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# Water-Quality Data of Soil Water from Three Watersheds, Shenandoah National Park, Virginia 1999–2000

By Karen C. Rice[1], Suzanne W. Maben[2], and James R. Webb[2]

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# Effects of Storm-Sampling Frequency on Estimation of Water-Quality Loads and Trends in Two Tributaries to Chesapeake Bay in Virginia

*By* Lori A. Sprague

**Water-Resources Investigations Report 01-4136**

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## CONVERSION FACTORS AND WATER-QUALITY UNITS

| Multiply | By | To obtain |
|---|---|---|
| | Area | |
| acre | 4,047 | square meter |
| acre | 0.4047 | hectare |
| mile | 1.609 | kilometer |
| square mile ($mi^2$) | 259.0 | hectare |
| square mile ($mi^2$) | 2.590 | square kilometer |
| | Flow | |
| foot per second (ft/s) | 0.3048 | meter per second |
| cubic foot per second ($ft^3/s$) | 0.02832 | cubic meter per second |
| | Mass | |
| pound (lb) | 0.4536 | kilogram |
| pound per acre (lb/acre) | 1.121 | kilogram per hectare |

**Water-Quality Units:** Chemical concentration is reported in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

# Effects of Storm-Sampling Frequency on Estimation of Water-Quality Loads and Trends in Two Tributaries to Chesapeake Bay in Virginia

*By* Lori A. Sprague

## ABSTRACT

Annual loads and flow-adjusted concentration trends were estimated by use of water-quality and streamflow data collected from 1990 through 1999 at monitoring stations on two tributaries to Chesapeake Bay in Virginia—James River at Cartersville, Va., and Rappahannock River near Fredericksburg, Va. The effects of storm-sampling frequency on the accuracy and precision of load and trend estimates were determined by use of data sets containing 0, 20, 40, 60, 80, and 100 percent of all storm samples collected in these two basins of different size, relief, and land use. Data sets included a range of dissolved and particulate constituents for the 10-year period from 1990 to 1999 and the 5-year period from 1995 to 1999.

Loads of dissolved constituents were estimated with greater accuracy and precision with fewer storm samples than loads of particulate constituents in both basins and for both time periods. All constituent loads were estimated with greater precision with fewer storm samples in the James River than in the Rappahannock River for both periods. The high relief and smaller drainage area of the Rappahannock River Basin caused quicker and more variable stream response than in the James River Basin, which led to less precise load estimates of all constituents, regardless of how many storm samples were included. For the James River, the magnitudes of the load estimates in the 5-year period were close to the estimates from the same years for the 10-year period for the dissolved constituents, but were smaller for the particulate constituents. Load estimates were more variable for the Rappahannock River than for the James River during the shorter period. In both basins, all estimates in the 5-year period had higher prediction errors than those in the 10-year period. Overall, loads of dissolved constituents were estimated with greater accuracy and precision with fewer storm samples than loads of particulate constituents; loads of all constituents were estimated with greater accuracy and precision over the longer time period; and load estimates of all constituents were more precise and required fewer storm samples in the larger and less flashy James River Basin than in the Rappahannock River Basin.

As with load estimates, estimates of flow-adjusted concentration trends were sensitive to the length of the monitoring period and the size of the basin; however, trend estimates generally were less sensitive than load estimates to the number of storm samples in the data set. Trends in flow-adjusted concentrations were estimated reasonably well with fewer storm samples for both dissolved and particulate constituents in the James River for the 10-year period, with the exception of total suspended solids. Data sets containing more storm samples were needed to obtain reasonable trend estimates for the 5-year period in this river. For the 10-year period in the Rappahannock River, more storm samples were necessary than in the James River to obtain reasonable estimates of trends for all constituents. No significant trends were observed for the 5-year period in this river, so the effect of storm-sampling frequency could not be determined. Because of the small number of significant trends throughout these data sets, it was not possible to determine whether fewer storm samples were required for estimating trends of dissolved constituents than particulate constituents. The results indicate that more storm

samples were necessary for accurate estimation of trends during the shorter time period and in the smaller and flashier Rappahannock River Basin.

## INTRODUCTION

Chesapeake Bay, the largest estuary in the United States, drains approximately 65,000 $mi^2$ of Virginia, West Virginia, Maryland, Delaware, Pennsylvania, New York, and the District of Columbia (fig. 1). The estuary extends nearly 200 mi from the mouth of the Susquehanna River in Maryland to the Atlantic Ocean along the southeastern coast of Virginia. From 1970 to 2000, the population in the Chesapeake Bay Watershed grew from a little more than 14 million to an estimated 15.5 million; by 2020, an estimated 18 million people will live in the watershed (U.S. Environmental Protection Agency, 1999). Population growth has led to substantial agricultural and urban development in the region, which has adversely affected the water quality of the Bay.

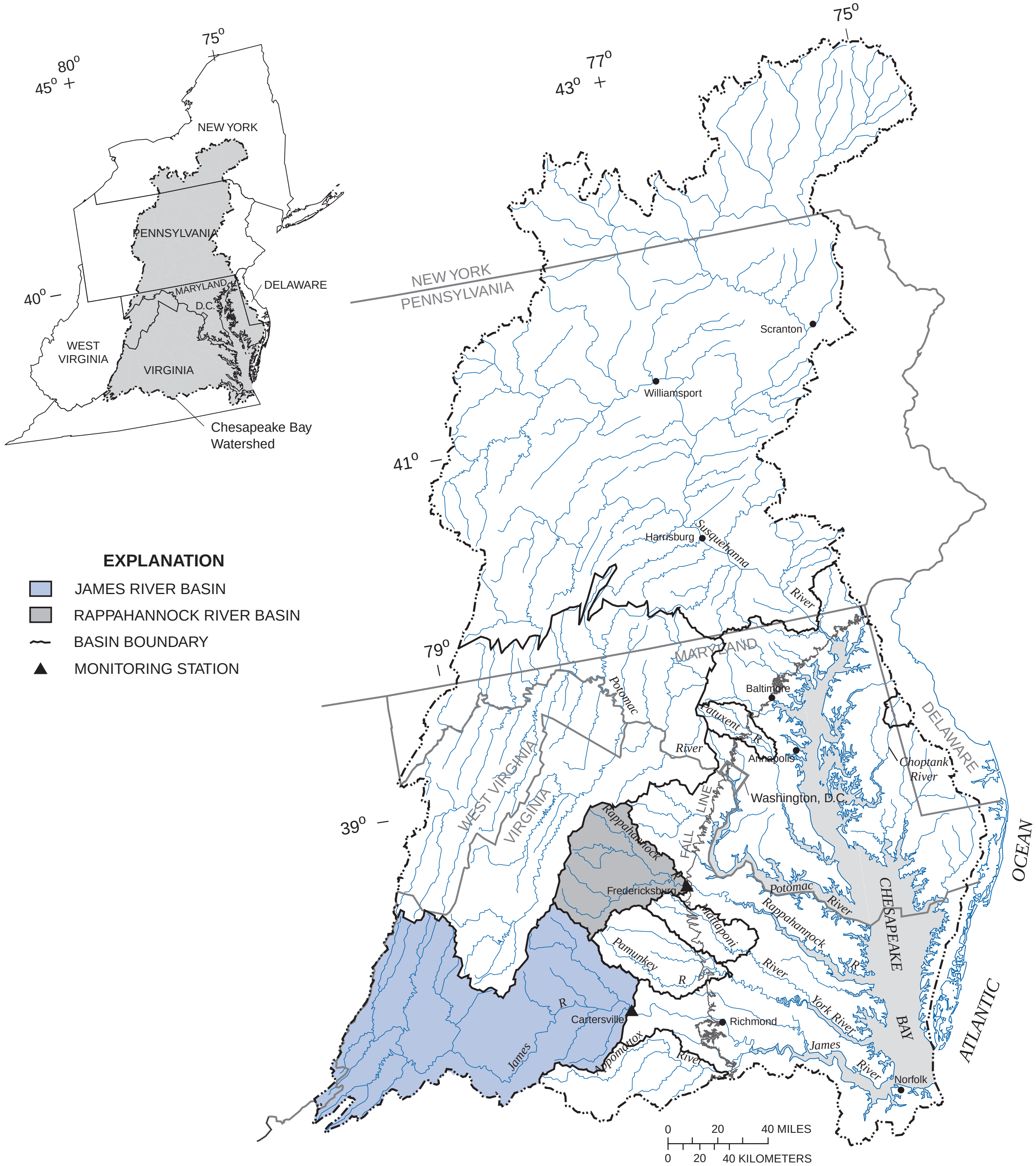
Excess nutrients and sediments enter the Bay and its tributaries from nonpoint sources such as urban and agricultural runoff and atmospheric deposition, and from point sources such as wastewater treatment plants. Elevated sediment concentrations and algal blooms caused by excess nutrients can deprive deep waters of sunlight needed to support the submerged aquatic vegetation that serves as a food supply and habitat for fish, shellfish, and other aquatic organisms. Subsequent decay of algae depletes the water of dissolved oxygen, further compromising the health of living resources in the Bay.

In 1987, the District of Columbia and the States of Virginia, Maryland, and Pennsylvania signed the Chesapeake Bay Agreement, a commitment to reduce controllable nutrient loads entering Chesapeake Bay (U.S. Environmental Protection Agency, 1988). In order to assess the effectiveness of nutrient and sediment reduction strategies, the U.S. Geological Survey (USGS) began the River Input Monitoring (RIM) Program in Virginia in 1988 in cooperation with the Virginia Department of Environmental Quality (VDEQ) and in Maryland in 1984 in cooperation with the Maryland Department of Natural Resources (MDNR) and the Metropolitan Washington Council of Governments (MWCOG). The purpose of the RIM Program is to monitor the water quality of the nine major tributaries that drain to Chesapeake Bay and to quantify loads and long-term trends in nutrient and sediment concentrations entering the Bay from these tributaries.

Water-quality monitoring conducted as part of the RIM Program is designed so that samples are obtained during a full range of hydrologic conditions, as in-stream concentrations are influenced by streamflow. For example, where point sources are the dominant nutrient source to a stream, dilution from an increase in streamflow decreases in-stream concentrations. In contrast, where nonpoint sources are the dominant nutrient source, increased streamflow from storm runoff generally increases in-stream concentrations. In-stream concentrations of particulate constituents derived primarily from surface runoff typically increase in response to storm events, whereas concentrations of dissolved constituents often decrease. Therefore, it is necessary to sample during both high-flow (elevated flow during and after storm events) and base-flow (background low flow between storm events) conditions to accurately monitor water quality in the tributaries to Chesapeake Bay.

Water-quality samples for the RIM Program in Virginia are obtained twice a month during base-flow conditions and periodically during high-flow conditions. VDEQ, which monitors additional sites in the Chesapeake Bay Watershed, collects water-quality samples once a month on pre-scheduled dates. This fixed-interval sampling typically results in the collection of samples during base-flow conditions; storm events are not targeted for additional sampling. To estimate loads and flow-adjusted concentration trends at all of the monitoring sites, the ESTIMATOR program is used to fit a log-linear regression model with explanatory variables of discharge, season, and time to the observed data (Cohn and others, 1992). Estimated daily concentrations from the model are used with daily mean discharges to calculate daily load estimates, which then are summed to provide monthly and annual load estimates.

In a previous study in which the regression model was used with data from large river basins in the Great Lakes region, fixed-interval sampling led to underestimates of the true total phosphorus load during a 2- to 3-year period (Preston and others, 1992). The addition of 12 high-flow samples per year reduced the bias and error of the estimates, particularly in the relatively small and rapidly responding basins. The effects of additional storm sampling on load and trend estimation in the Chesapeake Bay Watershed, where addi-




Base from U.S. Geological Survey Albers Equal-Area Conic projection
State lines from 1:100,000 TIGER files, 1990
Hydrography from USEPA River Reach Files Version 1 at 1:500,000, 1982
Watershed boundaries from 1:250,000 USGS Hydrologic Units, 1994

**Figure 1.** Drainage area and location of two monitoring stations in the Chesapeake Bay Watershed.

tional constituents are monitored and where the data sets typically cover a longer period, have not been examined thoroughly.

## Purpose and Scope

The purpose of this report is to determine the effects of storm-sampling frequency on (1) load and trend estimation in two basins of different size, relief, and land use in the Chesapeake Bay Watershed by comparing estimates from model simulations in which input data sets contained 0, 20, 40, 60, 80, and 100 percent of all storm samples; (2) load and trend estimation during two monitoring periods of different durations by comparing model estimates covering the 10-year period from 1990 to 1999 and the 5-year period from 1995 to 1999; and (3) estimation of a range of dissolved and particulate constituent loads and trends, including total nitrogen, dissolved nitrite-plus-nitrate (as N), dissolved orthophosphorus (as P), total phosphorus, and total suspended solids. Water-quality and streamflow data from 1990 through 1999 from two Virginia RIM stations—James River at Cartersville, Va. (02035000) and Rappahannock River near Fredericksburg, Va. (01668000)—were used in these analyses.

## Description of Study Area

Together, the James and Rappahannock River Basins comprise more than 50 percent of the Chesapeake Bay drainage area in Virginia, and about 20 percent of the total Chesapeake Bay drainage area (fig. 1). Both RIM stations are located near the Fall Line, the boundary between the Piedmont and the Coastal Plain Physiographic Provinces and the point farthest downstream unaffected by tides. Each station is co-located with an active USGS stream-gaging station.

The James River Basin, at 10,200 mi$^2$, is the third largest tributary basin in the Chesapeake Bay Watershed. The James River originates in the Appalachian Mountains near the Virginia-West Virginia border, flows through the Valley and Ridge, the Blue Ridge, the Piedmont, and the Coastal Plain Physiographic Provinces, and joins Chesapeake Bay near the city of Norfolk in southeastern Virginia. The monitoring station is in Cartersville, Va., about 40 mi upstream from the Fall Line. This location was selected because a long-term discharge record is available; no major streams enter the river between Cartersville and the Fall Line. The monitoring station receives drainage from about 60 percent of the James River Basin.

Land use upstream from the monitoring station is dominated by forest (80 percent) and agriculture (16 percent) (table 1). The agricultural areas are concentrated in the western part of the basin in Rockbridge, Botetourt, and Nelson Counties (Battaglin and Goolsby, 1994). Of the nine rivers monitored as part of the RIM Program, the James River contributes about 12 percent of the streamflow, 5 percent of the total nitrogen load, and 20 percent of the total phosphorus load to Chesapeake Bay, making it the third largest source of streamflow and nutrients to the Bay, after the Susquehanna and Potomac Rivers (Belval and Sprague, 1999).

The Rappahannock River Basin, at 2,800 mi$^2$, is the fourth largest tributary basin in the Chesapeake Bay Watershed. The Rappahannock River originates near the eastern edge of the Blue Ridge Physiographic Province and extends eastward through the Piedmont and Coastal Plain Physiographic Provinces. The monitoring station is located at the Fall Line just upstream from Fredericksburg, Va., where it receives drainage from about 57 percent of the Rappahannock River Basin. Upstream from the monitoring station, the basin's relief and steep slopes cause the river to respond rapidly to storm events.

**Table 1.** Land area and land use upstream from the monitoring stations

[USGS, U.S. Geological Survey; mi$^2$, square mile; land-use data from Vogelmann and others, 1998; land use expressed as a percentage of total land-surface area upstream from each monitoring station; other land use includes barren/transitional and water]

| USGS station number | Station name | Upstream land-surface area (mi$^2$) | Land use (percent) | | | |
|---|---|---|---|---|---|---|
| | | | Urban | Agricultural | Forested | Other |
| 02035000 | James River at Cartersville, Va. | 6,260 | 1 | 16 | 80 | 3 |
| 01668000 | Rappahannock River near Fredericksburg, Va. | 1,600 | 1 | 36 | 61 | 2 |

Land use upstream from the monitoring station is dominated by forest (61 percent) and agriculture (36 percent). The Rappahannock River Basin contains the highest percentage of agricultural land above the Fall Line of the five major tributary basins in Virginia. The agricultural areas are generally located in the central part of the basin, in Fauquier, Culpeper, Madison, and Orange Counties (Battaglin and Goolsby, 1994). Of the nine rivers monitored in the RIM Program, the Rappahannock River contributes about 3 percent of the streamflow, 2 percent of the total nitrogen load, and 8 percent of the total phosphorus load delivered annually from the nontidal part of the Chesapeake Bay Watershed (Belval and Sprague, 1999).

