Standards and Criteria

Most water-quality standards for surface water are determined by the applicable beneficial-use criteria (table 9) established for individual stream reaches. All streams in South Dakota are designated for the beneficial uses of irrigation and of wildlife propagation and stock watering. Additional beneficial uses are assigned to stream segments as applicable. Designated beneficial uses for specific stream segments are indicated by South Dakota Department of Environment and Natural Resources (2001a). Aquatic-life criteria are estimates of the highest constituent concentrations that aquatic life can be exposed to without adverse effects. The chronic criteria are based on extended exposures, and acute criteria are based on very short-term exposures. The aquatic criteria for several trace elements vary with stream hardness, as shown in figure 55. Drinking-water standards apply only to finished waters that are used for public consumption. These standards do provide another useful basis for comparison, however, and were presented previously in table 4.

Common-ion Chemistry

Common-ion chemistry of surface water in the study area is highly influenced by geology. Within this section, distinctive water-quality characteristics are described for the hydrogeologic settings (limestone headwater, crystalline core, artesian spring, and exterior settings) that were discussed previously (fig. 23). The loss zone setting is not characterized because the primary hydrologic influence is on streamflow, not water quality. Site information for sampling sites representative of the hydrogeologic settings was presented previously in table 5.

Specific conductance can provide an excellent indication of dissolved solids concentrations in surface water (fig. 56). Results of regression analyses (dissolved solids versus specific conductance) for samples available for sites representative of hydrogeologic settings are presented in table 10. Correlations between dissolved solids and specific conductance are strong for all of the hydrogeologic settings except the limestone headwater setting, for which variability in dissolved solids concentrations is small. Table 10 also includes regression information for all available samples for surface-water sites within the study area considered by Williamson and Carter (2001), which include numerous sites in addition to those that are representative of the hydrogeologic settings. The equation provided for all samples generally should provide reasonable estimates of dissolved solids concentrations (based on specific conductance) for surface water within the study area, regardless of hydrogeologic conditions. This equation would be most appropriate for locations where water quality is influenced by multiple hydrogeologic settings, which is a common circumstance within the study area.

Relations between specific conductance and streamflow for the hydrogeologic settings are shown in figure 57. Because of the large number of sites representative of the crystalline core setting, only five sites are shown for this setting. Measurements of specific conductance are abundant because measurements typically are obtained at USGS streamflow-gaging stations when streamflow is measured.

Sites representative of the crystalline core and exterior settings have large variability in streamflow and exhibit generally inverse relations between specific conductance and streamflow (fig. 57). Specific conductance values (and dissolved solids concentrations) generally decrease with increasing streamflow, primarily because of dilution by direct runoff.

Streamflow variability generally is small for the limestone headwater and artesian spring settings (fig. 57) because of dominance by ground-water discharge. Specific conductance values are nearly identical for all of the limestone headwater sites, where the primary geologic influences are outcrops of the Madison Limestone or outcrops of the Minnelusa Formation in areas where anhydrite beds have been removed by dissolution over geologic time.

Specific conductance characteristics are fairly distinct for each of the artesian spring sites (fig. 57). The lowest specific conductance values generally are for Cleghorn Springs, which is located within an outcrop of the Minnelusa Formation (fig. 35). The other artesian spring sites reflect larger influence from anhydrite beds within the Minnelusa Formation or possibly from dissolution of sulfate within other overlying geologic units. Minor influences (reduced specific conductance values) from occasional runoff events are apparent for several sites. Table 9. Surface-water-quality standards for selected physical properties and constituents

[All constituents in milligrams per liter unless otherwise noted. µS/cm, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; ⁰F, degrees Fahrenheit; ⁰C, degrees Celsius; ≥, greater than or equal to; --, no data available]

