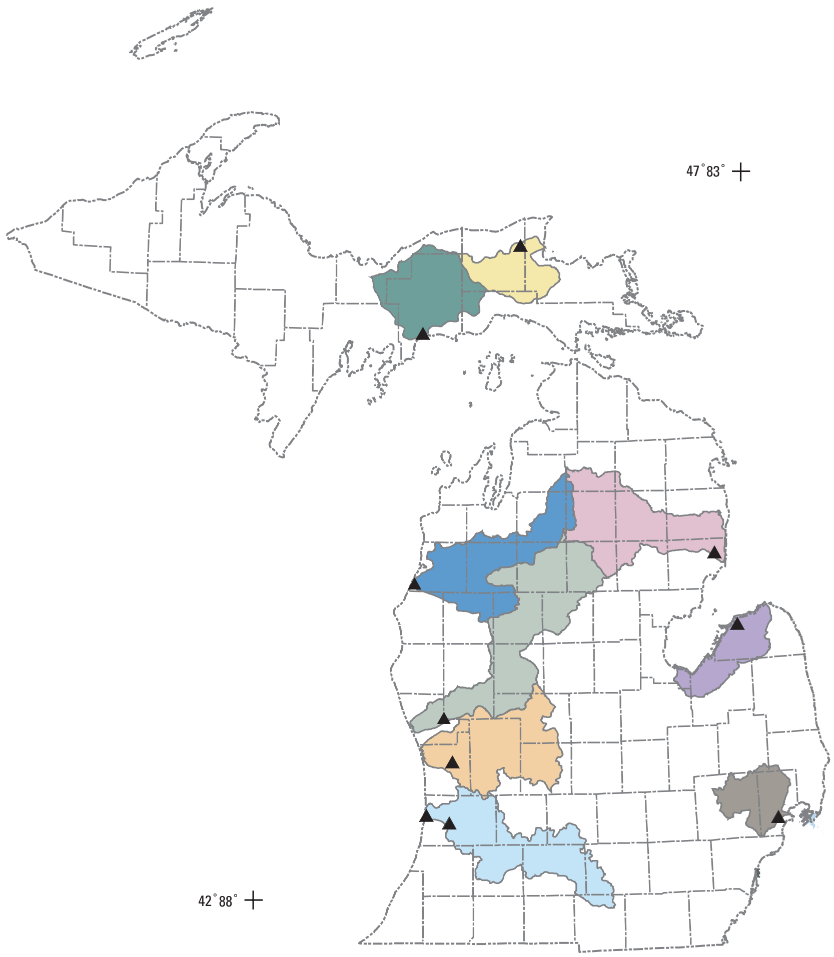
In cooperation with the
Michigan Department of Environmental Quality

Trends in Surface-Water Quality at Selected National Stream Quality Accounting Network (NASQAN) Stations, in Michigan



Scientific Investigations Report 2005-5158

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

Cover Illustration. Map of Michigan showing watersheds analyzed for trend tests in this study. (Illustration by Richard Jodoin, U.S. Geological Survey.)

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By Atiq U. Syed and Lisa R. Fogarty

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Conversion Factors and Abbreviations

Multiply	By	To obtain
	Area	
acre	4046.85	square meter (m^2)
square miles (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

Temperature in degree Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F = (1.8* °C) +32

Temperature in degree Fahrenheit (°F) may be converted to degree Celsius (°C) as follows:
°C = (°F-32)/1.8

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

Concentration of chemical constituents in water is given in milligrams per liter (mg/L). A milligram per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water.

Concentration of bacteria is given as cfu/100 ml. This pertains to the number of bacteria colonies formed from 100 ml of the sample.

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ABSTRACT

To demonstrate the value of long-term, water-quality monitoring, the Michigan Department of Environmental Quality (MDEQ), in cooperation with the U.S. Geological Survey (USGS), initiated a study to evaluate potential trends in water-quality constituents for selected National Stream Quality Accounting Network (NASQAN) stations in Michigan. The goal of this study is to assist the MDEQ in evaluating the effectiveness of water-pollution control efforts and the identification of water-quality concerns.

The study included a total of nine NASQAN stations in Michigan. Approximately 28 constituents were analyzed for trend tests. Station selection was based on data availability, land-use characteristics, and station priority for the MDEQ Water Chemistry Monitoring Project. Trend analyses were completed using the uncensored Seasonal Kendall Test in the computer program Estimate Trend (ESTREND), a software program for the detection of trends in water-quality data. The parameters chosen for the trend test had (1) at least a 5-year period of record (2) about 5 percent of the observations censored at a single reporting limit, and (3) 40 percent of the values within the beginning one-fifth and ending one-fifth of the selected period. In this study, a negative trend indicates a decrease in concentration of a particular constituent, which generally means an improvement in water quality; whereas a positive trend means an increase in concentration and possible degradation of water quality.

The results of the study show an overall improvement in water quality at the Clinton River at Mount Clemens, Manistee River at Manistee, and Pigeon River near Caseville. The detected trend for these stations show decreases in concentrations of various constituents such as nitrogen compounds, conductance, sulfate, fecal coliform bacteria, and fecal streptococci bacteria. The negative trend may indicate an overall improvement in agricultural practices, municipal and industrial wastewater-treatment processes, and effective regulations.

Phosphorus data for most of the study stations could not be analyzed because of the data limitations for trend tests. The only station with a significant negative trend in total phosphorus concentration is the Clinton River at Mount Clemens. However, scatter-plot analyses of phosphorus data indicate decreasing concentrations with time for most of the study stations.

Positive trends in concentration of nitrogen compounds were detected at the Kalamazoo River near Saugatuck and Muskegon River near Bridgeton. Positive trends in both fecal coliform and total fecal coliform were detected at the Tahquamenon River near Paradise. Various different point and nonpoint sources could produce such positive trends, but most commonly the increase in concentrations of nitrogen compounds and fecal coliform bacteria are associated with agricultural practices and sewage-plant discharges.

The constituent with the most numerous and geographically widespread significant trend is pH. The pH levels increased at six out of nine stations on all the major rivers in Michigan, with no negative trend at any station. The cause of pH increase is difficult to determine, as it could be related to a combination of anthropogenic activities and natural processes occurring simultaneously in the environment.

Trends in concentration of major ions, such as calcium, sodium, magnesium, sulfate, fluoride, chloride,

and potassium, were detected at eight out of nine stations. A negative trend was detected only in sulfate and fluoride concentrations; a positive trend was detected only in calcium concentration. The major ions with the most widespread significant trends are sodium and chloride; three positive and two negative trends were detected for sodium, and three negative and two positive trends were detected for chloride. The negative trends in chloride concentrations outnumbered the positive trends. This result indicates a slight improvement in surface-water quality because chloride as a point source in natural water comes from deicing salt, sewage effluents, industrial wastes, and oil fields.

For other major ions, such as magnesium and potassium, both positive and negative trends were detected. These changes in trends indicate changes in surface-water quality caused by a variety of point and non-point sources throughout Michigan, as well as natural changes in the environment.

INTRODUCTION

With over 36,000 mi of streams, surface waters are an important natural resource for the State of Michigan. Prior to the Clean Water Act of 1972 (Digest of Federal Resource laws, 1972), Michigan waters were severely affected by many different land-use activities such as urbanization, industrialization, and agricultural practices. Historically, industrial operations have left many of Michigan's waters contaminated with Poly Chlorinated Biphenyls (PCBs), solvents, metals, and other hazardous wastes. Agricultural and forestry practice has also affected waters by removing protective vegetation preventing erosion, and by introducing high levels of contaminants, such as nutrients, herbicides, and pesticides. The Clean Water Act of 1972, and its subsequent amendments, forced major changes in pollution prevention, controls, and clean-ups. The Act (1) made it unlawful for any person to discharge pollutants from a point source into navigable waters without obtaining proper permits, (2) financed municipal wastewater-treatment facilities, and (3) manages runoff pollution.

The U.S. Geological Survey (USGS) National Stream Quality Accounting Network (NASQAN) was established in 1973 to provide a national water-quality monitoring network (Ficke and Hawkinson, 1975). The design of the NASQAN program provided systematically collected water-quality data from numerous watersheds throughout the country with diverse climatic, physiographic, and cultural characteristics. The NASQAN program operated 34 water-quality stations in Michigan from 1973 to 1995 (Alexander and others, 1996). Documented information on sample collection, laboratory analysis, and quality assurance for the NASQAN program are presented in the USGS Digital Data Series publication DDS-37 (Alexander and others, 1996).

In 1998, the Water Chemistry Monitoring Project (WCMP) was established by the Michigan Department of Environmental Quality (MDEQ) in partnership with the USGS. The WCMP represented a first step towards improving water quality in Michigan since funding reductions in the mid-1990s resulted in severely restricted monitoring capabilities. The design of WCMP provides systematically collected annual water-chemistry data from stations located within the Great Lakes connecting channels, Saginaw Bay, Grand Traverse Bay, and 31 Great Lakes tributary watersheds. Annual reports, maps, as well as complete WCMP study design, are available upon request from the MDEQ or at www.michigan.gov.

To demonstrate the value of water-quality monitoring, the MDEQ in cooperation with the USGS, initiated a trend detection study to evaluate potential trends in water-quality constituents for selected NASQAN stations in Michigan. A trend in water quality is a change over time in the chemical, physical, or biological characteristics of water. Water quality is constantly changing in response to the changes in physical, chemical, and biological conditions. Changes may occur hourly, daily, seasonally, or over a period of years. Understanding water-quality trends aid in evaluating the effectiveness of water-pollution control efforts and the identification of emerging water-quality concerns. Water mangers and planners use trend information to evaluate the effectiveness of public expenditures for water-quality improvement, to assess progress towards achieving established water-quality goals, and to plan preventive actions. Therefore, long-term water-quality monitoring helps to improve management of Michigan's natural resources by characterizing surface-water quality and identifying changes in quality over time.

Purpose and Scope

The purpose of this report is to identify trends in selected water-quality constituents at nine NASQAN stations. Surface-water quality data collected in Michigan from 1973 to 1995 as part of the NASQAN program were used in this analysis. The report describes (1) the procedure for selection and preparation of data used in the trend analysis, (2) the statistical techniques used to perform the trend tests, and (3) evaluation of major constituent trends for the selected NASQAN stations in Michigan.

Detailed analyses of how these trends relate to watershed characteristics, land-use changes, population distribution, and site hydrology and geology is beyond the scope of this study. However, some supporting information is presented to provide a perspective on the interpretation of detected trends.

Study Sites

Site selection for this study was based on data availability, land-use characteristics, and site priority for the MDEQ, WCMP. A total of nine NASQAN stations (water-quality stations) were chosen with adequate data for trend detection (fig. 1). Station, as well as constituent selection for trend testing, is discussed in detail in the "Methods for the Detection of Trends in Water-quality Data" section of this report. A brief description of each station is given below.

Au Sable River near Au Sable, station number 04137500

The Au Sable River watershed drains an area of 1,932 mi^2 in north-central lower Michigan (fig. 1). The Au Sable River flows from its headwaters to Lake Michigan at Oscoda, Michigan (fig. 2). Designated as a "Natural River" by the MDEQ, the Au Sable River is known for its trout fishing. Most of the main stem of the Au Sable River runs through or adjacent to the Huron National Forest, an area of active canoeing. Dominated by 80-percent forest/woodland land coverage in 1978, a 30-percent reduction in forest/woodland and 27-percent increase in grass/shrub coverage resulted in the Au Sable River watershed by 2001 (table 1).

Clinton River at Mount Clemens, station number 04165500

The Clinton River watershed drains approximately 760 mi^2 in four southern Michigan counties. This drainage basin includes about 40 percent of eastern Oakland County, most of Macomb County, and small portions of southern Lapeer and St. Clair Counties (fig. 2). Clinton River and its tributaries flow through 60 rural, suburban, and urban communities with a total population of more than 1.4 million. The river's headwaters are located in Springfield and Independence Townships, and it flows into Lake St. Clair in Harrison Township (fig. 2).

In 1978, land coverage in the watershed was 36-percent urban with 28-percent agricultural (table 1). The northern portion of the watershed has remained rural with some agricultural land. The southern portion of the watershed has undergone rapid urbanization resulting in 51-percent urban land coverage in 2001 (table 1).

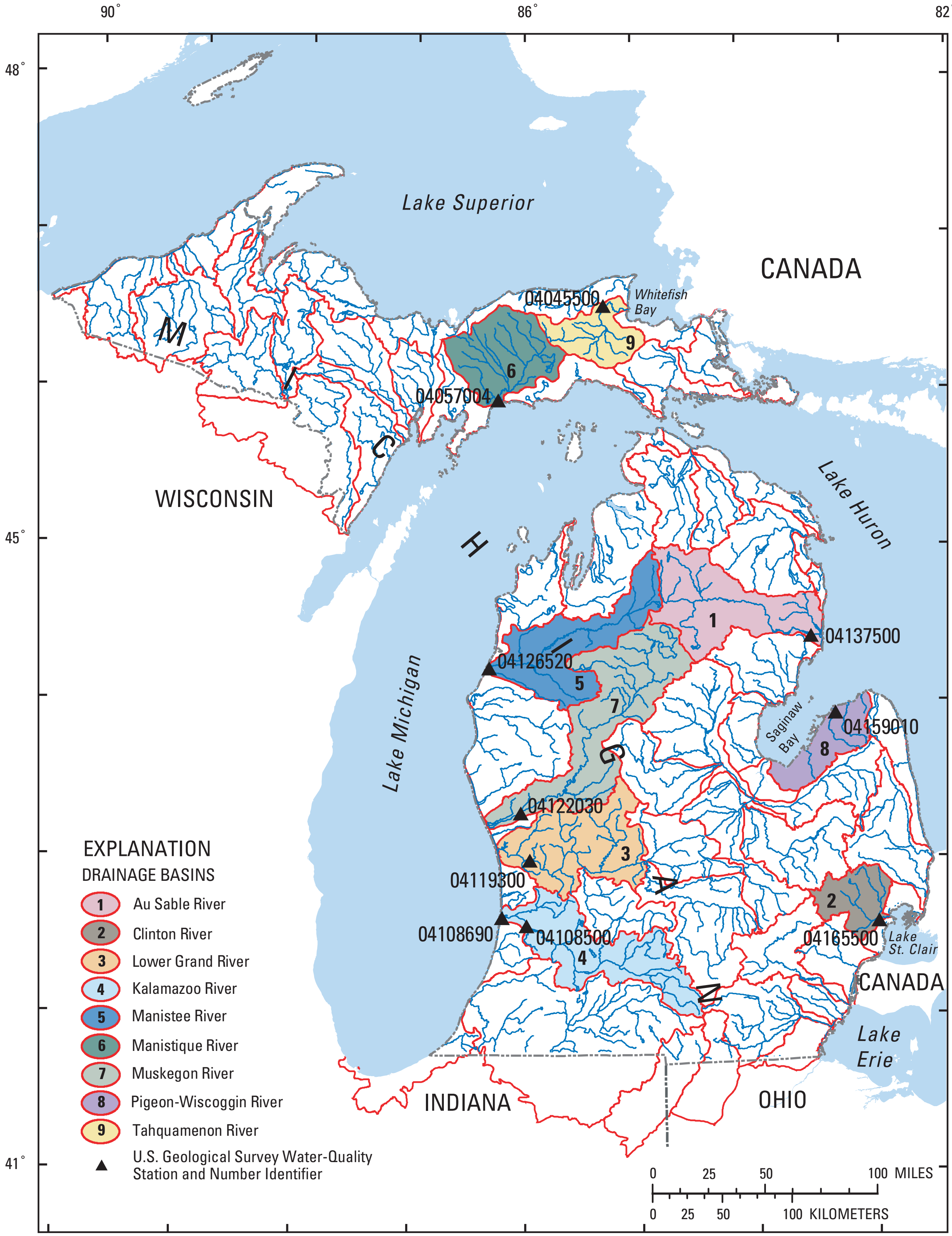
Although historical industrial and municipal discharges were the primary causes of environmental degradation in the Clinton River, and thus, of its designation as an Area of Concern (AOC), ongoing contamination problems are largely of nonpoint source origin (Clinton River Watershed Public Advisory Council and Michigan Department of Environemntal Quality, 1997). There are no major industrial discharges to the river or its tributaries of process water (only noncontact cooling water and stormwater), and most (though not all) municipal facilities have adequate industrial pretreatment programs and have implemented combined sewer-control plans. As such, stormwater runoff as a category is the single greatest source of water-quality degradation in the Clinton River watershed (Clinton River Watershed Public Advisory Council and Michigan Department of Environmental Quality, 1997).

