dissolved-magnesium concentrations were significant (*p*-values less than 0.10) and an upward trend in flow-adjusted dissolved-sodium concentrations was significant for water years 1991–2005. These flow-adjusted trends for the individual constituents are consistent with the upward trend in flow-adjusted SAR values during the same period because sodium is directly related to SAR, and calcium and magnesium are inversely related. The divergent trends in the flow-adjusted constituents that compose SAR at site P5 indicate a change in chemical composition that is apparently unrelated to streamflow variability during water years 1991–2005. No significant trends were determined (*p*-values greater than 0.10) for flow-adjusted dissolved-calcium, dissolved-magnesium, and dissolved-sodium concentrations at site P10 on the Little Powder River.

Trends in flow-adjusted SAR values and dissolved-calcium, dissolved-magnesium, and dissolved-sodium concentrations were not determined to be from CBNG development. Other land-use activities in the basins, such as traditional oil and gas development, irrigation and mining, also can affect streamflow and dissolved-constituent concentrations.

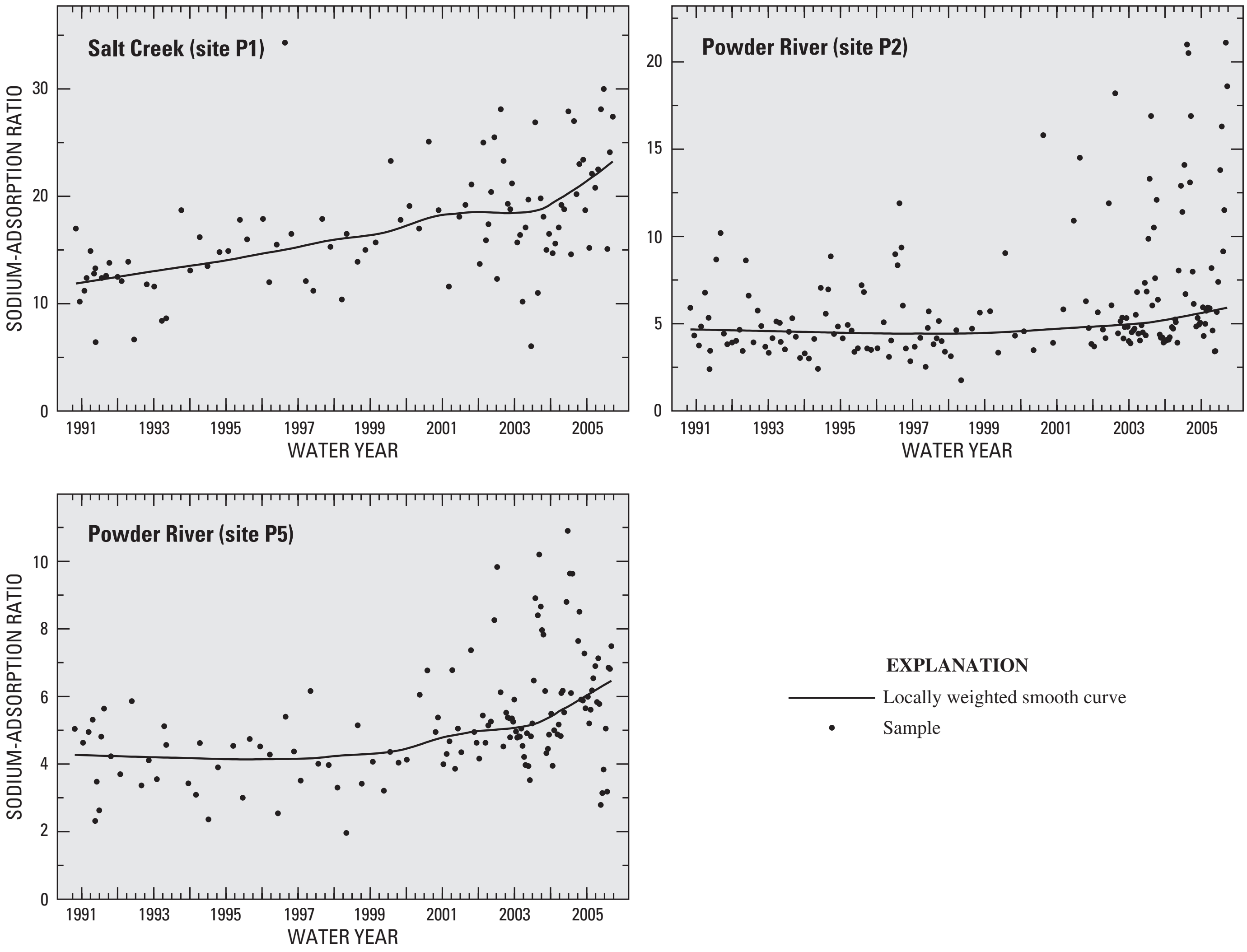

Figure 14. Time-series distribution of sodium-adsorption ratios for selected sampling sites in the Powder River drainage basin, Wyoming, water years 1991–2005.

The trends determined were monotonic for the entire trend period, and changes in flow-adjusted concentrations could have occurred at any time during water years 1991–2005; the changes were not determined to have occurred after the start of CBNG development. Also, trends may be an artifact of sampling frequency and conditions. Non-uniform sampling frequency through time could have resulted in different coverage of hydrologic conditions for the seasonal periods. The flow-adjustment procedure may not have completely removed all variability associated with streamflow; therefore, drought in the study area during the latter part of the trend period is a complicating factor that affects not only surface runoff but also ground-water/surface-water interactions.

The trend information presented in this report provides an initial assessment of long-term and basin-wide temporal patterns. Ongoing (2007) data-collection activities will enhance data sets for future trend testing. The period of record required for trend testing decreases with increased sampling frequency; therefore, current monthly sampling at many sites will allow trend-test eligibility sooner than what would be allowed by quarterly sampling. Also, more robust flow-adjusting statistical techniques are available for removing more of the variability associated with streamflow; however, the techniques require larger data sets than those available for this study. Spatial patterns are more likely to emerge with increased site density, potentially increasing the ability to determine cause and effect relations in trends.

