

Prepared in cooperation with the City of Spearfish and Lawrence County

Characterization of Ground-Water Flow and Water Quality for the Madison and Minnelusa Aquifers in Northern Lawrence County, South Dakota



Scientific Investigations Report 2007-5001

Cover: Photograph of collecting a water sample from the bottom of Mirror Lake near spring opening T. 7 N., R. 1 E., section 17 (photograph by Larry D. Putnam, U.S. Geological Survey)

Characterization of Ground-Water Flow and Water Quality for the Madison and Minnelusa Aquifers in Northern Lawrence County, South Dakota

By Larry D. Putnam and Andrew J. Long

Prepared in cooperation with the City of Spearfish and Lawrence County

Scientific Investigations Report 2007–5001

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

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

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2007

For product and ordering information:
World Wide Web: <http://www.usgs.gov/pubprod>
Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:
World Wide Web: <http://www.usgs.gov>
Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Putnam, L.D., and Long, A.J., 2007, Characterization of ground-water flow and water quality for the Madison and Minnelusa aquifers in northern Lawrence County, South Dakota: U.S. Geological Survey Scientific Investigations Report 2007-5001, 61 p.

Contents

Abstract.....	1
Introduction.....	2
Purpose and Scope	2
Description of Study Area	2
Acknowledgments.....	2
Hydrogeologic Setting.....	2
Methods.....	3
Mapping Potentiometric Surfaces.....	3
Dye Tracing Tests.....	10
Geochemical Tracers	10
Sample Collection and Analysis.....	10
Oxygen and Deuterium Isotopes.....	11
Chlorofluorocarbons	11
Tritium	11
Estimating Ground-Water Age from Chlorofluorocarbons	12
Water Quality.....	12
Characterization of Ground-Water Flow.....	13
Recharge.....	13
Areal Recharge	16
Streamflow Recharge	16
Spring Discharge	18
Potentiometric Surfaces.....	19
Flow Paths and Flow Rates Based on Dye Tracing.....	19
Fluorescein Injection.....	24
Rhodamine WT Injection	26
Ground-Water Flow Paths, Ages, and Mixing Based on Geochemical Tracers	29
Oxygen and Deuterium Isotopes.....	29
Chlorofluorocarbons	31
Ground-Water Age Distributions from Chlorofluorocarbon Data.....	33
Evidence for a Conduit Based on the Spatial Distribution of Apparent Ages	33
Tritium	34
Synopsis of Results from Geochemical Tracers.....	35
Characterization of Water Quality.....	36
Summary.....	44
References.....	45
Supplemental Information.....	49
Section A. Additional data	51
Section B. Dye Tracing Methods	58
Fluorescein.....	58
Rhodamine WT	58

Section C. Chlorofluorocarbon Age-Dating Methods and Background	60
Chlorofluorocarbons	60
Dissolved Gas Data.....	60

Figures

1. Map showing location of study area.....	4
2. Map showing hydrogeologic units of study area.....	6
3. Chart showing stratigraphic section for study area.....	8
4. Simplified hydrogeologic setting in the study area.....	9
5. Graph showing estimated 6-month tritium concentration in precipitation for the Black Hills, South Dakota.....	12
6. Graphs showing water-level hydrographs for observation wells completed in the Madison aquifer and the Minnelusa aquifer.....	14
7. Graph showing comparison of average annual streamflow and base flow for Crow Creek	18
8. Map showing generalized potentiometric surface of the Madison aquifer in 2004.....	20
9. Map showing generalized potentiometric surface of the Minnelusa aquifer in 2004.....	22
10–15. Graphs showing	
10. Fluorescein breakthrough curves for wells where dye was detected, March 2003–September 2004	24
11. Rhodamine WT breakthrough curves for wells where dye may be present, May 2003–September 2004	28
12. Water level in the Madison aquifer for observation well LA–88C near Spearfish during dye injections.....	29
13. Relation between $\delta^{18}\text{O}$ and δD in water samples collected from 1978 to 2005 from Madison and Minnelusa wells and springs, and surface water	31
14. Regression analysis of CFC–11 apparent age with distance to a possible major conduit.....	34
15. Regression analysis of tritium concentration with distance to a possible major conduit.....	35
16. Map showing specific conductance of water from the Madison aquifer	38
17. Map showing specific conductance of water from the Minnelusa aquifer.	40
18. Boxplot showing comparison of background, blank, and replicate samples for fluorescein dye analysis.....	58
19. Graph showing comparison of initial fluorescein concentrations with concentrations in samples that were stored for about 1 year.....	59
20. Boxplot showing comparison of background, blank, and replicate samples for Rhodamine WT dye analysis.....	59
21. Graph showing atmospheric concentrations of chlorofluorocarbons CFC–11, CFC–12, and CFC–113.....	60

Tables

1. Estimated average annual recharge to the Madison and Minnelusa aquifers in the study area	16
2. Streamflow loss to the Madison aquifer in upper reach of loss zone along Spearfish Creek.....	17
3. Streamflow gains or losses for selected reaches of Spearfish Creek.....	17
4. Streamflow losses to the Madison aquifer from Spearfish Creek	18
5. Summary of fluorometric analysis of water samples for fluorescein dye	25
6. Summary of fluorometric analysis of water samples for Rhodamine WT dye.....	27
7. Oxygen- and deuterium-isotope data for wells and springs in the study area	30
8. Chlorofluorocarbon and tritium data for wells and springs in the study area	32
9. Chemical analyses of selected ground-water samples from the Madison and Minnelusa aquifers.....	42
10. Observation wells used for monitoring water levels in the study area	51
11. Water wells completed in the Madison aquifer and used for interpretation of average potentiometric surface.....	52
12. Water wells completed in the Minnelusa aquifer and used for interpretation of average potentiometric surface.....	54
13. Analysis of fluorescein standards for concentrations of Rhodamine WT	59
14. Dissolved-gas data for selected wells and springs in the study area.....	61

Conversion Factors

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
	Volume	
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
gallon (gal)	3.785	cubic decimeter (dm ³)
million gallons (Mgal)	3,785	cubic meter (m ³)
cubic inch (in ³)	16.39	cubic centimeter (cm ³)

Multiply	By	To obtain
	Flow rate	
foot per day (ft/d)	0.3048	meter per day (m/d)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)
	Pressure	
pound per square inch (lb/in ²)	6.895	kilopascal (kPa)
	Transmissivity*	
foot squared per day (ft ² /d)	0.09290	meter squared per day (m ² /d)

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

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

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

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

*Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [(ft³/d)/ft²ft]. In this report, the mathematically reduced form, foot squared per day (ft²/d), is used for convenience.

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

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

Isotopic ratios are expressed in units of per mil (parts per thousand). Tritium concentrations are expressed in units of picocuries per liter (pCi/L) or tritium units (TU).

Water year is the 12-month period, October 1 through September 30, and is designated by the calendar year in which it ends. Thus, the water year ending September 30, 2003, is called "water year 2003."

Acronyms and Abbreviations

%	per mil
MCL	Maximum Contaminant Level
CFC	chlorofluorocarbon
pptv	parts per trillion by volume
pCi/L	picocuries per liter
SDDENR–WR	Water Rights Program of the South Dakota Department of Environment and Natural Resources
TU	tritium units
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
δD	² H/ ¹ H ratio compared to a reference composition
δ ¹⁸ O	¹⁸ O/ ¹⁶ O ratio compared to a reference composition
cm ³ /L	cubic meters per liter

Characterization of Ground-Water Flow and Water Quality for the Madison and Minnelusa Aquifers in Northern Lawrence County, South Dakota

By Larry D. Putnam and Andrew J. Long

Abstract

The Madison and Minnelusa aquifers are used extensively for water supplies for the city of Spearfish and other users in northern Lawrence County, South Dakota. Ground water in the Madison and Minnelusa aquifers in the study area generally flows north from outcrop areas where recharge from sinking streams and infiltration of precipitation occurs. Ground water that moves northward and eastward around the Black Hills enters the study area from the west and results in hydraulic heads that are several hundred feet higher on the western side of the study area than on the eastern side. The estimated average recharge rate of 38 cubic feet per second (ft³/s) on outcrops of the Madison Limestone and Minnelusa Formation is less than the total estimated average spring discharge rate of 51 ft³/s in the northwestern part of the study area.

Sixteen pounds of fluorescein dye were injected into Spearfish Creek on March 25, 2003, when streamflow was 6.6 ft³/s. The dye was detected in water samples from four wells completed in the Madison aquifer ranging from 2.6 to 4.5 miles north of the injection site. First arrival times ranged from 5 to 169 days, and ground-water velocities ranged from about 0.1 to 0.5 mile per day. Sixty-four pounds of Rhodamine WT was injected into Spearfish Creek at the same location on May 9, 2003, when streamflow was 5.6 ft³/s. Rhodamine WT dye concentrations measured in samples from the same four wells were about an order of magnitude less than measured fluorescein concentrations.

Oxygen- and deuterium-isotope values for samples from Cox Lake and McNenny Pond springs indicated a probable component of spring discharge that originates from outcrops of the Madison Limestone and Minnelusa Formation on the Limestone Plateau south of the study area. Oxygen- and deuterium-isotope values for samples from Mirror Lake spring indicated possible contributions from overlying aquifers and local recharge. Oxygen- and deuterium-isotope values for the combined springflow contributing to Crow Creek in the northwestern part of the study area indicated that the primary source of water is the Madison and Minnelusa aquifers. Oxygen- and deuterium-isotope values for Old Hatchery and Higgins Gulch springs, located north of Spearfish, indicated a source water

originating from the outcrops of the Madison Limestone and Minnelusa Formation within the study area.

Concentrations of three chlorofluorocarbons (CFC-11, CFC-12, and CFC-113) were used to characterize ground-water residence times in the study area. For the four wells where dye was detected, CFC-11 apparent ages ranged from 12 to 26 years, indicating that the wells contained months-old water mixed with years- to decades-old water. Logarithmic regression analysis of the CFC-11 apparent ages for water from 10 wells and distance to a possible conduit trending north through the area where dye was detected, yielded an r^2 value of 0.71. Straight-line regression analysis of the CFC-11 apparent ages for the six wells closest to the possible conduit had an r^2 value of 0.96. Two wells located relatively close to the outcrop areas had no or very low tritium values indicating relatively long residence times and diffuse ground-water flow. The tritium value of 7.2 TU in water from well COL where dye was detected, indicated that the water probably is a bimodal mixture, with a substantial portion that is older than 50 years. Water from well ELL, where dye was detected, had a tritium value of 19.7 TU and a CFC apparent age of 15 years, indicating that the sample from this well probably is a unimodal mixture with very little water older than 50 years. Comparison of the CFC apparent age for three spring sites (Cox Lake, 26 years; McNenny Pond, 26 years; Mirror Lake, 13 years) also indicated that Mirror Lake spring probably has a component of local recharge from formations that overlie the Minnelusa Formation.

In the Madison aquifer, specific conductance ranges from 18 to 945 microsiemens per centimeter. In the Minnelusa aquifer, specific conductance increases with distance from the outcrop and ranges from 2 to 3,000 microsiemens per centimeter. Water samples from two observation wells completed in the Madison and Minnelusa aquifers near Spearfish and two wells about 6 miles east of Spearfish were analyzed for physical properties, major ions, nutrients, trace elements, and radio-nuclides. U.S. Environmental Protection Agency Maximum Contaminant Levels were not exceeded for any of the constituents analyzed in water from the four wells. The U.S. Environmental Protection Agency Secondary Maximum Contaminant Level for sulfate (250 milligrams per liter) was exceeded in

water from the Minnelusa well located east of Spearfish, with a concentration of 392 milligrams per liter.

Introduction

The Madison and Minnelusa aquifers are used extensively for water supplies for the city of Spearfish and other users in northern Lawrence County, South Dakota, that include domestic, non-community, community, and irrigation users. A better understanding of ground-water flow in this complex hydrologic setting is needed to manage and protect these important water resources. The Madison Limestone and Minnelusa Formation have extensive fractures, solution-enhanced openings, and collapse features that result in large and variable secondary porosities and large heterogeneity in associated aquifer properties. For this reason, ground-water flow generally is complicated in these aquifers, and influences regarding water quality can be complex. A cooperative study between the U.S. Geological Survey (USGS), Lawrence County, and the city of Spearfish was initiated in 2000 to collect and analyze ground-water data to improve understanding of ground-water flow and water quality in these complex aquifers in northern Lawrence County.

Purpose and Scope

The purpose of this report is to present information that characterizes ground-water flow and water quality in the Madison and Minnelusa aquifers in northern Lawrence County. Most of the data included in this report were collected during 2000–2006. For the characterization of ground-water flow, this report includes estimates of recharge and spring discharge; potentiometric surfaces, flow paths and flow rates based on dye tracing; and ground-water flow paths, ages, and mixing based on geochemical tracing. The description of water quality for the Madison and Minnelusa aquifers focuses on selected wells and the general distribution of specific conductance.

Description of Study Area

The study area in northern Lawrence County consists of about 400 square miles (mi²) in the northwestern part of the topographically distinct Black Hills and adjacent foothills and plains to the north (fig. 1). Land-surface altitudes range from about 6,000 feet (ft) in the southwestern part of the study area to about 3,000–4,000 ft in the plains to the north, resulting in an orographically induced microclimate characterized generally by greater precipitation and lower temperatures at the higher altitudes. The lowest altitude is near 3,000 ft in the northeastern corner of the county. Average annual precipitation for 1961–1990 ranged from about 29 inches (in.) near Deadwood to about 18 in. in the northwestern part of the

study area (Driscoll and others, 2000). The average 30-year annual temperature is 46.5°F at Spearfish and 41.8°F at Lead (National Oceanic and Atmospheric Administration, 1997), which is located about 1 mi southwest of Deadwood.

Acknowledgments

The authors thank the city of Spearfish and residents of Lawrence County for their cooperation with data collection associated with this study. The Water Rights Program of the South Dakota Department of Environment and Natural Resources (SDDENR–WR) provided water-level records for observation wells and access to the observation wells for water-quality sampling. South Dakota Game Fish and Parks allowed access to spring-fed ponds for sampling. Numerous private entities also allowed access to wells and springs for sampling. The city of Spearfish provided extensive assistance with the collection of samples from municipal production wells for fluorescent dye tracing. The city of Spearfish and Homestake Mining Company also provided assistance with the streamflow measurements for Spearfish Creek.

Hydrogeologic Setting

Geologic formations in the study area have been grouped into hydrogeologic units and mapped for the Black Hills area based on similarity in hydraulic properties (Strobel and others, 1999). A generalization of that map (fig. 2) shows the surface exposures of the hydrogeologic units for the study area, labeled with the stratigraphic unit abbreviations for the grouped geologic formations (fig. 3). Precambrian igneous and metamorphic rocks in the southern part of the study area represent the northern extent of the central core of the Black Hills where the sedimentary rocks have been removed by erosion. Various outcrops of Tertiary-age intrusive rocks exist in the southern part of the study area (Lisenbee, 1985) that may include shallowly emplaced sills, laccoliths, dikes, and plugs. North of the Precambrian rocks are exposures of overlying limestone, sandstone, and shale. These bedrock sedimentary formations typically dip away from the uplifted Black Hills at angles that approach 15 to 20 degrees near the outcrops (Carter and Redden, 1999a, 1999b, 1999c), and decrease with distance from the uplift to about 2 degrees in the northeastern part of the study area. Unconsolidated units of Quaternary age include alluvium, colluvium, and gravel deposits. Mapped alluvial deposits along streams generally are widest in the northern part of the study area, where stream gradients generally are lowest.

The Madison and Minnelusa aquifers are contained within the Paleozoic-age Madison Limestone and Minnelusa Formation, and their relation to other sedimentary units is schematically illustrated in figure 4. The Minnelusa Formation is overlain by the Opeche Shale, and the Madison Limestone is underlain by the Englewood Formation. The hydraulic

connection between the Madison Limestone and Minnelusa Formation is spatially variable and probably results from faults, fractures, and breccia pipes. Collapse features resulting from the dissolution of anhydrite and gypsum in the Minnelusa Formation and from the dissolution of carbonates in the Madison Limestone may be pathways for vertical movement of water between these units. These features are described by several authors including Brobst and Epstein (1963), Bowles and Braddock (1963), Gott and others (1974), Hayes (1999), Greene (1999), and Long and Putnam (2002).

The Mississippian-age Madison Limestone is composed of limestone and dolomite, and thickness ranges from about 350 to 1,000 ft in the study area (Putnam, 2000). Secondary permeability generally is greater in the upper part of the formation because of solution openings and fractures (Greene, 1993). The upper surface of the formation is a weathered karst surface, unconformable with the overlying Minnelusa Formation (Cattermole, 1969). The aquifer is considered karstic because of the extensive solution enlargement of fractures that have resulted in a predominance of conduit flow. Secondary permeability in the lower part of the Madison Limestone generally is much smaller than in the upper part (Greene, 1993); however, the lower part of the unit can have greater permeability near outcrop areas, especially along stream channels. Well yields in the Madison aquifer are highly variable and most range from 10 to 200 gallons per minute (gal/min) with some yields ranging from 400 to 1,750 gal/min.

The Pennsylvanian- and Permian-age Minnelusa Formation is 350 to 650 ft thick in the study area. Bowles and Braddock (1963) describe the upper part as thick sandstone with thin limestone, dolomite, and mudstone, and the lower part as having less sandstone and more shale, limestone, and dolomite. Siltstone, gypsum, and anhydrite also can be present. At the base of the Minnelusa Formation is a red clay shale that ranges from 0 to 50 ft thick (Cattermole, 1969; Greene, 1993). This shale is an ancient residual soil developed on the surface of the Madison Limestone (Gries, 1996). The upper 200 to 300 ft of the Minnelusa Formation is more permeable than the lower part of the formation because of the coarser sandstone, solution openings, breccias, and other collapse features in the upper part (Peter and others, 1987; Greene, 1993). The lower part of the formation generally impedes flow between the Minnelusa and Madison aquifers (Kyllonen and Peter, 1987; Peter and others, 1987; Greene, 1993). Near outcrop areas and structural features, the lower part of the Minnelusa Formation can have increased permeability due to weathering and fracturing. Well yields are highly variable; most of the wells yield between 10 and 200 gal/min, many wells yield between 200 and 700 gal/min, and a few wells yield as much as 1,700 gal/min.

The Madison and Minnelusa aquifers are unconfined in and near the outcrop areas and confined in the rest of the study area north of the outcrops. When the confined portions of an aquifer are penetrated by wells, the water level rises above the top of the respective formation. A well drilled into such an aquifer is often referred to as an artesian well. When the

water in the well rises above the land surface, the well may be referred to as a flowing well. Also, springs that discharge to the land surface through openings in overlying confining layers often are referred to as artesian springs.

Transmissivity of the Madison and Minnelusa aquifers is very heterogeneous. Transmissivity values from aquifer tests that analyzed the formations at several different scales of area around a well stressed by aquifer tests (Greene and others, 1998) ranged over several orders of magnitude. Transmissivity values from testing production wells at a scale of 1,000–2,000 ft were about 10,000 feet squared per day (ft²/d) for the Minnelusa aquifer and about 40,000 ft²/d for the Madison aquifer. Confined storage coefficients ranged from 0.00007 to 0.0003. A summary of estimates of hydraulic conductivity, transmissivity, storage coefficient, and porosity for the Madison and Minnelusa aquifers in the Black Hills area is provided by Driscoll and others (2002, p. 27–28).

Methods

This section of the report describes methods used for mapping potentiometric surfaces, dye tracing tests, geochemical tracers, and water quality. Additional data for mapping potentiometric surfaces are provided in Supplemental Information Section A at the end of this report. Additional information regarding methods for dye tracing and chlorofluorocarbon (CFC) age-dating is provided in Supplemental Information Sections B and C, respectively, at the end of this report.

Mapping Potentiometric Surfaces

The potentiometric surface of an aquifer is equal to the altitude at which water will rise in tightly cased wells open to that aquifer (Lohman and others, 1972). In unconfined areas, such as outcrops of water-bearing rocks, this surface is equal to the water-table altitude. Potentiometric surfaces of the Madison and Minnelusa aquifers were defined based on water levels or pressures measured in public and private wells. For wells under pressure, pressure measurements were converted to equivalent feet of water above the land surface. The potentiometric surfaces represent water-level altitudes, which are referred to as hydraulic heads.

Water levels in wells were measured on various dates between 1905 and 2002 by the drillers at the time of well installation or by USGS personnel during previous studies. Because of difficulties related to access of private or public-supply wells, water levels were not measured as part of this study. Wells constructed since about 1993, when the last well inventory was completed, were site visited and locations and land-surface altitudes were determined. The static water level reported in the well completion report was used in addition to previous water-level measurements in creating the potentiometric maps. An attempt was made to adjust for low water levels that were measured during dry conditions and for high

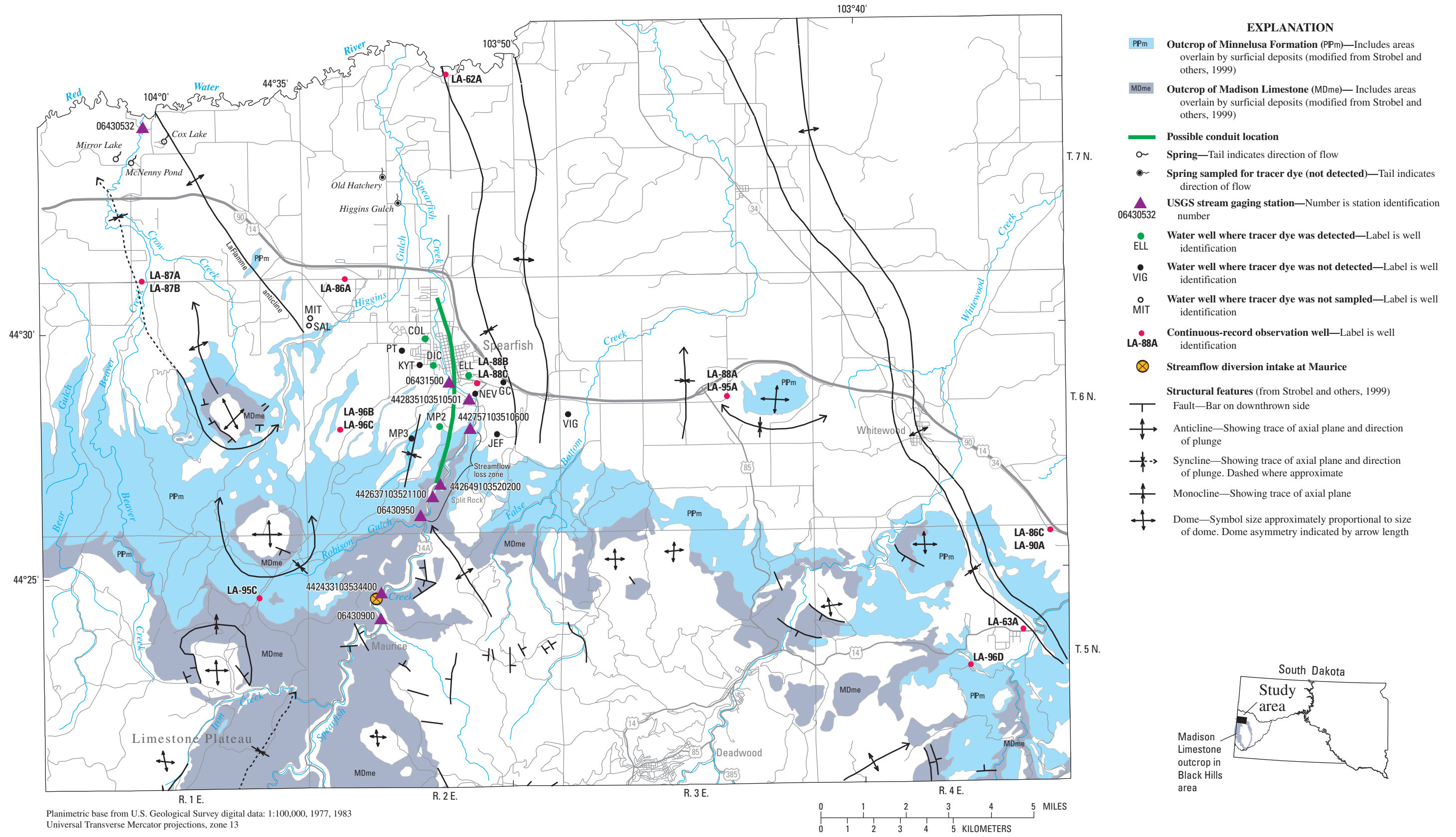


Figure 1. Location of study area.

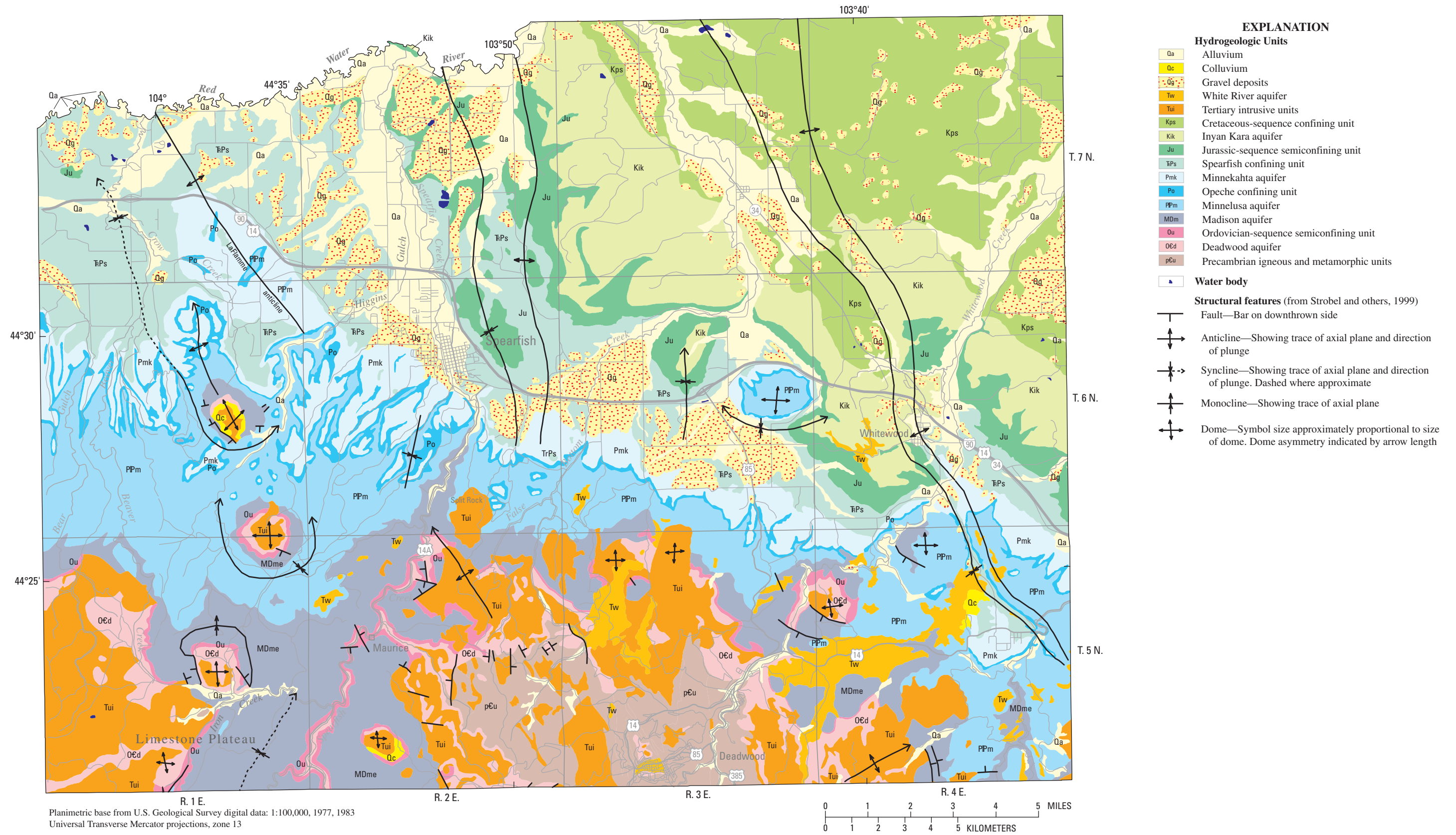


Figure 2. Hydrogeologic units of study area (modified from Strobel and others, 1999).