Grand River at Eastmanville, station number 04119300

The Grand River is the longest river in Michigan with the headwaters beginning in Jackson County, Mich., flows north to Lansing, then north-west to Lower Michigan at Grand Haven, and then ultimately discharges into Lake Michigan (figs. 1 and 2). The approximate drainage area of Grand River is 5,572 mi^2. The Grand River watershed is divided into the Upper and Lower Grand River watersheds. The Lower Grand River watershed drains an area of 3,020 mi^2 and contains two urban areas, the cities of Muskegon and Grand Rapids (fig. 2). The dominant land use in the watershed is agriculture; urban land use increased in the watershed from 10 percent in 1978 to 27 percent in 2001 (table 1). Based on the land-cover analysis, forested land decreased from 25 percent to 11 percent from 1978 to 2001 (table 1).

Kalamazoo River near Saugatuck, station number 04108690

Kalamazoo River watershed drains an area of 2,020 mi^2. The Kalamazoo River flows through south-western Michigan discharging into Lake Michigan at Saugatuck, Michigan (figs. 1 and 2). A variety of industries are present along the Kalamazoo River such as cereal production, pharmaceuticals, automotive, and paper mills. Historically, the Kalamazoo River was used for water-intake and discharges for many of these industries. These discharges contributed to PCB, and other industrial waste contamination of the river along with sewage. Portions of the Kalamazoo River are listed as U.S. Environmental Protection Agency (USEPA) Areas of Concern (AOCs) and included in the Superfund National Priorities List (U.S. Environmental Protection Agency, 2005a). The main land coverage of the Kalamazoo River watershed has remained nearly 50-percent agricultural from 1978 to 2001 (table 1). An increase of 12-percent urban land coverage has resulted in the watershed since 1978 (table 1).



Base map from State Boundaries in the United States for BASINS, 1:2,000,000, 1998
Michigan GeoRef Projection

Figure 1. Location of selected water-quality stations used in this study and their respective drainage basins in Michigan.

Base map from State Boundaries in the United States for BASINS, 1:2,000,000, 1998
Michigan GeoRef Projection

Figure 2. Location of lakes, counties, townships, and cities near selected water-quality stations in Michigan.

Table 1. Percent land use of the selected National Stream Quality Accounting Network Stations (NASQAN) in Michigan, 1978 and 2001.

[USGS, U.S. Geological Survey; no., number; mi^2, square miles]

USGS water-quality station name	USGS water-quality station no.	Drainage area (mi^2)	Percent Land Cover in 1978					
			Urban	Agricultural	Grass/ Shrub	Forest/ Woodland	Water	Wetlands
Au Sable River at Au Sable	04137500	1,932	4	4	7	80	2	3
Clinton Rive at Mt. Clemens	04165500	760	36	28	19	11	3	3
Grand River near Eastmanville	04119300	3,020	10	50	10	25	2	3
Kalamazoo River at Saugatuck	04108500	2,020	9	50	8	26	2	5
Manistee River at Manistee	04126520	1,780	2	11	10	73	1	3
Manistique River above Manistique	04057004	1,461	1	1	5	70	5	18
Muskegon River near Bridgeton	04122030	2,723	4	23	10	54	4	5
Pigeon River near Caseville	04159010	136	2	86	2	8	1	1
Tahquamenon River near Paradise	04045500	2,024	1	1	4	79	1	14

USGS water-quality station name	USGS water-quality station no.	Drainage area (mi^2)	Percent Land Cover in 2001					
			Urban	Agricultural	Grass/ Shrub	Forest/ Woodland	Water	Wetlands
Au Sable River at Au Sable	04137500	1,932	8	4	34	51	2	1
Clinton Rive at Mt. Clemens	04165500	760	51	25	13	9	2	0
Grand River near Eastmanville	04119300	3,020	27	47	12	11	1	1
Kalamazoo River at Saugatuck	04108500	2,020	21	52	12	12	2	1
Manistee River at Manistee	04126520	1,780	9	12	32	45	1	1
Manistique River above Manistique	04057004	1,461	3	1	16	60	5	15
Muskegon River near Bridgeton	04122030	2,723	12	22	25	36	4	1
Pigeon River near Caseville	04159010	136	15	77	2	4	1	1
Tahquamenon River near Paradise	04045500	2,024	3	1	9	73	1	13

Manistee River at Manistee, station number 04126520

The Manistee River watershed drains an area of 1,780 mi^2 in North-Western Lower Michigan (fig. 1). The Manistee River flows to Lake Michigan at Manistee, Mich. Numerous logging activities are present in the watershed. There has been a 28-percent decrease in the forest/woodland land coverage in the watershed from 1978 to 2001 (table 1). The watershed contains approximately 10-percent agriculture land during this period. Urban land has increased 7 percent from 1978 to 2001 (table 1).

Manistique River above Manistique, station number 04057004

The Manistique River watershed drains an area of 1,461 mi^2. The Manistique River flows southwest through the central Upper Peninsula, discharging into Lake Michigan at Manistique (figs. 1 and 2). Forest/woodland is the dominant land use in the Manstique River watershed. There has been a 10-percent decrease in forest/woodlands and an 11-percent increase in grass/shrubs from 1978 to 2001 (table 1). Little urbanization has occurred in the watershed. Urban areas have increased from 1 to 3 percent from 1978 to 2001 (table 1).

Muskegon River near Bridgeton, station number 04122030

The Muskegon River watershed is one of the largest watersheds in Michigan (figs. 1 and 2), draining about 2,723 mi^2. Located in north-central Michigan, the Muskegon River flows from its headwaters at Houghton and Higgins Lakes, to Muskegon Lake and eventually out into Lake Michigan (figs. 1 and 2). Forest/woodland covers most of the watershed; however, between 1978 and 2001, there was an 18-percent decrease in the forest/woodland land coverage. Urban areas increased by 8 percent from 1978 to 2001 (table 1).

Pigeon River near Caseville, station number 04159010

Located in the northern thumb area of the Lower Peninsula (figs. 1 and 2), the Pigeon River watershed drains an area of 136 mi^2. The Pigeon River flows northward and discharges into the Saginaw Bay (figs. 1 and 2). Agriculture has remained the dominant land use in the watershed; however, urban land use increased 13 percent from 1978 to 2001 (table 1). Drained by subsurface tiles directly into streams or into surface drains that lead to streams, agricultural practices appreciably affects water quality in the watershed.

Tahquamenon River near Paradise, station number 04045500

The Tahquamenon River watershed drains an area of 2,024 mi^2. The Tahquamenon River flows northeast through the northeastern section of the Upper Peninsula, discharging into Lake Superior White Fish Bay (figs. 1 and 2). The Tahquamenon River watershed is primarily forest/woodland with little urban land (table 1). Wetlands covered 14- and 13-percent of the watershed in 1978 and 2001, respectively. Tannic acid leaching from cedar tree bark in the wetland tributaries to the river has caused a light-brown coloring of the river waters.

METHODS FOR THE DETECTION OF TRENDS IN WATER-QUALITY DATA

The suitability of data for trend testing at an individual water-quality station is affected by the sample-collection schedule, sample-collection methods, analytical methods, and period of record. These factors were evaluated in the station selection process for this study. Besides data screening, the statistical procedure used for trend detection should not be affected by (1) the non-normal distribution of data, (2) seasonal variability, (3) missing values, (4) less than values, (5) variability related to discharge, and (6) outliers. The use of conventional parametric statistical procedures, which could be adversely affected by these factors, could produce errors in water-quality trend analysis. Therefore, the non-parametric uncensored Seasonal Kendall test in the Estimate Trend (ESTREND; Schertz and other, 1991) program was selected for the detection of trends in this study. The Seasonal Kendall test and associated procedures are not affected by non-normal data distribution, large seasonal variability, values below the detection limit, missing values, and outliers. Associated flow-adjustment procedures account for concentration variability related to discharge by defining a relation between concentration and discharge (Hirsch and others, 1981). Hirsch and others (1981) found that non-parametric trend test performed significantly better than its parametric counterparts for data sets with non-normal statistical characteristics.

A brief description of the period of record and data screening, season selection, flow adjustment, and uncensored Seasonal Kendall test is given in the sections below.

Period of Record, Data Screening, and Station Selection

The period of record for each NASQAN station varies (appendix A, tables A-1 to A-9); therefore, the period of record for trend analysis was chosen based on the study period of the NASQAN project for that station. The criteria used to determine which stations to include in the trend analysis for the selected period of record for a particular constituent are as follows (modified from Schertz and others, 1991).

(1) The period of record had to be at least 5 years.
(2) Less than 5 percent of the observations censored at a single reporting limit.
(3) At least 40 percent of the values had to be within the beginning one-fifth and ending one-fifth of the selected period.

On the basis of these criteria, 9 stations with approximately 28 constituents each were chosen for trend analysis. The properties and constituents selected for these nine stations represent the major categories of water-quality data from which the long-term changes and effects could be identified. Some of the selected constituents could not be tested for trends because of insufficient data points.

Season Definition and Selection

Water-quality constituents often vary seasonally. Seasonality may mean a source of variability that prevents the detection of trends (Schertz and others, 1991). A parametric approach for removal of the effects of seasonality in water-quality data is to include a cyclical function as an explanatory variable in a regression equation that relates water-quality data to time (Schertz and Hirsch, 1985).

The ESTREND program contains an automated procedure for determining the best seasonal choice for each constituent for a particular station (Schertz and others, 1991). The program combines the suggested season definition for the beginning 20 percent and ending 20 percent of the record and compares it to the middle 60 percent of the record. The selection procedure emphasizes the beginning and ending parts of the water-quality record; this emphasis ensures that the data adequately span the period of interest. Data gaps in the middle years of the record have less effect on the performance of the statistical procedures than gaps at the beginning or end of the record (Schertz and others, 1991). In case of multiple data values within season, the value that is closest to the midpoint of the season paired with the discharge (where applicable) is selected by the program to represent the season (Schertz and others, 1991).

In this study, 2, 3, 4, 6, or 12 possible seasons per year were present. The months included in each seasonal definition are shown in table 2. The season definition recommended for the beginning and ending parts of the record were used to define season for each station and constituent. The sampling frequency of a constituent may vary from station to station, and, consequently, the season definition for a constituent may vary from station to station.

Table 2. Season definition based on the ESTREND program used in this study.

Number of seasons per year	Months included
2	April-September; October-March
3	March-June; July-October; November-February
4	January-March; April-June; July-September; October-December
6	January-February; March-April; May-June; July-August; September-October; November-December
12	January; February; March; April; May; June; July; August; September; October; November; December

Flow Adjustment

Typically, the concentration of a given constituent is related to streamflow (discharge). The concentration of many dissolved water-quality constituents generally decreases as discharge increases because of dilution. On the other hand, the concentration of suspended sediments increases with an increase in discharge because of the transport of particulates by runoff. Therefore, a large part of the variance of constituent concentrations may be a result of the variation in the associated discharges (Schertz and others, 1991). Some constituents may show a combination of both effects. The removal of streamflow as a source of variance from the data makes trend-testing techniques more powerful by increasing the probability of detecting a trend, if present, and decreases the chances of detecting trends when it is only an artifact of trend in the associated discharges.

A flow-adjustment procedure in the ESTREND program discussed by Schertz and others (1991) was used for this study. The ESTREND program removes the effects of discharge on constituent concentrations by computing a time series of flow-adjusted concentrations (FAC) and testing this time series for trend. In statistical terms, the FAC is a residual and is defined as the actual constituent concentration minus the predicted concentration. The predicted concentration is computed from an equation describing the discharge-constituent relation (Schertz and others, 1991). The ESTREND package contains an automated procedure that selects the regression model “best fit” from 15 different models. The models are both linear and non-linear, and the model selected is based upon the residuals having the lowest variation. In cases where the regression models could not be used because a good fit was not possible (regression assumptions were violated), the LOWESS (locally weighted regression smoothing function) smoothing function was used to improve the fit.

Uncensored Seasonal Kendall Test

The statistical procedure used to detect trends for this study is the uncensored Seasonal Kendall test in the ESTREND program. The Seasonal Kendall test is a non-parametric test for monotonic trend in water quality (Hirsch and others, 1981). The magnitudes of the data in favor of the relative values or ranks of the data are ignored in the test, and the effects of seasonal variability in water-quality data are removed by restricting comparisons between pairs of data values to those values that are from the same season. The test makes all possible pairwise comparisons of a time-ordered set of water-quality values. If a later value (in time) is larger, a plus is recorded; if a later value is smaller, a minus is recorded. The test statistic is computed as the difference between the total number of pluses and the total number of minuses in the record. As the deviation of the test statistic from zero becomes larger, the likelihood of trend in the data is greater. For each water-quality record, a measure of the likelihood of trend, the p-value, is obtained from the standard normal distribution. The censored values are assigned one-half of their reporting limit. In the uncensored Seasonal Kendall test, water-quality records with more than about 5 percent of the observations censored at a single reporting limit were analyzed.

A trend in this study is defined as a one-directional (monotonic) change over time. A trend is considered to be statistically significant if the attained significance level of the trend test for a constituent is less than or equal to 0.05. The attained significance level, or p-value, is the probability that a detected trend resulted from a chance arrangement of the data rather than from an actual change in constituent concentration.

TREND RESULTS IN SURFACE-WATER QUALITY

Statistically significant water-quality trends for 9 NASQAN stations, each with approximately 28 constituents, are summarized in tables 3-8. In this study, a negative trend indicates a decrease in concentration of a particular constituent, which generally mean an improvement in water quality; whereas a positive trend indicates an increase in concentration and a possible degradation in water quality. Significant trends detected during the study only include constituents with flow-adjusted concentration. Details of trend results for each station are provided in appendix A at the back of the report. These results include period of record, number of observations, maximum values, minimum values, median, percentiles, and p-values.

Physical Properties

Trends were analyzed for three physical properties: temperature, specific conductance, and turbidity. Temperature is important for maintaining dissolved oxygen concentrations necessary for normal growth of aquatic plants and animals. Specific conductance is an indirect measure of the amount of dissolved matter in water. In general, the higher the concentration of ions, the greater the conductivity of the solution. Turbidity is a measure of the clarity of water, and is affected by suspended particles, dissolved matter, biological material, and color.

The only significant trend detected in physical properties is for specific conductance at the Pigeon River near Caseville station (fig. 1). No trends were detected in temperature or turbidity at any of the nine study stations.

Major Ions

Major dissolved ions and related constituents analyzed for trend in this study include dissolved calcium, magnesium, potassium, sodium, chloride, sulfate, fluoride, and silica. Trend results for major ions are shown in table 4.

