

Nutrient Budgets and Management Actions in the Patuxent River Estuary, Maryland

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Introduction

During the past several decades global use of phosphorus (P) and nitrogen (N) has increased at an alarming rate and is expected to further accelerate in some parts of the world. The quantitative extent of nutrient production (Vitousek et al. 1997) and use has been determined for many areas of the globe (e.g., Zheng et al. 2002; van Egmond et al. 2002) and estimates are now available concerning the magnitude of nutrient discharges to estuarine and coastal ecosystems at global (Krocze and Seitzinger 1998), national (Howarth et al. 2002) and regional scales (Van Breemen et al. 2002). The detrimental ecological effects of nutrient enrichment have also been examined for a variety of coastal ecosystems (Carpenter et al. 1998; Conley 2000; Rabalais 2002). A report by the National Research Council (2000) found nutrient over-enrichment to be the greatest pollution threat faced by coastal marine environments. A NOAA assessment concluded that some 40% of coastal waters of the USA exhibited advanced indications of nutrient stress (Bricker et al. 1999). While there is a rapidly accumulating body of knowledge concerning nutrients in estuarine and coastal marine waters, most of this information tends to be focused on particular issues rather than integrated at the ecosystem level where the relative importance of many processes can be compared, evaluated, better understood and used in management decisions.

A decade ago we used whole-system nutrient budgets as a quantitative framework to examine N and P in the nutrient-enriched Patuxent River estuary, a major tributary of Chesapeake Bay. Our goal was to examine the magnitude of nutrient sources, internal nutrient storages and losses and nutrient export from the estuary (Boynton et al. 1995). Results indicated that the Patuxent had moderate and high N and P loads, respectively, compared to other coastal and estuarine systems. Further, we found that relatively little N (~25%) and virtually no P passed out the mouth of the estuary and most of the N export was in dissolved or particulate organic forms rather than as compounds directly available to plant communities. Denitrification in sub-tidal sediments and long-term sediment burial of particulate N and P were important internal loss terms, the former a common feature of many estuaries but the latter important only in sediment-rich coastal plain ecosystems such as the Patuxent (Nixon et al. 1996; Boynton and Kemp 2005).

Some portions of the budget were better evaluated than others and several potentially important items were either neglected, because little or no data existed, or were entirely excluded because our biases and conceptual model of how things worked at the time did not include these processes. For example, we used input data from only two relatively dry years; there was no assessment of interannual variability because sufficient data were not available. The entire tidal estuary (e.g., tidal fresh, oligohaline and mesohaline regions) was treated as a single unit so there was no spatial resolution. The budgets also considered only total nitrogen and total phosphorus, nutrient exchanges with the Chesapeake Bay were estimated by difference (i.e., land plus atmospheric inputs minus internal losses), and the extensive tidal marshes of the Patuxent were considered to be neutral with regard to nutrient processes.

In the intervening years several things have led us to re-examine nutrient budgets for this estuary. First, there is now a substantial time-series of nutrient inputs from point, diffuse and atmospheric sources and this record includes wet, average and dry years. Associated with this input record are measurements of water column nutrient stocks,

phytoplankton primary production and biomass, zooplankton and benthic invertebrate biomass and sediment nutrient releases. Many of these measurements were made at monthly or finer time scales. Seasonal, as well as interannual, variability can now be examined. Second, several new data sets have been developed; burial rates of N and P in sub-tidal areas and intertidal marshes have been estimated (Merrill 1999; Greene 2005a) and denitrification rates have been measured in marsh and sub-tidal estuarine sediments using a more reliable technique (Kana et al. 1994, 1998). Third, the net flux of N and P between the oligohaline and mesohaline portions of the estuary and at the junction of the Patuxent with the Chesapeake Bay have been estimated using a box-model (Hagy et al. 2000) thus making it possible to have an estuarine nutrient budget with independent measurements for all major input and output terms (Nixon et al. 1996). Finally, during a decade long period, a nutrient management plan, focused on point source nutrient reductions, was implemented in the basin. During the mid-1980's phosphorus was removed at all major sewage treatment plants and by 1993 nitrogen was also being removed, only during warm seasons, at all the major treatment plants (D'Elia et al. 2003). Thus, this estuary was subjected to a major, system level management action.

The overall objective of this work is to produce a more thoroughly evaluated budget for N and P in this estuarine system. We have the relatively rare opportunity to assess how well we did the first time around. We also have the opportunity to examine issues related to interannual variability in nutrient inputs to an estuarine system and the manner in which estuarine processes respond to these variations in inputs. Finally, we can examine the effects of major management actions on the N and P budgets of a large coastal plain estuary.

Description of the Patuxent Basin and Estuary

The Patuxent River basin encompasses 2264 km² of land, 133 km² of tidal waters and 29 km² of tidal marshes (Table 1; Fig. 1). The Patuxent ranks sixth in drainage basin size, sixth in estuarine volume and seventh in freshwater inflow among the tributaries of the Chesapeake system (Cronin and Pritchard 1975). While it is far smaller than several other tributaries, it is still among the largest of the 60 tributaries that are part of the Chesapeake Bay complex and it is among the better known and studied because of a long history of management debate, court cases and eventual management actions aimed at water quality and habitat restoration (Malone et al. 1993; D'Elia et al. 2003; Kemp et al. 2005).

Several large land use changes occurred in this basin during the 370 years since European settlement and these are summarized here because they played a prominent role in the current nutrient ecology of the estuary. During the late 1600's, land use changes began in the Patuxent basin to support agricultural activities, especially tobacco production. Until the mid-1700's, traditional "hill and hoe" type agriculture remained dominant, a form of farming that was characterized by low erosion rates, retention of soil fertility and rotation between short production periods (6-8 years) followed by long (20 years) fallow periods (Walsh 2001). However, after 1780 agricultural practices shifted from traditional methods to newer "high farming" techniques developed in Europe and embraced by many large landowners in the United States. Land was plowed deeper, stumps and roots removed, fallow periods reduced, marginal lands brought into

production and plowing mainly directed down contours, rather than across, to ease the strain on plow animals (Walsh 2001). By the early 1800's some 40% of Southern Maryland land was cleared and by the late 1800's up to 80% of the land had been cleared (Cooper 1995). Earle and Hoffman (2001) vividly described agricultural changes in the Patuxent basin and the huge effects these had on land fertility, drainage patterns, rural economics and soil erosion rates.

Direct measurements of ecological conditions in the Patuxent watershed and estuary during these early periods do not exist, but other sources provide useful information. One of the earliest observations concerns filling of tidal river channels with soils eroded from surrounding lands associated with changes in farming practices. As early as 1780 some of the small, upper estuary ports of the Chesapeake had shoaled to the point where commercial vessels could not operate. Middleton (1953) lists Mattawoman Creek and Port Tobacco on the Potomac River, Elkridge on the Patapsco and Upper Marlboro on the Patuxent as among those affected. These ports had water depths of about 6m at settlement but these were reduced to less than 1 m by the late 1700's. Until 1815 a customs office operated at the Port of Queenstown on the Patuxent (river km 79; adjacent to the present town of Upper Marlboro, MD) where ships of 300 tons and drafts of 3.5 m came to trade. During the War of 1812, British war ships operated in the Patuxent as far upstream as the current town of Nottingham (river km 64; Khan and Brush, 1994) and until the 1730's barges operated 32 km upstream of Queenstown in support of an iron works (Donald Shomette, pers comm.). Since 1850 forest re-growth was a major ecological feature of the basin, a pattern that persisted until about 1985, when forested lands again started to decline as land was converted to urban and residential uses.

We also have limited descriptions of water quality from a century before direct measurements were initiated. Mr. J. Hungerford, a Baltimore lawyer, owned a plantation that bordered the lower Patuxent estuary. Escaping from a cholera epidemic in Baltimore during summer 1832, Hungerford spent time at the plantation and published a book that contained the following descriptions of the mesohaline estuary (Hungerford 1859):

"Of all the bright rivers that flow into it (Chesapeake Bay) there is not one which excels the Clearwater (Patuxent) in the purity of its waters"

and

"So transparent are its waters that far out from shore you may see, in the openings of the sea-weed forest, on its bottom the flashing sides of the finny tribes as they glide over the pearly sands"

While such descriptions are qualitative, the message is evident; the estuary was clearer than it has been in recent decades (Stankelis et al 2003).

Two paleoecological studies have also been conducted in the Patuxent and these provide more quantitative indications of past ecological conditions. Brush and Davis (1984) examined sediment cores collected from the tidal-fresh, oligohaline and mesohaline portions of the estuary and concluded there was little compositional change in diatom and macrophyte community composition for 300-1600 years prior to European settlement. During the post-settlement period, when land was being rapidly cleared, turbidity-intolerant diatom and macrophyte species disappeared from the upper portions

of the estuary, but similar changes were not as evident in mesohaline areas. However, following increased fertilizer use and sewage treatment plant discharges, submerged macrophyte communities also disappeared from the mesohaline portion of the estuary during the late 1960's (Stankelis et al. 2003).

In a more recent study, Khan and Brush (1994) obtained several cores from the tidal-fresh estuary and adjacent marshes (river km 73). Analyses of these cores indicated that the estuary in this region was deep enough for ocean-going vessels during the 1600's but began filling following initial land clearance. Erosion rates were very high during the mid to late 1800's (7-8 times the pre-settlement rates), during the period 1890-1910 and again during rapid urbanization of the upper basin (1960-1980). An important conclusion from this work was that the marsh edges adjacent to the tidal river were only about 100 years old. Supporting this conclusion, Flemer et al (1971) earlier examined US Geological Survey and Maryland Geological Survey maps of the upper Patuxent from 1904, 1938 and 1949 and found a high degree of consistency in the areal extent of marshes (~19 km²) during this half-century period. McCormick and Somes (1982) reported very similar areas of tidal wetlands for more recent times. Thus, these marshes appear to have been an extension of the channel filling processes that occurred during the previous two centuries. We have emphasized at some length land use and sedimentation patterns in this estuary because tidal marshes and abundant supplies of fine-grained sediments play central roles in the contemporary nutrient dynamics of this estuary.

Human population in the Patuxent basin was about 30,000 (13 people km⁻²) in 1900. The basin remained very rural until about 1960 when rapid population growth began, a trend that continues to the present (536,000; 235 people km⁻²; Table 1). During a recent 10 year period (1985-1995) population increased by 36, 14 and 50% in the upper, mid and lower basins, respectively. Population density in 1995 was highest in the upper basin (356 people km⁻²) and less than half that in the mid (154 people km⁻²) and lower (157 people km⁻²) basins. Population density in mid-Atlantic basins averaged 317 people km⁻², very similar to the upper portion of the Patuxent basin, but much higher than the mid and lower basins (Basta et al. 1990).

The dominant land use in the Patuxent basin remains forested lands (44%) and the percentage of forested lands decreases from the lower to upper basin. Urban and agricultural lands occupy about the same proportions in the upper and middle sub-basins (20-30%) while agricultural lands represent a smaller proportion of land use in the lower basin. Recent land use assessments have indicated that forested and agricultural lands are currently decreasing and are being converted mainly to residential and urban uses (Costanza et al. 1995).

The Patuxent River and estuary are about 170 km in total length and the lower 95 km are tidal (Fig. 1). The upper portion of the tidal estuary (rkm 40 -95) is narrow (50 - 300m), very turbid ($K_d = 3.0$), vertically well-mixed with a tidal range of 0.5 - 1.0m and average depth of 1.1 m. In addition, this portion of the estuary is flanked by extensive tidal freshwater and salt marshes with ratios of marsh area to river distance ranging from 0.4 to 0.8 km² km⁻¹ of river. The lower estuary (rkm 40 to mouth at Chesapeake Bay) is much wider (1 - 5 km), deeper ($z = 5.4$ m), clearer ($K_d = 0.9$) and seasonally stratified.

Conceptual Framework for Nutrient Budgets

In an earlier evaluation of nutrients for the Patuxent River estuary, a conceptual model was used to guide development of N and P budgets (Boynton et al. 1995). A more detailed conceptual model was developed for this evaluation but still represents a compromise between current understanding of major inputs, exports, storages, internal losses and cycling of N and P and the temporal and spatial availability of data with which to evaluate model terms (Fig. 2).

The drainage basin was treated as three distinct units (upper, middle and lower basins), with the upper basin draining into the upper estuary but having no estuarine waters within that unit of the model. The estuarine area of the basin was divided into upper and lower portions corresponding to the tidal fresh/oligohaline and mesohaline zones, respectively (Fig. 1). This model considers four classes of nutrient inputs, five loss terms for N and three for P, eight storage categories, three nutrient cycling pathways and two net nutrient transport terms.

The four classes of nutrient inputs, shown along the left and top of the diagram, include point, diffuse, septic and atmospheric sources. The atmospheric term only includes deposition of N and P to surface waters of the upper and lower estuary; atmospheric deposition of N and P to the watershed is included in the diffuse source terms. Point sources were all municipal sewage discharges. Diffuse sources were estimated at the head of tide (junction of upper and middle basin) based on extensive monitoring of river flow and nutrient concentrations; diffuse sources from the middle and lower basins were estimated using a land-use model. Septic sources were estimated separately based on population living in non-sewered homes. Nitrogen fixation was not directly evaluated in this budget but was probably a small source, as seems to be the case in most nutrient-rich, temperate zone estuarine systems (Howarth et al. 1988).

Loss terms in both upper and lower estuarine segments include burial of N and P in sub-tidal and tidal marsh sediments, denitrification in sub-tidal and marsh sediments, fisheries harvests (recreational and commercial yields) and net transport of N and P at the downstream boundary of the two estuarine segments. We recognize that the fisheries harvest term is incomplete; this term should include accumulation of N and P in fish that migrate into the estuary when individuals are small, grow rapidly during summer and then migrate from the system in the fall. However, satisfactory estimates of fish stocks and migrations were not available to attempt this calculation.

Major nutrient pools and several nutrient cycling processes were included in this analysis to allow estimates of turnover times and evaluation of the relative importance of "new" versus "recycled" nutrients. The evaluation of nutrient cycling terms is not complete because activities of water column bacteria, microzooplankton and soft-bodied zooplankton were not included, again because data were not available.

