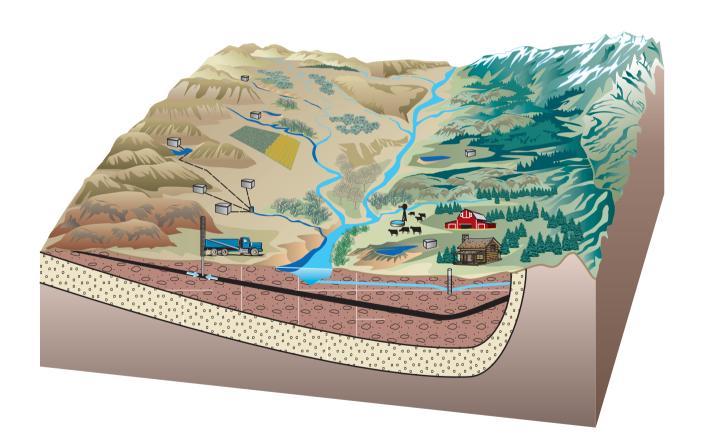


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Water-Resources Investigations Report 02-4045



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

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By Timothy T. Bartos and Kathy Muller Ogle

Water-Resources Investigations Report 02-4045

Prepared in cooperation with the

WYOMING STATE ENGINEER'S OFFICE and the BUREAU OF LAND MANAGEMENT

U.S. Department of the Interior

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
inch (in)	25.40	millimeter (mm)
inch (in)	72.540	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi ²)	2.590	square kilometer (km ²)
	Volume	
liter (L)	33.82	ounce (oz)
milliliter (mL)	0.0338	ounce (oz)
microliter (μL)	0.0000338	ounce (oz)
	Hydraulic Conductivity	
foot per day (ft/d)	0.3048	meter per day (m/d)
	Transmissivity	
foot squared per day (ft ² /d)	0.0929	meter squared per day (m ² /d)
	Concentration	
milligram per liter (mg/L)	1.0	part per million (ppm)
microgram per liter (μ g/L)	1.0	part per billion (ppb)

Temperature can be converted to degrees Fahrenheit (°F) or degrees Celsius (°C) as follows:

$$^{\circ}F = 9/5 \ (^{\circ}C) + 32$$

 $^{\circ}C = 5/9 \ (^{\circ}F - 32)$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called *Sea Level Datum of 1929*.

Abbreviated water-quality units used in this report:

% per mil or parts per thousand δ^2H deuterium/hydrogen isotopic ratio $\delta^{18}O$ oxygen-18/oxygen-16 isotopic ratio

 $\begin{array}{ll} meq/L & milliequivalents \ per \ liter \\ mg/L & milligram \ per \ liter \\ \mu g/L & microgram \ per \ liter \end{array}$

μm micrometer

μS/cm microsiemens per centimeter at 25 degrees Celsius

pCi/L picocuries per liter
TU tritium units

Abbreviations used in this report:

°C degrees Celsius
°F degrees Fahrenheit

 $^{2}\mathrm{H}$ deuterium $^{3}\mathrm{H}$ tritium $^{16}\mathrm{O}$ oxygen-16 oxygen-18

ANC acid-neutralizing capacity
BLM Bureau of Land Management

C carbon Ca calcium

CaCO₃ calcium carbonate

 ${
m CH_4}$ methane ${
m Cl}$ chloride ${
m cm}$ centimeter ${
m CO_2}$ carbon dioxide ${
m F}$ fluoride ${
m ft}$ foot

GMWL Global meteoric water line

H hydrogen H_2S hydrogen sulfide

 $\begin{array}{ccc} H_2O & water \\ HCO_3 & bicarbonate \\ K & potassium \\ m & meter \end{array}$

MCL maximum contaminant level

Mg magnesium Na sodium

NWQL National Water Quality Laboratory of U.S. Geological Survey

RPD relative-percent difference SAR sodium-adsorption ratio

Si silica

SMCL secondary maximum contaminant level

 SO_4 sulfate

TDS total dissolved solids

USEPA U.S. Environmental Protection Agency

USGS U.S. Geological Survey

VSMOW Vienna Standard Mean Ocean Water WSEO Wyoming State Engineer's Office

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ABSTRACT

Chemical analyses of ground-water samples were evaluated as part of an investigation of lower Tertiary aguifers in the eastern Powder River Basin where coalbed methane is being developed. Ground-water samples were collected from two springs discharging from clinker, eight monitoring wells completed in the Wasatch aquifer, and 13 monitoring or coalbed methane production wells completed in coalbed aquifers. The groundwater samples were analyzed for major ions and environmental isotopes (tritium and stable isotopes of hydrogen and oxygen) to characterize the composition of waters in these aquifers, to relate these characteristics to geochemical processes, and to evaluate recharge and ground-water flow within and between these aquifers. This investigation was conducted in cooperation with the Wyoming State Engineer's Office and the Bureau of Land Management.

Water quality in the different aquifers was characterized by major-ion composition. Samples collected from the two springs were classified as calcium-sulfate-type and calcium-bicarbonate-type waters. All ground-water samples from the coalbed aquifers were sodium-bicarbonate-type waters as were five of eight samples collected from the overlying Wasatch aquifer.

Potential areal patterns in ionic composition were examined. Ground-water samples collected during this and another investigation suggest that dissolved-solids concentrations in the coalbed aquifers may be lower south of the Belle Fourche River (generally less than 600 milligrams per liter). As ground water in coalbed aquifers flows to the north and northwest away from an inferred source of recharge (clinker in the study area), dissolved-solids concentrations appear to increase.

Variation in ionic composition in the vertical dimension was examined qualitatively and statistically within and between aguifers. A relationship between ionic composition and well depth was noted and corroborates similar observations by earlier investigators in the Powder River Basin in both Wyoming and Montana. This relationship results in two different water-quality zones with different characteristics – a shallow zone, comprising the upper part of the Wasatch aquifer, characterized by mixed cation composition and either sulfate or bicarbonate as the dominant anion; and a deeper zone, comprising the lower (deeper) part of the Wasatch aquifer and the underlying coalbed aquifers, characterized by sodium-bicarbonatetype waters. The zonation appears to be related to geochemical processes described by earlier investigators such as dissolution and precipitation of minerals, ion exchange, sulfate reduction, and mixing of waters. Qualitative and statistically significant differences were observed in sulfate concentrations between the coalbed aguifers and the overlying Wasatch aquifer. Ionic composition suggests that bacterially mediated redox processes such as sulfate reduction were probably the dominant geochemical processes in the anaerobic coalbed aquifers.

Tritium was used to qualitatively estimate the time of ground-water recharge. Tritium concentrations in both springs suggests that both were recharged after 1952 and contain modern water. Tritium was not detected at concentrations suggestive of modern water in any ground-water samples collected from the coalbed aquifers or in six of eight ground-water samples collected from the overlying Wasatch aquifer. Tritium concentrations in the remaining two wells from the Wasatch aquifer suggest a mixture between submodern (recharged before 1952) and modern water, although the low concentrations suggest that ground water in these two wells have very little modern water. The relative absence of modern water in all aquifers in the study area suggests that recharge processes to these aquifers are probably very slow.

Paired δ^2 H (deuterium/hydrogen isotopic ratio) and δ^{18} O (oxygen-18/oxygen-16 isotopic ratio) values for samples collected from the springs and all aquifers are close to the Global Meteoric Water Line, a meteoric water line for North American continental precipitation, and an estimated local meteoric water line, suggesting the water in the aquifers is of meteoric origin. The δ^2H and δ^{18} O values suggest that the waters were recharged in a colder climate or temperature, mid-latitudes, and mid-continent. In general, the samples do not form separate groups based on aquifer origin; this suggests either intermixing of the waters in the aquifers or that the different aquifers are subject to similar recharge and/or evolutional paths for the water. However, examination of the differences in the values of $\delta^2 H$ and $\delta^{18} O$, in combination with major-ion chemistry at three monitoring-well clusters, suggest that changes in the values with depth may represent different timing or sources of recharge to the different aquifers.

The areal distribution of $\delta^2 H$ was examined and an apparent break in the $\delta^2 H$ along a northwest to southeast trend was observed. In the coalbed aquifers, all but one ground-water sample (collected from the Big George coal bed), show a pattern where the $\delta^2 H$ values become more negative towards the center of the Powder River Basin and

values greater (less negative) than an arbitrary reference value of -140 ‰ (per mil or parts per thousand) were observed near the outcrop area of the Wyodak-Anderson coal zone. In the overlying Wasatch aquifer, the δ^2H values became less negative towards the center of the basin. The values more negative than -140 ‰ are near the outcrop area and the values that are less negative than -140 ‰ are closer to the basin center. It is unclear if this pattern is a result of sample size, different recharge mechanisms, geochemical processes, or if the processes producing these differences are independent or unrecognized.

Results of water-quality sampling were compared with selected regulatory and nonregulatory standards as well as commonly-used guidelines for proposed water uses. Dissolved solids was the measure that most frequently exceeded U.S. Environmental Protection Agency public water-supply standards and State of Wyoming domestic-use standards in ground-water samples collected from the Wasatch aquifer and coalbed aquifers. The State of Wyoming agricultural standards (irrigation) for sulfate and dissolved solids were exceeded in some samples collected from the Wasatch aquifer and coalbed aquifers. The State of Wyoming livestock standard for pH was exceeded in some samples collected from the Wasatch aquifer. Water from the Wasatch aquifer ranged from soft to very hard, and water from the coalbed aquifers ranged from moderately hard to very hard. Samples collected from wells completed in both the Wasatch aquifer and coalbed aquifers plotted in a wide range of both sodium- and salinity-hazard classes, but most samples clustered in or near the combined medium-sodium-hazard—high-salinityhazard classes.

INTRODUCTION

The Powder River Basin (fig. 1) in northeastern Wyoming is an important source of energy resources for the entire United States. Oil, conventional natural gas, uranium, coal, and most recently, coalbed methane (i.e., natural gas), are all developed in the basin. Since 1997, the development of coalbed methane has rapidly

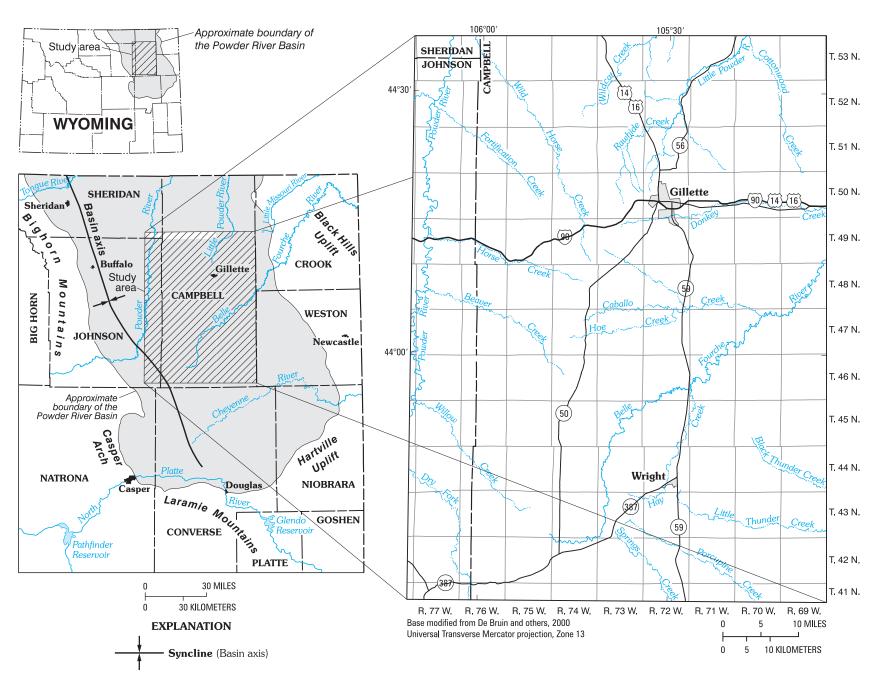


Figure 1. Location of the study area in the Powder River Basin, Wyoming.

increased as demand for natural gas has increased in the United States. Coalbed methane is produced by pumping water from wells installed in coal beds that contain methane. The removal and discharge of this water has renewed interest in hydrological and geochemical processes that control the water quality and volumes of produced water in the coalbed aquifers. Consequently, the U.S. Geological Survey (USGS), in cooperation with the Wyoming State Engineer's Office (WSEO) and the Bureau of Land Management (BLM), conducted an investigation to enhance the understanding of the characteristics of the aquifers associated with the development of this natural resource in the Powder River Basin. This report documents the results of the investigation.

Purpose and Scope

The purpose of this investigation was to increase understanding of the aquifers in the Wasatch and Fort Union Formations of lower Tertiary age in the eastern Powder River Basin in northeastern Wyoming. The scope of the investigation included the collection of ground-water samples from springs and wells and subsequent analysis of those samples for major ions, tritium, and oxygen and hydrogen isotopes to meet the following objectives:

- Determine possible hydrologic and geochemical relationships between different aquifers and/or aquifer systems in the lower Tertiary formations, using qualitative and quantitative (statistical) comparisons of major-ion chemistry and environmental isotopic composition between aquifers
- Determine spatial (areal) and vertical variation of major-ion chemistry and environmental isotopic composition within each aquifer
- Examine major-ion chemistry in the context of other studies of the same aquifers in the Powder River Basin
- Qualitatively estimate the time of ground-water recharge
- Determine what can be inferred about ground-water recharge by comparing concentrations of stable isotopes of oxygen and hydrogen with the global meteoric water line, the meteoric water line for North American continental precipitation, and an estimated local meteoric water line

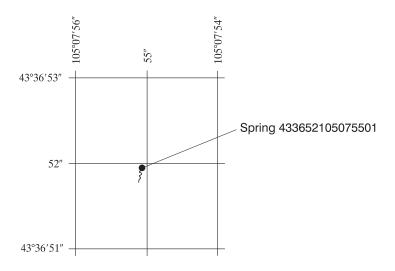
- Determine what can be inferred about potential ground-water flowpaths and recharge characteristics of the different aquifers using major-ion chemistry and environmental isotopic composition
- Characterize water quality in relation to waterquality standards using major-ion chemistry

In addition, a bibliography was compiled as part of this investigation. While all of these references may not be directly cited in this report, they are listed in the Selected References section of this report to assist readers searching for additional information about coalbed methane and the geology and hydrogeology of lower Tertiary formations in the Powder River Basin.

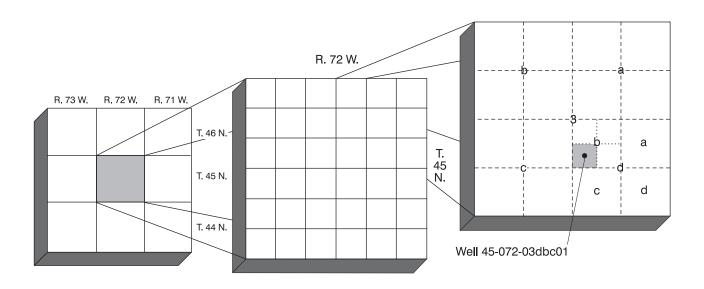
Numbering System for Wells and Springs

Wells and springs are identified by location using a 15 digit USGS well-identification number consisting of latitude, longitude, and a sequence number (fig. 2). For example, site 433652105075501 is the first site inventoried at a location having a latitude of 43 degrees, 36 minutes, and 52 seconds, and a longitude of 105 degrees, 7 minutes, and 55 seconds. The last two digits in the well-identification number (01) are a sequence number indicating the order of inventory.

A local well number also is assigned to wells and springs using the Federal township-range system of land subdivision. An example of a local number established for a well used in this report is 45-072-03dbc01 (fig. 2). The first number (45) denotes the township (T), the second number (072) denotes the range (R), and the third number (03) denotes the section. The first letter following the section number denotes the quarter section (160-acre tract); the second letter, the quarterquarter section (40-acre tract); and the third letter, if shown, the quarter-quarter section (10-acre tract). These subsections are designated a, b, c, and d in a counter-clockwise direction, beginning in the northeast quadrant. The last two digits in the local number are a sequence number indicating the order of inventory. For example, well 45-072-03dbc01 is the first well inventoried in the southwest quarter of the northwest quarter of the southeast quarter of section 3, T. 45 N., R. 072 W.



System for numbering springs and wells using latitude and longitude.



System for numbering springs and wells in surveyed townships.

Figure 2. Systems for numbering springs and wells.

Abbreviated site numbers are often used to describe well locations in place of USGS well-identification numbers, local well numbers, or local well names for all wells discussed in this report. For example, W1 indicates well W1 is completed in the Wasatch aquifer, and C1 indicates well C1 is completed in a coalbed aquifer. Site numbers, USGS well-identification numbers, and local well numbers are listed in the tables. Only site numbers are used in illustrations.

Methods of Investigation

Ground-water samples for water-quality analyses were collected during June 1999 from 27 locations in or near areas of coalbed methane development. Samples were collected from two springs discharging from clinker, eight BLM or WSEO monitoring wells completed in the Wasatch aquifer, seven BLM or WSEO monitoring wells completed in the coalbed aquifers, and ten coalbed methane production wells completed in the coalbed aquifers.

Different sampling devices and techniques were used to collect the various ground-water samples. Samples were collected from the springs by submerging sampling containers as close as possible to the point of discharge. In addition, samples were not collected from the springs if it had rained several days prior to arrival at the site to ensure that the samples represented discharge from the springs and were not influenced by surface-water runoff. Submersible pumps were used to collect samples from all but one monitoring well; the remaining well had sufficient gas and artesian pressure (hydraulic head) to sample without a pump. Coalbed methane production wells were sampled using submersible pumps already present in the wells. Attempts were made to remove (purge) a minimum of three casing volumes of water from each monitoring well and to allow onsite measurements (pH, specific conductance, and temperature) to stabilize prior to sample collection to ensure that the sample collected represented the ground water rather than water stored in the well casing. During purging at several wells, gas-lock of the pump or water-level drawdown prevented removal of three casing volumes; these wells were sampled after the pump could be restarted or after sufficient time was allowed for water-level recovery (because of drawdown). Purging, or removal of three casing volumes of water, was not conducted at coalbed methane production wells

because the wells are actively pumping water to produce methane; however, the wells were allowed to discharge water for some period of time prior to sample collection and onsite measurements of field parameters were monitored for stability.

Quality-assurance procedures involved calibration of all field meters, collection of quality-control samples (replicates), and use of standardized USGS sampling. processing, and analytical techniques. Field meters were calibrated prior to sampling at each well. Qualitycontrol samples consisted of two replicate (duplicate) ground-water samples. Water-quality samples were collected, preserved, and shipped according to standardized USGS techniques described in Book 9 of the USGS National Field Manual for the Collection of Water-Quality Data (Wilde and others; 1998; Wilde and Radtke, 1998; Wilde and others, 1999). Water-quality samples were analyzed at USGS laboratories using standardized USGS laboratory analytical methods and laboratory quality-assurance procedures as documented in Fishman and Friedman (1989). Ground-water samples were analyzed by the inductively coupled plasma method with atomic emission spectrometry for major ions (Fishman and Friedman, 1989; Fishman, 1993), tritium by electrolytic enrichment with gas counting (Ostlund and Dorsey, 1977), δ^2 H (deuterium/hydrogen isotopic ratio) by hydrogen equilibrium (Coplen and others, 1991) and δ^{18} O (oxygen-18/oxygen-16 isotopic ratio) by carbon dioxide equilibrium (Epstein and Mayeda, 1953). For this report, dissolved refers to constituents in water samples that passed through a 0.45-micrometer disposable cartridge filter during sample collection.

Each well was located using a military-grade Global Positioning System (GPS) receiver to obtain the latitude and longitude. The well was then plotted on the appropriate USGS Quadrangle maps (1:24,000 scale) to obtain land-surface elevations.

Water levels in monitoring wells were measured prior to sampling. Each monitoring well was equipped with a dedicated water-level recorder that was removed prior to water-quality sampling. Water levels measured by the recorders were noted immediately prior to removal. Water levels could not be measured in coalbed methane production wells, so water-level measurements from these wells were obtained from WSEO well permits. Well-completion information (i.e., well depths, casing material, screened or opened intervals) also was obtained from WSEO well permits.

Water-quality data commonly are not normally distributed and commonly contain censored data values (unquantified data reported as being less than some value, such as a minimum reporting level (MRL)). In addition, nonnormality is difficult to detect with small sample sizes. Nonparametric statistics do not rely on an assumption that data are normally distributed, are resistant to the effects of outliers, and are more appropriate when sample sizes are small (Helsel and Hirsch, 1992). Therefore, nonparametric statistical methods are used exclusively to describe and analyze water-quality data in this report. Individual methods are described in the sections where used.

DESCRIPTION OF STUDY AREA

Climate

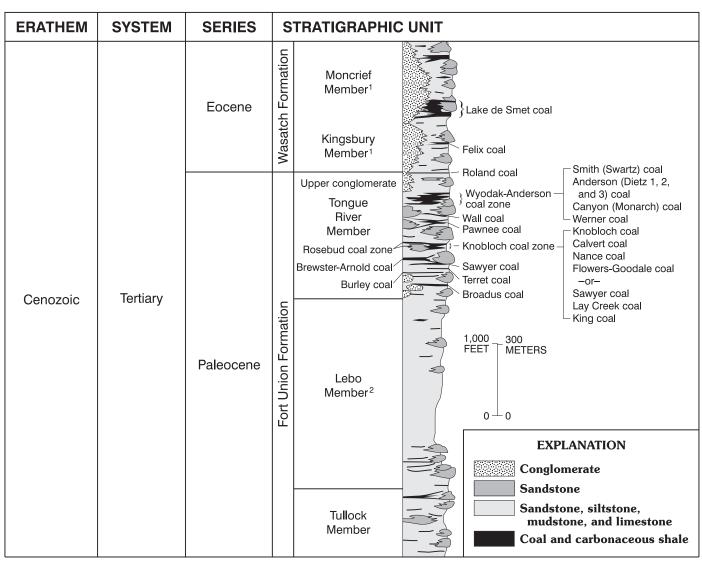
The climate of the study area is classified as a steppe climate typical of semiarid grassland prairies (Martner, 1986). The average mean temperature in Gillette for 1961 to 1990 was 44.2 degrees Fahrenheit, but temperature and precipitation vary widely, depending upon the season (Western Regional Climate Center, 2001). Mean annual precipitation for 1961 through 1990 in Gillette was 16.61 inches (Western Regional Climate Center, 2001). Estimated mean annual evaporation greatly exceeds mean annual precipitation in the study area; mean annual evaporation estimated from Class-A pans ranges from about 65 to 70 inches per year, while mean annual evaporation estimated from lakes ranges from about 45 to 50 inches per year (Martner, 1986, p. 177, and references therein). Estimated mean annual potential evapotranspiration also exceeds precipitation in most of the study area for 1951 through 1980 and was about 22 to 23 inches, based on the Thornthwaite method (Martner, 1986, p. 182). Wind in the study area is primarily from the west, and the average hourly wind velocity in the area is about 13 miles per hour (Lowry, Wilson, and others, 1986).

Geographic and Geologic Setting

The name Powder River Basin has been used to refer to both a structural basin and a drainage basin. The structural basin and the drainage basin do not coincide and both are frequently used interchangeably to define the area. In this report, Powder River Basin refers to the

structural basin. The Powder River Basin is an asymmetrical syncline formed during the Laramide orogeny (Late Cretaceous to early Tertiary age). The axis of the basin trends from southeast to northwest near the western margin of the basin (fig. 1), far from its geographic center. In Wyoming, the Powder River Basin is bounded by the Black Hills uplift in the northeast, the Hartville uplift in the southeast, the Laramie Mountains in the south, the Casper arch in the southwest, and the Bighorn Mountains in the west (fig. 1). The basin continues northward into Montana (not shown in fig. 1), where another structural feature, the Cedar Ridge anticline, separates it from the Williston Basin. The entire basin covers an area of more than 22,000 square miles (Flores and others, 1999). The Powder River drainage basin refers to the area in Wyoming and Montana drained by the perennial Powder River and its tributaries. The Powder River Basin includes not only the Powder River and associated tributaries, but also the upstream parts of the Belle Fourche River, Cheyenne River, and Tongue River drainage basins (fig. 1). The study area is in the eastern part of the Powder River Basin, within the unglaciated part of the Missouri Plateau of the Northern Great Plains and the Missouri River drainage basin. In the study area, the perennial Powder River and Little Powder River flow northward and the perennial Belle Fourche River flows northeastward (fig. 1). Tributaries to these rivers are primarily ephemeral, with streamflow resulting from precipitation (Lowry, Wilson, and others, 1986). Grasscovered plains, rolling hills, and tablelands dominate the landscape. Rivers and streams have eroded deeply in the area and have wide, flat streambeds and broad floodplains. Isolated flat-topped buttes, mesas, and ridges commonly are present several hundred feet above valley floors.

Within the study area, the geologic units of interest are lower Tertiary in age. In ascending stratigraphic order, these geologic units are the Fort Union Formation of Paleocene age and the Wasatch Formation of Eocene age (fig. 3). Sediments comprising both formations have been interpreted to be continental in origin. The Fort Union Formation in the Powder River Basin was deposited by northeastward-flowing fluvial systems consisting of braided, meandering, and anastomosed streams in the basin center; these fluvial systems were fed by alluvial fans at the basin margin associated with surrounding ancestral uplifts (Flores and Ethridge, 1985; Flores, 1986). The Wasatch Formation overlies the Fort Union Formation and is exposed at the surface



¹ Wasatch Formation not subdivided into members in study area (eastern Powder River Basin).

Figure 3. Generalized stratigraphic column of the Wasatch and Fort Union Formations in the central Powder River Basin, Wyoming (modified from Flores and Bader, 1999).

² Defined as the Lebo Shale Member of the Fort Union Formation in Montana.

throughout much of the Powder River Basin in Wyoming, including the study area (fig. 4). The Fort Union Formation is exposed primarily along the margins of the basin in Wyoming, including the eastern edge of the study area (fig. 4). The Wasatch Formation was deposited in conditions similar to those of the Fort Union Formation, primarily fluvial, lacustrine, and swampy environments (Seeland, 1992; Ellis and others, 1999a).

The Fort Union Formation in the Powder River Basin ranges in thickness from 2,300 to 6,000 ft (feet) (Curry, 1971) and is subdivided into three members – the Tullock, Lebo, and Tongue River Members (fig. 3). Along the eastern margin of the Powder River Basin, including the study area, the Fort Union Formation is nearly flat and dips to the west about 2 to 3 degrees (Glass, 1997). Near the western margin, the Fort Union Formation dips to the east from 10 to 25 degrees (Glass, 1997). The Tullock Member ranges in thickness from 370 to about 1,440 ft (Brown, 1993) and consists primarily of lenticular, discontinuous, fine to medium-grained sandstone beds interbedded with fine-grained sediments such as siltstone, claystone, mudstone, carbonaceous shale, rare limestone, and thin coal beds (Curry, 1971). The Lebo Member ranges in thickness from about 499 to about 1,700 ft (Law, 1975; Lewis and Hotchkiss, 1981) and consists primarily of shale or mudstone interbedded with lesser amounts of sandstone, siltstone, and sparse, very thin coal beds. Like the Tullock Member, the Tongue River Member (as much as 1,860 ft thick (Curry, 1971)) also consists primarily of lenticular, discontinuous, fine to medium-grained sandstone beds interbedded with fine-grained sediments such as siltstone, claystone, mudstone, carbonaceous shale, and limestone; however, in contrast, coal beds are more common, thicker, and laterally continuous in the Tongue River Member.

While there are many thick coal beds in the Tongue River Member, the thickest and most laterally continuous coal beds are associated with a coal zone present basinwide in Wyoming and Montana known as the Wyodak-Anderson coal zone (Averitt, 1975; Glass, 1980). The Wyodak-Anderson coal zone is composed of different coal beds (fig. 3) that split, merge, re-split, or pinch out (fig. 5). Goolsby and Finley (2000) recently suggested that the coal beds of the Wyodak-Anderson coal zone and some coal beds below the zone (fig. 3) may represent a single lithologic unit that was deposited in a corkscrew-type structure as the result of a depositional center that migrated over time. As many as six of

these coal beds can comprise the coal zone in any given location (Ellis, 1999). Currently, 11 individual coal beds have now been identified in the coal zone (Flores and others, 1999). The coal beds of the Wyodak-Anderson coal zone "were deposited in low-lying peat swamps and raised mires, and associated detrital rocks were deposited by trunk-tributary, meandering, anastomosed, and braided streams" (Flores, 1999, p. 6, and references therein). Historically, the naming of these many beds has been extremely complicated and the correlation of the beds controversial (Flores, 1999). Despite this complexity and as a result of much work by many investigators over many years, the Wyodak-Anderson coal zone has been correlated throughout the Powder River Basin in Wyoming. Many of the beds comprising the zone have been correlated throughout the basin and are laterally continuous over large distances (Glass, 1980, 1997; Ellis and others, 1999a; Flores, 1999; Flores and others, 1999) (fig. 5).

