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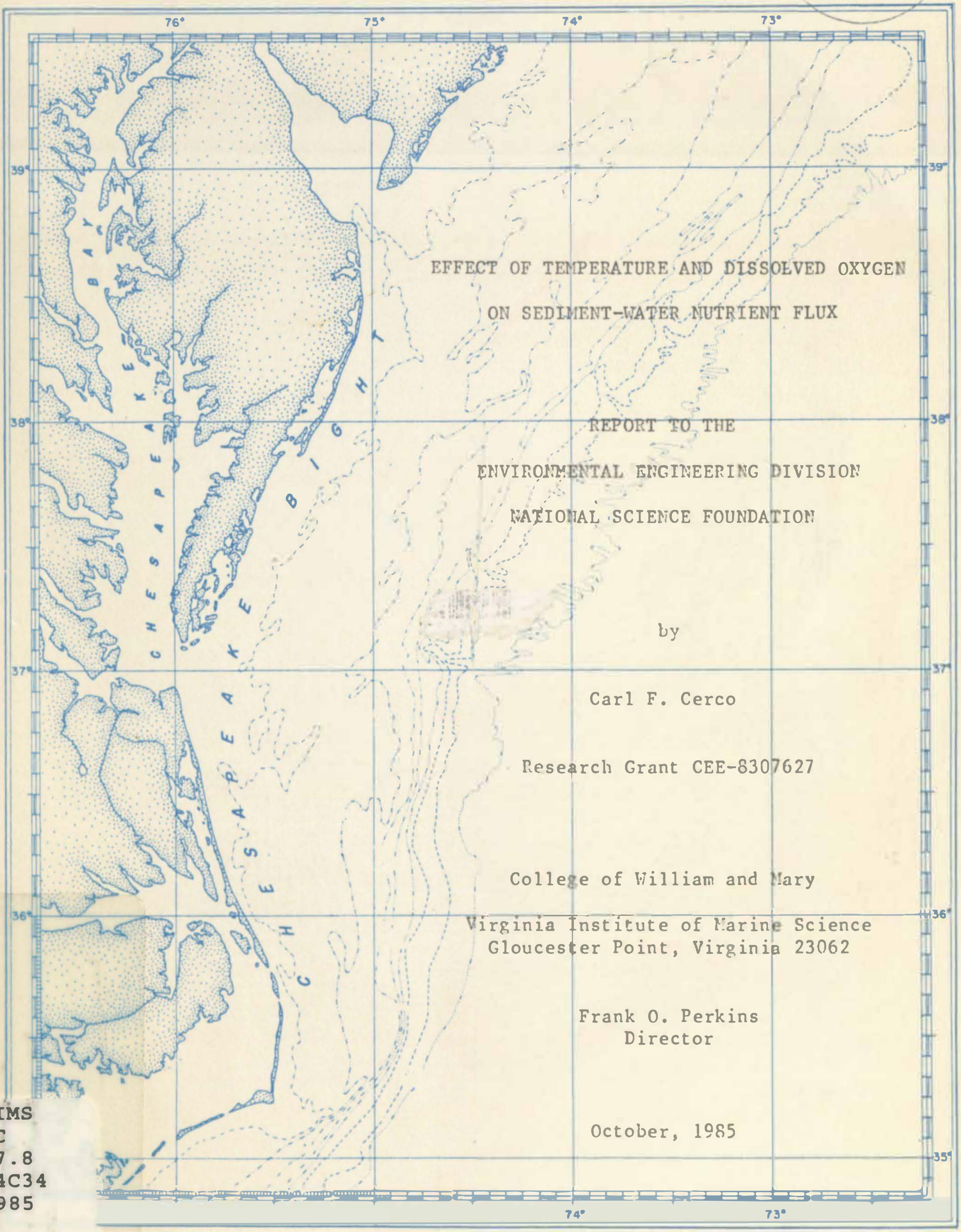

EFFECT OF TEMPERATURE AND DISSOLVED OXYGEN ON SEDIMENT-WATER NUTRIENT FLUX

REPORT TO THE
ENVIRONMENTAL ENGINEERING DIVISION
NATIONAL SCIENCE FOUNDATION

by

Carl F. Cerco

Research Grant CEE-8307627

College of William and Mary

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SUMMARY

A series of experiments was conducted in order to determine the influence of water-column temperature and dissolved oxygen on sediment-water nutrient flux. Three nutrients were considered: ammonium nitrogen, nitrate nitrogen, and ortho phosphorus. Results of the experiments indicated that nutrient concentration in the overlying water had to be considered, as well as temperature and dissolved oxygen, as an independent variable which affected sediment-water nutrient flux.

The apparatus used to control dissolved oxygen provided a record of sediment oxygen demand (SOD). Hence, the effects of water-column temperature and dissolved oxygen on SOD were examined also.

Experiments were conducted on intact sediment cores removed from Gunston Cove, Virginia, during the interval July to October, 1984. Gunston Cove is a shallow, freshwater tidal embayment tributary to the Potomac River and located 26 km downstream of Washington, D.C. The Cove is subject to blue-green algae blooms which persist despite stringent control of point-source nutrients discharged to the system. Sediments from Gunston Cove were selected for use in this study because sediment nutrient releases are suspected of supporting the algal blooms.

A total of eighteen different temperature-dissolved oxygen combinations were investigated. Temperature ranged from 10 to 30° C. Dissolved oxygen ranged from 0 to 8 mg/l. Measures at two temperature-dissolved oxygen combinations were repeated using sediments collected several weeks apart.

Ammonium was released from the sediments in 95% of the experiments. Release rates ranged from 44 to 276 mg/m^2/day. Release increased as a function of temperature and was greater at low dissolved oxygen concentrations than at high concentrations.

Nitrate was always taken up by the sediments. Uptake ranged from 17 to 509 mg/m^2/day. Uptake increased as a function of temperature and was greater at low dissolved oxygen concentrations than at high concentrations.

Ortho phosphorus moved into the sediments or out of the sediments with approximately equal frequency. Flux rates ranged from 16.4 mg/m^2/day sediment uptake to 8.9 mg/m^2/day sediment release. Release was higher under anoxic conditions and showed no relationship to temperature.

Sediment oxygen demand ranged from 0.4 to 3.3 gm/m^2/day. Demand increased as a function of temperature and was suppressed at low oxygen concentrations.

Quantitative relationships which expressed the effect of temperature, dissolved oxygen, and nutrient concentration on sediment-water fluxes were formulated. The relationships were consistent with both the theoretical relationships of these variables to flux and with the observations in the experiments. Parameters in the relationships were evaluated through nonlinear regression. Optimal parameter values were those which minimized the sum of the squared deviations between predictions and observations. The regression also was employed to evaluate the fraction of variability in the observations which could be attributed to each independent variable.

The most significant determinant of ammonium flux was temperature which accounted for 46% of the observed variability. Dissolved oxygen concentration accounted for an additional 9% of the variability and ammonium concentration exhibited no effect on flux.

The most significant determinant of nitrate flux was concentration in the water column which accounted for 52% of the observed variability. High concentration induced rapid uptake by the sediments. Temperature accounted for an additional 24% of the variability and dissolved oxygen accounted for 13%.

The most significant determinant of ortho phosphorus flux was concentration in the water column which accounted for 55% of the observed variability. High concentration induced rapid uptake by the sediments. Dissolved oxygen accounted for an additional 20% of the variability and temperature exhibited no effect on flux.

The most significant determinant of sediment oxygen demand was dissolved oxygen which accounted for 48% of the observed variability. Temperature accounted for an additional 20% of the variability.

Precision of the flux measures was monitored by running replicate cores in each experiment. Precision was quantified through the coefficient of variation (CV). Median CV of replicate cores for ammonium, nitrate, and SOD was approximately 0.2. Median CV for ortho phosphorus was 0.87.

Repeatability of the flux measures was examined twice using sediment cores collected several weeks apart. Repeatability was quantified through the coefficient of variation. The CV of the repeat measures was greater than the CV of replicate cores. Repeat measures of nitrate flux showed the closest agreement. Repeat measures of ammonium flux showed the least agreement.

No standard exists against which to judge the accuracy of the laboratory flux measures. The measures were compared, however, to in-situ flux measures and to flux measures completed in a different laboratory. The measures agreed only in direction and order of magnitude of flux. Little correspondence existed between individual flux measures conducted in the laboratory and in situ or in different laboratories. The root-mean-square difference in measures conducted by different methods was the same magnitude as the fluxes measured.

Sediment-water nutrient fluxes and sediment oxygen demand in Gunston Cove were compared to values reported for other systems. Sediment ammonium release measured in this study was typical of release rates measured elsewhere in the Chesapeake Bay system. Sediment nitrate uptake by Gunston Cove sediments was greater than in several similar water bodies. High nitrate concentration in the water was deemed responsible for the sediment uptake rate. Sediment oxygen demand measured in Gunston Cove was typical of demands measured elsewhere in Chesapeake Bay.

Sediment release of ortho phosphorus was small compared to several other systems. The low release rate and occasional sediment uptake of ortho phosphorus in Gunston Cove were unexpected in view of the release rate needed to support algal blooms. Two hypotheses were advanced to explain the minimal phosphorus release noted here. The first was that high nitrate concentrations during 1984 suppressed sediment phosphorus release. The second was that pH during 1984 was lower than during bloom years and enhanced the ability of sediment particles to sorb phosphorus. A recommendation was made to investigate the effect of both water-column nitrate and pH on sediment phosphorus release.

Chapter I. INTRODUCTION

In their management and model studies of receiving waters, engineers must account for all significant sources and sinks of the substances being modelled. In programs to eliminate eutrophication, these substances commonly include algal nutrients, oxygen, and oxygen-demanding materials. One significant source or sink is the flux of materials between the bottom sediments and the overlying waters. Although benthic cycling of phosphorus has long been recognized as an important process in lake eutrophication, and sediment oxygen demand (SOD) is commonly included in estuarine models, the effect of sediment nutrient fluxes on the quality of tidal waters has only lately been recognized. Sediment nutrient releases have been noted as supporting the algal population of the tidal Chowan (38) and Patuxent Rivers (37) and have frustrated the long-term efforts to prevent algal blooms in the tidal Potomac River (45).

Difficulties arise in incorporating sediment fluxes into receiving-water models because measures of sediment flux are scarce and because there is little understanding of how the fluxes are affected by such factors as temperature, dissolved oxygen (DO), and nutrient concentration in the overlying water.

A. Sediment Nutrient Fluxes in Gunston Cove

Gunston Cove is a shallow, freshwater tidal embayment situated on the Virginia shore of the Potomac River. In 1979, a study was commenced to survey water quality in the embayment, with particular respect to those substances which affect eutrophication, and to provide a mathematical model for use in management of the system. Early in the model study, it became apparent that a mass balance could not be achieved between observed substance concentrations in the embayment and measured inflows of these substances. Materials fluxes between the sediment and the water column were suspected of causing this imbalance. Consequently, in-situ measures of sediment nutrient flux were conducted and fluxes were incorporated into the water-quality model. It was concluded that sediment releases of phosphorus provided a significant portion of that nutrient needed to support algal blooms in Gunston Cove. Details of the model study and of the role of sediment nutrient fluxes may be found in (11).

In-situ measures of sediment nutrient flux collected during the study were erratic in magnitude and direction. It was unclear if the variability of the fluxes was an artifact of the measurement technique or reflected true variability of the processes being measured. Moreover, no consistent influence of temperature, dissolved oxygen, season, or other factors could be discerned in the data. Therefore, fluxes were incorporated into the model as constant values representative of the central tendency of a large number of measures. This approach was sufficient to obtain calibration and verification of the model, but compromised its use as a predictive tool. No means existed to project the effect of proposed management plans on existing sediment nutrient fluxes.

B. Objectives of this Study

The studies of Gunston Cove and of the previously-mentioned tidal water bodies indicate that management of water quality in these systems is not possible without reliable measures of benthic nutrient flux and without knowledge of the factors which influence benthic flux. This study was conducted in order to provide those measures and to contribute to that knowledge. The objectives were as follows:

1) Develop laboratory apparatus and methodology suitable to measure sediment nutrient fluxes.

2) Explore the effect of dissolved oxygen and temperature on sediment fluxes of the nutrients ammonium nitrogen, nitrate nitrogen, and ortho phosphorus.

No standard method of measuring sediment materials flux exists. Therefore, any examination of fluxes must start with construction of apparatus and development of methodology. Flux measures conducted in the laboratory were selected for use in this study as it was anticipated more accurate and precise measures could be conducted in the lab than in-situ. Laboratory measures also made it possible to control and alter the ambient conditions under which the fluxes are measured.

Evaluation of the accuracy of the laboratory measures through comparison with a known, standard flux is impossible. An evaluation which can be conducted, however, is to compare the measures detailed herein with fluxes measured by an alternate method. Therefore, the laboratory measures are compared to in-situ measures collected in Gunston Cove.

Three nutrients were selected for examination. Ammonium was selected for its role as a primary algal nutrient and because nitrification of ammonium contributes to oxygen demand in the water column. Nitrate was selected because it too is a nitrogenous algal nutrient and because observations of nitrate are often used to calibrate the nitrification rate in water-quality models. Ortho phosphorus was selected because it is a primary algal nutrient.

The effects of temperature and dissolved oxygen are examined because they are fundamental determinants of the nature and rate of biogeochemical processes. That these factors influence sediment nutrient flux has been established in numerous studies. Moreover, temperature and DO are readily measured, are commonly recorded, and are (to some extent) predictable. Therefore an understanding of the effect of temperature and dissolved oxygen on sediment nutrient flux will be of optimal use to engineers and managers seeking to incorporate these fluxes into their models and plans.

Nutrient concentration in the water overlying the sediments was not controlled in this investigation. Rather, the dissolved nutrient concentration at the initiation of each experiment was approximately equivalent to the concentration in Gunston Cove at the time water and sediment samples were collected. Therefore, the effect of nutrient concentration in the overlying water on sediment nutrient flux is included in the analyses although determination of this effect was not a primary objective of this study.

The system used to control dissolved oxygen in the laboratory apparatus also provided a record of sediment oxygen demand. Since SOD is a significant portion of the total oxygen demand in Gunston Cove and in similar water bodies, the effects of temperature and dissolved oxygen on sediment oxygen demand are examined here but are not emphasized.

Chapter II. THE STUDY AREA

Gunston Cove (Fig 2-1) is a tidal freshwater embayment located on the Viriginia side of the Potomac River approximately 26 km downstream of Washington, D.C. The Cove is formed by the confluence of two smaller embayments, Pohick Bay and Accotink Bay, which are the tidal termini of free-flowing Pohick and Accotink Creeks.

From the mouth of Gunston, it is approximately 5 km along the axes of Gunston and Pohick Bay to the point where the embayment narrows into Pohick Creek. Accotink Bay extends approximately 1.2 km upstream from its juncture with Gunston. Except at the mouth, where Gunston Cove merges with the Potomac River, depths in the embayments are shallow and of the order 1 to 2 meters. Tide range averages 61 cm. Dry-weather flows in the tributary creeks are small, 0.1 to 1.0 m^3/sec, although these flows may increase by an order of magnitude or more subsequent to rainstorms.

Flow in Pohick Creek is augmented by the Lower Potomac Water Pollution Control Plant which discharges into the creek approximtely 1.8 km above Pohick Bay. The design flow of the STP is 1.6 m^3/sec (36mgd) and it is the only point source which discharges to the embayment system. During the study period, nutrient concentrations in the STP effluent were in the range 8.1 to 9.4 mg/l ammonium, 4.6 to 5.9 mg/l nitrate, and 0.13 to 0.17 mg/l total phosphorus.

During the summer months, Gunston Cove is subject to nuisance algal blooms and accompanying undesirable dissolved oxygen fluctuations. Depth-average chlorophyll ´a´ concentrations in the range 100 to 200 μg/l are commonplace as are diurnal dissolved oxygen fluctuations of 8 to 10 mg/l. During bloom conditions, floating mats of the blue-green algae are apparent.

Sediment and water samples for this study were collected at a point approximately in the center of the embayment. Ambient temperature at this station was typically in the range 24 to 29°C, DO in the range 8 to 12 mg/l, and chlorophyll in the range 60 to 120 μg/l. Ammonium concentration varied by an order of magnitude from 0.1 to over 1 mg/l. Nitrate was 1 to 3 mg/l and total phosphorus was 0.08 to 0.25 mg/l, roughly equivalent to the concentration in the STP effluent.

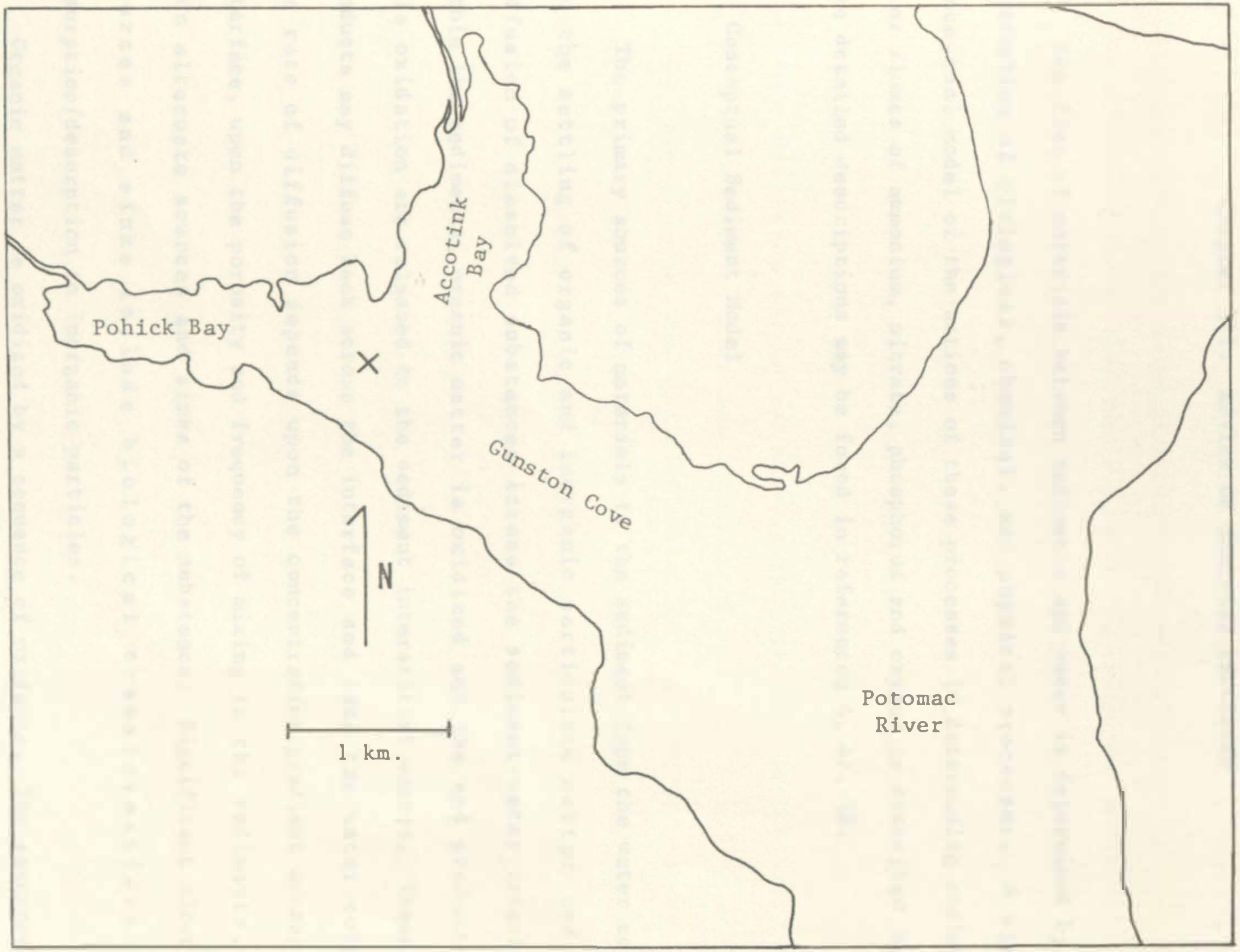


Figure 2-1. Gunston Cove. (X) indicates sample site.

Chapter III. REVIEW OF SEDIMENT PROCESSES

The flux of materials between sediments and water is determined by the interaction of biological, chemical, and physical processes. A simple conceptual model of the actions of these processes in determining sediment-water fluxes of ammonium, nitrate, phosphorus and oxygen is described here. More detailed descriptions may be found in references 4, 47, 48.

A. Conceptual Sediment Model

The primary sources of materials to the sediment from the water column are the settling of organic and inorganic particulate matter and the diffusion of dissolved substances across the sediment-water interface. Within the sediments, organic matter is oxidized and the end products of this oxidation are released to the sediment interstitial waters. These end products may diffuse back across the interface and into the water column. The rate of diffusion depends upon the concentration gradient across the interface, upon the porosity and frequency of mixing in the sediments, and upon alternate sources and sinks of the substance. Significant alternate sources and sinks include biological transformations and adsorption/desorption to inorganic particles.

