ESTIMATION AND ANALYSIS OF NUTRIENT AND SUSPENDED-SEDIMENT LOADS AT SELECTED SITES IN THE POTOMAC RIVER BASIN, 1993-95

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
pound, avoirdupois (lb)	0.4536	kilogram
ton	907.2	kilogram
cubic foot per second (ft^3/s)	0.02832	cubic meter per second

Chemical concentration in water is expressed in milligrams per liter (mg/L).

Water Year: A water year is the 12-month period from October 1 through September 30. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1993, is called the "1993 water year."

Estimation and Analysis of Nutrient and Suspended-Sediment Loads at Selected Sites in the Potomac River Basin, 1993-95

By Joy S. Lizárraga

ABSTRACT

Multiple surface-water samples were collected at 10 fixed sites during the first sampling phase of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) of the Potomac River Basin. Five fixed sites are at the outlets of small to intermediate subwatersheds characterized by a single land use or a representative combination of land uses (indicator sites) and five fixed sites are at the outlets of larger subwatersheds characterized by the combined effects of all natural and human water-quality factors (integrator sites). Selected water-quality data have been statistically summarized by site on the basis of the flow regime in which they were collected. At each fixed site, a load estimator program (ESTIMATOR, version 94.02) is used to estimate 1993-95 annual loads of total nitrogen, total nitrite plus nitrate, total organic plus ammonia (Kjeldahl) nitrogen, total phosphorus, and total suspended sediment. Average nutrient and sediment yields for each fixed site are calculated. At three of the five integrator sites, historical measurements of total nitrogen, total nitrite plus nitrate, and total phosphorus concentrations are combined with NAWQA measurements in order to estimate the base-flow contribution of these constituents to their annual loads during 1993-95.

INTRODUCTION

Reduction of nutrient and sediment loads to the Potomac River and to the Chesapeake Bay is vital to maintaining the health of the aquatic ecosystems that are present. Goals set out in the Chesapeake Bay Agreement in 1987, and signed by the Governors of Pennsylvania, Virginia, Maryland, and the Mayor of Washington, D.C., witness to the fact that reduction in nutrient and sediment loads is a priority for states with contributing drainage areas to the bay (Galloway, 1993).

Quantifying water-quality constituent loads is important for understanding the processes that affect loads, for directing control strategies, and for evaluating progress towards reduction of undesired contaminants. Determining whether or not certain water-quality constituents are principally transported in the base flow, which largely originates from ground-water sources, or in the total surface-water flow including stormwater, has implications for the choice of management practices.

Purpose and Scope

This report (1) presents a compilation of nutrient and sediment data from 10 fixed indicator and integrator sites from the first phase of Potomac NAWQA sampling; (2) statistically summarizes selected measured water-quality concentrations at these 10 surface-water sites during defined flow regimes; (3) presents 1993-95 annual load estimates for total nitrogen (TN), total nitrite plus nitrate (TNO23), total organic plus ammonia (Kjeldahl) nitrogen (TKN), total phosphorus (TP), and total suspended sediment (SED) at the fixed sites; and (4) estimates the 1993-95 base-flow load contribution of TN, TNO23, and TP at three larger NAWQA integrator sites using long-term historical monitoring data and the NAWQA data.

Previous Studies

The ESTIMATOR program, a regression analysis model for estimating water-quality constituent concentrations and loads, was developed by the U.S. Geological Survey (USGS) using data from the Chesapeake Bay region (Cohn and others, 1989; Cohn and others, 1992). The model was developed in 1989 using 1978-88 data from the Potomac, Susquehanna, Patuxent, and Choptank Rivers (Cohn and others, 1989). Cohn and others (1989) demonstrated that the ESTIMATOR model was a minimum variance unbiased estimator (MVUE) under the assumption that the model was correctly specified. The model was validated by Cohn and others (1992) through application to major Chesapeake Bay tributaries.

The USGS uses the ESTIMATOR program annually to estimate nutrient and sediment loads and trends at the Potomac River at Chain Bridge. For these annual estimates, the previous 10 years of sampling data collected by the USGS and the State of Maryland are used to calibrate the model. These estimates and data are reported in annual summary data reports published by the Maryland Department of the Environment (1990-95). Estimated loads for TN, TNO23, and TP at Chain Bridge during 1993-95 that have been reported by the State of Maryland are similar to estimates presented in this report.

Langland and others (1995) also present nutrient and sediment yields for sites throughout the Chesapeake Bay drainage area, including some of the sites in the Potomac Basin. These average yields are based on 1972-92 load estimates obtained by use of the ESTIMATOR program with historical data.

Some differences in load estimates at surface-water sites common to each of these previous studies and to this study can be largely explained by the following factors: (1) different versions and explanatory variables of the ESTIMATOR program are used in calculating the loads and yields, and (2) different calibration data sets are utilized.

Blomquist and others (1995) performed a retrospective analysis for the Potomac NAWQA study unit using historical data. Nutrient loads and the relation of these loads to land use, soils, and rock type were estimated for sites with available data. This report is intended to extend the work of Blomquist and others (1995) by using the newly collected NAWQA data to more accurately estimate the nutrient and sediment loads during 1993-95 at a larger number of sites, and to more fully evaluate the relation between loads and different environmental settings in the Potomac River Basin.

Location of Study and Hydrologic Conditions

The Potomac River Basin (fig. 1) is 14,670 mi^2 in area and covers Washington, D.C., and parts of Maryland, Virginia, and West Virginia. For purposes of the NAWQA sampling and characterization, the entire basin was stratified into subunits (Blomquist and others, 1995). Each subunit has a relatively distinct combination of physiography and lithology affecting the water quality of the streams that drain them (Fenneman and others, 1946; Blomquist and others, 1995).

In designing the NAWQA sampling plan, characterizing water quality in four of the eight subunits (Valley and Ridge, Great Valley Carbonate, Piedmont, and Triassic Lowlands) and from two land-use categories (agricultural and urban) was considered to be most important for the design by Blomquist and others (1995). This decision was based upon the distribution of population in the basin. These subunits and types of land use were used to prioritize surface-water sampling sites for water-quality assessment in the first intensive sampling phase in the basin. These sites, called fixed integrator and fixed indicator sites, were instrumented for surface-water sampling and analysis during the 1992-95 period (fig. 2).

Five of the ten fixed sites are integrator sites. Integrator sites drain large areas and represent the combined effects of all natural and human water-quality factors within the watershed. The other five fixed sites are indicator sites, chosen to represent small to intermediate watersheds characterized by a single land use or a representative combination of land uses within a subbasin (Gerhart and Brakebill, 1996). The percentage of different land uses, lithologies, and subunits within the drainage area of each fixed site is described in table 1. The highest percentage of each category is in bold type.

Surface-water samples were collected at all of the sites using the same flow-weighted and cross-sectionally integrated methods (Gerhart and Brakebill, 1996). Most of the samples were collected in water year 1994. The fixed sites were further grouped on the basis of frequency of sampling, basic or intensive. Water samples were collected approximately monthly and during selected high streamflow conditions at each basic fixed site. Three of the indicator sites and one integrator site are intensive fixed sites. At intensive fixed sites, in addition to sampling described for basic fixed sites, sampling frequency is increased to about weekly during one growing season. These sites and the year of intensive sampling are (1) Muddy Creek at Mt. Clinton, Va., 1993; (2) Monocacy River at Bridgeport, Md., 1994; (3) Accotink Creek near Annandale, Va., 1994; and (4) Shenandoah River near Millville, W. Va., 1993.

In the Potomac River Basin, the water years 1993 and 1994 were wetter than normal and water year 1995 was drier than normal. This conclusion is based on a comparison of annual mean discharges with average annual mean discharges for the period of record at 9 of the 10 surface-water gages at the fixed sites. In 1993, annual mean discharges ranged from 120 to 172 percent of the average annual mean discharges for the period of record. In 1994, annual mean discharges ranged from 120 to 169 percent of the average annual mean discharges for the period of record. In 1995, annual mean discharges ranged from 54 to 82 percent of the average annual mean discharges for the period of record.

Data Sources

Water-quality data used to apply the ESTIMATOR program for each fixed site were generated by the Potomac NAWQA Program. The mean daily values for surface-water discharges at the fixed sites were retrieved from the USGS National Water Information System.

