

PRELIMINARY ANALYSIS FOR TRENDS IN SELECTED WATER-QUALITY CHARACTERISTICS,
POWDER RIVER, MONTANA AND WYOMING, WATER YEARS 1952-85

by Lawrence E. Cary

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4050

Prepared in cooperation with the
MONTANA DEPARTMENT OF NATURAL
RESOURCES AND CONSERVATION



Helena, Montana
1989

DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, Director

For additional information
write to:

District Chief
U.S. Geological Survey
428 Federal Building
301 South Park, Drawer 10076
Helena, MT 59626-0076

Copies of this report can be
purchased from:

U.S. Geological Survey
Books and Open-File Reports Section
Federal Center, Bldg. 810
Box 25425
Denver, CO 80225-0425

CONTENTS

	Page
Abstract	1
Introduction	2
Purpose and scope.	2
Previous studies	4
Data availability.	5
Stations and periods of record	5
Water-quality characteristics.	6
Selection of data for trend analysis	7
Powder River near Locate, water years 1952-63.	8
Powder River near Locate, water years 1975-85.	9
Powder River at Sussex, water years 1967-68 and 1976-85.	9
Methods of trend analysis.	10
Methods available.	10
Flow-adjustment regressions.	10
Seasonal Kendall test.	15
Trends in water-quality characteristics.	17
Trends in unadjusted data.	17
Trends in flow-adjusted data	19
Factors affecting results.	21
Summary.	23
References cited	25

ILLUSTRATIONS

Figure 1. Map showing location of the Powder River and sampling stations used in the trend analysis.	3
2-4. Graphs showing:	
2. Monthly mean discharge, Powder River near Locate, Montana, water years 1952-63	14
3. Monthly mean sodium concentration, Powder River near Locate, Montana, water years 1952-63	14
4. Flow-adjusted monthly mean sodium concentration, Powder River near Locate, Montana, water years 1952-63	15

TABLES

Table 1. Hydrologic characteristics used in the trend analysis.	8
2. Type of regression equation selected for calculating flow-adjusted data for each station and time period.	13
3. Seasonal Kendall tests for trends in discharge of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming.	17
4. Seasonal Kendall tests for trends in unadjusted water-quality characteristics of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming.	18
5. Seasonal Kendall tests for trends in flow-adjusted characteristics of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming	20

Table 6. Seasonal Kendall tests for trends in flow-adjusted characteristics of the Powder River at Sussex, Wyoming, water years 1976-85. . . . 21

CONVERSION FACTORS

The following factors can be used to convert inch-pound units to metric (International System) units.

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
cubic foot per second (ft ³ /s)	0.028317	cubic meter per second
cubic foot per second per year	0.028317	cubic meter per second per year
mile (mi)	1.609	kilometer

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by the equation:

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

PRELIMINARY ANALYSIS FOR TRENDS IN SELECTED WATER-QUALITY
CHARACTERISTICS, POWDER RIVER, MONTANA AND WYOMING, WATER YEARS 1952-85

by

Lawrence E. Cary

ABSTRACT

Data for selected water-quality characteristics from two streamflow-gaging stations on the Powder River were statistically analyzed for trends. Included in the analyses were data for water years 1952-63 and 1975-85 from the Powder River near Locate, Montana, and for water years 1967-68 and 1976-85 from the Powder River at Sussex, Wyoming.

The seasonal Kendall test was applied to unadjusted and flow-adjusted water-quality characteristics. Flow-adjusted data were calculated as the residuals from a regression of the characteristics as a function of water discharge.

During the earlier period (water years 1952-63) for the Powder River near Locate, the reported analyses were composited from daily samples. Discharge-weighted monthly mean values were calculated and the test was applied to the mean values. Statistically significant (at the 0.10 level) trends were detected in flow-adjusted data for sodium and sodium-adsorption ratio. Flow-adjusted data increased 1.5 percent per year for sodium and 1.1 percent per year for sodium-adsorption ratio. No trends were detected in specific conductance, hardness, noncarbonate hardness, alkalinity, dissolved solids, or sulfate.

During the later period (water years 1975-85) for the Powder River near Locate, trends were detected in flow-adjusted data for specific conductance, sodium, sodium-adsorption ratio, and chloride. Flow-adjusted data increased 1.4 percent per year for specific conductance, 1.5 percent per year for sodium, 1.9 percent per year for sodium-adsorption ratio, and 3.1 percent per year for chloride. No trends were detected in hardness, noncarbonate hardness, alkalinity, dissolved solids, calcium, magnesium, potassium, or sulfate.

During water years 1967-68 and 1976-85 for the Powder River at Sussex, significant trends were detected in flow-adjusted data for sodium, sodium-adsorption ratio, sulfate, and chloride. Flow-adjusted data increased 1.1 percent per year for sodium, 2.6 percent per year for sodium-adsorption ratio, and 5.5 percent per year for chloride. Flow-adjusted data for sulfate decreased 1.8 percent per year. No trends were detected in specific conductance, alkalinity, or dissolved solids. When the 1967-68 data were deleted and the 1976-85 data were retested, only flow-adjusted data for sodium-adsorption ratio displayed a significant trend; the trend increased 3.3 percent per year.

Because the statistical analysis was exploratory, possible causes and effects were not considered. The results might have been affected by sample size, number of seasons, trend heterogeneity, significance level, serial correlation, and--for characteristics having little correlation with discharge--inadequate adjustment of the data.

INTRODUCTION

Increasing demands for water resources in parts of the semiarid Western United States are accompanied by interest in the suitability of water for its intended uses, including changes in the quality of the water that may affect its suitability. In some areas, concern for the quality of water is becoming as great as the concern for the quantity of water.

One such area is the drainage basin of the Powder River, which originates in Wyoming, flows northward into Montana, and joins the Yellowstone River near Terry, Montana (fig. 1). In Montana, water from the Powder River is used mostly to irrigate alfalfa. Concern has been expressed by irrigators and State agencies that salinity (dissolved-solids concentration) and sodium concentration in the river have been increasing and that continued increases will render the water unusable for irrigation.

In 1986, the U.S. Geological Survey conducted a study of the water quality of the Powder River in cooperation with the Montana Department of Natural Resources and Conservation. The study included preliminary statistical analysis of selected water-quality characteristics for trends (changes with time) based on available data.

