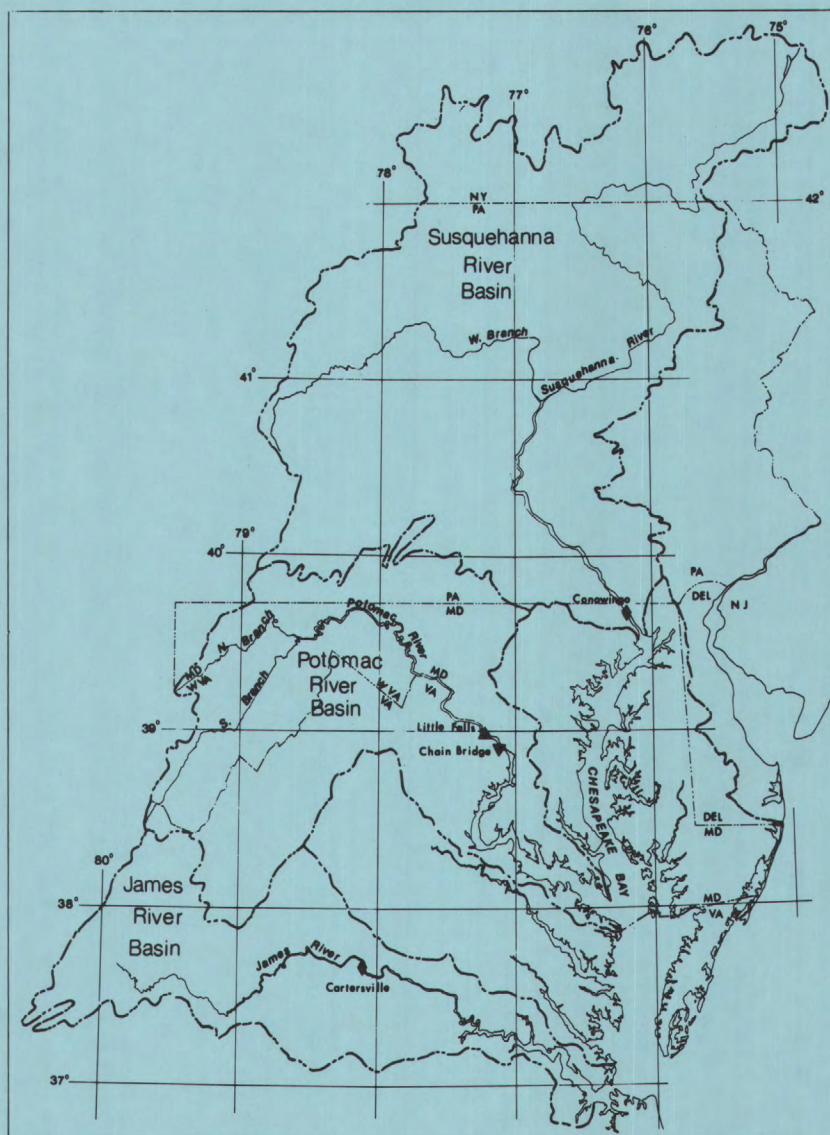


WATER-QUALITY OF THREE MAJOR TRIBUTARIES TO THE CHESAPEAKE BAY, THE SUSQUEHANNA POTOMAC, AND JAMES RIVERS, JANUARY 1979 – APRIL 1981

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 82-32



Prepared in cooperation with the

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May 1982

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES G. WATT, Secretary

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CONTENTS

	Page
Abstract	1
Introduction	2
Data collection	4
Basin land use and its effect on water quality	4
Hydrologic conditions	5
Methods of collection and laboratory analysis	5
Constituent loads	8
Load estimation techniques--nutrients and metals	8
Load estimation techniques--major cations and anions	16
Evaluation and limitation of the load estimates	18
Examination of selected water-quality constituents	20
Seasonal characterization of pesticides	20
Seasonal characterization of chlorophyll a	23
Chlorine	23
Total recoverable aluminum, iron, and manganese	27
Sulfate	27
Nutrients and their relationships to suspended sediment and discharge	31
Seasonal variability of nutrient transport	36
Comparison of nutrient data among the three Fall Line stations	42
Comparison of nutrient data with previous studies	46
Comparison of nutrient data at the Susquehanna River stations at Harrisburg, Pa., and Conowingo, Md.	51
Sediment transport characteristics	54
Susquehanna River	54
Potomac River	58
James River	58
Summary and conclusions	61
References	63

ILLUSTRATIONS

	Page
Figure 1. Map of study area showing location of drainage basins and sampling sites	3
2. Hydrograph showing mean monthly and long-term average monthly discharge for the three Fall Line stations	7
3. Hydrograph showing seasonal fluctuations in concentrations of 2,4-D at the Susquehanna and Potomac Fall Line stations	21
4. Hydrograph showing seasonal fluctuations in concentrations of atrazine at the Susquehanna and Potomac Fall Line stations	22
5. Hydrograph showing seasonal fluctuations of concentrations of chlorophyll a at the three Fall Line stations	24
6. Map showing location of chlorine-monitoring stations on selected tributaries to Chesapeake Bay	25
7. Hydrograph showing aluminum, iron, and manganese concentrations during February 20-26, 1981, at the Susquehanna River Fall Line station	28
8. Hydrograph showing aluminum, iron, and manganese concentrations during September 5-8, 1979, and March 21-24, 1980, at the Potomac River Fall Line station	29
9. Hydrograph showing aluminum, iron, and manganese concentrations during April 15-17, 1980, at the James River Fall Line station	30
10. Hydrograph showing nutrient concentrations during February 20-27, 1981, at the Susquehanna River Fall Line station	33
11. Hydrograph showing nutrient concentrations during September 5-8, 1979, and March 21-24, 1980, at the Potomac River Fall Line station	34
12. Hydrograph showing nutrient concentrations during April 15-17, 1980, at the James River Fall Line station	35
13. Hydrograph showing nutrient concentrations during February 25 - March 1, 1979, at the Potomac River Fall Line station	37

ILLUSTRATIONS--Continued

	Page
Figure 14. Bar graph showing monthly loads of nitrogen at the three Fall Line stations	43
15. Bar graph showing monthly loads of phosphorous at the three Fall Line stations	44
16. Hydrographs showing suspended-sediment transport for three high flows at the Susquehanna River at Harrisburg, Pa., and Conowingo, Md.	56
17. Hydrographs showing suspended-sediment transport for three high flows at the Potomac River at Chain Bridge at Washington, D.C.	59

TABLES

	Page
Table 1. Average discharge for study period and long-term average discharges for the three Fall Line stations	6
2. Least squares regression equations for load calculations of selected nutrients and metals with standard deviation (s^2) and coefficients of determination (r^2)	9
3. Monthly load estimates (in hundreds of thousands of pounds) for the Susquehanna River at Conowingo, Md.	10
4. Monthly load estimates (in hundreds of thousands of pounds) for the Potomac River at Chain Bridge at Washington, D.C.	12
5. Monthly load estimates (in hundreds of thousands of pounds) for the James River at Cartersville, Va.	14
6. Least squares regression equations for load calculations of selected cations and anions with standard deviation (s^2) and the coefficients of determination (r^2)	17
7. Nutrient loads (in millions of pounds) for the Potomac River at Chain Bridge at Washington, D.C., computed from the Potomac estuary and Fall Line monitoring study data	19
8. Schedule of low-molecular-weight, halogenated organic compounds analyzed in selected tributaries to the Chesapeake Bay	26

TABLES--Continued

	Page
Table 9. Sulfate loads in the Susquehanna, Potomac, and James Rivers from May 1980 to April 1981	32
10. Annual loads of selected nutrients (in millions of pounds) at the three Fall Line stations for calendar years 1979 and 1980	38
11. Seasonal fluctuations of selected nutrients for the three Fall Line stations	39
12. Total nutrient loads and discharge-weighted average nutrient concentrations for the period January 1979 to December 1980 at the three Fall Line stations	45
13. Average daily loads (in lbs/d) of selected nutrient species for the three Fall Line stations derived from different hydrologic investigations	47
14. Discharge-weighted average concentrations (in mg/L) of selected nutrient species for the three Fall Line stations derived from different hydrologic investigations	48
15. Estimates of nutrient loads (in lbs/d) at three different discharges for 1969-72 and 1979-81 data sets for the Susquehanna River at Conowingo, Md.	50
16. Water-quality constituent loads (in millions of pounds) for stations on the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 through March 1981	52
17. Relative proportions of orthophosphate, nitrite + nitrate, and ammonia + organic nitrogen to total phosphorous and nitrogen loads at the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 to March 1981	53
18. Discharge-weighted average concentrations (in mg/L) of water-quality constituents for stations on the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 through March 1981	55
19. Suspended-sediment loads (in tons) at the Harrisburg, Pa., and Conowingo, Md., stations on the Susquehanna River for three high-flow periods	57
20. Unit discharge sediment yields for the Potomac River at Chain Bridge at Washington, D.C., for three high-flow periods	60

CONVERSION OF MEASUREMENT UNITS

The following factors may be used to convert the inch-pound units published in this report to International System (SI) metric units.

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
<u>Length</u>		
inch (in.)	25.40	millimeter (mm)
	2.54	centimeter (cm)
foot (ft)	.3048	meter (m)
mile (mi)	1.609	kilometer (km)
<u>Area</u>		
square inch (in ²)	6.452	square centimeter (cm ²)
square mile (mi ²)	2.590	square kilometer (km ²)
<u>Volume</u>		
gallon (gal)	3.785	liter (L)
	.003785	cubic meter (m ³)
cubic foot (ft ³)	.02832	cubic meter (m ³)
<u>Flow</u>		
cubic foot per second (ft ³ /s)	28.32	liter per second (L/s)
	.02832	cubic meter per second (m ³ /s)
gallon per minute (gal/min)	.06309	liter per second (L/s)
	.00006309	cubic meter per second (m ³ /s)
<u>Temperature</u>		
degree Fahrenheit (°F)	-32 x 0.555	degree Celsius (°C)
<u>Concentration</u>		
pound per cubic foot	16055	milligram per liter (mg/L)
<u>Mass</u>		
pound per day (lb/d)	0.454	kilogram per day (kg/d)

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JANUARY 1979 - APRIL 1981

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ABSTRACT

Water-quality constituent loads at the Fall Line stations of the Susquehanna, Potomac, and James Rivers, the three major tributaries to the Chesapeake Bay, can be estimated with reasonable accuracy by regression techniques, especially for wet periods of 1 year or more. Net transport of all nutrient species and most other constituents, especially those found in greatest concentrations associated with suspended material, is dominated by a few spring and storm-related high-flow events. Atrazine and 2,4-D are the two herbicides most consistently detected at the Fall Line of the Susquehanna and Potomac Rivers. Concentrations of total residual chlorine and low-molecular-weight, halogenated hydrocarbons at selected sites in estuaries to the upper Bay are generally at or below detection limits. When compared to the two other major tributaries, the James River has the lowest discharge-weighted-sulfate concentrations, presumably because of the lack of coal mining activity in this basin. This river also has lower total nitrogen concentrations. Ammonia concentrations and loads are decreasing at all three Fall Line stations, as is orthophosphate in the Susquehanna and Potomac Rivers. Slight increases in total nitrogen and nitrite plus nitrate concentrations in the Susquehanna River from 1969 to 1980 may warrant continued monitoring.

Analyses of data for this report confirm the previous suggestion that when water discharge of the Susquehanna River at Conowingo, Maryland, is below about 400,000 cubic feet per second, sediment, with sorbed nutrients and other constituents, is deposited behind the three hydroelectric dams on this river between Harrisburg, Pennsylvania, and its mouth. Discharges above 400,000 cubic feet per second resuspend these sediments and transport constituent loads to the Bay well in excess of loads transported by the Susquehanna River at Harrisburg. In addition to precipitation quantity and intensity, antecedent conditions and season of the year play a major role in the transport of sediments and their associated chemical constituents at all three stations.

INTRODUCTION

The Chesapeake Bay is the largest estuary in the United States: 200 mi long; 8,000 mi of shoreline; and 4,400 mi² of water surface. It has a drainage area of 64,000 mi² and is fed by more than 150 tributaries (U.S. Dept. of the Army, Corps of Engineers, 1973). The three major tributaries of the Bay (Susquehanna, Potomac, and James Rivers) drain about 85 percent of the total Chesapeake Bay drainage basin.

The Bay supports substantial commercial and sport fishing and recreational industries. Its water also provides access to two major shipping ports--Baltimore, Md., and Hampton Roads, Va. Ship traffic on the Chesapeake Bay is increasing and is expected to continue growing as more coal is exported from Eastern United States.

In order to protect and preserve this valuable natural resource, the U.S. Environmental Protection Agency (EPA), under Congressional directive (Senate Report No. 94-326), conducted an in-depth study of the environmental quality of the Chesapeake Bay. As part of that study, the U.S. Geological Survey (USGS) assessed the water quality of the three major tributaries to the Bay [the Susquehanna, Potomac, and James Rivers (fig. 1)] at the Fall Line from January 1979 to April 1981. (The Fall Line is the boundary between the Coastal Plain and Piedmont physiographic provinces.)

This report presents the following water-quality information for the Susquehanna, Potomac, and James Rivers:

1. Estimated loads of major ions, suspended sediment, selected nutrient species, and selected trace metals for the 2-year, data-collection period.
2. An assessment of accuracy and limitations inherent in these estimates.
3. Seasonal characterization of nutrients, pesticides, and chlorophyll a collected during the study.
4. Relationships between discharge, specific conductance, and suspended sediment and selected nutrient and trace metal concentrations.
5. Comparisons of nutrient loads with other studies and the detection of trend in these loads.

The cooperation and assistance received from Mr. Howard Jarmon and staff of the Susquehanna Electric Company at Conowingo Dam are gratefully acknowledged.

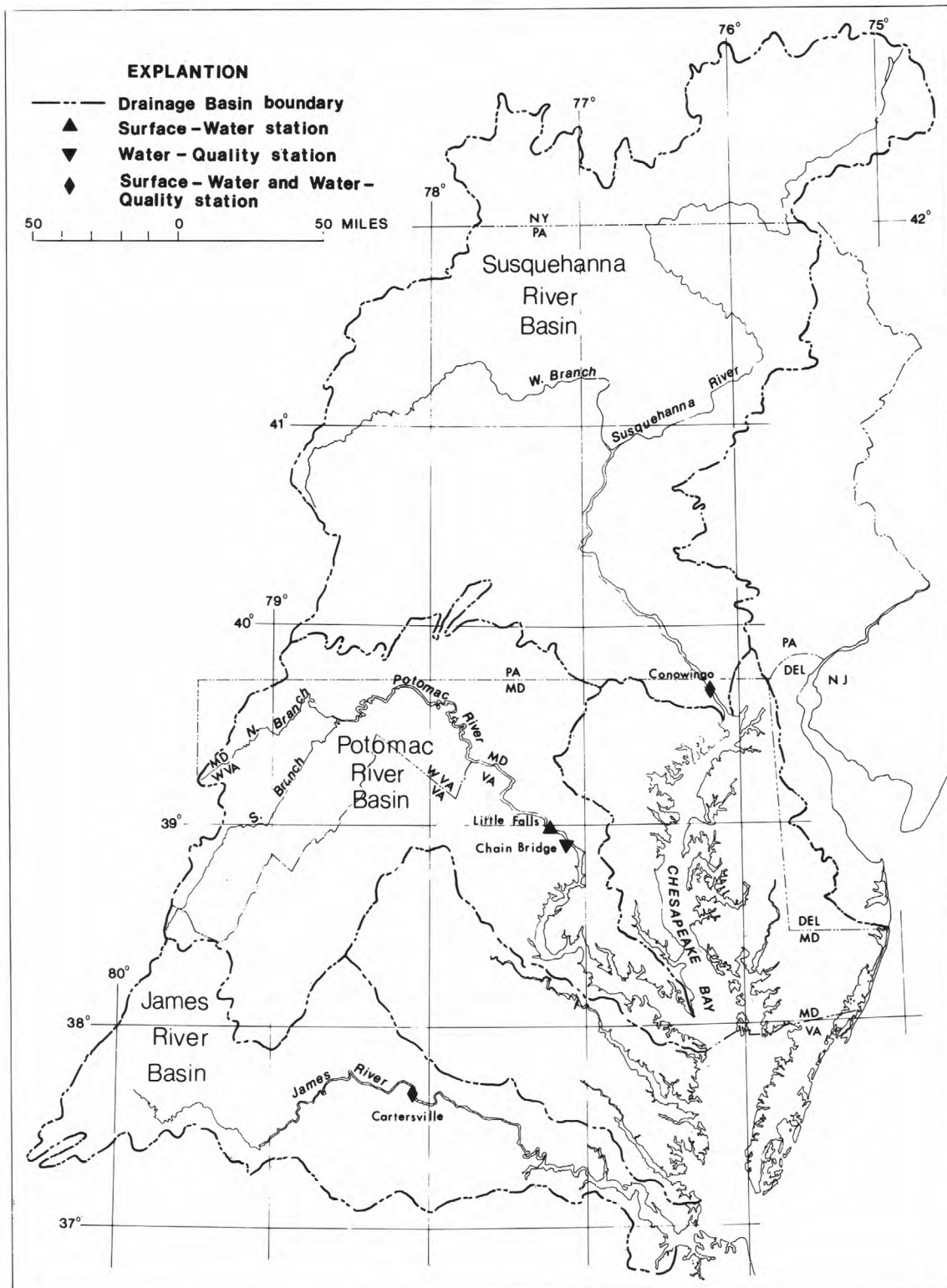


Figure 1.--Study area showing location of drainage basins and sampling sites.

DATA COLLECTION

Figure 1 shows the location of the water-quality monitoring stations used in the study. The Susquehanna River station is at Conowingo Dam, Conowingo, Md. From January 1979 to April 1981, if flow conditions permitted, base-flow water quality was measured every 2 weeks. The James River station is at Cartersville, Va., and the Potomac River site is at Chain Bridge at Washington, D.C.; during the study, both were sampled monthly. Water samples analyzed for both sediment and chemical quality were collected frequently during high flows at all three sites to better understand the mechanisms that affect the water quality during these critical periods of high mass transport.

The USGS continuously monitors stage and flow at the Cartersville and Conowingo sites. Potomac River flow is monitored at Little Falls, Md., half a mile upstream from Chain Bridge.

The Susquehanna River contributes almost half of the fresh-water inflow to the Bay. It is important to understand the net effects on water quality of the three hydroelectric dams located in the Susquehanna River between Harrisburg, Pa., and Conowingo, Md. This report presents only comparisons of selected constituent loads for these two stations. A more detailed analysis of the Harrisburg station data was made in another Geological Survey report, now in preparation.

Because the monitoring sites on the Potomac and James Rivers are not located at the mouths of these rivers, actual loads to the Chesapeake Bay were not measured. However, the samples collected at these stations are representative of constituents available to the Bay.

BASIN LAND USE AND ITS EFFECT ON WATER QUALITY

The following table indicates the percentages of each land-use category in the Susquehanna, Potomac, and James River basins. Land use in the Susquehanna and Potomac basins is similar with slightly more than half the area covered by forest. The James River basin contains 75-percent forest cover.

Land use	Susquehanna River at Conowingo, Md. drainage area = 27,100 mi ²	Potomac River at Chain Bridge at Washington, D.C. drainage area = 11,560 mi ²	James River at Cartersville, Va. drainage area = 6,257 mi ²
Agriculture and pastureland	35%	40%	22%
Forest	60%	55%	75%
Urban	5%	5%	3%

Land use has a significant effect on the water quality of any river. Areas with large forest cover normally have lower nutrient concentrations than agricultural areas. A study of 473 non-point source drainage areas in Eastern United States showed that nutrient concentrations are generally proportional to the percentage of agricultural land in the watershed (Omerik, 1976). In general, inorganic nitrogen makes up a larger percentage of total nitrogen concentration in streams with larger percentages of agricultural land. In that study, inorganic nitrogen was found to be 27 percent of the total nitrogen in streams which drained forested watersheds and over 75 percent in streams draining agricultural areas. Orthophosphate portion of total phosphorous remained unchanged at approximately 40 percent, regardless of land-use type. These observations are fairly consistent with the results of this report.

Coal mining along the tributaries to the Susquehanna and Potomac Rivers influences water quality at the Fall Line. Major coal fields are found in the Tioga, Juniata (both in the Susquehanna watershed), and North Branch Potomac River basins. Mining exposes pyritic rock surfaces to weathering and oxidation processes, which can cause a decrease in pH and elevate concentrations of iron, manganese, and sulfate in water emanating from these areas. Mine drainage with low pH characteristically contains iron and manganese in solution. When this water is diluted by inflow and the acids are neutralized, and if oxidizing conditions exist, these metals will precipitate and sorb onto sediment particles to be transported downstream. Iron and manganese are carried in this fashion from the mining areas into the Susquehanna and Potomac Rivers.

