Water-Quality Trend Analysis and Sampling Design for Streams in North Dakota, 1971-2000

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By Aldo V. Vecchia

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Abstract

This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the North Dakota Department of Health, to analyze historical water-quality trends in selected dissolved major ions, nutrients, and dissolved trace metals for 10 streams in southwestern and eastern North Dakota and to develop an efficient sampling design to monitor future water-quality trends. A time-series model for daily streamflow and constituent concentration was used to identify significant concentration trends, separate natural hydroclimatic variability in concentration from variability that could have resulted from anthropogenic causes, and evaluate various sampling designs to monitor future water-quality trends.

The interannual variability in concentration as a result of variability in streamflow, referred to as the annual concentration anomaly, generally was high for all constituents and streams used in the trend analysis and was particularly sensitive to the severe drought that occurred in the late 1980's and the very wet period that began in 1993 and has persisted to the present (2002). Although climatic conditions were similar across North Dakota during the trend-analysis period (1971-2000), significant differences occurred in the annual concentration anomalies from constituent to constituent and location to location, especially during the drought and the wet period.

Numerous trends were detected in the historical constituent concentrations after the annual concentration anomalies were removed. The trends within each of the constituent groups (major ions, nutrients, and trace metals) showed general agreement among the streams. For most locations, the largest dissolved major-ion concentrations occurred during the late 1970's and concentrations in the mid- to late 1990's were smaller than concentrations during the late 1970's. However, the largest concentrations for three of the Missouri River tributaries and one of the Red River of the North tributaries occurred during the mid- to late 1990's.

Concentration trends for total ammonia plus organic nitrogen showed close agreement among the streams for which that constituent was evaluated. The largest concentrations occurred during the early 1980's, and the smallest concentrations occurred during the early 1990's. Nutrient data were not available for the early 1970's or late 1990's. Although a detailed analysis of the causes of the trends was beyond the scope of this report, a preliminary analysis of cropland, livestock-inventory, and oil-production data for 1971-2000 indicated the concentration trends may be related to the livestock-inventory and oil-production activities in the basins.

Dissolved iron and manganese concentrations for the southwestern North Dakota streams generally remained stable during 1971-2000. However, many of the recorded concentrations for those streams were less than the detection limit, and trends that were masked by censoring may have occurred. Several significant trends were detected in dissolved iron and manganese concentrations for the eastern North Dakota streams. Concentrations for those streams either remained stable or increased during most of the 1970's and then decreased rapidly for about 2 years beginning in the late 1970's. The concentrations were relatively stable from the early 1980's to 2000 except at two locations where dissolved iron concentrations increased during the early 1990's.

The most efficient overall sampling designs for the detection of annual trends (that is, trends that occur uniformly during the entire year) consisted of balanced designs in which the sampling dates and the number of samples collected remained fixed from year to year and in which the samples were collected throughout the year

rather than in a short timespan. The best overall design for the detection of annual trends consisted of three samples per year, with samples collected near the beginning of December, April, and August. That design had acceptable sensitivity for the detection of trends in most constituents at all locations. Little improvement in sensitivity was achieved by collecting more than three samples per year.

The sampling designs that were first evaluated for annual trends also were evaluated with regard to their sensitivity to detect seasonal trends that occurred during three seasons--April through August, August through December, and December through April. Design results indicated that an average of one extra sample per station per year resulted in an efficient design for detecting seasonal trends. However, allocation of the extra samples varied depending on the station, month, and constituent group (major ions, nutrients, and trace metals).

INTRODUCTION

The quality of water in streams in North Dakota is important for human-health, ecological, aesthetic, and recreational concerns. Increasingly complex management decisions require water-quality monitoring programs that provide data for multiple purposes, including trend analyses to detect improvement or deterioration in water quality with time. Water-quality trend monitoring is necessary to determine if water quality has consistently improved, deteriorated, or remained constant over long (decadal) time scales, to determine if water quality has changed significantly because of natural or anthropogenic causes, and to explore potential causal mechanisms for water-quality changes.

The need to monitor water-quality trends must be balanced against the cost of obtaining the necessary data. The costs of water-quality sampling and laboratory analysis have increased in recent years, but the budgets for long-term water-quality monitoring in North Dakota have decreased. Therefore, to monitor potential future water-quality trends at the lowest cost, an efficient sampling design is needed for streams in North Dakota.

This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the North Dakota Department of Health, to analyze the historical water-quality trends in selected constituents and selected streams in North Dakota and to develop an efficient sampling design to monitor future trends. The constituents evaluated in this report include four dissolved major ions (calcium, sodium, sulfate, and chloride), two nutrients (total ammonia plus organic nitrogen and total phosphorus), and two dissolved trace metals (iron and manganese). The constituents were evaluated for 10 streams in North Dakota, including 5 tributaries of the Missouri River (the Little Missouri, Knife, Heart, Cannonball, and James Rivers) and 5 tributaries of the Red River of the North (the Wild Rice, Sheyenne, Maple, Goose, and Park Rivers). The dissolved major ions and trace metals were evaluated for all 10 streams, and the nutrients were evaluated for 5 streams (the Little Missouri, Knife, Heart, Cannonball, and Sheyenne Rivers). Too few recorded nutrient data were available to evaluate the constituents for the remaining five streams.

The water-quality trend analysis and sampling-design results are based on constituent-concentration and streamflow data for 1971-2000. The data were obtained from the U.S. Geological Survey National Water Information System (NWIS) and were collected through many Federal, State, and local programs, including the U.S. Geological Survey National Stream Water Quality Accounting Network (NASQAN), the Hydrologic Benchmark Network, the National Water Quality Assessment Program (NAWQA), and ongoing cooperative water programs with the North Dakota Department of Health, the North Dakota State Water Commission, and other State and local agencies. Sample-collection techniques and laboratory analyses followed strict, well-documented U.S. Geological Survey protocols (Wilde and others, 1998).

Trends were interpreted in relation to natural hydroclimatic variability. In particular, natural variability in constituent concentrations as a result of variability in streamflow was identified and separated from variability that presumably resulted from anthropogenic causes. Potential anthropogenic causes of water-quality trends include changes in land use, agricultural practices, mining, oil and gas production, and population inside a basin and atmospheric deposition of pollutants from sources inside or outside a basin. Although a complete interpretation of detected trends in relation to anthropogenic causes was beyond the scope of this report, some potential causes for the trends are indicated for possible further investigation.

STATIONS SELECTED FOR TREND ANALYSIS

The locations of the 10 long-term U.S. Geological Survey streamflow-gaging stations selected for the trend analysis are shown in figure 1. Contributing drainage areas for the stations range from about 690 square miles for the Park River at Grafton, N. Dak., station to about 8,310 square miles for the Little Missouri River near Watford City, N. Dak., station (table 1). Streamflow at four of the stations is affected by reservoir regulation. Lake Tschida, completed in 1949, is upstream from the Heart River near Mandan, N. Dak., station; Jamestown Reservoir, completed in 1953, and Pipestem Reservoir, completed in 1973, are upstream from the James River at LaMoure, N. Dak., station; Lake Ashtabula, completed in 1949, is upstream from the Sheyenne River near Kindred, N. Dak., station; and Homme Reservoir, completed in 1950, is upstream from the Park River station. Although these reservoirs may have altered pre-regulated downstream water quality, they did not affect the trend analysis described in this report because no substantial changes in reservoir operation occurred during the trend-analysis period (1971-2000). Although minor changes in regulation or diversion practices may have occurred at some of the stations during the trend-analysis period, none of the changes were considered major enough to significantly change streamflow or water-quality characteristics during that period.
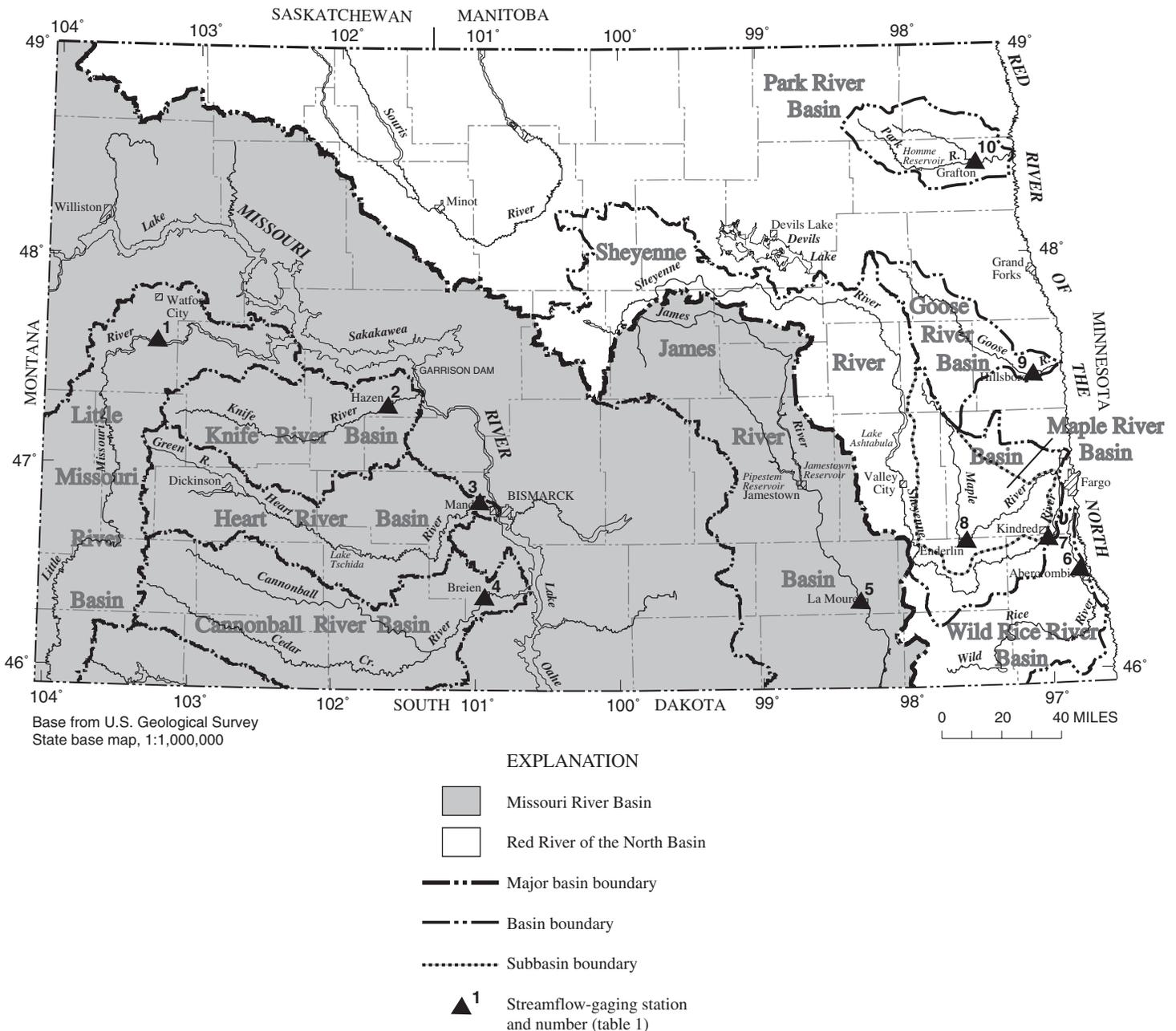
Figure 1. Locations of long-term U.S. Geological Survey streamflow-gaging stations selected for water-quality trend analysis.

Table 1. Streamflow-gaging stations selected for trend analysis

Map number (figure 1)	U.S. Geological Survey station number	Station name	Approximate contributing drainage area (square miles)	Latitude	Longitude	Major regulation
1	06337000	Little Missouri River near Watford City, N. Dak.	8,310	47°35'45"	103°15'45"	None
2	06340500	Knife River at Hazen, N. Dak.	2,240	47°17'07"	101°37'18"	None
3	06349000	Heart River near Mandan, N. Dak.	3,310	46°50'02"	100°58'27"	Lake Tschida
4	06354000	Cannonball River at Breien, N. Dak.	4,100	46°22'33"	100°56'03"	None
5	06470500	James River at LaMoure, N. Dak.	1,790	46°21'20"	98°18'15"	Jamestown Reservoir Pipestem Reservoir
6	05053000	Wild Rice River near Abercrombie, N. Dak.	1,490	46°28'05"	96°47'00"	None
7	05059000	Sheyenne River near Kindred, N. Dak.	3,020	46°37'54"	97°00'01"	Lake Ashtabula
8	05059700	Maple River near Enderlin, N. Dak.	800	46°37'18"	97°34'25"	None
9	05066500	Goose River at Hillsboro, N. Dak.	1,090	47°24'34"	97°03'39"	None
10	05090000	Park River at Grafton, N. Dak.	690	48°25'29"	97°24'42"	Homme Reservoir

CONCENTRATION AND STREAMFLOW DATA USED IN TREND ANALYSIS

The water-quality constituents selected for the trend analysis are given in table 2. The period of record chosen for the analysis was the 30-year period from January 1, 1971, through December 31, 2000. This was the longest period of record for which water-quality data were available for most stations. Nutrient data were not available for the early 1970's or the late 1990's, but the same historical period was used for all constituents regardless of the starting and ending dates of the water-quality sampling.

Table 2. Water-quality constituents selected for trend analysis

Constituent	Constituent number for report	Unit	National Water Information System parameter code
Calcium, dissolved	1	Milligrams per liter	00915
Sodium, dissolved	2	Milligrams per liter	00930
Sulfate, dissolved	3	Milligrams per liter	00945
Chloride, dissolved	4	Milligrams per liter	00940
Nitrogen, ammonia plus organic, total	5	Milligrams per liter	00625
Phosphorus, total	6	Milligrams per liter	00665
Iron, dissolved	7	Micrograms per liter	01046
Manganese, dissolved	8	Micrograms per liter	01056

The parametric time-series analysis procedure, or model, used in the trend analysis described in this report requires that, at most, three water-quality samples be included in the record for any one month and that the minimum spacing between any two consecutive sampling dates is 5 days. Thus, each month of the trend-analysis period was divided into three approximately 10-day intervals--the 1st day through the 10th day of the month, the 11th day through the 20th day of the month, and the 21st day through the end of the month. The number of samples for each station and each constituent then was reduced, if necessary, so data for no more than one sampling date were used during each 10-day interval and so at least 5 days separated each pair of sampling dates. Many of the stations had either no sampling dates or only one sampling date in any given month and, thus, no reduction in the number of samples was required. However, some of the stations had many sampling dates during the 1970's and early 1980's and some reduction in the number of samples was required.

A few nutrient samples and many trace-metal samples had concentrations that were less than the detection limit. Furthermore, the detection limit may have changed during the trend-analysis period. To ensure that changes in the detection limit did not cause false trends to be identified, concentrations that were less than or equal to the highest detection

limit in the record were set equal to the highest detection limit and treated as known concentrations. These concentrations actually are censored values (values that are known to be less than the detection limit but for which the exact value is not known). A moderate degree of censoring can be tolerated in the time-series analysis, but, as discussed in the "Water-Quality Trend Analysis" section of this report, care must be taken when interpreting trend results for censored data.

The number of samples for the concentration data and the number of censored values are given in table 3. The number of samples for the major ions ranged from less than 2 samples per year for many of the stations during various time intervals to about 17 samples per year for the Sheyenne River near Kindred, N. Dak., station during 1976-80. The largest number of samples for most stations was for 1976-80 when at least four samples per year were collected at each station. However, the number of samples generally decreased during the 1980's and early 1990's, and, during 1996-2000, two or fewer samples per year were collected at each station. No major-ion data were censored.

Table 3. Number of samples for concentration data and number of censored values

Map number (figure 1)	Station name	Number of samples for 1971-2000	Number of samples for						Number of censored values for 1971-2000
			1971-75	1976-80	1981-85	1986-90	1991-95	1996-2000	
Major ions (dissolved calcium, sodium, sulfate, and chloride)									
1	Little Missouri River near Watford City, N. Dak.	156	30	50	26	17	15	8	0
2	Knife River at Hazen, N. Dak.	144	27	48	24	19	16	10	0
3	Heart River near Mandan, N. Dak.	132	14	34	30	26	18	10	0
4	Cannonball River at Breien, N. Dak.	166	36	56	31	20	13	10	0
5	James River at LaMoure, N. Dak.	192	21	54	39	33	35	10	0
6	Wild Rice River near Abercrombie, N. Dak.	150	54	50	15	10	12	9	0
7	Sheyenne River near Kindred, N. Dak.	201	7	88	29	28	39	10	0
8	Maple River near Enderlin, N. Dak.	81	15	28	10	9	10	9	0
9	Goose River at Hillsboro, N. Dak.	80	17	24	8	10	12	9	0
10	Park River at Grafton, N. Dak.	70	12	20	9	9	11	9	0
Total ammonia plus organic nitrogen (detection limit of 0.2 milligram per liter)									
1	Little Missouri River near Watford City, N. Dak.	121	19	47	24	18	13	0	3
2	Knife River at Hazen, N. Dak.	134	18	60	25	19	12	0	4
3	Heart River near Mandan, N. Dak.	101	0	31	29	26	15	0	2
4	Cannonball River at Breien, N. Dak.	122	15	51	30	19	7	0	2
7	Sheyenne River near Kindred, N. Dak.	178	0	83	27	27	40	1	2
Total phosphorus (detection limit of 0.01 milligram per liter)									
1	Little Missouri River near Watford City, N. Dak.	125	19	50	25	18	13	0	4
2	Knife River at Hazen, N. Dak.	134	18	60	25	19	12	0	7
3	Heart River near Mandan, N. Dak.	102	0	32	29	26	15	0	27
4	Cannonball River at Breien, N. Dak.	127	15	56	30	19	7	0	8
7	Sheyenne River near Kindred, N. Dak.	179	0	84	27	27	40	1	0
Dissolved iron (detection limit of 10 micrograms per liter)									
1	Little Missouri River near Watford City, N. Dak.	91	19	17	19	14	14	8	12
2	Knife River at Hazen, N. Dak.	107	18	35	15	15	14	10	19
3	Heart River near Mandan, N. Dak.	72	14	12	14	11	11	10	26
4	Cannonball River at Breien, N. Dak.	105	27	18	22	17	11	10	36
5	James River at LaMoure, N. Dak.	88	20	9	6	17	26	10	30
6	Wild Rice River near Abercrombie, N. Dak.	52	9	6	8	10	10	9	9
7	Sheyenne River near Kindred, N. Dak.	147	7	79	14	11	27	9	46
8	Maple River near Enderlin, N. Dak.	79	13	28	10	9	10	9	5
9	Goose River at Hillsboro, N. Dak.	79	16	24	8	10	12	9	13
10	Park River at Grafton, N. Dak.	70	12	20	9	9	11	9	12

Table 3. Number of samples for concentration data and number of censored values—Continued

Map number (figure 1)	Station name	Number of samples for 1971-2000	Number of samples for						Number of censored values for 1971-2000
			1971-75	1976-80	1981-85	1986-90	1991-95	1996-2000	
	Dissolved manganese (detection limit of 10 micrograms per liter)								
1	Little Missouri River near Watford City, N. Dak.	95	19	17	19	17	15	8	61
2	Knife River at Hazen, N. Dak.	99	18	20	16	19	16	10	18
3	Heart River near Mandan, N. Dak.	90	14	12	21	18	15	10	66
4	Cannonball River at Breien, N. Dak.	112	27	18	24	20	13	10	41
5	James River at LaMoure, N. Dak.	116	20	9	9	33	35	10	0
6	Wild Rice River near Abercrombie, N. Dak.	55	10	6	8	10	12	9	9
7	Sheyenne River near Kindred, N. Dak.	173	7	79	20	20	37	10	24
8	Maple River near Enderlin, N. Dak.	81	15	28	10	9	10	9	0
9	Goose River at Hillsboro, N. Dak.	80	17	24	8	10	12	9	3
10	Park River at Grafton, N. Dak.	69	12	19	9	9	11	9	5

The number of samples for total ammonia plus organic nitrogen was largest during 1976-80 when at least six samples per year were collected at each station. Then, the number of samples steadily decreased until sampling was discontinued in the mid-1990's. The number of censored values for total ammonia plus organic nitrogen was less than 3 percent for all stations for which that constituent was evaluated.

The number of samples for total phosphorus was similar to the number of samples for total ammonia plus organic nitrogen. Except for the Heart River near Mandan, N. Dak., station, the number of censored values for total phosphorus was less than 7 percent for all stations. For the Heart River station, about 26 percent of the values were less than the detection limit of 0.01 milligram per liter.

The number of samples for iron ranged from two to four samples per year for most stations during the trend-analysis period, but some stations had a larger number of samples. The smallest number of samples generally was for 1996-2000 when two or fewer samples per year were collected at each station. Many iron concentrations were censored at a detection limit of 10 micrograms per liter. The smallest number of censored values was for the Maple River near Enderlin, N. Dak., station where about 6 percent of the recorded values were less than the detection limit, and the largest number of censored values was for the Heart River, Cannonball River at Breien, and James River at LaMoure, N. Dak., stations where about 35 percent of the values were less than the detection limit.

The number of samples for manganese was similar to the number of samples for iron. The James and Maple River stations had no censored values, and the Goose River at Hillsboro and Park River at Grafton, N. Dak., stations had fewer than 10 percent censored values. The largest number of censored values was for the Heart River station where about 73 percent of the recorded values were less than the detection limit.

Streamflow is an important variable in the analysis of water-quality trends because much of the variability in concentration is caused by variability in streamflow. Identifying and removing the streamflow-related variability in concentration increases the ability to detect trends in the presence of streamflow-related variability. Therefore, in the time-series analysis procedure used in this report, each month was divided into three approximately 10-day intervals as described previously for the concentration data, and each interval was assigned a streamflow value in the following manner. If a water-quality sample was available for a given interval, the streamflow value assigned for the interval was the mean daily streamflow for the day the water-quality sample was collected. If no water-quality sample was available for the interval, the streamflow value assigned for the interval was the mean daily streamflow for the 5th, 15th, or 25th day of the month, depending on whether the interval corresponded to the beginning, middle, or end of the month. Thus, a streamflow time series that consisted of 3 values per month, or 36 values per year, was obtained for each station. In contrast to the concentration time series, which was missing values for most intervals, the streamflow time series had values for each interval. The streamflow values used in the trend analysis are shown in figure 2. Values that were less than 0.1 cubic foot per second were set equal to 0.1 because the time-series analysis requires a logarithmic transformation of the values.
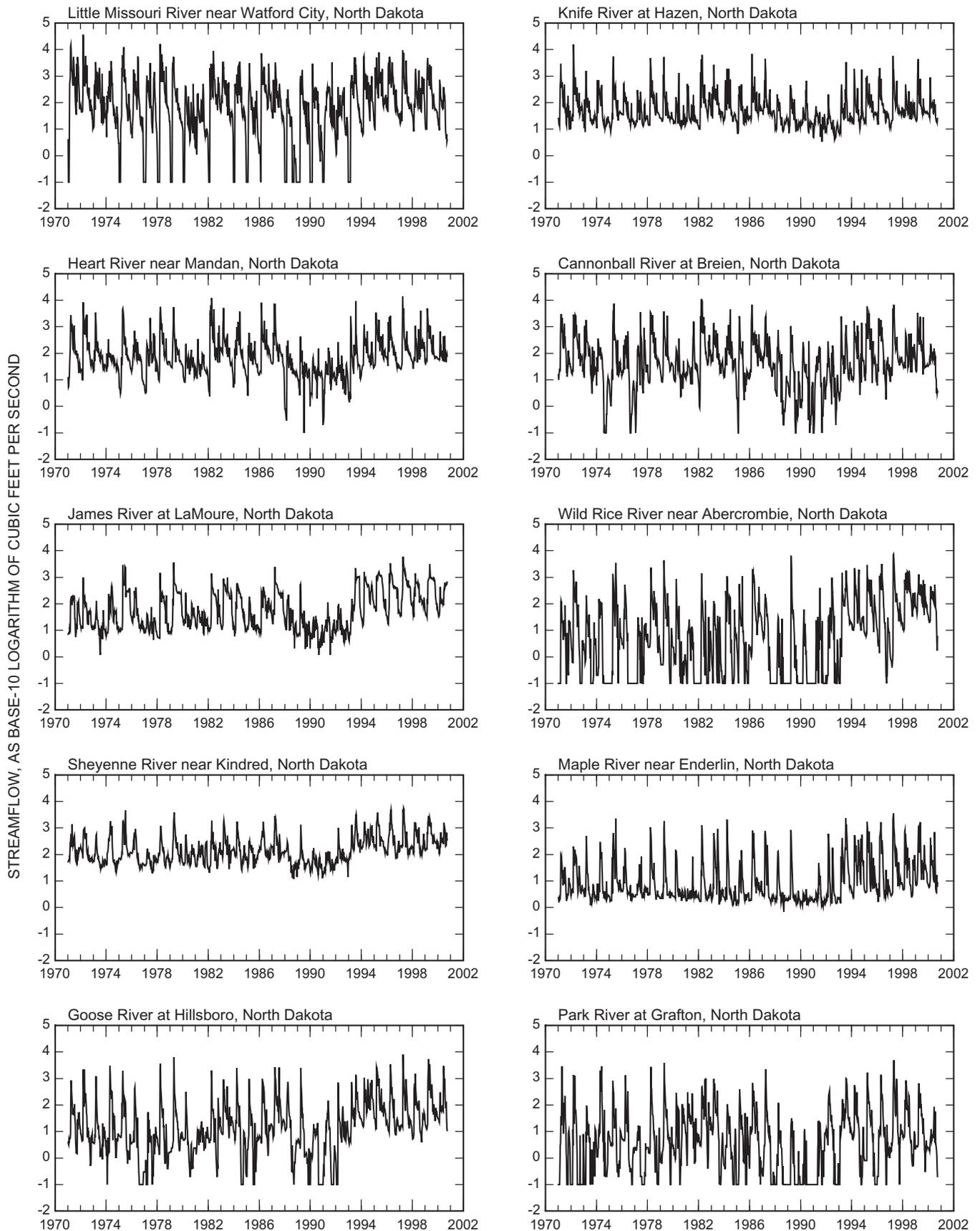
Figure 2. Daily streamflow for 1971-2000 (three values per month) for streamflow-gaging stations used in water-quality trend analysis.

TIME-SERIES MODEL USED IN TREND ANALYSIS

A parametric time-series analysis procedure was used in this report to detect the trends in constituent concentrations. The approach is described by Vecchia (2000) and has been used in other trend-analysis studies (Jones and Armstrong, 2001; Trench and Vecchia, 2002; Medalie and Smeltzer, in press). A brief description of the time-series model used is included in this section, and details on the theory and parameter estimation for the model are given in Vecchia (2000, appendix A).

To separate the natural variability in concentration as a result of variability in streamflow from the variability in concentration as a result of other factors (such as anthropogenic causes), the base-10 logarithm of daily streamflow for each station was divided into four components--a long-term mean, an annual streamflow anomaly, a seasonal streamflow anomaly, and a daily streamflow anomaly. The four components were defined as follows:

$$X(t) = M_x + A_x(t) + S_x(t) + U(t) \tag{1}$$

where

$X(t)$ is the base-10 logarithm of daily streamflow, in cubic feet per second, for time t;

t is time, in decimal years;

M_x is the mean of $X(t)$ for $1971 < t < 2001$, as base-10 logarithm of cubic feet per second;

$A_x(t)$ is the annual streamflow anomaly (dimensionless) for time t;

$S_x(t)$ is the seasonal streamflow anomaly (dimensionless) for time t; and

$U(t)$ is the daily streamflow anomaly (dimensionless) for time t.

The annual streamflow anomaly was computed by applying a 1-year centered moving average to $X(t) - M_x$ and represents annual variability in streamflow from the long-term mean. The seasonal streamflow anomaly was computed by fixing a particular time within the year and averaging $X(t) - M_x - A_x(t)$ for that time of year over all years in the record. The seasonal streamflow anomaly represents seasonal variability in streamflow from the annual mean. The daily streamflow anomaly was computed by subtracting $M_x + A_x(t) + S_x(t)$ from $X(t)$ and represents daily variability in streamflow from the annual and seasonal anomalies.

The annual streamflow anomalies for each station are shown in figure 3. A high degree of spatial coherence is evident in the annual anomalies, indicating that annual climatic conditions tend to be similar throughout North Dakota. The State experienced a severe drought from about 1988 to 1992, and annual streamflow was much less than normal during that period. A very wet period began in about 1993 and has persisted to the present (2002) as indicated by the consistently high annual streamflow anomalies from 1993 to 2001. The recent wet conditions are particularly strong in southeastern North Dakota--annual streamflows for the James, Wild Rice, Sheyenne, Maple, and Goose Rivers were much greater during 1993-2000 than for any period from 1971 to 1992.

As shown in figure 3, streamflow in North Dakota also is subject to a high degree of interannual variability. The annual streamflow anomalies for several stations ranged from less than -1 to greater than +1 base-10 logarithmic units, indicating that annual streamflow for those streams can range from less than one-tenth of normal to more than 10 times normal in any given year.