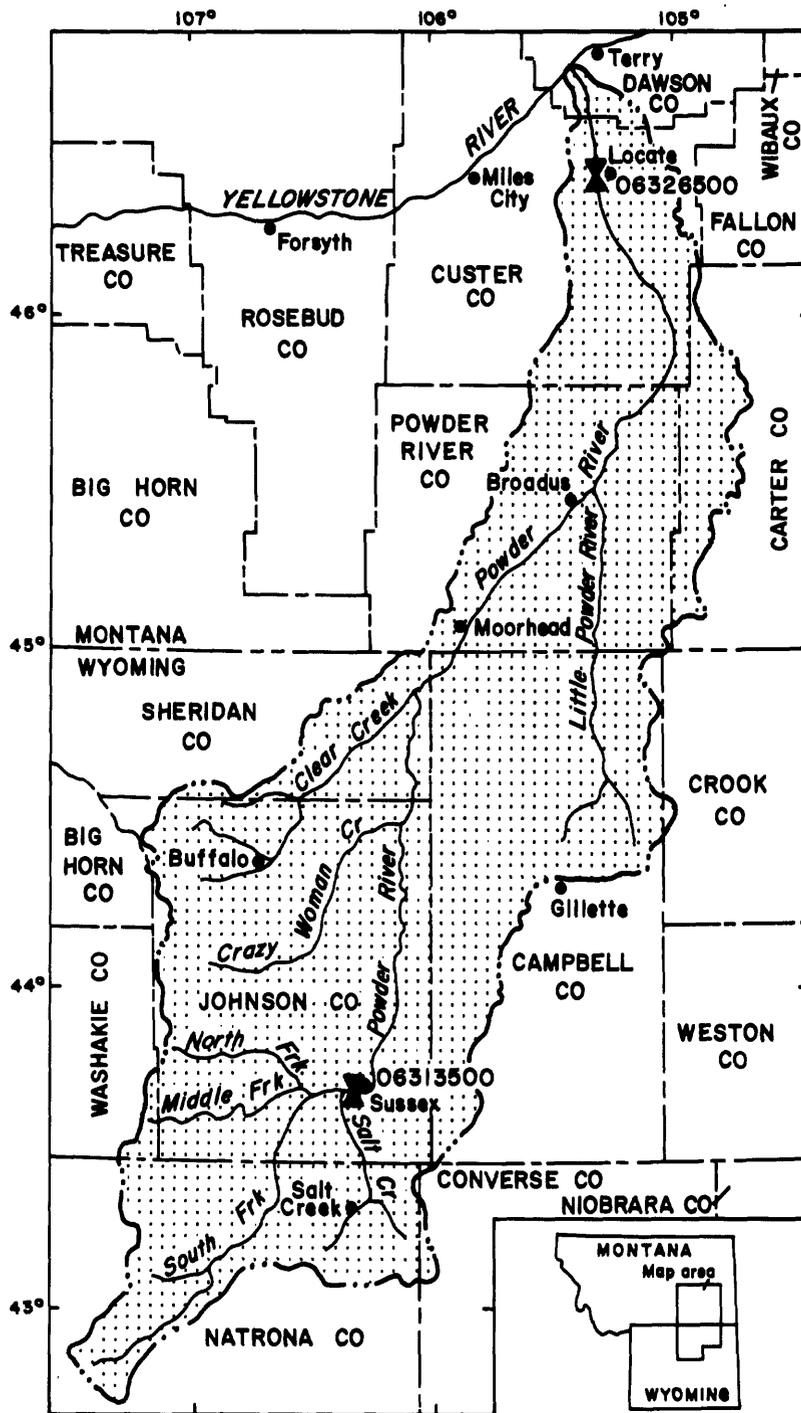
Purpose and Scope

The purpose of this report is to describe the methods of analysis and the trends in water quality of the Powder River. Results are provided for selected water-quality characteristics that reflect the chemical quality of the water, including salinity and relative sodium concentration.

Water-quality data from samples collected at two streamflow-gaging stations were used for analysis. One station was in the downstream part of the basin, near the basin outlet. The other station was at the most upstream site in the drainage that had adequate data for testing of trends. Data were available from an earlier period and a later period at both stations. The sampling technique and some of the laboratory methods used during the earlier period were different from those used during the later period. Therefore, the data from the two periods were analyzed separately.

Twelve water-quality characteristics were selected for testing. Water properties were specific conductance, hardness, noncarbonate hardness, sodium-adsorption ratio, and alkalinity. Dissolved solids was included to represent overall changes in salinity. The common ions were calcium, magnesium, sodium, potassium, sulfate, and chloride.

The trend test used for water-quality characteristics displaying seasonality was nonparametric. Variation in discharge can cause trends and also can mask



Base modified from U.S. Geological Survey, State base maps, Montana (1966) and Wyoming (1967), 1:1,000,000

0 20 40 MILES
0 20 40 KILOMETERS

EXPLANATION

- · · — DRAINAGE BASIN BOUNDARY
- 06313500 COMBINATION STREAMFLOW-GAGING AND WATER-QUALITY STATION AND NUMBER

Figure 1.--Location of the Powder River and sampling stations used in the trend analysis.

trends in water-quality characteristics caused by other factors. Therefore, the data were corrected for variation in discharge using a flow-adjusting procedure. Tests were applied to both unadjusted and flow-adjusted data. Trend tests were first applied to the unadjusted and the flow-adjusted data from the downstream station. The tests were repeated for data from the upstream station for those water-quality characteristics that displayed trends in unadjusted data for the downstream station.

Previous Studies

Several studies have evaluated the quality of water in the Powder River. Of particular interest are those that evaluated individual water-quality characteristics for trends. In demonstrating one method of trend analysis, Smith and others (1982) described the change in total phosphorus concentrations and loads at the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) stations. That study did not indicate a statistically significant trend in total phosphorus concentrations or loads at the station Powder River near Locate, Montana, for data collected during water years¹ 1975-79.

Later, Wells and Schertz (1983) reported the results of a trend analysis of dissolved-solids concentrations at NASQAN stations using regression. Those results indicated a significant, increasing trend in dissolved-solids concentrations at the station Powder River near Locate for water years 1975-81.

Smith and Alexander (1985) reported the results of nonparametric trend tests for concentrations of dissolved solids, inorganic nitrogen (nitrite plus nitrate), total phosphorus, and suspended sediment at NASQAN and National Hydrologic Benchmark Network water-quality monitoring stations. Data collected during water years 1975-81 were tested. No trends were detected in these water-quality characteristics in the Powder River near Locate.

Gallagher and others (1986) reported percentage changes in the monthly and seasonal mean values of selected water-quality characteristics for Powder River stations near Locate and at Moorhead, Montana. They compared monthly and seasonal mean values of the characteristics between years 1951-60 and 1975-81 near Locate, and between 1951-57 and 1972-84 at Moorhead. Monthly and seasonal mean values were compared for the irrigation season--May, June, July, and August. Characteristics evaluated included specific conductance, pH, sodium-adsorption ratio, adjusted sodium-adsorption ratio, and concentrations of calcium, magnesium, sodium, and bicarbonate at both stations. Boron also was evaluated at the Moorhead station. The mean values of all characteristics except calcium and magnesium concentrations were larger during the later periods at both stations. The mean boron concentrations were larger during the later periods at Moorhead. The changes ranged from a small increase (4 percent) in bicarbonate concentration at Moorhead during 1972-84 to a large increase (95 percent) in adjusted sodium-adsorption ratio at the same station during the same period.

¹A water year is the 12-month period October 1 through September 30. It is designated by the calendar year in which it ends.

DATA AVAILABILITY

Water-quality data have been collected at several streamflow-gaging stations on the Powder River and its tributaries. The time allotted to this exploratory study permitted analysis of data from two stations. The station Powder River near Locate, Montana (station 06326500), was selected as the downstream station because it is nearest the mouth (fig. 1). The station Powder River at Sussex, Wyoming (station 06313500), was selected as the upstream station because it is downstream from the mouths of Salt Creek and South Fork Powder River, which are plains streams that contribute substantial quantities of streamflow and dissolved solids to the Powder River (fig. 1).

Stations and Periods of Record

The streamflow-gaging station Powder River near Locate is 1.5 mi downstream from the bridge on old U.S. Highway 12 at Locate, Montana (fig. 1). The period of record for water discharge is March 1938 to 1985. The period of record for water-quality data is water years 1946, 1948-63, and 1975 to the present (1985).

One water-quality sample was collected in 1946. Beginning in August 1948, one sample was collected bimonthly until February 1949; thereafter, at least one sample was collected monthly from February through September 1949. During water year 1950, one sample was collected in December. Beginning in March 1951, one sample was collected monthly, except May, June, and July, when two samples were collected monthly. Beginning in October 1951, daily samples were collected and combined into composite samples before analysis, except for November 1951 when no samples were collected. Generally, three composites of 10-day samples were prepared each month. Each day's samples were added to the composite in proportion to the discharge for that day, creating a discharge-weighted composite. Although composite periods were usually for 10 days, the period varied if changes in discharge or specific conductance were large. This method of discharge weighting was continued through October 1962, when water-quality sampling ended.

Water-quality sampling was restarted during water year 1975, when the station Powder River near Locate was added to the NASQAN network. Each station in the network was on a fixed sampling schedule. Samples were collected approximately once monthly for the Powder River near Locate until 1982, when the sampling frequency was decreased to bimonthly through water year 1985.

The streamflow-gaging station Powder River at Sussex is located 0.6 mi west of Sussex, Wyoming (fig. 1). The station is 2.7 mi (0.5 mi prior to April 9, 1983) downstream from the mouth of Salt Creek. The period of record for water discharge is April 1938 to June 1940, February 1950 to September 1957, and October 1977 to September 1984. The period of record for water-quality data is water years 1949-53, 1967-68, and 1976 to the present (1985).

Water-quality samples were collected intermittently at Sussex during water years 1949-53. In 1949, one sample was collected. In 1950, nine samples were collected. During 1951-53, samples were collected about monthly, although some samples were collected bimonthly.

Water-quality samples also were collected during water years 1967-68 and from 1976 to the present (1985). Thirteen samples were collected in 1967, and nine

samples were collected in 1968. One sample per year was collected in 1976 and 1977. Samples were collected approximately once monthly from 1978 through 1981. The sampling frequency was decreased to bimonthly during 1982 and 1983. Eleven samples were collected in 1984 and eight samples were collected in 1985. From 1976 to the present, the station Powder River at Sussex was operated as part of the NASQAN network.