Table 10. Trend results for flow-adjusted dissolved-calcium, dissolved-magnesium, and dissolved-sodium concentrations for selected sampling sites in the Powder River drainage basin, Wyoming, water years 1991–2005.

[--, not determined]

Site number (fig. 1)	Number of samples	Test statistic	*p*-value	Trend direction
		Calcium, dissolved		
P1	55	([1])	([1])	--
P2	60	–0.136	0.242	No trend
P5	59	–.305	.005	Downward
P10	58	.031	.767	No trend
		Magnesium, dissolved		
P1	55	([1])	([1])	--
P2	60	–0.052	0.695	No trend
P5	59	–.291	.011	Downward
P10	58	–.051	.632	No trend
		Sodium, dissolved		
P1	55	0.184	0.202	No trend
P2	60	.200	.141	No trend
P5	59	.177	.030	Upward
P10	58	–.184	.137	No trend

[1] Regression relation between constituent and streamflow was not significant. Flow-adjusted trend was not computed.

Summary

Water-quality sampling was conducted regularly at stream sites within or near the Powder River structural basin in northeastern Wyoming and southeastern Montana during water years 2001–05 (October 1, 2000, to September 30, 2005) to characterize water quality in an area of coalbed natural gas development. The U.S. Geological Survey, in cooperation with the Wyoming Department of Environmental Quality, characterized the water quality at 22 sampling sites in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins. Data for general hydrology, field measurements, major-ion chemistry, and selected trace elements were summarized, and specific conductance and sodium-adsorption ratios were evaluated for relations with streamflow and seasonal variability. Trend analysis for water years 1991–2005 was conducted for selected sites and constituents to assess changes through time.

Average annual runoff was highly variable among the stream sites. Generally, streams that have headwaters in the Bighorn Mountains had more runoff as a result of higher average annual precipitation than streams that have headwaters in the plains. The Powder River at Moorhead, Mont., had the largest average annual runoff (319,000 acre-feet) of all sampling sites; however, streams in the Tongue River drainage basin had the highest runoff per unit area of the four major drainage basins. Average annual runoff at main-stem sites on the Tongue River, Powder River, and Belle Fourche River, which have some of the longest periods of record for streamflow, was less than average during water years 2001–05 because of drought conditions. Consequently, water-quality samples collected during the study period may not represent long-term water-quality conditions for all sites. Several of the streams that have headwaters in the plains had no streamflow during some site visits, making water-quality sampling impossible during these visits.

