Trends in Nutrients and Suspended Solids at the Fall Line of Five Tributaries to the Chesapeake Bay in Virginia, July 1988 through June 1995

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 96-4191

Prepared in cooperation with the

VIRGINIA DEPARTMENT OF ENVIRONMENTAL QUALITY,
CHESAPEAKE BAY AND COASTAL PROGRAMS

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

Richmond, Virginia

1996

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer
	Flow	
million gallons per day (Mgal/d)	0.04381	cubic meter per second
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)

Vertical datum: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Water-quality units: Chemical concentration is reported in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Specific electrical conductance of water is reported in microsiemens per centimeter at 25 degrees Celsius (µS/cm). Temperature in degree Celsius (°C) can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = 1.8 \times (°C) + 32.$$

Trends in Nutrients and Suspended Solids at the Fall Line of Five Tributaries to the Chesapeake Bay in Virginia, July 1988 through June 1995

By Clifton F. Bell, Donna L. Belval, and Jean P. Campbell

Abstract

Water-quality samples were collected at the Fall Line of five tributaries to the Chesapeake Bay in Virginia during a 6- to 7-year period. The water-quality data were used to estimate loads of nutrients and suspended solids from these tributaries to the non-tidal part of Chesapeake Bay Basin and to identify trends in water quality. Knowledge of trends in water quality is required to assess the effectiveness of nutrient management strategies in the five basins.

Multivariate log-linear regression and the seasonal Kendall test were used to estimate flow-adjusted trends in constituent concentration and load. Results of multivariate log-linear regression indicated a greater number of statistically significant trends than the seasonal Kendall test; however, when both methods indicated a significant trend, both agreed on the direction of the trend. Interpretation of the trend estimates for this report was based on results of the parametric regression method.

No significant trends in total nitrogen concentration were detected at the James River monitoring station from July 1988 through June 1995, though total Kjeldahl nitrogen concentration decreased slightly in base-flow samples. Total phosphorus concentration decreased about 29 percent at this station during the sampling period. Most of the decrease can be attributed to reductions in point-source phosphorus loads in 1988 and 1989, especially the phosphate detergent ban of 1988. No significant trends in total suspended solids were observed at the James River monitoring station, and no trends in runoff-derived constituents were interpreted for this river.

Significant decreases were detected in concentrations of total nitrogen, total Kjeldahl nitrogen, dissolved nitrite-plus-nitrate nitrogen, and total suspended solids at the Rappahannock River monitoring station between July 1988 and June 1995. A similar downward trend in total phosphorus concentration was significant at the 90-percent confidence level, but not the 95-percent confidence level. These decreases can be attributed primarily to reductions in nonpoint nutrient and sediment loads, and may have been partially caused by implementation of best management practices on agricultural and silvicultural land.

Flow-adjusted trends observed at the Appomattox, Pamunkey, and Mattaponi monitoring stations were more difficult to explain than those at the James and Rappahannock stations. Total Kjeldahl nitrogen and total phosphorus increased 16 and 23 percent, respectively, at the Appomattox River monitoring station from July 1989 through June 1995. Total phosphorus concentration increased about 46 percent at the Pamunkey River monitoring station between July 1989 and June 1995. At the Mattaponi River monitoring station, decreases in dissolved nitrite-plus-nitrate nitrogen were offset by increases in total Kjeldahl nitrogen, resulting in no net change in total nitrogen concentration from October 1989 through June 1995.

INTRODUCTION

The Chesapeake Bay is the largest and most productive estuary in the United States, extending nearly 200 mi from the mouth of the Susquehanna River in Maryland to where it discharges to the Atlantic Ocean along the southeastern coast of Virginia (fig. 1). The basin includes approximately 64,000 mi^2 of Delaware, Maryland, New York, Pennsylvania, Virginia, West Virginia, and the District of Columbia and has a population of more than 15 million people. In addition to providing habitats for coastal and marine wildlife, Chesapeake Bay is an important economic and recreational resource, providing thousands of jobs in commercial fishing, sport fishing, shipping, and other industries.

Intense agriculture, silviculture, and development in the Chesapeake Bay Basin have degraded the water quality of the Bay, and threatens its economic, recreational, and ecological value. The Chesapeake Bay Program, a partnership of government agencies and Bay-related organizations formed in 1983 to direct restoration efforts, has targeted three critical issues for intense investigation: (1) nutrient enrichment, (2) toxic substances, and (3) the decline of submerged aquatic vegetation. Nutrient enrichment has been identified as the primary cause of the decline in water quality of the Bay (Jordan and others, 1992). High concentrations of nitrogen and phosphorus cause excessive growth of algae, which deprives submerged aquatic vegetation of sunlight and, during decay, consumes dissolved oxygen. This in turn has a detrimental effect on fish, crabs, molluscs, and other species.

In order to address the problem of nutrient enrichment, the States of Maryland, Pennsylvania, Virginia, and the District of Columbia signed the Chesapeake Bay Agreement in 1987. This agreement commits Federal, State, and other agencies to work toward a 40 percent reduction in controllable nitrogen and phosphorus inputs to Chesapeake Bay by the year 2000, based on 1985 levels. The achievement of this goal will greatly restrict algal blooms in the Bay and will result in higher oxygen levels throughout the year.

Freshwater flow to Chesapeake Bay from its major tributaries is the single largest source of nutrients to the Bay. In 1992, The Chesapeake Bay Executive Council approved amendments to the 1987 agreement that committed member States to reduce nutrients inputs in the major river basins that discharge to the Bay. In response to the amendments, the member States are currently developing or implementing “tributary strategies,” which are documents that outline plans for meeting nutrient reduction goals for the 10 largest tributaries to the Bay.

In order to assess the effectiveness of tributary strategies and determine the effects of nutrients and sediment on water quality and living resources, loads and temporal trends of water-quality constituents at the Fall Line are quantified. The Fall Line is geographically defined as the boundary between the Piedmont and Coastal Plain Physiographic Provinces, and generally represents the upstream limit of tides (fig. 1). Load estimates at the Fall Line are particularly important for use as input to computer models of the Bay, and trends in water-quality at the Fall Line are a key indicator of the effectiveness of tributary strategies at reducing nutrient loads entering the estuary from the non-tidal part of its tributary basins.

In 1984, the U.S. Geological Survey (USGS), in cooperation with the Virginia Department of Environmental Quality (DEQ), began collecting water-quality samples at sites near the Fall Line on the James, Rappahannock, Pamunkey, and Mattaponi Rivers on a twice-per-month basis, with the purpose of quantifying loads of selected water-quality constituents contributed to the tidal part of the Bay Basin. In 1988, the monitoring program was expanded to include stormflow sampling at the James and Rappahannock Rivers; and in 1989, stormflow sampling was initiated at the Appomattox, Pamunkey, and Mattaponi Rivers. The Maryland District of the USGS, in cooperation with the Maryland Department of Natural Resources, has operated a similar monitoring program for the Susquehanna, Potomac, Patuxent, and Choptank Rivers since 1984. This information is now being used to assess the response of water quality to the implementation of nutrient reduction strategies.

Purpose and Scope

The purpose of this report is to: (1) Present flow-adjusted trends in nutrients and suspended solids for five major tributaries to Chesapeake Bay in Virginia near the Fall Line; (2) discuss possible factors that affect trends in water quality at these rivers, and (3) assess quality assurance/quality control results.

Water-quality samples were collected at the James and Rappahannock Rivers from July 1, 1988 through June 30, 1995; at the Appomattox and Pamunkey Rivers from July 1, 1989 through June 30, 1995; and at the Mattaponi River from September 1, 1989

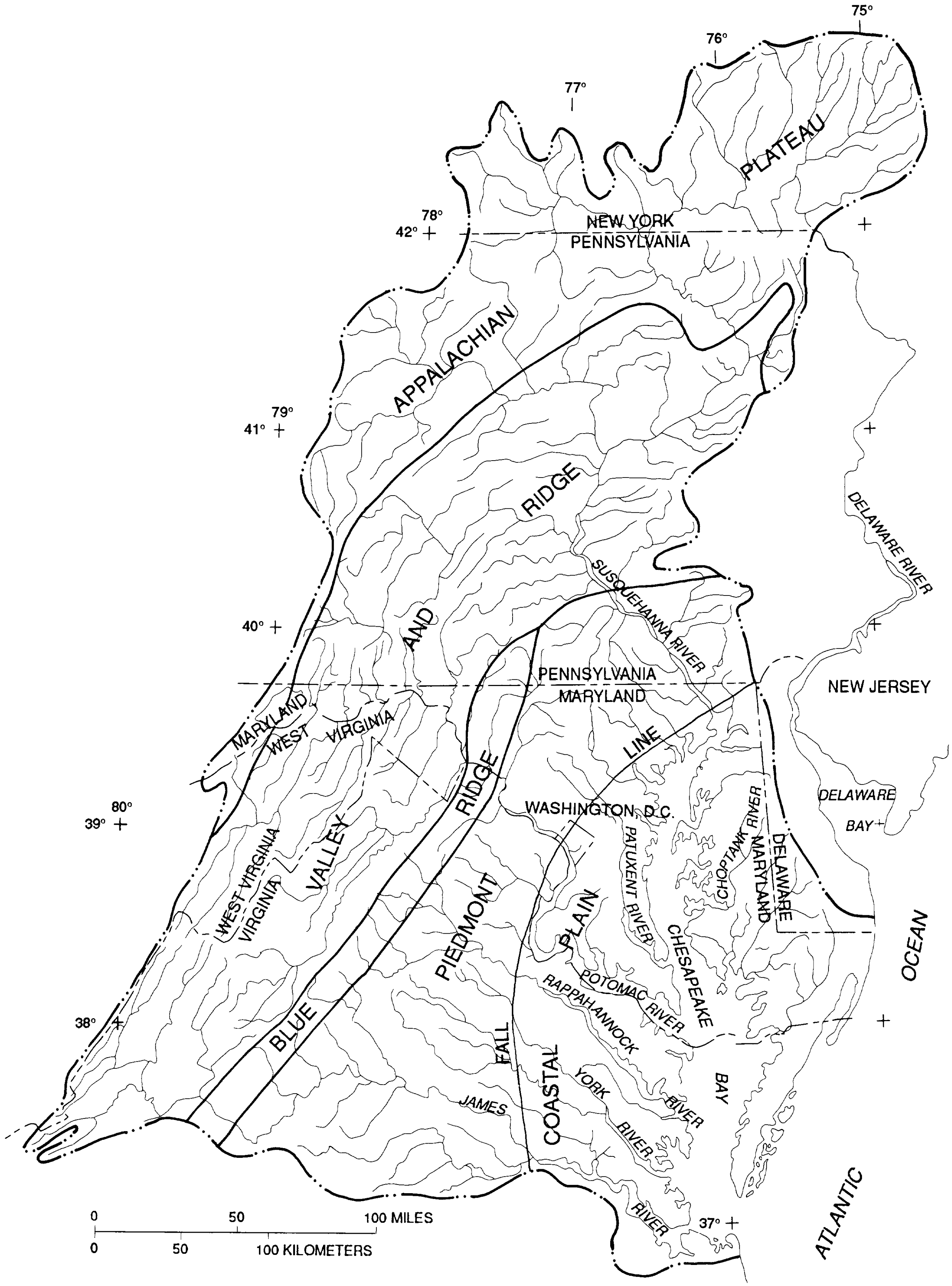

Figure 1. Chesapeake Bay drainage area.

through June 30, 1995. The samples were collected on a twice-per-month scheduled basis, most often during base-flow conditions, and also during high-flow events to cover a range in discharge conditions. Monthly loads and flow-adjusted trends of selected constituents were estimated by use of a seven-parameter log-linear-regression model (Cohn and others, 1992). Flow-adjusted trends also were estimated by use of the seasonal Kendall test.

Statistical summaries of concentrations, loads, and flow-adjusted trends of selected constituents are presented in tabular format. Time-series plots of constituent concentrations that exhibit significant trends are presented, as well as time-series plots of flow-adjusted residuals of the concentration/discharge regression, which are more useful for displaying flow-adjusted trends than time-series plots of the concentration data. Quality-assurance/quality-control procedures and results from July 1988 to June 1995 are presented in appendix A.

Previous Investigations

Several previous investigations provide information on water-quality monitoring and load estimation within the Chesapeake Bay Basin. Lang and Grason (1980) provided water-quality monitoring data for the Susquehanna, Potomac, and James Rivers. Lang (1982) computed loads of nutrients and metals from these rivers by use of a bivariate linear-regression equation method. Cohn and others (1992) used the minimum variance unbiased estimator of Bradu and Mundlak (1970) to estimate nutrient loads from the Susquehanna, Potomac, Patuxent, and Choptank Rivers near the Fall Line in Maryland. This method also was used to estimate constituent concentrations and loads in tributaries to the Chesapeake Bay from Pennsylvania (Ott and others, 1990; Fishel and others, 1991), from Maryland (Maryland Department of the Environment, 1993, 1994, 1995), and from Virginia (Belval and others, 1994; Belval and others, 1995).

All concentration data and load estimates used in the preparation of this report are presented in two previous reports (Belval and others, 1995; Belval and Campbell, 1996). Regression results used in this report to estimate trends are presented in Belval and Campbell (1996).

Description of Study Area

The contributing drainage areas discussed in this report collectively represent about 17 percent of the total Chesapeake Bay drainage area, and about 46 percent of the Virginia part of Chesapeake Bay Basin; the remainder of the Virginia part of Chesapeake Bay Basin consists mostly of the Virginia Coastal Plain Physiographic Province and the Virginia part of the Potomac River Basin. The locations of the five monitoring stations are shown in figure 2, and the station coordinates, drainage areas, land-use data, and upstream wastewater discharge for the five basins are listed in table 1.

The James River monitoring station is located at Cartersville and receives drainage from about 60 percent of the James River Basin. The river is the third largest source of freshwater to Chesapeake Bay, after the Susquehanna and Potomac Rivers. The James River Basin extends from the eastern part of West Virginia through four physiographic provinces (1) Valley and Ridge, (2) Blue Ridge, (3) Piedmont, and (4) Coastal Plain (fig. 1). The monitoring station is about 40-mi upstream of the Fall Line, but was selected because of the well-documented long-term discharge record, and because no major streams contribute to the discharge of the river between this station and the Fall Line at Richmond. Of the five basins discussed in this report, the James River Basin has the second highest percentage forested land upstream from the monitoring station (72 percent), the lowest percentage agricultural land (23 percent), and the greatest volume of wastewater discharge (table 1).

The Rappahannock River monitoring station is located upstream of Fredericksburg, Va. The area of the drainage basin upstream from the monitoring station is approximately 1,596 mi^2, which is about 56 percent of the Rappahannock River Basin. The river flows from the eastern edge of the Blue Ridge Physiographic Province through the Piedmont and Coastal Plain Physiographic Provinces to the Chesapeake Bay, and it is the second largest contributing stream to the Chesapeake Bay in Virginia. The high relief in the basin produces rapid or "flashy" streamflow peaks during storm events. The Rappahannock River can carry large loads of suspended solids and other constituents relative to the size of the basin (Belval and others, 1995). This basin has the highest percentage of agricultural land use upstream from the monitoring station (44 percent) of the five basins discussed in this report.