The Wyodak-Anderson coal zone and the individual beds comprising the zone vary widely in thickness and depend on geographic location. Although estimates vary widely, the most recent estimate suggests that the Wyodak-Anderson coal zone in the Powder River Basin in Wyoming and Montana "has a maximum net coal thickness (total thickness of all coal beds greater than 2.5 ft thick) of 284 ft" and that "the entire zone is more than 600 ft thick (measured from the top of the uppermost coal to the base of the lowermost coal) in the center part of the basin" (Ellis, 1999, p. 44). Throughout the basin, coal beds comprising the coal zone "average 25 ft in thickness, and are separated by clastic sedimentary rocks ranging from a few feet to 150 ft in thickness" (Ellis, 1999, p. 44). The coal beds of the Wyodak-Anderson coal zone outcrop or subcrop along the eastern margin of the basin (fig. 4). Consequently, this area is where most of the coal mining in the basin occurs. In the vicinity of the city of Gillette, several of the coal beds of the Wyodak-Anderson coal zone merge to form a single thick coal bed known as the Wyodak coal bed (location C, fig. 5). The Wyodak coal bed splits into several seams south, east, and north of Gillette (fig. 5). The maximum thickness of a single merged coal bed within the Wyodak-Anderson coal zone in the Gillette coal field is 145 ft (Ellis and others, 1999a). The complexity of the Wyodak-Anderson coal zone and associated coal beds is illustrated in several cross sections within the study area (fig. 6). The reader is referred to Flores (1999) and Flores and Bader (1999) for a detailed

historical review, discussion, and interpretation of the Wyodak-Anderson coal zone in the Powder River Basin in Wyoming and Montana.

Along the eastern part of the study area where the Wyodak-Anderson coal zone outcrops or subcrops (fig. 4), the coal beds have burned and baked the sediments around the beds to form rock known as clinker (also frequently referred to as scoria). Clinker is a distinct orange to red color throughout the basin and in the study area. The clinker covers about a 250-square mile area along the eastern boundary of the Gillette coal field east of Gillette and Wright (Heffern and Coates, 1997). The clinker is resistant to erosion and caps many of the topographically high locations in the area (Heffern and Coates, 1997).

The Wasatch Formation, like the Tongue River Member of the Fort Union Formation, consists primarily of fine- to coarse-grained lenticular, discontinuous sandstone beds interbedded with fine-grained sediments such as shale, siltstone, claystone, and mudstone. Consequently, the Wasatch Formation is difficult to distinguish from the underlying Fort Union Formation, especially in the subsurface, because of similarity both in lithology and in depositional history (Ellis and others, 1999a). The contact between these two formations and its relationship to the Paleocene-Eocene boundary remains controversial (Flores, 1999), but the contact commonly is placed above a coal bed, the Roland coal (Olive, 1957) (figs. 3 and 5). Palynostratigraphic differences (Tschudy, 1976; Nichols, 1994, 1998; Nichols and Brown, 1992) and mineralogical differences (Denson and others, 1989a, 1989b) typically are used to identify the two formations and locate the contact in the subsurface. The reader is referred to Flores (1999) and Flores and Bader (1999) for an overview and discussion of the contact between the Wasatch and Fort Union Formations. In the study area, many of the coal mines and coalbed methane developers consider the top of the Wyodak-Anderson coal zone as the contact, even though some of the Fort Union Formation may be present above the coal zone and below the overlying Wasatch Formation; this convention will be followed in this report. Dip of the Wasatch Formation is shallow, generally less than 4 degrees (Glass, 1997). The Wasatch Formation contains many coal beds, with the thickest beds in the western and central parts of the Powder River Basin outside the study area, particularly near Lake De Smet (fig. 5) (Glass, 1980, 1997). Clinker is present in the Wasatch Formation in

many locations (fig. 4) and frequently forms caprocks because it is more resistant to weathering than surrounding rock (Heffern and others, 1996; Heffern and Coates, 1999).

Methane (CH₄) is found in the coal beds of the study area and sometimes in lithological units, such as sandstone lenses, located immediately above or below the coal beds (Jones and De Bruin, 1990; Law and others, 1991; Rice, 1993). Coalbed methane is created by a series of processes (discussed in greater detail later in this report) that convert organic matter present in coal into methane. Coalbed methane in the Powder River Basin is composed almost entirely of methane, with a small amount of carbon dioxide (1.5 to 2 percent) (Law and others; 1991; Rice, 1993; De Bruin and others, 2000); composition is suspected to be very uniform throughout the basin (Rice, 1993). Based on the rank of the coal and the isotopic composition of the methane in the lower Tertiary coal beds of the Powder River Basin, it is believed that the coalbed methane was primarily generated from bacterial activity (biogenic) as opposed to heating (thermogenic) (Boreck and Weaver, 1984; Law and others, 1991; Rice and Flores, 1990, 1991; Rice, 1993; Gorody, 1999). Coalbed methane is believed to be stored in coal beds in four possible ways (Yee and others, 1993): (1) as free gas within small pores (micropores) and fractures (cleats); (2) as gas dissolved in water within the coal; (3) as gas adsorbed on surfaces of organic material, micropores, and cleats; and (4) as gas absorbed within the molecular structure of the coal molecules. De Bruin and others (2000) suggest the gas in the shallow coal beds of the study area is probably stored primarily as free gas and dissolved gas where good cleat development is present. The reader is referred to the recent publication by De Bruin and others (2000) for a discussion of coalbed methane in both the Powder River Basin and the State of Wyoming and recent publications by Rice (1997) and Nuccio (2000) for discussions of coalbed methane in the U.S.

Hydrogeologic Setting

The relations of Cenozoic stratigraphic units to assigned hydrogeologic units in this study are shown in figure 7. Only the hydrogeology of the geologic units overlying and associated with the Wyodak-Anderson

106°00′

Figure 4. Generalized geology, clinker in the study area, lines of geologic cross sections, and ground-water sampling locations in the eastern Powder River Basin, Wyoming, 1999.

DESCRIPTION OF STUDY AREA

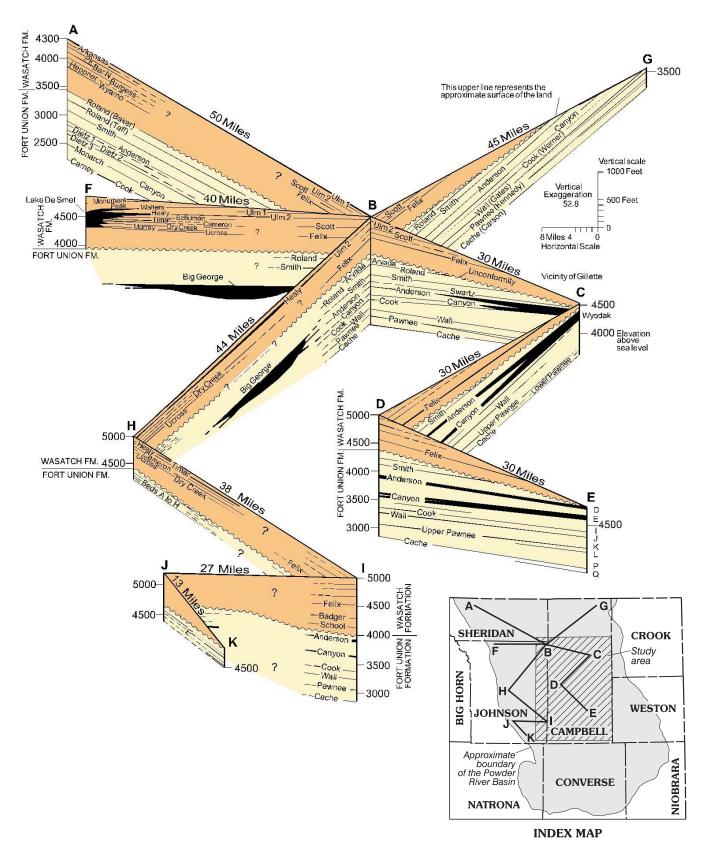


Figure 5. Correlation of coal beds in the Powder River coal field, eastern Powder River Basin, Wyoming (modified from Glass, 1997).

coal zone (Wasatch and Fort Union Formations) will be discussed. Convention in this report will be to use the geologic unit (i.e., member, formation, coal bed or coal zone) as the hydrogeologic unit or aquifer name, even though multiple aquifers may be present in any one geologic unit.

The Wyodak-Anderson coal zone and its associated coal beds comprise the most continuous hydrogeologic unit or aquifer in lower Tertiary deposits in the study area (Bloyd and others, 1986; Lowry, Wilson, and others, 1986; Martin and others, 1988). Because of the complicated history of the naming and correlation of the various coal beds comprising the Wyodak-Anderson coal zone, the aquifer within the coal zone has been referred to by many names, most frequently as the Wyodak coal aquifer or the Wyodak-Anderson coal or coalbed aguifer. The convention used in this report will be to use Wyodak-Anderson coalbed aquifer (fig. 7). Martin and others (1988) suggested that the aguifer can consist of not only the coal beds within the zone, but also the interbedded sandstone beds and the clinker along the coal outcrop. Aguifers present in other coal beds below the Wyodak-Anderson coal zone in the Tongue River Member of the Fort Union Formation will be combined with the coal zone in this report and will be collectively referred to as coalbed aquifers.

Water in the Wyodak-Anderson coalbed aquifer is typically unconfined near the outcrop along the eastern margin of the basin in the study area (Davis, 1976; Heffern and Coates, 1999) but becomes confined to the west, away from the outcrop and downdip (Davis, 1976; Martin and others, 1988). The aquifer is confined above by overlying low permeability shales or other fine-grained units in the Tongue River Member of the Fort Union Formation or Wasatch Formation and below by low permeability shale or other fine-grained units in the Tongue River Member (Martin and others, 1988). Artesian conditions can exist; Whitcomb and others (1966) also noted that the gas present within the coal beds or associated geologic materials (for example, sandstone lenses above or below the coal bed) can contribute significantly to hydraulic head in wells in the Powder River Basin and may cause water levels to rise higher than if only artesian pressure were present.

The amount of hydraulic connection under natural conditions between the Wyodak-Anderson coalbed aquifer and sandstone lenses comprising aquifers in the overlying Wasatch or Fort Union Formations is unclear. Many investigators have suggested that downward ver-

tical flow or leakage from overlying geologic units to the Wyodak-Anderson coalbed aquifer is small because of low vertical hydraulic conductivity of the overlying rocks (Davis and Rechard, 1977; Feathers and others, 1981; Bloyd and others, 1986), even though a downward vertical gradient between the coalbed aquifer and the overlying Wasatch aquifer is commonly present (Ground-Water Subgroup, 1974; Davis, 1976; Bureau of Land Management, 1999). However, some leakage probably occurs downward where the hydraulic gradient allows for downward vertical ground-water flow and where sandstone lenses may directly overlie the coalbed aquifer (Bureau of Land Management, 1999).

The Wyodak-Anderson coalbed aquifer is anisotropic; ground-water flow primarily occurs through fractures (cleats) in the coal bed (Ground-Water Subgroup, 1974; Brown, 1980; Rehm and others, 1980; Martin and others, 1988). Flow direction in this aquifer may change where the coal bed splits into other beds and is interbedded with other lithological units and where differences in the distribution and density of the fractures (cleats) in the coal occur (Martin and others, 1988). Anisotropy in coal beds in the Wasatch and Fort Union Formations of the Powder River Basin in both Wyoming and Montana has been examined or discussed by Stone and Snoeberger (1977), Rehm and others (1980), Stoner (1981), Dobson (1996), and Peacock (1997). In general, these investigators suggest that anisotropy in coals from both the Wasatch and Fort Union Formations in the Powder River Basin appears to be related to cleat orientation; cleat orientation may be oriented to major structural features (e.g., basin axis, lineaments, and faults).

Hydraulic conductivity values from aquifer tests conducted in the Wyodak-Anderson coalbed aquifer were summarized in Martin and others (1988) and Peacock (1997). Martin and others examined 357 aquifer tests conducted in the Wyodak-Anderson coalbed aquifer at coal mines in the Powder River Basin in Wyoming and noted hydraulic conductivity values approximated a lognormal distribution with a geometric mean of 0.8 ft per day. Peacock (1997) reported a geometric mean of about 0.5 ft per day for 166 aquifer tests conducted in the Wyodak-Anderson coalbed aquifer in the study area. Rehm and others (1980) summarized hydraulic conductivities from 193 aquifer tests conducted in Paleocene coal beds (Fort Union Formation or Group) in the Northern Great Plains (including the

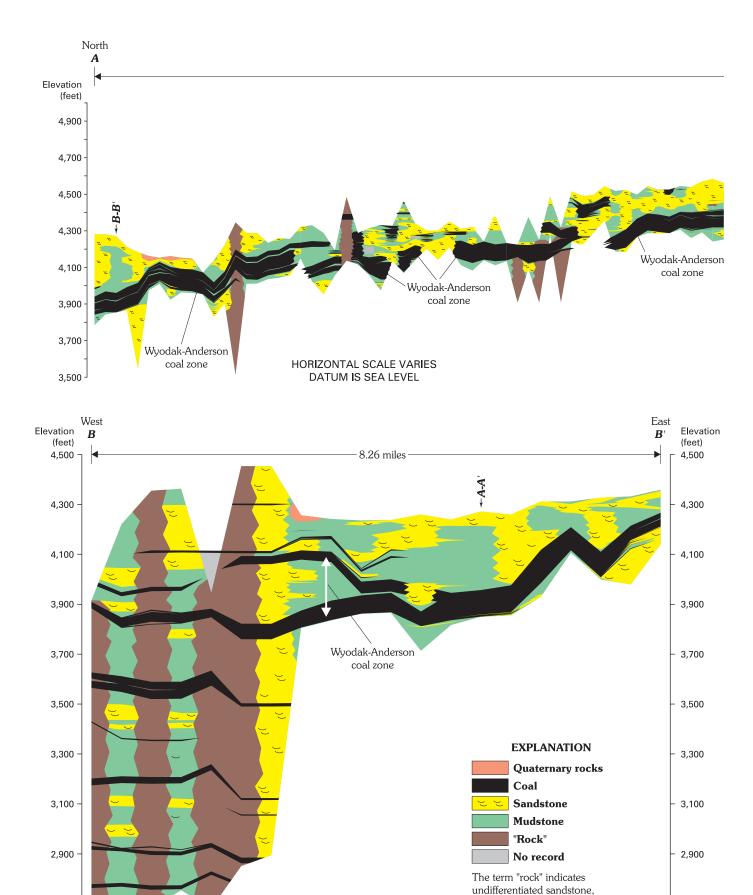


Figure 6. Geologic cross sections, eastern Powder River Basin, Wyoming (from Ellis and others, 1999a). Lines of section shown in figure 4.

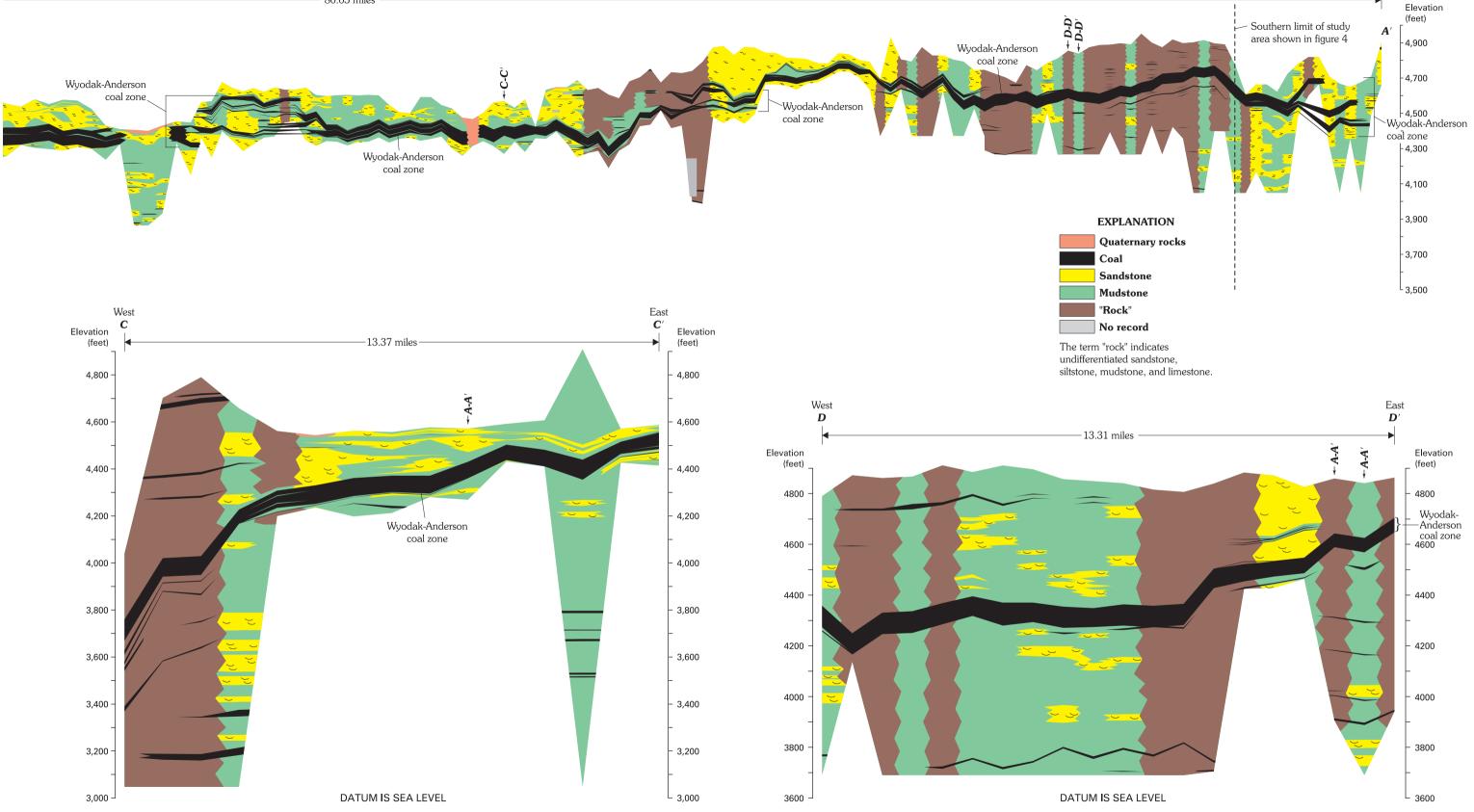
siltstone, mudstone, and limestone.

2,700

DATUM IS SEA LEVEL

2,700

14



South \boldsymbol{A}'

ERATHEM	SYSTEM	SERIES	STF	RATIGRAPHIC UNIT	HYDROGEOLOGIC UNIT
	Quaternary	Holocene and Pleistocene		Alluvium	Alluvial aquifers ¹
		Pliocene			
		Miocene		Not present in study area	Not present in study area
		Oligocene			
Cenozoic		Eocene	٧	Vasatch Formation	Wasatch aquifer ¹
		ene	rion	Wyodak-Anderson coal zone and other coal zones and coal beds	Confining unit Wyodak-Anderson coalbed aquifer and other coalbed aquifers Confining unit
		Paleocene	Fort Union Formation	Tongue River Member	Tongue River aquifer
		_ &	 ፫ ፫	Lebo Member ³	Lebo confining layer
				Tullock Member	Tullock aquifer

¹ Alluvial aquifers and Wasatch Formation combined into one hydrogeologic unit in Lewis and Hotchkiss (1981), Bloyd and others (1986), and Martin and others (1988).

Figure 7. Relation of Cenozoic stratigraphic units to hydrogeologic units, eastern Powder River Basin, Wyoming (modified from Lewis and Hotchkiss (1981), Bloyd and others (1986), and Martin and others (1988)).

Powder River Basin in Wyoming and Montana). The investigators reported the frequency distribution of coalbed conductivity values approximated a lognormal distribution with a geometric mean of about 0.9 ft per day.

Regional flow within the Wyodak-Anderson coalbed aquifer is suspected to be to the north and northwest, based on a potentiometric-surface map prepared by Daddow (1986) (fig. 8). Regional ground-water flow in the area near Porcupine Creek (fig. 8) may be to the north (Martin and others, 1988). The relationship between regional ground-water flow in the coalbed aquifers and the Fort Union Formation in the Powder River Basin has not been examined.

Recharge to the aquifer is suspected to occur primarily along the outcrop areas of clinker associated with the Wyodak-Anderson coal zone (Lowry and Cummings, 1966; Whitcomb and others, 1966; Davis, 1976; Martin and others, 1988; Heffern and Coates, 1999). In the study area, the clinker associated with the Wyodak-Anderson coalbed aquifer is located along the eastern margin, near the outcrop area (fig. 4). Recharge also may occur locally where the coal bed subcrops below the alluvium in the stream valleys (Davis, 1976; Davis and Rechard, 1977; Martin and others, 1988). Discharge is suspected to primarily occur in areas where the coal subcrops under the base of alluvium in valleys (Brown, 1980; Martin and others, 1988) or as downward leakage (Brown, 1980).

²The Tongue River Member of the Fort Union Formation, when present above the Wyodak-Anderson coal zone, was not included as part of the Wasatch aquifer in Bloyd and others (1986) and in Martin and others (1988).

³Defined as the Lebo Shale Member of the Fort Union Formation in Montana.

17

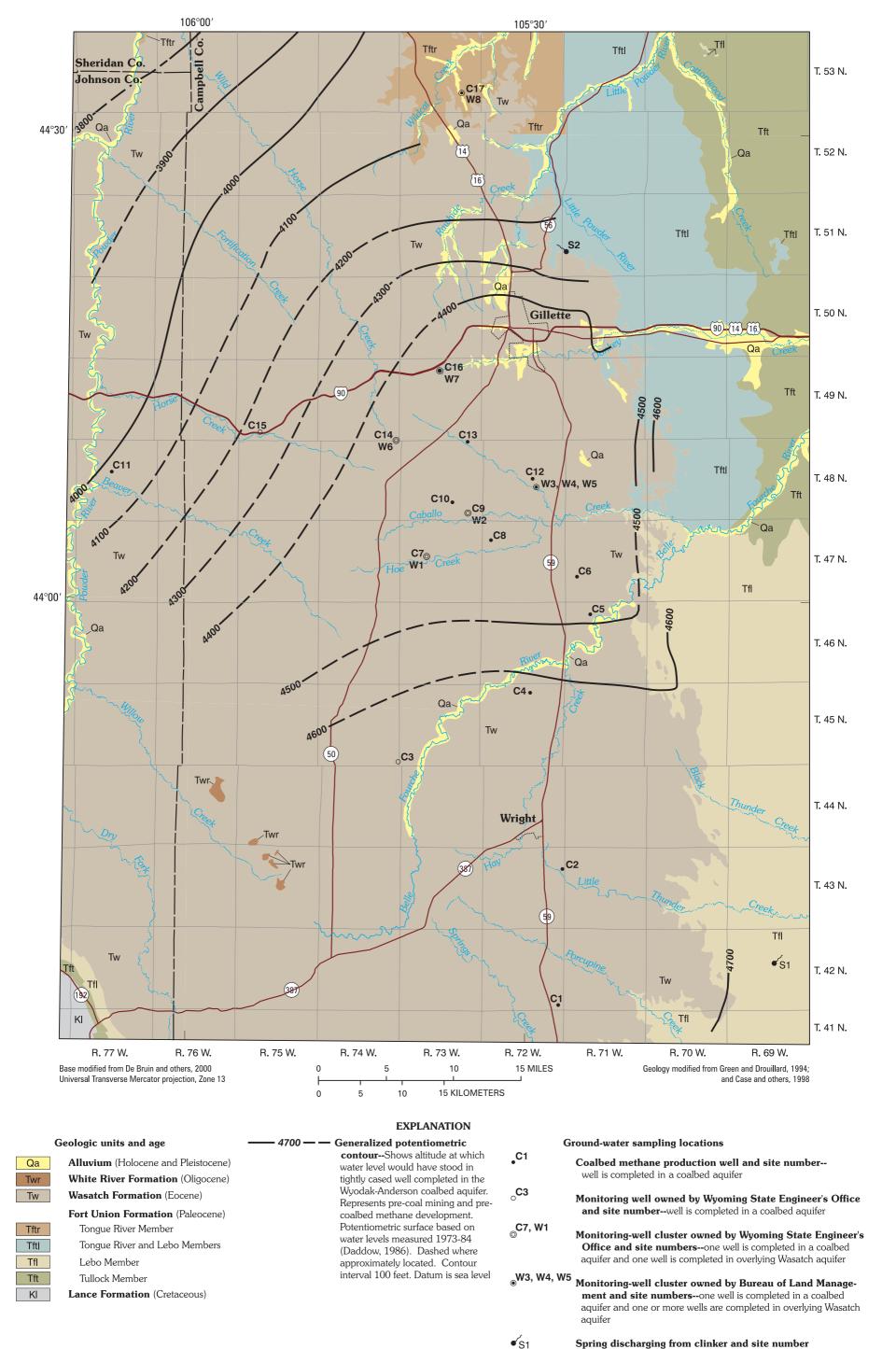


Figure 8. Generalized geology, potentiometric contours for Wyodak-Anderson coalbed aquifer, and ground-water sampling locations in the study area, eastern Powder River Basin, Wyoming, 1999. Potentiometric contours from Daddow (1986).

Clinker associated with and considered part of the Wyodak-Anderson coalbed aquifer by some investigators is highly permeable, may store large quantities of water, and may function locally as an unconfined or confined aquifer (Davis, 1976; Heffern and others, 1996; Heffern and Coates, 1999). Recharge of the clinker occurs vertically from precipitation, from streams that cross the clinker, and from lateral inflow from clinker or unburned coal and overburden updip (Heffern and Coates, 1999). Recharge rates to the clinker are suspected to be very high, especially compared to surrounding geologic units (Heffern and Coates, 1999). Transmissivities of the clinker are very high, and based on tests conducted at coal mines in the area, range from 10,000 to more than 1,000,000 feet squared per day (Heffern and Coates, 1999).

In a large part of the study area, the Wasatch Formation is exposed at land surface and overlies the Wyodak-Anderson coal zone. As stated previously and illustrated in figure 7, convention in this report will be to define the top of the Wyodak-Anderson coal zone and the aquifer contained within as the contact between the Fort Union Formation and the overlying Wasatch Formation and aquifer. The Wasatch aquifer consists primarily of discontinuous lenticular sandstone beds surrounded by fine-grained sedimentary rocks with low permeability such as siltstone, claystone, mudstone, carbonaceous shale, and limestone, although coal beds may be locally important if present. The discontinuous, lenticular sandstone beds are the actual geologic materials that primarily yield water to wells and comprise the aquifer (Littleton, 1950; Hagmaier, 1971; Hodson and others, 1973; Ground-Water Subgroup, 1974; Bloyd and others, 1986; Martin and others, 1988; Lowry and others, 1993).

Fine-grained sedimentary rocks in the Wasatch Formation do not yield sufficient quantities of water to be considered as an aquifer, even though they may be saturated and static water levels in wells completed in the fine-grained rocks may be the same as in adjacent beds of sandstone (Brown, 1980; Martin and others, 1988). The sandstone lenses have been considered as individual aquifers because they are surrounded by low permeability sedimentary rocks and they may be relatively hydraulically isolated from each other (Lowry and others, 1993). The yield of wells completed in the Wasatch aquifer is directly related to the number and thickness of sandstone lenses or beds penetrated by the well. Unconfined and confined conditions can exist in

the Wasatch aquifer (Littleton, 1950; Whitcomb and others, 1966; Davis, 1976), although the sandstone beds comprising the aquifer may be primarily confined (Lowry and others, 1993).

Hydraulic conductivity values for aquifer tests conducted in the sandstones comprising the Wasatch aquifer were summarized in Martin and others (1988) and Peacock (1997). Martin and others (1988, p. 19) noted that the frequency distribution "of the hydraulic conductivity of the Wasatch aquifer has a lognormal distribution with a geometric mean of 0.2 ft per day." Similarly, Peacock also noted a lognormal distribution and reported a geometric mean of about 0.3 ft per day for the Wasatch aguifer. Rehm and others (1980) reported a very similar geometric mean (0.35 ft per day) for sandstones of the Fort Union Group in the Northern Great Plains. The investigators also noted that fine-grained sedimentary rocks (e.g., siltstones, claystones, and mudstones) associated with the Fort Union Group were much less permeable and reported a geometric mean of 0.007 ft per day (Rehm and others, 1980).

Recharge to the Wasatch aquifer is suspected to be primarily from areal infiltration and percolation of precipitation (King, 1974; Ground-Water Subgroup, 1974; Brown, 1980). Infiltration to the Wasatch aquifer may be enhanced by clinker throughout the area (Davis, 1976; Bloyd and others, 1986; Martin and others, 1988).