Organic matter is oxidized by a sequence of oxidants. The sequence can be predicted based on the free energy yield of the reactions (17). The reactions which produce the largest amount of energy dominate until the oxidant is depleted and the next most efficient reaction becomes predominant. Reduction of oxygen yields the most energy in the oxidation of organic matter. Following oxygen, reduction of nitrate is the most important reaction in the tidal systems of interest.

The distribution of dissolved oxygen in the sediments is determined by the balance between the rate of consumption due to decomposition and the rate of supply from the water above. In the presence of an oxygenated water column, there usually will be an oxygen-bearing sediment layer in contact with the water and underlain by an oxygen-depleted sediment layer. Oxygen is maintained in the upper layer, typically 2 to 5 cm deep for mud (4), by molecular diffusion and by mixing due to physical disturbance of the sediments and biological reworking. This upper layer is variously referred to as the ´mixed´ layer, the ´oxidized´ layer, or the ´aerobic´ layer.

Below the mixed layer, the potential for oxygen consumption exceeds the rate at which oxygen is supplied by diffusion from above. Thus nitrate or another substance becomes the prime oxidant in the decomposition of organic matter. The extent of biological activity in the lower layer is determined by the porosity of the sediments and by the rate of input of organic substrate. The active zone may extend 25 to 30 cm deep (47) and is variously referred to as the ´reduced´ layer, the ´anoxic´ layer, or the ´anaerobic´ layer.

Decomposition of organic matter generally results in the liberation of nitrogen and phosphorus in the forms of ammonium and ortho phosphorus (32). A buildup of these forms in the interstitial water results in the eventual release of the end products of decompostion into the water column. This release may or may not occur, however, depending on additional processes which are active in the sediments.

In the oxidized layer, a portion of the ammonium produced by degradation is oxidized to nitrite and subsequently to nitrate via the nitrification process (4, 26, 42). Thus the quantity of ammonium available for export to the water column depends upon the rate at which production exceeds consumption. If consumption via nitrification equals the rate of production, no ammonium will escape the sediments.

Nitrate produced in nitrification may diffuse out of the sediments into the water column (4, 42) or down into the anoxic layer where it is reduced to a gaseous nitrogen form via the denitrification process (4, 26, 42). If sufficient nitrate is available in the water column, a portion of this nitrate may also diffuse into the anoxic (16, 35, 50) layer and be subsequently reduced as well.

Sediment-water fluxes of phosphorus are largely determined by the sorption/desorption of dissolved forms onto sediment particles, particularly ferric oxides. Under oxic conditions, ortho phosphorus has a far greater tendency to sorb to particulates than under anoxic conditions. The sorption coefficient of ortho phosphorus on one oxic marine sediment has been reported to be fifty times the sorption coefficient on an anoxic sediment (28). Thus little or no ortho phosphorus produced by decomposition of organic matter can escape the oxidized sediment layer unless the sorption capacity of the particulates is exceeded. Under anoxic conditions, however, the ability of particulates to sorb ortho phosphorus is much less and quantities of phosphorus may be recycled back to the water column.

In the event an oxidized sediment should become reduced, due to anoxia in the overlying water (18, 19) or to the rapid input of organic substrate (5), large quantities of previously-sorbed phosphate may be released. Phosphate releases may also be effected by an increase in water-column pH

(1, 43) or by physical disturbance of the sediment (3, 39). These phosphorus releases are of great consequence in contributing to the eutrophication of phosphorus-limited systems.

Chapter IV. APPARATUS AND METHODOLOGY

A. Description of Apparatus

The apparatus (Fig. 4-1) consisted of five transparent lucite columns, each 120 cm in length and 10 cm inside diameter. The columns were fashioned so that they were used as coring devices to withdraw sediment samples in the field.

Each column was capped to prevent the exchange of oxygen between the water column and the atmosphere. A Yellow Springs Instrument Model 5739 dissolved-oxygen (DO) probe was fitted to the cap and employed to sense DO within the water column. Passages placed in the cap permitted the introduction of compressed oxygen and nitrogen gas and allowed withdrawal of water samples. Mixing within the column was accomplished with a 2.9 cm diameter propeller connected by a shaft to an external motor. Mixing was enhanced by a series of internal baffles which insured complete circulation. The stirring rate, 2000 rpm, was selected in order to generate sufficient water motion for the DO probe to read accurately. Stirring the column was not sufficient to resuspend bottom sediments, however.

The columns were placed in a 61 cm diameter, 110 cm deep water-filled tank, insulated with 2 cm thick foam, which served as a constant-temperature bath. Temperature in the bath was regulated by a Haake EK51 external chiller of 380 watts capacity and a Haake E3 immersion heater of 1500 watts capacity. This system made it possible to maintain temperature in the bath at + or - 0.5^{o}C of the temperature specified for the experiment.

The experimental apparatus was controlled by a Commodore VIC-20 microprocessor fitted with an analog-digital conversion unit. The VIC continuously monitored DO within each column. When sediment oxygen demand drew DO below a specified concentration, a relay-operated valve was opened and gaseous oxygen bubbled through the column. When the desired DO concentration was again attained, the valve closed. This system regulated dissolved oxygen within + or - 0.25 mg/l of the concentration specified for the experiment. DO concentrations within each column and a record of valve operations were printed on an accessory printer. Analysis of this record allowed computation of sediment oxygen demand during the experiments.

B. Experimental Procedure

Sediment cores, 10 cm in diameter and 60 cm long, were collected by hand in the lucite tubes which were part of the laboratory apparatus. Following collection, the cores were examined for evidence of sediment disturbance or other factors which would render them unsuitable. At the same time a 25-liter Nalgene carboy was filled with ambient water. The cores and their overlying water were placed on ice and returned to the lab at Gloucester Point.

Upon return, the carboy water was pumped through a series of one-micron ´string filters´ in order to remove organic and inorganic particulate matter. Analysis indicated this system reduced total suspended solids (TSS) from the ambient level of 25 mg/l to below the detection level of 4 mg/l. Chlorophyll ´a´ was reduced from the ambient level to approximately 10 µg/l.

The water overlying the cores was siphoned off and replaced with 2.3 liters of the filtered water. This filled the columns to a depth of 30 cm. Siphoning and refilling were conducted gradually so as to cause minimal disturbance to the sediment surface.

The cores were placed in the constant-temperature bath, fitted with caps and DO probes, and allowed to attain the temperature and dissolved oxygen level specified for the experiment. When necessary, gaseous nitrogen was used to purge oxygen from the water. A mercury thermometer inserted in a spare core placed in the bath was used to monitor mud temperature. The initial water sample was collected as soon as the desired temperature and oxygen levels were achieved. Approximately twelve hours elapsed between removal of the cores from Gunston Cove and collection of the first sample.

Four mud cores were run simultaneously at two different dissolved oxygen concentrations. A single ´control´ column identical to the sediment columns but containing only water was employed to determine transformation rates in the water. The control was maintained at one of the specified DO concentrations for half the experiment. At the mid-point, the water was replaced and the control maintained at the second DO concentration.

At six-hour intervals, water samples were suctioned into 125 ml Nalgene bottles. The volume withdrawn was replaced with filtered water removed from Gunston Cove. A portion of the replacement water was reserved at each sample interval and analyzed along with the column samples in order to keep an exact mass balance of nutrients in the columns.

C. Sample Treatment and Analysis

Following collection, samples were placed in a cooler maintained at 4°C. Samples were analyzed within holding times recommended by the EPA or else preserved by recommended techniques (40).

1.) Ammonium Analysis - Samples for ammonium analysis were filtered through 0.45 micron millipore filters and analyzed by an automated phenate method (14) on a Technicon AAII autoanalyzer.

2.) Nitrate Analysis - Samples for analysis of nitrate + nitrite (subsequently referred to simply as nitrate) were filtered through 0.45 micron millipore filters and analyzed by the cadmium reduction method (14) on a Technicon AAII autoanalyzer.

3.) Ortho Phosphorus Analysis - Samples for analysis of ortho phosphorus were filtered through 0.45 micron millipore filters and analyzed via an ascorbic acid method (14) in a Bausch and Lomb Spectronic 20 spectrophotometer.

D. Calculation of Nutrient Flux Rates

The results of each experiment were time series of substance concentrations in each column. Nutrient flux rates were obtained from these via the relationship

$$F = \frac{V(C_n - C_o) + v \sum_{o}^{n} C_i - Cm_i}{A\, n\, \Delta t} \tag{4-1}$$

in which

F = mean flux rate (gm/m^2/day)

V = volume of water in column (m^3)

C_i = concentration at end of sample interval i (mg/l)

C_o = concentration at start of experiment (mg/l)

v = volume of sample withdrawn (m^3)

Cm = concentration of makeup water (mg/l)

A = cross-sectional area of column (m^2)

n = number of sample intervals

Δt = length of sample interval (days)

The first term in the numerator is the flux due to the concentration difference in the first and last samples collected. The second term is a correction to that flux due to sample withdrawal and replacement. Positive values of flux indicate movement of substances from the sediment into the water.

Experiments were conducted for a period of 42 to 48 hours. The results indicated, however, that the flux rates diminished after approximately 24 hours. Nutrients in the water approached depletion due to sediment uptake or approached a saturation concentration due to sediment release. Therefore, flux rates were computed based on no more than the first 24 hours of observations. If the observations indicated depletion or saturation in less than 24 hours, the computation period was shortened appropriately.

Nutrient concentrations in the water generally increased or decreased monotonically. Random deviations from monotonic behavior were observed, however. Typical time series of nutrient concentrations are shown in Figures 4-2 to 4-4 for ammonium, nitrate, and ortho phosphorus, respectively.

E. Calculation of Sediment Oxygen Demand

The rate of sediment oxygen demand was indicated by the amount of time elapsed between reaeration events. It was computed

$$SOD = \frac{V}{A} \frac{\sum_{1}^{n} C_b - C_e}{\sum_{1}^{n} \Delta t_i} \qquad (4\text{-}2)$$

SOD = mean sediment oxygen demand (gm/m^2/day)

C_b = concentration at which reaeration ceases (mg/l)

C_e = concentration at which reaeration starts (mg/l)

Δt_i = time elapsed during interval i (day)

n = number of instances of reaeration.

By convention, positive SOD indicates oxygen flux into the sediments. Intervals in which the oxygen balance was interupted by withdrawal of samples were omitted from analysis. In keeping with the computation of nutrient flux, only the first 24 hours of the SOD record were considered in Eq. 4-2.

Sediment oxygen demand was erratic and often increased during the first 24 hours of measurement. This increase is likely due to bacterial colonization of the column walls. A similar trend has been noted in another series of laboratory SOD measures and the same explanation offered (15). A typical time series of sediment oxygen demand is shown in Fig. 4-5.

F. Calculation of Net Sediment-Water Fluxes

The flux rates apparent in the columns containing sediment are the total of sediment-water fluxes and of transformations within the water only. The total fluxes may also include transfer of nutrients and oxygen between the column walls and the adjacent water due to abiotic sorption/desorption or due to bacterial colonization of the walls. In order to isolate the sediment-water fluxes, it is necessary to subtract from the total flux the transformation rates in the water and the interactions between the water and the walls. The sum of transformations in the water and interactions with the walls were obtained from the observations in the control column. Net sediment-water flux rates were computed by taking the average of the total fluxes in the two replicate sediment columns and subtracting the flux rate in the control column.

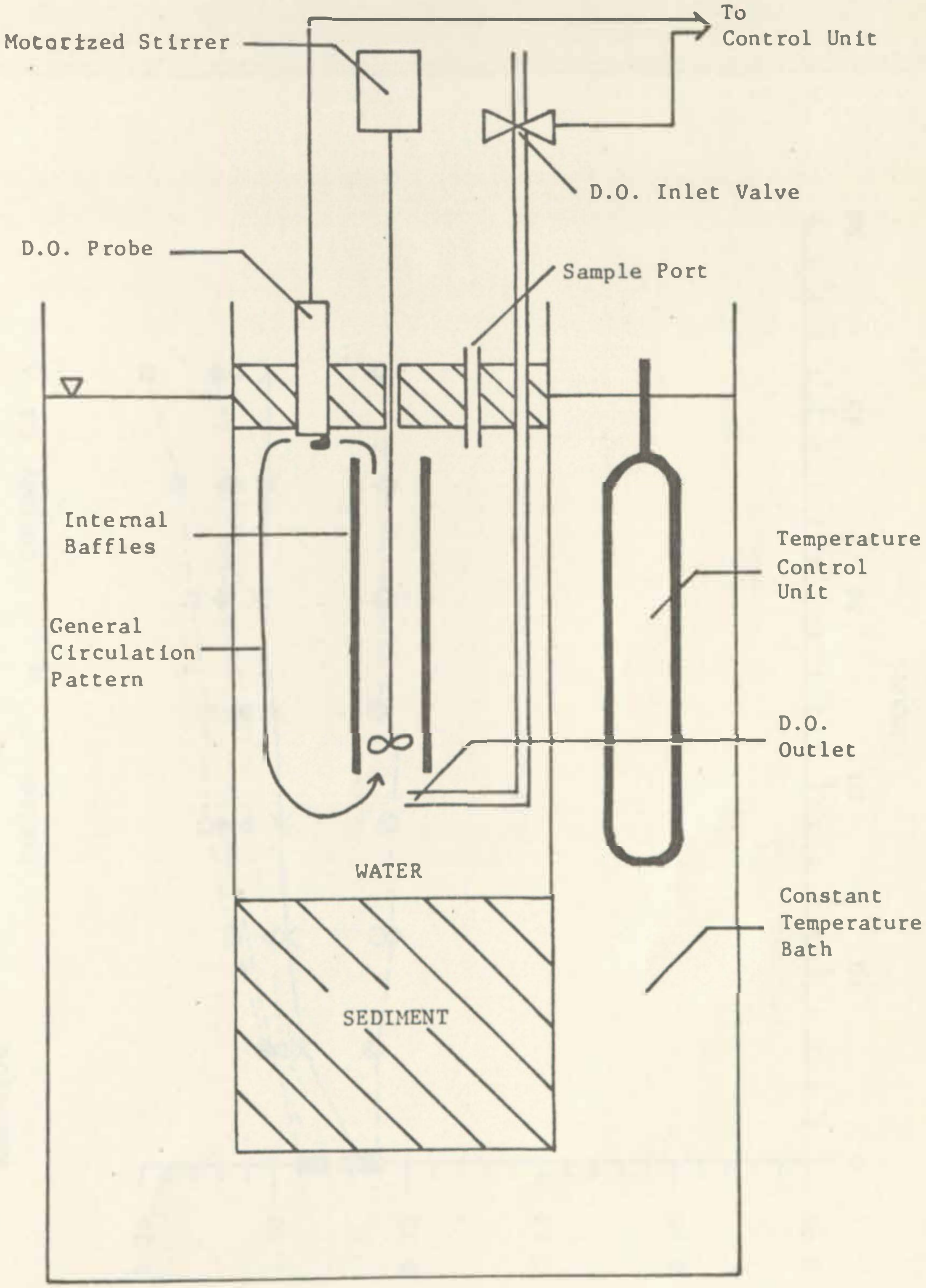


Figure 4-1. Schematic of a Sediment Column.

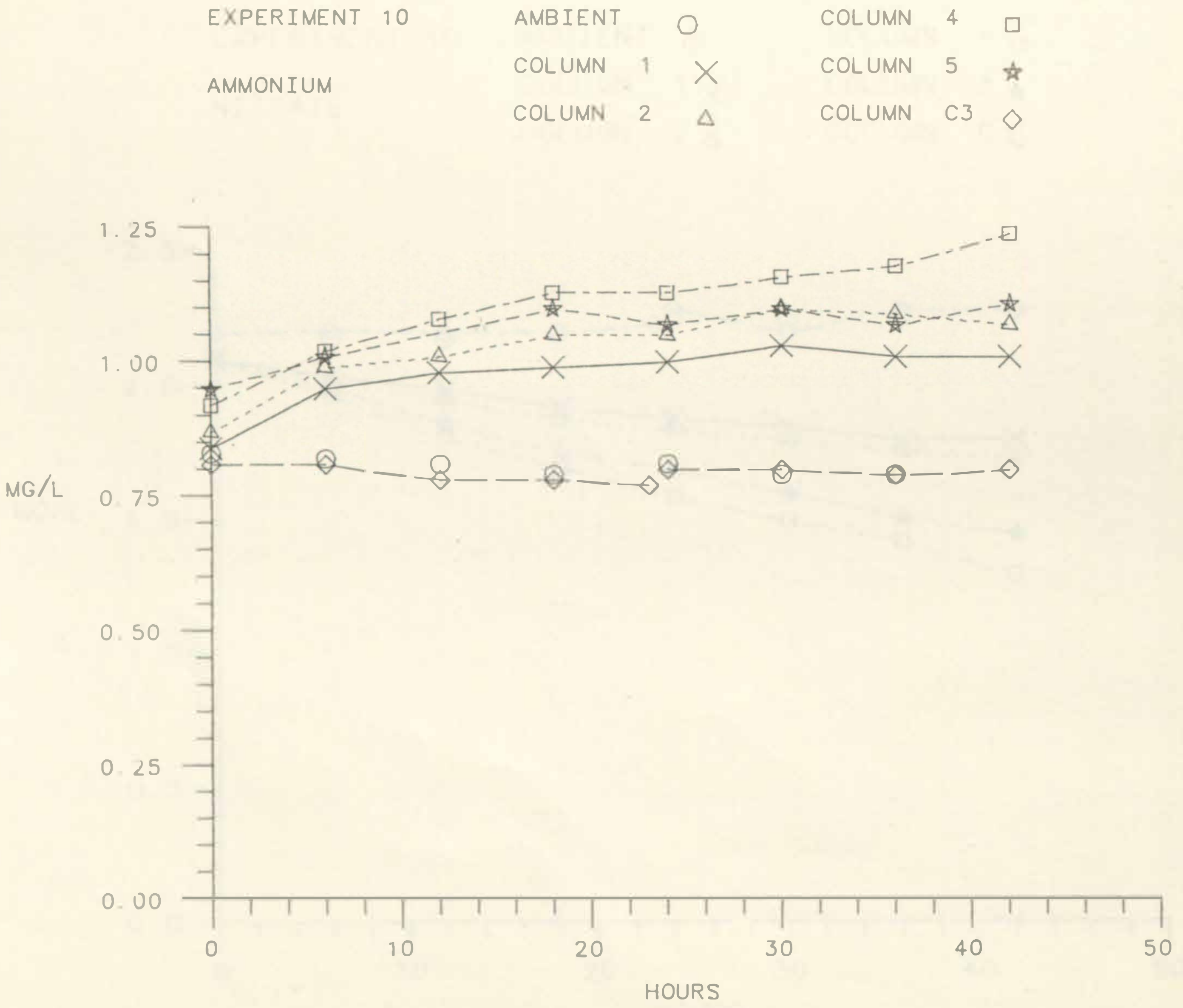


Figure 4-2. Ammonium Concentration vs. Time. Ambient indicates refill water. C3 indicates the control column.