Because of the smaller area, greater relief, and smaller percentage of forested land in the Rappahannock River Basin, the stream response to storm events is “flashy” relative to that of the James River Basin—stream levels rise and recede more quickly during and immediately after storm events in the Rappahannock River Basin. Corresponding stream discharge values can change rapidly during the course of a day, and the difference between the instantaneous discharge at the time of sampling and the daily mean discharge can be large. Because concentration values typically vary in response to streamflow, the difference between the instantaneous in-stream concentration at the time of sampling and the daily mean concentration also can be large. These factors may influence load estimation, because daily mean streamflow and concentration values are represented in the load regression model.

## Acknowledgments

The RIM Program is supported in Virginia through a cooperative agreement between VDEQ and USGS. The water-quality and streamflow data used in this report were collected by many USGS and VDEQ personnel. Dave Eckhardt and Joel Blomquist of the USGS and Rick Hoffman of VDEQ reviewed this report and provided many helpful comments.

# METHODS OF STUDY

The methods used to collect water-quality data and to estimate loads and trends are discussed below. In addition, the experimental design for determining the effects of storm-sampling frequency on load and trend estimation is described.

## Data Collection

Water-quality samples used in this study were collected from 1990 through 1999. Base-flow samples were collected twice a month—once by USGS personnel and once by VDEQ personnel at the James River monitoring station, and twice by USGS personnel at the Rappahannock River monitoring station. Samples were collected at the two monitoring stations by use of the equal-discharge increment (EDI) method, in which multiple samples from the centroids of equal-discharge increments across the river channel are composited (Wilde and others, 1999). The channels of both rivers are stable at the sampling locations, and the discharge ratings changed little each year. Samples were collected by USGS personnel with a depth-integrated sampler when streamflow velocities exceeded 1.5 ft/s; water enters this sampler at the same velocity as the stream at each depth and the intake comes as close to the stream bottom as possible without disturbing the bottom sediment. A weighted bottle was used at lower velocities at which depth-integrated samplers are not effective. All samples collected by VDEQ personnel at the James River monitoring station were obtained with a weighted bottle; if the stream velocity at the time of sampling exceeded 1.5 ft/s, the data were not used in this study.

In addition to the bimonthly base-flow samples, 30 to 40 high-flow samples per year were collected by USGS personnel at each site at the beginning of the study period. High-flow samples were defined as those collected above a gage height reached in each river about 40 times per year. During periods of extreme low flow, the sampling criteria were modified slightly to obtain the target number of high-flow samples. After 3 years, the number of storm samples was reduced to approximately 20 per year. Emphasis was placed on sampling throughout a range of rising, peak, and falling gage heights to avoid bias in concentrations. As a result of this sampling design, about half of the samples collected represented high-flow conditions.

Water samples collected for determination of nutrient and total suspended solids concentrations were analyzed at the Virginia Division of Consolidated Laboratory Services (VDCLS) in Richmond, Va. Quality-assurance samples were analyzed at VDCLS and the USGS National Water-Quality Laboratory in Denver, Colo. Quality-assurance procedures for the Virginia RIM Program are described in detail in Belval and others (1995) and Bell and others (1996).

## Load Estimation

Annual constituent loads at each station were estimated with the observed concentration and streamflow data as input to the ESTIMATOR model, a seven-parameter log-linear regression model that uses time, flow, and season terms to predict daily concentrations (Cohn and others, 1992). The model incorporates a minimum variance unbiased estimator to correct for log-transformation bias and an adjusted maximum likelihood estimator to assign concentration values to data below the detection limit (Cohn, 1988). The regression equation used is as follows:

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

where

$ln[]$ = the natural logarithm function,

$C$ = the constituent concentration (in mg/L),

$Q$ = the mean daily discharge (in $ft^3/s$),

$T$ = time (in years),

sin = the sine function,

cos = the cosine function,

$\pi$ = 3.14169,

$\beta$ = model coefficients,

$\varepsilon$ = model error, and

$\tilde{Q}$ and $\tilde{T}$ = centering variables.

$\beta_0$ through $\beta_6$ are the coefficients of the regression model that were computed from the observed concentration data. The model error ($\varepsilon$) is assumed to be independent and normally distributed with a mean of zero and constant variance. Centering variables simplify the numerical work and have no effect on the load estimates, so that the regression coefficients are statistically independent. This equation results in a predicted daily concentration. The predicted daily concentration values were multiplied by measured daily mean discharge values to estimate daily load values, which were summed to obtain annual load estimates.

Annual load estimates were compared on the basis of variance and bias. The standard error of prediction (SEP) is a measure of the variance, or precision, of the load estimate. All SEP values in this report were normalized to the total load estimate to facilitate comparisons among constituents, time periods, and basins, and are presented as percent SEP. The bias, or difference between the estimated load and the “true” load, is a measure of the accuracy of the load estimate. Because the true load cannot be determined without a continuous record of discharge and concentration, it was assumed that load estimates were converging toward the true load value as more storm samples were included. For the purposes of this study, convergence occurred when the median of the percent difference between the annual loads estimated with one storm data set and the annual loads estimated with the next highest storm data set was less than 5 percent. This generalized estimate of convergence is constrained by the fact that only six scenarios were tested.

The overall trend in flow-adjusted concentration was calculated by use of the beta coefficient of the linear time parameter ($\beta_3$) from the regression model. The trends are inherently flow-adjusted because the model separates variability in concentration due to variability in flow from that due to variability in time. The average percent change in flow-adjusted concentration over the time period was calculated as:

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

where

$\% \Delta C$ = percent change in flow-adjusted concentration,

$e$ = anti-log of the natural log,

$\beta_3$ = coefficient of the linear time parameter, and

$\Delta t$ = the period of time over which the regression model is calibrated.

The confidence interval of the trend was calculated by use of the standard deviation of $\beta_3$.

## Experimental Design

In order to determine the effect of the number of storm samples in a data set on load and trend estimation, subsets of storm samples were chosen randomly and removed from the full data sets of the James River and Rappahannock River RIM stations. Loads and trends were then estimated for each new, smaller data set.

### Streamflow Partitioning

The sampling design of the RIM Program is to obtain samples during a full range of flow conditions. The decision to sample a high-flow event is based in large part on regional precipitation amounts and gage-height fluctuations. To obtain a more rigorous designation of storm samples for this study, water-quality samples were classified as either “storm” or “base” on the basis of streamflow partitioning. The program PART was used to estimate daily base flow for the period of record from daily streamflow values (Rutledge, 1998). The method sets base flow equal to streamflow on days when surface runoff can be considered negligible (based on a requirement of antecedent recession) and linearly interpolates base-flow values on other days.

“Storm” samples were designated as those collected on days when base flow made up less than 60 percent of the total streamflow. Other studies that have described a similar storm-flow designation technique covered a wide range of threshold values. For example, in a study of base-flow and storm-flow yields in Kentucky, samples were not classified as base flow on days when base flow made up less than 90 percent of the total streamflow (Evaldi and Moore, 1994). In another study examining episodic acidification of streams in Virginia, samples were classified as storm flow on days when base flow made up less than 25 percent of the total streamflow (Eshleman and others, 1995). The 60-percent threshold chosen for this study is intermediate between these two values and covers the interquartile range of streamflow at the James and Rappahannock River monitoring stations (fig. 2).

Both the streamflow partitioning and the storm-sample designation procedures used in this study are arbitrary and have limitations. They do provide, however, a more consistent and quantitative classification of streamflow conditions at the time of sampling.

### Data-Set Construction

After base- and storm-flow samples had been designated, data sets with 0, 20, 40, 60, 80, and 100 percent storm samples (“storm data sets”) were created for each station, for the 10-year period from 1990 through 1999 and for the 5-year period from 1995 through 1999. All base-flow samples were retained in each data set, and storm samples were selected randomly with replacement for removal from each data set. The 100-percent data sets were the full data sets, including all base and storm samples. The 0-percent data sets included only base-flow samples; all storm samples were removed. The 80-percent data sets were created by removing 20 percent of the storm samples from each full data set; individual storm samples were selected randomly for removal. The 60-, 40-, and 20-percent data sets were created in a similar fashion. Appendix 1 lists the total number of storm-flow days in the daily streamflow record for each station during the 5- and 10-year periods and the number of storm-flow days in each data set on which a water-quality sample was collected. Figures 3 and 4 show all of the streamflow and water-quality sampling records for the James and Rappahannock Rivers, respectively.

The 0-, 20-, 40-, 60-, 80-, or 100-percent data-set designation refers to the percentage of the total number of storm samples in the full RIM data set that was left in the new data set—it does not represent the percentage of storms in the new data set. For example, the full Rappahannock River RIM data set (the designated 100-percent data set in this report) had 385 total samples from 1990 through 1999; 163 of those samples, or 42 percent, were storm samples. The 80-percent data set included 80 percent, or 130, of the 163 storm samples and all of the base-flow samples, resulting in a new data set with 37 percent storm samples (Appendix 1, figs. 3 and 4).

The number of storm events that corresponds to the 0-, 20-, 40-, 60-, 80-, or 100-percent designation differs depending on the station and time period. For example, for the period from 1990 through 1999, the 60-percent data set for the James River station contained 43 percent storm samples, whereas the 60-percent data set for the Rappahannock River station contained 31 percent storm samples.

## JAMES RIVER LOAD ESTIMATES

A wide range of hydrologic conditions occurred in the James River during the period from 1990 through 1999, making it an ideal period for examining the effects of storm-sampling frequency on load and trend estimation. The annual total streamflow from 1990 through 1999 at the James River monitoring station, along with the long-term mean-annual streamflow for the period of record (1899-1999), is shown in figure 5. Streamflow in 1990, 1993, 1994, 1996, and 1998 was above the long-term mean; in 1996, Hurricane Fran contributed to the highest annual total flow in the mon-

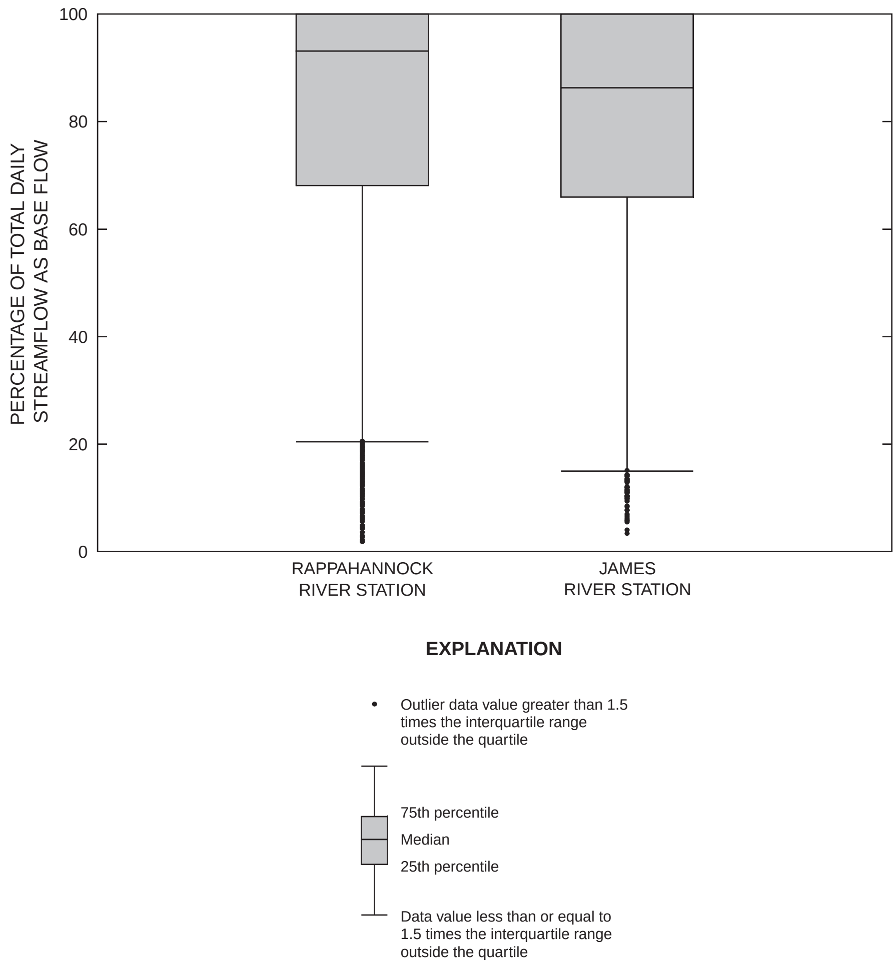



**Figure 2.** Percentage of total daily streamflow as base flow for the period of record at the monitoring stations.

itoring period. Streamflow in 1997 and 1999 was below the long-term mean; 1999 was a drought year and had the lowest annual total flow in the monitoring period.

## Ten-Year Loads

Annual loads for the 10-year period from 1990 through 1999 were estimated for a range of dissolved and particulate constituents—total suspended solids, total phosphorus, total nitrogen, dissolved nitrite-plus-nitrate, and dissolved orthophosphorus—with all storm data sets for the James River monitoring station (fig. 6). (The “dissolved” and “particulate” classification used throughout this report refers to the primary phase in which these constituents are found during both base- and storm-flow conditions.)

### Total Suspended Solids

Load estimates for total suspended solids varied among the storm data sets; they varied most during 1993, 1996, and 1998 and least during 1997 and 1999 (fig. 6). During all years, the data set without storm samples (the 0-percent data set) led to underestimates of total suspended solids loads relative to the data sets with storm samples. The 20-percent data set overestimated the loads relative to the higher percentage data sets during high-flow years, but during low-flow years the estimates were closer to those of the higher percentage data sets. The SEPs were highest with the lower percentage data sets, particularly the 0-percent data set (fig. 7). The relatively poor predictions in the lower percentage data sets were likely a result of the lack of a sufficient number of high concentration values in the input data set to constrain the model estimates at high

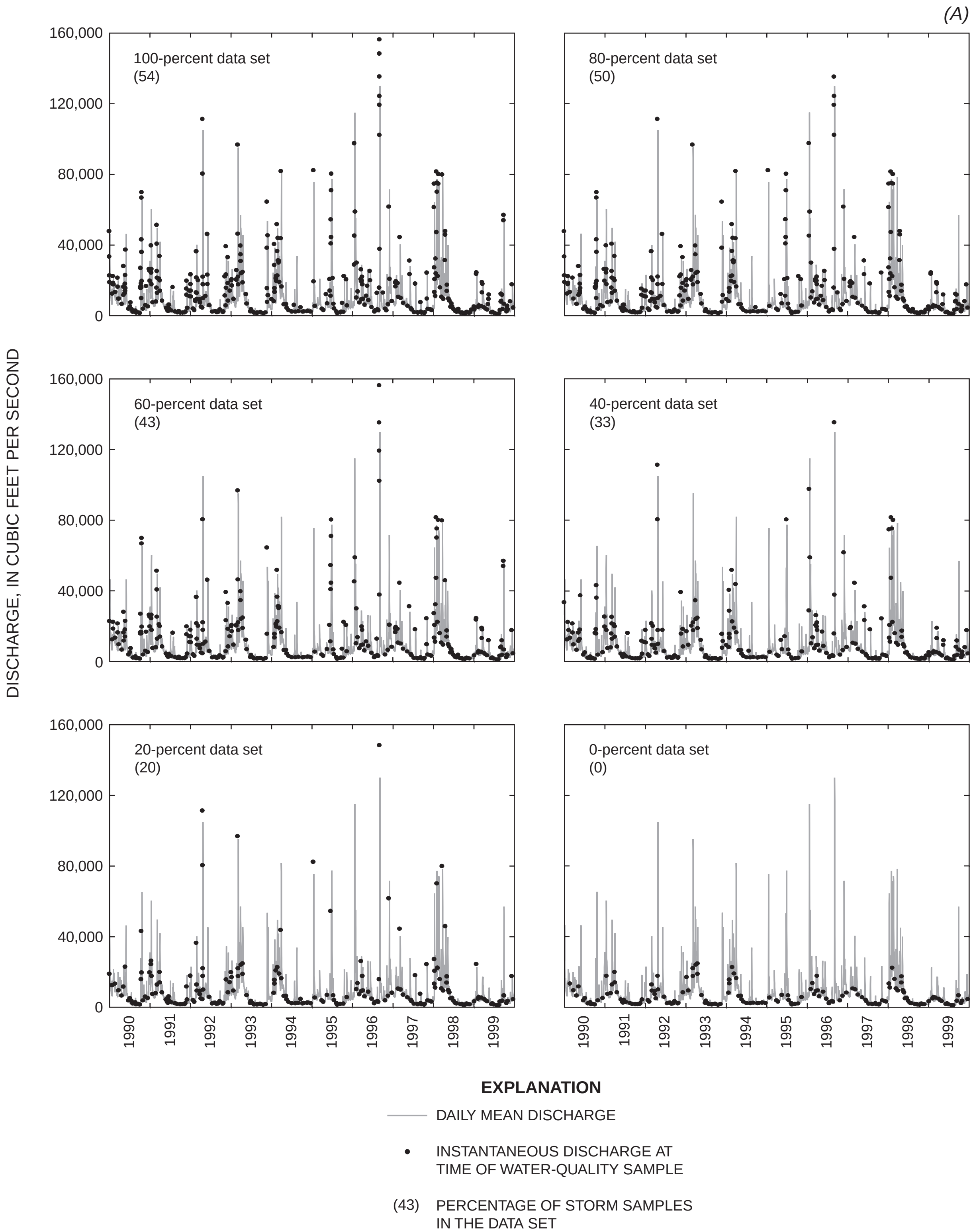



**Figure 3.** Water-quality samples and daily mean discharge at James River monitoring station for each storm data set, 1990 through 1995 *(A)* and 1995 through 1999 *(B)*.