Water-Quality Characteristics

For the station Powder River near Locate, the methods of analysis of water samples varied during water years 1946 and 1948-63. Beginning in October 1951, specific conductance of each daily sample was measured before the samples were composited. Both hardness and noncarbonate hardness were reported. Although alkalinity was not reported, bicarbonate was determined, and carbonate was determined when the pH value was sufficiently large. During water years 1949-56, dissolved-solids concentrations were reported as residue on evaporation at 180 °C. Later, values for the residue on evaporation and the sum of constituents were reported. Calcium and magnesium concentrations were not reported for all samples. Before 1951, sodium and potassium were reported as a combined concentration; after that date, sodium and potassium were reported separately. Sodium concentration was reported for nearly all samples, whereas potassium concentration was reported infrequently. The sodium-adsorption ratio was calculated for all samples. Sulfate and chloride concentrations were reported, with sulfate being analyzed more frequently than chloride.

When water-quality sampling was restarted in 1975 at the station Powder River near Locate, the number of characteristics reported commonly was greater than previously reported. Analyses for all the water-quality characteristics discussed above were reported for each water sample. In addition, onsite alkalinity was reported through 1980. Both onsite and laboratory determinations for alkalinity were reported during water years 1981-85. Dissolved-solids concentrations (residue on evaporation and sum of constituents) were reported for all water samples.

For the station Powder River at Sussex, the analyses of water samples were similar to the analyses reported for the Powder River near Locate. The same water-quality characteristics were reported for Sussex during water years 1949-53 as were reported for Locate during 1946 and 1948-63. Similarly, the water-quality characteristics reported for Sussex during water years 1967-68 and 1976-85 were the same as those reported for Locate during 1975-85.

Analytical methods and sampling techniques have changed through time. However, a review of the analytical methods and sampling techniques indicated that major changes did not occur during water years 1948-63. Thus, the analytical results within that period have not been affected by changes in analytical methods or sampling techniques. The review indicated that improved analytical techniques were adopted beginning in the late 1960's. Also, the practice of analyzing composited daily samples was almost completely abandoned in the 1970's in favor of analyzing discrete samples collected less frequently, for example, complete analyses of samples collected once monthly (Hem, 1985, p. 45). The analytical methods used during water years 1967-85 were similar. The reported results, therefore, were believed to be comparable. Owing to the differences between periods, the data were not consolidated but were analyzed separately.

Early methods of analysis are described by Rainwater and Thatcher (1960) and Brown and others (1970). More current methods are described by Skougstad and others (1985).

SELECTION OF DATA FOR TREND ANALYSIS

The measured properties of hardness and noncarbonate hardness were considered for trend analysis because of their relation to calcium and magnesium. Hardness includes the concentrations of calcium and magnesium and is expressed as equivalent quantities of calcium carbonate. Noncarbonate hardness is calculated as the difference between hardness and alkalinity and also is expressed as equivalent quantities of calcium carbonate. A test that indicates a trend in hardness would also indicate a trend in calcium and magnesium. Therefore, hardness data would be useful if analyses for calcium and magnesium are not reported. Trends in noncarbonate hardness might be affected by ions other than those contributing to hardness.

Alkalinity was considered for trend analysis because of its relation to bicarbonate and carbonate. Alkalinity is a measure of the combined activities of bicarbonate and carbonate. If alkalinity is not determined onsite or as part of a chemical analysis, it can be calculated from analyses of bicarbonate and carbonate as equivalent quantities of calcium carbonate. A test for trends in alkalinity could indicate trends in bicarbonate or carbonate.

Trends in specific conductance and dissolved solids could be caused by changes in the concentrations of constituents that were not included in the chemical analyses. Trends also could be caused by the sum of the effects of changes in concentration of individual constituents, which, when analyzed individually, failed to show statistically significant trends. Specific conductance may also change owing to a change in water composition, even though dissolved-solids concentration remains unchanged. Therefore, specific conductance and dissolved solids were considered for trend analysis.

The common ions were considered for trend analysis because they contribute most to dissolved solids in the Powder River and they were analyzed in both earlier and later periods. The common ions initially selected were the cations calcium, magnesium, sodium, and potassium and the anions sulfate and chloride.

The evaluation of water for its suitability for irrigation includes the assessment of the effects of sodium. One measure that commonly has been used is the sodium-adsorption ratio. Sodium-adsorption ratio was considered for trend analysis because of its importance in water used for irrigation.

The foregoing water-quality characteristics were evaluated with respect to the period of record, the sampling techniques, and the type of analyses for each station. After that evaluation, some characteristics during some time intervals were eliminated from consideration for trend analysis. The following sections describe the selection or rejection criteria of the data for each station and period of record. The final hydrologic characteristics used in the trend analysis are identified in table 1.

Table 1.--Hydrologic characteristics used in the trend analysis

[Units of measurement are milligrams per liter except as follows: discharge (cubic feet per second), specific conductance (microsiemens per centimeter at 25 °C) and sodium-adsorption ratio (units). Abbreviation: °C, degrees Celsius]

Characteristic	Powder River near Locate, Montana		Powder River at Sussex, Wyoming
	Water years 1952-63	Water years 1975-85	Water years 1967-68 and 1976-85
Discharge, water, monthly mean	Yes	No	No
Discharge, water, daily mean	No	Yes	Yes
Discharge, water, instantaneous	No	Yes	Yes
Specific conductance	Yes	Yes	Yes
Hardness ¹ , as CaCO ₃	Yes	Yes	No
Noncarbonate hardness, as CaCO ₃	Yes	Yes	No
Alkalinity ¹ , as CaCO ₃	Yes	Yes	Yes
Dissolved solids, residue at 180 °C	Yes	Yes	Yes
Calcium, dissolved, as Ca	No	Yes	No
Magnesium, dissolved, as Mg	No	Yes	No
Sodium, dissolved, as Na	Yes	Yes	Yes
Sodium-adsorption ratio (SAR) ²	Yes	Yes	Yes
Potassium, dissolved, as K	No	Yes	No
Sulfate, dissolved, as SO ₄	Yes	Yes	Yes
Chloride, dissolved, as Cl	No	Yes	Yes

¹Expressed in equivalent quantities of calcium carbonate.

²SAR =

$$\frac{(Na^+)}{\sqrt{\frac{(Ca^{+2}) + (Mg^{+2})}{2}}}$$

where Na, Ca, and Mg are expressed in milliequivalents per liter.

Powder River near Locate, Water Years 1952-63

Prior to the start of discharge-weighted compositing of water samples in October 1951, samples were only occasionally collected for analysis. Because discharge-weighted compositing was done from October 1951 through October 1962, data for this period (water years 1952-63) were selected for trend analysis and the earlier data (water years 1946 and 1948-51) were disregarded.

Characteristics with values reported for all compositing periods were selected for trend analysis. Those characteristics were specific conductance, hardness, noncarbonate hardness, alkalinity, and sodium-adsorption ratio. Monthly mean

values of each characteristic were computed from the discharge-weighted composite samples. The value of the characteristic was multiplied by the total discharge for the compositing period, then divided by the total discharge for the month. The results for each compositing period then were added, yielding a discharge-weighted, mean value of the characteristic for that month. Periods that included days from 2 months were prorated by the number of days of each month in the period. Because discharge-weighted monthly mean values of the water-quality characteristics were analyzed, monthly mean discharge was used instead of daily mean or instantaneous discharge.

Some characteristics were not analyzed for all composite samples, resulting in missing values. The missing values were so numerous for calcium, magnesium, potassium, and chloride that these constituents were not included in the trend analysis for this period. Dissolved solids and sodium each had two missing values; these values were estimated by linear regression. Values for dissolved solids were estimated from a relation developed between dissolved solids and specific conductance (coefficient of determination, 99 percent). Values for sodium were estimated from a relation developed between dissolved solids and sodium (coefficient of determination, 92 percent). Twenty-two percent of the sulfate values were missing. The missing values were too numerous to estimate without some risk of introducing bias into the data. Therefore, sulfate was analyzed using a smaller sample size.

Powder River near Locate, Water Years 1975-85

Data for the remaining period of record (water years 1975-85) at the Locate station were selected for trend analysis. A review of the water-quality data for that period indicated that instantaneous discharge was not measured at the time that seven of the samples were collected. Daily mean discharge was substituted for instantaneous discharge for these samples. The coefficient of determination between instantaneous and daily mean discharge was 99 percent.

