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# APPENDIX C

# RIVER FLOW AND NUTRIENT LOAD CHARACTERISTICS; WATER QUALITY CONDITIONS IN THE LOWER POTOMAC (MLE2.2); AND SEDIMENT-WATER FLUXES IN THE POTOMAC ESTUARY

Walter R. Boynton
Chesapeake Biological Laboratory
Solomons, MD
boynton@cbl.umces.edu

# POTOMAC RIVER INTEGRATED ANALYSIS PROJECT

- RIVER FLOW AND NUTRIENT LOAD CHARACTERISTICS
- WATER QUALITY CONDITIONS IN THE LOWER POTOMAC (MLE 2.2)
- SEDIMENT-WATER FLUXES IN THE POTOMAC ESTUARY

W. R. Boynton
Chesapeake Biological Laboratory
Box 38
Solomons, MD 20688

Tele: 1-410-326-7275
Fax: 1-410-326-7378
e-mail: boynton@cbl.cees.edu

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## INTRODUCTION

The Maryland Chesapeake Bay Water Quality Monitoring Program (Magnien et al. 1987) has multiple component programs, one of which is the Ecosystem Processes Component. This component of the monitoring program has been making measurements of sediment-water nutrient and oxygen exchanges at a number of sites (8-10) in mainstem Chesapeake Bay and tributary rivers during summer periods since 1985. In addition, this component of the monitoring program has been active in exploring the monitoring data base for relationships among water quality variables. Of particular interest are relationships between inputs of water, organic matter and nutrients to Chesapeake Bay, and sub-systems such as the Potomac River, and estuarine responses in terms of algal biomass, deep water oxygen conditions and sediment-water oxygen and nutrient exchanges.

### Estuarine eutrophication

During the past decade much has been learned about the effects of both natural and anthropogenic nutrient inputs (*e.g.*, nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and oxygen conditions in deep waters (Nixon, 1981, 1988; Kemp *et al.*, 1983 ; D'Elia *et al.*, 1983; Malone, 1992; and Kemp and Boynton, 1992). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production in surface waters and low dissolved oxygen conditions in deep waters are sustained through summer and early fall periods by sediment recycling of essential nutrients and sediment oxygen consumption, respectively and (3) deposition of organic matter from surface to deep waters links these processes of production and consumption (Boynton *et al.*, 1982a ; Garber *et al.*, 1989).

Research conducted in Chesapeake Bay and other estuaries indicates that estuarine sediments act as important storage sites for nutrients as well as sites of intense organic matter decomposition and oxygen consumption (Kemp and Boynton, 1984). For example, during summer periods in the Choptank and Patuxent estuaries, 40-70% of the total oxygen utilization was associated with sediments and 25-70% of algal nitrogen demand was supplied from estuarine sediments (Boynton *et al.*, 1982b). Processes of this magnitude have a pronounced effect on estuarine water quality and habitat conditions. Sediments in much of Chesapeake Bay, especially the upper bay and tributary rivers, contain significant amounts of carbon, nitrogen, phosphorus and other compounds (Boynton *et al.*, 1995). A large percentage of this material appears to reach sediments following the termination of the spring bloom and again after the fall bloom. A portion of this material is available to regenerative processes and once transformed into inorganic nutrients again becomes available for algal utilization. Nutrients and other materials deposited or buried in sediments represent the potential "water quality memory" of the bay.

Nutrients enter the bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on bay waters. Dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. Much of this particulate material then sinks to the bottom and is potentially available for remineralization. Essential nutrients released during the decomposition of organic matter may then again be utilized by algal communities. A portion of this newly produced organic matter sinks to the bottom, contributing to the development of anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative capacities and the potentially large nutrient storages in bottom sediments ensure a large return flux of nutrients from sediments to the water column and thus sustain continued phytoplankton growth. Continued growth supports deposition of organics to deep waters, creating anoxic conditions typically associated with eutrophication of estuarine systems (Figure 1). To a considerable extent, it is the magnitude of these processes which determines nutrient and oxygen water quality conditions in many zones of the bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings decrease, changes in the magnitude of sediment processes will serve as a guide in determining the effectiveness of strategies aimed at improving bay water quality and habitat conditions.

### Scope of this work

The schematic diagram in Figure 2 summarizes this conceptual eutrophication model where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced nitrogen and phosphorous loads lead to a restoration trajectory. Sediment processes play a prominent role in both trajectories. The working hypothesis is that if nutrient and organic matter loading to the bay decreases then the cycle of intense algal blooming, deposition of algal detritus to sediments, sediment oxygen demand resulting in poor deep water dissolved oxygen conditions, release of sediment nutrients and continued high algal production based on these recycled nutrients will also decrease. Because loads and water and sediment quality processes are linked, as described above, all three are considered in this component of the analysis. This work focuses on water and sediment quality conditions in the mesohaline portion of the Potomac River estuary (water quality monitoring station MLE 2.2) because this is the only site in the Potomac where both water quality and sediment process work has been conducted routinely for a decade. Work reported here is based on data collected during the period January 1986 through December 1995. Both monthly, seasonally averaged and annual data are examined.

## CHARACTERISTICS OF RIVER FLOW AND NUTRIENT LOADS (1986-1995)

### Annual patterns and trends

On an annual average basis, river flow ranged between 8000 to 12000 cfs during all years but 1993 and 1994 when annual average flows were much higher (16000 to 17000 cfs; Figure 3). Annual average falline plus Blue Plains nutrient loads of TN and TP generally followed river flow patterns with higher loads in wet years and lower loads in drier years. Loads for TN ranged between 60,000 and 75,000 kg per day except during 1993 and 1994 when TN loads averaged between 110,000 and 125,000 kg per day. Lowest TN loads occurred in 1986 and 1995, both low flow years. Interannual patterns of TP loading were similar. During the decade for which loads were examined there did not appear to be any strong trends of either increasing or decreasing TN or TP loads (Figure 4).

### Monthly patterns and trends

Monthly patterns of river flow are richer and more suggestive of differing ecological effects among years (Figure 5). For example, there were 2 very high flow years (1993 and 1994) and 4 very low flow years (1986, 1990, 1992 and 1995). Other years in this record were intermediate. In addition, the peak flows, which might reasonably be expected to have more influence on estuarine conditions than low flows, varied considerably among years in terms of when they occurred. There were four years with winter maximum flows, four with early spring maximum flows and two with late spring (May) maximum flows. The water quality consequences of winter versus spring inputs appear to be considerable, as will be discussed later. The monthly pattern in TN and TP load reflects river flow conditions and, because of this, there is substantial interannual variability in loads (> 2x for TN; > 3x for TP). Possibly the most important point is that the seasonal timing of maximum loads differs among years and this may have strong water quality consequences.

The N:P ratio of the falline load was calculated (on a molar basis) and is shown in Figure 6. This ratio has some utility as an indicator of potential N or P limitation of phytoplankton. Several interesting points emerged from inspection of this time series plot. First, there is great seasonal variability in the fall line load ratio which ranges from a low of about 22 to a high of 122. In most years the ratio is highest in winter-spring because diffuse source nutrient loads are typically much richer in N than P (nitrogen compounds, especially nitrate which is a major component of diffuse source nitrogen, is very soluable and moves readily with runoff). In terms of loading, the system is always rich in nitrogen relative to phosphorus. This is similar to other portions of Chesapeake Bay and tributaries that have important diffuse source nutrient loads. Surface water N:P ratios (atomic basis; DIN/PO4) were also computed for a mesohaline site in the Potomac River estuary (Sta MLE 2.2). Ratios were high in winter-spring and low in summer-fall and exhibited a greater range than in the fall line load ratio. The traditional Redfield value for balanced nutrient conditions is about 16:1(shown as a range between 10 and 20 in Figure 6). Note that values were seldom this low (~20% of all observations). However, Fisher et al (1997) have found, using a bioassay approach, that strong P limitation of phytoplankton growth does not generally emerge until this ratio is about 100-150. Of the 120 observations shown in Figure 6, only 36 have N:P values greater than 100 and all occurr in winter or early spring. This suggests summer through fall N limitation of phytoplanktonic growth, consistant with the work of Fisher et al (1997).

## CHLOROPHYLL-A CONDITIONS IN THE LOWER POTOMAC (Station MLE 2.2)

Monthly average water column chlorophyll concentrations exhibited large ranges during the period of observation at the water quality station in the mesohaline region of the Potomac River estuary (Figure 7). Of particular interest are the large spikes of chlorophyll-a during 1988, 1989 and 1990. The remaining years did not exhibit large spikes although seasonal patterns were evident. In general, maximum concentrations were observed in the late winter or spring; only in 1989 did high concentrations of chlorophyll-a persist through the summer period. No long term trend was obvious from inspection of the chlorophyll-a time series at this mesohaline site.

One of the main issues to be addressed for the Potomac River, as well as other locations in the Bay region, is establishing a nutrient loading rate that allows for resource restoration including a decline in algal blooming (as indicated by chlorophyll-a concentrations), restoration of higher bottom water dissolved oxygen concentrations and re-establishment of seagrass communities. Possible relationships between chlorophyll-a and nutrient loading rates were examined for the mesohaline region using data from water quality station MLE 2.2. TN load was plotted versus water column chlorophyll concentrations (monthly averages for both) and results are shown in Figure 8. No significant relationship emerged, as expected, from this simple treatment of the data. Considerably more interesting results emerged from two different groupings of data which included time lags between nutrient inputs at the fall line and chlorophyll-a responses in the mesohaline estuary (Figure 9). In the first case (top panel) peak chlorophyll-a concentrations which occurred in each year (in some cases a single monthly value if the peak was so defined; in cases of a protracted bloom several months were averaged to estimate peak concentrations) were plotted as a function of the monthly TN load 1-2 months prior to the time when peak chlorophyll conditions were observed. In this case the lag was introduced to account for the time required for nutrients (TN in this case) to be transported from the fall line to the mesohaline estuary and to then simulate phytoplanktonic growth. This sort of lag produces an unward sweeping curve that fits 9 of the 10 years of observation quite well. The 1990 chlorophyll-a data were strongly divergent wherein chlorophyll-a concentrations were much higher than would be predicted from lagged TN loads alone. The reason for this divergence is not clear at this time. Another approach used to examine the data base for load-chlorophyll-a relationships used the monthly TN load associated with the freshet (whenever it occured) in each year versus the peak water column chlorophyll concentrations that subsequently developed. In this case a humped curve results that has some interesting characteristics (Figure 9; lower panel). First, highest chlorophyll concentrations developed in association with late spring TN loads, as was the case in 1988 and 1989. These were not huge load years but they did develop very high chlorophyll concentrations. Very high load years (1987, 1993 and 1994) in which the peak load entered in March-April generated modest to low chlorophyll concentrations in the mesohaline estuary. This suggests that low temperature, limited sunlight and reduced residence times (because of high flow) combined to limit the development of algal stocks; inorganic nutrients may have been transported out of the lower Potomac to the Bay under these conditions. At the other extreme, small loads (whenever they occurred) produced low chlorophyll concentrations (except during 1990). Nutrients entering the system after some warming has occurred (i.e. May-June) have the ability to generate very large algal standing stocks.

## DISSOLVED OXYGEN CONDITIONS IN THE LOWER POTOMAC (Station MLE 2.2)

Bottom water dissolved oxygen conditions at this station in the mesohaline portion of the estuary are very poor during the summer months (Figure 10). During some months, average dissolved oxygen concentration in the bottom 6 m of the water column was just a few tenths of a milligram per liter. Despite a large range in river flows (which influences the strength of water column stratification and reaeration of deeper waters) and nutrient loads (which provide essential elements supporting algal biomass, the decomposition of which utilizes dissolved oxygen), very low dissolved oxygen concentrations were observed at this site in all years. Even under the lowest river flow and nutrient load conditions observed between 1996 and 1995 (which would favor higher bottom water dissolved oxygen conditions) low dissolved oxygen concentrations were always observed during summer periods.