The most numerous trends detected in major ions were in dissolved sodium and chloride concentrations. A total of three positive and two negative trends were detected in dissolved sodium concentrations, and three negative and two positive trends were detected in dissolved chloride concentrations. Positive trends in sodium concentration were detected at the Grand River at Eastmanville, Manistique River above Manistique, and the Tahquamenon River near Paradise stations; and negative trends were detected at the Manistee River at Manistee and Pigeon River near Caseville stations. Similarly, a positive trend in chloride concentrations was detected at the Au Sable River near Au Sable and the

Table 3. Summary statistics and trend results for physical properties at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04159010 (Pigeon River near Caseville); no., number; Max., maximum value; Min., minimum value; μS/cm, microsiemens per centimeter; -, negative trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Mean value	Percentile Values					p-value	Trend
					Max.	75	Median	25	Min.		
04159010	Specific Conductance (μS/cm)	1978-93	86	807	1230	902	800	724	214	0.024	-

Table 4. Summary statistics and trend results for major dissolved ions at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04137500 (Au Sable River near Au Sable), 04165500 (Clinton River at Mount Clemens), 04119300 (Grand River at Eastmanville), 04126520 (Manistee River at Manistee), 04057004 (Manistique River above Manistique), 04122030 (Muskegon River near Bridgeton), 04159010 (Pigeon River near Caseville); no., number; Max., maximum value; Min., minimum value; mg/L, milligrams per liter; -, negative trend; +, positive trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Mean value	Percentile Values					p-value	Trend
					Max.	75	Median	25	Min.		
04137500	Calcium (mg/L)	1978-94	114	43	49	45	43	41	33	0.024	+
04137500	Potassium (mg/L)	1978-94	114	0.6	0.9	0.7	0.6	0.5	0.1	.017	+
04137500	Chloride (mg/L)	1978-94	114	5.4	12	5.7	5.2	4.8	3.9	.008	+
04137500	Silica (mg/L)	1978-94	115	8.4	11	9.1	8.6	7.7	5.7	.050	-
04165500	Calcium (mg/L)	1974-95	139	70	90	76	70	65	45	.001	+
04165500	Magnesium (mg/L)	1974-95	139	20	26	22	21	19	12	.007	+
04165500	Chloride (mg/L)	1973-95	141	99	270	120	92	81	40	.006	+
04165500	Sulfate (mg/L)	1973-95	141	58	89	66	58	51	32	.003	-
04119300	Calcium (mg/L)	1979-94	97	71	91	79	72	63	43	.038	+
04119300	Sodium (mg/L)	1979-97	97	3.0	5.3	3.3	2.9	2.6	2.1	.035	+
04126520	Sodium (mg/L)	1974-94	157	13	24	15	12	9.7	5.8	.001	-
04126520	Potassium (mg/L)	1974-94	157	1.3	3.3	1.5	1.2	1.1	.5	.013	-
04126520	Chloride (mg/L)	1973-94	159	40	130	47	37	28	4.3	.016	-
04057004	Sodium (mg/L)	1975-86	100	1.3	1.9	1.5	1.3	1.2	.7	.001	+
04122030	Chloride (mg/L)	1973-90	124	17	27	20	18	16	2.4	.045	-
04122030	Fluoride (mg/L)	1974-90	123	.1	.4	.1	.1	.1	.1	.028	-
04159010	Sodium (mg/L)	1978-93	88	17	46	21	17	13	3.1	.046	-
04159010	Magnesium (mg/L)	1978-93	88	30	44	34	31	27	5.5	.026	-
04159010	Chloride (mg/L)	1978-93	86	49	85	56	47	41	10	.029	-
04159010	Sulfate (mg/L)	1978-93	86	109	200	130	115	88	25	.001	-
04159010	Fluoride (mg/L)	1978-93	88	.2	.4	.3	.2	.2	.1	.037	-
04045500	Sodium (mg/L)	1974-93	133	1.7	3.2	1.9	1.7	1.4	.7	.000	+
04045500	Potassium (mg/L)	1974-93	133	.7	1.1	.8	.7	.6	.3	.049	-

Clinton River at Mount Clemens; and negative trends were detected at the Manistee River at Manistee, Muskegon River near Bridgeton, and Pigeon River near Caseville stations (fig. 1).

Significant negative trends in sulfate concentration were detected at the Clinton River at Mount Clemens, Grand River at Eastmanville, and Pigeon River near Caseville stations. No significant trend in sulfate concentration was detected at the remaining six stations. Sulfate occurs naturally in water. Sulfate enters water from soils rock formations. Sulfate concentrations may be increased by municipal and industrial waste discharges and atmospheric deposition. Health concerns regarding sulfate in drinking water have been raised because of reports that diarrhea may be associated with the ingestion of water containing high sulfate concentrations (U.S. Environmental Protection Agency, 2005b).

Trend in concentrations of other major ions, such as calcium, magnesium, potassium, and silica, are detected in most of the study stations. Positive trend in calcium concentrations are detected at three out of nine stations with no negative trend at the remaining six stations. The stations with positive trends include the Au Sable River near Au Sable, Clinton River at Mount Clemens, and Grand River at Eastmanville.

A single positive and a single negative trend in magnesium concentration were detected at Clinton River at Mount Clemens and the Pigeon River near Caseville stations, respectively. One positive (Au Sable River near Au Sable) and two negative trends (Manistee River at Manistee and Tahquamenon River near Paradise) in potassium concentration were detected. A negative trend in silica concentration was detected at the Au Sable River near Au Sable; this trend is the only discernable trend for silica. Calcium, magnesium, and silica are important components of common rock types in Michigan.

Significant negative trend in fluoride concentration were detected at the Muskegon River near Bridgeton and Pigeon River near Caseville. The remaining seven stations showed no trends in fluoride concentration.

Nutrients

Nitrogen and phosphorus are important component of plants and animals. Waste matter produced by living organism, and material derived from their decomposition, are major sources of these elements in freshwater systems. Natural organic material, domestic industrial wastewater, agricultural and residential fertilizer, animal wastes, and combustion by products in the atmosphere contribute nitrogen and phosphorus to freshwater. A common nitrogen forms in streams include organic nitrogen, ammonia nitrogen, nitrate, and nitrite nitrogen. Common phosphorus form in the environment includes phosphate. Nitrogen and phosphorus transformations from one form to another can occur as a result of biological and chemical processes.

The station with the largest number of significant negative trends in nitrogen compounds was the Clinton River at Mount Clemens. Decreasing concentration of nitrogen compounds at this station include total ammonia, total ammonia plus organic nitrogen, total nitrogen, total organic nitrogen, and dissolved nitrite plus nitrate (mg/L as nitrogen) (table 5). Pigeon River near Caseville was the only other station with a negative trend in nitrogen compounds, such as total ammonia.

Table 5. Summary statistics and trend results for nutrients at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04165500 (Clinton River at Mount Clemens), 04108690 (Kalamazoo River near Saugatuck), 04122030 (Muskegon River near Bridgeton), 04159010 (Pigeon River near Caseville); no., number; Max., maximum value; Min., minimum value; mg/L, milligrams per liter; -, negative trend; +, positive trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Mean value	Percentile Values					p-value	Trend
					Max.	75	Median	25	Min.		
04165500	Total Ammonia (mg/L as nitrogen)	1977-92	70	0.17	0.73	0.19	0.14	0.1	0.01	0.008	-
04165500	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-95	136	1.1	4.9	1.2	1	.8	.19	.007	-
04165500	Total Nitrogen (mg/L)	1974-95	135	3.8	12	4.6	3.6	3	.75	.004	-
04165500	Total Organic Nitrogen (mg/L)	1978-95	99	.89	4.8	1.0	.82	.61	.35	.482	-
04165500	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-95	82	2.6	5	3	2.4	1.9	.25	.004	-
04165500	Total Phosphorus (mg/L)	1974-95	138	.21	.76	.26	.175	.12	.01	.001	-
04108690	Total Nitrogen (mg/L)	1974-86	106	1.8	3	2	1.8	1.6	.83	.022	+
04108690	Total Nitrite + Nitrate (mg/L as nitrogen)	1973-81	90	.78	2	.98	.82	.55	.01	.030	+
04122030	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-90	119	.54	2.9	.6	.47	.37	.1	.001	+
04122030	Total Nitrogen (mg/L)	1974-90	115	.82	3.3	.93	.74	.61	.26	.001	+
04122030	Total Organic Nitrogen (mg/L)	1977-90	76	.58	2.9	.64	.48	.38	.06	.003	+
04159010	Total Ammonia (mg/L as nitrogen)	1978-92	66	.11	1.1	.14	.07	.04	.01	.043	-

Significant positive trends (increasing concentrations) in nitrogen compounds were detected at the Kalamazoo River near Saugatuck and at the Muskegon River near Bridgeton. The Kalamazoo River near Saugatuck station showed positive trends in concentrations of total nitrogen and total nitrite plus nitrate (mg/L as nitrogen). The Muskegon River near Bridgeton station showed positive trends in concentrations of total ammonia plus organic nitrogen, total nitrogen, and total organic nitrogen.

Phosphorus data for most of the selected stations have 20 percent of the concentration data reported at less than the analytical detection limit with many stations having more than one censoring level. This condition is a limiting factor for detecting trends in surface-water quality constituents using the uncensored Seasonal Kendall test, and, therefore, the phosphorus data were not tested for trend. However, scatter-plot analyses of phosphorus data indicate decreasing phosphorus concentration for most of the study stations. The Clinton River at Mt. Clemens was the only station with a significant negative trend in total phosphorus concentration. The Muskegon River near Bridgeton also showed decreasing total phosphorus concentrations, but this cannot be considered a significant trend because the p-value is 0.07 (appendix A, table A-7).

Bacteria

Fecal coliform bacteria and fecal streptococci bacteria are groups of bacteria commonly associated with fecal contamination. Historically, the concentration of these organisms in the environment was used to indicate fecal contamination of humans or animals. The presence of these organisms indicated a potential health risk associated with pathogenic bacteria that might also be present in the fecal waste. During the time period of the NASQAN sampling, fecal coliforms and fecal streptococci were also collected and measured. The methods of analysis for these two groups changed in 1976. For the trend analysis study, only those samples collected after October 1976 were included. However, for sites in which there were pre-1976 data, all data were combined and called “total fecal coliforms” or “total fecal streptococci”. In 1976, the USEPA recommended fecal coliform bacteria concentrations not to exceed a geometric mean of 200 colonies per 100 ml of water. For recreational water, the USEPA in 1986 revised their recommendation for measuring water quality to include the use of E. coli (a member of the fecal coliform group) and/or enterococci (a sub-group of the fecal streptococci), and discouraged the use of fecal coliform and fecal streptococci (Environmental Protection Agency, 1986).

Bacteria samples analyzed for trends in this study include fecal coliform, total fecal coliform, fecal streptococci, and total fecal streptococci. Significant trends were detected at six sites for bacteria; these results are shown in table 6.

Negative trends in fecal coliform, total fecal coliform, fecal streptococci tests, and total fecal streptococci were detected at the Manistee River at Manistee. Positive trends in fecal coliform and total fecal coliform were detected at the Tahquamenon River near Paradise station. The remaining stations showed no significant trends in bacteria tests.

Table 6. Summary statistics and trend results for bacteria at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04126520 (Manistee River at Manistee), 04045500 (Tahquamenon River near Paradise); no., number; Max., maximum value; Min., minimum value; cfu/100 ml, colony forming units per hundred milliliters of the sample; -, negative trend; +, positive trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Percentile Values					p-value	Trend
				Max.	75	Median	25	Min.		
04126520	Fecal Coliform (cfu/100ml)	1976-94	125	1200	260	130	43	1	0.000	-
04126520	Total Fecal Coliform (cfu/100ml)	1976-94	147	1200	245	120	46.5	1	.001	-
04126520	Fecal Streptococci (cfu/100ml)	1976-94	127	1000	85	51	21	5	.003	-
04126520	Total Streptococci (cfu/100ml)	1974-94	156	3000	81.5	48	20	0	.040	-
04045500	Fecal Coliform (cfu/100ml)	1976-93	104	280	22	7.5	4	1	.034	+
04045500	Total Fecal Coliform (cfu/100ml)	1974-93	127	280	14	6	3	1	.029	+

pH and alkalinity

pH is a measure of the activity of the hydrogen ion (H+) and is represented by the negative logarithm to the base 10 (Snoeyink and others, 1998). Many precipitation, dissolution, oxidation-reduction and complexation reactions are determined by the value of pH in aqueous solutions. pH is affected by temperature; by reactions of dissolved carbon dioxide with water; by reactions in which solid materials are dissolved, precipitated, or oxidized; and by the photosynthetic activity of aquatic organisms, which take up dissolved carbon dioxide during the day and release it at night.

Significant positive trend in pH levels were detected at six out of nine stations on all the major rivers in Michigan. No negative trends in pH levels were detected at any stations. The stations showing increases in pH levels are Clinton River at Mount Clemens (04165500), Grand River at Eastmanville (04119300), Manistique River above Manistique (04057004), Manistee River at Manistee (041265200, Pigeon River near Caseville (04159010), and Tahquamenon River near Paradise (04045500). The positive trend in all the stations is within a standard unit pH range. The tendency of natural water to remain within a relatively narrow band of hydrogen-ion activity is due to the presence of buffers that resist pH changes. In a freshwater system, the buffering is related to the dissolved inorganic carbon species: carbon dioxide (CO_2), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{-2}), which scavenges the hydrogen and hydroxide ions.

Alkalinity is a measure of the capacity of water to neutralize strong acid (Snoeyink and others, 1998). In natural water, this capacity is attributed to bases, such as carbonates, bicarbonates and hydroxide, as well as to species often present in low concentrations such as silicates, borates, and organic bases. Concentrations of total bicarbonate, total hardness (mg/L as calcium carbonate), and total non-carbonate hardness (mg/L as calcium carbonate) were analyzed for trends.

Positive trend in total hardness (mg/L as calcium carbonate) were detected at the Clinton River at Mount Clemens and the Grand River at Eastmanville (table 7). The rest of the study stations showed no-significant trend in alkalinity concentration.

Suspended Sediments

Suspended sediment refers to those soil particles that stay in suspension for some extended period of time as a result of turbulence in the fluid flow. These soil particles are either detached during a rainfall-runoff event, which ultimately ends up in rivers and streams, which are brought in suspension by high velocity flow in the alluvial section of the river. Suspended sediment can be transported downstream many miles; the distance is dependent on the sediment transport capacity of the flow. Suspended-sediment concentrations and loads were analyzed for all the nine study stations. The only positive trend (increasing concentrations) in suspended-sediment concentration was detected at Manistee River at Manistee. No significant trends were detected at the remaining eight stations.

Table 7. Summary statistics and trend results for pH and alkalinity at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04165500 (Clinton River at Mount Clemens), 04119300 (Grand River at Eastmanville), 04126520 (Manistee River at Manistee), 04057004 (Manistique River above Manistique), 04159010 (Pigeon River near Caseville), 04045500 (Tahquamenon River near Paradise); no., number; mg/L as CaCO3, milligrams per liter as calcium carbonate; Max., maximum value; Min., minimum value; +, positive trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Mean value	Percentile Values					p-value	Trend
					Max.	75	Median	25	Min.		
04165500	pH (standard units)	1973-95	141	8.0	8.4	8.2	8	7	7.2	0.001	+
04165500	Total Hardness (mg/L as $CaCO_3$)	1974-95	99	72	120	84	74	64	37	.001	+
04119300	pH (standard units)	1979-94	97	8.2	8.8	8.4	8.2	8	7.1	.00027	+
04119300	Total Hardness (mg/L as $CaCO_3$)	1979-94	97	264	330	290	270	250	160	.035	+
04126520	pH (standard units)	1973-94	160	7.9	8.3	8.1	8	7.8	7	.042	+
04057004	pH (standard units)	1975-86	102	7.6	8.4	7.8	7	7.4	6.6	.005	+
04159010	pH (standard units)	1978-93	87	8.0	8.6	8.2	8.0	7.8	7.3	.039	+
04045500	pH (standard units)	1974-93	134	7.4	8.1	7.6	7.3	7.2	6.5	.010	+

Table 8. Summary statistics and trend results for suspended sediment at selected National Stream Quality Accounting Network stations in Michigan.