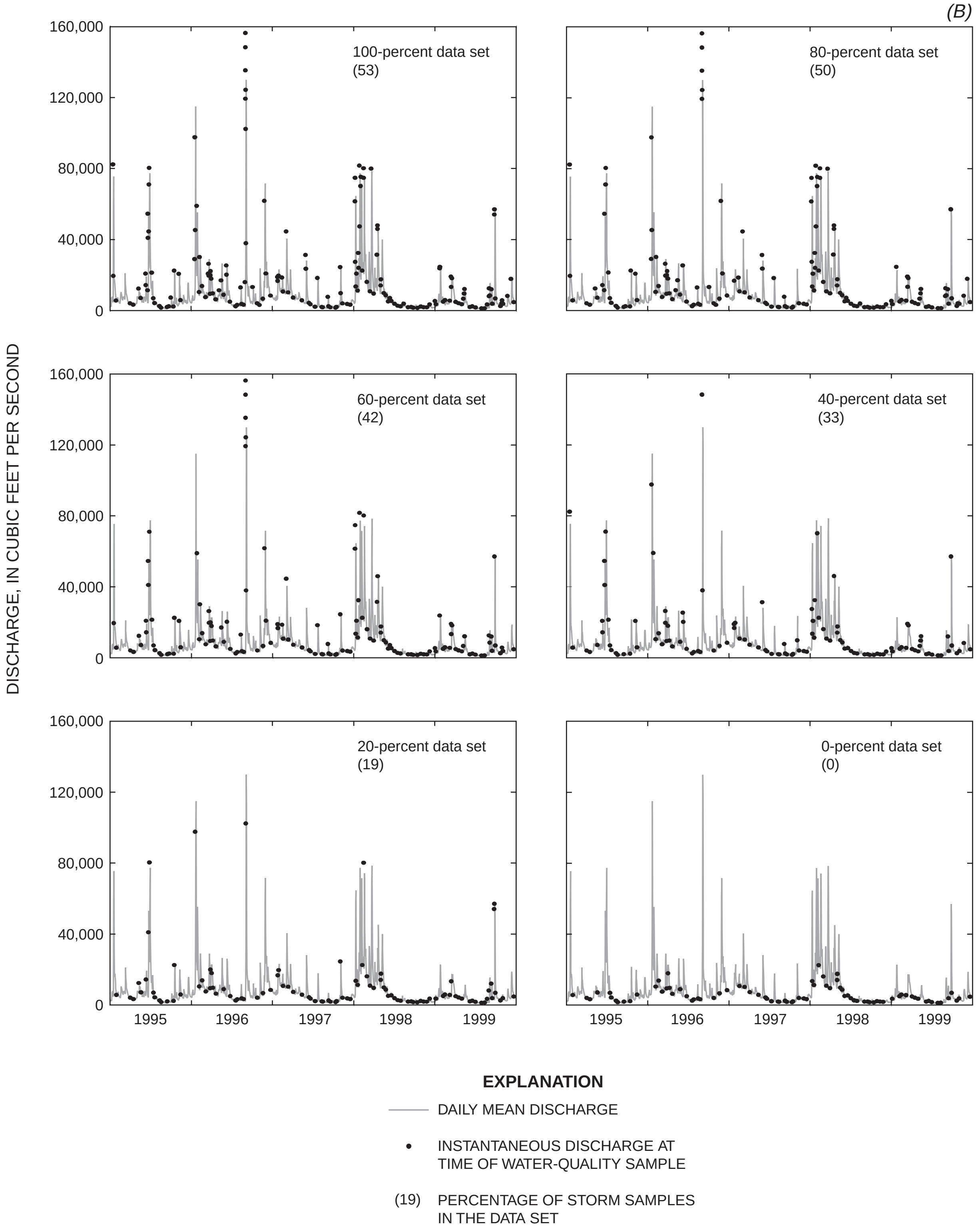



**Figure 3.** Water-quality samples and daily mean discharge at James River monitoring station for each storm data set, 1990 through 1995 *(A)* and 1995 through 1999 *(B)*—Continued.

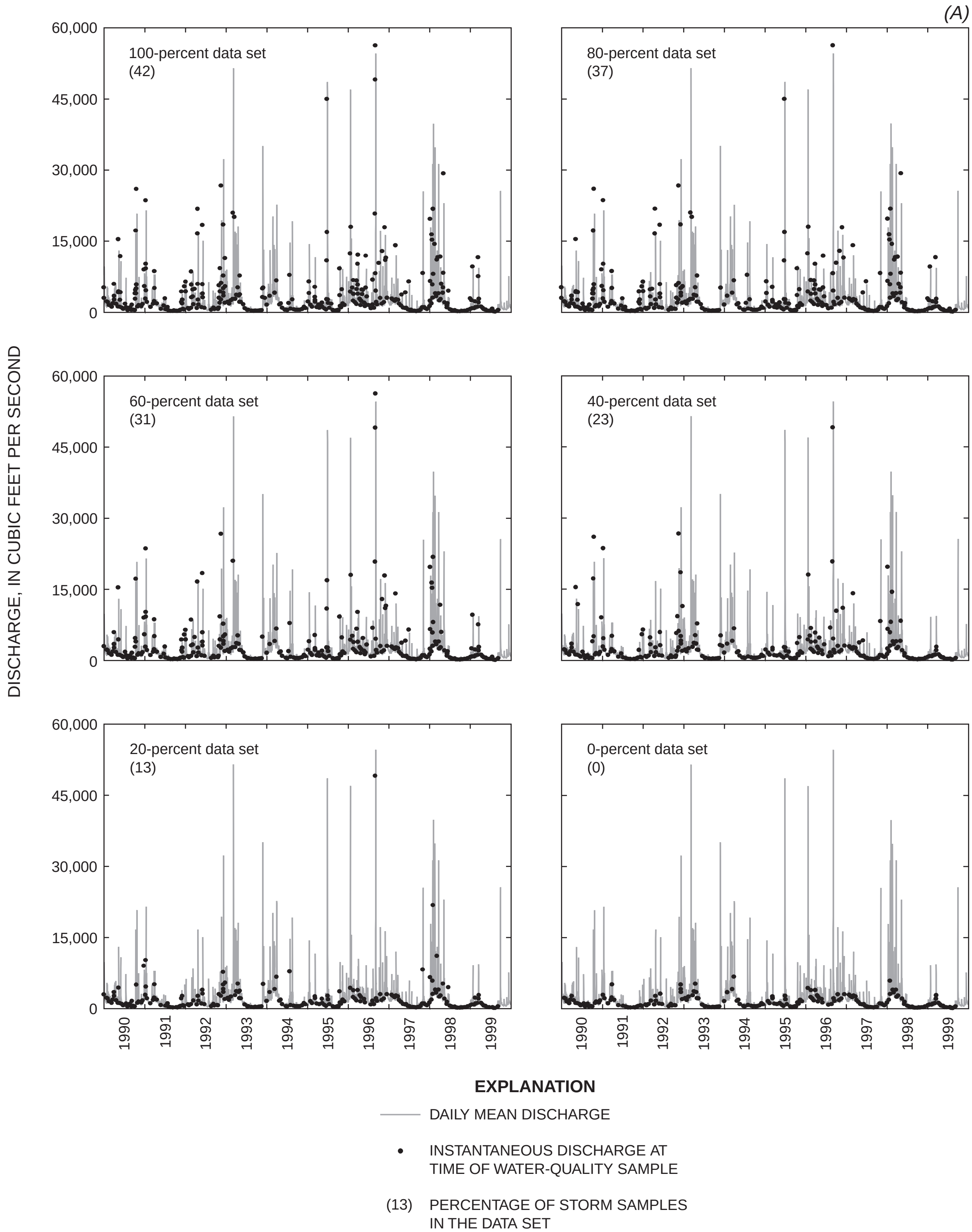



**Figure 4.** Water-quality samples and daily mean discharge at Rappahannock River monitoring station for each storm data set, 1990 through 1995 *(A)* and 1995 through 1999 *(B)*.

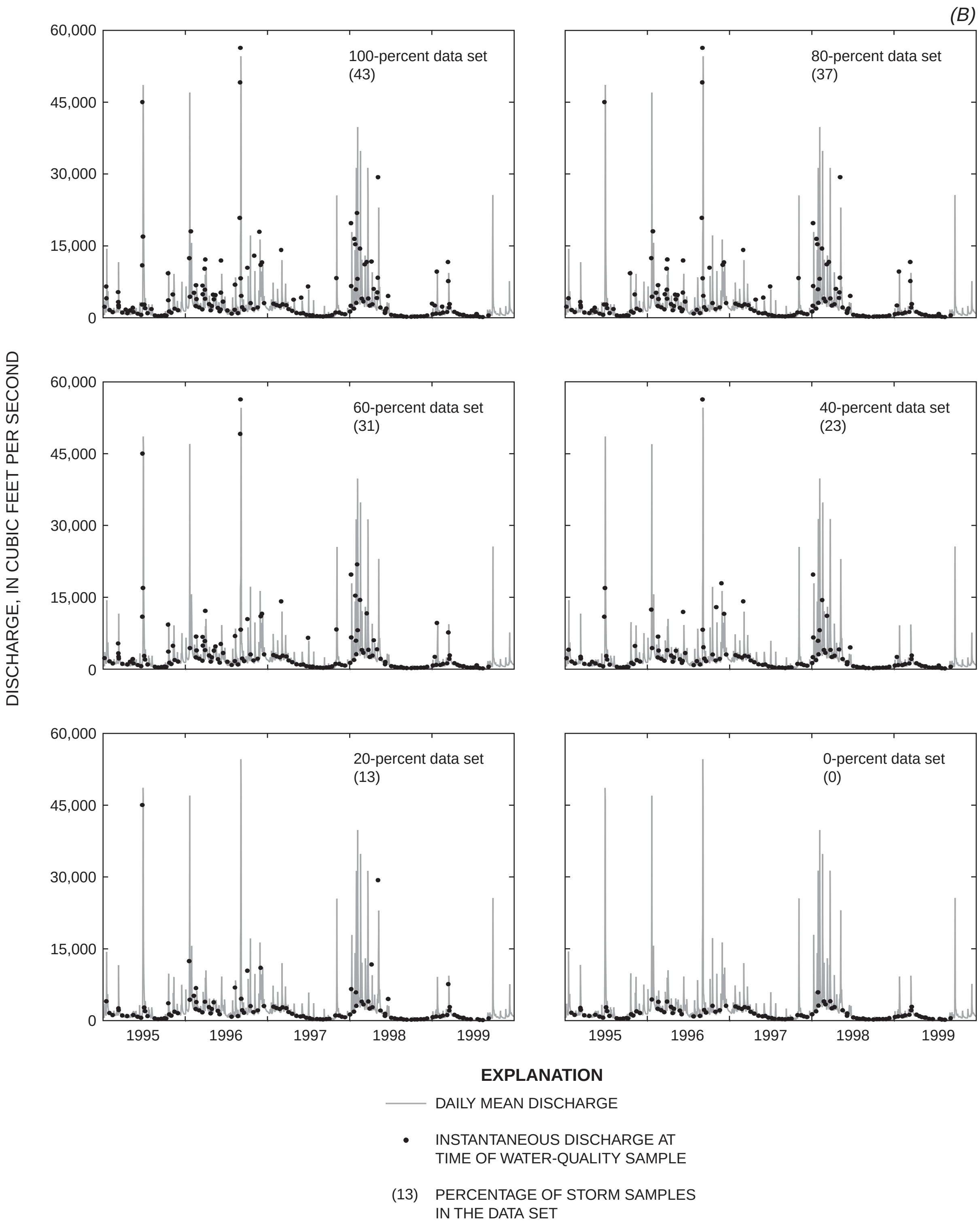



**Figure 4.** Water-quality samples and daily mean discharge at Rappahannock River monitoring station for each storm data set, 1990 through 1995 *(A)* and 1995 through 1999 *(B)*—Continued.

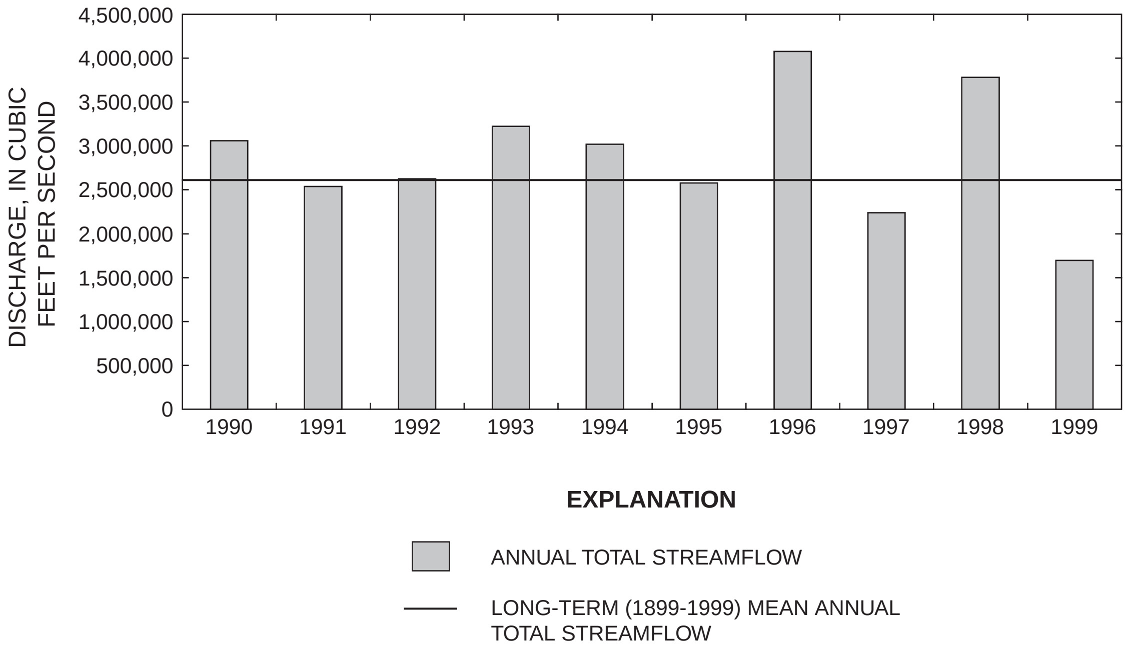



**Figure 5.** Annual total streamflow at the James River monitoring station, 1990 through 1999.

flows. Additional variability in load estimates among all data sets resulted from the high variability in the laboratory measurement of total suspended solids (Gray and others, 2000). As more storm samples were included beyond the 20-percent data set, load estimates varied less. Load estimates converged with the 80-percent data set, and no substantial reduction in SEPs occurred as more storm samples were added. As a result, data sets with at least 50 percent storm samples (the 80- and 100-percent data sets, fig. 3a) led to the most accurate and precise estimates of total suspended solids loads.

