ABSTRACT

Title of Thesis: FACTORS REGULATING VARIABILITY IN WATER QUALITY AND NET BIOGEOCHEMICAL FLUXES IN THE PATUXENT RIVER ESTUARY

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Net biogeochemical production and transport rates for several variables were computed for the Patuxent River estuary from 1985 to 2003 using a box model. Monthly rate estimates were analyzed for temporal patterns and variability in response to climatic factors and nutrient management. The middle estuary was the most productive estuarine region and was characterized by strong pelagic-benthic coupling. Phytoplankton biomass in this region peaked in spring as fueled by seaward nutrient inputs. Nutrients regenerated from decomposition of this spring bloom were required to support summer productivity.

Improvements of sewage treatment in the watershed resulted in declining point source nutrient loads to the estuary, but water quality did not improve in the mesohaline estuary. Poor water quality in the middle estuary was maintained by persistent non-point nutrient loads, while degrading water quality in the lower estuary correlated with increasing DIN inputs from Chesapeake Bay, high river flow, and declining herbivorous grazing.

FACTORS REGULATING VARIABILITY IN WATER QUALITY AND NET BIOGEOCHEMICAL FLUXES IN THE PATUXENT RIVER ESTUARY

By

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BACKGROUND AND INTRODUCTION

Estuarine ecosystems are among of the most productive systems in the biosphere. High estuarine productivity is due, in part, to the large fluxes of nutrients and carbon to estuaries from adjacent terrestrial and riverine systems (Nixon 1995). Retention and recycling of these nutrients and carbon inputs within estuaries can sustain high productivity in times of low exogenous inputs (Kemp and Boynton 1984), but nutrient cycling processes may be complex and involve non-linear feedbacks (Kemp et al. 2005). Estuarine primary productivity provides fuel for upper trophic levels, but productivity is also linked to water quality problems (e.g., hypoxia) that may adversely affect upper trophic levels (Breitburg et al. 2003). Because of the importance of primary productivity to food webs (which are ultimately harvested by humans), a great deal of interest has been focused on understanding the factors regulating productivity and nutrient cycling and how these factors change over time and space.

Anthropogenic activities and climatic variability influence estuarine productivity and nutrient cycling (Paerl et al. 2006). Perhaps the most notable of anthropogenic influences on coastal systems is the widespread, elevated input of nutrients since the mid-20th century (Nixon 1995). The resulting increase in productivity has led to many ecosystem-level changes in estuaries, including changes in phytoplankton species composition, elevated export of algal material to bottom waters, and reduced water clarity (Paerl 1988, Cloern 2001). Fluctuations of freshwater inputs cause responses similar to nutrient enrichment and are perhaps the most direct climatic influence on estuarine ecosystems. In many systems, high freshwater inputs are associated with reduced dissolved oxygen concentrations and water clarity and increased phytoplankton biomass (Malone et al. 1988, Justic et al. 1996, Boynton and Kemp 2000). Assessing the interactions between nutrient management and freshwater flow is important for improved understanding of estuarine primary productivity and water quality.

Chesapeake Bay and its tidal tributaries have changed markedly during the past several decades in response to nutrient enrichment (D'Elia et al. 2003, Kemp et al. 2005). High inter-annual variability in freshwater inputs has occurred contemporaneously with changes in nutrient loads (Kemp et al. 2005). In the Patuxent River estuary, the sixth largest tributary of Chesapeake Bay, nutrient enrichment has led to increased algal biomass, hypoxic volume, and decline of once-abundant submerged aquatic vegetations beds (D'Elia et al. 2003, Stankelis et al. 2003). Towards the goal of reversing the negative effects of nutrient enrichment, sewage treatment upgrades in the Patuxent River watershed have led to reductions in point source phosphorus and nitrogen loads in the watershed, beginning in the 1980s.

In response to eutrophication, and in part to monitor the effects of nutrient load reductions, an ambitious water quality monitoring program has been established in Chesapeake Bay and its tributaries. The Chesapeake Bay Monitoring Program has been measuring water quality (e.g., nutrient and oxygen concentrations, water clarity) and ecosystem processes (e.g., primary production, sediment oxygen and nutrient exchanges) at many stations in the Patuxent River estuary since 1985. The resulting data sets present opportunities to analyze ecosystem level responses to climatic variability and anthropogenic effects. Such data may also be utilized to develop empirical models (Hagy 1996) and as baseline data to calibrate complex water quality models (Lung and Bai 2003).

Empirical modeling, which involves building simple, direct relationships between biological, chemical, or physical rates and the variables that drive them, can be used as a first order method to predict the response of these rates to climatic and anthropogenic forcing or internal variability. Such models were successfully developed to predict the response of lakes to nutrient loading (Vollenweider 1976) and were later developed for estuarine systems (e.g., Boynton and Kemp 2000). Empirical methods are grounded in observations, yet observations may be too infrequent or the driving forces to complex to accurately predict the rates using such simple formulations. Alternatively, sophisticated numerical simulation models aim to capture the detail in mechanisms that drive ecological rates. Complex models are advantageous, as they may be used to capture fundamental ecological and biogeochemical processes and can be calibrated with monitoring data (Lung and Bai 2003, Fisher et al. 2006). The disadvantages of these models are that they are often complex and highly tuned, making their construction, implementation, and analysis expensive in terms of time and resources. While there is value in both the empirical and numerical approaches, the development of intermediate complexity models may offer an alternative to traditional approaches.

An example of an intermediate complexity model includes the coupling of a simple physical transport model (often called a "box model") to available nutrient and carbon concentrations provided by water quality monitoring programs. The result is the calculation of simple, empirical estimates and proxies for transformations of oxygen, carbon, and nutrients in estuaries (Smith et al. 1991, Hagy 1996). Such an approach can be mechanistic, in that the functional relationships between biogeochemical rates and their driving variables can be explored; yet the model is also empirical because the rates and relationships are derived from *in situ* observations. Such rates, if comparable to direct measurements of similar processes, may be used to assess ecological interactions in estuaries (e.g., pelagic-benthic coupling, net ecosystem production), the seasonal variability in the processes, and to evaluate their response to climatic variability and changes in nutrient loading. Considering the widespread availability of hydrologic, hypsographic, and water quality data in many of the nation's coastal systems, box models provide the opportunity to transform these abundant measurements into meaningful ecological rates. The LOICZ program (Land-Ocean Interactions in the Coastal Zone) has begun to make such calculations in many of the world's estuaries.

The purpose of this thesis is to analyze a nineteen-year monitoring data set to address important questions regarding estuarine ecological processes and the response of these processes to external forcing. Box models are presented as useful tools to transform routine monitoring data into regionally resolved rates of net ecosystem production and net nutrient production and transport along the axis of the Patuxent River estuary. The work in this thesis is an extension of the box model analysis of Hagy (1996) and Hagy et al. (2000) and was based upon formulations originally developed by Pritchard (1969) and Officer (1980). Chapter I includes an examination and quantification of the spatial and temporal coupling of nutrient inputs to net ecosystem production and nutrient regeneration along the axis of the estuary. In

Chapter II, a time series (1985 to 2003) of water quality measurements and box model computed net production and transport rates are used to evaluate the response of the Patuxent River estuary to nutrient management and to variability in river flow.

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CHAPTER I

Spatial and temporal variability of biogeochemical processes in the Patuxent River estuary: Inferences from water quality data

Abstract

Regional, seasonal, and inter-annual variations of nutrient inputs, net ecosystem production, and pelagic-benthic interactions were examined in the Patuxent River estuary, a tributary of Chesapeake Bay. Monthly rates of net biogeochemical production and physical transport of carbon, oxygen (O_2), and nutrients were calculated for six estuarine regions using a data-constrained salt- and water-balance model (box model) and a time series of water quality data. Assuming fixed metabolic stoichiometry for O_2, carbon, and silicate, we also derived estimates of net carbon production, particulate organic carbon (POC) sinking, and net diatom growth. Analyses of monthly mean rates revealed distinct regional and seasonal patterns in net O_2 production, including late spring peaks in surface layer rates (80 to 100 mmol O_2 m^{-2} d^{-1}) and summer peaks in bottom layer rates (-100 to -200 mmol O_2 m^{-2} d^{-1}). Net O_2 production and chlorophyll *a*, which reached annual maxima in spring when NO_3^- inputs to the estuary peaked, were highest in the middle region of the estuary and correlated with net DIN and DSi uptake. Rates of POC sinking (10 to 90 mmol C m^{-2} d^{-1}), which also peaked during the spring bloom, were correlated with bottom layer nutrient regeneration and O_2 consumption at annual, but not monthly, timescales. Correlations between surface layer carbon production/sinking and bottom layer nutrient regeneration (i.e., pelagic-benthic coupling) were strongest in the middle estuary, where rates were high, water depth was relatively shallow, and

interaction with adjacent landward and seaward sub-systems was minimal. The magnitude of net O_2 production and nutrient uptake rates was enhanced by flow. Rates of net O_2 production, POC sinking, and nutrient regeneration agree favorably with previously measured rates in the estuary. This analysis demonstrates the potential to infer patterns and regulating factors for biogeochemical processes using box modeling and statistical analyses of basic water quality and hydrologic data.

Introduction

Estuarine ecosystems form the transition zone between adjacent terrestrial, riverine, and oceanic regions (Smith et al. 1991). Biogeochemically reactive organic and inorganic materials enter estuaries from surrounding watersheds and the atmosphere and are processed within estuaries prior to transport to adjacent oceans (Webster et al. 2000). Estuarine transformations of anthropogenic and terrestrially derived materials are regulated by a balance between physical transport and biogeochemical uptake and recycling (Kemp and Boynton 1984, Smith et al. 1991, Howarth et al. 1996). Important transformations include both biological processes, such as organic carbon production and nutrient uptake/regeneration (Kemp and Boynton 1984), and physical-chemical reactions, such as flocculation and surface sorption/desorption (e.g., Sholkovitz 1976). Understanding the nature and magnitude of these transformation processes is essential for evaluating and managing estuarine production and nutrient cycling.

Inter-annual variations in river flow exert strong control over biogeocheimical transformation processes in estuaries. River flow may enhance phytoplankton biomass and productivity in mid-estuarine regions of temperate systems via enhanced nutrient inputs (Boynton and Kemp 2000), but flow may also reduce primary production in some systems where increased inputs of suspended particles tend to induce light-limited photosynthesis (Cloern et al. 1983, Howarth et al. 2000). Although elevated nutrient inputs delivered with high flow may enhance photosynthesis and associated net ecosystem production (D'Avanzo et al. 1996, Caffrey 2004), higher inputs of labile organic carbon tend to increase respiration, thereby decreasing net ecosystem production (Smith and Hollibaugh 1997). Higher freshwater inputs may also increase particulate organic matter sinking, as well as benthic respiration and nutrient regeneration (Boynton and Kemp 2000). Direct denitrification may be enhanced by flow if NO_3^- loading is elevated (Jorgensen and Sorensen 1988, Kana et al. 1998), while coupled nitrification and denitrification may be either enhanced with higher NH_4^+ recycling or depressed due to hypoxia (Seitzinger 1988, Kemp et al. 1990). Although river flow is a key driver of biogeochemical processes at decadal scales for whole estuaries, important variability also occurs at shorter temporal and spatial scales.

Many biogeochemical processes in estuaries vary widely over regional scales (Taft et al. 1978, Kemp et al. 1997, Harding et al. 2002). For example, phytoplankton biomass and productivity maxima in estuaries often develop where turbidity is low and nutrient limitation is relieved (Pennock and Sharp 1994). Regional variation in net ecosystem production is also common in many estuarine systems, ranging from net heterotrophy in landward waters to net autotrophy in seaward waters (Smith et al. 1991, Heath 1995, Howarth et al. 1996, Kemp et al. 1997). Benthic respiration and nutrient regeneration display distinct patterns of variation along salinity and depth gradients (Fisher et al. 1982, Boynton and Kemp 1985). Physical-chemical processes, such as flocculation of organic and inorganic materials, occur throughout estuaries, but tend to be concentrated in specific regions, such as the seawater-freshwater mixing zone (Sholkovitz 1976). Denitrification also varies along estuarine axes and is often influenced by gradients in nutrients and dissolved oxygen (Henriksen and Kemp 1988, Kemp et al. 1990). Consequently, patterns of nutrient uptake and production vary along estuarine salinity gradients (Fisher et al. 1988).

Estuarine biogeochemical processes also exhibit substantial seasonal variation. Although peak phytoplankton biomass may occur either in summer (Smith and Hollibaugh 1997) or spring (Harding et al. 2002), annual maxima in primary productivity generally occur in summer for temperate estuaries (Boynton et al. 1982, Malone et al. 1988). Net ecosystem production also varies seasonally, but the seasonality of peaks vary, depending on the magnitude and timing of annual hydrographs, terrestrial carbon inputs, and nutrient availability (Smith and Hollibaugh 1997, Kemp et al. 1997, Ram et al. 2003). Direct denitrification may peak during spring with high nitrogen inputs, while coupled nitrification-denitrification is characterized by summer minima in systems with bottom water hypoxia (Kemp et al. 1990). In systems where the water column is well oxidized throughout the year, denitrification may also peak in summer and fall (Nowicki 1994, Jorgensen and Sorensen 1988). Temperature maxima during summer often drive benthic nutrient regeneration (Fisher et al. 1982, Cowan and Boynton 1996), but high spring supplies of organic material may be regenerated prior to summer (Graf et al. 1982, Boynton and Rohland 2001).

Seasonal and regional patterns in biogeochemical processes are mediated by horizontal and vertical transport. Vertical exchanges of carbon and nutrients between surface and bottom waters connect pelagic and benthic habitats in coastal ecosystems (Kemp et al. 1999). Although the timing and magnitude of benthic respiration and nutrient regeneration are strongly regulated by temperature (Cowan and Boynton 1996), these processes often respond rapidly to vertical sinking of labile organic material (Graf et al. 1982). Elevated horizontal nutrient inputs fuel phytoplankton biomass and sinking (Boynton and Kemp 2000), but strong horizontal transport during high flow periods may cause regions of high productivity to be separated from depositional areas (Hagy 2005). In addition, sediment nutrient regeneration associated with benthic respiration of organic matter, which was deposited during previous periods, may be transported vertically to surface waters and fuel summer productivity (Kemp and Boynton 1984, Malone et al. 1988). Ultimately, the degree of interaction between surface and bottom layers is dependent on depth, where shallow systems exchange more material between surface and bottom water masses than deep systems (Kemp et al. 1999).

Estuarine transformations of nutrients and organic carbon are ultimately regulated by interactions between physical transport and biogeochemical processes. For example, a conceptual model for the Patuxent River and Chesapeake Bay suggests that large spring nutrient inputs are transformed from dissolved into particulate forms in the upper estuary, which subsequently sink and are transported seaward, where dissolved inorganic nutrients are regenerated via decomposition, dissolution, and/or desorption to fuel summer peaks in phytoplankton productivity

(Kemp and Boynton 1984, Malone et al. 1988). Although many of the ecological, biogeochemical, and physical transport processes relevant to this model have been measured at seasonal and regional scales in estuaries (Fisher et al. 1982, Pennock and Sharp 1994, Smith and Kemp 1995, Cowan and Boynton 1996, Roden et al. 1995), none of these studies have been sufficiently comprehensive to support an integrated assessment of this model. As a result, key questions remain to be addressed further in estuarine ecosystems. How do biogeochemical processes vary over seasonal and inter-annual time scales? How do these relationships vary regionally in the estuary? How do surface and bottom layer biogeochemical rates relate to each other? How does physical transport drive these processes and link adjacent regions?

The purpose of this chapter is to use a suite of integrated rates of net biogeochemical production and physical transport for nutrients, oxygen, and organic carbon to examine the spatial and temporal coupling of nutrient inputs and primary production along the axis of the Patuxent River estuary. Rates were computed using a previously developed salt- and water- balance "box" model (Hagy et al. 2000) applied to a 19-year water quality monitoring database. Net biogeochemical rates were derived by computing residual changes in concentrations of non-conservative materials after accounting for physical transport using net non-tidal velocities and diffusivities (Taft et al. 1978, Smith et al. 1991).

Methods

Study site and data availability

The Patuxent River estuary is a tributary system of Chesapeake Bay (USA, Fig. 1.1) that receives relatively high inorganic nutrient loads and that has been the target of nutrient reduction strategies for the past twenty five years (D'Elia et al. 2003). The estuary is ~65 km long, has a mean low-water estuarine volume of 577 x 10^6 m^3, and a surface area of 126 x 10^6 m^2. It averages 2.2 km in width and 6.0 m in depth over the most seaward 45 km of the estuary (Cronin and Pritchard 1975). The mean tidal range is 0.4 m at 9 km from the estuary mouth and increases landward to 0.8 m above 40 km from the mouth (Boicourt and Sanford 1988). Two-layered circulation occurs for most of the year in the lower estuary, with a seaward-flowing surface layer and a landward-flowing bottom layer. The upper estuary (above km 46) is vertically well mixed. Fall-line (99 km from mouth) freshwater discharge averaged 10.3 m^3 s^{-1} from 1977 to 2003 (USGS 2005). Water quality has been monitored at 9 stations along the estuarine axis since 1985, including measurements of salinity, temperature, O_2, chlorophyll *a*, nutrients, and organic carbon (CBP 2005, Fig. 1.1). In addition, a series of continuous water quality sensors (measurements include O_2, temperature, chlorophyll *a*) have been deployed from spring through fall at six stations throughout the estuary (MD DNR 2005, ACT 2005).

Computing salt and water transport

In this study, we computed the Patuxent estuary's time-dependent, seasonal mean circulation using mean monthly salinity and freshwater input data. Salinity data were acquired from the Chesapeake Bay Water Quality Monitoring Program (CBP 2005) and the freshwater input data (river flow and precipitation) were obtained from the United States Geological Survey (USGS 2005) and the National Oceanographic and Atmospheric Administration (NOAA 2005). This box modeling approach computes advective and diffusive exchanges of water and salt between adjacent control volumes and across end-member boundaries using the solution to non-steady state equations balancing salt and water inputs, outputs, and storage changes (Pritchard 1969, Officer 1980, Hagy et al. 2000). The control volumes, hereafter referred to as "boxes", are assumed to be well mixed. Stratified estuarine regions are represented by surface and bottom layers that capture the essential features of two-layered estuarine circulation (Pritchard 1969). Boundaries separating adjacent boxes were chosen based upon several factors: (1) data availability; (2) density stratification; and (3) relatively uniform salinity gradients and water volumes among boxes (Fig. 1.1).

The box model used in this analysis calculates advection and mixing between eleven boxes in the Patuxent River estuary (6 surface boxes, 5 lower boxes, Fig. 1.2, Hagy et al. 2000). The model computes lateral advective and diffusive exchanges in two directions, vertical advective and diffusive exchanges, and freshwater input. Thus, the salt balance for a surface layer box "*m*" in the two-dimensional scheme is described below (Fig. 1.2)

$$\mathrm{V_m}\frac{ds_m}{dt} = \mathrm{Q_{m-1}s_{m-1} + Q_{vm}s'_m - Q_m s_m + E_{vm}(s'_m - s_m)} \\ \mathrm{+ [E_{m-1,m}(s_{m-1} - s_m) + E_{m,m+1}(s_{m+1} - s_m)]} \qquad (1)$$

and the water balance is

$$\frac{dV_m}{dt} = 0 = \mathrm{Q_m - (Q_{m-1} + Q_{vm} + Q_{fm})} \qquad (2)$$

where $\mathrm{V_m}$ is the volume of the box, $\mathrm{Q_m}$ is the advective transport to the seaward box, $\mathrm{Q_{m-1}}$ is the advective transport from the landward box, $\mathrm{Q_{vm}}$ is the vertical advective input into the box, $\mathrm{Q_{fm}}$ is the freshwater input directly into the box, $\mathrm{E_{m-1,m}}$ is the diffusive exchange with the landward box, $E_{m,m+1}$ is the diffusive exchange with the seaward box, E_{vm} is the vertical diffusive exchange, s_m is the salinity in the upper layer box, s_{m-1} is the salinity in the landward box, s_{m+1} is the salinity in the seaward box, and s'_m is the salinity in the lower layer box. The left hand side of Eq. 1 is computed as the monthly salinity change (salinity distribution assumed to be uniform in each box), while the left hand side of Eq. 2 is assumed to be zero at monthly time scales.

In the case that all horizontal and vertical advective and non-advective terms from Eq. 1 were included in the computation, there would be more unknown exchange coefficients than equations and the system would not be solvable (Officer 1980, Hagy et al. 2000). To permit the system to be solvable, non-advective exchanges ($E_{m-1,m}$ and $E_{m,m+1}$) were assumed to be negligible in the region of the estuary with a consistent gravitational circulation (Boxes 2-6, Fig. 1.2, Hagy et al. 2000). Justification for this assumption and further detail of the box model is described in Hagy et al. (2000). The box model equations are solved using two equations at a time, allowing the derivation of closed expressions for the model solution and avoiding the need for a matrix approach (Hagy et al. 2000).

Nutrient transport and production rates

We computed monthly, seasonal, and annual rates of transport and net biogeochemical production of dissolved O_2, nutrients, and carbon for six regions of the Patuxent River estuary from 1985 to 2003. Physical transport rates for these non-conservative biogeochemical variables were computed by multiplying the solute concentration by the advective and non-advective fluxes (Q's and E's, respectively) for each box and month.

In this analysis, we calculated transport and net production rates for the following non-conservative variables: (1) dissolved inorganic nitrogen (DIN = NO_2^- + NO_3^- + NH_4^+), (2) dissolved inorganic phosphorus (DIP = PO_4^{3-}), (3) dissolved silicate (DSi = SiO_3^{2-}), (4) total organic carbon (TOC), and (5) dissolved O_2. Monthly mean values of salinity, nutrients, organic carbon, and dissolved O_2 were computed for each box (and upstream and downstream boundaries) using water quality monitoring data measured at 2-4 week intervals at 9 stations along the Patuxent axis (Fig. 1.1). The resulting mean values were calculated using a simple linear interpolation scheme with a grid of 477 cells spaced at 1 m vertical intervals, 1.85 km horizontal intervals, and spanning the width of the estuary (Hagy et al. 2000). Contour plots of the interpolated data were viewed to test for outlier measurements.

Mass balance equation(s) (Eq. 1 and 2) of the resulting nutrient transports into and out of each box, combined with the volume-weighted concentration change of the variable, yield a residual term (P_m) that represents the non-conservative net production rate (production – consumption) of nutrients, organic carbon, and O_2. For any surface layer Box *m* in the two-layer scheme of the box model, the mass balance equation is

$$V_m \frac{dc_m}{dt} = Q_{m-1}c_{m-1} + Q_{vm}c'_m + E_{vm}(c'_m - c_m) + E_{m+1,m}(c_{m+1} - c_m) - E_{m,m-1}(c_m - c_{m-1}) - Q_m c_m + P_m \tag{3}$$

which can be rearranged to calculate P_m

$$P_m = V_m \frac{dc_m}{dt} - Q_{m-1}c_{m-1} - Q_{vm}c'_m - E_{vm}(c'_m - c_m) - E_{m+1,m}(c_{m+1} - c_m)$$
$$+ E_{m,m-1}(c_m - c_{m-1}) + Q_m c_m \qquad (4)$$

Note that $E_{m,m-1} = 0$ for $m \neq 2$, $E_{m,m+1} = 0$ for $m \neq 1$, and $E_{vm} = 0$ and $Q_{vm} = 0$ for $m = 1$ (Fig. 1.2, 1.3). For any bottom layer Box *m*, the mass balance expression is

$$V'_m \frac{dc'_m}{dt} = Q'_{m+1}c'_{m+1} - Q_{vm}c'_m - Q'_m c'_m - E_{vm}(c'_m - c_m) + P'_m \qquad (5)$$

which can be rearranged to calculate bottom layer net production, P'_m

$$P'_m = V'_m \frac{dc'_m}{dt} - Q'_{m+1}c'_{m+1} + Q_{vm}c'_m + Q'_m c'_m + E_{vm}(c'_m - c_m) \qquad (6)$$

The variables used in Eq. 3-6 include V'_m, which represents the volume of bottom layer boxes, where the subscript, *m*, is the box identifier numbered 1 to 6 from the landward to the seaward ends, and prime notation indicates the bottom layer. In addition, c_m is the concentration of the non-conservative material, Q'_m is the advective fluxes to and from Box *m* in bottom layers, Q_{vm} is the vertical advection from bottom to surface layer, E_{vm} is the vertical diffusive exchange between the surface and bottom layers of Box *m*, and P'_m is the net production (or consumption) rate in bottom layers.

The non-conservative net production rates were calculated in units of mass per time within the box volume (i.e., mass fluxes, mmol d^{-1}). Rates were also computed in volumetric units (mmol m^{-3} d^{-1}) by dividing mass fluxes by either the mean low water volume for surface rates or the volume below the pycnocline for bottom rates. (Table 1.1). Depth-integrated rates were computed by dividing mass fluxes by the mean low-water surface area and vertical fluxes were calculated by dividing the mass fluxes by the pycnocline area (Table 1.1).

An input term for wet atmospheric deposition of DIN to all surface layer boxes was calculated using data for precipitation and concentrations of NO_3^- and NH_4^+ in precipitation. Mean annual nitrogen concentrations in precipitation were acquired from the National Atmospheric Deposition Program (NADP 2005) and were multiplied by monthly precipitation values, thus scaling the seasonal distribution of wet nitrogen deposition to precipitation and estimating a monthly mass flux of nitrogen to all surface layer boxes. This estimate of wet atmospheric deposition was added as an input term to the surface layer dissolved inorganic nitrogen balance.

Although we did not include direct non-point nutrient inputs to each box, we did test the effects of this omission for computing net production rates of DIN and DIP. Monthly non-point DIN/DIP loads to each box were derived from the Chesapeake Bay Watershed Model (Linker et al. 1996). We found that including these estimates for nutrient inputs altered calculations for monthly net production rates of DIN and DIP by less than 10% in Box 3-6 for DIN and in all boxes for DIP. The net production rates for DIN declined by 5-40% in Box 1 and 2 for DIN when direct non-point DIN loads were included. Although direct non-point source inputs of nutrients are important in the upper regions of the estuary (especially Box 2), they do not substantially alter the magnitude of rates computed for other regions of the estuary.

Computing net production or consumption of dissolved O_2 required two adjustments to the box model calculations: (1) a correction for diel variability relative to time of sample and (2) a correction for air-sea O_2 gas transfer. The first step to estimate net O_2 production with the non-conservative O_2 production rate is to correct the discrete O_2 measurements from the monitoring program to equivalent diel mean O_2 concentrations based on observed patterns of variation. Continuous dissolved O_2 data from moored sensors in the Patuxent's surface layer reveal that concentrations tend to vary consistently from 10-30% during each day due to effects of photosynthesis, respiration, and exchange with the atmosphere or adjacent water masses (Kemp and Boynton 1980). To make this correction, we first calculated hourly mean O_2 values (as % saturation) for each month of the year, using two years of data. Data were taken from four continuous (sample every 15 minutes) water quality sensors (Fig. 1.1) maintained by the Maryland Department of Natural Resources (MD DNR 2005) and the Alliance for Coastal Technologies (ACT 2005, Fig. 1.4) that span the estuarine axis. We then calculated a coefficient for each hour of the day in each month at each station to correct the monitoring program measurement. This unitless coefficient (kc_{hr}) is equal to the mean daily % O_2 saturation value for each month and station ($DOSAT_{day}$) divided by the mean hourly % O_2 saturation value for each month and station ($DOSAT_{hour}$).

$$kc_{hr} = \frac{DOSAT_{day}}{DOSAT_{hour}} \tag{7}$$

The corrected O_2 value was calculated by multiplying the measured monitoring O_2 concentration by the appropriate correction coefficient for time of day, month of year, and nearest sampling station.

O_2 concentrations corrected for diel variability were used in the box model to compute physical transport and net non-conservative production rates of dissolved

O_2. Net O_2 production rates in surface boxes were corrected for air-sea exchange. We computed the air-sea O_2 exchange on monthly time scales using O_2 values in the top 0.5 m of the water column following Caffrey (2003):

$$F_{A\text{-}O_2} = \alpha(1 - C_{O_2}/C_{O_2-s}) \qquad (8)$$

where α is the air-sea exchange coefficient (g O_2 m^{-2} h^{-1}), C_{O2} is the adjusted daily mean O_2 concentration at 0.5 m depth (g m^{-3}), $C_{O2\text{-}S}$ is the O_2 saturation value (g m^{-3}). We used a value for α of 0.5 g O_2 m^{-2} h^{-1} for all months, which is based on published relationships between α and wind speed (e.g., Hartman and Hammond 1984, Marino and Howarth 1993, Caffrey 2003) and monthly mean wind speed observed at the nearby Patuxent Naval Air Station. Analyses of the wind data suggested that there were significant variations in wind velocity on daily to weekly scales, but there were no significant monthly or seasonal trends.

Stoichiometric calculations

The net production rates computed with the box model were used to estimate additional biogeochemical processes by assuming fixed stoichiometric relationships between variables. Stoichiometric ratios used in this analysis were derived from traditional relationships for carbon, O_2, and DSi ("Redfield ratios"). We estimated the contribution of diatom photosynthesis to total net organic carbon production rates by applying a stoichiometric adjustment to the computed net rate of surface layer net DSi production rate:

$$PC(Si)_m = k_{C:Si}\,(-P(Si)_m) \qquad (9)$$

where $PC(Si)_m$ is the net carbon production attributed to diatoms (mmol C m^{-3} d^{-1}), $k_{C:Si}$ is the assumed carbon-silica ratio for diatoms of 6.625, and $P(Si)_m$ is the box model computed surface net silica production rate (mmol Si m^{-3} d^{-1}) (Hagy 1996). The net DSi production rate is multiplied by -1 because it is assumed that DSi uptake is associated with net carbon production. We also estimated the sinking flux of particulate organic carbon ($S(POC)_{m,}$ mmol C m^{-2} d^{-1}) across the pycnocline using box model computed net production rate estimates of O_2 and carbon in the surface layer in the stratified estuarine regions (Boxes 2-6) as follows:

$$S(POC)_m = k_{C:O}\, P(O_2)_m - P(TOC)_m \qquad (10)$$

where $P(O_2)_m$ is surface layer net O_2 production rate (mmol O_2 m^{-2} d^{-1}), and $P(TOC)_m$ is surface layer net production rate of total organic carbon (mmol C m^{-2} d^{-1}), and $k_{C:O}$ is the photosynthetic quotient (PQ = 1). This formulation assumes that, in the absence of particulate carbon sinking, net O_2 production (converted to carbon units) and total carbon production are equivalent.

Results

Seasonal changes in the concentration and distribution of chlorophyll *a*, salinity, and dissolved O_2 in the estuary during the winter, spring, and summer of 1995 (a year of average freshwater inputs) are shown in Figure 1.5. The chlorophyll *a* peak occurred in early spring during the period of maximum nitrate load (Kemp and Boynton 1984) and migrated seaward during the following month, eventually sinking in late spring in the middle regions of the estuary (Fig. 1.5). The peak extended to 7-10 meters in depth and 10-20 kilometers along the axis of the middle estuary (Fig.

1.5). Salinity stratification is most intense in spring, relaxing by early summer. Hypoxia ($O_2 < 2$ mg l^{-1}) develops in the same region where the majority of chlorophyll *a* sinking through the pycnocline occurred (Fig. 1.5). These dynamics have been described previously (e.g., Malone et al. 1988, Boynton and Kemp 2000) and are fundamental processes in estuarine ecology that link the terrestrial landscape to the estuarine ecosystem. In the following section, we display the ability of box models to assign rates to these processes and help quantify the interactions of surface and bottom layer processes with nutrient transport, production, and consumption.

Seasonal variation in non-conservative rates

Seasonal cycles of non-conservative production of O_2 in the surface layer can be summarized by spring-summer net heterotrophy in the upper estuary, giving way to spring net autotrophy in the middle and lower estuary surface layers (Fig. 1.6). Summer heterotrophy in the upper estuary (-80 mmol O_2 m^{-2} d^{-1}) corresponds with reduced net DIN and DSi uptake (< 2 mmol m^{-2} d^{-1}) and net DIP production in summer (Fig. 1.6). Surface net O_2 production (net autotrophy) peaked in late spring (60-80 mmol m^{-2} d^{-1}) in the middle and lower estuary and is linked to net DSi consumption (-5 mmol Si m^{-2} d^{-1}), though net DSi production (10-25 mmol Si m^{-2} d^{-1}) is dominant in summer (Fig. 1.6). Peak annual net DIN consumption of -5 mmol N m^{-2} d^{-1} lags 2-3 months behind peak net O_2 production (Fig. 1.6). Net DIP production in the surface layer and consumption in the bottom layer correlate; peaks occur in summer, though bottom production is 2-3 times higher than surface consumption per m^{-2}.