[USGS, U.S. Geological Survey; 04126520 (Manistee River at Manistee); no., number; Max., maximum value; Min., minimum value; mg/L, milligrams per liter; +, positive trend]

USGS water-quality station no.	Constituents and units	Period of record	No. of observations	Mean value	Percentile Values					p-value	Trend
					Max.	75	Median	25	Min.		
04126520	Suspended Sediment (mg/L)	1974-94	140	9	60	10	8	5	1	0.049	+

MAGNITUDE OF THE DETECTED TRENDS IN SURFACE-WATER QUALITY

The magnitude of the trend was estimated by the Thiel/Sen Slope estimator, described by Smith and others (1982). These slopes, expressed as a change in constituent concentration units per year, are ranked, and the median value is chosen to indicate the magnitude of the trend. Although the calculated trend slope indicates the general relation between values near the beginning and end of the record, this slope does not represent all the data variation within the selected period of record. The actual data may change linearly, may change in steps, or may reverse during portions of the selected period. However, the Thiel/Sen slope estimator provides a means of assessing the change in concentration over time based on the trend tests (figs. 3-15).

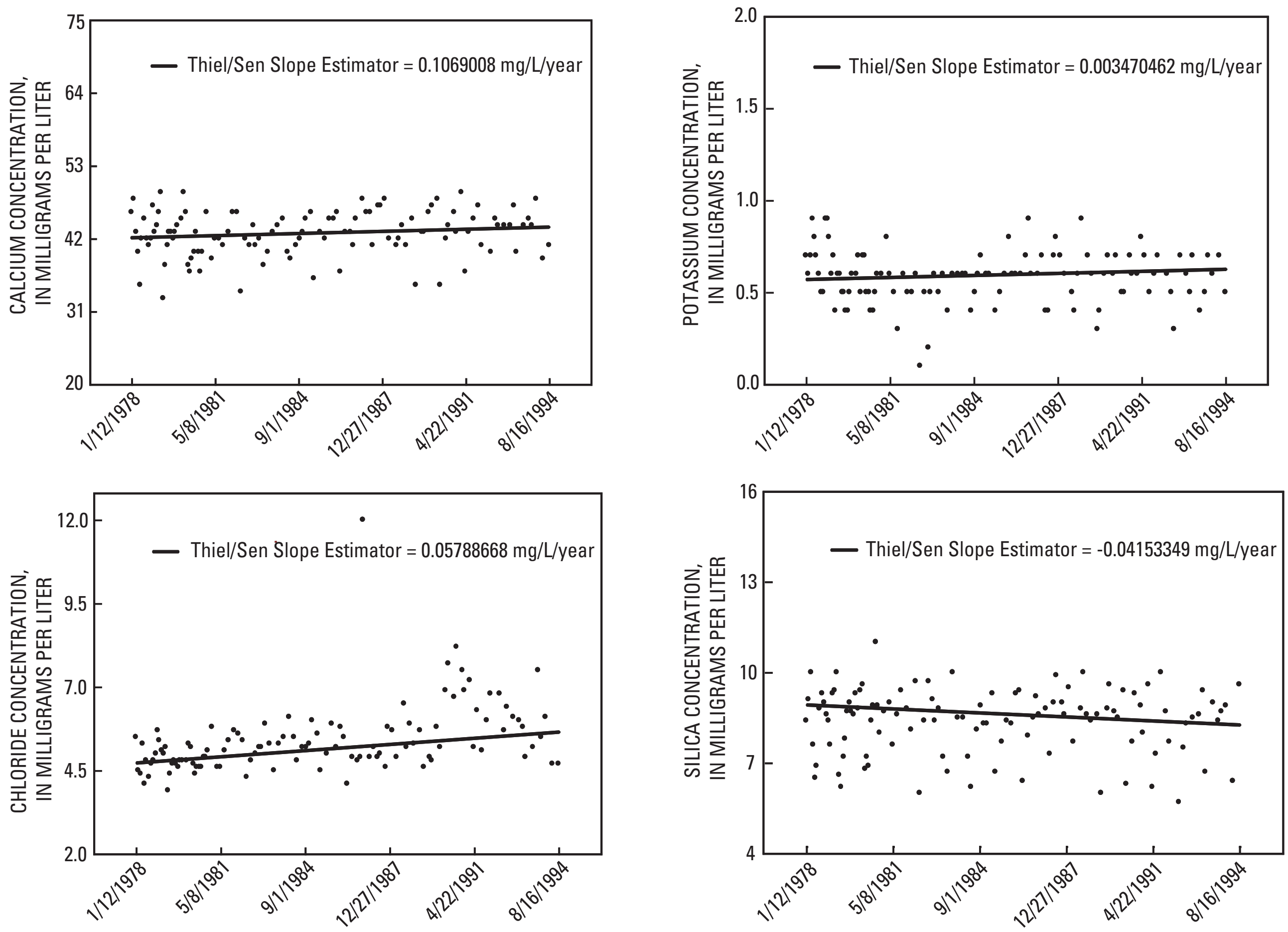


Figure 3. Significant trends detected in water-quality constituents at the Au Sable River near Au Sable (014137500), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

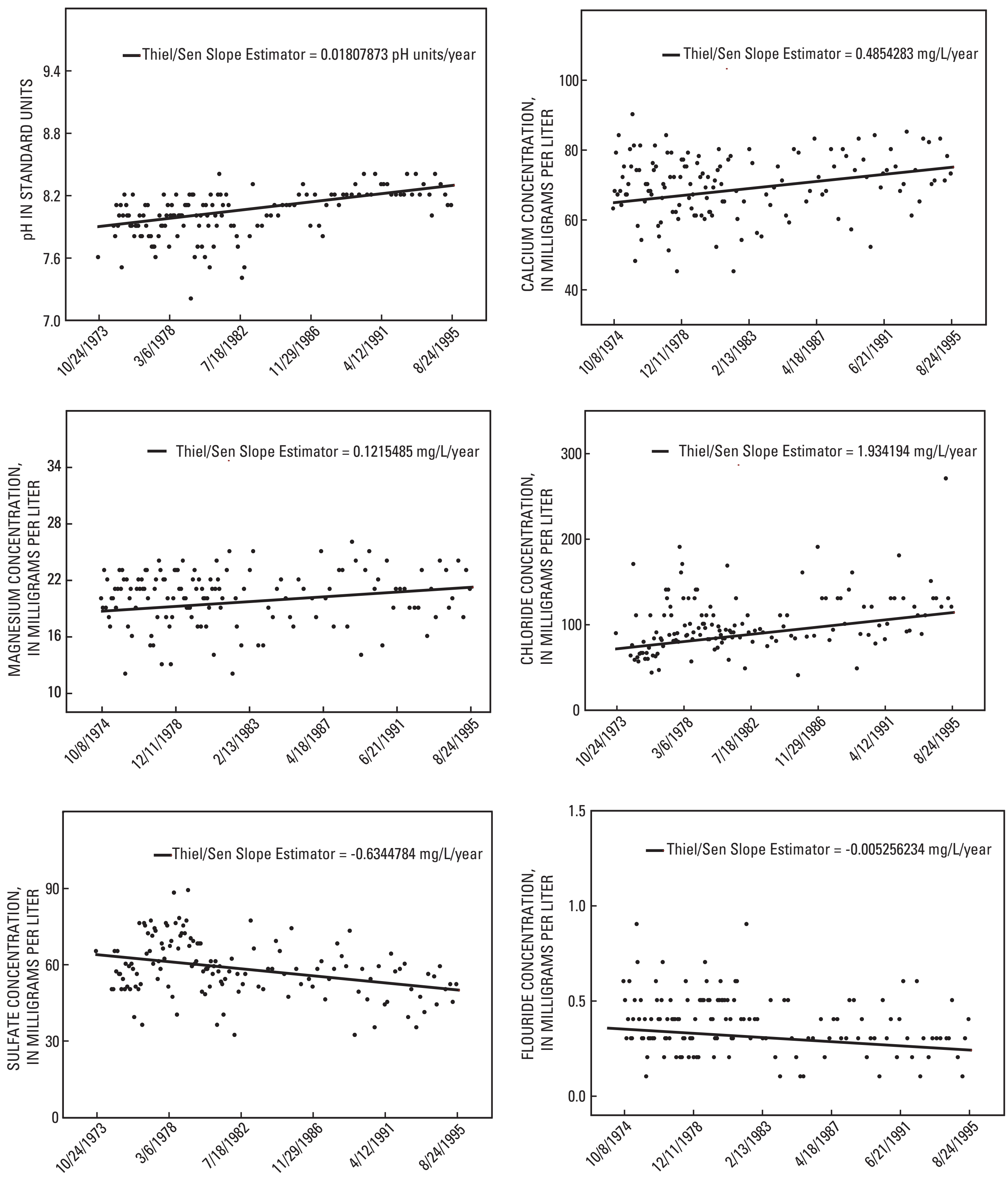


Figure 4. Significant trends detected in water-quality constituents at the Clinton River at Mount Clemens (04165500), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

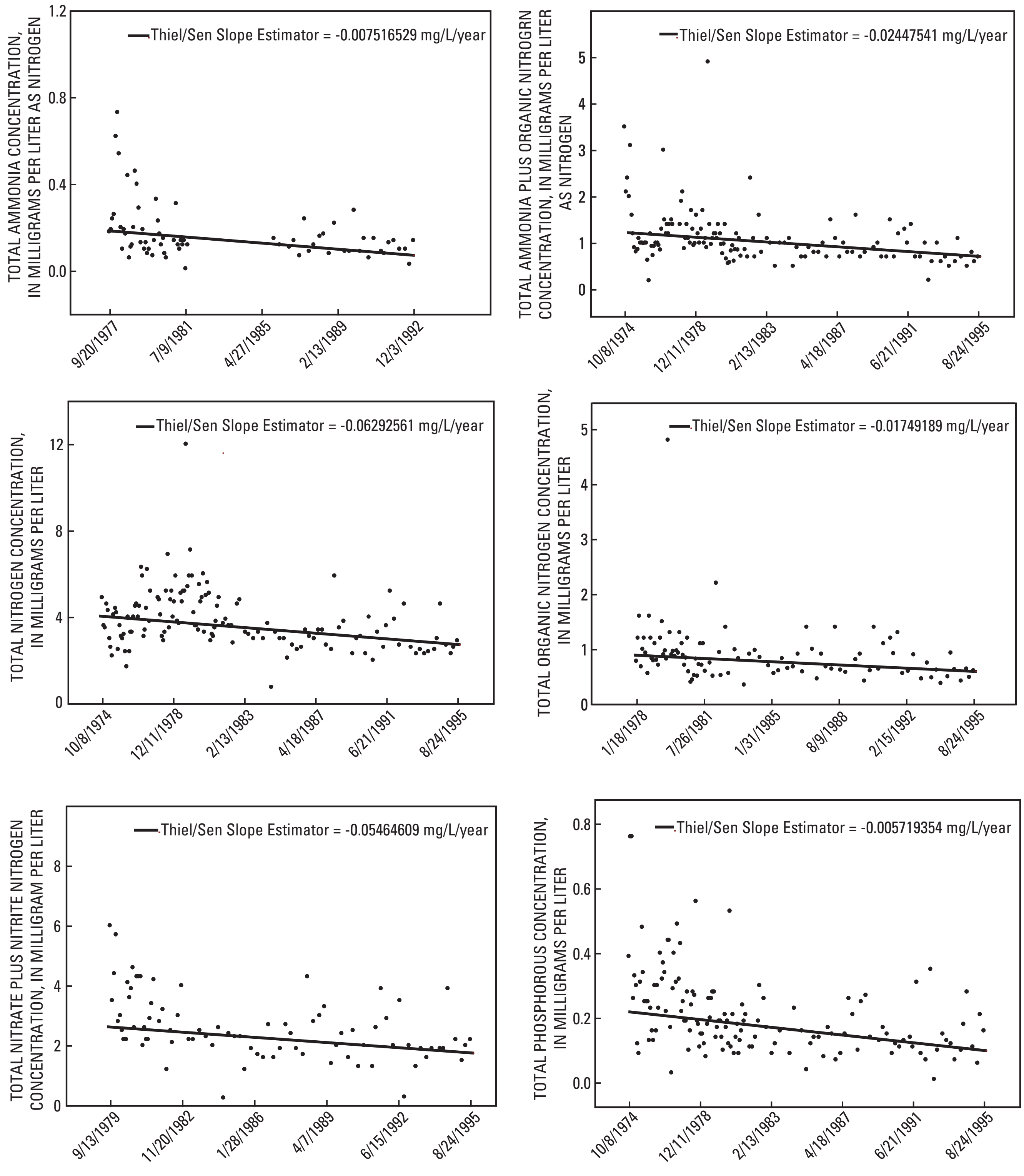


Figure 5. Significant trends detected in water-quality constituents at the Clinton River at Mount Clemens (04135500), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

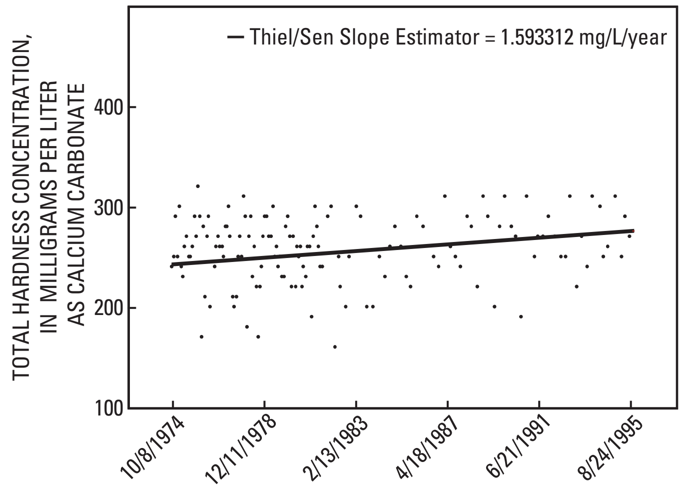


Figure 6. Significant trends detected in water-quality constituents at the Clinton River at Mount Clemens (04135500), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

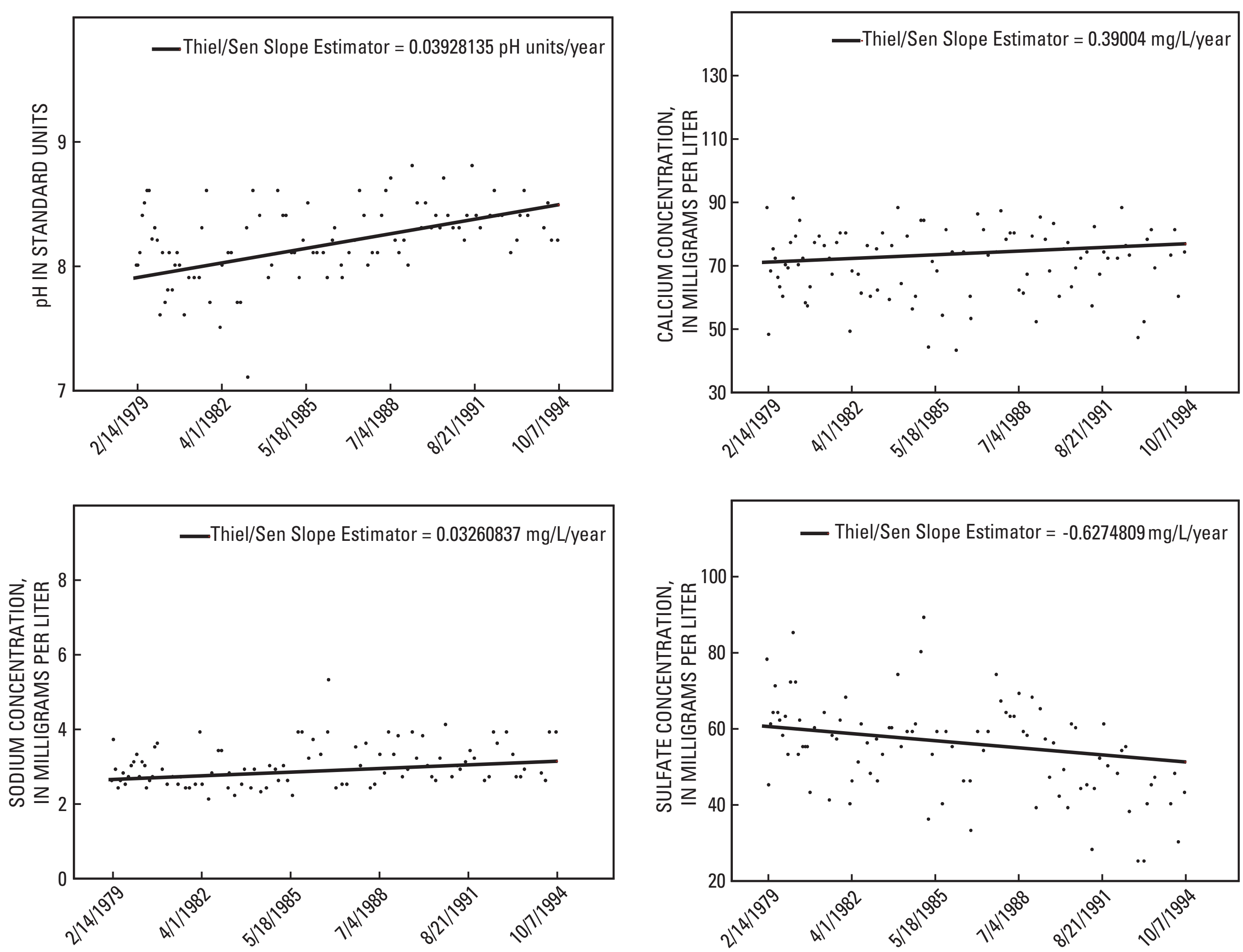


Figure 7. Significant trends detected in water-quality constituents at the Grand River at Eastmanville (04119300), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