The seasonal streamflow anomalies (fig. 4) are similar for all stations. The highest streamflows generally occurred in late March or early April as a result of snowmelt or rainfall on snow or partially frozen soils. Streamflow generally receded from late April through September as snowmelt runoff diminished and net evaporation (evaporation minus precipitation) increased. Secondary peaks occurred at some stations in October or November from fall precipitation, but streamflow during September through February usually was low and consisted primarily of baseflow from ground water or reservoir discharge.
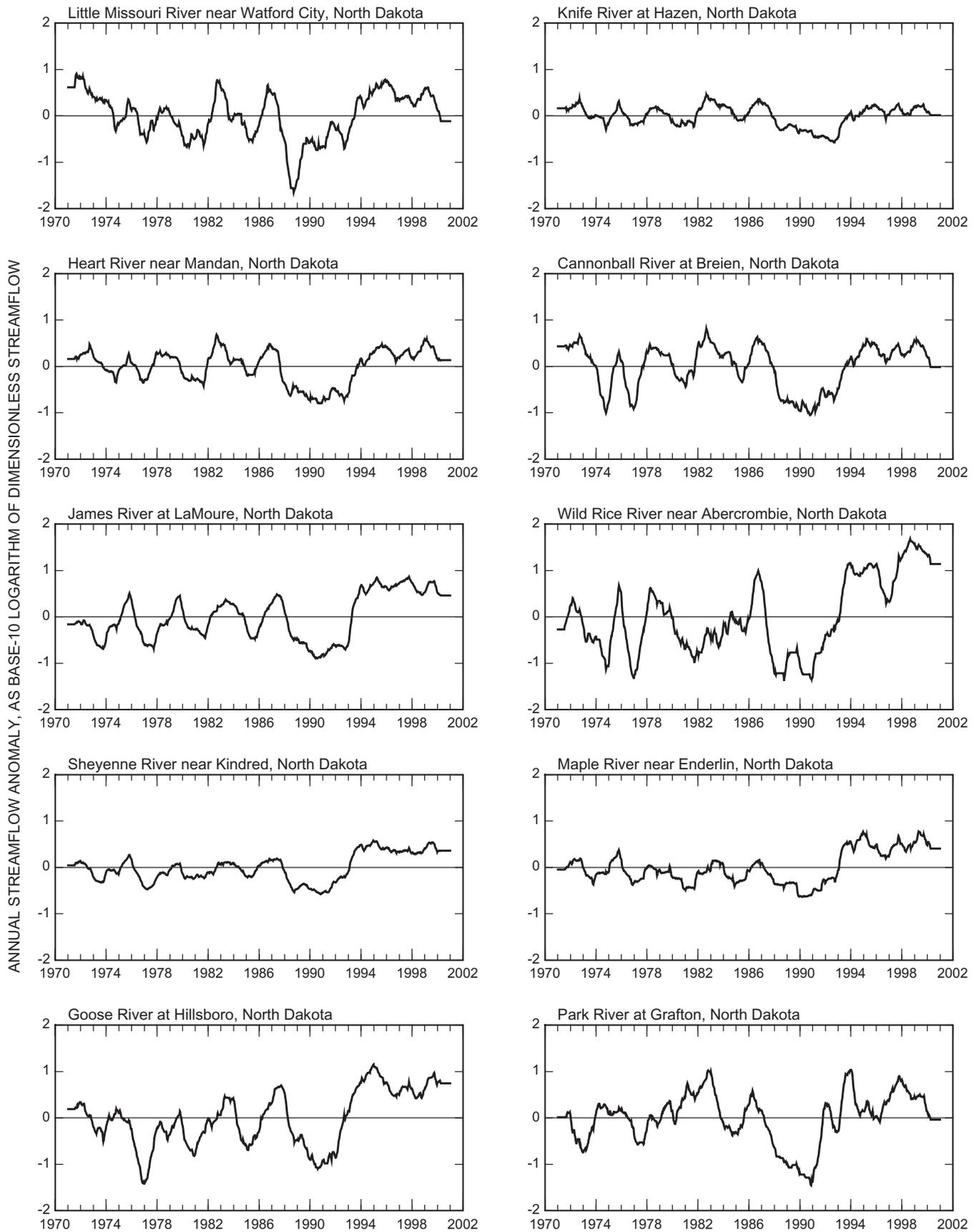
Figure 3. Annual streamflow anomalies for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Dimensionless streamflow is daily streamflow divided by the long-term geometric mean of daily streamflow.]
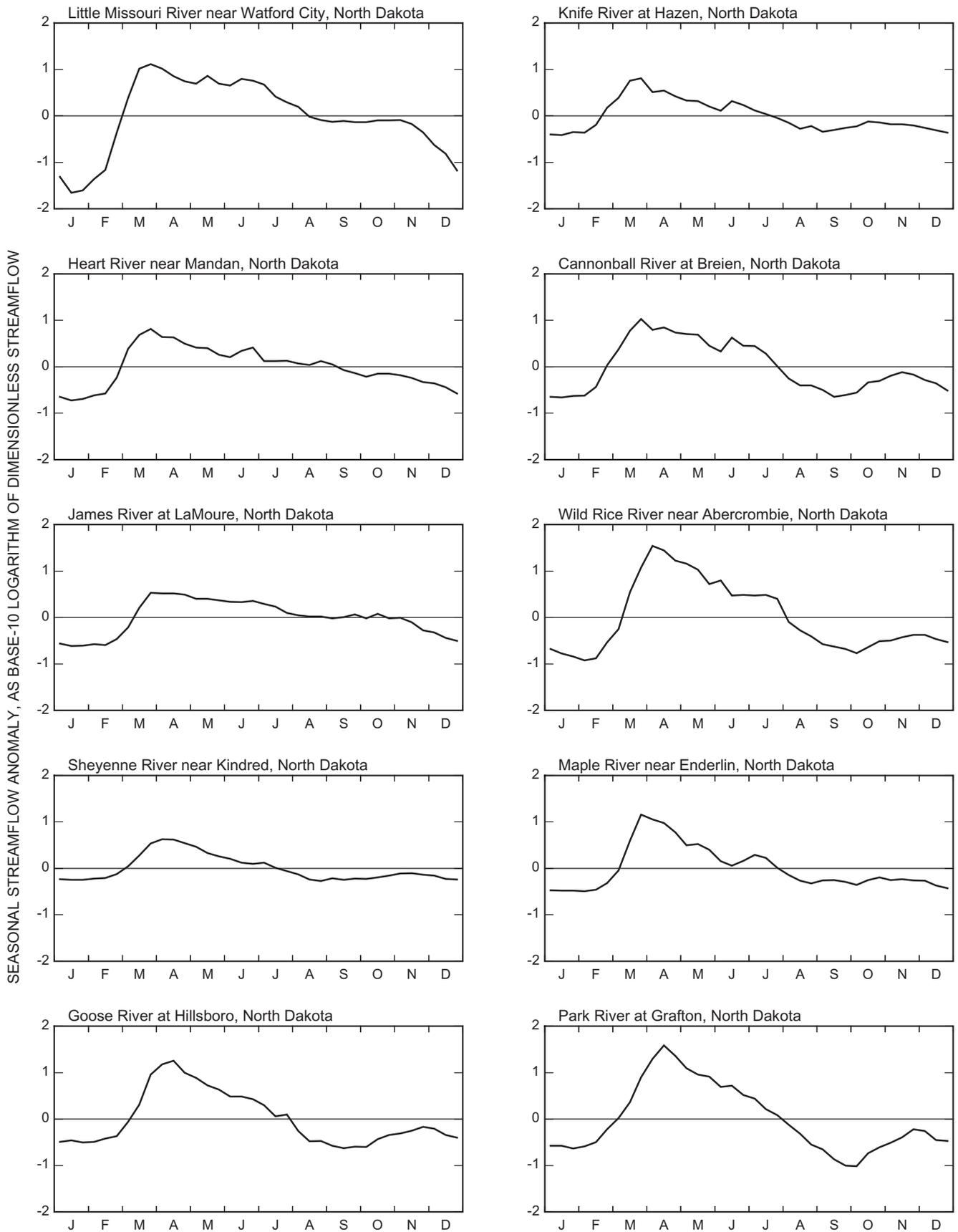
Figure 4. Seasonal streamflow anomalies for streamflow-gaging stations used in water-quality trend analysis. [Dimensionless streamflow is daily streamflow divided by the long-term geometric mean of daily streamflow.]

As shown in figure 4, streamflow in North Dakota also is subject to a high degree of seasonal variability. The range (maximum minus minimum value) of the seasonal streamflow anomalies at some stations was much greater than 2 base-10 logarithmic units, indicating that streamflow at those stations during spring runoff was more than 100 times higher, on average, than streamflow during low flow. Stations that have significant reservoir regulation generally had the least seasonal variability.

The daily streamflow anomalies for each station are shown in figure 5. The daily anomalies have a greater degree of high-frequency variability than the annual or seasonal streamflow anomalies because daily streamflow conditions depend on short-term meteorological conditions. Individual rainstorms, temperature changes, and many other factors contribute to the variability in the daily anomalies.

The high variability in the annual, seasonal, and daily streamflow anomalies that characterizes the streams in North Dakota and other streams throughout the north-central United States and south-central Canada introduces high variability in concentration from year to year, month to month, and day to day and makes the detection of water-quality trends particularly challenging. However, the time-series model removes as much of the natural variability in concentration as possible and makes trends easier to detect. To detect the trends for this report, the concentrations for each constituent were expressed in a form similar to equation 1:

$$Y(t) \;=\; M_y + A_y(t) + S_y(t) + \Gamma(t) + W(t) \tag{2}$$

where

$\quad Y(t)$ is the base-10 logarithm of concentration, in milligrams per liter or micrograms per liter, for time t;

$\quad M_y$ is the mean of $Y(t)$ for $1971 < t < 2001$, as base-10 logarithm of milligrams per liter or micrograms per liter;

$\quad A_y(t)$ is the annual concentration anomaly (dimensionless) for time t;

$\quad S_y(t)$ is the seasonal concentration anomaly (dimensionless) for time t;

$\quad \Gamma(t)$ is the concentration trend (dimensionless); and

$\quad W(t)$ is the daily concentration anomaly (dimensionless) for time t.

Although the components of equation 1 could be computed directly from the streamflow data, the components of equation 2 could not be computed from the concentration data because of the amount of missing data. Therefore, the components of equation 2 were expressed in terms of known explanatory variables that are functions of streamflow and time.

The annual concentration anomaly in equation 2 was expressed in terms of the annual streamflow anomaly as equation 3:

$$A_y(t) \;=\; \beta_1 A_x(t) + \beta_2 A_x(t-1) + \beta_3 A_x(t-2) \tag{3}$$

where

$\quad \beta_1$, β_2, and β_3 are model coefficients.

Only the concurrent annual streamflow anomaly, the first term on the right-hand side of equation 3, was used in earlier versions of the model (Vecchia, 2000). However, including the annual streamflow anomalies lagged by 1 and 2 years $[A_x(t-1)$ and $A_x(t-2)]$, in addition to including the concurrent anomaly, significantly improved the trend-analysis results for this report.

The seasonal concentration anomaly in equation 2 was expressed in equation 4 as given in Vecchia (2000, eq. A6):

$$S_y(t) \;=\; \beta_4 [S_x(t)]^+ + \beta_5 [S_x(t)]^- + \beta_6 \cos(2\pi t) + \beta_7 \sin(2\pi t) + \beta_8 \cos(4\pi t) + \beta_9 \sin(4\pi t) \tag{4}$$
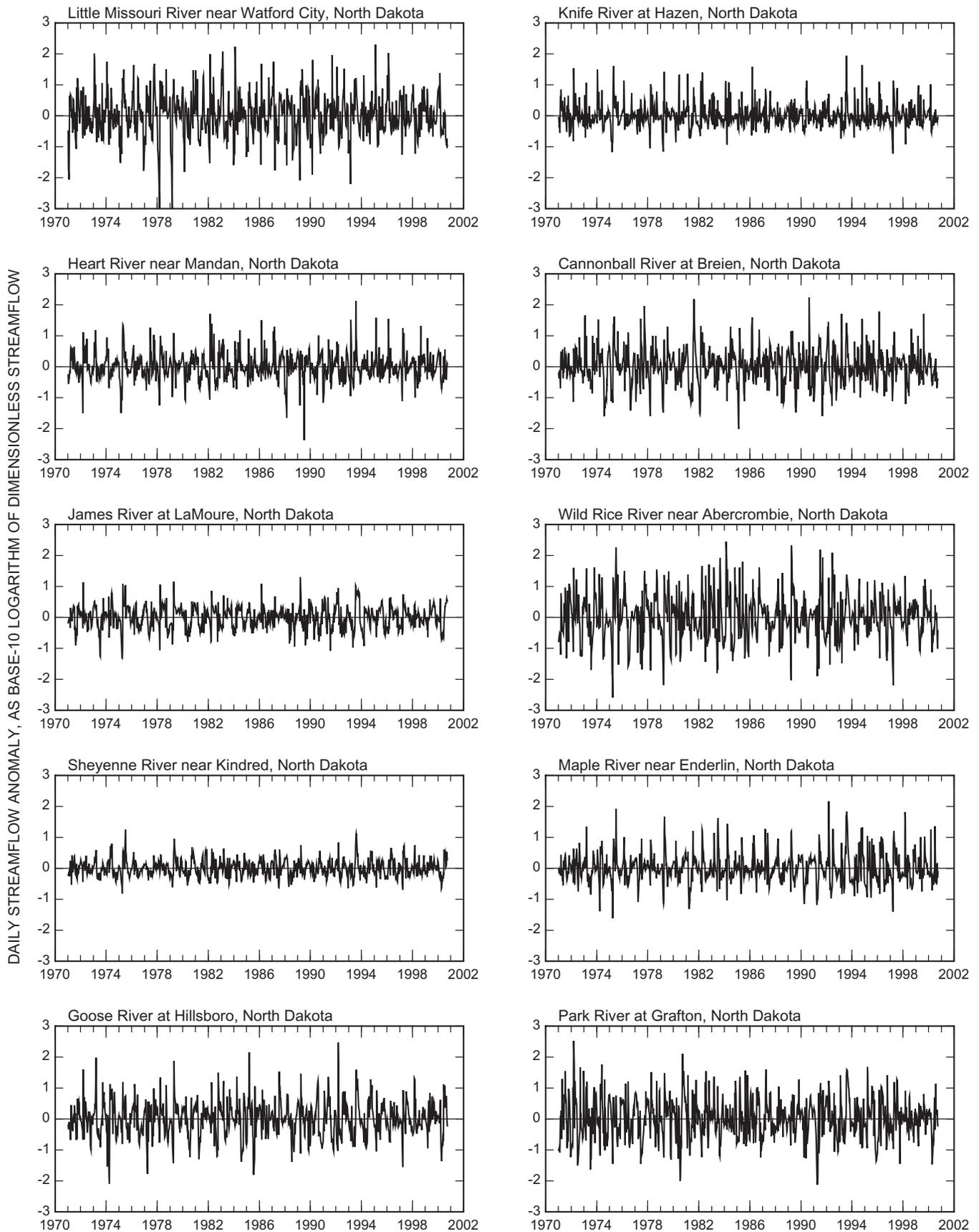
Figure 5. Daily streamflow anomalies for 1971-2000 (three values per month) for streamflow-gaging stations used in water-quality trend analysis. [Dimensionless streamflow is daily streamflow divided by the long-term geometric mean of daily streamflow.]

where

   β_4, ..., β_9 are model coefficients;

   $[S_x(t)]^+$ equals $S_x(t)$ if $S_x(t)$ is positive and zero otherwise;

   $[S_x(t)]^-$ equals $S_x(t)$ if $S_x(t)$ is negative and zero otherwise;

   $\cos(.)$ denotes the cosine function, and

   $\sin(.)$ denotes the sine function.

Including two terms in equation 4 for the seasonal streamflow anomaly (positive or negative) resulted in a better fit to the data than including only a single term involving $S_x(t)$ because concentrations may respond differently to streamflow during different times of the year. For example, when the seasonal streamflow anomaly is positive (that is, during the spring melt), concentrations of most constituents tend to decrease rapidly as streamflow increases (that is, β_4 tends to be negative and large in absolute value). However, when the seasonal streamflow anomaly is negative (that is, during low flow), concentrations tend to increase slowly as streamflow decreases (that is, β_5 tends to be negative but smaller in absolute value than β_4). In other cases, β_5 may be near zero, indicating that concentrations tend to be relatively constant as streamflow decreases. The sine and cosine terms were included in equation 4 because factors other than the seasonal streamflow anomaly also may affect the seasonal concentration anomaly. For example, fertilizer applications may be high during certain times of the year and nutrient concentrations may show an increase irrespective of streamflow conditions. Moreover, algal growth and, thus, nutrient concentrations may respond to temperature changes that follow different seasonal patterns than followed by the seasonal streamflow anomalies. Winter ice cover also may affect concentrations during low flow.

   The dimensionless concentration trend in equation 2 was assumed to be represented by equation 5:

$$\Gamma(t) = \gamma_1 f_1(t) + \gamma_2 f_2(t) + ... + \gamma_p f_p(t) \tag{5}$$

where

   γ_1, ..., γ_p are model coefficients;

   $f_1(t)$, ..., $f_p(t)$ are specified functions of t; and

   p is the number of coefficients in the trend model.

The trend functions in equation 5 can be specified using two approaches. In the first approach, the trend functions consist of time series of known covariates (acres of cropland, fertilizer applications, coal production, etc.) that possibly cause water-quality trends. In the second approach, which was used in this report, the trend functions consist of various piece-wise linear or step trends that are constructed to provide the best statistical fit to the data. The second approach is exploratory and iterative in nature and will be described in the "Examples of Trend Analysis" section of this report.

   The concentration trend in equation 2 represents systematic, interannual trends in $Y(t) - M_y - A_y(t) - S_y(t)$. These trends presumably are caused by changes inside or outside the basin that affect the amounts of major ions, nutrients, or trace metals that are available for suspension or solution in surface waters or that affect the processes that control the rate at which the various constituents are transported to or removed from the surface waters. For example, changes in land-use practices, such as reducing or increasing agricultural tillage, could change the amounts of chemical constituents that reach the streams whether or not climate and, thus, streamflow is changing. Other examples of potential changes that could affect water quality include changes in algal growth, mining practices, residential or agricultural fertilizer usage, livestock production, energy production, industrial and municipal effluents, and environmental sources of pollutants such as industrial or urban air emissions. All of these potential changes may be subject to complex interactions and may occur at different times, in different directions, and at different rates.

   To detect the concentration trends for this report, a joint time-series model was fitted to the concentration and streamflow data. The time-series model consists of equations 1 and 2, and the annual and seasonal concentration

anomalies and concentration trends were specified by equations 3 through 5. Because full specification of the time-series model requires that a statistical model be specified for the daily streamflow and concentration anomalies, $U(t)$ and $W(t)$, in equations 1 and 2, a particular type of bivariate, periodic autoregressive moving-average (PARMA) model (Salas and others, 1985; Jimenez and others, 1989) was used for the daily anomalies. The theory behind the PARMA model is given in Vecchia (2000) along with the procedure used to fit the model and estimate the model coefficients in equations 3 through 5. A general description of the procedure is given in the following discussion.

If the daily streamflow and concentration anomalies, $U(t)$ and $W(t)$, in equations 1 and 2 have no cross-correlation and no serial correlation (that is, values at different times are uncorrelated), the model coefficients in equations 3 through 5 can be estimated using classical multiple linear regression. However, the daily anomalies generally have significant cross-correlation and serial correlation because daily variability in streamflow is related to daily variability in concentration and because unusually high or low daily streamflows (for example, from a major spring storm or a major summer drought) tend to persist for some time before the return of more normal streamflow conditions. Therefore, the PARMA model was used to remove the variability in the daily concentration anomalies that was caused by cross-correlation with the daily streamflow anomalies and to remove the serial correlation in the daily concentration anomalies. In the process, the possibility of detecting false trends was decreased and the ability to detect true trends was increased. The PARMA model essentially separated the daily concentration anomalies into a "predictable" component plus random noise as follows:

$$W_i = W(t_i) = \tilde{W_i} + W_i^*$$ (6)

where

$\quad W_i$ or $W(t_i)$ is the daily concentration anomaly (dimensionless) for the ith recorded concentration;

$\quad t_i$ is the time of the ith recorded concentration, in decimal years;

$\quad \tilde{W_i}$ is the best (minimum mean-squared error) predictor of W_i (dimensionless) given the daily streamflow anomalies during or prior to time t_i and the nonmissing daily concentration anomalies prior to time t_i; and

$\quad W_i^*$ is the PARMA model residual for the ith recorded concentration (dimensionless).

The predicted values, $\tilde{W_i}$, and the PARMA model residuals, W_i^*, in equation 6 were computed using the periodic Kalman filter described in Vecchia (2000, appendix A). The computed residuals have less variability than the daily concentration anomalies and are uncorrelated. However, the variability of the residuals can differ for each recorded concentration because of the varying sampling times and because of differences in the ability to predict the daily concentration anomaly from season to season. For example, if two successive recorded concentrations are separated by 1 month, the residual for the second concentration might be smaller than if the recorded concentrations are separated by 1 year. Even if sampling times remain constant from year to year (for example, monthly sampling), the residuals might be more variable during spring breakup than during summer low flow because the daily concentration anomaly might be inherently harder to predict during spring breakup. The PARMA model accounted for the differences in the variability of the residuals when used to estimate the model coefficients in equations 3 through 5.

EXAMPLES OF TREND ANALYSIS

Several examples are presented in this section to illustrate the concepts described in the previous section. Results of the water-quality trend analysis for the constituents and streams used in this report will be presented in the next section.

The recorded dissolved sulfate concentrations for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., stations are shown in figure 6. The solid lines show the sum of the fitted mean, annual concentration anomaly, seasonal concentration anomaly, and concentration trend [the right-hand side of eq. 2 with $W(t)$ set equal to zero]. Trends, however, are not easily discerned from figure 6 because the annual and seasonal concentration anomalies are included along with the trends. Thus, the annual and seasonal concentration anomalies were removed to make the trends more evident.

The fitted annual concentration anomalies (fig. 7) indicate that annual streamflow variability may affect concentrations differently from station to station. For example, the annual concentration anomalies for the Heart and Cannonball River stations differ significantly despite the close geographic proximity of the two basins (fig. 1) and the similarities in the annual streamflow anomalies for the two stations (fig. 3). The annual concentration anomalies for the Heart River station tend to vary inversely with the annual streamflow anomalies--dry conditions produce high concentrations and wet conditions produce low concentrations. This behavior might be expected if a consistent source of sulfate in the basin readily supplies the stream during both wet and dry conditions. Because wet conditions tend to dilute the sulfate more than dry conditions, sulfate concentrations are lower during wet conditions than during dry conditions. In contrast to the annual concentration anomalies for the Heart River station, the annual concentration anomalies for the Cannonball River station tend to vary directly with the annual streamflow anomalies--dry conditions produce low concentrations and wet conditions produce high concentrations. This behavior might be expected if a large source of sulfate in the basin more readily supplies the stream during wet conditions than during dry conditions. Sulfate may build up in soils far from the stream channel during dry conditions and then be dissolved and transported to the stream channel during subsequent wet conditions. The differences in the annual concentration anomalies for the two stations also may be a result of streamflow regulation on the Heart River but not on the Cannonball River. Dry conditions in the Heart River Basin tend to increase the residence time of water in Lake Tschida and, thus, may increase dissolved ion concentrations in the lake water.
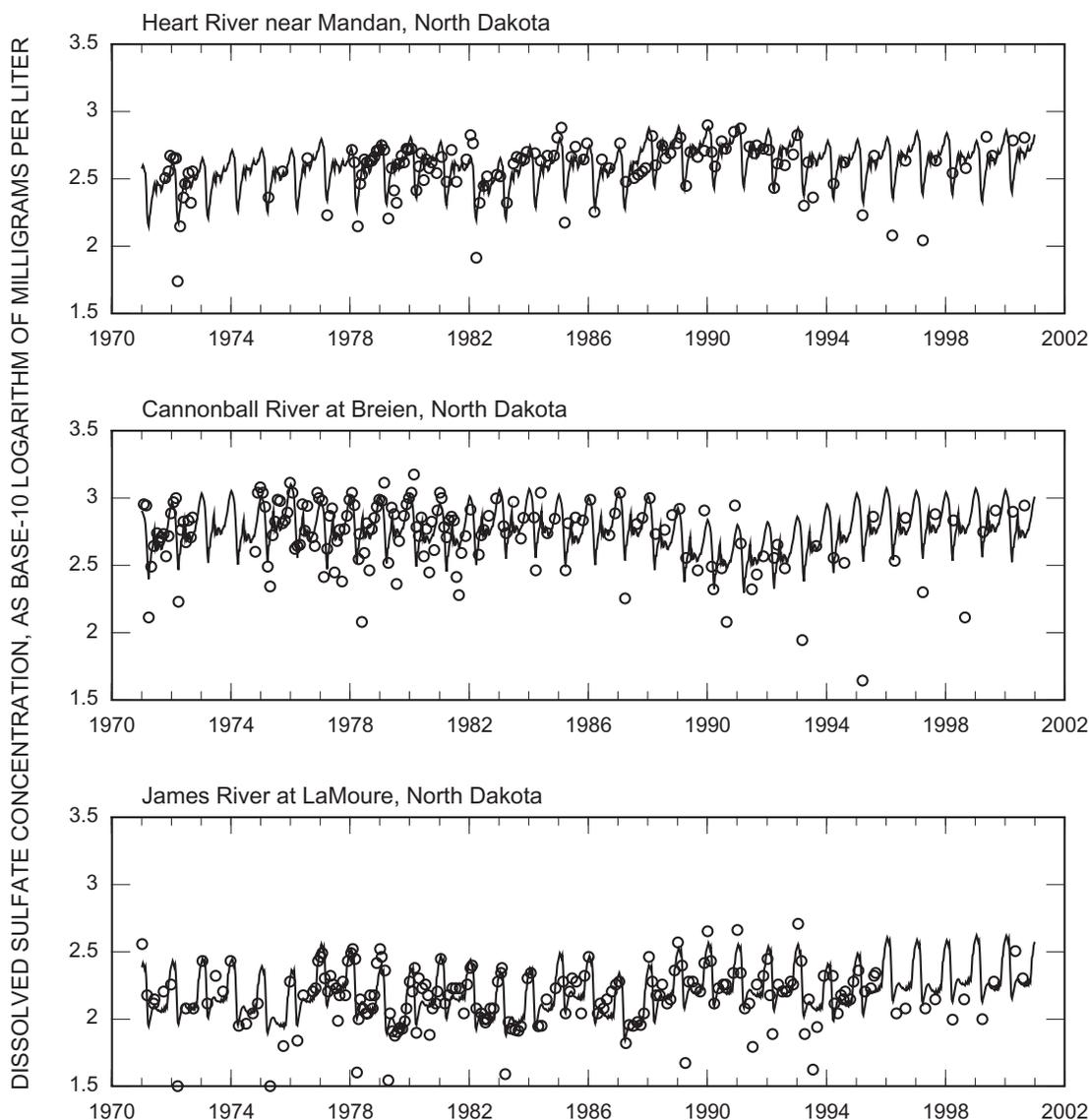
Figure 6. Recorded dissolved sulfate concentrations (points) and fitted low-frequency variability (lines) for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., streamflow-gaging stations.

The fitted annual concentration anomaly for the James River station (fig. 7) is similar to the fitted anomaly for the Heart River station although the two stations are separated geographically (fig. 1). The similarities may indicate that the two basins have similar hydrogeologic characteristics with respect to sulfate sources and transport, have similar effects from reservoir regulation, or have both.

The fitted model coefficients for the annual concentration anomalies (eq. 3) for the three stations are given in table 4. The first coefficient (which corresponds to the annual streamflow anomaly for the concurrent year) is the largest coefficient (in absolute value) for all three stations. The coefficient is negative for the Heart and James River stations and positive for the Cannonball River station. The coefficient is statistically different from zero at the 5-percent significance level in all three cases, as indicated by the fact that the 95-percent confidence intervals do not include zero. The second coefficient is positive for all three stations and is statistically different from zero for the Heart and Cannonball River stations. The third coefficient also is positive for all three stations, but only the coefficient for the James River station is statistically different from zero. Although the second and third coefficients are smaller in absolute value than the first coefficient, they are large enough to produce substantial multiyear lagged effects between the annual concentration anomaly and the annual streamflow anomaly that cannot be modeled using only the concurrent streamflow anomaly.
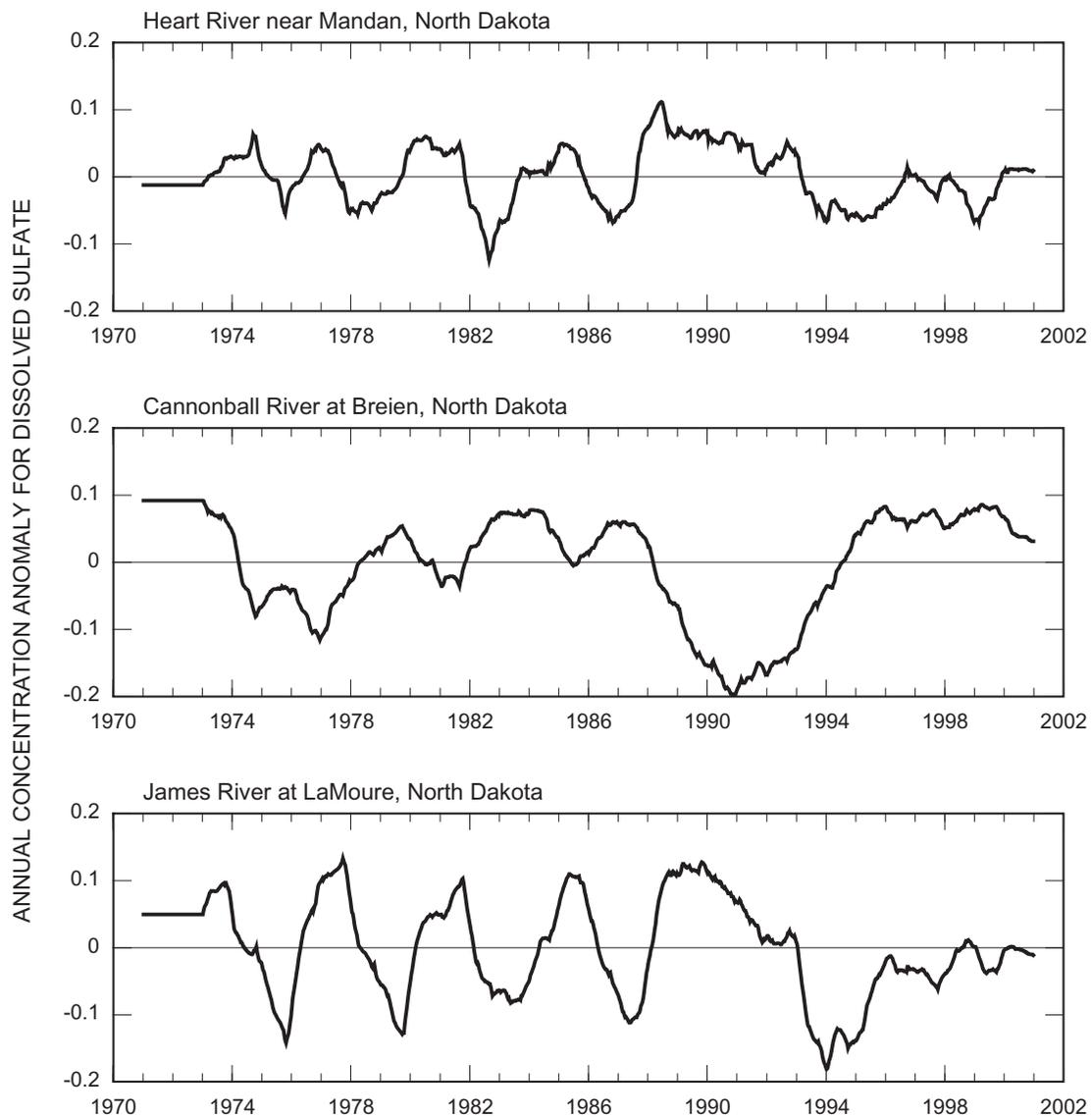
Figure 7. Fitted annual concentration anomalies for dissolved sulfate for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., streamflow-gaging stations.

Table 4. Fitted model coefficients for annual concentration anomalies for dissolved sulfate for selected streamflow-gaging stations

[Values in parentheses indicate 95-percent confidence intervals]

Station name	Explanatory variable (model coefficient)		
	Annual streamflow anomaly for concurrent year (β_1)	Annual streamflow anomaly lagged 1 year (β_2)	Annual streamflow anomaly lagged 2 years (β_3)
Heart River near Mandan, N. Dak.	-0.138 (-0.180, -0.096)	0.044 (0.005, 0.083)	0.034 (-0.002, 0.070)
Cannonball River at Breien, N. Dak.	0.104 (0.071, 0.138)	0.069 (0.032, 0.106)	0.034 (-0.001, 0.069)
James River at LaMoure, N. Dak.	-0.162 (-0.199, -0.124)	0.036 (-0.004, 0.076)	0.081 (0.042, 0.120)

The fitted seasonal concentration anomalies for the three stations are similar (fig. 8). The concentrations tend to be largest from December through mid-February, decrease rapidly from mid-February through late March, and increase slowly from late March through early June. The concentrations are stable from June through October and then increase again in November. The seasonal concentration anomalies for the three stations vary inversely with the seasonal streamflow anomalies (fig. 4) from December through early June. Streamflow from December through February consists mostly of baseflow under ice conditions and generally has the largest sulfate concentrations. The spring melt usually begins in late February or early March, and streamflow from March through early June is predominantly from snowmelt or rainfall on partially frozen soils and generally has small sulfate concentrations.

The seasonal concentration anomalies remain relatively constant from early June through October although the seasonal streamflow anomalies (fig. 4) continue to decrease during that time. Streamflow from June through October consists mostly of rainfall runoff from unfrozen soils and generally has sulfate concentrations that are larger than the concentrations from spring surface runoff but smaller than the concentrations from winter baseflow.

The seasonal concentration anomalies for the three stations are similar although the annual concentration anomaly for the Cannonball River station differs significantly from the anomalies for the remaining two stations. The annual and seasonal concentration anomalies represent entirely different processes. The annual concentration anomaly depends on long-term (multiyear) climatic trends, and the seasonal concentration anomaly depends on the annual climatic cycle. Thus, in the case of the Cannonball River station, although sulfate concentrations tend be larger during extended wet periods than during extended dry periods, sulfate concentrations during the year still tend to be smallest during spring runoff.

The trends in recorded sulfate concentrations for the three stations, after the annual and seasonal concentration anomalies were removed, were shown by rearranging equation 2 to obtain equation 7:

$$Y^*(t) = Y(t) - [A_y(t) + S_y(t)] = M_y + \Gamma(t) + W(t) \tag{7}$$

where

$Y^*(t)$ is the base-10 logarithm of concentration, in milligrams per liter, with annual and seasonal anomalies removed.