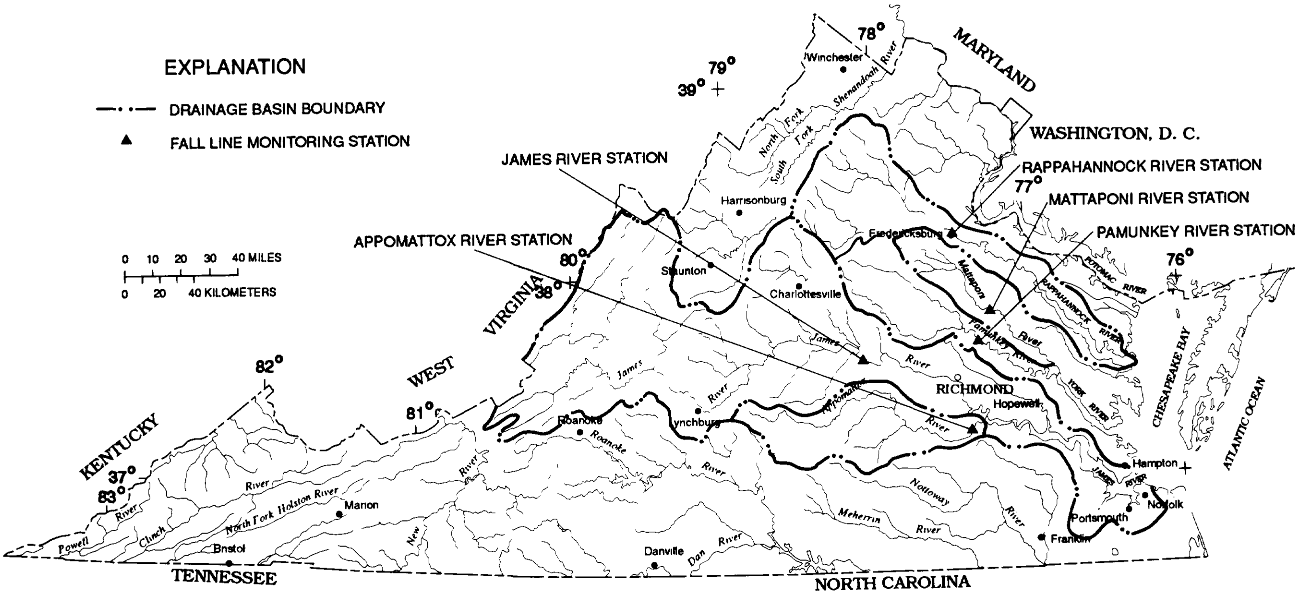

Figure 2. Locations of Fall Line monitoring stations in the James, Rappahannock, Appomattox, Pamunkey, and Mattaponi River Basins, Virginia.

Table 1. Location, drainage area, upstream land use, and major upstream wastewater discharge at the Fall Line monitoring stations in Virginia

[mi^2, square mile; Mgal/d, million gallons per day; land-use data from Langland and others, 1995; land use as percentage of total land-surface area in each drainage basin upstream from monitoring station; USGS, U.S. Geological Survey; VDEQ, Virginia Department of Environmental Quality]

USGS station number	VDEQ station number	Station name	Latitude	Longitude	Drainage area (mi^2)	Upstream land use: Developed (percent)	Upstream land use: Agricultural (percent)	Upstream land use: Forested[1] (percent	Major upstream wastewater discharge (Mgal/d)
02035000	TF5.1	James River at Cartersville	37°40'15"	78°05'10"	6,257	4	23	72	89.4
01668000	TF3.1	Rappahannock River near Fredericksburg	38°19'20"	77°31'05"	1,596	2	44	50	4.7
02041650	TF5.4A	Appomattox River at Matoaca	37°13'28"	77°28'32"	1,344	2	34	62	1.1
01673000	TF4.1	Pamunkey River near Hanover	37°46'03"	77°19'57"	1,081	2	35	59	5.0
01674500	TF4.3	Mattaponi River near Beulahville	37°53'02"	77°09'55"	601	2	28	69	.1

[1] Includes wetlands.

The Appomattox River Basin lies within the James River Basin but was monitored separately because the Appomattox River enters the James River below the Fall Line and is not included as a source to the James River monitoring station. The Appomattox River Basin begins in the Piedmont Physiographic Province, flows through a small part of the Coastal Plain Physiographic Province, and enters the James River estuary near Hopewell, Va. Discharge in the Appomattox River is affected by a dam 2.8-mi upstream of the monitoring station at Matoaca. This control acts to delay water-level rise during storm events, so that the water level is very slow to rise and fall in comparison with the other monitoring stations. Biogeochemical processes in Lake Chesdin, the lake formed by the dam, may strongly affect water quality at the Appomattox River monitoring station (Belval and others, 1995).

The York River Basin constitutes about 6.5 percent of the Virginia part of Chesapeake Bay Basin. The basin consists of the Pamunkey River, the Mattaponi River, and the coastal area below the confluence of these two rivers. Agriculture is an important component of the economy of the York River Basin, and the area is primarily rural. Although the Pamunkey and Mattaponi Rivers are often presented collectively as the York River Basin, each river has unique drainage basin, discharge, and water-quality characteristics and were monitored separately for this study.

The Pamunkey River Basin begins in the lower, eastern part of the Piedmont Physiographic Province where the relief is relatively low and extends into the Coastal Plain Physiographic Province. The drainage basin above the monitoring station represents about 40 percent of the York River Basin, and about 4 percent of the Virginia part of Chesapeake Bay Basin. The basin is of low relief and relatively wide, and tends to produce stormflow that is slow to peak and recede. Some regulation of the Pamunkey River occurs from the Lake Anna Dam, approximately 60-mi upstream of the monitoring station. The basin contains expanses of forested wetlands and marshes.

The total area of the Mattaponi River Basin above the monitoring station is approximately 601 mi^2, which is about 23 percent of the entire York River Basin, and 2 percent of the Virginia part of Chesapeake Bay Basin. Like the Pamunkey River, the Mattaponi River Basin has a relatively low relief and expanses of wetland areas. Stormflows are even slower to peak and recede than at the Pamunkey River.

Acknowledgments

The authors wish to thank Frederick Hoffman and Mark Bushing of the Virginia DEQ, Chesapeake Bay and Coastal Programs, for their assistance and guidance of the program. The majority of analyses for this project were performed by the Nutrients Laboratory and Non-metals Laboratory of the Virginia Division of Consolidated Laboratory Services (VDCLS), Bureau of Chemistry. Norma Roadcap of the Nutrients Laboratory provided assistance with water-quality data management, and some field-data collection was performed by the Piedmont Field Office of the Virginia DEQ. We thank all persons involved for their high-quality work.

METHODS OF STUDY

Methods of field-data collection and load estimation are described by Belval and others (1995). The following discussion pertains to methods used to (1) estimate temporal trends in water-quality data at the Fall Line; (2) perform streamflow partitioning for use in interpreting trends; and (3) present quality-assurance and quality-control results.

Trend Estimation

Trends in constituent concentration were estimated by two methods: (1) multivariate log-linear regression, and (2) the flow-adjusted seasonal Kendall test. The log-linear regression method is parametric and requires that certain assumptions regarding the fit of the water-quality data to the model are met, whereas the seasonal Kendall test is nonparametric and requires that the data are independent and are from the same statistical distribution (Schertz and others, 1991). Though the seasonal Kendall test requires fewer assumptions, parametric methods generally have more power to test hypotheses in situations where their use is appropriate. For this study, trends were interpreted primarily by use of the results of the log-linear regression. Other investigations of water-quality trends in the tidal part of Chesapeake Bay Basin have employed the seasonal Kendall test; therefore, results from the seasonal Kendall test are presented in this report for purposes of comparison.

Multivariate Log-Linear Regression

Trends in water-quality data were estimated by use of the same multivariate log-linear regression model that was used to estimate daily concentration and load for the data-collection period (Cohn and others, 1992; Belval and others, 1995). The regression model has the following form:

$$\ln(C) = \beta_0 + \beta_1\left[\ln\left(\frac{Q}{\tilde{Q}}\right)\right] + \beta_2\left[\ln\left(\frac{Q}{\tilde{Q}}\right)\right]^2 \qquad (1)$$

$$+ \beta_3[T - \tilde{T}] + \beta_4[T - \tilde{T}]^2 + \beta_5\sin(2\pi T)$$

$$+ \beta_6\cos(2\pi T) + \varepsilon,$$

where

C = the constituent concentration (in mg/L),
Q = the instantaneous discharge (in ft^3/s),
T = time (in years),
β = coefficient of the regression model,
ε = model error, and
$\tilde{Q}$ and $\tilde{T}$ = centering variables.

Equation (1) estimates daily concentration (or load) as a function of discharge, time, and seasonality. The minimum variance unbiased estimator (MVUE) of Bradu and Mundlak (1970) was employed to correct for the bias introduced by retransformation of concentration estimates from logarithmic space to real space. The adjusted maximum likelihood estimator (AMLE) (Cohn, 1988) was used to assign concentration values to censored data, which are data reported as less than a certain value, called the reporting limit.

Temporal trends in concentration are estimated by use of the coefficient of the time parameter (β_3) in the regression model, which represents the slope of the log-linear trend in concentration, independent of discharge and seasonality. The magnitude of the trend is calculated as follows:

$$\%\Delta C = 100\{e^{\beta_3 t} - 1\}, \qquad (2)$$

where $\%\Delta C$ is the percent change in concentration during any time t, with t expressed in years. The statistical significance of the trend may be determined from the probability value (p-value) of β_3, which is the estimated probability that random variation in concentration alone could produce the observed trend. For this report, a trend is considered significant if the p-value for β_3 is less than, or equal to, 0.05, which corresponds to a 95-percent confidence level. Some trends with p-values less than, or equal to, 0.10 are also considered significant.

Use of regression for trend analysis requires certain assumptions about the results of the regression model; specifically, that the model form is correct and that the regression residuals are independent, normally distributed, and homoscedastic (Helsel and Hirsch, 1992). Model results and residual plots were examined for each regression output before trends were calculated. Water-quality data and regression results from the Fall Line monitoring stations met the requirements for use of this method with the possible exception of model form; misspecification of model form could bias the magnitude of predicted trends. Model misspecification, however, is unlikely to affect the direction of the predicted trend. Trends were not calculated for dissolved orthophosphorus and ammonia because of the high percentage of censored data.

Trends estimated by the regression model are inherently flow-adjusted because multivariate regression separates variability in concentration that is due to variability in flow from that due to variability in time. If this is not done, trends in discharge can mask trends in concentration that are independent of discharge. Flow-adjusted trends in concentration calculated by this method are identical to flow-adjusted trends in load.

Flow-Adjusted Seasonal Kendall Test

The flow-adjusted seasonal Kendall test is described by Hirsch and others (1982), and was performed on Fall Line water-quality data by use of the program ESTREND, which is documented by Schertz and others (1991). This method is a variant of the Mann-Kendall test, which tests the hypothesis that the sum of the signs of the differences between temporally successive data is significantly different from zero. Flow-adjustment was accomplished by performing the seasonal Kendall test on the residuals from a locally weighted scatterplot smoothing (LOWESS) line fitted to the concentration/discharge relation. Seasonal adjustment was accomplished by restricting possible comparisons to residuals of water-quality data collected during the same month, and then summing the test statistics for all 12 months. All censored data were set to half the reporting limit for the seasonal Kendall test.

Trends detected by the seasonal Kendall test were considered significant if they had a p-value less than, or equal to, 0.05, which corresponds to a 95-percent confidence level. If significant, the magnitude of a trend was calculated as the median slope of all possible pairwise comparisons (Schertz and others, 1991).

Streamflow Partitioning

Each water-quality sample was labeled as a "base-flow" or "stormflow" sample to assist in the interpretation of the water-quality data and trend estimates. Daily base flow and stormflow were estimated at each station for the entire sampling period by use of the streamflow-partitioning program PART, which is described by Rutledge (1993). Water-quality samples were then labeled as base-flow samples if, on the day on which they were collected, base flow constituted at least 70 percent of the total streamflow. Otherwise, the sample was labeled as a stormflow sample.

Quality Assurance and Quality Control

A quality-assurance and quality-control (QA/QC) plan was developed for the Fall Line monitoring program to ensure the quality of data collected and analyzed for this study; copies of the QA/QC plan are on file at the Virginia District office of the USGS in Richmond, Va. The QA/QC plan includes the following: (1) A field component to ensure that water-quality samples were representative of river conditions; and (2) a laboratory component to assess the variance, accuracy, and bias of analytical results. A comprehensive discussion of quality-assurance results from July 1988 through June 1995 is presented in appendix A.

TRENDS IN NUTRIENTS AND SUSPENDED SOLIDS

Trend analysis for concentration and load was conducted on data collected during 1988–95 for the James and Rappahannock River monitoring stations, and on 1989–95 data for the Appomattox, Pamunkey, and Mattaponi River monitoring stations. Constituents for which trends were estimated include total nitrogen, total Kjeldahl nitrogen, dissolved nitrite-plus-nitrate nitrogen, total phosphorus, and total suspended solids. Flow-adjusted trends detected by multivariate regression and the seasonal Kendall test are presented in table 2, and flow-adjusted trends detected by regression are illustrated in figure 3. For comparison of water-quality characteristics between the five river basins, summary statistics of constituent load and concentration are presented in appendix B.

Time-series plots of concentrations with the corresponding LOWESS line are presented for those constituents that exhibited a significant trend in concentration and load. The LOWESS line is useful for displaying trends that might not be obvious from the raw water-quality data; however, these plots are not flow adjusted and the computations used to generate the LOWESS line are independent of those used to estimate the trends presented in table 2. Where appropriate, the time-series plots of base-flow and stormflow samples are displayed separately.

Also displayed are time-series plots of flow-adjusted residuals of the concentration/discharge regression, which are more useful for examining flow-adjusted trends than time-series plots of the concentration data. The time-series residual plots are prepared by performing a least-squares regression of the natural logarithm of discharge against time, regressing the natural logarithm of constituent concentration against the residuals of the first regression, and then plotting the residuals of the second regression against time with a LOWESS line. Trends in flow-adjusted concentration/discharge residuals are similar, but not identical, to trends calculated by the multivariate regression model.

The regression method was more likely to detect a significant trend in concentration and load than the seasonal Kendall test. Of the nine trends detected by regression and considered significant at the 95-percent confidence level, only three also were considered significant at this level by the seasonal Kendall test (table 2). The two methods agreed on the direction of the three trend results. Interpretation of trends in this section is based mostly on the results of the regression method.