Bottom layer rates of DSi (8-20 mmol Si m^{-2} d^{-1}), DIN (4-20 mmol N m^{-2} d^{-1}), and DIP (0.6-1.2 mmol P m^{-2} d^{-1}) production peak between May and September throughout the estuary concomitant with peaks in O_2 consumption (Fig. 1.6). DIP, NH_4^+, and DSi regeneration and bottom O_2 consumption were significantly correlated with temperature in the upper, middle, and lower estuary (Fig. 1.7). These relationships are strongest in the middle estuary and are exponential throughout the estuary (Fig. 1.7). The magnitudes of nutrient regeneration and O_2 consumption per m^{-2} are generally highest in the lower estuary (Fig. 1.9). Despite the significant relationships, 50-80% of the variation is not explained by temperature.

We tested for significant differences between monthly means for the entire data set of box model computed net production rates ($n = 228$) using a one-way ANOVA with month as the independent variable. There was significant seasonal variation between months for all variables except surface layer net O_2 production in the middle and lower estuary (Table 1.3). The significant seasonal variation exists despite high inter-annual variability in the box model computations (Chapter II).

Surface net O_2 production and surface nutrient consumption were generally enhanced in wet years (mean annual river flow > 20-year average), relative to dry years (mean annual river flow < 20-year average, Fig. 1.8). Surface net O_2 production was 10-15 mmol m^{-2} d^{-1} higher throughout the summer (May to September) in the middle and lower estuary and chlorophyll *a* was 10-15 μg l^{-1} higher (Fig. 1.8). Consequently, summer DIN consumption was 0.3-1.5 mmol m^{-3} d^{-1} higher during wet years and the summer peak persisted later in the year in the middle and lower estuary (Fig. 1.8). Surface layer O_2 production, chlorophyll *a*, and DIN consumption were significantly higher in the middle and lower estuary during wet years than dry years, but bottom layer rates were not significantly affected by flow (ANOVA, significance at $p < 0.05$).

Stoichiometric computations

Particulate organic carbon sinking (10-90 mmol C m^{-2} d^{-1}) and concentration (200-250 mmol C m^{-3}) peaked in late winter and spring (February to April) throughout the estuary (Fig. 1.11). Chlorophyll *a* and net diatom growth (~5 mmol C m^{-3} d^{-1}) peaked in the same time of year in these regions (Fig. 1.11). Particulate organic carbon sinking and concentration and chlorophyll *a* were higher in the middle region of the estuary than lower regions, though sinking estimates are not available for the upper estuary (Fig. 1.11). Particulate organic carbon sinking was minimal during June to August and increased to a fall peak of 10-30 mmol C m^{-2} d^{-1} (Fig. 1.11). Computed sinking rates (calculated as POC sinking flux divided by the POC concentration) ranged from 0.4-0.6 m d^{-1} during winter spring and 0.1-0.2 m d^{-1} during summer (Fig. 1.11).

Axial distributions of non-conservative rates

Rates of net O_2 production reveal a gradient from net heterotrophy in landward regions (Box 1, 2) to net autotrophy in seaward regions (Box 3-5, Fig. 1.9), with peak net O_2 production occurring in the middle and lower estuary (40-100 mmol O_2 m^{-2} d^{-1}). During wet years, chlorophyll *a* was elevated and the biomass peak shifted 20 km seaward (Fig. 1.9). DIN and DIP consumption were 20-50% higher in the middle estuary than the other regions and increased with river flow up to 30%

(Fig. 1.9). In fact, chlorophyll *a*, net O_2 production, and DIP consumption were reduced in the most landward reach of the upper estuary during wet years (Fig. 1.9). Mean bottom layer O_2 consumption, chlorophyll *a*, and DIP production were 5-30% higher in wet years relative to dry years, but these differences were not significant (Fig. 1.9). The axial distribution of rate magnitudes did not change with variation in freshwater inputs (Fig. 1.9).

Differences between the magnitude of the total surface layer O_2 production and bottom layer O_2 consumption changed in response to freshwater inputs (Fig. 1.10). Although freshwater flow resulted in 5-20% increases in net O_2 production in the surface layer, bottom layer rates were generally unaffected by freshwater flow (Fig. 1.10), resulting in higher differences between surface and bottom layer O_2 production in the middle estuary during periods of above average flow. Although surface O_2 production was higher than bottom consumption during years with lower freshwater flow in the middle estuary, surface and bottom layer rates were nearly balanced in the lower estuary (Fig. 1.10). The same was true for net DIN uptake in the surface layer and net DIN production in the bottom layer. Elsewhere in the estuary, however, surface net DIN consumption was an order of magnitude higher than bottom production in both wet and dry years (Fig. 1.10)

Pelagic-benthic coupling

The relationships between surface and bottom layer biogeochemical rates illustrate the coupling between surface and bottom processes and how this coupling varies along the axis of the estuary. We found significant ($p < 0.05$) positive correlations between annual mean surface layer net O_2 production and bottom layer O_2 consumption in the upper ($r^2 = 0.33$, $p < 0.02$), middle ($r^2 = 0.43$, $p < 0.01$), and lower estuary ($r^2 = 0.26$, $p < 0.05$, Fig. 1.12). The correlation is strongest and the surface and bottom layer rates were highest in the middle estuary (surface NEP = 10-40 10^3 kg O_2 d^{-1}, bottom O_2 consumption = 10-30 10^3 kg O_2 d^{-1}), with slightly lower rates in the lower estuary. Although the upper estuary was generally heterotrophic, the most positive surface layer production rates do correspond with the highest bottom layer consumption rates. In general, more O_2 is produced in the surface layer of the middle estuary than is consumed in the bottom layer (Fig. 1.12).

Positive correlations also exist between surface chlorophyll *a* and bottom layer O_2 consumption (Table 1.2, Fig. 1.12). The chlorophyll *a* versus O_2 consumption relationship is strongest in the middle estuary ($r^2 = 0.40$, $p < 0.01$) and is also statistically significant in the upper estuary (Table 1.2, Fig. 1.12). Chlorophyll *a* (in areal units) increases seaward, with highest chlorophyll in the lower and middle estuary, respectively (20-100 mg m^{-2} in lower, 20-80 mg m^{-2} in middle). Particulate organic carbon sinking is also positively correlated with bottom layer O_2 consumption on an annual scale in the middle estuary (Table 1.2). Similarly, chlorophyll *a* (in volumetric units) is significantly and positively correlated with box model computed POC sinking in the middle estuary (Table 1.2). Particulate organic carbon sinking during February to April was significantly correlated with bottom layer net NH_4^+, DIP, and DSi production in the middle estuary (Fig. 1.13) (NH_4^+: $r^2 = 0.25$, $p < 0.05$; DSi: $r^2 = 0.32$, $p < 0.05$; DIP: $r^2 = 0.51$, $p < 0.01$). We found that bottom layer net NH_4^+, DIP, and DSi production (i.e., bottom layer regeneration) were significantly and positively correlated with bottom layer O_2 consumption in the middle and lower estuary (Table 1.2). The correlation between NH_4^+ ($r^2 = 0.39$, $p < 0.01$), DIP ($r^2 = 0.23$, $p < 0.05$) regeneration and O_2 consumption is strongest in the lower estuary, but significant relationships exist in both the middle and lower estuary for NH_4^+, DIP, and DSi (Table 1.2). The nutrient production versus O_2 consumption correlations explained little variability and were not significant in the upper and lower estuary.

Nutrient transport rates

Rates of nutrient inputs to the surface layer of the middle estuary are important for driving biomass accumulation, net O_2 production, and pelagic-benthic coupling. DIN transport rates to the upper and lower estuary were dominated by spring seaward inputs and the magnitude of seaward inputs increased in more down-estuary boxes (Fig. 1.14). The magnitude of vertical transport of DIN to these waters was similar to seaward advection from May to October (3 mmol N m^{-2} d^{-1} in the middle, 5 mmol N m^{-2} d^{-1} in the lower). Conversely, DIN transport to the middle estuary was dominated by seaward advection in spring, but vertical imports dominated from May to October and were 50% higher than seaward inputs in the middle estuary (Fig. 1.14). Spring DIN inputs from seaward advection were sufficient to support spring net O_2 production, but vertical DIN inputs were required to support summer rates of net O_2 production (Fig. 1.14).

Discussion

Seasonal and regional variability in surface layer biogeochemistry

Net production rates for surface layer O_2, DIN, DIP, and DSi all exhibit distinct and significant seasonal cycles and regional distributions in the estuary (Fig. 1.6). Net negative rates of O_2 production (i.e., net consumption) are maintained in the upper estuary during spring and summer by the region's characteristic high turbidity (mean TSS = 70 mg l^{-1}, secchi depth = 0.4-0.6) and large allocthonous carbon inputs (annual mean = 125 mmol C m^{-2} d^{-1}). This pattern is common in temperate estuarine systems (Howarth et al. 1992, Hopkinson and Vallino 1995), where turbidity favors net O_2 consumption by reducing light for photosynthesis (Appendix I, Cloern et al. 1983), while allochthonous inputs of organic matter fuel respiration (e.g., Smith and Kemp 1995, Smith and Hollibaugh 1997). A transition from net heterotrophy in the upper estuary to autotrophy in the middle and lower estuary is also a common feature of temperature estuaries (Fig. 1.8, e.g., Kemp et al. 1997) and is consistent with the "river continuum" concept (Vannote et al. 1980).

Whereas phytoplankton production tends to peak in summer in the middle and lower estuary (data not shown) and in Chesapeake Bay (Harding et al. 2002) and other coastal systems (Radach et al. 1990, Paerl et al. 1998), seasonal maxima for net O_2 production coincide with spring chlorophyll *a* peaks in the Patuxent estuary (Fig. 1.6). Positive rates for net O_2 production in late spring and early summer, which have been observed in many temperate estuaries (Kenney et al. 1988, Hoppema 1991) including Chesapeake Bay (Smith and Kemp 1995), occur when diatom blooms dominate (Malone et al. 1988). With the onset of warm summer temperatures, net O_2

production declines as respiration increases (Howarth et al. 1992, Smith and Kemp 1995), though high pelagic respiration has been measured in cooler periods when phytoplankton biomass is high (L.M. Jensen et al. 1990). The seasonality and regional variation in box model estimates of net O_2 production compare favorably with similar computations for Chesapeake Bay (Kemp et al. 1997), while integrated rates of net O_2 production between -0.5 and 2.6 g O_2 m^{-2} d^{-1} are comparable to rates reported for Chesapeake Bay (Kemp et al. 1997).

We chose to quantify net ecosystem production (i.e., total system photosynthesis minus community respiration; Smith et al. 1991, Kemp et al. 1997) based on the non-conservative net production or consumption of O_2. An alternative method, which applies fixed stoichiometric assumptions to convert the net non-conservative DIP production rate into carbon units, has been widely used (e.g., Smith et al. 1991, LOICZ; Gordon et al. 1996). We were concerned that, for estuaries like the Patuxent, that DIP biogeochemistry is controlled by non-biological processes, including physical sorption-desorption (Jitts 1959, Pomeroy et al. 1965, Gunnars and Blomqvist 1997) and flocculation with Fe and Mn oxides and hydroxides (Sholkovitz 1976, Sundby et al. 1992), especially at low salinity. Given the limitations of using DIP to calculate net ecosystem production, O_2 appeared to be a more appropriate measure.

We were able to address directly two potential problems associated with using net O_2 production as a measure of net ecosystem production. We corrected instantaneous measurements of O_2 for systematic diel variations associated with photosynthesis and respiration (Fig. 1.4), but found that this correction altered the O_2

concentration by < 5%. We also corrected surface layer net O_2 production rates using conventional expressions for air-sea exchange and a measured exchange coefficient (α); we found that variations in α of ± 50% resulted in relatively small changes in net O_2 production, 5-10% in the middle and lower estuary (Box 3-6) and 5-15% in the upper estuary (Box 1, 2). In any case, box model estimates of net ecosystem production based on net O_2 production agree well with estimates using different techniques (Smith and Kemp 1995, Kemp et al. 1997).

Seasonal variations in net O_2 production appear to be linked to the annual DSi cycle. Because DSi does not react in chemical and physical sorption or precipitation processes at concentrations measured in Chesapeake Bay (Kamatani and Riley 1979) and because DSi dissolution is low at temperatures common during spring ($< 13^{o}$C, Yamada and D'Elia 1984), the net DSi production rate provides a useful indicator of net diatom DSi uptake. Spring peaks in net O_2 production and net DSi consumption in the middle and lower estuary are coincident with the typical timing of diatom spring blooms (Fig. 1.6, 1.11; Malone et al. 1988, Fisher et al. 1988). Converting net DSi uptake to equivalent carbon units (C:Si = 6.625) suggests diatoms comprises 50-80% of net O_2 production in the middle and lower estuary during spring (Fig. 1.6). Fall peaks in DSi uptake are consistent with fall peaks in the abundance of diatoms (*Skeletonema costatum*, *Cyclotella spp.*, and *Thalassiosira spp.*) in the Patuxent River estuary (Lacouture et al. 1993). During summer, a shift to net DSi production in all regions of the estuary indicates remineralization of DSi, which is a primarily chemical process that likely occurs in the shallow sediments contained in the surface layer box (D'Elia et al. 1983), not in the water column.

Strong seasonal patterns of surface layer DIN uptake (i.e., net negative production) rates were observed throughout the estuary, including spring peaks. DIN limitation has been found in the mesohaline region of the Patuxent River estuary in previous studies (e.g., D'Elia et al. 1986), and net O_2 production (i.e., net nutrient uptake) accounted for 80% of DIN uptake in the middle and lower estuary during February to March (O_2:N = 6.625), but less than 50% in May and June. Excess DIN uptake in spring and summer is attributed to denitrification rates of 2-4 mmol N m^{-2} d^{-1}, or 83-125 μmol N m^{-2} h^{-1}, which agree favorably with estimates obtained using ^{15}N tracer methods (Jenkins and Kemp 1984). In fact, box model computations of water column integrated net denitrification (Appendix II) suggest spring/ early summer peaks of 50-150 μmol N m^{-2} h^{-1}, which is comparable to these measurements. This surface layer denitrification is likely occurring in shallow water sediments along the flanks of the river, which are in contact with 75% of the surface layer (Table 1.1).

Coupling between net O_2 production and DIP production was less direct and consistent in the middle and lower estuary surface layer. Although net uptake of DIP would be expected to correlate with net O_2 production in autotrophic regions, the observed DIP uptake in the surface layer lagged behind O_2-based net production by 3-4 months in the middle and lower Patuxent estuary (Fig. 1.6). Surface layer DIP consumption rates of 0.1-0.4 mmol P m^{-2} d^{-1} in August of the lower estuary approach the expected uptake due to equivalent net O_2 production of 0.15-0.22 mmol P m^{-2} d^{-1} (assuming O_2:DIP = 106), but DIP and O_2 rates do not match during spring, winter, or fall.

These weak correlations suggest that net DIP production in the surface layer may also be controlled by physical or chemical processes. DIP can attach to organic and inorganic particles (Carpenter and Smith 1984) and sink out of the surface layer. Stratification and increased residence time (Hagy et al. 2000) during summer may allow for DIP scavenged onto particles to sink to the lower layer and be regenerated, but without quickly returning to the surface, as is true in many lakes (Jahnke 1992). Such a mechanism may allow for the large DIP net uptake rates observed during summer, which are larger than rates estimated for net DIN uptake using biological stoichiometry. DIP is also involved in diagenetic and sorption-desorption reactions in systems with strong O_2 and salinity gradients (Krom and Berner 1981, Fox et al. 1985), such as the Patuxent. Biological and chemical processes are likely interact to control net DIP consumption during summer.

Seasonal variability in bottom layer biogeochemistry

Summer peaks in bottom layer processes indicate the role of temperature in respiration and nutrient recycling. Correspondence between net rates of nutrient production and net O_2 consumption in bottom layers during summer (Table 1.2) is consistent with diagentic coupling between organic matter decomposition and nutrient regeneration, as is often measured in flux cores and benthic chambers (Cowan and Boynton 1996) and in mesocosm experiments (Kelly et al. 1985). Although it appears that a large proportion of fresh organic matter is delivered to sediments during spring (Fig. 1.11, Kanneworff and Christensen 1986, Boynton and Kemp 2000), O_2 consumption and DIN/DIP production do not peak until late spring and summer when temperature increases bacterial respiration rates and enzyme activity (Fig. 1.6, 1.7; Fisher et al. 1982, Shiah and Ducklow 1994). Summer peaks in aerobic respiration and nutrient regeneration are common in other temperate estuaries (Kamp-Nielsen 1992, Yoon and Benner 1992, Cowan et al. 1996). General agreement between box model estimated bottom layer net production rates and benthic chamber flux measurements in the Patuxent River estuary (Table 1.4, Boynton and Rohland 2001) indicate that benthic processes tend to dominate these seasonal patterns.

Although O_2 consumption and nutrient regeneration in the bottom layer are positively related with water temperature (Fig.1.7), temperature affects each nutrient via different chemical, physical, and biological mechanisms. For example, whereas temperature stimulation of organic matter hydrolysis and release of DIN and DIP occurs through effects of enzyme catalyzed biochemical reactions (Cowan and Boynton 1996), temperature enhancement of biogenic silica remineralization is attributable primarily to effects of physical-chemical dissolution (Yamada and D'Elia 1984, Chauvaud et al. 2000). Although DIP is remineralized initially via biochemical decomposition, physical-chemical processes tend to regulate DIP release from sediments to overlying water, including sorption to particles and flocculation with metal oxy-hydroxides. These processes are, in turn, regulated by seasonal variations in redox conditions within these sediment systems (Fisher et al. 1982, Cowan and Boynton 1996). A fraction of the net O_2 consumption in bottom layers is attributable to aerobic respiration; however, a large fraction of this O_2 uptake may be due to oxidation of sulfide (produced from sulfate reduction) via both chemical and microbial processes (Roden 1990, Roden et al. 1995). In Chesapeake Bay, Roden (1990) concluded that sulfate reduction could account for approximately 75% of summer organic matter oxidation in sediments. Under conditions of anoxic bottom water, a large fraction of the reduced sulfur (as hydrogen sulfide) diffuses vertically through the water column until it is oxidized near the pycnocline where free O_2 is abundant.

Temperature is not the only factor causing seasonal lags between surface nutrient uptake and bottom nutrient regeneration. A late spring O_2 consumption peak found throughout the estuary precedes the temperature maximum by 1-2 months, suggesting the respiration of recently deposited labile material (Fisher et al. 1982, Graf et al. 1982). Rates of sediment O_2 consumption measured in the Patuxent using benthic chambers also peaked in late spring and early summer before the seasonal temperature maxima (Boynton and Rohland 2001). Multiple regressions explained 40% more of the variability in bottom layer O_2 consumption using contemporaneous temperature and the previous month's bottom layer chlorophyll *a* than when using temperature alone (Hagy 1996). These relationships suggest the importance of labile organic matter deposition to bottom layer respiration and indicate that this vertical coupling is not instantaneous (Kanneworff and Christensen 1986, Kamp-Nielsen 1992, Kemp et al. 1999).

Assessing error in box model rates

The monitoring data used to compute mean concentrations for a given box are collected from mid-channel stations at 2-4 week intervals (Fig. 1.1). The boxes span the width of the estuary, containing both deep, two-layer regions near the estuarine channel and shallow (< 4 m) vertically mixed areas flanking the channel. These areas may have different water quality conditions (e.g., Ward et al. 1984), which could produce errors in computing monthly mean concentrations for an entire box from only the mid-channel data. Comparisons of point measurements in the channel with similar measurements from shallow water sensors in 2004 and 2005 (MD DNR 2005) indicate significant correlations between salinity ($r^2 = 0.91$-0.98), O_2 ($r^2 = 0.72$-0.95), and chlorophyll *a* ($r^2 = 0.36$-0.90, $n = 8$-20) with regression slopes ranging from 0.88-1.3. Similar agreements were found in comparing monthly means of the mid-channel and shallow water concentrations throughout Chesapeake Bay, where parallel measurements at mid-channel and adjacent nearshore areas were statistically indistinguishable 90% of the time when stations were < 2 km apart (Kemp et al. 2004).

In addition, relatively short-term (1-3 weeks) variability in nutrient concentrations may not be captured by the monthly and fortnightly monitoring program samples. To determine the potential error imposed by computing monthly means with data that does not capture short-term variability, we examined time series of continuously monitored nutrient data over 30-day periods in adjacent Chesapeake Bay tributaries (Choptank and Pocomoke Rivers, NAS-2E nutrient monitoring systems, L. Codispoti and V. Kelly, unpublished data). These analyses revealed that seasonal variability (monthly time scale) is greater than diel variability over 90% of the data set. Because seasons are the time scales of interest in this analysis, it appears that the shorter-term variability has little impact on seasonal trends, as long-term monthly averages reveal consistent seasonal nutrient cycles (Hagy 1996). Although episodic spikes in nutrient concentration observed in association with storm events could cause misrepresentation of the monthly mean nutrient concentrations, the actual sampling protocols generally preclude such problems.

Pelagic-benthic coupling

The contrast between O_2 production and nutrient uptake in the surface layer versus the bottom layer illustrates the dominance of autotrophy in the surface layer and heterotrophy in the bottom layer. Implicit in these patterns is a vertical connection of surface and bottom waters via particle sinking and vertical advection and diffusion. Such pelagic-benthic coupling has been described in many systems (e.g., Graf et al. 1982, Kamp-Nielsen 1992, Kemp et al. 1999) and includes a series of processes that is relevant to coastal zone management.

Box model computed POC sinking rates (per pycnocline area) of 20-90 mmol C m^{-2} d^{-1} in the middle estuary and 5-80 mmol C m^{-2} d^{-1} in the lower estuary (Fig. 1.11) are approximately the same magnitude as measured POC deposition rates of 10-150 mmol C m^{-2} d^{-1} measured at nearby Chesapeake Bay mesohaline sites (Roden et al. 1995) and in the lower Patuxent River (Kemp and Boynton 1984). POC sinking thus provides a mechanism to transport surface layer production to bottom layers (Graf et al. 1982, Kanneworff and Christensen 1986, Kemp et al. 1999). Coincident spring peaks of POC sinking, chlorophyll *a*, and net diatom growth support the view that diatom blooms comprise most of the spring vertical particle flux (Malone et al. 1988) and that a large fraction of the spring bloom is ungrazed (Peinert et al. 1982, Kanneworff and Christensen 1986). Box model computed POC sinking rates during winter-spring (0.4-0.6 m d^{-1}) agree with measured sinking rates of larger phytoplankton cells, such as diatoms (Bienfang 1981). Studies in different coastal systems observed a spring sinking peak, suggesting that sinking, not grazing, is the dominant loss term for spring phytoplankton blooms (Smetacek et al. 1978, Smetacek 1980, Peinert et al. 1982, Keller and Riebesell 1989).

Examination of annual mean rates of surface layer net O_2 production, bottom layer O_2 consumption, chlorophyll *a*, and POC sinking indicated that pelagic and benthic processes are tightly coupled in the middle region of the Patuxent River estuary, but more weakly connected in other regions. This is the case because the middle estuary is characterized by relatively shallow depths (Kemp et al. 1999, Bailey 2005), moderate residence times (Hagy et al. 2000), and low interaction with adjacent systems relative to other regions of the Patuxent (Sanford and Boicourt 1990, Gallegos et al. 1992, Fisher et al. 2006). Because we observed positive net O_2 production in the surface layer (i.e., production > respiration) and we equate O_2 production to carbon production, we expect this excess production to be exported to and respired in adjacent regions (Kemp et al. 1997). Significant correlations between surface net O_2 production and bottom net O_2 consumption (kg d^{-1}) suggest that net production tends to sink to the bottom layer (Fig. 1.12). Correlations between both surface chlorophyll *a* and POC sinking with bottom layer O_2 consumption in the middle estuary provide further evidence of direct pelagic-benthic coupling (Table 1.2, Fig. 1.12), which has been found in other temperate estuaries (Kamp-Nielsen 1992, Vidal et al. 1992, Yoon and Benner 1992). Correlations between POC sinking and surface chlorophyll *a* in the middle estuary indicate that much of the POC sinking is linked to plankton biomass (Table 1.2; Lignell et al. 1993, Hagy 2002, 2005). Such correlations are qualitative, however, and do not quantify how much of the bottom layer respiration is accounted for by organic matter sinking.

Independent estimates of rates of POC sinking and bottom layer respiration may be used to estimate what fraction of bottom layer respiration is due to POC sinking from the surface layer. We addressed the importance of annual mean POC sinking by comparing sinking rates to bottom layer O_2 consumption rates in the middle estuary (O_2 converted to carbon using RQ = 1 e.g., Hopkinson 1985). Because the surface layer overlies both the lower layer of deep channel water and bottom sediments in the shallow flanks, it is wider than the bottom layer. Thus, all of the sinking POC from the surface layer may not reach the central bottom layer. If we assume that POC sinking occurs uniformly throughout the surface layer and that carbon sinking to the bottom layer only occurs where the surface and bottom layer overlap (~25% of the total area of Boxes 3-5 at MLW, Table 1), POC sinking would account for 20-50% of bottom respiration. If we assume, on the other hand, that the entire POC flux from the surface layer was transported to the bottom layer within a year, POC sinking would account for 50 to > 100% of bottom respiration. The latter assumption requires that the majority of organic particles settling over the flanks are transported laterally down the slope toward the adjacent channel's lower layer (e.g., Kemp et al. 1997). This latter assumption is supported by measurements of plankton and benthic photosynthesis and respiration in Chesapeake Bay (Kemp, unpublished data), revealing net autotrophy in shallow water and net heterotrophy in deep water.

Distances between the shallow flanks and the main channel are shorter in the Patuxent (1-3 km wide) compared to the mainstem Chesapeake (10-15 km wide), suggesting that lateral carbon transport is likely. Previous studies have found that carbon sedimentation can account for a large fraction of sediment respiration (Kamp-Nielsen 1992, Cowan and Boynton 1996) and that respiration is elevated in regions where more organic material is present (Vidal et al. 1992, Yoon and Benner 1992).

Our calculations indicate that POC sinking from the surface layer will often, but not always provide the carbon necessary to support bottom layer respiration. Carbon deficits have also been found in other systems (e.g., 75% of bottom respiration unaccounted for in Kiel Bight) and were attributed to transport and benthic photosynthesis (Graf et al. 1982). Alternative sources of carbon to account for the additional respiration in the Patuxent could include landward carbon transport via gravitational circulation (Kemp et al. 1997). In fact, total organic carbon transport to the middle and lower estuary in the bottom layer is 30-70 10^3 kg d^{-1}, which is 3-4 times higher than the organic carbon sinking flux (10-25 10^3 kg C d^{-1}). A large fraction (up to 95%) of this horizontally imported carbon is exported from the region, however, and the net organic carbon inputs via advection and diffusion are 0.2-5.0 10^3 kg C d^{-1}, enough to satisfy the excess respiratory demand in some years, but not all. Carbon advected through the bottom layer likely originates as surface layer carbon from Chesapeake Bay and the lower Patuxent River estuary. By the time this material reaches the middle estuary, residual compounds may be less labile than locally produced surface carbon. POC sinking is thus the dominant carbon source to bottom waters, as suggested by the tight pelagic-benthic coupling in the middle estuary.

Estimated spring vertical transport of organic carbon to the bottom layer of the middle estuary is proportional to annual bottom layer net nutrient regeneration (Fig. 1.13). We use annual rates to represent the fact that regeneration may respond rapidly to carbon inputs (M.H. Jensen et al. 1990), or may lag with temperature effects (Kanneworff and Christensen 1986). Net bottom layer DSi production is correlated with both surface chlorophyll *a* ($r^2 = 0.61$) and spring POC sinking ($r^2 = 0.35$), indicating the role of sinking diatoms as a source of biogenic silica (Yamada and D'Elia 1984) and a link between surface productivity and DSi regeneration (Cowan and Boynton 1996). Correlations between both chlorophyll *a* and POC sinking with net bottom layer NH_4^+ and DIP production (Table 1.2) also support the link between nutrient remineralization and surface phytoplankton biomass (Nixon 1981, Cowan et al. 1996). In fact, POC sinking can account for 50-100% of NH_4^+, DIP, and DSi regeneration, while a smaller fraction of POC sinking is lost to long-term burial (e.g., Fisher et al. 1982). NH_4^+ regeneration has been correlated with phytoplankton productivity and sinking in Chesapeake Bay (Boynton and Kemp 2000), Danish coastal waters (M.H. Jensen et al. 1990), and in several other estuarine and coastal systems (Nixon 1981). These results suggest that organic matter deposition to the bottom layer affects the magnitude of nutrient regeneration, while temperature and O_2 consumption influence the timing of regeneration (Cowan and Boynton 1996, Cowan et al. 1996).

Bottom layer nutrient regeneration is an important source of nutrients for productivity during summer in many temperate estuaries, but not in spring (Kemp and Boynton 1984, Dollar et al. 1991). Although seaward DIN transport fuels "new" phytoplankton production (i.e., high chlorophyll *a* and net O_2 production) in the middle and lower estuary during spring (Fig 1.14, Malone et al. 1988, Magnien et al. 1992) vertical inputs of DIN from the bottom to the surface layer are large enough to satisfy 70-80% of summer surface DIN uptake (Fig. 1.14, Kemp and Boynton 1984). Approximately two-thirds of this vertically transported nitrogen is NH_4^+ (Hagy 1996), and more than half of this NH_4^+ was derived from bottom layer regeneration. Similar contributions of sediment nutrient regeneration, particularly NH_4^+, to summer phytoplankton productivity have been found in other temperate estuaries (Christian et al. 1991, Fisher et al. 1992, Malone et al. 1988). The additional 20-30% of N inputs during summer are probably derived from upstream sources, atmospheric inputs, and internal pelagic recycling processes (Nixon 1981, Paerl 1985). In the lower estuary, over 100% of the surface layer's net DIN demand could be supported by seaward DIN (both NO_3^- and NH_4^+) transport in all seasons. Seaward DIN transport may be comparable to vertical imports in the lower estuary because horizontal transport is amplified in a seaward direction in systems with two-layer circulation (Hagy et al. 2000). This analysis provides quantitative support for the concept that high spring DIN inputs generate net organic production that sinks to the lower layer, where organic N is remineralized in summer to support primary productivity (Kemp and Boynton 1984, Malone et al. 1988).

Effects of freshwater input

In many estuaries, high river flow supports increased phytoplankton productivity and biomass, due to elevated nutrient inputs (Malone et al. 1988, Paerl et al. 2006). This occurs in the lower and middle Patuxent estuary (Fig. 1.8, 1.9) where elevated summer chlorophyll *a* and net O_2 production during high flow years suggests that flow relieves nutrient limitation later into the year. Increased DIN consumption in wet years illustrates the nutrient demand of increased phytoplankton productivity in the middle and lower estuary (Fig. 1.8). Thus, a logical hypothesis is that elevated carbon production and nutrient uptake in years of high flow would lead to elevated bottom layer respiration and nutrient regeneration, as was found in Chesapeake Bay (Boynton and Kemp 2000).

Despite the significant positive effects of river flow on surface biomass and productivity, available data suggest that bottom layer respiration and regeneration are less affected (Fig. 1.9, 1.10). Particulate organic carbon sinking is positively, but not significantly related to flow ($r^2 = 0.15$, $p > 0.1$), while surface and bottom layer chlorophyll *a* increased significantly with flow (Fig. 1.8). These correlations suggest that flow does in fact lead to more deposition of recent phytoplankton biomass to the bottom layer. Previous studies in Chesapeake Bay have identified increased chlorophyll *a* deposition with elevated flow (Boynton and Kemp 2000, Hagy 2005) and increased NH_4^+ regeneration from sediments with elevated flow (Boynton and Kemp 2000, Boynton and Rohland 2001). In addition, surface net O_2 production and chlorophyll *a* are significantly correlated, thus we expect an increase in surface rates to cause an increase in bottom rates. Thus, why were rates of bottom layer O_2 consumption and nutrient regeneration not significantly enhanced with flow?

To begin to answer this question, we examined surface and bottom rates of net O_2 and DIN production/consumption in units of kg d^{-1} for each box. The magnitudes of surface layer and bottom layer net production rates in each region were not always equivalent (Fig. 1.10), suggesting that there may be an important mechanism for nutrient and carbon export. Horizontal transport is a large component of nitrogen and O_2 budgets in the boxes of the middle estuary (data not shown). The fact that surface layer O_2 production and DIN consumption exceed O_2 respiration and DIN regeneration in the bottom layer of the middle estuary suggest that some fraction of surface materials are transported out of the region represented by the box (Fig. 1.10).

