Nitrogen Dynamics in the Tidal Freshwater Potomac River, Maryland and Virginia, Water Years 1979-81

A Water-Quality Study of the Tidal Potomac River and Estuary

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By DAVID J. SHULTZ

UNITED STATES GEOLOGICAL SURVEY WATER-SUPPLY PAPER 2234-J

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FOREWORD

Tidal rivers and estuaries are very important features of the Coastal Zone because of their immense biological productivity and their proximity to centers of commerce and population. Most of the shellfish and much of the local finfish consumed by man are harvested from estuaries and tidal rivers. Many of the world's largest shipping ports are located within estuaries. Many estuaries originate as river valleys drowned by rising sea level and are geologically ephemeral features, destined eventually to fill with sediments. Nutrients, heavy metals, and organic chemicals are often associated with the sediments trapped in estuaries. Part of the trapped nutrients may be recycled to the water column, exacerbating nutrient-enrichment problems caused by local sewage treatment plants, and promoting undesirable algae growth. The metals and organics may be concentrated in the food chain, further upsetting the ecology and threatening the shell and finfish harvests. Our knowledge of the processes governing these phenomena is limited and the measurements needed to improve our understanding are scarce.

In response to an increasing awareness of the importance and delicate ecological balance of tidal rivers and estuaries, the U.S. Geological Survey began a 5-year interdisciplinary study of the tidal Potomac River and Estuary in October of 1977. The study encompassed elements of both the Water Resources Division's ongoing Research and River Quality Assessment Programs. The Division has been conducting research on various elements of the hydrologic cycle since 1894 and began intense investigation of estuarine processes in San Francisco Bay in 1968. The River Quality Assessment program began in 1973 at the suggestion of the Advisory Committee on Water Data for Public Use which saw a special need to develop suitable information for river-basin planning and water-quality management. The Potomac assessment was the first to focus on a tidal river and estuary. In addition to conducting research into the processes governing water-quality conditions in tidal rivers and estuaries, the ultimate goals of the Potomac Estuary Study were to aid water-quality management decision-making for the Potomac, and to provide other groups with a rational and well-documented general approach for the study of tidal rivers and estuaries.

This interdisciplinary effort emphasized studies of the transport of the major nutrient species and of suspended sediment. The movement of these substances through five major reaches or control volumes of the tidal Potomac River and Estuary was determined during 1980 and 1981. This effort provided a framework on which to assemble a variety of investigations:

(1) The generation and deposition of sediments, nutrients, and trace metals from the Holocene to the present was determined by sampling surficial bottom sediments and analyzing their characteristics and distributions.

(2) Bottom-sediment geochemistry was studied and the effects of benthic exchange processes on water-column nutrient concentrations ascertained.

(3) Current-velocity and water-surface-elevation data were collected to calibrate and verify a series of one- and two-dimensional hydrodynamic flow and transport models.

(4) Measurements from typical urban and rural watersheds were extrapolated to provide estimates of the nonpoint sources of sediments, nutrients, and biochemical oxygen demand during 1980 and 1981.

(5) Intensive summertime studies were conducted to determine the effects of local sewage-treatment-plant effluents on dissolved-oxygen levels in the tidal Potomac River.

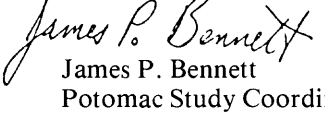
(6) Species, numbers, and net productivity of phytoplankton were determined to evaluate their effect on nutrients and dissolved oxygen.

(7) Wetland studies were conducted to determine the present-day distribution and abundance of submersed aquatic vegetation, and to ascertain the important water-quality and sediment parameters influencing this distribution.

(8) Repetitive samples were collected to document the distribution and abundance of the macrobenthic infaunal species of the tidal river and estuary and to determine the effects of changes in environmental conditions on this distribution and abundance.

The reports in this Water-Supply Paper series document the technical aspects of the above investigations. The series also contains an overall introduction to the study, an integrated technical summary of the results, and an executive summary which links the results with aspects of concern to water-quality managers.

Philip Cohen
Chief Hydrologist



James P. Bennett
Potomac Study Coordinator

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Nitrogen Dynamics in the Tidal Freshwater Potomac River, Maryland and Virginia, Water Years 1979–81

By David J. Shultz

Abstract

On an annual basis, river-supplied nitrate is the predominant form of nitrogen supplied to the tidal Potomac River from external sources. Much of the nitrate is associated with high flows that have rapid transit times through the tidal river. The Blue Plains Sewage-Treatment Plant (STP) at Washington, D.C., is the greatest source of all nitrogen species during low-flow periods. Prior to the fall of 1980, ammonia concentrations in depth-integrated, composited water samples were greatest (more than 1.00 mg/L (milligram per liter) as nitrogen) during summer periods near Alexandria, Va., because of loading from the nearby Blue Plains STP and reduced river discharge. After the fall of 1980, initiation of advanced wastewater treatment at the Blue Plains STP reduced ammonia loading to the river by 90 percent and increased nitrate loading by a similar percentage. As a result, concentrations of ammonia during the 1981 low-flow period were less than 0.20 mg/L as nitrogen at Alexandria, while nitrate concentrations were greater than 1.50 mg/L as nitrogen.

Concentrations of ammonia and nitrate at Alexandria were shown to be reasonably predictable by use of a simple dilution model that considers only loading from Chain Bridge and the Blue Plains STP. This apparently is the result of the short residence time through the Chain Bridge-to-Alexandria section of the tidal Potomac River, which precludes significant biological alterations. In marked contrast, the residence times of water parcels in the tidal Potomac River from Alexandria to Quantico, Va., are much greater because of the geometry of the reach. Biological nitrogen-cycle transformation processes affect nitrogen-species concentrations to a greater extent in this reach, especially during summer low-flow periods.

Mass-balance calculations that separate changes in transport mass from biological transformations indicatethat the tidal Potomac River was a net sink for all the nitrogen constituents during the 1980 and 1981 summer low-flow periods. However, during the 1980–81 winter period, some ammonia and nitrate was transported out of the tidal Potomac River into the transition zone.

Despite the reduced availability of ammonia, nitrogen-15 uptake studies showed that phytoplankton preferred ammonia to nitrate unless ammonia concentrations were less than 0.10 mg/L as nitrogen. Nitrification-rate studies during 1981 using a carbon-14 uptake technique indicate that rates did not vary with sample location, except for one sample from the head of the tidal river, where the rates were much higher. The numbers of *Nitrobacter* bacteria were highest in samples from near the Blue Plains STP and were greater than the numbers of *Nitrosomonas* bacteria. The predominance of *Nitrobacter* bacteria seemed to be associated with advanced wastewater treatment at the Blue Plains STP. Before advanced wastewater treatment, *Nitrosomonas* were numerically predominant and had the largest numbers near the Blue Plains STP. These results could be due to (1) loading of nitrifying bacteria in the Blue Plains sewage effluent that had been inhibited from further growth by an inhibitory substance or (2) the method used to measure nitrification rates, which measured only the ammonia oxidation stage; it is not possible to reject either mechanism on the basis of the data available.

Process models were used in conjunction with mass-balance determinations and individual process studies to estimate rates of processes that were not directly measured. It is estimated that denitrification removed 10 times as much nitrate from the water column during the summer of 1981 as during the summer of 1980. Sedimentation of particulate nitrogen is estimated to be the largest sink for nitrogen from the water column and was approximately equal to the external annual loading of all nitrogen constituents on a daily basis.

In summer, when river flows usually are low, the tidal Potomac River appears to be a partially closed system rather than one dominated by transport. Nitrogen constituents, primarily from point sources, are taken up by

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phytoplankton, converted to organic matter, and sedimented from the water column. Some of this nitrogen eventually becomes available again by means of benthic exchange. Removal, by transport, out of the tidal river is significant only during winter.

The differences for 1980 and 1981 resulting from advanced wastewater treatment are interesting. The shift to nitrate as the predominant form of nitrogen apparently resulted not only in a reduction in phytoplankton biomass but also in an increase in losses by denitrification. This is significant because denitrification is a route by which nitrogen is permanently removed from the system. Thus, the advanced-wastewater-treatment program may have short- and long-term benefits.

INTRODUCTION

Nitrogen, along with phosphorus and carbon, is one of the essential elements required by humans for growth. Rivers, lakes, and estuaries commonly contain elevated quantities of nitrogen as a result of human activities. The effect of these additional sources of nutrients, termed "cultural eutrophication," has been associated with degradation of water quality. Various programs have sought to stabilize or reverse this trend in the Nation's surface-water resources. In the Potomac River, point-source loadings of carbon, phosphorus, and nitrogen have been reduced in the last 10 years, despite population increases, by a major investment in local sewage-treatment facilities.

Purpose and Scope

This report quantifies the major sources of and sinks for nitrogen in the Potomac River and describes key nitrogen transformation processes. It focuses on the tidal freshwater part of the Potomac, because previous studies have shown that the perturbation caused by large inflows of sewage effluent is largely localized in this segment of the river. Data for this study were collected from August 1, 1977, through September 30, 1981.

The report includes synoptic and periodic data collected as part of the Potomac River Quality Assessment program (Smith and Herndon, 1979, 1980a, 1980b, 1980c; Blanchard and Hahl, 1981; Blanchard and Coupe, 1982; Blanchard and others, 1982). Information on the loading of nitrogen species into the tidal river from point, nonpoint, and upstream sources was obtained from Coupe and Webb (1984), Hickman (1987), and Blanchard and Hahl (1987). The studies of nitrification rates and ammonia and nitrate uptake were conducted during the summer of 1981.

Study Area

The Potomac River and Estuary is the largest subestuary to Chesapeake Bay (fig. 1). It is an example of an environmentally stressed system wherein large human inputs of nutrients enter the freshwater part of the river and become diluted by water from Chesapeake Bay. The Potomac River drains 38,000 km^2 (square kilometers) of land in West Virginia, Virginia, and Maryland. This area includes a population of more than 3.3 million people, approximately 2.8 million of whom reside in the Washington, D.C., metropolitan area. The Potomac River is the main source of drinking water for Washington, and also is the primary receptacle for the city's waste. The river receives large inputs (17.5 m^3/s (cubic meters per second)) of sewage effluent between Washington and Mt. Vernon, Va., most of which is added by the Blue Plains Sewage-Treatment Plant (STP) (fig. 2).

The river, 640 km (kilometers) long, is tidal throughout the lower 183 km of its course. The tidal part can be divided into three zones (fig. 1): (1) the tidal river above Quantico, Va., where the water is fresh (0 to 7 g/L (grams per liter) salinity), except in extremely dry years, and the net flow at all depths is seaward; (2) the transition zone of the estuary (oligohaline to mesohaline), where salinity is low (1 to 11 g/L) and extensive saltwater-freshwater mixing occurs; and (3) the lower mesohaline estuary (7 to 24 g/L salinity) (herein referred to as the "estuary"), which exhibits an internal circulation with reverse bottom flow, strong tidal currents, moderate vertical stratification, and considerable longitudinal variation in salinity. The tidal Potomac River and Estuary are relatively shallow, having an overall average depth of 6 m (meters). The greatest depth, about 36.5 m, is near Mathias Point, Va. (fig. 1). A typical cross section in the tidal river and estuary would show a deep channel with wide shallow flats on one or both sides.

On the basis of flow, the Potomac ranks 26th among all U.S. rivers and 8th among Atlantic-seaboard rivers. For the 51 years of record prior to 1981, the annual average freshwater flow at Little Falls Dam just upstream from Chain Bridge, Va. (fig. 1), was 313 m^3/s. The 60-day mean low flow before diversion (68.8 m^3/s for 1930–80) normally occurs during August and September. The maximum and minimum flows of record are 13,700 m^3/s in March 1936 and 3.43 m^3/s in September 1966, respectively (U.S. Geological Survey, 1981a, p. 329).

METHODS

Chemical Analyses and Field Measurements

The collection, shipment, and analysis of water samples from the tidal river are described in detail by Blanchard and Hahl (1981), Blanchard and Coupe (1982), and Blanchard and others (1982).

In situ water-column characteristics were determined at the same time water samples were collected. A Hydrolab digital 4041 water-quality system was used to measure

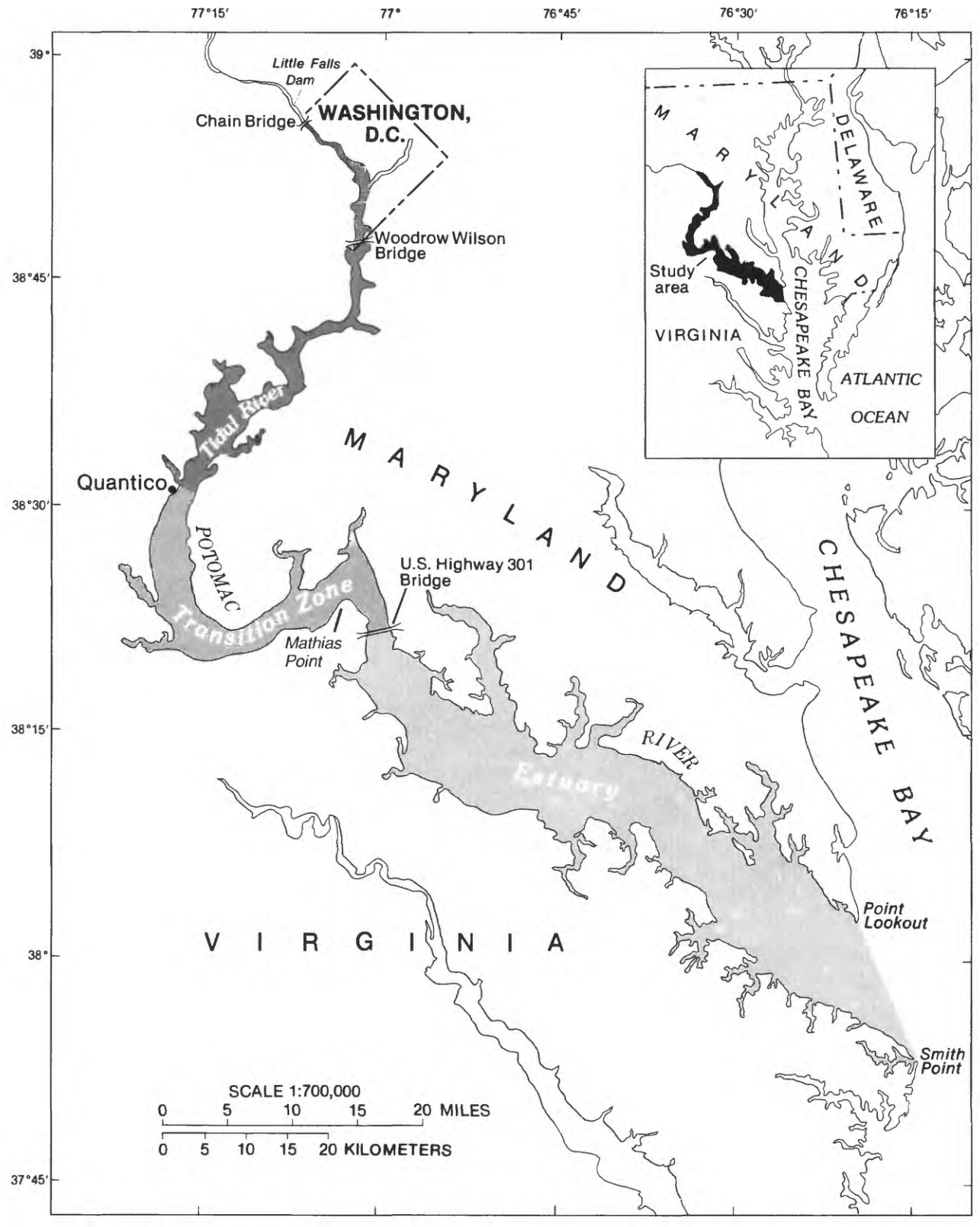

Figure 1. Tidal Potomac River and Estuary.

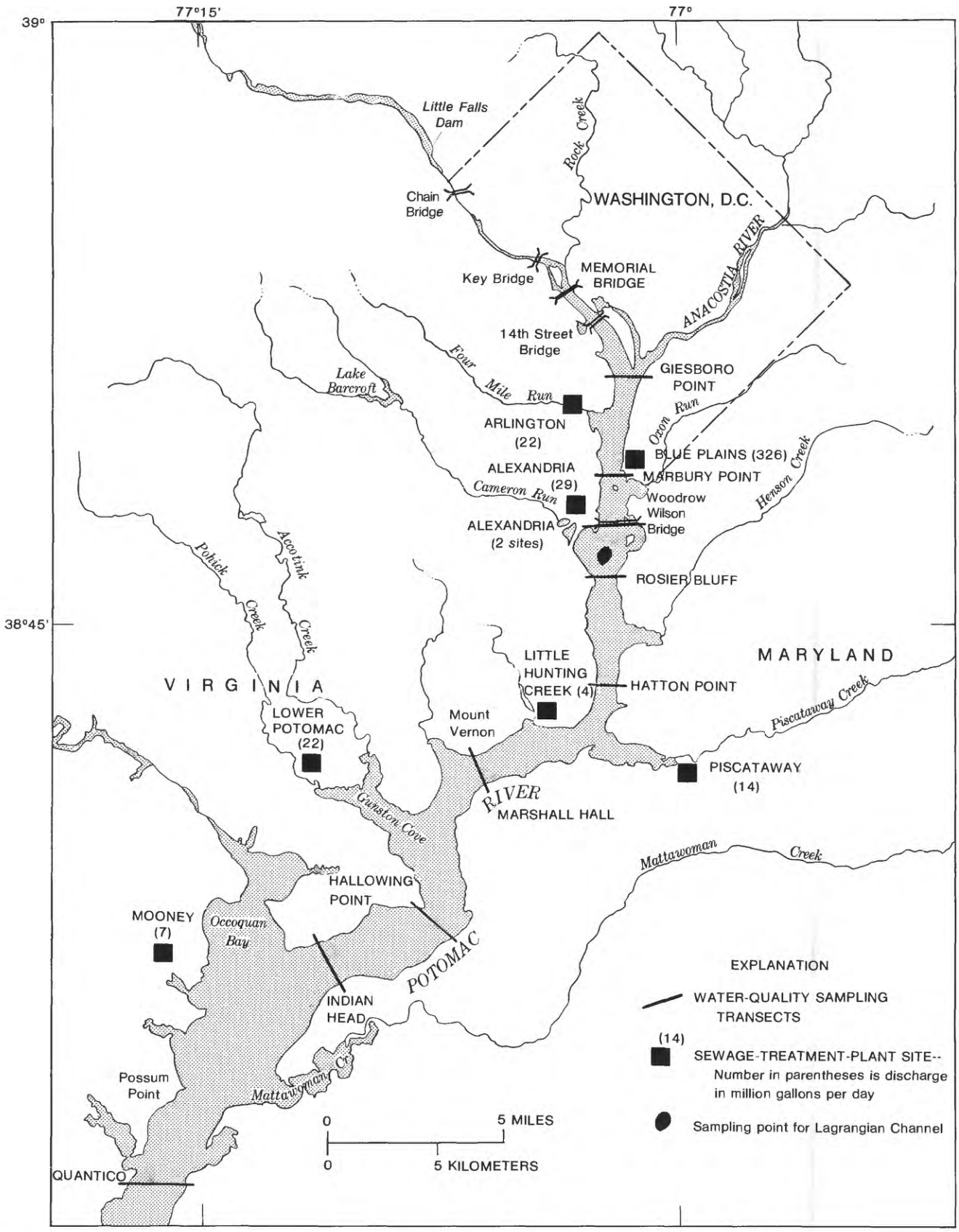

Figure 2. Tidal Potomac River study area, locations of water-quality sampling stations, and locations of sewage-treatment plants discharging more than 4 million gallons per day directly to tidal water in 1981.

specific conductance, pH, temperature, and dissolved oxygen. Details about the calibration of the Hydrolab are also reported in Blanchard and others (1982).

Measurement of the Most Probable Number of Nitrifying Bacteria

The most probable number of *Nitrosomonas* and *Nitrobacter* sp. was determined according to procedures in Greeson and others (1977). The sample tubes and blanks were incubated at room temperature (28±1 °C (degrees Celsius)) for at least 30 days. The most probable number of nitrifying bacteria was calculated by using equations from Hoskins (1933).

Sediment samples for determining the most probable number of nitrifying bacteria came from three cores. The samples were collected by using a Benthos gravity corer in which the plastic butyrate core liners (67-mm (millimeters) inner diameter) extended well below the metal parts of the coring rig. The corer was lowered to just above the sediment surface and allowed to penetrate the sediment by free-fall. The plastic core liner was removed from the core barrel while the coring assembly was oriented vertically. Supernatant water was removed by a siphon to within approximately 76 mm of the top of the core. The cores were transported to a shore-based laboratory for sampling, usually within 3 hours after collection.

The cores were extruded from the liners in 40-mm intervals. Samples were collected from each interval with a sterile plastic syringe barrel cut off at the end. Three cores were normally collected for a particular cross section on each sampling date, in order to collect a representative sample: one core in the channel and one core in the shallows on either side of the channel. The samples from the same depth interval for all three cores were composited in a sterile vial. A 1-mL (milliliter) aliquot of the composite sediment sample was added to 9 mL of sterile dilution water and then homogenized using a vortex mixer. Serial dilutions from 10^{-5} to 10^{-9} mL/mL were made.

Measurement of Nitrification Rates

Nitrification rates were determined using a ^{14}C tracer technique. The basis of the method is that $H^{14}CO_3$ uptake by *Nitrosomonas*, in the dark, can be separated from assimilation of bicarbonate by other micro-organisms using a specific inhibitor of nitrification. The difference between the inhibited and uninhibited aliquot was taken as the bicarbonate uptake resulting from nitrification. According to Billen (1976), the ratio of moles of ammonia oxidized by nitrification to moles of carbon fixed is 8.3.

The experimental protocol followed was that of Somville (1978). The nitrification inhibitor TCMP (2-chloro-6 (trichloromethyl) pyridine), commerically known as N-Serve, was added to one of two replicates of each sample to make a final concentration of 5 mg/L (milligrams per liter).. Samples were incubated in the dark under flowing water pumped from the river to simulate ambient conditions. At the termination of incubation, 0.2 mL of 10-percent formalin was added to each 60-mL sample bottle to stop ^{14}C incorporation. The samples were then processed according to the protocol of Janzer and others (1973). The ^{14}C activity was determined by liquid scintillation counting at the U.S. Geological Survey laboratory in Arvada, Colo. Carbonate alkalinity was determined by titrating to a pH of 4.5 using 0.01*N* HCl.