For three of the NAWQA fixed sites--Shenandoah River at Millville, W. Va., 1974-92; Monocacy River at Reich's Ford near Frederick, Md., 1969-83; and Potomac River at Chain Bridge at Washington, D.C., 1973-96--USGS historical water-quality and stream-discharge data were available. These data had been previously evaluated by Blomquist and others (1995). In general, the historical data were collected as part of local or national stream-gaging and sampling projects conducted by the USGS. Only USGS data were included in the data sets to ensure that comparable sampling and laboratory methods were utilized.

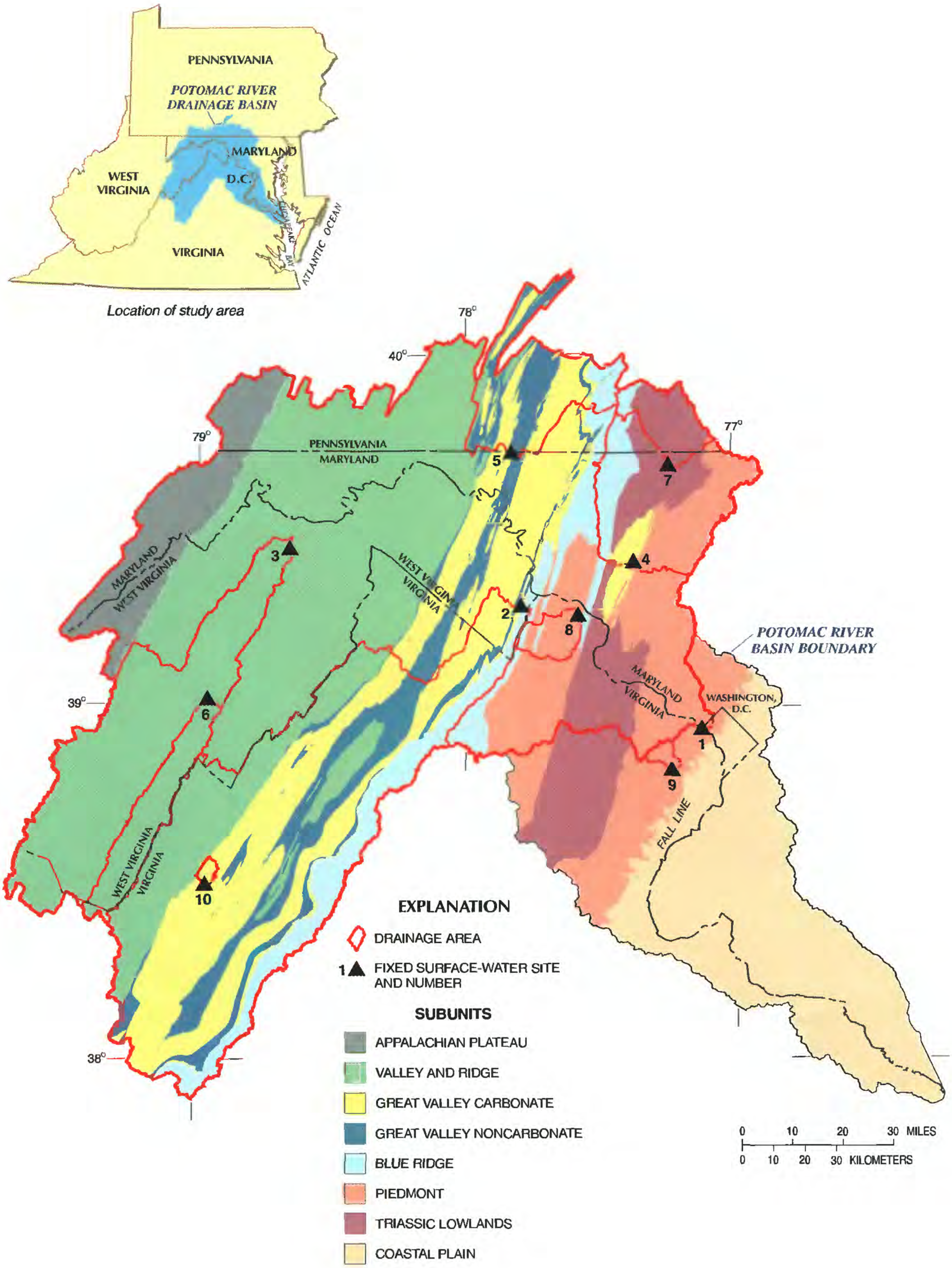

Figure 1. Subunits, fixed surface-water sites, and drainage areas in the Potomac River Basin.

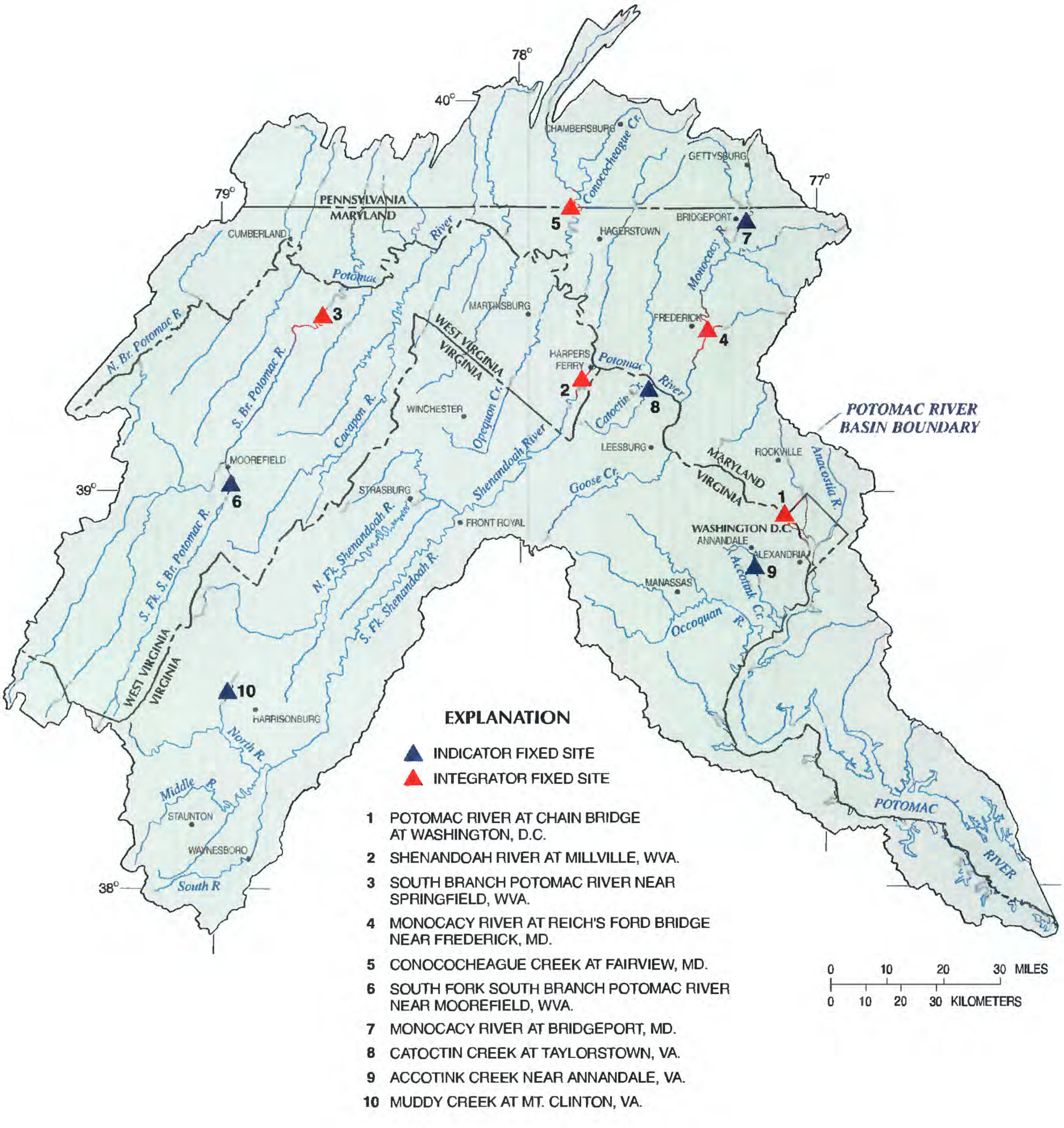

Figure 2. River network and integrator/indicator fixed sites in the Potomac River Basin.