Unlike the middle estuary, total masses of net O_2 and DIN production and consumption in surface and bottom layers are nearly equivalent in the lower estuary, especially during low flow periods. This suggests very little horizontal export out of the region (Fig. 1.10). Discrepancies between surface and bottom rates in the lower estuary are higher during high flow, much like the middle estuary, suggesting horizontal export seaward, but where does this material ultimately go? It does not appear that material potentially exported from the middle estuary sinks in the lower estuary, where sinking rates are low and surface and bottom layer O_2 and DIN production and consumption rates nearly match (Fig. 1.11). Boynton et al. (in prep) and Boynton et al. (1995) estimated net export of total nitrogen from the Patuxent estuary to Chesapeake Bay ($0.21\ 10^6$ kg N yr^{-1}), suggesting that production in the middle and lower estuary may be exported from the system altogether. Analyses of chlorophyll *a* deposition to Chesapeake Bay sediments suggest that particles are transported seaward from where they are produced during high flow periods (Hagy 2005). Although physical transport may cause export of particulates from the middle Patuxent estuary during high flow, the large scale of our regional analysis (5-10 km) might aggregate this process into a single box. Limited sediment chlorophyll data in the Patuxent River suggest that the highest levels are in the middle region of the estuary (Boynton and Rohland 1998), supporting the idea that regional maxima in surface biomass sink to the bottom layer locally.

Summary and Conclusions

This analysis leads to several important conclusions regarding factors regulating organic production and nutrient recycling. The following statements summarize the major processes: (1) The majority of "new" nutrients are delivered to the estuary during late winter and spring. (2) "New" nutrient inputs, most importantly NO_3^-, fuel a spring phytoplankton bloom that subsequently sinks across the pycnocline. (3) Organic material exported to the bottom layer is regenerated in late spring and summer in quantities generally proportional to those deposited. (4) POC sinking likely accounts for 50-100% of bottom layer respiration in the middle estuary and deficits are probably accounted for by the labile portion of organic carbon delivered in landward flowing water masses. (5) Bottom layer regeneration of particulate materials is necessary to support rates of net O_2 production and nutrient uptake in surface layers during summer. (6) Pelagic and benthic processes are most tightly linked in the middle estuary, which is highly productive and does not interact substantially with adjacent systems. (7) Elevated freshwater flow generally enhances surface layer processes more than bottom layer processes, indicating both vertical pelagic-benthic coupling and seaward transport of organic production under high flow conditions. These results generally agree with previously described conceptual models and are likely applicable to other temperate estuarine systems.

We therefore propose a refinement to the conceptual model of spatial and temporal coupling of nutrient inputs to net production in the Patuxent River estuary (Kemp and Boynton 1984). Although we do not propose that transformation of N and P to particulate forms in the oligohaline estuary during spring is unimportant, we suggest that seaward advection of inorganic nutrients is high enough during spring to support large phytoplankton blooms in the mesohaline estuary. These blooms are dominated by diatoms and sink to the lower layer following the senescence of the bloom. Deposited phytoplankton biomass is respired and regenerated in the bottom layer during late spring and summer, which allows export of NH_4^+ to surface waters to support summer productivity. Strong correlations between spring-dominated carbon sinking and summer-dominated nutrient regeneration support this assertion, and suggest that regeneration of particulate materials from oligohaline waters may not be as important as previously thought in the mesohaline regions.

Although net biogeochemical production rates estimated in this study are necessarily averaged over relatively large scales of months to decades and 10-30 km, significant regional and seasonal patterns were clearly evident. In addition, inter-annual variability in key biogeochemical processes was significantly related to changes in river flow and horizontal transport. Significant correlations between processes in vertically connected surface and bottom layers emphasize the importance of pelagic-benthic coupling at these scales. Using box modeling methods to interpret water quality monitoring data in terms of physical and biogeochemical rates provides a valuable tool to help understand large-scale processes and controls for estuaries such as the Patuxent, especially those with two-layered circulation. This technique has potential to be an important research and management tool in the growing number of well-monitored estuarine systems throughout the world, as it has already been applied in many systems (e.g., Chesapeake Bay; Taft et al. 1978, Baltic Sea; Wulff and Stigebrandt 1989, Tomales Bay; Smith et al. 1991, Patuxent River estuary; this study, the Scheldt Estuary; Gazeau et al. 2005).

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Unit	Layer	Box 1	Box 2	Box 3	Box 4	Box 5	Box 6
Volume (10^6 m^3)	Surface	17.6	29.7	63.8	104.0	110.0	100.0
	Bottom		3.5	17.9	33.5	44.0	62.8
Surface Area (10^6 m^2)	MLW	7.2	17.9	26.1	28.4	24.2	22.2
	Pycnocline		1.7	5.9	7.3	5.8	9.0
Depth (m)	Surface	2.43	1.66	2.45	3.67	4.53	4.50
	Bottom		2.03	3.03	4.57	7.59	6.95

Table 1.1: Physical dimensions of all boxes in for the box model of Hagy et al. (2000). Dimension information may be used to convert all box model computed nutrient transports and production rates to the desired units.

	Estuarine Region	Bottom Layer NH_4^+ Production (mmol m^{-3} d^{-1})	Bottom Layer DIP Production (mmol m^{-3} d^{-1})	Bottom Layer DSi Production (mmol m^{-3} d^{-1})	Bottom Layer O_2 Consumption (mmol m^{-3} d^{-1})	Surface Chlorophyll *a* (µg l^{-1})
Bottom Layer O_2 Consumption (mmol m^{-3} d^{-1})	Upper	$r^2 = 0.002$ $p > 0.1$	$r^2 = 0.00005$ $p > 0.1$	$r^2 = 0.02$ $p > 0.1$		$r^2 = 0.19$ $p < 0.1$
	Middle	**$r^2 = 0.12$** $p < 0.01$	**$r^2 = 0.12$** $p < 0.01$	**$r^2 = 0.18$** $p < 0.01$		**$r^2 = 0.40$** $p < 0.01$
	Lower	**$r^2 = 0.39$** $p < 0.01$	**$r^2 = 0.23$** $p < 0.01$	$r^2 = 0.06$ $p > 0.1$		$r^2 = 0.13$ $p > 0.1$
February - April POC Sinking (mmol m^{-2} d^{-1})	Upper					
	Middle	**$r^2 = 0.25$** $p < 0.05$	**$r^2 = 0.55$** $p < 0.05$	**$r^2 = 0.31$** $p < 0.02$	**$r^2 = 0.37$** $p < 0.01$	**$r^2 = 0.51$** $p < 0.01$
	Lower	$r^2 = 0.02$ $p > 0.1$	$r^2 = 0.03$ $p > 0.1$	$r^2 = 0.03$ $p > 0.1$	$r^2 = 0.01$ $p > 0.1$	$r^2 = 0.001$ $p > 0.1$
Temperature (°C)	Upper	$r^2 = 0.01$ $p > 0.1$	**$r^2 = 0.20$** $p < 0.001$	**$r^2 = 0.21$** $p < 0.001$	$r^2 = 0.01$ $p > 0.1$	
	Middle	**$r^2 = 0.18$** $p < 0.001$	**$r^2 = 0.42$** $p < 0.001$	**$r^2 = 0.20$** $p < 0.001$	**$r^2 = 0.24$** $p < 0.001$	
	Lower	**$r^2 = 0.31$** $p < 0.001$	**$r^2 = 0.40$** $p < 0.001$	**$r^2 = 0.18$** $p < 0.001$	**$r^2 = 0.22$** $p < 0.001$	

Table 1.2: Correlation coefficients and *p* values for the relationships (top panel rate versus side panel rate) between selected surface and bottom water biogeochemical rates and chlorophyll *a* in three regions (upper, middle, lower estuary) of the Patuxent River estuary. Rates include net biogeochemical production of bottom layer DSi, DIP, NH_4^+, and O_2 as computed with a box model, spring particulate organic carbon (POC) sinking, and chlorophyll *a*. Box model computed rates are monthly rates and chlorophyll *a* and POC sinking are annual means for the years 1985 to 2003 (O_2 data are annual means when related to these variables).

Layer	Region	O_2	Chl-a	DIN	DIP	Si
Surface	Upper	20.56**	3.34**	1.7	6.43**	3.53**
	Middle	1.02	5.09**	3.1**	10.46**	10.11**
	Lower	1.36	4.25**	3.33**	3.33**	3.18**
Bottom	Upper	1.76	5.69**	3.89**	9.43**	6.26**
	Middle	9.13**	11.76**	8.29**	17.08**	6.07**
	Lower	7.56**	14.05**	7.61**	19.59**	2.58*

Table 1.3: Resulting F-values of one-way ANOVA to test for significant differences between months for selected box model computed net production rates and chlorophyll *a*. Associated *p*-values < 0.01 indicated by ** and $p < 0.05$ indicated by *. Monthly means calculated for all data from 1985 to 2003 (n = 228) for the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary.

Region	Technique	DIP		NH_4^+		O_2 consumption	
		Spring	Summer	Spring	Summer	Spring	Summer
Middle	Box Model	0.03 - 0.12	0.20 - 0.60	0.08 - 3.10	3.00 - 6.60	40 - 80	115 - 150
	SONE	0.12 - 0.24	0.24 - 2.40	1.80 - 4.40	6.00 - 9.60	30 - 90	15 - 40
Lower	Box Model	0.01 - 0.08	0.20 - 1.10	1.20 - 2.80	8.7 - 15.10	40 - 75	130 - 220
	SONE	0.00 - 0.12	0.00 - 1.2	1.00 - 3.00	1.00 - 6.00	10 - 80	30 - 90

Table 1.4: Comparisons between non-conservative box model estimated rates of bottom layer nutrient regeneration and oxygen demand in the Patuxent river estuary with sediment-water oxygen and nutrient exchange (SONE) rates measured in the Patuxent. All rates are in units of mmol m^{-2} d^{-1}. SONE rates from Boynton and Rohland (2001).

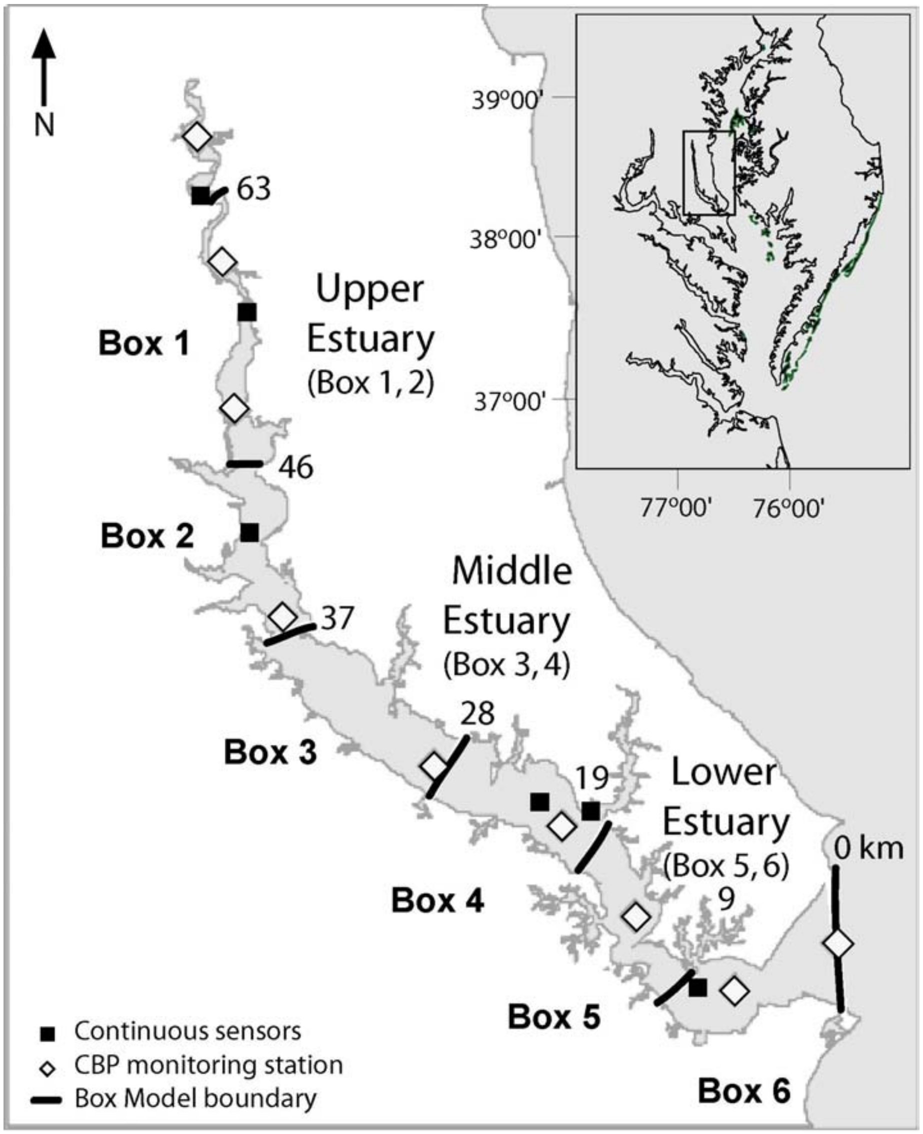

Figure 1.1: Map of the Patuxent River estuary with Chesapeake Bay (inset), including box model boundaries (Hagy 1996), Chesapeake Bay Program water quality monitoring stations (www.chesapeakebay.net), and the location of Maryland Department of Natural Resources' continuous water quality sensors (www.eyesonthebay.net). Chesapeake Bay Program station codes are to the left of each station and numbers at the right of box model boundaries indicate distance from the mouth of the estuary (km).

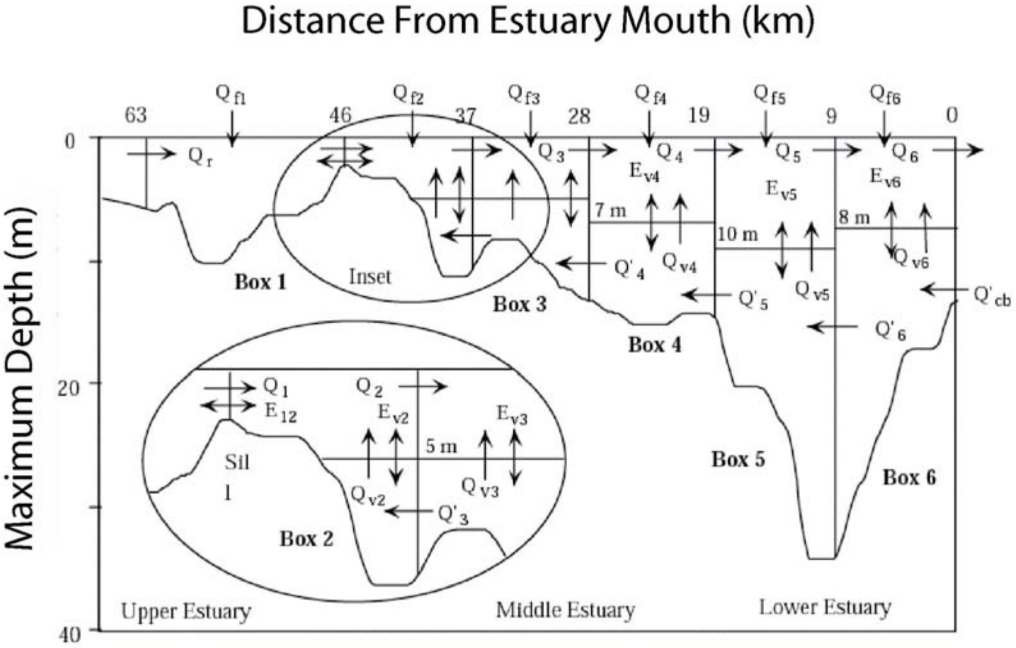

Figure 1.2: Schematic description of the box model structure (as seen in Hagy et al. 2000). Included are box model boundaries, exchange coefficients, and inputs. The estimated exchanges presented in this diagram are seaward advection (Q_m), landward advection (Q'_m), vertical advection (Q_{vm}), vertical diffusive exchange (E_{vm}), and horizontal dispersion ($E_{m,m+1}$). Included inputs are the volume of each box and the salt concentration (not included), river flow (Q_r), the input of freshwater to each box (Q_{fm}), and the salinity at the seaward boundary (not included).

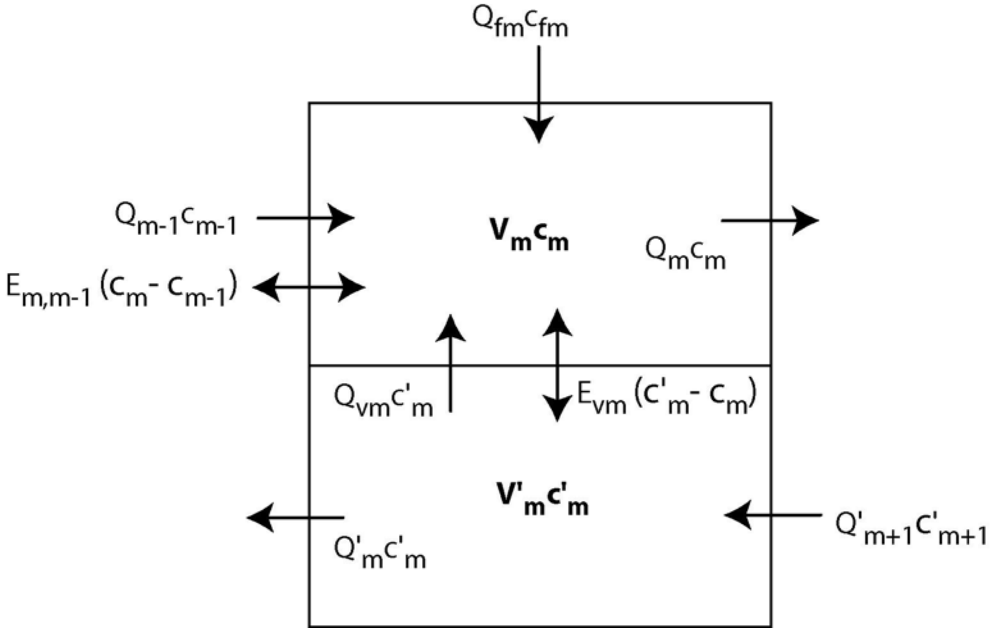

Figure 1.3: Generalized depiction of two-layer non-conservative box model for boxes 2-6. The non-advective exchange, $E_{m,m-1}(c_m - c_{m-1})$, is part of the calculation for Box 2 only. Notation is the same as in Figure 2 except for box volume (V) and up estuary (m-1) and down estuary (m+1) concentrations or water fluxes. Atmospheric inputs are included, though the non-conservative flux of DIN is the only rate where atmospheric inputs are included.

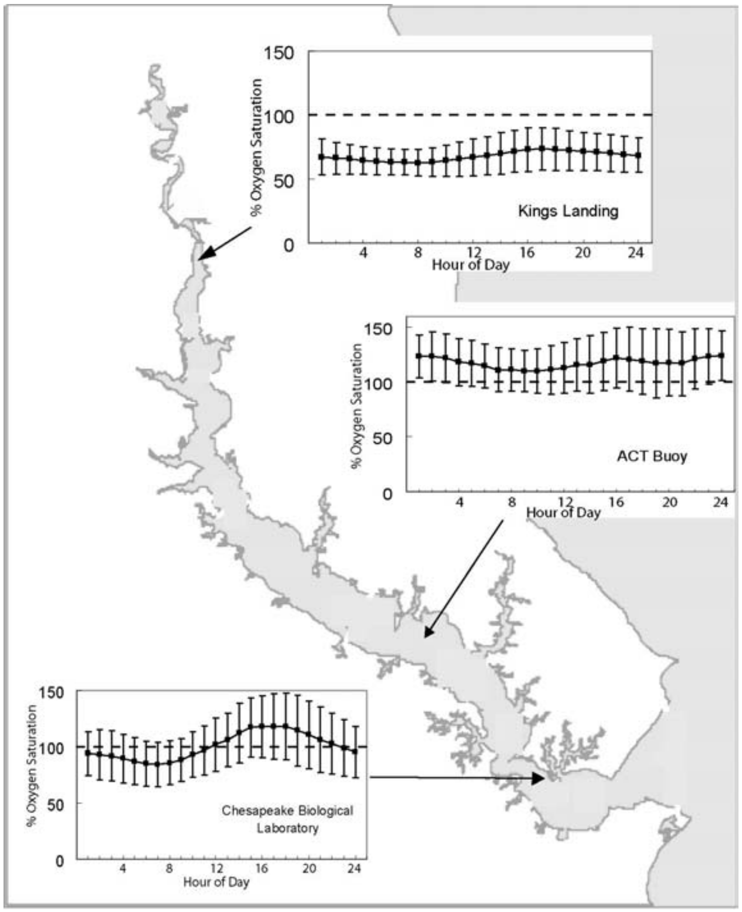

Figure 1.4: Average diel percent oxygen saturation curve for the month of August (2003 and 2004) in three regions of the Patuxent River estuary. The data were used to correct Chesapeake Bay Program monitoring data for the time of day sampled. Error bars represent one standard deviation of the mean. Data are from continuous water quality sensors maintained by the Maryland Department of Natural Resources (details of station location, depth, and available data can be found at www.eyesonthebay.net).

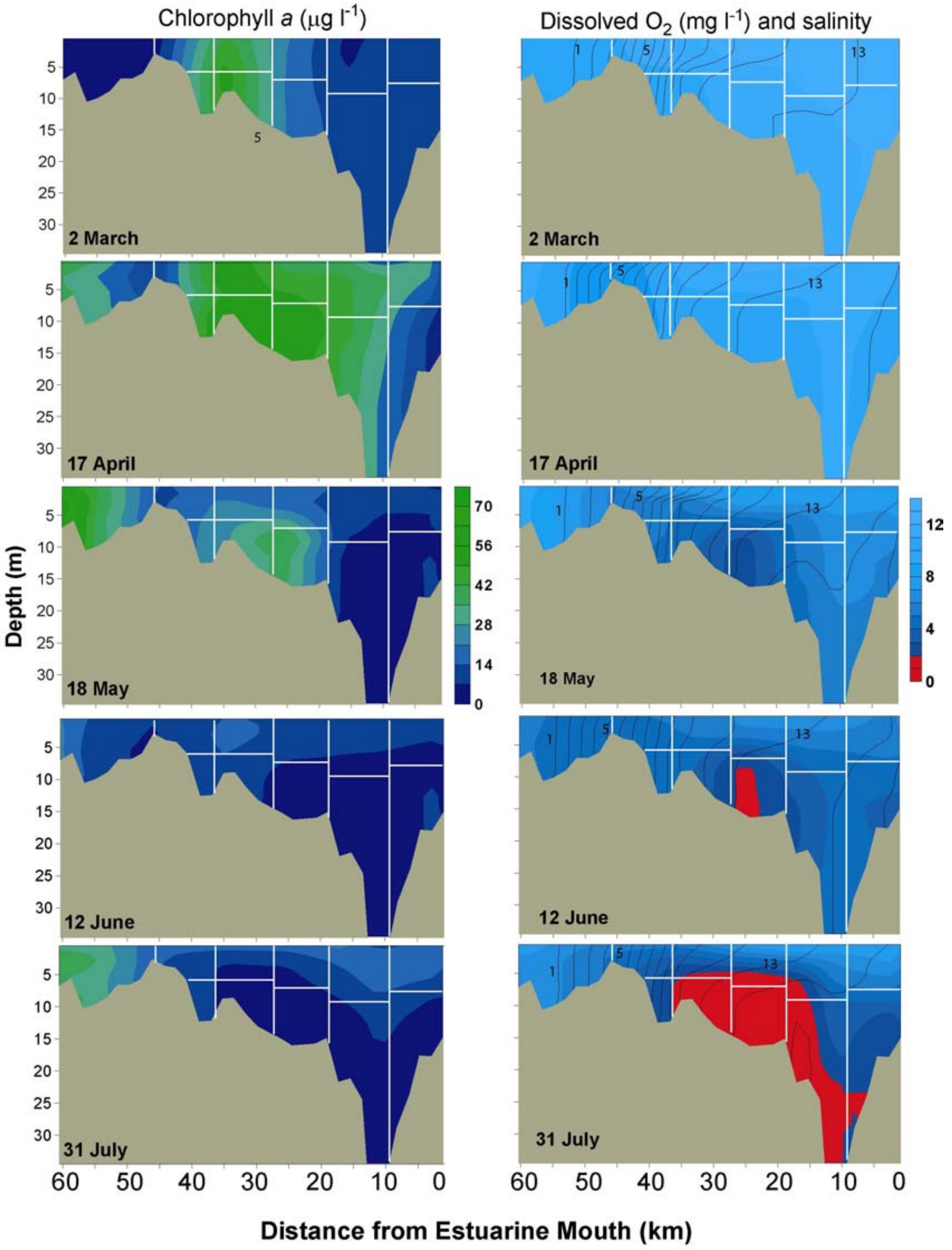

Figure 1.5: Contour plots of chlorophyll *a* (left panel) and dissolved oxygen/salinity (right panel) in the Patuxent River estuary in the winter, spring, and summer of 1995. Black lines represent salinity contours in the right panel and red area represents hypoxic water ($O_2 < 2$ mg l^{-1}). Box model boundaries are indicated by white lines. Salinity contours of 1, 5, and 13 are labeled.

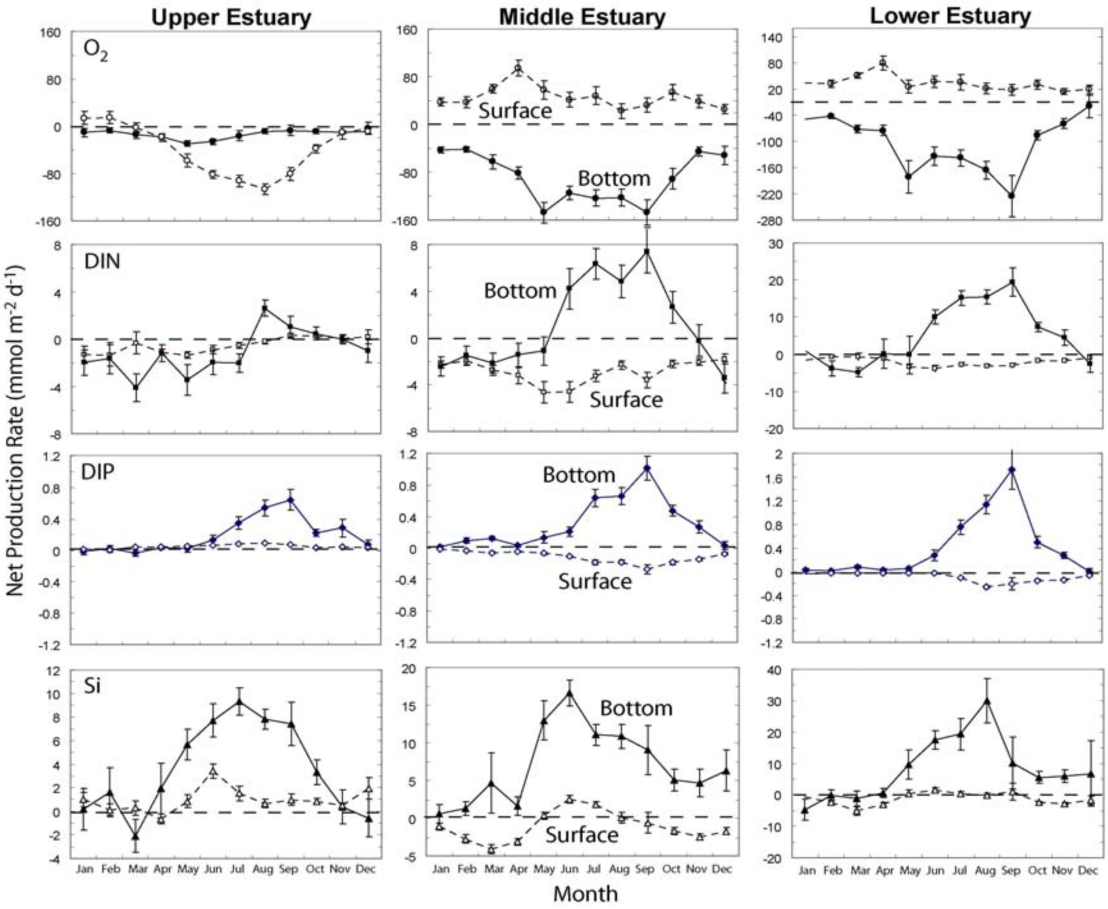

Figure 1.6: Monthly mean rates of net biogeochemical production of surface and bottom layer O_2 (surface rate corrected for air-sea exchange), DIN, DIP, and DSi computed by the box model for the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary. Monthly means (± SE) were calculated for all years from 1985 to 2003. Horizontal dashed lines are drawn at zero net production rates. Error bars represent one standard error of the mean.

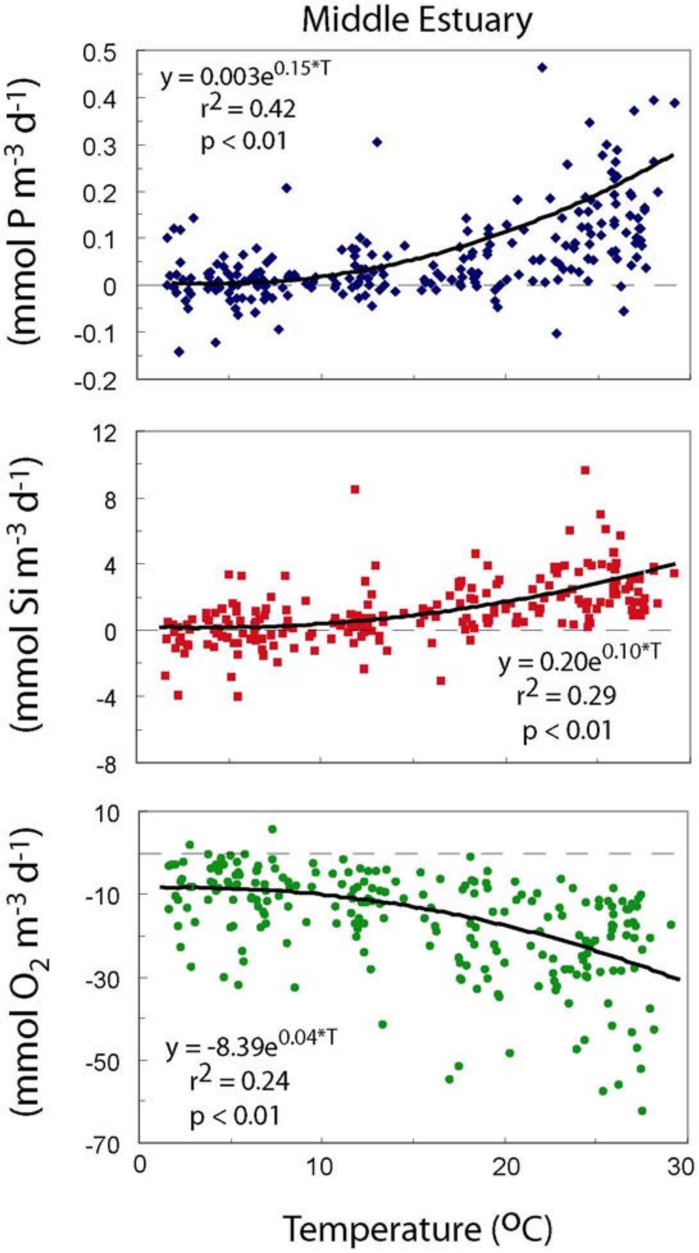

Figure 1.7: Relationships between temperature and monthly rates of bottom layer net production of DSi, DIP, and O_2, computed by the box model, in the middle region (Box 4) of the Patuxent River estuary.