					Beneficial-u	se criteria ¹					Aquatic-life
Property or constituent	Domestic water supply (mean/daily maximum)	Coldwater permanent fisheries	Coldwater marginal fisheries	Warmwater permanent fisheries	Warmwater semi- permanent fisheries	Warmwater marginal fisheries	Immersion waters	Limited contact waters	Wildlife propagation and stock- watering waters	Irrigation waters	criteria for fisheries ¹ (acute/ chronic) (µg/L)
Specific conductance (μS/cm)	:	1	1	:	:	:	1	:	² 4,000/7,000	² 2,500/4,375	1
pH range (standard units)	6.5-9.0	6.6-8.6	6.5-8.8	6.5-9	6.5-9	6.5-9	ł	ł	6.0-9.5	ł	ł
Temperature ^o F/ ^o C (maximum)	ł	65/18.3	75/24	80/27	90/32	90/32	ł	1	ł	ł	ł
Dissolved oxygen (minimum)	ł	≥6.0 ≥7 during spawning	≥5.0	≥5.0	≥5.0	≥4.0	≥5.0	≥5.0	ł	ł	ł
Total dissolved solids	$^{2}1,000/1,750$	1	1	ł	ł	ł	1	ł	² 2,500/4,375	1	-
Total suspended solids	1	² 30/53	² 90/158	² 90/158	² 90/158	² 150/263	1	:	1	1	ł
Sodium-adsorption ratio	1	1	1	1	ł	ł	1	1	1	10	1
Chloride	² 250/438	² 100/175	1	1	ł	1	1	1	1	1	1
Fluoride	4.0	ł	1	ł	1	1	ł	ł	1	ł	ł
Sulfate	² 500/875	1	;	;	1	ł	;	1	1	1	1
Nitrate (as N)	10	1	1	I	ł	ł	ł	ł	$^{2}50/88$	ł	ł
Un-ionized ammonia (as N)	ł	0.02	0.02	0.04	0.04	0.05	I	ł	1	ł	ł
Cyanide (free)	ł	1	ł	ł	ł	ł	I	ł	ł	ł	22/5.2
Dissolved arsenic	ł	1	ł	ł	ł	ł	ł	ł	ł	1	360/190
Dissolved barium	1.0	ł	ł	ł	ł	ł	ł	ł	ł	ł	1
Dissolved cadmium	ł	ł	ł	ł	ł	ł	ł	ł	ł	1	$^{3}3.7/^{3}1.0$
Dissolved copper	ł	ł	ł	ł	ł	ł	ł	ł	ł	ł	$^{3}17/^{3}11$
Dissolved lead	ł	ł	ł	ł	ł	ł	ł	ł	ł	ł	³ 65/ ³ 2.5
Dissolved mercury	ł	1	ł	ł	ł	ł	ł	ł	ł	ł	$2.1/^4 0.012$
Dissolved selenium	ł	ł	ł	ł	ł	ł	ł	ł	ł	1	20/5
Dissolved zinc	-	1	1	ł	1	1		1	1	ł	$^{3}110/^{3}100$
¹ South Dakota Depart ² 30-day average/daily ³ Hardness-dependent	ment of Environm maximum. criteria; value give	hent and Natural H en is an example	Resources (2001 based on hardne	a). ss of 100 millig	rams per liter a	s CaCO ₃ .					
⁻ Chronic criteria base	d on total recovera	able concentration									



Figure 55. Relations between hardness and freshwater aquatic-life standards for acute and chronic toxicity of selected trace elements (South Dakota Department of Environment and Natural Resources, 1998).



Figure 56. Relations between dissolved solids and specific conductance by hydrogeologic settings (from Williamson and Carter, 2001).

 Table 10.
 Summary of regression information (dissolved solids versus specific conductance), by hydrogeologic setting

Hydrogeologic setting	Equation of line	r ²	Number of samples
Headwater spring	S = 0.21K + 158.16	0.2437	261
Crystalline core	S = 0.55K + 15.83	.8914	136
Artesian spring	S = 0.93K - 194.22	.9614	13
Exterior	S = 0.85K - 249.50	.9676	174
All^1	S = 0.86K - 131.14	.9692	¹ 2,355

[S = dissolved solids, in milligrams per liter; K = specific conductance, in microsiemens per centimeter]

¹Includes numerous surface-water samples in addition to those available for sites representative of hydrogeologic settings.