Analyses for more water-quality characteristics were reported at Locate during water years 1975-85 than during the earlier period. The characteristics selected for trend analysis were specific conductance, hardness, noncarbonate hardness, onsite alkalinity, dissolved solids, calcium, magnesium, sodium, sodium-adsorption ratio, potassium, sulfate, and chloride. Onsite alkalinity was selected because of the greater number of values reported for onsite than for laboratory alkalinity.

Powder River at Sussex, Water Years 1967-68 and 1976-85

The water-quality data obtained during water years 1949-53 were not included in the study. The sample size for 1949-50, when periodic samples were collected at both stations, was not adequate for statistical analysis. The data for water years 1951-53 also were excluded because they were for discrete samples, whereas the data for the Powder River near Locate were for composite samples.

The data for the remaining period of record (water years 1967-68 and 1976-85) were selected for trend analysis. Instantaneous discharge was not measured when samples were collected during water years 1967-68. Daily mean discharge was substituted for instantaneous discharge for these samples. During water years 1976-85, instantaneous discharges were not available for four samples. Daily mean discharges were substituted for the missing values.

The characteristics selected for analysis for the Powder River at Sussex were those that displayed statistically significant trends in unadjusted data (not discharge weighted) at the station Powder River near Locate during water years 1975-85. Those characteristics were specific conductance, alkalinity, dissolved solids, sodium, sodium-adsorption ratio, sulfate, and chloride.

METHODS OF TREND ANALYSIS

Several methods are available to analyze data for trends. In selecting a method, the nature of the suspected trend is an important consideration. Sudden changes in conditions may cause a step trend--a sudden increase or decrease. A forest fire, a new dam, or a new analytical method may cause a relatively sudden change in the value of a water-quality property or in the concentration of a constituent. Gradual changes in conditions may cause a monotonic trend--a gradual increase or decrease. Such a trend in water quality may be the result of climatic variation, gradual changes in land use, or any other factor that causes a gradual increase or decrease in the value of a water-quality characteristic. For the Powder River, a cursory review of the history of the basin failed to indicate any cause for a step trend during the time that water-quality samples were collected. The trends in the water quality of the Powder River that have occurred are most likely monotonic.

Methods Available

Each method of data analysis has conditions that the data must meet before the method is applicable. Least-squares regression of a variable against time is a common trend-analysis technique. Inherent to this application of parametric statistics are the assumptions that the data are normally and identically distributed and are independent. However, water-quality characteristics commonly are not normally distributed. The probability distributions of each characteristic will change during the year, so they are not identically distributed. Also, the data are typically serially correlated, indicating a lack of independence.

Time-series analysis generally requires that the samples are equally spaced in time and that no values are missing. The water-quality data for the Powder River did not meet either requirement; therefore, the method of analysis was not applicable.

Many of the problems in applying parametric statistical and time-series methods to the analysis of water-quality data for trends can be avoided by the application of distribution-free (nonparametric) statistical tests. Hirsch and others (1982) and Smith and others (1982) modified Kendall's test (Kendall, 1975). The modified test, called the seasonal Kendall test, is used in analyzing data for trends when the data display seasonal patterns. The seasonal Kendall test was used in this study to analyze for trends in water-quality data.

Flow-Adjustment Regressions

Trends in many water-quality characteristics can be caused by variations in discharge or by changes in the processes that control the movement of constituents

to the stream and their subsequent fate, or both. Before analyzing for trends caused by changes in the controlling processes, the possible masking effects of variation in discharge need to be identified and removed. Hirsch and others (1982, p. 120) proposed a flow-adjusting procedure to accomplish this task. That procedure was followed in this study. A relation was developed between the characteristic and discharge using least-squares regression. Estimated values of the characteristic were calculated from the relation and subtracted from the measured values. The residuals then were tested for trends caused by changes in the underlying processes. Hirsch and others (1982, p. 120) defined the residuals as flow-adjusted concentrations. Because a measured property (specific conductance) and a calculated property (sodium-adsorption ratio) were included in this study in addition to concentrations of selected constituents and dissolved solids, the terminology "flow-adjusted data" is used in this report.

The first step in applying the seasonal Kendall test for trends is selecting an appropriate flow-adjustment equation. The equation that best describes the relation between stream discharge and the water-quality characteristics will not necessarily be the same for different characteristics or sampling locations. Crawford and others (1983, p. 11-12) included the following seven different types of equations in their flow-adjusting procedures:

$$\hat{C} = a + bQ \quad \text{linear} \quad (1)$$

$$\hat{C} = a + b \ln Q \quad \text{log-linear} \quad (2)$$

$$\hat{C} = a + b \left(\frac{1}{1 + dQ} \right) \quad \text{hyperbolic} \quad (3)$$

$$\hat{C} = a + b \left(\frac{1}{Q} \right) \quad \text{inverse} \quad (4)$$

$$\hat{C} = a + b_1 Q + b_2 Q^2 \quad \text{quadratic} \quad (5)$$

$$\ln \hat{C} = a + b \ln Q \quad \text{log-log} \quad (6)$$

$$\ln \hat{C} = a + b_1 \ln Q + b_2 (\ln Q)^2 \quad \text{log-quadratic log} \quad (7)$$

where

\hat{C} is the predicted value of the water-quality characteristic, with the same units as the actual water-quality characteristic;

a is the regression constant;

b, b_1 , b_2 , are regression coefficients;

Q is discharge, in ft^3/s ;

\ln signifies the natural logarithm; and

d is a constant typically in the range $10^{-3} Q^{-1} \leq d \leq 10^2 Q^{-1}$ where Q is mean discharge.

Eight different hyperbolic equations are generated in the procedures. An estimate of d is computed, then incremented by a constant quantity seven times, yielding eight hyperbolic equations.

Equations 1 through 5 were fitted to the data for the Locate station for the earlier period (water years 1952-63). The experience gained permitted the elimination of some equations from consideration when the data for the later period (water years 1975-85) for Locate and the data near Sussex were analyzed.

The equations selected for calculating flow-adjusted data are given in table 2. The equations were selected on the basis of the value of the coefficient of determination and an inspection of the plot of the relation between flow-adjusted data and the natural logarithm of flow. Often, the relation between the water-quality characteristics and discharge is not linear. Nonlinear equations (eqs. 2-5) better describe the relations. The hyperbolic equation (eq. 3) was included in the flow-adjusting procedures, in addition to the more common nonlinear equations (eqs. 2, 4, and 5) by Smith and others (1982, p. 8), because of its flexibility and usefulness in describing the relation between many dissolved constituents and discharge.

In some instances, the variability of the flow-adjusted data displayed a distinct pattern related to discharge. Usually, the data displayed increasing scatter with increasing discharge. In such situations, equations that related the natural logarithm of the variable to a function of discharge were used (eqs. 6 and 7), and the selection between alternate equations was based primarily on the inspection of the plots of the data.

Significant relations between each characteristic and discharge were obtained in all tests, at the 0.10 significance level. In each test, the value of the characteristic decreased with increasing discharge. Even though all relations were significant, the quantity of variation in the characteristic accounted for by changes in discharge was small in some instances. Failure to remove the smaller, but still significant, effects of discharge variation may result in a trend being detected that is discharge related. The data for all characteristics, therefore, were adjusted for changes in discharge.

Subsequent to equation selection, it is useful to inspect graphs of discharge, the water-quality data, and the flow-adjusted data as a function of time. Plots of these characteristics were inspected for all tests in the investigation. Information derived from the inspections included the nature of possible trends (step or monotonic), and the effects of changing discharge through time. Determining the possible nature of the trend is necessary because the seasonal Kendall test is applicable only for monotonic trends. If step trends occur, other tests are needed.

The graphs were too numerous to include in this report. However, examples are shown in figures 2-4. The graph of monthly mean discharge (fig. 2) reflects larger discharges in 1962 than in the previous years. No other distinct pattern is obvious. The graph of sodium concentration (fig. 3) does not show any clearly identifiable pattern. When the effect of discharge is removed and the flow-adjusted data are plotted (fig. 4), the data do not show any abrupt changes in concentration. A trend, if present, will be monotonic.