### Total Phosphorus

As with estimates of total suspended solids loads, total phosphorus load estimates varied most during 1996 and least during 1997 and 1999 (fig. 6). The data set without storm samples led to underestimates of loads relative to the data sets with storm samples during all years. During high-flow years, the 20-percent data set led to overestimates of total phosphorus loads relative to the higher percentage data sets; during the low-flow years, these load estimates were closer to those of the higher percentage data sets. As more storms were included beyond the 0- and 20-percent data set, load estimates varied less. The SEPs generally were highest with the 0- and 20-percent data sets (fig. 7), probably as a result of the lack of high-flow, high-concentration values in the input data set. Because load estimates converged with the 40-percent data set, and no substantial decrease in SEPs consistently occurred as more storm samples were included, data sets with at least 33 percent storm samples led to the most accurate and precise estimates of total phosphorus loads (fig. 3a).

### Total Nitrogen

Estimates of total nitrogen loads varied less than those of total phosphorus and total suspended solids loads (fig. 6). Differences in load estimates as more storms were included generally were smaller than those of total suspended solids and total phosphorus loads, likely because less of the total nitrogen loading occurs in response to storm events. The data set without storm samples led to underestimates of total nitrogen loads relative to the data sets with storm samples owing to the predominance of low-flow, low-concentration values in the data set. The SEPs with the 0-percent data set were as much as twice those of the other storm data sets (fig. 7). Because load estimates converged with the 20-percent data set, and no substantial decrease in SEPs consistently occurred as more storm samples

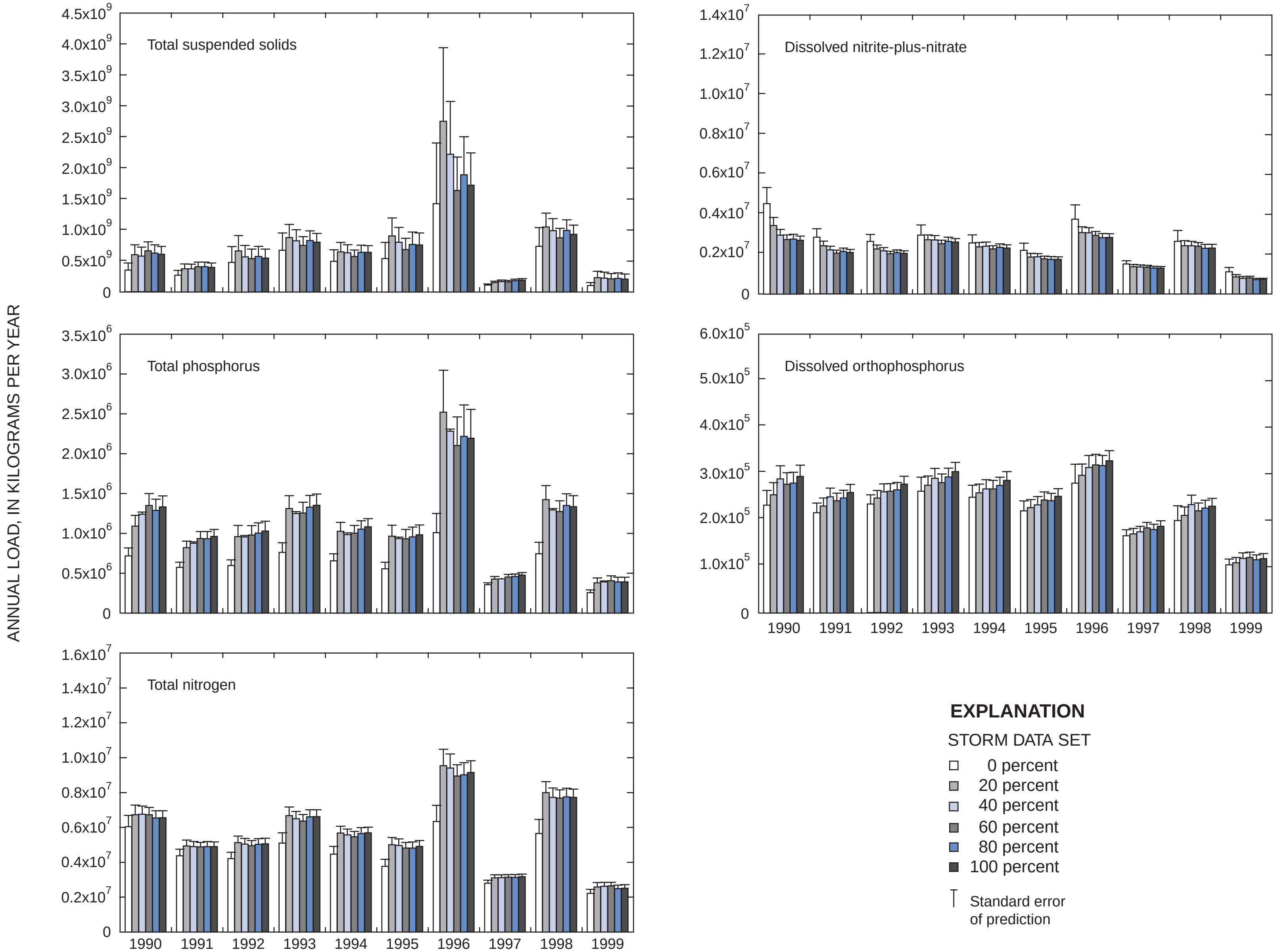



**Figure 6.** Annual loads of selected constituents at the James River monitoring station, 1990 through 1999.

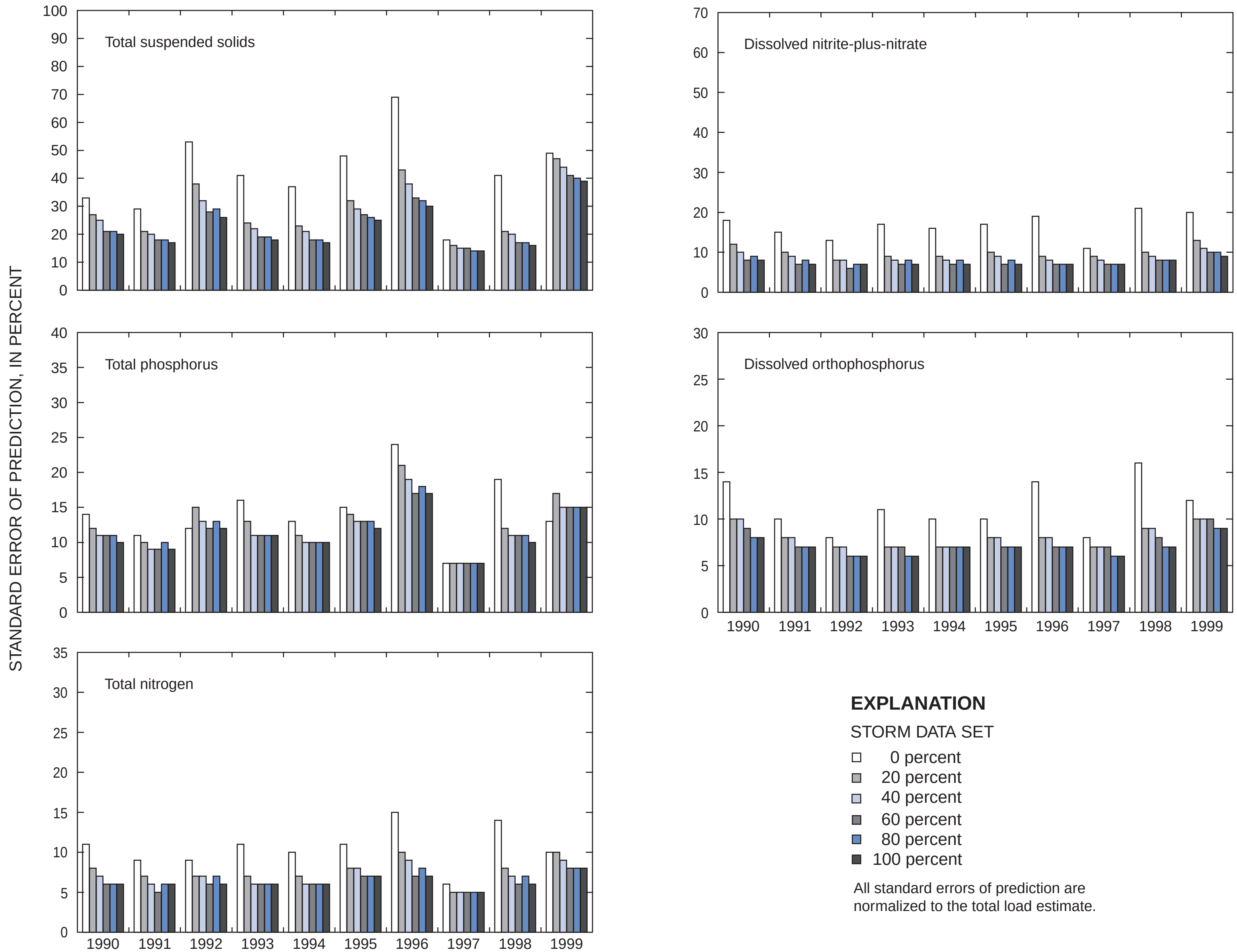



**Figure 7.** Standard error of prediction of selected constituent loads at the James River monitoring station, 1990 through 1999.

were included, data sets with at least 20 percent storm samples led to the most accurate and precise estimates of total nitrogen loads (fig. 3a).

### Dissolved Nitrite-plus-Nitrate

Dissolved nitrite-plus-nitrate load estimates varied the least of all the constituents considered as more storms were included (fig. 6). The data set without storm samples led to overestimates of these loads relative to the data sets with storm samples, but the relative magnitude of the difference was much smaller than with total suspended solids, total phosphorus, or total nitrogen. The SEPs with the 0-percent data set were nearly twice those with other storm data sets (fig. 7). This may be a result of the substantial groundwater input of nitrate to the James River; from 1985 to 1998 at the monitoring station, an average of 21 percent of the total nitrogen load in the river came from ground-water inputs of nitrate (Sprague and others, 2000). The under-representation of lower concentrations arising from dilution effects at high flows may have led to model predictions of higher concentrations at higher flows. Because load estimates converged with the 20-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included, data sets with at least 20 percent storm samples led to the most accurate and precise estimates of dissolved nitrite-plus-nitrate loads (fig. 3a).

### Dissolved Orthophosphorus

The data set without storm samples led to underestimates of dissolved orthophosphorus loads relative to the data sets with storm samples owing to the predominance of low-flow, low-concentration values in the input data set. Additionally, the SEPs with the 0-percent data set were nearly double those with the higher percentage data sets (fig. 7). No substantial decrease in SEPs consistently occurred beyond the 20-percent data set. Load estimates for dissolved orthophosphorus converged with the 40-percent data set, but continued to increase as the number of storm samples increased. This increase could be due in part to the desorption of orthophosphorus from particulate material that reaches the stream during storm events (Heathwaite and others, 2000). Because load estimates converged with the 40-percent data set, data sets with at least 33 percent storm samples led to the most accurate and precise estimates of dissolved orthophosphorus loads (fig. 3a).

These results show that data sets having little or no storm data resulted in variable and less precise load estimates for the constituents associated with particulate material, total suspended solids and total phosphorus, particularly in high-flow years when surface runoff of particulate material increased. In contrast, data sets with a small number of storm samples provided relatively accurate and precise load estimates of the dissolved constituents orthophosphorus and nitrite-plus-nitrate. The percentage of total samples as storm samples required for accurate and precise load estimation for the 10-year period in the James River ranged from 50 percent for total suspended solids to 20 percent for dissolved nitrite-plus-nitrate.

## Five-Year Loads

Annual loads for the 5-year period from 1995 through 1999 were estimated (fig. 8) and compared to those for the 10-year time period to determine whether the amount of storm sampling necessary for accurate and precise load estimation differed on the basis of the length of the data set.

### Total Suspended Solids

As with the 10-year load estimates, the data set without storm samples led to underestimates of total suspended solids loads relative to the data sets with storm samples in the 5-year period (fig. 8). The difference between the 0-percent data set and the higher percentage data sets was greatest in 1996, the year with the highest total flow. The SEPs for the 0-percent data set were as much as three times as high as those of the higher percentage data sets, with the largest difference occurring in 1996 (fig. 9). The relatively poor predictions with the lower percentage data sets were likely a result of the lack of high concentration values in the input data set and the variability associated with the laboratory measurement of total suspended solids. Because load estimates converged with the 60-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included, data sets with at least 42 storm samples led to the most accurate and precise estimates of total suspended solids loads (fig. 3b).

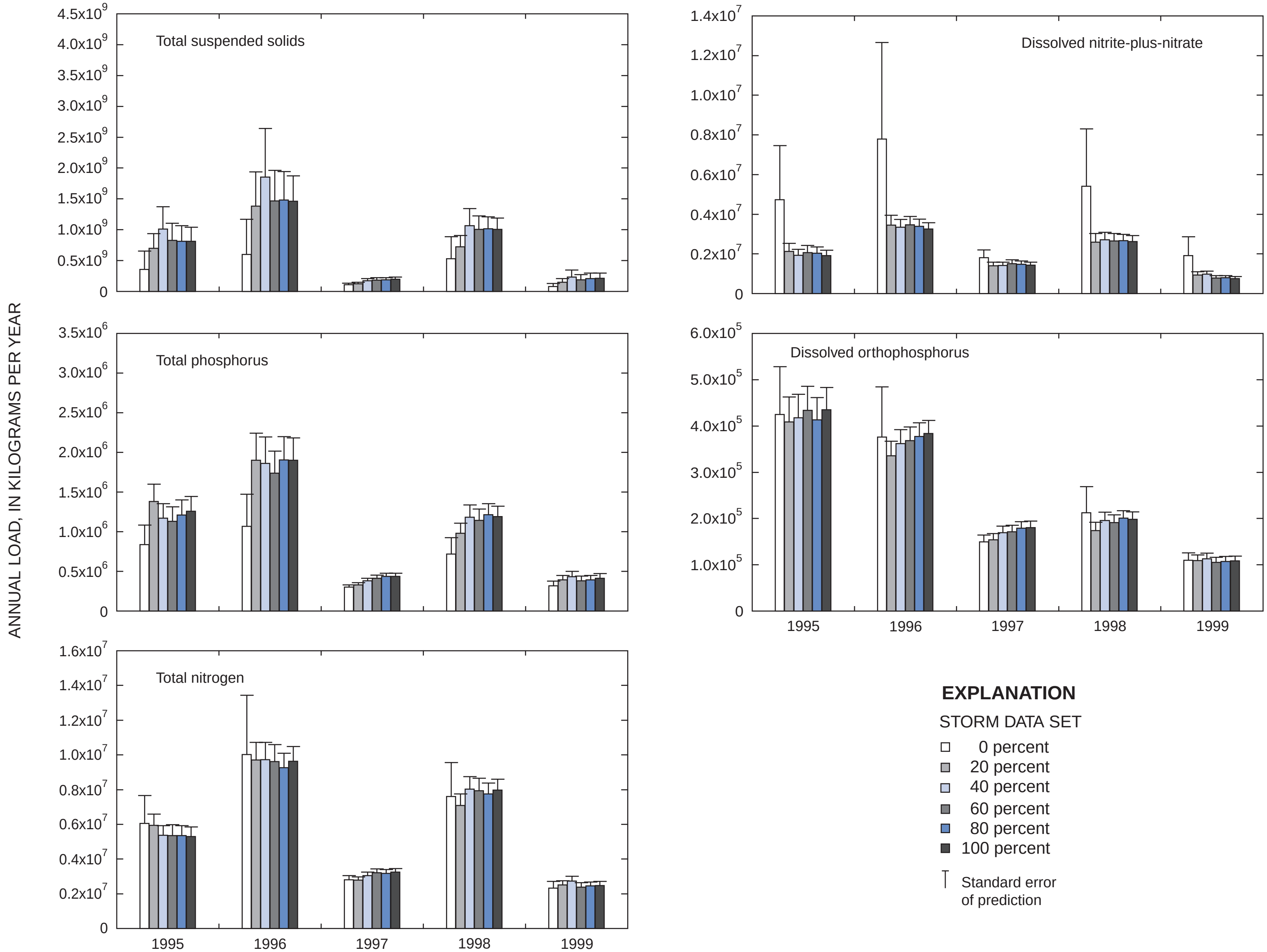



**Figure 8.** Annual loads of selected constituents at the James River monitoring station, 1995 through 1999.

During the 10-year period, more storm samples were necessary for the convergence of total suspended solids load estimates, but SEPs were lower across all storm data sets. Additionally, the magnitudes of total suspended solids load estimates in the 5-year period were generally lower than those in the same years during the 10-year period. Differences in magnitudes were greatest in 1996, the highest flow year, and were smallest in 1997 and 1999, the lowest flow years. Increasing the number of storm events beyond the 60-percent data set in the 5-year time period did not appear to close the gap in magnitude between the 5- and 10-year load estimates.