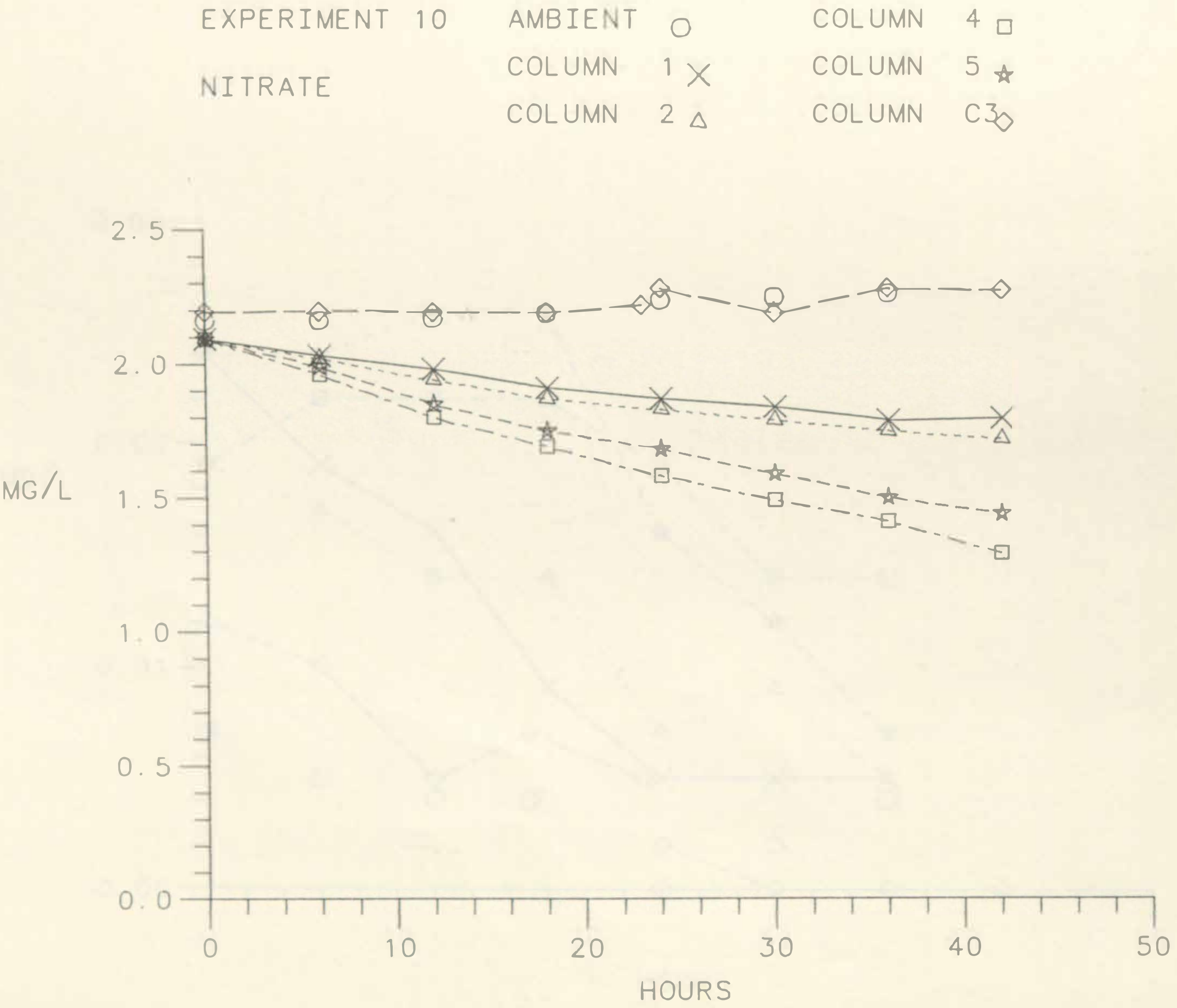


Figure 4-3. Nitrate Concentration vs. Time. Ambient indicates refill water. C3 indicates the control column.

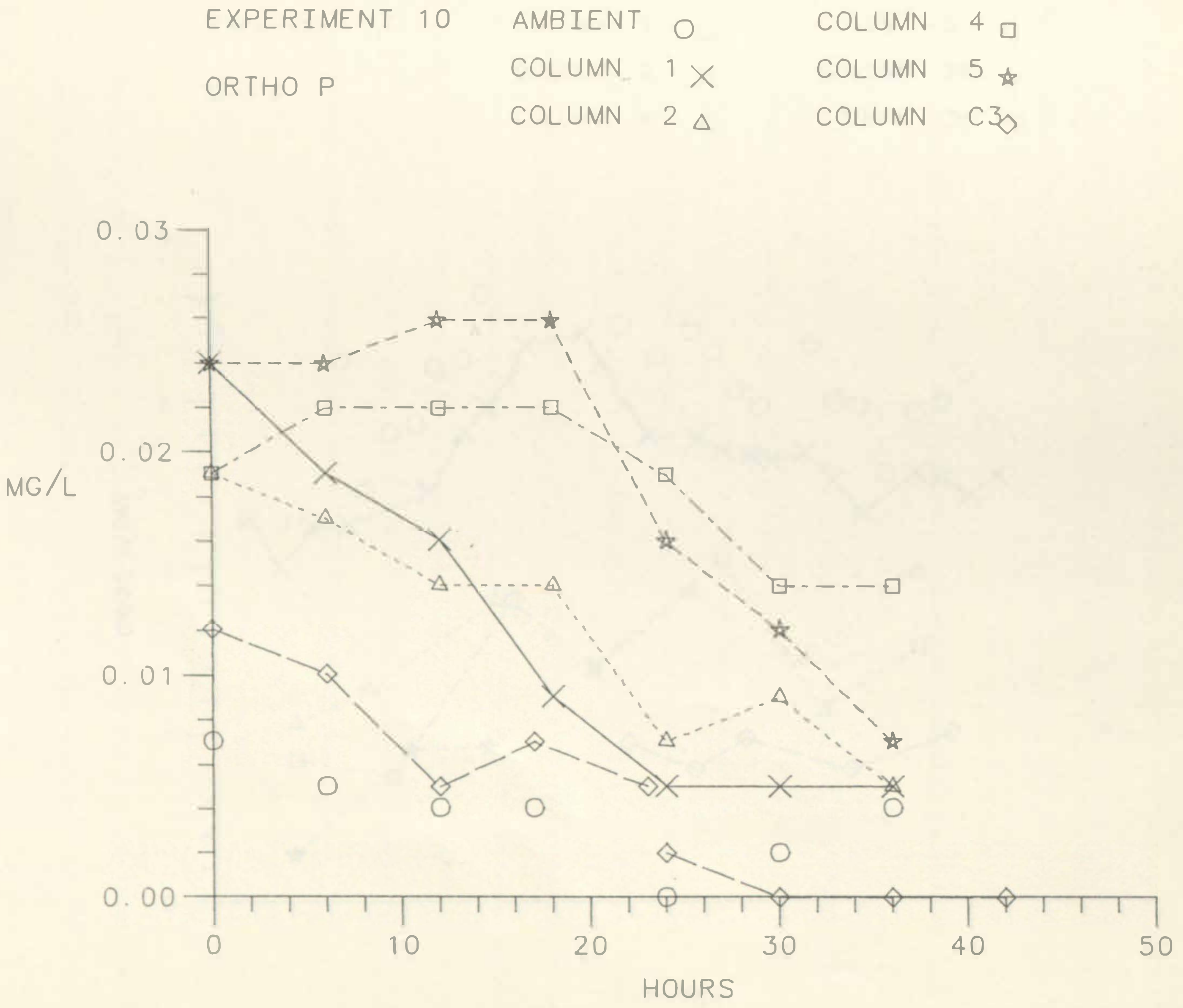


Figure 4-4. Ortho Phosphorus Concentration vs. Time. Ambient indicates refill water. C3 indicates the control column.

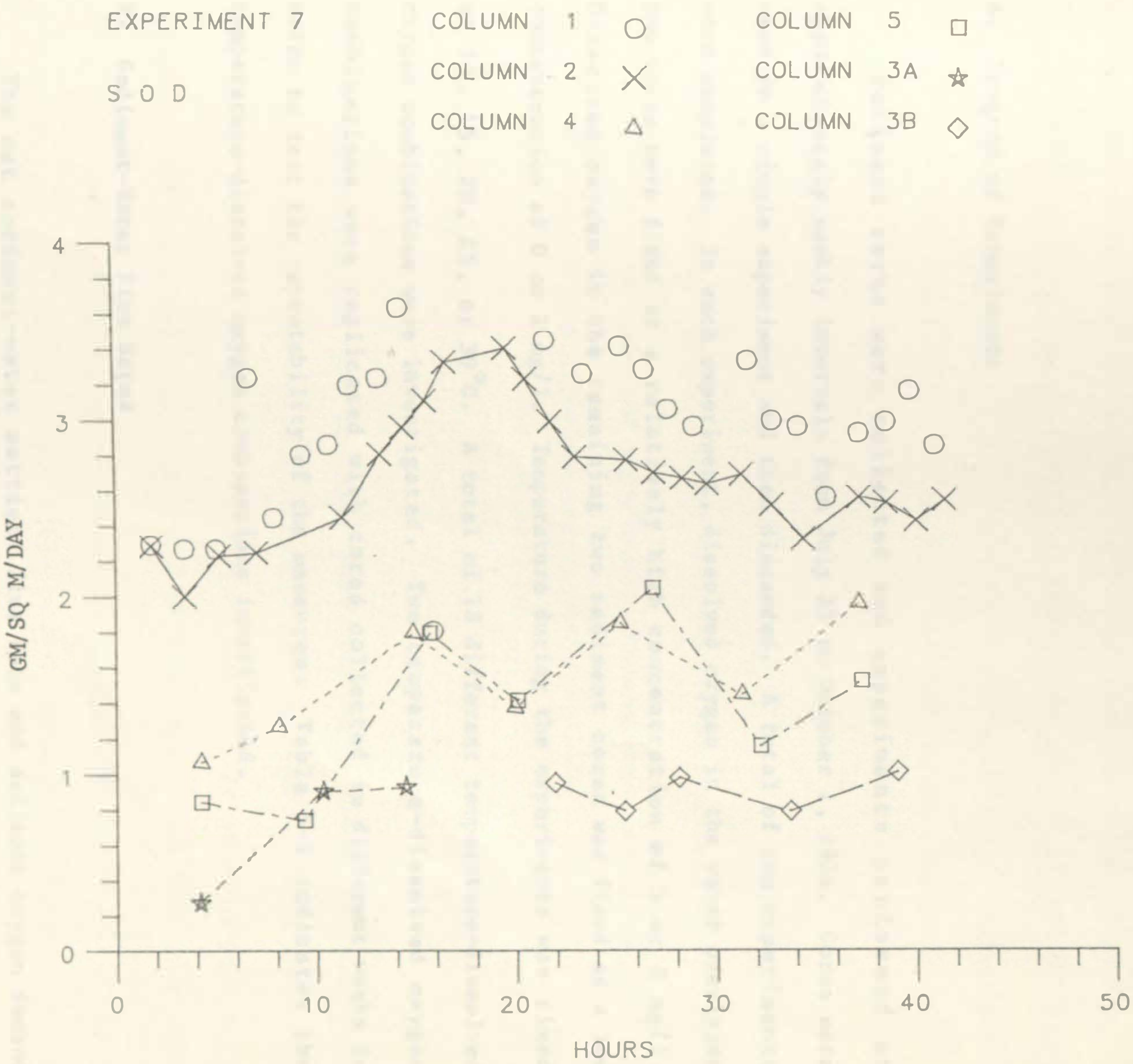


Figure 4-5. Sediment Oxygen Demand vs. Time. 3A and 3B indicate the control column.

Chapter V. PROGRAM OF EXPERIMENTS AND RESULTS

A. Program of Experiments

Sediment cores were collected and experiments performed at approximately weekly intervals from July 23 to October 1, 1984. Cores were used in a single experiment and then discarded. A total of ten experiments were completed. In each experiment, dissolved oxygen in the water overlying two cores were fixed at a relatively high concentration of 5 or 8 mg/l. Dissolved oxygen in the remaining two sediment cores was fixed at a low concentration of 0 or 2 mg/l. Temperature during the experiments was fixed at 10, 15, 20, 25, or 30°C. A total of 18 different temperature-dissolved oxygen combinations were investigated. Two temperature-dissolved oxygen combinations were replicated with cores collected in different weeks in order to test the repeatability of the measures. Table 5-1 indicates the temperature-dissolved oxygen combinations investigated.

B. Sediment-Water Flux Rates

The net sediment-water nutrient flux rate and sediment oxygen demand for each temperature-dissolved oxygen combination are presented in Tables 5-2 to 5-5 for ammonium, nitrate, ortho phosphorus, and SOD, respectively.

Positive nutrient fluxes indicate release from the sediment to the water. Positive SOD indicates transfer of oxygen from the water to the sediments.

C. Ammonium Flux

Ammonium flux was out of the sediments in 19 of the 20 cases investigated. The mean of all fluxes was 100 mg/m^2/day. Release was enhanced at high temperatures and at low dissolved oxygen concentrations.

D. Nitrate Flux

Nitrate moved from the water into the sediments in all observations. The mean flux rate was -160 mg/m^2/day. Uptake was enhanced at high temperatures and at low dissolved oxygen concentrations.

E. Ortho Phosphorus Flux

Ortho phosphorus was the only substance which showed no predominant direction of movement across the sediment water interface. Ortho phosphorus was released by the sediments in 47 per cent of the cases examined and taken up by the sediments in 53 per cent of the cases examined. The mean flux rate was -0.7 mg/m^2/day. Release was enhanced by low dissolved oxygen concentration in the overlying water but no effect of temperature was evident.

F. Sediment Oxygen Demand

Dissolved oxygen moved from the water to the sediments in all cases examined and sediment uptake of oxygen was enhanced at high temperatures. No SOD was observed while the overlying water was anoxic since no oxygen was available to move into the sediments. Sediment oxygen demand was highest when the dissolved oxygen concentration in the overlying water approached saturation. SOD was reduced at low DO concentrations in the overlying water. Mean sediment oxygen demand was 1.46 $gm/m^2/day$.

Table 5-1. Temperature-Dissolved Oxygen Combinations

Dissolved Oxygen (mg/l)	0	2	5	8
Temperature (^oC)				
10		x		x
15	x	x	x	x
20	x	2	x	2
25	x	x	x	x
30	x	x	x	x

(2) indicates replicate experiment.

Table 5-2. Sediment-Water Ammonium Flux (mg/m^2/day)

Dissolved Oxygen (mg/l)	0	2	5	8
Temperature (°C)				
10		75		76
15	78	46	61	72
20	161	44	48	-18*
20		111		79
25	160	138	50	98
30	134	276	180	124

Table 5-3. Sediment-Water Nitrate Flux (mg/m^2/day)

Dissolved Oxygen (mg/l)	0	2	5	8
Temperature (°C)				
10		-86		-35
15	-166	-91	-84	-17
20	-173	-165	-70	-64
20		-62		-64
25	-304	-440	-229	-244
30	-509	-170	-191	-39

*Treated as an outlier in subsequent analyses.

Table 5-4. Sediment-Water Ortho Phosphorus Flux (mg/m^2/day)

Dissolved Oxygen (mg/l)	0	2	5	8
Temperature (°C)				
10				0.2
15	2.1	-6.4	-1.9	-2.3
20	6.5	-0.8	-4.0	-16.4
20		8.9		-9.3
25	7.5	3.9	-1.6	0.0
30	6.4		-4.3	

Table 5-5. Sediment Oxygen Demand (gm/m^2/day)

Dissolved Oxygen (mg/l)	0	2	5	8
Temperature (°C)				
10		0.37		0.79
15		0.62	0.76	1.20
20		1.29	1.07	2.73
20		0.79		1.80
25		1.88	2.02	2.51
30		0.53	3.33	1.72

Chapter VI. ELEMENTARY NUTRIENT AND OXYGEN FLUX MODELS

A prime objective of this investigation was to determine the effect of water-column dissolved oxygen and temperature on sediment nutrient flux. These effects are expressed here in quantitative form as part of more general models of sediment nutrient flux. The models are intended to produce optimal agreement between predicted and observed fluxes. A constraint on the models, however, is that they be consistent with the processes known to affect sediment nutrient flux. A second constraint imposed on the models is simplicity. Water column temperature, dissolved oxygen, and substance concentration were the only variables recorded during the experiments. Hence, they are the only variables which can be incorporated into the models. The requirements of simplicity and minimum number of variables offer advantages, however. The proposed models can be easily incorporated into existing water quality models or employed to provide estimates for management purposes, since observations or projections of the independent variables are readily available.

A. Diffusion Model

One basic model of sediment water flux is a diffusion model in which transport across the sediment-water interface is proportional to the concentration gradient across that interface.

$$F = k\,(Cs - Cw) \qquad 6\text{-}1$$

in which

F = sediment-water flux rate ($M/L^2/T$)

Cs = substance concentration in interstitial water adjacent to the interface (M/L^3)

Cw = substance concentration in overlying water adjacent to the interface (M/L^3)

k = transport coefficient (L/T).

The transport coefficient is determined by factors including sediment porosity, physical mixing of the sediments, and bioturbation of the sediments. The interstitial water concentration is determined by the rate of production or consumption in the sediment, by transport across the sediment-water interface, and by transport to or from deeper sediments.

The diffusion model is not employed directly in this study since no observations of Cs are available. The model is significant, however, since it establishes that substance concentration in the overlying water influences the rate at which that substance is transported across the sediment water interface. The model also allows projection of the effect on transport of alterations in concentration.

B. Models Based on Temperature, Dissolved Oxygen, and Concentration

Understanding of the primary processes which govern sediment nutrient flux and examination of the laboratory results lead to models which are based on water-column temperature, dissolved oxygen, and concentration.

1. Ammonium. Ammonium is produced by decomposition of organic matter and is predominantly released by Gunston Cove sediments. Since decomposition is a metabolic process influenced by temperature, the rate of ammonium release should increase as a function of temperature.

A portion of the ammonium produced in the sediments is nitrified to nitrate and not released. Nitrification is suppressed at low dissolved oxygen concentrations (44), however. Therefore, the rate of ammonium release should be enhanced as the water column approaches anoxia.

Ammonium release is driven by the concentration gradient across the sediment water interface. If the interstitial water concentration is relatively constant, then release will be suppressed as the concentration in the water increases.

A quantitative expression of ammonium release, consistent with the conceptual model described above, is

$$F = F_o \; \Theta^{T-20} \; e^{\alpha DO} - b\,Cw \qquad 6\text{-}2$$

in which

F = ammonium flux rate (mg/m^2/day)

F_o = base ammonium flux rate at 20°C, 0 mg/l DO, 0 mg/l $NH4$

T = temperature (°C)

DO = dissolved oxygen (mg/l)

Θ = constant which expresses enhancement of flux by temperature

α = constant which expresses suppression of flux by dissolved oxygen (l/mg)

b = constant which expresses suppression of flux by ammonium in overlying water (mm/day).

2. Nitrate. Nitrate was exclusively taken up by Gunston Cove sediments. This indicates that the rate of reduction of nitrate in the decomposition process exceeds the rate of production by nitrification. Since decomposition is enhanced at higher temperatures, sediment uptake of nitrate should increase as a function of temperature.

Reduction of oxygen during decomposition yields more energy than reduction of nitrate. Therefore, reduction of oxygen will proceed before nitrate. As oxygen in the sediments becomes depleted, larger amounts of nitrate are employed. Lowering the DO concentration in the overlying water makes less oxygen available to the sediments and therefore should increase the rate of sediment nitrate uptake.

Nitrate transport into the sediments is driven by the concentration difference between the overlying water and the interstitial water. As the concentration in the overlying water increases, the rate of transport into the sediments should increase.

A quantitative expression of nitrate flux, consistent with the conceptual model described above, is

$$F = a\,Cw\,\Theta^{T-20}\,e^{\alpha DO} \qquad 6\text{-}3$$

in which

F = nitrate uptake rate (mg/m^2/day)

a = constant which relates uptake to concentration in overlying water (mm/day)

Θ = constant which expresses enhancement of flux by temperature

α = constant which expresses suppression of flux by dissolved oxygen (l/mg)

3. Ortho Phosphorus. Ortho phosphorus was taken up or released by the sediments with approximately equal frequency. A fundamental determinant of

the direction of phosphorus flux is the water-column dissolved oxygen concentration. When the water column approaches anoxia, phosphorus desorbs from sediment particles and is released to the water. When the water column is high in dissolved oxygen, phosphorus sorbs to sediment particles and release to the water column is suppressed.

A second consideration is the effect of temperature. As temperature increases, enhanced respiration enlarges the anoxic portion of the sediment and promotes desorption of phosphorus from particulates. A portion of the phosphorus previously bound in the organic matter is also released. Thus increasing temperature should increase the rate of ortho phosphorus flux from the sediments.

As with the other nutrients, transport of ortho phosphorus across the sediment-water interface is governed by the concentration gradient at that interface. If the interstitial water concentration remains constant, phosphorus release from the sediments will be enhanced by low concentrations in the water column and suppressed or reversed by high concentrations in the water column.

A quantitative expression of ortho phosphorus flux, consistent with the conceptual model described above, is

$$F = Fo\ \Theta^{T-20}\ e^{\alpha DO} - b\ Cw \qquad 6\text{-}4$$

in which

F = phosphorus flux rate (mg/m^2/day)

Fo = base flux rate at 20°C, 0 mg/l DO, 0 mg/l PO4

Θ = constant which expresses enhancement of flux by temperature

α = constant which expresses suppression of flux by dissolved oxygen (l/mg)

b = constant which expresses suppression of flux by ortho phosphorus in overlying water (mm/day).

4. Sediment Oxygen Demand. Sediment oxygen demand is largely created by the respiration of benthic organisms. As the temperature increases, the metabolism of these organisms increases and the rate of SOD should increase.

The employment of oxygen by benthic fauna depends upon its availability. As the water column approaches anoxia, oxygen becomes unavailable to the sediments and the rate of SOD must decrease.

A quantitative expression of SOD, consistent with the conceptual model described above, is

$$SOD = So\ \Theta^{T-20}\ (1 - e^{\alpha DO}) \qquad 6\text{-}5$$

in which

SOD = sediment oxygen demand (gm/m^2/day)

So = base sediment oxygen demand at 20 °C, 8 mg/l DO

Θ = constant which expresses enhancement of SOD by temperature

α = constant which expresses suppression of SOD by anoxia (l/mg).

C. Evaluation of Model Parameters

Each of the models described requires evaluation of three to four parameters or constants. These are evaluated through a technique known as "non-linear parameter estimation" or "non-linear regression" (NLR). NLR provides estimates of the model parameters which are optimal in that they minimize the difference between model predictions and observations. In the ordinary-least-squares method employed here, the difference between predictions and observations is expressed as the sum of the squared deviations

$$RSS = \sum_{1}^{n} (Yo_i - Yp_i)^2 \qquad 6\text{-}6$$

in which

RSS is the sum of the squared deviations

Yo_i = i^{th} observed flux

Yp_i = i^{th} predicted flux

n = number of observations.