The conceptual model of the nutrient budget can also be expressed as differential equations for TN and TP as follows;

$$\frac{dT_N}{dt}_{upper} = (I_{up} + I_{ud} + I_{ma} + I_{mp} + I_{md} + I_{ms}) - (L_{amb} + L_{mdn} + L_{ub} + L_{udn} + L_{of}) - T_{of}$$

$$dTN/dt_{\text{lower}} = T_{ul} + (I_{la} + I_{lp} + I_{ld} + I_{ls}) - (L_{lmb} + L_{lmdn} + L_{lb} + L_{ldn} + L_{lf}) - T_{lb}$$

$$dTP/dt_{\text{upper}} = (I_{up} + I_{ud} + I_{ua} + I_{up} + I_{ud}) - (L_{umb} + L_{ub} + L_{uf}) - T_{ul}$$

$$dTP/dt_{\text{lower}} = T_{ul} + (I_{la} + I_{lp} + I_{ld}) - (L_{lmb} + L_{lb} + L_{lf}) - T_{lb}$$

where: I's are input terms; L's are loss terms and T's are transport terms. The specific input, loss and transport terms are defined in **Figure 2**. In this analysis dTN/dt and dTP/dt were assumed to equal zero when averaged over several years.

Data Sources, Methods, and Computations

Nutrient Sources

Inputs of N and P included atmospheric deposition directly to surface waters of the estuary, point, diffuse and septic sources. Input data, in most cases, were available on a monthly basis from 1985 – 2000. In some instances the input record ended in 1997.

Atmospheric Deposition: Estimates of wet nitrogen loading to the surface waters of the estuary utilized data collected at the Wye, MD sample site (38° 54' 47", 76° 09' 09") of the National Atmospheric Deposition Program (**NADP 2001**). NADP reported monthly volume weighted mean concentrations of NH₄ and NO₃ and monthly total precipitation (cm). Concentrations of organic nitrogen in rainfall collected at two locations in the Chesapeake Bay region ranged from an average of 9.1 μM to 21 μM (**Scudlark et al. 1998; Jordan et al. 1995**). Insufficient data were available to compute seasonal deposition estimates; annual average concentration and average rainfall (~100 cm) were used to produce annual wet fall organic N. Estimates of HNO₃/NO₃ dry deposition were from the 1993-1997 Wye, MD AirMoNs dry study (**NADP 2001**). These data were modified in two ways. First, the HNO₃ deposition velocity over soil was reduced by a factor of three to represent over-water deposition velocity. This modification resulted in over-water deposition velocity that was similar to those reported by **Valigura (1995)**. Second, the original data were reported for one to three week intervals. These data were linearly interpolated to daily loads and then summed to monthly loads. Ammonia dry fluxes were based on data collected locally between March, 1997 and May, 1999. Generally there were 1 to 3 observations per month (**Larsen et al. 2001**). Atmospheric deposition of P is not nearly as important as it is for N. Accordingly, we put less effort into making estimates and it also appears that there are fewer estimates to consider. In the previous nutrient budget P inputs from the atmosphere were estimated to be 1.3 and 5.3 mg P m⁻² month⁻¹, for inorganic and total P, respectively (**Boynton et al. 1995**) and these were based on estimates reported by **Smullen et al. (1982)** and **Wies and O'Melia (1989)**. **Hu et al. (1998)** reported P concentrations in rainwater collected from Long Island Sound to range from below detection to 43 ug l⁻¹. The latter value is comparable to those reported by **Smullen et al (1982)** and we used the older values.

Point Sources: Estimates of point source N and P inputs were obtained from the **Chesapeake Bay Program (2001)** and details concerning these data are contained in **Wiedeman and Cosgrove (1998)**. In brief, all major point source discharges to the Patuxent were from municipal sewage treatment plants. Of the 34 plants discharging to the Patuxent, ten had daily discharges in excess of 1 million gallons per day ($3800 \text{ m}^3 \text{ d}^{-1}$) and were classified as major discharges. These discharges represented 97.2% of the total point source flow. Nine of the major plants were located above the head of tide (HoT) and one, the largest, was located just below HoT. Monthly data were available from 1985 – 1999 and included flow ($\text{m}^3 \text{ s}^{-1}$) and loads (kg d^{-1}) of ammonium, nitrite, nitrate, total nitrogen, dissolved inorganic P and total P.

Diffuse Sources: Diffuse source loads of N (ammonium, nitrite, nitrate, organic nitrogen and total nitrogen), P (dissolved inorganic phosphorus, organic phosphorus and total phosphorus) and total suspended sediments (TSS) were estimated by the Chesapeake Bay Program using Hydrologic Simulation Program-Fortran (HSPF), a widely used watershed model. The simulation time-step in the model was hourly but data used in this analysis were summed to monthly time intervals and covered the period 1985-1997. Details concerning the development and current configuration of this model are provided in a series of technical papers and reports (e.g., **Donigan et al. 1994; Linker et al. 1996; Linker et al. 1999; Linker et al. 2001; Shenk and Linker 2001**). In brief, HSPF is a continuous, physically-based, lumped parameter model that simulates hydrology, sediments and nutrients (or other pollutants) in soils and streams. The version of the model used by the Chesapeake Bay Program has nine different land-uses, including conventional-tilled cropland, conservation-tilled cropland, cropland in hay, pasture, pervious urban land, impervious urban land, mixed open space, forest and animal waste areas. Each land use has its own unit model which is simulated as a single acre unit and the results multiplied by the number of acres of that type of land use draining into a specific river segment. In the case of the Patuxent, diffuse source loads were estimated for three basin segments including: 1) the basin above HoT; 2) the coastal plain portion between the head of tide and Benedict, MD, an area that includes the upper estuary and almost all of the tidal marshes; 3) the smaller lower basin which surrounds the main mesohaline portion of the estuary. The USGS has maintained a flow and water quality monitoring station at the head of tide since 1978 (**Langland et al. 2001**). While the watershed model produced load estimates for the upper basin, we chose to use the USGS estimates because they were a more direct estimate of loads. Finally, nutrients derived from septic systems were not included in the watershed model. Septic system derived P was considered to be negligible. Nitrogen was computed based on the fraction of the population in the middle and lower basin served by septic systems, the average N excreted per person and the amount of N that actually reaches a stream segment (estimated at 40%; Shenk, pers. comm.; **Maizel et al. 1997**).

Nutrient Transport between Estuarine Zones and with Chesapeake Bay

Physical exchanges of TN and TP between the upper and lower estuary, and between the lower estuary and Chesapeake Bay, were computed using a salt-and-water balance model (Hagy et al. 2000). This model computes advective and dispersive transport of water and salt from a system of equations describing continuity of each for defined regions of the estuary. Assuming that the dissolved and suspended particulate N and P are transported in the same manner as salt, the fluxes of N and P can be computed as the products of physical transport and corresponding constituent concentrations (Hagy 1996). Physical exchange between the tidal fresh river and the upper estuary is dominated by seaward advection, but also includes a diffusive exchange flux. Thus, the net flux from the river to the upper estuary can be computed as

$$Q_r c_0 - E_{1,0}(c_1 - c_0)$$

where Q_r is the freshwater input from the tidal fresh river to the upper estuary, $E_{1,0}$ is the diffusive exchange between the upper estuary and the tidal fresh river, and c_0 and c_1 are the concentrations of N or P in the tidal fresh river and upper estuary, respectively. An identical advection and diffusion equation was applied to exchange between the upper estuary and lower estuary (Hagy et al. 2000). Two-layer gravitational circulation dominates the net horizontal transport within the lower estuary and between the lower estuary and Chesapeake Bay (Hagy et al. 2000). Therefore, the net exchange between Patuxent River and Chesapeake Bay was computed as the difference between the landward and seaward advective transport. This is

$$Q_6 c_6 - Q'_{cb} c'_{cb}$$

where Q_6 and Q'_{cb} are the rates of advection in the surface layer from the lower Patuxent River into Chesapeake Bay and in the bottom layer from Chesapeake Bay into the river. The values c_6 and c'_{cb} are the concentrations of N and P associated with advecting water.

The box model and resulting N and P fluxes were computed by month for the composite average years within the pre-BNR (1985-1990) and post-BNR (1993-1999) periods. Seasonal and annual average transport was computed from the monthly means.

Internal Storages of N and P

There were four categories of internal N and P storages evaluated in this budget** and these included water column (dissolved and particulate), surficial sediments (particulate in the surface 1 cm of sediments), macrobenthic infauna and zooplankton. In each case estimates were made for the upper and lower estuary. Seasonal estimates were also made for all categories except surficial sediments where there were not enough measurements to justify such an estimate. In addition, seasonal estimates were further categorized into pre and post-BNR periods for water column nutrient and zooplankton stocks; limited data precluded making such estimates for sediment and macroinfaunal N and P storages.

Water column nutrients: Data were obtained from the **Chesapeake Bay Water Quality Monitoring Program (2001)** and consisted of vertical profiles of dissolved and particulate N and P compounds (NO_3 , NO_2 , NH_4 , DON, PN, PO_4 , DOP, PP) collected 16-20 times per year from 1985–2000 at 13 locations along

the main axis of the estuary. Average volume-weighted concentrations for the upper and lower estuary were obtained using an interpolation algorithm developed by Hagy (1996). All subsequent seasonal and pre and post-BNR averaging was completed using the volume-weighted values.

Sediments: Storage of particulate N and particulate P in the surface 1 cm of sediments was based on samples collected using a box corer (Boynton and Rohland 2001) and from sources listed in Boynton et al (1995). Values of %N and %P from the upper and lower estuary were converted to mass per area using measured sediment dry weight per volume values.

Mesozooplankton: The N and P storage associated with mesozooplankton biomass was estimated using data collected by the **Chesapeake Bay Zooplankton Monitoring Program (2001)**. Samples were collected via stepped oblique tows using 202 μ m mesh paired bongo nets. Samples were mainly collected monthly between 1985 and 1999 at a site in the tidal fresh portion of the upper estuary and at a site in the middle of the mesohaline estuary. Numerical abundances were converted to biomass using conversion factors provided in **Chesapeake Bay Zooplankton Monitoring Program (2001)** and Jorgensen et al (1991). Conversion of dry weight biomass to N and P were based on conversion factors given in Walve and Larsson (1999).

Macrofauna: The N and P storage associated with macrobenthic biomass was estimated using data collected by the **Chesapeake Bay Benthic Monitoring Program (2001)**. Samples were collected at sites spaced throughout the estuary. Several sampling devices were used depending on water depth and bottom substrate but all samples were sieved through 0.5 mm screening and preserved in buffered formalin. Mean biomass (ash-free dry weight; AFDW) was computed by month and seasonal averages computed from the monthly means. Because there was a great deal less benthic sampling during the post-BNR period we did not compute pre and post-BNR means. Thus, seasonal and annual means include the period 1985-1999. We assumed that ash-free dry weight was 50% carbon. Percent N and P of AFDW were estimated to be 15% and 0.62%, respectively.

Water Column Uptake, Zooplankton Excretion and Sediment Recycling of N and P

There were three categories of N and P uptake and recycling evaluated in this budget and these included water column uptake of N and P by phytoplankton, net sediment releases of N and P and mesozooplankton excretion of N and P. In each case seasonal and annual (pre and post-BNR) estimates were made for the upper and lower estuary.

Mesozooplankton: Abundances were obtained from the **Chesapeake Bay Zooplankton Monitoring Program (2001)** for 1984-1999 from sampling stations located in tidal fresh and mesohaline portions of the estuary.

The sampling strategy changed during the course of the monitoring program from stratified tows to a single oblique tow. It was determined that

there were no clear differences in the abundance patterns based on sampling procedures. Zooplankton abundances were enumerated to species and were separated by life stage for some of the taxa. When life stages were present, average abundances were computed by life stage to account for differences in the sizes of the different life stages.

Nitrogen (NH_3) excretion rates were computed using the following equation (Mauchline 1998):

$$\log E = (-0.00941T + 0.8338)\log W + (0.02836T - 1.3665) \quad (1)$$

where E =excretion rate ($\mu\text{g NH}_3\text{-N copepod}^{-1} \text{ hr}^{-1}$), W =mg dry weight copepod⁻¹, and T =water temperature ($^{\circ}\text{C}$). Dry weights were obtained from literature sources (Heinle 1966; Jorgensen et al 1991; Chesapeake Bay Zooplankton Monitoring Program 2001). Monthly average water temperature for each station was computed from the Chesapeake Bay Water Quality Monitoring Program (2001).

Monthly mean abundances and NH_3 excretion rates were computed for the pre-BNR (1984-1990) and post-BNR years (1993-1999). In the post-BNR years, zooplankton abundance was not estimated for January and February. Therefore, for the purposes of computing seasonal and annual means, the January and February data for the pre-BNR years were used in the post-BNR years. Excretion rates per unit volume per hour were converted to areal rates using a mean depth of 2 m for the upper estuary and 5 m for the lower estuary and 24 hr day^{-1} .

Sediment Recycling: Data used to estimate N and P releases from sub-tidal estuarine sediments were obtained from Boynton and Rohland (2001) and from earlier work reported by Boynton et al (1982a). Most measurements of sediment nutrient fluxes were obtained from shipboard incubation of intact sediment cores; some values from the upper estuary were based on in-situ chamber measurements (Boynton et al 1982a). Sediment flux data were averaged by month and then used to estimate annual average fluxes for the upper and lower estuary. Data from December – March were limited for the upper estuary and not available for the lower estuary. Lower estuary sediment fluxes for N and P for those months were estimated to be zero. Because only summer data (June – September) had been routinely collected (1985-2000), only summer season pre and post-BNR values were computed for the upper and lower estuary.

Phytoplankton uptake: Nutrient uptake by phytoplankton was based on measured rates of primary production and Redfield stoichiometry. Primary production data were obtained from the Chesapeake Bay Phytoplankton Monitoring Program (2001). Rates were estimated using the C-14 technique with incubation (4 hr) in shipboard constant light incubators. Volumetric rates were converted to areal rates by assuming that the single measured volumetric rate was P_{max} and that production decreased in a linear fashion to the depth of

1% light. The euphotic depth was based on secchi disk measurements. Extrapolation of hourly rates to daily rates was accomplished by multiplying hourly rates by 80% of the daylight hours at the time of measurement. Finally, N and P uptake were estimated by assuming Redfield proportions of 106:16:1 for C:N:P. Measurements at these sites were routinely made 10-16 times per year from 1986 – 1999. Upper and lower estuary N and P uptake rates were computed for seasonal and annual periods during both the pre and post-BNR periods.

Internal Losses of N and P

The data sources for internal losses of N and P consisted of a combination of new data collected in the Patuxent and other literature sources. Specifically, we depended on measurements of marsh nutrient burial from the work of Merrill (1999), Merrill and Cornwell (2000) and Greene (2005a). Marsh denitrification measurements were from Merrill (1999) and Greene (2005a). Subtidal N and P burial rates were estimated from new measurements of ^{210}Pb -based sedimentation rates from cores collected in 2000, and estuarine denitrification rates were from measurements also made in 2000.