An estimate of the extent of hypoxia (water having less than 2 mg/l of dissolved oxygen) present in the mesohaline Potomac was also estimated. In the top panel of Figure 11 the cross-sectional area of the Potomac at Station MLE 2.2 having dissolved oxygen concentrations less than 2 mg/l was computed for each year. In the lower panel the result of intergrating the darken areas of the top panel is indicated. The hypoxic water mass has units of $m^2$-days rather than volume-days because there was only a single station in this region of the Potomac. If data from two mesohaline stations had been available, the more commonly computed hypoxic volume-days contained between two cross sections would have been reported . Hypoxic areas increased from 1986 through 1988, dropped sharply in 1989 and gradually increased to the present time. It is important to note that the interannual range in hypoxic cross-sectional days is relatively small compared to the interannual ranges in variables causing hypoxic conditions (river flow, nutrient loading rates, in-situ chlorophyll-a concentrations) suggesting an attenuated response of hypoxia, at least in this section of the estuary.

A number of regression analyses were completed to explore the data set for relationships between hypoxia in the mesohaline estuary and features causing hypoxia. Most did not yield significant results. However, in most years hypoxic conditions can be reasonably predicted as a function of average chlorophyll-a concentrations in the mesohaline estuary during the winter-spring period. In effect, summer season hypoxia can be predicted based on winter-spring season chlorophyll-a conditions in the water column (Figure 12). The basis for this model includes the following. In many areas of the bay there is an algal bloom (dominated by diatoms; the "spring bloom") which generally follows the late winter - early spring freshet. It appears that most of the algal material generated by this bloom is not grazed by herbivoures while still in the water column; rather, these algal cells sink to deep waters and sediments and when bottom water temperatures increase in late spring and summer is consumed by benthic hetertrophs, the activity of which creates hypoxic conditions. However, algal blooms which occur in late spring and summer seem to have less of an impact on deep water oxygen conditions based on examination of data from Sta MLE 2.2. It is probable that algal biomass generated from these blooms is consumed while still in surface waters rather than being first deposited to deep waters prone to oxygen depletion (Smith and Kemp 1995).

## SEDIMENT-WATER FLUXES IN THE POTOMAC RIVER ESTUARY

### Characteristics of sediment-water fluxes

Average monthly sediment-water exchanges of ammonium and phosphorus measured at five locations in the Potomac River estuary are summarized as a series of bar graphs in Figures 13a and 13b. Sediment-water exchange measurements are not available from sites in the Potomac River estuary during cooler periods of the year (November - April) but measurements made in other sections of Chesapeake Bay and tributary rivers all indicate that exchanges are low to very low during the cooler months (Boynton et al 1980). It is reasonable to assume that this is also the case in the Potomac and that the data displayed in Figure 13 encompass the period of the year when these processes have water quality significance.

Ammonium fluxes tended to be highest during the warmest month (August) at most stations. However, seasonal patterns are not very clear at the three most upriver stations because the sampling frequency was low (May and August at Anacostia River stations; May, July, August and October at Hedge Neck and Gunston Cove stations). The pattern observed at Ragged Point is based on monthly sampling between May and October for multiple years and probably represents the pattern which would emerge for other stations. Perhaps the most striking feature of the ammonium flux data is the decrease in the magnitude of fluxes from the tidal fresh region to the lower mesohaline region. We suspect that the reason for this pattern is that sediments in the upper estuary are exposed to high deposition rates of phytoplanktonic detritus which is labile and subject to rapid decomposition and release of ammonium under both aerobic and anaerobic sediment conditions. The station in the mesohaline region is exposed to generally lower organic matter deposition rates and is deeper and therefore more organic matter can be remineralized prior to reaching the sediment surface. Overall, rates of sediment ammonium release were high to very high compared to other sites in Chesapeake Bay and tributary rivers (Boynton et al 1996).

Phosphorus fluxes exhibited a very different pattern. Fluxes were uniformly low in the tidal fresh and low salinity portions of the estuary ( $< 15\ \mu mol\ m^{-2}\ hr^{-1}$) and very high ($> 30 \mu mol\ m^{-2}\ hr^{-1}$) in the mesohaline region. The probable mechanism responsible for this pattern involves the adsorbtion of dissolved sediment phosphorus to ferric oxides under aerobic conditions and the release of adsorbed phosphorus under anaerobic conditions (Kemp and Boynton 1992). It appears that there is ample phosphorus in sediments throughout the estuary to support high sediment exchanges (Boynton et al 1995) but the generally oxidized surface sediments of the shallower upper estuary prevent phosphorus release while the hypoxic conditions of the deeper mesohaline portion of the estuary promotes these releases. An example of the sensitivity of sediment phosphorus fluxes to dissolved oxygen conditions is shown in Figure 14; it appears that if bottom water dissolved oxygen concentrations fall below about 3 mg/l fluxes increase and if dissolved oxygen conditions decrease below 1 mg/l very large sediment phosphorus releases can occur.

It is also important to note that low dissolved oxygen levels is not the only mechanism that can solubilize phosphorus bound to sediment particles. In the relatively poorly buffered upper estuary, increases in water column pH (> 9.0) which can be caused by intense algal blooms (depleting inorganic carbon from the water column) will also lead to sediment phosphorus releases. This mechanism apparently played a role in sustaining a large algal bloom in the upper estuary during the 1980's (Seitzinger pers comm). Finally, it was noted earlier that the relative abundance of dissolved nitrogen to dissolved phosphorus in the water column in the mesohaline estuary during the warmer seasons of the year were much lower than the nitrogen to phosphorus ratio of nutrient inputs at the fall line. One reason for this large shift in the water column N:P ratio is that sediment releases of phosphorus in this zone of the estuary are particularly large and would have the effect of lowering the ratio in the mesohaline region and ultimately contribute to nitrogen limitation of phytoplankton growth.

## Status of Potomac fluxes relative to other portions of the Bay

A standardized protocol has been developed for scaling sediment-water flux data in order to compare fluxes from different regions of the Bay and tributary rivers (Figure 15). Several versions of this approach have evolved and the version described below has been adopted by the Chesapeake Bay Monitoring Program (Alden and Perry, 1997). The status bar for each sediment-water flux variable comprises a benchmark (with a gradient scale) and a pointer which indicates the current status or condition of sediment-water flux along the benchmark scale at a particular sampling site.

The complete sediment-water exchange data set (collected at eight stations in the Bay and tributary rivers from 1985 through 1996) was used to create a status bar for each parameter (*e.g.* sediment oxygen consumption [SOC]). Using all sediment-water exchange data assured that the widest observable range of variability due to factors such as river flow and nutrient loading rates were included. The 5th and the 95th percentile values were calculated for each exchange variable and were used to indicate the end points of the gradient scale. An additional two centiles, the 35th and 65th centiles, were used to scale the final benchmark such that it was delineated into three categories: poor, fair and good. A linear quantitative scale with "good" and "poor" end points was thus developed. The annual median for each sediment-water exchange variable at each station was calculated and placed on the status bar as a vertical arrow. Data from the Ragged Point station in the mesohaline Potomac River was used in developing the status bars for each sediment-water exchange variable; other stations in the Potomac were not used in developing the status bars because observations at these sites were too limited. Again, at the Ragged Point station, the current status (vertical arrow) of each sediment-water exchange variable was calculated as the average value for the years 1994, 1995 and 1996. This averaging of the last three years of data has the effect of eliminating the influence of extreme climatic conditions (*i.e.* very wet or very dry years) since such extremes do not usually occur for several years in succession. Average values were calculated for other stations in the Potomac using whatever sediment-water exchange data that were available (usually a single year).

### i Sediment Oxygen Consumption (SOC)

The current status of sediment oxygen consumption (SOC) fluxes at the five Potomac River estuary stations is indicated in Figure 15a. It seems appropriate to judge higher values of SOC as good in the context of this evaluation for several reasons despite the fact that high SOC rates indicate that sediments are using dissolved oxygen. The main reason for adopting this approach is that SOC rates are responsive to DO concentrations in the water. When dissolved oxygen concentrations in the water are high, SOC rates can potentially be high. Conversely, when dissolved oxygen concentrations in the water are low, SOC rates will always be low. Since restoration of increased dissolved oxygen in bottom waters is a goal of the management program we have adopted the position of treating higher SOC rates as indicative of healthy sediments in aerobic environments. Among the Potomac River estuary stations, three were considered to have SOC rates in the good range, one was in the fair range and one was in the poor range. The pattern of SOC fluxes in the provides substantiation that the benchmark is appropriate. SOC fluxes progress from good up-river to poor down-river. This pattern largely results because the water column is well mixed and well oxygenated up-river while the propensity for low water column dissolved oxygen (DO) conditions is high at the down-river site.

### ii. Ammonium ($NH_4^+$)

The current status of ammonium fluxes at the five Potomac River estuary stations is indicated in Figure 15b. In the case of ammonium fluxes it appears appropriate to judge high values as poor because of the well established linkage between ammonium availability and excessive phytoplankton biomass accumulation. Among the Potomac stations three were considered to have ammonium fluxes in the poor range and two were in the fair range. Two of the three stations in the poor range were actually off-scale, indicating extremely high values. Thus, sediment additions of ammonium to the water column are large relative to other regions of Chesapeake Bay and because of this have a larger impact on water quality conditions. It is expected that if nutrient loading rates from point and diffuse sources decrease then sediment ammonium releases will also decrease.

### iii. Nitrite plus Nitrate ($NO_2^- + NO_3^-$)

The current status of nitrite plus nitrate fluxes at the five Potomac River estuary stations is indicated in Figure 15c. In the case of nitrite plus nitrate fluxes it appears appropriate to judge high values (positive values; nitrate coming from sediments to the water column) as good because of the well established linkage between nitrite plus nitrate evolution from sediments (via complete nitrification) and oxidized sediment conditions. All of the Potomac stations were considered to have nitrite plus nitrate fluxes in the poor range and three of the stations were off-scale indicating particularly poor conditions relative to other areas of Chesapeake Bay. It is expected that stations would move from poor to fair or fair to good when dissolved oxygen conditions in bottom waters improve at deep stations (even if only enough to allow some nitrification activity to occur) and when water column concentrations of nitrate decrease, particularly at the more up-river sites.

### iv. Dissolved Inorganic Phosphorus ($PO_4^-$ or DIP)

The current status of dissolved inorganic phosphorus fluxes at the five Potomac River estuary stations is indicated in Figure 15d. In the case of phosphorus fluxes it appears appropriate to judge high values as poor because of the well established linkage between phosphorus availability and excessive phytoplankton biomass accumulation. Among the Potomac stations two were considered to have phosphorus fluxes in the good range, two were in the fair range and one was in the poor range. We would expect the site with a poor status to rapidly move towards the fair and good categories when dissolved oxygen conditions at this site improve (Jasinski 1996). If however, dissolved oxygen conditions degrade or if pH levels increase at the up-river sites we would expect these sites to rapidly move to status conditions of fair or poor for the reasons mentioned earlier.

## Annual and seasonal trends in sediment-water exchanges

A standardized protocol was adopted by the Chesapeake Bay Monitoring Program for determining interannual trends of each parameter (Eskin *et al.*, 1993). This approach uses the non-parametric seasonal Kendall test. In results presented here, sediment oxygen and nutrient exchange data were exposed to this test both before and after data were corrected for river flow conditions. In the following sections the procedures used to perform the standardized Kendall test for trends and the resulting trends for the single station in the mesohaline region of the Potomac River estuary (for which there is a long time-series of measurements available) are presented.