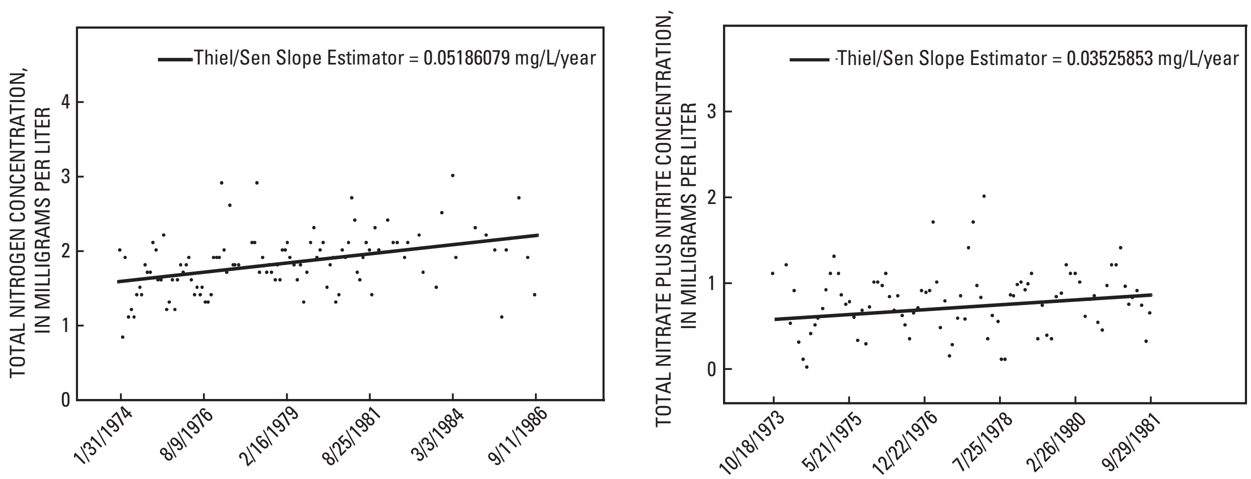


Figure 8. Significant trends detected in water-quality constituents at the Kalamazoo River near Saugatuck (04108690), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

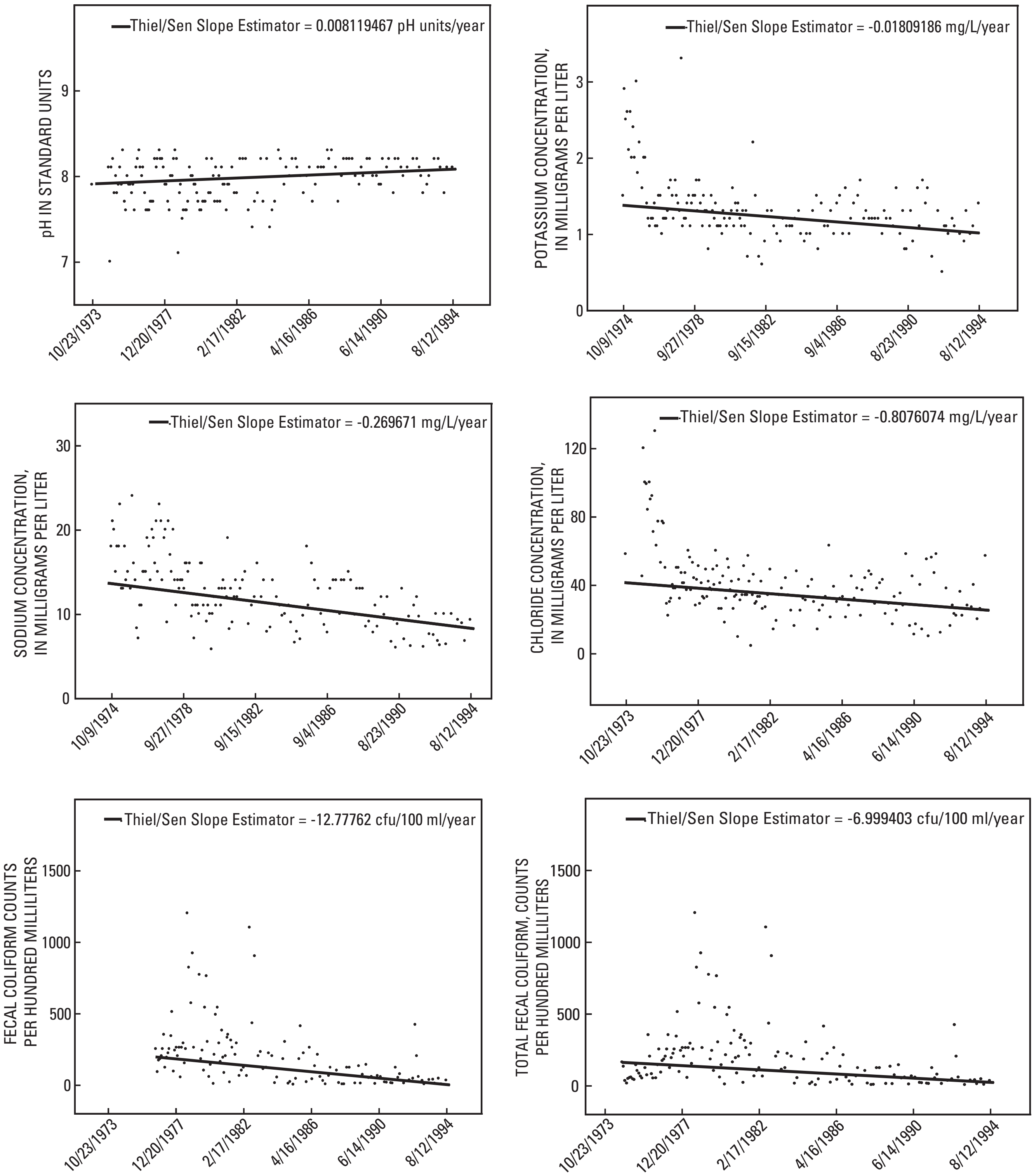


Figure 9. Significant trends detected in water-quality constituents at the Manistee River at Manistee (04126520), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year); colonies forming units per hundred milliliters of the sample per year (cfu/100ml/year)).

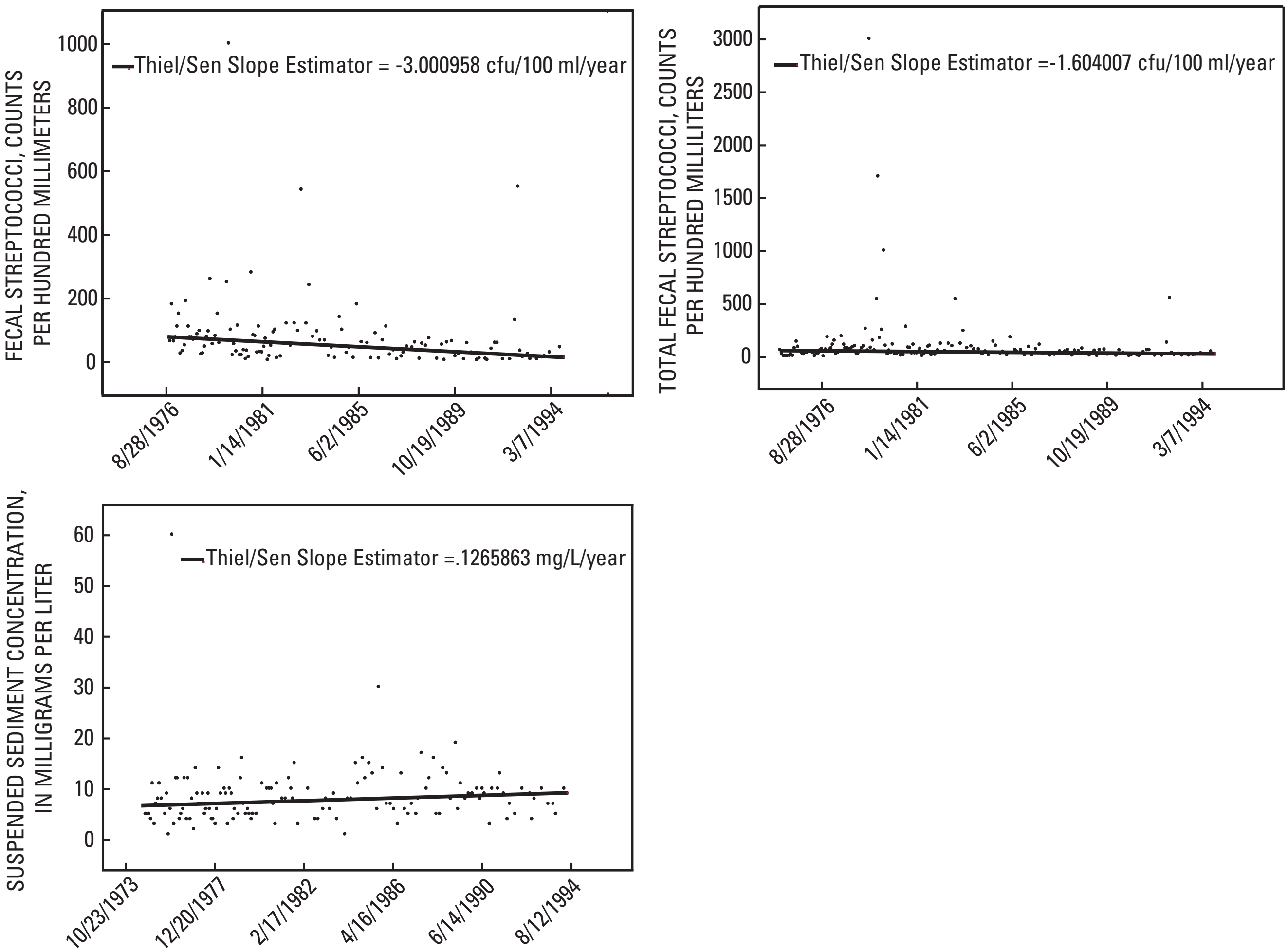


Figure 10. Significant trends detected in water-quality constituents at the Manistee River at Manistee (04126520), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year); colonies forming units per hundred milliliters of the sample per year (cfu/100ml/year)).

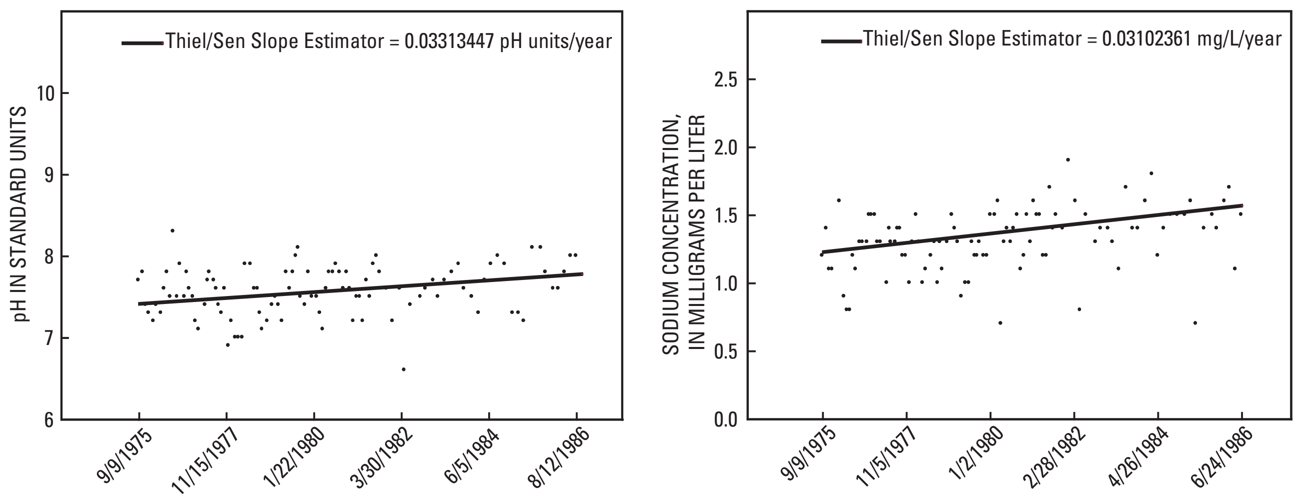


Figure 11. Significant trends detected in water-quality constituents at the Manistique River above Manistique (04157004), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