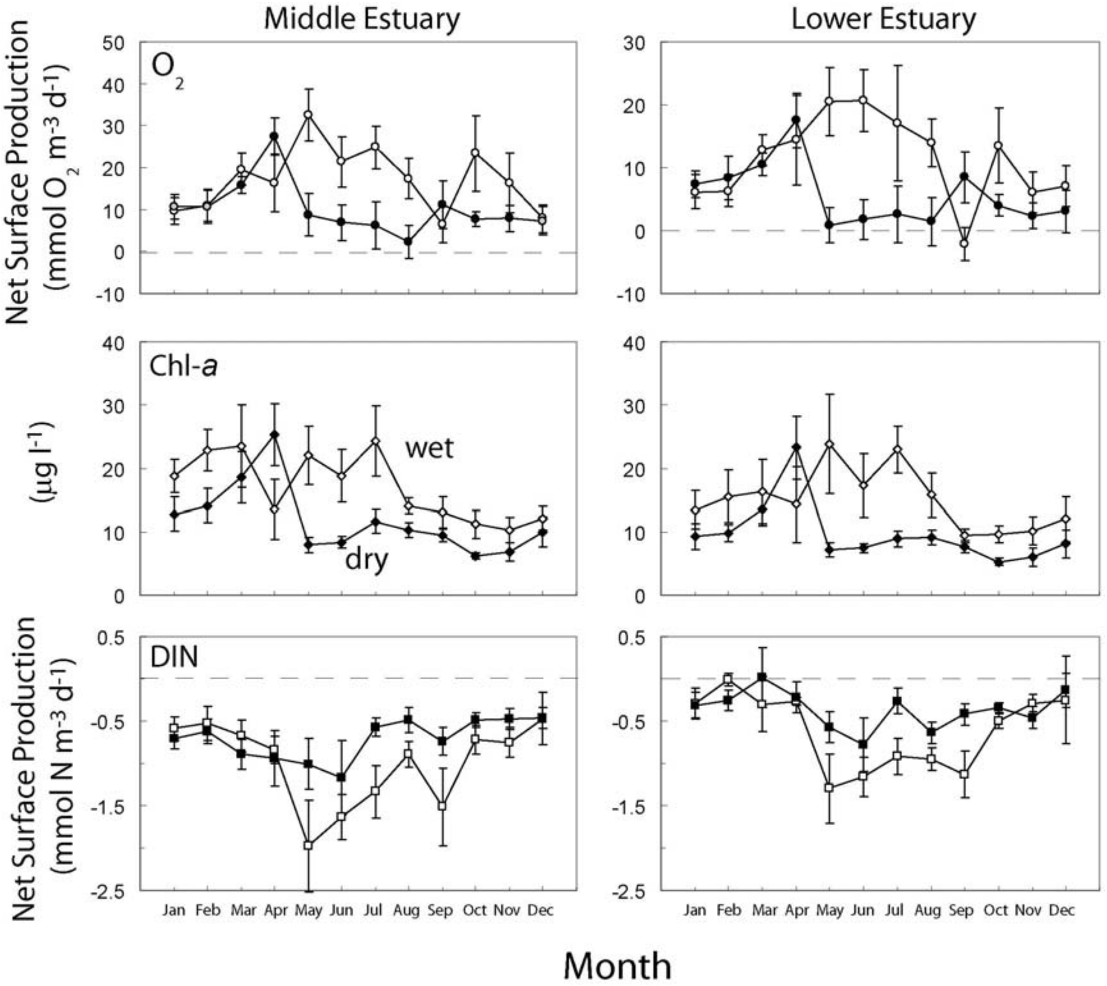

Figure 1.8: Monthly mean rates of net biogeochemical production of O_2 (corrected for air-sea exchange) and DIN computed for the surface layer by the box model, as well as chlorophyll *a* in the surface layer of the middle (Box 4) and lower (Box 5) regions of the Patuxent River estuary. Monthly mean values (± SE) were calculated for years of above average river flow (open shapes, flow > 20 year mean, n = 7) and below average river flow (shaded shapes, flow < 20 year mean, n = 9). Horizontal dashed lines are drawn at zero net production rates. Error bars represent one standard error of the mean.

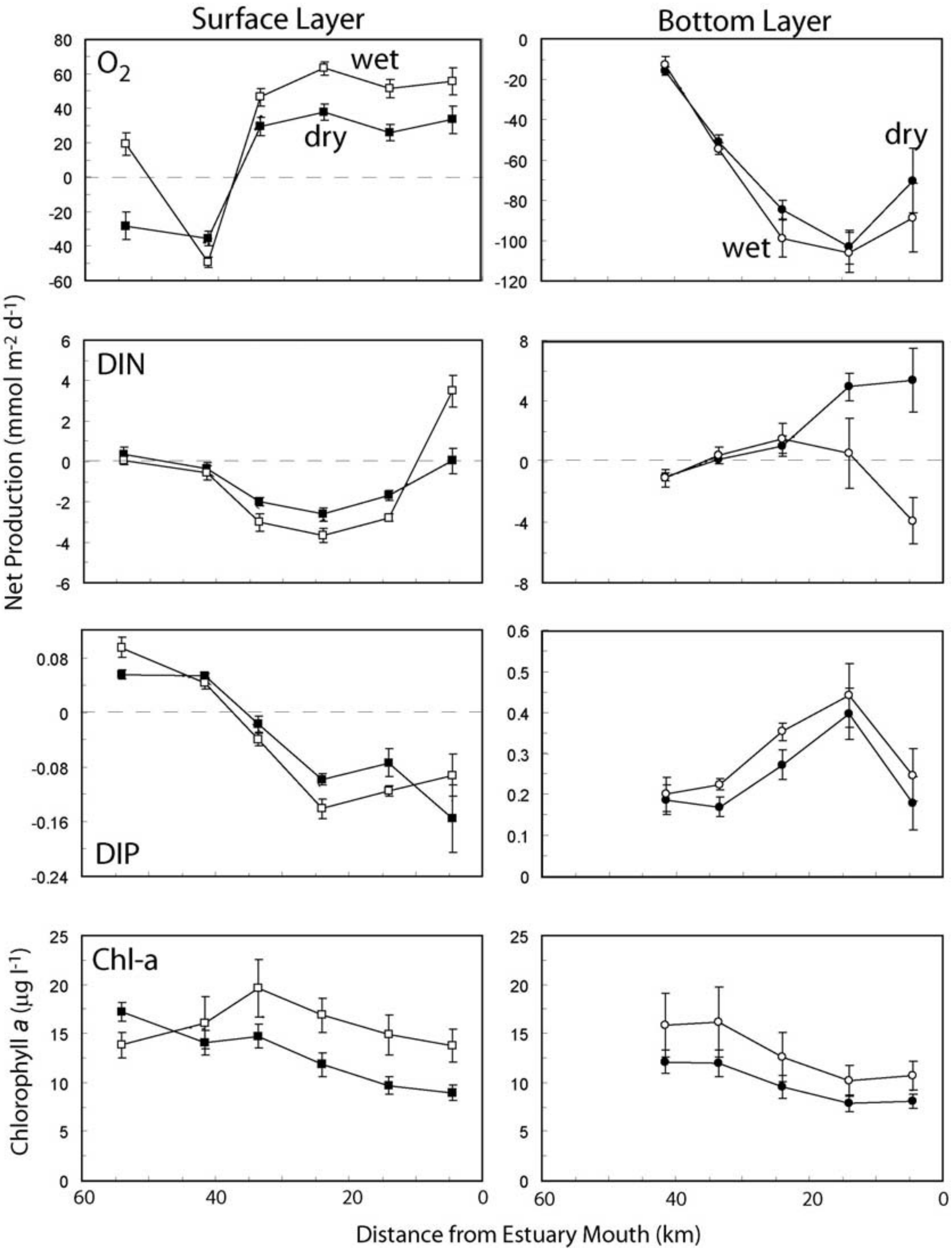

Figure 1.9: Mean annual rates of net biogeochemical production of surface and bottom layer DIN, DIP, and O_2 (surface rate corrected for air-sea exchange) computed by the box model, as well as chlorophyll *a* along the estuarine axis of the Patuxent River estuary. Annual means (± SE) were calculated for years of above average river flow (squares, flow > above 20 year mean + SE) and below average river flow (circles, flow < 20 year mean - SE). Error bars represent one standard error of the mean.

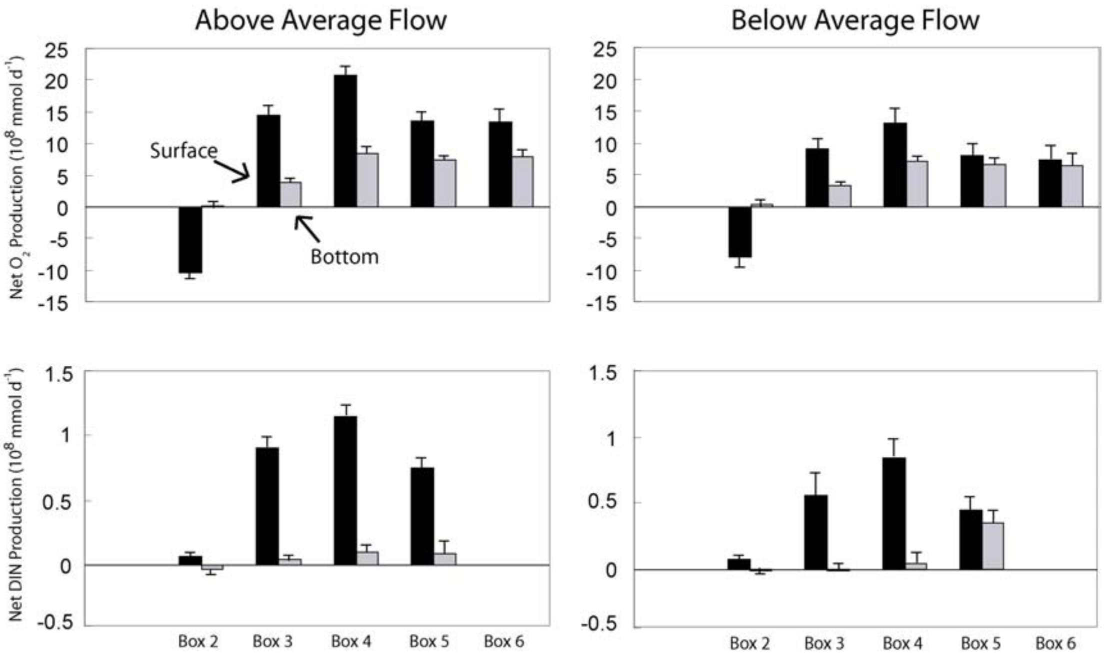

Figure 1.10: Mean annual rates of net biogeochemical production of surface and bottom layer O_2 (top panel, corrected for air-sea exchange) and DIN (bottom panel) along the estuarine axis of the Patuxent River estuary. Annual means were calculated for years of above average river flow (flow > above 20 year mean + SE) and below average river flow (flow < 20 year mean - SE). The rates are total mass fluxes in each layer in units of 10^8 mmol d^{-1}. Dark bars are surface layer rates and gray bars are bottom layer rates. Surface DIN consumption and bottom O_2 consumption rates were multiplied by -1 to simplify comparisons.

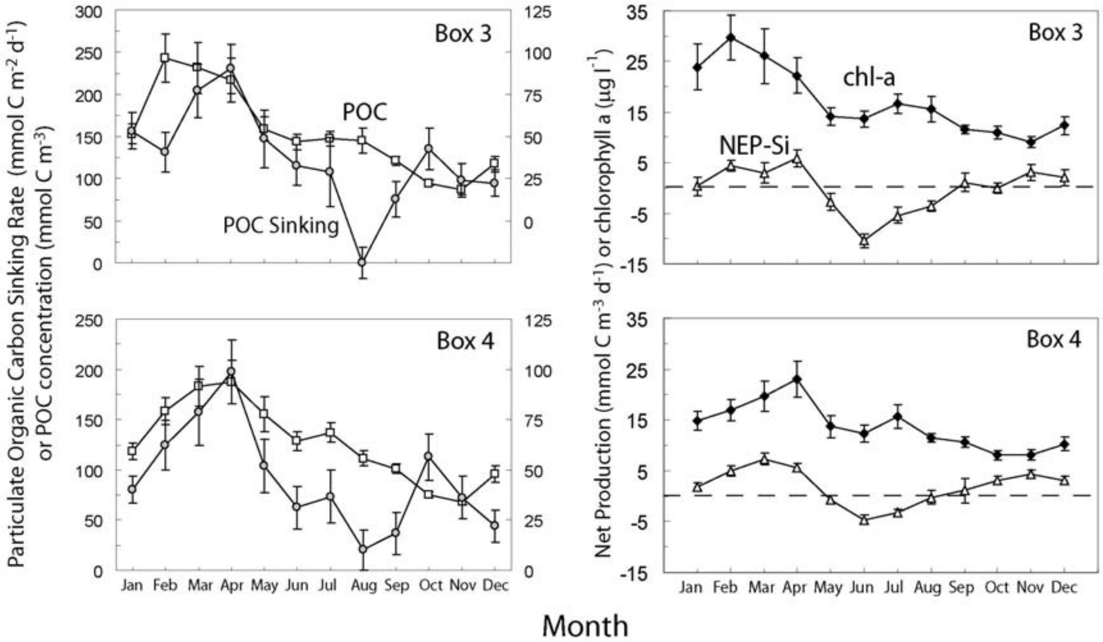

Figure 1.11: Mean monthly surface layer particulate organic carbon (POC) concentration and box model computed POC sinking (left panel), and surface layer net diatom growth (NEP_{Si}, right panel) and net surface layer chlorophyll *a* in the middle Patuxent River estuary (Box 3, 4). Monthly means (± SE) were calculated from 1985 to 2003 data. Horizontal dashed lines are drawn at zero. Error bars represent one standard error of the mean.

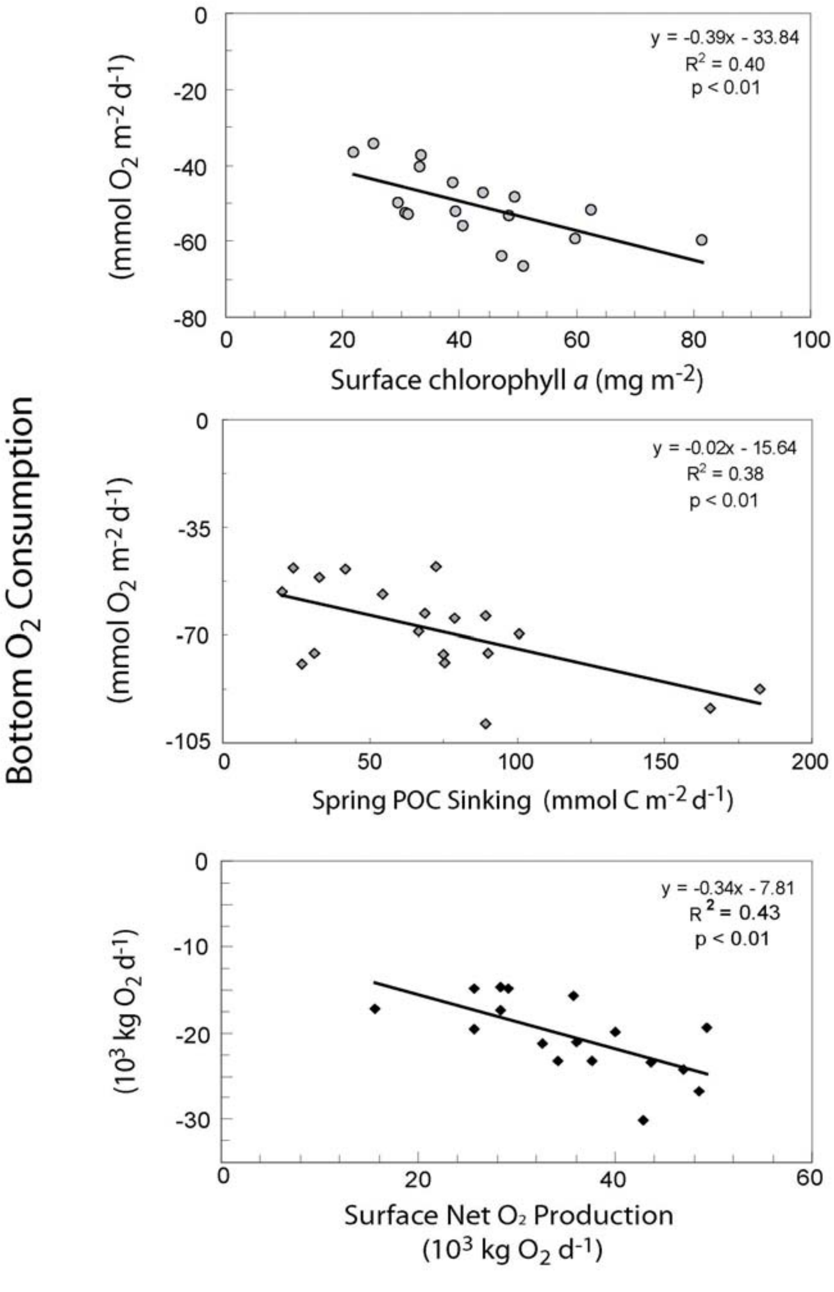

Figure 1.12: Correlation of mean annual rates of box model computed bottom layer O_2 consumption with mean annual surface chlorophyll *a* (top panel), spring POC sinking (middle panel), and surface net O_2 production (bottom panel, corrected for air-sea exchange) in the middle Patuxent River estuary. Data are annual means for the years 1985 to 2003.

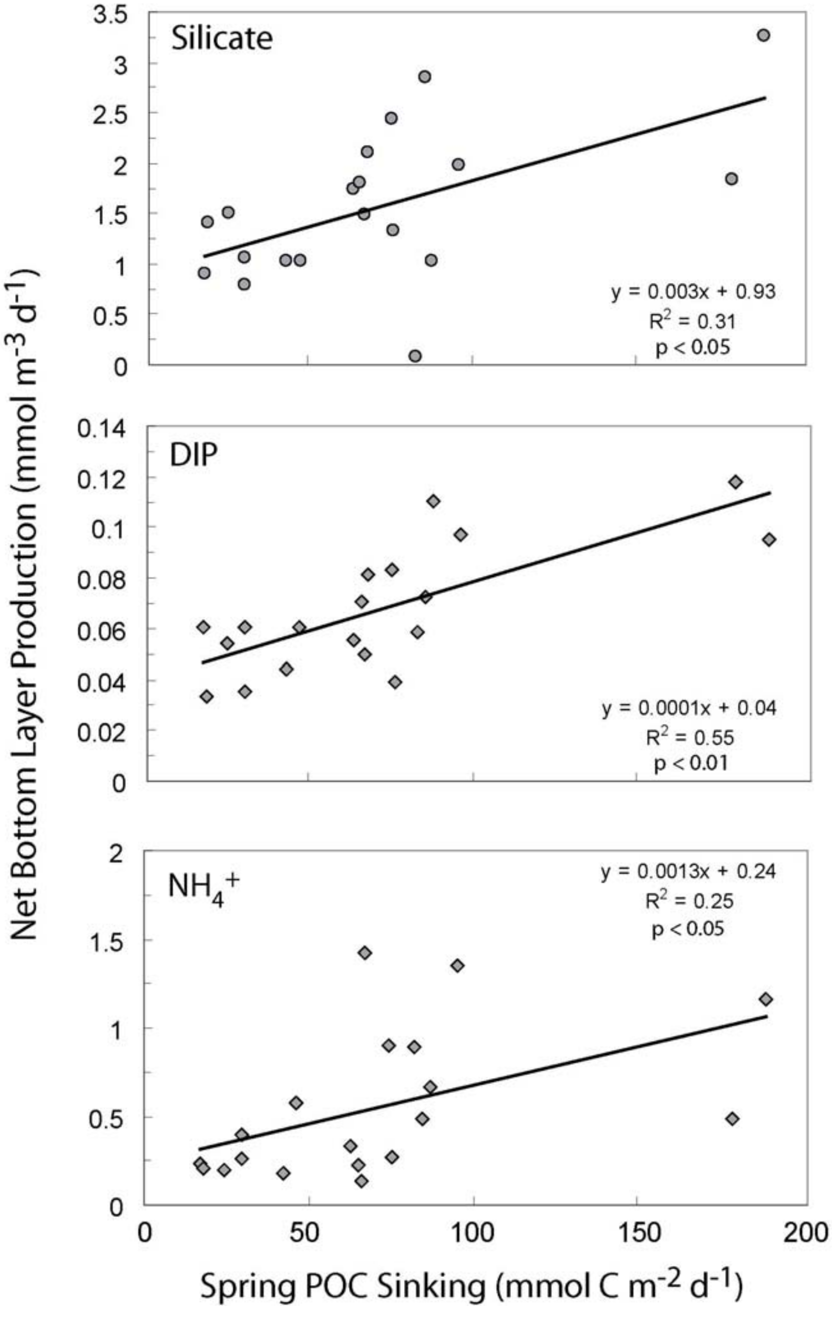

Figure 1.13: Correlation between mean annual box model compute spring POC sinking and bottom layer DSi, DIP, and NH_4^+ production in the middle region (Box 4) of the Patuxent River estuary. Data are annual means for the years 1985 to 2003.

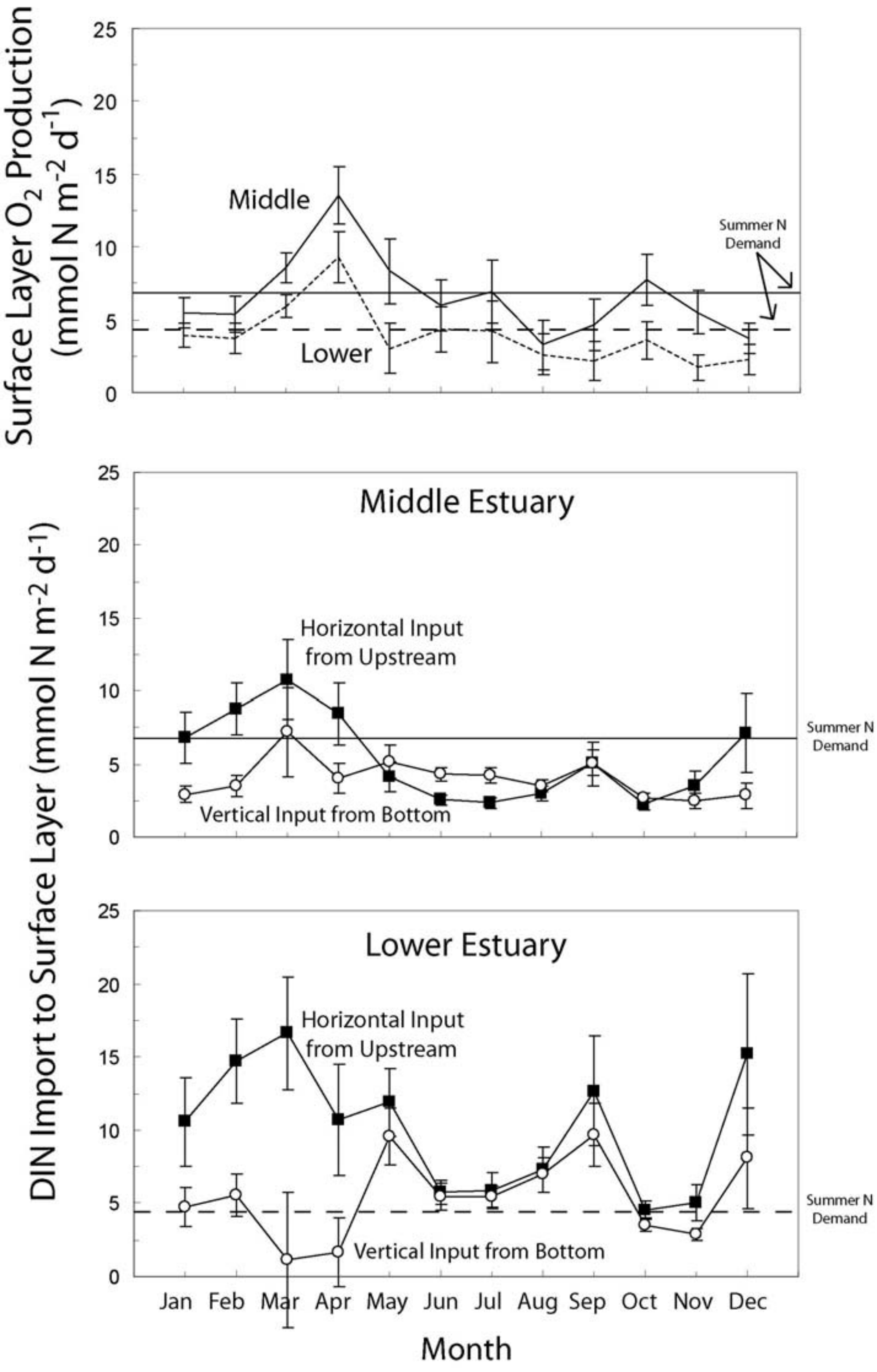

Figure 1.14: (Top panel) Monthly mean net O_2 production in the middle (solid line) and lower (dotted line) regions of the Patuxent River estuary. (Bottom panels) Monthly mean total inputs of DIN from seaward sources (squares) and vertical inputs from the bottom layer (circles) to the middle (Box 4) and lower (Box 5) regions of the Patuxent River estuary. Error bars represent one standard error of the mean.

CHAPTER II

Responses of water quality and biogeochemical fluxes to nutrient management and freshwater inputs in the Patuxent River estuary

Abstract

We conducted a quantitative assessment of estuarine ecosystem responses to variability in freshwater inputs and reduced phosphorus and nitrogen loading from sewage treatment facilities in the Patuxent River estuary. We analyzed a 19-year data set of climatic forcing, nutrient loading, and water quality conditions for six estuarine regions to compute monthly rates of net biogeochemical production and physical transport of dissolved oxygen (O_2), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), and dissolved silicate (DSi) using a salt- and water-balance model. Chlorophyll *a*, DIN and DIP concentration, surface net O_2 production, and bottom layer O_2 respiration were positively correlated with river flow on annual and seasonal time scales. Point source rates of DIN and DIP loading to the estuary, which declined by 40-60% following upgrades to sewage treatment plants, correlated with decreasing DIN and DIP throughout the Patuxent and declines in primary productivity and phytoplankton biomass in the tidal fresh region of the estuary. No clear trends in water quality and net O_2 production were apparent in the middle estuary, which appears to be due to persistently high nutrient loads from non-point sources. Despite declining seaward N and P transport to the region, chlorophyll *a* and surface net O_2 production have increased and water clarity has decreased in the lower estuary. Elevated chlorophyll *a* concentrations and net O_2 production rates in the lower estuary appear to be linked to above-average river flow in the 1990s, as

well as increasing net inputs of DIN into the estuary from Chesapeake Bay. In addition, significantly reduced grazing pressure from copepods during the time period favored increases in phytoplankton biomass and productivity. Thus, unexpected changes in external and internal factors have obscured the effects of nutrient management on water quality in the Patuxent River estuary.

Introduction

Effects of eutrophication are becoming increasingly evident in Chesapeake Bay (Kemp et al. 2005) and other coastal systems worldwide (Cloern 2001). Coastal eutrophication is driven by elevated inputs of key nutrients to ecosystems via anthropogenic sewage discharge, agricultural runoff, and atmospheric deposition (Nixon 1995, Jickells 2005). The structure and function of coastal ecosystems can change dramatically with eutrophication and responses include reduced cover of submerged aquatic vegetation (Duarte 1995), decreasing dissolved oxygen concentrations (Diaz 2001), increased frequency of toxic algae blooms (Paerl 1988), and food web shifts (Larsson et al. 1985, Smetacek et al. 1991). Effective management of coastal systems will require improved scientific understanding of ecological responses to changes in nutrient inputs (Cloern 2001).

Nutrient load reductions have been mandated for many estuaries and coastal systems in order to improve water quality conditions, including nutrient concentrations, phytoplankton biomass, water clarity, and dissolved oxygen concentrations (Conley et al. 2002, Kemp et al. 2005, Paerl et al. 2006). In general, eutrophication abatement has targeted phosphorus for most freshwater systems (Edmondson 1970, Schindler 1978), while more recent restoration efforts have emphasized both phosphorus and nitrogen in estuarine and coastal marine systems (Kemp et al. 2005, Paerl et al. 2006). In estuaries throughout the world where nutrient reduction mandates have been made, water quality monitoring programs are currently in place, in part to evaluate the response of the system to nutrient load reductions (Cloern 2001). Previous studies have used such data to demonstrate the recovery of water quality in coastal systems following nutrient load reduction (Smith et al. 1981, Lewis et al. 1998, Carstensen et al. 2006), while other studies have yielded less conclusive results, emphasizing the role of complicating physical and ecological factors (Kemp et al. 2005, Paerl et al. 2006).

Climatic variability also exerts dramatic influence on estuarine ecological processes. Fluctuations of freshwater inputs are perhaps the most notable consequence of climate and may mask the response of a system to nutrient management (Kimmerer 2002). Freshwater input affects residence time, salinity distribution, stratification, turbidity, and nutrient loads, all of which influence water quality and key ecosystem processes. In many estuaries, high freshwater inputs are associated with reduced dissolved oxygen concentrations and water clarity and increased phytoplankton biomass and nutrient loads (Malone et al. 1988, Justic et al. 1996, Boynton and Kemp 2000). Elevated freshwater flow can cause reduced phytoplankton productivity and biomass in other systems by inducing light limitation or reducing residence time (Cloern et al. 1983, Howarth et al. 2000). River flow tends to enhance hypoxia directly via increases in vertical stratification and indirectly via nutrient delivery and stimulation of primary production (Hagy et al. 2004). Assessing the interactions of nutrient management and freshwater flow is important for improved understanding of estuarine ecology and water quality for effective eutrophication management in coastal waters.

In one major tributary of Chesapeake Bay, the Patuxent River estuary, point source nitrogen and phosphorus loads have decreased substantially during the past two decades (D'Elia et al. 2003). Phosphorus load reductions began with a statewide ban on phosphate detergents in 1984, with subsequent upgrading of the eight major sewage treatments facilities in the Patuxent River basin to include phosphorus removal (Lung and Bai 2003). Reductions in nitrogen loads from sewage treatment plants in the watershed began in 1990 with the installation of biological nitrogen removal systems (BNR), in which the final nitrogen transformation is denitrification (Lung and Bai 2003). Freshwater flow to the estuary has been highly variable during the last two decades, including several sequential years with large differences in flow (Lung and Bai 2003). A monitoring program has produced spatially and temporally resolved water quality data in the estuary since 1985, in addition to measurements and estimates of nutrient loads and freshwater inflows. The Patuxent River estuary therefore provides a unique opportunity to evaluate the estuarine system response to long and short-term changes in water quality in response to nutrient loading and freshwater inputs (D'Elia et al. 2003, Jordan et al. 2003). Despite the available data sets, most previous studies have focused on particular aspects of the Patuxent River estuary's response to nutrient load reductions (Stankelis et al. 2003, Fisher et al. 2006). A comprehensive analysis of estuarine ecological responses to declines in nitrogen and phosphorus loading and to variability in freshwater flow remains to be achieved.

The purpose of this chapter is to analyze a multi-decade data set of water quality variables for the Patuxent River estuary to evaluate temporal trends in relation to contemporaneous nutrient management and to variations in freshwater flow. Consequently, this study will discern human impacts on water quality from hydrologic forcing. We hypothesize that point source nitrogen and phosphorus management has yielded generally improved water quality conditions in the Patuxent River (i.e., reduced phytoplankton biomass/productivity, nutrient concentrations, and respiration, but increased water clarity and dissolved oxygen concentrations), despite variability in freshwater flow.

Methods

We analyzed data for key water quality variables from stations along the Patuxent River estuarine salinity gradient for the periods 1963-1970, 1978, 1981, and 1985 to 2003. These data were assembled from unpublished technical reports and the Chesapeake Bay Monitoring Program. We analyzed the monitoring data (1985 to 2003) to estimate monthly and regional rates of net production and transport of nutrients, dissolved oxygen (O_2), and other water quality variables, using a simple model of salt- and water-balances. We examined relationships between nutrients, O_2 concentrations, and net production rates versus river flow and nutrient loading rates to evaluate the interacting roles of nutrient management and hydrologic variability in controlling water quality conditions and ecosystem processes.

Water Quality Data

We compiled water quality variables from the Chesapeake Bay Monitoring Program for the period 1985 to 2003, including inorganic and organic nutrients (NO_3^-, NH_4^+, PO_4^{-3}, TN, TP, mg l^{-1}), dissolved O_2 (mg l^{-1}), chlorophyll *a* (μg l^{-1}), secchi depth (m), and salinity. NO_3^- and NO_2^- are commonly reported as a sum value, with NO_2^- usually comprising a minor fraction of the sum; thus we hereafter report the sum as NO_3^-. Water samples were obtained from a submersible pump, filtered immediately, and stored for later analysis. The methods used for chemical analysis (Table 2.1) undergo routine robust QA/QC reviews. Unpublished data from technical reports and personal communications were also compiled (Flemer et al. 1970, MD DNR 1980, Boynton et al. 1981). With a few exceptions, similar methods for field sampling and chemical analysis were used to generate these data (Table 2.1). The sampling locations spanned the estuarine axis of the Patuxent River (Fig. 2.1).

Transport and production of non-conservative variables

We calculated net non-conservative production rates of dissolved O_2, dissolved inorganic phosphorus (DIP = PO_4^{3-}), dissolved inorganic nitrogen (DIN = $NO_3^- + NH_4^+$), and dissolved silicate (DSi = SiO_3^{2-}) in six regions of the estuary for each month from 1985 to 2003 using a modification of a previously described salt- and water-balance model, or "box model" (Pritchard 1969, Officer 1980). The boundaries of the estuarine regions, or "boxes" span the estuarine axis and were chosen to enclose at least one monitoring station (used to characterize the box) and to include similar volumes and areas for each box (Fig. 2.1). We analyzed and extended a previously constructed box model (Hagy et al. 2000) to calculate monthly mean non-conservative fluxes of nutrients and dissolved O_2 in the Patuxent River for the period 1985 to 2003. This box modeling approach allowed us to compute the time-dependent, monthly mean physical water transports between regions and across boundaries for the estuary using data for salinity and freshwater input. The box model for the Patuxent River estuary calculates advection and mixing between eleven control volumes, or "boxes" in the estuary, where the five most seaward boxes include a surface and a bottom layer (Fig. 2.2). Previous analyses of box models for this estuary indicate good agreement between computed velocities and mean values observed as direct measurements from a moored platform (Hagy 1996, Hagy et al. 2000).