### i. Description of seasonal Kendall test

Trend analysis is one method which can be use to assess the changes within the Bay system and the effectiveness of management programs designed to restore water quality conditions in the Bay. The seasonal Kendall test is non-parametric and is a generalization of the Mann-Kendall test. It is applied to data sets exhibiting seasonality. The test does not assume a specific parametric form. Details of the statistical method are given in Gilbert (1987).

Sediment-water exchange data were collected over a period of twelve years (1985 - 1996) during seven months (April through November) at one station in the Potomac River (Ragged Point). In order to characterize the data initially, manual QA/QC checks were completed. A plot of the complete data set for each flux variable was prepared. Extreme outliers were examined and in certain cases these data were discarded. Separate analyses were performed for each sediment oxygen and nutrient exchange variable by month of measurement, by season (e.g. July-August) and for each annual period (April - November). A probability level of 0.10 was used to assess the significance of the results.

### ii. Flow adjustment

River discharge rates often influence concentrations of nutrients and other materials in estuarine systems. For example, heavy rains may cause a dilution effect or may have the net result of increasing total nutrient loads. The use of flow adjusted concentrations (or some other variable) is an attempt to remove the influence of flow *per sae* from the inspection of a data set for interannual trends. So, for example, if nitrate concentration in a mesohaline zone of an estuary was a partial correlate of flow, flow correction would remove the influence of flow from the data set. In effect, the trend analysis is done on the residuals of the flow vs variable relationship. This is important because it is effects other than flow (*e.g.* managed nutrient concentration reductions) that are being sought, if they exist. In the case of sediment-water exchange variables an appropriate river flow (or river flow period) needed to be selected for flow correcting exchanges. In other portions of the Chesapeake Bay Monitoring Program flow lags of 7 -14 days appeared appropriate and were adopted. However, sediment-water exchange variables are influenced by river flow through a chain of events which taken together argue for a longer lag averaged over a substantial time period. Analyses presented in previous reports (Boynton *et al.*, 1994; Cowan and Boynton, 1996) suggest using river flow values averaged for December through February and applied to data collected between April and November as a reasonable solution. The sediment-water exchange data were "flow detrended" or adjusted to standardize the effects of river flow using a linear regression model. The independent variable of this model was the average of flow for the three winter months (December, January, and February) preceding data collections. The regression model was designed such that data for each month had a separate slope that described the flux as a function of flow. In the results, it was clear that exchange rates for some months were more strongly influenced by flow than rates for other months. The residuals from this flow correction analysis were then used to assess the data set for long-term trends using the seasonal Kendall test.

### iii. Results of Kendall tests for trends

Values are presented in a Table 1a for non-flow-corrected results and in Table 1b for flow corrected results; results were similar from both non-flow corrected and flow-corrected analyses. The tables include results for a total of six sediment-water exchange variables, including sediment oxygen consumption (SOC), ammonium, nitrite, nitrite plus nitrate, dissolved inorganic phosphorus and silicate at Ragged Point, the only station in the Potomac for which there is a long time-series of measurements.

Testing for trends at the annual time scale resulted in only one statistically significant result ($p < 0.10$). A significant trend was indicated for nitrite plus nitrate ($NO_2^- + NO_3^-$) at Ragged Point and the trend was towards increasing fluxes from water to sediments, a trend which would lead to a down-grading of status at this site. There were no significant annual trends for SOC, silicate, ammonium and dissolved inorganic phosphorus fluxes at Ragged Point in the Potomac River estuary. Despite a first-order correction for effects of river flow on these variables, it appears that there is sufficient interannual variability to obscure annual trends, if they exist.

Testing for trends at monthly and seasonal time scales revealed a few more significant trends at the Ragged Point site. SOC rates appear to be increasing at a slow rate during summer (June -September) months (a trend towards improved status), nitrite plus nitrate fluxes into sediments were increasing during summer months (a trend towards degrading status) and silicate fluxes were also increasing during summer months (a trend towards degrading status).

During the last 12 years both wet and dry years have been recorded (relatively high and low diffuse nutrient source loading years) which tend to produce high and low sediment fluxes. Since high/low load years have occurred without pattern, trends due either to climatic variability or management actions (reduced nutrient load) have not yet become apparent. These results were expected because substantial reductions in nitrogen loads (a particularly important nutrient in mesohaline regions of the bay system) have not yet been realized.

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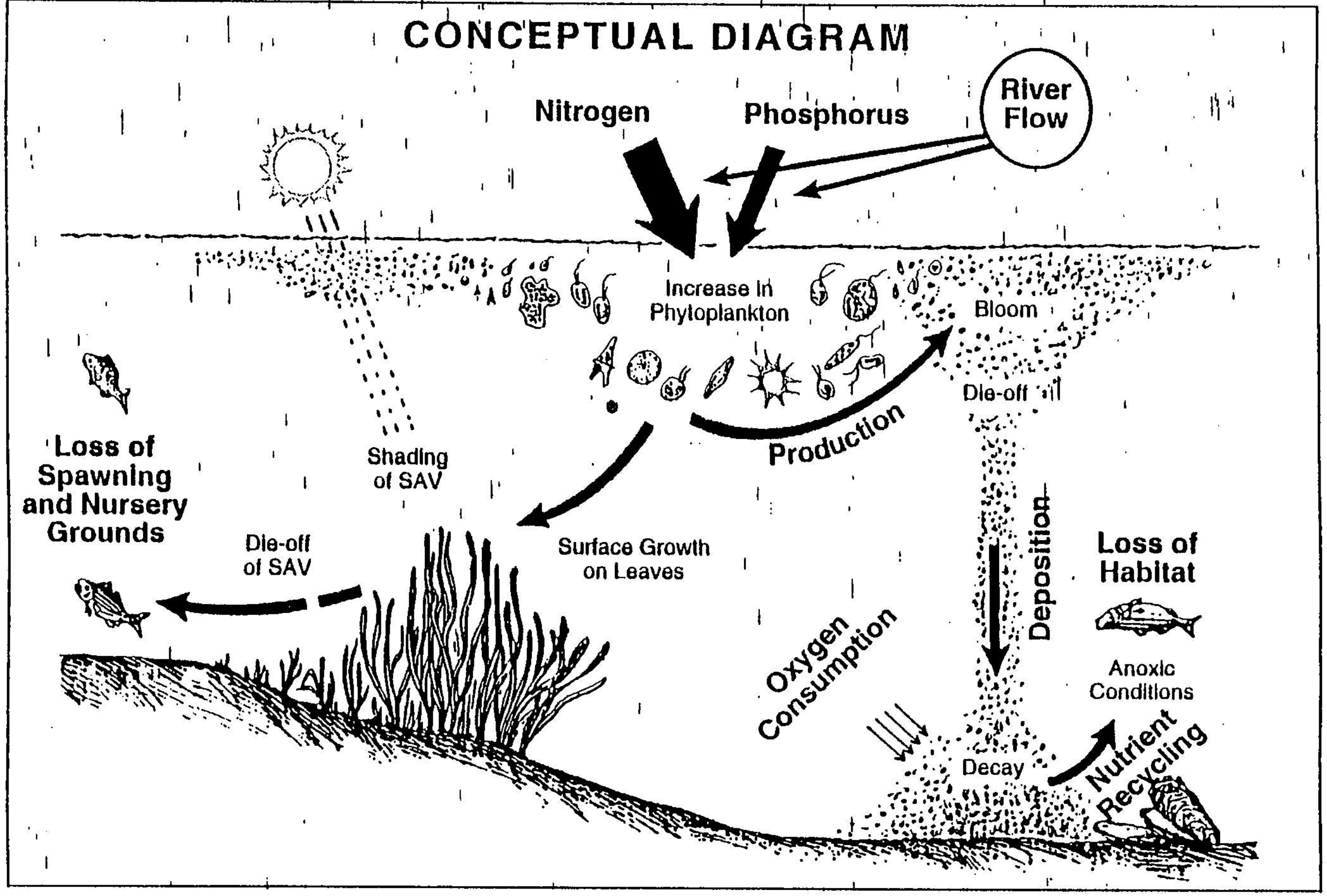


Figure 1. A conceptual diagram indicating some relationships between nutrient loading in estuarine systems and ecosystem responses. At the top of the diagram nutrients are shown entering the system, often associated with river flow. Nutrients promote phytoplankton growth which can reach bloom levels when nutrient loads are high. Such blooms eventually sink to deeper waters where decomposition (primarily by bacteria) processes use available dissolved oxygen from the water creating hypoxic (low oxygen) or anoxic (no oxygen) conditions. Dissolved nutrients are also released from sediments and can then be re-used by phytoplankton to create more bloom conditions. The left side of the diagram indicates that excessive nutrient inputs can decrease light availability to seagrasses resulting in the loss of these communities.

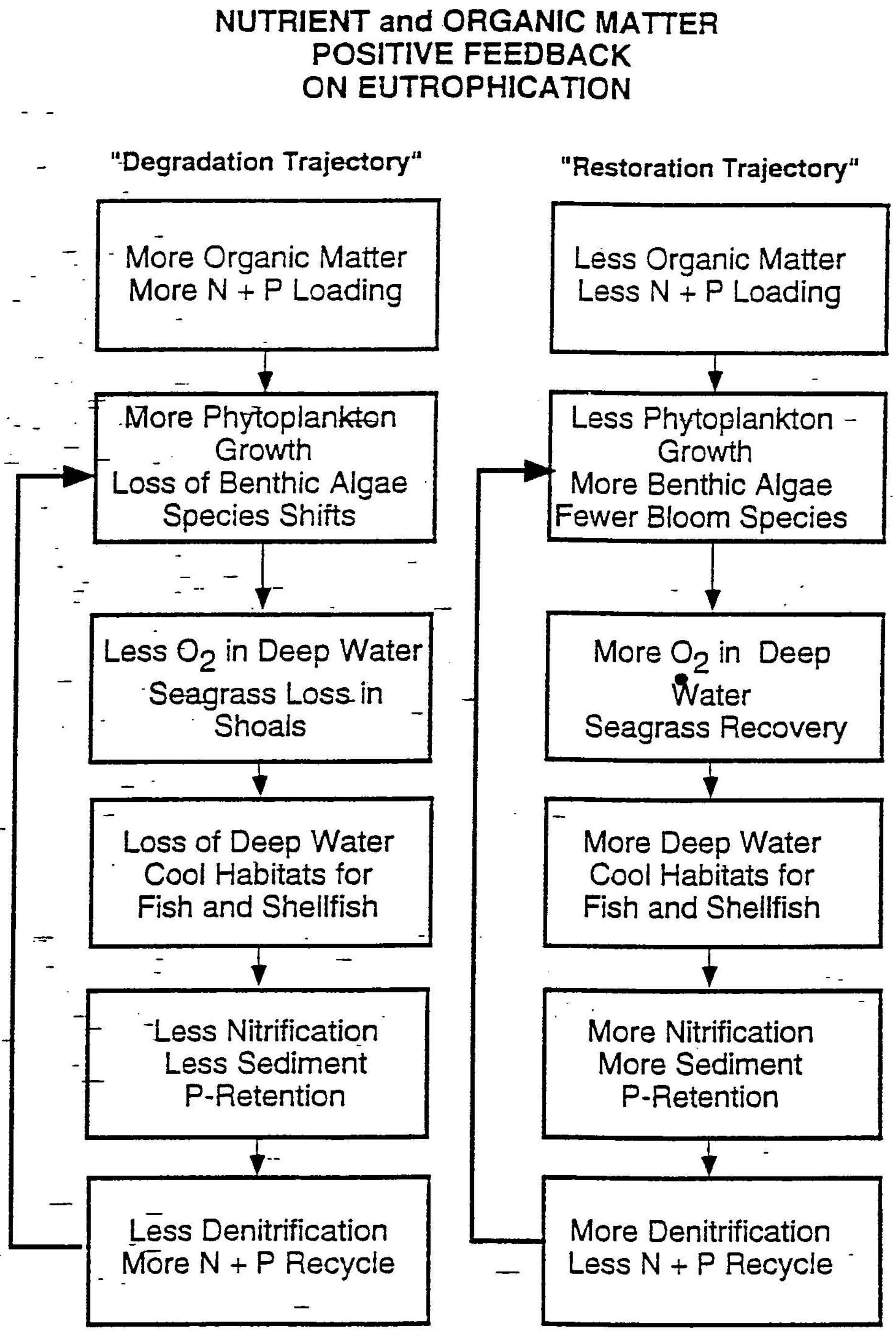


Figure 2. A simple schematic diagram indicating some of the key processes involved in the degradation and restoration trajectories of estuarine eutrophication. Also included are some of the major ecological consequences of eutrophication.