ERATHM	SYSTEM	ABBREVIATION FOR STRATIGRAPHIC INTERVAL	GEOLOGIC FORMATION	SUBSURFACE THICKNESS, IN FEET ¹	DESCRIPTION		
CENOZOIC	QUATERNARY & TERTIARY (?)	Qa, Qc, Qg	UNDIFFERENTIATED SANDS AND GRAVELS	~0-60	Sand, gravel, and boulders		
	TERTIARY	Tw	WHITE RIVER GROUP	~0-150	Light colored clays with sandstone channel fillings and local limestone lenses.		
MESOZOIC	CRETACEOUS	Tui	INTRUSIVE IGNEOUS ROCKS	---	Includes rhyolite, latite, trachyte, and phonolite.		
			BELLE FOURCHE SHALE	~150-850	Gray shale with scattered limestone concretions.		
		GRANEROS GROUP	Kps	MUDRY SHALE	~125-230	Clay spur bentonite at base.	
				DYNNESON SANDSTONE	~0-100	Light-gray siliceous shale. Fish scales and thin layers of bentonite.	
			NEWCASTLE	~150-270	Brown to light yellow and white sandstone.		
	SKULL CREEK SHALE	Kik	FALL RIVER FORMATION	~10-200	Dark gray to black siliceous shale.		
			Fusion Shale Minnewaste Limestone	~30-300	Massive to silty sandstone. Coarse gray to buff cross-bedded conglomeratic sandstone, interbedded with buff, red, and gray clay, especially toward top. Local fine-grained limestone.		
	JURASSIC	LAKOTA GROUP	MORRISON FORMATION	UNKPA PA SS	~0-150	Green to maroon shale. Thin sandstone.	
				UNKPA PA SS	~0-275	Massive fine-grained sandstone.	
		INYAN KARA GROUP	Ju	Redwater Member	~250-475	Greenish-gray shale, thin limestone lenses.	
Lak Member				~0-125	Glaucconitic sandstone; red sandstone near middle.		
Stockade Beaver Mem. Canyon Spr Member				~275-800	Red siltstone, gypsum, and limestone.		
SUNDANCE FORMATION	Pps	GYPSUM SPRING FORMATION	Red shale and sandstone.	~275-800	Red sandy shale, soft red sandstone and siltstone with gypsum and thin limestone layers.		
			Goose Egg Equivalent	~35-50	Gypsum locally near the base.		
			MINNEKAHTA LIMESTONE	~25-150	Thin to medium-bedded finely-crystalline, purplish gray laminated limestone.		
PERMIAN	PIPm	MINNELUSA FORMATION	OPECHE SHALE	~550-650	Yellow to red cross-bedded sandstone, limestone, mudstone, and anhydrite locally at top.		
			MINNELUSA FORMATION	~950-1000	Interbedded sandstone, limestone, dolomite, shale, gypsum, and anhydrite.		
			MINNELUSA FORMATION	~950-1000	Red shale with interbedded limestone and sandstone at base.		
PALEOZOIC	MISSISSIPPIAN	MDm	MADISON (PAHASAPA) LIMESTONE	~40-75	Massive light-colored limestone. Dolomite in part. Cavernous in upper part.		
			DEVONIAN	ENGLWOOD FORMATION	~0-150	Pink to buff limestone. Shale locally at base.	
				WHITEWOOD (RED RIVER) FORMATION	~0-110	Buff dolomite and limestone.	
			ORDOVICIAN	Ou	WINNIPEG FORMATION	~300-500	Green shale with siltstone.
					DEADWOOD FORMATION	~300-500	Massive to thin-bedded buff to purple sandstone. Greenish glauconitic shale, flaggy dolomite, and flatpebble limestone conglomerate. Sandstone, with conglomerate locally at the base.
	CAMBRIAN	OCd	PRECAMBRIAN	UNDIFFERENTIATED METAMORPHIC AND IGNEOUS ROCKS	~300-500	Schist, slate, quartzite, and arkosic grt. Intruded by diorite, metamorphosed to amphibolite, and by granite and pegmatite.	

Modified from information furnished by the Department of Geology and Geological Engineering, South Dakota School of Mines and Technology (written commun., January 1994)

¹ The subsurface thickness was modified from several references to provide a range that was the most specific to the study area.
² DeWitt and others, 1989.
³ Robinson and others, 1964.
⁴ Kyllonen and Peter, 1987.
⁵ Thickness estimated from subtracting surfaces created from structure contours of the tops of Madison Limestone and Minnelusa Formation (Carter and Redden, 1999b; 1999a).
⁶ Thickness estimated from subtracting surfaces created from structure contours of the tops of Deadwood Formation and Madison Limestone (Carter and Redden, 1999c; 1999b). The subsurface thicknesses of the Madison Limestone greater than 700 feet are in the northeast part of the study area.

Figure 3. Stratigraphic section for study area.

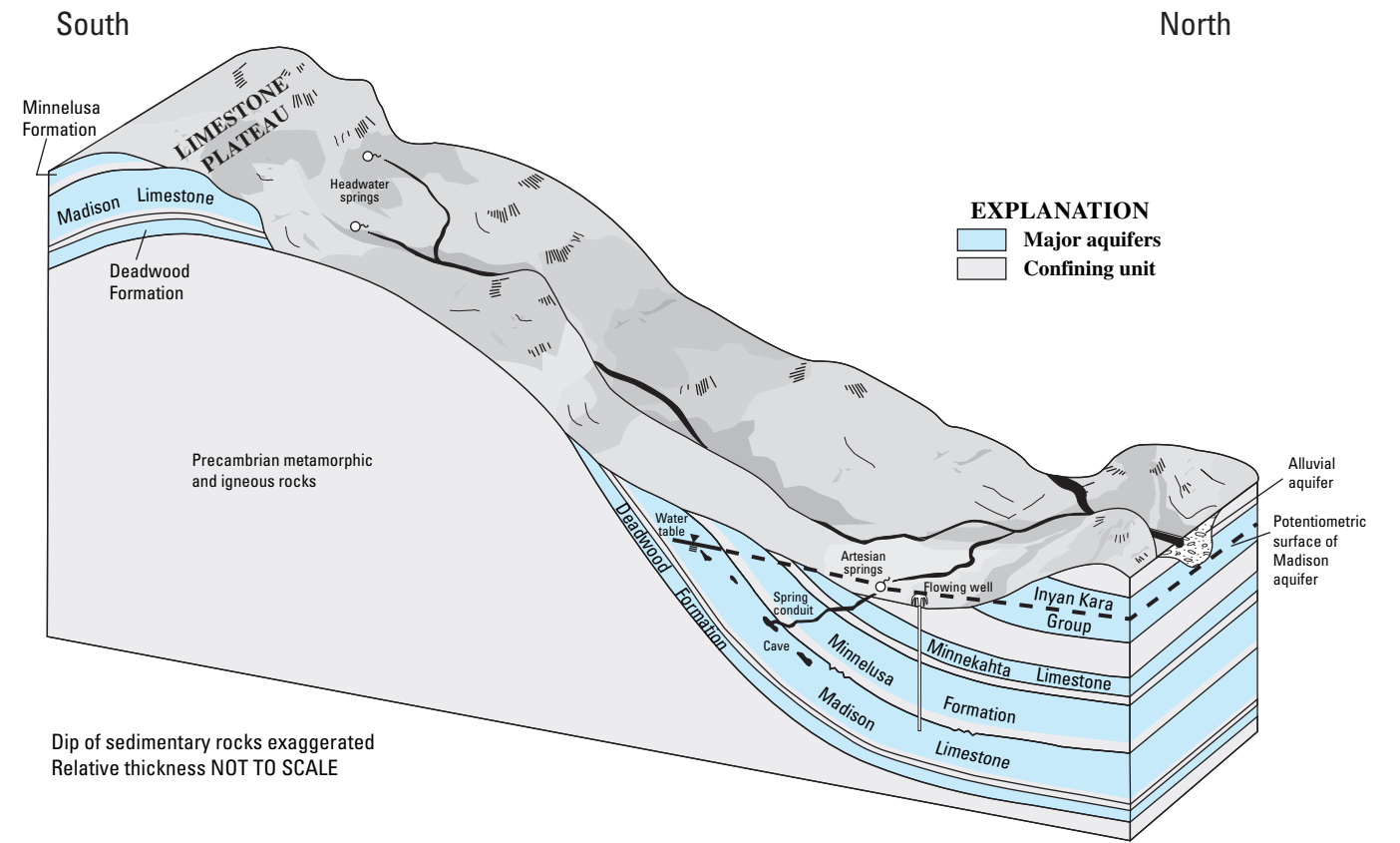


Figure 4. Simplified hydrogeologic setting in the study area.

water levels measured during wet conditions. To create a contemporaneous potentiometric surface, it was necessary to estimate water levels that represent current conditions. Therefore, measured water levels were adjusted based on records from continuous water-level observation wells in the study area to approximate potentiometric surfaces representing current conditions. The similarity of water level records for observation wells at various locations (as described in the “Characterization of Ground-Water Flow” section) indicates that water levels in nearby wells with single measurements probably also changed similarly to water levels in the observation wells. September 15, 2004, was selected as the date for which potentiometric surfaces would be estimated. Thus, measured water levels were adjusted to a water level that was estimated for each well based on the nearest observation well open to the same aquifer (table 10 in Supplemental Information Section A). If the date of measurement was prior to the measured period of record for the nearest observation well, the adjustment was made on the basis of well LA-63A, which had the longest water-level record in the study area (1969–2006) and is open to the Minnelusa aquifer. The magnitude and sign of each adjustment was equal to the difference in hydraulic head in the observation well between September 15, 2004, and the measurement date. For example, if the water level in the nearest observation well declined 12 ft between the date at which a

private well was measured and September 15, 2004, then 12 ft were subtracted from the measured water level for the private well. For the Minnelusa aquifer, seven wells had water-level measurements prior to the period of record for LA-63A, and thus these water levels could not be adjusted. Although some error is accepted, the adjustments were considered an improvement over no adjustment. The mean and standard deviation for the absolute values of the adjustments were 16.9 ft and 1.6 ft, respectively, for the Madison aquifer and 9.5 ft and 0.9 ft, respectively, for the Minnelusa aquifer. Considering the total relief in the potentiometric surfaces (2,200 ft and 2,000 ft, respectively), the adjustments are relatively small and thus did not substantially effect the overall potentiometric surface. Only sites where the location has been verified were used in constructing potentiometric-surface maps. In some locations, the data indicate excessive spatial variability in hydraulic head at local scales, which probably does not represent the potentiometric surface. This variability may result from measurement errors or errors in estimating the land-surface altitude at the well. One-hundred-foot contour intervals were constructed with the intent of showing the smoothest potentiometric surface possible within the constraints of the data. Therefore, local hydraulic-head variability within contour intervals sometimes was ignored by assuming the strict

linear interpolation between contour lines need not necessarily apply to each data point. In addition, about 9 percent of these data points did not reasonably fit between appropriate contours without introducing improbable bends or unlikely closed contours. These data points were assumed to be in error, were not used in constructing the potentiometric surface, and are not shown on the potentiometric surface. Data for all site-visited wells in the study area used for interpretation of average potentiometric surfaces and those not used are listed in Supplemental Information Section A (tables 10–12).

The land-surface altitude of a spring in an outcrop area is approximately equal to the water-table altitude at that location, and thus selected springs were used in constructing potentiometric-surface maps. However, some springs may discharge from perched aquifers and thus do not represent the main water-table altitude. Springs at unusually high altitudes were assumed to discharge perched water and therefore were not used in constructing potentiometric-surface maps. Artesian springs discharging water into Cox Lake, Mirror Lake, and the McNenny Fish Hatchery rearing pond probably flow from the Madison and Minnelusa aquifers (Klemp, 1995). Because these aquifers are buried at these locations, hydraulic head must be above the land surface to compensate for head losses incurred as water is forced to the land surface. It was assumed that hydraulic head was at least within 100 ft of the land surface at these springs. This situation may be similar to Jackson-Cleghorn Springs in Rapid City, South Dakota, which is a large relatively steady spring discharging primarily from the Madison aquifer with a hydraulic head about 20 ft above the land surface (Long and Putnam, 2002).

Dye Tracing Tests

Two fluorescent dye injections into the Madison aquifer were accomplished during spring 2003 by injecting dye into Spearfish Creek in a “streamflow loss zone” within the outcrop of the Madison Limestone. Streamflow entering the loss zone was about 6 ft³/s and extended about 0.75 mile (mi) south of station 06430950 (fig. 1) before disappearing. Fluorescein—a yellow green dye—was used for the first injection, and Rhodamine WT—a red dye—was used for the second injection. The first injection was intended as a reconnaissance injection to be followed by an injection of a larger amount of Rhodamine WT, which can be detected at lower concentrations than fluorescein.

One method of dye injection is to introduce a slug of dye instantaneously in a swallow hole and trace the concentrations with a time series of samples from wells and springs located downgradient. No specific swallow holes were readily identifiable in Spearfish Creek because of alluvial deposits that were thick enough to obscure individual swallow holes. Thus, dye was injected into Spearfish Creek upstream from the loss zone over a period of about 1 hour. The dye was assumed to be thoroughly mixed with the water below the injection point because of the turbulence in the stream. This allowed dye to enter the

aquifer at all locations where streamflow losses were occurring. A small amount of dye dispersion may have occurred as the stream water moved through the alluvium to the underlying Madison Limestone. Fluorescein dye is photochemically unstable (Jones, 1984); therefore, the fluorescein dye injection was initiated at dusk. Periodic water samples were collected from wells and springs for about 18 months after injection and were stored in opaque plastic bottles to minimize degradation of dye from sunlight exposure.

The methods used for the fluorometric analysis of water samples and quality-control data are described in Supplemental Information Section B. Natural waters often have some fluorescent characteristics that need to be established before dye is injected; therefore, samples were collected prior to dye injection to quantify background fluorescence. Replicate samples were used to test the effects of storing samples and instrument variability.

Geochemical Tracers

For this study, several geochemical tracers were used as tools to improve understanding of ground-water flow in the Madison aquifer in the study area. In addition to data available from previous studies, samples from selected wells and springs were collected and analyzed for stable isotopes of oxygen and deuterium, CFCs, other dissolved gases, and tritium.

Sample Collection and Analysis

Samples for analysis of stable isotopes of oxygen and deuterium were collected during the inventory of private wells in the study area. A grab sample of raw water was collected as close as possible to the pumping well in 60-milliliter (mL) glass bottles with polyseal caps. Samples were analyzed at the USGS Reston Stable Isotope Laboratory. A description of the analytical method is available at <http://isotopes.usgs.gov/Quality.htm#samples>. Two replicate samples analyzed for delta (δ)¹⁸O had a difference of less than 1 percent. Two replicate samples analyzed for δ D had a difference of less than 2 percent.

CFC samples were collected from wells and springs by sequentially filling five welded glass ampoules for each sample. The method for filling and welding the glass ampoules is described at <http://water.usgs.gov/lab/chlorofluorocarbons/sampling/ampoules>. Refrigeration grade copper tubing and a Bennet pump were used for sampling to avoid contact with materials that can contaminate CFC samples. The spring samples were collected by placing the Bennet pump in the spring-fed lakes near the openings where the springs entered the bottom of the lakes to prevent any contact with the atmosphere. Three of the five ampoules for each sample set were analyzed at the USGS Reston Chlorofluorocarbon Laboratory by methods described at http://water.usgs.gov/lab/chlorofluorocarbons/lab/analytical_procedures. The CFC concentrations used in this report are an average of these three

values. For 11 of the 13 sample sets, the difference between the average of the three samples in the set and the individual samples was less than 20 percent, with an average difference of 2.2 percent. The percent difference for two samples was as high as 50 percent, with an average difference of 12.7 percent. These two samples had very low concentrations of CFCs; therefore, a small difference between samples resulted in a large difference when described as a percentage.

The dissolved gas data were collected with the same equipment and materials as used for CFCs. Two 150-mL septum bottles were filled for each sample by submerging the bottles in a beaker of the sample of water and inserting the sample tube into the bottle. A stopper was inserted in the bottles after filling while submerged to prevent exposure of the sample to the atmosphere. More details on the method of collecting the dissolved gas samples are available at <http://water.usgs.gov/lab/dissolved-gas/sampling>. Both samples were analyzed at the USGS Reston Chlorofluorocarbon Laboratory by methods described at http://water.usgs.gov/lab/dissolved-gas/lab/analytical_procedures. For dissolved gases, the difference between the values for the duplicate samples was less than 29 percent with an average difference of 2.0 percent.

Oxygen and Deuterium Isotopes

Stable isotopes of oxygen and hydrogen have more neutrons and thus greater atomic weight than typical oxygen and hydrogen atoms. Meteorological processes result in isotopic fractionation that may impart a unique signature in space and time to water that recharges aquifers. Delta (δ)¹⁸O is a measure of the ¹⁸O/¹⁶O ratio compared to a reference composition expressed in parts per thousand or per mil (‰) and is given by the following equation:

$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{reference}}} - 1 \right) \times 1000 \text{‰ VSMOW}$$

where VSMOW is the Vienna Standard Mean Ocean Water, which is used as the reference composition (Clark and Fritz, 1997). Similarly, the delta notation for deuterium (δ D) is a metric describing the ²H/¹H ratio compared to a reference composition. Thus, δ values are expressed as a difference from the value of the reference composition. For example, a sample with a value of -20 ‰ is isotopically depleted by 20 parts per thousand (2 percent) relative to the reference composition. Isotope values in δ notation are commonly described as light (more negative) or heavy (more positive), which is analogous to low or high for concentration.

Chlorofluorocarbons

CFCs are tracers that can be used to characterize ground-water residence times. The atmospheric concentrations of three CFCs (CFC–11, CFC–12, and CFC–113) have been changing over time, generally increasing from small concentrations in the 1960s and peaking in the 1990s. Residence times or ages of ground water often are estimated by comparing concentrations in ground-water samples to historical atmospheric concentrations. The three CFCs have different atmospheric concentrations, and examining all three of these tracers in conjunction with tritium can be helpful when characterizing ground-water mixtures. Because CFCs are dissolved gases, the results are expressed as parts per trillion by volume (pptv). This volumetric ratio is a function of the pressure and temperature at which recharge occurred, and dissolved gas data were used to estimate these parameters. Additional background information on CFC and dissolved gas analyses is described in Supplemental Information Section C.

Tritium

Tritium, a radioactive isotope with a half-life of 12.5 years, also can be helpful in characterizing ground-water age. Naturally occurring background concentrations of tritium in continental precipitation are estimated to range from 1 to 20 tritium units (TU), depending on location (Michel, 1989). One TU is defined as 1 ³H atom per 1,180 atoms of hydrogen, which is equivalent to 3.19 picocuries per liter (pCi/L) in water (International Atomic Energy Agency, 1981). Because of nuclear testing during the 1950s and 1960s and a subsequent treaty limiting such tests, tritium concentrations in atmospheric water increased sharply in 1953, peaked in 1963, and since then have been declining.

Naus and others (2001) compiled estimates of annual average tritium concentrations for precipitation recharge for the Black Hills area for 1953–1998. These estimates were weighted by monthly precipitation rates for the Black Hills. By using a method similar to that used by Naus and others (2001), average 6-month tritium concentrations in precipitation were estimated for the Black Hills for 1953–2002. The estimated record for the Black Hills was based on four stations with long-term tritium data (Bismarck, North Dakota; Lincoln, Nebraska; Ottawa, Quebec; and Albuquerque, New Mexico) and was not weighted by precipitation (fig. 5).

The Bismarck record (1963–1984) and the Lincoln record (1962–1986) were selected because of proximity to the Black Hills and because the Black Hills is located approximately equidistant and between these two stations. For the Bismarck and Lincoln records, data prior to 1962 or 1963 were estimated based on linear regression with the Ottawa station (1953–2002), and data after 1984 or 1986 were estimated based on

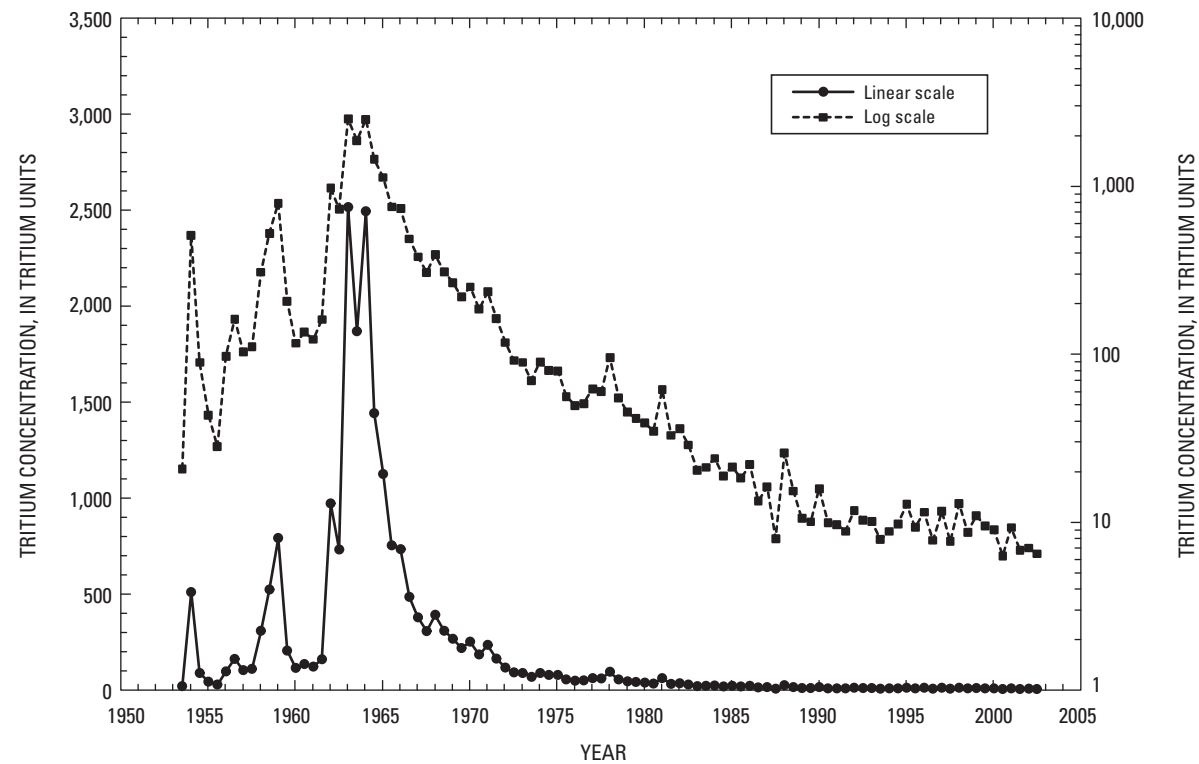


Figure 5. Estimated 6-month tritium concentration in precipitation for the Black Hills, South Dakota.

linear regression with the Albuquerque station (1962–2002). The Ottawa and Albuquerque stations were selected because of their record lengths and because they had tritium concentrations similar to the Bismarck and Lincoln stations. Although the Ottawa station could have been used to estimate all of the missing data, tritium concentrations for this station deviate upward beginning in about 1984 in comparison to most other stations in North America that have data after 1984. This may have resulted from a local source of tritium near the Ottawa station in recent years (Naus and others, 2001). Therefore, the Albuquerque station was used to estimate the recent data for Bismarck and Lincoln. The Ottawa and Albuquerque records also were used to estimate any missing data within the periods of record for Bismarck and Lincoln. The record for the Black Hills (1953–2002) was estimated by averaging the measured or estimated data for the Bismarck and Lincoln stations. Finally, 6-month averages were calculated from the estimated monthly record for the Black Hills.

Estimating Ground-Water Age from Chlorofluorocarbons

One way to get a general sense of relative ground-water age is to apply a simple piston-flow model, in which all of the water in a sample is assumed to have the same transit time with no dispersion (Maloszewski and Zuber, 1982; Plummer

and Busenberg, 2005). The piston date is the date at which the historical concentration in precipitation was equal to that of the sample, for example, the date that a hypothetical non-dispersive piston of water would have entered the aquifer. The apparent age (piston-flow age) is equal to the date sampled minus the piston date. Because the apparent age is not necessarily equal to the mean transit time, the apparent age for any single location is not particularly meaningful. Furthermore, the piston-flow model is inadequate to describe the range of ages in a sample, especially for karst aquifers, where the velocities in conduits can be orders of magnitude faster than in other parts of the aquifer, and a sample may contain a mixture of fast and slow moving ground water. However, the apparent age can be useful when assessing the relative ages for different sites. As the fraction of water less than 1 year old increases, the apparent age generally decreases, which indicates fast flow and possibly the presence of a major karst conduit.

Water Quality

Water-quality samples from two observation wells in the Madison aquifer and two in the Minnelusa aquifer were collected in August 2005 and processed using standard USGS techniques (U.S. Geological Survey, 1997–2006). The observation wells are 5-in. steel cased wells with open hole in the Madison Limestone or Minnelusa Formation. The depth of the

wells ranged from 220 to 780 ft, and the pumping rate ranged from 3 to 10 gal/min. Polyethylene tubing and a pump with brass components were used to extract water from the wells. Field parameters for these samples were determined with a YSI multiparameter monitoring system. Specific conductance values were determined with a specific conductance meter in the field for water samples collected from wells during the well inventory for this study. Also, specific conductance values determined in previous studies with collection dates that ranged from 1956 to 1998 were used in describing the distribution of specific conductance for the aquifers. Historical specific conductance data were retrieved from the USGS National Water Information System.