The water and salt balance equations follow the general form for box "*m*" in a two-layered, estuarine region (Fig. 2.2). The possible salt exchanges include axial advective and diffusive exchanges in two directions, vertical advective and diffusive exchanges, and freshwater input. Thus, the salt balance is described below

$$V_m \frac{ds_m}{dt} = Q_{m-1}s_{m-1} + Q_{vm}s'_m - Q_m s_m + E_{vm}(s'_m - s_m) + [E_{m-1,m}(s_{m-1} - s_m) - E_{m,m+1}(s_{m+1} - s_m)] \qquad (1)$$

and the water balance is

$$\frac{dV_m}{dt} = 0 = Q_m - (Q_{m-1} + Q_{vm} + Q_{fm}) \qquad (2)$$

where V_m is the volume of the box, Q_m is the advective transport to the seaward box, Q_{m-1} is the advective transport from the landward box, Q_{vm} is the vertical advective input into the box, Q_{fm} is the freshwater input into the box, $E_{m-1,m}$ is the diffusive exchange with the landward box, $E_{m,m+1}$ is the diffusive exchange with the seaward box, E_{vm} is the vertical diffusive exchange, s_m is the salinity in the surface layer box, s_{m-1} is the salinity in the landward box, s_{m+1} is the salinity in the seaward box, and s'_m is the salinity in the bottom layer box. The left hand side of equation 1 is computed as the monthly salinity change, while the left hand side of equation 2 is assumed to be zero at monthly time scales. Provided a box model with a total of *n* boxes, the total of the salt- and water-balances yields 2*n* equations. To limit the number of unknown exchanges to 2*n*, horizontal diffusive exchanges were assumed to be zero, except between Box 1 and 2 (Officer 1980, Hagy et al. 2000).

The equations used to estimate the advective and non-advective transports for non-conservative variables (i.e., DIN, DIP, DSi, and O_2) are similar to the salt balance equations except salinity is replaced by a non-conservative variable. For non-conservative variables, the mass balance equations also must include a residual term. This residual term provides a measure of the net production or consumption rate (P_m) of the non-conservative variable. For any surface layer box *m* in the two-layer scheme of the box model, the equation is as below.

$$V_m \frac{dc_m}{dt} = Q_{m-1}c_{m-1} + Q_{vm}c'_m + E_{vm}(c'_m - c_m) + E_{m+1,m}(c_{m+1} - c_m)$$
$$+ E_{m,m-1}(c_m - c_{m-1}) - Q_m c_m + P_m \qquad (3)$$

This above equation is rearranged to calculate the net production rate in the box (P_m).

$$P_m = V_m \frac{dc_m}{dt} - Q_{m-1}c_{m-1} - Q_{vm}c'_m - E_{vm}(c'_m - c_m) - E_{m+1,m}(c_{m+1} - c_m)$$
$$- E_{m,m-1}(c_m - c_{m-1}) + Q_m c_m \qquad (4)$$

Note that $E_{m,m-1} = 0$ for $m \neq 2$, $E_{m+1,m} = 0$ for $m \neq 1$, and $E_{vm} = 0$ and $Q_{vm} = 0$ for $m = 1$ (Fig. 2.2, 2.3). For any bottom layer box *m*, the mass balance expression is

$$V'_m \frac{dc'_m}{dt} = Q'_{m+1}c'_{m+1} - Q_{vm}c'_m - Q'_m c'_m - E_{vm}(c'_m - c_m) + P'_m \qquad (5)$$

The above equation can be rearranged to calculate P'_m

$$P'_m = V'_m \frac{dc'_m}{dt} - Q'_{m+1}c'_{m+1} + Q_{vm}c'_m + Q'_m c'_m + E_{vm}(c'_m - c_m) \qquad (6)$$

The variables used in equation 3 through 6 include V'_m, which represent the volume of the bottom layer boxes, where the subscript, *m*, is the box identifier numbered 1-6 from the landward to the seaward ends, and prime notation indicates the bottom layer. In addition, c'_m is the concentration of the non-conservative material, Q'_m is the advective fluxes to and from box *m* in bottom layers, Q_{vm} is the vertical advection from bottom to surface layer, E_{vm} is the vertical diffusive exchange between the surface and bottom layers of box *m*, and P'_m is the net production (or consumption) rate in bottom layers.

O_2 concentrations measured at varying times within the day were adjusted to daily mean estimates using patterns of diel variability based on continuous sensor observations at nearby sites (ACT 2005, MD DNR 2005). These estimates of daily mean O_2 were used in the box model to compute physical transport and net non-conservative production rates of dissolved O_2, the latter of which were corrected (surface layer only) for air-sea exchange. Organic carbon and nutrients do not exchange significantly with the atmosphere, so similar adjustments do not have to be made for those variables. We estimated the air-sea O_2 exchange on monthly time scales using the estimated daily mean O_2 values in the top 0.5 m of the water column following Caffrey (2003):

$$F_{A\text{-}O_2} = \alpha\,(1 - C_{O_2}/C_{O_2\text{-}S}) \tag{7}$$

where α is the air-sea exchange coefficient (g O_2 m^{-2} h^{-1}), C_{O2} is the adjusted daily mean O_2 concentration at 0.5 m depth (g m^{-3}), $C_{O2\text{-}S}$ is the O_2 saturation value (g m^{-3}). We used a value for α of 0.5 g O_2 m^{-2} h^{-1}, which is a median value measured for Chesapeake Bay and its tributaries (Kemp and Boynton 1980) and based on published relationships with wind speed exchange (e.g., Hartman and Hammond 1984, Marino and Howarth 1993, Caffrey 2003). Analysis of annual variations in wind speed and direction (observed at the nearby Patuxent Naval Air Station) suggested that, while there were significant variations in wind velocity on daily to weekly scales, there were no significant monthly or seasonal trends.

The sum of net O_2 production in the surface and bottom layers provides an estimate of net ecosystem production (NEP = total system carbon production – total system carbon respiration (see Hagy 1996, Howarth et al. 1996). We tested the sensitivity of calculated surface layer net O_2 production rates to increases and decreases in α of ± 50%. Rates varied by 5-10% in the middle and lower estuary (Box 3-6), where net O_2 production is highest, and by 5-15% in the upper estuary (Box 1, 2).

Hypoxia

We calculated hypoxic volume as the volume of water in the estuary with a dissolved O_2 concentration less than 2 mg l^{-1}. Vertical dissolved O_2 profiles at monitoring stations (Fig. 2.1) were interpolated to 1-meter intervals and then extrapolated horizontally at constant depth. The resulting 2-dimensional interpolated grid (1-meter x 1-nautical mile) was coupled to cross-sectional volumes along the axis of the Patuxent River (Cronin and Pritchard 1975) to yield volumes of 477 cells within the estuary. For each sampling date from 1985 to 2003, hypoxic volume was calculated by summing the volume of the cells with O_2 less than 2 mg l^{-1}. The integrated area under the time series of hypoxic volume for each year is equivalent to hypoxic volume days, a time-volume integrated value that represents hypoxia (m^3 d yr^{-1}).

Nutrient load and freshwater flow data

We assembled data for daily river flow and total nitrogen (TN) and phosphorus (TP) inputs to the estuary from a stream gauge (Bowie, MD; USGS 2005) for the period 1985 to 2003. Monthly averages were computed from daily rates of river flow and total nutrient inputs to match the time scale of the box model rates and water quality variables. Data for inputs of TN, TP, and water from sewage treatment plants were obtained from the Chesapeake Bay Program nutrient input monitoring program from 1985 to 2003. In addition, we also obtained estimates non-point TN and TP loads to the Patuxent River above and below Box 2 (Fig. 2.1) produced from the Chesapeake Bay Watershed Model for the period 1985 to 1997 (Linker et al. 1996).

Statistical analyses

We examined temporal trends in water quality data and computed nutrient production rates from 1985 to 2003 using two approaches. First, we used Model I linear regressions for the annual means of chlorophyll *a*, secchi depth, DIN and DIP concentrations, and net O_2 production. We also performed trend analyses on the monthly means of the same water quality variables using a Seasonal Kendall test. The Seasonal Kendall test accounts for seasonality in the data and determines if the slope of the trend lines was significantly different from zero. We reported Kendall's tau values (similar to correlation coefficient), slopes of trend lines, and *p*-values for all trends calculated with the Seasonal Kendall tests. We consider significant slopes to occur when the p-value is < 0.01. Lastly, we removed the effect of river flow from time series of annual mean chlorophyll *a* and surface layer net O_2 production in the upper, middle, and lower estuary by fitting linear regressions to the river flow versus chlorophyll *a* and river flow versus net O_2 production relationships, and then analyzed the residual values of the temporal trends.

Results

Temporal trends in nutrient loading

Point source discharges of total nitrogen (TN) declined by up to 50% (0.75 10^3 kg d^{-1} decline above the fall line, 0.5 10^3 kg d^{-1} below) after the incorporation of BNR at sewage treatment facilities in 1990 (Fig. 2.3). Similarly, point source discharge of total phosphorus (TP) declined sharply in 1986 (> 50% decline) after the statewide phosphate ban from detergents, as well as sewage treatment plant upgrades.

Winter discharges of TN from sewage plants remained high because of seasonally varying treatment protocols, which was especially evident below the fall line (Fig. 2.3). Total water discharge from all sewage treatment facilities in the watershed increased steadily since 1985, concomitant with population increases in the watershed (Fig. 2.3, D'Elia et al. 2003). In the upper estuary, point source loads comprised 50-60% of total nitrogen loads before BNR, but now comprise only 20-30%. Following sewage treatment upgrades, declining trends in TN and TP concentrations were significant ($p < 0.01$) in the non-tidal freshwater region of the river through 2002 (Fig. 2.4). Elevated TP concentrations in 2003 were associated with sustained high river flow (Fig. 2.4). Total nitrogen loads from upstream waters into the mesohaline estuary declined significantly ($p < 0.01$) after BNR installation. Average declines approached 100 kg N d^{-1} from 1985-2002, but loads are elevated during periods of high river flow (Fig. 2.4, 2.5). Total phosphorus loads from upstream waters into the mesohaline estuary declined significantly ($p < 0.01$) after phosphate removal. Average declines approached 116 kg P d^{-1} from 1985-2002, but loads are elevated during periods of high river flow (Fig. 2.4). River flow has been higher on average during the 15 years after BNR (19.2 ± 2.3 m^3 s^{-1}) than in the mid to late 1980s (14.4 ± 1.8 m^3 s^{-1}) when phosphorus loads were higher (Fig. 2.4). Despite reduced mean inputs of total nitrogen into the estuary per unit river flow after BNR, the highest flow and load periods on record occurred episodically after BNR (Fig. 2.5). Total nitrogen and phosphorus loads from non-point sources were elevated in the 1990s (3.0 ± 0.37 10^3 kg d^{-1}) relative to the 1980s (2.0 ± 0.26 10^3 kg d^{-1}; Fig. 2.6). Following BNR, non-point TN and TP loads are similar or higher than point loads to the lower estuary.

Temporal trends in water quality

By combining data from individual studies between 1970 and 1980 with the Chesapeake Bay Monitoring Program data (1985 to 2003 data, CBP 2005), we analyzed long-term trends in water quality. This analysis suggests that DIP concentrations increased by 50% and NO_3^- increased by 10-20% between 1970 and 1980 in the upper and middle estuary, with concentrations observed in the late 1970s being similar to those in 1985 (Fig. 2.7). Since BNR was established, NO_3^- concentrations in the middle estuary have been reduced to levels observed in the 1960s, but concentrations in the upper estuary have remained elevated (Fig. 2.7). Recent (2001-2003) concentrations of NO_3^- and DIP have not returned to levels observed in the 1960s in the upper estuary following sewage treatment upgrades (Fig. 2.7). Chlorophyll *a* values were lower in the 1960s than in the years after 1970 and annual variability in chlorophyll *a* was also lower in the 1960s than any other decade (Fig. 2.7). Trends in chlorophyll *a* are not significant.

Analyses of data from 1985 to 2003 reveal significant declines (Table 2.2) in annual mean DIN concentration throughout the estuary (upper, middle, and lower regions). Mean DIN concentration was 30-50% lower after BNR than before (Fig. 2.8). DIP concentrations also declined in all regions of the estuary in the mid 1980s, following the phosphate detergent ban and sewage treatment upgrades (Table 2.2, Fig. 2.8). Declining trends in DIN and DIP concentrations over time were significant using both Model I linear regressions and the Seasonal Kendall test (Table 2.2). Although DIN concentrations were elevated to pre-BNR levels during the high river flow years of the mid-1990s and DIN was positively correlated with river flow in the upper estuary, but not the lower and middle ($r^2 = 0.1 - 0.2$, $p > 0.1$; Fig. 2.8), DIP responded negatively and insignificantly to river flow ($p > 0.1$; Fig. 2.8). We found a significant correlation between total sewage nitrogen load and DIN concentration in the upper estuary ($p < 0.01$), but not in the middle and lower estuary (Fig. 2.9). During four mid-1990s years with high river flow (1993, 1994, 1996, 1997), DIN concentrations in the middle and lower estuary were as high or higher than before sewage upgrades. DIN concentrations, however, were lower than all previous years during four years of below average flow (1999 to 2002, Fig. 2.9). For the remaining years, DIN concentrations in the middle and lower estuary were significantly related to sewage TN load ($p < 0.01$).

Chlorophyll *a* in the lower estuary was generally higher after the implementation of BNR than before BNR, and two statistical tests indicated positive trends in all regions of the estuary (Fig. 2.10). Positive trends were significant in the upper and middle estuary based on the Seasonal Kendall test, but not for the linear regression (Table 2.2). Lower estuary trends in chlorophyll *a* were significant at $p < 0.1$ for the Model I linear regression and $p < 0.01$ for the Seasonal Kendall test in the middle and lower estuary (Table 2.2). Trends in mean summer (June to August) chlorophyll *a* in the lower estuary were significantly ($p < 0.05$) positive from 1985 to 2003 (Fig. 2.11). Chlorophyll *a* was also significantly correlated with river flow in the middle ($r^2 = 0.35$, $p < 0.01$) and lower ($r^2 = 0.53$, $p < 0.01$) estuary (Fig. 2.12). An examination of the time series of the chlorophyll *a* versus river flow residuals, which indicates factors controlling chlorophyll *a* aside from river flow, reveals concave curves for the middle and lower estuary, with a negative trend occurring during the first 8-9 years of the data set (Fig. 2.12). An increasing trend in the residuals (i.e., more chlorophyll *a* than expected from flow) occurred from 1998 to 2003 in all regions of the estuary (Fig. 2.12).

Annual mean secchi depth decreased over time (i.e., water clarity declined) in all regions of the estuary, which corresponds with the increasing chlorophyll *a* trends (Fig. 2.10, see Appendix I). The trends are significant for both the Model I linear regression and the Seasonal Kendall test in the middle estuary (Table 2.2). Computations of k_d, made using an empirical light model for mesohaline-polyhaline of Chesapeake Bay water (Wu et al. 2005), suggest that chlorophyll contributes more to light attenuation (20% of total k_d) than TSS (3 %) in the lower Patuxent estuary. Trends in mean summer (June-August) secchi depth in the lower estuary were also significantly negative from 1985 to 2003 (Fig. 2.12). In general, the significance of trends calculated with the Seasonal Kendall test for monthly mean chlorophyll *a* and secchi depth generally agree with significance of the simple linear regression computed for the annual means of chlorophyll *a* and secchi depth. We did not perform a residual analysis for secchi depth because only weak relationships existed between secchi depth and river flow.

Temporal trends in net O_2 production and biogeochemical fluxes

We found no clear trends of declining surface layer net O_2 production over the period 1985 to 2003 in the upper (Box 2) and middle (Box 4) estuary. Net O_2 production was 50% higher after BNR than before in the lower estuary (Box 5; Fig. 2.13). Surface net O_2 production appeared to increase in the middle and lower estuary over the 19-year record; however, only the trend calculated with a Model I linear regression for the lower estuary was significant (Table 2.2, Fig. 2.13). Inter-annual variability in river flow influenced net O_2 production, with annual mean river flow explaining 72% of the variability in surface net O_2 production in the upper estuary ($p < 0.01$). Relationships were weaker for the middle and lower estuary, as river flow explained 15% ($p = 0.09$) and 36% ($p < 0.01$) of variability in net O_2 production, respectively (Fig. 2.14). There was no clear trend in the residuals of the relationship between net O_2 production and river flow for any regions of the estuary, but positive residuals (i.e., more net O_2 production than expected from river flow) are more frequent in the lower estuary after BNR than before (Fig. 2.14). Bottom layer O_2 consumption was generally lower (i.e., less negative) in the upper estuary during years following BNR, but no significant differences were found between the periods. Bottom layer O_2 consumption was generally higher (i.e., more negative) in the middle and lower estuary in the post-BNR years, but no significant differences between the periods were found (Fig. 2.13). Surface layer net O_2 production and bottom layer O_2 consumption were significantly correlated on annual time scales in Box 4 ($r^2 = 0.43$, $p < 0.01$).

No clear trends in annual rates of net production of DIN, DIP, and DSi were evident from 1985 to 2003 for the surface or bottom layer in all estuarine regions. Rates of net DSi production in the bottom layer of the middle and lower estuary appear to be higher in the mid 1990s when freshwater inputs were high and river flow explained 40% (middle, $p < 0.01$) and 27% (lower, $p = 0.02$) of inter-annual variability. Annual mean rates of surface DIN and DIP net consumption are significantly correlated with annual mean river flow in the middle estuary ($r^2 = 0.35$, $p < 0.01$ and $r^2 = 0.49$, $p < 0.01$, respectively).

Trends and controls on Hypoxia

Bottom waters of the Patuxent River estuary often experience hypoxia between May and September. The extent and severity of hypoxia varied among years (1985 to 2003) with no trend over time (Fig. 2.15). Temporal integrals for the volume of hypoxia in bottom waters were significantly correlated with river flow (Fig. 2.16) for both annual mean flow ($r^2 = 0.35$, $p < 0.01$) and spring (February to May) flow ($r^2 = 0.49$, $p < 0.01$). Net bottom layer O_2 consumption rates were also higher in the hypoxic region of the estuary (Box 3-5) than other regions (Fig. 2.13). There was no significant response of hypoxia to point source nutrient management, as hypoxic volumes remained high following sewage treatment upgrades (Fig. 2.15). Hypoxia correlated with box model-computed physical O_2 inputs (horizontal advection, vertical diffusion) to the hypoxic region (Box 4, Fig. 2.17).

Discussion

Water quality responses to point source nutrient load reductions have varied in different regions of the Patuxent estuary. Definitive declines in DIN and DIP concentrations in all regions of the estuary correspond to declines in sewage plant nutrient loads (Fig. 2.3, 2.8). The return of nutrient concentrations to near historical (1965 to 1970) levels in the middle estuary (Fig. 2.7) can also be attributed to effective nutrient management of point sources. There is evidence that chlorophyll *a* and plankton productivity have declined in the tidal fresh region of the river (data not shown), indicating that regions of the estuary in close proximity to point sources are recovering faster than seaward regions. Submerged aquatic plants in the oligohaline and tidal fresh Patuxent River increased dramatically after BNR was initiated, suggesting that water clarity or epiphytic algal biomass declined following sewage treatment upgrades (Kemp et al. 2005, Fisher et al. 2006).

Similar water quality improvements in response to point source nutrient load reductions have been reported for other estuarine systems. In the tidal upper Potomac River, Carter and Rybicki (1986) found increased spatial extent of submerged macrophytes less than a decade after phosphorus load reductions occurred concomitant with increased water clarity, although other factors may have also contributed to improved water clarity (Phelps 1994). In the Neuse River estuary, phosphorus load reductions to the estuary resulted in measurable declines in annual mean chlorophyll *a* in upstream sections of the estuary, but without concomitant nitrogen load reductions, water quality remained poor in more saline regions of the system (Paerl et al. 2004). Nutrient management has also been successful in Tampa Bay, where water quality improvements following nitrogen load reductions allowed the seagrass population to recover from historical declines (Lewis et al. 1998). Similar success in achieving nutrient concentration reductions through point source management (Smith et al. 1981, Carstensen et al. 2006) suggests that this management tool can be quite effective.

Despite reductions in point source loads to the estuary, nutrient concentrations and seaward transport rates in the Patuxent were higher during several years after point source load reductions (Fig. 2.8). High concentrations during 1993, 1994, 1996, and 1997 correspond to above-average freshwater flow and associated elevated non-point nutrient loads (Fig. 2.4, 2.6). In addition, high point source loads below the fall line in winter probably contributed to high nutrient concentrations (Fig. 2.3). Higher nutrient concentrations are often caused by increased freshwater flow and the resulting delivery of nutrients to estuarine waters (Boynton and Kemp 2000, Paerl et al. 2006). High flow contributes to elevated nutrient loads to the Patuxent River from non-point sources, particularly because non-point loads were 2 to 3 times higher than point source loads in the 1990s (Fig. 2.7, Boynton et al., in prep). In addition to elevated non-point loads, BNR is not currently activated in winter months and consequently, rates of nitrogen loading to the middle and lower estuary in the 1990s and 2000s were higher than before BNR (Fig. 2.3).

Increases in loads from other direct sources of nutrients do not, however, fully explain high nutrient concentrations during the mid 1990s. Trends in atmospheric inputs of nitrogen have been stable since the 1980s (NADP 2005), suggesting this source is not contributing to the observed persistently poor water quality. Although contributions of groundwater NO_3^- are significant for some coastal regions (e.g., Charette et al. 2001, Pearl 1997), analyses in Chesapeake Bay and its tributaries suggest that direct inputs of NO_3^- and freshwater from groundwater are less significant, ranging from < 5-10% of total inputs (Hussain et al. 1999, Charette and Buesseler 2004).

Boynton et al. (in prep) computed nitrogen and phosphorus loads to the estuary from all sources (atmospheric, non-point, point) during 1985 to 1997 and determined that total annual N loads to the upper estuary were stable and total phosphorus loads had increased over time. This suggests that nutrient input reductions from point sources had been replaced by non-point nutrient loading during recent years of above average freshwater inputs (1993 to 1997). Despite these stable trends, DIP and DIN concentrations throughout the estuary declined substantially by the late 1990s relative to the 1980s (Fig. 2.8), concomitant with declining nutrient transport to the middle (Fig. 2.5) and lower estuary (Seaward DIN transport: 2.7 ± 0.3 10^3 kg N d^{-1} (1985 to 1990) and 1.7 ± 0.4 10^3 kg N d^{-1} (1992 to 2003).

Persistent or increasing non-point loads of total nitrogen and phosphorus may be responsible for the relative stability of net O_2 production, chlorophyll *a*, and secchi depth in the middle estuary after the implementation of BNR at sewage treatment plants (Fig. 2.6, 2.10, 2.13, Boynton et al., in prep). The magnitude of non-point total nitrogen load to the upper estuary (above Box 2, ~1500 kg d^{-1}) is indeed comparable to point source loads before BNR and is two times higher than point source loads after BNR (Fig. 2.4, 2.6). In two regions of the middle estuary (Box 3 and 4), surface net O_2 production is correlated with total nitrogen loads (point + non-point, 1985 to 1997 data), suggesting that net O_2 production in this region is sensitive to both point and non-point loads (Fig. 2.18). Similar regressions are not strong in the upper and lower estuary, indicating that other factors tend to regulate net O_2 production. Spring (February to April) chlorophyll *a* also correlates with non-point loads in the middle estuary (Box 4; $r^2 = 0.38$, $p < 0.05$). Because secchi depth is correlated with chlorophyll *a* in many regions of the Patuxent and Chesapeake Bay (Appendix I, Xu et al. 2005) and other systems (e.g., Sanden and Hakansson 1996, Conley et al. 2002), we would expect parallel responses of these two variables to changes in nutrient load.

Non-point source nitrogen and phosphorus management likely needs to improve in order to allow further improvements in water quality to occur in this estuary.

In many estuaries, freshwater flow indirectly drives plankton productivity by delivering nutrients and suspended materials and altering residence times (Cloern et al. 1983, Malone et al. 1988, Paerl et al. 2006). For the Patuxent, a 20% increase in mean annual river flow (10 m^3 s^{-1}) tends to increase nitrogen delivery to the estuary by an amount equal to the N removal achieved by full-scale BNR at all sewage treatment plants in the estuary (Fig. 2.5). As a result, annual mean levels of phytoplankton biomass and net productivity in the middle and lower Patuxent estuary correlate strongly with river flow (Fig. 2.12, 2.14). Similar relationships have been reported for Chesapeake Bay and other temperate estuaries (Sin et al. 1999, Boynton and Kemp 2000, Paerl et al. 2006). Positive relationships between flow and net O_2 production suggest that flow tends to enhance productivity more than respiration, which is likely due to higher nutrient inputs (D'Avanzo 1996). In addition, lower water temperatures, which are often associated with high flow years, tend to reduce respiration rates (Smith and Kemp 1995, Howarth et al. 1996, Fisher et al. 2006). Thus, the unexpected increases in chlorophyll *a*, light attenuation, and net O_2 production that we found in the mesohaline Patuxent estuary must, in part, be driven by the unusually high freshwater flow in the 1990s, compared to the previous decade (Fig. 2.4, 2.11, 2.14).

Conversely, flow generally reduced biomass and productivity in the tidal fresh region of the estuary. Chlorophyll *a* and spring river flow were negatively correlated ($r^2 = 0.26$, $p < 0.05$) in the tidal fresh region, because flow generally produces increased turbidity and flushing rates, which is the case in upper regions of most coastal plain estuaries (Kemp et al. 1997, Hagy et al. 2000, Howarth et al. 2000). For the upper Patuxent, secchi depth was negatively correlated with flow ($r^2 = 0.22$, $p < 0.1$) because of higher inputs of suspended material (Appendix I).

Removing the effects of freshwater flow from chlorophyll *a* and net O_2 production rates permits an analysis of how other forcing variables affect these ecosystem properties. Initial declines in chlorophyll *a* residuals from 1985 to 1997 in all regions of the estuary support the assertion that point source nutrient reductions did indeed reduce phytoplankton biomass per unit freshwater input (Fig. 2.12). A distinct reversal of this trend toward more biomass per unit flow from 1998 to 2003 in the middle and lower estuary suggests, however, that nutrient loading was increasing, accepting that the phytoplankton community is nutrient limited (D'Elia et al. 1986, Fisher et al. 2006). Positive residuals in the lower estuary from 1994 to 2003 suggest other factors, such as increases in local nutrient sources or increased grazing were sustaining higher phytoplankton biomass than expected from flow. In the middle estuary, increases in non-point N and P inputs since the mid-1990s may account for this increasing trend in chlorophyll *a* and net O_2 production in this region and time period (Fig. 2.18). Increases in non-point nutrient inputs are not likely to be important in the lower estuary because the sub-watershed of this region is small (~50 km^2) compared to the upper estuary (~180 km^2) and because seaward N and P transports to the lower estuary were the lowest on record from 1998-2002.

Given the fact that watershed nitrogen inputs to the lower estuary have generally declined since 1991, it is difficult to explain the contemporaneous increases in chlorophyll *a* and net O_2 production in this region and time period. Alternative macronutrients, primarily DIP and DSi, have been declining since 1985 in the lower estuary (Fig. 2.8). Furthermore, DIN/DSi ratios < 1 and DSi/DIN ratios > 16 in all seasons (data not shown) suggest that DSi is not limiting phytoplankton growth (D'Elia et al. 1983, Conley and Malone 1992). DIN/DIP ratios suggest P-limitation during early spring and N-limitation during summer (D'Elia et al. 1986, Fisher et al. 1992, Fisher et al. 1999). Because the summer is the period of most substantial chlorophyll *a* increases since 1985, nitrogen is the relevant nutrient supporting the phytoplankton biomass increases.

Trends of increasing chlorophyll *a* and net O_2 production are most significant in the lower estuary and are not correlated with N or P inputs from point, non-point, or atmospheric sources (Fig. 2.3, 2.6, 2.10, 2.13). The lower estuary is situated adjacent to Chesapeake Bay, which is a large and nutrient-enriched system (Kemp et al. 2005). As computed by the box model, the net input of DIN to the Patuxent from Chesapeake Bay, has nearly tripled since 1990 and has increased steadily since 1985 (Fig. 2.20). From 1991 to 2003, seaward N transport to the lower estuary declined by $2.5\ 10^3$ kg N d^{-1}, while net DIN input from Chesapeake Bay increased by $1.0\text{-}1.5\ 10^3$ kg, N d^{-1}. DIN inputs from Chesapeake Bay, which enter the Patuxent in the bottom layer, are transported to surface waters via vertical upwelling and diffusive exchange to support plankton production. Indeed, vertical DIN inputs to surface waters were the dominant (or co-dominant) source of DIN to the lower estuary in the mid to late 1990s when seaward inputs were declining and vertical inputs were increasing (Fig. 2.20). During this period, increases in net DIN inputs from Chesapeake Bay co-occurred with increases in net O_2 production and chlorophyll *a* in the lower estuary surface layer (Fig. 2.20). Stoichiometric conversions of the upwelling DIN flux to O_2 units (O_2:C using PQ = 1.0, C:N = 6.625) in the surface layer indicate that vertical DIN transport was adequate to support 80-100% of net O_2 production in the lower estuary.

In the lower estuary, annual mean net O_2 production and annual mean net DIN from Chesapeake Bay were significantly correlated ($r^2 = 0.53$, $p < 0.01$), suggesting that DIN exchange with Chesapeake Bay could be influencing Patuxent water quality (Fig. 2.21). In addition, summer mean chlorophyll *a* and mean annual net DIN inputs from the bay were also strongly correlated in this region ($r^2 = 0.50$, $p < 0.01$; Fig. 2.14). Most of the DIN entering the Patuxent River from Chesapeake Bay is delivered in during May, June, and July (Fisher et al. 2006), and trends of increasing summer mean chlorophyll *a* and secchi depth from 1985 to 2003 were more pronounced than the corresponding trends for annual means (Fig. 2.10, 2.12). In general, DIN is most limiting for phytoplankton biomass and production in summer months (Fisher et al. 1992), suggesting the seasonal importance of DIN supplied by Chesapeake Bay. The importance of nitrogen import from Chesapeake Bay was also inferred for phytoplankton blooms in other tributary estuaries (Jordan et al. 1991, Sin et al. 1999), and such results underscore the need to resolve nutrient loads at regional scales (D'Elia et al. 2003, Paerl et al. 2006).

A number of environmental factors may have contributed to the observed temporal trends of increasing net input of DIN from Chesapeake Bay. Two potential mechanisms were considered: (1) increased net DIN advection to the Patuxent from the Bay via increased gravitation circulation and (2) increased net DIN advection to the Patuxent from the Bay due to an increased DIN concentration gradient from the Bay to the Patuxent. Although there was no significant trend in advective water transport from the Bay to the Patuxent during the time period (1991-2003), the normalized difference in DIN concentration between the Bay and the Patuxent ("normalized" = DIN_{BAY}-DIN_{PAX} /(DIN_{BAY}+DIN_{PAX})/2) was significantly higher from 1992 to 2003 (0.21 ± 0.02 mg N l^{-1}) than from 1985 to 1990 (0.13 ± 0.01 mg N l^{-1}) (t = 2.8, $p = 0.013$). The net exchange of DIN at the estuary mouth was, in fact, significantly correlated ($r^2 = 0.52$, $p < 0.05$) with this normalized DIN concentration difference from 1985 to 2003. Furthermore, the non-normalized difference between Bay and Patuxent DIN was significantly correlated with annual Patuxent River flow (1985 to 2003; $r^2 = 0.71$, $p < 0.01$), suggesting an effect of river flow on DIN concentration gradient and net exchange.

If net inputs of DIN from Chesapeake Bay are contributing to increasing phytoplankton productivity and biomass in the lower Patuxent estuary, how could DIN concentrations be declining? Despite declining DIN concentrations and seaward total nitrogen (TN) transport to the lower estuary, TN concentrations have remained stable in this region (Fig. 2.19). Given the stable TN concentrations over the last two decades, declining DIN indicates that concentrations of dissolved and/or particulate organic nitrogen (DON, PON) must have been increasing. Because DON has been declining from 1985 to 2003 (slope = -0.0001, $p < 0.01$), PON concentrations must have been increasing over this period in the lower estuary. This inferred PON increase corresponds with observed chlorophyll *a* increases from 1985 to 2003 (Fig.

2.10, 2.11). Thus, trends of decreasing DIN inputs from the watershed and increasing net DIN inputs from the Bay resulted in a stable pattern of TN concentration in the lower estuary. The contemporaneous trends of decreasing DIN and increasing PON, however, require further explanation.

One possible explanation for this shift in the partitioning of TN from DIN to PON would involve a decrease in grazing pressure on phytoplankton biomass. Reduced grazing pressure would decrease phytoplankton mortality in the lower estuary, allowing algal cells to assimilate more DIN. In fact, recent analyses in Chesapeake Bay, the Patuxent estuary, and other tributaries suggest that the abundance of the planktivorous ctenophore (*Mnemiopsis leidyi*) has increased during the last decade (Purcell and Decker 2005, Breitburg and Fulford, in prep). It appears that this trend may have, in turn, led to decreased abundance of the herbivorous copepod, *Acartia tonsa*, in Chesapeake Bay (Pucell and Decker 2005).