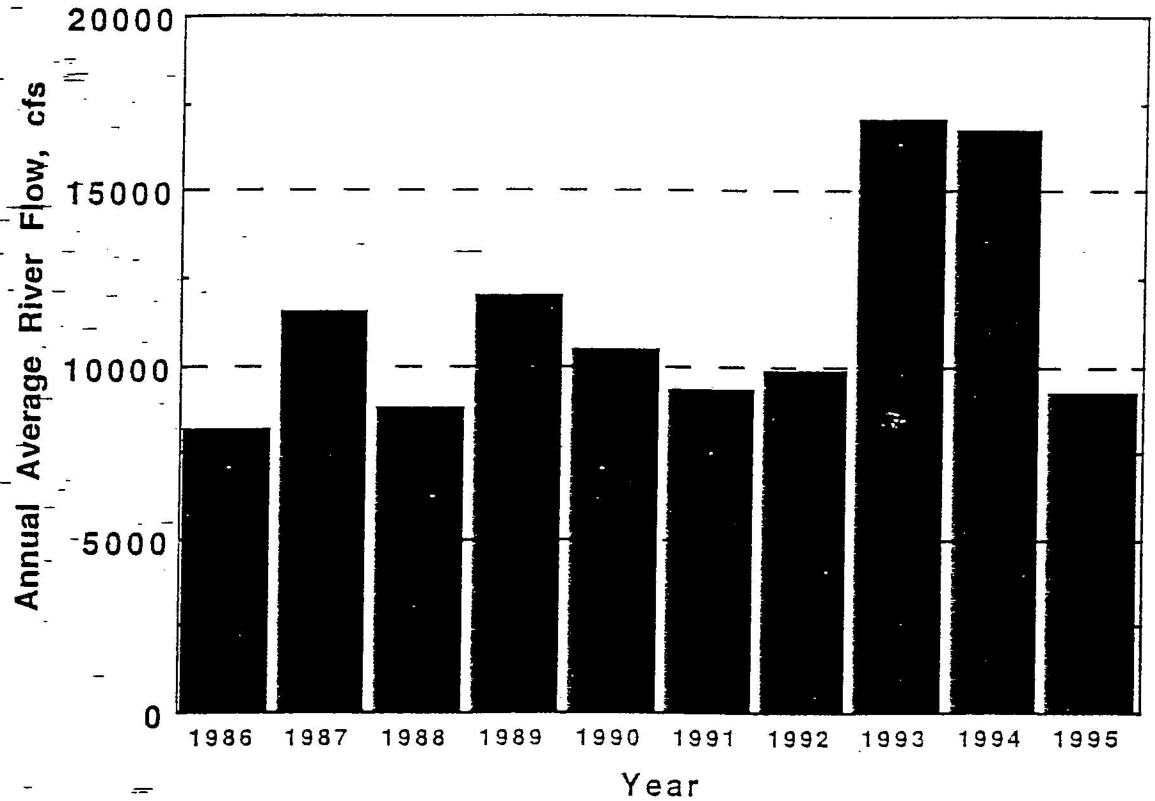


Figure 3. Annual average river flow (cfs) measured at the fall line of the Potomac River from 1986 - 1995. Data are from the United States Geological Survey.

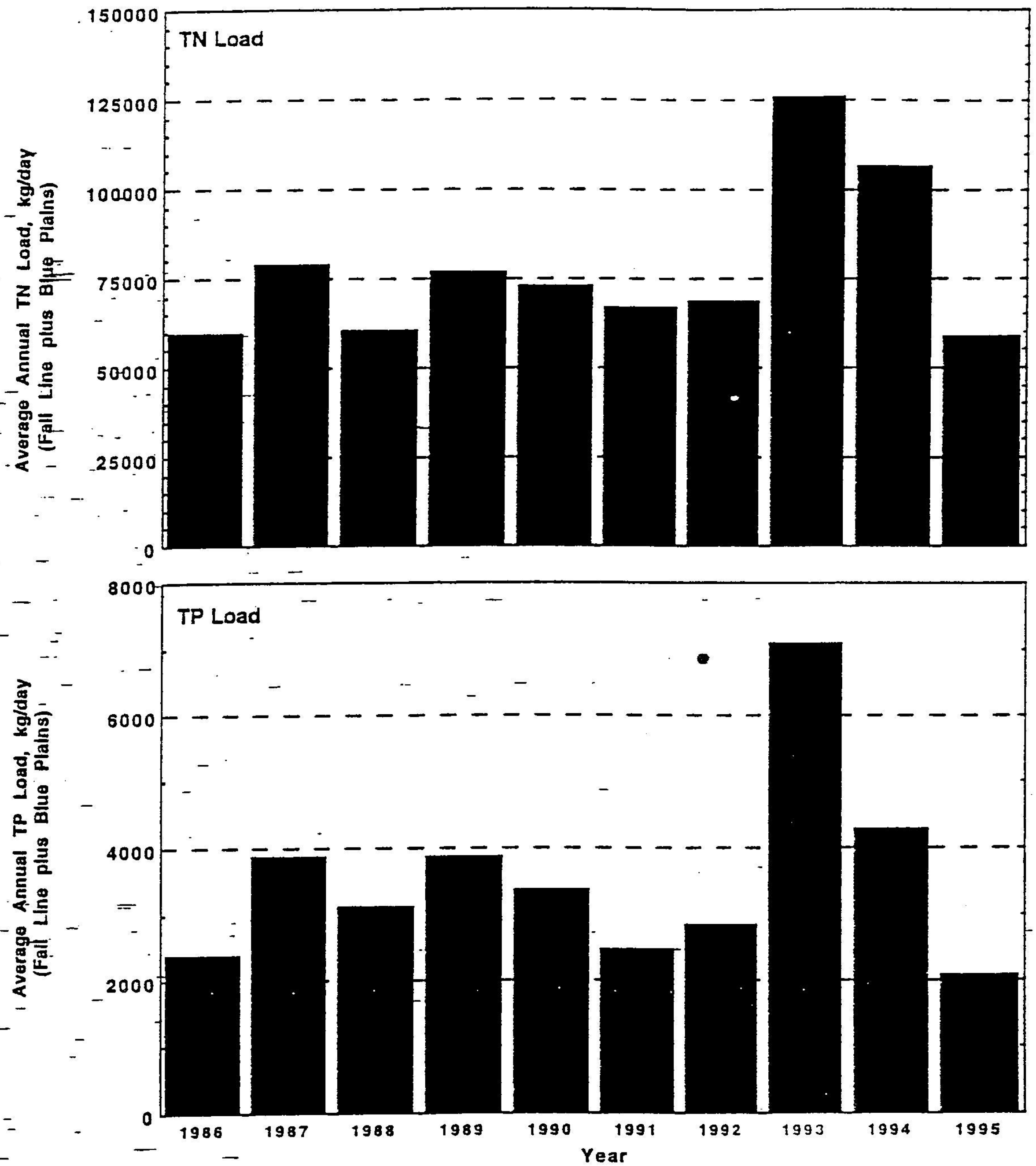


Figure 4. A series of bar graphs indicating average annual loads of total nitrogen (TN) and total phosphorus (TP) entering the Potomac River estuary during the period 1986-1995. These loads include the fall line load plus discharges of TN and TP from the Blue Plains sewage treatment plant. Other point and diffuse sources entering the estuary downstream of the fall line are not included. In addition, atmospheric deposition of TN and TP to surface waters of the Potomac are not included. Data are from the United States Geological Survey Fall Line Monitoring Program.

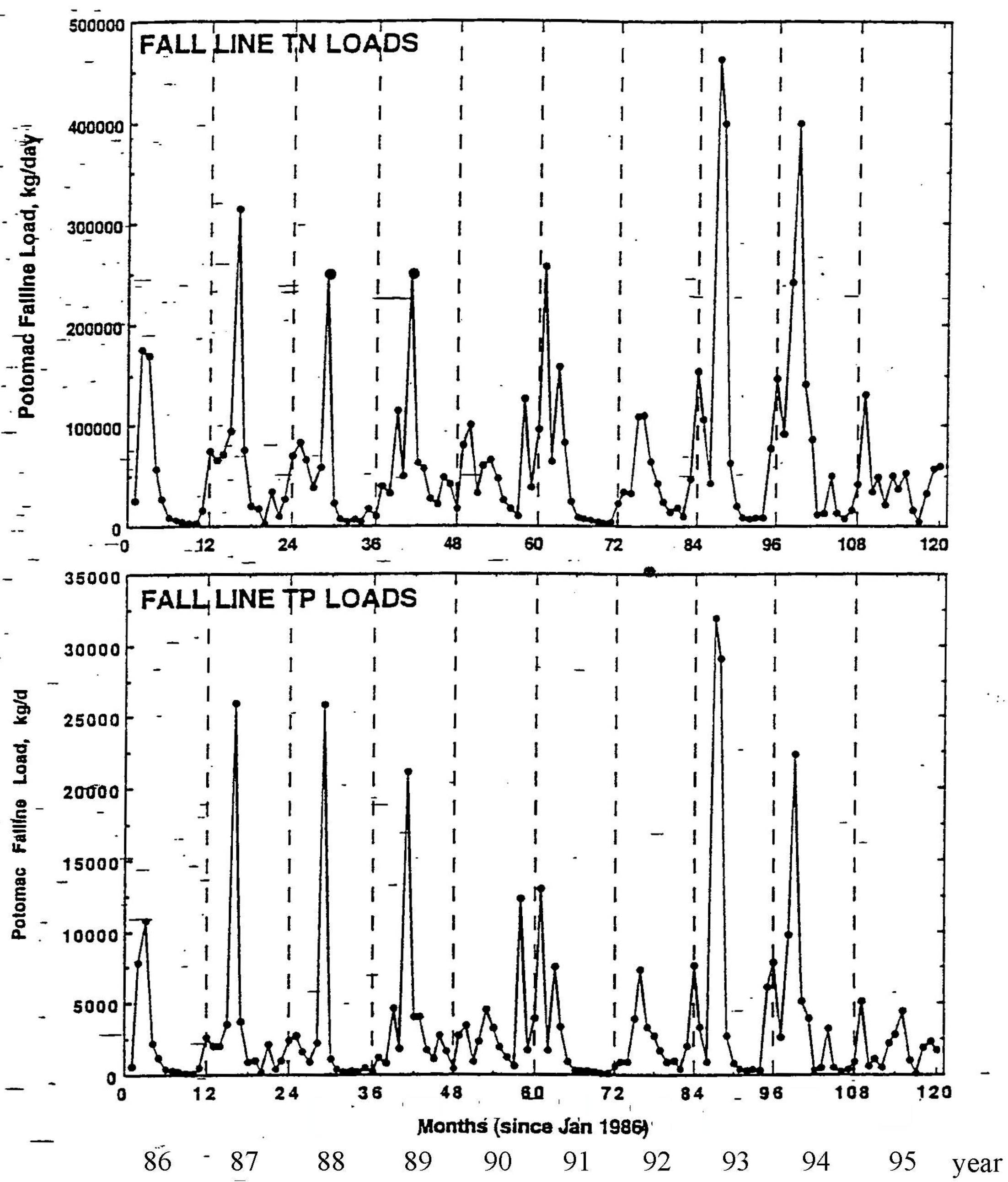


Figure 5. Monthly average total nitrogen (TN) and total phosphorus (TP) loads measured at the fall line of the Potomac River estuary from January, 1996 through December, 1995. Point source and diffuse source loads entering the estuary below the fall line are not included. Atmospheric deposition of TP and TP directly to surface waters of the estuary is also not included.