Analyses for major ions, trace elements, and low-level nutrients were done at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, by methods described by Fishman (1993) and Faires (1993). Analyses for mercury were done at the NWQL in Denver, Colorado, by cold vapor–atomic fluorescence spectrometry (Garbarino and Damrau, 2001). Analyses for gross alpha and beta radioactivity were performed at Eberline Services in Richmond, California, using U.S. Environmental Protection Agency (USEPA) approved methods for drinking water (<http://www.epa.gov/OGWDW/methods/methods.html>). For a replicate sample set, the difference between the replicate and the reported value for all constituents was less than 50 percent with an average difference of 1.8 percent. The constituents that had differences between reported and replicate values greater than 10 percent were near the reporting limit for the constituent.

Characterization of Ground-Water Flow

Ground water in the Madison and Minnelusa aquifers in the study area generally flows north from the outcrop areas (fig. 1) where ground-water recharge from sinking streams (streamflow recharge) and infiltration of precipitation (areal recharge) occurs. Outcrops of the Madison Limestone and Minnelusa Formation extend south beyond the study area along the western flank of the Black Hills (Strobel and others, 1999), which is referred to as the Limestone Plateau (fig. 1). Recharge to the Madison and Minnelusa aquifers on the Limestone Plateau west of a ground-water flow divide (Carter, Driscoll, Hamade, and Jarrell, 2001) flows west into Wyoming where it merges with regional ground-water flow. The general direction of this regional flow in Paleozoic aquifers in the northern Great Plains is to the northeast (Downey and Dinwiddie, 1988; Whitehead, 1996). Ground water originating as recharge in the northern part of the Limestone Plateau moves northward where it encounters regional flow, then moves eastward around the northern flank of the Black Hills. Based on an analysis of regional flow paths using geochemical information, Naus and others (2001) concluded that water in the Madison and Minnelusa aquifers in the study area originates from the central Black Hills area and does not

include recharge from areas west of the Black Hills. Regional hydraulic heads, however, probably influence hydraulic heads in the study area. For purposes of discussion, ground-water movement around the northern flank of the Black Hills is referred to as the eastern flow component, and ground water originating from recharge within the study area is referred to as the northern flow component. The eastern and northern flow components merge in the northwestern part of the study area, the hydraulics of which are influenced by large spring discharges.

Generalized potentiometric surfaces for the Madison and Minnelusa aquifers in the Black Hills area (Strobel and others, 2000a, 2000b) show that hydraulic heads are several hundred feet lower on the eastern side of the study area than on the western side. Spring discharges in the northwestern part of the study area, which are discussed in more detail in the “Spring Discharge” section, are very steady, indicating relatively small changes in hydraulic heads over time in this area. Recharge, which is discussed in more detail in the “Recharge” section, on average is less than total spring discharge in the study area. Transient changes in recharge are substantial between wet periods and dry periods (Carter, Driscoll, Hamade, and Jarrell, 2001).

Water-level hydrographs for SDDENR–WR observation wells in the study area (fig. 6) show the response of Madison and Minnelusa aquifer hydraulic heads to dry and wet periods from 1990 to 2005. The wells are located in the study area (fig. 1) with the label beginning with LA–xx. The early 1990s were dry followed by a wet period in the late 1990s followed by another dry period beginning in 2000. Hydraulic-head changes in wells LA–87A and LA–88B on the western side of the study area were substantially less than changes in wells LA–90A and LA–86C on the eastern side of the study area.

Recharge

Recharge to the Madison and Minnelusa aquifers occurs as areal recharge (infiltration of precipitation on outcrop areas) and streamflow recharge (infiltration of streamflow as streams cross outcrops). Carter, Driscoll, and Hamade (2001) estimated an average annual recharge rate of 334 ft³/s for the Madison and Minnelusa aquifers in the Black Hills for the period 1931–1998, with a minimum rate of 61 ft³/s and a maximum rate of 847 ft³/s. This relatively large difference in recharge between dry and wet periods could result in considerable differences in how the northern and eastern flow components interact. The length of the flow paths, the storage capacity of rocks in the Limestone Plateau area, and the influence of gradual changes in flow in the regional system probably buffer the transient changes in the eastern flow component. The northern flow component probably is more responsive than the eastern flow component to changes in recharge associated with dry and wet cycles. Estimated average annual recharge rate to the Madison and Minnelusa aquifers in the study area is about 38 ft³/s (table 1).

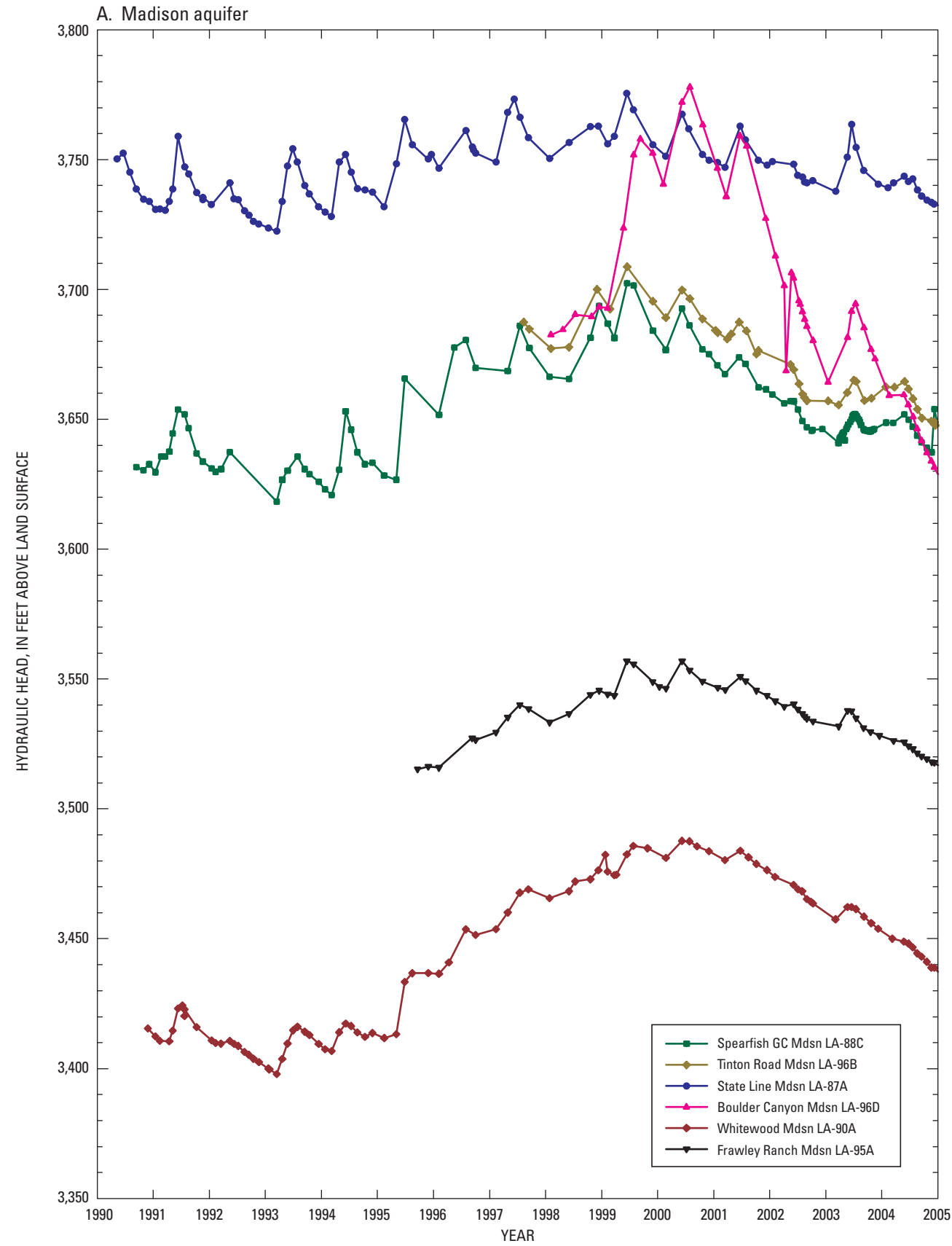


Figure 6. Water-level hydrographs for observation wells completed in (A) the Madison (MDSN) aquifer and (B) the Minnelusa (MNLS) aquifer.

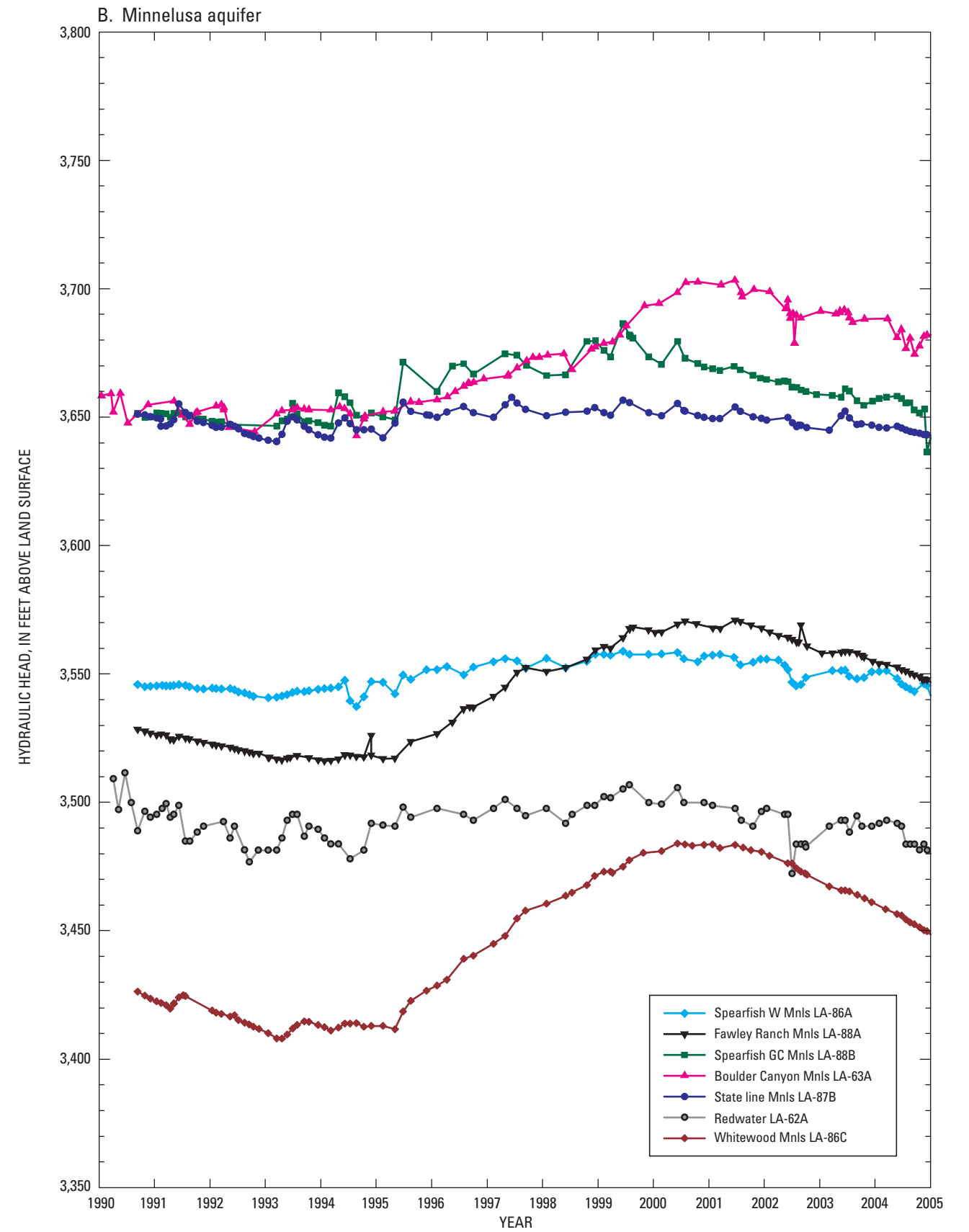


Figure 6. Water-level hydrographs for observation wells completed in (A) the Madison (MDSN) aquifer and (B) the Minnelusa (MNLS) aquifer.—Continued

Table 1. Estimated average annual recharge to the Madison and Minnelusa aquifers in the study area.

[--, not determined]

Recharge component	Average annual recharge rate (cubic feet per second)		
	Madison aquifer	Minnelusa aquifer	Combined Madison and Minnelusa aquifers
Areal recharge	8.0	12.6	20.6
Streamflow recharge			
Bear Gulch	--	--	2.0
Beaver Creek	--	--	4.0
Spearfish Creek	6.5	.5	7.0
False Bottom Creek	2.0	2.5	4.5
Total	--	--	38.1

Areal Recharge

The average annual areal recharge rate for the Madison and Minnelusa aquifers ranges from about 6 inches per year (in/yr) in the southwestern part of study area to less than 3 in/yr for the northern and western outcrop areas (Carter, Driscoll, and Hamade, 2001). Areal extent of the Madison Limestone outcrop in the study area, including overlying surficial deposits and intrusive rocks within outcrops, was estimated to be 28.6 mi². Infiltration occurring on the Madison Limestone outcrop south of Iron Creek and adjacent to Spearfish Creek upstream from the loss zone was assumed to discharge as base flow to Spearfish Creek and thus was not included in the estimated 28.6 mi² recharge area. The area of the Minnelusa Formation outcrop contributing to areal recharge in the study area was 57.7 mi². A discretized grid of spatially variable recharge rates (Carter, Driscoll, and Hamade, 2001) on the outcrop areas was used to calculate volumetric areal recharge rates of 8.0 and 12.6 ft³/s for the Madison and Minnelusa aquifers, respectively.

Streamflow Recharge

An important source of recharge to the Madison and Minnelusa aquifers is streamflow loss that occurs as streams cross outcrops of the Madison Limestone and Minnelusa Formation. Streamflow recharge occurs from Bear Gulch, Beaver Creek, Spearfish Creek, and False Bottom Creek (fig. 1). On the basis of annual streamflow recharge estimates for 1992–1998 for Bear Gulch, Beaver Creek, and False Bottom Creek, and for 1950–1998 for Spearfish Creek (Carter, Driscoll, and Hamade, 2001), an average annual recharge rate was estimated for each of the four streams (table 1). The combined annual streamflow recharge rate in the study area was estimated to be about 17.5 ft³/s.

Streamflow in Spearfish Creek upstream from outcrops of the Madison Limestone and Minnelusa Formation usually is diverted around these outcrops at the Spearfish diversion intake at Maurice (fig. 1) through an aqueduct to a power plant located near Spearfish. This diversion intake is located about 2 mi upstream from the Madison Limestone outcrop. When streamflow in Spearfish Creek is greater than about 115 ft³/s (Hortness and Driscoll, 1998), water flows over the diversion structure, and usually disappears in the reach that crosses the Madison Limestone outcrop except during high-flow conditions when flow in the creek is sustained downstream from the outcrop. An analysis of streamflow for Spearfish Creek at USGS gaging station 06431500 (fig. 1) indicates that streamflow exceeds 94 ft³/s only 5 percent of the time (Miller and Driscoll, 1998). Therefore, opportunities to characterize streamflow recharge to the Madison and Minnelusa aquifers from Spearfish Creek are limited. In addition, before streamflow measurements can be made to estimate loss, the unsaturated alluvium overlying the bedrock formations needs to be saturated. Hortness and Driscoll (1998) estimated a streamflow loss threshold of about 21 ft³/s for the Madison Limestone on the basis of four streamflow measurements upstream and downstream from the outcrop. The streamflow loss threshold is the maximum rate of streamflow loss that occurs when flow is sustained through the loss zone.

In October 2000, streamflow measurements were made within an upper reach of the Madison Limestone loss zone to quantify loss characteristics. Streamflow measurements and computations were made with a current meter in downstream sequence using USGS standard methods described by Rantz and others (1982). Streamflow was allowed to bypass the diversion structure in conjunction with tunnel maintenance and assistance from Barrick Corporation. Streamflow bypass began the morning of October 2, 2000, and lasted until October 7, 2000. The bypass flow rate was increased each morning during this period, and streamflow measurements were made each morning after the bypass flow rate had been constant for about 24 hours (fig. 1 and table 2) so that streamflow would be approaching equilibrium conditions. A rise in stream stage causes an increased amount of storage in the alluvium. When the stage stabilizes for a sufficient amount of time and equilibrium conditions are met, the difference in flow between an upstream and downstream location would be equal to the loss rate if evapotranspiration is assumed negligible. No tributaries were contributing flow within the intervening reach. Although it is uncertain whether 24 hours was sufficient time to attain equilibrium, a longer period of bypass flow was not possible. Rantz and others (1982) describe the potential sources of error in streamflow measurements with a current meter. A measurement rated as good has a cumulative measurement error of ±5 percent. To provide a range of potential errors associated with the estimated streamflow loss, the sum of a 5-percent error for each measurement involved in the calculated loss is listed in table 2. Under these limitations and assumptions, the estimated streamflow loss rate for this stream reach on Spearfish Creek most likely is between 4 and 8 ft³/s.

Table 2. Streamflow loss to the Madison aquifer in upper reach of loss zone along Spearfish Creek.

[ft³/s, cubic feet per second]

Date of measurement	Streamflow (ft ³ /s)		Streamflow loss (ft ³ /s)	Potential measurement error in calculated loss (ft ³ /s)
	Station 06430950 (upstream)	Station 442637103521100 (downstream)		
10–03–2000	3.26	0.00	3.26	0.2
10–04–2000	6.92	2.18	4.74	.5
10–05–2000	14.1	7.72	6.38	1.1
10–06–2000	26.7	17.9	8.80	2.2
10–07–2000	48.2	39.2	9.00	4.4

During spring 2006, runoff following a large snowfall event created streamflow in Spearfish Creek that was able to saturate the alluvium and sustain flow through the loss zone for several days. The USGS, in cooperation with the city of Spearfish, conducted a series of streamflow measurements at five sites on Spearfish Creek between the diversion intake and

Spearfish (fig. 1 and table 3). Gains or losses were calculated for each set of measurements for the four reaches between these gaging sites (table 3). The measurements were made in downstream order to minimize the effects that changes in streamflow during the measurements would have on calculated gains and losses.

Table 3. Streamflow gains or losses for selected reaches of Spearfish Creek.

[ft³/s, cubic feet per second; e, estimated value; --, not applicable]

Description of stream reach	Date	Streamflow at gaging station (ft ³ /s)		Streamflow gain or loss (ft ³ /s)	Potential measurement error in calculated gain or loss (ft ³ /s)
		442433103534400	06430950		
				Gain	
Diversion intake to above Madison Limestone outcrop	05–05–2006	41.2	51.6	10.4	4.6
	05–07–2006	27.4	40.2	12.8	3.4
	05–12–2006	32.0	37.7	5.7	3.5
	06–08–2006	.4	4.6	4.2	.2
		06430950	442649103520200	Loss	
Above Madison Limestone outcrop to Split Rock	05–05–2006	51.6	43.4	8.2	4.8
	05–07–2006	40.2	32.7	7.5	3.6
	05–12–2006	37.7	34.3	3.4	3.6
	05–18–2006	24.3	18.9	5.4	2.2
	06–08–2006	4.6	.0	4.6	.2
		442649103520200	442757103510600	Loss	
Split Rock to below Madison Limestone outcrop	05–05–2006	43.4	27.4	16.0	3.5
	05–07–2006	32.7	14.5	18.2	2.4
	05–12–2006	34.3	15.7	18.6	2.5
	05–18–2006	18.9	5.2	13.7	1.2
	06–08–2006	.0	.0	--	--
		442757103510600	442835103510501	Loss	
Below Madison Limestone outcrop to above Power Plant	05–12–2006	15.7	e5	10.7	--
	05–17–2006	12.2	4.2	8.0	0.8
	05–18–2006	5.2	e.2	5.0	--

The reach between the diversion intake and the Madison Limestone outcrop was always a gaining stream and the reaches that overlie the Madison Limestone outcrop were always losing reaches. The measurements made above and below the Madison Limestone outcrop are compared in table 4. The streamflow losses to the Madison Limestone below Split Rock generally are about twice the loss that occurs above Split Rock. The measured losses are very close to the streamflow loss threshold of 21 ft³/s that was previously estimated by Hortness and Driscoll (1998). Some unexplainable variability is inherent in estimation of streamflow losses. On the basis of previous and more recent measurements, it is concluded that the streamflow loss threshold for Spearfish Creek probably is in the range of 20–25 ft³/s. On the basis of three measurements above the Power Plant, additional substantial losses probably occur downstream from the Madison Limestone outcrop.

Spring Discharge

Total artesian springflow for the Redwater River above Belle Fourche, which flows along the northwestern part of the study area (fig. 1), has been estimated to be about 94 ft³/s (Carter, Driscoll, Hamade, and Jarrell, 2001). Sources in the northwestern part of the study area that include springflow contributing to Crow Creek and discharge from Cox Lake accounted for about 41 ft³/s of that total. Artesian springs contributing to Spearfish Creek accounted for about 10 ft³/s of that total. On the basis of streamflow measurements (U.S. Geological Survey, 1977–2003), Higgins Gulch and Old Hatchery springs make up most of this spring discharge to Spearfish Creek. The combined total of this estimated spring discharge rate (51 ft³/s) is more than the estimated average recharge rate (38 ft³/s) in the study area.

The relatively steady spring discharge in the northwestern part of the study area is illustrated by analysis of the base flow for Crow Creek and Cox Lake. Average annual base flow

for station 06430532 (fig. 1) for water years 1994–2004 was estimated using a hydrograph separation program (Sloto and Crouse, 1996), and the fixed interval method using an interval of 11 days, which was selected to minimize the influence of alluvial bank storage. Comparison of base flow to streamflow for Crow Creek (fig. 7) indicates a consistently large contribution of springflow with an average base flow of 36.0 ft³/s. During the relatively dry years during 2002–2004, base flow declined slightly to about 33 ft³/s. A similar analysis for Cox Lake for water years 1992–1995 indicated base flow was very steady at 4.2 ft³/s.

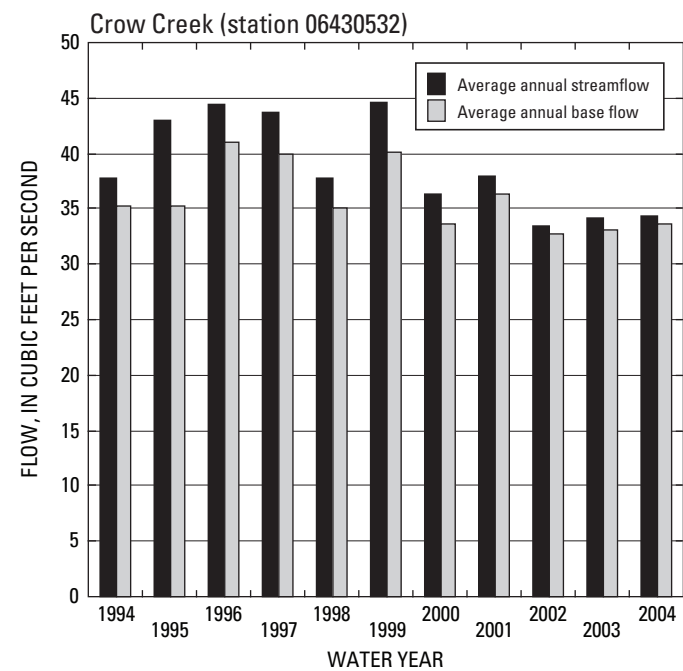


Figure 7. Comparison of average annual streamflow and base flow for Crow Creek.

Table 4. Streamflow losses to the Madison aquifer from Spearfish Creek.

[ft³/s, cubic feet per second]

Description of stream reach	Date	Streamflow at gaging station (ft ³ /s)		Streamflow loss (ft ³ /s)	Potential measurement error in calculated loss (ft ³ /s)
		06430950	442757103510600		
Above Madison Limestone outcrop	05–05–2006	51.6	27.4	24.2	3.9
Limestone outcrop to below Madison Limestone outcrop	05–07–2006	40.2	14.5	25.7	2.7
	05–12–2006	37.7	15.7	22.0	2.7
	05–18–2006	24.3	5.2	19.1	1.5
	06–08–2006	4.6	.0	4.6	.2

¹Insufficient flow for inclusion in loss threshold estimate

On the basis of geochemical modeling (Klemp, 1995), the source of the spring discharge was presumed to originate primarily from the Madison and Minnelusa aquifers. An analysis of oxygen and deuterium isotope data described in a subsequent section generally agrees with this assumption, except that additional data indicate possible small contributions from other sources.

Potentiometric Surfaces

Generalized potentiometric surfaces of the Madison and Minnelusa aquifers are shown in figures 8 and 9, respectively. The potentiometric contours near the perimeter of the study area where there are no control points were estimated on the basis of potentiometric maps for the Black Hills area (Strobel and others, 2000a; 2000b). Ground-water flow in the Madison and Minnelusa aquifers in the study area generally is toward the northeast. In isotropic aquifers, the direction of flow is perpendicular to potentiometric contour lines. However, in an aquifer with possible anisotropic transmissivity, such as the Madison aquifer, flow direction can deviate from that perpendicular direction. Therefore, the potentiometric surface of the Madison aquifer does not indicate precise flow directions. Flow directions in the Minnelusa aquifer, however, probably are approximately perpendicular to the potentiometric contours in most locations.

Hydraulic gradients become progressively less steep with distance from outcrops for both aquifers and is indicated by the decreasing density of the potentiometric contours to the north (figs. 8 and 9). Steeper hydraulic gradients near recharge areas are expected; however, recharge alone probably does not explain the large change in gradient. Another factor that can cause steeper gradients is lower relative transmissivity. On the eastern flank of the Black Hills, however, transmissivity in the Madison aquifer generally is higher near outcrops than with distance from the outcrops (Long and Putnam, 2002). Ground-water flow that moves northward and eastward around the Black Hills in the study area might contribute to anomalies in the hydraulic gradient because of converging flow paths; however, the specific boundary conditions and structural features that could explain the changes in gradient are not well understood. The large discharge from artesian springs, which is greater than the estimated recharge in the study area, as discussed previously, probably influences hydraulic gradients to a large degree. Spring discharge in the northwestern part of the study area probably contributes to lowered hydraulic heads in the Minnelusa aquifer (fig. 8). Near observation well LA–62A (fig. 9), there is a confirmed hydraulic gradient that decreases to the west toward the springs. Hydraulic head at well LA–62A was 3,500 ft on December 1, 1999, and the closest well to the west (7N 2E18ABBA) had a shut-in pressure of 32 pounds per square inch (lb/in²) reported by the driller 2 days earlier, which is equivalent to a hydraulic head of 3,464 ft. Although data are sparse for the Madison aquifer

in the northern part of the study area, it is assumed that the potentiometric surface is similar to that of the Minnelusa aquifer near the springs because the springs discharge from both aquifers. Geochemical modeling has indicated that the predominant source of spring discharge at Cox Lake and McNenny Pond is the Madison aquifer, whereas the spring source of Mirror Lake is a 1:1 ratio of water from the Madison and Minnelusa aquifers (Klemp, 1995). Because the majority of the spring discharge probably originates from the Madison aquifer, hydraulic head was assumed to be higher for the Madison aquifer than for the Minnelusa aquifer near the springs.

