

# Sediment/Water-Column Flux of Nutrients and Oxygen in the Tidal Patuxent River and Estuary, Maryland

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# Sediment/Water-Column Flux of Nutrients and Oxygen in the Tidal Patuxent River and Estuary, Maryland

By Bruce M. Lantrip, Robert M. Summers, Daniel J. Phelan, and William Andrlle

## ABSTRACT

An intensive study was made of the flux of nutrients and oxygen between the water column and the sediments of the tidal Patuxent River and Estuary. Eleven stations, located between the mouth of the estuary and the head of navigation, were monitored on a quarterly basis over a 2-year period. Flux rates were calculated based on the change in concentration of various nutrient species within in situ benthic respirometers. The constituents measured included dissolved ammonium ( $\text{NH}_4^+$ ), dissolved ammonium plus dissolved organic nitrogen ( $\text{NH}_4^+$  + organic N), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), dissolved reactive phosphorus, total dissolved phosphorus, and oxygen ( $\text{O}_2$ ).

The data are presented graphically and summarized by median and quartile values. For the comparison of different salinity, oxygen, and hydrodynamic regimes, stations were segregated into tidal river, transition, estuary, and anoxic estuary zones. In general, all sediments were a source for ammonium and a sink for nitrite plus nitrate. The estuarine anoxic sediment was a consistently higher source of ammonium, while the tidal river showed greater flux of nitrite plus nitrate in both directions. Dissolved reactive phosphorus flux was generally into the sediment in the tidal river and transition zones and from the sediment in the estuary. Sediment oxygen demands were variable, but median values were generally consistent among the different zones.

A major feature of the data is the large spatial and temporal variability in sediment nutrient flux and oxygen demand. This variability reflects the influence but lack of dominance of many interacting factors, including sediment nutrient concentrations, sediment grain size, water temperature, oxygen availability, benthic macro-organism and micro-organism populations, and meteorological conditions. Part of this variation is due to spatial or seasonal differences in controlling factors, but year-to-year differences at individual stations during a given season are also large.

## INTRODUCTION

The basic objective of this study was to determine the magnitude and spatial and temporal variability of the

benthic flux of nitrogen and phosphorus species and the sediment oxygen demand over the tidal Patuxent River and Estuary system. Water-column and sediment characteristics were measured concurrently to provide the basis for assessing the degree of influence of these factors over sediment nutrient fluxes and sediment oxygen demand.

Bottom sediment affects the quality of the overlying water through the release of nutrients to the water column and through the oxygen demand exerted by the metabolism of organic materials in the sediment. Previous studies on the Patuxent and other estuaries have indicated that releases from the sediments are important sources of the nutrients fueling eutrophication (Boynton and others, 1982; Callender and Hammond, 1982). Sediment oxygen demand contributes to the depressed dissolved oxygen concentrations observed in the deeper, stratified portions of estuaries (Boynton and others, 1982). However, in the tidal Patuxent River and Estuary, these factors have not been quantified sufficiently to address basic water quality management issues (O'Connor and others, 1981).

## Purpose and Scope

The purpose of this report is to present the results of this study and to provide an analysis of the magnitude of sediment nutrient flux and sediment oxygen demand as well as the temporal and spatial trends in the data. A preliminary assessment of the influence of sediment grain size and synoptic water quality conditions on sediment nutrient fluxes and oxygen demand is also provided.

Eight cruises, each of approximately 2 weeks' duration, were conducted during 1982 and 1983 to determine sediment oxygen demand and the magnitude and direction of the flux of nitrogen and phosphorus species at the interface between the sediment and the water column at eleven stations. Figure 1 shows the study area and the station locations along the Patuxent. Temporal and spatial resolution was achieved by conducting the cruises seasonally along the entire reach of the tidal Patuxent

River and Estuary from the head of navigation (Wayson's Corner) to the mouth. The specific sites occupied were chosen to provide the best possible spatial coverage of the reach of the Patuxent under investigation. In addition, a four-station cross section of the midestuary, near Marsh Point, was monitored to assess lateral variability in nutrient fluxes and sediment oxygen demand.

Benthic respirometers were used for the in situ measurement of nutrient flux rates and sediment oxygen demand. The nutrients observed during the flux measurements were dissolved ammonium ( $\text{NH}_4^+$ ), dissolved ammonium plus dissolved organic nitrogen ( $\text{NH}_4^+$  + organic N), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), dissolved reactive phosphorus, total dissolved phosphorus, and oxygen. Organic nitrogen determinations were dropped from the analyses after the first year due to the erratic nature of the dissolved organic nitrogen concentrations in the respirometers. The erratic numbers are suspected to be a function of problems with the analytical technique not of the environment. Nitrite ( $\text{NO}_2^-$ ) analyses were included during the second year.

In addition to the chemical analysis of samples from the respirometers, initial water-column samples were collected for the same chemical constituents. Measurements of pH, conductivity, temperature, and dissolved oxygen were made hourly at approximately 1-m intervals in the water column. Sediment samples from each site were analyzed for grain-size distribution.

This project was supported under a joint funding agreement between the U.S. Geological Survey (USGS) and the Maryland Office of Environmental Programs (OEP). The study plan was cooperatively developed by the USGS staff and the OEP Ecological Modeling Section staff. The data reduction, analysis, and preparation of this report were also joint efforts.

## Study Area

The Patuxent River is the largest intrastate river in Maryland, with a length of 175 km and a watershed (drainage area) of 2,230 km<sup>2</sup>. This represents 8.7 percent of the land area of Maryland. In relation to the Chesapeake Bay, the Patuxent River is the sixth largest tributary in volume ( $7.57 \times 10^7$  m<sup>3</sup>), the second in mean depth (5.37 m), and the seventh in surface area ( $1.41 \times 10^7$  m<sup>2</sup>).

The Patuxent River traverses two distinct geologic regimes—the upper 25 percent of the river basin is in the Piedmont Plateau and the remaining 75 percent meanders through the Coastal Plain. This project was concerned with the sediment/water-column exchange of nitrogen and phosphorus species in the Coastal Plain portion of the tidal river and estuary.

The Patuxent River is tidally affected below Hills Bridge (Wayson's Corner), river kilometer 88.7. The lower river can be separated into three subdivisions: (1) tidal

river, (2) transition zone, and (3) estuary. The tidal river is the freshwater portion of the river that is tidally affected and extends from kilometer 99 to the upper boundary of the transition zone. The transition zone begins where measurable quantities of sea salt appear in the water, generally below kilometer 75. It extends downstream to the portion of the estuary below the marked salinity gradient and turbidity maximum zone (kilometers 50–35). The downstream boundary of the transition zone is subject to considerable variability that is predominantly a function of riverflow.

The estuarine portion of the Patuxent extends from the downstream boundary of the transition zone to the mouth. Physiographically, the tidal river and transition zone are characterized by broad, low-lying marshes. The estuary, however, deepens and widens downstream with bluffs replacing the marshes.

Average freshwater discharge measured at river kilometer 99 (Bowie, Md., USGS station 01594440) is 0.79 m<sup>3</sup>/s (USGS, 1983). Below river kilometer 34 (Benedict, Md.), the estuary develops a two-layer circulation pattern, and in the vicinity of Solomons, Md., a three-layer circulation has been observed occasionally (Boynton and others, 1982). The mean tidal ranges are 0.37 m at the mouth and 0.46 m at the upstream limit.

Between 1900 and 1970, the population nearly increased tenfold from 27,000 to 260,000. The land use distribution in 1930 was 50 percent agricultural, 10 percent urban, and 40 percent forested (Mihursky and Boynton, 1978). In the basin as a whole, this distribution has been changing as agricultural lands give way to urbanization and reforestation. The most recent available land-use percentages are 37 percent agricultural, 12 percent urban, and 51 percent forested (Maryland Department of State Planning, MAGI data, 1982). While urbanization is mainly confined to the upper basin, its impact may be felt throughout the region.

The economic base of the lower basin has been predominantly agriculture, but the estuary has supported a commercial fishery, harvesting oysters, crabs, clams, and finfish (such as shad, herring, white perch, spot, and striped bass).

## Acknowledgments

The authors wish to thank Barbara Schultz and Edward Callender of the USGS in Reston, Va., for their laboratory and field assistance throughout this project. Thanks are also extended to the Maryland Geological Survey, particularly to Gerald Cox, captain, and Richard Younger, mate, of the research vessel *Discovery*, for their assistance and guidance throughout the project. Appreciation is expressed to Ellen Osborne, Ward Staubit, Michael Haire, and Nauth Panday for their efforts in bringing the project to fruition.

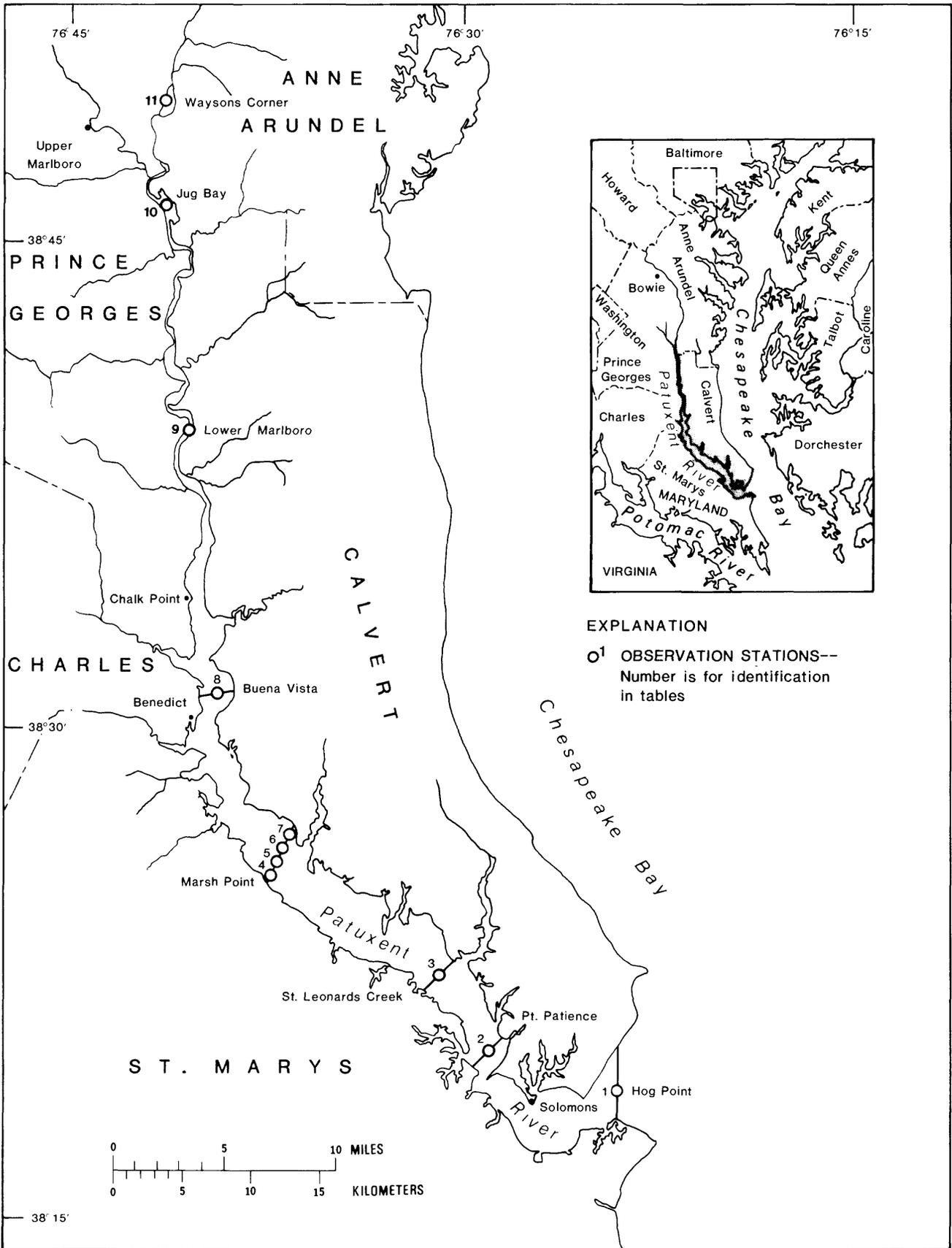


Figure 1. Location of study area and observation stations.

## PREVIOUS STUDIES

### Nutrient-Recycling Processes

The sediment-water interface is the site of many chemical and microbiological interactions regulating the dynamics of macronutrient (nitrogen and phosphorus species) cycling and transfer between sediments and the overlying water. The processes of diffusion and bioturbation represent interactions of many physical, chemical, and biological activities that are neither spatially nor temporally homogeneous for natural water systems in temperate climates.

The one-dimensional flux of material can be described by Fick's first law (Thibodeaux, 1979), which is shown below:

$$J_{AZ} = -C_2 D_{A2} \frac{dX_A}{dz},$$

where  $J_{AZ}$  is flux per area of component  $A$ ;  $C_2$  is molar density of the fluid;  $X_A$  is molar fraction of  $A$  in the fluid;  $Z$  is distance, in centimeters; and  $D_{A2}$  is the diffusion coefficient and a constant depending on the nature of the substance, in square centimeters per second.

The above equation describes the movement of constituents across the interface by diffusion. In natural bodies of water, this relationship is most closely realized during the winter months, when biological activity is minimal. During other periods of the year, the transport of solutes across the interface is additionally enhanced by disturbances or flushing actions associated with the various benthic organisms present.

Two methods have been used to estimate or measure nutrient flux rates. The first method estimates a flux rate based on a profile of the interstitial water in the sediments. These profiles are generally based on representative core samples taken from the sediments in question. The second method involves trapping a known volume of water over a known surface area and measuring concentration changes in the trapped water parcel over time. Several variants of this technique have been used: benthic respirometers have been placed on the sediment surface for an extended period, box cores have been taken and incubated onboard ship, and smaller cores have been taken back to the laboratory and incubated there. The advantages of the benthic respirometer method used in this study are that it integrates the flux rate over a larger sediment surface area and also incorporates the effects of benthic organisms that are present. When comparing flux rates determined by both methods, Callender and Hammond (1982) found that fluxes measured in situ were generally higher than calculated fluxes.

Nutrient flux rates from the sediment represent the net result of various microbiological, chemical, and

hydrodynamic processes. A brief description and explanation of the nutrient-recycling processes involved is presented below.

The macronutrients discussed below were limited to nitrogen and phosphorus species because enrichment with those species coincides with or induces eutrophication. The processes involved with the transfer of these constituents across the sediment-water interface are diffusive flux, irrigation, or pumping by benthic invertebrates; resuspension of bottom material; and possibly ground-water flow.

### Nitrogen

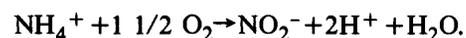
The nitrogen cycles in lakes are microbial in nature (Wetzel, 1975); this assumption can reasonably be extended to include rivers and estuaries. Alexander (1977) divides the nitrogen process into the two broad categories of mineralization and immobilization. Mineralization of nitrogen includes the processes by which organic compounds are decomposed and converted to ammonium and nitrate. This pool of compounds includes proteins, polypeptides, amino acids, nucleic acids, and other organic compounds. Nitrogen immobilization is the assimilation of simple nitrogen compounds into complex biological molecules.

The major nitrogen-related processes that occur in the aquatic environment are ammonification, nitrification, and denitrification. Microbial fixation of molecular nitrogen from the atmosphere, an important terrestrial activity, occurs to a much lesser extent and only under certain conditions in the aquatic environment. When inorganic nitrogen is unavailable, some bacteria and certain blue-green algae (cyanobacteria) can fix molecular nitrogen ( $N_2$ ) to be used for growth and reproduction.

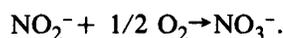
Ammonification is the process by which ammonia is produced as the primary end product of heterotrophic bacterial decomposition of organic matter. In water, ammonium is generally present as  $NH_4^+$  and as undissociated  $NH_4OH$ , the ratio of which is pH and temperature dependent. The following table from the work of Hutchinson (1957) shows the approximate  $NH_4^+$  to  $NH_3$  ratios:

pH	$NH_4^+ : NH_3$
6	3,000:1
7	300:1
8	30:1
9.5	1:1

Nitrification encompasses the microbial conversions of ammonium ( $NH_4^+$ ) to nitrite ( $NO_2^-$ ) and nitrite to nitrate ( $NO_3^-$ ). The first step of this conversion is predominantly mediated by bacteria of the genus *Nitrosomonas* (Alexander, 1977). This reaction is characterized by

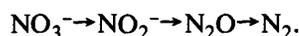


The second step in the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  is the conversion of  $\text{NO}_2^-$  to  $\text{NO}_3^-$ . This step is predominantly mediated by bacteria of the genus *Nitrobacter* and is characterized by



Nitrification, while an aerobic process, will continue down to oxygen concentrations of 0.3 mg of  $\text{O}_2$  per liter (Wetzel, 1975). The oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  requires 2 mole of  $\text{O}_2$  per mole  $\text{NH}_4^+$ ; this has direct bearing on the occurrence of nitrification in greatly reduced sediments. Essentially, in reduced sediments, nitrification is limited to the surficial oxidized layer, and during summer stratification, the oxidation of  $\text{NH}_4^+$  by *Nitrosomonas* and *Nitrobacter* may be of minor importance. Below pH 5, nitrification is severely restricted in the aquatic environment (Alexander, 1977).

Denitrification is predominantly the bacterial reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to nitrogen gas ( $\text{N}_2$ ). The general reaction is



In contrast to nitrification, where a limited group of bacteria mediate the reactions, denitrification is mediated by a large cross section of facultatively anaerobic bacteria. Alexander (1977) lists members of the genera *Pseudomonas*, *Achromobacter*, *Escherichia*, *Bacillus*, and *Micrococcus* as microbes capable of using nitrate as an exogenous terminal  $\text{H}^+$  acceptor. The reduction of nitrate or nitrite in the concomitant oxidation of glucose yields approximately as much energy as does the aerobic oxidation of glucose (Hutchinson, 1957).

Because denitrification does not require oxygen, it can proceed vigorously under anoxic conditions where abundant oxidizable organic substrates are present, that is, anoxic sediments and hypolimnia of eutrophic lakes. Denitrification is temperature dependent with little activity below 2° C (Wetzel, 1975).

## Phosphorus

Phosphorus dynamics cannot be categorized into neatly separated compartments as can the nitrogen dynamics. Phosphorus is in both the organic and the inorganic form, and according to Wetzel (1975), routinely greater than 90 percent of the phosphorus in lakes is in the organic form. The categories of organic and inorganic phosphorus can be further subdivided into particulate and dissolved forms. Particulate phosphorus includes organisms and cellular components such as nucleic acids, proteins, enzymes, and nucleotides (adenosine 5'-triphosphate and adenosine 5'-diphosphate); clay particles with associated adsorbed phosphorus; and particulate matter or

organic debris. The forms of phosphorus occur as orthophosphate ( $\text{PO}_4^{-3}$ ), polyphosphate, and organic colloids.

Sediment/water-column exchange processes are particularly important with respect to phosphorus cycling in natural waters. Both inorganic and organic forms of phosphorus undergo sorption-desorption and (or) form complexes in natural waters. The extent of these interactions will depend on the concentration and species of phosphorus present, the metal ion concentrations, the pH, and the presence of other ligands. The phosphorus moved from the water column to the sediments by these processes may either be returned to the water column through recycling processes or be buried and remain in the sediments (Syers and others, 1973).

The processes that return phosphorus to the water column are complex. Changes in redox conditions with the development of anoxia can mobilize phosphorus that was previously complexed with metal ions; additionally, changes in pH can mobilize previously complexed phosphorus. Organic phosphorus compounds can be degraded and the phosphorus mobilized by microbial activity; this remineralization can be achieved directly or indirectly by altering the ambient environmental conditions. Mobilized phosphorus can then be returned to the water column by diffusive flux, irrigation by benthic invertebrates, or resuspension of the sediments.

## Water Quality of the Patuxent River and Estuary

The tidal Patuxent River and Estuary have been the focus of a multitude of water quality investigations since the 1930's (Nash, 1947). However, instead of recounting the individual research efforts, the authors will focus on recent exhaustive reviews of the Patuxent data base by Mihursky and Boynton (1978) and Boynton and others (1982). The purpose is to provide a general description of the water quality of the Patuxent. The primary, inter-related water quality problems in the Patuxent have been linked to sedimentation, turbidity, dissolved oxygen, chlorophyll or phytoplankton, phosphorus, and nitrogen excesses or deficiencies.

## Sedimentation

Sediment yield to the Patuxent increased after 1949, coincident with increases in the population of metropolitan Washington, D.C., after World War II. Estimates of area-weighted mean sediment yields were the following: urban, 257 ( $\text{Mg}/\text{km}^2$ )yr; rural, 80 ( $\text{Mg}/\text{km}^2$ )yr; and rural with construction, 268 ( $\text{Mg}/\text{km}^2$ )yr (Fox, 1975). According to this study, increased activity and growth without adequate sediment controls deliver more sediment to the river and estuary.

Numerous estimates (Mihursky and Boynton, 1978) of deposition rates in the Patuxent ranged from 1.2 mm/yr

to 37 mm/yr. Sediment deposition and discharge are important factors in the water quality of the Patuxent, but a wide range exists in the magnitude of these activities. Mihursky and Boynton (1978) also cited work by Biggs that stated that “. . . bathymetry and bottom sediments near the mouth of the Patuxent suggest no evidence of sediment contributions from the Patuxent to the Bay.”

### **Turbidity**

Sediment contributes to the turbidity of water, but not all turbidity is caused by sediment. Comparison of historical and recent data (Mihursky and Boynton, 1978) suggests that the turbidity of the Patuxent increased during the period of 1930–70.

The turbidity maximum in an estuary corresponds to the front of the salt wedge, and its position moves as a function of the freshwater inflow. In the Patuxent, the turbidity maximum ranges between river kilometers 50 and 80, and during periods of low freshwater input, two simultaneous turbidity maximums have been observed.

### **Dissolved Oxygen**

Mihursky and Boynton (1978) discuss the large number of dissolved oxygen studies conducted on the Patuxent. The general trends suggest a similarity between surface and bottom water in the Patuxent Estuary from October to March, representative of a mixed water column and lessened phytoplankton activity. From March to September, the data show that surface and bottom water dissolved oxygen concentrations are different. An important point that Mihursky and Boynton emphasize is that surface to bottom differences vary from year to year. This is a natural variation caused by environmental and climatic conditions.

The bottom water of the Patuxent River near Solomons, Md., has been characteristically low in dissolved oxygen, even during the 1930's and 1940's (Mihursky and Boynton, 1978), but there is concern that the areal extent of low or no dissolved oxygen water is extending. Nash (1947) suggested that the development of the dissolved oxygen minimums resulted from the vertical stability of the water column to a greater extent than from the temperature. It will be shown below that the development of anoxic conditions can have a tremendous effect on observed fluxes of ammonium and phosphorus.

### **Chlorophyll *a***

Significant year-to-year variations in the chlorophyll *a* concentrations are observed (Mihursky and Boynton, 1978) in the Patuxent without definite discernible trends in the chlorophyll *a* data. One possible cause for the variability of chlorophyll *a* data is changes that have

occurred in methodologies for estimating chlorophyll concentrations.

### **Phosphorus**

Dissolved inorganic phosphate and total phosphate both show sharp declines in concentration in a downriver (fresh to saline) direction (Mihursky and Boynton, 1978). Seasonal patterns are not distinct at Lower Marlboro, a tidal river station, but phosphorus concentrations at the estuarine stations appeared to increase during the summer.

### **Nitrogen**

Prior to the location of sewage treatment plants on the Patuxent River, only nitrate concentrations were measured in the water (Mihursky and Boynton, 1978). Clear, seasonal patterns do exist for nitrate in the estuary, with high concentrations in the winter and low concentrations in the summer. No definite reason for this is provided, but the relative impact of nitrifying bacteria over the denitrifying bacteria during the winter and the inverse during the summer is offered as one explanation. At Upper Marlboro, another tidal river station, no seasonal pattern was observed. Nitrate concentrations appear to be correlated with riverflow, and large increases in the concentration were observed after 1936 and again after 1963.

Ammonium concentrations in the Patuxent River are inversely correlated with flow, the highest concentrations being observed in the upper estuary during low-flow periods. In the summer, ammonium is the primary source of nitrogen available to the primary producers in the lower estuary.

### **Primary Productivity and Limiting Nutrients**

Primary productivity measures the activity of the primary or photosynthetic production of organic matter. In the Patuxent River, it is chiefly from phytoplankton. Nutrient enrichment tends to stimulate algal growth with resulting increases in photosynthesis and algal biomass. This cycle has a direct effect on the dissolved oxygen balance of the estuary. The increase in photosynthetic activity results in increased daily oxygen concentrations where phytoplankton are present, and the increased algal biomass represents both an increased demand for oxygen by algal respiration and a larger feedstock for other heterotrophic organisms. Heterotrophic consumption of oxygen during respiration can result in lowering the oxygen minimums sufficiently to alter normal estuarine ecology. Mihursky and Boynton (1978), in reviewing the data available, suggest that primary productivity in the lower Patuxent Estuary is increasing. They also suggest that primary productivity in the upstream portions has remained similar, with wide annual fluctuations. The

authors also state that the primary productivity values observed in the Patuxent are as high or higher than those of other east coast estuaries and in the range of highly eutrophic systems such as the Potomac River. As would be expected, Mihursky and Boynton show that there is a seasonality to primary productivity, with the lowest rates during the winter (November–February).

Over recent decades, the tidal Patuxent River and Estuary have been subjected to increased population growth in the basin with subsequent increases in sediment, turbidity, nutrients transported to the water column, and the areal extent of low dissolved oxygen bottom water in the estuary. If adequate controls were placed on the transport of nutrients to the Patuxent, what would be the contribution of the river sediments to the water-column nutrient concentrations and dynamics? This question was addressed by Boynton and others (1982) for the upper estuary and the lower tidal river near the Chalk Point Power Station. The purpose of the current study was to follow up and extend the areal and temporal coverage of Boynton and others.

## METHODS

### Data Collection and Analysis

In situ benthic flux rates were measured by trapping a parcel of water above the sediment-water interface and determining the rate of change of nutrient concentration in that parcel. For this purpose, four benthic respirometers were constructed of marine aluminum (see fig. 2). Three of these were identical and open on the bottom to hold the water parcel in contact with the sediment surface. The fourth was modified to trap a water parcel 1 m above the bottom to be used as the water-column process control. The respirometers were outfitted with dissolved oxygen probes, circulating pumps, sampling lines, and two check valves to maintain stable internal pressure. The circulating pumps were operated to maintain an internal water velocity of approximately 7 cm/s to provide well-mixed conditions inside the respirometers. Speeds higher than this resulted in significant resuspension of bed material at some stations.

At the beginning of each incubation period, all four respirometers were suspended beneath the vessel with the circulating pumps running to ensure that all air was evacuated from the domes. The control respirometer was then lowered to a point 1 m above the bottom and flushed three times; the final flush was trapped to serve as the water-column control. The pumps were then stopped on the three remaining respirometers, which were then slowly lowered to the bottom. To allow any resuspended sediment material to resettle, the circulating pumps were left off for 15 min and then restarted.

### Dissolved Oxygen

Dissolved oxygen concentrations inside the respirometers were measured with YSI Model 57<sup>1</sup> dissolved oxygen meters and probes. Dissolved oxygen meters were calibrated using a Winkler titration protocol described by Shultz and Stephens (1977). Saturated air calibration was used for dissolved oxygen calibration on the June 1982 cruise. When either the meter or the probe malfunctioned, dissolved oxygen concentrations were determined by the Winkler method at the beginning and end of each incubation.

### Water-Column Data

Water-column-specific conductance, dissolved oxygen, pH, and temperature were measured hourly at intervals of 1–2 m with a Hydrolab 4000 series portable meter outfitted with a flow-through cell mounted to the probe sonde. The intake hose for the flow-through cell was marked to allow for the measurement of depth and was attached to a small 12-V pump as an energy source for pumping water from the various depths.

Water-column samples were collected from the flow-through cell discharge, with the intake 1 m above the sediment surface. The initial water-column samples at each site were analyzed for the same chemical constituents as were the benthic respirometer samples.

<sup>1</sup>The mention of brand names is for identification purposes and does not constitute endorsement by the USGS.

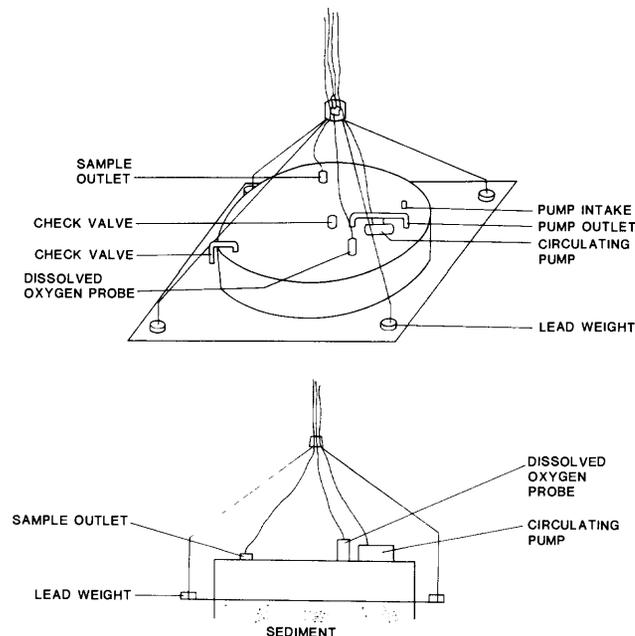


Figure 2. Schematic of benthic respirometer (two views).

## Bottom Samples and Velocity

Bottom samples for sediment-size fraction analysis were collected at each site and sent to the USGS Sediment Laboratory in Harrisburg, Pa.

Current velocities were measured hourly at a point 0.3 m above the bottom for all sites. On cruises after November 1982, current velocities were also measured at eight-tenths and at two-tenths of total depth, using standard USGS techniques (Rantz and others, 1982).

## Chemical Analysis

The following list details the chemical constituents that were measured and for which subsequent flux rates were determined during the study. All chemical analyses were conducted in accordance with USGS procedures (Skougstad and others, 1979).

## Collection Procedures

For sampling purposes, each respirometer was out-fitted with 6.35-mm outside-diameter tygon tubing, with one end attached to the inside of the respirometer and the other, shipboard. Samples were removed from each respirometer approximately hourly over a 4-hour period. For phosphorus, a separate set of samples was taken each hour from the water column about 1 m above the bottom. All samples were immediately filtered and refrigerated onboard ship. Nitrogen samples were placed on ice and mailed to the USGS Laboratory in Atlanta, Ga.; phosphorus samples were transported on ice to Reston, Va., for analysis. Mercuric chloride was added to the nitrogen samples as an additional preservative.

The measurement of the respirometer volume is essential in determining flux rates. To this end, 100 mL of a lithium chloride solution followed by 200 mL of

*Chemical constituents collected during the Patuxent River nutrient flux project*

WATSTORE				
Laboratory	Dates	Parameter code	Constituent name	Units
Atlanta (USGS)	June-November 1982	00623	Nitrogen, dissolved ammonium plus organic	mg/L as N
Atlanta (USGS)	March 1983 - end	00613	Nitrogen, dissolved nitrate	mg/L as N
Atlanta (USGS)	All sampling trips	00608	Nitrogen, ammonium dissolved	mg/L as N
Atlanta (USGS)	All sampling trips	00631	Nitrogen, dissolved nitrite plus nitrate	mg/L as N
Reston (USGS)	All sampling trips	DRP	Dissolved reactive phosphorus	μmoles/L as P
Reston (USGS)	All sampling trips up to June 1983	TDP	Total dissolved phosphorus	μmoles/L as P

deionized water were injected into each respirometer while the circulating pumps were operating. The lithium was mixed for 15 min prior to sampling. Samples of the injected lithium, diluted lithium, and a lithium background sample were analyzed at the USGS Laboratory in Reston, Va. (Skougstad and others, 1979). The volume was computed by the following equation:

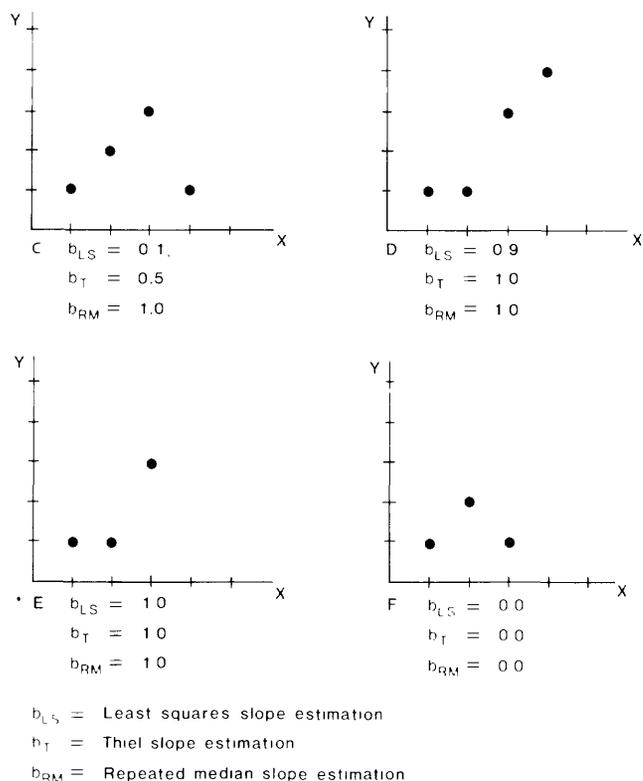
$$V_I C_I = V_R C_R,$$

where  $V_I$  is volume injected, in liters;  $C_I$  is concentration of injected lithium, in milligrams per liter;  $V_R$  is volume

of respirometer, in liters; and  $C_R$  is concentration of lithium in the respirometer, in milligrams per liter.

