Minnelusa Aquifer

Water from the Minnelusa aquifer generally is low in radionuclide concentrations, but may be high in some areas. In the Minnelusa aquifer, uranium concentrations are highest in the southern and eastern Black Hills. The highest gross beta concentrations (as cesium-137 and strontium/yttrium-90) are in the southern Black Hills. The highest thorium concentrations are in the eastern and southern Black Hills, whereas the highest tritium concentrations are in the eastern and northern Black Hills.

Of the 11 samples analyzed for alpha radioactivity as thorium-230, three samples exceed the MCL of 15 pCi/L for gross alpha; all of the samples that exceed the MCL were from the southern Black Hills. One of 17 samples exceeds the MCL for the combined radium-226 and radium-228; this sample was from a well located in the eastern Black Hills.

Inyan Kara Aquifer

Uranium was discovered in the Black Hills area in Fall River County in 1951 in the basal 100 to 150 feet of the Lakota Formation of the Inyan Kara Group (Page and Redden, 1952). Following the first discovery, numerous other uranium deposits were discovered in the southern Black Hills. Uranium may be introduced into the Inyan Kara Group through the artesian recharge of water from the Minnelusa aquifer (Gott and others, 1974). As water in the Inyan Kara aquifer flows downgradient, geochemical conditions favor the precipitation of uranium (Gott and others, 1974). Therefore, it is not surprising that some water from the Inyan Kara aquifer, especially in the southern Black Hills, contains relatively high concentrations of radionuclides.

Concentrations of several radionuclides vary with well depth (fig. 26). Gross alpha as U-natural in picocuries per liter, gross beta as cesium-137, and radium-226 generally increase with increasing well depth associated with increasing distance from the outcrop. Other concentrations vary with geographic location. The highest uranium and thorium concentrations are from wells located in the southern Black Hills.

Almost 18 percent of the samples (6 of 34 samples) collected from the Inyan Kara aquifer exceed the MCL for combined radium-226 and radium-228; all but one of these samples are from wells in the southern Black Hills. About 4 percent of the samples (3 of 77 samples) exceed the MCL for uranium; all these samples are from wells located in the southern Black Hills.

Minor Aquifers

Excluding analyses from alluvial aquifers, the MCL of 30 µg/L for uranium is the only drinking-water standard that is exceeded by samples from other aquifers in the study area. However, few analyses exist for gross alpha, radium, and radon for the minor aquifers in the study area. In addition to the uranium concentrations in the alluvial aquifers, 1 of 9 samples from the Spearfish aquifer, 2 of 6 samples from the Morrison aquifer, 5 of 28 samples from the Pierre aquifer, and 1 of 10 samples from the Graneros aquifer exceed the MCL for uranium.

Samples from alluvial aquifers may be high in uranium concentrations, especially in the southern Black Hills. About 17 percent of the samples (5 of 29 samples) exceed the MCL for uranium, and all were collected from wells located in the southern Black Hills. In addition to uranium, thorium concentrations were highest in the southern Black Hills. One of four samples from alluvial aquifers exceeds the proposed MCL for radon in States without an active indoor air program, but this sample does not exceed the proposed MCL for radon in States with an active indoor air program.

Summary for Aquifers in Relation to Water Use

Concentrations exceeding the SMCL's or MCL's may affect the use of water in some areas for many aquifers within the study area. Most concentrations exceeding standards are for various SMCL's and generally only affect the aesthetic quality of the water. Radionuclide concentrations may be especially high in some of the major aquifers within the study area and preclude the use of water in some areas. Hard water may require special treatment for certain uses. Other factors, such as the SAR and specific conductance, may affect irrigation use.

High concentrations of iron and manganese occasionally may hamper the use of water from Precambrian aquifers. None of the samples from the Precambrian aquifers exceeded drinking-water standards for radionuclides, although few samples with radionuclide analyses were available.

The principal deterrents to use of water from the Deadwood aquifer are the high concentrations of radionuclides, including radium-226 and radon. In addition, concentrations of iron and manganese can be high.

Water from the Madison aquifer can contain high concentrations of iron and manganese that may deter its use. Water from the Madison aquifer is hard to very

hard and may require special treatment for certain uses. In downgradient wells (generally deeper than 2,000 feet), concentrations of dissolved solids and sulfate also may deter use of water from this aquifer. In deep wells and in the Hot Springs area, hot water may not be desirable for some uses. Radionuclide concentrations in the Madison aquifer generally are acceptable.

The principal properties or constituents in the Minnelusa aquifer that may hamper the use of water from this aquifer include hardness and high concentrations of iron and manganese. Generally, downgradient wells (generally deeper than 1,000 feet) also have high concentrations of dissolved solids and sulfate. In deep wells, hot water may be undesirable for some uses. Arsenic may be a problem for some wells if the MCL is lowered to 10 µg/L. Only a few samples exceed the MCL's for various radionuclides.

Water from the Minnekahta aquifer generally is suitable for all water uses because few samples exceed SMCL's or MCL's and no samples available for this study from the Minnekahta aquifer exceed drinking-water standards for any radionuclides; however, samples are available only from shallow wells near the outcrop. Water from the Minnekahta aquifer is harder than that from any of the other major aquifers in the study area, and may require special treatment for certain uses.

The use of water from the Inyan Kara aquifer may be hampered by high concentrations of dissolved solids, iron, sulfate, and manganese. In the southern Black Hills, radium-226 and uranium concentrations also may preclude its use. Hard water from wells located on or near the outcrop of the Inyan Kara Group may require special treatment. Suitability for irrigation may be affected by high specific conductance and the adjusted SAR.

The use of water from minor aquifers may be hampered by hardness and concentrations of dissolved solids and sulfate. Concentrations of radionuclides, with the exception of uranium, generally are acceptable in samples from these minor aquifers. Selenium concentrations may be an additional deterrent to the use of water from the Sundance aquifer. Water from the Pierre and Sundance aquifers generally is not suitable for irrigation. Water from the other minor aquifers generally is suitable, but may not be in specific instances if either the specific conductance or the SAR is high.

Water from alluvial aquifers generally is very hard and may require special treatment for certain uses.

In alluvial deposits that overlie the Cretaceous-age shales, the high concentrations of dissolved solids, sulfate, iron, and manganese may limit the use of water from these aquifers. In the southern Black Hills, uranium concentrations can be high in alluvial aquifers in many locations.

Water-Quality Characteristics of Selected Surface-Water Sites

The water-quality characteristics for selected surface-water sites (fig. 7; table 16 in the Supplemental Information section), including streams and springs within the study area, are presented in this section. Surface-water quality depends largely on the geology of the area. Selected sites are used within this section to characterize the geologic influences based on the hydrogeologic settings presented in figure 7. These sites include headwater springs, crystalline core sites, artesian springs, and exterior sites. Headwater springs originate from the Paleozoic units (fig. 2) on the western side of the study area, and each spring tends to have relatively constant water-quality characteristics. Other streams originate in the Precambrian rocks of the crystalline core and tend to have more variability than the headwater springs. Artesian springs occur downgradient from the loss zones and contribute much of the base flow to exterior streams beyond the Black Hills. Additional exterior streams originate around the periphery of the Black Hills and represent sites having greater fluctuations in water-quality characteristics than the representative sites for other settings. The selected representative sites for the hydrogeologic settings generally have longer periods of record and more closely represent sites with characteristics that depend largely on the geologic influences. These sites have been used as representative sites in other reports produced as part of the Black Hills Hydrology Study. Many other surface-water sites from throughout the Black Hills are included in an "other" category to provide indications of the wider ranges that can occur and represent the combination of influences on water-quality characteristics within the study area.

Mineralized areas in the northern Black Hills as well as the generally drier climate of the southern Black Hills influence water-quality characteristics. Changes that occur within a basin as streams flow downslope from headwater areas to the exterior plains also will be examined (fig 7a).

Boxplots and summary statistics are presented for physical properties, common ions, nutrients, trace elements, and radionuclides. Figures illustrating spatial variations as well as trilinear and Stiff diagrams (Stiff, 1951), which indicate water type, also are presented.

Concentrations are compared to drinking-water standards as well as beneficial-use and aquatic-life criteria. Drinking-water standards are directly relevant to a limited number of stream segments with the beneficial use of domestic water supply, but concentrations that exceed these standards may be of interest to local users as a precautionary measure. Many of the aquatic criteria are dependent on hardness. If a concentration exceeds the aquatic criteria that is based upon a hardness of 100 mg/L, the appropriate hardness-calculated criterion is presented. Drinking-water standards are for total concentrations, and results reported by the USGS as dissolved concentrations may be less than those obtained for similar samples analyzed for total concentrations. A summary of how water-quality characteristics may affect the water use for selected sites within the study area is presented at the end of this section.

Physical Properties

The physical properties of the surface-water samples include measurements for discharge, specific conductance, pH, water temperature, dissolved oxygen, carbon dioxide, hardness, and alkalinity. Statistical comparisons identified similarities and differences between the groups of sites—headwater springs, crystalline core sites, artesian springs, exterior sites, and other sites. Summary statistics are presented in table 9, and the significance of the properties is described in table 1. Boxplots are presented in figure 28 for each of the properties by group.

Streamflow and the physical properties of the water can vary with the hydrogeologic settings. Seasonal variability and range in discharge for a representative site from each hydrogeologic setting (fig. 29) illustrate discharge variability by group. Relations commonly exist between discharge and specific conductance (fig. 30) and between temperature and dissolved oxygen (fig. 31).

Group Comparisons

Discharge at headwater springs displays little variability (fig. 28) compared to most other groups, with only artesian springs having similar flow charac-

teristics. Discharge from the artesian springs is relatively constant at each individual site with more variability between sites. Artesian springs generally do not display large seasonal or historic variability in discharge (fig. 29). Discharge for crystalline core sites displays wider ranges in variability and generally varies with season with increasing flows during the spring and summer when snowmelt and precipitation result in greater runoff. The greatest variability in discharge is measured at exterior sites, which have much larger drainage basins than the other groups.