Ground-water flow in the Wasatch aquifer is suspected to be primarily local and related to topography, with discharge occurring primarily along streams adjacent to local recharge areas (Hagmaier, 1971; King, 1974; Bloyd and others, 1986; Martin and others, 1988) and possibly underflow out of the study area (Bloyd and others, 1986). Brown (1980) also noted that discharge to clinker may occur in some areas. Investigators differ on whether regional ground-water flow in the Wasatch aquifer occurs and the relationship between local ground-water flow and possible intermediate and regional ground-water flow is unclear (see discussions in Fogg and others (1991) and Lindner-Lunsford and Wilson (1992)). However, Martin and others (1988) suggest regional ground-water flow in the Wasatch aguifer occurs and flow is to the north, although the volume of flow is suspected to be small and the flow rate probably slow because of the low permeability of many of the rocks in the Wasatch Formation.

In the northern part of the study area, lithologic units comprising the Tongue River Member of the Fort Union Formation are exposed at land surface and directly overlie the Wyodak-Anderson coalbed aquifer (fig. 8). As discussed earlier, the Wasatch Formation and the Tongue River Member of the Fort Union Formations are very similar, both lithologically and hydrogeologically, and properties are expected to be similar. Consequently, some investigators combine the Wasatch Formation and the upper part of the Fort Union Formation (i.e., Tongue River Member, excluding the Wyodak-Anderson and other coalbed aquifers) into a single aquifer or hydrogeologic unit (Feathers and others, 1981; Lewis and Hotchkiss, 1981; Koch and others, 1982; Slagle and others, 1985; Hotchkiss and Levings, 1986; Bloyd and others, 1986). Convention in this report will be to assume that properties of the upper lithologic units of the Tongue River Member of the Fort Union Formation (i.e., above the Wyodak-Anderson coalbed aquifer) are similar to the Wasatch aquifer and the Tongue River Member above the Wyodak-Anderson coalbed aquifer will be considered as part of the Wasatch aquifer for all comparisons with the underlying coalbed aquifers (fig. 7).

Resource Extraction

The study area is located within the Powder River coal field. The Powder River coal field coincides with the boundary of the Powder River Basin (fig. 1) and has the largest coal resources of any coal field in the contiguous United States (Glass, 1997). Coals are present in both Cretaceous and lower Tertiary geologic formations in the basin, but the thickest and most frequently mined are the two formations of lower Tertiary age discussed previously—the Wasatch Formation of Eocene age and the Fort Union Formation of Paleocene age. Most of the coal mining occurs in the Wyoming part of the Powder River Basin; much of the mining in Wyoming occurs along the eastern margin and includes the study area, as indicated by the large number of coal-lease areas (fig. 9). Most of the coal in the basin and in the study area is mined from the Wyodak-Anderson coal zone in the Tongue River Member of the Fort Union Formation, the most important and well known coal bed or coal zone within the Powder River coal field.

The coal is primarily subbituminous in rank and low in trace elements (Stricker and others, 1998); the

coal also is low in sulfur and ash content (Ellis and others, 1998). Consequently, coal from the Wyodak-Anderson coal zone is very suitable for coal-fed power plants concerned with meeting increasingly stringent air-quality standards and is shipped to many states in the U.S. The coal is removed using strip-mining methods because the Wyodak-Anderson coal zone is present at or near the land surface in the eastern Powder River Basin.

Recently, there has been increased interest in the potential for coalbed methane production in the Powder River Basin. Methane suspected to be related to coal beds in the Powder River Basin in Wyoming was first reported by Olive (1957). Subsequently, Whitcomb and others (1966) and Lowry and Cummings (1966) published gas analyses from several water wells in the Powder River Basin in Wyoming indicating high concentrations of methane. Commercial extraction of coalbed methane began in the mid- to late-1980's in the Powder River coal field (Jones and De Bruin, 1990). Extraction greatly increased around 1997, when over 200 coalbed methane wells were in production and monthly methane production reached one billion cubic feet (De Bruin and Lyman, 1999). Since then, development continues rapidly as "the coalbed methane play in the Powder River Coal Field is currently the most active gas play in the United States" (De Bruin and Lyman, 1999, p. 67). More than 3,000 wells have been drilled as of July 2000, many more have been permitted (fig. 9), and thousands more are expected to be installed in the future.

Methane is removed from the coal by pumping water (dewatering) from coalbed methane production wells installed in coal beds. The wells are completed by installing well casing to the top of the coal bed, reaming the coal bed, and then leaving the coal bed open to the hole. Water is then removed from the well by installing a submersible pump in the open coal bed; pumping reduces hydrostatic pressure in the coal that allows the methane to be released (desorption). The gas is transported to the surface in the space between the tubing attached to the submersible pump and the well casing and the produced water is discharged to the surface via the tubing.

Because of the importance of the coal and gas resources in the area, many studies of the geology and hydrogeology of the area have been, and continue to be conducted. The rapid development of the Wyodak-Anderson coal zone as a source of coalbed methane has renewed interest in hydrologic processes throughout the Powder River Basin.

Acknowledgments

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WATER-LEVEL MEASUREMENTS

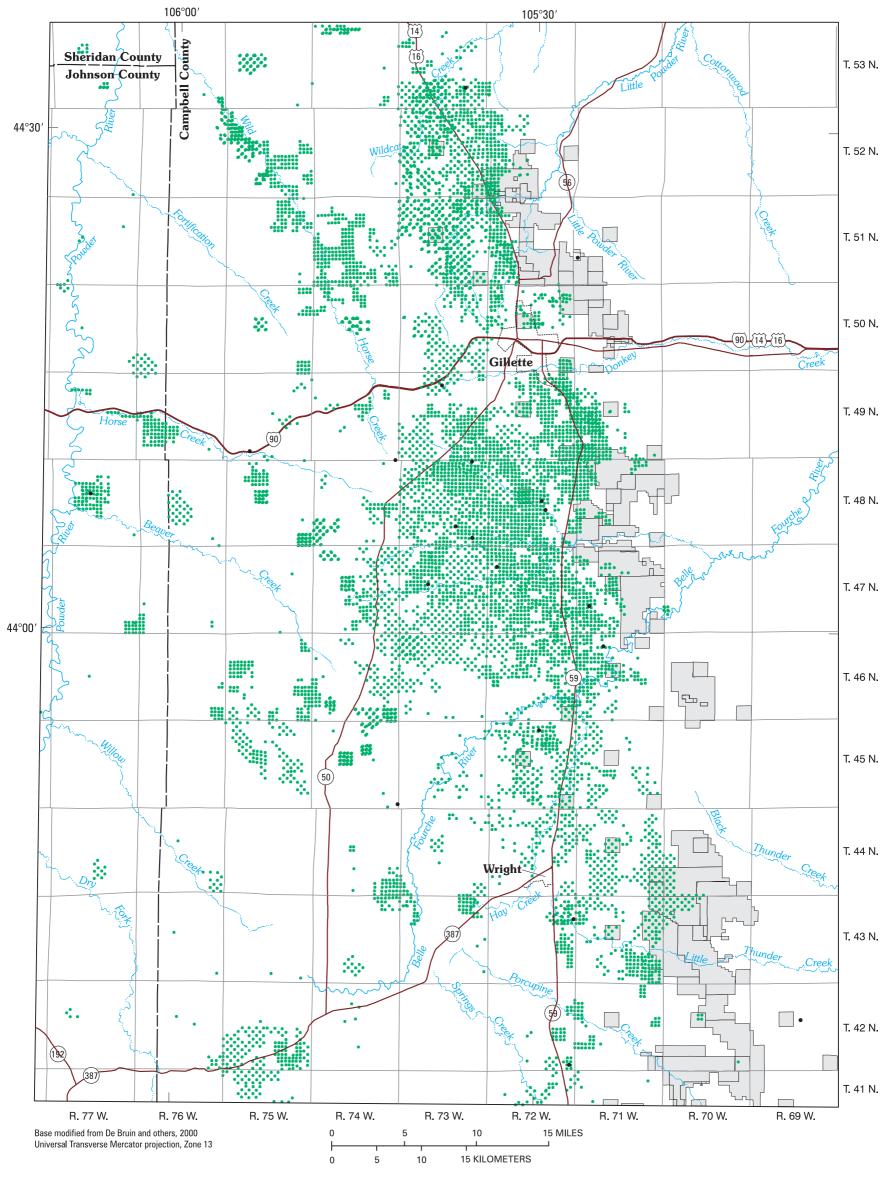
Well-completion information, water levels, and the identified aquifer for all wells sampled as part of this study are summarized in table 1. If a well was completed in the Wyodak-Anderson coal zone, individual coal beds within the zone were identified from well permits if possible. All but one of seventeen wells completed in a coalbed aquifer were in the Wyodak-Anderson coal zone or equivalent zone or bed (i.e., one well was completed in the Big George coal bed); well C15 was suspected to be completed in a coal bed located below the zone. Well locations are shown on figure 8.

Water levels were measured in all monitoring wells prior to sampling, including one monitoring-well cluster comprising three wells completed successively deeper in the Wasatch aquifer and five monitoring-well clusters comprising two wells each (one well completed in the Wasatch aquifer and one well completed successively deeper in the Wyodak-Anderson coalbed aquifer) (table 1). A monitoring-well cluster is a series of wells located close to each other where each well is drilled

and completed at a different depth. Water levels measured in successively deeper wells completed as part of a well cluster can be used to evaluate the hydraulic potential (differences in hydraulic head) for vertical ground-water flow at the location. There was a relatively strong vertical gradient within the Wasatch aquifer at the site of the well cluster (table 2) containing wells W3, W4, and W5. The decreasing hydraulic head with depth indicates that there was a hydraulic potential for downward ground-water flow in the Wasatch aquifer in the vicinity of this location if geologic conditions allow. There was a downward vertical gradient from the Wasatch aquifer to the Wyodak-Anderson coalbed aquifer as measured in three of the four well clusters (table 2) that were completed in both zones. This decreasing hydraulic head between aquifers indicated the potential for downward vertical flow from the Wasatch aquifer to the underlying Wyodak-Anderson coalbed aquifer. The fourth well cluster indicated hydraulic head increases with depth at one well cluster (table 2, wells W8 and C17), indicating an apparent hydraulic potential for upward ground-water flow, based on a water level measured below land surface in a well completed in the Wasatch aquifer (W8) and a flowing well discharging a mixture of gas and water completed deeper in the underlying Canyon coal bed of the Wyodak-Anderson coalbed aquifer (C17). The hydraulic potential for vertical ground-water flow could not be evaluated in one well cluster (wells W6 and C14) because the well completed in the Wasatch aquifer (W6) had just been installed and well development recently completed; therefore, the water level was not used because it did not represent the static water level in the aquifer.

It should be noted that all of these monitoring-well clusters are located within active coalbed methane production fields (fig. 9) and areas of coal mining. Significant drawdown has been observed in the Wyodak-Anderson coalbed aquifer in some of these areas as a result of both of these activities (Meyer, 1999); therefore, water levels measured in these monitoring wells may have been affected depending on hydraulic connection between the individual wells in the clusters. However, a downward vertical gradient in the Wasatch and Fort Union Formations in the study area prior to much development has been noted previously (Ground-Water Subgroup, 1974; Davis, 1976). In addition, the water-level measurements represent a discrete measurement at one point in time and water levels may vary with time.

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EXPLANATION

Coal-lease area

- Coalbed methane well--Permitted or production well (as of June 2000)
- Ground-water sampling site--spring discharging from clinker, monitoring well, or coalbed methane production well sampled as part of this study

Figure 9. Coal-lease areas, coalbed methane permitted or production wells, and ground-water sampling sites in the study area, eastern Powder River Basin, Wyoming, 1999.

Table 1. *Identification numbers, well-completion information, water levels, geologic* [P, perforated well casing; S, commercial well screen; O, open hole; L, well liner; --, water

Site number (fig. 8)	U.S. Geological Survey site-identification number	Local well number	Land-surface elevation (feet above sea level)	Depth of well (feet below land surface)	Elevation of bottom of well (feet above sea level)	Date of water- level measure- ment
W1	440253105385702	47-073-16cbc02	4,850	910	3,940	6-16-99
W2	440542105351802	48-073-36bcc02	4,740	700	4,040	6-17-99
W3	440724105291301	48-072-22adc01	4,574	410	4,164	6-24-99
W4	440724105291302	48-072-22adc02	4,574	185	4,385	6-25-99
W5	440724105291303	48-072-22adc03	4,574	80	4,490	6-25-99
W6	441019105414502	49-074-36ddc02	4,915	1,100	3,815	
W7	441451105375502	^{1,2} 49-073-03cc 02	4,775	750	4,025	6-17-99
W8	443241105360801	53-073-26dba01	4,045	³ 200	3,844	6-29-99
C1	433408105270101	² 42-072-36db 01	4,998	765	4,233	⁴ 5-17-98
C2	434252105264301	² 43-072-12da 01	4,861	⁵ 650	4,211	⁴ 5-08-99
C3	434941105412001	45-074-36dad01	4,883	⁶ 1,220	3,663	6-22-99
C4	435411105294001	45-072-03dbd01	4,876	⁷ 703	4,173	⁴ 12-20-96
C5	435915105242201	46-071-05dda01	4,625	340	4,285	⁴ 2-18-97
C6	440139105253301	47-071-30aaa01	4,709	399	4,310	⁴ 6-18-96
C7	440253105385701	47-073-16cbc01	4,850	1,219	3,631	6-15-99
C8	440358105331401	² 47-072-07ac 01	4,776	853	3,603	⁴ 4-22-98
C9	440542105351801	48-073-36bcc01	4,740	905	3,835	6-16-99
C10	440623105364101	48-073-27dac01	4,836	⁸ 1,057	3,779	⁴ 5-21-99
C11	440808106070601	² 48-077-16ac 01	4,093	⁹ 1,224	2,869	⁴ 6-18-99
C12	440756105293301	² 48-072-15dc 01	4,613	565	4,048.4	⁴ 5-24-93
C13	441017105352201	² 48-073-02aa 01	4,718	842	3,876.3	⁴ 2-04-98
C14	441019105414501	49-074-36ddc01	4,915	¹⁰ 1,234	3,681	6-23-99
C15	441047105535401	49-075-32adb01	4,439	¹¹ 1,795	2,598	6-24-99
C16	441451105375501	² 49-073-03cc 01	4,775	905	3,870	6-17-99
C17	443241105360802	53-073-26dba02	4,044	297	3,747	⁴ 10-9-98

¹Plots in section 4 when using Global Positioning System (GPS) location; well is assigned to section 3 on well permit, so this location was

²Well located in center of quarter-quarter section.

³Well was drilled to a depth of 201 feet below land surface but was completed to a depth of 200 feet below land surface.

⁴Water level from Wyoming State Engineer's Office well permit.

⁵Well was drilled to a depth of 675 feet below land surface but was completed to a depth of 650 feet below land surface.

⁶Well was cased to a depth of 1,220 feet below land surface but was perforated 1,050 to 1,070 feet below land surface.

⁷Well was drilled to a depth of 722 feet below land surface but was completed to a depth of 703 feet below land surface.

⁸Well was drilled to a total depth of 1,066 feet below land surface, and well casing was installed to a depth of 980 feet below land surface; well is open from 980 to 1,057 feet below land surface.

⁹Well is open to sandstone and shale from 1,003 to about 1,070 feet below land surface and coal from 1,070 to 1,224 feet below land surface.

¹⁰Well was drilled to a total depth of 1,263 feet below land surface but was completed to a depth of 1,234 feet below land surface.

¹¹Well was drilled to a total depth of 1,868 feet below land surface, plugged back to 1,841 feet below land surface, cased to 1,841 feet below land surface, and perforated from 1,728 to 1,795 feet below land surface.

units, and assigned hydrogeologic units for wells sampled in the study area

level not recovered from well installation; LS, water level at land surface]

Water level (feet below land surface)	Water-level elevation (feet above sea level)	Open interval (feet below land surface)	Type of open interval	Date con- struction completed	Geologic unit	Hydrogeologic unit
365.9	4,484.1	850-910	P	10-06-98	Wasatch Formation	Wasatch aquifer
260.2	4,479.8	670-700	P	10-24-98	Wasatch Formation	Wasatch aquifer
94.6	4,479.4	340-410	P	02-07-93	Wasatch Formation	Wasatch aquifer
36.0	4,534.0	140-180	S	04-22-98	Wasatch Formation	Wasatch aquifer
17.5	4,552.5	15-80	S	04-22-98	Wasatch Formation	Wasatch aquifer
		1,050-1,100	P	06-18-99	Wasatch Formation	Wasatch aquifer
291.3	4,483.7	690-750	P	10-14-98	Wasatch Formation	Wasatch aquifer
21	4,024.0	³ 140-200	S	05-21-98	Tongue River Member of the Fort Union Formation above Wyodak-Anderson coal zone	Wasatch aquifer
⁴ 406	⁴ 4,592.0	667-765	O	05-17-98	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 272	⁴ 4,589.0	⁵ 531-650	O	05-08-99	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
241.7	4,641.3	⁶ 1,050-1,070	P	12-11-98	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 319.5	⁴ 4,556.5	⁷ 661-703	O	12-20-96	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 155	⁴ 4,470.0	275-340	O	02-18-97	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 338	⁴ 4,371.0	340-399	O	06-18-96	Wyodak-Anderson coal zone	Coalbed aquifers
410.9	4,439.1	1,187-1,219	P	10-26-98	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 278	⁴ 4,498.0	760-853	O	05-28-99	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
307.6	4,432.4	860-905	P	10-22-98	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 360	⁴ 4,476.0	⁸ 980-1,057	O	05-21-99	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
⁴ LS	⁴ 4,093	⁹ 1,003-1,224	O	06-11-99	Big George coal bed	Coalbed aquifers
⁴ 203	⁴ 4,410.4	482-565	O	05-24-93	Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 703	⁴ 4,015.3	768.5-842.0	O	02-04-98	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
481.4	4,433.6	¹⁰ 1,156-1,234	L	11-17-98	Wyodak-Anderson coal zone	Coalbed aquifers
133.16	4,305.8	¹¹ 1,728-1,795	P	02-10-90	Coal bed or zone below the Wyodak-Anderson coal zone	Coalbed aquifers
328.9	4,446.1	845-905	L	10-11-98	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers
⁴ 32.8	⁴ 4,011.2	221-297	O	07-06-96	Canyon coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers

Table 2. Differences in water-level elevations and hydraulic potential for vertical ground-water flow in monitoring-well clusters

[--, water level not recovered from well installation; NC, not calculated; NA, not applicable because difference was not calculated because one well is discharging a mixture of gas and water]

Site number (fig. 8)	Geologic unit	Hydrogeologic unit	Water-level elevation	Difference in water-level elevations	Hydraulic potential for vertical ground-water flow
W1	Wasatch Formation	Wasatch aquifer	4,484.1	45	Downward
C7	Wyodak-Anderson coal bed of the Fort Union Formation	Coalbed aquifer	4,439.1		Downward
W2	Wasatch Formation	Wasatch aquifer	4,479.8	47.4	Downward
C9	Wyodak-Anderson coal bed of the Fort Union Formation	Coalbed aquifer	4,432.4		Downward
W6	Wasatch Formation	Wasatch aquifer			Cannot evaluate because
C14	Wyodak-Anderson coal bed of the Fort Union Formation	Coalbed aquifer	4,433.6	NC	water level not recovered from installation of well W6 prior to measurement
W7	Wasatch Formation	Wasatch aquifer	4,483.7	37.6	
C16	Wyodak-Anderson coal bed of the Fort Union Formation	Coalbed aquifer	4,446.1		Downward
W8	Tongue River Member of the Fort Union Formation	Wasatch aquifer	4,024.0		
C17	Wyodak-Anderson coal bed of the Fort Union Formation	Coalbed aquifer	Flowing	NA	Upward
W5	Wasatch Formation	Wasatch aquifer	4,552.5	18.5	5
W4	Wasatch Formation	Wasatch aquifer	4,534.0		Downward
W3	Wasatch Formation	Wasatch aquifer	4,479.4	54.6	Downward

GROUND-WATER QUALITY

Many natural factors can affect ground-water quality; however, the primary factors include the source and chemical composition of recharge water, the lithological and hydrological properties of the geologic unit, the various chemical processes occurring within the geologic unit, and the amount of time the water has remained in contact with the geologic unit (residence time). All of these factors can affect the type and quantities of dissolved constituents in ground water. The most abundant dissolved constituents measured are the major ions, which can be both positively charged (cations) and negatively charged (anions). Because of the

requirements of electroneutrality, cations and anions are present at equal concentrations in water and comprise most of the dissolved solids in ground water. The most abundant cations present in water are calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K); the most abundant anions are bicarbonate (HCO₃), chloride (Cl), and sulfate (SO₄). By measuring the concentrations of these ions in ground-water samples, the ionic composition of the water is determined and the chemical quality of the water can be characterized and described. A brief summary of the source or cause of these and other dissolved constituents and physical and general mineral characteristics commonly present in ground water is presented in table 3.

Table 3. Source or cause, and significance of dissolved-mineral constituents and physical properties of water (modified from Popkin, 1973, p. 85)

[mS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter]

Constituent or property	Source or cause	Significance
Specific conductance (μS/cm)	Mineral content of the water.	Indicates degree of mineralization. Specific conductance is a measure of the capacity of the water to conduct an electric current. Varies with temperature, concentration, and degree of ionization of the constituents.
рН	Acids, acid-generating salts, and free carbon dioxide lower the pH. Carbonates, bicarbonates, hydroxides, phosphates, silicates, and borates raise the pH.	pH is a measure of the activity of hydrogen ions. A pH of 7 indicates neutrality of a solution. Values higher than 7 denote increasing alkalinity; values lower than 7 indicate increasing acidity. Corrosiveness of water generally increases with decreasing pH. However, excessively alkaline water also may be corrosive.
	In most water, nearly all the hardness is due to calcium and magnesium. All metallic cations other than the alkali metals also cause hardness.	Consumes soap before a lather will form and deposits soap curd on bathtubs. Hard water forms scale in boilers, water heaters, and pipes. Hardness equivalent to or less than the bicarbonate and carbonate concentration is called carbonate hardness. Any hardness in excess of this is called noncarbonate hardness. Water with hardness of 60 mg/L or less is considered soft; 61 to 120 mg/L, moderately hard; 121 to 180 mg/L, hard; more than 180 mg/L, very hard.
magnesium (Mg)	Dissolved from many rocks and soil, but especially from lime- stone, dolomite, and gypsum. Calcium and magnesium are detected in large quantities in some brines. Magnesium is present in large quantities in seawater.	Causes most of the hardness and scale-forming properties of water; soap consuming (see hardness).
Sodium (Na) and potassium (K)	Dissolved from many rocks and soil; also in ancient brines, seawater, industrial brines, and sewage.	Large concentrations, in combination with chloride, give a salty taste. Moderate concentrations have little effect on the usefulness of water for most purposes. Sodium salts may cause foaming in steam boilers. A large sodium concentration may limit the use of water for irrigation.
	Action of carbon dioxide in water on carbonate rocks such as limestone and dolomite.	Bicarbonate and carbonate produce alkalinity. Bicarbonates of calcium and magnesium decompose in steam boilers and hot-water facilities to form scale and release corrosive carbon dioxide gas. In combination with calcium and magnesium, causes carbonate hardness.
Sulfate (SO ₄)	Dissolved from rocks and soil containing gypsum, iron sulfides, and other sulfur compounds. Commonly present in mine water and in some industrial wastes.	Sulfate in water containing calcium forms hard scale in steam boilers. In large concentrations, sulfate in combination with other ions gives bitter taste to water, and may have a laxative effect on some people. Some calcium sulfate is considered beneficial in the brewing process.
	Dissolved from rocks and soil. Present in sewage and found in large concentrations in ancient brines, seawater, and industrial brines.	In large concentrations in combination with sodium, gives salty taste to drinking water. In large concentrations increases the corrosiveness of water towards some metals.
Fluoride (F)		Fluoride in drinking water reduces the incidence of tooth decay when the water is consumed during the period of enamel calcification. However, it may cause mottling of the teeth and renal dysfunction, depending on the concentration of fluoride, the age of the child, quantity of drinking water consumed, and susceptibility of the individual.
_	Dissolved from many rocks and soil, commonly less than 30 mg/L. Large concentrations, as much as 250 mg/L, generally occur in alkaline water.	Forms hard scale in pipes and boilers. Transported in steam of high-pressure boilers to form deposits on blades of turbines. Inhibits deterioration of zeolite-type water softeners.
Dissolved solids	Primarily mineral constituents dissolved from rocks and soil.	Water containing more than 1,000 mg/L dissolved solids is unsuitable for many purposes.

The ionic composition of water is used to classify it into ionic types based on the dominant dissolved cation and anion, expressed in milliequivalents per liter (meq/L). A milliequivalent (meq) is a measurement of the molar concentration of the ion, normalized by the ionic charge of the ion. The dominant dissolved ion must be greater than 50 percent of the total. For example, water classified as a sodium-bicarbonate-type water contains more than 50 percent of the total cation milliequivalents as sodium and more than 50 percent of the total anion milliequivalents as bicarbonate. If no cation or anion is dominant (greater than 50 percent), the water is classified as mixed and the two most common cations or anions in decreasing order of abundance are used to describe the water type. For example, a water containing 45 percent sodium, 35 percent calcium, and 20 percent magnesium, and 55 percent bicarbonate, 30 percent sulfate, and 15 percent chloride would be classified as a sodium-calcium-bicarbonatetype water.

Quality Assurance and Quality Control

A review of water-quality analyses (appendix table 1) in this study suggested that four sampled monitoring wells (C3, C7, C9, and C14, fig. 8) were contaminated by grout during well completion. The pH values for ground-water samples collected from these wells were very alkaline (pH = 9.6, 10.5, 11.3, and 11.7), were much higher than for similar wells completed in the coalbed aguifers in the study area (Rice and others, 2000), and were uncommonly high for natural aquifers (Hem, 1985). High pH values in this range are typical for wells contaminated with alkaline grout (cement and/or bentonite) used to seal the annular space during well completion (Nielson, 1991). Nielson (1991, p. 585) described four ways that very alkaline water from annular seals can enter well screen areas and be sampled: "(1) Wells located in low permeability units with strong vertical gradients (i.e., grout bleeds directly downward); (2) Grout injected into the screened area of the well; (3) Bentonite seals too thin or ineffective; and (4) Fractured rock providing channels around bentonite seals." It is unclear which of these may have affected the water-quality analyses, but the approach used in this investigation was to remove all water-quality analyses for samples from these four wells.

Ion balances were calculated and examined for each ground-water sample as a quality-assurance check of the chemical analyses. The ion balance was calculated (in meg/L) as the total dissolved-cation concentration minus the total dissolved-anion concentration divided by the total concentration of ions dissolved in solution. The total cation concentration was calculated as the sum of calcium, magnesium, sodium, and potassium; the total anion concentration was calculated as the sum of acid-neutralizing capacity, chloride, fluoride, and sulfate. Inorganic nitrogen species (nitrite plus nitrate and ammonium) were not included in the calculations because neither was measured in the ground-water samples. Nineteen of twenty-one ground-water samples (about 90 percent) had ion balances within the +/- 6 percent range, indicating that the major-ion analyses were of good quality. The remaining two samples had ion balances of about 9 and 12 percent; these samples are still included and considered acceptable in this study because the ion balances are still relatively low, and unmeasured constituents such as organic anions, nutrients, and trace metals may contribute to higher ion balances (Hem, 1985).

A replicate sample (duplicate) is a ground-water quality-control sample collected sequentially after a regular sample (normal environmental sample); both are analyzed for the same constituents to assess the combined effects of field and laboratory procedures on measurement variability. Constituents measured in both samples are compared by calculating the relative-percent difference (RPD) using the equation given below. The RPD cannot be calculated for compounds that are below the minimum reporting level (MRL).

RPD = absolute value
$$\left(\frac{sample1-sample2}{\left(\frac{sample1+sample2}{2}\right)}\right) \times 100 (1)$$

Two replicate samples were collected during this study. Results of the RPD calculations are shown in table 4. RPD values greater than zero but less than 1 percent are reported as less than 1 percent (< 1 percent) in the table.