Table 2.--Type of regression equation selected for calculating flow-adjusted data for each station and time period

Characteristic	Type of equation (equation No.)	Coefficient of determination ¹ (percent)
<u>Powder River near Locate, Montana, water years 1952-63</u>		
Specific conductance	Hyperbolic (3)	51
Hardness	Hyperbolic (3)	27
Noncarbonate hardness	Hyperbolic (3)	15
Alkalinity	Log-log (6)	35
Dissolved solids	Hyperbolic (3)	46
Sodium	Hyperbolic (3)	70
Sodium-adsorption ratio	Log-log (6)	60
Sulfate	Hyperbolic (3)	33
<u>Powder River near Locate, Montana, water years 1975-85</u>		
Specific conductance	Hyperbolic (3)	47
Hardness	Hyperbolic (3)	35
Noncarbonate hardness	Hyperbolic (3)	21
Alkalinity	Log-log (6)	33
Dissolved solids	Hyperbolic (3)	47
Calcium	Hyperbolic (3)	28
Magnesium	Hyperbolic (3)	41
Sodium	Hyperbolic (3)	50
Sodium-adsorption ratio	Log-log (6)	43
Potassium	Log-quadratic log (7)	23
Sulfate	Hyperbolic (3)	39
Chloride	Log-quadratic log (7)	44
<u>Powder River at Sussex, Wyoming, water years 1967-68 and 1976-85</u>		
Specific conductance	Hyperbolic (3)	47
Alkalinity	Log-log (6)	37
Dissolved solids	Hyperbolic (3)	47
Sodium	Hyperbolic (3)	62
Sodium-adsorption ratio	Log-log (6)	50
Sulfate	Hyperbolic (3)	43
Chloride	Log-quadratic log (7)	19

¹Coefficient of correlation squared for all types except the log-quadratic log type, which is the multiple correlation coefficient squared.

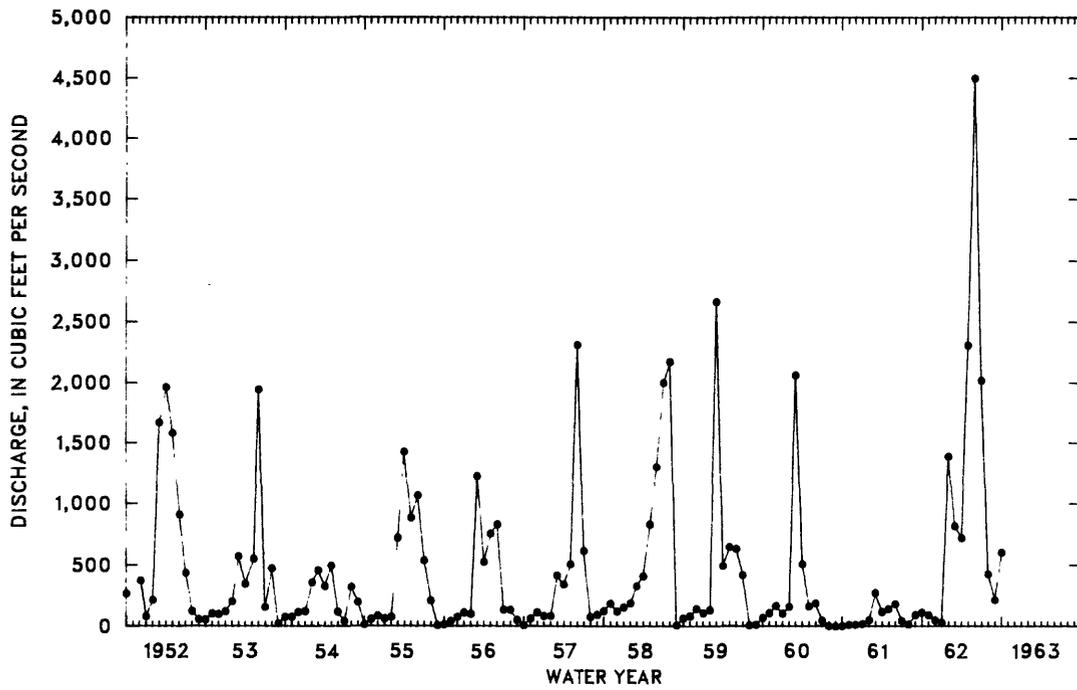


Figure 2.--Monthly mean discharge, Powder River near Locate, Montana, water years 1952-63.

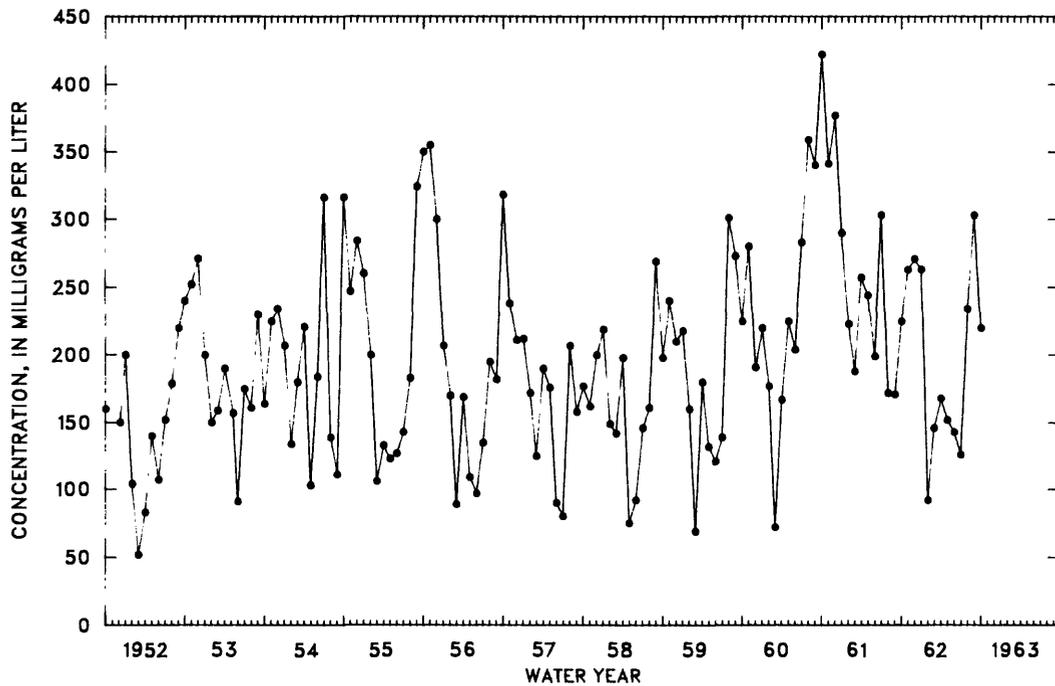


Figure 3.--Monthly mean sodium concentration, Powder River near Locate, Montana, water years 1952-63.

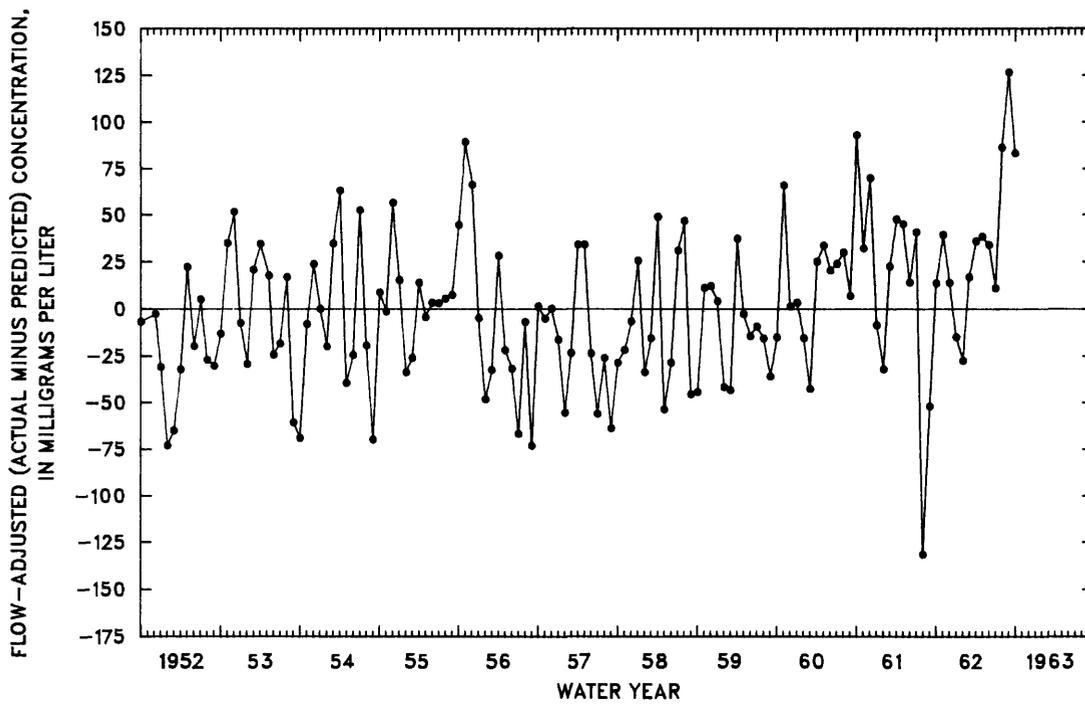


Figure 4.--Flow-adjusted monthly mean sodium concentration, Powder River near Locate, Montana, water years 1952-63.