The set of parameters which minimize RSS is considered optimal. Details of the method employed here may be found in (41).

Quantification of the agreement between the model and the data is desirable. One measure is the RSS. Smaller values of RSS imply better agreement between predictions and observations. Raw values of RSS are difficult to interpret, however. Thus, it is customary to normalize RSS. The quantity employed in the normalization is the sum of the squared deviations betweeen the observed fluxes and the mean flux

$$SSY = \sum_{1}^{n} (Yo_i - Ym)^2 \qquad 6\text{-}7$$

in which

SSY = sum of the squared deviation between observations and the mean

Ym = mean of the observed flux.

The normalization is carried out so that the familiar quantity R^2 results

$$R^2 = \frac{SSY-RSS}{SSY} \qquad 6\text{-}8$$

The quantity R^2 is limited to values between zero and unity. Higher values of R^2 indicate improved agreement between predictions and observations. A value of unity indicates perfect agreement. One interpretation of R^2 is that it is the fraction of veriability in the observations which can be accounted for by the model.

D. Results of Ammonium Model

Additional insight into the factors which affect sediment-water nutrient flux is gained by entering variables into the models singly, in order of importance. The importance of a variable is determined by the proportion of variability in the experimental results attributed to it. This proportion is quantified through the squared correlation coefficient, R^2.

Application of the stepwise evaluation of model parameters for ammonium is summarized in Table 6-1. A plot of predicted versus observed ammonium flux is shown as Figure 6-1. The analysis indicates that temperature is the most significant determinant of ammonium flux, accounting for 46% of the variability observed in the experiments. Dissolved oxygen is the next most significant determinant, although it accounts for only 9% of the observed variability. Water-column ammonium concentration exerted no consistent effect on observed ammonium flux and it is therefore dropped from the proposed model. The simplified model is

$$F = F_o \Theta^{T-20} e^{\alpha DO} \qquad 6\text{-}9$$

Optimal parameter values are reported in Table 6-1. A plot of Equation 6-9, illustrating the effects of temperature and dissolved oxygen on ammonium release, is shown as Figure 6-2.

Parameters evaluated and effects noted in this study are compared with results of some other studies in Table 6-2. The effect of temperature is quantified by various investigtors through the parameters Θ or Q10 or as linear or logarithmic functions. In order to be consistent with the parameter employed in this study, temperature effects are converted to equivalent values of Θ whenever possible.

The value of Θ obtained in this study is somewhat lower than reported elsewhere and temperature, in this study, explains a smaller fraction of the observed variability in ammonium flux than in other investigations. These findngs indicate that factors not examined in this study are influential in determining ammonium flux in Gunston Cove.

Ammonium release was enhanced by 50% as dissolved oxygen concentration was reduced from approximately saturation (8 mg/l) to zero. Other studies have reported tripling of ammonium release due to anoxia (18) or else no effect (19). The amount by which release increases depends on the proportion of ammonium which is nitrified in the sediments. If a large proportion of ammonium produced is nitrified, then release will be greatly enhanced in the event nitrification is suppressed due to anoxia. If only a small proportion is nitrified, then the effect of anoxia will be reduced. Results of these experiments indicate that roughly a third of the ammonium produced in Gunston Cove sediments is nitrified under oxic conditions.

The concentration of ammonium in the water column exerted no consistent effect on ammonium flux, a finding in agreement with the results of other studies (12, 23). This behavior may be explained by noting that flux is driven by the difference in ammonium concentration between the interstitial and overlying water (Eq. 6-1). If the concentration in the interstitial water is relatively constant, then flux will be determined by the concentration in the overlying water. If the interstitial concentration is variable, however, observations of concentration in the overlying water alone are of little use in the prediction of sediment-water flux.

Almost half the variability in observed ammonium flux remains unexplained. A portion of this unexplained variability is likely due to spatial and temporal inhomogeneities in the sediments employed. Relatively large differences exist in the ammonium flux from sediments collected within a circle of a few meters radius during a single summer season. Quantification of the spatial and temporal variability will be presented in a subsequent chapter.

E. Results of Nitrate Model

Application of the stepwise evaluation of model parameters for nitrate is summarized in Table 6-3. A plot of predicted versus observed nitrate flux is shown as Figure 6-3. The analysis indicates that nitrate concentration is the most significant determinant of sediment nitrate uptake, accounting for 52% of the variability observed in the experiments. Temperature is the next most significant determinant and accounts for 24% of the variability. The remaining variable, dissolved oxygen, accounts for 13% of the observed variability.

A plot illustrating the effects of temperature and dissolved oxygen on sediment nitrate uptake is presented as Figure 6-4. Effects noted and parameters evaluated in this investigtion are compared to the results of other studies in Table 6-4. Reported temperature effects have been converted to the parameter Θ whenever possible.

A tendency for sediment uptake of nitrate to increase as a function of the water column concentration has been noted in several systems (7, 8, 12). In this study, uptake has been found to be linearly proportional to concentration. Other investigators (34, 35, 49) have described the effect of concentration on flux in terms of a rate-saturation equation commonly referred to as the "Michaelis-Menten" equation. Half-saturation concentrations have been found to be in the range 3 to 50 mg/l nitrate. Nitrate concentrations in this study were generally less than 2.5 mg/l. Employing these relatively low concentrations in the reported rate-saturation equations yields functions which are approximately linear, indicating that the functional forms in this and other studies are consistent.

An interesting comparison can be made between the proportionality constant ´a´ derived in this and another study. The parameter ´a´ relates nitrate flux to concentration in the overlying water. Considering its dimensions, length/time, it may be conceived as a scale velocity at which nitrate is transferred across the sediment-water interface. The value obtained herein, a = 102 mm/day is approximately sixteen times larger than the value, a = 6 mm/day, which can be derived from data presented by Van Kessel (49). One explanation for the discrepancy is that intact sediment cores were employed herein while sieved, homogenized sediments were employed in the other study. This indicates that treatment of the sediments may greatly affect rates of sediment-water column nutrient exchange.

The temperature parameter, $\Theta = 1.068$, derived in this study is centrally located within the range of values reported in other lab studies. It is noteworthy that two in-situ studies found no effect of temperature on nitrate flux. The in-situ temperature effect is likely masked by the influence of concentration and by other factors.

Sediment nitrate uptake was almost doubled under anoxic conditions compared to uptake under a water column approximately saturated with dissolved oxygen. This ratio of anoxic to oxic uptake is at the upper range of reported values. Several characteristics of the individual systems will affect the enhancement of nitrate uptake under anoxic conditions. Systems in which the rate of nitrate reduction is initially low relative to the rate of oxygen reduction, in which sufficient nitrate is available in the water column, and in which the diffusion of nitrate through the sediments is rapid, will tend to exhibit high ratios of enhancement under anoxic conditions. Systems in which the reduction of nitrate is relatively large compared to the reduction of oxygen and in which the supply of nitrate to the sediments is limited, will exhibit low enhancements of sediment nitrate uptake under anoxic conditions.

The proposed model, Equation 6-3, accounts for 89% of the variability observed in nitrate uptake. Nitrate uptake is more predictable than ammonium release. Quantitative examination of spatial and temporal inhomogenieties in nitrate flux will be presented in a subsequent chapter.

F. Results of Phosphorus Model

Application of the stepwise evaluation of model parameters is summarized in Table 6-5. A plot of predicted versus observed ortho phosphorus flux is shown as Figure 6-5. The analysis indicates that ortho phosphorus concentration is the most significant determinant of sediment-water phosphorus flux, accounting for 55% of the variability observed in the experiments. Dissolved oxygen is the next most significant determinant and accounts for 20% of the variability. Temperature accounts for none of the observed variability and is therefore dropped from the proposed model. The revised model is

$$F = Fo\ e^{\alpha DO} - b\ Cw \qquad (6\text{-}10)$$

Optimal parameter values are given in Table 6-5. A plot of Equation 6-10, illustrating the effects of phosphorus and dissolved oxygen concentrations on phosphorus flux, is shown as Figure 6-6. Parameters evaluated and effects noted in this study are compared with the results of some other studies in Table 6-6.

The lack of temperature effect, noted here, conflicts with the results of numerous other studies, although the results reported here are not unique. Sediments in other systems have been noted to take up phosphorus at low temperatures and release it at high temperatures (21, 24) or else to release phosphorus at a rate which is enhanced as temperature increases (7, 19, 23, 36).

Correlations which exist between temperature and sediment phosphorus flux may be indicative of an association rather than a cause and effect mechanism. For example, during winter, ortho phosphorus concentration in Gunston Cove exceeds 0.02 mg/l, due to point-source and non-point source inputs to the system, and temperature is below 10°C. In-situ measures indicate phosphorus moves into the sediments during this period. During summer, ortho phosphorus concentrations may be an order of magnitude less, due to algal uptake, and temperature approaches 30°C. In summer ortho phosphorus commonly moves out of the sediments. Thus, Gunston Cove sediments exhibit a tendency to take up phosphorus in winter and release phosphorus in summer. A correlation between temperature and phosphorus flux may be obtained, but the model (Eq. 6-10) indicates the correlation is due to seasonal trends in phosphorus concentration rather than temperature.

Studies exist, however, in which the effect of temperature on phosphorus flux cannot be explained by the influence of concentration. A strong increase in sediment phosphorus release was noted in Narragansett Bay sediments during the winter-spring warming period (36). Moreover, increases in water-column phosphorus did not diminish sediment release, as would be predicted by the model expressed in Equation 6-10. Intact lake sediment cores incubated successively at different temperatures also exhibited a trend of increasing phosphorus release with increasing temperature (24).

The problem of temperature dependence of sediment phosphorus release can be resolved by noting that release is influenced by abiotic and biotic processes. The abiotic sorption/desorption of ortho phosphorus to mineral particles is independent of temperature in the range commonly encountered in the environment (29, 31). The biotic processes, respiration, remineralization, and bioturbation, are temperature dependent. Temperature-induced increases in respiration can promote phosphorus release by depleting interstitial dissolved oxygen, thereby causing phosphorus to desorb from sediments. Increases in the remineralization rate may promote release by raising the quantity of mineral phosphorus in the sediments. Increased bioturbation may promote release by raising the diffusion coefficient at the sediment-water interface. An influence of temperature on phosphorus flux will or will not be present depending on whether biotic or abiotic processes are predominant. This mechanism aids in the explanation of the tendency of some sediments to take up phosphorus at low temperatures and release it at high temperatures. At low temperatures, abiotic processes are dominant and sediments sorb phosphorus. At higher temperatures, biotic processes are dominant and sediments are induced to release phosphorus. Examination of data from estuary (21) and lake (24) sediments indicates the change in dominance of abiotic and biotic processes occurred in these systems at approximately 10°C. During the study period, however, Gunston Cove sediments were dominated by abiotic processes at all temperatures.

The sediment phosphorus flux model derived here indicates that anoxia in the water column increases phosphorus release by a factor of four compared to flux under a dissolved-oxygen-saturated water column containing no phosphorus. The increase in flux is due to anoxia-induced desorption of phosporus from sediment particles (9, 28). Other studies indicate an increase of phosphorus release of from two times to infinity under anoxic conditions compared to oxic conditions. The extreme ratios of anoxic to oxic conditions occur in systems which release little or no phosphorus into an oxic water column. In systems which generally release phosphorus, the anoxic to oxic ratio is roughly five or ten to one. Gunston Cove sediments are at the lower end of this range but not distinctly different.

The primary variable affecting phosphorus flux in Gunston Cove sediments was ortho phosphorus concentration in the overlying water. Under oxic conditions, phosphorus would move into or out of the sediment depending on conditions in the water column. This evidence indicates the existence of an ´equilibrium´ ortho phosphorus concentration. When phosphorus in the water column exceeds the equilibrium concentration, phosphorus moves into the sediments. When phosphorus in the water column is below the equilibrium concentration, phosphorus moves out of the sediments. Solution of Equation 6-10 indicates that at 8 mg/l dissolved oxygen, the equilibrium ortho phosphorus concentration is 0.018 mg/l.

The process proposed here is consistent with the theory proposed for Doboy Sound, GA, that estuarine sediments exert a buffering action on phosphorus in the water column (39). Measurements of sorption-desorption on sediments removed from that system indicated an equilibrium concentration of 0.03 mg/l ortho phosphorus. Sediments in other systems, as well, have exhibited a tendency to take up phosphorus under high water-column concentrations and release it under low concentrations. Lake Memphramagog sediments indicated an equilibrium concentration of 0.005 mg/l (46) and, at low temperatures, Narragansett Bay sediments have been stated to buffer the water colunn at 0.03 mg/l (23).

The model proposed here indicates that the equilibrium concentration is dependent upon dissolved oxygen in the water column. As DO decreases, concentration of ortho phosphorus in the sediment interstitial water increases and phosphorus is released to the water column until a new equilibrium is established. This principle is consistent with experiments conducted on lake sediments (20). Under oxic conditions, the sediments were a sink of phosphorus. Under anoxic conditions, the sediments were a source of phosphorus until the water column attained 1 to 1.4 mg/l ortho phosphorus. In that concentration range, no more phosphorus was released. The equilibrium concentration under anoxic conditions predicted here, 0.07

mg/l, is much less than the concentration noted in that series of experiments, however.

G. Results of the Sediment Oxygen Demand Model

Application of the stepwise evaluation of the parameters in the sediment oxgen demand model is summarized in Table 6-7. A plot of predicted versus observed SOD is shown as Figure 6-7. The analysis indicates that dissolved oxygen concentration is the most significant determinant of sediment oxygen demand, accounting for 48% of the variability observed in the experiments. Temperature, the remaining determinant, accounts for 20% of the variability. A plot illustrating the effects of temperature and dissolved oxygen on sediment oxygen demand is presented as Figure 6-8. Effects noted and parameters evaluated in this investigation are compared to the results of other studies in Table 6-8.

Sediment oxygen demand must decline as the supply of oxygen to the sediments is restricted. Reported studies indicate two patterns of decline. In the first, SOD is dependent on dissolved oxygen throughout its range (13,15, 16). In the second, SOD is independent of dissolved oxygen until dissolved oxygen falls below a limiting value of approximately 2 mg/l (18, 21). Sediments in Gunston Cove fit the first pattern described. Edwards and Rolley (16) indicated a resolution of the two patterns when they suggested that "shallow layers of mud behave like bacterial suspensions and that oxygen consumption is dependent on oxygen concentration only when the mud depth increases." They, themselves, noted no correlation between mud depth and SOD, however. Their theory is supported here although it is maintained that the rate and depth of dissolved oxygen diffusion into the mud are of more importance than the thickness of the mud.

General agreement exists that sediment oxygen demand is severely restricted as water-column dissolved oxygen falls below 2 mg/l. This occurs in systems in which SOD is affected only when DO falls below 2 mg/l (18, 21) and in systems in which a sharp change in the dependence of SOD on DO occurs at approximately 2 mg/l (15, 16). This suggests that bacterial respiration is limited at dissolved oxygen concentrations less than 2 mg/l. In sediments in which the rate and extent of dissolved oxygen diffusion are rapid and thorough compared to respiration, interstitial dissolved oxygen will be equivalent to the overlying water and SOD will be limited only when DO concentrations in the water are low enough to restrict respiration. In sediments in which the rate and/or extent of dissolved oxygen diffusion are limited relative to respiration, interstitial dissolved oxygen will be less than the overlying water and a region in the sediments will exist in which respiration is limited by low DO. The extent of the limited-respiration region will depend on the gradient-driven supply of dissolved oxygen to the sediments from above. Hence, sediment oxygen demand will be dependent on water-column dissolved oxygen.

The value of Θ obtained here is in the range of reported values (15, 16, 23), although at the lower end. More noteworthy is the lower proportion of variability in SOD attributed to temperature here than elsewhere (7, 23). A plausible explanation is that the range of dissolved oxygen, 0 to 8 mg/l, employed here caused larger variability in SOD than in the comparable systems. If the range of DO had been less, the total variability would have been less and the proportion of that variability attributed to temperature greater.

Table 6-1. Ammonium Model

Variables	Model	Total R^2	Marginal R^2
temperature	$Fo\ \Theta^{T-20}$	0.46	0.46
temperature, dissolved oxygen	$Fo\ \Theta^{T-20}\ e^{\alpha DO}$	0.55	0.09
temperature, dissolved oxygen, concentration	$Fo\ \Theta^{T-20}\ e^{\alpha DO}\ -b\ Cw$	0.55	0

Final Parameter Values

Fo = ~~10.9~~ 109 mg/m^2/day
Θ = 1.065
α = -0.051 liter/mg
b = eliminated from model

Table 6-2. Comparison of Factors Affecting Ammonium Flux

Influence of Temperature

θ	Temperature	R^2	Comments	Reference
1.065	10 to 30	0.46	This study.	
1.102	13 to 24		Lab incubations of marsh sediment	6
1.078 to 1.084	12 to 22	0.82	In-situ measures in Narragansett Bay	23
	3 to 29	0.83	In-situ measures in Patuxent Estuary	7

Influence of Dissolved Oxygen

Effect	Ratio			Comments	Reference
	Anoxic	:	Oxic		
Anoxia enhances release	1.5	:	1	This study.	
Anoxia enhances release	3	:	1	Lab incubations of synthetic sludge	18
None				Lab incubations of river and lake sediments.	19

Influence of Ammonium Concentration

Effect	Comments	Reference
None	This study.	
None	In-situ measures in James Estuary	12
None	In-situ measures in Narragansett Bay	23

Table 6-3. Nitrate Model

Variable	Model	Total R^2	Marginal R^2
concentration	$a\ Cw$	0.52	0.52
concentration, temperature	$a\ Cw\ \Theta^{T-20}$	0.76	0.24
concentration, temperature, dissolved oxygen	$a\ Cw\ \Theta^{T-20}\ e^{\alpha DO}$	0.89	0.13

Final Parameter Values

a = 102 mm/day
Θ = 1.068
α = -0.083 liter/mg

Table 6-4. Comprison of Factors Affecting Nitrate Flux

Influence of Temperature

Θ	Temperature	R^2	Comments	Reference
1.068	10 to 30	0.24	This study.	
1.025 to 1.043	17 to 28		Lab incubations of Patuxent Estuary sediments.	26
1.10	14 to 35		Lab incubations of Lake Okeechobee sediments.	34
1.036 to 1.088	2 to 15	0.35 to 0.46	Lab incubations of Narragansett Bay sediments.	42
1.082	10 to 20		Lab incubations of Great Lakes sediments.	27
	3 to 22	none	In-situ measures in Narragansett Bay.	23
	19 to 29	none	In-situ measures in James Estuary.	12

Influence of Dissolved Oxygen

Effect	Ratio Anoxic : Oxic	Comments	Reference
Anoxia enhances uptake	1.9 : 1	This study.	
Anoxia enhances uptake	1.15 to 1.18 : 1	Lab incubations of freshwater sediments	49
Variable	0.62 to 1.95 : 1	Lab incubations of lake sediments	25

Influence of Concentration

Effect	Comments	
Uptake linearly proportional to concentration	This study.	
Uptake proportional to concentration but exhibits saturation, half-saturation at 3 mg/l NO3	Lab incubations of Lake Okeechobee sediments.	34
Half-saturation at 4.5 mg/l NO3	Lab incubations of marsh sediments	35
Half-saturation greater than 50 mg/l NO3	Lab incubations of freshwater sediments	49

Table 6-5. Phosphorus Model

Variables	Model	Total R^2	Marginal R^2
concentration	$Fo - b\,Cw$	0.55	0.55
concentration, dissolved oxygen	$Fo\, e^{\alpha DO} - b\,Cw$	0.75	0.20
concentration, dissolved oxygen, temperature	$Fo\, \Theta^{T-20}\, e^{\alpha DO} - b\,Cw$	0.75	0

Final Parameter Values

Fo = 10.2 mg/m^2/day
b = 134 mm/day
α = -0.184 liter/mg
Θ = eliminated from model

Table 6-6. Comparison of Factors Affecting Phosphorus Flux

Influence of Temperature

Θ	Temperature	R^2	Comments	Reference
1	10 to 30	0	This study.	
1.04 to 1.17	24 to 30		Lab incubation of river and lake sediments.	19
1.07 to 1.12	5 to 25		Lab incubation of Narragansett Bay sediments.	36
1.08 to 1.16	12 to 22	0.71	In-situ measures in Narragansett Bay	23
	3 to 29	0.73	In-situ measures in Patuxent Estuary	7
1	5 to 19	0	Lab incubation of lake sediments	1