Table 2. Flow-adjusted trends in concentration and load of selected constituents at the Fall Line monitoring stations in Virginia

[Trends expressed as percent change in constituent concentration during the sampling period; trends in shaded areas are considered significant at the 95-percent confidence level corresponding to a *p*-value less than 0.05]

James River at Cartersville, Va. **Trend period: July 1988 through June 1995**

Water-quality constituent	Trend from regression	*p*-value from regression	Trend from seasonal Kendall test	*p*-value from seasonal Kendall test
Total nitrogen	−9	0.196	−11	0.340
Total Kjeldahl nitrogen	−18	.075	−6	.447
Dissolved nitrite-plus-nitrate nitrogen	−6	.430	−9	.395
Total phosphorus	−29	.003	−13	.561
Total suspended solids	−12	.425	0	.964

Rappahannock River near Fredericksburg, Va. **Trend period: July 1988 through June 1995**

Water-quality constituent	Trend from regression	*p*-value from regression	Trend from seasonal Kendall test	*p*-value from seasonal Kendall test
Total nitrogen	−27	0.000	−20	0.261
Total Kjeldahl nitrogen	−29	.003	−21	.037
Dissolved nitrite-plus-nitrate nitrogen	−29	.031	−16	.182
Total phosphorus	−24	.069	−24	.070
Total suspended solids	−48	.004	−16	.043

Appomattox River at Matoaca, Va. **Trend period: July 1989 through June 1995**

Water-quality constituent	Trend from regression	*p*-value from regression	Trend from seasonal Kendall test	*p*-value from seasonal Kendall test
Total nitrogen	+6	0.337	+15	0.093
Total Kjeldahl nitrogen	+16	.022	+9	.212
Dissolved nitrite-plus-nitrate nitrogen	−19	.075	+30	.303
Total phosphorus	+23	.025	+32	.255
Total suspended solids	+18	.163	−22	.357

Table 2. Flow-adjusted trends in concentration and load of selected constituents at the Fall Line monitoring stations in Virginia—Continued

[Trends expressed as percent change in constituent concentration during the sampling period; trends in shaded areas are considered significant at the 95-percent confidence level corresponding to a p-value less than 0.05]

Pamunkey River near Hanover, Va.		**Trend period: July 1989 through June 1995**		
Water-quality constituent	**Trend from regression**	***p*-value from regression**	**Trend from seasonal Kendall test**	***p*-value from seasonal Kendall test**
Total nitrogen	+5	0.401	−5	0.871
Total Kjeldahl nitrogen	+4	.600	−7	.704
Dissolved nitrite-plus-nitrate nitrogen	+9	.269	+26	.175
Total phosphorus	+46	.000	+31	.082
Total suspended solids	+37	.075	−40	.704

Mattaponi River near Beulahville, Va.		**Trend period: October 1989 through June 1995[1]**		
Water-quality constituent	**Trend from regression**	***p*-value from regression**	**Trend from seasonal Kendall test**	***p*-value from seasonal Kendall test**
Total nitrogen	+3	0.533	−5	0.819
Total Kjeldahl nitrogen	+11	.081	−4	.481
Dissolved nitrite-plus-nitrate nitrogen	−33	.000	−55	.000
Total phosphorus	+12	.165	−6	.871
Total suspended solids	−11	.501	−37	.093

[1] Though sampling began at the Mattaponi River in September 1989, discharge data was not available until October 1989.

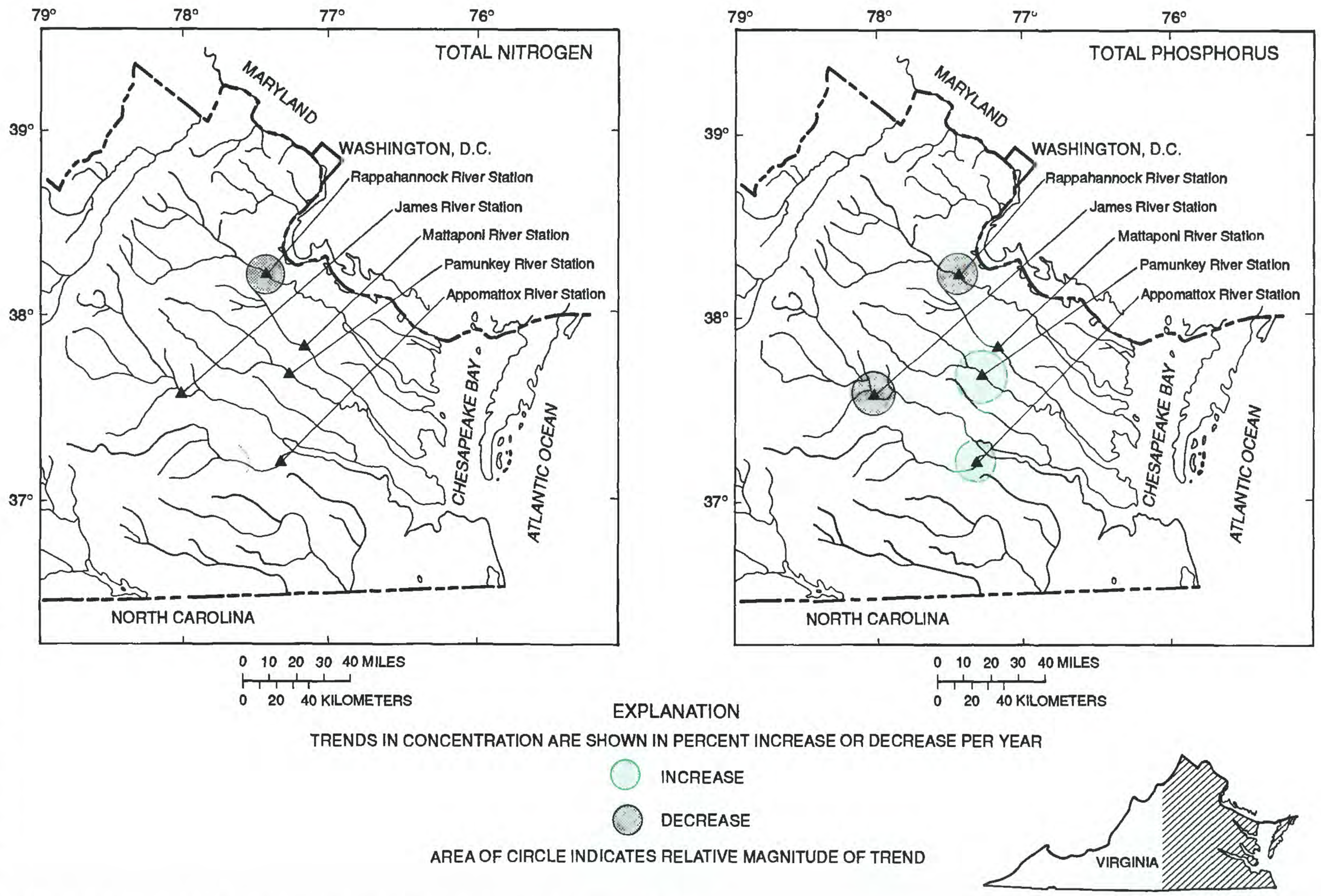

Figure 3. Significant trends in total nitrogen and total phosphorus for the period of study.

James River

No significant flow-adjusted trend in total nitrogen concentration was detected at the James River monitoring station (table 2). The regression model did detect a slight decrease in total nitrogen concentration in base flow caused by a 37 percent decrease in total Kjeldahl nitrogen (TKN) concentration in base flow; the 18 percent decrease in overall TKN concentration is considered significant at the 90-percent confidence level but not at the 95-percent confidence level. This decrease was not large enough to cause an overall trend in total nitrogen concentration. The cause of the decrease in TKN concentration in base flow is unclear; estimates of total nitrogen loads from point sources delivered to the Fall Line on the James River indicate an increase of approximately 20 percent during 1989–94 (Virginia Department of Environmental Quality, written commun., 1996). The decrease in base-flow TKN concentration might be caused by decreased nitrogen concentration in ground-water discharge, which in turn might be related to reductions in total nitrogen load contributed by agriculture or silviculture to the James River.

A significant downward flow-adjusted trend in total phosphorus concentration (–29 percent) was detected by the regression model at the James River monitoring station for the period July 1988 through June 1995 (table 2). A time-series plot of total phosphorus concentration in base flow and stormflow (fig. 4*A*) shows little trend in stormflow concentration, but shows a marked decrease in total phosphorus concentration in base flow during late 1988–91, and then a leveling-off, or slight increase, for the remainder of the sampling period. Similarly, a time-series plot of flow-adjusted residuals from the concentration/discharge regression (fig. 4*B*) shows a dramatic decrease during 1988–90, and then a leveling-off. No significant trends were detected by limiting the model input data to stormflow samples, or by limiting the model input data to samples collected from January 1, 1990 through June 30, 1995.

The large flow-adjusted trend in total phosphorus concentration for the sampling period appears to be mostly owing to a dramatic decrease in dissolved orthophosphorus concentration in base flow during 1988–90. The most important cause for this decrease is the Statewide phosphate detergent ban that went into effect in 1988. About 90 Mgal/d of treated municipal and industrial wastewater enters the James River above the monitoring station (table 1), and point-source total phosphorus load to the James River decreased more than 30 percent during 1985–89 (Virginia Department of Environmental Quality, written commun., 1996). Point-source total phosphorus loads, however, increased during 1990–94, with the 1994 level approaching the 1985 level (Virginia Department of Environmental Quality, written commun., 1994). Therefore, increases in point-source load may be partially erasing the improvements caused by the detergent ban.

The lack of trends in runoff-associated constituents, such as total suspended solids and nutrients in stormflow, suggests that the contribution of nutrients and sediment from nonpoint sources, such as agricultural and forested land, did not significantly change during the sampling period. The James River Basin has the lowest percentage of agricultural land use upstream from the monitoring station (about 23 percent) of the five basins (table 1); thus, the effect of best-management practices (BMP's) may be masked by contributions from other nonpoint sources, or offset by increasing development. In addition, BMP's that reduce nitrogen concentration in ground water may take many years to affect water quality in the James River due to low rates of ground-water flow.

Rappahannock River

The regression model detected significant downward flow-adjusted trends in concentrations of total nitrogen (–27 percent), TKN (–29 percent), dissolved nitrite-plus-nitrate nitrogen (–29 percent), and total suspended solids (–48 percent) at the Rappahannock River monitoring station (table 2) from July 1988 through June 1995. The seasonal Kendall test detected a significant decrease in TKN concentration and load for this same period. The regression model also detected a –24 percent flow-adjusted trend in total phosphorus concentration, which was significant at the 90-percent confidence level but not at the 95-percent confidence level (*p*-value = 0.07).

Time-series plots of constituent concentrations and flow-adjusted residuals of the concentration/discharge relations clearly illustrate the trends in total nitrogen (fig. 5), total Kjeldahl nitrogen (fig. 6), dissolved nitrite-plus-nitrate nitrogen (fig. 7), total phosphorus (fig. 8), and total suspended solids (fig. 9) for the sampling period. Flow-adjusted trend in dissolved nitrite-plus-nitrate nitrogen concentration was upward during the first 3 years of the sampling period, then became downward, resulting in an overall decrease for this constituent.

The Rappahannock River Basin has the largest percentage of agricultural land use upstream from the monitoring station (about 44 percent) of the five basins (table 1), and nonpoint sources contribute the majority of nutrient loads from this basin (Belval and others, 1995). Decreases in nutrients probably were caused by reduced runoff of particulate and dissolved nutrients from nonpoint sources, such as agricultural and silvicultural land. The large flow-adjusted decrease in total suspended solids concentration suggests that rates of soil erosion decreased during the sampling period, possibly resulting from the implementation of BMP's.

The Virginia Department of Conservation and Recreation estimates that between 1985 and 1993 there was a reduction in nitrogen (−11.2 percent) and in phosphorus (−17.5 percent) from nonpoint sources (Virginia Department of Conservation and Recreation, written commun., 1996) in the entire Rappahannock River Basin due to the implementation of different BMP's, including conservation tillage, nutrient management, highly erodible land retirement, and forest harvesting practices. Similar nutrient reductions, however, have been predicted for other basins in Virginia where no dramatic improvement in water quality has been observed. It is unknown which basin characteristics (for example, slope, land use, or percentage of land affected by BMP's) might be responsible for the unique response of the Rappahannock River to BMP's, if these are a cause of the observed trends. Despite the reductions in nutrient and sediment concentrations in the Rappahannock River Basin, this basin still has the highest yield of total nitrogen, total phosphorus, and total suspended solids of the five Virginia river basins (Belval and others, 1995).

Appomattox River

The regression model detected significant upward flow-adjusted trends in concentration and load of TKN (+16 percent) and total phosphorus (+23 percent) from July 1989 through June 1995 at the Appomattox River monitoring station (table 2). Dissolved nitrite-plus-nitrate nitrogen showed a decrease (−19 percent) that was significant at the 90-percent confidence level but not the 95-percent confidence level (table 2). The model detected no significant trend in total suspended solids, and the seasonal Kendall test detected no significant trends in any constituent.

Time-series plots of TKN concentration (fig. 10) and total phosphorus concentration (fig. 11) show a similar pattern. Constituent concentrations increased during the first part of the sampling period, and then decreased toward the end of the sampling period. For example, total phosphorus concentration increased during 1989–93, with the highest concentration in 1993, and then decreased during 1993–95 (fig. 11*A*). Similarly, a time-series plot of the flow-adjusted residuals of the concentration/discharge regression (fig. 11*B*) shows that flow-adjusted total phosphorus concentration peaked by 1993 and actually decreased during 1993–95.

The causes of trends in TKN and total phosphorus in the Appomattox River are unclear. The only major point source upstream of the monitoring station is a treatment plant at Farmville which releases about 1.1 Mgal/d municipal wastewater (table 1); this plant probably does not have a large effect on nutrient concentrations at the Fall Line monitoring station. Biogeochemical processes in Lake Chesdin, on the other hand, may strongly affect water quality at the monitoring station. The marginally significant decrease in dissolved nitrite-plus-nitrate nitrogen for the sampling period suggests that increased uptake of this constituent by phytoplankton could be responsible for the increase in TKN, with no net effect on total nitrogen concentration. The similarity in temporal pattern of TKN and total phosphorus suggests that trends in both constituents might have been caused by a trend in some suspended material, even though no significant trend in suspended solids was detected.

Pamunkey River

The regression model detected no trends in nitrogen species at the Pamunkey River monitoring station from July 1989 through June 1995. Total phosphorus concentration, however, increased about 46 percent (table 2). This trend is more pronounced in base-flow samples than in stormflow samples, as revealed in time-series plots of both base-flow and stormflow total phosphorus concentration (fig. 12*A*). A similar flow adjusted trend in total suspended solids (+37 percent) was considered significant at the 90- but not the 95-percent confidence level. Visual inspection of dissolved orthophosphate concentration suggests that increases in this constituent are at least partly responsible for the increase in total phosphorus. A time-series plot of flow-adjusted residuals of the total phosphorus concentration/discharge regression (fig. 12*B*) shows that the flow-adjusted total phosphorus concentration increased during 1989–92, then leveled off.

