Water-Quality Characteristics of Five Tributaries to the Chesapeake Bay at the Fall Line, Virginia, July 1988 through June 1993

By D.L. Belval, J.P. Campbell, S.W. Phillips, and C.F. Bell

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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATED WATER-QUALITY UNITS, AND TRADE-NAME DISCLAIMER

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer
	Volume	
gallon (gal)	3.785	liter
gallon (gal)	0.003785	cubic meter
million gallons (Mgal)	3,785	cubic meter
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second
	Mass	
kilogram	0.4536	pound, avoirdupois (lb)

Temperature

Water temperature is expressed in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F = 1.8\ (°C) + 32$$

Sea level: 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.

Abbreviated water-quality units: Chemical concentration is reported in milligrams per liter (mg/L) or micrograms per liter (mg/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).

Trade-name disclaimer: Any use of trade, product, or firm names used in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

Water-Quality Characteristics of Five Tributaries to the Chesapeake Bay at the Fall Line, Virginia, July 1988 Through June 1993

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

ABSTRACT

Development in the Chesapeake Bay region has adversely affected the water quality of the Bay. The general degradation in the Bay has resulted in the decline of commercial fishing industries and has reduced the area of aquatic vegetation that provides food and habitat for fish and shellfish. In order to assess the effectiveness of programs aimed at reducing the effects of excess nutrients and suspended solids on Chesapeake Bay, it is necessary to quantify the loads of these constituents into the Bay, and to evaluate the trends in water quality. This report presents the results of a study funded by the Virginia Department of Environmental Quality—Chesapeake Bay and Coastal Programs and the U.S. Geological Survey, to monitor and estimate loads of selected nutrients and suspended solids discharged to Chesapeake Bay from five major tributaries in Virginia. The water-quality data and load estimates provided in this report also will be used to calibrate computer models of Chesapeake Bay.

Water-quality constituents were monitored in the James and Rappahannock Rivers over a 5-year period, and in the Pamunkey, Appomattox, and Mattaponi Rivers over a 4-year period. Water-quality samples were collected from July 1, 1988 through June 30, 1993, for the James and Rappahannock Rivers; from July 1, 1989 through June 30, 1993, for the Pamunkey and Appomattox Rivers; and from September 1, 1989 through June 30, 1993, for the Mattaponi River. Water-quality samples were collected on a scheduled basis and during stormflow to cover a range in discharge conditions. Monitored water-quality constituents, for which loads were estimated include total suspended solids (residue, total at 105° Celsius), dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, total Kjeldahl nitrogen, total nitrogen, total phosphorus, dissolved orthophosphorus, total organic carbon, and dissolved silica. Organic nitrogen concentrations were calculated from measurements of ammonia and total Kjeldahl nitrogen, and organic nitrogen loads were estimated using these calculations. Other selected water-quality constituents were monitored for which loads were not calculated. Daily mean load estimates of each constituent were computed by use of a seven-parameter log-linear-regression model that uses variables of time, discharge, and seasonality.

Concentration of total nitrogen ranged from less than 0.14 to 3.41 mg/L (milligrams per liter), with both extreme values occurring at the Rappahannock River. Concentration of total Kjeldahl nitrogen ranged from less than 0.1 mg/L in the James, Rappahannock, and Appomattox Rivers to 3.0 mg/L in the James River. Organic nitrogen was the predominant form of nitrogen at all stations except the Rappahannock River, where nitrite-plus-nitrate nitrogen was predominant, and organic nitrogen comprised the majority of the measured total Kjeldahl nitrogen at all stations, ranging from 0.01 mg/L in the Appomattox River to 2.86 mg/L in the James River. Concentration of dissolved ammonia nitrogen ranged from 0.01 mg/L in the Pamunkey River to 0.54 mg/L at the James River. Concentration of nitrite-plus-nitrate nitrogen ranged from 0.02 to 1.05 mg/L in the James River. Concentrations of total phosphorus ranged from less than 0.01 mg/L in the Rappahannock and the Mattaponi Rivers to 1.4 mg/L in the James River. Dissolved orthophosphorus ranged from less than 0.01 mg/L in all five rivers to 0.51 mg/L in the James River. Total suspended solids ranged from a concentration of less than 1 mg/L in all five rivers to 844 mg/L in the

Rappahannock River. Total organic carbon ranged from 1.1 mg/L in the Appomattox River to 110 mg/L in the Rappahannock River. Dissolved silica ranged from 2.4 mg/L in the James River to 18 mg/L in the Appomattox River.

The James and Rappahannock Rivers had high median concentrations and large ranges in concentrations for most constituents, probably because of a greater number of point and nonpoint sources of nutrients and suspended solids, and differences in land use when compared with the other basins. A significantly higher median concentration and greater range of dissolved orthophosphorus generally occurred at the James River than in all other rivers, which primarily is due to the greater number of point sources, such as municipal waste-water treatment plants. The Rappahannock River had significantly higher median concentrations and greater ranges of dissolved nitrite-plus-nitrate nitrogen and total nitrogen than other rivers, probably derived from agricultural sources. Total organic carbon was highest in the Mattaponi and Pamunkey River Basins that contain expanses of wetlands. The Appomattox River had the highest concentration of dissolved silica.

The median monthly load of total nitrogen ranged from 16,500 kg (kilogram) in the Mattaponi River to 371,000 kg in the James River. Total Kjeldahl nitrogen ranged from a median monthly load of 12,500 kg in the Mattaponi River to 205,500 kg, also in the James River. Organic nitrogen comprised the majority of the total Kjeldahl nitrogen load in all five rivers, ranging from a median monthly load of 11,251 kg in the Mattaponi River to 3,299,500 kg in the James River. The median monthly load of dissolved ammonia nitrogen was 1,130 kg in the Mattaponi River and was as much as 21,050 kg in the James River, whereas nitrite-plus-nitrate nitrogen ranged from a median monthly load of 4,065 kg in the Mattaponi River to 156,500 kg in the James River. The median monthly load of total phosphorus ranged from 1,670 kg in the Mattaponi River to 61,600 kg in the James River, whereas the median monthly load of dissolved orthophosphorus ranged from 350 kg in the Mattaponi River to 25,900 kg in the James River. Total suspended solids ranged from a median monthly load of 241,500 kg in the Mattaponi River to 20,050,000 kg in the James River. Total organic carbon ranged from a median monthly load of 167,000 kg in the Mattaponi River to 2,100,000 kg in the James River. The median monthly load of dissolved silica ranged from 209,500 kg in the Mattaponi River to 3,625,000 kg in the James River.

In general, annual loads for complete years of data collection were greatest at the James River for all constituents, probably because of the much higher discharge, greater basin size, and higher rates of runoff. Yields, or computations of loads per square mile of basin area, were generally highest at the Rappahannock River for total suspended solids, total Kjeldahl nitrogen, nitrite-plus-nitrate nitrogen, and total nitrogen. Dissolved orthophosphorus was the only constituent with a yield consistently greater at the James River. Yields of total phosphorus were highest for the James and Rappahannock River basins, whereas yields of dissolved ammonia nitrogen, total organic carbon, and dissolved silica were similar for all five river basins.

Quality-assurance analyses that compare the results of the Virginia Division of Consolidated Laboratory Services and the U.S. Geological Survey Laboratory indicate that there are statistically significant differences between the laboratories for several constituents. Differences between laboratories were found to be caused by differences in analytical reporting limits, differences in analytical technique, or a slight bias at both laboratories. Quality-assurance data were used to address analytical technique problems, and to qualify final concentrations and loads.

INTRODUCTION

The Chesapeake Bay is the largest estuary in the United States, extending nearly 200 mi from the mouth of the Susquehanna River in Maryland to where it discharges along the southeastern coast of Virginia into the Atlantic Ocean (fig. 1). The drainage area contains parts of Delaware, Pennsylvania, Maryland, New York, Virginia, West Virginia, and the District of Columbia and is approximately 64,000 mi^2 in area. The Bay contains areas of freshwater and saltwater, tidal and nontidal wetlands, open and protected waters that provide habitats for wildlife, and extensive commercial fishing and recreational industry. In addition, the bay economy has created thousands of jobs directly and indirectly within the watershed.

Development in the Chesapeake Bay region has adversely affected the water quality of the Bay. The general degradation of the quality of water in the Bay has resulted in the decline of important commercial fish and oyster industries and has reduced the number of acres populated by aquatic vegetation that provides food and habitat for fish and shellfish. The Chesapeake Bay

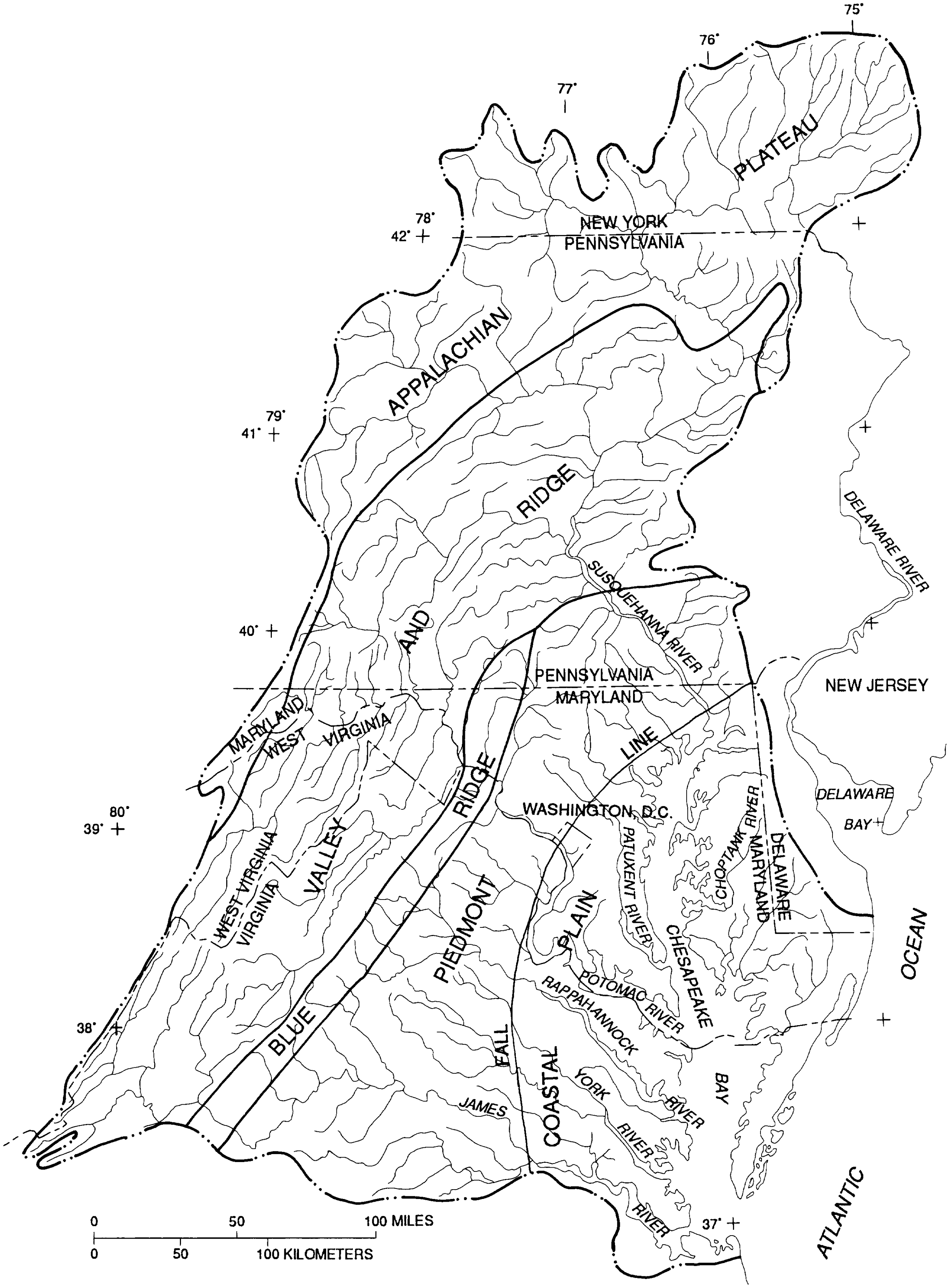

Figure 1. Chesapeake Bay drainage area.

Program, established in 1978 to restore the water quality and the water-quality resources of the Bay, identified three critical areas of concern for intensive investigation: (1) nutrient enrichment, (2) toxic substances, and (3) the decline of submerged aquatic vegetation (U.S. Environmental Protection Agency, 1982). The sources of nutrients and toxic substances entering the Bay include nonpoint and point sources, such as agriculture, urban runoff, atmospheric deposition, weathering of soil and rock, decomposition of plant material, and waste-water discharges.

The Chesapeake Bay Agreement, which was signed in 1987 by the Governors of Virginia, Maryland, and Pennsylvania, the Mayor of Washington, D.C., the Administrator of the U.S. Environmental Protection Agency, and representatives of the Chesapeake Bay Commission, commits Federal, State, and other agencies to work toward improving the quality of water in the Bay by reducing nutrient and toxic inputs and by continuing to monitor water, plant, and animal resources. The agreement set a goal to reduce controllable nutrient input into the Bay by 40 percent by the year 2000. In order to achieve this goal, several nutrient-control strategies have been implemented within the river basins discharging to the Bay.

In order to determine the effects that nutrients and suspended solids have on the ecosystems of the Bay, and to assess the effectiveness of programs aimed at reducing the consequences of these effects on the Bay, it is necessary to quantify the loads of water-quality constituents into the Bay over time and to evaluate trends in water-quality. Load estimates also can be used to calibrate and validate computer models of the Bay.

Nutrient and suspended-solid monitoring began in Virginia in 1984 by the U.S. Geological Survey (USGS), in cooperation with the Virginia Department of Environmental Quality (DEQ)—Chesapeake Bay and Coastal Programs, with the goal of quantifying loads of nutrients and solids entering the Bay from its major rivers. The initial monitoring program consisted of collecting water-quality data on a twice-per-month scheduled basis at sites near the Fall Line on four tributaries to the Bay, the James, Rappahannock, Pamunkey, and Mattaponi Rivers. The Fall Line is geographically defined as where the Piedmont Physiographic Province meets the Coastal Plain Physiographic Province. In most instances the Fall Line corresponds to the point farthest downstream that is unaffected by tides. Therefore, load estimates at the Fall Line of each river collectively represent all sources of nutrients and suspended solids to the Chesapeake Bay above the tidal area. Because loads of nutrients and suspended solids are greatest during stormflow, the monitoring program was expanded in 1988 to include more frequent collection of water-quality data during stormflow conditions at the two major tributaries to the Bay from Virginia, the James and Rappahannock Rivers. In July 1989, the Pamunkey, Mattaponi, and Appomattox Rivers were added to the existing stormflow-monitoring network. A parallel monitoring program has been conducted on four tributaries in Maryland, by the USGS, in cooperation with the Maryland Department of the Environment since 1982.

A multivariate log-linear-regression model that requires input variables of discharge, seasonality, and time was used to estimate the concentration of selected water-quality constituents for those days when no water-quality data were available. Estimated constituent concentration and daily mean discharge were used to calculate daily mean load estimates, which were then summed to provide monthly loads.

Purpose and Scope

The purpose of this report is as follows: (1) Discuss possible factors that affect concentrations and loads of selected water-quality constituents, (2) describe the relation between concentrations of selected nutrients and suspended solids to discharge and to seasonality for five major tributaries to Chesapeake Bay in Virginia near the Fall Line, (3) compare water-quality data and load estimates among rivers, (4) assess quality-assurance/quality-control results, and (5) present monthly loads of nutrients and suspended solids.

Water-quality samples were collected at the James and Rappahannock Rivers from July 1, 1988 through June 30, 1993; at the Appomattox and Pamunkey Rivers from July 1, 1989 through June 30, 1993; and at the Mattaponi River from September 1, 1989 through June 30, 1993. Water-quality samples were collected on a twice-per-month scheduled basis, which most often occurred during base-flow conditions. Samples also were collected during stormflow to cover a range in discharge conditions. Monthly loads of selected constituents were estimated by use of a seven-parameter log-linear-regression model. Approximately 30 to 40 stormflow samples per year were needed for accurate estimation of load using the log-linear regression model selected for this study.

Relation between concentration of water-quality constituents and discharge is shown in graphs for selected river basins. Relations between concentration and seasonality is shown by use of boxplots. Estimated annual load and yield of water-quality constituents for each river basin also are presented in graphs. Appendix A provides a complete review of quality-assurance/quality-control procedures and results, and appendix B provides a summary of the regression model results and tables of the seven-parameter log-linear-regression model equations for each river. Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear-regression model are stored on diskette, in American International Standard Code for Information Exchange (ASCII) format using MS-DOS operating system, at the back of this report. Also stored on the diskette is an ASCII text file that lists all tables on the diskette.

Previous Studies

Several previous investigations provide information for constituent monitoring in the Chesapeake Bay Basin and methods for loads computation. Lang and Grason (1980) provide water-quality-monitoring data for the Susquehanna, Potomac, and James Rivers—three major tributaries to the Chesapeake Bay. Lang (1982) computed loads of nutrients and metals from these three rivers by use of a bivariate linear-regression equation method. Cohn and others (1989) provide a review of statistical methods used for estimating constituent concentrations and loads of nutrients and suspended solids, and they determined that the minimum variance unbiased estimator of Bradu and Mundlak (1970), which uses a seven-parameter log-linear-regression equation, provides the best estimates. This regression equation was used by Cohn and others (1992) to estimate nutrient loads using water-quality data from the Susquehanna, Patuxent, Choptank, and Potomac Rivers in Maryland. This method also was used to estimate constituent concentrations 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).

Description of Study Area

The contributing basins for this report together compose about 22 percent of the total Chesapeake Bay drainage area. The James and Rappahannock River Basins represent approximately 13 and 4 percent, respectively, of the Chesapeake Bay drainage area; the Appomattox River Basin, part of the lower James River Basin, represents another 2.5 percent; and the Pamunkey and Mattaponi River Basins represent about 2 and 1 percent, respectively, of the total Chesapeake Bay drainage area. The remainder of Chesapeake Bay drainage area in Virginia consists of the Potomac River Basin and its tributaries, including the Shenandoah River. These tributaries are monitored by the Maryland District office of the USGS, and are not included in this report.

The locations of the five river basins and the Fall Line monitoring stations are shown in figure 2. The rivers are referred to throughout this report in decreasing order of basin area. Table 1 lists the locations of the Fall Line monitoring stations, presents the basin size, the percentage land use in Chesapeake Bay drainage area, the percentage land use in Virginia, and the percentage land use within each of the basins monitored for this report.

The James River Basin encompasses a land area of approximately 10,206 mi^2, which constitutes about 25 percent of the State of Virginia. 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.

The James River monitoring station represents the upstream contributing area (6,257 mi^2) to the Bay from the James River Basin near the Fall Line, or about 60 percent of the James River basin. This station is about 40-mi upstream of the Fall Line, but was selected because of the well-documented long-term discharge record, and because there are no major streams contributing to the discharge between this station and the Fall Line at Richmond. Because of the large size of the basin upstream of the monitoring station, streamflow varies widely with time, depending on precipitation patterns that can result in either very localized or widespread stormflow events.

The Rappahannock River Basin encompasses a land area of approximately 2,848 mi^2 that constitutes about 7 percent of the State of Virginia. 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 is the second largest contributing stream to the Chesapeake Bay in Virginia.

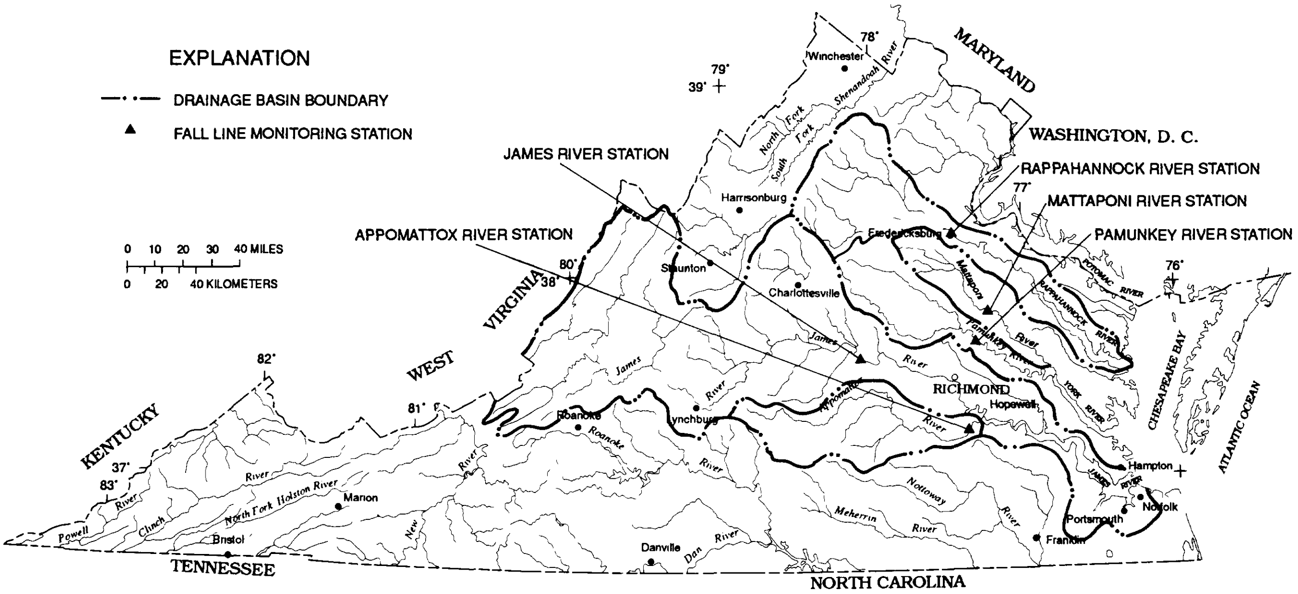

Figure 2. Location of Fall Line monitoring stations in the James, Rappahannock, Appomattox, Pamunkey, and Mattaponi River Basins.

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. Upstream from the station, most of the basin is in the uplands, or western part of the Piedmont Physiographic Province, and because of the high relief, the river produces rapid or "flashy" streamflow peaks during storm events. The river can carry large loads of suspended solids and other constituents relative to the size of the basin. The agricultural land use and increased development within the basin affect the water quality of the river by increasing concentrations of sediment in runoff and increasing concentrations of nutrients associated with the sediment, such as phosphorus. This station is inaccessible during extreme storm events; during these conditions stormflow samples were collected from the Interstate-95 (I-95) bridge about 1-mi downstream of the monitoring station. There are no major contributors of discharge to the river between the two sites.

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 total basin area is 1,600 mi^2, approximately 16 percent of the James River Basin and 4 percent of the area of Virginia. The Appomattox River Basin begins in the Piedmont Physiographic Province, flows through a small part of the Coastal Plain Physiographic Province, and empties into the James River near Hopewell.

The drainage area of the Appomattox River Basin above the monitoring station is approximately 1,344 mi^2. Discharge in the Appomattox River is controlled by a dam 2.8-mi upstream of the monitoring station. 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. The steep gradient from the rapid elevation change results in expanses of rocky rapids between the dam and the monitoring station.

The York River Basin encompasses an area of approximately 2,650 mi^2, which constitutes about 6.5 percent of the State of Virginia. The basin is composed of the Pamunkey River, the Mattaponi River, and the coastal area below the monitoring stations. 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 collec-

Table 1. Location of the Fall Line monitoring stations, and land use for Chesapeake Bay, Chesapeake Bay drainage area in Virginia, and selected river basins in Virginia

[NA, not applicable; mi^2, square mile; Mgal/d, million gallons per day; land-use data from Neumiller and others, 1995 and from Chesapeake Bay Program, written commun., 1994; land use as percentage of total land-surface area in each drainage basin; USGS, U.S. Geological Survey, VDEQ, Virginia Department of Environmental Quality]

USGS station number	VDEQ station number	Drainage basin or station name	Latitude	Longitude	Land-surface area (mi^2)	Urban (percent)	Agricultural (percent)	Forested[1] (percent)	Major upstream municipal discharge (Mgal/d)
NA	NA	Entire Chesapeake Bay	NA	NA	64,000	8	33	58	NA
NA	NA	Chesapeake Bay in Virginia	NA	NA	40,815	10	31	58	NA
02035000	TF5.1	James River near Cartersville	37°40'15"	78°05'10"	10,206	8	25	65	50.2
01668000	TF3.1	Rappahannock River near Fredericksburg	38°19'20"	77°31'05"	2,848	6	40	54	7.8
02041650	TF5.4A	Appomattox River at Matoaca	37°13'28"	77°28'32"	1,600	3	33	61	2.0
01673000	TF4.1	Pamunkey River near Hanover	37°46'03"	77°19'57"	1,474	3	35	59	NA
01674500	TF4.3	Mattaponi River near Beulahville	37°53'02"	77°09'55"	911	2	27	69	NA

[1] Includes wetlands.

tively as the York River Basin, each river has unique basin, discharge, and water-quality characteristics and were monitored separately for this study.

The total area of the Pamunkey River Basin is 1,474 mi^2, or about 4 percent of the area of Virginia. 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 basin contains expanses of forested wetlands and marshes that are significant sources of wildlife productivity (Virginia Water Control Board, 1991).

The area of the drainage basin above the monitoring station is approximately 1,081 mi^2, which is about 40 percent of the York River Basin, and about 4 percent of the area of Virginia. 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 a dam approximately 100-mi upstream of the monitoring station.

The Mattaponi River Basin is 911 mi^2, or 2 percent of the area of Virginia, and is located within the Piedmont and Coastal Plain Physiographic Provinces. Like the Pamunkey River, the Mattaponi River has expanses of wetland areas (Virginia Water Control Board, 1991). The wetland areas reduce river velocities, and stormflows are slower to peak and recede than at the Pamunkey River. 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 area of Virginia.

Acknowledgments

The authors gratefully acknowledge Frederick Hoffman and Mark Bushing of the Virginia Department of Environmental Quality, Chesapeake Bay and Coastal Programs, for their assistance and guidance of the program. The majority of analyses for this project were performed by the Virginia Division of Consolidated Laboratories, Bureau of Chemistry, specifically the Nutrients Laboratory and the Non-metals Laboratory. Field-data collection was provided by numerous personnel from the Virginia DEQ, Piedmont Field Office, and the USGS, Virginia District Office. We thank all of these people for their high-quality work.

METHODS OF STUDY

Methods of study for this project are divided into the following categories: (1) field-data collection, (2) estimation of loads, and (3) quality assurance/quality control. The details of these methods of study follow.

Field-Data Collection

Stormflow-sampling criteria were determined by establishing a gage height reached at each river about 40 times per year. At progressively higher stages, the water level would be reached on a fewer number of days. Emphasis was placed on sampling throughout the range in stormflow conditions that existed throughout the data-collection period. The streamflow guidelines used for sample collection at each river are listed in the Fall Line Monitoring Program Quality Assurance Plan (FLQAP); data on file in the Virginia District office of the USGS in Richmond, Va. In order to determine when to collect stormflow samples, telemetry equipment was installed at selected stream-gage stations upstream of the Fall Line monitoring stations to observe changes in water level. Whenever possible, and as permitted by discharge conditions, water samples were collected during the rise, peak, and fall of the river stage.

In addition to stormflow sampling, base-flow samples were collected on a scheduled basis. These base-flow samples were collected once per month by Virginia DEQ personnel and once per month by USGS personnel at the James River monitoring station, Pamunkey River monitoring station, and the Mattaponi River monitoring station. Samples were collected twice per month by USGS personnel at the Rappahannock River monitoring station and the Appomattox River monitoring station.

Water-quality samples were collected by the Virginia DEQ and USGS personnel during base-flow and stormflow conditions by use of an equal-discharge increment (EDI) method or an equal-width increment (EWI) method, so that a sample representative of stream conditions was obtained. Samples were collected using a USGS-designed depth-integrating sampler (designation D-74 or D-74AL) when average streamflow velocities exceeded 1.5 ft/s, or a weighted sample bottle at lower velocities when depth-integrating samplers were not effective. These methods are documented by Edwards and Glysson (1988) and Ward and Harr (1990). The rationale for use of the EDI or EWI method at each of the five Fall Line rivers and the criteria for equipment use based on the discharge at each site are documented in the FLQAP. The majority of samples collected were analyzed by the Virginia Division of Consolidated Laboratory Services (VDCLS) in Richmond, Va. Quality-assurance samples were analyzed by VDCLS and also by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo.

Collected water samples were packed in ice and transported to the VDCLS. Samples were filtered and analyzed by VDCLS under criteria established by Clesceri and others (1989) and the USEPA Environmental Monitoring and Support Laboratory (1983). Water samples collected on weekends were chilled to 4°C and held until they could be accepted by VDCLS during working hours on the following week. Approximately 1 of every 10 samples was sent to both the VDCLS and the NWQL in Arvada, Colo., as a quality-assurance check of the analytical results. Analytical methods used at NWQL are documented in Fishman and Friedman (1989).

Field measurements for water temperature, pH, specific conductance, dissolved oxygen, barometric pressure, and air temperature were routinely made on days when nutrient and suspended-solids samples were collected. Temperature, dissolved oxygen, specific conductance, and pH were measured in the field. Temperature and dissolved oxygen were measured in the stream after sampling by use of a YSI (model 54A) dissolved oxygen meter. The dissolved oxygen meter was calibrated to water-saturated air in a stainless steel calibration chamber immersed in the stream. Specific conductance and pH were measured on unfiltered water samples using an Orion (model 122) specific conductance meter with a DIP conductivity cell and Orion (SA 250) pH meter with epoxy-bodied pH electrode, respectively. The calibration of the specific conductance meter was checked using three solutions of known conductance. The pH meters were calibrated before each use with two solutions of known pH values (usually pH 4.0 and 7.0).

Load Estimation

In order to estimate the monthly and annual loads of nutrients and suspended solids at the Fall Line monitoring stations, first it is necessary to estimate the daily concentration of these constituents for the entire period of study. This estimate of daily constituent concentration was obtained by use of a a seven-parameter log-linear regression equation that uses the minimum variance unbiased estimator (MVUE) of Bradu and Mundlak

(1970). The MVUE corrects for the retransformation bias associated with multivariate log-linear models. The Adjusted Maximum Likelihood Estimator (AMLE) (Cohn, 1988) was employed in the regression analyses to statistically handle censored data (values below analytical reporting limits) and multiple detection limits. Censored data are assigned true concentration values through an in-line analysis inherent in the AMLE technique.

The estimation of constituent load was conducted in two steps (1) daily constituent concentration was estimated by use of a multivariate log-linear model; and (2) constituent load was computed as the product of discharge and the estimated daily constituent concentration. The regression equation used to estimate daily constituent concentration is as follows (Cohn and others, 1992):

$$\begin{aligned}\ln[C] &= \beta_0 + \beta_1(\ln[Q/\tilde{Q}]) + \beta_2(\ln[Q/\tilde{Q}])^2 \\ &+ \beta_3[T-\tilde{T}] + \beta_4[T-\tilde{T}]^2 + \beta_5 \sin[2\pi T] + \\ &\beta_6 \cos[2\pi T] + \varepsilon\end{aligned} \tag{1}$$

where

$ln[]$ = the natural logarithm function,
C = the constituent concentration (in mg/L),
Q = the instantaneous discharge (in ft^3/s),
T = time (in years),
sin = the sine function,
cos = the cosine function,
$\pi = 3.14169$,
β = coefficient of the regression model,
ε = model error, and
$\tilde{Q}$ and $\tilde{T}$ = centering variables.

β_0 through β_6 are the coefficients of the regression model that were computed from the constituent concentration data collected. The model error (ε) is assumed to be independent and normally distributed with a mean of zero and constant variance (σ^2). Centering variables simplify the numerical work and have no effect on the load estimates being defined, so that the regression coefficients are statistically independent. This equation results in an estimate of daily constituent concentration.