Measurement of Ammonia and Nitrate Uptake

The methods used to measure ammonia and nitrate uptake were similar to those of Dugdale and Goering (1967). In these experiments, 100 µL (microliters) of stock solution of 140 µg/L (micrograms per liter) $^{15}NH_4Cl$ or $Na^{15}NO_3$ were added to 1-L ground-glass-stoppered bottles containing the samples to make a final spike concentration of 14 µg/L of ^{15}N. This represents an increase over ambient concentrations of less than 10 percent. The water samples were incubated at ambient temperatures, with flowing river water, under neutral density screens, to give light-level conditions of 100 percent, 55 percent, 23 percent, and 0 percent of incident solar radiation. The incubations were usually begun by 10 a.m. and ended 3 to 4 hours later.

After incubation, Lugol's acetic acid solution was added to kill the phytoplankton and halt nitrogen incorporation. The phytoplankton were filtered from solution onto glass-fiber filters and stored in a vacuum desiccator in plastic Petri dishes. The subsequent sample preparation and mass-spectrometric analyses were performed by a commercial laboratory. The organic nitrogen on the filters was combusted using a modified Dumas procedure (Barsdate and Dugdale, 1965) in closed tubes. The condensable gases in the combusted samples were removed by means of a vacuum-line procedure, and any oxidized nitrogen was reduced to nitrogen gas using a high-temperature CuO heated tube. The isotope ratio of the sample was determined on an isotope-ratio mass spectrometer, the isotope ratio was converted to atom percent ^{15}N, and the enrichment over the normal atom percent ^{15}N (0.37) of the organic material was calculated. The quantity of ammonium or nitrate taken up by phytoplankton was computed using the following equation from Stanley and Hobbie (1977):

$$\rho = \frac{PON \cdot A_f}{\Delta t \cdot A_i}, \qquad (1)$$

where

ρ=uptake rate of ammonia or nitrate as N, in milligrams per liter per hour;

PON=concentration of particulate organic matter as N exposed to the isotope, in milligrams per liter;

A_f=atom percent excess ^{15}N in organic matter at the end of incubation;
Δt=incubation time, in hours; and
A_i=atom percent excess ^{15}N in organic matter at the start of incubation.

NITROGEN DYNAMICS

Loads of Dissolved Nitrogen Species

One of the major objectives of the Potomac River Quality Assessment study was to determine the loading of the nutrient species into the tidal river, the transition zone, and the estuary. This section summarizes results from other investigators in the study concerning the loading of nitrogen constituents into the tidal river.

Point-source loads were calculated from National Pollution Discharge Elimination System reports on the eight sewage-treatment plants in the tidal river area (Coupe and Webb, 1984). Nonpoint-source loads included loads from tributary streamflows, Washington, D.C., combined sewer overflow, and rainfall on the tidal water surface (Hickman, 1987). Data on only total nitrate plus nitrite nitrogen loads were available, but, typically, almost all of this is in the dissolved form in river water. Loads from upriver coming past Chain Bridge, Va., into the tidal river were calculated from data collected by the transport study (Blanchard and Hahl, 1987). No dissolved-ammonia analyses were done for the 1979 water year. For a more detailed description of the transport study and the methods used to compute loads, see Blanchard and Hahl (1987).

Upriver Loading

Nitrate and nitrite account for 75 percent of the total nitrogen concentration and 63 percent of the total nitrogen load from upriver (table 1) that enter the tidal freshwater portion of the Potomac River. Much of the nitrate probably originates from agricultural applications. Of the three major rivers discharging into Chesapeake Bay, the Potomac River at Chain Bridge had the highest discharge-weighted average concentration of nitrate plus nitrite, 1.20 mg/L, the Susquehanna River had 1.14 mg/L, and the James River, 0.30 mg/L, in a 28-month monitoring study conducted by the U.S. Geological Survey from 1979 through 1981 (Lang, 1982). The difference between the three rivers was attributed by Lang to the larger part of the Potomac and Susquehanna River basins involved in agriculture.

Lang (1982) also noted that the average concentration of nitrate plus nitrite in the Potomac River at Chain Bridge decreased slightly from 1966 through 1980. Regressions of nitrate plus nitrite concentration with river flow did not establish statistically significant correlations (Blanchard and Hahl, 1987). However, Blanchard and Hahl pointed out that the annual-average concentrations for the years 1979–81 were quite similar despite substantial differences in high-flow runoff patterns and annual-average discharge. They concluded that variations in the annual load result mostly from changes in discharge rather than changes in the annual-average concentrations of nitrate plus nitrite.

The load of dissolved ammonia from upriver into the tidal river averages about 5 percent of the nitrate plus nitrite loads. Lang (1982) found that the average concentration and loads of ammonium decreased from 1969 through 1980. This trend was also observed in the Susquehanna River at Conowingo, Md., and the James River at Cartersville, Va. There was no significant correlation between dissolved-ammonium concentrations and discharge for water years 1979 through 1981, but the annual-average concentrations were similar (Blanchard and Hahl, 1987). However, annual loads can vary because of differences in discharge.

Dissolved organic nitrogen loads were about 20 and 23 percent of 1980 and 1981 total annual dissolved-nitrogen loads, respectively, and approximately 30 and 36 percent during the summer (July–August) of 1980 and 1981, respectively. Blanchard and Hahl (1987) found that the concentrations of nitrogen constituents showed little consistent seasonal change; however, there was a seasonal trend in loads resulting from seasonal changes in runoff.

Nonpoint-Source Loading

Ammonia loads from nonpoint sources were lower than loads from the other sources. Nonpoint-source loads of nitrate plus nitrite, dissolved organic nitrogen, and particulate organic nitrogen were on the same order of magnitude as estimated point-source loads but were still much less than upriver loads (table 1).

The annual pattern for nonpoint-source loading during the study period follows the same pattern as for upriver loading, whereby loads increase during high-flow periods. Hickman (1987) did not find any significant correlation between concentration and discharge for any of the nitrogen constituents except for nitrate plus nitrite in the Rock Creek watershed (see fig. 2), where the concentration decreased with increasing discharge.

Point-Source Loading

Approximately 70 percent of the total point-source loading of nitrogen species to the tidal Potomac River was from the Blue Plains STP; the other 30 percent was contributed by smaller treatment plants (fig. 2). During low-flow conditions, the point-source loads of nitrogen made up almost all of the total nitrogen loading to the tidal river. During high-flow conditions, the point-source loads of nitrogen made up a smaller proportion of total nitrogen loading. The decrease in the proportion of point-source loads to total loads was attributable to increased nonpoint-source and upriver loading (not to decreased point-source

Table 1. Annual daily loads of nitrogen species to the tidal Potomac River from point, nonpoint, and upriver sources during water years 1979–81

[kg/d, kilograms per day; %, percentage of total; —, not determined. Totals are rounded to three significant figures]

Source	Ammonia as N						Nitrate + nitrite as N						Dissolved organic nitrogen as N						Particulate ammonia as N						Particulate organic nitrogen as N					
	1979		1980		1981		1979		1980		1981		1979		1980		1981		1979		1980		1981		1979		1980		1981	
	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%	kg/d	%
Point[1]	19,900	--	21,800	82	7,560	84	1,320	3	2,980	6	14,000	45	[4]1,960	--	[4]1,660	11	[4]1,930	24	--	--	--	--	--	--	[5]1,150	6	[5]977	8	[5]1,140	19
Nonpoint[2]	1,315	--	718	3	356	4	4,450	9	3,030	6	1,130	4	5,190	--	2,730	18	1,280	16	540	--	222	--	52	--	2,640	14	1,360	12	534	9
Upriver[3]	--	--	4,200	16	1,100	12	42,200	88	47,500	88	15,800	51	--	--	11,000	71	4,720	60	--	--	--	--	--	--	[6]15,200	80	[6]9,180	80	[6]4,240	72
Total	--	--	26,700	100	9,020	100	48,000	100	53,500	100	30,900	100	--	--	15,400	100	7,930	100	--	--	--	--	--	--	19,000	100	11,500	100	5,910	100

(1) Data from Coupe and Webb (1984).

(2) Data from Hickman (1987).

(3) Data from Blanchard and Hahl (1987).

(4) Point-source dissolved organic nitrogen estimated by subtracting dissolved ammonia load from total Kjeldahl nitrogen load and multiplying result by 0.63 (the ratio DON/(DON + PON)) for a limited number of samples of Blue Plains Sewage-Treatment Plant effluent (Blanchard and others, 1982).

(5) Point-source particulate organic nitrogen loads were not directly determined but were estimated by subtracting dissolved ammonia loads from total Kjeldahl loads and multiplying by 0.37 (the ratio PON/(DON + PON)) for a limited number of samples of Blue Plains Sewage-Treatment Plant effluent (Blanchard and others, 1982).

(6) River particulate organic nitrogen loads were not directly determined but were estimated by subtracting dissolved Kjeldahl nitrogen loads from total Kjeldahl nitrogen loads.

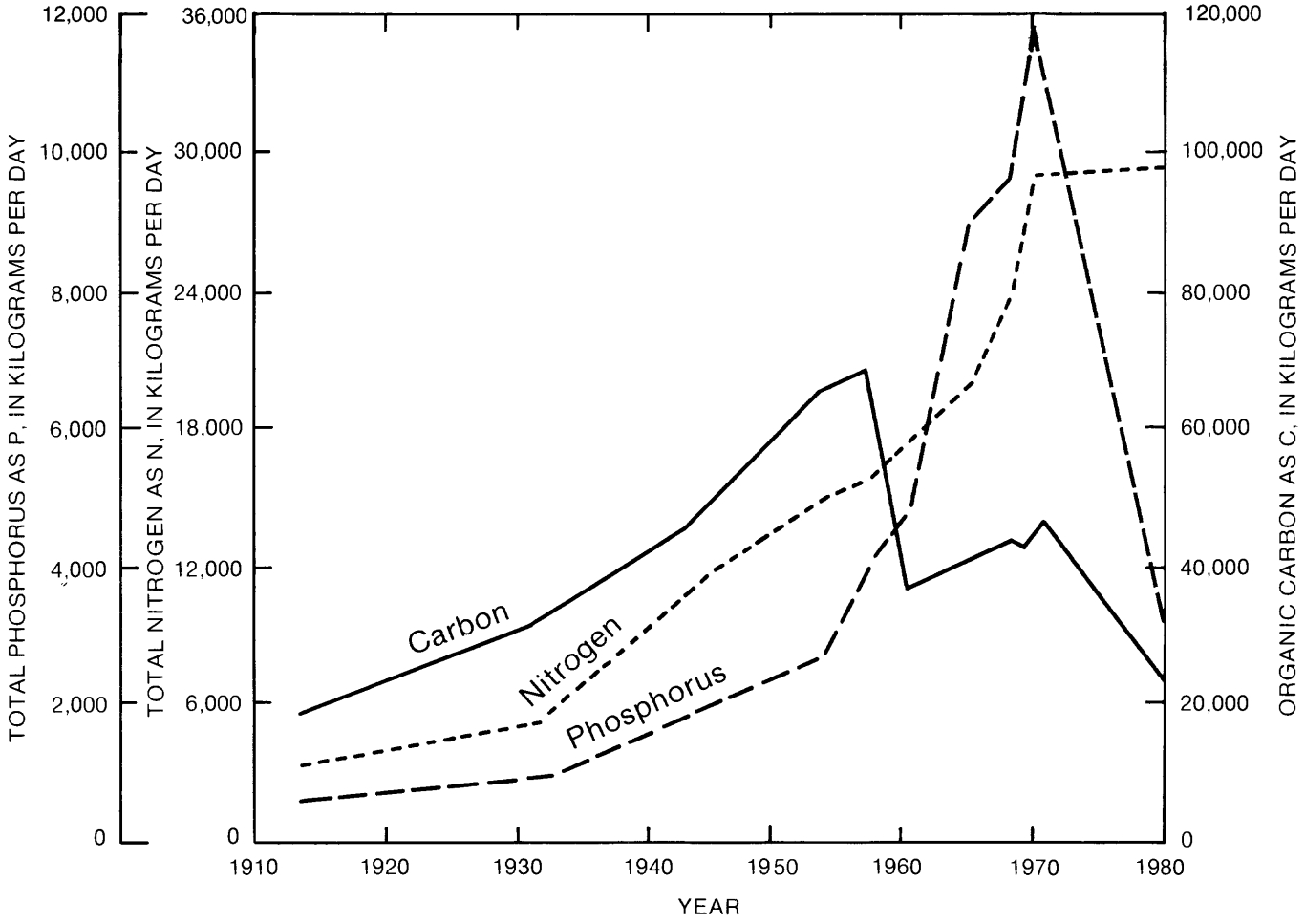

Figure 3. Trends in nutrient enrichment from wastewater in the tidal Potomac River, 1910–80 (modified from Jaworski and others, 1971).

loading). Temporally, the loading from the point sources was relatively constant (Coupe and Webb, 1984).

The point-source loads observed during this study were smaller than those observed during the late 1960's and early 1970's (fig. 3). This is a result of procedures instituted in 1977 to reduce phosphorus loading by the coagulation technique (Champ and others, 1981). Some nitrogen evidently was removed along with the phosphorus.

In September 1980, a program of advanced wastewater treatment was instituted at the Blue Plains STP that had the effect of converting most of the ammonia to nitrate by using nitrification reactors. Ammonia loads were reduced and nitrate loads increased after September 1980. Actually, reductions in ammonia loading were apparent as early as July 1980 (Coupe and Webb, 1984), apparently associated with the initial startup of the reactors. However, the official startup date was in September, and the ammonia loading is consistent with that date (Coupe and Webb, 1984). As a result of advanced wastewater treatment, ammonia was 31 percent of the total nitrogen point-source load in 1981, whereas in 1979 and 1980 it represented 82 and 80 percent, respectively (table 1).

Summarizing, on an annual basis, loading from upriver is the largest source of nitrogen to the tidal river. The nitrogen predominantly is in the form of nitrate, because high river discharge during wet periods of the year brings large loads of nitrogen species into the tidal river, even though correlation of concentration with discharge is not predictable. The fate of these large loads is discussed in other sections of this report. During the summer low-flow months, which were the focal point of the Potomac River Quality Assessment study, the loading from point sources is the most important. During the period of the River Quality Assessment study (1979–81), ammonia was the predominant form of nitrogen loaded from point sources until September 1980, when nitrate became the predominant form.

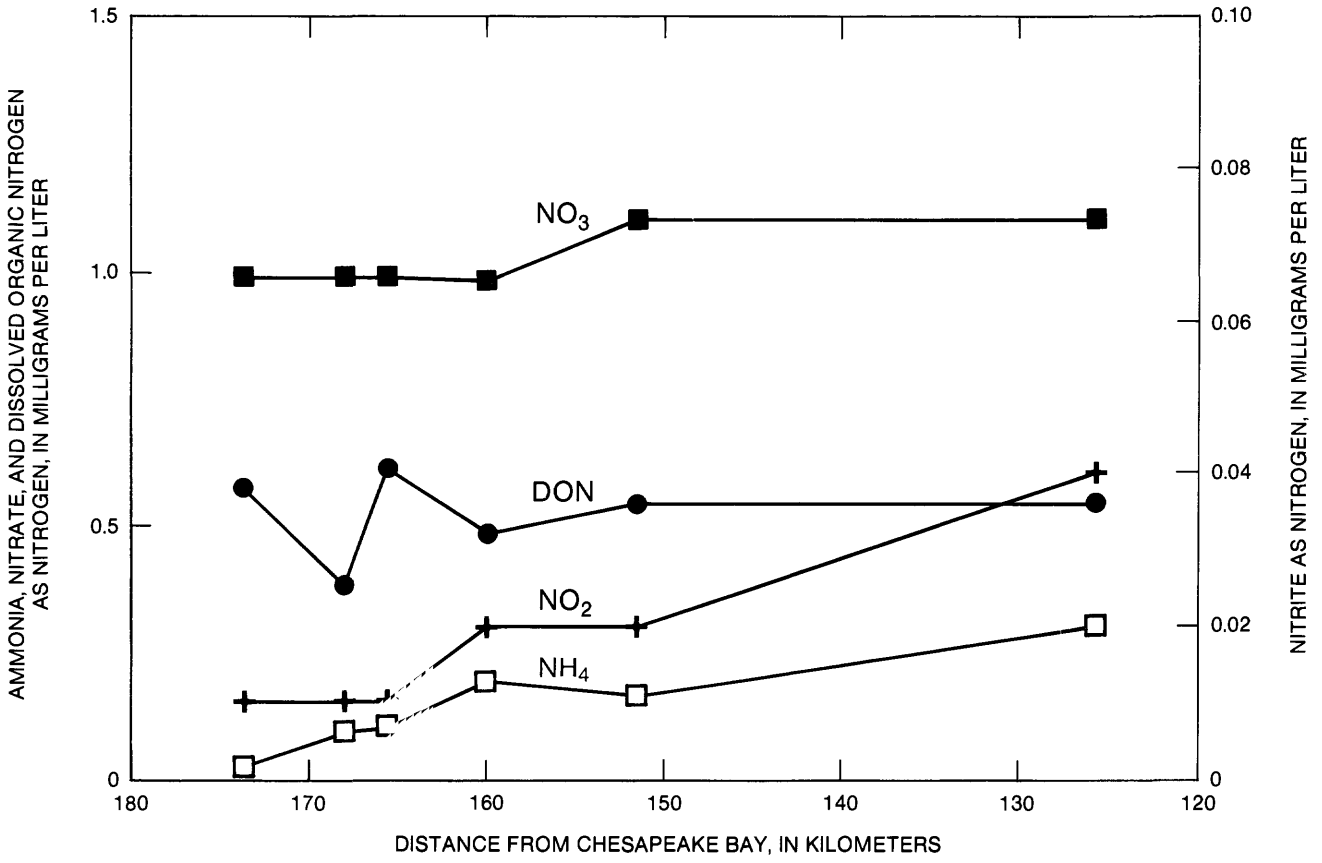

Figure 4. Concentrations of ammonia, nitrite, nitrate, and dissolved organic nitrogen as a function of distance from Chesapeake Bay, October 6, 1979.

Factors Controlling Longitudinal Distribution of Dissolved-Nitrogen Species in the Tidal River

The longitudinal variations in concentrations of nitrogen species in the tidal Potomac River often were quite large. These variations were a function of loading, river discharge, and net effect of source and sink processes. The source and sink processes vary seasonally, primarily because of temperature variations; seasonal variations in loading and river discharge were discussed in the preceding section.

Another significant factor affecting longitudinal variation is the geometry of the tidal river. Downstream from river kilometer 168 (Woodrow Wilson Bridge, Alexandria, Va.), the tidal river widens and the volume increases. The volume of the tidal river from river kilometer 180 to 168 (Memorial Bridge to Woodrow Wilson Bridge) is 62.1×10^6 m^3 (cubic meters), or an average of 5.4×10^6 m^3/km (cubic meters per kilometer) (Cronin, 1971). The volume from river kilometer 168 to 126 (Woodrow Wilson Bridge to Quantico, Va.) is 515×10^6 m^3, or an average of 12.3×10^6 m^3/km (Cronin, 1971). The effect of the river geometry is that traveltimes of water parcels are much shorter through the upper part of the tidal river (river kilometer 187 to 168) than through the lower part (river kilometer 168 to 126).