### Total Phosphorus

As in the 10-year period, the data set without storm samples led to underestimates of the total phosphorus loads relative to the data sets with storm samples in the 5-year period (fig. 8). The greatest difference in load estimation between the 0-percent data set and the higher percentage data sets occurred in 1996. The SEPs for the 0-percent data set were more than twice those for the higher percentage data sets in some years; the difference was largest in 1996 (fig. 9). As in the longer time period, the poor predictions with the 0-percent data set probably resulted from the lack of high concentration values in the input data set. Because load estimates for total phosphorus converged with the 40-percent data set in the 5-year period as they did in the 10-year period, and no substantial decrease in SEPs consistently occurred as more storm samples were included, data sets with at least 33 percent storm samples led to the most accurate and precise estimates of total phosphorus loads (fig. 3b).

The magnitudes of the total phosphorus load estimates in the 5-year period were generally lower than those in the same years during the 10-year period for all storm data sets, particularly in 1996. In addition, the SEPs in the 5-year period were slightly higher than those in the 10-year period, particularly with the 0-percent data set. Increasing the percentage of storm samples beyond the 40-percent data set in the 5-year time period did not close the gap in magnitudes between the 5- and 10-year load estimates.

### Total Nitrogen

The data set without storm samples resulted in load estimates of total nitrogen that were closer in magnitude to those for the data sets with storm samples in the 5-year period than in the 10-year period under all flow conditions (fig. 8). The SEPs for the 0-percent data set, however, were as much as three times as high as those for the other storm data sets in the 5-year period (fig. 9). Because load estimates for total nitrogen in the 5-year period converged with the 40-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included, data sets with at least 33 percent storm samples led to the most accurate and precise estimates of total nitrogen loads (fig. 3b).

Despite the slightly greater variability in load estimates for the 10-year period, these estimates converged with fewer storm samples and SEPs were lower across all storm data sets relative to the 5-year period. The magnitudes of the total nitrogen load estimates in the 5-year period were generally close to those in the same years during the 10-year period for all storm data sets, though they were slightly lower during high-flow years.

### Dissolved Nitrite-plus-Nitrate

The data set without storm samples led to much greater overestimates of dissolved nitrite-plus-nitrate loads relative to data sets with storm samples in the 5-year period than in the 10-year period (fig. 8). The SEPs for the 0-percent data set in the 5-year period were as much as six times as high as those for the higher percentage data sets (fig. 9). This may be a result of the lack of high-flow, low-concentration data in the input data set. As in the 10-year period, load estimates in the 5-year period converged with the 20-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included (fig. 9). Therefore, data sets with at least 19 percent storm samples led to the most accurate and precise estimates of dissolved nitrite-plus-nitrate loads (fig. 3b). With the exception of the 0-percent data set, the magnitudes of the load estimates in the 5- and 10-year periods were similar for all storm data sets. Of the five constituents considered, dissolved nitrite-plus-nitrate loads were the most similar between the two time periods under all hydrologic conditions.

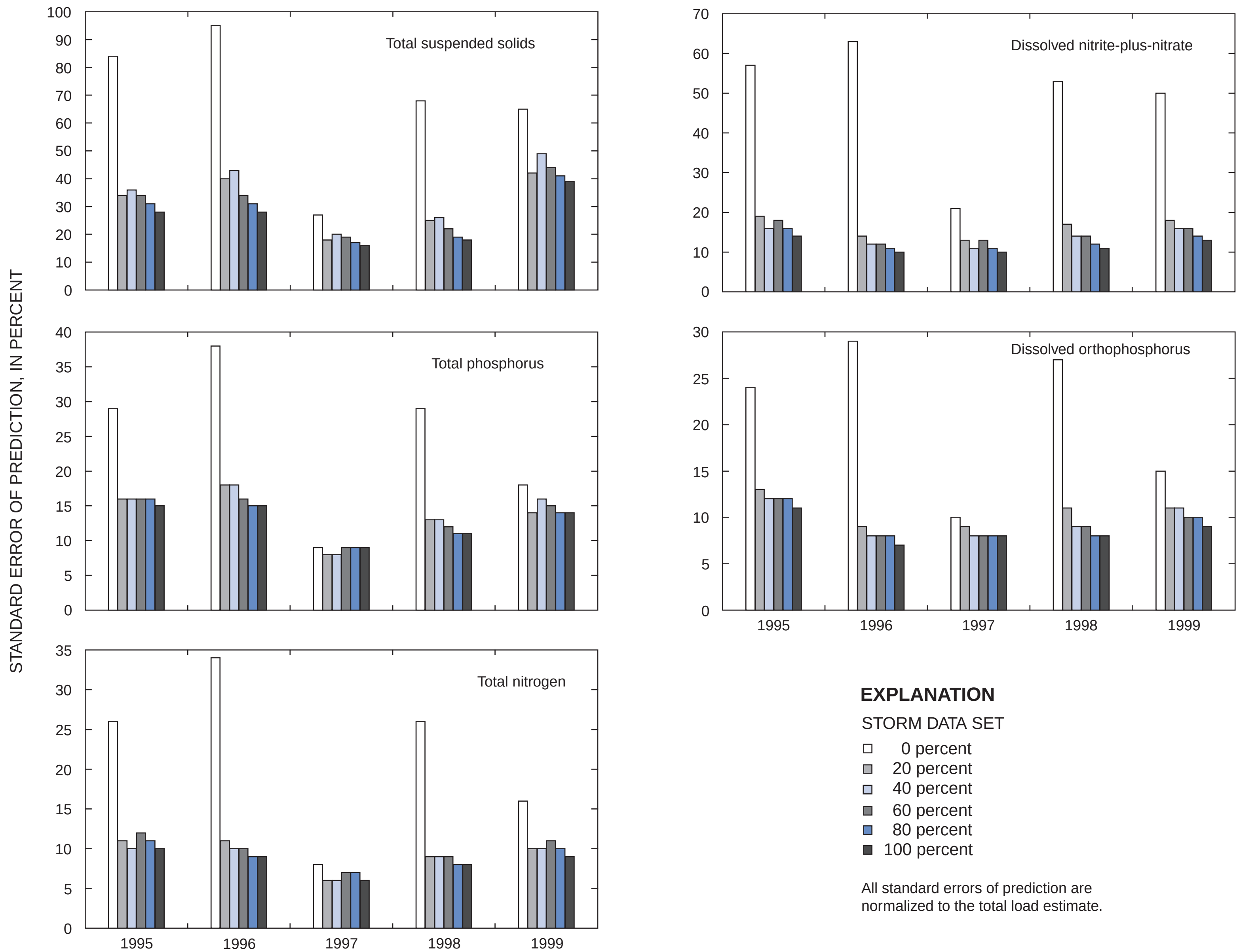



**Figure 9.** Standard error of prediction of selected constituent loads at the James River monitoring station, 1995 through 1999.

### Dissolved Orthophosphorus

The data set without storm samples appeared to result in load estimates of dissolved orthophosphorus that were closer in magnitude to those for the data sets with storm samples in the 5-year period than in the 10-year period (fig. 8). The SEPs for the 0-percent data set, however, were as much as four times as high as those for the higher percentage data sets in the 5-year period, whereas in the 10-year period, the SEPs for the 0-percent data set were only as much as twice as high (figs. 7 and 9). Because load estimates for dissolved orthophosphorus converged with the 0-percent data set in the 5-year period, and no substantial decrease in the SEPs consistently occurred beyond the 20-percent data set, data sets with at least 19 percent storm samples led to the most accurate and precise estimates of dissolved orthophosphorus loads (fig. 3b). Even with the convergence, the magnitudes of the load estimates in the 5-year period differed from those in the same years during the 10-year period, though they were not consistently lower or higher.

## Comparison of Ten-Year and Five-Year Loads

These results indicate that load estimates for the constituents associated with particulate material in the 5-year period were generally lower than those in the same years in the 10-year period for all storm data sets. Differences in magnitude were greatest in 1996, the highest flow year, and were smallest in 1997 and 1999, the lowest flow years. In addition, the SEPs in the 5-year period were higher than those in the same years in the 10-year period, particularly with the 0-percent data sets and in the higher flow years. Thus, loads of particulate constituents were estimated more accurately and precisely in the longer time period, when a greater number of moderate-flow samples was included in the data set (figs. 3a, b).

In contrast, load estimates for the dissolved constituents in the 5-year period generally were closer to those in the same years in the 10-year period for all storm data sets, regardless of the annual flow conditions. This result indicates that the model better predicted loads of dissolved constituents than particulate-associated constituents during the shorter period. The inclusion of a greater number of high- and moderate-flow samples in the overall 10-year data set was not as important with the dissolved constituents, as much of their loading occurs during lower flow conditions. Consequently, 5 years of data led to load estimates that were similar in magnitude to those obtained from 10 years of data, though they were less precise in the shorter period.

The percentage of total samples as storm samples required for convergence of the load estimates in the 10-year period in the James River ranged from 50 percent for total suspended solids to 20 percent for dissolved nitrite-plus-nitrate. In the 5-year period, the range was from 42 percent for total suspended solids to 19 percent for dissolved nitrite-plus-nitrate and dissolved orthophosphorus. Though fewer storm samples were necessary for accurate load estimates during the shorter time period, these estimates were less precise for all constituents, regardless of the number of storm samples included.

# RAPPAHANNOCK RIVER LOAD ESTIMATES

The 1,600-$mi^2$ area that drains to the Rappahannock River monitoring station is approximately one-fourth the size of the area that drains to the James River monitoring station. The smaller basin size, in addition to the greater relief and smaller percentage of forested area, causes the Rappahannock River to respond more rapidly to storm events than the James River. The annual total streamflow from 1990 through 1999, along with the long-term mean annual total for the period of record (1907-1999), is shown in figure 10. Streamflow in 1993, 1994, 1996, and 1998 was above the long-term mean—the highest annual total flow in the monitoring period occurred in 1996. Streamflow in 1991, 1997, and 1999 was below the long-term mean—the lowest annual total flow in the monitoring period occurred in 1999.

## Ten-Year Loads

Annual loads for the 10-year period from 1990 through 1999 were estimated for total suspended solids, total phosphorus, total nitrogen, dissolved nitrite-plus-nitrate, and dissolved orthophosphorus with all storm data sets for the Rappahannock River monitoring station (fig. 11). These load estimates were compared to the 10-year load estimates for the James River Basin

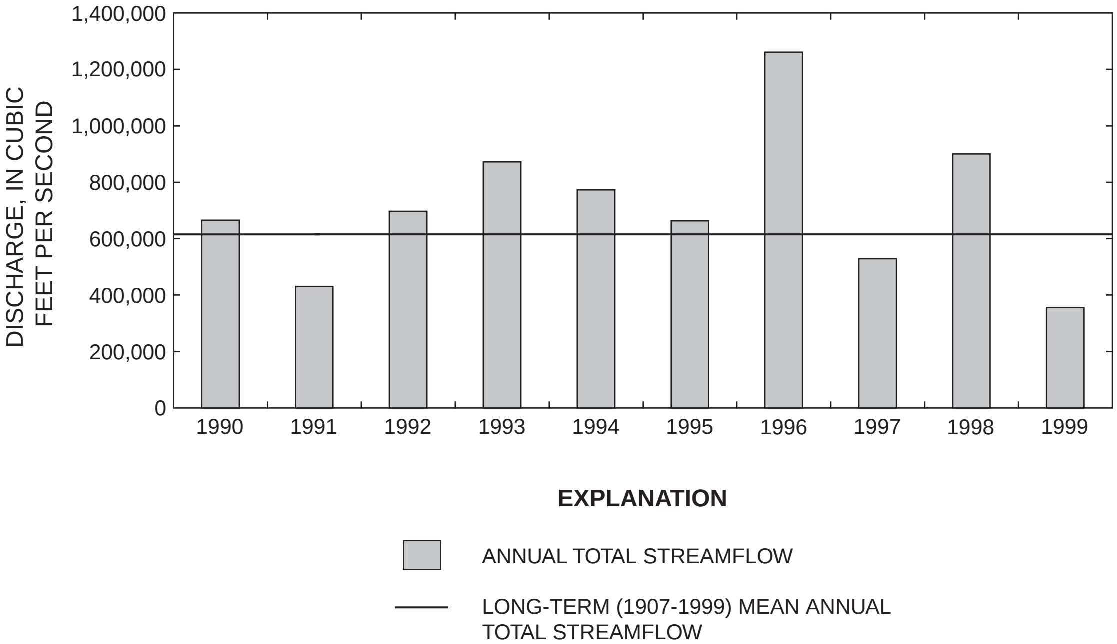



**Figure 10.** Annual total streamflow at the Rappahannock River monitoring station, 1990 through 1999.

to assess the effects of storm-sampling frequency on load estimation in basins with different drainage areas and basin characteristics.

### Total Suspended Solids

Load estimates for total suspended solids were highly variable (fig. 11). The quick response of the Rappahannock River makes it difficult to collect a storm sample that represents the daily mean concentration used in the model. In addition to the environmental variability, there is high variability in the laboratory measurement of total suspended solids (Gray and others, 2000). The regression model diagnostics indicate that the model for total suspended solids did not adhere to the underlying assumptions and therefore was not valid for the 0-, 20-, 40-, and 60-percent data sets—plots of residuals against the predicted values indicated heteroscedasticity and probability plots of the residuals were not normally distributed. The homoscedasticity and normality assumptions were met with the 80- and 100-percent data sets, but the SEPs were still high (fig. 12). Because only the 80- and 100-percent data sets adhered to the model assumptions, data sets with at least 37 percent storm samples (fig. 4a) were required to estimate total suspended solids loads in the Rappahannock River, though even these estimates had large prediction errors.

### Total Phosphorus

The 0- and 20-percent data sets underestimated total phosphorus loads relative to the higher percentage data sets, particularly during high-flow years (fig. 11). The relatively poor predictions were likely a result of the under-representation of high-flow, high-concentration values in the input data set. The SEPs were variable among all storm data sets, and the model fit was not consistently better as more storm samples were included (fig. 12). This may be a consequence of the difficulty of collecting storm samples representing the daily mean concentration. Because load estimates converged with the 60-percent data set, and the SEPs did not consistently decrease with the inclusion of more storm samples, data sets with at least 31 percent storm samples led to the most accurate and precise estimates of total phosphorus loads (fig. 4a).