Most of the other physical properties (including specific conductance, hardness, and alkalinity) at headwater springs also display limited variability (fig. 28). The stable nature of both discharge and specific conductance at headwater springs is apparent in figure 30. Specific conductance at crystalline core sites generally decreases as flow increases (fig. 30) due to dilution. Specific conductance varies considerably from one artesian spring to another; however, specific conductance is relatively constant at each site. At exterior sites, specific conductance generally is much higher than that for other hydrogeologic settings with a mean of 3,400 µS/cm and a maximum of 9,250 µS/cm. Compared to sites in the other hydrogeologic settings, much stronger relations exist between discharge and specific conductance at the exterior sites, with more pronounced decreases in specific conductance with increasing discharge (fig. 30).
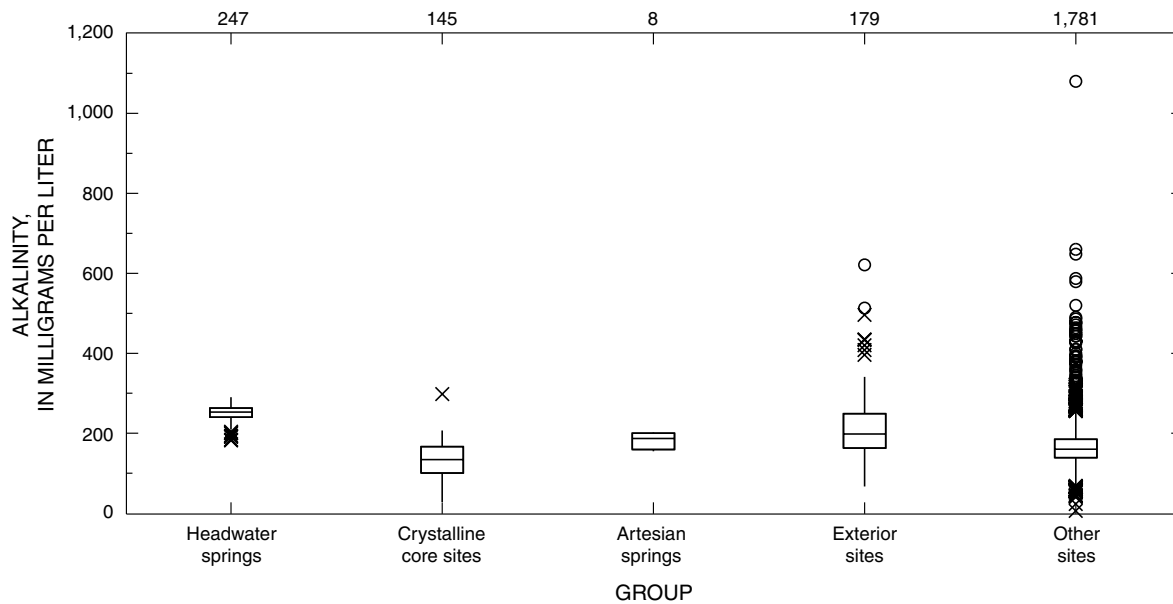
Twenty-one percent of the samples (56 of 263 samples) from headwater springs exceed the SMCL upper limit of 8.5 for pH, with concentrations exceeding standards for three of the four headwater springs included in this summary. Most values exceeding the SMCL for pH occurred at Castle Creek above Deerfield Reservoir (06409000); samples from this site composed more than 90 percent of the headwater spring samples. There also were 28 samples exceeding the coldwater permanent fisheries criteria (upper limit of 8.6) and 6 samples exceeding the coldwater marginal fisheries criteria (upper limit of 8.8), accounting for 11 and 2 percent of samples, respectively. Fifteen percent of the samples from crystalline core sites exceed the SMCL for pH, and 7 percent and 2 percent exceed the coldwater permanent and marginal criteria, respectively. The pH values for artesian springs are much lower than at headwater springs and crystalline core sites, and generally are less than 8.5. One percent of the pH values at exterior sites exceed the SMCL upper limit of 8.5, and no samples exceed the fisheries beneficial-use pH criteria (table 2).
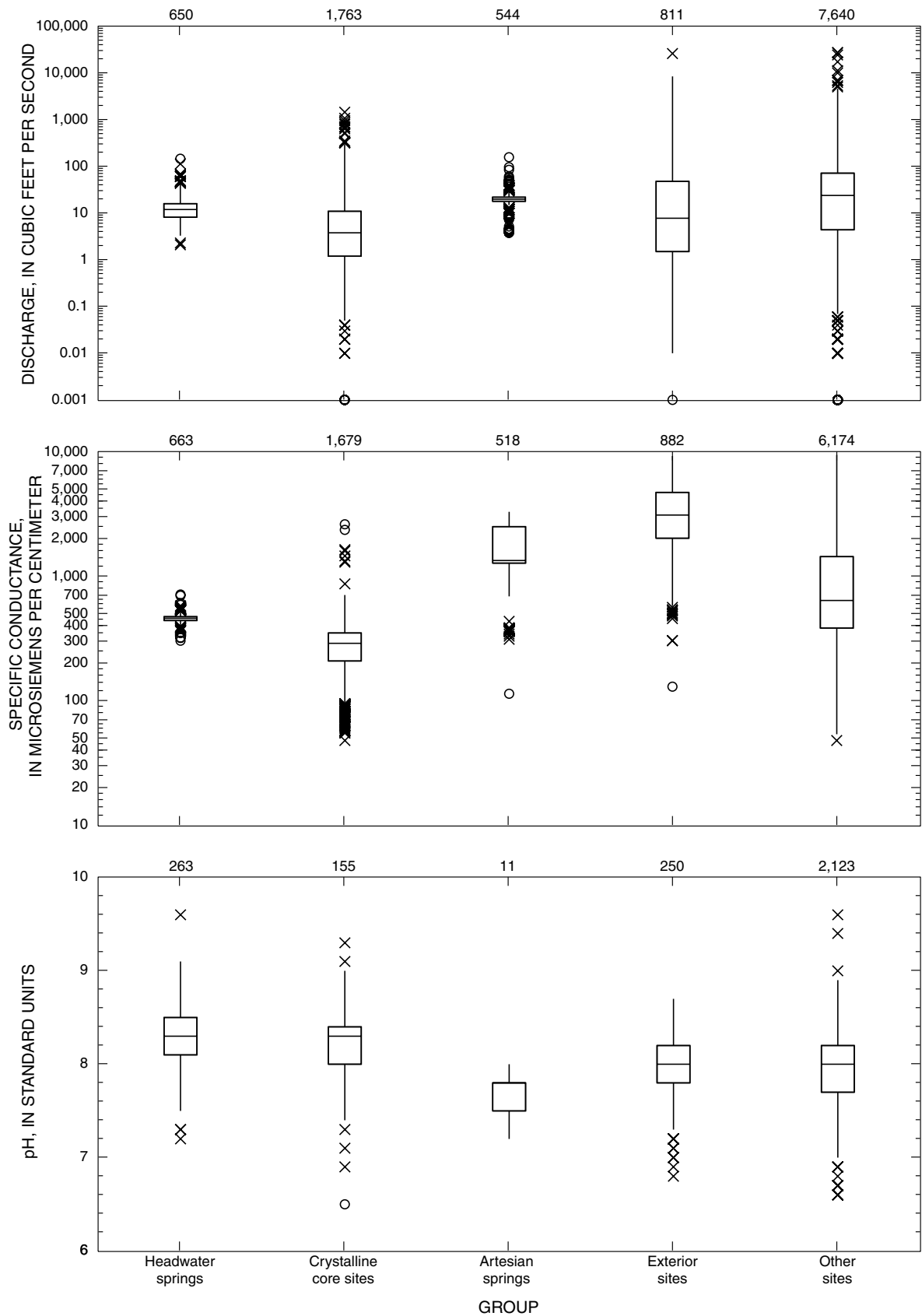
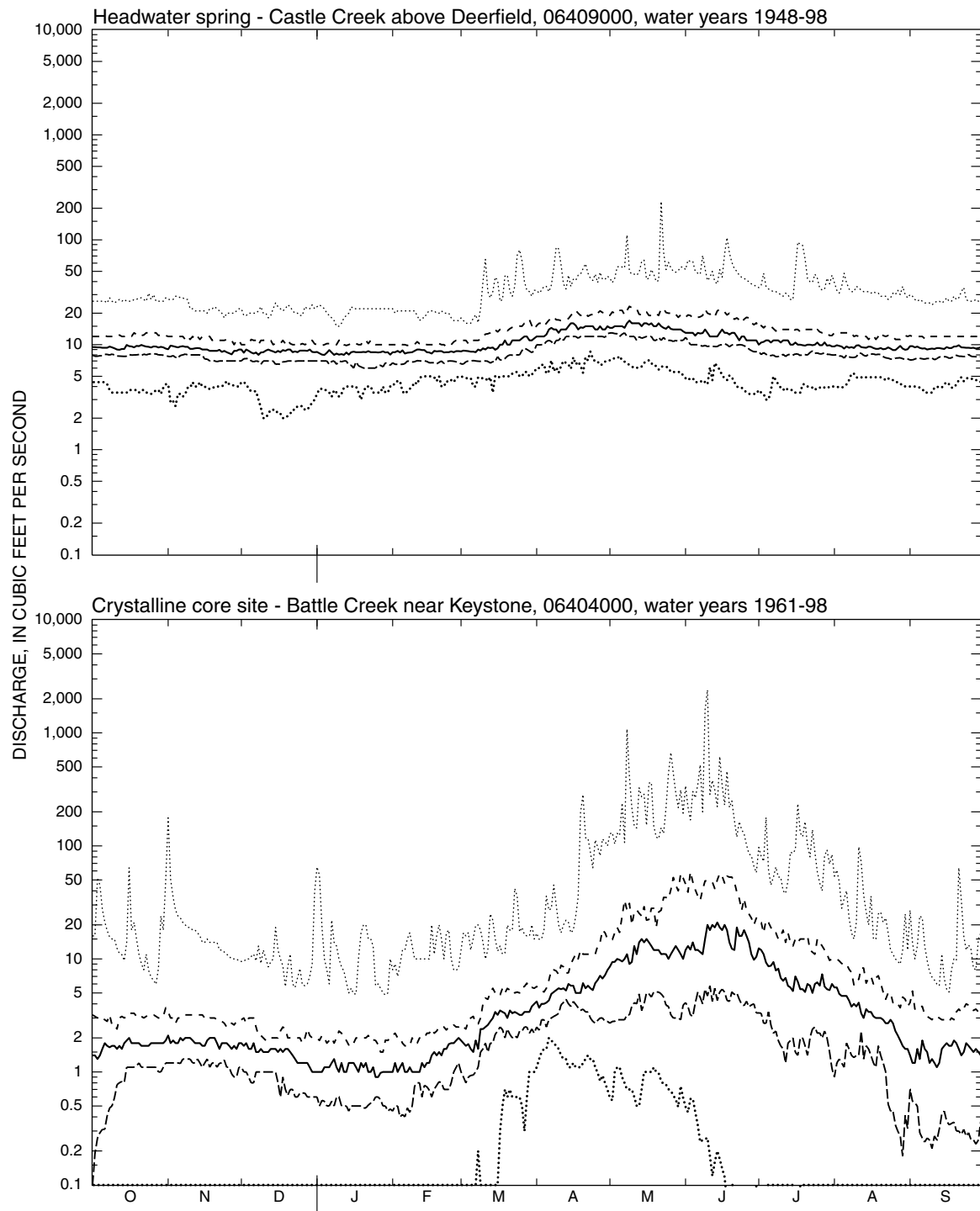**Figure 28.** Boxplots of concentrations of selected properties by surface-water group.
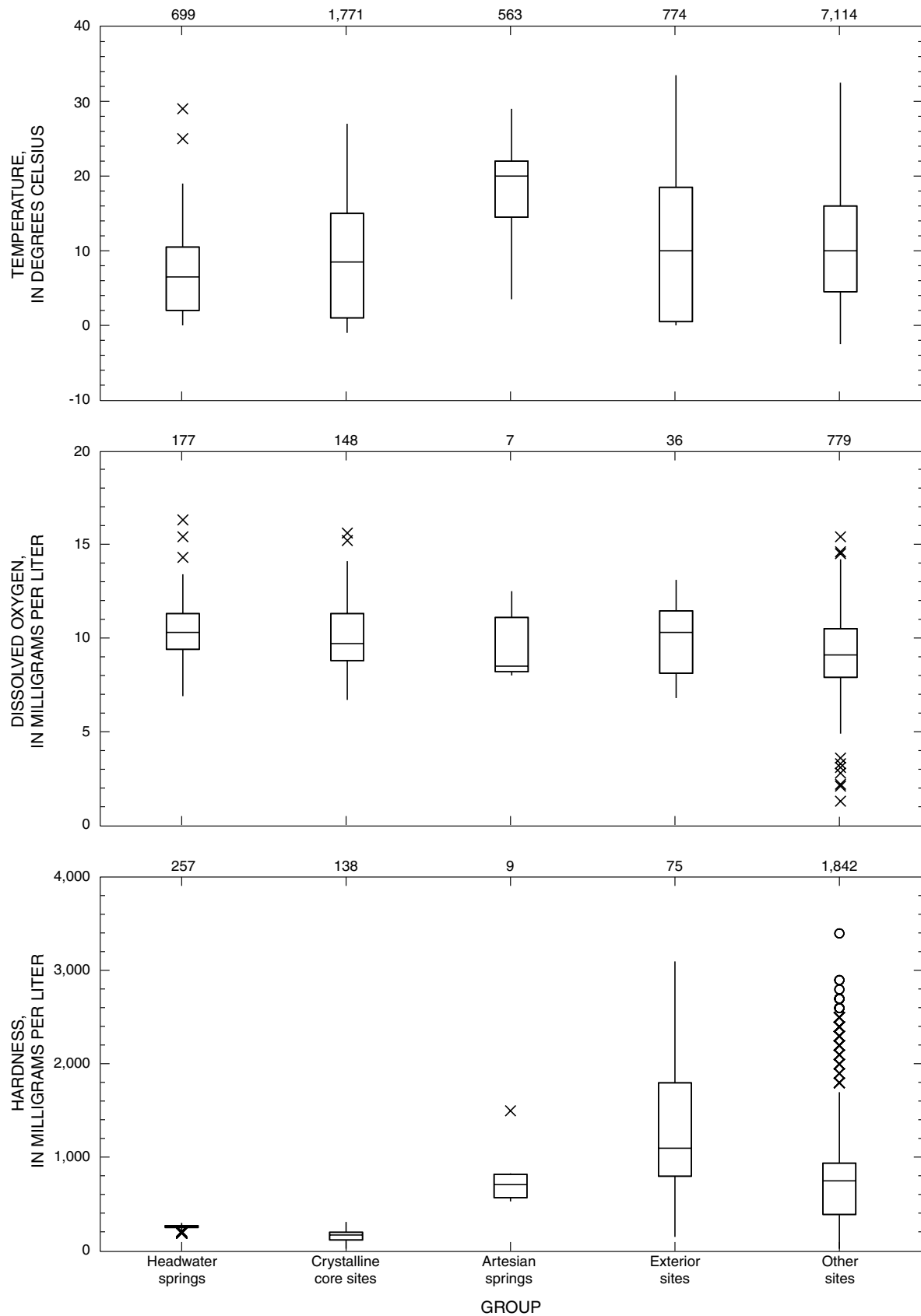
Figure 28. Boxplots of concentrations of selected properties by surface-water group.--Continued
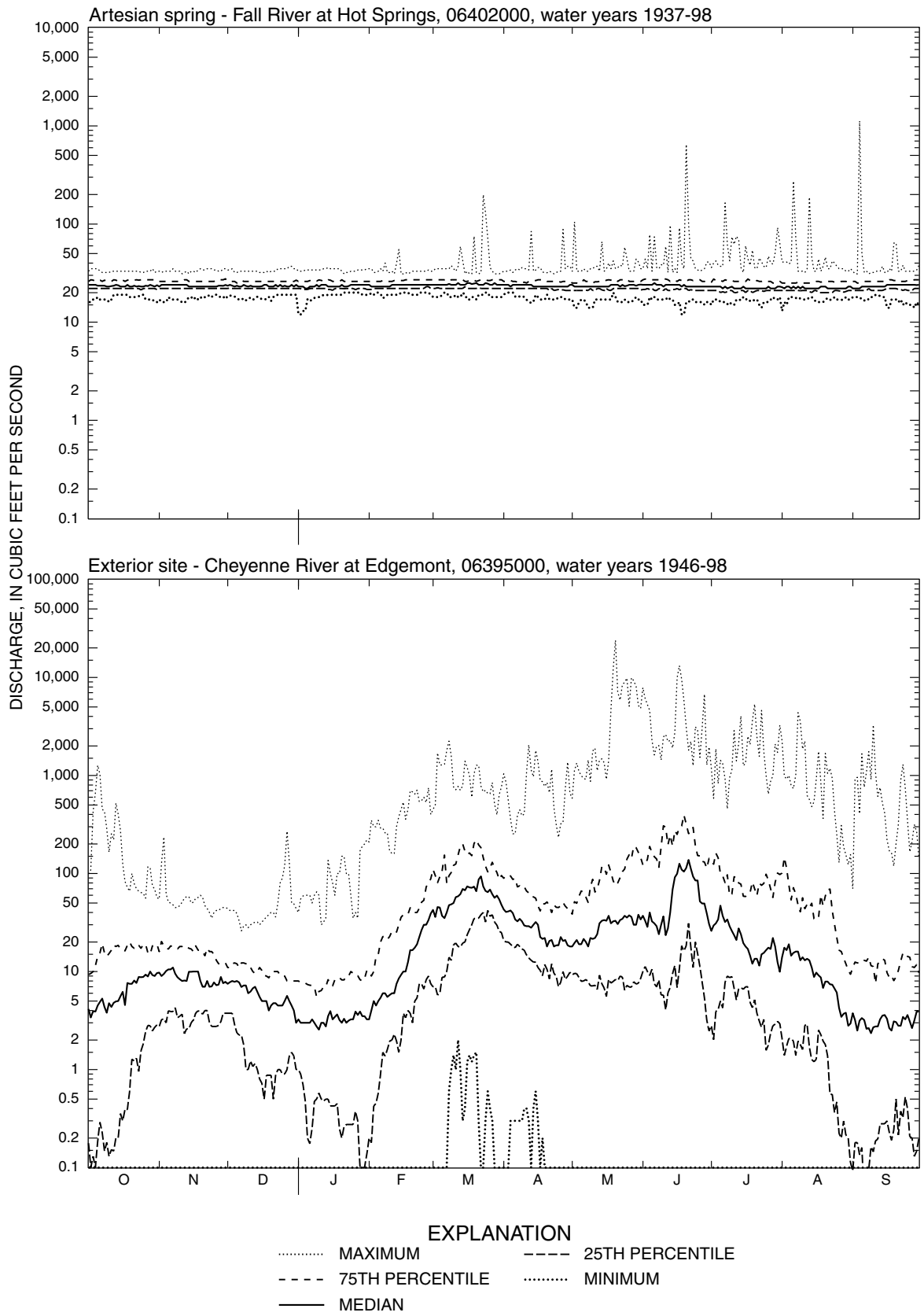
Figure 28. Boxplots of concentrations of selected properties by surface-water group.--Continued

Figure 29. Duration hydrographs of daily mean flow for selected headwater, crystalline, artesian, and exterior surface-water group sites.

Figure 29. Duration hydrographs of daily mean flow for selected headwater, crystalline, artesian, and exterior surface-water group sites.--Continued

**Table 9.** Summary of physical properties in surface water by group

[Results based on data stored in U.S. Geological Survey National Water Information System water-quality database. Results in milligrams per liter except as indicated. One milligram per liter is approximately equal to one part per billion. ft³/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius]

| Property or dissolved constituent	Number of samples	Mean	Median	Minimum	Maximum
Headwater springs					
Discharge (ft³/s)	650	14.1	12.0	2.1	147
Specific conductance (µS/cm)	663	460	460	304	715
pH (standard units)	263	8.3	8.3	7.2	9.6
Temperature (°C)	699	6.8	6.5	0.0	29.0
Dissolved oxygen	177	10.4	10.3	6.9	16.3
Hardness	257	258	260	190	300
Alkalinity	247	249	253	182	290
Crystalline core sites					
Discharge (ft³/s)	1,763	19.4	3.8	0.0	1,460
Specific conductance (µS/cm)	1,679	297	290	48	2,620
pH (standard units)	155	8.2	8.3	6.5	9.3
Temperature (°C)	1,771	8.9	8.5	-1.0	27.0
Dissolved oxygen	148	10.1	9.7	6.7	15.6
Hardness	138	158	170	29	310
Alkalinity	145	130	134	28	298
Artesian springs					
Discharge (ft³/s)	544	20.5	20.0	3.8	158
Specific conductance (µS/cm)	518	1,692	1,340	114	3,300
pH (standard units)	11	7.7	7.8	7.2	8.0
Temperature (°C)	563	18.9	20.0	3.5	29.0
Dissolved oxygen	7	9.5	8.5	8.0	12.5
Hardness	9	769	710	530	1,500
Alkalinity	8	181	187	155	202
Exterior sites					
Discharge (ft³/s)	811	177.6	7.8	0.0	26,300
Specific conductance (µS/cm)	882	3,400	3,110	130	9,250
pH (standard units)	250	7.9	8.0	6.8	8.7
Temperature (°C)	774	10.7	10.0	0.0	33.5
Dissolved oxygen	36	9.9	10.3	6.8	13.1
Hardness	75	1,296	1,100	150	3,100
Alkalinity	179	215	198	67	621

Table 9. Summary of physical properties in surface water by group—Continued

[Results based on data stored in U.S. Geological Survey National Water Information System water-quality database. Results in milligrams per liter except as indicated. One milligram per liter is approximately equal to one part per billion. ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius]

