ESTIMATION OF NUTRIENT AND SUSPENDED-SEDIMENT LOADS IN THE PATUXENT RIVER BASIN, MARYLAND, WATER YEARS 1986-90

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ESTIMATION OF NUTRIENT AND SUSPENDED-SEDIMENT LOADS IN THE PATUXENT RIVER BASIN, MARYLAND, WATER YEARS 1986-90

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ABSTRACT

Water-quality data collected at stream sites in the Patuxent River Basin during the 1986 through 1990 water years were used to estimate loads of nutrients and other constituents. Tests were performed to determine the adequacy of the water-quality data for load estimation and to evaluate load-estimation methods. Sampling frequencies and patterns were inconsistent during the study period because equipment failures limited the number of high-streamflow-discharge samples during the early stages of the study.

A regression-based estimator and a ratio estimator were used to estimate loads. Comparisons indicated that the estimators provided similar levels of accuracy when concentration data were available from the entire discharge range. When high-discharge concentration data were not available, it appeared that the regression-based estimator overestimated loads of some constituents, whereas the ratio estimator appeared to underestimate some loads. The ratio estimator was selected for application in this study because the temporal inconsistencies in the sampling frequencies and patterns represented violations of the assumptions of the regression-based method and could cause substantial load-estimate bias. Ratio estimator load-estimate quality varied because high-flow concentration data were not available during some years.

Because of the load-estimate quality limitations and other complications, consistent differences in loading among the monitored subbasins were only apparent for total nitrogen. Preliminary estimation of the base-flow percentages of total loads was performed by calculating conservatively high and conservatively low base-flow load estimates to provide limits for the actual base-flow percentage. The highest base-flow percentages--at the Unity, Savage, and Killpeck Creek monitoring sites--were for total nitrogen because nitrate from ground water constitutes the largest percentage of total nitrogen in streamflow at those sites.

INTRODUCTION

Excessive nutrient loading, and its associated ecological effects, is considered to be a significant threat to the water quality and economic vitality of the Chesapeake Bay. Elevated nutrient concentrations stimulate algal productivity and can result in an increase in algal biomass. Dense algal biomass can affect fisheries by causing the depletion of dissolved-oxygen concentrations in the water and by reducing the habitat that is made available to fish by submerged aquatic vegetation (SAV). Such effects diminish the recreational and economic value of the Chesapeake Bay. The amount of nutrients that enter the bay needs to be controlled to prevent these effects.

Nutrients originate from point and nonpoint sources in the Chesapeake Bay watershed and are transported to the bay by its tributaries. Efforts to control point sources of nutrients have been established and include the upgrading of sewage-treatment plants for nutrient removal. In conjunction with these efforts water-quality improvements and nutrient-level reductions have been documented in some tributaries (Maryland Department of the Environment, 1993). Further reductions will require the control of both point and nonpoint sources of nutrients.

Nonpoint-source (NPS) nutrient loading is commonly related to land-use patterns within the watershed. Agricultural land use contributes nutrients to waterways by the washoff of excess fertilizer and animal waste. "Best management practices" (BMP's) are land-management practices that are specifically designed to minimize the transport of nutrients from agricultural lands. Much of the Chesapeake Bay watershed has experienced land development and a gradual shift from primarily agricultural to more urban and residential land uses. Developed areas also represent potential nonpoint sources of nutrients; however, the overall effect of development on water quality is not clear.

Background

In order to gain further understanding of the processes that contribute to NPS nutrient loading to the Chesapeake Bay, the U.S. Geological Survey (USGS), in cooperation with Maryland Department of the Environment (MDE), initiated a study of the Patuxent watershed. The purpose of the study is to quantify NPS nutrient loading at various locations in the basin, to gain further understanding of the relation between land use and water quality, and to evaluate the potential effectiveness of BMP's. To achieve those goals, a data-collection effort was established that included the compilation of hydrologic, meteorologic, geographic, and water-quality data from the Patuxent watershed. A model is being developed with the data that will allow simulation of the hydrology and water quality of the basin and investigation of the effect of different land-use alternatives on water quality.

The Patuxent watershed was selected as the study basin because of its importance to the State of Maryland and because it is representative of other Chesapeake Bay subbasins. The Patuxent is important to the State because it is the one major Chesapeake Bay subbasin that lies entirely within Maryland. The Patuxent is also important because it traverses the corridor between the two major metropolitan areas of Baltimore and Washington, D.C. Because of its location, the Patuxent watershed has experienced a substantial amount of development, and in that way, is representative of much of the Chesapeake Bay region. Growth in the region is expected to continue, and the State of Maryland has a strong interest in evaluating the effects of that development on water quality and in developing methods for planning future development.

Water-quality degradation associated with elevated nutrient and suspended-sediment loads has been documented in the Patuxent estuary. A comprehensive review of historical water-quality data for 1936-76 (Mihursky and Boynton, 1978) showed trends of increased nutrient concentrations, increased algal growth, decreased water-column transparency, and extended oxygen depletion in the bottom waters of the lower Patuxent estuary. Heinle and others (1980) reported similar conditions of water-quality degradation and highlighted the spatial and temporal increase of low dissolved-oxygen waters in the lower Patuxent and increased peak algal concentrations. These changes in Patuxent water quality were ultimately expressed in the declining health of living resources of the aquatic system. A significant loss of SAV was reported, with an associated loss of food sources and vital habitat. Harvests of commercially important species, such as striped bass and oysters, were reported to have declined substantially (U.S. Environmental Protection Agency, 1990).

In an effort to identify specific solutions for these problems, the State of Maryland initiated studies designed to evaluate existing controls of water quality in the Patuxent estuary. Existing water-quality data were analyzed, and a monitoring program was initiated to collect the information necessary to develop a water-quality model of the Patuxent estuary. Results of the modeling analysis (O'Conner and others, 1981) indicated that a point-source phosphorus-control policy would result in the greatest water-quality benefits in the Patuxent. The State initiated plans to institute a point-source phosphorus-control policy for the Patuxent. However, the analysis and the phosphorus-control policy were the subject of considerable controversy, which led to a lawsuit brought by three southern rural counties of Maryland (Calvert, Charles and St. Marys Counties) against the U.S. Environmental Protection Agency, the State of Maryland, and the four northern developed counties of Maryland (Anne Arundel, Howard, Montgomery and Prince Georges Counties).

In an effort to resolve the conflict, the State convened an intensive arbitration workshop in December 1981. Referred to as the "Charrette," the workshop involved representatives from local, State, and Federal governments, utility agencies, and other user groups. The Charrette resulted in the adoption of water-quality, fishery-productivity, esthetic, and recreational goals for the Patuxent watershed. The Charrette successfully reached a consensus for action which included: (1) acceptance of the water-quality model results; (2) agreement that a watershed-wide nutrient control strategy was needed; (3) acknowledgment that both phosphorus and nitrogen loading would be reduced; and (4) recognition that additional research and modeling were needed to improve understanding of related processes.

As a foundation for management actions, the 208 Water Quality Management Plan for the Patuxent River Basin was developed. The plan outlined a broad approach for improving water quality in the estuary by (1) formally adopting specific goals for nitrogen and phosphorus control from point and nonpoint sources, (2) proposing that efforts to protect the river go forward based on the best available information at that time, (3) calling for an intensive monitoring, research, and modeling effort to improve understanding of the river, and (4) proposing that the management strategy be adjusted as new information became available.

Following adoption of the Water Quality Management Plan, the State of Maryland developed and initiated the Patuxent Nutrient Control Strategy (Office of Environmental Programs, 1983). The Patuxent Nutrient Control Strategy identified specific nitrogen- and phosphorus-reduction goals as follows:

(1) Point-source phosphorus loads were to be reduced to 420 lbs/d. This goal would be achieved by requiring any facility that discharged more than 500,000 gal/d to meet an effluent limit of 1.0-mg/L phosphorus and to plan for a possible 0.3-mg/L limit.

(2) Point-source nitrogen loads were to be reduced to 4,040 lbs/d. The State would require specific facilities to incorporate nitrogen removal to the 3-mg/L level and for all facilities to plan for that level.

(3) Nonpoint-source nitrogen loads were to be reduced by 2,000 lbs/d from 1981 loads. It was expected that phosphorus nonpoint-source loads would be reduced through control of sediment runoff to be achieved under agricultural and stormwater cost-share programs.

The strategy also called for development of a comprehensive monitoring, modeling, and research program to reduce scientific uncertainty and to confirm the response of the Patuxent watershed to management actions. The monitoring program developed to meet the requirements of the Patuxent nutrient-reduction strategy includes both a tidal and nontidal water-quality sampling effort. The modeling component includes both watershed and estuarine water-quality models that are calibrated and verified with the appropriate monitoring data. Together, the monitoring and modeling projects are used by the State to analyze alternative management strategies and to evaluate progress for meeting nutrient-load-reduction goals.

In order to fulfill the need for water-quantity and water-quality data in the nontidal part of the basin, the USGS and MDE initiated a long-term study to measure stream discharge and key water-quality constituents at sites in the Patuxent watershed. The purpose of the study is to quantify nutrient and suspended-sediment loads from various parts of the basin. The monitoring program also provides the data necessary to calibrate and verify the watershed water-quality model. Water-quality data have been collected since September 1985 and will be collected for some years into the future.

Purpose and Scope

This report provides a description and analysis of water-quantity and water-quality data that were collected during water years 1986-90 as part of the ongoing study of the Patuxent watershed. The purpose of the report is to (1) summarize the available data for key constituents in the water-quality data base, (2) compare methods of load estimation to identify the most appropriate methodology for continued application in the Patuxent Basin, and (3) provide interim estimates of constituent mass load during the 5-year period.

Acknowledgments

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DESCRIPTION OF STUDY AREA

The Patuxent River Basin is representative of much of the Chesapeake Bay region in that it is extremely diverse. Stream characteristics in the basin range from narrow and free flowing in the upper basin to broad and sluggish in the central and southern areas. The main Patuxent channel is a freshwater stream in the upper basin but becomes a large estuary in the lower reaches. Land use ranges from sparsely populated agricultural regions in the northern and southern extremes to densely populated urban and residential areas in the central part of the basin. Similar diversity occurs in many basins throughout the Chesapeake Bay region, thus making the Patuxent an appropriate test basin for detailed study.

Location and Physiography

The Patuxent River Basin is located entirely in the State of Maryland and extends from northwestern Howard County in a southeastern or southern direction toward the Chesapeake Bay (fig. 1). The main channel is 110 mi long and extends through parts of seven Maryland counties. In the upper area of the basin, the main stem of the Patuxent represents the boundary between Howard and Montgomery Counties. In proceeding downstream, the Patuxent traverses the Baltimore-Washington, D.C. corridor and separates Anne Arundel and Prince Georges Counties. The lower Patuxent represents the western boundary of Calvert County and the eastern boundaries of Charles and St. Marys Counties.

The Patuxent River Basin is long and narrow, and traverses three physiographic zones. The basin covers an area of approximately 930 mi^2 and rarely exceeds a width of 15 mi. The upper one-third of the basin is located in the Piedmont Physiographic Province, which can be characterized by rolling hills and rugged terrain. In this area the Patuxent Basin includes a network of small streams that join to form the main channel. In the vicinity of Laurel, Maryland, the Patuxent River traverses the Fall Line, which represents the boundary between the Piedmont and Coastal Plain Physiographic Provinces (fig. 1 and 2). Below the Fall Line, the Patuxent River traverses the Coastal Plain Province. This area is characterized by a relatively shallow gradient, slow meandering streams, and progressively greater tidal effects.

In the upper part of the basin, the Patuxent consists of three main branches and numerous smaller branches (fig. 1 and 2). Of the three main

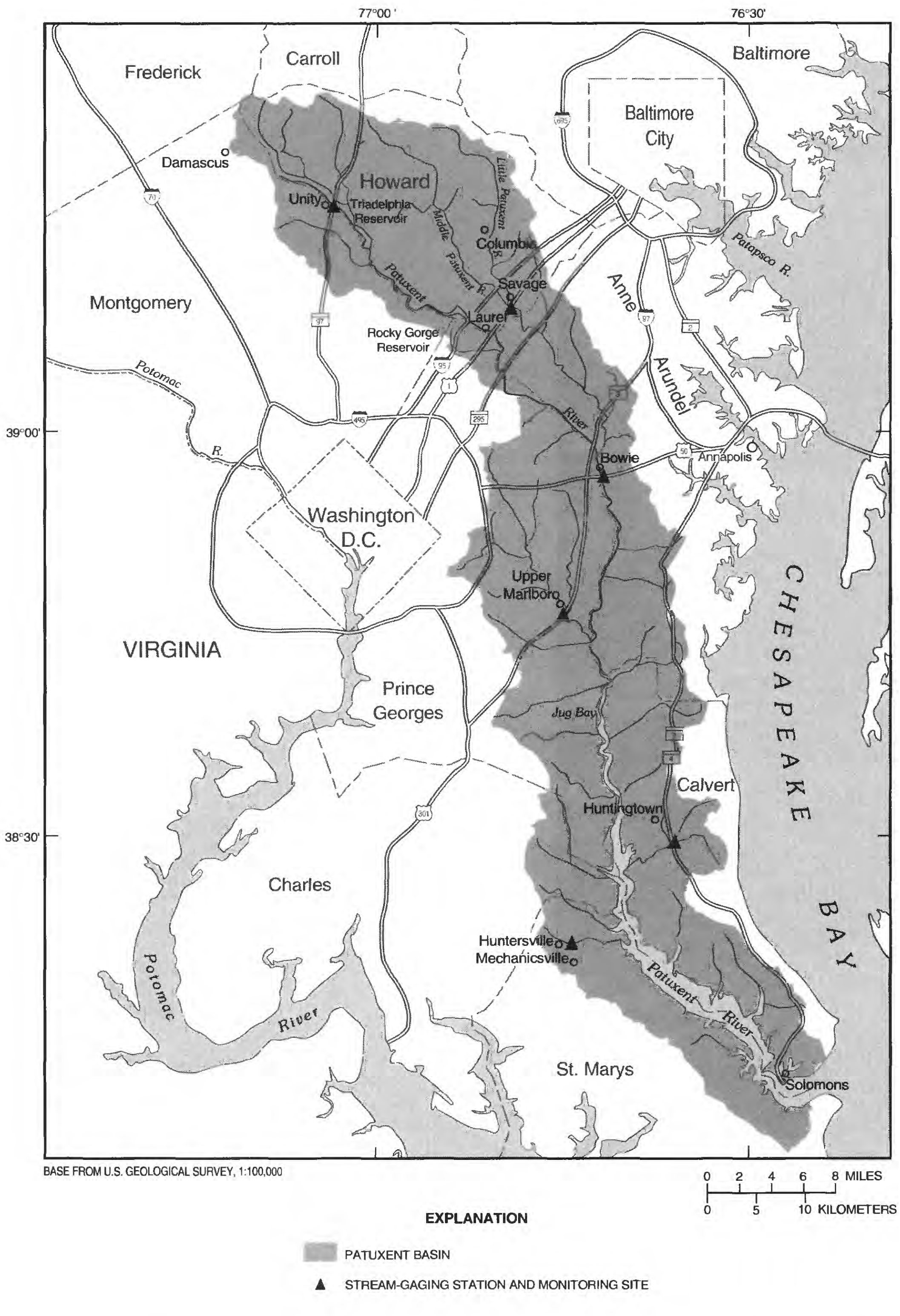
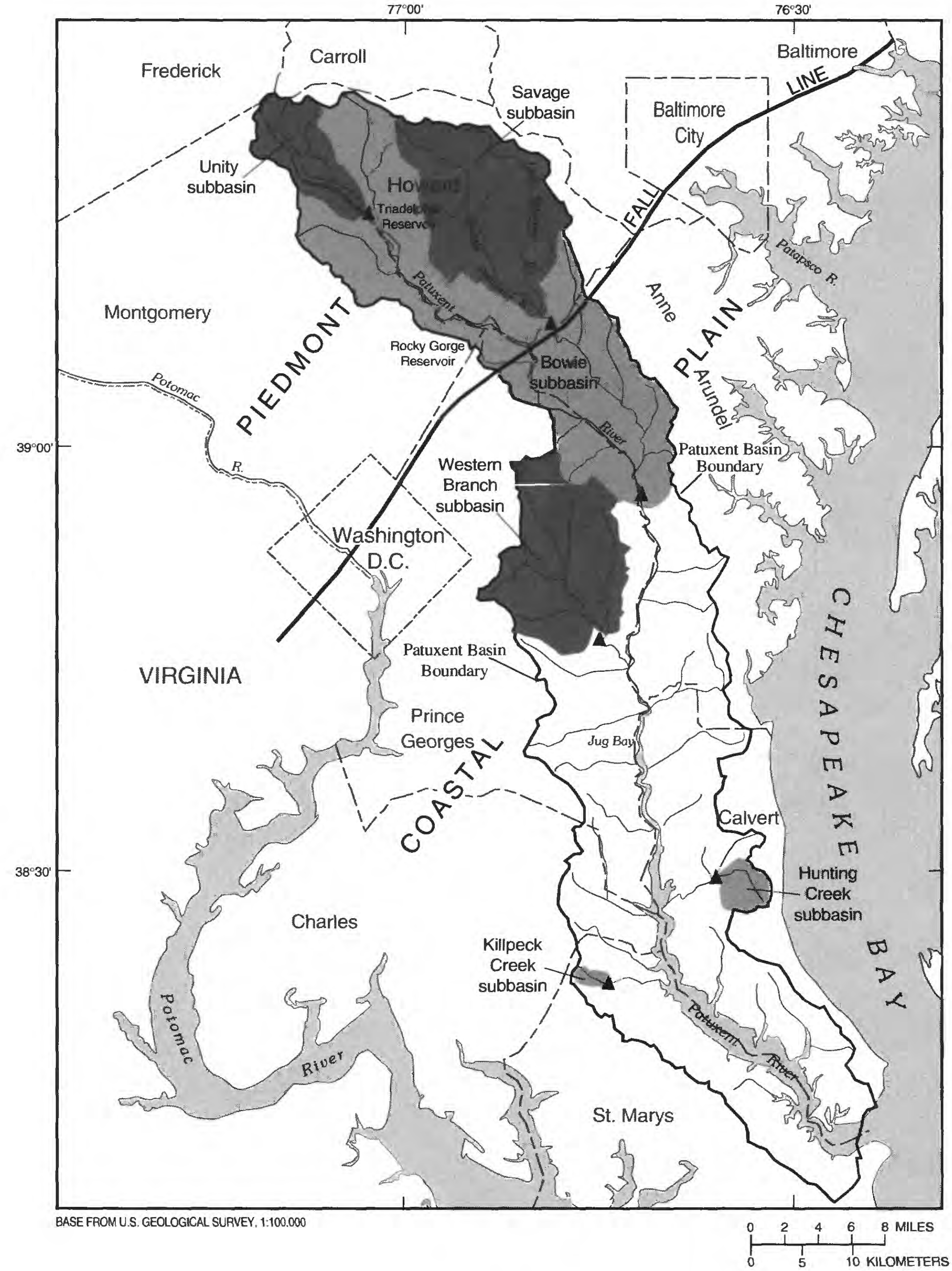


Figure 1. The Patuxent River Basin, monitoring sites and surrounding areas in Maryland and Virginia.



EXPLANATION

▲ STREAM-GAGING STATION AND MONITORING SITE

Figure 2. The Patuxent River Basin, monitoring sites and associated drainage subbasins.

branches, the Little Patuxent and Middle Patuxent Rivers are northeast of the main stem and reach their confluence just downstream from the town of Columbia and upstream of the Fall Line. The main stem of the Patuxent is dammed in two locations to form two major impoundments, the Triadelphia and the Rocky Gorge Reservoirs. The main stem of the Patuxent and the Little Patuxent River reach their confluence near the town of Bowie.

In the central and lower parts of the basin, the Patuxent River widens to form a major estuary (fig. 1). At its start the estuary is fed by the main stem of the Patuxent and by Western Branch. Western Branch is a relatively large tributary that drains much of Prince Georges County and discharges to the Patuxent just above Jug Bay. In the lower estuary, numerous streams and creeks drain the small subbasins that occur within the Patuxent watershed in Calvert and St. Marys Counties. The Patuxent discharges to the Chesapeake Bay at the town of Solomons in Calvert County (fig. 2).

Population and Land Use

In part because of its proximity to the two major metropolitan areas of Baltimore, Md. and Washington, D.C., population has continued to increase in the upper basin of the Patuxent watershed. For 1950-80, population in the basin increased 245 percent. The population is expected to continue to grow during the foreseeable future and is expected to increase by another 90 percent before the year 2000 (Alliance for the Chesapeake Bay, 1990).

Data provided by the Maryland Office of State Planning (MOSP) indicate that land use in the watershed varies with location (Fisher, 1991). In the extreme upper end of the basin, land use is predominantly agricultural. For example, in the upper part of the main-stem subbasin, land use is 55 percent agricultural, 34 percent forest, and only 10 percent urban and residential. Near the Baltimore-Washington, D.C., corridor, the fraction of urban and residential land use is much higher (30 percent), although the largest fraction of land use is forest (49 percent). In the lower part of the basin, the fraction of total land dedicated to urban and residential land use is low (5 percent), and forest is the predominant land use (55 percent).

Because of the rapid growth in population, land use in the Patuxent watershed has shifted from primarily forest and agricultural toward urban and residential uses. This is especially true in the upper part of the basin but has been true to some extent throughout the watershed. It has been reported that for 1950-80, non-agricultural land use increased from 20,000 to 213,000 acres, which represents more than a tenfold increase in area (Alliance for the Chesapeake Bay, 1990).

Monitoring-Site Descriptions

Six stream sites were selected for detailed hydrologic and water-quality monitoring to represent various subbasins, physiographic provinces, and mix of land uses in the watershed (fig. 1 and 2). Two of the selected sites are located on the main stem of the Patuxent River, two are located on major tributaries, and two are located in small Coastal Plain basins that discharge directly to the Patuxent estuary.

The site that is farthest upstream is near Unity, Md., where Route 97 crosses the main stem of the Patuxent, immediately upstream of the Triadelphia Reservoir at an established USGS streamflow-gaging station (01591000). The Unity site was selected to represent an area of rural land use in the Piedmont part of the basin. Land use in the Unity subbasin during 1985 was primarily agricultural (64 percent) and forest (32 percent).

One site was selected to measure the water quality of the Middle and Little Patuxent Rivers. That site is just south of Savage, Md., where Route 1 crosses the Little Patuxent River. The site at Savage is located just downstream of the confluence of the Middle and Little Patuxent Rivers, and is directly downstream from the developed area of Columbia. Land use in the Savage subbasin during 1985 was mostly agricultural (35 percent), but a large fraction of land area was urban and residential (31 percent). Forest area accounted for approximately 32 percent of the basin area.

A second main-stem site is located near Bowie at the Route 50 Patuxent River bridge. The Bowie site is at an established USGS streamflow-gaging station (01594440) and is just upstream of tidal effects and downstream of the Fall Line. Data collected at the Bowie site are used by both the Patuxent and the River Input studies. The objective of the River Input study is to quantify loads of various constituents from the major tributaries of the Chesapeake Bay. The combined effort of the Patuxent and River Input studies has resulted in a more detailed data record at the Bowie site than is available at the other sites. Land use in the Bowie subbasin during 1985 was 22 percent urban and residential, 31 percent agricultural, and 44 percent forest.

Western Branch is a large tributary that is located in the Coastal Plain and discharges directly to the Patuxent estuary. As a result, a water-quality monitoring site was established on Western Branch at Upper Marlboro. Land use in the Western Branch subbasin in 1985 included 24 percent urban and residential, 30 percent agriculture, and 38 percent forest.

Two subbasins were selected to represent the numerous small Coastal Plain subbasins that are located along the Patuxent estuary in the lower part of the Patuxent watershed. In Calvert County, the Hunting Creek subbasin was selected, and a monitoring site was established at the Route 263 crossing. In St. Marys County, the Killpeck Creek subbasin was selected, and a monitoring site was established near Huntersville. In both subbasins, land use in 1985 was predominantly forest (63-76 percent) and agriculture (20-26 percent), with the remainder being urban and residential.

METHODS OF DATA COLLECTION AND PROCESSING

In order to provide quality data for nutrient and suspended-sediment load estimation, substantial resources were expended for data collection and processing. At each of the monitoring sites, semipermanent housing was established to shelter data-collection equipment. Because of the potential for damage from high, fast-flowing water and storms, the housing and equipment configurations were designed to withstand substantial external weathering. Furthermore, because data collection was expected to continue into the foreseeable future, the stations were designed to last for a long period of time. After the sites were established, substantial resources were expended to maintain and monitor the equipment and to retrieve data as collected. Finally, after the data were collected, a substantial amount of effort was expended to process the data and to integrate them in a way that would allow load estimation and other evaluations of the hydrology and water quality of the basin. At all stages of data collection and processing, care was taken to ensure the dependability of data-collection equipment and the quality of the final data base.

Data Collection

In order to perform load estimation, discharge and water-quality-constituent concentration data need to be collected. The characteristics of the two types of data are much different because of the methods used to collect them. Discharge data are collected automatically and in high frequency by recording stream stage at regular intervals. Constituent-concentration data are collected intermittently by taking discrete water samples from the stream and performing laboratory analysis. The frequency of the concentration measurements is relatively low because of the expense of sample collection and laboratory analysis. In comparison, the discharge data are quasi-continuous and can be used to estimate concentration. In that way the more detailed discharge record can be used to supplement the concentration record during periods when samples were not collected (Cohn and others, 1989). Thus, it is important that the discharge record be complete throughout the load-estimation period.

Measurement of Discharge

Discharge measurements were made using standard USGS streamflow-gaging procedures (Buchanan and Somers, 1982). Stage was sensed automatically using either a float and stilling-well system or a gas-purge manometer system. Stage was recorded using automated digital recorders. These recorders were powered by a battery that allowed them to run unattended for 60 to 90 days. Stage was recorded by punching holes in a paper tape at intervals of 15 minutes. The paper tapes were collected at regular intervals, and the stage measurements were read, computerized, and entered into the USGS discharge data base.

Discharge data were calculated from stage data through the use of an empirical relation called a discharge rating. Discharge measurements were made at each site using (1) current meters to measure velocity at points across the width of the stream and (2) the cross-sectional area of the stream. Discharge measurements were collected for a range of stages, and a mathematical or graphical relation was developed for that range. After the development of the discharge rating, discharge measurements were continued on a regular basis so that any shifts caused by changes in the streambed or control could be detected. Further details on stage measurement or discharge calculation are described by Carter and Davidian (1968).

Sample Collection and Analysis

Water-quality samples were collected during base-flow and high-flow conditions to ensure coverage of the full range of discharge. Water-quality data covering the entire discharge range are important because they can ensure the accuracy and precision of a number of types of water-quality evaluations. A large fraction of the total load is carried during high-flow periods, and measurement of water quality during high flow will enhance load-estimate accuracy. In addition, load variability tends to increase during high-flow periods, and collecting more samples during high-flow periods, therefore, can improve load-estimate precision. Finally, changes in water quality induced by high-flow conditions are important to the simulation of NPS loads, and high-flow measurements of water quality are essential for adequate calibration of watershed loading models.

High-flow samples were collected using automated sampling devices that initiated sampling as the stream reached a specified actuation level. Actuation levels were selected specifically for each site and represent the discharge level above which the stream is dominated by surface runoff. Sampling equipment at each site included (1) a flow meter that recorded the discharge through time and indicated when samples were collected, (2) a sampler that pumped water from the stream or mixing chamber and stored it in separate sample bottles, and (3) an actuator that "turned on" the sampler and flow meter as the actuation level was reached. At most sites, as many as 24 samples were collected and composited to yield from one to four samples per storm. Samplers were either refrigerated or iced before a storm began to preserve the samples as they were collected. Samples were retrieved and processed within 48 hours of collection.

In most cases storm samples were collected on a flow-proportional basis and composited manually based on the characteristics of the storm. Flow-proportional sampling is performed by collecting a sample each time that a specific volume of flow is measured by the flow meter. In that way flow-proportional sampling increases the frequency of samples collected during high flows and increases the probability that samples will be collected during the highest flows.

Compositing of samples was performed to collect an appropriate number of concentration data for a particular storm. In most cases, when many samples were collected during a storm, the hydrograph was used as the basis for defining composites. Samples were composited to represent specific portions of the hydrograph such as the rising and falling limbs, and the peak flow. Individual samples were composited in a churn splitter and aliquots were withdrawn for laboratory analysis to determine constituent concentration. Concentration data from composite samples were associated with discharge values that were defined by digitizing the portion of the hydrograph where the samples were collected.

Tests were performed to verify that samples collected through the sampler intake were representative of the stream (Koterba and others, 1994). As part of the tests, samples were collected manually in the stream and simultaneously using the automatic sampler. Comparison of the results indicated that the two methods provided data that were nearly equivalent throughout a range of discharges. Suspended sediment was the only constituent that exhibited slight differences between the two methods; suspended-sediment concentrations in samples collected by the automatic sampler were slightly lower than those in samples collected manually from the stream.

Base-flow samples were collected monthly using the equal-width-increment (EWI) method described by Edwards and Glysson (1988). The

EWI method was used to collect samples that were depth and width integrated and were representative of the entire stream cross section. The EWI method uses vertically integrated subsamples, collected at equal increments across the width of the stream and then composited to form the whole sample. The technique is designed to provide a sample that is horizontally and vertically integrated and that will not be affected by variations in concentration within the stream cross-section. In most cases, base-flow samples were processed immediately and transported to the laboratory within 24 hours.

Five constituents were selected for load estimation and included measures of total nutrients and sediment concentration. Constituents for which loads were estimated included total phosphorus, total nitrogen, total organic carbon, total suspended solids and suspended sediment. Laboratory analyses that were used to measure each of these constituents are listed in table 1. Total nitrogen is determined as the sum of ammonium and organic nitrogen determined by the total Kjeldahl method (Fishman and Friedman, 1989) and nitrate plus nitrite determined by colorimetry (U.S. Environmental Protection Agency, 1979). All laboratory analyses were performed by the Maryland Department of Health and Mental Hygiene (MDHMH) laboratory, except for the suspended-sediment analyses, which were performed by the USGS sediment laboratory in Lemoyne, Pa. Actual data may be found in the reports by James and others (1991 and 1992).