### Total Nitrogen

Estimates of total nitrogen loads varied less across storm data sets than those of total phosphorus and total suspended solids loads (fig. 11), likely because less of the total nitrogen loading occurs in response to storm events. During high-flow years, the 0-percent data set just slightly overestimated total nitrogen loads relative to the higher percentage data sets; during the low-flow years, load estimates were

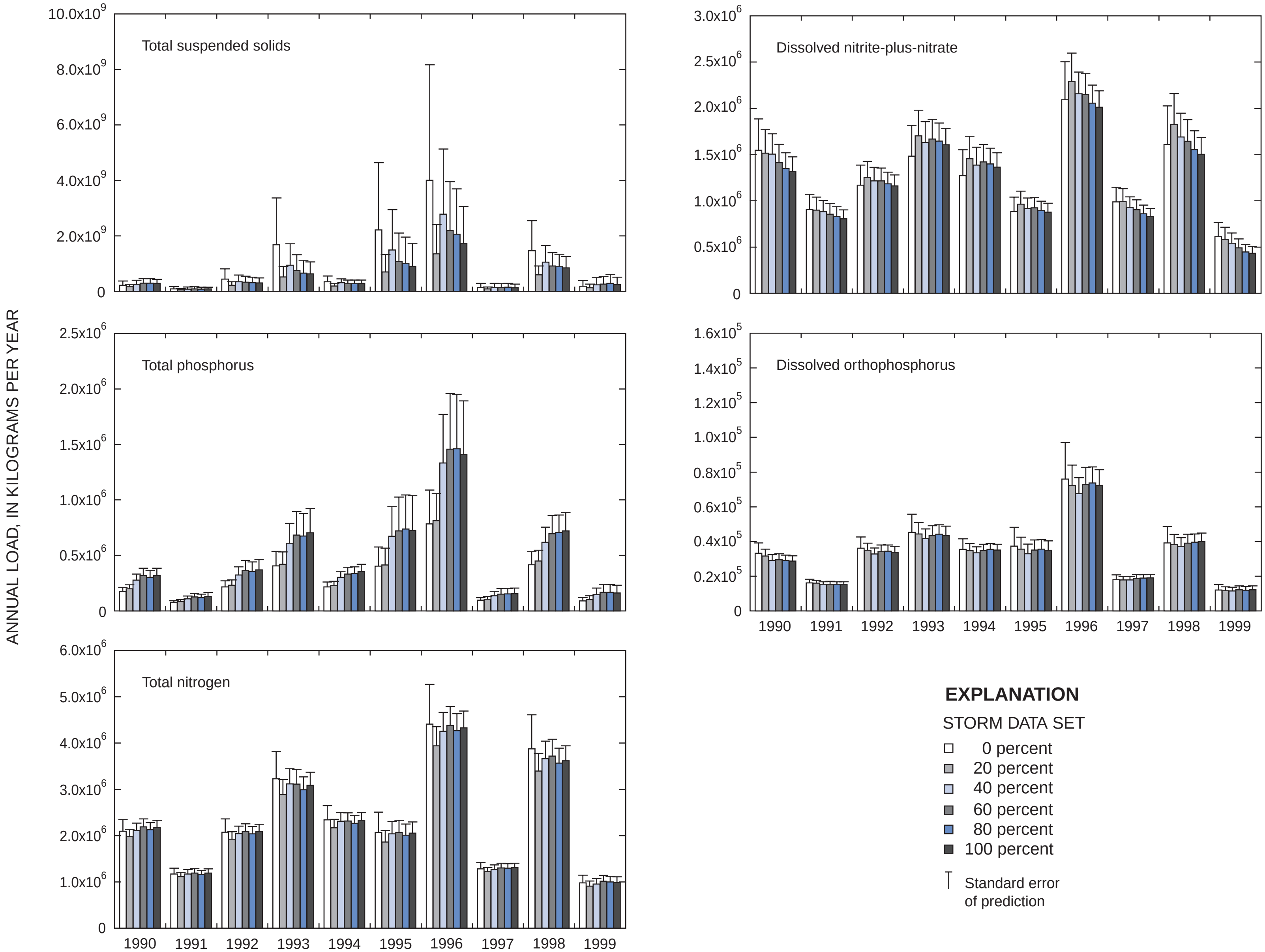



**Figure 11.** Annual loads of selected constituents at the Rappahannock River monitoring station, 1990 through 1999.

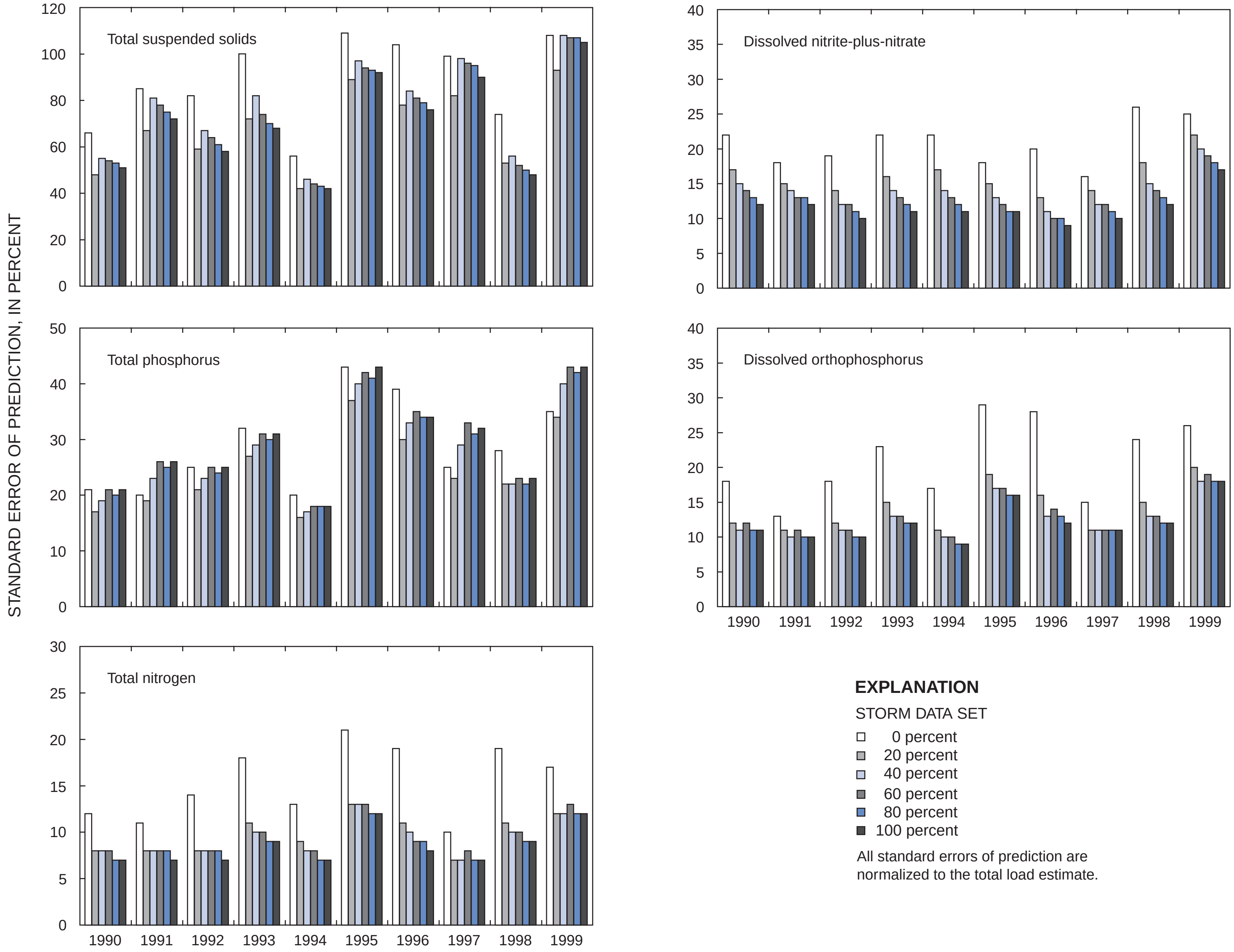



**Figure 12.** Standard error of prediction of selected constituent loads at the Rappahannock River monitoring station, 1990 through 1999.

closer to those of the higher percentage data sets. The SEPs were as much as twice as high with the 0-percent data set as with any other storm data set (fig. 12). Because load estimates converged with the 40-percent data set, and no substantial decrease in SEPs consistently occurred as more storm samples were included, data sets with at least 23 percent storm samples led to the most accurate and precise estimates of total nitrogen loads (fig. 4a).

### Dissolved Nitrite-plus-Nitrate

The 0-percent data set did not lead consistently to under- or overestimates of dissolved nitrite-plus-nitrate loads relative to the higher percentage data sets (fig. 11), though the SEPs were always higher (fig. 12). The inclusion of more high-flow, low-concentration values led to continually decreasing load estimates as more storms were included in the data set. This decrease was greater than in the James River, in part because ground-water inputs of nitrate are higher (26 percent) at the Rappahannock River monitoring station (Sprague and others, 2000). Despite the continuing decrease, load estimates converged with the 20-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included. Therefore, data sets with at least 13 percent storm samples led to the most accurate and precise estimates of dissolved nitrite-plus-nitrate loads (fig. 4a).

### Dissolved Orthophosphorus

Estimates of dissolved orthophosphorus loads varied the least of all the constituents considered among storm data sets in the Rappahannock River (fig. 11). The data set without storm samples led to load estimates that were similar to those for the data sets with storm samples, though the SEPs were as much as twice as high (fig. 12). No substantial decrease in SEPs occurred for data sets containing more storm samples than the 20-percent data set. Load estimates for dissolved orthophosphorus converged with the 0-percent data set, but because the SEPs were much higher with the 0-percent data set, more precise load estimates were obtained with the 20-percent and higher data sets. Therefore, data sets with at least 13 percent storm samples led to the most accurate and precise estimates of dissolved orthophosphorus loads (fig. 4a).

These results show that data sets with little or no storm data resulted in variable and less precise load estimates for the constituents associated with particulate material than for the dissolved constituents in the Rappahannock River, particularly in high-flow years. In contrast, data sets with a relatively small number of storm samples provided more precise load estimates of the dissolved constituents orthophosphorus and nitrite-plus-nitrate. The percentage of total samples as storm samples required for reasonably accurate and precise load estimation for the 10-year period in the Rappahannock River ranged from 37 percent for total suspended solids to 13 percent for dissolved nitrite-plus-nitrate and dissolved orthophosphorus.

In general, fewer storm samples were necessary for accurate load estimation in the Rappahannock River than in the James River, but the estimates were less precise than those in the James River for all storm data sets. More storm samples were required just to meet the model assumptions for total suspended solids, in large part because the stream response in the Rappahannock River Basin is quicker and more variable than in the James River Basin. The quicker and more variable streams response also led to less precise load estimates, regardless of how many storm samples were included. Additionally, the difference in load estimates as more storms were included was slightly greater in the Rappahannock River, indicating that the influence of storm-sampling frequency on load estimation was greater in this smaller and flashier basin.

## Five-Year Loads

Annual loads for the 5-year period from 1995 through 1999 were estimated for a range of particulate and dissolved constituents with all Rappahannock River storm data sets (fig. 13). The 5-year load estimates were compared to those for the 10-year period to determine whether the amount of storm sampling necessary for accurate and precise load estimation in this basin differed on the basis of the length of the data set. These load estimates also were compared to the 5-year load estimates for the James River to assess the effects of storm-sampling frequency on load estimation for a shorter time period in basins with different drainage areas and basin characteristics.

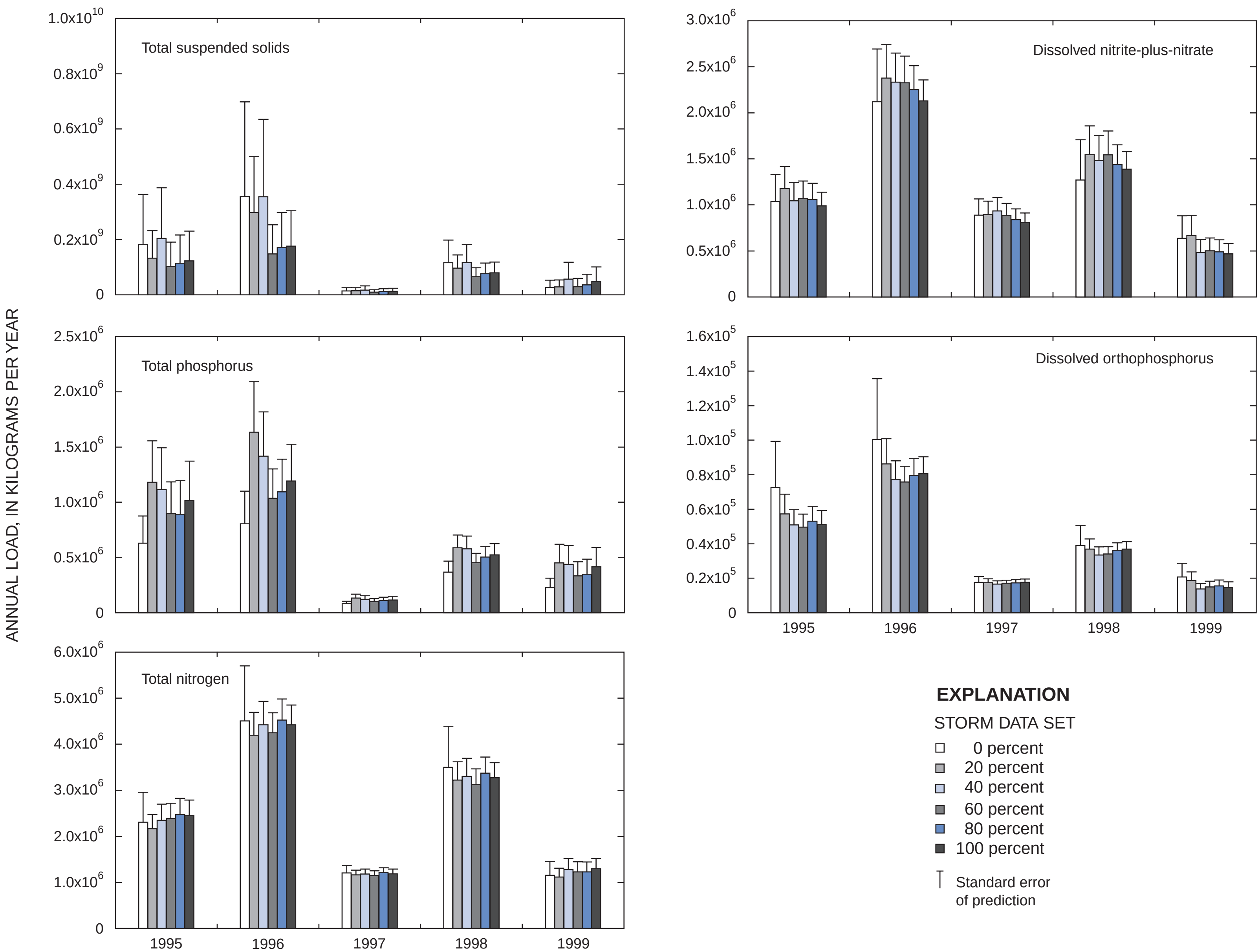



**Figure 13.** Annual loads of selected constituents at the Rappahannock River monitoring station, 1995 through 1999.

### Total Suspended Solids

Load estimates for total suspended solids were highly variable (fig. 13). The model diagnostics indicate that, as with the 10-year model, the 5-year model for total suspended solids did not adhere to the assumptions of normality and homoscedasticity of the residuals for the 0-, 20-, 40-, and 60-percent data sets. The assumptions were met with the 80- and 100-percent data sets, but the SEPs were still very high (fig. 14). Because load estimates converged with the 80-percent data, and no substantial decrease in SEPs occurred as more storm samples were included, data sets with at least 37 percent storm samples led to the most accurate and precise estimates of total suspended solids loads (fig. 4b). It is difficult to compare the magnitudes of the estimates between the 5- and 10-year data sets because load estimates were poor for both time periods, even with 100 percent of the storm samples included.

### Total Phosphorus

As in the 10-year period, the 0-percent data set in the 5-year period led to underestimates of total phosphorus loads relative to higher percentage data sets, particularly during high-flow years (fig. 13). The estimates with the other storm data sets in the 5-year period, unlike those in the 10-year period, were variable and did not converge. The SEPs for the 5-year period did not decrease consistently as more storms were included, indicating that even with 100 percent of the storm samples included, the number of high-flow samples was insufficient to produce a good model fit (fig. 14). In contrast, load estimates converged at a reasonable value in the 10-year period. The behavior of total phosphorus in this basin is therefore better characterized in the longer time period, for which a greater number of moderate-flow samples is included in the data set.

### Total Nitrogen

Estimates of total nitrogen loads with the 0-percent data set were similar in magnitude to those with the higher percentage data sets (fig. 13); however, SEPs were as much as twice as high with the 0-percent data set (fig. 14). Because estimates of total nitrogen loads in the 5-year period converged with the 20-percent data set, and no substantial decrease in SEPs occurred as more storm samples were included, data sets with at least 13 percent storm samples led to the most accurate and precise estimates of total nitrogen loads (fig. 4b). The magnitudes of the total nitrogen load estimates in the 5-year period were generally similar to those in the same years during the 10-year period for all storm data sets, though SEPs were higher.

### Dissolved Nitrite-plus-Nitrate

The 0-percent data set led to estimates of dissolved nitrite-plus-nitrate loads that were not consistently under- or overestimated relative to the higher percentage data sets (fig. 13). The SEPs were always higher, particularly during high-flow years (fig. 14). Load estimates in the 5-year period were similar to those in the 10-year period and converged with the 20-percent data set; no substantial decrease in SEPs occurred as more storm samples were included. Therefore, data sets with at least 13 percent storm samples led to the most accurate and precise estimates of dissolved nitrite-plus-nitrate loads (fig. 4b). The magnitudes of the load estimates in the 5- and 10-year periods were similar for all storm data sets, though there were slight differences in high-flow years.