Denitrification in Estuarine and Marsh Sediments: Subtidal denitrification was determined from flux cores using time courses of N_2 changes based on N_2 :Ar ratio changes (Kana et al. 1994; Owens et al. submitted). At 6 sites in May and December of 2000, we examined fluxes in duplicate cores fitted with magnetic stirrers. Flux cores (7 cm inside diameter) were incubated at *in situ* temperatures for ~6 hours; samples were collected for dissolved gases using 7 mL ground glass tubes with Hg used as a preservative. Samples were analyzed using a membrane inlet mass spectrometer, with O_2 and N_2 ratios to Ar measured (i.e. Kana and Weiss 2004). The slope of the N_2 concentration versus time, minus that of control cores without sediments, was used to estimate denitrification rates. In the case of tidal freshwater marsh sediments, similar cores (10 cm inside diameter) were collected, flooded with ambient river water, and denitrification measured as with subtidal cores (Merrill 1999; Merrill and Cornwell 2000; Greene 2005a).

Burial in Estuarine and Marsh Sediments: Subtidal cores were collected using a Benthos gravity corer, extruded into 2 cm segments to 10 cm depth, 5 cm segments from 10-30 cm depth, and 10 cm segments to the bottom of the core (75-110 cm). The analysis of ^{210}Pb , total P and total N followed that of Cornwell et al. (1996). Sedimentation rates were calculated via regression of cumulative mass versus excess ^{210}Pb . Marsh cores were collected using a MacAuley or Russian peat corer to minimize compaction and nutrient burial calculations were similar to those of the subtidal cores (Merrill 1999). A total of 29 marsh cores were collected throughout the marsh ecosystem, including several transects from the marsh bank to the upland area. We grouped the nutrient burial rates on the basis of the vegetation community (Merrill and Cornwell 2000; Greene 2005a).

Results and Discussion

Nutrient Inputs

Inter-Annual Variability

We begin by examining TN, TP and DIN and DIP loads from all sources to this estuarine system on an annual time scale for a 13 year period (1985-1997). TN and DIN loading rates ranged from 4300 to 8600 kg N d⁻¹ and 3200 to 5500 kg N d⁻¹, respectively, and averaged 6200 and 4300 kg N d⁻¹ (Fig. 3). Annually averaged DIN loads were correlated with TN loads ($r^2=0.71$; $p<0.01$) and represented an average of 69 % of TN loads during the study period. TP and DIP loading rates ranged from 207 to 690 kg P d⁻¹ and 113 to 414 kg P d⁻¹, respectively, and averaged 453 and 242 kg P d⁻¹ during the same period (Fig. 3). DIP loads also closely tracked TP loads ($r^2=0.92$; $p<0.01$) and represented an average of 53 % of TP loads. Inter-annual range in loads, both total and inorganic, was about a factor of two for N and 3.5 for P. Similar levels of variability have been observed in other large basins of the Chesapeake Bay (USGS 2004). Such levels of inter-annual variability exceed the annual load reductions (~40%) that local, state and federal agencies are trying to achieve in this estuary.

Relationships to Regional Climate Conditions

A portion of the variability in nutrient loading rates was associated with variability in local weather conditions (Fig 4). Annual average river flow at the head of tide (HoT) ranged from 5.5 to 17.5 m³ s⁻¹ and averaged 10.3 m³ s⁻¹ during the 25 year period flow has been gauged at this site (1978-2003). On a seasonally averaged basis, river flows were generally highest during the winter and/or spring and considerably lower during summer and/or fall. However, during two drought years (1992 and 1995) river flow was low all year while during 1996 flow remained relatively high all year. During 1989 flow was lowest during the winter and highest during spring and summer, almost a complete reversal of the most common pattern.

Typically, N concentrations at HoT were highest during winter and spring (100-200 µM) coinciding with periods of highest flow and generally lower in summer and fall (25-75 µM). Thus, loads tend to be higher in wet years, especially when river flows are highest in winter or spring. Hagy et al (1998) reconstructed upper Patuxent River TN and TP loading rates at HoT for the period 1960-1997 and found a strong relationship between river flow and loads with the slope of the TN and TP relationships to flow being 180 kg N d⁻¹/m³ s⁻¹ and 65 kg P d⁻¹/m³ s⁻¹, respectively. TN and TP loads for the entire basin exhibited the same general relationship although there was more scatter. Higher and lower loads were clearly associated with wetter and drier years, respectively.

Later in this analysis the impact of instituting biological nitrogen removal (BNR) during warm portions of the year at all major sewage treatment plants in the basin is examined. Upgrading plants to BNR was initiated in the early 1990's and was completed by 1993. In subsequent analyses the years 1985-1990 and 1993-1997 were considered to be from the pre and post-BNR periods, respectively. Four of the six pre-BNR years were relatively dry (average river flow = 8.8 m³ s⁻¹) while during the post-BNR period wetter conditions prevailed for four of the five years (average river flow = 13.0 m³ s⁻¹; Fig. 4).

To place the effect of inter-annual climate variability in perspective, loading rates of TN, TP, DIN, and DIP from all external sources were summed for each year and the

years with the highest and lowest loading rates identified (Table 2). Results indicate both the importance of local climate variability and the impact of management actions on nutrient loading rates. Specifically, the lowest loads for all nutrient groups occurred during 1991, a dry year. Highest loads for all nutrient groups, except DIP, occurred during wet years (1989, 1993, and 1996). Highest DIP loads occurred during 1985, a relatively dry year, but this was the last year in this record before P was effectively removed from major sewage discharges throughout the basin. Thus, for this compound, management actions at sewage treatment plants were evident at the scale of whole estuary DIP inputs. However, the highest and lowest loading years for TN occurred after and before implementation of BNR, respectively, clearly indicating the importance of sources other than point sources in the TN budget at the scale of the whole estuary. Additionally, lowest TN and DIN loads were observed during 1991, prior to implementation of BNR. However, there was a clear reduction in both P and N loads from the upper basin (above HoT), where 9 of the 10 major sewerage treatment plants are located, after implementation of P and then N removal from discharges. Thus, at a sub-basin scale, load reductions in both nutrient groups were evident.

Loading Rates Relative to Other Estuarine Systems

In an earlier nutrient budget analysis **Boynton et al (1995)** assembled nutrient input data (TN and TP) for 18 estuarine sites. That effort was expanded and input data for 34 sites are shown in **Figure 5**. Annual loading rates ranged from 1.1 to 188 g N m⁻² yr⁻¹ and from 0.1 to 32 g P m⁻² yr⁻¹ or by factors of 170 and 320 for TN and TP, respectively. Of the 34 sites, 6 had TN loading rates in excess of 50 g N m⁻² yr⁻¹, 15 had loads less than 10 g N m⁻² yr⁻¹ and 13 locations had loads between these extremes. Loads of both TN and TP to the Patuxent River estuary were moderate compared to other sites. Inspection of the multi-year data for the Patuxent River estuary provides a clear indication that many of the points shown on the diagram might be better represented as clouds of points, if such data were available. Multi-year TN and TP input data for whole estuaries are not very common so there remains uncertainty about the magnitude of inter-annual scales variability, but variability may be large. For example, wet and dry year input data were available for the Guadaloupe estuary and TN and TP loads varied by factors of 3.7 and 2.5, respectively. Similar values for the Patuxent River estuary were 2.0 and 2.6 for TN and TP, respectively. TN and TP loads to Kaneohe Bay were adjusted downward by factors of 2.0 and 4.5, respectively, due to management actions related to sewage diversions.

The bold line in **Figure 5** represents the Redfield ratio expressed on a weight basis (N: P = 7.2:1). In this selection of sites, N: P ratios of inputs ranged from 2 to 38. About a quarter of these locations (9 of 34) had load ratios that were considerably lower (<5.0) than the Redfield ratio while 50% (18 of 34) had ratios equal to or higher than 9.0. **Boynton et al (1995)** suggested that point source dominated systems would favor lower load ratios because of the abundance of P relative to N in sewage and the opposite in diffuse sources. However, it is clear that this is not always the case. For example, Himmerfjargen had a very high load ratio (38) even though point sources were the dominant nutrient sources because P (and not N) was removed from treatment plant effluent. A similar situation was also present in the Back and Potomac River estuaries

where N: P ratios were elevated but point sources (with P removal) were a component of nutrient inputs.

It would be useful to be able to compare nutrient loading rates from different estuarine ecosystems and come to some conclusions regarding water quality and habitat conditions. In such a simple conceptual model, those systems with low inputs would have oligotrophic characteristics (e.g., seagrasses important, limited phytoplankton accumulations, absent or rare HABs, well-developed microphytobenthic and macroinfaunal communities) while those with the highest loads would have eutrophic characteristics (e.g., large phytoplankton biomass accumulations, HABs, hypoxia/anoxia, degraded benthic communities). To a limited extent this may be true. For example, those systems with very high nutrient loads (e.g., Tokyo Bay, Back River, W. Scheldt) have severe water quality problems while those with low loads (e.g., Maryland coastal bays, Buzzards Bay) have few symptoms of eutrophication. However, there are numerous exceptions and these indicate there are other important processes influencing trophic condition besides loading rate (Vollenweider 1976; Wulff et al. 1990). Loading rates to the Baltic Sea are relatively low (Larsson et al. 1985) but persistent stratification and very long water residence times produce large volumes of hypoxic/anoxic water. Conversely, TN loading rates to Mobile Bay and the Potomac River estuary are similar but only the Potomac has severe indications of eutrophication, possibly because of much greater depth, longer water residence time and seasonal stratification. However, the selection of estuaries presented here was based on availability of nutrient load data and is very diverse, including coastal waters, estuaries, fjords and lagoons. It might be argued that nutrient loads from more similar or localized groups of systems might be more prescriptive. Nedwell et al (2002) organized inorganic N and P loads to 93 estuaries of the United Kingdom and found several significant relationships between loads and biological responses in adjacent coastal waters. However, even in this relatively localized analysis there was substantial unresolved variability, again indicating influence of other factors.

Components of Nitrogen and Phosphorus Loads

Atmospheric Deposition

An annual time-series of total atmospheric nitrogen deposition was constructed for the years 1985-1999 (NADP 2001). In this time series TN was composed of wet deposition of NH_3 and NO_3 , dry deposition of HNO_3 and NO_3 , and net dry exchange of NH_3/NH_4 (Fig. 6). Atmospheric deposition ranged from about 575 to 1125 $\text{mg N m}^{-2} \text{ yr}^{-1}$ and was generally higher in wet years (e.g., 1989, 1994) than in dry years (e.g., 1985, 1987, 1992) but there were exceptions where dry or wet year deposition remained higher (e.g., 1987) or lower (e.g., 1998) than expected. Overall, TN inputs from atmospheric deposition varied by about a factor of two, in the same range as for TN loading from all sources. Monthly TN deposition rates ranged from about 30 to 120 $\text{mg N m}^{-2} \text{ month}^{-1}$ and were higher during late spring and summer than during fall and winter (Fig. 7). This pattern is significant because the generally much larger diffuse source inputs are at a minimum during summer and fall. In addition, much of the atmospheric N deposition going directly to the surface waters of the estuary is in a chemical form directly available to phytoplankton (Paerl 1997). The dominant form of N deposition was $\text{NH}_x + \text{NO}_3$ in

wet fall, comprising about 67% of the total followed by organic N (17%) and all measured forms of dry fall N (15%; **Table 3**).

Little information was available concerning atmospheric P deposition in this region, but indicated that loading rates were a small portion of total P inputs to the estuary on both seasonal and annual time scales.

As expected, direct N deposition to the surface waters of the estuary was largest in the lower estuary where estuarine surface area was also large and minor in the upper estuary. In the lower estuary annual loads of atmospheric deposition averaged about 360 kg N day⁻¹ and were larger in spring and summer than in fall and winter. As we will show later, direct atmospheric deposition during summer was a significant source of N to the lower estuary.

The full contribution of atmospheric deposition of N to the estuary is greatly underestimated when only direct deposition to the surface waters is considered. However, this approach has the advantage of being readily and more directly estimated from a variety of concentration measurements and rainfall. However, regional assessments of nitrogen additions and losses from landscapes have become more common and some have focused on estimating the portion of N losses from landscapes coming from atmospheric deposition of N (**Howarth et al. 1996; Jaworski et al. 1997**). In the case of the Chesapeake Bay basin **Fisher and Oppenheimer (1991)** and more recently **Castro et al (2003)** estimated about 25% and 22%, respectively, of atmospheric N deposition to the landscape makes it to estuarine waters. No estimate is available for the Patuxent basin. However, if the most recent estimate of 22% is applied to the Patuxent basin, about 990 kg N m⁻² day⁻¹ would reach estuarine waters as a component of diffuse source loading. This turns out to be a substantial portion of the total diffuse source load.

Point Sources

Point sources of N and P were substantially reduced due to sewage treatment plant modifications, with first P removal (1986) and then seasonal N removal (1993). Point source loads of TP declined from about 250 kg P day⁻¹ before upgrades to about 50 kg day⁻¹ following upgrades (**Fig. 8**). TN sewage loads prior to seasonal N removal varied between 1200 – 1900 kg day⁻¹ and were reduced to annual averages of about 700 kg day⁻¹. During the post-BNR period TN loads were higher during winter (~900 – 1000 kg N day⁻¹) than during summer periods (500 – 600 kg N day⁻¹; **Fig 8**).

During the pre-BNR period N and P loads did not vary appreciably during the year as might be expected for sewage treatment plant operations having relatively constant daily inputs and discharges (**Table 4**). However, during the post-BNR period TN and DIN loads exhibited considerable seasonal change with summer and fall loads about 30% lower than winter and spring loads due to the higher N-removal efficiencies at higher temperatures. There were very small variations in P loads among seasons of the year.

One strong distinguishing feature of point source N and P loads concerns the distribution between dissolved inorganic and total N and P. For sewage N, 92% and 82% of the load was DIN during the pre and post-BNR periods, respectively. The remaining N was mainly dissolved organic nitrogen. Sewage P was 78% and 80% DIP during the pre and post-BNR periods, respectively. While point source N and P were not the single

largest sources of N or P to the estuary, the fact that most was in chemical forms directly available to plant communities enhances the importance of this source.

Diffuse Sources

The substantial interannual variability in loading rates is largely the result of interannual changes in diffuse source inputs of N and P (Fig. 3). For example, annual TN loads from the middle basin ranged from 760 to 3469 kg N day⁻¹ and averaged 1716 and 2659 kg N day⁻¹ for the pre and post-BNR periods, respectively. For the same region, P loads ranged from 37 to 415 kg P day⁻¹ and averaged 114 and 284 kg P day⁻¹ during the pre and post-BNR periods, respectively (Fig. 9). In general, higher and lower loads were associated with wet and dry years, respectively, although there was substantial variability not accounted for by climate conditions alone. Presumably, the time of year when flows were high or low, intensity of rain events, large storm events and changing land uses and practices all played a role in determining annual loads. In any case, diffuse source loads of N were the largest single source both before and after BNR implementation; diffuse sources of P were slightly smaller than point sources before P removal at point sources was implemented after 1985.