Property or dissolved constituent	Number of samples	Mean	Median	Minimum	Maximum
		Other sites			
Discharge (ft^3/s)	7,640	110.6	24.0	0.0	27,700
Specific conductance (µS/cm)	6,174	1,035	640	48	9,450
pH (standard units)	2,123	7.9	8.0	6.6	9.6
Temperature (°C)	7,114	10.5	10.0	-2.5	32.5
Dissolved oxygen	779	9.2	9.1	1.3	15.4
Hardness	1,842	769	750	28	3,400
Alkalinity	1,781	170	160	4.0	1,080
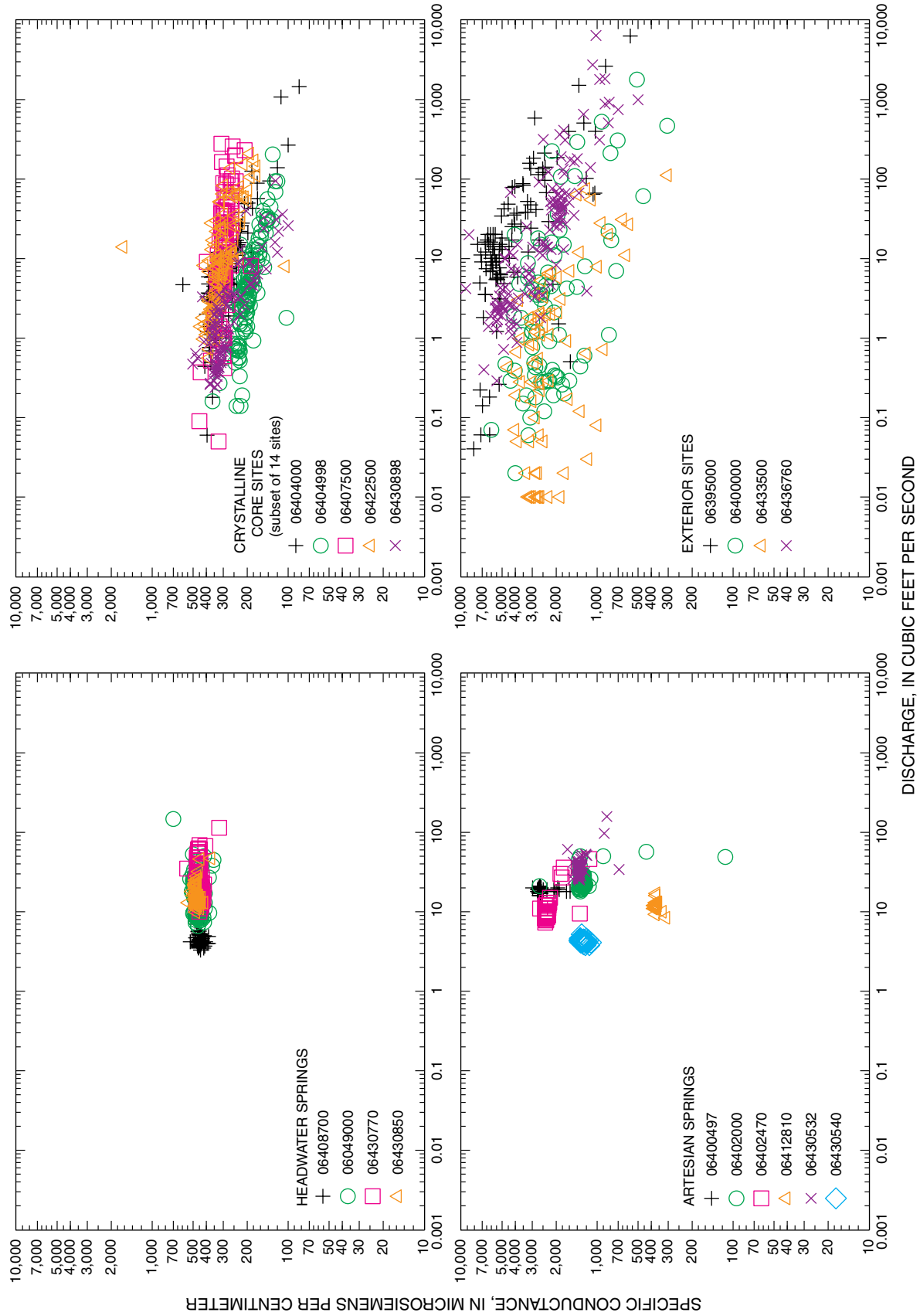
Figure 30. Relations between discharge and specific conductance for selected sampling sites by surface-water group.
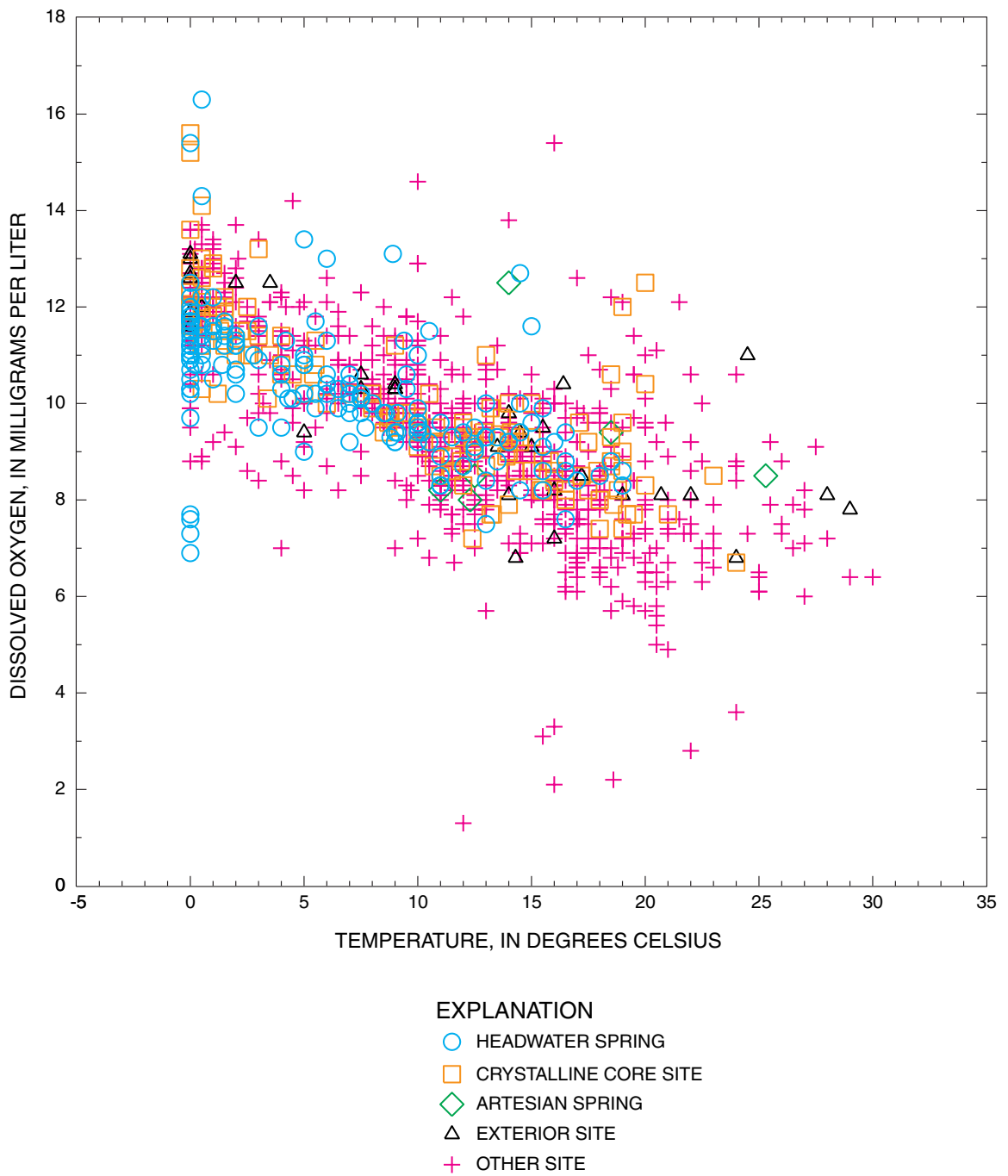
Figure 31. Relations between temperature and dissolved oxygen for selected surface-water groups.

Variations in water temperature occur primarily as seasonal fluctuations. Dissolved oxygen concentrations generally vary with temperature, with lower dissolved oxygen concentrations occurring during periods of higher temperature (fig. 31). For headwater springs, seven samples (1 percent of the samples) exceed the coldwater permanent fisheries criteria for temperature (18.3°C), and two samples exceed the coldwater marginal fisheries temperature criteria (24°C), indicating that temperature may stress fish during unusually warm summer periods with lower flows. Dissolved oxygen concentrations rarely are less than 7 mg/L, the minimum criteria during spawning periods. Almost 12 percent of the water temperature measurements for crystalline core sites exceed the coldwater permanent fisheries criteria of 18.3°C (210 of 1,771 samples), and less than 1 percent exceed the coldwater marginal fisheries criteria of 24°C. The artesian springs generally have higher temperatures (fig. 28) than other groups because of the ground-water contribution to the springs. Water-temperature statistics for the artesian springs are strongly influenced by Fall River at Hot Springs (06402000), which is a warm-water spring in the southern Black Hills. Fall River displays little variability with season, and freezing temperatures have not been recorded at this site. Temperature and dissolved oxygen concentration ranges at exterior sites are similar to the other groups. Dissolved oxygen concentrations in water from the exterior sites generally remain greater than 6 mg/L even at higher temperatures, and ranges of 6 to 12 mg/L are not uncommon for temperature ranges of 10 to 30°C (fig. 31).

Dissolved oxygen concentrations of 2.1, 2.2, and 3.6 mg/L have been measured at an urban runoff site within the Rapid Creek Basin (06416300, Meade Street Drain). Two additional sites with low dissolved oxygen concentrations are Cottonwood Creek near Buffalo Gap and Cheyenne River near Buffalo Gap. In addition, low dissolved oxygen concentrations have been reported at exterior sites (including the Cheyenne River and tributaries) when temperatures are high and flows are very low (Hoof, 1998).

Water from headwater springs generally is very hard with concentrations greater than 190 mg/L (table 9). The median alkalinity for the headwater springs of 253 mg/L (table 9) is the highest of the surface-water groups. Water at the crystalline core sites ranges from soft to very hard, with the soft water occurring primarily because of minimal exposure to limestone and sandstone units, which are a source of calcium and magnesium. Alkalinity at the crystalline core sites ranges from 28 to 298 mg/L. Water from the artesian springs is very hard with alkalinity ranging from 155 to 202 mg/L (table 9). Hardness and alkalinity at exterior sites are higher than or similar to upslope sites with the water being hard to very hard. The maximum alkalinity concentration of 1,080 mg/L occurred at Horse Creek near Vale (06436800, other site group) and approached the wildlife propagation and stock-watering criteria daily maximum of 1,313 mg/L.

Additional Comparisons

Urbanization is one factor that influences natural conditions of streams. Increased runoff during storms, permitted discharges, and factors such as channelization and increased public use, can affect stream quality. Limited urbanization exists in the Black Hills currently, but population in the area continues to grow rapidly. Both Rapid City and Spearfish have experienced recent growth that challenges city and county managers with protection of water and natural conditions while providing for economic growth.

Within a basin, changes in discharge include losses of water as streams cross loss zones and then gains downstream (Hortness and Driscoll, 1998). Additional streamflow losses and gains can occur due to effects from urbanization and agriculture including irrigation. Other physical properties, such as specific conductance and hardness, generally increase downstream with additional exposure to and dissolution of calcium, magnesium, sodium, and sulfate as shown by increasing concentrations in the Rapid Creek Basin from its headwaters to near its confluence with the Cheyenne River (fig. 32, fig. 7a).

Water-quality changes have been identified in streams in the northern Black Hills where sulfide ores have been exposed by mining (Williamson and Hayes, 2000). In areas of acid-mine drainage or naturally occurring iron-bog areas, pH values can be very low, often less than 6. A downstream progression of pH values for two streams (False Bottom and Deadwood Creeks) affected by mining activities is presented in figure 33. Upstream from mining activities, pH levels in the stream are normal for the area. The stream pH then decreases to low levels immediately downstream of mining activities. Farther downstream from mining activities, pH values generally increase to near normal levels again after exposure to the calcium-rich sediments common to the area (Torve, 1991).
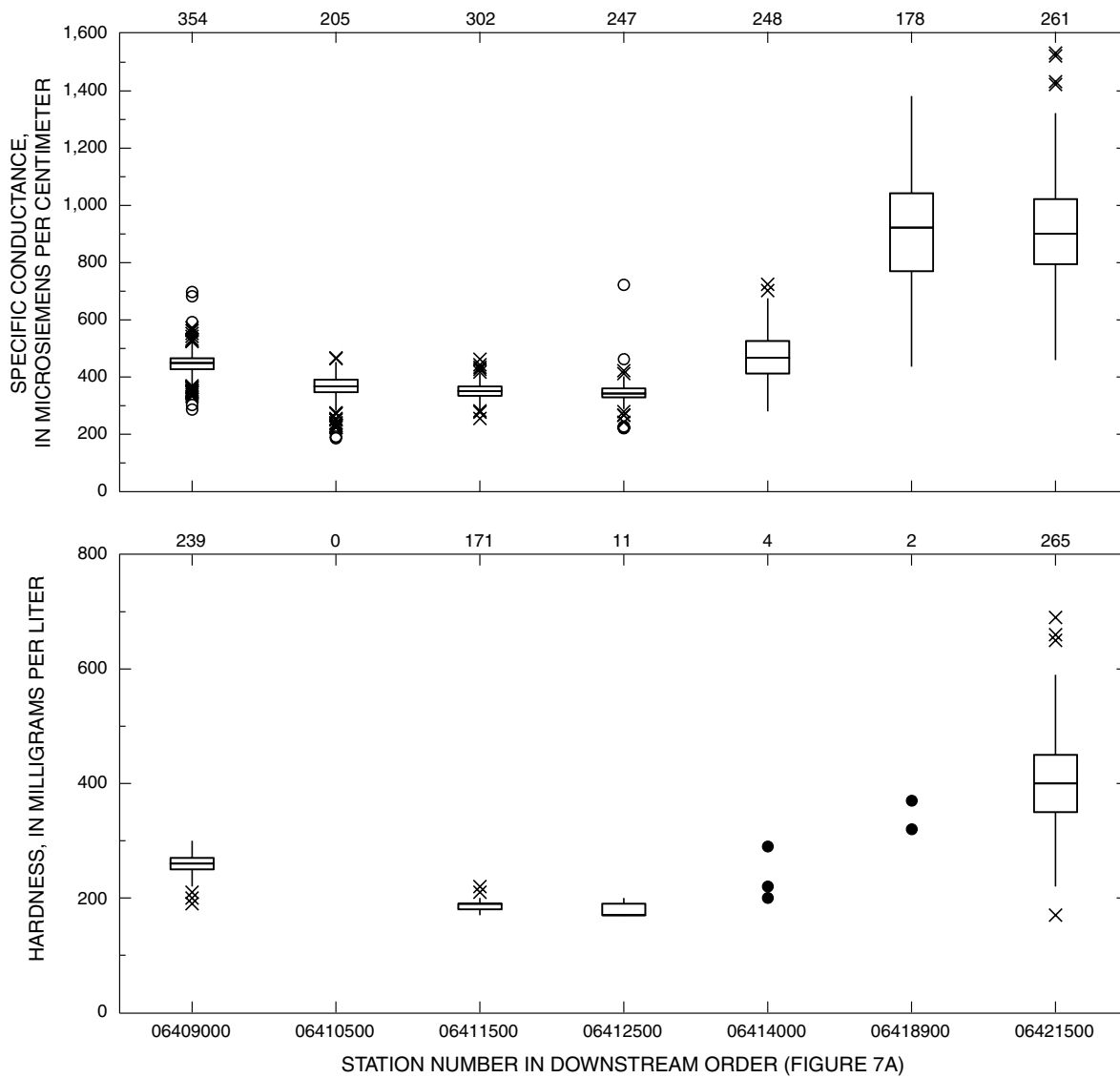
Figure 32. Boxplots of specific conductance and hardness for selected surface-water sites in Rapid Creek Basin.
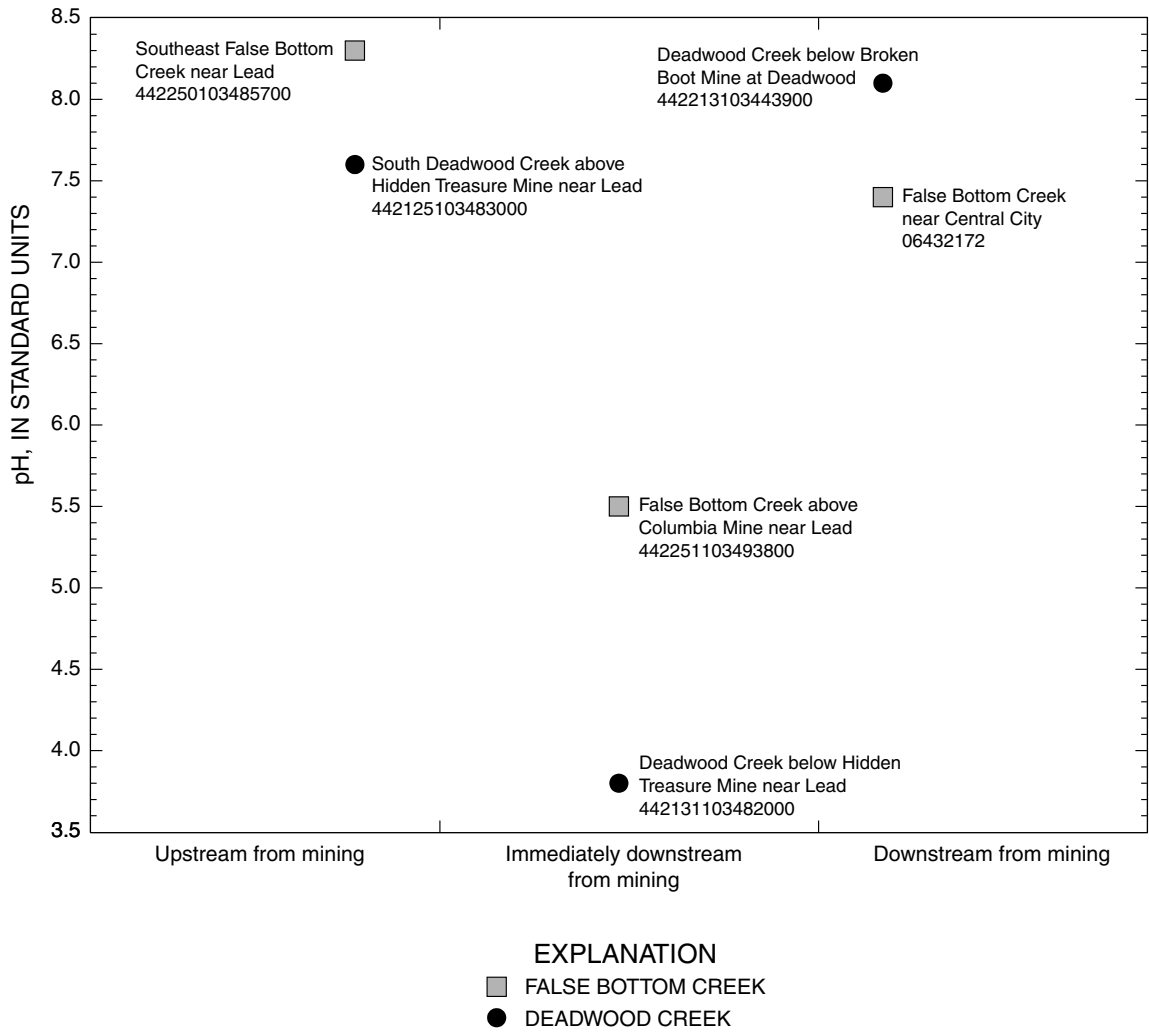
Figure 33. Downstream progression of pH for selected streams influenced by acid mine drainage.