## Estimation of Flux Rate

In an effort to select the most appropriate estimator, three different estimators were used initially in calculating  $b_i$ , the rate of change in a water-chemistry concentration over time for respirometer  $i$ . These are the classical least squares estimator, the Theil estimator, and Siegel's



**Figure 3.** Numerical comparisons of how three estimators are affected by variable data with small sample sizes.

repeated median estimator. A detailed discussion of the statistical analysis of flux rate estimation can be found in the work of Salvo (1984).

Numerical comparisons of how the three rate estimators are affected by variable data (given sample sizes of three and four) are presented in figure 3. When only three points are present (see E and F of fig. 3), all three estimators perform equally. When four points are present with one outlier (see C and D of fig. 3), the repeated median will perform well regardless of where the outlier is. The Theil and least squares estimates will be adversely affected when the outlier is at the extreme range of X (time in these graphs).

In summary, observe that the least squares estimate will always be affected adversely by any outlier. The Theil estimate will be adversely affected only if the outlier is located at the extreme range of X. The repeated median estimate provides the best representative picture of how the slope behaves. The least squares estimator, however, has two advantages over Siegel's repeated median estimator if the model is correct and if the errors are approximately Gaussian. The least squares estimator is the most efficient estimator, and it provides an estimated interval measure of uncertainty.

To determine which estimator was appropriate for the Patuxent River nutrient flux data, box plots were prepared for the flux rates that compared the three estimators by station over all cruises. Very little difference was noticed in any of the three estimators (Salvo, 1984). This similarity can be explained by the fact that the variability of the nutrient concentrations within a given chamber is small, so that each estimator tends to give the same estimate of flux rate. In fact, the different estimators can be regarded as "fine-tuning" adjustments in the analysis, so that regardless of the estimator used the gross overall trends will be the same. Because of this close similarity between estimates and the fact that the least squares estimate is a simpler computational procedure, only the least squares estimates will be used in any further analysis.

## CHEMICAL AND PHYSICAL CHARACTERISTICS OF WATER COLUMN AND SEDIMENTS

### Water-Column Quality

Table 1 shows the observed median, maximum, and minimum values over all depths for all stations over the period of the project. Salinity values in table 1 show that Wayson's Corner and Jug Bay constitute the tidal river, or freshwater, stations. Lower Marlboro can be considered a transition zone station, and Buena Vista, St. Leonard's Creek, Point Patience, Hog Point, and the four Marsh Point transect stations are the estuarine stations.

Salinities encountered during the project varied from less than 0.1 to greater than 17. Temperature ranged from 5 to 29° C. Dissolved oxygen ranged from essentially below detection to greater than 16 mg/l. Both observations occurred at Marsh Point stations. The maximum (16 mg/l) observation occurred during a spring dinoflagellate phytoplankton bloom while the water temperature was still below 10° C (Kevin Sellner, oral commun., 1983). The minimum dissolved oxygen value was also observed at a Marsh Point station. Marsh Point was a transect with four stations—one each in the shallows on the Calvert and St. Marys County sides of the river (stations 4 and 7, respectively) and two in the main body of the river (stations 5 and 6). Marsh Point station 6 was in the channel with a depth of approximately 10 m; stratification of the water column and anoxia in the bottom water developed early at this station. Marsh Point station 6 will be discussed separately because of its uniqueness among the estuarine stations. Figures 4 and 5 show the longitudinal profiles for the observed maximum, minimum, and median values for salinity and dissolved oxygen, respectively. Marsh Point stations are actually located at river kilometer 27, but for elucidation of the data, the Marsh Point stations are offset by a kilometer.

**Table 1.** Observed median, maximum, and minimum values of salinity, temperature, pH, and dissolved oxygen at each station over all depths

Station	Salinity				Temperature, in Degrees Celsius			
	Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	183	14.20	17.35	6.99	184	21.50	27.0	3.0
2. Point Patience	179	14.41	16.95	6.38	180	23.15	27.3	5.1
3. St. Leonard's Creek	176	13.88	16.48	5.99	195	22.60	27.2	5.3
4. Marsh Point 4	39	10.11	13.75	9.47	45	24.30	25.8	7.5
5. Marsh Point 3	110	10.85	15.40	5.00	110	23.90	28.1	6.0
6. Marsh Point 2	211	12.04	16.34	4.68	212	23.60	27.3	5.5
7. Marsh Point 1	80	11.84	14.21	5.31	80	24.00	26.1	15.1
8. Buena Vista	152	10.59	14.41	3.19	154	24.55	28.8	6.5
9. Lower Marlboro	179	2.04	4.70	0.05	182	24.30	27.7	9.3
10. Jug Bay	105	0.10	0.39	0.05	105	22.50	26.8	9.6
11. Wayson's Corner	136	0.09	0.12	0.05	136	20.30	23.9	9.7

Station	Dissolved Oxygen				pH			
	Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	182	6.65	12.6	3.5	159	7.70	8.2	6.9
2. Point Patience	180	7.45	14.1	3.6	145	7.70	8.3	7.0
3. St. Leonard's Creek	195	8.00	13.8	1.8	180	7.80	8.2	6.7
4. Marsh Point 4	43	6.40	13.9	2.8	45	7.60	8.2	6.9
5. Marsh Point 3	107	6.80	16.7	1.3	78	7.60	9.0	6.8
6. Marsh Point 2	212	5.10	13.3	0.1	121	7.20	8.4	6.1
7. Marsh Point 1	80	7.50	11.8	3.0	56	7.50	8.0	6.9
8. Buena Vista	134	5.65	11.4	2.0	123	7.20	8.4	6.7
9. Lower Marlboro	166	7.20	9.9	4.4	149	7.10	8.1	6.6
10. Jug Bay	81	7.80	11.8	5.3	81	6.80	7.3	6.5
11. Wayson's Corner	121	7.20	8.9	5.0	108	6.75	7.7	6.5

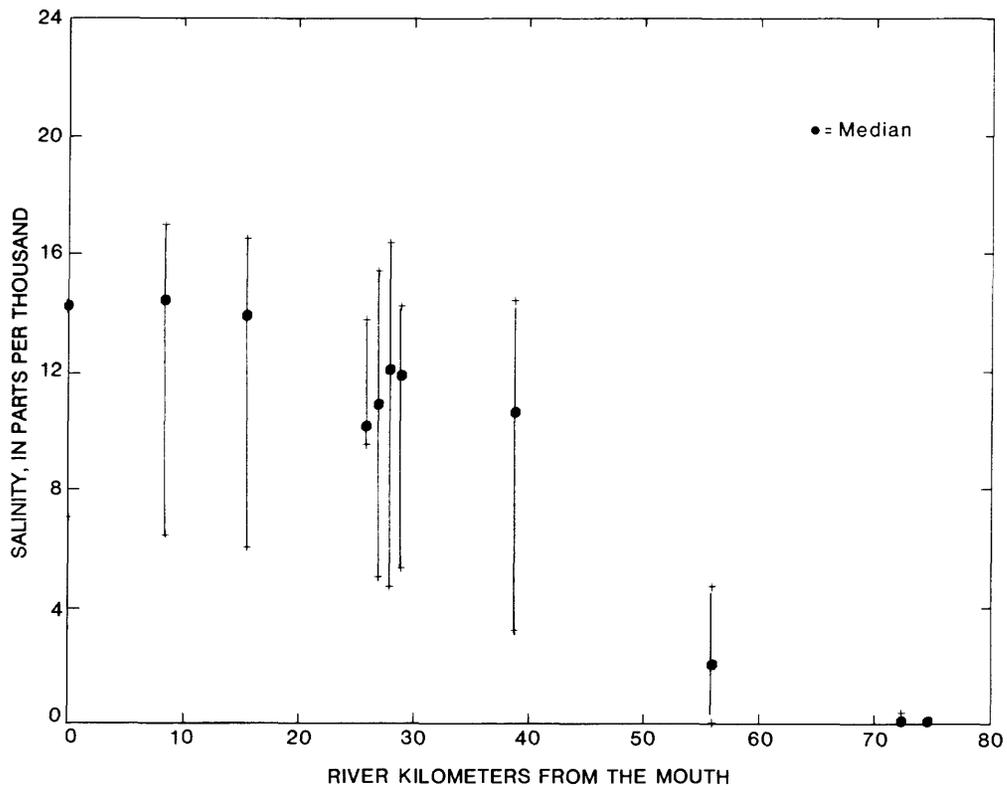
## Sediment Nutrient Flux and Oxygen Demand

The observed flux rates for measured nutrients are shown in table 2. The rates are comparable to previous rates reported for the Patuxent near the Chalk Point Power Plant (Boynton and others, 1982). They reported ranges of  $-105$  to  $1,584$  micromoles meter<sup>-2</sup> hour<sup>-1</sup> ( $-105$  to  $1,584$   $\mu\text{Mm}^{-2}\text{h}^{-1}$ ) as N for ammonium,  $1$  to  $295$   $\mu\text{Mm}^{-2}\text{h}^{-1}$  as P for dissolved inorganic phosphorus, and  $0.5$  to  $4.1$  g of  $\text{O}_2$  m<sup>-2</sup>d<sup>-1</sup> for sediment oxygen demand. The rates reported here ranged from  $-297$  to  $3,040$   $\mu\text{Mm}^{-2}\text{h}^{-1}$  as N,  $-166$  to  $698$   $\mu\text{Mm}^{-2}\text{h}^{-1}$  as P, and  $0.1$  to  $3$  g m<sup>-2</sup>d<sup>-1</sup> for ammonium, dissolved reactive phosphorus, and sediment oxygen demand, respectively. The present data exhibit a wider range because of the more extensive temporal and spatial coverage in this project.

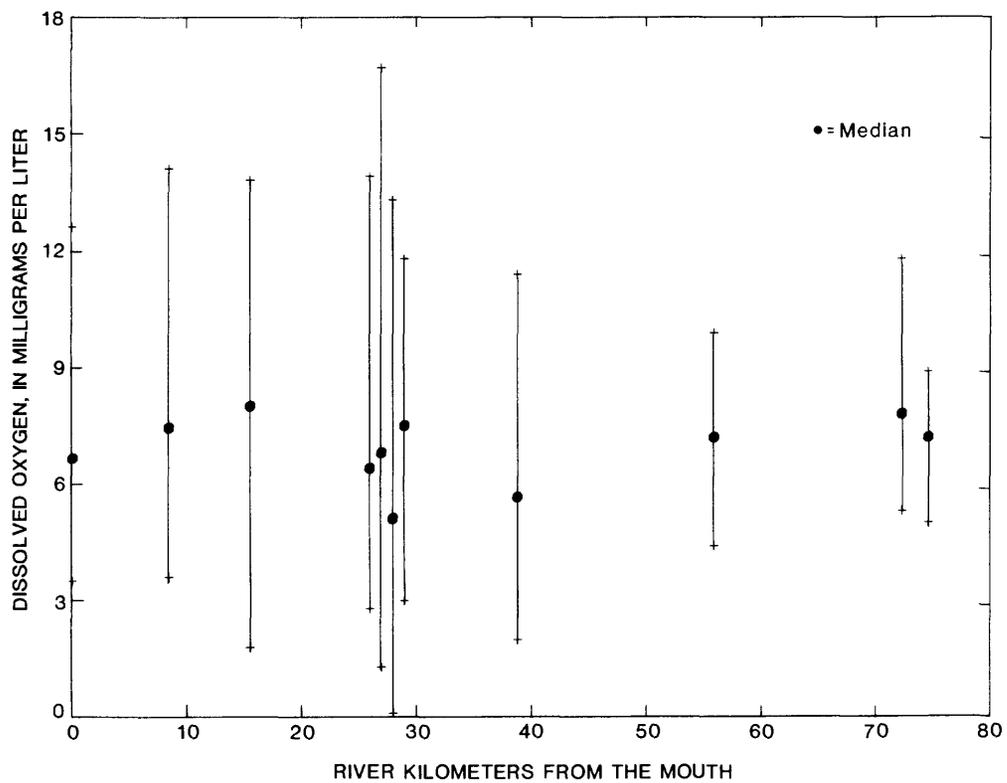
Figures 6 through 13 show the longitudinal distributions for the observed nutrient fluxes and the percentage

of sand composition of the sediment. Figure 13 represents the percentage of bed material in the sand-size category. The remaining amount (100 percent minus the percentage of sand) is considered the percentage of fine-grained (silt and clay) sediments. Values for each observation and the median values for each station are shown on these plots.

The median, maximum, and minimum initial nutrient and dissolved oxygen concentrations measured inside the respirometers are shown in table 3. These values represent the water-column concentrations just above the sediment surface. Examination of the maximum and minimum values shows the fluctuation in nutrient concentrations that can occur over a yearly cycle. The lowest and the highest initial dissolved oxygen values were recorded in the estuary; this is consistent with previous statements that the ranges between the maximum and the minimum values are greater in the estuary than in the tidal river (Mihursky and Boynton, 1978).



**Figure 4.** Observed maximum, minimum, and median values for water-column salinity during all cruises.



**Figure 5.** Observed maximum, minimum, and median values in water-column dissolved oxygen during all cruises.

**Table 2.** Median values and ranges of sediment nutrient flux and sediment oxygen demand rates for each station over all cruises

[All fluxes except dissolved oxygen are in micromoles meter<sup>-2</sup> day<sup>-1</sup> N or P as appropriate. Oxygen is in grams O<sub>2</sub> meter<sup>-2</sup> day<sup>-1</sup>.]

Station	River kilometer	Dissolved ammonium plus organic nitrogen				Dissolved ammonium			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.10	6	97.51	1,068.16	-20	19	241.116	798.13	-401.26
2. Point Patience	8.50	21	491.91	5,861.86	-4,885	33	355.206	756.62	43.04
3. St. Leonard's Creek	15.60	12	1.67	7,446.90	-1,396	26	55.660	434.42	-290.95
4. Marsh Point 4	26.00	6	883.26	2,538.87	-710	9	82.268	325.51	-162.77
5. Marsh Point 3	27.00	9	629.02	3,515.44	-326	21	63.443	592.39	-134.51
6. Marsh Point 2	28.00	9	377.64	3,196.88	-13,648	34	639.347	3,043.13	79.99
7. Marsh Point 1	29.00	7	241.45	5,117.85	-813	16	162.349	626.63	-24.39
8. Buena Vista	38.90	12	-258.95	3,881.78	-2,162	23	191.364	653.88	-173.11
9. Lower Marlboro	56.00	14	777.01	5,683.41	-655	26	355.282	1,940.51	-228.59
10. Jug Bay	72.40	15	44.27	1,113.63	-2,857	27	99.548	1,778.92	-297.48
11. Wayson's Corner	74.70	12	-802.96	5,286.60	4,985	24	109.398	1,191.19	-271.16

Station	River kilometer	Dissolved nitrate plus nitrite				Dissolved nitrite			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	19	-14.83	34.96	-295.4	14	-5.61	47.95	-37.52
2. Point Patience	5.5	33	-1.84	2,602.58	-1,298.5	12	37.62	63.54	-42.31
3. St. Leonard's Creek	15.5	25	16.91	190.24	-283.5	14	6.0	45.06	-10.67
4. Marsh Point 4	26.0	9	2.53	52.12	-23.5	3	0.0	0.0	-0.0
5. Marsh Point 3	27.0	21	0.00	89.84	-180.9	12	-8.63	12.73	-112.12
6. Marsh Point 2	28.0	34	-50.63	112.51	-252.4	25	5.69	34.75	-115.04
7. Marsh Point 1	29.0	16	6.62	120.75	-588.5	9	18.94	129.77	-2.54
8. Buena Vista	38.9	23	20.61	535.11	-59.3	11	2.05	18.15	-11.89
9. Lower Marlboro	56.0	25	11.45	3,372.62	-867.2	12	16.05	62.80	-73.79
10. Jug Bay	72.4	27	-215.83	2,270.87	3,869.8	12	8.2	239.14	-62.85
11. Wayson's Corner	74.7	24	-263.67	1,320.78	-745.4	12	4.13	98.03	-27.16

Station	River kilometer	Dissolved reactive phosphorus				Total dissolved phosphorus			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	22	10.14	45.8	-2.94	11	17.75	59.74	-5.70
2. Point Patience	8.5	33	14.88	39.13	-18.91	24	20.48	46.67	-11.33
3. St. Leonard's Creek	15.6	26	5.99	36.55	-15.03	15	11.402	22.09	-38.05
4. Marsh Point 4	25.0	9	9.28	29.72	1.72	9	4.19	33.76	-3.53
5. Marsh Point 3	27.0	21	4.71	38.32	-18.08	12	12.92	37.49	-17.13
6. Marsh Point 2	28.0	34	70.54	698.40	0.57	12	326.10	718.33	-4.92
7. Marsh Point 1	29.0	16	9.82	25.09	1.58	8	2.13	48.36	-14.48
8. Buena Vista	38.9	23	14.78	57.22	3.12	14	10.60	33.20	-12.36
9. Lower Marlboro	56.0	26	-2.85	18.20	-43.19	17	-0.80	17.95	-11.60
10. Jug Bay	72.4	27	-6.90	187.02	-165.86	18	-6.35	262.37	-294.14
11. Wayson's Corner	74.7	24	-4.29	24.42	-133.81	15	-0.46	40.66	-83.52

Station	River kilometer	Dissolved oxygen demand			
		Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	15	-2.0196	-3.85	1.1088
2. Point Patience	8.5	17	-2.5059	-4.87	-1.0601
3. St. Leonard's Creek	15.6	20	-1.7195	-2.90	2.6564
4. Marsh Point 4	26.0	9	-2.3820	-3.10	-1.6617
5. Marsh Point 3	27.0	17	-1.9268	-3.42	-0.3410
6. Marsh Point 2	28.0	21	-1.5415	-3.82	-0.4238
7. Marsh Point 1	29.0	14	-1.3898	-3.50	-0.3788
8. Buena Vista	38.9	23	-2.2713	-3.11	0.3588
9. Lower Marlboro	56.0	19	-1.1658	-6.06	-0.6669
10. Jug Bay	72.4	19	-1.0770	-3.53	3.5246
11. Wayson's Corner	74.7	20	-1.1916	-2.43	0.2529

**Table 3.** Median, maximum, and minimum initial nutrient and oxygen concentrations

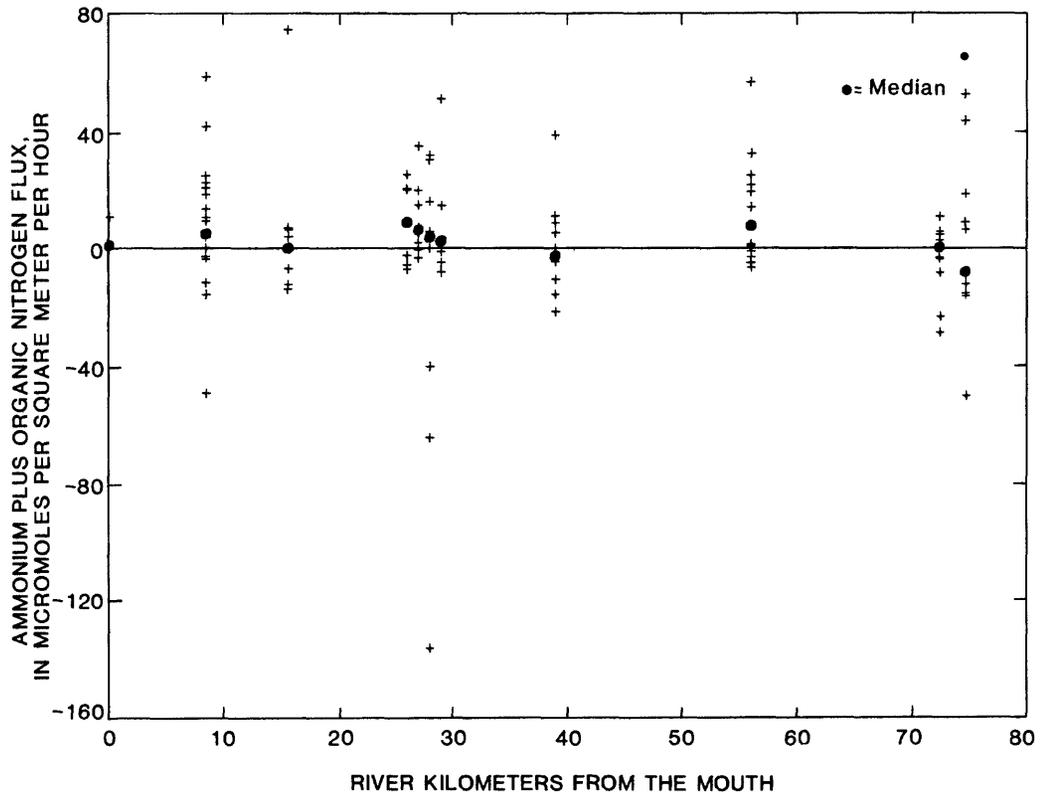
[All concentrations are in milligrams per liter as N or P or O<sub>2</sub> where appropriate.]

Station	River kilometer	Initial concentration of ammonium plus organic nitrogen				Initial concentration of ammonium			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	8	25.00	35.71	7.14	27	13.07	26.50	5.86
2. Point Patience	8.5	28	35.71	221.43	7.14	44	16.04	24.36	6.65
3. St. Leonard's Creek	15.6	16	14.29	42.86	7.14	34	14.11	66.29	4.29
4. Marsh Point 4	26.0	8	28.57	50.00	14.29	12	12.39	15.36	9.00
5. Marsh Point 3	27.0	12	21.43	35.71	14.29	28	10.39	19.07	5.64
6. Marsh Point 2	28.0	12	46.43	300.00	7.14	46	17.50	33.29	4.29
7. Marsh Point 1	29.0	9	50.00	157.14	21.43	21	9.29	16.86	3.86
8. Buena Vista	38.9	16	28.57	64.29	14.29	31	12.29	20.50	7.14
9. Lower Marlboro	56.0	26	42.86	100.00	28.57	41	9.36	38.64	1.50
10. Jug Bay	72.4	20	35.71	64.29	21.43	36	10.14	27.36	.36
11. Wayson's Corner	74.7	17	50.00	335.71	7.14	33	17.21	43.00	11.71

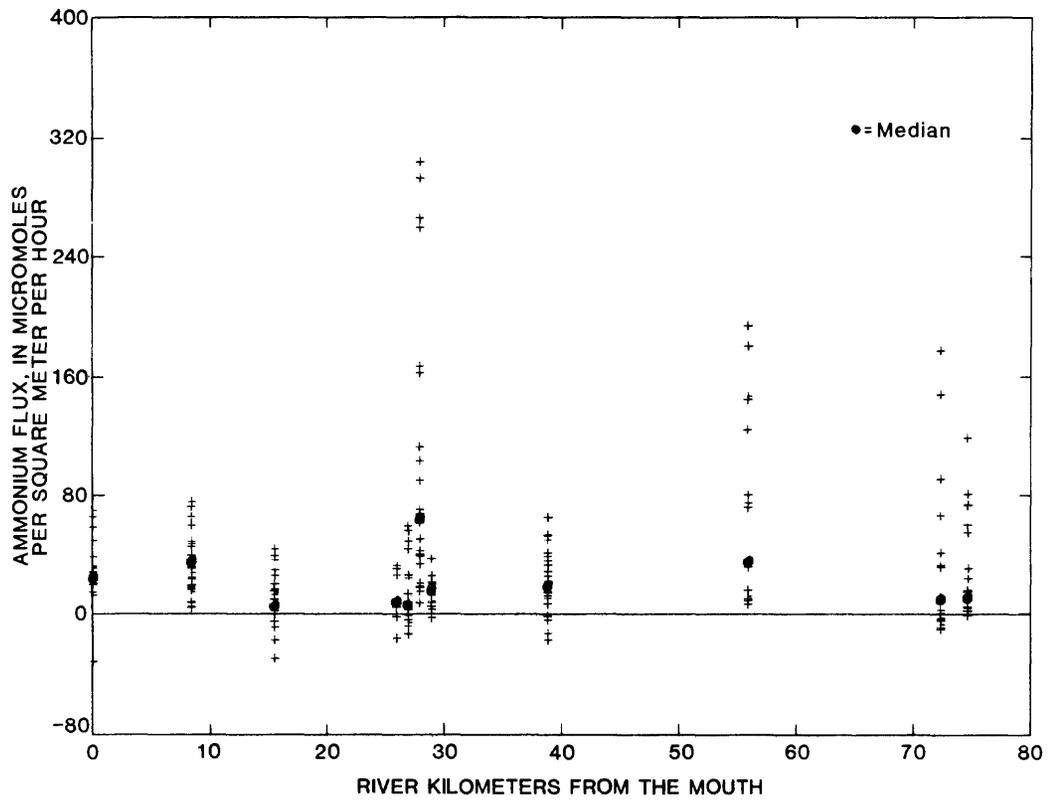
Station	River kilometer	Initial concentration of nitrite plus nitrate				Initial concentration of nitrite			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	27	4.29	24.79	2.00	20	0.71	2.14	0.05
2. Point Patience	6.6	44	3.93	22.29	1.79	16	1.29	3.60	.71
3. St. Leonard's Creek	15.5	34	3.36	17.07	.71	18	.79	4.29	.39
4. Marsh Point 4	25.0	12	4.43	21.71	1.71	4	.71	.71	.71
5. Marsh Point 3	27.0	28	7.14	13.36	2.14	16	.71	5.71	.00
6. Marsh Point 2	25.0	46	7.93	15.79	.71	34	1.11	10.00	.14
7. Marsh Point 1	29.0	21	4.07	7.86	1.00	12	1.04	7.86	.50
8. Buena Vista	38.9	31	7.07	43.93	3.57	15	.79	6.43	.57
9. Lower Marlboro	56.0	41	9.50	107.14	2.50	16	1.43	7.14	.21
10. Jug Bay	72.4	36	125.00	185.71	49.36	16	2.68	5.71	1.43
11. Wayson's Corner	74.7	33	164.29	250.00	100.00	16	4.18	10.00	2.86

Station	River kilometer	Initial concentration of dissolved reactive phosphorus				Initial concentration of total dissolved phosphorus			
		Number of observations	Median	Maximum	Minimum	Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	31	0.44	0.75	0.14	15	0.61	1.05	0.19
2. Point Patience	8.5	44	.56	1.24	.00	32	.69	1.56	.12
3. St. Leonard's Creek	15.6	36	.54	1.30	.00	21	.75	1.34	.25
4. Marsh Point 4	26.0	12	1.21	2.00	.20	12	1.52	2.14	.28
5. Marsh Point 3	27.0	28	1.17	2.49	.15	16	1.08	2.72	.29
6. Marsh Point 2	28.0	46	1.25	7.56	.17	16	2.49	7.94	.51
7. Marsh Point 1	29.0	22	1.44	1.78	.12	11	1.48	2.69	.69
8. Buena Vista	38.9	31	1.52	3.41	.68	19	1.77	3.01	.75
9. Lower Marlboro	56.0	42	1.58	2.29	1.13	30	1.70	2.21	1.34
10. Jug Bay	72.4	36	2.35	8.11	.56	24	2.44	9.68	.83
11. Wayson's Corner	74.7	34	6.07	12.60	2.51	22	4.81	10.30	2.79

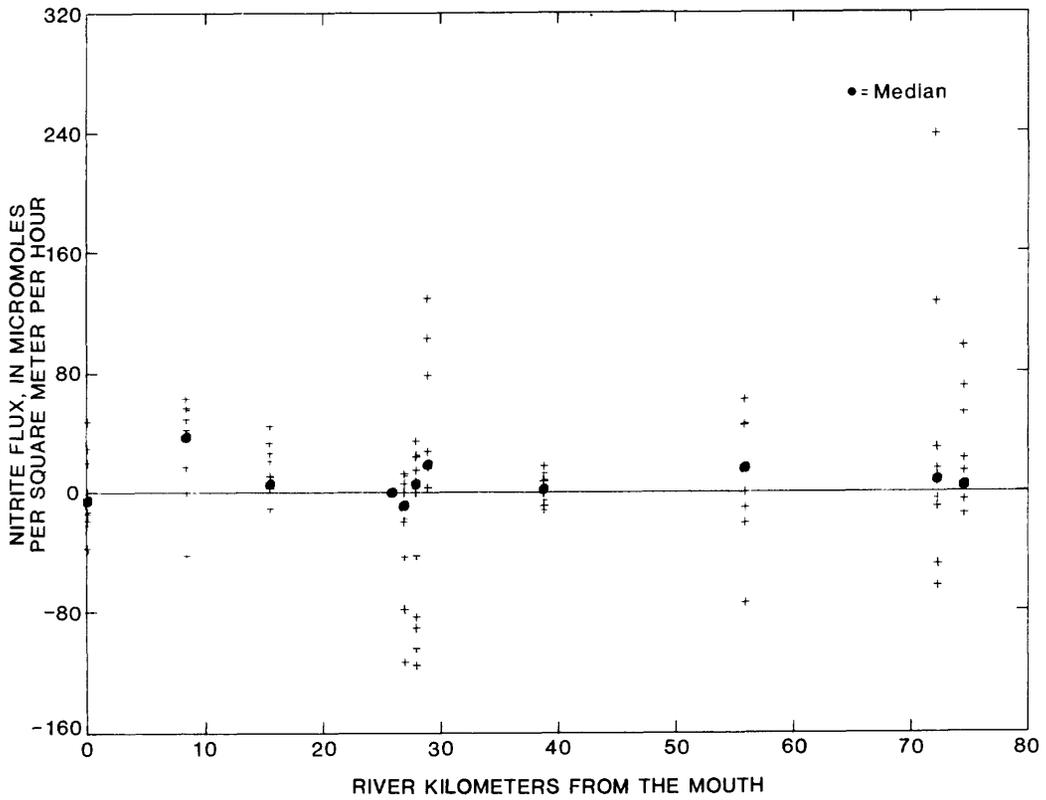
Station	River kilometer	Initial concentration of dissolved oxygen			
		Number of observations	Median	Maximum	Minimum
1. Hog Point	0.1	27	6.90	17.60	2.65
2. Point Patience	8.5	35	5.60	12.50	1.95
3. St. Leonard's Creek	15.6	32	5.90	9.70	2.75
4. Marsh Point 4	26.0	12	8.70	13.60	6.10
5. Marsh Point 3	27.0	27	4.70	13.10	.75
6. Marsh Point 2	28.0	33	3.35	11.40	.15
7. Marsh Point 1	29.0	20	6.95	11.50	1.70
8. Buena Vista	38.9	31	6.10	11.60	3.10
9. Lower Marlboro	56.0	29	7.23	11.10	4.00
10. Jug Bay	72.4	27	7.70	9.75	3.60
11. Wayson's Corner	74.7	29	5.80	9.50	4.00



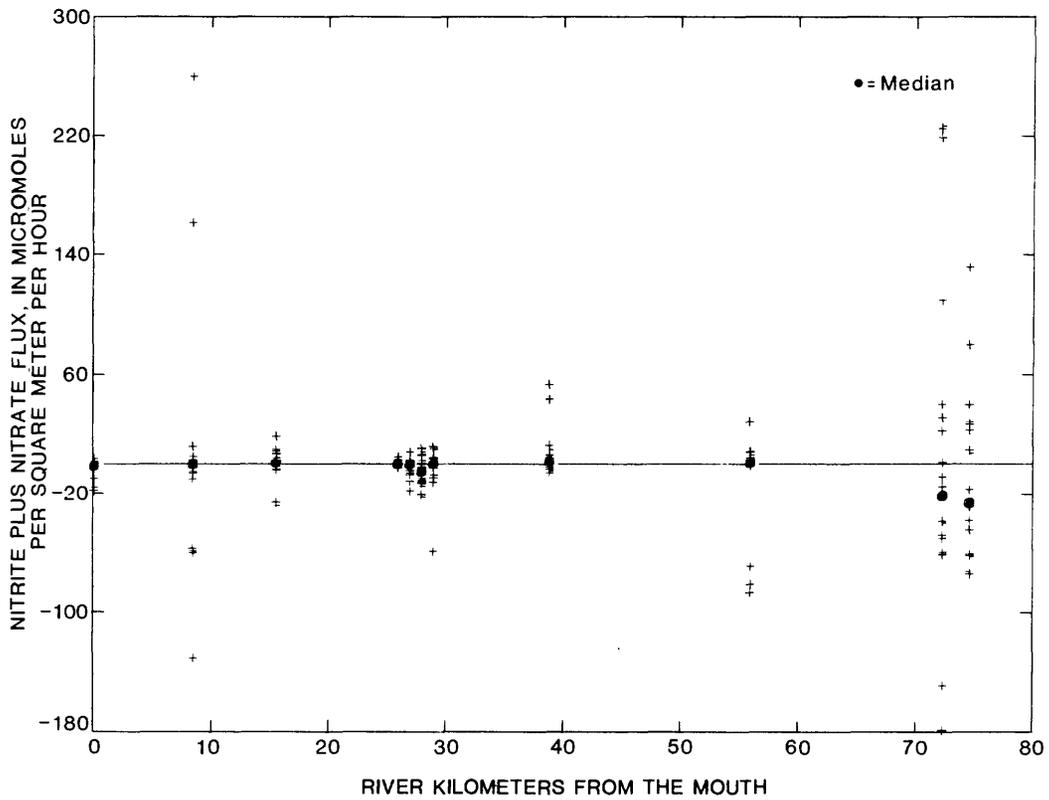
**Figure 6.** Relation of observed dissolved ammonium plus organic nitrogen flux rates to river kilometer during all cruises.