Daily estimates of constituent concentration are multiplied by daily mean discharge to produce a daily mean load using the following equation:

$$L_d = Q_d \times C_e \times K \tag{2}$$

where:

L_d = the daily mean load (in kg/d),
Q_d = the daily mean discharge (in ft^3/s),
C_e = the estimated daily concentration (in mg/L), and
$K = 2.447$, the correction factor for unit conversion.

The estimation procedure described above was used to estimate nutrient and suspended solids loads for the five rivers. Although the seven model variables for discharge, season, and time were included in each of the model runs for each constituent and river, not all variables were significant in explaining the variance in constituent concentration data. Inclusion of non-significant parameters, however, does result in slightly larger standard error of estimate, which causes an overestimation of confidence limits for the estimates. Overestimation of confidence limits results in a slight understatement of accuracy of the estimates, and therefore a conservative estimate of the load.

Quality Assurance and Quality Control

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 the variance, accuracy, and bias of analytical results. A comprehensive discussion of quality-assurance results for the laboratory component of the QA/QC plan, the objectives of the QA/QC plan, and a description of the types of samples collected are presented in appendix A.

Results of the field component of the QA/QC plan were within established guidelines for the quality of field data collection for the USGS and the Virginia Fall Line monitoring project. The results of the field component of the QA/QC plan are on file in the Richmond District office of the USGS.

GENERAL FACTORS AFFECTING WATER QUALITY

A summary and description of general water-quality characteristics are presented in this section. A general discussion of the sources and chemical behavior of water-quality constituents is presented first, followed by a discussion of streamflow conditions and seasonal variation during the period of study.

Sources and Chemical Behavior of Water-Quality Constituents

Water-quality constituents in a river are derived from both natural and anthropogenic sources. Natural sources of water-quality constituents include nonpoint sources, such as the weathering of rocks and soils, atmospheric deposition, and decay of natural organic material. Water-quality constituents from these sources can enter a river by surface runoff, direct precipitation, or from base flow, which is ground water that discharges to a river or stream. Anthropogenic sources include point-source discharge from industrial and waste-water treatment plants and nonpoint sources such as land affected by agriculture or urban/suburban development. Atmospheric deposition can be considered an anthropogenic source if it has been affected by industrial and (or) automobile emissions. Differences in concentrations and loads among the rivers can be related to differences in several interrelated characteristics, including (1) land use, (2) point sources, (3) basin size, (4) runoff characteristics, (5) streambed and flood-plain characteristics, (6) streamflow velocities, and (7) hydrogeologic setting.

Nitrogen and phosphorus are of particular importance to the health of Chesapeake Bay and its estuaries because they can cause eutrophication, which is the excessive growth of undesirable plants and algae. Algal blooms in the Bay deprive submerged aquatic vegetation of sunlight and their decay consumes oxygen, which in turn has a detrimental effect on fish, crabs, molluscs, and other species. Sources of nitrogen, phosphorus, and other selected water-quality constituents are discussed below.

Nitrogen Species.—Nitrogen exists in natural waters as one of several different forms or a combination of these forms, depending on the source and the environmental conditions. Common forms include organic nitrogen, which can be either dissolved or particulate, and the inorganic ions ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-). The nitrogen cycle is a series of biologically catalyzed reactions by which one form of nitrogen is transformed into another.

Certain micro-organisms, such as blue-green algae and bacteria associated with the roots of leguminous plants, have the capability to transform atmospheric nitrogen (N_2) to ammonium by a process commonly termed "nitrogen fixation." Other bacteria catalyze the oxidation of ammonium to nitrite and then to nitrate, a process termed "nitrification," which occurs rapidly under aerobic conditions. Under low dissolved oxygen conditions, bacteria can reduce nitrate to nitrogen gas, a process termed "denitrification," or back to nitrite and then to ammonium, termed "nitrogen reduction." Alternately, inorganic nitrogen species can be taken up by organisms and incorporated into organic material (amination), which in turn can decay and release nitrogen in the form of ammonia (deamination). All of these processes affect nitrogen transport in ground water and surface water.

Three different analyses for nitrogen were performed on water-quality samples from the Fall Line monitoring stations: dissolved ammonia nitrogen, dissolved nitrite-plus-nitrate nitrogen, and total Kjeldahl nitrogen (TKN), which is composed of both organic and ammonia nitrogen. Concentration of total nitrogen is computed as the sum of TKN and nitrite-plus-nitrate nitrogen, and concentration of organic nitrogen is computed by subtracting dissolved ammonia nitrogen from TKN.

Because nitrogen is so readily converted from one form to another according to environmental conditions, identifying sources of nitrogen from analyses of different forms at a single monitoring station is difficult. However, nitrogen from specific sources enters the hydrologic cycle in characteristic forms. Sources of TKN include the decay of organic material such as plant material and animal wastes and urban and industrial disposal of sewage and organic waste. Large amounts of ammonia and organic nitrogen are applied to cropland as fertilizer. Both ammonia and organic nitrogen are relatively immobile in soils and ground water because of adsorption on soil surfaces and particulate filtering, but are susceptible to nitrification under aerobic conditions.

Nitrite-plus-nitrate nitrogen can be derived from nitrification of TKN, and thus shares all the potential sources of TKN. Nitrite-plus-nitrate concentrations commonly exceed 10 mg/L in rivers affected by fertilizer application and animal wastes (Hem, 1989). Unlike ammonium ions and organic nitrogen, nitrate is highly mobile in ground water; nitrate derived from agricultural fertilizer, animal waste, or decaying plant material can infiltrate ground water, which in turn can discharge to streams. Nitrogen oxides discharged to the atmosphere by plants and the burning of fossil fuels are transformed to nitrate that is present in rain water (Drever, 1988); ammonium ions also are present in rain water (Feth, 1966). Important sinks for nitrite-plus-nitrate nitrogen in streams include incorporation into organic matter and denitrification.

Phosphorus species and total suspended solids.—Like nitrogen, phosphorus is present in natural waters in several different forms: orthophosphate, which includes species of PO_4^{3-}; polyphosphates and metaphosphates, formed by the condensation of two or more orthophosphate groups; and organic phosphorus. Orthophosphate is the most thermodynamically stable and biochemically available form of phosphorus in natural waters, and micro-organisms catalyze the hydrolysis of condensed phosphates to orthophosphate. However, 30 to 60 percent of the phosphorus present in many natural waters is organically bound (Snoeyink and Jenkins, 1980). Water-quality samples from this study were analyzed for dissolved orthophosphate and total phosphorus.

Most phosphate salts have low solubility in water, and the positive charge on phosphate ions causes them to adsorb strongly onto particles in soils, suspended solids, and streambed sediments. Precipitation/adsorption onto sediments, and the uptake of dissolved orthophosphate by biota usually limit typical concentrations of dissolved phosphorus to no more than a few tenths of a milligram per liter (Hem, 1989). Phosphorus has low mobility in ground water, and is the limiting nutrient for vegetative growth in many surface waters.

The tendency of phosphorus to precipitate/adsorb onto soil surfaces causes a positive correlation between total phosphorus and suspended solids in many streams. Common nonpoint sources for both of these constituents is weathering of natural soils and rocks and runoff from agricultural land. Phosphate from fertilizers binds to soils, which erode during storm events adding considerable amounts of suspended phosphate to streams (Hem, 1989). Total suspended solids also are contributed to a river by soil erosion in response to lumbering and construction practices. The most important point source of phosphorus is municipal waste-water discharge, which discharges phosphate as orthophosphate and organic phosphorus.

Organic carbon.—Total organic carbon is present as dissolved organic carbon (DOC) and particulate organic carbon (POC) in surface water. Sources of both DOC and POC include decomposition of plant material and municipal wastewater discharge. Like phosphorus, POC in streams can be derived from erosion of soils by way of surface runoff; thus POC correlates positively with suspended solids and discharge. The amount of DOC in a river will vary based on the size of a river, climate, vegetation, and season. Large concentrations of DOC are expected during periods of increased decomposition, such as during the summer, or high organic deposition, such as during the fall. Many streams have more particulate than suspended organic carbon.

Dissolved silica.—Most dissolved silica observed in natural waters results originally from the chemical breakdown of silicate minerals in irreversible processes of weathering, and most streams in the Northeastern United States have dissolved silica concentrations less than 10 mg/L (Hem, 1989). Aquatic organisms (primarily diatoms) extract and use silica in their shells and skeletons in freshwater and in seawater, including Chesapeake Bay.

Field measurements.—Field measurements, such as pH, specific conductance, and dissolved oxygen, can be used to compare chemical conditions at the rivers during the sampling period. For example, pH is affected by natural sources of acidity or alkalinity in the basin and point sources. Examples of natural sources affecting pH include the following: (1) weathering of limestone, which will result in a higher pH, (2) production of higher concentrations of organic acids in wetland areas, which will lower pH, and (3) the introduction of carbon dioxide into the water by algae, which will lower pH. The effect of algae is more apparent in summer months, when algal growth rates are high and discharge is low.

Specific conductance is an indicator of the ability of water to conduct an electric current, and usually has a strong positive correlation with total dissolved solids. Diverse factors affect the specific conductance of streams, including flow conditions, bedrock geology, and contributions of dissolved solids from different point and nonpoint sources.

Dissolved oxygen concentration is normally higher during winter months because water has a greater oxygen capacity at lower temperatures. Dissolved oxygen also is high where the waters have an opportunity to be churned or mixed with air, such as in rapids. Elevated dissolved oxygen concentration in summer months can be caused by release of oxygen by photosynthetic plants. Low dissolved oxygen concentration is found in waters that are warm and not well-mixed, such as in slow-moving streams in summer. Algal growth and decomposition of organic material in the stream and streambed sediments are major sinks of dissolved oxygen in streams; both of these processes are more active during summer months.

Streamflow

Knowledge of streamflow conditions is important to any water-quality monitoring strategy. First, streamflow data is necessary to compute constituent loads. In addition, sampling that covers the range of streamflow conditions is necessary to determine the relation of discharge

Table 2. Historic streamflow conditions and streamflow conditions for the period of study for the Fall Line monitoring stations in Virginia

[ft^3/s, cubic foot per second; ft/s, foot per second; NA, not applicable]

Time period (month/year)	Mean discharge (ft^3/s)	Median discharge (ft^3/s)	Instantaneous peak discharge (ft^3/s)	Instantaneous low discharge (ft^3/s)	Mean velocity at median discharge (ft/s)	Mean velocity at bankfull discharge (ft/s)
James River						
Period of record	7,077	4,460	362,000	316	2.0	4.4
07/88–06/93	7,983	4,900	113,000	801	NA	NA
Rappahannock River						
Period of record	1,660	984	140,000	5.0	.55	5.7
07/88–06/93	1,745	1,050	57,800	101	NA	NA
Appomattox River						
Period of record	1,384	695	40,800	26	1.8	4.6
07/89–06/93	1,163	657	12,500	82	NA	NA
Pamunkey River						
Period of record	1,110	620	29,900	47	1.8	2.6
07/89–06/93	1,030	544	13,300	47	NA	NA
Mattaponi River						
Period of record	583	374	16,900	5.9	1.2	1.8
09/89–06/93	519	251	4,810	6.3	NA	NA

to concentrations and loads of water-quality constituents. Some water-quality constituents, such as phosphorus, enter a stream primarily by surface runoff, and thus concentrations will be expected to rise during storm events. Other water-quality constituents, such as nitrate, often have higher concentrations in base flow than in surface runoff, and thus can be diluted during storm events. Even if concentrations decrease during storms, the majority of the annual load of a water-quality constituent can occur during high-discharge conditions. In addition to stormflow sampling, sampling at periodic intervals throughout the year helps determine the variability in the concentration of each constituent in response to seasonal changes in discharge, land use, point-source inputs, and biologic processes.

Sampling during the rise, peak, and fall of the river stage during a single storm is necessary to accurately characterize the water quality of the stream, as concentrations change over the stormflow period. High-discharge conditions preceded by a period of low-discharge conditions can lead to what is termed a "first-flush" effect, whereby rapidly rising water levels transport high concentrations of water-quality constituents early in the storm event. During the first flush, therefore, high concentrations of water-quality constituents can be associated with a low (but rapidly rising) discharge.

An overview of the streamflow conditions at all five monitoring stations is shown in table 2 and figure 3. Table 2 gives information on the central values of the streamflow (mean and median), as well as the extremes. In figure 3, monthly mean discharge is plotted with the normal range of monthly discharges to illustrate the pattern of streamflow during the period of sample collection. The monthly mean discharge is computed by averaging the daily mean discharges in each month. The normal range of monthly discharge is the range of discharges that could be expected for any individual month and represents discharge conditions that are not considered exceptionally high or low. The normal range for a specific month is calculated by ranking all monthly mean discharge values for that month during (over) the period-of-streamflow record. The 25th percentile, or that discharge that is exceeded by 75 percent of the monthly mean discharges, and the 75th percentile, or that discharge that is exceeded by 25 percent of the monthly mean discharges, are then determined. The normal range is the range in

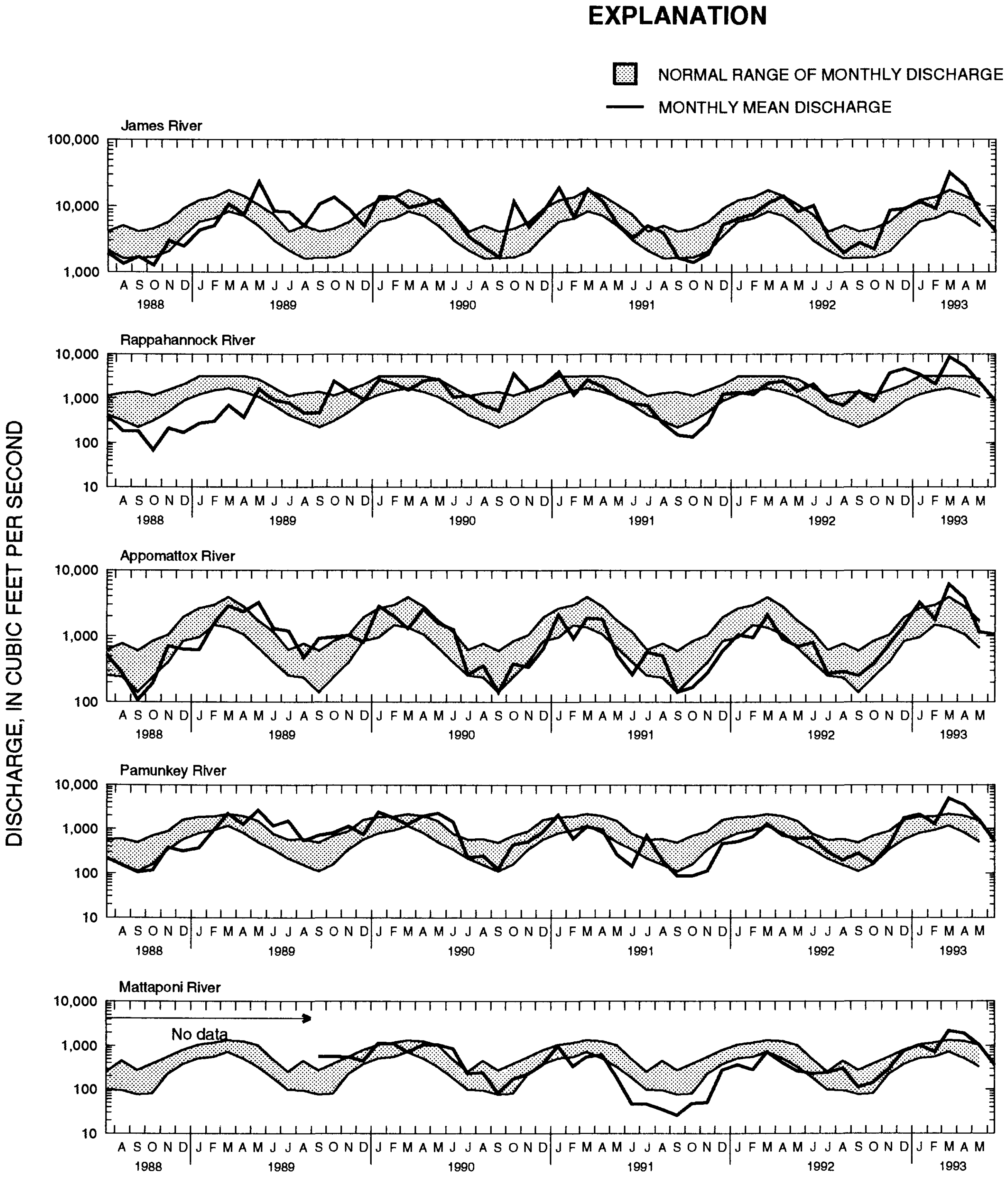

Figure 3. Relation of discharge to time for the James, Rappahannock, Appomattox, Pamunkey, and Mattaponi River stations, Virginia.

discharge between these two values. Historically, the monthly mean discharge is in the normal range 50 percent of the time.

Streamflow conditions at the five monitoring stations indicate similar trends with respect to the normal range of discharge for the data-collection period (fig. 3). Streamflow was generally below the normal range during the fall of 1988 through the winter of 1989 at the four stations where streamflow data were collected. Spring rains increased streamflows; three of the four stations had discharges above the normal range from approximately May 1989 through November 1989. The exception was the Rappahannock River, where discharges remained in the normal range during that period except for the month of October, where discharges were above the normal range. Streamflow-data collection resumed in September 1989 at the Mattaponi River station with discharges above the normal range for 2 months, which indicates trends similar to the other stations. Streamflows generally remained within the normal range at all five monitoring stations from December 1989 through March 1991. This time period was followed by streamflows below the normal range or near the lower normal-range value at the five monitoring stations from April through December 1991. The smaller basins (Pamunkey and Mattaponi Rivers) had streamflows well below the normal range during this period.

The streamflow at most of the stations had increased into the normal range by the spring of 1992. Streamflow generally remained within the normal range at all five monitoring stations until the winter of 1993, where streamflow increased above the normal range at all stations except the Mattaponi River. Streamflow increased to well above the normal range at all five monitoring stations in March 1993 because of widespread precipitation during three storms. This series of storms caused flooding throughout the Chesapeake Bay Basin and resulted in the highest monthly mean discharge for the James River station since streamflow-data collection began in 1899 and the highest monthly mean discharge at the other stations for the data-collection period.

Seasonal Variation

Knowledge of the interrelation between seasonality, discharge, and water-quality constituent concentration is important in interpreting concentration and load estimates. A definite seasonal pattern to the long-term monthly mean discharge shows the lowest discharge in the summer months and the highest in winter months (fig. 3). These seasonal patterns are caused by storms of longer duration in the winter and spring, as opposed to shorter, more intense summer thunderstorms, and higher evapotranspiration rates in summer and fall because of the higher ambient temperatures and uptake by plants.

Seasonality is defined based on the following Virginia DEQ guidelines:

Water temperature	Month of year	Season
<10°C	any	Winter
10–24°C	January–June	Spring
>24°C	any	Summer
10–24°C	July–December	Fall

Seasons defined by the above criteria agreed well with calendar seasons under low-discharge conditions, whereas lower water temperature during storm events caused disagreement with calendar seasons. Seasons for selected stormflow samples were corrected to the season for the base-flow samples before and after the storm. The locations of temperature measurement also affect the seasonal definition for some samples; temperatures measured along the stream bank differ from temperatures measured in the center of a stream, resulting in abnormally high or low temperature measurements. Defined seasons for these samples were corrected based on the defined season of the previous and subsequent samples.

Seasonal changes other than discharge can significantly affect concentrations of water-quality constituents. For example, total organic carbon can increase in the fall as leaves drop and decay. Aquatic vegetation, algae, and micro-organisms flourish during warm weather months but die back during cold weather; thus, in-stream uptake of nutrients by biota increases during spring and summer months. Concentrations of constituents associated with soils, such as total suspended solids or total phosphorus can increase during periods when less vegetative ground cover is available to prevent erosion, such as during the winter and spring. Seasonal farming practices, such as plowing and fertilizing fields during spring and summer can facilitate the release of suspended solids and nutrients to streams. Biological uptake of nutrients such as nitrogen, phosphorus, and silica, however, increases during the spring and summer growing seasons, which can result in low concentrations.

CONSTITUENT CONCENTRATION AND LOADS

This section presents ranges in selected constituent concentrations and loads for each river and discusses the relation of discharge and basin characteristics to water quality for each river. Results of the seven-parameter log-linear regression model are discussed with significance to discharge and to seasonality by constituent concentration for each river. Methods used to interpret water-quality results included the use of scatterplots, boxplots, bar charts, and results of the log-linear model.

The maximum, minimum, and median concentrations of selected water-quality constituents and values of selected field parameters for each river are listed in table 3. Although maximum and minimum concentrations are important in understanding the differences in ranges among rivers, and can indicate basin response to changes in discharge and seasonality, these concentrations can occur during extreme conditions, such as droughts or storm events, and therefore are not representative of "normal" conditions. Median concentrations represent the midpoint of a group of concentrations and are unaffected by the value of the highest and (or) lowest extreme concentrations, and thus are more useful in comparing concentration differences among the rivers. On the basis of reporting limits for some constituents, minimum concentration can be affected by the specific analytical technique done by the laboratory. A summary of the calculated loads for each river is presented in table 4.

For this report, scatterplots consist of all data points for a specified constituent plotted against the discharge for that point, to show the concentration/discharge relation for a specific river. Plotted with each scatterplot is a Locally Weighted Scatterplot Smoothing, or LOWESS line (Cleveland, 1979). LOWESS uses a moving subset of the data points to compute a central value for those data. The smooth line is used to indicate patterns in the data that may not be obvious from the scatterplot. Boxplots are used to show the median, the 25th and 75th percentiles, and ranges in concentration for a certain river and (or) for a certain time period, and the boxplots are used to compare those statistics among rivers. Bar charts are used to show relative loads of related constituents for each river; to compare loads among rivers; and to compare yield, or load per area, among rivers.

Summaries of the regression results from the seven-parameter log-linear model for each river are presented in appendix B. For each regression analysis, residuals were examined to identify any pattern that would be indicative of non-normal distribution; no pattern was observed in residual plots for the water-quality constituents monitored. The significance of discharge to concentration for each water-quality constituent, according to the regression model results for each river is presented in table 5, and the significance of seasonality to concentration for each water-quality constituent is presented in table 6.

James River

Nitrogen species.—Concentration of total nitrogen in the James River ranged from 0.27 to 3.3 mg/L, with a median of 0.74 mg/L (table 3). On the basis of median concentration, the predominant species of nitrogen was organic nitrogen, which had a median concentration of 0.36 mg/L and made up the majority of TKN measured. Dissolved nitrite-plus-nitrate nitrogen (which is mostly nitrate) had a slightly lower median concentration than organic nitrogen. Ammonia was the least prevalent form of nitrogen in the James River, with a median concentration of 0.04 mg/L.

All the nitrogen species concentrations have a significant relation to discharge at the James River (table 5), and there are several distinct constituent/discharge relations. The relation between TKN and discharge is nonlinear (fig. 4). The concentration increase with discharge becomes apparent during storm events, particularly when discharge exceeded 20,000 ft^3/s. In contrast, concentrations of dissolved nitrite-plus-nitrate nitrogen showed an increase with discharge at low-discharge conditions, then a leveling-off of concentration at high discharges (fig. 5). The model results (table 6) indicated there is no significant relation between concentrations of total nitrogen and dissolved nitrite-plus-nitrate and season, but a relation does exist for concentrations of both TKN and ammonia to season. TKN and dissolved ammonia were highest in the winter (fig. 6); the increase in TKN in the winter can be attributed to the increase in dissolved ammonia.

The concentration ranges for the nitrogen species in the James River are typical for a basin having mixed land use and point-source influences. Organic nitrogen (and thus TKN) is derived probably from a combination of sources, including waste-water discharge (table 1) and surface runoff from agricultural and forested land. In addition, some organic nitrogen can be derived from instream uptake of ammonia and nitrate by algae and other biota. The increase in concentration of organic nitrogen with discharge, especially during large storm events

Table 3. Summary statistics for selected water-quality constituents for rivers monitored near the Fall Line of Virginia

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; <, less than]

Statistic	Oxygen, dis solved (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							
Minimum	6.3	60	6.1	0.27	<0.1	0.02	0.06	0.02	0.03	<.01	<1	1.3	2.4
Median	9.9	123	7.3	.74	.4	.04	.36	.29	.15	.04	50	4.1	7.2
Maximum	16.9	345	8.9	3.3	3.0	.54	2.86	1.05	1.4	.51	800	25	15
						Rappahannock River							
Minimum	6.0	40	5.8	<.14	<.1	.03	.06	<.04	<.01	<.01	<1	1.2	3.5
Median	9.8	76	7.1	1.07	.4	.04	.36	.60	.10	.01	36	4.0	9.6
Maximum	15.0	138	8.4	3.41	2.8	.27	2.63	1.03	1.1	.06	844	110	13
						Appomattox River							
Minimum	6.3	38	6.1	.20	<.1	<.04	.01	<.04	.01	<.01	<1	1.1	6.4
Median	10.7	83	7.1	.60	.4	.05	.36	.16	.05	.01	9	5.7	14
Maximum	14.8	135	8.1	1.14	.8	.22	.76	.54	.18	.08	50	20	18
						Pamunkey River							
Minimum	5.6	46	5.5	.36	.2	.01	.13	.06	.02	<.01	<1	1.6	6.1
Median	9.8	80	6.9	.69	.45	.04	.38	.23	.07	.01	18	5.9	10
Maximum	14.1	250	8.5	2.23	2.0	.17	1.92	.61	.50	.10	347	15	15
						Mattaponi River							
Minimum	4.8	33	5.3	.31	.2	.02	.06	<.04	<.01	<.01	<1	1.2	2.8
Median	9.8	53	6.6	.60	.4	<.038	.38	.14	.06	.01	7	6.7	7.8
Maximum	14.0	95	8.1	1.19	.9	.14	.86	.87	.23	.10	156	48	13

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

Table 4. Summary of load statistics for the Fall Line stations 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 (July 1988 through June 1993)										
Minimum monthly	47,600	46,000	3,060	39,710	6,730	14,500	7,380	224,000	439,000	513,000
Median monthly	371,000	205,500	21,050	187,050	156,500	61,600	25,900	20,050,000	2,100,000	3,625,000
Maximum monthly	2,620,000	2,030,000	126,000	1,904,000	712,000	766,000	93,600	480,000,000	23,000,000	15,400,000
Mean annual[2]	5,705,000	3,610,500	310,500	3,299,500	2,175,000	1,266,000	359,500	585,000,000	30,600,000	51,275,000
Rappahannock River (July 1988 through June 1993)										
Minimum monthly	2,080	2,030	210	1,820	414	196	103	5,390	26,600	66,200
Median monthly	96,550	43,100	3,895	39,185	58,100	8,815	1,405	3,795,000	392,000	1,010,500
Maximum monthly	995,000	769,000	40,900	728,100	446,000	315,000	9,150	384,000,000	6,330,000	5,100,00
Mean annual[2]	1,885,000	1,076,250	80,225	996,000	948,000	334,250	24,900	277,300,000	7,950,000	14,225,000
Appomattox River (July 1989 through June 1993)										
Minimum monthly	5,940	3,780	348	3,415	1,820	288	145	20,800	59,300	163,000
Median monthly	34,600	26,950	3,520	23,830	9,905	2,700	726	544,000	373,000	889,500
Maximum monthly	375,000	255,000	25,700	229,300	137,000	55,500	4,840	8,960,000	4,780,000	4,710,000
Mean annual[2]	479,000	349,000	45,200	303,500	136,000	45,800	9,310	9,400,000	4,770,000	11,300,000
Pamunkey River (July 1989 through June 1993)										
Minimum monthly	3,820	2,370	216	2,145	1,430	338	200	13,900	28,500	62,500
Median monthly	35,200	22,800	2,490	20,325	12,300	3,815	834.5	1,595,000	286,000	516,000
Maximum monthly	292,000	194,000	17,800	176,200	98,400	35,700	3,160	13,600,000	3,550,000	3,100,000
Mean annual[2]	505,000	343,000	34,400	308,000	162,000	52,300	10,550	24,600,000	4,150,000	7,190,000
Mattaponi River (September 1989 through June 1993)										
Minimum monthly	1,080	853	60	793	214	119	36	5,700	11,400	14,100
Median monthly	16,500	12,500	1,130	11,251	4,065	1,670	350	241,500	167,000	209,500
Maximum monthly	106,000	82,500	7,120	75,380	24,800	10,600	1,430	1,540,000	1,780,000	981,000
Mean annual[2]	216,000	160,700	15,100	146,000	57,700	21,900	4,550	3,830,000	2,670,000	2,730,000

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

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

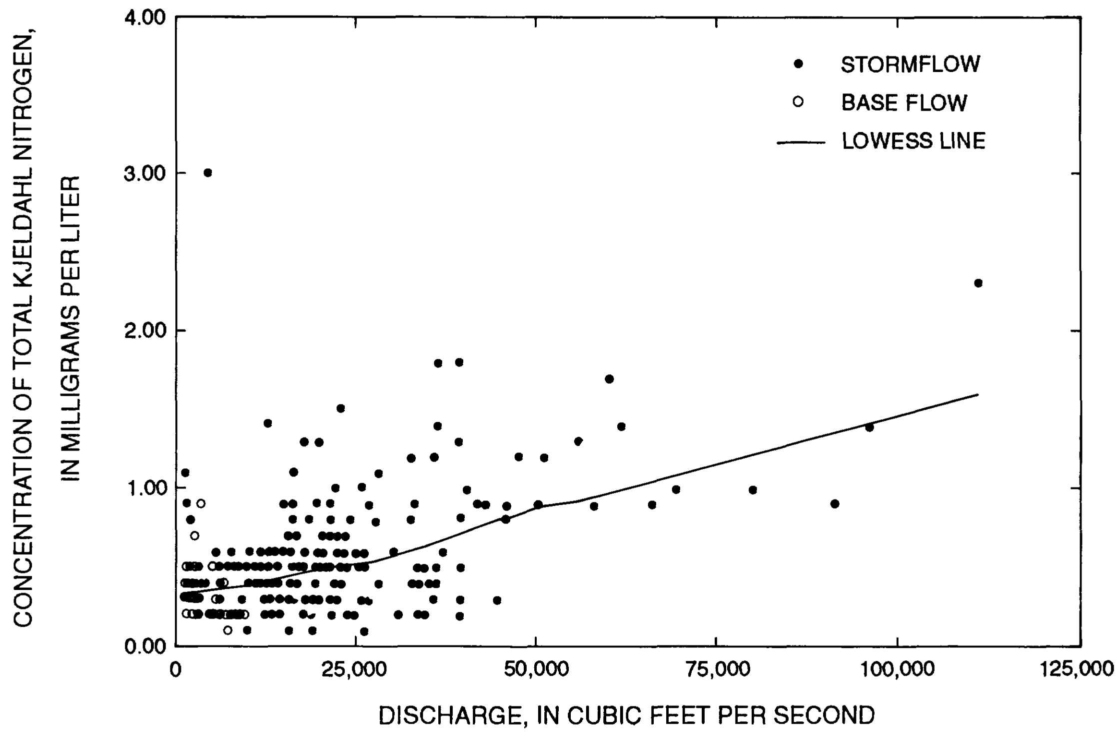


Figure 4. Relation of total Kjeldahl nitrogen concentration to discharge at the James River station, Virginia.