The proportion of diffuse source loads as DIN varied from 44 to 85% of TN and averaged 67%, well less than for point sources. The same ratio for P from diffuse sources was about 60%, again much less than point source P.

There was a consistent seasonal pattern of diffuse source inputs, as might be expected based on river flows which were generally highest during winter-spring and lowest during summer-fall. For example, TN loads at HoT averaged about 2300 kg N day⁻¹ during winter-spring and about 1450 kg N day⁻¹ during summer-fall in the pre-BNR years. During the generally wetter post-BNR years these averages were 2700 kg N day⁻¹ and 1200 kg N day⁻¹, for winter-spring and summer-fall, respectively. Thus, there is a substantial difference in the seasonality of nutrient inputs from this important source compared to direct atmospheric deposition and point sources.

Septic Sources

At the basin level, N and P estimated to come from septic systems was small (< 5% of total N inputs to the middle basin and < 2% of total N loads to the lower basin) and has not changed much during the pre and post-BNR periods (Table 5). However, in a few heavily developed residential areas adjacent to tidal creeks, septic system N appeared to be an important local source (Barnes et al. 2004). Septic system P was assumed to be effectively bound to sub-surface soils and not contribute to diffuse source P loads.

Input Summary

Annual average inputs of TN and TP from all external sources were compiled for the pre and post-BNR periods (Fig. 10) and several important findings emerged. First, improved treatment of point source discharges had a substantial effect on both N and P loads entering the estuary from the upper and middle basin. For example, TN and TP loads from point sources located in the upper basin decreased from 1577 to 744 kg N day⁻¹ and from 124 to 57 kg P day⁻¹, respectively. Smaller reductions were also observed in the middle basin where point sources of TN and TP decreased from 744 to 454 kg N day⁻¹

¹ and from 60 to 50 kg P day⁻¹, respectively. Overall, point sources represented 37 % of TN and 46 % of TP inputs during the pre-BNR period and were reduced to 18 % of TN and 19 % of TP during the post-BNR period. Thus, due to the changes in sewage treatment plant operations, there were substantial changes in the relative importance of sources. Secondly, direct atmospheric deposition of N and P to the surface waters of the estuary were relatively small during the pre and post-BNR periods (TN~ 7%; TP~ 7-10%) as was TN derived from septic system drainage (~5%). The largest inputs of TN and TP were from diffuse sources during both the pre and post-BNR periods. TN and TP from diffuse sources represented 51% and 48% of total inputs during the pre-BNR period and 70% and 77% during the post-BNR period. The post-BNR period was wetter than the pre-BNR period and this is reflected in substantial increases in diffuse source loading during the latter period. In fact, total loading of TN and TP to the estuary was about 6% and 43% larger during the period following sewage treatment plant improvements, again emphasizing the importance of diffuse sources in this system.

Major Storages of N and P

Four N and P storages in the estuary were evaluated, including water column dissolved and particulate nutrient stocks, macrobenthic invertebrate and macrozooplankton biomass and surficial sediment stocks (Table 6). Detailed seasonal and spatial distributions of N and P concentrations in the water column have been described for this estuary elsewhere (Mihursky and Boynton 1978; Kemp and Boynton 1984). In brief, TN concentrations were higher in both the upper and lower estuary during winter-spring than summer-fall and were 20-30% higher in the upper than lower estuary during all seasons (Table 7). On an annual basis, about 50% of the TN in the water column was DIN, mostly nitrate, in the upper estuary while about 26% of TN was DIN, again mostly nitrate, in the lower estuary. There was a decrease in TN concentration in the upper estuary of about 30% between the pre and post-BNR periods and a much smaller decrease in TN concentration in the lower estuary (~7%). At the scale of the full estuary the average annual total mass of TN in the water column was about 580 and 520 x 10³ kg N during the pre and post-BNR periods, respectively. There were also clear spatial and seasonal differences in P concentrations in the estuary. TP concentrations tended to be higher during summer-fall than during winter-spring and only about 20% higher in the upper estuary compared to the lower estuary. In addition, dissolved inorganic P (DIP) was a smaller fraction of TP than was the case for the ratio TN:DIN, comprising about 20% and 30% of TP in the upper and lower estuary, respectively. At the scale of the full estuary the total mass of TP in the water column was about 48 and 36 x 10³ kg P during the pre and post-BNR periods, respectively, a decrease of about 25% following implementation of BNR technology (Table 6).

Monthly estimates of benthic invertebrate biomass ranged from 4 to 19 gAFDW m⁻² in the upper estuary and from about 1 to 10 gAFDW m⁻² in the lower estuary and averaged 12.5 and 4.2 gAFDW m⁻², respectively (Table 8). In both the upper and lower estuary biomass was highest during spring and lowest during fall and winter seasons. When these annual average biomass estimates were converted to N and P equivalents, there were 119 x 10³ kg N and 5 x 10³ kg P in the system associated with benthic animal biomass. This represented only about 4.4% and 0.7% of the N and P in the system (Table 6).

While clearly an important part of pelagic estuarine food webs, macrozooplankton contained a very small fraction of the N and P in the system. Average annual N and P in macrozooplankton stocks amounted to 4.9×10^3 kg N and 0.83×10^3 kg P or about 0.2 and 0.1% of the total N and P, respectively (Table 6).

Most of the N and even more of the P in this system were contained in the sediments (Table 9). We have somewhat arbitrarily used only the upper 2 cm of the sediment column in this analysis but we did this to include only the relatively recently deposited N and P. If a deeper sediment column were used, an even higher percentage of N and P would be associated with sediments. Average surface sediment N content averaged 0.35 and 0.31% of sediment dry weight in the upper and lower estuary, respectively, and sediment P content averaged 0.125 to 0.093 % in the same areas. About 75% of TN and about 93% of TP in the system were in sediments (Table 6). We did not have a time series of sediment composition data sufficient to consider either seasonal or pre and post-BNR changes these features.

One simple way of relating nutrient stocks to nutrient dynamics of the whole system is to compute turnover times for N and P stocks. If all nutrient storages are combined (Table 6) and divided by average annual inputs (Fig. 3), turnover times of about 1.2 and 4.2 years result for TN and TP, respectively. Thus, if we have considered storages correctly, especially the very large sediment storage, it appears that there is not a huge reservoir of nutrients in the system compared to new inputs of N and P. If we delete sediment storage of TN and TP from turnover computations, seasonal-scale turnover times result (0.3 years for both TN and TP). This observation is consistent with other nutrient-related measurements such as primary production rates, algal biomass accumulation, volumes of hypoxic/anoxic water and sediment-water nutrient and oxygen exchanges, all of which respond on seasonal or even shorter time scales to changes in nutrient delivery rates (Boynton and Kemp 2000; Hagy et al. 2004; Kemp et al. 2005; Fisher et al. 2005). Thus, it also seems reasonable to expect rapid responses of such processes as those indicated above to either increases or decreases in nutrient loading rates associated with continued development of the drainage basin and effective management actions, respectively.

One striking aspect of this evaluation of nutrient stocks is that most of the N and P in this moderately eutrophic estuary is contained in sediments and is detrital organic matter in the case of N and particulate inorganic material in the case of P. A very small fraction is in living biota. It seems likely that the fraction contained in living biota was once much higher for several reasons. First, it appears that benthic infaunal biomass has been substantially reduced from earlier levels. D'Elia et al. (2003) make reference to the substantial commercial fishery, especially for oysters and crabs, which once flourished in this estuary and is now largely absent. Compared to benthic biomass estimates assembled by Herman et al. (1999), Patuxent values were 2 to 3 times lower than those observed at similar levels of primary production in other estuarine systems. Second, Stankelis et al. (2003) assembled available data concerning seagrass communities in the Patuxent at present and as far back in time as the late 1930's. It is clear that seagrasses were a large feature of the Patuxent and represented a substantial storage of nutrients in living tissue. Old records from the Academy of Natural Sciences of Philadelphia (1965-1975) also indicated that epiphytic and benthic diatoms were a significant feature of the Patuxent but these autotrophs have largely been lost in recent decades. The status

of fish stocks, both commercial and forage, are far less clear although long-term residents uniformly insist that fish were far more abundant prior to the 1970's. These observations suggest that the partitioning of N favored living as opposed to detrital storages prior to the estuary becoming eutrophic. If any of this is true, it would seem like these longer-lived N storages would represent a nutrient buffer, restricting nutrient recycling to rates below those associated with very rapid bacterial remineralization of labile substrates commonly observed under present conditions.

Nutrient Transport

Box models (Hagy et al. 2000) were constructed to compute monthly average physical transport of nitrate plus nitrite, ammonium, TN, DIP and TP for the pre and post-BNR periods. Nutrient transport was evaluated at two locations in the estuary. The first was at a location between the narrow, shallow, turbid and vertically well-mixed upper estuary where it joins the wider, deeper, clearer and seasonally stratified mesohaline portion of the system (Fig.11). About 90% of the tidal marshes of the Patuxent are located upstream of this location. The second site was at the junction of the Patuxent estuary with Chesapeake Bay. These locations were chosen, in the first case, to obtain closure of the budget at a location between very different portions of the estuary and, in the second case, to have an export/import estimate for the whole estuarine system.

Transport from Upper to Lower Estuary

During both the pre and post-BNR periods there were very strong seasonal patterns in DIN and TN transport between the upper and lower estuary (Fig. 11a). Transport was highest during winter and early spring, intermediate during fall and early winter and lowest during summer, generally following seasonal patterns in river flow and ambient nutrient concentrations. It is interesting, and discouraging from a management viewpoint, to note that both TN and DIN transport estimates were higher during the post-BNR winter seasons than during pre-BNR winters. This likely reflected the fact that the post-BNR period included several years characterized by particularly high river flow (1993, 94, 96, 98) and only two low flow years (1995 and 1999). In contrast, flow was below average during much of the pre-BNR period. Moreover, BNR does not routinely reduce N loading from sewage treatment plants during cold seasons. During summer, when BNR was active and river flow differences were less dramatic, reductions in N loading to the lower estuary were substantial. Seasonal average DIN loading for summer and fall decreased by 46% and 50%, respectively. Decreases in TN loading were smaller, but still substantial at 33% during summer and 21% during fall. However, annual mean DIN and TN loading to the lower estuary decreased by only 6% and 7%, respectively, following adoption of seasonal BNR technology.

There were also clear seasonal patterns evident for P transport between the upper and lower estuary. Again, rates were highest during winter and spring and lowest during summer and fall. For the most part, pre-BNR rates were lower than post-BNR rates, again probably because of higher river flows and more diffuse source inputs from the landscape during the wetter post-BNR period. There were almost no differences in annual average DIP and TP inputs to the lower estuary between the pre and post-BNR periods.

Exchange at the Seaward Margin

Nutrient exchange at the seaward margin of the estuary was more variable than transport between the upper and lower estuary (Fig. 11b). This reflects the fact that the net direction of this transport depends only on the difference in N concentration in the seaward (outward) flowing surface water and the landward (inward) flowing bottom water. The net N or P transport results from a relatively small vertical concentration gradient, which can easily change.

On an annual average basis, DIN was imported from the Bay to the Patuxent during both pre- and post-BNR periods, while TN was always exported to the Bay. Inflow of DIN was greater in the post-BNR period by 582 kg d^{-1} , increasing from an annual average of 136 to 718 kg d^{-1} . This increase was about half the size of the decrease in DIN input (1074 kg d^{-1}) from landside point sources due to BNR implementation, leading to a smaller than expected reduction in overall DIN input to the lower Patuxent estuary. TN export from the estuary during the pre-BNR and post-BNR period averaged 1250 and 869 kg d^{-1} , respectively, and contrasted sharply with DIN exchanges. TN was consistently exported during the pre-BNR period and exports were largest during spring and fall. During the post-BNR period TN was exported as well but at a lower rate (870 kg N d^{-1}) and there were periods during spring and fall when TN was imported into the estuary. Both TP and DIP were exported from the estuary during almost all months of the year. Annual DIP export averaged 105 and 40 kg P d^{-1} during the pre-BNR and post-BNR periods, respectively. During both periods, exports were highest during late summer and fall. TP exports averaged about 125 kg P d^{-1} during both pre-BNR and post-BNR periods. However, seasonal patterns were quite different. Exchanges were variable during the pre-BNR period and monotonic, with a summer maximum, during the post-BNR period.

There are currently three estimates available of nutrient exchanges at the mouth of the Patuxent River estuary (Table 10). The first was generated by subtraction of internal losses of TN and TP from all terrestrial plus direct atmospheric inputs of N and P, the second was computed from a coupled hydrodynamic/water quality model and the third was based on the box model computations described above. Estimates of TN export were remarkably similar, ranged from 0.21 to $0.45 \text{ kg N} \times 10^6 \text{ y}^{-1}$, and all were directed from the estuary to the Bay. The range in estimates of TP exchange was larger (-0.06 to $0.05 \text{ kg P} \times 10^6 \text{ y}^{-1}$) and one estimate indicated a small import of TP from the Bay to the estuary. On the one hand it is comforting to largely see convergence of these estimates indicating export from the estuary to the Bay but it remains difficult to judge the accuracy of these estimates. Several of these estimates were made using data from the same years but the two estimates based on box model computations were made using data averaged for multiple years. Nixon et al (1986a) indicated that making estimates of net nutrient exchange at the mouths of estuaries is extremely difficult largely because of large bi-directional water flows and small and variable nutrient concentration gradients associated with these water flows.

Ecosystem Level Export Comparisons

The current estimates of nutrient export from the estuary can be compared to total nutrient inputs from all external sources and from this some understanding of nutrient retention versus export characteristics of the estuary can be developed. Using export

estimates based on box model computations, about 20% and 13% of TN was exported to the Bay during pre and post-BNR periods, respectively. In the case of TP about 34% and 23% of total inputs were exported to the Bay. For both nutrients, export was not a major pathway of loss, especially not for N. To provide some perspective we can compare these levels of export to those summarized by Nixon et al (1996) for a selection of estuaries and lakes. They reported a strong inverse relationship between percent of nutrient inputs exported and the log mean of estuarine water residence time. This strong relationship suggests that if estuarine communities have time to process nutrients, they will, in effect reducing the nutrients exported as a function of the time available for nutrient uptake, sinking to sediments, burial or denitrification. Thus it appears estuaries can act as either "pipes" where transport rather than transformation/loss is the dominant process or as "sinks", largely as a function of how long water remains in the system. However, the Patuxent appears to remove substantially more nutrients than expected, based on water residence times. Some of this difference may simply be the result of accumulated errors in developing these budgets. However, it is interesting to note that the Patuxent is a "sediment-rich" and eutrophic system; there are both abundant particulate nutrients and sediments to facilitate burial. Of the estuaries examined by Nixon et al (1996) only the Chesapeake systems had substantial burial losses, probably because of these features and moderately long water residence times. In addition, the Patuxent also has substantial areas of tidal marshes in the upper estuary and these marshes have been found to sequester both N and P (Merrill 1999; Greene 2005a). Thus, it's possible that some estuarine features, such as tidal marshes or extensive seagrass communities, may further modify nutrient export characteristics (Valiela et al 2001).