For the first replicate sample, RPDs for all but two measured constituents were less than 1 percent in one normal environmental sample and associated replicate sample, indicating very good precision (reproducibility) (table 4). The RPD was 4 percent for calcium and

Table 4. Calculated relative-percent differences between normal environmental and replicate ground-water samples

[mg/L, milligrams per liter; CaCO₃, calcium carbonate; TU, tritium units; < MRL, less than minimum reporting level; NC, not calculated because both normal environmental sample and replicate sample were less than minimum reporting level; ‰, per mil or parts per thousand]

		Sample 1		Sample 2			
Characteristic or constituent	Normal environmental sample	Replicate sample	Relative- percent difference ¹	Normal environmental sample	Replicate sample	Relative- percent difference ¹	
Acid-neutralizing capacity (ANC), laboratory (mg/L as CaCO ₃)	580	580	0	267	267	0	
Dissolved solids, calculated sum (mg/L)	624	622	< 1	4,020	4,020	0	
Hardness, total (mg/L as CaCO ₃)	120	120	0	2,500	2,500	0	
Sodium-adsorption ratio (SAR)	8	8	0	2	2	0	
Calcium, dissolved (mg/L)	25	26	4	550	550	0	
Magnesium, dissolved (mg/L)	14	14	0	280	270	¹ 4	
Sodium, dissolved (mg/L)	190	190	0	270	260	¹ 4	
Potassium, dissolved (mg/L)	13	12	8	14	14	0	
Bicarbonate, calculated from ANC ² (mg/L)	707	707	0	326	326	0	
Chloride, dissolved (mg/L)	7	7	0	18	17	3	
Sulfate, dissolved (mg/L)	1.2	1.2	0	2,700	2,700	0	
Fluoride, dissolved (mg/L)	1.1	1.1	0	0.3	0.3	0	
Silica, dissolved (mg/L)	20	20	0	17	16	6	
Tritium, TU	< MRL	< MRL	NC	6	9	40	
$\delta^2 H$ (‰)	-151.0	-150.3	< 1	-147.8	-147.2	< 1	
$\delta^{18}O$ (‰)	-19.99	-19.94	< 1	-19.03	-19.02	< 1	

¹Value rounded to nearest percent.

8 percent for potassium. In the second sample, RPDs for all but five constituents were less than 1 percent. RPDs for magnesium, sodium, chloride, and silica were about 3 to 6 percent. The RPD for tritium is high (about 40 percent), indicating poor precision between the two sample types; the source of the poor precision is unclear. Therefore, precision between all constituents but tritium is very good in the second set of samples.

Major-Ion Chemistry

Ground-water-quality data for samples collected from springs and wells are presented in the Appendix, and summary statistics for samples collected from wells are presented in tables 5 and 6. Visual descriptions and comparisons of data collected from springs and wells in the Wasatch aquifer are provided by plotting individual data values because the sample sizes are less than 10 (figs. 10, 11, and 12). Percentiles and boxplots were constructed for characteristics and constituents measured, analyzed, or calculated in samples collected from coalbed aquifers.

Dissolved solids are reported as a concentration value in mg/L (milligrams per liter) calculated by summing all major ions; dissolved-solids concentrations often are used to compare water quality between different groups of water samples. Dissolved-solids concentrations were used to compare data collected as part of this study to data collected by several other investigations with larger sample sizes (n > 30).

²Equivalent bicarbonate concentrations calculated from acid-neutralizing capacity (ANC) concentrations by dividing ANC concentrations (expressed as milligrams per liter of calcium carbonate) by 0.8202 (Hem, 1985, p. 57).

Table 5. Summary of water-quality data for ground-water samples collected from wells completed in the Wasatch aquifer [MRL, minimum reporting level; °C, degrees Celsius; NA, not applicable; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; CaCO₃, calcium carbonate]

Characteristic or constituent	Number of detections/ number of samples	Highest MRL	Minimum	50th percentile (Median)	Maximum
	Physical cha	aracteristics			
Water temperature, field measurement (°C)	8/8	NA	14	18	20
pH, field measurement (standard units)	8/8	0.1	7.2	7.8	8.9
	General minera	l characteristics			
Acid-neutralizing capacity (ANC), laboratory (mg/L as CaCO ₃)	7/7	1.0	129	378	1,020
Specific conductance, field measurement (μ S/cm at 25°C)	8/8	1.0	438	1,382	4,330
Dissolved solids, calculated sum (mg/L)	7/7	NA	263	1,010	4,020
Hardness, total (mg/L as CaCO ₃)	8/8	NA	22	97.5	2,500
Sodium-adsorption ratio (SAR)	8/8	NA	2	9	13
Major ions, in milligrams per liter, dissol	ved (sample filte	ered through 0.4	5-micrometer	· disposable car	rtridge filter)
Calcium	8/8	0.02	6.2	15.5	550
Magnesium	8/8	0.01	1.5	15.4	280
Sodium	8/8	0.09	97	225	480
Potassium	8/8	0.24	2.2	9.4	18
Bicarbonate, calculated from ANC ¹	7/7	NA	157	461	1,244
Chloride	7/8	0.3	5	9.6	18
Sulfate	8/8	0.3	10	130	2,700
Fluoride	7/8	0.1	0.3	0.85	1.5
Silica	8/8	0.1	8	10	17

¹Equivalent bicarbonate concentrations calculated from acid-neutralizing capacity (ANC) concentrations by dividing ANC concentrations (expressed as milligrams per liter of calcium carbonate) by 0.8202 (Hem, 1985, p. 57).

Despite small sample size (n = 7), the median dissolved-solids concentration for ground-water samples collected from wells completed in the Wasatch aquifer in the study area (1,010 mg/L) is the same (1,010 mg/L) as reported by Lowry, Wilson, and others (1986) for the Powder River drainage basin in Wyoming and Montana, and similar to the median dissolved-solids concentration (1,220 mg/L) reported by Larson (1984) for samples collected from the Wasatch aquifer in Campbell County (Wyoming), suggesting good comparability. In contrast, the median dissolved-solids concentration (1,010 mg/L) is about one-half the median dissolved-solids concentration (2,215 mg/L) reported by Martin and others (1988) for

samples collected from wells completed in the Wasatch Formation in the Powder River Basin. The difference may be attributable to the location and depth of the wells examined by Martin and others (1988). Those wells were located at coal mines at relatively shallow depths along the eastern margin of the study area. As will be discussed later in this report, the ionic composition of the shallow part of the Wasatch Formation is believed to be different than deeper parts of the formation; this apparent relationship between depth and ionic composition in the Wasatch Formation may explain the observed differences in median dissolved-solids concentrations between this study and the study by Martin and others (1988).

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Table 6. Summary of water-quality data for ground-water samples collected from wells completed in coalbed aquifers

[MRL, minimum reporting level; °C, degrees Celsius; NA, not applicable; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; CaCO₃, calcium carbonate; NC, not calculated because percentile is less than highest minimum reporting level]

	Number of detections /number of	Highest		10th	25th	50th percentile	75th	90th	
Characteristic or constituent	samples	MRL	Minimum	percentile	percentile	(Median)	percentile	percentile	Maximum
		Ph	ysical chara	cteristics					
Water temperature, field measurement (°C)	13/13	NA	14	15.2	17	19	20	26.6	27
pH, field measurement (standard units)	13/13	0.1	6.9	6.9	7.1	7.2	7.4	7.6	7.8
		Genera	al mineral cl	naracteristic	S				
Acid-neutralizing capacity (ANC), laboratory (mg/L as CaCO ₃)	13/13	1.0	346	349.6	432	584	788	1,924	2,570
Specific conductance, field measurement $(\mu S/cm \text{ at } 25^{o}C)$	13/13	1.0	665	672.6	839	1,070	1,610	3,504	4,180
Dissolved solids, calculated sum (mg/L)	13/13	NA	382	387.2	483	644	959	2,296	2,720
Hardness, total (mg/L as CaCO ₃)	13/13	NA	74	75.2	100	150	245	446	550
Sodium-adsorption ratio (SAR)	13/13	NA	5	5.4	6	7	8	19	26
Major ions, in milligra	ms per liter, o	lissolved (sa	mple filtere	d through 0.	45-micromet	er disposabl	e cartridge f	ilter)	
Calcium	13/13	0.02	15	15.8	20	36	50	59	62
Magnesium	13/13	0.01	8.4	8.5	11.4	15	28	37	39
Sodium	13/13	0.09	120	124	160	210	300	736	1,000
Potassium	13/13	0.24	4.9	5.2	7.3	12	13	35	48
Bicarbonate, calculated from ANC ¹	13/13	NA	422	426	527	712	1,103	2,350	3,134
Chloride	13/13	0.29	6.9	6.9	8	9.1	14	23	24
Sulfate	5/13	0.3	< 0.3	NC	NC	NC	0.95	1.6	1.8
Fluoride	13/13	0.1	0.6	0.68	1.0	1.2	1.4	1.8	1.9
Silica	13/13	0.1	7.4	8.1	9.8	10	11	16	20

¹Equivalent bicarbonate concentrations calculated from acid-neutralizing capacity (ANC) concentrations by dividing ANC concentrations (expressed as milligrams per liter of calcium carbonate) by 0.8202 (Hem, 1985, p. 57).

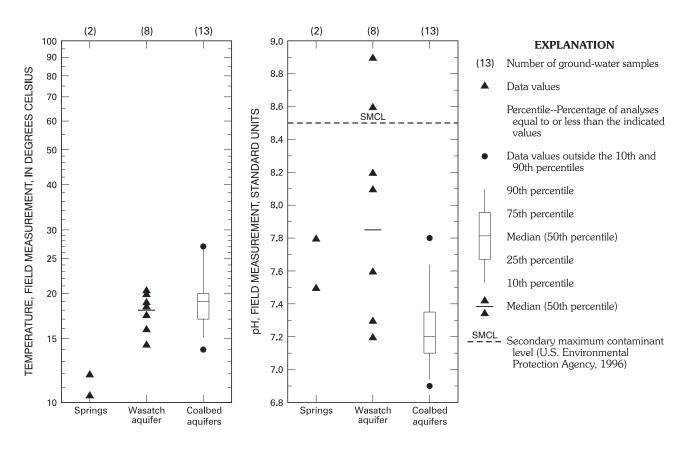


Figure 10. Physical characteristics of ground water, eastern Powder River Basin, Wyoming, 1999.

The median dissolved-solids concentration for 13 ground-water samples collected from wells completed in the coalbed aquifers (644 mg/L) is lower than reported by Martin and others (1988), 1,310 mg/L for 379 samples collected from 88 wells at coal mines. The 88 wells were located at the coal mines at relatively shallow depths along the eastern margin of the study area. Water quality of the coalbed aquifers in this area may be different because of the location of the wells in relation to clinker deposits and/or the burn line (the contact between the unburned coal or overburden) (Heffern and Coates, 1999); this will be discussed later in the report. In contrast, the median dissolved-solids concentration (644 mg/L) in this study is very similar to the median dissolved-solids concentration calculated for groundwater samples (680 mg/L) collected from 36 wells completed in coalbed aquifers in the study area as part of another investigation (Rice and others, 2000). That dataset represents a better comparison because groundwater samples were collected from coalbed aquifers throughout the study area.

Classification of Ionic Composition and Comparisons Between Aguifers

The relative ionic composition of ground-water samples collected from springs and wells in the study area are plotted on a trilinear diagram (fig. 13). A trilinear diagram, also frequently referred to as a Piper diagram (Piper, 1944), provides a convenient method to classify and compare water types based on the ionic composition of different water samples (Hem, 1985). Cation and anion concentrations for each ground-water sample are converted to total meq/L and plotted as percentages of their respective totals in two triangles (fig. 13). The cation and anion relative percentages in each triangle are then projected into a quadrilateral polygon that describes the water type or hydrochemical facies.

Samples collected from two springs in the study area both had the same dominant cation, calcium, but different dominant anions, sulfate and bicarbonate (fig. 13); samples collected from these springs would be classified as calcium-sulfate-type and calcium-bicarbonate-type waters.

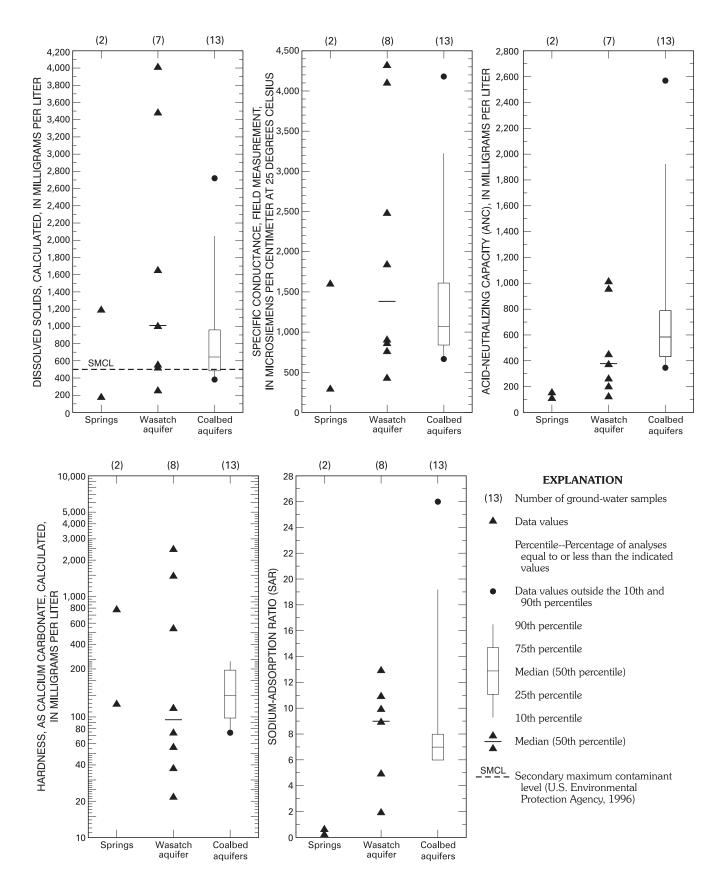


Figure 11. General mineral characteristics of ground water, eastern Powder River Basin, Wyoming, 1999.

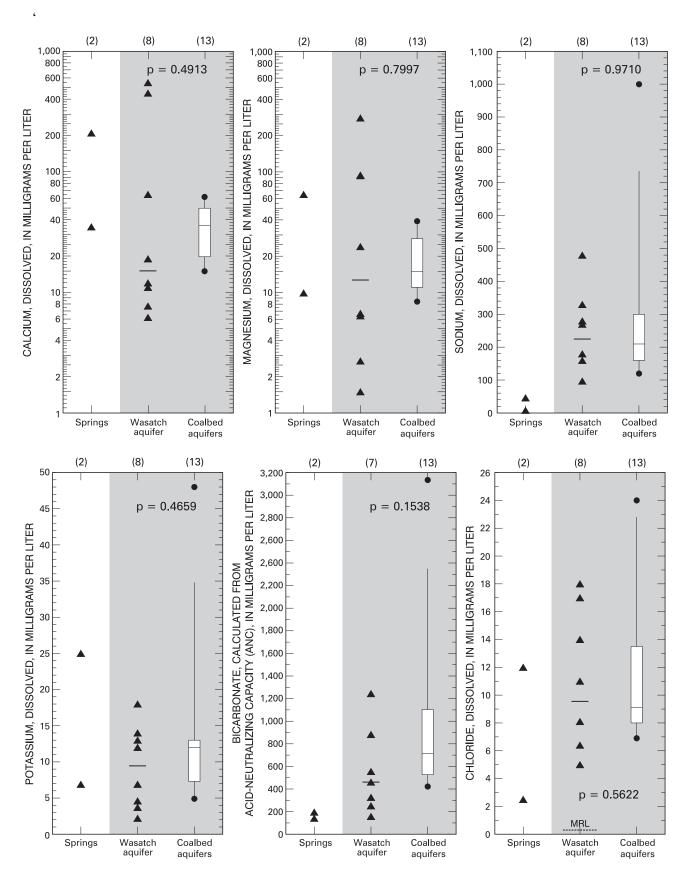
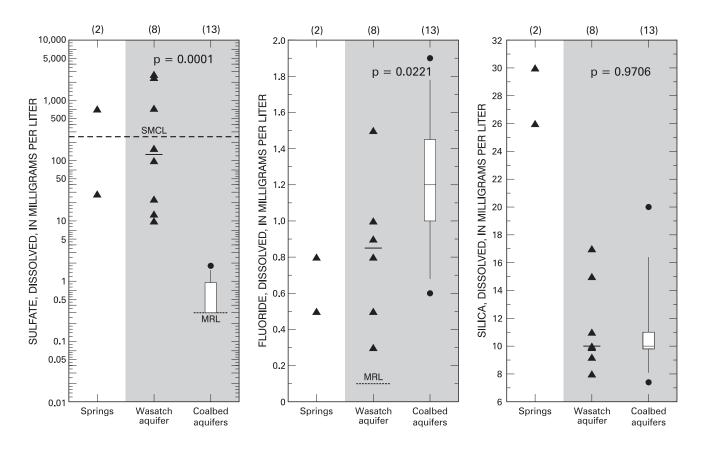


Figure 12. Concentrations of major ions in ground water, eastern Powder River Basin, Wyoming, 1999.



EXPLANATION

- (8) Number of ground-water samples
- ▲ Data values

Percentile--Percentage of analyses equal to or less than the indicated values

Data values outside the 10th and 90th percentiles

90th percentile

75th percentile

Median (50th percentile)

25th percentile

10th percentile

Median (50th percentile)

MRL

Highest minimum reporting level (MRL)

- SMCL -- Secondary maximum contaminant level (U.S. Environmental Protection Agency, 1996)

 $p=0.0221\,$ The two-sided probability (p-value) from the rank-sum statistical test. Conducted to compare median concentrations between samples collected from the Wasatch aquifer and the coalbed aquifers (shaded area). Probabilities (p-values) less than 0.05 are assumed to be statistically significant

Figure 12. Continued.

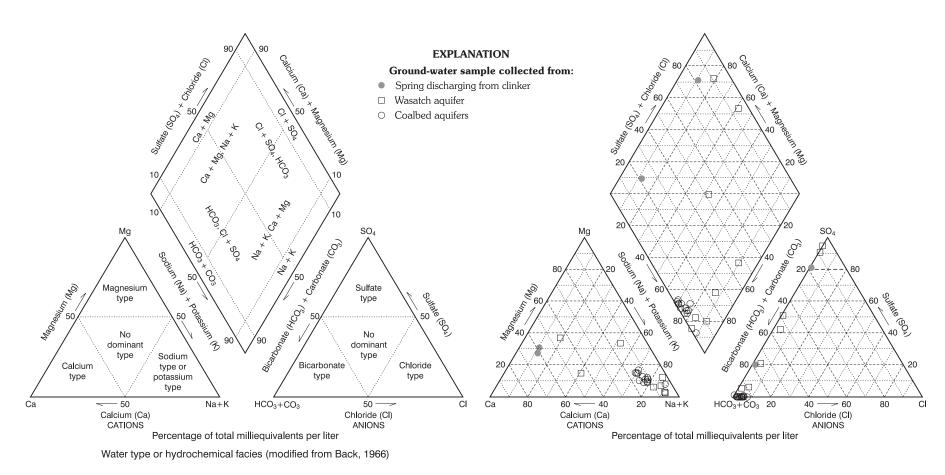


Figure 13. Trilinear diagram showing water types for ground-water samples collected from springs, Wasatch aquifer, and coalbed aquifers, eastern Powder River Basin, 1999. Nondetections set to 0.0 milligrams per liter.

Ground-water samples collected from wells had a different ionic composition than samples collected from the springs, but had very similar compositions with respect to each other, regardless of aquifer (fig. 13). All ground-water samples collected from the coalbed aquifers were sodium-bicarbonate-type waters and only three of eight samples collected from the Wasatch aquifer were not classified the same. Coalbed aquifers in the Powder River Basin in Wyoming and Montana are characterized by sodium-bicarbonate-type waters, as noted by other investigators (Law and others, 1991; VanVoast, 1991; Rice and others, 2000; Rice, 2000). Two of the three samples collected from the overlying Wasatch aguifer that were not sodium-bicarbonate-type waters were similar in ionic composition, with mixed cations, and with the same dominant anion, sulfate. The other sample was a mixed type, and plots in the sodium-magnesium-sulfate-bicarbonate part of the trilinear diagram. The similarity in water type between most ground-water samples suggests that similar geochemical processes may be controlling major-ion chemistry in these aquifers and that the waters had the same or similar origins.

The two-sided version of the rank-sum test (Helsel and Hirsch, 1992), also known as the Wilcoxon ranksum test (Wilcoxon, 1945) or Mann-Whitney test (Mann, 1945), is a nonparametric hypothesis test that was used to determine the probability that the median dissolved-solids and major-ion concentrations between aguifers were the same. The rank-sum test, like most nonparametric hypothesis tests, requires no assumptions about the population distribution, is resistant to outliers, and is more appropriate for small sample sizes where nonnormality is more difficult to detect. The null hypothesis of identical median concentrations between aguifers was rejected if the probability (p-value) of obtaining identical medians by chance was less than 0.05. Results of the hypothesis testing are provided in table 7 and in figure 12.

Median concentrations of all but two major ions were statistically the same between coalbed and overlying aquifers (p-values > 0.05). Fluoride concentrations were significantly different between aquifers (p-value = 0.0221). It is unclear why fluoride concentrations differ between aquifers, although it has been suggested that differences in fluoride concentrations within the Wasatch and Fort Union Formations may be due to local lithological variation (Wyoming Water Development Commission, 1985). While median sulfate concentrations are low in the overlying Wasatch

aquifer (130 mg/L), sulfate concentrations are very low in samples collected from the coalbed aquifers, as indicated by greater than 50 percent of data values at concentrations less than detectable limits. This contrast is easily seen on the boxplot and plotting of individual data values presented earlier (fig. 12). Results of the rank-sum test indicate that these differences are statistically significant (p-value = 0.0001) between aquifers. It should be noted that the severe censoring of sulfate concentrations in samples collected from the coalbed aquifers may reduce the ability of the rank-sum test to reject the null hypothesis when actually false (Helsel and Hirsch, 1992); however, the very low p-value (0.0001) for sulfate would indicate that this is not the case.

Table 7. Results of rank-sum tests between Wasatch aquifer and coalbed aquifers

[Bold text indicates a statistically significant difference with a p-value less than 0.05]

Constituent or major ion	Rank-sum test probability (p-value)
Dissolved solids	0.5261
Calcium	0.4913
Magnesium	0.7997
Sodium	0.9710
Potassium	0.4659
Bicarbonate	0.1538
Chloride	0.5622
Sulfate	0.0001
Fluoride	0.0221
Silica	0.9706

Areal Distribution

The ionic composition of ground-water samples can be represented by another type of water-quality diagram – the stiff diagram (Stiff, 1951). Stiff diagrams are used to compare the ionic composition of water samples between different locations, depths, or aquifers. The stiff diagram is a polygon created from three horizontal axes extended on both sides of a vertical axis. Cations are plotted on the left side of the axis and anions are plotted on the right side, both in meq/L. A greater distance from the vertical axis represents a larger ionic concentration. The cation and anion concentrations are connected to form an asymmetric polygon known as a

stiff diagram, where the size is a relative indication of the dissolved-solids concentration.

The areal distribution of stiff diagrams constructed for all water samples collected as part of this study are shown in figure 14. The horizontal axis units are the same on all stiff diagrams to aid comparisons between different sampling locations and aquifers. The color of the stiff diagrams indicates the aquifer and the number above each diagram is the calculated dissolved-solids concentration.

Like the trilinear diagram presented and discussed earlier, the stiff diagrams show and reinforce the similarity in ionic composition (sodium-bicarbonate-type water) observed in most ground-water samples, regardless of aquifer. Stiff diagrams constructed for samples collected from wells completed in the Wasatch aquifer show no areal pattern in water type (all but three are sodium-bicarbonate-type waters) or obvious areal pattern in dissolved-solids concentrations; this suggests that well location, in addition to aquifer, may not be related to water type. However, there may be a relationship between well depth and ionic composition in the Wasatch aquifer.

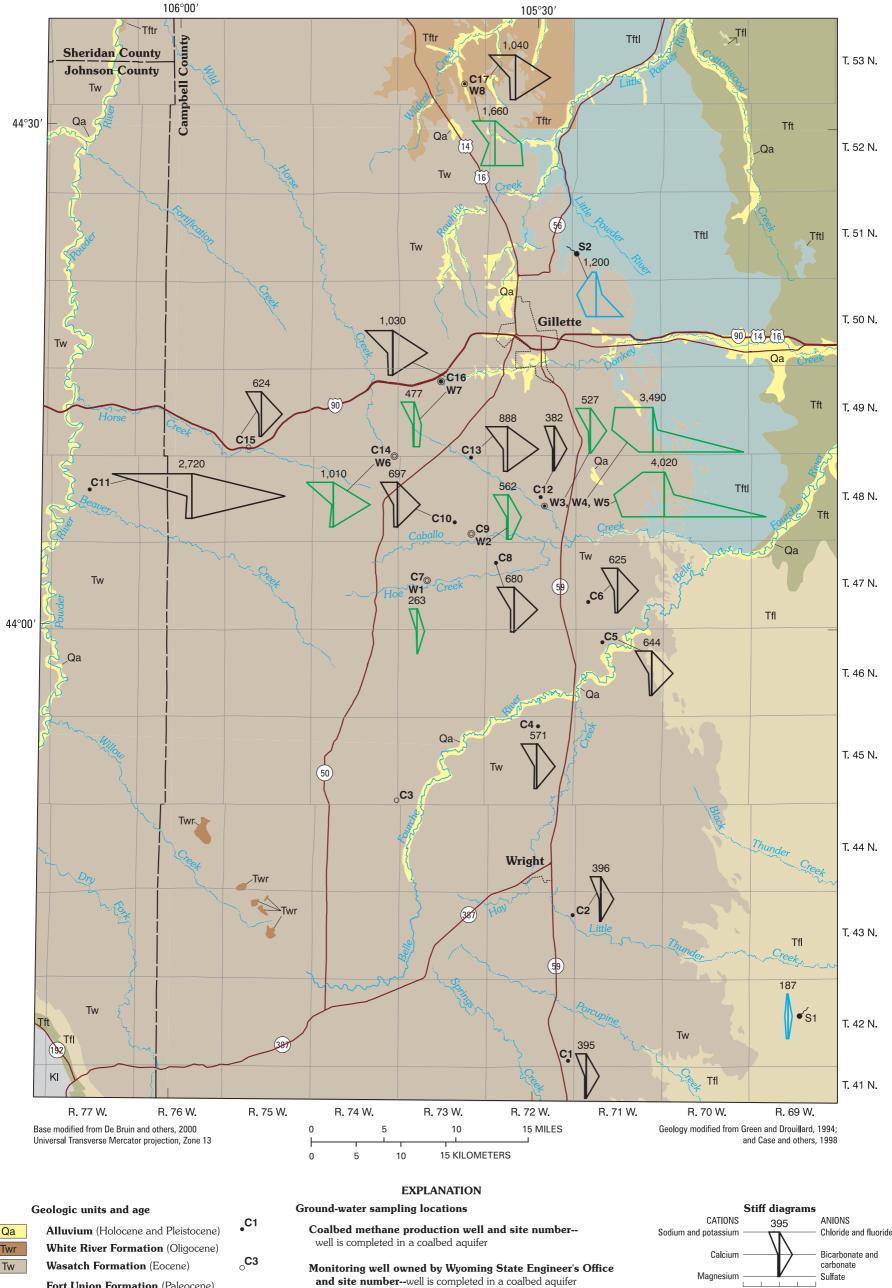
Stiff diagrams constructed for ground-water samples collected from wells completed in the coalbed aquifers also show no spatial pattern because the water type is the same (sodium-bicarbonate type) for all samples. The dissolved-solids concentration in the sample collected from well C11 (fig. 14), the most western site in the study area, is much higher than all other samples collected from wells completed in coalbed aquifers; this sample was collected from a well completed in the Big George coal bed, a coal bed considered equivalent to the Wyodak-Anderson coal zone (Flores and Bader, 1999). The Big George coal bed is both deeper and possibly older (Flores, 1999) than other coal beds in the Wyodak-Anderson coal zone (fig. 5). It should be noted that this well also is completed in sandstone and shale overlying the coal bed, and the effect on resulting water quality cannot be determined. However, another waterquality sample collected from this coal bed in the same area was similar in both water type (sodium-bicarbonate type) and high dissolved-solids concentration (Rice and others, 2000).

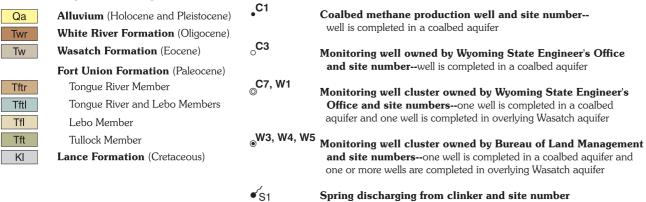
On the basis of ground-water samples collected during this study and additional samples collected in the area as part of another study (Rice and others, 2000), dissolved-solids concentrations in the Wyodak-

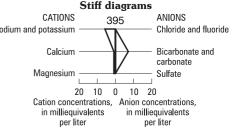
Anderson coalbed aquifer appear to be lower (generally less than 600 mg/L) south of the Belle Fourche River, near the southern Rochelle Hills (an area with clinker in the Lebo Member of the Fort Union Formation). Clinker in this area has been speculated to provide much recharge to coalbed aquifers downdip to the west in the study area (Davis, 1976; Daddow, 1986; Lowry, Wilson, and others, 1986; Martin and others, 1988; Heffern and others, 1996; Bureau of Land Management, 1999; Heffern and Coates, 1999).