Seasonal Kendall Test

The Kendall test involves comparing paired values in a data set. If the second member of the pair is larger than the first, a +1 is assigned; if smaller than the first, a -1 is assigned; and if they are equal, a 0 is assigned. The sum of these scores is the test statistic, S , which is approximately normally distributed.

Streamflow and water-quality characteristics display seasonal patterns. Therefore, any comparison between data from different times of the year may result in misleading conclusions. As a result, a study of trends involving comparison of data collected during the fall (a period of generally little discharge in this region) with data collected during the spring (a period of generally greater discharge) might indicate a false trend.

The seasonal Kendall test of Hirsch and others (1982, p. 109-110) and Smith and others (1982, p. 31) calculates an S_i ($i = 1$ to n , the number of seasons per year) for each season. That is, if monthly values of a characteristic are being compared, an S_i statistic is calculated by comparing values for adjacent years for each month. The test statistic, S , is the sum of the seasonal values, S_i . Missing values pose no problem; if data are missing for a particular season and year (or years), no score is assigned. If more than one value occurs, the median of the values is used for that season and year. Kendall's tau is computed as S divided by $n(n-1)/2$, where n is the number of valid comparisons in the respective season. Tau is a type of rank correlation coefficient between the characteristic and time. It has values between -1 and +1. Negative values of tau signify a decreasing trend and positive values an increasing trend (Crawford and others, 1983, p. 61).

The standard normal variate, Z, is computed as the S value (with a continuity correction) divided by the standard deviation of the S values. If the seasonal S value is 0, then Z is 0 (Hirsch and others, 1982, p. 110; Smith and others, 1982, p. 31). The probability level of the test is the probability corresponding to the value of Z. It is the probability of obtaining a Z value as large as or larger than the computed value when there is no trend (the null hypothesis is true) (Crawford and others, 1983, p. 60). The probability level is obtained from statistical tables or computed from statistical functions available on computer systems.

The significance level is the probability of concluding that a trend exists when it does not. A related error is concluding that a trend does not exist when, in fact, it does. The probability of making the second error is not generally known. However, the errors are inversely related. The probability of making the second error can be decreased by increasing the significance level. In testing for trends, a significance level of 0.01, 0.05, or 0.10 typically is chosen. The probability level corresponding to the value of Z is compared with the significance level. If the probability is equal to or larger than the significance level, the conclusion is that no trend exists. If the probability level is smaller than the significance level, the conclusion is that there is a trend.

Estimates of the magnitudes of trends may be obtained using methods of Hirsch and others (1982, p. 117) and Smith and others (1982, p. 6), who calculated the trend magnitude by first computing the slopes of trends as the difference between the ordered pairs of data divided by the time interval between them. The slope estimate, which is the median value of these slopes, provides an estimate of the median magnitude of a trend during the time interval.

To make comparisons between characteristics easier, the slope estimate can be expressed as a percentage (Smith and others, 1982, p. 13, 20). The procedure is to divide the slope estimate by the mean value of the characteristic, then multiply by 100. When the natural logarithm of the characteristic is analyzed for trend, the slope estimate (b) is converted to a percentage as follows: $100 \cdot (\exp(b)-1)$ (Crawford and others, 1983, p. 12-13). In this study, all slope estimates were converted to percentages using these procedures.

The slope estimate can be 0 for some characteristics. Even though Kendall's tau and the significance level indicate a significant trend, the slope estimate can be 0 when many paired values of the characteristic are equal (Hirsch and others, 1982, p. 117).

Crawford and others (1983) developed seasonal Kendall test procedures for trends in water-quality data using the Statistical Analysis System². These procedures, which are stored in the U.S. Geological Survey's central computer system, were used in this study.

Following selection of a flow-adjustment equation, the seasonal Kendall test was applied. Values of Kendall's tau, probability level, and slope estimate are computed for discharge, the unadjusted water-quality characteristics, and the flow-adjusted water-quality characteristics.

²Use of firm or trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

TRENDS IN WATER-QUALITY CHARACTERISTICS

Trends in Unadjusted Data

The results of the tests for trends in discharge are summarized in table 3. During water years 1975-85, the instantaneous discharge of the Powder River near Locate indicated a significant, decreasing trend. The probability level was less than the selected significance level of 0.10, indicating a trend. The magnitude of the trend was about $-13 \text{ ft}^3/\text{s}$ per year.

Table 3.--Seasonal Kendall tests for trends in discharge of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming

[Probability level: *, trend is significant at 0.10 level]

Station	Time period (water years)	Number of observations	Number of seasonal values	Tau	Probability level	Slope estimate (cubic feet per second per year)
Powder River near Locate	1952-63	132	117	-0.067	0.374	-2.8
Powder River near Locate	1975-85	107	101	-.246	.003*	-13
Powder River at Sussex	1967-68, 1976-85	101	94	-.071	.421	-.96

Tests for trends in the water-quality characteristics before flow adjustment can provide useful information regarding the detection of discharge-related trends. A discharge-related trend is indicated when a trend is detected before flow adjustment but not after. The results of seasonal Kendall tests of the unadjusted characteristics are listed in table 4.

In the Powder River near Locate during water years 1952-63, increasing trends in the unadjusted data occurred in specific conductance, dissolved solids, sodium, sodium-adsorption ratio, and sulfate. During water years 1975-85 at the same station, trends occurred in the same characteristics as during the earlier period. In addition, increasing trends were detected in alkalinity and chloride during the later period. In the Powder River at Sussex during water years 1967-68 and 1976-85, increasing trends were detected in sodium, sodium-adsorption ratio, and chloride; a decreasing trend was detected in sulfate.

Table 4.--Seasonal Kendall tests for trends in unadjusted water-quality characteristics of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming

[Probability level: *, trend is significant at 0.10 level]

Characteristic	Number of observations	Number of seasonal values	Tau	Probability level	Slope estimate (percent per year)
<u>Powder River near Locate, water years 1952-63</u>					
Specific conductance	132	117	0.141	0.057 *	1.6
Hardness	132	117	.084	.264	.9
Noncarbonate hardness	132	117	.113	.128	1.2
Alkalinity	132	114	.072	.344	.5
Dissolved solids	132	117	.138	.064 *	1.3
Sodium	132	117	.230	.002 *	2.4
Sodium-adsorption ratio	131	116	.197	.004 *	0
Sulfate	103	92	.145	.099 *	2.6
<u>Powder River near Locate, water years 1975-85</u>					
Specific conductance	107	101	.203	.013 *	2.9
Hardness	107	101	.099	.233	1.2
Noncarbonate hardness	107	101	.020	.826	.1
Alkalinity	93	87	.242	.008 *	2.0
Dissolved solids	107	101	.213	.009 *	2.4
Calcium	107	101	.061	.464	0
Magnesium	107	101	.089	.288	.9
Sodium	107	101	.223	.006 *	3.1
Sodium-adsorption ratio	102	96	.291	.001 *	2.4
Potassium	107	101	.041	.638	.4
Sulfate	107	101	.195	.017 *	2.4
Chloride	107	101	.324	.001 *	5.2
<u>Powder River at Sussex, water years 1967-68 and 1976-85</u>					
Specific conductance	85	80	.142	.147	.6
Alkalinity	63	58	.049	.295	.3
Dissolved solids	101	94	.089	.310	.6
Sodium	101	94	.280	.001 *	1.5
Sodium-adsorption ratio	100	93	.393	.001 *	2.1
Sulfate	101	94	-.193	.024 *	-2.1
Chloride	101	94	.360	.001 *	6.5

Trends in Flow-Adjusted Data

The results of the application of the seasonal Kendall test to the flow-adjusted data are summarized in table 5. Inspection of the results indicates that the flow-adjusted data for the Powder River near Locate did not have significant trends in specific conductance, dissolved solids, or sulfate during water years 1952-63, or in alkalinity, dissolved solids, or sulfate during water years 1975-85. These results indicate that trends in these characteristics before flow adjustment are due to discharge variability. Unlike the Powder River near Locate, flow adjustment of the data at the Powder River at Sussex did not eliminate trends present in the unadjusted data. The adjustment caused a decrease in the slope estimates for sodium, sulfate, and chloride; an increase in the slope estimate for sodium-adsorption ratio, and an increase in the probability level for sodium by an order of magnitude. The trends were significant at the 0.10 level.