HYDROLOGIC CONDITIONS

Average discharge at each of the Fall Line sites for the study period was about 20 percent greater than the long-term averages for the Potomac and James Rivers, but 4 percent less than the long-term averages for the Susquehanna River (table 1). Streamflow was unevenly distributed over the 28-month study period, with discharge generally well above normal during the winter and fall of 1979 (fig. 2). However, from summer of 1980 to the end of the data-collection period in April 1981, flow at all three stations was well below the long-term averages, with the exception of a brief period in February 1981.

METHODS OF COLLECTION AND LABORATORY ANALYSIS

All water-quality and suspended-sediment samples were collected by USGS personnel using depth-integrating methods described by Guy and Norman (1970). All water-quality samples were preserved in the field according to methods described in the National Handbook of Recommended Methods for Water Data Acquisition (U.S. Geological Survey, 1977) and analyzed at the USGS Central Laboratory in Doraville, Ga. Pesticide residues, low-molecular-weight halogenated hydrocarbons, and organic carbon were determined according to methods described by Goerlitz and Brown (1972), and inorganic constituents were analyzed according to procedures cited by Skougstad and others (1979). Samples for analysis of chlorine were collected and analyzed using methods described in another section of this report. Sediment samples were analyzed in the USGS sediment laboratory in Harrisburg, Pa., by methods described by Guy (1969).

Table 1.--Average discharge for study period and long-term average discharges for the three Fall Line stations

Period of average	Average discharge for study period (ft ³ /s)	Long-term average discharge (ft ³ /s)	Percent difference from long- term average
<u>SUSQUEHANNA RIVER AT CONOWINGO, MD.</u>			
Jan.-Dec. 1979	52,300	¹ 38,900	+ 34
Jan.-Dec. 1980	28,400	¹ 38,900	- 27
Jan.-Apr. 1981	45,900	¹ 56,700	- 19
Jan. 1979-Apr. 1981	41,100	¹ 42,900	- 4
<u>POTOMAC RIVER AT CHAIN BRIDGE AT WASHINGTON, D.C.</u>			
Jan.-Dec. 1979	20,400	11,500	+ 79
Jan.-Dec. 1980	11,000	11,500	- 3
Jan.-Apr. 1981	9,060	15,300	- 41
Jan. 1979-Apr. 1981	14,800	12,000	+ 23
<u>JAMES RIVER AT CARTERSVILLE, VA.</u>			
Jan.-Dec. 1979	12,000	7,050	+ 70
Jan.-Dec. 1980	7,790	7,050	+ 11
Jan.-Apr. 1981	3,180	10,000	- 68
Jan. 1979-Apr. 1981	8,950	7,470	+ 20

¹ Based on long-term discharge record for the Susquehanna River at Harrisburg, Pa., and drainage area relationships.

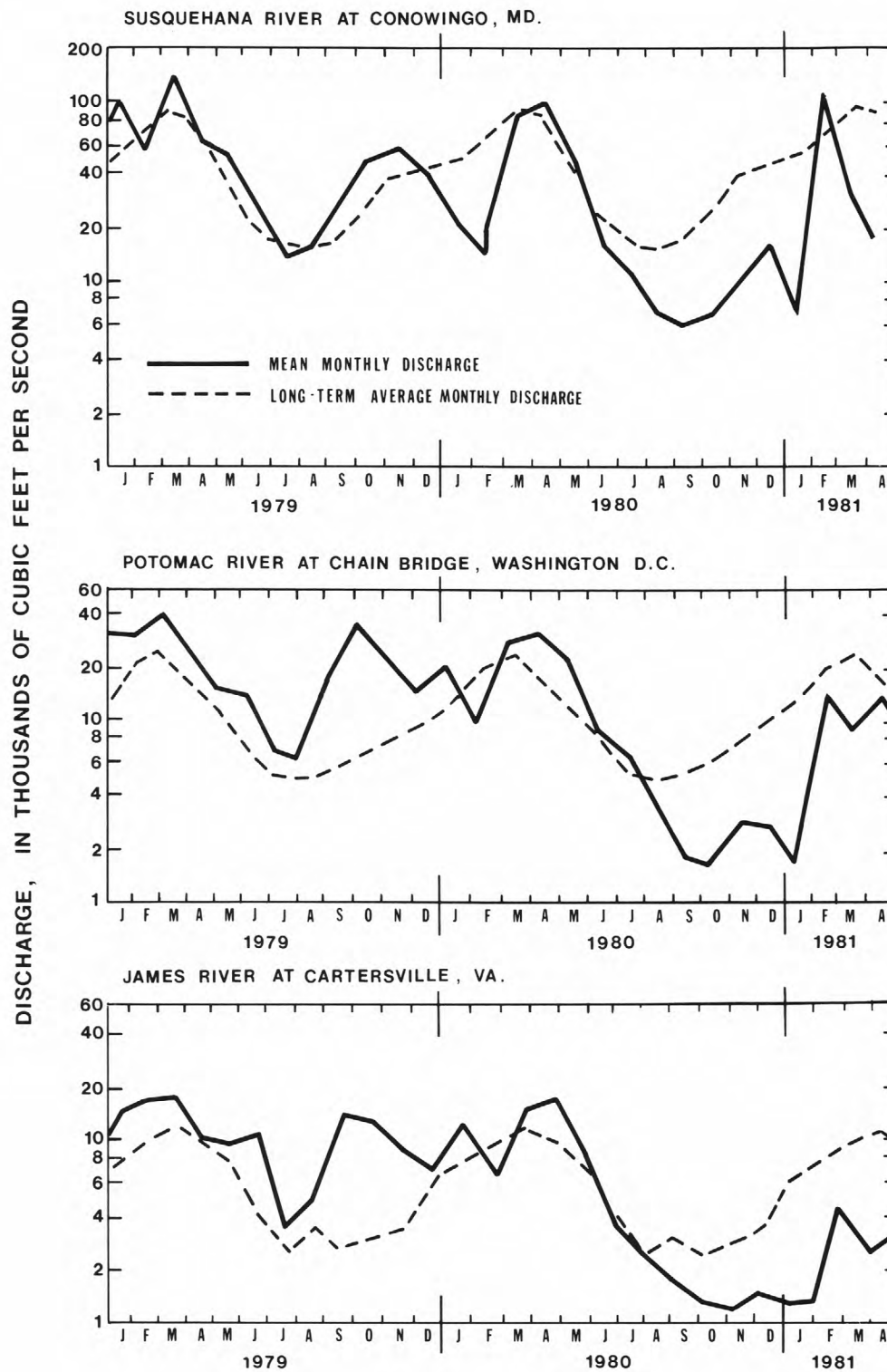


Figure 2.--Mean monthly and long-term average monthly discharge for the three Fall Line stations.

CONSTITUENT LOADS

Load Estimation Techniques--Nutrients and Metals

Bivariate linear regression equations were used to estimate all loads in this study. Instantaneous constituent concentrations and discharges were used to formulate the equations, which were then used with either mean daily discharges or daily sediment loads to obtain daily constituent loads.

Instantaneous constituent loads were computed for each sample collected using the following equation:

$$L = C \times Q \times 5.38$$

where

- L = nutrient or metal load at time of sample,
in lbs/d;
- C = nutrient or metal concentration at time of sample,
in mg/L;
- Q = instantaneous discharge at the time of sample, in ft³/s; and
- 5.38 = conversion factor.

The log of this instantaneous load was regressed against the log of the instantaneous discharge and the log of the instantaneous suspended-sediment load at the time of sampling. Regression equations were fitted analytically by the method of least squares.

Three criteria were then used for selecting either the discharge or sediment regression to calculate loads: (1) The chosen equation should have a low standard deviation. (2) A large percentage of the variance in the dependent variable (loads) should be explained or accounted for by the regression. The coefficient of determination (r^2) is a measure of this. The greater r^2 is, the better the regression line fits the observed data points, and the more highly correlated one variable is to another. (3) The signs of all significant regression coefficients should agree with accepted chemical and physical principles.

Table 2 presents the regression equations and related statistics derived from the above regression analysis and used to calculate constituent loads. Both equations, using either discharge or suspended sediment as the independent variable, are shown. An asterisk notes the equation selected for determination of constituent loads found in tables 3, 4, and 5. The selected equation is in the form:

$$\text{Log}_{10} L = a + b (\text{log}_{10} \bar{Q})$$

or

$$\text{Log}_{10} L = a + b (\text{log}_{10} SS)$$

where

- $\frac{L}{Q}$ = daily nutrient or metal load, in lbs/d;
- \bar{Q} = mean daily discharge, in ft³/s;
- SS = daily sediment load, in lbs;
- a = constant defining y intercept; and
- b = constant defining slope of regression.

The mean daily discharge or suspended-sediment load is then substituted to obtain daily constituent load. These daily loads are then summed to obtain the monthly totals found in tables 3, 4, and 5.

Table 2.--Least squares regression equations for load calculations of selected nutrients and metals with standard deviations(s^2) and coefficients of determination (r^2)

[Equations are of the form $\text{Log}_{10} L = a + b \text{Log}_{10} X$, where L = constituent load (lb/d); a and b are regression constants; and $X = Q$ (discharge in ft^3/s) or SS (suspended sediment load in lb/d). Asterisk notes equation which was used to calculate loads found in tables 3, 4, and 5.]

Constituent	Susquehanna River at Conowingo, Md.	s^2	r^2	Potomac River at Chain Bridge, Washington, D.C.	s^2	r^2	James River at Cartersville, Va.	s^2	r^2
Aluminum, total recoverable ($\mu\text{g/L}$ as Al)	-2.54 + 1.62(Log Q) -0.38 + 0.82(Log SS)*	0.35 .27	0.82 .89	-2.79 + 1.80(Log Q) -0.86 + 0.86(Log SS)*	0.47 .37	0.78 .88	-2.90 + 1.88(Log Q)* -0.38 + 0.80(Log SS)	0.26 .22	0.94 .96
Carbon, organic, total (mg/L as C)	+0.13 + 1.23(Log Q)* +1.87 + 0.61(Log SS)	.20 .22	.90 .88	+0.18 + 1.31(Log Q) +1.61 + 0.60(Log SS)*	.19 .15	.92 .95	+0.61 + 1.21(Log Q)* +2.33 + 0.51(Log SS)	.27 .28	.85 .86
Iron, total recoverable ($\mu\text{g/L}$ as Fe)	-2.39 + 1.63(Log Q) -0.29 + 0.84(Log SS)*	.42 .34	.76 .84	-3.30 + 1.99(Log Q) -0.97 + 0.90(Log SS)*	.53 .42	.77 .86	-3.04 + 1.98(Log Q)* -0.45 + 0.85(Log SS)	.30 .17	.93 .98
Manganese, total recoverable ($\mu\text{g/L}$ as Mn)	-1.65 + 1.35(Log Q) +0.35 + 0.66(Log SS)*	.27 .28	.83 .82	-3.86 + 1.87(Log Q) -1.62 + 0.84(Log SS)*	.36 .23	.86 .95	-3.57 + 1.78(Log Q)* -1.31 + 0.77(Log SS)	.33 .13	.90 .98
Nitrogen, ammonia, total (mg/L as N)	-1.05 + 1.16(Log Q)* +0.91 + 0.53(Log SS)	.32 .36	.71 .65	-1.94 + 1.34(Log Q) -0.24 + 0.59(Log SS)*	.40 .39	.74 .75	-0.88 + 1.05(Log Q)* +0.50 + 0.44(Log SS)	.31 .30	.79 .81
6 Nitrogen, ammonia + organic, total (mg/L as N)	-0.10 + 1.10(Log Q)* +1.65 + 0.52(Log SS)	.22 .26	.83 .78	-1.03 + 1.38(Log Q) +0.50 + 0.64(Log SS)*	.28 .21	.89 .92	-1.30 + 1.43(Log Q)* +0.61 + 0.61(Log SS)	.26 .27	.90 .90
Nitrogen, organic, total (mg/L as N)	-0.34 + 1.13(Log Q)* +1.46 + 0.53(Log SS)	.26 .29	.79 .74	-1.34 + 1.43(Log Q) +0.41 + 0.64(Log SS)*	.29 .23	.86 .91	-1.34 + 1.43(Log Q)* -0.59 + 0.61(Log SS)	.26 .26	.90 .91
Nitrogen, nitrite + nitrate, total (mg/L as N)	+0.45 + 1.07(Log Q)* +0.91 + 0.53(Log SS)	.14 .36	.92 .65	+0.01 + 1.18(Log Q)* +1.69 + 0.50(Log SS)	.15 .28	.94 .81	-0.11 + 1.08(Log Q)* +1.37 + 0.45(Log SS)	.16 .22	.93 .88
Nitrogen, total (mg/L as N)	+0.55 + 1.08(Log Q)* +2.45 + 0.48(Log SS)	.12 .23	.94 .79	-0.15 + 1.27(Log Q)* +1.55 + 0.55(Log SS)	.13 .21	.96 .90	-0.58 + 1.31(Log Q)* +1.20 + 0.55(Log SS)	.17 .20	.94 .93
Phosphorus, orthophosphate, total (mg/L as PO_4)	-0.68 + 1.06(Log Q)* +1.24 + 0.47(Log SS)	.36 .40	.65 .57	-1.10 + 1.21(Log Q)* -0.21 + 0.56(Log SS)	.33 .29	.75 .81	+1.17 + 0.68(Log Q)* +1.90 + 0.31(Log SS)	.27 .23	.66 .77
Phosphorus, total (mg/L as PO_4)	-2.08 + 1.43(Log Q)* +0.05 + 0.70(Log SS)	.28 .29	.84 .84	-2.22 + 1.59(Log Q) -0.49 + 0.74(Log SS)*	.32 .23	.88 .93	-0.39 + 1.18(Log Q)* +0.97 + 0.53(Log SS)	.30 .21	.82 .92

Table 3.--Monthly load estimates (in hundreds of thousands of pounds) for the
Susquehanna River at Conowingo, Md.

[Dashes indicate missing data]

Month	Mean discharge (ft ³ /s)	Aluminum, total recoverable as Al	Calcium, dissolved as Ca	Carbon, organic, total as C	Chloride, dissolved as Cl	Iron, total recoverable as Fe	Magnesium, dissolved as Mg	Manganese, total recoverable as Mn
January 1979	101,200	-	-	636	-	-	-	-
February	47,600	-	-	245	-	-	-	-
March	143,000	-	-	969	-	-	-	-
April	65,200	57.0	-	342	-	90.0	-	21.7
May	43,900	34.5	-	224	-	54.4	-	13.8
June	26,900	15.7	-	120	-	24.6	-	7.0
July	13,000	4.7	624	50.2	309	7.4	192	2.7
August	16,140	6.7	688	65.2	340	10.3	212	3.5
September	28,000	16.3	1,060	125	530	25.6	317	7.3
October	48,900	45.6	1,780	256	893	77.0	519	19.6
November	48,300	35.9	1,710	248	858	61.0	499	15.0
December	44,200	42.7	1,490	225	748	72.3	426	18.0
Calendar year total	52,300	-	-	3,510	-	-	-	-
January 1980	27,200	10.9	1,009	122	504	18.0	294	5.9
February	13,100	2.8	614	47.2	304	4.4	188	2.0
March	70,400	119.3	2,170	426	1,093	209.2	610	38.4
April	108,000	126.7	2,650	648	1,350	219.5	700	44.3
May	46,500	44.9	1,480	235	743	75.7	420	19.5
June	17,500	13.5	700	69.5	349	22.1	210	7.3
July	12,300	4.3	593	46.9	294	6.8	180	3.0
August	8,450	3.1	438	29.8	217	4.9	135	2.3
September	4,740	1.8	278	14.5	137	2.9	87	1.5
October	6,270	4.3	397	21.3	196	6.9	125	2.9
November	9,800	5.2	685	35.9	336	8.4	219	3.3
December	16,800	5.3	793	69.4	393	8.5	241	3.5
Calendar year total	28,400	342	11,800	1,770	5,920	587	3,410	134
January 1981	7,170	5.1	395	24.6	195	8.3	123	3.3
February	104,000	221.5	2,800	622	1,420	394.2	779	63.0
March	35,500	20.0	1,220	174	615	33.2	352	10.0
April	36,800	-	-	171	-	-	-	-
Total January 1979 to April 1981	-	-	-	6,260	-	-	-	-

Table 3.--Monthly load estimates (in hundreds of thousands of pounds) for the
Susquehanna River at Conowingo, Md.--Continued

Month	Nitrogen, ammonia, total as N	Nitrogen, organic, total as N	Nitrogen, ammonia + organic, total as N	Nitrogen, nitrite + nitrate, total as N	Nitrogen, total as N	Phosphorous, ortho- phosphate, total as PO ₄	Phosphorous, total as PO ₄	Sodium, dissolved as Na	Sulfate, dissolved as SO ₄
January 1979	18.4	63.9	80.7	201	285.0	13.2	42.0	-	-
February	7.3	25.7	32.8	82.8	116.8	5.5	15.3	-	-
March	27.4	94.0	117.8	291	413.0	19.1	68.7	-	-
April	10.4	36.8	47.3	120	169.0	8.0	19.7	-	-
May	6.9	24.7	32.0	82	115.0	5.5	12.3	-	-
June	3.8	13.9	18.2	47.1	65.8	3.1	6.1	-	-
July	1.7	6.3	8.4	22.3	31.0	1.5	2.2	210	1,210
August	2.2	8.0	10.6	28.1	39.0	1.9	2.9	233	1,340
September	4.0	14.5	18.9	49.1	68.6	3.3	6.3	350	2,000
October	7.8	28.0	36.1	92.1	129.4	6.1	14.5	570	3,280
November	7.6	26.9	34.7	88.3	124.1	5.9	14.2	549	3,160
December	6.9	24.9	32.2	83.0	115.8	5.5	12.4	470	2,700
Calendar year total	104	368	470	1,190	1,670	78.6	217	-	-
January 1980	3.9	14.3	18.8	48.9	68.3	3.3	6.0	324	1,863
February	1.6	5.9	7.9	21.0	29.0	1.4	2.0	206	1,190
March	12.4	43.5	55.2	138.0	195.5	9.1	27.3	670	3,860
April	18.8	65.6	83.0	207	293.5	13.7	41.9	780	4,490
May	7.3	26.1	33.8	86.7	121.6	5.8	12.8	460	2,650
June	2.3	8.5	11.3	29.6	41.2	2.0	3.1	230	1,320
July	1.6	6.0	7.9	21.1	29.2	1.4	2.0	198	1,140
August	1.0	4.0	5.3	14.1	19.5	1.0	1.2	148	849
September	.52	2.0	2.7	7.4	10.1	.5	.53	95	549
October	.74	2.8	3.8	10.3	14.3	.7	.82	137	786
November	1.2	4.5	6.0	15.9	22.0	1.0	1.6	239	1,370
December	2.3	8.4	11.2	29.4	40.9	2.0	3.2	264	1,520
Calendar year total	53.7	192	247	629	885	41.8	102	3,751	21,600
January 1981	0.9	3.3	4.4	11.9	16.4	0.8	1.0	134	770
February	17.7	61.0	76.6	189.7	269.3	12.5	43.1	862	4,950
March	5.4	19.6	25.5	65.5	91.8	4.4	9.4	388	2,230
April	5.4	19.4	25.3	65.3	91.5	4.4	8.9	-	-
Total January 1979 to April 1981	188	663	848	2,150	3,030	143	381	-	-

Table 4.--Monthly load estimates (in hundreds of thousands of pounds) for the Potomac River at Chain Bridge at Washington, D.C.