Common Ions

Summary statistics for selected common ions are presented in table 10, and the significance of the various common ions is described in table 1. Boxplots are presented in figure 34 for each of the common ions, except dissolved solids (residue at 180°C), percent sodium, and SAR.

Group Comparisons

Specific conductance can be used to estimate the concentration of dissolved solids. Linear regression was performed using specific conductance (field and laboratory), and concentrations of dissolved solids (sum of constituents or residue) for each group, and results are presented in table 11 and figure 35. The regression of specific conductance and dissolved solids for headwater springs yields a weak relation due to the small variability in both specific conductance and dissolved solids. For headwater springs, specific conductance ranged from 304 to 705 µS/cm, and dissolved solid concentrations (sum of constituents) ranged from 186 to 294 mg/L. The relation between specific conductance and dissolved solids is much stronger for crystalline core sites, artesian springs, and exterior sites where greater variability of specific conductance and dissolved solids occurs. Dissolved solids concentrations (sum of constituents) ranges from 44 to 362 mg/L at crystalline core sites, from 834 to 2,240 mg/L at artesian springs, and from 346 to 6,460 mg/L at exterior sites (table 10).

The variation in water type for the surface-water groups is shown by trilinear diagrams (fig. 36) and Stiff diagrams (fig. 37). Calcium and magnesium are the dominant cations (40 to 60 percent of total cations), and bicarbonate the dominate anion (80 to 99 percent of total anions) for headwater springs (figs. 36 and 37) similar to samples from the Madison aquifer (fig. 17) from wells located on or near the Madison Limestone outcrop. Generally, only crystalline core sites have lower concentrations of common ions than headwater springs (fig. 37). Crystalline core sites generally are a calcium bicarbonate type water or calcium bicarbonate sulfate type water (fig. 36) and are similar to samples from the Precambrian aquifers (fig. 17) with slightly higher sulfate and chloride.

Water from the artesian springs is a calcium sulfate type (fig. 37). Increased sulfate at artesian springs is the most notable difference from headwater springs and crystalline core sites. Sources of sulfate include rock/water interactions in the Minnelusa Formation from upwelling Madison aquifer and/or Minnelusa aquifer water (primary source water for these springs) or exposure to shale units such as the Spearfish Formation at or near land surface. The range of sulfate concentrations, based on the limited data set (eight samples), is similar to ranges found in ground-water samples from the Spearfish aquifer and from the Minnelusa aquifer within the sulfate transition zone (fig. 21). Sulfate concentrations from the artesian springs are all greater than the SMCL of 250 mg/L (table 10).

Exterior sites generally have sodium calcium magnesium sulfate type waters (fig. 36). Increased sodium and sulfate concentrations are the most notable differences for the exterior sites (fig. 37). Sixty-six percent of the samples from the exterior sites have sulfate concentrations greater than 1,000 mg/L. Three of the 73 samples have sulfate concentrations less than the SMCL of 250 mg/L. The SAR does not exceed 10, so the sodium generally does not limit the use of this water for irrigation. Chloride also generally is much higher at these sites than at the headwater springs, crystalline core sites, and artesian springs. Of the 73 samples analyzed for chloride, 26 percent of the samples exceed the SMCL of 250 mg/L, and 10 percent of the samples exceed 500 mg/L. All of the concentrations that exceeded the SMCL are from Cheyenne River at Edgemont.

Concentrations of common ions for the other-sites group are very similar to those of the hydrogeologic settings groups, with maximum concentrations similar to exterior sites and minimum concentrations similar to headwater springs and crystalline core sites (table 10). Two bicarbonate concentrations greater than 800 mg/L and eight chloride concentrations greater than 400 mg/L have been determined for water from Horse Creek near Vale. The minimum bicarbonate concentration of 28 mg/L is for water from False Bottom Creek. All but one sulfate concentrations greater than 1,000 mg/L have occurred in water from exterior sites along the Cheyenne River, Belle Fourche River, or prairie tributaries. The exception is an urban runoff sample within the Rapid Creek Basin with a sulfate concentration of 1,100 mg/L.

Table 10. Summary of concentrations of common ions in surface water by group

[Results based on data stored in U.S. Geological Survey National Water Information System water-quality database. Results in milligrams per liter except as indicated. One milligram per liter is approximately equal to one part per million; <, less than]

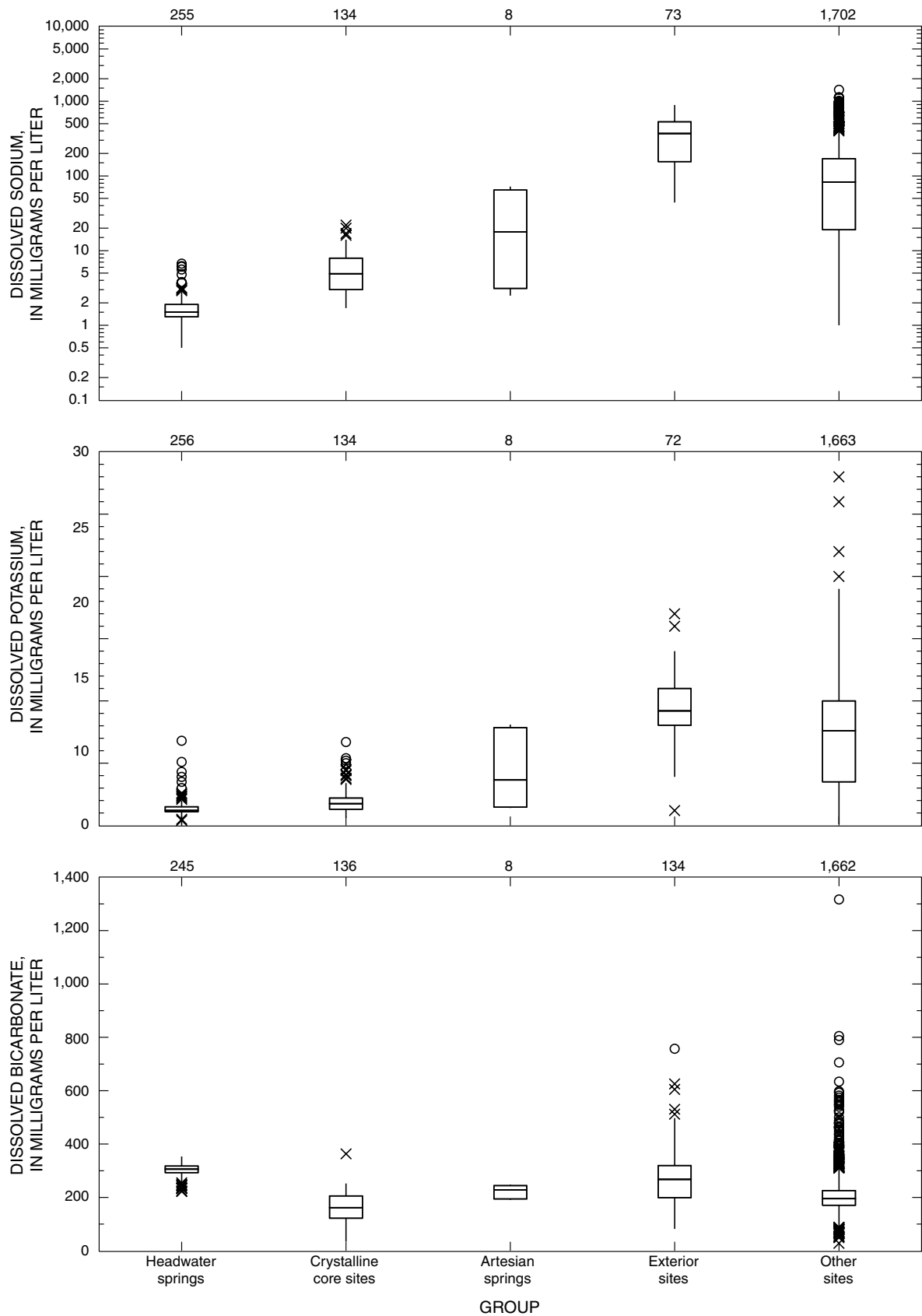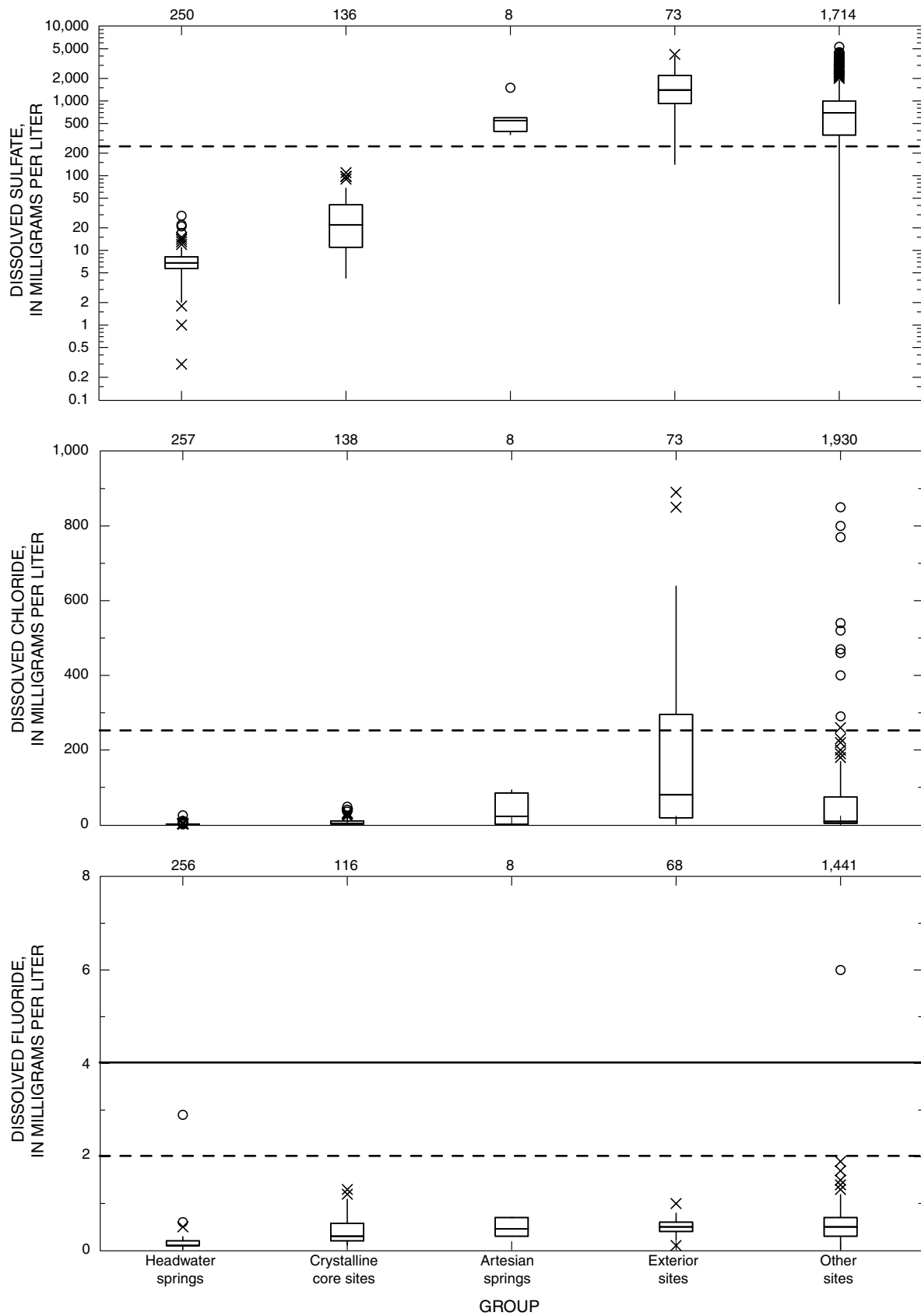| Dissolved constituent	Number of samples	Number of censored samples	Mean	Median	Minimum	Maximum
Headwater springs						
Solids, residue at 180°C	224	0	249	252	147	476
Solids, sum of constituents	251	0	255	258	186	294
Calcium	255	0	55	56	25	70
Magnesium	255	0	29	30	20	40
Sodium	255	0	1.7	1.5	0.5	6.7
Sodium, percent	254	0	1.4	1.0	0.0	5.0
Sodium-adsorption ratio	254	0	0.0	0.0	0.0	0.2
Potassium	256	0	1.4	1.2	0.4	6.8
Bicarbonate	245	0	302	306	222	354
Sulfate	250	1	7.2	7.0	<1.0	29
Chloride	257	1	1.6	1.2	<0.1	25
Fluoride	256	8	0.2	0.1	<0.1	2.9
Silica	255	0	8.9	9.0	0.1	21
Crystalline core sites						
Solids, residue at 180°C	100	0	184	192	53	350
Solids, sum of constituents	134	0	191	200	44	362
Calcium	134	0	41	41	8.6	79
Magnesium	134	0	13	14	1.8	28
Sodium	134	0	6.2	4.9	1.7	22
Sodium, percent	132	0	8.6	7.0	3.0	27
Sodium-adsorption ratio	132	0	0.2	0.2	0.1	0.7
Potassium	134	0	2.0	1.8	0.6	6.7
Bicarbonate	136	0	157	162	34	363
Sulfate	136	0	28	22	4.2	110
Chloride	138	0	7.1	3.7	0.2	48
Fluoride	116	4	0.4	0.3	<0.1	1.3
Silica	113	0	13	13	6.8	21
Artesian springs						
Solids, residue at 180°C	6	0	936	990	206	2,130
Solids, sum of constituents	8	0	1,110	966	834	2,240
Calcium	8	0	248	245	150	470
Magnesium	8	0	43	38	33	83
Sodium	8	0	31	18	2.5	72
Sodium, percent	8	0	8.6	2.5	1.0	21

Table 10. Summary of concentrations of common ions in surface water by group—Continued

[Results based on data stored in U.S. Geological Survey National Water Information System water-quality database. Results in milligrams per liter except as indicated. One milligram per liter is approximately equal to one part per million; <, less than]