Trilinear diagrams showing ionic proportions (by hydrogeologic setting) for available samples for representative sites are shown in figure 58. Median concentrations for each setting are shown in figure 59. Proportions of common ions are similar for some sites representative of the limestone headwater and crystalline core settings (fig. 58); however, many of the crystalline core sites have smaller proportions of bicarbonate and larger proportions of chloride than limestone headwater sites. The limestone headwater and crystalline core settings have the lowest median concentrations of common ions (fig. 59), which is consistent with low concentrations of dissolved solids, relative to the artesian spring and exterior settings (fig. 56).



Figure 58. Trilinear diagrams showing proportional concentrations of common ions by hydrogeologic setting (from Williamson and Carter, 2001).



Figure 59. Stiff diagrams (Stiff, 1951) showing median concentrations by hydrogeologic setting (from Williamson and Carter, 2001).

Concentrations of dissolved solids for most sites representative of the artesian spring setting are higher than for the limestone headwater and crystalline core sites (fig. 56). The representative artesian spring sites generally have calcium sulfate water types (figs. 58 and 59), resulting from increased sulfate concentrations. Most water discharged by artesian springs probably originates primarily from the Madison and/or Minnelusa aquifers (Naus and others, 2001); however, high sulfate concentrations probably result primarily from rock/water interactions in the Minnelusa Formation. Other potential sulfate sources may be in contact with shale confining units such as the Spearfish Formation. Several artesian springs with low sulfate concentrations are located upgradient from the anhydrite transition zone in the Minnelusa aquifer (fig. 35).

Exterior sites generally have sodium calcium magnesium sulfate type waters (figs. 58 and 59), with high concentrations of dissolved solids (fig. 56), relative to other sites. Although no stream reaches within the exterior setting are classified for domestic water supply, most samples for exterior sites have dissolved solids concentrations that exceed the 30-day average and maximum criteria of 1,000 and 1,750 mg/L,

respectively (table 9). The criteria for wildlife propagation and stock watering also are exceeded for many samples.

Median concentrations of sodium, chloride, magnesium, and sulfate are much higher for the exterior sites than for sites representative of the other settings (fig. 59). Specific conductance values for many of the exterior samples (fig. 56) exceed the criteria for irrigation waters (table 10); however, no samples for this setting exceed the criterion for sodium-adsorption ratio (Williamson and Carter, 2001). The highest chloride concentrations occur in the Cheyenne River at Edgemont, where numerous samples exceed the SMCL of 250 mg/L. Figure 60 presents a spatial distribution of median sulfate concentrations for the study area, including numerous sites in addition to those that are representative of the hydrogeologic settings. The highest sulfate concentrations are for sites within the exterior hydrogeologic setting, which results from contact with outcrops of Cretaceous shales within this area (figs. 9 and 14). Several streams with large influence from artesian springs also have relatively high sulfate concentrations.



Figure 60. Spatial distribution of median sulfate concentrations in surface water (from Williamson and Carter, 2001).

Anthropogenic Effects

Various human activities, including agriculture, mining, and urban/suburban development, have potential to influence the water quality of streams within the study area. In many cases, anthropogenic influences on water quality cannot necessarily be distinguished from naturally occurring influences. Water-quality sampling for the Black Hills Hydrology Study was performed primarily for the purpose of identifying baseline waterquality conditions; extensive investigations to evaluate effects of anthropogenic influences were not performed as part of the study. Much of the information summarized in this section was obtained from results of sitespecific studies by previous investigators. A detailed summary of previous investigations is provided in Williamson and Carter (2001).

Extensive studies of potential effects of irrigation drainage were performed under the National Irrigation Water Quality Program (NIWQP) during the late 1980's by Greene and others (1990) for the Angostura Reclamation Unit and by Roddy and others (1991) for the Belle Fourche Reclamation Project. Concentrations of pesticides in water, bottom sediment, and biota were less than laboratory reporting limits for most samples collected by these investigators. Results of follow-up sampling efforts were presented by Sando and others (2001), who concluded that for both irrigation projects, available data were insufficient to confidently quantify potential increases in dissolved solids loading resulting from irrigation operations.