Total suspended solids and suspended sediment are both measures of the amount of particulate matter in the sample. Total suspended solids is measured by performing gravimetric analysis on a subsample that is collected from the whole sample using a graduated cylinder (American Public Health Association, 1975). Suspended sediment is measured by performing gravimetric analysis on the entire volume of a sample that was collected solely for that analysis (Guy, 1969). MDE commonly uses total suspended solids in evaluating the particulate loads of streams; USGS usually uses suspended sediment. Load estimation was performed using both measures to accommodate the preferences of both agencies and to allow comparison with other studies that have used either total suspended solids or suspended sediment.

Various types of quality-control data were collected throughout the study period to evaluate sampling and analytical error. Duplicate base-flow samples were collected on a monthly basis. During some years, the MDHMH laboratory participated in laboratory audits that were sponsored by the USGS and were designed to verify analytical accuracy. As part of the evaluation of automatic samplers described previously in this report and by Koterba and others (1994), data were collected to investigate the potential for contamination from the sampling equipment. In general, all of these types of quality-assurance/quality-control (QA/QC) data confirmed that the water-quality data were accurate and representative of stream concentrations. Some QA/QC data have been published in the reports by James and others (1991and 1992). Further information on the QA/QC aspects of the study and the QA/QC data can be obtained from the authors of this report.

Table 1. *Analytical methods used for selected water-quality constituents*

[MDHMH, Maryland Department of Health and Mental Hygiene, Baltimore, Md.; USGS, U.S. Geological Survey sediment laboratory, Lemoyne, Pa.]

Constituent	Laboratory	Methodology	Reference
Total phosphorus as P	MDHMH	Digeston/ Colorimetry	Fishman and Friedman (1989)
Total nitrogen as N	MDHMH	Digeston/ Colorimetry	Fishman and Friedman (1989); U.S. Environmental Protection Agency (1979)
Total organic carbon	MDHMH	U/V-Persulfate Oxidation	American Public Health Association (1975)
Total suspended solids	MDHMH	Filtration	American Public Health Association (1975)
Suspended sediment	USGS	Filtration	Guy (1969)

Data Processing

Discharge data were processed using standard USGS methods in which discharge is estimated through the application of a rating curve to measured stream stage data. A more detailed description of these techniques can be found in Kennedy (1983).

Water-quality data were obtained from the MDHMH laboratory in the form of data sheets and were entered manually into SAS (Statistical Analysis System [1]) data sets by MDE. SAS is a statistical computer language that offers extensive data-management and data-analysis capability. SAS water-quality data sets were transferred to the USGS, where they were checked, corrected, and merged with discharge and sediment data. All water-quality data were converted to eastern standard time for consistency. Corrected instantaneous discharge values were integrated with the water-quality data by retrieving the appropriate values from ADAPS, the USGS discharge data-base system. The corrected water-quality data were stored in QWDATA, the USGS water-quality data-base system.

ESTIMATION OF NUTRIENT AND SUSPENDED-SEDIMENT LOADS

SAS water-quality data sets were modified slightly to perform load estimation. Many statistical estimators are based on the assumption of a maximum frequency at which sampling can be performed. That maximum frequency defines the sample population and the total number of samples that are possible in the population. For load estimation at annual and monthly time scales, the maximum sampling frequency usually is assumed to be daily, and the sample population is defined as measurements of concentration on individual days. In some cases, more than one concentration value was available on a given day because duplicates were collected for quality-control purposes or because samples were collected more frequently during a storm. To provide consistent data for load estimation, constituent data sets were compressed by calculating the daily mean of duplicate or multiple storm samples.

A common problem when estimating constituent loads is finding effective methods of estimating loads in the presence of constituent measurements that are less than reporting limits. Actual concentration values for measurements that are less than reporting limits range from zero to the reporting limit; thus, for the purpose of load estimation, attributing a value of zero to less-than reporting limit measurements will cause underestimation of the true load, and conversely, attributing the value of the reporting limit to the measurement will cause overestimation of the true load. The significance of these errors usually depends upon the characteristics of the data, such as the proportion of measurements that are less-than reporting limits and the number that occur during high discharge periods. At the Patuxent monitoring sites, the fraction of constituent measurements that were less than reporting limits was usually small, and most measurements were associated with low discharge values and consequently low loading rates. For those reasons, reporting limits were used where actual constituent-concentration measurements were less than reporting limits. It is expected that substituting reporting limits for values less than reporting limit led to slight overestimation of the actual load, which was insignificant relative to the overall level of load-estimate error.

Data Used in Load Estimations

Data used to estimate constituent loads at the Patuxent monitoring sites are summarized in the form of tables and time-series plots. The tables present various types of descriptive statistics for discharge and concentration data. The mean daily discharge values for each site in each water year are summarized in table 2. Constituent concentration data for each water year are summarized by site in tables 3-8. Time-series plots that indicate the distribution of concentration and discharge values for the period of record are shown in figures 3-8. Sampling was not consistent for the period of

[1] The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 2. *Summary of mean daily discharge data used for load estimation at the Patuxent monitoring sites, water years 1986-90*

[--, no data]

Monitoring site name (fig. 2)	Monitoring site number	Water year	Mean daily discharge (cubic feet per second)					
			Number of data values	Mean	Standard deviation	Coefficient of variation	Minimum	Maximum
Unity	01591000	1986	365	21.7	21.1	0.97	2.8	165
		1987	365	34.0	46.2	1.36	2.5	397
		1988	366	41.4	51	1.23	8.1	514
		1989	365	40.9	78.6	1.92	8.1	1,390
		1990	365	34	27.6	.81	9.7	264
Savage	01594000	1986	365	63.4	66.3	1.04	8.5	605
		1987	365	88.1	112	1.27	8	1,090
		1988	366	92.8	108	1.16	14	1,100
		1989	365	137	222	1.62	17	3,150
		1990	365	114	111	.97	30	906
Bowie	01594440	1986	365	201	165	.82	56	1,200
		1987	365	290	302	1.04	57	2,600
		1988	366	329	325	.98	84	2,720
		1989	365	447	601	1.34	83	8,400
		1990	365	359	301	.84	102	2,530
Western Branch	01594526	1986	365	54.8	69.2	1.26	3.2	665
		1987	365	76.2	94.1	1.23	2.8	864
		1988	366	73.8	100.3	1.35	3.8	731
		1989	212	82.6	98.5	1.19	7.2	750
		1990	--	--	--	--	--	--
Hunting Creek	01594670	1986	--	--	--	--	--	--
		1987	--	--	--	--	--	--
		1988	--	--	--	--	--	--
		1989	365	12.7	17.7	1.39	.1	195
		1990	365	14.7	18.7	1.27	1.8	221
Killpeck Creek	01594710	1986	365	3.51	3.7	1.05	.4	47
		1987	365	3.89	3.93	1.01	.31	42
		1988	366	2.43	2.63	1.08	.35	32
		1989	365	4.42	4.52	1.02	.49	36
		1990	365	5.33	5.02	.94	1.6	69

record, and time-series plots are presented to evaluate the accuracy of load estimates that are based on the overall number of data and the number of concentration data collected during high-discharge events.

Complete records of daily mean discharge are available for most of the monitoring sites throughout the study period (table 2). Discharge data from the Western Branch site are not available for part of water year 1989 and all of water year 1990 because road construction necessitated the removal of all gaging and sampling equipment. Complete discharge records are not available for the Hunting Creek site during water years 1986, 1987, or 1988 because of equipment failure. Some discharge data are available for the Hunting Creek site for water year 1987; however, the number was not adequate for load estimation. Differences in discharge among the Patuxent sites are primarily a function of the size of the drainage basin. Annual mean discharge is highest at the Bowie site because its drainage area is the largest.

Table 3. *Summary of water-quality data used for load estimation at the Unity monitoring site, water years 1986-90*

[mg/L, milligrams per liter]

Constituent	Water year	Number of data values	Water-quality data: Number of data values less than reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	17	0	0.073	0.039	0.030	0.170
	1987	27	0	.200	.475	.040	2.30
	1988	26	0	.140	.323	.010	1.70
	1989	24	0	.120	.192	.010	.900
	1990	27	2	.110	.139	.010	.600
Total Nitrogen (mg/L as N)	1986	16	0	2.3	.62	1.60	3.35
	1987	27	0	2.9	1.51	1.65	9.10
	1988	26	0	3.1	1.00	2.25	7.79
	1989	24	2	2.9	.58	2.20	5.10
	1990	25	2	3.0	.56	1.78	4.40
Total Organic Carbon (mg/L as C)	1986	17	0	2.1	.72	1.37	4.42
	1987	27	4	4.3	5.80	1.11	25.9
	1988	24	0	2.3	2.24	.56	11.8
	1989	23	1	2.3	3.66	.80	18.9
	1990	28	2	2.7	2.93	.65	14.3
Total Suspended Solids (mg/L)	1986	17	1	11	12	1	42
	1987	27	5	128	433	1	2,090
	1988	25	6	17	51	1	262
	1989	25	4	11	17	1	58
	1990	28	4	48	103	1	343
Suspended Sediment (mg/L)	1986	8	0	19	11	4	35
	1987	16	0	53	94	3	384
	1988	13	0	190	342	2	901
	1989	14	0	219	757	2	2,850
	1990	15	0	85	151	3	543

Table 4. *Summary of water-quality data used for load estimation at the Savage monitoring site, water years 1986-90*

[mg/L, milligrams per liter]

Constituent	Water year	Number of data values	Water-quality data: Number of data values below reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	7	0	0.040	0.014	0.030	0.070
	1987	11	0	.093	.130	.020	.480
	1988	12	1	.150	.290	.015	1.03
	1989	15	1	.200	.270	.010	1.00
	1990	17	2	.210	.240	.010	.650
Total Nitrogen (mg/L as N)	1986	5	0	1.3	.36	.97	1.8
	1987	10	0	1.9	.49	1.3	2.6
	1988	12	0	2.3	.55	1.7	3.7
	1989	15	0	2.4	.44	1.9	3.3
	1990	15	0	2.7	.53	2.1	3.7
Total Organic Carbon (mg/L as C)	1986	7	0	2.6	.63	1.8	3.8
	1987	11	0	2.6	.79	1.5	3.9
	1988	12	0	3.7	4.3	.72	16
	1989	16	0	3.5	2.6	1.2	11
	1990	18	0	5.5	4.4	1.2	17
Total Suspended Solids (mg/L)	1986	7	2	2	1	1	3
	1987	12	6	7	10	1	34
	1988	12	5	65	160	1	540
	1989	16	1	29	79	1	323
	1990	18	1	148	221	1	693
Suspended Sediment (mg/L)	1986	7	0	7	4	3	13
	1987	11	0	14	11	3	39
	1988	10	0	131	316	2	1,000
	1989	14	0	170	306	1	894
	1990	21	0	172	259	1	926

Table 5. *Summary of water-quality data used for load estimation at the Bowie monitoring site, water years 1986-90*

[mg/L, milligrams per liter]

Constituent	Water year	Number of data values	Water-quality data: Number of data values below reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	64	0	0.393	0.182	0.130	1.28
	1987	80	1	.235	.118	.040	.720
	1988	68	0	.224	.107	.070	.700
	1989	47	0	.260	.298	.085	1.90
	1990	31	0	.165	.117	.050	.490
Total Nitrogen (mg/L as N)	1986	63	0	5.3	1.6	2.60	8.1
	1987	78	1	4.1	1.6	2.24	8.5
	1988	68	0	3.8	1.3	1.95	7.2
	1989	46	2	3.1	1.2	1.42	5.3
	1990	31	2	2.9	.90	1.45	4.8
Total Organic Carbon (mg/L as C)	1986	59	0	6.2	3	3.29	18
	1987	80	0	5.6	1.8	3.00	12
	1988	62	0	4.9	2.7	1.58	15
	1989	42	0	5.7	2.4	2.31	13
	1990	31	0	6.0	2.4	2.41	11
Total Suspended Solids (mg/L)	1986	40	0	23	38	1	175
	1987	51	1	37	69	1	387
	1988	59	2	37	59	1	304
	1989	14	1	16	16	1	54
	1990	5	0	24	21	6	354
Suspended Sediment (mg/L)	1986	40	0	60	100	4	550
	1987	52	0	75	95	7	450
	1988	44	0	87	115	6	611
	1989	34	0	70	82	6	354
	1990	31	0	70	71	4	282

Table 6. *Summary of water-quality data used for load estimation at the Western Branch monitoring site, water years 1986-90*

[mg/L, milligrams per liter; --, no data]

Constituent	Water year	Number of data values	Water-quality data: Number of data values below reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	25	0	0.072	0.187	0.050	0.770
	1987	32	0	.120	.074	.050	.420
	1988	31	0	.120	.090	.045	.440
	1989	22	0	.260	.270	.035	.900
	1990	--	--	--	--	--	--
Total Nitrogen (mg/L as N)	1986	23	1	1.1	.47	.38	2.1
	1987	32	0	1.1	.39	.63	2.5
	1988	31	2	1.0	.29	.57	1.6
	1989	21	1	1.4	.46	.78	2.4
	1990	--	--	--	--	.58	--
Total Organic Carbon (mg/L as C)	1986	24	0	5.1	2.1	2.4	11
	1987	32	0	4.8	1.5	2.7	9.7
	1988	30	0	3.7	1.7	1.3	8.6
	1989	18	1	5.5	1.7	2.3	13
	1990	--	--	--	3.3	--	--
Total Suspended Solids (mg/L)	1986	25	2	16	21	1	86
	1987	32	6	15	25	1	107
	1988	30	4	9	11	1	55
	1989	22	2	18	18	1	86
	1990	--	--	--	--	--	--
Suspended Sediment (mg/L)	1986	08	0	34	44	1	137
	1987	12	0	30	26	8	87
	1988	09	0	34	59	6	188
	1989	11	0	181	247	7	857
	1990	--	--	--	--	--	--

Table 7. *Summary of water-quality data used for load estimation at the Hunting Creek monitoring site, water years 1986-90*

[mg/L, milligrams per liter; --, no data]

Constituent	Water year	Number of data values	Water-quality data: Number of data values below reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	--	--	--	--	--	--
	1987	--	--	--	--	--	--
	1988	--	--	--	--	--	--
	1989	9	0	0.161	0.125	0.020	0.450
	1990	21	0	.137	.069	.060	.300
Total Nitrogen (mg/L as N)	1986	--	--	--	--	--	--
	1987	--	--	--	--	--	--
	1988	--	--	--	--	--	--
	1989	9	3	.79	.23	.41	1.2
	1990	19	1	.77	.37	.43	2.0
Total Organic Carbon (mg/L as C)	1986	--	--	--	--	--	--
	1987	--	--	--	--	--	--
	1988	--	--	--	--	--	--
	1989	8	0	6.7	3.7	2.4	13
	1990	24	0	6.4	1.9	3.1	9.5
Total Suspended Solids (mg/L)	1986	--	--	--	--	--	--
	1987	--	--	--	--	--	--
	1988	--	--	--	--	--	--
	1989	10	0	18	32	1	105
	1990	25	1	33	40	1	188
Suspended Sediment (mg/L)	1986	--	--	--	--	--	--
	1987	--	--	--	--	--	--
	1988	--	0	--	--	--	--
	1989	11	0	28	39	2	131
	1990	22	0	31	30	3	100

Table 8. *Summary of water-quality data used for load estimation at the Killpeck Creek monitoring site, water years 1986-90*

[mg/L, milligrams per liter]

Constituent	Water year	Number of data values	Water-quality data: Number of data values below reporting limits	Mean	Standard deviation	Minimum	Maximum
Total Phosphorus (mg/L as P)	1986	7	0	0.123	0.040	0.080	0.200
	1987	10	0	.087	.032	.040	.150
	1988	11	0	.076	.020	.050	.110
	1989	19	1	.307	.331	.040	1.36
	1990	22	0	.442	.446	.050	1.40
Total Nitrogen (mg/L as N)	1986	7	0	1.7	.28	1.4	2.3
	1987	10	0	1.9	.29	1.3	2.3
	1988	11	0	1.9	.62	.70	2.7
	1989	16	0	2.0	.74	1.4	4.4
	1990	21	0	2.1	.72	1.1	3.8
Total Organic Carbon (mg/L as C)	1986	8	0	2.9	.54	2.1	3.8
	1987	9	0	2.8	.73	1.7	4.1
	1988	10	0	2.2	.72	1.4	3.8
	1989	15	0	7.3	5.7	2.1	21
	1990	25	0	9.3	9.7	2.1	48
Total Suspended Solids (mg/L)	1986	8	0	8	6	2	16
	1987	10	3	5	4	1	13
	1988	11	1	7	6	1	16
	1989	19	0	29	32	1	94
	1990	25	0	575	1,620	3	8,100
Suspended Sediment (mg/L)	1986	5	0	18	8	10	32
	1987	10	0	19	16	5	58
	1988	09	0	30	35	8	120
	1989	19	0	236	325	1	1,037
	1990	28	0	632	1,060	5	5,365

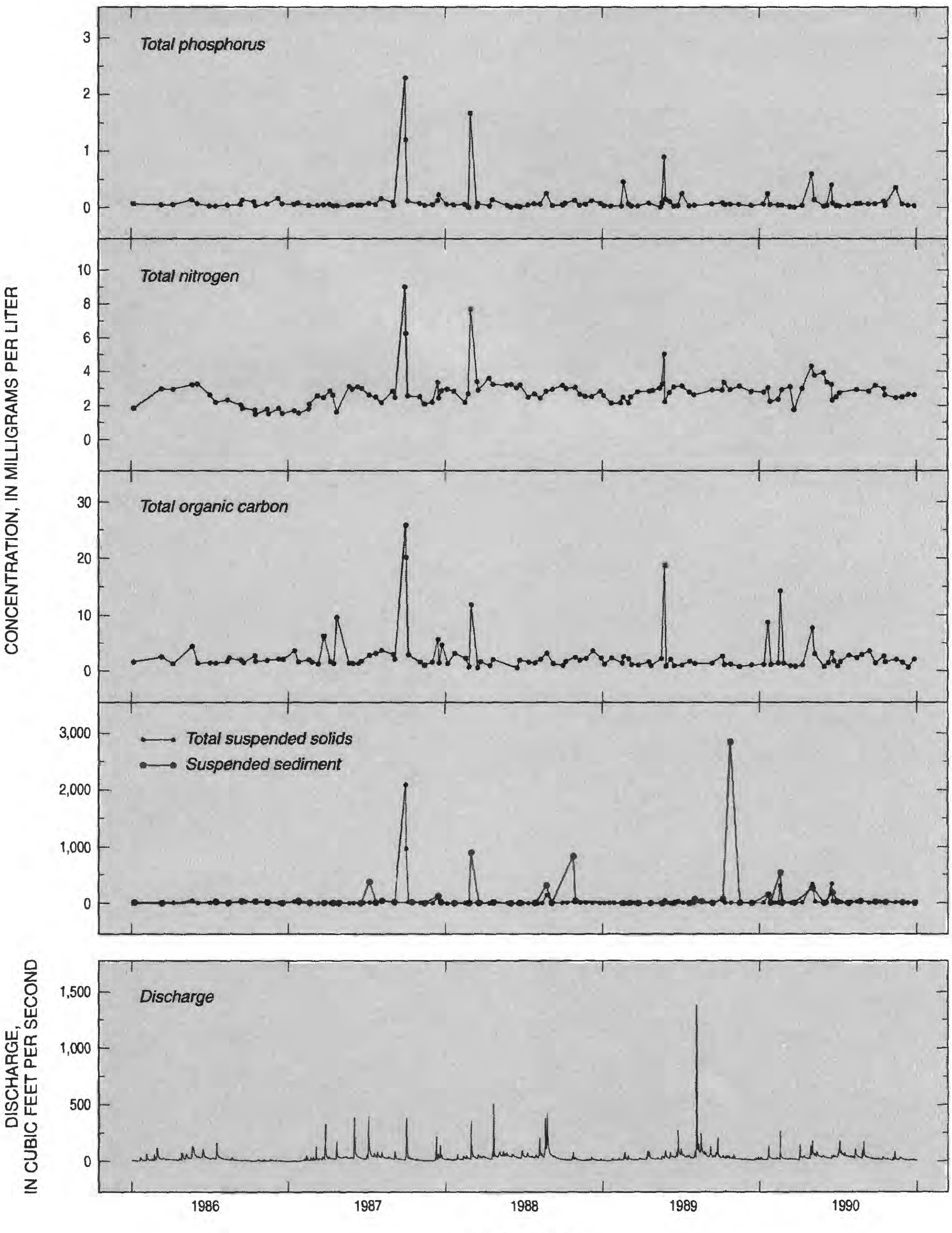


Figure 3. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Unity monitoring site, water years 1986-90.

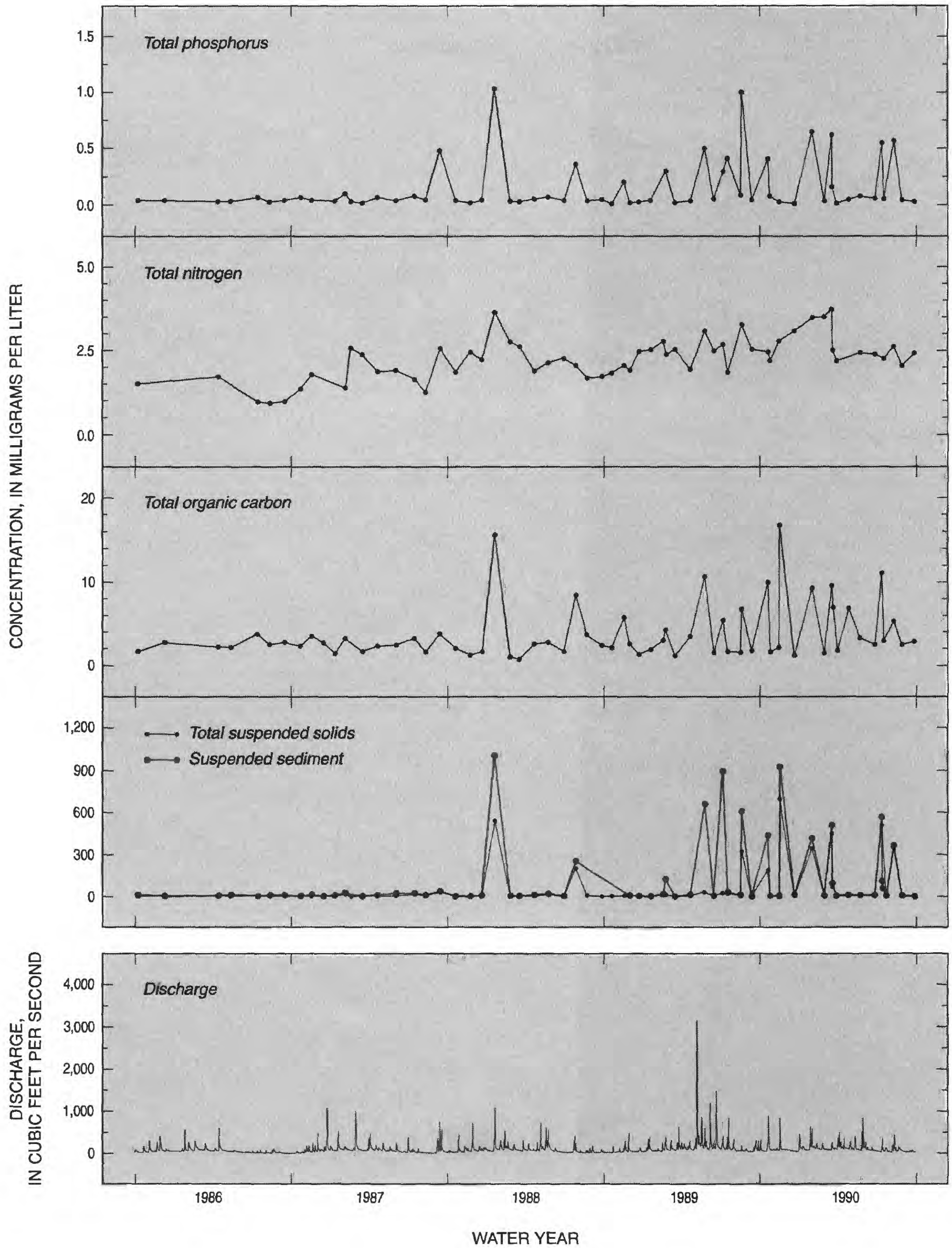


Figure 4. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Savage monitoring site, water years 1986-90.

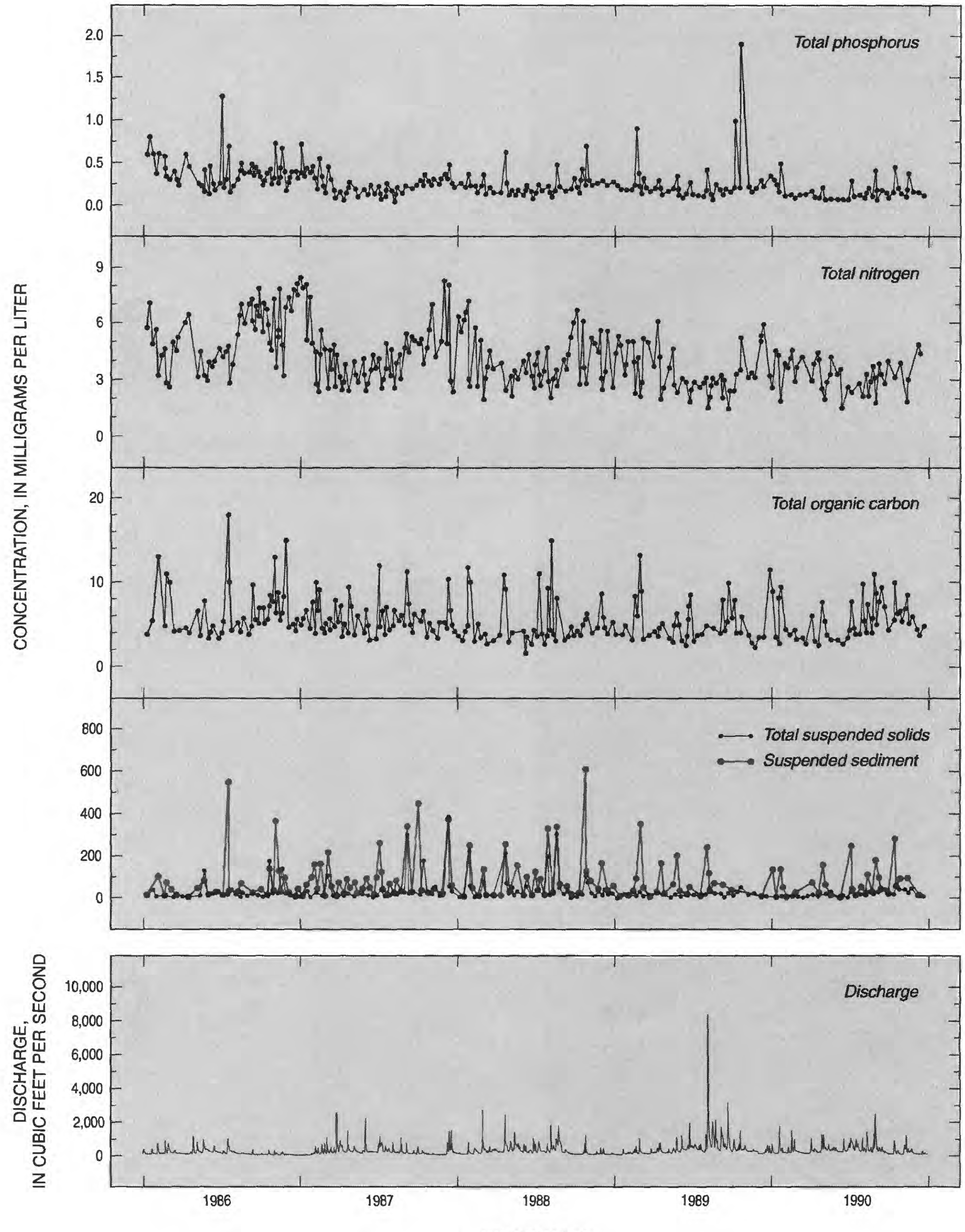


Figure 5. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Bowie monitoring site, water years 1986-90.

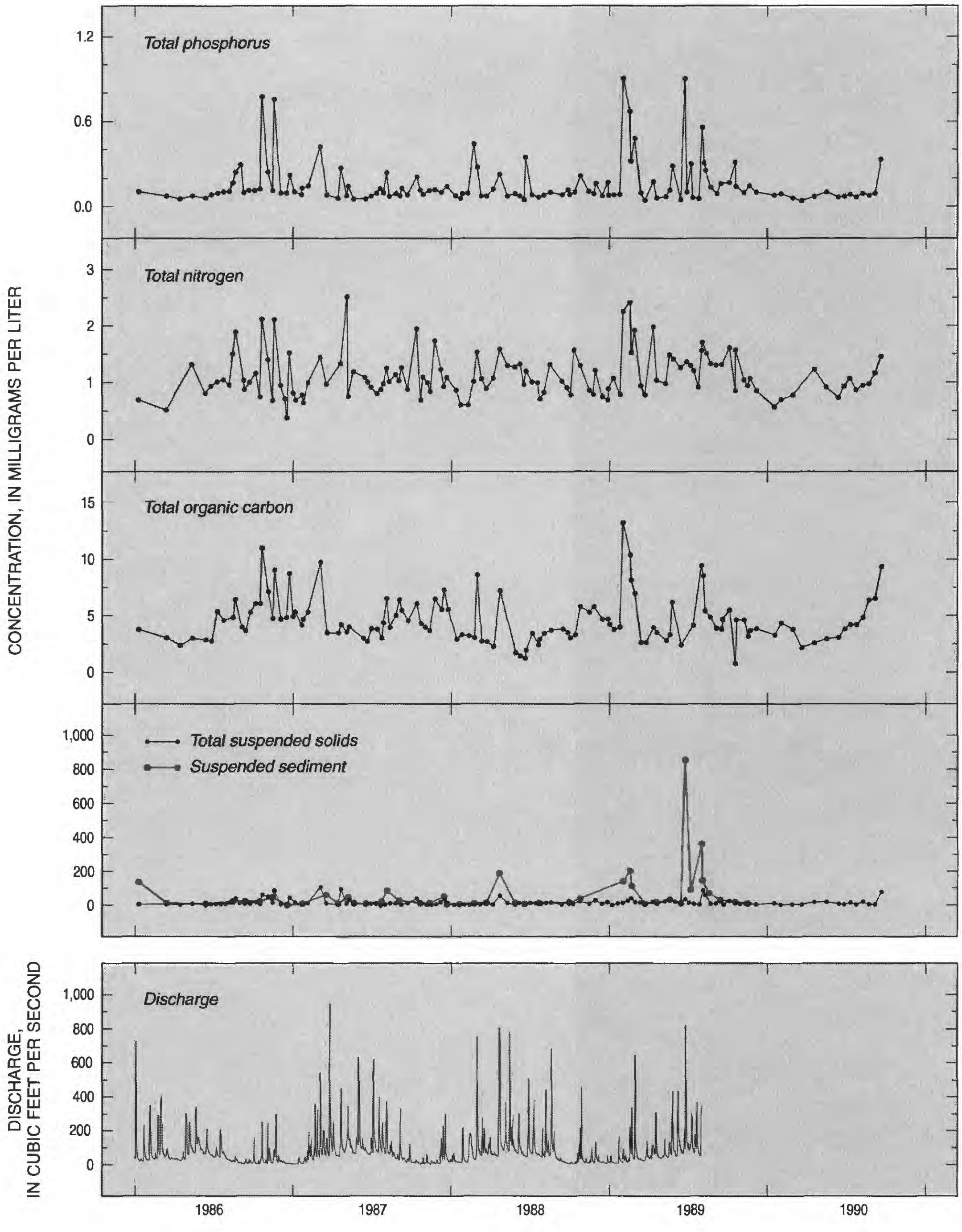


Figure 6. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Western Branch monitoring site, water years 1986-90.