Table 5. Results of log-linear regression model for the Fall Line monitoring stations showing the relation of discharge to constituent concentration

[× indicates model determined discharge is significant; analyses are for the dissolved constituent unless otherwise noted]

Water-quality constituent	James River	Rappahannock River	Appomattox River	Pamunkey River	Mattaponi River
Nitrogen, total	×	×	×	×	×
Kjeldahl nitrogen, total	×	×	×	×	×
Ammonia nitrogen,	×	×	×	×	
NO_2+NO_3 nitrogen,	×	×	×		×
Phosphorus, total	×	×	×	×	×
Orthophosphorus	×	×			
Suspended solids, total	×	×	×	×	×
Organic carbon, total	×	×	×	×	×
Silica	×	×	×	×	×

Table 6. Results of log-linear regression model for the Fall Line monitoring stations showing the relation of seasonality to constituent concentration

[× indicates model determined seasonality is significant; analyses are for the dissolved constituent unless otherwise noted]

Water-quality constituent	James River	Rappahannock River	Appomattox River	Pamunkey River	Mattaponi River
Nitrogen, total				×	×
Kjeldahl nitrogen, total	×	×	×	×	×
Ammonia nitrogen,	×		×		
NO_2+NO_3 nitrogen,		×	×	×	×
Phosphorus, total	×	×		×	×
Orthophosphorus	×	×		×	×
Suspended solids, total	×	×	×	×	
Organic carbon, total	×	×		×	
Silica	×		×	×	×

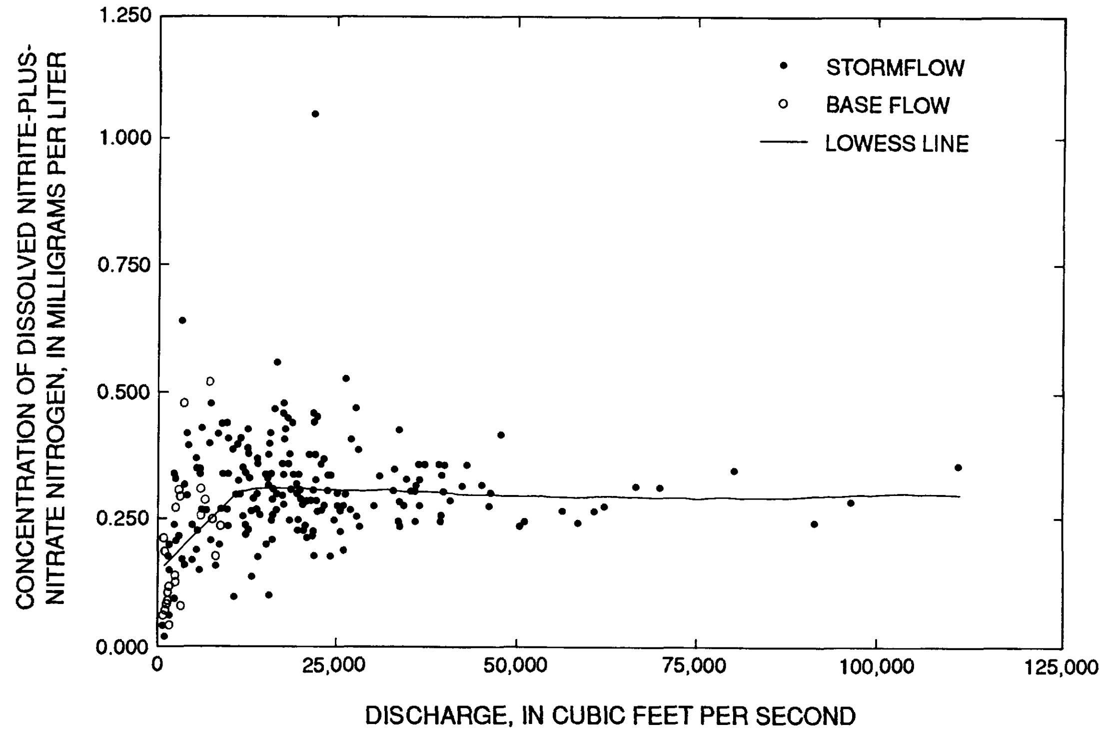


Figure 5. Relation of dissolved nitrite-plus-nitrate nitrogen concentration to discharge at the James River station, Virginia.

(fig. 4), suggests that surface runoff is a major source of this constituent. The consistently low dissolved ammonia concentration is expected for an oxygenated stream in which ammonia will be rapidly nitrified or incorporated into organic material. Concentrations of TKN and ammonia may be highest in the winter because low temperatures inhibit nitrification.

Major sources of nitrate in the James River Basin include the following: (1) In-stream conversion of TKN, from sources discussed above; (2) ground water discharged to streams as base flow that contains nitrate derived from agricultural and forested land; and (3) surface runoff from agricultural and forested land. If ground water was the only major source of nitrate, then concentrations would be expected to decrease by dilution during periods of high discharge; conversely, if surface runoff were the only major source, then concentrations of nitrate would be expected to increase with increased discharge. The nonlinear relation of dissolved nitrite-plus-nitrate nitrogen to discharge (fig. 5) suggests that nitrate in the James River is controlled by a combination of sources and in-stream processes.

The median monthly load (defined as the median value of all computed monthly loads during the sampling period) of total nitrogen in the James River was 371,000 kg (table 4). The mean annual total nitrogen load consisted of approximately 57 percent organic nitrogen, 38 percent dissolved nitrite-plus-nitrate, and 5 percent dissolved ammonia nitrogen. The highest total nitrogen load occurred in March 1993 and, in general, the highest loads are related to periods of high discharge (fig. 7). The other nitrogen species showed similar load distribution during the period of sample collection, and the results are summarized in table 4.

Phosphorus and total suspended solids.—Concentrations of total phosphorus and total suspended solids in the James River ranged over approximately two orders of magnitude (table 3). The median concentration of dissolved orthophosphorus was 0.04 mg/L compared to the 0.15 mg/L median concentration for total phosphorus. Thus, most of the total phosphorus is not dissolved but is associated with suspended solids and organic material.

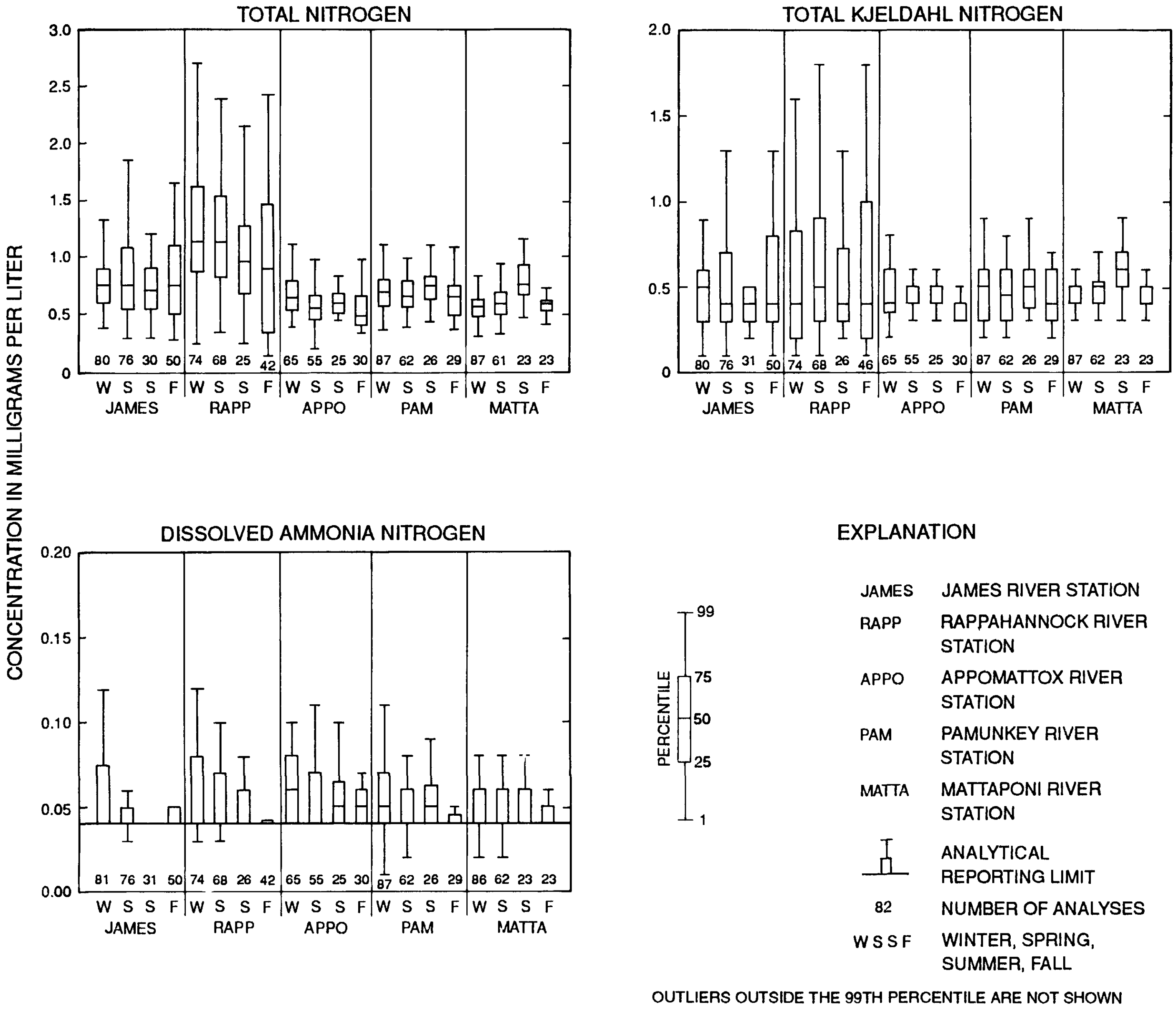
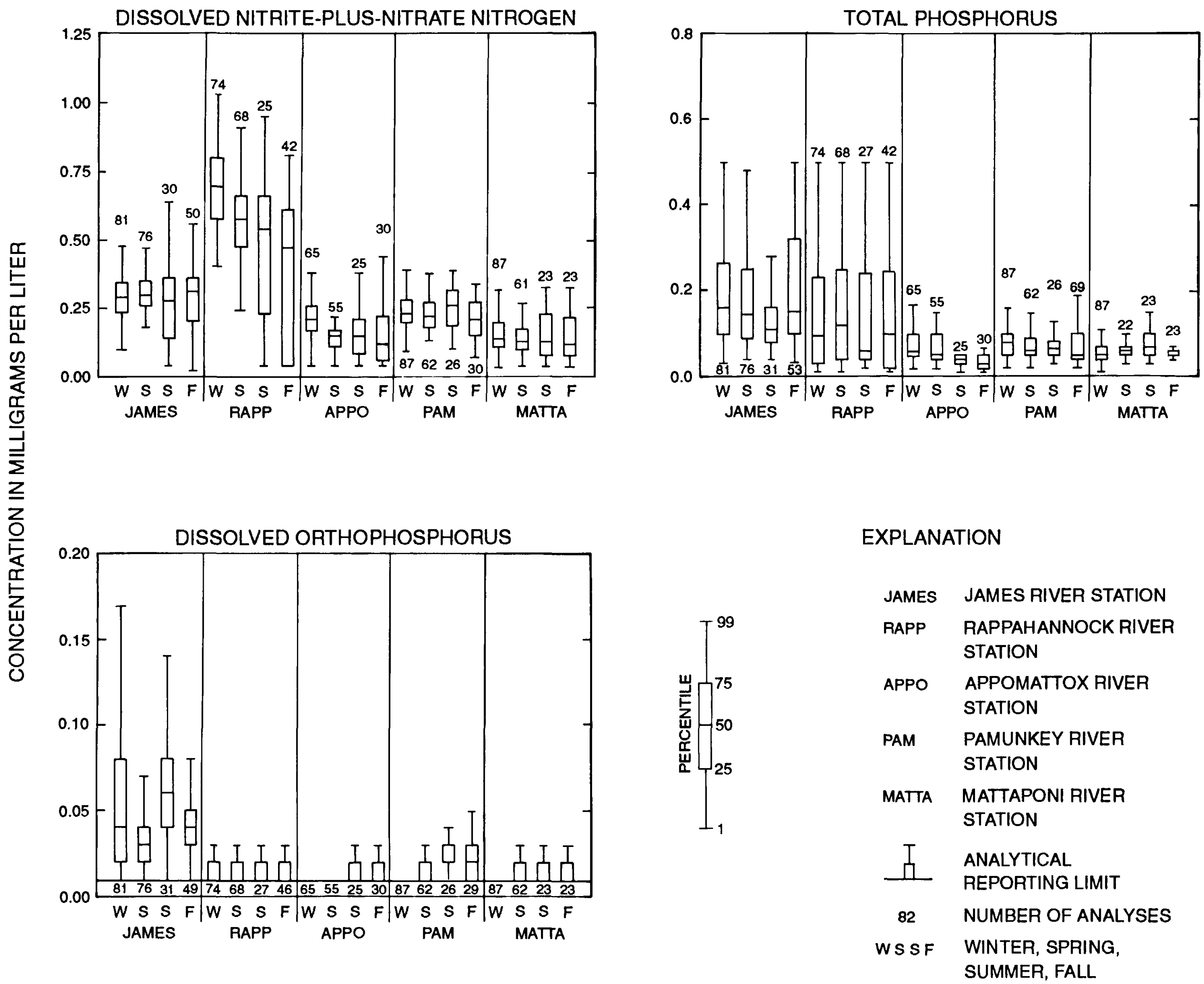
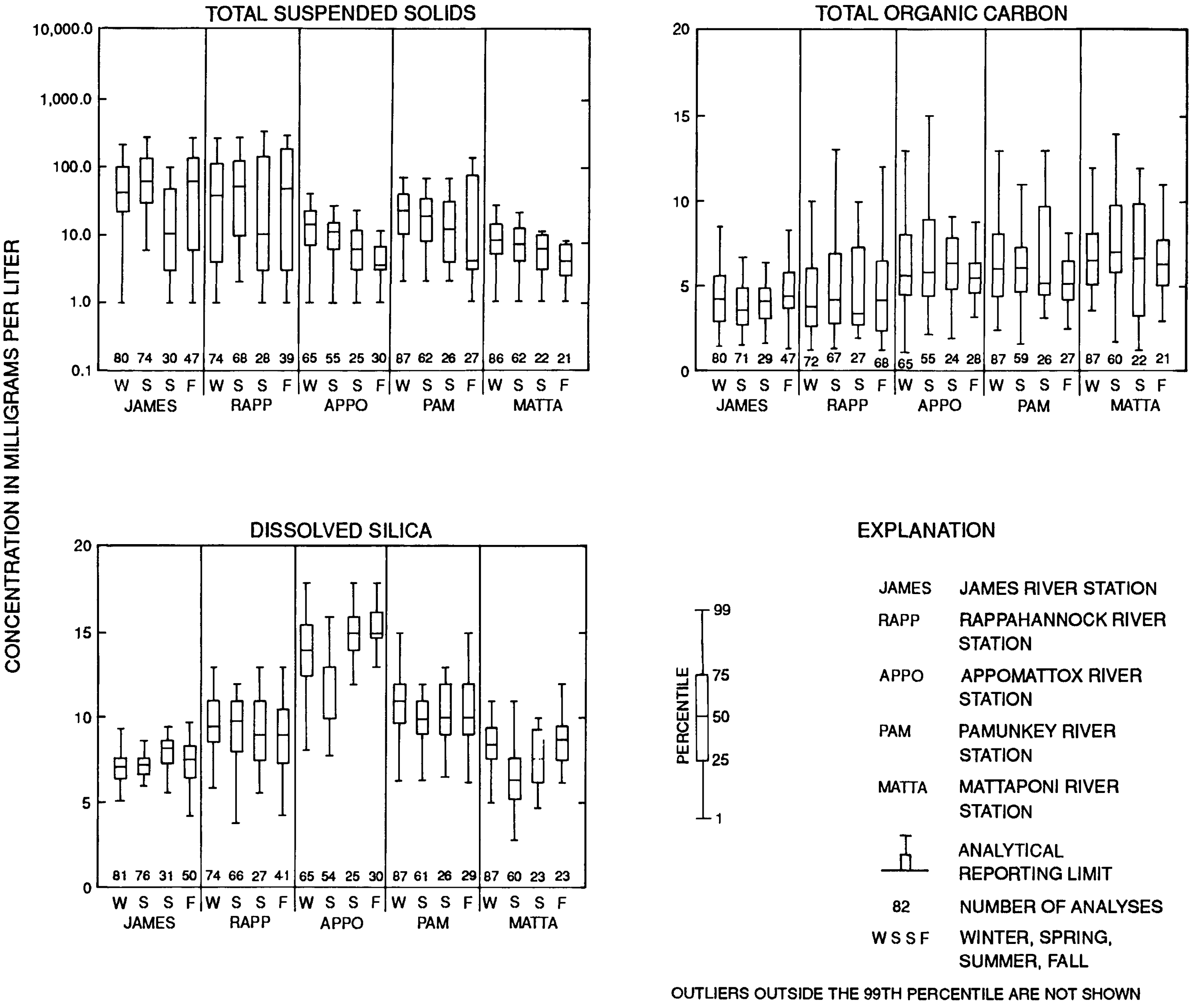


Figure 6. Seasonal concentrations of selected constituents at the Fall Line stations, Virginia.



OUTLIERS OUTSIDE THE 99TH PERCENTILE ARE NOT SHOWN

Figure 6. Seasonal concentrations of selected constituents at the Fall Line stations, Virginia--Continued.



TOTAL SUSPENDED SOLIDS

TOTAL ORGANIC CARBON

DISSOLVED SILICA

EXPLANATION

Figure 6. Seasonal concentrations of selected constituents at the Fall Line stations, Virginia--Continued.

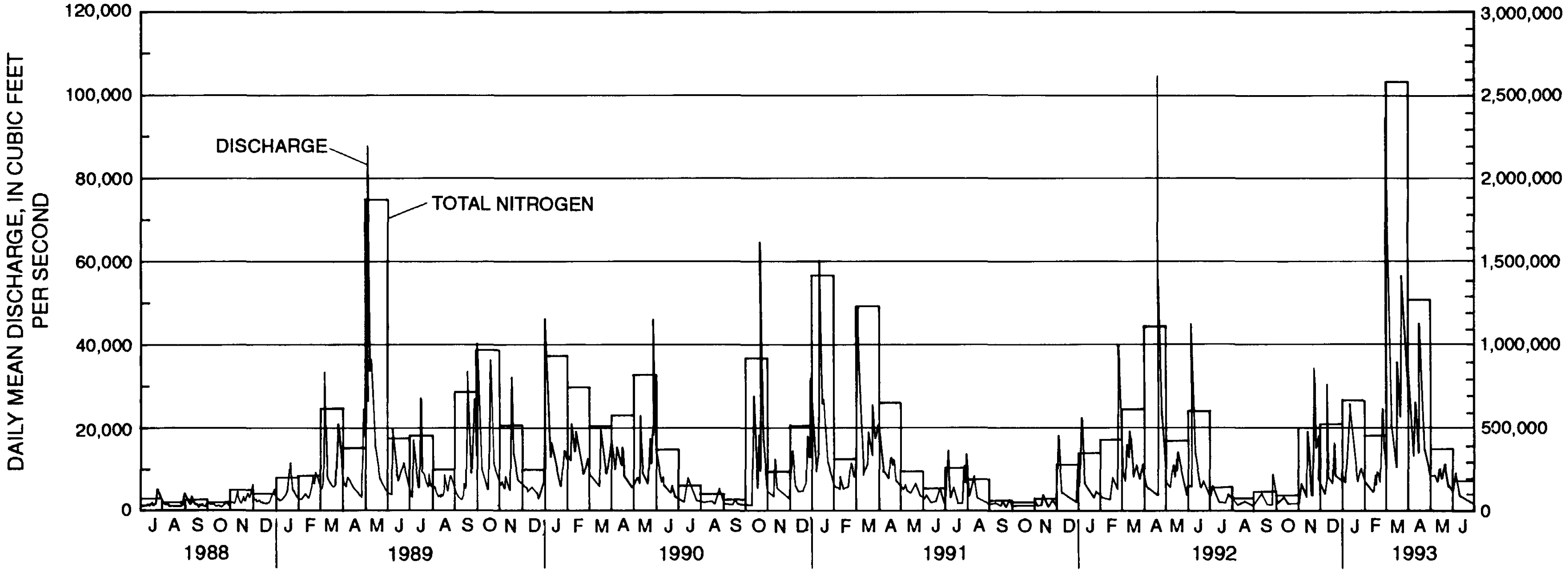


Figure 7. Relation of discharge to total nitrogen load at the James River station, Virginia, July 1988 through June 1993.

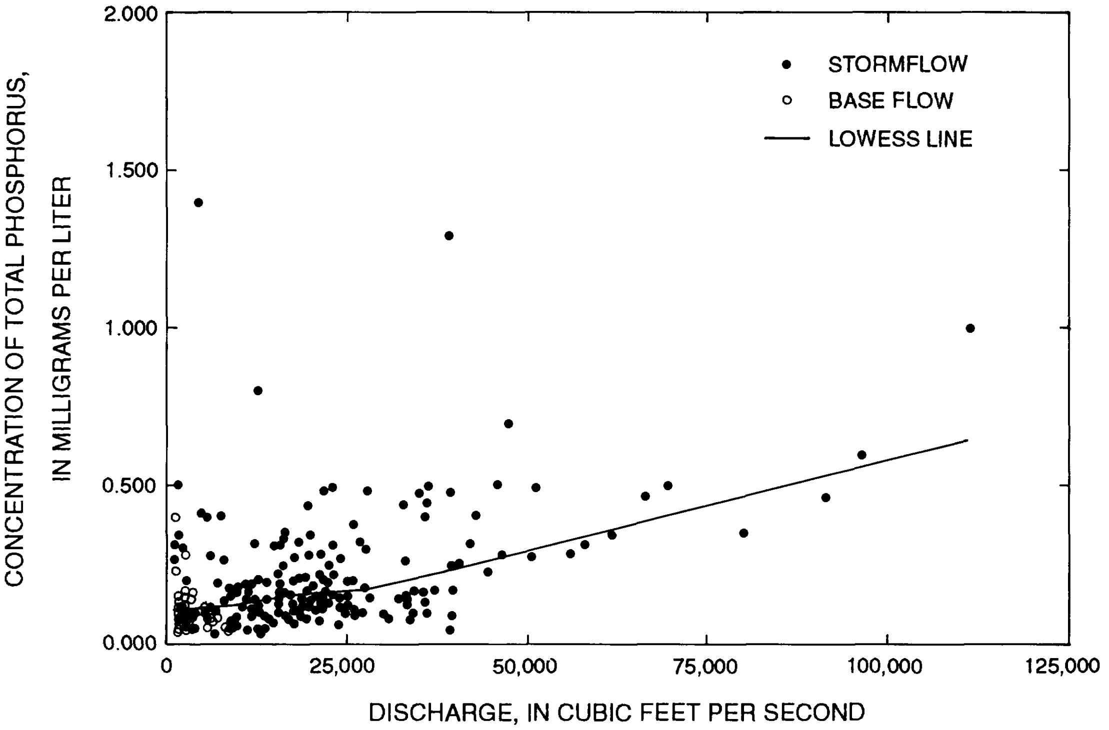


Figure 8. Relation of total phosphorus concentration to discharge at the James River station, Virginia.

Concentrations of total phosphorus and total suspended solids increased with discharge (table 5 and fig. 8), whereas concentration of dissolved orthophosphorus decreased with increasing discharge (fig. 9). These constituents correlated significantly to season (table 6), with total suspended solids and total phosphorus lowest in the summer, whereas orthophosphorus was highest in the summer (fig. 6).

The positive relation of total phosphorous and total suspended solids to discharge indicates that the primary source of these constituents in the James River is overland runoff during storm events. Runoff from agricultural lands probably contributes most of the total phosphorus; although, weathering of natural soils and rocks can also contribute significant amounts of total phosphorus. In contrast, most dissolved orthophosphorus probably originates from point-source discharges on the James River, indicated by dilution during periods of high streamflow. The steady decrease in dissolved orthophosphorus during the period of sample collection can be attributed to upgrades in sewage treatment plants and the Statewide phosphorus detergent ban that went into effect in 1989.

The median monthly load of total phosphorus in the James River was 61,600 kg (table 4), and the median monthly load of dissolved orthophosphorus was 25,900 kg (table 4). During the data-collection period, the percentage of total phosphorus load contributed by dissolved orthophosphorus decreased from 35 percent in 1989 to 19 percent in 1992 (fig. 10). It should be noted that estimated loads near the beginning of the sampling period are greater for dissolved orthophosphorus than for total phosphorus, of which dissolved orthophosphorus is actually a component. This discrepancy was caused probably by the lower variability in dissolved orthophosphorus concentrations compared to the total phosphorus concentrations, or the small number of samples collected that affected how the model computed loads for that period of time. Loads in the James River were highest in March 1993 for both total suspended solids and total phosphorus, and lowest in October 1988 and October 1991, respectively. The median monthly load of total suspended solids was 20,050,000 kg for the sampling period.

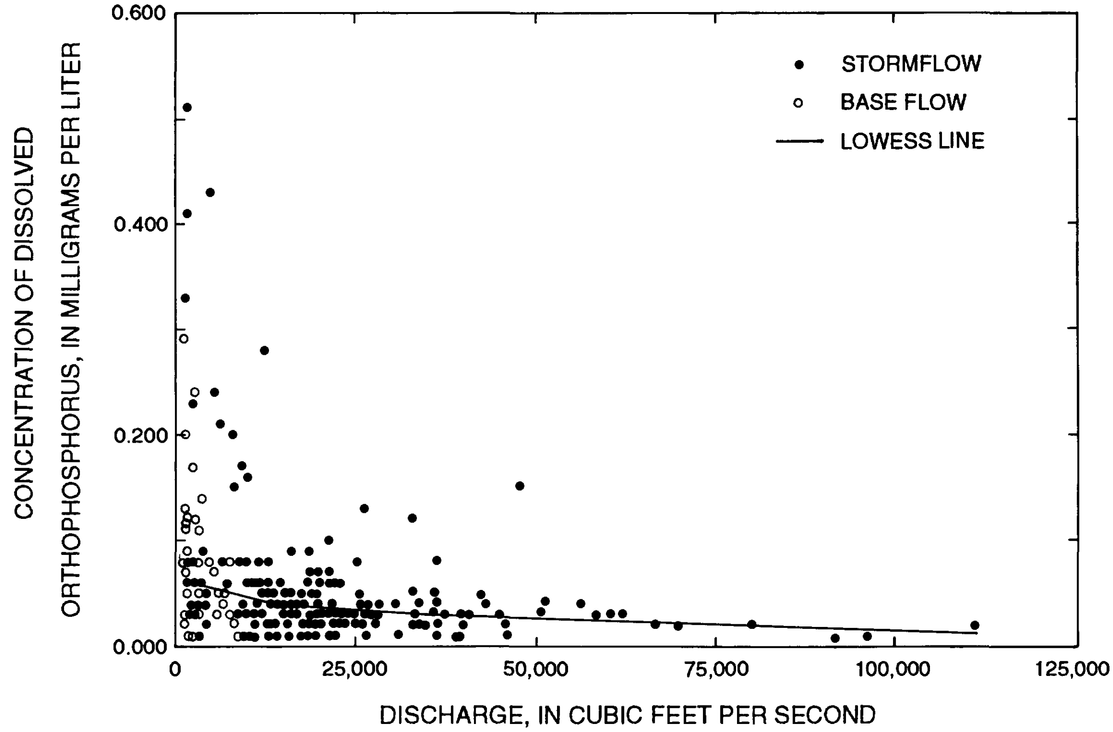


Figure 9. Relation of dissolved orthophosphorus concentration to discharge at the James River station, Virginia.

Total organic carbon, silica, and field measurements.—Concentration of total organic carbon ranged from 1.3 to 25 mg/l (table 3).Total organic carbon concentration had a positive relation to discharge (table 5) and was related to season (table 6), but the median for each season was similar except for a low value in the spring (fig. 6). The increase of total organic carbon with discharge suggests that a majority of the total organic carbon is derived from surface runoff, and that the majority of total organic carbon is particulate rather than dissolved. The increase of concentration with discharge and the seasonal variation can be correlated to increased total organic carbon entering the system in runoff from forested and agricultural areas during the fall and winter.

Loads of total organic carbon were lowest in October 1988 and highest in March 1993 (fig. 11). The load of total organic carbon during storm events of May 1989 seems relatively low compared with the storm events in March 1993, which possibly is due to the reduced runoff because of increased vegetative cover in May. The median monthly load was 2,100,000 kg (table 4).

The results from the regression model indicated that concentrations of dissolved silica had a positive relation with discharge at the James River (table 5), but the LOWESS line in figure 12 shows a slight decrease in concentration during very high-discharge conditions. Silica concentration was correlated to season (table 5) and was generally high in the summer (fig. 6). The dilution of silica concentration at high discharge and a high median concentration in the summer during low discharge suggests that a primary source of dissolved silica is ground-water discharge to the James River. Silica can enter the ground-water system from weathering of silicate minerals in the aquifers underlying the James River Basin. Additional dissolved silica can be derived from in-stream dissolution of silicate minerals in suspended sediments and the stream bed. The median monthly load was 3,625,000 kg for dissolved silica (table 4). Loads of dissolved silica were lowest in October 1988 and highest in March 1993.

The James River had a median pH value of 7.3, with a range from 6.1 to 8.9 (table 3). Of the six pH values above 8.5, five were collected in the summer, and all six

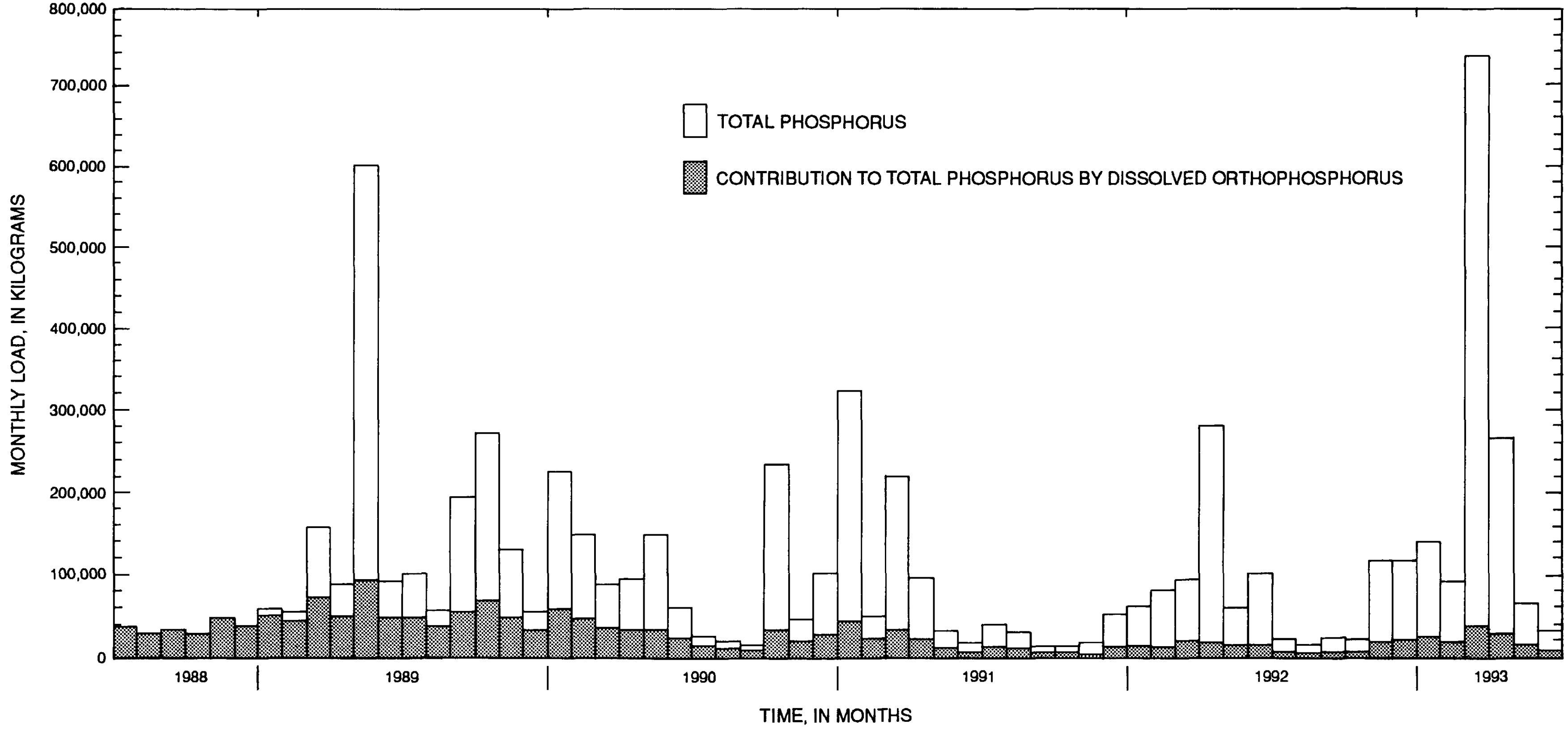


Figure 10. Load of total phosphorus and contribution to total phosphorus load by dissolved orthophosphorus at the James River station, Virginia, July 1988 through June 1993.