Trends in concentration of nutrients in base flow usually are caused by point source or ground-water contributions to the river. Estimates of point-source loads delivered to the Fall Line in the York River Basin (most of which come from the Pamunkey River Basin) suggest that point-source phosphorus load did not increase during 1989–94 (Virginia Department of Environmental Quality, written commun., 1996). The increase of total phosphorus in base flow, therefore, may be caused by undocumented point sources, or by nonpoint sources such as agriculture or increased land development. Increased development in the basin, such as that in Hanover County, around Lake Anna, and along the I-95 corridor, may be contributing additional phosphorus to the river, and may also be causing the marginally significant trend in total suspended solids concentration.

Mattaponi River

The regression model detected an upward flow-adjusted trend in TKN (+11 percent, significant at the 90- but not the 95-percent confidence level) from October 1989 through June 1995 at the Mattaponi River monitoring station (table 2). Conversely, both the regression model and the seasonal Kendall test detected downward flow-adjusted trends in dissolved nitrite-plus-nitrate nitrogen concentration (–33 and –55 percent, respectively). Trends in these two nitrogen species seemed to offset each other, so that there was no significant change in the concentration and load of total nitrogen. No significant flow-adjusted trends were detected in total phosphorus or total suspended solids concentrations and loads at this site.

The upward trend in TKN is more pronounced in base flow than in stormflow (fig. 13*A*). Similarly, the downward flow-adjusted trend in dissolved nitrite-plus-nitrate nitrogen concentration is more pronounced in base-flow samples than in stormflow samples, as illustrated by a time-series residual plot (fig. 14*B*) though the decrease is observed in both kinds of samples. Only about 0.1 Mgal/d wastewater discharges to the Mattaponi River upstream of the monitoring station (table 1); therefore, trends in point-source contributions probably did not cause the trends in nitrogen species. Concentrations of both TKN and dissolved nitrite-plus-nitrate nitrogen show significant seasonal variations at the Mattaponi River monitoring station (Belval and others, 1995). The trends in both nitrogen species may have been caused by increased uptake of dissolved inorganic nitrogen by phytoplankton (especially algae), which converts nitrate to organic nitrogen forms.

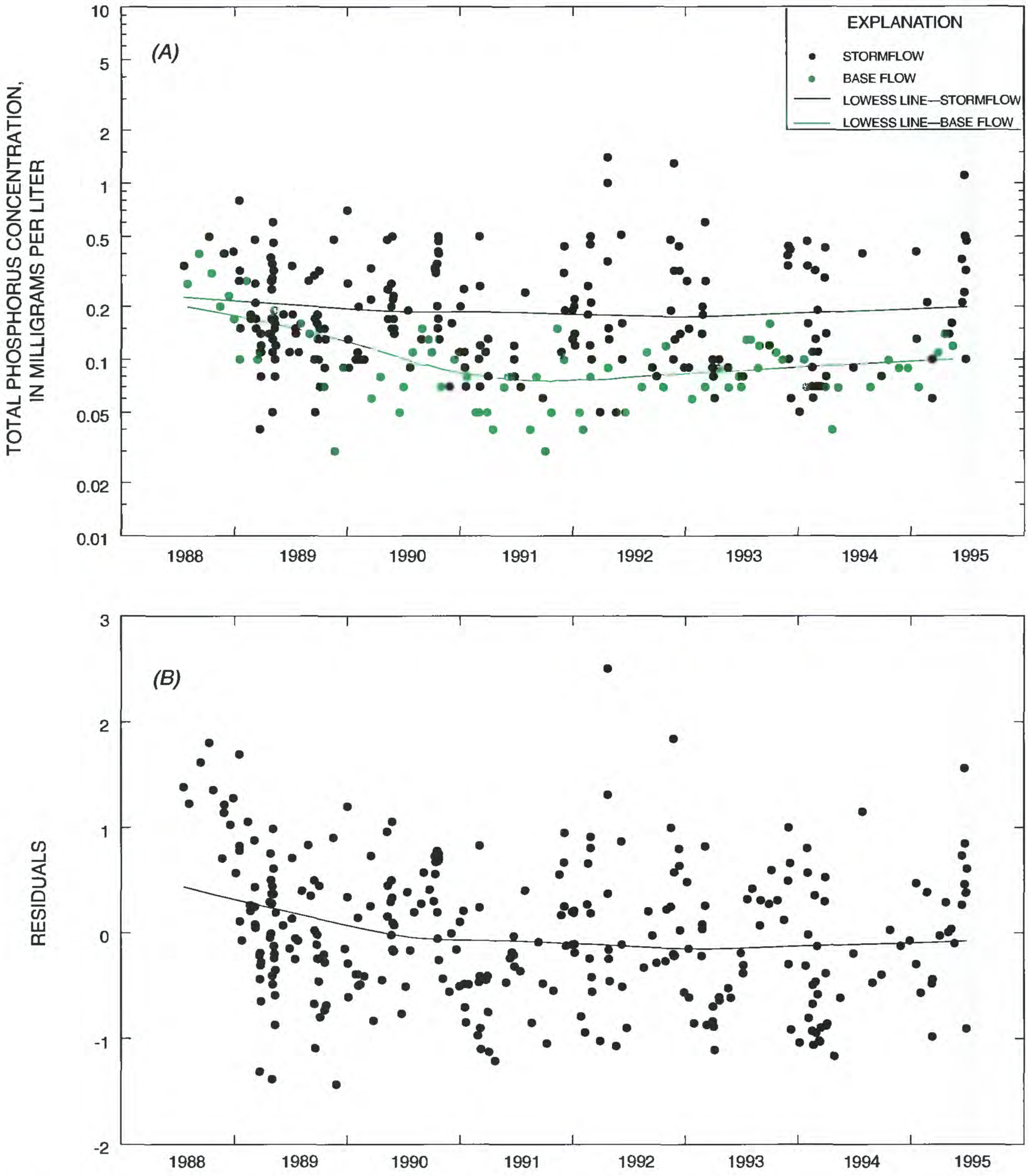

Figure 4. Relation of total phosphorus concentration in base flow and in stormflow *(A)*, and flow-adjusted residuals of the total phosphorus concentration/discharge regression *(B)* to time at the James River monitoring station, Cartersville, Virginia.

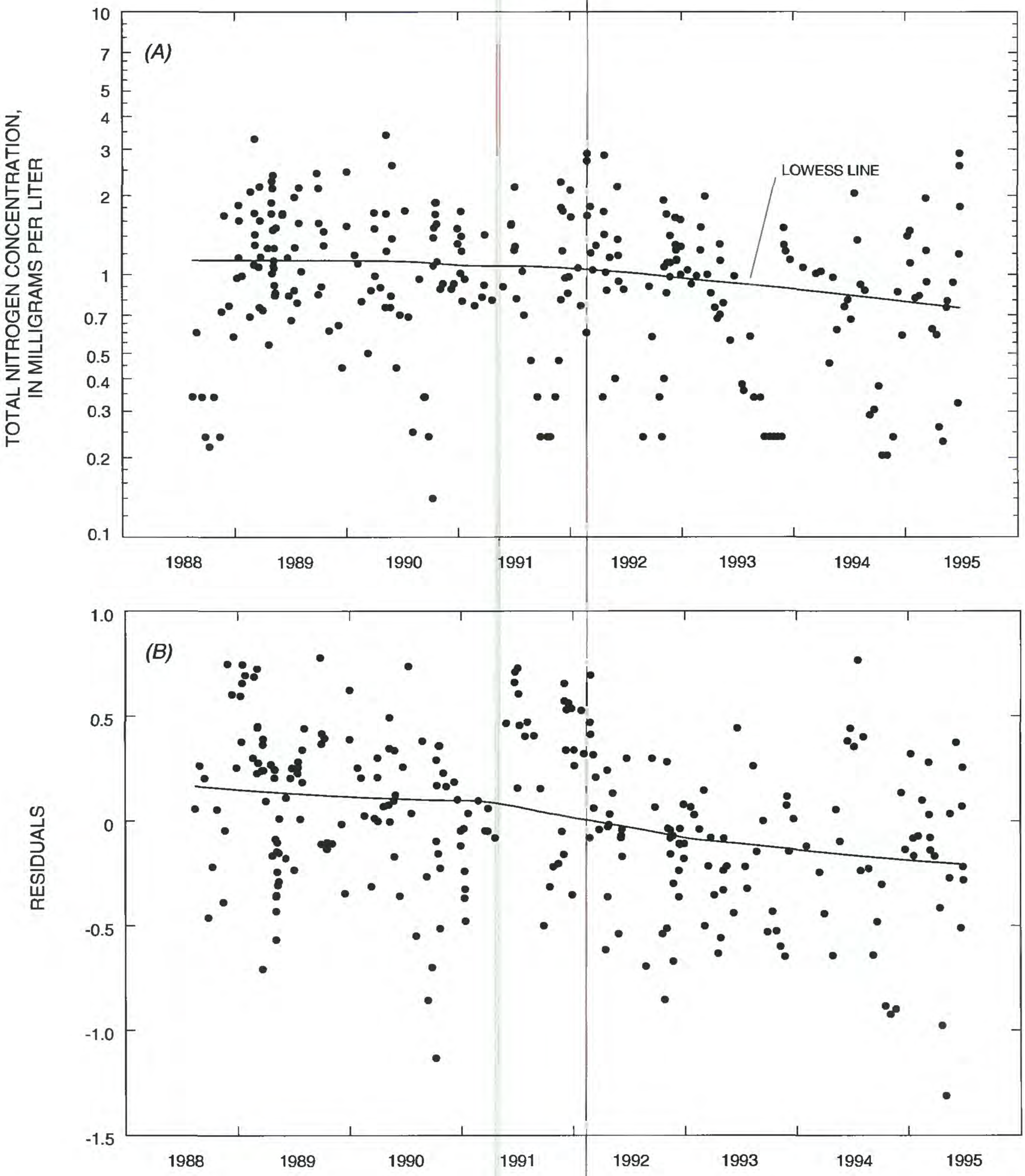

Figure 5. Relation of total nitrogen concentration *(A)*, and flow-adjusted residuals of the total nitrogen concentration/ discharge regression *(B)* to time at the Rappahannock River monitoring station near Fredericksburg, Virginia.

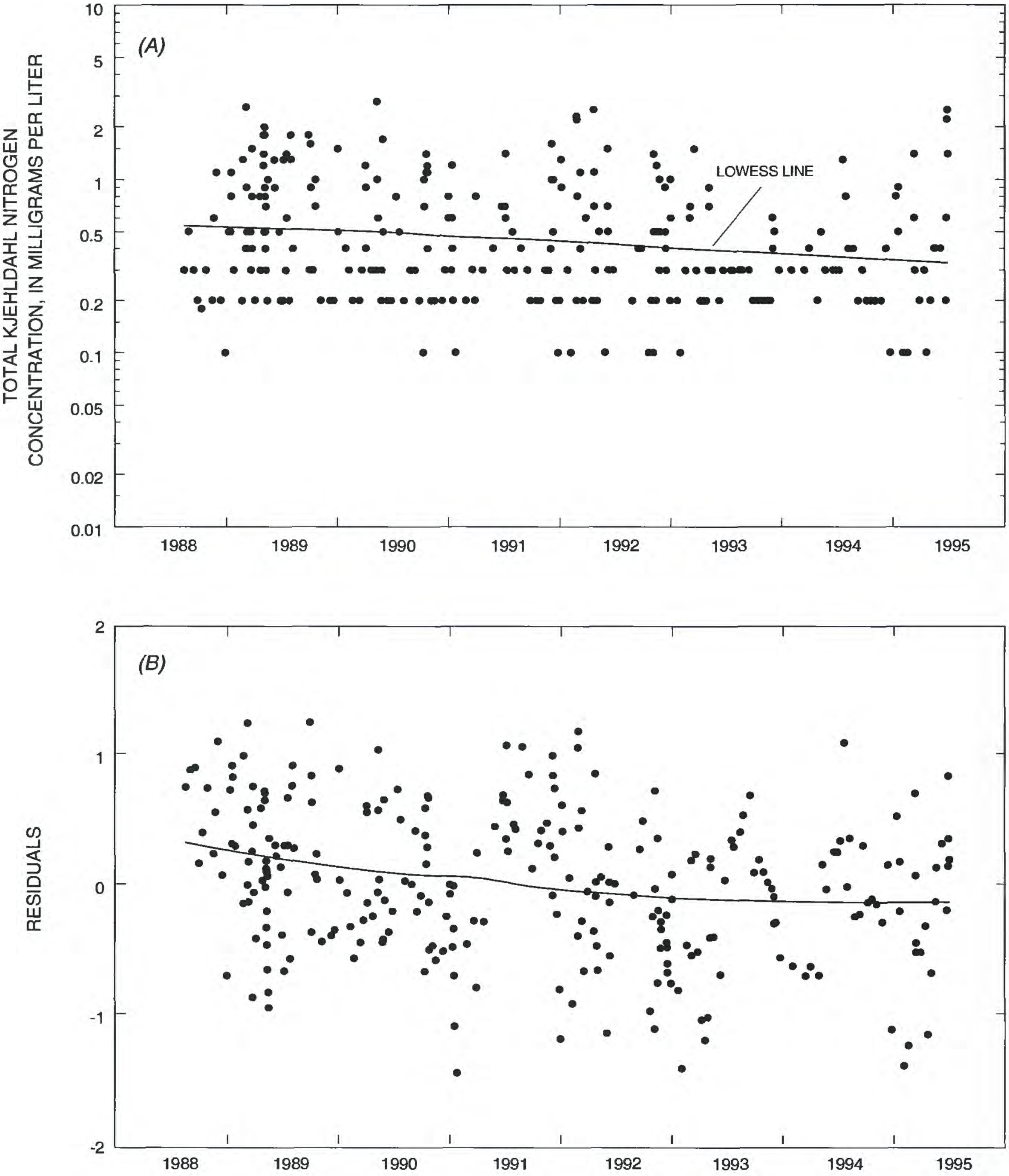

Figure 6. Relation of total Kjeldahl nitrogen concentration *(A)*, and flow-adjusted residuals of the total Kjeldahl nitrogen concentration/discharge regression *(B)* to time at the Rappahannock River monitoring station near Fredericksburg, Virginia.