The mean, M_y, was included with the trend so the trend could be expressed in the same units as the recorded concentrations. The sulfate concentrations with annual and seasonal anomalies removed are shown in figure 9 along with the fitted trends. The fitted trends consist of continuous piece-wise linear functions of time with breakpoints, or slope changes, that occur at specified times. The model first was fitted with no breakpoints (that is, a single linear trend for the entire historical period), and then breakpoints were added one at a time with the time of the breakpoint chosen to maximize the log-likelihood function (Vecchia, 2000, appendix A). Likelihood ratio tests were used to determine if each additional breakpoint resulted in a significant improvement in the model when using a 1-percent significance level. Breakpoints were added until no significant improvement could be obtained. Then, the slope between each pair of breakpoints was examined and, if the slope was not significantly different from zero when using a 2-percent significance level, the slope was set equal to zero and the model was refitted using a zero slope for that time interval.
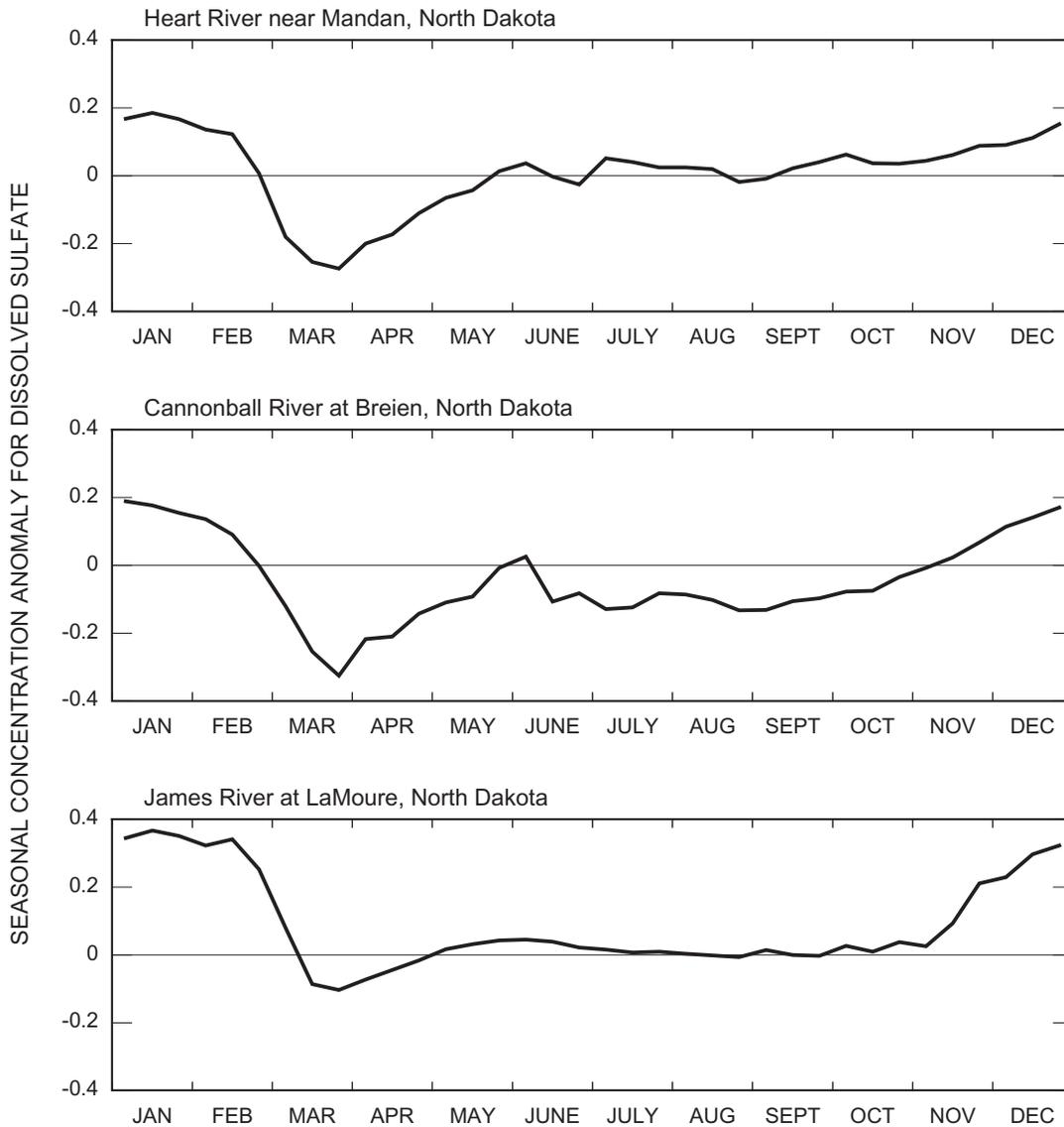
Figure 8. Fitted seasonal concentration anomalies for dissolved sulfate for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., streamflow-gaging stations.

The daily concentration anomalies for sulfate vary considerably about the fitted trends shown in figure 9. As indicated previously, some of the variability was reduced by using the PARMA model to remove the effects of cross-correlation between the daily streamflow anomalies and the daily concentration anomalies and the effects of serial correlation in the daily concentration anomalies. By combining equations 6 and 7, the concentrations were refined further by using equation 8:

$$Y_i^{**} = Y_i^* - \widetilde{W_i} = M_y + \Gamma_i + W_i^* \tag{8}$$

where

Y_i^{**} is the time-series model adjusted value of the base-10 logarithm of concentration, in milligrams per liter, for the ith record; and

Y_i^* is the base-10 logarithm of concentration, in milligrams per liter, for the ith record with annual and seasonal anomalies removed (eq. 7 with $t = t_i$).
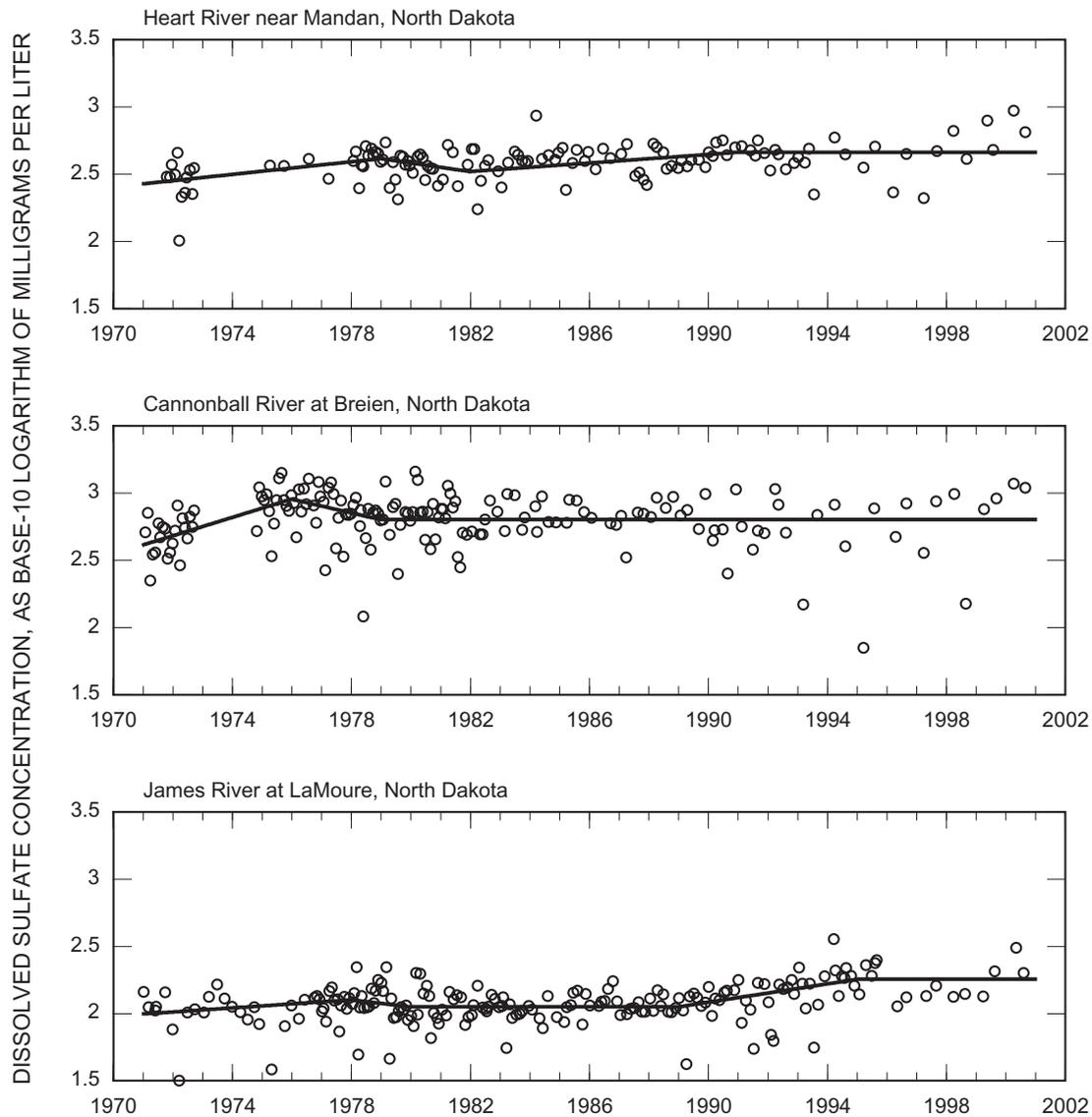
Figure 9. Dissolved sulfate concentrations with annual and seasonal anomalies removed (points) and fitted trends (lines) for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., streamflow-gaging stations.

The time-series model adjusted concentrations (eq. 8) will, henceforth, be referred to as the model-adjusted concentrations. The model-adjusted sulfate concentrations for the three stations are shown in figure 10 along with the fitted trends. A comparison of figures 9 and 10 indicates considerably less variability about the fitted trends shown in figure 10. The latter years of the record show less reduction in variability because few recorded data are available for those years and, thus, less information was available to predict the daily concentration anomalies.

The model-adjusted concentrations are estimates of the concentrations that would have been measured during "ideal" conditions--that is, when streamflow was the same year after year and when concentrations were measured when daily streamflow equaled median daily streamflow. Thus, the estimated concentrations could be referred to as "flow-adjusted" concentrations. However, in water-quality trend literature, flow-adjusted concentrations generally refer to residuals from a regression (either parametric or nonparametric) of concentration on streamflow (Hirsch and others, 1982). The time-series model used in this report is much more robust than a regression model that relates concentration and streamflow and generally is able to remove more variability in concentration than would a simple flow-adjustment process.

The recorded total ammonia plus organic nitrogen concentrations for the Heart River, Cannonball River, and Sheyenne River near Kindred, N. Dak., stations are shown in figure 11. The fitted annual concentration anomalies for the Cannonball

and Sheyenne River stations are similar (fig. 12) although the two stations are separated geographically (fig. 1) and the drainage basins have different hydrogeologic characteristics. The annual concentration anomalies for the two stations tend to vary directly with the annual streamflow anomalies (fig. 3), and the magnitude of the variability is similar. Much less variability occurs in the annual concentration anomaly for the Heart River station, and the annual concentration anomaly for that station is not closely correlated (either positively or negatively) with the annual streamflow anomaly. The fitted model coefficients for the annual concentration anomalies (table 5) indicate that the coefficients for the Heart River station are not significantly different from zero at the 5-percent significance level. However, the first two coefficients for the Cannonball River station and the first coefficient for the Sheyenne River station are positive and significantly different from zero.

The fitted seasonal concentration anomalies for total ammonia plus organic nitrogen for the three stations are similar from December through May but differ from June through November (fig. 13). The seasonal concentration anomalies tend to be relatively small during December and January, increase from late January through mid-March or early April, and decrease in April and May. The seasonal concentration anomalies for the three stations vary directly with the seasonal streamflow anomalies (fig. 4) from December through May, and the concentrations tend to peak slightly before streamflow peaks. However, secondary peaks in the seasonal concentration anomalies occur for the Heart and Cannonball River stations during the summer, and the concentrations peak about as high as those during the spring. The concentrations for
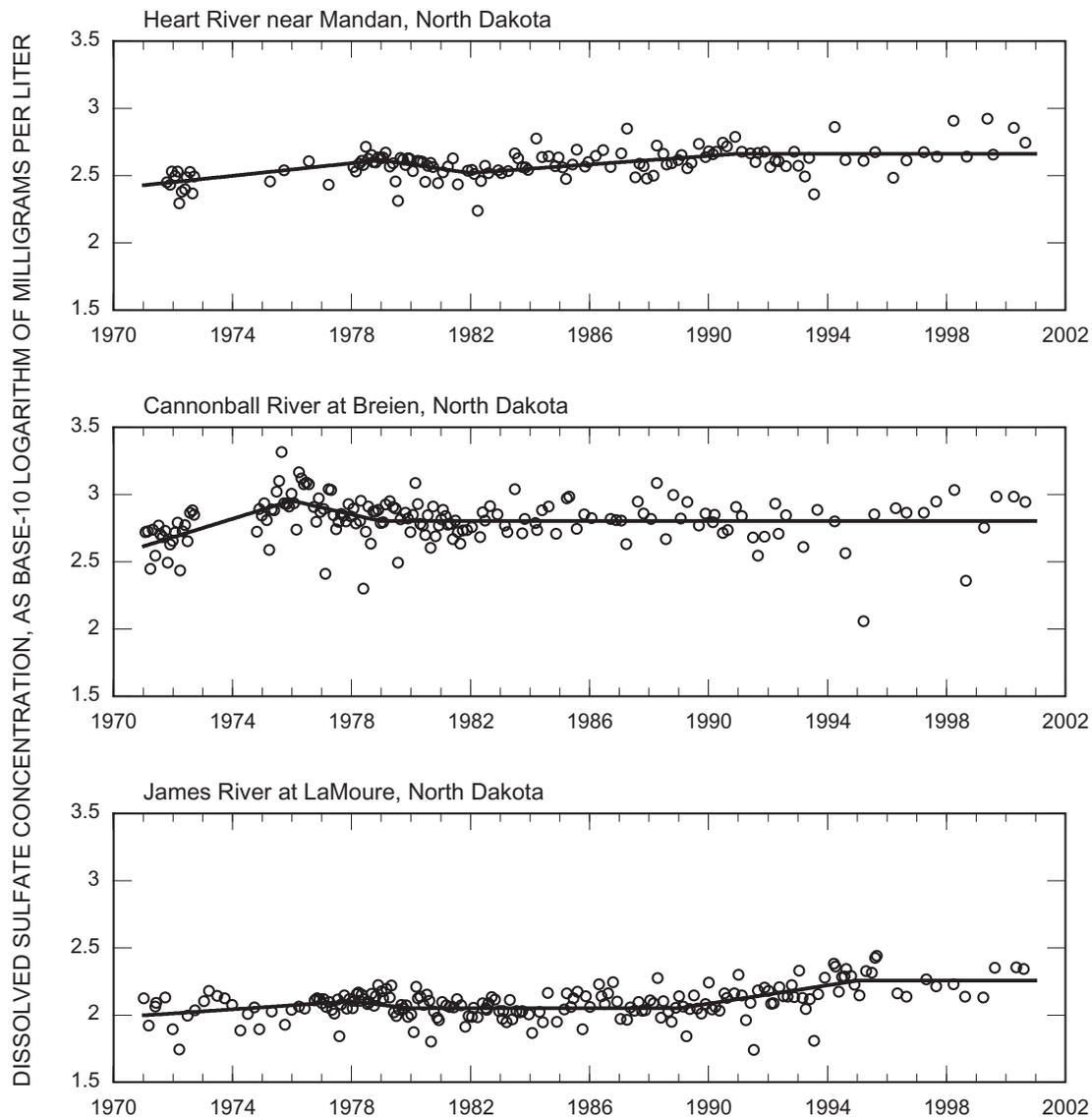
Figure 10. Model-adjusted dissolved sulfate concentrations (points) and fitted trends (lines) for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and James River at LaMoure, N. Dak., streamflow-gaging stations.

the Heart River station show a decrease in September and October and tend to be lower during those months than during December and January. The concentrations for the Sheyenne River station continue to decrease from May through October and do not show a secondary peak in the summer.

The annual concentration anomalies for total ammonia plus organic nitrogen for the Heart and Cannonball River stations (fig. 12) are similar to the annual concentration anomalies for sulfate (fig. 7), especially for the Cannonball River station. However, the seasonal concentration anomalies for total ammonia plus organic nitrogen for those two stations (fig. 13) are in sharp contrast to the seasonal concentration anomalies for sulfate (fig. 8). Thus, although the climatically induced interannual variability in total ammonia plus organic nitrogen is similar to that in sulfate, the seasonal variability differs. As indicated previously, the annual and seasonal concentration anomalies represent entirely different processes and, thus, may behave differently for different constituents and locations.

The model-adjusted total ammonia plus organic nitrogen concentrations for the three stations are shown in figure 14 along with the fitted trends obtained using the same procedure as described previously for sulfate. In addition to the piece-wise linear trends, a step trend also was included in the fitted trend for total ammonia plus organic nitrogen to account for a laboratory analysis bias that occurred at the U.S. Geological Survey National Water Quality Laboratory during 1986-91 (Patton and Truitt, 2000; Trench and Vecchia, 2002). Recorded concentrations for total ammonia plus organic nitrogen
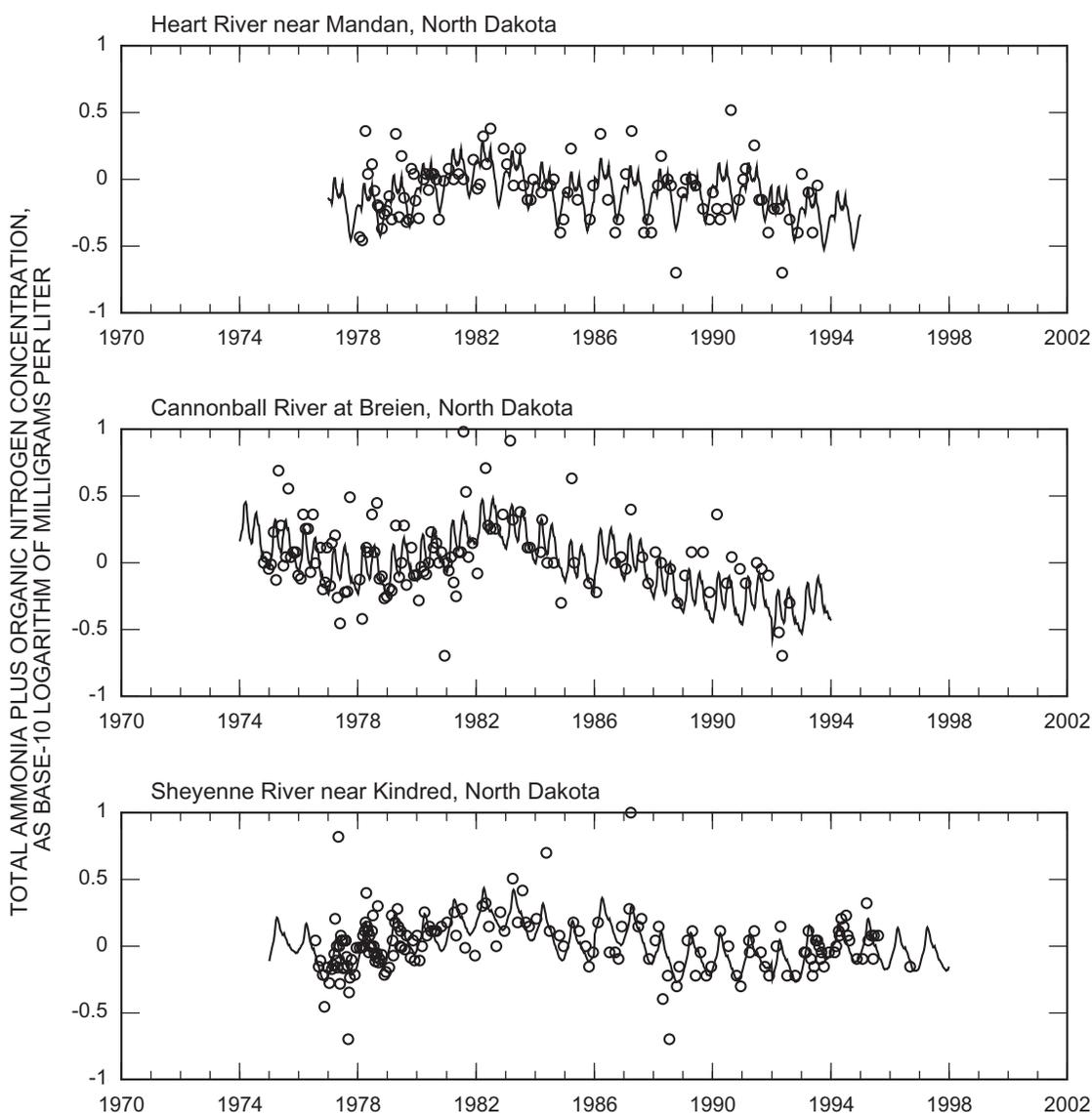
Figure 11. Recorded total ammonia plus organic nitrogen concentrations (points) and fitted low-frequency variability (lines) for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and Sheyenne River near Kindred, N. Dak., streamflow-gaging stations.
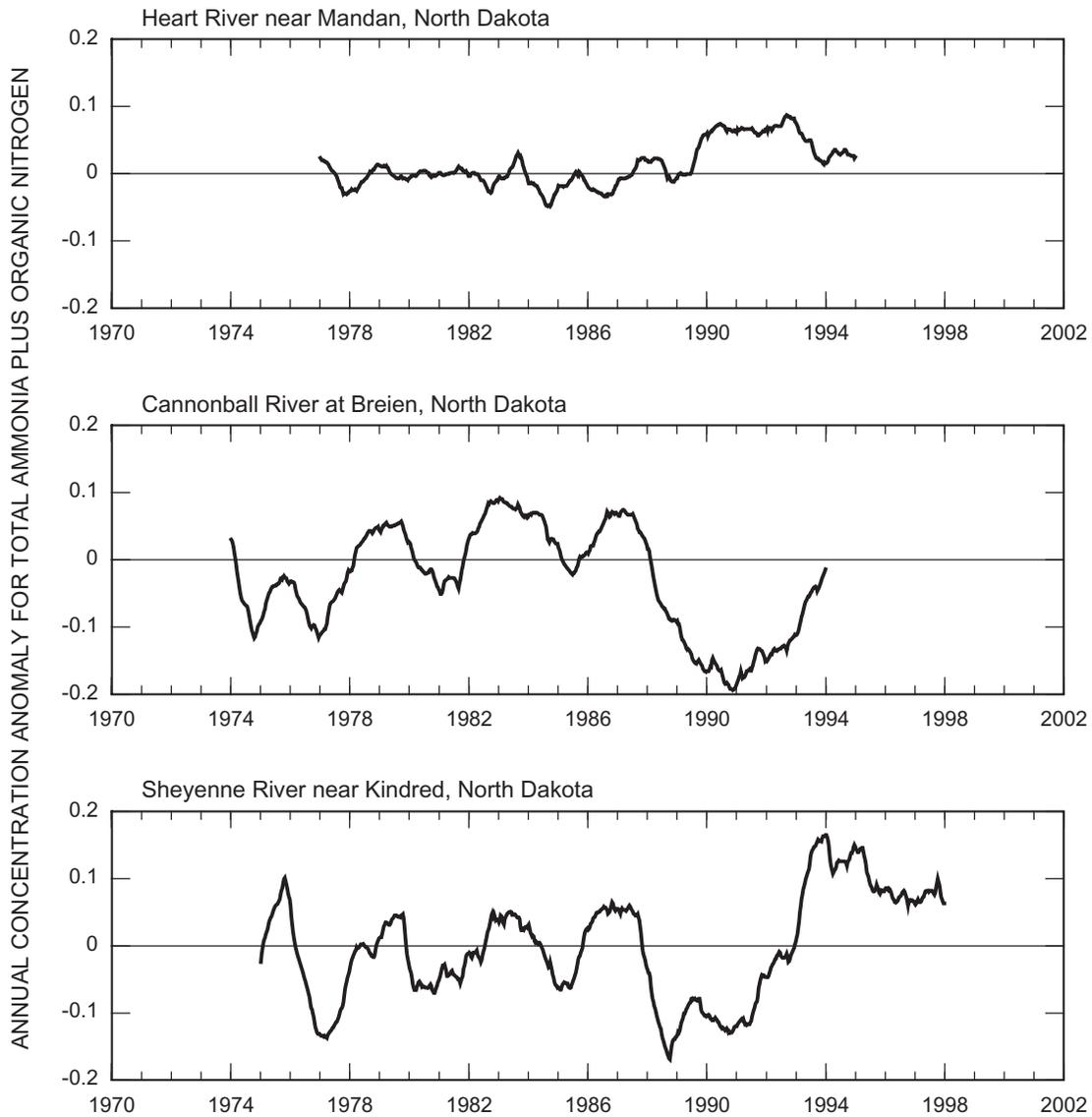
Figure 12. Fitted annual concentration anomalies for total ammonia plus organic nitrogen for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and Sheyenne River near Kindred, N. Dak., streamflow-gaging stations.

during 1986-91 generally are biased high because of a method change during that time, and significant positive bias was detected for the three stations for 1986-91 (fig. 14).

WATER-QUALITY TREND ANALYSIS

The historical water-quality trend analysis for the constituents and streams described in this report is summarized in this section. The time-series methods used to analyze the data were described in the previous examples. Emphasis in this section is placed on describing the annual concentration anomalies, which model the interannual variability in concentrations as a result of variability in streamflow, and on describing the trends, which model the interannual variability in concentration as a result of factors other than streamflow. Potential causes for the trends are discussed in a later section. The estimated trends in constituent concentrations are given in appendix A, and the recorded constituent concentrations, model-adjusted constituent concentrations, and fitted trends are shown in appendix B.

Table 5. Fitted model coefficients for annual concentration anomalies for total ammonia plus organic nitrogen for selected streamflow-gaging stations

[Values in parentheses indicate 95-percent confidence intervals]

Station name	Explanatory variable (model coefficient)		
	Annual streamflow anomaly for concurrent year (β_1)	Annual streamflow anomaly lagged 1 year (β_2)	Annual streamflow anomaly lagged 2 years (β_3)
Heart River near Mandan, N. Dak.	-0.058 (-0.166, 0.050)	0.015 (-0.093, 0.123)	-0.067 (-0.165, 0.031)
Cannonball River at Breien, N. Dak.	0.125 (0.081, 0.169)	0.062 (0.020, 0.104)	0.010 (-0.032, 0.052)
Sheyenne River near Kindred, N. Dak.	0.301 (0.215, 0.387)	-0.065 (-0.145, 0.015)	-0.023 (-0.107, 0.061)

Major Ions

Annual Concentration Anomalies

The fitted annual concentration anomalies for calcium, sodium, sulfate, and chloride are shown in figure 15. To facilitate discussion of the annual anomalies and allow comparisons among the constituents, the annual anomalies, [$A_y(t)$ in eq. 2], were exponentiated and divided by their respective values, or normalized, for the beginning of the trend-analysis period (January 1, 1971). Thus, for example, the annual anomalies for sodium, sulfate, and chloride for the Little Missouri River near Watford City, N. Dak., station were more than twice as high during 1988 than during 1971. Generally, a high degree of persistence exists in the annual anomalies. The annual anomalies can consistently increase or decrease for many years or remain low or high for many years before returning to more normal levels. Also, the variability in the annual anomalies often may be large. This indicates the importance of detecting and removing the annual anomalies before analyzing the concentration trends so that the trends are not hidden among the annual anomalies or misinterpreted entirely.

Although the annual concentration anomalies for all four major ions show a similar pattern of variability for most stations, substantial differences occur for some stations (fig. 15). For example, for the Cannonball River at Breien, N. Dak., station, the annual anomalies for calcium and sulfate differ substantially from the annual anomalies for sodium and chloride, and, for the Sheyenne River near Kindred, N. Dak., station, the annual anomaly for chloride differs substantially from the annual anomalies for the remaining ions. Thus, annual climate variability evidently affects major ions differently even within the same basin.

Although some similarities in the annual concentration anomalies exist between stations, the annual anomalies tend to show a different pattern of variability from station to station (fig. 15) despite similarities in the annual streamflow anomalies (fig. 3). Thus, climate variability evidently affects major-ion concentrations differently, depending on the hydrogeologic properties of the basins.

The ratio between the maximum and minimum values of the annual concentration anomaly for a given constituent is a measure of the variability of the anomaly. The annual anomalies for the Knife River at Hazen, N. Dak., station have low variability, with ratios less than 2 for all four major ions. The annual anomalies for the Heart River near Mandan, Cannonball River, Wild Rice River near Abercrombie, Sheyenne River, and Maple River near Enderlin, N. Dak., stations have moderate variability, with ratios less than 4 for all four major ions. The annual anomalies for the remaining stations have high variability, with ratios greater than 4 for one or more major ions. The annual anomalies for chloride tend to be the most variable, and the annual anomalies for calcium tend to be the least variable.

Differences in the annual concentration anomalies from constituent to constituent and from location to location are more prevalent during 1988-2001 than during the early years of the record, indicating that prolonged, extremely dry or wet periods have cumulative effects on major-ion concentrations and that the effects may differ among constituents and among locations. A severe drought occurred from 1988 to 1992, and a very wet period began in 1993 and has persisted to the present (2002). However, climatic conditions during the early years of the record were less extreme (fig. 3). Thus, extreme climatic conditions that last several years evidently can cause substantial changes in the hydrology and geochemistry of drainage basins and, in turn, change the water quality of surface runoff.

Concentration Trends

 The fitted concentration trends and the model-adjusted concentrations for calcium, sodium, sulfate, and chloride are shown in appendices A and B. To facilitate discussion of the trends, the fitted trends were exponentiated and divided by their respective values, or normalized, for January 1, 1971. The resulting normalized fitted trends (fig. 16) indicate periods of stable concentrations interspersed with abrupt changes in the concentrations. The concentrations at many of the stations increased significantly from 1971 through the mid- to late 1970's and then decreased for about 2 to 3 years. Although the time at which the decrease began differs somewhat from station to station (the earliest decreases occurred in 1976 for the Cannonball and Wild Rice River stations, and the latest decrease occurred in 1982 for the Little Missouri River station), the decreases generally began in about 1979. The Sheyenne and Maple River stations were the only stations that did not indicate a significant increase in concentrations of at least two major ions in the 1970's.

 Major-ion concentrations for the streams in southwestern North Dakota (the Little Missouri, Knife, Heart, and Cannonball River stations) showed two distinct patterns following the abrupt decrease in concentrations in the late 1970's or early 1980's (fig. 16). Concentrations for the Little Missouri and Cannonball River stations stabilized at levels that were higher than those in the early 1970's and remained stable for the remainder of the record. However, concentrations for the
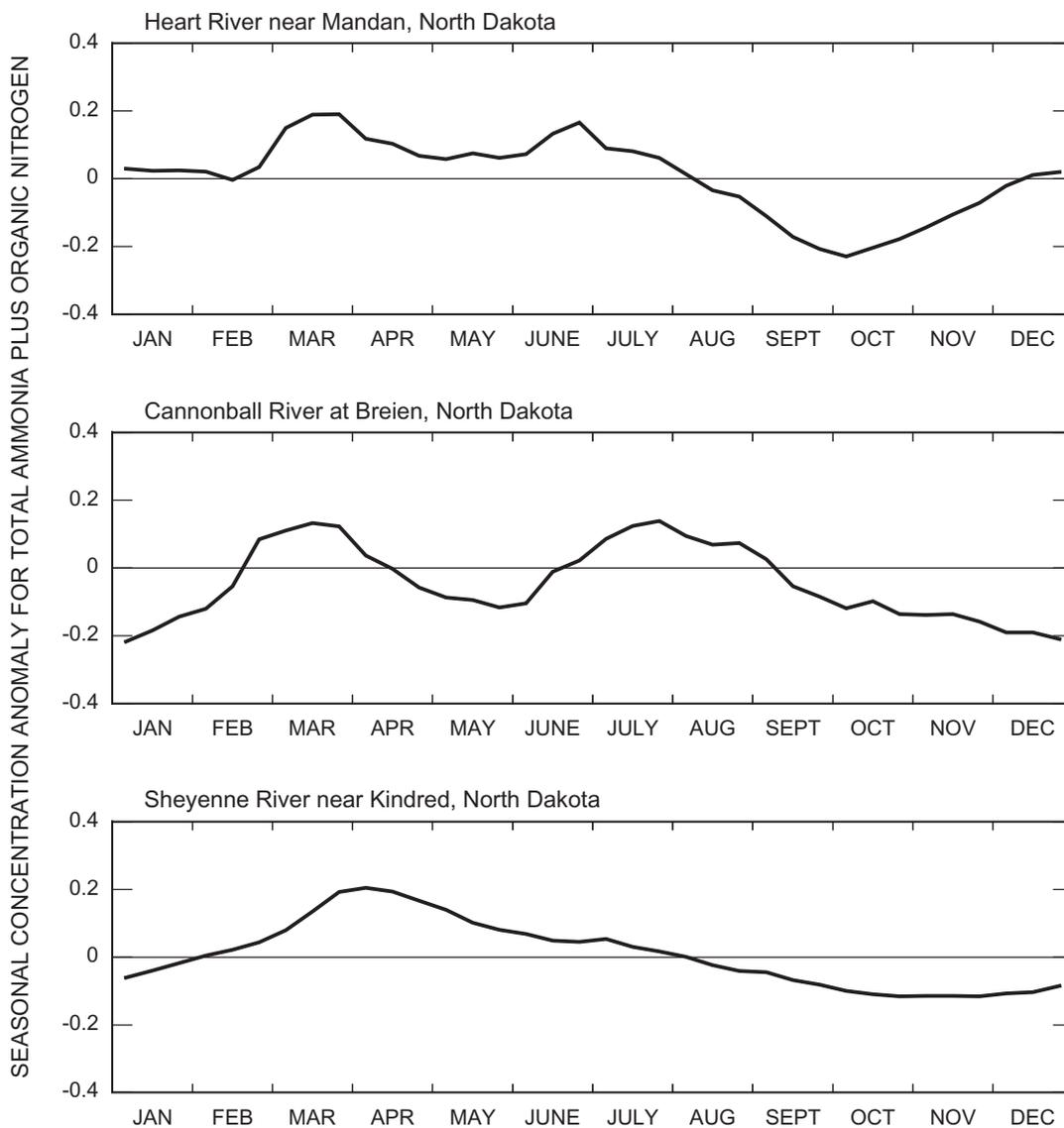
Figure 13. Fitted seasonal concentration anomalies for total ammonia plus organic nitrogen for the Heart River near Mandan, Cannonball River at Breien, and Sheyenne River near Kindred, N. Dak., streamflow-gaging stations.

Knife and Heart River stations increased during the 1980's before stabilizing in the early 1990's at levels that were higher than those in the late 1970's. Chloride concentrations increased the most compared to the other constituent concentrations for all four stations, and concentrations at the end of the record were about twice as high as those in 1971. Calcium concentrations increased the least, and concentrations at the end of the record were 20 to 50 percent higher than those in 1971.