[Dashes indicate missing data]

Month	Mean discharge (ft ³ /s)	Aluminum, total recoverable as Al	Calcium, dissolved as Ca	Carbon, organic, total as C	Chloride, dissolved as Cl	Iron, total recoverable as Fe	Magnesium, dissolved as Mg	Manganese, total recoverable as Mn
January 1979	31,100	133	1,045	341	352	216	219	15.9
February	30,600	138	-	255	-	237	-	16.2
March	38,300	80.9	-	271	-	126	-	9.9
April	18,900	24.9	-	111	-	37.2	-	3.1
May	17,400	24.6	729	114	277	36.4	161	3.1
June	14,600	31.6	561	133	208	47.5	123	3.9
July	5,960	3.8	317	35.6	133	5.1	73.6	.51
August	5,940	7.7	-	56.2	-	10.6	-	1.0
September	21,900	99.8	791	274	284	161	170	12.0
October	33,700	103	1,084	310	285	164	233	12.6
November	18,300	30.8	318	119	126	47.2	72.0	3.8
December	13,200	10.0	604	56	235	14.5	135	1.3
Calendar year total	20,400	689	-	2,080	-	1,100	-	83.3
January 1980	18,400	14.7	609	76.6	227	21.4	133	1.9
February	8,050	4.0	341	30.3	137	5.5	77.5	.52
March	23,300	49.7	-	170	-	77.8	-	6.1
April	31,000	63.2	-	236	-	96.4	-	7.8
May	25,300	63.2	65.1	217	25.0	98.2	14.5	7.8
June	7,910	6.2	368	48	149	8.4	83.9	.81
July	4,280	3.6	259	33	110	4.7	60.4	.47
August	3,400	2.0	222	20.4	96.2	2.6	52.3	.27
September	1,670	.44	112	7.6	49.0	.53	26.5	.06
October	1,700	.50	138	7.9	62.7	.61	33.4	.07
November	3,710	2.7	264	21.1	117	3.7	63.0	.35
December	3,550	1.1	215	14.3	91.5	1.4	50.3	.15
Calendar year total	11,000	211	-	882	-	321	-	26.3
January 1981	1,680	0.41	108	7.3	49.5	0.49	26.2	0.06
February	13,700	42.3	583	153	229	65.2	131	5.2
March	7,550	3.8	359	33.3	141	5.0	80.7	.50
April	13,100	-	352	-	131	-	77.0	-
Total January 1979 to April 1981	-	947	-	3,150	-	1,490	-	115

Table 4.--Monthly load estimates (in hundreds of thousands of pounds) for the Potomac River at Chain Bridge at Washington, D.C.--Continued

Month	Nitrogen, ammonia, total as N	Nitrogen, organic, total as N	Nitrogen, ammonia + organic, total as N	Nitrogen, nitrite + nitrate, total as N	Nitrogen, total as N	Phosphorous, ortho- phosphate, total as PO ₄	Phosphorous, total as PO ₄	Sodium, dissolved as Na	Sulfate, dissolved as SO ₄
January 1979	4.56	44.2	54.3	65.8	125.0	6.96	34.2	251	1,024
February	5.53	34.8	42.8	68.0	140.9	7.20	30.7	-	-
March	5.80	33.9	41.6	82.9	158.5	8.82	23.8	-	-
April	2.04	13.3	16.3	33.5	59.3	3.48	8.3	-	-
May	1.87	13.5	16.7	31.3	54.9	3.24	8.4	232	1,517
June	1.49	16.0	19.7	25.1	43.8	2.58	10.3	170	1,219
July	.40	3.8	4.7	8.2	12.8	.81	1.82	125	650
August	.40	6.3	7.7	8.2	12.9	.81	3.3	-	-
September	2.80	35.1	43.2	42.3	78.3	4.47	26.5	221	1,744
October	5.00	39.4	48.5	72.6	137.5	7.68	28.9	296	2,403
November	2.06	14.5	17.8	33.6	59.7	3.48	9.6	112	672
December	1.35	6.5	7.9	23.4	40.2	2.40	3.7	202	1,289
Calendar year total	33.3	261	321	495	924	51.9	190	-	-
January 1980	2.16	8.9	11.0	35.1	62.6	3.60	5.3	186	679
February	.63	3.3	4.1	12.1	19.7	1.20	1.7	123	-
March	3.06	21.0	25.9	47.1	86.4	4.95	14.6	-	-
April	4.12	29.1	35.8	62.1	115.3	6.60	19.6	-	-
May	3.39	27.0	33.2	51.6	95.2	5.43	18.7	21.3	1,064
June	.65	5.3	6.5	12.4	20.1	1.23	2.7	134	770
July	.29	3.6	4.4	6.2	9.5	.60	1.7	104	528
August	.21	2.1	2.6	4.7	7.1	.45	.98	93.0	448
September	.08	.74	.91	1.9	2.7	.18	.28	47.8	224
October	.08	.78	.96	2.1	2.9	.21	.30	63.1	198
November	.26	2.3	2.8	5.3	8.4	.54	1.2	116	368
December	.23	1.5	1.8	5.0	7.5	.48	.61	86.8	284
Calendar year total	15.2	106	130	247	438	25.5	67.8	-	-
January 1981	0.09	0.71	0.87	2.2	3.1	0.21	0.26	50.1	156
February	1.43	18.8	23.2	23.3	41.4	2.40	12.8	200	697
March	.63	3.6	4.4	12.1	19.6	1.20	1.7	124	430
April	1.46	11.8	-	24.0	42.4	2.49	-	107	391
Total January 1979 to April 1981	52.1	402	480	804	1,470	83.7	273	-	-

Table 5.--Monthly load estimates (in hundreds of thousands of pounds) for the James River at Cartersville, Va.

[Dashes indicate missing data]

Month	Mean discharge (ft ³ /s)	Aluminum, total recoverable as Al	Calcium, dissolved as Ca	Carbon, organic, total as C	Chloride, dissolved as Cl	Iron, total recoverable as Fe	Magnesium, dissolved as Mg	Manganese, total recoverable as Mn
January 1979	16,400	46	393.7	179	164.5	93	80.6	3.5
February	18,200	115	-	207	-	261	-	7.9
March	20,100	64.4	463.5	225	172.4	132	93.7	4.9
April	9,690	12.6	264.6	90.1	-	23.1	56.5	1.1
May	9,190	12.1	261.4	87.7	155.7	22.3	55.9	1.0
June	13,800	51.4	316.1	149	-	110	64.4	3.7
July	3,580	1.9	122.8	28.8	93.3	3.1	27.3	.18
August	3,000	1.5	106.4	23.8	828	2.4	23.7	.14
September	16,100	60.0	353.2	176	-	127	71.1	4.4
October	16,000	40.0	391.5	171	172.5	79.4	80.6	3.1
November	11,900	20.0	307.0	115	164.0	37.6	64.7	1.6
December	7,110	7.4	213.5	65	137.8	13.1	46.1	.64
Calendar year total	12,000	432	-	1,520	-	904	-	32.2
January 1980	14,600	35.1	364.6	155	167.6	69.6	75.4	2.8
February	6,540	5.5	188.5	54.6	126.0	9.6	41.0	.49
March	17,900	46.6	431.3	194	182.2	93	88.4	3.6
April	21,500	67.3	264.6	234	155.5	138	56.4	5.1
May	8,040	9.1	236.2	74.7	147.6	164	50.8	.78
June	3,590	2.0	118.3	28.3	89.0	3.4	26.2	.19
July	2,350	.9	86.2	17.7	69.8	1.4	19.3	.09
August	1,820	.5	69.8	13.1	58.8	.8	15.8	.05
September	1,420	.3	53.5	9.1	46.7	.5	12.2	.03
October	1,410	.3	56.2	9.7	48.8	.5	12.8	.03
November	2,020	.7	73.3	14.4	60.6	1.1	16.5	.07
December	1,860	.6	71.0	13.4	59.6	.9	16.0	.06
Calendar year total	7,790	169	2,010	819	1,210	483	431	13.4
January 1981	1,680	0.51	65.3	11.9	55.6	0.7	14.8	0.05
February	4,760	3.6	137.1	37.2	95.8	6.2	30.0	.32
March	2,650	1.1	95.3	20.4	75.8	1.8	21.4	.10
April	3,640	1.9	120.6	28.3	91.3	3.1	26.8	.18
Total January 1979 to April 1981	-	608	-	2,430	-	1,400	-	46.3

Table 5.--Monthly load estimates (in hundreds of thousands of pounds) for the
James River at Cartersville, Va.--Continued

Month	Nitrogen, ammonia, total as N	Nitrogen, organic, total as N	Nitrogen, ammonia + organic, total as N	Nitrogen, nitrite + nitrate, total as N	Nitrogen, total as N	Phosphorous, ortho- phosphate, total as PO ₄	Phosphorous, total as PO ₄	Sodium, dissolved as Na	Sulfate, dissolved as SO ₄
January 1979	1.1	18.0	18.9	8.7	29.6	3.2	12.4	115.4	240.0
February	1.1	27.1	28.5	9.3	39.3	2.7	14.5	-	-
March	1.4	23.4	24.7	10.8	38.0	3.7	15.7	123.9	277.3
April	.61	7.3	7.7	4.7	13.3	2.3	6.2	-	172.1
May	.59	7.0	7.4	4.6	13.0	2.2	6.1	102.6	170.6
June	.90	16.1	16.9	7.2	25.5	2.6	10.4	-	191.3
July	.22	1.8	1.9	1.7	3.7	1.2	2.0	59.5	85.0
August	.18	1.4	1.5	1.4	3.0	1.1	1.6	52.6	74.1
September	1.1	19.4	20.3	8.4	30.6	2.9	12.3	-	209.8
October	1.1	16.7	17.6	8.5	28.0	3.2	11.9	119.7	240.8
November	.75	10.0	10.6	5.9	17.8	2.6	8.0	110.0	195.7
December	.45	4.9	5.2	3.5	9.2	1.9	4.5	89.8	141.8
Calendar year total	9.5	153	161	74.7	251	29.6	106	-	-
January 1980	0.97	14.9	15.7	7.7	25.1	3.0	10.7	115.4	226.0
February	.39	3.9	4.2	3.0	7.6	1.7	3.8	81.6	126.2
March	1.2	19.1	20.1	9.5	31.9	3.5	13.5	127.5	263.4
April	1.4	24.5	25.8	11.3	39.7	3.8	16.3	102.7	172.1
May	.52	5.8	6.1	4.0	10.8	2.1	5.2	96.6	155.8
June	.21	1.8	1.9	1.6	3.7	1.1	1.9	56.8	81.7
July	.14	.98	1.0	1.1	2.1	.89	1.2	44.2	60.7
August	.11	.67	.7	.8	1.5	.75	.89	37.0	49.7
September	.08	.43	.5	.6	1.0	.60	.6	29.3	38.5
October	.08	.47	.5	.6	1.0	.63	.7	30.7	40.4
November	.12	.78	.8	.9	1.7	.77	1.0	38.2	51.9
December	.11	.70	.7	.8	1.6	.76	.9	37.5	50.5
Calendar year total	5.3	74.0	78	41.9	128	19.5	56.7	798	1,320
January 1981	0.10	0.60	0.6	0.7	1.4	0.71	0.8	35.0	46.6
February	.27	2.6	2.8	2.1	5.1	1.3	2.6	61.7	92.8
March	.16	1.2	1.2	1.2	2.5	.97	1.4	48.1	66.8
April	.21	1.8	1.9	1.6	3.7	1.2	1.9	58.2	83.4
Total January 1979 to April 1981	15.6	233	246	122	391	53.3	169	-	-

Load Estimation Techniques--Major Cations and Anions

Because specific conductance is directly related to the number of dissolved ions in water, it is appropriate to use this parameter to predict loads of major cations and anions in the three rivers. The James River specific conductance data were not sufficient, thus log Q was substituted as the independent variable. The relationships used were:

$$C = a + b (SC)$$

or

$$C = a + b (\log Q)$$

where

- C = major ion concentration at the time of sample, in mg/L;
- SC = specific conductance at the time of sample, in $\mu\text{mhos}/\text{cm}^2$;
- Q = instantaneous discharge at the time of sample, in ft^3/s ;
- a = constant defining y intercept; and
- b = constant defining slope of regression.

Instantaneous constituent concentrations were regressed against the daily specific conductance or the log of the instantaneous discharge and the above equations fitted analytically by the method of least squares. By substituting the daily specific conductance or log of the mean daily discharge into the equations instead of the value at the time of sample, an average daily concentration \bar{C} was calculated:

$$\bar{C} = a + b (SC_d)$$

or

$$\bar{C} = a + b (\log \bar{Q}).$$

Then, the daily load was computed by:

$$L = \bar{C} \times \bar{Q} \times 5.38$$

where

- \bar{C} = average daily ion concentration, in mg/L;
- SC_d = daily specific conductance value, in $\mu\text{mhos}/\text{cm}$;
- \bar{Q} = mean daily discharge, in ft^3/s ;
- L = daily load in lbs/d;
- a = constant defining y intercept;
- b = constant defining slope of regression; and
- 5.38 = conversion factor.

Daily major cation and anion loads are summed to obtain monthly loads and are tabulated in tables 3, 4, and 5. The regression equations used to estimate them are presented in table 6.

Table 6.--Least squares regression equations for load calculations of selected cations and anions with standard deviation (s^2) and the coefficients of determination (r^2).

[Equations are of the form $C = a + b(X)$, where C = major ion concentration; a and b are regression constants; X = SC (specific conductance in $\mu\text{mhos}/\text{cm}^2$) or log Q (\log_{10} of daily discharge)]

Constituent	Susquehanna River at Conowingo, Md.	s^2	r^2	Potomac River at Chain Bridge, Washington, D.C.	s^2	r^2	James River at Cartersville, Va.	s^2	r^2
Calcium, dissolved (mg/L as Ca)	$-0.87 + 0.11(\text{SC})$	2.45	0.90	$+1.57 + 0.106(\text{SC})$	2.94	0.88	$+50.0 - 8.26(\text{Log Q})$	4.14	0.53
Chloride, dissolved (mg/L as Cl)	$+0.01 + 0.051(\text{SC})$	2.25	.72	$-3.26 + 0.057(\text{SC})$	2.84	.70	$+61.3 - 12.8(\text{Log Q})$	4.94	.66
Magnesium, dissolved (mg/L as Mg)	$-1.59 + 0.037(\text{SC})$.83	.91	$-0.70 + 0.028(\text{SC})$	1.00	.82	$+12.3 - 2.17(\text{Log Q})$.63	.77
Sodium, dissolved (mg/L as Na)	$-1.58 + 0.042(\text{SC})$	1.24	.85	$-6.67 + 0.065(\text{SC})$	1.94	.87	$+37.3 - 7.66(\text{Log Q})$	2.95	.66
Sulfate, dissolved (mg/L as SO_4)	$-9.10 + 0.23(\text{SC})$	4.73	.92	$-13.1 + 0.186(\text{SC})$	5.07	.89	$+40.2 - 7.29(\text{Log Q})$	3.60	.54

Evaluation and Limitation of the Load Estimates

In tables 3, 4, and 5, and in subsequent listings, all constituent loads are calculated independently from their regression equations, regardless of the relationships that are known to exist among the parameters. For example, total nitrogen concentration equals the sum of nitrite + nitrate and ammonia + organic nitrogen concentrations for each individual sample. If the load estimation techniques are accurate, the sums of monthly or yearly loads of nitrite + nitrate, and ammonia + organic nitrogen should be nearly the same as loads for total nitrogen for the same periods. Also, the summed loads of ammonia nitrogen and organic nitrogen should be the same as ammonia + organic nitrogen. The agreement or disagreement of the constituent loads and the sums of their component species is an indication of the ability of the regression technique to accurately estimate those constituent loads for the specific period.

To test further the accuracy of this technique, yearly constituent loads calculated by this regression method were compared to those obtained by a totally different method for Potomac River at Chain Bridge (table 7). The USGS's Potomac Estuary Project personnel independently collected data on selected nutrient species at this site through calendar years 1979 and 1980. For their load computations, they had access to a large data base of which only part was used in this report to obtain regression equations and to compute constituent loads. The Estuary Project group calculated their loads using the hydrograph method (Porterfield, 1972). In this technique, enough data must be available to estimate a continuous plot of constituent concentrations. This, along with a continuous plot of discharge, is used to obtain a continuous measure of constituent loads, subdividing days as necessary. This is a more direct and, hence, accurate method of load computation.

The comparisons in table 7 show relatively small differences in annual total loads. Month-by-month comparisons do not compare as well because the regression technique does not allow for seasonal- and antecedent-flow variations, which are accounted for in the hydrograph technique. Similar results can be expected from the Susquehanna and James Rivers.

The regression load-estimation technique requires intensive sampling of high discharges, which carry the majority of most constituent loads. An inconsistent or incomplete, high-flow sampling program will not cover the full range of hydrologic events and may incorrectly bias the regression equations to only those high-flow events that are sampled.

The regression load-estimation technique is most accurate in wet years having a wide range of flow. Factors not taken into account in the regression technique, such as season and time since the previous flow peak, have a greater relative effect on constituent loads during sustained low-flow periods. Based only on low-flow constituent loads, the regression line has higher standard deviation, which leads to a lower coefficient of determination.

The basic data used in calculating loads for the Susquehanna and Potomac Rivers are available in USGS annual reports titled "Water Resources Data for Maryland and Delaware;" the James River data is found in the USGS publication titled "Water Resources Data for Virginia."

Table 7.--Nutrient loads (in millions of pounds) for the Potomac River at Chain Bridge at Washington, D.C., computed from the Potomac estuary and Fall Line monitoring study data

Constituent	1979 calendar year			1980 calendar year			Totals Jan. 1979 - Apr. 1981		
	Potomac estuary study	Fall Line study	Percent difference	Potomac estuary study	Fall Line study	Percent difference	Potomac estuary study	Fall Line study	Total percent difference
Nitrogen, ammonia, dissolved as N	(¹)	(¹)	(¹)	8.49	9.44	+11.7	² 15.7	² 16.4	² +4.4
¹⁹ Nitrogen, ammonia + organic, total as N	290	321	+10.7	114	130	+14.0	447	494	+10.5
Nitrogen, nitrite + nitrate, total as N	457	495	+8.3	260	245	-5.8	794	802	+1.0
Phosphorus, dissolved as P	17.3	17.3	0	7.40	8.45	+14.2	27.4	27.9	+1.8
Phosphorus, total as P	61.6	63.3	+2.7	19.6	22.6	+15.3	90.0	93.6	+4.0

¹Ammonia data collection began October 1979.

²Comparison includes data from October 1979 to April 1981.

EXAMINATION OF SELECTED WATER-QUALITY CONSTITUENTS

Seasonal Characterization of Pesticides

Pesticide residue data (organochlorine and organophosphorous insecticides and chlorophenoxy acid herbicides) were collected monthly and during high flows at each of the Fall Line stations. Only 2, 4 dichlorophenoxyacetic acid (2,4-D) and atrazine were consistently detected at the Conowingo and Chain Bridge stations. Pesticide concentrations at the Chain Bridge site were generally less than at Conowingo. Maximum concentrations detected at Conowingo were 0.30 and 1.2 µg/L for 2,4-D and atrazine, respectively. At Chain Bridge, maximum concentrations were 0.14 and 0.4 µg/L for 2,4-D and atrazine, respectively. Atrazine, 2,4-D, and silvex were detected at James River at Cartersville several times, but concentrations were at the lower limit of detection.

Both 2,4-D and atrazine concentrations show strong seasonal patterns in the Susquehanna and Potomac Rivers (figs. 3 and 4). Both rivers have 2,4-D and atrazine concentration peaks in late spring and summer. This is reasonable because herbicides are usually applied just before and during spring planting, and both 2,4-D and atrazine are readily soluble in water. Therefore, runoff from cropland and residential areas in late spring and summer usually carries higher than normal concentrations of these herbicides in solution to nearby tributaries and streams. These streams, in turn, carry the herbicides into the estuaries of the Chesapeake Bay.

The highest concentrations of 2,4-D in the Susquehanna River occurred during low-flow periods in fall 1980 and spring 1981. As streamflow decreased, the concentration of 2,4-D in the Susquehanna River increased. This trend continued until high flows in February diluted the concentration to much lower levels. Following this high-flow event, 2,4-D concentrations again increased in March 1981. This type of concentration-discharge relationship is typical of a constant, continual input of a constituent into a variable flow system; runoff during high flows dilutes the constituent to low concentrations, but concentrations begin to rise during base flow. Considering 2,4-D is a widely-used domestic herbicide, it is possible that input of 2,4-D to the Susquehanna River could be from shallow ground-water sources or point discharges. However, more data are needed to determine the source of 2,4-D in the Susquehanna River which keeps concentrations high (0.20-0.30 µg/L) even during winter months when herbicide applications are at a minimum. In contrast, the Potomac basin, which has similar land-use practices as the Susquehanna, had very small concentrations (<0.05 µg/L) during the same low-flow periods in fall 1980 and spring 1981.