Table 1. *Percentage of different land uses, lithologies, and subunits within drainage areas of fixed sites in the Potomac River Basin*

[mi^2, square miles; Ag, agricultural; For, forested; Urb, urban; N, siliciclastic; CN, carbonate/siliciclastic; C, carbonate; S, unconsolidated sediment; X, crystalline; AP, Appalachian Plateau; VR, Valley and Ridge; GVC, Great Valley Carbonate; GVNC, Great Valley Noncarbonate; BR, Blue Ridge; TR; Triassic; PD, Piedmont. Numbers in **bold** represent the highest percentage. --, indicate less than 1 percent]

Site no. (fig. 2)	Site name	Site type	Drainage area (mi^2)	Annual land use [a] (nearest percent)			Lithology (nearest percent)					Subunits (nearest percent)						
				Ag	For	Urb	N	CN	C	S	X	AP	VR	GVC	GVNC	BR	TR	PD
1	Potomac River at Chain Bridge at Washington, D.C.	Integrator	11,670	39	**54**	6	**52**	7	21	--	19	6	**44**	19	8	8	6	10
2	Shenandoah River at Millville, W. Va.	Integrator	3,040	40	**51**	7	36	7	**43**	--	14	--	26	43	17	14	--	--
3	South Branch Potomac River near Springfield, W. Va.	Integrator	1,470	22	**78**	--	**77**	15	6	3	--	--	**100**	--	--	--	--	--
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	Integrator	817	**71**	23	5	38	--	7	--	**54**	--	--	6	--	18	**43**	33
5	Conococheague Creek at Fairview, Md.	Integrator	494	**59**	36	5	**51**	--	39	--	10	--	11	38	41	10	--	--
6	South Fork South Branch Potomac River near Moorefield, W. Va.	Indicator	283	14	**86**	--	**86**	7	5	2	--	--	**100**	--	--	--	--	--
7	Monocacy River at Bridgeport, Md.	Indicator	173	**77**	20	4	**75**	--	--	--	24	--	--	--	--	11	**88**	1
8	Catoctin Creek at Taylorstown, Va.	Indicator	89.6	**81**	18	1	--	--	--	--	**99**	--	--	--	--	15	--	**85**
9	Accotink Creek near Annandale, Va.	Indicator	23.5	--	2	**98**	--	--	--	--	**100**	--	--	--	--	--	--	**100**
10	Muddy Creek at Mt. Clinton, Va.	Indicator	14.2	**73**	22	5	--	--	**100**	--	--	--	--	**100**	--	--	--	--

[a] Land use determined by Anderson and others (1976) and updated by Hitt (1994). Land-use types described in Mitchell and others (1977).

Methods of Calculation

The methods of calculation used in this study were developed by the USGS. A multiple regression equation and a hydrograph separation procedure were used for load estimation of total and base-flow loads.

Estimation of Nutrient and Sediment Loads

The ESTIMATOR program (version 94.02) was used in developing load estimates for the Potomac fixed sites. The Adjusted Maximum Likelihood Estimator (AMLE), discussed in Cohn (1988) and Cohn and others (1995) is implemented in the ESTIMATOR program. The AMLE allows for the use of data sets containing censored values. For data sets without censored values, the AMLE is equivalent to the MVUE.

In the ESTIMATOR program, available discharge and water-quality data can be used to calibrate a multiple regression equation of the form

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

where

ln is the natural logarithm function;

$\beta_0 - \beta_6$ are the beta coefficients of the explanatory variables;

C is the measured concentration (milligrams per liter or micrograms per liter);

Q is the mean daily discharge on the day the sample was taken;

Q is the centered discharge;

T is the time, converted to decimal form;

$\bar{T}$ is the centered time, converted to decimal form, and

ε is the combined independent random error, assumed to be normally distributed with zero mean and variance.

The output from the model include model diagnostics and plots of residuals and month, residual and simulated values, residuals and flow, and residuals and time. The model diagnostics were used to select the explanatory variables that were considered to be significant to the regression equation; a variable was kept if the beta coefficient had a p-value less than 0.1. The residual plots were examined to ensure that there were no patterns in the residuals in relation to simulated values, flow, and time.

For the regression equations for the 1993-95 data, the $\{T- \bar{T}\}^2$ explanatory variable was dropped because it was not considered to be a relevant parameter for such a short time period. To determine trends using historical data records, this explanatory variable was included if the beta coefficient was significant (p-value less than 0.1). The resulting regression equations were then used with mean daily discharge values and time to simulate daily concentrations and loads. Daily loads were summed to provide annual load estimates for a particular water-quality constituent.

For the ESTIMATOR program, it is optimal to have 60 or more measured concentrations with about half of the concentrations measured at higher discharges (T.A. Cohn, USGS, written commun., 1996). However, the program will allow a model to be formulated without that much data. In the following applications of the ESTIMATOR, fewer data points were available (see tables 2-6 for number of samples used in each regression), and these were collected over a relatively short timeframe. This could have an effect on load-estimate accuracy and precision and load estimates should be evaluated with that in mind.

There is another potential source of error in the estimates presented below. In the version of the ESTIMATOR program used in this study, water-quality concentrations measured during a routine site visit are regressed against mean daily discharge, not against instantaneous discharge. For this reason, load estimates at larger basin sites may be more accurate because measured concentrations generally have less diurnal variability. Concentrations measured at smaller basin sites can be highly variable because stages rise and fall quickly during storms. Sites with large diurnal water-quality variations may cause errors in load estimates. This kind of error in loads may not be reflected in the standard error of the regression equation and bias may be introduced.

An example of the ESTIMATOR program output at an intensive fixed site is presented in figure 3. This graph shows measured instantaneous and simulated daily concentrations of TNO23 concentrations at Muddy Creek at Mt. Clinton, Va.

Calculation of Yields

Load estimates over time can be used to compute a yield for the contributing drainage area of the site. Yield is an area-normalized load performed for the purposes of site comparison and defined as:

$$Yield = \frac{\sum_{i=1}^{N} \frac{L_i}{N}}{DA} ,$$

where

L_i is the calculated load in year i,
N is the total number of years, and
DA is the drainage area of the basin.