Influence of Dissolved Oxygen

Effect	Ratio Anoxic : Oxic	Comments	Reference
Anoxia enhances release	4.4 : 1	This study.	
Anoxia enhances release	5 : 1	Lab incubation of synthetic sludge	18
Anoxia enhances release	5.6 to 11 : 1	Lab incubation of river and lake sediments.	19
Anoxia enhances release	2.1 to ∞ : 1	Lab incubation of lake sediments	3
Anoxia enhances release	10 : 1	Lab incubation of lake sediments	24
Anoxia enhances release	5.1 to 13 : 1	Lab incubation of Narragansett Bay sediments.	36
Anoxia enhances release	>164 : 1	Lab incubation of lake sediments	33

Table 6-6 (Cont'd)

Influence of Phosphorus Concentration

Effect	Comments	Reference
Sediments buffer oxic water column at 0.018 mg/l	This study.	
Sediments buffer anoxic water column at 0.076 mg/l	This study.	
Sediments buffer oxic water column at 0.03 mg/l	Lab measures of adsorption on Doboy Sound sediments.	39
Sediments buffer oxic water column at 0.005 mg/l	Lab incubation of lake sediments.	46
Sediments buffer cold, oxic water column at 0.03 mg/l	In-situ measures in Narragansett Bay sediments.	23
Sediments buffer anoxic water column at 1 to 1.4 mg/l	Lake incubation of lake sediments.	20
No effect	Lab incubation of Narragansett Bay sediments.	36

Table 6-7. Sediment Oxygen Demand Model

Variables	Model	Total R^2	Marginal R^2
dissolved oxygen	$So\ (1-e^{\alpha DO})$	0.48	0.48
dissolved oxygen, temperature	$So\ \Theta^{T-20}\ (1-e^{\alpha DO})$	0.68	0.20

Final Parameter Values

$So = 1.86$ gm/m^2/day
$\Theta = 1.046$
$\alpha = -0.34$ liter/mg

Table 6-8. Comparison of Factors Affecting Sediment Oxygen Demand

Influence of Temperature

Θ	Temperature	R^2	Comments	Reference
1.046	10 to 30	0.21	This study.	
1.067 to 1.080	10 to 20		Lab incubation of river sediments	16
1.040 to 1.130	5 to 25		Lab incubation of sediments	15
1.047	12 to 22	0.53	In-situ measures of Narragansett Bay sediments.	23
	3 to 29	0.67	In-situ measures of Patuxent Estuary sediments.	7

Influence of Dissolved Oxygen

Effect	Comments	Reference
SOD dependent on DO at all concentrations	This study.	
SOD dependent on DO at all concentrations	In-situ measures of Saginaw River sediments.	13
SOD dependent on DO at all concentrations	Lab incubations of river sediments	16
SOD dependent on DO at all concentrations	Lab incubation of sediments	15
SOD dependent on DO only below 2 mg/l	Lab incubation of synthetic sludge	18
SOD dependent on DO only below 2 mg/l	In-situ measures of estuary sediments	21

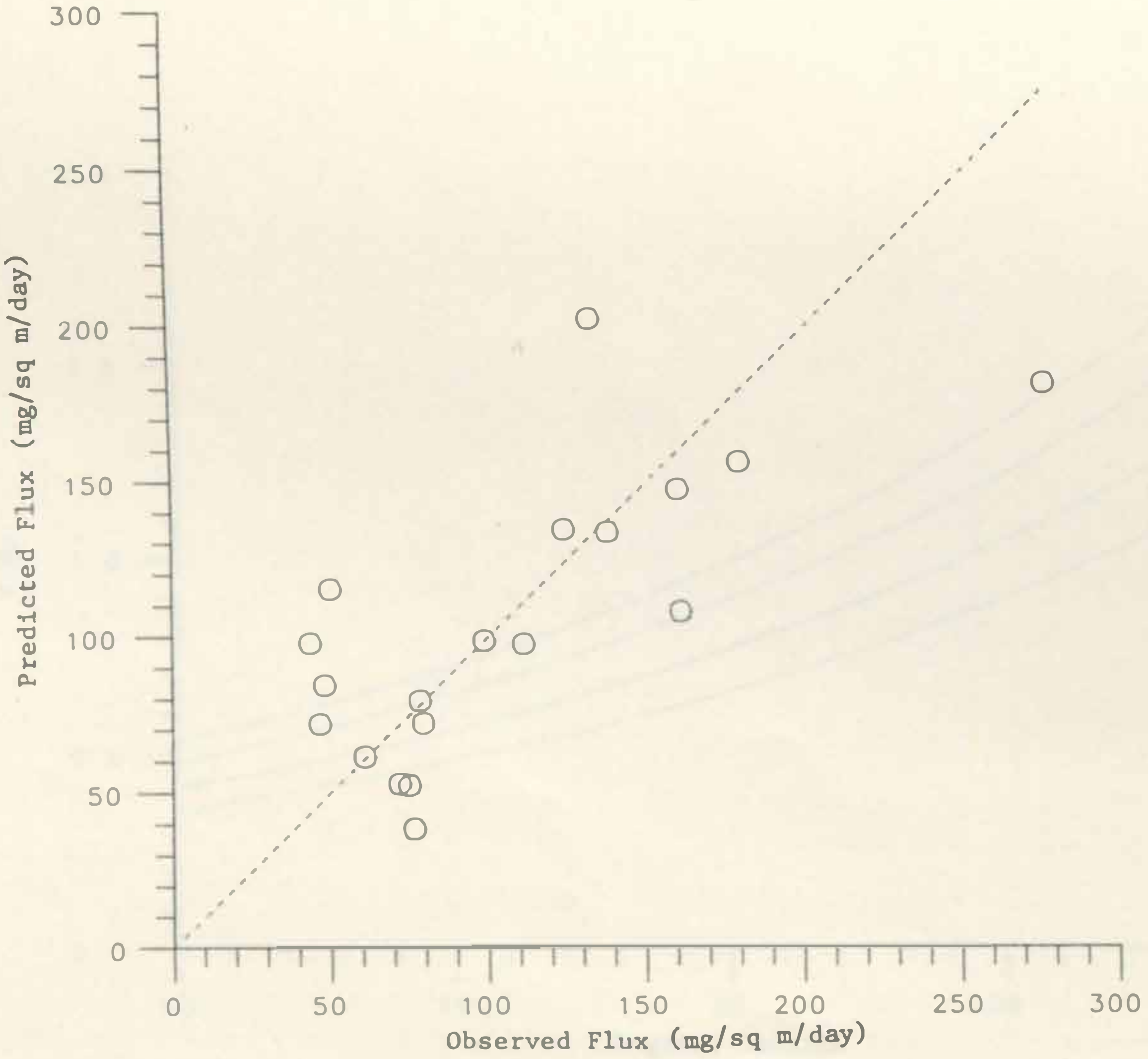


Figure 6-1. Predicted vs. Observed Ammonium Flux.

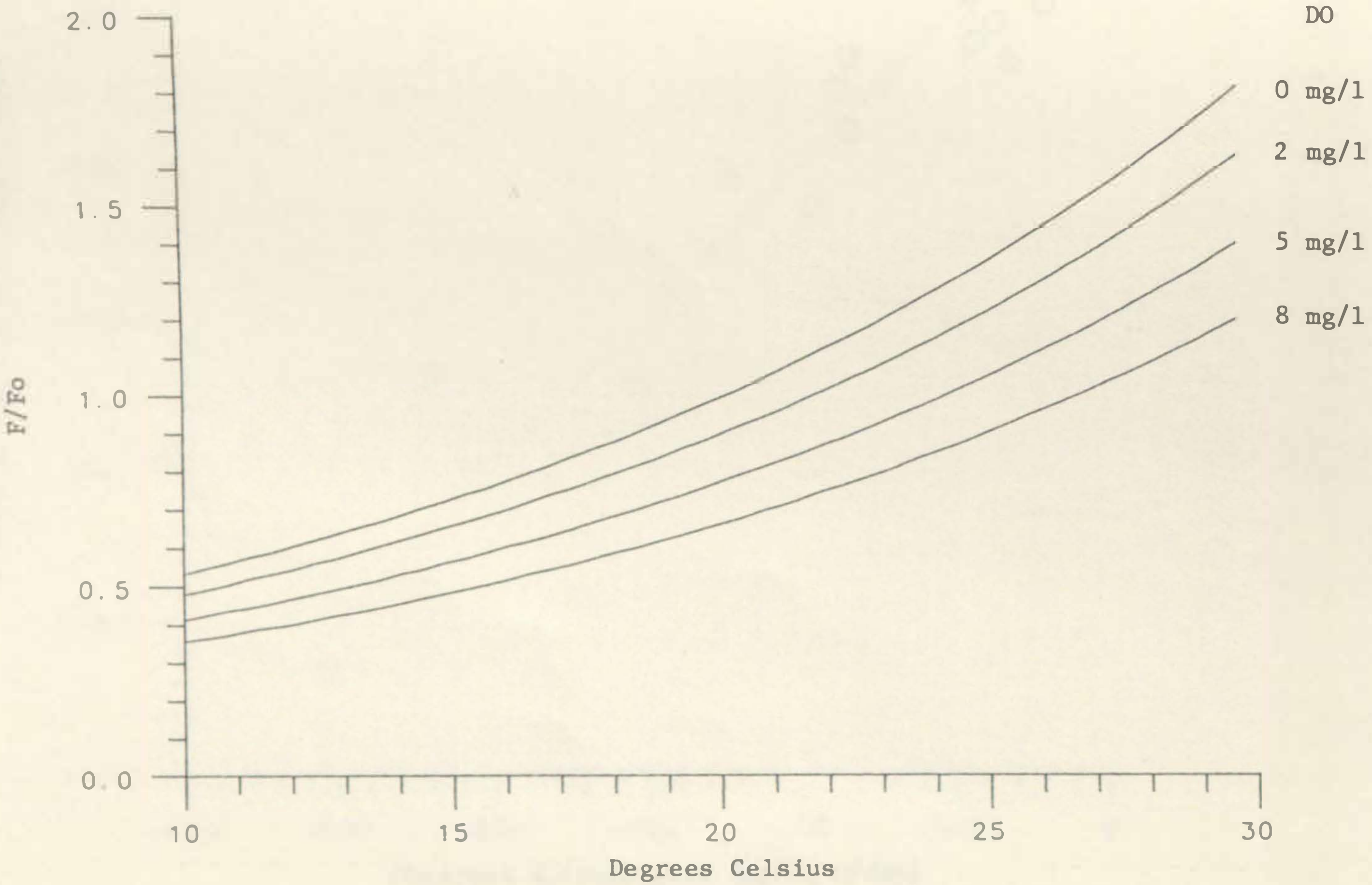


Figure 6-2. Effect of Temperature and DO on Ammonium Flux.

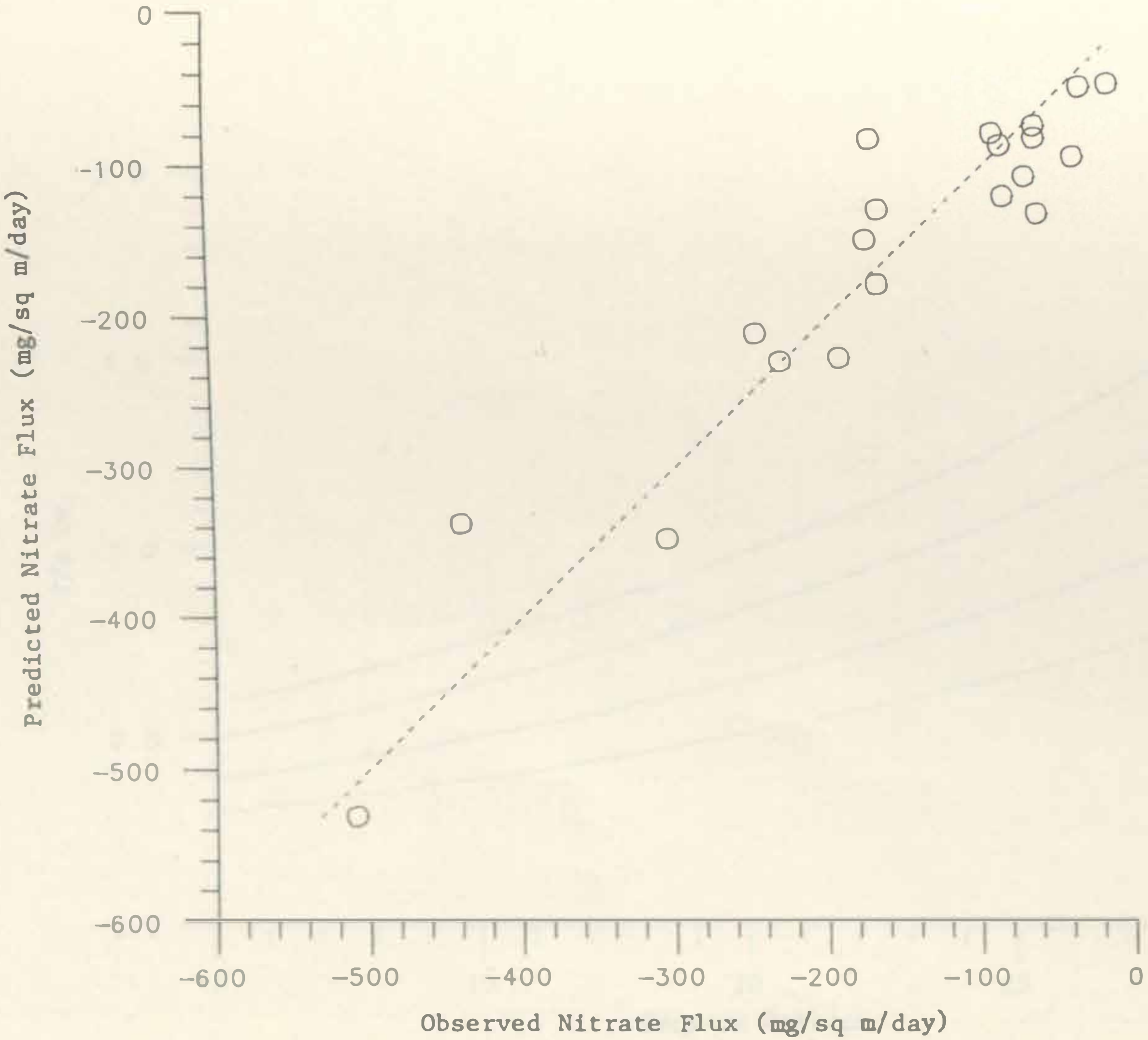


Figure 6-3. Predicted vs. Observed Nitrate Flux.

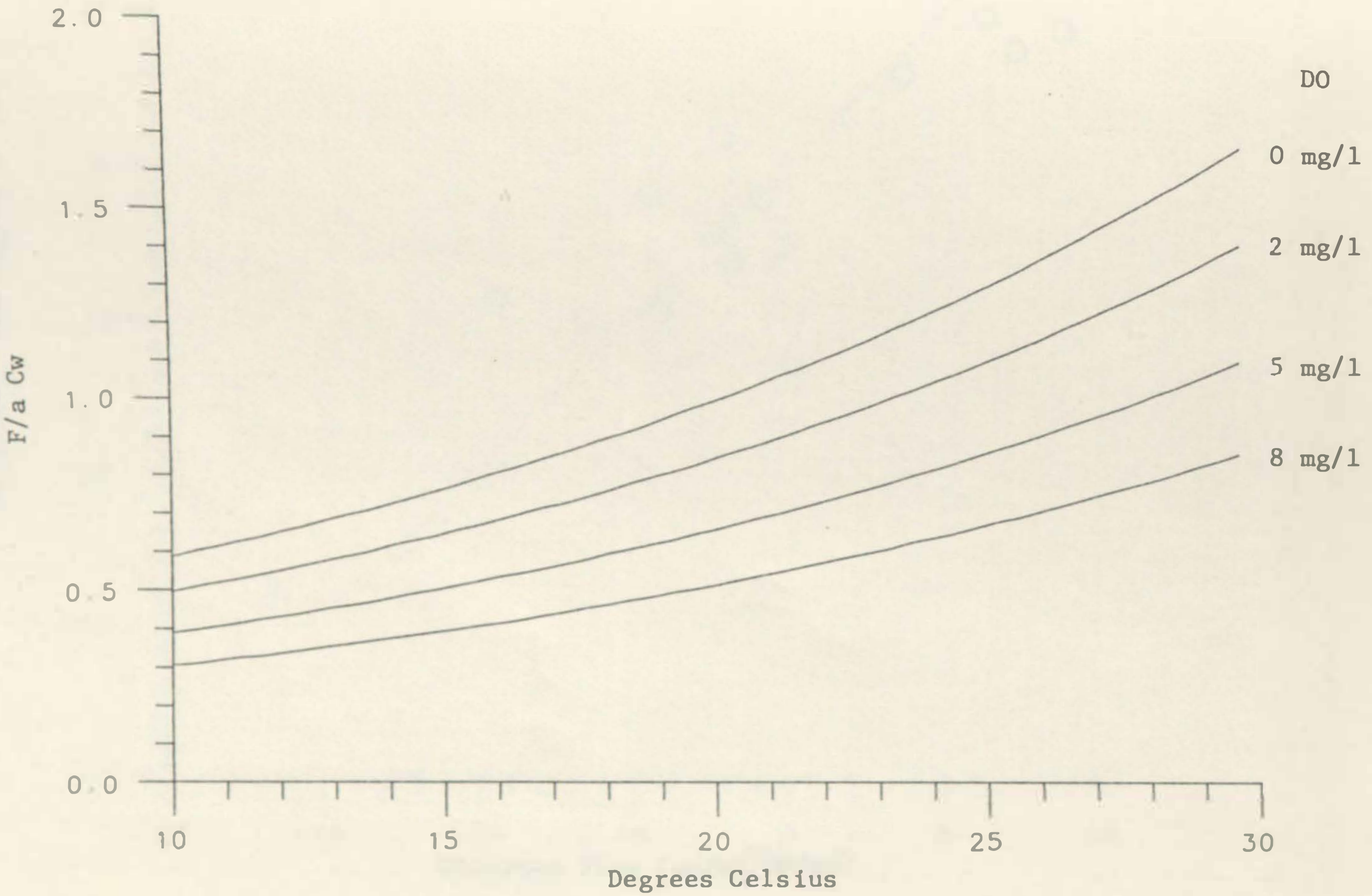


Figure 6-4. Effect of Temperature and DO on Nitrate Flux.

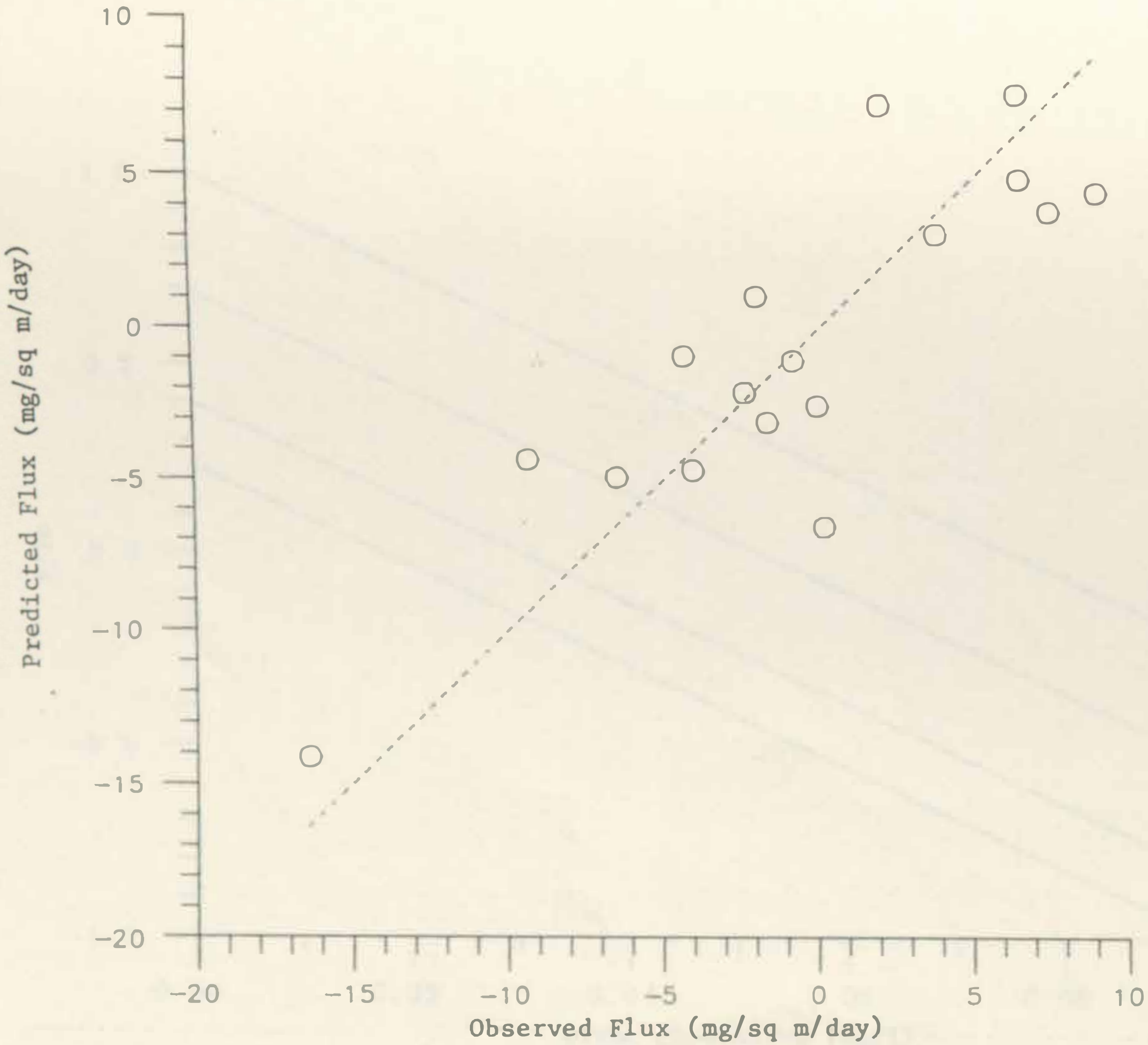


Figure 6-5. Predicted vs. Observed Ortho Phosphorus Flux.