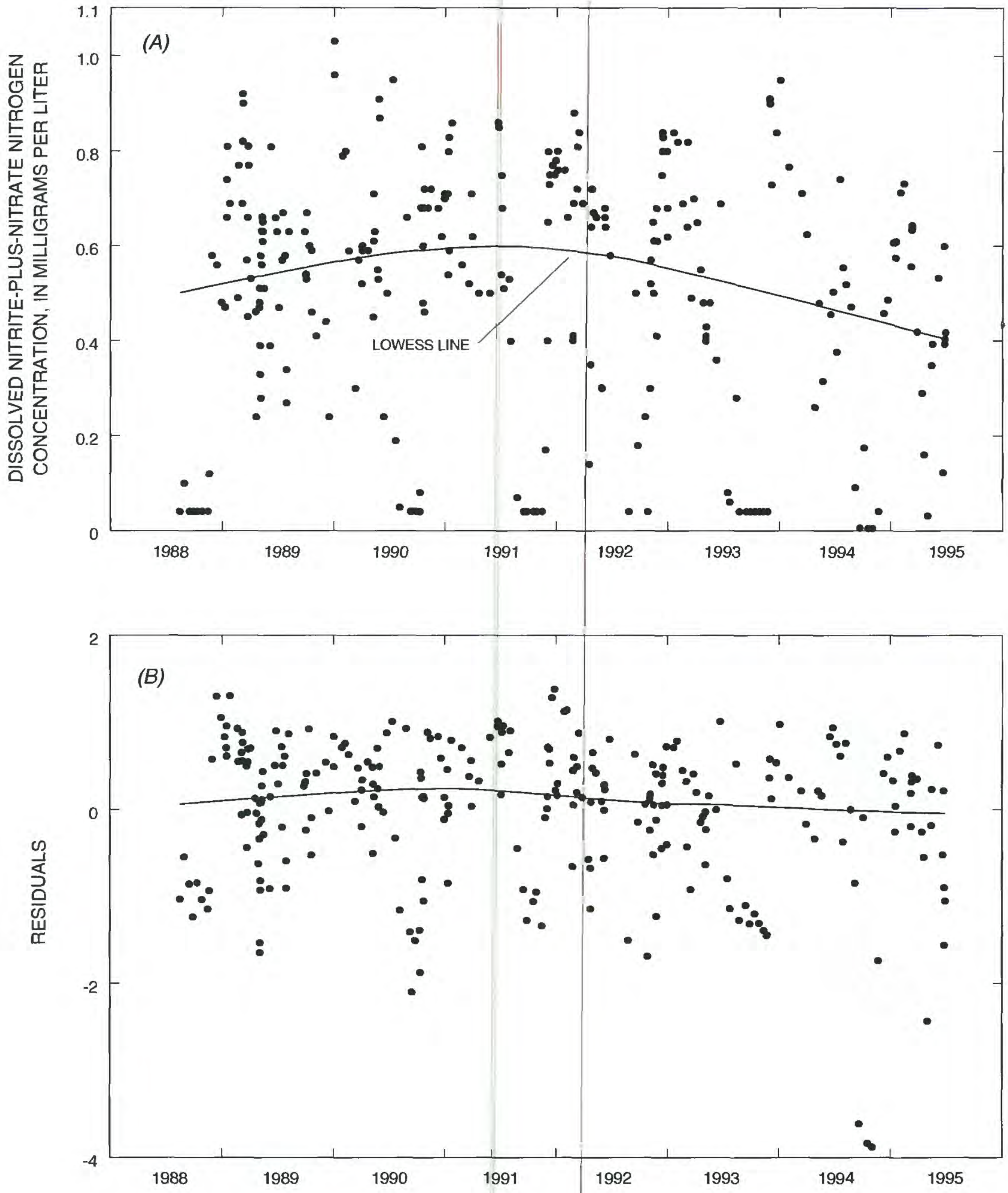

Figure 7. Relation of dissolved nitrite-plus-nitrate nitrogen concentration *(A)*, and flow-adjusted residuals of the dissolved nitrite-plus-nitrate nitrogen concentration/discharge regression *(B)* to time at the Rappahannock River monitoring station near Fredericksburg, Virginia.

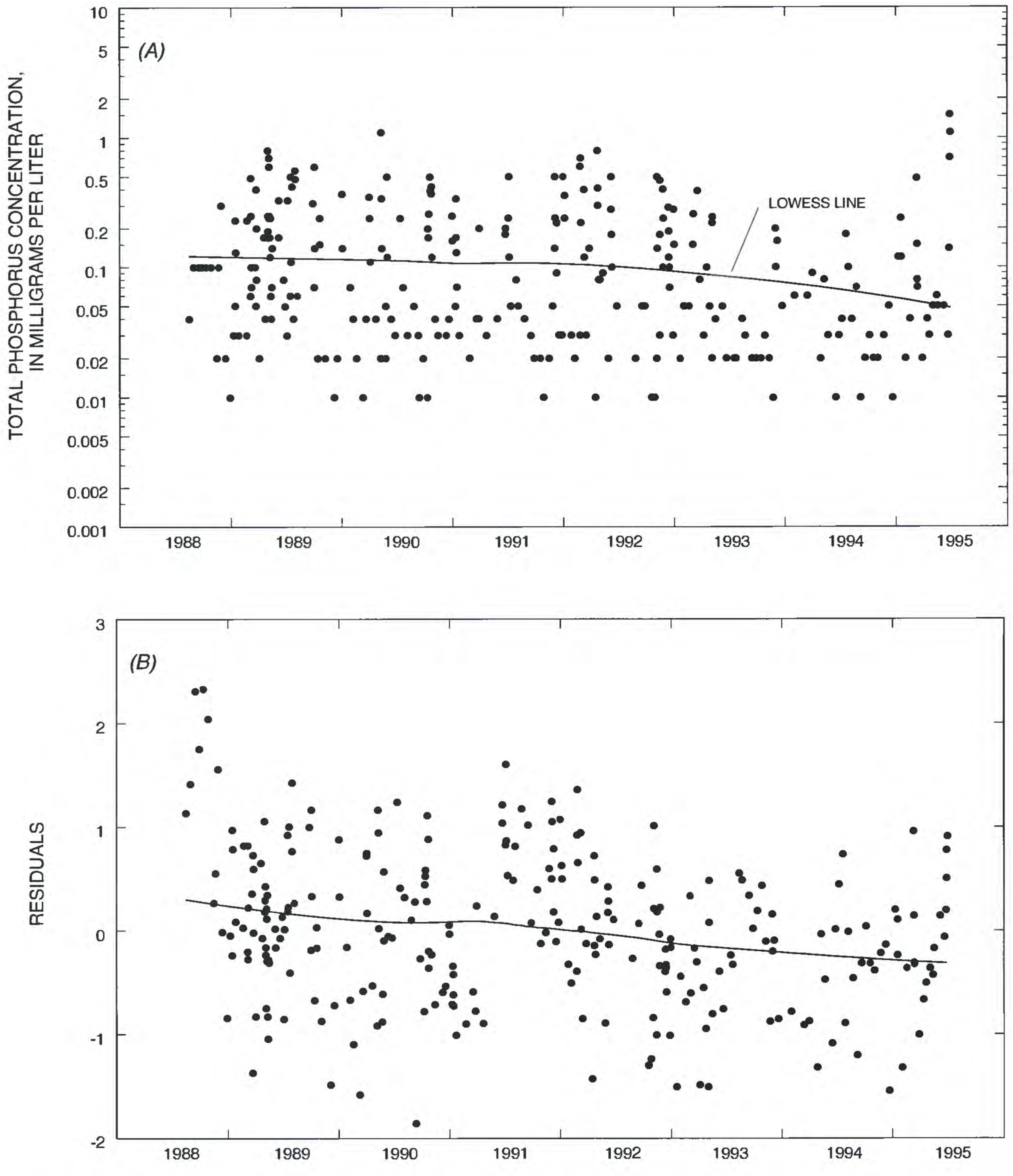

Figure 8. Relation of total phosphorus concentration *(A)*, and flow-adjusted residuals of the total phosphorus concentration/discharge regression *(B)* to time at the Rappahannock River monitoring station near Fredericksburg, Virginia.

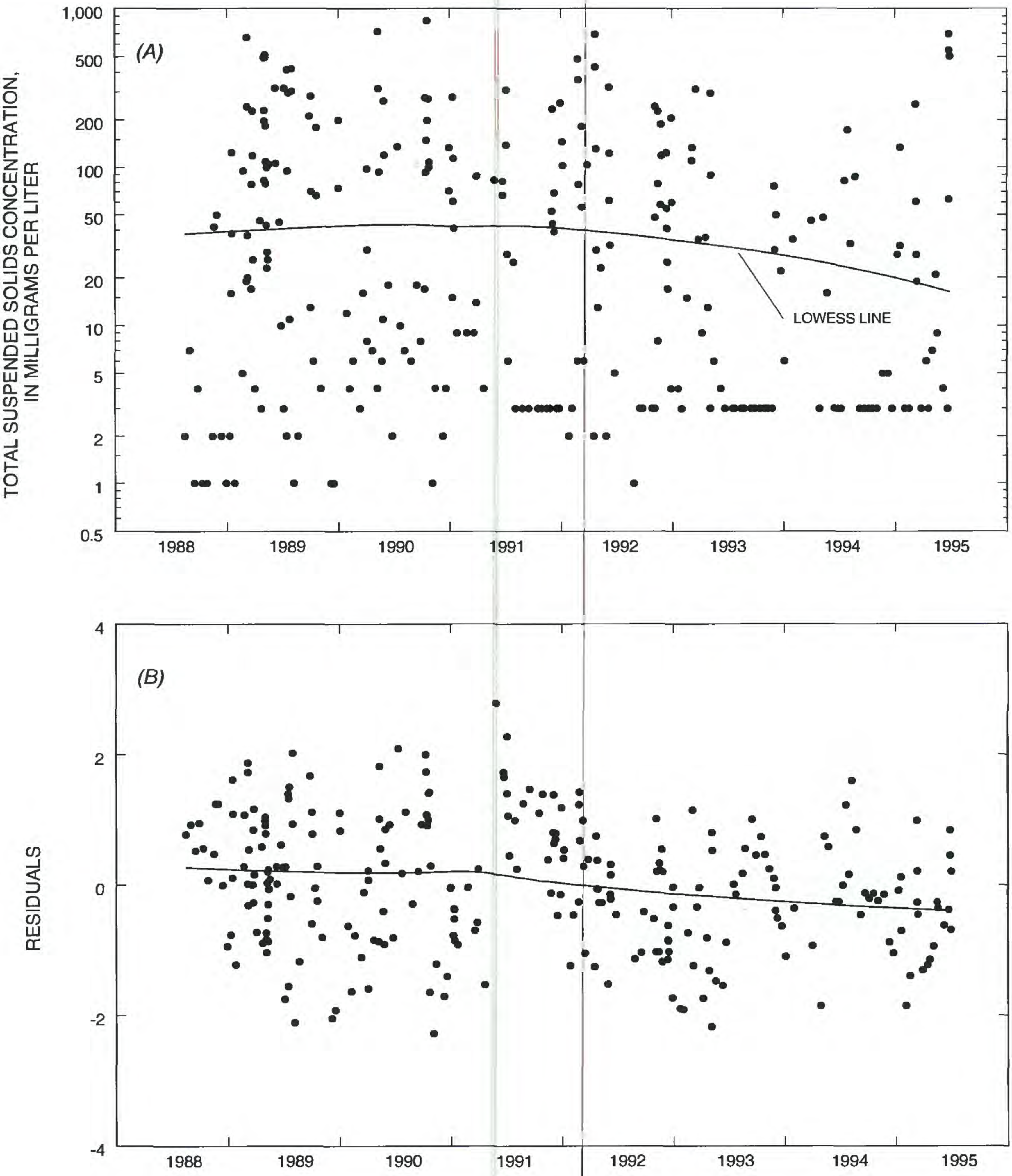

Figure 9. Relation of total suspended solids concentration *(A)*, and flow-adjusted residuals of the total suspended solids concentration/discharge regression *(B)* to time at the Rappahannock River monitoring station near Fredericksburg, Virginia.

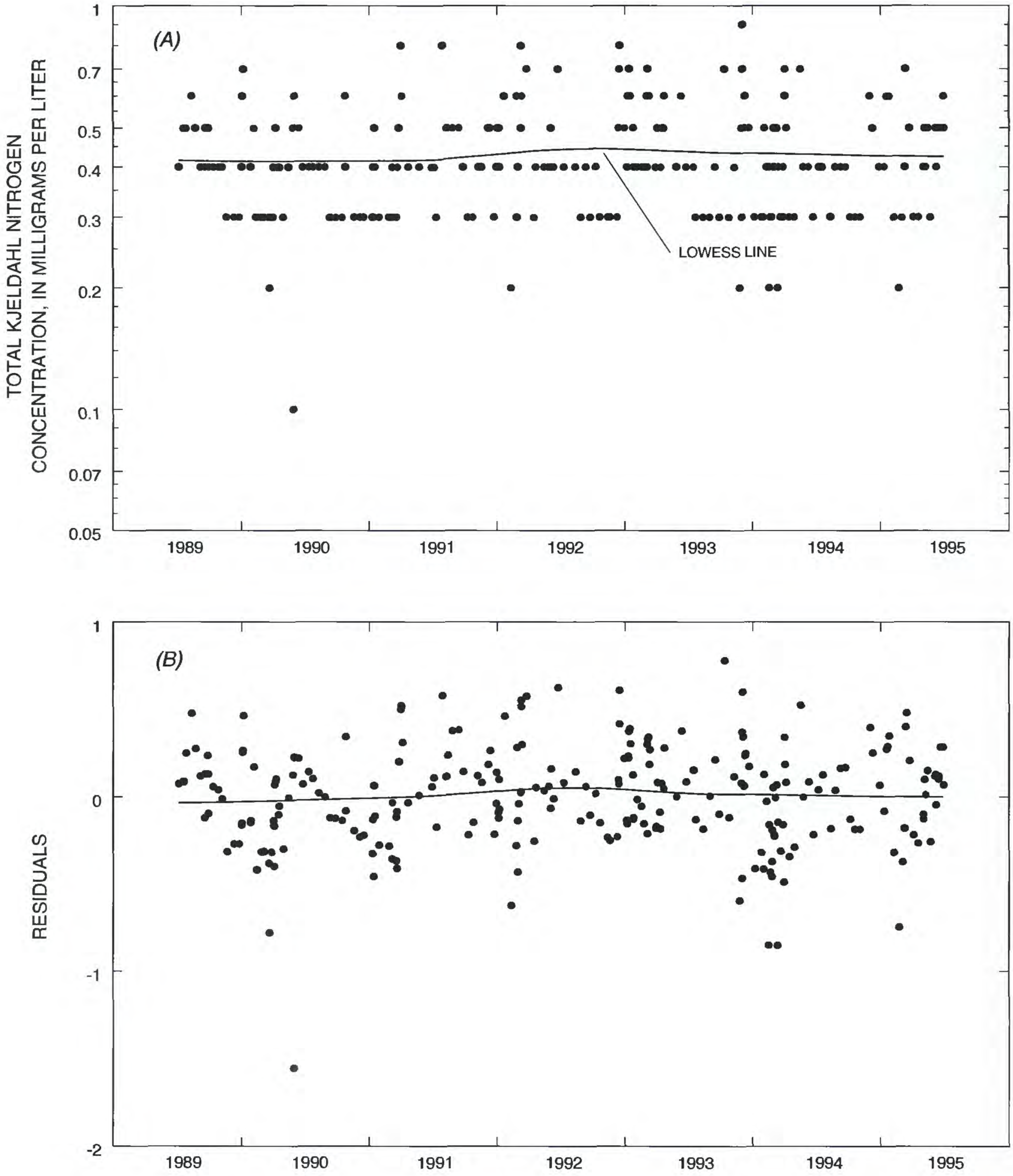

Figure 10. Relation of total Kjeldahl nitrogen concentration *(A)*, and flow-adjusted residuals of the total Kjeldahl nitrogen concentration/discharge regression *(B)* to time at the Appomattox River monitoring station, Matoaca, Virginia.