The Powder River near Locate during water years 1952-63 exhibited statistically significant trends in flow-adjusted data for sodium and sodium-adsorption ratio. The flow-adjusted data for sodium increased at a rate of 2.9 mg/L per year, or 1.5 percent of the mean concentration (195 mg/L) per year. The flow-adjusted data for sodium-adsorption ratio increased 0.04 unit per year, or 1.1 percent of the mean ratio (3.5 units) per year. No trends were detected in specific conductance, hardness, noncarbonate hardness, alkalinity, dissolved solids, or sulfate.

The Powder River near Locate during water years 1975-85 exhibited significant trends in flow-adjusted data for specific conductance, sodium, sodium-adsorption ratio, and chloride. Flow-adjusted data for specific conductance increased 29 $\mu\text{S}/\text{cm}$ (microsiemens per centimeter at 25 °C) per year, or 1.4 percent of the mean value (2,104 $\mu\text{S}/\text{cm}$) per year. Flow-adjusted data for sodium increased 4.2 mg/L per year, or 1.5 percent of the mean concentration (282 mg/L) per year. Flow-adjusted data for sodium-adsorption ratio increased 0.1 unit per year, or 1.9 percent of the mean ratio (5.3 units) per year. Flow-adjusted data for chloride increased 4.2 mg/L per year, or 3.1 percent of the mean concentration (134 mg/L) per year. No trends were detected in hardness, noncarbonate hardness, alkalinity, dissolved solids, calcium, magnesium, potassium, or sulfate.

Of the characteristics tested for trend in the Powder River at Sussex during water years 1967-68 and 1976-85, flow-adjusted data exhibited significant trends for sodium, sodium-adsorption ratio, sulfate, and chloride. Flow-adjusted data for sodium increased 5.7 mg/L per year, or 1.1 percent of the mean concentration (520 mg/L) per year. The flow-adjusted data for sodium-adsorption ratio increased 0.25 unit per year, or 2.6 percent of the mean ratio (9.5 units) per year. The trend in flow-adjusted data for sulfate decreased 13 mg/L per year, or about -1.8 percent of the mean concentration (720 mg/L) per year. Flow-adjusted data for chloride increased 22 mg/L per year, or 5.5 percent of the mean concentration (400 mg/L) per year. No trends were detected in specific conductance, alkalinity, or dissolved solids.

Data for water years 1967-68 were included in the preceding analysis at Sussex to increase sample size. Because the period at Sussex (1976-85) was nearly the same duration as near Locate (1975-85), the data for water years 1967-68 were deleted, and the remaining data were reanalyzed to determine the effect, if any, of inclusion of the 1967-68 data. Trend analysis was performed on the characteristics that earlier displayed significant trends (sodium, sodium-adsorption ratio, sulfate, and chloride). The results are summarized in table 6.

Table 5.--Seasonal Kendall tests for trends in flow-adjusted characteristics of the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming

[Probability level: *, trend is significant at 0.10 level]

Flow-adjusted characteristic	Number of observations	Number of seasonal values	Tau	Probability level	Slope estimate (percent per year)
<u>Powder River near Locate, water years 1952-63</u>					
Specific conductance	132	117	0.093	0.214	0.5
Hardness	132	117	.026	.741	.2
Noncarbonate hardness	132	117	.037	.630	.3
Alkalinity	132	114	.025	.753	.1
Dissolved solids	132	117	.048	.526	.4
Sodium	132	117	.219	.003 *	1.5
Sodium-adsorption ratio	130	115	.137	.067 *	1.1
Sulfate	103	92	.037	.693	.7
<u>Powder River near Locate, water years 1975-85</u>					
Specific conductance	107	101	.165	.045 *	1.4
Hardness	107	101	.018	.851	.2
Noncarbonate hardness	107	101	-.048	.574	-.4
Alkalinity	93	87	.074	.434	.6
Dissolved solids	107	101	.124	.133	1.0
Calcium	107	101	-.048	.574	-.2
Magnesium	107	101	.089	.288	.9
Sodium	107	101	.200	.015 *	1.5
Sodium-adsorption ratio	102	96	.212	.013 *	1.9
Potassium	107	101	-.008	.950	-.3
Sulfate	107	101	.094	.260	.8
Chloride	107	101	.246	.003 *	3.1
<u>Powder River at Sussex, water years 1967-68 and 1976-85</u>					
Specific conductance	85	80	-.021	.861	-.1
Alkalinity	62	57	.041	.341	.1
Dissolved solids	101	94	.119	.173	.6
Sodium	101	94	.202	.019 *	1.1
Sodium-adsorption ratio	100	93	.372	.001 *	2.6
Sulfate	101	94	-.256	.003 *	-1.8
Chloride	101	94	.342	.001 *	5.5

Table 6.--Seasonal Kendall tests for trends in flow-adjusted characteristics of the Powder River at Sussex, Wyoming, water years 1976-85

[Probability level: *, trend is significant at 0.10 level]

Flow-adjusted characteristic	Number of observations	Number of seasonal values	Tau	Probability level	Slope estimate (percent change per year)
Sodium	81	74	0.090	0.400	1.3
Sodium-adsorption ratio	78	72	.270	.010 *	3.3
Sulfate	81	74	.130	.215	1.0
Chloride	81	74	.065	.552	.5

The flow-adjusted data for sodium-adsorption ratio exhibited a statistically significant trend at the 0.10 level. The slope estimate was an increase of 3.3 percent per year, compared to 2.6 percent per year when water years 1967-68 were included. Statistically significant trends were no longer present for sodium, sulfate, or chloride.

The statistically significant trends in flow-adjusted data for sodium and sodium-adsorption ratio indicate that the sodium concentration increased during water years 1952-63 and 1975-85 near Locate, and during water years 1967-68 and 1976-85 at Sussex. The fact that the increase in sodium-adsorption ratio during water years 1975-85 near Locate and 1976-85 at Sussex implies that the increase may be due, in part, to activities upstream from Sussex.

Factors Affecting Results

Several factors may affect the results of trend tests made in this study. Some of the test results were variable, and in two instances, were contradictory: an increasing trend in specific conductance but not dissolved solids near Locate, for water years 1975-85, and an increasing trend in sodium-adsorption ratio but not sodium at Sussex for water years 1976-85.

The ability of a test to detect an existing trend depends, in part, on sample size (Hirsch and others, 1982, p. 111). The sample size is the number of valid data pairs formed in the seasonal Kendall test. Smith and others (1982, p. 3) explained the effects of sample size as follows:

"A trend which now exists may have existed for only a few years and may even be a reversal of a previous trend. The use of a long record tends to mask a current trend. On the other hand, a very short record may not contain enough data to distinguish a trend from natural variability in the data."

When data for water years 1967-68 were deleted from the data for the Powder River at Sussex, the number of data pairs was decreased by 21 percent, which may have affected the trend results.

The selection of the time periods used for the seasons may also affect the results. Because S is computed as the sum of S_i ($i=1$ to n , the number of seasons per year), the S values depend on the number of valid data pairs in each season. In this study, the total number of observations (and data pairs that were formed) varied, owing to the sampling schedules near Locate during water years 1975-85 and at Sussex during water years 1967-68 and 1976-85.

S is a summary statistic for the entire period of record and does not indicate trends in individual seasons. Trend heterogeneity, increasing trends in some seasons and decreasing trends in other seasons, can result in a value of S that is close to zero. The small value of S can result in the conclusion that no trend exists when significant trends in opposing directions are actually present (Hirsch and others, 1982, p. 111).

The significance level can result in the conclusion that a trend exists, when in fact, it does not. A significance level of 0.10 means that there is a 10-percent chance of wrongly concluding that a trend exists. This might be one explanation for the detection of trends in specific conductance but not dissolved solids near Locate, and for the detection of a trend in the sodium-adsorption ratio but not in sodium at Sussex.