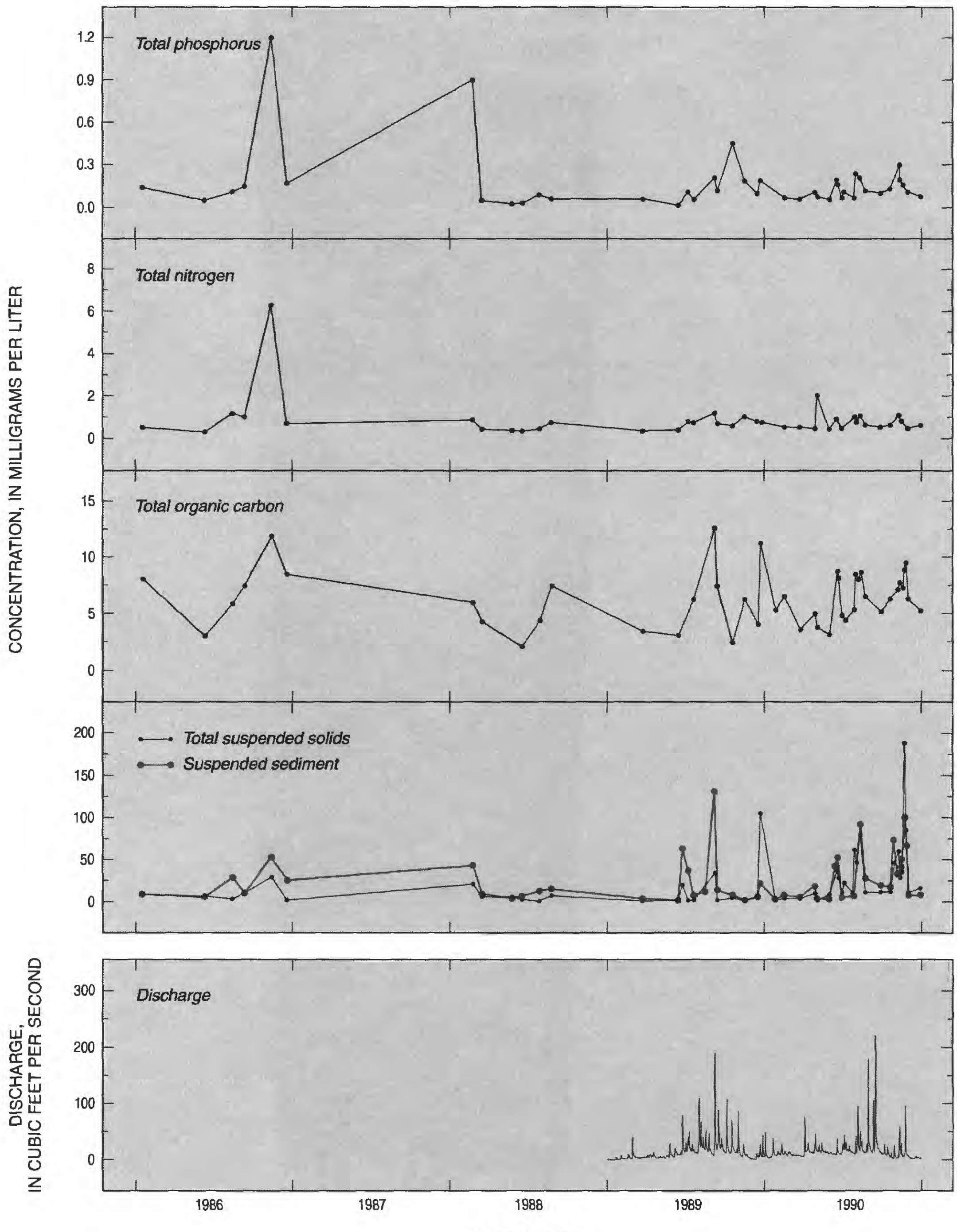


Figure 7. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Hunting Creek monitoring site, water years 1986-90.

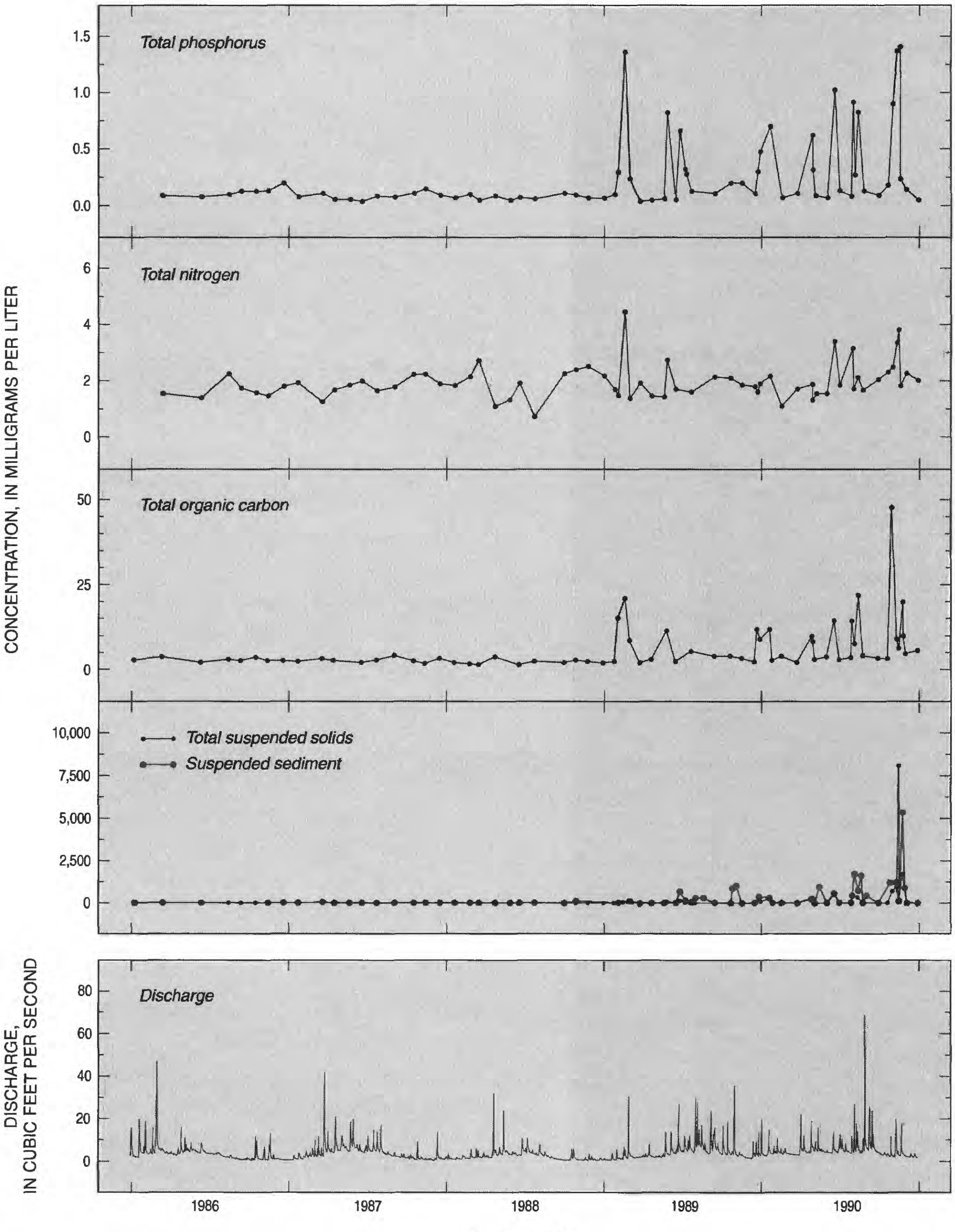


Figure 8. Total phosphorus, total nitrogen, total organic carbon, total suspended-solids and suspended-sediment concentrations, and discharge time series at the Killpeck Creek monitoring site, water years 1986-90.

Constituent concentration data are summarized in tables 3-8. Included in these tables are the number of data available for load estimation, the number of data that are less than reporting limits and descriptive statistics. The number of data available is important to interpret the quality of load estimates because accuracy and precision often are related to the number of sample data. At many sites, data frequency increased through the period of record as sampling methods and equipment were refined and improved. The number of constituent concentrations less than a reporting limit is important to assess the potential effect of substituting reporting limits for values less than reporting limit.

For most constituents in most water years, the number of constituent concentrations that were less than reporting limits is small. The largest number of constituent concentrations less than a reporting limit value was for total suspended solids, because suspended-solids concentrations are normally quite low during base-flow sampling. Substitution of reporting limits for actual total suspended solids data is expected to have minimal effect on the accuracy of load estimates, because the reporting limit is quite low (less then 1.0 mg/L) and because most total suspended-solids concentrations that are less than reporting limits are measured during low-flow conditions. Thus, loads during periods when suspended-solids concentrations were less than reporting limits are a small part of the total loads.

Data availability is illustrated further by time-series plots in which the daily constituent concentrations and discharges are plotted against time for each site (figs. 3-8). Time-series figures are included to indicate temporal variations in the numbers and the types (base-flow or storm) of sample data. The type of sample data is important for interpreting estimate quality because the number of high-discharge data affects load-estimate accuracy and precision.

The temporal consistency of water-quality data collection varies by monitoring site. Bowie is the only monitoring site at which the number and type of data are consistent throughout the record. At the Savage, Hunting Creek, and Killpeck Creek sites, data were collected less frequently during the first three water years, and high-discharge concentration data were recorded most frequently during water years 1989 and 1990. At the Unity and Western Branch monitoring sites, high-discharge concentration data were collected sporadically during the entire study period. Complete mean daily discharge records are available for most of the sites during the water years in which load is estimated; water year 1989 at the Western Branch site was the only partial discharge record used for load estimation.

Descriptions of Selected Load Estimators

In order to estimate constituent loads for the Patuxent monitoring sites, two statistical estimators were considered. The seven-parameter model described by Cohn and others (1989) is a statistical regression model that predicts concentration on non-sample days on the basis of trend, seasonality and hydrologic variability. The model is designed to be used in situations where there are water-quality data for more than 10 years that can be used for model calibration. Water-quality data for most of the Patuxent monitoring sites are available for 5 years or less, with varying data frequencies. For that reason, a simpler statistical model also was considered. The ratio estimator was originally proposed for load estimation by Dolan, Yui, and Geist (1981) and has been shown to provide unbiased load estimates for modest sampling rates (Young, DePinto, and Heidtke, 1988). The ratio estimator typically provides unbiased estimates but might not always provide a level of precision that is greater than other estimators.

Constituent loading in tributaries is a continuous process that can be represented as the product of concentration and discharge through time. Tributary mass load is defined as the cumulative load for a specified period of time and can be defined mathematically as the integral of the product of concentration and discharge through time:

$$L = \int_{1}^{T} C(t)\, Q(t)\, dt \quad , \qquad (1)$$

where

L = the load through the time period (mass);

$C(t)$ = concentration at time t (mass/volume);

$Q(t)$ = discharge at time t (volume/time); and

T = load estimation time period.

Typically, discharge is measured continuously with automatic data recorders and stage-discharge relations. Concentrations usually are measured discretely, however, by collecting water samples for laboratory analysis. Thus, tributary loads need to be estimated discretely by using a finite number of concentration data.

Collected samples are assumed to be representative of a tributary cross section and a specified time period (Δt). The total period (T) for which the load is to be estimated is divided into a finite number of smaller periods (Δt). The total number of smaller periods (N) represents the pool from which a relatively small number of samples (n) is drawn. Assuming that the sampling periods are equally weighted and evenly divided, the discrete approximation of equation (1) can be expressed as:

$$L = \sum_{i=1}^{T/\Delta t} C_i Q_i \Delta t \quad , \qquad (2)$$

where

C_i = i th concentration, and

Q_i = discharge associated with the i th concentration measurement.

Typically, mass load is estimated for a year during which the maximum sampling frequency is daily (N=365). A monthly sampling program would collect samples from 12 of the 365 potential sample days, for a sampling rate of 3.3 percent.

The size of the sampling fraction (n/N) is determined on the basis of the constraints of the sampling program. Error can be minimized by collecting a large number of samples. Concentration measurements are expensive, however, and a practical balance needs to be maintained between an acceptable level of error and cost. Concentration measurements are usually collected in low frequency; for example, less than 10 percent of the possible samples. Thus, the optimal placement and use of those data are important objectives for limiting the amount of error.

Load-estimate error can be minimized by use of a statistical model (estimator) to predict concentration on nonsample days. Typically, mass-load estimators use sample data to define a concentration-discharge relation. That concentration-discharge relation then is used to predict concentrations on days when only discharge data might be available. Mass loads then are estimated using actual and predicted concentration data in equation 2. Concentration-discharge relations for mass-load estimation are often defined using regression models. For example, rating curves (log-log concentration-discharge regression models) commonly have been used to estimate the loads of dissolved and particulate water-quality constituents (Walling, 1977). Other estimators use estimates of concentration-discharge covariance and combine them with aggregation methods for mass-load estimation (El-Shaarawi and others, 1986).

The seven-parameter model considered in this study is a multivariate log-linear regression model that predicts concentration on the basis of discharge and temporal trend variables (Cohn and others, 1992). The form of the seven-parameter model is:

$$\begin{aligned} ln(C) = {} & \beta_0 + \beta_1 ln\left[\frac{Q}{\overline{Q}}\right] + \beta_2 ln\left[\frac{Q}{\overline{Q}}\right]^2 \\ & + \beta_3(T-\overline{T}) + \beta_4(T-\overline{T})^2 \\ & + \beta_5 \sin(2\pi T) + \beta_6 \cos(2\pi T) + \varepsilon \, , \qquad (3) \end{aligned}$$

where

β_0 - β_6 = model parameters;

T = time (years);

$\bar{Q}$ and $\bar{T}$ = centering variables (Cohn and others, 1992); and

ε = model error.

The model has a maximum of seven parameters: an intercept, two discharge parameters and four time parameters. Of the seven parameters, a subset usually is selected on the basis of the ability of individual terms to account for variations in concentration. Thus, the appropriate number of parameters in the model (as many as seven) is determined statistically in order to maximize the precision of concentration estimates.

Independent variables in the seven-parameter model are both linear and nonlinear. A quadratic discharge term is included to account for the possibility of a nonlinear log relation between concentration and discharge. Similarly, linear and quadratic time variables are included to account for possible nonlinear trends in the long-term average of concentration. Cyclical variations in concentration often occur on a seasonal basis; thus, trigonometric functions are included to account for possible seasonal effects. $\bar{Q}$ and $\bar{T}$ are "centering" variables that are defined to reduce covariance among the independent variables and enhance estimate precision (Cohn and others, 1992).

Estimates from log-linear models often suffer from bias caused by retransformation from log to real space. That bias is usually corrected by multiplying the estimate by a term that is commonly referred to as a "bias correction factor" (BCF). Cohn and others (1989) evaluated the BCF of Bradu and Mundlak (1970) and found that it was more accurate than other proposed BCF's and that it provided theoretically defined minimum-variance estimates. The BCF of Bradu and Mundlak (1970) was incorporated, therefore, as part of the normal application of the seven-parameter model.

In order to evaluate load-estimate quality, precision often is assessed using statistical formulas that have been derived for each estimator. Gilroy and others (1990) derived an expression for calculating load-estimate variance from the minimum-variance unbiased estimator (MVUE) of Bradu and Mundlak (1970). Evaluation of that expression indicated that it accurately estimated MVUE load-estimate variance. Because the method was developed for the MVUE and was found to be accurate, standard errors of load estimates from the seven-parameter model were estimated using the expression derived by Gilroy and others (1990).

The seven-parameter model has been used to estimate nutrient and suspended-sediment loads from major Chesapeake Bay tributaries including the Susquehanna, Potomac, Patuxent, and Choptank Rivers (Maryland Department of the Environment, 1993). In that study, the seven-parameter model was used to estimate the loads of various water-quality constituents for a 10-year period.

Data requirements for the seven-parameter model are greater than those of simpler load-estimation models. Data should be available for a substantial length of time to estimate temporal component parameters accurately. Data also should be available in sufficient numbers to precisely estimate all seven model parameters. Data from the Patuxent monitoring sites were recorded only for a short period of time (less than 5 years) and for varying frequencies. Application of the seven-parameter model with insufficient data could lead to poor load-estimate accuracy and precision.

As an alternative to the seven-parameter model, the ratio estimator also was applied for load estimation at the Patuxent monitoring sites. The ratio estimator is much simpler than the seven-parameter model in that it is based on a simple relation between load and discharge and requires estimation of only one parameter value. Evaluations have indicated that the ratio estimator usually provides unbiased load estimates at modest sampling rates but might not provide the minimum-variance estimate (Young, DePinto, and Heidtke, 1988; Preston, Bierman, and Silliman, 1992). Lack of bias (accuracy) is a valuable quality in that it indicates that the estimate will, on average, be correct. Variance should be evaluated by calculating confidence intervals for load estimates.

Different forms of the ratio estimator have been proposed in the statistical literature and have been compared for load estimation (Preston, Bierman, and Silliman, 1989). Beale's ratio estimator (Tin, 1965) performed as well or better than the other ratio estimator forms and was selected because it has been commonly applied for load estimation. Beale's ratio estimator is defined by the expression:

$$\hat{L} = Q\hat{R}\left[\frac{1+\left[\frac{1-f}{n}\right]\left[\frac{S_{lq}}{(\bar{l})(\bar{q})}\right]}{1+\left[\frac{1-f}{n}\right]\left[\frac{S_q^2}{\bar{q}^2}\right]}\right], \qquad (4)$$

where

$\hat{L}$ = estimated mass load;

Q = total discharge volume for estimation period;

$\hat{R}$ = load/discharge ratio;

f = sampling fraction (n/N);

n = number of samples collected;

N = total number of possible samples;

S_{lq} = sample covariance between load and discharge;

S_q^2 = sample variance of discharge;

$\bar{l}$ = mean load; and

$\bar{q}$ = mean discharge.

The parameter $\hat{R}$ is the ratio between load and discharge and is defined by:

$$\hat{R} = \left[\frac{\bar{l}}{\bar{q}}\right]. \qquad (5)$$

The simple ratio estimator consists of the total flow volume (Q) multiplied by the load-discharge ratio ($\hat{R}$). The bracketed term in equation 4 is designed to counteract statistical bias.

Empirical evaluations indicate that the ratio estimator provides unbiased mass-load estimates for modest sampling rates and for a broad range of tributary types (Preston, Bierman, and Silliman, 1992). The ratio estimator is known to be a "Best Linear Unbiased Estimator" (BLUE) under two conditions (Cochran, 1977):

(1) The relation between l_i (load) and q_i (discharge) is a straight line through the origin; and

(2) The variance of l_i about this line is proportional to q_i.

These conditions usually are approximated by the relation between load and discharge. For that reason, the ratio estimator typically provides unbiased estimates.

Because the ratio estimator is sometimes less precise than other estimators, it is important for interpretation of load-estimate quality to be able to estimate confidence intervals for the load estimate. Tin (1965) derived expressions for estimating ratio-estimator precision. Tin's expression for the variance of Beale ratio estimates is:

$$V(\hat{L}) = Q^2\hat{R}^2\left[\left[\frac{1-f}{n}\right]\left[\frac{S_q^2}{\bar{q}^2}+\frac{S_l^2}{\bar{l}^2}-\frac{2S_{lq}}{\bar{l}\bar{q}}\right] + \left[\frac{1-f}{n}\right]^2\left[\frac{2S_q^4}{\bar{q}^4}-\frac{4S_q^2S_{lq}}{\bar{q}^3\bar{l}}+\frac{S_{lq}^2}{\bar{l}^2\bar{q}^2}+\frac{S_q^2S_l^2}{\bar{q}^2\bar{l}^2}\right] + \frac{2}{N}\left[\frac{1-f}{n}\right]\left[\frac{S_q^3}{\bar{q}^3}-\frac{2S_q^2S_l}{\bar{q}^2\bar{l}}+\frac{S_qS_l^2}{\bar{q}\bar{l}^2}\right]\right], \qquad (6)$$

where

$V(\hat{L})$ = load-estimate variance, and

S_i^2 = sample variance of load.

Bodo and Unny (1984) used a modified version of Tin's expression for estimating the variance of load estimates that were calculated using Beale's ratio estimator. The modified version of equation 6 included the first two terms within the brackets but dropped the third term under the assumption that it was insignificant. Equation 6 has received little evaluation for estimating the variance of tributary mass-load estimates.

Comparison of Estimators at the Bowie Monitoring Site

In order to provide a basis of estimator evaluation, the seven-parameter model and Beale's ratio estimator were used to estimate constituent loads at the Bowie monitoring site. True evaluation of the estimators cannot be performed because the actual load at the Patuxent monitoring sites is unknown; however, comparison of two different models could indicate primary causes of load-estimate error. The seven-parameter model has received detailed statistical evaluation using data from the Bowie monitoring site (Cohn and others, 1992). Comparison of the ratio estimator to the more detailed seven-parameter model at a site where it has already been evaluated provides a basis for verification of the accuracy and precision of the ratio estimator.

The Bowie monitoring site was used for estimator evaluation because it has a more extensive set of concentration and discharge data than the other Patuxent sites. Constituent loads at the Bowie site are assumed to be representative of loads entering the tidal part of the Patuxent River from the nontidal part of the watershed. For that reason, the Bowie site has been given greater importance than other Patuxent sites. Consequently, sampling was performed more frequently and for a longer period of time than at other sites. Concentration data are available from 1978 to the present, although only data from 1978-1988 have been used here for comparison of methods.

Both the seven-parameter model and the ratio estimator were used to estimate annual and monthly constituent loads at Bowie. Use of the seven-parameter model for annual and monthly load estimation has been described by Cohn and others (1992) and Maryland Department of the Environment (1993). Because the seven-parameter model can account for temporal shifts, only one set of parameters was estimated for the entire study period. The ratio estimator cannot account for long-term shifts and was applied separately for each year of record. Annual load estimates were disaggregated to form monthly load estimates by applying the monthly discharge volume to the annual estimate of the ratio; thus, monthly loads were estimated as:

$$\hat{L}_i = Q_i \hat{R} \left[\frac{1 + \left[\frac{1-f}{n}\right]\left[\frac{S_{lq}}{(\bar{l})(\bar{q})}\right]}{1 + \left[\frac{1-f}{n}\right]\left[\frac{S_q^2}{\bar{q}^2}\right]} \right] , \qquad (7)$$

where $\hat{L}_i$ and Q_i are the load and flow volume, respectively, in month *i*. All other parameters were estimated on an annual basis.

The ratio estimator was applied in an unstratified and in a stratified form. Stratification is a technique in which separate estimates are calculated for high and low discharge and then combined for a total load (Cochran, 1977). The technique provides improved estimate precision when sufficient data are available in all strata. The technique provides the greatest benefits when the sampling program is designed for it, but improved precision also can be achieved by stratifying data after they are collected. In this study, the ratio estimator was applied in an unstratified form during all years and in a stratified form if sufficient data were available during high-flow periods.

To compare the seven-parameter model and the ratio estimator, annual and monthly loads of four constituents (total phosphorus, total nitrogen, total organic carbon, and suspended sediment) were estimated from 1978 to 1988. Comparisons of the three types of estimates are indicated in figures 9 through 12 (annual load estimates) and in figures 13 through 16 (monthly load estimates). Precision was evaluated by comparing the standard errors of the estimators, which are illustrated by shaded areas around the estimates in figures 17 through 20.

For most constituents, during most years, all three types of estimators are consistent in the estimation of annual loads (figs. 9-12). Large differences are apparent for total phosphorus, total organic carbon, and suspended sediment during 1979, however, and for suspended sediment during 1983. In each of these cases, loads from the seven-parameter model were substantially higher than loads from both types of ratio estimators. Reasons for these differences cannot be determined with certainty because the actual loads are unknown. Study of the conditions under which the estimators are applied indicates possible reasons for the differences, however.

Comparison of monthly load estimates (figs. 13-16) indicates that the seven-parameter model load estimates are higher than those of the ratio estimator during months in which high discharge events occurred. Figure 21 illustrates the annual, monthly, and daily discharge time series for the Patuxent River at Bowie monitoring site. Some of the highest flows of the study period occurred during February and September of calendar year 1979, and the seven-parameter model predicted total phosphorus, total organic carbon, and suspended-sediment loads during those months that were much higher than average. Those three constituents increased substantially with high discharge and exhibited increasing concentration-discharge relations. Therefore, it can be inferred that the differences between the two estimators could be related to the way that the seven-parameter model predicts the high-discharge concentrations of constituents with substantially increasing concentration-discharge relations.

The differences between the two types of estimators is most likely related to the assumptions that are implicit in applying them outside of the range of discharge for which concentration data are available for calibration. At the Bowie monitoring site, concentration data are available for a discharge range that is much smaller than the range for which estimation should be performed. For example, 8 of 439 total phosphorus data used for calibration are associated with discharge values greater than 2,000 ft^3/s, and no total phosphorus data are available for discharges greater than 4,000 ft^3/s. Total phosphorus loads need to be estimated at discharges that exceed 8,000 ft^3/s, however. Given that it is necessary to extrapolate beyond the calibration range for load estimation at the Bowie monitoring site, the assumption that the concentration-discharge relation does not change as discharge increases is implicit to the use of either type of estimator.

On the basis of the results of model calibration, the seven-parameter model indicates that total phosphorus concentrations are diluted at low discharge but then continue to increase as discharge increases (Cohn and others, 1992; Maryland Department of the Environment, 1993). Total phosphorus concentration would be expected to increase through a part of the discharge range in conjunction with sediment resuspension, and evaluation of the calibration data confirms that total phosphorus increases in the discharge range of 1,000 to 4,000 ft^3/s. It is not clear, however, that phosphorus concentration will continue to increase through the highest discharges observed at the site. It is possible, therefore, that the seven-parameter model could overestimate the loads of some constituents during high-discharge periods.