Dissolved constituent	Number of samples	Number of censored samples	Mean	Median	Minimum	Maximum
Artesian springs—Continued						
Sodium-adsorption ratio	8	0	0.4	0.2	0.0	1.0
Potassium	8	0	4.4	3.6	1.4	8.1
Bicarbonate	8	0	221	228	190	247
Sulfate	8	0	614	545	350	1,500
Chloride	8	0	39	22	0.7	94
Fluoride	8	0	0.5	0.5	0.3	0.7
Silica	8	0	16	14	11	23
Exterior sites						
Solids, residue at 180°C	126	0	3,274	3,180	363	7,020
Solids, sum of constituents	72	0	2,768	2,605	346	6,460
Calcium	73	0	284	270	44	820
Magnesium	73	0	146	110	4.9	430
Sodium	73	0	371	370	44	890
Sodium, percent	72	0	37	38	19	60
Sodium-adsorption ratio	72	0	4.4	5.0	1.0	9.0
Potassium	72	0	9.6	9.2	1.2	17
Bicarbonate	134	0	273	268	82	757
Sulfate	73	0	1,667	1,400	140	4,200
Chloride	73	0	172	80	1.5	890
Fluoride	68	2	0.5	0.5	<0.1	1.0
Silica	61	0	7.1	6.3	0.9	38
Other sites						
Solids, residue at 180°C	816	0	1,316	1,085	81	9,450
Solids, sum of constituents	1,646	0	1,368	1,150	78	8,380
Calcium	1,701	0	187	200	3.7	590
Magnesium	1,701	0	73	55	3.0	545
Sodium	1,702	0	134	83	1.0	1,420
Sodium, percent	1,641	0	20	20	1.0	63
Sodium-adsorption ratio	1,610	0	1.8	1.0	0.0	11
Potassium	1,663	1	7.6	7.6	<0.1	28
Bicarbonate	1,662	0	207	195	28	1,317
Sulfate	1,714	0	806	700	1.9	5,300
Chloride	1,930	4	39	8.8	<3.0	850
Fluoride	1,441	6	0.5	0.5	<0.1	6.0
Silica	1,418	0	8.9	8.6	0.0	41
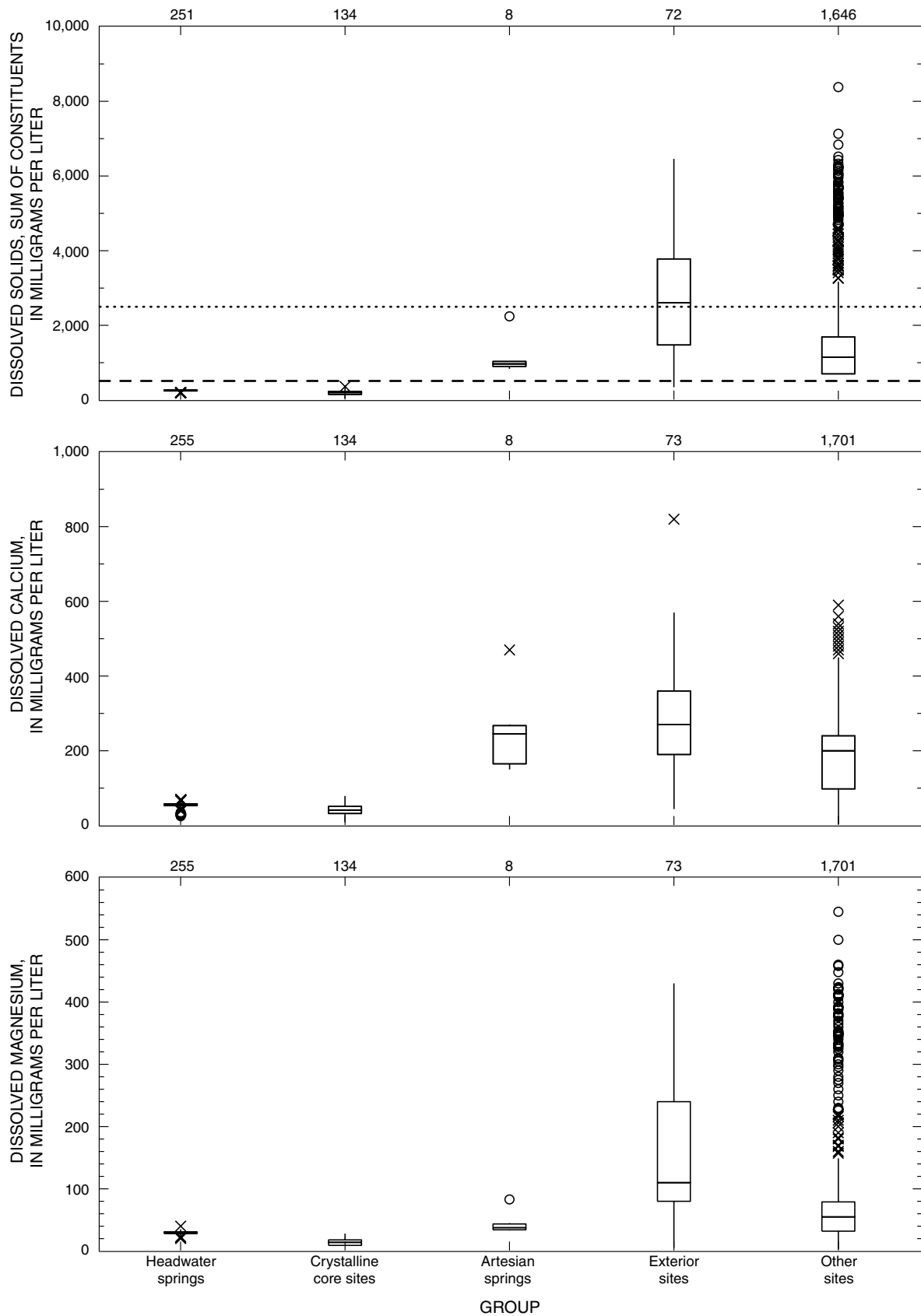
Figure 34. Boxplots of concentrations of selected ions by surface-water group.

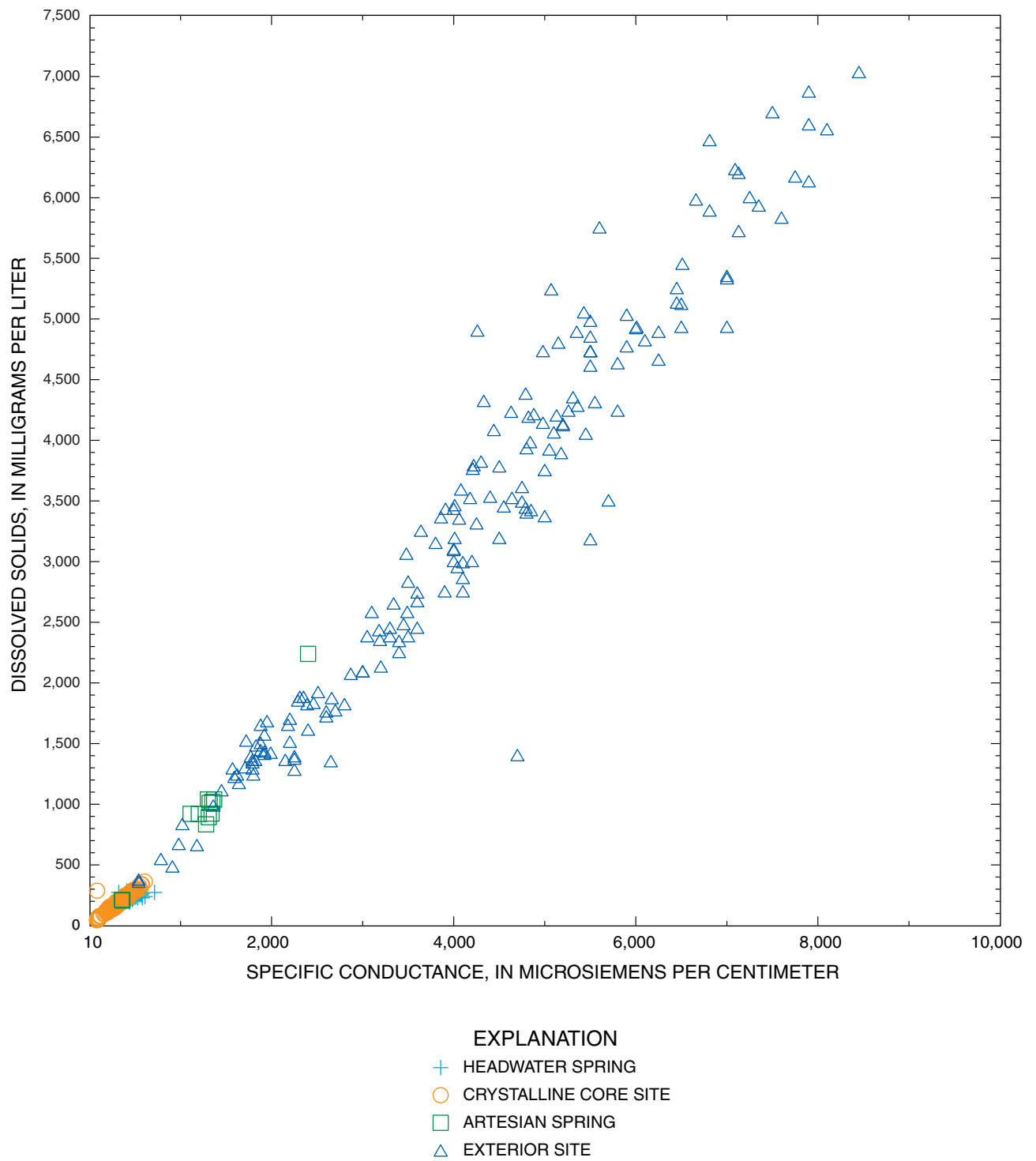**Figure 34.** Boxplots of concentrations of selected ions by surface-water group.--Continued

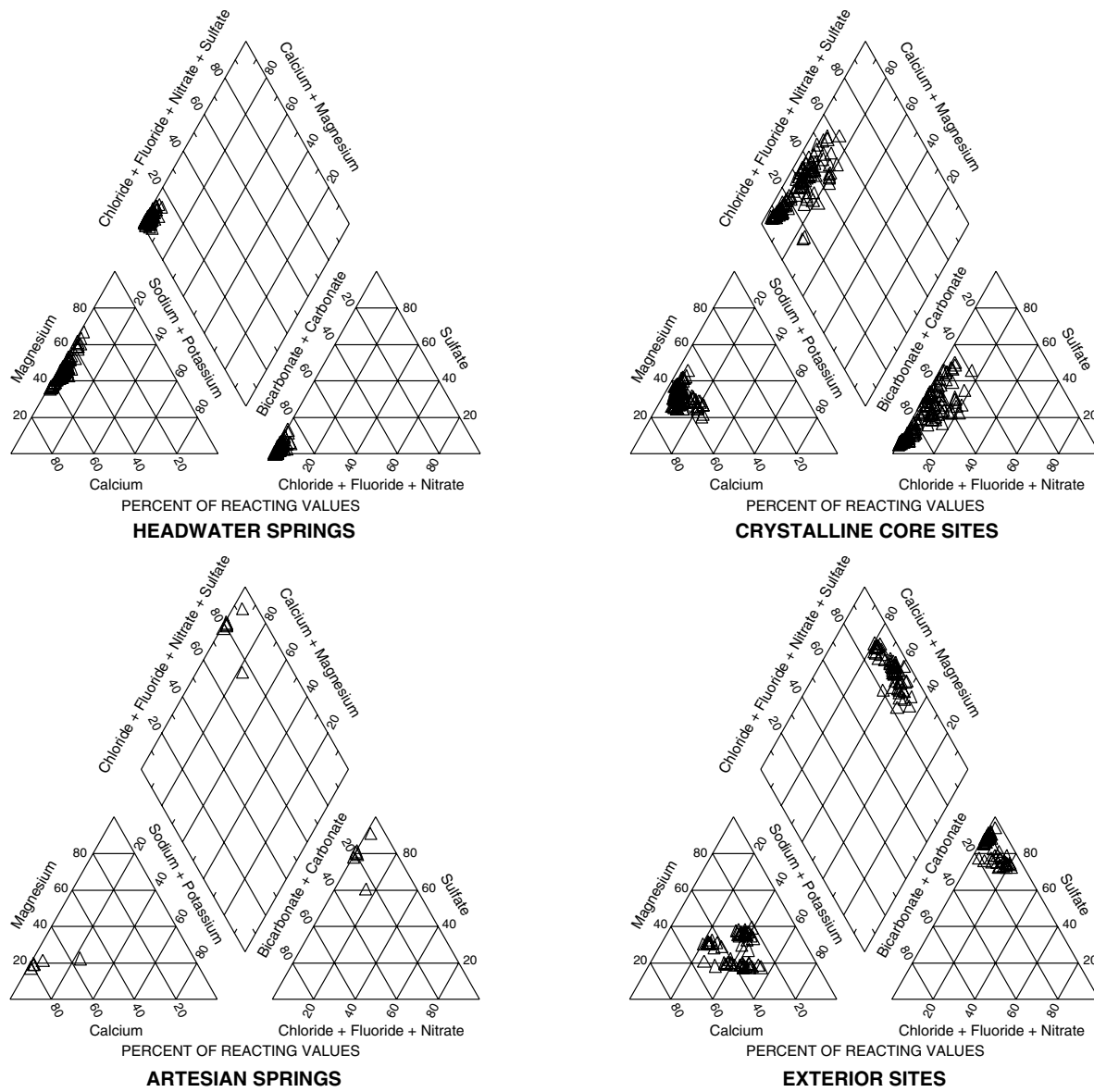**Figure 34.** Boxplots of concentrations of selected ions by surface-water group.--Continued

Figure 34. Boxplots of concentrations of selected ions by group.--Continued

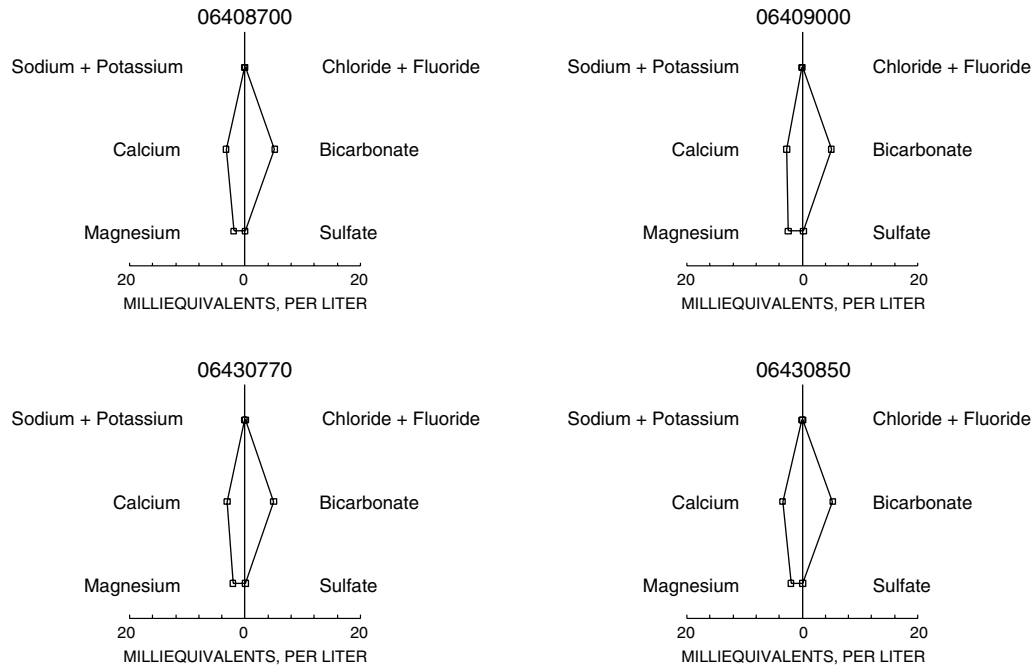**Figure 35.** Relation between specific conductance and dissolved solids by surface-water group.

HEADWATER SPRINGS

CRYSTALLINE CORE SITES

ARTESIAN SPRINGS

EXTERIOR SITES

Figure 36. Trilinear diagrams showing proportional concentrations of major ions by surface-water group.

HEADWATER SPRINGS

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

50   0   50
MILLIEQUIVALENTS, PER LITER

CRYSTALLINE CORE SITES

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

50   0   50
MILLIEQUIVALENTS, PER LITER

ARTESIAN SPRINGS

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

50   0   50
MILLIEQUIVALENTS, PER LITER

EXTERIOR SITES

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

50   0   50
MILLIEQUIVALENTS, PER LITER

STIFF DIAGRAMS OF MEDIAN CONCENTRATIONS (BY GROUP)