Dissolved-solids concentrations represent total ions dissolved in solution; concentrations typically are lower near recharge sources where ground-water residence times (time in contact with aquifer materials) are relatively short and increase as ground water flows away from the source of recharge and residence times increase. As stated earlier, potentiometric contours suggest regional ground-water flow in the Wyodak-Anderson coalbed aguifer may be towards the west and northwest, away from clinker in the area (Daddow, 1986) (fig. 8). If the clinker in this area is the source of most of the recharge to the coalbed aquifers in the study area, dissolved-solids concentrations should increase as ground water flows away from the clinker deposits, a pattern that may be present and may explain the apparent increase in dissolved-solids concentrations as ground water flows north of the Belle Fourche River. Alternatively, the lower dissolved-solids concentrations in the area may not represent a true spatial pattern and may simply be the result of natural or random variation, different processes in the area, or a product of small sample size in the area.

Dissolved-solids concentrations in the Wyodak-Anderson coalbed aquifer appears to increase northeast of the Belle Fourche River and outside of the study area. Rice and others (2000) noted that dissolved-solids concentrations in the Wyodak-Anderson coalbed aquifer appears to increase from south to north and from east to west in the Powder River Basin in Wyoming. The investigators suggest that "this trend may be a result of increased water-rock interaction along a flowpath, an increase or change in composition of the ash content of the coal, or other factors not yet recognized" and "the increase in TDS (total dissolved solids) is generally a result of an increase in sodium and bicarbonate content of the water" (Rice and others, 2000, p. 4).







Number above stiff diagram is calculated dissolved-solids concentration, in milligrams per liter. Stiff diagram color indicates waterquality sample was collected from: black, coalbed aquifer; green, Wasatch aquifer; aquifer; blue, springs discharging from clinker

Vertical Distribution Within Aquifers

Dissolved-solids and major-ion concentrations in

ground-water samples collected from wells were com-

pared with well depth to determine if there was a statis-

tically significant relationship. Kendall's tau test statistic (Helsel and Hirsch, 1992), a nonparametric

measure of the monotonic correlation between two continuous variables, was calculated to measure the strength of this relationship. Kendall's tau is a correlation coefficient calculated using the ranks of the data rather than actual data values: therefore, the test statistic is resistant to outliers and can be used for datasets with moderate censoring. Tau is dimensionless and ranges between -1 and 1; when one variable increases as the second increases, tau is positive. If the variables vary in opposite directions, tau is negative. If a strong correlation is observed, tau, like any statistical correlation coefficient, does not explain the cause of the relationship. Kendall's tau correlation coefficients were considered statistically significant when probabilities (p-values) were less than 0.05; the null hypothesis of no correlation between dissolved-solids or major-ion concentrations and well depth was rejected if the probability of obtaining this correlation by chance was less than this value. The exact form of the test was used for the samples collected from the Wasatch aquifer because the sample size was less than 10; the large sample approximation was used for samples collected from the coalbed

Kendall's tau correlation coefficients and resulting probabilities (p-values or attained levels of significance) between dissolved solids or major ions and well depth for eight samples collected from the Wasatch aquifer are shown in table 8. Bicarbonate and fluoride were positively correlated with well depth; all other major ions were negatively correlated with well depth. Correlation between calcium and well depth is very strong (tau = -0.93) and statistically significant (p-value = 0.0004); correlation between sulfate and well depth was strong (tau = -0.79) and also is statistically significant (p-value = 0.0056). These statistically significant correlations between calcium and sulfate and well depth are illustrated in scatterplots (figure 15). The correlation between dissolved solids and well depth is relatively strong (tau = -0.62) and close to statistical significance (p-value = 0.07). Similar nonsignificant correlations were observed between magnesium and well depth (tau = -0.57, p-value = 0.062) and fluoride and well depth (tau = 0.54, p-value = 0.084).

aquifers because sample size was greater than 10.

Table 8. Kendall's tau correlation coefficients and resulting probabilities (p-values) between dissolved solids or major ions and well depth, Wasatch aquifer

[Bold text indicates a statistically significant correlation with a p-value less than 0.05]

Constituent or major ion	Kendall's tau correlation coefficient	Probability (p-value)
Dissolved solids	-0.62	0.07
Calcium	-0.93	0.0004
Magnesium	-0.57	0.062
Sodium	-0.46	0.144
Potassium	-0.43	0.178
Bicarbonate	0.24	0.562
Chloride	-0.36	0.360
Sulfate	-0.79	0.0056
Fluoride	0.54	0.084
Silica	-0.14	0.72

Kendall's tau correlation coefficients and resulting probabilities (p-values) between dissolved solids or major ions and well depth for 13 samples collected from coalbed aquifers are shown in table 9. Chloride and fluoride were negatively correlated with well depth; all other major ions were positively correlated with well

Table 9. Kendall's tau correlation coefficients and resulting probabilities (p-values) between dissolved solids or major ions and well depth, coalbed aquifers

[Bold text indicates a statistically significant correlation with a p-value less than 0.05; NC, not calculated because greater than 50 percent of data values are less than minimum reporting level]

Constituent or major ion	Kendall's tau correlation coefficient	Probability (p-value)
Dissolved solids	0.179	0.393
Calcium	0.115	0.5822
Magnesium	0.217	0.297
Sodium	0.167	0.4228
Potassium	0.462	0.0256
Bicarbonate	0.231	0.2721
Chloride	-0.256	0.2224
Sulfate	NC	NC
Fluoride	-0.026	0.902
Silica	0.308	0.1301

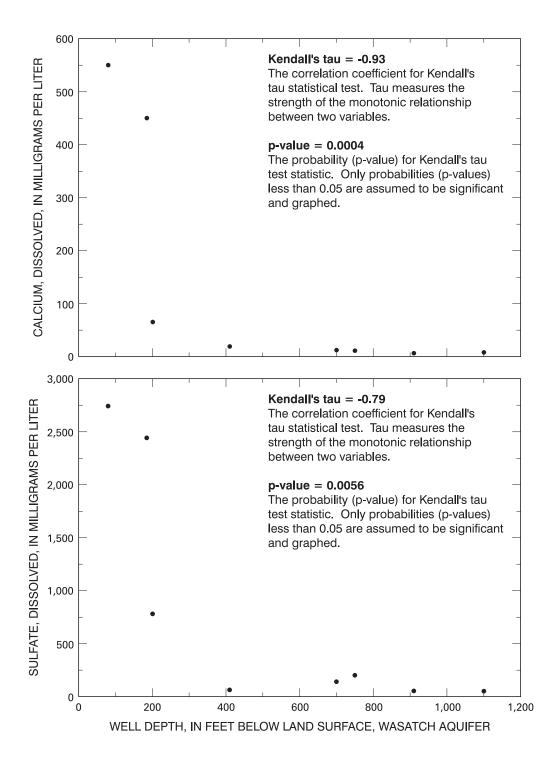


Figure 15. Calcium and sulfate concentrations in relation to well depth, Wasatch aquifer, eastern Powder River Basin, Wyoming, 1999.

The strongest correlation was observed between potassium and well depth; this positive correlation (tau = 0.462) is statistically significant (p-value = 0.0256), but not strong. The statistically significant correlation between potassium and well depth is illustrated in a scatterplot (fig. 16). Kendall's tau was not calculated for sulfate because greater than 50 percent of the data values were censored (less than the MRL).

Vertical Distribution Between Aquifers

Major-ion chemistry in the vertical dimension was examined qualitatively in three areas with monitoring-well clusters, including one area with a monitoring-well cluster where three wells are completed in the Wasatch aquifer (W5, W4, W3) and overlie a nearby well (C12) completed in the Wyodak-Anderson coalbed aquifer (fig. 14); each well is completed progressively deeper (fig. 17). Water-level measurements indicated the hydraulic potential for downward vertical ground-water flow at this location. Major-ion composition was sim-

ilar in ground-water samples collected from the two shallowest wells (W5 and W4) with both having mixed cations (calcium, magnesium, and sodium) and the same dominant anion, sulfate. The ionic composition was similar in samples collected from the two deepest wells (W3 and C12)—both were sodium-bicarbonatetype waters. As illustrated in figure 17, calcium, magnesium, and sulfate concentrations decrease with increasing well depth; these decreases correspond with a large decrease (from 4,020 mg/L to 382 mg/L) in dissolved-solids concentrations with increasing depth. Sodium concentrations increase with depth between the two shallowest wells (W5 and W4) but decrease with increasing well depth in all the other wells (W4, W3, and C12) completed successively deeper. Bicarbonate concentrations decrease with increasing well depth in the two shallowest wells (W5 and W4), increase with depth between the next two deepest wells (W4 and W3), and then decrease between the two deepest wells (W3 and C12).

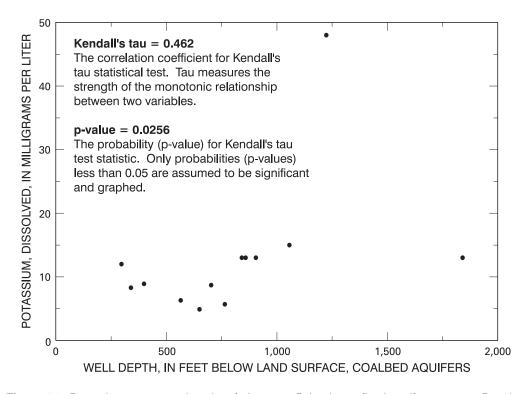


Figure 16. Potassium concentrations in relation to well depth, coalbed aquifers, eastern Powder River Basin, Wyoming, 1999.

Major-ion chemistry in the vertical dimension between the Wasatch aguifer and the underlying coalbed aquifers also was examined at two additional monitoring-well clusters composed of one well completed in the Wasatch aquifer and one well completed in the underlying coalbed aquifers (figs. 18 and 19). The major-ion chemistry in these two well clusters show a similar pattern to that of the well cluster previously discussed (Wells W5, W4, W3, and C12) where shallowest wells have a different ionic composition (i.e., water type) than the well completed deeper in the Wasatch aquifer or underlying coalbed aquifer. The groundwater samples collected from the monitoring-well cluster composed of wells W8 and C17 (fig. 18) indicate the water in the shallow well completed in the Wasatch aquifer is a mixed type and the water in the underlying coalbed aguifer is a sodium-bicarbonate type; calcium concentrations are about the same in the two wells, but magnesium, sulfate, and dissolved solids decrease with depth while sodium and bicarbonate concentrations increase. The ground-water samples collected from the well cluster composed of wells W7 and C16 (fig. 19) indicate the water in the well completed in the Wasatch aquifer is a sodium-bicarbonate-sulfate type and the water in the underlying coalbed aquifer is a sodiumbicarbonate type; calcium, magnesium, bicarbonate, and dissolved-solids concentrations increase with increasing depth, and sodium and sulfate concentrations decrease with depth (fig. 19).

All ground-water samples collected from coalbed aquifers during this study were sodium-bicarbonatetype waters. Ground-water samples collected from the overlying Wasatch aguifer were either mixed-type waters or sodium-bicarbonate-type waters; the mixedtype waters in these aguifers were from relatively shallow wells, generally completed to depths less than about 200 feet, and the sodium-bicarbonate waters were from deeper wells. Results from the rank-sum statistical test (table 7) indicated statistically significant differences in median concentrations of both fluoride and sulfate between ground-water samples collected from the Wasatch aquifer and ground-water samples collected from the underlying coalbed aquifers. Statistically significant correlations were observed between calcium and sulfate concentrations and well depth for groundwater samples collected from the Wasatch aquifer (table 8); nonsignificant correlations were observed between dissolved solids, magnesium, fluoride, and well depth. A statistically significant correlation was

observed between potassium and well depth in samples collected from the coalbed aquifers (table 9). All of these comparisons, both qualitative and statistical, show the most striking differences in ionic composition between the Wasatch aquifer and the underlying coalbed aquifers are observed in sulfate concentrations; this difference appears to be related to depth.

Geochemical Processes

Qualitative and statistical examination of the majorion chemistry of ground-water samples collected during this study suggests there is a relationship between depth and ionic composition in the Wasatch aquifer overlying the coalbed aquifers. A relationship between well depth and major-ion composition of ground water from lower Tertiary aguifers in the Powder River Basin has been noted by many other investigators. The relationship is reflected by the presence of two major-ion compositional systems—generally, a shallow system with mixed cation composition (calcium, magnesium, and lesser amounts of sodium) and either bicarbonate or sulfate as the dominant anion, and a deeper, underlying system where sodium and bicarbonate are the dominant ions. This apparent "zonation" in major-ion composition was first noted by Whitcomb and others (1966) for groundwater samples collected from the Fort Union Formation in Johnson County, Wyoming; the investigators reported that "the quality of water in the Fort Union Formation seems to be related to the depth of the water-bearing zone" (Whitcomb and others, 1966, p. 69). They noted that water from wells less than 500 feet deep in Johnson County, Wyoming, is typically of a sodium-sulfate, calcium-sodium sulfate, or calcium-sulfate type with high dissolved-solids concentrations, and water from deeper wells is sodium-bicarbonate type with lower dissolved solids.

In a study of the geochemistry of waters in the Wasatch and Fort Union Formations in the Powder River Basin within Wyoming, Hagmaier (1971) noted changes in major-ion chemistry with depth in lower Tertiary aquifers and suggested three "divisions" or "zones" with different water types—"shallow ground water, deep ground water from the Wasatch Formation, and deep ground water from the Fort Union Formation" (Hagmaier, 1971, p. 6). In Hagmaier's classification, shallow ground water is typically represented by calcium-sodium-sulfate-bicarbonate-type water in recharge areas

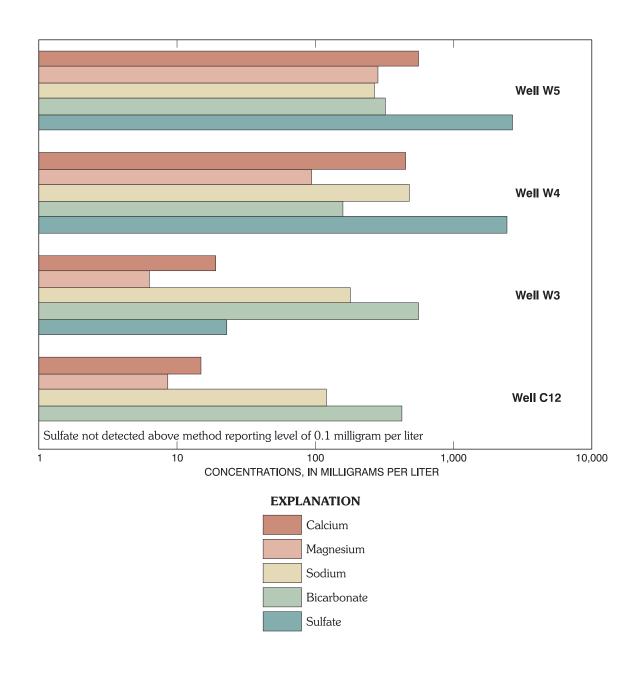
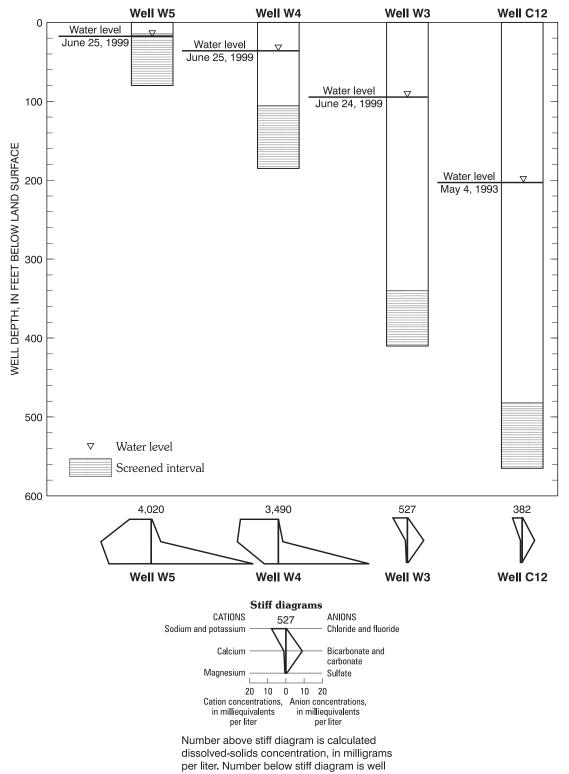


Figure 17. Calcium, magnesium, sodium, bicarbonate, and sulfate concentrations in relation to the clustered wells W5, W4, W3, and C12 in the eastern Powder River Basin, Wyoming, 1999.



number. Wells W5, W4, and W3 are completed in the Wasatch aquifer and well C12 is completed in the Wyodak-Anderson coalbed aquifer.

Figure 17. Continued.

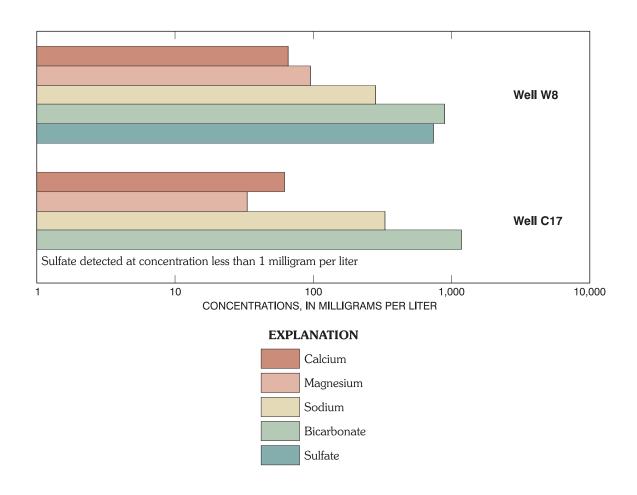
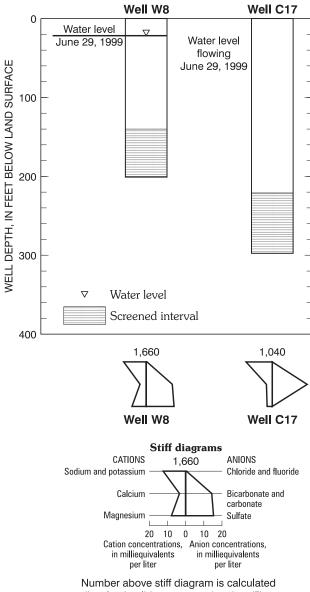


Figure 18. Calcium, magnesium, sodium, bicarbonate, and sulfate concentrations in relation to the clustered wells W8 and C17 in the eastern Powder River Basin, Wyoming, 1999.



Number above stiff diagram is calculated dissolved-solids concentration, in milligrams per liter. Number below stiff diagram is well number. Well W8 is completed in the Wasatch aquifer and well C17 is completed in the Wyodak-Anderson coalbed aquifer.

Figure 18. Continued.

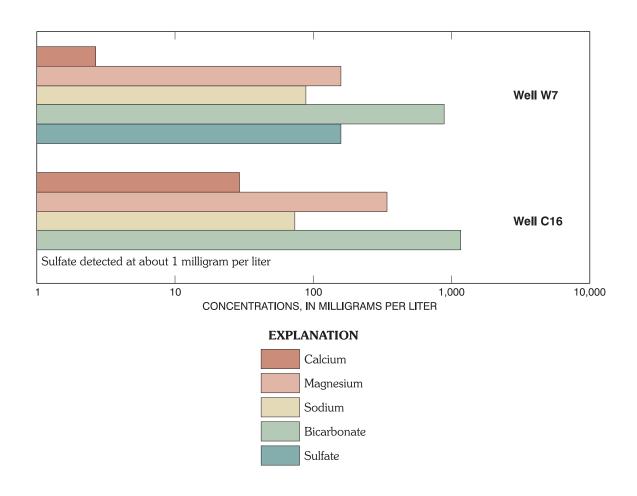
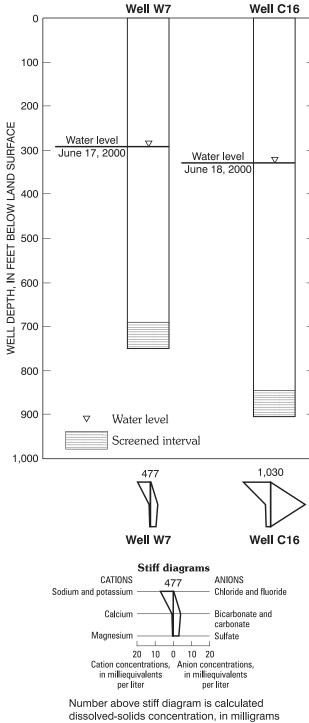


Figure 19. Calcium, magnesium, sodium, bicarbonate, and sulfate concentrations in relation to the clustered wells W7 and C16 in the eastern Powder River Basin, Wyoming, 1999.



Number above stiff diagram is calculated dissolved-solids concentration, in milligrams per liter. Number below stiff diagram is well number. Well W7 is completed in the Wasatch aquifer and well C16 is completed in the Wyodak-Anderson coalbed aquifer.

Figure 19. Continued.

and sodium-calcium-bicarbonate-sulfate-type water in local discharge areas; deep ground water from the Wasatch Formation is typically represented by sodium-calcium-sulfate-bicarbonate-type water; and deep ground water from the Fort Union Formation is typically represented by a sodium-bicarbonate-type water. Similarly, a study conducted by the Ground-Water Subgroup (1974) suggested that water from shallow aquifers in the Wasatch and Fort Union Formations in the Gillette area is generally a "calcium and/or magnesium-sulfate water" and "as depth to the aquifer increases, calcium and magnesium ions give way to sodium ions, and sulfate is at least partially replaced by bicarbonate ions," resulting in a sodiumbicarbonate-type water (Ground-Water Subgroup, 1974, p. 35). Lee (1981), in a comprehensive evaluation of the geochemistry of waters in the Fort Union Formation of the Powder River Basin in southern Montana, noted the presence of two distinct geochemical systems—a shallow, localized system generally less than about 200 ft deep that is chemically dynamic with highly variable water chemistry, and a deeper, regional system greater than about 200 ft deep that is chemically stagnant with water chemistry characterized by sodium and bicarbonate. The shallow geochemical system probably coincides with local ground-water flow, while the deeper geochemical system probably is dominated by regional ground-water flow (Lee, 1981; Slagle and others, 1985). Feathers and others (1981) also noted that ionic composition in waters from the Wasatch and Fort Union Formations in the Powder River Basin in Wyoming have a relationship to well depth. Lowry, Wilson, and others (1986, p. 99, fig. 8.4.3-2) noted the same compositional change for waters from lower Tertiary and Upper Cretaceous aquifers in the Powder River drainage basin in Wyoming and Montana occurs and at a depth similar to that noted by Lee (about 200 feet). Rankl and Lowry (1990) examined major-ion composition with depth in lower Tertiary and Upper Cretaceous aquifers in the Powder River Basin in Wyoming and Montana and noted the same changes in ionic composition, although at a depth up to 500 feet (same as Whitcomb and others (1966)). Conceptually, and using nomenclature similar to that presented by Lee (1981), the relation of water type to aquifers in the study area is shown in figure 20.

Although some of these investigators were often discussing water-quality characteristics and geochemi-

cal processes in the Fort Union Formation, or combining the Wasatch and Fort Union Formations into a single hydrogeologic unit in the Powder River Basin, the Wasatch Formation, as discussed earlier, is very similar to and essentially indistinguishable from the Fort Union Formation in depositional and lithological composition (Lowry and Cummings, 1966; Davis, 1976; Flores and others, 1999), although it has been suggested that coal beds and sandstone deposits may be less common in the Wasatch Formation (Lowry and Cummings, 1966, p. 37). Consequently, many of these investigators have noted that the same geochemical processes probably control water chemistry in both lower Tertiary formations (Lowry and Cummings, 1966; Ground-Water Subgroup, 1974; Feathers and others, 1981; Lowry, Wilson, and others, 1986; Rankl and Lowry, 1990). It also should be noted that many of these discussions are referring to the entire Fort Union Formation or combined Fort Union and Wasatch Formations and that processes may differ or be somewhat altered within a single coal bed or zone.

Cation exchange is the chemical reaction frequently cited to explain the high percentage of sodium compared to calcium and magnesium in water from the Fort Union Formation in the Powder River Basin (Renick, 1924; Riffenburg, 1925; Lowry and Cummings, 1966; Whitcomb and others, 1966; Hagmaier, 1971; Lee, 1981; Woessner and others, 1981; Lowry, Wilson, and others, 1986; VanVoast and Reiten, 1988; VanVoast, 1991) in Wyoming and Montana, and correspondingly in the Wasatch Formation in Wyoming (Lowry and Cummings, 1966; Whitcomb and others, 1966; Hagmaier, 1971). Cation exchange is a reaction in which the calcium and magnesium in the water are exchanged for sodium that was adsorbed to aquifer solids such as clay minerals, resulting in higher sodium concentrations and softer water (decreased calcium and magnesium concentrations). The generalized reactions (Hem, 1985, p. 13) are as follows:

$$Na_2X + Ca^{2+} \rightleftharpoons CaX + 2Na^+$$
 (2)

$$Na_2X + Mg^{2+} \stackrel{\longrightarrow}{\leftarrow} MgX + 2Na^+$$
 (3)

Where Na^+ = sodium ion

 Ca^{2+} = calcium ion

 Mg^{2+} = magnesium ion

X = aquifer solid

Hagmaier (1971) and Lee (1981) both noted that calcium and magnesium cations change from dominant to subordinate cations in relation to total cations with increasing depth and as ground water flows away from sources of recharge. Similar conclusions were reached earlier by Hamilton (1970) in western North Dakota and Riffenburg (1925) in the Northern Great Plains of the United States.

Sulfate reduction in water in the Fort Union Formation in Wyoming and Montana was suggested by investigators based on the relatively high percentage of bicarbonate in comparison to sulfate and by the detection of hydrogen sulfide and hydrocarbon gases such as methane in the water at many locations (Riffenburg, 1925; Lowry and Cummings, 1966; Whitcomb and others, 1966; Hagmaier, 1971; Dockins and others, 1980; Lee, 1981; Woessner and others, 1981; Lowry, Wilson, and others, 1986; Van Voast and Reiten, 1988; Van Voast, 1991). These observations, in combination with geochemical modeling at two coal mines, led Martin and others (1988) to conclude that sulfate reduction is likely an ongoing process at some locations in the Powder River Basin. Sulfate reduction is a process where bacteria obtain energy for metabolism from oxidation of relatively simple organic compounds. That oxidation is coupled to sulfate reduction. Byproducts of this activity are bicarbonate and hydrogen sulfide. This process generally occurs when no free oxygen is available (anaerobic or reducing conditions). The generalized reaction (Drever, 1997, p. 161) for sulfate reduction is as follows:

$$SO_{4}^{2} + 2C_{\text{organic}} + 2H_{2}O = H_{2}S + 2HCO_{3}^{2}$$
 (4)

The presence of hydrogen sulfide (H_2S) is often indicated by the presence of a "rotten-egg" odor; this odor was frequently detected in ground-water samples collected from the Wasatch aquifer and coalbed aquifers during this study. Dockins and others (1980), using stable isotopes of sulfur, showed that bacterially-mediated sulfate reduction is probably responsible for low sulfate concentrations and most of the sulfide production in the Fort Union Formation in the Powder River Basin in southeastern Montana. The investigators also noted that sulfate-reducing bacteria were detected in 25 of 26 of their ground-water samples.

Most of these investigators suggest both processes in combination may explain the observed ionic composition and zonation of water from the Wasatch and Fort Union aquifers in the Powder River Basin of both Wyoming and Montana. The general underlying assumption is that ground water associated with recharge (probably areas 1, 2, and 3 in the Wyodak-Anderson coal zone and area 4 in the shallow geochemical zone, fig. 20) is represented by water dominant in calcium, magnesium, and sulfate, with lesser amounts of sodium and bicarbonate (Hagmaier, 1971; Lee, 1981; Woessner and others, 1981). As ground water flows away from the source of recharge, the interaction between water and rock increases. Sodic lithologic units are encountered as the ground water moves along a flowpath and calcium and magnesium ions are exchanged for sodium ions attached to aquifer solids. Anaerobic sulfate-reducing bacteria, in the presence of organic material in coals and carbonaceous shales, also act on the ground water as it moves along a flowpath. Therefore, both reactions result in a decrease in calcium, magnesium, and sulfate, and a corresponding increase in sodium and bicarbonate as ground water flows away from the source of recharge and results in a water that evolves to a sodium-bicarbonate type (areas 5 and 7 in the deep geochemical zone and area 6 in the Wyodak-Anderson coal zone, fig. 20).