Selenium, which can be concentrated by irrigation operations, was a special concern of NIWQP because of toxicity and prevalence in irrigation areas in the western United States. Selenium is abundant in the Cretaceous shales surrounding the Black Hills area (figs. 9 and 14), which is reflected in the maximum selenium concentrations measured at selected sites within the study area (fig. 61). Selenium concentrations below the laboratory reporting limit of $1 \mu g/L$ have been reported for numerous additional sites (not shown in fig. 61), most of which are located within the limestone headwater, crystalline core, or artesian spring settings. Sando and others (2001) concluded that selenium routinely occurs in concentrations that could be problematic, both upstream and downstream from both irrigation projects. Increased selenium loading resulting from irrigation operations was not discernible for the Angostura Reclamation Unit; however, increased loading probably occurs from return flows in

Horse Creek, within the Belle Fourche Reclamation Project.

Effects of mining activity on water quality can be difficult to quantify because natural influences in mineralized areas may have similar effects on water quality. Mining activities generally have been most extensive in the northern Black Hills, primarily in the vicinity of Tertiary intrusive units (fig. 14) where the largest deposits of gold ores tend to be located.

One potential effect of mining is acid-mine drainage, which can result from weathering and oxidation of sulfide minerals that occur in some locations. Torve (1991) examined pH conditions and metals concentrations near abandoned mines along Deadwood Creek and False Bottom Creek. Measured pH values for sites (fig. 62) upstream, immediately downstream, and farther downstream of the mines are presented in figure 63. The pH values are depressed in the immediate vicinity of the mines, but increase farther downstream as a result of the buffering effect of carbonate minerals. Similar areas of low pH also exist in naturally occurring bog-iron areas, which can be found in various locations in the Black Hills area (Luza, 1969; Rice, 1970).

Low pH conditions can cause increased solubility of various metals, which can be abundant in mineralized areas where mining has occurred. Torve (1991) documented elevated concentrations of dissolved cadmium, copper, and zinc that approached or exceeded aquatic-life criteria near mines along Deadwood Creek and False Bottom Creek. Decreased concentrations of dissolved metals were documented farther downstream, where pH levels increased. Approximately 900 abandoned or inactive mines exist throughout the Black Hills area (South Dakota Department of Environment and Natural Resources, 2001b); similar pH and trace-metal conditions occur at a limited number of these locations (Rahn and others, 1996).

Acid-mine drainage has been a problem at the Gilt Edge mine (a large, open-pit, heap-leach-recovery gold mine that was operated during 1986-98), which was listed as a Superfund site by USEPA in 2000 (South Dakota Department of Environment and Natural Resources, 2001b). The mine area is drained by Strawberry Creek, which is a tributary to Bear Butte Creek. Copper concentrations have frequently exceeded aquatic standards in Bear Butte Creek (fig. 64). In addition, dissolved solids concentrations have increased since 1994 in Bear Butte Creek downstream of the confluence with Strawberry Creek, primarily from increases in sodium and sulfate concentrations (Williamson and Carter, 2001).



Figure 61. Spatial distribution of maximum selenium concentrations in surface water (from Williamson and Carter, 2001).





Figure 62. Locations of selected water-quality sampling sites used for analysis of anthropogenic effects in (A) Lawrence County and (B) Rapid Creek Basin.



Figure 63. Downstream progression of pH for selected streams influenced by acid-mine drainage (from Williamson and Carter, 2001).



Figure 64. Comparison of dissolved copper concentrations to hardness-dependent chronic and acute aquatic-life criteria for Bear Butte Creek near Deadwood (06437020) (from Williamson and Carter, 2001).

Acid-mine drainage from the Richmond Hill Mine resulted in depressed pH levels in headwater reaches of Squaw Creek (Durkin, 1996). This condition resulted in a need for substantial reclamation efforts in closing the mine, which consisted of capping large deposits of sulfide minerals to prevent exposure to air and water.