Magnitude of Nutrient Recycling and Nutrient Demand

Recycling rates for N and P were organized for several time periods, seasons and location within the estuary to allow for comparisons between the magnitudes of new versus recycled nutrient inputs to this estuary and phytoplanktonic nutrient demand (Dugdale and Goering 1967). Recycling rates of N and P associated with sediments and macrozooplankton are summarized in Tables 11 and 12, respectively, and estimates of phytoplanktonic nutrient demand are provided in Table 13. Unfortunately, no direct estimates water column nutrient recycling associated with microzooplankton and bacterial communities were available.

Annual average rates of N and P releases from sediments were substantial, being about twice as large as modal rates summarized for 48 other estuarine systems by Bailey (2005). This result was not surprising given the eutrophic condition of this estuary (Fig. 5). Sediment releases of N and P were best documented for warm periods of the year. However, it still appears that there was strong seasonality in flux magnitude with highest values observed during summer and lowest values during winter. Fluxes of both N and P were higher (23-45%) in the upper than lower estuary and this may be related to the supply rate of labile organic matter from the water column to sediments which is probably higher in the upper estuary, especially during summer (Cowan and Boynton 1996; Hagy 1996). Ammonium and phosphate fluxes were also consistently higher during the post-BNR period, although differences were not large (< 30%).

Excretion rates of N by macrozooplankton were based on size/temperature relationships developed by **Mauchline (1998)**. Dominant zooplankton included the copepods *Acartia* spp., *Eurytemora* spp., and *Bosmina* spp.; *Bosmina* was only found in the upper estuary and was extremely abundant during the post-BNR period. As a result of enhanced *Bosmina* abundances N excretion rates in the upper estuary were 2 to 12 times higher during the post-BNR period than during earlier years or during any time period in the lower estuary (**Table 12**). In most cases N recycling by zooplankton was highest during either spring or summer and much lower during fall and winter. We were not able to find a suitable size/temperature relationship to estimate P excretion by zooplankton.

Phytoplankton primary production rates ranged from 191 to 582 g C m⁻² yr⁻¹ during the pre-BNR period and from 172 to 458 g C m⁻² yr⁻¹ during the post-BNR period (**Table 13**). Rates estimated for the mesohaline region were high relative to measurements available for many other estuarine systems (**Boynton and Kemp 2005**). Rates were highest in the mesohaline region, intermediate in the tidal freshwater region and lowest in the oligohaline areas. It is probable that the extreme turbidity (secchi disk depth ~0.3-0.5 m) associated with the oligohaline region acts to limit primary production rates (**Hagy 1996**). During both pre and post-BNR periods and in all salinity zones, rates were highest during summer, lowest during winter and intermediate during spring and fall.

The purpose of developing estimates of nutrient recycle and phytoplankton productivity was to extrapolate these values to the scale of the whole estuary and compare the relative importance of new nutrient inputs to recycled nutrients and to phytoplankton nutrient demand (**Table 14**). Inputs of new DIN were highest during winter associated with higher river flows and lowest during summer; these seasonal differences were much larger for the lower than upper estuary. In addition, new inputs of DIN and DIP were not substantially different during the pre and post-BNR periods.

Recycle of DIN in the upper estuary was smaller than new inputs, especially during winter, when new inputs were about 6 times larger than recycle rates. In contrast, DIP recycle rates were larger than new inputs, especially during summer, and were about twice new inputs on an annual basis. Except for the winter period, both DIN and DIP recycling rates were higher during the post-BNR period. While we do not have experimental evidence to explain these differences they are likely due to wetter conditions that prevailed during the post-BNR period (**Fig.4**). Wetter conditions lead to higher inputs of nutrients, larger phytoplankton crops, and, ultimately, more organic matter available for recycling from sediments (**Cowan and Boynton 1996**). Finally, estimated phytoplankton nutrient demand was similar to nutrient recycle rates and always much smaller than the combined rates of new inputs plus nutrients supplied via recycling. This result is not surprising since this zone of the estuary almost never shows any nutrient limitation but is often severely light limited (**Fisher et al 1999**).

In contrast, recycle of DIN in the lower, mesohaline estuary was larger than new inputs, except during winter. Summer recycling rates, largely from sediments, were about 7 times larger than new inputs of DIN. DIP recycle rates were also much larger than new inputs, even during winter. Both DIN and DIP recycling rates were higher during the post-BNR period and the reason is probably the same as suggested above. Finally, estimated phytoplankton nutrient demand in the mesohaline estuary was always

greater, or much greater, than nutrient recycle rates evaluated here and always exceeded the combined rates of new inputs plus nutrients supplied via the two recycling pathways evaluated. During the pre and post-BNR periods recycle plus new inputs of DIN and DIP supplied an average of 32% and 41% of phytoplankton demand, respectively.

There was a large discrepancy between phytoplankton nutrient demand in the mesohaline region and the supplies of nutrients from both external sources and the two recycle pathways evaluated. The most obvious missing source is nutrients recycled in the water column by bacteria and other microheterotrophs, a pathway we could not directly evaluate because such measurements have not been made in the Patuxent. However, we can make some crude estimates based on water column respiration measurements coupled with Redfield ratios of respired material. **Boynton et al (1982a) and Mikita (2002)** made a series of plankton community respiration measurements in the mesohaline estuary. Respiration rates in the lower estuary ranged from about $0.8 \text{ g C m}^{-2} \text{ day}^{-1}$ during winter to $2.0 \text{ g C m}^{-2} \text{ day}^{-1}$ during summer. Similar rates were reported by **Smith (2000)** for the mesohaline portion of Chesapeake Bay. If typical summer respiration rates are converted to nitrogen and phosphorus equivalents (assuming C:N:P ratio of 106:16:1) and extrapolated to the area of the estuary, this represents N and P recycle rates of about $42,000 \text{ kg N day}^{-1}$ and $5,700 \text{ kg P day}^{-1}$ in the lower estuary. These rates are large enough to satisfy estimated phytoplanktonic nutrient demand when coupled with smaller, but still significant, sediment nutrient releases.

Several interesting points emerge from these whole-estuary computations. First, new inputs of N and P during any season do not approach phytoplanktonic nutrient demand in the lower estuary. Even during winter, when inputs of new N and P are highest and demand lowest, about 25% of demand is supplied by new nutrients. During summer, and on an annual average basis, sediments supply more recycled N and P than is derived from new inputs of these compounds but the sediment source is still much smaller than estimated plankton demand. **Kemp et al (1992)** were able to put sediment and water column respiration (a proxy here for nutrient regeneration) in perspective by examining the percentage of community respiration (water column plus sediments) attributable to sediments as a function of water column depth using data from about a dozen estuaries. They found a sharp decline in the relative importance of sediment processes with increasing depth. Using their relationship, and 6m average depth of the Patuxent, sediments would constitute about 30% of total community respiration, similar to the percentage of N and P recycled by sediments found in this evaluation (**Table 14**). It appears that even in relatively shallow estuaries, such as the Patuxent, water column nutrient recycling dominates N and P recycling.

Internal Nutrient Losses

Internal nutrient losses included denitrification and burial of particulate N and P in sub-tidal and tidal marsh habitats. Nutrient losses due to commercial and recreational fisheries extraction were not considered here because they were found to be small in an earlier analysis (**Boynton et al. 1995**) and no new information was available to substantially revise these estimates.

Denitrification rates for sub-tidal areas were based on measurements reported by **Jenkins and Kemp (1984)**, **Twilley and Kemp (1987)** and measurements made during this study (**Greene 2005a; Cornwell, unpublished data**). Lower estuary rates ranged

from about 6 to 50 $\mu\text{Moles N m}^{-2} \text{hr}^{-1}$ during spring and from 0.0 to 102 $\mu\text{Moles N m}^{-2} \text{hr}^{-1}$ during late fall. Summer rates in the lower estuary were non-detectable, probably because of low oxygen conditions and resultant lack of sediment nitrification activity (Kemp et al. 1990; Rysgaard et al 1994). A similar seasonal pattern of denitrification was evident in the upper estuary. Annual average rates for the upper and lower estuary were about 38 and 32 $\mu\text{Moles N m}^{-2} \text{hr}^{-1}$, respectively (Table 15).

Rates of denitrification for tidal marsh areas were based on a limited number of measurements made by Merrill (1999) and a considerably larger number of more recent measurements made in low, mid and high marsh locations by Greene (2005a). Rates ranged from non-detectable during late winter to over 500 $\mu\text{Moles N m}^{-2} \text{hr}^{-1}$ in the high marsh during spring. There was a clear decrease in denitrification rates from the high to the low marsh and a general decrease in rates from early spring through fall. Annual average rates were computed using both temporal and spatial weightings related to season and marsh type (e.g., extent of high, mid or low marsh areas) and found to be about 111 $\mu\text{Moles N m}^{-2} \text{hr}^{-1}$ (Table 15). Most of the tidal marshes of the Patuxent are located in the upper estuary (~80 %) where all tidal marsh denitrification measurements were collected. However, small tidal marshes are associated with most of the tributary creeks flowing into the lower estuary and we used a slightly smaller denitrification rates for these marshes as suggested by the lower rates associated with mid and low marshes characterizing these smaller marshes. When these rates were extrapolated to include all sub-tidal and marsh areas, denitrification removed about $0.91 \times 10^6 \text{ kg N yr}^{-1}$ from the system; sub-tidal sediments removed about 60 % and tidal marshes the remaining 40%.

Estimates for sediment deposition rates in sub-tidal areas were based on Pb^{210} measurements made by Cornwell (unpublished data) and similar measurements from Merrill (1999) and Greene (2005a) for tidal marshes. Largest deposition rates were found for the sub-tidal upper estuary ($2722 \text{ g dry sediment m}^{-2} \text{yr}^{-1}$) and smallest rates for the lower estuary ($1143 \text{ g dry sediment m}^{-2} \text{yr}^{-1}$; Table 16). Rates were variable in the tidal marshes but yielded estimates of about $2140 \text{ g dry sediment m}^{-2} \text{yr}^{-1}$ when deposition rates for low, mid and high marsh were spatially weighted. We assumed these rates were also characteristic of the small marshes in the lower estuary. Sediment PN and PP concentrations in sub-tidal areas (at sediment depths of 10-15 cm) were higher in the upper than lower estuary, especially for PP. Marsh values for PP were similar to those observed in sub-tidal areas of the upper estuary. In contrast, sediment PN values in tidal marsh sediments were about twice those in the sub-tidal areas (Table 16). Areal estimates of PN burial ranged from 2.9 to $12.6 \text{ g N m}^{-2} \text{yr}^{-1}$; burial rates were greater in the upper than lower estuary. Burial rates of PP ranged from 0.6 to $3.4 \text{ g P m}^{-2} \text{yr}^{-1}$ and were much higher in the upper than lower estuary.

When these rates of PN and PP burial were extrapolated to include all sub-tidal and marsh areas, long-term burial removed about $0.89 \times 10^6 \text{ kg N yr}^{-1}$ and $0.21 \times 10^6 \text{ kg P yr}^{-1}$ from the system; about 41 % and 59 % of PN was buried in marshes and sub-tidal sediment, respectively. About 30% of PP burial occurred in tidal marshes and the rest in sub-tidal sediments.

While we benefited from having many more observations of these processes than were available for earlier nutrient budget analyses there are certainly errors associated with these estimates of whole system denitrification and burial. Until far more measurements of both processes are made, not a likely event in the near future, rigorous

estimates of error are not possible. However, we can compare our estimates to those made in other estuarine and tidal marsh ecosystems and thereby obtain a qualitative sense as to whether our estimates are within the range of others made in similar environments. In a recent summary, **Greene (2005b)** assembled a large number of denitrification rate measurements from a variety of coastal habitats and found about 66% of measured rates were less than $100 \mu\text{Moles N m}^{-2} \text{ hr}^{-1}$ and median rates for coastal wetlands and estuaries were 71 and $31 \mu\text{Moles N m}^{-2} \text{ hr}^{-1}$, respectively. Rates used for marshes in our analysis were slightly higher than this median value and values for sub-tidal sediments were very close to the median value. Thus, our whole system values reflect rates that have been commonly observed; in fact, we would not have reached substantially different conclusions if we had based our analysis on median literature values.

A similar situation exists regarding burial rates. The data set has improved but there is ample room for further measurement and more formal error analysis. In lieu of this we have examined burial rates observed in other coastal systems (**Table 17**) and found rates for PN and PP burial to range from 6 to $25 \text{ g N m}^{-2} \text{ yr}^{-1}$ and from 0.1 to $2.6 \text{ g P m}^{-2} \text{ yr}^{-1}$, respectively. Again, burial rates used in this analysis were very comparable to those observed elsewhere. An additional step we took to help judge the adequacy of our measurements was to organize data concerning sediment sources. Essentially we asked, is there enough sediment entering the system to support the measured accretion rates. In the lower Patuxent estuary, like other mesohaline regions of Chesapeake Bay, a primary source of fine sediments is from shoreline erosion (**Yarbro et al. 1983; Hobbs et al. 1992**). In the case of the lower Patuxent, **Halka (personal communication)** estimated shoreline erosion yielded sufficient fine-grained sediments to support an average annual deposition rate of about $750 \text{ g (dry sediment) m}^{-2} \text{ yr}^{-1}$, close to the value estimated using ^{210}Pb technique in the mesohaline region of the estuary. In the upper estuary we combined multi-year (1984-1997) average inputs of sediments at the head of tide with the same multi-year estimates of sediment load from the land-use model and found that these sources provided enough sediment to support deposition rates of about $2900 \text{ g (dry sediment) m}^{-2} \text{ yr}^{-1}$ in the upper estuary. Again, this spatially averaged rate is very similar to those used in the upper estuary (**Table 16**). These considerations suggest that our estimates of deposition are not wrong by a large margin.