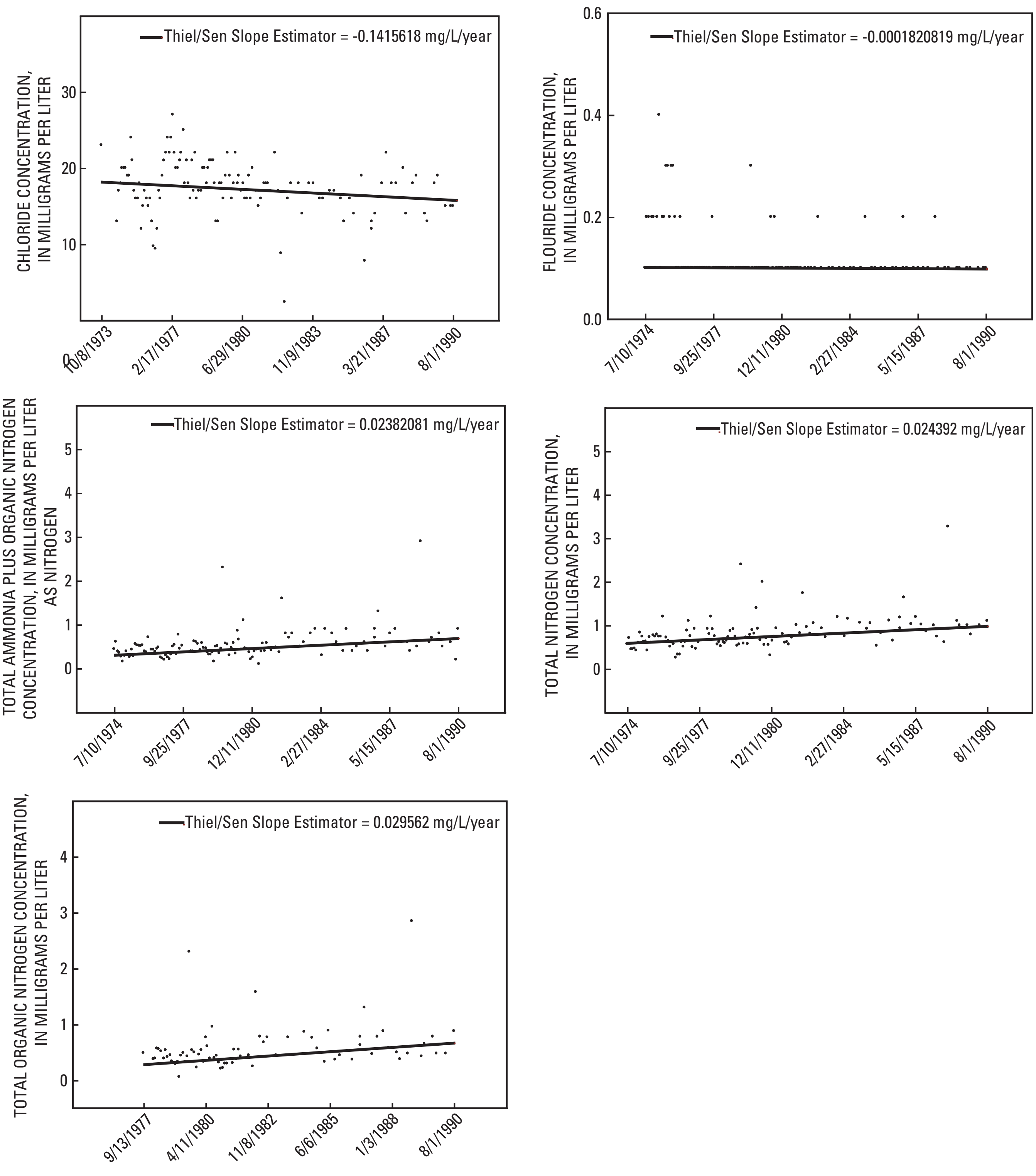


Figure 12. Significant trends detected in water-quality constituents at the Muskegon River near Bridgeton (04122030), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

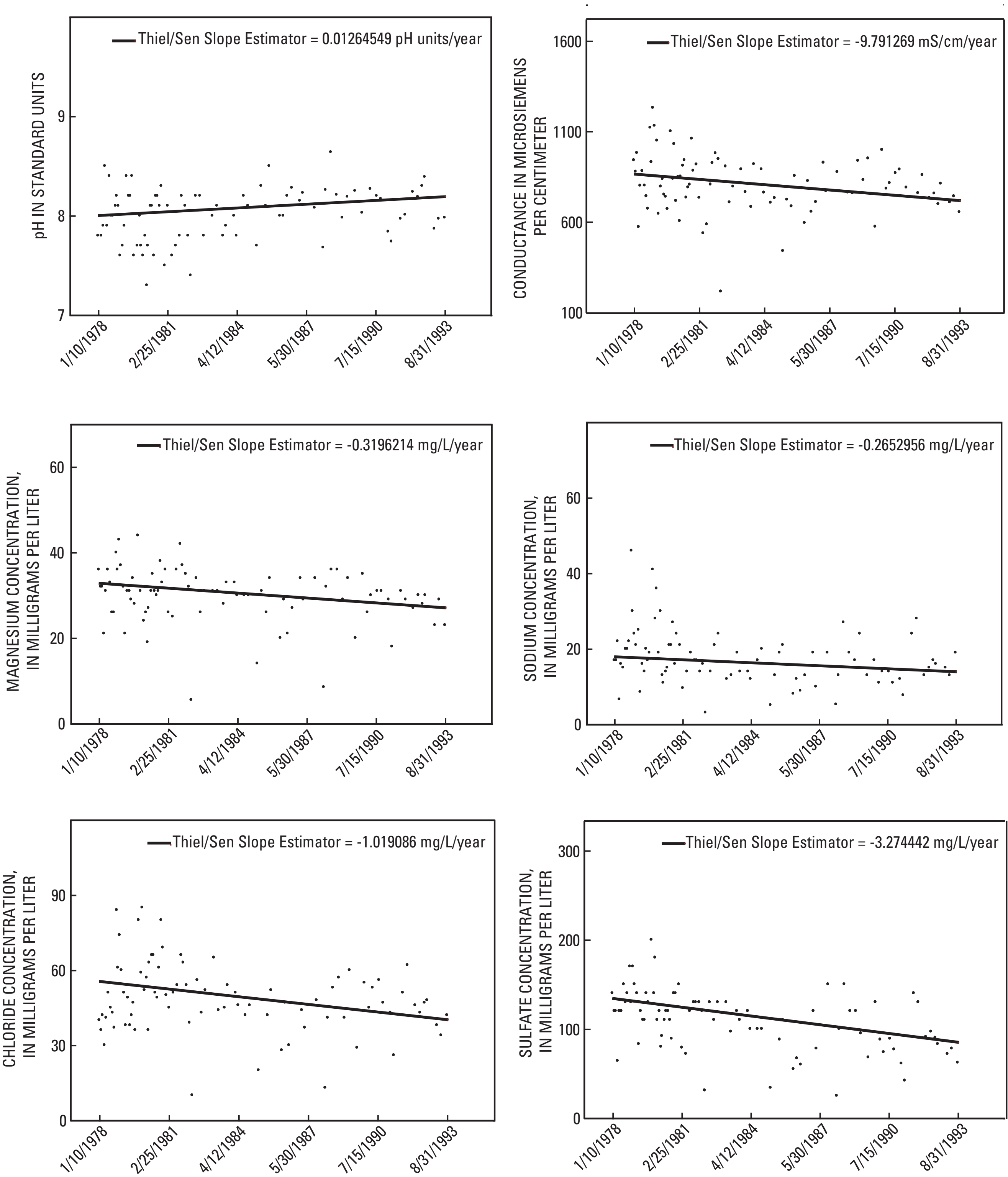


Figure 13. Significant trends detected in water-quality constituents at the Pigeon River near Caseville (04159010), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year); microsiemens per centimeter per year (µS/cm/year)).

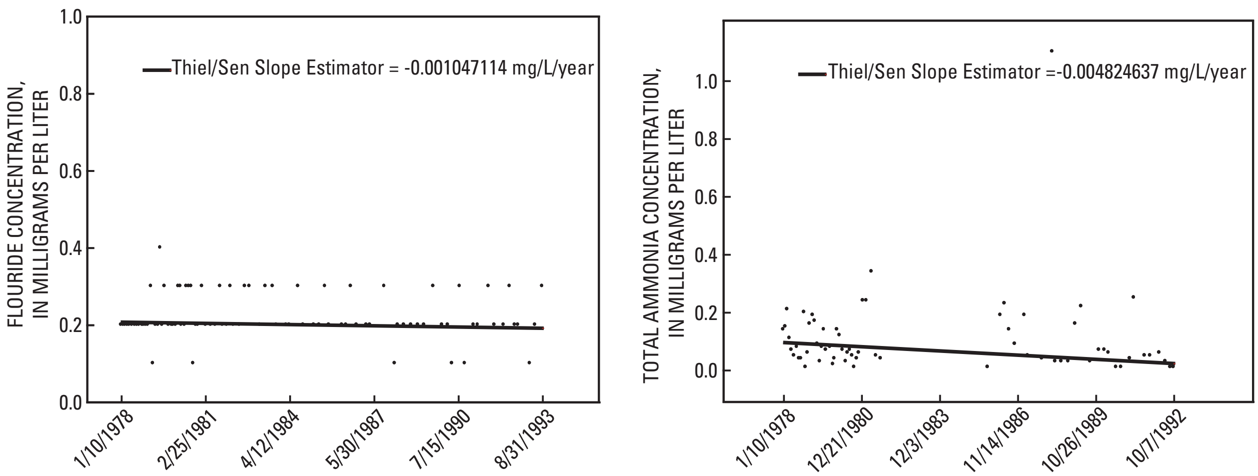


Figure 14. Significant trends detected in water-quality constituents at the Pigeon River near Caseville (04159010), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year)).

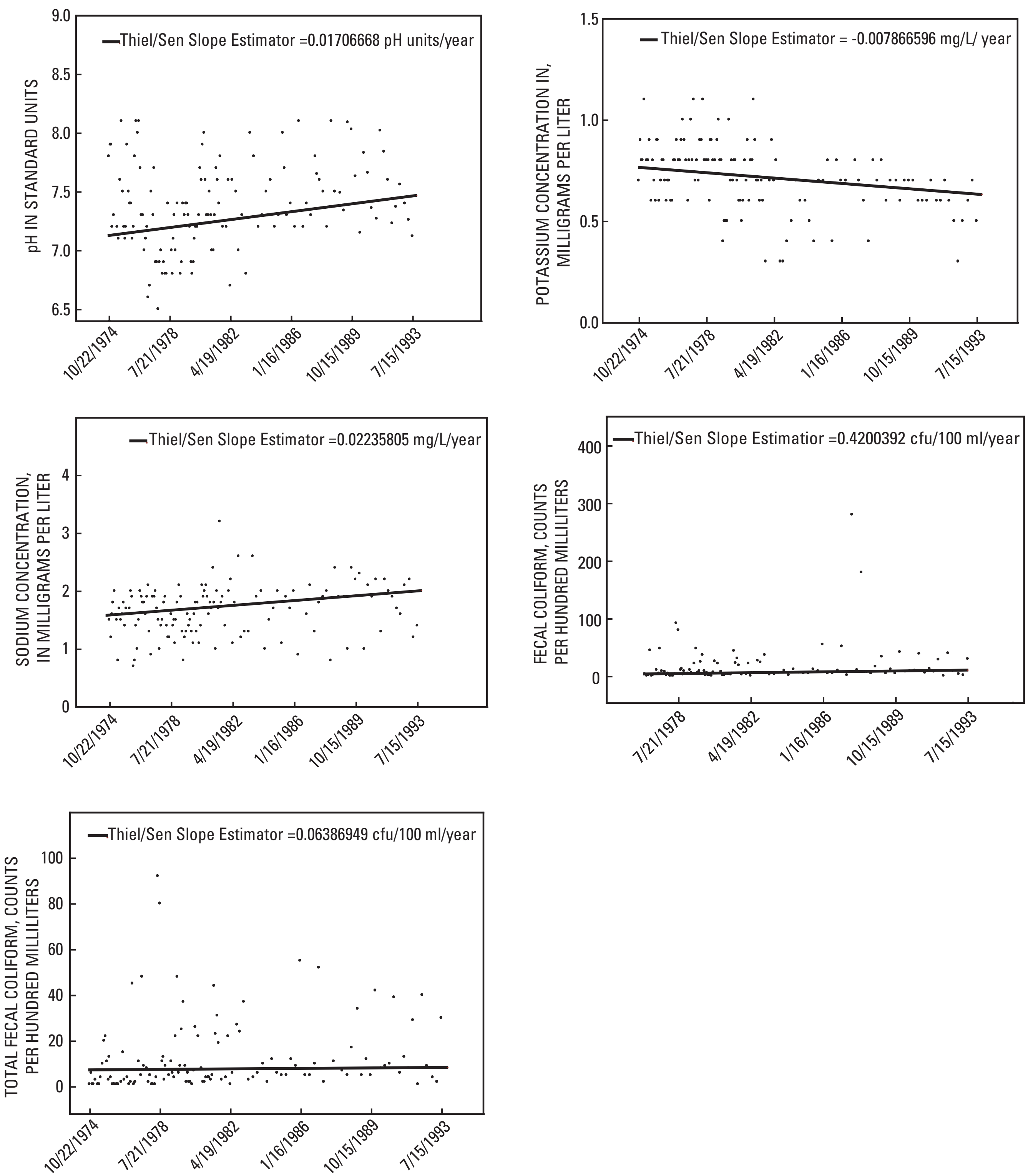


Figure 15. Significant trends detected in water-quality constituents at the Tahquamenon River near Paradise (04045500), Michigan. (The Thiel / Sen Slope estimator shows changes in constituent concentrations in milligrams per liter per year (mg/L/year); colonies forming units per hundred milliliters of the sample per year (cfu/100ml/year)).

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey (USGS) National Stream Quality Accounting Network (NASQAN) program operated 34 surface-water quality stations in the State of Michigan from 1973 to 1995. Sampling frequencies varied from monthly at the beginning of the program to between four and five samples annually in the early 1990's. The program was eventually discontinued in 1995. Water-quality sampling was reinstated through a cooperative effort known as the Clean Michigan Initiative (CMI) with the Michigan Department of Environmental Quality (MDEQ). To demonstrate the value of long-term, water-quality monitoring, the USGS, in cooperation with the MDEQ, initiated this study to evaluate the NASQAN data for use in identifying trends in water-quality constituents for nine selected stations. The results from this study would help the MDEQ in assessing the effectiveness of water-pollution control efforts since the initiation of the Clean Water Act in 1972.

For this study, a total of 9 NASQAN stations were selected and approximately 28 constituents were evaluated at each station. Station selection was based on data availability, land-use characteristics, and station priority for the MDEQ Water Chemistry Monitoring Project (WCMP). The trend analyses were completed using the ESTREND statistical software package. ESTREND is a statistical program used mainly for the investigations of trends in water-quality data. Changing seasons, water-quality records with missing values, censored ("less-than") data, and flow-adjusted constituent concentration are accounted for in the trend tests. The water-quality data chosen for the trend tests had: (1) at least a 5-year period of record, (2) less than 5 percent of the observations censored at a single reporting limit, and (4) 40 percent of the values within the beginning one-fifth and ending one-fifth of the selected period. Sampling parameters that did not meet these criteria were not included for trend-test analyses. In this study, a negative trend indicates, a decrease in concentration of a particular constituent, which generally means an improvement in water quality; whereas a positive trend indicates an increase in concentration of a particular constituent and possible degradation of water quality. Significant trends detected during the study represent constituents with flow-adjusted concentrations.

Results of the trend analyses showed an overall improvement in water quality at the Clinton River at Mount Clemens, Manistee River at Manistee, and Pigeon River near Caseville stations. The detected trends for these stations showed decreases in concentration of various constituents including nitrogen compounds, specific conductance, sulfate, fecal coliform bacteria, and fecal streptococci bacteria. The station with the most significant improvement in bacterial contamination was the Manistee River at Manistee. Significant negative trends were detected in fecal coliform, total fecal coliform, fecal streptococci, and total fecal streptococci at this station. Similarly, the Clinton River at Mount Clemens station had significant decreases in nitrogen compound concentrations. At this station, negative trends in concentrations were detected in total ammonia, total ammonia plus organic nitrogen, total organic nitrogen, total nitrite plus nitrate (mg/L as nitrogen), and total nitrogen. These negative trends may indicate an overall improvement in agricultural practices, municipal and industrial wastewater-treatment processes, and effective regulations.

The Pigeon River near Caseville station indicated water-quality improvements (negative trends) in a variety of constituents including conductance, chloride, sodium, sulfate, and total ammonia.

Phosphorus data for most of the selected stations have 20 percent of the concentrations less than the analytical detection limit with more than one censoring level. This condition is a limiting factor for detecting trends in surface-water quality constituents using the uncensored Seasonal Kendall test. The only station with a significant negative trend in total phosphorus concentration is the Clinton River at Mount Clemens. However, scatter-plot analyses of phosphorus data indicate decreasing phosphorus concentrations at most of the study stations.