### Dissolved Orthophosphorus

The load estimates for dissolved orthophosphorus were slightly more variable among storm data sets for the 5-year period than among those for the 10-year period (fig. 13). For the 5-year period, the 0-percent data set slightly overestimated loads of dissolved orthophosphorus relative to those for the higher percentage data sets, and the SEPs were nearly three times as high during some years (fig. 14). Because load estimates for dissolved orthophosphorus converged with the 40-percent data set in the 5-year period, and no substantial decrease in the SEPs consistently occurred as more storms were included, data sets with at least 23 percent storm samples led to the most accurate and precise estimates of dissolved orthophosphorus loads (fig. 4b). After the load estimates converged, their magnitudes in the 5-year period were similar to those in the same years in the 10-year period.

## Comparison of Ten-Year and Five-Year Loads

These results indicate that the length of the data set had a greater effect on the load estimation of particulate constituents than dissolved constituents in the

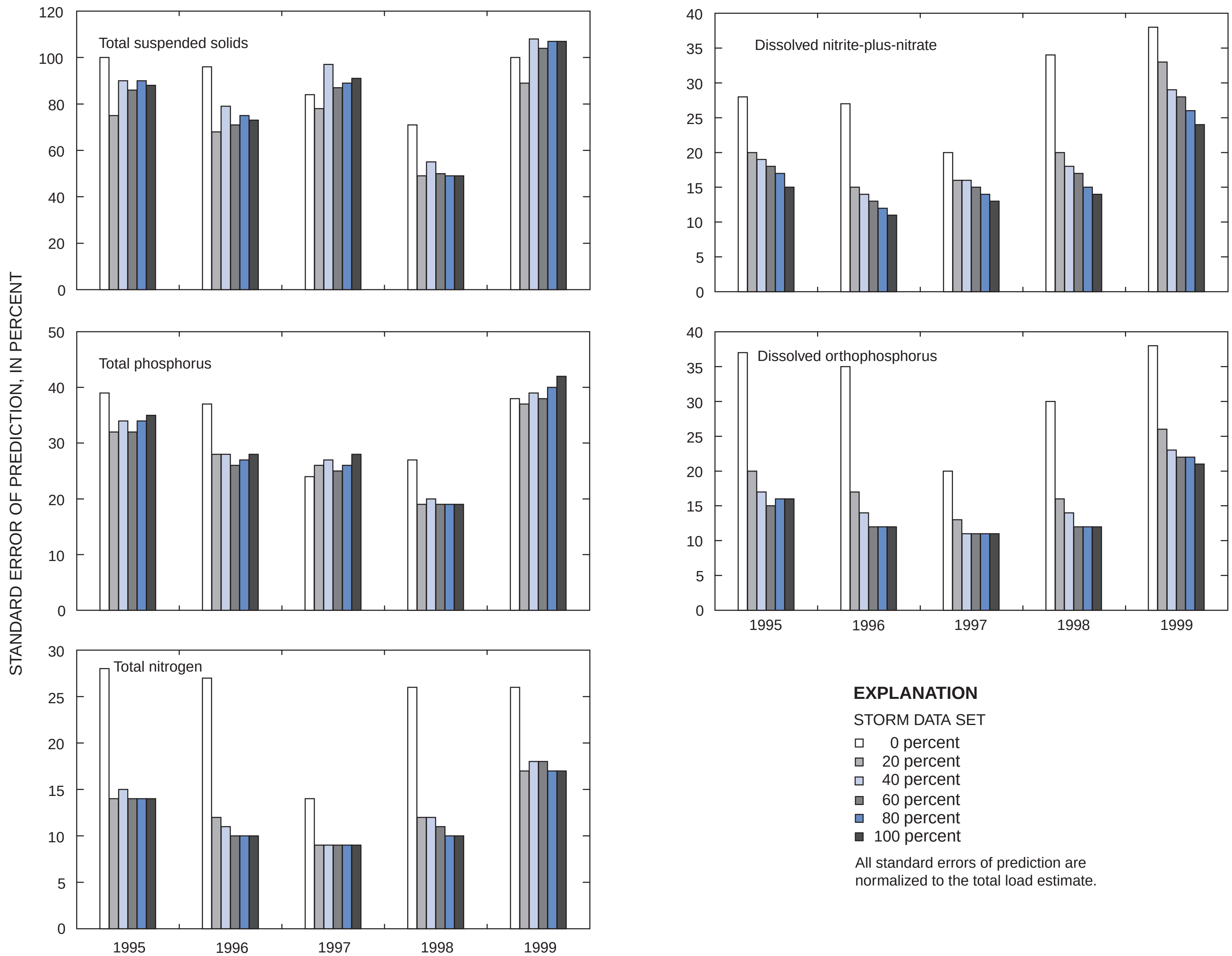



**Figure 14.** Standard error of prediction of selected constituent loads at the Rappahannock River monitoring station, 1995 through 1999.

Rappahannock River. Loads of particulate constituents were estimated more precisely with data from the longer time period when a greater number of moderate-flow samples was included in the data set (fig. 3). Both total phosphorus and total suspended solids loads were poorly estimated for the 5-year period, but total phosphorus loads were estimated reasonably well for the 10-year period. The SEPs for the 5-year period were higher than those in the same years for the 10-year period, particularly with the 0-percent data sets and in the higher flow years. In contrast, dissolved constituent loads in the Rappahannock River were estimated reasonably well with data sets that included a small number of storm samples during both the 10- and 5-year periods, though the SEPs were higher during the shorter period. The percentage of storm samples required for reasonably accurate and precise load estimation during a 5-year period in the Rappahannock River ranged from 37 percent for total suspended solids to 13 percent for total nitrogen and dissolved nitrite-plus-nitrate. Reasonable load estimates for total phosphorus could not be obtained even with the inclusion of 100 percent of the storm samples collected in this study.

For the 5-year period in the James River, whereas estimates of some constituent loads converged with a higher percentage of storm samples, all estimates had lower SEPs than in the Rappahannock River. In addition, as observed for the 10-year period, the difference in load estimates as more storm samples were included was slightly greater in the Rappahannock River, indicating that the influence of storm events on load estimation is greater in the Rappahannock River Basin for both time periods. The James River responds more slowly and consistently to storm events than does the Rappahannock River. As a result, loads in this basin can be estimated with greater accuracy and precision over shorter time periods and often with fewer storm samples.

Several changes in load estimates as more storm samples were included could not be explained. The method of storm data set construction used in this study may have led to results that were particularly sensitive to the nature of the single, random subset of data, and differences in load estimates may have resulted in part from differences between the individual distribution of sample populations in each storm data set. More detailed analyses for some constituents, perhaps by use of Monte Carlo simulations, would provide additional insight into the differences in load estimates as storm-sampling frequency increases.

Additionally, both of the basins examined in this study are relatively large, and the conclusions drawn in this study likely do not apply to smaller basins. In smaller basins, the response of streamflow and in-stream concentration values to storm events would be quicker than in either the James or the Rappahannock River Basins. Storm sampling in smaller basins can lead to positively biased and less precise load estimates because measured concentrations during storm events are often higher than the daily mean concentrations employed in the regression model (Robertson and Roerish, 1999).

## TREND ESTIMATES

Trends in flow-adjusted concentrations of total suspended solids, total phosphorus, total nitrogen, dissolved nitrite-plus-nitrate, and dissolved orthophosphorus were estimated with storm data sets covering both time periods at the James River and Rappahannock River RIM stations. The 5-year trend estimates were compared to those from the 10-year period to determine whether the amount of storm sampling necessary for reasonable trend estimates differed on the basis of the length of the data set. The James River trend estimates also were compared to the Rappahannock River trend estimates to assess the effects of storm-sampling frequency in basins with different sizes and characteristics.

For the 10-year period in the James River, the estimates of flow-adjusted concentration trends (eq. 2) were similar in magnitude and significance with all storm data sets for all constituents except total suspended solids (table 2). The 95-percent confidence intervals for the trend magnitudes decreased slightly as more storm samples were included, indicating that the model better estimated the “true” trends with the inclusion of a greater number of storm samples. Trend estimates for total suspended solids were significant with the 60-percent and higher data sets, and magnitudes were similar for the 80- and 100-percent data sets. A Type I error occurred with the 0-percent data set—at a significance level of 0.05, the null hypothesis that the $\beta_3$ coefficient (eq. 1) did not differ from zero was inappropriately rejected. This error was suggested by the acceptance of the null hypothesis with the 20- and 40-

**Table 2.** Trends in flow-adjusted concentrations of selected constituents at the James River monitoring station for each of the storm data sets, 1990 through 1999

[Trends expressed as percent change. The lower and upper magnitudes represent the 95-percent confidence interval of the trend. Trends that were significant with p-value less than or equal to 0.05 are shown in bold type. <, less than]

| Data set | Lower magnitude | Mean magnitude | Upper magnitude | p-value |
|---|---|---|---|---|
| | | **Total suspended solids** | | |
| **100%** | **-43** | **-26** | **-4** | **.0216** |
| **80%** | **-44** | **-26** | **-3** | **.0281** |
| **60%** | **-52** | **-35** | **-12** | **.0037** |
| 40% | -44 | -23 | +6 | .1014 |
| 20% | -48 | -26 | +5 | .0794 |
| **0%** | **-54** | **-34** | **-4** | **.0222** |
| | | **Total phosphorus** | | |
| **100%** | **-55** | **-45** | **-33** | **<.0001** |
| **80%** | **-54** | **-44** | **-31** | **<.0001** |
| **60%** | **-55** | **-45** | **-32** | **<.0001** |
| **40%** | **-53** | **-42** | **-29** | **<.0001** |
| **20%** | **-49** | **-35** | **-18** | **.0003** |
| **0%** | **-51** | **-37** | **-20** | **.0002** |
| | | **Total nitrogen** | | |
| **100%** | **-32** | **-22** | **-11** | **.0003** |
| **80%** | **-33** | **-22** | **-10** | **.0007** |
| **60%** | **-30** | **-19** | **-7** | **.0028** |
| **40%** | **-32** | **-20** | **-7** | **.0038** |
| **20%** | **-34** | **-21** | **-5** | **.0106** |
| **0%** | **-40** | **-26** | **-10** | **.0030** |
| | | **Dissolved nitrite-plus-nitrate** | | |
| **100%** | **-52** | **-43** | **-31** | **<.0001** |
| **80%** | **-55** | **-45** | **-33** | **<.0001** |
| **60%** | **-47** | **-36** | **-22** | **<.0001** |
| **40%** | **-55** | **-43** | **-28** | **<.0001** |
| **20%** | **-60** | **-47** | **-31** | **<.0001** |
| **0%** | **-62** | **-48** | **-28** | **.0001** |
| | | **Dissolved orthophosphorus** | | |
| **100%** | **-53** | **-42** | **-29** | **<.0001** |
| **80%** | **-52** | **-41** | **-27** | **<.0001** |
| **60%** | **-50** | **-38** | **-22** | **<.0001** |
| **40%** | **-55** | **-42** | **-26** | **<.0001** |
| **20%** | **-55** | **-41** | **-24** | **.0001** |
| **0%** | **-57** | **-41** | **-20** | **.0006** |

percent data sets. The results indicate that over a 10-year period at the James River monitoring station, trends in flow-adjusted concentrations can be estimated reasonably well with a small number of storm samples for both dissolved and particulate constituents, with the exception of total suspended solids.

For the 5-year period in the James River, the trend estimates were not significant for total suspended solids or total nitrogen with all storm data sets (table 3). The trend estimates were strongly significant for dissolved orthophosphorus with all storm data sets, though the confidence intervals decreased as more storm samples were added. Owing to the predominance of point-source inputs of dissolved orthophosphorus, much of the decrease likely occurred within the lower flow samples included in all data sets. The downward trends in flow-adjusted concentrations of total phosphorus and dissolved nitrite-plus-nitrate were smaller in magnitude and were significant with only the 60-percent and higher data sets. Trend estimates for these two constituents were similar in significance and magnitude with the 60-, 80-, and 100-percent data sets, but the p-values decreased slightly as more storm samples were included. These results indicate that reasonable trend estimates for the 5-year period in the James River were obtained for both dissolved and particulate constituents with data sets in which at least 42 percent of the samples were storm samples (fig. 3b). More storm samples are required at this monitoring station for trend estimation for the 5-year period than for the 10-year period. Because no significant trends were observed in several of the constituents for the 5-year period, there was no clear evidence that dissolved-constituent trends were better estimated with fewer storm samples than particulate-constituent trends.

More storm samples were necessary for trend estimation in the Rappahannock River than in the James River for the 10-year period. The p-values for trends in dissolved nitrite-plus-nitrate in the Rappahannock River decreased steadily as the number of storm samples increased; the trend estimate was significant only when 100 percent of the storm samples were included (table 4). Trends in dissolved orthophosphorus were significant with the 0-, 20-, and 40-percent data sets, but were not significant with the data sets containing more storm samples. It is possible that the increases in contributions from nonpoint sources at higher flows offset decreases in contributions from point sources and, as a result, a false overall trend in orthophosphorus was detected when the higher flow samples were not included. Trends in total phosphorus were significant and the magnitudes were similar for the 40-percent and higher data sets. Trends in total suspended solids and total nitrogen were not significant with all data sets (with the exception of an apparent Type I error in the total suspended solids trend with the 40-percent data set). There was no clear evidence that trends in dissolved constituents were better estimated with fewer storm samples than trends in constituents associated with particulate material. To predict particulate- and dissolved-constituent trends for the 10-year period in the Rappahannock River, it was necessary to include 100 percent of the possible storm samples in this study, or 42 percent of the samples in the data sets as storm samples (fig. 4a).

For the 5-year period in the Rappahannock River, trends were not significant for any constituents except dissolved orthophosphorus (table 5). Downward trends in flow-adjusted concentrations of dissolved orthophosphorus were large and were detected with all storm data sets. There was no consistent decrease in p-values for the other constituents as more storm samples were included, and it appears that including more storm samples would not lead to better trend estimates. It is likely that the true trends during this period were not significant. Therefore, the amount of storm sampling necessary for reliable trend estimation for both dissolved and particulate constituents in this basin for the 5-year period could not be determined.

## SUMMARY AND CONCLUSIONS

Annual loads and flow-adjusted concentration trends were estimated from water-quality and streamflow data collected from 1990 through 1999 at monitoring stations on two tributaries to the Chesapeake Bay in Virginia—James River at Cartersville, Va., and Rappahannock River near Fredericksburg, Va. The effects of storm-sampling frequency on load and trend estimates in these two basins of different size, relief, and land use were determined by use of input data sets that included 0, 20, 40, 60, 80, and 100 percent of all available storm samples; all available base-flow samples were used in each data set. Loads and trends were estimated for total suspended solids, total phosphorus, total nitrogen, dissolved nitrite-plus-nitrate, and dissolved orthophosphorus in order to determine the effects of storm-sampling frequency on estimation of dissolved and particulate constituent loads and trends.