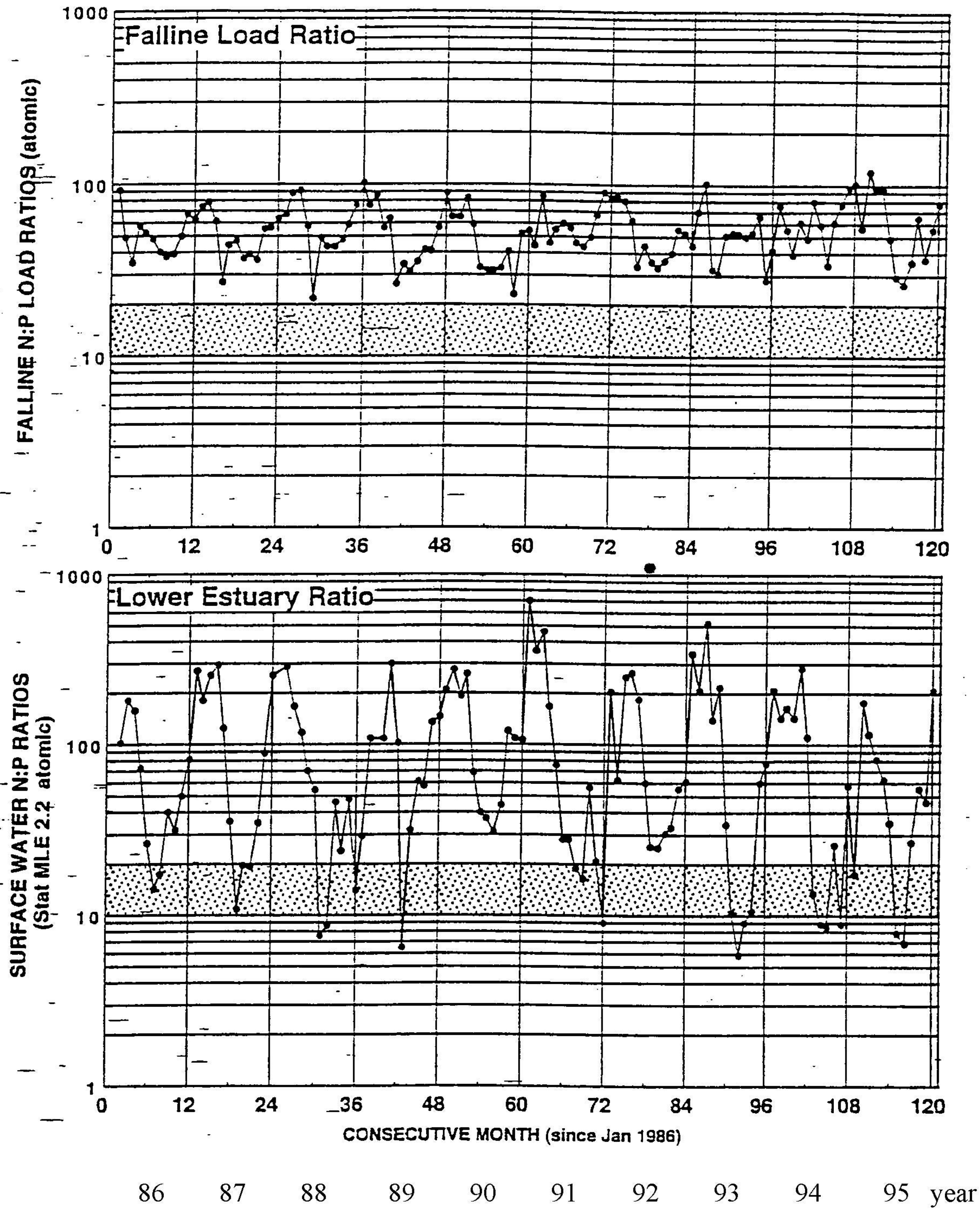


Figure 6. Average monthly ratios of total nitrogen to total phosphorus (TN : TP) of the fall line load and of surface waters in the mesohaline region (Sta. MLE 2.2) of the Potomac River estuary. Data were collected between January, 1986 and December, 1995 by the Maryland Chesapeake Bay Water Quality Monitoring Program. The shaded area on each figure indicates the approximate range of TN : TP ratios where potential N or P limitation is unlikely; values below 10 suggest possible N limitation and values above 20 suggest possible P limitation of phytoplankton communities.

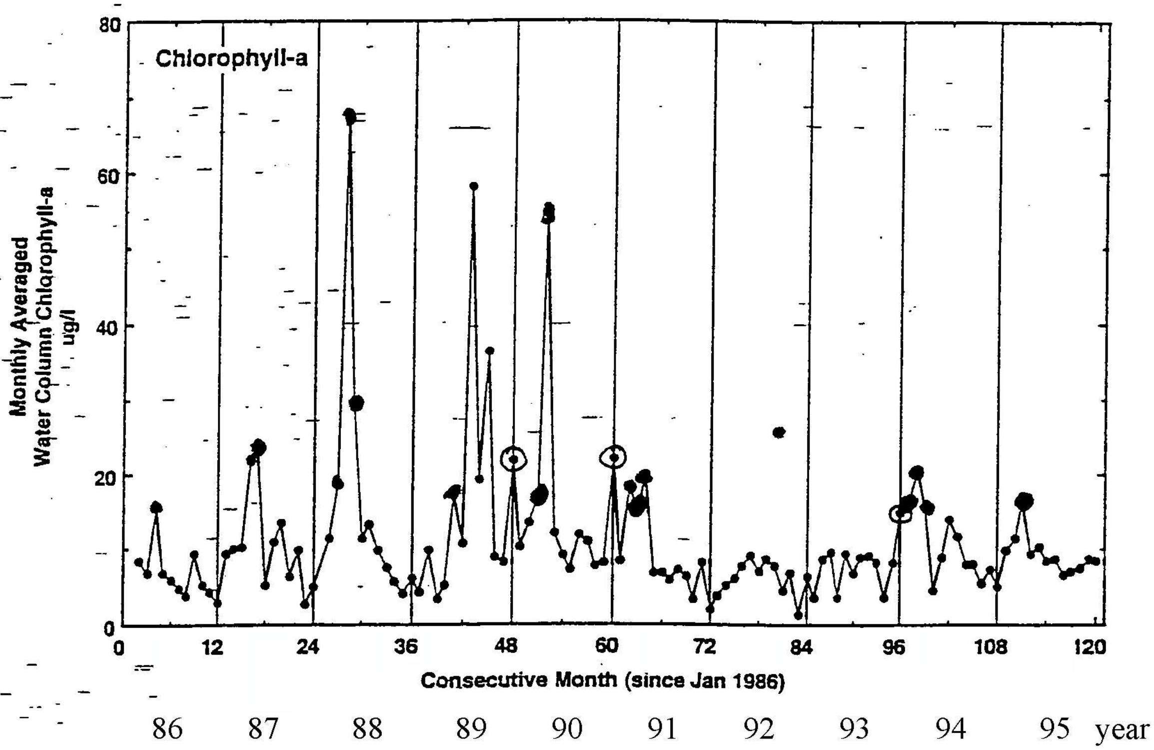


Figure 7. A plot of water column averaged chlorophyll-a concentrations at Sta MLE 2.2 located in the mesohaline region of the Potomac River estuary. Data were collected by the Maryland Chesapeake Bay Water Quality Monitoring Ptogram from January, 1986 through December, 1995.

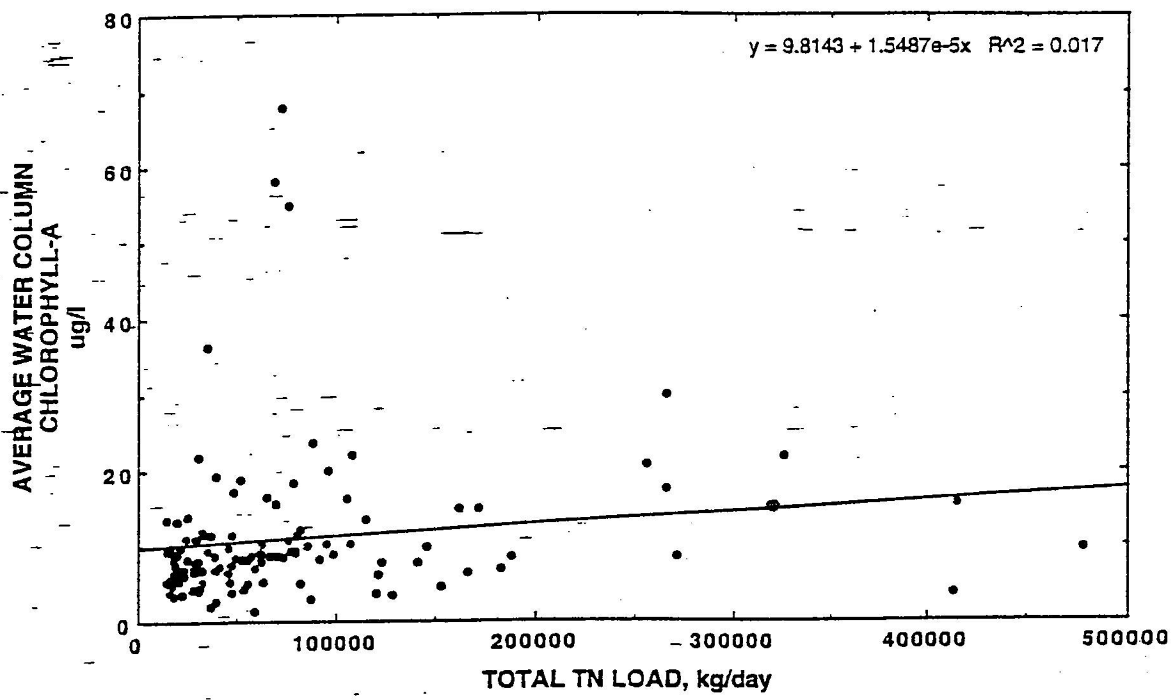


Figure 8. A scatter plot of water column averaged chlorophyll-a at a mesohaline station (MLE 2.2) versus total nitrogen (TN) loading rate measured at the fall line of the Potomac River. In this plot paired load and chlorophyll-a data were collected in the same month; there are no time lags between load and chlorophyll-a in this plot. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