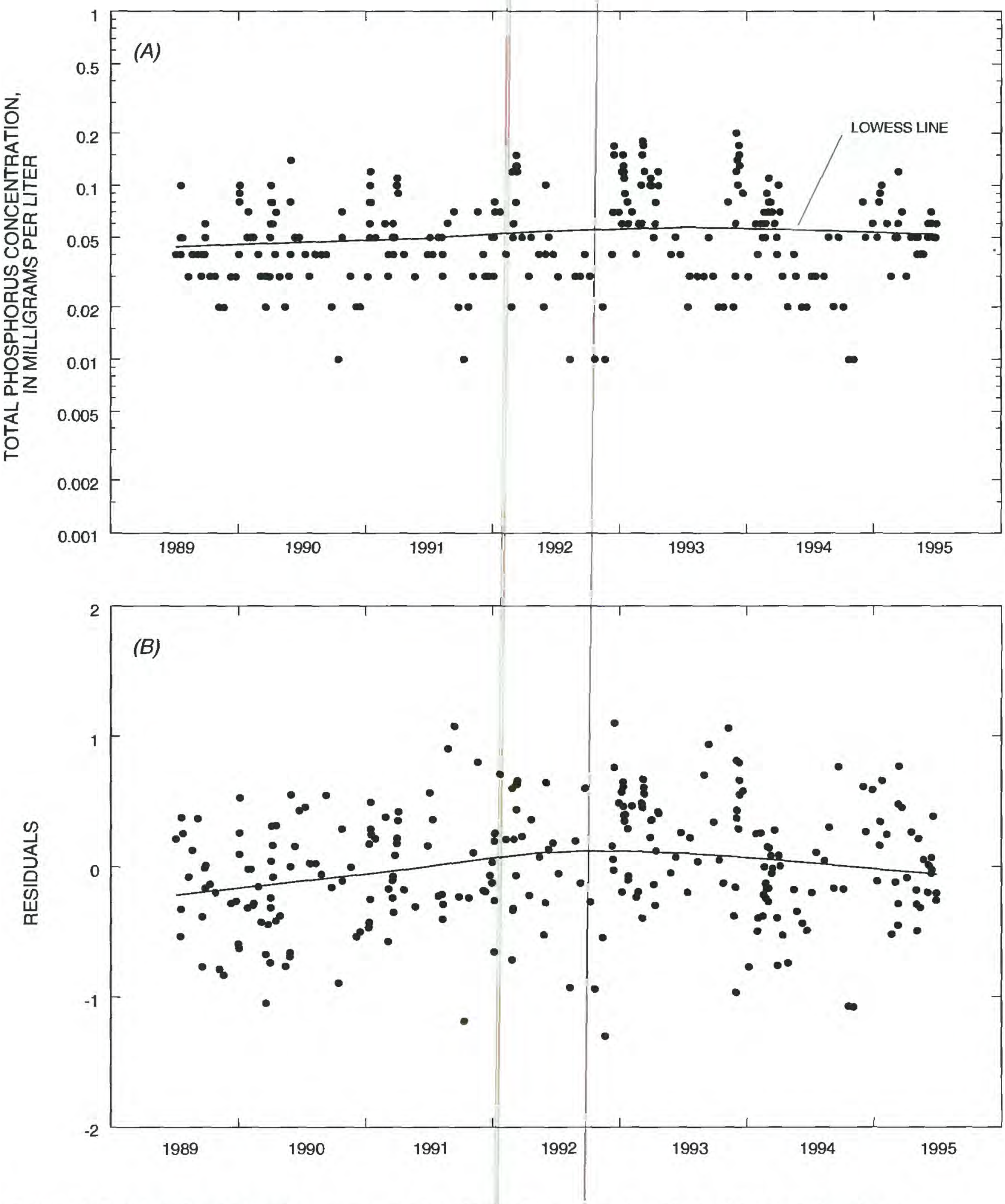

Figure 11. Relation of total phosphorus concentration *(A)*, and flow-adjusted residuals of the total phosphorus concentration/discharge regression *(B)* to time at the Appomattox River monitoring station, Matoaca, Virginia.

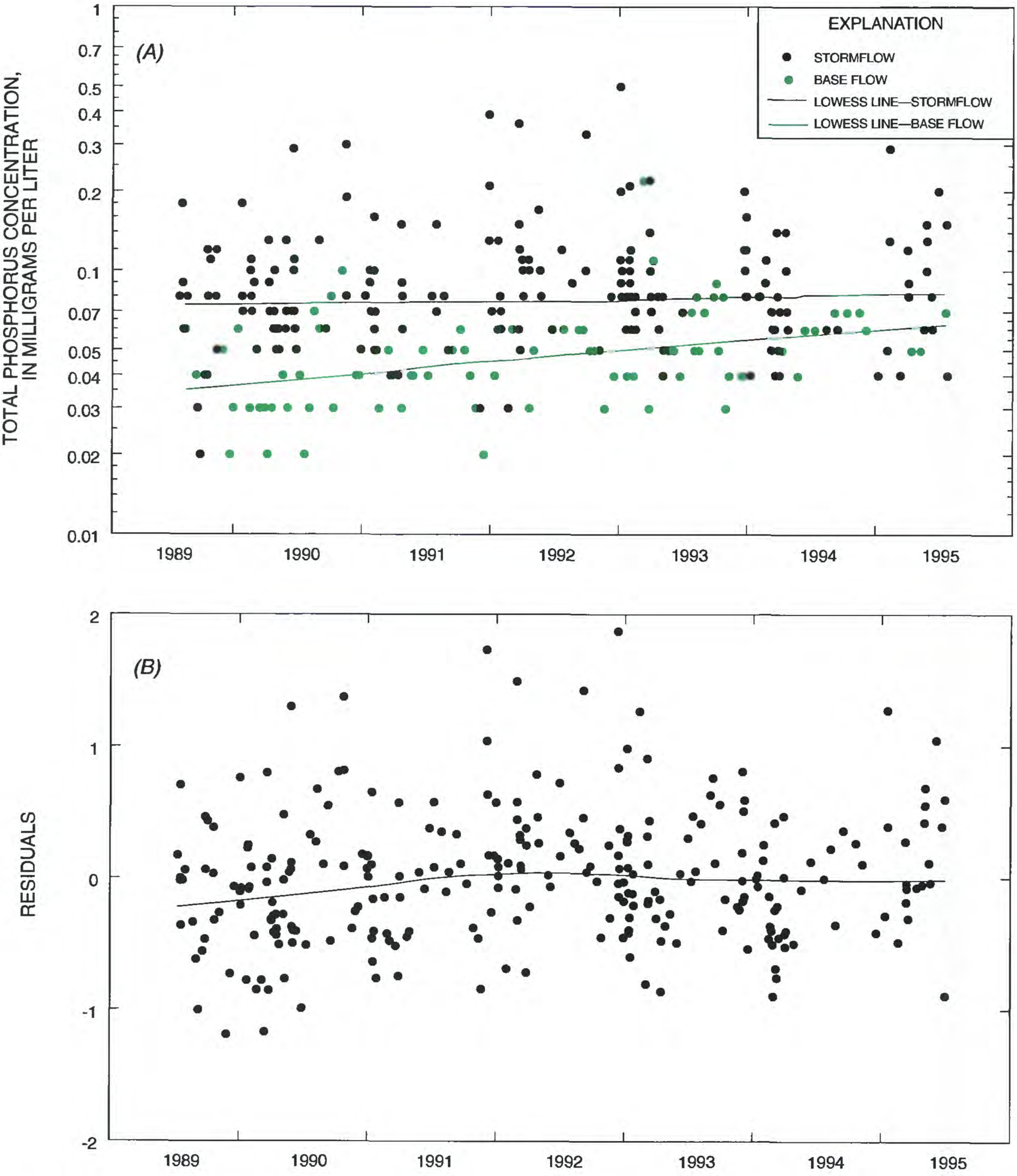

Figure 12. Relation of total phosphorus concentration in base flow and in stormflow *(A)*, and flow-adjusted residuals of the total phosphorus concentration/discharge regression *(B)* to time at the Pamunkey River monitoring station near Hanover, Virginia.

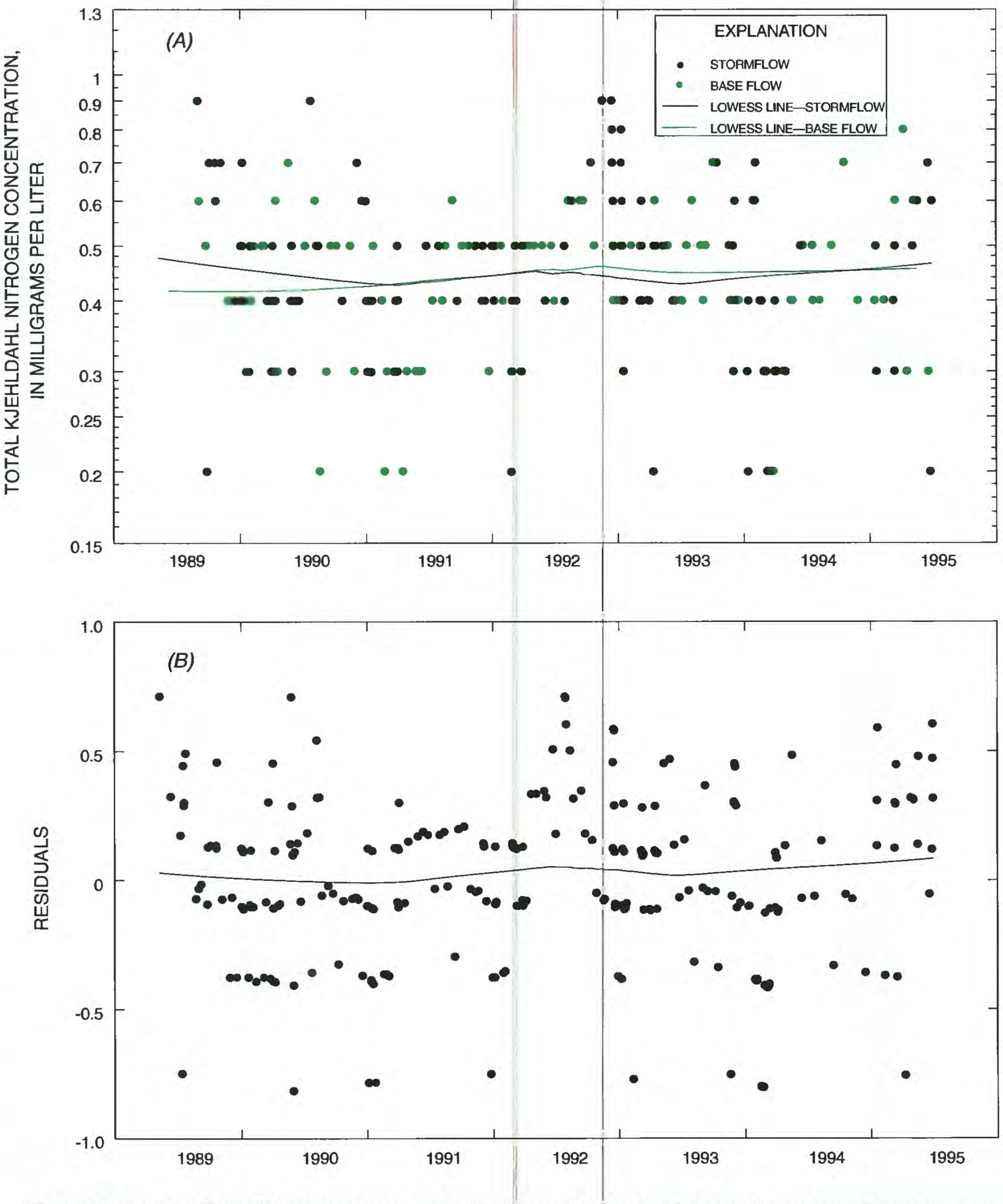

Figure 13. Relation of total Kjeldahl nitrogen concentration in base flow and in stormflow *(A)*, and flow-adjusted residuals of the total Kjeldahl nitrogen concentration/discharge regression *(B)* to time at the Mattaponi River monitoring station near Beulahville, Virginia.

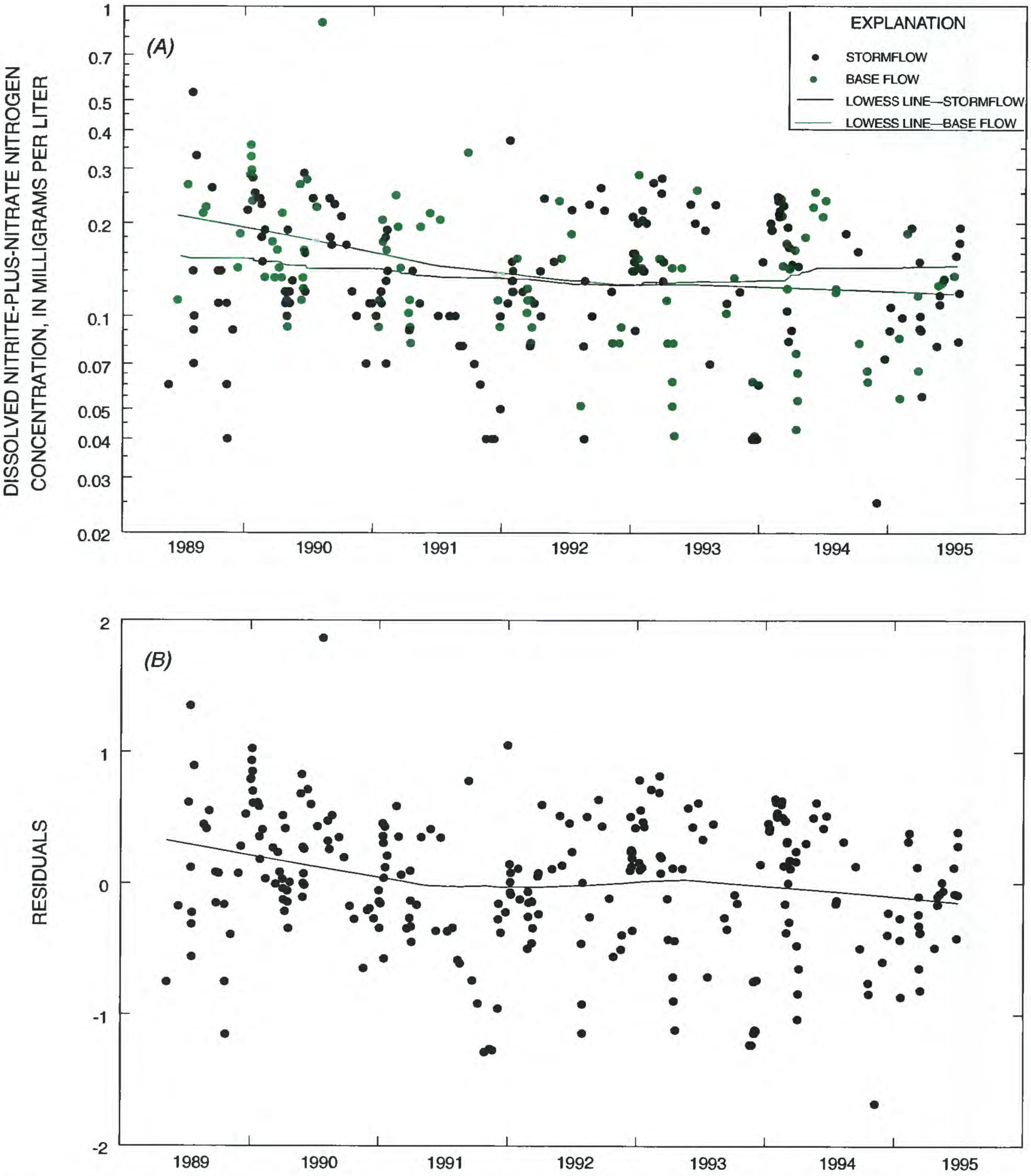

Figure 14. Relation of dissolved nitrite-plus-nitrate nitrogen concentration in base flow and in stormflow *(A)*, and flow-adjusted residuals of the dissolved nitrite-plus-nitrate nitrogen concentration/discharge regression *(B)* to time at the Mattaponi River monitoring station near Beulahville, Virginia.