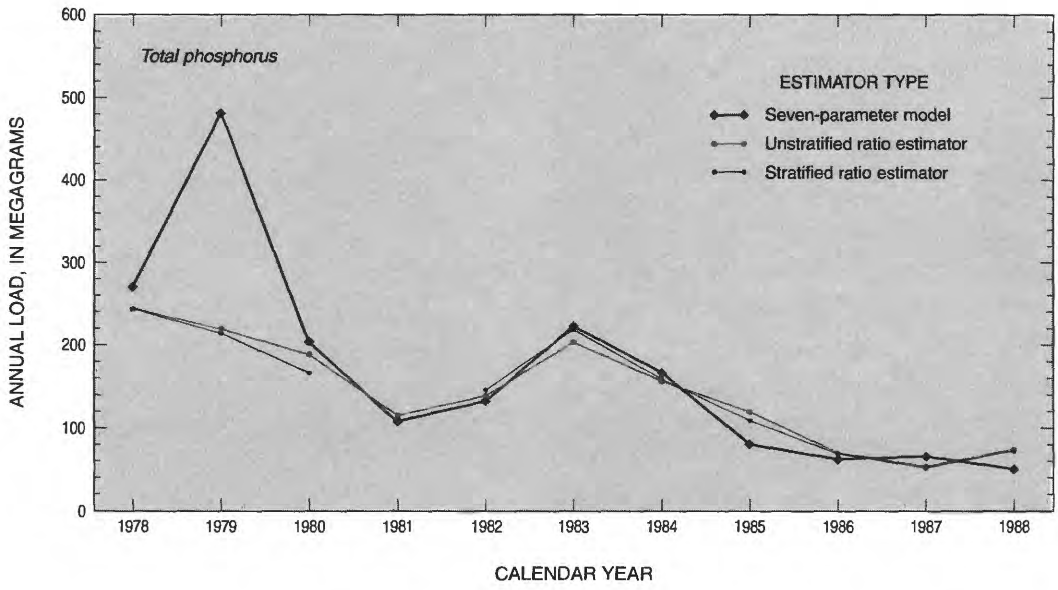


Figure 9. Annual total phosphorus load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

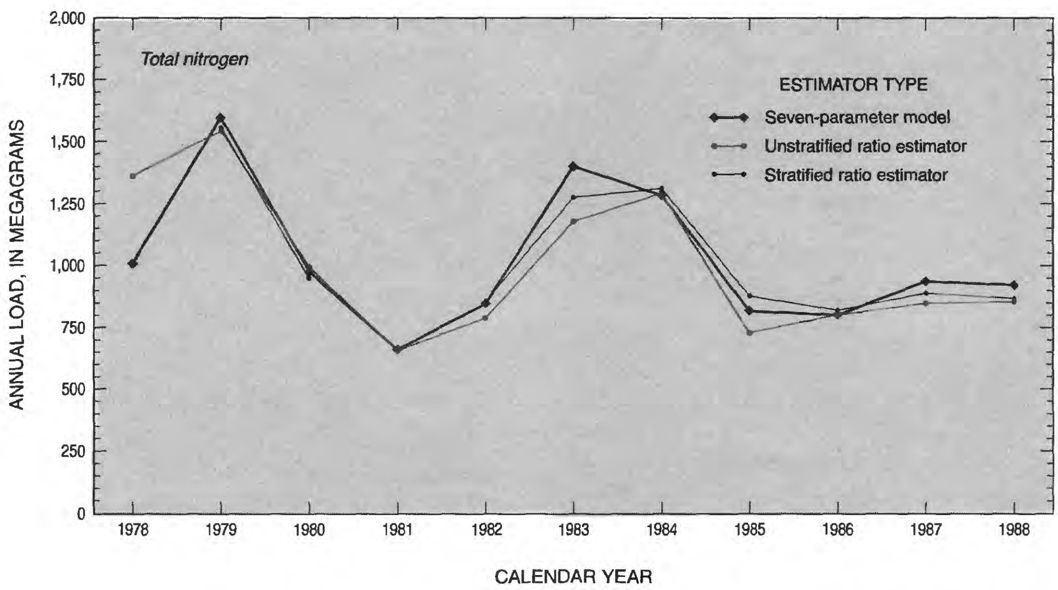


Figure 10. Annual total nitrogen load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

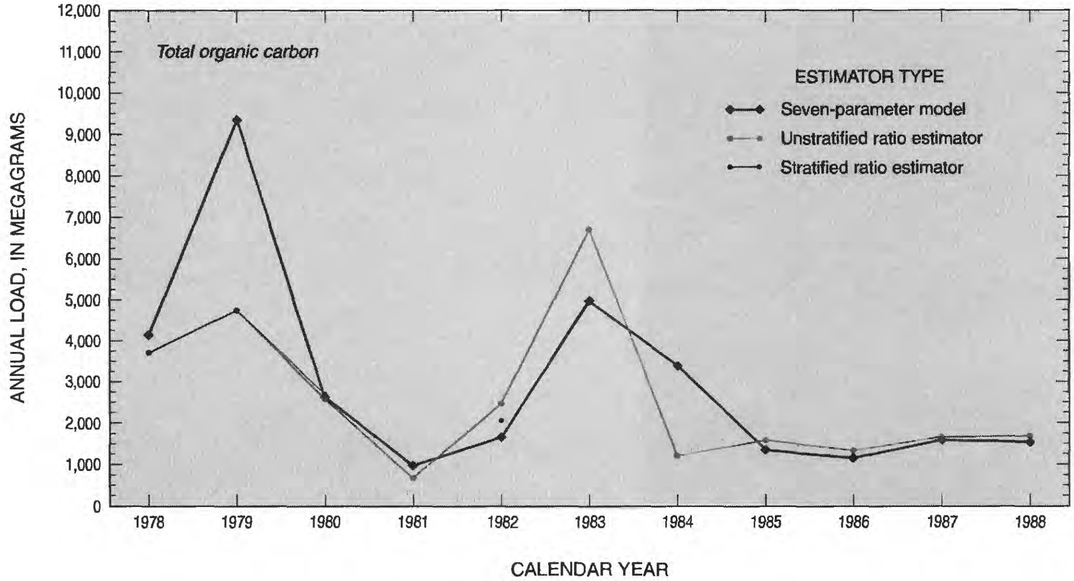


Figure 11. Annual total organic carbon load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

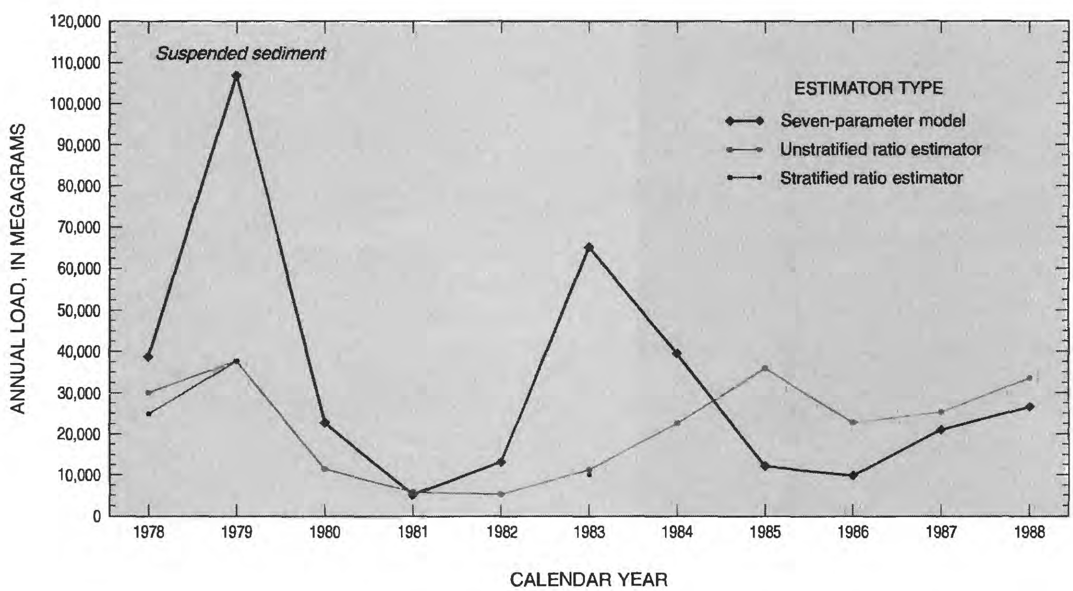


Figure 12. Annual suspended-sediment load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

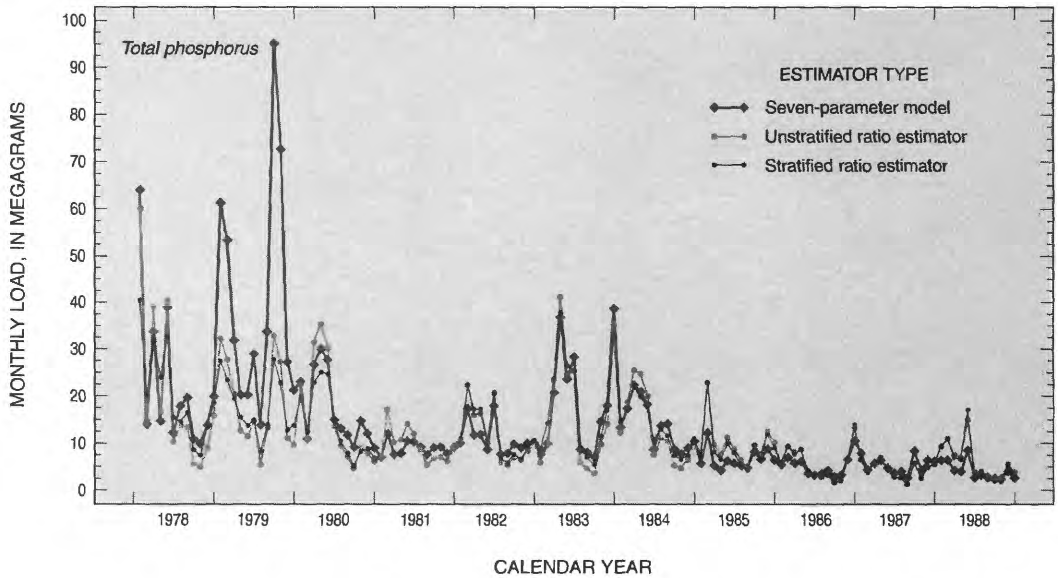


Figure 13. Monthly total phosphorus load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

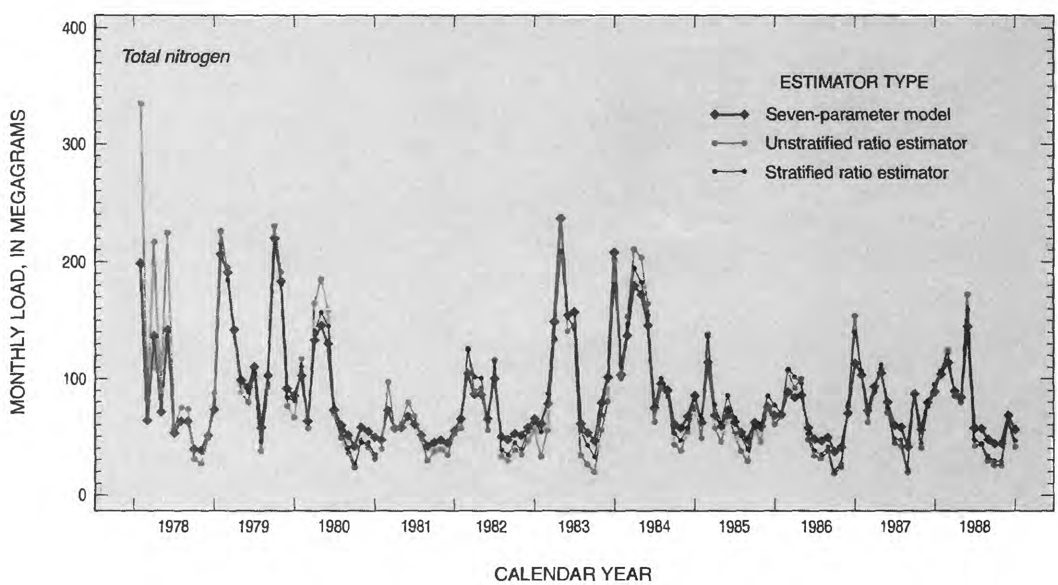


Figure 14. Monthly total nitrogen load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

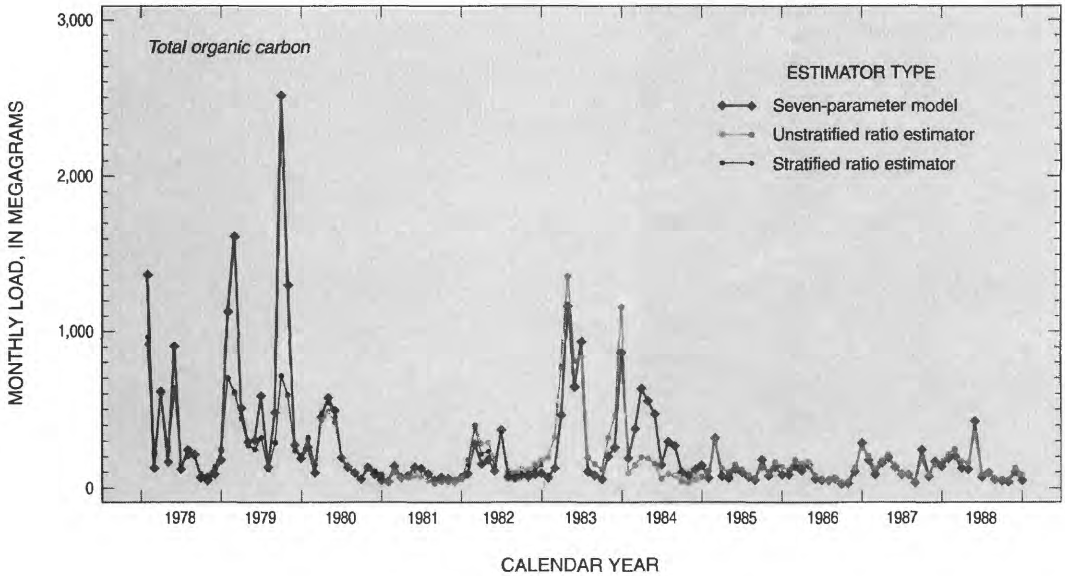


Figure 15. Monthly total organic carbon load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

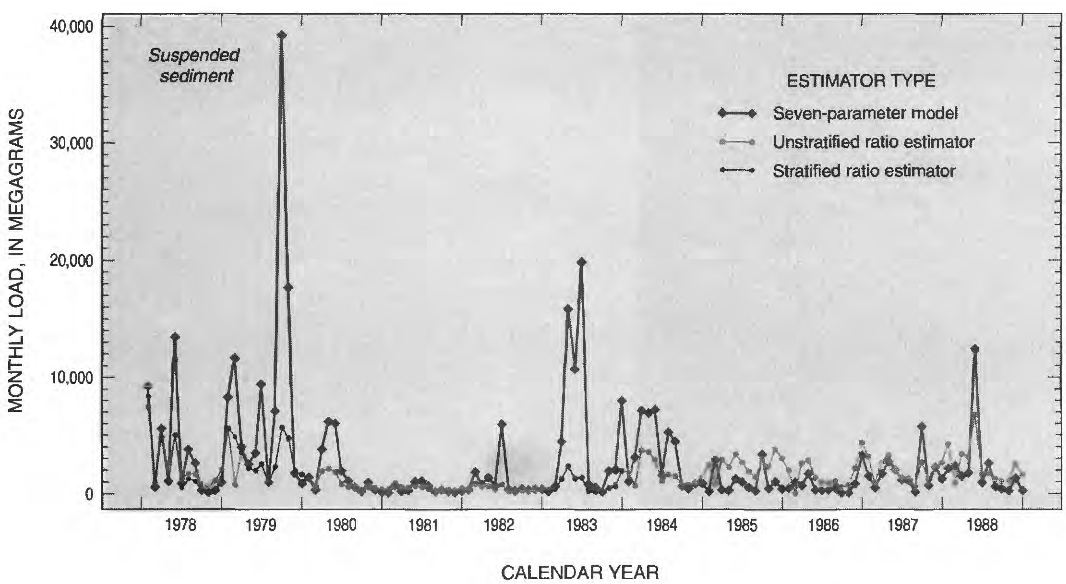


Figure 16. Monthly suspended-sediment load estimates for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

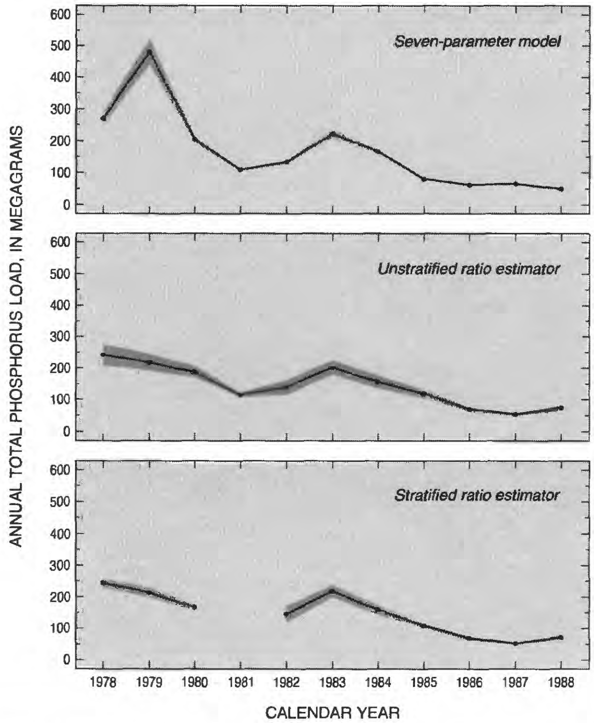


Figure 17. Annual total phosphorus load estimates and standard errors for the Patuxent River at Bowie monitoring site, calendar years 1978-88. [Darker shading represents one standard error above and below the load estimate.]

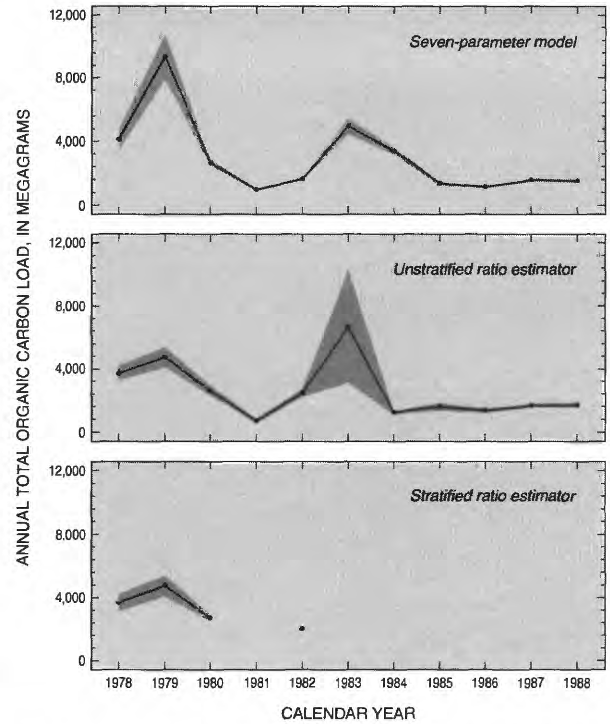


Figure 19. Annual total organic carbon load estimates and standard errors for the Patuxent River at Bowie monitoring site, calendar years 1978-88. [Darker shading represents one standard error above and below the load estimate.]

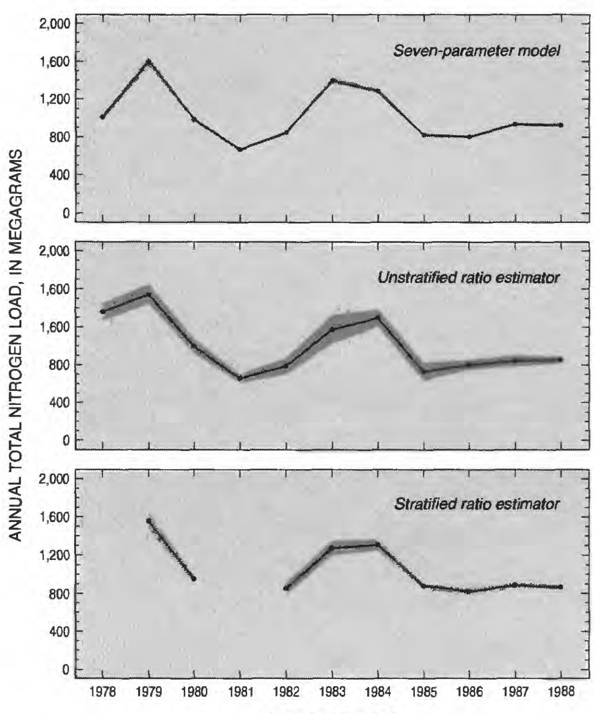


Figure 18. Annual total nitrogen load estimates and standard errors for the Patuxent River at Bowie monitoring site, calendar years 1978-88. [Darker shading represents one standard error above and below the load estimate.]

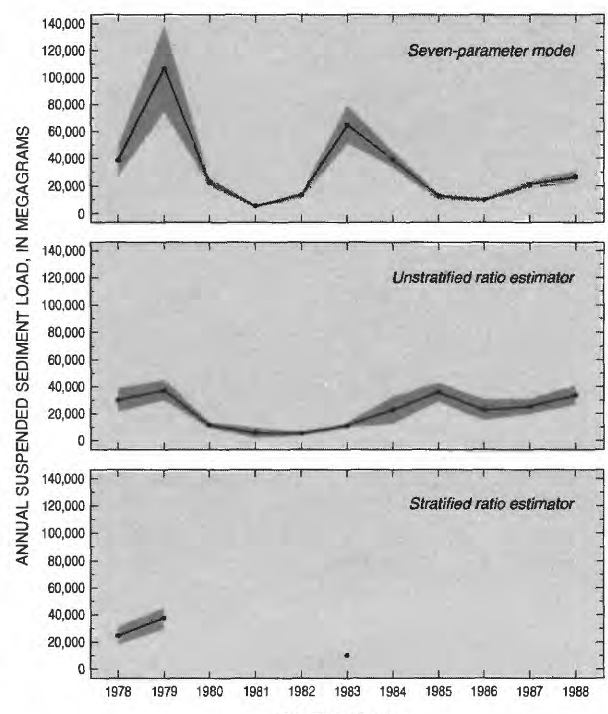


Figure 20. Annual suspended-sediment load estimates and standard errors for the Patuxent River at Bowie monitoring site, calendar years 1978-88. [Darker shading represents one standard error above and below the load estimate.]

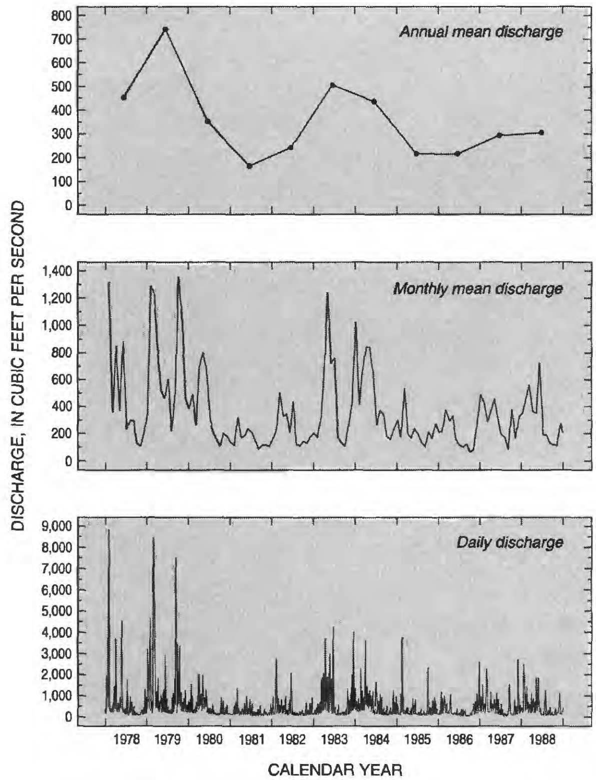


Figure 21. Annual, monthly, and daily discharge time series for the Patuxent River at Bowie monitoring site, calendar years 1978-88.

In contrast to the seven-parameter model, the ratio estimator assumes that the relation between load and discharge is consistent throughout the discharge range. Typically, the ratio estimator is unbiased, provided that sufficient data are available throughout the discharge range. Insufficient numbers of data in the high-flow range could lead to underestimation of loads, however. Because the ratio estimator is applied here on an annual basis, the number of high-flow data is potentially insufficient during any given year and would thus cause underestimation of load. For example, during 1979, only 4 of 22 samples were collected at discharges greater than 1,000 ft^3/s, and no samples were collected at discharges greater than 2,500 ft^3/s. Since discharges ranged to as much as 8,400 ft^3/s during 1979, it is possible that the ratio estimator could have underestimated loads for that year.

In general, the two estimators provide similar load estimates provided that adequate data are available throughout the range of discharge. Because adequate data are not always available, the assumptions of each estimator should be understood and the quality of load estimates should be assessed on the basis of how well the data meet the estimator assumptions. On the basis of application of the estimators to data for the Patuxent River at Bowie monitoring site, the seven-parameter model could overestimate loads of some constituents in years with discharges beyond the calibration range. Similarly, the ratio estimator could underestimate loads if an insufficient number of high discharge samples are collected. If sufficient data were available throughout the discharge range, it is likely that the loads from all estimators would converge even during extreme high-discharge periods.

Precision is a measure of the random error about a given estimate. Typically, precision is assessed by calculating the standard error of the estimate using sample data; a smaller standard error indicates a more precise estimate. Assuming that the estimate is accurate, the standard error can be used to estimate a range in which the actual load is likely to occur. A narrower range indicates greater certainty in the estimate.

Precision of the load estimates for Patuxent River at Bowie is indicated by shaded areas in figures 17 through 20 that are defined by one standard error above and below the estimate. For most constituents in most years, the seven-parameter model provides very precise annual load estimates. The ratio estimator is less precise, but standard errors are within 10 percent of the estimate for most years. Stratification is a statistical technique that is designed to enhance estimate precision and as might be expected, the stratified ratio estimator is more precise than the unstratified version for years where adequate numbers of high-discharge concentration data are available.

The precision of both the seven-parameter model and ratio-estimator estimates is greatest for total phosphorus and total nitrogen. The seven-parameter model precision is lower for total organic carbon and for suspended sediment during high discharge years because the model was used to estimate concentrations beyond the calibration range of discharge. Precision of the total organic carbon load estimates using the unstratified ratio-estimator is poor for 1983 because the concentration of total organic carbon was quite variable during that year. The ratio estimator may be more susceptible to high variability during any given year because it is applied on a year-by-year basis. Because the seven-parameter model is applied to the entire time period, it may be less likely to be affected by high variability during any single year.

Comparison of Estimators at Patuxent Monitoring Sites During Calendar Years 1986-89

In order to further evaluate the estimators, the seven-parameter model and the ratio estimator were compared by using them to estimate loads at all Patuxent monitoring sites for calendar years 1986-89. Constituent data from most Patuxent sites are available in lower frequency and for a shorter time period than data from the Bowie site. Estimator performance needs to be evaluated when applied using shorter, less detailed data records, and comparison of the two types of estimators provides a basis for evaluation. The seven-parameter model and the ratio estimator were applied on a calendar year basis because the seven-parameter model is designed to estimate calendar-year loads.

In order to compare load estimates at the Patuxent sites for the 4-year period, estimators were applied as described in the previous section. The ratio estimator was applied in both unstratified and stratified forms and was calibrated separately for each year. The seven-parameter model was applied at the Bowie monitoring site in the manner described by Cohn and others (1992) and Maryland Department of the Environment (1993). Calibration was performed for a 10-year window that extended through the period immediately preceding the end of the last estimation year. For example, seven-parameter model loads for calendar years 1986-89 were estimated using a model that was calibrated for 1980-89. For all other sites, seven-parameter model loads were estimated using models that were calibrated with all available data from calendar years 1986-89.

An advantage of the seven-parameter model is that statistical diagnostics can be used to evaluate load-estimate quality. A great deal of research has focused on refining multiple-regression techniques, and the use of statistical diagnostics has become a normal part of regression-model application. Statistical diagnostics, such as the coefficient of determination (r^2), provide an indication of the amount of variance explained by the model. Other diagnostics (T-tests) indicate the relative importance of different model components in accounting for constituent variability. The information gained from statistical diagnostics is often an important clue to determining the quality of load estimates that are based on model calibration.

Statistical diagnostics and parameter estimates for the seven-parameter model applications are summarized in table 9. All regressions were significant at the significance level (α) of 0.05, although the coefficients of determination were often quite low (for example r^2=16.8 for total nitrogen at Killpeck Creek). The amount of variance accounted for varied by monitoring site and constituent. Of all sites, the Savage site had the highest coefficient of determination values for all constituents, with values of 67.3 percent or greater. Strong relations between nutrient concentration and suspended sediment have been observed at this site. High coefficients of determination could be an indication that sediment transport induced by high discharge is a dominant factor affecting constituent loading.

Asterisks next to parameter values summarized in table 9 indicate significance at the $\alpha = 0.05$ level. In all except two cases (total nitrogen

Table 9. *Regression-model parameter estimates for the Patuxent monitoring sites during water years 1986-89*

[*ln*, natural logarithm; Q, flow factor; T, time; sin, sine; π, pi; cos, cosine; r^2, coefficient of determination; s, standard error; *, indicates significance at the α=0.05 level]

Monitoring site	Constituent	Constant	$(Q-\bar{Q})$	$[ln(Q-\bar{Q})]^2$	$(T-\bar{T})$	$(T-\bar{T})^2$	sin (2πT)	cos (2πT)	s	r^2
Unity	Total phosphorus	-2.75*	0.671*	0.100	-0.084	0.067	-0.502*	-0.330*	0.746	38.3
	Total nitrogen	1.09*	.182*	-.025	.019	-.008	-.031	-.014	.213	40.1
	Total organic carbon	.611*	.543*	.076	-.134*	.068	-.344*	-.164*	.542	42.6
	Total suspended solids	1.67*	1.30*	.166	-.128	.209*	-.528*	-.801*	1.09	53.4
	Suspended sediment	2.31*	1.16*	.260	-.110	.230	-.559	.856*	1.20	55.0
Savage	Total phosphorus	-2.79*	1.13*	.130*	-.128	.110	-.550*	-.511*	.610	75.9
	Total nitrogen	.840*	.111*	-.019	.105*	-.019	.049	.103*	.176	69.2
	Total organic carbon	.818*	.521*	.153*	-.015	.111*	-.177*	-.173*	.414	67.3
	Total suspended solids	1.67*	1.62*	.200	.107	.177	-.711*	-.637*	1.06	73.2
	Suspended sediment	2.46*	1.71*	.303*	-.139	.152	-.354	-.625*	.959	77.6
Bowie	Total phosphorus	-.914*	-.008	.040*	-.170*	-.012*	-.307*	-.112	.437	60.2
	Total nitrogen	1.26*	-.336*	.059*	-.009*	-.010*	-.016	-.003	.196	75.0
	Total organic carbon	1.92*	.338*	.037	-.067*	-.009*	-.227*	-.160*	.367	38.8
	Total suspended solids	3.22*	1.01*	-.031	-.068*	-.010	-.218*	-.642*	.747	48.6
	Suspended sediment	4.32*	.948*	-.232*	-.006	-.021*	-.381*	-.622*	.728	58.2
Western Branch[1]	Total phosphorus	-2.38*	.308*	.076*	-.125	.051	-.357*	-.398*	.440	45.3
	Total nitrogen	-.024	.169*	.011	-.038	.019	-.013	-.167*	.276	33.0
	Total organic carbon	1.27*	.204*	.060*	-.173*	.016	-.354*	-.406*	.204	76.1
	Total suspended solids	1.29*	.684*	.232*	-.153	.323	-.358*	-.806*	.858	48.3
	Suspended sediment	2.66*	.748*	.116	-.186	.091	-.397	-.727*	.798	53.9
Hunting Creek[1]	Total phosphorus	-1.93*	.334*	-.005	.252	-1.24*	-.243*	-.540*	.388	69.1
	Total nitrogen	-.271*	.148	.029	.003	-.380	-.042	-.104	.365	21.9
	Total organic carbon	1.76*	.186*	.040	.156	-.165	-.058	-.162	.341	38.5
	Total suspended solids	2.20*	.727*	.074	1.82*	.198	.004	-.229	.991	59.8
	Suspended sediment	2.50*	.876*	.061	1.02*	.685	.077	-.264	.751	68.1
Killpeck Creek	Total phosphorus	-2.28*	.595*	.212*	.095	.081	-.283*	-.230	.677	55.6
	Total nitrogen	.563*	-.012	.030	.052	.012	-.050	-.094	.288	16.8
	Total organic carbon	1.18*	.547*	.091	.071	.058	-.216*	-.091	.479	64.9
	Total suspended solids	1.52*	1.04*	.316*	.451*	.395*	-.079	-.186	1.23	65.8
	Suspended sediment	3.14*	1.20*	.264*	.234	.260*	-.002	-.795*	1.13	69.8

[1] Shortened calibration period due to limitations on discharge data--see table 2.

at the Hunting and Killpeck Creek monitoring-sites), discharge or squared discharge parameters were significant in the models. In most cases the estimated discharge parameters were positive, which indicates that constituent concentration increased with discharge. A negative discharge parameter for total nitrogen at the Bowie site, however, indicates a decrease in concentration with discharge, possibly caused by dilution (Maryland Department of the Environment, 1993). At least one of the time parameters was significant for all constituents at the Bowie site. A longer period of record at Bowie allows more definitive determination of long-term trends. Decreasing trends of most constituents at the Bowie site are assumed to be the result of upgrades of sewage-treatment plants directly upstream (Maryland Department of the Environment, 1993). Trends at other Patuxent sites are less definite because of the shorter period of record and because of changing frequency of data collection through the study period. Seasonal parameters are significant at many of the sites and indicate seasonal variation in the frequency of high-discharge events.