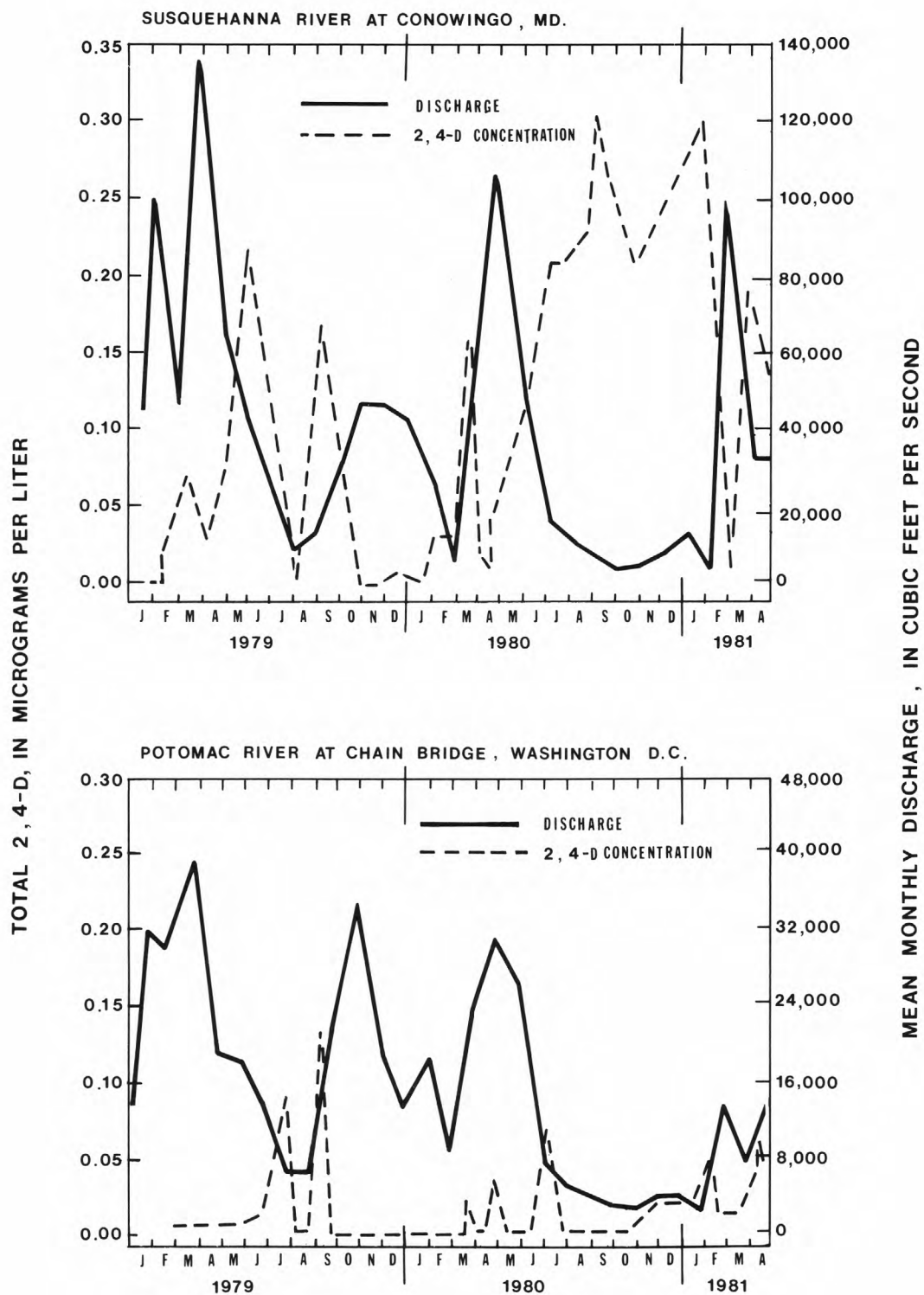


Figure 3.--Seasonal fluctuations in concentrations of 2,4-D at the Susquehanna and Potomac Fall Line stations.

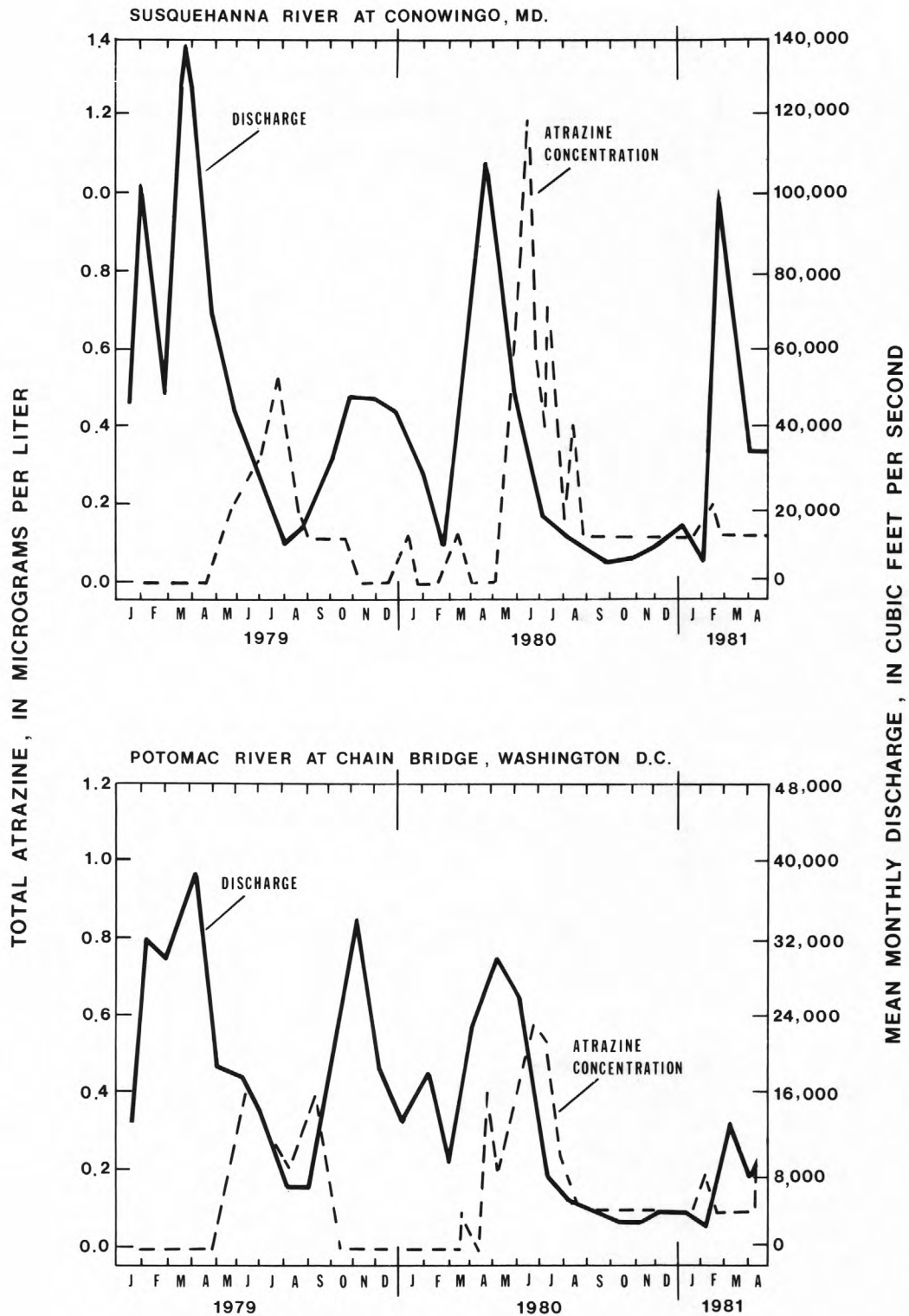


Figure 4.--Seasonal fluctuations in concentrations of atrazine at the Susquehanna and Potomac Fall Line stations.

Seasonal Characterization of Chlorophyll A

Chlorophyll a is the primary pigment of all oxygen-evolving photosynthetic organisms and is present in all algae and photosynthetic organisms, except some photosynthetic bacteria (Wetzel, 1975). Figure 5 presents the chlorophyll a concentrations for each of the Fall Line stations. Maximum chlorophyll a concentrations at all three sites occur during spring runoff. Increased spring concentrations may be caused by high-velocity runoff carrying with it fragments of underdeveloped and emerging plankton or a spring accumulation of periphytic chlorophyll. Concentration peaks of lesser magnitude occur during the late spring and summer months, but these are generally not related to discharge. The summer peaks may be related to increased biological activity which accompanies warmer temperatures, increased daylight, and rapid nutrient recycling.

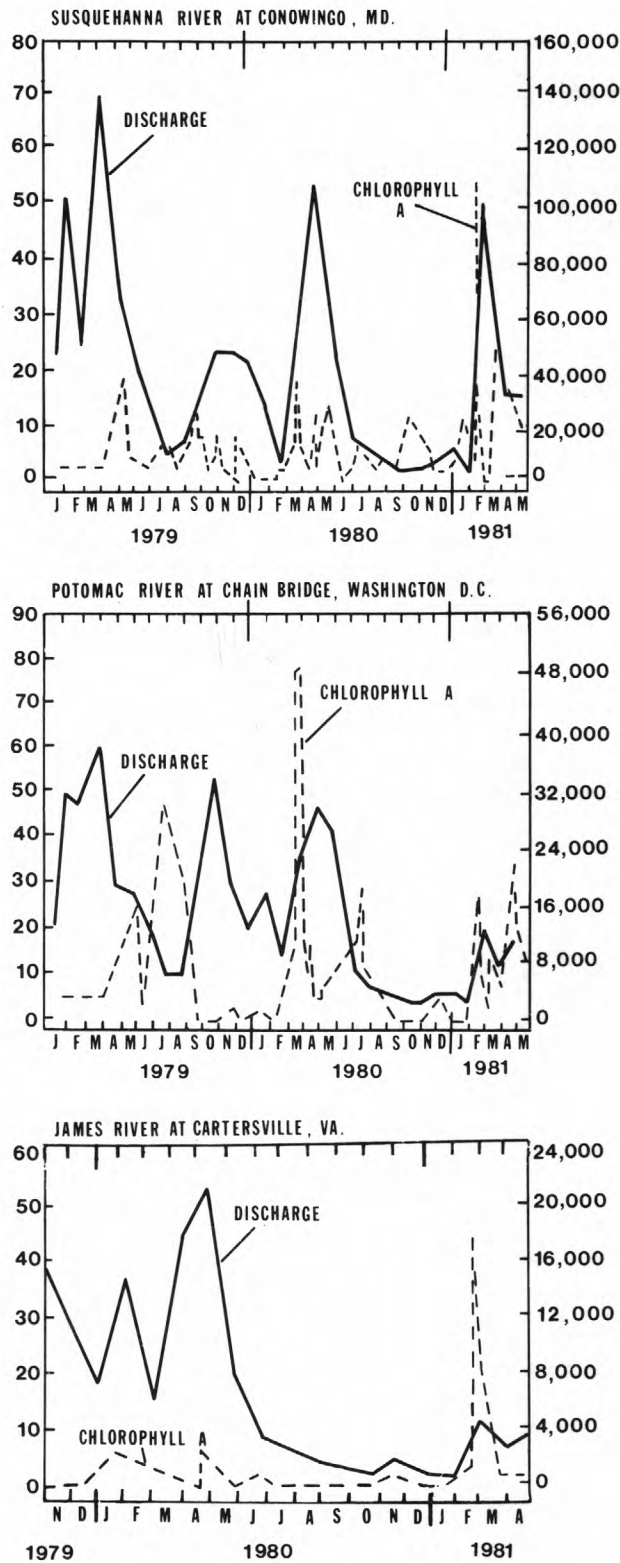
Chlorine

Because of recent interest in the effects of chlorine on marine life, water samples were collected and field-analyzed for total residual chlorine at five sites on tributaries to the Chesapeake Bay (fig. 6). At the same time, additional samples were collected and sent to the laboratory for analysis of low-molecular-weight halogenated hydrocarbons listed in table 8. The sites are: (1) Susquehanna River at Conowingo, Md.; (2) Potomac River at Chain Bridge at Washington, D.C.; (3) Potomac River at Woodrow Wilson Bridge at Alexandria, Va.; (4) Patuxent River near Bowie, Md.; and (5) Back River at Edgemere, Md.

The total residual (free residual and combined) chlorine analysis employed (American Public Health Association, 1976) was an amperometric titration technique which measures the total oxidants in the water. Therefore, significant concentrations of constituents such as bromine, iodine, chlorine dioxide, or permanganate in the sample may produce erroneously high values for total residual chlorine.

The five stations shown in figure 6 were each sampled in December 1980 or January 1981 and again in June or July 1981. All samples had total residual chlorine concentrations of less than or equal to the lower limit of detection for the technique, 0.01 mg/L. In three instances the chemicals listed in table 8 were detected. Trichloroethylene (TCE) concentrations of 0.005 and 0.009 mg/L were reported for the Back and Patuxent River sites, respectively, on July 1, 1981. On June 26, 1981, a benzene concentration of 0.002 mg/L was detected for the Potomac River at Alexandria, Va. The limits of detection for both TCE and benzene are 0.001 mg/L.

CHLOROPHYLL-A PHYTOPLANKTON, IN MICROGRAMS PER LITER



MEAN MONTHLY DISCHARGE, IN CUBIC FEET PER SECOND

Figure 5.--Seasonal fluctuations of concentrations of chlorophyll a at the three Fall Line stations.

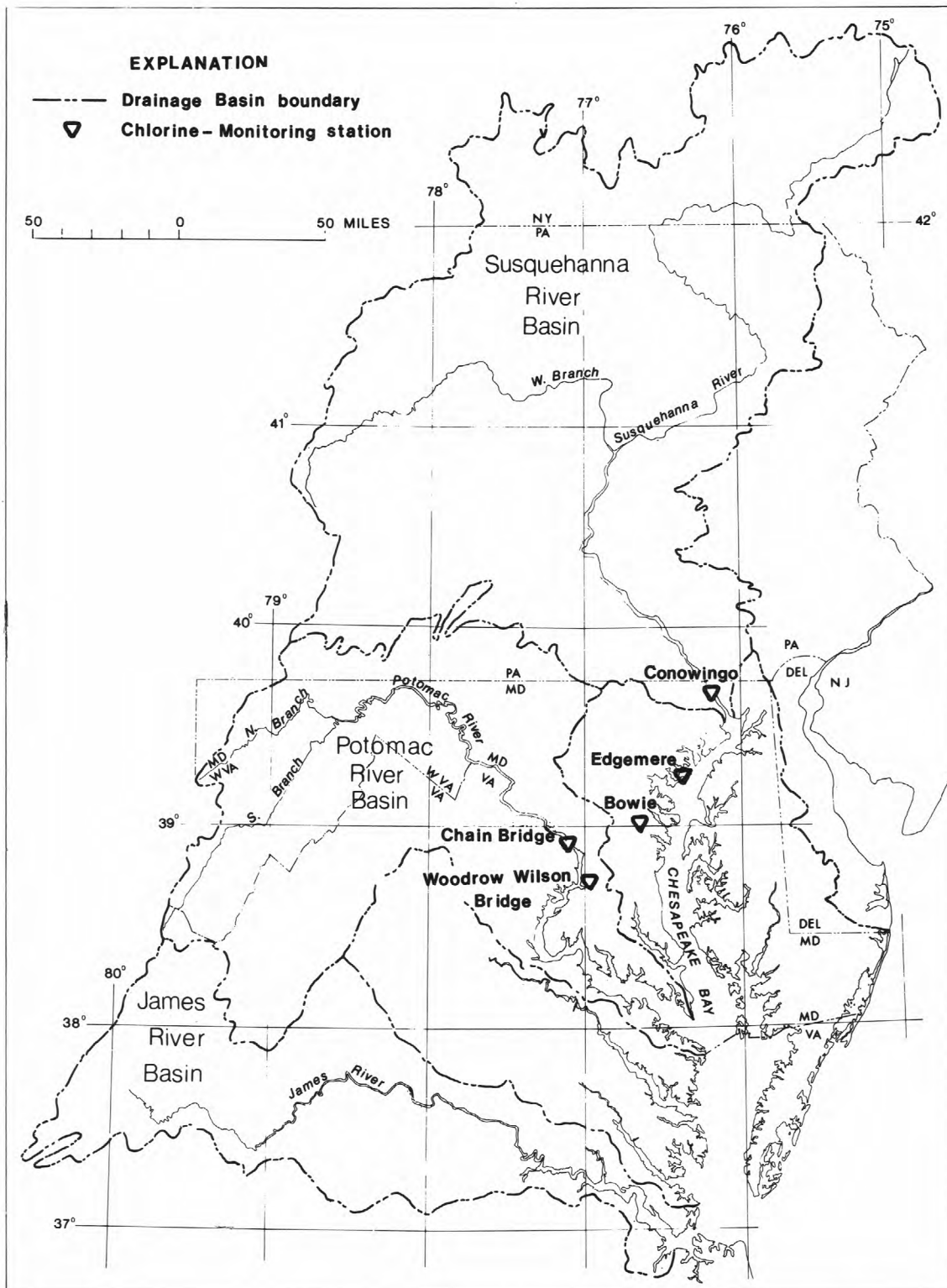


Figure 6.--Location of chlorine-monitoring stations on selected tributaries to Chesapeake Bay.

Table 8.--Schedule of low-molecular-weight, halogenated organic compounds analyzed from selected tributaries to Chesapeake Bay. All samples were collected at base flow and performed on unfiltered, water-sediment mixtures.

Benzene
 Bromoform
 Carbon tetrachloride
 Chlorobenzene
 Chlorodibromomethane

 Chloroethane
 2-Chloroethyl vinyl ether
 Chloroform
 Dichlorobromoethane
 Dichlorodifluoromethane

 1,1-Dichloroethane
 1,2-Dichloroethane
 1,1-Dichloroethylene
 1,2-trans-Dichloroethylene
 1,2-Dichloropropane

 1,3-Dichloropropene
 Ethylbenzene
 Methylbromide
 1,1,2,2-Tetrachlorethane

 Tetrachloroethylene
 Toluene
 1,1,1-Trichloroethane
 1,1,2-Trichloroethane
 Trichloroethylene

 Trichlorofluoromethane
 Vinyl chloride

Total Recoverable Aluminum, Iron, and Manganese

The term "total recoverable" refers to the amount of a particular constituent that is in solution after a water/suspended-sediment mixture sample has been digested by dilute acid. Complete dissolution of all particulate matter by this method is not achieved or desirable. The purpose of the digestion is to remove those constituents readily recoverable from the surfaces of the sediment particles without breaking down the crystalline structure of the sediments. Minerals within this crystalline structure are considered essentially unavailable for biological uptake under normal conditions existing in the estuaries of the Chesapeake Bay.

Computed loads for total recoverable aluminum, iron, and manganese are presented in tables 3, 4, and 5. The greatest loads for each constituent were carried in the Susquehanna River basin, whereas the smallest loads were found in the James River basin. Figures 7, 8, and 9 show aluminum, iron, manganese, and suspended-sediment concentrations, and discharge at the three Fall Line stations for selected high-flow periods. Regression data from table 2 for the Susquehanna River show higher correlations of aluminum, iron, and manganese with suspended sediment than with discharge. Because of the three dams in the lower Susquehanna River, this correlation is not evident in figure 7.

Aluminum, iron, and manganese correlated very well with suspended sediment in the Potomac River at Chain Bridge (table 2 and fig. 8). As suspended-sediment concentrations increased, so did concentrations of aluminum, iron, and manganese. All three metals had peak concentrations that were greater during the high flow in March than in September.

Figure 9 shows slightly different relations at the James River. Although manganese and suspended-sediment concentrations increased proportionally with discharge, aluminum and iron decreased at the peak of both suspended sediment and discharge. This sag may be caused by different quality and arrival times of water coming from upstream tributaries. No other storms were intensively sampled to verify whether this phenomenon occurs frequently.

Sulfate

Sulfate is not a major constituent in the earth's outer crust (Hem, 1970). It is commonly derived from metallic sulfides which occur in both igneous and sedimentary rocks. As these sulfides come into contact with aerated water, they are oxidized to sulfates. The oxidation of sulfur-containing minerals, such as pyrite, is especially common in coal areas.

Sulfate concentrations generally are inversely related to discharge. Because rainwater contains very small concentrations of sulfate as compared to streams, sulfate concentrations drop sharply during runoff events. During low-flow periods, streams are fed principally from ground-water sources, which have relatively high concentrations of sulfate due to prolong and intimate contact with sulfate-yielding minerals.