The spatial distribution of maximum arsenic concentrations for the study area is shown in figure 65. None of the samples have exceeded the aquatic-life criteria (table 9); however, concentrations exceeding the revised MCL of 10 μ g/L (table 4) have been measured at seven sites. One concentration exceeding 50 µg/L has been measured. Concentrations below the laboratory reporting limit of $1 \,\mu g/L$ have been reported for numerous additional sites (not shown in fig. 65). Arsenic commonly is associated with gold ores, with most of the elevated concentrations occurring within the crystalline core setting in locations where mining activities have occurred. Arsenic also is relatively abundant in the Cretaceous shales surrounding the Black Hills area, with concentrations above 5 µg/L measured at upstream locations on the Chevenne and Belle Fourche Rivers.

Potential effects of mining operations on arsenic concentrations generally cannot be quantified because background samples (prior to mining activities) are not available. Elevated arsenic concentrations in Whitewood Creek and downstream reaches of the Belle Fourche River have been attributed to long-term discharge of mine tailings, which resulted in designation of an 18-mi reach as a Superfund site by USEPA in 1983 (Goddard, 1989). Other constituents of concern along Whitewood Creek include cadmium, copper, cyanide, iron, manganese, mercury, and silver. The largest concentrations of dissolved arsenic typically occur during storm-flow recessions and result from seepage from tailings deposits in the adjacent flood plain. Concentrations of total arsenic exceeding 100 µg/L are common during storm flows when sediments are mobilized.

A variety of factors influencing the solubility of arsenic have been identified by previous investigators. Arsenic is most soluble within a pH range of 8.1 to 8.6; however, adsorption/desorption processes also can affect the mobility of arsenic (Fuller and Davis, 1989; Fuller and others, 1993). The abundance of calcite and ferrihydrite in bed sediments was identified by Williamson and Hayes (2000) as important factors in controlling adsorption/desorption of arsenic. Solubility of arsenic is increased by abundance of calcite because of associated increases in pH. Solubility of arsenic is reduced by abundance of ferrihydrite, which provides iron surfaces for adsorption of arsenic. The highest concentrations of dissolved arsenic typically occur in streams with limited quantities of ferrihydrite in bed sediments. Photosynthesis and respiration by aquatic vegetation within a stream can cause diurnal changes in pH, resulting in fluctuations in arsenic concentrations (Fuller and Davis, 1989).

Arsenic concentrations in Annie Creek that consistently approached the former MCL of 50 μ g/L resulted in USEPA designation of a 5-acre site on the National Priorities List (Driscoll and Hayes, 1995). A failed tailings impoundment from an abandoned mine had resulted in large deposits of arsenic-rich tailings along the stream channel. Natural geology and the Annie Creek Mine, which occupies much of the Annie Creek drainage basin, also may contribute to elevated arsenic concentrations in Annie Creek. An important influence is small concentrations of ferrihydrite in bed sediments (Williamson and Hayes, 2000), which limits adsorption/coprecipitation on ferrihydrite and contributes to high concentrations of dissolved arsenic.

Elevated concentrations of nitrite plus nitrate in Annie Creek, with two samples exceeding the MCL of 10 μ g/L in 1995 and 1996, were noted by Williamson and Carter (2001). The concentrations probably result from the breakdown of blasting agents (ammonium nitrate mixed with diesel fuel) and cyanide, which is used in the heap-leach extraction process. Two denitrification facilities were installed within the Annie Creek Basin in 1997 and have been effective in reducing nitrite plus nitrate concentrations (South Dakota Department of Environment and Natural Resources, 1998).

Elevated nitrite plus nitrate concentrations also can result from various other influences including fertilizers, animal and human waste, and natural processes that occur within stream riparian systems. Nitrite plus nitrate concentrations for sites representative of hydrogeologic settings are shown in figure 66. In this figure, Annie Creek is separated from other crystalline core sites because of the substantial influence from mining operations, as previously discussed. Concentrations for most sites representative of individual hydrogeologic settings are below 1 μ g/L, which probably is indicative of conditions with little human influence. Numerous samples for sites that are not representative of individual hydrogeologic settings are included in an "other sites" category. Most of the elevated concentrations for this category were collected prior to 1980 from Horse Creek near Vale (Williamson and Carter, 2001), which is influenced by irrigation return flows.



Figure 65. Spatial distribution of maximum arsenic concentrations in surface water (modified from Williamson and Carter, 2001).