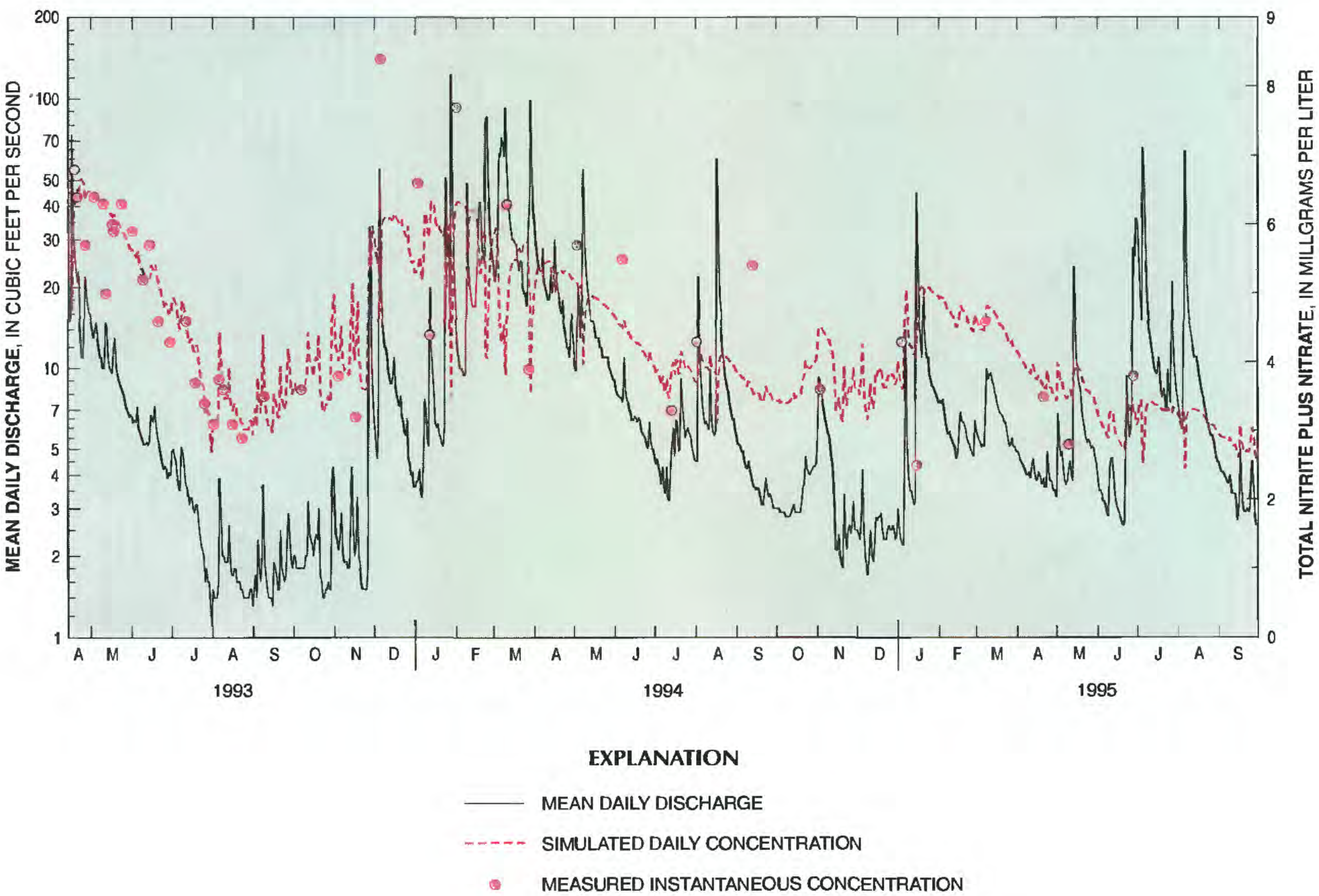

Figure 3. Mean daily discharge, simulated daily concentrations of total nitrite plus nitrate, and measured instantaneous concentrations of total nitrite plus nitrate at Muddy Creek at Mt. Clinton, Virginia, 1993-95.

Differences in yields between sites for the same time period may be attributable not only to differences in land use, geology, types of rock, and anthropogenic factors (such as point sources of nutrients), but to differences in the amount of precipitation that the sites receive over the same time period. In the following calculations, annual loads from 1994 and 1995 are used to calculate yields for the fixed sites. These years were chosen because most of the data were collected in this timeframe and because hydrologic conditions were generally similar at the sites in comparison to their respective periods of record.

Hydrograph Separation

In order to determine if water-quality samples are collected during days of base flow or during days of higher discharge, a hydrograph separation procedure (Sloto and Crouse, 1996) was used to separate base-flow discharge from mean daily discharge. The local minimum method was selected for use in this study (Sloto and Crouse, 1996). The base-flow discharges are compared to the daily discharges to determine the days during which the base flow accounted for 70 percent or more of the total streamflow. Water-quality samples collected on these days are designated as "base-flow samples." An example of a hydrograph separation and determination of which samples were collected during base flow is presented in figure 4.

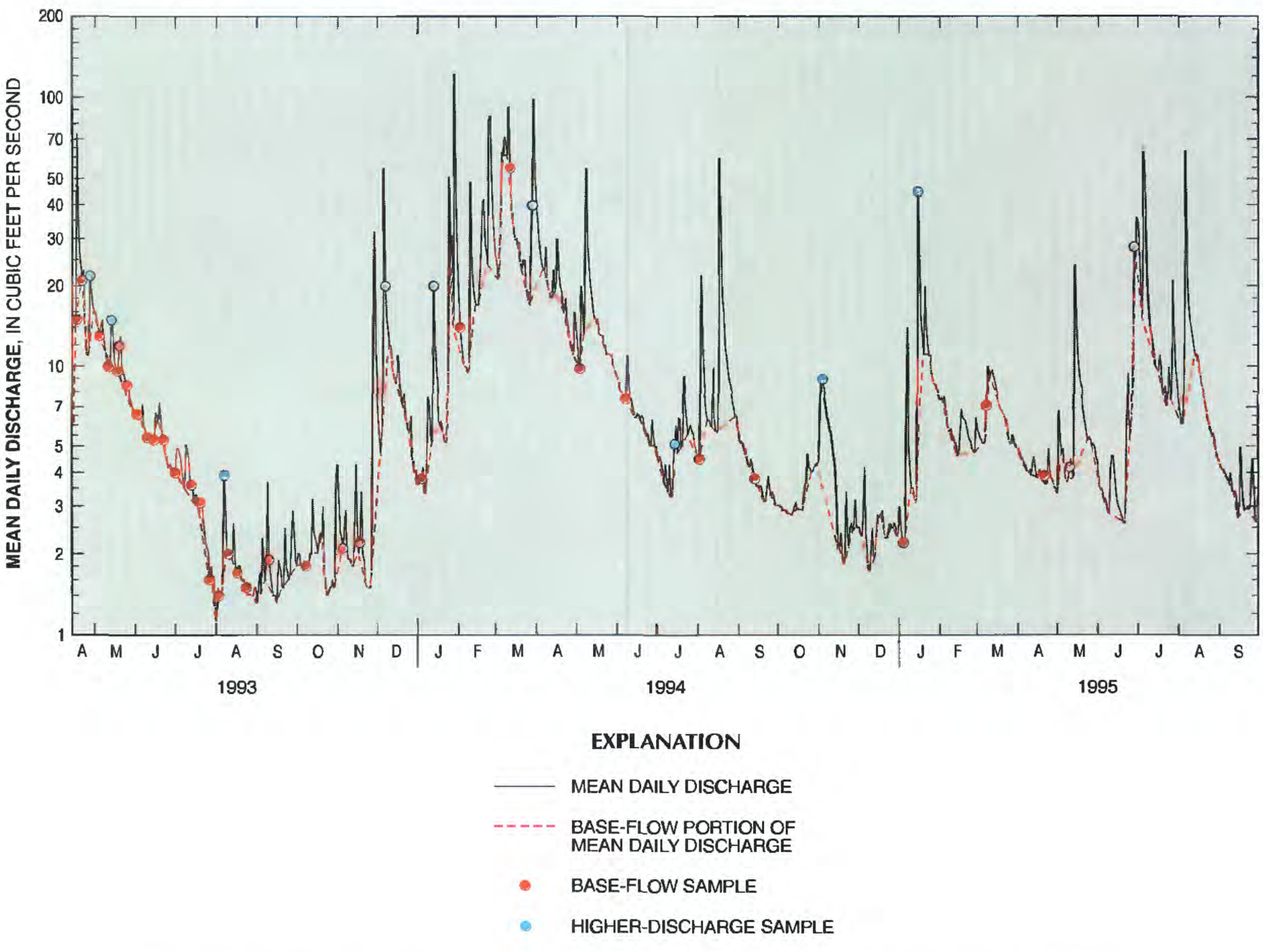

Figure 4. Hydrograph separation and sample types at Muddy Creek at Mt. Clinton, Virginia, 1993-95.

NUTRIENT AND SEDIMENT LOADS AND YIELDS AT NAWQA FIXED SITES, 1993-95

Annual nutrient and sediment loads are estimated for each of the NAWQA fixed sites for the 1993-95 water years. The coefficient of determination (R^2) for each parameter at each site is a measure of how well the six possible explanatory variables in the regression equation explain the variability in the measured concentrations. The standard error of prediction and error range of the loads and yields is based on the difference between the actual instantaneous concentrations and the predicted daily concentrations.

Nitrogen Loads and Yields

The loads and yields of TKN, TNO23, and TN from the fixed sites are presented in tables 2-4. Total nitrogen concentrations at a particular site are determined in the laboratory as the summation of the TKN and TNO23 concentrations. Theoretically, therefore, the estimated loads of TKN and TNO23 should add up to the estimated TN load at a particular site. Any error is due to the formulation of the regression equations.

Model standard error of prediction for TN loads were fairly reasonable, ranging from 3 to 17 percent. Standard error of prediction for TKN loads were higher than for TN loads, ranging from 10 to 30 percent. Standard error of predictions for TNO23 loads also were higher than for TN loads, ranging from 6 to 32 percent. Although the R^2 sometimes was quite low (for example, 0.01 for the TKN model at Monocacy River at Reich's Ford Bridge near Frederick, Md.), the results are presented. The poor fit of some equations may be attributable to point sources, but the reasons are not clear based on the collected data. The standard error of prediction is a better measure to consider when comparing the yields among sites.