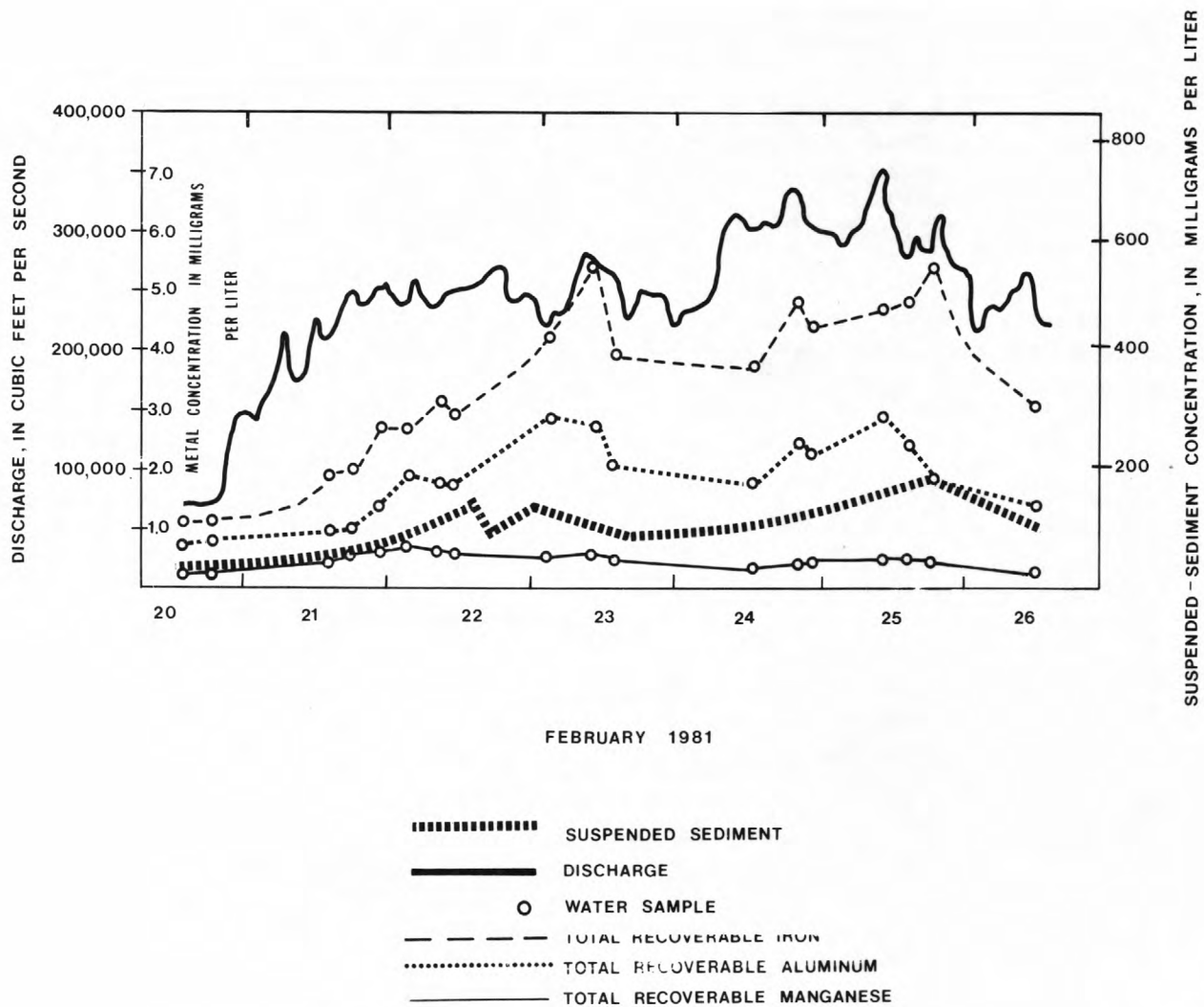


Figure 7.--Aluminum, iron, and manganese concentrations during February 20-26, 1981, at the Susquehanna River Fall Line station.

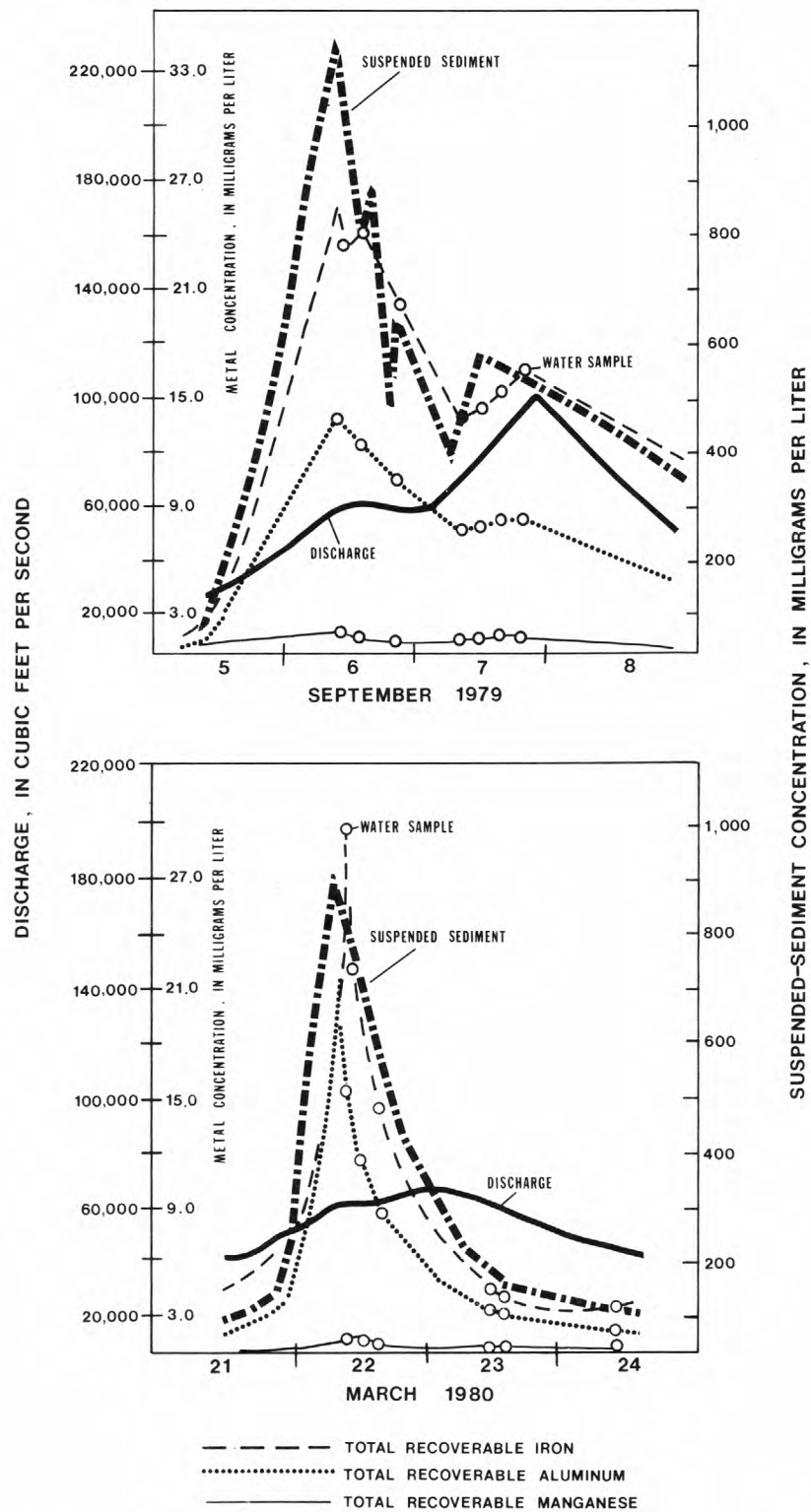


Figure 8.--Aluminum, iron, and manganese concentrations during September 5-8, 1979, and March 21-24, 1980, at the Potomac River Fall Line station.

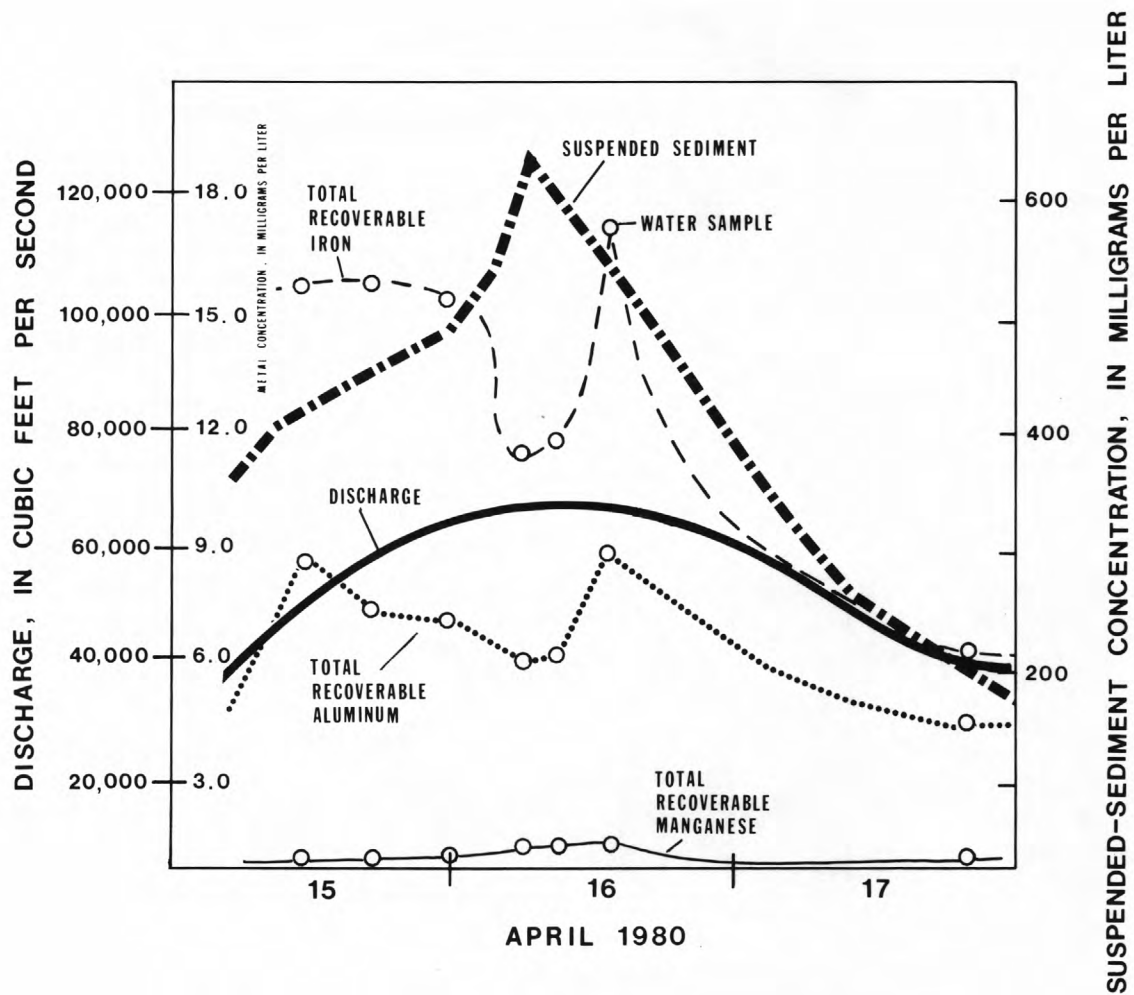


Figure 9.--Aluminum, iron, and manganese concentrations during April 15-17, 1980, at the James River Fall Line station.

Table 9 compares sulfate loads for the three Fall Line stations for the period May 1980 to April 1981. This period was chosen because it contained the most complete set of data for each of the stations, primarily during base-flow periods. The James River site carried 8.3 percent of the water discharge for the three stations but only 3.2 percent of the sulfate load. Both the Susquehanna and Potomac Rivers carried slightly more than their share of sulfate loads, when compared to their flow contributions for the same period. The discharge-weighted average concentrations of sulfate also point out that the Susquehanna and Potomac Rivers carry greater amounts per unit discharge of sulfate than the James River. The increased sulfate concentrations may be the result of drainage from coal areas in the Susquehanna and Potomac River basins. Very little coal is mined in the James River basin.

Nutrients and Their Relationships to Suspended Sediment and Discharge

Nutrients, chemical species of phosphorous, nitrogen, and carbon necessary for the growth of plant life, are found in water in the dissolved form associated with clay particles and as suspended organic matter. Certain nutrient species, such as orthophosphate, nitrite, and nitrate, are usually found dissolved in water. Most of the organic phosphorous and organic nitrogen is usually suspended. Ammonia and carbon can be found in the dissolved or suspended phase.

Generally, the highest concentrations of all nutrients occur during storms when water discharge and suspended-sediment concentrations are highest (figs. 10, 11, and 12). Nitrite + nitrate and orthophosphate loads correlate closely with discharge at all three Fall Line stations (table 2). All of the nutrient species data for the Susquehanna River at Conowingo correlate more closely with discharge; whereas, for the Potomac River at Chain Bridge, some parameters correlate better with suspended sediment while others correlate better with discharge. In general, nutrient parameters known to associate with suspended material relate better to suspended sediment, and constituents with greater solubility relate better to discharge.

For the Susquehanna River site, the hydroelectric dams between Harrisburg and Conowingo alter the natural riverine, sediment-flow patterns. During most years, suspended sediment becomes trapped behind these dams (Williams and Reed, 1972). The effect that the dams between Harrisburg and Conowingo have on the sediment transport of the lower Susquehanna River is discussed in more detail in a later section. However, those nutrients normally in suspension obviously have their transport regulated by the dams on the lower Susquehanna. Figure 10 shows the nutrient and suspended-sediment concentrations at Conowingo for the largest storm during the 1981 water year. None of the water-quality parameters show clear relationships with either suspended sediment or discharge, although both nitrite-nitrate and ammonia + organic nitrogen both have their highest concentrations occurring at the discharge and suspended-sediment peak.

Table 9.--Sulfate loads in the Susquehanna, Potomac, and James Rivers from May 1980 to April 1981

Station	Mean daily discharge for period (ft ³ /s)	Volume of streamflow for period (ft ³)	Sulfate load in millions of pounds	Percent of total volume of discharge for three stations	Percent of total sulfate load for three stations	Discharge weighted average concentrations of sulfate for period (mg/L)
Susquehanna River at Conowingo, Md.	25,500	8.03×10^{11}	1,930	71.3	75.1	38.6
Potomac River at Chain Bridge at Washington, D.C.	7,300	2.30×10^{11}	556	20.4	21.6	38.8
James River at Cartersville, Va.	2,970	0.94×10^{11}	82	8.3	3.2	14.2

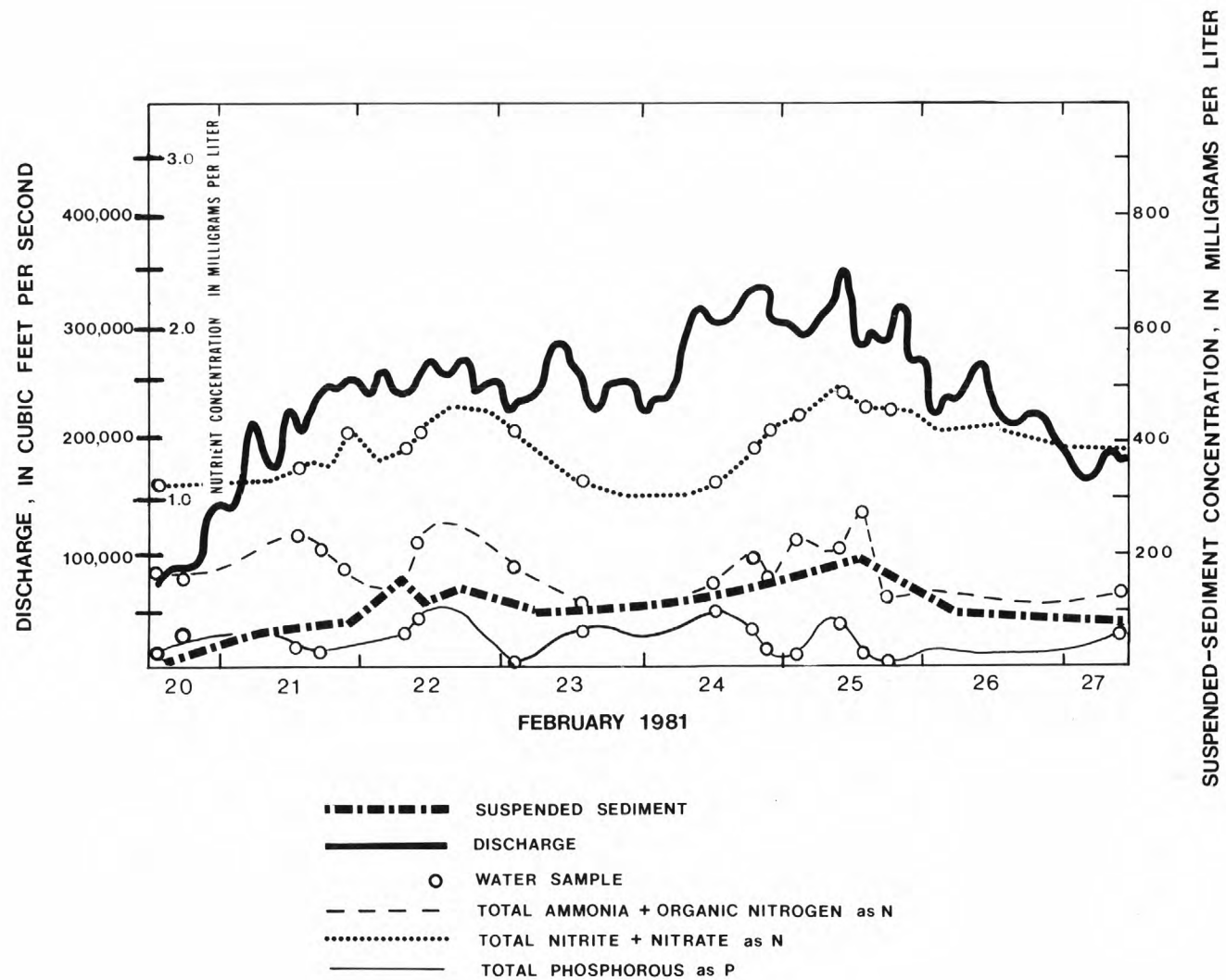


Figure 10.--Nutrient concentrations during February 20-27, 1981, at the Susquehanna River Fall Line station.

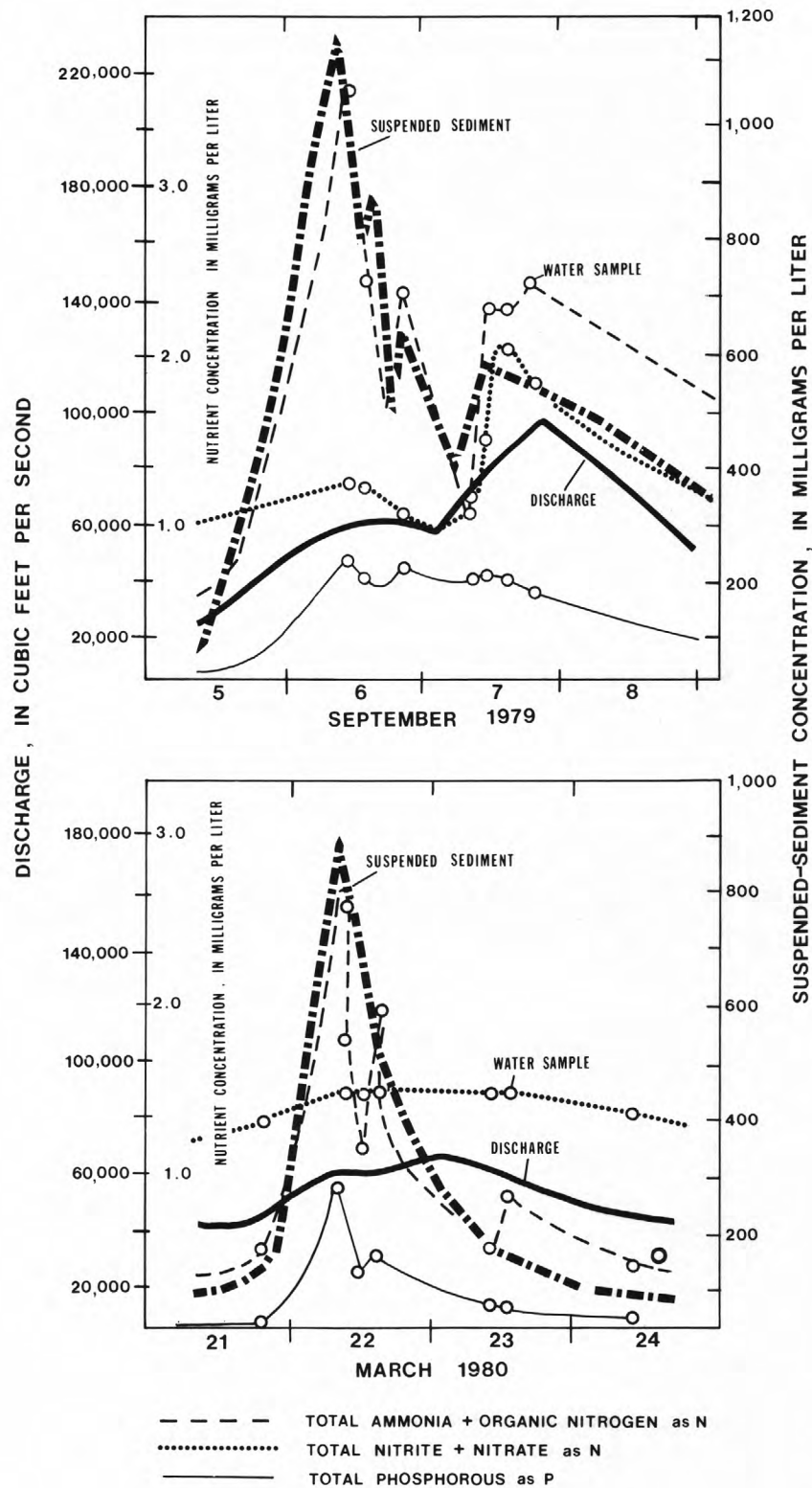


Figure 11.--Nutrient concentrations during September 5-8, 1979, and March 21-24, 1980, at the Potomac River Fall Line station.