Major-ion concentrations for the streams in eastern North Dakota show two distinct patterns of increase for the 1980's and 1990's (fig. 16). For the James River at LaMoure, N. Dak., and Sheyenne River stations, the concentrations increased significantly from about 1989 through 1994. For the Sheyenne River station, the increase in calcium and sulfate concentrations during that period was interrupted by a sharp decrease in 1993. This decrease is highly significant, but the cause for the decrease is not known. For the Wild Rice River, Maple River, and Park River at Grafton, N. Dak., stations, an abrupt increase in concentrations occurred in the mid- to late 1980's.

Except for the James and Sheyenne River stations, no significant trends in major-ion concentrations were detected from 1990 to the end of the record. However, because few samples were collected during the 1990's, some trends may not have been detected.
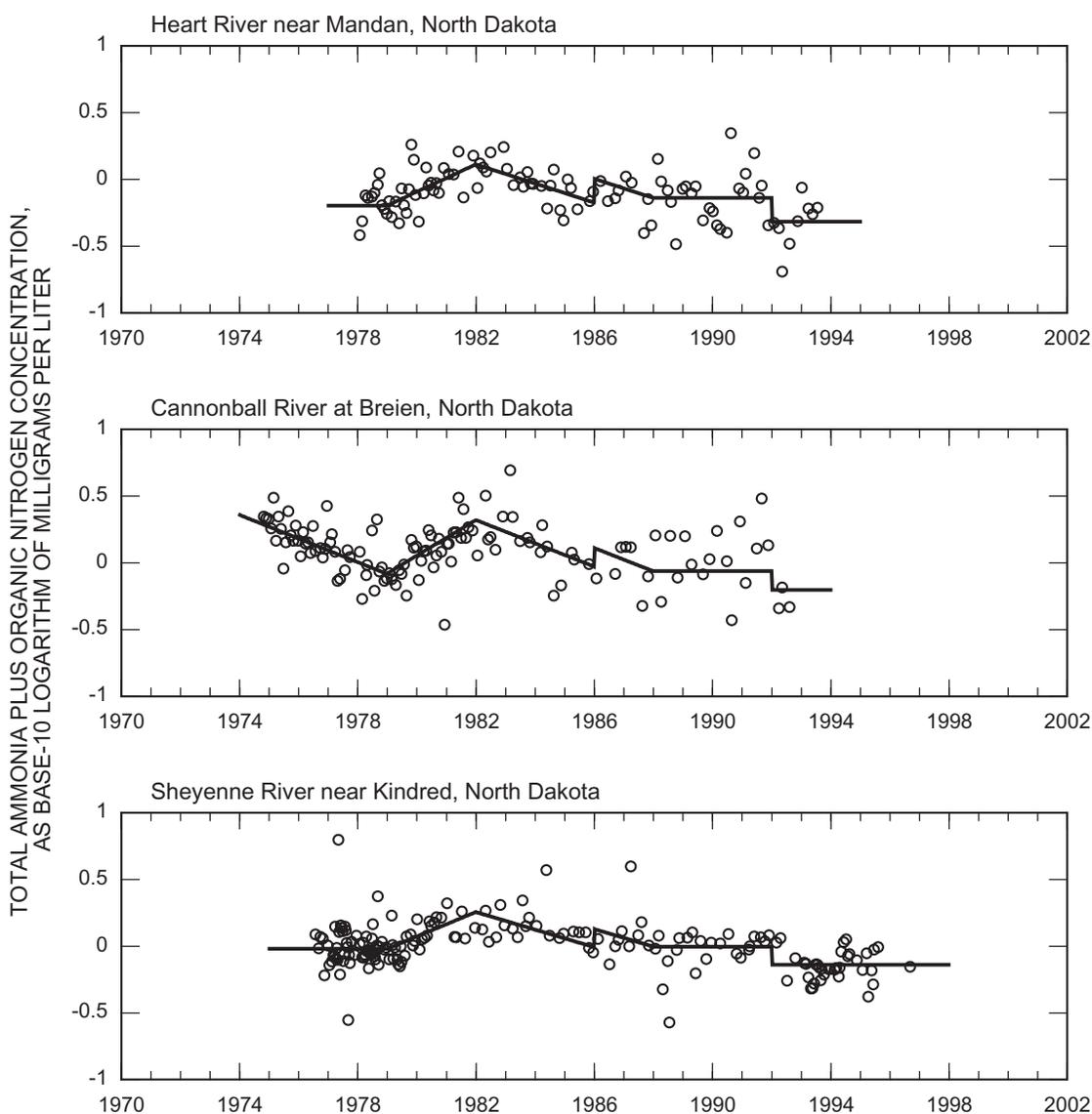
Figure 14. Model-adjusted total ammonia plus organic nitrogen concentrations (points) and fitted trends (lines) for 1971-2000 for the Heart River near Mandan, Cannonball River at Breien, and Sheyenne River near Kindred, N. Dak., streamflow-gaging stations.
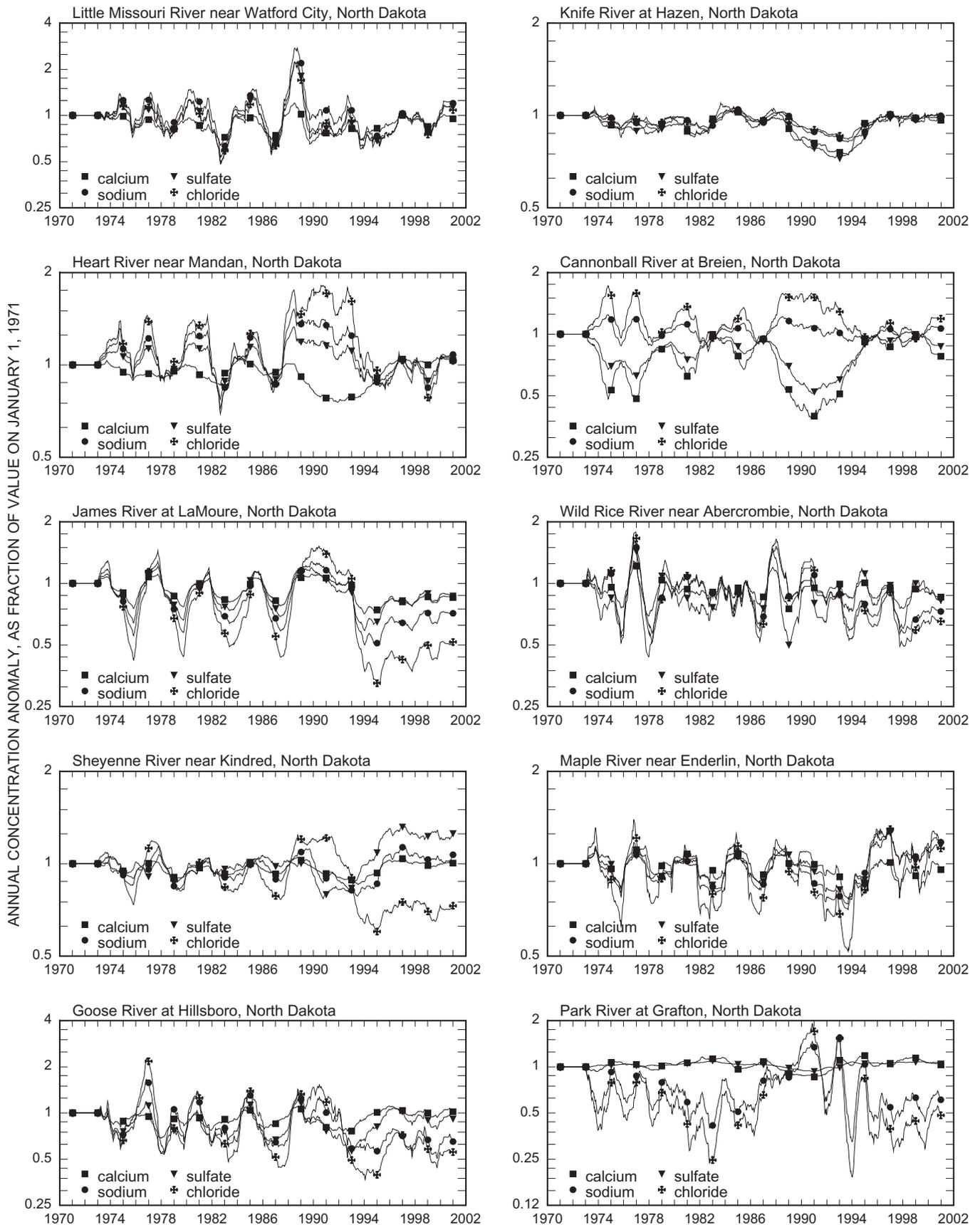
Figure 15. Normalized fitted annual concentration anomalies for dissolved calcium, sodium, sulfate, and chloride for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]
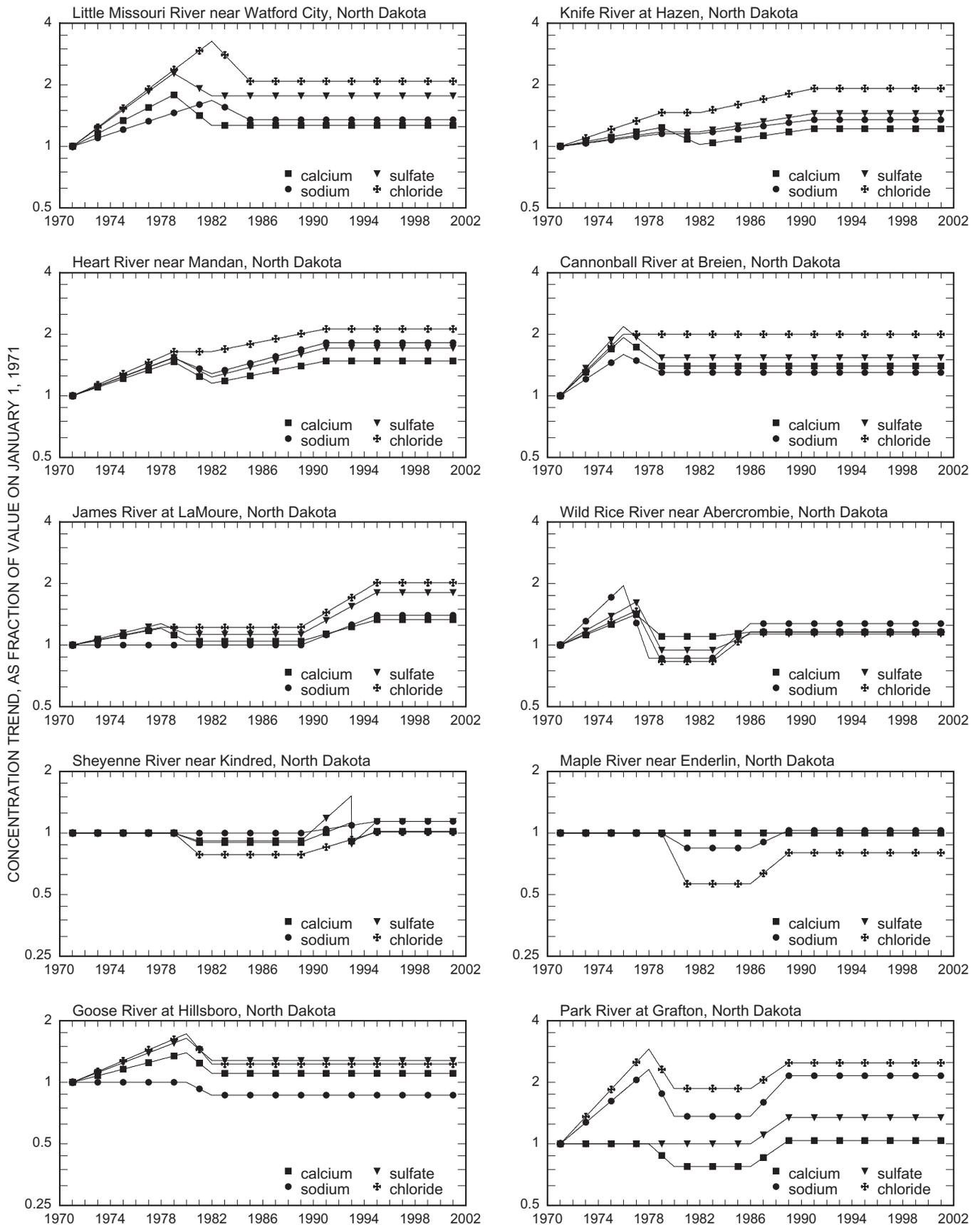
Figure 16. Normalized fitted concentration trends for dissolved calcium, sodium, sulfate, and chloride for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]

Chloride concentrations increased the most compared to the other constituent concentrations during the analysis period at 6 of the 10 stations (fig. 16). Chloride concentrations in 2001 for the Little Missouri, Knife, Heart, Cannonball, James, and Park River stations were about twice as high as those in 1971. However, chloride concentrations in 2001 for the Wild Rice River, Sheyenne River, and Goose River at Hillsboro, N. Dak., stations were about the same as those in 1971, and chloride concentrations in 2001 for the Maple River station were less than those in 1971. Substantial increases also occurred in sulfate concentrations. Sulfate concentrations in 2001 for the Little Missouri and James River stations were about twice as high as those in 1971, and sulfate concentrations in 2001 for the Knife, Heart, and Cannonball River stations were about 1.5 times as high as those in 1971. In addition, sodium concentrations in 2001 for the Park River station were about twice as high as those in 1971, and moderate increases in sodium and calcium occurred at several stations.

Nutrients

Annual Concentration Anomalies

The normalized fitted annual concentration anomalies for total ammonia plus organic nitrogen and total phosphorus are shown in figure 17. The annual anomalies were divided by their respective values for January 1, 1979, rather than January 1, 1971, because data were not available for the Heart River before 1979. The normalized fitted annual anomalies for both nutrients showed a similar pattern of variability for the Knife River at Hazen and Sheyenne River near Kindred, N. Dak., stations but differed substantially for the Little Missouri River near Watford City, Heart River near Mandan, and Cannonball River at Breien, N. Dak., stations. Thus, as with major ions, annual climate variability evidently affects nutrients differently even within the same basin. For example, the annual anomaly for total ammonia plus organic nitrogen for the Cannonball River station decreased by about 50 percent from the beginning to the end of the drought (1988-92), but the annual anomaly for total phosphorus more than doubled during the same period. Although the pattern of variability for the two nutrients differed, the magnitude of variability was similar for all stations except the Little Missouri River station. The annual anomaly for that station for total phosphorus was much more variable than the annual anomaly for total ammonia plus organic nitrogen, and the annual anomalies for both nutrients were much more variable than for the remaining stations.

Concentration Trends

The fitted concentration trends and the model-adjusted concentrations for total ammonia plus organic nitrogen and total phosphorus are shown in appendices A and B. As mentioned previously and indicated in the appendices, a laboratory analysis bias occurred during 1986-91 for total ammonia plus organic nitrogen. A laboratory analysis bias also occurred before 1991 for total phosphorus. Thus, total phosphorus concentrations determined by the U.S. Geological Survey National Water Quality Laboratory may be slightly negatively biased before that year (Zimmerman and others, 1996; Trench and Vecchia, 2002). As indicated in the appendices, the potential biases for both total ammonia plus organic nitrogen and total phosphorus were estimated and removed before the normalized fitted trends shown in figure 18 were computed.

The normalized fitted concentration trends for total ammonia plus organic nitrogen show close agreement among the stations (fig. 18). A significant decrease in concentration occurred from 1974 through 1978 for the Little Missouri, Knife, and Cannonball River stations. For the Heart River station, data were not collected until 1978 so, although a decrease may have occurred before then, the decrease was not detected. For the Sheyenne River station, data were collected beginning in 1976 and the frequency of recorded data for 1976-78 is high. However, no decrease was detected for that period. Total ammonia plus organic nitrogen concentrations increased significantly at all stations from 1979 through the end of 1981. Concentrations nearly doubled during that time for the Sheyenne River station, more than doubled for the Knife, Heart, and Cannonball River stations, and nearly quadrupled for the Little Missouri River station. Concentrations at all stations decreased from 1982 through the late 1980's or early 1990's before stabilizing at levels slightly lower than those in 1979.

The normalized fitted concentration trends for total phosphorus (fig. 18) indicate a significant decrease in concentration from 1974 through 1978 for the Little Missouri River station. The remaining stations showed no trends during that time. Significant increases in concentration occurred from 1979 through 1981 for the Little Missouri, Knife,
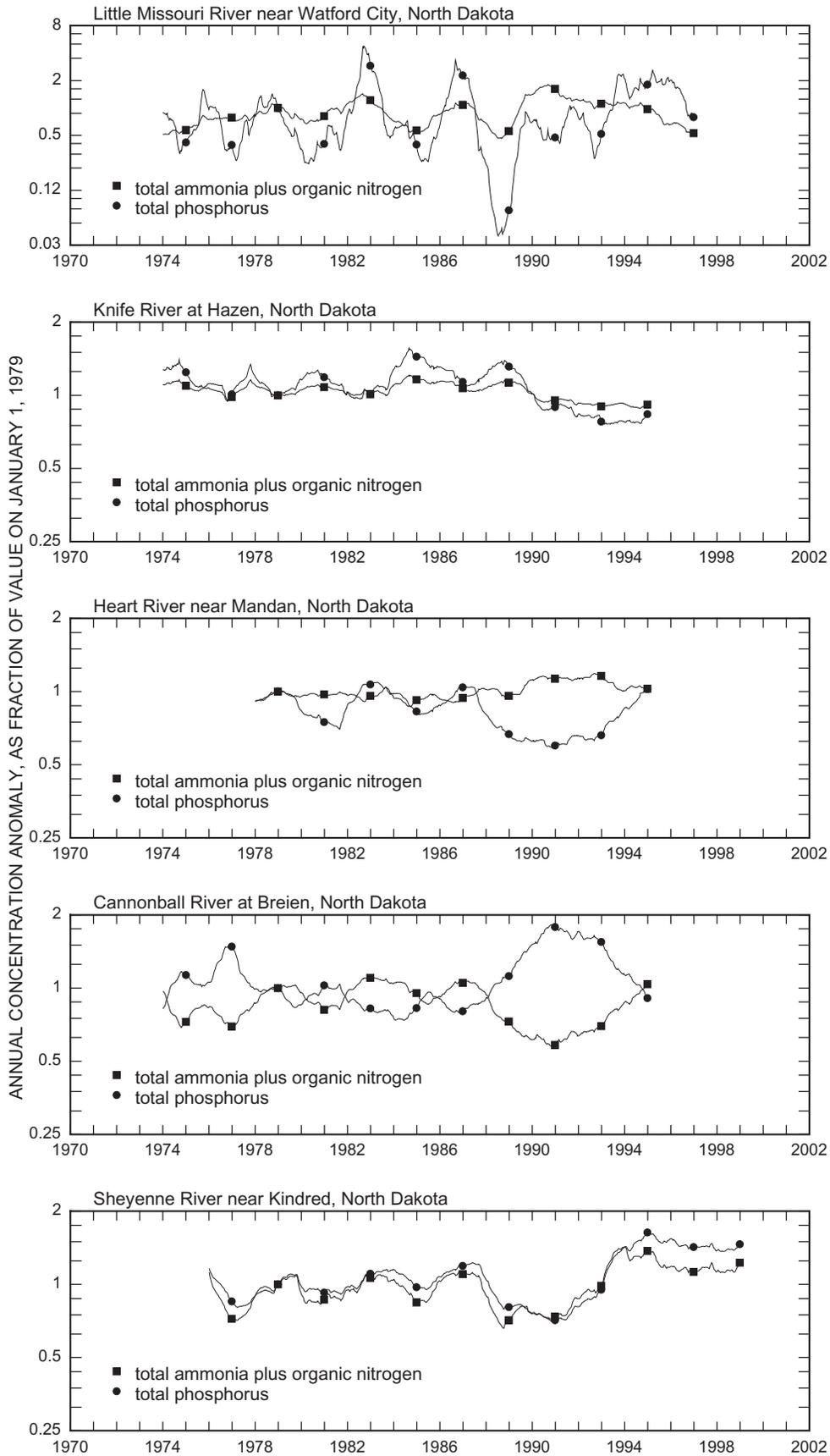
Figure 17. Normalized fitted annual concentration anomalies for total ammonia plus organic nitrogen and total phosphorus for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]
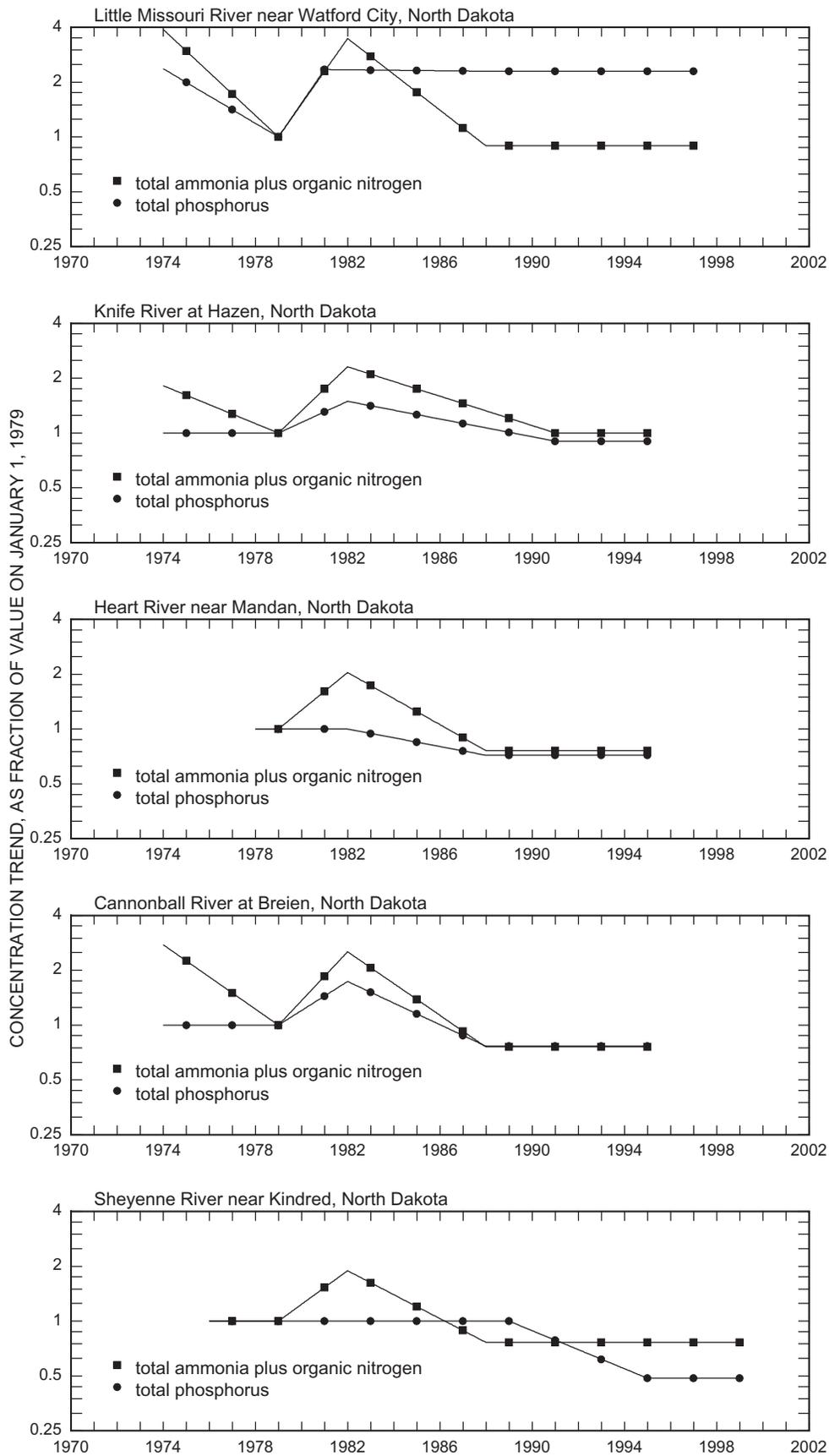
Figure 18. Normalized fitted concentration trends for total ammonia plus organic nitrogen and total phosphorus for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]

and Cannonball River stations. The largest increase occurred for the Little Missouri River station where concentrations more than doubled during a 2-year period. Significant decreases in concentration occurred from 1982 through 1987 for the Heart and Cannonball River stations, from 1982 through 1990 for the Knife River station, and from 1989 through 1994 for the Sheyenne River station. The lowest total phosphorus concentrations for all stations except the Little Missouri River station occurred at the end of the record.

The significant trends for total phosphorus were in the same direction as the corresponding trends for total ammonia plus organic nitrogen, but the trends for total phosphorus generally were smaller in magnitude than the trends for total ammonia plus organic nitrogen. Total phosphorus trends were not detected for many of the intervals that showed total ammonia plus organic nitrogen trends. However, because total phosphorus concentrations generally are close to the method detection limit and subject to more variability than total ammonia plus organic nitrogen concentrations, the trends in total phosphorus were more difficult to detect.

Trace Metals

Annual Concentration Anomalies

The normalized fitted annual concentration anomalies for iron and manganese, like those for calcium, sodium, sulfate, and chloride, show substantial persistence and variability for most stations (fig. 19). The annual anomalies for iron and manganese were similar for the Little Missouri River near Watford City, Knife River at Hazen, Heart River near Mandan, James River at LaMoure, and Sheyenne River near Kindred, N. Dak., stations but were different for the Cannonball River at Breien, Wild Rice River near Abercrombie, Goose River at Hillsboro, and Park River at Grafton, N. Dak., stations. The annual anomalies for manganese for the Little Missouri, Heart, Cannonball, and Sheyenne River stations have low variability compared to the annual anomalies for the remaining stations. Manganese concentrations for those four stations were highly censored (table 3), and the censoring may be masking the actual anomalies. The annual anomalies for iron have low to moderate variability except for the Cannonball River, Maple River near Enderlin, N. Dak., and Goose River stations. The annual anomalies for those stations have high variability.

Concentration Trends

The iron concentrations for the streams in eastern North Dakota show more trends than the iron concentrations for streams in southwestern North Dakota (fig. 20). The only trend for the southwestern streams was a decrease in concentration during 1971-81 for the Little Missouri River station. That trend is notable because it was the only decrease detected for the early to mid-1970's. However, a breakpoint in the late 1970's may not have been detected (possibly because of censored values), and the trend for the Little Missouri River station for 1971-81 may be more like the trends for the eastern streams. Trends may have occurred for the remaining southwestern streams as well, but the trends for those streams were not detected using the time-series model, possibly as a result of censored values.

The fitted trends for iron for the eastern streams show nearly unanimous agreement from 1971 through 1988 (fig. 20) and indicate two stable periods separated by an abrupt decrease in the late 1970's or early 1980's. The only exception is for the Park River station, which showed a significant increase from 1971 to 1978. The only trends detected for the last half of the record were increases for the James and Sheyenne River stations from 1989 to 1994. For every station, iron concentrations in 2001 were less than or equal to those in 1971.

The manganese concentrations for the streams in eastern North Dakota (fig. 20) also show more significant trends than the manganese concentrations for the streams in southwestern North Dakota. An increase in concentration was detected for the Knife River station for 1982-90, but no other trends were detected for the southwestern streams. The fitted trends for manganese for the Wild Rice, Goose, and Park River stations show large increases from 1971 to the late 1970's. The increases were followed by a rapid decrease that lasted about 2 years (fig. 20). The James, Sheyenne, and Maple River stations showed no trends for most of the 1970's, but concentrations for the Sheyenne and Maple River stations decreased during the late 1970's or early 1980's. The only trend in manganese concentrations after the early 1980's was an increase for the Wild Rice River station from 1983 through 1985. Manganese concentrations for the Wild Rice, Goose, and Park River stations were much higher in 2001 than in 1971.
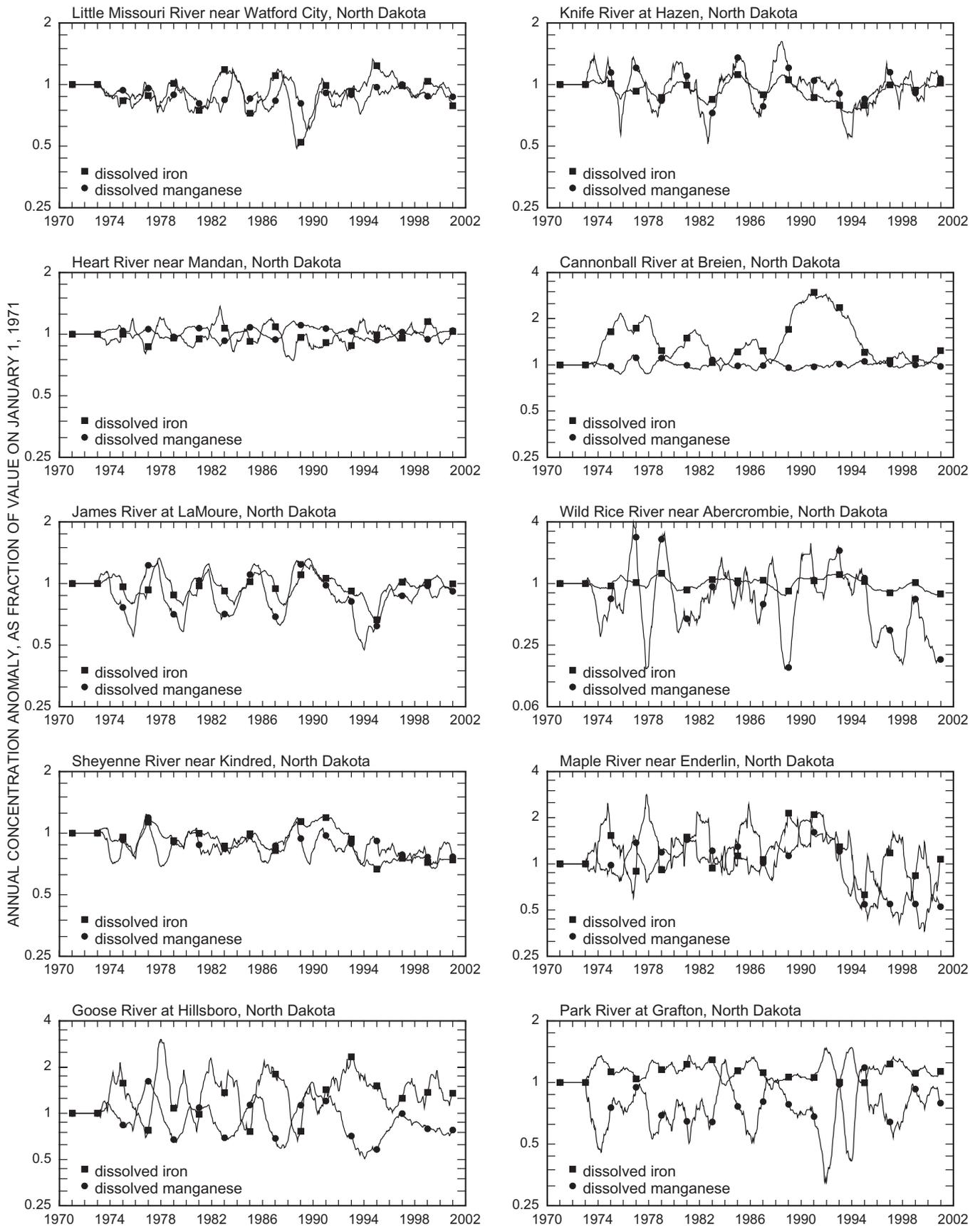
Figure 19. Normalized fitted annual concentration anomalies for dissolved iron and dissolved manganese for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]
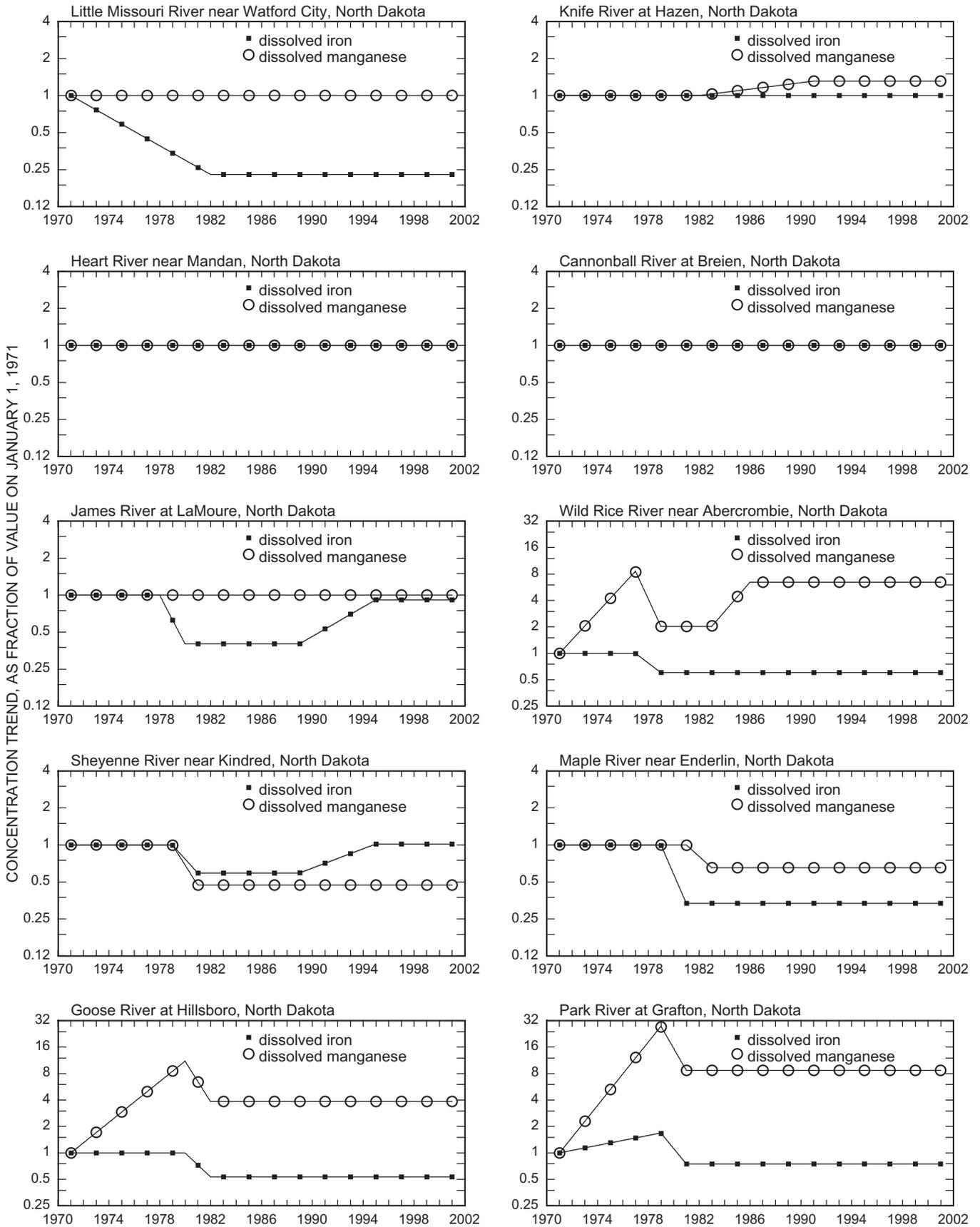
Figure 20. Normalized fitted concentration trends for dissolved iron and dissolved manganese for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis. [Vertical scales are indicated as log scales.]