There is greater variation in the yields of TNO23 from site to site than there is in the yields of TKN. The TNO23 load generally makes up a higher percentage of the TN load than does TKN for all the sites, with the possible exception of Accotink Creek. TNO23 load makes up the highest percentage of the TN load at the sites with the highest yields of TN--Conococheague Creek at Fairview, Muddy Creek at Mt. Clinton, and Monocacy River at Bridgeport.

Phosphorus Loads and Yields

The loads and yields of TP from the fixed sites are presented in table 5. Model standard error of prediction for total phosphorus loads were quite high, ranging from 13 to 70 percent.

Suspended-Sediment Loads and Yields

The loads and yields of total suspended sediment from the fixed sites are presented in table 6. Standard error of prediction for these loads were high, ranging from 13 to 70 percent; this result reflects the related variability of total suspended-sediment concentrations and flow. Differences in total suspended-sediment loads and yields among sites are more pronounced for the wetter years (1993 and 1994).

Summary of Loads and Yields

The load estimates for the period 1993-95 presented in tables 2-6 indicate that, of the integrator sites sampled, two major tributaries from mostly agricultural regions (table 1)--Conococheague Creek at Fairview, Md. (fig. 2, site 5) and Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4)--had the greatest yields of TN, TP, and SED in the Potomac River Basin. Similar conclusions for other time periods have previously been documented (Blomquist and others, 1995; Langland and others, 1995). The integrator site with the highest yields of TN, TP, and SED was Conococheague Creek at Fairview, Md. (site 5), a largely agricultural site located primarily in the Great Valley subunits underlain by siliciclastic and carbonate rock. The site with the second highest yields of TN, TP, and SED was Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4). The Monocacy River site has a higher percentage of agricultural land use than the Conococheague Creek site, but is located primarily in the Triassic and Piedmont subunits, and is underlain by crystalline and siliciclastic rock.

At the smaller indicator sites, two agricultural sites and one urban site have the highest yields of nutrients and sediment for 1993-95. The indicator

Table 2. *Loads of total nitrogen from fixed sites in the Potomac River Basin, 1993-95*

[N, number of samples used in ESTIMATOR program; R^2, coefficient of determination for the concentration regression equation; WY, water year; Load, thousands of pounds per year; SEP, percent standard error of prediction; Average yield, thousands of pounds per square mile per year; --, data not available]

Site no. (fig. 2)	Site name	N	R^2	WY 1993		WY 1994		WY 1995		WY 1994-95
				Load	SEP	Load	SEP	Load	SEP	Average yield
1	Potomac River at Chain Bridge at Washington, D.C.	20	0.88	73,294	4	64,632	3	23,558	3	3.78 ± 0.11
2	Shenandoah River at Millville, W. Va.	25	.38	13,770	7	14,824	7	6,601	5	3.52 ± 0.23
3	South Branch Potomac River near Springfield, W. Va.	13	.62	2,870	12	4,473	11	1,629	11	2.06 ± 0.23
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	21	.60	10,842	8	7,917	5	3,734	8	7.13 ± 0.43
5	Conococheague Creek at Fairview, Md.	23	.42	8,135	5	8,695	5	3,986	4	12.84 ± 0.60
7	Monocacy River at Bridgeport, Md.	44	.38	1,224	15	1,202	17	666	14	5.40 ± 0.86
8	Catoctin Creek at Taylorstown, Va.	19	.64	507	14	410	12	88	11	2.78 ± 0.33
9	Accotink Creek near Annandale, Va.	38	.34	134	11	154	12	62	8	4.60 ± 0.50
10	Muddy Creek at Mt. Clinton, Va.	48	.69	--	--	179	5	68	7	8.70 ± 0.48

Table 3. *Loads of total Kjeldahl nitrogen from fixed sites in the Potomac River Basin, 1993-95*

[N, number of samples used in ESTIMATOR program; R^2, coefficient of determination for the concentration regression equation; WY, water year; Load, thousands of pounds per year; SEP, percent standard error of prediction; Average yield, thousands of pounds per square mile per year; --, data not available]

Site no. (fig. 2)	Site name	N	R^2	WY 1993		WY 1994		WY 1995		WY 1994-95
				Load	SEP	Load	SEP	Load	SEP	Average yield
1	Potomac River at Chain Bridge at Washington, D.C.	22	0.40	13,139	14	14,281	14	5,915	10	0.87 ± 0.11
2	Shenandoah River at Millville, W. Va.	30	.12	3,752	16	4,039	16	1,651	12	0.94 ± 0.14
3	South Branch Potomac River near Springfield, W. Va.	28	.62	1,168	26	1,722	23	441	23	0.73 ± 0.17
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	21	.01	2,123	24	1,830	23	866	17	1.65 ± 0.35
5	Conococheague Creek at Fairview, Md.	23	.49	926	20	1,389	17	617	19	2.03 ± 0.36
7	Monocacy River at Bridgeport, Md.	46	.56	450	12	472	14	236	12	2.05 ± 0.27
8	Catoctin Creek at Taylorstown, Va.	22	.66	163	14	119	10	39	10	0.89 ± 0.09
9	Accotink Creek near Annandale, Va.	42	.53	37	30	66	24	31	16	2.06 ± 0.44
10	Muddy Creek at Mt. Clinton, Va.	48	.18	--	--	40	24	18	30	2.04 ± 0.53

Table 4. *Loads of total nitrite plus nitrate from fixed sites in the Potomac River Basin, 1993-95*

[N, number of samples used in ESTIMATOR program; R^2, coefficient of determination for the concentration regression equation; WY, water year; Load, thousands of pounds per year; SEP, percent standard error of prediction; Average yield, thousands of pounds per square mile per year; --, data not available]

Site no. (fig. 2)	Site name	N	R^2	WY 1993		WY 1994		WY 1995		WY 1994-95 Average Yield
				Load	SEP	Load	SEP	Load	SEP	
1	Potomac River at Chain Bridge at Washington, D.C.	22	0.74	59,531	8	50,640	6	18,331	6	2.96 ± 0.18
2	Shenandoah River at Millville, W. Va.	30	.43	7,804	12	13,192	11	3,984	11	2.83 ± 0.31
3	South Branch Potomac River near Springfield, W. Va.	27	.42	2,092	13	2,727	9	922	10	1.23 ± 0.11
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	21	.76	9,691	8	6,338	5	2,851	7	5.62 ± 0.32
5	Conococheague Creek at Fairview, Md.	23	.48	7,668	6	7,041	5	3,236	6	10.40 ± 0.55
6	South Fork South Branch Potomac River near Moorefield, W. Va.	29	.43	494	20	667	20	271	18	1.66 ± 0.32
7	Monocacy River at Bridgeport, Md.	41	.08	1,014	29	1,102	32	478	29	4.57 ± 1.42
8	Catoctin Creek at Taylorstown, Va.	21	.66	324	16	298	15	121	14	2.34 ± 0.34
9	Accotink Creek near Annandale, Va.	42	.41	64	15	66	14	33	10	2.11 ± 0.27
10	Muddy Creek at Mt. Clinton, Va.	48	.64	--	--	128	5	49	6	6.23 ± 0.33

Table 5. *Loads of total phosphorus from fixed sites in the Potomac River Basin, 1993-95*

[N, number of samples used in ESTIMATOR program; R^2, coefficient of determination for the concentration regression equation; WY, water year; Load, thousands of pounds per year; SEP, percent standard error of prediction; Average yield, thousands of pounds per square mile per year; --, data not available]