To the extent that these food web changes have occurred in the Patuxent, increased ctenophore grazing on copepods could have caused a top-down cascade that favors elevated phytoplankton biomass. Data from a station in the mesohaline Patuxent River estuary (Box 3, 4; CBP 2005) reveal a 5-fold increase in *Mnemiopsis* abundance and biovolume during June, July, and August since 1994, concomitant with a 5-fold decline in *Acartia tonsa* concentration (Fig. 2.22). Chlorophyll *a* has been stable during June-August at this station and seaward regions despite nutrient input declines, suggesting that a release of top-down control on phytoplankton could have occurred. Assuming similar food web changes have occurred in the nearby lower estuary, reduced grazing may explain why chlorophyll *a* in the Patuxent has increased more in the months of May, June, and July, the time of year when grazing is an important control on phytoplankton (White and Roman 1992) and when gelatinous zooplankton are abundant (Purcell et al. 1994).

To quantify the potential effect of reduced *Acartia tonsa* abundance on phytoplankton biomass, we multiplied measured clearance rates (14.5 ml copepod^{-1} d^{-1}, Reaugh 2005) by summer copepod concentrations for all years from 1992 to 2003 (CBP 2005). These computations indicate that *A. tonsa* filtration declined from 15-20% of the water column per day in summer prior to 1995 to < 1% between 1997 and 2002. At the higher filtration rates, copepods could substantially impact summer phytoplankton abundance in Chesapeake Bay (Sellner and Kachur 1987). Although copepods also prey on microzooplankton in summer (White and Roman 1992, Reaugh 2005) and summer phytoplankton communities are numerically dominated by phytoflagellates (Marshall and Alden 1990), larger, more edible, phytoplankton species (e.g., *Thalassiosira* sp., *Gymnodinium* sp., and *Cyclotella* sp.) are also abundant (CBP 2005).

Hypoxia

A common goal of coastal nutrient management is the elevation of summer O_2 concentrations in bottom waters (e.g., Diaz 2001, Kemp et al. 2005). This goal is motivated by the fact that hypoxic waters cause physiological stress, growth reduction, and mortality for many estuarine organisms (e.g., Breitburg et al. 2003). Previous analyses reported a slightly shortened period of summer anoxic conditions in the Patuxent River estuary following point source nutrient management (Magnien

1999). Our analysis indicates that nutrient management (BNR) has not relieved total hypoxia in the Patuxent (Fig. 2.15) and Fisher et al. (2006) found no trend in bottom water dissolved O_2 concentrations in the mesohaline Patuxent. Provided the results of our analysis of phytoplankton and water quality dynamics over the past two decades, these trends are not surprising. First, significant correlations between freshwater flow and hypoxia (Fig. 2.16) imply that the high river flow of the 1990s increased hypoxia via elevated stratification and nutrient delivery (Boicourt 1992, Hagy et al. 2004). Secondly, hypoxia was fueled by organic matter derived from stable or elevated phytoplankton biomass and net O_2 production in the middle and lower estuary, the regions where bottom water hypoxia occurs (Fig. 2.10, 2.11, 2.13). Lastly, hypoxia was correlated with physical O_2 inputs (landward advection and vertical diffusion) from 1985 to 2003 (Fig. 2.17), illustrating how environmental controls can override management effects on hypoxia (Breitburg 1990, Fisher et al. 2006).

Summary and Conclusions

Our analysis of a time series water quality data and net O_2 production reveals different responses to nutrient management and climate variability in different regions of the estuary. Water quality in the upper estuary (above Benedict Bridge) was generally stable, and in some cases, improved, while water quality conditions appeared to be stable in middle estuary and degrading in the lower estuary. Thus, nutrient load reductions have led to improved water quality in regions that are closely coupled to watershed nutrient inputs, but not in regions that may be influenced by nutrient inputs from other sources.

The degrading trends in water quality that occurred in the lower estuary provide insight into the interaction of internal and external forces in controlling water quality. Food web changes may have allowed for increased phytoplankton biomass via increased predation on copepods by a gelatinous predator. Periods of high freshwater input to the estuary induced substantial fluctuations in algal biomass and nutrient concentrations and may obscure the expected benefits of nutrient management. Net nitrogen inputs to the Patuxent estuary from Chesapeake Bay are currently similar in magnitude to seaward DIN inputs to the lower estuary and underscore the need for whole ecosystem restoration and water quality management.

Although the results of this study may not be encouraging to managers interested in controlling N and P inputs to estuaries, water quality in this system would surely be degraded beyond what is currently observed if no nutrient management was in place. This analysis displays the utility of box models to compute net O_2 production rates and advective and diffusive nutrient transports. Such rates are quite useful for management-related research and provided critical information to this analysis.

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	Chesapeake Bay Program	Flemer et al. 1970
Variable	Analytical Methods	Analytical Methods
Dissolved Oxygen (O_2)	Determined by a YSI calibrated periodically with Winkler titrations	Not measured
Ammonium (NH_4^+)	Determined by the alkaline phenol hypochlorite method (EPA 350.1 or equivalent) using an autoanalyzer	Determined as NO_2^-after ammonia is oxidized by alkaline hypochlorite and excess oxidant destroyed by arsenite
Nitrate plus Nitrite ($NO_2^- + NO_3^-$)	Determined as NO_2^- using the diazo method with an autoanalyzer (EPA Method 353.2) with NO_3^- reduced to NO_2^- with cadmium	Determined colorimetrically as NO_2^- by diazotizing with sulphanilamide and coupling with N-(1-napthyl) - ethylenediamine
Orthophosphate (PO_4^{3-})	Determined as an antimony-phospho-molybdate complex, which turns blue after reacting with ascorbic acid and is measured colorimetrically (EPA Method 365.1)	Composite reagent method (Strickland and Parsons 1968)
Active Chlorophyll-a	Determined by acetone extraction from a ground filter followed by spectrophotometric analysis before and after acidification	Determined by extraction from a ground filter followed by flurometric analysis before and after acidification (Flurometer was periodically calibrated with a spectrophotometer)

Table 2.1: Summary of analytical methods used by the Chesapeake Bay Program and in Flemer et al. (1970) to measure several water quality variables.

Method	Region	Statistics		
Regression		r^2	Slope	*p* value
DIN	Upper	0.47	-0.014	**< 0.01**
	Middle	0.31	-0.008	**< 0.01**
	Lower	0.31	-0.007	**< 0.01**
DIP	Upper	0.51	-0.001	**< 0.01**
	Middle	0.55	-0.001	**< 0.01**
	Lower	0.49	-0.001	**< 0.01**
Chlorophyll *a*	Upper	0.14	0.359	0.11
	Middle	0.08	0.306	0.23
	Lower	0.18	0.312	0.07
Secchi Depth	Upper	0.27	-0.008	**< 0.05**
	Middle	0.34	-0.017	**< 0.01**
	Lower	0.38	-0.019	**< 0.01**
Net O_2 production	Upper	0.01	-0.080	0.68
	Middle	0.06	0.148	0.30
	Lower	0.15	0.197	0.10
Seasonal Kendall		Tau	Slope	*p* value
DIN	Upper	-0.23	-0.009	**< 0.01**
	Middle	-0.36	-0.006	**< 0.01**
	Lower	-0.38	-0.007	**< 0.01**
DIP	Upper	-0.33	-0.001	**< 0.01**
	Middle	-0.34	0.000	**< 0.01**
	Lower	-0.34	0.000	**< 0.01**
Chlorophyll a	Upper	0.17	0.276	**< 0.01**
	Middle	0.13	0.227	**< 0.01**
	Lower	0.15	0.175	**< 0.01**
Secchi Depth	Upper	-0.17	-0.006	**< 0.01**
	Middle	-0.17	-0.013	**< 0.01**
	Lower	-0.16	-0.014	**< 0.01**
Net O_2 production	Upper	-0.02	-0.102	0.74
	Middle	0.02	0.096	0.69
	Lower	0.04	0.155	0.37
Maximum carbon fixation	Upper	-0.16	-1.241	**< 0.01**
	Middle	-0.07	-0.943	0.12

Table 2.2: Comparison of trend test results for 1985 to 2003 from linear regression and Seasonal Kendall models. Significant *p*-values are those less than 0.05 and are bold.

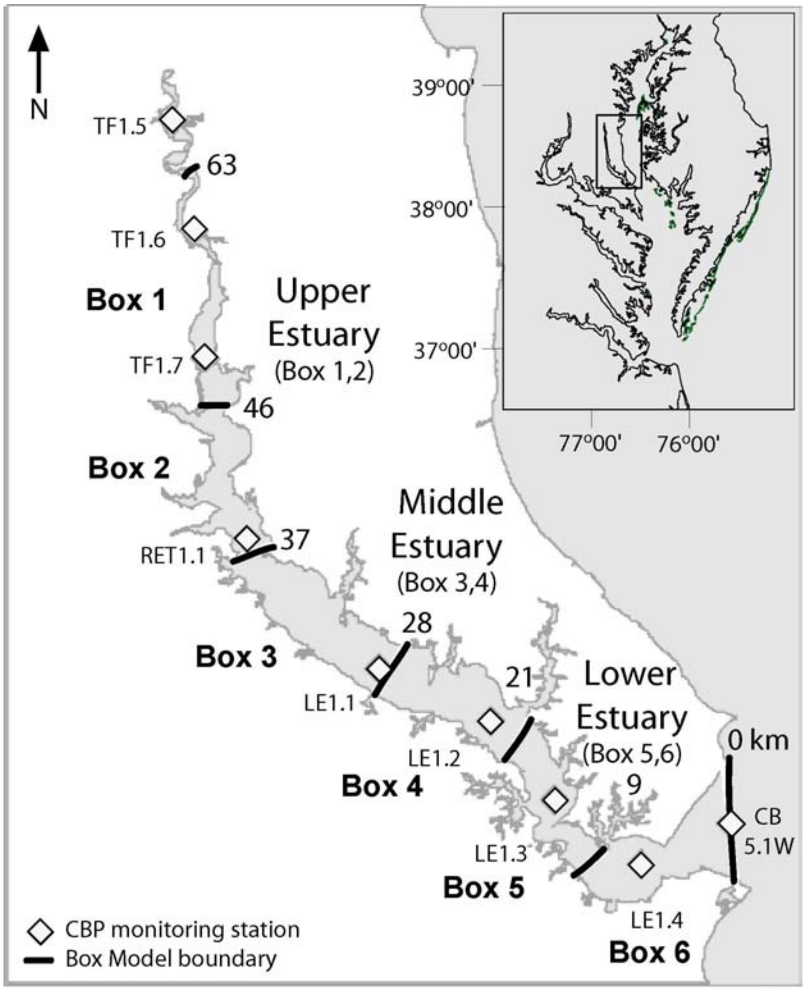

Figure 2.1: Map of the Patuxent River estuary with Chesapeake Bay (inset), including box model boundaries and Chesapeake Bay Program water quality monitoring stations. Chesapeake Bay Program station codes are to the left of each station and numbers at the right of box model boundaries indicate distance from the mouth of the estuary (km). Map based upon image in Hagy et al. 2000.

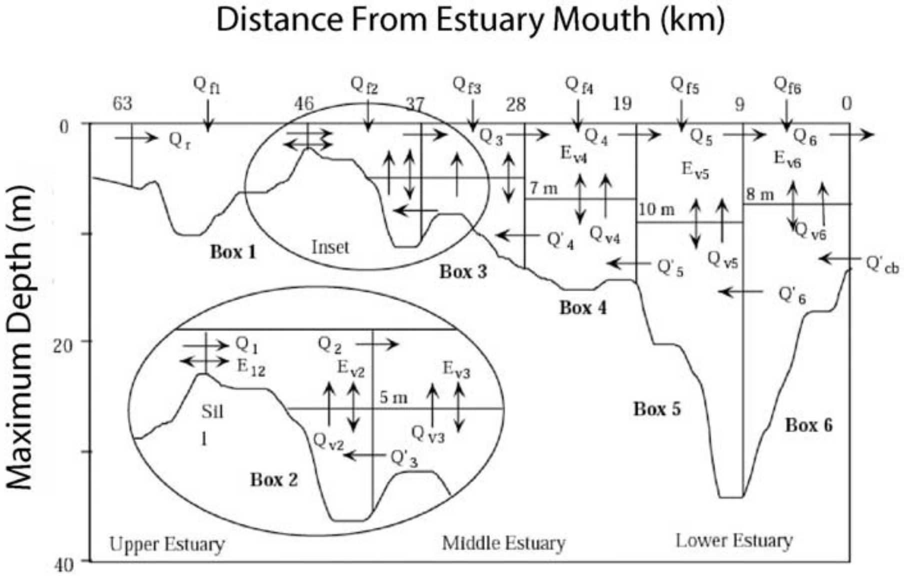

Figure 2.2: Schematic description of the box model structure (as seen in Hagy et al. 2000). Included are box model boundaries, exchange coefficients, and inputs. The estimated exchanges presented in this diagram are seaward advection (Q_m), landward advection (Q'_m), vertical advection (Q_{vm}), vertical diffusive exchange (E_{vm}), and horizontal dispersion ($E_{m+1,m}$). Included inputs are the volume of each box and the salt concentration (not included), river flow (Q_r), the input of freshwater to each box (Q_{fm}), and the salinity at the seaward boundary (not included).

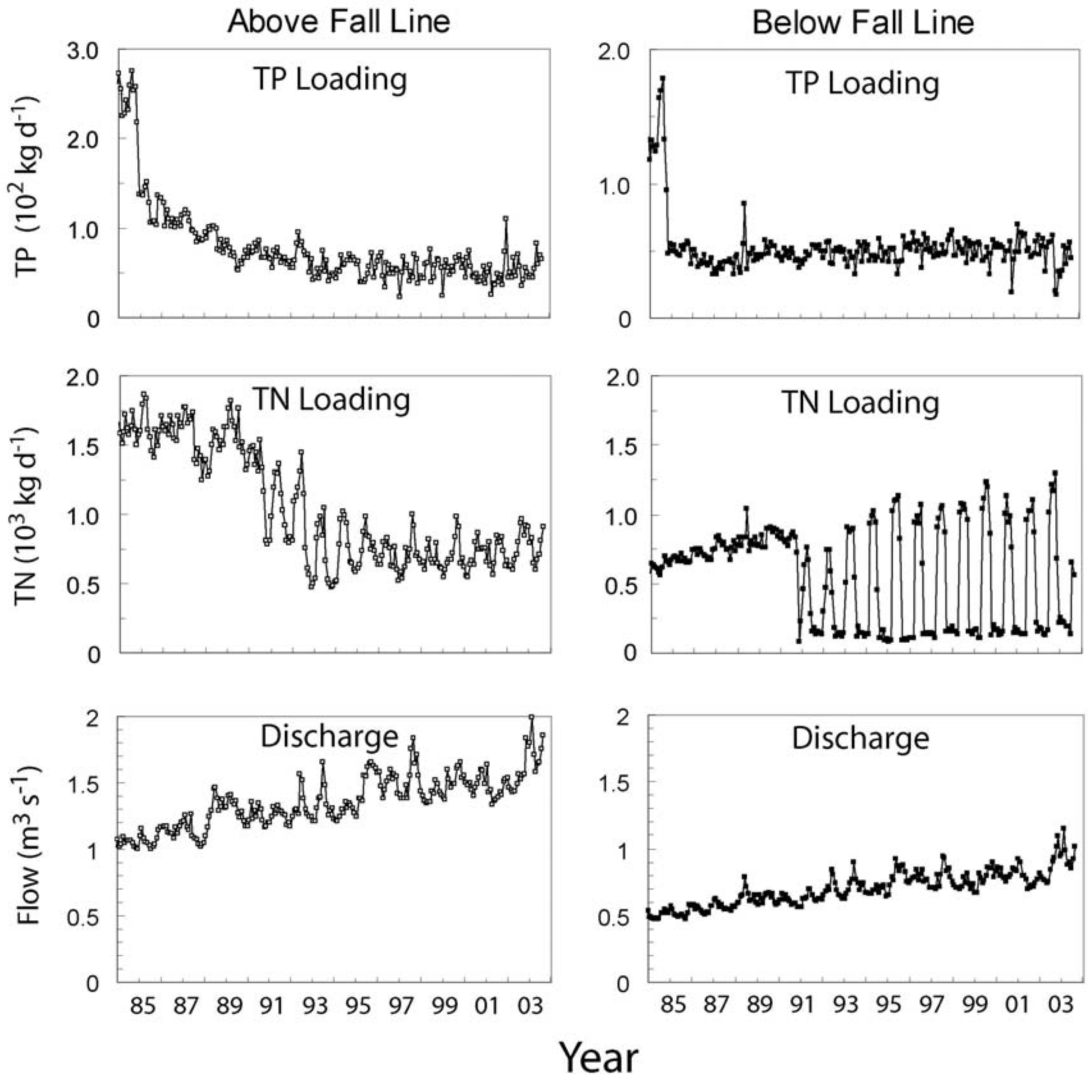

Figure 2.3: Mean monthly inputs of total phosphorus (TP), total nitrogen (TN) and water (discharge) from all sewage treatment facilities on the Patuxent River from 1985 to 2003. Inputs are presented as discharges released into waters above and below the fall line. Data are from the Chesapeake Bay Program's Point Source Nutrient Database (www.chesapeakebay.net).

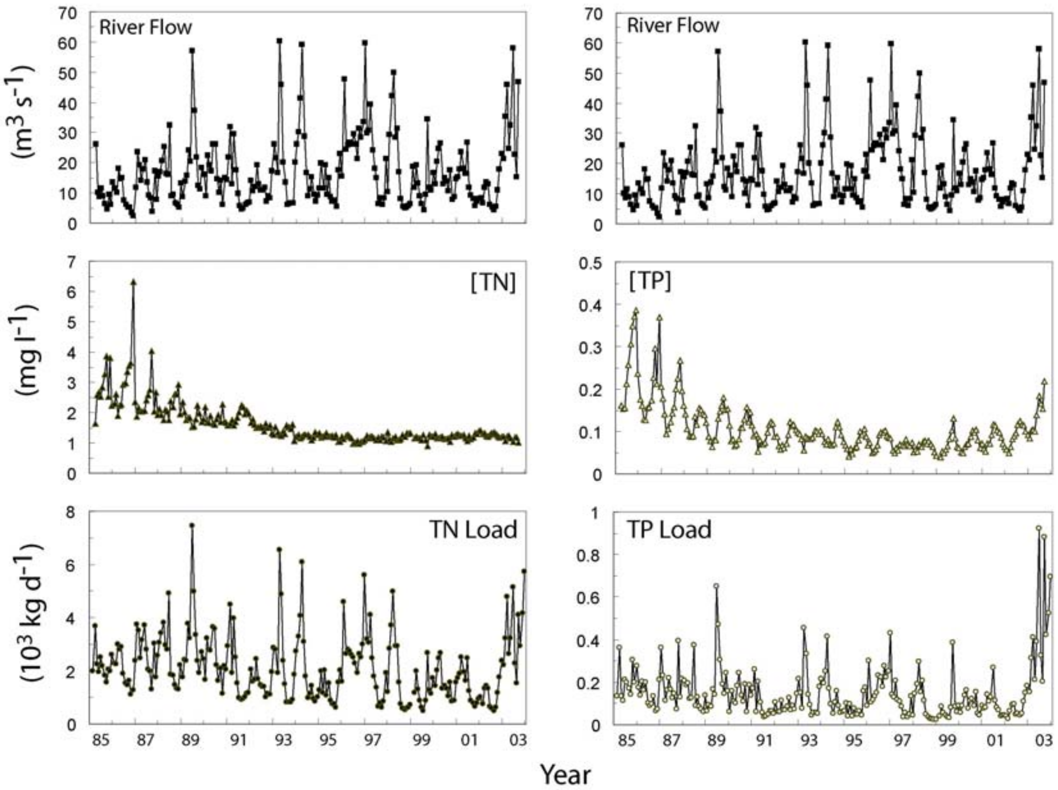

Figure 2.4: Time series (1985 to 2003) of mean monthly river discharge (top panel), total nitrogen and phosphorus concentrations (middle panel), and total nitrogen and phosphorus loading at the USGS gauging station at Bowie, MD (www.usgs.gov).

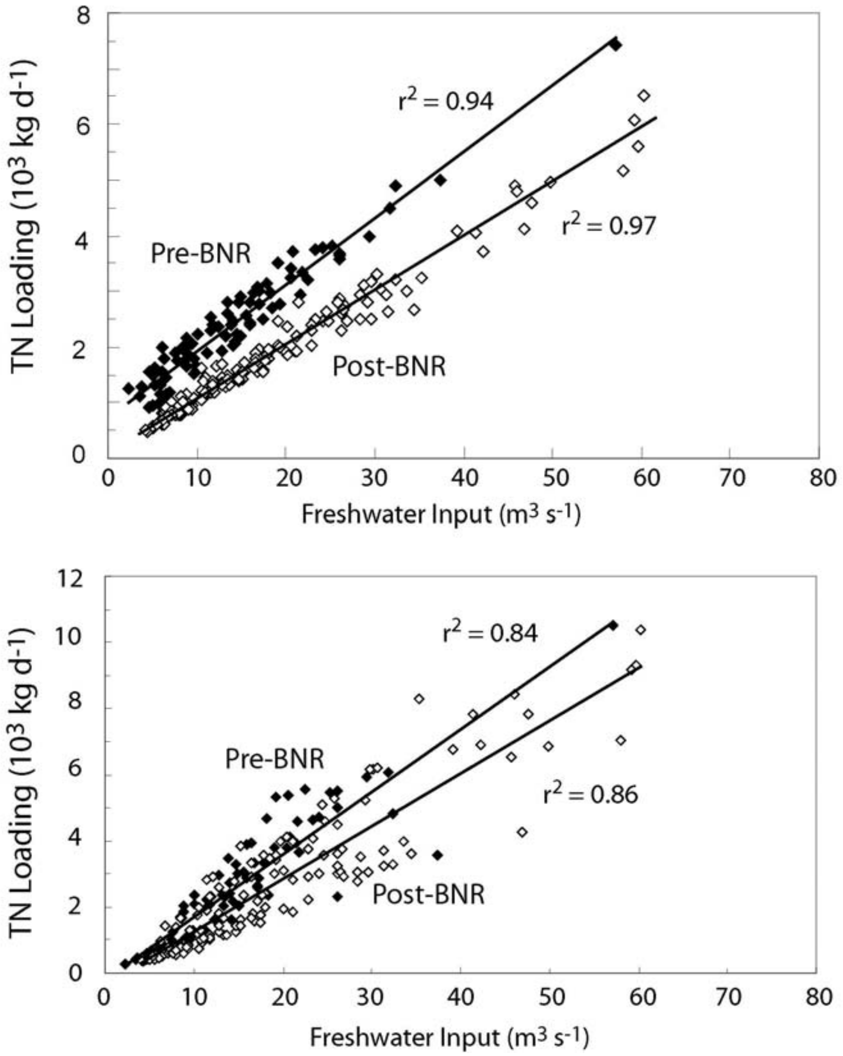

Figure 2.5: Plot of mean monthly river flow and mean monthly advective total nitrogen load to the Patuxent River estuary at the fall line (top panel) and at the landward boundary of Box 2 (bottom panel). Data are from the years 1985 to 2003 and were assembled from USGS river flow and solute gauging at Bowie, MD (www.usgs.gov) and from box model computed transports. Data are separated as months before BNR was implemented and months after BNR. The linear fits were created using all pre- and post-BNR data.

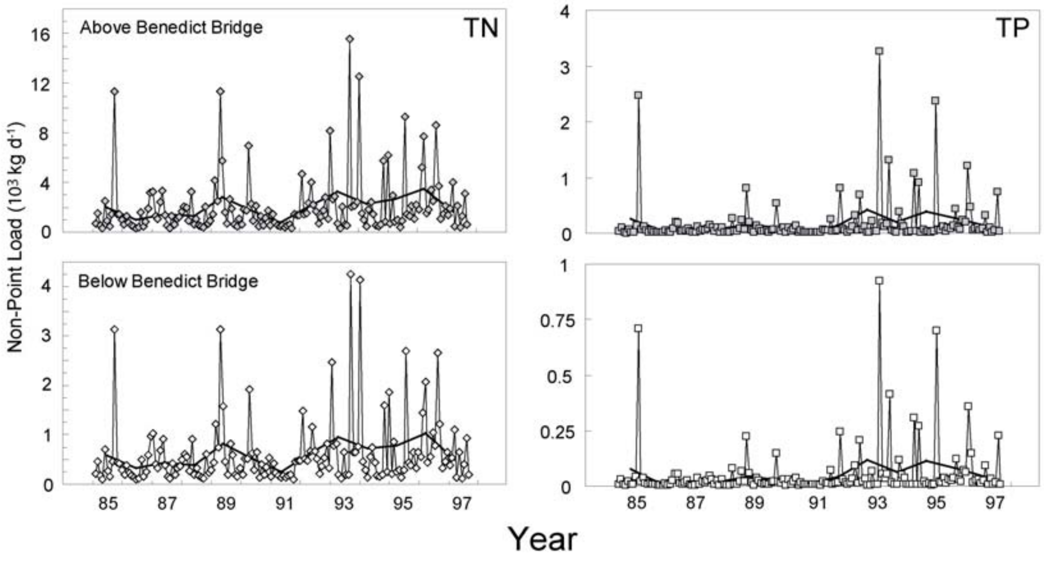

Figure 2.6: Time series (1985 to 1997) of non-point source total nitrogen (left panel) and total phosphorus (right panel) loading to the Patuxent River estuary, above and below Benedict Bridge, which is located at the seaward boundary of Box 2. Solid black lines are the annual averages of total load. Data are output from the Chesapeake Bay Watershed Model for the Patuxent watershed (Linker et al. 1996).

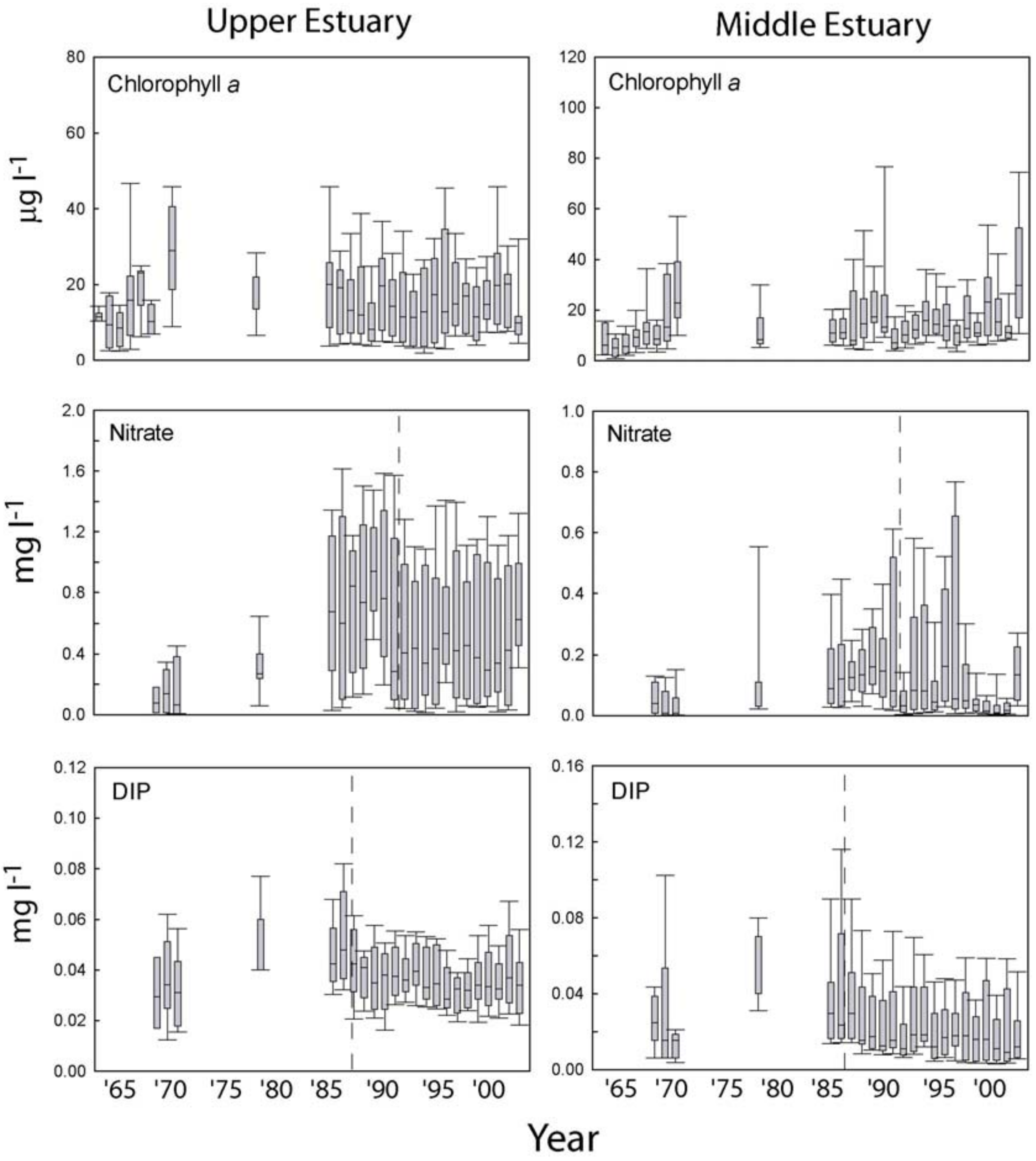

Figure 2.7: Box plots of temporal trends (1963 to 2003) of chlorophyll *a* (top panel), nitrate (middle panel), and DIP (bottom panel) concentrations in the upper and middle regions of the Patuxent River estuary. Data are from the Chesapeake Bay Program Water Quality Monitoring Program (1985 to 2003), The Department of Natural Resources (1978), and Flemer et al. (1970) (1968 to 1974). Vertical dashed lines indicate the beginning of BNR implementation (nitrate) and the initiation of phosphorus removal (DIP) at sewage plants. The top of the boxes indicates the 75th percentile, the bottom of the boxes are the 25th percentile, the line in the box is the median, and the error bars are the 10th and 90th percentile.

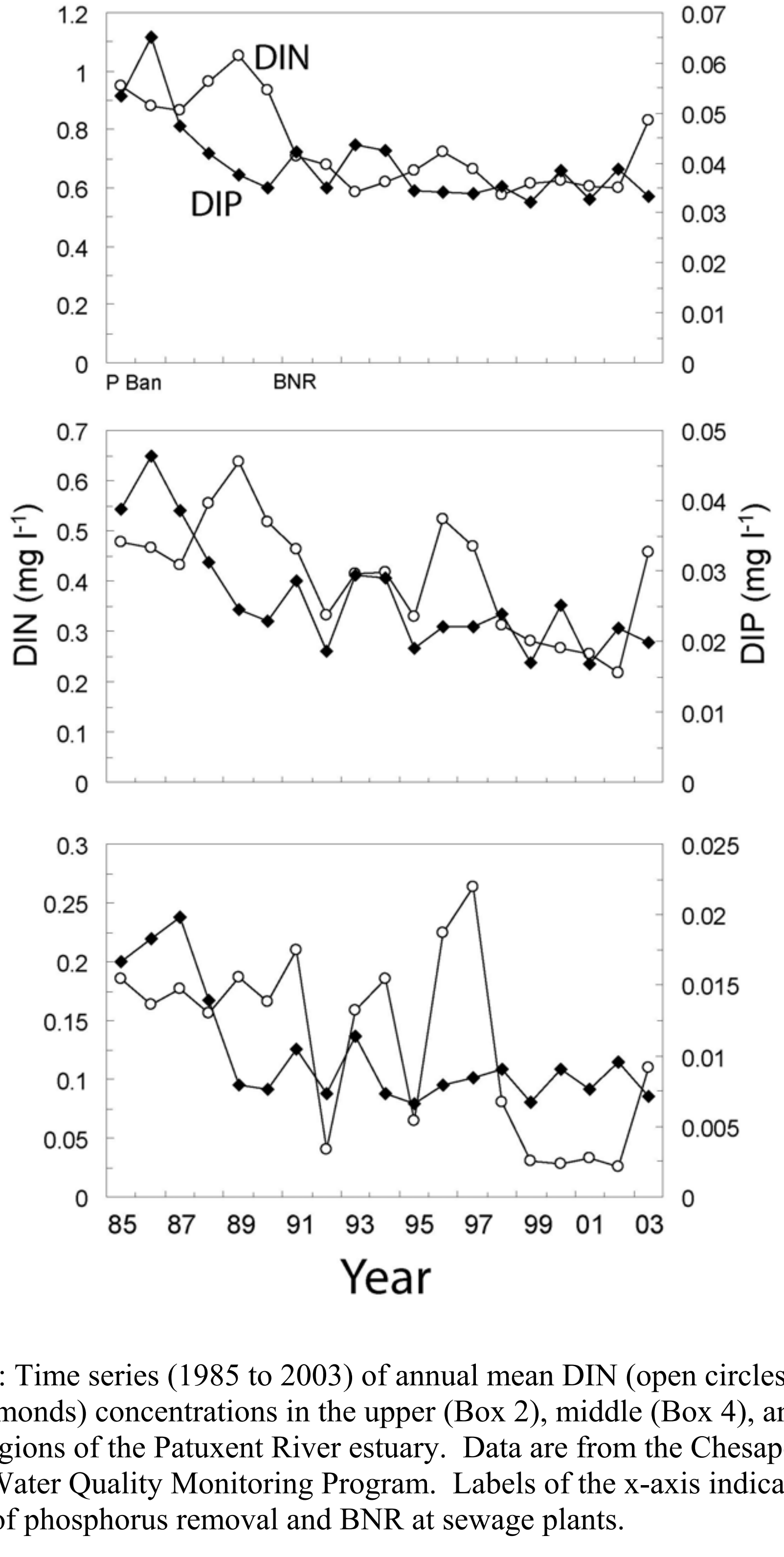

Figure 2.8: Time series (1985 to 2003) of annual mean DIN (open circles) and DIP (black diamonds) concentrations in the upper (Box 2), middle (Box 4), and lower (Box 5) regions of the Patuxent River estuary. Data are from the Chesapeake Bay Program Water Quality Monitoring Program. Labels of the x-axis indicate the initiation of phosphorus removal and BNR at sewage plants.