The effluent discharge point for the Blue Plains STP is at river kilometer 170. Hearn (1985), using dye, found that the flow path of the effluent was confined to an embayment on the eastern side of the river for a distance of 4 km below the outfall. Peak concentrations of many constituents therefore are often downstream from river kilometer 170. Because the loading from the Blue Plains STP is relatively constant (Coupe and Webb, 1984), increased river discharge will have the effect of lowering the concentration of a given nitrogen constituent by dilution. The combined effect of increased river volume downstream and dilution of Blue Plains effluent as a function of river discharge means that, even for conservative constituents, there can be longitudinal changes in concentration not caused by source and sink processes. Longitudinal distributions of nitrogen species on two dates (October 6, 1979, and December 16, 1980) are shown in figures 4 and 5 to illustrate further the effects of discharge. These dates were chosen because the effects of biological processes at these times are smaller than during summer low-flow periods. October 6, 1979, was preceded by a period of unseasonably

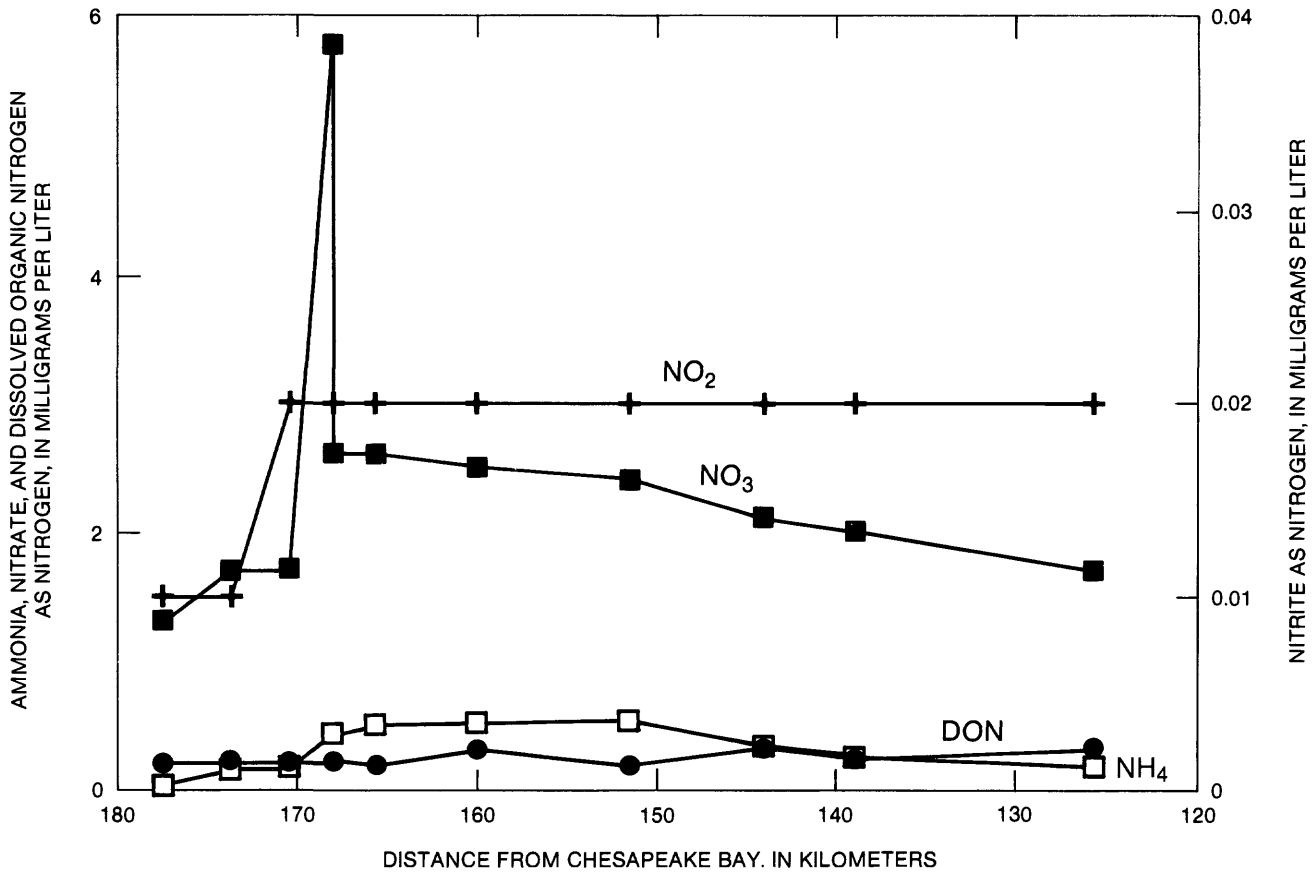

Figure 5. Concentrations of ammonia, nitrite, nitrate, and dissolved organic nitrogen as a function of distance from Chesapeake Bay, December 16, 1980.

wet weather. The mean flow for the 6 days preceding the day the longitudinal samples were collected was 1,250±300 m^3/s. On the basis of a plug-flow model, a parcel entering the tidal river at Memorial Bridge (river kilometer 180) would take 5 days to reach the downstream end of the tidal river (river kilometer 126, Quantico). Although the spatial coverage of these data was sparse, a spike in ammonia and nitrate concentrations caused by the Blue Plains STP effluent was absent. The concentrations of ammonia, nitrite, and nitrate increase downstream from river kilometer 160, probably as a result of lower river discharge. The discharge hydrograph shows that the day the longitudinal samples were collected was on the rising limb of a high-flow event (U.S. Geological Survey, 1981a). This means that the water at the downstream end of the tidal river had flowed past Blue Plains when discharge was lower, and thus that less dilution occurred.

The longitudinal sampling on December 16, 1980 (fig. 5), was preceded by 13 days of relatively low and constant flow (mean flow, 124±12 m^3/s). This is particularly interesting because the river discharge is close to values typical of summer low-flow periods. A parcel entering the tidal river at the start of this period (December 3, 1980) would have reached river kilometer 152 by December 16. There was a clear increase in ammonia, nitrite, and nitrate concentrations at river kilometer 168, just upstream from where the Blue Plains STP effluent enters the main stem of the tidal Potomac (Hearn, 1985). The combined effects of the change at Blue Plains and the discharge hydrograph preceding December 16, 1980, resulted in two features in the longitudinal nitrogen concentrations (fig. 5) that are worth noting. First, the peak nitrate concentration at river kilometer 168 was higher on December 16, 1980, than on October 6, 1979; this is consistent with the lower river discharge preceding December 16 than preceding October 6, 1979, as well as the changes at Blue Plains in September 1980, which resulted in a sevenfold increase in nitrate plus nitrite loads to the tidal river (Coupe and Webb, 1984). Second, the discharge hydrograph preceding December 3 is on the falling limb of a high-flow event (U.S. Geological Survey, 1981b). The water at the downstream end of the tidal river had flowed past Blue Plains when discharge was higher than on the day of the sampling, and, as a result, dilution would have caused ammonia, nitrite, and nitrate concentrations to decrease. Thus, the October 6, 1979, and December 16, 1980,

Table 2. Mean discharge and water temperature of the tidal Potomac River and mean solar radiation at Alexandria, Va., for the 5 weeks preceding August 24, 1977, August 28, 1978, August 6, 1980, and August 6, 1981

[n.d., not determined]

	Mean discharge (cubic meter per second)	Mean temperature (degrees Celsius)	Mean solar radiation (calories per square centimeter per day)
August 24, 1977	48 ± 16	26 ± 1	n.d.
August 28, 1978	290 ± 210	28 ± 2	n.d.
August 6, 1980	120 ± 40	29 ± 2	440 ± 130
August 6, 1981	120 ± 70	27 ± 2	440 ± 150

longitudinal data are qualitatively consistent with a dilution-transport model for periods when biologic activity is not as pronounced as during summer.

Flows normally decrease during summer and fall, when biological processes are most active. The longitudinal profiles of the nitrogen species reflect a dynamic system during these seasons. Figures 6 through 9 show longitudinal data collected on August 24 and 25, 1977, August 28, 1978, August 6, 1980, and August 6, 1981. The first two collections were part of a preliminary survey of the tidal river in which the samples were collected at discrete points, filtered, and analyzed onboard ship (Smith and Herndon, 1979, 1980c). The latter two collections were part of the River Quality Assessment data-collection program in which the samples were collected as composites, filtered, and shipped to the U.S. Geological Survey central laboratory in Atlanta, Ga. (Blanchard and Coupe, 1982; Blanchard and others, 1982). Despite the differences in methodologies, the two groups of data are presented together because sampling occurred at approximately the same time of year and were preceded by periods of relatively constant river discharge. Mean discharge and mean temperature for the entire tidal river, as well as mean solar radiation at Alexandria, Va., arbitrarily calculated for the 5-week periods preceding the four collections, are shown in table 2.

The August 24–25, 1977, longitudinal sampling (fig. 6) was preceded by several months of low and steady flow. At the average discharge calculated for the preceding 5 weeks, a parcel entering the tidal river 35 days before August 24, 1977, would have reached somewhere between Hatton Point and Marshall Hall, Md. (river kilometer 160 to 151), by the sampling date. The longitudinal variations in ammonia, nitrite, and nitrate concentrations are quite large and also obviously are not due to variations in river discharge preceding sampling. The peak concentrations for ammonia, nitrite, and nitrate are at river kilometers 170, 157, and 150, respectively. This is a classic pattern that has been observed previously in the Potomac and is interpreted to mean that nitrification is occurring in the water column (Jaworski and others, 1972; Elkins and others, 1981).

The longitudinal data from August 28, 1978 (fig. 7), was preceded by completely different river flow conditions than was the same period in 1977. The discharge hydrograph (fig. 7A) shows a high-flow event several weeks before the sampling. At the 35-day average discharge preceding sampling (290 m^3/s), a parcel entering the tidal river would have been transported out the downstream end in 23 days. The longitudinal variations in ammonia, nitrite, and nitrate concentration are also quite different than in the previous year (fig. 6). The longitudinal distribution of ammonia conforms to what would be expected from constant loading from the Blue Plains STP, dilution by river flow (figure 7C), and some downstream loss due to a sink process. The higher concentrations of nitrite and nitrate downstream from the ammonia peak were either due to nitrification or associated with upriver loading. The nitrate plus nitrite concentrations at Chain Bridge (fig. 7B) for 33 days preceding sampling (Blanchard, 1983) show that loading from upriver would explain the longitudinal distribution on August 28, 1978 (fig. 7C). If the downstream nitrate peak were due to nitrification, one would expect it to be at least as high as the ammonia peak.

The August 6, 1980, longitudinal sampling was, with the exception of one high-flow event, preceded by low and steady flow (fig. 8A). A parcel entering the tidal river 35 days earlier at the 35-day discharge would have been located somewhere between Hallowing Point, Va., and Indian Head, Md. (river kilometer 144 to 139), on August 6. The ammonia distribution (fig. 8B) was again consistent with loading by the point source at the Blue Plains STP and subsequent loss by one or more ammonia-using process. The data show no clear downstream progression of ammonia, nitrite, and nitrate. The peak concentrations of ammonia and nitrate are approximately the same, but the nitrite peak concentration is lower by a factor of four. The monthly loads of ammonia during June, July, and August were 559, 320, and 251 Mg (megagrams), respectively, and for nitrate plus nitrite, 8, 176, and 220 Mg (Coupe and Webb, 1984). The distribution of ammonia cannot be explained by dilution and transport alone, since ammonia loading was decreasing through June, July, and August. At least one ammonia-using process must account for the longitudinal distribution. If the ammonia-using process was nitrification, the nitrate concentrations should increase with distance downstream, unless a nitrate-using process was removing it from the water column.

The August 6, 1981, longitudinal sampling was preceded by hydrologic conditions very similar to those of the preceding year (fig. 9A). The longitudinal distribution of ammonia concentration was remarkably different from the distribution in August 1977, 1978, and 1980. This was due, in part, to reduced ammonia loading from the Blue Plains STP. The ammonia loads for June, July, and August 1981 were 68, 50, and 40 Mg (Coupe and Webb, 1984), about a tenfold reduction from the preceding year. Nitrate

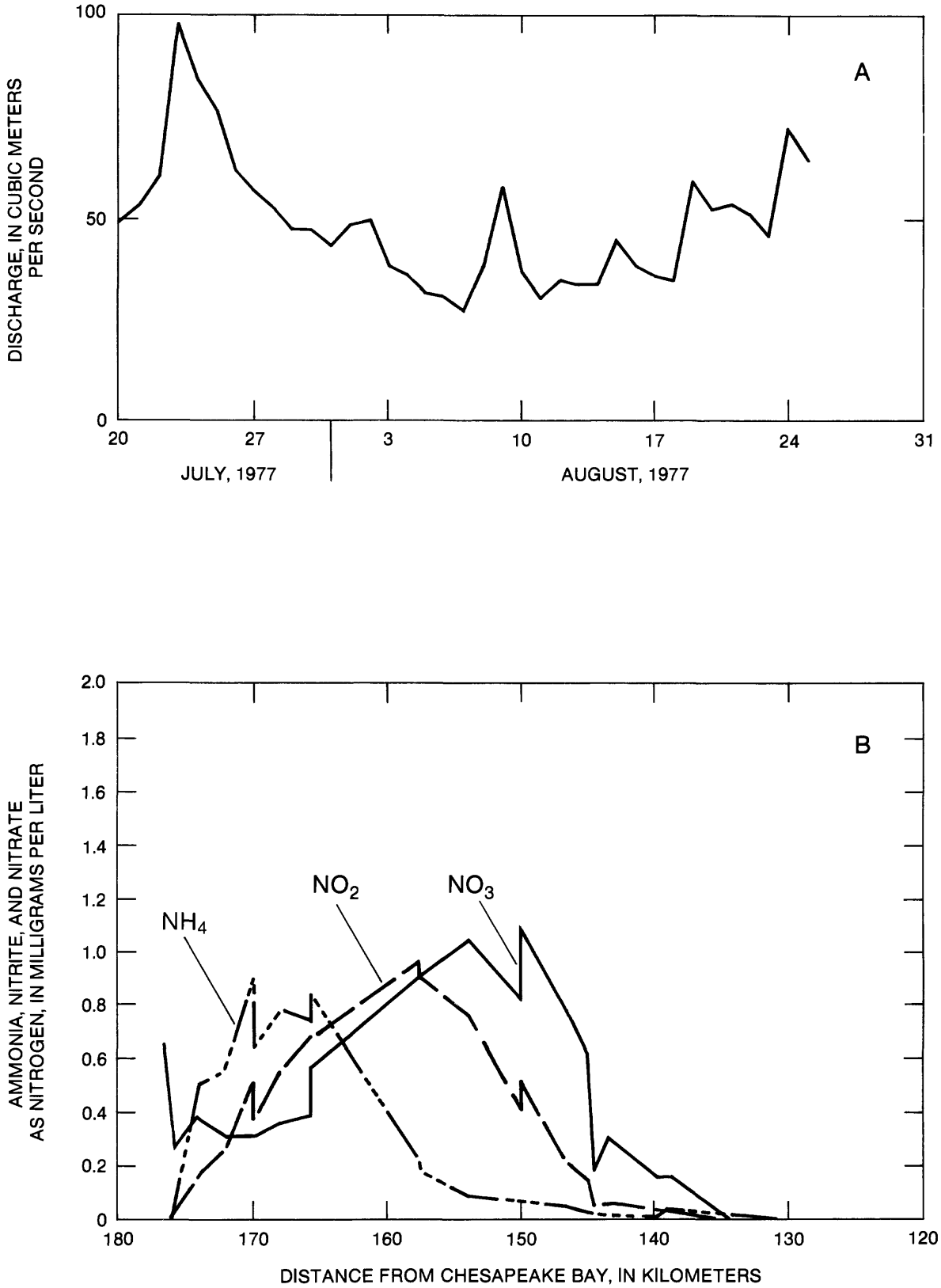

Figure 6. A, Freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C., from July 20 to August 25, 1977; and B, Concentrations of ammonia, nitrite, and nitrate in point samples as a function of distance from Chesapeake Bay, August 24 and 25, 1977.

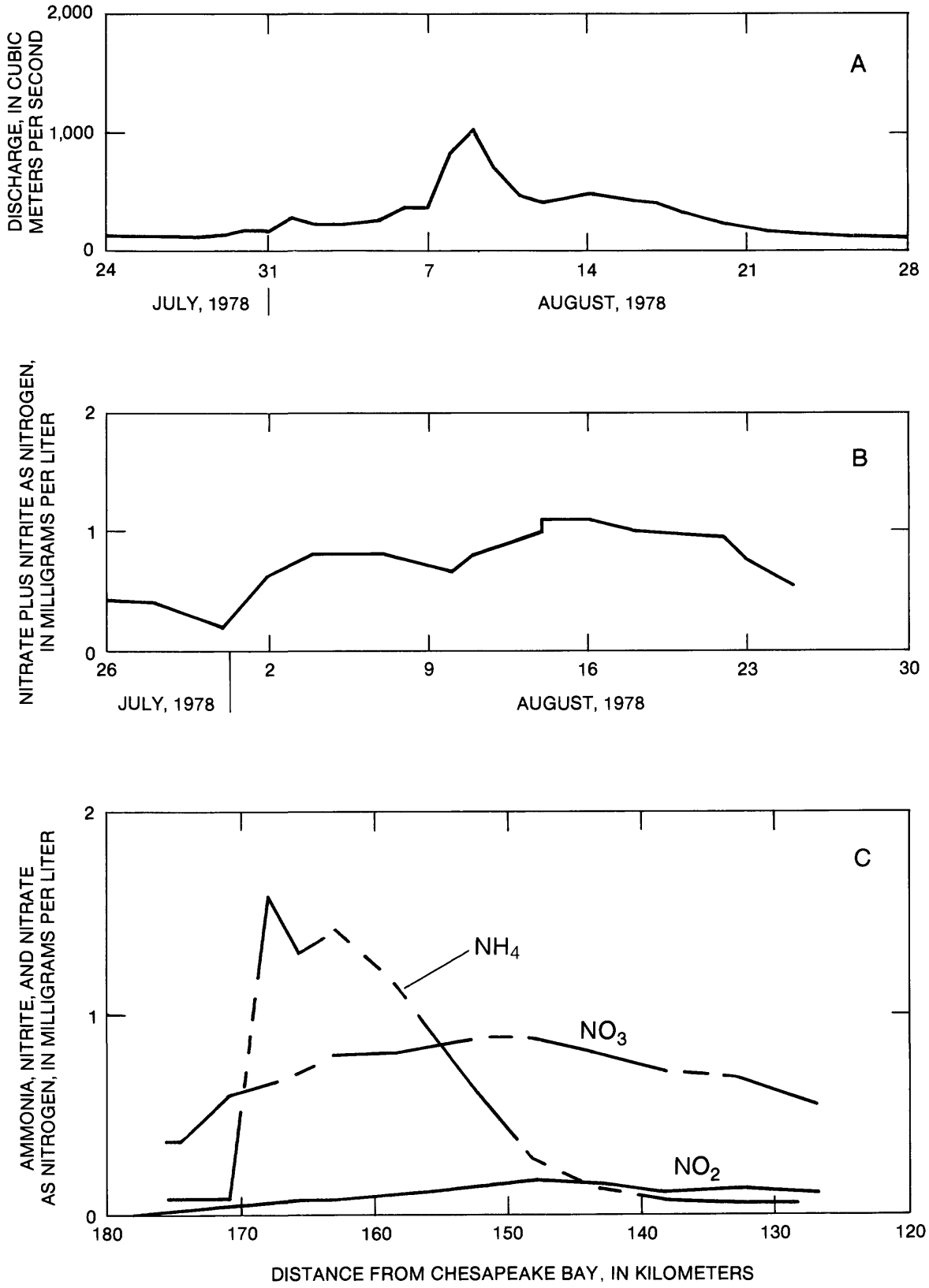

Figure 7. A, Freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C., from July 24 to August 28, 1978; B, Nitrate plus nitrite concentrations at Chain Bridge, near Washington, D.C., from July 26 to August 25, 1978; and C, Concentrations of ammonia, nitrite, and nitrate in point samples as a function of distance from Chesapeake Bay, August 28, 1978.

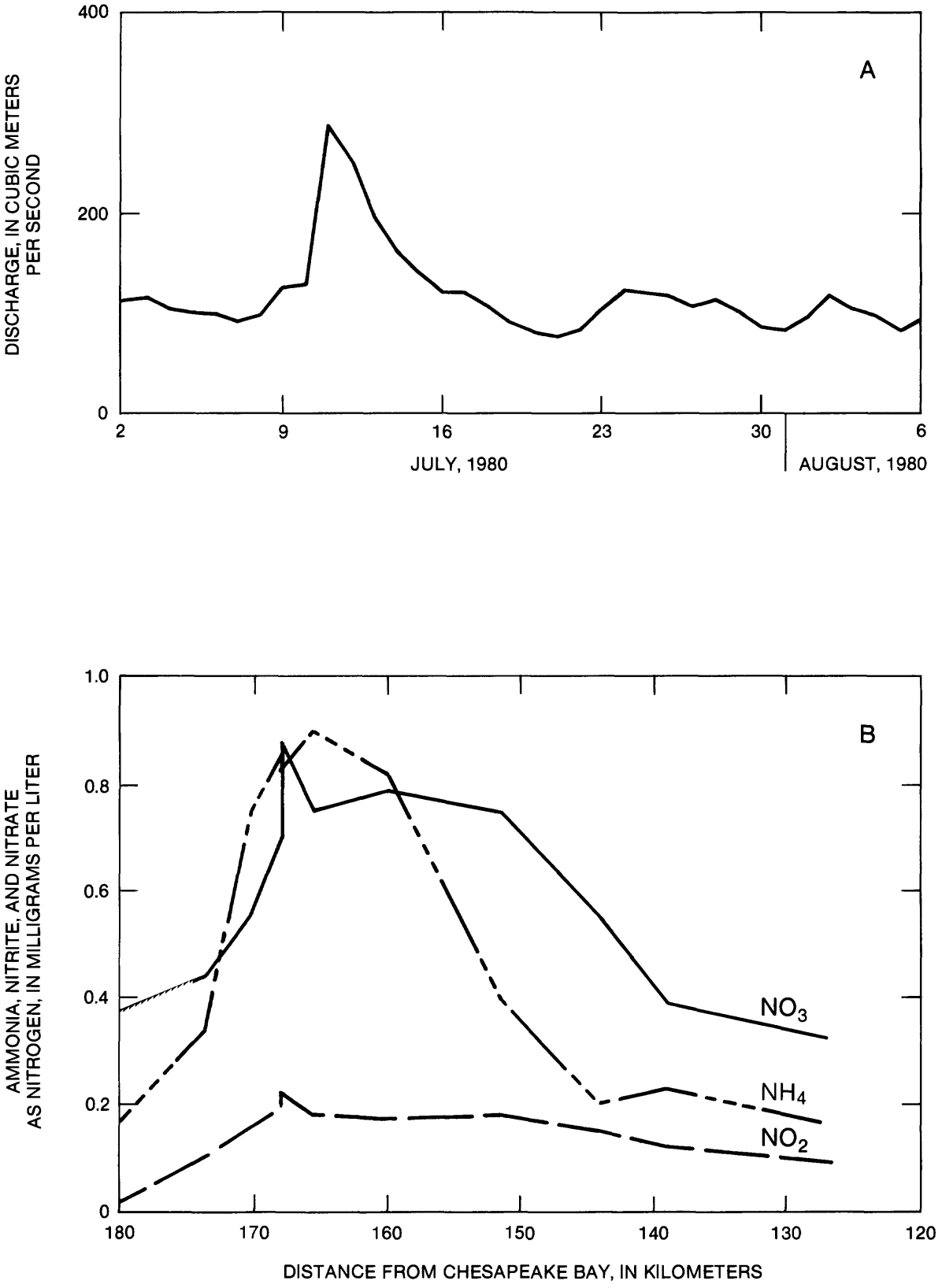

Figure 8. A, Freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C., from July 2 to August 6, 1980; and B, Concentrations of ammonia, nitrite, and nitrate in depth-integrated, composited samples as a function of distance from Chesapeake Bay, August 6, 1980.