Higher relative transmissivity near the springs than near outcrop areas might explain the lower hydraulic gradient in the northwestern part of the study area. Long and Putnam (2002) concluded that the area surrounding Jackson-Cleghorn Springs, a large spring discharging from the Madison aquifer in the east-central part of the Black Hills, had high relative transmissivity as a result of enhanced ground-water circulation, which resulted from greater karst development than in surrounding areas. Total artesian springflow for the study area was estimated to be about 51 ft³/s (see “Spring Discharge” section), which is substantially larger than the estimated discharge of 22 ft³/s for Jackson-Cleghorn Springs (Long and Putnam, 2002). Thus, potential for karst development in the northwestern part of Lawrence County is large.

Flow Paths and Flow Rates Based on Dye Tracing

Dye tracing is a useful tool that has been widely used to describe ground-water flow in formations with enlarged openings or conduits that result from dissolution of limestone. Ground-water flow paths in the Madison Limestone that extend for several miles with velocities as high as 1,000 feet per day (ft/d) have been documented by dye tracing in the Black Hills area (Rahn, 1971; Greene, 1993). These previous tracer studies involved injecting dye in swallow holes associated with sinking streamflow. Characterizing these major flow paths can be a useful starting point in understanding ground-water flow in karst aquifers.

Spearfish Creek, the largest stream in the study area, was selected as a site for injecting dye because the maximum streamflow recharge rate for the Madison and Minnelusa aquifers south of Spearfish (fig. 1) is about 21 ft³/s (Hortness and Driscoll, 1998), which is the largest streamflow recharge rate in the northern Black Hills. This focused recharge often is associated with enlarged openings or conduits in the aquifer that can rapidly move water downgradient.

Two fluorescent dye injections into the Madison aquifer were made during spring 2003. Fluorescein—a green dye—was used for the first injection, and Rhodamine WT—a red dye—was used for the second injection.

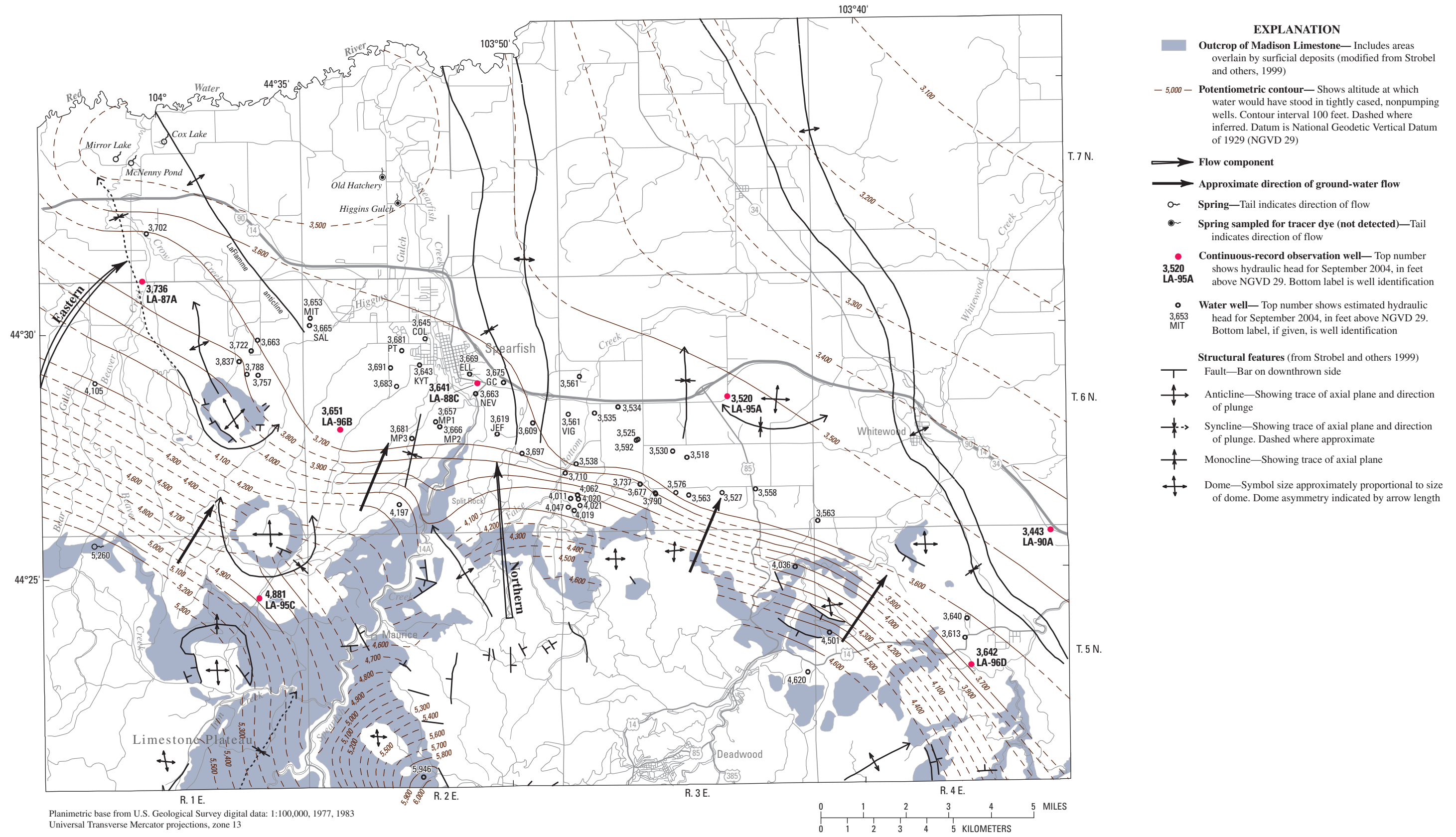


Figure 8. Generalized potentiometric surface of the Madison aquifer in 2004.

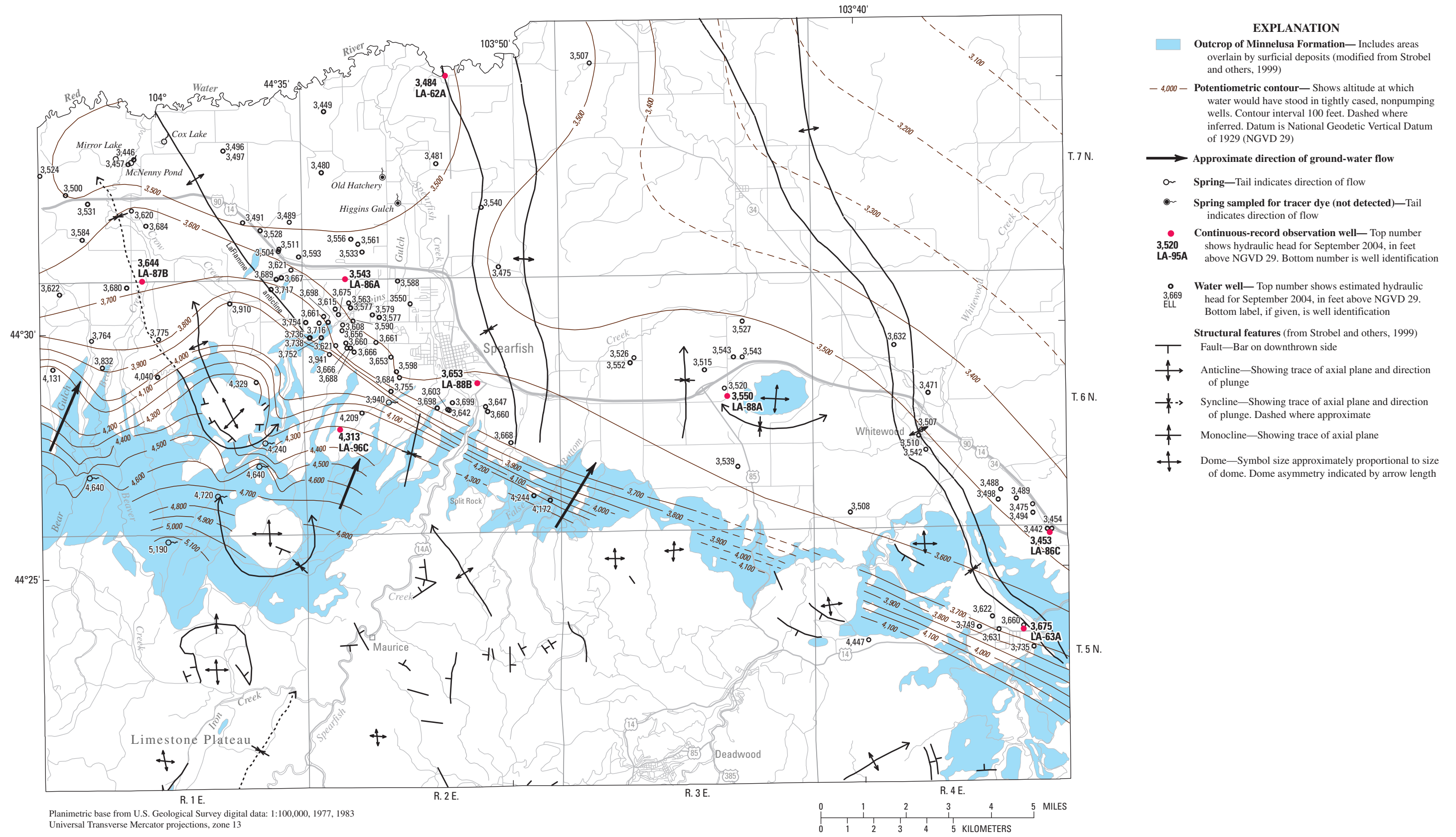


Figure 9. Generalized potentiometric surface of the Minnelusa aquifer in 2004.

Fluorescein Injection

Sixteen pounds (lb) (dry weight) of fluorescein dye were injected in Spearfish Creek during the evening of March 25, 2003. Measured streamflow was 6.6 ft³/s at the time of injection. Periodic water samples were collected from 10 wells and 2 springs (table 5 and fig. 10) and analyzed for dye with a Turner Model TD700 filter fluorometer. Samples were collected daily at the beginning of the injection, and the interval was increased to several days for some wells and springs as the dye study progressed.

Fluorescein dye was detected in water samples from four wells ranging in distance from 2.6 to 4.5 mi from the injection point (table 5). Dye breakthrough curves for the four wells (fig. 10) indicate first arrival times that ranged from 5 to 169 days. Some gaps in the dye breakthrough curve were the result of well operation and maintenance issues. During the periods when the concentrations for well MP2 drop to background levels (fig. 10), water was being supplied to the sampling point by a different well connected to the distribution system. Sampling from well DIC was discontinued 154 days after the injection because of well repair work.

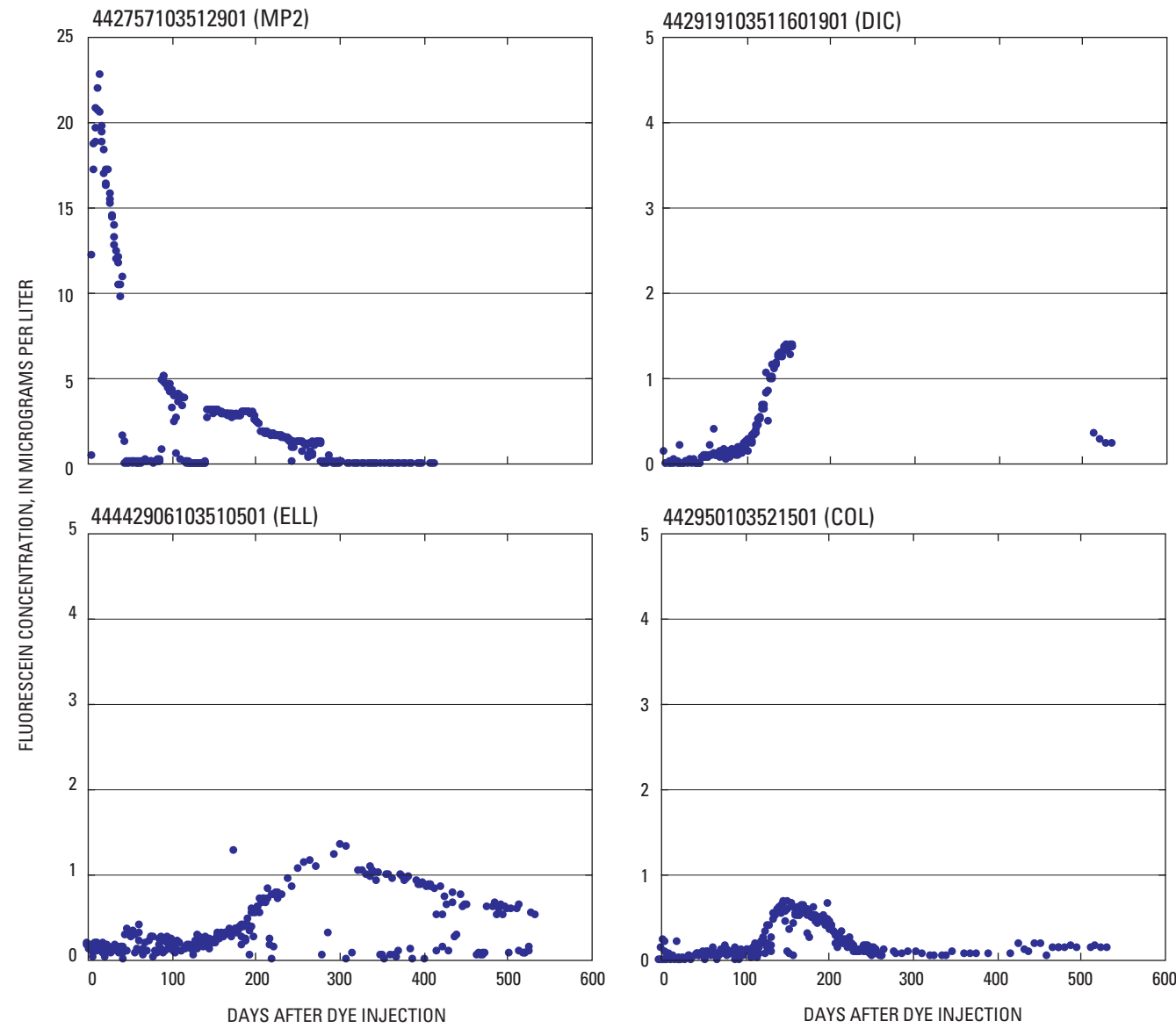


Figure 10. Fluorescein breakthrough curves for wells where dye was detected, March 2003–September 2004.

Table 5. Summary of fluorometric analysis of water samples for fluorescein dye.

Station number	Other Identifier	Beginning date of sampling period	Ending date of sampling period	Number of samples	Concentration (micrograms per liter)		Distance from injection point (miles)	Days to first arrival of dye	Days to peak dye concentration
					Maximum	Minimum ¹			
442748103524501	MP3	03-24-2003	10-15-2003	116	0.25	-0.04	2.3	-	-
442757103512901	MP2	03-24-2003	05-12-2004	322	22.77	-1.16	2.6	5	15
442752103501901	JEF	03-20-2003	² 05-13-2003	81	.30	-0.02	2.9	-	-
442842103505501	NEV	03-25-2003	05-03-2004	236	.32	-1.12	3.5	-	-
442906103510501	ELL	03-20-2003	09-07-2004	293	1.35	-0.06	3.8	169	301
442919103511601	DIC	03-20-2003	³ 09-07-2004	154	1.39	-0.06	3.9	109	-
442855103503501	GC	03-20-2003	07-21-2003	29	.23	-0.20	4.0	-	-
442936103530001	PT	03-25-2003	05-03-2004	202	.15	-0.08	4.3	-	-
442815103481701	VIG	⁴ 07-09-2003	09-07-2004	133	.32	-0.07	4.4	-	-
442950103521501	COL	03-26-2003	09-07-2004	295	.69	-0.08	4.5	130	153
443309103532401	OH (Old Hatchery Spring)	05-13-2003	02-27-2004	28	.32	.02	8.1	-	-
443237103525801	HG (Higgins Gulch Spring)	05-13-2003	11-19-2003	23	.35	.05	7.8	-	-

¹Negative concentrations are not possible and represent instrument noise.

²Well not sampled from May 10, 2003, to July 8, 2003.

³Well not sampled from August 16, 2003, to August 17, 2004, because of well repairs.

⁴Well not sampled until July 9, 2003, because of well repairs.

On the basis of first arrival times, ground-water velocities ranged from about 0.1 mi/d for the three wells downgradient to about 0.5 mi/d for well MP2. The peak concentration of about 23 µg/L for the closest well (MP2) occurred 15 days after injection, then gradually decreased; however, concentrations greater than 1 µg/L were still measured about 9 months later. First arrival for wells DIC, COL, and ELL was interpreted to range from 109 to 169 days. The observed concentrations for wells COL and ELL intermittently decreased to near background (natural fluorescence) levels. A possible explanation for this could be that the dye was being drawn toward the wells by pumping. When the wells were only pumped briefly to collect a sample, the drawdown created by pumping may not have been large enough to intersect the conduits of the main flow path that was transporting the dye.

Detectable dye concentrations for well ELL were observed for about 400 days compared to about 100 days for well COL. The detection of dye in both wells DIC and ELL could be the result of pumping and anastomosis of conduits along the approximate location of a possible main conduit as shown in figure 1. Assuming such a conduit exists, it may trend in the direction of Old Hatchery (OH) and Higgins Gulch (HG) springs. Conduits in karst aquifers typically propagate downgradient from swallow holes and upgradient from springs (Clemens and others, 1997). Although detectable dye concentrations were not observed for springs OH and HG, the location of the springs several miles farther downgradient could have resulted in dilution of the dye beyond the point of detection. Spearfish Creek streamflow of about 5 ft³/s at the time of injection was small in relation to the loss threshold of about 21 ft³/s. Streamflow entering the loss zone probably decreased during the summer; therefore, the flow velocity in conduits associated with the Spearfish Creek loss zone also may have slowed as the dye test progressed.

A comparison of dye breakthrough curves, apparent age of water samples from wells on the basis of CFCs, and the distance of the wells from a possible conduit indicate that the generalized location of the conduit may be plausible. A least-squares, straight-line regression analysis of apparent age and distance for the six closest wells had an r² value of 0.96 (see "Ground-Water Flow Paths, Ages, and Mixing Based on Geochemical Tracers" section).

Rhodamine WT Injection

The fluorescein injection was followed by an injection of 64 lb (dry weight) of Rhodamine WT dye on May 9, 2003, at the same location. Measured streamflow was 5.6 ft³/s or about 1 ft³/s less than during the fluorescein injection. Periodic water samples were collected from 10 wells and 2 springs (table 6 and fig. 11) and analyzed for dye with a Turner Model TD700 filter fluorometer. Samples were collected daily at the beginning of the injection, and the interval was increased to several days for some wells and springs as the dye study progressed.

Because streamflow conditions were similar to those of the first injection, it was assumed that injecting about four

times the amount of injected fluorescein dye would cause the Rhodamine WT concentrations in wells to be greater than the fluorescein concentrations; however, the measured Rhodamine WT concentrations were about an order of magnitude less than the measured fluorescein concentrations. First arrival and peak concentrations were not estimated for well MP2 because the well was not in operation during a brief period when the first arrival and peak probably would have occurred. The Rhodamine WT concentrations in wells ELL, DIC, and COL were near background levels, and thus there is uncertainty in estimating dye arrival or peak traveltimes for these wells. However, the general shape and magnitude of the concentration breakthrough curves were similar to those for fluorescein, except with a dilution of more than an order of magnitude. In the analysis of samples with a filter fluorometer, some overlap in the fluorescent bandwidths of fluorescein and Rhodamine WT can occur (Jones, 1984). An evaluation of samples with standard concentrations of fluorescein (Supplemental Information Section B) indicated that any overlap between fluorescein and Rhodamine WT in the analysis was small.

The small change in streamflow between the fluorescein and Rhodamine WT injections does not explain the degree of dilution in measured Rhodamine WT dye concentrations in comparison to the measured fluorescein concentrations. Greater absorption of Rhodamine WT or other degradation of the dye in the alluvium in Spearfish Creek compared to fluorescein dye may be possible. However, the large difference in concentrations cannot be explained by absorption or degradation alone.

Examination of the hydraulic head in the area (fig. 8) provides some insight on dilution possibilities. The relatively flat gradient in hydraulic head in the area where dye was detected probably is the result of solution-enlarged openings associated with recharge in the Spearfish Creek loss zone and indicates an area of high transmissivity. This high transmissivity would result in ground water moving easily to the north. Because of the current diversion of water around the loss zone, there is less streamflow recharge than before water was diverted around the loss zone. Water levels in the Madison aquifer have been estimated to have decreased about 100 ft as the result of the diversion (Greene and others, 1998).

A large proportion of recharge on the outcrop of the Madison Limestone occurs when snowmelt and spring precipitation infiltrate and fill cave-like openings in the unconfined area with water. As these openings fill with water, additional openings are utilized in the downgradient movement of ground water. Part of this water probably moves toward the highly conductive conduits underlying the streamflow loss zone. Water-level response in Madison aquifer observation well LA-88C located about 1 mi north of the loss zone (fig. 1) is consistent with this flow mechanism. Water levels generally rise quickly in early spring and then decline gradually through the summer and winter (Driscoll and others, 2000) (fig. 12). The injection of fluorescein on March 25, 2003, was near the beginning of this typical water-level rise, whereas when the Rhodamine WT was injected on May 9, 2003, water levels

Table 6. Summary of fluorometric analysis of water samples for Rhodamine WT dye.

[--, no data]

Station number	Other identifier	Beginning of sample period	End of sample period	Number of samples	Concentration (micrograms per liter)		Distance from injection point (miles)	Days to first arrival of dye	Days to peak dye concentration
					Maximum	Minimum ¹			
442748103524501	MP3	03-24-2003	10-15-2003	116	0.25	-0.04	2.3	--	--
442757103512901	MP2	05-07-2003	01-28-2004	239	1.02	-0.02	2.6	(²)	(²)
442752103501901	JEF	03-20-2003	³ 05-13-2003	81	.30	-0.02	2.9	--	--
442842103505501	NEV	03-25-2003	05-03-2004	236	.32	-0.12	3.5	--	--
442906103510501	ELL	03-20-2003	09-07-2004	273	.27	-0.07	3.8	(⁴)	(⁴)
442919103511601	DIC	03-20-2003	⁵ 09-07-2004	111	.13	-0.02	3.9	(⁴)	(⁴)
442855103503501	GC	03-20-2003	07-21-2003	29	.23	-0.20	4.0	--	--
442936103530001	PT	03-25-2003	05-03-2004	202	.15	-0.08	4.3	--	--
442815103481701	VIG	07-09-2003	⁶ 09-07-2004	133	.32	-0.07	4.4	--	--
442950103521501	COL	03-26-2003	09-07-2004	248	.09	-0.05	4.5	(⁴)	(⁴)
443309103532401	OH (Old Hatchery spring)	05-13-2003	02-27-2004	28	.32	.02	8.1	--	--
443237103525801	HG (Higgins Gulch spring)	05-13-2003	11-19-2003	23	.35	.05	7.8	--	--

¹Negative concentrations are not possible and represent instrument noise.

²First arrival and peak probably occurred when pump was out of service.

³Well not sampled from May 10, 2003, to July 8, 2003.

⁴First arrival and peak not determined because concentrations are too close to background and instrument noise.

⁵Well not sampled from August 16, 2003, to August 17, 2004, because of well repairs.

⁶Well not sampled until July 9, 2003, because of well repairs.

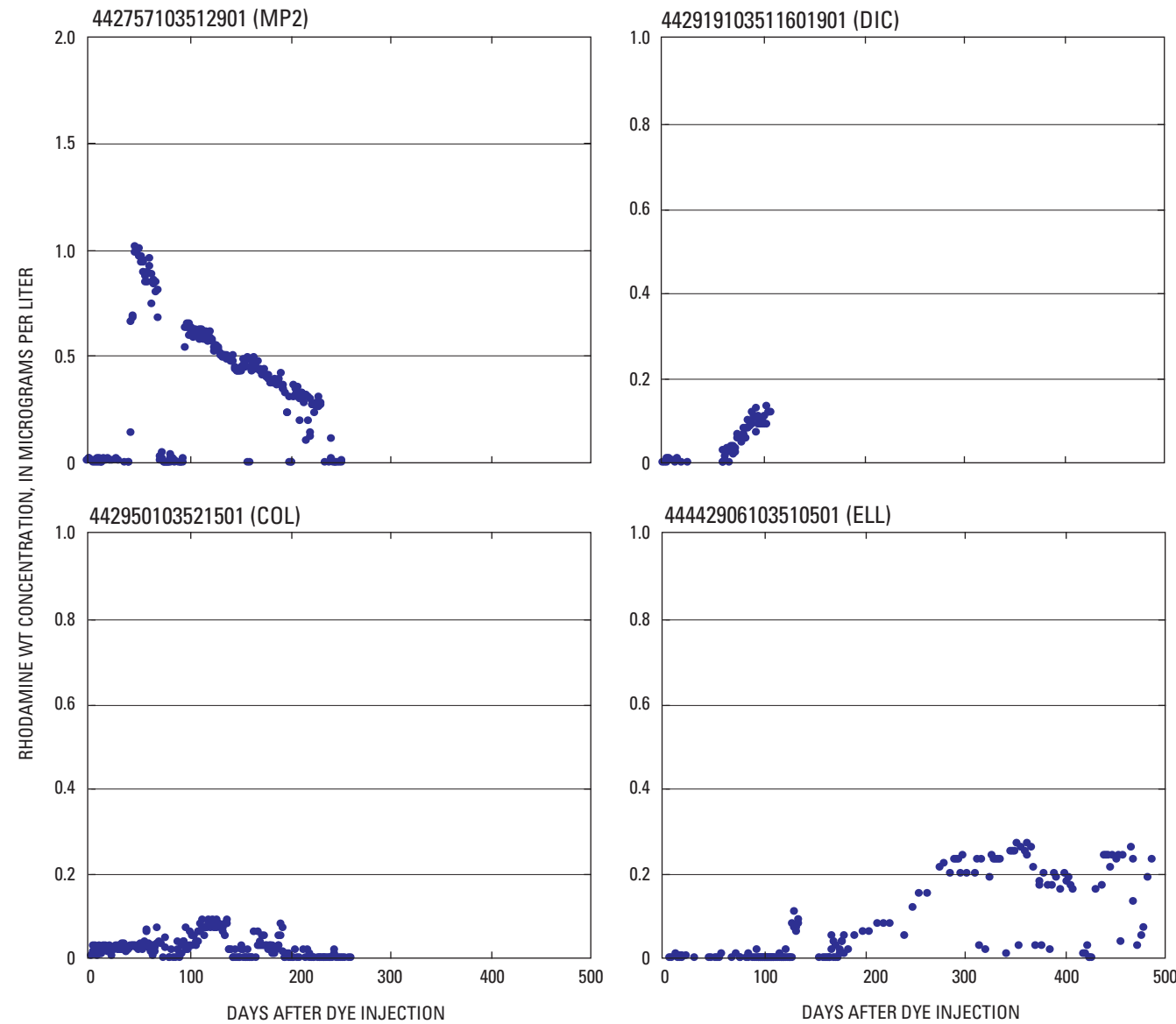


Figure 11. Rhodamine WT breakthrough curves for wells where dye may be present, May 2003–September 2004.