06408700

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

20   0   20
MILLIEQUIVALENTS, PER LITER

06409000

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

20   0   20
MILLIEQUIVALENTS, PER LITER

06430770

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

20   0   20
MILLIEQUIVALENTS, PER LITER

06430850

Sodium + Potassium   Chloride + Fluoride

Calcium   Bicarbonate

Magnesium   Sulfate

20   0   20
MILLIEQUIVALENTS, PER LITER

STIFF DIAGRAMS FOR SELECTED HEADWATER SPRINGS

Figure 37. Stiff diagrams for surface-water groups and selected sites.
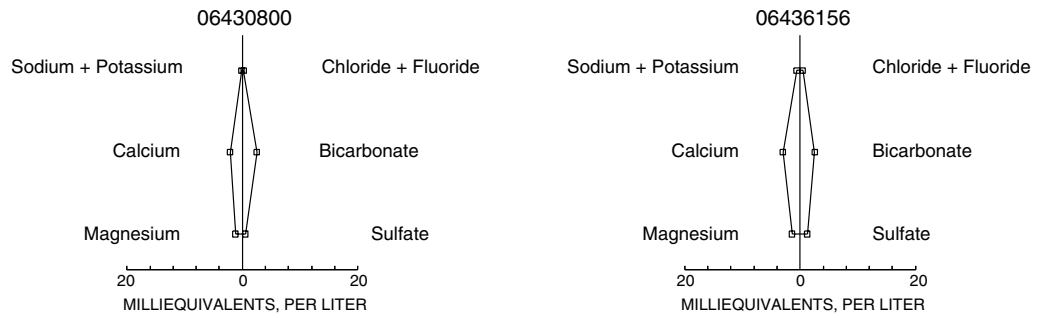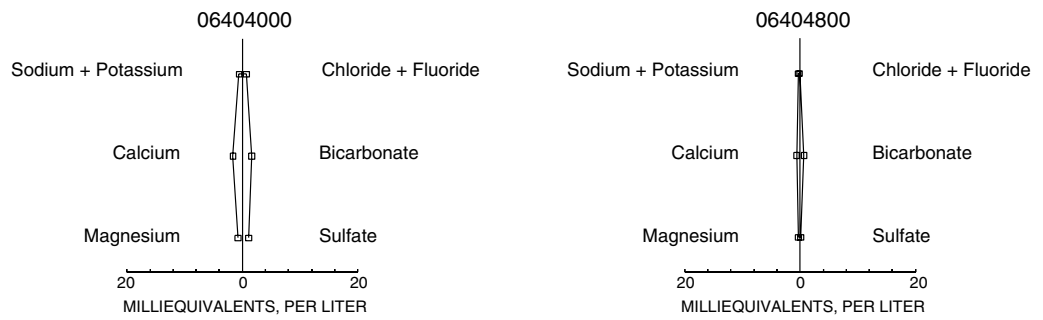
STIFF DIAGRAMS FOR SELECTED CRYSTALLINE CORE SITES
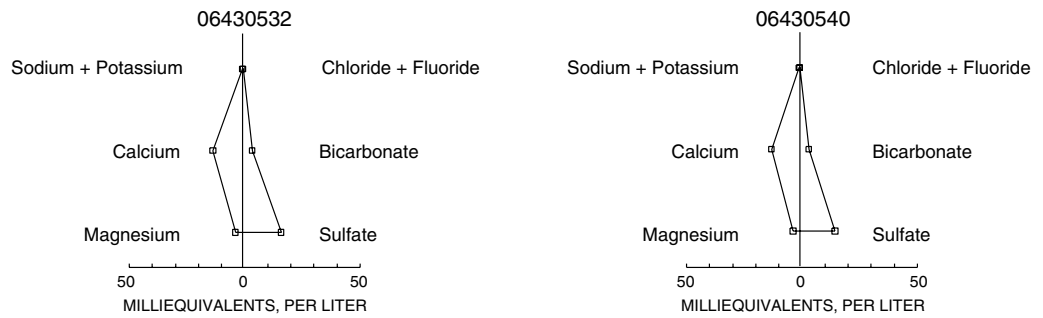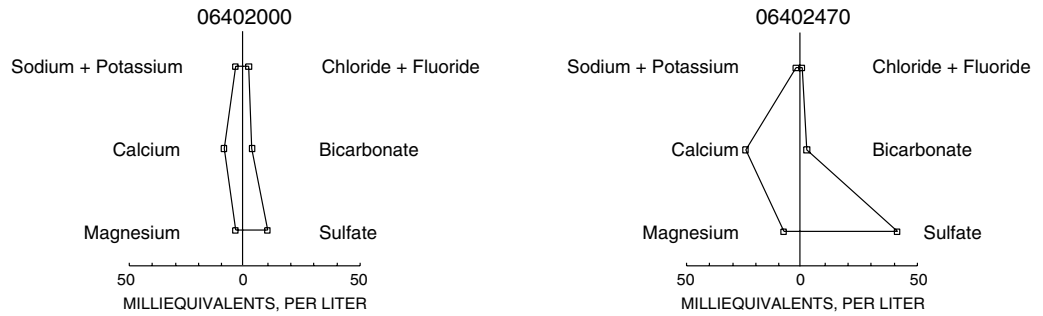
STIFF DIAGRAMS FOR SELECTED ARTESIAN SPRINGS

Figure 37. Stiff diagrams for surface-water groups and selected sites.--Continued

STIFF DIAGRAMS FOR SELECTED EXTERIOR SITES
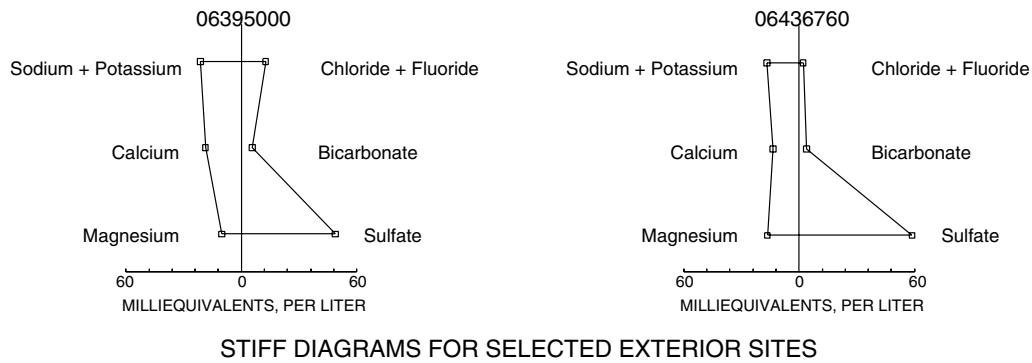
Figure 37. Stiff diagrams for surface-water groups and selected sites.--Continued

Table 11. Relation between specific conductance and dissolved solids for selected surface-water groups

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

Group	Equation of line	R^2	Number of samples
All	$S = 0.86K - 131.14$	0.9692	2,355
Headwater springs	$S = 0.21K + 158.16$	.2437	261
Crystalline core sites	$S = 0.55K + 15.83$	.8914	136
Artesian springs	$S = 0.93K - 194.22$	.9614	13
Exterior sites	$S = 0.85K - 249.50$	.9676	174

Generally, common ion concentrations tend to increase after the streams come in contact with the Cretaceous-age marine shales surrounding the Black Hills, which results in increased concentrations of sulfate complexed with calcium or sodium. Other ions such as chloride, magnesium, and potassium also tend to increase. figures 38 and 39 present spatial distributions of mean calcium and sulfate concentrations, respectively, for the study area. Specific conductance follows this same general pattern and linear relations commonly exist between specific conductance and selected common ion concentrations (fig. 40).

Additional Comparisons

A downstream progression of calcium and sulfate concentrations for Rapid Creek is shown in figure 41. Downstream from Rapid Creek above Canyon Lake, 06412500, concentrations of calcium and sulfate increase notably, which is consistent with the increased exposure to limestone and then Cretaceous-age marine shales.

Changes in ion concentrations over time often can provide indications of land-use changes near a site. Dissolved solids, sodium, and sulfate concentrations in the water from Bear Butte Creek near Deadwood, 06437020, display increases during 1996 and 1997 (fig. 42). In January 1996, the DENR issued a permit for mining in the Strawberry Creek Basin (South Dakota Department of Environment and Natural Resources, 1998), a tributary immediately upstream of the Bear Butte Creek site. Increases in sodium and sulfate may indicate that mining and reclamation activities were affecting the stream. A mining area in the Strawberry Creek Basin recently has been listed on the Superfund National Priorities List (South Dakota Department of Environment and Natural Resources, 2001).
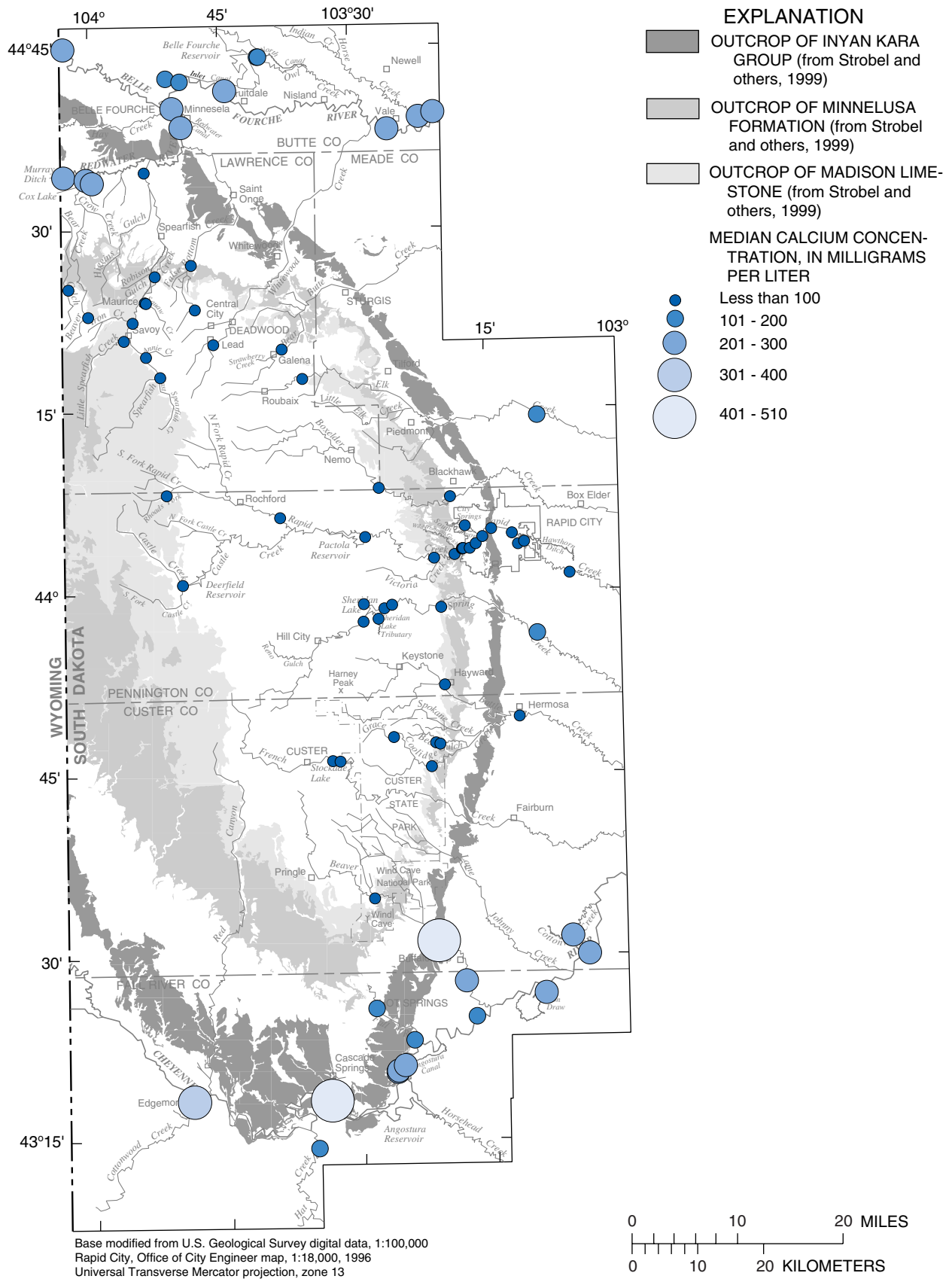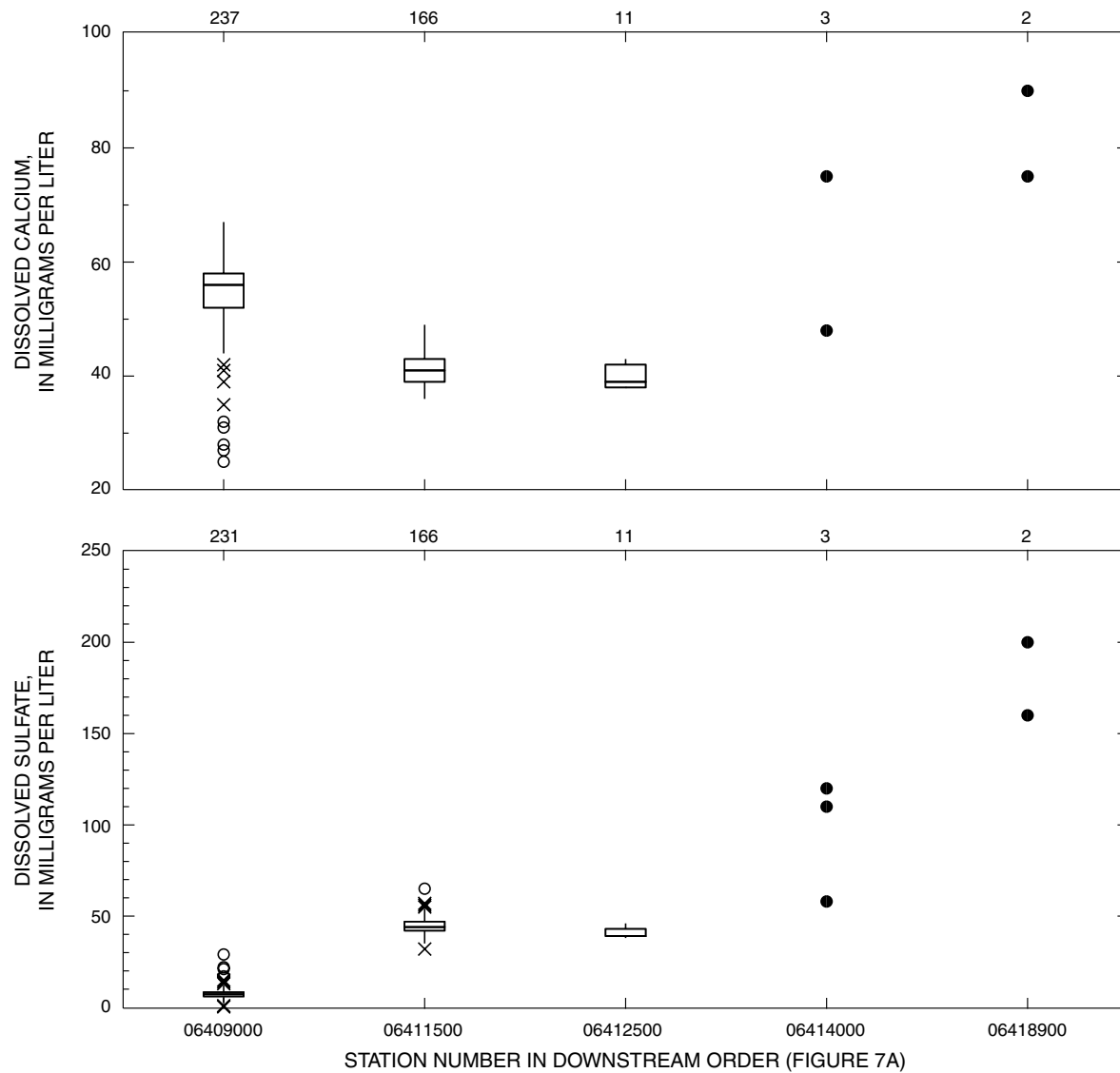
Figure 38. Spatial distribution of median calcium concentrations in surface water.
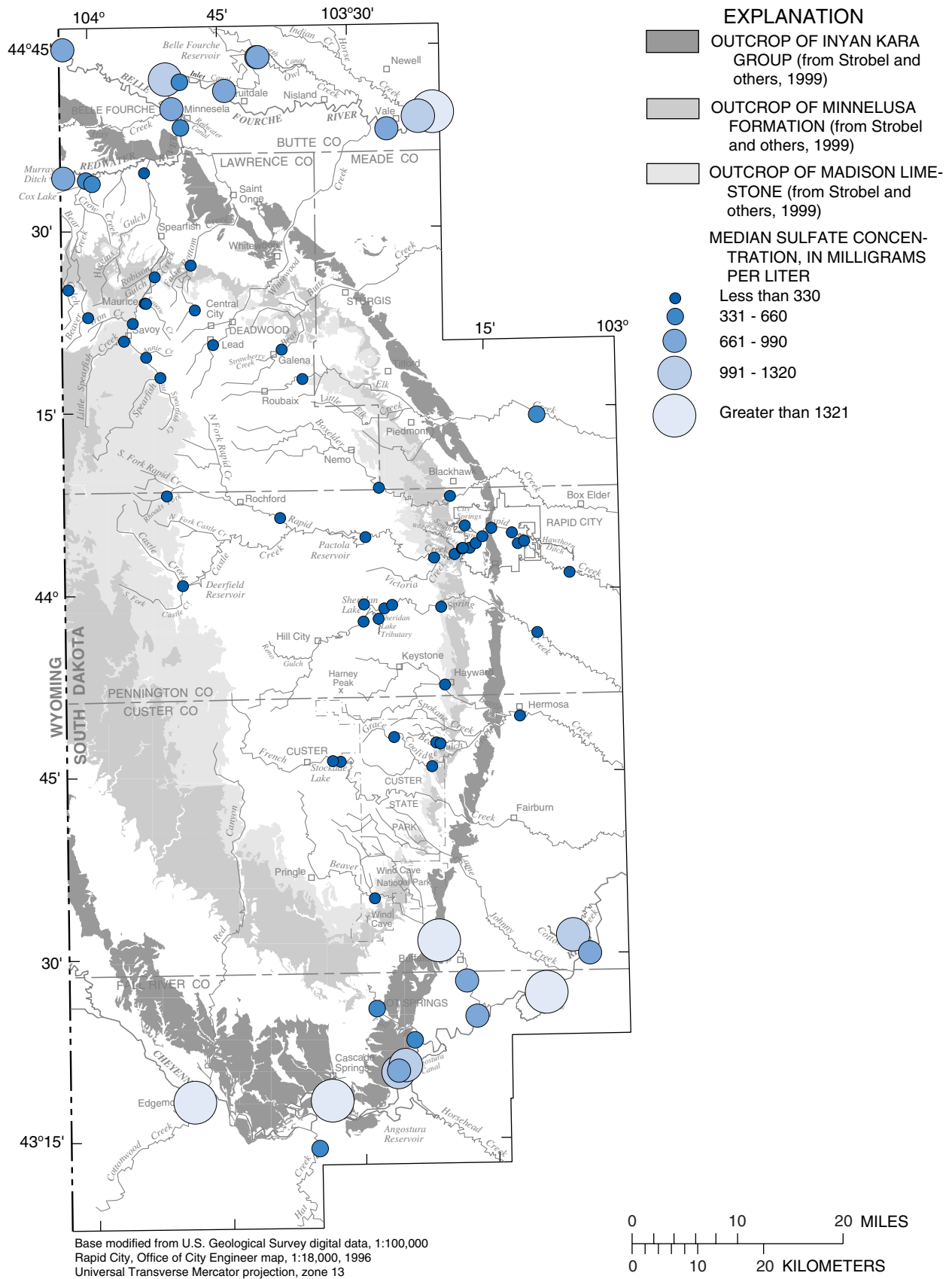
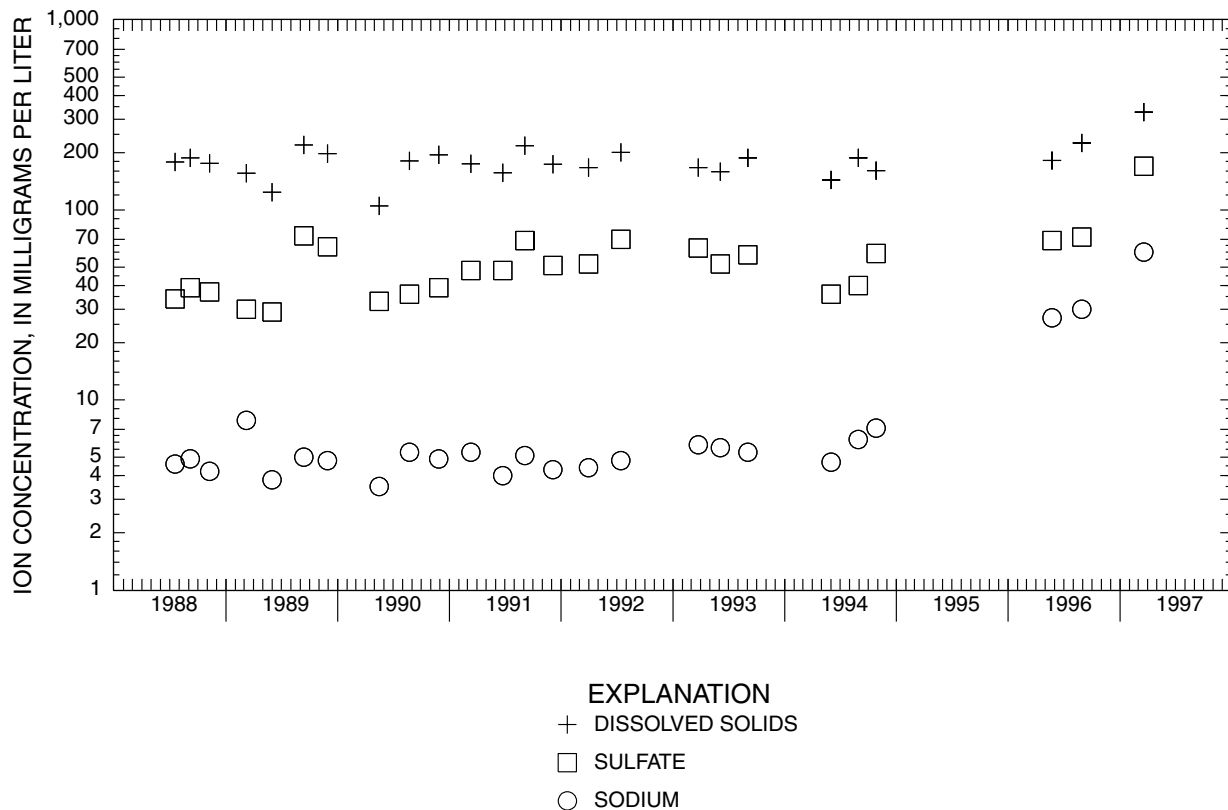**Figure 39.** Spatial distribution of median sulfate concentrations in surface water.
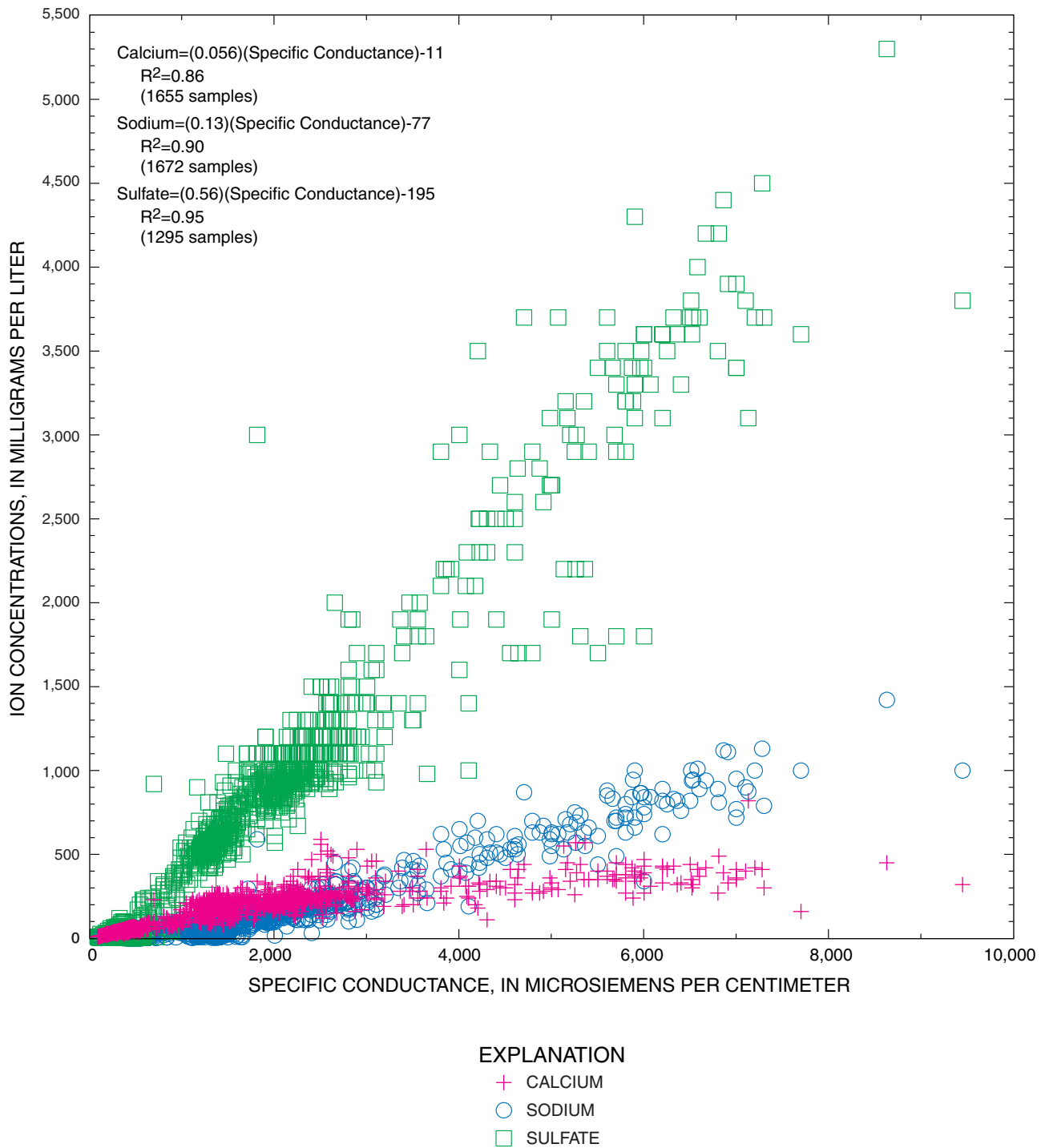
Figure 40. Relation between specific conductance and calcium, sodium, and sulfate concentrations in surface water.