The fitted trends for iron and manganese for the eastern streams (fig. 20) show many similarities to the fitted trends for calcium, sodium, sulfate, and chloride (fig. 16). Thus, the factors that affect trace-metal concentrations in the eastern streams may be similar to the factors that affect major-ion concentrations. However, the strong trends in major-ion concentrations for the southwestern streams were not evident in the trace-metal concentrations for those streams. Thus, the factors that affect major-ion concentrations in the southwestern streams may not affect trace-metal concentrations, or the effect may be masked by censoring or variability in the trace-metal concentrations close to the method detection limit.

POTENTIAL CAUSES OF HISTORICAL WATER-QUALITY TRENDS

The historical trend analysis in this report was used to detect statistically significant changes in constituent concentrations as a result of factors other than natural variability in streamflow. The trend analysis indicated numerous periods of significant improvement or deterioration in water quality across North Dakota during the past 3 decades. However, the analysis was exploratory rather than predictive in nature and, thus, cannot be used to determine the exact causes for the trends or to predict future water-quality changes. Therefore, this section presents a rudimentary example of how, with more extensive data gathering and model development, the time-series model used for the trend analysis can be used to obtain a better understanding of the potential causes of water-quality trends. The example pertains to total ammonia plus organic nitrogen concentrations for the Knife River at Hazen, Heart River near Mandan, and Cannonball River at Breien, N. Dak., stations.

The trends described previously for the model-adjusted total ammonia plus organic nitrogen concentrations (fig. 14) provided the best statistical fit to the data, assuming the trend consisted of a continuous piece-wise linear function of time superimposed with a step trend to account for the potential method bias that occurred during 1986-91. However, the general trend function (eq. 5) could instead consist of a linear combination of known covariates that possibly cause trends in total ammonia plus organic nitrogen concentrations. The large magnitudes of the historical concentration trends and the general agreement in the directions and times of the trends among the stations (fig. 18) indicate that the trends probably were caused by major changes that affected large parts of the Knife, Heart, and Cannonball River Basins. Several activities that occur throughout substantial parts of the basins are farming, livestock production, and oil production. Fertilizer applications associated with cropland, soil erosion and manure associated with livestock, and soil erosion associated with oil production could affect total ammonia plus organic nitrogen concentrations in streams. To fully evaluate how, or if, those activities affected the total ammonia plus organic nitrogen concentrations, detailed histories of crop production, fertilizer usage, livestock grazing and feedlot operations, oil drilling and exploration, etc., would be needed for each basin. Although those data could be obtained from existing databases of various State and Federal agencies, such a detailed analysis was beyond the scope of this report. Therefore, for this example, three readily available time series that are related to farming, livestock production, and oil production were used to determine which activities could have affected the total ammonia plus organic nitrogen concentrations.

The data used for this example (fig. 21) consist of annual total cropland data for calendar years 1970-2001 for eight North Dakota counties that overlap the Knife, Heart, and Cannonball River Basins; annual total livestock-inventory (cattle, sheep, and pig) data for January 1, 1970-2001, for the same eight counties; and annual total oil-production data for North Dakota for calendar years 1970-2001. The oil-production data were not readily available by county, but most of the oil from North Dakota is produced in the southwestern part of the State. The cropland and livestock-inventory data were obtained from the U.S. Department of Agriculture National Agricultural Statistics Service (accessed June 25, 2002), and the oil-production data were obtained from the North Dakota State Industrial Commission (accessed June 26, 2002). Although definitive cause-and-effect relations cannot be established without more detailed data, a preliminary analysis of the data can indicate the areas where more detailed data and a more detailed analysis could be useful for explaining the concentration trends.

As indicated in figure 21, substantial changes have occurred in the annual time series for cropland, livestock, and oil production during the past 30 years. These changes, in turn, may have affected the total ammonia plus organic nitrogen concentrations in the Knife, Heart, and Cannonball River Basins. Thus, if the preliminary analysis of the data indicates that a reasonable statistical relation exists between the model-adjusted total ammonia plus organic nitrogen concentrations and the cropland, livestock-inventory, or oil-production data, then a more detailed analysis of the cause of the relation may be warranted. However, if the preliminary analysis indicates that no statistical relation exists, then the total ammonia plus

organic nitrogen concentrations are not being affected by the farming, livestock inventory, or oil production in the basins, or the effect may be difficult to distinguish with the available concentration data.

To establish a "reasonable" statistical relation, three general constraints were used. The first general constraint was that the changes in the total ammonia plus organic nitrogen concentrations needed to lag the changes in the explanatory variables (cropland area, livestock inventory, or oil production) for a valid cause-and-effect relation to exist. The second general constraint was that the lag time between the changes in the explanatory variables and the changes in the concentrations needed to be short enough to avoid spurious correlations. For example, the adjusted total ammonia plus organic nitrogen concentrations were highly correlated with the livestock-inventory data lagged by 10 years but were only slightly correlated with the data lagged by less than 5 years. Thus, a 10-year lag time between the total ammonia plus organic nitrogen concentrations and the livestock-inventory data resulted in a better statistical fit than a shorter lag time. However, the effect of livestock inventory on the total ammonia plus organic nitrogen concentrations probably would not be minimal for many years and then increase 10 years later. Therefore, terms that relate the concentrations to lagged values of the explanatory variables were limited to lag times of 5 years or less. The third general constraint was that the relation between the concentrations and the lagged values of the explanatory variables needed to be monotonic. For example, if an
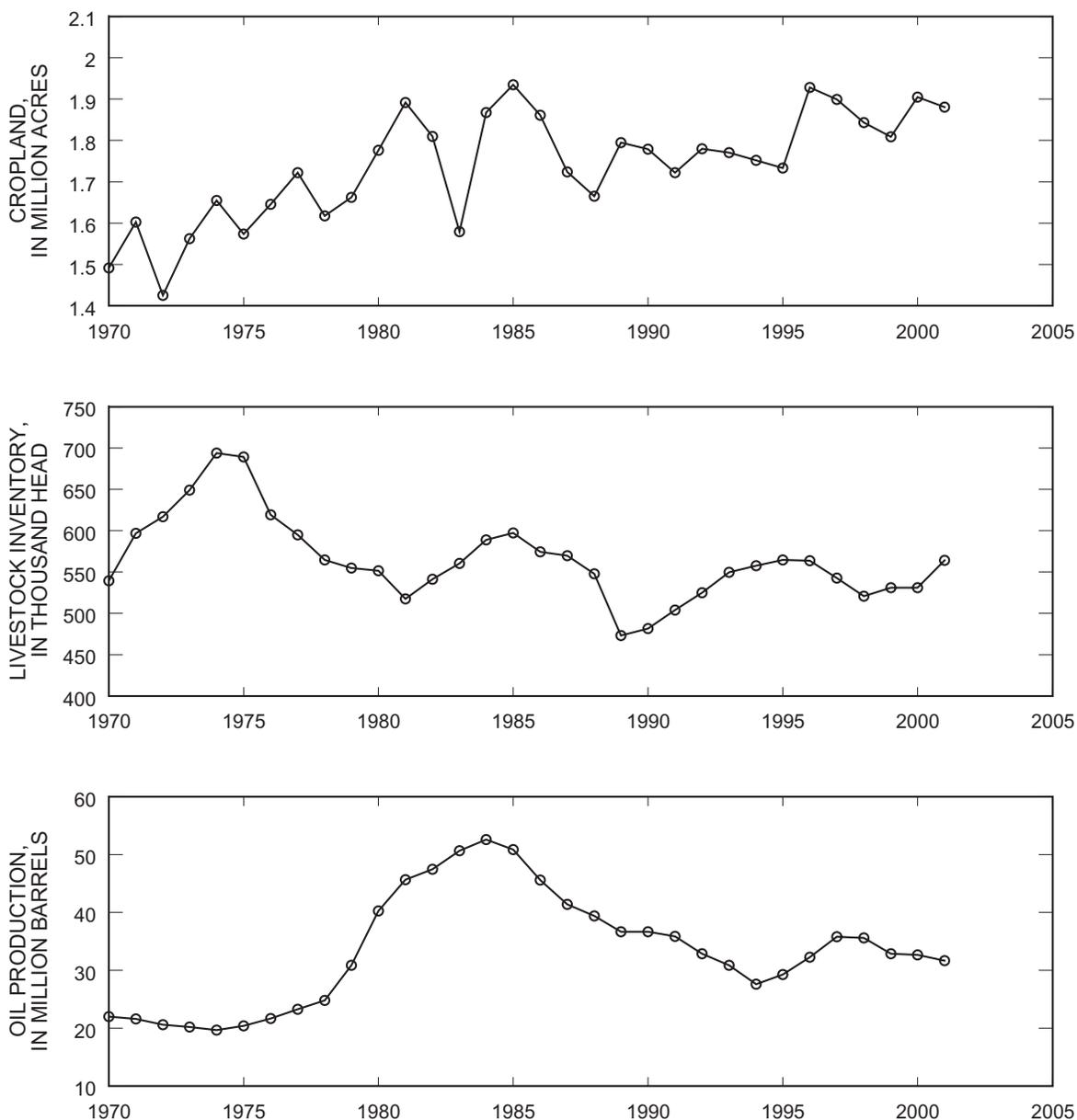

Figure 21. Annual total cropland for southwestern North Dakota, annual total livestock inventory for southwestern North Dakota, and annual total oil production for North Dakota for 1970-2001.

increase in oil production led to an increase in concentration, then a decrease in oil production could not also lead to an increase in concentration.

Various monotonic functions of the explanatory variables, for lags of 1 to 5 years, were considered as explanatory variables in the preliminary analysis. An all-subsets regression (S-Plus Statistical software package) then was used to determine the best combination of the explanatory variables for the adjusted total ammonia plus organic nitrogen concentrations. Because no combination of explanatory variables was found to provide a close match to the historical trends, the list of potential explanatory variables was expanded to include livestock inventory for the concurrent year (lag zero) and oil production for lead times of either 1 or 2 years. Because the livestock-inventory data are for January 1 of each year, allowing a lag-zero term was reasonable because livestock inventory at the beginning of the year might affect water quality for the remainder of the year. Allowing lead times for oil production also might be reasonable because the total ammonia plus organic nitrogen concentrations may be related more to oil exploration and drilling than to oil production, and changes in exploration and drilling probably lead to changes in production. Using all-subsets regression with the expanded list of explanatory variables, the best fitted trend for the Knife River was calculated with equation 9:

$$\Gamma(t) \ = \ -0.148 + 2.53\log\left[\frac{L(t)}{550}\right]^* + 1.65\log\left[\frac{O(t+1)}{32}\right]^* \tag{9}$$

where

$\Gamma(t)$ is the fitted trend in the adjusted total ammonia plus organic nitrogen concentration for year t;

$L(t)$ is the livestock inventory for January 1 of year t, in thousand head;

$O(t+1)$ is the oil production for year $t+1$, in million barrels; and

$[\ ]^*$ indicates that the value in brackets is replaced by 1 if the value is less than or equal to 1.

The fitted trend (eq. 9) explained 32 percent of the variability in historical adjusted total ammonia plus organic nitrogen concentrations and is similar to the piece-wise linear trend (fig. 22). However, the piece-wise linear trend shows an abrupt peak in the concentrations in 1982, and the fitted trend (eq. 9) shows a more rounded peak in about 1984. Because equation 9 is a threshold model, the explanatory variables have an effect on the total ammonia plus organic nitrogen concentrations only when the explanatory variables exceed a certain threshold (550,000 head of livestock or 32 million barrels of oil). Thus, if both variables are less than the threshold, the concentrations are not sensitive to fluctuations in the variables.

The fitted trend for the Heart River was calculated with equation 10:

$$\Gamma(t) \ = \ -0.357 + 1.85\log\left[\frac{O(t+2)}{32}\right]^*. \tag{10}$$

The fitted trend explained 42 percent of the variability in the historical adjusted total ammonia plus organic nitrogen concentrations and is similar to the piece-wise linear trend (fig. 22). Although no significant relation occurred between the total ammonia plus organic nitrogen concentrations and livestock inventory for the Heart River, the concentrations may have been affected by livestock inventory during the mid-1970's. The mid-1970's were years of high livestock inventory in the Heart River Basin, but no concentration data were available for the Heart River before 1978.

The fitted trend for the Cannonball River was calculated with equation 11:

$$\Gamma(t) \ = \ -0.138 + 4.13\log\left[\frac{L(t)}{550}\right]^* + 2.88\log\left[\frac{O(t+2)}{40}\right]^*. \tag{11}$$

The fitted trend explained 37 percent of the variability in the historical adjusted total ammonia plus organic nitrogen concentrations and is similar to the piece-wise linear trend (fig. 22). The threshold for oil production in the Cannonball
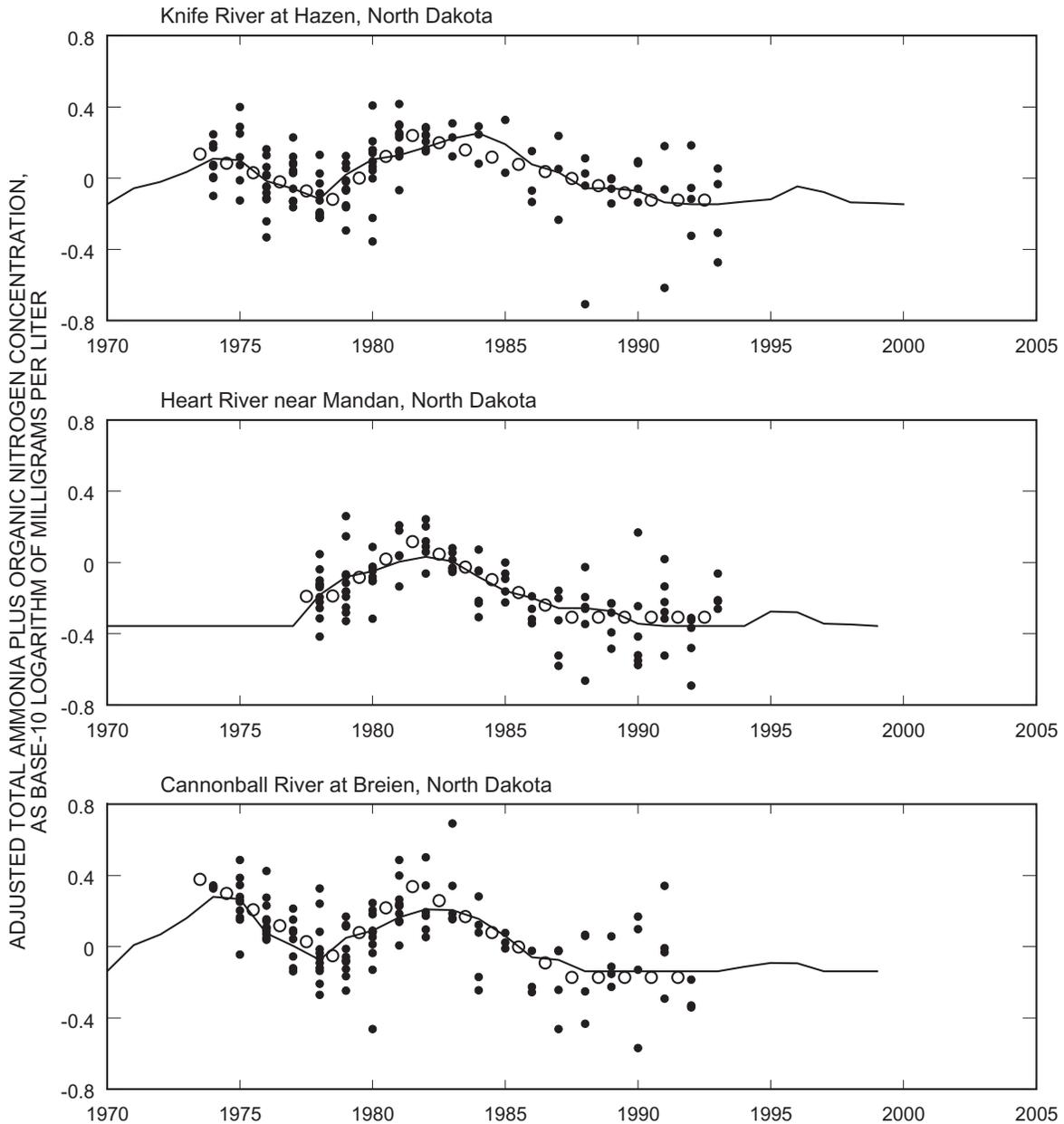
Figure 22. Model-adjusted total ammonia plus organic nitrogen concentrations (points), fitted trends based on piece-wise linear functions (circles), and fitted trends based on livestock-inventory and oil-production data (lines) for the Knife River at Hazen, Heart River near Mandan, and Cannonball River at Breien, N. Dak., streamflow-gaging stations.

River Basin was increased to 40 million barrels because smaller values for the threshold resulted in a much poorer fit to the data.

The preliminary analysis of the data indicated that increases in livestock grazing or feedlot operations might lead to increases in total ammonia plus organic nitrogen concentrations, which is a reasonable relation given that livestock waste is a potential source of ammonia and organic nitrogen. However, the relation between the total ammonia plus organic nitrogen concentrations and oil production is unclear. Perhaps extensive oil-production activities led to an increase in soil erosion and, thus, an increase in the amount of organic nitrogen entering the streams. Or, perhaps the large total ammonia plus organic nitrogen concentrations that occurred in the early 1980's were related to factors other than oil production, and oil production just happened to be high at that time. More detailed data and a more detailed analysis of the data could lead to a better understanding of the processes that affect water quality and allow conjectures based on the preliminary analysis to be confirmed or refuted on the basis of sound scientific evidence.

SAMPLING DESIGNS TO MONITOR FUTURE WATER-QUALITY TRENDS

The time-series model used to detect concentration trends for this report also can be used to evaluate various sampling designs to monitor future water-quality trends. As indicated in the previous example, the interpretation of trends in terms of cause and effect can be difficult and, although the data used in the preliminary analysis definitely indicate that trends are occurring, establishing a cause for the trends may require more extensive data gathering and model development. However, to evaluate the various sampling designs for this report, no interpretation of cause and effect was needed because the designs depend only on the statistical properties of the daily streamflow and concentration anomalies (eqs. 1 and 2) and the statistical properties of the daily anomalies are independent of the trends.

To evaluate various sampling designs, the number of samples collected (on average) each year needs to be considered along with the sampling dates and whether the number of samples or sampling dates should be fixed (the same year after year). To determine whether the number of samples or the sampling dates should be fixed or variable, an objective of the trend analysis needs to be specified. For example, if the objective of the trend analysis is to determine whether livestock inventory affects water quality, then the number of samples collected should be increased when livestock inventory is changing rapidly and decreased when livestock inventory is remaining relatively stable. Historically (fig. 21), this would indicate that the most advantageous times to sample would have been during the 1970's and the late 1980's. Without specific trend-analysis objectives and assuming that trends can occur at any time, in any direction, and for any duration, the best approach for trend monitoring is to collect a fixed number of samples each year. The sampling dates also should remain relatively fixed from year to year because varying the dates adds more variability and makes trend detection more difficult. However, sampling on the exact same days each year is neither feasible nor necessary.

Given that the number of samples and the sampling dates remain fixed from year to year, two related concepts-- sensitivity and efficiency--are used to evaluate sampling designs. Sensitivity measures the ability of a design to detect a trend--the smaller the trend that can be detected, the more sensitive the design. An efficient design maximizes the sensitivity to detect a trend for a fixed cost, which for this report was measured in terms of the number of samples per year. The only way to increase the sensitivity of an efficient design is to increase the cost--that is, to collect samples more frequently. For example, among all possible two-sample designs, the best (most efficient) design might be to sample once during April and once during August, and among all possible three-sample designs, the best design might be to sample once in March, once in May, and once in August. The best three-sample design is more sensitive than the best two-sample design but also is more costly. Therefore, to determine whether three samples are preferable to two samples, judgment is needed as to whether the increased sensitivity is worth the increased cost.

Given the fitted time-series models for historical streamflow and constituent concentrations (eqs. 1 and 2), the sampling designs for this report could be evaluated for any given constituent at any given location. The potential future data were assumed to consist of the daily streamflow anomalies and the daily concentration anomalies plus a linear trend by using equations 12 and 13:

$$X^*(t) \; = \; U(t) \tag{12}$$

and

$$Y^*(t) \; = \; \gamma t + W(t) \tag{13}$$

where

$X^*(t)$ is the future streamflow data (dimensionless) for time t ($t \geq 0$, where $t = 0$ corresponds with an arbitrary time origin);

$Y^*(t)$ is the future concentration data (dimensionless) for time t; and

γ is the slope of the concentration trend.

The assumptions were made that a streamflow gage would continue to be operated at each station (so that the daily streamflow anomalies could be computed) and that concentration data would be collected no more than once each month. Concentration data potentially could be collected as often as three times each month, but the cost of such data collection would be prohibitive. The assumption also was made that the concentration data would be collected near the fifth day of the month. However, the actual sampling date could vary from 1 week before to 1 week after the fifth day without appreciably changing the results of the design analysis.

Given the framework defined by equations 12 and 13, the sensitivity of a design could be determined using the PARMA model for the daily streamflow and concentration anomalies. The sensitivity is a function of the standard error of the estimated slope of the trend, which was defined as follows:

$$\sigma(D, n) = [V(\hat{\gamma}|D, n)]^{1/2} \tag{14}$$

where

$\sigma(D, n)$ is the standard error of the estimated slope for design D and duration n;

D is a design that specifies when concentration data are collected each year;

n is the duration of the trend, in years;

$V(\hat{\gamma}|D, n)$ is the variance of the estimated slope for design D and duration n; and

$\hat{\gamma}$ is the maximum-likelihood estimator of the slope based on the fitted PARMA model for the daily streamflow and concentration anomalies.

The methodology for computing σ is described by Vecchia (2000, appendix A).

The sensitivity of a sampling design depends on the duration of the trend. If concentrations are increasing at a rate of 5 percent per year, the chance of detecting the trend after only 1 year may be extremely small. However, if the trend persists for 5 years, the chance of detecting the trend increases dramatically. In contrast to the sensitivity of a design, the efficiency of a design is not dependent on the duration of the trend. If a particular four-sample (per year) design is most efficient for detecting a trend that persists for 5 years, that design generally also will be most efficient for detecting a trend that persists for 2 years or 10 years. Therefore, a 5-year duration was used as a benchmark to determine which designs in the design analysis were most efficient.

Sampling designs cannot detect trends with absolute certainty or prove that no trends exist with absolute certainty. Therefore, the size of the trend that can be detected depends on the acceptable level of tolerance for incorrectly identifying a trend. For this report, the acceptable level of tolerance was controlled by specifying two parameters--the probability that a true trend was detected and the probability that a trend was detected when no true trend existed. Because the selection of an efficient design is not highly dependent on the values specified for the two probabilities, for this analysis, the first probability was set equal to 0.8 and the second probability was set equal to 0.1. The designs then were compared in terms of their characteristic trend (Vecchia, 2000, appendix A):

$$CT(D) = 100(10^{2.123\sigma(D, 5)} - 1) \tag{15}$$

where

$CT(D)$ is the characteristic trend for design D.

The characteristic trend is interpreted as the increase in concentration, in percent per year, that has an 80-percent chance of being detected (using a significance level of 10 percent) after 5 years of sampling. Trends larger than the characteristic trend have more than an 80-percent chance of being detected, and trends smaller than the characteristic trend have less than

an 80-percent chance of being detected. The characteristic trend served as a benchmark for comparing the sensitivity of the various sampling designs.

Sampling designs first were evaluated with regard to their sensitivity to detect annual trends--that is, trends that occur uniformly throughout the year. Then, the designs were evaluated with regard to their sensitivity to detect trends that occurred during three 5-month seasons--December through April, April through August, and August through December. Additional samples were added to the annual design, if warranted, to increase the sensitivity to detect trends in certain constituents during the three seasons.

In the following discussion, a sampling design is said to have low sensitivity for a given constituent if the characteristic trend is greater than 15 percent for major ions, 18 percent for total ammonia plus organic nitrogen, 30 percent for total phosphorus, or 45 percent for trace metals. A design is said to have high sensitivity if the characteristic trend is less than 10 percent for major ions, 12 percent for total ammonia plus organic nitrogen, 20 percent for total phosphorus, or 30 percent for trace metals. A design with neither high nor low sensitivity is said to have moderate sensitivity. A good design is one in which all constituents have either moderate or high sensitivity.

Detection of Annual Trends

A total of 4,095 potential sampling designs with at most one sample per month were analyzed for detection of annual trends for this report. However, detailed analysis of the sensitivity of the designs indicated that designs with three to six samples per year generally were good designs for detecting annual trends. Designs with only one or two samples per year had low sensitivity for detecting trends in some constituents, and designs with more than six samples per year generally resulted in only small improvements in sensitivity over designs with six samples per year. Among the designs with three to six samples per year, balanced designs (those for which samples were allocated equally throughout the year) tended to be more efficient than unbalanced designs (those for which samples were allocated more heavily toward a particular season). For example, the sensitivities of 23 designs with 1 to 12 samples per year are shown in figure 23 for the Knife River at Hazen, N. Dak., station. All one-sample designs (1 through 4) have low sensitivity for several constituents. Design 1, with a single sample in October, has low sensitivity for dissolved chloride, total ammonia plus organic nitrogen, total phosphorus, and dissolved iron. Design 3, with a single sample in April, has low sensitivity for all constituents except dissolved calcium and manganese, and design 4, with a single sample in July, has low sensitivity for dissolved sodium, sulfate, chloride, and iron. The two-sample designs (5 through 12) tend to be more sensitive than the one-sample designs whether samples are collected in successive months or are collected several months apart. However, most of the two-sample designs have low sensitivity for one or more constituents. Of the three-sample designs, the balanced designs (17 through 20) are good designs and tend to be more efficient than the unbalanced designs (13 through 16). Design 19 (December, April, and August) is a good three-sample design for all constituents, but design 15 (April, May, and June) has low sensitivity for dissolved sulfate and iron. Both balanced six-sample designs (21 and 22) have high sensitivity for all constituents. Design 21 has better sensitivity than design 19, particularly for nutrients and trace metals, but design 21 is twice as costly as design 19 and the improved sensitivity may not justify the added cost. Increasing from 6 samples to 12 samples per year (design 23) produced little improvement in sensitivity.

Sampling design results for the Sheyenne River near Kindred, N. Dak., station (fig. 24) again show that all one-sample designs have low sensitivity for some constituents and that the balanced designs tend to have better sensitivity overall than the unbalanced designs. Several two-sample designs (9, 10, and 12) are good designs, but design 11 has low sensitivity for some constituents. Design 11, with samples in April and August (one sample collected near or shortly after spring peak flow and one sample collected during summer low flow), has been ongoing since about 1990 at most of the stations. Design 19 (December, April, and August) has high sensitivity for detecting annual trends in all constituents and, thus, may be preferable to design 11. Some improvement in sensitivity for dissolved chloride and manganese can be gained by increasing from three to six samples per year (for example, from design 19 to design 21), but the improvement may not justify the added cost. Sampling more than six times per year produced little improvement in sensitivity.

In summary, sampling design results for the Knife and Sheyenne River stations (figs. 23 and 24) and for the remaining stations (not shown in figures) indicated that balanced designs consisting of three samples per year, with about 4 months between samples, generally are good overall designs for detecting annual trends in major ions, nutrients, and trace metals for the streams analyzed. The specific months in which the samples are collected are not important as long as about
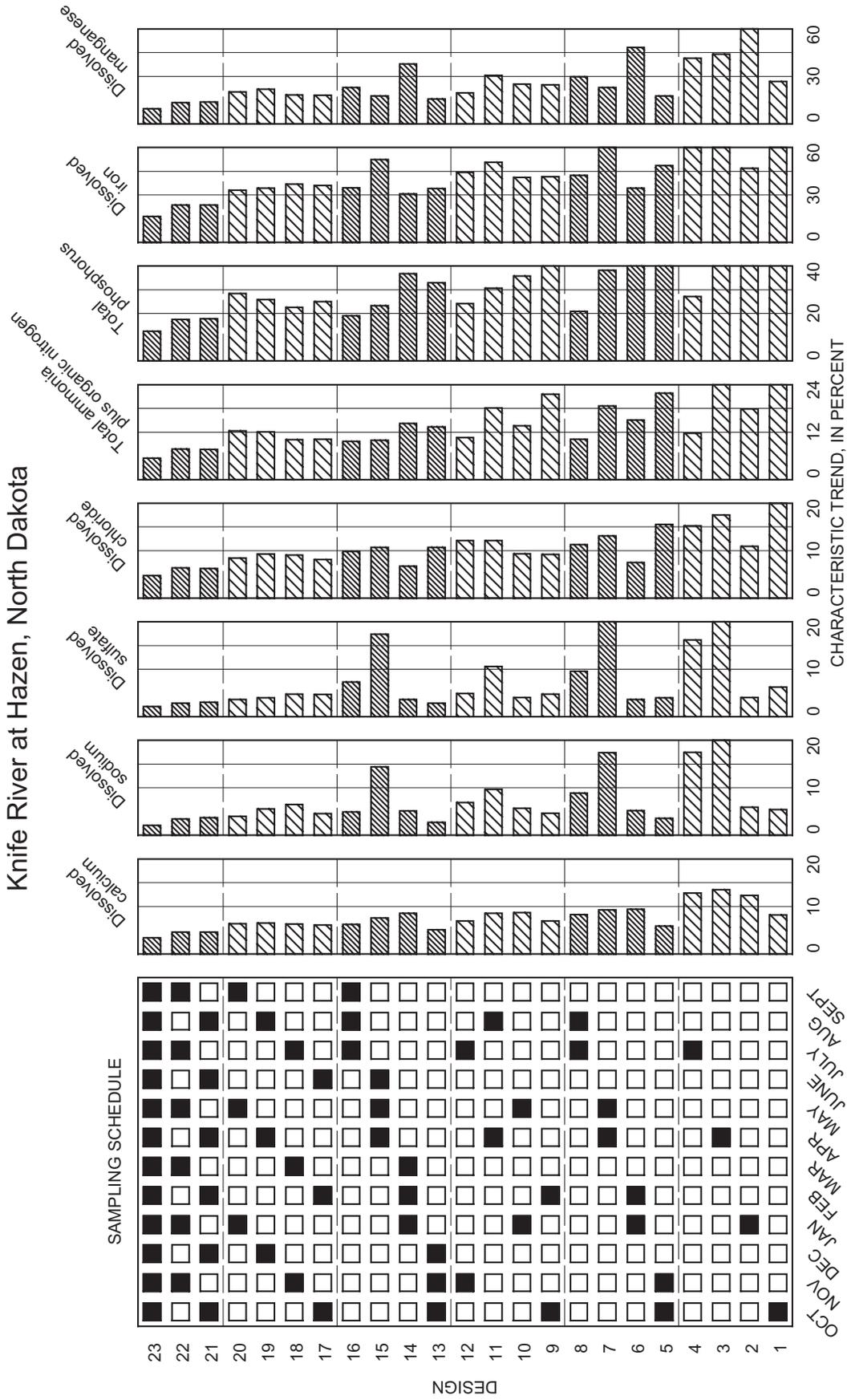
Figure 23. Characteristic trends of selected sampling designs for detection of annual trends in major ions, nutrients, and trace metals for the Knife River at Hazen, N. Dak., streamflow-gaging station.