Serial correlation has the effect of increasing the actual probability level. Thus, a significant trend may be indicated when it actually is not significant (Hirsch and Slack, 1984, p. 727). Crawford and others (1983, p. 50) indicated that, for monthly data, the serial correlations generally are in the range such that the actual probability levels may be twice as large as the calculated probability levels. However, in most instances in this study, the calculated probability levels were such that if the actual level were twice as large, the conclusions would not change.

In this study, each variable was adjusted for the effects of discharge prior to the application of the seasonal Kendall test by the calculation of flow-adjusted data. Discharge was used as the independent (or explanatory) variable because of its good correlation with many water-quality characteristics. For some characteristics, Crawford and others (1983, p. 11) stated that adjustment by some other characteristic may be appropriate. For example, it might be appropriate to adjust some biological constituents by solar radiation or air temperature.

Additional studies would be useful in evaluating the factors that might be affecting the trends found. Water-quality models could be used to help discern reasons for the trends determined. The trend analysis could be expanded to include other stations and data collected since 1985. The effects of trend heterogeneity could be evaluated by analyzing each season separately. The effects of serial correlation could be investigated, and, if found to be affecting the tests for trends, the covariance correction described by Hirsch and Slack (1984, p. 728) could be used. Alternative means of adjusting the data for characteristics having small correlation with discharge could be examined.

SUMMARY

Data for major water-quality characteristics were evaluated for trends at two streamflow-gaging stations on the Powder River. The stations were the Powder River near Locate, Montana, and the Powder River at Sussex, Wyoming.

Water-quality data for the Powder River near Locate were available for water years 1946, 1948-63 and 1975-85. Because composite samples were collected consistently from October 1951 through October 1962, data for this period (water years 1952-63) were selected for trend analysis and the earlier data (water years 1946 and 1948-51) were not. Daily samples were composited for three or more periods each month, depending on variation in discharge or specific conductance. Monthly mean values of each characteristic were computed by weighting the values reported for each period. The value of the characteristic was multiplied by the ratio of total discharge for the period to total discharge for the month, then the weighted values for each month were added. Compositing periods that overlapped months were prorated between the months.

Water-quality sampling was restarted during water year 1975 near Locate, and samples were collected on a fixed schedule. Samples were collected approximately once monthly until 1982, when the sampling frequency was decreased to bimonthly through water year 1985.

Water-quality data for the Powder River at Sussex were collected during water years 1949-53, 1967-68, and 1976-85. The sampling schedule varied. In 1949, 1976, and 1977, one sample per year was collected. During the other water years, the schedule ranged from one sample every other month to one sample each month.

Samples from the later period (water years 1975-85) near Locate and water years 1967-68 and 1976-85 at Sussex were analyzed separately. In the few instances where discharge was not measured when the water sample was collected, daily mean discharge was substituted for instantaneous discharge.

The seasonal Kendall test was applied to both unadjusted and flow-adjusted data. The trend tests were first applied to the unadjusted and flow-adjusted data for the Powder River near Locate for water years 1952-63 and 1975-85. The tests also were applied to data for the Powder River at Sussex for water years 1967-68 and 1976-85 for those characteristics that displayed statistically significant trends in unadjusted data at the Powder River near Locate during water years 1975-85. The slope estimate was calculated for each characteristic, which provided a measure of the magnitude of trends.

Flow-adjusted data for the Powder River near Locate during water years 1952-63 had statistically significant trends in sodium and sodium-adsorption ratio. Flow-adjusted data increased 1.5 percent per year for sodium and 1.1 percent per year for sodium-adsorption ratio. No trends were detected in specific conductance, hardness, noncarbonate hardness, alkalinity, dissolved solids, or sulfate.

Flow-adjusted data for the Powder River near Locate during water years 1975-85 had significant trends in specific conductance, sodium, sodium-adsorption ratio, and chloride. Flow-adjusted data increased by 1.4 percent per year for specific conductance, 1.5 percent per year for sodium, 1.9 percent per year for sodium-adsorption ratio, and 3.1 percent per year for chloride. No trends were detected in hardness, noncarbonate hardness, alkalinity, dissolved solids, calcium, magnesium, potassium, or sulfate.

Flow-adjusted data for the Powder River at Sussex during water years 1967-68 and 1976-85 had significant trends in sodium, sodium-adsorption ratio, sulfate, and chloride. Flow-adjusted data increased 1.1 percent per year for sodium, 2.6 percent per year for sodium-adsorption ratio, and 5.5 percent per year for chloride. Flow-adjusted data for sulfate displayed a significant, decreasing trend of 1.8 percent per year. No trends were detected in specific conductance, alkalinity, or dissolved solids.

To compare similar periods at Sussex (water years 1976-85) and Locate (water years 1975-85), the data for water years 1967-68 at Sussex were deleted, and the 1976-85 data were reanalyzed. The sodium-adsorption ratio was the only characteristic exhibiting a statistically significant trend. The flow-adjusted data indicated an increasing trend of 3.3 percent per year.

Trend results indicated increases in sodium-adsorption ratio near Locate (water years 1975-85) and at Sussex (water years 1976-85). The fact that the increase was nearly concurrent at the two stations implies that the increase may be due, in part, to activities upstream from Sussex.

Several factors may have affected the results of trend tests that were made in this study. Sample size may have been too small. The time periods used in the analyses may not have included trends in some characteristics. The number of valid data pairs, in addition to the total number of pairs, used in each season may have affected the results. A single test statistic is formed from the sum of the seasonal statistics. If the trends were heterogeneous (increasing in some seasons, decreasing in others), a nonsignificant test statistic might be computed when, in fact, significant trends exist during some seasons. At the 0.10 significance level, there is a 10-percent chance that the conclusion will be drawn that a trend exists when it does not; this might explain the detection of trends in specific conductance and sodium-adsorption ratio but not in dissolved-solids and sodium concentrations. Serial correlation was assumed to be negligible in this study. If significant serial correlation exists, the conclusion might be drawn that trends exist, when in fact, they do not. In this study, the data were adjusted to account for changes in flow. Adjustment using some characteristic other than discharge may be necessary to indicate trends for some water-quality characteristics. Additional studies of available data would be useful in evaluating the factors that might be affecting the results of trend analysis.

REFERENCES CITED

- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 160 p.
- Crawford, C.G., Slack, J.R., and Hirsch, R.M., 1983, Nonparametric tests for trends in water-quality data using the Statistical Analysis System: U.S. Geological Survey Open-File Report 83-550, 102 p.
- Gallagher, Kathleen, Garvin, J.P., and Schafer, W.M., 1986, Powder River Basin water-quality study [Montana]: Unpublished report prepared for the Powder River Conservation District, Powder River County, Montana, 100 p.
- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- Hirsch, R.M., and Slack, J.R., 1984, A nonparametric trend test for seasonal data with serial dependence: Water Resources Research, v. 20, no. 6, p. 727-732.
- Hirsch, R.M., Slack, J.R., and Smith, R.A., 1982, Techniques of trend analysis for monthly water-quality data: Water Resources Research, v. 18, no. 1, p. 107-121.
- Kendall, M.G., 1975, Rank correlation methods: London, Charles Griffin and Co., Ltd., 202 p.
- Rainwater, F.H., and Thatcher, L.L., 1960, Methods of collection and analysis of water samples: U.S. Geological Survey Water-Supply Paper 1454, 301 p.
- Skougstad, M.W., Fishman, M.J., Freedman, L.C., Erdmann, D.E., and Duncan, S.S., eds., 1985, Methods for determination of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 709 p.
- Smith, R.A., Hirsch, R.M., and Slack, J.R., 1982, A study of trends in total phosphorus measurements at NASQAN stations: U.S. Geological Survey Water-Supply Paper 2190, 34 p.
- Smith, R.A., and Alexander, R.B., 1985, Trends in concentrations of dissolved solids, suspended sediment, phosphorus, and inorganic nitrogen at U.S. Geological Survey National Stream Quality Accounting Network stations, in National water summary 1984: U.S. Geological Survey Water-Supply Paper 2275, p. 66-73.
- Wells, F.C., and Schertz, T.L., 1983, Statistical summary of daily values data and trend analysis of dissolved-solids data at National Stream Quality Accounting Network (NASQAN) stations: U.S. Geological Survey Water-Resources Investigations Report 83-4172, 526 p.