Water-quality characteristics were highly variable because of streamflow variability, geologic controls, and potential land-use effects. The range of median specific-conductance values among sites was smallest in the Tongue River drainage basin. Median values in that basin ranged from 643 microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C) on the Tongue River to 1,460 μS/cm at 25°C on Prairie Dog Creek. The Tongue River drainage basin has the largest percentage of area underlain by Mesozoic-age and older rocks and by more resistant rocks. In addition, the higher annual precipitation and a steeper gradient in this basin compared to basins in the plains produce relatively fast

stream velocities, which result in a short contact time between stream waters and basin materials. The Powder River drainage basin, which has the largest drainage area and most diverse site conditions, had the largest range of median specific-conductance values among the four major drainage basins. Median values in that basin ranged from 680 µS/cm at 25°C on Clear Creek to 5,950 µS/cm at 25°C on Salt Creek. Median specific-conductance values among sites in the Cheyenne River drainage basin ranged from 1,850 µS/cm at 25°C on Black Thunder Creek to 4,680 µS/cm at 25°C on the Cheyenne River. The entire Cheyenne River drainage basin is in the plains, which have low precipitation, soluble geologic materials, and relatively low gradients that produce slow stream velocities and long contact times. Median specific-conductance values among sites in the Belle Fourche River drainage basin ranged from 1,740 µS/cm at 25°C on Caballo Creek to 2,800 µS/cm at 25°C on Donkey Creek.

Water in the study area ranged from a magnesium-calcium-bicarbonate type for some sites in the Tongue River drainage basin to a sodium-sulfate type at many sites in the Powder, Cheyenne, and Belle Fourche River drainage basins. Water in the Powder River changed from a sodium-sulfate type at the upstream sites to a sodium-calcium-magnesium-sulfate type at Moorhead, Mont. The main source of the change is the addition of waters from Clear Creek, which has a diluting effect on the Powder River. Water in the Belle Fourche River changed from a sodium-sulfate type at the upstream site to a calcium-sulfate type at the downstream site near Hulett, Wyo., probably reflecting changes in geology and effects from a reservoir in the lower basin.

Based on sampling results for the 22 sampling sites, the Tongue River and its tributary streams generally had the smallest major-ion concentrations, sodium-adsorption ratios, and dissolved-solids concentrations of the four major drainage basins assessed as part of this study. Major-ion concentrations, sodium-adsorption ratios, and dissolved-solids concentrations in the Powder, Cheyenne, and Belle Fourche River drainage basins generally were larger and much more variable than concentrations in the Tongue River drainage basin. Little Goose Creek, Goose Creek, and Tongue River in the Tongue River drainage basin and Clear Creek in the Powder River drainage basin consistently had the smallest or near smallest medians for most major-ion constituents, sodium-adsorption ratios, and dissolved solids. These sites share the common characteristic of having their headwaters in the Bighorn Mountains.

Streams that have headwaters in the plains, such as Wild Horse Creek, the Little Powder River, and the Cheyenne River, tended to have large dissolved-sodium concentrations, sodium-adsorption ratios, dissolved-sulfate concentrations, and dissolved-solids concentrations. Salt Creek and Antelope Creek also had large constituent concentrations; however, the water quality of those streams may not be typical of a plains stream. Salt Creek, which had the largest dissolved-sodium concentrations and sodium-adsorption ratios of all sites, receives discharges of saline ground waters from conventional oil and gas production that affect its water quality. Large dissolved-chloride concentrations frequently occurred in samples collected from Salt Creek. These concentrations often were larger than the State of Wyoming water-quality criteria for chloride. Relatively small concentration ranges for constituents in samples from Antelope Creek indicate ground water predominates the water quality in that stream. The water-quality characteristics of Caballo Creek in the Belle Fourche River drainage basin, also a plains tributary, may be affected by coalbed-natural-gas-produced waters although other land-use changes also may have occurred.