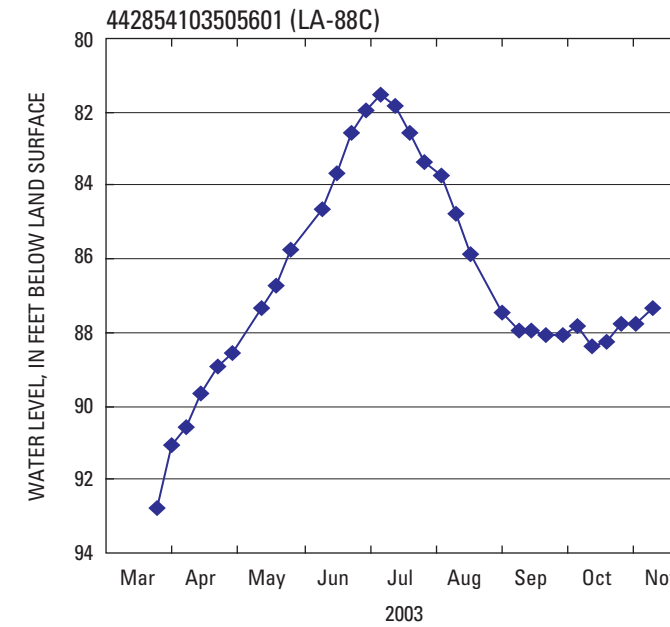


Figure 12. Water level in the Madison aquifer for observation well LA-88C near Spearfish during dye injections.

were rising rapidly and had already risen about 5 ft. A combination of this water-level rise, the diversion of streamflow around the loss zone, and the highly transmissive conduits associated with streamflow loss may explain the transient differences in dilution of dye concentrations.

Ground-Water Flow Paths, Ages, and Mixing Based on Geochemical Tracers

Geochemical tracers used in previous studies to characterize ground-water flow in the Black Hills area (Naus and others, 2001) include stable isotopes of oxygen and hydrogen (deuterium) and the radioisotope tritium. For this study, several geochemical tracers were used as tools to better understand ground-water flow in the Madison aquifer in the study area. In addition to the data available from previous studies, samples from selected wells and springs were collected and analyzed for oxygen and deuterium isotopes, tritium, CFCs, and dissolved gases that included nitrogen, argon, oxygen, carbon dioxide, and methane. CFCs are young age-dating tracers, and the dissolved-gas analyses provide additional information that is useful in interpreting CFC data. These tracers provide insights on ground-water flow paths, ages, and mixing, which are described in the following sections. Conjunctive analysis of several tracers was useful in understanding ground-water flow in selected locations as described in the “Synopsis of Results from Geochemical Tracers” section.

Oxygen and Deuterium Isotopes

Meteorological processes that affect stable-isotope distributions for the Black Hills area and the generalized distribution of oxygen and deuterium isotopes were described in Naus and others (2001). Water recharging the Madison and Minnelusa aquifers in the northern Black Hills generally has $\delta^{18}\text{O}$ values lighter than -16‰ , with values becoming heavier in an outward direction from the central part of the Black Hills. Oxygen- and deuterium-isotope values for samples collected for this study are listed in table 7. Additional oxygen- and deuterium-isotope values reported in Naus and others (2001) were used in the interpretation of ground-water flow in the study area.

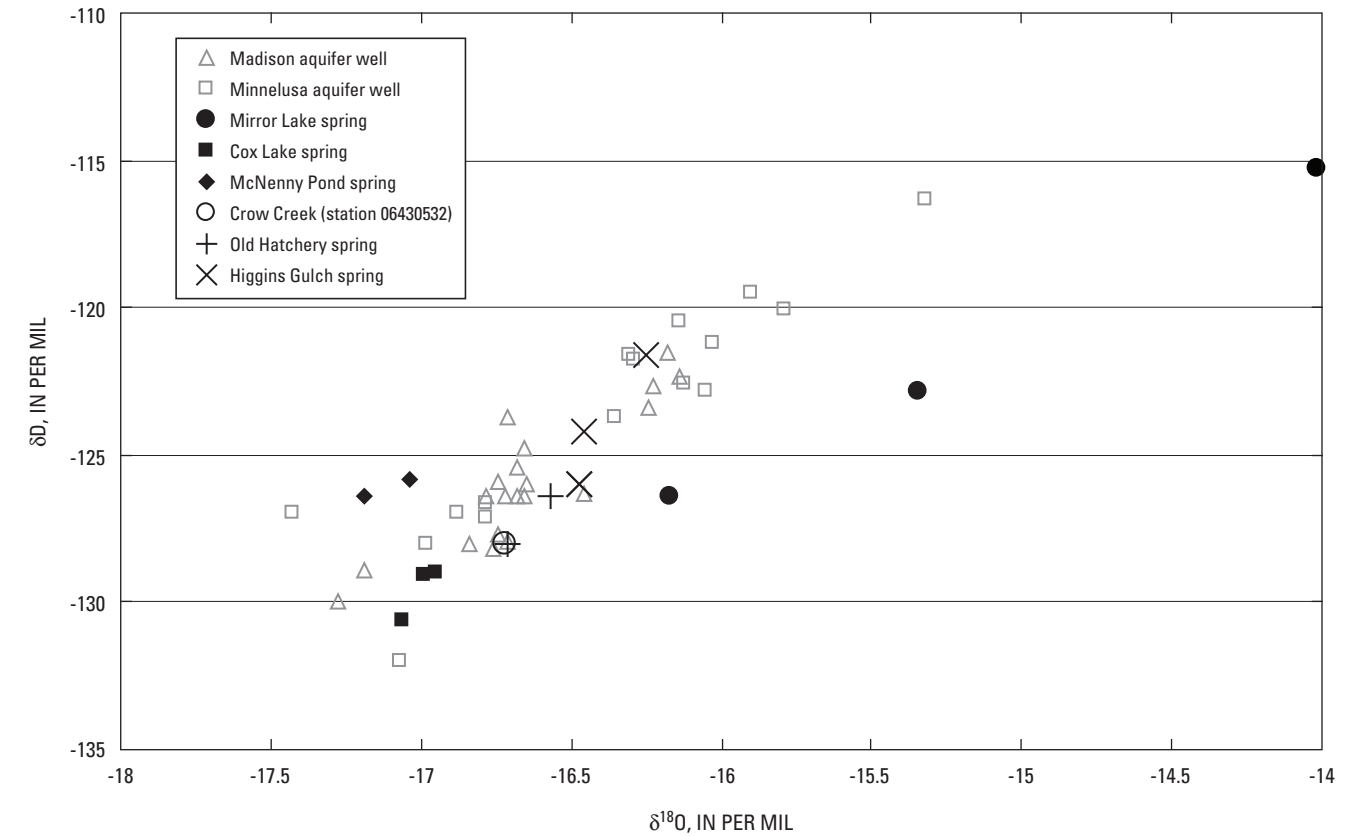
Comparison of $\delta^{18}\text{O}$ and δD values for water from Madison and Minnelusa wells and springs (fig. 13) provides information that is relevant to ground-water flow interpretations. On the basis of the generalized distribution of $\delta^{18}\text{O}$ for the Black Hills (Naus and others, 2001), ground water moving around the northern flank of the Black Hills from the Limestone Plateau probably would have lighter isotope values than the recharge from outcrops in the study area. Values from samples from Cox Lake (COX) and McNenny Pond (McNEN) springs plot with the lightest isotope values observed for wells, which is consistent with the interpretation of a component of spring discharge originating from outcrops of the Madison Limestone and Minnelusa Formation in the Limestone Plateau area. Values for the three isotope samples from Mirror Lake (MIR) spring are heavier and more variable than values from springs COX and McNEN, indicating possible contributions from overlying formations and local recharge. The overlying Minnekahta aquifer is a potential source of water to MIR spring discharge. An observation well completed in the Minnekahta aquifer about 2 mi southwest of Mirror Lake had a $\delta^{18}\text{O}$ value of -15.6‰ (Naus and others, 2001).

The oxygen- and deuterium-isotope values for surface-water samples collected at station 06430532 (Naus and others, 2001), which represents the combined springflow contributing to Crow Creek, were more similar to springs COX and McNEN than to spring MIR. Geochemical modeling by Klemp (1995) indicated that McNenny Pond primarily was little-evolved Madison aquifer water, Cox Lake was Madison aquifer water with influence from the Minnelusa aquifer, and Mirror Lake was a mixture of water from the Madison and Minnelusa aquifers. The geologic processes involved in the formation of these springs are complex and include karst development in gypsum layers as well as limestone units and collapse features associated with these dissolution processes (Epstein and Putnam, 2005). The general location of the LaFlamme anticline (Strobel and others, 1999) in relation to Crow Creek and Cox Lake indicates that structural features also influence the development of ground-water flow paths to springs. Although movement of water in overlying formations contributes to spring discharge, isotope data indicate that

Table 7. Oxygen- and deuterium-isotope data for wells and springs in the study area.

[Mdsn, Madison; Mnls, Minnelusa; --, none]

Station identification number	Local number	Other identifier	Name	Site type	Sample date	$\delta^{18}\text{O}$ (per mil)	δD (per mil)
443237103525801	7N 2E28BACD	HG	Higgins Gulch below I-90	Spring	09-10-2001	-16.46	-124
443012103544700	--	--	Higgins Gulch above Spearfish	Spring	09-10-2001	-16.25	-122
443309103532401	7N 2E20DAAD	OH	Old Hatchery	Spring	09-10-2001	-16.57	-126
443330104003401	7N 1E21BBCD	McNEN	McNenny Pond	Spring	11-05-2001	-17.04	-131
443335104010001	7N 1E20AABC	MIR	Mirror Lake	Spring	11-06-2001	-16.17	-126
443335104010001	7N 1E20AABC	MIR	Mirror Lake	Spring	09-10-2001	-14.02	-115
443356103593701	7N 1E16DADC	COX	Cox Lake	Spring	11-05-2001	-17.06	-131
443356103593701	7N 1E16DADC	COX	Cox Lake	Spring	09-10-2001	-16.99	-129
442752103501901	6N 2E23DBCA	JEF	--	Mdsn well	10-31-2001	-16.74	-128
442752103501901	6N 2E23DBCA	JEF	--	Mdsn well	08-16-2001	-16.74	-126
442826103503801	6N 2E23BABB	--	--	Mnls well	06-13-2001	-16.78	-127
442757103512901	6N 2E22CBAB	MP2	--	Mdsn well	06-13-2001	-16.71	-124
442822103514001	6N 2E22BADB	--	--	Mnls well	08-16-2001	-16.12	-123
442823103514301	6N 2E22BAAC	--	--	Mnls well	08-16-2001	-16.35	-124
442918103523001	6N 2E16AAB	KYT	--	Mdsn well	10-30-2001	-16.46	-126
442918103523001	6N 2E16AAB	KYT	--	Mdsn well	06-14-2001	-16.66	-126
442918103523001	6N 2E16AAB	KYT	--	Mdsn well	06-14-2001	-16.68	-125
442919103511601	6N 2E15BBBB	DIC	--	Mdsn well	10-19-2001	-16.72	-126
442906103510501	6N 2E15AADC	ELL	--	Mdsn well	05-29-2001	-16.78	-127
442842103505501	6N 2E14CBCC	NEV	--	Mdsn well	10-30-2001	-16.71	-128
442842103505501	6N 2E14CBCC	NEV	--	Mdsn well	06-14-2001	-16.68	-126
442855103503501	6N 2E14ACDC	GC	--	Mdsn well	11-01-2001	-16.78	-126
442950103521501	6N 2E 9ADDB	COL	--	Mdsn well	05-29-2001	-16.76	-128
442956103542701	6N 2E 8CCDA	--	--	Mnls well	08-16-2001	-15.32	-116
442953103551801	6N 2E 7BDDA	--	--	Mnls well	08-15-2001	-16.31	-122
443005103553801	6N 2E 7BBDB	SAL	--	Mdsn well	10-22-2001	-16.24	-123
443005103553801	6N 2E 7BBDB	SAL	--	Mdsn well	08-14-2001	-16.23	-123
443011103552101	6N 2E 7BAAB	--	--	Mnls well	08-14-2001	-16.14	-120
443012103550601	6N 2E 7ABBA	--	--	Mnls well	08-14-2001	-16.03	-121
443021103544801	6N 2E 6DDBD	--	--	Mnls well	08-15-2001	-16.05	-123
443016103545801	6N 2E 6DCDA	--	--	Mnls well	08-15-2001	-16.29	-122
443017103553601	6N 2E 6CCDA	MIT	--	Mdsn well	11-01-2001	-16.18	-122
443017103553601	6N 2E 6CCDA	MIT	--	Mdsn well	06-07-2001	-16.14	-122
443013103542301	6N 2E 5CCDC	--	--	Mnls well	08-16-2001	-15.79	-120

**Figure 13.** Relation between $\delta^{18}\text{O}$ and δD in water samples collected from 1978 to 2005 from Madison and Minnelusa wells and springs, and surface water (data prior to 2001 from Naus and others, 2001).

the primary sources of water for these spring inflows to Crow Creek are the Madison and Minnelusa aquifers.

Oxygen- and deuterium-isotope values for samples from springs OH and HG were heavier than values for springs COX and McNEN in the northwestern part of the study area. This heavier isotope signature is consistent with source water originating from outcrops of the Madison Limestone and Minnelusa Formation primarily within the study area rather than from ground-water flow originating in the Limestone Plateau area and entering the study area along the eastern flow component that was described earlier (fig. 8). Oxygen- and deuterium-isotope values for spring OH were lighter than values for spring HG, which is located about 1 mi southeast of spring OH and closer to the outcrops in the study area. This could indicate a small fraction of water from the eastern flow component contributing to spring OH.

Chlorofluorocarbons

Concentrations of three CFCs (CFC-11, CFC-12, and CFC-113) were used to characterize ground-water residence times in the study area. Ten wells completed in the Madison aquifer and three springs were sampled for CFCs (fig. 1 and table 8). For the four wells where dye was detected, at least part of the mixture contains water that is less than 1 year old because dye reached these wells within 1 year. For these four wells, the apparent age ranged from 12 to 26 years, indicating that the samples contained months-old water mixed with years- to decades-old water. The following section summarizes a method described in Long and Putnam (2006) and used to model ground-water age distributions for the data shown in table 8.

Table 8. Chlorofluorocarbon and tritium data for wells and springs in the study area.

[CFC, chlorofluorocarbon; pptv, parts per trillion by volume; pCi/L, picocuries per liter; TU, tritium units; Mdsn, Madison; Mnl, Minnelusa; --, none or no data]

Site identification number	Local number	Other identifier	Other identifier	Site type	Sample date	CFC concentration (pptv)						Apparent age (years)						Tritium (TU)	Tritium 2-sigma (pCi/L)	Tritium (pCi/L)
						CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113	Mean					
443017103553601	6N 2E 6CCDA	MIT	--	Mdsn well	11-01-2001	49.7	14.2	0.0	39.2	40.2	--	40	--	--	--	--	--			
443005103553801	6N 2E 7BDB	SAL	--	Mdsn well	10-22-2001	5.3	.2	.0	53.1	54.1	--	54	--	--	0.0	1	0			
442950103521501	6N 2E 9ADDB	COL	--	Mdsn well	05-29-2001	201.3	74.0	21.2	27.7	29.7	21.7	26	--	--	23	1.6	7.2			
442855103503501	6N 2E14ACDC	GC	--	Mdsn well	11-01-2001	--	--	--	--	--	--	--	--	--	48	3.2	15.0			
442854103505601	6N 2E14BCCC	LA-88B	Spearfish GC Mnl	Mdsn well	08-18-2005	--	--	--	--	--	--	--	--	--	61.4	3.8	19.2			
442854103505602	6N 2E14BCCC2	LA-88C	Spearfish GC Mnl	Mdsn well	08-17-2005	--	--	--	--	--	--	--	--	--	13.8	1	4.3			
442842103505501	6N 2E14CBCC	NEV	--	Mdsn well	10-30-2001	398.1	165.2	47.9	16.7	22.2	16.2	18	--	--	--	--	--			
442842103505501	6N 2E14CBCC	NEV	--	Mdsn well	06-14-2001	--	--	--	--	--	--	--	--	--	68	4.5	21.3			
442906103510501	6N 2E15AADC	ELL	--	Mdsn well	05-29-2001	480.5	201.0	57.9	12.2	17.7	13.7	15	--	--	63	3.8	19.7			
442919103511601	6N 2E15B BBB	DIC	--	Mdsn well	10-19-2001	445.9	164.3	47.9	14.6	22.1	16.1	18	--	--	--	--	--			
442918103523001	6N 2E16AAB	KYT	--	Mdsn well	10-30-2001	18.3	46.4	.0	39.7	38.7	--	39	--	--	1	1	.3			
442918103523001	6N 2E16AAB	KYT	--	Mdsn well	06-14-2001	--	--	--	--	--	--	--	--	--	34	2.6	10.7			
442757103512901	6N 2E22CBAB	MP2	--	Mdsn well	06-13-2001	()	254.5	78.0	--	13.3	11.2	12	--	--	72	4.5	22.6			
442752103501901	6N 2E23DBCA	JEF	--	Mdsn well	10-31-2001	421.3	169.5	50.8	15.7	21.7	15.7	18	--	--	--	--	--			
442833103434601	6N 3E15DDDA	LA-88A	Frawley Ranch Mnl	Mdsn well	08-17-2005	--	--	--	--	--	--	--	--	--	106.9	6.4	33.5			
442833103434602	6N 3E15DDDA2	LA-95A	Frawley Ranch Mnl	Mdsn well	08-16-2005	--	--	--	--	--	--	--	--	--	.3	.6	.1			
442815103481701	6N 3E19BBDC	VIG	--	Mdsn well	08-24-2005	48.1	64.2	3.5	43.5	35.4	39.5	39	--	--	21.8	1.6	6.8			
443356103593701	7N 1E16DADC	COX	Cox Lake	Spring	11-05-2001	255.0	82.3	18.8	25.2	29.7	23.2	26	--	--	--	--	--			
443356103593701	7N 1E16DADC	COX	Cox Lake	Spring	09-10-2001	--	--	--	--	--	--	--	--	--	43	2.6	13.5			
443335104010001	7N 1E20AABC	MIR	Mirror Lake	Spring	11-06-2001	524.6	217.6	65.5	8.7	16.2	13.2	13	--	--	--	--	--			
443335104010001	7N 1E20AABC	MIR	Mirror Lake	Spring	09-10-2001	--	--	--	--	--	--	--	--	--	35	2.6	11.0			
443330104003401	7N 1E21BBDC	McNEN	McNenny Pond	Spring	11-05-2001	232.7	93.4	25.1	26.7	28.7	21.2	26	--	--	--	--	--			
443309103532401	7N 2E20DAAD	OH	Old Spearfish Hatchery	Spring	09-10-2001	--	--	--	--	--	--	--	--	--	42	2.6	13.2			
443012103544700	--	--	Higgins Gulch above Spearfish	Spring	09-10-2001	--	--	--	--	--	--	--	--	--	55	3.2	17.2			
443237103525801	7N 2E28BACD	HG	Higgins Gulch below I-90	Spring	09-10-2001	--	--	--	--	--	--	--	--	--	73	4.5	22.9			

¹CFC-12 for samples was contaminated.

²CFC-11 value is average of two samples because one of three samples was contaminated. All other values are the average of three samples.

Ground-Water Age Distributions from Chlorofluorocarbon data

The mixture of young and old ground water in a sample can be described quantitatively by a ground-water age distribution. The type and shape of the age distribution provides important information related to ground-water mixing and the complex nature of flow networks in karst aquifers. Long and Putnam (2006) used CFC concentrations to evaluate various age distributions for different areas of the Madison aquifer. One type of age distribution was classified as bimodal because the age categories were separated into two distinct groups that were separated by as much as two decades. For example, a bimodal age distribution could indicate that 30 percent of the water in a sample is less than 2 years old and 40 percent is from 20 to 40 years old. This distribution also might indicate that water from 3 to 19 years old and from 41 to 50 years is not present or negligible. Because CFCs only can be used to estimate ground-water age less than about 50 years old, the remaining 30 percent would be of an unknown age that is older than 50 years. Another type of age distribution was classified as unimodal, which had one age category where 100 percent of the water was young, generally less than a few years old.

Results of the Long and Putnam (2006) study indicated that water sampled near presumed conduits with generally younger ages probably are unimodal and dominated by conduit flow, possibly mixed with intermediate flow. Water from wells near the possible conduit (fig. 1) was better characterized by the unimodal distribution than the bimodal distribution. For some of the wells where dye was detected and whose water was characterized by unimodal distributions, mixing with intermediate flow could explain apparent ages of 12 to 26 years. Bimodal distributions were determined to be generally more applicable to areas farther from conduits that have older ground-water ages. The two components of a bimodal age distribution are interpreted as representing two components of flow (or storage) such as conduit and diffuse flow, and as much as two decades may separate the impulse responses of these components. Results of the Long and Putnam (2006) study indicated that bimodal distributions with a large age gap similar to this might characterize water sampled from many sites in the study area. Wells in these areas probably have good hydraulic connection to both diffuse and conduit flow. The large age gap between flow components may indicate that little mixing of components occurs naturally; however, mixing of these distinct flow components probably occurs at the well during pumping, which induces flow from both components.

Evidence for a Conduit Based on the Spatial Distribution of Apparent Ages

An analysis was conducted to provide possible evidence for the existence of a major conduit, which could be useful for describing a physical basis for the different types of age distributions, especially the bimodal distribution. The objective of this analysis was to show that the spatial distribution

of apparent ages may provide evidence for the presence of a conduit, but not to locate a conduit precisely. The spatial variability of apparent ages provides evidence that different flow components exist, such as conduit and diffuse flow.

Water supplied by major conduits is assumed to represent the youngest water in the Madison aquifer, and thus a relation may exist between apparent age and proximity to conduits. A north-trending line, which is centered on the four wells in which tracer dyes were detected, represents the possible location of a major conduit (fig. 1). The southern end of this line trends toward the dye injection point, and the northern end points toward springs OH and HG, for which the primary source is the Madison aquifer (Klemp, 1995). Because dye was not detected at springs OH and HG, orienting the conduit toward the springs is somewhat speculative; however, springs are a common discharge point for conduit flow (Clemens and others, 1997). Springs OH and HG emerge from streambeds and could not be located precisely, so dye samples were collected downstream from the springs. Possible tracer dye in these samples would have been diluted with small amounts of runoff and may have been degraded by organic matter in the stream and sunlight. Therefore, tracer dye probably would have been detected only with relatively high concentrations. In addition, if the conduit is assumed to be not farther from well COL than from the other wells where dye was detected, then the conduit near well COL would trend slightly toward the west, orienting it approximately toward the springs. The exact position chosen for this conduit was, to some extent, arbitrary, and alternative positions may result in equally good or better relations of apparent age and conduit proximity.

Dye tracers injected into Spearfish Creek were transported mainly toward the north but also were dispersed in an east-west transverse direction, as detection locations indicate (fig. 1). All wells where dye was detected are large production wells, which are more likely to draw water from a nearby conduit than are wells having smaller zones of influence. In addition, transverse flow could be the result of an anastomosing conduit network near a major central conduit or possibly from flushing of dye into the matrix (along fractures or bedding planes) especially during high flow.

To test the hypothesis that ground-water age is related to its proximity to a conduit, apparent age was used as a metric to assess relative age and was plotted in relation to distance to the possible conduit shown in figure 1. Three of the CFC-113 samples from wells had concentrations of 0, which prevented an age estimate from that tracer, other than the knowledge that the water was more than about 50 years old. For CFC-12, one of the samples was contaminated, which prevented an age estimate from that tracer. For CFC-11, however, apparent ages were determined for all sites sampled for CFCs, and for consistency, only these apparent ages were included in the analysis of spatial distribution. In addition, the three springs in the northwest corner of the study area near Crow Creek were not included because the hydraulic gradient in this area slopes toward the northeast, and thus the source of water to these springs is unlikely to be a conduit near the city of Spearfish.

Figure 14 shows the results of a least-squares regression analysis of apparent age and distance to the possible conduit for the 10 wells with CFC-11 apparent ages. A logarithmic curve fit the 10 data points with an r^2 value of 0.71. For only the six closest wells to the conduit (fig. 1) (wells MP2, ELL, DIC, NEV, COL, and KYT), a straight-line regression had an r^2 value of 0.96. Because the six closest wells also are large production wells, the better fit for these data could result from either closer proximity to the conduit or from having larger zones of influence. Because the conduit is hypothetical, its location is approximate, and thus the regression analysis indicates that a plausible relation exists between apparent age and an approximate conduit location. Although this spatial analysis of age alone is not conclusive for the existence of a conduit, it provides additional evidence when considered in conjunction with other information such as locations of swallow holes and springs and other tracer data.

Tritium

Tritium values for samples collected for this study ranged from 0 to 33.5 TU (table 8). With complex mixtures a possibility, characterizing residence time from tritium data alone

is often difficult; however, low values can indicate that a large portion of water is greater than 50 years old. This can be useful in understanding ground-water flow especially in the Madison aquifer. Two wells completed in the Madison aquifer had nondetectable (well SAL) or very low tritium concentrations (well LA-95A, 0.1 TU) (table 8). These wells are located about the same distance or closer to the outcrop areas than many wells (fig. 1) that have higher tritium concentrations, indicating that they are not located near a conduit and that water is largely derived from storage in the surrounding matrix (diffuse flow). Two tritium samples were collected from well KYT and had tritium concentrations of 0.3 and 10.1 TU. A possible explanation for the large difference is that the well may be drawing water from the Minnelusa aquifer in addition to the Madison aquifer, with pumping changing the mixture.