**Figure 7.** Relation of observed dissolved ammonium flux rates to river kilometer during all cruises.



**Figure 8.** Relation of observed dissolved nitrite flux rates to river kilometer during all cruises.



**Figure 9.** Relation of observed dissolved nitrite plus nitrate flux rates to river kilometer during all cruises.

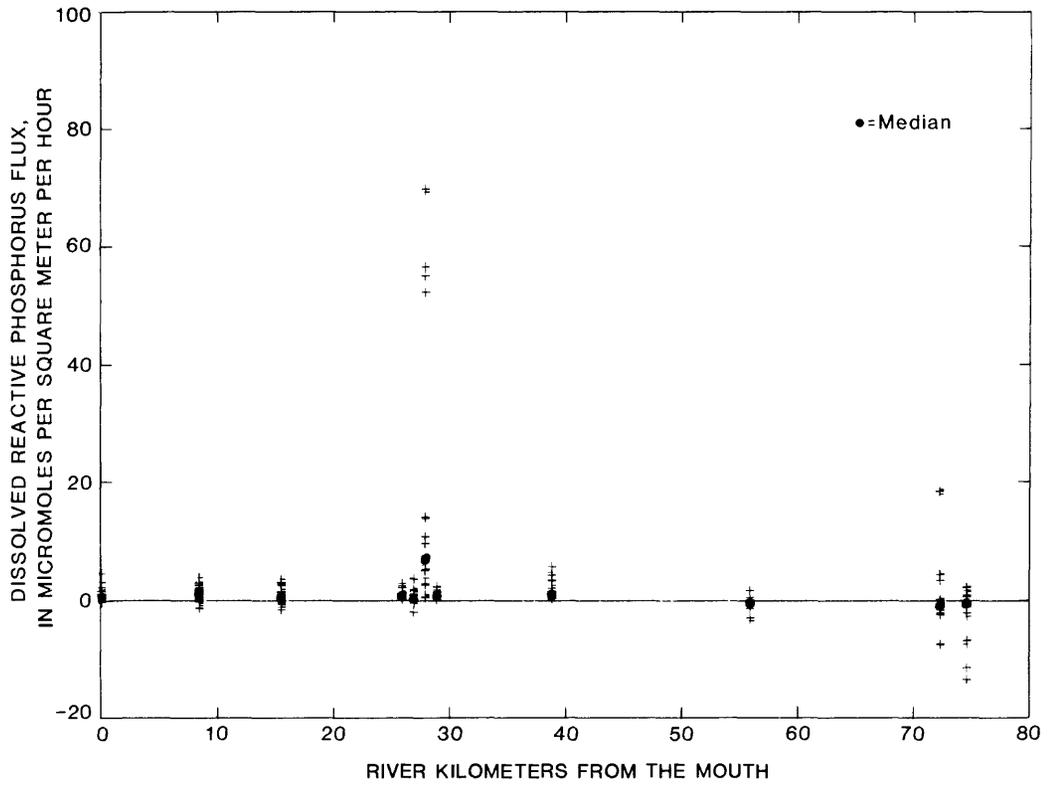


Figure 10. Relation of observed dissolved reactive phosphorus flux rates to river kilometer during all cruises.

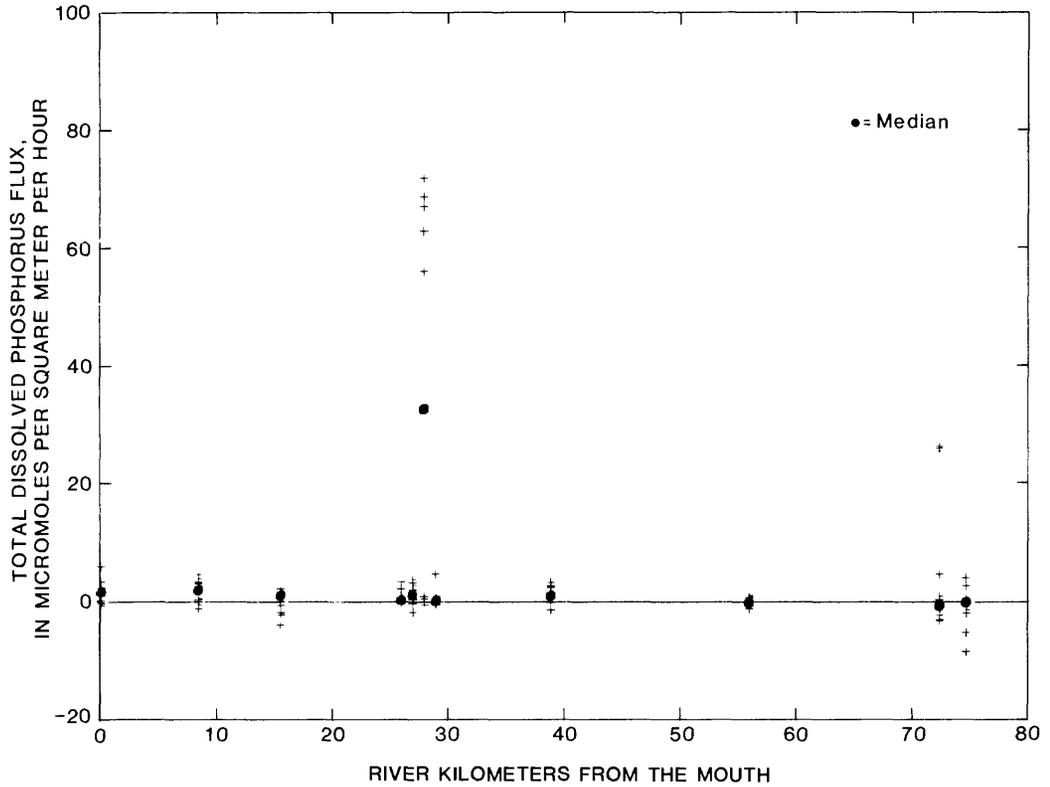
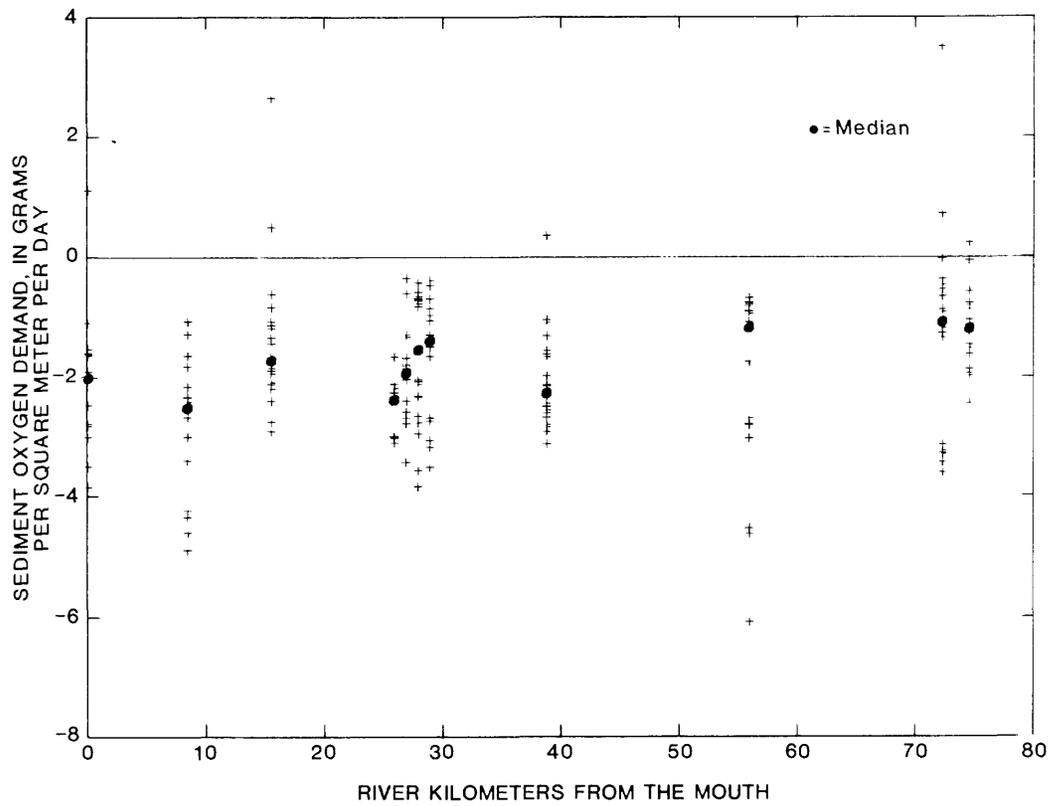
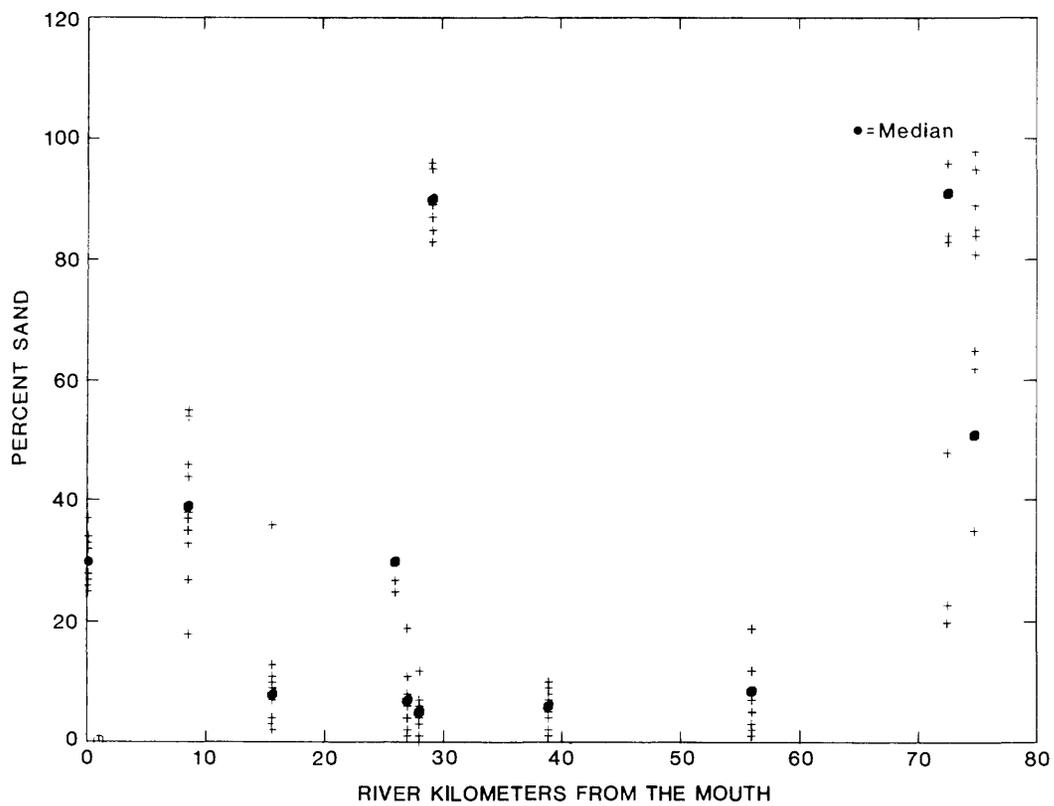


Figure 11. Relation of observed total dissolved phosphorus flux rates to river kilometer during all cruises.



**Figure 12.** Relation of observed sediment oxygen demand to river kilometer during all cruises.



**Figure 13.** Relation of observed percentage of sand in sediments to river kilometer during all cruises.

## Sediment Particle Size and Nutrient Concentrations

In conjunction with the estimation of nutrient fluxes and sediment oxygen demand, data were collected on the sediment-size fractionation among sand, silt, and clay. On two cruises, sediment was collected for nutrient concentrations (carbon, nitrogen, and phosphorus). Tables 4 and 5 show sediment-size fractionation and nutrient concentrations, respectively.

The sediment-size data shown in table 4 were collected in close proximity to the benthic respirometers. During the first year, single samples were collected at each station, but three samples were collected at each station during the second year. These three samples were used to assess the variability in sediment size.

The sediment nutrient concentrations shown in table 5 were determined for sediment collected during the final cruises of the project and represent sediment nutrient concentrations during the late summer and fall of 1983. The samples were collected with a benthos gravity corer, and the extruded cores were partitioned into 0- to 2.5-cm and 2.5- to 5.0-cm segments. When a core could not be collected, occasionally a subsample of a grab sample was used for nutrient concentrations. The analyses were conducted by the USGS Laboratory in Atlanta, Ga. Nutrient concentrations were similar along the estuary, exceptions being Marsh Point stations 1 and 2. Sediment nutrient concentrations in the freshwater, with the exception of Wayson's Corner, were within the range of the estuarine samples.

Marsh Point station 7 shows extremely low nutrient concentrations in comparison with the other stations; Marsh Point station 7 also has the highest percentage of sand of any of the stations. The association of finer grained sediments with organic material is known. Therefore, both the sediment and the nutrient characteristics may be related to the depositional properties of the station.

After an initial review of the data of the first year, sediment nutrient concentrations were added to the sampling scheme in the hope of explaining some of the observed flux rate variability. Budgetary constraints limited the sampling to two cruises. Preliminary analyses of the sediment nutrient concentrations and corresponding flux rates did not yield any trends. Therefore, further use or analysis of these data were not attempted for this report.

## TRENDS AND VARIABILITY IN SEDIMENT NUTRIENT FLUX AND OXYGEN DEMAND

The first step taken in analyzing these data was to characterize the observed fluxes by station to determine if the observed flux rates were normally distributed. On

the basis of the univariate analysis (SAS Institute Incorporated, 1982), the flux data were not consistent. Flux rate estimates for some parameters were normally distributed at some stations but not at others; the data set was subdivided into "cold weather" and "warm weather." Again, the SAS procedure univariate analysis did not reveal consistently normal data; however, fewer of the parameters were discernibly different from normal at the 5 percent level than they were when the data were lumped without regard to temperature. Because the data were not consistently normally distributed, it was decided that the use of parametric statistics to characterize (summarize) the data was not appropriate. Instead, all data are shown graphically in figures 6 to 13. The median values and quartiles have been highlighted on these figures to show the central tendency of the data. On the basis of an assessment of these plots, three parameters—dissolved  $\text{NH}_4^+$  plus organic N, total dissolved phosphorus, and  $\text{NO}_2^-$ —will be dropped from further evaluation. The  $\text{NH}_4^+$  plus organic N values were erratic and were dropped because of the low confidence placed on the rate approximations. The dissolved phosphorus flux appears to be dominated by dissolved reactive phosphorus. This dominance plus a lack of consistency in the total dissolved phosphorus measurements led to the removal of total dissolved phosphorus as a measured parameter after the first year. The  $\text{NO}_2^-$  analyses will not be discussed further because of the dominance of the  $\text{NO}_2^- + \text{NO}_3^-$  fraction. However, a listing of the complete data set can be found at the end of this report in the supplemental data.

The removal of these parameters from consideration does not imply problems with the procedures; rather, it suggests that the analytical methods might not be sensitive enough to detect consistently the small changes in concentration observed during this project.

## Spatial and Seasonal Trends

### Nutrients

*Ammonium fluxes.*—The majority of the ammonium flux observations are positive (fig. 7), indicating that the sediments are generally a source of ammonium to the overlying water. The preponderance of the data points lie between 0 and  $500 \mu\text{Mm}^{-2}\text{h}^{-1}$ . Maximum values occurred at Marsh Point station 6. Higher values were also observed at the tidal river stations (kilometer 56 and above).

With the exception of station 6 (kilometer 28), the dissolved ammonium profiles shown in figure 7 suggest greater variability in ammonium fluxes from the Patuxent freshwater sediments (stations 9, 10, and 11) than from the estuary, with observed ranges of  $-297$  to  $1,940 \mu\text{Mm}^{-2}\text{h}^{-1}$  in the freshwater in comparison with  $-401$  to  $798 \mu\text{Mm}^{-2}\text{h}^{-1}$  as N in the estuary. Station 6 ammonium flux values ranged from 80 to  $3,040 \mu\text{Mm}^{-2}\text{h}^{-1}$ .

**Table 4.** Observed sediment-size fractionation in the tidal Patuxent River and Estuary

Station	Cruise		Particle size analysis, in percent		
			Sand	Silt	Clay
1. Hog Point	June	1982	26	40	34
	August-September	1982	34	34	32
	October-November	1982	34	50	16
	March	1983	30	58	12
	June	1983	28	33	39
			37	34	29
			32	34	34
	September	1983	25	63	12
			28	38	34
			28	50	22
	October-November	1983	27	41	32
			29	47	24
33			45	22	
2. Point Patience	June	1982	39	25	36
	August-September	1982	37	28	35
	October-November	1982	35	51	14
	March	1983	44	46	10
	June	1983	46	21	35
			55	20	25
			33	40	27
	September	1983	38	26	36
			27	49	24
			18	45	37
	October-November	1983	44	28	28
			39	46	15
54			30	16	
3. St. Leonard's Creek	August-September	1982	4	56	40
	October-November	1982	8	33	59
	March	1983	12	47	42
	June	1983	36	22	42
			9	43	48
			7	39	54
	September	1983	3	57	40
			2	64	34
			13	55	32
	October-November	1983	10	49	41
			13	67	20
			11	57	32
4. Marsh Point 4	June	1982	60	14	26
	August-September	1982	27	28	45
	October-November	1982	30	24	46
	March	1983	25	50	25
	June	1983	36	29	35

**Table 4.** Observed sediment-size fractionation in the tidal Patuxent River and Estuary—Continued

Station	Cruise		Particle size analysis, in percent			
			Sand	Silt	Clay	
5. Marsh Point 3	June	1982	19	27	54	
	August-September	1982	7	54	39	
	October-November	1982	8	50	42	
	March	1983	11	31	58	
	June	1983		4	24	72
				7	41	52
				11	21	68
	September	1983		1	59	40
				4	53	43
				6	27	67
	October-November	1983		4	45	51
				7	54	39
				2	56	42
	6. Marsh Point 2	June	1982	5	2	93
August-September		1982	6	47	47	
October-November		1982	9	15	76	
March		1983	3	55	42	
June		1983	3	15	82	
September		1983		4	55	41
				12	78	10
				5	61	34
				1	35	64
				6	0	94
October-November		1983		7	60	33
				8	60	32
				1	50	49
				0	52	48
				7	59	34
			6	64	30	
7. Marsh Point 1	June	1982	96	1	3	
	August-September	1982	90	4	6	
	October-November	1982	95	1	4	
	June	1983		87	4	9
				89	4	7
				90	4	6
	September	1983		83	11	6
				89	4	7
				87	6	7
	October-November	1983		87	6	7
				87	6	7
				85	7	8
8. Buena Vista	June	1982	5	23	72	
	August-September	1982	10	22	68	
	October-November	1982	9	21	70	
	March	1983	6	43	51	
	June	1983		5	25	70
				7	20	73
			1	28	71	

**Table 4.** Observed sediment-size fractionation in the tidal Patuxent River and Estuary—Continued

Station	Cruise		Particle size analysis, in percent		
			Sand	Silt	Clay
(8. Buena Vista--Continued)					
	September	1983	8	45	47
			4	65	31
			8	29	63
	October-November	1983	8	24	68
			10	47	43
			2	36	62
9. Lower Marlboro					
	June	1982	8	26	66
			25	29	46
	August-September	1982	19	33	48
			8	31	61
	October-November	1982	10	32	58
			1	35	64
	March	1983	12	35	53
	June	1983	8	27	65
			9	36	55
			7	36	57
	September	1983	3	67	30
			2	73	25
			5	76	19
	October-November	1983	7	63	30
			7	65	28
			7	53	40
10. Jug Bay					
	June	1982	87	6	7
			95	1	4
	August-September	1982	96	1	3
			94	1	5
	October-November	1982	83	8	9
			91	3	6
	March	1983	84	7	9
	June	1983	48	39	13
			84	10	6
			32	53	15
	September	1983		All Leaves	
	October-November	1983	20	43	37
			20	33	47
			23	32	45
11. Wayson's Corner					
	June	1982	51	27	22
	August-September	1982	51	25	24
	October-November	1982	65	22	13
	March	1983	85	7	8
	June	1983	89	5	6
			98	0	2
			84	9	7
	September	1983	35	31	34
			81	7	12
			62	29	9
	October-November	1983	85	9	6
			64	23	13
			95	1	4

**Table 5.** Observed sediment nutrient concentrations in the tidal Patuxent River and Estuary

Cruise	Depth of sample below surface (cm)	Nitrogen (mg/kg)	Phosphorus (mg/kg)	Carbon (g/kg)
<u>Hog Point</u>				
September 1983	0 - 2.5	8,300	440	17.0
September 1983	2.5 - 5	14,000	430	17.0
October 1983	0 - 2.5	8,300	560	15.0
October 1983	2.5 - 5	3,200	180	13.0
<u>Point Patience</u>				
September 1983	0 - 2.5	6,300	330	17.0
September 1983	2.5 - 5	29,000	350	15.0
November 1983	0 - 2.5	9,900	170	14.0
November 1983	2.5 - 5	4,700	290	9.3
<u>St. Leonard's Creek</u>				
September 1983	0 - 2.5	12,000	840	30.0
September 1983	2.5 - 5	7,000	370	25.0
November 1983	0 - 2.5	13,000	570	26.0
November 1983	2.5 - 5	11,000	2,100	23.0
<u>Marsh Point station 5</u>				
September 1983	0 - 2.5	16,000	1,000	46.0
September 1983	2.5 - 5	5,900	710	24.0
November 1983	0 - 2.5	6,600	550	24.0
November 1983	2.5 - 5	6,200	410	22.0
<u>Marsh Point station 6</u>				
September 1983	0 - 2.5	73,000	1,300	34.0
September 1983	2.5 - 5	28,000	970	28.0
November 1983	0 - 2.5	11,000	260	27.0
November 1983	2.5 - 5	13,000	640	25.0
<u>Marsh Point station 7</u>				
September 1983	0 - 2.5	2,000	130	3.8
September 1983	2.5 - 5	4,000	72	3.2
November 1983	0 - 2.5	780	86	2.5
November 1983	2.5 - 5	680	28	1.4
<u>Buena Vista</u>				
September 1983	0 - 2.5	7,800	1,800	29.0
September 1983	2.5 - 5	23,000	1,200	27.0
November 1983	0 - 2.5	3,600	1,600	25.0
November 1983	2.5 - 5	11,000	850	24.0
<u>Lower Marlboro</u>				
September 1983	0 - 2.5	53,000	2,000	33.0
September 1983	2.5 - 5	15,000	2,300	34.0
November 1983	0 - 2.5	19,000	-	35.0
November 1983	2.5 - 5	11,000	2,300	35.0
<u>Jug Bay</u>				
September 1983	0 - 2.5	20,000	3,000	71.0
September 1983	2.5 - 5	8,000	3,700	92.0
November 1983	0 - 2.5	12,000	620	35.0
November 1983	2.5 - 5	7,400	1,500	47.0
<u>Wayson's Corner</u>				
November 1983	0 - 2.5	2,100	540	10.0
November 1983	2.5 - 5	450	260	12.0

Station 6 is unique with respect to the other stations in that it is in a highly depositional environment which becomes anoxic over extended periods in the summer. The higher flux of ammonium here may be the result of the higher organic content of the sediments (see table 5) and (or) the reduction of nitrite and nitrate occurring under anoxic conditions.

In an effort to separate seasonal variability from spatial variability, the flux data have been plotted in seasonal categories. Spring includes the June 1982 and 1983 cruises when water temperatures throughout the study area ranged between 20 and 27°C. Summer includes cruises in late August and early September of both years when temperatures were similar to those observed in the spring. Fall cruises occurred in late October and early November when water temperatures were between 10 and 19°C. Winter data consist of a single cruise in March 1983 when temperatures were from 5 to 11°C.

Ammonium flux data segregated by season are shown in figure 14. Spring and summer fluxes are similar at each station. In the fall, values are somewhat lower, with the exception of station 9 at Lower Marlboro. By winter, the fluxes are minimal at all stations. This seasonal cycle is probably the result of lower temperatures and associated reduced biological activity.

*Nitrite plus nitrate fluxes.*—The dissolved nitrite plus nitrate flux observations are plotted in figure 9, and the seasonal groupings are shown in figure 15. The median flux rates over all cruises at the transition and estuarine stations (1–9, below kilometer 57) are in the range of  $\pm 50 \mu\text{Mm}^{-2}\text{h}^{-1}$  (see table 2). The tidal river stations, Jug Bay (kilometer 72) and Wayson's Corner (kilometer 74), had median flux rates of  $-215.83$  and  $-263.67 \mu\text{Mm}^{-2}\text{h}^{-1}$ , respectively. Although the tidal river stations were also subject to greater variability, there is a predominance of negative flux rates, which indicates that the tidal fresh sediments are acting as a sink for nitrite plus nitrate.

The wide variability in flux rates in the freshwater stations appears to be the result of a strong seasonal cycle (fig. 15). During the fall and spring, the sediments are more often a source of nitrite and nitrate to the water column. During the summer, the sediments are most often a sink for nitrite and nitrate, and in winter, flux rates are minimal.

The estuarine results for this study show the sediments to be predominantly a sink for nitrite plus nitrate in the spring and summer. In the fall and winter, values were generally near or above zero. This is consistent with results obtained by Boynton and others (1982) for sediments near the Chalk Point Power Plant (river kilometer 40).

Based on the amounts measured in the water column, nitrite and nitrate are the dominant dissolved nitrogen species in the tidal Patuxent River. The water-column concentrations (table 3) and fluxes (table 2) are

nearly double those for dissolved ammonium; this is similar to observations in the Potomac River (Callender and others, 1984). The nitrogen balance between the water column and sediments in the tidal river is probably controlled by several factors. The high concentration of dissolved nitrite and nitrate is due to high concentrations in the inflowing river water. Simple equilibrium reactions may control sediment/water-column exchange. For example, high water-column concentrations due to reduced riverflow in the summer coincide with maximum nitrite and nitrate losses to the sediment. In addition, the exchange may be governed by deposition-resuspension, denitrification processes, and (or) ground-water flow.

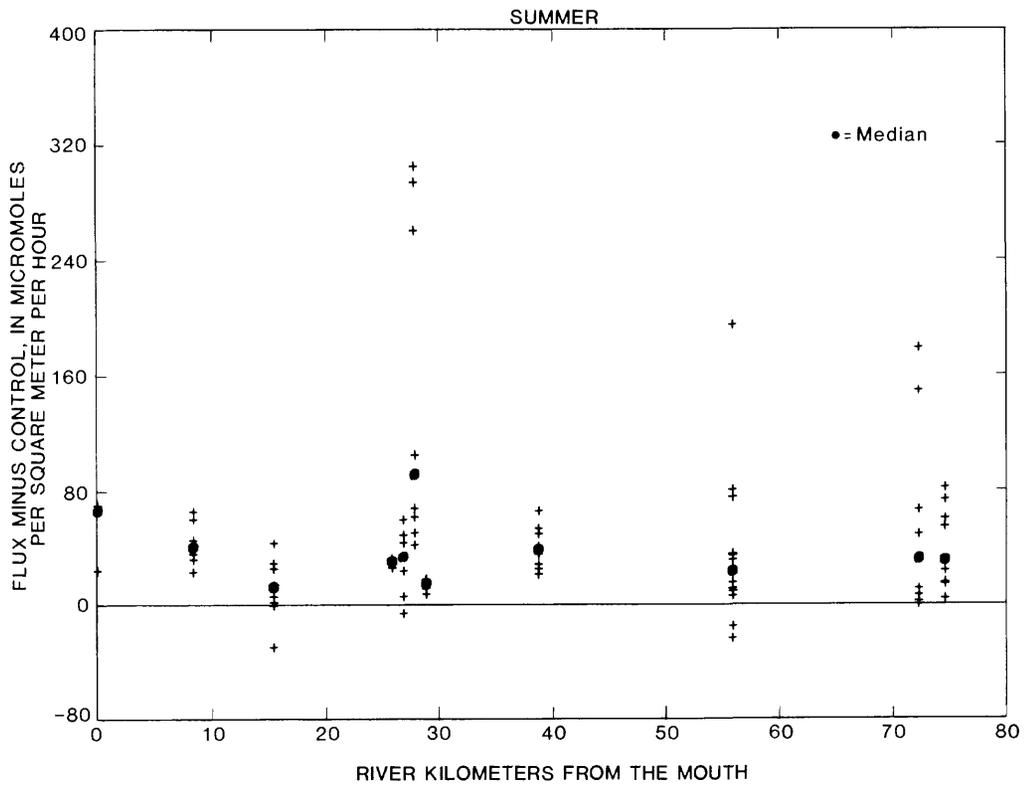
In the estuary, the dominant form of nitrogen is ammonium. This is true for this study, for the Patuxent (Boynton and others, 1982), for the Potomac (Callender and others, 1984), and for two North Carolina estuaries (Fisher and others, 1982). This dominance is most likely due to the regeneration of ammonium from the metabolism of organic material. However, the loss of nitrite plus nitrate to the sediments in summer, particularly at the anoxic station (Marsh Point station 6), coincident with the increased flux of ammonium from the sediment suggests that reduction of nitrite plus nitrate in the sediment may also be a factor.

*Dissolved reactive phosphorus.*—The striking aspect of the dissolved reactive phosphorus profile (fig. 10) is Marsh Point station 6 (kilometer 28), where the median flux rate of  $71 \mu\text{Mm}^{-2}\text{h}^{-1}$  as P is nearly fivefold greater than the closest rate of  $15 \mu\text{Mm}^{-2}\text{h}^{-1}$  as P at Point Patience (kilometer 8.5) and Buena Vista (kilometer 39). The range of observed fluxes was  $1\text{--}698 \mu\text{Mm}^{-2}\text{h}^{-1}$  as P at Marsh Point station 6. The probable mechanism for this phosphorus release involves the development of anoxia in the water column, resulting in the creation of reducing conditions in the sediments, with concomitant changes in the iron-phosphorus complexes. In an oxidizing environment, the iron is in insoluble ferrous form. The change to a reducing environment with the development of anoxia converts the iron to the soluble ferric form, releasing the bound phosphorus (Thibodeaux, 1979).