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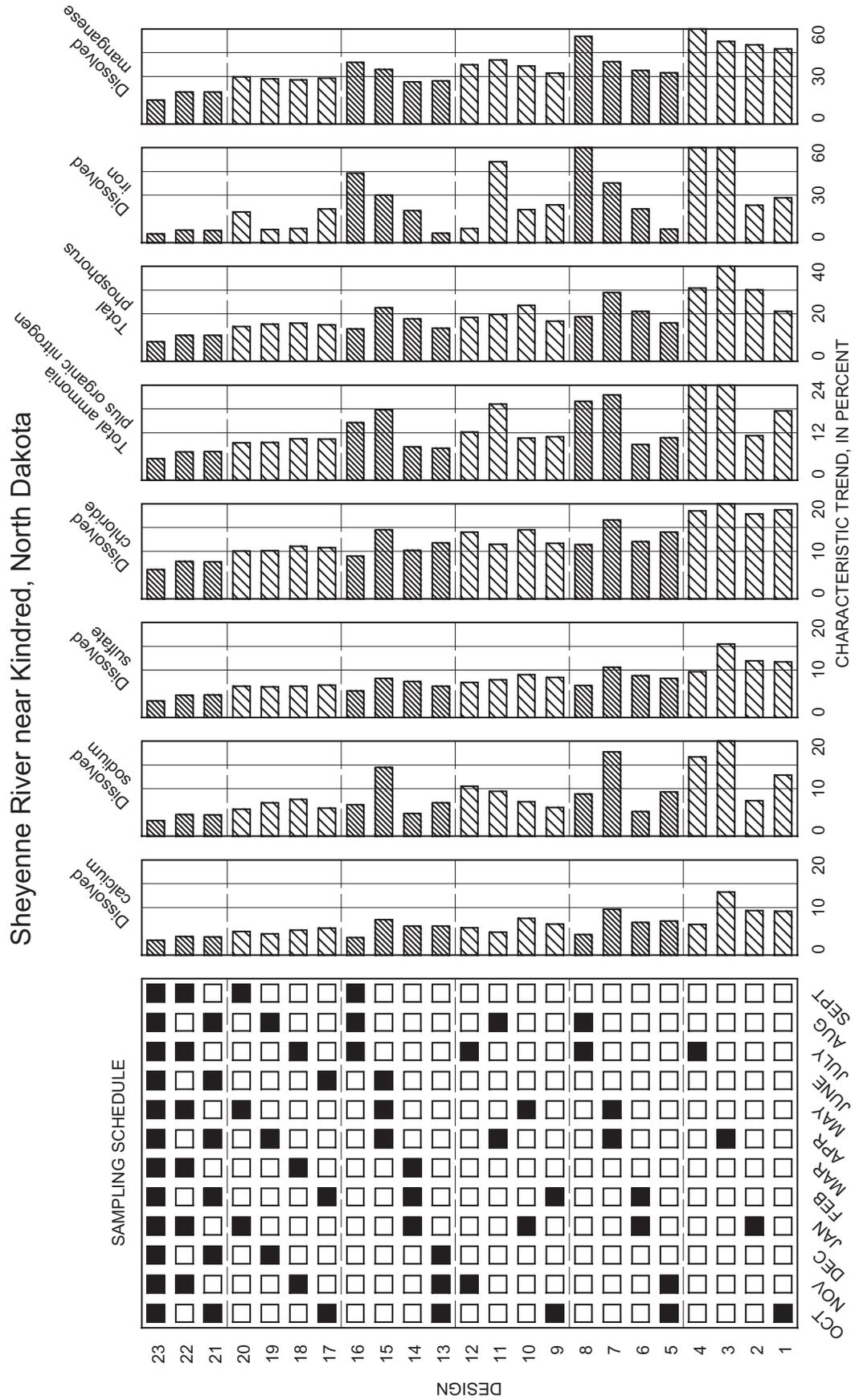
Figure 24. Characteristic trends of selected sampling designs for detection of annual trends in major ions, nutrients, and trace metals for the Sheyenne River near Kindred, N. Dak., streamflow-gaging station.

4 months separate the samples. A three-sample design with samples collected near the beginning of December, April, and August is a good choice because such a design would include samples collected during high flow and low flow along with an additional sample in late fall.

Detection of Seasonal Trends

Sampling designs that are sensitive for the detection of annual trends may not be sensitive for the detection of seasonal trends. The best months to collect samples for the detection of annual trends generally correspond with the months in which the variability in the daily concentration anomaly is low and trends can be distinguished most effectively from variability in the daily anomaly. However, in some cases, the most critical months for monitoring trends are those in which the variability in the daily concentration anomaly is high. Furthermore, monitoring programs may have objectives other than trend monitoring that also may require concentration data. For example, the estimation of annual constituent loads generally requires more concentration data for high-flow conditions than does the detection of trends (Gilroy and others, 1990). Thus, additional samples may be collected during those conditions although the samples may not be necessary for the detection of annual trends. For other applications, certain constituent concentrations during the fall or winter may be of primary importance, and more samples may be collected during those seasons although the samples may not be necessary for the detection of annual trends. Therefore, the best three-sample design for detecting annual trends (design 19) (December, April, and August) was evaluated with respect to its sensitivity to detect trends during three 5-month seasons-- April through August, which typically overlaps the beginning of spring high flow through the end of the hydrograph recession (fig. 4); August through December, which typically overlaps the beginning of summer low flow through the end of the open-water season; and December through April, which typically overlaps the beginning of winter freezeup through the end of the spring melt. The April through August season accounts for most of the surface runoff from a basin and, thus, probably is the most important season for detecting trends in constituents that have sources that extend over large parts of the basin. However, the other seasons may be important for detecting trends in constituents that originate primarily from ground-water discharge, irrigation return flow, or point sources near the stream or for detecting trends in constituents that are affected by seasonal variations in temperature or other climatic conditions.

The sensitivities of various sampling designs for detecting seasonal trends for the Knife River near Hazen, N. Dak., station are shown in figure 25. The annual design with three samples per year (design 19) consists of a combination of the seasonal designs with two samples per season (designs 1, 6, and 11). Although design 19 is a good design for detecting annual trends, it has low sensitivity for some constituents during the April through August (design 1) and December through April (design 11) seasons. Therefore, design 19 may need to be augmented with extra samples to improve the sensitivity to detect trends in those seasons. Designs 1, 6, and 11 are good designs for all four major ions so no extra samples would need to be added in any season. For nutrients and trace metals, design 6 is a good design so no extra samples would need to be added in the August through December season. However, adding a sample in June (design 2) would greatly improve the sensitivity of design 1 for nutrients and trace metals, and adding a sample in February (design 12) would greatly improve the sensitivity of design 11 for nutrients and trace metals. Adding a sample in January (design 13) would further improve sensitivity over design 12 for nutrients and trace metals, but adding a sample in January may not be necessary unless trends during the winter season are of primary importance. In summary, a good overall design for detecting both annual and seasonal trends for the Knife River station consists of collecting major-ion, nutrient, and trace-metal samples in December, April, and August and collecting extra nutrient and trace-metal samples in June and February.

The sensitivities of various sampling designs for detecting seasonal trends for the Sheyenne River near Kindred, N. Dak., station are shown in figure 26. Although design 19 is a good design for detecting annual trends, it has low sensitivity for total ammonia plus organic nitrogen and dissolved iron during the April through August (design 1) season. Adding a sample in June (design 2) would greatly improve the sensitivity for both total ammonia plus organic nitrogen and dissolved iron. Thus, design 2 is a good alternative to design 1 for detecting trends in nutrients and trace metals. Adding a sample in February (design 12) also might be considered for improving sensitivity for dissolved chloride. In summary, a good overall design for detecting both annual and seasonal trends for the Sheyenne River station consists of collecting major-ion, nutrient, and trace-metal samples in December, April, and August and collecting extra nutrient and trace-metal samples in June.
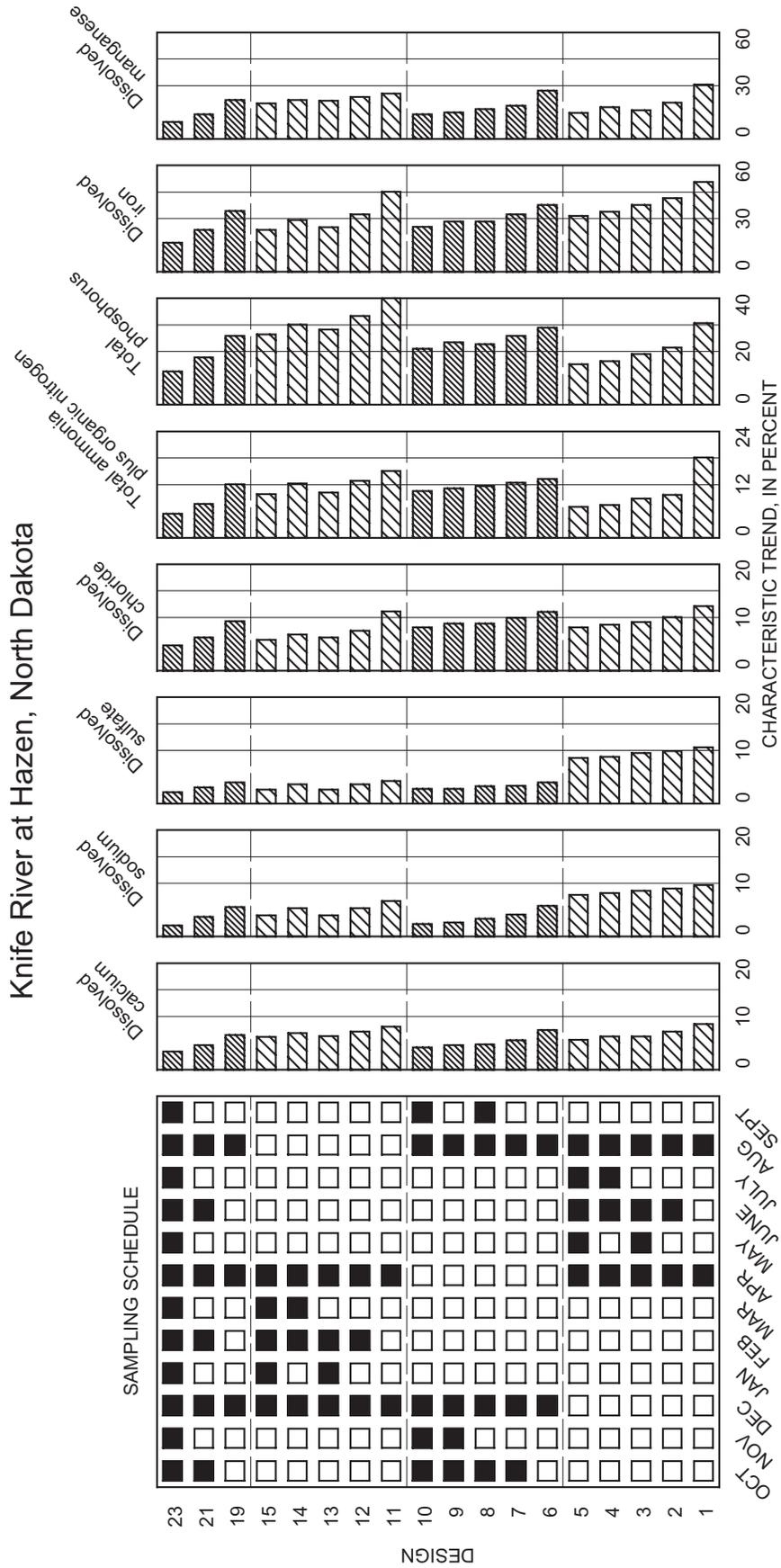
Figure 25. Characteristic trends of selected sampling designs for detection of seasonal trends in major ions, nutrients, and trace metals for the Knife River at Hazen, N. Dak., streamflow-gaging station.
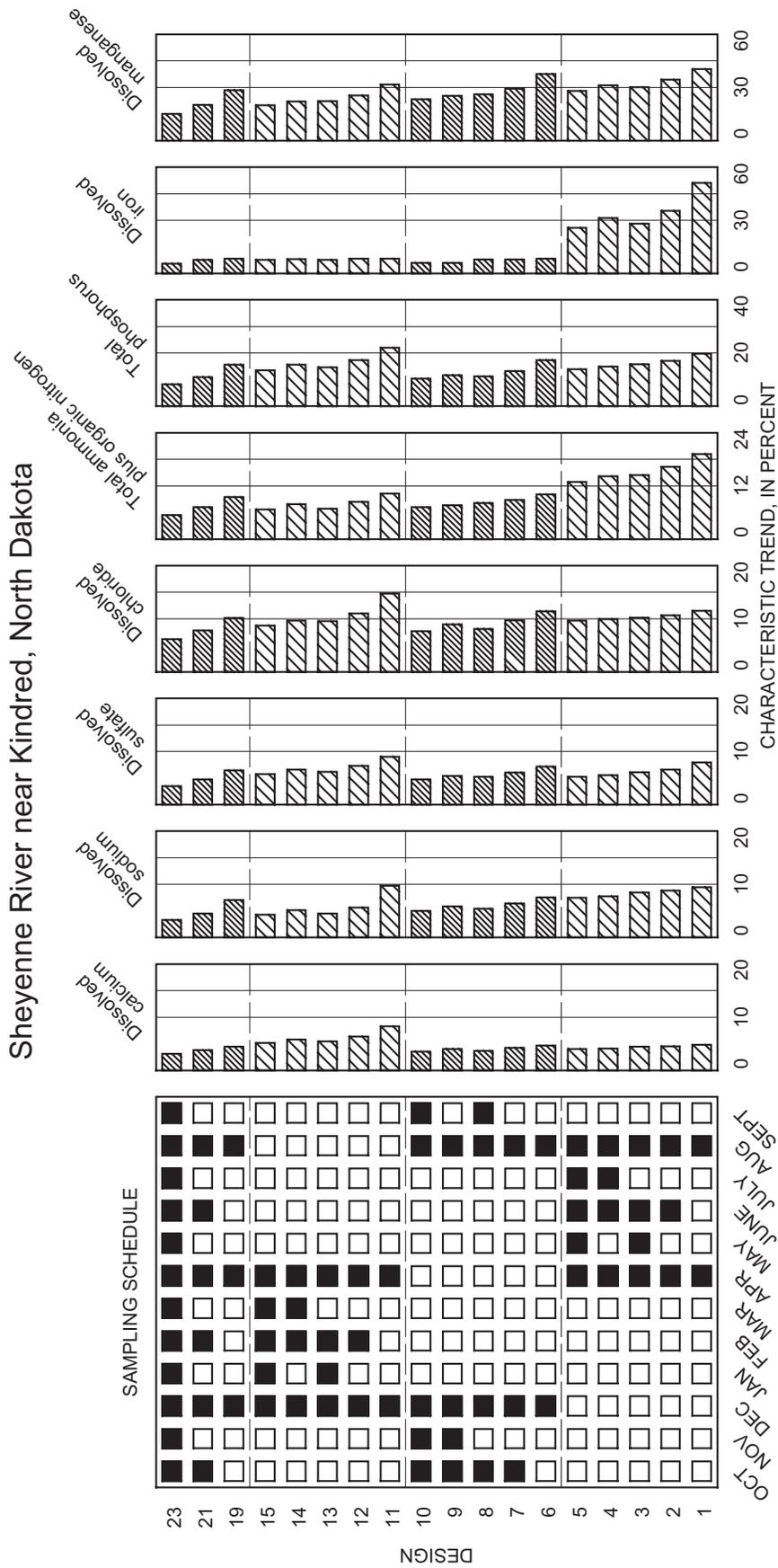
Figure 26. Characteristic trends of selected sampling designs for detection of seasonal trends in major ions, nutrients, and trace metals for the Sheyenne River near Kindred, N. Dak., streamflow-gaging station.

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The sensitivities of various sampling designs for detecting seasonal trends for the Goose River at Hillsboro, N. Dak., station are shown in figure 27. Design 1 has low sensitivity for dissolved sodium and chloride and adding a sample in June (design 2) would greatly improve the sensitivity for both constituents. Thus, design 2 is a good alternative to design 1 for detecting trends in major ions. Design 2 also may be a good alternative to design 1 for trace metals because of the substantial improvements in sensitivity for both dissolved iron and manganese. Design 6 has low sensitivity for dissolved iron and manganese and adding a sample in October (design 7) would greatly improve the sensitivity for both of those constituents. Thus, design 7 is a good alternative to design 6 for trace metals. Design 11 has low sensitivity for dissolved iron and adding a sample in February (design 12) would somewhat improve the sensitivity for that constituent. However, the small improvement in sensitivity may not justify the extra sample. In summary, a good overall design for detecting both annual and seasonal trends for the Goose River station consists of collecting major-ion and trace-metal samples in December, April, and August and collecting an extra major-ion sample in June and an extra trace-metal sample in October.

The previous sampling design results and results for the remaining stations (not shown in figures) indicate that an efficient design for detecting both annual and seasonal trends for most constituents is the three-sample design with samples in December, April, and August augmented with one or more extra samples in June, October, or February. The historical sampling frequency for 1996-2000 (table 3) consisted of two or fewer samples per year with samples collected either during spring high flow or summer low flow. That sampling frequency would not be adequate for monitoring trends in major ions, nutrients, or trace metals as indicated by the large characteristic trends for most constituents for design 6 (figs. 25 through 27). Conversely, the historical sampling frequency for major ions and nutrients for 1976-80 (table 3) when about 9 or 10 samples per year were collected at each station would be higher than necessary for monitoring trends. This is indicated by the small improvement in sensitivity that can be achieved by sampling more frequently than six times per year. The historical sampling frequency for 1981-95 consisted of about four samples per year for most constituents (table 3). As indicated in the previous examples, this sampling frequency appears to be a good "middle-ground" for monitoring trends provided sample collection is efficiently allocated among stations and among months. However, some stations may require only three samples per year, but others may require four, five, or six samples per year. Given an average of four samples per

Goose River at Hillsboro, North Dakota
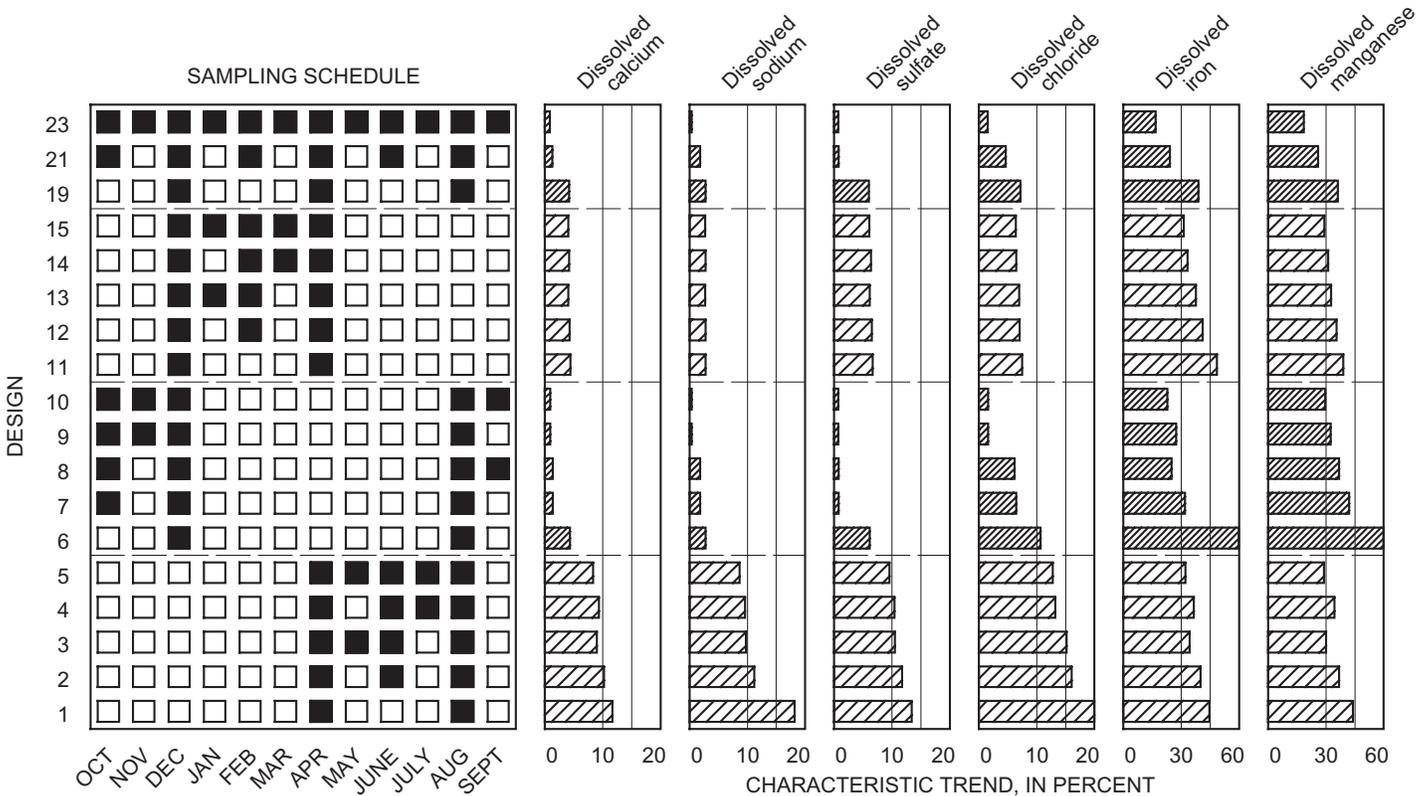
Figure 27. Characteristic trends of selected sampling designs for detection of seasonal trends in major ions, nutrients, and trace metals for the Goose River at Hillsboro, N. Dak., streamflow-gaging station.

year per station (40 samples at the 10 stations), high sensitivity, or even moderate sensitivity, may not be achieved for every constituent and every station. Therefore, a procedure for prioritizing placement of the extra samples among the various seasons and stations was needed to make the most efficient use of limited resources.

The characteristic trends of the seasonal sampling designs were used to efficiently allocate extra samples among seasons and stations. The characteristic trends for each of three pairs of seasonal designs (A1 and A2, B1 and B2, and C1 and C2) are given in table 6. The highest priority for extra samples was given to months and/or stations where the extra sample would result in the largest decrease in the characteristic trends. Thus, the benefit of an extra sample for a given station, month, and constituent was given by equation 16:

$$B(i, j, k) \ = \ CT1(i, j, k) - CT2(i, j, k) \tag{16}$$

where

$B(i, j, k)$ is the benefit of an extra sample for station i, month j, and constituent k;

$i \ = \ 1, 2, ... 10$ is the station number (table 1);

$j \ = \ 1, 2,$ or 3, with $j \ = \ 1$ corresponding to June, $j \ = \ 2$ to October, and $j \ = \ 3$ to February;

$k \ = \ 1, 2, ... 8$ is the constituent number (table 2);

$CT1$ is the characteristic trend of design A1 (if $j \ = \ 1$), B1 (if $j \ = \ 2$), or C1 (if $j \ = \ 3$); and

$CT2$ is the characteristic trend of design A2 (if $j \ = \ 1$), B2 (if $j \ = \ 2$), or C2 (if $j \ = \ 3$).

The overall benefit of an extra sample for a constituent group (major ions, nutrients, or trace metals) was defined as the average of the benefits for each individual constituent in the group with equations 17 through 19:

$$BI(i, j) \ = \ \frac{[B(i, j, 1) + B(i, j, 2) + B(i, j, 3) + B(i, j, 4)]}{4}; \tag{17}$$

$$BN(i, j) \ = \ \frac{[B(i, j, 5) + B(i, j, 6)]}{2}; \tag{18}$$

and

$$BT(i, j) \ = \ \frac{[B(i, j, 7) + B(i, j, 8)]}{2} \tag{19}$$

where

BI is the benefit of an extra major-ion sample for station i and month j;

BN is the benefit of an extra nutrient sample for station i and month j; and

BT is the benefit of an extra trace-metal sample for station i and month j.

The benefits of extra major-ion samples could be computed for all 10 stations. However, the benefits of extra nutrient samples could be computed only for the five stations that had historical nutrient data. Although all 10 stations had historical trace-metal data that were used in the trend analysis, one station (the Wild Rice River near Abercrombie, N. Dak., station) did not have sufficient dissolved iron or dissolved manganese data to compute the benefit of extra trace-metal samples and, thus, was not included in the computation. The Little Missouri River near Watford City and Heart River near Mandan, N. Dak., stations did not have sufficient dissolved manganese data so, for those stations, only dissolved iron data were used to compute the benefit of extra trace-metal samples.

Table 6. Characteristic trends of selected sampling designs for major ions, nutrients, and trace metals

[The characteristic trend is the increase in concentration, in percent per year, that has an 80-percent chance of being detected after 5 years of sampling; (I), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in major ions; (N), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in nutrients; (T), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in trace metals]

Station name	Constituent	Design (months in which samples are collected)					
		A1	A2	B1	B2	C1	C2
		April August	April June August	August December	August October December	December April	December February April
Little Missouri River near Watford City, N. Dak.	Calcium, dissolved	16	12(I)	17	11(I)	14	13
	Sodium, dissolved	13	10(I)	13	11(I)	16	16
	Sulfate, dissolved	14	11(I)	13	10(I)	12	12
	Chloride, dissolved	17	14(I)	19	15(I)	21	17
	Nitrogen, ammonia plus organic, total	43	37(N)	10	10	10	3
	Phosphorus, total	125	78(N)	14	14	14	14
	Iron, dissolved	68	61	110	48(T)	79	72
Knife River at Hazen, N. Dak.	Calcium, dissolved	8	7	7	5	8	7
	Sodium, dissolved	10	9	6	4	6	5
	Sulfate, dissolved	11	10	4	4	4	4
	Chloride, dissolved	12	10	11	10	11	7
	Nitrogen, ammonia plus organic, total	18	9(N)	13	12	15	13(N)
	Phosphorus, total	31	22(N)	29	26	42	33(N)
	Iron, dissolved	51	43	37	32	45	32
	Manganese, dissolved	31	20	26	18	24	22
Heart River near Mandan, N. Dak.	Calcium, dissolved	8	6	6	5	6	5
	Sodium, dissolved	8	7	5	4	6	5
	Sulfate, dissolved	11	10	7	5	7	6
	Chloride, dissolved	18	17	12	8	13	12
	Nitrogen, ammonia plus organic, total	19	16	18	15	16	13
	Phosphorus, total	27	22	33	26	26	22
	Iron, dissolved	47	32(T)	23	21	25	21
Cannonball River at Breien, N. Dak.	Calcium, dissolved	16	12(I)	8	7	8	7
	Sodium, dissolved	14	12(I)	5	4	5	5
	Sulfate, dissolved	21	16(I)	8	7	8	7
	Chloride, dissolved	20	15(I)	16	11	15	13
	Nitrogen, ammonia plus organic, total	20	16(N)	32	4(N)	19	16
	Phosphorus, total	49	38(N)	41	30(N)	36	31
	Iron, dissolved	53	45	52	41(T)	42	30
	Manganese, dissolved	32	30	35	21(T)	30	24

Table 6. Characteristic trends of selected sampling designs for major ions, nutrients, and trace metals—Continued

[The characteristic trend is the increase in concentration, in percent per year, that has an 80-percent chance of being detected after 5 years of sampling; (I), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in major ions; (N), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in nutrients; (T), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in trace metals]

Station name	Constituent	Design (months in which samples are collected)					
		A1 April August	A2 April June August	B1 August December	B2 August October December	C1 December April	C2 December February April
James River at LaMoure, N. Dak.	Calcium, dissolved	9	7(I)	8	6	9	8
	Sodium, dissolved	15	10(I)	11	9	10	9
	Sulfate, dissolved	13	10(I)	10	8	10	8
	Chloride, dissolved	15	12(I)	14	12	14	13
	Iron, dissolved	36	32	34	26(T)	42	26(T)
	Manganese, dissolved	55	40	61	49(T)	53	42(T)
Wild Rice River near Abercrombie, N. Dak.	Calcium, dissolved	16	10(I)	13	11	11	10(I)
	Sodium, dissolved	22	17(I)	22	19	19	14(I)
	Sulfate, dissolved	23	16(I)	22	20	17	13(I)
	Chloride, dissolved	17	13(I)	17	17	18	14(I)
Sheyenne River near Kindred, N. Dak.	Calcium, dissolved	4	4	4	4	8	6
	Sodium, dissolved	9	8	7	6	10	5
	Sulfate, dissolved	8	7	7	6	9	7
	Chloride, dissolved	12	11	12	10	15	11
	Nitrogen, ammonia plus organic, total	19	16	10	8	10	8
	Phosphorus, total	20	17	18	13	22	17
	Iron, dissolved	51	35(T)	8	8	8	8
	Manganese, dissolved	41	34(T)	38	30	32	24
Maple River near Enderlin, N. Dak.	Calcium, dissolved	7	5(I)	3	2	3	3
	Sodium, dissolved	13	8(I)	11	7	10	9
	Sulfate, dissolved	8	3(I)	3	3	3	3
	Chloride, dissolved	21	12(I)	16	15	13	11
	Iron, dissolved	35	32	61	31(T)	40	36
	Manganese, dissolved	33	22	4	4(T)	3	3
Goose River at Hillsboro, N. Dak.	Calcium, dissolved	12	10(I)	5	2(I)	4	4
	Sodium, dissolved	18	11(I)	3	2(I)	3	3
	Sulfate, dissolved	13	12(I)	6	1(I)	6	6
	Chloride, dissolved	22	16(I)	11	6(I)	7	7
	Iron, dissolved	45	40	60	32(T)	48	41
	Manganese, dissolved	44	37	63	41(T)	39	36

Table 6. Characteristic trends of selected sampling designs for major ions, nutrients, and trace metals—Continued

[The characteristic trend is the increase in concentration, in percent per year, that has an 80-percent chance of being detected after 5 years of sampling; (I), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in major ions; (N), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in nutrients; (T), indicates cases where an extra sample in June, October, or February would be most beneficial for detecting trends in trace metals]

Station name	Constituent	Design (months in which samples are collected)					
		A1	A2	B1	B2	C1	C2
		April August	April June August	August December	August October December	December April	December February April
Park River at Grafton, N. Dak.	Calcium, dissolved	8	8(I)	2	2	2	2
	Sodium, dissolved	25	20(I)	3	2	3	3
	Sulfate, dissolved	15	10(I)	2	2	2	2
	Chloride, dissolved	27	22(I)	4	4	4	4
	Iron, dissolved	27	26	31	29	23	7(T)
	Manganese, dissolved	26	26	47	42	24	5(T)

Of the 40 major-ion samples per year (an average of 4 samples per station for 10 stations), the first 30 were allocated to December, April, and August for each station. The remaining 10 were allocated to the stations and months that had the 10 highest values of $BI(i, j)$. The allocation of the 10 extra samples is indicated in table 6 by the symbol (I). Of the 10 extra samples, 7 were allocated to June, 2 to October, and 1 to February. The Little Missouri, Wild Rice, and Goose River stations each received two extra samples, the Cannonball River at Breien, James River at LaMoure, Maple River near Enderlin, and Park River at Grafton, N. Dak., stations each received one extra sample, and the remaining stations received no extra samples.

Of the 20 nutrient samples per year (an average of 4 samples per station for 5 stations), the first 15 were allocated to December, April, and August for each station. The remaining five were allocated to the stations and months that had the five highest values of $BN(i, j)$. As indicated in table 6 by the symbol (N), three extra nutrient samples were allocated to June, one was allocated to October, and one was allocated to February. The Knife and Cannonball River stations each received two extra samples, the Little Missouri River station received one extra sample, and the Sheyenne River station received no extra samples.

Of the 36 trace-metal samples (an average of 4 samples per year for 9 stations), the first 27 were allocated to December, April, and August for each station. The remaining nine were allocated to the stations and months that had the nine highest values of $BT(i, j)$. As indicated in table 6 by the symbol (T), two extra samples were allocated to June, five were allocated to October, and two were allocated to February. The James River station received two extra samples, the Knife River station received no extra samples, and the remaining stations each received one extra sample.

SUMMARY

This report presents the results of a study conducted by the U.S. Geological Survey, in cooperation with the North Dakota Department of Health, to analyze historical water-quality trends during 1971-2000 in selected dissolved major ions (calcium, sodium, sulfate, and chloride), nutrients (total ammonia plus organic nitrogen and total phosphorus), and dissolved trace metals (iron and manganese) for 10 streams in southwestern and eastern North Dakota and to develop an efficient sampling design to monitor future water-quality trends. The selected constituents were evaluated for five tributaries of the Missouri River and five tributaries of the Red River of the North. A time-series model for daily streamflow and constituent concentration was used to identify significant concentration trends, separate natural hydroclimatic variability in concentration from variability that could have resulted from anthropogenic causes, and evaluate various sampling designs to monitor future water-quality trends.