Tritium was used as a metric to characterize ground-water age in the area near a possible conduit. A straight line fit by linear regression between tritium concentration and distance to the possible conduit shown in figure 15 for the six wells closest to the conduit shows an inverse relation between these two parameters (fig. 15). As distance from the conduit increases, samples may contain larger fractions of pre-1950 water that would not have detectable tritium concentrations

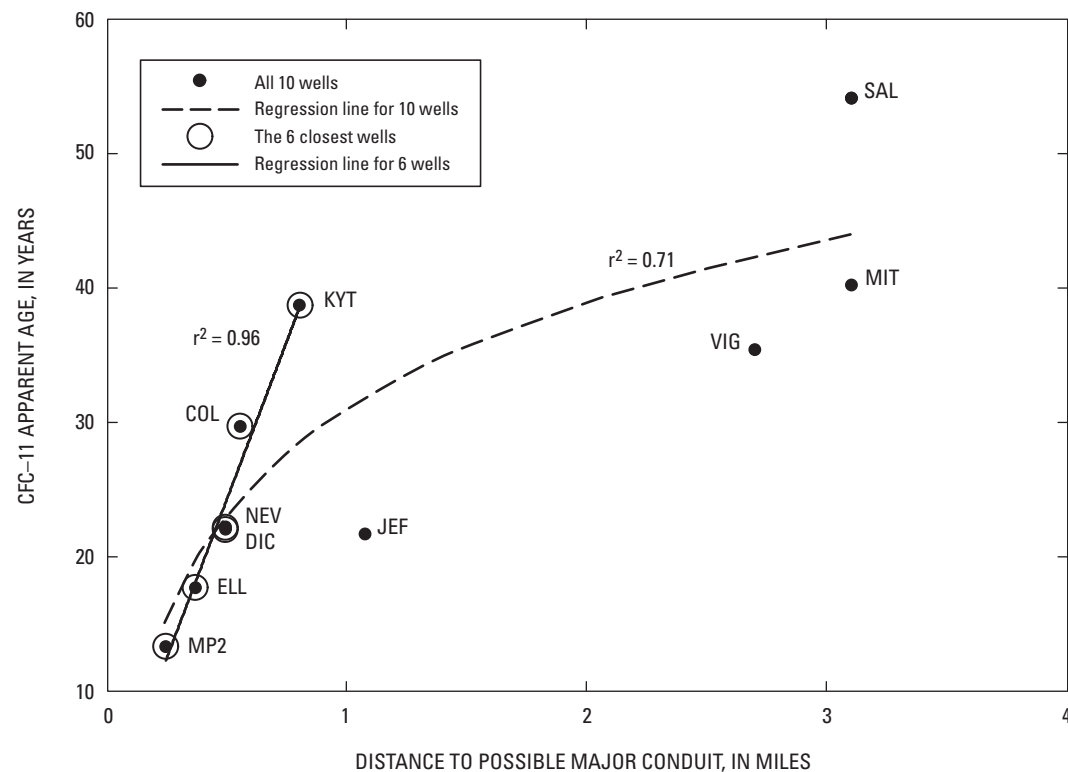


Figure 14. Regression analysis of CFC-11 apparent age with distance to a possible major conduit.

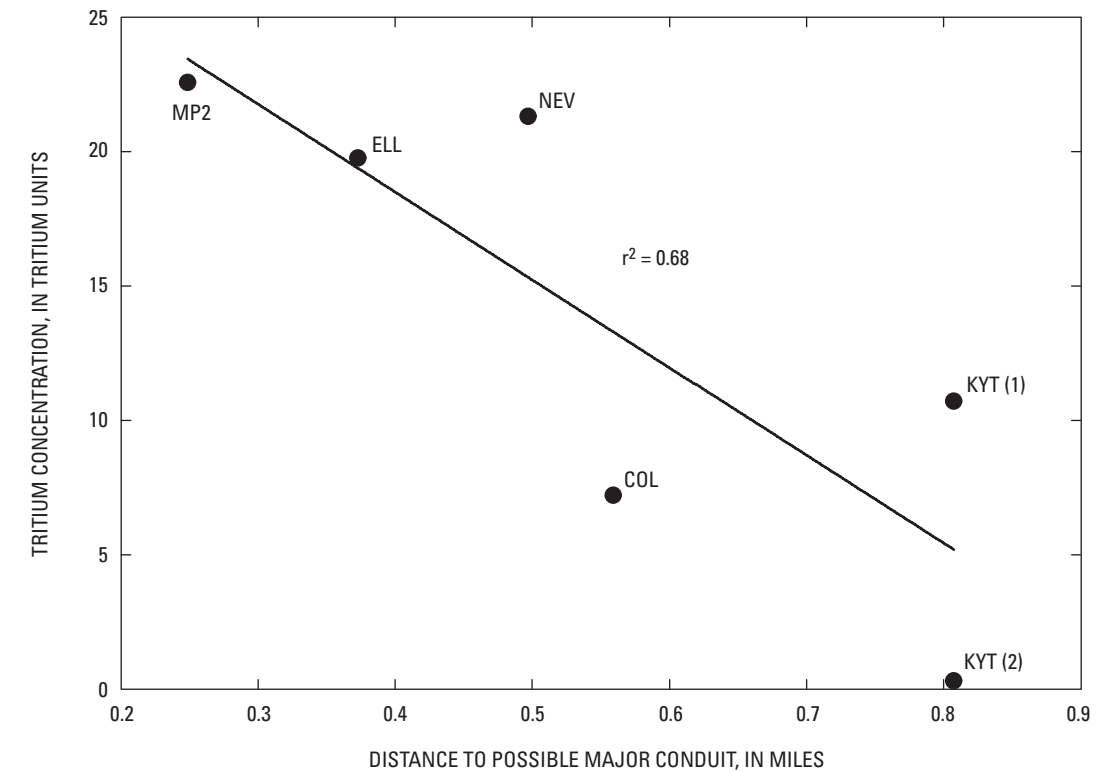


Figure 15. Regression analysis of tritium concentration with distance to a possible major conduit.

because of low concentrations in precipitation for that period and subsequent radioactive decay. The correlation coefficient for the tritium regression ($r^2 = 0.68$) is lower than that of the CFC-11 apparent-age regression (fig. 14). Tritium may be a less reliable age indicator than are CFCs because tritium concentrations in precipitation have risen and declined over time in contrast to CFCs, which have risen steadily up until about 2000.

Synopsis of Results from Geochemical Tracers

Water from wells VIG, LA88C, and COL (fig. 1 and table 8) had low tritium concentrations indicating that a portion of the water probably is older than 50 years. Comparison of the tritium concentration of 7.2 TU for the Madison production well COL (fig. 1) to the tritium concentration in precipitation (fig. 5) indicates that even though dye was detected, a substantial portion of the water probably is older than 50 years when CFC data also are considered. Water from well ELL (fig. 1), in which dye also was detected, had a CFC apparent age of 15 years and a tritium concentration of 19.7 TU, which is about the same concentration as a unimodal mixture

of water from precipitation averaged over the last 20 years with very little water older than 50 years. Comparison of CFC apparent ages for these two wells (COL, 26 years; ELL, 15 years) is consistent with two different mixing scenarios, bimodal and unimodal, respectively, as described previously.

Age-dating parameters also can be useful in conjunction with other tracers in characterizing source waters. Comparison of the CFC apparent age for the three spring sites (COX, 26 years; McNEN, 26 years; and MIR, 13 years) located in the northwest part of study area (fig. 1) is consistent with the interpretation from oxygen- and deuterium-isotope data that spring MIR probably has a local source of recharge from formations that overlie the Madison Limestone and Minnelusa Formation. Analysis of potential mixing models (Long and Putnam, 2006) indicated that a bimodal distribution of a young fraction mixed with an older fraction is probable for springs COX and McNEN. This is consistent with the interpretation that spring flow from the Madison and Minnelusa aquifers in the northwest part of the study area represents a mixture of water with different flow paths and residence times. The relatively steady base flow in Crow Creek probably is related to this mixture of source waters with different hydraulic responses to stress over time.

Characterization of Water Quality

Specific conductance is a measure of electrical conductivity, which is in general directly proportional to the concentration of dissolved solids in water. The general distributions of specific conductance for the Madison and Minnelusa aquifers are shown in figures 16 and 17. In addition to specific conductance values determined for this study, values in the USGS National Water Information System database with collection dates that ranged from 1956 to 1998 were used to describe the distribution of specific conductance. In the Madison aquifer, specific conductance ranges from 18 to 945 microsiemens per centimeter. In the Minnelusa aquifer, specific conductance ranges from 2 to 3,000 microsiemens per centimeter. In the Minnelusa aquifer, specific conductance increases with distance from the outcrop (downgradient) and probably is proportional to the amount of time that ground water is in contact with aquifer material. The spatial distribution of specific conductance in the Madison aquifer is less ordered than in the Minnelusa aquifer and is not necessarily related to distance from the outcrop. This may result from the greater heterogeneity of the Madison aquifer. The existence of fast flow paths, such as conduits, probably has a large influence on the spatial distribution of ground-water residence times and thus specific-conductance values. The mixing of young and old ground water at well intakes (see “Ground-Water Flow Paths, Ages, and Mixing Based on Geochemical Tracers” section) also could be a factor in the distribution of specific conductance.

Water samples from four observation wells completed in the Madison and Minnelusa aquifers in Spearfish (wells LA-88B and LA-88C) and about 6 mi east of Spearfish (wells LA-88A and LA-95A) (fig. 1) were analyzed for physical properties, major ions, nutrients, trace elements, and radionuclides (table 9). A description of water-quality characteristics for these constituent groups in ground water in the Black Hills area is available in Williamson and Carter (2001), which also describes water-quality criteria, standards or recommended limits, and general significance for selected properties.

USEPA Maximum Contaminant Levels (MCLs) are established for contaminants that, if present in drinking water, may cause adverse human-health effects; MCLs are enforceable health-based standards (U.S. Environmental Protection Agency, 2006a). USEPA Secondary Maximum Contaminant Levels (SMCLs) are established for contaminants that can adversely affect the taste, odor, or appearance of water and may result in discontinuation of use of the water; SMCLs are nonenforceable, generally non-health-based standards that are related to the aesthetics of water use (U.S. Environmental Protection Agency, 2006b).

No MCLs were exceeded for any of the constituents analyzed for samples from the four wells. The SMCL of 250 mg/L for sulfate (U.S. Environmental Protection Agency, 2006b) was exceeded in samples from the Minnelusa well LA-88A, with a concentration of 392 mg/L. Sulfates of calcium and magnesium form hard scale. Large concentrations of sulfate also have a laxative effect on some people and in combination with other ions give water a bitter taste. A potential source of the sulfates in the Minnelusa Formation are anhydrite and gypsum lenses (both minerals composed of calcium sulfate). A calcium concentration of 194 mg/L for this well sample also was relatively high compared to the median value of 68 mg/L for 250 Minnelusa aquifer well samples in the Black Hills area (Williamson and Carter, 2001).

Calcium and magnesium cause most of the hardness and scale forming properties in water. Hardness greater than 180 mg/L (as CaCO_3) is considered very hard (Heath, 1983). Hardness was 631 mg/L in water from Minnelusa well LA-88A and 263 mg/L in water from Minnelusa well LA-88B.

The major species of nitrogen usually found in ground water is nitrate. Nitrate is very mobile in ground water and moves with little or no retardation (Freeze and Cherry, 1979). Concentrations greater than local background levels may indicate pollution by feedlot runoff, sewage, or fertilizer. For samples from Minnelusa wells LA-88A and LA-88B, nitrite plus nitrate values of 2.41 mg/L and 0.58 mg/L, respectively, were relatively high compared to the median value of 0.2 mg/L for 157 Minnelusa aquifer well samples in the Black Hills area (Williamson and Carter, 2001).

This page intentionally left blank.

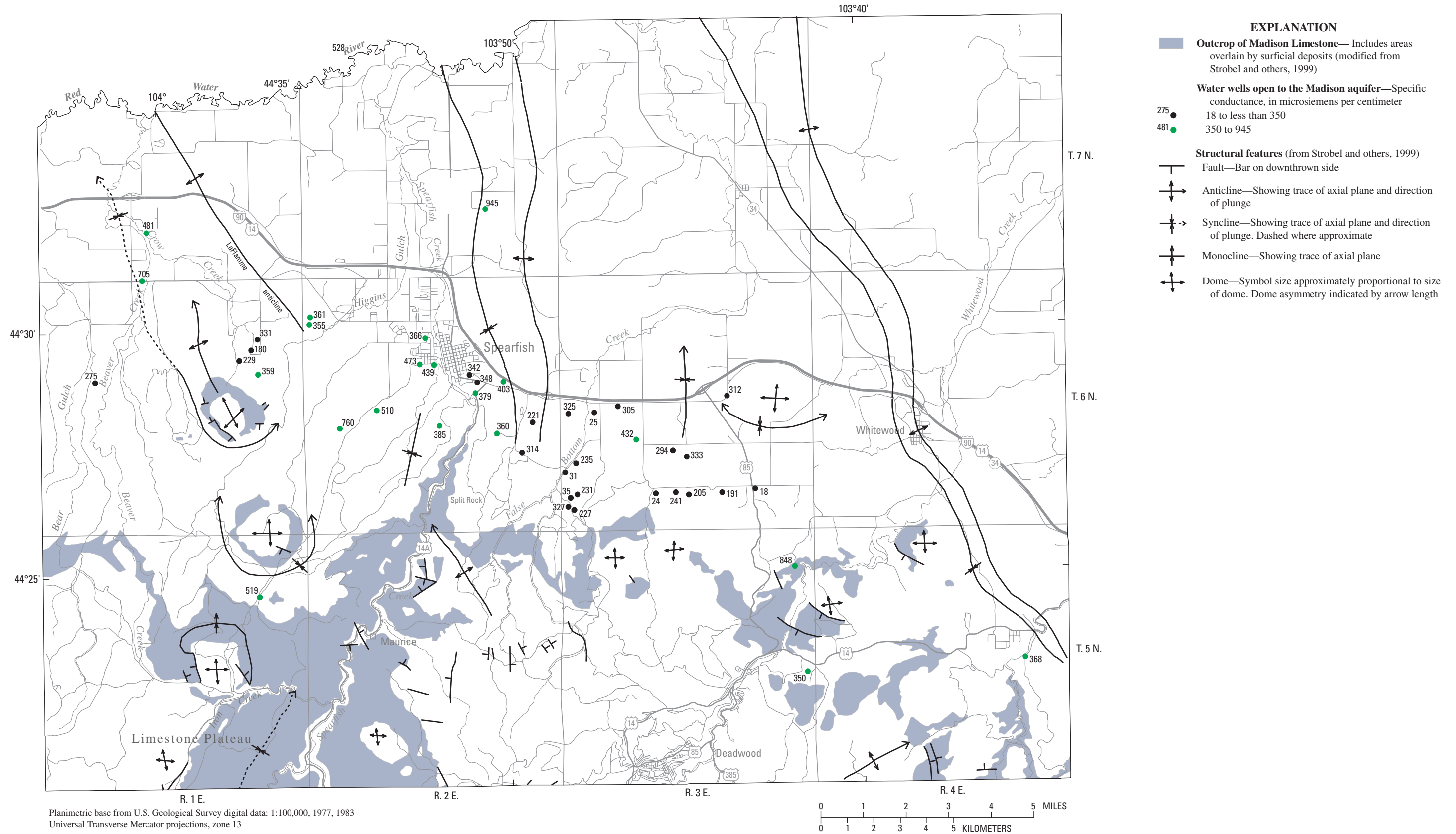


Figure 16. Specific conductance of water from the Madison aquifer (data from U.S. Geological Survey National Water Information System, 1956–2005).

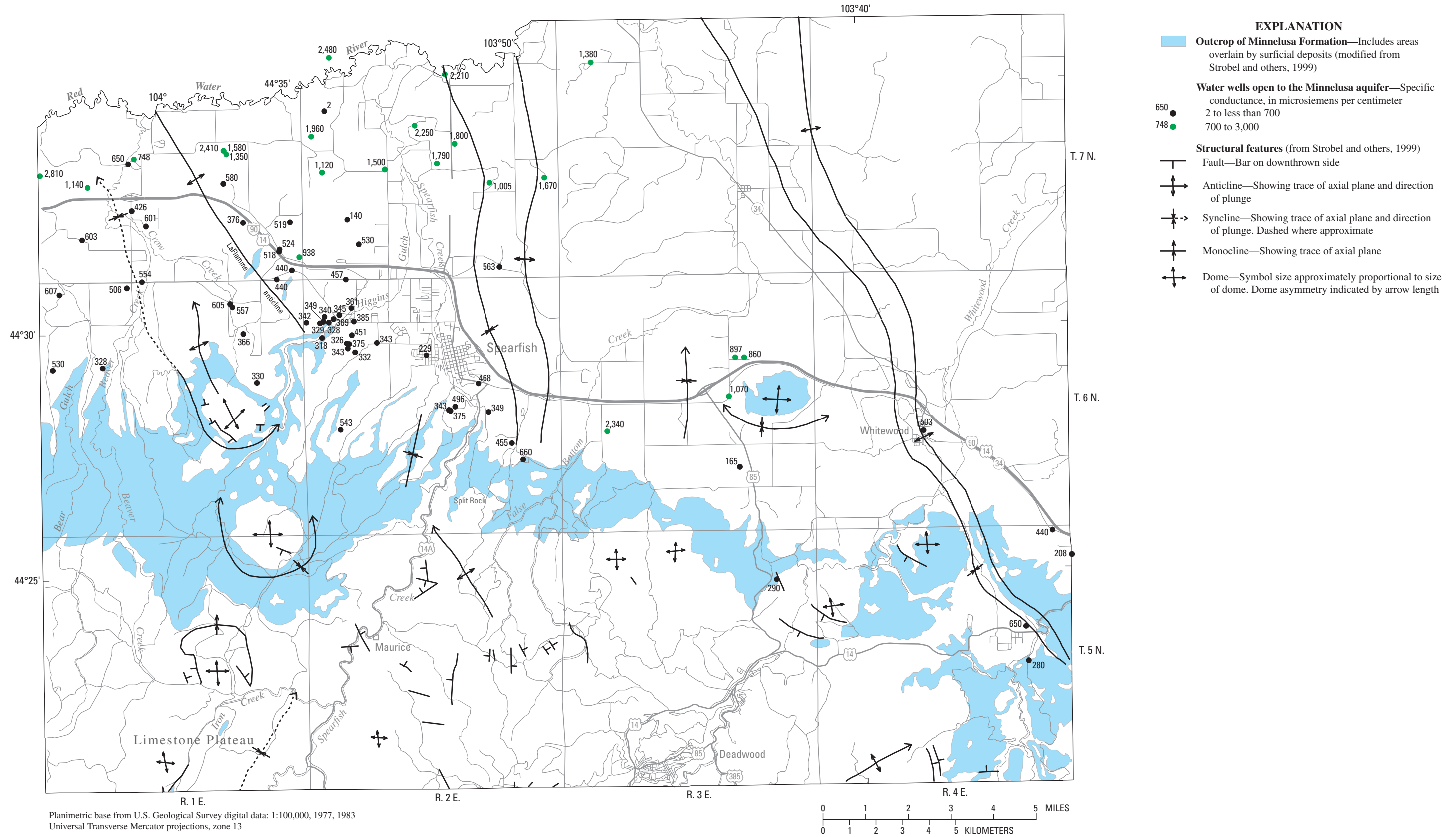


Figure 17. Specific conductance of water from the Minnelusa aquifer (data from U.S. Geological Survey National Water Information System, 1956–2005).

Table 9. Chemical analyses of selected ground-water samples from the Madison and Minnelusa aquifers.

[Number in parentheses below constituent is U.S. Geological Survey National Water Information System parameter code. FET, fixed end point titration; IT, incremental titration; gal/min, gallons per minute; µS/cm, microsiemens per centimeter; deg C, degrees Celsius; mm of Hg, millimeters of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter; Mdsn, Madison aquifer; Mnls, Minnelusa aquifer; e, estimated; <, less than]

Station number	Local number	Other identifier	Sample date	Flow rate (gal/min) (00059)	Specific conductance (µS/cm) (000950)	pH, water whole, field (standard units) (00400)
442833103434602	6N 3E15DDDA2	Frawley Ranch Mdsn (LA-95A)	08-16-2005	7.5	312	6.7
442833103434601	6N 3E15DDDA	Frawley Ranch Mnls (LA-88A)	08-17-2005	6.0	1,070	6.8
442854103505602	6N 2E14BCCC2	Spearfish GC Mdsn (LA-88C)	08-17-2005	3.0	348	8.7
442854103505601	6N 2E14BCCC	Spearfish GC Mnls (LA-88B)	08-18-2005	10.0	468	6.6

Other identifier	Temperature, air (deg C) (00020)	Temperature, water (deg C) (00010)	Barometric pressure (mm of Hg) (00025)	Oxygen, dissolved (mg/L) (00300)	Oxygen, dissolved (percent saturation) (00301)	Hardness total (mg/L as CaCO ₃) (00900)	Alkalinity, filtered, IT field, (mg/L as CaCO ₃) (00410)	Calcium, dissolved (mg/L as Ca) (00915)	Magnesium, dissolved (mg/L as Mg) (00925)
LA-95A	32.2	13.2	672	5.0	54	175	156	37.1	19.2
LA-88A	26.7	13.1	665	8.3	91	631	200	194	35.4
LA-88C	26.7	9.1	665	.7	6	84	¹ e33	7.1	16.2
LA-88B	23.9	9.2	670	11.3	97	263	221	64.2	24.9

Other identifier	Sodium, dissolved (mg/L as Na) (00930)	Potassium, dissolved (mg/L as K) (00935)	Bicarbonate, dissolved, IT, field (mg/L as HCO ₃) (00453)	Carbonate, dissolved, IT, field (mg/L as CO ₃) (00452)	Sulfate, dissolved (mg/L as SO ₄) (00945)	Chloride, dissolved (mg/L as Cl) (00940)	Fluoride, dissolved (mg/L as F) (00950)	Silica, dissolved (mg/L as SiO ₂) (00955)
LA-95A	2.47	1.47	189	0	6.3	0.40	0.3	12.0
LA-88A	5.92	2.86	242	5	392	3.36	.2	11.9
LA-88C	19.5	22.4	¹ e22	¹ e8	4.0	67.5	.2	.2
LA-88B	3.22	.98	268	0	25.0	2.80	.2	12.8

Table 9. Chemical analyses of selected ground-water samples from the Madison and Minnelusa aquifers.—Continued

[Number in parentheses below constituent is U.S. Geological Survey National Water Information System parameter code. FET, fixed end point titration; IT, incremental titration; gal/min, gallons per minute; µS/cm, microsiemens per centimeter; deg C, degrees Celsius; mm of Hg, millimeters of mercury; mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter; Mdsn, Madison aquifer; Mnls, Minnelusa aquifer; e, estimated; <, less than]

Other identifier	Nitrogen, ammonia dissolved (mg/L as N) (00608)	Nitrogen, nitrite dissolved (mg/L as N) (00613)	Nitrogen, NO ₂ +NO ₃ dissolved (mg/L as N) (00631)	Phosphorus, dissolved (mg/L as P) (00666)	Phosphorus ortho, dissolved (mg/L as P) (00671)	Aluminum, dissolved (µg/L as Al) (01106)	Antimony, dissolved (µg/L as Sb) (01095)	Arsenic, dissolved (µg/L as As) (01000)
LA-95A	<0.010	<0.002	0.1	0.008	e0.005	<2	<0.20	2.5
LA-88A	.016	<.002	2.41	.021	.017	<2	<.20	3.8
LA-88C	.063	<.002	<.016	.041	e.004	<2	<.20	<.2
LA-88B	<.010	<.002	.579	.021	.016	<2	<.20	2.6

Other identifier	Barium, dissolved (µg/L as Ba) (01005)	Beryllium, dissolved (µg/L as Be) (01010)	Boron, dissolved (µg/L as B) (01020)	Cadmium, dissolved (µg/L as Cd) (01025)	Chromium, dissolved (µg/L as Cr) (01030)	Cobalt, dissolved (µg/L as Co) (01035)	Copper, dissolved (µg/L as Cu) (01040)	Iron, dissolved (µg/L as Fe) (01046)
LA-95A	157	<0.06	9	<0.04	<0.8	0.307	<0.4	85
LA-88A	13	<.06	91	<.04	<.8	.418	3.7	30
LA-88C	15	<.06	11	e.03	<.8	.016	.4	17
LA-88B	277	<.06	9	<.04	<.8	.502	.8	e5

Other identifier	Lead, dissolved (µg/L as Pb) (01049)	Lithium, dissolved (µg/L as Li) (01130)	Manganese, dissolved (µg/L as Mn) (01056)	Mercury, dissolved (µg/L as Hg) (71890)	Molybdenum, dissolved (µg/L as Mo) (01060)	Nickel, dissolved (µg/L as Ni) (01065)	Selenium, dissolved (µg/L as Se) (01145)	Silver, dissolved (µg/L as Ag) (01075)
LA-95A	<0.08	5.0	40.7	<0.01	1.8	4.68	1.6	<0.2
LA-88A	<.08	13.6	1.9	<.01	1.9	7.79	1.5	<.2
LA-88C	<.08	56.2	16.8	<.01	10.8	.39	<.4	<.2
LA-88B	<.08	3.0	.5	<.01	.5	2.77	.7	<.2

Other identifier	Strontium, dissolved (µg/L as Sr) (01080)	Thallium, dissolved (µg/L as Tl) (01057)	Vanadium, dissolved (µg/L as V) (01085)	Zinc, dissolved (µg/L as Zn) (01090)	Alpha radioactivity (pCi/L) (04126)	Gross beta radioactivity (pCi/L) (03515)	Tritium (pCi/L) (07000)	Tritium 2-sigma (pCi/L) (75985)	Uranium natural, dissolved (µg/L as U) (22703)
LA-95A	189	e0.02	2.0	0.7	0.9	1.2	0.3	0.60	1.50
LA-88A	2,610	<.04	3.1	3.4	4.4	1.3	107	6.4	2.77
LA-88C	174	<.04	<.1	1.1	-2	13.5	13.8	1.0	<.04
LA-88B	222	<.04	2.8	2.2	2.4	1.4	61.4	3.8	1.13

¹Carbonate endpoint and theoretical titration curve did not fit data well.

Summary

The Madison and Minnelusa aquifers are used extensively for water supplies for the city of Spearfish and other users in northern Lawrence County, South Dakota. The Madison and Minnelusa aquifers are contained within the Paleozoic-age Madison Limestone and Minnelusa Formation, and the hydraulic connection between the Madison and Minnelusa aquifers is spatially variable. Transmissivity of the Madison and Minnelusa aquifers is very heterogeneous with values determined from aquifer tests that range over several orders of magnitude.

Ground water in the Madison and Minnelusa aquifers in the study area generally flows north from outcrop areas where ground-water recharge from sinking streams and infiltration of precipitation occurs. Ground water that moves northward and eastward around the Black Hills enters the study area from the west and results in hydraulic heads that are several hundred feet higher on the western side of the study area than on the eastern side. The estimated average recharge rate of 38 cubic feet per second (ft³/s) on outcrops of the Madison Limestone and Minnelusa Formation is less than the total estimated average spring discharge rate of 51 ft³/s in the northwestern part of the study area. Potentiometric contours for the Madison and Minnelusa aquifers show that the hydraulic gradient is steeper near outcrop areas than in the northern part of the study area.

The maximum potential streamflow recharge rate to Madison and Minnelusa aquifers along Spearfish Creek is about 21 ft³/s. Sixteen pounds of fluorescein dye were injected into Spearfish Creek on March 25, 2003, when streamflow was 6.6 ft³/s. The dye was detected in water samples from four wells completed in the Madison aquifer ranging from 2.6 to 4.5 miles north of the injection site. First arrival times ranged from 5 to 169 days, and ground-water velocities ranged from about 0.1 to 0.5 mile per day. A peak concentration of about 23 micrograms per liter (µg/L) at the nearest well occurred 15 days after injection, then decreased gradually; however, concentrations greater than 1 µg/L were present about 9 months later. Detectable dye concentrations were observed for as long as 400 days in a well farther downgradient. Sixty-four pounds of Rhodamine WT were injected into Spearfish Creek at the same location as the fluorescein dye injection on May 9, 2003, when streamflow was 5.6 ft³/s. Rhodamine WT dye concentrations measured in samples from the same four wells were about an order of magnitude less than measured fluorescein concentrations. A combination of recharge characteristics, the diversion of streamflow around the Spearfish Creek loss zone, and highly transmissive conduits associated with streamflow loss may explain transient differences in dye concentrations.