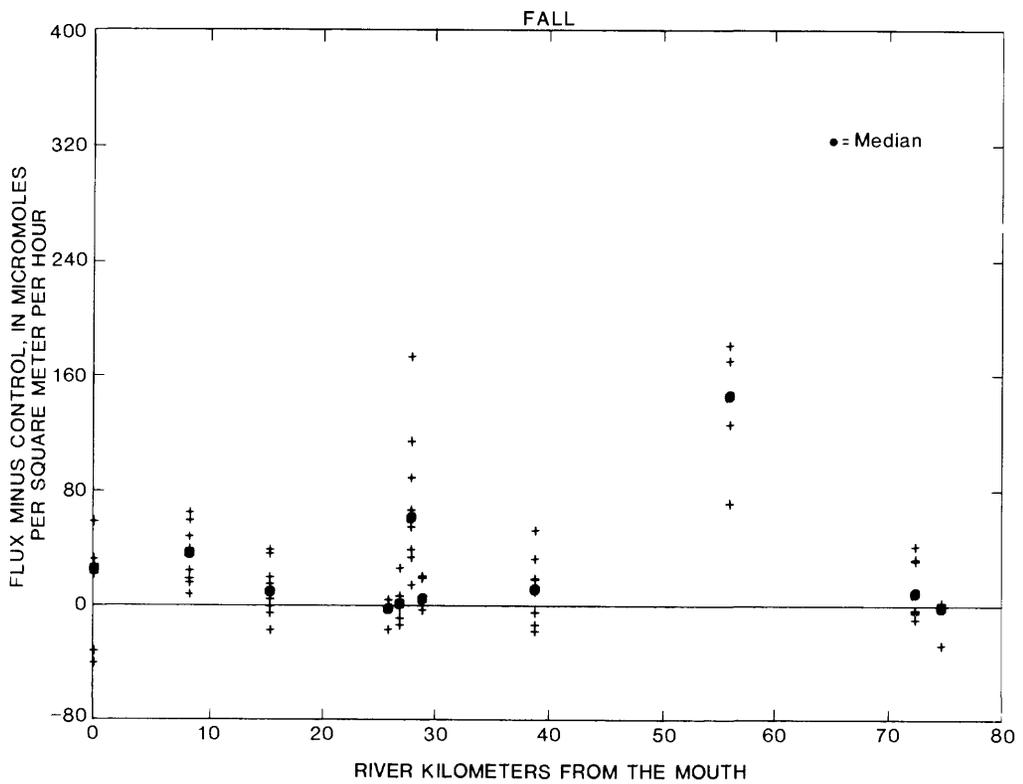
The vast majority of the dissolved reactive phosphorus fluxes in the tidal river were directed to the sediments in the transition zone (station 9, kilometer 56). Values were clustered around zero, and in the estuary the fluxes were predominantly to the water column.

Previous estimates (Boynton and others, 1982) of dissolved inorganic phosphorus fluxes ranging from  $-60$  to  $70 \mu\text{Mm}^{-2}\text{h}^{-1}$  as P were similar to the estimates of this study of  $-43$  to  $57 \mu\text{Mm}^{-2}\text{h}^{-1}$  as P (excepting station 6) for the same general reach of the river. Boynton and others also noted that the fluxes were smallest in the tidal river and often directed to the sediments.

Seasonal groupings of the dissolved reactive phosphorus flux rate observations are shown in figure 16. For



**Figure 14.** Dissolved ammonium flux rates plotted by season.



**Figure 14.** Dissolved ammonium flux rates plotted by season—Continued.

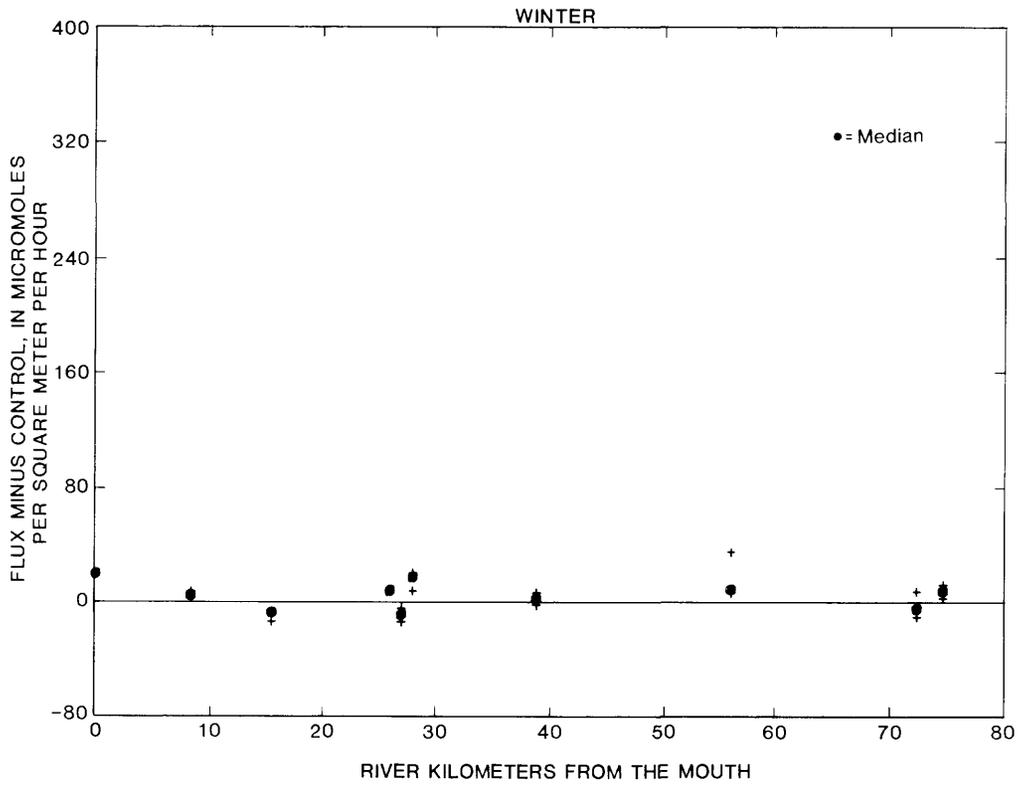


Figure 14. Dissolved ammonium flux rates plotted by season—Continued.

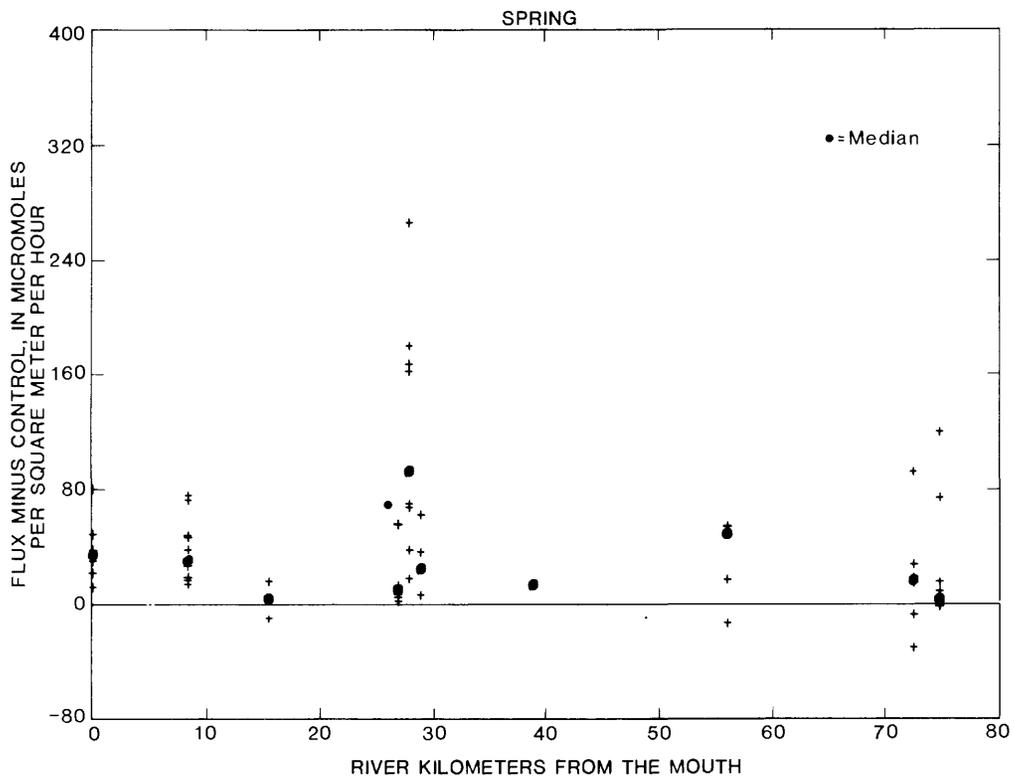
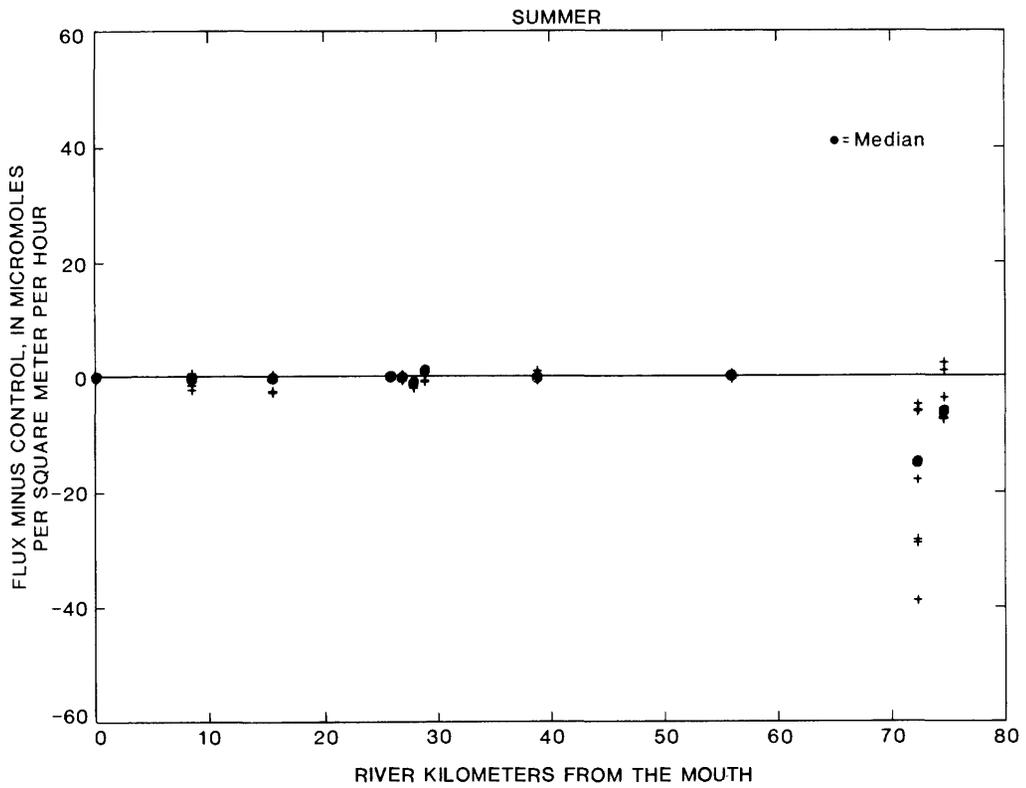
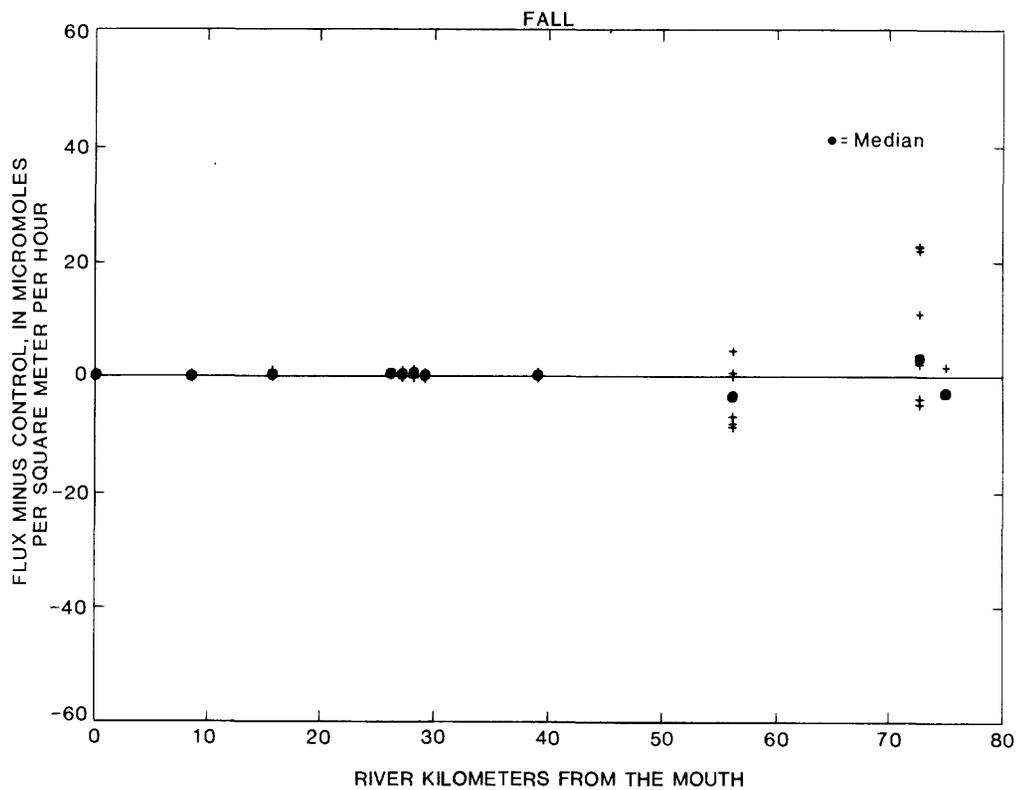


Figure 14. Dissolved ammonium flux rates plotted by season—Continued.



**Figure 15.** Dissolved nitrite plus nitrate flux rates plotted by season.



**Figure 15.** Dissolved nitrite plus nitrate flux rates plotted by season—Continued.

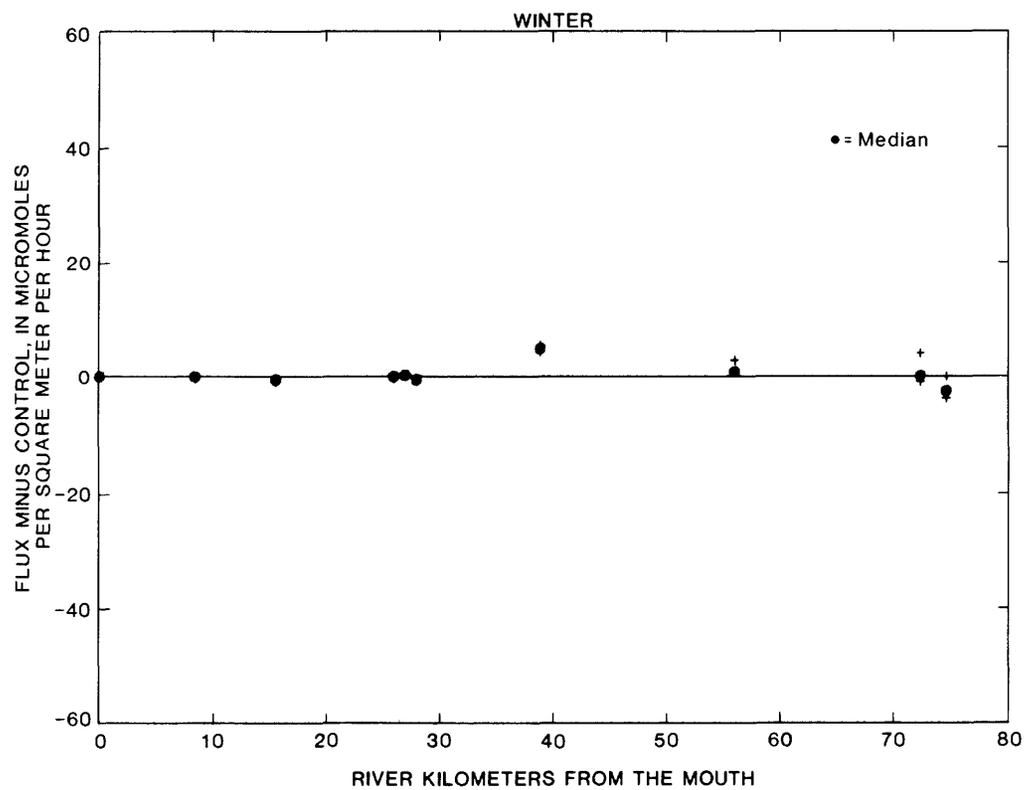


Figure 15. Dissolved nitrite plus nitrate flux rates plotted by season—Continued.

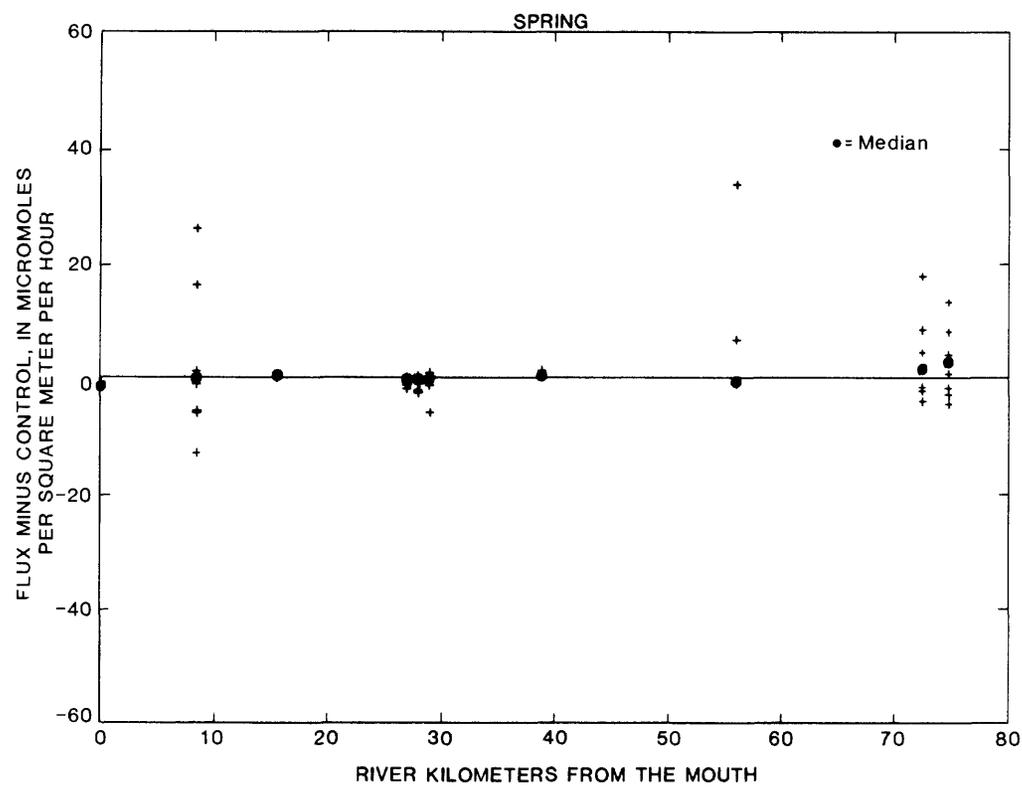
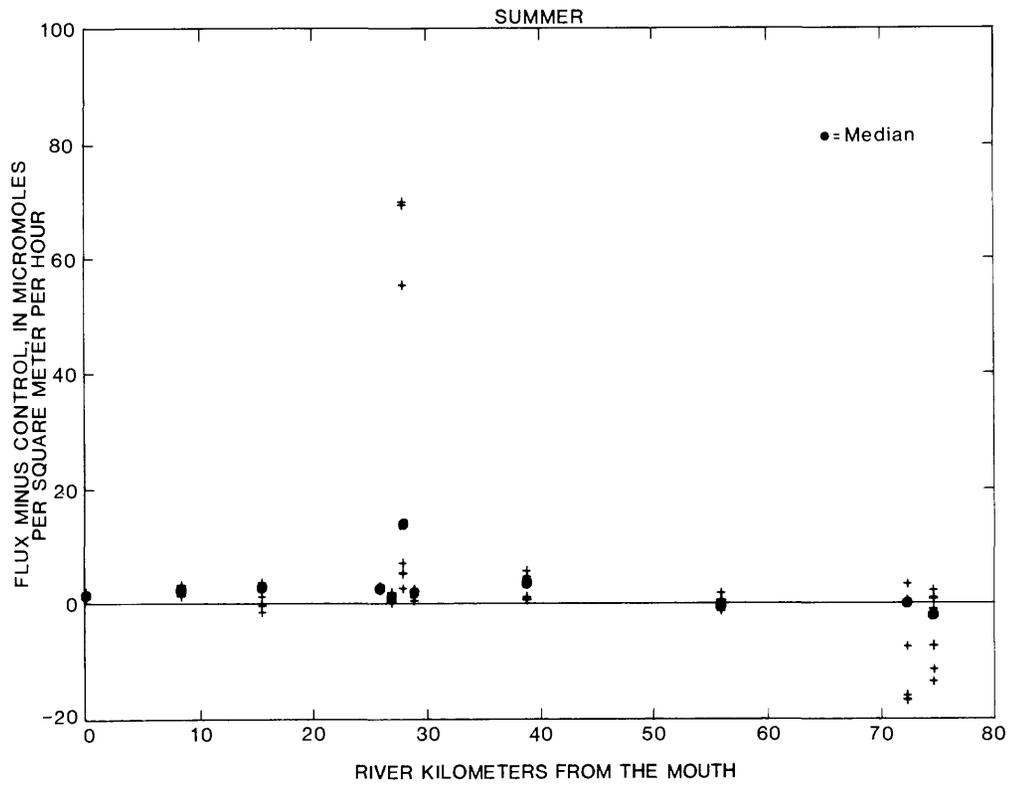
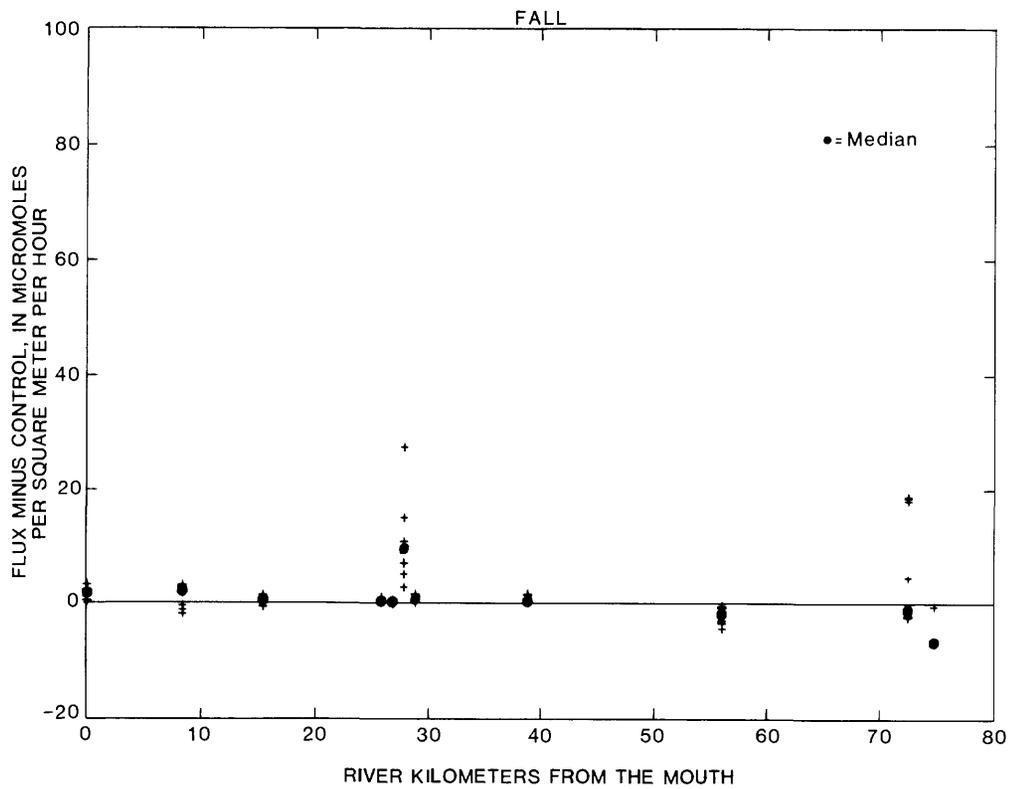


Figure 15. Dissolved nitrite plus nitrate flux rates plotted by season—Continued.



**Figure 16.** Dissolved reactive phosphorus flux rates plotted by season.



**Figure 16.** Dissolved reactive phosphorus flux rates plotted by season—Continued.

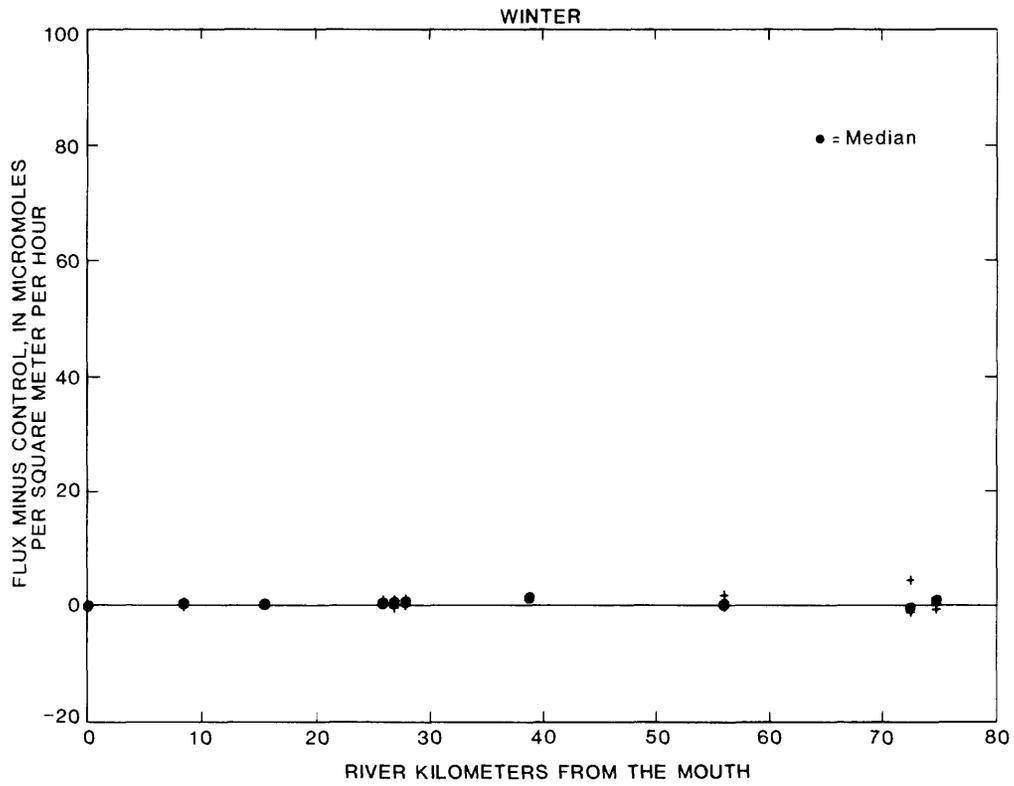


Figure 16. Dissolved reactive phosphorus flux rates plotted by season—Continued.

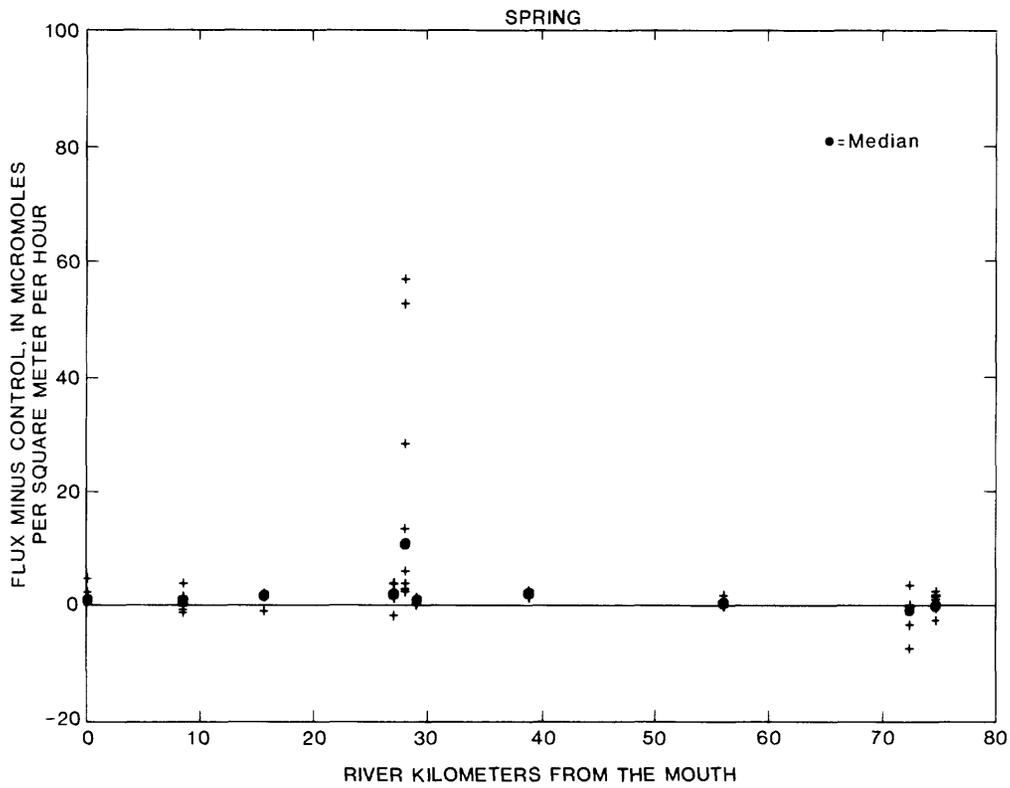


Figure 16. Dissolved reactive phosphorus flux rates plotted by season—Continued.

the midchannel station at Marsh Point (station 6, kilometer 28), there is a clear seasonal cycle with elevated fluxes in the spring and summer and reduced fluxes in the fall, reaching a minimum in the winter. This cycle apparently coincides with the development of anoxia in the overlying water. At the remaining estuarine stations, there is a similar but much less pronounced seasonal cycle. This is probably simply a function of the seasonal cycle in water temperature.

At the tidal river and transition stations, a somewhat different seasonal cycle was observed. In the summer, the majority of the flux measurements were directed to the sediments. Otherwise, fluxes were distributed above and below zero. This increased flux of phosphorus to the sediments in the summer may be the result of elevated water-column phosphorus concentrations caused by the reduced riverflow.

### Sediment Oxygen Demand

Observations of sediment oxygen demand fell predominantly in the range of 0 to  $-4 \text{ g m}^{-2}\text{d}^{-1}$  (fig. 12); maximum values ( $-4$  to  $-6 \text{ g m}^{-2}\text{d}^{-1}$ ) occurred at Point Patience (kilometer 8) and Lower Marlboro (kilometer 57). Sediment oxygen demand was highly variable along the longitudinal profile of both the tidal river and the estuary. As a result of this variability, there were no demonstrable or consistent trends in sediment oxygen demand in the Patuxent River. Figure 17 shows the seasonal pattern of sediment oxygen demand observations. With the exception of Marsh Point (station 6), where low dissolved oxygen in the summer caused sediment oxygen demand to be near zero, there are no clear seasonal trends that can be distinguished in the sediment oxygen demand data.

Figure 18 shows initial water-column concentrations for ammonium, nitrite plus nitrate, dissolved reactive phosphorus, and dissolved oxygen. Ammonium concentration variability obscures any longitudinal trends in the data. Nitrite plus nitrate and dissolved reactive phosphorus concentrations are higher in the tidal river and decline gradually in a downstream direction. This may reflect the importance of river sources for these constituents. There is an aberration in the dissolved reactive phosphorus profile at Marsh Point (station 6), where higher values and greater variability were observed. This is probably due to the increased sediment flux of phosphorus under anoxic conditions. Dissolved oxygen concentrations are variable and generally uniform throughout the river. The increased range in dissolved oxygen concentrations observed in the estuary is indicative of the effect of phytoplankton and water-column stratification on dissolved oxygen concentrations.