Site no. (fig. 2)	Site name	N	R^2	WY 1993		WY 1994		WY 1995		WY 1994-95 Average yield
				Load	SEP	Load	SEP	Load	SEP	
1	Potomac River at Chain Bridge at Washington, D.C.	21	0.94	2,227	21	2,518	21	873	16	0.15 ± 0.03
2	Shenandoah River at Millville, W. Va.	30	.28	1,151	28	1,246	28	395	21	0.27 ± 0.07
3	South Branch Potomac River near Springfield, W. Va.	28	.71	148	44	256	34	68	44	0.11 ± 0.04
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	21	.46	525	17	465	18	247	13	0.44 ± 0.07
5	Conococheague Creek at Fairview, Md.	23	.60	194	19	315	17	185	21	0.51 ± 0.09
6	South Fork South Branch Potomac River near Moorefield, W. Va.	29	.58	18	44	29	40	9	64	0.07 ± 0.01
7	Monocacy River at Bridgeport, Md.	45	.68	108	17	117	22	60	18	0.51 ± 0.11
8	Catoctin Creek at Taylorstown, Va.	22	.60	55	45	40	38	11	40	0.28 ± 0.11
9	Accotink Creek near Annandale, Va.	42	.58	13	53	26	70	4	33	0.64 ± 0.42
10	Muddy Creek at Mt. Clinton, Va.	48	.27	--	--	11	35	7	47	0.63 ± 0.25

Table 6. *Loads of total suspended sediment from fixed sites in the Potomac River Basin, 1993-95*

[N, number of samples used in ESTIMATOR program; R^2, coefficient of determination for the concentration regression equation; WY, water year; Load, thousands of pounds per year; SEP, percent standard error of prediction; Average yield, thousands of pounds per square mile per year; --, data not available]

Site no. (fig. 2)	Site name	N	R^2	WY 1993		WY 1994		WY 1995		WY 1994-95 Average yield
				Load	SEP	Load	SEP	Load	SEP	
1	Potomac River at Chain Bridge at Washington, D.C.	16	0.95	994	15	1,331	13	342	18	0.07 ± 0.01
2	Shenandoah River at Millville, W. Va.	23	.85	232	23	273	23	98	38	0.06 ± 0.02
3	South Branch Potomac River near Springfield, W. Va.	19	.85	89	43	127	37	25	46	0.05 ± 0.02
4	Monocacy River at Reich's Ford Bridge near Frederick, Md.	17	.49	96	36	75	38	22	28	0.06 ± 0.02
5	Conococheague Creek at Fairview, Md.	14	.80	116	40	253	73	40	64	0.30 ± 0.21
7	Monocacy River at Bridgeport, Md.	25	.47	7	52	6	50	10	82	0.05 ± 0.03
8	Catoctin Creek at Taylorstown, Va.	20	.90	26	53	16	32	4	40	0.11 ± 0.4
9	Accotink Creek near Annandale, Va.	42	.77	10	44	21	60	2	29	0.49 ± 0.29
10	Muddy Creek at Mt. Clinton, Va.	48	.37	--	--	4	48	1	44	0.18 ± 0.08

sites with the highest yields of TN and TNO23 were agricultural sites--Monocacy River at Bridgeport (fig. 2, site 7) and Muddy Creek at Mt. Clinton (site 10). These sites are located in the Great Valley and the Triassic, respectively, and are underlain by combinations of carbonate, crystalline, and siliciclastic rock. The urban indicator site, Accotink Creek near Annandale (site 9), had the highest yield of SED. This urban site is located in the Piedmont subunit and is underlain by crystalline rock. TKN and TP were higher in these two agricultural and one urban site. Another agricultural indicator site, Catoctin Creek at Taylorstown, located in the Piedmont subunit and underlain by crystalline rock, generally had lower yields of nutrients and sediment than the other agricultural sites and the urban site.

The integrator and indicator sites on South Branch Potomac River (sites 3 and 6) with the largest percentages of forested land always had the lowest yields of nitrogen and phosphorus for 1993-95. In fact, a sufficient number of water-quality measurements of TKN over the detection limit were not available to estimate a TKN or TN load at the forested indicator site, South Fork South Branch Potomac River near Moorefield.

CONCENTRATIONS AND LOADS FROM BASE FLOW AT NAWQA FIXED SITES, 1993-95

Base-flow loads are attributed to ground-water discharges and point sources, whereas samples collected during higher discharges can contain storm runoff as well. In developing nutrient and sediment control strategies, it is important to understand the relative importance of base flow and total streamflow in contributing loads and carrying concentrations.

In the following section, the concentrations of samples collected during the first sampling phase of the Potomac NAWQA are statistically summarized. Base-flow loads are estimated at three integrator sites by combining historical base-flow measurements with the 1993-95 NAWQA base-flow measurements and applying the ESTIMATOR program. Base-flow loads could not be estimated at all of the fixed sites due to the lack of historical data and the limited number of NAWQA base-flow samples collected during the first sampling phase of NAWQA.

Concentration Statistics at NAWQA Fixed Sites

Boxplots for four parameters--TN, TNO23, TP, and SED--display the concentration data for the 10 fixed sites (figs. 5 and 6). The total number of samples taken in each flow regime at each site also are noted on the boxplot figures (figs. 5 and 6).

Boxplots of TN concentrations for each site (fig. 5a) show that TN concentrations are significantly lower in the base-flow samples than in the higher discharge samples at two integrator sites with high percentages of forested land use--South Branch Potomac River (fig. 2, site 3) and Potomac River at Chain Bridge (site 1)--and at one agricultural indicator site, Monocacy River at Bridgeport (site 7). A forested indicator site, South Fork South Branch Potomac River near Moorefield (site 6), had significantly higher concentrations of TN in base-flow samples than in higher discharge samples. The highest TN concentrations in both base-flow and higher discharge samples were measured at two agricultural sites in the Great Valley--Conococheague Creek at Fairview, Md. (site 5), and Muddy Creek at Mt. Clinton, Va. (site 10).

Median TP and SED concentrations are higher at all sites when measured at higher discharges (fig. 6a and 6b) than when measured during base-flow conditions. The TP concentrations are significantly higher in higher discharge samples than in base-flow samples at five sites. The SED concentrations are significantly higher in higher discharge samples than in base-flow samples at seven sites. The highest TP median concentrations were measured in higher discharge samples at two agricultural sites--Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4), and Muddy Creek at Mt. Clinton, Va. (site 10). The highest SED concentrations measured in higher discharges were from Accotink Creek near Annandale, Va. (site 9), and Muddy Creek at Mt. Clinton, Va. (site 10), an urban site and an agricultural site, respectively.

The Potomac River at Chain Bridge at Washington, D.C. (site 1), was the only site where concentrations for all four plotted parameters (TN,