With the possible exception of Hagmaier (1971), Lee's evaluation of the water quality in the Fort Union Formation in the Powder River Basin in southern Montana is still the most comprehensive examination of the water chemistry in relation to hydrogeologic and geochemical conditions. However, it should be noted that many of the conclusions reached by Lee (1981) are very similar to conclusions reached by Hagmaier (1971) for the geochemistry of waters in the same aquifers in the Powder River Basin in Wyoming, even though both investigators appear to have reached their conclusions independently. As discussed previously, Lee suggests the presence of two distinct geochemical systems: a shallow, localized, chemically dynamic system generally less than 200 feet (area 4 in the shallow geochemical zone, fig. 20) and an underlying deeper, regional, chemically static system (areas 5 and 7 in the deep geochemical zone and area 6 in the Wyodak-Anderson coal zone, fig. 20). At topographically high locations and from springs, water from the shallow system probably represents recharge waters and the dominant ions are magnesium, calcium, sodium, and bicarbonate, with moderate amounts of sulfate and low concentrations of chloride. At topographically low locations, water in the shallow system is dominant either in sodium and sulfate

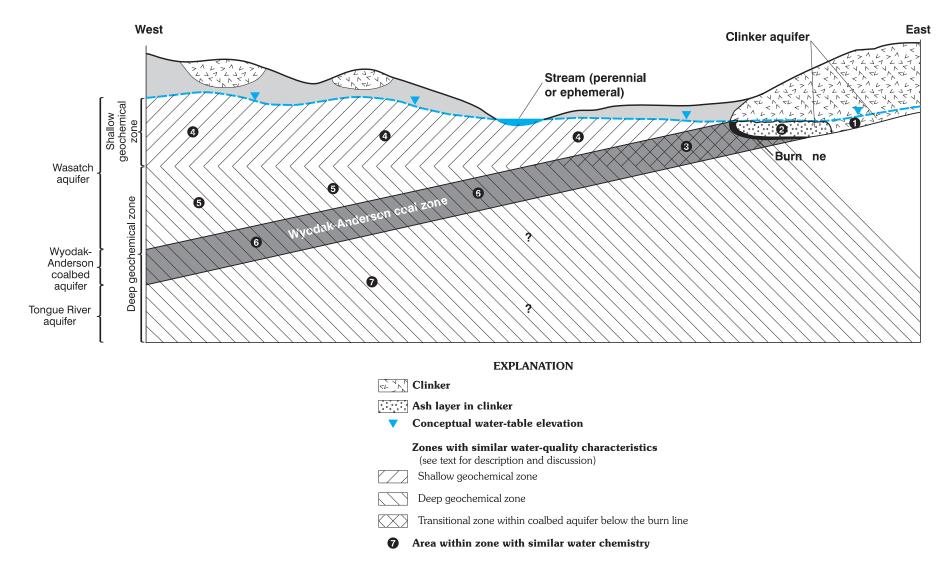


Figure 20. Conceptual model of major-ion composition in relation to hydrogeologic units, eastern Powder River Basin, Wyoming. Water types associated with numbered areas within geochemical zones are described and discussed in text.

with lower concentrations of magnesium, calcium, and bicarbonate, or is dominant in sodium and bicarbonate with lower concentrations of magnesium, calcium, and sulfate.

Lee proposed three general trends in the major-ion composition of ground water as it flows away from recharge areas as well as the geochemical processes that might produce the trends. The three trends are: (1) enrichment in sodium and sulfate, (2) enrichment in sodium and depletion of sulfate, and (3) depletion of sodium and sulfate. Lee found the first trend was the most common trend in the shallow system, although all three trends were observed. Lee concluded that the primary chemical reactions that contribute to sodium enrichment are dissolution of minerals such as sodium feldspars by infiltrating recharge waters in combination with cation-exchange on clay minerals, although other reactions of less significance also may occur. Direct sulfate enrichment may be attributed to the weathering of pyrite and dissolution of gypsum (also noted in Dockins and others (1980)), or indirectly by precipitation of calcium and magnesium carbonates that remove bicarbonate from solution (also suggested by Hagmaier (1971)). As ground water continues to flow away from the source of recharge, the trend towards sulfate enrichment is reversed and relative depletion of sulfate is commonly observed (second trend).

Bacterially mediated sulfate reduction is the chemical reaction suspected to explain the decreases in sulfate in both the shallow and deeper systems. Lee proposed that the observed trend of sodium and sulfate depletion (third trend) may be explained by mixing of infiltrating ground water with older ground water that results in dilution. In addition, water in the deeper system, typically with sodium-bicarbonate-type waters, may locally leak upward into the shallow system and decrease the relative percentage of sulfate. In the chemically stagnant deeper system, Lee suggests bacterially mediated sulfate reduction was the dominant geochemical process and results in water that is primarily sodium-bicarbonate type.

Carbonate equilibria also may be controlling the amount of dissolved calcium and magnesium in solution. The presence of dissolved constituents at relatively high concentrations (i.e., sodium and bicarbonate concentrations in most samples collected from all aquifers in the study area) can control the amount of calcium and magnesium in solution through the precipitation of carbonate minerals. The reader is referred to Hem (1985), Stumm and Morgan (1996), and Drever (1997) for more

detailed discussions of carbonate equilibria and equilibrium water chemistry.

Waters in the coalbed aquifers in some areas may evolve to a sodium-bicarbonate-type water through a different combination of hydrological and geochemical processes. Heffern and Coates (1999) examined majorion composition in clinker associated with the Wyodak-Anderson coalbed aquifer along the eastern margin of the basin and study area (Rochelle Hills area) and speculated on the processes responsible for the composition of the waters in the deposits. As described earlier, the clinker in this area is often directly updip and in hydraulic connection with the Wyodak-Anderson coalbed aquifer (fig. 20) and the deposits in this area are suspected to be the source of much of the recharge to the aquifer in the study area. The investigators noted several trends in major-ion chemistry in the clinker: (1) Waters upgradient of the burn line (the contact between the clinker and unburned coal or overburden) are highly oxygenated with low dissolvedsolids concentrations and are primarily calciumbicarbonate-type waters (area 1 in the Wyodak-Anderson coal zone, fig. 20), and (2) waters "ponded" adjacent to or near the burn line are frequently characterized by high sulfate concentrations and high dissolved-solids concentrations (area 2 in the Wyodak-Anderson coal zone, fig. 20). Waters in the Wyodak-Anderson coalbed aquifer immediately downgradient of the burn line (and in hydraulic connection with the clinker) are frequently characterized by moderate dissolved-solids concentrations and sodiumbicarbonate-type waters typically seen in the coalbed aquifers in the study area (areas 3 and 6 in the Wyodak-Anderson coal zone, fig. 20). The investigators speculate on the processes that result in the observed chemistry. The following quotation is from Heffern and Coates (1999, p. 249) and explains their hypothesis:

Mine permits show that wells drilled into ponded clinker water near this contact commonly have high levels of sulfate and TDS. We postulate that these high concentrations are due to dissolution of: 1) sulfates and pyrite in the coal near the burn line, and 2) minerals in the ash layer at the base of the clinker, as highly oxygenated ground water flows downdip through the clinker towards the coal. As this water moves downdip into and through the coal, calcium and sulfate precipitate out in fractures as gypsum, and magnesium and sulfate as epsomite (Davis, 1976). Water in the coal, and in clinker downdip from the coal, is typically of the sodium-bicarbonate type, with moderate TDS levels.

Coalbed methane in the Powder River Basin is believed to be biological in origin (biogenic) (Law and others, 1991; Rice, 1993; Gorody, 1999), a product of anaerobic bacterial decomposition of organic matter through a series of redox reactions. In samples collected from the coalbed aquifers during this study, the high percentage of sulfate nondetections (greater than 50 percent) and low sulfate concentrations when detected is suggestive of waters that have undergone or are undergoing sulfate reduction. VanVoast (1991, p. 1.143) noted that methane encountered in the Powder River Basin "invariably coincides with conditions of chemically reduced groundwater containing Na and HCO₃ as the principal ions." In addition, the author noted that "a chemical model accounting for methane and the associated water-quality conditions requires the exchange of cations Ca and Mg (to clays) for Na (to water) followed by: $4CH_2O$ (coal) + SO_4 + H_2O \rightarrow H₂S +3HCO₃ + CH₄" (VanVoast, 1991, p. 1,143). Rice and others (2000) also observed similar low concentrations and nondetections of sulfate in ground-water samples collected from 47 wells completed in the coalbed aquifers; similarly, the investigators noted that the low sulfate concentrations "are consistent with water in contact with a coal reservoir that has undergone or is undergoing methanogenesis" (Rice and others, 2000, p. 5).

Methanogenesis is another type of redox chemical reaction. The anaerobic bacterial decomposition of organic matter occurs as a series of redox chemical reactions - each series or stage of redox reactions occur in a specific order (succession) and are mediated by different types of bacteria (Chapelle and others, 1993; Chapelle, 2001); this series of reactions essentially represents a microbial "food chain" where different types of bacteria utilize relatively simple organic matter or compounds as a source of energy (Chapelle and others, 1993; Chapelle, 2001). Sulfate reduction (described earlier) is one of these reactions. After all or most sulfate has been consumed through the process of sulfate reduction, the anaerobic bacterial decomposition of organic matter occurs in three stages and each stage or reaction is mediated by a different type of bacteria – the final stage or process is known as methanogenesis (Rice, 1993) and the bacteria that mediate the process are known as "methanogens." Although these redox chemical reactions occur in successive stages, both sulfate reduction and methanogenesis can exist within separate zones of the same aquifer (Chapelle and others, 1993; Chapelle, 2001). The methanogens utilize relatively simple organic compounds (produced in two prior stages of anaerobic decomposition by the breakdown of complex organic matter by acetogenic and fermentative bacteria such as hydrogen (H₂), carbon dioxide (CO₂), acetate, formate, and simple alcohols, to produce methane). There are two metabolic pathways used by bacteria to produce methane after sulfate reduction has ended—methyl-group fermentation and reduction of carbon dioxide (Schoell, 1980; Wolternate and others, 1984; Jenden and Kaplan, 1986; Whiticar and others, 1986). The two generalized reactions (Chapelle, 2001) showing the metabolic pathways for bacterial conversion of simple organic matter into methane are as follows:

Methyl-group fermentation
$$CH_3COOH \rightarrow CH_4 + CO_2$$
 (5)
acetic acid

Carbon dioxide reduction
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 (6)

Rice (1993) examined stable isotopes of gas and water and suggested that the second reaction, carbon dioxide reduction, was the metabolic pathway responsible for most (about 80 percent) of the biogenic generation of methane in coal beds of the Powder River Basin and methyl-group fermentation was responsible for the rest. Similarly, Gorody (1999) also examined the isotopic composition of gas and water from the coal beds and also concluded that reduction of carbon dioxide by methanogenic bacteria rather than methyl-group fermentation is probably responsible for most of the large quantities of methane present in the Wyodak-Anderson coal zone in the Powder River Basin. Rice (1993) suggests that biogenic methane generation in the Powder River Basin occurred between 10 and 35 million years ago, the time of estimated maximum burial of the coal beds. In contrast, Gorody (1999) suggests that methane generation may have continued to at least the Pleistocene age.

In the past, both sulfate reduction and methanogenesis have affected the chemistry of waters in the Wasatch aquifer and coalbed aquifers. On the basis of work in this and other studies described herein, sulfate reduction was likely the dominant geochemical process responsible for the sodium-bicarbonate-type waters in the deep aquifers in the study area. The low to nondetectable concentrations of sulfate in coalbed aquifers in the study area documented in this study and in Rice and others (2000), in combination with earlier work by

Dockins and others (1980) and other studies described earlier, suggests that sulfate reduction may be an ongoing process in some locations in aquifers in the study area. Presumably, the sulfate reduction is occurring primarily in the Wasatch aguifer overlying the coalbed aquifers (except possibly along eastern basin margin – see discussion in Heffern and Coates (1999) and discussion herein) because the near absence of sulfate in the coalbed aguifers indicates the waters in the coalbed aquifers are past sulfate reduction in terms of terminal electron-accepting processes (see discussion in Chapelle (2001)). Because of the absence of sulfate, waters in the coalbed aquifers can undergo methanogenesis if the organic precursors necessary for activity by methanogenic bacteria are present in the aquifers. Work to answer these questions is well outside the scope of this study. Future work will hopefully determine the location and extent of active sulfate reduction and determine if methanogenesis in the aquifers is occuring in any of the study area and throughout the Powder River Basin.

Results from this and previous studies suggest that reducing conditions exist in significant portions of the Wasatch and coalbed aquifers. Very reducing conditions can affect the chemistry (i.e., mobility) of many other constituents, particularly redox-sensitive species (Hem, 1985; Stumm and Morgan, 1996; Drever, 1997). Iron and manganese are detected at relatively high concentrations in the Wasatch aquifer and coalbed aquifers, often at concentrations greater than regulatory standards (Martin and others, 1988; Rice and others, 2000). Both iron and manganese are highly sensitive to redox conditions and both are more soluble in reducing conditions (Hem, 1985).

Low to nondetectable concentrations of many trace elements in waters from the coalbed aquifers in the Powder River Basin in Wyoming have been reported by other investigators (Drever and others, 1977; Martin and others, 1988; Rice and others, 2000); when detected, concentrations of many trace elements are well below any applicable USEPA regulatory standards. Hydrogen sulfide (H₂S) produced by sulfate reduction can strongly affect (decrease) the solubility of many metals (Drever, 1997). In addition, the low to nondetectable sulfate concentrations in the coalbed aquifers can influence the solubility of trace elements such as barium. Rice and others (2000) noted that barium is frequently detected in the coalbed aquifers at concentrations higher than typically seen for most

ground waters. The solubility of barium is primarily controlled by barite (barium sulfate) (Hem, 1985), so the absence of sulfate may be responsible for the relatively high concentrations observed in the waters.

Environmental Isotopes

Isotopes are atoms of the same element that have the same numbers of protons and electrons but different numbers of neutrons. The difference in the number of neutrons between different isotopes of the same element means they have the same atomic number but different atomic masses. Environmental isotopes are naturally occurring isotopes of elements commonly found in the natural environment (typically hydrogen, carbon, nitrogen, oxygen, and sulfur). Isotopes are called stable if not involved in any natural radioactive decay or called radioactive if they undergo radioactive decay. Stable isotopes are typically used in hydrogeology as "tracers of water, carbon, nutrient, and solute cycling" (Clark and Fritz, 1997, p. 5) whereas radioactive isotopes are typically used "to estimate the age or circulation of ground-water" (Clark and Fritz, 1997, p. 5). Both radioactive and stable isotopes were examined during this study.

Tritium

Tritium (³H) is a radioactive isotope of hydrogen (H) commonly used as a tool to provide an approximate age for ground water. Tritium atoms are unstable and undergo radioactive decay with a half-life of 12.43 years (Plummer and others, 1993). Unlike other radioisotopes, tritium atoms can substitute for other hydrogen atoms in the water molecule. The incorporation of tritium directly into the water molecule makes tritium an excellent tool for qualitatively age-dating ground water. Tritium is produced by cosmic radiation naturally in the upper atmosphere at very low concentrations and is incorporated into precipitation. However, atmospheric testing of thermonuclear devices beginning in the early 1950's and continuing through the early 1960's increased tritium concentrations by several orders of magnitude above natural levels, resulting in a global atmospheric spike in tritium concentrations measured in precipitation. The atmospheric spike occurred during and after thermonuclear device testing and "created a tritium reservoir in the stratosphere which contaminated global precipitation

systems for over four decades" (Clark and Fritz, 1997, p. 177). A test-ban treaty was signed in 1963, effectively ending large-scale atmospheric testing of thermonuclear devices and the resulting large increases in atmospheric tritium. Non-signatory nations (France and China) conducted small atmospheric tests of thermonuclear devices until 1980 (Clark and Fritz, 1997) but these tests probably contributed little to tritium concentrations in precipitation (Michel, 1989). Atmospheric concentrations decreased after the test-ban treaty by decay in the atmosphere and loss to the hydrologic cycle (primarily the oceans). Tritium concentrations in precipitation have only recently (about 1990) approached natural levels. Concentrations probably will never completely return to natural levels because low concentrations of tritium continue to be released by other anthropogenic sources such as nuclear power plants and weapons plants (Clark and Fritz, 1997).

Tritium in ground water is primarily from precipitation that infiltrated downward to the aquifer (groundwater recharge). Recharge to ground water originates as precipitation, therefore, increased levels of tritium present in precipitation during and after nuclear device testing can be measured in ground-water samples to qualitatively estimate the time that the water entered the aquifer and became isolated from the atmospheric source of tritium. Tritium is generally used as a qualitative dating tool because tritium concentrations have varied considerably, both spatially and temporally (Michel, 1989). The presence of elevated levels of tritium in ground water is considered an indicator of recent or active ground-water recharge that has occurred since the early 1950's and has become the standard for defining "modern" ground water (Plummer and others, 1993; Clark and Fritz, 1997). Because modern ground water is defined by the very presence of tritium, water with detectable concentrations also is frequently referred to as post-bomb water or ground water with some component of recharge after 1952. Ground water with little or no detectable tritium is defined as "submodern" or older and often is referred to as pre-bomb water or ground water recharged prior to 1952.

Tritium concentrations are expressed in picocuries per liter (pCi/L) or tritium units (TU) where 1 TU is equal to 1 ³H atom in 10¹⁸ atoms of H, or 1 TU is equal to about 3.24 pCi/L (Plummer and others, 1993). From a practical standpoint, tritium concentrations in ground water recharged prior to nuclear device testing (sub-

modern or pre-bomb water) would be less than about 0.8 TU or 2.6 pCi/L; greater concentrations would indicate modern water that has been recharged after atmospheric thermonuclear device testing began (modern or post-bomb water) or ground water that is a mixture of submodern and modern water (Plummer and others, 1993; Clark and Fritz, 1997).

Concentrations detected in the water samples discussed in this report are compared to qualitative interpretations of tritium concentrations in ground water for continental regions as presented in Clark and Fritz (1997, p. 185), and reproduced here in its entirety for convenience:

< 0.8 TU Submodern – recharged prior to 1952 0.8 to ~ 4 TU Mixture between submodern and recent recharge

5 to 15 TU Modern (< 5 to 10 years) 15 to 30 TU Some "bomb" tritium present > 30 TU Considerable component of recharge from

the 1960's or 1970's

> 50 TU Dominantly the 1960's recharge

Tritium concentrations in ground-water samples collected from springs, monitoring wells, and coalbed methane production wells as part of this study are presented in table 10; for convenience, concentrations are presented in both pCi/L and TU.

Tritium concentrations in water samples collected from spring S1 (about 24 TU) and spring S2 (about 16 TU) suggest that both were recharged after 1952 and contain modern or post-bomb water (table 10). The tritium concentrations are both within the "some bomb tritium present" category presented by Clark and Fritz (1997), indicating that both springs were recharged after 1952 and are likely discharging modern or post-bomb water. The presence of modern water in both springs is indicative of recent recharge; both springs had calcium and magnesium as dominant cations and the presence of modern water confirmed suggestions by other investigators (discussed earlier) that these two cations would be dominant in recharge waters in the study area.

Ground-water samples were collected from eight monitoring wells completed in the Wasatch aquifer to examine tritium concentrations in aquifers overlying the coalbed aquifers (table 10). Tritium was not detected in two of eight monitoring wells completed in the Wasatch aquifer. Detectable tritium concentrations in the

Table 10. Tritium concentrations in ground-water samples collected from springs and wells

[pCi/L, picocuries per liter; TU, tritium units; < MRL, less than minimum reporting level; NA, not applicable because concentration is less than minimum reporting level]

Site number	Hydrogeologic unit	Minimum reporting level (pCi/L)	Analytical uncertainty ¹ (+/- pCi/L)	Tritium concentration (pCi/L)	Tritium concentration (TU)
S1	Springs discharging from clinker	1	4	76	24
S2	Springs discharging from clinker	1	3	52	16
W1	Wasatch aquifer	1	1	< MRL	NA
W2	Wasatch aquifer	1	1	9	2.8
W3	Wasatch aquifer	1	1	2	0.6
W4	Wasatch aquifer	1	1	< MRL	NA
W5	Wasatch aquifer	1	1	6	1.8
W6	Wasatch aquifer	1	1	2	0.6
W7	Wasatch aquifer	1	1	1	0.3
W8	Wasatch aquifer	1	1	< MRL	NA
C1	Coalbed aquifers	1	1	< MRL	NA
C2	Coalbed aquifers	1	1	< MRL	NA
C4	Coalbed aquifers	1	1	1	0.3
C5	Coalbed aquifers	1	1	< MRL	NA
C6	Coalbed aquifers	1	1	< MRL	NA
C8	Coalbed aquifers	1	1	1	0.3
C10	Coalbed aquifers	1	1	2	0.6
C11	Coalbed aquifers	1	1	1	0.3
C12	Coalbed aquifers	1	1	< MRL	NA
C13	Coalbed aquifers	1	1	< MRL	NA
C15	Coalbed aquifers	1	1	< MRL	NA
C16	Coalbed aquifers	1	1	< MRL	NA
C17	Coalbed aquifers	1	1	1	0.3

¹Also known as two-sigma precision estimate.

remaining six wells ranged from the MRL (about 0.3 TU or 1 pCi/L) to about 2.8 TU. Therefore, tritium concentrations in six of eight water samples collected from wells completed in the Wasatch aquifer overlying the coalbed aquifers suggest the water is submodern or pre-bomb (tritium concentration less than 0.8 TU). Tritium concentrations in the remaining two samples are in the category (0.8 to 4 TU) that suggests a mixture between submodern (pre-bomb) and modern (postbomb) water, although the low concentrations suggest that ground water in these wells have very little modern water.

Tritium was not detected in eight of thirteen ground-water samples collected from monitoring wells and coalbed methane production wells completed in coalbed aquifers (table 10). Of the five wells with detectable concentrations, tritium was detected at the MRL (about 0.3 TU) in four wells and at a concentration of 0.6 TU in one well. The absence of any tritium at concentrations above 0.8 TU suggests that ground water in the coalbed aquifers probably is submodern or pre-bomb, indicating that no recharge water is likely to have entered the aquifers and traveled to the vicinity of the sampled wells since at least the early 1950's.

Stable Isotopes of Oxygen and Hydrogen

Ratios of the stable isotopes of oxygen (oxygen-18/ oxygen-16, or ¹⁸O / ¹⁶O) and hydrogen (deuterium/ hydrogen, or ²H/H) in the water samples were examined in relation to meteoric water lines, to vertical distribution in monitoring-well clusters, and to spatial distribution. Hydrogen-2 (deuterium or ²H) is a stable heavy isotope of hydrogen containing an extra neutron, and oxygen-18 (¹⁸O) is a stable heavy isotope of oxygen containing two extra neutrons. The variation in the number of neutrons in an element results in a different mass. This difference in mass causes fractionation to occur by a process known as Rayleigh fractionation (Clark and Fritz, 1997). Isotopic data are reported as ratios because isotopic ratios are determined more precisely than actual abundances. The isotopic concentration or ratio is expressed as the difference between the measured ratios of the sample and the reference water divided by the ratio of the measured reference water. Vienna Standard Mean Ocean Water (VSMOW) is generally used as the standard reference water for $\delta^{18}O$ and δ^2 H. The ratio, commonly known as delta (δ), is expressed in units of parts per thousand or per mil (‰)

because the differences are very small. For example, a sample with a $\delta^{18}O$ of -20 ‰ is depleted in $\delta^{18}O$ by 2 percent, or 20 ‰ relative to the standard. This ratio is calculated as follows (example for $\delta^{18}O$):

$$\delta^{18}$$
O sample (in ‰) = (7)

$$\left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}}\right) \times 1000$$

An equation of the same form is used to calculate $\delta^2 H$. The analytical precision for $\delta^{18} O$ values in a given laboratory is usually about +/- 0.2 ‰ and for $\delta^2 H$, the analytical precision is usually +/- 1.0 ‰ (Clark and Fritz, 1997). In this study, a field replicate collected at well C15 had a difference of 0.7 ‰ for $\delta^2 H$ and 0.05 ‰ for $\delta^{18} O$ between the normal environmental sample and the field replicate (table 11).

The values of $\delta^{18}O$ and $\delta^{2}H$ in precipitation become progressively lighter from the equator towards the poles, from lower to higher elevations, and with the distance inland from the ocean. When paired $\delta^{18}O$ and $\delta^{2}H$ values of precipitation throughout the world are plotted, they fall closely to a straight line known as the global meteoric water line (GMWL) (Craig, 1961) which is defined as follows:

$$\delta^2 H = 8 \, \delta^{18} O + 10 \tag{8}$$

Similarly, paired δ^{18} O and δ^{2} H values for North American continental precipitation have been plotted and they also fall closely to a straight line that has the same slope but is shifted downward from GMWL (Gat, 1980).

 $\delta^2 H$ and $\delta^{18} O$ values in ground water are representative of values in precipitation that recharge the ground water, unless some process after the water reaches the earth's surface as precipitation causes isotopic fractionation, and consequently, deviation from meteoric water lines. Some processes that cause fractionation are evaporation, exchange with the aquifer matrix, or recharge that occurred at a different temperature or under a different climate. Local meteoric water lines also may deviate from the GMWL. Shifts in $\delta^{18} O$ values may be affected by interaction with the aquifer matrix. Calcite interactions in carbonate aquifers or more complex

Table 11. $\delta^2 H$ (deuterium/hydrogen isotopic ratio) and $\delta^{18} O$ (oxygen-18/oxygen-16 isotopic ratio) values for ground-water samples collected from springs discharging from clinker and wells completed in the Wasatch aquifer and coalbed aquifers

[‰, parts per thousand or per mil]

Site number	Hydrogeologic unit	δ ² Η (‰)	δ ¹⁸ Ο (‰)
S1	Springs discharging from clinker	-138.5	-18.04
S2	Springs discharging from clinker	-142.6	-18.41
W1	Wasatch aquifer	-139.0	-18.03
W2	Wasatch aquifer	-124.0	-15.57
W3	Wasatch aquifer	-140.7	-18.40
W4	Wasatch aquifer	-148.6	-19.02
W5	Wasatch aquifer	-147.8	-19.03
W6	Wasatch aquifer	-131.1	-18.14
W7	Wasatch aquifer	-146.5	-18.95
W8	Wasatch aquifer	-138.9	-18.46
C1	Coalbed aquifers	-137.9	-17.84
C2	Coalbed aquifers	-141.9	-18.31
C4	Coalbed aquifers	-144.2	-18.54
C5	Coalbed aquifers	-138.1	-17.92
C6	Coalbed aquifers	-140.9	-18.25
C8	Coalbed aquifers	-143.5	-18.79
C10	Coalbed aquifers	-143.4	-18.51
C11	Coalbed aquifers	-132.9	-17.80
C12	Coalbed aquifers	-136.6	-18.56
C13	Coalbed aquifers	-141.3	-18.40
C15 ¹	Coalbed aquifers	-151.0 ² -150.3	-19.99 ² -19.94
C16	Coalbed aquifers	-134.9	-18.66
C17	Coalbed aquifers	-143.7	-18.78

 $^{^{1}}$ A petroleum product is present in this well but it is unlikely to affect δ^{2} H and δ^{18} O values (Carol Kendall, oral comm., 2000).

²Replicate sample.

exchanges with the rock matrix in geothermal systems are commonly observed causes of shifts in the $\delta^{18}O$ values. In general, there are fewer shifts in the $\delta^2 H$ in aquifer systems because fifty percent or more of the total oxygen in the system is usually resident in the rocks, but almost all of the hydrogen in the system is in the water (Drever, 1997). Coalbed aquifers are exceptions to that general rule, because significant amounts of hydrogen are tied up in the coal. In addition, interaction between gases and water may introduce a more complex model, particularly when methanogenesis is present. As described earlier, the biogenic production of methane is a complex process of a mixed bacterial population and results in the production of carbon dioxide and hydrogen gases as well as methane. δ^2 H values have been observed to shift in water samples collected from landfills because of active methane production (Siegel and others, 1990; Hackley and others, 1996; Clark and Fritz, 1997).

Collection of δ^2 H and δ^{18} O in precipitation was not possible as part of this study and no local values were available; therefore, the δ^2 H and δ^{18} O values in ground-water samples (table 11) were plotted and compared to published values for precipitation (fig. 21). The values plotted close to the GMWL, the meteoric water line for North American continental precipitation, and a local meteoric water line estimated by Gorody (1999) for the Powder River Basin. The close proximity to the meteoric water lines, including samples from two springs with modern water, suggests that the water was of meteoric origin, in contrast to water present in the aquifer materials during deposition (connate). The samples also plotted in the more negative area (i.e., left side) of the graph, which is appropriate for waters recharged at colder temperatures or in a colder climate, mid-latitudes, and mid-continent. Many of the values plotted slightly below all three meteoric water lines, despite different aquifers of origin, suggesting some isotopic fractionation, possibly by evaporation. The water samples were intermixed on the plot and did not group into separate areas of the graph based on the aquifer of origin. This could indicate that there was intermixing of the waters in the aquifers or it could indicate that the different aquifers were subject to similar recharge and or evolutional paths for the water, so that the net difference in the $\delta^2 H$ and $\delta^{18}O$ values was minimal. Similar $\delta^{2}H$ and $\delta^{18}O$ values were observed in four ground-water samples collected from the Wyodak-Anderson coalbed aquifer

at two coal mines in the southern part of the Powder River Basin (Martin and others, 1988).