Figure 41. Boxplots of selected ions for selected surface-water sites in Rapid Creek Basin.

Figure 42. Changes in selected ions at Bear Butte Creek near Deadwood (06437020), 1988-97.

Nutrients

Nitrogen occurs in surface water as nitrite (NO_2^-), nitrate (NO_3^-), and as ammonium (NH_4^+), as well as other oxidation states. Nitrate is the form most commonly found in oxygenated surface waters. Nitrate concentrations in drinking water above 10 mg/L (U.S. Environmental Protection Agency, 1994a) can cause methemoglobinemia (blue-baby syndrome) in small children. Some sources of nitrate in water include septic systems, barnyards where animals are confined to small areas, fertilizers, impacts from mining including explosives and the breakdown of cyanide, as well as nitrification associated with in-stream riparian systems.

Summary statistics for selected nutrients are presented in table 12, and the significance of the various nutrients is described in table 1. Boxplots are presented in figure 43 for selected nutrients.

Group Comparisons

Nutrient concentrations for headwater springs are relatively low with most concentrations of nitrite below the laboratory reporting limit, and nitrate and nitrite plus nitrate concentrations much less than the MCL of 10 mg/L. For all sites, ammonia concentrations generally are low (less than 1 mg/L), with a few concentrations greater than 1 mg/L at exterior sites. Phosphate and orthophosphate concentrations generally also are less than 1 mg/L. Nutrient concentrations for crystalline core sites generally are higher than headwater springs but similar in magnitude to the other groups. The crystalline core sites do, however, have several nitrate and nitrite plus nitrate concentrations that exceed the MCL. The high concentrations are from Annie Creek near Lead (06430800). Nitrite plus nitrate concentrations at Annie Creek increased during the 1990's (fig. 44), with the highest concentrations in 1995 and 1996. Johnson (1992) concluded that mining effects were the cause of the higher nitrate levels in Annie Creek. Denitrification facilities were put in place within the Annie Creek Basin in 1997. Various levels of nitrate reduction by these facilities have been achieved (South Dakota Department of Environment and Natural Resources, 1998b).
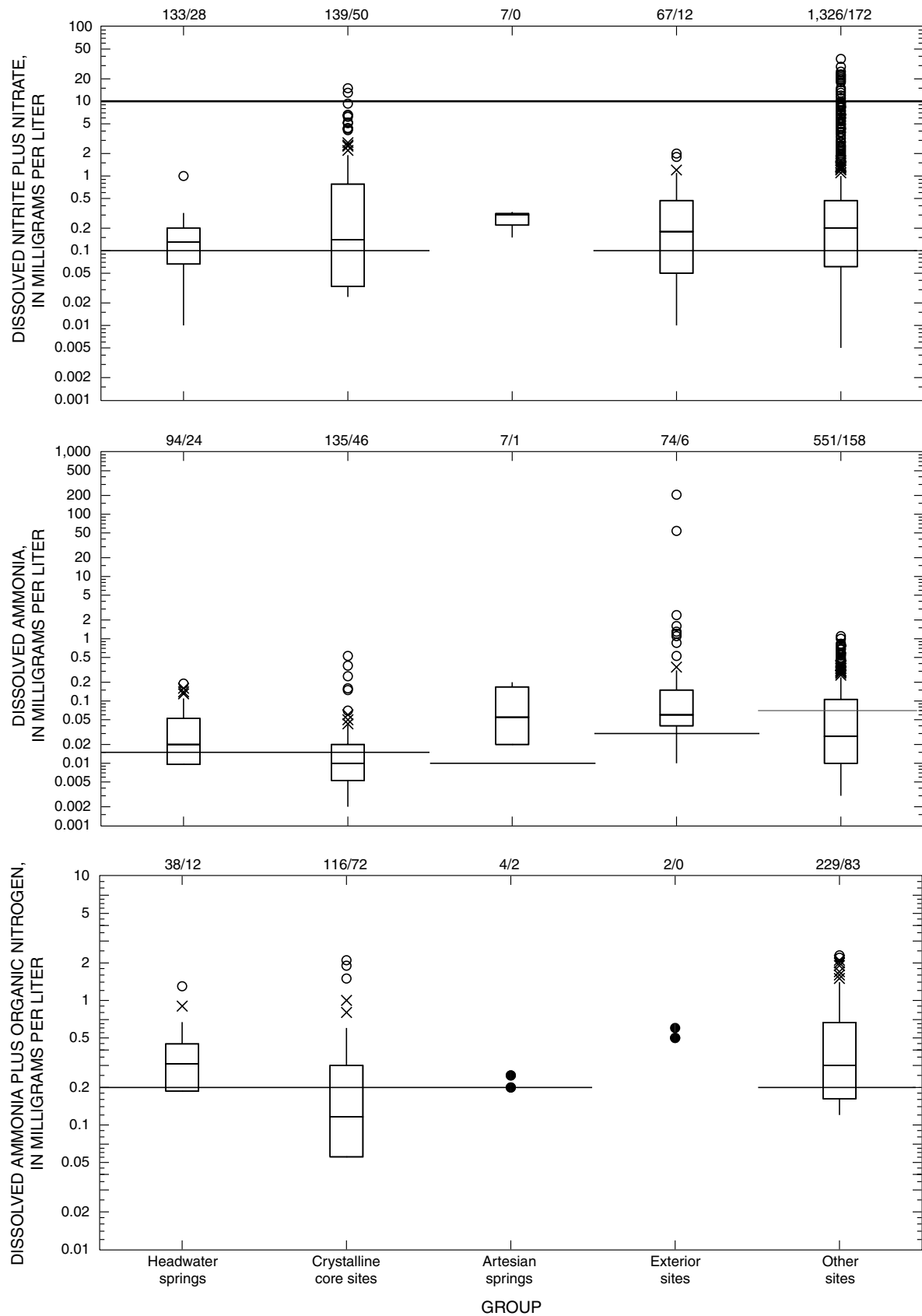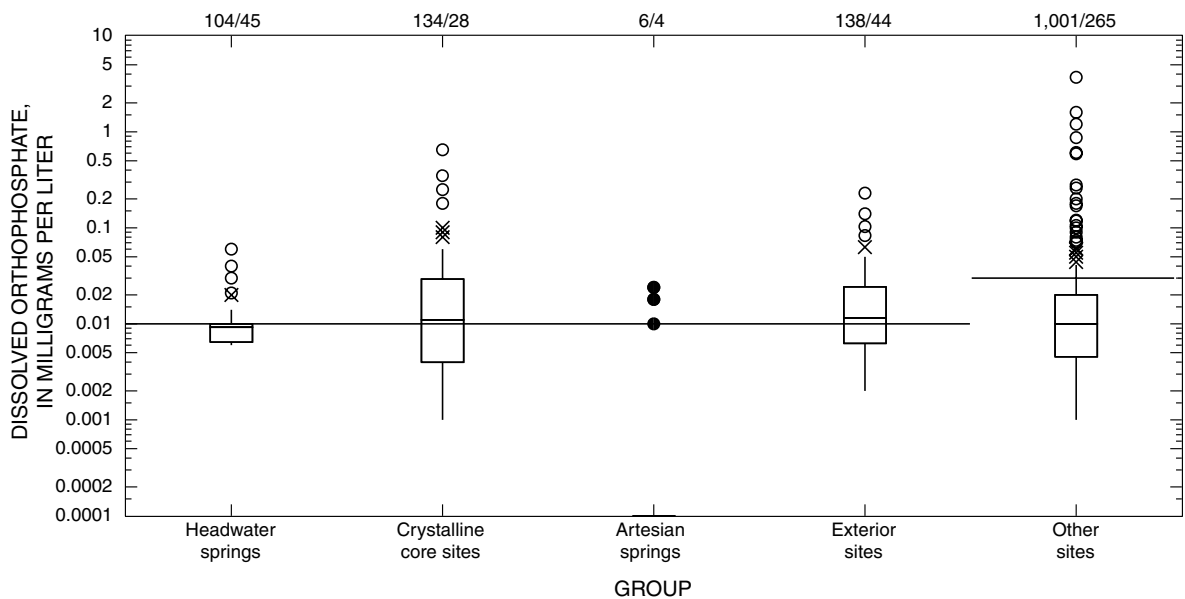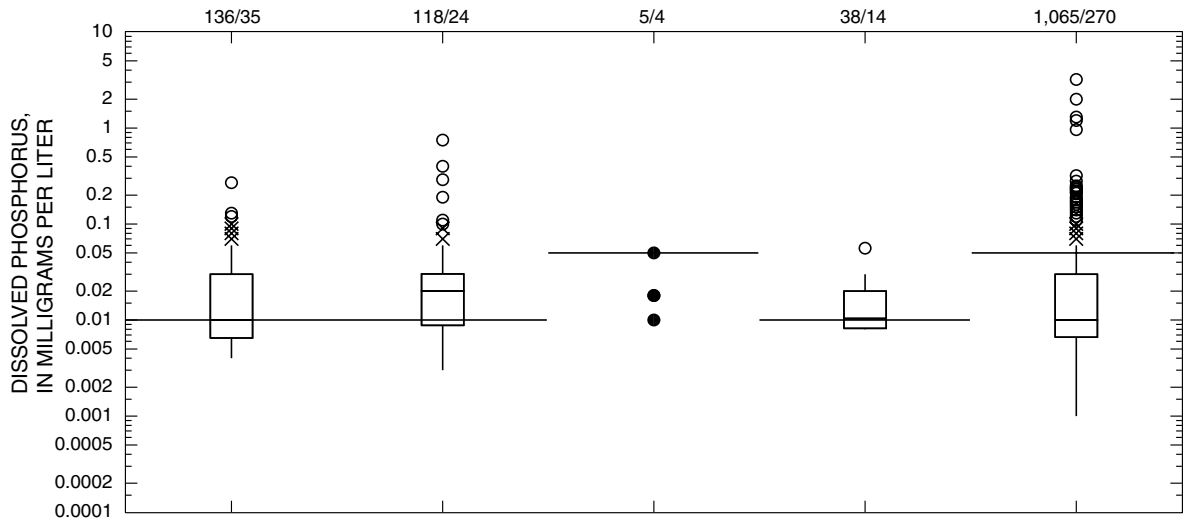
Figure 43. Boxplots of concentrations of selected nutrients by surface-water group.