The data have been presented in graphical form showing all data and the median values for the appropriate

groupings of the data. On the basis of this graphical analysis and the comparison of median values and quartile ranges shown in table 6, the generalizations presented in table 6 can be made.

### Temporal Variability

In this section, temporal variability within station groups is presented to assess year-to-year fluctuations in the data, in contrast to the preceding seasonal grouping of data over the longitudinal profile of the river. Rather than including separate plots for each station, the stations have been divided into four groups—the tidal river, the transition zone, the estuary, and the anoxic estuary. These groupings were selected to reflect differences in the salinity, dissolved oxygen, and hydrodynamic conditions at the stations. The tidal river includes stations 10 and 11 (above kilometer 56). The river is narrow and subject to strong tidal currents; however, the salinity was never above 0.4. The transition zone includes only station 9. The river is hydrodynamically similar to the tidal river, but salinity ranges from fresh to nearly 5. The estuarine group includes stations 1 through 8, with the exception of station 6 (which is the anoxic group). The estuary is broader and not subject to as strong a current system as the tidal river and transition zones. Salinities ranged from 3 to 17. Station 6 was the only station that exhibited consistent anoxia over the spring and summer; for this reason, this station was segregated in its own group.

### Dissolved Ammonium

Ammonium flux rates for each group over the duration of the project are shown in figure 19. In the tidal river there was a clear maximum observed in late summer of the second year, but in the first year, flux rates were fairly consistent throughout the year. At the transition zone station, ammonium flux peaked in the fall for both years. At the anoxic station, fluxes peaked in summer during the first year and were roughly equivalent in the spring, summer, and fall of the second year. In the estuary, winter and early spring fluxes were slightly lower than those at other times of the year. Estuarine ammonium fluxes were much less variable than fluxes at other stations.

In general, there is a seasonal cycle in flux rates, with maximum fluxes occurring in summer and fall. However, year-to-year differences can be as large as seasonal differences; this was observed at the tidal river and anoxic stations in particular. Here, the year-to-year variability in fluxes is most likely to be a reflection of riverflow variation and associated changes in sediment load and nutrient concentrations. At the estuarine stations, the impact of changes in stratification due to meteorologic events affects dissolved oxygen and fluxes as well. This suggests

**Table 6.** Summary of results of sediment oxygen demand and sediment nutrient flux measurements [75%, 75th percentile; 25%, 25th percentile; Med, Medium]

Chemical constituent	Tidal river			Transition zone			Estuary (oxic)			Estuary (anoxic)		
	75%	Med	25%	75%	Med	25%	75%	Med	25%	75%	Med	25%
Dissolved ammonium ( $\mu\text{mole}/\text{m}^2/\text{hr}$ )	Positive flux generally lower than other groups except in summer.											
Spring	283	97	-5	543	492	28	469	252	141	1,733	921	533
Summer	681	317	105	651	239	78	435	299	156	2,766	903	562
Fall	263	9	-41	1,727	1,457	1,119	275	113	-15	1,007	608	368
Winter	90	54	-58	353	91	65	81	46	-67	205	178	80
Dissolved nitrite plus nitrate ( $\mu\text{mole}/\text{m}^2/\text{hr}$ )	Large negative (to sed.) flux in summer, slightly negative in winter; otherwise generally positive.											
Spring	803	271	-216	2,015	-65	-77	41	-2	-148	0	-32	-215
Summer	-572	-622	-1,560	31	11	-25	6	-20	-58	-108	-116	-141
Fall	1,918	201	-359	158	-341	-825	38	21	2	95	60	-12
Winter	111	-43	-278	288	87	79	23	2	-25	-29	-54	-71
Dissolved reactive phosphorus ( $\mu\text{mole}/\text{m}^2/\text{hr}$ )	Negative flux in summer and fall; negligible in winter and spring.											
Spring	15	-1	-8	13	5	0	22	13	5	405	107	34
Summer	5	-15	-119	5	-4	-7	31	20	12	623	138	53
Fall	146	-13	-23	-6	-18	-36	16	6	2	129	94	61
Winter	19	2	-8	18	1	-2	8	3	0	11	6	1
Sediment oxygen demand ( $\text{g}/\text{m}^2/\text{d}$ )	Slightly lower oxygen demand than in estuary.											
Spring	0.0	-0.8	-1.3	ND	ND	ND	-1.4	-2.1	-2.9	-2.1	-2.3	-2.7
Summer	-0.9	-1.6	-2.4	-1.1	-2.7	-4.1	-1.6	-2.0	-2.8	-0.6	-0.7	-0.7
Fall	-0.6	-1.2	-3.1	-0.7	-0.8	-1.3	-1.5	-2.1	-2.6	-1.1	-2.0	-2.4
Winter	0.0	-0.4	-0.9	-0.9	-0.9	-0.9	-1.1	-1.7	-2.2	-2.9	-3.2	-3.6
Dissolved nitrite	Generally weak flux, but more outliers than estuarine stations; in fall, strong negative flux.											
Dissolved nitrate	Negligible to small negative flux in spring and summer; negligible to small positive flux in fall and winter.											
Dissolved nitrite plus nitrate	Weak negative flux except in fall when it is positive at an equivalent magnitude.											
Dissolved reactive phosphorus	Positive flux peaking in summer; negligible in winter.											
Dissolved ammonium	Large positive flux in all seasons, peaking in summer.											
Sediment oxygen demand	Consistent SOD in spring, summer and fall; slightly less in winter.											
Sediment oxygen demand	Maximum SOD in winter; comparable to the estuary in spring and fall; low SOD in summer because of anoxia.											



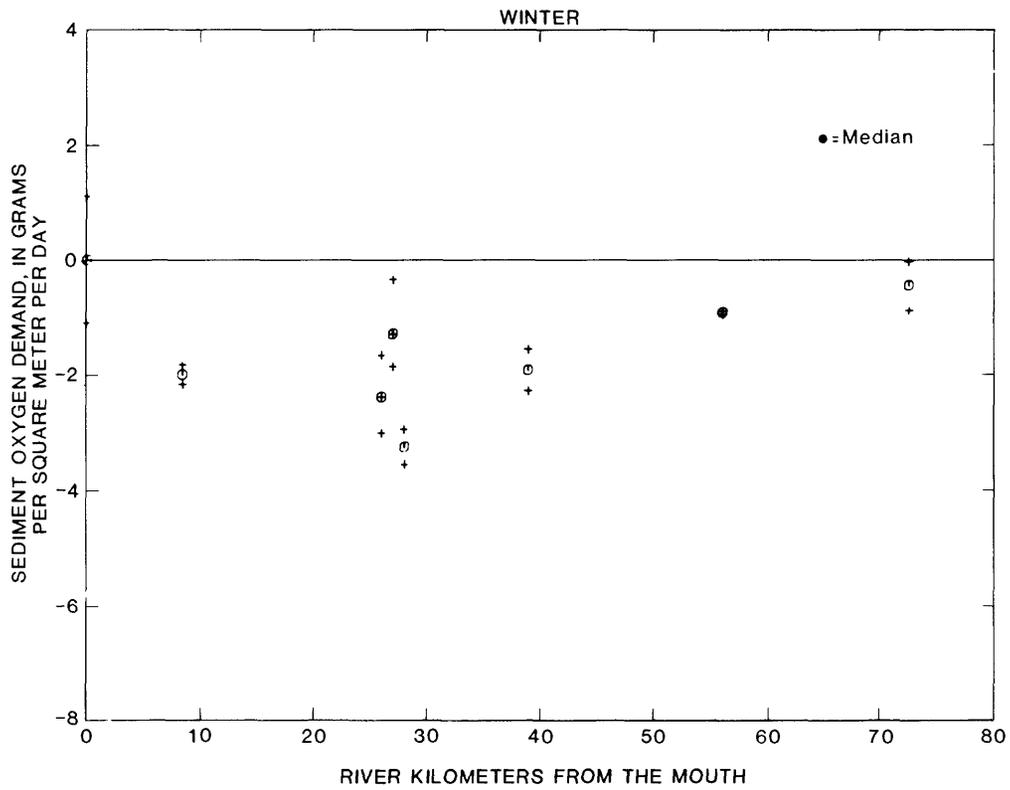
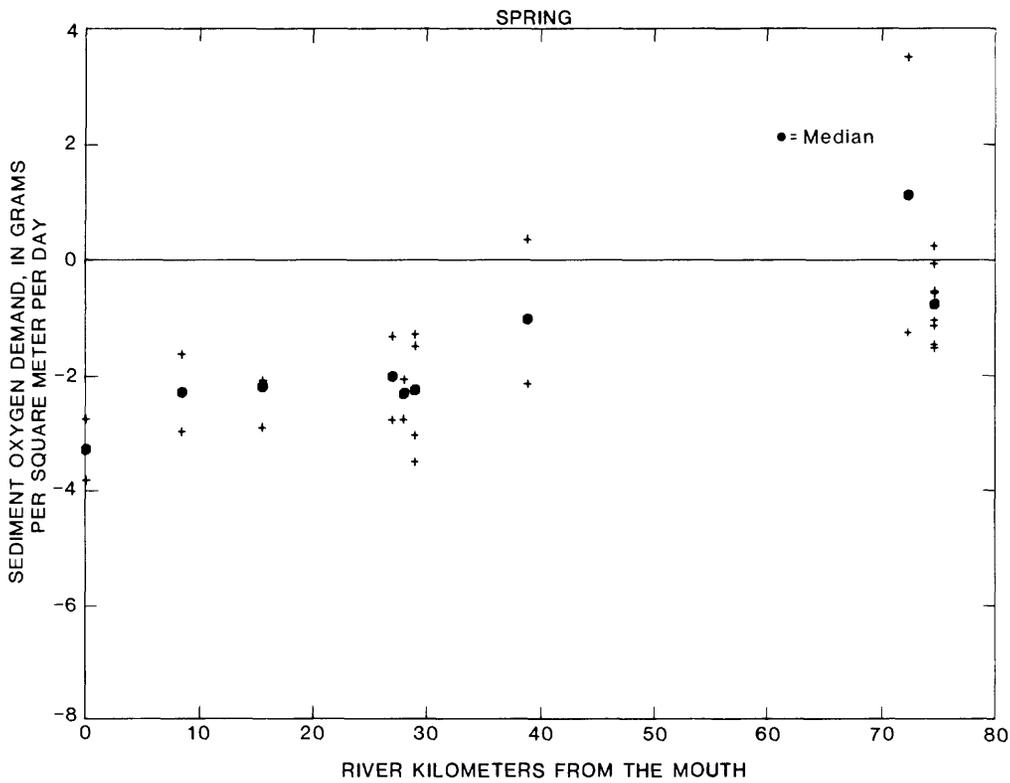
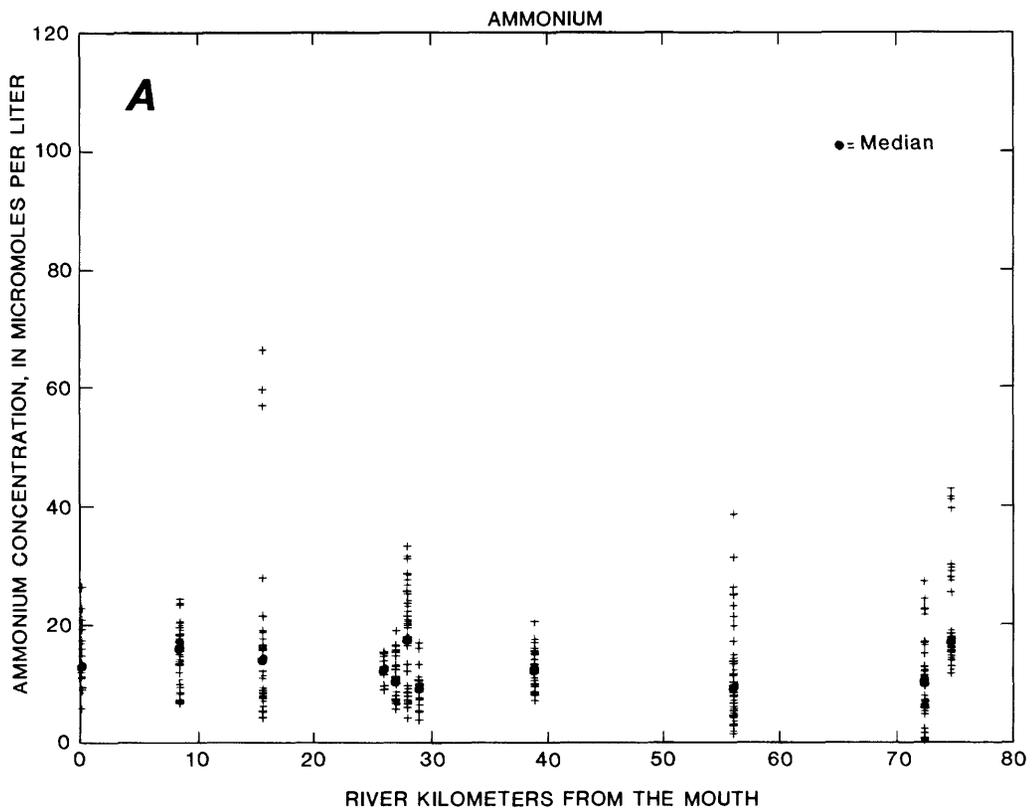
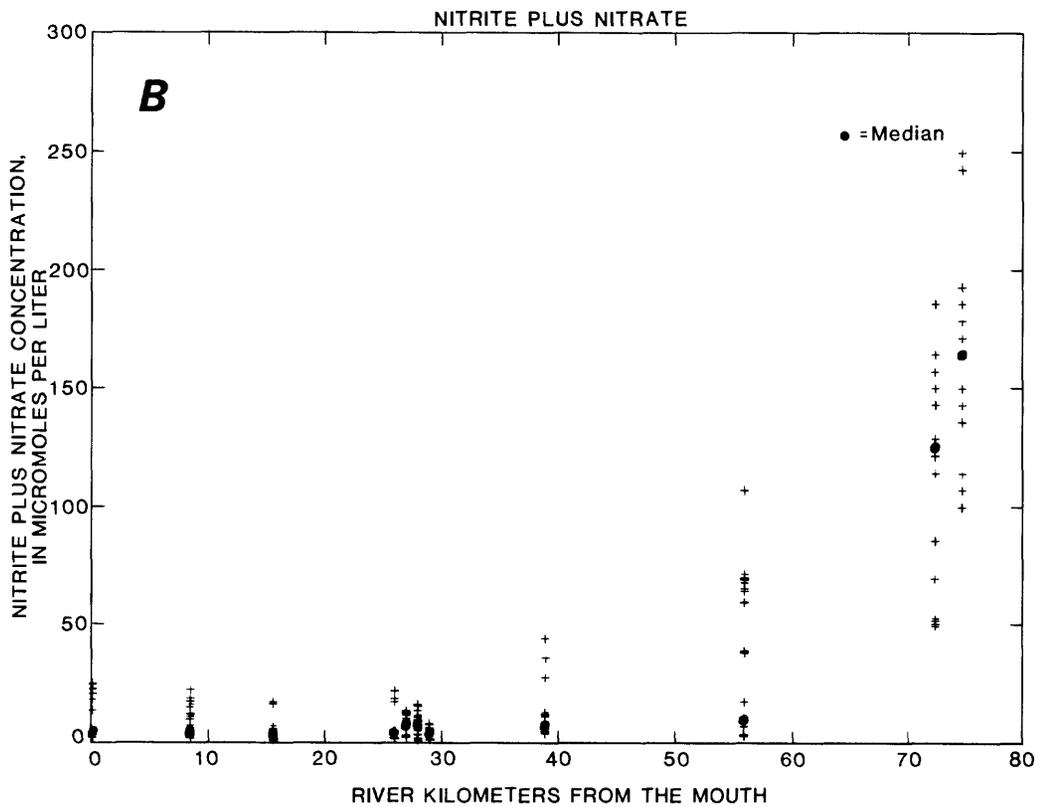


Figure 17. Sediment oxygen demand flux rates plotted by season—Continued.

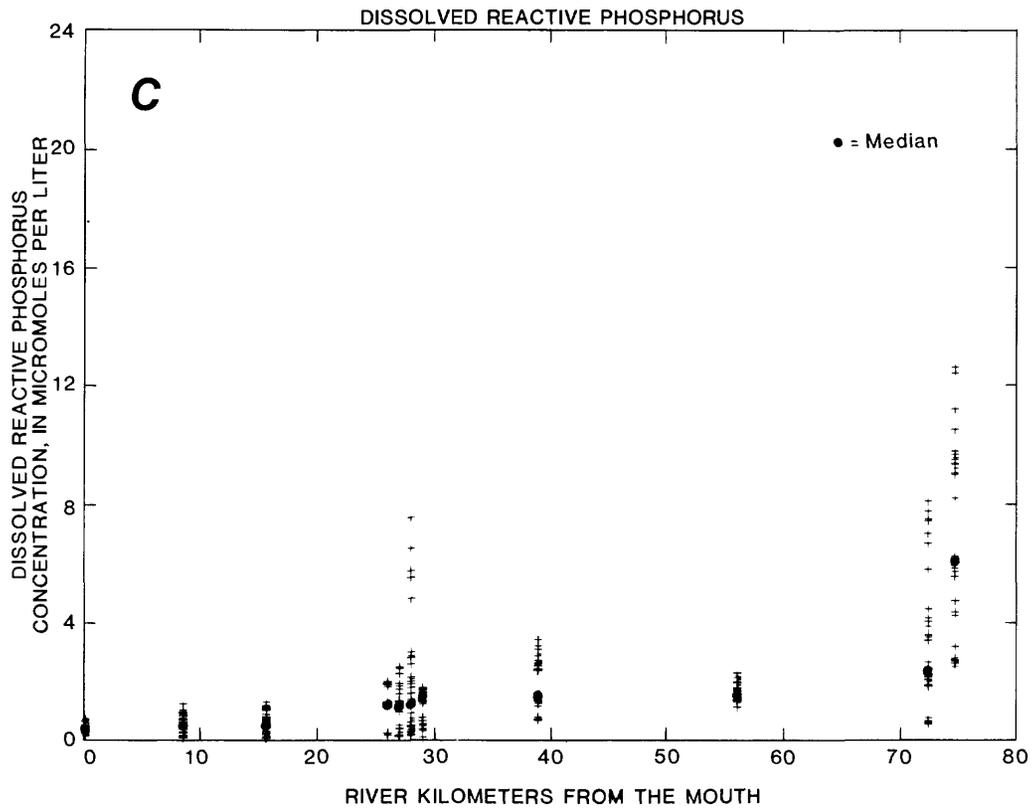




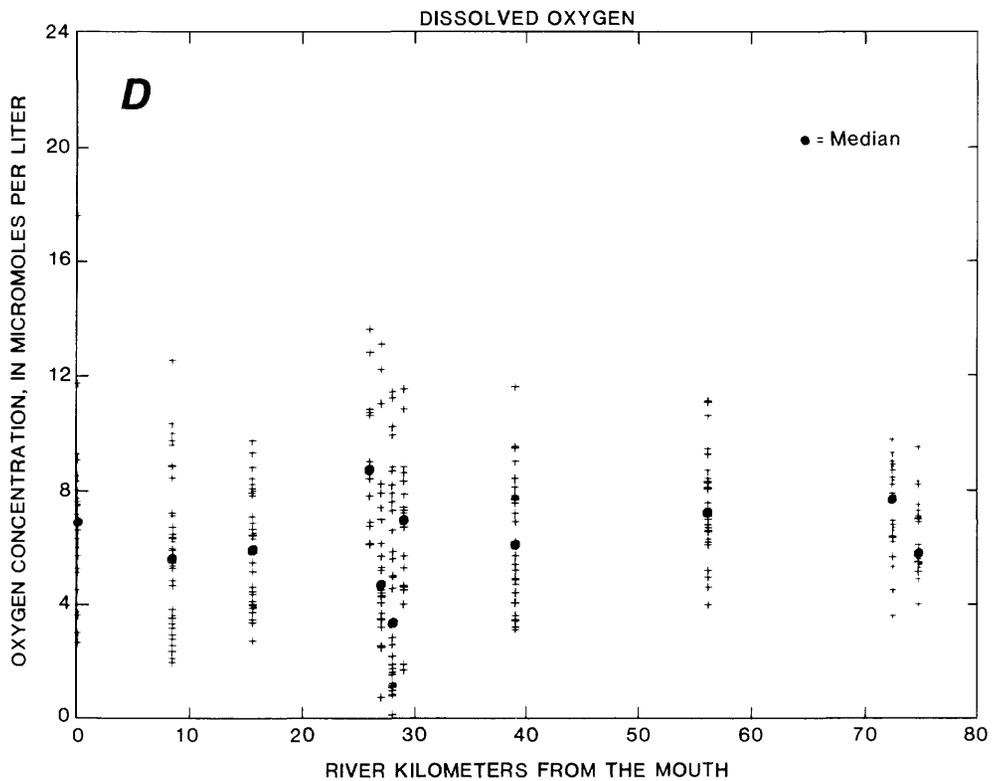
**Figure 18.** Relation of observed median initial nutrient concentrations in benthic respirometers to river kilometer, during all cruises, for (A) ammonium, (B) nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved oxygen.



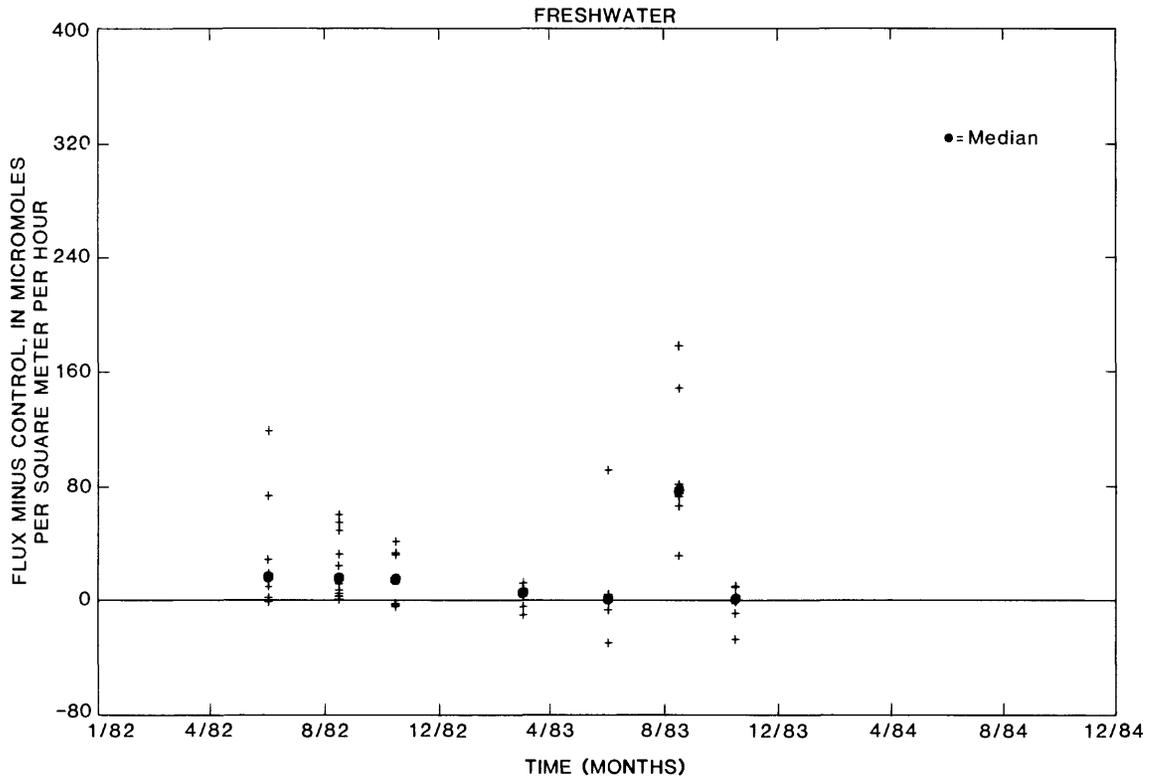
**Figure 18.** Relation of observed median initial nutrient concentrations in benthic respirometers to river kilometer, during all cruises, for (A) ammonium, (B) nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved oxygen—Continued.



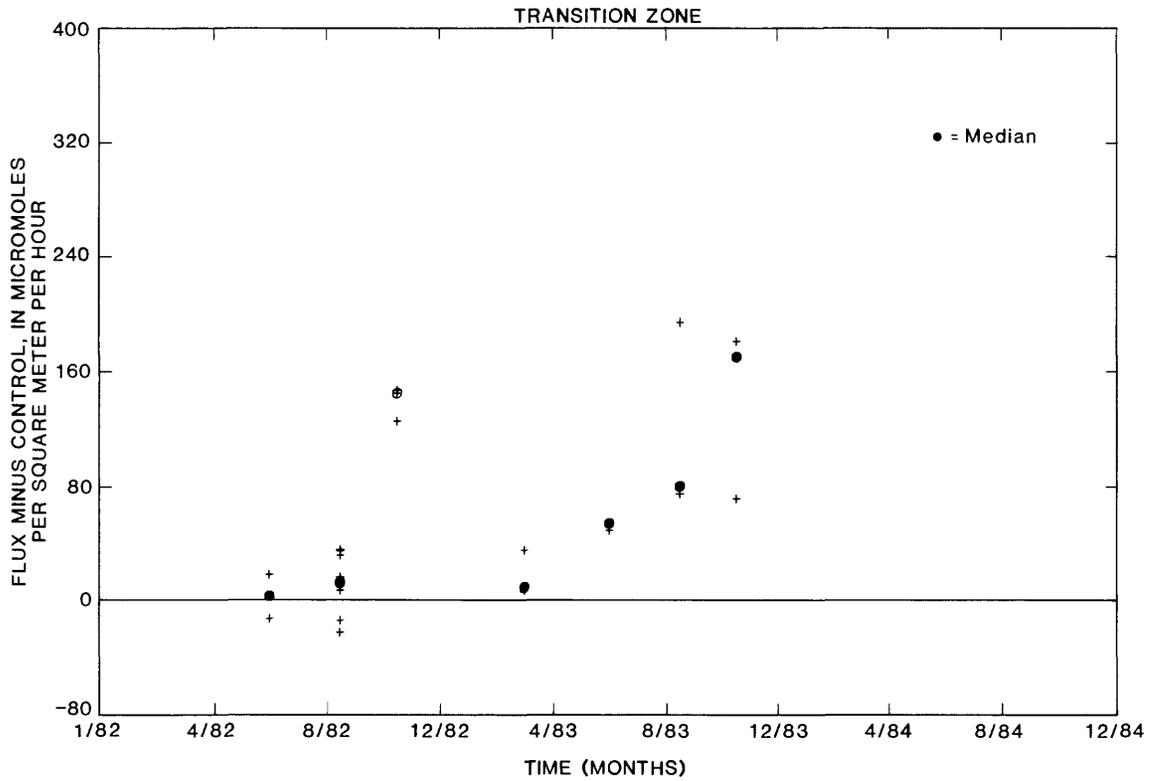
**Figure 18.** Relation of observed median initial nutrient concentrations in benthic respirometers to river kilometer, during all cruises, for (A) ammonium, (B) nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved oxygen—Continued.



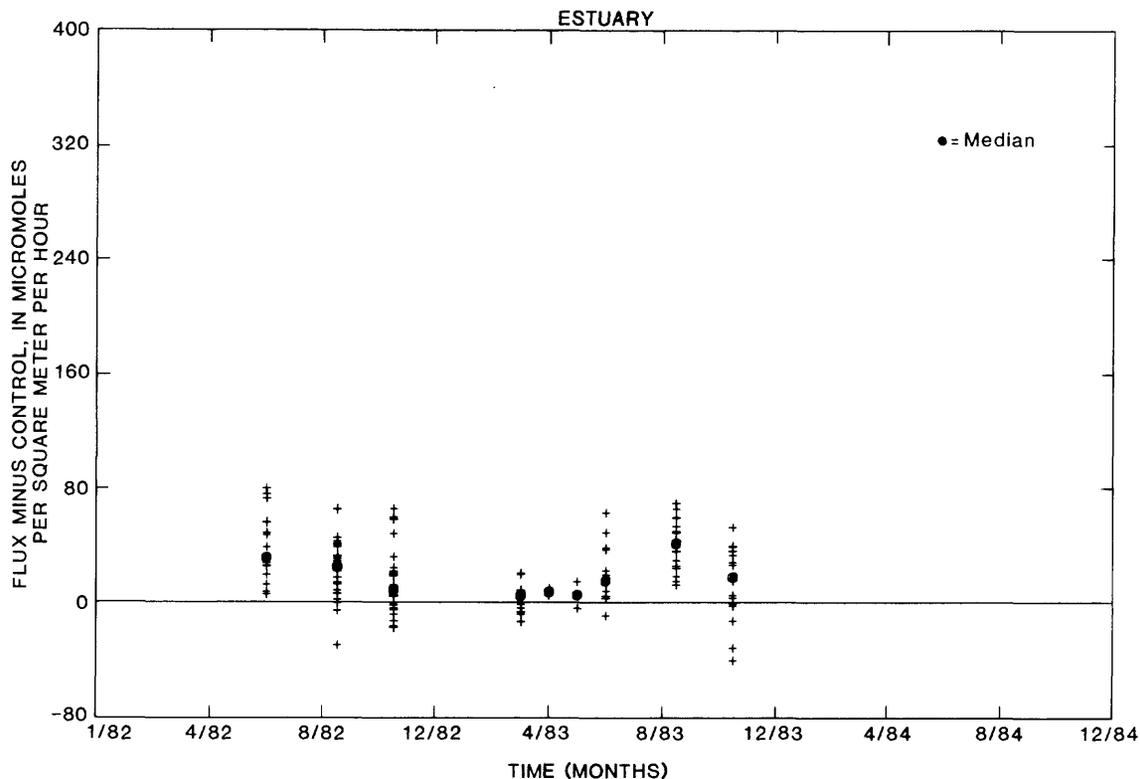
**Figure 18.** Relation of observed median initial nutrient concentrations in benthic respirometers to river kilometer, during all cruises, for (A) ammonium, (B) nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved oxygen—Continued.



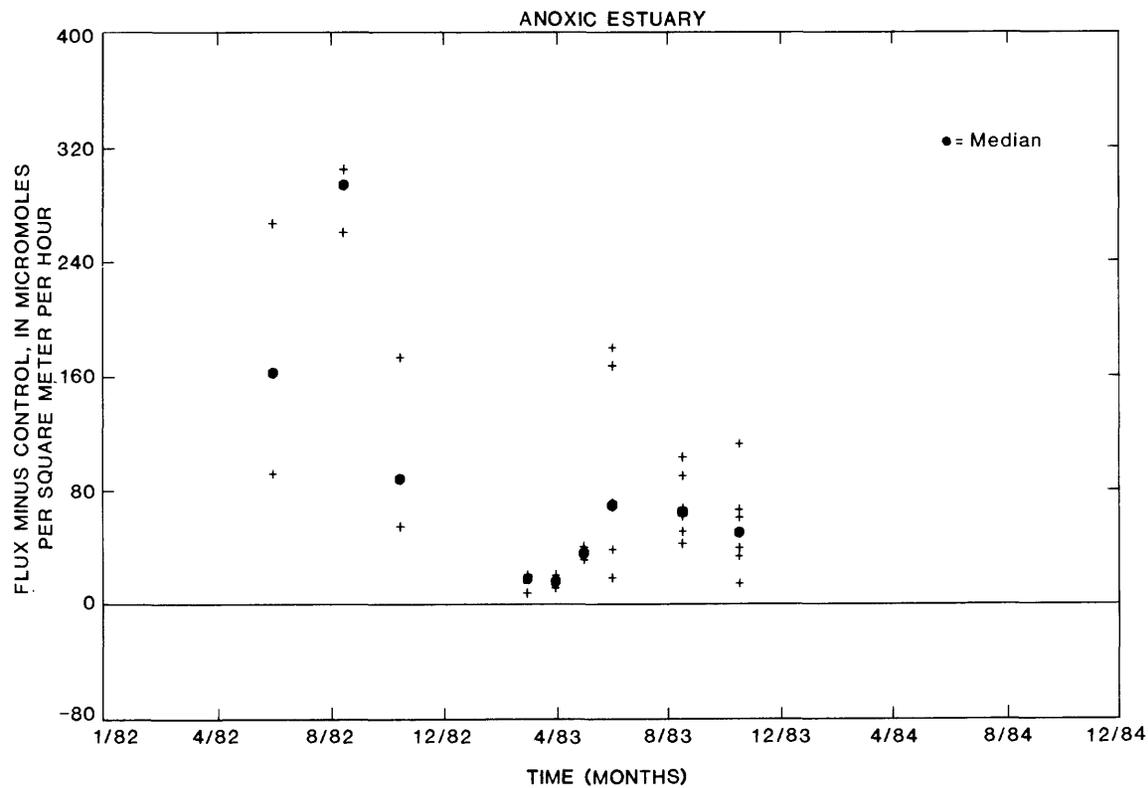
**Figure 19.** Observed ammonium flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments.