**Table 3.** Trends in flow-adjusted concentrations of selected constituents at the James River monitoring station for each of the storm data sets, 1995 through 1999

[Trends expressed as percent change. The lower and upper magnitudes represent the 95-percent confidence interval of the trend. Trends that were significant with p-value less than or equal to 0.05 are shown in bold type. <, less than]

| Data set | Lower magnitude | Mean magnitude | Upper magnitude | p-value |
|---|---|---|---|---|
| **Total suspended solids** | | | | |
| 100% | -44 | -13 | +36 | .5341 |
| 80% | -43 | -8 | +49 | .7196 |
| 60% | -51 | -16 | +44 | .5106 |
| 40% | -48 | -8 | +63 | .7597 |
| 20% | -54 | -21 | +37 | .3745 |
| 0% | -59 | -21 | +53 | .4438 |
| **Total phosphorus** | | | | |
| **100%** | **-52** | **-34** | **-9** | **.0103** |
| **80%** | **-54** | **-35** | **-9** | **.0111** |
| **60%** | **-53** | **-32** | **-2** | **.0369** |
| 40% | -43 | -18 | +17 | .2569 |
| **20%** | **-55** | **-37** | **-11** | **.0070** |
| 0% | -50 | -25 | +11 | .1361 |
| **Total nitrogen** | | | | |
| 100% | -31 | -11 | +14 | .3569 |
| 80% | -33 | -13 | +14 | .3043 |
| 60% | -38 | -16 | +13 | .2332 |
| 40% | -22 | +3 | +36 | .8038 |
| 20% | -36 | -16 | +9 | .1792 |
| 0% | -44 | -21 | +10 | .1439 |
| **Dissolved nitrite-plus-nitrate** | | | | |
| **100%** | **-58** | **-40** | **-12** | **.0078** |
| **80%** | **-61** | **-41** | **-10** | **.0128** |
| **60%** | **-65** | **-44** | **-9** | **.0163** |
| 40% | -47 | -16 | +32 | .4272 |
| 20% | -57 | -28 | +20 | .1894 |
| 0% | -59 | -21 | +52 | .4594 |
| **Dissolved orthophosphorus** | | | | |
| **100%** | **-81** | **-74** | **-64** | **<.0001** |
| **80%** | **-80** | **-72** | **-61** | **<.0001** |
| **60%** | **-82** | **-74** | **-64** | **<.0001** |
| **40%** | **-79** | **-70** | **-57** | **<.0001** |
| **20%** | **-79** | **-70** | **-55** | **<.0001** |
| **0%** | **-79** | **-68** | **-50** | **<.0001** |

**Table 4.** Trends in flow-adjusted concentrations of selected constituents at the Rappahannock River monitoring station for each of the storm data sets, 1990 through 1999

Trends expressed as percent change. The lower and upper magnitudes represent the 95-percent confidence interval of the trend. Trends that were significant with p-value less than or equal to 0.05 are shown in bold type]

| Data set | Lower magnitude | Mean magnitude | Upper magnitude | p-value |
|---|---|---|---|---|
| **Total suspended solids** | | | | |
| 100% | -42 | -12 | +34 | .5380 |
| 80% | -40 | -7 | +43 | .7220 |
| 60% | -48 | -19 | +28 | .3592 |
| 40% | -47 | -15 | +37 | .4787 |
| 20% | -49 | -19 | +29 | .3593 |
| 0% | -53 | -24 | +22 | .2350 |
| **Total phosphorus** | | | | |
| **100%** | **-45** | **-29** | **-9** | **.0063** |
| **80%** | **-40** | **-23** | **-2** | **.0291** |
| **60%** | **-45** | **-29** | **-8** | **.0081** |
| **40%** | **-44** | **-27** | **-7** | **.0111** |
| 20% | -38 | -21 | +1 | .0528 |
| **0%** | **-37** | **-21** | **0** | **.0445** |
| **Total nitrogen** | | | | |
| 100% | -26 | -13 | +1 | .0605 |
| 80% | -24 | -11 | +4 | .1584 |
| 60% | -26 | -12 | +3 | .1188 |
| 40% | -28 | -14 | +2 | .0746 |
| 20% | -26 | -12 | +5 | .1457 |
| 0% | -26 | -11 | +8 | .2497 |
| **Dissolved nitrite-plus-nitrate** | | | | |
| **100%** | **-44** | **-26** | **-1** | **.0391** |
| 80% | -44 | -25 | +2 | .0667 |
| 60% | -43 | -20 | +11 | .1792 |
| 40% | -43 | -19 | +16 | .2559 |
| 20% | -40 | -11 | +33 | .5759 |
| 0% | -41 | -8 | +44 | .7225 |
| **Dissolved orthophosphorus** | | | | |
| 100% | -32 | -15 | +6 | .1310 |
| 80% | -34 | -18 | +2 | .0661 |
| 60% | -36 | -19 | +4 | .0859 |
| **40%** | **-39** | **-23** | **-1** | **.0382** |
| **20%** | **-45** | **-30** | **-10** | **.0049** |
| **0%** | **-47** | **-31** | **-9** | **.0078** |

**Table 5.** Trends in flow-adjusted concentrations of selected constituents at the Rappahannock River monitoring station for each of the storm data sets, 1995 through 1999

[Trends expressed as percent change. The lower and upper magnitudes represent the 95-percent confidence interval of the trend. Trends that were significant with p-value less than or equal to 0.05 are shown in bold type. <, less than]

| Data set | Lower magnitude | Mean magnitude | Upper magnitude | p-value |
|---|---|---|---|---|
| **Total suspended solids** | | | | |
| 100% | -3 | +90 | +275 | .0561 |
| 80% | -4 | +96 | +302 | .0590 |
| 60% | -32 | +42 | +199 | .3316 |
| **40%** | **-3** | **+106** | **+338** | **.0469** |
| 20% | -17 | +65 | +225 | .1306 |
| 0% | -26 | +39 | +159 | .2933 |
| **Total phosphorus** | | | | |
| 100% | -21 | +12 | +58 | .5188 |
| 80% | -15 | +21 | +72 | .2752 |
| 60% | -28 | +2 | +45 | .8929 |
| 40% | -4 | +36 | +92 | .0793 |
| 20% | -4 | +33 | +83 | .0773 |
| 0% | -13 | +16 | +54 | .3108 |
| **Total nitrogen** | | | | |
| 100% | -11 | +15 | +50 | .2688 |
| 80% | -13 | +15 | +51 | .3117 |
| 60% | -17 | +11 | +48 | .4709 |
| 40% | -7 | +25 | +68 | .1242 |
| 20% | -11 | +18 | +57 | .2462 |
| 0% | -15 | +17 | +63 | .3203 |
| **Dissolved nitrite-plus-nitrate** | | | | |
| 100% | -45 | -11 | +45 | .6316 |
| 80% | -48 | -12 | +50 | .6349 |
| 60% | -50 | -10 | +61 | .7195 |
| 40% | -53 | -11 | +68 | .7085 |
| 20% | -43 | +11 | +117 | .7474 |
| 0% | -44 | +21 | +163 | .6116 |
| **Dissolved orthophosphorus** | | | | |
| **100%** | **-63** | **-49** | **-31** | **<.0001** |
| **80%** | **-63** | **-49** | **-29** | **.0001** |
| **60%** | **-65** | **-50** | **-29** | **.0001** |
| **40%** | **-68** | **-53** | **-33** | **.0001** |
| **20%** | **-60** | **-41** | **-14** | **.0060** |
| **0%** | **-65** | **-47** | **-21** | **.0018** |

Estimates of loads and trends for the 10-year period from 1990 to 1999 were compared to those for the 5-year period from 1995 to 1999 to determine whether the length of the data set had an effect on the frequency of storm sampling required to obtain accurate load and trend estimates.

For the 10-year period in the James River, the percentage of storm samples required for accurate and precise load estimation ranged from 50 percent for total suspended solids to 20 percent for dissolved nitrite-plus-nitrate. For the 5-year period, the percentage of total samples as storm samples required for convergence of the load estimates ranged from 42 percent for total suspended solids to 19 percent for dissolved nitrite-plus-nitrate and dissolved orthophosphorus. The magnitudes of the load estimates in the 5-year period were close to those for the same years in the 10-year period for the dissolved constituents, but were lower for the particulate constituents. Additionally, all estimates in the 5-year period had higher prediction errors than those in the 10-year period. Therefore, the model better predicted loads of dissolved constituents than loads of particulate constituents with fewer storm samples for both time periods in the James River, though all constituent loads were better predicted for the longer time period.

For the 10-year period in the Rappahannock River, the percentage of storm samples required for reasonably accurate and precise load estimation ranged from 37 percent for total suspended solids to 13 percent for dissolved nitrite-plus-nitrate and dissolved orthophosphorus. For the 5-year period, a similar percentage of storm samples provided reasonable estimates of dissolved constituent loads and total suspended solids loads, but the prediction errors were much higher than for the 10-year period. Load estimates for total phosphorus never converged when data from the 5-year period were used, and the prediction errors did not decrease consistently as more storms were included, indicating that even when 100 percent of the available storm samples were included, the number of high-flow values was insufficient to accurately estimate total phosphorus loads during the shorter period. The load estimates for the 5-year period were not consistently higher or lower than those for the same years in the 10-year period for any constituent. As with the James River, all estimates had higher prediction errors for the 5-year period than for the 10-year period. Therefore, the model better predicted loads of dissolved constituents than particulate constituents with fewer storm samples for both periods, though, as observed in the James River, all constituent loads were better predicted in the longer time period.

Loads of dissolved and particulate constituents were estimated with fewer storm samples and were slightly more accurate and precise in the James River than in the Rappahannock River during both periods. The high relief and smaller drainage area of the Rappahannock River Basin cause quicker and more variable stream response than in the James River Basin, which led to less precise load estimates, regardless of how many storm samples were included. In addition, the difference in load estimates as more storms were included was slightly greater in the Rappahannock River during both periods, indicating that the influence of storm events on load estimation is greater in this smaller and flashier basin. Overall, the results of this study indicate that loads in the larger and less flashy James River Basin can be estimated with greater accuracy and precision over shorter time periods and usually with fewer storm samples than in the Rappahannock River Basin.

Trends in flow-adjusted concentrations were estimated reasonably well with few storm samples for both dissolved and particulate constituents in the James River for the 10-year period, with the exception of total suspended solids. Data sets having more storm samples—at least 42 percent of the total number of samples—were needed to obtain reliable trend estimates for the 5-year period. For the 10-year period in the Rappahannock River, at least 42 percent storm samples was necessary for reasonable estimates of trends in both dissolved and particulate constituents. No significant trends were observed for the 5-year period, so the minimum number of storm samples for trend estimation could not be determined. Because of the small number of significant trends throughout these data sets, it was not possible to determine whether dissolved constituent trends were better estimated with fewer storm samples than particulate constituent trends. The results do indicate that, as with load estimation, more storm samples were necessary for trend estimation during shorter time periods and in the smaller and flashier Rappahannock River Basin. Both load and trend estimates were sensitive to the length of the monitoring period and the size of the basin; however, load estimates were more sensitive to the number of storm samples in the data set than were trend estimates.

The best overall monitoring strategy for accurate and precise load and trend estimation of particulate and dissolved constituents in the James and Rappahannock River Basins was found to consist of 50 percent base-flow samples and 50 percent storm samples. If total suspended solids—a constituent that has large associated measurement errors—were not considered, however, a minimum of 33 percent storm samples would be sufficient.

The results of this study indicate that the optimal sampling design of monitoring programs in large river basins will differ depending on the basin size and hydrologic response, the length of the monitoring program, and the constituents of interest. Flashier basins will require collection of a greater number of storm samples, particularly if particulate constituents are monitored, though lengthening the monitoring period may reduce the amount of storm sampling required. Many monitoring programs begin as short-term efforts, however, making it impractical to initially design a sampling strategy that will be optimal over long periods. If the monitoring period is extended after several years of relatively high-intensity storm sampling, a significant reduction in storm-sampling frequency may bias trend estimates in the long term. The potential for this bias should be investigated prior to making substantial changes to a monitoring program.

## REFERENCES CITED


Battaglin, W.A., and Goolsby, D.A., 1994, Spatial data in geographical information system format on agricultural chemical use, land use, and cropping practices in the United States, 1985-91: U.S. Geological Survey Water-Resources Investigations Report 94-4176, 87 p.

Bell, C.F., Belval, D.L., and Campbell, J.P., 1996, Trends in nutrients and suspended solids at the Fall Line of five tributaries to the Chesapeake Bay in Virginia, July 1988 through June 1995: U.S. Geological Survey Water-Resources Investigations Report 96-4191, 37 p.

Belval, D.L., Campbell, J.P., Phillips, S.W., and Bell, C.F., 1995, Water-quality characteristics of five tributaries to the Chesapeake Bay at the Fall Line, Virginia, July 1988 through June 1993: U.S. Geological Water-Resources Investigations Report 95-4258, 71 p.

Belval, D.L., and Sprague, L.A., 1999, Monitoring nutrients in the major rivers draining to Chesapeake Bay: U.S. Geological Survey Water-Resources Investigations Report 99-4238, 8 p.

Cohn, T.A., 1988, Adjusted maximum likelihood estimation of the moments of lognormal populations from type I censored samples: U.S. Geological Survey Open-File Report 88-350, 34 p.

Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., and Summers, R.M., 1992, The validity of a simple log-linear model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 28, no. 9, p. 2353-2364.

Eshleman, K.N., Miller-Marshall, L.M., and Webb, J.R., 1995, Long-term changes in episodic acidification of streams in Shenandoah National Park, Virginia: Water, Air and Soil Pollution, v. 85, no. 2, p. 517-522.

Evaldi, R.D., and Moore, B.L., 1994, Yields of selected constituents in base flow and stormflow in urban watersheds of Jefferson County, Kentucky, 1988-92: U.S. Geological Survey Water-Resources Investigations Report 94-4065, 70 p.

Gray, J.R., Glysson, G.D., Turcios, L.M., and Schwarz, G.E., 2000, Comparability of suspended-sediment concentration and total suspended solids data: U.S. Geological Water-Resources Investigations Report 00-4191, 20 p.

Heathwaite, Louise, Haygarth, Phil, and Dils, Rachel, 2000, Pathways of phosphorus transport, *in* Sharpley, A.N., ed., Agriculture and phosphorus management—The Chesapeake Bay: Boca Raton, Fla., CRC Press, p. 107-130.

Preston, S.D., Bierman, V.J., and Silliman, S.E., 1992, Impact of flow variability on error in estimation of tributary mass loads: Journal of Environmental Engineering, v. 118, no. 3, p. 402-419.

Robertson, D.M., and Roerish, E.D., 1999, Influence of various water quality sampling strategies on load estimates for small streams: Water Resources Research, v. 35, no. 12, p. 3747-3759.

Rutledge, A.T., 1998, Computer programs for describing the recession of ground-water discharge and for estimating mean ground-water recharge and discharge from streamflow records—Update: U.S. Geological Survey Water-Resources Investigations Report 98-4148, 43 p.

Sprague, L.A., Langland, M.J., Yochum, S.E., Edwards, R.E., Blomquist, J.D., Phillips, S.W., Shenk, G.W., and Preston, S.D., 2000, Factors affecting nutrient trends in major rivers of the Chesapeake Bay Watershed: U.S. Geological Survey Water-Resources Investigations Report 00-4218, 98 p.

U.S. Environmental Protection Agency, 1988, Chesapeake Bay Agreement, *in* Comprehensive research plan: An agreement commitment report from the Chesapeake Executive Council (variously paged).

U.S. Environmental Protection Agency, 1999, Population trends, accessed December 5, 2000, at URL http://www.chesapeake.net/pop.htm/.

Vogelmann, J.E., Sohl, T.L., Campbell, P.V., and Shaw, D.M., 1998, Regional land cover characterization using Landsat Thematic Mapper data and ancillary data sources, Third EMAP Research Symposium, Albany, N.Y., April 8-11, 1997: Environmental Monitoring and Assessment, v. 51, p. 415-428.

Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., 1999, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, 103 p.

# APPENDIX

**Appendix 1.** Number of storm-flow days in the streamflow record, number of days on which a water-quality sample was collected, and number of storm-flow samples at the James and Rappahannock River monitoring stations for each data set

| Data set | Number of samples | Number of storm-flow samples | Percent storm-flow samples |
|---|---|---|---|
| **James River, 1990-99** | | | |
| **Streamflow Record (days)** | **3,652** | **729** | **20** |
| [1]100% | 407 | 221 | 54 |
| 80% | 355 | 177 | 50 |
| 60% | 312 | 133 | 43 |
| 40% | 266 | 88 | 33 |
| 20% | 225 | 44 | 20 |
| 0% | 182 | 0 | 0 |
| **James River, 1995-99** | | | |
| **Streamflow Record (days)** | **1,826** | **344** | **19** |
| [1]100% | 178 | 94 | 53 |
| 80% | 151 | 75 | 50 |
| 60% | 134 | 56 | 42 |
| 40% | 116 | 38 | 33 |
| 20% | 98 | 19 | 19 |
| 0% | 80 | 0 | 0 |
| **Rappahannock River, 1990-99** | | | |
| **Streamflow Record (days)** | **3,652** | **752** | **21** |
| [1]100% | 385 | 163 | 42 |
| 80% | 352 | 130 | 37 |
| 60% | 320 | 98 | 31 |
| 40% | 287 | 65 | 23 |
| 20% | 255 | 33 | 13 |
| 0% | 222 | 0 | 0 |
| **Rappahannock River, 1995-99** | | | |
| **Streamflow Record (days)** | **1,826** | **384** | **21** |
| [1]100% | 182 | 78 | 43 |
| 80% | 166 | 62 | 37 |
| 60% | 152 | 47 | 31 |
| 40% | 135 | 31 | 23 |
| 20% | 120 | 16 | 13 |
| 0% | 104 | 0 | 0 |

[1] 100% data set is the full data set with all base-flow and storm-flow samples included.