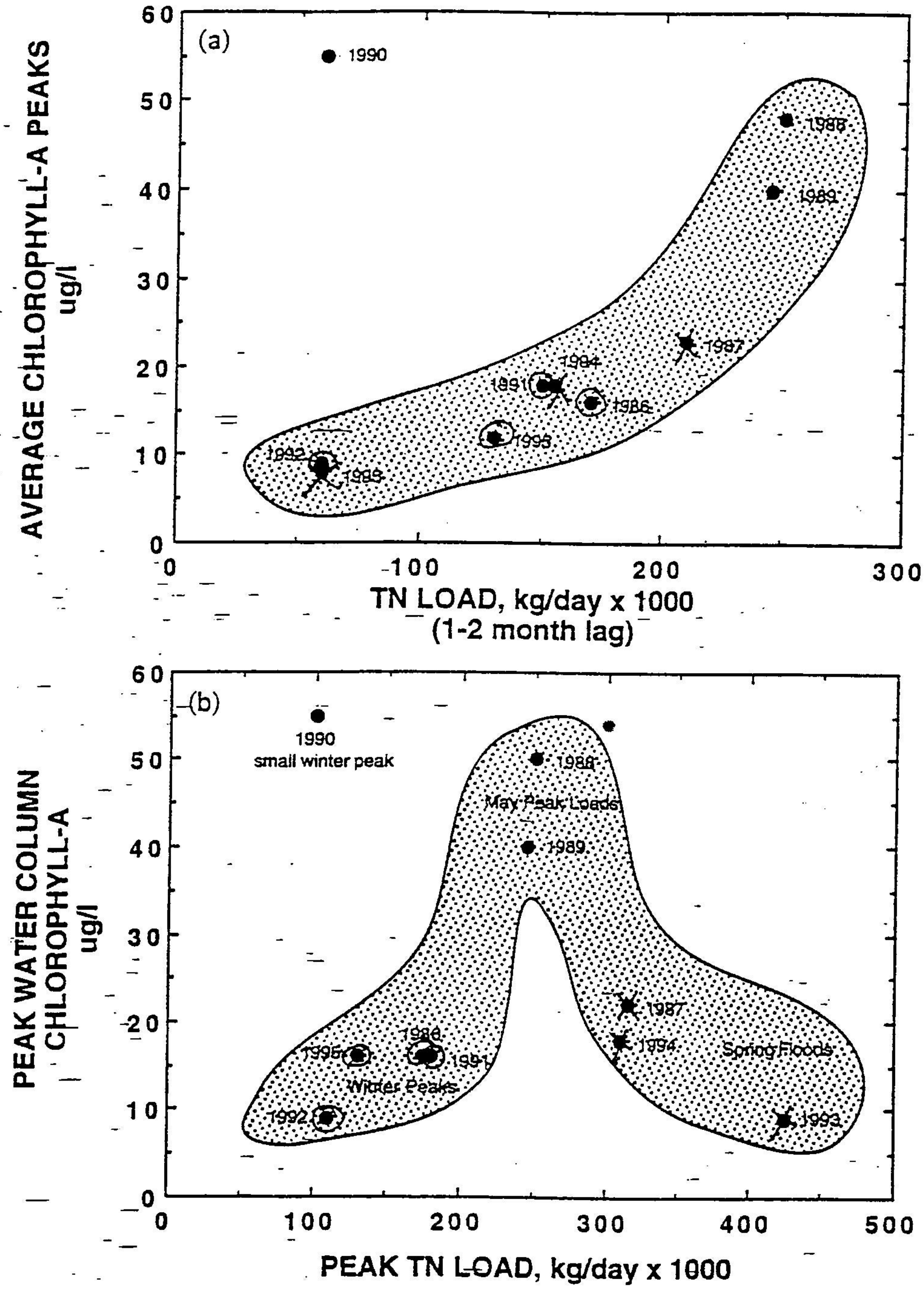


Figure 9. Scatter plots of water column averaged chlorophyll-a at a mesohaline station (MLE 2.2) versus several different functions of total nitrogen (TN) loading rate measured at the fall line of the Potomac River estuary. In (a) average peak chlorophyll-a concentrations were regressed against TN load measured 1-2 months prior to the chlorophyll-a peak. In (b) peak water column chlorophyll-a concentrations were regressed against peak TN load occurring prior to the chlorophyll-a peak. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

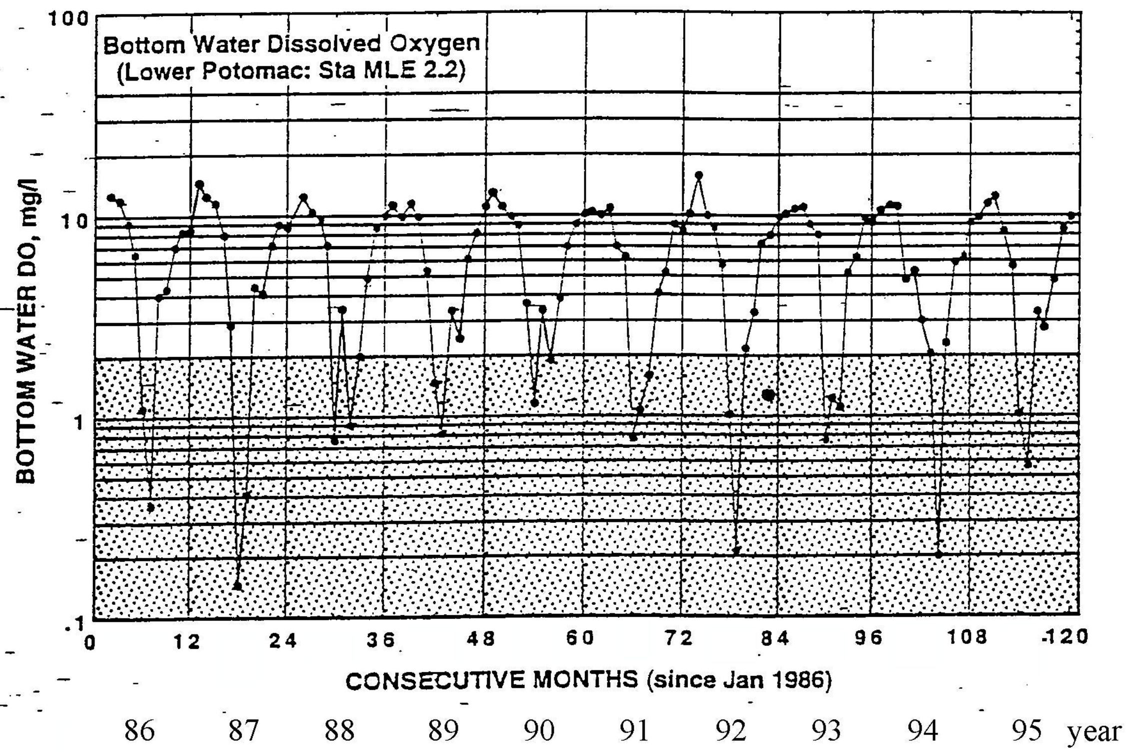


Figure 10. A summary of average monthly bottom water dissolved oxygen concentrations at a station in the mesohaline region of the Potomac River estuary (Sta MLE 2.2). The stippled area of the figure indicates observations with dissolved oxygen concentrations less than 2 mg/l. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

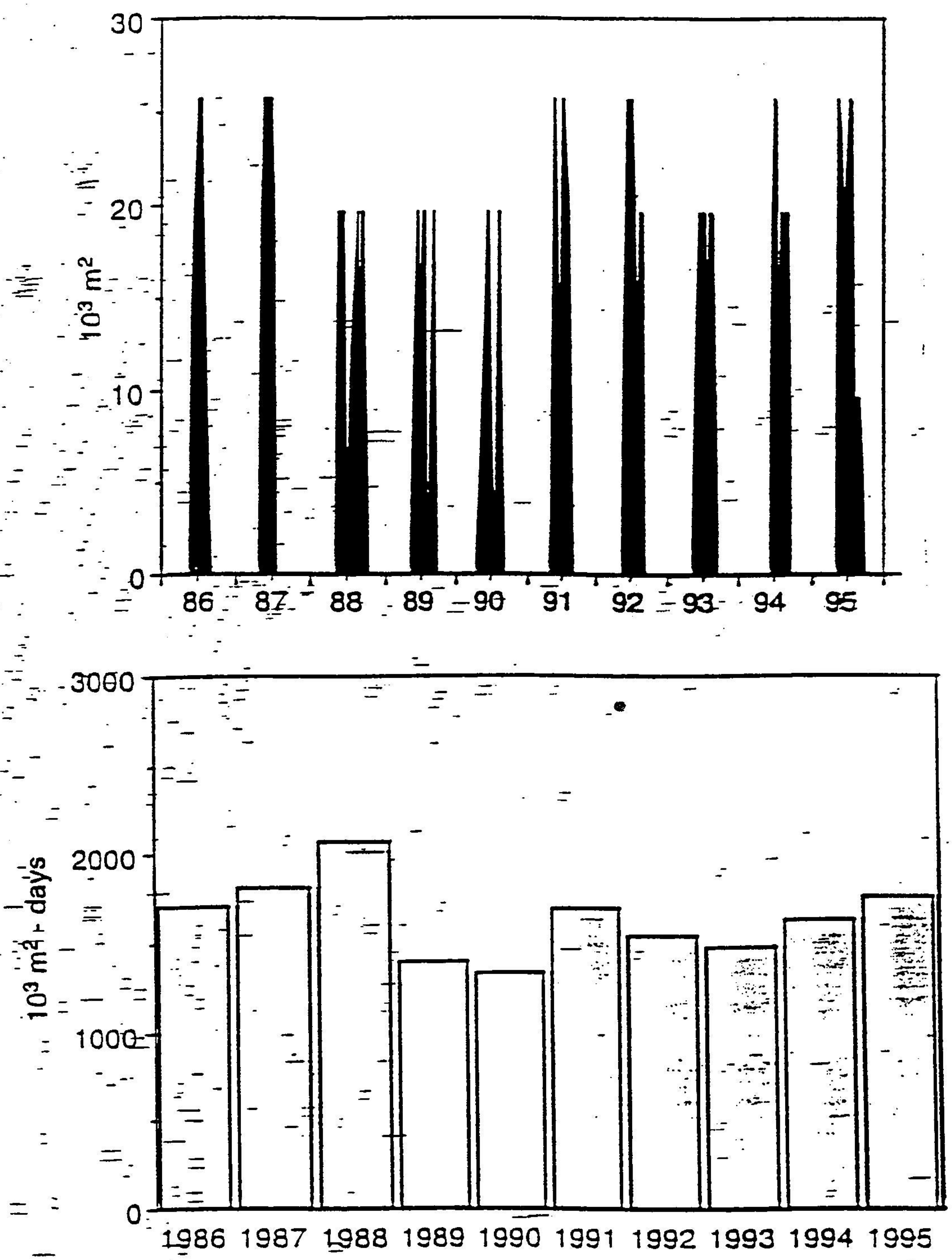


Figure 11. Annual estimate of the hypoxic (DO < 2.0 mg/l) cross-sectional area at a mesohaline site (river cross-section at Sta MLE 2.2) in Potomac River estuary and hypoxic cross-sectional area days at the same location. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

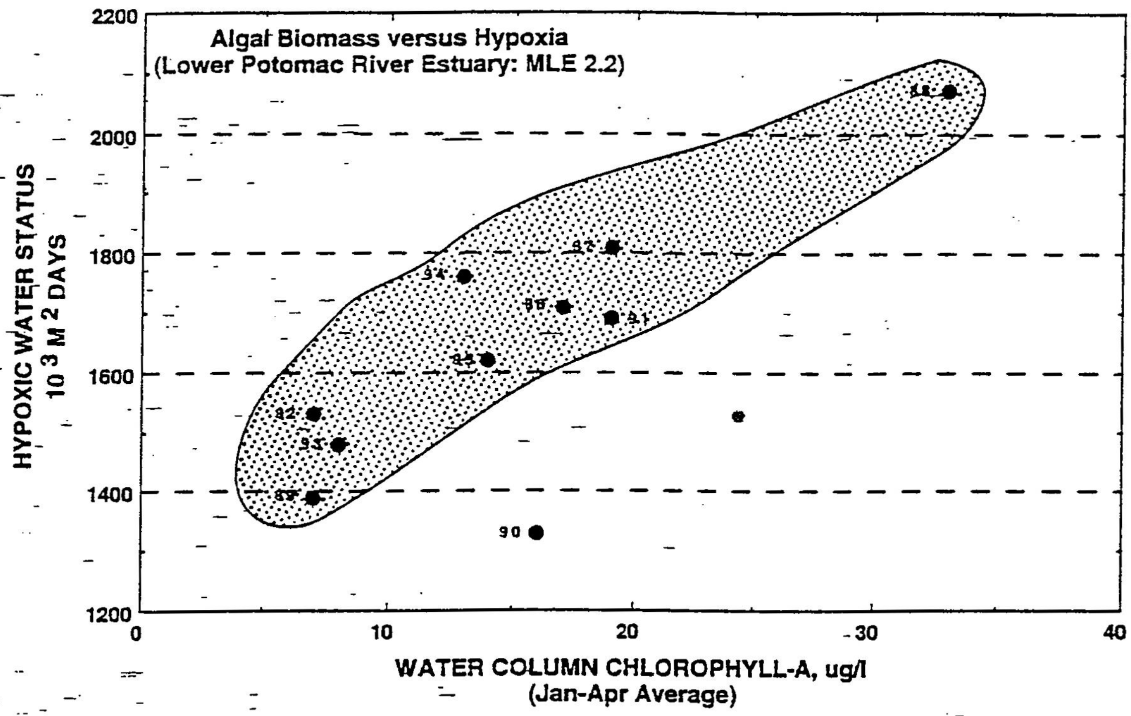


Figure 12. A scatter plot of annual hypoxic (< 2 mg/l) water status versus seasonal (average of January - April) water column chlorophyll-a concentrations at a station in the mesohaline region of the Potomac River estuary. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program. Hypoxic water status represents the product of the cross-sectional area of the Potomac River at station MLE 2.2 which had dissolved oxygen concentrations below 2 mg/l multiplied by the number of days this condition persisted.