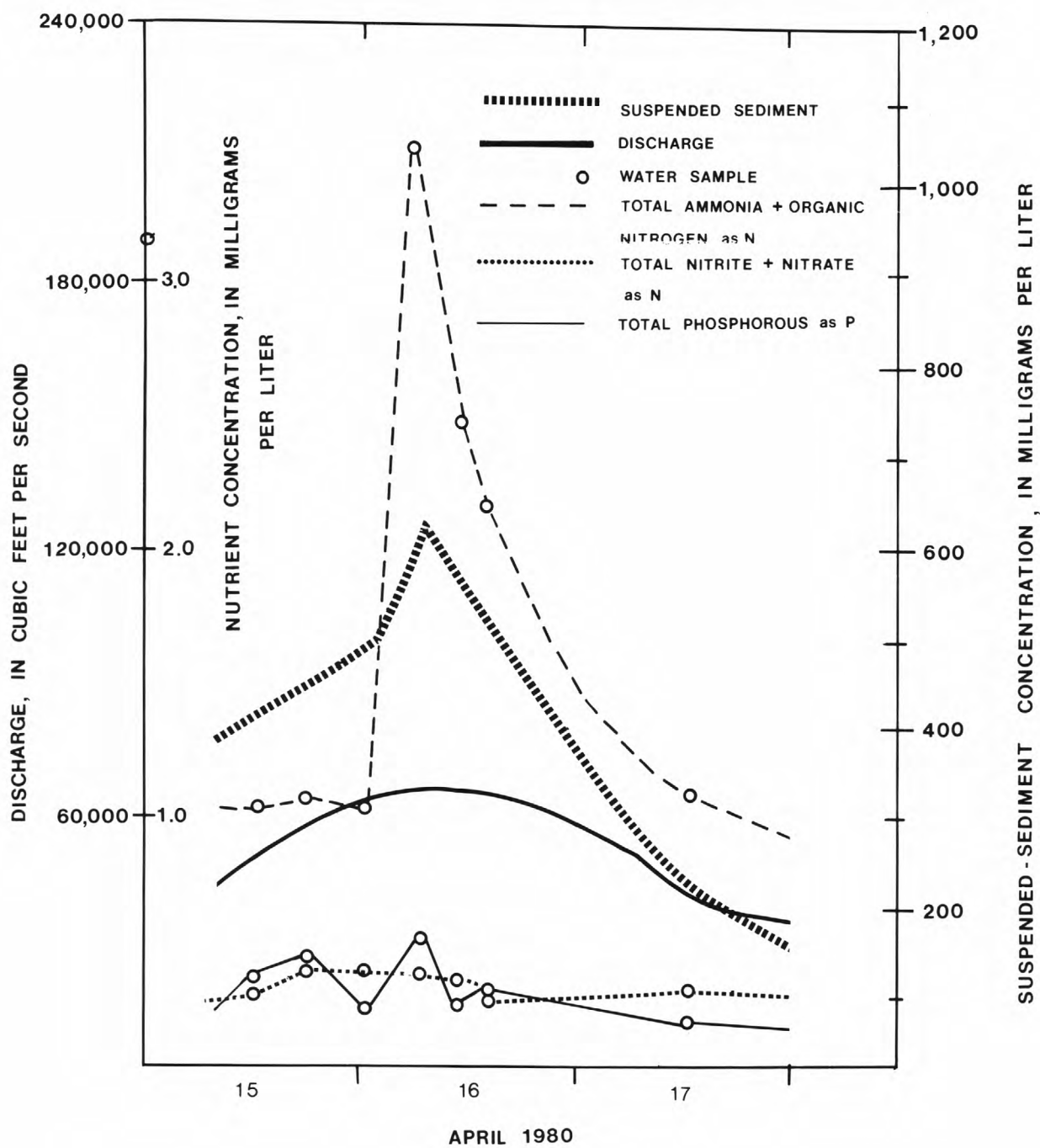


Figure 12.--Nutrient concentrations during April 15-17, 1980, at the James River Fall Line station.

In figures 11 and 12, ammonia + organic nitrogen is clearly related to the suspended-sediment hydrograph at both the Chain Bridge and Cartersville sites. Nitrite-nitrate nitrogen relates better to discharge at these two sites. Total phosphorous shows good correlation with suspended sediment at the Chain Bridge station and less correlation with suspended sediment at the Cartersville site.

During the high-flow events, it is critical to sample intensively before, during, and after both the discharge and suspended-sediment peaks to provide data sufficient for accurate nutrient load estimates. At the Chain Bridge and Cartersville stations, suspended-sediment concentration peak precedes the discharge peak by 8 to 40 hours (figs. 11 and 12). If samples are collected only between the peaks, one might wrongly conclude that certain nutrient parameters, such as total phosphorous and organic nitrogen, are inversely related to discharge during storm periods; the loads of these constituents would then be underestimated.

In only one instance in the 2-year data-collection period did nutrient concentrations decrease significantly during a high-flow event. For the Potomac River at Chain Bridge in February 1979 (fig. 13), the rise of nutrient concentrations at the beginning of the flow peak was reversed, probably because of a dilution effect from snowmelt (fig. 13). However, when the snow cover had been melted and the rain came in contact with the land surface, the concentrations of nitrite + nitrate, ammonia + organic nitrogen, and total phosphorous again increased.

Table 10 presents annual loads of selected nutrient species and annual mean discharges at the three Fall Line stations for 1979 and 1980. This table shows that at each of the stations, mean streamflow during 1980 was approximately one-half that of 1979; likewise, all listed nutrient loads are reduced by about half. This suggests the possibility of using annual mean discharges to approximate annual nutrient loads for past and future years.

Seasonal Variability of Nutrient Transport

Table 11 lists the transported loads of selected nutrients at the three Fall Line stations for 2 complete calendar years. The period of data collection is divided into 4-month intervals: (1) January-April, which represents the late winter and early spring high-flow period; (2) May-August, the most intense part of the growing season when flows are low, except during hurricane-related storms; and (3) September-December, when flows are low to moderate (except during hurricane-related storms) and biological activity for the year is declining. Data from January to April 1981 are not included in order to limit this analysis to two complete yearly cycles.

The data in table 11 show that for all three stations, the January-through-April period transports most of the loads of these nutrient species. Sixty-one percent of the total nitrogen and about two-thirds of the total phosphorous and organic carbon loads at the Susquehanna River at Conowingo accompany the high runoff occurring in late winter and early spring. At the Potomac and James River Fall Line stations, the January-through-April period contributes 50 to 61 percent of the loads for these three constituents.

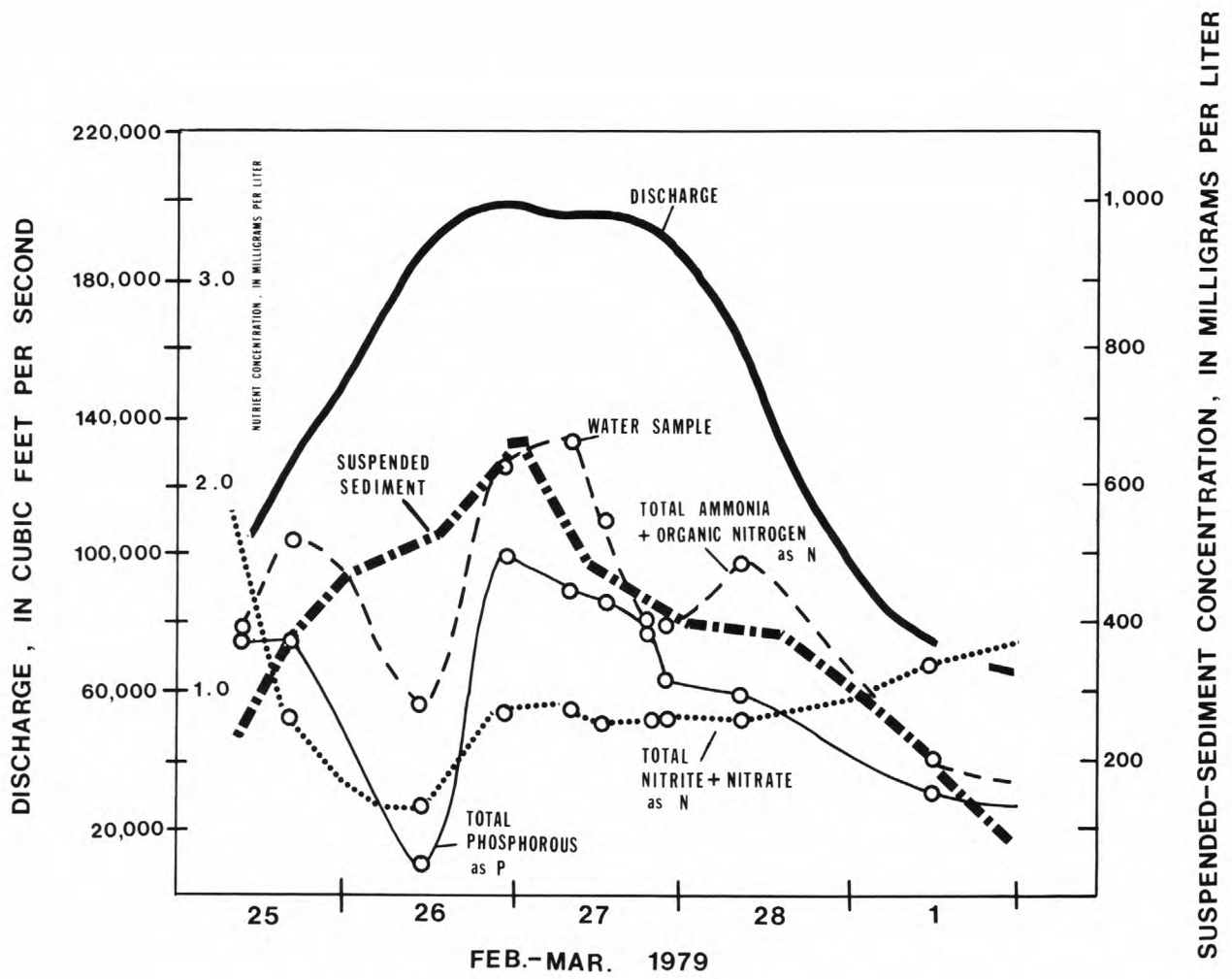


Figure 13.--Nutrient concentrations during February 25 - March 1, 1979, at the Potomac River Fall Line station.

Table 10.--Annual loads of selected nutrients (in millions of pounds) at the three Fall Line stations for calendar years 1979 and 1980

Constituent	Susquehanna River at Conowingo, Md.		Potomac River at Chain Bridge at Washington, D.C.		James River at Cartersville, Va.	
	1979	1980	1979	1980	1979	1980
Nitrogen, nitrite + nitrate, total as N	119	62.9	49.5	24.7	7.47	4.19
Nitrogen, ammonia, total as N	10.4	5.37	3.33	1.52	0.95	0.53
Nitrogen, ammonia + organic, total as N	47.0	24.7	32.1	13.0	16.1	7.80
Nitrogen, organic, total as N	36.8	19.2	26.1	10.6	15.3	7.40
Nitrogen, total as N	167	88.5	92.4	43.8	25.1	12.8
Phosphorus, orthophosphate, total as PO ₄	7.86	4.18	5.19	2.55	2.96	1.95
Phosphorous, total as PO ₄	21.7	10.2	19.0	6.78	10.6	5.67
Carbon, organic, total as C	351	177	208	88.2	152	81.9
Mean discharge (ft ³ /s)	52,300	28,400	20,400	11,000	12,000	7,790

Table 11.--Seasonal fluctuations of selected nutrients for the three Fall Line stations

Period	Nitrogen, nitrite + nitrate, total as N		Nitrogen, ammonia + organic total as N		Nitrogen, total as N		Phosphorous, orthophosphate total as PO ₄		Phosphorous, total as PO ₄		Carbon, total as C	
	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period
<u>SUSQUEHANNA RIVER AT CONOWINGO, MD.</u>												
January-April 1979	69.5	58	27.9	59	98.4	59	4.58	58	14.50	67	219	63
May-August 1979	17.9	15	6.9	15	25.1	15	1.20	15	2.40	11	45.9	13
September-December 1979	31.3	26	12.2	26	43.8	26	2.03	27	4.70	22	85.4	24
Calendar year total	119	100	47.0	100	167	100	7.86	100	21.6	100	350	100
January-April 1980	41.5	66	16.5	67	58.6	66	2.75	66	7.7	75	124	70
May-August 1980	15.1	24	5.8	23	21.2	24	1.02	24	1.91	19	38.1	22
September-December 1980	6.3	10	2.4	10	8.7	10	.42	10	.61	6	14.1	8
Calendar year total	62.9	100	24.7	100	88.5	100	4.18	100	10.2	100	177	100
Combined 2 year totals												
January-April (1979, 1980)	111.0	61	44.4	62	157	61	7.33	61	22.2	69	344	65
May-August (1979, 1980)	33.0	18	12.7	18	46.3	18	2.22	18	4.31	14	84.0	16
September-December (1979, 1980)	37.6	21	14.6	20	52.5	21	2.50	21	5.31	17	99.5	19
Total loads for period January 1979 - December 1980	182	100	71.7	100	256	100	12.0	100	31.8	100	527	100

Table 11.--Seasonal fluctuations of selected nutrients for the three Fall Line stations--Continued

Period	Nitrogen, nitrite + nitrate, total as N		Nitrogen, ammonia + organic total as N		Nitrogen, total as N		Phosphorous, orthophosphate total as PO ₄		Phosphorous, total as PO ₄		Carbon, total as C	
	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period
POTOMAC RIVER AT CHAIN BRIDGE, WASHINGTON, D.C.												
January-April 1979	25.0	50	15.5	49	48.4	52	2.65	51	9.7	51	97.8	47
May-August 1979	7.3	15	4.9	15	12.4	14	.74	14	2.4	13	33.9	16
September-December 1979	17.2	35	11.7	36	31.6	34	1.80	35	6.9	36	75.9	37
Calendar year total	49.5	100	32.1	100	92.4	100	5.19	100	19.0	100	208	100
January-April 1980	15.6	64	7.68	59	28.4	65	1.64	64	4.12	61	51.3	58
May-August 1980	7.5	30	4.67	36	13.2	30	.77	30	2.41	35	31.8	36
September-December 1980	1.4	6	.65	5	2.2	5	.14	6	.24	4	5.1	6
Calendar year total	24.6	100	13.0	100	43.8	100	2.55	100	6.77	100	88.2	100
Combined 2 year totals												
January-April (1979,1980)	40.6	55	23.2	52	76.8	56	4.29	55	13.8	54	149	50
May-August (1979,1980)	14.8	20	9.6	21	25.6	19	1.51	20	4.81	19	65.7	22
September-December (1979,1980)	18.6	25	12.4	27	33.8	25	1.94	25	7.14	27	81.0	28
Total loads for period												
January 1979 - December 1980	74.1	100	45.1	100	136	100	7.74	100	25.8	100	296	100

Table 11.--Seasonal fluctuations of selected nutrients for the three Fall Line stations--Continued

Period	Nitrogen, nitrite + nitrate, total as N		Nitrogen, ammonia + organic total as N		Nitrogen, total as N		Phosphorous, orthophosphate total as PO ₄		Phosphorous, total as PO ₄		Carbon, total as C	
	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period	Total load in 1,000,000 LBS	Percent of total load in period
JAMES RIVER AT CARTERSVILLE, VA.												
January-April 1979	3.35	45	7.98	50	12.0	48	1.19	40	4.88	46	70.1	46
May-August 1979	1.49	20	2.77	17	4.52	18	.71	24	2.01	19	28.9	19
September-December 1979	2.63	35	5.37	33	8.56	34	1.06	36	3.67	35	52.7	35
Calendar year total	7.47	100	16.1	100	25.1	100	2.96	100	10.6	100	152	100
January-April 1980	3.15	75	6.58	84	10.4	82	1.20	62	4.43	78	63.8	78
May-August 1980	.75	18	.97	13	1.81	14	.48	25	.92	16	13.4	16
September-December 1980	.29	7	.25	3	.53	4	.27	14	.32	6	4.66	6
Calendar year total	4.19	100	7.80	100	12.8	100	1.95	100	5.67	100	81.9	100
Combined 2 year totals												
January-April (1979,1980)	6.50	56	14.6	61	22.4	59	2.39	49	9.31	57	134	57
May-August (1979,1980)	2.24	19	3.74	16	6.33	17	1.19	24	2.93	18	42.3	18
September-December (1979,1980)	2.92	25	5.62	23	9.09	24	1.33	27	3.99	25	57.4	25
Total loads for period January 1979 - December 1980	11.7	100	24.0	100	37.8	100	4.91	100	16.2	100	234	100

During the May-through-August period, transport of nitrogen, phosphorous, and organic carbon is at a minimum. Streamflow is normally low and biological uptake of nutrients is high. During the September-through-December period, while evapotranspiration, temperature, and biological uptake of nutrients decline, stream flow and nutrient concentrations show marked increases.

Figures 14 and 15 graphically present monthly nitrogen and phosphorous species loads from the three Fall Line stations. As shown in table 11, much of the load is delivered during the first few months of each year when streamflow is above average. Also worth noting are the very small loads which were carried by the three rivers during the summer and fall of 1980 when streamflow was below normal. Nitrogen and phosphorous loads are not evenly distributed throughout the year, but are delivered mainly during high-flow periods.

Comparison of Nutrient Data Among the Three Fall Line Stations

Of the three stations, the Potomac River at Chain Bridge had the highest discharge-weighted average concentration of total nitrogen, 2.20 mg/L (table 12); the Susquehanna value had 1.61 mg/L, followed by the James River average concentration of 0.96 mg/L.

Most of the total nitrogen load transported by the Susquehanna and Potomac Rivers at their Fall Line is in the nitrite + nitrate form (table 12 and fig. 14). Nitrite + nitrate comprised 71 and 55 percent of the total nitrogen at the Conowingo and Chain Bridge sites, respectively. On the other hand, at the James River at Cartersville, nitrite + nitrate comprised only 31 percent of the total nitrogen load, with the remainder being mostly in the form of organic nitrogen. Since a much larger portion of the Susquehanna and Potomac River basins is involved in agriculture, this agrees with the results of Omerik (1976) mentioned previously.

The Susquehanna River at Conowingo has discharge-weighted average concentrations of both total phosphorous and orthophosphate notably lower than the other two rivers (table 12).

Orthophosphate comprises 38, 31, and 32 percent of the total phosphorous load at the Susquehanna, Potomac, and James River stations, respectively. The remainder is in the form of organic or acid hydrolyzable phosphorous. Figure 15 breaks down the transport loads of each of the phosphorous species for the 28-month data-collection period.

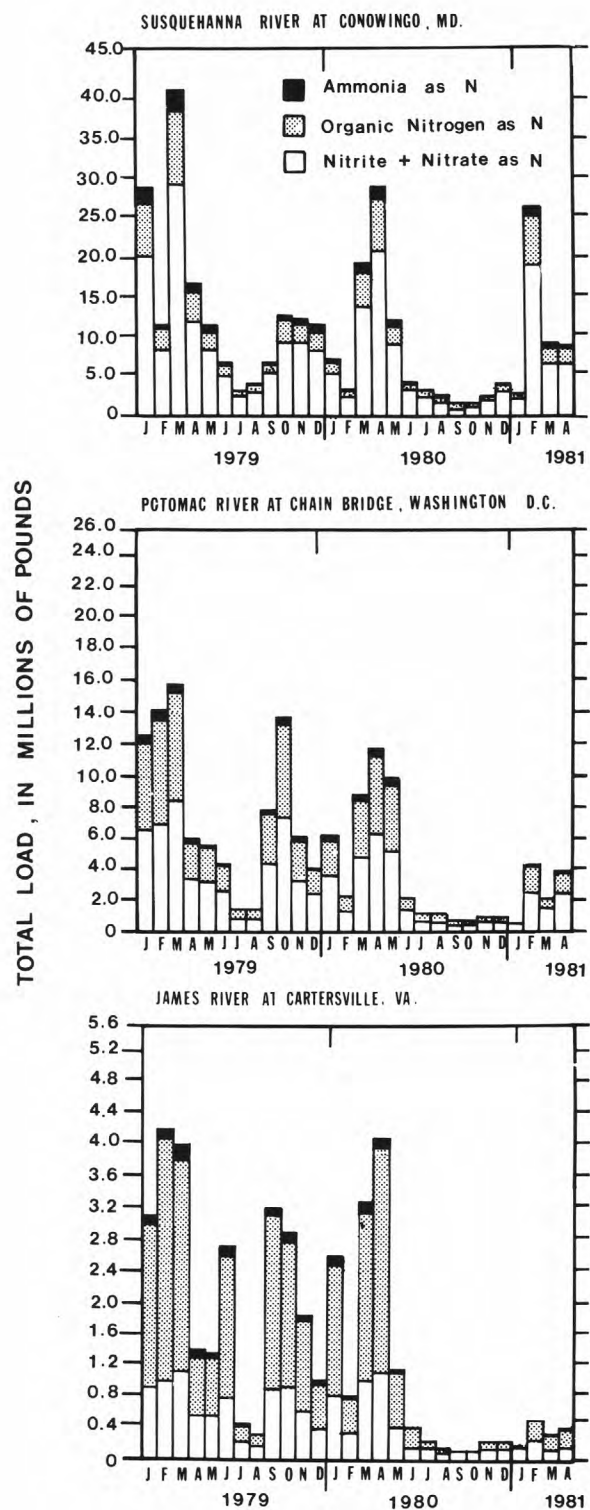


Figure 14.--Monthly loads of nitrogen at the three Fall Line stations.