The interannual variability in concentration as a result of variability in streamflow, referred to as the annual concentration anomaly, generally was high for all constituents and streams used in the trend analysis. The annual concentration anomalies for most constituents and streams showed several periods of consistent increases or decreases during the trend-analysis period (1971-2000) and were particularly sensitive to the drought that occurred in the late 1980's and the wet period that began in 1993 and has persisted to the present (2002). Although climatic conditions were similar across North Dakota during 1971-2000, significant differences occurred in the annual concentration anomalies from constituent to constituent and location to location, especially during the drought and the wet period. Although a definitive cause for the differences is not known, extended wet or dry periods may result in changes in soil-moisture conditions, changes in water storage in wetlands and small lakes, and changes in ground water that, in turn, may result in changes in concentrations of surface runoff and base flow.

Numerous trends were detected in the historical constituent concentrations after the annual concentration anomalies were removed. The trends within each of the constituent groups (major ions, nutrients, and trace metals) showed general agreement among the streams. Concentrations of dissolved major ions increased in most streams from the early 1970's through the mid- to late 1970's and then decreased for about 2 to 3 years. Concentrations then remained stable or increased during various time intervals from the early 1980's to 2001, depending on the location. The largest concentrations for three of the Missouri River tributaries and one of the Red River of the North tributaries occurred during the mid- to late 1990's.

Concentration trends for total ammonia plus organic nitrogen showed close agreement among the streams for which that constituent was evaluated. Concentrations decreased during the mid- to late 1970's, increased from 1979 through the end of 1981, and then decreased from about 1982 through the late 1980's or early 1990's. The largest concentrations

occurred during the early 1980's, and the smallest concentrations occurred during the early 1990's. Nutrient data were not available for the early 1970's or late 1990's. Although a detailed analysis of the causes of the trends was beyond the scope of this report, a preliminary analysis of cropland, livestock-inventory, and oil-production data for 1971-2000 indicated the concentration trends could be related to the livestock-inventory and oil-production activities in the basins.

Dissolved iron and manganese concentrations for the southwestern North Dakota streams generally remained stable during 1971-2000. However, many of the recorded concentrations for those streams were less than the detection limit, and trends may have been masked by censoring of the data. Several significant trends were detected in dissolved iron and manganese concentrations for the eastern North Dakota streams. Concentrations for those streams either remained stable or increased during most of the 1970's and then decreased rapidly for about 2 years beginning in the late 1970's. The concentrations were relatively stable from the early 1980's to 2001 except at two stations where dissolved iron concentrations increased during the early 1990's.

Sampling design results indicated that the most efficient overall designs for the detection of annual trends (that is, trends that occur uniformly during the entire year) in major-ion, nutrient, and trace-metal concentrations consisted of balanced designs in which the sampling dates and the number of samples collected remained fixed from year to year and in which the samples were collected throughout the year rather than in a short timespan. All designs with only one sample per year had low or very low sensitivity for some constituents, no matter when the sample was collected. The designs with two samples per year were much more sensitive than the one-sample designs but usually had low sensitivity for one or more constituents. The designs with three samples per year generally were good designs for the detection of annual trends in most constituents. The best overall design for the detection of annual trends consisted of three samples per year, with samples collected near the beginning of December, April, and August. That design had acceptable sensitivity for the detection of trends in most constituents at all locations. Little improvement in sensitivity for detecting annual trends was achieved by collecting more than three samples per year.

The sampling designs that were first evaluated for annual trends also were evaluated with regard to their sensitivity to detect seasonal trends that occurred during three seasons--April through August, August through December, and December through April--because designs that are sensitive for the detection of annual trends may not be sensitive for the detection of seasonal trends. Design results indicated that an average of one extra sample per station per year (in addition to the annual design consisting of three samples per year at each station) resulted in an efficient design for detecting seasonal trends. However, allocation of the extra samples varied depending on the station, month, and constituent group (major ions, nutrients, and trace metals).

The design for major ions was improved by adding a sample in June for 7 of 10 stations, adding a sample in October for 2 of 10 stations, and adding a sample in February for 1 of 10 stations. The design for nutrients was improved by adding a sample in June for three of five stations, adding a sample in October for one of five stations, and adding a sample in February for one of five stations. The design for trace metals was improved by adding a sample in June for two of nine stations, adding a sample in October for five of nine stations, and adding a sample in February for two of nine stations.

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APPENDIX A

Table A1. Estimated trends in major-ion concentrations

[Values in parentheses indicate 95-percent confidence intervals]

Station name	Time interval	Estimated trend in concentration (percent per year)			
		Calcium	Sodium	Sulfate	Chloride
Little Missouri River near Watford City, N. Dak.	1971-78	7.6 (4.3, 11.1)	--	10.9 (8.3, 13.6)	--
	1971-81	--	4.9 (2.8, 7.2)	--	11.4 (8.1, 14.8)
	1979-81	-10.9 (-14.1, -7.5)	--	-8.2 (-10.7, -5.6)	--
	1982-84	--	-7.1 (-10.5, -3.5)	--	-13.9 (-18.6, -8.9)
Knife River at Hazen, N. Dak.	1971-78	2.8 (1.1, 4.5)	1.9 (0.7, 3.0)	2.1 (1.0, 3.2)	5.0 (3.1, 6.8)
	1979-81	-6.2 (-9.3, -3.1)	--	--	--
	1982-90	2.1 (0.9, 3.3)	1.9 (1.1, 2.6)	2.3 (1.6, 3.0)	3.0 (1.9, 4.2)
Heart River near Mandan, N. Dak.	1971-78	5.0 (3.3, 6.6)	5.4 (4.1, 6.7)	5.4 (3.9, 7.0)	6.4 (4.4, 8.5)
	1979-81	-7.7 (-10.7, -4.7)	-5.8 (-8.3, -3.3)	-7.1 (-10.1, -4.0)	--
	1982-90	2.8 (1.7, 3.9)	4.0 (3.0, 5.0)	3.7 (2.5, 5.0)	2.8 (1.5, 4.2)
Cannonball River at Breien, N. Dak.	1971-75	14.0 (9.6, 18.6)	9.9 (7.1, 12.8)	16.9 (12.0, 22.1)	15.1 (10.8, 19.5)
	1976-78	-10.0 (-13.1, -6.9)	-6.4 (-8.5, -4.4)	-11.1 (-14.4, -7.6)	--
James River at LaMoure, N. Dak.	1971-77	2.8 (0.6, 5.0)	--	3.5 (0.8, 6.3)	2.8 (0.3, 5.4)
	1978-79	-6.9 (-10.5, -3.1)	--	-5.8 (-10.4, -1.0)	--
	1989-94	4.0 (2.7, 5.3)	5.9 (4.1, 7.8)	8.1 (6.3, 10.0)	8.6 (6.6, 10.7)
Wild Rice River near Abercrombie, N. Dak.	1971-75	--	14.3 (9.4, 19.4)	--	--
	1971-76	5.9 (2.2, 9.8)	--	8.4 (2.7, 14.4)	6.7 (3.0, 10.4)
	1976-77	--	-33.5 (-38.7, -27.8)	--	--
	1977-78	-11.7 (-18.4, -4.5)	--	-23.8 (-32.1, -14.4)	-24.8 (-30.8, -18.4)
	1983-85	--	13.8 (7.1, 20.8)	6.4 (0.1, 13.6)	11.7 (5.4, 18.4)
Sheyenne River near Kindred, N. Dak.	1979-80	-5.2 (-7.3, -2.9)	--	-4.5 (-7.5, -1.4)	-11.5 (-15.6, -7.2)
	1989-94	5.7 (3.0, 8.4)	2.1 (0.5, 3.7)	13.5 (9.5, 17.6)	4.2 (1.8, 6.7)
Maple River near Enderlin, N. Dak.	1979-80	--	-8.2 (-15.0, -0.1)	--	-25.0 (-34.0, -14.8)
	1986-88	--	6.9 (1.3, 12.8)	--	12.2 (2.9, 22.3)
Goose River at Hillsboro, N. Dak.	1971-79	3.8 (2.3, 5.2)	--	5.7 (4.2, 7.2)	6.2 (2.5, 9.9)
	1980-81	-10.9 (-14.0, -7.6)	-7.1 (-13.0, -0.9)	-11.7 (-14.9, -8.3)	-15.7 (-26.2, -3.6)
Park River at Grafton, N. Dak.	1971-77	--	12.7 (8.7, 16.9)	--	16.7 (11.3, 22.3)
	1978-79	-11.9 (-17.1, -6.4)	-23.1 (-28.3, -17.5)	--	-20.0 (-28.5, -10.5)
	1986-88	10.4 (6.0, 15.0)	16.4 (11.1, 22.0)	10.4 (5.2, 15.9)	10.2 (1.2, 19.9)

Table A2. Estimated trends in nutrient concentrations

[Values in parentheses indicate 95-percent confidence intervals]

Station name	Time interval	Estimated trend in concentration (percent per year)	
		Total ammonia plus organic nitrogen	Total phosphorus
Linear trends in log-transformed concentrations			
Little Missouri River near Watford City, N. Dak.	1974-78	-23.8 (-28.8, -18.4)	-15.9 (-24.9, -5.7)
	1979-81	51.4 (41.8, 61.6)	53.1 (29.9, 80.4)
	1982-87	-20.2 (-23.7, -16.6)	--
Knife River at Hazen, N. Dak.	1974-78	-11.2 (-15.4, -7.0)	--
	1979-81	32.1 (23.9, 40.9)	14.3 (3.0, 26.8)
	1982-90	-8.8 (-12.6, -4.8)	-5.4 (-10.3, -0.1)
Heart River near Mandan, N. Dak.	1979-81	26.8 (16.6, 37.8)	--
	1982-87	-15.1 (-19.8, -10.1)	-5.4 (-10.0, -0.5)
Cannonball River at Breien, N. Dak.	1974-78	-18.3 (-22.1, -14.4)	--
	1979-81	36.1 (28.2, 44.5)	20.2 (2.8, 40.7)
	1982-87	-18.2 (-22.1, -14.0)	-12.7 (-20.5, -4.1)
Sheyenne River near Kindred, N. Dak.	1979-81	23.6 (17.6, 29.9)	--
	1982-87	-14.1 (-16.6, -11.6)	--
	1989-94	--	-11.3 (-20.5, -1.0)
Step trends in log-transformed concentrations[1]			
Little Missouri River near Watford City, N. Dak.	1984-91	0.270 (0.156, 0.384)	--
	1971-90	--	-0.443 (-0.702, -0.184)
Heart River near Mandan, N. Dak.	1986-91	0.178 (0.081, 0.275)	--
	1971-90	--	-0.096 (-0.286, 0.094)
Cannonball River at Breien, N. Dak.	1986-91	0.139 (0.029, 0.249)	--
Sheyenne River near Kindred, N. Dak.	1986-91	0.135 (0.070, 0.200)	--
	1971-90	--	-0.223 (-0.442, -0.004)

[1]Step trends in total ammonia plus organic nitrogen indicate positive laboratory method bias (measured concentrations larger than actual concentrations) during trend interval, and step trends in total phosphorus indicate negative laboratory method bias (measured concentrations less than actual concentrations) during trend interval.

Table A3. Estimated trends in trace-metal concentrations

[Values in parentheses indicate 95-percent confidence intervals]

Station name	Time interval	Estimated trend in concentration (percent per year)	
		Iron	Manganese
Little Missouri River near Watford City, N. Dak.	1971-81	-12.5 (-19.5, -4.9)	--
Knife River at Hazen, N. Dak.	1982-89	--	3.0 (0.1, 6.1)
James River at LaMoure, N. Dak.	1978-79	-36.6 (-48.1, -22.6)	--
	1989-94	14.8 (4.8, 25.8)	--
Wild Rice River near Abercrombie, N. Dak.	1971-76	--	43.2 (27.7, 60.6)
	1977-78	-22.4 (-38.8, -1.6)	-51.5 (-65.7, -31.4)
	1983-85	--	47.2 (26.0, 80.0)
Sheyenne River near Kindred, N. Dak.	1979-80	-23.1 (-29.7, -15.8)	-31.4 (-40.1, -21.6)
	1989-94	9.4 (3.4, 15.8)	--
Maple River near Enderlin, N. Dak.	1979-80	-42.2 (-52.3, -30.0)	--
	1981-82	--	-19.3 (-31.0, -5.6)
Goose River at Hillsboro, N. Dak.	1971-79	--	30.6 (17.9, 44.6)
	1980-81	-26.9 (-41.4, -8.8)	-41.0 (-57.2, -18.6)
Park River at Grafton, N. Dak.	1971-78	6.7 (4.2, 9.2)	51.7 (49.0, 54.4)
	1979-80	-33.5 (-44.5, -20.2)	-43.9 (-53.6, -32.2)