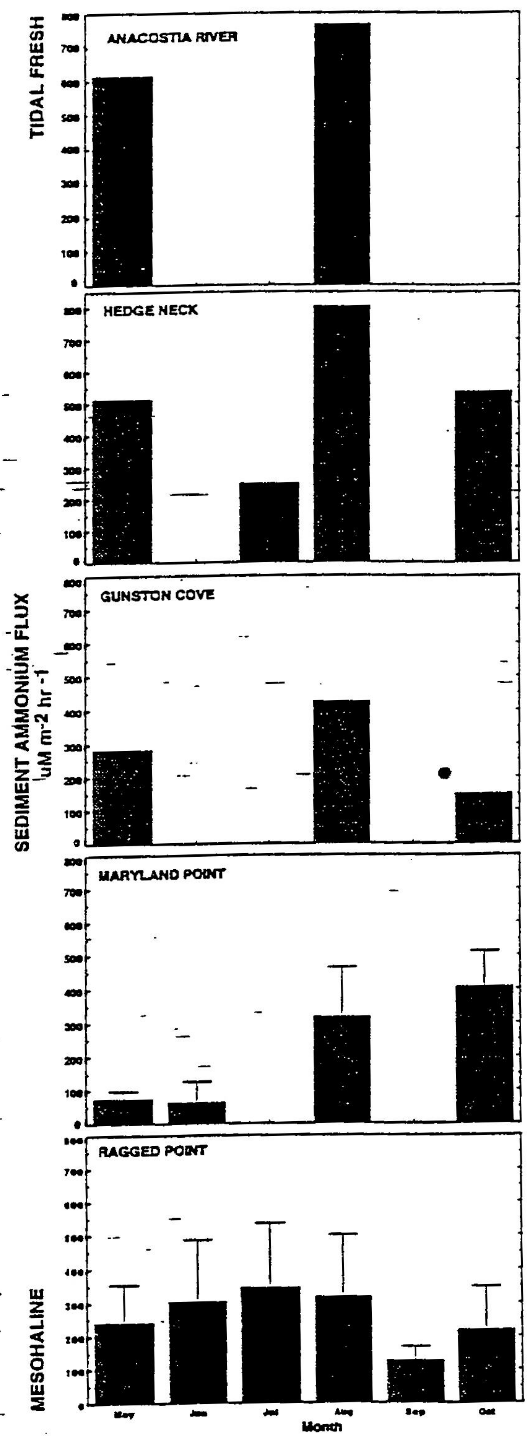


Figure 13 a. Monthly average sediment-water exchanges of ammonium at stations located along the Potomac River estuary from tidal fresh to mesohaline regions. Average monthly fluxes at Ragged Point were based on measurements collected between 1985 and 1996; average fluxes at Maryland Point were based measurements collected between 1985 and 1988 and 1992; fluxes at remaining stations were based on a single year of observation. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

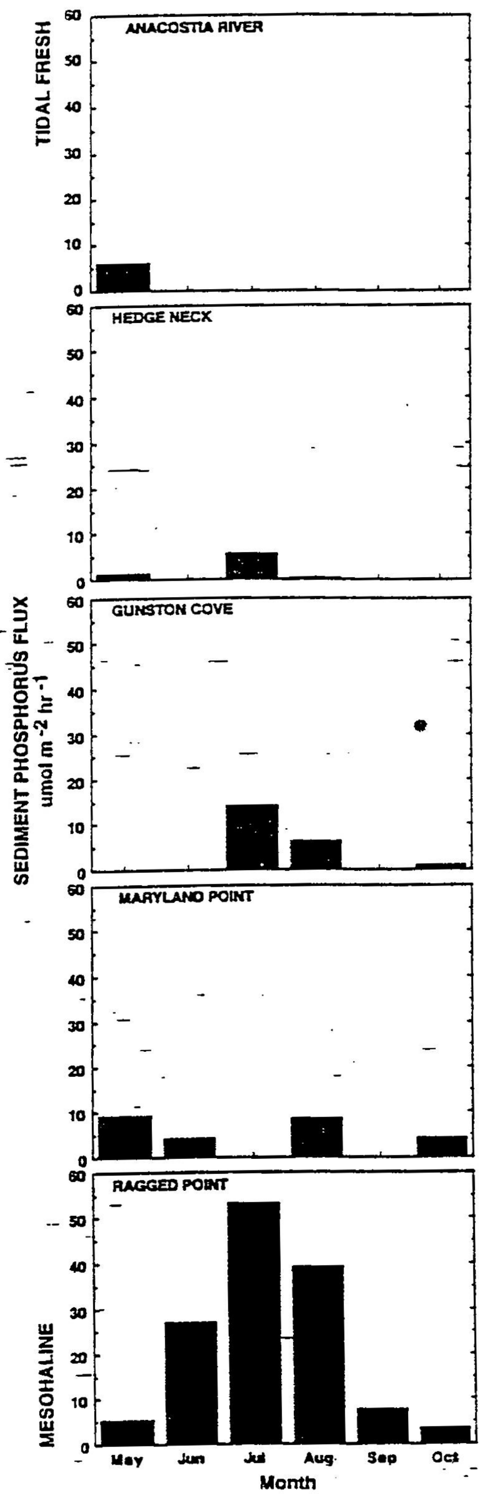


Figure 13 b. Monthly average sediment-water exchanges of phosphorus at stations located along the Potomac River estuary from tidal fresh to mesohaline regions. Average monthly fluxes at Ragged Point were based on measurements collected between 1985 and 1996; average fluxes at Maryland Point were based measurements collected between 1985 and 1988 and 1992; fluxes at remaining stations were based on a single year of observation. Data are from the Maryland Chesapeake Bay Water Quality Monitoring Program.

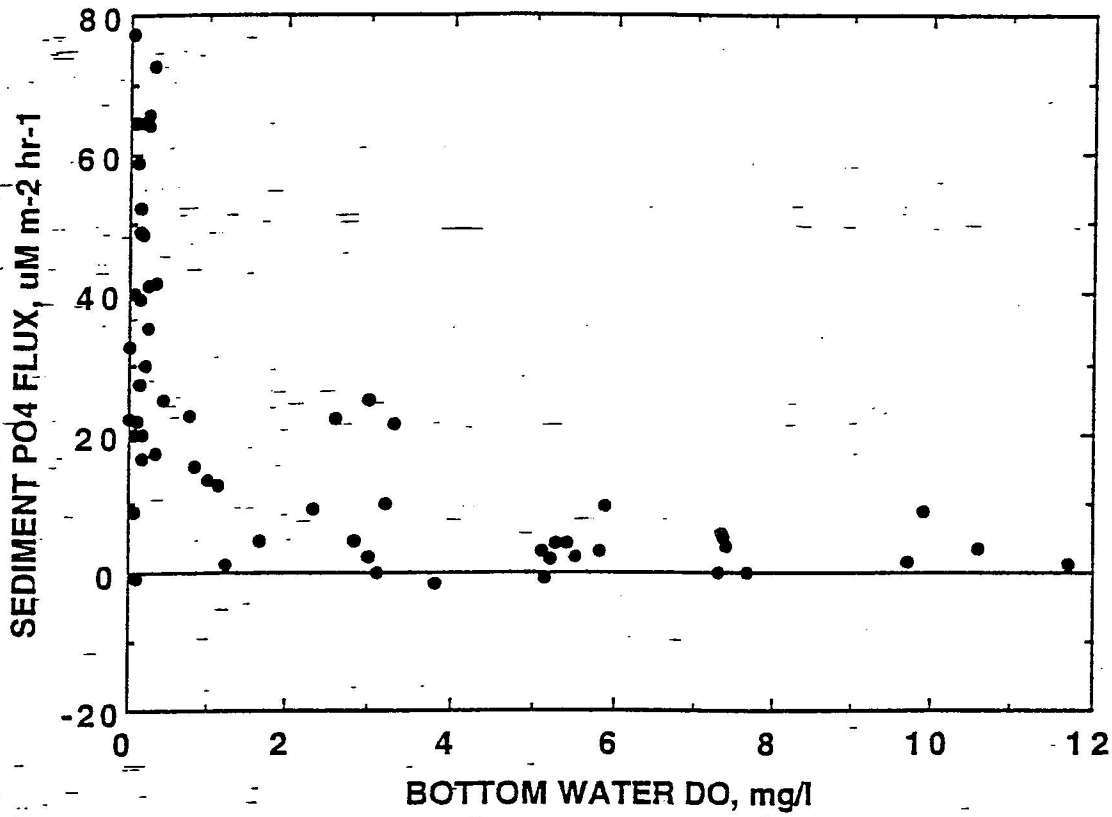


Figure 14. A scatter plot of sediment-water phosphorus fluxes versus bottom water dissolved oxygen concentrations from a station in the mesohaline region of the Potomac River estuary (Sta. MLE 2.2). Positive and negative values on the Y-axis represent fluxes from sediments to water and water to sediments, respectively. All of the larger phosphorus fluxes (> 10 umol $m^{-2}$ $hr^{-1}$) occurred under hypoxic conditions.