Positive trends in concentrations of nitrogen compounds were detected at the Kalamazoo River near Saugatuck and Muskegon River near Bridgeton. Positive trends in both fecal coliform and total fecal coliform were detected at the Tahquamenon River near Paradise station. Various different point and nonpoint sources could produce such increases, but most commonly the increase in concentrations of nitrogen compounds and fecal coliform bacteria are related to changes in agricultural practices or sewage-plant discharges.

pH levels increased at six out of nine stations on all the major rivers. No negative trends (decreasing concentration) in pH levels were detected at any of the stations. The possible causes of pH increase are difficult to determine. pH changes may be affected by many factors, such as temperature; by reactions of dissolved carbon dioxide with water; by reactions in which solid materials are dissolved, precipitated, or oxidized; and by the photosynthetic activity of aquatic organisms, which take up dissolved carbon dioxide during the day and release it at night. Increases in pH may be related to decreasing concentration of ammonia, or changes in regulatory requirements concerning the neutralization of municipal and industrial wastewater.

In addition to pH, numerous trends were detected in chloride and sodium concentrations on all the major rivers. A total of three positive and two negative trends were detected in sodium concentration, and three negative and two positive trends were detected in chloride concentrations. Anthropogenic sources of chloride commonly include deicing salt, sewage effluents, industrial wastes, and oil fields.

Trends in concentrations of other major ions, such as calcium, magnesium, sulfate, fluoride and potassium, were detected at stations throughout Michigan. Negative trends were detected only in sulfate and fluoride concentrations; on the contrary, only positive trends were detected in calcium concentrations. For other major ions, such as magnesium and potassium, both positive and negative trends were detected.

It is important to note that the period of record for this study encompasses a period of improvement and sophistication in sampling methods and analytical techniques. Improvements in analytical methods for most constituents may be related, in part, to measurement bias, which is difficult to take into account in water-quality trend tests. This difficulty arises because of the relative effects and the magnitude change in constituent concentrations in most cases is difficult to determine. Therefore, it can be assumed that in this study the detected trends in some water-quality constituents may be biased because of the improved analytical techniques and sampling methods.

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Appendix A.

Summary statistics and Trend-Test Results for selected National Stream Quality Accounting Network (NASQAN) stations in Michigan

Appendix A-1. Summary statistics and trend test results of water-quality data for the Au Sable River near Au Sable (04137500), Mich.

[USGS, U.S. Geological Survey; Max., maximum value; Min., minimum value; ºC, degrees Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; cfu/100 ml, colony forming units per hundred milliliters of the sample ; “a” , less than 40-percent of the data in the ending one-fifth of the data set; insufficient data, does not meet the criteria for trend test because of limitations in the number of data points or period of record; ––, no data]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1974-93	136	8.8	26	18	7	0	0	1.000
00076	Turbidity (NTU)	1978-93	89	2	5	2.4	2	1.5	0.2	0.090
00300	Dissolved Oxygen (mg/L)	1974-93	132	8.3	13	9.4	8	7.4	3.6	.254
00400	pH (standard units)	1974-93	134	7.4	8.1	7.6	7.3	7.2	6.5	.010
00095	Specific Conductance (µS/cm)	1974-93	132	135	198	164	145	110	42	.792
00915	Dissolved Calcium (mg/L)	1974-93	133	19	29	23	20	15	5.4	.852
00925	Dissolved Magnesium (mg/L)	1974-93	133	5.0	9.1	6	5.3	3.9	1.6	.988
00930	Dissolved Sodium (mg/L)	1974-93	133	1.7	3.2	1.9	1.7	1.4	.7	.000
00400	Dissolved Chloride (mg/L)	1974-93	132	2.0	4.5	2.3	2.0	1.7	.7	.558
00945	Dissolved Sulfate (mg/L)	1974-93	132	11.7	26	14	12	9.1	3.8	.690
00950	Dissolved Fluoride (mg/L)	1975-93	133	0.1	0.4	0.1	0.1	0.1	0	% censoring exceeds 5
00955	Dissolved Silica (mg/L)	1974-93	133	6.9	12	8.3	7	5.5	2.3	.640
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-93	72	.04	.09	.05	.04	.02	.01	% censoring exceeds 5
00610	Total Ammonia (mg/L as N)	1977-92	78	.04	.1	.05	.04	.02	.01	.133
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-93	128	.54	1.9	.69	.5	.38	.07	.141
00600	Total Nitrogen (mg/L)	1974-93	101	.62	2.23	.74	.57	.46	.22	a
00605	Total Organic Nitrogen (mg/L)	1977-93	87	.55	1.84	.66	.47	.36	.09	1.000
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1974-92	93	.10	.35	.14	.08	.04	.01	a
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-93	75	.11	.33	.14	.1	.08	.02	.572
71887	Total Nitrogen (mg/L as nitrate)	1974-92	83	2.6	4.9	3.2	2.5	1.9	1	a
00666	Dissolved Phosphorus (mg/L)	1977-93	97	.01	.06	.02	.01	.01	.01	.840
00665	Total Phosphorus (mg/L)	1974-93	131	.03	.35	.03	.02	.02	.01	.883
00440	Total Bicarbonate (mg/L)	1974-87	88	72	119	89	75	58	20	a
00900	Total Hardness (mg/L as calcium carbonate)	1974-93	133	68	100	82	71	54	20	.782
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1974-87	88	11	32	14	11	7	0	a
80154	Suspended Sediment (mg/L)	1974-93	126	5	22	6	5	3	0	.843
80155	Suspended Sediment Load (tons/day)	No Data	0	––	––	––	––	––	––	––
31625	Fecal Coliform (cfu/100ml)	1976-93	104	18	280	22	7.5	4	1	.034
31673	Fecal Streptococci (cfu/100ml)	1976-93	102	49	1200	38	15	5	1	.650

Appendix A-2. Station 04165500 Clinton River at Mt. Clemens, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values Max.	75	Median	25	Min.	p-value
00010	Temperature (degrees Celsius)	1973-95	143	12	26	20	13	3	0	0.544
00076	Turbidity (NTU)	1978-95	96	13	180	15	6.8	3.4	0.2	.076
00300	Dissolved Oxygen (mg/L)	1974-95	134	9.4	17	12	8.9	6.8	5.2	.474
00400	pH (standard units)	1973-95	141	8.0	8.4	8.2	8	7	7.2	.001
00095	Specific Conductance (µS/cm)	1973-95	141	784	1270	864	789	700	355	.059
00915	Dissolved Calcium (mg/L)	1974-95	139	70	90	76	70	65	45	.001
00925	Dissolved Magnesium (mg/L)	1974-95	139	20	26	22	21	19	12	.007
00930	Dissolved Sodium (mg/L)	1974-95	139	58	160	70	55	47	22	.066
00935	Dissolved Potassium (mg/L)	1974-95	139	5	9	5	5	4	3	.257
00400	Dissolved Chloride (mg/L)	1973-95	141	99	270	120	92	81	40	.006
00945	Dissolved Sulfate (mg/L)	1973-95	141	58	89	66	58	51	32	.003
00950	Dissolved Fluoride (mg/L)	1974-95	140	0.4	0.9	0.5	0.4	0.3	.1	.444
00955	Dissolved Silica (mg/L)	1974-95	140	5.3	8.1	6.2	5.4	4.6	2	.622
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-95	81	.13	.31	.16	.12	.08	.01	.456
00610	Total Ammonia (mg/L as N)	1977-92	70	.17	.73	.19	.14	.1	.01	.008
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-95	136	1.1	4.9	1.2	1	.8	.19	.007
00600	Total Nitrogen (mg/L)	1974-95	135	3.8	12	4.6	3.6	3	.75	.004
00605	Total Organic Nitrogen (mg/L)	1978-95	99	.89	4.8	1.0	.82	.61	.35	.482
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1973-92	93	3.0	6.9	3.8	2.9	2.1	.29	a
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-95	82	2.6	5	3	2.4	1.9	.25	.004
71887	Total Nitrogen (mg/L as nitrate)	1974-92	87	19	52	22	18	15	7.5	a
00666	Dissolved Phosphorus (mg/L)	1977-95	104	.10	.35	.13	.09	.0675	.01	.670
00665	Total Phosphorus (mg/L)	1974-95	138	.21	.76	.26	.175	.12	.01	.001
00440	Total Bicarbonate (mg/L)	1973-87	87	226	280	249	230	201	150	Insufficient Data
00900	Total Hardness (mg/L as calcium carbonate)	1974-95	139	257	320	280	260	240	160	.001
00902	Total Noncarbonate Hardness (mg/L as calcium carbon-ate)	1974-90	87	72	120	84	74	64	37	a
80154	Suspended Sediment (mg/L)	1974-95	138	40	511	48	26	16	3	.162
80155	Suspended Sediment Load (tons/day)	1974-95	136	98	1100	84	27	11	1.9	.393
31625	Fecal Coliform (cfu/100ml)	1976-95	113	30,007	110000	1,800	630	320	70	.196
31673	Fecal Streptococci (cfu/100ml)	1976-95	113	1,546	18000	1,800	560	200	21	.602

Appendix A-3. Station 04119300 Grand River near Eastmanville, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; cfu, colony forming units; ––, no data]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values: Max.	75	Median	25	Min.	p-value
00010	Temperature (degrees Celsius)	1979-97	100	13	27	20.3	14	4.9	0	0.831
00076	Turbidity (NTU)	1979-94	96	12	210	15	6.7	3.8	0.5	0.512
00300	Dissolved Oxygen (mg/L)	1979-94	99	11	16.6	12.7	11.2	9.3	5.7	0.977
00400	pH (standard units)	1979-94	97	8.2	8.8	8.4	8.2	8	7.1	0.000
00095	Specific Conductance (µS/cm)	1979-94	97	593	787	651	610	541	350	0.117
00915	Dissolved Calcium (mg/L)	1979-94	97	71	91	79	72	63	43	0.038
00925	Dissolved Magnesium (mg/L)	1979-94	97	21	27	24	22	20	12	0.296
00930	Dissolved Sodium (mg/L)	1979-97	97	3	5.3	3.3	2.9	2.6	2.1	0.035
00935	Dissolved Potassium (mg/L)	1979-97	97	22	44	28	22	17	7.6	0.264
00400	Dissolved Chloride (mg/L)	1979-94	96	39	77	48	39	32	16	0.560
00945	Dissolved Sulfate (mg/L)	1979-94	95	55	77	62	39	32	16	0.156
00950	Dissolved Fluoride (mg/L)	1979-94	96	0.19	0.3	0.2	0.2	0.2	.1	0.619
00955	Dissolved Silica (mg/L)	1979-97	97	5.7	10	7.7	5.6	3.7	.06	0.153
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-94	88	.22	.89	.30	.18	.11	.01	0.180
00610	Total Ammonia (mg/L as N)	1979-92	64	.25	.88	.34	.215	.12	.01	0.318
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1979-94	100	1.2	3.4	1.4	1.2	.9	.2	0.506
00600	Total Nitrogen (mg/L)	1979-97	98	2.6	7	3.2	2.4	2.0	.35	0.318
00605	Total Organic Nitrogen (mg/L)	1979-94	93	.97	3.21	1.13	.91	.66	.2	0.948
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1979-92	36	1.50	5.4	2.0	1.4	.85	.11	Insufficient Data
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-94	94	1.4	5.1	1.9	1.3	.73	.21	0.837
71887	Total Nitrogen (mg/L as nitrate)	No Data	––	––	––	––	––	––	––	––
00666	Dissolved Phosphorus (mg/L)	1979-94	99	.04	.2	.06	.03	.01	.01	0.375
00665	Total Phosphorus (mg/L)	1979-94	99	.11	.29	.14	.1	.07	.01	0.275
00440	Total Bicarbonate (mg/L)	1979-87	34	264	320	268	240	223	150	Insufficient Data
00900	Total Hardness (mg/L as calcium carbonate)	1979-94	97	264	330	290	270	250	160	0.035
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1979-90	41	64	110	76	63	53	27	Insufficient Data
80154	Suspended Sediment (mg/L)	1979-94	96	35.5	294	39.5	26.5	19.8	1	0.952
80155	Suspended Sediment Load (tons/day)	1979-94	94	670	8,930	747	300	165	4.7	0.883
31625	Fecal Coliform (cfu/100ml)	1979-94	91	310	5,200	900	230	85	1	0.204
31673	Fecal Streptococci (cfu/100ml)	1979-94	91	774	12,000	665	230	64	4	0.265

Appendix A-4. Station 04108690 Kalamazoo River at Saugatuck, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1973-86	113	12	28	21	11	2.5	0	0.338
00076	Turbidity (NTU)	1978-86	57	7.3	50	8.5	6	3	0.3	.413
00300	Dissolved Oxygen (mg/L)	1974-86	104	10	16	12	10	8.7	4.9	.928
00400	pH (standard units)	1973-86	113	8	8.8	8.2	8	7.8	7.1	.589
00095	Specific Conductance (µS/cm)	1973-86	113	547	715	592	561	510	344	.979
00915	Dissolved Calcium (mg/L)	1974-86	109	65	43	71	65	61	40	.385
00925	Dissolved Magnesium (mg/L)	1974-86	109	20	24	22	21	19	12	.414
00930	Dissolved Sodium (mg/L)	1974-86	110	19	28	22	19	16	8	.886
00935	Dissolved Potassium (mg/L)	1974-86	109	2.1	3	2.3	2.1	1.9	1.3	.304
00400	Dissolved Chloride (mg/L)	1973-86	111	31	43	36	32	27	13	.873
00945	Dissolved Sulfate (mg/L)	1973-86	109	45	63	49	46	41	21	.767
00950	Dissolved Fluoride (mg/L)	1974-86	109	.2	0.5	0.2	0.2	0.2	.1	.509
00955	Dissolved Silica (mg/L)	1974-86	109	6.1	10	8	6.5	4.7	.1	.620
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-86	43	.13	.42	.18	.11	.04	.01	Insufficient Data
00610	Total Ammonia (mg/L as N)	1977-86	50	.19	1	.24	.15	.07	.03	a
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-86	107	1	1.8	1.1	.96	.83	.31	.570
00600	Total Nitrogen (mg/L)	1974-86	106	1.8	3	2	1.8	1.6	.83	.022
00605	Total Organic Nitrogen (mg/L)	1977-86	63	.89	1.7	1	.82	.695	0	.666
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1973-81	90	.78	2	.98	.82	.5475	.01	.030
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-86	45	.91	1.6	1.1	.95	.67	.1	Insufficient Data
71887	Total Nitrogen (mg/L as nitrate)	1974-81	85	7.8	13	8.7	7.9	6.8	3.7	a
00666	Dissolved Phosphorus (mg/L)	1977-86	67	.04	.14	.05	.04	.03	.01	.379
00665	Total Phosphorus (mg/L)	1974-86	110	.11	.24	.1375	.11	.08	.01	.264
00440	Total Bicarbonate (mg/L)	1973-82	94	248	300	270	250	237	149	.309
00900	Total Hardness (mg/L as calcium carbonate)	1973-86	110	245	280	260	250	230	150	.686
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1973-86	97	41	75	51	40	31	0	a
80154	Suspended Sediment (mg/L)	1974-86	102	16	66	21	14	9.3	1	.872
80155	Suspended Sediment Load (tons/day)	1974-86	93	86	490	109	64	36	3.5	.824
31625	Fecal Coliform (cfu/100ml)	1976-86	62	157	1,300	200	84	46	6	.542
31673	Fecal Streptococci (cfu/100ml)	1976-86	67	514	8,000	395	120	43	3	.414