**Figure 19.** Observed ammonium flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



**Figure 19.** Observed ammonium flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



**Figure 19.** Observed ammonium flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.

that fluxes are significantly affected by external events and cannot a priori be assumed to follow a consistent seasonal pattern.

#### Dissolved Nitrite Plus Nitrate

Nitrite plus nitrate fluxes versus time for each group over the duration of the project are shown in figure 20. At the tidal river stations, flux rates were directed into the sediments with peak water-column loss to the sediments occurring in the summer of both years. The data for the first year showed greater variability with predominantly positive flux in the spring. In the second year, variability was reduced and spring flux was predominantly negative. At the transition station, a strong negative flux was observed in the fall of the first year but not in the second year. At the anoxic station, negative fluxes were observed in the summer of both years and in the spring of the second year. Otherwise, fluxes were near zero. The estuarine group showed very little or no seasonal pattern.

A consistent seasonal cycle was observed only at the tidal river and anoxic stations, with nitrite plus nitrate fluxes directed to the sediment in the summer. The tidal river cycle was much more pronounced. Year-to-year variation in magnitude was observed; however, it was not as extreme as it was in the case of ammonium flux. Again, fluxes appear to be strongly influenced by year-to-year variation in meteorologic conditions and associated changes in riverborne sediment as well as nutrient loads, stratification-induced anoxia, and other external factors.

#### Dissolved Reactive Phosphorus

Figure 21 shows dissolved reactive phosphorus flux rates versus time over the duration of the project. The tidal river stations are variable, but a slight trend toward greater negative fluxes in summer was observed in both years. At the transition station, a consistent seasonal pattern was not observed. In the first year, flux rates were fairly constant, but in the second year, more strongly negative fluxes were observed in the fall. The anoxic station exhibited depressed phosphorus flux in the winter. Spring, summer, and fall fluxes were much greater in the first year than in the second. Other estuarine stations exhibited only slightly diminished winter fluxes and seasonal or year-to-year variation was not clearly evident.

#### Sediment Oxygen Demand

Figure 22 shows the variation in sediment oxygen demand in each group over the course of the project. At the tidal freshwater stations, maximum sediment oxygen demand occurred in the summer and fall of both years, although some difference in magnitude was apparent.

Maximum sediment oxygen demand occurred in the summer at the transition station as well. During the first year at the anoxic station, few sediment oxygen demand measurements could be obtained due to the lack of oxygen in bottom waters. Peak sediment oxygen demand was observed in winter, since limited or no oxygen was available at other times. Estuarine stations exhibited no seasonal trend in sediment oxygen demand.

#### Correlation of Flux Rates with Initial Nutrient Concentrations, Initial Dissolved Oxygen Concentrations, and Sediment Particle Size

Flux rates may be controlled by or related to concentration gradients in the sediments and between the sediments and water column. The following section addresses the observed relationships between the flux rates and their respective initial nutrient concentrations. The nitrite plus nitrate flux rates were plotted against the initial dissolved ammonium concentrations. The flux rates were also plotted against the initial oxygen concentrations to evaluate the effect of oxygen dynamics on flux rates.

Figure 23 shows the plots of flux rates on initial nutrient concentrations. On a system-wide basis, no apparent relationships exist between the initial nutrient concentrations and the flux rates. The Spearman correlation coefficients ( $r$ ) (SAS Institute Incorporated, 1982; Proc Corr procedure) for the regressions are shown in table 7. Some of the correlation coefficients are significant at the 5-percent level; however, in none of these cases is the proportion of explained variance ( $r^2$ ) greater than 15 percent. This suggests that there is not a strong relationship between flux and water-column concentration at the concentrations observed in this study.

The regression of the flux rates on the initial dissolved oxygen concentrations are shown in figure 24. The corresponding correlation coefficients are also shown in table 7. Greater ranges of flux rates for dissolved ammonium and dissolved reactive phosphorus were observed at lower initial dissolved oxygen concentrations. This observation is overwhelmingly due to the inclusion of Marsh Point station 2 data. If Marsh Point station 2 data are removed, no trend between flux rates and initial dissolved oxygen concentration is apparent. Again, while some of the correlations were significant at the 5 percent level, the proportion of explained variance is extremely low.

As can be seen in table 7, the correlations between the percentage of sand in the sediment and flux rates were of similar magnitude to those discussed previously. Only the percentage of sand is shown here because it represents the traditional division between coarse and fine sediments. A similar lack of correlation was noted between flux rates and the other sediment-size fractions.

**Table 7.** Correlation coefficients for regression of observed flux rates against initial concentrations of nutrients and oxygen

Observed initial nutrient concentrations and nutrient flux rates	Observed flux rates			
	Dissolved ammonium	Nitrite plus nitrate	Dissolved reactive phosphorus	Sediment oxygen demand
Initial dissolved ammonium	<sup>1</sup> 0.17938 <sup>2</sup> 0.0040 <sup>3</sup> 256	0.00684 0.9138 253	0.13598 0.0296 256	0.18533 0.0107 189
Initial nitrite plus nitrate	-0.12266 0.0513 253	-0.14099 0.0241 256	-0.27050 0.0001 256	0.25129 0.0004 192
Initial dissolved reactive phosphorus	0.13173 0.0344 258	-0.07935 0.2040 258	-0.04299 0.4892 261	0.30895 0.0001 194
Initial dissolved oxygen	-0.39001 0.0001 214	0.24085 0.0004 214	-0.37105 0.0001 217	-0.01395 0.8469 194
Percentage of sand	-0.17775 0.0085 218	-0.04967 0.4657 218	-0.22311 0.0008 221	-0.02807 0.7123 175
Dissolved ammonium	1.00000 0.0000 258	-0.15365 0.0140 255	0.35547 0.0001 258	-0.10657 0.1455 188
Nitrite plus nitrate	-0.15365 0.0140 255	1.00000 0.0000 258	0.07004 0.2623 258	-0.07113 0.3282 191
Dissolved reactive phosphorus	0.35547 0.0001 258	0.07004 0.2623 258	1.00000 0.0000 261	-0.15780 0.0292 191
Sediment oxygen demand	-0.10657 0.1455 188	-0.07113 0.3282 191	-0.15780 0.0292 191	1.00000 0.0000 194

<sup>1</sup> Spearman correlation coefficient (R).

<sup>2</sup> Probability greater than R.

<sup>3</sup> Number of observations.

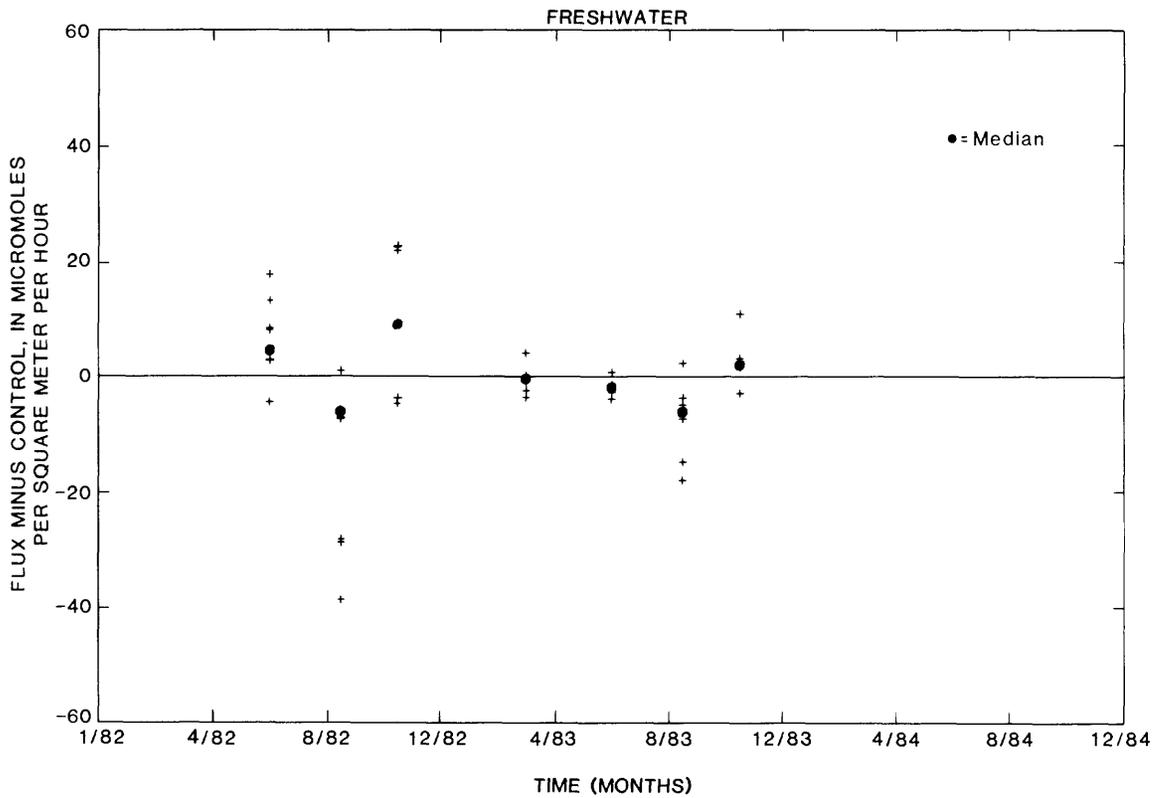
Table 7 also includes correlation statistics among the fluxes and sediment oxygen demand. Again, no significant relationships were observed.

The lack of notable correlation between flux rates and any one of the factors discussed above reflects the dependency of flux rates on many interacting factors. It is not that the above factors are not important but rather that no single factor dominates flux rates to an extent that it supersedes the others.

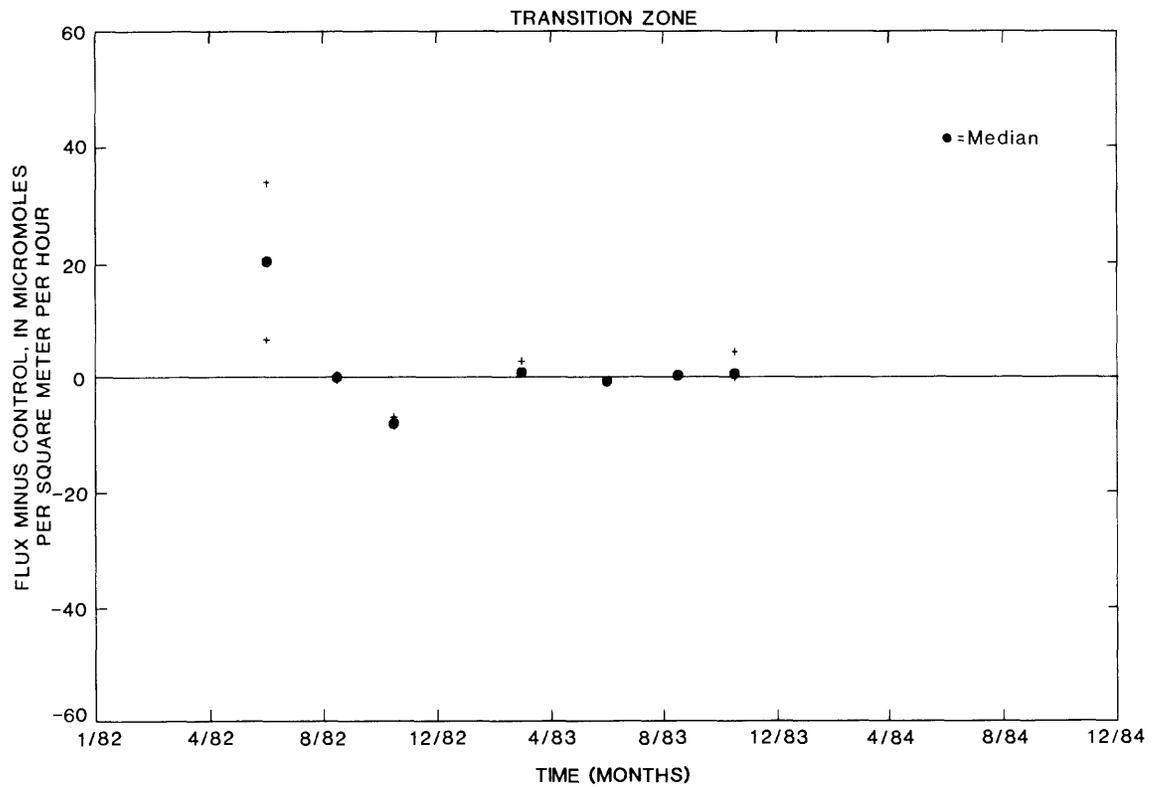
## SUMMARY AND CONCLUSIONS

The Patuxent Nutrient Flux Project was a 2-year assessment of the sediment nutrient flux and sediment oxygen demand in the tidal Patuxent River and Estuary. Ben-

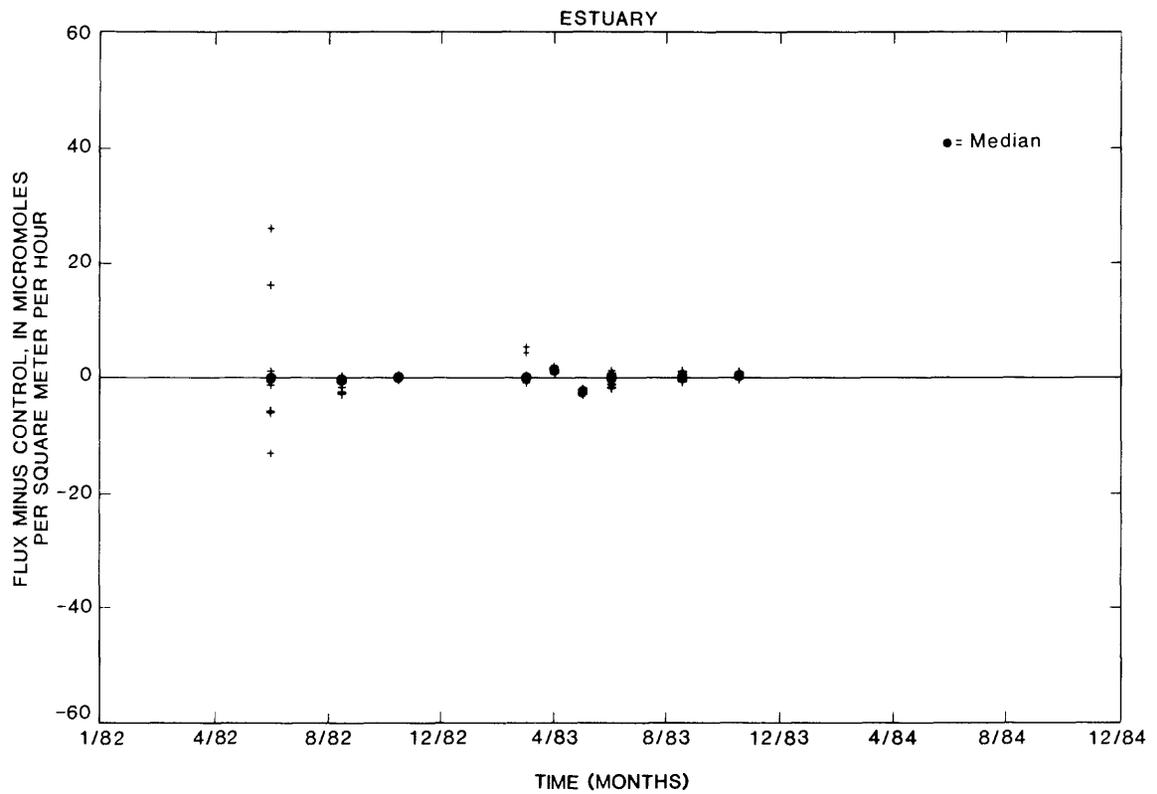
thic respirometers were used for the in situ measurement of nitrogen, phosphorus, and oxygen fluxes at 11 stations during each of 8 cruises from March 1982 to November 1983. The six chemical constituents measured were limited to the dissolved forms of ammonium, ammonium plus organic nitrogen, nitrite, nitrite plus nitrate, dissolved reactive phosphorus, and total dissolved phosphorus. Three parameters—ammonium plus dissolved organic nitrogen, nitrite, and total dissolved phosphorus—were not discussed in detail in the data analysis. The ammonium plus organic nitrogen results were considered too erratic to provide reliable flux rate estimates. The other two parameters, total dissolved phosphorus and nitrite, were predominantly accounted for by dissolved reactive phosphorus and nitrite plus nitrate, which are discussed in detail.



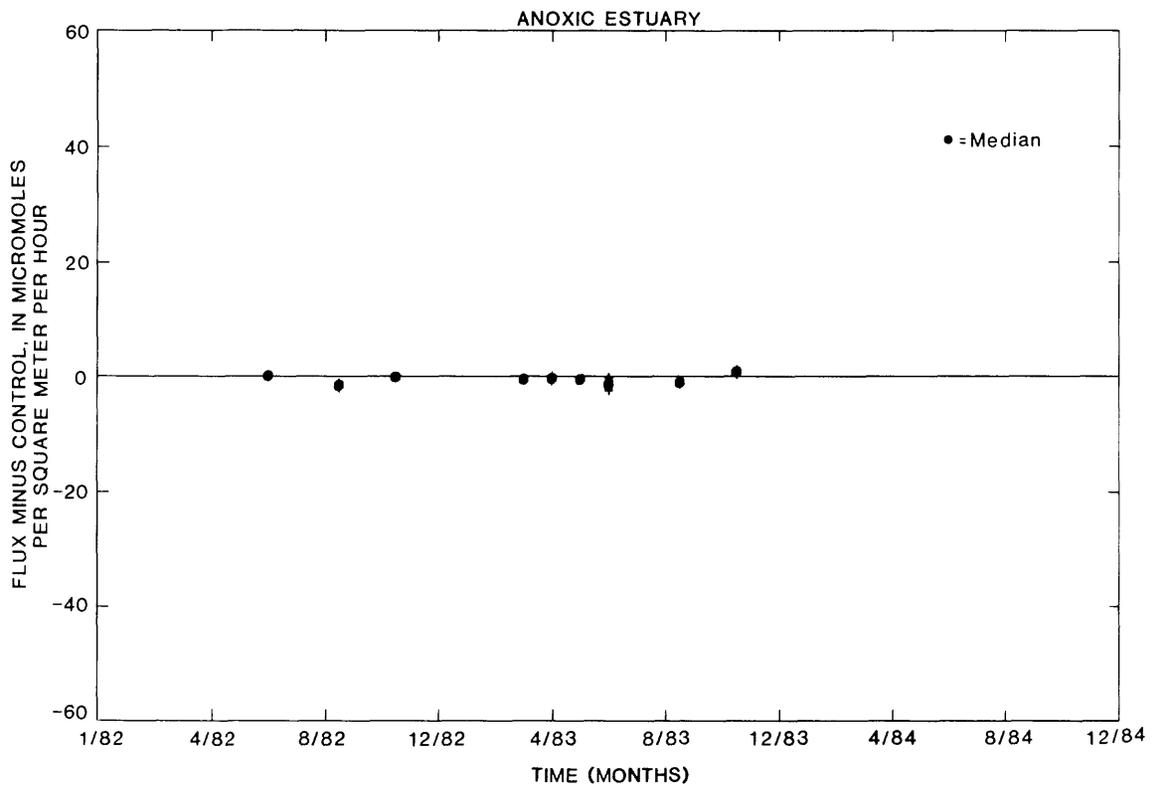
**Figure 20.** Observed nitrite plus nitrate flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments.



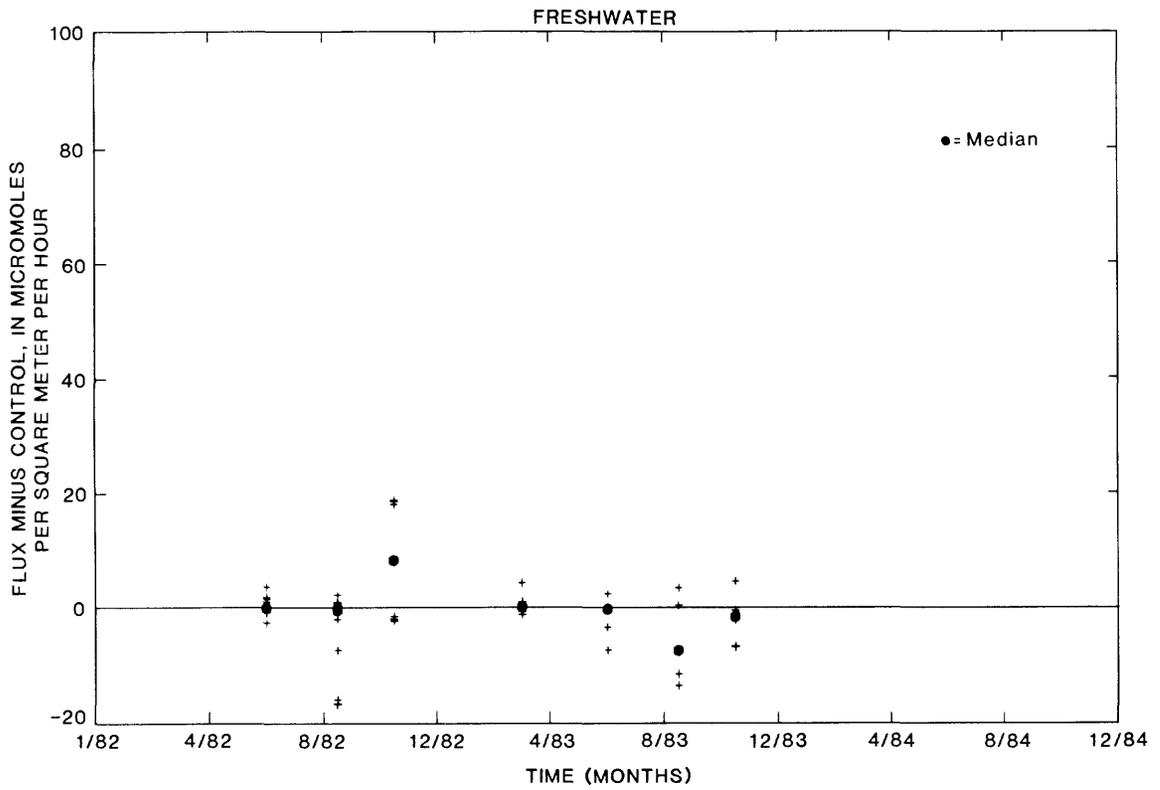
**Figure 20.** Observed nitrite plus nitrate flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



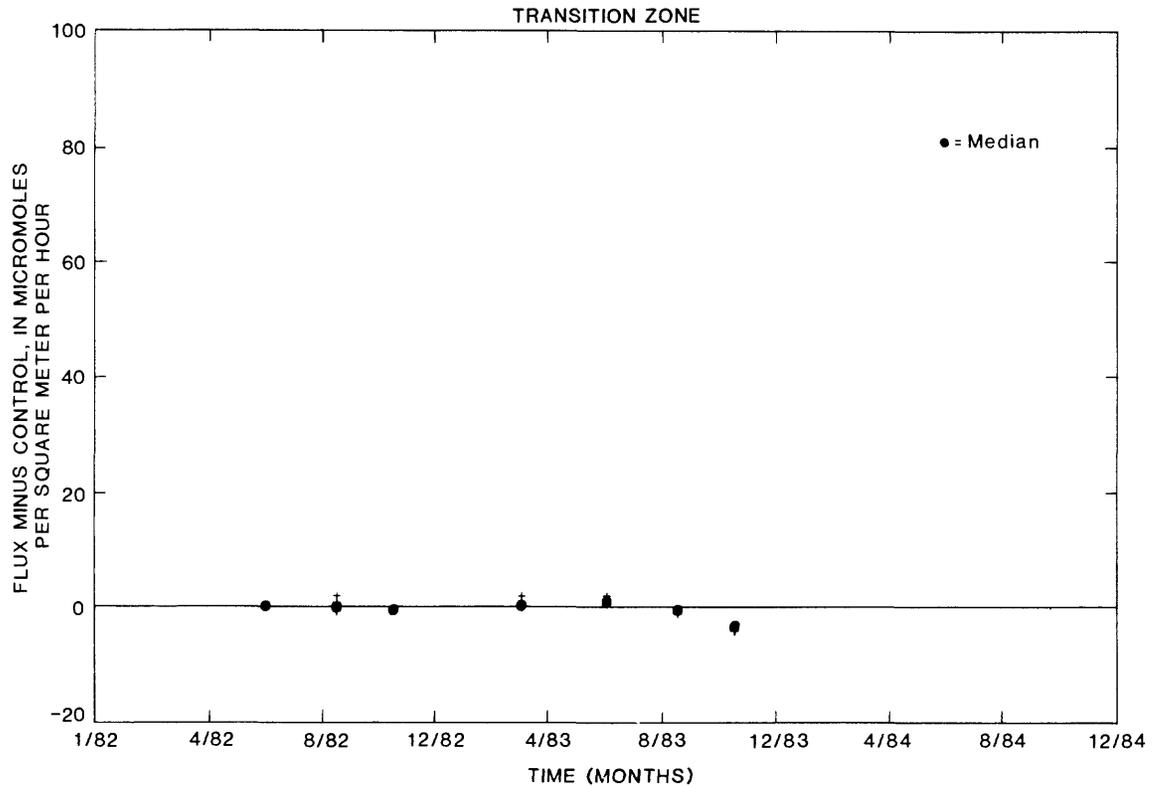
**Figure 20.** Observed nitrite plus nitrate flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



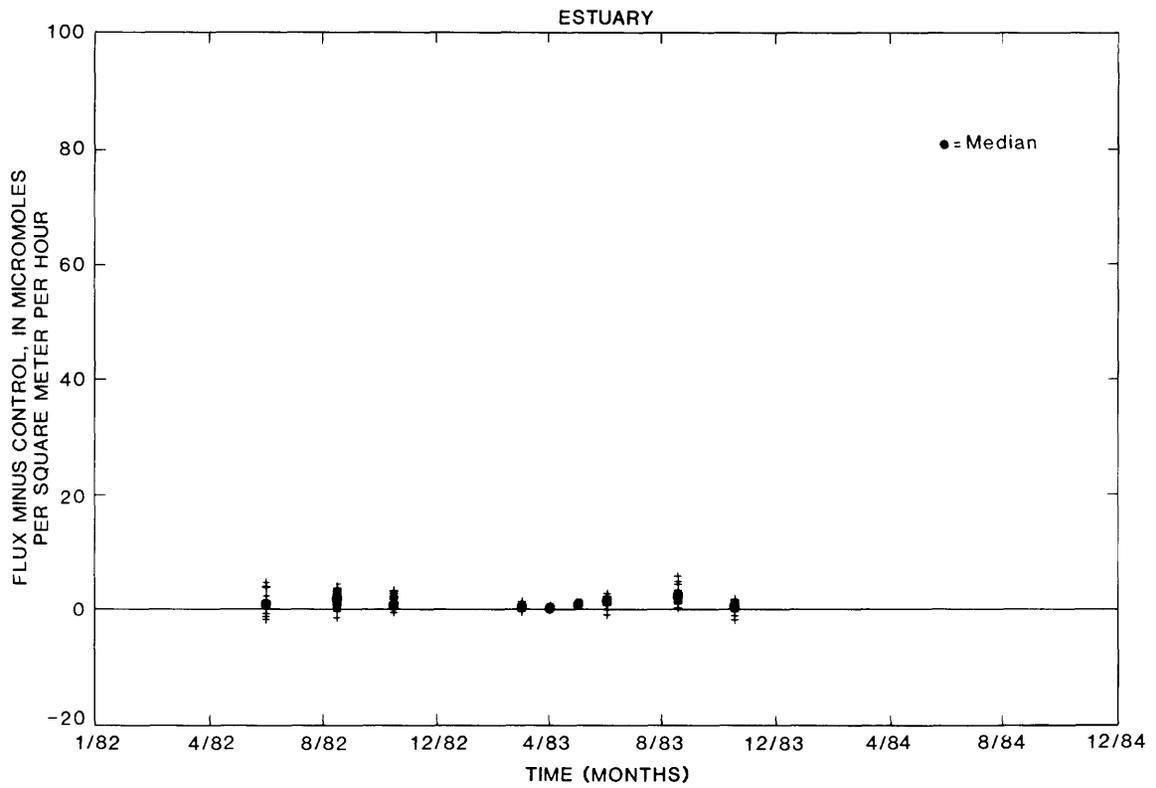
**Figure 20.** Observed nitrite plus nitrate flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



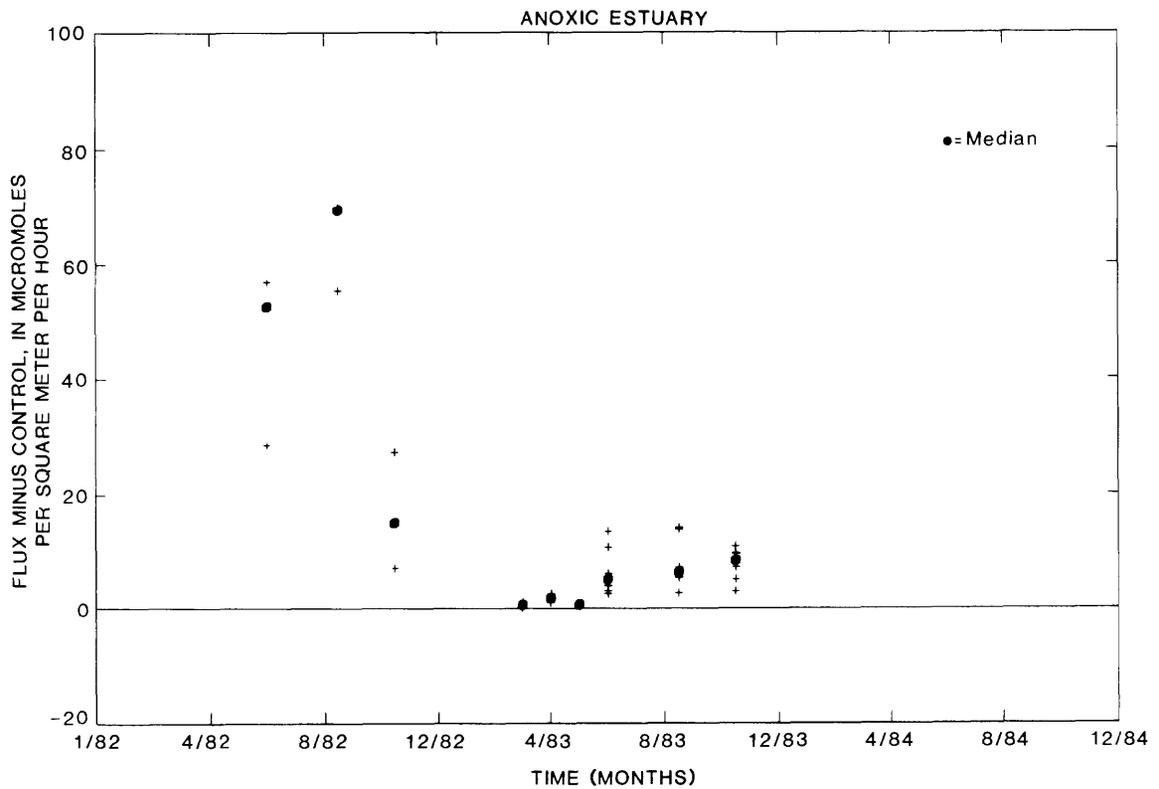
**Figure 21.** Observed dissolved reactive phosphorus flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments.