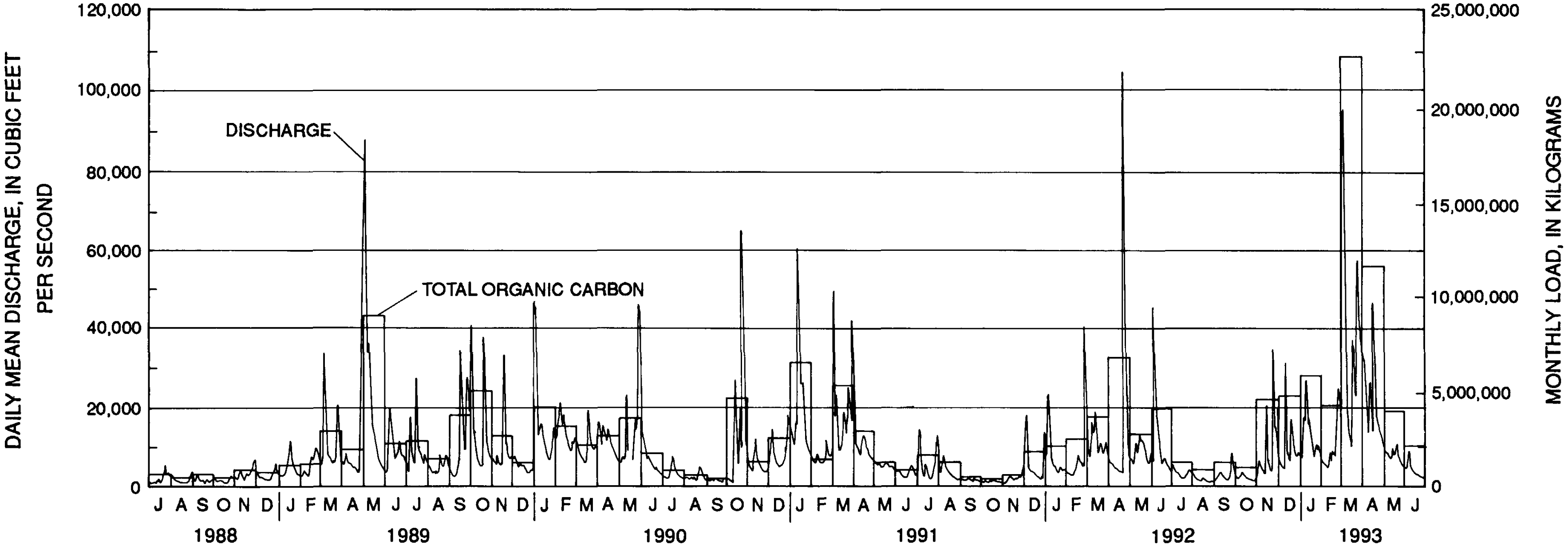


Figure 11. Relation of discharge to total organic carbon load at the James River station, Virginia, July 1988 through June 1993.

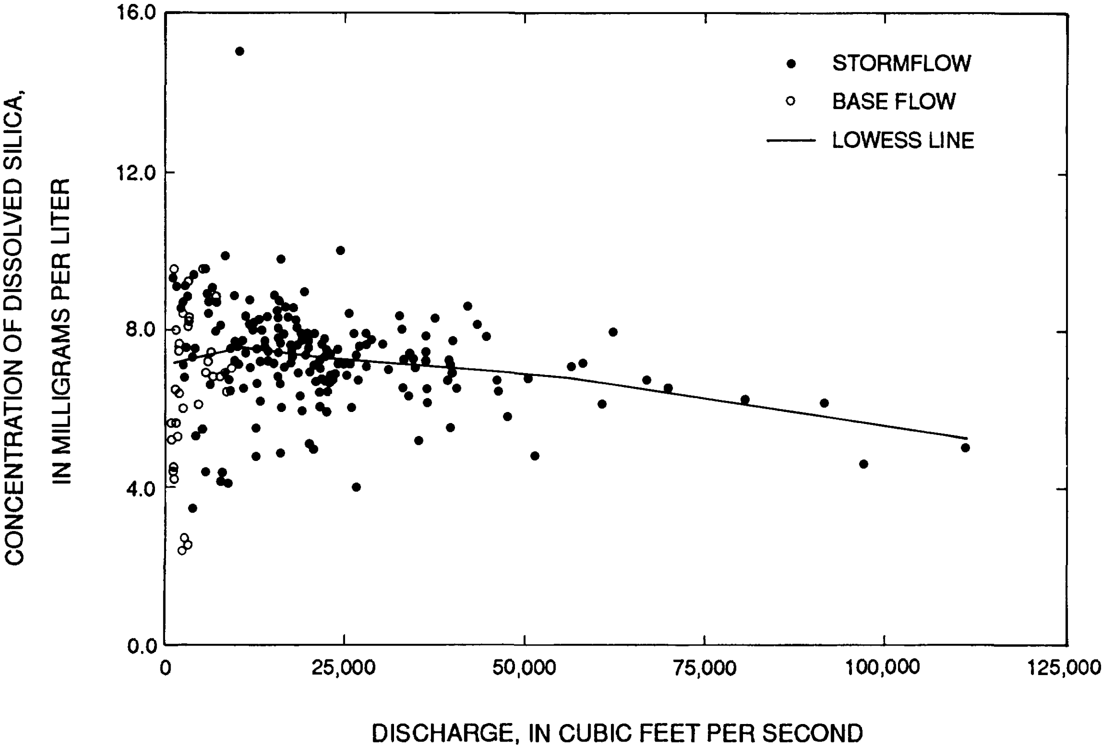


Figure 12. Relation of dissolved silica concentration to discharge at the James River station, Virginia.

were during low-discharge conditions. As expected, ground-water discharge to the James River has higher pH than surface runoff because of reaction with carbonates and other buffering minerals in aquifers. In-stream biochemical processes such as algal respiration and decay of organic material also can affect pH in the James River. During the data-collection period for this report, dissolved oxygen concentration never was below the State aquatic life criteria of 4.0 mg/L. Specific conductance ranged from 60 to 345 µS/cm.

Rappahannock River

Nitrogen species.—Concentration of total nitrogen in the Rappahannock River ranged from less than 0.14 to 3.41 mg/L, with a median concentration of 1.07 mg/L (table 3). The predominant nitrogen species, based on median concentration, was dissolved nitrite-plus-nitrate nitrogen; although, organic nitrogen also was present in significant concentrations and comprised the majority of the measured TKN. Dissolved ammonia nitrogen was the least prevalent form of nitrogen in the Rappahannock River.

All of the nitrogen species concentrations were related to discharge (table 5), and distinct relations for each species were apparent. It should be noted that only two samples were collected at discharges above 30,000 ft^3/s, both of which were collected on the same day. Because samples at those extreme discharges are collected infrequently, the relation above 30,000 ft^3/s is not well-defined for all constituents at the Rappahannock River. The positive relation between discharge and concentration of TKN at the Rappahannock River is shown in figure 13; organic nitrogen and dissolved ammonia concentration separately showed this same relation to discharge. An increase in concentration of dissolved nitrite-plus-nitrate nitrogen with discharge during low-discharge conditions and a dilution effect during high discharge conditions are shown in figure 14. The regression model results indicated that both TKN and dissolved nitrite-plus-nitrate nitrogen concentrations were correlated to season (table 6). The median concentration of

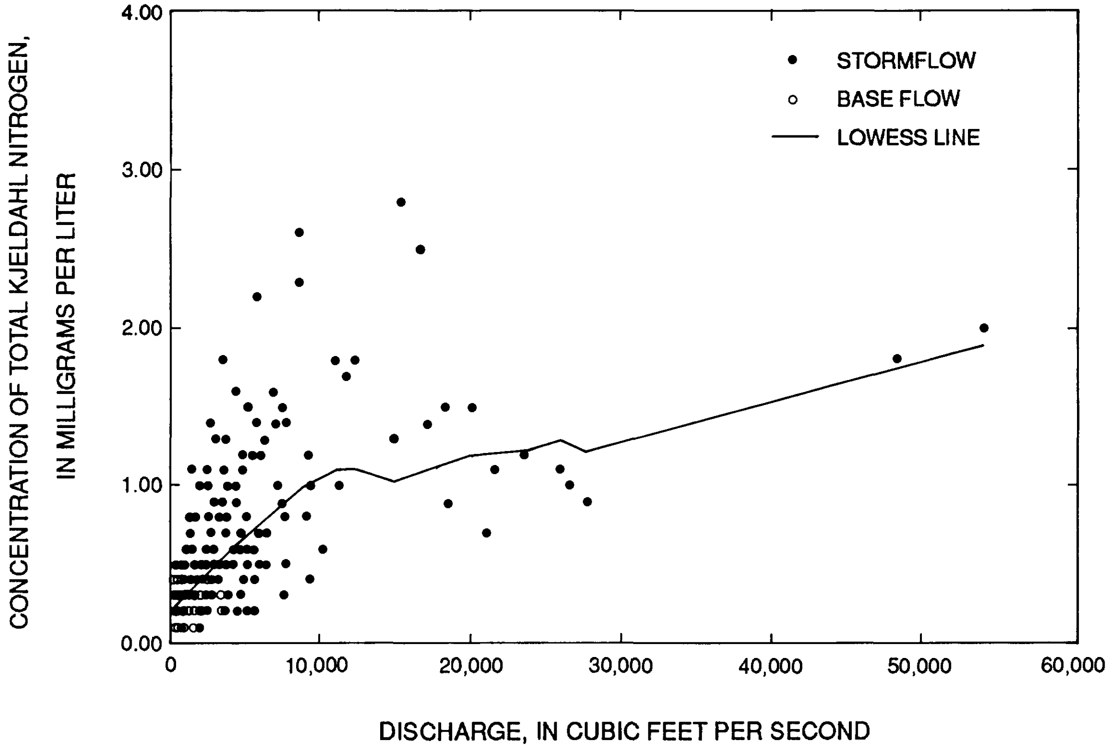


Figure 13. Relation of total Kjeldahl nitrogen concentration to discharge at the Rappahannock River station, Virginia.

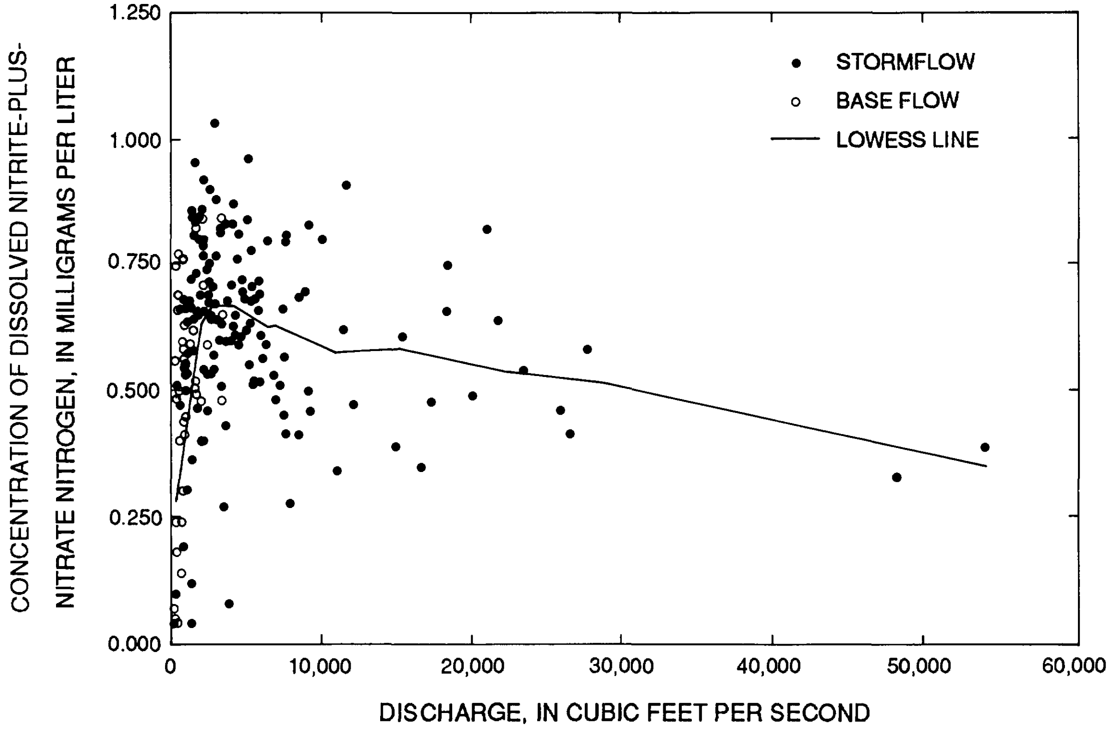


Figure 14. Relation of dissolved nitrite-plus-nitrate nitrogen concentration to discharge at the Rappahannock River station, Virginia.

TKN was highest in the spring (fig. 6), whereas the highest median for dissolved nitrite-plus-nitrate nitrogen occurred in the winter.

The Rappahannock River is generally considered to be nonpoint-source dominated (oral commun., Frederick Hoffman, Virginia Department of Environmental Quality, 1995). This basin has approximately 40 percent of its land devoted to agricultural activities, which probably contribute a large amount of nitrogen to the river by way of surface runoff and ground-water discharge. Base flow is the major source of nitrate, based on the dilution of nitrate at high discharges during storm events; although, nitrification of TKN also probably contributes nitrate to the river. Organic nitrogen is derived mainly from surface runoff from agricultural and forested land and instream biological uptake of dissolved ammonia and nitrate.

The median monthly load for total nitrogen in the Rappahannock River was 96,550 kg (table 4). Although median monthly concentration of dissolved nitrite-plus-nitrate nitrogen was higher than organic nitrogen, the mean annual loads of these two constituents were very similar—each compose about half of the mean annual total nitrogen load. During the period of sample collection, the lowest median monthly load of total nitrogen was in October 1991, with the highest in March 1993 (fig. 15), which was the highest monthly mean discharge for the sampling period.

Phosphorus and suspended sediment.—Concentration of total phosphorus in the Rappahannock River ranged from less than 0.01 to 1.1 mg/L, with a median concentration of 0.10 mg/L (table 3). The median concentration for total phosphorus was significantly higher than the median concentration for dissolved orthophosphorus (0.01 mg/L), indicating that the majority of the phosphorus is in the particulate phase and is associated with the suspended solids. Total suspended solids showed a range in concentration variation of almost three orders of magnitude. The maximum total suspended solids concentration of 844 mg/L occurred in response to a quick, intense storm, when the daily mean discharge rose from 1,720 to 11,900 ft^3/s over a 2-day period.

Concentrations of total phosphorus, dissolved orthophosphorus, and total suspended solids all showed a positive relation to discharge at the Rappahannock River (table 5), and these water-quality constituents were also related to season (table 6). Total phosphorus and total suspended solids concentrations were lowest in the summer. The relation of concentrations of total phosphorus, dissolved orthophosphorus, and total suspended solids to discharge and to season indicate a nonpoint source for these constituents, probably runoff from agricultural lands and weathering of natural rocks and soils. Some dissolved orthophosphorus also can be contributed by municipal waste-water dischargers to the river.

The median monthly load of total phosphorus was 8,815 kg, whereas the median monthly total suspended solids load was 3,795,000 kg (table 4). Loads for both total phosphorus and for total suspended solids were highest in May 1989, as a result of a storm event that caused the highest daily mean discharge for 1989 (fig. 16). The lowest loads were in October 1991 for both total suspended solids and total phosphorus. The annual load of dissolved orthophosphorus for the data-collection period ranged from 6 to 11 percent of the total phosphorus load.

Total organic carbon, silica, and field parameters.—Concentration of total organic carbon ranged from 1.2 to 110 mg/L (table 3). The maximum concentration of 110 mg/L was the highest concentration of total organic carbon of all five rivers. The concentration of total organic carbon had a positive relation to discharge and to season. (tables 5 and 6). The median monthly load of total organic carbon was 392,000 kg. It should be noted that the maximum concentration for total organic carbon resulted in a difference in load computations of about 6 percent.

Dissolved silica ranged in concentration from 3.5 to 13 mg/L (table 3), and had a statistically significant negative relation to discharge (table 5) that suggests much of the dissolved silica is derived from base flow. The median monthly load was 1,010,500 kg (table 4). The pH ranged from 5.8 to 8.4, and specific conductance ranged from 40 to 138 μS/cm (table 3). The minimum concentration of dissolved oxygen was 6.0 mg/L and was well above the State aquatic life criteria minimum of 4.0 mg/L.

Appomattox River

Nitrogen species.—Concentration of total nitrogen in the Appomattox River ranged from 0.20 mg/L to 1.14 mg/L, and the median concentration of total nitrogen was 0.60 mg/L. Organic nitrogen was the predominant species, followed by dissolved nitrite-plus-nitrate nitrogen and then dissolved ammonia nitrogen. All the nitrogen species concentrations had a relation to discharge (table 5): total nitrogen, TKN, organic nitrogen, and dissolved ammonia nitrogen had positive relations to discharge in

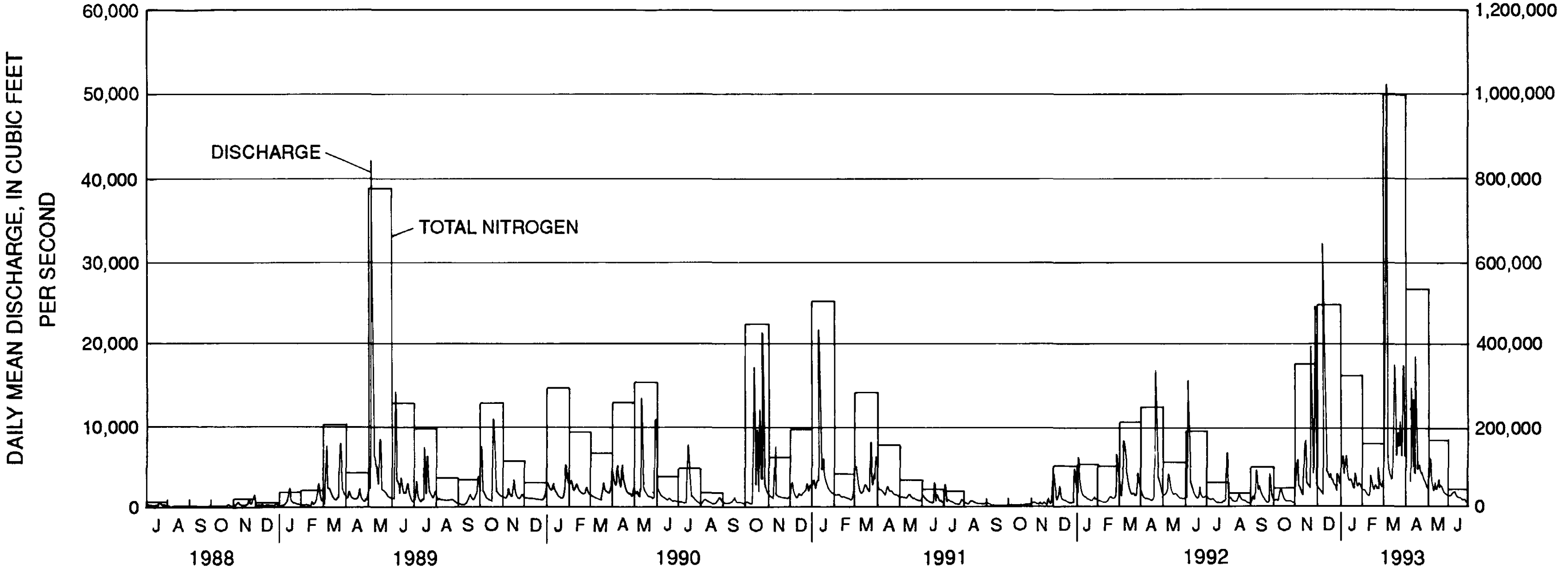


Figure 15. Relation of discharge to total nitrogen load at the Rappahannock River station, Virginia, July 1988 through June 1993.

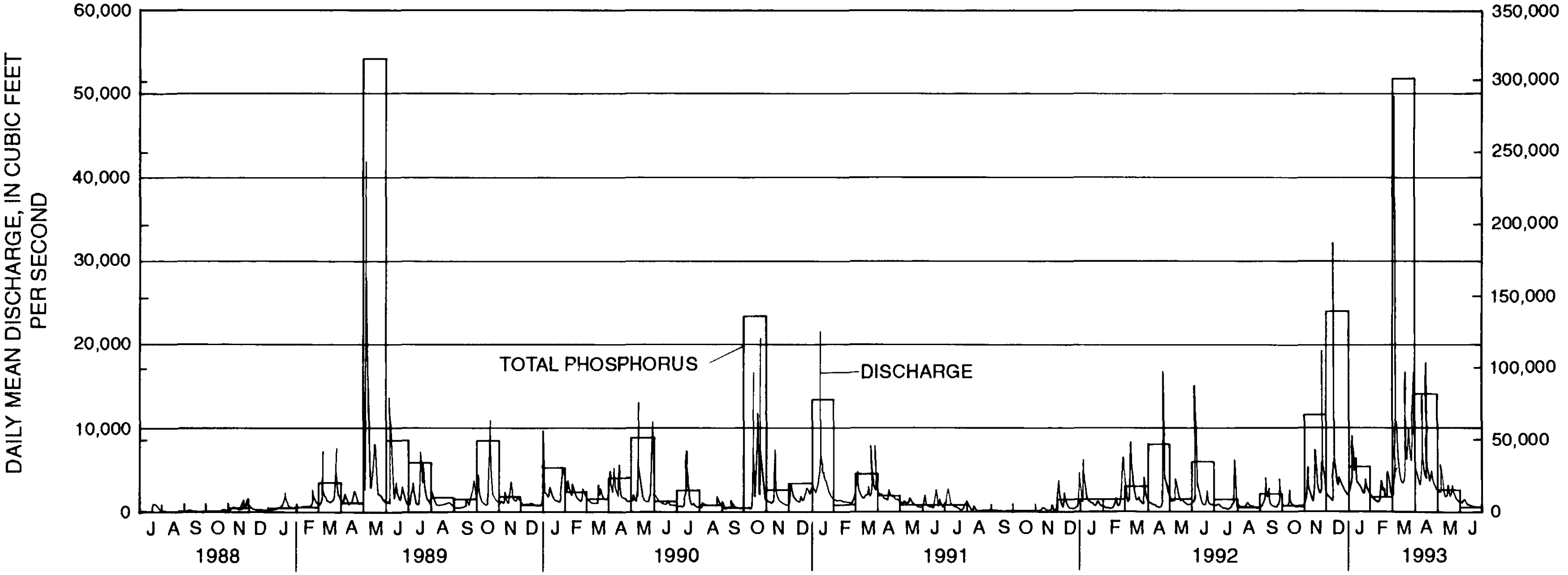


Figure 16. Relation of discharge to total phosphorus load at the Rappahannock River station, Virginia, July 1988 through June 1993.

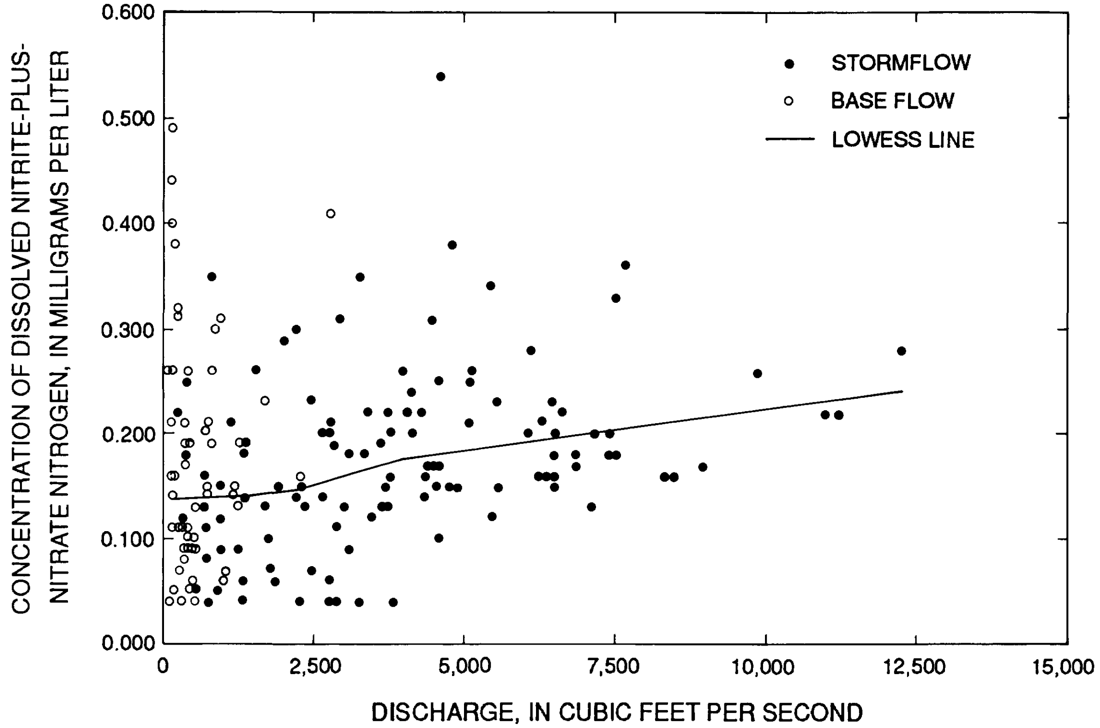


Figure 17. Relation of dissolved nitrite-plus-nitrate nitrogen concentration to discharge at the Appomattox River station, Virginia.

the Appomattox River. Concentration of dissolved nitrite-plus-nitrate nitrogen also had a positive relation to discharge but did not show a large concentration increase until discharge exceeded 2,500 ft^3/s (fig. 17). Many of the high concentrations of nitrite-plus-nitrate nitrogen were measured in samples collected during low-discharge conditions. All of the individual nitrogen species, except total nitrogen, were related to season (table 6). Seasonal variation of the nitrogen species was small (fig. 6).

Surface runoff from agricultural and forested areas contributes nitrogen in all three forms of interest to the Appomattox River, as indicated by the positive relations to discharge. Significant amounts of nitrate also may be derived from base flow, and in-stream biological uptake and decay probably affects the distribution of nitrogen among species.

The median monthly load of total nitrogen in the Appomattox River was 34,600 kg (table 4). The mean annual nitrogen load consisted of approximately 63 percent organic nitrogen, 28 percent dissolved nitrite-plus-nitrate nitrogen, and 9 percent dissolved ammonia nitrogen. Monthly loads of total nitrogen were lowest in September 1991 and highest in March of 1993 (fig. 18). The period from January through April 1993 included the first, second, and third highest monthly loads for the total nitrogen of the data-collection period.

Phosphorus and total suspended sediment.—The median total phosphorus concentration in the Appomattox River monitoring station was 0.05 mg/L, whereas the median dissolved orthophosphorus concentration was 0.01 mg/L, indicating that most of the phosphorus is in the particulate phase. The median concentration of total suspended solids was 9 mg/L. The results of the regression model indicated that total phosphorus and total suspended solids have a positive relation to discharge (table 5), but that only total suspended solids was correlated to season (table 6). Dissolved orthophosphorus concentration was often measured at the detection limit, and showed no relation to discharge or to season. Biological uptake of dissolved orthophosphorus in Lake Chesdin may explain the consistently low concentration of this constituent. Median concentrations of total phosphorus and total suspended solids were highest in the winter and spring (fig. 6). High total phosphorus and total suspended solids concentrations can be attributed to the higher

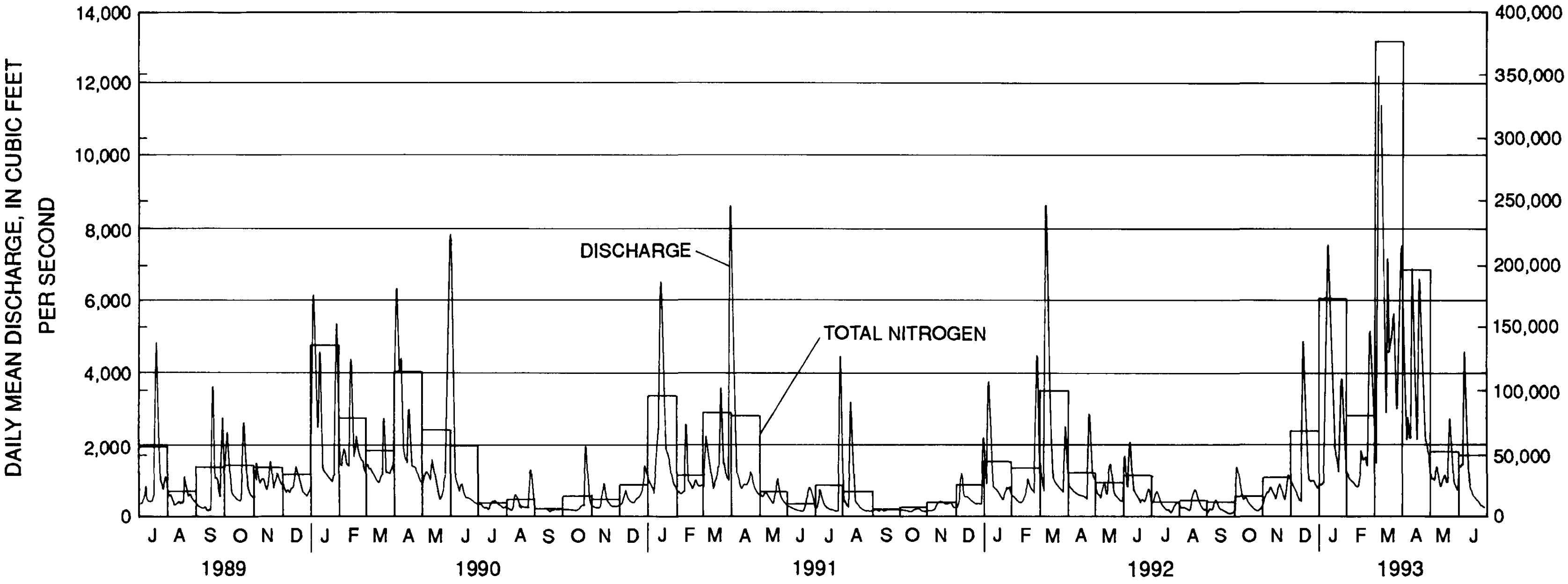


Figure 18. Relation of discharge to total nitrogen load at the Appomattox River station, Virginia, July 1989 through June 1993.

discharge periods for the Appomattox River in the winter and spring; Lake Chesdin does not totally prevent the transport of constituents associated with suspended sediment.

The median monthly load for total phosphorus was 2,700 kg, whereas the median monthly load for total suspended solids was 544,000 kg (table 4). Loads for both total phosphorus and total suspended solids were highest in March 1993 and lowest in September 1990. The annual load of dissolved orthophosphorus ranged from 18 to 20 percent of the annual load of total phosphorus.

Total organic carbon, silica, and field measurements.—Concentration of total organic carbon in the Appomattox River ranged from 1.1 to 20 mg/L, and silica concentration ranged from 6.4 to 18 mg/L (table 3). Total organic carbon concentration increased as the discharge increased, whereas dissolved silica concentration decreased as discharge increased (table 5). Total organic carbon concentration was not correlated to season, whereas dissolved silica did show a relation to season (table 6). The positive correlation between discharge and total organic carbon concentration suggests that much of the total organic carbon is associated with suspended organic carbon and is transported during high-discharge events. Median values for dissolved silica were lowest in the spring and winter. The dilution effect of silica concentration with increasing discharge and high concentrations during low-discharge conditions suggest that base flow is a major source of dissolved silica.