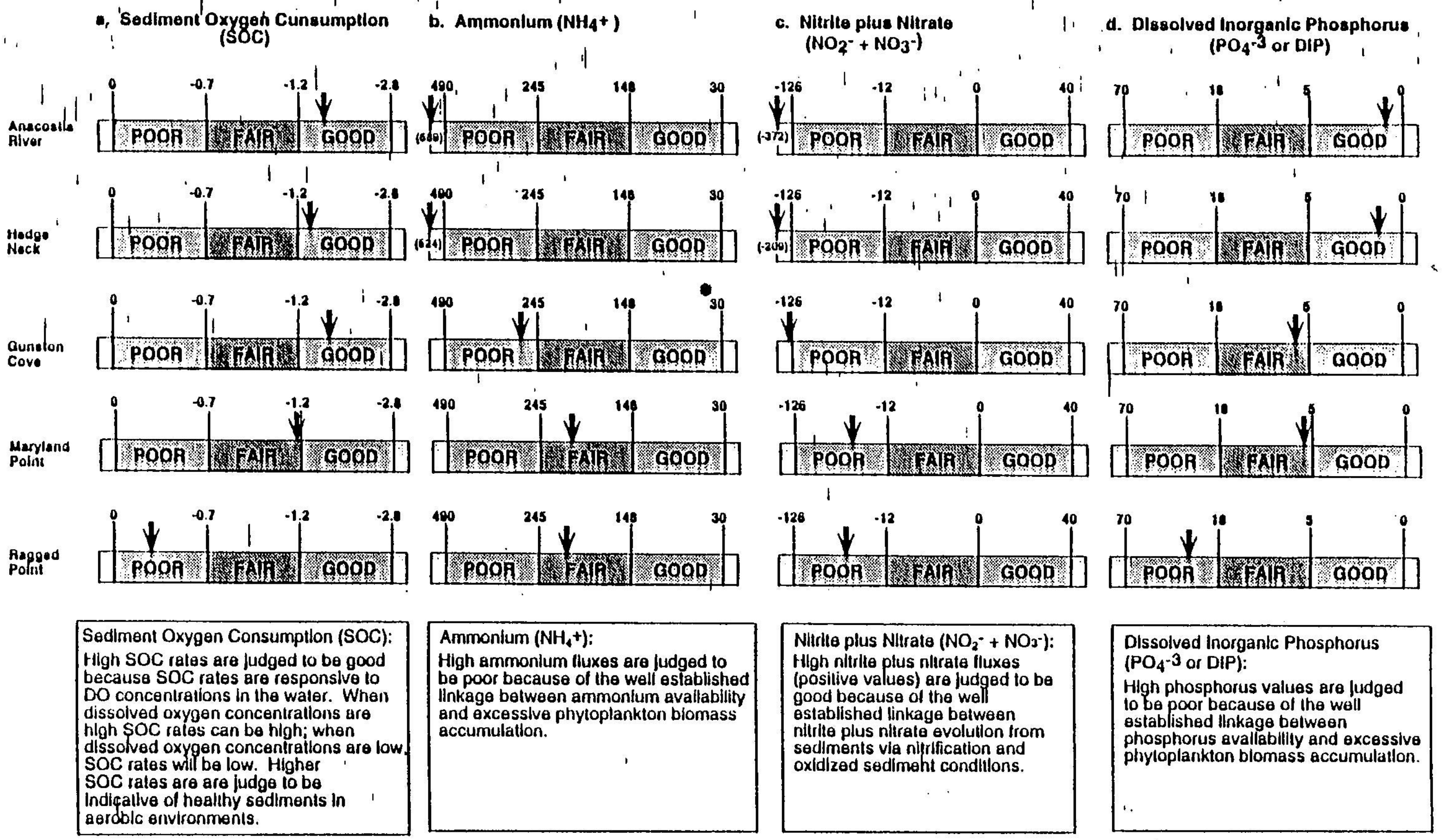


Figure 15. A summary of the status of sediment-water oxygen and nutrient exchanges for several locations in the Potomac River estuary. Stations are arranged from up-river (top of diagram) to down-river (bottom of diagram). Details concerning the development and scaling of status bars is provided in the text. In brief, for each flux variable (e.g. SOC) all data collected at 8 regularly sampled (1985 - 1996) stations in Chesapeake Bay (including one station in the lower Potomac River; Ragged Point) were combined and the 5th, 95th, 35th and 65th percentiles determined. In each status bar these are indicated by vertical lines separating the catagories of poor, fair and good and the numerical value of the flux separating each catagory is indicated. Downward pointing arrows on each bar represent the current status of a sediment-water flux variable. The status at Ragged Point is based on the mean of fluxes observed during the period 1994-1996; at Maryland Point status is based on the mean of fluxes measured from 1985-1988 and 1992; status at the remaining stations is based on measurements made during a single year. In a few cases fluxes measured in the Potomac exceeded the range of previously measured values and in these cases the actual flux value is indicated in parentheses at one end of the status bar. At the base of the figure the general criteria for judging flux status as good, fair or poor is provided and further discussed in the text. The development of these status bars exactly follows the procedure adopted by the Chesapeake Bay Program; determination of current status at Ragged Point also exactly follows that procedure but status at the remaining stations was determined using data from any year in which measurements were available.

Table 1a. Summary of seasonal Kendall test statistics (not flow adjusted) based on data collected at a station in the mesohaline portion of the Potomac River (Ragged Point) for six sediment-water flux variables. Data were collected from 1985 - 1996 and 4 to 6 measurements were made during each year. The term "not flow adjusted" indicates that flux data were not modified prior to statistical testing in any way because of freshwater flow conditions during the period of measurement. Significance: + p = 0.10; * p = 0.05; ** p = 0.01; *** = 0.001

**a. Sediment Oxygen Consumption (SOC; [g $O_2$ $m^{-2}$ $day^{-1}$ $yr^{-1}$])**

| Ragged Point (RGPT) | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Sign | 1 | 6 | -9 | -13 | -22 | 2 | -3 | 1 | -37 |
| p value | | 0.55 | 0.53 | | 0.08+ | | 0.77 | | 0.11 |
| n | 3 | 8 | 11 | 8 | 11 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -42 | -44 | -35 |
| p value | 0.04* | 0.03* | 0.02* |

**b. Ammonium ($NH_4$; [µM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| Ragged Point (RGPT) | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Sign | -1 | -4 | -2 | -8 | -12 | 5 | -1 | -3 | -26 |
| p value | | 0.72 | 0.95 | 0.40 | 0.45 | 0.47 | 1.00 | | 0.32 |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -17 | -22 | -20 |
| p value | 0.48 | 0.34 | 0.25 |

**c. Nitrite ($NO_2$; [µM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| Ragged Point (RGPT) | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Sign | 0 | -5 | -6 | 10 | -1 | 1 | 5 | 0 | 4 |
| p value | | 0.47 | 0.58 | 0.28 | | 1.00 | 0.47 | | 0.86 |
| n | 1 | 6 | 8 | 8 | 8 | 6 | 6 | 1 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | 4 | 3 | 9 |
| p-value | 0.84 | 0.87 | 0.48 |

Table 1a (continued). Summary of seasonal Kendall test statistics (not flow adjusted) based on data collected at a station in the mesohaline portion of the Potomac River (Ragged Point) for six sediment-water flux variables. Data were collected from 1985 - 1996 and 4 to 6 measurements were made during each year. The term "not flow adjusted" indicates that flux data were not modified prior to statistical testing in any way because of freshwater flow conditions during the period of measurement. Significance: + p = 0.10; * p = 0.05; ** p = 0.01; *** = 0.001.

**d. Nitrite plus nitrate ($NO_2 + NO_3$; [μM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT)+ | | | | | | | | | |
| Sign | -3 | 2 | -28 | -10 | -21 | 8 | 1 | -1 | -52 |
| p value | | 0.90 | 0.06+ | 0.28 | 0.17 | | 1.00 | | 0.04* |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -51 | -59 | -31 |
| p value | 0.03* | 0.01** | 0.07+ |

**e. Dissolved Phosphorus ($PO_4^-$; [μM P $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | 3 | -6 | 4 | -8 | -6 | 7 | 11 | -1 | 4 |
| p value | | 0.55 | 0.84 | 0.40 | 0.73 | 0.27 | 0.14 | | 0.91 |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -3 | -10 | -14 |
| p value | 0.93 | 0.68 | 0.44 |

**f. Silicate ($Si(OH)_4$; [μM Si $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | -3 | -2 | 7 | -5 | 31 | 2 | -3 | -1 | 24 |
| p value | | 0.90 | 0.64 | 0.47 | 0.005** | 0.75 | 0.77 | | 0.28 |
| n | 3 | 8 | 11 | 6 | 10 | 4 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | 35 | 33 | 26 |
| p-value | 0.06+ | 0.07+ | 0.04* |

Table 1b. Summary of seasonal Kendall test statistics (flow adjusted) based on data collected at a station in the mesohaline portion of the Potomac River (Raggec Point) for six sediment-water flux variables. Data were collected from 1985 - 1996 and 4 to 6 measurements were made during each year. The term "flow adjusted' indicates that flux data from each month and for groups of months were regressed against river flow averaged for the January through April period of the same year Residuals from this analysis were then used in the seasonal Kendall test. Flow correction represents an attempt to exclude natural effects (river flow variability) anc test for trends related to management actions (nutrient load reduction). Significance: + $p = 0.10$; * $p = 0.05$; ** $p = 0.01$; *** = 0.001

**a. Sediment Oxygen Consumption (SOC; [g $O_2$ $m^{-2}$ $day^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | -1 | 8 | -9 | -12 | -16 | 7 | -3 | -1 | -27 |
| p value | | 0.40 | 0.53 | 0.18 | 0.24 | 0.27 | 0.77 | | 0.26 |
| n | 3 | 8 | 11 | 8 | 11 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -30 | -37 | -28 |
| p value | -0.16 | 0.07+ | 0.07+ |

**b. Ammonium ($NH_4$; [µM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | -1 | -8 | -12 | -8 | -12 | 9 | -1 | -1 | -34 |
| p value | | 0.40 | 0.45 | 0.40 | 0.45 | 0.14 | 1.00 | | 0.19 |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -23 | -32 | -20 |
| p value | 0.33 | 0.16 | 0.25 |

**c. Nitrite ($NO_2$; [µM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])**

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | 0 | -3 | 2 | 4 | -8 | -3 | -9 | 0 | -17 |
| p value | | 0.72 | 0.90 | 0.72 | 0.40 | 0.72 | 0.14 | | 0.34 |
| n | 1 | 6 | 8 | 8 | 8 | 6 | 6 | 1 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -5 | -2 | -4 |
| p-value | 0.79 | 0.94 | 0.79 |

Table 1b (continued). Summary of seasonal Kendall test statistics (flow adjusted) based on data collected at a station in the mesohaline portion of the Potomac River (Ragged Point) for six sediment-water flux variables. Data were collected from 1985 - 1996 and 4 to 6 measurements were made during each year. The term "flow adjusted" indicates that flux data from each month and for groups of months were regressed against river flow averaged for the January through April period of the same year. Residuals from this analysis were then used in the seasonal Kendall test. Flow correction represents an attempt to exclude natural effects (river flow variability) and test for trends related to management actions (nutrient load reduction). Significance: + p = 0.10; * p = 0.05; ** p = 0.01; *** = 0.001.

d. Nitrite plus nitrate ($NO_2 + NO_3$; [µM N $m^{-2}$ $hr^{-1}$ $yr^{-1}$])

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | -1 | 6 | -24 | -6 | -26 | 9 | -3 | -1 | -46 |
| p value | | 0.55 | 0.11 | 0.55 | 0.09+ | 0.14 | 0.77 | | 0.07+ |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | -47 | -56 | -32 |
| p value | 0.04* | 0.01** | 0.06+ |

e. Dissolved Phosphorus ($PO_4^-$; [µM P $m^{-2}$ $hr^{-1}$ $yr^{-1}$])

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | 1 | -8 | -4 | -2 | 8 | 9 | 9 | -1 | 2 |
| p value | | 0.40 | 0.84 | 0.90 | 0.95 | 0.14 | 0.24 | | 0.97 |
| n | 3 | 8 | 12 | 8 | 12 | 6 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | 1 | -8 | -4 |
| p value | 1.00 | 0.75 | 0.86 |

f. Silicate ($Si(OH)_4$; [µM Si $m^{-2}$ $hr^{-1}$ $yr^{-1}$])

| | April | May | June | July | August | September | October | November | Annual |
|---|---|---|---|---|---|---|---|---|---|
| Ragged Point (RGPT) | | | | | | | | | |
| Sign | -1 | -4 | 57 | -5 | 27 | 2 | -3 | -1 | 20 |
| p value | | 0.72 | 0.76 | 0.47 | 0.02* | 0.75 | 0.77 | | 0.37 |
| n | 3 | 8 | 11 | 6 | 10 | 4 | 7 | 3 | |

| | Jun-Sep | Jun-Aug | Jul-Aug |
|---|---|---|---|
| Sign | 29 | 27 | 22 |
| p-value | 0.12 | 0.15 | 0.09+ |