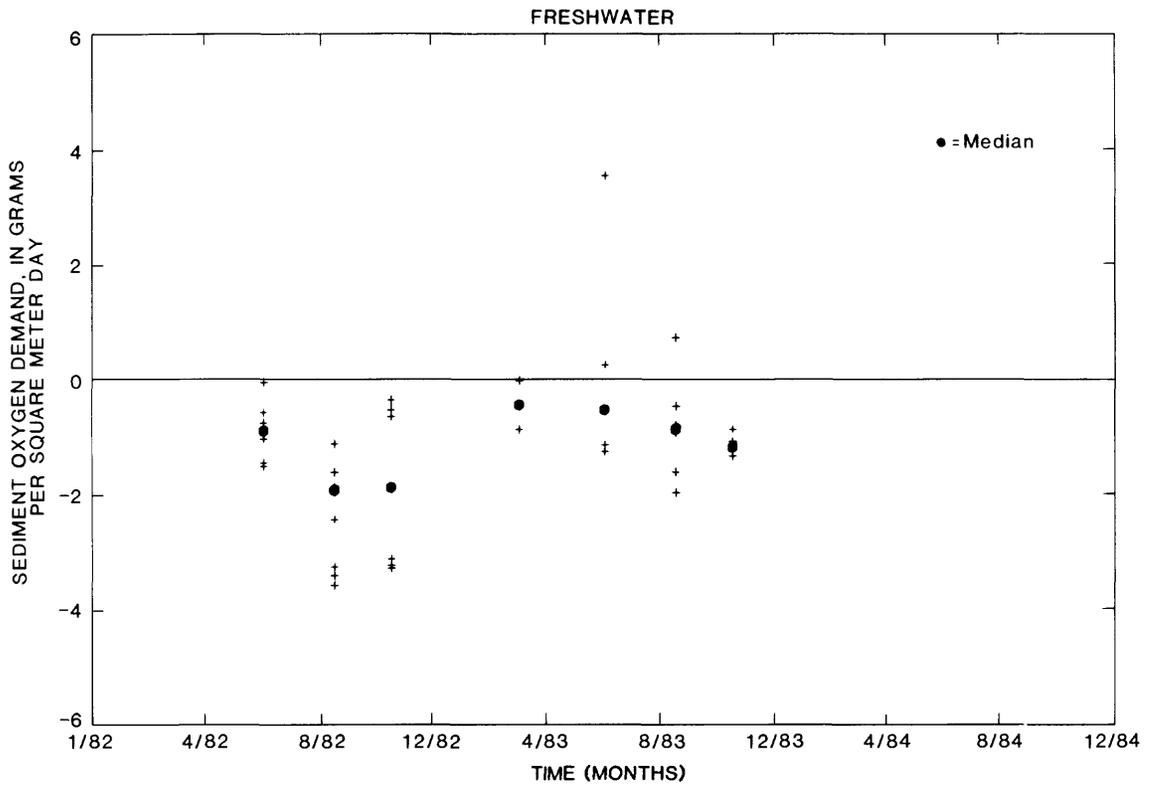
**Figure 21.** Observed dissolved reactive phosphorus flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



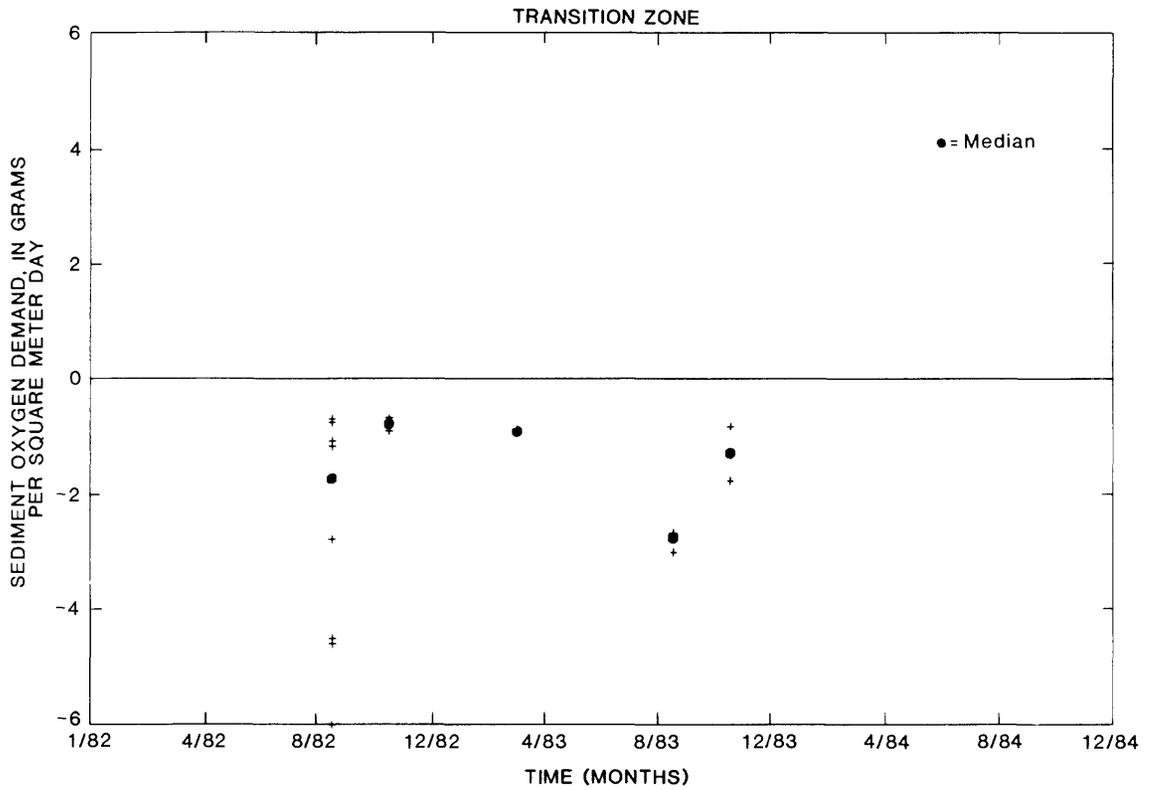
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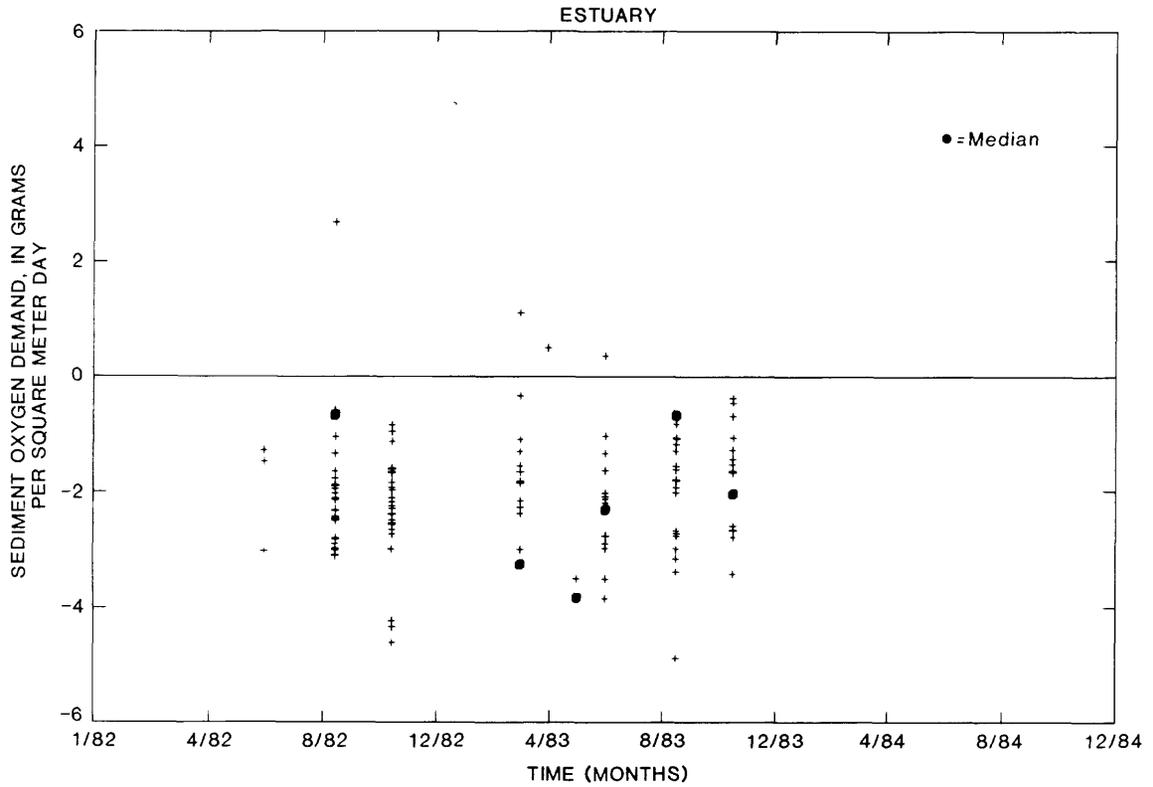
**Figure 21.** Observed dissolved reactive phosphorus flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



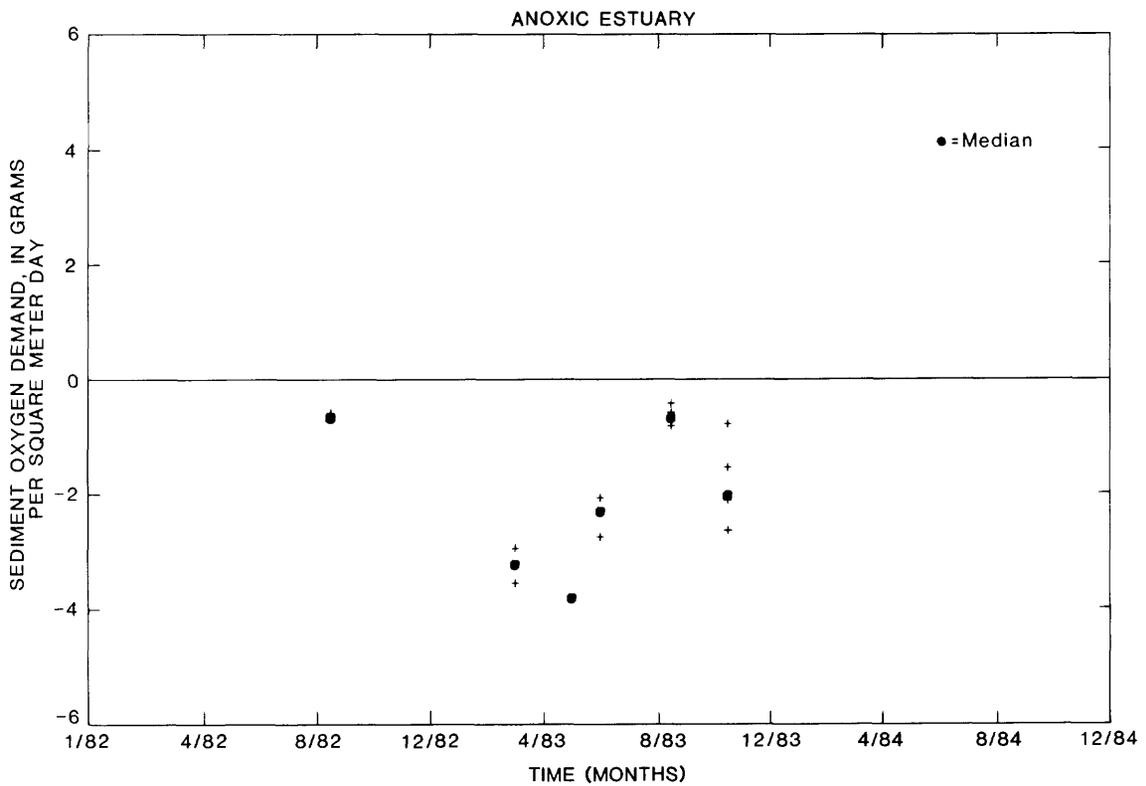
**Figure 22.** Observed sediment oxygen demand flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments.



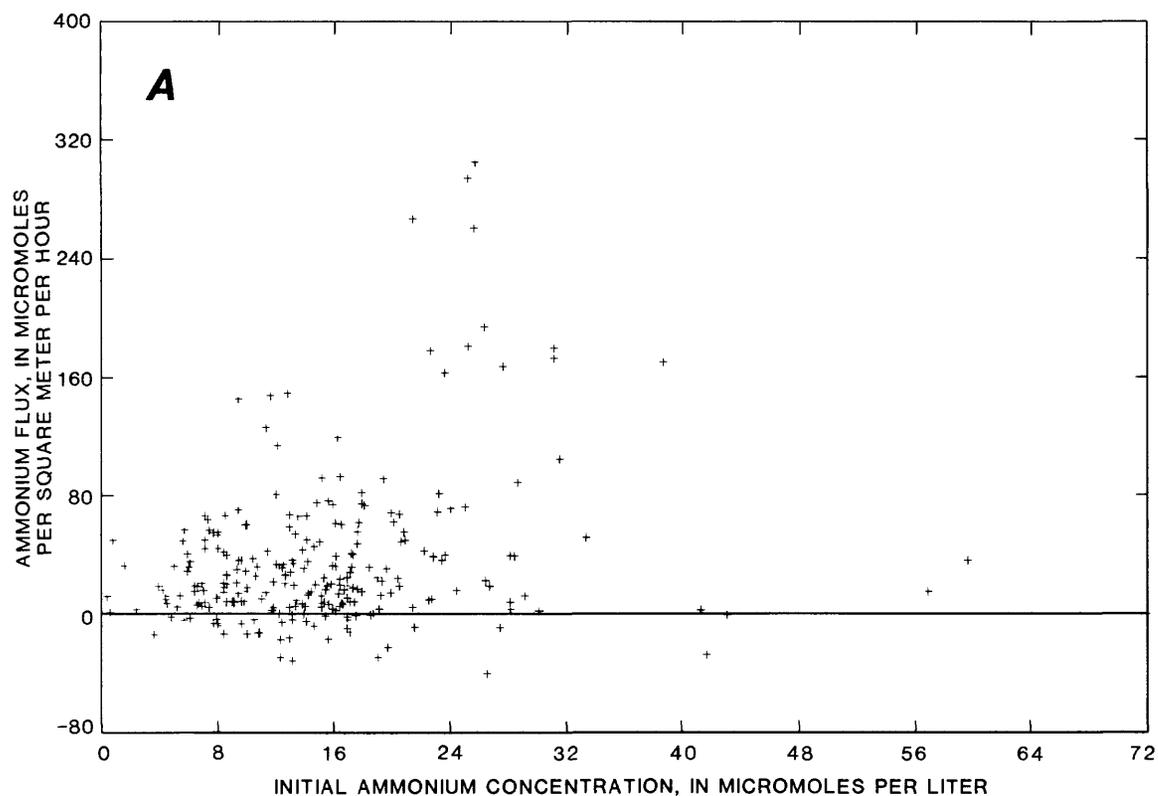
**Figure 22.** Observed sediment oxygen demand flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



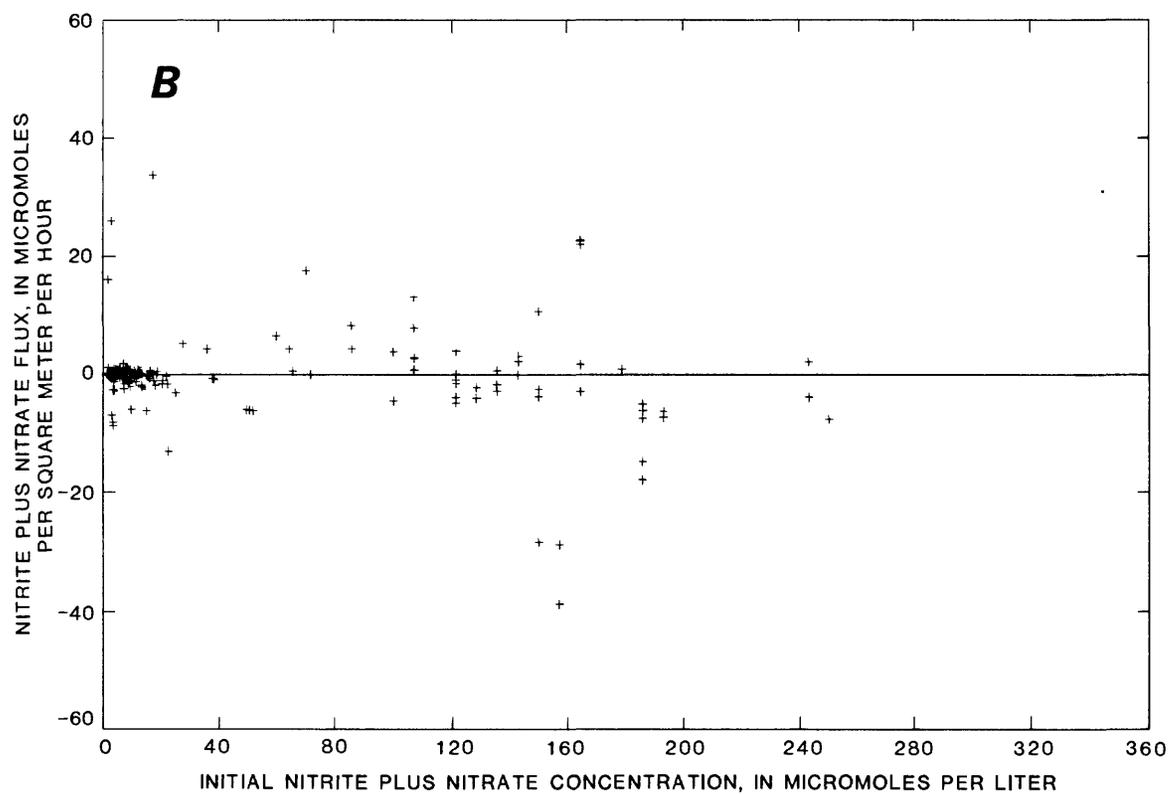
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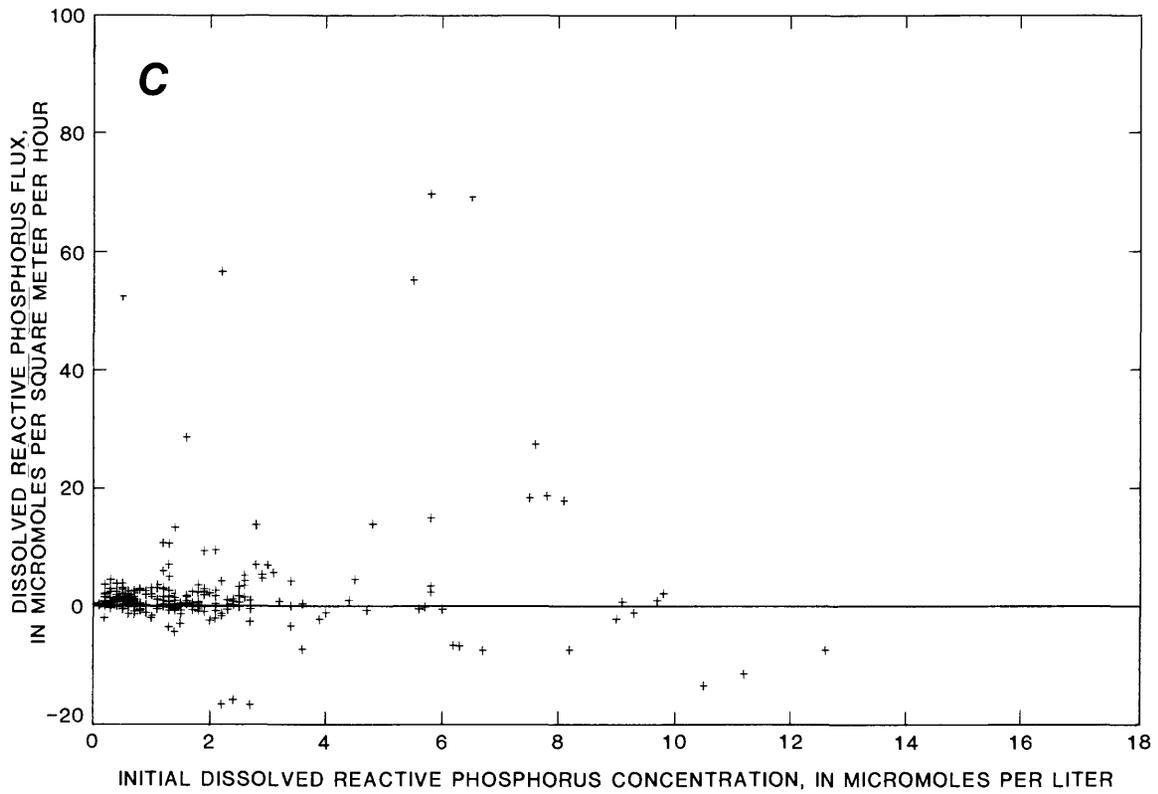
**Figure 22.** Observed sediment oxygen demand flux rates in tidal river, transition zone, estuarine, and anoxic estuarine environments—Continued.



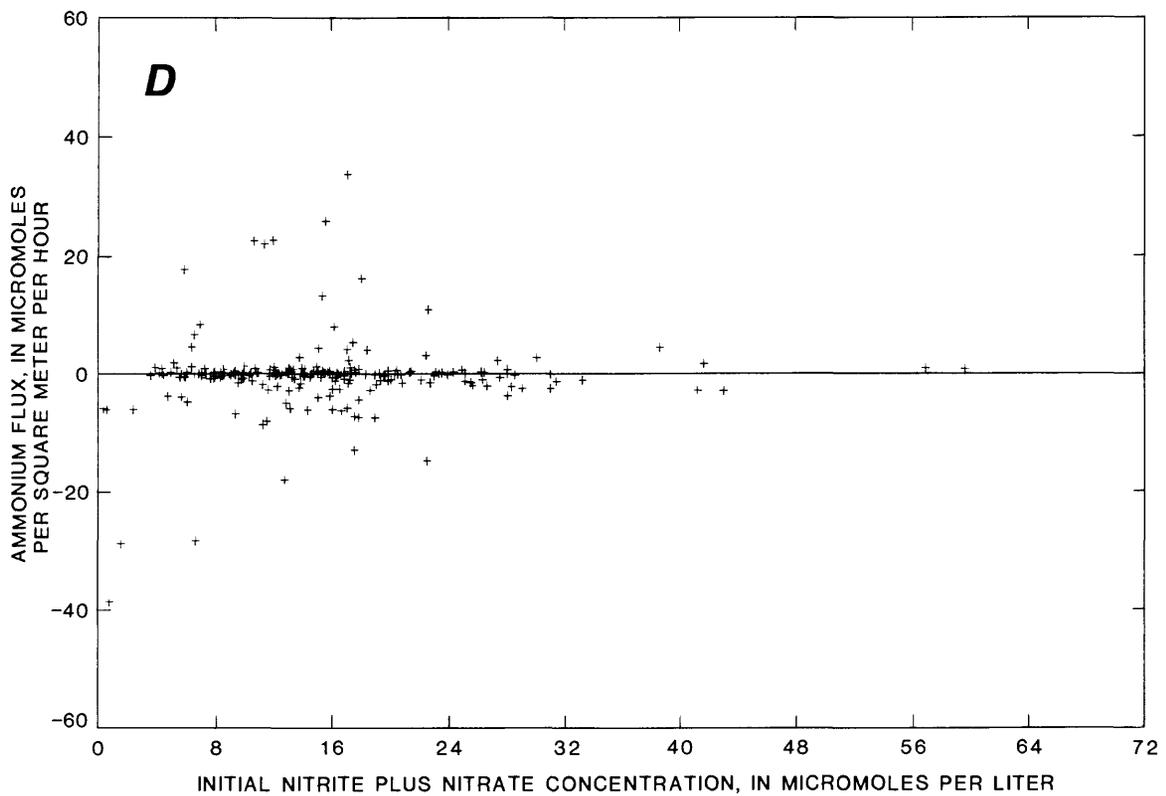
**Figure 23.** Relation of observed nutrient flux rates to initial nutrient concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved nitrite plus nitrate flux to initial ammonium concentration.



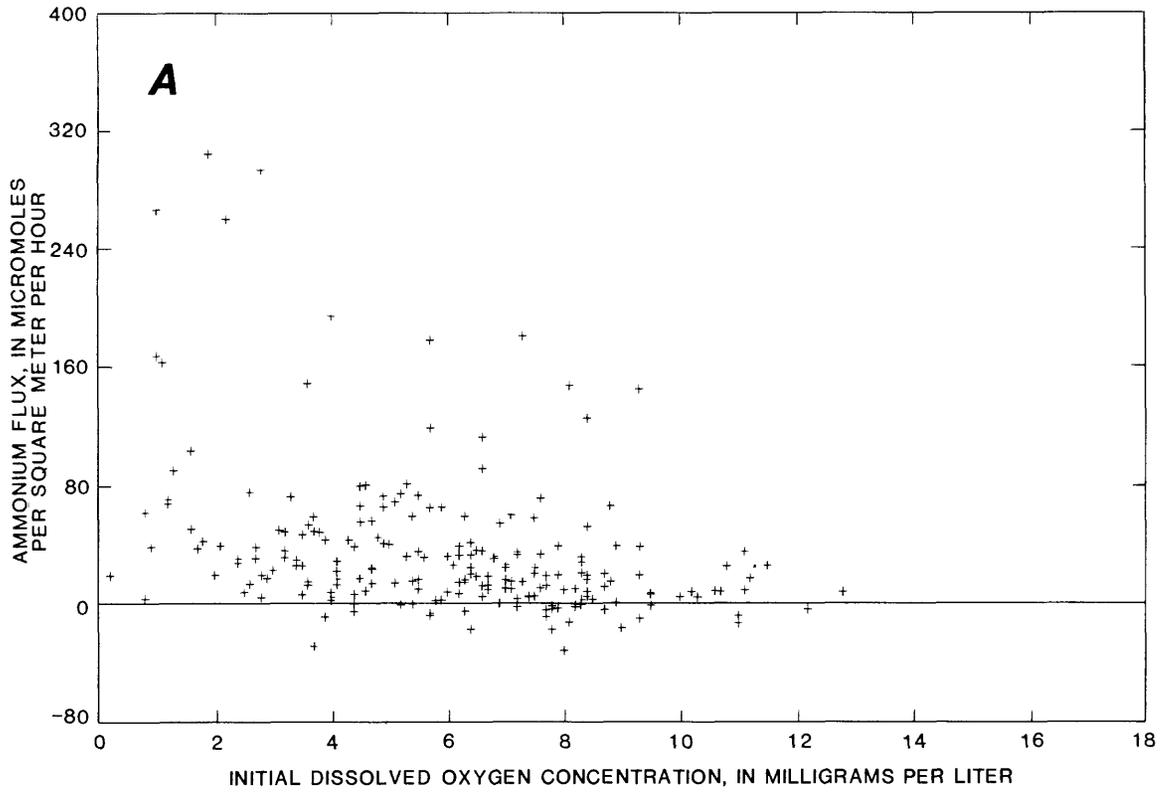
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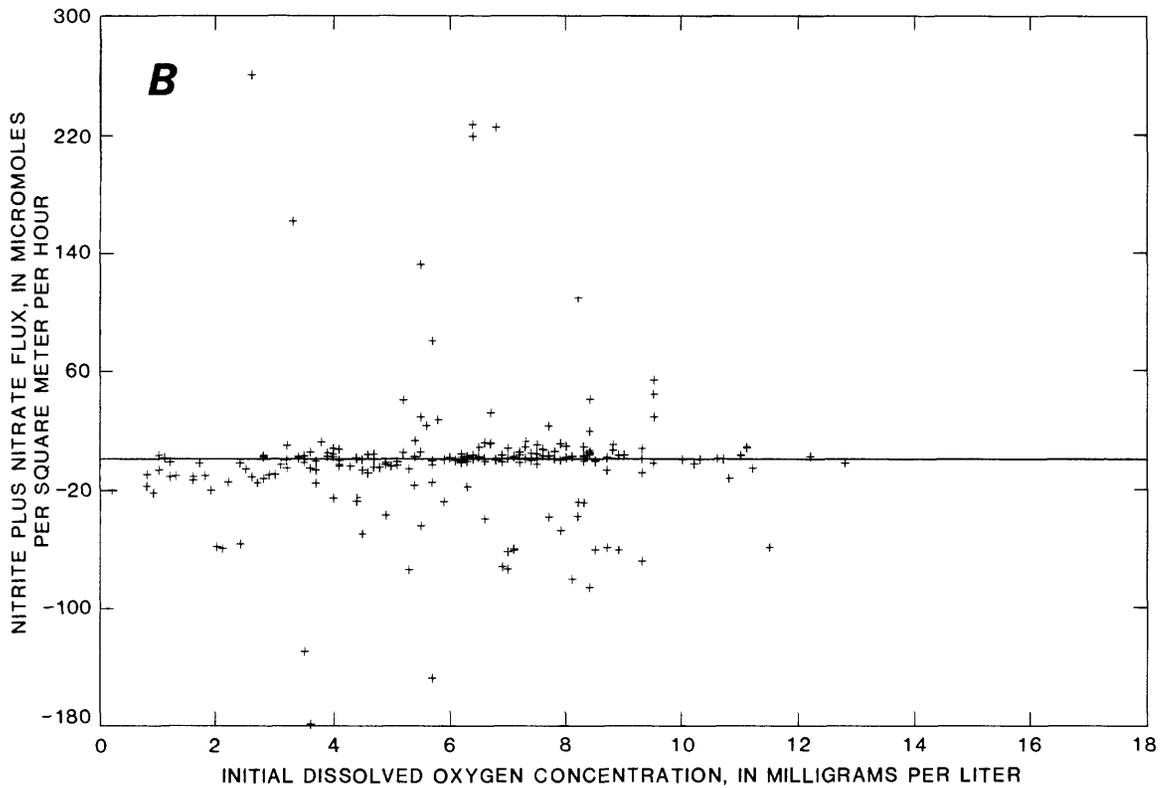
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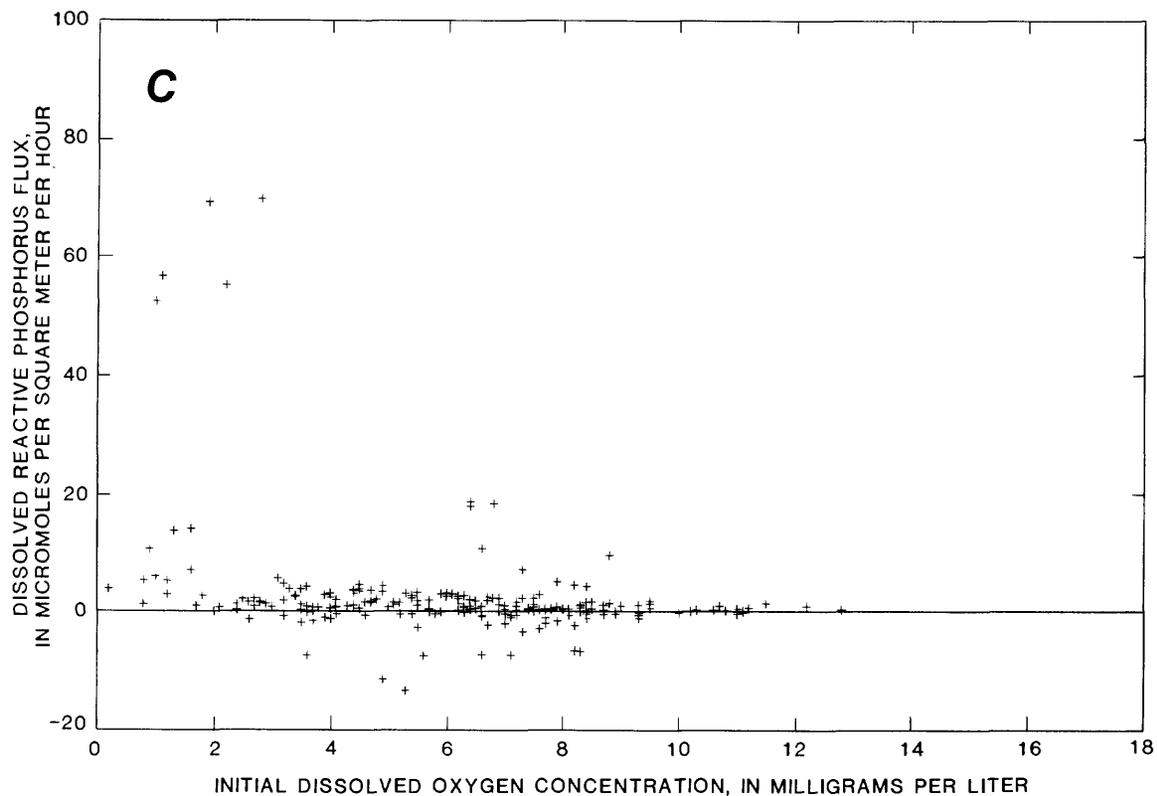
**Figure 23.** Relation of observed nutrient flux rates to initial nutrient concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) dissolved nitrite plus nitrate flux to initial ammonium concentration—Continued.