Unfortunately, we have no time-series of burial or denitrification rates to evaluate interannual variability and this is unfortunate because we had such information for nutrient inputs. It would be very instructive to see how responsive these important losses are relative to changes in inputs. It does seem intuitively clear that burial rates would be higher during wet than dry years and that this would lead to enhanced burial of particulate nutrients. For example, **Schubel and Zabawa (1977)** found very large deposition rates in the upper portion of Chesapeake Bay following tropical storm Agnes in 1972. **Khan and Brush (1994)** reported substantial variation in deposition rates in the upper Patuxent in response to decadal-scale changes in land uses and **Roberts and Pierce (1974)** found very large increases in sediment inputs in response to urbanization, particularly during wet years. Thus, it seems reasonable that climate variability (i.e., wet or dry years), large storms, and land use changes would lead to inter-annual variability in particulate nutrient burial, but quantification of this remains a challenge.

Similarly, we suspect inter-annual variability in denitrification rates to be substantial. It is well known that denitrification rates respond to changes in nitrate

concentrations at seasonal (e.g., **Rysgaard et al 1995**) and shorter time scales (**Greene 2005a**). In the Patuxent estuary, there were large differences in nitrate loads between wet and dry years (**Table 2**) and this would presumably enhance denitrification rates in wet years. Additionally, wet years produce larger phytoplankton communities and possibly more organic matter deposition to the bottom, as has been observed in Chesapeake Bay (**Boynton and Kemp 2000**). Thus, it seems likely that denitrification rates would be larger during wet than dry years. However, larger supplies of labile organic matter from phytoplankton production also contribute to hypoxic conditions in deep waters, particularly in wet years (**Fisher et al. 2005**), and this seriously impedes coupled nitrification-denitrification during summer periods (**Jenkins and Kemp 1984; Rysgaard et al (1994)**). **Hagy and Kemp (2002)** developed a preliminary LOICZ-type budget (**Gordon et al 1996**) for the lower Patuxent estuary for a 12 year period. This approach yielded estimates of annual net denitrification and these rates ranged from 24 to 78 $\mu\text{moles m}^{-2} \text{hr}^{-1}$, spanning the range of rates used in the current budget analysis. During the period of time analyzed with the LOICZ approach there several wet and dry years; higher denitrification rates were associated with wet years and lowest rates with drought years. Thus, while we do not have direct measurements of inter-annual variability, indirect evidence indicates that internal loss rates (burial and denitrification) are in proportional to external loading rates.

Patuxent Estuary Responses to Nutrient Loading Rates

The long-term record of water quality data collected for Patuxent estuary shows that water quality, specifically algal biomass and hypoxia, varies predictably on an interannual basis in response to external forcing of the system by nutrient loading and freshwater inflow. The observed patterns of water quality can also be understood reasonably well in terms of known and often quantified ecosystem processes. Earlier research on Patuxent estuary water quality (**Hagy 1996**) also showed that different regions of the estuary had different seasonal patterns of water quality and responded differently to external forcing. A qualitative understanding of the ecological processes controlling water quality patterns was used to inform the development and interpretation of simple quantitative models of ecosystem response (**Fig. 12**). These models reflect the same general responses observed by **Hagy (1996)**, but now with greater certainty due to the addition of 10 years' additional data.

Summer algal biomass (chlorophyll-a concentration) in tidal fresh surface water varied within a broad range of 30-60 $\mu\text{g l}^{-1}$ during periods of normal summertime freshwater inflow. During above average summer (June-August) freshwater inflow, however, algal biomass tended to be much lower, approximately 10 $\mu\text{g l}^{-1}$ (**Fig. 12**). This pattern likely reflects the large increase in flushing of this region as flow increases (**Hagy et. al. 2000**). Low winter biomass may reflect the combination of slow algal growth and rapid flushing rate which occurs in most winters. Whereas winter average biomass was nearly always low, biomass increased several-fold in 2002, to 10 $\mu\text{g l}^{-1}$, when record low flow occurred in winter-spring. Tidal fresh algal biomass did not respond discernibly to the decrease in nitrogen loading at HoT which occurred in the early 1990s. This pattern likely reflects the apparent dominance of physical controls on phytoplankton biomass over nutrient limitation. In contrast, submersed aquatic vegetation increased robustly

after nutrient loadings decreased, perhaps in response to nutrient input reductions (Fisher et al. 2005).

Phytoplankton biomass and production in the mesohaline portion of the estuary proceeds through several distinct phases during the year. During late winter, nutrient concentrations are high, while biomass remains low, suggesting light limitation associated with short photoperiod and a well-mixed water column (Hagy 1996, Hagy et al. 2000). In late winter to early spring, a phytoplankton bloom develops throughout the well-mixed water column, responding to compensating light levels. This bloom usually concludes in late spring. High algal biomass during summer, apparently controlled by nutrients and grazing, occurs only in surface waters. Algal biomass declines into fall until the lowest levels are reached in late fall. Annual mean values for chlorophyll-a in surface waters of the mesohaline Patuxent estuary were significantly correlated with both annual mean total nitrogen (TN) loading ($r^2=0.46$) and annual mean freshwater inflow as measured at HoT ($r^2=0.59$). Average chlorophyll-a values for the mesohaline estuary were better correlated with freshwater flow (Fig. 12) than with TN loading; it is probable that freshwater inflow correlates with factors affecting delivery of nutrients to the mesohaline portion of the estuary. For example, freshwater flow correlates with both diffuse nutrient loading from the middle portion of the watershed and downstream transport of nutrients from HoT to the mesohaline estuary. In addition, TN loading measured at HoT was affected by large decreases in point source discharges within the upper watershed. Within the lower watershed, the Western Branch treatment plant implemented biological N removal, but also increased the quantity of discharge (Fisher et al. 2005). Thus, it is very likely that freshwater flow tracks N availability to phytoplankton in the lower watershed better than TN loading at HoT.

Hypoxia and anoxia occur annually in mesohaline bottom waters of the Patuxent estuary, affecting at times nearly all of the below-pycnocline volume, but usually a smaller volume. Hagy (1996) observed that hypoxia usually occurs within an approximately 20 km stretch of the middle estuary, at the up-stream limit of landward circulation. At times, apparent intrusions of hypoxic bottom water from Chesapeake Bay affect the lower reaches of the estuary as well, dramatically increasing the volume of water affected (Fisher et al. 2005). The annual extent of hypoxia during 1986-2004 was significantly ($p<0.01$) correlated with freshwater inflow at HoT, averaged in any of several reasonable ways (e.g., October-August, January-August). March-August average inflow was the best predictor of hypoxic volume (Fig. 12), whereas a much weaker correlation was obtained when the average did not include the high-flow period in late spring. As with algal biomass, average TN loading at HoT did not predict the extent of hypoxia as well as freshwater inflow.

Hypoxia in 1987 and 1993 was more extensive than expected from inflow due to large hypoxic volumes associated with intrusions of hypoxic water from Chesapeake Bay. Hypoxia was substantially less extensive than expected in some other years (e.g., 1996, 1998), for unknown reasons. Whereas Hagy (1996) excluded the 1987 observation before fitting a regression, to better characterize typical system behavior during 1985-1992, the addition of 12 years' data renders this unnecessary. The general pattern of hypoxia in relation to freshwater flow is now more clearly rendered, as is the frequency of years in which hypoxia is unusually extensive or limited.

Budget Synthesis and Comparisons with Earlier Budgets

In the previous sections we described various individual N and P processes, transport and storages. In this section we put the pieces together in the quantitative framework of a budget and examine the results of our measurements and current level of understanding.

The annual scale TN budget appeared to be well balanced with inputs closely approximating internal losses plus export (Fig. 13a and 13b). To our knowledge this is the first estuarine nutrient budget where all terms were independently evaluated; all previous budgets had at least one term that was estimated by difference (Nixon et al. 1996). The rather close agreement between inputs and the sum of internal losses and export suggests we have captured most of the significant processes.

In addition to finding a closely balanced budget, there are other important aspects that emerge from this budget evaluation. In the case of the Patuxent, most of the TN input is to the upper estuary (5389 kg N day⁻¹; ~80% of total; Fig. 12a). However, in this portion of the system about 47% of these inputs were lost via long-term burial and denitrification. Loss processes occurring in the adjacent tidal marshes accounted for 64% of all losses in this region of the estuary. In the upper estuary long-term burial and denitrification were of about equal importance as loss terms. While this region represents only 12% of estuarine surface area (25% if adjacent tidal marshes are included) about 45% of all internal losses occur in this zone of the estuary. In the lower estuary losses associated with tidal marshes were small because of limited marsh area in this zone of the estuary. Denitrification and long-term burial in sub-tidal estuarine sediments were again of equal importance. Of the total annual TN load to the lower estuary, 75% is lost to burial and denitrification and the rest, mainly as DON and PON, exported to the Chesapeake Bay. Overall, only about 13% of the TN load to the entire estuarine system reaches Chesapeake Bay. The clear message here is that this estuary does not act as a passive pipe conveying nitrogen from the drainage basin to Chesapeake Bay.

The annual scale TP budget also appeared to be reasonably balanced but not to the same degree as the TN budget (Fig. 12b). Burial of TP in both tidal marshes and sub-tidal sediments was particularly important in the upper estuary. While the upper estuary constitutes only 25% of the area of the entire marsh-estuary system, about 61% of all TP inputs are buried in this region. Burial also sequestered a large fraction of inputs to the lower estuary (~95%). Box model-based estimates of TP transport to the lower estuary are more than twice that estimated by subtracting internal losses from external inputs (310 vs 120 kg P day⁻¹) indicating possible over-estimates of burial rates, an over-estimate of transport or an under-estimate of new TP inputs. The same result occurred in the lower estuary wherein TP transport to the Bay exceeded the residual obtained by subtracting internal losses from inputs. However, in both cases, these differences are not huge and neither changed the direction of transport. It is difficult to identify the most probable source of error leading to the discrepancies in the TP budget. Evaluations by Williams et al (2005) and Jordan et al (2003) both argue that accurately measuring TP inputs to the estuary is extremely difficult because such a large fraction of P travels attached to sediment particles. TSS transport is responsive to rain and storm events and very transitory; it is quite possible to miss quantitatively important but very short-lived runoff events. While the number of accretion rate estimates for marshes and sub-tidal

area has improved substantially since we last produced a budget, additional sediment accretion rate measurements would be useful to further refine loss rate estimates.

One of the objectives of this work was to compare the earlier budget for the Patuxent (Boynton et al. 1995) with this more intensive effort; in a sense, see if we got it right the first time (Table 18). At the outset, it seemed like this exercise would be straightforward, but it turned out to be more complicated than expected. Both management actions (i.e., improved treatment of point source discharges) and climate variability (wetter in recent years) complicated the comparison. Inputs of TN were larger (~40%) in the current budget because wetter conditions resulted in larger diffuse source TN inputs that more than off-set TN reductions at sewage treatment plants. TP inputs, in contrast, were smaller (~12%) because decreases in point source TP inputs were larger than the increased TP inputs from diffuse sources. When these inputs were expressed on an areal basis, differences were small and certainly not large enough to suggest either an increased or decreased trophic condition. Internal losses of both TN and TP were computed to be larger (TN by 28 %; TP by 6 %) in the current budget and this is consistent with larger inputs in more recent times. In addition, the earlier budget did not include tidal marshes while in this effort they appeared to be important sinks for both N and P. Had marshes not been included there would have been a good deal of N and P not accounted for by the sum of internal losses and export, particularly in the upper estuary. Williams et al (2005) reported that the degree of overprediction of water column NO_3^- concentration by a water quality model for the upper estuary was proportional to the area of adjacent tidal marshes. The addition of marshes to this evaluation clearly influenced the results and supports the ideas expressed by Valiela et al (2001) concerning the importance of exchanges of materials among adjacent coastal community types. Finally, TN exports to Chesapeake Bay constituted about 13 % of total inputs in both budgets. While export was arrived at differently in these budgets the answer in both is the same; not much nitrogen escapes from this estuary. However, there were substantial differences in TP export. The earlier budget indicated a net import (negative export) of TP amounting to about 30 % of total landside inputs of TP. The current TP budget indicates a net export, also close to 30 % of landside inputs. Thus, there is a difference in both the direction and magnitude of TP exchange with Chesapeake Bay.

Management Issues and Ecosystem-Scale Experiment

There has been considerable effort expended to reduce nutrient inputs, mainly from point sources, and thereby restore the Patuxent estuary to a less eutrophic condition (Malone et al. 1993; D'Elia et al. 2003). However, there has not been a quantitative evaluation of all nutrient inputs, storages, internal losses, and exchanges with Chesapeake Bay before and after these management actions occurred. Nutrient budgets are a useful framework for such an evaluation and we summarize here the main management-related point derived from this budgeting effort.

There is clear evidence of nutrient load reduction at the head of the estuary. This pattern, for both TN and TP, is substantial (25 % for TN and 23 % for TP) and caused by decreased nutrient concentrations in point source discharges (Table 4). Load reductions occurred earlier for P and were caused by the P-ban in detergents and improved P-removal at sewage plants. Reductions in N occurred later, were not as large and were caused by use of biological N removal technologies (denitrification) at sewage treatment

plants. These load reductions have been broadly touted as evidence of progress towards meeting Chesapeake Bay restoration goals. However, there is no evidence that annual time-scale nutrient loads to the much larger lower estuary have declined in response to these management actions. Pre and post-BNR TN and TP fluxes from the upper to the lower estuary were almost identical (Fig. 11). In fact, if TN and TP loads to this estuarine system were ranked from largest to smallest, the largest occurred during a wet year in the post-BNR period (1996) and the smallest during a dry year in the pre-BNR period (1991). Thus, diffuse sources, particularly those from the middle portion of the drainage basin, dominate the nutrient input signature for this estuary. Water quality improvements will not likely occur until there are substantial reductions in diffuse source inputs. Further reductions in N concentrations (to $\sim 3 \text{ mg N l}^{-1}$) in point source discharges are planned; these reductions, if implemented, could reduce N loads by about 20-25 % to the upper estuary and about 9 % when all N sources to the estuary are considered.

There has been a prolonged debate concerning the relative importance of Patuxent basin versus Chesapeake Bay nutrient sources contributing to the eutrophication of the Patuxent estuary (e.g., Domotor et al. 1989). Some agencies claim that Patuxent basin nutrient reductions would be ineffective because large amounts of N and P are imported from the nutrient enriched Chesapeake Bay to the Patuxent estuary. Several estimates of nutrient exchange at the mouth of the Patuxent indicate that this is not the case; TN and TP are exported from the Patuxent to the Chesapeake Bay rather than the reverse (Fig. 11). In addition, regression models relating nutrient loading rates to algal biomass accumulation and to hypoxic volumes account for much of the variability, suggesting that nutrients derived from the Patuxent basin are centrally involved (Hagy 1996). Finally, spring algal blooms and development of hypoxic waters first occur within the Patuxent rather than in the adjacent Chesapeake Bay; there is little evidence for importation of these features from the Bay to the Patuxent. Thus, nutrient load reductions in the Patuxent should, if of sufficient size, contribute to a lessening of eutrophic characteristics.