Samples from selected wells and springs in the study area were collected and analyzed for oxygen and deuterium isotopes, chlorofluorocarbons (CFCs), and tritium. Oxygen- and deuterium-isotope distributions in precipitation for northern Lawrence County generally are lightest (more

negative) in the southeast and become heavier (more positive) in an outward direction from the central part of the Black Hills. Oxygen- and deuterium-isotope values for samples from Cox Lake and McNenny Pond springs are similar to the lightest oxygen and deuterium values for water from wells, indicating a probable component of spring discharge that originates from outcrops of the Madison Limestone and Minnelusa Formation on the Limestone Plateau south of the study area. Oxygen- and deuterium-isotope values for three samples from Mirror Lake spring are heavier than values for Cox Lake and McNenny Pond springs, indicating possible contributions from overlying aquifers and local recharge. The oxygen- and deuterium-isotope values for the combined springflow contributing to Crow Creek in the northwestern part of the study area are similar to the values for Cox Lake and McNenny Pond springs indicating that the primary sources of water for the large spring discharge are the Madison and Minnelusa aquifers. Oxygen- and deuterium-isotope values for Old Hatchery and Higgins Gulch springs, located north of Spearfish, were heavier than values for Cox Lake and McNenny Pond springs, indicating a source water originating from the outcrops of the Madison Limestone and Minnelusa Formation within the study area rather than ground-water moving into the study area from the west.

Concentrations of three CFCs (CFC-11, CFC-12, and CFC-113) were used to characterize ground-water residence times in the study area. For the four wells where dye was detected, at least a portion of the water was less than 1 year old. CFC apparent ages ranged from 12 to 26 years, indicating that the wells contained months-old water mixed with years-to decades-old water.

Logarithmic regression analysis of the CFC-11 apparent ages for water from 10 wells where dye was detected and distance to a possible conduit trending north through the area, yielded an r² value of 0.71. Straight-line regression analysis of the CFC-11 apparent ages for the six wells closest to the possible conduit had an r² value of 0.96. Although spatial analysis of age alone is not conclusive for the existence of a conduit, it provides additional evidence when considered in conjunction with other hydrologic and chemical data.

Two wells located relatively close to the outcrop areas had no or very low tritium values indicating relatively long residence times and diffuse ground-water flow. The low tritium value of 7.2 TU in water from well COL where dye was detected, indicates that the water probably is a bimodal mixture, with a substantial portion that is older than 50 years. Water from well ELL, in which dye also was detected, had a CFC apparent age of 15 years and a tritium concentration of 19.7 TU, which is about the same concentration as a unimodal mixture of water from precipitation averaged over the last 20 years with very little water older than 50 years. Comparison of the CFC apparent age for the three spring sites (Cox Lake, 26 years; McNenny Pond, 26 years; Mirror Lake, 13 years) also indicates that Mirror Lake spring probably has a component of local recharge from aquifers that overlie the Minnelusa Formation.

In the Madison aquifer, specific conductance ranges from 18 to 945 microsiemens per centimeter. In the Minnelusa aquifer, specific conductance ranges from 2 to 3,000 microsiemens per centimeter. The spatial distribution of specific conductance in the Madison aquifer is less ordered than in the Minnelusa aquifer and probably is the result of heterogeneity and the existence of solution conduits.

Water samples from two observation wells completed in the Madison and Minnelusa aquifers near Spearfish and two wells about 6 miles east of Spearfish were analyzed for physical properties, major ions, nutrients, trace elements, and radionuclides. U.S. Environmental Protection Agency Maximum Contaminant Levels were not exceeded for any of the constituents analyzed in water from the four wells. The U.S. Environmental Protection Agency Secondary Maximum Contaminant Level for sulfate (250 milligrams per liter) was exceeded in water from a Minnelusa well located east of Spearfish, with a value of 392 milligrams per liter.

References

- Bowles, C.G., and Braddock, W.A., 1963, Solution breccias of the Minnelusa Formation in the Black Hills, South Dakota and Wyoming, *in* Geological Survey Research—Short papers in geology and hydrology, articles 60–121: U.S. Geological Survey Professional Paper 475–C, art. 83, p. C91–C95.
- Brobst, D.A., and Epstein, J.B., 1963, Geology of the Fanny Peak quadrangle, Wyoming-South Dakota: U.S. Geological Survey Bulletin 1063–1, 377 p., 2 pl.
- Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl₃F and CCl₂F₂) as hydrologic tracers and age-dating tools—the alluvium and terrace system of Central Oklahoma: *Water Resources Research*, v. 28, no. 9, p. 2257–2283.
- Busenberg, Eurybiades, Plummer, L.N., and Bartholomay, R.C., 2001, Estimated age and source of the young fraction of ground water at the Idaho National Engineering and Environmental Laboratory: U.S. Geological Survey Water-Resources Investigations Report 01–4265, 144 p.
- Carter, J.M., Driscoll, D.G., and Hamade, G.R., 2001, Estimated recharge to the Madison and Minnelusa aquifers in the Black Hills area, South Dakota and Wyoming, water years 1931–98: U.S. Geological Survey Water-Resources Investigations Report 00–4278, 66 p.
- Carter, J.M., Driscoll, D.G., Hamade, G.R., and Jarrell, G.J., 2001, Hydrologic budgets for the Madison and Minnelusa aquifers, Black Hills of South Dakota and Wyoming, water years 1987–96: U.S. Geological Survey Water-Resources Investigations Report 01–4119, 53 p.
- Carter, J.M., and Redden, J.A., 1999a, Altitude of the top of the Minnelusa Formation in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–744–C, 2 sheets, scale 1:100,000.
- Carter, J.M., and Redden, J.A., 1999b, Altitude of the top of the Madison Limestone in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–744–D, 2 sheets, scale 1:100,000.
- Carter, J.M., and Redden, J.A., 1999c, Altitude of the top of the Deadwood Formation in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–744–E, 2 sheets, scale 1:100,000.
- Cattermole, J.M., 1969, Geologic map of the Rapid City west quadrangle, Pennington County, South Dakota: U.S. Geological Survey Geologic Quadrangle Map GQ–828, scale 1:24,000.
- Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrogeology: Boca Raton, Florida, Lewis Publishers, 328 p.
- Clemens, T., Hueckinghaus, D., Sauter, M., Liedl, R., and Teutsch, G., 1997, Modelling the genesis of karst aquifer systems using a coupled reactive network model: Hard Rock Hydrosystems, Proceedings of Rabat Symposium S2, May 1997, International Association of Hydrological Sciences 241, p. 3–10.
- Cook, P.G., and Solomon, D.K., 1997, Recent advances in dating young groundwater—chlorofluorocarbons, ³H/³He, and ⁸⁵Kr: *Journal of Hydrology*, v. 191, p. 245–265.
- Cook, P.G., Solomon, D.K., Sanford, W.E., Busenberg, Eurybiades, Plummer, L.N., and Poreda, R.J., 1996, Inferring shallow groundwater flow in saprolite and fractured rock using environmental tracers: *Water Resources Research*, v. 32, no. 6, p. 1501–1509.
- DeWitt, Ed, Redden, J.A., Buscher, David, and Wilson, A.B., 1989, Geologic map of the Black Hills area, South Dakota and Wyoming: U.S. Geological Survey Map I–1910, scale 1:250,000.
- Downey, J.S., and Dinwiddie, G.A., 1988, The regional aquifer system underlying the Northern Great Plains in parts of Montana, North Dakota, South Dakota, and Wyoming—summary: U.S. Geological Survey Professional Paper 1402, 64 p.
- Driscoll, D.G., Carter, J.M., Williamson, J.E., and Putnam, L.D., 2002, Hydrology of the Black Hills area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 02–4094, 150 p.

- Driscoll, D.G., Hamade, G.R., and Kenner, S.J., 2000, Summary of precipitation data for the Black Hills area of South Dakota, water years 1931–98: U.S. Geological Survey Open-File Report 00–329, 151 p.
- Epstein, J.B., and Putnam, L.D., 2005, Mirror Lake—sinkholes, gypsum dissolution front, and hydrology of resurgent springs, Field Trip Guide 2 *in* U.S. Geological Survey Karst Interest Group Proceedings: U.S. Geological Survey Scientific Investigations Report 2005–5160, p. 251–260.
- Even, H., Carmi, I., Magaritz, M., and Gerson, R., 1986, Timing the transport of water through the upper vadose zone in a karstic system above a cave in Israel: *Earth Surface Processes and Landforms*, v. 11, no. 2, p. 181–191.
- Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 92–634, 28 p.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.
- Freeze, R.A., and Cherry, J.A., 1979, *Groundwater*: Englewood Cliffs, N.J., Prentice-Hall, 604 p.
- Garbarino, J.R., and Damrau, D.L., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of organic plus inorganic mercury in filtered and unfiltered natural water with cold vapor–atomic fluorescence spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01–4132, 16 p.
- Gott, G.B., Wolcott D.E., and Bowles, C.G., 1974, Stratigraphy of the Inyan Kara Group and localization of uranium deposits, southern Black Hills, South Dakota and Wyoming: U.S. Geological Survey Professional Paper 763, 57 p., 4 pl.
- Greene, E.A., 1993, Hydraulic properties of the Madison aquifer system in the western Rapid City area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 93–4008, 56 p.
- Greene, E.A., 1999, Characterizing recharge to wells in carbonate aquifers using environmental and artificially recharged tracers, *in* Morganwalp, D.W., and Buxton, H.T., eds., Proceedings of the Technical Meeting, Charleston, S.C., March 8–12, 1999, Toxic Substances Hydrology Program: U.S. Geological Survey Water-Resources Investigations Report 99–4018–C, p. 803–808.
- Greene, E.A., Shapiro, A.M., and Carter, J.M., 1998, Hydrogeologic characterization of the Minnelusa and Madison aquifers near Spearfish, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 98–4156, 64 p.
- Gries, J.P., 1996, *Roadside geology of South Dakota*: Missoula, Montana, Mountain Press Publishing Co., 358 p.
- Hayes, T.S., 1999, Episodic sediment-discharge events in Cascade Springs, southern Black Hills, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 99–4168, 34 p.
- Heath, R.C., 1983, Basic ground-water hydrology: U.S. Geological Survey Water-Supply Paper 2220, 84 p.
- Hortness, J.E., and Driscoll, D.G., 1998, Streamflow losses in the Black Hills of western South Dakota: U.S. Geological Survey Water-Resources Investigations Report 98–4116, 99 p.
- International Atomic Energy Agency, 1981, Statistical treatment of environmental isotope data in precipitation: Technical Report Series No. 206, 256 p.
- Jones, W.K., 1984, Dye tracer tests in karst areas: *National Speleological Society Bulletin*, v. 46, no. 2, p. 3–9.
- Klemp, J.A., 1995, Source aquifers for large springs in northwestern Lawrence County, South Dakota: Rapid City, South Dakota School of Mines and Technology, unpublished M.S. thesis, 175 p.
- Kyllonen, D.P., and Peter, K.D., 1987, Geohydrology and water quality of the Inyan Kara, Minnelusa, and Madison aquifers of the northern Black Hills, South Dakota and Wyoming, and Bear Lodge Mountains, Wyoming: U.S. Geological Survey Water-Resources Investigations Report 86–4158, 61 p.
- Lisenbee, A.L., 1985, Tectonic map of the Black Hills uplift, Montana, Wyoming, and South Dakota: State of Wyoming Geological Survey Map Series 13, scale 1:24,000.
- Lohman, S.W., and others, 1972, Definitions of selected ground-water terms—revisions and conceptual refinements: U.S. Geological Survey Water-Supply Paper 1988, 21 p.
- Long, A.J., and Putnam, L.D., 2002, Flow-system analysis of the Madison and Minnelusa aquifers in the Rapid City area, South Dakota—conceptual model: U.S. Geological Survey Water-Resources Investigations Report 02–4185, 100 p., 3 pl.
- Long, A.J. and Putnam, L.D., 2006, Translating CFC-based piston ages into probability density functions of ground-water age in karst: *Journal of Hydrology*, v. 330, p. 735–747.
- Maloszewski, P., and Zuber, A., 1982, Determining the turnover time of groundwater systems with the aid of environmental tracers—1. Models and their applicability: *Journal of Hydrology*, v. 57, p. 207–231.
- Michel, R.L., 1989, Tritium deposition in the continental United States, 1953–83: U.S. Geological Survey Water-Resources Investigations Report 89–4072, 46 p.
- Miller, L.D., and Driscoll, D.G., 1998, Streamflow characteristics for the Black Hills of South Dakota, through water year 1993: U.S. Geological Survey Water-Resources Investigations Report 97–4288, 322 p.
- National Oceanic and Atmospheric Administration, 1997, Climatological data annual summary, South Dakota: National Oceanic and Atmospheric Administration, v. 102, no. 13, 30 p.
- Naus, C.A., Driscoll, D.G., and Carter, J.M., 2001, Geochemistry of the Madison and Minnelusa aquifers in the Black Hills area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 01–4129, 118 p.
- Oster, H., Sonntag, C., and Munnich, K.O., 1996, Groundwater age dating with chlorofluorocarbons: *Water Resources Research*, v. 32, no. 10, p. 2989–3001.
- Peter, K.D., Kyllonen, D.P., and Mills, K.R., 1987, Geologic structure and altitude of the top of the Minnelusa Formation, northern Black Hills, South Dakota and Wyoming, and Bear Lodge Mountains, Wyoming: U.S. Geological Survey Water-Resources Investigations Report 85–4053, 1 sheet.
- Plummer, L.N., and Busenberg, Eurybiades, 2005, Chlorofluorocarbons: accessed August 31, 2005, at <http://water.usgs.gov/lab/cfc/background/>, excerpt from Cook, P., and Herczeg, A., eds., 1999, *Environmental tracers in subsurface hydrology*: Norwell, Massachusetts, Kluwer Academic Publishers, 552 p.
- Putnam, L.D., 2000, Sensitivity of ground water to contamination, Lawrence County, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 00–4103, 55 p.
- Rahn, P.H., 1971, The hydrologic significance of the November, 1986 dye test on Boxelder Creek, Black Hills, South Dakota: Proceedings, South Dakota Academy of Science, v. 50, p. 52–56.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow—Volume 1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, p. 1–285.
- Robinson, C.S., Mapel, W.J., and Bergendahl, M.H., 1964, Stratigraphy and structure of the northern and western flanks of the Black Hills uplift, Wyoming, Montana, and South Dakota: U.S. Geological Survey Professional Paper 404, 134 p.
- Sloto, R.A., and Crouse, M.Y., 1996, HYSEP—a computer program for streamflow hydrograph separation and analysis: U.S. Geological Survey Water-Resources Investigations Report 96–4040, 46 p.
- Strobel, M.L., Galloway, J.M., Hamade, G.R., and Jarrell, G.J., 2000a, Potentiometric surface of the Minnelusa aquifer in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–745–C, 2 sheets, scale 1:100,000.
- Strobel, M.L., Galloway, J.M., Hamade, G.R., and Jarrell, G.J., 2000b, Potentiometric surface of the Madison aquifer in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–745–D, 2 sheets, scale 1:100,000.
- Strobel, M.L., Jarrell, G.J., Sawyer, J.F., Schleicher, J.R., and Fahrenbach, M.D., 1999, Distribution of hydrogeologic units in the Black Hills area, South Dakota: U.S. Geological Survey Hydrologic Investigations Atlas HA–743, 3 sheets, scale 1:100,000.
- Szabo, Zoltan, Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., and Schlosser, P., 1996, Age-dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flowpath analysis, southern New Jersey coastal plain: *Water Resources Research*, v. 32, no. 4, p. 1023–1038.
- U.S. Environmental Protection Agency, 2006a, National Primary Drinking Water Regulations: accessed November 27, 2006, at <http://www.epa.gov/safewater/contaminants/index.html#primary>
- U.S. Environmental Protection Agency, 2006b, National Secondary Drinking Water Regulations: accessed November 27, 2006, at <http://www.epa.gov/safewater/contaminants/index.html#sec>
- U.S. Geological Survey, 1977–2003, Water resources data for South Dakota, water years 1976–2002: U.S. Geological Survey Water-Data Reports SD–76–1 to SD–02–1 (published annually).
- U.S. Geological Survey, 1997–2006, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, 2 v., variously paged. [Available online at <http://pubs.water.usgs.gov/twri9A>. Chapters were originally published from 1997–1999; updates and revisions are ongoing and are summarized at <http://water.usgs.gov/owq/FieldManual/mastererrata.html>.]

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

Whitehead, R.L., 1996, Ground water atlas of the United States—segment 8, Montana, North Dakota, South Dakota, Wyoming: U.S. Geological Survey Hydrologic Investigations Atlas 730–I, 24 p.

Williamson, J.E., and Carter, J.M., 2001, Water-quality characteristics in the Black Hills area, South Dakota: U.S. Geological Survey Water-Resources Investigations Report 01–4194, 196 p.

Wilson, J.F., Cobb, E.D., and Kilpatrick, F.A., 1986, Fluorometric procedures for dye tracing: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A12, 34 p.

Supplemental Information

Section A. Additional data

Table 10. Observation wells used for monitoring water levels in the study area.

[NGVD 29, National Geodetic Vertical Datum of 1929; Mdsn, Madison; Mnl, Minnelusa]

Station identification number	Local number	Other identifier	Other identifier	Aquifer	Hydraulic head, September 2004 (feet above NGVD 29)	Land-surface altitude (feet above NGVD 29)
442435103571101	5N 1E11DABA	Big Hill Trailhead Mdsn	LA-95C	Mdsn	4,881	5,530
442545103343701	5N 4E 1ABBD	Whitewood Mnl	LA-86C	Mnl	3,453	3,629
442545103343702	5N 4E 1ABBD2	Whitewood Mdsn	LA-90A	Mdsn	3,443	3,630
442344103253401	5N 4E14ADD	Boulder Canyon Mnl	LA-63A	Mnl	3,675	3,882
442301103365501	5N 4E22ADDA	Boulder Canyon Mdsn	LA-96D	Mdsn	3,642	4,062
443100103543001	6N 2E 5BBBB	Spearfish W Mnl	LA-86A	Mnl	3,543	3,678
442854103505601	6N 2E14BCCC	Spearfish GC Mnl	LA-88B	Mnl	3,653	3,734
442854103505602	6N 2E14BCCC2	Spearfish GC Mdsn	LA-88C	Mdsn	3,641	3,735
442802103544601	6N 2E19DABA	Tinton Rd Mdsn	LA-96B	Mdsn	3,651	4,590
442802103544602	6N 2E19DABA2	Tinton Rd Mnl	LA-96C	Mnl	4,313	4,591
442833103434601	6N 3E15DDDA	Fawley Ranch Mnl	LA-88A	Mnl	3,550	3,768
442833103434602	6N 3E15DDDA2	Fawley Ranch Mdsn	LA-95A	Mdsn	3,520	3,768
443100104002001	7N 1E33CCDD	State line Mdsn	LA-87A	Mdsn	3,736	3,667
443100104002002	7N 1E33CCDD2	State line Mnl	LA-87B	Mnl	3,644	3,668
443515103513901	7N 2E10BADC	Redwater	LA-62A	Mnl	3,484	3,218

Table 11. Water wells completed in the Madison aquifer and used for interpretation of average potentiometric surface.

[NGVD 29, National Geodetic Vertical Datum of 1929; --, none]

Station identification number	Local number	Other identifier	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
441134103590301	3N 1E27DBAA	--	6,269	LA-63A	6,545	420
441700103535401	4N 2E29AACB	--	5,505	LA-63A	5,525	50
442113103524101	5N 2E33DCAA2	--	5,946	LA-63A	6,040	480
442504103415301	5N 3E 1DCCB	--	4,036	LA-63A	4,360	550
442255103413401	5N 3E24ADCA	--	4,620	LA-63A	4,680	145
¹ 443146103362301	5N 4E14BBB	--	3,742	LA-63A	4,130	870
442358103370101	5N 4E15ABCA	--	3,640	LA-63A	4,260	900
442334103370501	5N 4E15DBCB	--	3,613	LA-63A	4,210	700
442344103405601	5N 4E18BDCCD	--	4,501	LA-63A	4,800	540
442951103570701	6N 1E11ADDB	--	3,663	LA-63A	4,140	725
442925103573901	6N 1E11CDDD	--	3,837	LA-96B	4,340	962
442938103571801	6N 1E11DACB	--	3,722	LA-63A	4,175	680
442908103570701	6N 1E14AADC	--	3,757	LA-63A	4,330	750
442909103572601	6N 1E14ABDC	--	3,788	LA-63A	4,365	1,070
442900104014601	6N 1E17BCBC	--	4,105	LA-87A	4,285	760
443017103553601	6N 2E 6CCDA	MIT	3,653	LA-63A	4,105	810
443005103553801	6N 2E 7BBDB	SAL	3,665	LA-63A	4,155	1,262
442950103521501	6N 2E 9ADDB	COL	3,645	LA-88C	3,640	741
442936103530001	6N 2E 9CAC2	PT	3,681	LA-63A	3,762	855
442855103503501	6N 2E14ACDC	GC	3,675	LA-63A	3,805	1,180
442842103505501	6N 2E14CBCC	NEV	3,663	LA-88C	3,760	842
¹ 442906103510501	6N 2E15AADC	ELL	3,669	LA-88C	3,720	800
442918103523001	6N 2E16AAB	KYT	3,643	LA-88C	3,840	925
442917103525601	6N 2E16BADD	--	3,548	LA-63A	3,900	760
442907103530801	6N 2E16BBBC	--	3,691	LA-63A	3,930	620
442853103530001	6N 2E16CBAB	--	3,683	LA-63A	4,020	600
442748103524501	6N 2E21DCBC	MP3	3,681	LA-63A	4,230	965
442813103520501	6N 2E22BCCA	MP1	3,657	LA-63A	4,220	1,140
442757103512901	6N 2E22CBAB	MP2	3,666	LA-88C	4,240	870
442752103501901	6N 2E23DBCA	JEF	3,619	LA-88C	4,020	720
442805103491801	6N 2E24BDCCD	--	3,609	LA-88C	4,030	708

Table 11. Water wells completed in the Madison aquifer and used for interpretation of average potentiometric surface.—Continued

[NGVD 29, National Geodetic Vertical Datum of 1929; --, none]

Station identification number	Local number	Other identifier	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
442727103493701	6N 2E25BBCA	--	3,697	LA-63A	4,115	615
442636103480301	6N 2E31BADB	--	4,062	LA-88C	4,530	660
442627103530801	6N 2E33BCAC	--	4,197	LA-96B	4,835	1,285
442856103475701	6N 3E18BDAD	--	3,561	LA-63A	3,900	900
442818103472501	6N 3E19AACD	--	3,535	LA-63A	3,970	740
442815103481701	6N 3E19BBDC	VIG	3,561	LA-88C	3,965	863
442823103465201	6N 3E20BAAC	--	3,534	LA-95A	3,940	902
442652103472801	6N 3E20DDAC	--	3,592	LA-63A	4,015	680
442742103462101	6N 3E20DDCA	--	3,525	LA-63A	4,025	820
¹ 442736103461401	6N 3E20DDDC	--	3,974	LA-63A	4,020	720
¹ 442715103432301	6N 3E26BDBD	--	3,727	LA-63A	3,898	880
442720103445501	6N 3E27BCBB	--	3,518	LA-95A	3,970	980
442727103451901	6N 3E28ABCA	--	3,530	LA-63A	3,970	950
442651103460401	6N 3E29DDDB	--	3,737	LA-63A	4,190	700
442714103480501	6N 3E30BDDB	--	3,538	LA-88C	4,160	980
442703103482401	6N 3E30CBDB	--	3,710	LA-88C	4,145	580
442631103480201	6N 3E31BADD	--	4,020	LA-88C	4,525	660
442632103481501	6N 3E31BBDD	--	4,011	LA-88C	4,440	640
442621103481901	6N 3E31BCDD	--	4,047	LA-88C	4,540	765
442623103485901	6N 3E31BDDA	--	4,021	LA-88C	4,500	760
442617103480901	6N 3E31CABB	--	4,019	LA-88C	4,500	700
442637103451501	6N 3E33AACB	--	3,576	LA-95A	4,220	894
442637103451901	6N 3E33BABC	--	3,677	LA-63A	4,190	760
442636103454901	6N 3E33BACB	--	3,790	LA-95A	4,220	660
442636103435601	6N 3E34AACA	--	3,527	LA-95A	4,055	820
442640103444501	6N 3E34BBCA	--	3,563	LA-63A	4,200	922
442640103425901	6N 3E35ABBA	--	3,558	LA-63A	4,035	1,140
442600103411301	6N 4E31CCBA	--	3,563	LA-63A	4,080	705
443204104001301	7N 1E28CDAC	--	3,702	LA-87A	3,535	1,530

¹ The hydraulic head for this site displays excessive variability at the local scale and probably does not represent the potentiometric surface; therefore, the hydraulic head was not used in interpretation of the potentiometric surface.

Table 12. Water wells completed in the Minnelusa aquifer and used for interpretation of average potentiometric surface.