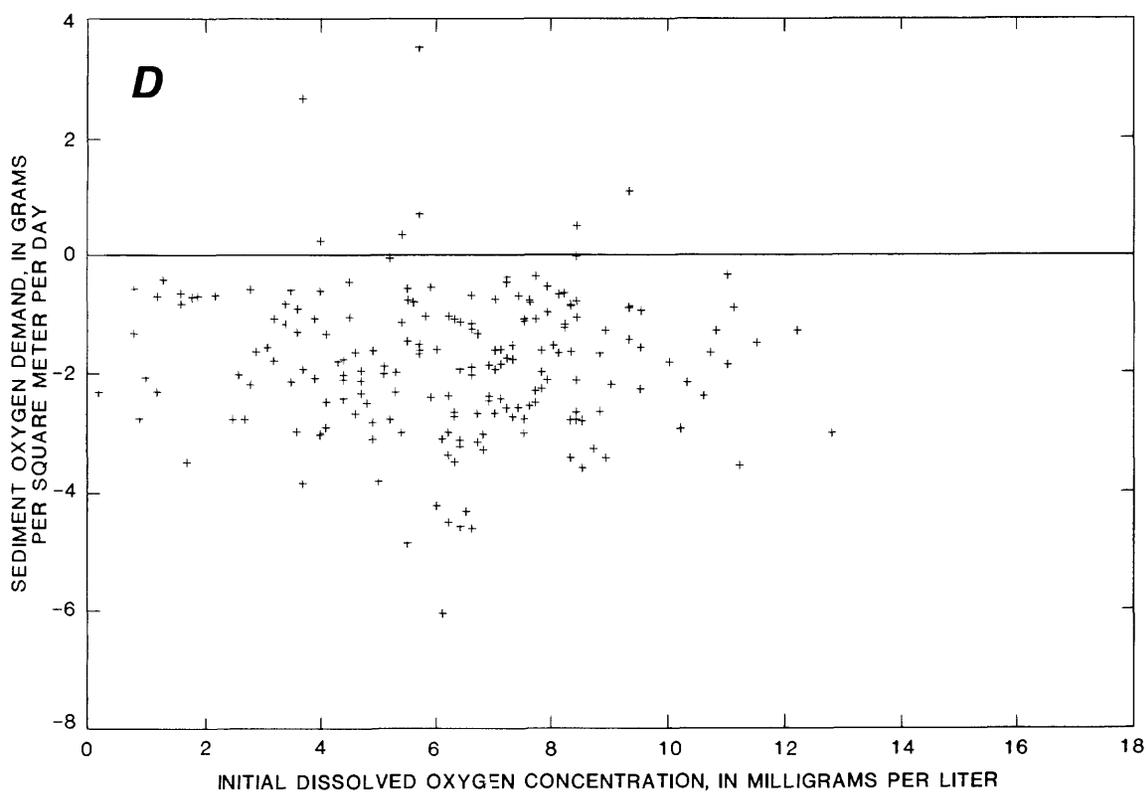
**Figure 24.** Relation of observed nutrient flux rates and sediment oxygen demand to initial dissolved oxygen concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) sediment oxygen demand.



**Figure 24.** Relation of observed nutrient flux rates and sediment oxygen demand to initial dissolved oxygen concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) sediment oxygen demand—Continued.



**Figure 24.** Relation of observed nutrient flux rates and sediment oxygen demand to initial dissolved oxygen concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) sediment oxygen demand—Continued.



**Figure 24.** Relation of observed nutrient flux rates and sediment oxygen demand to initial dissolved oxygen concentrations for (A) dissolved ammonium, (B) dissolved nitrite plus nitrate, (C) dissolved reactive phosphorus, and (D) sediment oxygen demand—Continued.

## Nutrients

*Dissolved Ammonium Flux.*—Tidal river and estuarine sediments are predominantly a source for ammonium to the water column. Sediment contributions are greater in anoxic areas. The higher ammonium concentrations in the sediments at the anoxic site may be an important factor in this observation. In addition, the observed loss of nitrite and nitrate to the sediments under anoxic conditions suggests that reduction of these species may be a factor. Greater variability in ammonium flux was observed at the tidal river stations than at other stations. A general reduction in flux rates was noted in winter, which may reflect a temperature or biological community dependency.

*Dissolved Nitrite Plus Nitrate Flux.*—In the estuarine and transition zone, the absolute value of the nitrite plus nitrate flux was low in comparison with that in the tidal river and with ammonium flux rates in general. In spring and summer, estuarine sediments were predominantly a sink for nitrite plus nitrate, while in fall and winter they were predominantly a source. As is mentioned above, the loss of nitrite plus nitrate to the sediments coincident with elevated ammonium flux, particularly at the anoxic station, suggests that reduction to ammonium may be a factor. The tidal river stations exhibited a large median flux to the sediments but also greater variability than other stations. This was the result of a strong seasonal cycle with large losses of nitrite plus nitrate to the sediment in summer and significant flux from the sediments in spring and fall.

*Dissolved Reactive Phosphorus Flux.*—In general, the estuarine sediments were a source of phosphorus throughout the year, peaking in the summer, while transition and tidal river sediments were a sink in the summer and fall. A prominent feature of the phosphorus flux was that the anoxic station median flux rate in spring, summer, and fall was at least seven times higher than that at other estuarine stations. This elevated flux appears to result from low-oxygen conditions in bottom waters at this station.

## Sediment Oxygen Demand

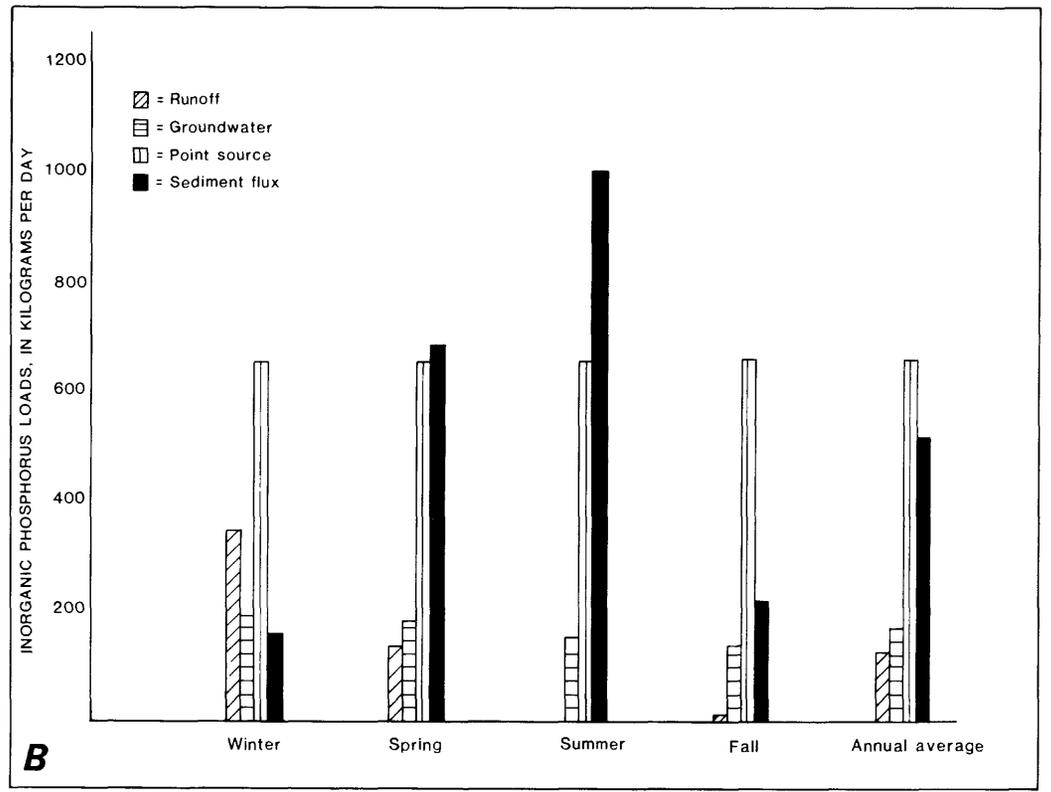
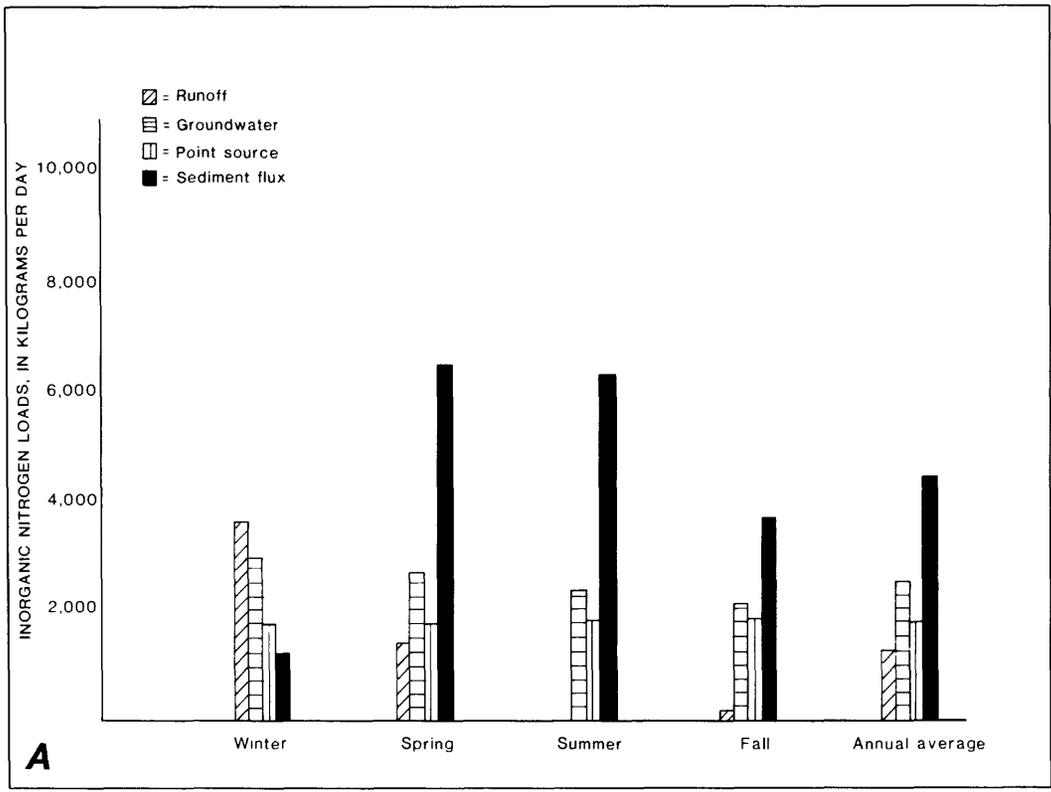
Oxygen fluxes were overwhelmingly directed into the sediments. Sediment oxygen demand was variable, but, except for a slight reduction in winter, there was no seasonal cycle. The exception to this was the anoxic station, where sediment oxygen demand peaked in winter. This was probably due to the extremely organically rich sediment and the lack of sufficient oxygen at other times of the year. Only slight differences in the magnitude of

sediment oxygen demand were observed between station groups (table 6).

The observed median values of the data summarized above were generally consistent with other studies on the Patuxent (Boynton and others, 1982). However, because these data include a more extensive spatial and temporal coverage, the range in the data is greater. The flux rates reported here, like those of Boynton and others (1982), are among the highest reported for east coast estuaries. Generally, flux rate estimates reported for the tidal Potomac River and Estuary by Callender and Hammond (1982) were comparable to the Patuxent flux rates reported here; the major exception was that Callender and Hammond did not observe nutrient fluxes from anoxic estuarine sediments of the magnitude observed at Marsh Point station 6 on the Patuxent. Additionally, as was observed by Callender and Hammond (1982), the tidal river and estuary are distinct environments and should be treated as such when evaluating sediment nutrient fluxes.

An obvious characteristic of the data is its variability. Spatial and temporal variability is a large part of this. However, even when the data are grouped to account for these elements, considerable variability remains. The reasons for this are manifold. Many of the microbiological and chemical processes that recycle nutrients are temperature dependent and are generally affected by the presence or absence of oxygen (oxidation-reduction conditions). In addition, the observed rates vary with regard to the presence or absence of benthic communities (such as clams, worms, and oysters). Sediment nutrient concentrations, meteorological conditions affecting riverflow and estuarine stratification, sedimentation, sediment grain size, and other factors are also important. The within season variability from one year to the next observed in this project is a direct result of the year-to-year variability in external factors mentioned above. The Patuxent River is not unique in its inherent variability; many of the nutrient-recycling processes on the Potomac have been shown to exhibit considerable year-to-year variability as well (Ealkins and others, 1982; D. J. Shultz, oral commun., 1984).

A comparison of nutrient loads from sediment/water-column flux and other sources is provided in figure 25. Sediment nutrient loads were calculated based on the median of observed flux rates, and estimates of the sediment surface area in each zone were taken from O'Connor and others (1981). Runoff, ground water, and upstream point source estimates are from O'Connor and others (1981). The authors recognize that the load estimates of O'Connor and others (1981) are based on limited data and, as a result, are subject to a great deal of uncertainty. It should also be noted that the load estimates provided in figure 25 do not include the potentially large nutrient loads contributed by the Chesapeake



**Figure 25.** Comparison of estimated nutrient loads from the sediments with other estimated nutrient loadings to the tidal Patuxent River and Estuary. (A) Inorganic nitrogen, (B) Inorganic phosphorus.

Bay. Nevertheless, these estimates provide a general perspective on the importance of sediment nutrient regeneration to the total nutrient load.

Estuarine sediment flux of inorganic nitrogen ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$ ) dominates the other sources in every season except winter, when runoff and ground-water dominate. Inorganic phosphorus loads are dominated by upstream point sources in the winter and fall, by both point sources and estuarine sediment in the spring, and by estuarine sediment in the summer.

The above summary of the results of this study raises as many questions as it answers. Because of the large size of the data set, the authors could not cover all of the possibilities for analysis in a single document. In the future, many of the questions raised in the above discussion will be addressed in separate publications. For example, the magnitude of nutrient and oxygen fluxes between the water column and the sediment and their spatial and temporal variability have been quantified, but no single factor has been found that controls the flux rates throughout the system. A number of relationships are suggested in the discussion of the data. However, these must be investigated in more detail before any conclusions can be drawn. In depth, multivariate analysis of these data will be the subject of future publications.

The brief comparison provided in this report illustrates the importance of sediment nutrient loads in relation to other major nutrient loads to the system. As is noted above, the available estimates are highly uncertain due to the sparsity of the data. Efforts are underway to address these issues. Another OEP-USGS cooperative effort is currently underway to improve the point source, ground water, and runoff load estimates. In addition, OEP has proposed more detailed water quality modeling efforts for the estuary, including characterization of Patuxent-Chesapeake Bay exchange of nutrients. The results of the sediment oxygen and nutrient flux study will be of great value in this effort.

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## SUPPLEMENTAL DATA

[Observed nutrient and oxygen flux rates and ancillary environmental data]

- CRUISE - Each cruise consists of a complete geographic coverage of the river and estuary over the period of 10 days or more. Eight cruises were conducted; the first was a trial run and the data were not used in this analysis.
- MONTH - Calendar month, 1 to 12.
- DAY - Calendar day.
- YEAR - Calendar year (1982-83).
- STATION - Each sampling location was assigned a station number from 1 to 11.
- RIV KIL - Distance from the mouth of the estuary to the station, in kilometers.
- INCUBAT - In the event that more than one 4-hour measurement was conducted at a given station on the same day, a variable "INCUBATION" was established to distinguish the measurements.
- CHAMBER - A numerical value was assigned to each benthic respirometer. Chambers 1-3 were for sediment flux measurements and chamber 4 was the control. If more than one "incubation" was conducted at the same station on the same cruise, the numbers 5-8, 9-12, etc., were used.

### CHEMICAL PARAMETERS

The chemical parameter values are designated using a prefix, followed by the chemical symbol. The prefix denotes the type of data, while the chemical symbol indicates which parameter the data are associated with.

- N "symbol" - Denotes the number of chemical concentration observations taken in order to calculate the flux rate.
- F "symbol" - This is the raw flux rate before it is adjusted based on the control chamber.
- FA "symbol"- This is the flux adjusted based on the control chamber.
- IN "symbol"- This is the initial concentration of the parameter in the chamber at the start of the measurement.
- NH<sub>4</sub>ORG - Dissolved ammonium ion plus dissolved organic nitrogen (mg/L as N).
- NH<sub>4</sub> - Dissolved ammonium (mg/L as N).
- NO<sub>2</sub> - Dissolved nitrite (mg/L as N).
- NO<sub>2</sub>NO<sub>3</sub> - Dissolved nitrite plus nitrate (mg/L as N).
- TDP - Total dissolved phosphorus (mg/L as P).
- DRP - Dissolved reactive phosphorus (mg/L as P).
- DO - Dissolved oxygen (mg/L).

### OTHER PARAMETERS

- OXYG DEM - Oxygen demand in the chamber, uncorrected for the control.
- SOD1 - Sediment oxygen demand in each chamber, corrected by the control.
- PERCLAY - Percent clay-size fraction (by weight) in sediment from the sampling site.
- PERSAND - Percent sand-size fraction.
- PERSILT - Percent silt-size fraction.









OB S	CR U I S E	M O N T H	D A Y	Y E A R	S T A T I O N	R I V K I L	C H A M B E R	N I N H 4 O R G	F I N H 4 O R G	F F N H 4	F F N O 2	F N O 2	F T D P	F I D R P	O X Y G I D E M	F A N H 4 D R G
73	3	9	10	82	1	0.1	1					-5.23	15.869	8.789	-80.50	
74	3	9	10	82	1	0.1	1					-1.71	20.862	16.546	-118.01	
75	3	9	10	82	1	0.1	1					-7.62	21.559	11.845	-103.89	
76	3	9	10	82	1	0.1	1					9.60	0.000	0.000	-0.91	
77	3	9	15	82	2	8.5	1	0.0	0.0	686.12		-88.36	27.653	16.455	0.0	
78	3	9	15	82	2	8.5	1	0.0	0.0	462.58		-243.36	0.000	16.455	0.0	
79	3	9	15	82	2	8.5	1	0.0	0.0	437.44		-162.37	15.048	22.630	0.0	
80	3	9	15	82	2	8.5	1	0.0	0.0	35.52		-2.88	-17.331	-3.762		
81	3	9	14	82	2	8.5	3	1142.2	1142.2	326.17		-33.00	14.215	14.748	-73.14	1046.3
82	3	9	14	82	2	8.5	3	1153.6	1153.6	411.64		-43.49	34.036	29.688	-72.41	1057.6
83	3	9	14	82	2	8.5	3	470.2	470.2	546.31		-33.82	59.690	19.438	-79.86	374.3
84	3	9	14	82	2	8.5	3	96.0	96.0	94.04		18.19	13.704	-1.343	24.55	
85	3	9	14	82	3	15.6	1	2270.5	2270.5	356.72		-42.89	13.775	1.766	-114.73	687.1
86	3	9	14	82	3	15.6	1	371.5	371.5	367.74		-48.31	7.454	17.335	-137.64	-1211.9
87	3	9	14	82	3	15.6	1	882.2	882.2	-63.52		-21.17	-24.949	-9.387	51.68	-701.2
88	3	9	14	82	3	15.6	1	1583.4	1583.4	227.43		-8.64	13.099	5.643	-59.01	0.0
89	3	9	14	82	3	15.6	2	-0.0	-0.0	153.41		15.52	14.191	4.091	-25.28	0.0
90	3	9	14	82	3	15.6	2	-1396.4	-1396.4	194.42		18.26	6.466	3.910	-88.27	-1396.4

OB S	F A N H 4	F A T D P	F A N O 2	F A N O 3	F A D R P	S O D 1	I N N H 4 O	I N N H 4	I N N O 2	I N N O 2	I N T D P	I N D R P	P E R S I L T	P E R S A N D	P E R C L A Y
73		17.749	8.789	4	4	-1.9102					0.62	0.65	6.60000	32	34
74		22.743	16.546	4	4	-2.8104				2.0714	0.69	0.71	8.50000	32	34
75		23.440	11.845	4	4	-2.4716				2.0000	0.69	0.65	6.90000	32	34
76				3	3					2.0714	0.76	0.65	7.60000	32	34
77	650.60	1.322	31.414	4	4		14.2857	13.5000		3.7143	1.56	0.97			
78	427.06	17.331	20.167	4	4		7.1429	13.7850		7.1400	1.20	0.86			
79	401.92	32.379	26.392	4	4		7.1429	17.2140		7.1400	1.20	0.91			
80				4	4		7.1429	10.7857		2.5000	1.12	0.74			
81	232.13	0.511	16.091	4	4	-2.3446	21.4286	16.3571		4.1429	1.27	1.02	4.65000	35	37
82	317.60	20.332	31.031	4	4	-2.3271	14.2857	16.0714		4.3572	1.27	0.97	5.26000	35	37
83	452.26	45.986	20.782	4	4	-2.5059	35.7143	14.6429		4.1429	1.05	0.97	4.82000	35	37
84				4	4		21.4286	7.0714		1.8572	0.69	0.63	9.70000	35	37
85	128.28	0.676	-3.877	4	4	-1.3375	7.1429	14.2143		3.2857	1.20	1.13	4.10000	40	44
86	140.31	-5.645	11.692	4	4	-1.8871	7.1429	14.2143		4.2143	1.34	1.02	5.14000	40	44
87	-290.95	-38.048	-15.029	4	4	2.6564	7.1429	19.0000		4.2143	1.27	1.02	3.70000	40	44
88				4	4		7.1429	7.5714		1.5714	0.91	0.80	7.90000	40	44
89	20.98	22.090	31.176	4	4	-0.6052	7.1429	16.0714		3.9286	1.12	1.19	4.00000	40	44
90	61.99	14.366	30.995	4	4	-2.1170	35.7143	16.5714		3.4286	1.27	1.08	4.44000	40	44

OB S	CR U S E	MO N T H	DA Y	EA R	ST A T I O N	RI V E R	IN C U B	CH A M B E R	N H O R G	N O 2	N T D P	N N D O	F N H O R G	F N O 2	F T D P	F D R P	O X Y G D E M	F A N H O R G
91	3	9	14	82	3	15.6	2	7	4	4	4	4	15	-7.12	8.074	9.469	-73.69	0.0
92	3	9	14	82	3	15.6	2	8	3	4	4	4	16	276.39	-7.900	-27.085	-0.06	0.0
93	3	9	9	82	4	26.0	2	1	4	4	4	4	10	-17.39	26.410	25.000	-122.65	2039.0
94	3	9	9	82	4	26.0	2	2	4	4	4	4	9	-0.85	26.776	22.951	-123.96	2538.9
95	3	9	9	82	4	26.0	2	3	4	4	4	4	8	-1.65	38.593	29.723	-127.16	2001.8
96	3	9	9	82	4	26.0	2	4	4	4	4	4	9	4.80	4.837	0.000	2.07	0.0
97	3	9	9	82	5	27.0	1	4	4	4	4	4	10	11.10	8.477	-85.13	1974.3	
98	3	9	9	82	5	27.0	1	2	4	4	4	4	10	5.66	11.367	15.465	-81.78	1499.2
99	3	9	9	82	5	27.0	1	3	4	4	4	4	3	23.58	0.472	-25.00	629.0	
100	3	9	9	82	5	27.0	1	4	4	4	4	4	11	1.15	-2.418	-0.00	0.0	0.0
101	3	9	8	82	6	28.0	3	1	4	4	4	4	11	-150.56	541.479	559.276	-48.79	3028.9
102	3	9	8	82	6	28.0	3	2	4	4	4	4	10	-125.24	697.976	705.049	-44.65	564.9
103	3	9	8	82	6	28.0	3	3	4	4	4	4	9	-203.53	666.333	700.099	-49.58	3196.9
104	3	9	8	82	6	28.0	3	4	4	4	4	4	11	-0.00	-20.354	6.650	-20.46	0.0
105	3	9	8	82	7	29.0	1	2	4	4	4	4	12	7.06	8.714	6.086	-37.16	1462.1
106	3	9	8	82	7	29.0	1	3	4	4	4	4	13	-10.92	13.070	16.824	-62.40	274.5
107	3	9	8	82	7	29.0	1	4	4	4	4	4	12	79.65	3.762	0.672	6.39	0.0
108	3	9	7	82	8	38.9	1	1	4	4	4	4	10	-65.44	-10.158	15.030	-94.89	1103.5

OB S	FA N O 2	FA N O 3	FA T D P	FA D R P	FA S O D 1	IN H O	IN H 4	IN N O 2	IN N O 2	IN N O 2	IN T D P	IN D R P	IN D O	PER S I L T	PER S A N D	PER C L A Y
91	-1.43	-283.5	15.97	36.55	-1.7670	7.143	18.7143	3.643	1.34	1.13	1.05	1.30	4.35000	4	4	40
92	325.51	-22.2	21.57	25.68	-2.9933	14.286	12.2143	2.071	1.05	1.30	1.05	1.30	4.60000	4	4	40
93	304.09	-5.7	21.94	22.95	-3.0246	35.714	13.8571	1.714	2.07	2.00	2.07	2.00	6.15000	27	27	45
94	262.10	-6.4	33.76	29.72	-3.1015	35.714	12.5714	1.714	1.85	1.89	1.85	1.89	6.75000	27	27	45
95	-55.28	9.9	15.10	10.89	-2.0431	50.000	11.5000	2.143	2.07	1.83	2.07	1.83	6.80000	27	27	45
96	241.18	4.5	37.48	17.88	-1.9627	21.429	12.3571	2.357	2.50	2.27	2.50	2.27	4.40000	7	7	39
97	63.44	22.4	13.15	2.89	-0.6000	28.571	15.6429	2.786	2.65	2.49	2.65	2.49	4.65000	7	7	39
98	2599.13	-150.6	561.83	552.63	-0.6800	14.286	12.4286	2.143	2.72	2.44	2.72	2.44	3.45000	7	7	39
99	2934.49	-125.2	718.33	698.40	-0.5807	7.143	25.6429	8.643	6.20	1.94	6.20	1.94	5.30000	7	7	39
100	3043.13	-203.5	686.69	693.45	-0.6989	35.714	25.2143	8.857	5.91	5.75	5.91	5.75	2.83000	6	6	47
101	174.53	-72.6	4.95	5.41	-1.0451	57.143	25.7143	9.214	6.71	6.52	6.71	6.52	1.90000	47	47	67
102	84.01	-90.6	9.31	16.15	-1.6509	21.429	9.6429	4.786	2.28	2.00	2.28	2.00	5.85000	6	6	47
103	218.14	-45.0	-12.36	8.27	-2.4894	50.000	10.0000	4.071	1.78	1.78	1.78	1.78	4.50000	6	6	90
104						64.286	9.7857	3.786	1.85	1.62	1.85	1.62	4.60000	6	6	90
105						85.714	9.6429	2.500	1.85	1.73	1.85	1.73	4.65000	6	6	90
106						14.286	11.7857	5.786	2.79	2.36	2.79	2.36	4.05000	68	68	0.0





























OB S	CR UI S E	MO N T H	DA Y	Y E A R	ST A T I O N	R I V K I L	IN C U B A T	CH A M B E R	N H 4 O R G	N O 2 N O 3	N T D R P	N D O	F N H 4 O R G	F N H 4	F N O 2	F T D P	F D R P	O X Y G D E M	F A N H 4 O R G
361	8	10	31	83	5	27.0	3	4	4	4	4	5	7.71	17.250	-21.09		-2.821	18.03	
362	8	10	31	83	6	28.0	1	1	4	4	4	6	277.99	4.642	71.53		33.589	-30.46	
363	8	11	4	83	6	28.0	1	1	5	5	5	7	253.29	-6.954	18.47		71.614	-36.93	
364	8	10	31	83	6	28.0	1	2	4	4	4	4	549.06	-8.907	33.23		98.908		
365	8	11	4	83	6	28.0	1	2	4	4	4	4	1234.85	2.433	47.10		107.662	-57.84	
366	8	10	31	83	6	28.0	1	3	4	4	4	6	603.30	-4.642	63.70		100.659	-100.69	
367	8	11	4	83	6	28.0	1	3	4	4	4	6	489.00	-8.126	40.61		51.268	-60.86	
368	8	10	31	83	6	28.0	1	4	4	4	4	6	-59.47	-1.908	3.22		4.433	1.52	
369	8	11	4	83	6	28.0	1	4	4	4	4	8	103.83	-32.319	-65.41		-0.100	27.30	
370	8	10	25	83	7	28.0	1	1	4	4	4	8	75.54	9.534	22.49		4.618	-40.82	
371	8	10	25	83	7	29.0	1	2	4	4	4	8	0.00	-2.446	32.85		1.723	-31.48	
372	8	10	25	83	7	29.0	1	3	4	4	4	8	56.61	-0.827	30.20		8.269	-27.75	
373	8	10	25	83	7	28.0	1	4	4	4	4	8	24.39	-18.738	-15.96		-0.791	-11.96	
374	8	11	3	83	8	38.9	3	1	4	4	4	4	247.72	-11.894	59.11		10.249	-107.72	
375	8	11	3	83	8	38.9	3	2	4	4	4	4	53.01	-14.775	0.00		11.440	-104.49	
376	8	11	3	83	8	38.9	3	3	4	4	4	4	-86.93	-0.840	82.03		10.588	-112.54	
377	8	11	3	83	8	38.9	3	4	4	4	4	4	-276.30	-2.888	21.09		-5.239	3.71	
378	8	11	2	83	9	56.0	1	1	4	4	4	7	753.72	-34.358	-87.17		-22.524	-39.69	

OB S	FA N H 4	FA N O 2	FA T D P	FA D R P	S O D D 1	IN NH 4 O	IN NH 4	IN N O 2	IN T D P	IN D R P	IN D O	PER S I L T	PER S A N D	PER C L A Y
361	337.46	6.549		29.156	-0.7677		11.071	0.143		0.98	7.90000			
362	149.47	25.365		71.714	-1.5415		13.214	0.143		1.20	7.60000	33	7	60
363	608.53	-7.000		94.474			17.929	1.500		1.33	7.30000	48	0	52
365	1131.02	34.751		107.762	-2.0435		17.714	0.286		1.92		49	8	60
366	662.78	6.549		96.226	-2.6452		12.143	0.929		1.16	6.60000	34	7	59
367	395.17	24.193		51.368	-2.1158		20.500	0.143		2.09	8.80000	49	1	50
368							17.286	1.214		1.27	7.90000	30	6	64
369							13.214	0.357		0.76	8.20000			
370	51.15	28.272		5.410	-0.6927		13.214	1.286		0.94	9.90000			
371	-24.39	16.291		2.514	-0.4684		13.286	0.929		1.75	7.40000	7	87	6
372	32.22	17.911		9.060	-0.3788		16.857	1.071		1.75	7.20000	7	87	6
373							15.929	1.214		1.58	7.20000	8	85	7
374	526.02	-9.005		15.489	-2.6743		15.929	1.000		1.52	8.80000	68	8	24
375	331.31	-11.886		16.680	-2.5968		8.000	0.571		1.33	8.40000	43	10	47
376	191.36	2.049		15.828	-2.7900		12.500	1.071		1.16	7.20000	62	2	36
377							20.500	0.571		1.44	8.40000			
378	719.32	-10.296		-28.982	-0.8133		14.143	0.929		1.27	9.00000	30	7	63
							25.000	2.571		1.46	7.61000			



## METRIC CONVERSION FACTORS

The following factors may be used by readers who wish to convert the metric (International System) units used in this report to inch-pound units.

Multiply Metric Unit	By	To Obtain Inch-Pound Unit
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.39	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
gram (g)	0.002205	pound (lb)
megagram (Mg)	1.102	ton, short
liter (L)	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	35.31	cubic foot (ft <sup>3</sup> )
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m <sup>3</sup> /s)	35.31	cubic foot per second (ft <sup>3</sup> /s)
degree Celsius (°C)	$F = 9/5^{\circ}C + 32$	degree Fahrenheit (°F)