Nixon et al (1996) compiled N and P budgets for about a dozen estuaries. The magnitude and characteristics of inputs, losses and exports varied widely, as might be expected from a selection of estuaries that ranged from shallow lagoons to deeper, stratified coastal plain estuaries. However, they found a striking relationship between the percent of N and P exported and the log mean residence time of estuarine water. Thus, in rapidly flushed estuaries a large percent of inputs were exported while in more slowly flushed systems a smaller percent of inputs were exported. The Patuxent exported (as a percent of inputs) even less than predicted by the Nixon et al (1996) analysis. The practical issue here is that the Patuxent does not rapidly export nutrients. In fact, only about 13 % and 23% of TN and TP inputs, respectively, are exported. Most of the TN and TP exported are as dissolved or particulate organic compounds, indicating that they have been transformed from dissolved inorganic forms during transit through the estuary. Because of these large internal losses, the Patuxent contributes little to the eutrophication of Chesapeake Bay and probably even less than suggested by export estimates because a large fraction of the TN and TP exported is in forms not immediately utilizable by phytoplankton communities.

One of the unexpected outcomes of this budget analysis was the importance of the tidal marshes as sinks for both N and P. Investigations elsewhere (e.g., **Bricker and Stevenson 1996; Stevenson et al. 2002**) have reached similar conclusions. Marshes removed about 30 and 31 % of all TN and TP inputs, respectively, despite the fact they are a small part of the land/seascape (1.3 %) of the Patuxent basin and 18% of the estuarine/marsh system. Thus, accreting marshes, such as those in the Patuxent, seem to act as an efficient "ecosystem-scale kidney" and should continue to be protected for the many values they provide. However, should the tidal marshes of the Patuxent fail to keep pace with rising sea level, as has occurred in about 50% of other Chesapeake Bay tidal marshes (**Kearney et al. 2002**), the nutrient buffering effect of marshes would be lost; further still, eroding marshes could serve as a source of organic matter and nutrients, reversing the current role marshes appear to play (**Stevenson et al. 2002**).

There is substantial recycling of N and P from both the water column and sediments, especially during the warm periods of the year. Water column recycling, while large, can not support further increases in algal biomass but only maintain existing biomass. Nutrient releases from sediments, however, represent a "new" source of nutrients to the euphotic zone and can support increased algal standing stocks. There is field evidence from the Patuxent and other portions of Chesapeake Bay that deep water hypoxic/anoxic conditions facilitate efficient recycling of N and P from estuarine sediments (**Boynton and Kemp 1985; Cowan and Boynton 1996; Kemp et al. 2005**). We would expect sediment nutrient releases to diminish under conditions in which sediments remain oxidized through the summer months. Under such conditions P releases would be reduced due to reactions with oxidized iron at the sediment-water interface and N releases would also be reduced because coupled nitrification-denitrification would remain active. Thus, nutrient input reductions sufficient to relieve seasonal hypoxic/anoxic conditions might lead to larger improvements in water quality than expected because sediment nutrient recycling processes become less efficient. The quantitative impact of a drop in sediment nutrient recycling efficiency is not available at this time. However, we might expect there to be something other than a linear response to load reductions, possibly similar to the more complex hysteresis in ecosystem response observed in the Potomac River estuary (**Jones 2000**).

Our analyses indicate that major features of the estuary can be related to nutrient load changes. For example, the volume of hypoxic water and the size of algal standing crop were proportional to nutrient loading rates. In addition, time-series measurements of community metabolism and sediment releases of N also appear to be related to nutrient loading rates (**Boynton and Rohland 1998; Sweeney 1995**) in the Patuxent and mainstem Chesapeake Bay (**Boynton and Kemp 2000**). The practical aspect of these findings is that these processes, central to water quality, are very responsive to changes in nutrient inputs. There does not seem to be a large nutrient memory embedded in the sediments or water column of the Patuxent or other portions of Chesapeake Bay (**Boynton and Kemp 2000**). Should substantial nutrient reductions occur, we would predict measurable improvements in water quality conditions within a year or slightly longer period.

A central issue concerning eutrophication of the Patuxent concerns how much nutrient load reduction is needed. The Patuxent is currently among the aquatic systems in Maryland cited as not being in compliance with water quality guidelines; a Total Daily

Maximum Load (TMDL) computation is currently being developed for this estuary. Much of the TMDL result will be based on values computed from coupled land-use and water quality models and will thus be a function of how well those models capture features of the land and estuary. There are also several approaches to estimating needed load reductions based on field measurements; in the long run, use of both approaches would be useful. Fisher et al (2005) examined deep water dissolved oxygen concentrations in the Patuxent for an 18 year period (1986-2004). During summer average oxygen concentrations were below 1 mg l^{-1} for 6 of those years and below 2 mg l^{-1} for 10 additional years. During two drought years (1986 and 1992) summer dissolved oxygen concentration were at or slightly above 2 mg l^{-1} . Whole system TN and TP loads during those years averaged 5100 and 313 $\text{kg N and P day}^{-1}$, about 80 % and 70%, respectively, of average loads and 60 % and 45 %, respectively, of loads during high flow years. TN input reductions on the order of 1500 to 2500 kg N day^{-1} and TP reductions on the order of 100 kg P day^{-1} would be needed to be consistent with load conditions associated with deep water dissolved oxygen concentrations at or above 2 mg l^{-1} . We recognize that factors other than nutrient inputs (e.g., freshwater input and resultant strength of water column stratification, storm frequency and resultant vertical mixing) play a role in determining water quality conditions so these values are most useful as a first approximation rather than as firm targets. An alternative approach is to examine nutrient loading rates when the estuary exhibited few symptoms of eutrophication (Mihursky and Boynton 1978; Heinle et al 1980). The earliest load estimates were developed by Hagy et al (1998) and extend back to 1960, a period before sewage treatment plants were a significant feature of the basin (Domotor et al 1989) and before intensive urban/suburban development was initiated in the watershed (D'Elia et al 2003). TN and TP inputs at HoT averaged about 1200 kg N day^{-1} and 224 kg P day^{-1} during the decade of the 1960's. TP loads at the head of tide are now lower than during the 1960's by almost a factor of two. However, TN loads at the same location are still a factor of 1.6 greater than the earlier loads, despite BNR technology at the sewage treatment plants located above the head of tide. This comparison suggests the need for modest reductions in TN. However, about 70% of the contemporary TN load to the estuary comes from the basin located downstream of HoT. If we apply a modest diffuse TN yield for the basin area below HoT (areal rate = $5 \text{ kg N ha yr}^{-1}$) to represent inputs appropriate for the 1960's, a total TN load to the estuary of 3100 kg N day^{-1} results. This is about half of average contemporary TN loads and about 30% higher than TN loads estimated for recent dry years. While also crude, this analysis reaches a conclusion not dissimilar from the previous one; TN loads need to be decreased on the order of 2500 - 3000 kg N day^{-1} to be comparable to loads associated with far less eutrophic conditions of the 1960's. The second estimate is somewhat larger than the first and this might reflect the fact that the first only required that deep water dissolved oxygen conditions be above 2 mg l^{-1} in summer while the latter estimate was associated with an ecosystem having a vibrant seagrass community, well developed benthos and oyster reefs as well as better deep water oxygen conditions.

Whatever nutrient input reductions are eventually agreed to during the TMDL process, several things seem clear. First, TN reduction will need to be substantial to reduce hypoxic conditions during normal and wet years and larger still to restore other community components (SAV, benthos) to this ecosystem in addition to improving

oxygen conditions in deep waters. Second, further reductions in point source discharges are technically possible and, if instituted, will measurably reduce loads. However, most of the needed reductions will involve diffuse sources and to date there appears to have been little progress in dealing with this source of nutrients.

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tide (HoT), from the basin region between HoT and Benedict, MD and from the basin between Benedict and Chesapeake Bay (Fig. 1). Abbreviations WC, Biota, and Seds refer to multi-year, average annual TN and TP concentrations in the water column, animal biota and sediments, respectively. Abbreviations M and ST refer to tidal marsh and sub-tidal areas of the estuary. All flows have units of kg N or P day⁻¹ and all stocks have units of kg N or P x 10³.

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Table 12. Summary of macrozooplankton abundance and excretion rates in the Patuxent River estuary. Zooplankton abundance data were from Chesapeake Bay Zooplankton Monitoring Program (2001). Macrozooplankton excretion rates were computed using the relationship developed by Mauchline (1998). Data were not available for the oligohaline portion of the estuary.

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Table 1. Summary of pre (1985) and post (1995) BNR human population and 1990 land uses for three sub-basins and the full Patuxent River basin. Sub-basin divisions are shown in Figure 1. Tilled land includes both conventional and conservation tillage, Urban includes both pervious and impervious residential and urban areas, Open Space is non-agricultural and non-forest lands (e.g., golf courses). Data are from Chesapeake Bay Watershed Model Land Use and Linkages to the Airshed and Estuarine Models (2000).

<i>Locations</i>	<i>Pop Density, indiv km⁻²</i>		<i>%</i>	<i>Forest</i>	<i>Tilled Land</i>	<i>Pasture and Hay</i>	<i>Urban</i>	<i>Open Space</i>	<i>Non-Tidal Waters</i>	<i>Totals</i>
	<i>Pre-BNR</i>	<i>Post-BNR</i>								
<i>Upper Basin</i>	261	356	<i>km²</i>	364	129	94	209	106	7	910
			<i>%</i>	40.0	14.2	10.3	23.0	11.7	0.8	
<i>Middle Basin</i>	135	154	<i>km²</i>	419	137	78	239	109	9	991
			<i>%</i>	42.0	14.0	8.0	24.0	11.0	1.0	
<i>Lower Basin</i>	104	157	<i>km²</i>	211	35	20	74	32	5	377
			<i>%</i>	56.0	9.0	5.0	20.0	8.0	1.0	
<i>Basin Totals</i>	181	235	<i>km²</i>	995	302	191	522	247	21	2278
			<i>%</i>	44.0	13.0	8.0	23.0	11.0	1.0	

Table 2. Highest and lowest average daily nutrient loading rates, and years when these were observed, during the 13 year time-series. All point, diffuse, direct atmospheric and septic inputs were included. Data sources listed in Tables 3-5 and Figure 9.

Loading Category	Average Loads, kg N or P day ⁻¹			
	TN	DIN	TP	DIP
Highest	8574	6153	759	414
(year)	1996	1999	1993	1985
Lowest	4276	3218	207	113
(year)	1991	1991	1991	1991

Table 3. Estimates of atmospheric N and P loads directly to the surface waters of the Patuxent estuary. The upper portion of the table indicates areal N delivery rates based on data collected at Wye, MD (NADP 2001). P delivery rates are the same as those used in Boynton et al. (1995). The lower table provides N and P delivery rates to the upper (HoT to Benedict) and lower estuary (Benedict to estuary mouth). Direct atmospheric deposition to surface waters was not estimated for the region above HoT because of the very small surface area of the river. Pre and post BNR periods are not differentiated. Nitrogen wet fall data were averaged from 1984-1999, NH_x dry deposition from 1997-1999 and HNO_3/NO_3 dry deposition from 1992-1997. Seasonal average total N deposition rates do not include estimates of organic N. Units in the upper and lower table are $\text{mg N or P m}^{-2} \text{ month}^{-1}$ and $\text{kg N or P day}^{-1}$, respectively.

LOCATION	SEASON	N Wet Fall ($\text{NH}_x + \text{NO}_3$)	NHx Dry Deposition	HNO3/NO3 Dry Deposition	Organic N Deposition	Total N Deposition	P Wet Fall (PO4)	Total P Wet Fall
NADP Site at Wye, MD	Winter	50.0	11.5	10.5	na	72.0	na	na
	Spring	74.7	3.8	14.2	na	92.7	na	na
	Summer	91.6	-6.3	12.9	na	98.2	na	na
	Fall	49.4	6.0	8.5	na	63.9	na	na
	Ann Avg	66.4	3.8	11.5	17.4	99.0	1.3	5.3
Patuxent Estuary	SEASON	N Wet Fall ($\text{NH}_x + \text{NO}_3$)	NHx Dry Deposition	HNO3/NO3 Dry Deposition	Organic N Deposition	Total N Deposition	P Wet Fall (PO4)	Total P Wet Fall
Benedict	Spring	63.8	3.2	12.1	na	79.2		
	Summer	78.3	-5.4	11.0	na	83.9		
	Fall	42.2	5.1	7.2	na	54.6		
	Ann Avg	56.8	3.2	9.8	14.8	84.7	1.1	4.5
Benedict to Mouth	Winter	182.4	42.0	38.3	na	262.7		
	Spring	272.6	13.9	51.8	na	338.3		
	Summer	334.2	-23.0	47.1	na	358.3		
	Fall	180.3	21.9	30.9	na	233.1		
	Ann Avg	242.4	13.7	42.0	63.3	361.4	4.7	19.3

Table 4. A summary of point source N and P loads to the Patuxent River above and below the HoT. All entries have units of kg N or P day⁻¹. The pre and post BNR periods are 1986-1990 and 1993-2000, respectively. The location of HoT and major sewage treatment plants are shown in Figure 1. DIN = ammonium, nitrite, and nitrate; TN = DIN plus dissolved and particulate organic N; DIP = dissolved inorganic phosphorus; TP = DIP plus dissolved organic and particulate phosphorus. Seasons were defined as: winter (Dec-Feb), Spring (Mar-May), Summer (Jun-Aug), and Fall (Sep-Nov). Data in this table were from Chesapeake Bay Program (2001) and Wiedeman and Cosgrove (1998).

LOCATION	SEASON	DIN		TN		DIP		TP	
		Pre-BNR	Post-BNR	Pre-BNR	Post-BNR	Pre-BNR	Post-BNR	Pre-BNR	Post-BNR
Above HoT	Winter	1387	741	1614	909	85.1	33.6	131.9	56.4
	Spring	1443	638	1656	815	85.3	42.7	127.5	63.3
	Summer	1339	457	1511	591	82.4	35.5	116.1	52.5
	Fall	1349	528	1527	659	84.0	44.0	120.0	54.8
	Ann Avg	1379	591	1577	744	84.2	38.9	123.9	56.7
Below HoT	Winter	699	908	752	966	45.7	43.6	53.2	48.9
	Spring	894	249	763	298	53.8	41.2	61.3	45.7
	Summer	674	91	724	132	57.2	50.4	64.2	53.3
	Fall	696	372	739	421	54.5	47.3	61.3	50.9
	Ann Avg	691	405	744	454	52.8	45.8	60.0	49.7

Table 5. Estimates of septic system N discharges to the middle and lower Patuxent River estuary. Data were from Chesapeake Bay Watershed Model Land Use and Linkages to the Airshed and Estuarine Models(2000).