CONCLUSIONS

The five rivers discussed in this report showed markedly different flow-adjusted trends in nutrients and suspended solids at the Fall Line, between the late 1980's and 1995, that correspond to different basin characteristics. The James River is the only river with a large number of point-source nutrient sources upstream of the Fall Line, and this river responded measurably to reductions in point-source phosphorus loads. The phosphate detergent ban of 1988 probably is responsible for much of the 29 percent decrease in total phosphorus in the James River. Point-source phosphorus loads, however, are once again increasing in this basin, and further reductions in total phosphorus may be dependent on additional nutrient control strategies. No trends in runoff-derived constituents are interpreted for the James River Basin, because the positive effects of BMP's are being (1) masked by contributions from other sources, (2) delayed by ground-water residence time, or (3) offset by increased development or agriculture.

In contrast to the James River, water quality of the Rappahannock River is dominated by nonpoint sources, such as agriculture and silviculture. The consistent decrease of nitrogen, phosphorus, and suspended solids for the sampling period makes the Rappahannock River the "most-improved" of Virginia's monitored tributaries to the non-tidal part of Chesapeake Bay Basin. Management practices may have contributed to the observed decreases; however, the Rappahannock River still has the highest yields of nitrogen, phosphorus, and suspended solids of the five rivers.

Trends in water quality of the Appomattox, Pamunkey, and Mattaponi Rivers were less consistent than trends in the James and Rappahannock Rivers. Total phosphorus concentration increased in both the Appomattox and Pamunkey Rivers, whereas trends in total nitrogen concentration were not observed in the Appomattox and Mattaponi Rivers. In general, none of these three rivers displayed consistent trends in nutrients or suspended solids for the entire sampling period.

Continued monitoring of nutrient concentrations in streams at the Fall Line will improve understanding of the effects of changes in land use, management practices, and point sources on overall water quality. The effects of ground-water residence time on nitrogen concentrations and loads are particularly interesting to monitor; specifically, whether base-flow nitrate concentrations decrease in response to reductions in agricultural nitrogen applications. Trend analysis of water-quality data from the James and Rappahannock River monitoring stations suggests that point-source reductions and BMP's can improve water quality on a basin-wide scale. Future trends in nutrients and suspended solids, however, will depend on the complex interaction of these efforts and the effects of increased population, land development, and agriculture.

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APPENDIXES

APPENDIX A.—QUALITY-ASSURANCE AND QUALITY-CONTROL PROCEDURES AND RESULTS

A quality-assurance/quality-control (QA/QC) plan was developed for the Fall Line monitoring program to ensure the quality of data collected and analyzed for this study. The QA/QC plan includes the following: (1) A field component to ensure that water quality samples were representative of river conditions; and (2) a laboratory component to assess variance and bias of analytical results, as well as verification that clean techniques were used to collect and analyze samples. Much of the discussion of QA/QC procedures presented in this appendix has been taken from the U.S. Geological Survey Water-Resources Investigations Report 95–4258; however, all QA/QC results have been updated to include analysis of data collected through June 1995.

General results.—Results of the field component of the QA/QC plan indicate that representative samples were collected, samples were collected for a range in discharge conditions, and proper sampling techniques and equipment were used by field personnel. Field blank results show a need to identify a source of low-level contamination for dissolved ammonia nitrogen, total phosphorus, and dissolved orthophosphorus.

Results of the laboratory component follow. Duplicate data showed good agreement between samples, therefore no qualification of constituent concentration or load was necessary. Total variance for duplicate samples depends on the concentration range of the constituent of interest, whereas measurement variance depends on the number of ties between sample pairs and the range of constituent concentration. A value of 10 percent, or less for percent of total variance, caused by measurement variance is acceptable for these data. The percent of total variance from measurement variance for seven of the constituents sampled ranged from 0.9 to 7.8 percent. Dissolved ammonia nitrogen showed 25-percent total variance from measurement variance. Concentrations for dissolved ammonia nitrogen showed a small range in total variability because more than half of the data was censored and measurement variability was limited by 62-percent ties between sample pairs. Loads were not calculated for dissolved ammonia nitrogen because of the large percentage of censored data.

Results of the Wilcoxon signed-rank test on laboratory-split samples between Virginia Division of Consolidated Laboratory Services (VDCLS) and the U.S. Geological Survey (USGS) National Water-Quality Laboratory (NWQL) in Arvada, Colo. showed a statistically significant difference between the laboratories for dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, total phosphorus, total organic carbon, and dissolved silica. Investigation revealed that concentration of total organic carbon in storm samples was underestimated by VDCLS during the period August 1988 through February 1992, causing total organic carbon load to also be underestimated. Differences between laboratories for the remaining four constituents had no environmental significance with respect to concentration or load.

Procedures.—The field component of the QA/QC plan consists of documentation of field conditions, collection procedures, and equipment as follows:

1. Water-quality samples were collected according to approved USGS guidelines to ensure that samples were representative of the river cross section (Horowitz and others, 1994). These guidelines ensured the collection of a representative, composite sample from the horizontal and vertical cross section of the river.
2 Sampling criteria based on discharge characteristics were documented to ensure that water-quality samples were collected over a range in discharge conditions. In addition, detailed documentation of field procedures ensured consistency of procedures between field personnel.
3. Proper use of sampling equipment and sample-collection techniques by field personnel was verified through in-house testing of procedures and through comparisons of field- and laboratory-analyzed results.

The laboratory component of the QA/QC plan consisted of the collection of duplicate, laboratory-split, and field blank samples as follows:

1. Duplicate samples document the variance of the analytical results. Duplicate samples were prepared by withdrawing two subsamples of the full-sample volume collected, with both samples being analyzed by VDCLS. The second subsample was disguised as an environmental sample by labeling it with a different time from the first subsample. Approximately ten percent of the samples collected at each site were duplicate samples.
2. Laboratory-split samples document bias in the analytical results. Laboratory-split samples were collected in a similar manner to duplicate samples;

however, one subsample was analyzed by VDCLS and the other subsample was analyzed by NWQL to assess the comparability of results between the two laboratories. Approximately ten percent of the samples collected at each site were laboratory-split samples.

3. Field blank samples document the ability of field personnel to collect a clean sample and/or the laboratory to perform analytical procedures without contaminating the sample. A field blank is prepared by passing carbon-free deionized water through all equipment used to collect and process a sample at the field site. A portion of the blank sample water also passes from the churn through the capsule filter for analysis of dissolved constituents. Approximately two percent of the samples collected at each site during the study period were field blanks.

Quality-assurance samples were collected at all five rivers throughout the period of study. All data were reviewed for transcription errors and corrected. Concentrations below the minimum reporting limit ("censored") were considered equal to the minimum reporting limit for all QA/QC calculations.

Duplicate samples.—The duplicate samples, which provide an indication of variability or spread in the data, were compared by determining total variance, measurement variance, and the percentage of the total variance from measurement variance. Total variance is the variability within the regularly scheduled samples. Total variance equals the sum of the variability in the measurement process and naturally occurring environmental variability. Measurement variance is a measure of the variability between the regularly scheduled sample and a duplicate sample. The source of measurement variability can be either field-collection techniques or laboratory analytical procedures and should ideally be ten percent or less of the total variability. Transformations are often applied to water-quality data to make these data more symmetric. Log-transformation was determined to be inappropriate for these data because of a large percentage of ties, or zero differences, between the regular and duplicate samples.

Eight water-quality constituents were included in the analysis of duplicate samples for this study. Results of variance calculations on raw concentration data for duplicate samples are presented in table A–1.

Total suspended solids has the highest total variance. The naturally occurring variability between base-flow and stormflow samples results in concentration ranges of more than several orders of magnitude for this constituent. Constituents with about half of the concentrations in the range of 4.0 to 11.0 mg/L, such as total organic carbon and dissolved silica, show larger total variability than nitrogen and phosphorus

Table A–1. Results of variance computations for duplicate quality-assurance samples analyzed by the Virginia Division of Consolidated Laboratory Services

[(mg/L)^2, milligrams per liter squared]

Constituent	Total variance (mg/L)^2	Measurement variance (mg/L)^2	Percent of total variance from measurement variance	Percent ties	Percent censored data	Number of sample pairs
Suspended solids, total	17,211	317	1.8	31	12	135
Nitrite-plus-nitrate nitrogen, dissolved	.0469	.0018	3.8	47	5.7	139
Ammonia nitrogen, dissolved	.0008	.0002	25	62	33	138
Kjeldahl nitrogen, total	.2163	.0049	2.3	59	.7	138
Phosphorus, total	.0486	.0014	2.9	51	2.9	138
Orthophosphorus, dissolved	.0031	.00003	1.0	73	19	138
Organic carbon, total	16.48	1.285	7.8	15	0	119
Silica, dissolved	10.54	.0979	.9	64	0	137

species, which generally have concentrations below 1.0 mg/L. Dissolved ammonia nitrogen showed the smallest total variability because of the high percentage of censored data for this constituent (51 percent of the regular sample concentrations were less than, or equal to, the minimum reporting limit).

Measurement variance followed a pattern similar to total variance, where larger variances occurred with high concentration ranges. Tied values, or zero difference between the regular and duplicate sample, showed no variability between the sample pairs. Dissolved orthophosphorus had the highest percentage of tied values between regular and duplicate samples and, therefore, had the lowest measurement variance. The low concentration range for dissolved orthophosphorus (50 percent of the values were from 0.01 to 0.03 mg/L) caused a high percentage of tied values and thus limited the measurement variability. The limiting effect of ties on variability had the greatest impact on nutrient species because of the low concentration ranges of these constituents compared to total suspended solids and total organic carbon. Measurement variance for dissolved silica was small because 64 percent of the 137-sample pairs were ties. Total organic carbon, with only 15-percent ties, has the best estimate of measurement variance of the eight constituents.

The percentage of total variance from measurement variance as shown in table A–1 is not affected by the concentration range of the constituent of interest. The higher the percentage of measurement variance, the greater the effect of laboratory analytical technique on total variance. The high percentage for dissolved ammonia nitrogen, however, is due to the low total variance and measurement variance for this constituent. A value of 10 percent, or less, for percent of total variance from measurement variance is acceptable for these data.

Sample water for both regular and duplicate samples was collected according to USGS guidelines and stored in one churn prior to processing; therefore, the duplicates represent variability in the analysis of identical samples by VDCLS. Concurrent replicate sampling, which quantifies variance in the field sampling process, involves the use of two churns to collect two samples simultaneously. Two verticals are collected at each cross section and are stored separately in two churns. Differences between concurrent replicates could be caused by field collection techniques, short-term variability of in-stream concentrations, and (or) differences in laboratory precision.

Low-level analyses by the VDCLS began January 1, 1994, for the following constituents: dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, and dissolved orthophosphorus. Although the minimum reporting limit was lowered to parts per billion for these constituents, 86 percent of the duplicate data reflects the higher reporting limits. As the percentage of duplicate data analyzed under the new, lower reporting limit increases, measurement variance will also increase because the number of tied values will decrease. Total variance will also increase owing to the lower minimum value.

Laboratory-split samples.—A nonparametric test, the Wilcoxon signed-rank test, was used to analyze the data for laboratory-split and standard-reference samples, which provided an indication of laboratory bias. A nonparametric test was chosen because it computes statistics using the median value of a population. The median value, as opposed to the mean value in parametric tests, was used because it is unaffected by outliers that are common in water-quality data and by data censoring less than 50 percent. The Wilcoxon signed-rank test has more power to detect differences between two groups of paired data in most situations than other nonparametric tests, such as the sign test, and does not require normality of the data.

The null hypothesis associated with the Wilcoxon signed-rank test indicates that for a given constituent the median of the differences between concentration reported by NWQL and the concentration reported by the VDCLS is equal to zero. Probability (p) is the significance level reached by the test, or the probability of incorrectly rejecting the null hypothesis when it is true. If $p > 0.05$ then no statistical difference between laboratories was inferred. If $p \leq 0.05$ then a significant bias by one or both laboratories was indicated. Results of the Wilcoxon signed-rank test for laboratory-split samples, including a two-sided probability value for raw concentrations; the median of the differences between the laboratories (also referred to as median bias), and the highest value used as the minimum reporting limit for each constituent from August 1988 through June 1995 are listed in table A–2.

No statistically significant differences ($p > 0.05$) were found for total suspended solids, total Kjeldahl nitrogen, or dissolved orthophosphorus. A statistically

Table A–2. Results of the Wilcoxon signed-rank test comparing constituent concentration analyzed by the Virginia Division of Consolidated Laboratory Services with constituent concentration analyzed by the National Water-Quality Laboratory

[Two-sided probability values less than, or equal to, 0.05 show a statistical difference between laboratories]

Constituent	Two-sided probability value	Median of differences	Highest reporting limit	Number of sample pairs
Suspended solids, total	0.196	0	3.0	217
Nitrite-plus-nitrate nitrogen, dissolved	.035	.002	.10	228
Ammonia nitrogen, dissolved	.000	−.013	.04	229
Kjeldahl nitrogen, total	.421	0	.20	230
Phosphorus, total	.000	−.01	.01	231
Orthophosphorus, dissolved	.299	0	.01	231
Organic carbon, total	.000	.4	1.0	192
Silica, dissolved	.000	0	.10	229

significant difference ($p \leq 0.05$) was observed in the median of the differences between the two laboratories for the following constituents: dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, total phosphorus, total organic carbon, and dissolved silica. These statistics do not specify the source of the difference, but only that a difference exists in the analytical method, preservation method, holding time, and (or) the environment of each laboratory.