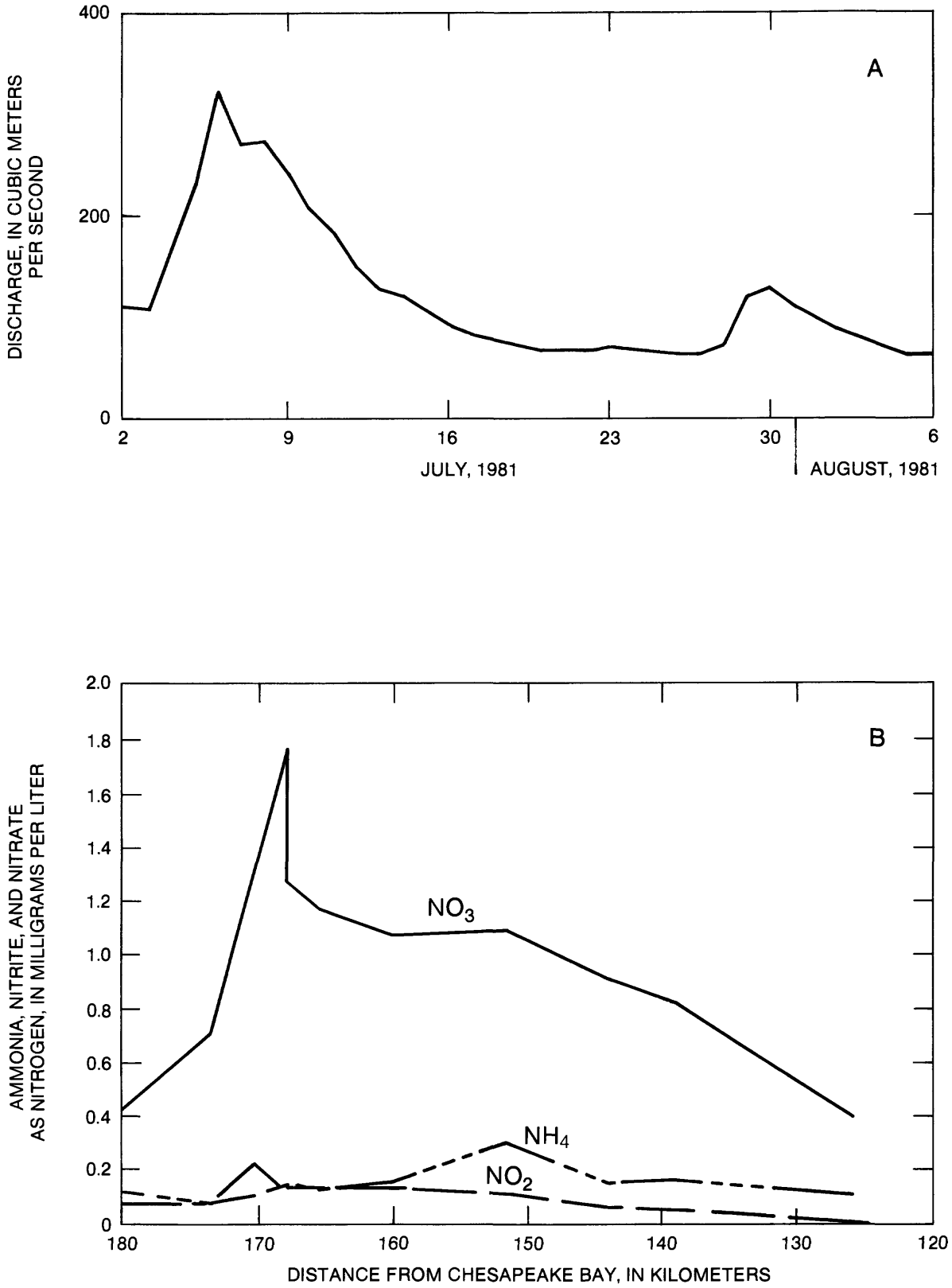

Figure 9. A, Freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C., from July 2 to August 6, 1981; and B, Concentrations of ammonia, nitrite, and nitrate in depth-integrated, composited samples as a function of distance from Chesapeake Bay, August 6, 1981.

loading was 526, 433, and 473 Mg (Coupe and Webb, 1984) for the same months in 1981, a substantial increase over the same period in 1980. The increased nitrate loads account for the elevated nitrate concentrations in the 1981 plume, and, taken together with the higher flows 3 weeks before August 6, 1981, the nitrate data give no clear evidence of a source or sink process.

In summary, the physical processes of loading and mixing can account for the distribution of the dissolved inorganic nitrogen species upstream from river kilometer 168 throughout the year. Effluent from the Blue Plains STP was the single most important source of dissolved-nitrogen species in the tidal river during the summer. The effect of biologic processes became more apparent downstream from river kilometer 168 during summer under low-flow conditions. This was due in part to the higher dissolved-nitrogen species concentrations in the Blue Plains effluent and in part to the longer residence times of water through this segment of the tidal river. Decreases in river discharge increased nutrient concentrations at the beginning of the reach because of reduced dilution and increased residence time.

Factors Controlling Temporal Variations in Dissolved-Nitrogen Species

The transport stations at Chain Bridge and Quantico, Va., define the upstream and downstream boundaries of the tidal river; the station at Alexandria, Va. (river kilometer 168), is just downstream from the Blue Plains STP effluent discharge. Examination of monthly variations in ammonia, nitrate, nitrite, and dissolved organic nitrogen concentrations over the study period reveal interannual patterns that might be obscured by examination of annual variations.

No pattern is apparent in the Chain Bridge and Alexandria ammonia data, but there is a clear pattern in the Quantico ammonia data (fig. 10): concentrations are lower during summer and fall and higher during winter and spring. Since there is no pattern at either Chain Bridge or Alexandria, the pattern at Quantico must be due to source and sink processes occurring in the river between Alexandria and Quantico. It is interesting that even though ammonia concentrations at Alexandria decreased after September 1980, because of the initiation of advanced wastewater treatment at Blue Plains, the patterns at Quantico for 1980 and 1981 are similar.

A simple dilution model was used to predict ammonia (fig. 11) and nitrate (fig. 13) concentrations at Alexandria. The equation used to predict the concentrations at Alexandria was

$$C_{Alex}=\frac{Q_{CB}\cdot C_{CB}+Q_{BP}\cdot C_{BP}}{Q_{CB}+Q_{BP}}, \qquad (2)$$

where

C_{Alex}=concentration of ammonia or nitrate in Potomac River at Alexandria, in milligrams per liter as N;

Q_{CB}=discharge of Potomac River at Chain Bridge, in cubic meters per second;

C_{CB}=concentration of ammonia or nitrate in Potomac River at Chain Bridge, in milligrams per liter as N;

Q_{BP}=discharge of effluent from Blue Plains STP, in cubic meters per second; and

C_{BP}=concentration of ammonia or nitrate in Blue Plains STP effluent, in milligrams per liter as N.

This simple model assumes that no source or sink processes occurred during a water parcel's transit between Chain Bridge and Alexandria. The time of travel of a parcel from Chain Bridge to Alexandria is also ignored. Finally, daily fluctuations in discharge and concentration at the Blue Plains STP are ignored. A regression of calculated to observed ammonia concentrations indicates that 40 percent of the variance of the ammonia concentrations at Alexandria could be explained by the dilution model.

Interestingly, there is an obvious interannual pattern in the nitrate concentrations at Chain Bridge (fig. 12). Since Blanchard and Hahl (1987) did not find any significant correlation between concentration and discharge, this pattern must be due to some process that is independent of discharge. The interannual pattern is somewhat obscured at Alexandria. Factors included in the mixing model (fig. 13) account for 50 percent of the variance of the nitrate concentrations at Alexandria.

The pattern in interannual variations in nitrate concentrations at Quantico is clear (fig. 12) and is similar to the pattern for ammonia, in that concentrations are higher in winter and spring than in summer and fall. Unlike ammonia, however, the effect of increased nitrate loads is reflected downstream at Quantico during winter and spring 1981.

The pattern of increased nitrite concentrations during summer low-flow periods at Alexandria and Quantico (fig. 14) has an interesting implication. The downstream pattern must be caused either by loading or by source and sink processes, because there is no pattern at Chain Bridge (fig. 14).

In 1980, the nitrite pulse occurred at Quantico earlier than at Alexandria. This argues against it being a result of loading and transport from point sources. Periodic nitrite pulses have been reported in Chesapeake Bay and other estuaries during late summer and early fall (McCarthy and others, 1977; Webb and D'Elia, 1980; D'Elia and others, 1981; Webb, 1981). Kemp and others (1982) hypothesized that these pulses are due to the first stage of nitrification (oxidation of ammonia to nitrite) occurring at a faster rate than the second stage (oxidation of nitrite to nitrate). If oxidation of ammonia to nitrite occurred in the water column, one would expect to see a lower nitrite pulse in 1981 because of reduced ammonia concentrations. This does not appear to be the case. However, if the nitrification

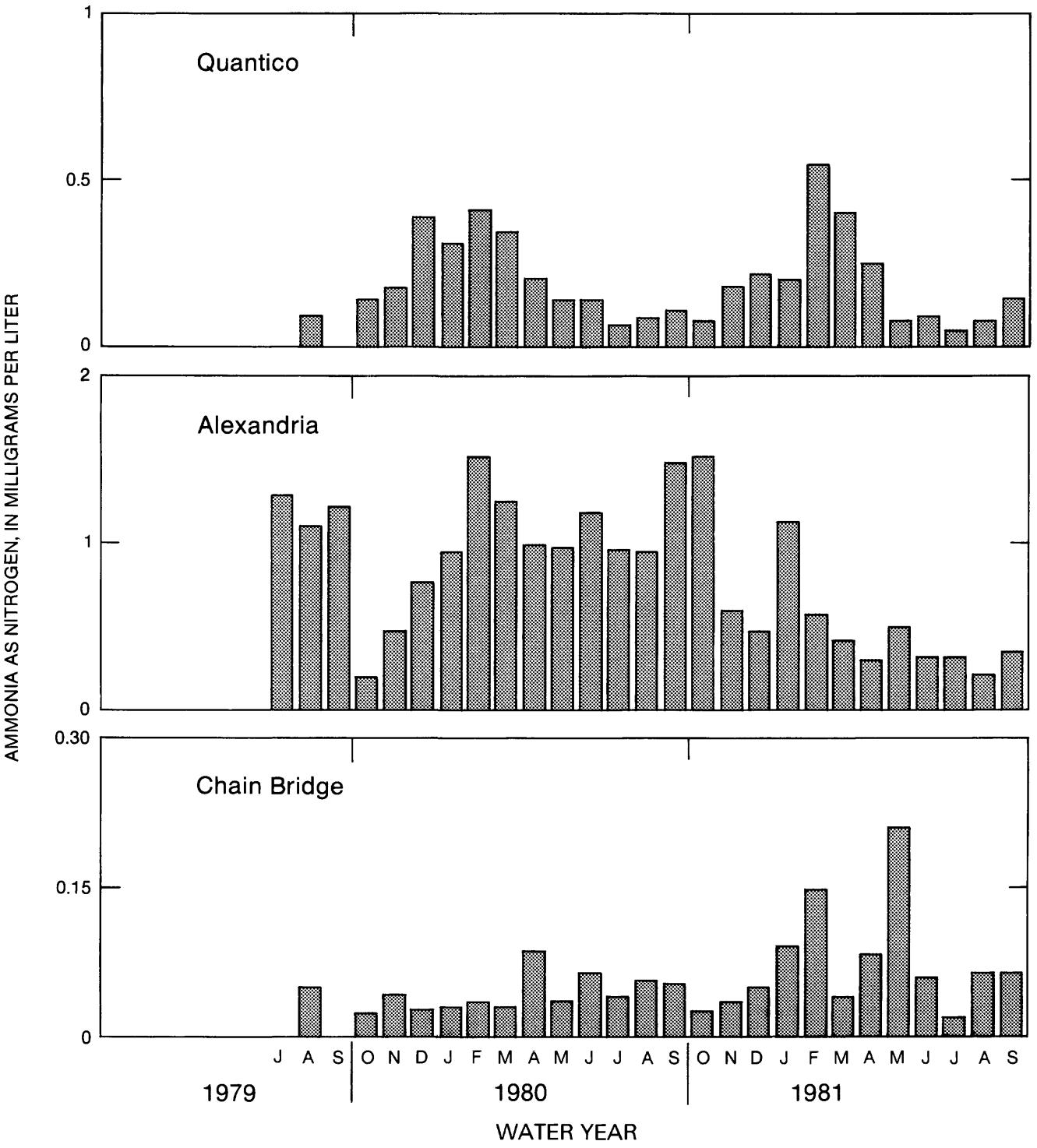

Figure 10. Average monthly ammonia concentrations at three transport stations, water years 1979–81.

occurred primarily in the sediments, then the linkage between water column ammonia and nitrite concentrations may not be direct. Benthic flux measurements usually reveal positive ammonia gradients from the sediments to the water column, indicating ammonia export (Callender and Hammond, 1982). Nitrification in the sediment would also be consistent with the nitrite pulse occurring simultaneously over broad reaches of the tidal river.

There is no apparent seasonal pattern for dissolved organic nitrogen concentrations at any of the three stations

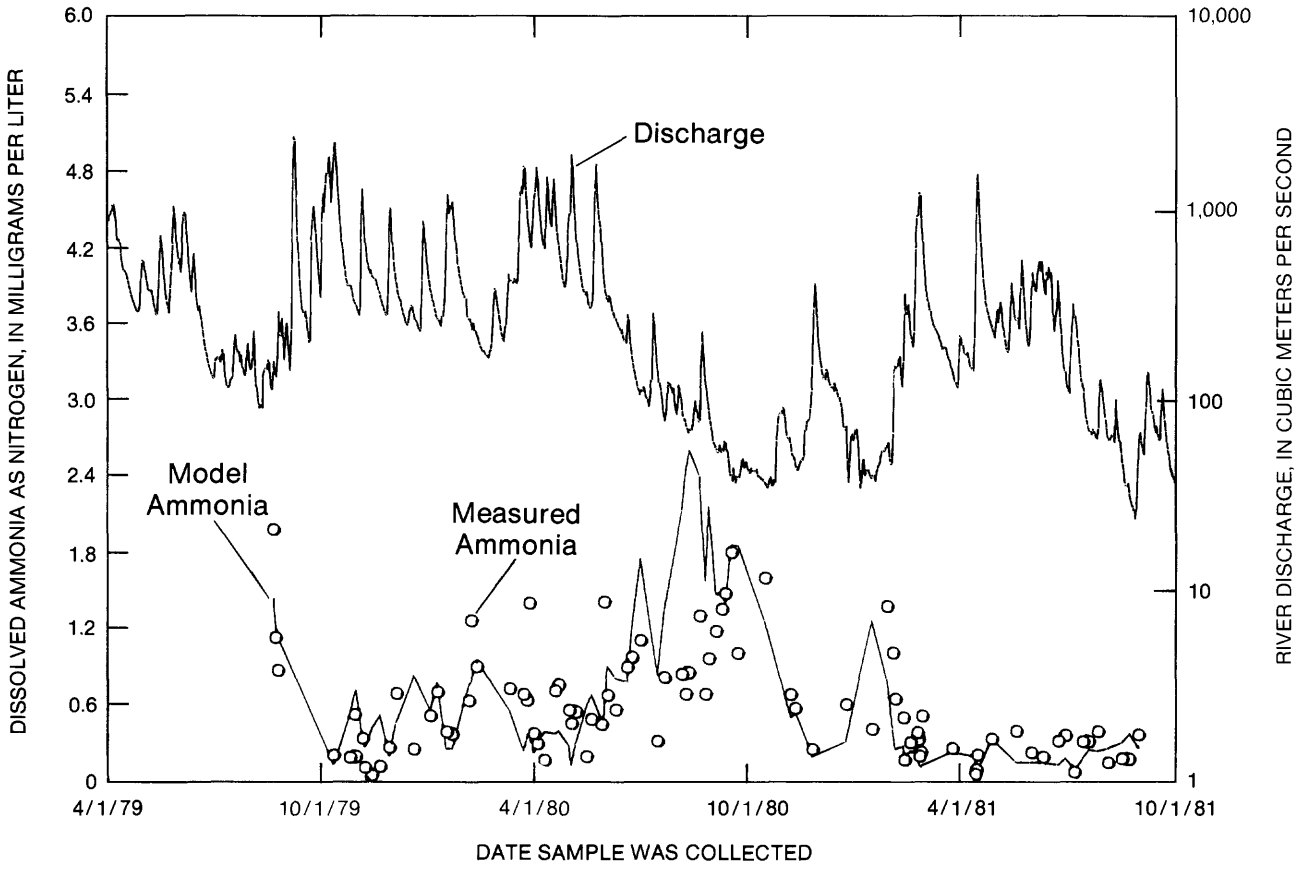

Figure 11. Actual and dilution-model depth-integrated, composited ammonia concentrations in the tidal Potomac River at Alexandria, Va., for water years 1979–81, and freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C.

(fig. 15). The variations are greater at Alexandria and Quantico than at Chain Bridge.

Mass-Balance Calculations

The examples discussed in the preceding section show that even with detailed data on river flow and loading, interpreting longitudinal data to determine relevant biological and geochemical processes is extremely difficult. Another approach to separating loading and transport from biological and geochemical processes is a mass-balance approach. Longitudinal concentrations and the volumes of specific tidal river segments were used to calculate the mass of a particular constituent in the tidal river on a given date. The mass input from river, point, and nonpoint sources was computed from the loading tables in Blanchard and Hahl (1987), Coupe and Webb (1984), and Hickman (1987). Advected mass transport out the downstream end of the tidal river was computed by multiplying the discharge at Chain Bridge and the Blue Plains STP by concentration. For these calculations, the station at Hallowing Point, Va. (river kilometer 144), was considered the downstream end of the tidal river because flow was often in two layers at the Indian Head (river kilometer 139) and Quantico (river kilometer 126) stations during summer low-flow periods. The outgoing advection term (eq. 3) included a correction for dispersion, which was computed by multiplying a value of 28 m^3/s, determined experimentally for the tidal Potomac by Hetling and O'Connell (1966), by the mean concentration gradient of the constituent during the time period. A final mass was calculated using the following equation:

$$\textit{Final mass} = \textit{Initial mass} + \textit{Mass input} - \textit{Advected mass output}\ , \quad (3)$$

where

Final mass=mass of a particular constituent in the tidal Potomac River at the end of a particular time period, in megagrams;

Initial mass=mass of a particular constituent in the tidal Potomac River at the start of a particular time period, computed by summing mass

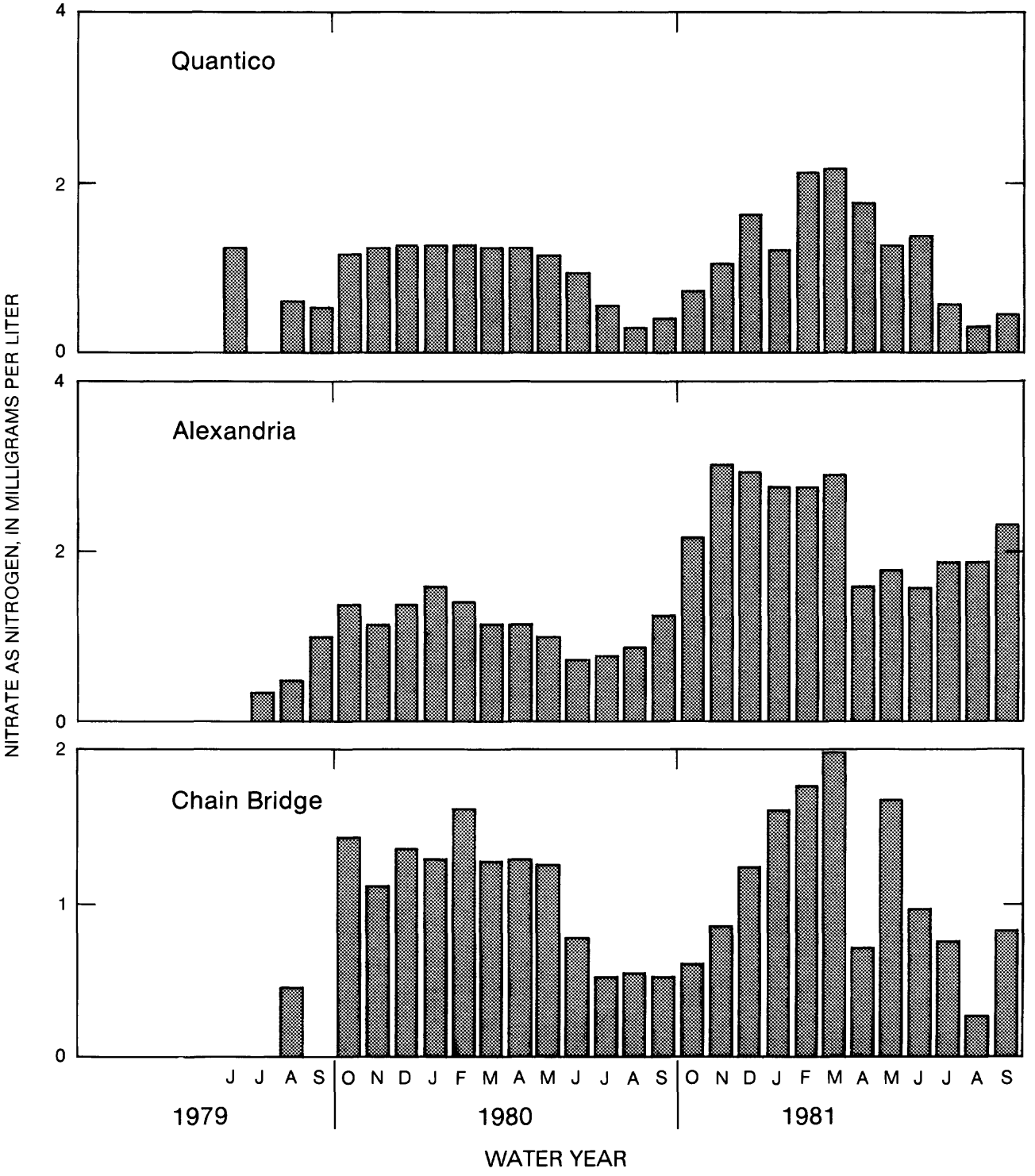

Figure 12. Average monthly nitrate concentrations at three transport stations, water years 1979–81.