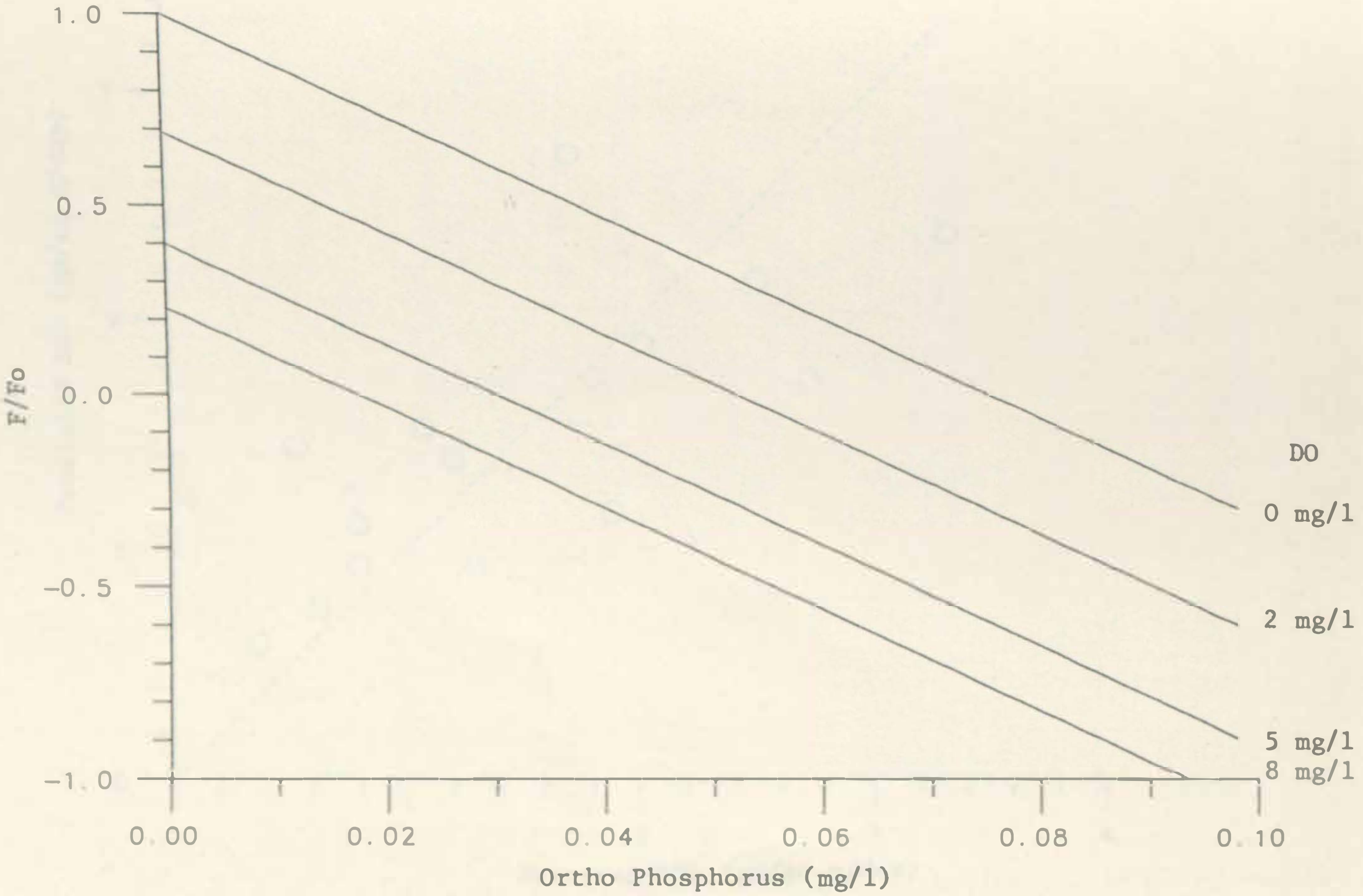


Figure 6-6. Effect of Concentration and DO on Ortho Phosphorus Flux.

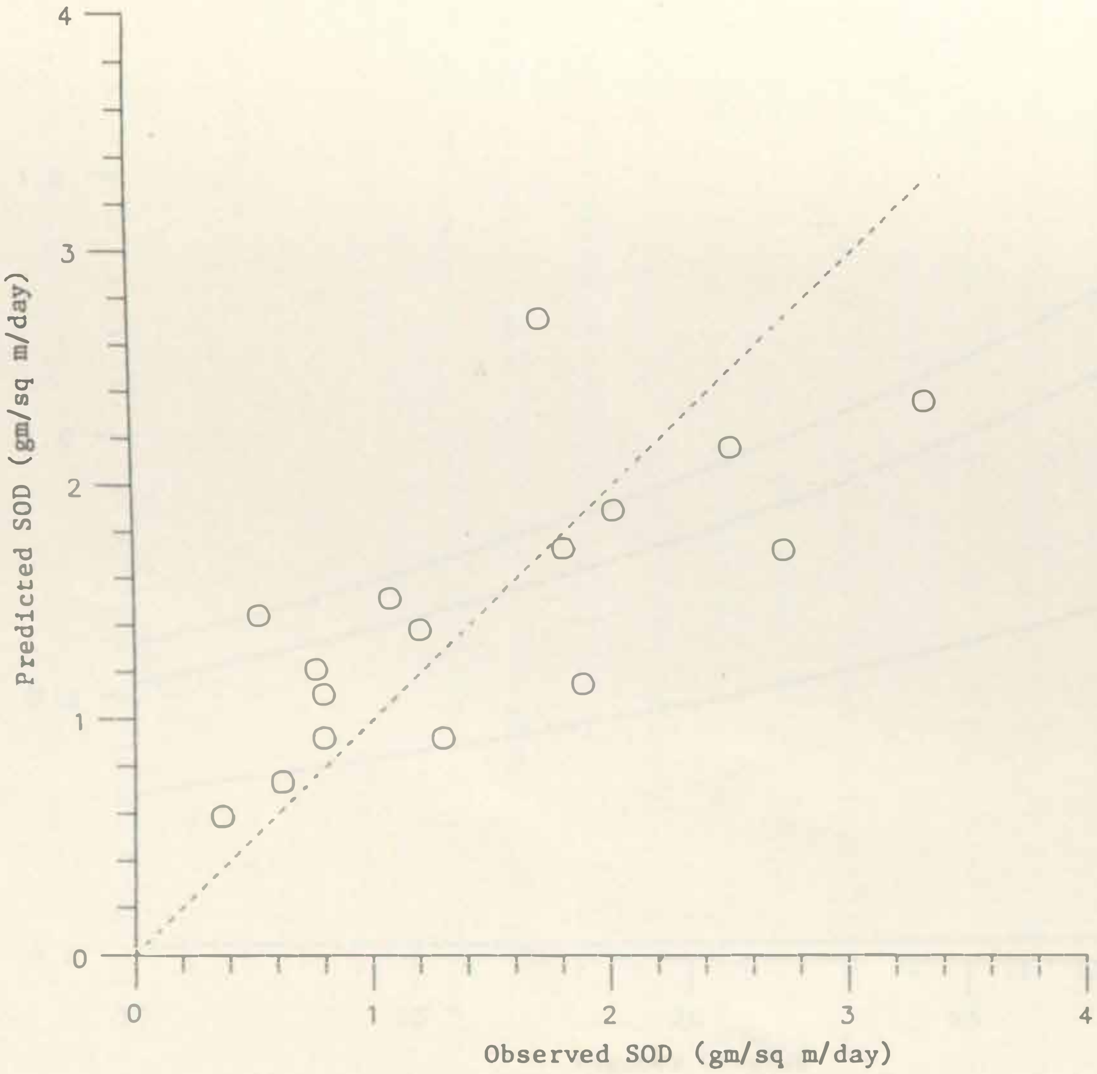


Figure 6-7. Predicted vs. Observed Sediment Oxygen Demand.

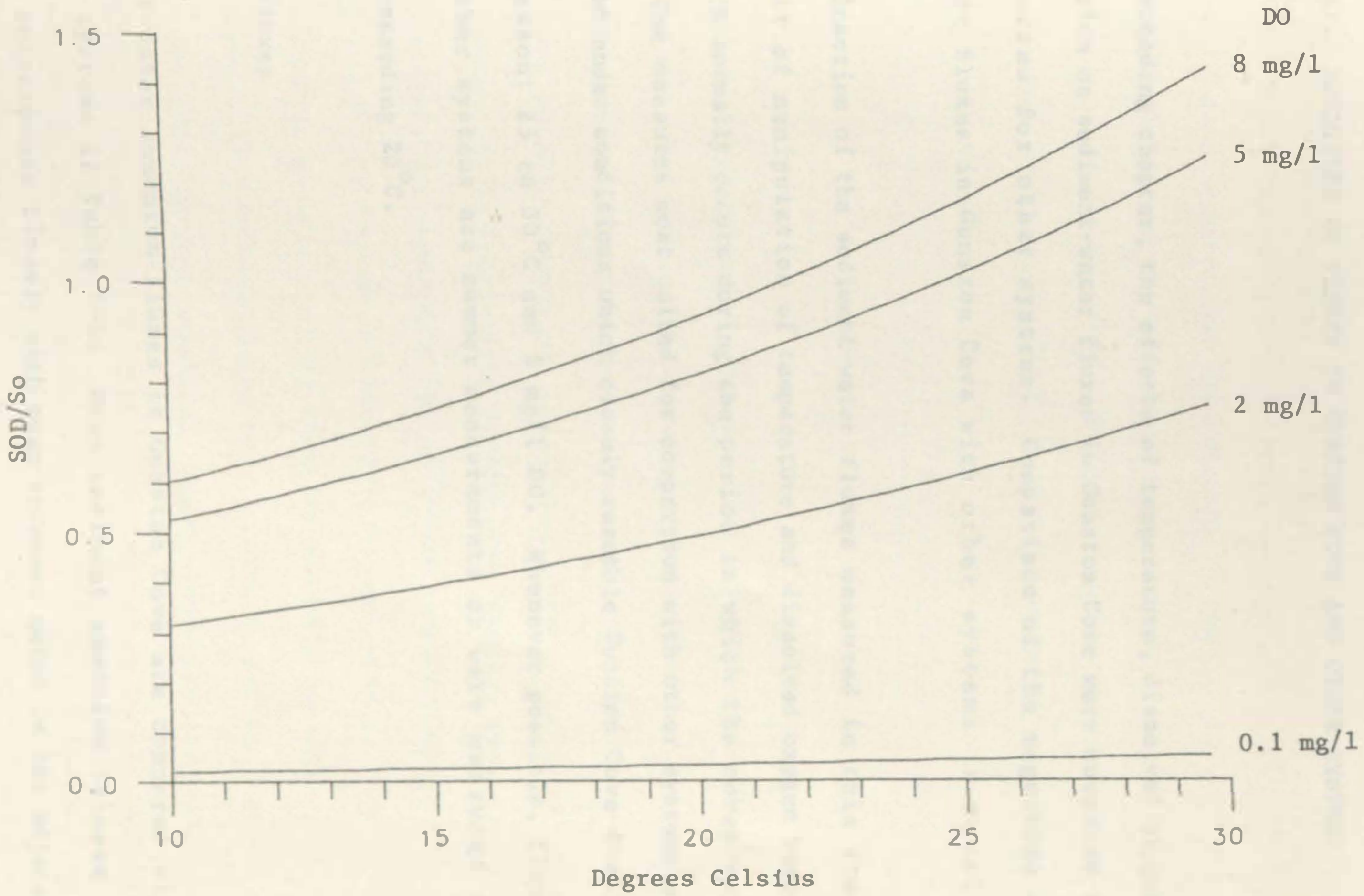


Figure 6-8. Effect of Temperature and DO on Sediment Oxygen Demand.

Chapter VII. MAGNITUDE OF FLUXES IN GUNSTON COVE AND OTHER SYSTEMS

In the preceding chapter, the effects of temperature, dissolved oxygen, and concentration on sediment-water fluxes in Gunston Cove were compared to effects reported for other systems. Comparison of the magnitude of sediment-water fluxes in Gunston Cove with other systems is equally worthwhile.

A large fraction of the sediment-water fluxes measured in this study are the result of manipulation of temperature and dissolved oxygen beyond the range which normally occurs during the period in which the cores were collected. The measures most suited for comparison with other systems are those conducted under conditions which closely resemble Gunston Cove during the summer season: 25 to 30°C and 8 mg/l DO. Whenever possible, fluxes quoted for other systems are summer measurements or were measured at temperatures exceeding 20°C.

A. Ammonium Fluxes

Sediment-water ammonium fluxes in Gunston Cove are compared with several other systems in Table 7-1. Mean sediment ammonium release in Gunston Cove corresponds closely with mean releases noted in the adjacent tidal, freshwater portion of the Potomac Estuary and with Chesapeake Bay. Mean and range of ammonium release are generally lower than corresponding measures in the tidal, freshwater James Estuary and in the Patuxent Estuary. Reported fluxes for the James are unusually high, however, due to the existence of extreme releases near the head of tide in the vicinity of several waste discharges (12). The limited number of measures and the high temporal variability of ammonium fluxes make it difficult to determine if the difference between Gunston and the Patuxent is real or an artifact of the methodologies employed, of the low accuracy of the measures and of the natural variability of ammonium flux. Basically, summer sediment releases of ammonium in Gunston Cove are typical of values measured elsewhere in Chesapeake Bay and its tributaries.

B. Nitrate Fluxes

Sediment-water nitrate fluxes in Gunston Cove are compared with several other systems in Table 7-2. Sediment nitrate uptake in Gunston Cove exceeds uptake noted elsewhere except in unusual circumstances. Nitrate uptake in Gunston Cove more closely resembles freshwater stream sediments than estuarine sediments. It is interesting to note that Gunston sediments take up nitrate at the same time Chesapeake Bay sediments release nitrate.

The anomalous nitrate uptake in Gunston Cove sediments is largely due to the presence of high nitrate concentrations in the water column. In the preceding chapter, it has been shown that sediment nitrate uptake is proportional to water-column concentration. Average nitrate concentration at the initiation of the measures reported here was 1.6 mg/l. By contrast, nitate concentration in the Chowan River, in which little sediment uptake was noted, averaged 0.002 mg/l (30). In the James Estuary, nitrate fluxes were into the sediment when water-column concentration exceeded 0.18 mg/l and were out of the sediment when concentration fell below 0.18 mg/l (12). In the Patuxent, nitrate fluxes "were into the sediment in winter when water column concentrations were high" (7). Although no concentration was specified, sediment nitrate uptake in winter ranged from 34 to 226 $mg/m^2/hr$. These values are similar to summer values in Gunston Cove. The dependence of flux on concentration noted in Gunston Cove and elsewhere indicates the high sediment uptake rate in Gunston is due to the large quantity of nitrate dissolved in the water column rather than unique characteristics of the sediment.

C. Ortho Phosphorus Fluxes

Gunston Cove is in the minority of systems which exhibit a mean sediment uptake of ortho phosphorus (Table 7-3). In view of the limited number and range of observations, the direction of the mean is of dubious significance, however. Gunston is similar to numerous other systems in that ortho phosphorus flux occurs in both directions across the sediment-water interface.

The measures reported here indicate that sediment-water ortho phosphorus flux in Gunston Cove is small and of indeterminate direction. These measures conflict with previous estimates of the flux and with the notion that algal blooms in Gunston Cove are supported by sediment phosphorus release. Model studies indicate that releases of 20 $mg/m^2/day$ ortho phosphorus were needed to support the algal populations observed in 1979, 1982 (11), and 1983 (45).

Why are the fluxes reported here so low? Two hypotheses may be formed. The first is based on the influence of pH on the sorption and desorption of ortho phosphorus from sediment particles. The second is based on the ability of nitrate to suppress sediment phosphorus release.

Several studies indicate that the capacity of sediment particles to sorb phosphorus decreases as pH increases (29, 31). Based on findings such as these, the hypothesis has been formed that sediment phosphorus release occurs in Gunston Cove when the water-column pH is extremely high, in the vicinity of 10 (45). The pH is raised to this level by the action of algae which deplete water-column carbon dioxide and increase dissolved oxygen. This hypothesis is supported by a limited number of experiments conducted on intact sediment cores removed from Gunston Cove (43).

Water-column pH was not monitored in this portion of the study. Ambient chlorophyll concentrations were monitored, however, and indicate chlorophyll did not exceed approximately 150 μg/l during summer 1984. In bloom years, such as 1983, chlorophyll concentrations may exceed 250 μg/l. An empirical relationship between chlorophyll and pH (unpublished data) indicates that pH during these studies was lower, pH 8 to 9, than during algal blooms, pH approximately 10. Thus, the ortho phosphorus fluxes reported here may be lower than during algal blooms due to differences in water-column pH.

High concentrations of nitrate, 1 to 5 mg/l, in the water column have been found to suppress phosphorus release from anoxic lake hypolimnia (2, 5). This effect is explained by the ability of nitrate to act as an electron acceptor in the oxidation of organic matter. This reaction fixes the oxidation-reduction potential of the sediment at a level such that the desorption of phosphorus which normally occurs under anoxic conditions cannot take place.

The ability of nitrate to suppress sediment phosphorus release has been observed under oxic conditions as well. Nitrate concentrations in excess of 0.5 mg/l were noted to eliminate sediment phosphorus releases in oxic lake hypolimnia (2). The suppression of phosphorus release by nitrate under an oxic water column can be explained by noting that only a small fraction of the sediments are oxic. In Gunston Cove, the light brown surface layer characteristic of oxidized sediments is a centimeter or less thick. Below this layer lie anoxic sediments despite oxygen saturation in the water column. Desorption of phosphorus from the anoxic sediments and diffusion through the thin oxic layer back into the water column is possible. Diffusion of nitrate from the water through the oxic sediments into the anoxic sediments and subsequent reduction of nitrate may prevent the desorption of phosphorus in the anoxic sediments and reduce or eliminate the release of phosphorus into the oxic water column.

The average nitrate concentration at the initiation of the measures reported here was 1.6 mg/l. By contrast, nitrate in lower Gunston Cove was approximately 0.5 mg/l during much of the late July to early September 1983 algal bloom (45). The high nitrate concentration in 1984 may have suppressed phosphorus release to far below the level needed to support the 1983 bloom.

Both the theories of enhanced release of phosphorus at high pH and of suppressed release of phosphorus at high nitrate concentration appear valid. Both require additional investigation so that their role in the regulation of sediment phosphorus release may be better understood.

D. Sediment Oxygen Demands

Sediment oxygen demand in Gunston Cove is compared with several other systems in Table 7-4. The mean and range correspond with measures collected in the freshwater portion of the Potomac Estuary, in Chesapeake Bay, and in the Patuxent Estuary. Although SOD in Gunston appears to be higher than in the freshwater portion of the James Estuary, it is typical of the range of values reported for Chesapeake Bay and its tributaries.

Table 7-1. Reported Ammonium Fluxes

Mean	Range	Comments
111	73 to 135	Gunston Cove. 25 to 30 C. This study.
95		Tidal freshwater portion of Potomac Estuary. August. (10).
271	-72 to 1560	Tidal freshwater portion of James Estuary. July to October. (12).
117	34 to 270	Chesapeake Bay. August. (8).
	185 to 530	Patuxent Estuary. August. (7).
31	2 to 168	Chowan River. Tidal freshwater. June (30).
75	24 to 153	Neuse Estuary. (21).
	50 to 92	Narragansett Bay. T > 20 C. (23).
32		Anaerobic lake sediments. (22).
	120 to 360	Eutrophic river and lake sediments. 24 to 30 C. (19).
270		Anaerobic sludge. 22 C. (18).

All fluxes in mg N/m^2/day. Positive fluxes indicate sediment release.