Comparisons of load estimates for the Patuxent monitoring sites are illustrated in figures 22 through 26. Estimators are compared by plotting annual load estimates with error bars (one standard error) for each constituent at each site. These figures do not include comparisons for the Bowie monitoring site, which were summarized previously in figures 9 through 20.

In most cases, estimators provide similar load estimates for all constituents at all sites; however, estimate precision varies substantially among years for some constituents. For example, suspended-sediment loads at the Unity monitoring site are similar for 1986 through 1988. In 1989, however, the seven-parameter model load estimate is substantially higher in value and is much less precise than the ratio estimators. Similar effects are observed at the Savage monitoring site.

Poor precision of the seven-parameter model estimates for 1989 is related to estimation beyond the calibration range. The highest sample discharge at the Unity site during the entire study period was 957 ft^3/s. During 1989, however, the mean daily discharge reached 1,390 ft^3/s. Similarly, the highest sample discharge at the Savage site was 1,334 ft^3/s, and mean daily discharge reached 3,150 ft^3/s during 1989. At these sites the model was used to estimate concentration values for days during which discharge far exceeded the calibration range. As indicated by total phosphorus loads at the Bowie site during 1979 (fig. 18), the seven-parameter model estimates tend to be much higher than ratio-estimator estimates when discharges exceeded the calibration range. The Unity and Savage sites have fewer high-flow samples and a shorter period of record, which make them more susceptible to error caused by estimation beyond the calibration range.

The effects of applying the seven-parameter model outside of its calibration range are observed primarily for constituents that increase substantially in concentration as discharge increases. Total suspended solids, suspended-sediment, and, to a lesser degree, total phosphorus loads, therefore, are most affected. Total nitrogen loads do not appear to be substantially affected because total nitrogen does not increase with discharge as much as other constituents do.

Load estimates made using the unstratified ratio estimator differ from estimates made using the seven-parameter model and the stratified ratio estimator in some cases. For example, unstratified ratio-estimator load estimates are higher and less precise than estimates made using the other estimators for all constituents at the Unity monitoring site for 1987. Similar examples were observed during 1988 at the Savage, Western Branch, and Killpeck Creek sites, and during 1989 at the Hunting Creek site.

The unstratified ratio estimator assumes that the same load-discharge relation exists during both low flow and high flow; thus, the potential for bias and poor precision can be created when samples are not collected in proportion to discharge. For example, if most samples are collected during low flow, the unstratified ratio estimator will extrapolate the low-flow load-discharge relation to high-flow conditions, which can result in an underestimation of load. These effects can be minimized by stratification. Research has demonstrated that, if sufficient data are available, the stratified ratio estimator can improve both

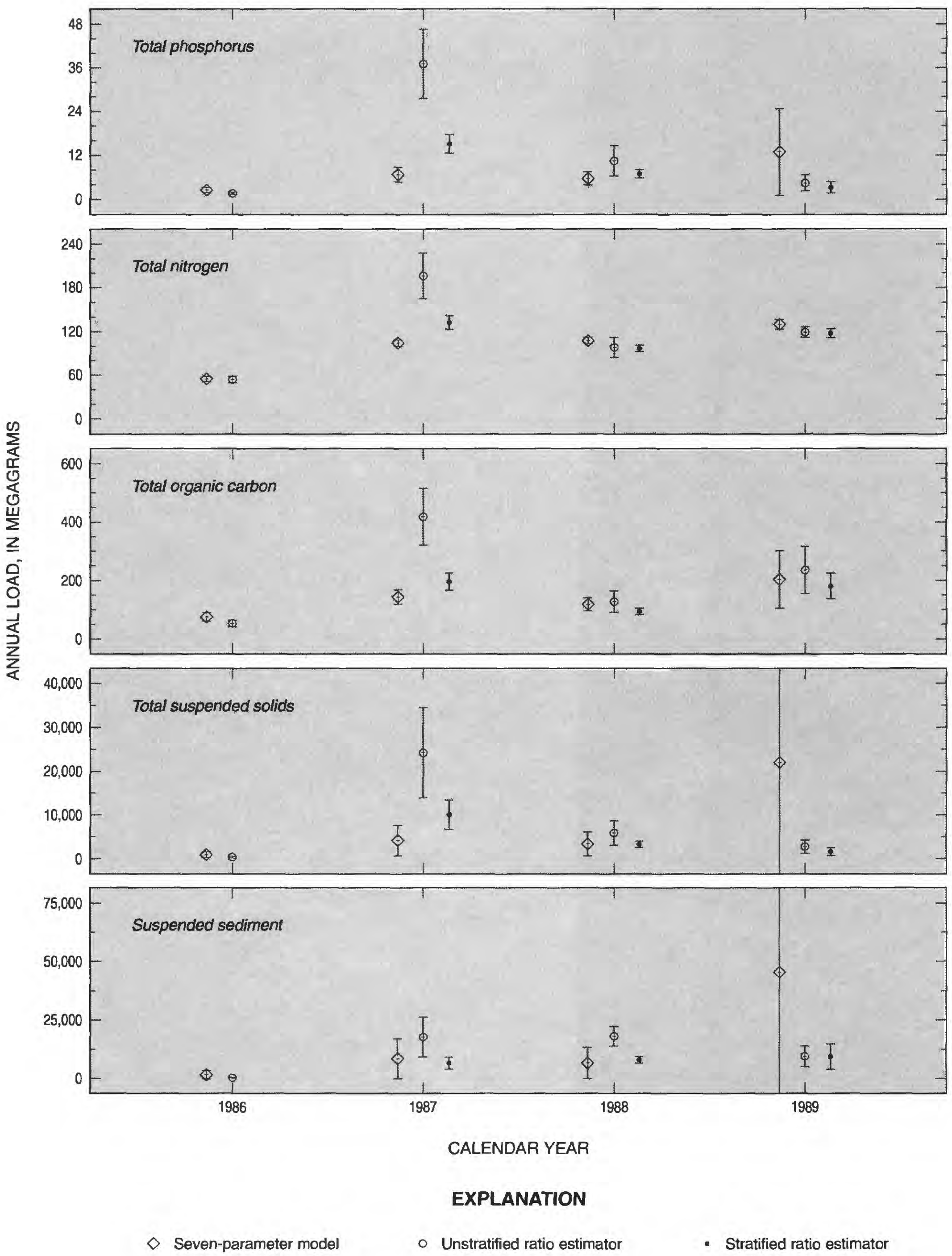


Figure 22. Comparison of annual estimates of constituent load for the Patuxent River at Unity, calendar years 1986-89. [Load estimates include those determined using the seven-parameter model, the unstratified ratio estimator, and the stratified ratio estimator. Error bars represent one standard deviation above and below the estimate.]

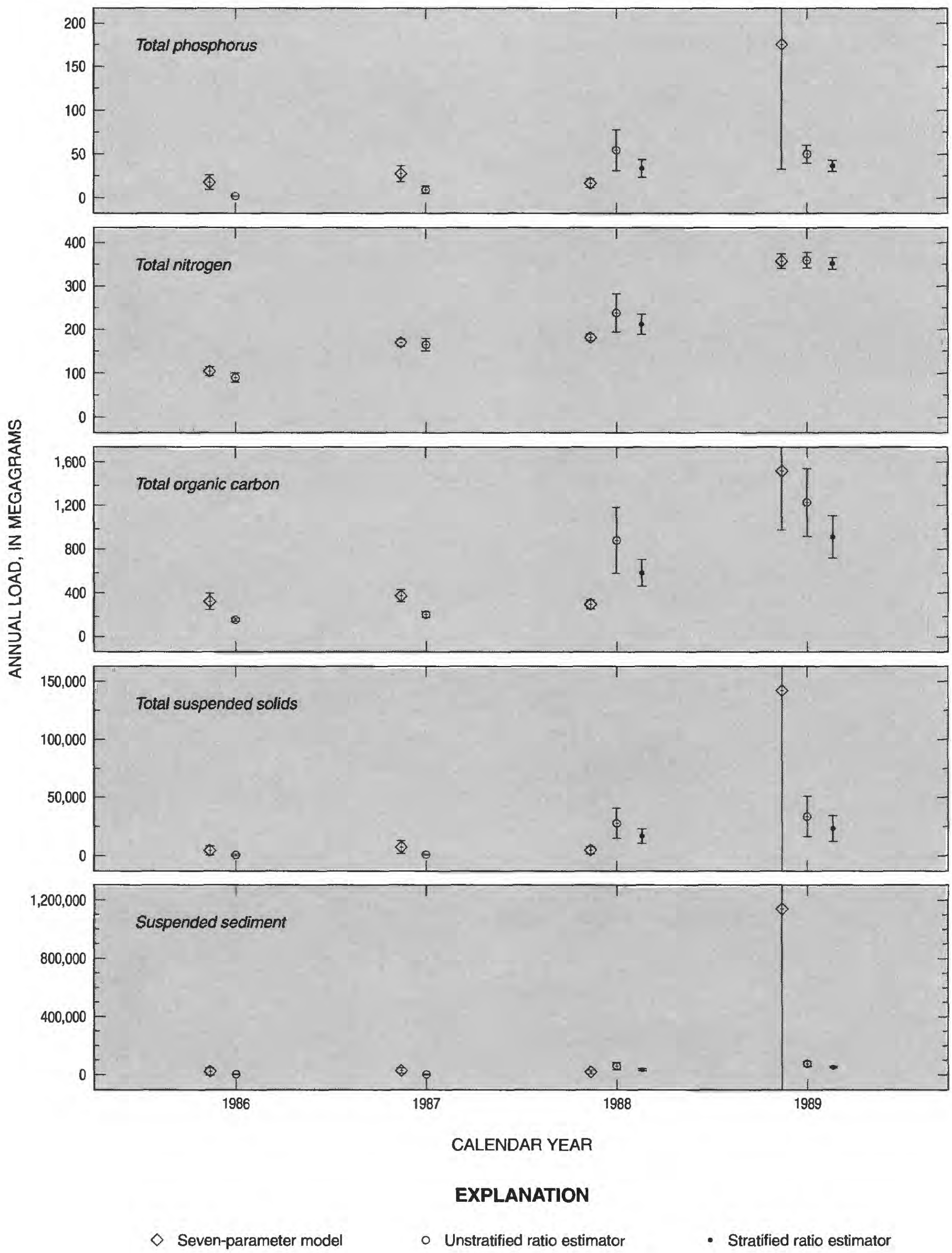


Figure 23. Comparison of annual estimates of constituent load for the Little Patuxent River at Savage, calendar years 1986-89. [Load estimates include those determined using the seven-parameter model, the unstratified ratio estimator, and the stratified ratio estimator. Error bars represent one standard deviation above and below the estimate.]

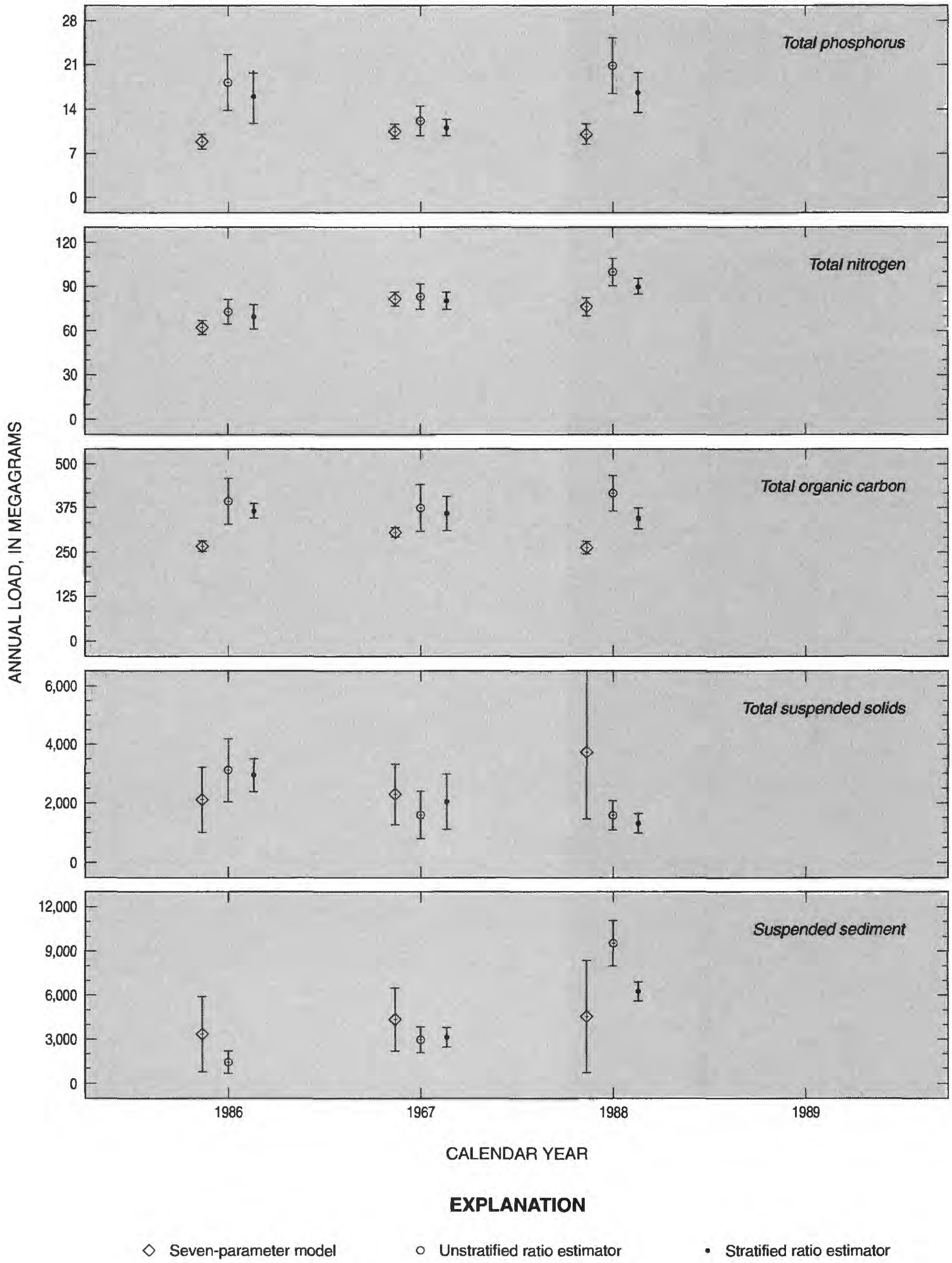


Figure 24. Comparison of annual estimates of constituent load for Western Branch at Upper Marlboro, calendar years 1986-89. [Load estimates include those determined using the seven-parameter model, the unstratified ratio estimator, and the stratified ratio estimator. Error bars represent one standard deviation above and below the estimate.]

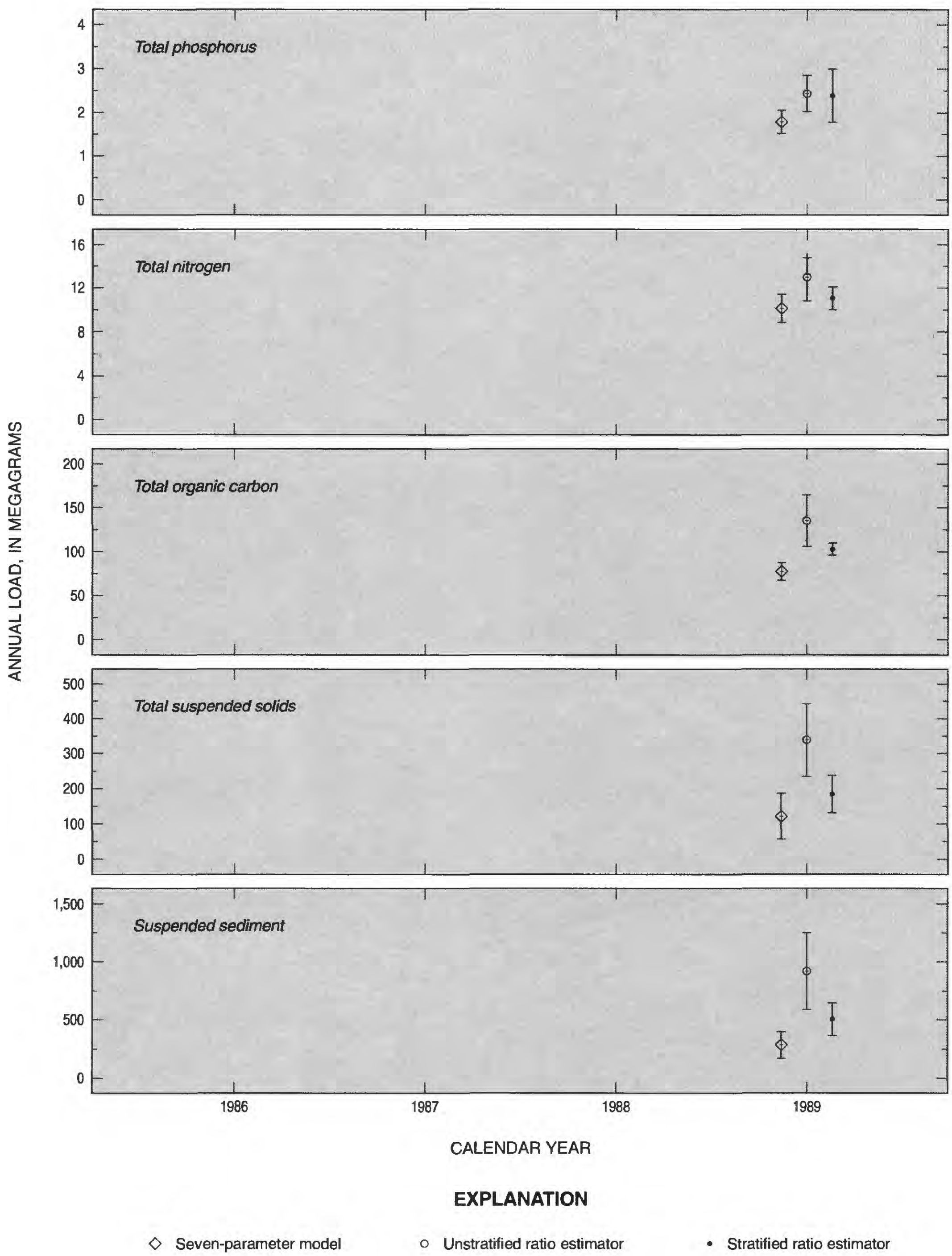


Figure 25. Comparison of annual estimates of constituent load for Hunting Creek near Huntingtown, calendar years 1986-89. [Load estimates include those determined using the seven-parameter model, the unstratified ratio estimator, and the stratified ratio estimator. Error bars represent one standard deviation above and below the estimate.]

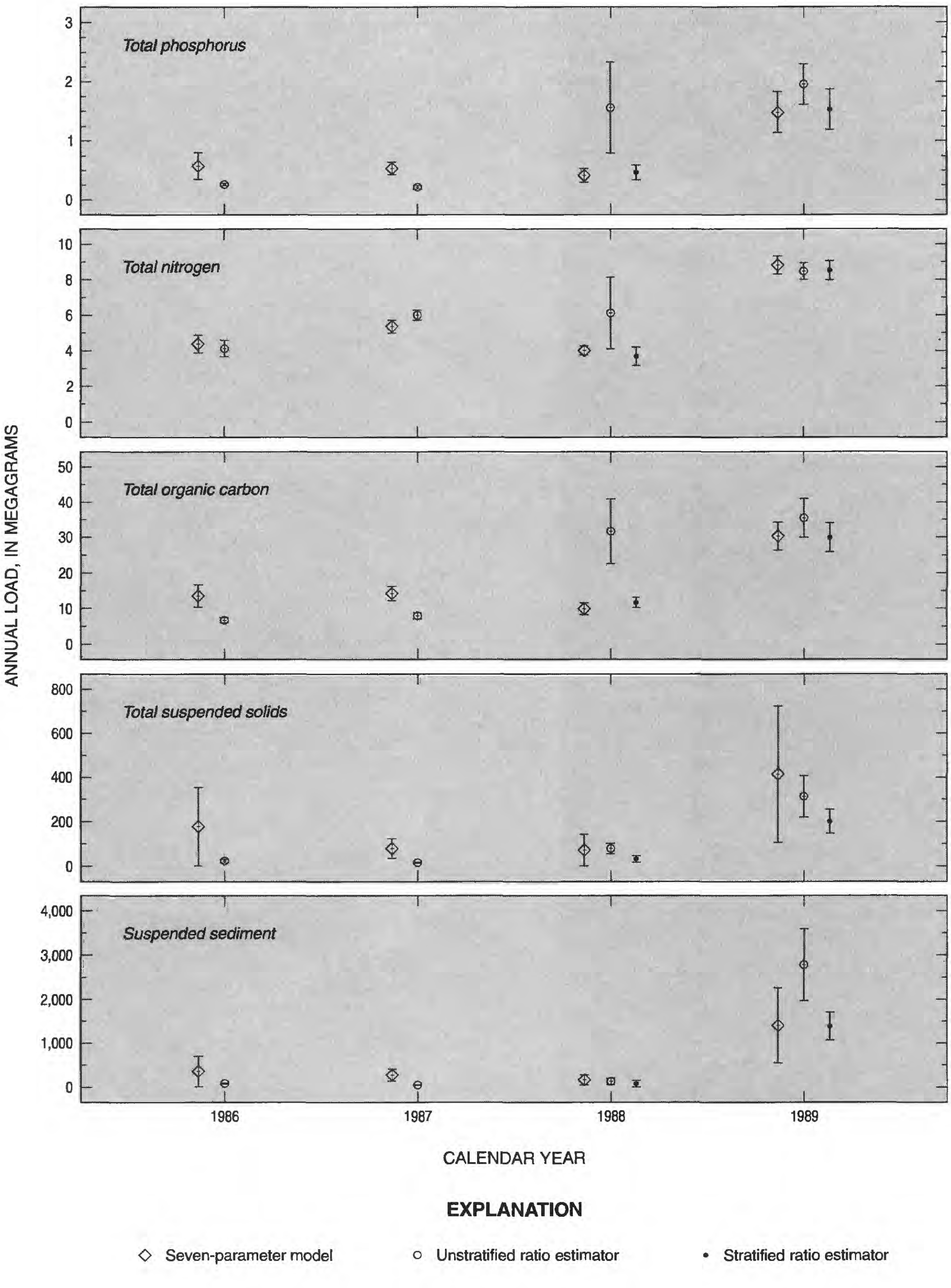


Figure 26. Comparison of annual estimates of constituent load for Killpeck Creek near Huntersville, calendar years 1986-89. [Load estimates include those determined using the seven-parameter model, the unstratified ratio estimator, and the stratified ratio estimator. Error bars represent one standard deviation above and below the estimate.]

accuracy and precision of load estimates (Young and others,1988; Preston and others, 1989). At the Unity monitoring site during 1987, a relatively high number of samples (47 percent) were collected during high flow. The unstratified ratio estimator, therefore, tended to overestimate loads for that year. Estimates made using the stratified version of the ratio estimator generally agreed with those made using the seven-parameter model.

Estimation of Patuxent Monitoring Site Loads For Water Years 1986-90

On the basis of comparisons made in previous sections, the ratio estimator was selected for estimating loads at the Patuxent River monitoring sites. The ratio estimator provides estimates that are comparable to those of the seven-parameter model but is less subject to overestimation when data are not available throughout the estimation range. The ratio estimator is known to be less precise than the seven-parameter model when a detailed data set is available. Given the limitations of the Patuxent data sets, however, the ratio estimator might be a more conservative approach. In other words, the ratio estimator might not achieve the levels of precision of the seven-parameter model, but it does not appear to produce large inaccuracies caused by estimation beyond the calibration range.

Because of its apparent advantages, the ratio estimator was used to estimate annual (water year) constituent loads at sites in the Patuxent Basin. Whenever sufficient data were available for stratification, the stratified ratio-estimator loads were assumed to be the most accurate and precise. During some years, however, there were few high-discharge events and the number of high-discharge concentration measurements was too small for stratification. For those years, the unstratified ratio estimator was assumed to be accurate. For other years, there were a substantial number of high-discharge events, but an inadequate number of water-quality samples were collected. Estimates for those years were identified as potentially inaccurate.

Annual load estimates and information about the load-estimation data sets are summarized for each of the Patuxent monitoring sites in tables 10 through 15. In each of the tables, load estimates and their associated standard errors are listed. Next to the load estimates are indications of whether the unstratified (u) or stratified (s) version of the ratio estimator was used. Loads that are assumed to be underestimated, because of an inadequate number of high-discharge samples, are indicated by asterisks. Monthly loads are illustrated as time series in figures 27 through 32.

Other types of information are included in tables 10 through 15 that can provide an indication of the adequacy of the sampling rate in the high-discharge range. The total number of samples and the fraction of samples that fall into the high-flow stratum are listed to indicate the relative sample-collection frequency between high- and low-flow strata. A small percentage of samples in the high-flow stratum could indicate that the estimate is biased toward low-flow conditions. The number of days with mean daily discharge higher than the stratification level and the percentage of high-flow days when samples were collected are also listed. A small percentage of high-flow days sampled could indicate poor representation of high-flow conditions which would lead to low load-estimate accuracy and precision. Finally, the maximum calibration discharge and maximum estimation discharge are listed. A maximum sample discharge (used for calibration) that is much lower than the maximum mean daily discharge (used for estimation) indicates poor representation of the discharge range and indicates underestimation by the ratio estimator.