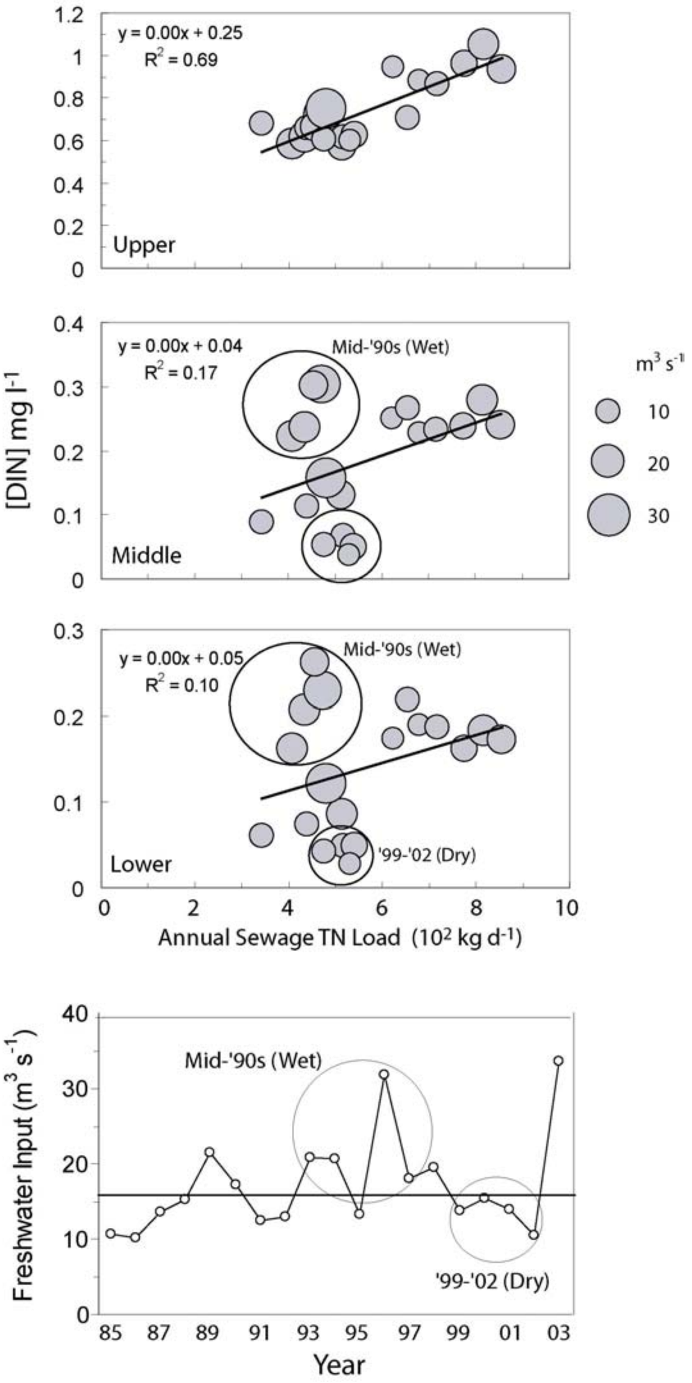

Figure 2.9: Correlations between annual mean sewage total nitrogen load below the fall line and annual mean surface layer dissolved inorganic nitrogen in the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary (left panel, 1985 to 2003). Size of circles indicates the relative magnitude of annual mean river flow. Sewage load data from the Chesapeake Bay Program nutrient input monitoring data set (www.chesapeakebay.net). Time series of annual mean freshwater input with circles around years in the wet mid-1990s (1993, 1994, 1996, 1997) and the dry '99-'02 (right panel). Dark horizontal line represents 19-year average.

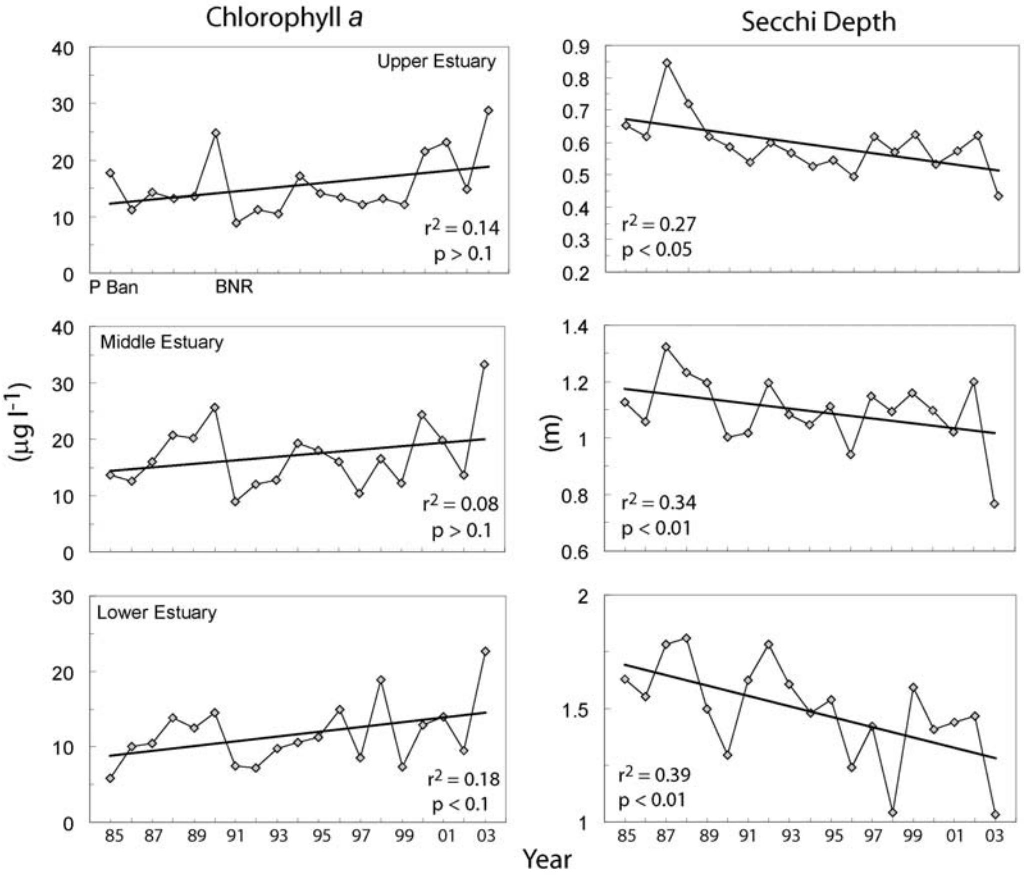

Figure 2.10: Time series (1985 to 2003) of annual mean chlorophyll *a* (left panel) and secchi depth (right panel) in surface waters of the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary. Data are from the Chesapeake Bay Program and x-axis labels indicate the beginning of phosphorus removal and BNR at sewage treatment plants in the watershed. Trend lines are simple linear regressions and correlation coefficient and *p*-value are indicated for each region and variable.

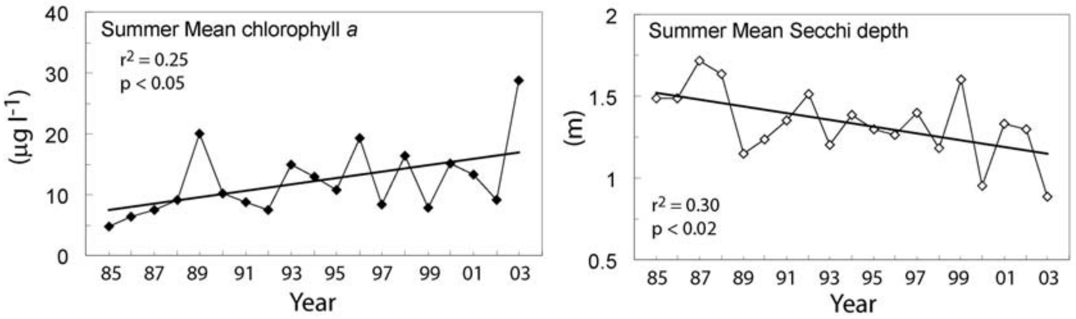

Figure 2.11: Time series (1985 to 2003) of mean summer chlorophyll *a* (left panel) and secchi depth (right panel) in surface waters the lower estuary. Data are from the Chesapeake Bay Program. Trend lines are simple linear regressions and correlation coefficient and *p*-value are indicated for each region and variable.

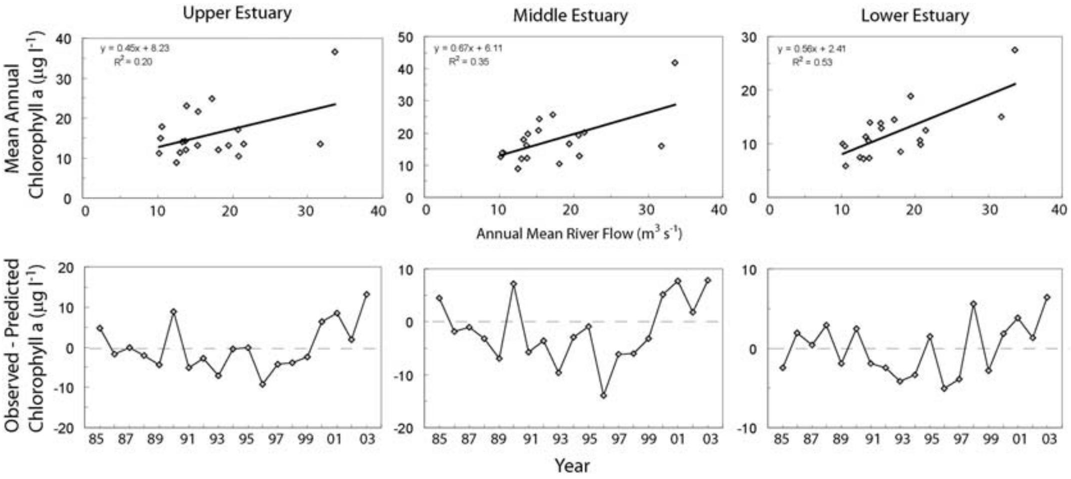

Figure 2.12: Correlations between annual mean river flow and annual mean chlorophyll *a* biomass in the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary (top panel, 1985 to 2003). Time series (1985 to 2003) of residuals (observed – predicted) of chlorophyll *a* versus river flow relationship in the same three regions as above (bottom panel). Dashed horizontal lines indicate the zero value.

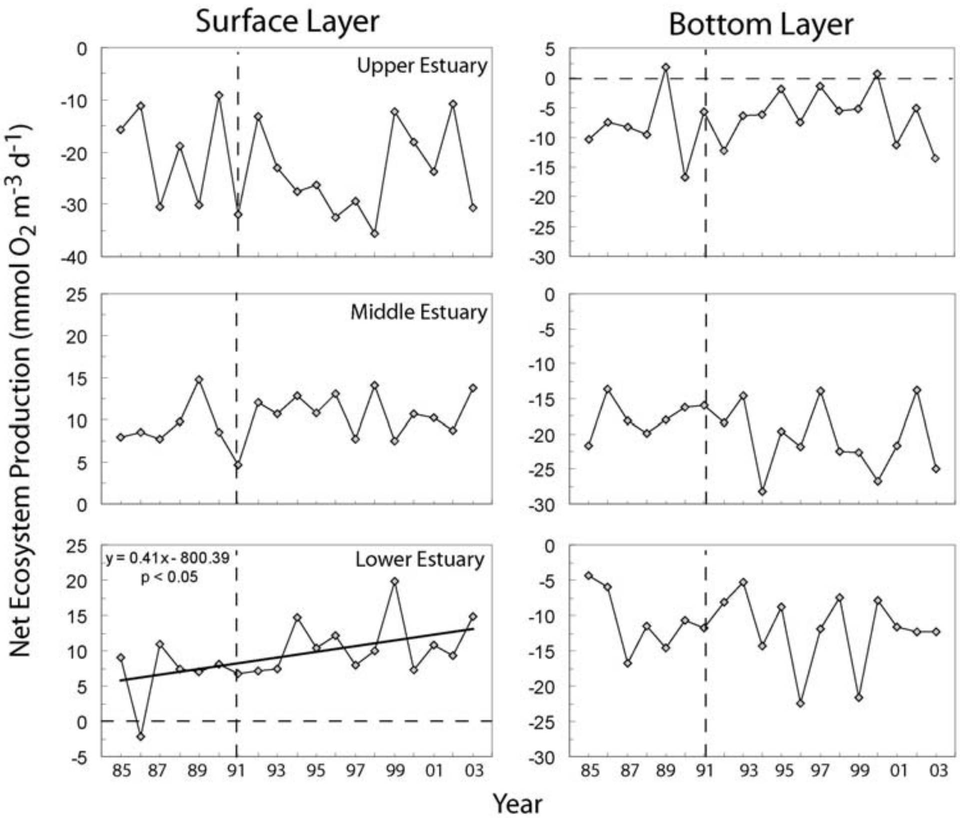

Figure 2.13: Time series (1985 to 2003) of surface and bottom layer net O_2 production in the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary. Data are annual means and surface layer net O_2 production is calculated by adding an air-sea exchange flux to the box model estimate of net O_2 production. Vertical dashed lines indicate the beginning of BNR implementation and horizontal dashed lines indicate net O_2 production of zero.

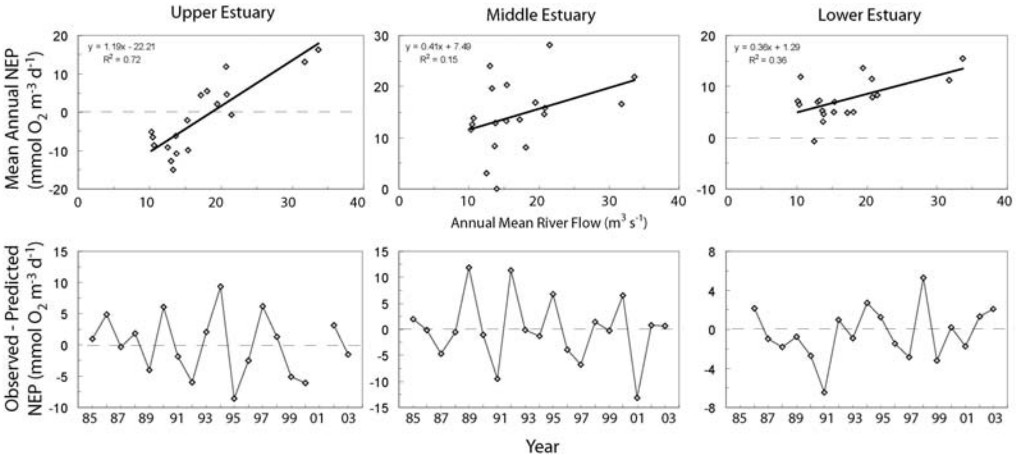

Figure 2.14: Correlations between annual mean river flow and annual mean net O_2 production in the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary (top panel, 1985 to 2003). Time series (1985 to 2003) of residuals (observed – predicted) of net O_2 production versus river flow relationship in the same three regions as above (bottom panel). Dashed horizontal lines indicate the zero value.

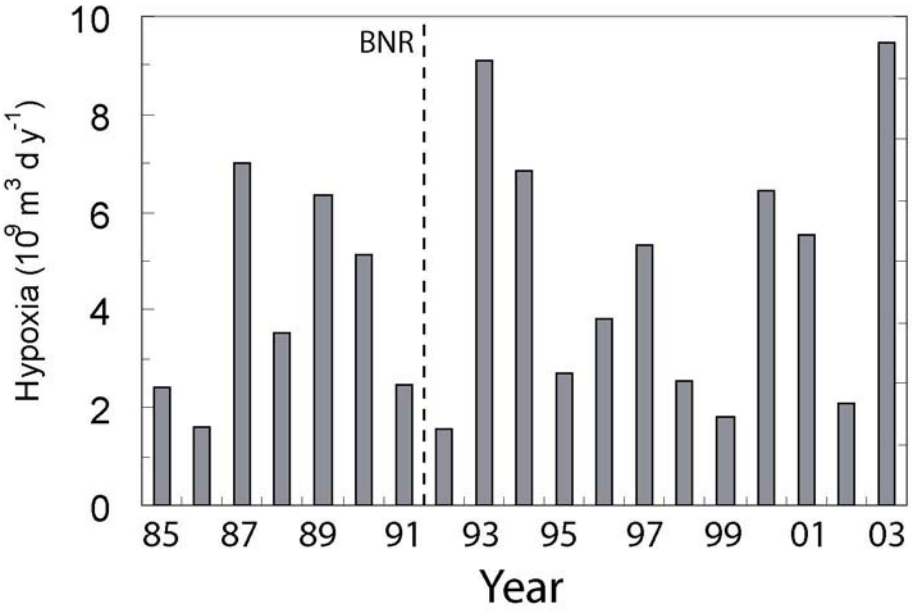

Figure 2.15: Time series (1985 to 2003) of hypoxic volume days in the Patuxent River estuary. The vertical dashed line indicates the initiation of BNR.

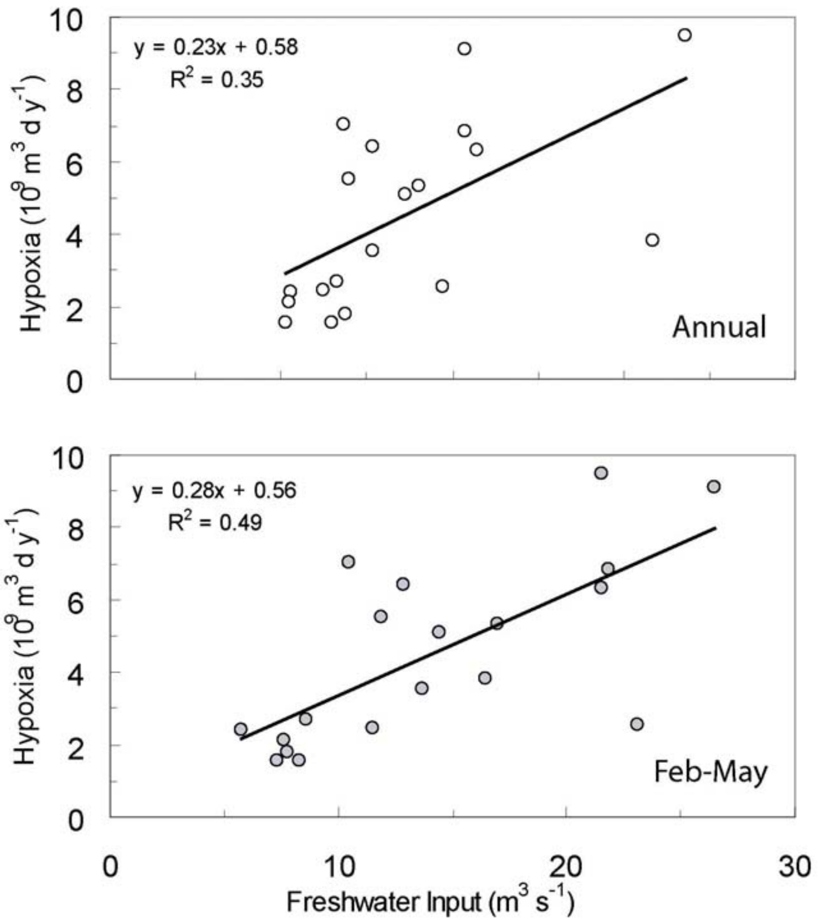

Figure 2.16: Regression of annual hypoxia (hypoxia = $O_2 < 2$ mg l^{-1}) to annual mean freshwater inputs and February to May (Spring) freshwater inputs.

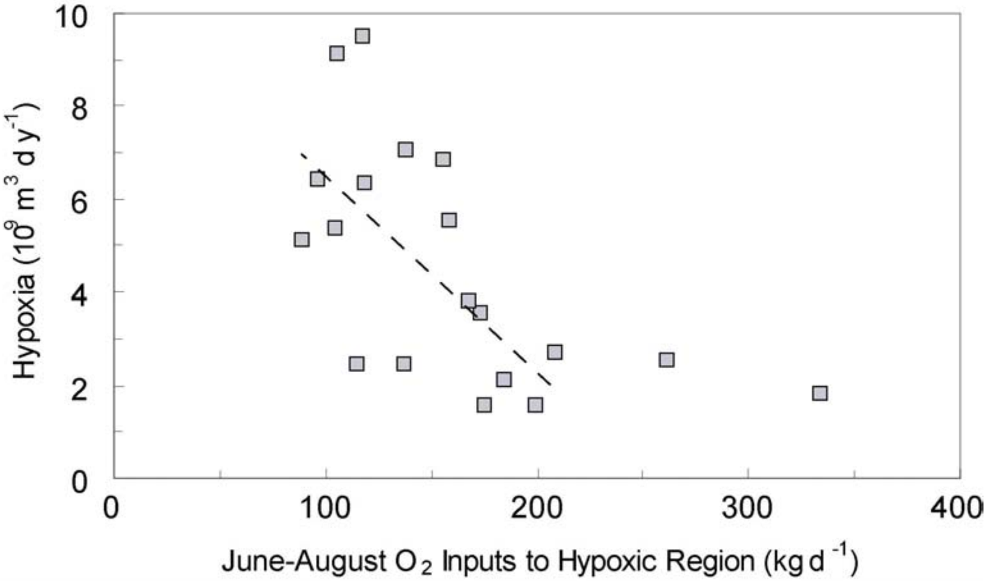

Figure 2.17: Regression of hypoxic volume with June-August dissolved O_2 inputs into Box 3 and 4 from landward advection and vertical diffusion (1985 to 2003 data).

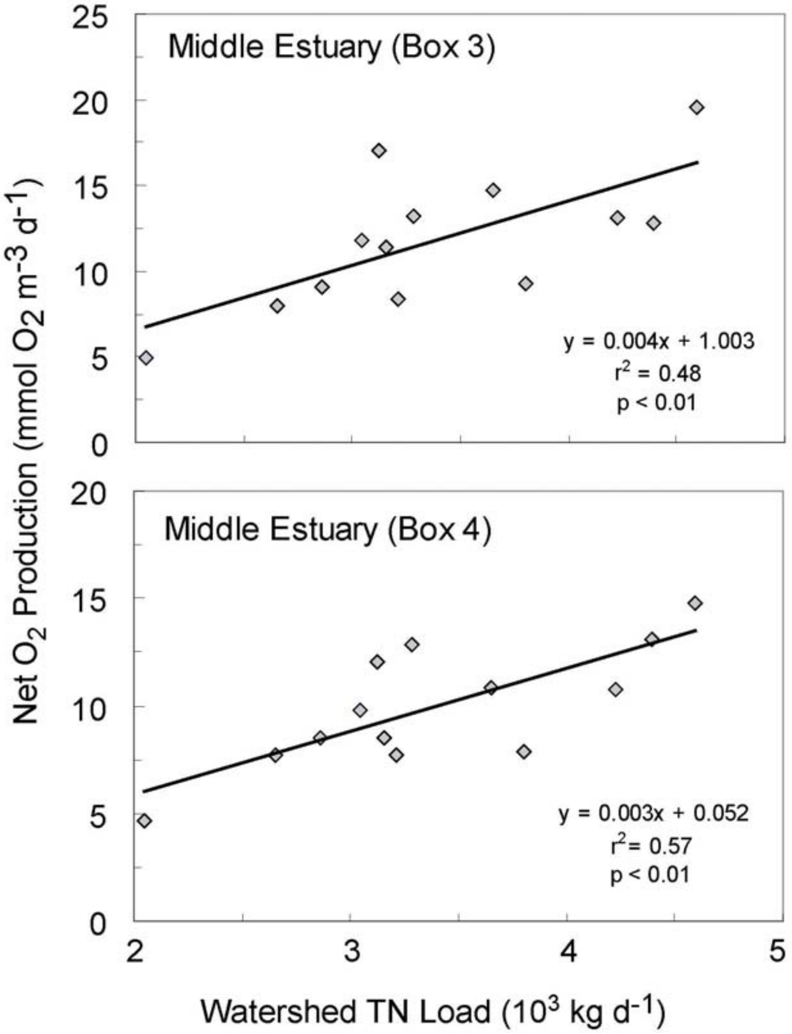

Figure 2.18: Regression of total nitrogen load (non-point + septic + point loads) above Benedict Bridge with net O_2 production in the surface layer of Box 3 and Box 4 (middle estuary). Total nitrogen loads for the region above Benedict Bridge are output from the Chesapeake Bay Watershed Model for the Patuxent River. Data include the years 1985 to 1997 and are annual means. Trend lines are simple linear regressions and correlation coefficient and *p*-value are indicated for each region and variable.

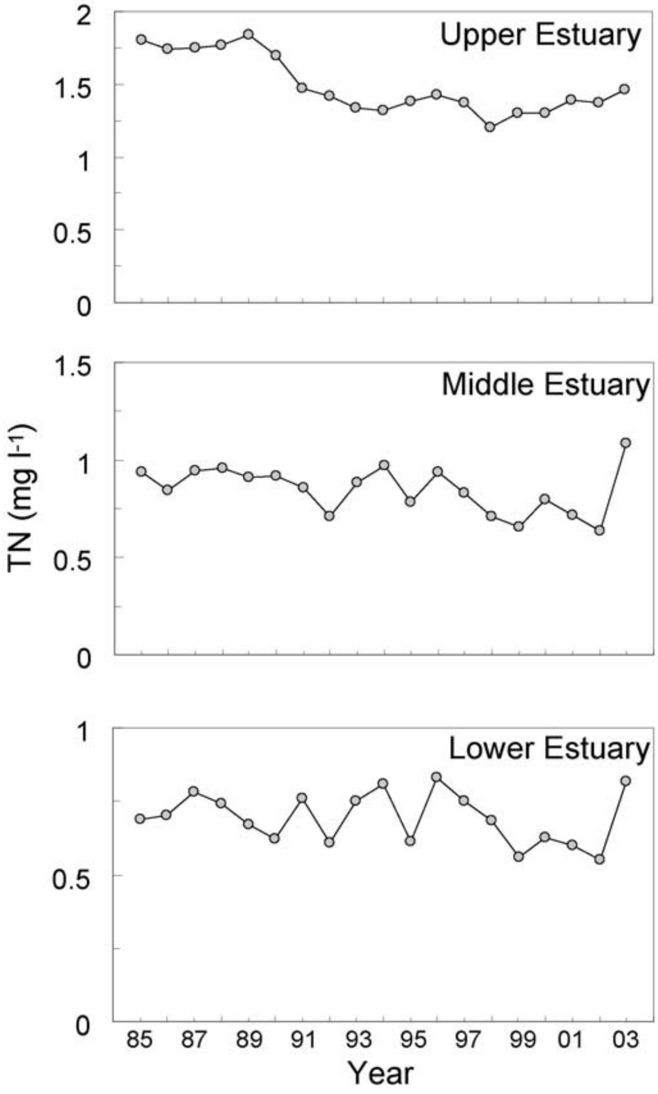

Figure 2.19: Time series (1985 to 2003) of annual mean total nitrogen (TN) concentrations the upper (Box 2), middle (Box 4), and lower (Box 5) regions of the Patuxent River estuary. Data are from the Chesapeake Bay Program Water Quality Monitoring Program.

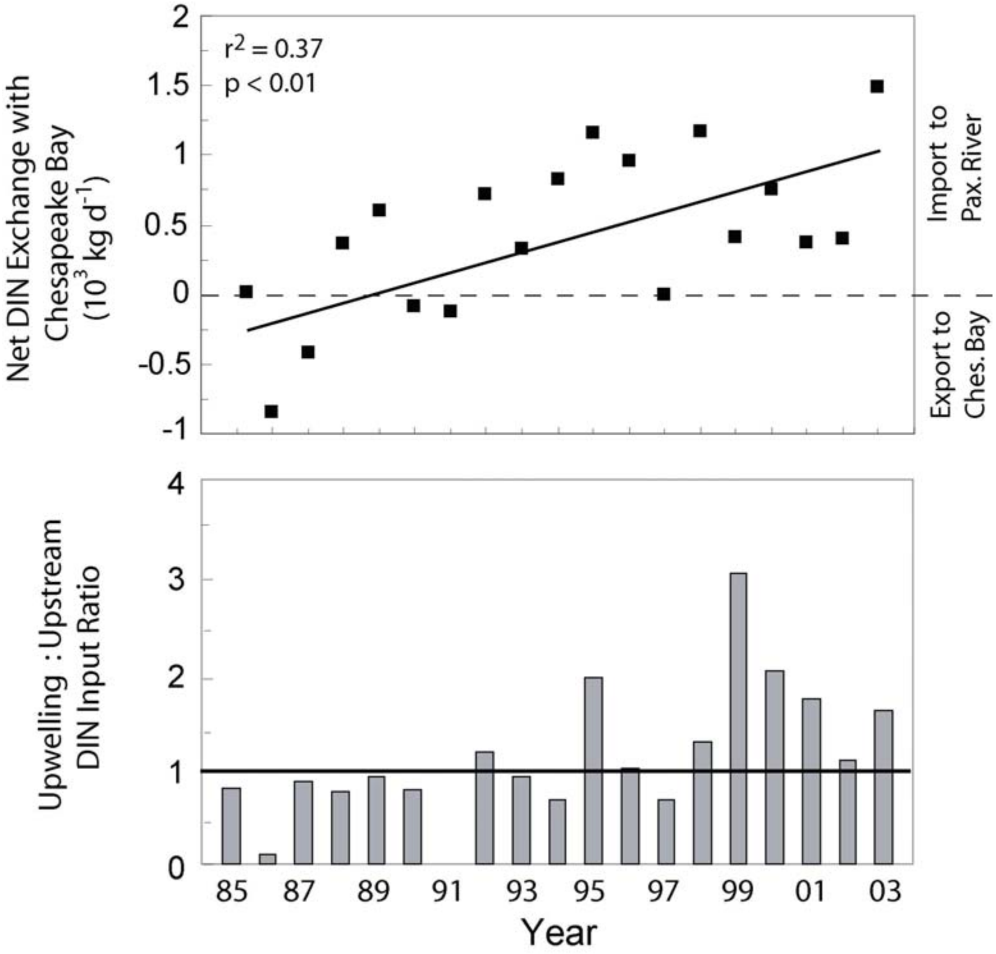

Figure 2.20: Time series (1985 to 2003) of box model computed annual mean net exchange of DIN between the Patuxent River estuary and mainstem Chesapeake Bay (top panel). Positive values indicate net input into the Patuxent River estuary. Time series (1985 to 2003) of the ratio of vertical DIN inputs to horizontal DIN inputs from upstream to the surface layer of Box 5 (bottom panel). Solid black line indicates a ratio of one, where horizontal inputs are equal to vertical inputs.

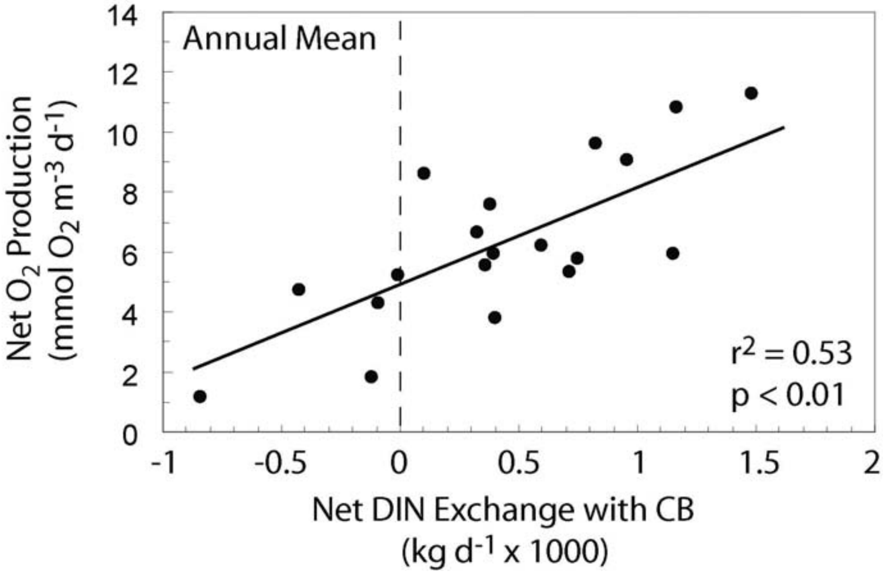

Figure 2.21: Regression of annual mean net DIN exchange between the Patuxent River estuary and mainstem Chesapeake Bay with annual mean net O_2 production in the surface layer of Box 5 (lower estuary). Trend lines are simple linear regressions and correlation coefficient and *p*-value are presented.