Table 7-2. Reported Nitrate Fluxes

Mean	Range	Comments
-141	-14 to -300	Gunston Cove. 25 to 30 C. This study.
	-22 to 22	Tidal freshwater portion of Potomac Estuary. August. (10).
-39	-240 to 96	Tidal freshwater portion of James Estuary. July to October. (12).
	0 to 97	Chesapeake Bay. August. (8).
	0 to 8	Patuxent Estuary. August. (7).
0.4	-8 to 9	Chowan River. Tidal freshwater. June. (3).
1	0 to 2	Neuse Estuary. (21).
	-1 to 6	Narragansett Bay. July. (42).
	-11 to -171	Freshwater stream sediments. 21 C. (52).
-913		Sewerage drainage ditch. 19 C. (50).

All fluxes in mg N/m^2/day. Positive fluxes indicate sediment release.

Table 7-3. Reported Ortho Phosphorus Fluxes

Mean	Range	Comments
-2.1	-5.9 to 3.7	Gunston Cove. 25 to 30 C. This study.
6.2		Tidal freshwater portion of Potomac Estuary. August. (10).
-21	-280 to 46	Tidal freshwater portion of James Estuary. July to October. (12).
	-4 to 34	Chesapeake Bay. August. (8).
	31 to 219	Patuxent Estuary. August. (7).
3	-1.4 to 11.2	Chowan River. Tidal freshwater. June. (30).
10.4	-1.7 to 34	Neuse Estuary. (21).
21.4		Narragansett Bay. 20 C. (36).
	7 to 30	Narragansett Bay. T >20. (23).
23		Anaerobic lake sediments. (22).
	0.9 to 68	Aerobic lake sediments. T >20 C. (24).
154		Anaerobic sludge. 22 C. (18).

All fluxes in mg P/m^2/day. Positive fluxes indicate sediment release.

7-4. Reported Sediment Oxygen Demand

Mean	Range	Comments
2.1	0.7 to 3.0	Gunston Cove. 25 to 30 C. This study.
	2.5 to 2.7	Tidal freshwater portion of Potomac Estuary. August. (10).
1.1	0 to 1.9	Tidal freshwater portion of James Estuary. July to October. (12).
2.1	1.5 to 4.5	Chesapeake Bay. August. (8).
	2.0 to 3.5	Patuxent Estuary. August. (7).
0.5	0 to 2.3	Chowan River. Tidal freshwater. June. (30).
1.2	0.6 to 1.7	Neuse Estuary. (21).
1.6	0.7 to 4.2	Houston Ship Channel. 24 C. (51).
	1.7 to 2.7	Eutrophic river and lake sediments. 24 to 30 C. (19).
7		Aerobic sludge. (18).

All demands in gm oxygen/m^2/day. Positive values indicate sediment uptake.

Chapter VIII. EXAMINATION OF METHODOLOGY

Assessment of the precision and accuracy of sediment-water flux measurements is problematical. No standard method of measuring these fluxes exists, nor can measurements be compared to a known, standard sample. The precision of the measures can be evaluated by including replicate samples in an experiment or by running replicate experiments, but accuracy of the measures cannot be directly addressed. One approach to the problem of accuracy is to compare the results of measures conducted by different, independent methodologies. That approach is adopted here. The laboratory measures of sediment-water flux are compared to in-situ measures collected at the site in Gunston Cove from which the sediment cores were removed. A second, unique evaluation of measures is presented by comparison of the lab measures reported here with lab measures conducted in an alternate, independent investigation.

A. Precision of Laboratory Measures

Two approaches to evaluating the precision of the laboratory measures are possible. In the first, fluxes in replicate cores collected at the same time are compared. Two sets of replicates were run in each experiment conducted here. In the second approach, fluxes measured in replicate experiments using sediments collected in different surveys are compared.

Replicate experiments were performed for two temperature-dissolved oxygen combinations using sediments collected three to six weeks apart.

The parameter employed to quantify precision is the coefficient of variation (CV), defined as the absolute value of the ratio of the standard deviation of a set of observations to the arithmetic mean of the observations. The coefficient of variation of replicate cores and of replicate experiments is presented in Table 8-1.

Replicate cores exhibited a range of CV from approximately zero to greater than unity for fluxes of all substances. The median CV was approximately 0.2 for fluxes of ammonium, nitrate, and oxygen. Median CV for ortho phosphorus was more than four times higher than the other substances, indicating that measures of ortho phosphorus flux are much less precise than measures of the other fluxes.

The coefficients of variation for replicate experiments are mostly larger than median coefficients of variation for replicate cores. The causes and implications of the CV´s of replicate experiments cannot be generalized for all substances.

Ammonium fluxes measured in replicate columns were among the most repeatable of any substance, yet the experiments were the least repeatable. Since the experimental conditions were well-controlled, the low repeatability of the experiments must be due to changes in the character of the sediments. The changes occur in a time scale of a few weeks and may be caused, for example, by variations in the rate of input of organic matter or by alterations in the rate of bioturbation. Alterations in the properties of the sediment in the course of these experiments partially accounts for the relatively low fraction of variability in flux explained by temperature and dissolved oxygen.

The repeatability of nitrate measures in different experiments is greater than ammonium indicating that the sediment properties which determine nitrate uptake are not as variable as the properties which determine ammonium release.

Ortho phosphorus flux exhibits a high coefficient of variation both for replicate columns and replicate experiments. The CV for replicate columns indicates that small-scale spatial variabilities in the sediments exert a significant influence on ortho phosphorus flux. The spatial variabilities occur on a scale smaller than the ten-meter radius in which the cores were collected. One process which varies on that spatial scale and which can account for the flux variability is bioturbation. The action of bioturbation is dependent upon the random distribution of benthic fauna in a sediment sample.

A portion of the coefficient of variation of ortho phosphorus flux in replicate experiments is attributed to differences in the concentration of the overlying water rather than temporal variations in sediment properties. Initial concentrations in one set of repeat experiments were 0.06 vs 0.02 mg/l and were 0.12 vs 0.05 mg/l in the second set. Variations in flux measured in repeat experiments is therefore expected in view of the strong dependence of flux on concentration. Although ortho phosphorus flux varies from week to week, the success of the model, Eq 6-10, indicates a large fraction of the variation is predictable if the water-column dissolved oxygen and ortho phosphorus concentrations are known.

Sediment oxygen demand in replicate experiments exhibited a surprisingly low coefficient of variation. The CV for replicate SOD experiments was comparable to the CV for replicate nitrate experiments. Summed over all experiments, the SOD was less predictable than nitrate flux.

Therefore, SOD measures were expected to be less repeatable than nitrate flux measures. The sample size of repeat measures is small, however, and the apparently low CV of replicate SOD measures may be an artifact of the sample size.

B. Comparison of Fluxes Measured by Different Methodologies

The laboratory measures reported in this study are compared to in-situ measures conducted at the site in Gunston Cove from which the cores were removed. Six in-situ measures were collected at approximately two-month intervals from July, 1984, to June, 1985. The in-situ or "dome" measures were conducted by sealing a hemispherical dome, 46 cm in diameter and displacing 25 liters, to the sediment-water interface. By monitoring the time course of dissolved substance concentration in the entrapped water, materials fluxes into or out of the sediment were inferred. Two sediment domes and a single control dome, which contained water not in contact with the sediments, were employed in each masurement. Duration of the measures was seven hours. Details of the measurement technique may be found in (12). Sample dates, ambient conditions, and results of the measures are presented in Table 8-2.

Several comparisons may be made between the laboratory and in-situ measures. The first is a direct comparison of fluxes measured under similar conditions of temperature and dissolved oxygen. Not all of the field measures have a directly corresponding lab measure, however. Only three of the field measures are suited for direct comparison with lab measures.

A second approach is to compare the performance of the models based on laboratory measures with the in-situ measures. This method is advantageous in that predictions of flux can be made based on the exact conditions of temperature, dissolved oxygen, and substance concentration which prevailed in the domes. The measure of comparison is the root-mean-square (RMS) difference between the laboratory and field measures and between the model results and field measures.

1. Direct Comparison of Lab and In-Situ Measures

Three laboratory and in-situ measures are compared directly in Table 8-3. The difference in fluxes measured by the two methods is of the same magnitude as the fluxes themselves. Although correspondence between individual measures is small, nitrate flux and sediment oxygen demand measured in the lab and in-situ do agree in order of magnitude and direction. At temperatures exceeding 25°C, ammonium fluxes measured by the two methods agree in magnitude and direction although the in-situ measures are two to four times larger than the lab measures. The ammonium fluxes are in different directions, however, at 10 to 12°C. Only a single comparison is possible for ortho phosphorus flux. In that case, laboratory and field measures differ in magnitude and direction.

Sediments for the laboratory were generally collected while ambient temperatures were 25 to 30°C. Agreement is therefore expected between the laboratory measures and the in-situ measures of ammonium flux conducted in that temperature range. Lack of agreement at low temperatures occurs because in-situ measures collected in April are compared to lab measures using sediments collected in August. Characteristics of the sediment, most likely the benthic fauna, are different in these two months and different fluxes occur even though temperatures during the two measures are in agreement. The effects of temperature on ammonium flux reported here are the effects on sediment collected in a twelve-week, late summer period. Caution must be used in extrapolating these effects to predict sediment activity at a different time of year.

No ortho phosphorus flux was detected in several of the dome emplacements. In both cases, ambient ortho phosphorus was 0.005 mg/l or less and no meaningful temporal trend could be detected in the concentration data. At that low concentration, sediment ortho phosphorus release should occur, as predicted by the model, Eq. 6-10. During the July measures, release must have occurred in order to sustain the algae population of the cove. No trend was detected because the algae were assimilating the ortho phosphorus as rapidly as it was released. In order to avoid this problem, measures of total phosphorus flux were collected in subsequent field measures. An increase in total phosphorus in the dome but no change in ortho phosphorus indicates sediment ortho phosphorus release and simultaneous biotic uptake. This strategy was not always successful, however, because particulate phosphorus occasionally was stirred off the bottom during dome emplacement and because particulates in the water column showed a tendency to settle during the emplacement. It was not always possible to segregate the increase of particulate phosphorus due to biotic uptake from resuspension or settling of particulate phosphorus.

The difficulty in measuring phosphorus flux in-situ when ortho phosphorus is near the detection limit can be reduced by conducting laboratory measures instead. In the lab, a large fraction of the organic and inorganic particulates are filtered from the water and care can be taken not to resuspend sediments.

The large discrepancy in the single available comparison between laboratory and in-situ ortho phosphorus flux is partially explained by the difference in concentration during the two measures. The initial concentration during the in-situ measure was 0.009 mg/l vs 0.053 mg/l in the lab measures. Since ortho phosphorus flux is strongly dependent on water-column concentration, discrepencies between the field and lab masures are expected.

2. Comparison of In-Situ Measures and Model Predictions

A limited number of laboratory and field measures correspond sufficiently in temperature and dissolved oxygen for direct comparisons to be performed. Comparisons of nitrate and ortho phosphorus flux are further compromised by differences in water-column concentration during lab and field measures. The data base can be enlarged by comparing the in-situ measures with fluxes predicted to occur under the ambient conditions which prevailed when the measures were collected. The models based on the laboratory observations are used to provide the predictions. This method is advantageous in that all field observations are utilized and predictions can be based on the temperature, dissolved oxygen, and concentration which were observed in the domes.

Six sets of predicted and observed fluxes are presented in Table 8-4. The same comparisons are shown graphically in Figure 8-1. The results echo the results of the direct comparisons. RMS differences in the predicted and observed fluxes are of the some order of magnitude as the fluxes themselves. Predicted and observed nitrate fluxes and SOD generally agree in magnitude and direction. Predicted and observed ammonium fluxes agree in magnitude and direction at temperatures equal to or greater than 18°C. At lower temperatures, in situ ammonium fluxes tend to be into the sediments while predicted fluxes are out of the sediments. Predicted and observed ortho phosphorus fluxes agree in direction but may disagree in magnitude.

The figure indicates that predicted and observed fluxes correspond while fluxes are small but the observations exhibit extreme values not reproduced by the model. The in-situ observations also exhibit occasional outlying values, in this case exemplified by an abnormally low nitrate flux, which cannot be reproduced by the model.

C. Comparison of Fluxes Measured by Different Investigators

During the period this study was conducted, an investigation of sediment nutrient flux aimed at determining the role of sediments in the 1983 Potomac River blue-green algae bloom was conducted by the Philadelphia Academy of Sciences (PAS) under the sponsorship of the United States Environmental Protection Agency (43). One station in the PAS study was in Gunston Cove, a few hundred meters downstream of the site from which cores were collected in this study. Availability of the PAS data presents a unique opportunity for comparison of fluxes measured by different investigators employing similar methodologies and sediments.

Mean and range of nutrient fluxes measured in the two investigations are compared in Table 8-5. An in-situ measure collected in the summer of 1984 under conditions similar to the lab is also reported. The two lab measures agree in magnitude and direction of ammonium flux but are an order of magnitude lower than the in-situ observation of flux. Mean nitrate fluxes are into the sedments in all methods, but the laboratory results differ by an order of magnitude from each other. The replicate in-situ nitrate fluxes varied by such a wide margin that the significance of the mean flux is questionable. Mean ortho phosphorus fluxes in the two lab studies differ in direction but indicate agreement that the flux is small and variable. Ortho phosphorus was below detection level in the field study and no flux could be determined.

Several differences exist in the laboratory methods employed in this study and the PAS study. These include the diameter of the cores, 10 cm (this study) vs 6.7 cm (PAS), and the time elapsed between collection of the cores and initiation of measurements, hours (this study) vs days (PAS). The influence of these differences on the measurements is debatable. They may be of no influence, as the fluxes measured in different laboratories exhibit the same standards of agreement as the fluxes measured by different methodologies.

D. Assessment of Methodologies

Several additional statistics which aid in the assessment of methodologies can be developed. One statistic is the coefficient of variation of replicate "dome" measurements. The in-situ apparatus were deployed in pairs just as the laboratory cores were monitored in pairs. The CV of the in-situ devices is compared to the laboratory cores in Table 8-1. For this comparison, the in-situ measures reported in Table 8-2 are combined with measures collected elsewhere in Gunston Cove so that a total of nine dome pairs are available. Median coefficients of variation of replicate measures by the two methodologies are similar for nitrate fluxes, ortho phosphorus fluxes, and SOD. The CV for in-situ ammonium flux is much higher than for ammonium flux measured in the laboratory, however. This low precision may account for some of the extreme deviation of observed from predicted ammonium flux.

A second statistic of interest is the ratio of control-column (or dome) activity to sediment-column (or dome) activity. The columns containing sediment actually measure the total of sediment-water fluxes and substance transformations within the water. In order to isolate the sediment-water fluxes, transformations in the water alone must be measured and subtracted from the total. A desirable characteristic of field and lab methodology is that the transformation in the water be only a small fraction of the total of sediment-water flux and water transformation. If the water transformation is of similar magnitude to the total, then the sediment-water flux obtained by subtraction of the control from the sediment column is of dubious magnitude and direction. If the water transformation is of the same sign but much greater magnitude than the sediment-water flux (e.g. an uptake of phosphorus in both sediment and water), subtraction of the control from the sediment column yields a sediment-water flux significant in direction but highly dependent on the accuracy of the measure in the control column. A similar situation exists if the water transformation is of greater magnitude then the sediment-water flux but of different sign. In this study, as in most studies, less emphasis was placed on measures in the control column than in the sediment column. It is undesirable, therefore, for the accuracy of the reported sediment-water fluxes to be highly dependent upon the accuracy of the control measures.

The principles outlined above can be restated simply that the absolute value of the ratio of control-column (or dome) transformations to sediment-column (or dome) transformations should be much less than unity. The median and range of ratios for both laboratory and in-situ measures are reported in Table 8-6.

The median ratios for nitrate and ortho-phorphorus fluxes are comparable for laboratory and in-situ measures although the ratio for ortho phorphorus is undesireably high. The in-situ measures exhibit lower ratios than the lab measures for ammonium flux and SOD. The relatively high activity in the control column compared to the control dome is surprising since the laboratory water is passed through a one-micron filter and the dome water is not. The activity in the control column may be due more to colonization of the column walls than to activity in the water. This hypothesis is supported by noting that the volume-to-surface-area ratio of the domes is 5 cm but only 1.1 cm in the columns, due to their small diameter and the presence of internal baffles. Opportunity for colonization is also greater in the columns, which are in contact with water for 36 hours, than in the domes, which are in contact with water only 8 hours.

Inevitably, the question arises: Which methodology is better? Laboratory or in-situ? The answer lies in the preferences of the investigator and in the purpose of the measurements. Fluxes measured by the two methods do not closely agree, but neither can be claimed more accurate. No consistent difference exists in the methods in terms of coefficient of variation of fluxes observed in replicate devices or in the ratio of water to sediment activity.

In-situ methods are advantageous in that they measure fluxes which occur under the prevailing conditions of temperature, dissolved oxygen, nutrient concentration, pH, benthic activity and a host of other factors. Reproduction in the laboratory of all ambient conditions observed in the field is impossible. The laboratory permits control and manipulation of the ambient conditions, however. An important contrast is that dissolved oxygen can be kept constant in the laboratory columns but always declines in the in-situ devices.

The primary difference between laboratory and field measures lies in the difficulty of collecting the measures and in the frequency of failed measurements. Great care is needed to seal the domes to the sediment-water interface and the work must be conducted by a diver working in virtual darkness. Certainty that the dome has been installed properly and with minimal disturbance to the sediments is not possible. Failures are common due to erosion of the seal beween the dome and the sediments or leaks in the circulation system. By contrast, successful laboratory measures are assured once the cores are collected. Individual cores can be inspected to determine their suitability, and set-up of the experiment is conducted by investigators working in light and atmosphere. In terms of ease and reliability, laboratory measures are greatly preferred over in-situ measures.

Phosphorus is the most important of the sediment-water fluxes in Gunston Cove. Sediment phosphorus release has been implicated as supporting the algae blooms which continue to occur despite stringent point-source phosphorus control. Quantification and understanding of sediment-water phosphorus flux is crucial to the control of algae blooms. The behavior of phosphorus and the factors which influence its flux make it, unfortunately, the most difficult flux to measure and predict. Phosphorus flows both ways across the sediment-water interface and therefore influences the water-column concentration and is influenced by it. Phosphorus flux measurements are the least precise and among the most difficult to repeat of the substances investigated here. Sediment activity of phosphorus is difficult to discern from activity in the water. In the laboratory, sediment fluxes of uncertain magnitude and direction are sometimes obtained due to high activity in the water. In the field, no fluxes are detected when biotic uptake equals sediment release.

In the laboratory, several steps can be taken to improve the accuracy of the phosphorus flux measures. The first is to increase the number of sediment cores per measurement. The second is to increase the number of control columns or, preferably, to decrease the activity of phosphorus in the water. The decrease can be effected by filtering the water through a filter which passes less particulates or by decreasing the surface area available for colonization. Surface area can be decreased by using a device which has a higher volume-to-surface ratio or, in this study, by removing the internal baffle system.

Table 8-1. Coefficients of Variation

NH4	NO3	PO4	SOD	Comments
0.22	0.18	0.87	0.21	Median CV of replicate cores.
0.03 to 1.31	0.04 to 1.29	0.04 to 2.34	0.01 to 1.58	Range of CV of replicate cores.
0.62 to 2.22	0 to 0.64	0.39 to 1.68	0.29 to 0.34	CV of replicate experiments.
0.88	0.27	0.97	0.22	Median CV of replicate domes.
0.22 to 10.3	0.10 to 7.63	0.01 to 2.69	0.03 to 0.45	Range of CV of replicate domes.

Table 8-2. In-Situ Flux Measures in Gunston Cove

	C°	NH4	NO3	PO4	SOD
840723	29				
concentration		1.00	1.27	0.010	5.0
flux		432	-15	ND	1.8
841016	18				
concentration		0.12	2.22	0.005	7.7
flux		89	-198	ND	3.1
841213	5				
concentration		2.17	1.84	0.012	9.0
flux		8	-35	0.89	1.0
850228	10				
concentration		6.87	1.11	0.047	6.8
flux		-14	-23	-0.62	1.5
850403	12				
concentration		2.86	1.47	0.005	9.5
flux		-39	-37	ND	1.2
850606	25				
concentration		1.29	0.77	0.009	5.2
flux		223	-141	17.7	3.5

NH4, NO3, PO4 flux in mg/m^2/day, positive out of sediments. SOD in gm/m^2/day, positive into sediments. Concentrations of NH4, NO3, PO4 are the initial concentrations in the dome, in mg/l. Dissolved oxygen concentration is average during emplacement, in mg/l. ND indicates ´none detected´.

Table 8-3. Direct Comparison of Laboratory and In-Situ Measures

Date or Experiment	Temperature	DO Concentration	NH4 Flux	NO3 Flux	PO4 Flux	SOD	
Experiment 4	10	8.0	76	-35	0.2	0.8	Lab
850403	12	9.5	-39	-37	ND	1.2	Field
Experiment 8	25	5.0	50	-229	-1.6	2.0	Lab
850606	25	5.2	223	-141	17.7	3.5	Field
Experiment 9	30	5.0	180	-191	-4.3	3.3	Lab
840703	29	5.0	432	-15	ND	1.8	Field
		RMS Difference	189	114		1.2	

Temperature in C^o. Dissolved oxygen concentration in mg/l. Fluxes in mg/m^2/day, except SOD in gm/m^2/day. ND indicates 'none detected'.