The median monthly load for total organic carbon was 373,000 kg (table 4). Monthly total organic carbon loads were highest in September 1990 and lowest in March 1993. The first, second, and third total organic carbon loads, as for total nitrogen, were during the period from January to April 1993, during the extended period of high-discharge conditions. The median monthly load of dissolved silica was 889,500 kg. Monthly dissolved silica loads were lowest in September 1991 and highest in March 1993. Dissolved oxygen concentrations were never below the State aquatic life criteria of 4.0 mg/L. The pH ranged from 6.1 to 8.1, and specific conductance ranged from 38 to 135 µS/cm (table 3).

Pamunkey River

Nitrogen species.—The concentration of total nitrogen in the Pamunkey River ranged from 0.36 to 2.23 mg/L, with a median concentration of 0.69 mg/L (table 3). The predominant nitrogen species was organic nitrogen; although, dissolved nitrite-plus-nitrate nitrogen also was present in significant concentrations. Total nitrogen, TKN, and dissolved ammonia nitrogen each showed a relation to discharge at the Pamunkey River (table 5); although, the concentration/discharge relation varied for each constituent. Total nitrogen concentration increased with increasing discharge up to about 5,000 ft^3/s, with a slight decrease in concentration as discharge increased. TKN, which is mostly organic nitrogen, also showed an increase with discharge to about 5,000 ft^3/s, but did not change significantly above 5,000 ft^3/s (fig. 19). Dissolved ammonia nitrogen (fig. 20) showed an increase with discharge to about 2,000 ft^3/s and a concentration decrease with increasing discharge. No significant relation existed between dissolved nitrite-plus-nitrate nitrogen and discharge in the Pamunkey River (table 5). All constituents except for ammonia were correlated to season (table 6); although, there was not a large range in median concentrations between seasons for any of the nitrogen species (fig. 6).

The Pamunkey River has no major municipal point-source discharges upstream of the monitoring station (table 1), so nitrogen is derived primarily from nonpoint sources, such as forest, agricultural land, and wetlands. Upstream of the monitoring station there is fairly low relief and a wide flood plain, which lowers streamflow velocities during high-discharge conditions. The low velocities allow constituents associated with the sediment transport to settle out of the water column as they move downstream. The lack of a positive relation between TKN and discharge at high discharges can be partially explained by the settling out of particulate organic nitrogen during high-discharge conditions. The median monthly load of total nitrogen for the sampling period was 35,200 kg (table 4). The highest total nitrogen load was in March 1993, whereas the lowest load was in September and October 1991 (fig. 21).

Phosphorus and total suspended sediment.—Concentration of total phosphorus ranged from 0.02 to 0.50 mg/L, with a median of 0.07 mg/L (table 3). Most of the phosphorus is transported in the particulate phase based on a comparison with median values of total phosphorus and dissolved orthophosphorus. Both total phosphorus and total suspended solids concentrations increased with discharge at the Pamunkey River (table 5) for discharges between 1,000 and 5,000 ft^3/s. Above 5,000 ft^3/s, the total phosphorus concentration did not increase significantly with discharge, whereas the total suspended solids concentration actually decreased at higher discharges (fig. 22). Dissolved orthophosphorus did not show any

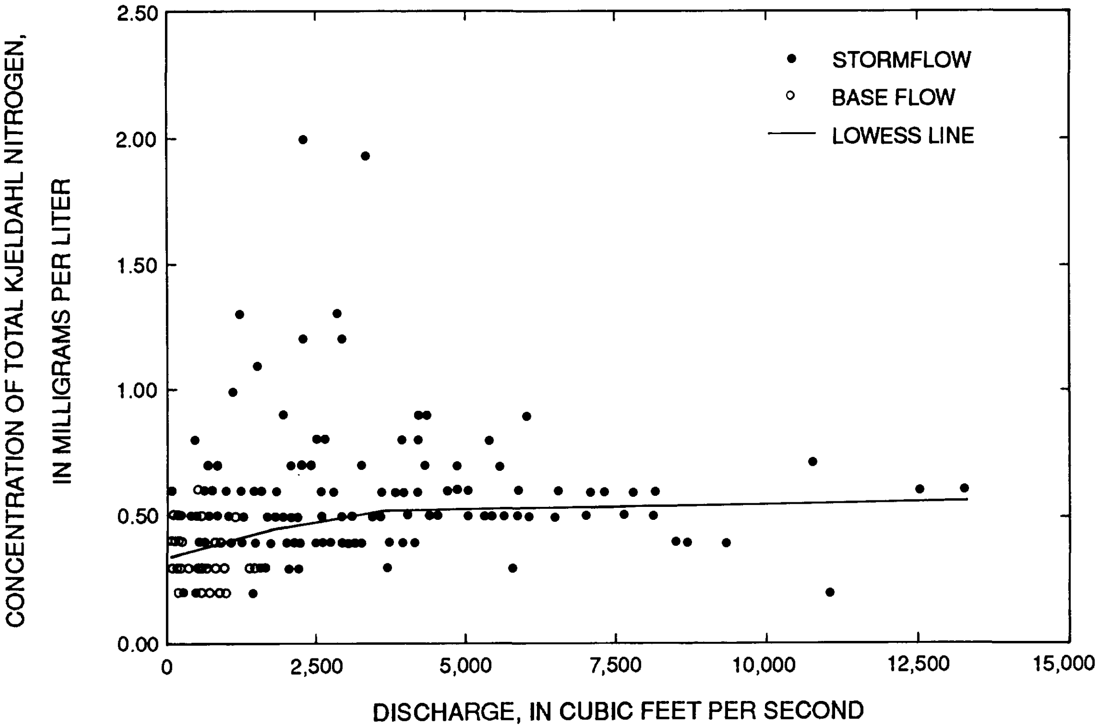


Figure 19. Relation of total Kjeldahl nitrogen concentration to discharge at the Pamunkey River station, Virginia.

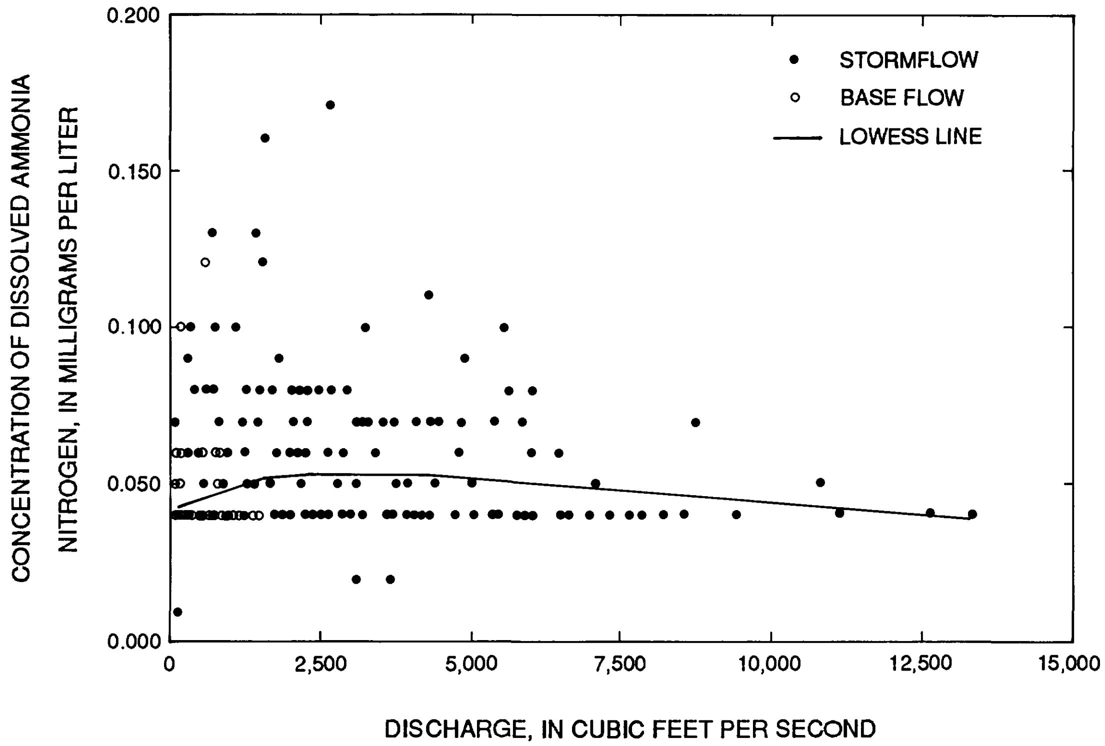


Figure 20. Relation of dissolved ammonia nitrogen concentration to discharge at the Pamunkey River station, Virginia.

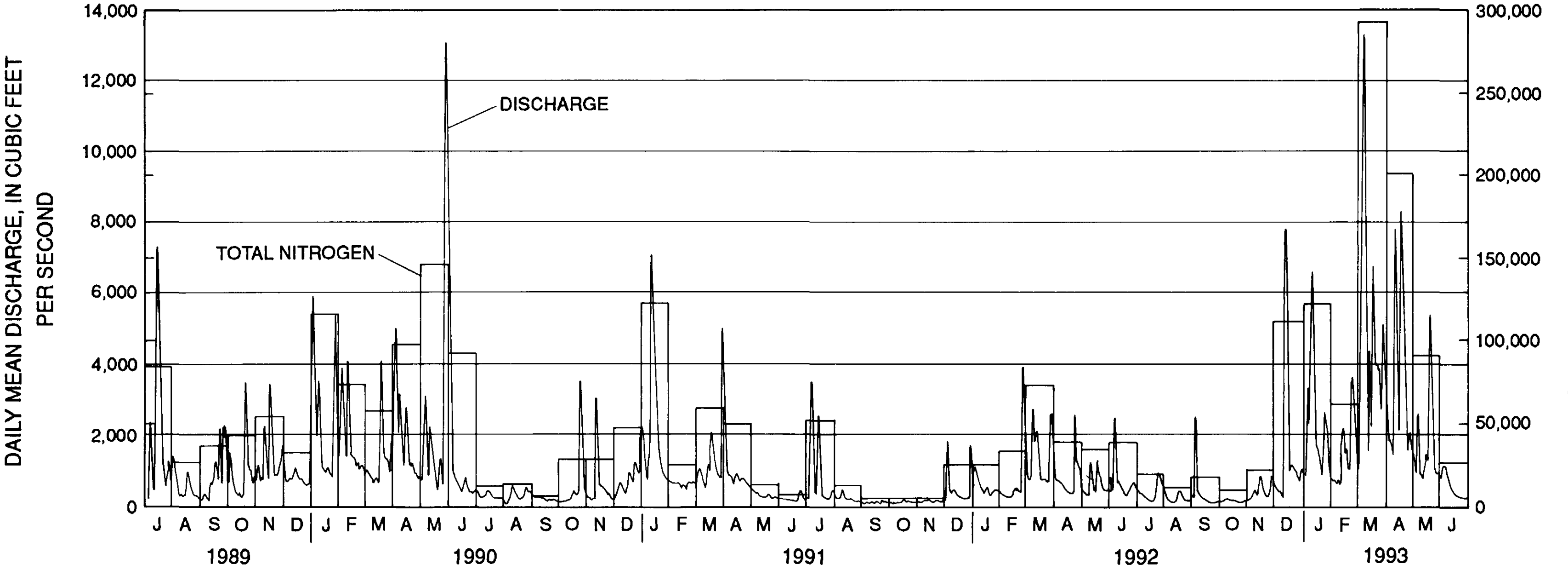


Figure 21. Relation of discharge to total nitrogen load at the Pamunkey River station, Virginia, July 1989 through June 1993.

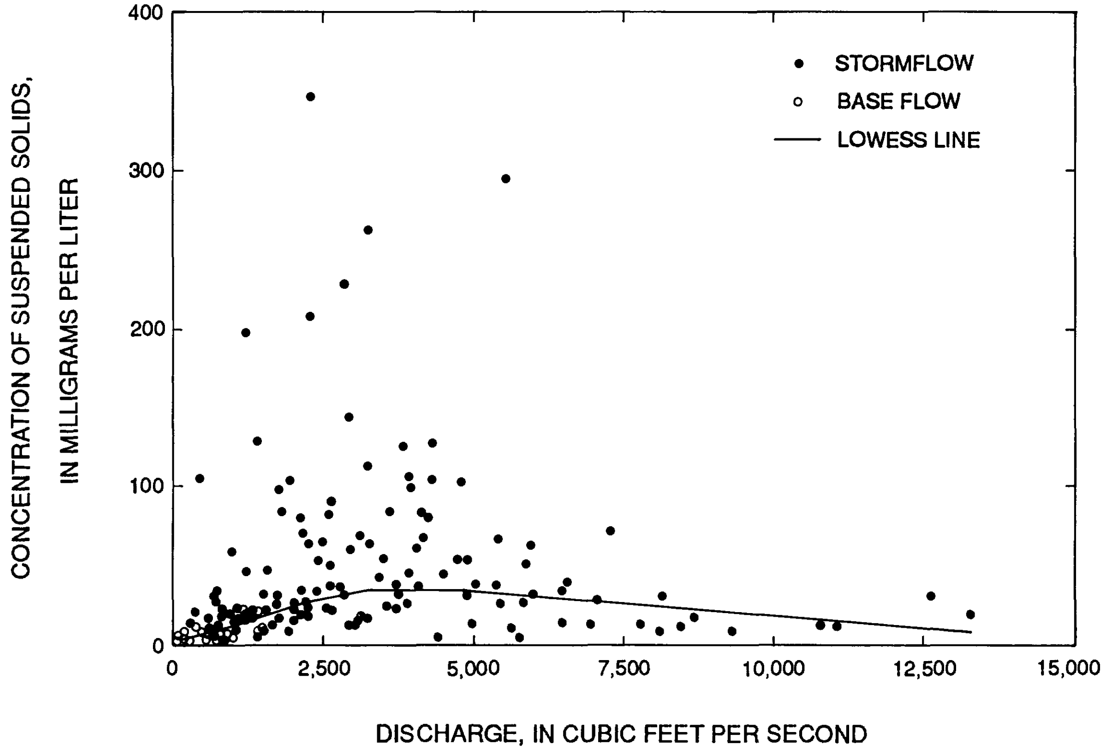


Figure 22. Relation of total suspended solids concentration to discharge at the Pamunkey River station, Virginia.

significant change in concentration with discharge. Both phosphorus species and total suspended solids correlated with season (table 6). Median concentrations of total phosphorus was slightly higher in the winter and median concentration of total suspended solids values was highest in the winter and spring. The median concentration of dissolved orthophosphorus was highest in the summer. As with TKN, the decrease of total suspended solids and total phosphorus during high-discharge events probably is caused by particulate settling.

Monthly loads for both total phosphorus and for total suspended solids were highest in March 1993, whereas the lowest monthly loads were in October and September 1991, respectively. The median monthly load for total phosphorus was 3,815 kg and was 1,595,000 kg for total suspended solids, (table 4). The annual load of dissolved orthophosphorus ranged from 16 to 20 percent of the total phosphorus load.

Total organic carbon, silica, and field measurements.—Concentration of total organic carbon ranged from 1.6 to 15 mg/L (table 3). Concentration of total organic carbon showed a positive relation to discharge (table 5), and was related to season (table 6). The total organic carbon median concentration was slightly higher in the winter and spring (fig. 6). Total organic carbon showed an increase with discharge (fig. 23) despite the decrease in total suspended solids. This relation suggests either that particulate organic carbon does not settle out as much as inorganic suspended solids, or that the increase in total organic carbon during high discharge is due to an increase in dissolved organic carbon from wetlands. Dissolved silica decreased with discharge at the Pamunkey River, and thus is derived primarily from base flow.

The median monthly load of total organic carbon was 286,000 kg, and was 516,000 kg for dissolved silica (table 4). Total organic carbon loads were lowest in October 1991 and highest in March 1993 during the extended high-discharge period, and dissolved silica loads were lowest in September 1991 and highest in March 1993. The first and second highest monthly loads for the study period occurred in 1993, during March and April, for both constituents. Dissolved oxygen concentration never was below the State aquatic life criteria of 4.0 mg/L. Specific conductance ranged from 46 to 250 µS/cm (table 3).

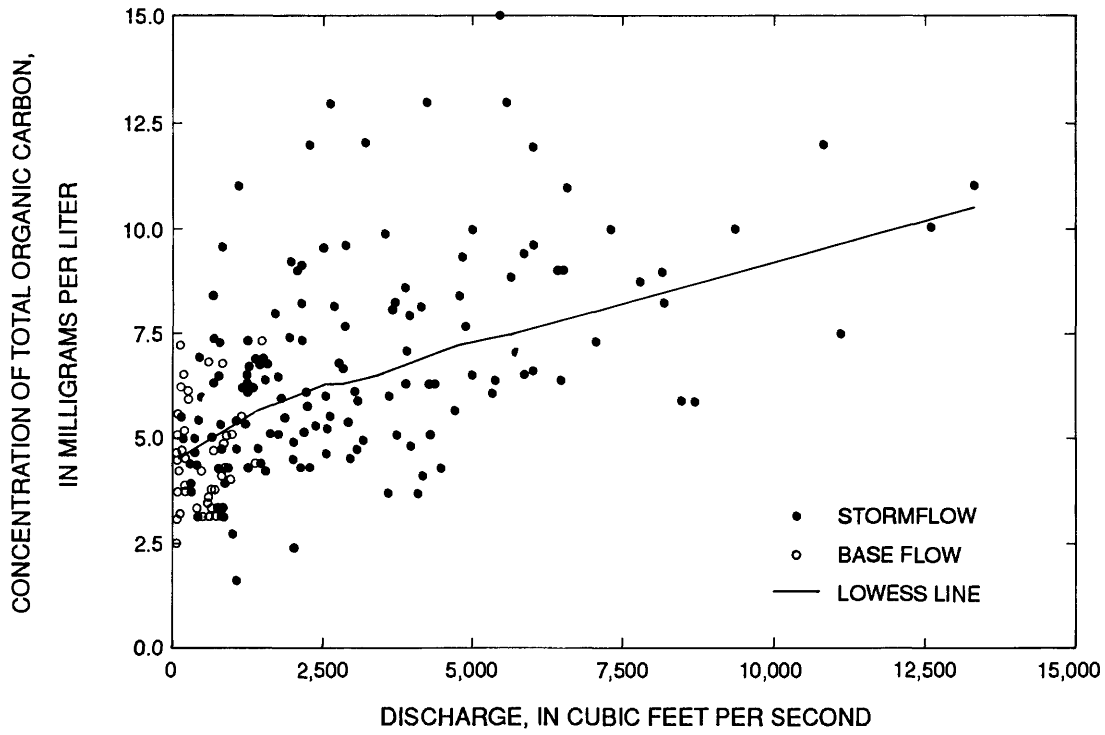


Figure 23. Relation of total organic carbon concentration to discharge at the Pamunkey River station, Virginia.

Mattaponi River

Nitrogen species.—Concentration of total nitrogen ranged from 0.31 to 1.19 mg/L in the Mattaponi River, with a median concentration of 0.60 mg/L. The predominant nitrogen species was organic nitrogen; the median dissolved ammonia concentration was below the detection limit. All the nitrogen species except for dissolved ammonia nitrogen were related to discharge (table 5). At discharges as much as 800 ft^3/s, total nitrogen and TKN concentrations decreased with discharge (fig. 24) but at high discharges these constituents increased with discharge. Dissolved nitrite-plus-nitrate nitrogen showed a negative relation with discharge. All the nitrogen species except ammonia were related to season (table 6); organic nitrogen was significantly higher in the summer than during other seasons (fig. 6).

The Mattaponi River Basin does not contain wastewater treatment plants so organic nitrogen is derived primarily from nonpoint sources such agricultural land (about 30 percent of the basin), forested land (almost 70 percent of the basin), wetlands, and in-stream biological uptake of nitrate and dissolved ammonia. A negative relation with discharge suggests that nitrate probably is delivered to the river mostly from base flow and in-stream nitrification.

Monthly load values for total nitrogen in the Mattaponi River were lowest in September 1991 and highest in March of 1993 (fig. 25). The second and third highest monthly load also occurred in early 1993.

Phosphorus and total suspended sediment.—The median concentration of total phosphorus in the Mattaponi River was 0.06 mg/L, whereas dissolved orthophosphorus had a median concentration of 0.01 mg/L, indicating that most of the phosphorus is transported in the particulate phase. Dissolved orthophosphorus was often near the detection limit, and so showed no relation to discharge (table 5). Total phosphorus and total suspended sediment exhibited an increase with discharge during low-discharge conditions and decreased at discharges exceeding 1,000 ft^3/s. As with the Pamunkey River, the decrease in concentration of total phosphorus and suspended solids at high discharges can be attributed to low streamflow velocities that allow settling of

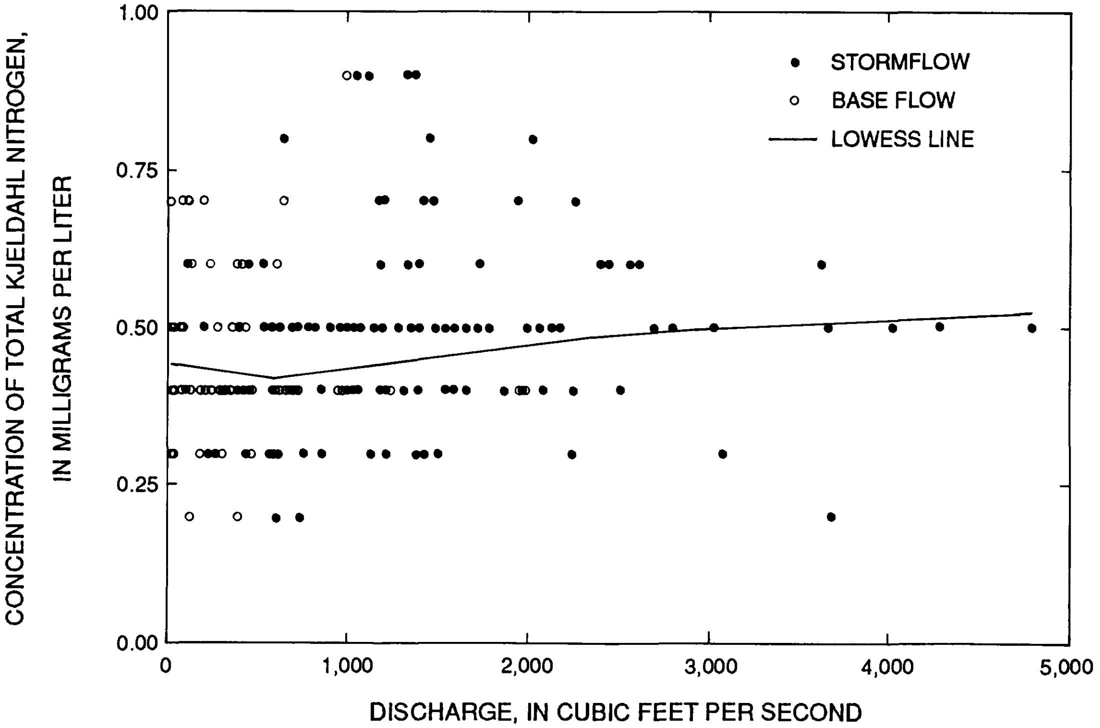


Figure 24. Relation of total Kjeldahl nitrogen concentration to discharge at the Mattaponi River station, Virginia.

suspended material. Both phosphorus species concentrations were correlated to season, and concentration of total suspended solids was not correlated to season (table 6).

The median monthly load for total phosphorus was 1,670 kg, and the median monthly load for total suspended solids was 241,500 kg (table 4). Monthly loads for both total phosphorus and total suspended solids were highest in March 1993, with the second highest in April 1993, and lowest in September 1991. The annual load of dissolved orthophosphorus ranged from 18 to 22 percent of the total phosphorus load.

Total organic carbon, silica, and field measurements.—Concentration of total organic carbon in the Mattaponi River ranged from 1.2 to 48 mg/L (table 3), and much of the carbon is derived probably from the large wetland systems upstream of the monitoring station. Total organic carbon correlated positively with discharge despite the general decrease of total suspended solids with discharge. This suggests either that particulate organic carbon does not settle out as much as inorganic suspended solids, or that the increase in total organic carbon during high discharge is due to an increase in dissolved organic carbon from the wetlands.

Dissolved silica ranged from 2.8 to 13 mg/L in the Mattaponi River (table 3). This constituent had a negative relation to discharge (table 5) at the Mattaponi River and was correlated to season (table 6). Most dissolved silica is derived from base flow, as indicated by the decrease in silica concentration with increasing discharge.

Total organic carbon loads and dissolved silica loads were lowest in September 1991 and highest in March 1993. The second and third highest monthly loads for total organic carbon also were during early 1993. The median monthly load for total organic carbon was 167,000 kg, and the median monthly load for dissolved silica was 209,500 kg (table 4) in the Mattaponi River. Dissolved oxygen concentrations were never below the State aquatic life criteria of 4.0 mg/L. Specific conductance ranged from 33 to 95 µS/cm, and pH ranged from 5.3 to 8.1.

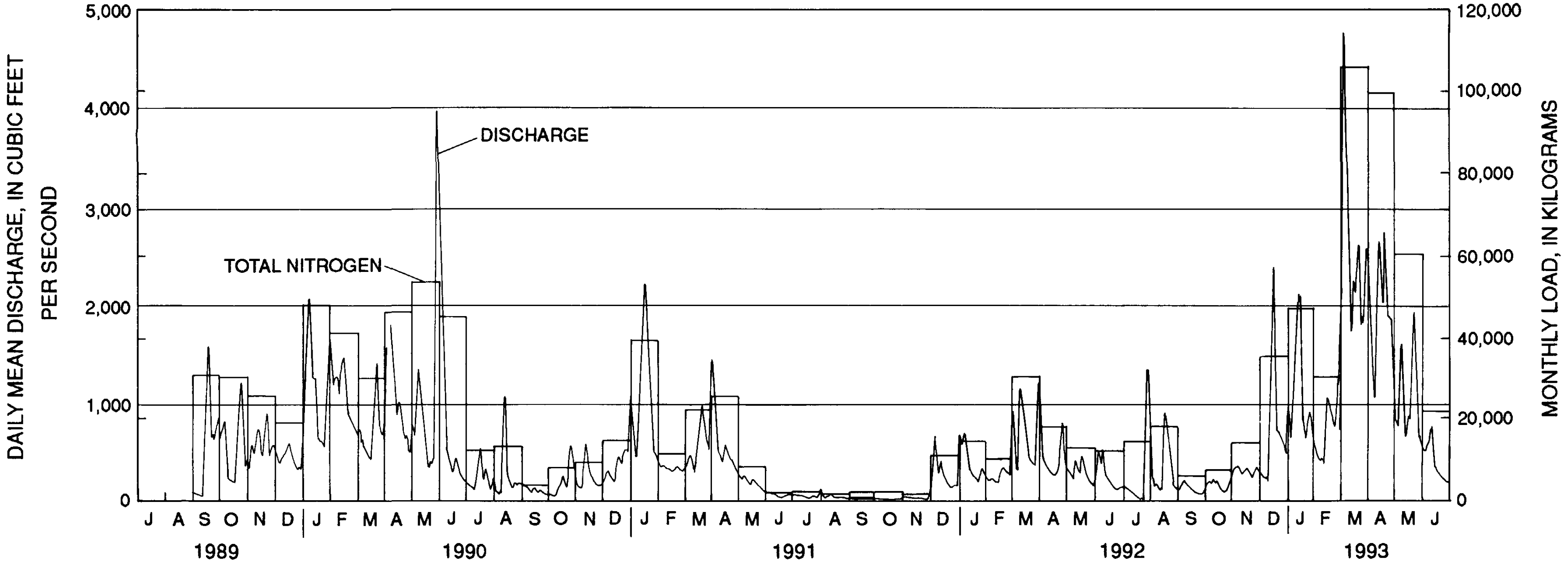


Figure 25. Relation of discharge to total nitrogen load at the Mattaponi River station, Virginia, September 1989 through June 1993.

COMPARISON OF WATER-QUALITY CHARACTERISTICS AMONG RIVERS

The comparison of constituent concentrations among rivers is presented in this general order: nitrogen species, total suspended solids with phosphorus species, and total organic carbon with dissolved silica. A comparison of constituent concentrations between rivers is followed by a comparison of loads between rivers. Figures are used to compare the annual load and yield for selected constituents in each river by year. Only years with complete monthly loads were included for comparison. Yield was computed by dividing the annual load delivered at each station, in kilogram, by the area of the basin upstream of the station, in square mile. Relatively high discharges in 1989 for all rivers caused corresponding high loads for many constituents; similarly, the extreme low discharges in 1991 resulted in the lowest loads observed during the period of data collection for many constituents.

Nitrogen Species

Organic nitrogen was the predominant form of total nitrogen at the James, Appomattox, Pamunkey, and Mattaponi Rivers, and accounts for more than 85 percent of the mean annual load of TKN for all five rivers. The percentage of total nitrogen load contributed by each river as TKN ranged from a median of 44 percent at the Rappahannock River to 77 percent at the Mattaponi River (table 4). The median concentration of TKN varied little among the five rivers. The greatest range and highest concentration of TKN were in the James River, whereas the Rappahannock River had a slightly lower, but similar range. The smallest ranges of TKN was observed in the Mattaponi and Appomattox Rivers. The Pamunkey River had a concentration range about twice that of the Mattaponi River.

Model results indicate that the concentration of TKN was correlated to discharge (table 5) and to season (table 6) in all five rivers. The James and Rappahannock Rivers showed marked increases of TKN concentration with discharge, whereas the other three rivers had less well-defined relations of TKN concentration to discharge. The seasonal variation in median TKN concentration in the James and Rappahannock Rivers was greater than in other rivers. The James River had the greatest range in the winter, the Rappahannock had the greatest range in the spring, and both rivers showed the least range in the summer. The Pamunkey and Mattaponi Rivers had their greatest median TKN concentration during the summer months, and the Appomattox River showed little obvious seasonal variation, with many concentrations at or near the detection limit.

Dissolved ammonia nitrogen contributed less than 10 percent of total nitrogen load for all five rivers. Median concentration of dissolved ammonia varied little among the five rivers; most median concentrations were very close to the detection limit because of the large number of censored values. The greatest median concentration of dissolved ammonia nitrogen was 0.05 mg/L (table 3) at the Appomattox River. This median concentration was only slightly greater than the reporting limit of 0.04 mg/L. The lowest median concentration and the smallest range of dissolved ammonia nitrogen were found at the Mattaponi River. The James River had the largest range in ammonia concentration (0.52 mg/L). The Rappahannock and Appomattox Rivers had similar ranges (about 0.2 mg/L), and the Pamunkey and Mattaponi Rivers had the smallest range (about 0.15 mg/L). Model results indicated that ammonia was related to discharge in all rivers except the Mattaponi River (table 5). In general, ammonia concentration increased with discharge at low discharges, but decreased or stabilized at high discharges. Model results indicated that ammonia was correlated to season only in the James and Appomattox Rivers (table 6).

Nitrite-plus-nitrate nitrogen was the predominant species of nitrogen at the Rappahannock River with 54 percent of the total nitrogen load in this form; this constituent was the second most predominant nitrogen species in the other four rivers. The highest median concentration of nitrite-plus-nitrate nitrogen was in the Rappahannock River (0.60 mg/L) (table 3), which was two to four times greater than the median concentration in the other rivers. The James and Pamunkey Rivers had similar median concentrations (0.29 and 0.23 mg/L, respectively), whereas the Appomattox and Mattaponi Rivers had the lowest median concentrations. The largest ranges in concentration were at the James and Rappahannock Rivers. The Appomattox River had the smallest concentration ranges, but the Pamunkey and Mattaponi Rivers also had small concentration ranges. Model results indicate that nitrite-plus-nitrate nitrogen concentration was correlated to discharge in all rivers except the Pamunkey River (table 5). Most of the rivers showed an increase in nitrite-plus-nitrate nitrogen concentration at lower discharges, and then a decrease in concentration with increasing discharge. Only at the Appomattox River did nitrite-plus-nitrate concentration consistently increase with increasing discharge. The model indicated that nitrite-plus-nitrate was correlated to season in all rivers except the James River (table 6). The highest seasonal medians and largest difference between seasonal medians were observed in the Rappahannock River.