(concentration times volume) for each segment, in megagrams;

Mass input=sum of loads of a particular constituent delivered by upriver, point, and nonpoint sources to

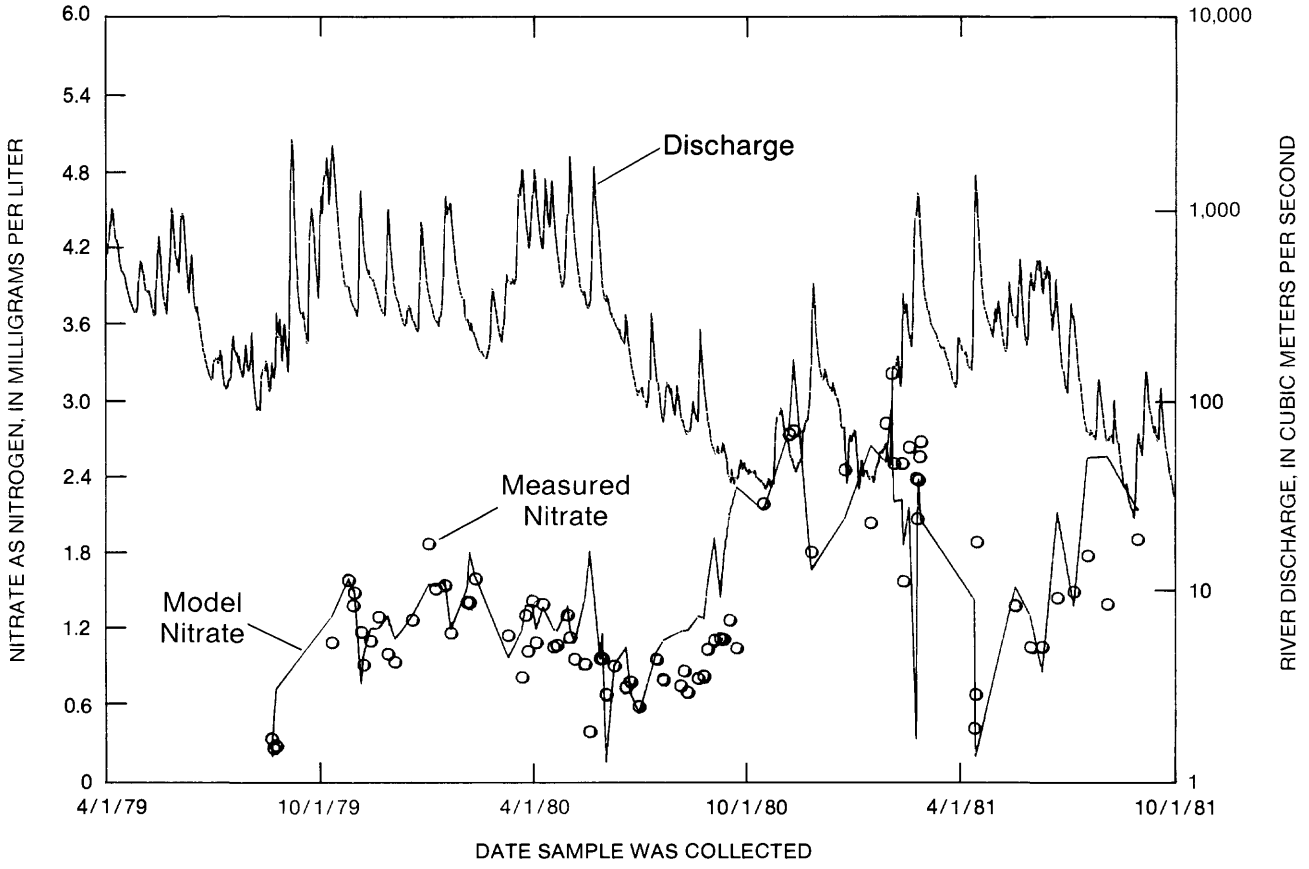

Figure 13. Actual and dilution-model depth-integrated, composited nitrate concentrations in the tidal Potomac River at Alexandria, Va., for water years 1979–81, and freshwater discharge at the streamflow-gaging station at Little Falls, Va., near Washington, D.C.

the tidal Potomac River over the period of calculation, in megagrams; and

Advected mass output=load of a particular constituent transported out of the tidal Potomac River over the period of calculation, in megagrams.

For comparison, the net source or sink rate was computed as follows:

$$Net\ source\text{-}sink\ rate = \frac{Mass_{obs} - Mass_{calc}}{\Delta t}, \qquad (4)$$

where

Net source-sink rate=appearance or disappearance of a particular constituent, unrelated to loading and transport, in megagrams per day;

$Mass_{obs}$=final mass observed for a particular constituent, computed by multiplying the concentration of the depth-integrated, composited sample by the volume of water in the river segment where the sample was collected, then summing these masses for the entire tidal river, in megagrams;

$Mass_{calc}$=final mass of a particular constituent calculated by equation 3, in megagrams; and

Δt=elapsed time between successive longitudinal sampling trips taken to determine $Mass_{calc}$, in days.

The net source-sink rate represents the net effect of a number of different processes that may be unevenly distributed in time and space. Periods when river discharge was relatively constant were chosen for comparison; the periods were in the summer of 1980 and 1981 and the winter of 1980–81.

A positive value represents a net source, and a negative value represents a net sink. The only positive values (table 3) calculated for dissolved constituents were for ammonia and nitrate during the winter period, when biologically mediated processes have reduced rates. Ammonia, rather than nitrate, had the largest net sink during the

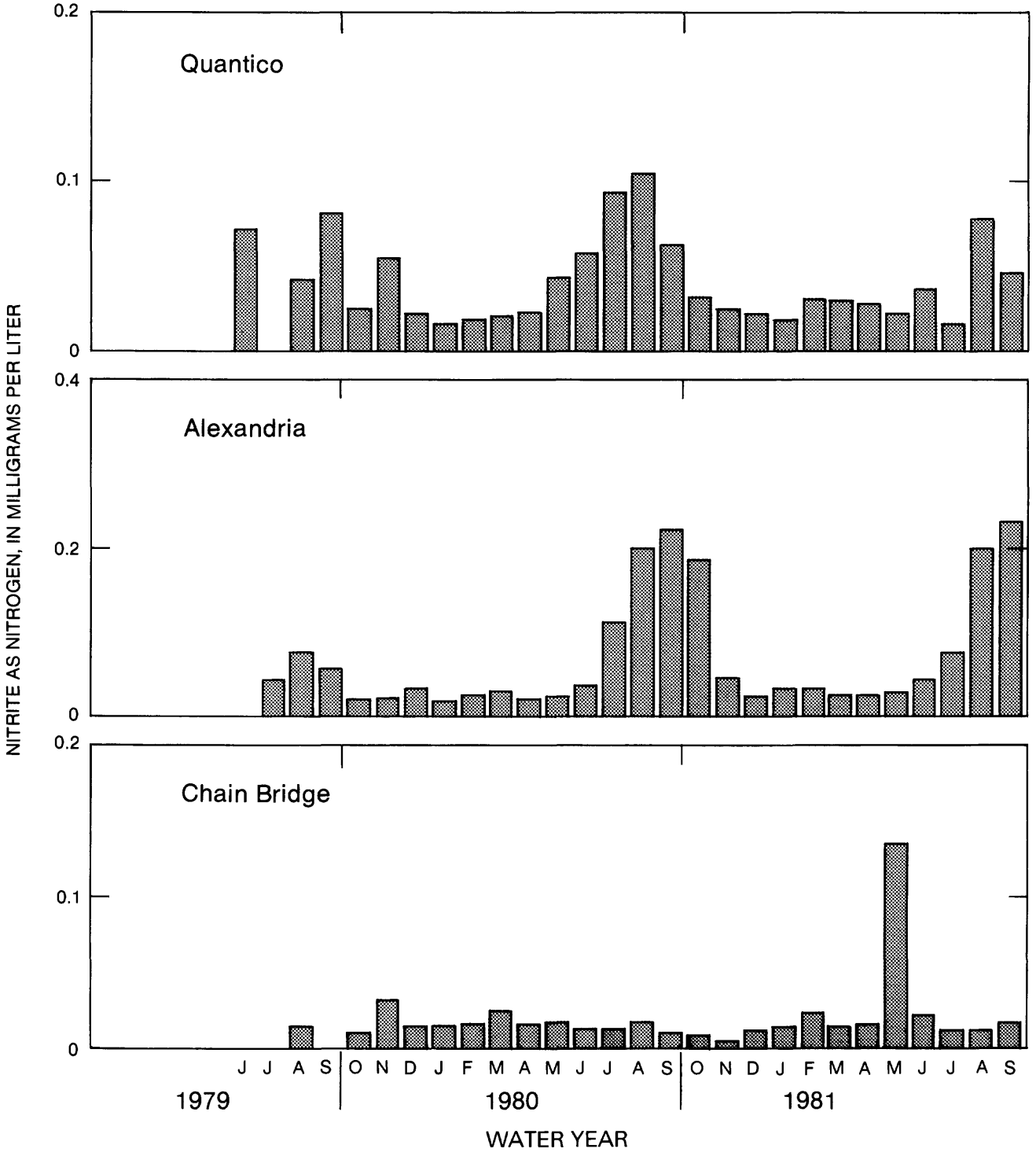

Figure 14. Average monthly nitrite concentrations at three transport stations, water years 1979–81.

summer 1980 period, while the reverse was true for the summer 1981 period. Qualitatively, this corresponds to the switch from predominantly ammonia loading to nitrate loading at the Blue Plains STP in September 1980.

The mass and rate calculations integrated the net results of a number of processes acting on a particular constituent over fairly long periods of time and space. The results indicate that the tidal river acted as a trap for

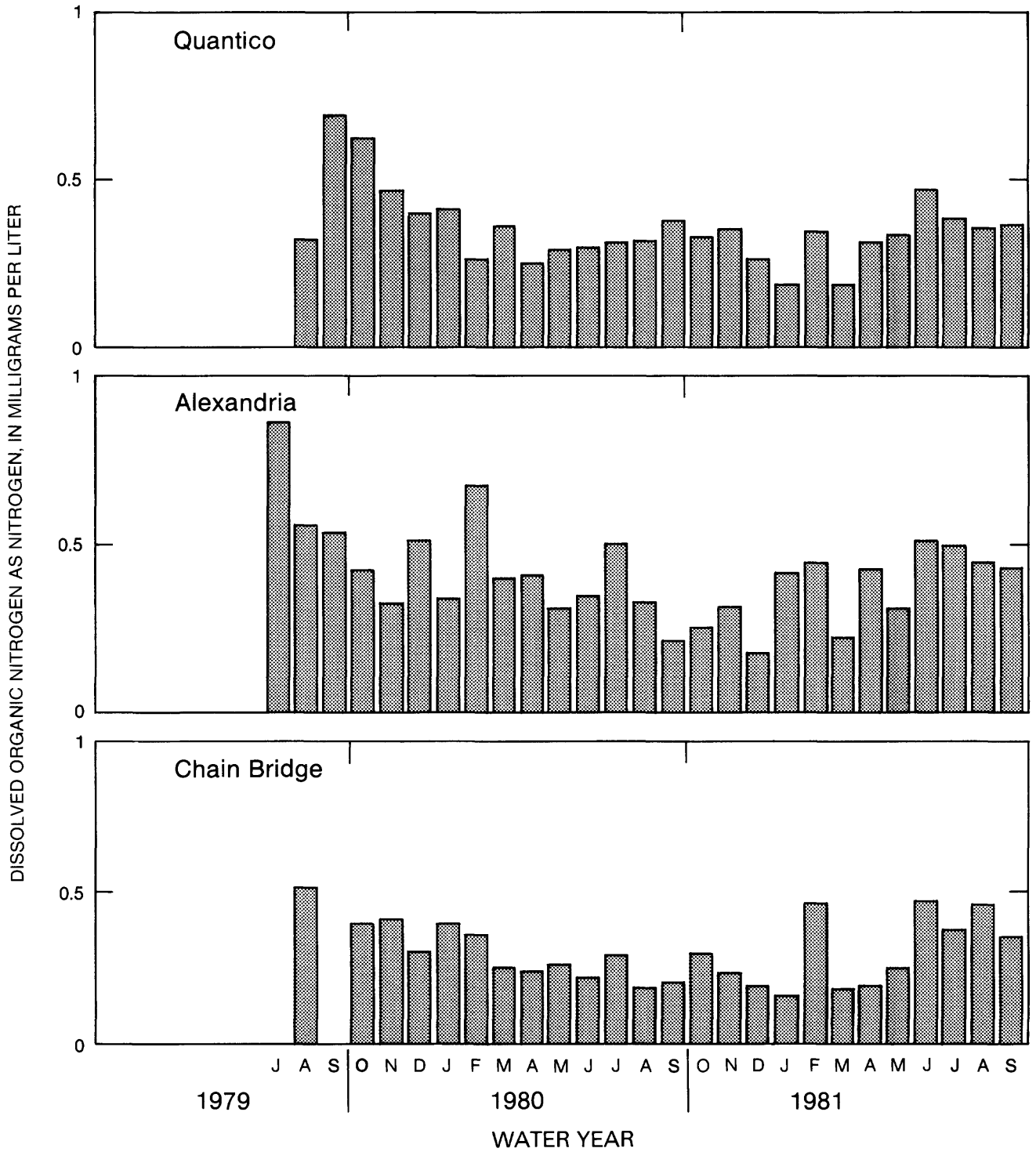

Figure 15. Average monthly dissolved organic nitrogen concentrations at three transport stations, water years 1979–81.

nitrogen and phosphorus, particularly during the summer periods of this study.

The net sink decreased for ammonia and increased for nitrate during the summer of 1981 relative to the summer of 1980. The ammonia and nitrate source-sink terms also show the greatest change from summer to winter. This is consistent with the biological nature of the main source and sink processes that affect ammonia and nitrate. The seasonal variation in dissolved reactive phosphorus is similar to the variations in ammonia and nitrate, in that net sink decreased

Table 3. Difference between calculated and observed final mass for dissolved and particulate constituents in the tidal Potomac River normalized for three time periods

[In megagrams per day. Positive value indicates net source, negative value net sink]

	July 30 - Aug. 20, 1980	Aug. 6 - Aug. 26, 1981	Dec. 15, 1980 - Feb. 4, 1981
Dissolved constituents			
Ammonia	- 12	- 6.4	+ 1.9
Nitrate	- 5.8	- 13	+ .28
Nitrite	- .068	- 2.8	- 2.0
Organic Nitrogen	- 4.2	- 1.9	- 4.0
Phosphate (dissolved reactive phosphorus)	- 1.4	- 1.4	- .94
Silica	- 49	- 33	- 32
Particulate constituents			
Organic nitrogen	- 1.3	- 3.7	- 3.3
Phosphorus	+ .86	- .42	- .79
Chlorophyll	+ .77	+ .11	+ .018

during the winter period. Hearn (1985), in a detailed study of dissolved reactive phosphorus downstream from the Blue Plains STP outfall, found that adsorption of dissolved reactive phosphorus onto particulate material and diurnal uptake by phytoplankton were major sinks removing dissolved reactive phosphorus from solution. Temperature might be expected to have a greater effect on phytoplankton uptake of phosphorus than it does on adsorption of phosphorus by particulate material. Therefore, if adsorption is the major sink for phosphorus, one might expect very little difference between the net sink values for the summer and winter periods. In fact, the net source-sink values in table 3 tend to support this view. The summer net source-sink values, in 1980 and 1981, for phosphorus were negative and 1.5 times greater than the winter net source-sink value, which was also negative. In comparison, the summer net source-sink values, in 1980 and 1981, for ammonia, which is also used by phytoplankton, were negative and 7.3 and 4.4 times lower, respectively, than the winter net source-sink value, which was positive.

Constituents associated with particulate material (organic nitrogen, chlorophyll, and particulate phosphorus) are also considered in table 3 but will not be discussed in detail here except to mention that the results for chlorophyll are consistent with the above discussion. As one would expect for a constituent associated with phytoplankton, which increase in number during summers, the net source-sink values for chlorophyll were positive for the 1980 and 1981 summer periods and were 43 and 6 times greater, respectively, than the winter value, which was also positive. The large difference in the net source for chlorophyll between the summers of 1980 and 1981 probably is associated with the higher concentrations of phytoplankton in the tidal river in 1980 compared with those in 1981 (Blanchard and Coupe, 1982; Blanchard and others, 1982).

Nitrogen-Cycle Processes

Uptake of Ammonia and Nitrate by Phytoplankton

Phytoplankton extract ammonia and nitrate from solution and transform the nitrogen into organic nitrogen compounds. A large mass of phytoplankton is not only unsightly but is often implicated in a number of water-quality problems. Water-quality improvement has often centered around strategies to reduce standing crops of phytoplankton. One approach to phytoplankton control is based on the concept of the growth-limiting nutrient, which assumes that if several nutrients are necessary for growth, the one in shortest supply will control not only the rate of growth but also the size of the standing crop (biomass). From a water-quality-management standpoint, this approach has appeal because it suggests that eutrophic bodies of water can be improved by focusing control measures on only one element. Jaworski and others (1972) suggested that nitrogen may be the growth-limiting nutrient during late summer in the tidal freshwater Potomac.

Many of the discussions and findings about potential growth-limiting nutrients are based on analyses of the ratio of dissolved inorganic nitrogen to dissolved inorganic phosphorus concentrations. This approach may be misleading because it is based not on uptake rates but on bulk estimates of available nitrogen and phosphorus. A more direct approach is to measure uptake rates of ammonia and nitrate utilizing isotopically labeled substrates. Determination of uptake rates does not directly yield any information about which element is growth limiting, but it is probably less ambiguous than nitrogen to phosphorus ratios.

Phytoplankton uptake of ammonia and nitrate was measured in the summer of 1981 using ^{15}N-labeled ammonia and nitrate. Six experiments using water samples collected throughout the tidal river were conducted over the period August 11 to September 25, 1981.

The experimental conditions for the six water samples for which the ^{15}N tracer studies were performed are noted in table 4. The uptake rates for ammonia and nitrate, calculated by equation 1, are shown in table 5. Also computed is the growth rate (V_{NH_4} or V_{NO_3}) in terms of nitrogen, which is equal to the uptake rate divided by the concentration of particulate organic nitrogen.

The high initial $\delta^{15}N$ shown in table 5 for some of the experiments is probably an artifact of not killing the initial spiked sample quickly enough. Apparently, ammonia and nitrate uptake is rapid enough that a delay of several minutes before killing the sample with Lugol's solution can result in appreciable uptake. The uptake rates were calculated using the initial $\delta^{15}N$; therefore, the calculated rates

Table 4. Experimental conditions for nitrogen-15 uptake experiments using tidal Potomac River water samples

[°C, degrees Celsius; µg/L, micrograms per liter; mg/L, milligrams per liter; $\delta^{15}N$, isotope ratio; ‰, per mil; n.d., not determined. Location of stations shown in fig. 2]

Station	Date	Incubation temperature (°C)	Chlorophyll-a (µg/L)	Initial concentration NH_4 (mg/L as N)	Initial concentration NO_3 (mg/L as N)	Blank $\delta^{15}N$ (‰)	Sterile control[1] NH_4 $\delta^{15}N$ (‰)	Sterile control[1] NO_3 $\delta^{15}N$ (‰)
Lagrangian Channel[2]	8/11/81	29.0	45.8	0.14	0.94	79.7	14.8	28.0
Rosier Bluff, Maryland	8/18/81	26.8	68.6	0.07	.59	17.0	47.2	19.0
Memorial Bridge	9/04/81	25.5	14.0	0.13	.28	76.8	n.d.	n.d.
Marbury Point, Maryland	9/04/81	25.5	35.4	0.37	1.57	10.4	24.2	18.7
Hatton Point, Maryland	9/25/81	19.9	33.1	0.32	1.96	9.1	n.d.	n.d.
Hallowing Point, Virginia	9/25/81	19.9	25.4	0.13	1.50	17.4	24.6	27.7

[1]The sterile controls were autoclaved for 15 minutes and cooled, the $^{15}NH_4$ or $^{15}NO_3$ spikes were then added and incubated at 100-percent light.

[2]A depth-integrated composite collected in the channel during a Lagrangian experiment where a parcel of water was followed over a 24-hour period. At the time of sampling, the parcel was located in the vicinity of river kilometer 165.

may underestimate the actual rates. Comparison of the $\delta^{15}N$ values for the blank and sterile controls shows that the isotope ratios of the blank (live-unspiked) and sterile (dead-spiked) controls were quite similar and were less than the initial sample. This means there was no uptake by abiologic processes.

In general, the ammonia uptake rates were higher than the nitrate uptake rates, even though nitrate was far more abundant in 1981 than was ammonia. It also is interesting that there was usually appreciable uptake of ammonia but not of nitrate in the dark (0 percent light). A way of comparing the relative preference of the phytoplankton for ammonia from different samples is to calculate the ratio of nitrate uptake to nitrate uptake plus ammonia uptake, where a value of 1.0 represents only nitrate uptake and a value of 0.0 represents only ammonia uptake; this eliminates errors due to varying amounts of particulate nitrogen detritus between samples (Dugdale and Goering, 1967). The ratios shown in table 5 are plotted in figure 16. Ammonia was the preferred source of nitrogen in five of the six experiments. Eighty to ninety percent of the nitrogen taken up was in the form of ammonia. In one experiment (Memorial Bridge), in which the ambient ammonia concentration was smaller than 0.10 mg/L as N, only 40 to 60 percent of the nitrogen taken up was in the ammonia form. Similar results were found by McCarthy and others (1975) in Chesapeake Bay and by Stanley and Hobbie (1977) in the Chowan River in North Carolina.

Several investigations have shown that phytoplankton will preferentially use ammonia over nitrate until ammonia concentrations are below 0.014 mg/L as N (Pomeroy, 1970; Morris, 1974; McCarthy, 1980). One implication is that before 1981, when ammonia concentrations in the Potomac River were higher, phytoplankton nitrogen requirements were supplied primarily by ammonia. The only time nitrate was likely to have been a significant source of phytoplankton nitrogen is in the latter stages of a bloom, when ammonia concentrations were reduced to less than 0.10 mg/L as N.