Table 10. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Unity monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	1.64 (u)	0.395	17	5.9	19	5.3	86	165
	1987	12.9 (s)	3.43	27	29.6	32	25	591	397
	1988	14.6 (s)	7.49	26	11.5	45	6.7	957	514
	1989	3.42 (s)*	1.71	24	25.0	49	12.2	589	1,390
	1990	4.98 (s)	.945	27	11.1	31	9.7	165	264
Total nitrogen	1986	55.1 (u)	4.01	16	6.3	19	5.3	86	165
	1987	115 (s)	10.6	27	29.6	32	25	591	397
	1988	138 (s)	29.2	26	11.5	45	6.7	957	514
	1989	110 (s)	7.42	24	20.8	49	10.2	87.3	1,390
	1990	96.0 (s)	4.57	25	12.0	31	9.7	165	264
Total organic carbon	1986	51.6 (u)	12.2	17	5.9	19	5.3	86	165
	1987	216 (s)	37.5	27	29.6	32	25	591	397
	1988	148 (s)	43.3	24	12.5	45	6.7	956	514
	1989	111 (s) *	50.3	23	21.7	49	10.2	87.3	1,390
	1990	122 (s)	18.0	28	14.3	31	12.9	165	264
Total suspended solids	1986	385 (u)	156	17	5.9	19	5.3	86	165
	1987	9,973 (s)	3,252	27	29.6	32	25	591	397
	1988	3,820 (s)	799	25	8.0	45	4.4	957	514
	1989	598 (s)*	70.9	25	35.3	49	12.2	589	1,390
	1990	2,494 (s)	353	28	14.3	31	12.9	244	264
Suspended sediment	1986	327 (u)	93.0	8	0	19	0	--	165
	1987	1,364 (s)	511	16	43.8	32	21.9	133	397
	1988	10,508 (s)	1,503	13	30.8	45	8.9	957	514
	1989	5,511 (s)*	4,747	14	21.4	49	6.1	146	1,390
	1990	3,042 (s)	826	15	26.7	31	12.9	244	264

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

Table 11. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Savage monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	2.12 (u)	0.248	7	0	32	0	--	605
	1987	10.3 (u) *	5.11	11	9.1	56	1.8	146	1,090
	1988	42.2 (s)	8.32	12	16.7	65	3.1	1,242	1,100
	1989	33.7 (s) *	7.80	15	60	109	8.3	663	3,150
	1990	27.7 (s)	3.28	17	41.2	94	7.4	864	906
Total nitrogen	1986	85.1 (u)	11.4	5	0	32	0	--	605
	1987	158 (u)	16.6	10	10	56	1.8	146	1,090
	1988	242 (s)	20.2	12	16.7	65	3.1	1,242	1,100
	1989	316 (s)	13.7	15	60	109	8.3	663	3,150
	1990	278 (s)	16.4	15	40	94	6.4	864	906
Total organic carbon	1986	140 (u)	11.5	7	0	32	0	--	605
	1987	221 (u) *	23.4	11	9.1	56	1.8	146	1,090
	1988	693 (s)	89.1	12	16.7	65	3.1	1,242	1,100
	1989	553 (s) *	90.2	16	62.5	109	9.2	663	3,150
	1990	741 (s)	114	18	44.4	94	8.5	1,334	906
Total suspended solids	1986	98.9 (u)	26.5	7	0	32	0	--	605
	1987	819 (u) *	345	12	8.3	56	1.8	146	1,090
	1988	21,217 (s)	4,176	12	16.7	65	3.1	1,242	1,100
	1989	4,776 (s) *	2,966	16	62.5	109	9.2	663	3,150
	1990	22,838 (s)	5,727	18	44.4	94	8.5	1,334	906
Suspended sediment	1986	357 (u)	119	7	0	32	0	--	605
	1987	1,470 (u) *	387	11	9.1	56	1.8	146	1,090
	1988	39,368 (s)	9,266	10	20	65	4.6	1,242	1,100
	1989	39,693 (s) *	11,286	14	64.3	109	8.3	663	3,150
	1990	29,245 (s)	6,901	21	47.6	94	10.6	1,334	906

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

Table 12. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Bowie monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams per liter; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	71.4 (s)	4.69	64	9.4	13	46.2	1,037	1,200
	1987	56.4 (s)	3.62	80	12.5	28	35.7	2,380	2,600
	1988	70.3 (s)	4.48	68	13.2	37	24.3	3,152	2,720
	1989	82.7 (s)	8.78	47	48.9	58	39.7	9,080	8,400
	1990	47.3 (s)	4.2	31	48.4	44	34.1	3,120	2,530
Total nitrogen	1986	821 (s)	31.5	63	9.5	13	46.2	1,037	1,200
	1987	890 (s)	37.1	78	14.1	28	39.3	2,380	2,600
	1988	917 (s)	27.6	68	14.7	37	27.0	3,152	2,720
	1989	1,076 (s)	56.5	46	50	58	39.7	9,080	8,400
	1990	925 (s)	42.2	31	48.4	44	34.1	3,120	2,530
Total organic carbon	1986	1,278. (s)	97	59	8.5	13	38.5	1,037	1,200
	1987	1,572 (s)	51.5	80	15	28	42.9	2,380	2,600
	1988	1,836 (s)	88.9	62	12.9	37	21.6	2,760	2,720
	1989	2,413 (s) *	115	42	42.9	58	31.0	3,260	8,400
	1990	1,792 (s)	73.7	31	48.4	44	34.1	3,120	2,530
Total suspended solids	1986	7,930 (u)	2,715	40	2.5	13	7.7	1,037	1,200
	1987	24,160 (s) *	6,942	51	5.9	28	10.7	1,070	2,600
	1988	16,651 (s)	4,089	59	11.9	37	18.9	3,152	2,720
	1989	8,299 (s) *	3,041	14	42.9	58	10.3	2,630	8,400
	1990	8,133 (u) *	2,855	5	0.	44	0	--	2,530
Suspended sediment	1986	13,670 (s)	3,192	40	15	13	46.2	1,031	1,200
	1987	23,822 (s)	4,108	52	23.1	28	42.9	2,380	2,600
	1988	29,547 (s)	4,735	44	20.5	37	24.3	3,152	2,720
	1989	30,324 (s)	4,735	34	50	58	29.3	9,080	8,400
	1990	17,368 (s)	4,111	31	48.4	44	34.1	3,120	2,530

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

Table 13. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Western Branch monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	16.4 (u) *	6.30	25	4	43	2.3	231	665
	1987	13.8 (s)	2.62	32	18.8	77	7.8	547	864
	1988	12.1 (s)	1.12	31	9.7	68	4.4	739	731
	1989	--	--	22	--	--	--	1,219	--
	1990	--	--	--	--	--	--	--	--
Total nitrogen	1986	71.5 (u)	10.4	23	4.3	43	2.3	231	665
	1987	81.8 (s)	5.34	32	18.8	77	7.8	547	864
	1988	87.5 (s)	2.99	31	9.7	68	4.4	739	731
	1989	--	--	21	--	--	--	1,219	--
	1990	--	--	--	--	--	--	--	--
Total organic carbon	1986	320 (u) *	66.8	24	4.2	43	2.3	231	665
	1987	391 (s)	58.4	32	18.8	77	7.8	547	864
	1988	365 (s)	36.6	30	9.7	68	4.4	739	731
	1989	--	--	18	--	--	--	1,219	--
	1990	--	--	--	--	--	--	--	--
Total suspended solids	1986	1,518 (u) *	480	25	3.3	43	2.3	231	665
	1987	3,287 (s)	890	32	15.6	77	6.5	547	864
	1988	2,197 (s)	737	30	6.7	68	2.9	739	731
	1989	--	--	22	--	--	--	1,219	--
	1990	--	--	--	--	--	--	--	--
Suspended sediment	1986	1,497 (u) *	1,052	8	0	43	0	--	665
	1987	3,526 (s)	752	12	16.7	77	2.6	238	864
	1988	9,978 (s)	3,858	9	11.1	68	1.5	739	731
	1989	--	--	11	--	--	--	1,219	--
	1990	--	--	--	--	--	--	--	--

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

Table 14. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Hunting Creek monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	--	--	0	--	--	--	--	--
	1987	--	--	0	--	--	--	--	--
	1988	--	--	0	--	--	--	--	--
	1989	2.25 (s)	0.595	9	33.3	41	7.3	169	195
	1990	1.93 (s) *	.178	21	38.1	35	22.9	89.7	221
Total nitrogen	1986	--	--	0	--	--	--	--	--
	1987	--	--	0	--	--	--	--	--
	1988	--	--	0	--	--	--	--	--
	1989	10.1 (s)	.911	9	33.3	41	7.3	169	195
	1990	10.8 (s) *	1.26	19	36.8	35	20	89.7	221
Total organic carbon	1986	--	--	0	--	--	--	--	--
	1987	--	--	0	--	--	--	--	--
	1988	--	--	0	--	--	--	--	--
	1989	93 (s)	7.2	8	25.0	41	4.9	169	195
	1990	88.3 (s) *	6.08	24	41.7	35	28.6	130	221
Total suspended solids	1986	--	--	0	--	--	--	--	--
	1987	--	--	0	--	--	--	--	--
	1988	--	--	0	--	--	--	--	--
	1989	173 (s)	49.2	10	40.0	41	9.8	169	195
	1990	415 (s) *	60.6	25	44.0	35	31.4	130	221
Suspended sediment	1986	--	--	0	--	--	--	--	--
	1987	--	--	0	--	--	--	--	--
	1988	--	--	0	--	--	--	--	--
	1989	473 (s)	131	11	45.5	41	12.2	169	195
	1990	465 (s) *	70	22	36.4	35	22.9	130	221

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

Table 15. *Summary of ratio-estimator annual constituent load estimates and sample distribution at the Killpeck Creek monitoring site, water years 1986-90*

[ft^3/s, cubic feet per second; Mg, megagrams; --, not determined]

Constituent	Water year	Annual constituent load estimate (Mg)	Load estimate standard error	Total number of samples	Percentage of samples in high-flow stratum	Total number of high-flow days	Percentage of high-flow days sampled	Maximum sample discharge (ft^3/s) (instantaneous)	Maximum mean daily discharge (ft^3/s)
Total phosphorus	1986	0.302 (u) *	0.032	7	0	24	0	--	47
	1987	0.248 (u) *	.036	10	0	40	0	--	42
	1988	0.162 (u) *	.017	11	0	8	0	--	32
	1989	1.58 (s)	.384	19	47.4	50	18.0	34.1	36
	1990	1.69 (s)	.190	22	54.5	51	23.5	27.4	69
Total nitrogen	1986	5.03 (u)	.441	7	0	24	0	--	47
	1987	6.31 (u)	.271	10	0	40	0	--	42
	1988	3.16 (u)	.536	11	0	8	0	--	32
	1989	8.90 (s)	1.18	16	37.5	50	12.0	27	36
	1990	9.59 (s)	.488	21	57.1	51	23.5	27.4	69
Total organic carbon	1986	9.30 (u) *	1.15	8	0	24	0	--	47
	1987	9.47 (u) *	.902	9	0	40	0	--	42
	1988	6.06 (u) *	1.07	10	0	8	0	--	32
	1989	33.9 (s)	6.00	15	40.0	50	12.0	27	36
	1990	37.0 (s)	4.24	25	56.0	51	27.5	45.5	69
Total suspended solids	1986	24.1 (u) *	7.43	8	0	24	0	--	47
	1987	17.7 (u) *	3.01	10	0	40	0	--	42
	1988	20.1 (u) *	5.07	11	0	8	0	--	32
	1989	136 (s)	35.1	19	47.4	50	18.0	34.1	36
	1990	1,682 (s)	546	25	56.0	51	27.5	45.5	69
Suspended sediment	1986	61.6 (u) *	18.5	5	0	24	0	--	47
	1987	60.3 (u) *	16	10	0	40	0	--	42
	1988	63.7 (u) *	15	9	0	8	0	--	32
	1989	1,257 (s)	301	19	52.6	50	20.0	89.8	36
	1990	2,483 (s)	668	28	64.3	51	35.3	50.1	69

* Loads that were assumed to be underestimated, because of an inadequate number of high-discharge samples; u, unstratified; s, stratified.

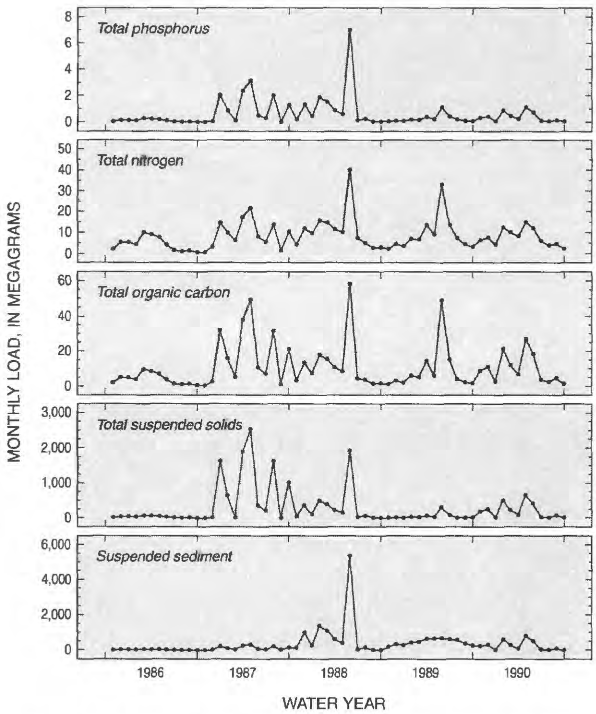


Figure 27. Monthly constituent load estimate time series for the Patuxent River at Unity, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

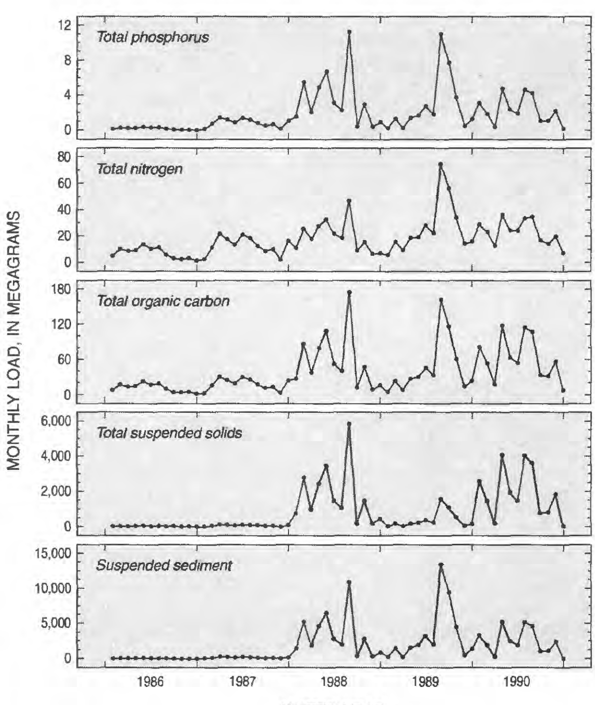


Figure 28. Monthly constituent load estimate time series for the Little Patuxent River at Savage, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

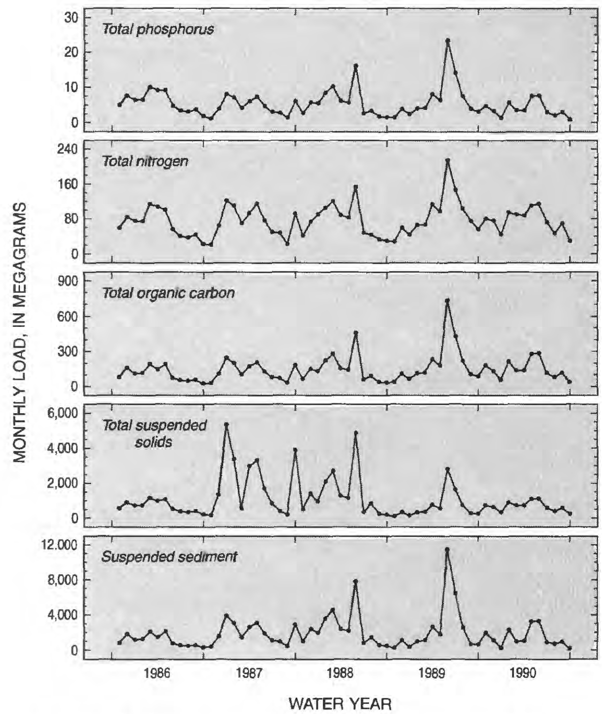


Figure 29. Monthly constituent load estimate time series for the Patuxent River at Bowie, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

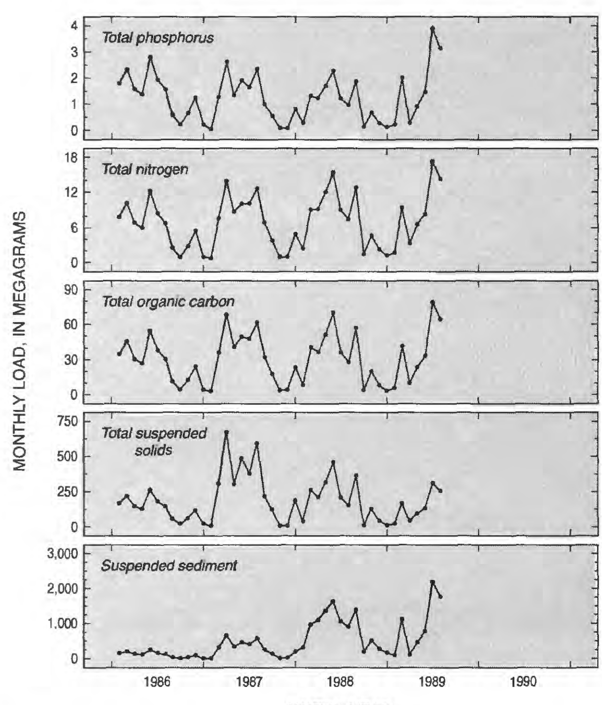


Figure 30. Monthly constituent load estimate time series for the Western Branch at Upper Marlboro, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

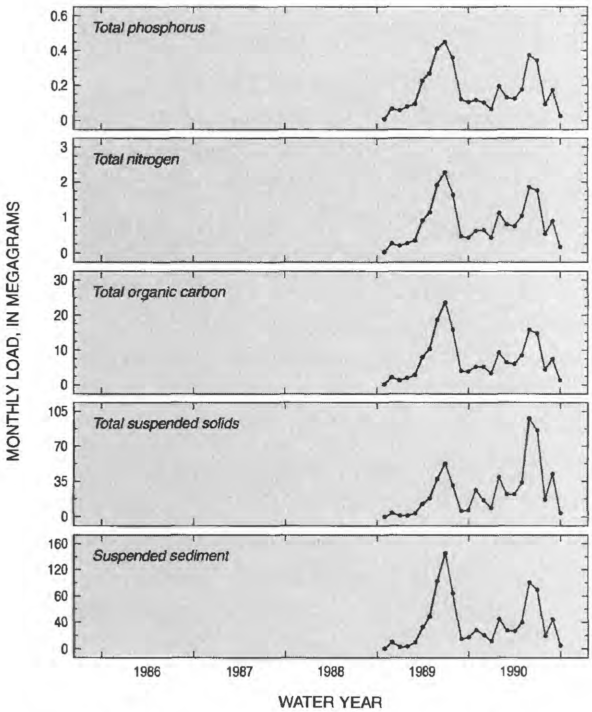


Figure 31. Monthly constituent load estimate time series for Hunting Creek near Huntingtown, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

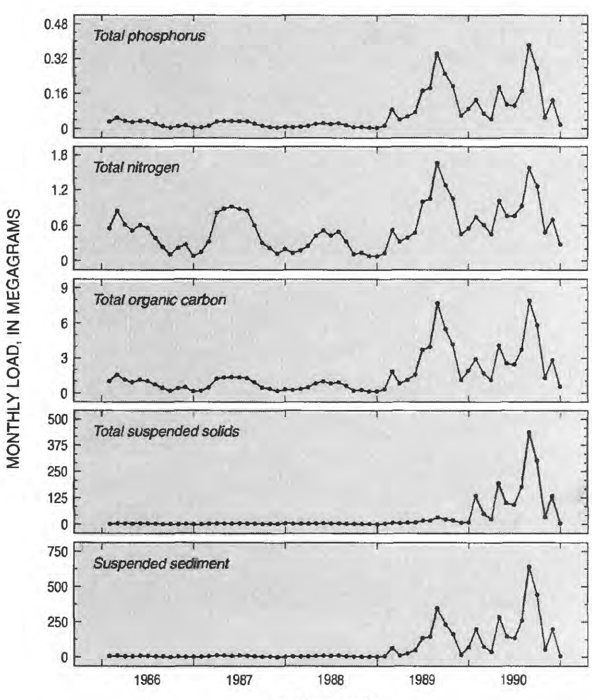


Figure 32. Monthly constituent load estimate time series for Killpeck Creek near Huntersville, water years 1986-90. [Load estimates were made using the unstratified or stratified ratio estimator for each water year.]

Retrospective evaluation of load-estimate quality is difficult to do objectively. Determination of load-estimate quality should include judgments that are based on prior knowledge of load-estimator performance and on the types of error that are caused by different types of data conditions. The conditions that lead to load-estimate error often are related to the frequency and distribution of high-discharge concentration measurements. There is no objective scheme, however, to use discharge information to determine load-estimate quality. For the purposes of this report, only those estimates determined with data sets that clearly do not represent the high-flow range will be identified as possibly being underestimated.

At the Unity monitoring site, sampling rates were adequate for most constituents during most years (table 10). The total number of samples ranged from 8 to 28, but in most cases the number of samples was greater than 20. A sampling rate of 24 samples per year is comparable to a semimonthly sampling program and is considered to be a moderate sampling rate. During most years, at least 10 percent of the samples were in the high-flow stratum, and the stratified ratio estimator could be applied. During 1986, however, there were few high-discharge events and only a few samples were collected during high-flow conditions. Because few high-discharge events occurred during 1986, little benefit would be expected from stratification, and the unstratified ratio estimator was applied.

During most years at the Unity site, the number of high-flow samples was small, but most of the discharge range was adequately represented (table 10). The number of high-flow samples was less than 10 in all cases and included less than 30 percent of the high-flow days. Sample discharges exceeded the maximum daily discharge in 1987 and 1988 and reached at least 50 percent of the maximum daily discharge in all years except 1989, when a large high-flow event was not sampled. Because of the missed high-flow event, the maximum sample discharge in 1989 was less than 50 percent of the maximum mean daily discharge for all constituents and less than 11 percent for total nitrogen, total organic carbon, and suspended sediment. Because the high-flow sampling frequency and the range of discharges were low during 1989, all load estimates except total nitrogen were considered to be underestimated. Total nitrogen was not considered to be underestimated because it did not increase with discharge as much as the other constituents and did not appear to be affected by unsampled high discharges in previous comparisons (for example in figures 10 and 23).

Constituent loads at the Unity site were highest during water years 1987 and 1988 and lowest during 1986. Figure 27 illustrates the monthly time series for constituent loads at the Unity site. Constituent loads were low during 1986 because of low discharge during most of the year. A large number of high-discharge events occurred during 1987, and as a result, loads of most constituents were higher and more variable than in 1986. Water year 1988 was the wettest of the 5-year period with the highest mean annual discharge, and the annual loads of all constituents, except for total suspended solids, were highest during that year (table 10). A large loading peak during May of water year 1988 (fig. 27) was caused by an extended period (2 weeks) of mean daily discharges greater than 60 ft^3/s. Loading peaks only appear for some constituents during May of water year 1989 when the maximum mean daily discharge (1,390 ft^3/s) occurred. The absence of loading peaks during that month could be due to possible underestimation of loads during that year or could be due to the short duration (1 day) of the high-discharge event.

At the Savage monitoring site, sampling rates were lower than at the Unity site throughout the study period. The total number of samples ranged from 5 to 21 per year but was between 10 and 18 in most cases (table 11). Many of the samples that were collected were from the high-flow stratum (18 to 65 percent in most cases). High-flow samples still represent a relatively low sampling rate, however, and in all but one case, less than 10 percent of high discharge days were sampled. The number of data collected during high flows was adequate for stratification only for water years 1988, 1989, and 1990. In water year 1986, few high-flow events occurred, and application of the unstratified ratio estimator for that year was appropriate. A significant number of high-flow events occurred during water year 1987 but were not sampled. Use of the unstratified ratio estimator for water year 1987, therefore, was necessary but not optimal.

High-discharge samples at the Savage monitoring site spanned the range of mean daily discharge during only 2 of the 5 water years (table 11). During water years 1988 and 1990, sample discharges were near or exceeded the maximum mean daily discharge. During water years 1987 and 1989, however, sample discharges were less than 25 percent of the maximum mean daily discharge. During May of 1989, the Savage site experienced a high-discharge event, similar to the one at the Unity site, that was not sampled. Because of the missed high-discharge event, the maximum sample discharge did not approach the maximum mean daily discharge during that water year. Given the low sampling rates and the small range of discharge represented during 1987 and 1989, estimates of all constituents other than total nitrogen were considered to be possibly underestimated.

Constituent loading at the Savage monitoring site was highest during water years 1989 and 1990 because discharge was highest during those years (tables 2 and 11). The monthly time series for constituent loading at the Savage site is illustrated in figure 28. Monthly loads appear to be constant during 1986 and 1987; however, this pattern could be partly due to underestimation caused by low sampling rates and poor representation of the discharge range. The same pattern was not observed in water years 1988 and 1990 because the discharge range was adequately represented. The highest loading periods occurred during the spring of water years 1988 and 1989 and were the result of extended periods of high discharge.

Sampling rates at the Bowie monitoring site were higher than at all other sites because of the combined sampling effort there (table 12). The total number of samples ranged from 5 to 80 but was higher than 30 in almost all cases. Sampling rates of total suspended solids were lower during 1989 and 1990 because the Fall Line study ended the collection of total suspended solids data during that period. The percentage of samples collected during high flows was larger than 13 in most cases but was smaller during 1986 because few high-flow events occurred during that year. Because of the high sampling rates, the numbers of high-flow samples were sufficient for stratification in all cases except for total suspended solids during water years 1986 and 1990.

Compared to the other Patuxent monitoring sites, high-flow samples at the Bowie site were collected more frequently and were collected for the entire discharge range. High-flow days at the Bowie site were sampled at a rate of more than 22 percent for all cases except total suspended solids. At the Unity and Savage sites, high-flow days were sampled at rates of less than 15 percent in most cases. Coverage of the discharge range was greater at the Bowie site; maximum sample discharges were near or greater than the maximum mean daily discharge in almost all cases. Similar to the Unity and Savage sites, a high-discharge event occurred at the Bowie site during water year 1989. Unlike the Unity and Savage sites, however, samples were collected at the Bowie site during the 1989 high-discharge period. Load data sets that did not span the entire discharge range included total organic carbon during water year 1989 and total suspended solids during water years 1987, 1989, and 1990. In all of those cases, the maximum sample discharge was less than 50 percent of the maximum mean daily discharge, and for that reason, the constituent loads for those years were considered to be possibly underestimated.

Loads of most constituents at the Bowie site were low during water years 1986 and 1990 and higher during water years 1988 and 1989 (table 12), similar to loads at the Unity and Savage sites. Loads of most constituents were highest in water years 1988 and 1989 because of extended wet periods during those water years. The monthly load time series (fig. 29) indicate that, similar to the Unity and Savage sites, loading peaks occurred during May of both water years as a result of high discharge (fig. 5). Nutrient loads (total nitrogen and total phosphorus) were lowest in 1990 (table 12) despite having the second highest mean discharge during that year. All other loads were lowest in water year 1986, which had the lowest mean annual discharge. Low nutrient loads during 1990 could be partly due to recent improvements at sewage-treatment plants that include the establishment of nutrient-removal processes (Maryland Department of the Environment, 1993).

Only 3 full years of data were collected at the Western Branch monitoring site because of construction that began in 1989. During water years 1986, 1987, and 1988, sampling rates ranged between 8 and 32 samples per year, but in most cases at least 20 samples were collected per year (table 13). Suspended-sediment samples were collected less frequently, compared to the other constituents throughout the study period. During water years 1987 and 1988, samples collected during high flows represented at least 7 percent of the total number of samples. During water year 1986, fewer high-flow events occurred, and few high-flow samples were collected (0 to 4.3 percent). For all constituents, the number of high-flow samples was adequate for stratification during water years 1987 and 1988 but not for water year 1986.

For all constituents, high-flow samples were collected less frequently, compared to the number of high-flow days but spanned most of the discharge range during 2 of the 3 years (table 13). In all cases, less than 10 percent of the high-flow days were sampled, which indicates that few high-flow events were sampled. During water years 1987 and 1988, the maximum sample discharge was at least 60 percent of the maximum mean daily discharge, however, which indicates that most of the discharge range was sampled. During water year 1986, the maximum sample discharge was less than 35 percent of the maximum mean daily discharge, which indicates poor coverage of the discharge range; thus, loads of all constituents except total nitrogen were considered to be possibly underestimated.

Temporal trends are not consistent for constituent loads at the Western Branch monitoring site (table 13). Total organic carbon and total suspended solids loads were highest during water year 1987 when discharge was also highest (table 2); however, total nitrogen and suspended-sediment loads were highest in water year 1988, and total phosphorus loads were highest in water year 1986. The monthly loading time series (fig. 30) indicates seasonal periodicity in the loading of total nitrogen, total phosphorus, and total organic carbon. Total suspended-solids and suspended-sediment loads were low throughout water year 1986 because few high-discharge events occurred.

Suspended-sediment loads were low during water year 1987 (fig. 30), which could be due to underestimation caused by poor representation of high-discharge conditions.

At the Hunting Creek monitoring site, data were collected during only 2 water years (table 14). During water year 1989 the sampling rate was low (8-11 samples per year), but included high-flow samples that spanned most of the discharge range. During 1989, high-flow samples represented at least 25 percent of the total sample number but that represented only a small percentage (4.9-12.2 percent) of the high-discharge days during that water year. During water year 1990, the sampling rate was higher than in 1989 (19-25 samples per year), and the percentage of high-flow samples ranged from 36 to 44 percent. High-flow samples were collected on 20 to 31 percent of the high-discharge days and spanned most of the discharge range. During both water years, loads of all constituents were highest during the months of May and June when discharge was the highest (fig. 31).

At the Killpeck Creek site, sampling rates were relatively low during the first few years but increased through the study period (table 15). Fewer than 10 samples (5-8) were collected for all constituents during water year 1986, but the sampling rate increased to more than 20 per year (21-28) during water year 1990. The fraction of high-flow samples also increased through the study period. No high-flow samples were collected during water years 1986, 1987, and 1988; however, high-flow samples represented more than 38 percent of the total number of samples during water years 1989 and 1990. Stratification was only possible for water years 1989 and 1990 because of the lack of high-flow samples during water years 1986, 1987, and 1988.

High-flow samples spanned a major part of the discharge range only during water years 1989 and 1990 (table 15). During water years 1986, 1987, and 1988, sample discharges never exceeded the stratification discharge. As a result, high-discharge conditions were not characterized during those years, and all load estimates were considered to be possibly underestimated. During water years 1989 and 1990, 12 to 35 percent of the high-flow days were sampled and the maximum sample discharges were at least 50 percent of the maximum mean daily discharges in nearly all cases.

All constituent loads appear to increase through the period of study (table 15). Annual load estimates of all constituents were low for water years 1986, 1987, and 1988 but were substantially higher for water years 1989 and 1990. Similarly, monthly load estimates of all constituents, except total nitrogen, varied little during water years 1986, 1987, and 1988 (fig. 32) but were higher and more variable for water years 1989 and 1990. Lower loads during water years 1986, 1987, and 1988 are consistent with lower discharge during those years (table 2). The primary reason for lower loads during the initial 3 water years may be related to possible underestimation caused by poor representation of the high-discharge range.

Comparison of Areal Load Estimates

In order to compare load estimates among monitoring sites, annual loads were normalized by dividing by the area of each subbasin. Annual discharge volumes usually were related to basin size because area determines the amount of rainfall that is captured in the basin. Differences in annual loads among basins could be partly due to differences in basin size because the discharge part of the total load is related to basin size. Loads can be normalized by dividing by basin area, and in that way, some of the interbasin hydrologic differences can be accounted for. Remaining interbasin differences could be attributable to differences in rainfall volume or to basin characteristics that contribute to constituent loading, such as land-use practices. Annual water yields (discharge volume normalized to basin area) and annual areal loads of the five constituents in each of the six subbasins are illustrated in figures 33 through 38.

Water yield is presented in units of depth to indicate the amount of rainfall that is converted to discharge. Water yield is affected by many factors, but it is expected to be higher at sites that have received more rainfall or that have a higher percentage of impervious area. Among the monitored subbasins, differences in water yield appear to be due primarily to differences in the amount of rainfall received rather than to differences in basin characteristics (fig. 33).

Rainfall amounts often differ between the northern and southern parts of the Patuxent Basin, and differences in water yield among sites could be related primarily to those rainfall differences. For example, rainfall in the vicinity of the Killpeck Creek monitoring site (the southernmost site, fig. 2) was 33.7 in. during 1986 and 40.2 in. during 1990 [National Oceanic and Atmospheric Administration (NOAA) meteorological site at Damascus]. Rainfall at the Unity monitoring site (the northernmost site, fig. 2) was 36.6 in. during 1986 and 49.4 in. during 1990 (NOAA meteorological site at Mechanicsville). During both water years, precipitation was higher at the southern site and water yield was also higher. Conversely, during water year 1988, rainfall near the Killpeck Creek site (36.0 in.) was lower than at the Unity site (46.2 in.) and water yield was lower.

Few consistent differences in areal total phosphorus loads are apparent among the monitored subbasins (fig. 34). Loads at sites in the northern part of the watershed (Unity and Savage) were highest during water year 1988 and lowest during water year 1986. Loads at the Killpeck Creek site were low during the first 3 water years but were the highest of all the sites during water years 1989 and 1990. Differences are most likely due to differing amounts of rainfall and to underestimation of total phosphorus loads. At the Unity and Savage sites, areal total phosphorus loads were high when annual discharge was high, except during water year 1989. Total phosphorus loads in 1989 could have been underestimated at the two northern sites because of the high-discharge event that was not sampled. Similarly, Killpeck Creek areal total phosphorus loads were high compared to the other sites during water years 1989 and 1990 when rainfall and discharge were highest. Low total phosphorus loads at the Killpeck Creek site during water years 1986, 1987, and 1988 could have been due to underestimation of loads (table 15).