The annual load of total nitrogen for years of complete data is shown in figure 26. The James River provided most of the total nitrogen load to Chesapeake Bay from Virginia during the study period, and the Rappahannock River provided approximately one-third of the total nitrogen load of the James River, and the other three rivers provided substantially less. Conversely, the Rappahannock River provided a greater yield of nitrogen than the James River in 3 of 4 complete years of data (fig. 27), and the Appomattox, Pamunkey, and Mattaponi Rivers provided from about one-third to one-half the nitrogen yield of the Rappahannock River.

Because nitrogen is so readily converted between species in a river, knowledge of the distribution of nitrogen among species by itself gives little information as to source(s) of the nitrogen. The effect of discharge on concentration and species distribution, however, can provide some insight into sources. Results of this study indicate that the majority of the total nitrogen load from all five rivers was derived probably from nonpoint sources; although, municipal waste-water discharges contribute significant amounts of nitrogen to the James and Rappahannock Rivers.

TKN (which mostly is organic nitrogen) is derived primarily from surface runoff from agricultural and (or) forested land in all five rivers, as indicated by positive or non-negative relations between discharge and TKN concentration. In the Pamunkey and Mattaponi Rivers, significant TKN also can be contributed by wetlands that fringe the rivers upstream of the monitoring stations. Municipal waste-water discharge probably contributes significant amounts of TKN to the James and Rappahannock Rivers, but much of this TKN may be nitrified before it reaches the monitoring stations. TKN yields were highest in the James and Rappahannock Rivers, which is due possibly to municipal waste-water discharge. Alternately, the higher yields of TKN can be related to the high concentration of suspended solids in the James and Rappahannock Rivers, which in turn are caused by high stream gradients and erosion rates.

Concentration of nitrite-plus-nitrate appears to be controlled by a combination of processes in all five rivers. The general decrease of nitrite-plus-nitrate concentration at high discharges for all rivers except the Appomattox suggests that base flow is a major contributor of this constituent. However, the observed increase in concentration at low discharges for most rivers indicates that surface runoff can also contribute nitrite-plus-nitrate. Much of the nitrite-plus-nitrate can be derived from in-stream nitrification of TKN from sources discussed above; in this case, nitrite-plus-nitrate is diluted during high flows because the nitrification process does not occur as rapidly as TKN is introduced to the streams. Only in the Appomattox River does surface runoff appear to be the dominant source of nitrite-plus-nitrate, as indicated by the consistently positive discharge/concentration relation. It should be noted, however, that water-quality samples collected from the Appomattox River during low-discharge conditions contain many of the highest concentrations observed for that river; this may be explained by the long hydraulic residence time in Lake Chesdin that allows more complete conversion of TKN to nitrate.

The percentage of agricultural land use in each basin seems to be reflected in the nitrate concentrations and yields, except in the James River Basin. The high nitrite-plus-nitrate concentrations and yields in the Rappahannock River reflect that 40 percent of the land use in this basin is agricultural, which is the highest percentage of all the basins. The Pamunkey River Basin had the second highest percentage of agricultural land use (35 percent) and had the third highest median concentration and yield of nitrate. The Appomattox and the Mattaponi River Basins had the next lowest percentages of agricultural land use (33 percent and 27 percent, respectively) and also the lowest median concentrations of nitrate. The low nitrate concentration in the Appomattox River is also probably affected by biological uptake of nitrate in Lake Chesdin.

The James River had the lowest percentage of agricultural land (25 percent) yet had the second highest median concentration and yield of nitrite-plus-nitrate. The high nitrite-plus-nitrate concentration may be explained by the large amount of municipal waste water discharged to the James River, which is introduced to the river mostly as TKN but is nitrified by in-stream bacteria.

Phosphorus Species and Total Suspended Solids

On the basis of a comparison of the median concentrations and mean annual loads of total phosphorus and dissolved orthophosphorus, most of the phosphorus was particulate in all five rivers. The greatest median

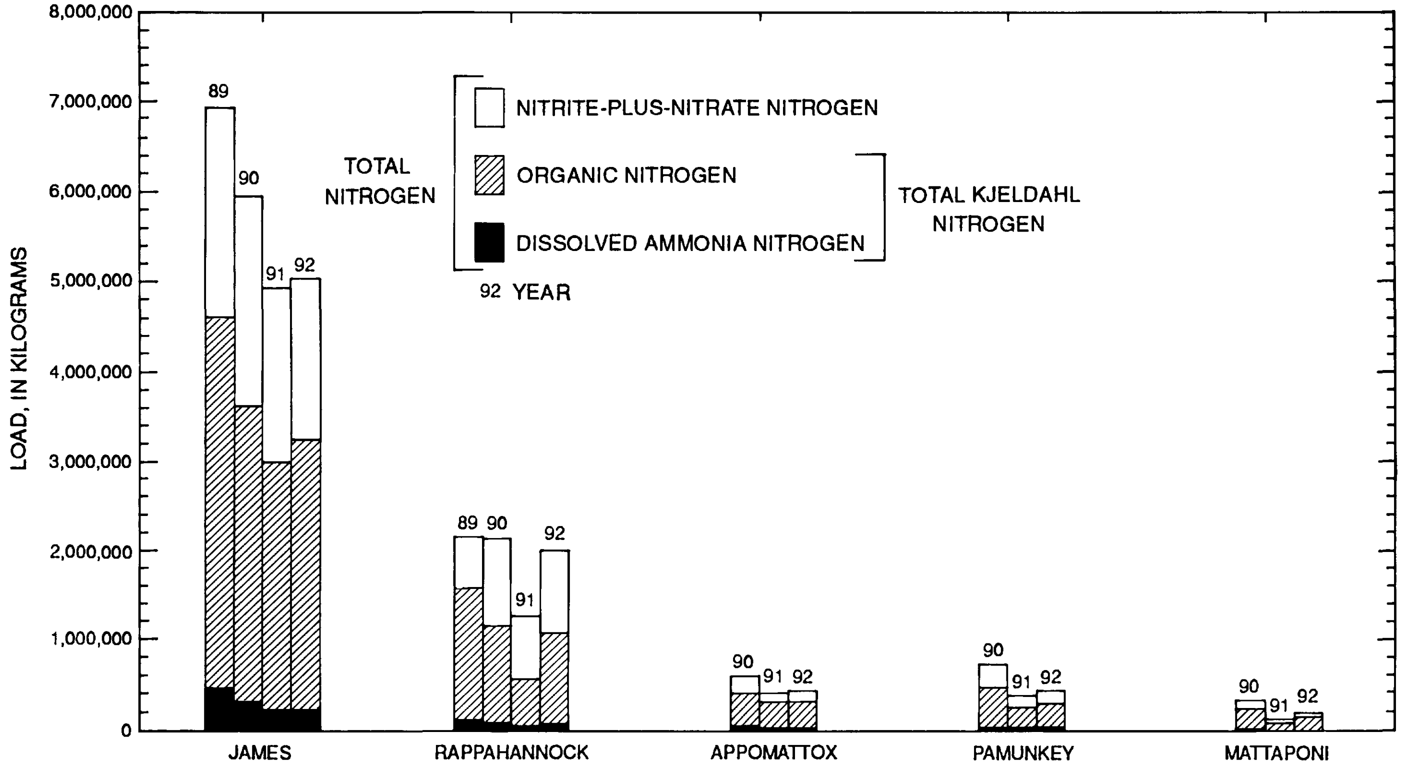


Figure 26. Annual load of total nitrogen contributed by nitrite-plus-nitrate nitrogen, organic nitrogen, and dissolved ammonia nitrogen at the Fall Line stations in Virginia in selected years.

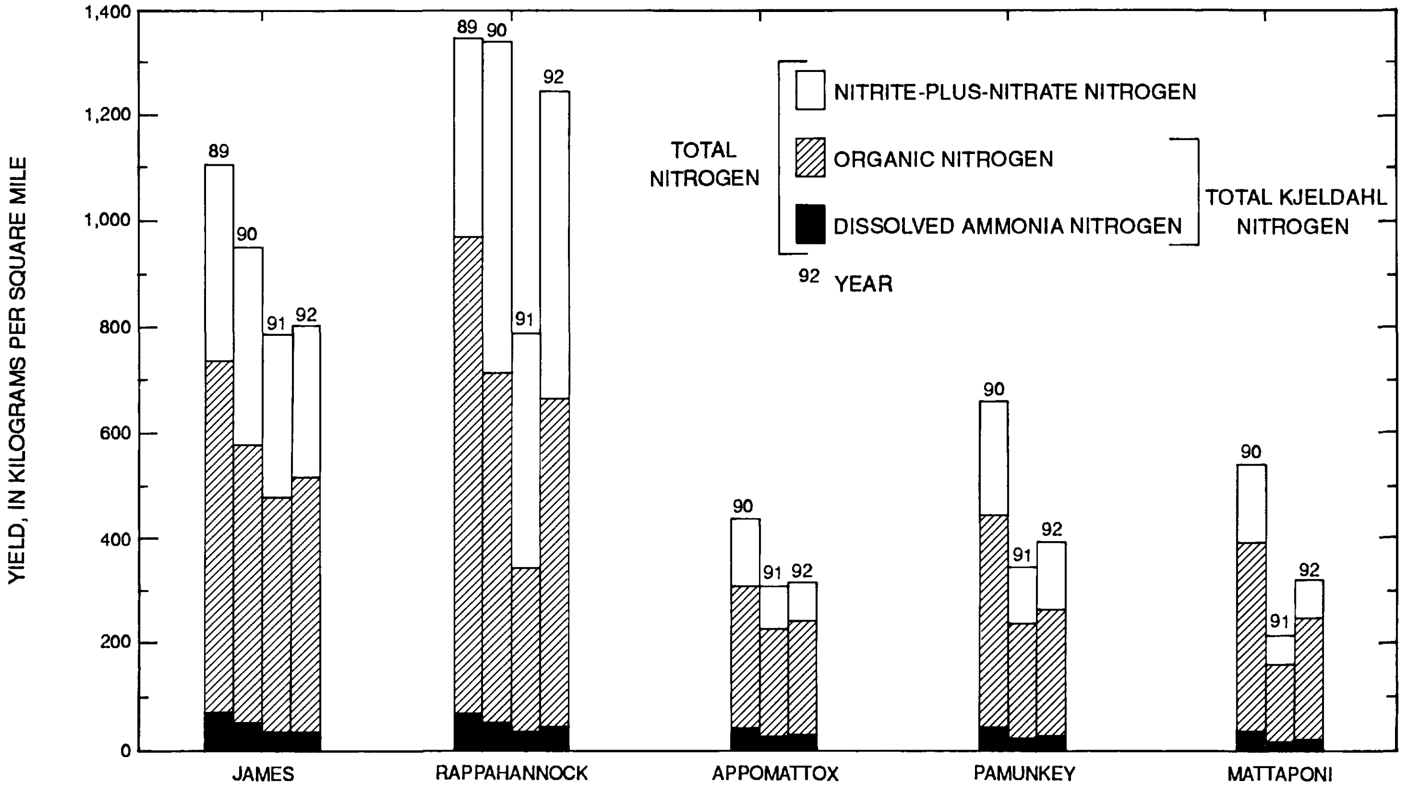


Figure 27. Yield of total nitrogen contributed by nitrite-plus-nitrate nitrogen, organic nitrogen, and dissolved ammonia nitrogen at the Fall Line stations in Virginia in selected years.

concentration of total phosphorus was 0.15 mg/L at the James River, with the next highest median of 0.10 mg/L at the Rappahannock River (table 3). The Appomattox, Pamunkey, and Mattaponi Rivers had similar medians (0.05 to 0.07 mg/L). The greatest range in total phosphorus was in the James River (about 1.4 mg/L), whereas the smallest range was in the Appomattox and the Mattaponi Rivers.

The model indicated that total phosphorus was correlated to discharge in all five rivers (table 5), generally having a positive relation with discharge. In the James, Rappahannock, and Appomattox Rivers, total phosphorus concentration increased during the entire observed range of discharge. In the Pamunkey and Mattaponi Rivers, however, total phosphorus increased with discharge at low discharges, then leveled-off at high discharges. Total phosphorus was related to season in all the rivers except the Appomattox River (table 6). In the James and Rappahannock Rivers, median concentrations of total phosphorus were lowest in the summer, and there was a less noticeable pattern in the other three rivers.

The median concentration for dissolved orthophosphorus of 0.04 mg/L at the James River was four times greater than the medians (0.01) of the other rivers (table 3). The maximum dissolved orthophosphorus concentration was at least five times greater in the James River than the maximum concentrations found among the other rivers. Orthophosphorus ranges and maximum concentration in the other rivers were similar. According to model results, dissolved orthophosphorus concentrations were correlated to discharge in only two rivers—the James and Rappahannock Rivers (table 5). Concentration decreased with high discharge in the James River and increased with high discharges in the Rappahannock River. Orthophosphorus was correlated to season in all the rivers except the Appomattox River (table 6).

The mean annual load of total phosphorus at the Fall Line monitoring stations is shown in figure 28. The greatest load is again provided by the James River, with the Rappahannock River providing up to a third of the total phosphorus load provided by the James River. The yield of total phosphorus provided by the James and the Rappahannock Rivers, however, are comparable (fig. 29), with the Appomattox, Pamunkey, and Mattaponi Rivers providing substantially less phosphorus per unit of basin area. The annual load of dissolved orthophosphorus at the five Fall Line monitoring stations is also shown in figure 28. The James River contributed both the greatest load and the greatest yield of dissolved orthophosphorus of the five Fall Line monitoring stations (fig. 29). All four of the remaining monitoring stations showed substantially less load and yield of dissolved orthophosphorus than the James River.

The highest median concentration for total suspended solids was found at the James River, and the lowest median concentration was found in the Appomattox and Mattaponi Rivers. The highest total suspended solids concentrations (844 mg/L) and greatest range was in the Rappahannock River; the highest concentration in the James River was comparable (800 mg/L). The smallest range was found in the Appomattox River (about 50 mg/L). Model results indicated that total suspended solids concentration was related to discharge in all five rivers (table 5). In the James, Rappahannock, and Appomattox Rivers, total suspended solids concentration had a positive relation to discharge throughout the range in discharge, and suspended solids in the Mattaponi and Pamunkey Rivers increased with discharge only at low discharges. Total suspended solids was correlated to season in all the rivers except the Mattaponi River (table 6).

Load of total suspended solids was highest in the James River, with the Rappahannock River load equal to about two-thirds of the James River load (fig. 30). The remaining three rivers had much smaller loads. Yield of total suspended sediment was highest in the Rappahannock River, especially in 1989 (fig. 31).

The effects of municipal waste-water discharge on the water quality of the James River is exhibited by the high concentration, yield, and concentration/discharge relations to dissolved orthophosphorus. Point source discharges do not contribute nearly as much dissolved orthophosphorus to the other four rivers. In the Appomattox River Basin, for example, the positive discharge/concentration correlation indicates that most dissolved orthophosphorus is derived from surface runoff, probably from agricultural land.

Non-point source influences, particularly agricultural land use, affect the total phosphorus and total suspended solids concentration in all the rivers. Total phosphorus and total suspended solids yields were highest in the Rappahannock River Basin, which also has the greatest percentage of agricultural land use and increased construction in response to the urban development within the Metropolitan Washington, D.C., area. The James River also had high total phosphorus yields. In addition to agricultural land use, the high yields in these two rivers are related to basin characteristics. Much of the James and Rappahannock River Basins are at higher elevation and have higher relief than the Appomattox, Pamunkey, and Mattaponi River Basins, especially in the headwaters.

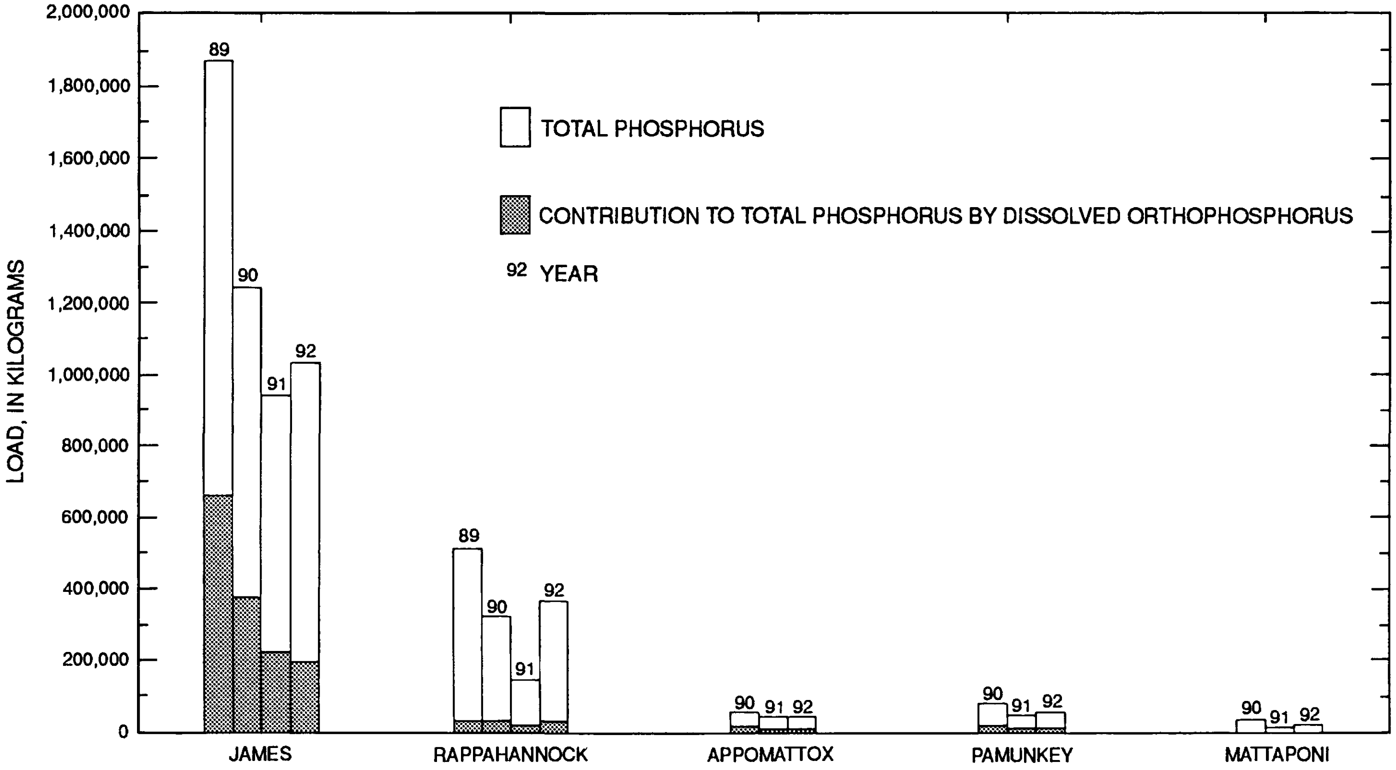


Figure 28. Annual load of total phosphorus and contribution by dissolved orthophosphorus at the Fall Line stations in Virginia in selected years.

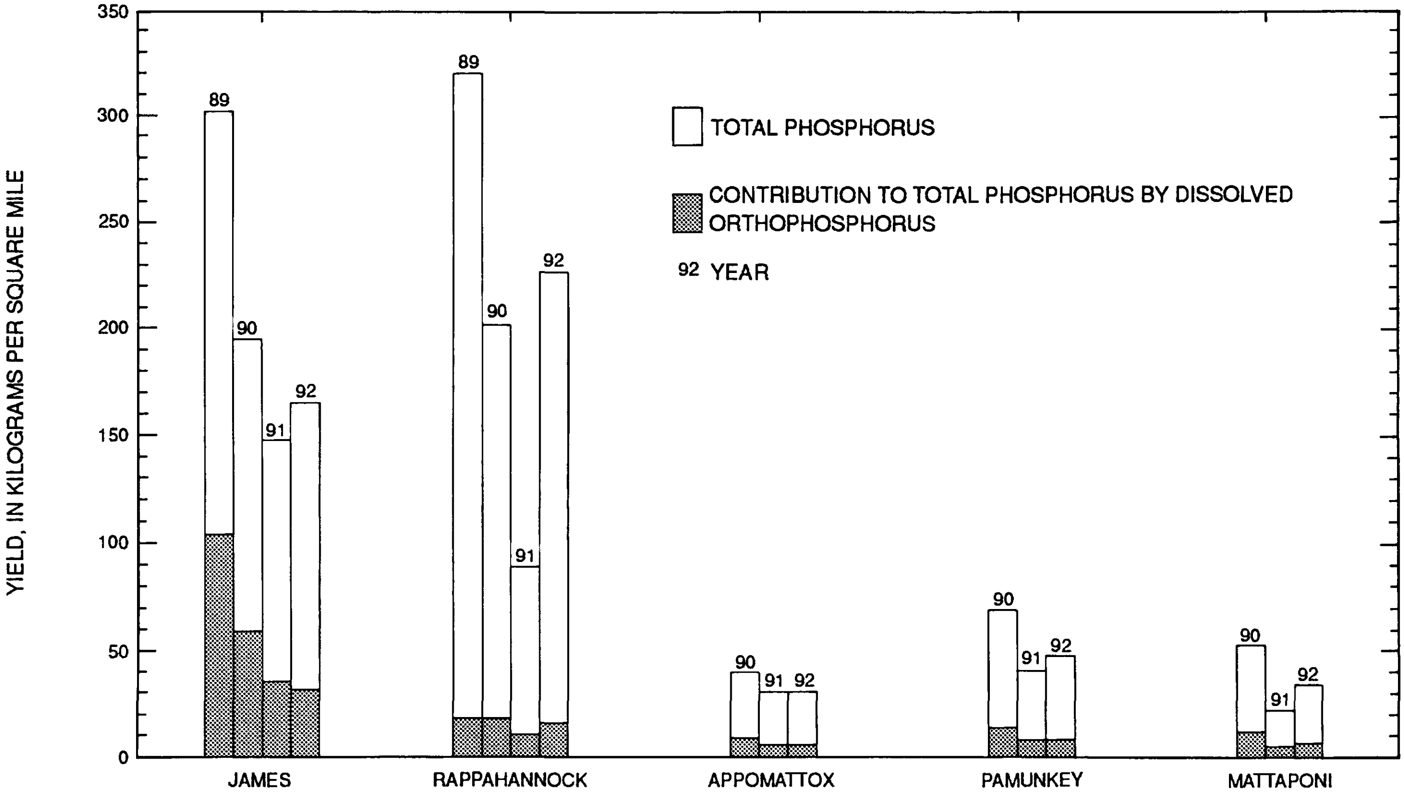


Figure 29. Yield of total phosphorus and contribution by dissolved orthophosphorus at the Fall Line stations in Virginia in selected years.

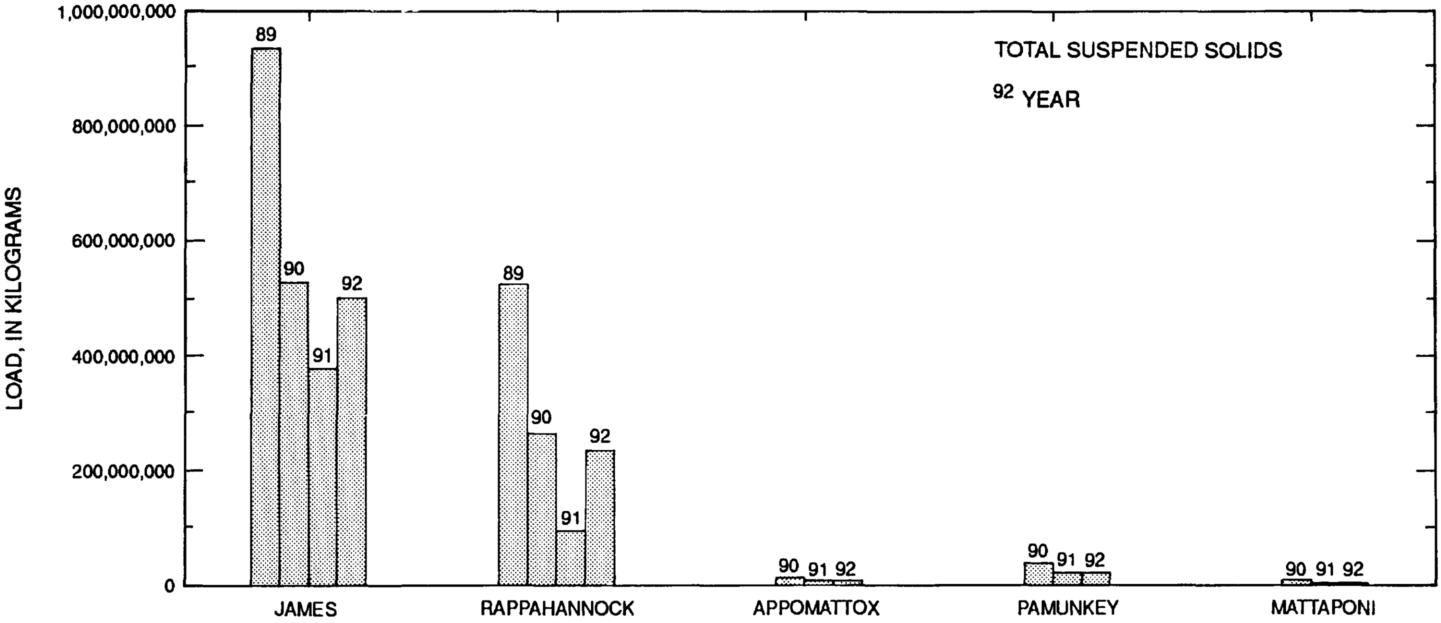


Figure 30. Annual load of total suspended solids at the Fall Line stations in Virginia in selected years.

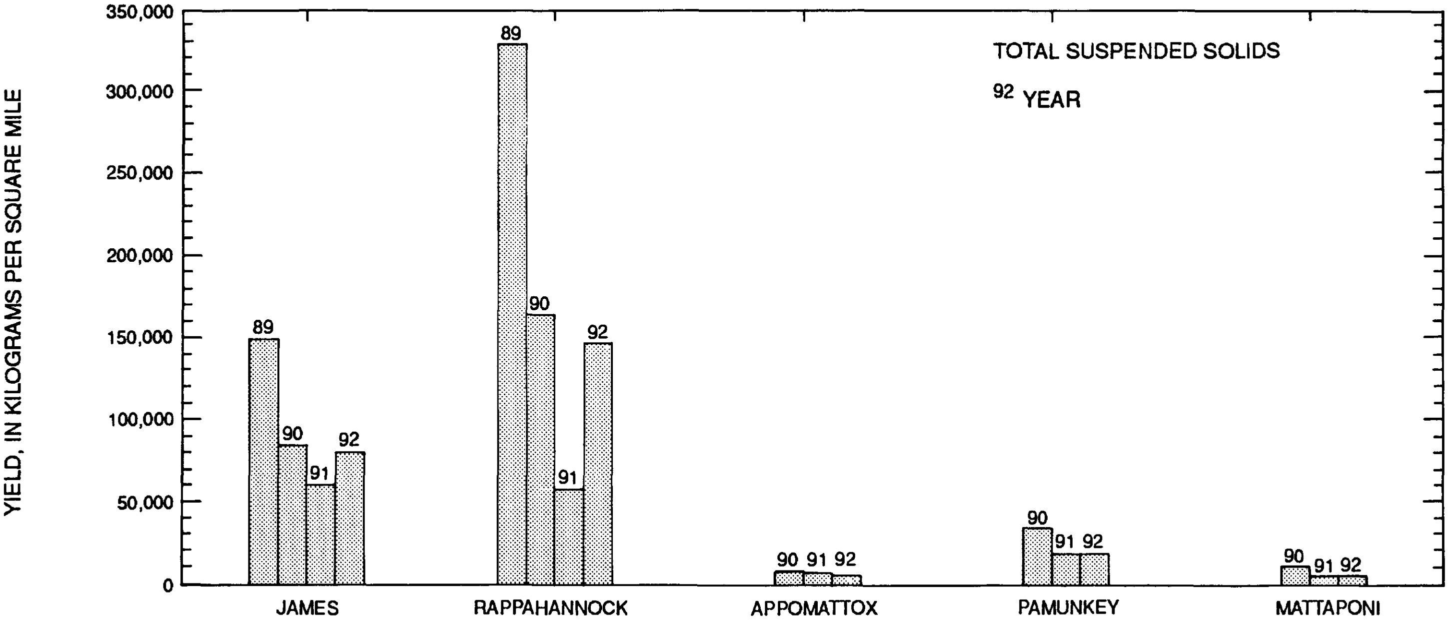


Figure 31. Yield of total suspended solids at the Fall Line stations in Virginia in selected years.

During storms, the Rappahannock River responds rapidly and flows at high velocity, allowing greater transport of suspended solids and constituents associated with suspended solids. The James River Basin is at least three times as large as the Rappahannock River Basin and area-wide rainfall causes high discharges from many tributaries in the headwaters above the monitoring station, causing high velocities and contributing suspended solids to the river.

The yield of total phosphorus and total suspended solids at the Appomattox, Pamunkey, and Mattaponi Rivers was much lower than that of the James and Rappahannock Rivers. The lake and dam upstream of the Appomattox River lowers the velocity of the river as it discharges into the lake, and tends to allow settling of particulates in Lake Chesdin. The Pamunkey and Mattaponi Rivers have low streamflow velocities compared to the other rivers because of lower overall gradients and wide flood plains; therefore, these rivers cannot transport as much suspended material as the James or Rappahannock Rivers. The higher total phosphorus and total suspended solids concentrations in the Pamunkey River, compared to the Appomattox and Mattaponi, is probably directly related to the higher percentage of agricultural land use relative to the other two basins.

Total Organic Carbon, Silica, and Selected Field Measurements

The median concentration for total organic carbon was highest in the Mattaponi River (6.7 mg/L). The Appomattox and Pamunkey Rivers had slightly lower, but similar median concentration of total organic carbon (about 5.8 mg/L), and the James and Rappahannock Rivers had the lowest median concentration (about 4.0 mg/L). The Rappahannock River had the highest concentration and highest range of total organic carbon. A maximum concentration of 110 mg/L was measured in the Rappahannock River, and was confirmed by VDCLS. Although the concentration was out of the historic range for the station, the sample had been collected after a quick, intense storm event in the fall, when organic input from fallen leaves is high. The Mattaponi River had the next highest maximum concentration and range for total organic carbon. The high median concentrations of organic carbon in the Mattaponi and Pamunkey Rivers are derived probably from plant decomposition in wetland areas. Model results indicate that total organic carbon was correlated to discharge at all of the rivers; concentrations generally increased with discharge. Total organic carbon concentrations in the James, Rappahannock, and Pamunkey Rivers were correlated to season.

The annual loads of total organic carbon from each river are shown in figure 32. The James River contributed the greatest load of the five Fall Line monitoring stations, with the four remaining stations not significantly different from each other. Correspondingly, the yield of total organic carbon is comparable among the five monitoring stations (fig. 33).

The highest median concentration of dissolved silica occurred in the Appomattox River (table 3). Silica concentration decreased with discharge in each of the five rivers, indicating that most dissolved silica is contributed by base flow. All rivers but the Rappahannock River showed a significant seasonal variation for dissolved silica (table 6). The highest median dissolved silica concentration was found in the Appomattox River during all four seasons, with the highest median concentration in the fall. The annual load of dissolved silica at the Fall Line monitoring stations is shown in figure 34; the James River provided the greatest load, and the other four stations provided substantially less. The Rappahannock River provided the highest yields for 1991 and 1992 (fig. 35).