 δ^2 H and δ^{18} O values were examined in the vertical dimension at the three monitoring-well clusters where major-ion chemistry was previously discussed. In the monitoring-well cluster composed of wells W5, W4, and W3, and nearby coalbed methane production well C12, depth to water increased with the depth of the well (fig. 22). The water level in the coalbed well was measured before the well was pumped to remove water for gas production, while the water levels in the wells completed in the Wasatch aquifer were collected after pumping of the coalbed methane production field began. The water level in the coalbed well (C12) probably had drawn down farther by 1999 than is presented in figure 22 because this well was a production well that produced water and gas in 1999. Hydraulic head (fig. 22) decreased with depth and indicated a hydraulic potential for downward ground-water flow if geologic conditions allow.

 δ^2 H values generally increased (became less negative) with depth (fig. 22). δ^2 H values in the two shallow Wasatch wells (W5and W4) are about the same, although the middle Wasatch well (W4) was slightly more negative than the uppermost well (W5); the difference between the two δ^2 H values is probably within the precision of the δ^2 H analysis. δ^2 H increased dramatically between the two shallow Wasatch wells (W5 and W4) and the deepest Wasatch well (W3). Similarly, δ^{18} O values were about the same between the two shallowest Wasatch wells but increased with depth between the middle Wasatch well (W4) and the deepest Wasatch well (W3). Physical and chemical processes such as methanogenesis and hydrogen-sulfide exchange reactions can shift δ^2 H values towards less negative values (deuterium enrichment) without corresponding shifts in δ^{18} O values (Hackley and others, 1996, and references therein). If the sandstone lenses screened by the wells were assumed to be hydraulically connected, one of these processes could increase δ^2 H values as ground water moves downward. However, a shift in δ^{18} O is observed between the two shallow Wasatch wells (W5 and W4) and the deep Wasatch well (W3) and suggests that these processes have probably not affected the $\delta^2 H$ values between these wells. The shifts observed in $\delta^2 H$ and $\delta^{18}O$ between the two shallow Wasatch wells and the deepest Wasatch well almost parallels the meteoric water lines (fig. 21) and this type of deviation from the meteoric water lines may be more

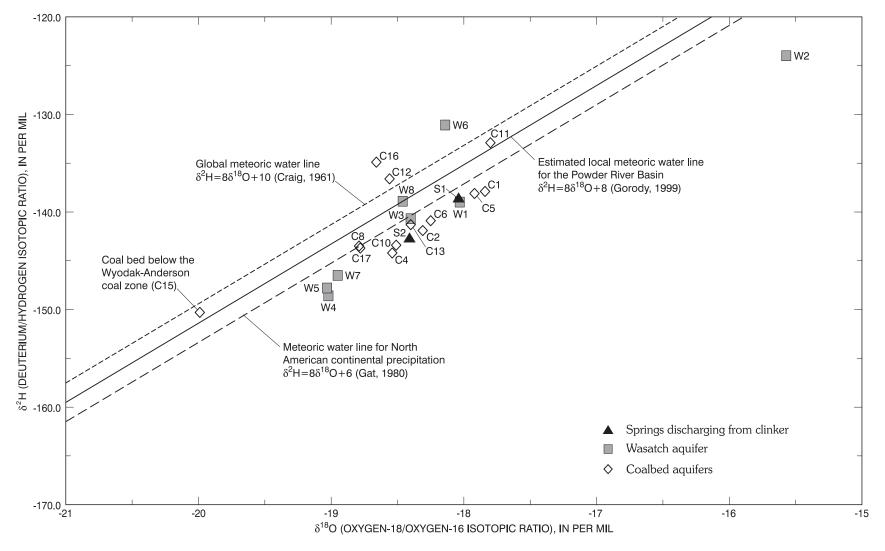


Figure 21. Relation between δ^{18} O (oxygen-18/oxygen-16 isotopic ratio) and δ^{2} H (deuterium/hydrogen isotopic ratio) for ground-water samples collected from springs discharging from clinker, the Wasatch aquifer, and coalbed aquifers, eastern Powder River Basin, Wyoming, 1999.

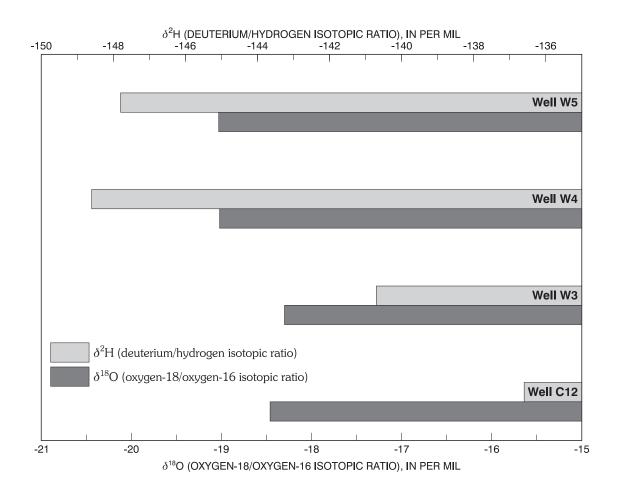
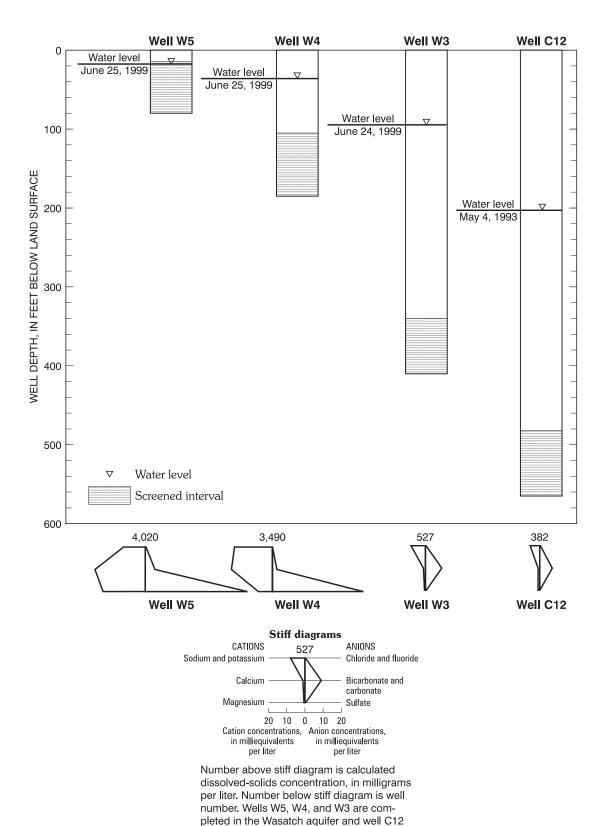


Figure 22. δ^2 H (deuterium/hydrogen isotopic ratio), δ^{18} O (oxygen-18/oxygen-16 isotopic ratio), and major-ion chemistry in relation to the clustered wells W5, W4, W3, and C12 in the eastern Powder River Basin, Wyoming, 1999.



is completed in the Wyodak-Anderson coalbed

aquifer.

Figure 22. Continued.

indicative of differences in recharge temperatures rather than processes such as methanogenesis or hydrogen-sulfide exchange reactions. In addition, it is interesting to note that the shift in δ^2H between the two shallowest Wasatch wells and the deepest Wasatch well corresponds to a change in water type (fig. 22) and a decrease in sulfate concentrations (figs. 17 and 22).

 δ^2 H continued to increase with depth between the deepest Wasatch well (W3) and the underlying Wyodak-Anderson coalbed well (C12) (figs. 17 and 22). Waters in both wells were sodium-bicarbonate type. Sulfate concentrations continued to decrease with depth, with a concentration of about 2,400 mg/L in the deep Wasatch well (W3) and less than the MRL of 0.1 mg/L in the coalbed well (C12). In this case, $\delta^2 H$ shifted to a less negative value without a corresponding shift in the δ^{18} O values (fig. 22). As mentioned previously, this pattern is sometimes observed where waters have undergone or were undergoing methanogenesis or hydrogen-sulfide exchange reactions and might be observed if the waters in both wells were assumed to be originally isotopically the same, in hydraulic connection, and moving downward. Future work will hopefully determine if either geochemical process affected or currently affects the water chemistry in the deep wells.

In the monitoring-well cluster composed of wells W7 (completed in Wasatch aguifer) and C16 (completed in Wyodak-Anderson coalbed aguifer) (fig. 23), δ^2 H increased (became less negative) with depth; δ^{18} O also slightly increased (became less negative) with depth, but the difference in the $\delta^{18}O$ values is probably within the precision of the analysis. Hydraulic head decreased with depth, indicating the potential for downward ground-water flow. Waters in both wells were sodium-bicarbonate type. Sulfate concentrations decreased with depth (fig. 19), with a concentration of about 160 mg/L in the Wasatch well (W7) and about 1 mg/L in the coalbed well (C16). This pattern in stable isotope values, hydraulic gradient, and major-ion chemistry is very similar to the pattern just described for wells W3 and C12 in the monitoring-well cluster.

In contrast, a very different pattern was observed in the monitoring-well cluster composed of wells W8 and C17 (fig. 23). Both $\delta^2 H$ and $\delta^{18} O$ decreased (became more negative) with depth. Unlike the other two monitoring-well clusters, hydraulic head increased with depth, indicating the potential for upward ground-water flow. Major-ion chemistry also was different, as the

water from the Wasatch well (W8) immediately overlying the coalbed aquifer was a mixed type, and the water in the coalbed well (C17) was a sodium-bicarbonate type. Sulfate concentrations decreased with depth (fig. 18), with a concentration of about 740 mg/L in the Wasatch well (W8) and less than 1 mg/L in the coalbed well (C17). In the other two monitoring-well clusters, the waters in samples collected from the Wasatch wells immediately overlying the coalbed aquifer were sodium-bicarbonate-type waters, the same as the waters in the underlying coalbed aquifers.

Two explanations or hypotheses are proposed to explain the observed changes in stable isotope values and major-ion chemistry with increasing well depth at the three monitoring-well cluster locations. The first hypothesis requires an assumption of hydraulic connection between the intervals screened by successively deeper wells. In this case, the observed changes with depth are the result of geochemical processes (described earlier for the Powder River Basin) as ground water moves downward through the Wasatch Formation into the underlying coalbed aquifer. The second explanation is that there are two different aquifers or aquifer systems with minimal hydraulic connection -(1) the upper Wasatch Formation, represented by the two sandstone lenses screened by the two shallow Wasatch wells (wells W5 and W4) in the first monitoring-well cluster discussed, and (2) the coalbed aquifers and overlying deep Wasatch sandstone lenses, represented by the deep Wasatch well (W3) and coalbed well (C12) in the first monitoring-well cluster discussed, and Wasatch well W7 and coalbed well C16 in the second monitoringwell cluster discussed. At the third monitoring-well cluster examined, the shallow Wasatch well (W8) and underlying coalbed well (C17) would represent the same two different aguifers or aguifer systems. In this second hypothesis, each of the two aguifers or aguifer systems have different major-ion chemistry and stable isotope values because the waters in the different aquifers or aquifer systems are subject to different recharge and/or evolutional paths.

The shallow aquifer or aquifer system would be part of the "shallow geochemical zone" described earlier for the Powder River Basin (and associated geochemical processes, primarily in the context provided by Lee (1981)) while the deeper aquifer or aquifer system would be part of the "deep geochemical zone" described earlier (see fig. 20 and related discussion in earlier section, Major-Ion Chemistry).

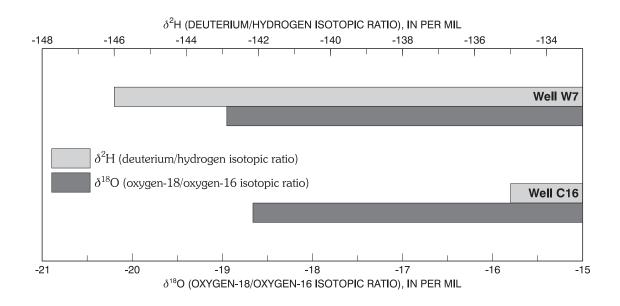
 δ^2 H values were examined spatially (figs. 24 and 25) for both wells completed in the Wasatch aquifer and the coalbed aquifers. Springs discharging from clinker were included with the wells completed in the Wasatch aquifer. A break in δ^2 H values can be observed along a northwest to southeast trend with both groups. An inferred -140 % δ^2 H value line is shown in both figures as an arbitrary reference value to examine relative increases or decreases in δ^2 H values. Samples collected from wells completed in the coalbed aquifers, except for the sample from the Big George coal bed, followed a pattern where the more negative $\delta^2 H$ values plotted towards the center of the basin, whereas the less negative values plotted near the outcrop area. The pattern for the samples collected from the Wasatch aquifer and the springs was opposite. The values more negative than -140 ‰ plotted near the outcrop area, while the values less negative than -140 ‰ plotted towards the basin center. The δ^2 H -140 % line in the coalbed aguifer and the δ^2 H -140 % line in the overlying Wasatch aquifer spatially were relatively close to each other given the size of the dataset. Further investigation of this possible spatial relation is required. The pattern may be the result of sample size, different recharge mechanisms, or geochemical processes, or the processes producing these differences may be independent.

HYDROGEOLOGIC IMPLICATIONS OF OBSERVED MAJOR-ION CHEMISTRY AND ENVIRONMENTAL ISOTOPES

Examination of data from this study, in combination with work by previous investigators, suggests several possibilities to help explain the composition of samples collected from the Wasatch aquifer and the underlying coalbed aquifers in this study. All interpretations of data were provided in previous sections, along with references to previous conclusions reached by other investigators. It should be noted that interpretations presented herein are a combination of past investigations and data collected as part of this investigation. Sample size for this study was limited, and as more data are collected in other areas of the basin, these interpretations may be modified or refined.

In the previous section, two possible concepts were hypothesized to explain the observed major-ion chemistry and stable isotope values at three locations with monitoring-well clusters in the study area. The first concept proposes that the changes observed with depth at the three monitoring-well cluster locations are the result of geochemical processes that occur as ground water moves vertically through successively deeper, hydraulically connected sandstone lenses in the Wasatch Formation and finally, into the underlying coalbed aquifer. This investigation, along with earlier investigations described herein, has noted a hydraulic potential for downward ground-water flow within the Wasatch Formation. If geologic conditions are favorable to vertical ground-water flow, geochemical processes such as dissolution, precipitation, ion exchange, sulfate reduction, and mixing of waters are the processes that may occur as ground water moves downward through the Wasatch Formation and evolves the water to the sodium-bicarbonate type observed in the deeper part of the Wasatch Formation and the coalbed aguifers.

The second concept assumes the presence of two different aquifers or aquifer systems to explain the differences in major-ion chemistry and stable isotope values observed at the three monitoring-well clusters. Three ground-water samples were collected from shallow wells in this study and all three were collected from the shallow part of the Wasatch Formation (less than about 200 ft below land surface). The wells had mixed cation composition (but generally dominant in calcium and magnesium) with either sulfate or bicarbonate as the dominant anion: all three wells were located at the monitoring-well clusters previously discussed. These wells could be part of a shallow aguifer or aguifer system represented by the "shallow geochemical zone" discussed previously. All ground-water samples collected from wells completed deeper in the Wasatch Formation and the underlying coal beds were sodiumbicarbonate-type waters; these wells could be representative of the underlying, deeper, chemically stagnant geochemical system described by Lee (1981) (described herein as the "deep geochemical zone" composed of the deep sandstone lenses present in the Wasatch Formation and underlying coal beds). In this explanation, little vertical hydraulic connection is present between successively deeper sandstone lenses in the Wasatch Formation and between the shallow sandstone lenses and the underlying coalbed aquifers; very little vertical flow, and therefore, intermixing of waters between the shallow and deep geochemical zones would occur. Heterogeneity and anisotropy, related to discontinuous



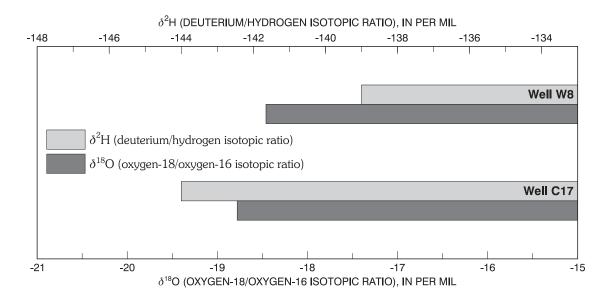


Figure 23. δ^2 H (deuterium/hydrogen isotopic ratio), δ^{18} O (oxygen-18/oxygen-16 isotopic ratio), and major-ion chemistry in relation to the clustered wells W7 and C16 and clustered wells W8 and C17 in the eastern Powder River Basin, Wyoming, 1999.

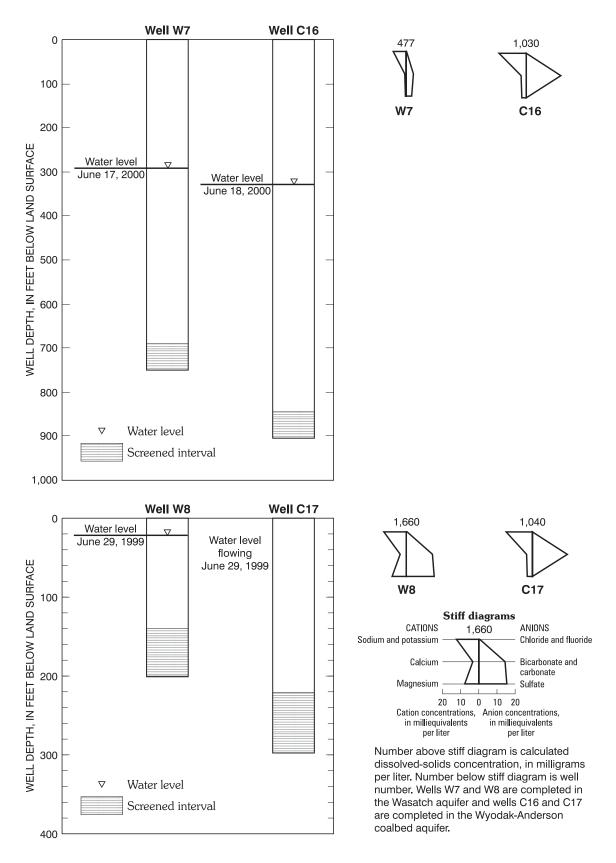


Figure 23. Continued.

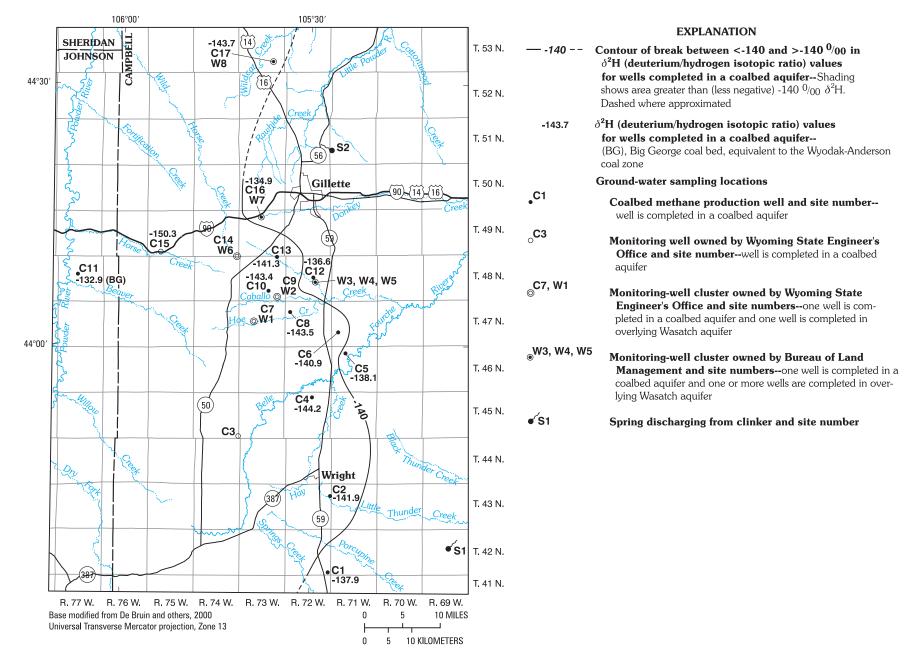


Figure 24. δ^2 H (deuterium/hydrogen isotopic ratio) values for coalbed aquifers in the study area, eastern Powder River Basin, Wyoming, 1999.

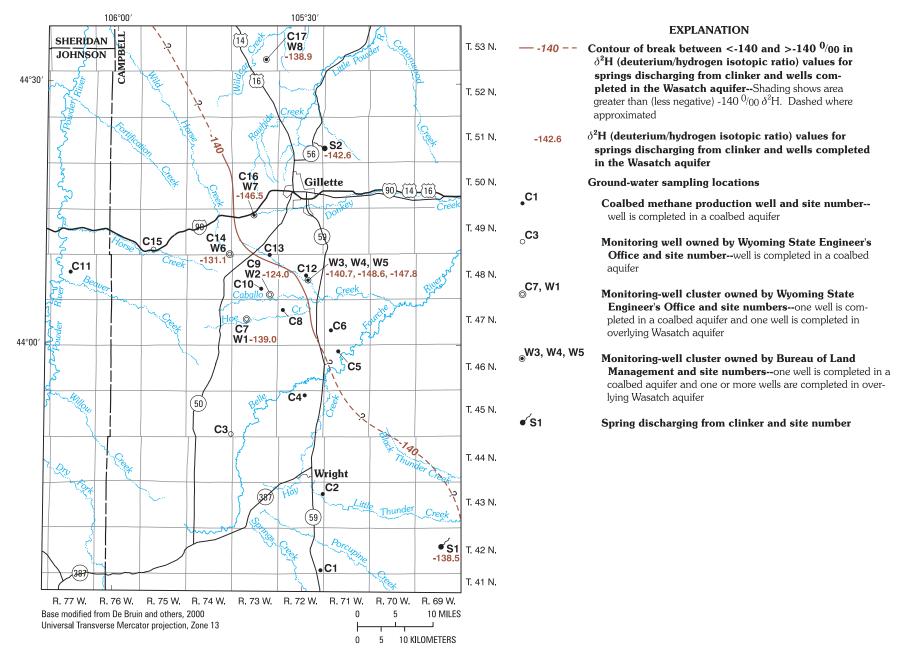


Figure 25. δ^2 H (deuterium/hydrogen isotopic ratio) values for springs discharging from clinker and for wells completed in the Wasatch aquifer in the study area, eastern Powder River Basin, Wyoming, 1999.

sandstone lenses surrounded by a predominantly finegrained lithology present in the Wasatch Formation, could have a large effect relative to the actual groundwater flow direction and result in ground-water flow that is primarily horizontal. Other investigators such as Feathers and others (1981) and Lowry and others (1993) have suggested that there is very little vertical ground-water flow in the Wasatch and Fort Union Formations because of the predominantly fine-grained lithology, and that ground-water flow in these formations is primarily horizontal through the discontinuous sandstone lenses present. Therefore, well depth (and consequently, differences in ionic composition and stable isotope values) may simply reflect the relative distance water has flowed through the aquifer and different hydrological and geochemical origins and evolutional paths. Waters from the "shallow geochemical zone" may represent waters in local ground-water flow systems with relatively short flowpaths, whereas waters from the "deep geochemical zone" may be representative of a deep, regional ground-water flow system. This explanation also is consistent with differences in water chemistry noted in this and earlier studies, assuming very little vertical ground-water flow through the Wasatch Formation and into underlying hydrogeologic units such as the coalbed aquifers.

Both of the proposed concepts can explain the observed composition of waters in the Wasatch Formation and sodium-bicarbonate composition of waters in the coalbed aquifers at the locations examined. In addition, the concept proposed by Heffern and Coates (1999) discussed earlier also can evolve the water in the coalbed aquifers to a sodium-bicarbonate type. At the basin scale, it is possible, and perhaps most likely, that all three concepts of the ground-water system are correct - the predominant hydrogeologic and geochemical processes at any given location are probably dependant on site-specific geologic and hydrogeologic conditions. In areas where many sandstone lenses are "vertically stacked" above coal beds and the hydraulic gradient allows for downward vertical flow, ground water may move downward through the Wasatch Formation and into the underlying coal beds. In other areas where the sandstones are relatively isolated with limited hydraulic connection, vertical ground-water flow is restricted and flow is primarily horizontal. Despite the localized differences in processes, the overall net effect at the basin scale is the system currently observed. The number of locations where vertical changes in major-ion

chemistry and stable isotope values were examined during this study was limited to three locations. Examination of both major-ion chemistry and stable isotope values at additional locations throughout the Powder River Basin may help to refine or alter these proposed concepts of the ground-water system.

Six of eight wells completed in the Wasatch aquifer had no post-bomb water, and two of the eight wells (W2 and W5) had concentrations suggesting a mixture of pre- and post-bomb water, although the low concentrations are suggestive of very little modern water (table 10). One of these two wells (W5) is the shallowest well completed in the Wasatch aquifer (probably the only water-table well). This well had very low concentrations of tritium, indicating that some post-bomb water may be present near the water table. Additional samples at the water table in the Wasatch aquifer should be collected to determine if some modern water is present at or near the water table at more locations in the basin. However, if there was a significant amount of areal recharge, it would be expected that post-bomb water would be distributed throughout the shallow zone of the Wasatch aquifer. The absence of post-bomb water in the shallow zone would suggest that processes responsible for recharge to the Wasatch aquifer in the Powder River Basin are probably very slow. As discussed earlier, most recharge to the coalbed aquifers is suspected to occur in or near clinker. It is possible that the majority of recharge from precipitation to the Wasatch aquifer may occur in the highly permeable clinker scattered throughout the basin; additional recharge also probably occurs from surface-water drainages in the study area. More accurate age-dating techniques and measurement of recharge rates would be required to understand recharge processes to the Wasatch aquifer.

Based on the absence of any post-bomb water in samples collected from the coalbed aquifers, it appears that ground water may be flowing very slowly away from the suspected source of recharge, the clinker (which has modern or post-bomb water). Since no tritium data has been collected from wells completed in the coalbed aquifer adjacent to and immediately downgradient of suspected recharge areas (i.e., clinker), the rate at which water enters the coalbed aquifers from its recharge areas is not known.

COMPARISON OF WATER QUALITY TO REGULATORY STANDARDS

An important purpose in studying and describing the general and physical characteristics and ionic composition of water is to determine its suitability for proposed uses. In the study area, water from wells completed in the lower Tertiary aguifers (Wasatch aguifer and coalbed aquifers) and not used in relation to resource extraction (petroleum production, coal mining, or coalbed methane production) is used primarily for public supply, domestic, or agricultural purposes (Feathers and others, 1981; Wyoming Water Development Commission, 1985; Martin and others, 1988). To aid the determination of suitability for the intended uses, results of water-quality sampling are compared to U.S. Environmental Protection Agency (USEPA) and State of Wyoming water-quality levels and standards and several additional commonly used guidelines for the proposed uses.

Public Supply and Domestic Use

The U.S. Environmental Protection Agency (1991, 1996) has established drinking-water regulations for public supplies of drinking water. The regulations specify maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs). The MCLS are health-based and are legally enforceable standards while the SMCLs are nonenforceable, recommended standards. Although MCLs and SMCLs apply

only to public supplies of drinking water, not individual well owners, the levels are useful to determine the suitability of water for drinking. Standards also have been developed by the State of Wyoming to evaluate groundwater quality for domestic use (Wyoming Department of Environmental Quality, 1993).

Results of ground-water-quality sampling of wells conducted as part of this study are compared to selected applicable MCLs and SMCLs in table 12 and State of Wyoming domestic standards in table 13. Dissolved solids was the constituent or characteristic with the highest percentage of exceedances. More than 50 percent of concentrations from both the Wasatch aquifer and coalbed aquifers exceeded USEPA levels and State of Wyoming standards. The ground-water sample collected from spring S1 (appendix table 1) does not exceed any levels or standards. The sample collected from spring S2 (appendix table 1) exceeds the MCL, SMCL, and Wyoming standard for both sulfate and dissolved solids.