Areal total nitrogen loads were highest at the Unity, Savage and Bowie monitoring sites during most water years (figure 35). Areal total nitrogen loads at the Killpeck Creek site were higher than those at the Savage site during water years 1986 and 1987 and were nearly equal those at the Unity, Savage, and Bowie sites during 1990. In all other cases, however, areal total nitrogen loads at the northern sites were higher than those at the southern sites. Reasons for these differences could be partly related to the amount of rainfall received in the basins. Killpeck Creek received more rain during water years 1986, 1987, and 1990 when areal nitrogen loads approached those of some northern sites. Reasons for higher areal nitrogen loads at the northern sites also could be related to land uses in all of the basins and to point sources (sewage-treatment plants) in the Bowie subbasin. Agriculture is the predominant land use in the Piedmont (northern) Province of the Patuxent Basin. Land use in the Coastal Plain (southern) Province of the Patuxent Basin is predominantly forest cover.

Areal total organic carbon loads are similar for the six monitoring sites during the early water years but differ toward the end of the study period (fig. 36). Total organic carbon loads were highest at the Hunting Creek and Killpeck Creek sites during water years 1989 and 1990. Total organic carbon loads would be expected to be higher at the southern sites because wetlands make up a significant fraction of the land use in the lower Patuxent subbasins, and wetlands are known to be significant sources of dissolved and colloidal organic carbon. Low total organic carbon loads at the Killpeck Creek site during water years 1986, 1987, and 1988 could be due to underestimation during those years.

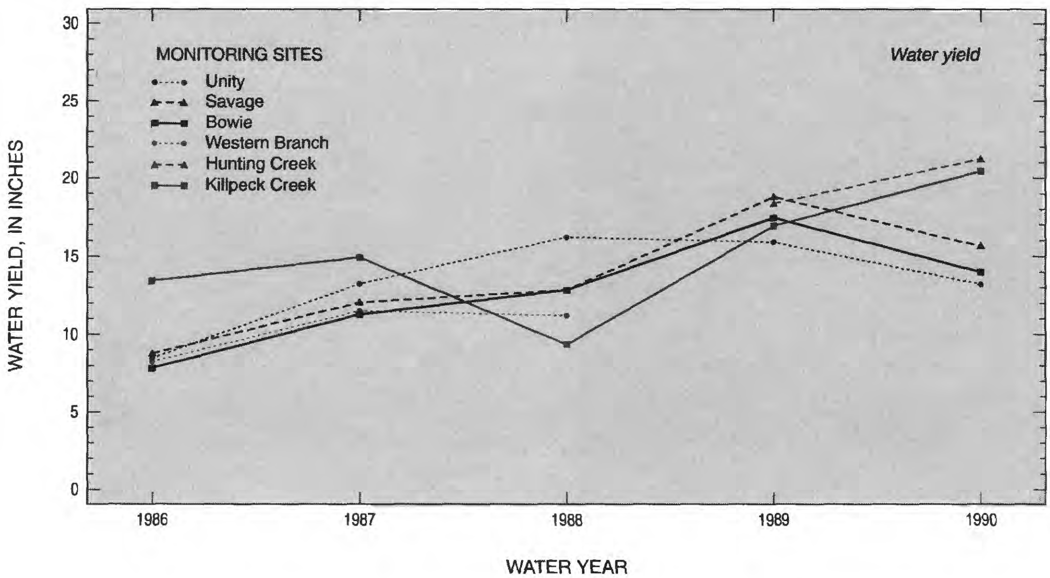


Figure 33. Annual water yield of Patuxent subbasins, water years 1986-90.

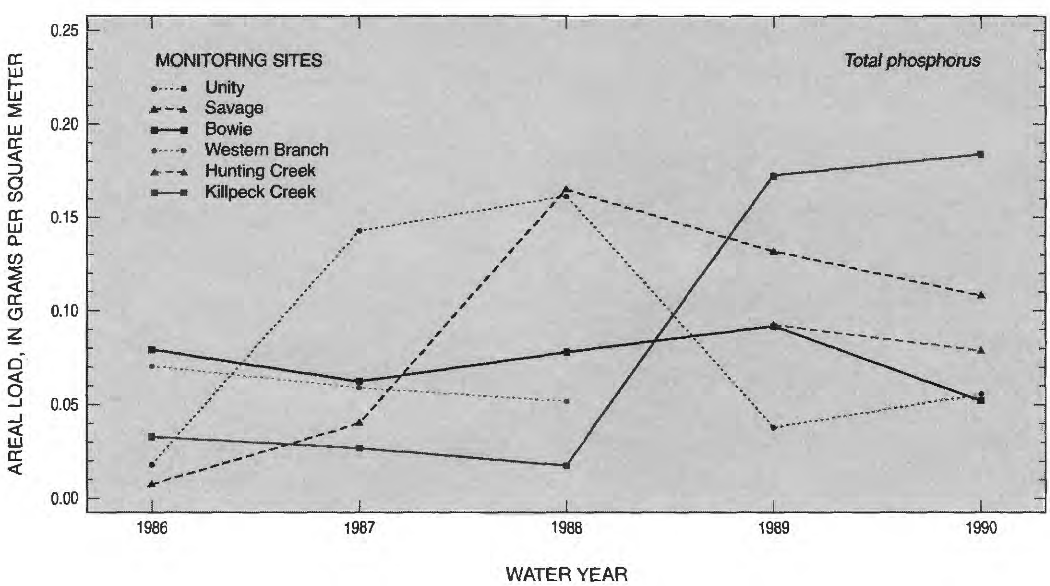


Figure 34. Annual areal total phosphorus loads of Patuxent subbasins, water years 1986-90.

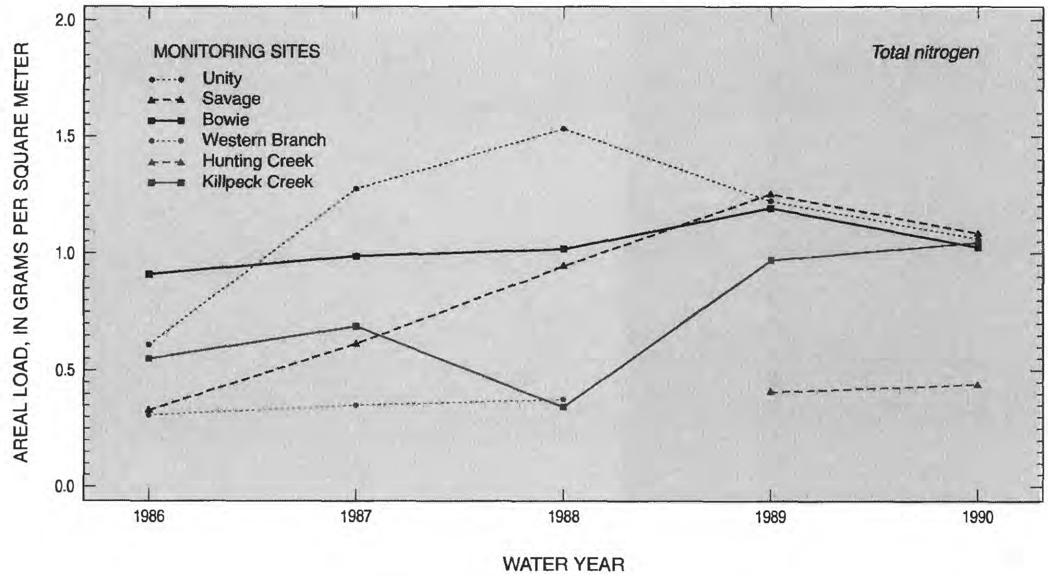


Figure 35. Annual areal total nitrogen loads of Patuxent subbasins, water years 1986-90.

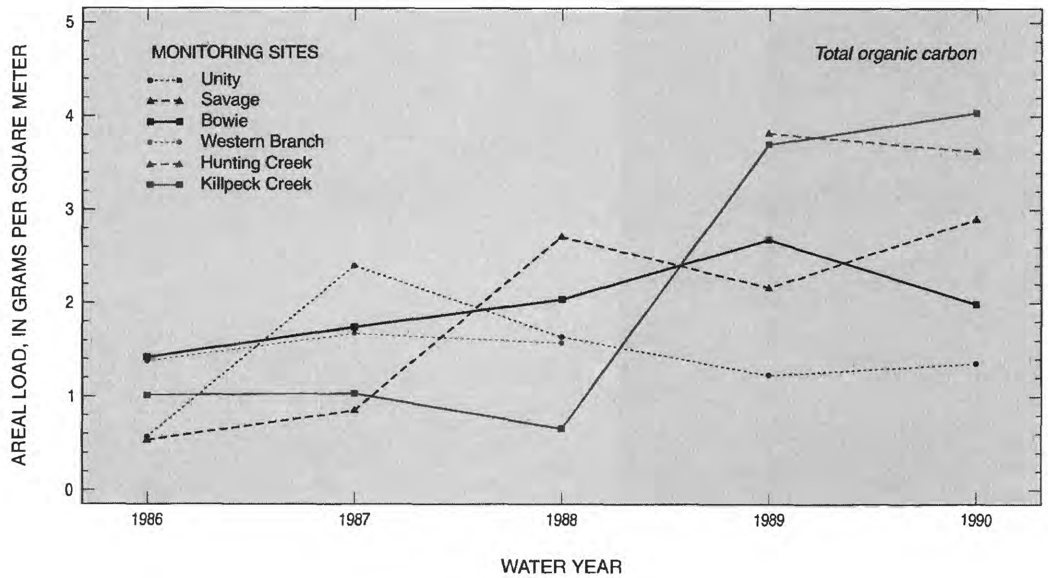


Figure 36. Annual areal total organic carbon loads of Patuxent subbasins, water years 1986-90.

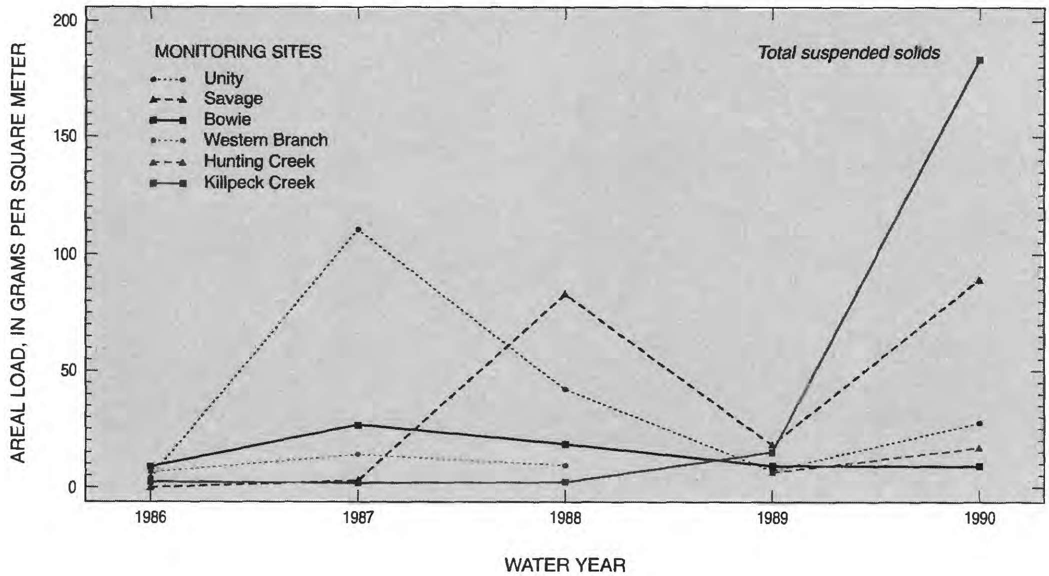


Figure 37. Annual areal total suspended-solids loads of Patuxent subbasins, water years 1986-90.

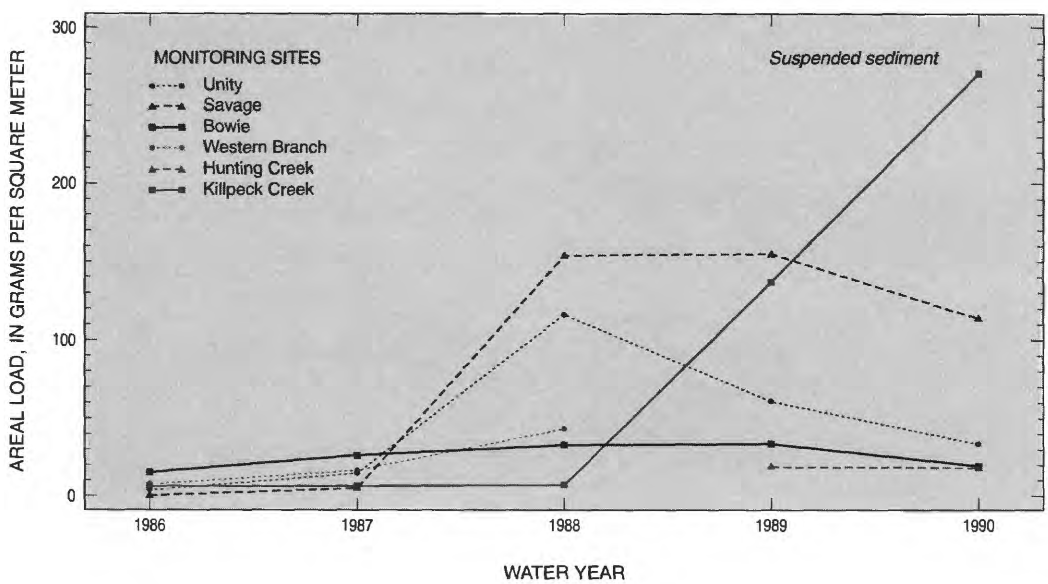


Figure 38. Annual areal suspended-sediment loads of Patuxent subbasins, water years 1986-90.

No consistent differences are apparent in areal total suspended solids or areal suspended-sediment loads among the six monitoring sites (figs. 37-38). Suspended-sediment loads at the Unity and Savage sites were highest during water years 1988, 1989, and 1990. Total suspended-solids and suspended-sediment loads at the Killpeck Creek site were high during water years 1989 and 1990. Reasons for these differences are not entirely clear but appear to be related to variations in the annual discharge volume and to possible underestimation of the loads. Discharge volumes at the Killpeck Creek site were highest during water years 1989 and 1990. Total suspended solids typically increase exponentially as discharge increases above a threshold level. Since both concentration and discharge increase simultaneously, loads of total suspended solids can increase drastically when high discharges occur. Furthermore, no high-discharge samples were collected at the Killpeck Creek site during 1986, 1987, and 1988 (table 15), and it is likely that the loads were underestimated.

Estimation of Base-Flow Components of Loads

Identification of the primary pathways of constituent loading to streams can be an important aid to understanding the processes that affect nonpoint-source loading. Total load estimates can be used to imply causes of constituent loading in a watershed (for example, by relating total loads to land use in basins). However, total load estimates provide no direct information on the pathways and mechanisms of constituent loading to streams. Two of the primary pathways for nonpoint-source nutrient loading in the Patuxent Basin are direct runoff and ground water. Runoff contributes suspended solids and particle-associated constituents to streams when rainfall exceeds infiltration capacity. Ground water (base flow) contributes dissolved constituents to streams during runoff and non-runoff periods. Identification of the relative importance of these two pathways can be useful in the design of effective nonpoint-source management strategies.

The relative importance of direct runoff and base flow to fluvial loading can be evaluated by first separating stream discharge into base flow and direct runoff and then estimating the loading for each component. Typically, stream discharge is separated into runoff and base-flow components using hydrograph-separation techniques to identify base-flow portions of the total flow. During extended periods of flow recession, stream discharge is assumed to be made up entirely of base flow, and all loading from point sources, ground-water contribution, or other sources that are not related to direct runoff can be attributed to base flow. During runoff periods, discharge is separated into runoff and base-flow components using assumptions about the amount of area under the hydrograph that should be attributed to base flow. When streamflow consists of both runoff and base flow, separation of constituent loads into runoff and base-flow contributions is more difficult because water from all sources is mixed. When runoff occurs, therefore, loads can be separated into runoff and base-flow components only on the basis of assumptions and on prior knowledge of nonpoint-source loading processes in the basin.

Total loads are separated into runoff and base-flow components to estimate the importance of loading by direct runoff compared to loading by all other sources. Loading during non-runoff periods is referred to here as the "base-flow" percentage. The term "base flow" refers to the source of discharge, however, and not necessarily the constituent source. Loading during non-runoff conditions could be related to many sources and is not intended to be attributed entirely to one source (for example, ground water).

Many methods have been proposed for separating total discharge into runoff and base-flow components (Pettyjohn and Henning, 1979; Linsley and others, 1982; Rutledge, 1992). Most methods identify runoff periods, use hydrograph-separation techniques to identify runoff during those periods, and attribute the remaining discharge to base flow. Runoff periods usually are identified as starting with a rise in the streamflow hydrograph and ending after a period of continuous recession. Methods usually differ in the definition of the recession period and in the hydrograph-separation technique applied during runoff periods. Many of the proposed hydrograph-separation techniques are defined arbitrarily and have not been confirmed by rigorous experimental evaluation. Detailed description of the relative merits of the techniques is beyond the scope of this report.

The streamflow partitioning method of Rutledge (1992) was used in this study. Rutledge (1992) defines runoff periods as starting with a rise in the streamflow hydrograph and ending after the period of continuous recession that is assumed to be due to runoff. The length of the runoff recession period is defined by an empirical relation between basin area and the duration of runoff recession (Linsley and others, 1982). The end of the runoff is defined as the end of a period of continuous recession that is equal in length to the empirically defined runoff recession period. The hydrograph is separated by linear interpolation between the start and the end of each runoff event. Discharge volume above the separation line is attributed to runoff; discharge volume below the separation line is attributed to base flow. All discharge during non-runoff periods is attributed to base flow.

Results of hydrograph separation for each of the Patuxent monitoring sites are summarized by water years in table 16 and by months in figures 39 and 40. The mean annual discharge and mean annual base flow are listed in table 16 for each water year at each site. The base-flow percentage presented in table 16 is simply the percentage of total discharge that is made up of base flow (in other words, mean annual base flow divided by mean annual discharge). The time series of mean monthly discharge and mean monthly base flow are presented in figures 39 and 40.

At the northern monitoring sites (Unity, Savage, and Bowie), the base-flow percentage tended to be highest during dry years and during years when runoff events were infrequent (table 16). At the Unity and Savage sites, the base-flow percentage was highest during water years 1986 and 1990 when high-discharge events were infrequent. The base-flow percentage was lowest during water years 1987, 1988, and 1989, when high-discharge events were either frequent (1987 and 1988) or exceptionally high (1989) (table 16, figs. 3-4). During water year 1989, the base-flow percentage was low at the Unity, Savage, and Bowie sites because a large runoff event during May of that year contributed much of the total discharge (table 16, fig. 39).

As observed at the northern monitoring sites, base-flow percentages at the southern monitoring sites (Western Branch, Hunting Creek, and Killpeck Creek) tended to be highest during dry years and during years when runoff events were infrequent (table 16). For example, at the Killpeck Creek site the base-flow percentage was highest during water year 1988 when high-discharge events were relatively small and infrequent (table 16, figs. 8 and 40). Base-flow percentages at the Killpeck Creek site differed from those at the northern sites in that they were consistently high and were never less than 74 percent. Higher porosity of the surficial strata in the Coastal Plain Province could contribute to high base-flow percentages in the Killpeck Creek subbasin. In contrast, base-flow percentages at the Western Branch monitoring site were consistently low and were never higher than 59 percent. A large percentage of area with urban land use contributes to greater imperviousness in the Western Branch subbasin which increases runoff and decreases the base-flow percentage.

As stated previously, separation of total constituent loads into runoff and base-flow contributions is complicated by the mixing that occurs during runoff. When total discharge in the stream is equal to base flow, all loading can be attributed to base flow. Mixing of runoff and base

Table 16. *Summary of annual discharges and estimated base-flow percentages at the Patuxent monitoring sites, water years 1986-90*

[ft^3/s, cubic feet per second; -- insufficient data]

Monitoring site	Water year	Annual mean discharge (ft^3/s)	Annual base-flow discharge (ft^3/s)	Base-flow percentage
Unity	1986	21.7	17.3	79.4
	1987	34.0	22.2	65.3
	1988	41.4	29.5	71.3
	1989	40.9	28.5	69.7
	1990	34	26.5	77.9
Savage	1986	63.4	45.6	71.9
	1987	88.1	53.0	60.2
	1988	92.8	58.0	62.5
	1989	137	76.8	56.1
	1990	114	75.0	75.5
Bowie	1986	201	148	73.6
	1987	290	164	56.6
	1988	328	204	62.2
	1989	447	245	54.8
	1990	359	210	58.5
Western Branch	1986	54.8	32.1	58.6
	1987	76.2	42.4	55.6
	1988	73.8	40.3	54.6
	1989	--	--	--
	1990	--	--	--
Hunting Creek	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	12.7	8.03	63.2
	1990	14.7	9.70	66.0
Killpeck Creek	1986	3.51	2.63	75.1
	1987	3.89	2.94	75.6
	1988	2.43	1.92	78.9
	1989	4.43	3.16	71.3
	1990	5.33	3.96	74.3

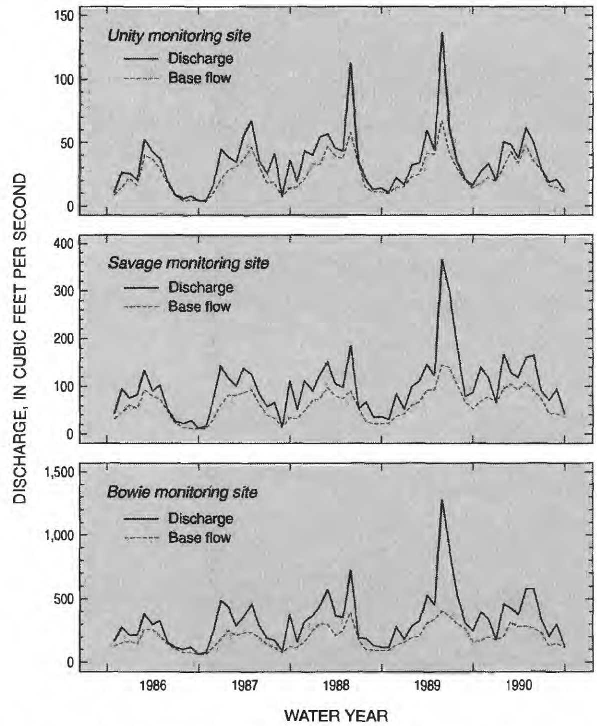


Figure 39. Monthly stream discharge and estimated base flow at the Unity, Savage, and Bowie monitoring sites, water years 1986-90.

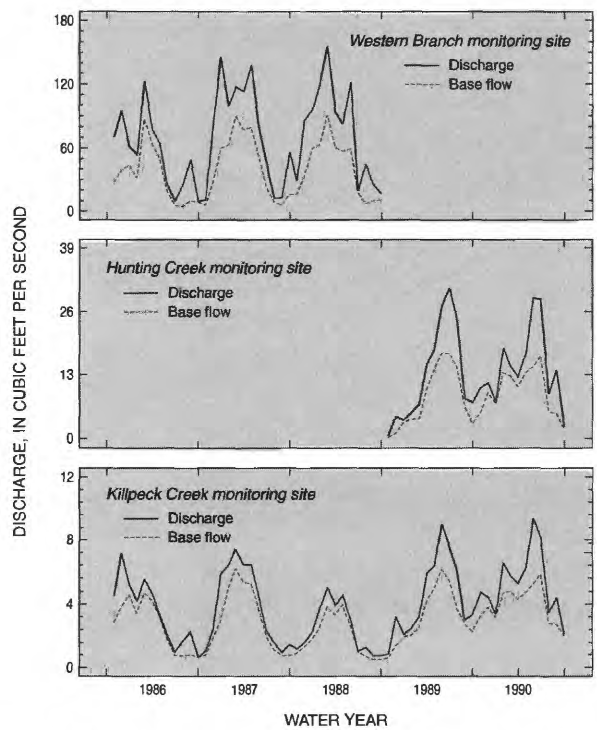


Figure 40. Monthly stream discharge and estimated base flow at the Western Branch, Hunting Creek, and Killpeck Creek monitoring sites, water years 1986-90.

flow, however, complicates separation of loads because the original concentrations of each source are unknown. For the purposes of this study, assumptions are made about the potential loading from each source so that total loads can be separated and, in that way, provide initial estimates of loading attributable to runoff and base flow.

Because direct estimation of runoff and base-flow loads is not possible, conservative high and low base-flow loads were estimated that can be expected to bracket the actual value. In that way, base-flow loads were defined within a specific range that could be refined further with additional study. In order to make the bracket estimates, assumptions were made about the minimum and maximum potential for loading from base flow.

During periods of direct runoff, the base-flow component of load might be considered negligible because the runoff contribution of some constituents (for example, suspended sediment) far outweighs contributions from other sources. In reality, the assumption that the base-flow percentage of loading is zero during runoff causes underestimation because contributions from ground water, point sources, and within-stream processes are neglected. Assuming that the base-flow percentage of loading during runoff is zero, therefore, will provide conservatively low estimates and a lower limit for the actual base-flow contribution.

In contrast, it might be assumed that runoff and base-flow loading are equivalent in rate and differ only by volume. Such an assumption is conservatively high, provided that the runoff concentration is not lower than the base-flow concentration and that dilution does not occur. Most particle-related constituents are contributed primarily by runoff, and their concentration in a stream tends to increase as runoff increases. At the Patuxent monitoring sites, stream concentration increases with discharge in all cases except one (total nitrogen at the Bowie site). The assumption that runoff and base-flow loading rates are equivalent, therefore, should cause overestimation of the contribution of base flow to the total load.

In order to estimate runoff and base-flow component loads, the discharge volumes determined by hydrograph separation were combined with the ratio estimators previously determined. When the unstratified ratio estimator was used, both the runoff and base-flow volumes were multiplied by the ratio estimator as in equation 4. This was performed for the lower limit of base-flow load estimation (where base-flow loading during runoff periods is assumed to be negligible) and for the upper limit (where runoff and base-flow loading are assumed to differ only in volume). In this case, the upper limits of the base-flow percentages of total load are equivalent to the base-flow percentages of total discharge because the ratio estimator is the same during high- and low-flow conditions. When the stratified ratio estimator was used, base-flow loads were estimated the same way, except that the low-flow ratio was used when total discharge was below the stratification discharge and the high-flow ratio was used when total discharge was above the stratification discharge.

Results of the load separation procedure are presented in a manner that is similar to presentation of the hydrograph-separation results (table 16; figs. 39-40). For each monitoring site, tables 17-22 list the total annual load for each constituent along with the lower and upper limits of base-flow load percentages. Figures also are presented for each site that illustrate the monthly time series of total load and the lower and upper base-flow load estimates for each constituent at each site (figs. 41-46).

At the Patuxent monitoring sites, lower and upper base-flow load estimates typically differ by 20 to 40 percent (tables 17-22). Differences tend to be low during dry periods when there is little runoff because most of the load is attributed to base flow. During periods with high runoff, the differences between the lower and upper estimates increase substantially (figs. 41-46). Estimation ranges of 20 to 40 percent are too wide for precise evaluation of load sources but can be sufficient as preliminary estimates, which will be used to aid the calibration and validation of the Patuxent watershed-loading

Table 17. *Summary of annual constituent loads and estimated base-flow percentages at the Unity monitoring site, water years 1986-90*

[Mg, megagrams]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	1.64	46.7	79.4
	1987	12.9	11.8	32.4
	1988	14.6	11.5	44.7
	1989	3.42	27.1	66.1
	1990	4.98	16.5	56.6
Total nitrogen	1986	55.1	46.7	79.4
	1987	115	26.9	54.8
	1988	138	30.3	64.9
	1989	110	28.9	68.4
	1990	96	34.6	75.5
Total organic carbon	1986	51.6	46.7	79.4
	1987	216	16.2	38.9
	1988	148	20.0	53.8
	1989	111	20.7	57.3
	1990	122	18.1	58.3
Total suspended solids	1986	385	46.7	79.4
	1987	9,973	9.0	28.1
	1988	3,820	9.1	42.2
	1989	598	16.1	51.1
	1990	2,494	7.5	47.1
Suspended sediment	1986	327	46.7	79.4
	1987	1,364	15.0	37.1
	1988	10,508	8.5	41.5
	1989	5,511	39.0	82.2
	1990	3,042	6.3	45.9

Table 18. *Summary of annual constituent loads and estimated base-flow percentages at the Savage monitoring site, water years 1986-90*

[Mg, megagrams]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	2.12	36.7	71.9
	1987	10.3	28.8	60.2
	1988	42.2	3.3	34.6
	1989	33.7	9.9	39.9
	1990	27.7	8.7	45.8
Total nitrogen	1986	85.1	36.7	71.9
	1987	158	28.8	60.2
	1988	242	22.7	55.7
	1989	316	22.0	54.7
	1990	278	24.8	64.1
Total organic carbon	1986	140	36.7	71.9
	1987	221	28.8	60.2
	1988	693	7.2	38.8
	1989	553	14.4	45.3
	1990	741	13.2	50.9
Total suspended solids	1986	98.9	36.7	71.9
	1987	819	28.8	60.2
	1988	21,217	1.3	32.4
	1989	4,776	9.0	38.8
	1990	22,838	5.2	41.8
Suspended sediment	1986	357	36.7	71.9
	1987	1,470	28.8	60.2
	1988	39,368	1.3	32.4
	1989	39,693	8.5	38.1
	1990	29,245	5.6	42.3

model. Further studies are being performed that are expected to refine the preliminary base-flow load estimates that are presented here.

At the northern monitoring sites (Unity, Savage, and Bowie), base-flow percentages of most constituent loads were lowest during water years when high-discharge events were frequent and highest during dry water years (tables 17, 18, and 19). The lowest base-flow load percentages varied by site, but all occurred during water years when high discharge events were most frequent. Base-flow percentages of most constituent loads were low during water years 1987 and 1988 at the Unity site and during water years 1988-90 at the Savage site. At all sites, base-flow load percentages were highest in water year 1986, which was the driest of the study period.