Nitrification

Nitrification is a series of bacterially mediated processes wherein ammonia is oxidized to nitrite by autotrophic bacteria of the genus *Nitrosomonas* and nitrite is oxidized to nitrate by autotrophic bacteria of the genus *Nitrobacter*. Since 4.57 g (grams) of oxygen are used per 1.00 g of ammonia oxidized, nitrification may be a significant oxygen-demanding process. Nitrification can take place in either the water column or oxidized sediments (Curtis and others, 1975; Matulewich and Finstein, 1978). Jaworski and others (1972) interpreted the downstream progression of ammonia and nitrate peaks in the tidal Potomac River, downstream from the Blue Plains STP, as evidence of water-column nitrification. Wofsy and others (1981), using a modeling approach with data collected between 1971 and

Table 5. Experimental results and calculated uptake rates in tidal Potomac River water samples containing nitrogen-15 labeled ammonia and nitrate amendments

[$\delta^{15}N$, isotope ratio; V, growth rate; ρ, uptake rate; (mg/L)/hr, milligram per liter per hour; n.d., not determined. —, negative value for V_{NO_3} or ρ_{NO_3}. Location of stations shown in fig. 2]

		$^{15}NH_4$ Spikes				$^{15}NO_3$ Spikes				$\frac{\rho_{NO_3}}{\rho_{NH_4} + \rho_{NO_3}}$
Station	Percent light	Initial $\delta^{15}N$	Final $\delta^{15}N$	V_{NH_4} (per hour)	ρ_{NH_4} ((mg/L)/hr)	Initial $\delta^{15}N$	Final $\delta^{15}N$	V_{NO_3} (per hour)	ρ_{NO_3} ((mg/L)/hr)	
Lagrangian Channel[1]	0	271	n.d.	n.d.	n.d.	35	19.4	—	—	n.d.
	25		4,439	.0570	0.0238		127	.0082	.00034	.014
	100		4,174	.0535	.0223		211	.0151	.00634	.22
	100		3,357	.0426	.0179		231	.0168	.00706	.28
Rosier Bluff, Maryland	0	591	1,609	.0088	.0062	15	n.d.	n.d.	n.d.	n.d.
	25		3,781	.0210	.0147		374	.0157	.0110	0.43
	55		n.d.	n.d.	n.d.		376	.0157	.0110	n.d.
	100		3,698	.0206	.0144		836	.0360	.0252	0.64
	100		3,956	.0220	.0154		n.d.	n.d.	n.d.	n.d.
Memorial Bridge	0	313	1,678	.0157	.0022	27.9	19.9	—	—	n.d.
	25		3,551	.0334	.0047		105.5	.0018	.00025	.051
	55		3,834	.0361	.0050		130.8	.0023	.00032	.060
	100		3,740	.0352	.0049		152.8	.0028	.00039	.074
Marbury Point, Maryland	0	81.7	430	0.0124	0.0035	18.5	14.4	—	—	n.d.
	0		n.d.	n.d.	n.d.		22.8	.00052	.00015	n.d.
	25		760	.0225	.0063		13.5	—	—	n.d.
	55		1,357	.0498	.0114		20.7	.00025	.00007	0.0061
	100		1,477	.0444	.0124		17.0	—	—	n.d.
Hatton Point, Maryland	0	34.9	258.9	.0054	.00059	20	10.2	—	—	n.d.
	25		718.5	.0161	.00177		25.9	—	—	n.d.
	55		804.6	.0180	.00198		23.9	—	—	n.d.
	100		755.6	.0169	.00186		35.9	.00114	.00013	.065
Hallowing Point, Virginia	0	523	751.3	.0066	.00125	29.3	25.5	—	—	n.d.
	25		2,542	.0231	.00439		n.d.	n.d.	n.d.	n.d.
	55		2,547	.0231	.00439		34.9	.00070	.00013	.029
	100		2,434	.0221	.00420		35.9	.00079	.00015	.034

[1]A depth-integrated composite taken in the channel during a Lagrangian experiment where a parcel of water was followed over a 24-hour period. At the time of sampling, the parcel was located in the vicinity of river kilometer 165.

1979 in the tidal freshwater Potomac, concluded that nitrification is the single most important process affecting nitrogen. They also found that the ammonia oxidation rate varied inversely with river discharge.

Nitrification-rate experiments were performed using the method of Somville (1978), which is based on uptake of $H^{14}CO_3^-$ during oxidation of ammonia to nitrite. Fourteen nitrification-rate experiments were performed over a 5-month period on samples from eight locations in the tidal freshwater river. Sample locations, dates of incubation, incubation temperatures, and results are shown in table 6.

From previous research (Jaworski and others, 1972; Wofsy and others, 1981), it was expected that the results would show elevated nitrification rates in the region of the tidal river closest to the Blue Plains STP. The experimental nitrification rates determined for this study (fig. 17A) show very little increase in the tidal river immediately upstream or downstream from the Blue Plains STP (river kilometer 170). In fact, the highest nitrification rate was for a sample collected at Memorial Bridge (river kilometer 180), which is considered to be outside the influence of the Blue Plains STP effluent plume. The results seem to be more highly

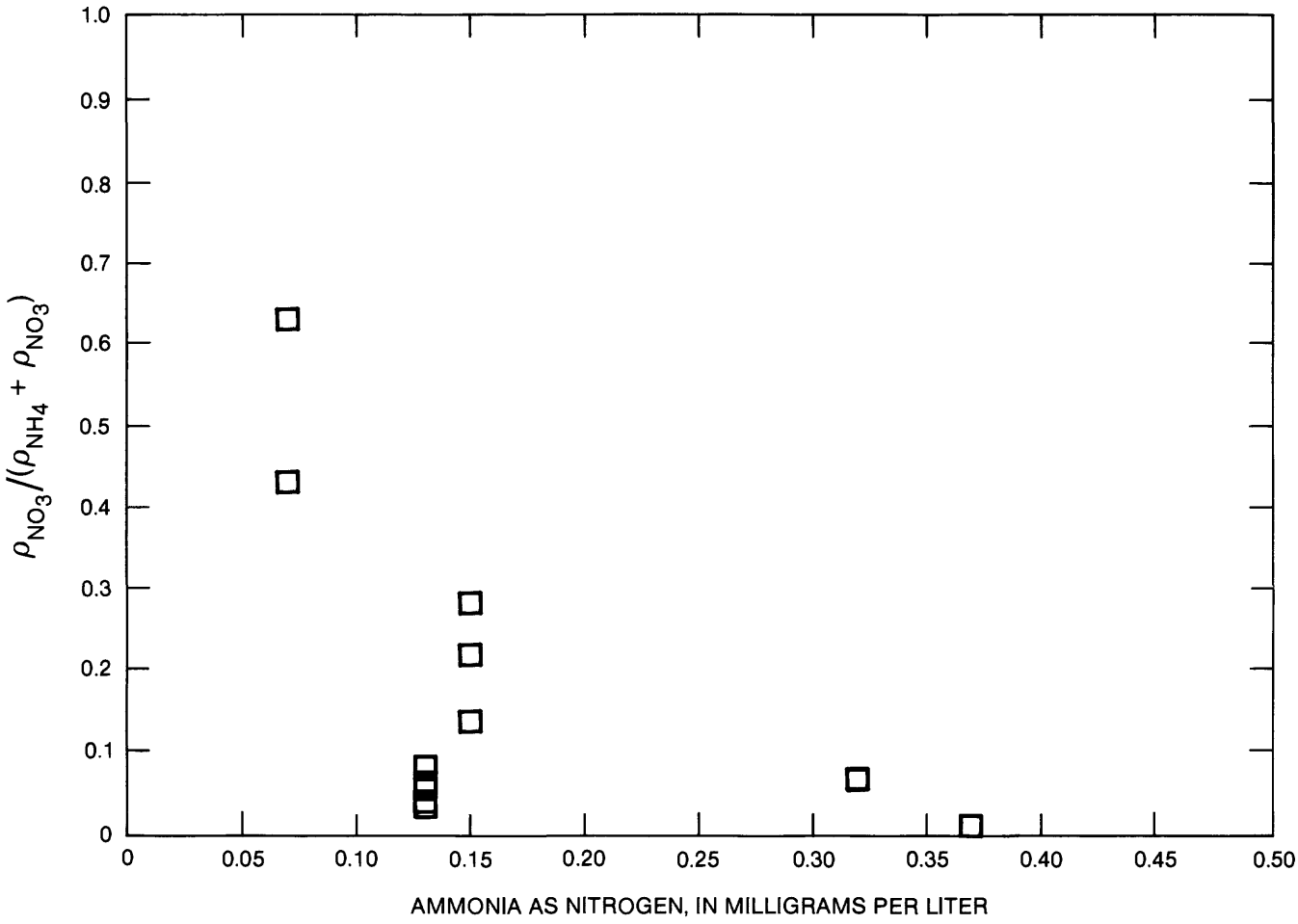

Figure 16. Effect of increasing ammonia concentration on the fraction of N uptake that is nitrate, from ^{15}N-uptake experiments in the tidal Potomac River, August–September 1981.

correlated with temperature (fig. 17B) than with sample location or ammonia concentration.

If it is assumed that nitrification is a first-order process, then a first-order rate constant can be calculated from the measured nitrification rates and the initial ammonia concentration using the following equation:

$$k = \frac{-\log_e\left(1 - \frac{rate \cdot \Delta t}{C_o}\right)}{\Delta t}, \quad (5)$$

where

k=first-order rate constant, per hour;

$\log_e$=natural logarithm;

rate=experimentally determined nitrification rate, in milligrams per liter as N per hour;

Δt=incubation time, in hours; and

C_o=initial ammonia concentration, in milligrams per liter as N.

To compare the first-order rate constants, independent of the effects of temperature, the first-order rate constant at the ambient temperature was converted to a first-order rate constant at 20 °C using the following equation:

$$k_{20} = \frac{k_t}{e^{m(t-20)}} \quad (6)$$

where

k_{20}=first-order rate constant at 20 °C, per hour;

k_t=first-order rate constant at temperature t, per hour;

e=2.71;

m=slope of $\log_e k_t$ as a function of t, in per degree Celsius; and

t=temperature at which incubations were performed, in degrees Celsius.

The regression of $\log_e k_t$ as a function of t gave a slope of 0.127 °C (r^2=0.39). Jaworski and others (1972) reported a value of 0.172 for the Potomac based on nitrification rate constants determined from biochemical oxygen demand incubations. It is interesting that when the resulting first-order rate constants are plotted as a function of longitudinal position (fig. 17C), the rate constants are uniformly low, except for the one sample at Memorial Bridge (river kilometer 180). One interpretation of these

Table 6. Experimental conditions, results, and computed nitrification rates from carbon-14 labeled bicarbonate uptake incubations in tidal Potomac River water samples, July–December 1981

[°C, degrees Celsius; MPN, most probable number; mL, milliliters; mg/L, milligrams per liter, (μg/L)/hr, micrograms per liter per hour]

Date	Station	Kilometers from mouth	Incubation temperature (°C)	Hours incubated	Nitrosomonas MPN per 100 mL	Initial NH_4 concentration (mg/L as N)	NH_4 assimilation rate ((μg/L)/hr)
07/29/81	Memorial Bridge	179.5	26.0	3.0	230	0.04	2.7
10/16/81	Memorial Bridge	179.5	16.0	4.0	230	.08	[1]0
09/10/81	14th St. Bridge	175.8	23.9	4.1	230	.09	[1]0
10/16/81	Marbury Point, Md.	170.4	16.0	4.0	90	.55	[1]0
12/01/81	Alexandria, Va.	168.0	6.5	1.0	4,600	.77	.31
12/01/81	Alexandria, Va.	168.0	6.5	3.0	4,600	.77	.17
12/01/81	Alexandria, Va.	168.0	6.5	4.0	4,600	.77	.27
08/26/81	Rosier Bluff, Md.	165.9	25.0	4.0	230	.15	.63
09/10/81	Rosier Bluff, Md.	165.9	23.9	4.1	16,000	.17	.48
10/16/81	Rosier Bluff, Md.	165.9	16.0	4.0	90	.41	[1]0
07/29/81	Hatton Point, Md.	160.0	26.0	3.0	230	.33	1.3
10/16/81	Hatton Point, Md.	160.0	16.0	4.0	230	.32	.081
09/10/81	Marshall Hall, Md.	151.6	23.9	4.1	600	.06	.046
09/10/81	Indian Head, Md.	138.9	23.9	4.1	2,300	.10	.20

[1] ^{14}C uptake greater in N-Serve blocked sample than in unblocked sample; therefore, the amount of NH_4 assimilated was assumed to be 0.

results might be that a nitrification-inhibiting substance is present. Evidence presented later in the report supports this interpretation.

The rate constant resulting from the incubation of the Memorial Bridge sample was significantly different from those of the remaining incubations. In the following calculation of the amount of ammonia oxidized by nitrification, the rate constant associated with the Memorial Bridge sample was excluded so as not to bias the results. This seems justified because the volume of water in the river segment between Memorial Bridge and Marbury Point represents only a fraction of 1 percent of the total volume of the tidal river.

Using the mean rate constant of 0.00078 ± 0.00086 per hour for 13 of the 14 incubations, a first-order rate constant of 0.035 ± 0.039 per day at 25 °C (the mean water temperature of the tidal river in August 1981) was calculated using equation 6. The amount of ammonia oxidized was calculated using the first-order formulation (equation 5 solved for rate), with the initial ammonia concentration estimated by dividing the total ammonia mass in the tidal river by total volume of water.

Even though the rate constant derived in these calculations was based on incubations performed in 1981, it has also been used in the calculation for the 1980 period. The calculations for the July 30–August 20, 1980, and August 6–26, 1981, periods, used in the calculation of the net source-sink values (table 3), yielded rates for ammonia oxidized by nitrification of 3.8 and 1.2 Mg/d (megagrams per day), respectively. This represents 31 and 18 percent of the ammonia net source-sink for August 1980 and 1981 (table 3), respectively. The variance of the rate constants derived from the incubations indicates that the ammonia oxidation rates given above could differ by a factor of two.

Another approach to assessing nitrification was determining the most probable number of nitrifying bacteria in water and surficial sediment samples. The reproducibility of results obtained by this approach is low, especially with sediment samples. Furthermore, numbers of bacteria do not necessarily give any information about activity. The most probable number calculated from two sets of longitudinal samples collected on September 15, 1980, and August 26, 1981, are shown in figures 18 and 19. Qualitatively, these data show a switch from predominance of *Nitrosomonas* in 1980 to predominance of *Nitrobacter* in 1981. In 1980, the Blue Plains STP was still loading dissolved inorganic nitrogen predominantly in the form of ammonia. The increase in numbers of *Nitrosomonas* occurred at the point where Blue Plains STP effluent discharges into the tidal Potomac. This increase could be due either to effluent loading or to inriver growth of *Nitrosomonas*. If the latter mechanism is the cause, one might expect that at some place in the tidal river *Nitrobacter* most probable number values would increase, reflecting the second stage of nitrification (oxidation of nitrite to nitrate). This was not apparent in the September 15, 1980, samples. The August 26, 1981, samples (fig. 19) show a completely different distribution of nitrifying bacteria, with *Nitrobacter* more numerous than *Nitrosomonas*. Because one of the differences between the 1980 and 1981 samples was the switch to advanced wastewater treatment at Blue Plains, one explanation of the nitrifying bacteria distribution is that the *Nitrobacter* bacteria are being loaded into the river with the STP effluent. Table 7 lists results of most probable number

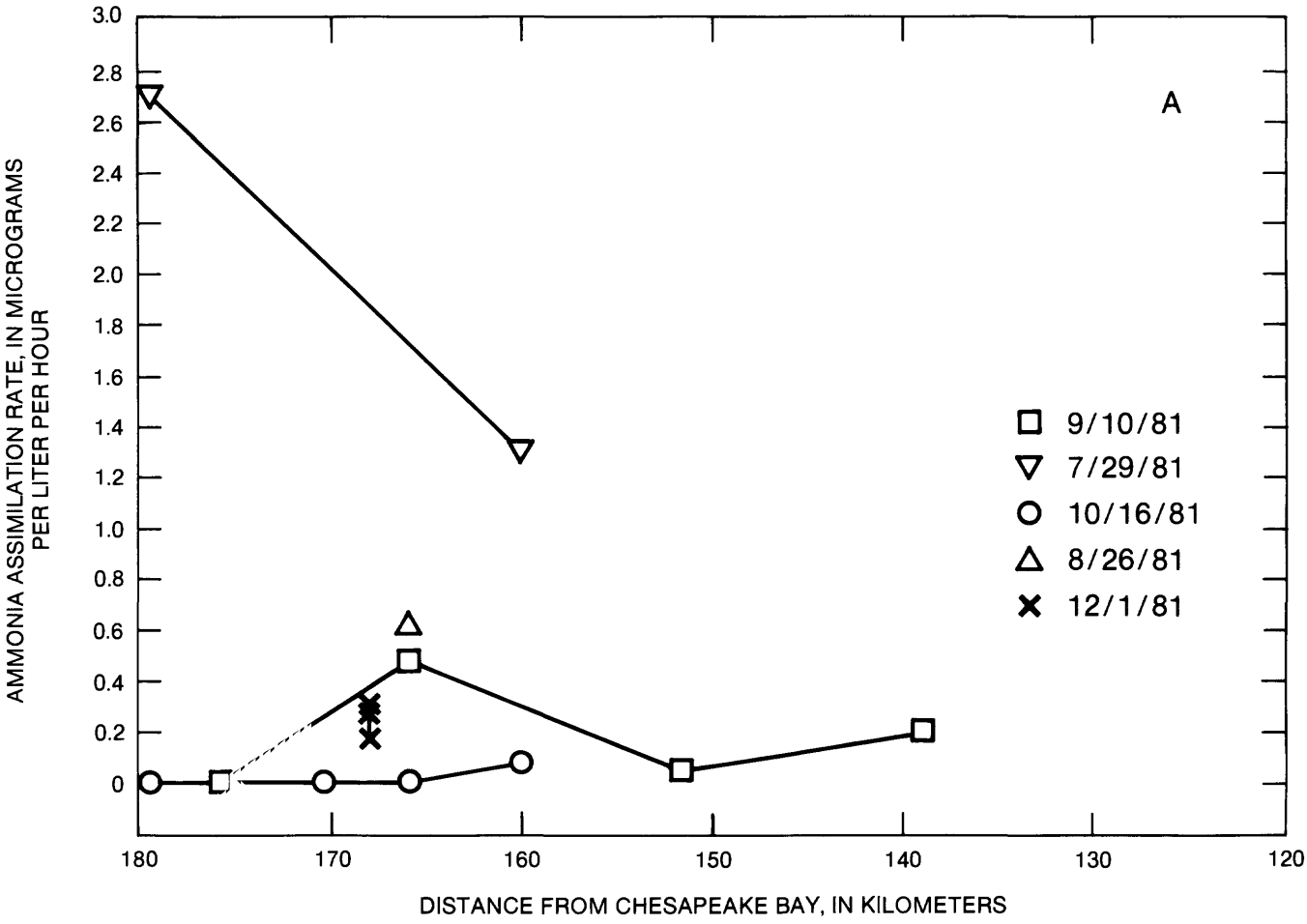

Figure 17A. Ammonia assimilation rates determined from uptake of $H^{14}CO_3$ in parallel incubations of nitrification blocked (N-Serve) and unblocked samples as a function of distance from Chesapeake Bay, July–December 1981.

determinations on samples taken from the Blue Plains STP unchlorinated primary and tertiary and chlorinated tertiary effluent streams. Raw samples as well as tenfold and hundredfold dilutions were incubated. Interestingly, the most probable number values increased with increasing dilution of the raw sample. One interpretation of this result is that some growth-inhibiting substance is present and that the dilution minimizes the effect of the inhibiting substance. However, there was not the expected predominance of *Nitrobacter* over *Nitrosomonas* in either the raw samples or the dilutions.

Another explanation of the observed predominance of *Nitrobacter* over *Nitrosomonas* in the September 1981 samples is that it is in response to higher loads of nitrite from the Blue Plains STP. Because the nitrification process in advanced wastewater treatment involves bacterial oxidation of ammonia to nitrite and then to nitrate, an incomplete reaction could result in increased loads of nitrite being discharged into the tidal river. The loading values for 1980 and 1981 for Blue Plains (Coupe and Webb, 1984) were computed as nitrite plus nitrate, so it is not possible to verify this hypothesis directly. The nitrite concentrations in samples collected in 1981 are not significantly different from concentrations in 1980 samples. If nitrite were actively oxidized in the water column, a comparison of nitrite concentrations between the 2 years would not be a valid test of the hypothesis. The hypothesis cannot be rejected, however, because the first-order nitrification rate constants were longitudinally uniform (fig. 17C). The nitrification rates were determined using a method (Somville, 1978) that measures only the first stage of nitrification (ammonia oxidation). It might be possible to have a population of *Nitrobacter* actively oxidizing nitrite and yet determine low ammonia-oxidation rates. Similarly, the hypothesis cannot be rejected because water-column nitrite concentrations were similar in 1980 and 1981. Time-course sampling of bacterial and substrate concentrations might allow inferences about activity, but inferring activity from isolated values of substrate concentrations in the water column is not valid.