Figure 66. Boxplots of concentrations of dissolved nitrite plus nitrate by hydrogeologic setting, with Annie Creek separated from other crystalline core sites.

Nitrite plus nitrate concentrations for selected sites within the Rapid Creek Basin (fig. 62) are presented in figure 67. Concentrations for the farthest site upstream (06409000, Castle Creek above Deerfield) generally are slightly higher than for the next two sites downstream. One possible nitrogen source, based on land-use activities, is cattle grazing upstream from the farthest site upstream. Rapid Creek at Rapid City (06414000) shows minor influences of nitrite plus nitrate from various possible urban sources. Concentrations at Rapid Creek near Farmingdale (06421500) increase markedly, reflecting various possible influences including non-point urban/suburban sources, effluent discharge from the Rapid City municipal wastewater treatment plant, and various possible influences from agricultural activities.

Numerous constituents in addition to nitrite plus nitrate can influence water quality in urban environments. Williamson and others (1996) documented increased concentrations of various trace metals contributed to Rapid Creek by the Rapid City municipal wastewater treatment plant. Goddard and others (1989) summarized data collected during a USEPA National Urban Runoff Program study in the Rapid City area. In an interpretation of this data set, Harms and others (1983) documented increases in numerous constituents in Rapid Creek associated with urban runoff.

Additional Factors Relative to In-Stream Standards

Beneficial uses for various stream reaches can be influenced by several other factors in addition to those that have been previously discussed. Detailed discussions of low pH conditions associated with acid-mine drainage were presented previously. Low pH values below the desirable range (table 9) also can occur naturally, especially in areas with bog-iron deposits (Luza, 1969). Occurrences generally are in limited stream reaches within the crystalline core setting. Occasional occurrences of pH values exceeding the desirable range have been noted in the limestone headwater and crystalline core settings (Williamson and Carter, 2001).

Beneficial uses for some stream reaches also can be limited by temperature and dissolved oxygen concentrations. In-stream temperatures exceeding beneficial-use criteria for fisheries (table 9) occasionally occur, especially during low-flow conditions. Concentrations of dissolved oxygen below desirable ranges also can occur occasionally, especially during low-flow conditions and when elevated temperatures reduce oxygen solubility. Low concentrations of dissolved oxygen associated with urban runoff also have been documented (Harms and others, 1983).

Concentrations of suspended solids exceeding beneficial-use criteria are relatively common in the Black Hills area. The largest (and most frequent) exceedances typically occur in the exterior setting, where fine-grained particulates associated with clay soils are easily mobilized during high-flow conditions. High concentrations of suspended solids also typically occur during urban runoff events (Harms and others, 1983).

HYDROLOGIC BUDGETS

The quantification of various hydrologic budget components is important for managing and understanding the water resources in the Black Hills area. This section contains summaries of hydrologic budgets that were developed by previous investigators for ground water, surface water, and the combined groundwater/surface-water system. A detailed hydrologic budget for the Madison and Minnelusa aquifers in the Black Hills of South Dakota and Wyoming for 1987-96 was presented by Carter, Driscoll, Hamade, and Jarrell (2001). Detailed hydrologic data sets were available for this period, during which changes in ground-water storage were considered negligible. Basic hydrologic budgets for the Black Hills of South Dakota for 1950-98 were presented by Driscoll and Carter (2001) for: (1) the Madison and Minnelusa aquifers; (2) other bedrock aquifers; (3) surface water; and (4) the combined ground-water/surface-water system. This timeframe includes an extended period of particularly dry climatic conditions that occurred during the 1950's (fig. 8) and the particularly wet conditions that occurred during the middle to late 1990's.

All hydrologic budgets were developed from the following basic continuity equation, which states that for any designated volume:

$$\Sigma Inflows - \Sigma Outflows = \Delta Storage \tag{2}$$

where:

 Σ *Inflows* = sum of inflows; Σ *Outflows* = sum of outflows; and

 $\Delta Storage = change in storage.$

Thus, a positive $\Delta Storage$ results when inflows exceed outflows.



Protection Agency, 1994a)

Figure 67. Boxplots of concentrations of dissolved nitrite plus nitrate within the Rapid Creek Basin.