Preservation method and holding time differ between laboratories for nutrient samples, and therefore results for dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen and total phosphorus may have been affected by these differences. Nutrient samples sent to VDCLS were preserved by chilling at 4°C and were usually analyzed within a 24-hour period. Samples sent to NWQL were preserved with mercuric chloride, chilled in a dark bottle, and shipped to the laboratory in Arvada, Colo. These nutrient samples were usually analyzed within 1 week. The NWQL discontinued use of mercuric chloride as a preservative for nutrient samples on October 1, 1994 because a NWQL comparison of sample preservation techniques determined that chilling nutrient samples gave results that were comparable to those preserved with mercuric chloride or sulfuric acid. The NWQL also was concerned about potential environmental contamination from the storage, use, and disposal of mercuric chloride. Nutrient samples sent to NWQL were preserved by chilling to 4°C after the October 1994 date.

Dissolved nitrite-plus-nitrate nitrogen showed a statistically significant difference between laboratories (p=0.035). These data were checked for symmetry and were found to be random around zero difference. The reporting limit for this analysis was lowered to parts per billion by VDCLS on January 1, 1994; however, a higher reporting limit provided by the NWQL, 0.10 mg/L, was the limiting factor for this constituent. The median of the differences in concentrations between laboratories (0.002 mg/L) is much lower than the highest minimum reporting limit throughout the study period (0.10 mg/L), indicating this bias has no significance with respect to concentrations or loads.

The difference in concentrations reported by VDCLS and NWQL for dissolved ammonia nitrogen showed a statistically significant difference from zero (p=0.000). The minimum reporting limit for dissolved ammonia nitrogen at VDCLS was 0.04 mg/L from August 1988 through December 1993 and was lowered by the laboratory to 0.004 mg/L on January 1, 1994, whereas the minimum reporting limit for dissolved ammonia nitrogen was 0.01 mg/L at NWQL throughout the entire period. The VDCLS results for dissolved ammonia nitrogen before January 1994 contained a large percentage of censored data that caused difficulties in data interpretation. Results of the Wilcoxon signed-rank test on 40 cases available from January 1, 1994 through June 30, 1995 showed no significant difference between the laboratories (p=0.127). The median of the differences (in absolute value) between the two laboratories was lowered by an order of magnitude, from 0.013 mg/L for the entire data set to 0.002 mg/L after January 1994, by lowering the minimum reporting limit to parts per billion. Analyses for dissolved ammonia nitrogen have been acceptable throughout the period of study. Data after January 1994 show a significant lowering of the median bias for this constituent.

A statistically significant difference was shown between the laboratories for total phosphorus ($p=$ 0.000). The median bias for total phosphorus, 0.01 mg/L, is the same as the minimum reporting limit for both laboratories and, therefore, has no environmental significance.

Total organic carbon showed a statistically significant difference ($p=0.000$) between the two laboratories. From August 1988 through February 1992, VDCLS used a technique that did not allow mixing a sample before withdrawing an aliquot for analysis. Therefore, concentrations and loads for storm samples were underestimated for total organic carbon during this period. Data for total organic carbon were divided into two groups based on the technique change at the VDCLS on March 1, 1992. The 103 cases available from August 1988 through February 1992 showed a significant difference between laboratories ($p=0.000$). The 89 cases available from March 1992 to June 1995 showed no statistical difference between laboratories ($p=0.906$) and the median bias was zero for these data. The estimates for total organic carbon loads from August 1988 through February 1992 are lower for stormflow samples than if analytical methods appropriate for large sediment concentrations were used. Samples after March 1, 1992, have no consistent bias present; therefore, the analyzed concentrations better represent in-stream conditions.

The Wilcoxon signed-rank test showed a significant difference between the laboratories for dissolved silica. The median of the differences between the laboratories was zero, which indicates that a difference does not exist, however, the p-value was 0.000. The Wilcoxon signed-rank test is an evaluation of the hypothesis that the median of the population for the difference between two variables is equal to zero, based on the proportion of the differences above and below zero. Of the 229 cases available for analysis, 45 percent showed differences greater than zero, whereas only 24 percent showed differences less than zero, indicating these data are not symmetric around zero. A positive bias at NWQL for dissolved silica has been documented by the USGS Branch of Quality Assurance in Golden, Colo. This bias caused the statistical test to fail for dissolved silica. The largest variability between laboratories occurred when the concentration of dissolved silica was greater than 10 mg/L; however, there is no statistically significant difference for dissolved silica based on the median bias of zero difference between the laboratories for this constituent.

Field blank samples.—Field blanks are processed under actual field conditions and, therefore, are subject to the same potential contamination sources during sample collection, field processing, preservation, transportation, and laboratory handling as environmental samples. Contamination found in a field blank could also be the result of improper cleaning of sampling equipment by field personnel prior to sample collection. District-prepared deionized water (carbon-free) was used as a blank solution for most of the field blank samples. Laboratory blanks containing deionized water were sent to NWQL for analysis and showed no contamination of the constituents of interest for this project. Collection of field blank samples by USGS personnel began in September 1991. Field blanks were submitted to VDCLS for analysis simultaneously with environmental samples.

A summary of the number of samples showing concentrations greater than the minimum reporting limit is shown in table A–3. The following constituents are listed in table A–3 twice because their minimum reporting limits were lowered from parts per million to parts per billion on January 1, 1994: dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, and dissolved orthophosphorus.

No field blanks had concentrations of total suspended solids or total Kjeldahl nitrogen that were greater than the minimum reporting limits (no "hits"). Total organic carbon and dissolved silica each had one hit at concentrations much higher than the reporting limit; these hits may have been caused by a mix up with an environmental sample. Blanks analyzed for total phosphorus showed seven hits in the range 0.02 to 0.04 mg/L. Environmental samples with concentrations of total phosphorus at or below 0.04 mg/L should be interpreted with caution.

The VDCLS lowered the minimum reporting limit for dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, and dissolved orthophosphorus on January 1, 1994. Field blanks for these constituents were grouped into two categories based

Table A–3. Summary of the number of field blanks with concentrations greater than the minimum reporting limit for samples analyzed by the Virginia Division of Consolidated Laboratory Services

[mg/L, milligrams per liter]

Constituent	Number of samples greater than the minimum reporting limit	Number of samples	Minimum reporting limit (mg/L)
Suspended solids, total	0	27	3.0
Nitrite-plus-nitrate nitrogen, dissolved	0	11	.04
Nitrite-plus-nitrate nitrogen, dissolved	2	16	[1].004
Ammonia nitrogen, dissolved	0	11	.04
Ammonia nitrogen, dissolved	12	16	[1].004
Kjeldahl nitrogen, total	0	27	.10
Phosphorus, total	7	27	.01
Orthophosphorus, dissolved	0	11	.01
Orthophosphorus, dissolved	10	16	[1].002
Organic carbon, total	1	11	1.0
Silica, dissolved	1	27	.10

[1] Minimum reporting limit lowered to parts per billion on January 1, 1994.

on whether they were analyzed before or after the reporting limit was lowered. There were no hits before January 1994 for any of the three constituents. Dissolved nitrite-plus-nitrate nitrogen had two hits after January 1994. Dissolved ammonia nitrogen showed 12 hits in the range of 0.005 to 0.015 mg/L. Therefore, environmental samples with dissolved ammonia nitrogen concentrations at or below 0.015 mg/L should be interpreted with caution. Dissolved orthophosphorus showed 10 hits in the range of 0.003 to 0.006 mg/L. Environmental samples with concentrations of dissolved orthophosphorus below 0.007 mg/L should also be interpreted with caution. The low-level contamination of dissolved ammonia nitrogen and dissolved orthophosphorus in field blanks was below the minimum reporting limit in use for each constituent before January 1994.

Field blank results show a need to pinpoint the source of contamination for dissolved ammonia nitrogen, total phosphorus, and dissolved orthophosphorus. Preparing a blank before each step in the sample collection process as well as a laboratory blank will help to identify possible sources of this contamination.

Although low-level concentrations for dissolved ammonia nitrogen, total phosphorus, and dissolved orthophosphorus should be interpreted with caution, load estimates for these constituents were not markedly affected by contamination. Concentrations of constituents derived from contamination were not high enough to significantly raise the concentrations in environmental samples that are used as input to the load estimation model.

APPENDIX B.—SUMMARY STATISTICS OF CONSTITUENT CONCENTRATION AND LOAD

Presented in this appendix are summary statistics for constituent concentrations (table B–1) and loads (table B–2) for all five rivers for the sampling period. Summary statistics are useful for comparing the water-quality characteristics of the five river basins. A discussion of the factors affecting water quality in these basins is provided in Belval and others (1995).

Table B–1. Summary statistics for selected water-quality constituents at the Fall Line monitoring stations in Virginia during the period of data collection

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; <, less than]

Statistic	Oxygen, dissolved (mg/L, as O_2)	Specific conductance (µS/cm)	pH	Nitrogen, total (mg/L, as N)	Total Kjeldahl nitrogen (mg/L, as N)	Nitrogen, ammonia, dissolved (mg/L, as N)	Nitrogen, organic[1] (mg/L)	Nitrogen, $NO_2 + NO_3$, dissolved (mg/L, as N)	Phosphorus, total (mg/L, as P)	Phosphorus, ortho, dissolved (mg/L, as P)	Total suspended solids, residue at 180°C (mg/L)	Carbon, organic (mg/L, as C)	Silica, dissolved (mg/L, as SiO_2)
James River monitoring station (July 1988—June 1995)													
Minimum	5.2	60	6.1	0.191	<0.1	<.004	0.046	0.029	0.03	<.01	<1	1.3	2.4
Median	10.	125	7.3	.73	.4	<.04	.36	.29	.14	.04	45	4.1	7.2
Maximum	16.9	352	8.9	3.3	3.0	.54	2.86	1.05	1.4	.51	800	25	15
Rappahannock River monitoring station (July 1988—June 1995)													
Minimum	6.0	40	5.8	.14	<.1	.004	.06	<.004	<.01	.002	<1	1.2	3.5
Median	9.8	77	7.1	1.	.4	.04	.34	.57	.08	.01	26	3.75	9.5
Maximum	15.0	159	8.4	3.41	2.8	.27	2.63	1.03	1.5	.06	844	110	18
Appomattox River monitoring station (July 1989—June 1995)													
Minimum	4.3	38	6.1	.27	<.1	.005	.01	.02	<.01	.004	<1	1.1	6.4
Median	10.7	81	7.1	.59	.4	.04	.36	.16	.05	.01	9	5.7	14
Maximum	14.8	135	8.1	2.91	2.8	.22	2.72	.54	.20	.04	70	20	23
Pamunkey River monitoring station (July 1989—June 1995)													
Minimum	5.4	41	5.5	.34	.2	<.004	.13	.04	.02	.006	<1	1.6	5.8
Median	9.7	80	6.9	.68	.4	.04	.38	.23	.07	.013	18	5.9	10
Maximum	14.1	263	8.5	2.23	2.0	.17	1.92	.61	.50	.10	347	17	18
Mattaponi River monitoring station (September 1989—June 1995)													
Minimum	4.8	33	5.3	.21	.2	<.004	.06	.025	<.01	.004	<1	1.2	2.8
Median	9.7	53	6.6	.59	.4	<.04	.38	.132	.06	.01	7	6.6	7.7
Maximum	14.2	95	8.1	1.19	.9	.14	.86	.87	.23	.10	156	48	13

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[1] Computed as difference between concentration of total Kjeldahl nitrogen and concentration of dissolved ammonia nitrogen.

Table B–2. Summary of load statistics for the Fall Line monitoring stations in Virginia during the period of data collection

[kg, kilogram]

Statistic	Nitrogen, total (kg)	Total Kjeldahl nitrogen (kg)	Nitrogen, ammonia, dissolved (kg)	Nitrogen, organic[1] (kg)	Nitrogen, $NO_2 + NO_3$, dissolved (kg)	Phosphorus, total (kg)	Phosphorus, ortho, dissolved (kg)	Total suspended solids, residue at 180°C (kg)	Carbon, organic (kg)	Silica, dissolved (kg)
James River monitoring station (July 1988—June 1995)										
Minimum monthly	50,700	40,800	2,350	26,900	6,800	14,800	8,020	221,000	386,000	494,000
Median monthly	328,500	179,500	17,450	155,500	135,500	60,100	24,000	16,650,000	2,080,000	3,410,000
Maximum monthly	2,580,000	1,810,000	114,000	1,720,000	744,000	621,000	97,600	433,000,000	16,000,000	15,300,000
Mean annual[2]	5,830,000	3,690,000	289,500	3,440,000	2,195,000	1,290,000	325,500	637,000,000	35,200,000	51,700,000
Rappahannock River monitoring station (July 1988—June 1995)										
Minimum monthly	2,310	2080	186	2,030	277	186	72	3320	27,600	62,900
Median monthly	91,500	40250	3,685	40,350	56,550	7935	1,340	3,435,000	398,000	975,000
Maximum monthly	1,140,000	1,040,000	46,500	941,000	537,000	586,000	10900	497,000,000	6,750,000	5,050,000
Mean annual[2]	2,150,000	1,970,000	81,000	1,630,000	1,182,500	407,000	27,400	288,950,000	9,950,000	15,700,000
Appomattox River monitoring station (July 1989—June 1995)										
Minimum monthly	3,490	2,320	140	2,180	1,280	188	89	7,740	38,200	95,600
Median monthly	35,300	25,800	3,195	24,350	9,415	2,945	654	517,000	351,500	864,000
Maximum monthly	326,000	238,000	17,300	229,000	90,900	47,800	5,000	11,100,000	3,820,000	4,890,000
Mean annual[2]	682,000	498,000	52,500	479,000	191,000	75,200	12,500	16,600,000	7,280,000	13,900,000
Pamunkey River monitoring station (July 1989—June 1995)										
Minimum monthly	3,210	1,900	125	1,650	1,290	300	190	6,860	28,600	53,700
Median monthly	36,900	22,650	2,265	21,600	12,950	3,980	988	1,420,000	283,500	544,000
Maximum monthly	306,000	216,000	13,400	205,000	91,700	40,300	5,080	17,800,000	3,360,000	3,170,000
Mean annual[2]	708,000	480,500	41,500	461,000	230,000	82,300	15,200	35,500,000	6,345,000	9,640,000
Mattaponi River monitoring station (October 1989—June 1995[3])										
Minimum monthly	1,050	789	55	751	225	106	30	4,260	12,000	13,400
Median monthly	16,700	12,350	1,065	11,650	4,315	1,590	428	229,000	180,500	201,500
Maximum monthly	105,000	82,100	4,350	77,700	22,200	11,100	1,740	2,070,000	1,620,000	1,080,000
Mean Annual[2]	297,000	227,500	17,200	218,000	72,300	30,400	5,990	5,140,000	3,690,000	3,490,000

[1] Organic nitrogen is computed as the difference between the concentration of total Kjeldahl nitrogen and the concentration of dissolved ammonia nitrogen.

[2] Mean annual load is computed from complete years of data.

[3] Though sampling began at the Mattaponi River in September 1989, discharge data was not available until October 1989.