The Appomattox River had the highest median concentration of dissolved oxygen, probably because water is aerated as it passes over or through the gates at the dam, and then is further aerated in the rapids between the dam and the monitoring station. The lowest median dissolved oxygen concentration of 9.8 mg/L was measured the Pamunkey, the Mattaponi, and the Rappahannock Rivers, and the lowest minimum dissolved oxygen concentration of 4.8 mg/L was measured at the Mattaponi River. The comparatively low dissolved oxygen concentration in the Pamunkey and Mattaponi Rivers is due to the low velocities that result in less aeration than at other rivers.

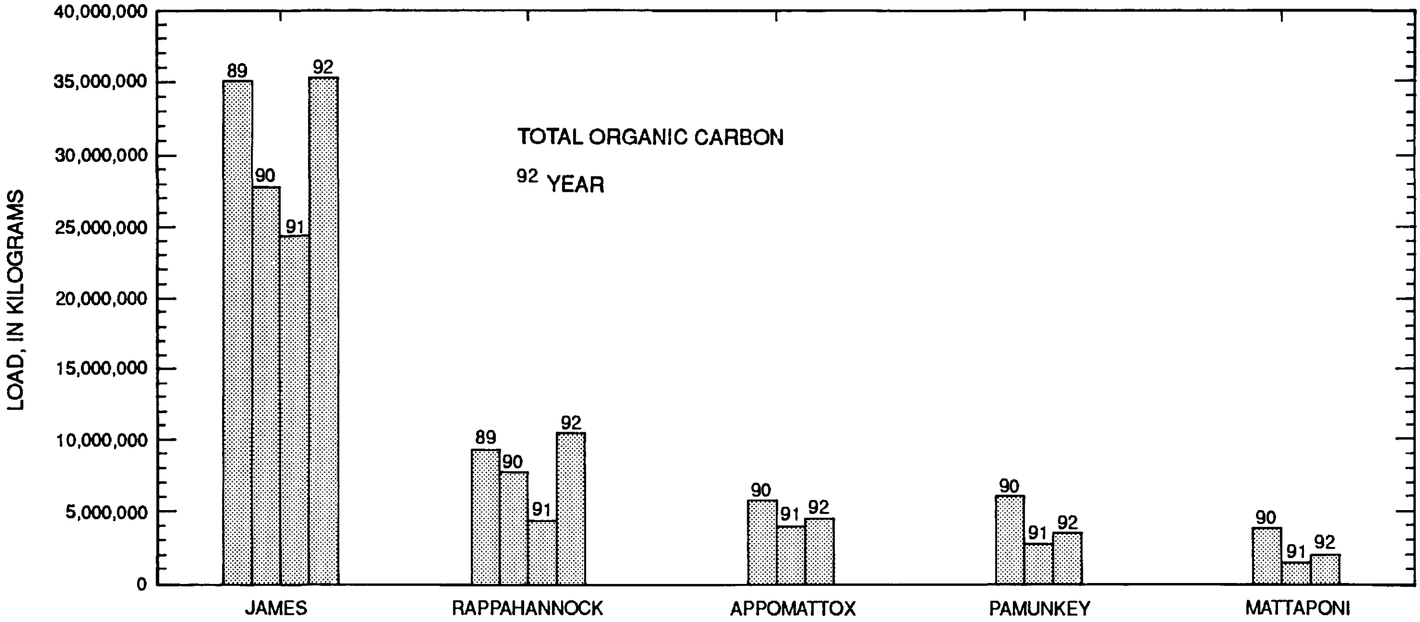


Figure 32. Annual load of total organic carbon at the Fall Line stations in Virginia in selected years.

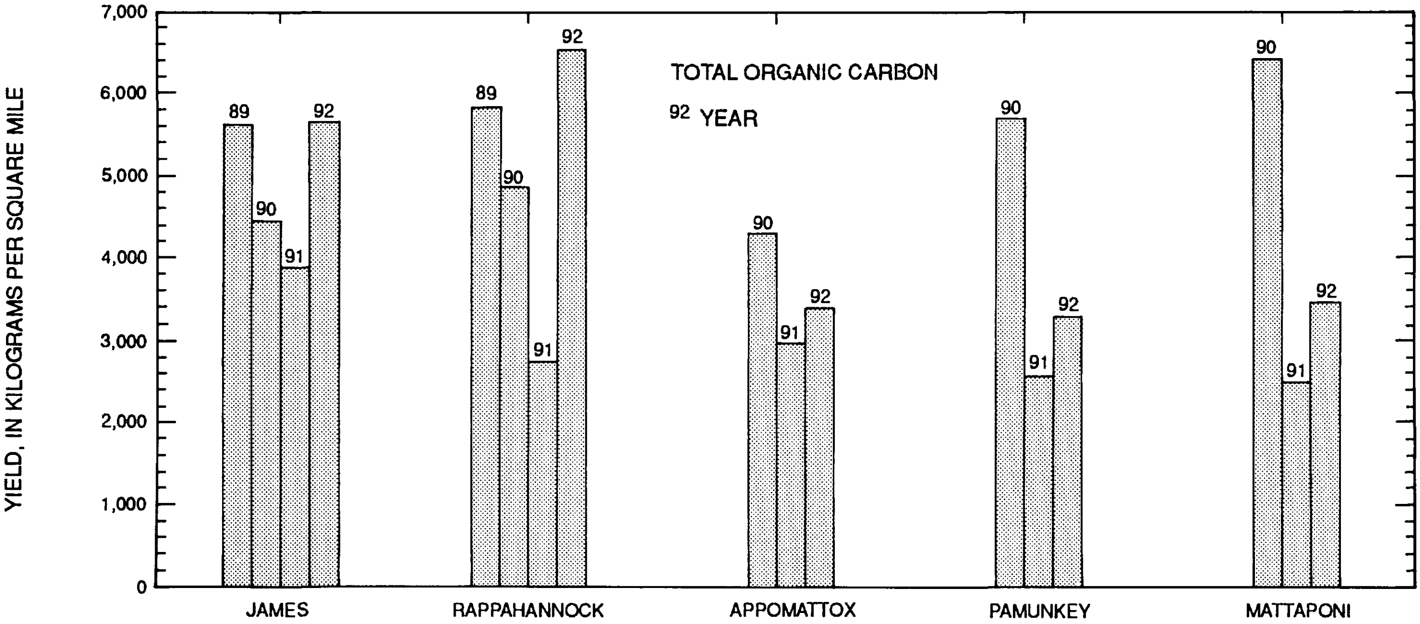


Figure 33. Yield of total organic carbon at the Fall Line stations in Virginia in selected years.

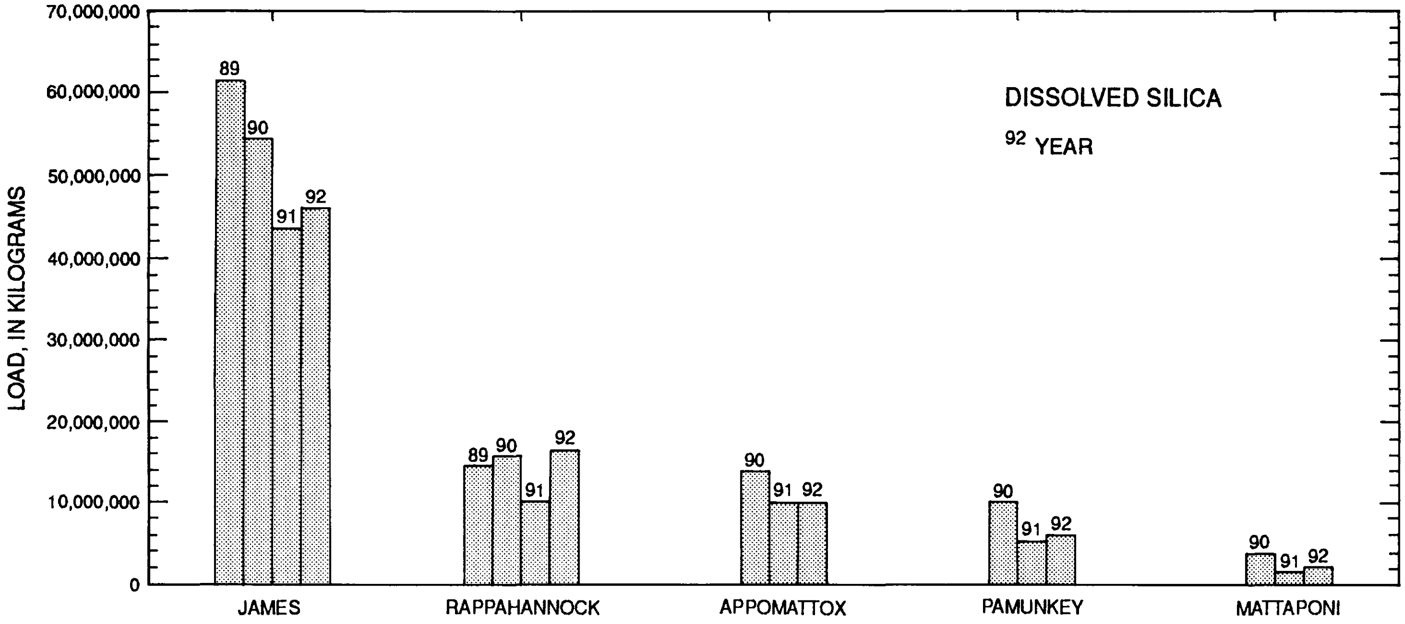


Figure 34. Annual load of dissolved silica at the Fall Line stations in Virginia in selected years.

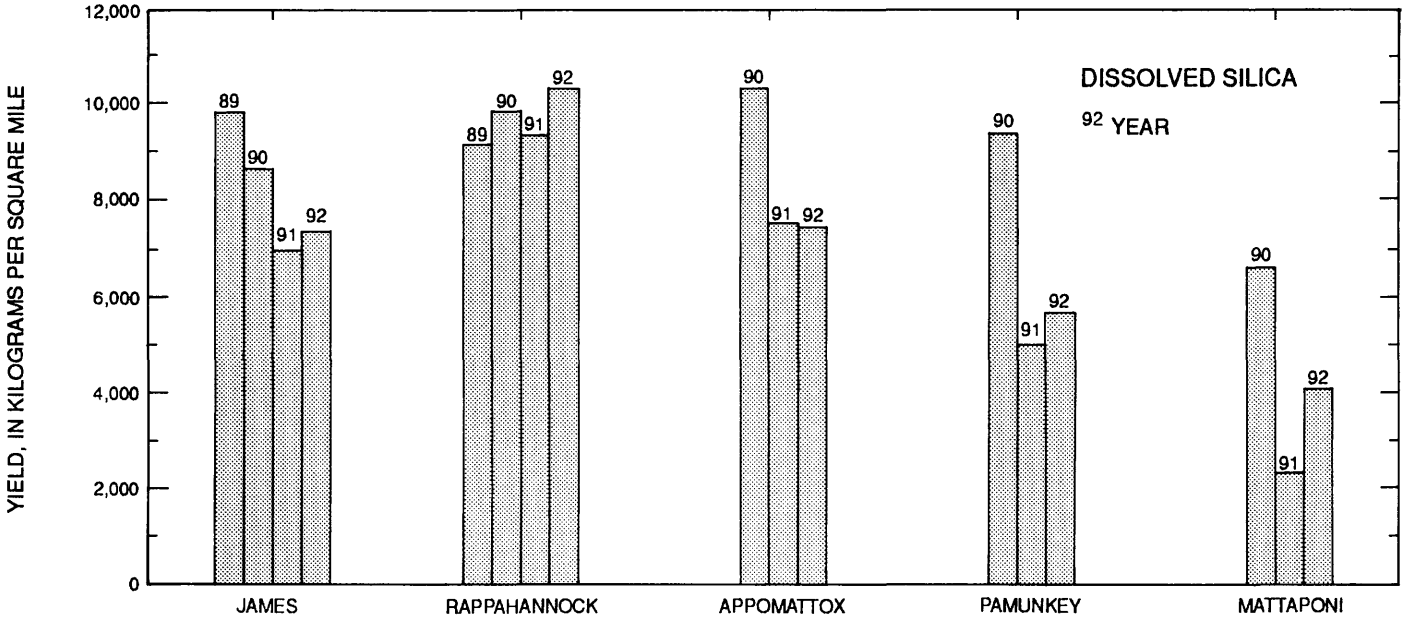


Figure 35. Yield of dissolved silica at the Fall Line stations in Virginia in selected years.

SUMMARY

This report characterizes the water-quality of five major tributaries to the Chesapeake Bay in Virginia near the Fall Line by (1) explaining possible factors that affect concentration and loads of nutrients and suspended solids, (2) discussing relations of discharge and season to concentrations of selected constituents, (3) comparing concentration data and load estimates between rivers, (4) assessing quality-assurance results in order to describe the quality of the analyses provided by the participating laboratories, and (5) presenting monthly loads of nutrients and suspended solids.

Water-quality constituents were monitored in the James and Rappahannock Rivers during a 5-year period, and the Appomattox, Pamunkey, and Mattaponi Rivers during a 4-year period. Water-quality samples were collected from July 1, 1988 through June 30, 1993, for the James and Rappahannock Rivers; from July 1, 1989 through June 30, 1993, for the Pamunkey and Appomattox Rivers; and from September 1, 1989 through June 30, 1993, for the Mattaponi River. Samples were collected on a scheduled basis and during stormflow conditions in order to cover a range in discharge conditions. Monitored water-quality constituents for which loads were estimated included total suspended solids (residue, total at 105° Celsius), dissolved nitrite-plus-nitrate nitrogen, dissolved ammonia nitrogen, TKN, total nitrogen, total phosphorus, dissolved orthophosphorus, total organic carbon, and dissolved silica. Other selected constituents also were monitored for which loads were not calculated. Daily mean load estimates of each constituent were computed by use of a multivariate log-linear regression model with variables of time, discharge, and seasonality.

Concentration of total nitrogen ranged from less than 0.14 to 3.41 mg/L, with both high and low concentrations measured in the Rappahannock River. TKN concentration ranged from less than 0.1 mg/L in the James, Rappahannock, and Appomattox Rivers to 3.0 mg/L in the James River, and organic nitrogen ranged from 0.01 to 2.86 mg/L. Organic nitrogen was the predominant form of nitrogen at all stations except the Rappahannock River, where nitrite-plus-nitrate nitrogen was predominant. Dissolved ammonia nitrogen concentration ranged from less than 0.01 in the Pamunkey River to 0.54 mg/L in the James River. Concentration of nitrite-plus-nitrate nitrogen ranged from 0.02 mg/L at the James River to 1.05 mg/L, also at the James River. Concentration for total phosphorus ranged from less than 0.01 mg/L in the Rappahannock and the Mattaponi Rivers to 1.4 mg/L in the James River. Dissolved orthophosphorus concentration ranged from less than 0.01mg/L in all five rivers to 0.51mg/L in the James River. Concentration of total suspended solids ranged from less than 1 mg/L in all five rivers to 844 mg/L in the Rappahannock River. Concentration of total organic carbon ranged from 1.1 mg/L in the Appomattox River to 110 mg/L in the Rappahannock River. Dissolved silica ranged from 2.4 mg/L at the James River to 18 mg/L in the Appomattox River.

The James and Rappahannock Rivers had comparable high median concentrations and ranges for most constituents. Dissolved orthophosphorus had a significantly higher median concentration and greater range at the James River than all other rivers, which partially caused by a greater number of point sources such as municipal waste-water treatment plants. Concentrations of dissolved nitrite-plus-nitrate nitrogen and total nitrogen had significantly higher medians and ranges in the Rappahannock River, which probably is due to the high proportion of agricultural land use in the basin. Total organic carbon concentrations were highest in the Mattaponi and Pamunkey Rivers; these rivers have expanses of fringing wetlands that contribute large amounts of decaying plant material.

The median monthly load of total nitrogen ranged from 16,500 kg in the Mattaponi River to 371,000 kg in the James River. TKN ranged from a median monthly load of 12,500 kg in the Mattaponi River to 205,500 kg in the James River. Median monthly loads of organic nitrogen ranged from 11,251 kg in the Mattaponi River to 187,050 kg in the James River. The median monthly load of dissolved ammonia nitrogen was 1,130 kg in the Mattaponi River and was as much as 21,050 kg in the James River, whereas total nitrite-plus-nitrate nitrogen ranged from a median monthly load of 4,065 kg in the Mattaponi River to 156,500 kg in the James River. The median monthly load of total phosphorus ranged from 1,670 kg in the Mattaponi River to 61,600 kg in the James River, whereas the median monthly load of dissolved orthophosphorus ranged from 350 kg in the Mattaponi River to 25,900 kg in the James River. Total suspended solids ranged from a median monthly load of 241,500 kg in the Mattaponi River to 20,050,000 kg in the James River. Total organic carbon ranged from a median monthly load of 167,000 kg in the Mattaponi River to 2,100,000 kg in the James River. The median monthly load of dissolved silica ranged from 209,500 kg in the Mattaponi River to 3,625,000 kg for the James River.

Annual loads were greatest at the James River for all constituents, probably because of the much higher discharge, greater basin size, and topography, which causes higher rates of runoff. Yields, or computations of loads per square mile of basin area, were generally highest at the Rappahannock River for total suspended solids, TKN, dissolved nitrite-plus-nitrate nitrogen, and total nitrogen. Dissolved orthophosphorus was the only constituent with a yield consistently greater at the James River, which probably is due to municipal waste-water discharge. Yields of total phosphorus were comparable between the James and Rappahannock River Basins, and yields of dissolved ammonia nitrogen, total organic carbon, and dissolved silica were comparable between the five river basins

Quality-assurance analyses that compare the results of the Virginia Division of Consolidated Laboratory Services and the USGS National Water Quality Laboratory indicate that there are statistically significant differences between the laboratories for several constituents. Differences between laboratories were found to be caused by differences in analytical reporting limits, differences in analytical technique, or a biases at both laboratories. Quality assurance data were used to address technique problems, and to qualify final concentrations and loads.

The water-quality data and load estimates provided in this report will be used to calibrate the computer-modeling efforts of the Chesapeake Bay region; to evaluate the water quality of the Bay and the major effects on the water quality; and to assess the results of best-management practices in Virginia.

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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 the variance, accuracy, and bias of analytical results.

General results.—No qualification of constituent concentration or load was necessary based on analysis of duplicate samples. 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 samples and the range of constituent concentration. A minimum value of the percentage of total variance caused by measurement variance is preferred. The percentage of total variance from measurement variance for the constituents sampled ranged from 1.1 to 38 percent. The highest percentage (38 percent) was for dissolved ammonia nitrogen, which was because of the low concentration values and resultant low values for total variance and measurement variance. This does not indicate a problem at the Virginia Division of Consolidated Laboratory Services (VDCLS) for this analysis.

Results of the Wilcoxon signed-rank test on laboratory-split samples between 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 ammonia nitrogen, total phosphorus, total organic carbon, and dissolved silica. Of these four constituents, load of total organic carbon was underestimated for storm samples collected during the period August 1988 to February 1992.

The median bias for dissolved ammonia nitrogen of the differences in concentrations between laboratories (0.02 mg/L) was less than the minimum reporting limit of 0.04 mg/L by the VDCLS, indicating the bias shown by one or both laboratories has no significance with respect to concentrations or loads. The median bias for total phosphorus (0.01 mg/L) is the same as the minimum reporting limit for both laboratories and, therefore, also is not significant.

Total organic carbon showed a statistically significant difference (p =0.000) between the two laboratories. From August 1988 to February 1992, VDCLS used a technique that did not allow mixing a sample before withdrawing an aliquot for analysis. Therefore, concentration and load for storm samples and loads were underestimated for total organic carbon during this period. A new analytical technique, which required mixing the samples, was implemented on March 1, 1992, and produced results that were comparable to NWQL (p =0.694).

Dissolved silica showed a statistically significant difference (p =0.000) between laboratories because of a positive bias at NWQL that was documented by the USGS Branch of Quality Assurance (BQA) in Golden, Colo. The greatest variability between laboratories occurred when the concentration of dissolved silica was greater than 10 mg/L.

Results of the Wilcoxon signed-rank test on standard-reference samples showed a statistically significant difference between VDCLS analytical results and known concentration standards for total suspended solids and dissolved ammonia nitrogen. No qualification of concentration or load based on the results of standard-reference analyses was needed.

Total suspended solids showed a statistically significant difference (p =0.024) between analytical results and expected results from standard-reference samples. Results of reference samples from VDCLS at low concentrations were good, whereas only 40 percent of results at higher concentrations (234 to 363 mg/L) were within the 95-percent confidence interval of the expected concentration. Because both VDCLS and NWQL reported concentrations within the 95-percent confidence interval, the technique used for sample preparation by USGS personnel was examined more closely, was determined to be questionable, and was revised.

Dissolved ammonia nitrogen also showed a significant difference (p =0.001) between analytical results and expected results from standard-reference samples. Although all samples analyzed were within the 95-percent confidence interval, indicating good agreement between analytical results from VDCLS and known concentrations, a negative bias (-0.02 mg/L) was strong enough to affect statistical calculations for this constituent. Because the minimum reporting limit was 0.04 mg/L, this bias had no 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 using approved USGS guidelines to ensure the collection of samples that were representative of the river cross section. 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 during a range in discharge conditions. In addition, detailed documentation of field procedures and paperwork 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 standard-reference 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 10 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 10 percent of the samples collected at each site were laboratory-split samples.
3. Standard-reference samples document the accuracy of a laboratory to analyze samples of known concentrations and to check for bias in analytical results. Standard-reference samples were prepared in the USGS laboratory and submitted to VDCLS and NWQL for analysis.

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 (or "censored") were considered equal to the minimum reporting limit for calculations presented in this appendix, unless more than 25 percent of the data were censored. The maximum likelihood estimator (MLE) was used in the few cases where censoring was greater than 25 percent (Helsel and Cohn, 1988). Calculations for duplicate samples also were performed with the censored data equal to zero to define the range of variance for each constituent.

Duplicate samples.—The duplicate samples, which provided 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 samples and a duplicate sample. The source of measurement variability can be either field collection techniques or laboratory analytical procedures and should ideally be a small percentage 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 concentrations ranging more than several orders of magnitude. Constituents with about half of the concentrations in the range of 3.0 to 10.0 mg/L, such as total organic carbon and dissolved silica, show larger total variability than nitrogen and phosphorus species, which generally have concentrations below 1.0 mg/L. Dissolved ammonia nitrogen showed the smallest total variability because about 40 percent of the concentrations were equal to, or less than, the minimum reporting limit of 0.04 mg/L.

Measurement variance followed a pattern similar to total variance, where the large variances occurred with high concentration ranges. Tied values, or zero difference, between regular and duplicate samples showed no variability between the samples. Dissolved orthophosphorus had the highest percentage of tied values between

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

Constituent	Total variance	Measurement variance	Percent of total variance from measurement variance	Percent ties	Percent censored data	Number of sample pairs
Solids, total, suspended	20,542	392	1.9	28	9.1	109
Nitrogen, nitrite + nitrate, dissolved	.0484	.0022	4.5	48	5.3	113
Nitrogen, ammonia, dissolved	.0008	.0003	38	66	35	112
Nitrogen, ammonia + organic, total	.2545	.0057	2.2	60	.9	112
Phosphorus, total	.0564	.0018	3.2	47	2.7	112
Phosphorus, ortho, dissolved	.0037	.00004	1.1	81	21	112
Carbon, organic, total	33.53	8.245	25	14	0	106
Silica, dissolved	10.01	.1071	1.1	63	0	111

regular and duplicate samples and, therefore, had the lowest measurement variance. The low concentration range for dissolved orthophosphorus along with the minimum reporting level by the VDCLS caused a high percentage of tied values, thus limiting the measurement variability. The limiting effect of ties on variability had the greatest effect on nutrient species because of the low concentrations of these constituents as compared with total suspended solids, total organic carbon, and dissolved silica.

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, the greater the effect of laboratory analytical technique on total variance. The high percentage for dissolved ammonia nitrogen, however, probably is because of the low total variance and measurement variance for this constituent. Total organic carbon, with only 14 percent ties, is the least affected by the minimum reporting limit of the constituents analyzed for variance.

Calculations of total variance were recomputed setting the censored data equal to zero to define a range in variance for the six constituents with censored data. Measurement variance also was recomputed setting the censored data equal to zero for regular samples, and equal to the minimum reporting limit for duplicate samples. Total variance and measurement variance were slightly high for all constituents with censored data. The decision to set the censored data equal to the minimum reporting limit was seen to represent accurately the true variance because the results were only slightly different when the censored data were equal to zero.

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 variance 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 and (or) differences in laboratory precision. Collection of field blanks quantifies the source of measurement variability by ensuring that clean techniques were followed by field personnel.

The minimum reporting limits provided by the VDCLS caused a large percentage of tied values between regular and duplicate samples; therefore, the variance estimates are downwardly biased (underestimated). Low-level analyses began January 1, 1994, for the following constituents: dissolved ammonia, dissolved orthophosphorus, and dissolved nitrite plus nitrate (Norma Roadcap, Virginia Division of Consolidated Laboratory Services, oral commun., 1994). The change in analytical technique from part per million to part per billion should reduce the number of ties for these constituents and will improve calculations of variance in the future. Improvements in quality-assurance data-collection procedures were made to further quantify the source of measurement variability.

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 that was reached by the test. If $p > 0.05$ then there was no statistical difference between laboratories. If $p \leq 0.05$ then a significant bias was shown by one or both laboratories. Results of the Wilcoxon signed-rank test for laboratory-split samples, including two-sided probability values for raw concentrations, and the percent censored data reported by the NWQL and VDCLS for each constituent are listed in table A-2.

A statistically significant difference ($p \leq 0.05$) was observed in the median of the differences between the two laboratories for the following constituents: 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 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. 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. Holding time is thought to affect sample results as chemical processes are ongoing even after a sample has been collected.

Results from two quality-assurance projects conducted by the BQA were used to evaluate the NWQL and VDCLS analyses of the four water-quality constituents that showed a statistically significant difference between laboratories to identify the source of the difference. The external blind sample quality-assurance project was used to evaluate the quality of the NWQL results during the study. Reference samples, disguised as environmental samples, were sent periodically to the NWQL from USGS offices throughout the United States for analysis. An extensive data base of quality-assurance results exists for this project. USGS Open-File Report 90-162 provides instructions for the use of QADATA, a program that allows users to retrieve these results (Lucey, 1990). The USGS evaluation program for standard-reference samples was used to evaluate the accuracy of results for both the NWQL and VDCLS. Reference materials were supplied to participating laboratories semiannually to provide quality-assurance testing for this program. Numerous open-file reports exist that document the results of this study and are available from H. Keith Long (BQA).

The difference in concentrations reported by VDCLS and NWQL for dissolved ammonia nitrogen showed a statistically significant difference from zero. The NWQL showed a positive bias for dissolved ammonia nitrogen for both the standard-reference samples and blind samples, however, the accuracy was good for this constituent. The VDCLS showed no bias and good accuracy for dissolved ammonia nitrogen in the standard-reference sample program. The minimum reporting limit for dissolved ammonia nitrogen is 0.04 mg/L at VDCLS, whereas the minimum reporting limit for dissolved ammonia nitrogen is 0.01 mg/L at NWQL. The VDCLS results for dissolved ammonia nitrogen contained 48-percent censored data, whereas the NWQL results only contained 11-percent censored data. The median bias of the differences between the two laboratories (0.02 mg/L) has no environmental significance because this median bias is less than the minimum reporting limit at the VDCLS. No conclusions about laboratory performance can be drawn for this constituent with respect to the difference in reporting limits between the two laboratories and the high percentage of censored data reported by the VDCLS. The VDCLS lowered their minimum reporting limit to 0.004 mg/L on January 1, 1994 (Norma Roadcap, Virginia Division of Consolidated Laboratory Services, oral

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

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

Constituent	Two-sided probability value	Percent censored data NWQL	Percent censored data VDCLS	Number of sample pairs
Solids, total, suspended	0.357	7.1	10	166
Nitrogen, nitrite + nitrate, dissolved	.136	8.4	2.7	177
Nitrogen, ammonia, dissolved	.000	11	48	178
Nitrogen, ammonia + organic, total	.955	12	0.6	177
Phosphorus, total	.000	2.2	0.4	178
Phosphorus, ortho, dissolved	.389	28	19	178
Carbon, organic, total	.000	0	0	155
Silica, dissolved	.000	0	0	177

commun., 1994), and therefore it should be possible to make conclusions about laboratory performance for this constituent in the future.

Total phosphorus results from both quality assurance projects were examined for accuracy and bias since the median of the difference between the two laboratories for this constituent showed a significant difference from zero. The NWQL changed analytical techniques for total phosphorus two times during the data-collection period of this report. The change on May 1, 1990, was a dilution change that affected total phosphorus values exceeding 1.0 mg/L, and those samples with high sediment concentrations (greater than 50 mg/L suspended sediment). The maximum concentration of total phosphorus was 0.54 mg/L from August 1988 through April 1990. Two samples out of 45 had total suspended sediment concentrations in the range of 91 to 100 mg/L, and 3 samples were in the range 58 to 63 mg/L. The dilution change implemented by the NWQL on May 1, 1990, had minimal effect on the total phosphorus concentrations observed in the rivers for this study. The second technique change happened on October 1, 1991, when a new method was implemented. The data before October 1, 1991, showed a negative bias and fair accuracy for total phosphorus. Blind sample results after October 1, 1991 showed a 31 percent increase in the number of samples with zero difference between the NWQL result and the most probable value (MPV), which is the median result of all of the participating laboratories. The accuracy of the NWQL changed from fair (9.8 percent of the results were greater than two standard deviations from the MPV) to good (3.4 percent of the results were greater than two standard deviations from the MPV). A negative bias was still evident for total phosphorus; however, the number of values lower than the MPV decreased by about 10 percent. The new method provided substantial improvement in the accuracy of total phosphorus determination by the NWQL.

The VDCLS results for total phosphorus from the standard-reference sample program showed a positive bias and questionable accuracy, as 29 percent of the low-level samples were greater than two standard deviations from the MPV. The questionable accuracy by the VDCLS for total phosphorus was because of the use of analytical equipment with a minimum reporting limit of 0.1 mg/L for high-level phosphorus determinations. Sample results were reported to only two significant figures using this technique, whereas the concentrations provided by other laboratories in the program were reported to three or four significant figures. The MPV's used by Keith Long (BQA) for computations of accuracy were also reported to four significant figures; therefore, the rounded concentrations reported by the VDCLS appeared to be inaccurate. However, the VDCLS used a low-level phosphorus analysis for this study, with a minimum reporting limit of 0.01 mg/L. Load was computed using low-level total phosphorus concentration accurate to three significant figures that are within established guidelines for this study.

The total phosphorus data collected for this study were divided into two groups in order to further analyze the difference between laboratories: results from August 1988 to September 1991 and results from October 1991 to June 1993. Both groups showed a statistically significant difference between the laboratories for total phosphorus concentrations. After October 1991 the number of ties, where both laboratories got an identical result, increased from 15 to 23 percent of the reported values. Bias was shown by the number of times the NWQL result was lower than the VDCLS result increasing from 55 to 61 percent of the values analyzed. Bias in the differences between the NWQL and VDCLS for total phosphorus over time are shown in figure A-1. The positive bias by VDCLS along with the negative bias by NWQL affected results of the Wilcoxon signed-rank test performed on raw concentrations (p =0.000) for the 74 cases available from October 1, 1991 to June 30, 1993.

In summary, a statistical difference continues to exist between the laboratories for total phosphorus. The concentrations determined by the VDCLS are generally from 0.005 to 0.01 mg/L higher than those reported by the NWQL. This difference is not significant because the minimum reporting limit is 0.01 mg/L for both laboratories.

A statistically significant difference was observed between values reported by VDCLS and NWQL for total organic carbon. Total organic carbon samples were collected according to two different field sampling protocols. The sample collected for the VDCLS was a cross-sectional composite sample withdrawn from the churn and sent to the laboratory in a plastic container. The sample sent to NWQL was collected in the center of discharge in the river and shipped in a baked-glass bottle.