Table 19. *Summary of annual constituent loads and estimated base-flow percentages at the Bowie monitoring site, water years 1986-90*

[Mg, megagrams]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	71.4	28.1	75.1
	1987	56.4	12.0	55.8
	1988	70.3	14.7	55.5
	1989	82.7	11.0	50.2
	1990	47.3	11.8	49.4
Total nitrogen	1986	821	28.8	76.2
	1987	890	12.8	58.4
	1988	917	20.1	65.5
	1989	1,076	16.1	60.9
	1990	925	18.3	63
Total organic carbon	1986	1,278	25.0	69.4
	1987	1,572	10.8	52.2
	1988	1,836	12.9	52.2
	1989	2,413	10.3	48.6
	1990	1,792	12.5	50.9
Total suspended solids	1986	7,930	27.2	73.4
	1987	24,160	3.7	29.8
	1988	16,651	8.9	44.7
	1989	8,299	7.3	42.3
	1990	8,133	16.2	58.5
Suspended sediment	1986	13,670	23.8	67.1
	1987	23,822	9.8	49.2
	1988	29,547	11.5	49.6
	1989	30,324	5.0	37.5
	1990	17,368	7.0	39.2

Table 20. *Summary of annual constituent loads and estimated base-flow percentages at the Western Branch monitoring site, water years 1986-90*

[Mg, megagrams; --, no data]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	16.4	27.5	58.6
	1987	13.8	14.2	44.1
	1988	12.1	15.4	44.2
	1989	--	--	--
	1990	--	--	--
Total nitrogen	1986	71.5	27.5	58.6
	1987	81.8	22.3	52.6
	1988	87.5	20.0	49.4
	1989	--	--	--
	1990	--	--	--
Total organic carbon	1986	320	27.5	58.6
	1987	391	20.4	50.6
	1988	365	14.3	42.8
	1989	--	--	--
	1990	--	--	--
Total suspended solids	1986	1,518	27.5	58.6
	1987	3,287	9.1	38.9
	1988	2,197	8.6	36.1
	1989	--	--	--
	1990	--	--	--
Suspended sediment	1986	1,497	27.5	58.6
	1987	3,526	15.7	45.7
	1988	9,978	24.3	54.6
	1989	--	--	--
	1990	--	--	--

The base-flow percentages of the total nitrogen loads were the highest for the constituents that were considered at all three sites. The lower estimates of the base-flow percentage of the total nitrogen load always exceeded 26 percent at the Unity site, 22 percent at the Savage site, and 12 percent at the Bowie site (tables 17-19). The upper estimates always exceeded 55 percent at the Unity and Savage sites and 58 percent at the Bowie site (tables 17-19). In contrast, the lower estimates of the base-flow load percentage of total phosphorus, total suspended solids, and suspended sediment were often less than 15 percent at the Unity and Savage, and Bowie sites.

The base-flow percentage of the total nitrogen loads at the Unity and Savage sites is high because nitrate is present in high concentrations during base flow. Ground water is the primary source of nitrate

Table 21. *Summary of annual constituent loads and estimated base-flow percentages at the Hunting Creek monitoring site, water years 1986-90*

[Mg, megagrams; --, no data]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	2.25	33.3	63.2
	1990	1.93	28.9	57.8
Total nitrogen	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	10.1	26.6	57
	1990	10.8	34.0	64.1
Total organic carbon	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	93	20.4	51.3
	1990	88.3	32.8	62.6
Total suspended solids	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	173	7.9	39.7
	1990	415	19.0	45.4
Suspended sediment	1986	--	--	--
	1987	--	--	--
	1988	--	--	--
	1989	473	7.6	39.4
	1990	465	23.6	51.2

Table 22. *Summary of annual constituent loads and estimated base-flow percentages at the Killpeck Creek monitoring site, water years 1986-90*

[Mg, megagrams]

Constituent	Water year	Annual load (Mg)	Lower base-flow percentage	Upper base-flow percentage
Total phosphorus	1986	0.302	44.6	75.1
	1987	.248	45.3	75.6
	1988	.162	48.5	78.9
	1989	1.58	29.1	61.9
	1990	1.69	18.9	50.6
Total nitrogen	1986	5.03	44.6	75.1
	1987	6.31	45.3	75.6
	1988	3.16	48.5	78.9
	1989	8.90	37.0	68.7
	1990	9.59	40.0	69.6
Total organic carbon	1986	9.30	44.6	75.1
	1987	9.47	45.3	75.6
	1988	6.06	48.5	78.9
	1989	33.9	26.8	60
	1990	37	23.6	54.8
Total suspended solids	1986	24.1	44.6	75.1
	1987	17.7	45.3	75.6
	1988	20.1	48.5	78.9
	1989	136	26.7	59.9
	1990	1,682	7.5	40.3
Suspended sediment	1986	61.6	44.6	75.1
	1987	60.3	45.3	75.6
	1988	63.7	48.5	78.9
	1989	1,257	14.0	49.1
	1990	2.483	8.0	40.7

to the total flow in the Unity and Savage subbasins, and during base flow 70 to 80 percent of the total nitrogen consists of nitrate. During runoff, nitrate makes up a smaller percentage of total nitrogen because particulate nitrogen is transported by suspended solids. The monthly time series of total nitrogen, nitrate-nitrite, and discharge at the Unity, Savage, and Bowie sites are illustrated in figure 47. As indicated by the figure, most of the total nitrogen at the Unity and Savage sites consists of nitrate, and total nitrogen is significantly greater than nitrate only during some runoff events (especially at the Savage site). Furthermore, the increase in total nitrogen during runoff events is often small because nitrate is often diluted as particulate nitrogen increases. As compared to other constituents, therefore, base flow contributes a large percentage of the total nitrogen load because total nitrogen concentrations do not increase as much as other constituents during periods of high runoff.

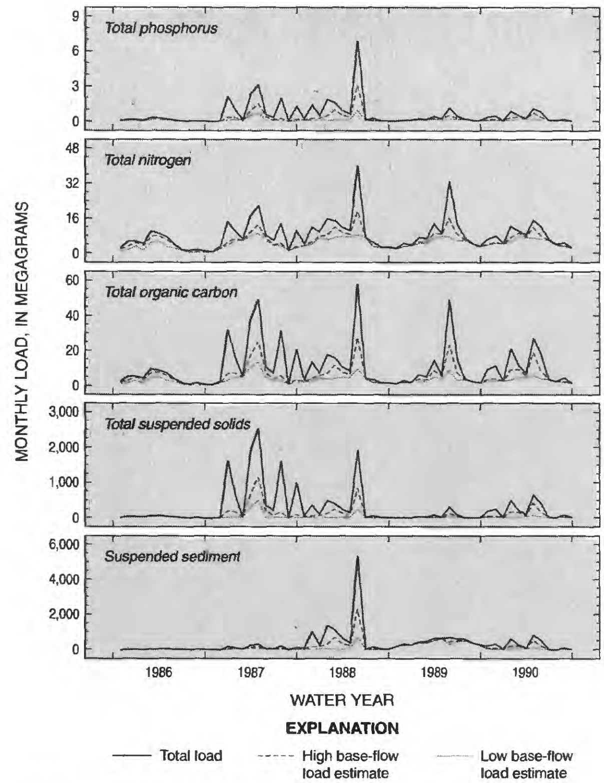


Figure 41. Monthly total load and high and low estimates of load carried during base flow at the Unity monitoring site, water years 1986-90.

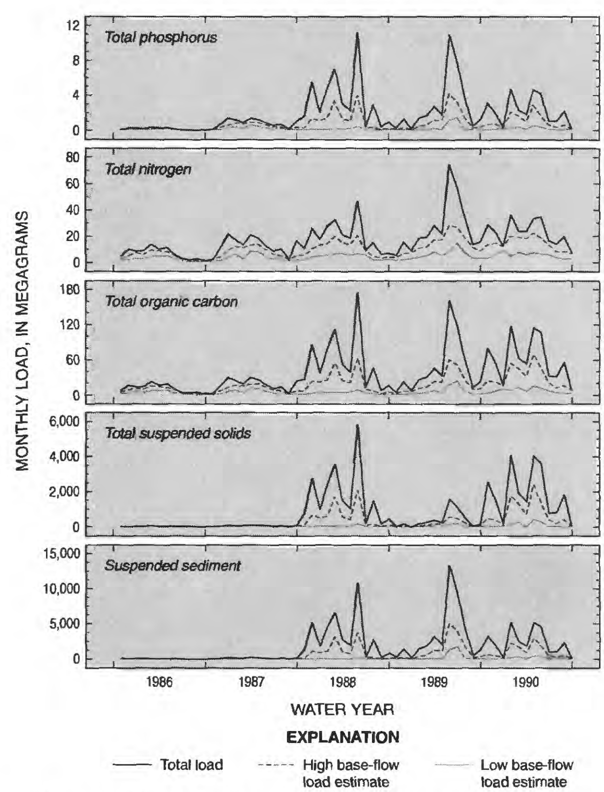


Figure 42. Monthly total load and high and low estimates of load carried during base flow at the Savage monitoring site, water years 1986-90.

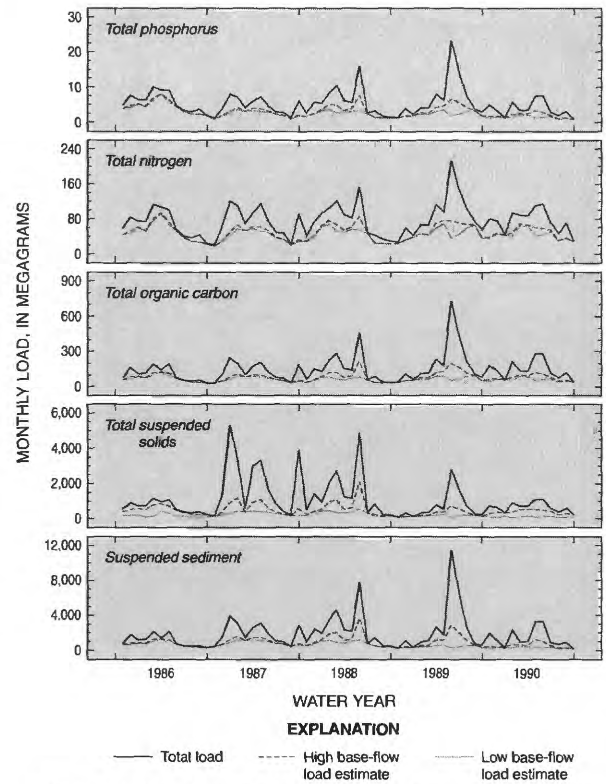


Figure 43. Monthly total load and high and low estimates of load carried during base flow at the Bowie monitoring site, water years 1986-90.

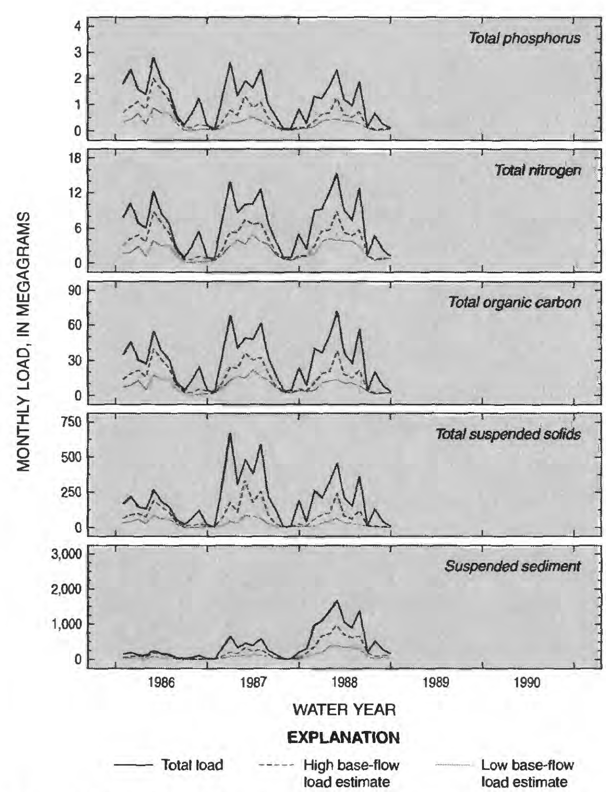


Figure 44. Monthly total load and high and low estimates of load carried during base flow at the Western Branch monitoring site, water years 1986-88. [Data were not collected during 1989 and 1990.]

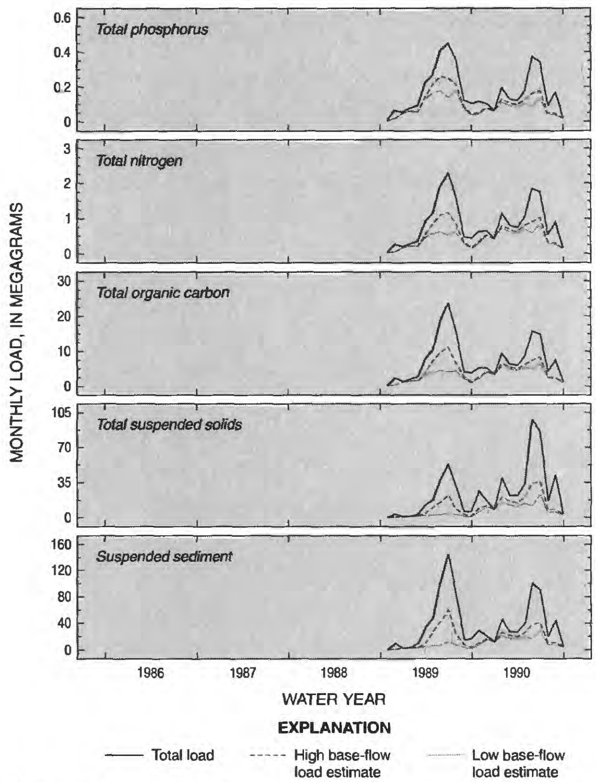


Figure 45. Monthly total load and high and low estimates of load carried during base flow at the Hunting Creek monitoring site, water years 1989-90. [Data were not collected during water years 1986, 1987, and 1988.]

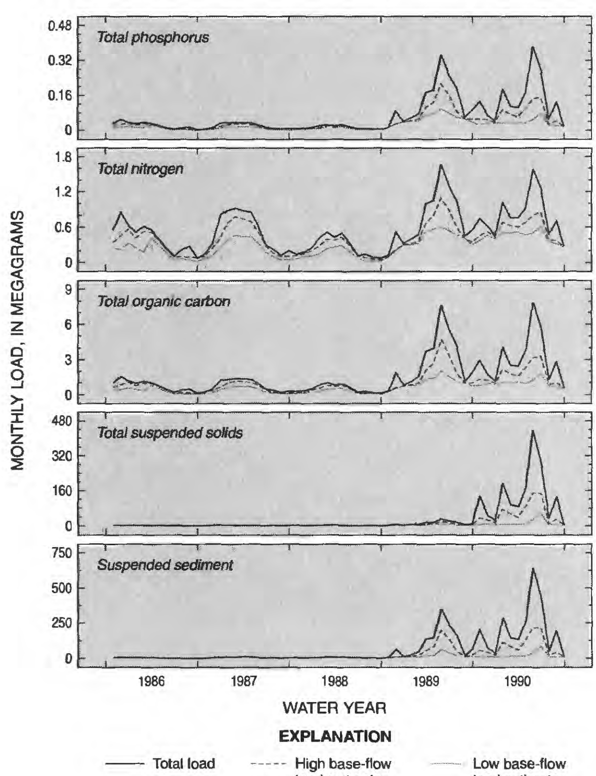


Figure 46. Monthly total load and high and low estimates of load carried during base flow at the Killpeck Creek monitoring site, water years 1986-90.

Total nitrogen concentrations at the Bowie monitoring site decrease with runoff in contrast to concentrations at the Unity and Savage monitoring sites. Most of the total nitrogen consists of nitrate; however, total nitrogen and nitrate appear to decrease at the same rate during periods of high runoff (fig. 47). Total nitrogen concentrations are diluted at the Bowie site because sewage-treatment plants located upstream are the primary source of nitrogen. Nitrogen concentrations are much higher at the Bowie site than at the Unity and Savage sites, and as a result, runoff tends to reduce stream concentrations by dilution. Sewage-treatment plants also are the dominant source of total phosphorus, which is diluted by runoff in a similar manner. As stated previously, dilution negates the assumption that is used to make a conservative estimate for the upper limit of the base-flow load percentage. The upper estimates of base-flow percentages of total phosphorus and total nitrogen loads at the Bowie site may not, therefore, be conservative upper limits.

At the Western Branch monitoring site, the base-flow load percentages for particle-related constituents were lowest during years with more frequent high discharge events (table 20). In general, the base-flow percentages of total phosphorus, total suspended-solids, and suspended-sediment loads were all low during 1987-88 when discharge was highest. All these constituents increase in concentration during runoff conditions, and as a result, high discharge carries a greater proportion of the total load. Total nitrogen and total organic carbon increase only slightly with discharge and base flow carries a greater proportion of the total load of those constituents. Nitrate is a significant percentage of total nitrogen at the Western Branch monitoring site (30 to 50 percent); however, the relation between nitrate concentrations and total nitrogen loading is not as clear as at other sites (fig. 48).

At the Hunting Creek site, base-flow percentages of all constituent loads, except total phosphorus, were higher in water year 1990 than in water year 1989 (table 21). Reasons for higher base-flow loads during 1990 are not entirely clear because discharge was highest during that year. Much of the discharge during 1990 was apparently

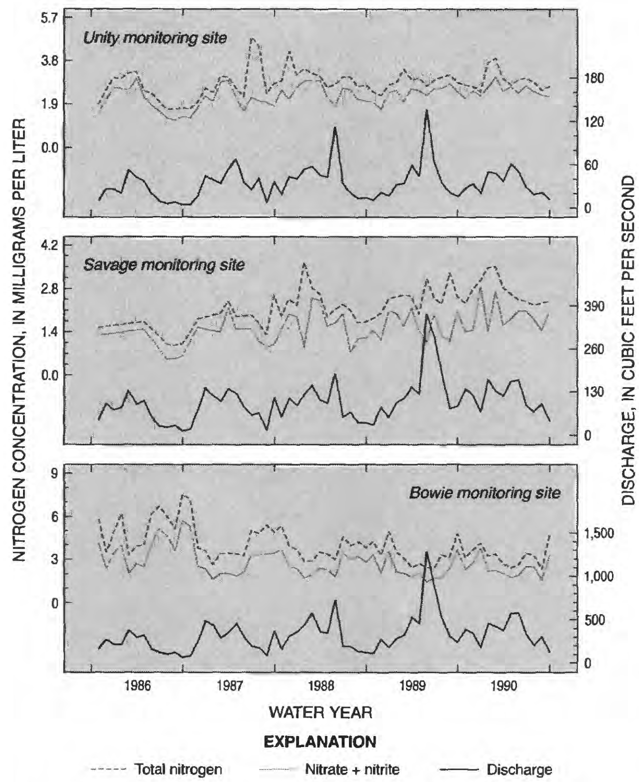


Figure 47. Monthly discharge, total nitrogen, and nitrate + nitrite time series at the Unity, Savage, and Bowie monitoring sites, water years 1986-90.

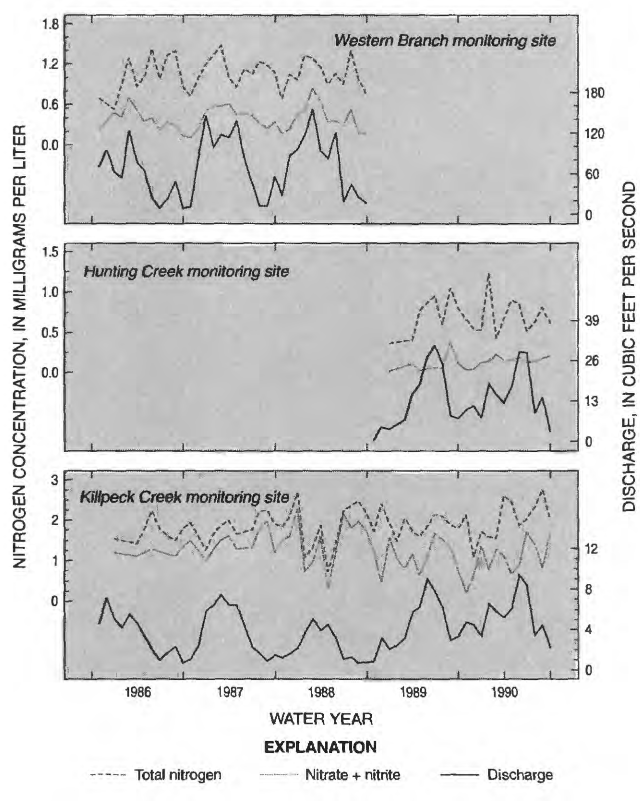


Figure 48. Monthly discharge, total nitrogen, and nitrate + nitrite time series at the Western Branch, Hunting Creek, and Killpeck Creek monitoring sites, water years 1986-90.

attributed to base flow by the hydrograph-separation technique (table 16). Also, sample numbers were low during 1989 and 1990, and possible load estimate error complicated any comparison at the site. Nitrate at the Hunting Creek site is the smallest percentage of total nitrogen of all the sites considered (less than 20 percent), and dilution of nitrate by runoff is not apparent (fig. 48).

At the Killpeck Creek site, base-flow load percentages are highest during water years 1986, 1987, and 1988 for all constituents except total nitrogen (table 22). Loads were assumed to be underestimated during each of those years, and high estimated base-flow percentages during those years could be related to the underestimation of total loads. The frequency of runoff events and total discharge, however, was lowest during 1986, 1987, and 1988, and the base-flow load percentages would be expected to be higher during those years. During water years 1989 and 1990, the base-flow percentages were highest for total nitrogen loads (table 22). Nitrate consistently is 70 to 80 percent of the total nitrogen load at the Killpeck Creek site and ground water is assumed to be the primary contributor; thus, the base-flow percentage of the total nitrogen load might be assumed to be higher than those of the other constituents.

SUMMARY AND CONCLUSIONS

Estimation of constituent loads in streams is often complicated because available estimators and data sets are not optimal. Some constituent loads must be estimated retrospectively using data that have already been collected. Data sets used for load estimation, therefore, might not be optimal for specific statistical estimators. In such a situation, the sensitivity of the estimator to inadequacies in a data set should be known because it might be necessary to evaluate load-estimate quality retrospectively.

Currently, no statistical estimators of constituent loads are optimal for all conditions. The two estimators applied in the study of the Patuxent River Basin, Maryland, described here have been used for load estimation, but are less than optimal and can be seriously flawed under certain conditions. The seven-parameter model is a minimum-variance, unbiased estimator that is based on the assumption of a specific model structure. Given the sampling rates of most load-estimation programs, however, it can never be assured that the model structure is appropriate. The ratio estimator is not a minimum-variance estimator, but it is usually unbiased for typical sampling rates.

Comparison of the seven-parameter model and the ratio-estimator load estimates at the Bowie monitoring site confirm that there are situations when the estimators diverge. In such situations it is usually unclear which of the estimators is correct, and evaluations should be performed retrospectively. It is possible that the seven-parameter model overestimates loads when calibration data are not available for extreme high discharges. Such a situation requires that the seven-parameter model predict constituent concentration outside of the calibration range, at the same time assuming that the concentration-discharge relationship remains constant. It is possible that such extrapolation could lead to overestimation when concentration tends to increase with discharge. In contrast, the ratio estimator could underestimate loads when concentration data are not available during high discharges because the load-discharge covariance has not been adequately quantified. Such conditions were observed when constituent loads were estimated for the Bowie monitoring site during 1979.

Estimator accuracy and precision can be seriously affected by inadequacies in the load-estimation data set. Constituent-concentration data that are collected infrequently can affect load-estimate precision and could prohibit the use of a detailed estimator, such as the seven-parameter model. Similarly, constituent-concentration data that are not representative of the range of discharge can cause substantial bias regardless of the type of estimator used. The adequacy of the data set is, therefore, critical to accurate load estimates.

Load-estimation data-set quality from the Patuxent monitoring sites was variable but tended to improve as the study progressed. Due to equipment failures and other problems, data sets compiled from samples that were collected in the early phase of the study are not always representative of the discharge range. As a result, seven-parameter model estimates were erratic in some cases because the few high-discharge concentration data collected toward the end of the study period appeared as outliers in the model; thus, the assumptions of the model were violated, and the accuracy and precision of the seven-parameter model estimates were apparently low. Similarly, ratio-estimator load estimates for years in which the entire discharge range of streams in the basin was not represented appeared to be biased (underestimated). In most cases, data sets from the Patuxent monitoring sites were adequate for load estimation; however, the inadequacies of some of the data sets and the subsequent poor quality of the load estimates emphasized the necessity of high-discharge samples. As a result, efforts have continued to upgrade and improve the high-discharge sampling efforts at all sites.

Given the inadequacies of some of the load-estimation data sets from the Patuxent monitoring sites, the ratio estimator was selected for load estimation. Some of the load-estimation data sets contained low-frequency concentration measurements that were collected during a shifting sampling pattern (that is, a shift from primarily base-flow sampling to high-discharge sampling). Such data-set characteristics inhibit the application of the seven-parameter model and could cause low accuracy and precision for estimates if the seven-parameter model were used. The ratio estimator is simpler and less rigid than the seven-parameter model. For that reason, the ratio estimator could be less susceptible to the error caused by inadequacies in some of the data sets. The primary limitation of the ratio estimator is that it is not a minimum-variance estimator. Application of the ratio estimator to long-term load-estimation data sets from the Bowie monitoring site, however, indicate that the ratio-estimator standard errors are, in most cases, only slightly larger than those of the seven-parameter model (figs. 18-21). The ratio estimator was accordingly selected because it is more flexible than the seven-parameter model and provides estimates that appear to have acceptable precision.

The ratio-estimator load estimates appear to be reasonable for all data sets with concentration measurements that are representative of the discharge range. At all sites, some data sets were compiled in which the highest sampled discharge was substantially lower than the maximum daily discharge for the water year. It is expected that loads estimated from such data sets using the ratio estimator are biased and underestimate the actual load. In particular, all of the loads estimated for the Killpeck Creek site during the first 3 years of study were probably underestimated because of a lack of samples in the high-discharge range. Such results emphasize the necessity of sampling during high-discharge periods and of sampling the highest discharges.

Comparison of load estimates among the sampling locations can facilitate the evaluation of the effect of land use on constituent loading. For the purposes of this study, subbasin loads were compared by calculating the areal load (yield) for each site. Few consistent differences were observed among the sites for most constituents; however, comparison of the sites was complicated by differences in the amount of precipitation among subbasins and by errors caused by underestimation of loads at some of the sites. Consistent differences were apparent among subbasin total nitrogen yields. Total nitrogen yields were almost always lower at the Coastal Plain sites than at the Piedmont sites, and total nitrogen yields at the Western Branch and Hunting Creek sites were substantially lower than at the Piedmont sites. Coastal Plain sites tend to be more heavily forested than the other sites, with less agricultural land use, which could be one reason for observed differences in total nitrogen yields. Further evaluation will be necessary to identify reasons for the differences with more certainty, however, and to explain why total nitrogen yields at the Killpeck Creek site are higher than at the other two Coastal Plain sites.

Estimating the magnitude of runoff and base-flow components of nutrient loads is an important objective for management of nonpoint sources of nutrients. Various types of land-management practices, called best management practices (BMP's), have been proposed, and their effectiveness varies depending on the primary transport pathway of the constituent of interest. For example, tillage practices can affect the amount of sediment and total phosphorus that is transported by surface runoff and also can increase the amount of nitrogen that enters ground water. If nitrogen transport by base flow is the largest component of the total nitrogen load, then certain BMP's could be ineffective for reducing nonpoint-source nitrogen loading. Understanding the primary transport pathways to the streams, therefore, is essential to the design of effective land-management practices.

Because of the need to define the primary transport pathways of nonpoint-source loading, efforts were made in this study to estimate the percentages of total constituent loads attributable to runoff and base flow. Separating total loads into their runoff and base-flow components is complicated by the mixing of various water sources in the stream. Hydrographs can be separated to estimate runoff and base-flow volumes; however, the constituent concentrations of individual sources are unknown because of mixing in the stream, so that total loads can be separated only by making assumptions about the capacity of loading from different transport pathways. Such an approach allows the establishment of limits on runoff and base-flow percentages of total loads. Such limits do not provide precise definition of loading percentages but are valuable as preliminary estimates that can be refined further with additional study.

Hydrograph separation revealed that most of the total discharge at the Patuxent monitoring sites is from base flow. Base-flow percentages generally range from 50 to 75 percent and vary with location and with the amount and distribution of precipitation throughout the year. Ground water is the primary source of streamflow during base-flow conditions at most of the Patuxent sites, and because nitrate is commonly transported by ground water, it could be the primary source of nitrate to streams in some of the monitored subbasins.

Further evidence of the possible effect of ground-water inflow on nitrogen loading of streams is indicated by the separation of total loads into runoff and base-flow components. At all the sites, the base-flow percentages of the total nitrogen load are higher than those of all other constituents. At the Unity and Savage sites, base-flow percentages of total nitrogen are substantially higher than those of the other constituents because most of the total nitrogen consists of nitrate that could be transported by ground water in the subbasins. At the Western Branch and Hunting Creek sites, the base-flow percentages of total nitrogen are only slightly higher than those of the other constituents because the base-flow volumes are lower and because nitrate comprises a much smaller percentage of the total nitrogen.

Reasons for differences in nitrogen loading among the monitored subbasins are unclear in some cases. At the Unity and Savage sites, total nitrogen is made up primarily of nitrate, and ground water appears to be a primary source of nitrogen to the stream. In the Unity and Savage subbasins, agriculture is an important land use, and increased nitrogen concentrations during base flow could be due to the application of fertilizer. Nutrient concentrations at the Bowie site are dominated by point sources upstream where runoff tends to dilute the concentrations of nitrogen and phosphorus. At the Western Branch and Hunting Creek sites, nitrate concentrations tend to be substantially lower than at northern sites (Unity and Savage), possibly because the percentage of agricultural area in those basins (Western Branch and Hunting Creek) is much lower. Nitrate at the Killpeck Creek site is higher than at the other two Coastal Plain sites, however, and is nearly as high as at the Unity and Savage sites. Further study is necessary to define the reasons for high nitrate concentrations at the Killpeck Creek site.

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