Hardness is another water-quality characteristic commonly used to characterize the suitability of water for public-supply and domestic use. Hardness usually is characterized on the basis of four classes (Hem, 1985, p. 158-159). Hardness values calculated for groundwater samples collected from wells as part of this study are summarized by aquifer in relation to the four classes in table 14. Both ground-water samples collected from springs (appendix table 1) were very hard (130 mg/L for sample collected from spring S1 and 790 mg/L for sample collected from spring S2).

Table 12. Comparison of ground-water-quality samples collected from wells with selected U.S. Environmental Protection Agency maximum and secondary maximum contaminant levels for public drinking-water supplies (Contaminant levels from U.S. Environmental Protection Agency, 1991, 1996. Results of sampling individual wells are listed in appendix table 1.)

[All constituent or characteristic concentrations are in milligrams per liter except as indicated; --, no established level; N/A, not applicable]

Constituent or characteristic	Maximum contaminant level (MCL)	Percentage and number of samples collected from Wasatch aquifer that exceed MCL	Percentage and number of samples collected from coalbed aquifers that exceed MCL	Secondary maximum contaminant level (SMCL)	Percentage and number of samples collected from Wasatch aquifer that exceed SMCL	Percentage and number of samples collected from coalbed aquifers that exceed SMCL
Chloride		N/A	N/A	250	0	0
Fluoride	4	0	0	2	0	0
Sulfate	500	38 (3/8)	0	250	38 (3/8)	0
Dissolved solids		N/A	N/A	500	86 (6/7)	77 (10/13)
pH, standard units		N/A	N/A	6.5-8.5	25 (2/8)	0

Table 13. Comparison of ground-water-quality samples collected from wells with selected State of Wyoming standards for domestic use

(Standards from Wyoming Department of Environmental Quality, 1993, p. 9. Results of sampling individual wells are listed in appendix table 1.) [All constituent or characteristic concentrations are in milligrams per liter except as indicated]

Constituent or characteristic	Domestic-use standard	Percentage and number of samples collected from Wasatch aquifer that exceed standard	Percentage and number of samples collected from coalbed aquifers that exceed standard
Chloride	250	0	0
Fluoride	¹ 1.4-2.4	² 12 (1/8)	² 31 (4/13)
Sulfate	250	38 (3/8)	0
Dissolved solids	500	86 (6/7)	77 (10/13)
pH, standard units	6.5-9.0	0	0

¹Dependent on the annual average of the maximum daily air temperature: 1.4 milligrams per liter corresponds with a temperature range of 26.3 to 32.5 degrees Celsius, and 2.4 milligrams per liter corresponds with a temperature of 12 degrees Celsius and below.

Table 14. *Hardness classification of ground-water-quality samples collected from wells* (Hardness classification from Hem, 1985. Results of sampling individual wells are listed in appendix table 1.) [CaCO₃, calcium carbonate; mg/L, milligrams per liter]

Hardness as CaCO ₃ (mg/L)	Hardness classes	Percentage ¹ and number of samples collected from Wasatch aquifer within class	Percentage ¹ and number of samples collected from coalbed aquifers within class
0-60	Soft	38 (3/8)	0
61-120	Moderately hard	25 (2/8)	38 (5/13)
121-180	Hard	0	23 (3/13)
more than 180	Very hard	38 (3/8)	38 (5/13)

¹Individual percentages for each hardness class, when summed, do not equal 100 percent due to rounding.

Agricultural Use

Agricultural use includes water used to irrigate crops and water given to livestock. The State of Wyoming has established standards for both uses (Wyoming Department of Environmental Quality, 1993). Ground-water samples collected from wells are compared to selected applicable State of Wyoming agricultural standards in table 15.

The ground-water sample collected from spring S1 (appendix table 1) does not exceed any Wyoming agri-

cultural (irrigation) or livestock standards. In contrast, the ground-water sample collected from spring S2 (appendix table 1) exceeds the agricultural-use standard (irrigation) for sulfate and dissolved solids.

A classification system to evaluate the suitability of water for irrigation use was developed by the U.S. Salinity Laboratory Staff (1954). The classification system is based on two characteristics, the salinity hazard and sodium (alkali) hazard of the water. Salinity hazard is divided into four classes using the specific

²Percentage and number of samples presented for concentrations equal to or exceeding lower standard (1.4 milligrams per liter).

Table 15. Comparison of ground-water-quality samples collected from wells with selected State of Wyoming standards for agricultural (irrigation) and livestock use

(Standards from Wyoming Department of Environmental Quality, 1993. Results of sampling individual wells are listed in appendix table 1.)

[All constituent or characteristic concentrations are in milligrams per liter except as indicated]

Constituent or characteristic	Agricultural-use standard (irrigation)	Percentage and number of samples collected from Wasatch aquifer that exceed standard	Percentage and number of samples collected from coalbed aquifers that exceed standard	Livestock-use standard	Percentage and number of samples collected from Wasatch aquifer that exceed standard	Percentage and number of samples collected from coalbed aquifers that exceed standard
Chloride	100	0	0	2,000	0	0
Sulfate	200	75 (6/8)	8 (1/13)	3,000	0	0
Dissolved solids	2.000	25 (2/8)	8 (1/13)	5,000	0	0
pH, standard units	4.5-9.0	0	0	6.5-8.5	25 (2/8)	0

conductance of the water. The characteristics of the salinity-hazard classes and specific-conductance ranges are as follows:

	Specific	
Salinity- hazard class	conductance (μS/cm) ¹	Characteristics
Low	0-250	Low-salinity water can be used for irrigation on most soil with minimal likelihood that soil salin- ity will develop.
Medium	251-750	Medium-salinity water can be used for irrigation if a moderate amount of drainage occurs.
High	751-2,250	High-salinity water is not suitable for use on soil with restricted drainage. Even with adequate drainage, special management for salinity control may be required.
Very high	More than 2,250	Very high-salinity water is not suitable for irrigation under normal conditions.

¹μS/cm, microsiemens per centimeter at 25 degrees Celsius.

The sodium hazard also is divided into four classes using the sodium-adsorption ratio (SAR). The SAR is a dimensionless ratio that is calculated to indicate the tendency of sodium to replace calcium and magnesium in soils. The replacement of calcium and magnesium with sodium can damage the soil structure and reduce the permeability of the soil to water infiltration (Hem, 1985). However, the SAR should be used in conjunc-

tion with information about the soil characteristics and irrigation practices in the area being examined. The SAR is calculated by converting ion concentrations to meq/L and substituting into the SAR equation as follows:

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \tag{9}$$

SAR values can then be compared to characteristics of the four sodium-hazard classes as follows:

-	Sodium- hazard class	Sodium- adsorption ratio (SAR)	Characteristics
-	Low	0-10	Low-sodium water can be used for irriga- tion on most soil with minimal danger of harmful levels of exchangeable sodium.
	Medium	>10-18	Medium-sodium water will present an appreciable sodium hazard in fine-textured soil having high cation-exchange capacity.
	High	>18-26	High-sodium water may produce harmful levels of exchangeable sodium in most soil.
	Very high	>26	Very high-sodium water is generally unsatisfactory for irrigation purposes.

Typically, both salinity hazard and sodium hazard are combined into a single plot to evaluate the suitability of water for irrigation (U.S. Salinity Laboratory

Staff, 1954). Results from analyses of ground-water samples collected from springs and wells (appendix table 1) are shown in figure 26. Samples collected from both springs plot in the low sodium-hazard (S1) class but plot in the medium (C2) and high (C3) classes for salinity hazard. Ground-water samples collected from the Wasatch aquifer plot in the range from low (S1) to high (S3) sodium-hazard classes and medium (C2) to very high (C4) salinity-hazard classes. Ground-water samples collected from the coalbed aquifers also plot in

the range from medium (C2) to very high (C3) salinity-hazard classes, but plot in range from low (S1) to very high (S4) sodium-hazard classes. The sample that plots the highest in both the salinity- and sodium-hazard classes from all aquifers was collected from the Big George coal bed. Although this suggests that samples collected from wells completed in all aquifers plot in a wide range of both sodium and salinity-hazard classes, most samples cluster in or near the combined medium-sodium-hazard—high-salinity-hazard (S2-C3) class.

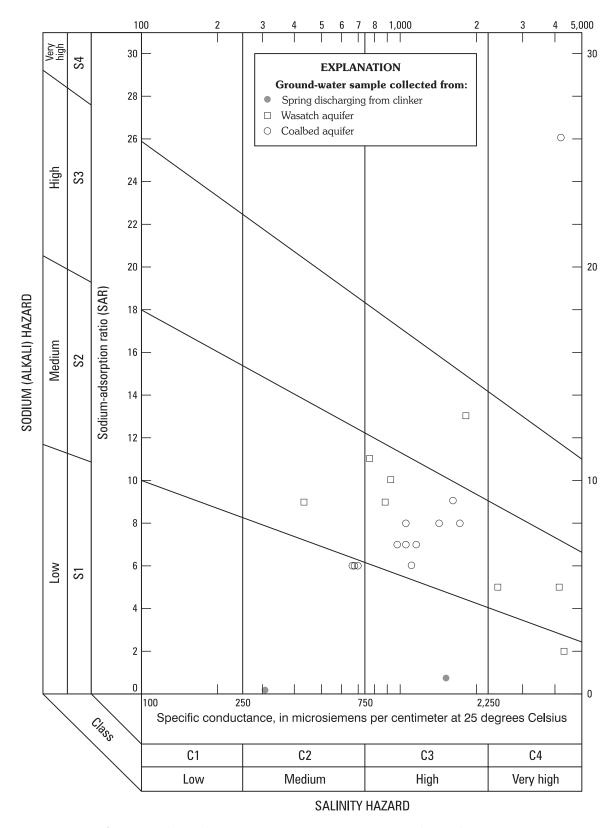


Figure 26. Suitability of water for use in irrigation based on analyses of water from springs, Wasatch aquifer, and coalbed aquifers, eastern Powder River Basin, Wyoming, 1999. Diagram modified from U.S. Salinity Laboratory Staff (1954). Data are listed in appendix table 1.

SUMMARY

Ground-water samples collected from wells in coalbed aquifers of the Fort Union Formation and from springs and wells in overlying aquifers displayed distinct differences and trends between and within the aquifers and areally within the Powder River Basin. Data on water levels, major-ion composition, and isotopic composition of the water support the conclusion that the changes in water composition are likely the result of geochemical processes that occur as groundwater moves vertically and horizontally, as well as possible hydraulic connection between the aquifers.

Major-ion composition of samples in this study varied, primarily in relation to depth or proximity to suspected recharge areas. Ground-water samples collected from springs discharging from clinker were classified as calcium-sulfate-type and calciumbicarbonate-type waters. Two ground-water samples collected from wells completed in the Wasatch aquifer had mixed cation composition with sulfate as the dominant anion, and one sample was a sodium-magnesiumsulfate-bicarbonate-type water; all three samples were collected from wells completed to depths less than 200 feet. Ground-water samples collected from wells completed in the coalbed aquifers and 5 of 8 wells completed in the Wasatch aquifer were all sodiumbicarbonate-type waters. All five Wasatch wells with sodium-bicarbonate-type waters were collected from wells completed at depths greater than 200 feet. Statistically and qualitatively, major-ion composition of samples from the coalbed aquifers and the overlying Wasatch aquifer was not significantly different except for two constituents, sulfate and fluoride, with sulfate showing the most striking difference. The median sulfate concentration in the Wasatch aquifer was low (130 mg/L), but concentrations were much lower in the coalbed aquifers, with more than 50 percent of the values below detection limits.

Major-ion data and water levels in monitoringwell clusters composed of wells completed in coalbed aquifers and the overlying Wasatch aquifer indicated changes in water composition that may be related to depth and possible hydraulic connection between aquifers. Water-level measurements at most of the monitoring-well clusters (4 out of 5) indicated a potential for downward ground-water flow from the Wasatch aguifer to the coalbed aguifers, with the one remaining well cluster indicating a potential for upward movement. Both increases and decreases in major ions (Ca, Mg, SO₄, Na, HCO₃) with depth and dissolved-solids concentrations were noted in the well clusters, with no consistent trend for any of the constituents except sulfate, which dramatically decreased with depth. In the Wasatch aquifer, statistically significant correlations were noted between calcium and sulfate concentrations and well depth, and correlations close to statistical significance were noted for dissolved solids, magnesium, and fluoride with increasing well depth. In the coalbed aquifers, a statistically significant correlation was found between potassium concentrations and well depth, but qualitatively, again the most striking difference was the decrease in sulfate with depth.

No clear areal pattern in water type was noted because samples collected from most wells, regardless of aquifer type, were sodium-bicarbonate-type waters. However, a pattern in dissolved-solids concentrations in waters from the coalbed aquifers was noted. Samples from this study and another recent investigation (Rice and others, 2000) suggests that dissolved-solids concentrations may be lower (less than 600 mg/L) south of the Belle Fourche River and that concentrations appear to increase northward in the Powder River Basin in Wyoming.

Tritium was used to qualitatively estimate the time of ground-water recharge. Tritium concentrations in water samples collected from two springs suggest that both were recharged after 1952 and contain modern (or post-bomb) water. Tritium concentrations in six of eight ground-water samples collected from wells completed in Wasatch aquifer overlying the coalbed aquifers suggest the water is submodern (or pre-bomb). Tritium concentrations in the remaining two wells suggest a mixture between submodern and modern water, although the low concentrations suggest that ground water in these wells has very little modern water. Tritium concentrations above pre-bomb concentrations were not detected in any wells completed in the coalbed aquifers, suggesting that ground water in the coalbed aquifers in the shallow coal beds of the Tongue River Member of the Fort Union Formation probably is submodern, and that no recharge water is likely to have reached the portions of the aguifers sampled in this study since at least the early 1950's. This suggests recharge to the Wasatch aguifer and the coalbed aguifers is probably very slow.

The $\delta^2 H$ and $\delta^{18} O$ values from waters in this study suggest that the waters are of meteoric origin. Paired δ^2 H and δ^{18} O values were plotted in relation to the Global Meteoric Water Line, a meteoric water line for North American continental precipitation, and a local meteoric water line constructed for the Powder River Basin (Gorody, 1999). The values plot close to all meteoric water lines, indicating that the water in ground-water samples collected during this investigation is of meteoric origin. The isotopic values suggest that the waters were recharged in a colder climate or at a cold temperature, mid-latitudes, and mid-continent. Samples do not group together based on aquifer origin; this suggests either intermixing of the waters in the aquifers or it suggests that the different aquifers are subject to similar recharge and/or evolutional paths for the water so that the difference in the δ^2 H and δ^{18} O values is minimal.

The areal distribution of $\delta^2 H$ was examined and an apparent break in δ^2 H values along a northwest to southeast trend was observed. In the coalbed aquifers, all but one ground-water sample (collected from the Big George coal bed), show a pattern where the $\delta^2 H$ values become more negative towards the center of the Powder River Basin, and values greater than an arbitrary reference value of -140 ‰ (parts per thousand or per mil) were observed near the outcrop area of the Wyodak-Anderson coal zone. The pattern in samples collected from the overlying Wasatch aquifer was reversed. The values more negative than -140 % are near the outcrop area, and the values that are less negative than -140 \% are closer to the basin center. It is unclear if this pattern is a result of sample size, different recharge mechanisms, methanogenesis, or if the processes producing these differences are independent.

Results of ground-water-quality sampling were compared to selected USEPA and State of Wyoming regulatory and nonregulatory standards and several additional commonly used guidelines to determine the suitability of water for possible uses. The public drinking-water supply and domestic-use standards for dissolved solids were the standards most frequently exceeded in samples collected from both the Wasatch aquifer and the coalbed aquifers. The State of Wyoming agricultural-use (irrigation) standard for sulfate was exceeded in 75 percent of samples collected from the Wasatch aquifer and 8 percent of samples collected from the coalbed aquifers. The State of Wyoming agricultural-use (irrigation) standard for dissolved sol-

ids was exceeded in 25 percent of samples collected from the Wasatch aquifer and 8 percent of samples collected from the coalbed aquifers. The only State of Wyoming standard for livestock use exceeded was pH; 25 percent of samples collected from the Wasatch aquifer exceeded the standard. Water from the Wasatch aquifer ranged from soft to very hard and water from the coalbed aquifers ranged from moderately hard to very hard. Samples collected from wells completed in both the Wasatch aquifer and coalbed aquifers plotted in a wide range of both sodium- and salinity-hazard classes, but most samples clustered in or near the combined medium-sodium-hazard—high-salinity-hazard classes.

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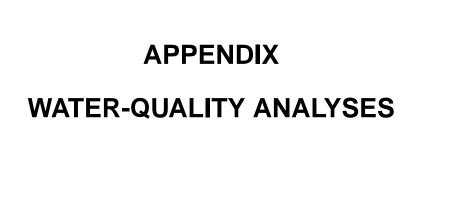


Table 1. Physical properties, general mineral characteristics, and major ions in ground-water samples collected [μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; ANC, acid-neutralizing

Site number	U.S. Geological Survey site- identification number	Local well number	Geologic unit	Hydrogeologic unit	Date of collection	Sample time	Specific conduc- tance, field mea- surement (μS/cm)	pH, field measure- ment
S1	433652105075501	42-069-15dbb01	Clinker in Tongue River Member of the Fort Union Formation	Springs discharging from clinker	06-14-99	1545	303	7.8
S2	442232105264101	51-071-30bac01	Clinker in Tongue River Member of the Fort Union Formation	Springs discharging from clinker	06-21-99	1530	1,610	7.5
W1	440253105385702	47-073-16cbc02	Wasatch Formation	Wasatch aquifer	06-16-99	1000	438	8.6
W2	440542105351802	48-073-36bcc02	Wasatch Formation	Wasatch aquifer	06-17-99	1121	914	8.2
W3	440724105291301	48-072-22adc01	Wasatch Formation	Wasatch aquifer	06-24-99	1720	870	8.1
W4	440724105291302	48-072-22adc02	Wasatch Formation	Wasatch aquifer	06-25-99	0935	4,110	7.6
W5	440724105291303	48-072-22adc03	Wasatch Formation	Wasatch aquifer	06-25-99	1035	4,330	7.2
W6	441019105414502	49-074-36ddc02	Wasatch Formation	Wasatch aquifer	06-23-99	1024	1,850	7.6
W7	441451105375502	^{2,3} 49-073-03cc 02	Wasatch Formation	Wasatch aquifer	06-17-99	1640	770	8.9
W8	443241105360801	53-073-26dba01	Tongue River Member of the Fort Union Formation above Wyodak-Anderson coal zone	Wasatch aquifer	06-29-99	1535	2,490	7.3
C1	433408105270101	³ 42-072-36db 01	Wyodak-Anderson coal zone	Coalbed aquifers	06-29-99	1150	688	7.2
C2	434252105264301	³ 43-072-12da 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1420	684	7.1
C4	435411105294001	45-072-03dbd01	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1320	990	7.2
C5	435915105242201	46-071-05dda01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1230	1,070	7.2
C6	440139105253301	47-071-30aaa01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1135	1,060	7.1
C8	440358105331401	³ 47-072-07ac 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1040	1,150	7.2
C10	440623105364101	48-073-27dac01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	0955	1,210	7.4
C11	440808106070601	³ 48-077-16ac 01	Big George coal bed ³	Coalbed aquifers	06-24-99	1330	4,180	6.9
C12	440756105293301	³ 48-072-15dc 01	Wyodak-Anderson coal zone	Coalbed aquifers	06-25-99	0905	665	7.4
C13	441017105352201	³ 48-073-02aa 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	0915	1,520	7.0
C15	441047105535401	49-075-32adb01	Coal bed or zone below the Wyodak-Anderson coal zone	Coalbed aquifers	06-24-99	1110	1,060	7.3
C16	441451105375501	³ 49-073-03cc 01	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-18-99	1005	1,700	7.3
C17	443241105360802	53-073-26dba02	Canyon coal bed of the Wyo- dak-Anderson coal zone	Coalbed aquifers	06-29-99	1600	1,790	7.8

¹Replicate sample.

²Plots in section 4 when using Global Positioning System (GPS) location; well is assigned to section 3 on well permit, so this location was used.

³Well located in center of quarter-quarter section.

⁴Big George coal bed considered equivalent to the Wyodak-Anderson coal zone (Flores and Bader, 1999)

from springs discharging from clinker and wells completed in the Wasatch aquifer and coalbed aquifers capacity; CaCO₃, calcium carbonate; NR, not reported because of problem with ANC analysis]

Temper- ature (degrees Celsius)	Cal- cium, dis- solved (mg/L)	Magne- sium, dis- solved (mg/L)	Sodium, dis- solved (mg/L)	Sodium- adsorp- tion ratio	Potas- sium, dis- solved (mg/L)	Chlo- ride, dis- solved (mg/L)	ANC, (mg/L as CaCO ₃)	Bicar- bonate, dis- solved (mg/L)	Sulfate, dis- solved (mg/L)	Fluo- ride, dis- solved (mg/L)	Silica, dis- solved (mg/L)	Dis- solved solids, calculated (mg/L)	Hard- ness, (mg/L as CaCO ₃)
12	35	9.9	8.1	0.3	6.9	2.5	116	141	28	0.5	26	187	130
10.5	210	65	46	0.7	25	12	160	195	720	0.8	30	1,200	790
20	6.2	1.5	97	9	2.2	8.1	206	251	13	0.8	11	263	22
20.5	12	6.7	180	10	6.9	17	378	461	100	0.9	10	562	57
17.5	19	6.4	180	9	4.6	6.4	455	555	23	1	9.9	527	75
14.5	450	93	480	5	12	5	129	157	2,400	< 0.1	9.2	3,490	1,500
14.5	550 ¹ 550	280 1270	270 ¹ 260	$^{2}_{^{1}2}$	14 1 ₁₄	18 ¹ 17	267 ¹ 267	326 ¹ 326	2,700 12,700	0.3 1 _{0.3}	17 ¹ 16	4,020 ¹ 4,020	2,500 12,500
18.5	7.7	24	330	13	13	0.3	1,020	1,244	10	1.5	10	1,010	120
19	11	2.7	160	11	3.7	11	NR	NR	160	0.9	8	NR	38
16	6.5	94	280	5	18	14	723	882	740	0.5	15	1,660	550
19.5	17	8.7	130	6	5.7	6.9	360	439	< 0.1	1.9	11	395	80
19	17	8.4	130	6	4.9	9.3	355	433	1.8	1.2	10	396	77
17	23	15	190	7	8.7	24	504	615	< 0.1	1.5	10	571	120
17	32	14	210	8	8.3	15	584	712	< 0.1	1.4	9.1	644	140
17	37	15	200	7	8.9	12	573	699	< 0.1	1.1	9.7	625	150
20	40	22	210	6	13	8.5	632	771	< 0.1	1.2	11	680	190
20	36	23	210	7	15	9.1	647	789	0.9	1.3	11	697	180
26	51	39	1,000	26	48	21	2,570	3,134	< 0.3	1.2	7.4	2,720	290
20	15	8.7	120	6	6.3	8.9	346	422	< 0.1	1.6	9.9	382	74
18.5	49	27	270	8	13	7.7	853	1,040	< 0.1	0.8	10	888	230
27	25 ¹ 26	14 114	190 ¹ 190	8 1 ₈	13 1 ₁₂	7 ¹ 7	580 ¹ 580	707 ¹ 707	1.2 11.2	1.1 ¹ 1.1	20 120	624 ¹ 622	120 1120
17	54	29	340	9	13	8.3	956	1,166	1	0.9	10	1,030	260
14	62	33	330	8	12	11	962	1,173	0.7	0.6	11	1,040	290

Table 2. Radioactive and stable-isotope values for ground-water samples collected from springs discharging from clinker and wells completed in the Wasatch aquifer and coalbed aquifers

[pCi/L, picocuries per liter; δ^2 H, deuterium/hydrogen isotopic ratio; δ^{18} O, oxygen-18/oxygen-16 isotopic ratio; ‰, parts per thousand or per mil; <MRL, value less than minimum reporting level of 1 picocurie per liter]

Site number	U.S. Geological Survey site- identification number	Local well number	Geologic unit	Hydrogeologic unit	Date of collection	Sample time	Tritium (pCi/L)	Analytical uncer- tainty ¹ (+/-pCi/L)	δ ² Η (‰)	δ ¹⁸ Ο (‰)
S1	433652105075501	42-069-15dbb01	Clinker in Tongue River Member of the Fort Union Formation	Springs discharging from clinker	06-14-99	1545	76	4	-138.5	-18.04
S2	442232105264101	51-071-30bac01	Clinker in Tongue River Member of the Fort Union Formation	Springs discharging from clinker	06-21-99	1530	52	3	-142.6	-18.41
W1	440253105385702	47-073-16cbc02	Wasatch Formation	Wasatch aquifer	06-16-99	1000	<mrl< td=""><td>1</td><td>-139.0</td><td>-18.03</td></mrl<>	1	-139.0	-18.03
W2	440542105351802	48-073-36bcc02	Wasatch Formation	Wasatch aquifer	06-17-99	1121	9	1	-124.0	-15.57
W3	440724105291301	48-072-22adc01	Wasatch Formation	Wasatch aquifer	06-24-99	1720	2	1	-140.7	-18.40
W4	440724105291302	48-072-22adc02	Wasatch Formation	Wasatch aquifer	06-25-99	0935	<mrl< td=""><td>1</td><td>-148.6</td><td>-19.02</td></mrl<>	1	-148.6	-19.02
W5	440724105291303	48-072-22adc03	Wasatch Formation	Wasatch aquifer	06-25-99	1035	6 2 ₉	1 1	-147.8 ² -147.2	-19.03 ² -19.02
W6	441019105414502	49-074-36ddc02	Wasatch Formation	Wasatch aquifer	06-23-99	1024	2	1	-131.1	-18.14
W7	441451105375502	^{3,4} 49-073-03cc 02	Wasatch Formation	Wasatch aquifer	06-17-99	1640	1	1	-146.5	-18.95
W8	443241105360801	53-073-26dba01	Tongue River Member of the Fort Union Formation above Wyodak-Anderson coal zone	Wasatch aquifer	06-29-99	1535	<mrl< td=""><td>1</td><td>-138.9</td><td>-18.46</td></mrl<>	1	-138.9	-18.46
C1	433408105270101	⁴ 42-072-36db 01	Wyodak-Anderson coal zone	Coalbed aquifers	06-29-99	1150	<mrl< td=""><td>1</td><td>-137.9</td><td>-17.84</td></mrl<>	1	-137.9	-17.84
C2	434252105264301	⁴ 43-072-12da 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1420	<mrl< td=""><td>1</td><td>-141.9</td><td>-18.31</td></mrl<>	1	-141.9	-18.31
C4	435411105294001	45-072-03dbd01	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1320	1	1	-144.2	-18.54
C5	435915105242201	46-071-05dda01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1230	<mrl< td=""><td>1</td><td>-138.1</td><td>-17.92</td></mrl<>	1	-138.1	-17.92
C6	440139105253301	47-071-30aaa01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1135	<MRL	1	-140.9	-18.25
C8	440358105331401	⁴ 47-072-07ac 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	1040	1	1	-143.5	-18.79
C10	440623105364101	48-073-27dac01	Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	0955	2	1	-143.4	-18.51
C11	440808106070601	⁴ 48-077-16ac 01	Big George coal bed ⁵	Coalbed aquifers	06-24-99	1330	1	1	-132.9	-17.80
C12	440756105293301	⁴ 48-072-15dc 01	Wyodak-Anderson coal zone	Coalbed aquifers	06-25-99	0905	<mrl< td=""><td>1</td><td>-136.6</td><td>-18.56</td></mrl<>	1	-136.6	-18.56
C13	441017105352201	⁴ 48-073-02aa 01	Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-30-99	0915	<mrl< td=""><td>1</td><td>-141.3</td><td>-18.40</td></mrl<>	1	-141.3	-18.40
C15	441047105535401	49-075-32adb01	Coal bed or zone below the Wyodak-Anderson coal zone	Coalbed aquifers	06-24-99	1110	<mrl< td=""><td>1</td><td>-151.0</td><td>-19.99</td></mrl<>	1	-151.0	-19.99
		4					² <mrl< td=""><td>1</td><td>²-150.3</td><td>²19.94</td></mrl<>	1	² -150.3	² 19.94
C16	441451105375501	⁴ 49-073-03cc 01	Upper Wyodak coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-18-99	1005	<mrl< td=""><td>1</td><td>-134.9</td><td>-18.66</td></mrl<>	1	-134.9	-18.66
C17	443241105360802	53-073-26dba02	Canyon coal bed of the Wyodak-Anderson coal zone	Coalbed aquifers	06-29-99	1600	1	1	-143.7	-18.78

¹Also known as two-sigma precision estimate.

²Replicate sample.

³Plots in section 4 when using Global Positioning System (GPS) location; well is assigned to section 3 on well permit, so this location was used.

⁴Well located in center of quarter-quarter section.

⁵Big George coal bed considered equivalent to the Wyodak-Anderson coal zone (Flores and Bader, 1999).