[NGVD 29, National Geodetic Vertical Datum of 1929; --, not applicable]

Station identification number	Local number	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
442546103344101	5N 4E 1ABBC	3,454	LA-63A	3,618	310
442546103343301	5N 4E 1ABBD3	3,442	LA-63A	3,625	400
442337103350401	5N 4E13CCAC	3,735	LA-63A	3,870	315
442340103345001	5N 4E14ADA	3,660	--	3,860	400
442400103362001	5N 4E14BBDA	3,622	LA-63A	4,030	620
442344103360601	5N 4E14BDCA	3,631	LA-63A	3,990	630
¹ 442347103364001	5N 4E15ADDA	3,655	LA-63A	4,075	560
442347103364002	5N 4E15ADDB2	3,749	LA-63A	4,175	560
442331103401401	5N 4E17CACB	4,447	LA-63A	4,480	70
443053103564301	6N 1E 1BAC	3,717	LA-63A	3,980	480
443036103575401	6N 1E 2CABB	3,910	LA-63A	3,930	160
443057104005001	6N 1E 5AADB	3,680	LA-87B	3,690	515
443049104024501	6N 1E 6BDAB	3,622	LA-63A	3,785	430
442952104015101	6N 1E 8BCBC	3,764	LA-63A	3,900	320
442953103595601	6N 1E 9ACBC	3,775	--	3,840	189
¹ 442959103573201	6N 1E11ACBA	3,693	LA-87B	4,090	620
442859103571001	6N 1E14ADDB	4,329	LA-96C	4,415	752
442903103595601	6N 1E16ACBB	4,040	--	4,180	263
442919104013301	6N 1E17BBA	3,832	LA-87B	4,140	402
442917104025801	6N 1E18BBAA	4,131	LA-63A	4,300	300
443101103530601	6N 2E 4BBAA	3,588	LA-63A	3,548	300
443028103522801	6N 2E 4DBCC	3,550	LA-63A	3,562	420
443029103542701	6N 2E 5CBBC	3,577	LA-86A	3,662	280
443035103543001	6N 2E 5CBDB	3,563	LA-86A	3,655	290
443013103542301	6N 2E 5CCDC	3,590	LA-86A	3,670	238
443020103525001	6N 2E 5DC2	3,579	LA-63A	3,625	285
443017103533801	6N 2E 5DDCB	3,577	LA-86A	3,615	300
443025103544501	6N 2E 6DACC	3,615	LA-63A	3,710	267
¹ 443016103545801	6N 2E 6DCDA	3,702	LA-86A	3,895	380
443019103551301	6N 2E 6DCDC	3,661	LA-86A	3,920	500
443021103544801	6N 2E 6DDBD	3,675	LA-86A	3,738	480
443008103544101	6N 2E 7AAAB	3,608	LA-86A	3,700	260
443001103544201	6N 2E 7AADC	3,656	LA-86A	3,795	240
443012103550601	6N 2E 7ABBA	3,698	LA-86A	3,965	480

Table 12. Water wells completed in the Minnelusa aquifer and used for interpretation of average potentiometric surface.—Continued

[NGVD 29, National Geodetic Vertical Datum of 1929; --, not applicable]

Station identification number	Local number	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
443011103552101	6N 2E 7BAAB	3,716	LA-86A	4,120	620
443012103554401	6N 2E 7BBBA	3,754	LA-86A	4,150	560
442953103553801	6N 2E 7BCBB	3,738	LA-86A	3,790	77
442953103553701	6N 2E 7BCBD	3,736	LA-86A	3,790	74
442953103551801	6N 2E 7BDDA	3,752	LA-86A	3,780	51
442946103543601	6N 2E 7DAAA	3,660	LA-86A	3,820	498
442942103545201	6N 2E 7DABC	3,621	LA-86A	3,838	320
443026103550401	6N 2E 7DCBA	3,941	LA-63A	4,080	220
442946103534401	6N 2E 8ACDD	3,661	LA-63A	3,700	180
¹ 442945103543201	6N 2E 8CBBB	3,706	LA-86A	3,807	440
442940103543401	6N 2E 8CBBC	3,666	LA-86A	3,840	472
442935103542201	6N 2E 8CBDD	3,666	LA-86A	3,822	540
442940103542801	6N 2E 8CBDD1	3,688	LA-86A	3,800	410
442921103463101	6N 3E 8DDAC	3,526	LA-88A	3,815	662
442935103530301	6N 2E 9CCB	3,653	LA-63A	3,820	205
442831103513501	6N 2E15CDDA	3,699	LA-63A	3,940	520
442903103530501	6N 2E16BCAD	3,684	LA-96C	3,970	440
442910103531001	6N 2E16BDBD	3,598	LA-96C	3,930	560
442901103530001	6N 2E16CBCB	3,755	LA-96C	4,110	500
442820103541001	6N 2E20BACA	4,209	LA-63A	4,280	200
442823103514301	6N 2E22BAAC	3,603	LA-88B	4,030	560
442822103514001	6N 2E22BADB	3,642	LA-88B	4,060	620
442825103520101	6N 2E22BBDC	3,698	LA-63A	4,000	520
442826103503801	6N 2E23BABB	3,647	LA-88B	3,790	180
442820103503501	6N 2E23BBBA	3,660	LA-88B	3,740	415
442741103495601	6N 2E23DD	3,668	LA-63A	4,042	540
¹ 442729103493601	6N 2E25BBDD	3,939	LA-63A	4,100	260
442630103485001	6N 2E36A	4,172	LA-63A	4,240	200
442636103491801	6N 2E36BACA	4,244	LA-63A	4,520	600
443006103431701	6N 3E11BAAC	3,527	LA-63A	3,665	775
442922103433301	6N 3E11CCDC	3,543	LA-88A	3,680	430
442923103431501	6N 3E11CDDC	3,543	LA-88A	3,660	430
¹ 442834103431501	6N 3E14CDA	3,715	LA-63A	3,750	100
442907103442301	6N 3E15BADD	3,515	LA-63A	3,840	598

Table 12. Water wells completed in the Minnelusa aquifer and used for interpretation of average potentiometric surface.—Continued

[NGVD 29, National Geodetic Vertical Datum of 1929; --, not applicable]

Station identification number	Local number	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
442844103434901	6N 3E15DAD	3,520	--	3,740	300
442913103465401	6N 3E17ABAA2	3,552	LA-63A	3,830	700
¹ 442822103433501	6N 3E26BDBB	3,685	LA-63A	3,880	438
442708103432801	6N 3E26CBAA	3,539	LA-88A	3,950	560
¹ 442622103420601	6N 3E36DBBB	3,981	LA-63A	4,020	165
442950103374701	6N 4E 8DADD	3,632	LA-88A	3,680	242
442835103380101	6N 4E16DDBB	3,471	LA-63A	3,560	1,442
442749103381401	6N 4E21DBCD	3,507	LA-86C	3,620	630
442746103381301	6N 4E21DCBC	3,510	LA-86C	3,645	480
442728103381201	6N 4E28ABD	3,542	LA-63A	3,680	552
442610103401701	6N 4E31ADDD	3,508	LA-63A	4,040	700
¹ 442606103402301	6N 4E31DACD	3,462	LA-88A	3,970	730
¹ 442708103382001	6N 4E33ABDC	3,656	LA-86C	3,750	460
442624103353301	6N 4E35ADBC	3,489	LA-86C	3,560	315
442652103354201	6N 4E35BADA	3,488	LA-86C	3,583	495
442623103360401	6N 4E35BDCA	3,498	LA-63A	3,720	300
¹ 442610103345501	6N 4E36ACD	3,504	LA-63A	3,604	400
442610103350001	6N 4E36CBAA	3,475	LA-86C	3,595	460
442611103350301	6N 4E36CBDD	3,494	LA-86C	3,590	310
443536104004801	7N 1E 5DDAB	3,482	LA-87B	3,490	990
443355103574501	7N 1E14CCDD	3,496	--	3,480	460
443355103574502	7N 1E14CCDD2	3,497	LA-63A	3,474	620
443320104030001	7N 1E19BCCC	3,524	LA-63A	3,520	825
443255104020301	7N 1E19DCCC	3,500	LA-63A	3,520	645
443320104004501	7N 1E20AAD	3,457	LA-63A	3,400	281
443320104003501	7N 1E21BBC	3,446	LA-63A	3,379	220
443202103581101	7N 1E25CCBC	3,528	LA-63A	3,620	240
443215103561501	7N 1E25DBDA	3,489	LA-86A	3,510	500
443215103573001	7N 1E26ACD	3,491	LA-87B	3,524	270
443231104004001	7N 1E28BCBC	3,620	LA-87B	3,485	740
443212104001601	7N 1E28CACD	3,684	LA-63A	3,535	1,530
443240104024001	7N 1E30AAAD	3,531	LA-63A	3,480	615
443150104020001	7N 1E30DDDC	3,584	LA-63A	3,510	985
443132103555501	7N 1E36ADDD	3,593	LA-86A	3,630	310
443141103562301	7N 1E36BDAA	3,511	LA-63A	3,655	240
443143103563001	7N 1E36BDAD	3,504	LA-86A	3,675	300

Table 12. Water wells completed in the Minnelusa aquifer and used for interpretation of average potentiometric surface.—Continued

[NGVD 29, National Geodetic Vertical Datum of 1929; --, not applicable]

Station identification number	Local number	Adjusted hydraulic head (feet above NGVD 29)	Observation well used for adjustment	Land-surface altitude (feet above NGVD 29)	Well depth (feet)
443105103563401	7N 1E36CDDC	3,689	LA-86A	3,930	480
443032103562501	7N 1E36CDDD	3,667	LA-63A	3,930	480
¹ 443117103560101	7N 1E36DCBC	3,716	LA-86A	3,890	500
443116103560801	7N 1E36DDBB	3,621	LA-86A	3,820	500
443430103550901	7N 2E18ABBA	3,449	LA-86A	3,390	1,076
443420103551001	7N 2E19CAAA	3,480	--	3,405	700
443323103515501	7N 2E22BCA	3,481	--	3,437	1,218
443230103504101	7N 2E26BCDA	3,540	LA-63A	3,400	825
443117103541301	7N 2E32BAC	3,561	LA-63A	3,570	500
443427103540201	7N 2E32BB	3,556	LA-63A	3,560	540
443115103540001	7N 2E32BDD	3,533	LA-63A	3,590	545
443117103501301	7N 2E35DCBA	3,475	LA-88B	3,545	717
443515103473001	7N 3E 7AABA	3,507	LA-63A	3,360	1,653

¹The hydraulic head for this site displays excessive variability at the local scale and probably does not represent the potentiometric surface; therefore, the hydraulic head was not used in interpretation of the potentiometric surface.

Section B. Dye Tracing Methods

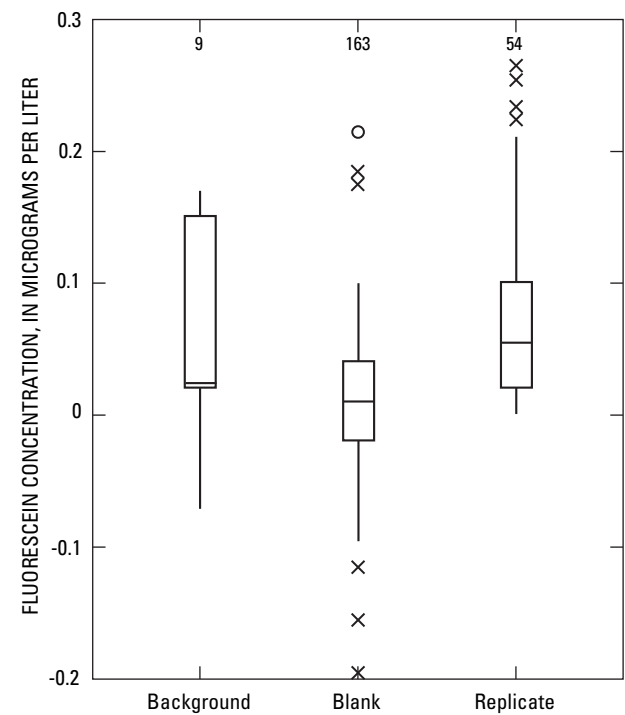
Fluorescent dyes can be detected at very low concentrations in water samples by analysis of glass ampoules containing the sample in a filter fluorometer. This instrument causes the dye in the sample to fluoresce when exposed to light of a particular bandwidth. The light emitted has a specific bandwidth that is characteristic for a particular dye. The fluorometer measures the relative magnitude of this emitted light, which is then calibrated to known standard concentrations of the dye in units of mass per volume. A Turner Designs Model TD-700 Laboratory fluorometer was used for the analyses in this study. Jones (1984) and Wilson and others (1986) provide more detailed technical information regarding operation of filter fluorometers.

Two types of tracer dyes were used in this study, fluorescein and Rhodamine WT. The two dyes emit fluorescence at different ranges of bandwidths with a small overlap; thus, a sample containing a mixture of the two dyes can be analyzed for each dye separately with little interference.

Fluorescein

Fluorescein is a green dye that can be detected at concentrations as low as 0.1 µg/L (Jones, 1984). Background water samples not containing dye often can have fluorometer readings at higher levels than this. Some constituents in natural waters, such as clay and organic substances such as humic acids have fluorescent properties, and instrument noise may be a factor. Boxplots of background concentrations for water samples collected prior to dye injection at selected wells and blank samples indicate that background concentrations generally were less than 0.2 µg/L (fig. 18). Variability in blank samples generally was less than ±0.1 µg/L, with some outliers of about 0.2 µg/L. The differences between sample concentrations and replicate analyses of the same samples were less than 0.1 µg/L for 75 percent of the samples. On the basis of this information, the calculated detectable dye concentrations at first arrival was estimated to be about 0.35 µg/L. An isolated sample at this concentration may not indicate the presence of dye; however, an increasing trend beginning at this concentration was assumed to indicate the presence of fluorescein dye.

Because fluorescein concentrations are sensitive to sunlight exposure, samples were collected in opaque bottles. To test the loss of fluorescence, samples from well MP2 were stored for about 1 year and then reanalyzed and compared with the original analysis (fig. 19). The loss in dye concentration over this period averaged about 20 percent. Dye samples were usually collected over a several week period before analysis, and some loss of dye in sample storage is possible.



EXPLANATION

- 9 Number of samples
- Outlier data value greater than 3 times the interquartile range outside the quartile
- × Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- 75th percentile
- Median
- 25th percentile
- Interquartile range

Replicate is a second analysis of the same sample

Figure 18. Comparison of background, blank, and replicate samples for fluorescein dye analysis.

Rhodamine WT

Rhodamine WT is bright red at high concentrations and can be detected at concentrations as low as 0.01 µg/L with a fluorometer (Jones, 1984). The same considerations regarding background levels and instrument noise as described for fluorescein apply to Rhodamine WT except that the dye is

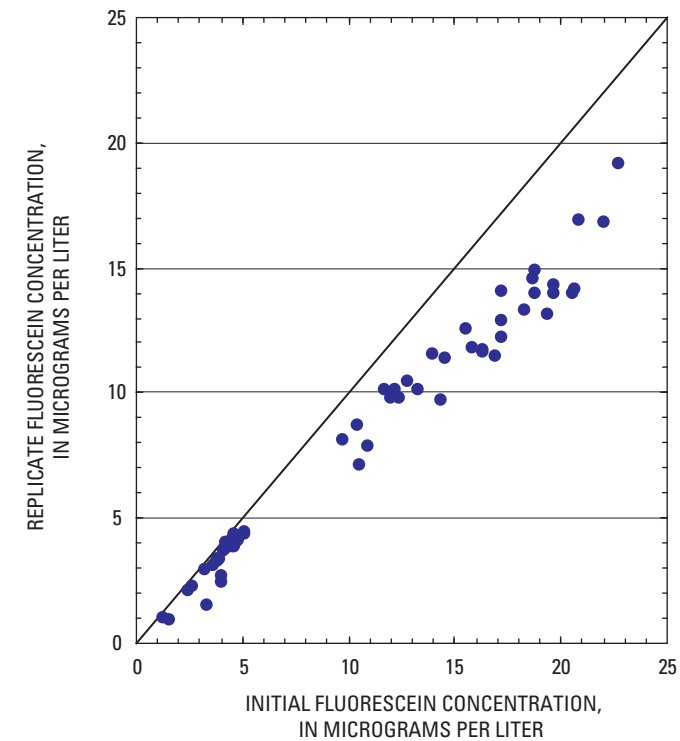
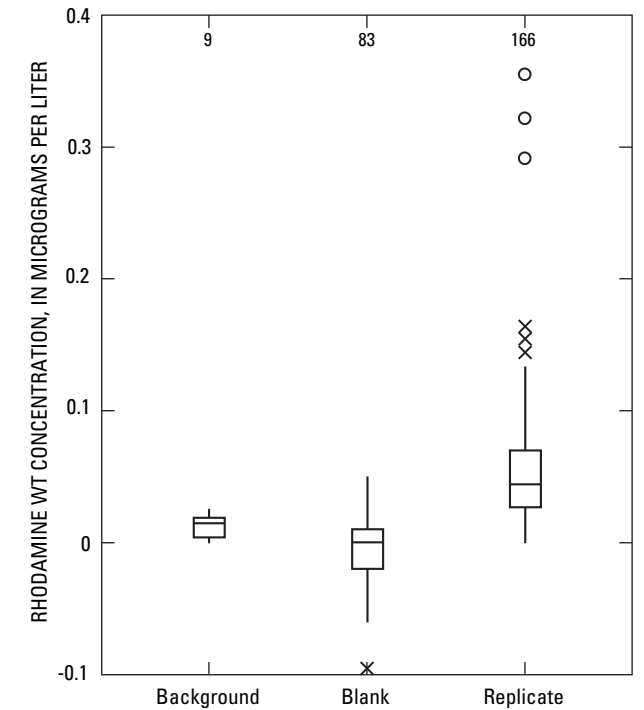


Figure 19. Comparison of initial fluorescein concentrations with concentrations in samples that were stored for about 1 year.

not as sensitive to sunlight exposure. Boxplots of background concentrations for water samples collected prior to dye injection at selected wells indicate that background concentrations generally were less than 0.03 µg/L (fig. 20). Variability in blank samples generally was less than ±0.10 µg/L. The differences between sample concentrations and replicate analyses of the same samples were less than 0.08 µg/L for 75 percent of the samples. On the basis of this information, the calculated detectable dye concentrations at first arrival was estimated to be about 0.10 µg/L. An isolated sample greater than this concentration may not indicate the presence of dye; however, an increasing trend beginning at this concentration was assumed to indicate the arrival of Rhodamine WT dye. Some isolated samples containing suspended sediment had concentrations greater than 0.10 µg/L.

In the analysis of samples with a filter fluorometer, there is a small area of overlap in the excitation wavelength between fluorescein and Rhodamine WT around 550 nanometers (Jones, 1984). Samples with standard concentrations of fluorescein were analyzed using the Rhodamine filters to quantify this potential overlap in wavelengths (table 13). The analysis of several different concentrations of fluorescein standards indicated that the presence of fluorescein dye would not interfere with the analysis of samples for Rhodamine WT.



EXPLANATION

- 9 Number of samples
- Outlier data value greater than 3 times the interquartile range outside the quartile
- × Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- 75th percentile
- Median
- 25th percentile
- Interquartile range

Replicate is a second analysis of the same sample

Figure 20. Comparison of background, blank, and replicate samples for Rhodamine WT dye analysis.

Table 13. Analysis of fluorescein standards for concentrations of Rhodamine WT.

[µg/L, micrograms per liter]

Fluorescein concentration (µg/L)	Apparent Rhodamine WT concentration (µg/L)
4	0.037
20	.074
100	.094
190	.023

Section C. Chlorofluorocarbon Age-Dating Methods and Background

Chlorofluorocarbons

Chlorofluorocarbons (CFCs) are anthropogenic tracers that are useful for estimating ground-water age (Busenberg and Plummer, 1992; Cook and others, 1996; Oster and others, 1996; Szabo and others, 1996; Cook and Solomon, 1997; Plummer and Busenberg, 2005). These compounds have been used in a variety of industrial and refrigerant applications and are present in the atmosphere where they become assimilated into rain and snow as dissolved gases and infiltrate to ground water. Because atmospheric concentrations have been changing over time, the residence time or age of ground water often can be estimated by comparing concentrations in ground-water samples to historical atmospheric concentrations. Three species of CFCs that are used as tracers include CFC-11, CFC-12, and CFC-113. The atmospheric concentrations of these tracers (fig. 21) for Niwot Ridge, Colorado, increased between the 1940s and 1990s and recently (2002) began declining slightly (Plummer and Busenberg, 2005). Production and release of CFCs to the atmosphere rose rapidly during the 1970s and 1980s (Alternative Fluorocarbons Environmental Acceptability Study, written commun., 2002).

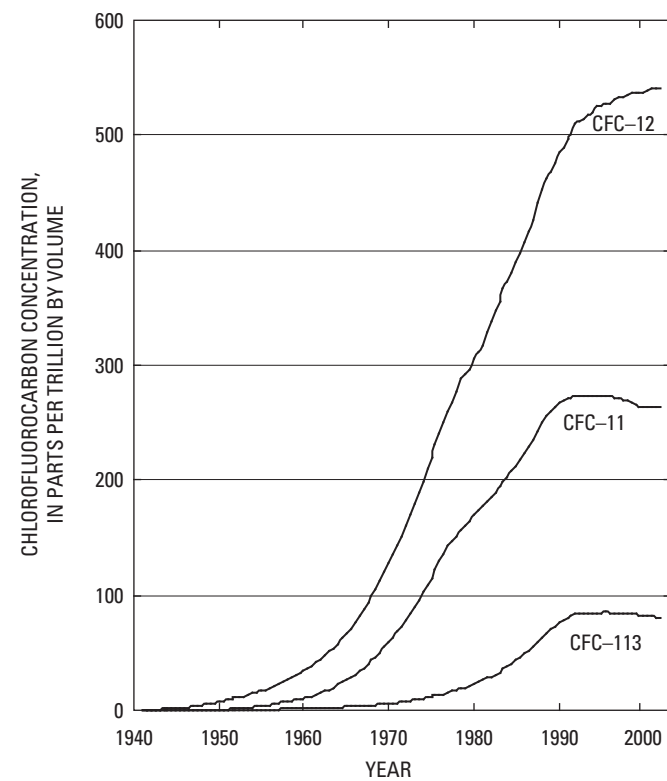


Figure 21. Atmospheric concentrations of chlorofluorocarbons CFC-11, CFC-12, and CFC-113 (Plummer and Busenberg, 2005).

In water that is exposed to the atmosphere, CFC concentrations become equilibrated with atmospheric concentrations; however, in ground water not in contact with the open atmosphere, CFC concentrations generally remain stable at the concentration of the recharge water. Shallow ground water remains closed to gas exchange because molecular diffusion coefficients of gases are about five orders of magnitude smaller in water than in air (Plummer and Busenberg, 2005). The gas concentration in water can be modified by gas exchange between the water at the water table and the unsaturated-zone atmosphere. Although the exchange can affect the concentration in the top few centimeters of this zone, the gases are confined below about 1 meter and do not exchange with the unsaturated zone atmosphere (Busenberg and others, 2001). For most dating applications, CFC confinement is thought to occur rapidly some time between the seasonal high and low water table (Cook and Solomon, 1997).

In karstic aquifers, infiltrating rainwater and snowmelt can be stored above the confined part of the aquifer for years or decades in features such as perched caves or the epikarstic zone (Even and others, 1986). The water table may be in contact with the current atmosphere as caves and other openings breathe in and out due to changes in barometric pressure. As water levels change in these cave-like openings, some of the stored water could be re-exposed to the atmosphere during mixing as perched water spills and cascades downgradient. In the study area, water table conditions can exist in wells that are greater than 1,000 ft deep. Some resetting of the CFC clock may occur, and estimated ages may indicate a larger proportion of younger water than that indicated by tritium dating.

Henry's Laws of solubilities of CFCs in water are known, and equilibration with atmospheric concentrations can be calculated with estimates of pressure and temperature. CFC-11, CFC-12, and CFC-113 all can be degraded under anaerobic conditions. Ground-water samples were analyzed for selected dissolved gases to assist with interpretation of CFC data.

Dissolved Gas Data

Dissolved gases including nitrogen, argon, oxygen, carbon dioxide, and methane (table 14) are useful in calculating recharge temperature and excess air, and in assessing potential degradation of CFCs. The ratio of nitrogen to argon can be used to calculate the temperature of the recharge water on the basis of the large differences in the solubility of nitrogen and argon at different temperatures (Weiss, 1970). Recharge temperature affects the solubility of CFCs and is used in determining the atmospheric mixing ratio in parts per trillion by volume (pptv). Recharge temperatures for 10 wells and springs

ranged from 3.4 to 7.7°C, with an average of 6.2°C. A 1°C difference in the recharge temperature results in about a 5 percent difference in the calculated CFC mixing ratio; thus, calculating recharge temperatures from dissolved gases improves the accuracy of calculated CFC mixing ratios.

Excess air can be trapped in recharge water and dissolved under increased hydrostatic pressure resulting in increases in CFCs (Plummer and Busenberg, 2005). Excess air can be determined from nitrogen and argon ratios and generally is less than 6 cubic centimeters per liter (cm³/L). Calculated

excess air for 10 sites ranged from 0.4 to 6.4 cm³/L, with an average of 2.8 cm³/L. When excess air is small as in this study, the effect on CFCs can be ignored in most ground-water cases (Busenberg and Plummer, 2005). Potential degradation of CFCs resulting from microbial processes and reducing conditions is indicated by the concentrations of carbon dioxide, dissolved oxygen, and methane. Dissolved oxygen was present at all sites, and methane concentrations were low, both indicating little potential for degradation of CFCs from reducing conditions for the samples collected for this study.

Table 14. Dissolved-gas data for selected wells and springs in the study area.

[NGVD 29, National Geodetic Vertical Datum of 1929; deg C, degrees Celsius, cm³/L, cubic centimeters per liter]

Station Number	Other identifier	Sample date	Dissolved concentration (milligrams per liter)					Estimated recharge altitude (feet above NGVD 29)	Recharge temperature (deg C)	Excess air (cm ³ /L)
			Nitrogen	Argon	Oxygen	Carbon dioxide	Methane			
442752103501901	JEF	10-31-2001	22.043	0.7340	7.33	10.94	0.0000	5,000	5.7	5.1
442752103501901	JEF	10-31-2001	22.042	.7315	5.94	11.98	.0000	5,000	6.0	5.2
442815103481701	VIG	08-24-2005	18.671	.6774	7.52	5.63	.0000	5,000	3.8	1.3
442815103481701	VIG	08-24-2005	18.864	.6847	7.32	5.90	.0000	5,000	3.4	1.3
442842103505501	NEV	10-30-2001	23.684	.7732	8.00	10.10	.0000	5,000	3.7	6.4
442842103505501	NEV	10-30-2001	23.490	.7677	7.25	10.69	.0000	5,000	4.0	6.3
442918103523001	KYT	10-30-2001	20.462	.6841	3.04	23.24	.0000	5,000	7.4	4.6
442918103523001	KYT	10-30-2001	20.546	.6867	3.42	22.61	.0000	5,000	7.3	4.6
442919103511601	DIC	10-19-2001	20.663	.7052	6.25	13.41	.0000	5,000	5.4	4.0
442919103511601	DIC	10-19-2001	20.979	.7127	6.38	13.56	.0000	5,000	5.2	4.2
443005103553801	SAL	10-22-2001	17.852	.6439	3.93	16.05	.0000	5,000	6.9	1.7
443005103553801	SAL	10-22-2001	17.881	.6461	3.84	16.35	.0000	5,000	6.7	1.6
443017103553601	MIT	11-01-2001	18.091	.6511	3.92	16.40	.0000	5,000	6.6	1.8
443017103553601	MIT	11-01-2001	18.287	.6555	4.04	16.41	.0000	5,000	6.4	2.0
443330104003401	McNEN	11-05-2001	17.582	.6354	5.46	18.58	.0000	5,000	7.3	1.6
443330104003401	McNEN	11-05-2001	17.518	.6324	5.68	18.55	.0000	5,000	7.6	1.6
443335104010001	MIR	11-06-2001	16.990	.6360	6.54	6.89	.0010	4,000	7.6	.4
443335104010001	MIR	11-06-2001	17.078	.6387	7.75	6.45	.0010	4,000	7.4	.5
443356103593701	COX	11-05-2001	17.360	.6297	3.26	22.59	.0057	5,000	7.6	1.4
443356103593701	COX	11-05-2001	17.213	.6257	3.19	22.62	.0043	5,000	7.7	1.4

Manuscript approved for publication, January 2, 2007.

Prepared by the Helena Publishing Service Center.

For more information concerning the research in this report, contact:

U.S. Geological Survey
Director, South Dakota Water Science Center
1608 Mountain View Road
Rapid City, SD 57702
<http://sd.water.usgs.gov/>



Printed on recycled paper