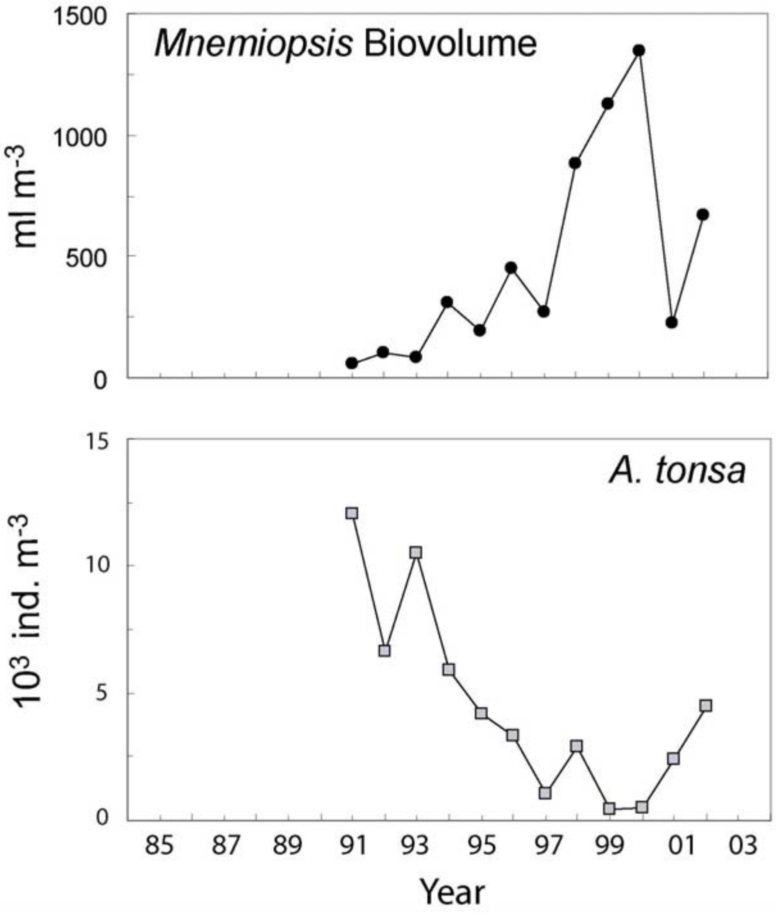

Figure 2.22: Time series (1991 to 2003) of mean summer (June to August) *Mnemiopsis leidyi* biovolume (top panel) and adult *Acartia tonsa* concentration (bottom panel) in the middle Patuxent River estuary (Box 3, 4; Chesapeake Bay Monitoring Station LE1.1).

SUMMARY AND SYNTHESIS

The Patuxent River estuary is a well-studied and well-monitored estuarine system, for which rich water quality databases and numerous biogeochemical rate measurements over the last 2-3 decades permit the analyses presented in this thesis. Although monitoring data may be used directly to evaluate trends and make comparisons between regions and years (Chapter II), I extended the work of Hagy et al. (2000) to apply a box-modeling approach for transforming data on solute concentrations into quantitative rates of net biogeochemical production and physical transport at regional and seasonal scales (Chapter I, II). I use this approach to address both fundamental scientific questions concerning coupling of ecological interactions (Chapter I) and applied science questions on ecological responses to nutrient management (Chapter II). This thesis demonstrates that box models provide a readily accessible tool that can be used to examine relationships between physical transport and biogeochemical processing of nutrients, organic carbon, and other non-conservative substances for the growing number of well-monitored estuarine systems worldwide.

This approach, however, is not without limitations. The ecological rates one can calculate with a box model are strictly “net” rates, that is, they provide an aggregated sum of many biogeochemical processes into a single rate. In this study of the partially stratified Patuxent River estuary, a two-layered box model provides separate rates for surface and bottom layers, where surface rates in the euphotic zone are generally positive for production of O_2 and negative for production of dissolved inorganic nutrients, while the opposite is true for aphotic bottom layers.

Consequently, the sum of these surface and bottom rates (absolute values) provides a sense of “gross” behavior for some biogeochemical processes. In the case of a single box without vertical separation of layers, however, production and consumption processes may be of similar magnitude, making the net rates approach zero and difficult to interpret. A second limitation to the box model approach is the inherent difficulty in estimating error. Complex box models typically average point measurements of concentrations over large space and time scales and also calculate numerous transport rates using the sparse input data. The potential for error in such a computation may be large, but the general lack of finer scale observations make it difficult to quantify. In the case of a well-monitored system, like the Patuxent, error evaluation can be performed for some processes (Chapter I).

On the other hand, the scales at which box models provide computations are appropriate to address many relevant ecological questions. The key variability for several important biogeochemical processes (e.g., phytoplankton productivity, hypoxia, nutrient regeneration) operates at seasonal and regional scales, permitting the use of box models to explore the controlling factors for these processes. Issues of ecological responses to climatic forcing and nutrient pollution may also be addressed, and box models provide a simple and accessible tool for managers to investigate nutrient transport and exchange.

In Chapter I, a conceptual model of temporal and spatial coupling of nutrient cycles and primary productivity developed for the Patuxent River estuary (Kemp and Boynton 1984) was expanded to include how horizontal and vertical transport are necessary to produce the spring phytoplankton bloom, regenerate the material from the bloom in summer, and deliver regenerated nutrients back to the surface layer. Longitudinal peaks of phytoplankton biomass in the middle estuary coincide with similar peaks in nutrient uptake, particulate sinking, nutrient regeneration, and vertical export to this middle region of the estuary. Kemp and Boynton (1984) described a Patuxent estuary with a predominantly summer biomass peak, which is true in the tidal fresh and oligohaline estuary, but waters seaward of river kilometer 40 are characterized by a spring bloom. Thus, despite the transformation of inorganic nutrients into particulate forms in the oligohaline estuary during spring (as noted by Kemp and Boynton 1984), large quantities of inorganic nitrogen are still transported to the middle and lower estuary in spring. Summer productivity is dependent on nutrient regeneration and export from the bottom layer of the middle and lower estuary and this regeneration is coupled to the particulate organic carbon deposited to the bottom layer following the breakup of the spring bloom.

In Chapter II, I explain inter-annual variability in water quality and net O_2 production and the response of the Patuxent estuary to nutrient load reductions from sewage treatment plants. Although chlorophyll *a* declined in the tidal fresh region of the river and nutrient concentrations declined throughout the estuary, chlorophyll *a*, net O_2 production, and water turbidity were stable or increased in the mesohaline estuary. Persistently poor water quality was due, in part, to elevated freshwater inputs during the latter period of the data set and associated high non-point nutrient loads from the upper watershed. Degrading water quality in the lower estuary also correlated with trends of increasing net inputs of DIN from Chesapeake Bay and declining herbivorous grazing. The practical primary conclusion of this chapter is that further nutrient load reductions will be required (e.g., winter operation of BNR, improved non-point source management) before substantial water quality improvements will occur in the mesohaline reaches of the system. Additionally, this study illustrates that water quality benefits of nutrient management may be masked in tributary estuaries because of nutrient exchange with nutrient-rich seaward waters. Fortunately, nutrient load reductions are being pursued throughout the Chesapeake Bay watershed, which would lead to nutrient declines in the mainstem and the tributaries and reduce the importance of the Bay as a nutrient source for upper tributaries.

As was shown in both Chapters I and II, freshwater inputs are an important forcing function for the Patuxent, as well as other estuarine ecosystems. High freshwater inputs have many of the same effects of nutrient enrichment, such as elevated productivity and reductions in water clarity and bottom water O_2. The implications of these effects are as follows; (1) the prevailing climatic conditions must be considered during short term ecological studies in systems such as the Patuxent estuary to include flow effects in data interpretation, (2) high variability in freshwater input trends obscure the interpretation of water quality trends attributable to nutrient management, and (3) predicted increases in precipitation and flow in the Mid-Atlantic region associated with global atmospheric changes during the next century might counteract ambitious nutrient management plans.

This thesis has answered many questions concerning the biogeochemistry of the Patuxent River estuary, but many new questions have been raised in the process. Tight links were found between the magnitude of surface productivity and bottom respiration in the middle estuary, but why is this vertical coupling not as strong in the upper and lower estuary? What transport mechanisms decouple surface and bottom layer processes? Is the sinking of unrespired surface carbon production in the middle estuary the reason that hypoxia develops in this region each year, or is landward bottom layer delivery of low O_2 water and labile carbon also important? In respect to Chapter II, an unequivocal explanation for the increasing phytoplankton biomass in the lower estuary was not established. In addition, the relative importance of increased algal biomass (via reduced grazing) causing net import of DIN from the Bay into the Patuxent versus the net nutrient import causing the algal biomass increase is unclear. It appears that river flow and physical O_2 inputs control inter-annual variations in hypoxia more than do changes in phytoplankton biomass or net O_2 production. Do physical forces control the extent and duration of hypoxia or has the stable phytoplankton biomass in the middle and lower estuary caused the persistent hypoxia? Further studies including analyses of box model computations should help resolve these important questions.

The potential application of the box model technique to aid in the management of coastal ecosystems has been implied throughout the text of this thesis. One utility of box models is the conversion of routine hydrologic and water quality monitoring data to nutrient transport and exchange rates. Such rates permit managers to measure the extent to which nutrient load reductions in the watershed translate into nutrient transport reductions along the axis of the estuary (Chapter II). A second and perhaps more useful approach to box modeling is to estimate box model transport and production rates needed to meet criteria for total maximum daily load (TMDL) mandates. Such an approach might involve (1) developing empirical relationships between nutrient loads and box model rates; (2) developing relationships between box model rates and water quality criteria (e.g., bottom layer O_2 consumption and hypoxia, Chapter II); and (3) using theses empirical relationships to identify the maximum nutrient loading needed to maintain water quality conditions within criteria or standards. These analyses, once developed, have the potential to provide important information to managers at minimal cost.

APPENDIX I

Relationships between chlorophyll *a*, total suspended solids, and secchi depth along the estuarine axis of the Patuxent River

We analyzed water quality monitoring data from the Chesapeake Bay Program (CBP 2005) to evaluate the causative factors driving secchi depth (or light extinction) in the Patuxent River estuary, MD. We developed relationships between secchi depth and both total suspended solids (TSS) and chlorophyll *a* at six stations in the oligohaline and mesohaline regions of the estuary (Fig. AI.1). We also developed relationships between 1/secchi depth (~light extinction coefficient = k_d, m^{-1}) and both total suspended solids (TSS) and chlorophyll *a* (Fig. AI.2). Station TF1.6 is the most upstream station, while station LE1.4 is closest to Chesapeake Bay.

We found that a significant fraction ($p < 0.05$) of the variability in secchi depth and light extinction is explained by TSS in the oligohaline regions of the estuary (Fig. AI.1: TF1.6: $r^2 = 0.29$, TF1.7: $r^2 = 0.44$, and RET1.1: $r^2 = 0.38$, and Fig. AI.2: TF1.6: $r^2 = 0.13$, TF1.7: $r^2 = 0.16$, and RET1.1: $r^2 = 0.14$), but not by chlorophyll *a*. Conversely, we found that more of the variability in secchi depth and light extinction is explained by chlorophyll *a* in the mesohaline region of the estuary (Fig. AI.1: LE1.3: $r^2 = 0.32$, LE1.4: $r^2 = 0.34$, and Fig. AI.2: LE1.3: $r^2 = 0.37$, LE1.4: $r^2 = 0.39$) than by TSS. The secchi depth versus chlorophyll *a* relationship in the lower estuary is negative, which indicates that plankton biomass is attenuating light more than inorganic/organic solids.

Our results indicate that light attenuation is driven by different factors in the oligohaline estuary than in the mesohaline estuary. Strong correlations between TSS and secchi depth in the tidal fresh/oligohaline estuary indicate that characteristically high inorganic solid concentrations in this region are the most important factor driving light attenuation. As inorganic solid concentrations are lower in the mesohaline region relative to the oligohaline, plankton biomass is more important in attenuating light in the mesohaline estuary. The significant correlation between chlorophyll *a* and secchi depth in the mesohaline estuary indicates that the temporal trends in these variables we found in Chapter II are related to each other.

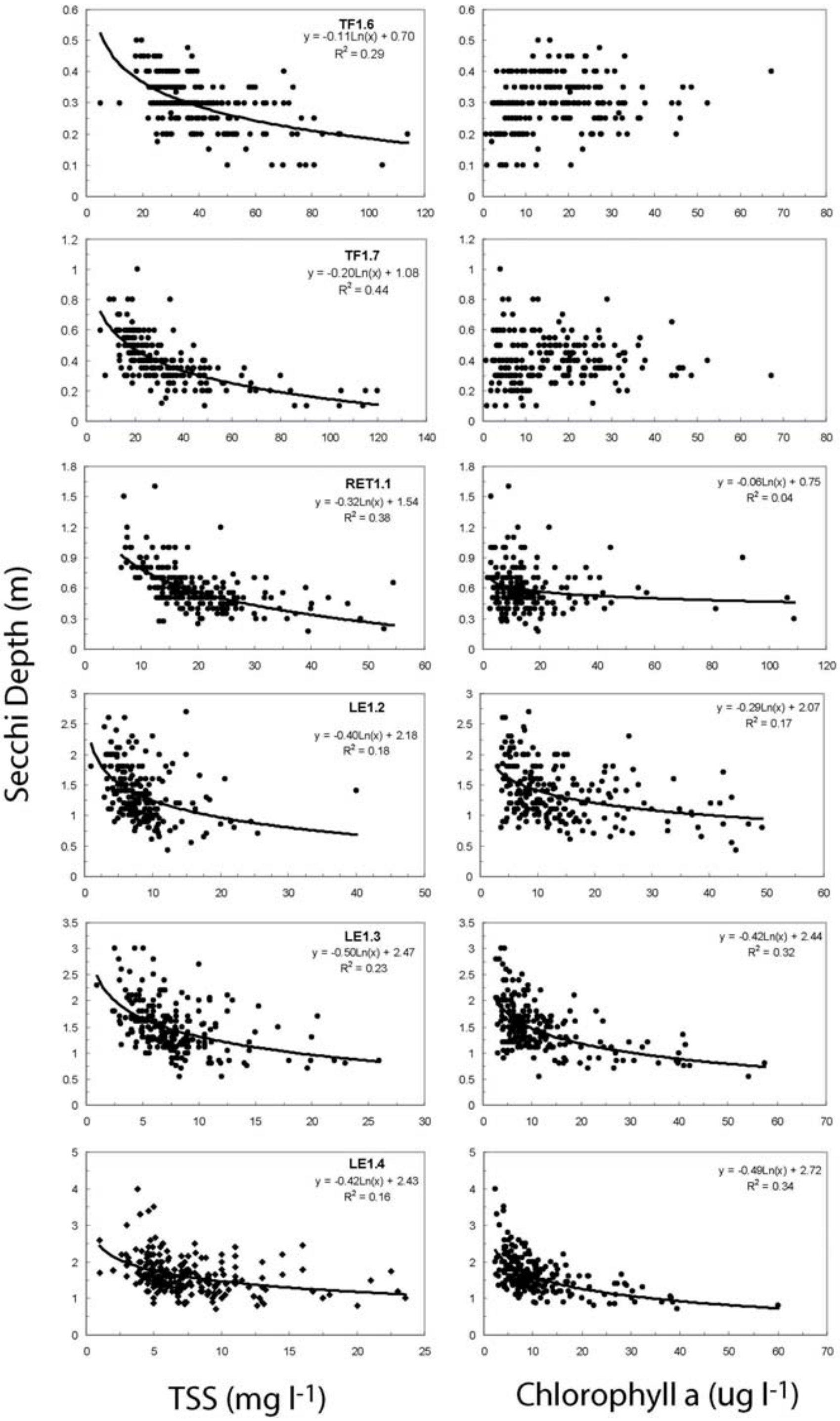

Figure AI.1: Correlations between mean monthly secchi depth and total suspended solids (TSS, left panel) and between secchi depth and chlorophyll *a* (right panel) at six stations spanning the tidal fresh (Station TF1.6) to mesohaline (Station LE1.4) regions of the Patuxent River estuary (see Chapter I, Fig. 1.1 for station location). Data for all months from 1985 to 2003 (n = 228).

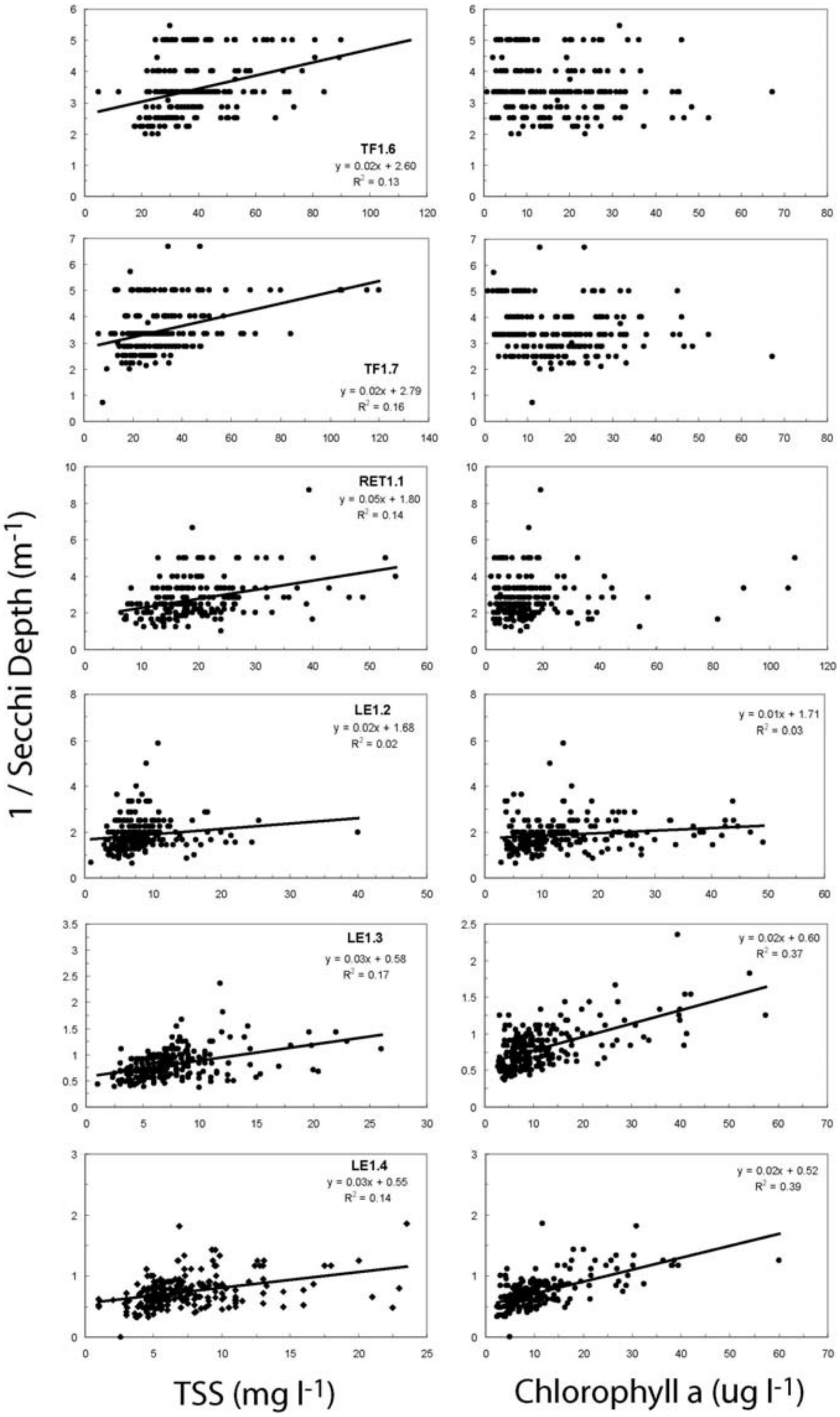

Figure AI.2: Correlations between mean monthly 1/secchi depth (~ k_d, m^{-1}) and total suspended solids (TSS, left panel) and between 1/secchi depth and chlorophyll *a* (right panel) at six stations spanning the tidal fresh (Station TF1.6) to mesohaline (Station LE1.4) regions of the Patuxent River estuary (see Chapter I, Fig. 1.1 for station location). Data for all months from 1985 to 2003 (n = 228).

APPENDIX II

Estimating denitrification using non-conservative fluxes of nitrogen and phosphorus: Approach and comparison with different methods

Nitrogen cycling is an important component of estuarine biogeochemical dynamics in that nitrogen is limiting to phytoplankton growth in many coastal systems (D'Elia et al. 1986). Denitrification is a process where NO_3^- is used as a terminal electron acceptor by denitrifying bacteria, resulting in the production of gaseous forms of nitrogen (N_2, N_2O). Because nitrogenous gases cannot be assimilated by most species of estuarine phytoplankton, denitrification provides an important sink for excess nitrogen in coastal marine ecosystems (Kemp et al. 1990).

We estimated net denitrification (denitrification – nitrogen fixation) by quantifying the deviation of the net TDN production rate from the net TDP production rate:

$$P_{N_2m} = k_{TDN:TDP}\,(P_{DIPm} + P_{DOPm}) - (P_{DINm} + P_{DONm}) \qquad (1)$$

where P_{N2m} is net denitrification (mmol m^{-3} d^{-1}), $k_{TDN:TDP}$ is the assumed nitrogen-phosphorus molar ratio of 16, and P_{DIPm}, P_{DOPm}, P_{DINm}, and P_{DONm} are the box model computed net production rates (mmol m^{-3} d^{-1}) for dissolved inorganic and organic phosphorus and nitrogen, respectively (Smith et al. 1991). The computation of net denitrification using the difference between net production rates of TDN and TDP has been used in previous studies (e.g., Smith et al. 1991) and is specified for denitrification calculations as part of LOICZ biogeochemical budgets (Land-Ocean Interactions in the Coastal Zone, Webster et al. 2000). If the amount of nitrogen released from organic matter oxidation is less than that expected from phosphorus releases, the "missing" quantity of nitrogen is attributable to loss via denitrification. Positive values indicate a nitrogen sink, such as denitrification, while negative values indicate nitrogen fixation. Net denitrification rates are expressed below in units of μmol N m^{-2} h^{-1} to simplify comparisons with rate measurements.

Seasonal patterns in box model computed net denitrification rates vary along the estuarine axis (Fig. AII.1). Net denitrification peaks in early spring and later in summer in the upper estuary (~150 μmol N m^{-2} h^{-1}), but March-May peaks were found in the middle and lower estuary. Seasonal peak rates of net denitrification were highest in the upper and middle estuary (Fig. AII.1: 100-180 μmol m^{-2} h^{-1}, annual mean = 75-125 μmol m^{-2} h^{-1}). Net denitrification reached seasonal minima of 0-50 μmol N m^{-2} h^{-1} in July-September in the middle and lower estuary (Fig. AII.1). Mean integrated net denitrification, averaged over Box 2 to Box 6, was significantly and positively correlated with mean annual river flow ($r^2 = 0.66$, $p < 0.01$, n = 19).

Box model computed rates of net denitrification compare favorably with rate measurements made in the Patuxent and adjacent Chesapeake Bay (Jenkins and Kemp 1984, Kemp et al. 1990, Greene 2005). Significant correlations between denitrification and mean annual river flow suggest that the large amounts of NO_3^- delivered from terrestrial systems to the estuary during high flow fuels direct denitrification throughout the estuary (Fig. AII.2) and coupled denitrification in the middle and lower estuary associated with increased organic matter deposition to sediments (Nielsen et al. 1995, Kana et al. 1998, Cornwell et al. 1999). River flow, however, may decrease denitrification by causing reduced bottom water O_2 concentrations (see Chapter II), which might limit coupled nitrification-denitrification

(Cornwell et al. 1999). Perhaps the positive effects of NO_3^- loading on denitrification offset the negative effects of hypoxia. Seasonal rates of denitrification in the middle and lower estuary indicate peaks in March-May when river flow and NO_3^- concentration are high (Kemp et al. 1990, Nielsen et al. 1995) and seasonal minima in summer when hypoxia develops in the region and low O_2 restricts coupled nitrification-denitrification (Kemp et al. 1990). Net denitrification remains high in summer in the upper estuary, where seasonal hypoxia does not develop. Such trends agree with seasonal measurements of NO_3^-, denitrification, and dissolved O_2 concentrations in Chesapeake Bay, where low O_2 inhibits nitrification, preventing the buildup of NO_3^- substrate for denitrification (Kemp et al. 1990). Rates of denitrification are also highest in the upper and middle region of the estuary, where NO_3^- concentrations are high relative to the lower estuary and where organic matter sinking to the bottom layer is highest (Fig. AII.2, see Chapter I). Thus, high carbon sinking in the middle estuary may enhance water column denitrification (Cornwell et al. 1999).

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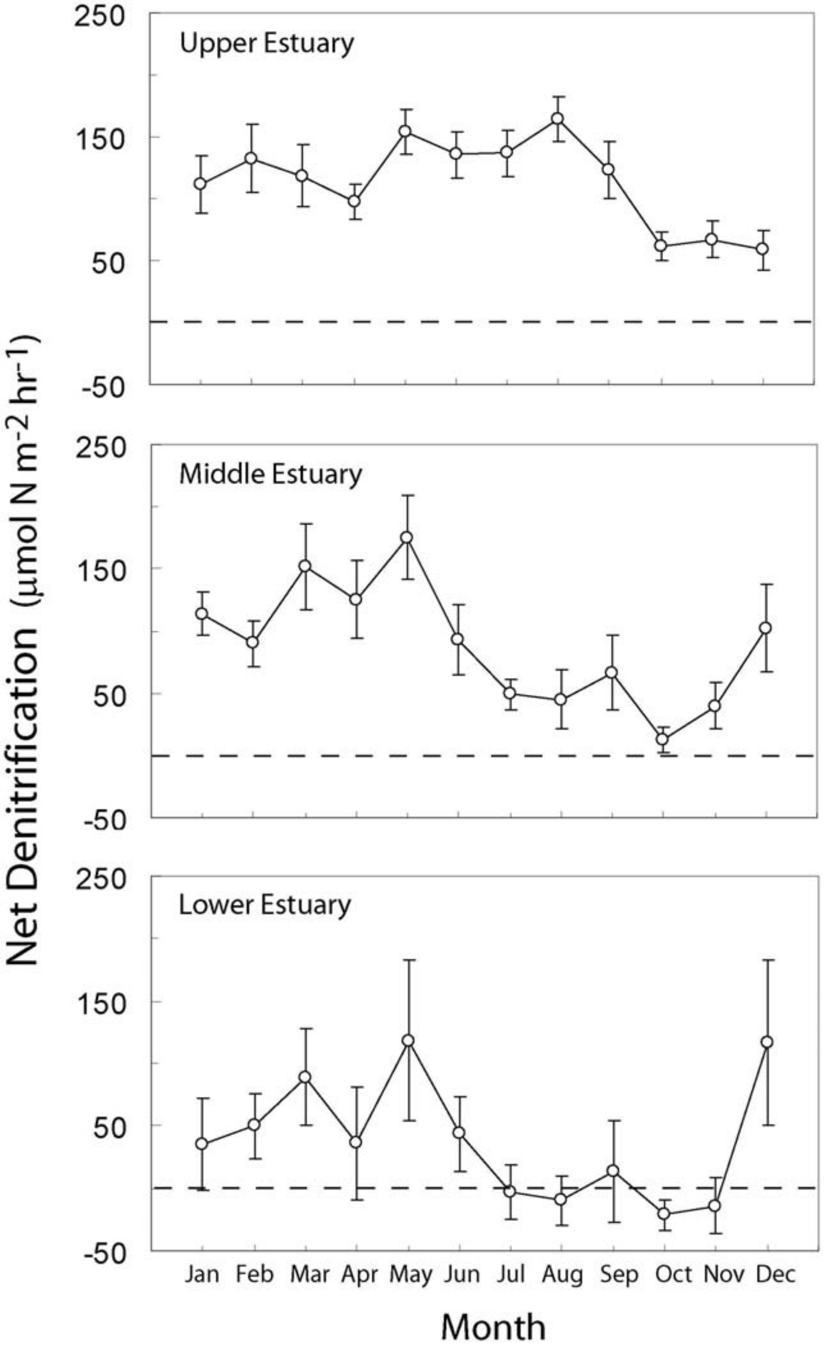

Figure AII.1: Mean monthly integrated net denitrification (denitrification- nitrogen fixation) computed by the box model in the upper (Box 2), middle (Box 4), and lower (Box 5) Patuxent River estuary. Monthly means (± SE) were calculated from 1985 to 2003 data. Horizontal dashed lines are drawn at zero net denitrification. Error bars represent one standard error of the mean.

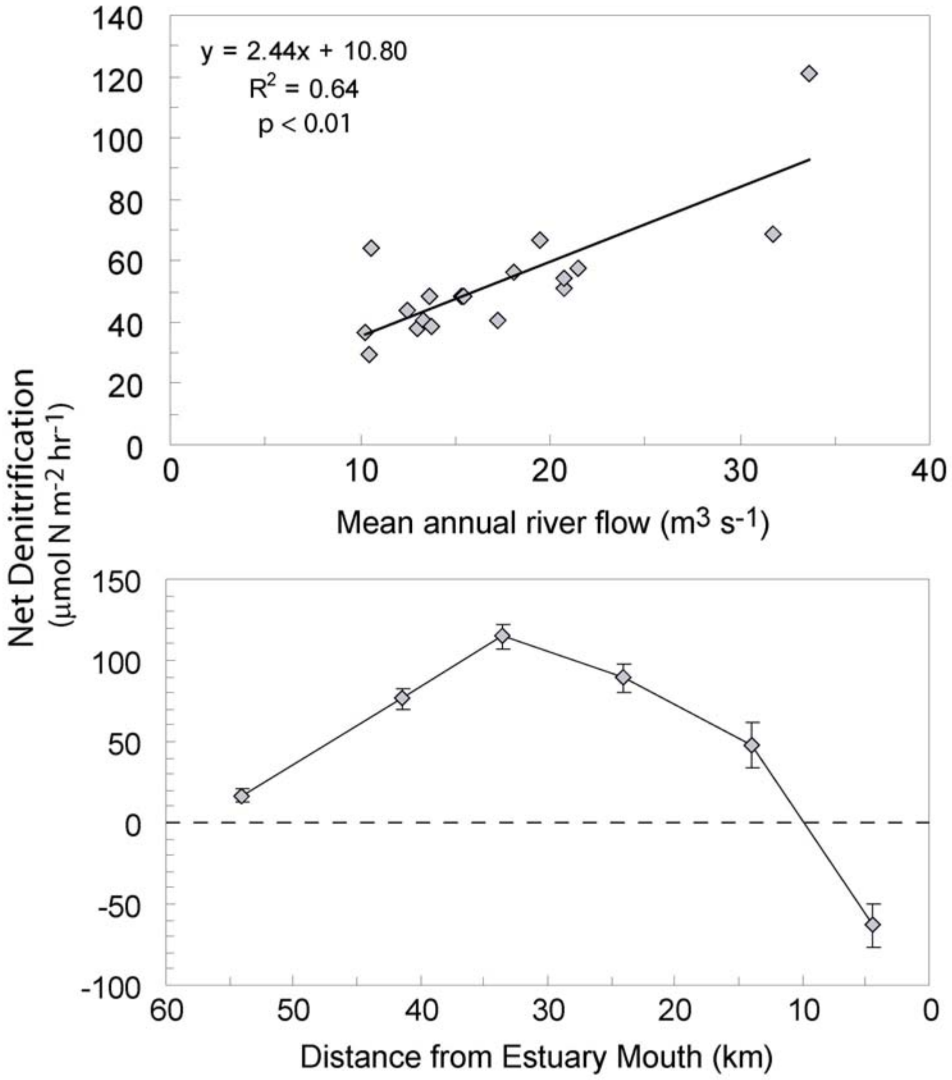

Figure AII.2: Correlations between mean annual box model computed net denitrification and mean annual freshwater flow measured at the fall line (top panel) and distribution of box model computed net denitrification along the axis of the Patuxent river estuary (bottom panel). Error bars in the lower panel represent one standard error of the mean for all data from 1985 to 2003.

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