Generally, dissolved constituents in streams tend to become more concentrated as waters flow downstream and across the plains. Typical changes that occur in dissolved solids as a stream flows from the mountains to the plains were observed in samples from sites on Clear Creek. An increase in the medians was observed from upstream to downstream for all major-ion constituents (except chloride and silica), sodium-adsorption ratios, and dissolved solids. In contrast, median dissolved-solids concentrations in samples collected from the Powder River are larger at upstream sites than at the downstream site at Moorhead, Mont. In this case, diluting flows from Clear Creek decrease constituent concentrations on the Powder River. Likewise, medians for several major-ion constituents, sodium-adsorption ratios, and dissolved solids for samples collected from the Belle Fourche River also show a pattern of larger concentrations at the upstream sites compared to the downstream site at Hulett, Wyo. The Belle Fourche River headwaters are in the plains, and diluting inflows from areas underlain by the more resistant rocks of the Black Hills in the lower basin and reservoir effects may be the reasons for the smaller concentrations.

Total-aluminum, dissolved-arsenic, total-barium, total-beryllium, dissolved-iron, dissolved-manganese, and total-selenium concentrations were variable across the drainage basins. Median total-aluminum concentrations were greater than 100 micrograms per liter at most sites, primarily as a function of suspended-sediment concentrations. In contrast, concentrations of other constituents, such as total beryllium, generally were small; median concentrations for beryllium were less than 0.1 microgram per liter at many sites. Total aluminum and dissolved manganese were the trace elements that most frequently occurred in concentrations larger than established water-quality criteria for Wyoming. More than 75 percent of the samples collected from sites on the Powder River in Wyoming had total-aluminum concentrations greater than aquatic-life criteria. Dissolved-manganese concentrations were greater than the human-health criterion in at least one sample from all streams where the criterion applies—Little Goose Creek, Goose Creek, Prairie Dog Creek, Powder River, Crazy Woman Creek, Clear Creek, Little Powder River, Cheyenne River, and Belle Fourche River—although most of the waters are not used as drinking-water supplies.

An analysis of specific conductance and sodium-adsorption ratios indicated both constituents generally had inverse relations with streamflow; thus, the largest concentrations tended to occur during low flows when ground water composes a large part of the streamflow. Land-use activities may have weakened the constituent and streamflow relations at some sites. Seasonal variability in specific conductance and sodium-adsorption ratios generally were significant (*p*-values less than 0.10) in streams that have headwaters in mountainous areas. Median specific-conductance values and sodium-adsorption ratios for these streams tended to be smallest during April through June as a result of snowmelt runoff. Seasonal variability was not significant (*p*-values greater than 0.10) for specific conductance for several plains streams. Seasonal variability was observed more often in sodium-adsorption ratios for the plains sites; however, the season that had the largest median value varied among sites.

Eight sites in the Tongue, Powder, and Belle Fourche River drainage basins were evaluated for trends in unadjusted and flow-adjusted specific-conductance values during water years 1991–2005. Upward trends in unadjusted specific-conductance values were significant (*p*-values less than 0.10) at a site on Goose Creek, a site on the Tongue River, a site on the Powder River at Sussex, Wyo., and a site on the Powder River at Arvada, Wyo. No significant trends in unadjusted specific-conductance values were determined (*p*-values greater than 0.10) for sites on Salt Creek, the Powder River at Moorhead, Mont., the Little Powder River, and the Belle Fourche River. Trends in specific conductance were not significant (*p*-values greater than 0.10) at the eight sites when values were flow-adjusted for streamflow variability.

Four sites in the Powder River drainage basin were evaluated for trends in unadjusted and flow-adjusted sodium-adsorption ratios during water years 1991–2005. Upward trends in unadjusted sodium-adsorption ratios were significant (*p*-values less than 0.10) for sites on Salt Creek, the Powder River at Sussex, Wyo., and the Powder River at Arvada, Wyo. Upward trends in flow-adjusted sodium-adsorption ratios also were significant at these sites, indicating streamflow variability may not have been the cause of the trends. A downward trend in flow-adjusted sodium-adsorption ratios was significant (*p*-values less than 0.10) for a site on the Little Powder River. The cause of the downward trend was not determined. Ongoing (2007) data-collection activities in the Tongue, Powder, Cheyenne, and Belle Fourche River drainage basins will enhance data sets for future trend testing.

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