APPENDIX B
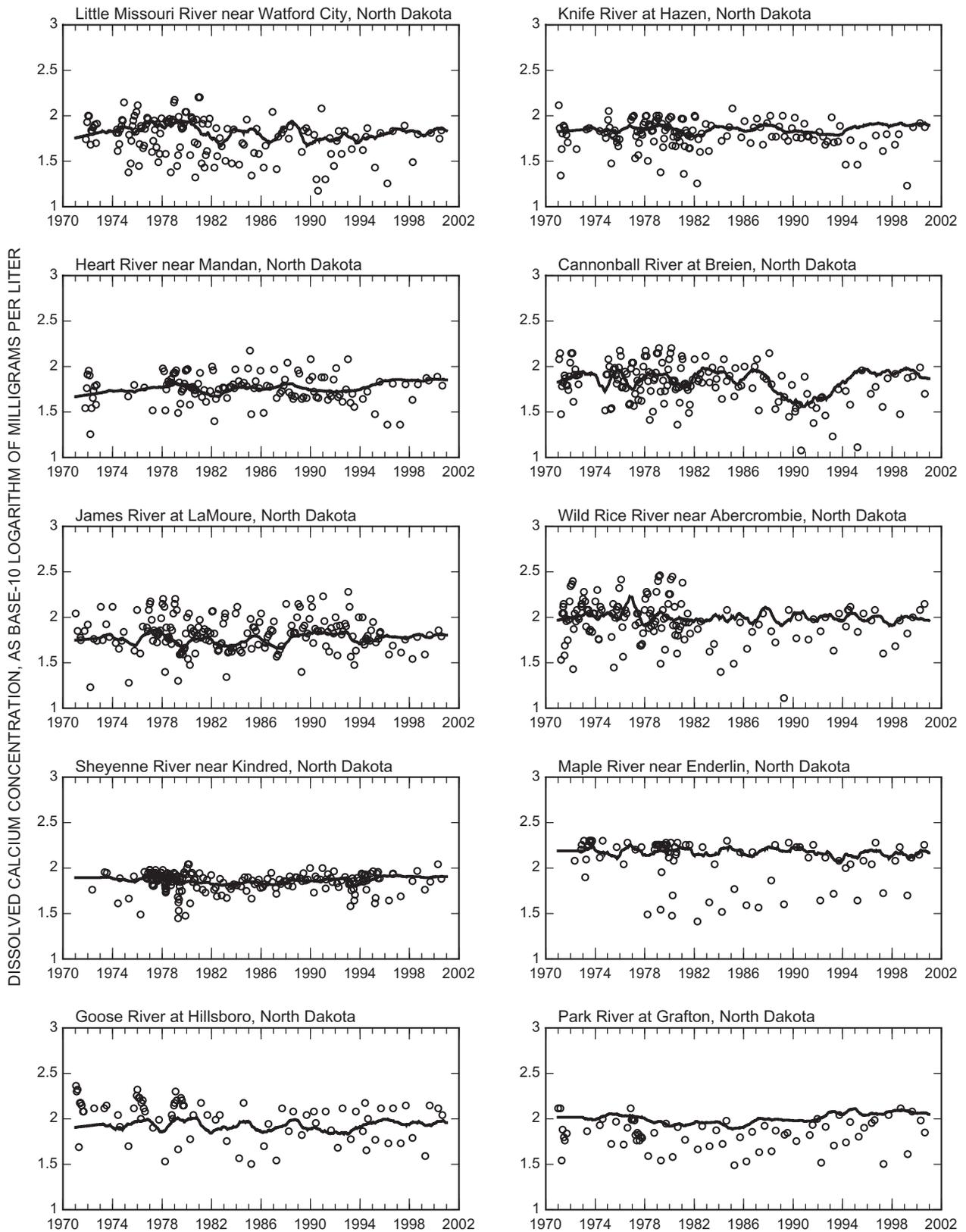
Figure B1. Dissolved calcium concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
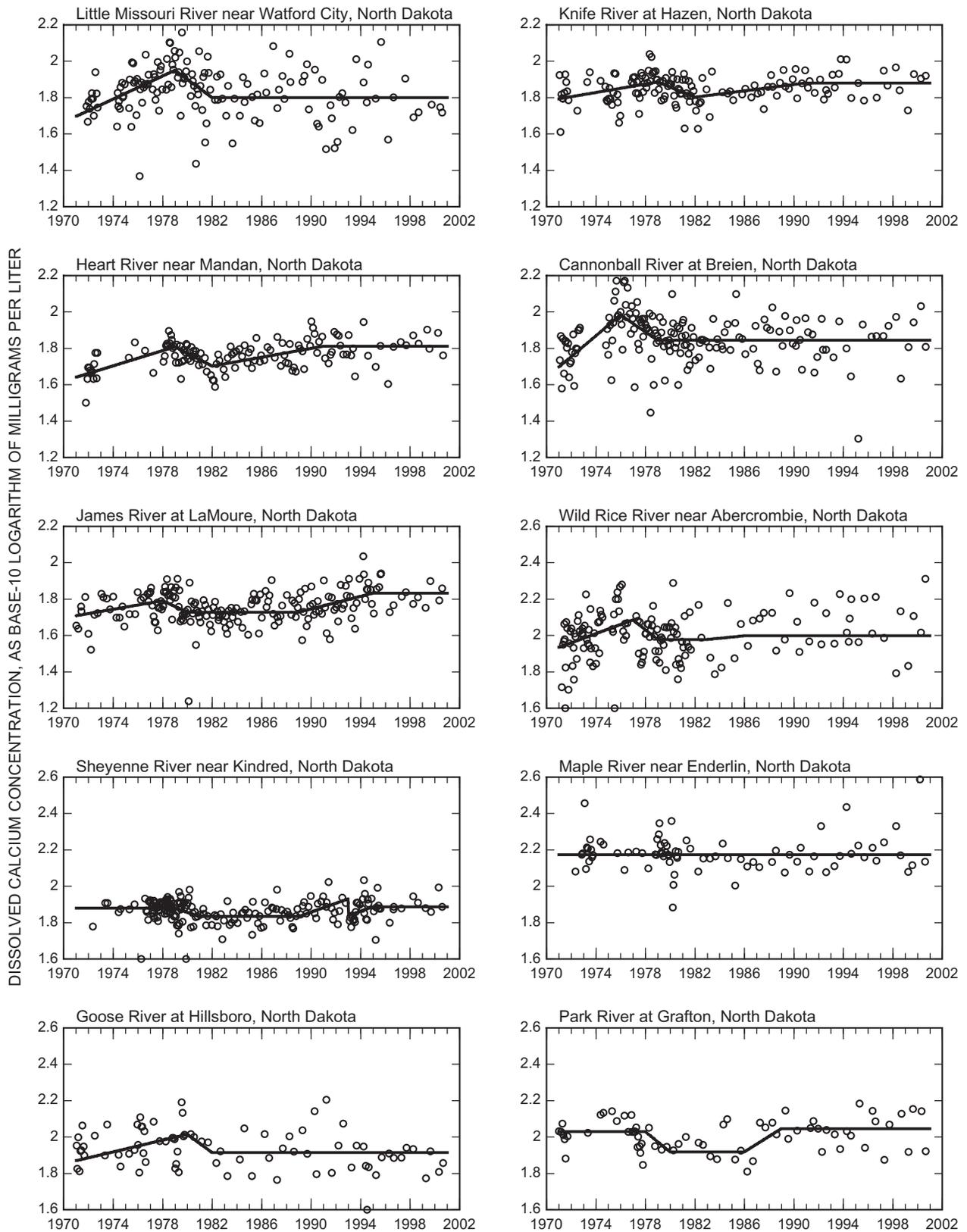
Figure B2. Model-adjusted dissolved calcium concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
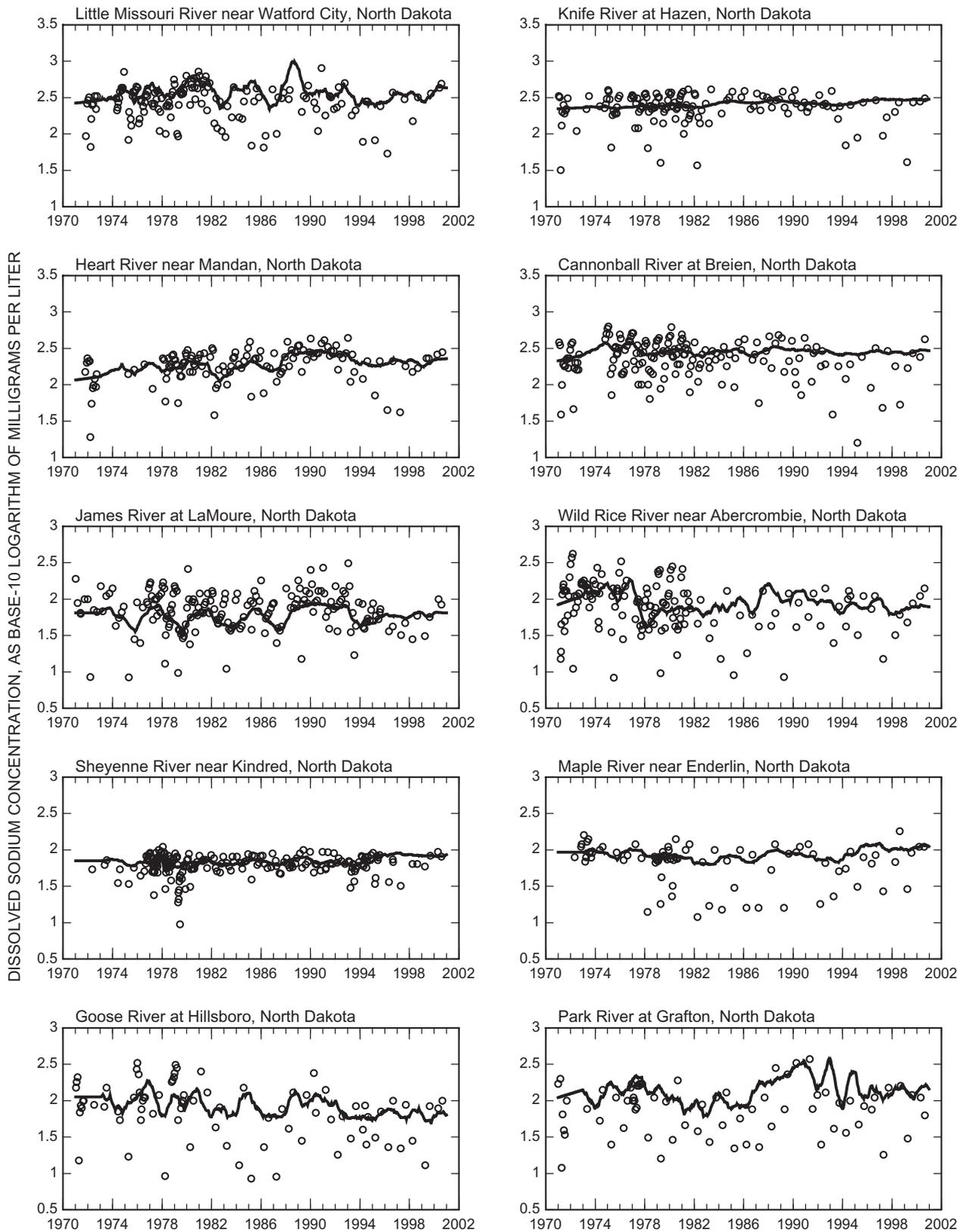
Figure B3. Dissolved sodium concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
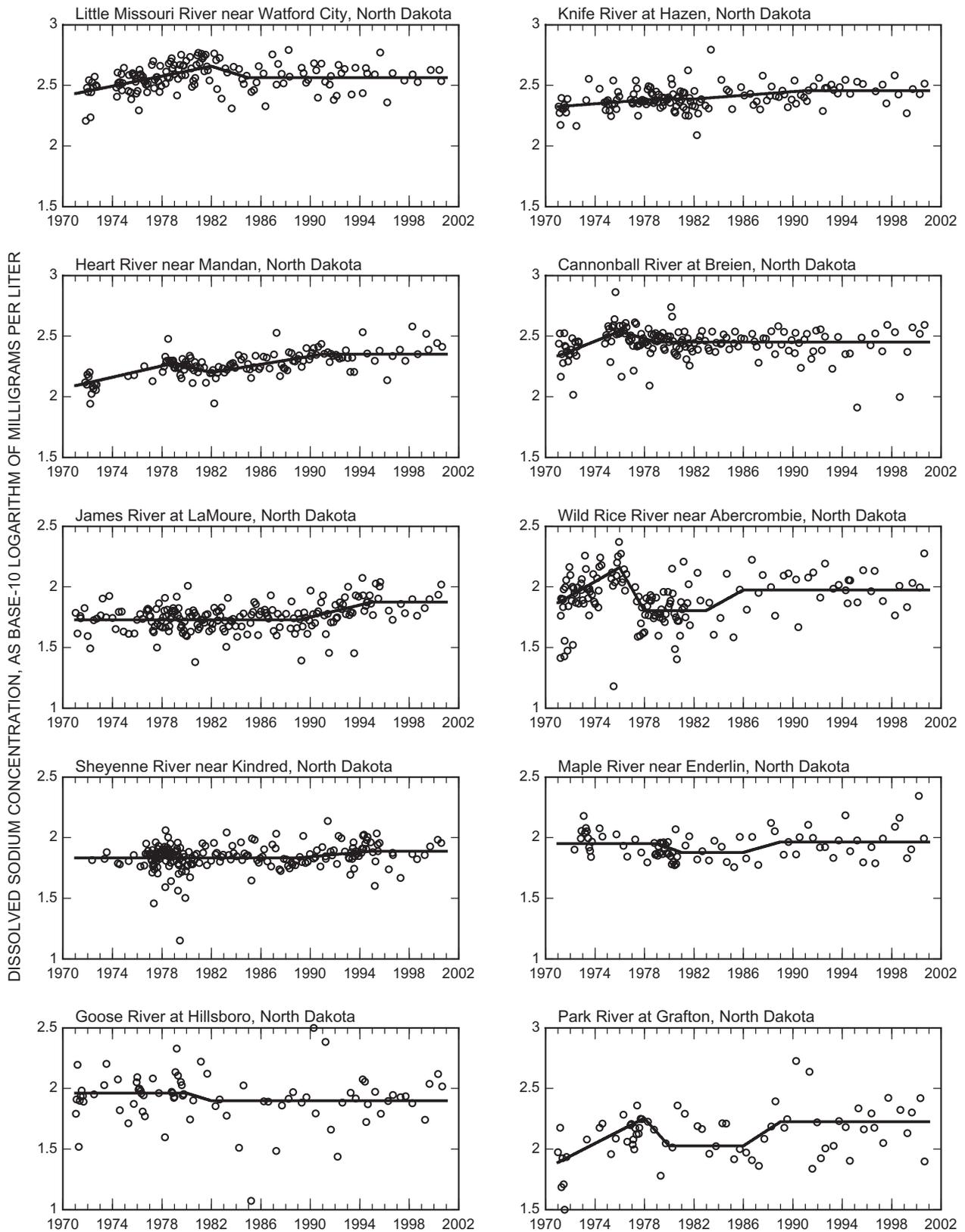
Figure B4. Model-adjusted dissolved sodium concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
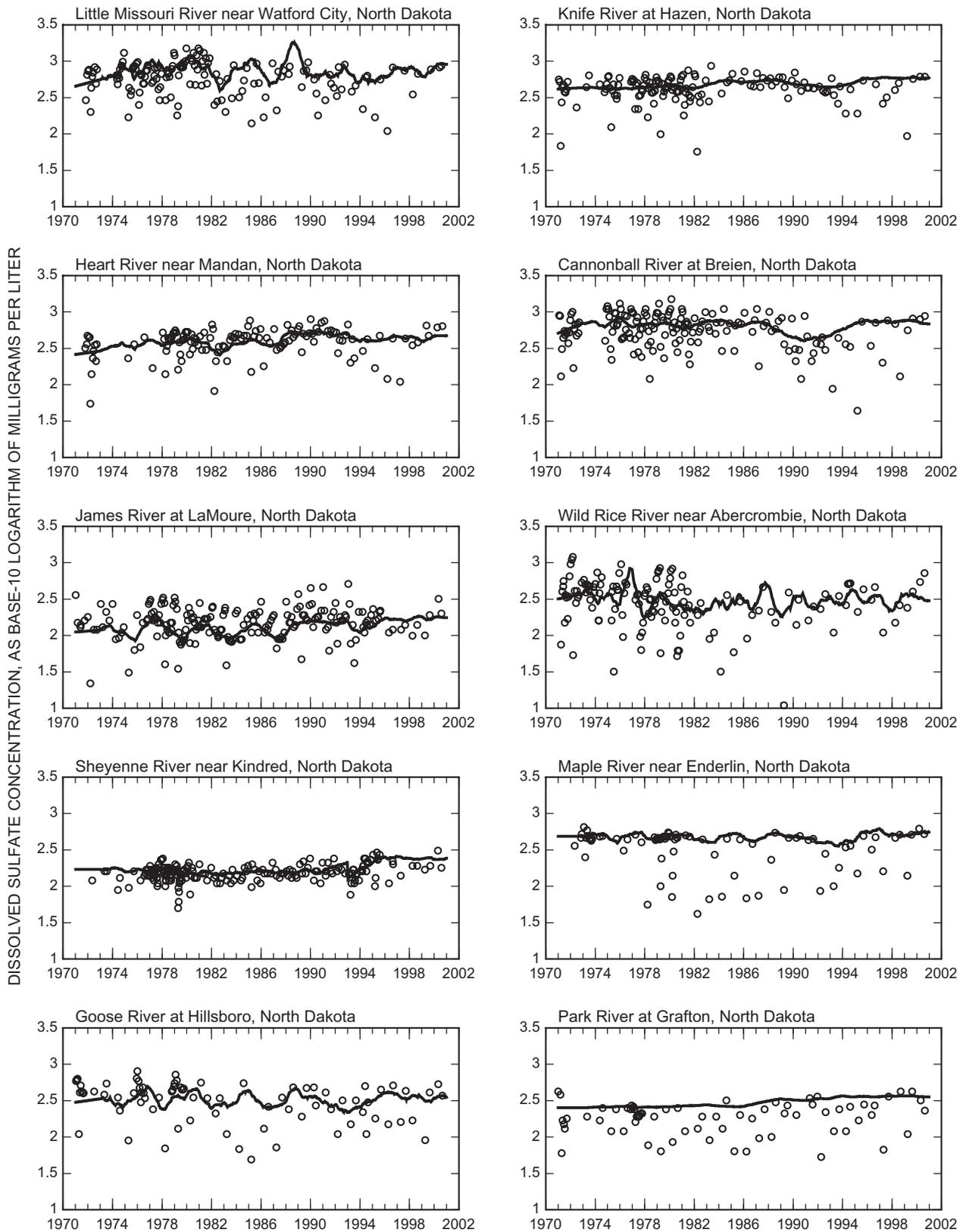
Figure B5. Dissolved sulfate concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
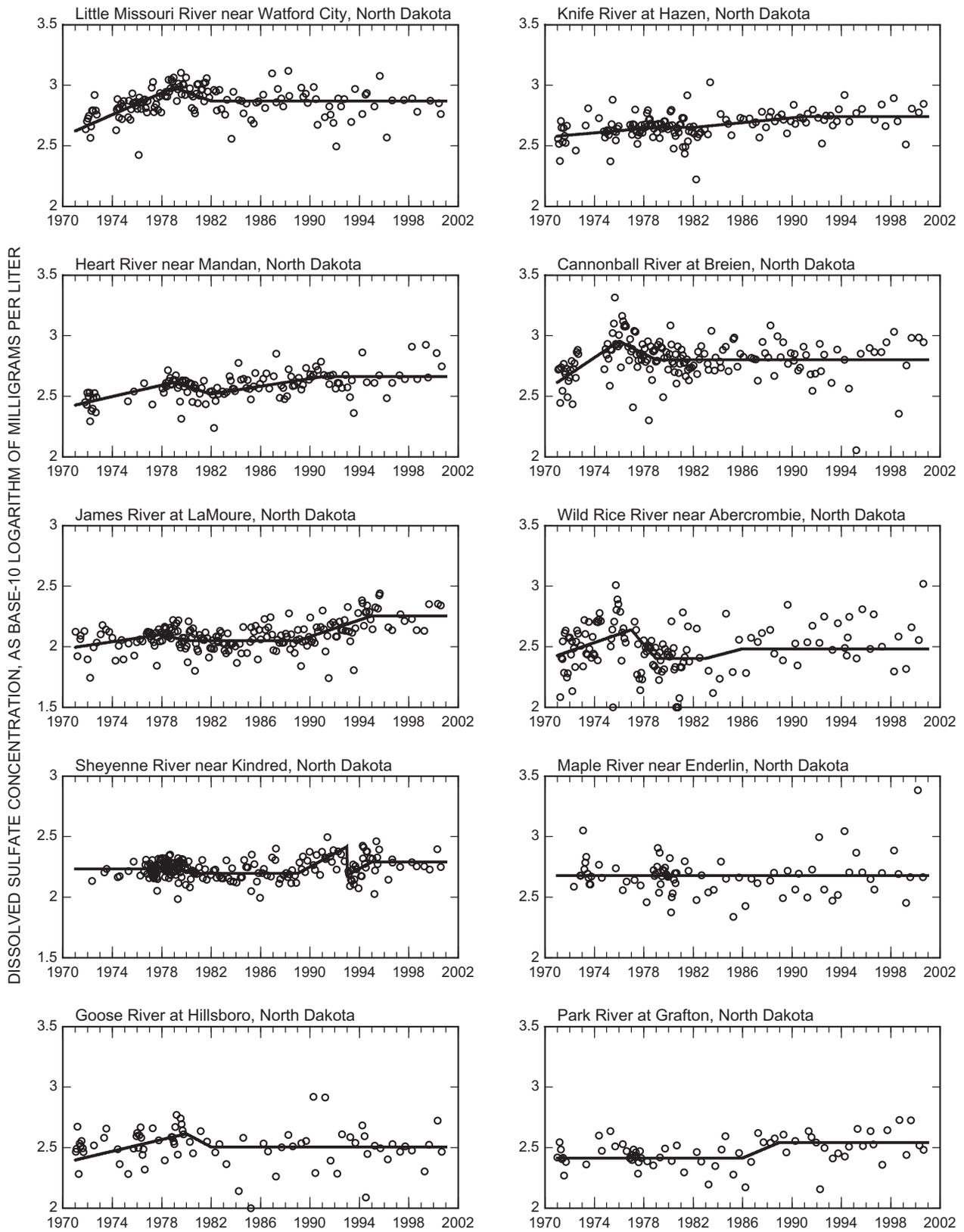
Figure B6. Model-adjusted dissolved sulfate concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
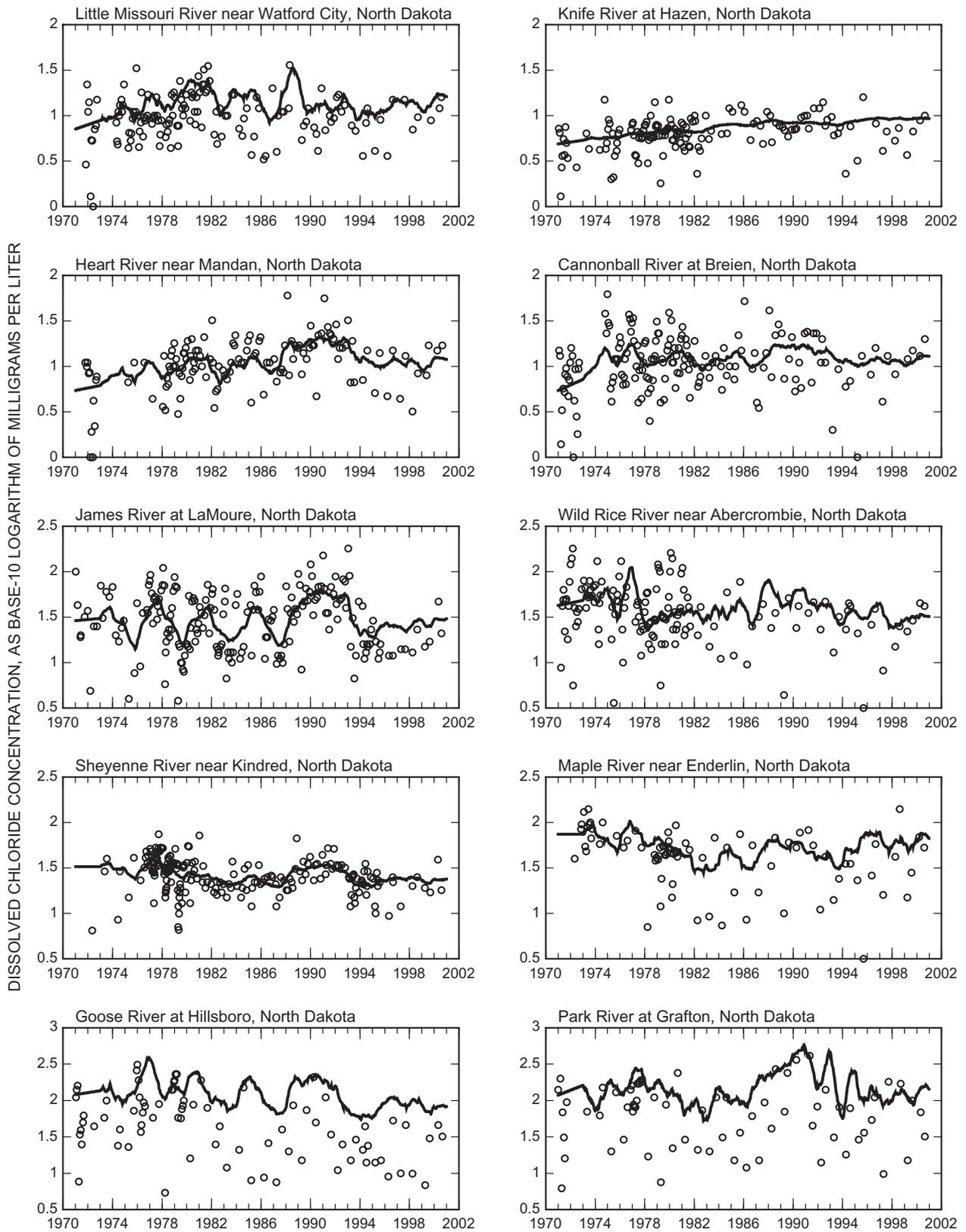
Figure B7. Dissolved chloride concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
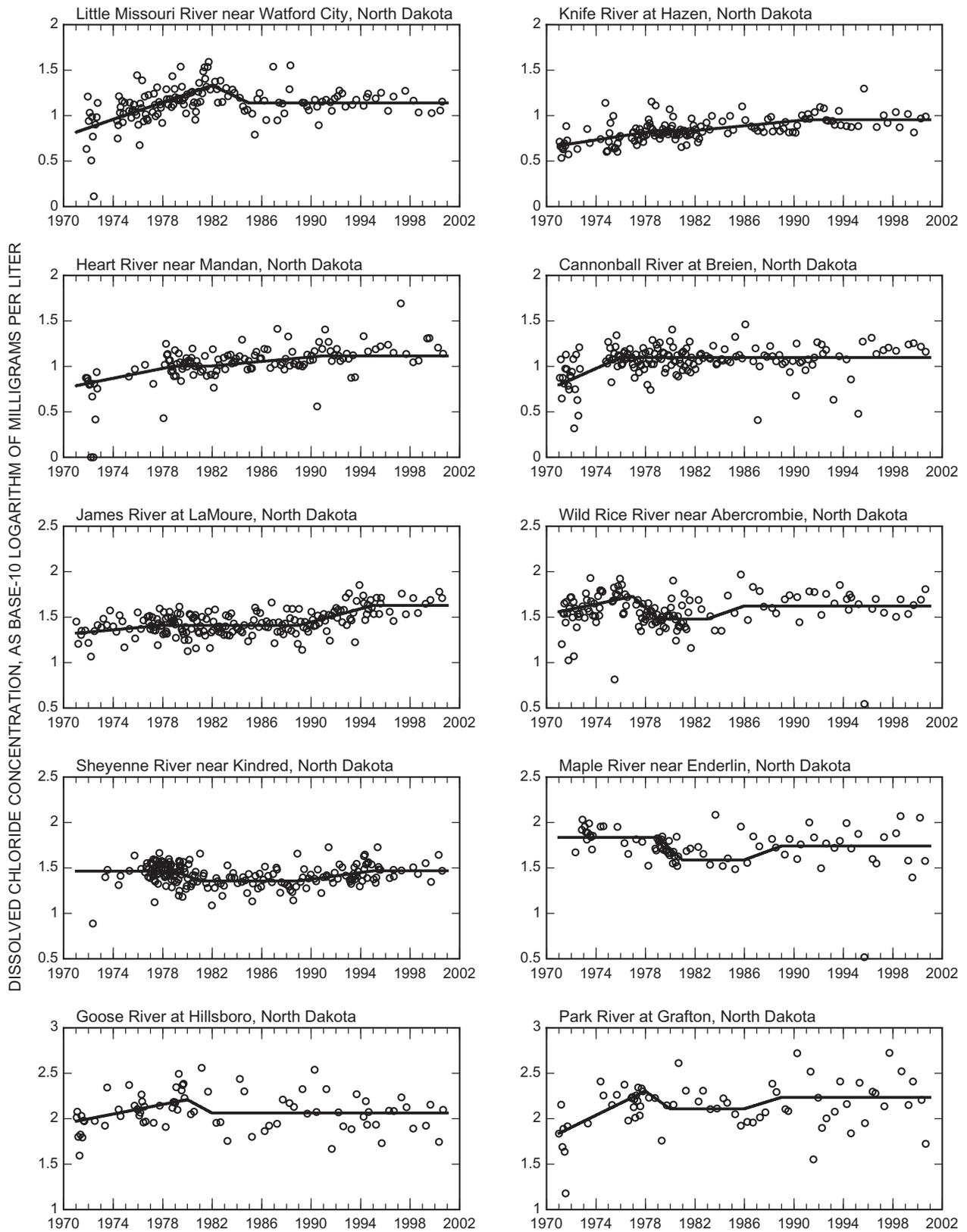
Figure B8. Model-adjusted dissolved chloride concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
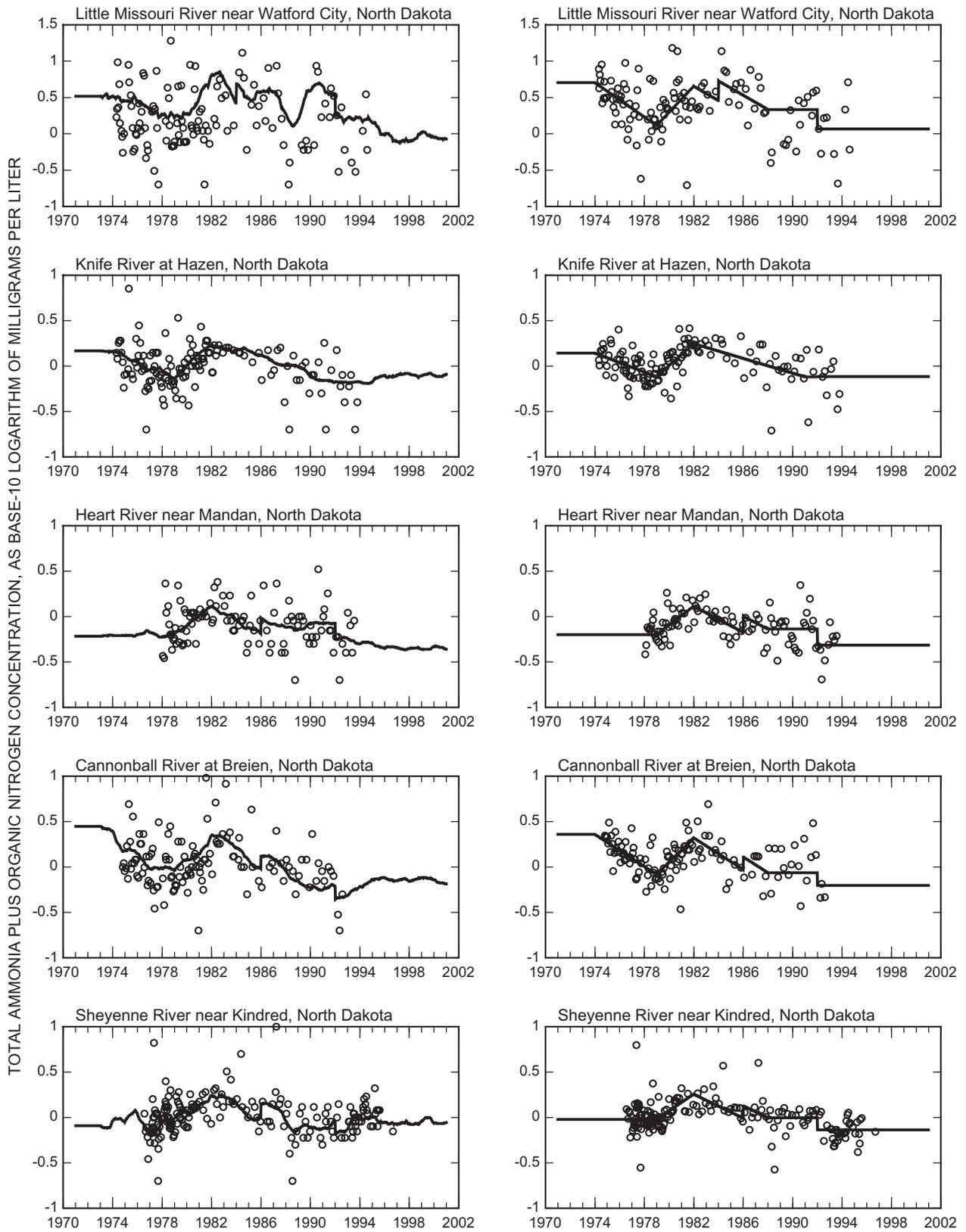
**Figure B9.** Total ammonia plus organic nitrogen concentrations (points, left-hand plots); fitted trends plus annual anomalies (lines, left-hand plots); model-adjusted concentrations (points, right-hand plots); and fitted trends (lines, right-hand plots) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
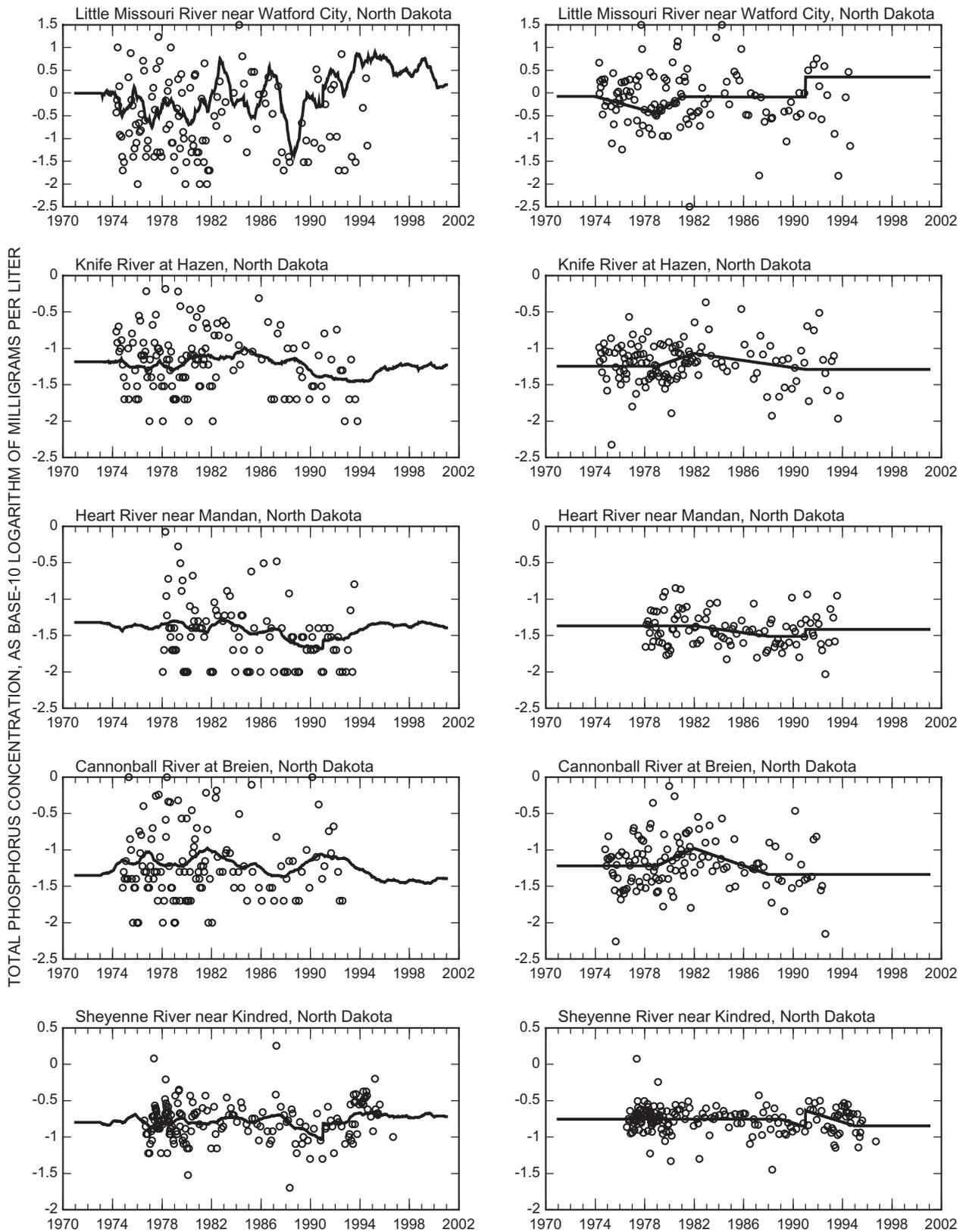
Figure B10. Total phosphorus concentrations (points, left-hand plots); fitted trends plus annual anomalies (lines, left-hand plots); model-adjusted concentrations (points, right-hand plots); and fitted trends (lines, right-hand plots) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
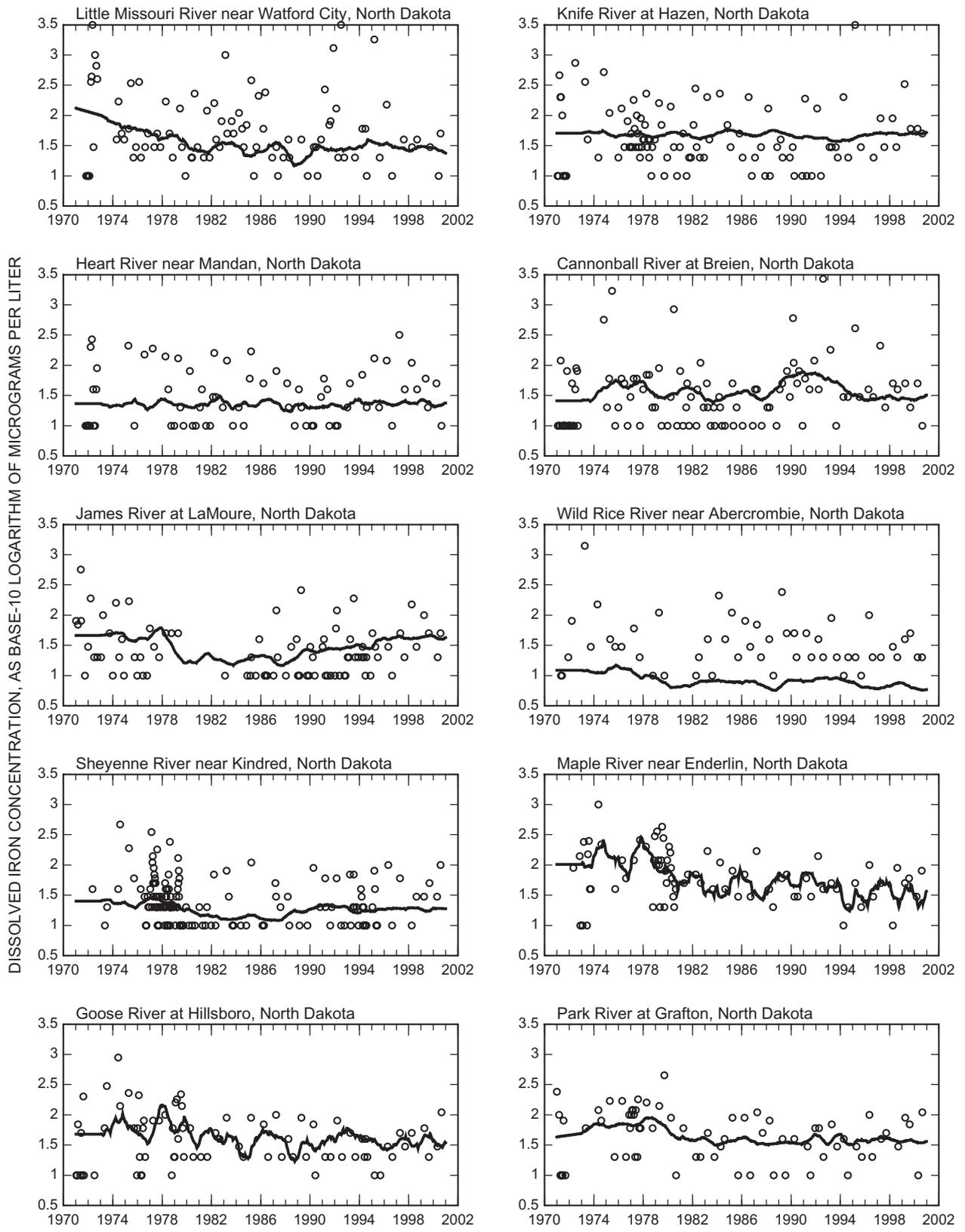
Figure B11. Dissolved iron concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
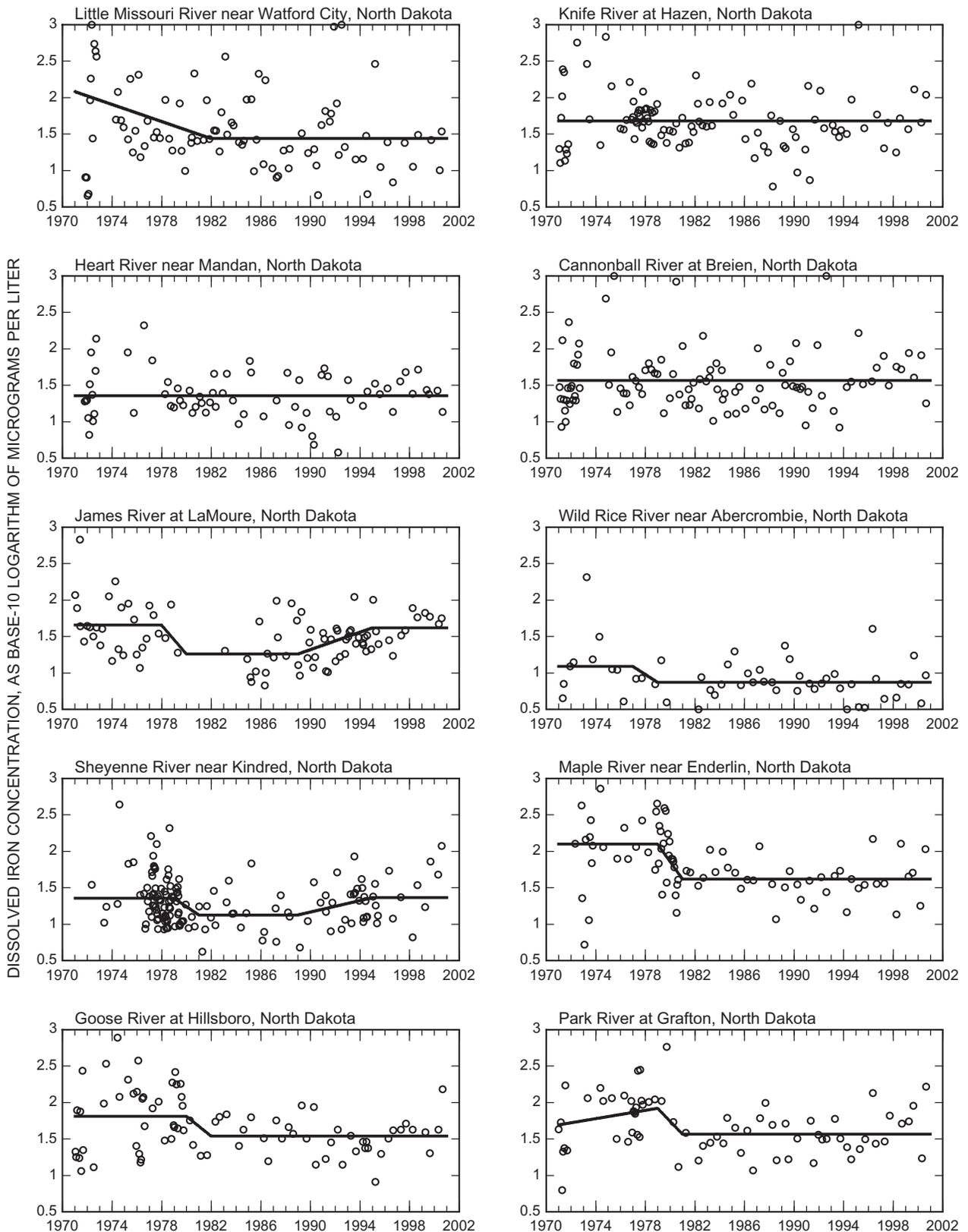
Figure B12. Model-adjusted dissolved iron concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
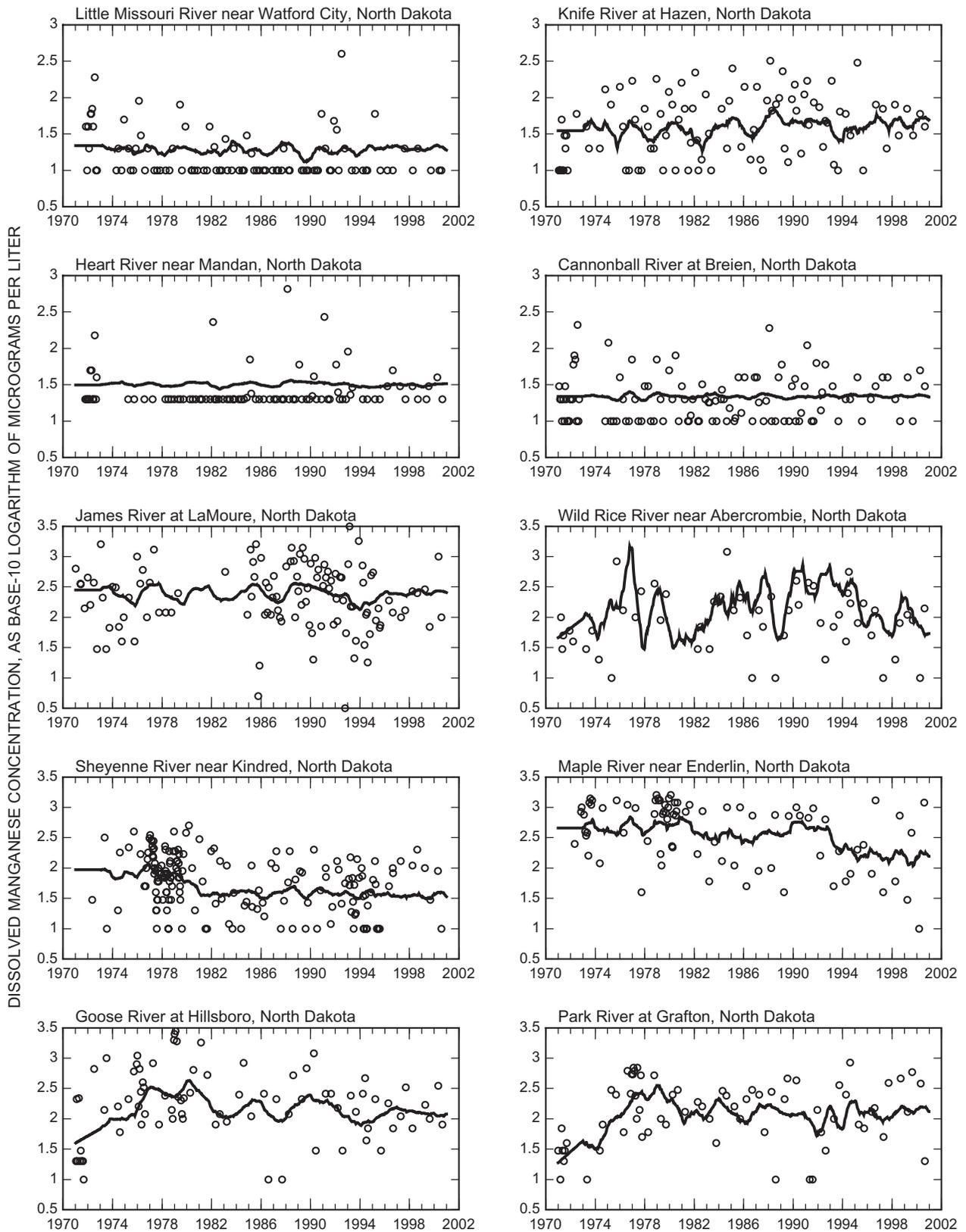
Figure B13. Dissolved manganese concentrations (points) and fitted trends plus annual anomalies (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.
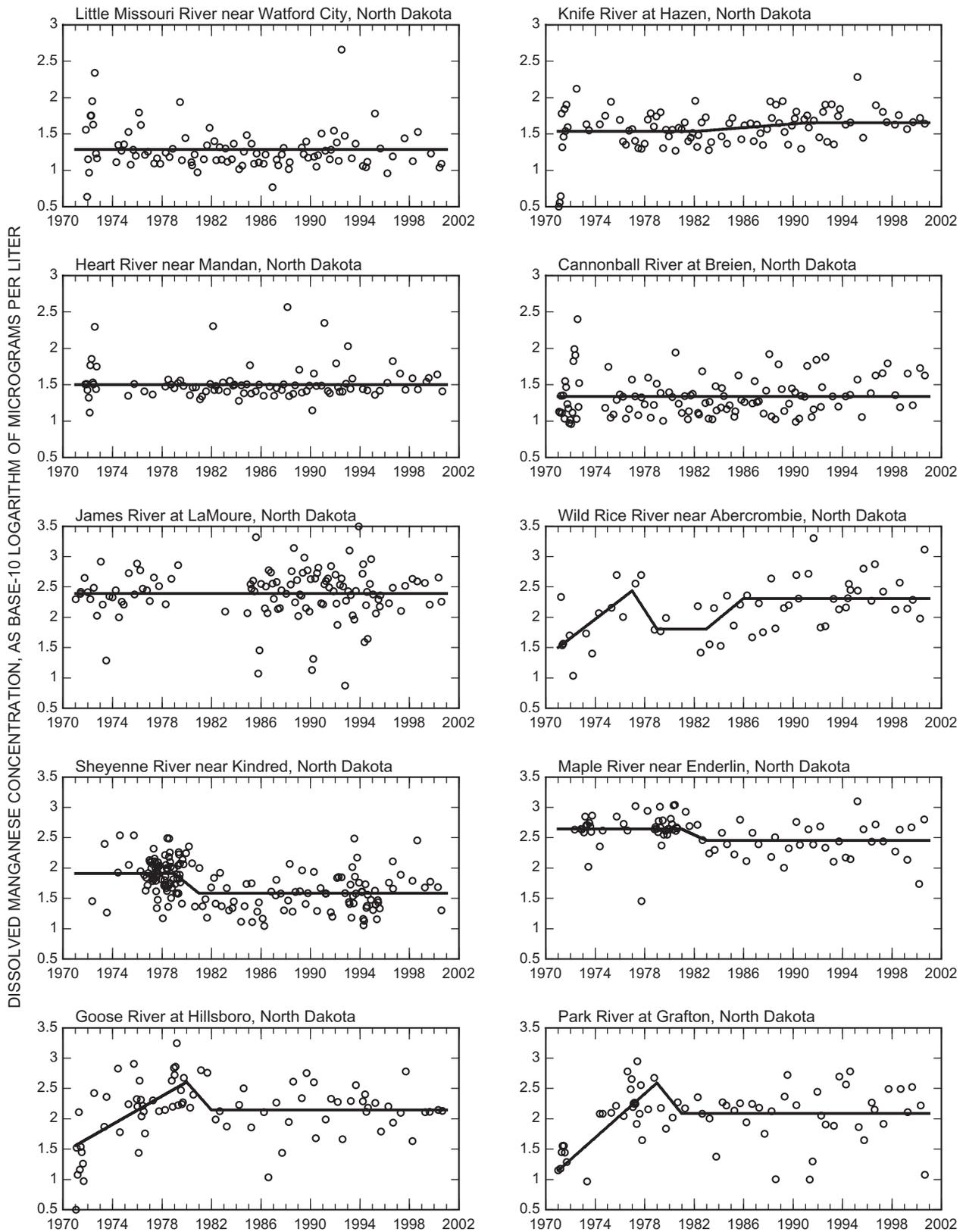
Figure B14. Model-adjusted dissolved manganese concentrations (points) and fitted trends (lines) for 1971-2000 for streamflow-gaging stations used in water-quality trend analysis.