The procedure followed by VDCLS to analyze total organic carbon did not require mixing the sample before withdrawing an aliquot for analysis, thus particles in the sample were allowed to settle. Total organic carbon in samples collected during stormflow would, therefore, be underestimated by the VDCLS analytical technique. This procedure was changed by VDCLS on March 1, 1992. The total organic carbon data were divided into results before and after this change in technique to further analyze the quality-assurance data. The VDCLS concentration data from August 1988 to February 1992 indicated a negative bias with respect to the NWQL that produced results that were not comparable (p =0.000). The 53 cases available for analysis from March 1992 to June 1993 indicated that the improved laboratory technique used by the VDCLS produced results that were comparable to the NWQL (p =0.694). The number of times the NWQL result was greater than the VDCLS result changed from 78 percent using the old method to 45 percent with the new method. The negative bias by VDCLS for total organic carbon over time is shown in figure A-2. The plot showed the differences between NWQL and VDCLS were consistently greater than zero before March 1992, and showed random variability around zero after that date. The estimates for total organic carbon loads from August 1988 to February 1992 are lower for samples collected during high discharge than if analytical methods appropriate for large sediment concentrations were used. Samples collected after March 1, 1992, exhibit random variability, with no consistent bias present; therefore, the loads should be a better representation of 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. The 177 differences available between NWQL and VDCLS for dissolved silica showed a positive bias. Of these, 85 sample pairs showed the NWQL concentration to be higher, whereas 33 sample pairs showed the VDCLS concentration to be higher. The remaining 59 values were zero difference (ties) between sample pairs. The large number of ties caused the median bias to be zero; however, the median concentration of NWQL results is +0.3 when compared to the median concentration of VDCLS results for dissolved silica.

The blind-sample project showed a positive bias for dissolved silica determination by the colorimetric method at the NWQL from 1988 to 1990, and for 1993. However, when all quality-assurance samples from August 1988 to June 1993 were grouped, no bias was evident. The accuracy of the NWQL was good for this analysis, with less than 2 percent out of 1,082 samples being greater than two standard deviations from the most probable value and less than 1 percent being greater than six standard deviations from the most probable value. Results for the NWQL for dissolved silica, colorimetric method, were not available for the standard-reference sample program; but eight samples analyzed by VDCLS for dissolved silica for the standard-reference sample program were available for this report. The samples showed good to excellent results except the January 1992 sample, which showed poor results. Most of the data are to the right of the x=y line, meaning that the data are consistently higher at NWQL than at VDCLS as shown in figure A-3. The largest variability occurred when the concentration of dissolved silica was greater than 10 mg/L, which may affect loads for this constituent. The positive bias at

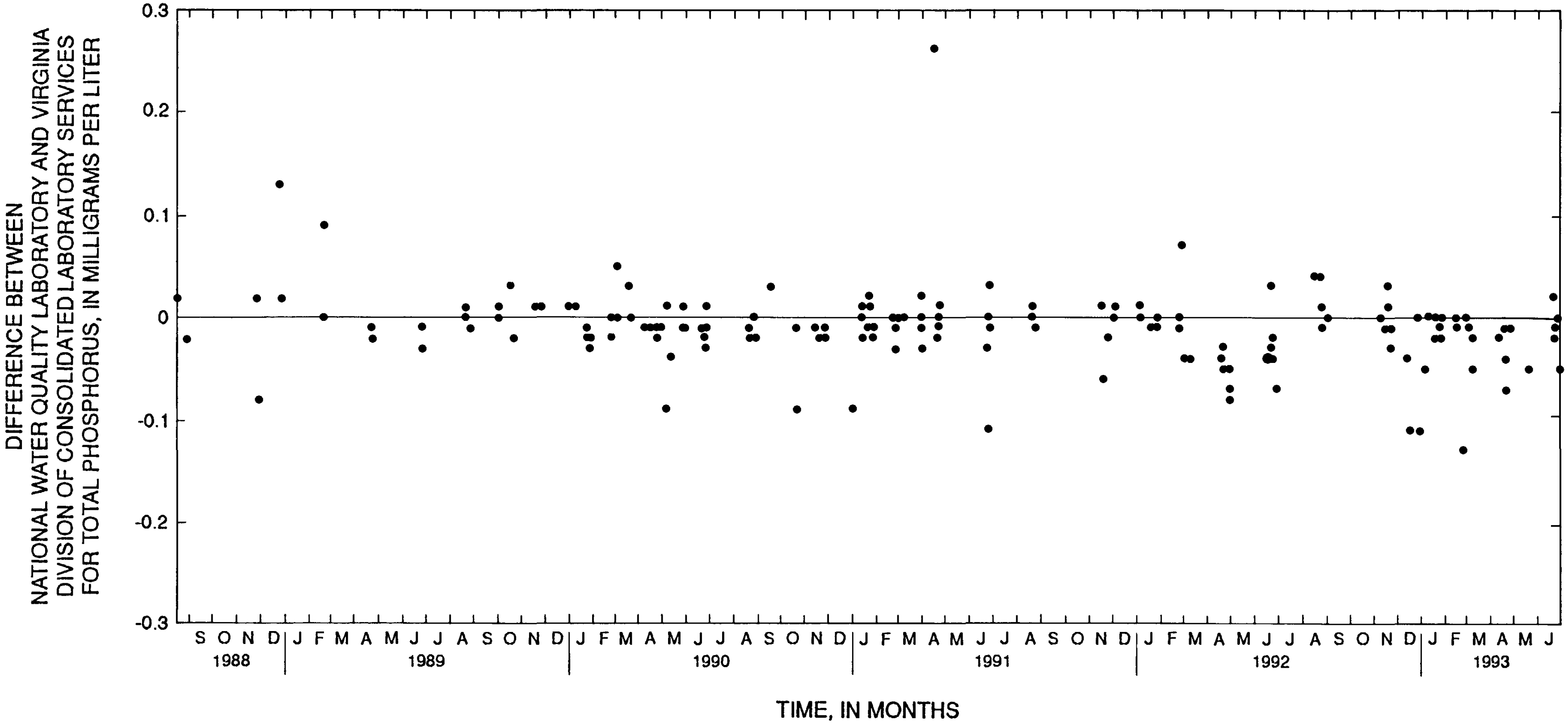

Figure A-1. Relation of the difference between laboratories for total phosphorus by time.

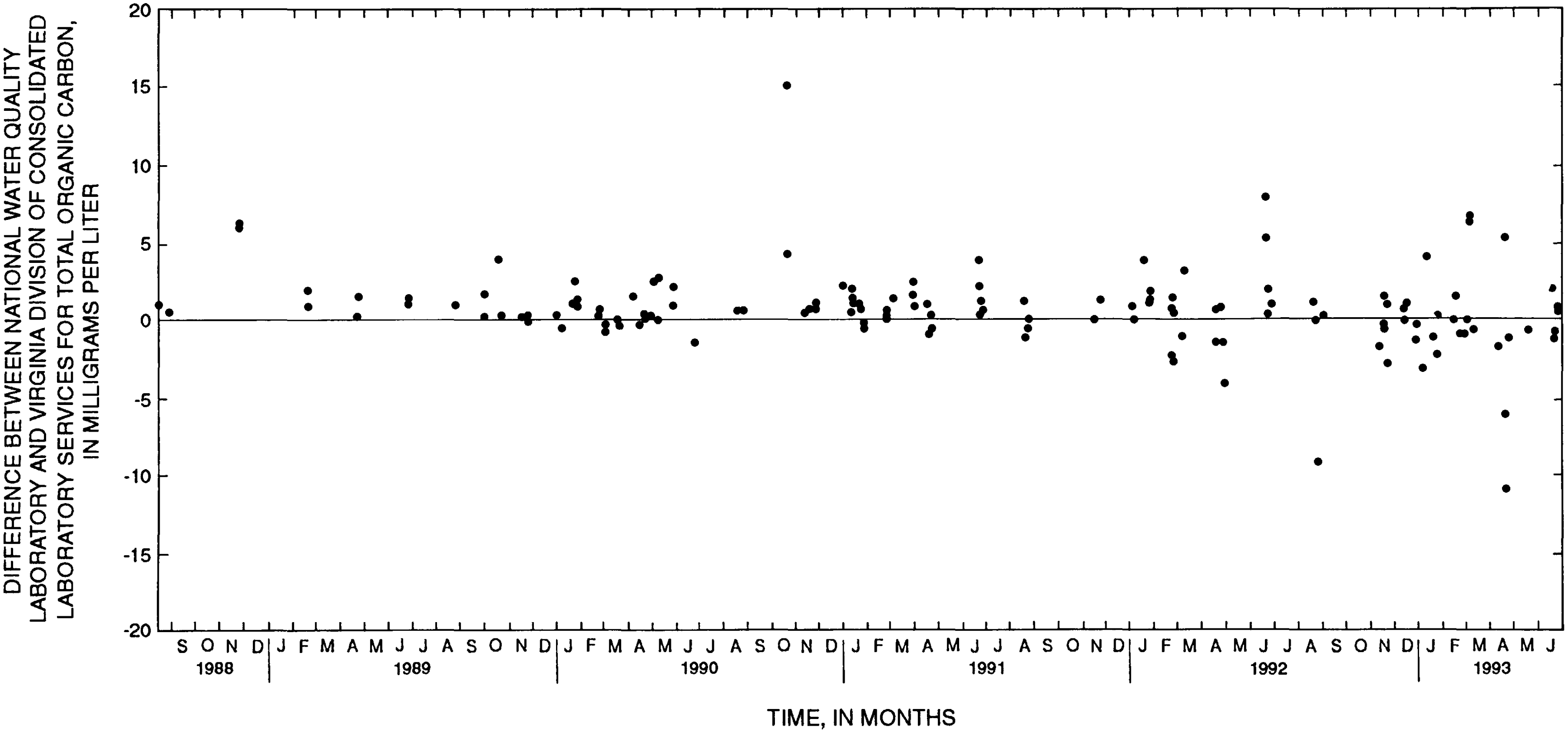

Figure A-2. Relation of the difference between laboratories for total organic carbon by time.

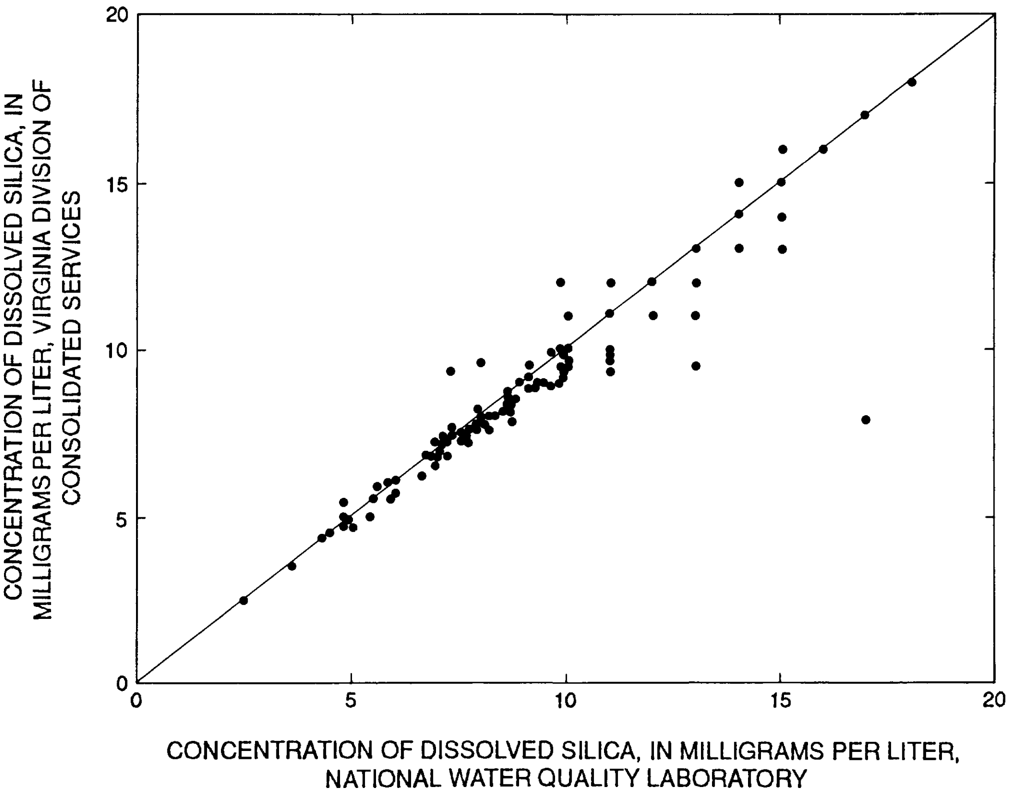

Figure A-3. Relation of dissolved silica concentration analyzed by the Virginia Division of Consolidated Laboratory Services to dissolved silica concentration analyzed by the National Water Quality Laboratory.

NWQL for dissolved silica along with a slight negative bias at VDCLS caused the results from NWQL to be consistently higher than VDCLS results for dissolved silica.

Standard-reference samples.—Standard-reference samples were sent to the VDCLS to check for bias in analytical procedures and to check the accuracy of the laboratory in analyzing known concentrations within a 95-percent confidence interval of the mean value. Reference samples were provided by the U.S. Environmental Protection Agency (USEPA) Environmental Monitoring Systems Laboratory in Cincinnati, Ohio, and from commercial laboratories. Quality-control sample concentrates were supplied by the laboratories along with instructions for preparation of reference samples. The true value, mean, standard deviation, and 95-percent confidence interval were reported by the USEPA and commercial laboratories for each lot of reference samples. Equations were provided to calculate the above statistics when the sample was prepared by diluting to a volume other than what was presented in the instructions.

A summary of statistics comparing constituent concentrations analyzed by the VDCLS to known concentrations of standard-reference samples is shown in table A-3. Five of seven constituents showed p-values >0.05, indicating no statistically significant difference between VDCLS results and known concentration standards.

Total suspended solids showed a statistically significant difference ($p = 0.024$), and only 50 percent of samples were within the 95-percent confidence interval. Three low-level samples (32 to 67 mg/L) analyzed showed excellent agreement with known concentrations, whereas only 6 out of 15 higher-level samples (234 to 363 mg/L) were within the 95-percent confidence interval. Samples outside of the 95-percent confidence interval were considered to be out-of-range for the discussion that follows. Eight of nine out-of-range samples were below the minimum value of the confidence interval. Four total suspended solids reference samples sent to both the VDCLS and NWQL showed good agreement between the laboratories for one low-level sample, and a similar pattern of out-of-range results for three high-level samples. Concentrations reported by both laboratories were below the minimum value of the 95-percent confidence interval for the high-level samples.

Reference samples for total suspended solids are difficult to prepare because the powdered solids do not resuspend well in organic-free water and tend to adsorb onto the inside wall of the flask when the subsamples are

Table A-3. Summary of statistics comparing constituent concentrations analyzed by the Virginia Division of Consolidated Laboratory Services to standard-reference samples approved by the U.S. Environmental Protection Agency

[two-sided probability values ≤.05 show a statistical difference between laboratory results and known standards; NA, not applicable]

Constituent	Number of Samples	Number of samples within 95 percent confidence interval	Percent samples within 95 percent confidence interval	Two-sided probability value
Solids, total, suspended	18	9	50	0.024
Nitrogen, nitrite + nitrate, dissolved	21	20	95	.273
Nitrogen, ammonia, dissolved	21	21	100	.001
Nitrogen, ammonia + organic, total	21	21	100	.061
Phosphorus, total	21	17	81	.780
Phosphorus, ortho, dissolved	21	20	95	.237
Carbon, organic, total	18	11	61	.163
Silica, dissolved[1]	0	NA	NA	NA

[1] Dissolved silica unavailable as a standard-reference sample.

being poured off. Both the VDCLS and NWQL reported concentrations below the expected value, indicating that not all of the solids were present in the sample for analysis. The technique problem has a greater effect on the high-level samples because larger quantities of solids are present. A technique that involves several rinses of the flask with known volumes of organic-free water will be implemented in the future.

Dissolved ammonia nitrogen showed a statistically significant difference ($p = 0.001$); however, 100 percent of the samples analyzed were within the 95-percent confidence interval. Out of 21 available samples, 19 differences were negative (VDCLS reported concentration was less than known concentration), resulting in a median bias of -0.02 mg/L for this constituent. This negative bias was not significant with respect to the concentrations because the minimum reporting limit was 0.04 mg/L. VDCLS results for prepared samples for dissolved ammonia nitrogen were excellent.

Nitrite-plus-nitrate nitrogen showed that 95 percent of the samples were within the 95-percent confidence interval. One out-of-range sample was investigated and the concentration confirmed by the VDCLS. Total phosphorus showed that 81 percent of the samples were within the 95-percent confidence interval. Four samples were out-of-range because of rounding by the laboratory to the nearest tenth. Dissolved orthophosphorus showed that 95 percent of the samples were within the 95-percent confidence interval. One out-of-range sample was confirmed by the VDCLS internal quality-control check. The concentration was approximately 0.3 mg/L higher than the maximum expected value.

Total organic carbon showed 61 percent of the samples analyzed were within the 95-percent confidence interval, however, there was no statistical difference ($p = 0.163$) for this constituent. Six high-level samples (23.0 mg/L) showed excellent agreement with known concentrations, whereas only 5 out of 12 low-level samples (4.0 to 8.8 mg/L) were within the 95-percent confidence interval. The out-of-range sample (lower than the minimum expected concentration) on February 6, 1991 also was analyzed by NWQL. The NWQL showed three similar samples analyzed for total organic carbon on that day to be less than the 95-percent confidence interval. This indicates perhaps a different lot number (with different confidence limits) was used to prepare these samples or an error occurred diluting the sample to volume in the USGS laboratory. Four out-of-range samples (greater then the maximum confidence interval) with concentrations from 5.4 to 6.1 mg/L occurred from October 1989 to March 1990, but were in good agreement with each other. The USEPA records of reference samples sent during this period were not available, so further investigation of these data is not possible. These samples do not appear to signify any problem with the VDCLS but represent an unknown problem within the USEPA or USGS.

APPENDIX B—REGRESSION MODEL RESULTS

Regression coefficients from the seven-parameter model provide information on the relation between concentration and each of the variables in the equation, which include discharge, time, and seasonality. In the following section, the coefficients of the model variables for discharge and season are used to help define how concentration changes with discharge and season. The regression summary tables (tables B-1–B-5) include: variable coefficients; the coefficient of variation, R^2; the number of data points used in developing equations, n; and the standard error of the regression, s.

A variable that has a T value with an absolute value greater than 2 is considered to be significant for that constituent, which means that the variable can explain some variance in the data set. The R^2 is the percentage of the variance explained by the regression equation. For example, an R^2 of 0.74 indicates that approximately 74 percent of the variance in the actual data is explained by the variables in the equation. The resultant 26 percent is assumed to be natural variability in the river system.

Two variables for discharge are used in the regression equation to explain the relation between discharge and constituent concentration: (1) a linear term, β_1 and (2) a quadratic term, β_2.The relation between concentration and discharge can be examined using the coefficients of the discharge variables. For this report, an underline of the variable in the summary regression tables indicates that this is a significant coefficient in the model in describing the relation between this constituent and streamflow (a T value greater than 2). A positive sign for the discharge coefficient, β_1, indicates a positive relation to concentration meaning that as discharge increases, concentration increases. A negative sign for β_1 indicates that as discharge increases, concentration decreases, and the constituent is diluted. The quadratic term, β_2, allows for curvature in the linear relation between concentration and discharge.The significance of the quadratic discharge term indicates that the relation between concentration and discharge becomes non-linear (either accelerating or decelerating) as discharges increase. If either β_1 or β_2 is significant as either a positive or negative value, then there is a relation between concentration and discharge for that constituent at that station.

Temporal changes in concentrations during the sample collection period are represented in the log-linear regression equation by variables β_3 and β_4. These changes in concentration can be representative of, for example: (1) increased or decreased atmospheric deposition that may not be apparent within short time frames, (2) upgrades to a number of water-treatment plants during the period of sample collection, or (3) other basin-wide changes, such as the implementation of best management practices by farmers, and at lumbering and construction sites that may reduce sediment and nutrients entering the river.

Seasonal changes in concentrations of water-quality constituents during the period of sample collection are represented in the log-linear regression equation by variables β_5 and β_6. Results of the regression model were used along with boxplots of concentration by season to help characterize the relation between seasonality and discharge for each river. The summary of regression coefficients from the model for β_5 and β_6 indicates that constituents are significantly related to season. If either the β_5 or β_6 is significant, then seasonality is important in explaining some of the variance in the water-quality data.

The sample coefficient of determination, denoted R^2, is a general indicator of the "goodness-of-fit" of the regression equation to the data. This statistic expresses the proportion of the total variance of the dependent variable (daily constituent concentration) that can be explained by variance in the independent variables (time, discharge, and season). Low values of R^2 occur when apparently random variations in concentrations of a constituent are much greater than variations in concentration associated with changes in discharge, season, and time, or when unaccounted-for variables strongly affect the constituent concentration. Low values of R^2 commonly are observed when the model is used to estimate concentrations of dissolved constituents, whereas higher R^2 values reflect constituents for which the concentrations are heavily dependent on discharge and (or) seasonality.

For each regression analysis, residuals were examined to identify any pattern that would be indicative of variability in the data set that is not explained by the seven model variables. No pattern was observed in residual plots for the constituents monitored.

Table B-1. Regression summary for the seven-parameter log-linear model used to estimate concentrations at the James River station[1]

[s, standard deviation of the residuals from ordinary least squares fit; r^2, coefficient of determination; n, number of observations used to fit the model; β_0, constant; β_1, coefficient of natural logarithm of streamflow; β_2, coefficient of natural logarithm of streamflow, squared; β_3, coefficient of time; β_4, coefficient of time, squared; β_5, coefficient of sine (time); β_6, coefficient of cosine (time); underline shows coefficients T value greater than 2, which indicates significance]

s	r^2	n	β_0	β_1	β_2	β_3	β_4	β_5	β_6
Total nitrogen									
0.35001	38	235	$\underline{-0.3842}$	$\underline{0.2766}$	$\underline{0.0434}$	-0.0008	-0.019	-0.0694	0.0154
Total Kjeldahl nitrogen									
.53013	29	236	$\underline{-1.0742}$	$\underline{.2896}$	$\underline{.1573}$	-.0141	.0039	$\underline{-.1275}$	.0402
Dissolved ammonia nitrogen									
.54279	25	237	$\underline{-3.5468}$	$\underline{.1146}$	.0270	$\underline{-.1462}$	$\underline{.0973}$	.0198	$\underline{.2293}$
Dissolved nitrite plus nitrate nitrogen									
.37327	51	236	$\underline{-1.1192}$	$\underline{.2911}$	$\underline{-.1927}$	.0347	$\underline{-.0385}$	-.0143	-.0449
Total phosphorus									
.56795	36	236	$\underline{-2.3124}$	$\underline{.3378}$	$\underline{.1758}$	$\underline{-.0936}$	$\underline{.0692}$	$\underline{-.1934}$	$\underline{.1199}$
Dissolved orthophosphorus									
.52675	59	236	$\underline{-3.3572}$	$\underline{-.3534}$	-.0064	$\underline{-.3375}$	$\underline{.0991}$	-.0881	$\underline{.1175}$
Total suspended solids									
.74988	77	229	$\underline{3.3044}$	$\underline{1.4342}$	$\underline{-.1129}$	-.0273	.0385	$\underline{-.3359}$	$\underline{-.1962}$
Total organic carbon									
.43259	32	226	$\underline{1.1684}$	$\underline{.1891}$	$\underline{.0825}$	$\underline{.1199}$	$\underline{.0853}$	$\underline{-.1684}$	.0004
Dissolved silica									
.19196	25	237	$\underline{2.0388}$	$\underline{.0606}$	$\underline{-.0756}$	.0118	-.0029	$\underline{-.1104}$	$\underline{-.0791}$

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[1] Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear regression model are stored on diskette at the back of this report.

Table B-2. Regression summary for the seven-parameter log-linear model used to estimate concentrations at the Rappahannock River station[1]

[s, standard deviation of the residuals from ordinary least squares fit; r^2, coefficient of determination; n, number of observations used to fit the model; β_0, constant; β_1, coefficient of natural logarithm of streamflow; β_2, coefficient of natural logarithm of streamflow, squared; β_3, coefficient of time; β_4, coefficient of time, squared; β_5, coefficient of sine (time); β_6, coefficient of cosine (time); underline shows coefficients T value greater than 2, which indicates significance]

s	r^2	n	β_0	β_1	β_2	β_3	β_4	β_5	β_6
Total nitrogen									
0.36638	70	209	0.0537	$\underline{0.4324}$	$\underline{-0.0745}$	$\underline{-0.0519}$	-0.0249	0.0462	0.0327
Total Kjeldahl nitrogen									
.55113	52	210	$\underline{-.8878}$	$\underline{.4780}$	$\underline{.0505}$	$\underline{-.1073}$	-.0183	$\underline{-.1468}$	$\underline{-.1254}$
Dissolved ammonia nitrogen									
.57224	30	210	$\underline{-3.3247}$	$\underline{.2259}$	.0092	$\underline{-.01567}$	.0271	.1189	.1098
Dissolved nitrite plus nitrate nitrogen									
.54323	67	209	$\underline{-.5443}$	$\underline{.4127}$	$\underline{-.2271}$	.0005	-.0315	$\underline{.2536}$	$\underline{.1654}$
Total phosphorus									
.72184	62	210	$\underline{-2.5546}$	$\underline{.7940}$	.0466	-.0682	-.0173	$\underline{-.2188}$	$\underline{-.1881}$
Dissolved orthophosphorus									
.54057	22	211	$\underline{-4.2845}$	$\underline{.2306}$	-.0012	$\underline{-.0748}$	-.0349	$\underline{-.2326}$	-.0074
Total suspended solids									
1.05136	74	209	$\underline{3.1775}$	$\underline{1.4995}$	-.0610	$\underline{-.1571}$	-.0643	$\underline{-.2433}$	$\underline{-.3252}$
Total organic carbon									
.51163	36	204	$\underline{1.2522}$	$\underline{.3139}$	.0335	.0250	$\underline{.0466}$	$\underline{-.1386}$	-.0694
Dissolved silica									
.19167	39	210	$\underline{2.3306}$	.0047	$\underline{-.0780}$	.0167	-.0004	-.0375	.0137

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[1] Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear regression model are stored on diskette at the back of this report.

Table B-3. Regression summary for the seven-parameter log-linear model used to estimate concentrations at the Appomattox River station[1]

[s, standard deviation of the residuals from ordinary least squares fir; r^2, coefficient of determination; n, number of observations used to fit the model; β_0, constant; β_1, coefficient of natural logarithm of streamflow; β_2, coefficient of natural logarithm of streamflow, squared; β_3, coefficient of time; β_4, coefficient of time, squared; β_5, coefficient of sine (time); β_6, coefficient of cosine (time); underline shows coefficients T value greater than 2, which indicates significance]

s	r^2	n	β_0	β_1	β_2	β_3	β_4	β_5	β_6
Total nitrogen									
0.27072	22	170	-0.6799	0.0813	0.0540	0.0255	0.0296	-0.0161	0.0067
Total Kjeldahl nitrogen									
.29863	21	170	-.8777	.1401	.0086	.0591	-.0022	-.1157	-.0691
Dissolved ammonia nitrogen									
.41072	23	170	-2.9086	.1664	-.0856	.0022	.0397	-.2003	.0200
Dissolved nitrite plus nitrate nitrogen									
.52746	27	170	-2.4542	-.0739	.1678	-.0489	.1438	.2861	.2582
Total phosphorus									
.42117	53	170	-3.1724	.3052	.0644	.1001	-.0098	.0515	.0205
Dissolved orthophosphorus									
.49011	8.7	170	-4.7427	-.0946	.0495	-.0841	.0563	.0311	.0955
Total suspended solids									
.56634	66	170	2.1686	.7281	-.0587	.0338	-.984	-0.2749	-.0141
Total organic carbon									
.38368	25	167	1.5458	.0868	.0652	.0906	.0833	-.0061	-.0621
Dissolved silica									
.13132	54	169	2.7154	-.0037	-.0319	-.0358	-.0263	-.1285	.0384

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[1] Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear regression model are stored on diskette at the back of this report.

Table B-4. Regression summary for the seven-parameter log-linear model used to estimate concentrations at the Pamunkey River station[1]

[s, standard deviation of the residuals from ordinary least squares fit; r^2, coefficient of determination; n, number of observations used to fit the model; β_0, constant; β_1, coefficient of natural logarithm of streamflow; β_2, coefficient of natural logarithm of streamflow, squared; β_3, coefficient of time; β_4, coefficient of time, squared; β_5, coefficient of sine (time); β_6, coefficient of cosine (time); underline shows coefficients T value greater than 2, which indicates significance]

s	r^2	n	β_0	β_1	β_2	β_3	β_4	β_5	β_6
Total nitrogen									
0.26813	26	194	-.02519	0.1615	-0.0146	0.0548	-0.0688	-0.1555	-0.1206
Total Kjeldahl nitrogen									
.33417	33	194	-.6299	.2441	-.0158	.0611	-.1155	-.2380	-.1371
Dissolved ammonia nitrogen									
.45266	11	194	-2.9653	.1143	-.0641	.0441	-.0477	-.0966	-.0041
Dissolved nitrite plus nitrate nitrogen									
.33095	5.6	195	-1.5194	-0.0102	-.0040	.0334	.0330	.0475	-.0786
Total phosphorus									
.45414	41	194	-2.4097	.3703	-.0296	.1390	-.1704	-.3712	-.1433
Dissolved orthophosphorus									
.52632	32	194	-4.1216	-.0690	.0165	-.0601	-.0902	-.3366	-.1926
Total suspended solids									
.83592	64	192	3.3349	1.0492	-.2336	.1141	-.2494	-.5858	-.3574
Total organic carbon									
.27099	47	195	1.6550	.1989	.0270	.0877	.0241	-.1056	-.1363
Dissolved silica									
.10737	64	193	2.4219	-.0727	-.0556	-.0037	.0094	-.0158	.0721

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[1] Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear regression model are stored on diskette at the back of this report.

Table B-5. Regression summary for the seven-parameter log-linear model used to estimate concentrations at the Mattaponi River station[1]

[s, standard deviation of the residuals from ordinary least squares fit; r^2, coefficient of determination; n, number of observations used to fit the model; β_0, constant; β_1, coefficient of natural logarithm of streamflow; β_2, coefficient of natural logarithm of streamflow, squared; β_3, coefficient of time; β_4, coefficient of time, squared; β_5, coefficient of sine (time); β_6, coefficient of cosine (time); underline shows coefficients T value greater than 2, which indicates significance]

s	r^2	n	β_0	β_1	β_2	β_3	β_4	β_5	β_6
Total nitrogen									
0.20572	27	179	-0.5090	0.0615	-0.0144	0.0365	0.0308	-0.1131	-0.1663
Total Kjeldahl nitrogen									
.23831	32	180	-.7741	1.056	-.0045	.0681	-.0115	-.1671	-.2161
Dissolved ammonia nitrogen									
.50408	7.1	179	-3.3289	.0763	-.0357	.0061	.0729	-.1116	-.1002
Dissolved nitrite plus nitrate nitrogen									
.47344	13	179	-2.0768	-.0915	-.0473	-.0511	.1535	.1442	.0168
Total phosphorus									
.34314	31	180	-2.7606	.2004	.0051	.0644	-.0808	-.2970	-.2800
Dissolved orthophosphorus									
.48549	20	180	-4.3426	-.0077	.0054	-.0630	-.0612	-.2306	-.2071
Total suspended solids									
.78965	31	177	1.9794	.4849	-.0904	-.0797	-.1412	-.1552	-.0609
Total organic carbon									
.40618	20	179	1.6453	.1017	.0523	.0484	.0570	-.0010	-.0010
Dissolved silica									
.17783	51	182	2.1027	.0299	-.0448	-.0114	-.0075	-.2137	.0972

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[1] Selected chemical and physical water-quality characteristics used as input variables to the seven-parameter log-linear regression model are stored on diskette at the back of this report.