Other studies have found that nitrification often occurs in the surficial sediments if dissolved oxygen is

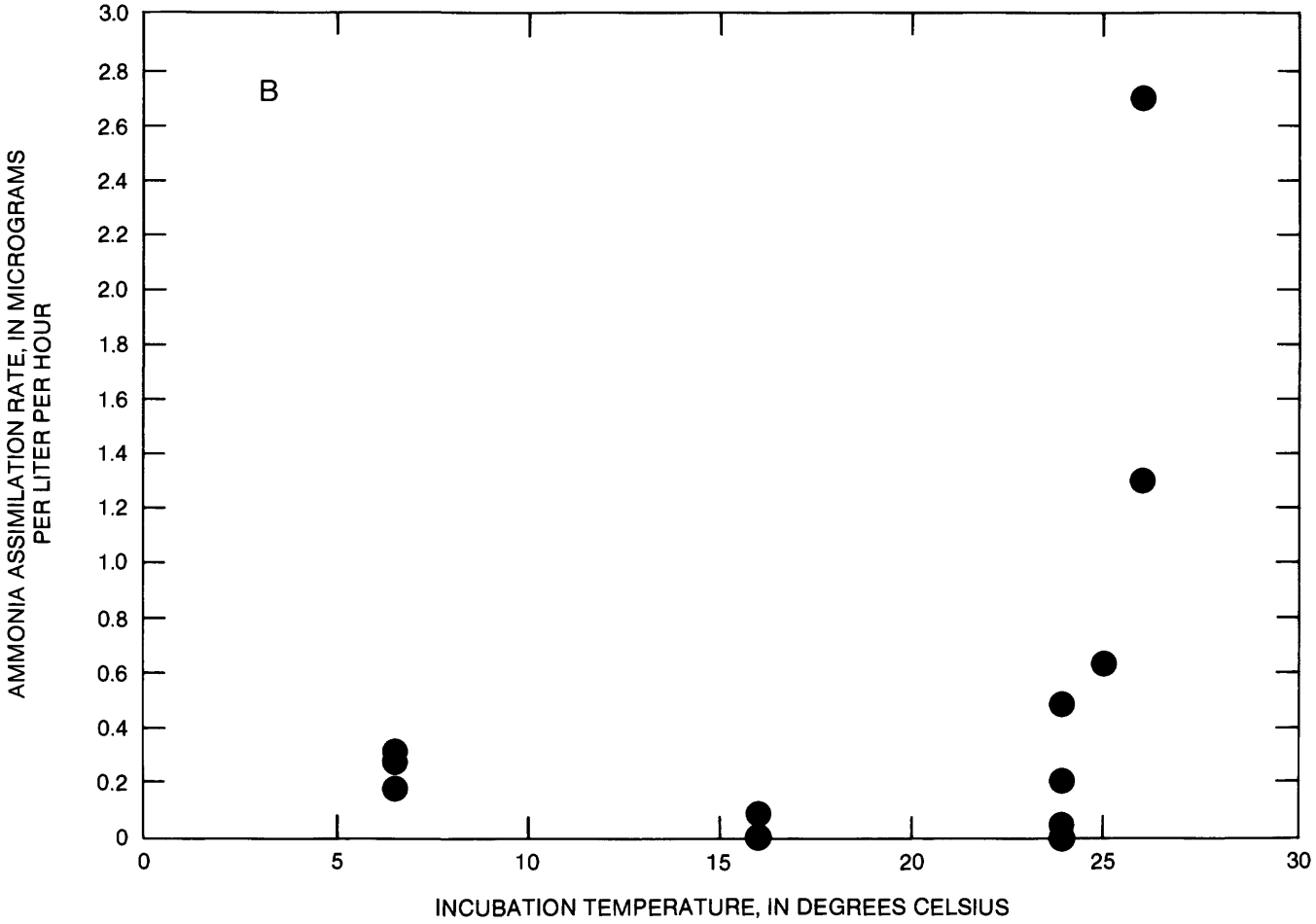

Figure 17B. Ammonia assimilation rates as a function of incubation temperatures, July–December 1981.

present in the water column overlying the sediments (Jenkins, 1981). The most probable number values for *Nitrosomonas* and *Nitrobacter* in surficial sediment samples collected in 1981 show that on a volumetric basis there was as much as three orders of magnitude more nitrifying bacteria in the sediment than in the water column. The most probable number values for sediment samples from the same site collected on different dates were not significantly different. Therefore, all the sediment most probable number data from the same site were pooled; the means and standard errors of the means are plotted in figures 20A and 20B. The large standard errors are a reflection of the sampling variability and the large analytical variability inherent in determining the most probable number in sediment samples. Nevertheless, there is a trend toward higher most probable number values of both *Nitrosomonas* and *Nitrobacter* in the sediments (river kilometer 168) near the area of the Blue Plains STP outfall (river kilometer 170). This is consistent with a study by McElroy and others (1978), who suggested that nitrification in the tidal river sediments was responsible for the longitudinal variations of N_2O they observed in the water column. McElroy and others (1978) reported that the peak concentration of N_2O, which is a reaction product of nitrification, was often in the vicinity of the Blue Plains STP outfall.

In summary, the results of these investigations in 1980 and 1981 show that the rates of ammonia oxidation were low (<2.7 μg/L (micrograms per liter) of N per hour), that there was a shift from *Nitrosomonas* to *Nitrobacter* predominance between September 1980 and September 1981, and that numerically there were more nitrifying bacteria in the surficial sediments than in an equal volume of the overlying water.

Because rates of nitrification in the sediments were not measured, the relative importance of the sediments to the water column cannot be determined. A qualitative change in the distribution of ammonia, nitrite, and nitrate was observed downstream from the Blue Plains STP compared with earlier studies. In the 1970's, several studies (Jaworski and others, 1972) showed downstream progression of ammonia, nitrite, and nitrate. This was interpreted as evidence that nitrification was occurring in the water column. The longitudinal profiles for 1979–81 show no evidence of this downstream progression. It is not clear

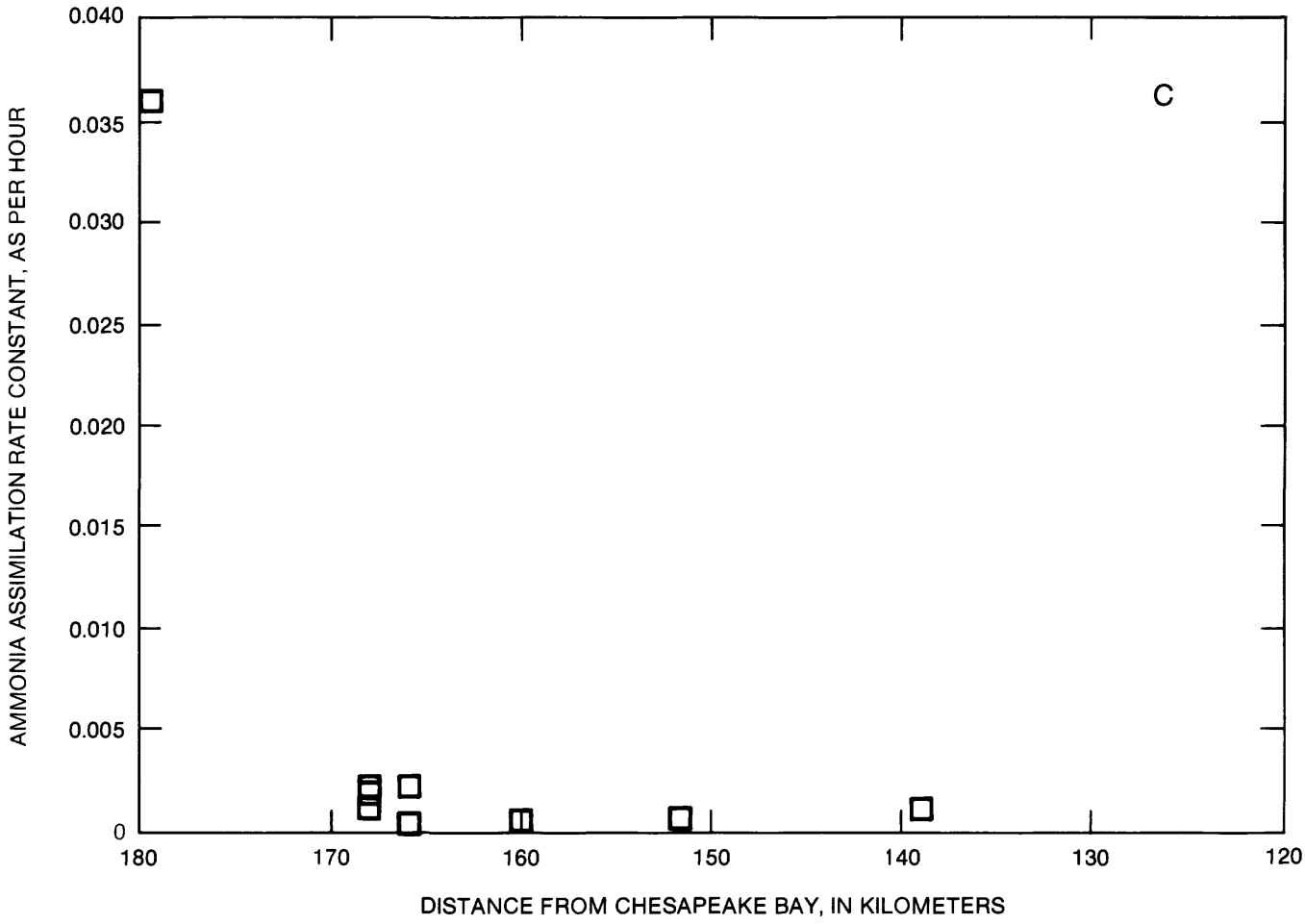

Figure 17C. Ammonia assimilation rate constants, at 20 degrees Celsius, as a function of distance from Chesapeake Bay, July–December 1981.

what changes in the tidal river or at the Blue Plains STP could account for such a difference. However, if the downstream progression of ammonia, nitrite, and nitrate is evidence of water-column nitrification, it follows that the lack of such a progression implies little or no water-column nitrification.

Wofsy and others (1981), using data collected during 1970–79, found that the mass of ammonia in the tidal river increased as a linear function of discharge. They attributed this to an increase in the nitrification rate as discharge decreased. The present study found no correlation between the mass of ammonia and river discharge for the data collected prior to advanced wastewater treatment. This indicates that the first stage of nitrification (ammonia oxidation to nitrite) was probably not as significant in the water column during the study period as had been observed in earlier studies. This result was not anticipated, and the reasons for the apparent change in a basic water-column process in a major system are not apparent.

Exchange of Benthic Nutrients

The exchange of dissolved substances across the sediment-water interface is an important process affecting nutrient concentrations in rivers and estuaries (Nixon and others, 1976; Billen, 1978; Peterson, 1979). The direction of the net exchange depends on the processes supplying or using the particular constituent and the relative concentrations in the sediment and water column. Mechanisms affecting the physical transfer include molecular diffusion, stirring of the sediments by currents (Hammond and others, 1977; Vanderborght and others, 1977) and benthic invertebrates (Robbins and others, 1977), irrigation of sediments by macrobenthos (Goldhaber and others, 1977; Grundmanis and Murray, 1977; Hammond and Fuller, 1979; Aller and Yingst, 1980; McCaffrey and others, 1980), and transport through bubble tubes (Martens and others, 1980; Klump and Martens, 1981).

Two general methods have been used to estimate nutrient flux rates. The diffusive benthic flux method

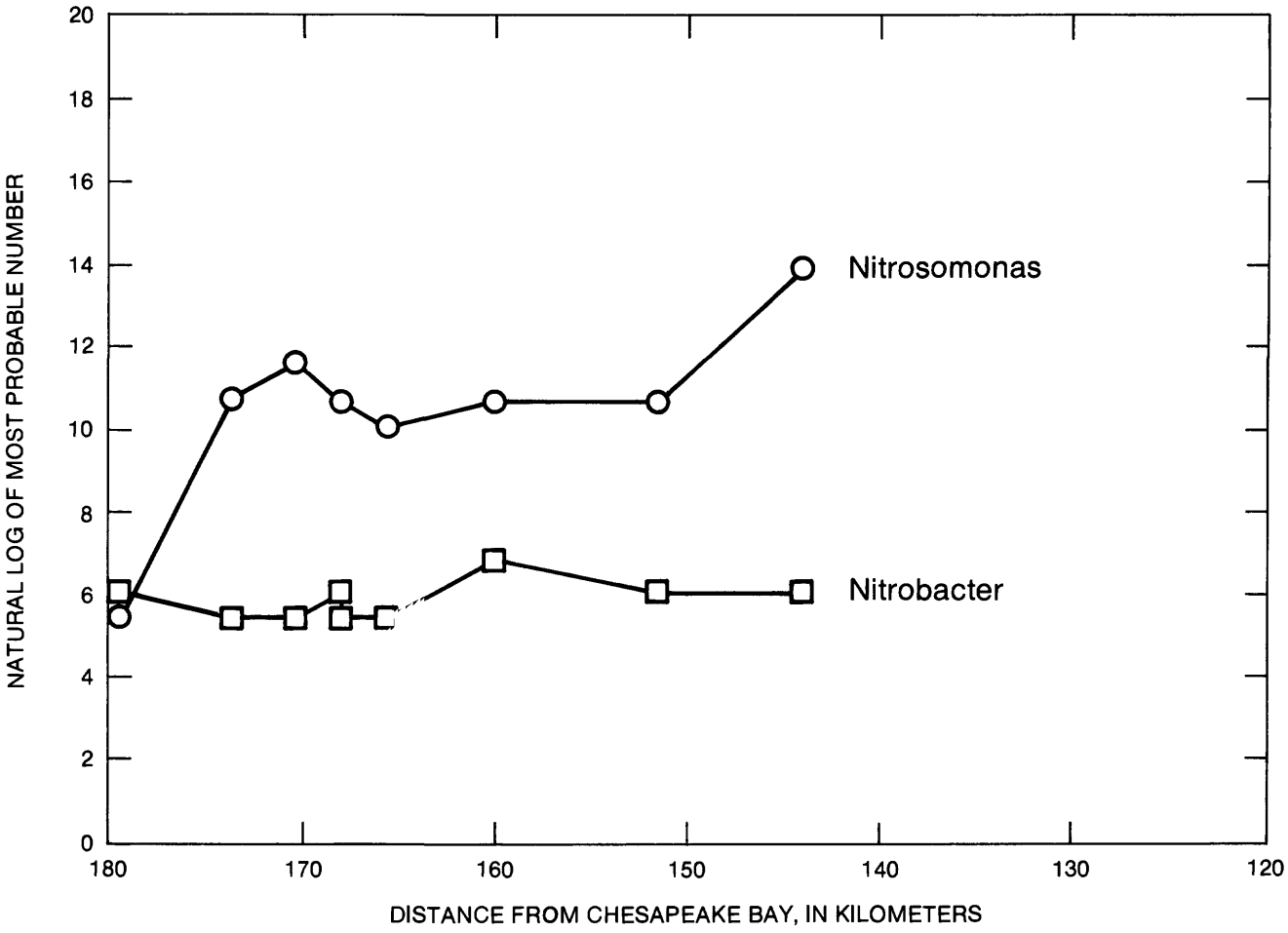

Figure 18. Natural logarithm of the most probable number of *Nitrosomonas* and *Nitrobacter* in depth-integrated, composited water samples as a function of distance from Chesapeake Bay, September 15, 1980.

(Callender and Hammond, 1982) uses the profile of dissolved nutrients in the interstitial water of sediments and Fick's law to calculate the diffusive flux rate. The in situ benthic-flux method (Boynton and others, 1980; Klump and Martens, 1981) involves trapping a known volume of water over a known surface area of sediment and measuring the nutrient concentration changes in the water over time.

Callender and Hammond (1982) showed that in situ flux rates were often higher than diffusive flux rates, because, in areas having significant benthic invertebrate populations, irrigation of worm tubes facilitates a higher rate of transfer of nutrients from the sediments to the water column. Callender and Hammond reported mean flux rates for in situ ammonia and nitrate in the tidal Potomac of $5.6\pm0.83\times10^{-6}$ and $-0.91\pm3.1\times10^{-6}$ $(mg/m^2)/s$ (milligrams per square meter per second), respectively. These flux rates were converted to loads using a surface area of 5.56×10^7 m^2 (square meters) for the tidal river (between Memorial Bridge and Hallowing Point) (Cronin, 1971), with the result for ammonia and nitrate of 5.2 ± 1.3 and -0.9 ± 2.9 Mg/d (megagrams per day), respectively. The negative sign for nitrate is interpreted to mean that the nitrate is moving from the water column into the sediments.

Denitrification

Denitrification is a bacterially mediated process wherein the micro-organisms use nitrate as the terminal hydrogen acceptor. It is potentially important in aquatic environments because the end products are gases, primarily N_2, which can be lost from the system through volatilization (Hattori, 1983). Unless anoxic conditions develop in the water column, one would normally expect any denitrification to occur in the anoxic sediment layer immediately below the oxidized surficial sediments. Estimates of the percentage of total nitrogen input removed by denitrification range from 5 to 6 percent in Duffin Creek, Ontario, Canada (Hill, 1979), to 20 percent in the tidal Potomac River (Elkins and others, 1981).

It was assumed at the start of this study that denitrification would not be important in the water column because there was no reason to believe there would be any

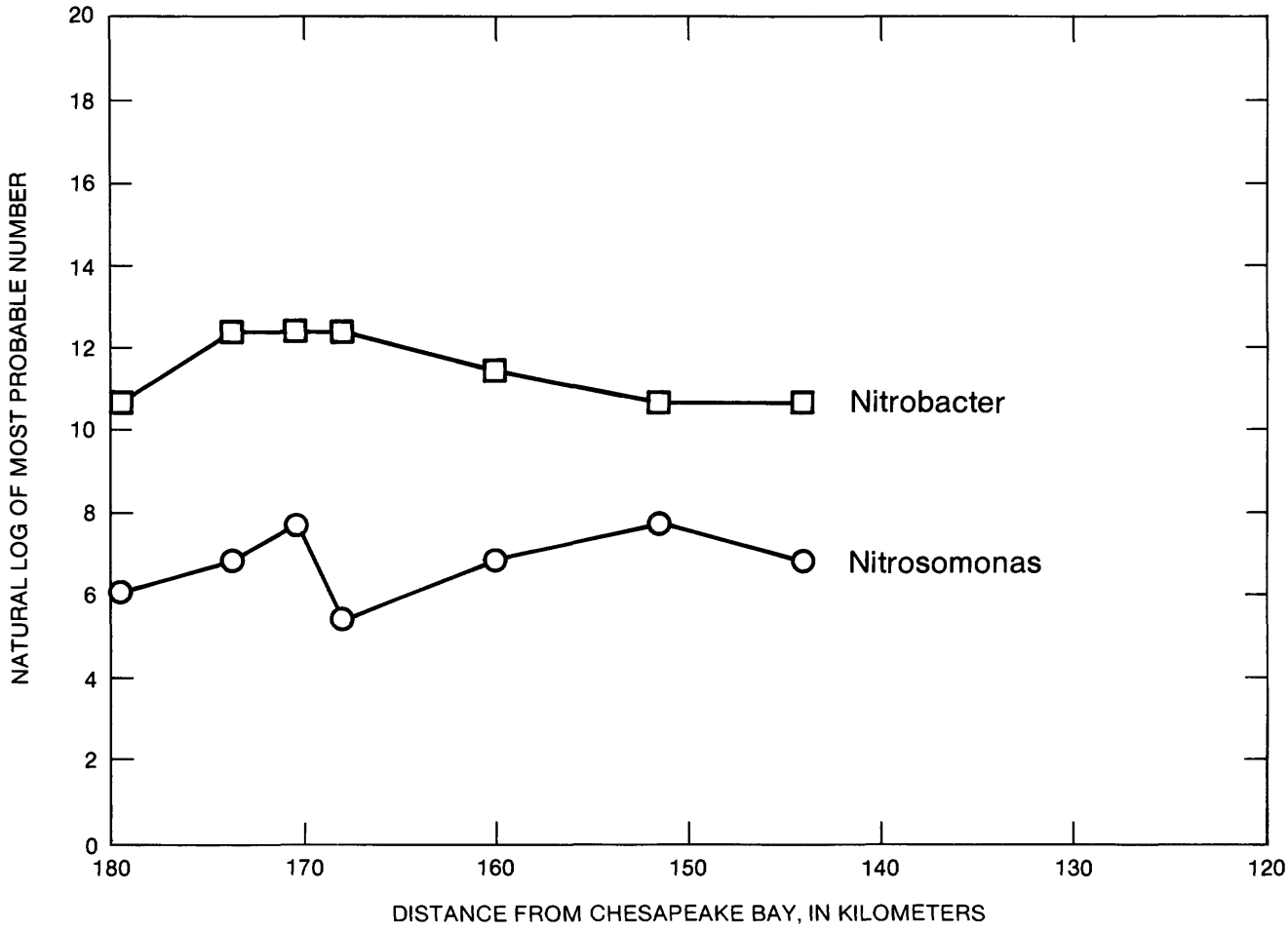

Figure 19. Natural logarithm of the most probable number of *Nitrosomonas* and *Nitrobacter* in depth-integrated, composited water samples as a function of distance from Chesapeake Bay, August 26, 1981.

anoxic periods. However, it appears from the mass-balance calculations that there was a major sink for nitrate nitrogen. The nitrate uptake rates determined from the ^{15}N uptake studies seem to rule out phytoplankton uptake of nitrate as the only removal process. This indicates that denitrification in the sediments may be causing nitrate removal. This is an important point because after September 1980 most of the nitrogen loaded into the Potomac from the Blue Plains STP was in the form of nitrate.

One method to estimate benthic denitrification would be to use the in situ benthic flux rate for nitrate from the work of Callender and Hammond (1982). However, since water-column nitrate concentrations were higher in 1981 samples, one might expect benthic denitrification to be higher than when the in situ benthic flux rates were measured in 1979. In addition, the in situ benthic flux rates for nitrate were quite variable, only a few measurements were reported, and the technique measures the net effect of all nitrate-demanding and nitrate-producing processes.

Another method that can be used to estimate sediment denitrification rates is a process model. Processes demanding or producing nitrate are summarized in the following equation:

$$Net\ nitrate = Nit_{NO_2} + BNit_{NO_2} - PU_{NO_3} - DEN_{NO_3}, \quad (7)$$

where

Net nitrate=net source-sink rate calculated from mass-balance calculations (table 3), in megagrams;

Nit_{NO_2}=water-column nitrification of NO_2 to NO_3, in megagrams per day;

$BNit_{NO_2}$=benthic nitrification of NO_2 to NO_3, in megagrams per day;

PU_{NO_3}=phytoplankton uptake of NO_3, in megagrams per day; and

DEN_{NO_3}=benthic denitrification of NO_3 to NO_2, in megagrams per day.

As previously discussed, water-column nitrification (Nit_{NO_2}) for the July 30–August 20, 1980, and August 6–26, 1981, periods is assumed to be 3.8 and 1.2 Mg/d. It will be assumed that water-column nitrification for the

Table 7. Most probable number of nitrifying bacteria in Blue Plains Sewage-Treatment Plant effluent at different dilutions

[n.d., not determined; <, less than]

	Unchlorinated tertiary-treated water			Chlorinated tertiary-treated water			Unchlorinated primary-treated water		
	1:1	1:10	1:100	1:1	1:10	1:100	1:1	1:10	1:100
Nov. 6, 1981									
Nitrosomonas[1]	430	2,300	23,000	9,800	9,300	43,000	n.d.	n.d.	n.d.
Nitrobacter[1]	230	2,300	23,000	<30	<300	<3,000	n.d.	n.d.	n.d.
Jan. 15, 1982									
Nitrosomonas[1]	9,300	15,000	9,000	4,600	4,300	0	3,900	9,300	23,000
Nitrobacter[1]	430	2,300	23,000	<30	<300	<30,000	230	2,300	9,000

[1]All values are MPN/100 mL corrected for the sample dilution; a sample diluted 1:100 with a resulting MPN of 230 would be reported as 23,000.