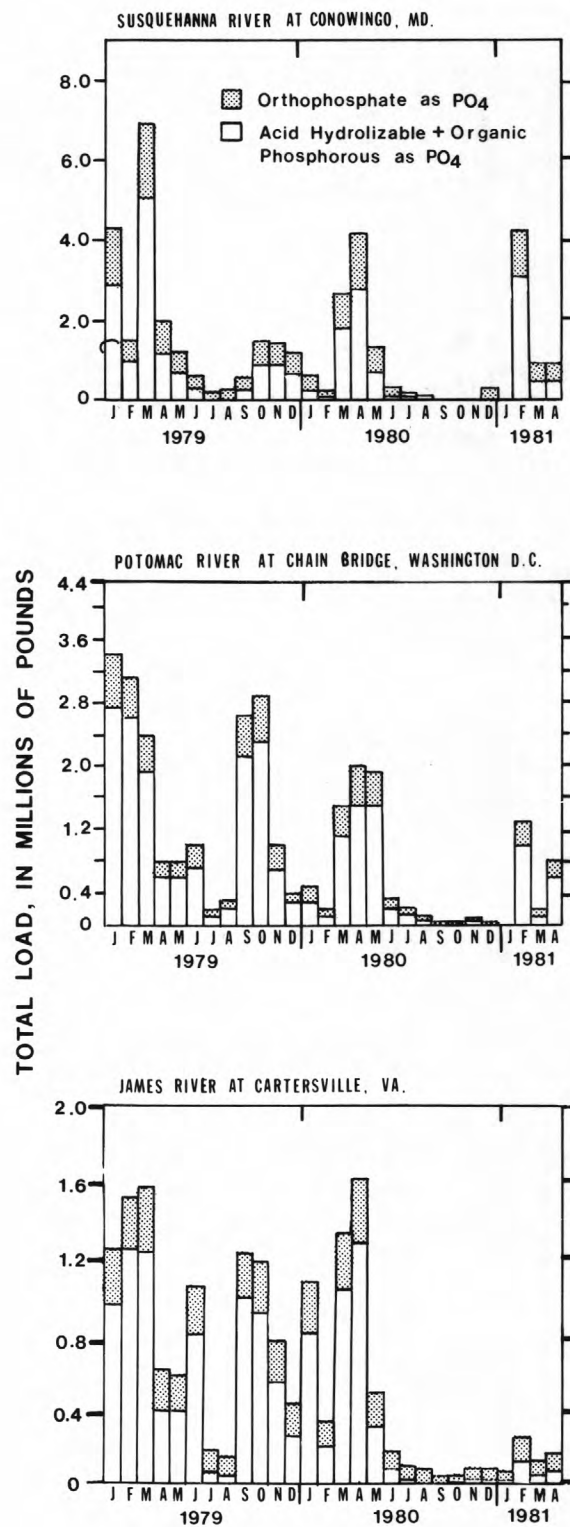


Figure 15.--Monthly loads of phosphorous at the three Fall Line stations.

Table 12.--Total nutrient loads and discharge-weighted average nutrient concentrations for the period
January 1979 to December 1980 at the three Fall Line stations

Constituent	Susquehanna River at Conowingo, Md.		Potomac River at Chain Bridge at Washington, D.C.		James River at Cartersville, Va.	
	Mean daily discharge for period January 1979-December 1980 = 40,300 ft ³ /s; total volume of streamflow for period = 2.55x10 ¹² ft ³		Mean daily discharge for period January 1979-December 1980 = 15,700 ft ³ /s; total volume of streamflow for period = 0.99x10 ¹² ft ³		Mean daily discharge for period January 1979 - December 1980 = 9,910 ft ³ /s; total volume of streamflow for period = 0.63x10 ¹² ft ³	
	Total load in million pounds	Discharge-weighted average concentrations in mg/L	Total load in million pounds	Discharge-weighted average concentrations in mg/L	Total load in million pounds	Discharge-weighted average concentrations in mg/L
Nitrogen, nitrite + nitrate, total as N	182	1.14	74.2	1.20	11.7	0.30
Nitrogen, ammonia, total as N	15.8	.10	4.85	.08	1.48	.04
Nitrogen, ammonia + organic, total as N	72.1	.45	45.1	.72	23.9	.61
Nitrogen, total as N	256.0	1.61	136	2.20	37.9	.96
Phosphorous, orthophosphate, total as PO ₄	12.0	.08	7.74	.13	4.91	.12
Phosphorous, total as PO ₄	31.9	.20	25.8	.42	16.3	.41
Carbon, organic, total as C	528	3.32	296	4.79	234	5.95

Comparison of Nutrient Data with Previous Studies

Tables 13 and 14 compare average nutrient loads and concentrations obtained from different hydrologic studies conducted at the Fall Line stations since 1966. At the Chain Bridge station, the period of the Jaworski (1969) report (January through December, 1966) was the driest in over 50 years of record. The loads and concentrations of Guide and Villa (1972) were computed for a period (June 1969 to May 1970) when Potomac River flow was 4 percent below normal. The Fall Line monitoring comparisons were made during a period (January 1979 to December 1980) when streamflow was 38 percent above average. However, even with these differences in flow, conclusions can be drawn from the data in tables 13 and 14.

From 1969 to 1980, average concentrations and loads of ammonia decreased at all three Fall Line stations; this is true even though the mean discharges for the sampling periods increased in all cases. The average concentrations and loads of orthophosphate at the Susquehanna and Potomac River sites also declined. The average concentration of nitrite + nitrate decreased slightly at the Potomac River from 1966 to 1980. At Conowingo, an increase in nitrite + nitrate concentrations was noted.

As another basis for evaluating trends in nutrient loads, the regression equations for the Susquehanna, Potomac, and James Rivers used by Guide and Villa (1972) were applied to the mean daily discharge data from January 1979 to December 1981. These hypothetical loads and average concentrations better reflect a true trend in nutrient loads because the same flow regime is utilized in each comparison (Hirsch^{1/}, oral commun., 1982). Tables 13 and 14 show hypothetical loads and average concentrations which would have occurred if the 1972 regressions were valid during 1979 and 1980.

In most cases, the hypothetical average concentrations for the Susquehanna and Potomac Rivers are nearly the same as those derived by Guide and Villa (1972). In table 14, these data support the previous conclusion that ammonia and orthophosphate concentrations have decreased. The James River results are inconclusive. Examination of the data used to calculate the 1972 regressions show that there were a significant number of high-flow samples collected at the Susquehanna and Potomac River stations. This is not true for the James River. In order to properly predict loads over a wide range of stages by regression, samples should be collected over this wide range. It is extremely difficult to accurately extrapolate high-flow loads from low-flow data. The only trend in James River water quality apparent from the data in tables 13 and 14 is a decrease in the ammonia loads and average concentrations.

Analysis of covariance was applied to the Guide and Villa (1972) and the Fall Line data for the nutrients found in tables 13 and 14. Results indicate a significant difference in all population means at a 5-percent significance level. There were no analytical changes in procedure for determining nitrite + nitrate, orthophosphate,

^{1/} Hirsch, R. M., Chief, U.S. Geological Survey Systems Analysis Group, Reston, Va.

Table 13.--Average daily loads (in lbs/d) of selected nutrient species for the three Fall Line stations derived from different hydrologic investigations

Investigation and period of coverage	Average daily discharge for sampling period (ft ³ /s)	Phosphorous, total as PO ₄	Phosphorous, ortho-phosphate, total as PO ₄	Nitrogen, nitrite + nitrate, total as N	Nitrogen, ammonia + organic, total as N	Nitrogen, ammonia, total as N	Carbon, organic, total as C
<u>SUSQUEHANNA RIVER AT CONOWINGO, MD</u>							
Guide & Villa (1972); June 1969 - May 1970	¹ 36,000	37,800	23,300	174,000	101,000	30,800	568,000
Fall Line Monitoring Study; January 1979 - December 1980	¹ 40,300	43,600	16,400	249,000	98,600	21,600	722,000
Hypothetical loads ²	¹ 40,300	46,600	30,300	203,000	110,000	32,200	633,000
<u>POTOMAC RIVER AT CHAIN BRIDGE AT WASHINGTON, D.C.</u>							
Jaworski (1969); January 1966-December 1966	³ 6,740	17,000	-	49,000	5,700	-	-
Guide and Villa (1972); June 1969 - May 1970	³ 10,500	24,800	11,000	65,600	37,400	6,700	285,000
Fall Line Monitoring Study; January 1979 - December 1980	³ 15,900	35,300	10,600	102,000	61,700	6,600	405,000
Hypothetical loads ²	³ 15,900	38,400	18,200	144,000	52,800	9,670	377,000
<u>JAMES RIVER AT CARTERSVILLE, VA.</u>							
Guide & Villa (1972) ⁴ June 1969 - May 1970	⁵ 6,880	8,670	5,100	18,200	21,600	5,130	159,000
Fall Line Monitoring Study; January 1979 - December 1980	⁶ 9,910	22,300	6,700	16,000	32,700	2,000	320,000
Hypothetical loads ²	⁶ 9,910	23,700	13,100	33,900	48,600	18,300	229,000

¹ Mean annual discharge for this station is 38,900 ft³/s, based on records at Harrisburg, Pa.

² Based on regressions from Guide and Villa (1972) and streamflow from Fall Line study.

³ Mean annual discharge for this station is 11,500 ft³/s.

⁴ Station is located at Huguenot Bridge in Richmond, Va., about 40 miles downstream.

⁵ Mean annual discharge for this station is 7,610 ft³/s.

⁶ Mean annual discharge for this station is 7,110 ft³/s.

Table 14.--Discharge-weighted average concentrations (in mg/L) of selected nutrient species for the three Fall Line stations derived from different hydrologic investigations

Investigation and period of coverage	Average daily discharge for sampling period (ft ³ /s)	Phosphorous, total as PO ₄	Phosphorous, ortho-phosphate, total as PO ₄	Nitrogen, nitrite + nitrate, total as N	Nitrogen, ammonia + organic, total as N	Nitrogen, ammonia, total as N	Carbon, organic, total as C
<u>SUSQUEHANNA RIVER AT CONOWINGO, MD</u>							
Guide & Villa (1972); June 1969 - May 1970	¹ 36,000	0.20	0.12	0.89	0.52	0.16	2.92
Fall Line Monitoring Study; January 1979 - December 1980	¹ 40,300	.20	.08	1.14	.45	.10	3.32
Hypothetical concentrations ²	¹ 40,300	.21	.14	.94	.51	.15	2.92
<u>POTOMAC RIVER AT CHAIN BRIDGE AT WASHINGTON, D.C.</u>							
Jaworski (1969); January 1966-December 1966	³ 6,740	0.47	-	1.35	0.16	-	-
Guide and Villa (1972); June 1969 - May 1970	³ 10,500	.44	.20	1.16	.66	.12	5.06
Fall Line Monitoring Study; January 1979 - December 1980	³ 15,900	.42	.13	1.20	.72	.08	4.79
Hypothetical concentrations ²	³ 15,900	.45	.21	1.69	.62	.11	4.42
<u>JAMES RIVER AT CARTERSVILLE, VA.</u>							
Guide & Villa (1972) ⁴ ; June 1969 - May 1970	⁵ 6,880	0.23	0.14	0.49	0.58	0.14	4.30
Fall Line Monitoring Study; January 1979 - December 1980	⁶ 9,910	.41	.12	.30	.61	.04	5.95
Hypothetical concentrations ²	⁶ 9,910	.44	.24	.64	.91	.34	4.29

¹ Mean annual discharge for this station is 38,900 ft³/s, based on records at Harrisburg, Pa.

² Based on regressions from Guide and Villa (1972) and streamflow from Fall Line study.

³ Mean annual discharge for this station is 11,500 ft³/s.

⁴ Station is located at Huguenot Bridge in Richmond, Va., about 40 miles downstream.

⁵ Mean annual discharge for this station is 7,610 ft³/s.

⁶ Mean annual discharge for this station is 7,110 ft³/s.

and total phosphorous that would influence the results of comparisons between the two studies (Erdmann^{2/}, written commun., 1981; and Villa^{3/}, written commun., 1981). Because of a more thorough digestion process, ammonia concentration values recorded during the Fall Line study may actually be higher than during the 1972 study by Guide and Villa. It has been noted previously that ammonia concentrations apparently decreased during the Fall Line study. This is the opposite of what would be expected if the more thorough digestion influenced the results.

Table 15 compares nutrient loads for the Susquehanna River at Conowingo computed by Clark, Donnelly, and Villa (1973) to loads calculated for the period of this report. Both studies use the same load versus discharge regression technique to compute loads, although each uses a different regression equation. Therefore, load estimates can be made for any chosen discharge. In the table, loads are listed for three discharges (10,000, 50,000, and 100,000 ft³/s), which represent low, medium, and high flows at this station. Because the comparisons of estimated loads are made at the same discharges for the two data periods, differences in the loads may represent trends in water-quality characteristics rather than reflect the combined effects of varying amounts of rainfall, runoff, or ground-water infiltration.

The comparisons in table 15 verify the apparent reductions in loads of ammonia and orthophosphate at this site, as previously noted. They also reinforce the suggestion of an increase in nitrite + nitrate. If nitrogen is the limiting nutrient for algal growth in the upper Chesapeake Bay, as reported by Clark, Donnelly, and Villa (1973), this trend in particular warrants continued monitoring.

With mixed results, previous investigations have attempted to correlate discharge with nutrient concentrations. In most instances, there was either no correlation or discharge directly related to nutrient concentration. However, in several instances, investigators detected an inverse correlation of discharge with concentrations of certain nutrient species. Guide and Villa (1972) noted this inverse correlation for ammonia + organic nitrogen at the Susquehanna River at Conowingo; for total phosphorous at the Potomac River at Great Falls (about 8 mi upstream from Chain Bridge); and for nitrite + nitrate at the James River at Cartersville. Clark, Guide, and Pfeiffer (1974) also noted an inverse relationship between concentrations of total phosphorous or ammonia + organic nitrogen and discharge at the Susquehanna River at Conowingo site. Jaworski (1969) noted a similar correlation for total phosphorous and discharge at the Potomac River Fall Line site.

^{2/} Erdmann, D. E., Chief, U.S. Geological Survey National Water-Quality Laboratory, Atlanta, Ga., June 1981.

^{3/} Villa, Orterio, Chief, U.S. Environmental Protection Agency, Region III Laboratory, Annapolis, Md., May 1981.

Table 15.--Estimates of nutrient loads (in lb/d) at three different discharges for 1969-72 and 1979-81 data sets for the Susquehanna River at Conowingo, Md.

Constituent	Discharge of Estimate (ft ³ /s)					
	10,000		50,000		100,000	
	Data Set		Data Set		Data Set	
	1969-72 ¹	1979-81	1969-72 ¹	1979-81	1969-72 ¹	1979-81
Phosphorus, total as PO ₄	7,500	4,370	50,000	43,800	120,000	117,000
Phosphorus, orthophosphate, total as PO ₄	3,500	3,360	30,000	20,000	75,000	41,700
Nitrogen, organic, total as N	² 22,000	14,700	² 100,000	90,300	² 200,000	197,000
Nitrogen, inorganic, total as N	58,000	³ 59,700	300,000	³ 330,000	600,000	³ 694,000
Nitrogen, nitrite + nitrate, as N	40,000	53,700	250,000	301,000	530,000	631,000
Nitrogen, ammonia + organic, total as N	⁴ 40,000	20,000	⁴ 150,000	117,000	⁴ 270,000	251,000
Nitrogen, ammonia, total as N	⁵ 18,000	3,900	⁵ 50,000	25,200	⁵ 70,000	56,200
Nitrogen, total as N	80,000	74,100	400,000	423,000	800,000	891,000

¹1969-72 data from Clark, Donnelly, and Villa (1973).

²Calculated by (Total nitrogen) - (Total inorganic nitrogen).

³Calculated by (Total nitrogen) - (Total organic nitrogen).

⁴Calculated by (Total nitrogen) - (Nitrite + Nitrate nitrogen).

⁵Calculated by (Total inorganic nitrogen) - (Nitrite + nitrate nitrogen).

Concentrations of all nutrient parameters analyzed for this report correlate directly with discharge including data for total phosphorous, ammonia + organic nitrogen, and nitrite + nitrate. Figures 10, 11, and 12 present typical relationships between discharge, suspended sediment, and nutrient species for the three Fall Line stations during storms. The direct relationships between discharge or suspended sediment and nutrient parameters are clearly apparent for the Potomac and James River stations. Regulation of the lower Susquehanna River obscures these relationships somewhat at the Conowingo station.

Clark, Donnelly, and Villa (1973) stated that inorganic nitrogen and the total nitrogen loads in the upper Chesapeake Bay were generally constant regardless of the Susquehanna River flow. The previous discussion has shown that in the Susquehanna, for calendar years 1979 and 1980, nitrite + nitrate (which is the majority of inorganic nitrogen) and total nitrogen transport are dependent on river discharge; more than half of their total load is transported by spring high flows (table 10). The fate of these nutrients in the water of the upper Bay is crucial to the development of control strategy and requires further study.

Comparison of Nutrient Data at the Susquehanna River Stations at Harrisburg, Pa., and Conowingo, Md.

From April 1980 to March 1981, the water quality of the Susquehanna River was intensively monitored at both Conowingo, Md., and Harrisburg, Pa. The results of sampling at these two stations are presented in tables 16 and 17 where water-quality constituent loads for the period are compared. All load computations were by methods previously described in an earlier section.

The three hydroelectric dams on the Susquehanna River between Harrisburg and Conowingo influence the transport of many water-quality constituents. For the period of concurrent sampling, the suspended-sediment load at the Conowingo site is 45 percent lower than the Harrisburg site, even though the drainage area at the downstream site is 13 percent greater. It is reasonable to assume then that those constituents which are mainly sorbed to suspended-sediment particles or are contained in suspended material should also have smaller loads at Conowingo. The data in table 16 show that this is indeed true for total phosphorous, organic and ammonia + organic nitrogen, organic carbon, aluminum, iron, and manganese. A more thorough analysis of the reductions of the suspended-sediment loads between the two stations on the Susquehanna River is presented in a subsequent section.

The data in table 17 point out that orthophosphate and nitrite + nitrate make up a greater percentage of the total phosphorous and nitrogen loads at the Conowingo station than at the Harrisburg site. This is also reasonable since these constituents are usually dissolved in streams, and their concentrations are not diminished by the settling of suspended sediment behind the dams. There is also a large percentage of agriculture in the area between the two stations. As previously noted, agricultural areas normally have higher nitrite + nitrate concentrations because of the use of nitrogen based fertilizers.

Table 16.--Water-quality constituent loads (in millions of pounds) for stations on the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 through March 1981

Constituent	Susquehanna River at Harrisburg, Pa. ¹	Susquehanna River at Conowingo, Md. ²
Phosphorous, total as PO ₄	18.3	12.1
Phosphorous, orthophosphate, total as PO ₄	3.14	4.58
Nitrogen, organic, total as N	28.2	21.2
Nitrogen, nitrite + nitrate, total as N	53.4	68.9
Nitrogen, ammonia + organic, total as N	33.6	27.2
Nitrogen, ammonia, as N	4.23	6.00
Nitrogen, total as N	90.8	97.0
Carbon, organic, total as C	237	199
Manganese, total recoverable as Mn	20.4	16.6
Aluminum, total recoverable as Al	50.5	46.0
Iron, total recoverable as Fe	162	78.8
Solids, dissolved	5,550	7,200
Sediment, suspended	4,600	2,540

¹Mean daily discharge for the period is 26,500 ft³/s.

²Mean daily discharge for the period is 31,400 ft³/s.

Table 17.--Relative proportions of orthophosphate, nitrite + nitrate, and ammonia + organic nitrogen to total phosphorous and nitrogen loads at the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 to March 1981

Constituent	Susquehanna River at Harrisburg, Pa. ¹		Susquehanna River at Conowingo, Md. ²	
	Load (in millions of pounds)	Percent of total PO ₄ or N	Load (in millions of pounds)	Percent of total PO ₄ or N
Phosphorous, total as PO ₄	18.3	100	12.1	100
Phosphorous, orthophosphate, total as PO ₄	3.5	17	4.56	38
Nitrogen, total as N	³ 870	100	³ 961	100
Nitrogen, nitrite + nitrate, total as N	534	61	689	72
Nitrogen, ammonia + organic, total as N	336	39	272	28

¹Mean daily discharge for the period 26,500 ft³/s.