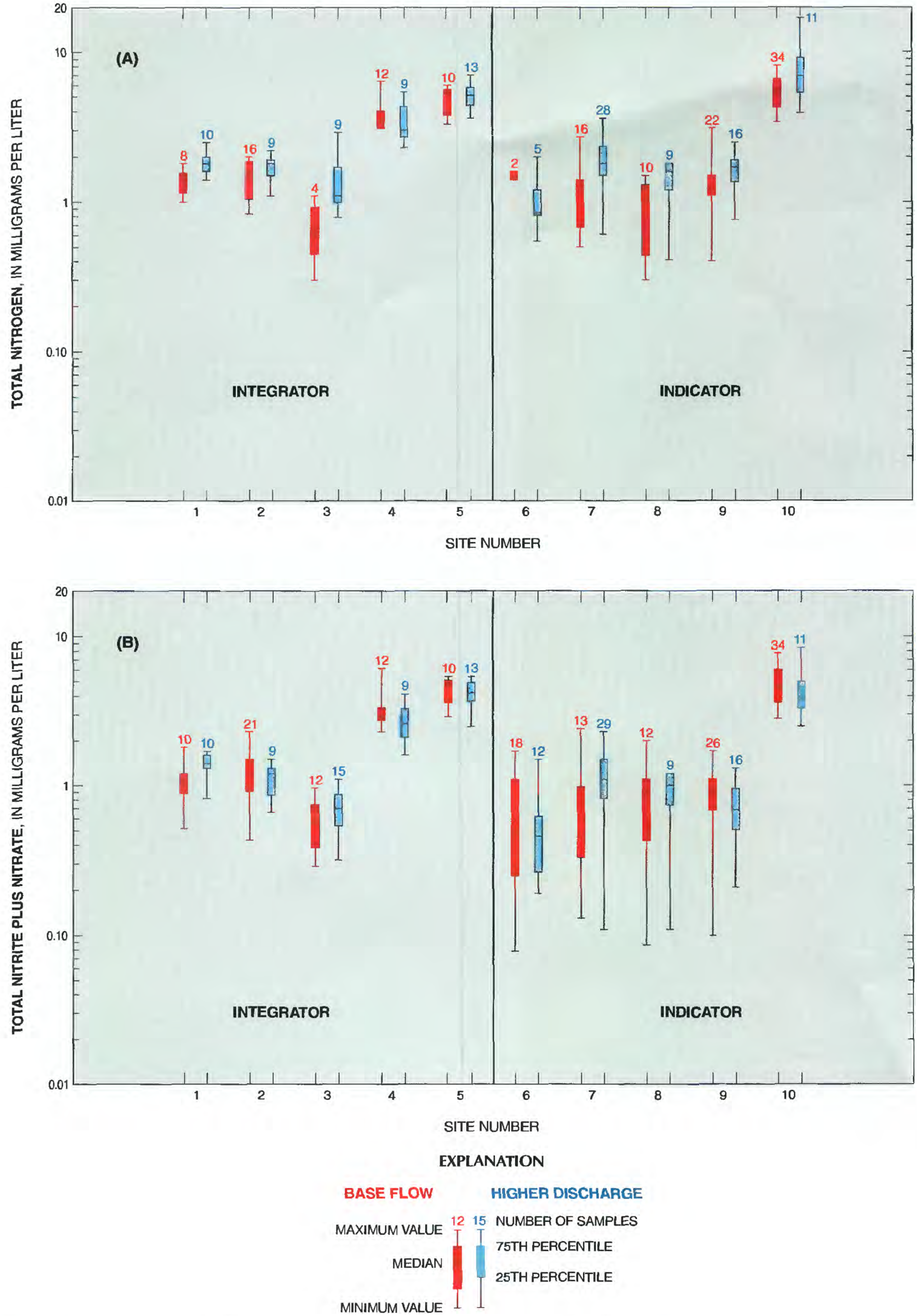

Figure 5. Base-flow and higher discharge concentrations at the NAWQA fixed sites for **(A)** total nitrogen, and **(B)** total nitrite plus nitrate.

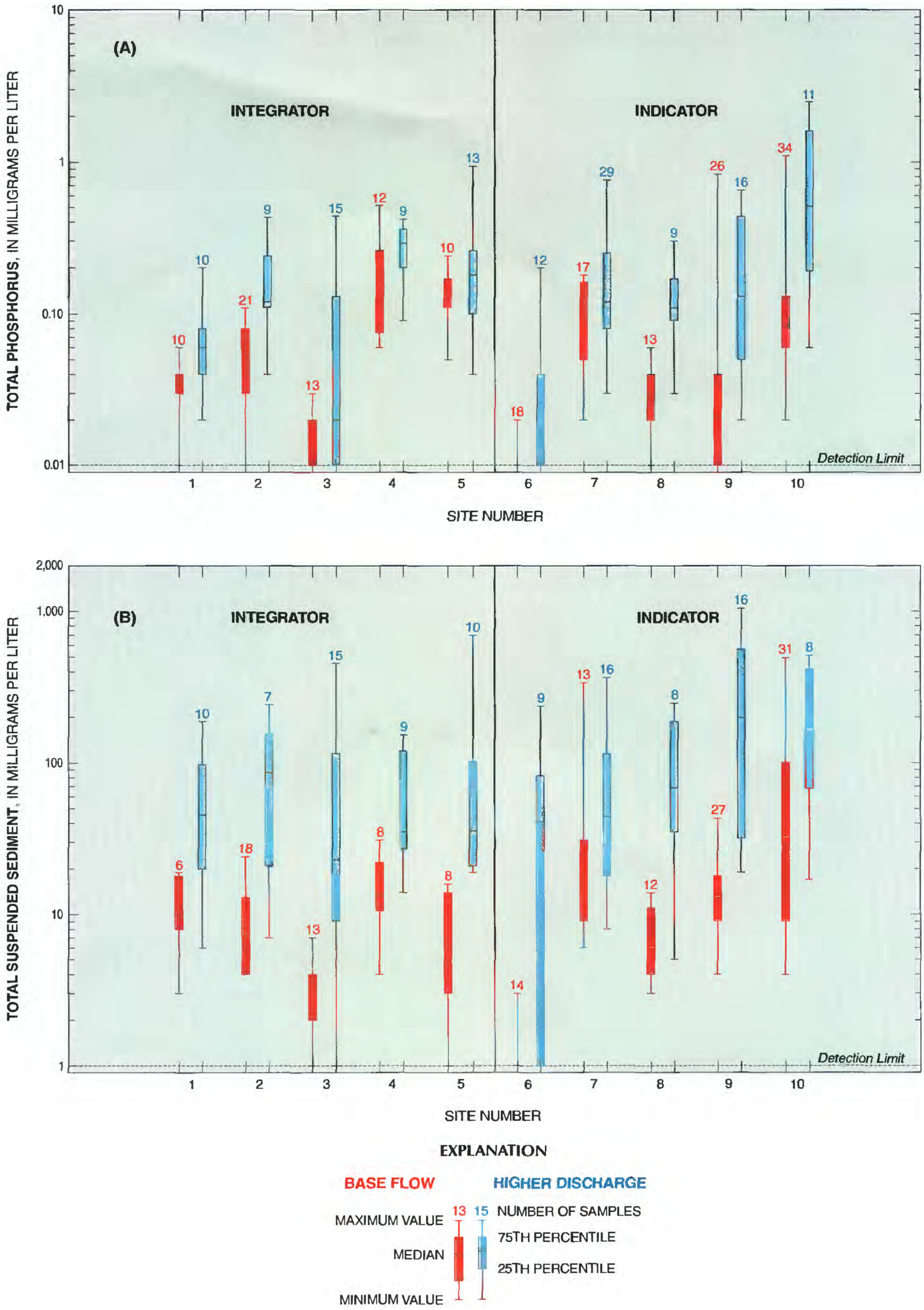

Figure 6. Base-flow and higher discharge concentrations at the NAWQA fixed sites for **(A)** total phosphorus, and **(B)** total suspended sediment.

TNO23, TP, and SED) were significantly lower for base-flow conditions than conditions of higher discharge. This is the only site with these results for TNO23.

Estimated Total and Base-flow Loads of Total Nitrite plus Nitrate, Total Nitrogen, and Total Phosphorus at Three NAWQA Sites Using Historical and NAWQA Data

At three integrator sites, there are sufficient long-term and NAWQA water-quality monitoring data to estimate a new total load (based on a longer data record) and the base-flow contribution of TNO23, TN, and TP to this total load (table 7, fig. 7). These sites include the Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4), the Shenandoah River at Millville, W. Va. (site 2), and the Potomac River at Chain Bridge at Washington, D.C. (site 1).

TNO23 constitutes the predominant form of nitrogen transported during base-flow conditions (table 7, fig. 7). Base-flow loads of TNO23 were often estimated to be greater than the base-flow loads of TN based on the separate regression analyses. This, however, is probably an artifact of slightly different regression parameters and associated errors.

Total and base-flow loads are greatest in the wet years (1993 and 1994) and lowest in the dry year (1995), but base-flow loads make up a greater percentage of total loads during dry years. At the Potomac River at Chain Bridge site, base-flow loads account for approximately 40 to 60 percent of the TN load, 50 to 60 percent of the TNO23 load, and less than 30 percent of the TP load. Compared to the Potomac River site, the percentage of the nutrient load contributed by base flow at the Monocacy River site and the Shenandoah River site is higher for TN, TNO23, and TP during the wet years (1993 and 1994) and higher for TNO23 and TP during the dry year (1995). Although the Monocacy River site has a higher yield of TN and TP than the Shenandoah River site, the percentage of the loads contributed from base flow at the two sites is about the same.