Appendix A-5. Station 04126520 Manistee River at Mansitee, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; “a” , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1973-94	160	10	25	19	10	2	0	0.325
00076	Turbidity (NTU)	1978-94	113	3.3	10	4.1	3	2	0.4	.120
00300	Dissolved Oxygen (mg/L)	1974-94	151	10	15	12	9.9	8.4	3.6	.721
00400	pH (standard units)	1973-94	160	7.9	8.3	8.1	8	7.8	7	.042
00095	Specific Conductance (µS/cm)	1973-94	156	426	729	458	417	378	276	.105
00915	Dissolved Calcium (mg/L)	1973-94	157	54	98	56	52	44	32	.321
00925	Dissolved Magnesium (mg/L)	1973-94	158	12	29	13	12	12	8.1	.459
00930	Dissolved Sodium (mg/L)	1974-94	157	13	24	15	12	9.7	5.8	.001
00935	Dissolved Potassium (mg/L)	1974-94	157	1.3	3.3	1.5	1.2	1.1	.5	.013
00400	Dissolved Chloride (mg/L)	1973-94	159	40	130	47	37	28	4.3	.016
00945	Dissolved Sulfate (mg/L)	1973-94	159	13	18	15	13	12	5.1	.496
00950	Dissolved Flouride (mg/L)	1974-94	156	0.1	0.4	0.1	0.1	0.1	.1	.736
00955	Dissolved Silica (mg/L)	1974-94	157	7.5	9.7	8.2	7.6	6.8	5	.633
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-94	100	.05	.25	.05	.04	.03	.01	.977
00610	Total Ammonia (mg/L as N)	1977-92	92	.05	.09	.06	.05	.0375	.01	.551
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-94	153	.39	3.6	.44	.3	.21	.1	.934
00600	Total Nitrogen (mg/L)	1974-94	129	.62	3.8	.64	.55	.43	.28	a
00605	Total Organic Nitrogen (mg/L)	1977-94	104	.37	3.5	.44	.28	.22	.03	.400
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1973-92	97	.21	.42	.29	.19	.14	.03	.531
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-94	100	.23	2	.27	.2	.12	.07	.660
00666	Dissolved Phosphorus (mg/L)	1977-94	119	.02	.12	.02	.01	.01	.01	.393
00665	Total Phosphorus (mg/L)	1974-94	155	.03	.14	.03	.02	.02	.01	.231
00440	Total Bicarbonate (mg/L)	1973-87	97	179	219	190	180	170	130	a
00900	Total Hardness (mg/L as calcium carbonate)	1973-94	157	185	300	200	180	170	130	.200
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1973-86	94	44	150	52	35	28	6	.028
80154	Suspended Sediment (mg/L)	1974-94	140	8	60	10	8	5	1	.086
80155	Suspended Sediment Load (tons/day)	1974-94	136	64	411	77	53	33	4.7	.184
31625	Fecal Coliform (cfu/100ml)	1976-94	125	2,443	1,200	260	130	43	1	.000
31673	Fecal Streptococci (cfu/100ml)	1976-94	131	1,800	1,000	85	51	21	5	.003

Appendix A-6. Station 04057004 Manistique River above Manistique, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1975-1986	101	8.8	24	16	7.5	0.00005	0	0.302
00076	Turbidity (NTU)	1978-1986	68	4	25	4	3.0	2.2	0.5	.461
00300	Dissolved Oxygen (mg/L)	1975-1986	98	10	13.7	11.175	9.7	8.7	7.2	.463
00400	pH (standard units)	1975-1986	102	7.6	8.4	7.8	7	7.4	6.6	.005
00095	Specific Conductance (µS/cm)	1975-1986	98	170	247	194	175	151	58	.486
00915	Dissolved Calcium (mg/L)	1975-1986	101	25	38	29	26	22	8.6	.257
00925	Dissolved Magnesium (mg/L)	1975-1986	101	5.5	7.8	6.2	5.7	4.9	2	1.000
00930	Dissolved Sodium (mg/L)	1975-1986	100	1.3	1.9	1.5	1.3	1.2	.7	.001
00935	Dissolved Potassium (mg/L)	1975-1986	101	0.6	0.9	0.7	0.6	.6	.1	.222
00400	Dissolved Chloride (mg/L)	1975-1986	101	1.7	3.1	2	1.7	1.5	.4	.897
00945	Dissolved Sulfate (mg/L)	1975-1986	101	21	41	25	22	18	7.4	.854
00950	Dissolved Fluoride (mg/L)	1975-1976	101	.1	.3	.1	.1	.1	0	.190
00955	Dissolved Silica (mg/L)	1975-1986	101	6.0	8.8	7	6.2	5.2	.6	.781
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-1986	53	.05	.26	.06	.03	.01	.01	.676
00610	Total Ammonia (mg/L as nitrogen)	1977-1986	53	.05	.12	.06	.04	.02	.01	.252
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1975-1986	96	.04	1.4	.5	.43	.32	.1	.809
00600	Total Nitrogen (mg/L)	1975-1986	78	.58	1.3	.64	.52	.42	.28	a
00605	Total Organic Nitrogen (mg/L)	1978-1986	64	.57	1.38	.47	.4	.31	.19	.804
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1976-1981	71	.45	.86	.13	.09	.07	.02	.903
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-1986	53	.10	.22	.12	.1	.09	.01	.575
71887	Total Nitrogen (mg/L as nitrate)	1975-1971	65	2.5	5.9	2.8	2.3	1.8	1.2	.929
00666	Dissolved Phosphorus (mg/L)	1977-1986	77	.01	.04	.01	.01	.01	.01	1.000
00665	Total Phosphorus (mg/L)	1975-1986	98	.02	.05	.02	.02	.01	.01	.649
00440	Total Bicarbonate (mg/L)	1975-1981	73	83	120	95	87	70	33	.754
00900	Total Hardness (mg/L as calcium carbonate)	1975-1986	101	85	120	97	90	76	30	.326
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1975-1985	75	19	36	25	19	14	0	a
80154	Suspended Sediment (mg/L)	1975-1986	96	6	35	6	5	3	1	1.000
80155	Suspended Sediment Load (tons/day)	1975-1986	91	43	985	40	16	8.4	0	.982
31625	Fecal Coliform (cfu/100ml)	1976-1986	83	9	46	15	3	2	1	.586
31673	Fecal Streptococci (cfu/100ml)	1976-1986	81	24	330	25	8	3	1	.674

Appendix A-7. Station 04122030 Muskegon River near Bridgeton, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS param-eter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1973-90	125	11	25	19	12	3	0	0.893
00076	Turbidity (NTU)	1978-90	74	4.5	140	2.8	1.9	1.1	0.2	.534
00300	Dissolved Oxygen (mg/L)	1974-90	120	10	16	13	10	8.7	3.5	.691
00400	pH (standard units)	1973-90	124	8.1	8.6	8.3	8.1	7.9	7.5	.558
00095	Specific Conductance (µS/cm)	1973-90	120	356	461	387	259	332	206	.878
00915	Dissolved Calcium (mg/L)	1974-90	122	44	53	47	44	41	27	.418
00925	Dissolved Magnesium (mg/L)	1974-90	122	13	17	14	13	12	7.5	.831
00930	Dissolved Sodium (mg/L)	1974-90	122	9.7	14	11	9.9	8.6	4.4	.721
00935	Dissolved Potassium (mg/L)	1974-90	122	1.2	2.4	1.4	1.2	1.1	.8	.470
00400	Dissolved Chloride (mg/L)	1973-90	124	17	27	20	18	16	2.4	.045
00945	Dissolved Sulfate (mg/L)	1973-90	124	20	27	22	18	16	2.4	.759
00950	Dissolved Fluoride (mg/L)	1974-90	123	0.1	0.4	0.1	0.1	0.1	.1	.028
00955	Dissolved Silica (mg/L)	1974-90	124	5.6	9.2	6.7	5.3	4.5	2.6	.773
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-90	60	.03	.13	.04	.03	.02	.01	.610
00610	Total Ammonia (mg/L as nitrogen)	1977-90	68	.04	.17	.05	.03	.02	.01	.347
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-90	119	.54	2.9	.6	.47	.37	.1	.001
00600	Total Nitrogen (mg/L)	1974-90	115	.82	3.3	.93	.74	.61	.26	.001
00605	Total Organic Nitrogen (mg/L)	1977-90	76	.58	2.9	.64	.48	.38	.06	.003
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1974-81	84	.26	.86	.36	.23	.14	.01	.157
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-90	60	.28	.53	.39	.26	.16	.01	.418
71887	Total Nitrogen (mg/L as nitrate)	1974-81	79	3.2	11	3.5	2.9	2.5	1.2	.557
00666	Dissolved Phosphorus (mg/L)	1977-90	82	.02	.09	.02	.01	.01	.01	.903
00665	Total Phosphorus (mg/L)	1974-90	122	.04	.7	.04	.03	.02	.01	.069
00440	Total Bicarbonate (mg/L)	1973-87	94	178	364	190	180	170	112	a
00900	Total Hardness (mg/L as calcium carbonate)	1973-90	123	165	200	180	170	150	98	.670
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1973-86	90	23	110	29	24	15	4	a
80154	Suspended Sediment (mg/L)	1974-90	120	25	312	28	15	11	1	.160
80155	Suspended Sediment Load (tons/day)	1974-90	116	307	10,700	231	93	41	12	.233
31625	Fecal Coliform (cfu/100ml)	1976-90	86	167	2,500	69	18	8	1	a
31673	Fecal Streptococci (cfu/100ml)	1976-90	89	352	12,000	88	34	12	1	.613

Appendix A-8. Station 04159010 Pigeon River near Pigeon, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1978-1993	88	10	25	18	10	1.4	0	0.978
00076	Turbidity (NTU)	1978-1993	82	8.0	210	5.8	3	1.8	0.3	.663
00300	Dissolved Oxygen (mg/L)	1978-1993	86	10	16	12	10	8	4.3	.514
00400	pH (standard units)	1978-1993	87	8.0	8.6	8.2	8.0	7.8	7.3	.039
00095	Specific Conductance (µS/cm)	1978-1993	86	807	1230	902	800	724	214	.024
00915	Dissolved Calcium (mg/L)	1978-1993	88	107	150	120	110	91	28	.119
00925	Dissolved Magnesium (mg/L)	1978-1993	88	30	44	34	31	27	5.5	.026
00930	Dissolved Sodium (mg/L)	1978-1993	88	17	46	21	17	13	3.1	.046
00935	Dissolved Potassium (mg/L)	1978-1993	88	4.2	8.7	4.9	3.7	3.2	2.5	.174
00400	Dissolved Chloride (mg/L)	1978-1993	86	49	85	56	47	41	10	.029
00945	Dissolved Sulfate (mg/L)	1978-1993	86	109	200	130	115	88	25	.001
00950	Dissolved Fluoride (mg/L)	1978-1993	88	0.2	0.4	0.3	0.2	0.2	.1	.037
00955	Dissolved Silica (mg/L)	1978-1993	88	4.5	10	6.5	4.6	1.9	.1	.781
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-1993	67	.12	1.1	.13	.05	.03	.01	.874
00610	Total Ammonia (mg/L as nitrogen)	1978-1992	66	.11	1.1	.14	.07	.04	.01	.043
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1978-1993	85	.96	3.6	1.3	.81	.66	.3	.857
00600	Total Nitrogen (mg/L)	1978-1993	81	5.9	20	8.7	4.3	1.8	.56	.189
00605	Total Organic Nitrogen (mg/L)	1978-1993	81	.85	2.5	1.2	.75	.55	.23	.959
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1978-1992	51	4.7	18	6.85	2.9	.76	.01	a
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-1993	67	5.08	19	8.7	3.4	.2	.02	a
00666	Dissolved Phosphorus (mg/L)	1978-1993	87	.09	.4	.11	.07	.04	.01	.108
00665	Total Phosphorus (mg/L)	1978-1993	87	.12	.53	.16	.09	.06	.01	.124
00440	Total Bicarbonate (mg/L)	1978-1993	47	296	390	365	310	245	86	Insufficient Data
00900	Total Hardness (mg/L as calcium carbonate)	1978-1993	87	392	560	445	400	350	93	.056
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1978-1993	49	159	250	190	160	130	0	Insufficient Data
80154	Suspended Sediment (mg/L)	1978-1993	86	31	295	41	19	7.3	2	1.000
80155	Suspended Sediment Load (tons/day)	1978-1993	82	20	536	7.2	1.2	.28	.01	.735
31625	Fecal Coliform (cfu/100ml)	1978-1993	84	667	18,000	418	205	86	1	.954
31673	Fecal Streptococci (cfu/100ml)	1978-1993	85	3,974	100,000	870	360	120	5	.939

Appendix A-9. Station 04045500 Tahquamenon River near Paradise, Mich.

[No., number; Max., maximum value; Min., minimum value; C, Celsius; NTU, nephelometric turbidity units; mg/L, milligrams per liter; µS/cm, mirosiemens per centimeter; "a" , less than 40-percent of the data in the ending one-fifth of the data set; cfu, colony forming units; ––, no data]

USGS parameter code	Constituents and units	Period of Record	No. of Observations	Mean Value	Percentile Values					p-value
					Max.	75	Median	25	Min.	
00010	Temperature (degrees Celsius)	1974-93	136	8.8	26	18	7	0	0	1.000
00076	Turbidity (NTU)	1978-93	89	2	5	2.4	2	1.5	0.2	0.090
00300	Dissolved Oxygen (mg/L)	1974-93	132	8.3	13	9.4	8	7.4	3.6	.254
00400	pH (standard units)	1974-93	134	7.4	8.1	7.6	7.3	7.2	6.5	.010
00095	Specific Conductance (µS/cm)	1974-93	132	135	198	164	145	110	42	.792
00915	Dissolved Calcium (mg/L)	1974-93	133	19	29	23	20	15	5.4	.852
00925	Dissolved Magnesium (mg/L)	1974-93	133	5.0	9.1	6	5.3	3.9	1.6	.988
00930	Dissolved Sodium (mg/L)	1974-93	133	1.7	3.2	1.9	1.7	1.4	.7	.000
00400	Dissolved Chloride (mg/L)	1974-93	132	2.0	4.5	2.3	2.0	1.7	.7	.558
00945	Dissolved Sulfate (mg/L)	1974-93	132	11.7	26	14	12	9.1	3.8	.690
00950	Dissolved Fluoride (mg/L)	1975-93	133	0.1	.4	0.1	0.1	0.1	0	% censoring exceeds 5
00955	Dissolved Silica (mg/L)	1974-93	133	6.9	12	8.3	7	5.5	2.3	.640
00608	Dissolved Ammonia (mg/L as nitrogen)	1979-93	72	.04	.09	.05	.04	.02	.01	% censoring exceeds 5
00610	Total Ammonia (mg/L as N)	1977-92	78	.04	.1	.05	.04	.02	.01	.133
00625	Total Ammonia + organic nitrogen (mg/L as nitrogen)	1974-93	128	.54	1.9	.69	.5	.38	.07	.141
00600	Total Nitrogen (mg/L)	1974-93	101	.62	2.23	.74	.57	.46	.22	a
00605	Total Organic Nitrogen (mg/L)	1977-93	87	.55	1.84	.66	.47	.36	.09	1.000
00630	Total Nitrite + Nitrate (mg/L as nitrogen)	1974-92	93	.10	.35	.14	.08	.04	.01	a
00631	Dissolved Nitrite + Nitrate (mg/L as nitrogen)	1979-93	75	.11	.33	.14	.1	.08	.02	.572
71887	Total Nitrogen (mg/L as nitrate)	1974-92	83	2.6	4.9	3.2	2.5	1.9	1	a
00666	Dissolved Phosphorus (mg/L)	1977-93	97	.01	.06	.02	.01	.01	.01	.840
00665	Total Phosphorus (mg/L)	1974-93	131	.03	.35	.03	.02	.02	.01	.883
00440	Total Bicarbonate (mg/L)	1974-87	88	72	119	89	75	58	20	a
00900	Total Hardness (mg/L as calcium carbonate)	1974-93	133	68	100	82	71	54	20	.782
00902	Total Noncarbonate Hardness (mg/L as calcium carbonate)	1974-87	88	11	32	14	11	7	0	a
80154	Suspended Sediment (mg/L)	1974-93	126	5	22	6	5	3	0	.843
80155	Suspended Sediment Load (tons/day)	No Data	0	––	––	––	––	––	––	––
31625	Fecal Coliform (cfu/100ml)	1976-93	104	18	280	22	7.5	4	1	.034
31673	Fecal Streptococci (cfu/100ml)	1976-93	102	49	1200	38	15	5	1	.650

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