²Mean daily discharge for the period 31,400 ft³/s.

³Total nitrogen load is the sum of this station's nitrite + nitrate and ammonia + organic nitrogen loads (as N) for the period.

Table 18 presents the discharge-weighted average concentrations for water-quality constituents sampled at both Susquehanna River stations. Reductions in a downstream direction are again noted in the concentration of those parameters generally associated with suspended sediment. The largest reductions are noted in total phosphorous, organic nitrogen, and organic carbon. Orthophosphate and nitrite + nitrate concentrations show slight increases at the Conowingo site when compared to the Susquehanna River at Harrisburg. Some of these differences are probably attributed to the large amount of agriculture present between the two stations.

Sediment Transport Characteristics

Susquehanna River

In an average year, the Susquehanna River transports 1.8 million tons of sediment to the Chesapeake Bay (Williams and Reed, 1972). Most of the load is carried to the Bay during spring high flows or hurricane-related storms.

According to Williams and Reed (1972), dams on the lower Susquehanna constructed before 1931 reduce the natural suspended-sediment load by 40 percent. Between April 1980 and March 1981, 2.3 million tons of suspended sediment were measured at the Susquehanna River at Harrisburg, and 1.3 million tons at Conowingo--a 56-percent reduction even though the drainage area at Conowingo is 13 percent greater. The pools behind the dams on the lower Susquehanna River act as sediment traps during low and medium flows.

However, at high flow, the dams are suspended-sediment sources. Ritter (1974) reports that 7.5 million tons of suspended sediment were measured at the Harrisburg site during Hurricane Agnes in June 1972. Gross and others (1978) estimate that for the same period, the river at Conowingo transported 27 million tons to the Bay, or about a 360-percent increase. They suggest that during major floods (discharges greater than about 400,000 ft³/s), previously deposited sediment is eroded from behind the dams and transported downstream. This discharge has a recurrence interval of approximately 4 years at Conowingo based on 110 years of streamflow data at Harrisburg and adjusted for drainage-area difference between Harrisburg and Conowingo.

A comparison of recent suspended-sediment transport data for the Susquehanna River at the Harrisburg and Conowingo stations supports the suggestion that above a discharge of 400,000 ft³/s, sediment is scoured from behind the dams. Suspended-sediment concentrations at the Harrisburg and Conowingo sites during the three highest discharge peaks from March 1979 to April 1981 are shown in figure 16. The March 5-11, 1979 storm, which had a peak discharge of about 500,000 ft³/s, transported 67 percent more sediment at Conowingo than at Harrisburg (table 19). The other storms in figure 16 had peak discharges of 240,000 and 353,000 ft³/s. During these storms, the suspended-sediment transport at Conowingo was about 50 percent less than that of Harrisburg. The only time in this data-collection period when suspended-sediment transport on the Susquehanna River at Conowingo exceeded that of the Harrisburg station was during the March 5-11, 1979 storm.

Table 18.--Discharge-weighted average concentrations (in mg/L) of water-quality constituents for stations on the Susquehanna River at Harrisburg, Pa., and Conowingo, Md., from April 1980 through March 1981

Constituent	Susquehanna River at Harrisburg, Pa. ¹	Susquehanna River at Conowingo, Md. ²
Phosphorous, total as PO ₄	0.35	0.20
Phosphorous, orthophosphate, total as PO ₄	0.06	0.07
Nitrogen, organic, total as N	0.54	0.34
Nitrogen, inorganic, total as N	1.20	1.22
Nitrogen, nitrite + nitrate, total as N	1.03	1.11
Nitrogen, ammonia + organic, total as N	0.65	0.44
Nitrogen, ammonia, total as N	0.08	0.10
Nitrogen, total as N	1.74	1.57
Carbon, organic, total as C	4.54	3.27
Manganese, total recoverable as Mn	0.39	0.27
Aluminum, total recoverable as Al	0.97	0.75
Iron, total recoverable as Fe	3.12	1.28
Solids, dissolved	107	117
Sediment, suspended	88	41

¹Mean daily discharge for the period is 26,500 ft³/s.

²Mean daily discharge for the period is 31,400 ft³/s.

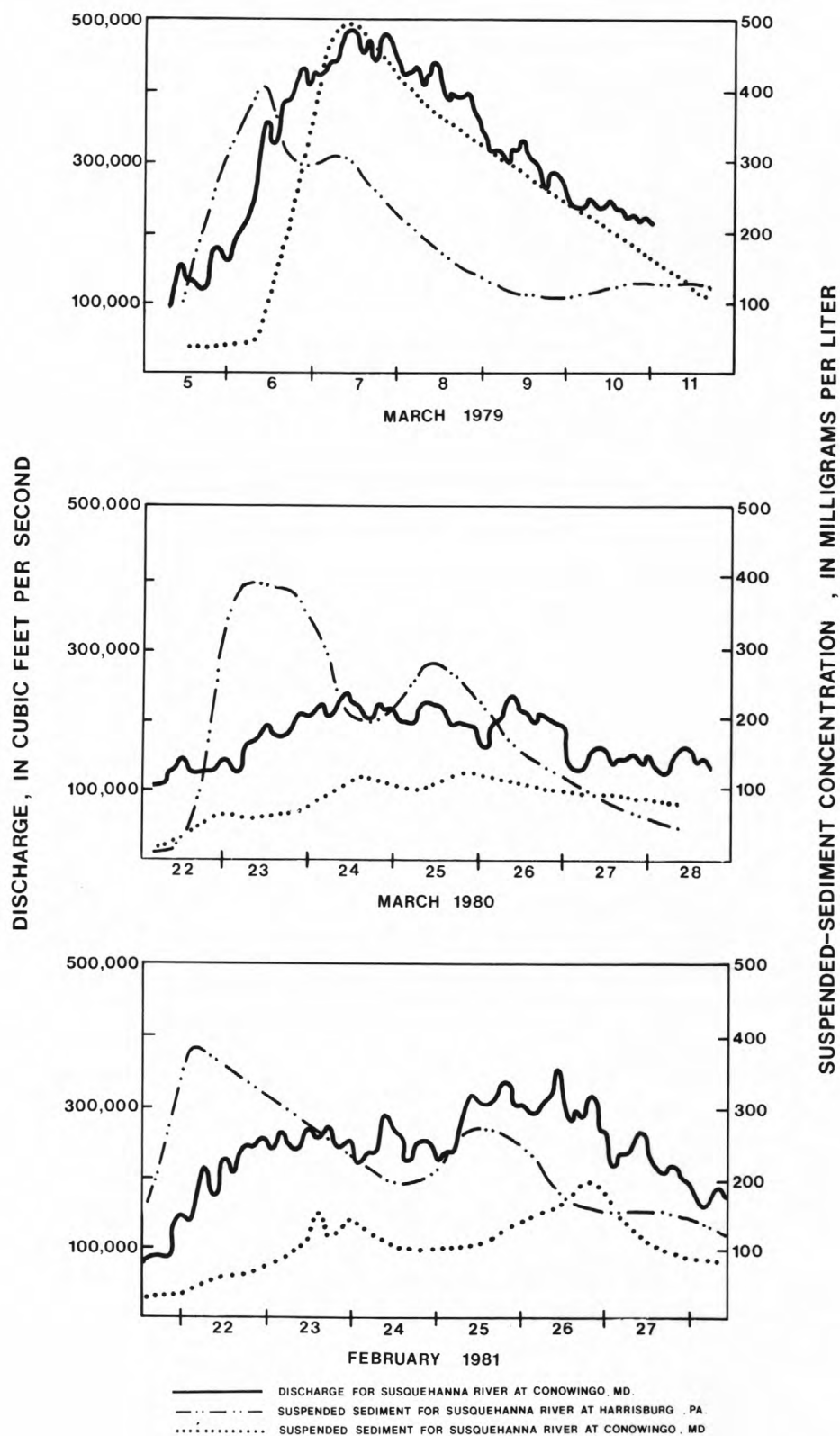


Figure 16.--Suspended-sediment transport for three high flows at the Susquehanna River at Harrisburg, Pa., and Conowingo, Md.

Table 19.--Suspended-sediment loads (in tons) at the Harrisburg, Pa., and Conowingo, Md., stations on the Susquehanna River for three high-flow periods

Date	Susquehanna River at Harrisburg, Pa. (Drainage area is 24,100 mi ²)	Susquehanna River at Conowingo, Md. (Drainage area is 27,100 mi ²)
March 5, 1979	32,300	15,300
March 6	284,000	184,000
March 7	316,000	568,000
March 8	149,000	412,000
March 9	90,100	236,000
March 10	69,700	136,000
March 11	<u>30,000</u>	<u>67,800</u>
Total load for high-flow period	971,100	1,619,100
March 21, 1980	33,200	13,500
March 22	152,000	28,000
March 23	132,000	57,500
March 24	116,000	63,300
March 25	55,200	46,900
March 26	<u>31,600</u>	<u>34,700</u>
Total load for high-flow period	520,000	243,900
February 21, 1981	196,000	31,600
February 22	183,000	78,200
February 23	127,000	76,600
February 24	199,000	90,800
February 25	142,000	137,000
February 26	78,400	70,500
February 27	<u>30,200</u>	<u>36,200</u>
Total load for high-flow period	955,600	520,900

Potomac River

During the 1979 water year (Oct. 1978 to Sept. 1979), the suspended-sediment load at the Potomac River at Chain Bridge at Washington, D.C., was 2.64 million tons (Lang and Grason, 1980). Water year 1979 had the second highest annual mean discharge in this station's 86-year period. Periods of exceptionally intense runoff in January, February, March, and September 1979 were the principal causes of the high yearly discharge and sediment load (fig. 17). Feltz (1976) estimated the average annual suspended-sediment load to be 1.5 million tons from 1964 to 1975 at the Potomac River at Great Falls, 8 mi (and 99 percent of the drainage area) upstream from Chain Bridge.

Figure 17 shows the importance of antecedent conditions to sediment transport at the Chain Bridge station. Depicted in this figure are the three highest discharge peaks occurring during the study period. Even though the peak and total discharges for the January 22-27, 1979 storm are very much less than the February 25 -March 1, 1979 storm, suspended sediment reaches higher concentrations during the January storm. The most readily available sediments were probably transported in the January storm, and the February storm occurred less than 1 month later before much more material was available for transport. The snow cover during February also dampened any effect the precipitation had impacting the land surface and loosening soil particles. This would also reduce the sediment erosion rate.

The September 6-8, 1979 discharge peak, which occurred as a result of Tropical Storm David, is only 51 percent that of the February 25 - March 1 peak, but it has a peak suspended-sediment concentration of 1,140 mg/L, nearly twice as high as that in February. The intensity of the rainfall from the tropical storm and the relatively dry period preceding it greatly increased the unit discharge yields of suspended sediment during this high-flow event (table 20).

The hydrograph and suspended-sediment plots resulting from Tropical Storm David both show a double peak (fig. 17). Other storm hydrographs for this station do not show this double-peak pattern. Its cause during the September 5-8, 1979 high flow may be related to the timing of tributary inflow or may have resulted from two separate periods of intense precipitation during this storm.

James River

Because of problems in establishing and maintaining a daily sediment station for the James River at Cartersville, suspended-sediment data were incomplete and no storm comparisons or annual totals were available.

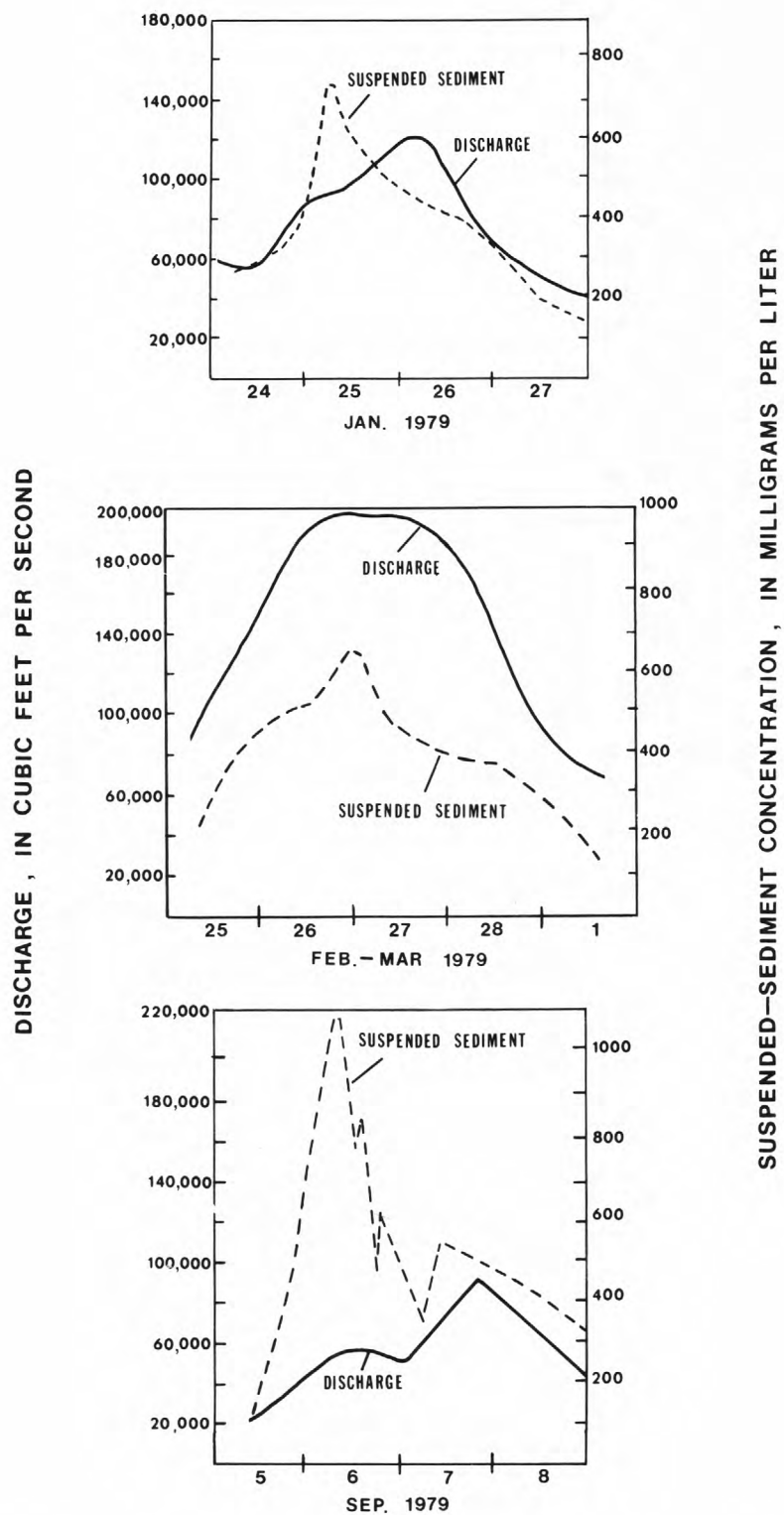


Figure 17.--Suspended-sediment transport for three high flows at the Potomac River at Chain Bridge at Washington, D.C.

Table 20.--Unit discharge sediment yields for the Potomac River at Chain Bridge at Washington, D.C.,
for three high-flow periods

High-flow period	Mean daily discharge for period (ft ³ /s)	Peak sediment concentration in mg/L	Total volume of streamflow for period (ft ³)	Total suspended- sediment load for period (tons)	Unit discharge yield of suspended sediment for high-flow period ($\frac{\text{Total suspended sediment load}}{\text{Total volume of streamflow}}$)	
					(tons/ft ³)	(mg/L)
Jan. 22-27, 1979	72,700	705	3.77×10^{10}	5.05×10^5	1.34×10^{-5}	430
Feb. 25 - Mar. 1, 1979	144,000	675	6.23×10^{10}	8.30×10^5	1.34×10^{-5}	430
Sept. 6-8, 1979	70,900	1,140	1.84×10^{10}	3.25×10^5	1.77×10^{-5}	568

SUMMARY AND CONCLUSIONS

1. Loads of water-quality constituents estimated in this report were using linear regression relations and daily values of either streamflow, suspended-sediment concentration, or specific conductance. Comparison of these estimates to loads calculated by a more data-intensive and accurate technique (Porterfield, 1972) for selected constituents at the Potomac River Fall Line station showed good agreement (within 10.5 percent), when considering the 2-year data set as a whole. The regression technique is more accurate for years when precipitation and streamflow are above average.
2. The only two pesticide residues consistently detected at the Susquehanna and Potomac River Fall Line stations were 2,4-D and atrazine. The concentrations of both generally peak at these stations in the late spring and summer, although 2,4-D concentrations at the Susquehanna River site remained high during the fall and winter of 1980-81. In this case, 2,4-D may have entered the stream in ground-water inflow.
3. Generally, the highest concentrations of chlorophyll *a* occurred at the three Fall Line stations during spring high flows. These peak concentrations may have been caused by high velocity runoff carrying fragments of underdeveloped and emerging plankton or spring accumulation of periphytic chlorophyll.
4. Samples collected at five sites in tributaries to the northern part of Chesapeake Bay were analyzed for total residual chlorine and selected low-molecular-weight hydrocarbons. The results of all the chlorine analyses were less than or equal to the detection limit of 0.01 mg/L. There were three instances when those organic compounds listed in table 8 were detected. Trichloroethylene (TCE) was detected at low levels at Back and Patuxent River sites on July 1, 1981; a 0.002 mg/L concentration of benzene was found in the Potomac River at Alexandria, Va., on June 26, 1981.
5. For the Susquehanna and Potomac River Fall Line stations, concentrations of total recoverable aluminum, iron, and manganese correlated closely with suspended sediment. However, the character of this correlation differs for the two sites and from one storm to the next at each site. For the James River at Cartersville, there was lesser correlation between suspended sediment and these metals.
6. When measured at their Fall Line stations, the Susquehanna and Potomac Rivers had significantly greater discharge-weighted-average sulfate concentrations than the James River. Significant areas of active coal mining in the Susquehanna and Potomac basins may account for this.
7. Concentrations and loads of all nutrient species were highest during spring and storm-related high flows for the three Fall Line stations.
8. At each of the Fall Line stations, there was a close correlation between mean annual water discharge and the corresponding annual nutrient loads. This relationship may provide a basis for estimating specific nutrient loads in years for which load estimates are not now available.

9. Of the three Fall Line stations, the Potomac River at Chain Bridge had the highest discharge-weighted average concentration of total nitrogen, 2.20 mg/L, and the James River station had the lowest, 0.96 mg/L. Most of the total nitrogen load at the Susquehanna (71 percent) and Potomac River (55 percent) sites was in the form of nitrite and nitrate. However, 69 percent of the total nitrogen at the James River station was ammonia + organic nitrogen, and only 31 percent is nitrite + nitrate nitrogen.
10. Of the three rivers sampled, the Susquehanna River had the lowest discharge-weighted average concentrations of total phosphorous and orthophosphate, 0.20 and 0.08 mg/L, respectively.
11. Based on comparisons with previous studies, ammonia concentrations and loads decreased at all three Fall Line stations from 1969 to 1981. Orthophosphate concentrations and loads in the Susquehanna and Potomac Rivers also declined.
12. If nitrogen is the limiting nutrient for algal growth in the upper Chesapeake Bay, as suggested by Clark, Donnelly, and Villa (1973), the slight increases in total nitrogen, principally as nitrite + nitrate, at the Susquehanna River at Conowingo may signal the need for further monitoring.
13. Generally, nutrient concentrations were proportional to streamflow. The data in this report do not support suggestions from some previous investigations that certain nutrient species are inversely proportional to streamflow. The majority of the nutrient loads transported by the three rivers occurred during spring storm events. This is particularly significant in light of the conclusions of Clark, Donnelly, and Villa (1973), who suggested that total and inorganic nitrogen loads in the upper Chesapeake Bay are generally constant regardless of Susquehanna River flow.
14. Comparison of data for the Susquehanna River at Harrisburg and Conowingo indicated that loads of dissolved constituents such as orthophosphate and nitrite + nitrate, increased in the downstream direction. Both orthophosphate and nitrite + nitrate comprised a larger fraction of the total phosphorous and nitrogen loads at Conowingo than at Harrisburg.
15. The data in this report support the suggestion by Gross and others (1978) that at discharges below about 400,000 ft³/s at the Susquehanna River at Conowingo, sediment accumulates behind the three hydroelectric dams between Harrisburg and the mouth. Above that peak discharge, sediment is scoured and resuspended for transport to the Bay. The recurrence interval for this flow is approximately 4 years.
16. Sediment transported by the Potomac River at Chain Bridge is heavily influenced by seasonal variations, type of precipitation, rainfall intensity, and antecedent conditions. Peak concentrations of suspended sediment for a late-winter flow peak were half that of a late-summer high flow, although the winter storm peak discharge was twice that of the summer storm.

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