Table 7. *Base-flow loads of total nitrite plus nitrate, total nitrogen, and total phosphorus at three integrator fixed sites in the Potomac River Basin, 1993-95*

[TNO23, total nitrite plus nitrate, TN, total nitrogen, TP, total phosphorus. Sites are shown in figure 2]

	Base-flow load, in thousands of pounds per year *(Percent of total load)* [a]								
	Potomac River at Chain Bridge at Washington, D.C. (site 1)			Shenandoah River at Millville, W. Va. (site 2)			Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4)		
Year	TNO23	TN	TP	TNO23	TN	TP	TNO23	TN	TP
1993	40,501 *(55)*	32,756 *(43)*	432 *(10)*	8,854 *(70)*	7,851 *(52)*	264 *(28)*	5,165 *(60)*	5,379 *(50)*	143 *(25)*
1994	40,580 *(48)*	37,064 *(45)*	377 *(10)*	9,341 *(66)*	7,873 *(48)*	256 *(26)*	4,923 *(64)*	5,143 *(55)*	137 *(26)*
1995	24,319 *(63)*	17,214 *(60)*	181 *(27)*	1,759 *(66)*	3,878 *(58)*	159 *(46)*	2,619 *(64)*	2,992 *(63)*	106 *(39)*

[a] Base-flow and new total load estimates were determined using a regression equation that was formulated with combined historical and NAWQA data sets.

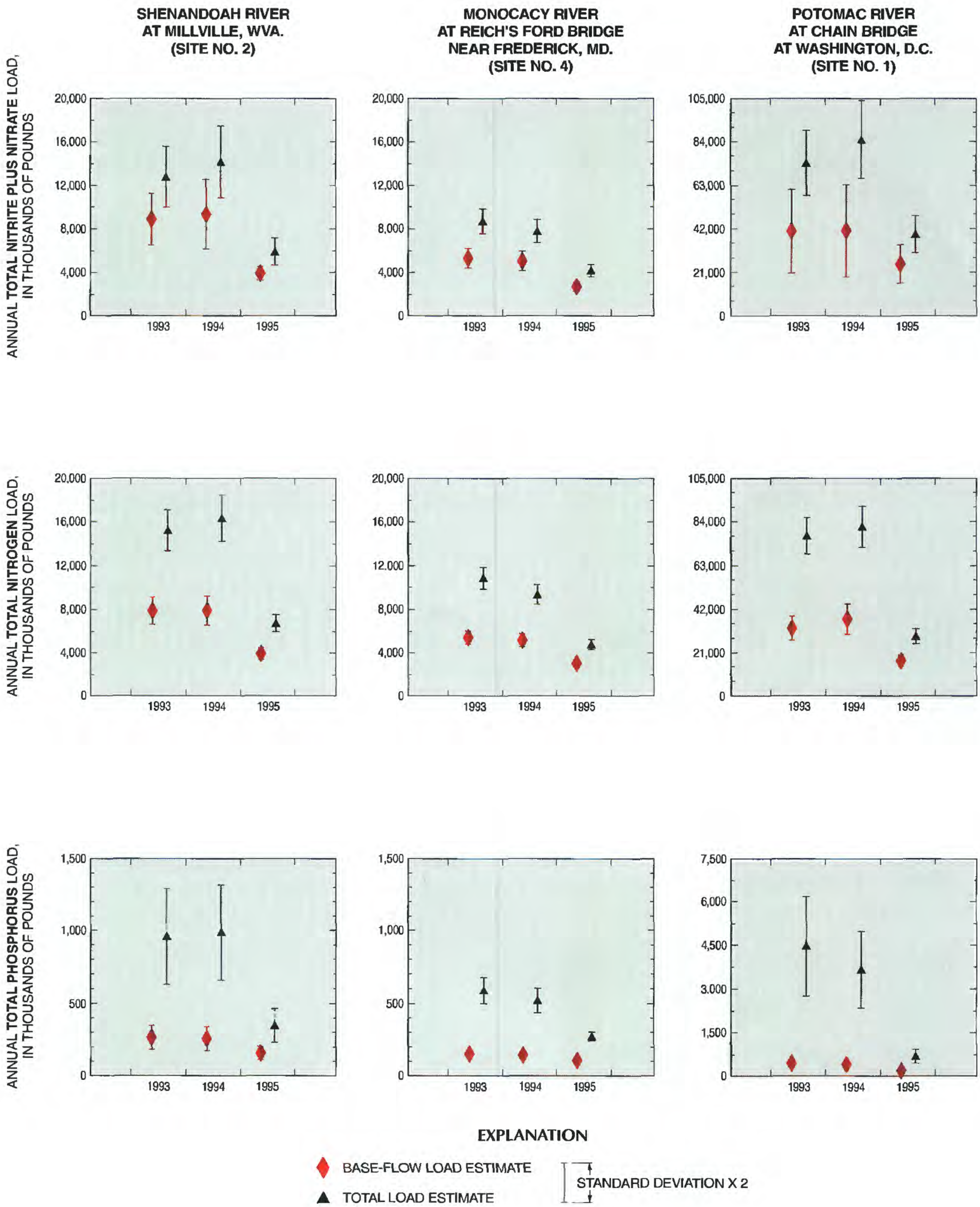

Figure 7. Base-flow and total loads of total nitrogen, total nitrite plus nitrate, and total phosphorus at three integrator fixed sites in the Potomac River Basin, 1993-95.

SUMMARY

Multiple surface-water samples were collected at 10 fixed sites during the first sampling phase of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) of the Potomac River Basin. Five fixed sites are at the outlets of small to intermediate subwatersheds characterized by a single land use or a representative combination of land uses (indicator sites) and five fixed sites are at the outlets of larger subwatersheds characterized by the combined effects of all natural and human water-quality factors (integrator sites).

Based upon estimated loads and yields, two integrator sites draining primarily agricultural regions overlying combinations of siliciclastic, carbonate, and crystalline rock types have the greatest 1993-95 yields of total nitrogen (TN), total phosphorus (TP), and total suspended sediment (SED) in the Potomac River Basin. These sites are the Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4) and the Conococheague Creek at Fairview, Md. (site 5). Similar conclusions have previously been documented. At the smaller indicator sites, two agricultural sites--Monocacy River at Bridgeport, Md. (site 7) and Muddy Creek at Mt. Clinton, Va. (site 10)--and one urban site, Accotink Creek at Annandale, Va. (site 9)--have the highest 1993-95 yields of nutrients and sediment. The agricultural indicator site, underlain by only crystalline rock, Catoctin Creek at Taylorstown, Va. (site 8), did not have high yields compared to the other indicator sites for those years. The integrator and indicator sites on South Branch Potomac River (sites 3 and 6)--the sites with the largest percentages of forested land--always had the lowest 1993-95 yields of nitrogen and phosphorus.

TN concentrations are significantly lower in the base-flow samples than in the higher discharge samples at two integrator sites with high percentages of forested land use--South Branch Potomac River near Springfield, Va. (site 3) and Potomac River at Chain Bridge at Washington, D.C. (site 1)--and at one agricultural indicator site, Monocacy River at Bridgeport, Md. (site 7). A forested indicator site, South Fork South Branch Potomac River near Moorefield, W. Va. (site 6), had significantly higher concentrations of TN in base-flow samples than in higher discharge samples. The highest TN median concentrations were measured at two agricultural sites in the Great Valley--Muddy Creek at Mt. Clinton, Va. (site 10) and Conococheague Creek at Fairview, Md. (site 5); these concentrations were significantly higher than the concentrations in both base-flow and higher discharge samples at all other sites.

Median TP and SED concentrations are higher at all sites during higher discharges. The highest TP median concentrations measured during higher discharges were from two agricultural sites--Monocacy River at Reich's Ford Bridge near Frederick, Md. (site 4) and Muddy Creek at Mt. Clinton, Va. (site 10). The highest SED concentrations measured in higher discharges were from Accotink Creek near Annandale, Va. (site 9), and Muddy Creek at Mt. Clinton, Va. (site 10), an urban and an agricultural site, respectively.

The Potomac River at Chain Bridge at Washington, D.C. (site 1) was the only site where concentrations for four plotted parameters (total nitrogen, total nitrite plus nitrate (TNO23), total phosphorus, and total suspended sediment) were significantly lower for base-flow conditions than conditions of higher discharge. This is the only site with these results for TNO23.

At the three integrator sites where historical data were available for base-flow load estimation, total and base-flow loads were greatest in the wet years (1993 and 1994) and lowest in the dry year (1995), and base-flow loads made up a greater percentage of total loads during the dry year. TNO23 constitutes the predominant form of nitrogen transported during base-flow conditions. Compared to the Potomac River site, the percentage of the nutrient load contributed by base flow at the Monocacy and Shenandoah sites is higher for TNO23, TN, and TP during the wet years (1993 and 1994) and higher for TNO23 and TP during the dry year (1995).

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