Figure 43. Boxplots of concentrations of selected nutrients by surface-water group.--Continued

Table 12. Summary of concentrations of nutrients in surface water by group

[Results based on data stored in U.S. Geological Survey National Water Information System water-quality database. Results in milligrams per liter. One milligram per liter is approximately equal to one part per million; --, not analyzed or determined; <, less than]

Dissolved constituent	Number of samples	Number of censored samples	Mean	Median	Minimum	Maximum
Headwater springs						
Nitrate, as N	30	0	0.174	0.18	0.01	0.41
Nitrite, as N	62	54	[1]--	[1]--	<0.01	<0.05
Nitrite plus nitrate, as N	133	28	0.141	0.13	0.01	1
Ammonia, as N	94	24	0.034	0.02	<0.01	0.19
Ammonia plus organic nitrogen, as N	38	12	0.355	0.31	<0.2	1.3
Phosphorus, as P	136	35	0.023	0.01	0.004	0.27
Orthophosphate, as P	104	45	0.012	0.009	0.006	0.06
Crystalline core sites						
Nitrate, as N	20	0	1.588	0.139	0.019	14.1
Nitrite, as N	114	92	[1]--	[1]--	0.001	0.93
Nitrite plus nitrate, as N	139	50	0.950	0.14	<0.005	15
Ammonia, as N	135	46	0.026	0.01	<0.002	0.53
Ammonia plus organic nitrogen, as N	116	72	0.213	0.116	<0.2	2.1
Phosphorus, as P	118	24	0.036	0.02	0.003	0.75
Orthophosphate, as P	134	28	0.027	0.011	<0.001	0.65
Artesian springs						
Nitrate, as N	0	0	--	--	--	--
Nitrite, as N	6	6	[1]--	[1]--	<0.01	<0.01
Nitrite plus nitrate, as N	7	0	0.265	0.302	0.15	0.33
Ammonia, as N	7	1	0.081	0.055	<0.01	0.2
Ammonia plus organic nitrogen, as N	4	2	[1]--	[1]--	<0.2	0.25
Phosphorus, as P	5	4	[1]--	[1]--	<0.01	0.05
Orthophosphate, as P	6	4	[1]--	[1]--	<0.01	0.024
Exterior sites						
Nitrate, as N	36	0	0.365	0.205	0.01	2
Nitrite, as N	25	16	0.007	0.006	<0.01	0.03
Nitrite plus nitrate, as N	67	12	0.359	0.18	0.01	2
Ammonia, as N	74	6	3.708	0.06	<0.01	206
Ammonia plus organic nitrogen, as N	2	0	0.55	0.55	0.5	0.6
Phosphorus, as P	38	14	0.016	0.010	0.008	0.056
Orthophosphate, as P	138	44	0.020	0.012	0.002	0.23
Other sites						
Nitrate, as N	171	0	0.716	0.233	0.003	29
Nitrite, as N	312	182	0.008	0.004	<0.001	0.16
Nitrite plus nitrate, as N	1326	172	0.821	0.2	<0.005	37
Ammonia, as N	551	158	0.083	0.027	<0.002	1.1
Ammonia plus organic nitrogen, as N	229	83	0.464	0.3	0.12	2.3
Phosphorus, as P	1065	270	0.033	0.01	<0.001	3.2
Orthophosphate, as P	1001	265	0.027	0.01	<0.001	3.7

[1]Percent of censored values is greater than 80 percent. Mean and median are not reported because they are unreliable.
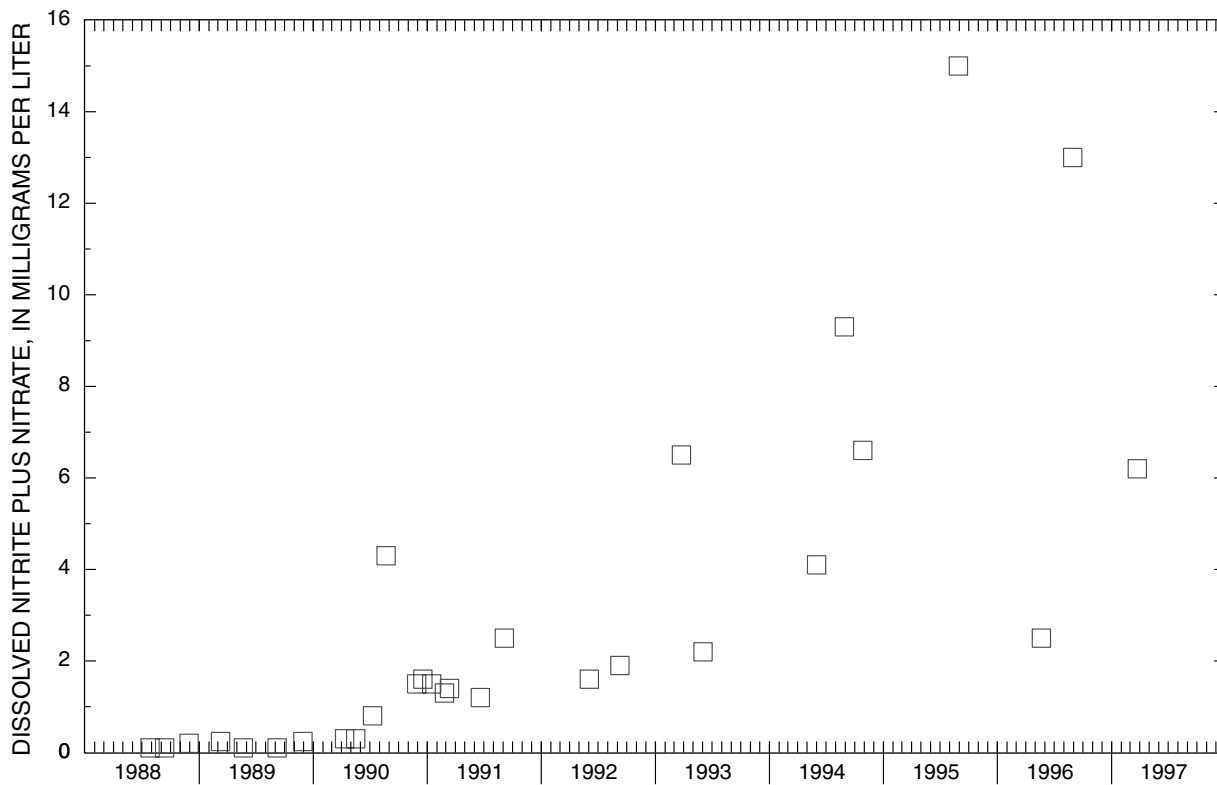
Figure 44. Nitrite plus nitrate concentrations in Annie Creek near Lead (06430800), 1988-97.

Based on a relatively limited data set, nutrient concentrations from the artesian springs are similar to other hydrogeologic settings. With ground water (primarily from the Madison and/or Minnelusa aquifers) as the source for these springs, the low nutrient concentrations provide an indication that at least for these limited sites, impacts from septic systems, mining, or other nutrient contamination sources are not currently taking place to the ground-water system. Because major sources of recharge to these regional aquifers are the outcrop areas upstream from these springs, contamination is a concern, including continued urban development and the placement of rural septic systems. Delineation of source-water protection areas and education are ongoing efforts by State and local governmental agencies.

Exterior sites have low nutrient concentrations with the exception of a few high ammonia concentrations. The two ammonia concentrations above 5 mg/L were from the Cheyenne River at Edgemont (06395000) during January and February of 1975. Both concentrations (54 mg/L and 206 mg/L) are more than two orders of magnitude higher than monthly samples collected prior to and after these samples. Possible causes of high ammonia concentrations could be related to stagnant/semi-stagnant conditions under ice, which causes reducing conditions. With reducing conditions, ammonia would be the end-product of the breakdown of organic material in the sediments. The corresponding pH values were the lowest of record for this site, which would be consistent with consumption of oxygen and dissolution of carbon dioxide.

The majority of nutrient concentrations from the other-sites group are similar to concentrations from the hydrogeologic setting groups. Some high nitrate and nitrite plus nitrate concentrations occurred at Horse Creek near Vale (06436800) during the 1970's, but concentrations decreased by the early 1980's (fig. 45). It is unknown if these levels were due to irrigation or farming practices during that time period. Horse Creek drains a portion of the irrigated lands that are part of the Belle Fourche Irrigation Project. Further sampling during the late 1980's and early 1990's at Horse Creek above Vale (06436760), which is located about 1.5 miles upstream, indicated concentrations similar to those from the early 1980's at Horse Creek near Vale. Slight seasonal trends are apparent at the Horse Creek above Vale site with higher concentrations during late fall and winter when ground-water discharge from alluvial aquifers likely would constitute most of the

streamflow. Additionally, relatively high nitrate levels are not uncommon to the shales in western South Dakota (South Dakota Department of Environment and Natural Resources, 2000).

Additional Comparisons

Nutrient concentrations in Rapid Creek generally are low but do show a slight increase with distance downstream and a notable increase in nitrite plus nitrate and orthophosphate from samples at Rapid Creek near Farmingdale (06421500) (fig. 46). Limited data exist between just above Rapid City to Farmingdale for orthophosphates, so increases may be more gradual than indicated by the data. Trends indicate that urbanization and/or agricultural practices may be affecting Rapid Creek, although concentrations are relatively low.
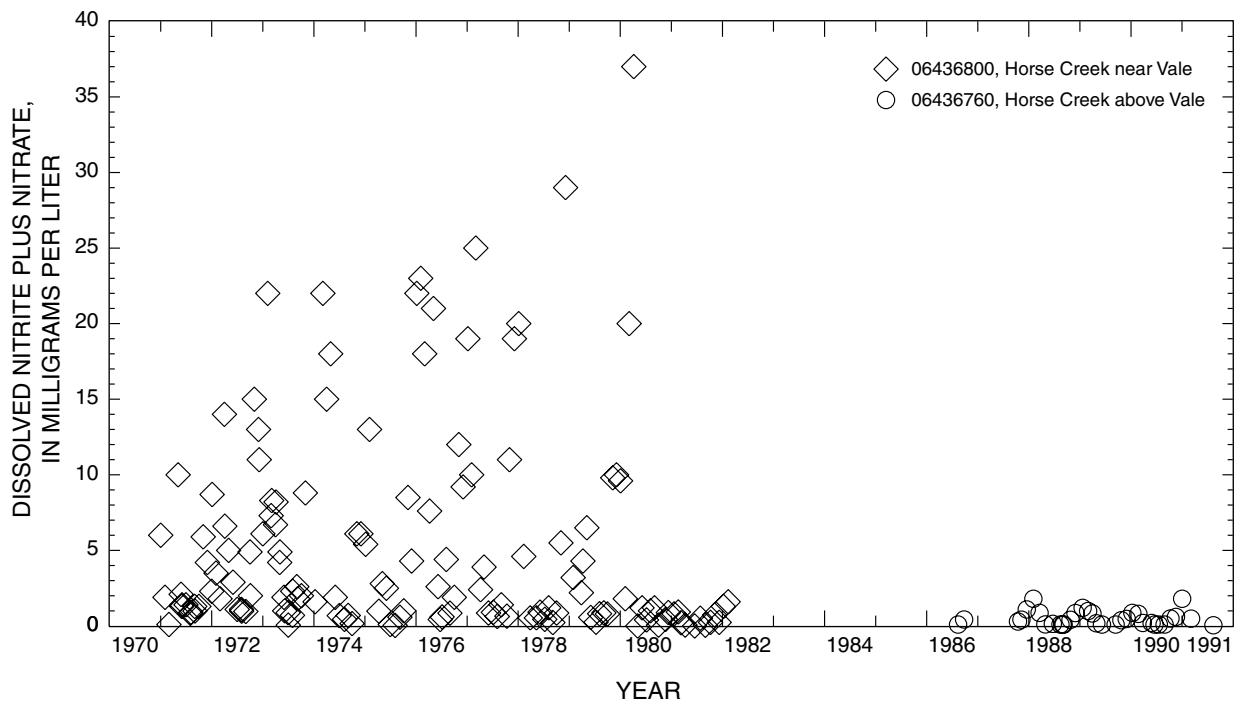
Figure 45. Nitrite plus nitrate concentrations at Horse Creek near Vale (06436800) and Horse Creek above Vale (06436760).
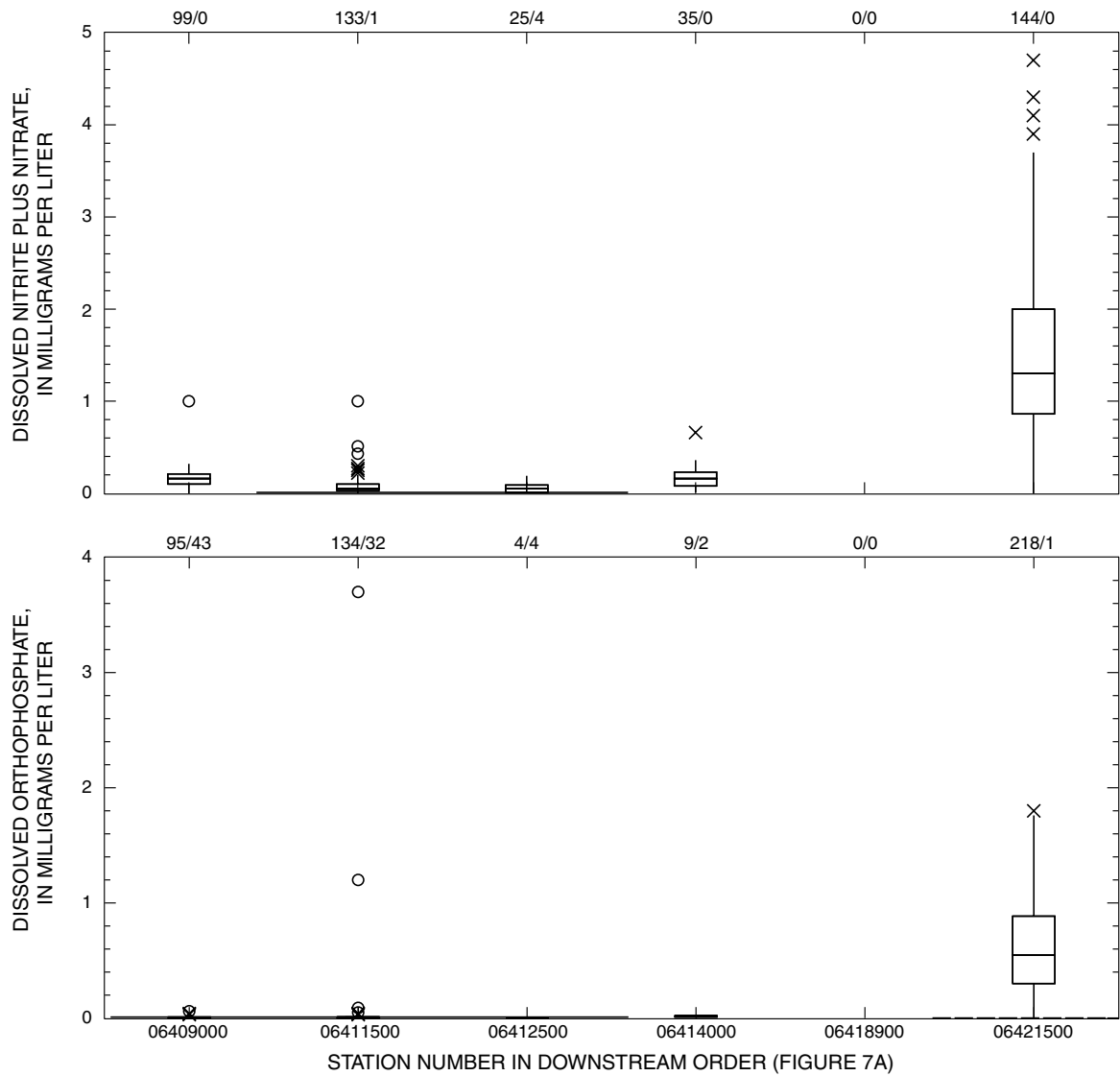
Figure 46. Boxplots of selected nutrients for selected surface-water sites in Rapid Creek Basin.