December 15, 1980–February 4, 1981, period was zero, because previous studies have shown that nitrifying bacteria at temperatures below 10 °C have only 10 percent of the activity at 35 °C (Jones and Hood, 1980). The net effect of benthic nitrification is included in the in situ benthic flux (*BF*) measurements:

$$BF_{NO_3}=BNit_{NO_2}-DEN_{NO_3}. \quad (8)$$

Therefore, equation 7 simplifies to

$$Net\ nitrate=Nit_{NO_2}+BF_{NO_3}-PU_{NO_3}. \quad (9)$$

In 1980, before the switch to advanced wastewater treatment at the Blue Plains STP, water-column nitrate concentrations were similar to the nitrate concentrations in 1979 samples. Therefore, for the 1980 period the BF_{NO_3} value calculated from the data of Callender and Hammond (1982) was used to solve equation 9 for PU_{NO_3} (table 8). For the summer 1981 and winter 1980–81 periods, using the same value for BF_{NO_3} would not be justified, and no experimental values were available. Therefore, the PU_{NO_3} values for the winter 1980–81 and summer 1981 periods were estimated by multiplying the 1980 PU_{NO_3} value by the ratio of the depth-integrated primary productivity at Hatton Point in 1981 and 1980 (Cohen and Pollock, 1983). The resulting rate for PU_{NO_3} for the summer 1981 period is about one-third the rate for the summer 1980 period. This is consistent with the lower net increase in chlorophyll computed in the mass-balance calculations (table 3).

Equation 9 was rearranged and solved for BF_{NO_3} using the estimated PU_{NO_3} values. The result for the summer of 1981 (table 8) was 13 times the value Callender and Hammond (1982) reported for 1979. It is interesting to speculate on whether the shift to nitrate predominance may have reduced phytoplankton biomass and increased nitrogen loss from the tidal river through increased sediment denitrification.

Sedimentation of Particulate Material

Nitrogen can also be removed from the tidal-river water column when particulate material containing nitrogen falls to the surface of the sediments. The sedimentary particulate material could be phytoplankton cells, bacterial cells, organic material transported from upstream, or nitrogen adsorbed to inorganic material. There was no attempt in this study to measure the sedimentation rate directly.

One method of estimating sedimenting nitrogen is to use the mass-balance results with a process model. In general, the effects of individual processes tend to cancel out one another when considering a mass balance for total nitrogen ($TN=DON+PON+NH_4+NO_2+NO_3$), unless the process involves addition or removal of a nitrogen constituent from the water column, as follows:

$$Net\ total\ nitrogen = BF_{NH_4}+BF_{NO_3}+NFIX-SED_{PON}-VOL_{NH_4}, \quad (10)$$

where

Net total nitrogen=net source-sink rate computed from mass-balance calculations, in megagrams per day;

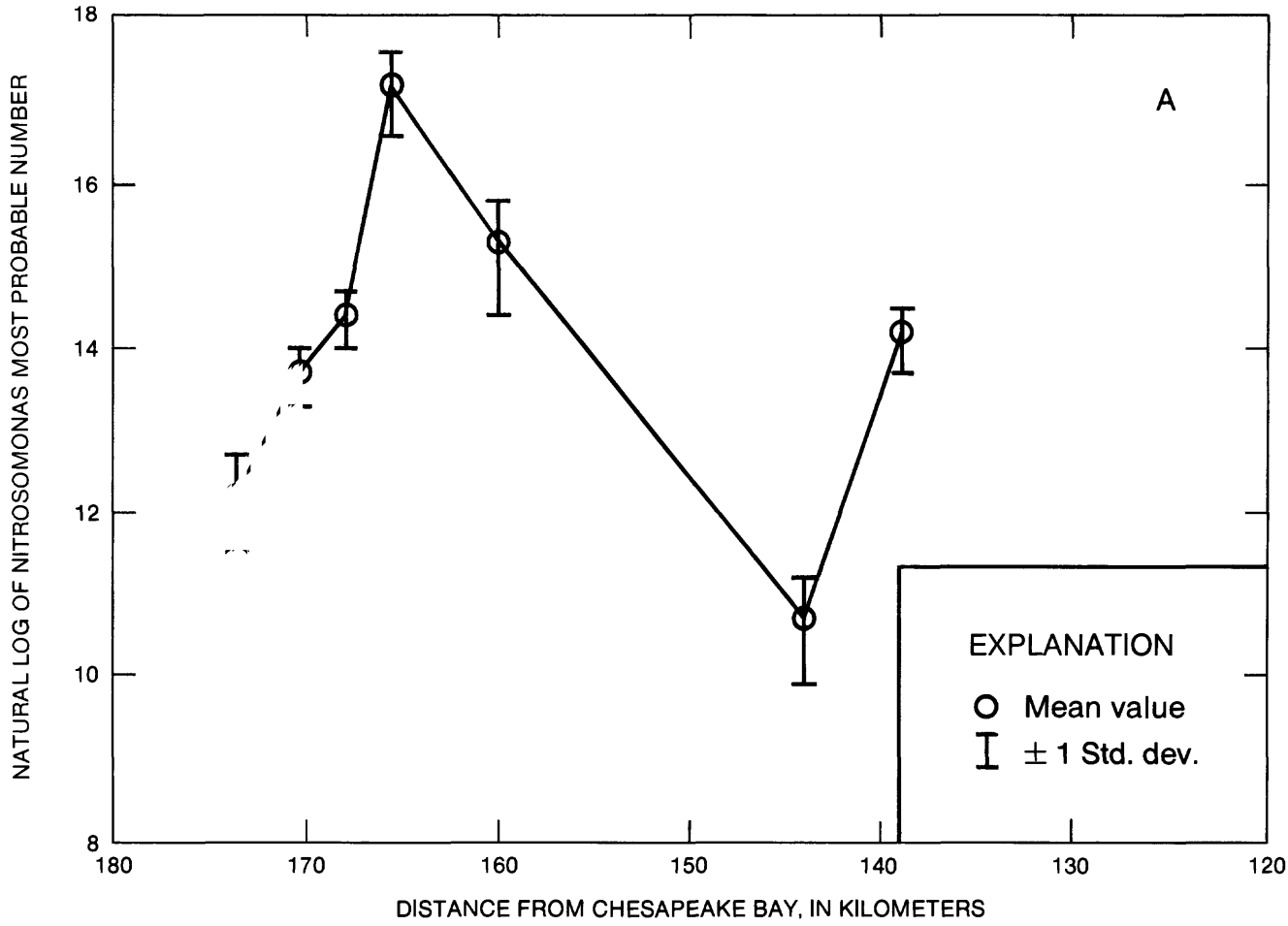

Figure 20A. Natural logarithm of the most probable number of *Nitrosomonas* in surficial sediments as a function of distance from Chesapeake Bay.

BF_{NH_4}=benthic flux of ammonia, in megagrams per day;

BF_{NO_3}=benthic flux of nitrate, in megagrams per day;

$NFIX$=nitrogen fixation, in megagrams per day;

SED_{PON}=sedimentation of particulate organic nitrogen out of the water column, in megagrams per day; and

VOL_{NH_4}=volatilization of ammonia from the water column to the atmosphere, in megagrams per day.

The process of nitrogen fixation involves the reduction of nitrogen gas to ammonia, which is used for subsequent protein synthesis. The very stable nitrogen-gas triple bond is split by the enzyme system, nitrogenase. The process of nitrogen fixation is mediated by several genera of bacteria and blue-green algae. In aquatic environments the latter are probably the most common nitrogen fixers (Horne and Fogg, 1970; Horne and Goldman, 1972). The role of nitrogen-fixing bacteria living in surface muds has not been determined, but the short-term contributions appear to be negligible (Horne, 1977).

For eutrophic systems, the possibility of nitrogen fixation has been of concern in nutrient-abatement programs. If controls are placed on nitrogen inputs to control algal biomass, nitrogen fixation could supply unwanted nitrogen. The role of nitrogen fixation in large, slow-moving rivers like the tidal Potomac has not been thoroughly studied. It was hypothesized that nitrogen fixation was not likely to be a significant nitrogen-cycle process in the tidal Potomac during the study period since it was not likely to be important where large amounts of ammonia or nitrate were readily available for growth (Fogg, 1962).

The distribution of ammonia between the dissolved nonionized molecule (NH_3) and its ionic form (NH_4^+) is pH dependent. In aquatic systems having a pH below 7, more than 90 percent of the ammonia is in the ionic form. At pH values higher than 7, which are common during the day in highly productive waters, equilibrium processes shift the distribution in favor of the gaseous form (Goering, 1972).

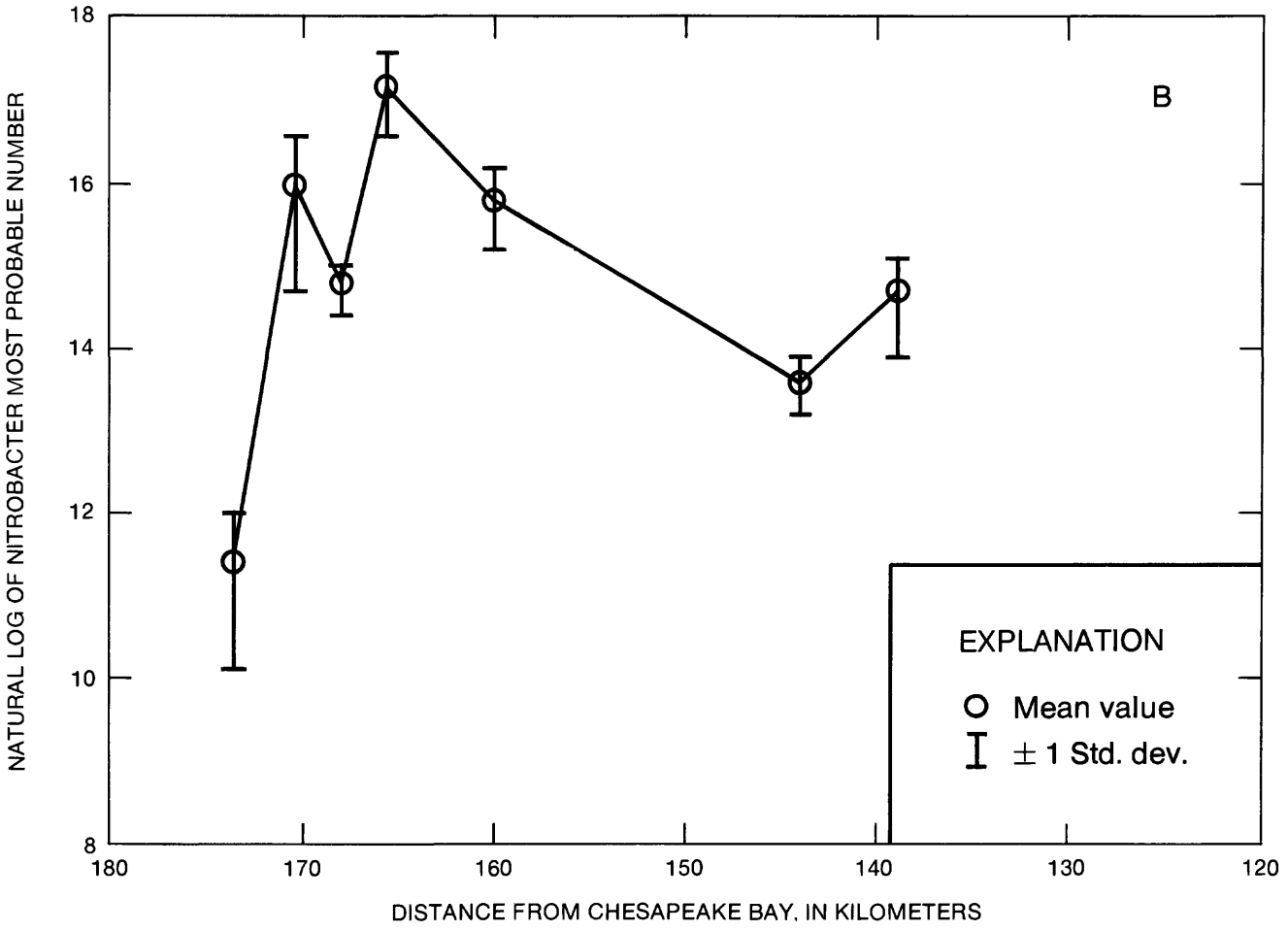

Figure 20B. Natural logarithm of the most probable number of *Nitrobacter* in surficial sediments as a function of distance from Chesapeake Bay.

Ammonia is subject to transfer from solution to the atmosphere, and the rate of transfer is partly a function of temperature, wind velocity, and water turbulence. Several studies have concluded that volatilization losses of ammonia can be significant (Hutchinson and Viets, 1969; Stratton, 1969). In this study, pH values measured in the field rarely exceeded 8.0, so it was assumed that losses of ammonia due to volatilization were insignificant.

If it is assumed that both *NFIX* and VOL_{NH_4} were zero, then equation 10 can be simplified and solved for SED_{PON}:

$$SED_{PON}=BF_{NH_4}+BF_{NO_3}-Net\ total\ nitrogen. \quad (11)$$

The values for net total nitrogen were obtained by summing the net sources and sinks for individual nitrogen species from table 3. The benthic flux terms, discussed previously, represent a major uncertainty in the calculation. Table 9 summarizes the values of the terms used to solve for SED_{PON} (eq. 11) for each of the sampling periods and the calculated value of SED_{PON}. If the benthic flux terms were in error by 100 percent, the resulting SED_{PON} would change by approximately 20, 30, and 40 percent for the summer of 1980, the summer of 1981, and the winter of 1980–81, respectively. Cohen and others (1984) reported that large populations of the Asian clam *Corbicula fluminea* were found between Alexandria and Hallowing Point. They estimated, on the basis of feeding studies, that the clams removed substantial amounts of phytoplankton from the water column. This mechanism for removal of phytoplankton would be indistinguishable from settling in the calculations summarized in table 9.

Obviously, some of the particulate nitrogen sedimenting to the bottom is recycled back to the water column or is lost via denitrification. The net effect of this recycling is contained in the benthic flux terms. The magnitude of this calculated sink for particulate nitrogen is on the same order as the sum of all external loads (river, point, and nonpoint) of all forms of nitrogen to the tidal river (table 10).

These results are consistent with studies of sediment trapping efficiency conducted in Chesapeake Bay. Biggs (1970), using a box model approach, concluded that 90

Table 8. Values of terms used to calculate in situ benthic flux rates for three periods after the switch to advanced wastewater treatment at the Blue Plains Sewage-Treatment Plant

[In megagrams per day. Negative numbers for BF_{NO_3} indicate that nitrate has moved from the water column into sediments]

	July 30, - August 20, 1980	August 6, - August 26, 1981	December 15, 1980 - February 4, 1981
Net Nitrate[1]	-5.8	-13	0.28
Nit_{NO_2}	3.8	1.2	0
PU_{NO_3}	7.9	[2]2.6	[3]5.1
BF_{NO_3}	[4]-1.7	[5]-12.	[5]5.4

[1]From mass-balance calculations (table 3).

[2]Computed by multiplying the value of PU_{NO_3} for the July 30 to August 20, 1980, period times the ratio of the mean ^{NO_3} depth-integrated primary productivity (at Hatton Point, Md.) for July 8 to August 20, 1981, divided by the mean depth-integrated primary productivity (at Hatton Point, Md.) for July 23 to August 26, 1980. The depth-integrated primary productivity values were obtained from table 7 in Cohen and Pollock (1983).

[3]Computed by multiplying the value of PU_{NO_3} for the July 30 to August 20, 1980, period times the ratio of the mean ^{NO_3} depth-integrated primary productivity (at Hatton Point, Md.) for December 16, 1980 to February 5, 1981, divided by the mean depth-integrated primary productivity (at Hatton Point, Md.) for July 23 to August 26, 1980. The depth-integrated primary productivity values were obtained from table 7 in Cohen and Pollock (1983).

[4]Computed from Callender and Hammond (1982) benthic flux data (table 1).

[5]Calculated from equation (9) by solving for BF_{NO_3} and substituting the values for net nitrate and PU_{NO_3} shown in this ^{NO_3} column.

Table 9. Values of terms used to calculate particulate nitrogen settling rate, for three periods, in the tidal Potomac River

[In megagrams per day]

Term	Period		
	July 30 - Aug. 20, 1980	Aug. 6 - Aug. 26, 1981	Dec. 15, 1980 Feb. 4, 1981
[1]BF_{NH_4}	5.2	5.2	5.2
[2]BF_{NO_3}	- 0.90	- 12	5.4
[3]TN	- 23	- 28	- 7.1
[4]SED_{PON}	+ 27	+ 21	+ 18

[1]From Callender and Hammond, 1982.

[2]From table 8.

[3]From table 3 where TN=total nitrogen=ammonia+nitrate+nitrite+dissolved organic nitrogen+particulate organic nitrogen.

[4]Calculated from equation 11 by solving for SED_{PON} and substituting the value for BF_{NH_4}, BF_{NO_3}, and TN shown in this column.

Table 10. Comparison of external loading of all forms of nitrogen from all sources with calculated sedimentation rates for particulate nitrogen and denitrification rates

Average annual daily loads of all forms of N from external sources (river, point and non point) (megagrams per day)	Year	Sedimentation of PON[1,2] (megagrams per day)	Denitrification[2] (megagrams per day)	Period
38	1980	27	0.9	July 30 - Aug. 20, 1980
		18		Dec. 15, 1980 - Feb. 4, 1981
38	1980	21	11.0	Aug. 6 - Aug. 26, 1981

[1]PON is particulate organic nitrogen.

[2]The sedimentation and denitrification rates are for the reach of the tidal Potomac River between Memorial Bridge and Hallowing Point, Va. which has an area, excluding tributaries, of 54.7 square kilometers (Cronin, 1971).

percent of the sediment input to Chesapeake Bay by the Susquehanna River was trapped in the northern third of the estuary. Bennett (written commun., 1987) summarized the monthly budgets for dissolved and particulate nitrogen in the tidal Potomac River using a box model approach. Trapping efficiencies (the percentage of incoming material that is not transported out) for total nitrogen from Bennett's box model results for August 1980, August 1981, and December 1980–January 1981 were 61, 66, and 39 percent, respectively. Bennett's approach treats any losses of nitrogen from the water column by denitrification as sedimentation, and his values are for a slightly larger area of the tidal Potomac River (Chain Bridge to Quantico), but they are on the same order as reported in table 10 of this report.

SUMMARY

On an annual basis, river-supplied nitrate is the predominant form of nitrogen supplied to the tidal Potomac River from external sources. Much of this nitrate is associated with high-flow periods that have rapid transit times through the tidal river. Prior to the fall of 1980, depth-integrated, composited ammonia concentrations were high est (more than 1.00 mg/L as N) during summer periods near Alexandria, Va., because of loading from the nearby Blue Plains STP and reduced river discharge. After the fall of 1980, initiation of advanced wastewater treatment at the Blue Plains STP reduced ammonia loading to the river by 90 percent and increased nitrate loading by a similar percentage. As a result, concentrations of ammonia during the 1981 low-flow season were less than 0.20 mg/L as N at Alexandria, while nitrate concentrations were greater than 1.50 mg/L as N. Despite the reduced availability of ammonia, phytoplankton were found to prefer ammonia to nitrate unless ammonia concentrations were less than 0.10 mg/L as N.

Nitrification-rate studies during 1981 indicate that rates did not vary with sample location, except for one sample from near the head of the tidal river (river kilometer 180). The numbers of *Nitrobacter* bacteria were highest in samples from near the Blue Plains STP and were greater than the numbers of *Nitrosomonas* bacteria. The predominance of *Nitrobacter* bacteria seemed to be associated with advanced wastewater treatment at Blue Plains. Before advanced wastewater treatment, *Nitrosomonas* were numerically predominant and had the highest numbers near the Blue Plains STP. These results could be due to loading of nitrifying bacteria in the Blue Plains sewage effluent that were inhibited from further growth by an inhibitory substance; a second explanation is that the method used to measure nitrification rates measured only the ammonia oxidation stage. It is not possible to reject either mechanism on the basis of the data available.

It is estimated that sediment denitrification removed 10 times as much nitrate from the water column during a summer period in 1981 as during a similar period in 1980. This may be due to the greater supply of nitrate during 1981, but there is no direct evidence to accept or reject this hypothesis. The rate of particulate nitrogen sedimentation was calculated to be approximately the same as the annual daily rate of supply to the tidal river from external sources.

Mass-balance calculations indicate that the tidal Potomac River functioned as a net trap for all nitrogen constituents during both the 1980 and 1981 summer periods. However, during the 1980–81 winter period, some ammonia and nitrate was transported out of the tidal Potomac River into the transition zone.

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METRIC CONVERSION FACTORS

For readers who wish to convert measurements from the metric system of units to the inch-pound system of units, the conversion factors are listed below.

Multiply metric unit	By	To obtain inch-pound unit
	Length	
millimeter (mm)	0.03937	inch
	0.003281	foot
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
	Area	
square meter (m^2)	10.76	square foot
square kilometer (km^2)	0.3861	square mile
	Volume	
cubic meter (m^3)	264.2	U.S. gallon
	35.31	cubic foot
liter (L)	0.2642	U.S. gallon
milliliter (mL)	2.642×10^{-4}	U.S. gallon
microliter (μL)	2.642×10^{-7}	U.S. gallon
	Flow	
cubic meter per second (m^3/s)	35.31	cubic foot per second
	Weight	
gram (g)	2.205×10^{-3}	pound
megagram (Mg)	1.102	short ton (2,000 pounds)
milligram (mg)	2.205×10^{-6}	pound
microgram (μg)	2.205×10^{-9}	pound
	Concentration	
grams per liter (g/L)	1.0	parts per thousand
milligrams per liter (mg/L)	1.0	parts per million
micrograms per liter (μg/L)	1.0	parts per billion
	Flux rate	
milligram per square meter per second [$(mg/m^2)/s$]	2.045×10^{-7}	pounds per square foot per second [$(lb/ft^2)/s$]
	Radiometric unit of measure	
calories per square centimeter per day [$(cal/cm^2)/d$]	0.4847	watts per square meter
	Temperature	
Temp °F=1.8(temp °C)+32		

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