Table 8-4. Comparison of In-Situ and Predicted Sediment-Water Fluxes

Date	Temperature	DO Concentration	NH4 Flux	NO3 Flux	PO4 Flux	SOD	
840723	29	5.0	432	-15	ND	1.8	Observed
			149	-155	2.72	2.3	Predicted
841016	18	7.7	89	-198	ND	3.1	Observed
			65	-105	1.80	1.6	Predicted
841213	5	9.0	8	-35	0.89	1.0	Observed
			27	-33	0.34	0.9	Predicted
850228	10	6.8	-14	-23	-0.62	1.5	Observed
			41	-33	-3.38	1.1	Predicted
850403	12	9.5	-39	-37	ND	1.2	Observed
			41	-40	1.11	1.2	Predicted
850606	25	5.2	223	-141	17.7	3.5	Observed
			115	-71	2.71	1.9	Predicted
	RMS Difference		130	74	8.8	0.9	

Temperature in C°. Dissolved oxygen concentration in mg/l. Fluxes in mg/m^2/day, except SOD in gm/m^2/day. ND indicates none detected.

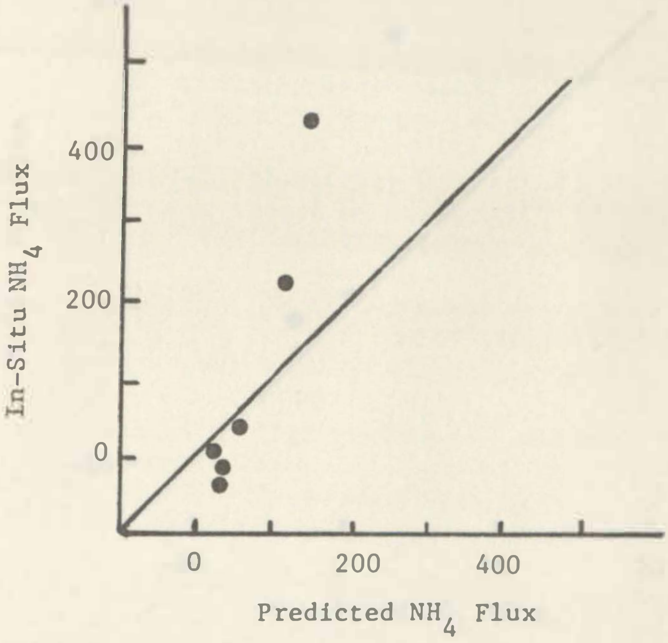
Table 8-5. Comparison of Fluxes Measured by Three Methods

Date	Temperature	DO Concentration	NH4 Flux	NO3 Flux	PO4 Flux		Comments
Sept. 1984	25	5	50	-229	-1.6	mean	Lab cores,
			43 to 57	-218 to -240	-4.3 to 1.1	range	this study.
Sept., Oct. 1984	22 to 24	aerobic	17	-28	1.2	mean	Lab cores,
			-23 to 37	-7 to -43	-2.1 to 4.2	range	PAS (43).
July 1984	29	5	432	-15	ND	mean	In-situ measures,
			310 to 554	-93 to 64		range	this study

Temperature in C^{o}. Dissolved oxygen concentration in mg/l. Fluxes in mg/m^{2}/day.
ND indicates 'none detected'.

Table 8-6. Ratio of Water to Combined Sediment and Water Activity

		NH4	NO3	PO4	SOD
Laboratory	median	0.43	0.18	0.89	0.39
	range	0 to 9.5	0 to 0.67	0 to 17.5	0 to 0.87
In-Situ	median	0.23	0.20	0.94	0.11
	range	0.07 to 0.93	0 to 5.8	0 to 3.9	0 to 0.51



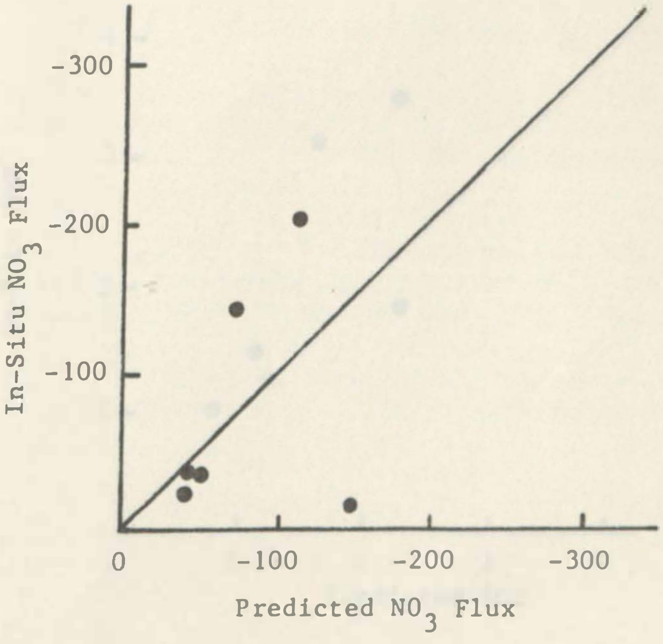


Figure 8-1. In-Situ vs. Predicted Flux. NH_4 and NO_3 fluxes in mg/sq m/day.

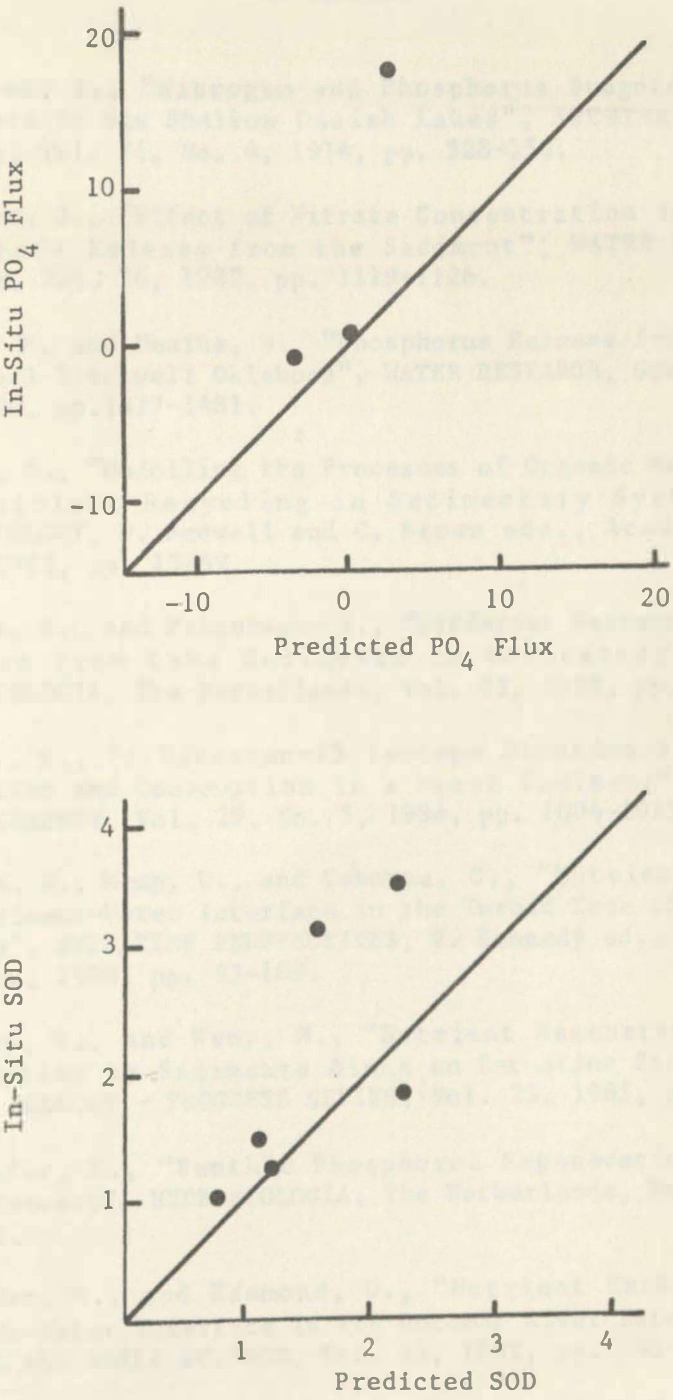


Figure 8-1. Continued. PO$_4$ flux in mg/sq m/day. SOD in gm/sq m/day.

REFERENCES

1. Andersen, J., "Nitrogen and Phosphorus Budgets and the Role of Sediments in Six Shallow Danish Lakes", ARCHIVA HYDROBIOLOGIA, Germany, Vol. 74, No. 4, 1974, pp. 528-550.

2. Andersen, J., "Effect of Nitrate Concentration in Lake Water on Phosphate Release from the Sediment", WATER RESEARCH, Great Britain, Vol. 16, 1982, pp. 1119-1126.

3. Bates, M. and Neafus, N., "Phosphorus Release from Sediments from Lake Carl Blackwell Oklahoma", WATER RESEARCH, Great Britain, Vol. 14, 1980, pp.1477-1481.

4. Billen, G., "Modelling the Processes of Organic Matter Degradation and Nutrient Recycling in Sedimentary Systems", SEDIMENT MICROBIOLOGY, D. Nedwell and C. Brown eds., Academic Press, New York, 1982, pp. 15-52.

5. Bostrom, B., and Pettersson K., "Different Patterns of Phosphorus Release from Lake Sediments in Laboratory Experiments", HYDROBIOLOGIA, The Netherlands, Vol. 92, 1982, pp. 415-429.

6. Bowden, W., "A Nitrogen-15 Isotope Dilution Study of Ammonium Production and Consumption in a Marsh Sediment", LIMNOLOGY AND OCEANOGRAPHY, Vol. 29, No. 5, 1984, pp. 1004-1015.

7. Boynton, W., Kemp, W., and Osborne, C., "Nutrient Fluxes Across the Sediment-Water Interface in the Turbid Zone of a Coastal Plain Estuary", ESTUARINE PERSPECTIVES, V. Kennedy ed., Academic Press, New York, 1980, pp. 93-109.

8. Boynton, W., and Kemp, W., "Nutrient Regeneration and Oxygen Consumption by Sediments Along an Estuarine Salinity Gradient", MARINE ECOLOGY - PROGRESS SERIES, Vol. 23, 1985, pp. 45-55.

9. Callender, E., "Benthic Phosphorus Regeneration in the Potomac River Estuary", HYDROBIOLOGIA, The Netherlands, Vo. 92, 1982, pp. 431-446.

10. Callender, E., and Hammond, D., "Nutrient Exchange Across the Sediment-Water Interface in the Potomac River Estuary", ESTUARINE, COASTAL AND SHELF SCIENCE, Vol. 15, 1982, pp. 395-413.

11. Cerco, C., "Water Quality in a Virginia Potomac Embayment: Gunston Cove", College of William and Mary, Gloucester Pt., Va., 1985.

12. Cerco, C., "Sediment-Water Column Exchanges of Nutrients and Oxygen in the Tidal James and Appomattox Rivers", College of William and Mary, Gloucester Pt., Va., 1985.

13. Chiaro, P., and Burke, D., "Sediment Oxygen Demand and Nutrient Release", JOURNAL OF THE ENVIRONMENTAL ENGINEERING DIVISION ASCE, Vol. 106, No. EE1, 1980, pp. 177-195.

14. "Determination of Inorganic Nonmetallic Constituents", EXAMINATION OF WATER AND WASTEWATER, 14th edition, M. Franson ed., American Public Health Association, Washington D.C., 1976, pp. 273-509.

15. Edberg, N., and Hofsten, B., "Oxygen Uptake of Bottom Sediments Studied In Situ and in the Laboratory", WATER RESEARCH, Great Britain, Vol. 7, 1973, pp. 1285-1294.

16. Edwards, R., and Rolley, H., "Oxygen Consumption of River Muds", JOURNAL OF ECOLOGY, Vol. 52, No. 1, 1965, pp. 1-19.

17. Faust, S., and Aly, O., "Oxidation Reduction Conditions of Natural Waters and Environs", CHEMISTRY OF NATURAL WATERS, Ann Arbor Science, Ann Arbor, Mich., 1981, pp. 169-204.

18. Fillos, J., and Molof, A., "Effect of Benthic Deposits on Oxygen and Nutrient Economy of Flowing Waters", JOURNAL OF THE WATER POLLUTION CONTROL FEDERATION, Vol. 44, No. 4, 1972, pp. 644-662.

19. Fillos, J., and Swanson, W., "The Release Rate of Nutrients from River and Lake Sediments", JOURNAL OF THE WATER POLLUTION CONTROL FEDERATION, Vol. 44, No. 5, 1975, pp. 1032-1042.

20. Fillos, J., and Biswas, H., "Phosphate Release and Sorption by Lake Mohegan Sediments", JOURNAL OF THE ENVIRONMENTAL ENGINEERING DIVISION ASCE, Vol. 102, No. EE2, 1976, pp. 239-249.

21. Fisher, T., Carlson, P., and Barber, R., "Sediment Nutrient Regeneration in Three North Carolina Estuaries, ESTUARINE COASTAL AND SHELF SCIENCE, Vol. 14, 1982, pp. 101-116.

22. Freedman, P., and Canale, R., "Nutrient Release from Anaerobic Sediments", JOURNAL OF THE ENVIRONMENTAL ENGINEERING DIVISION, ASCE, Vol. 103, No. EE2, 1977, pp.233-244.

23. Hale, S., "The Role of Benthic Communities in the Nitrogen and Phosphorus Cycles of an Estuary", MINERAL CYCLING IN SOUTHEASTERN ECOSYSTEMS, F. Howell, J. Gentry, and M. Smith eds., ERDA Symposium Series, 1975, pp. 291-308.

24. Holdren, G., and Armstrong, D., "Factors Affecting Phosphorus Release from Intact Lake Sediment Cores", ENVIRONMENTAL SCIENCE AND TECHNOLOGY, Vol. 14, No. 1, 1980, pp. 79-87.

25. Jacobsen, O., and Jorgensen, S., "A Submodel for Nitrogen Release from Sediments", ECOLOGICAL MODELLING, Vol. 1, 1975, pp. 147-151.

26. Jenkins, M., and Kemp, W., "The Coupling of Nitrification and Dentrification in Two Estuarine Sediments", LIMNOLOGY AND OCEANOGRAPHY, Vol. 29, No. 3, 1984, pp. 609-619.

27. Klapwijk, A., and Snodgrass, W., "Experimental Measurement of Sediment Nitrification and Denitrification in Hamilton Harbour, Canada", HYDROBIOLOGIA, The Netherlands, Vol. 91, 1982, pp. 207-216.

28. Krom, M., and Berner, R., "Adsorption of Phosphate in Anoxic Marine Sediments", LIMNOLOGY AND OCEANOGRAPHY, Vol. 25, No. 5, 1980, pp. 797-806.

29. Ku, W., DiGiano, F., and Feng, T., "Factors Affecting Phosphate Adsorption Equilibria in Lake Sediments", WATER RESEARCH, Great Britain, Vol. 12, 1978, pp. 1069-1074.

30. Kuenzler, E., Stone, K., and Albert, D., "Phytoplankton Uptake and Sediment Release of Nitrogen and Phosphorus in the Chowan River, North Carolina", UNC-WRRI-82-186, Water Resources Research Institute of the University of North Carolina, Raleigh N.C., Sept. 1982.

31. Lake, C., and MacIntyre, W., "Phosphate and Tripolyphosphate Adsorption by Clay Minerals and Estuarine Sediments", VPI-VWRRC-BUL 109, Virginia Water Resources Research Center, Blacksburg Va., June 1977.

32. Malcolm, S., and Stanley, S., "The Sediment Environment", SEDIMENT MICROBIOLOGY, D. Nedwell and C. Brown eds., Academic Press, New York, 1982, pp. 1-14.

33. Mawson, S., Gibbons, H., Funk, W., and Hartz, K., "Phosphorus Flux Rates in Lake Sediments", JOURNAL OF THE WATER POLLUTION CONTROL FEDERATION, Vol. 55, No. 8, 1983, pp. 1105-1110.

34. Messer, J., and Brezonik, P., "Laboratory Evaluation of Kinetic Parameters for Lake Sediment Dentrification Models", ECOLOGICAL MODELLING, Vol. 21, 1984, pp. 277-286.

35. Nedwell, D., "Exchange of Nitrate, and the Products of Bacterial Nitrate Reduction Between Seawater and Sediment from a U.K. Saltmarsh", ESTUARINE, COASTAL AND SHELF SCIENCE, Vol. 14, 1982, pp. 557-566.

36. Nixon, S., Kelly, J., Furnas, B., Oviatt, C., and Hale, S., "Phosphorus Regeneration and the Metabolism of Coastal Marine Bottom Communities", MARINE BENTHIC DYNAMICS, K. Tenare and B. Coull eds., University of South Carolina Press, Columbia, S. C., 1980, pp. 219-242.

37. O´Connor, D., Callagher, T., and Hallden, J., "Water Quality Analysis of the Patuxent River", HSMY 0011, Hydroqual Inc., Mahwah, N.J., Aug. 1981.

38. Paerl, H., "Environmental Factors Promoting and Regulating Nitrogen-Fixing Blue-Green Algal Blooms in the Chowan River, N.C.", UNC-WRRI-82-176, Water Resources Research Institute of the University of North Carolina, Raleigh N.C., Jan. 1982.

39. Pomeroy, L., Smith, E., and Grant, E., "The Exchange of Phosphate Between Estuarine Water and Sediments", LIMNOLOGY AND OCEANOGRAPHY, Vol. 10, No. 2, 1965, pp. 167-172.

40. "Required Containers, Preservation Techniques, and Holding Times", FINAL DRAFT AMENDMENT to 40 CFR PART 136, United States Environmental Protection Agency Region III, Philadelphia Pa., 1981.

41. Robinson, J., "Determining Microbial Kinetic Parameters Using Nonlinear Regression Analysis", ADVANCES IN MICROBIAL ECOLOGY, K. Marshall ed., Vol. 8, Plenum Press, New York, 1985, pp. 61-114.

42. Seitzinger, S., Nixon, S. and Pilson, M., "Dentrification and Nitrous Oxide Production in a Coastal Marine Ecosystem", LIMNOLOGY AND OCEANOGRAPHY, Vol. 29, No. 1, 1984, pp. 73-83.

43. Seitzinger, S., "The Effect of Oxygen Concentration and pH on Sediment-Water Nutrient Fluxes in the Potomac River", REPORT NO. 85-2, The Academy of Natural Sciences of Philadelphia, Philadelphia Pa., Jan. 1985.

44. Sharma, B., and Ahlert, R., "Nitrification and Nitrogen Romoval", WATER RESEARCH, Great Britain, Vol 11, 1977, pp. 897-925.

45. Thomann, R., Jaworski, N., Nixon. S., Paerl, H., and Taft, J., "The 1983 Algal Bloom in the Potomac Estuary", Potomac Strategy State/EPA Management Committee, United States Environmental Protection Agency Region III, Philadelphia, Pa., March 1985.

46. Twinch, A., and Peters, R., "Phosphate Exchange Between Littoral Sediments and Overlying Water in an Oligotrophic North-Temperate Lake", CANADIAN JOURNAL OF FISHERIES AND AQUATIC SCIENCE, Canada, Vol. 41, 1984, pp. 1609-1617.

47. Vanderborght, J., Wollast, R., and Billen, G., "Kinetic Models of Diagenesis in Distrubed Sediments. Part 1. Mass Transfer Properties and Silica Diagenesis", LIMNOLOGY AND OCEANOGRAPHY, Vol. 22, No. 5, 1977, pp. 787-793.

48. Vanderborght, J., Wollast, R., and Billen, G., "Kinetic Models of Diagenesis in Disturbed Sediments. Part 2. Nitrogen Diagenesis", LIMNOLOGY AND OCEANOGRAPHY, Vol. 22, No. 5, 1977, pp. 794-803.

49. Van Kessel, J., "Factors Affecting the Dentrification Rate in Two Water-Sediment Systems", WATER RESEARCH, Great Britain, Vol 11, 1977, pp. 259-267.

50. Van Kessel, J., "Removal of Nitrate from Effluent Following Discharge on Surface Water", WATER RESEARCH, Great Britain, Vol. 11, 1977, pp. 533-537.

51. Ward, G., "The Measurement of Benthal Oxygen Demand in the Houston Ship Channel", JOURNAL OF THE WATER POLLUTION CONTROL FEDERATION, Vol. 56, No. 2, 1984, pp. 183-191.

52. Wyer, M., and Hill, A., "Nitrate Transformations in Southern Ontario Stream Sediments", WATER RESOURCES BULLETIN, Vol. 20, No. 5, 1984, pp. 729-737.

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Effect of temperature and dissolved oxygen on sediment-water nutrient flux