Time Period	Middle Basin (kg day ⁻¹)	Lower Basin (kg day ⁻¹)
Pre-BNR (1985-1990)	222	72
Post-BNR (1993-1997)	258	84

Table 6. A summary of annual average N and P stocks in the upper (tidal fresh and oligohaline) and lower (mesohaline) regions of the Patuxent River estuary. Pre and post-BNR data have been averaged in this summary. All values as kg N or P x 10³. Data sources and details were provided in Tables 7 - 10.

Nutrient Stock	Nutrient Type	Upper Estuary	Lower Estuary	Total
Water Column	TN	89	465	554
	TP	10	33	43
	DIN	46	123	169
Sediments	DIP	2	9	11
	TN	460	1580	2040
Benthic Invertebrates	TP	160	470	630
	TN	49	70	119
Macro-Zooplankton	TP	2	3	5
	TN	1.05	3.80	4.85
Totals	TP	0.13	0.70	0.83
	TN			2718
	TP			679

Table 7. Mean seasonal and annual N and P concentrations in the water column for the upper and lower Patuxent River estuary during pre (1986-1990) and post (1993-2000) BNR periods. Data are from the Chesapeake Bay Water Quality Monitoring Program (2001).

Nitrogen Concentrations, mg N l ⁻¹							Phosphorus Concentrations, mg P l ⁻¹				
Pre-BNR							Pre-BNR				
Upper Estuary			Lower Estuary				Upper Estuary		Lower Estuary		
Month	TN	NO ₂₊₃	NH ₄	TN	NO ₂₊₃	NH ₄	Month	TP	PO ₄	TP	PO ₄
Winter	2.39	1.35	0.22	0.82	0.18	0.04	Winter	0.193	0.029	0.050	0.009
Spring	2.00	1.07	0.13	0.92	0.27	0.06	Spring	0.198	0.035	0.051	0.010
Summer	1.40	0.36	0.10	0.77	0.07	0.12	Summer	0.211	0.054	0.074	0.026
Fall	1.63	0.62	0.11	0.72	0.09	0.08	Fall	0.209	0.047	0.077	0.026
AVG	1.86	0.85	0.14	0.81	0.15	0.08	AVG	0.203	0.041	0.063	0.018
Post-BNR							Post-BNR				
Upper Estuary			Lower Estuary				Upper Estuary		Lower Estuary		
Month	TN	NO ₂₊₃	NH ₄	TN	NO ₂₊₃	NH ₄	Month	TP	PO ₄	TP	PO ₄
Winter	1.98	1.18	0.19	0.75	0.20	0.02	Winter	0.148	0.025	0.033	0.004
Spring	1.44	0.69	0.08	0.95	0.30	0.04	Spring	0.153	0.029	0.045	0.007
Summer	0.99	0.18	0.06	0.73	0.05	0.07	Summer	0.148	0.045	0.058	0.016
Fall	1.08	0.24	0.06	0.58	0.03	0.02	Fall	0.172	0.037	0.052	0.018
AVG	1.37	0.57	0.10	0.75	0.15	0.04	AVG	0.155	0.034	0.047	0.011

Summary of macrobenthic infaunal biomass and N and P stock in the upper and lower of the Patuxent River estuary. Data were averaged by month for the period 1985-1999 averaged by seasons (Winter = Dec-Feb; Spring = Mar-May; Summer = Jun-Aug; Fall =). Percent nitrogen and phosphorus of ash-free dry weight material was taken to be 15%, respectively. Biomass data were from the Chesapeake Bay Benthic Monitoring (2001).

<i>Infaunal Biomass</i>		<i>Infaunal N and P Stock</i>			
<i>Upper Estuary</i>	<i>Lower Estuary</i>	<i>Upper Estuary</i>		<i>Lower Estuary</i>	
<i>g (AFDW) m⁻²</i>	<i>g (AFDW) m⁻²</i>	<i>g N m⁻²</i>	<i>g P m⁻²</i>	<i>g N m⁻²</i>	<i>g P m⁻²</i>
8.1	1.9	1.22	0.050	0.29	0.012
15.1	7.8	2.27	0.094	1.17	0.048
13.4	5.5	2.01	0.083	0.82	0.034
13.3	1.7	2.00	0.082	0.26	0.011
12.5	4.2	1.87	0.077	0.83	0.026

Table 9. Estimates of annual average particulate nitrogen (PN) and phosphorus (PP) in the surface 2 cm of sediments in the Patuxent River estuary. Data are from Boynton et al. (1980), Boynton et al. (1995) and Boynton and Rohland (1998). There were not sufficient data available to make pre and post-BNR estimates. Seasonal variations in surficial sediment PN and PP were small and erratic.

Estuary Region	Sediment PN, % wgt	Sediment PP, % wgt	Sediment Volume g cm ⁻³	PN Stock g N m ⁻²	PP Stock g P m ⁻²
Lower Estuary	0.31	0.093	0.23	14.3	4.3
Upper Estuary	0.35	0.125	0.25	17.5	6.3

Table 10. Summary of estimates of annual TN and TP exports from the Patuxent River estuary to Chesapeake Bay. Negative value indicates net annual import of TP from Chesapeake Bay to the Patuxent River estuary.

Study / Computation	Observation Years	TN kg N x 10 ⁶ y ⁻¹	TP kg P x 10 ³ y ⁻¹	Source
Patuxent Nutrient Budget (Inputs - Internal Losses)	1985-1986	0.21	-0.060	Boynton et al. 1995
Hydrodynamic/Water Quality Model	1985-1986	0.33	0.020	Cerco and Cole (1992) in Boynton et al (1995)
Patuxent Box Model				This study
Pre-BNR	1986-1990	0.45	0.050	
Post-BNR	1993-2000	0.32	0.046	

Table 11. Summary of sediment ammonium and phosphate releases in the oligohaline and mesohaline regions of the Patuxent River estuary. Data were from Boynton et al (1982a) and Boynton and Rohland (1998). Data were not available for the tidal/fresh portion of the estuary. Most data were collected during summer periods, fewer during spring and fall and only scattered observations during winter. Composite seasonal patterns of ammonium and phosphate flux indicated that highest values always occurred during summer. Spring and fall fluxes were about 40% of summer values and winter fluxes were about 10% of summer values. These proportions are reflected in the values in the table.

Pre-BNR (1986-1990) Seasons	Oligohaline		Mesohaline	
	Ammonium uMoles N m ⁻² h ⁻¹	Phosphate uMoles P m ⁻² h ⁻¹	Ammonium uMoles N m ⁻² h ⁻¹	Phosphate uMoles P m ⁻² h ⁻¹
Winter	31	4.1	23	2.2
Spring	126	16.3	93	8.9
Summer	314	40.7	232	22.2
Fall	126	16.3	93	8.9
Annual	149	19.4	110	10.6
Post-BNR (1993-1999) Seasons	Ammonium uMoles N m ⁻² h ⁻¹	Phosphate uMoles P m ⁻² h ⁻¹	Ammonium uMoles N m ⁻² h ⁻¹	Phosphate uMoles P m ⁻² h ⁻¹
Winter	43	4.2	30	3.2
Spring	171	18.8	119	13.0
Summer	428	42.2	298	32.4
Fall	171	18.8	119	13.0
Annual	203	20.0	142	15.4

Table 12. Summary of macrozooplankton abundance and excretion rates in the Patuxent River estuary. Zooplankton abundance data were from Chesapeake Bay Zooplankton Monitoring Program (2001). Macrozooplankton excretion rates were computed using the relationship developed by Mauchline (1998). Data were not available for the oligohaline portion of the estuary.

Pre-BNR (1986-1990) Seasons	Tidalfresh		Mesohaline	
	Zooplankton Abundance	Zooplankton NH ₃ Recycle	Zooplankton Abundance	Zooplankton NH ₃ Recycle
	Number m ⁻³	mg N m ⁻² d ⁻¹	Number m ⁻³	mg N m ⁻² d ⁻¹
Winter	10395	1.8	8856	0.9
Spring	27966	11.9	36283	22.5
Summer	14715	11.3	8446	11.5
Fall	6514	2.0	7349	5.8
Annual	14898	6.7	15233	10.2
Post-BNR (1993-1999) Seasons	Zooplankton Abundance	Zooplankton NH ₃ Recycle	Zooplankton Abundance	Zooplankton NH ₃ Recycle
	Number m ⁻³	mg N m ⁻² d ⁻¹	Number m ⁻³	mg N m ⁻² d ⁻¹
	Winter	123712	15.6	7239
Spring	173055	87.3	49967	31.7
Summer	110915	99.0	11643	12.3
Fall	29212	12.3	8437	4.7
Annual	109223	53.5	19322	12.5

Table 13. A summary of seasonal and annual primary production estimates from three locations in the Patuxent River estuary during pre and post-BNR periods. Data were collected by the Chesapeake Bay Phytoplankton Monitoring Program (2001). Measurements were based on C^{14} incubations in constant light incubators. Volumetric rates were converted to areal rates by assuming measured rate represented P_{max} at the surface and production was a linear function of light to the depth of 1% light penetration. Euphotic depth was determined from secchi measurements.

Pre-BNR (1986-1990)	Tidalfresh	Oligohaline	Mesohaline
Seasons^k	(mg C m⁻² d⁻¹)	(mg C m⁻² d⁻¹)	(mg C m⁻² d⁻¹)
Winter	30	491	1003
Spring	599	232	1632
Summer	1656	1017	2486
Fall	1147	358	1256
Annual Average	858	524	1594
Annual Total (g C m ² y ⁻¹)	313	191	582
Post-BNR (1993-1999)	Tidalfresh	Oligohaline	Mesohaline
Seasons	(mg C m⁻² d⁻¹)	(mg C m⁻² d⁻¹)	(mg C m⁻² d⁻¹)
Winter	40	55	654
Spring	677	393	1585
Summer	1332	943	1750
Fall	858	489	1026
Annual Average	727	472	1254
Annual Total (g C m ² y ⁻¹)	266	172	458

Table 14. Whole system scale estimates of nitrogen (NH_4 and DIN) and phosphorus (PO_4) inputs, recycle rates from estuarine sediments (Table 11) and macrozooplankton (Table 12) and phytoplankton uptake rates of NH_4 and PO_4 . Phytoplankton demand for N and P was estimated using a Redfield C:N:P ratio of 106:16:1 and primary production rates provided in Table 13. Surface areas for upper and lower estuary were 26×10^6 and $117 \times 10^6 \text{ m}^2$, respectively.

Input/Recycle/Uptake Component	Upper Estuary, kg day^{-1}						Lower Estuary, kg day^{-1}						
	Annual		Summer		Winter		Annual		Summer		Winter		
	NH_4/DIN	PO_4	NH_4/DIN	PO_4	NH_4/DIN	PO_4	NH_4/DIN	PO_4	NH_4/DIN	PO_4	NH_4/DIN	PO_4	
Pre-BNR (1986-1999)													
New inputs	4122	128	3558	129	4191	125	2510	80	1320	68	3702	68	
Recycle													
Sediments	2524	252	2743	787	655	38	4580	966	9120	1824	912	192	
Macrozooplankton	175	24	294	41	47	nd	266	37	300	41	106	nd	
Total	2699	276	3037	828	702	39	4846	1003	9420	1965	1017	192	
Uptake													
Phytoplankton	-3349	-463	-6484	-876	-1264	-175	-34726	-4806	-64362	-7526	-21640	-3023	
Post-BNR (1993-1999)													
New inputs	3576	243	2541	159	4177	189	2478	110	1136	75	4226	98	
Recycle													
Sediments	1856	309	3739	816	374	81	5857	1430	11715	2820	1172	282	
Macrozooplankton	1362	193	2074	356	408	nd	324	46	320	44	140	nd	
Total	3248	502	6313	1172	780	81	6181	1455	12035	2864	1312	282	
Uptake													
Phytoplankton	-2905	-402	-5508	-766	-252	-35	-27300	-3776	-38220	-5289	-14196	-1977	

Table 15. A summary of nitrogen losses due to denitrification in tidal marshes and sub-tidal estuarine sediments of the Patuxent River estuary.

Estuarine Zone	Area of Zone (m ² * 10 ⁶)	Annual Average Denitrification Rate (μmol N m ⁻² hr ⁻¹) ^a	Total Denitrification (Kg N yr ⁻¹) ^b
Sub-Tidal Estuarine Sediments			
Upper estuary	22.3	38	103925
Lower estuary	111.0	32	<u>435617</u>
			Total 539542
Tidal Marshes			
Upper estuary	22.8	111	310377
Lower estuary	5.9	80	<u>57886</u>
			Total 368263
		System Total	907806

^a Estimates of sub-tidal denitrification rates for the upper estuary were from Twilley and Kemp (1987) as reported in Boynton et al. (1995). Lower estuary rates were based on data from Jenkins and Kemp (1984) and Cornwell (unpublished data). Tidal marsh rates of denitrification were from Greene (2005) and were spatially weighted (high, mid and low marshes) for upper estuary marshes but not weighted for the much smaller lower estuary marshes.

^b Total denitrification was estimated as the product of marsh area and annual average denitrification rate.

Table 16. Summary of sub-system areas, sediment deposition rates, sediment composition, and areal and whole-system annual PN and PP burial rates for major subsystems of the upper and lower Patuxent River estuary.

Location	Sub-System Area (km ²)	Sediment Deposition Rate ^a (g dry sed m ⁻² yr ⁻¹)	Sediment Composition ^b		Annual Burial Rate ^c		Total Burial Rate ^d			
			PN (mgN g dry sediment ⁻¹)	PP (mgP g dry sediment ⁻¹)	PN (g N m ⁻² yr ⁻¹)	PP (g P m ⁻² yr ⁻¹)	PN (kg N yr ⁻¹)	PP (kg P yr ⁻¹)		
Upper Estuary										
tidal marsh	22.8	2140	5.9	1.05	12.6	2.2	287873	51232		
sub-tidal estuary	22.3	2722	3.5	1.25	9.5	3.4	212452	75876		
							total	500325	127107	
Lower Estuary										
tidal marsh	5.9	2140	5.9	1.05	12.6	2.2	74493	13257		
sub-tidal estuary	111	1143	2.5	0.55	2.9	0.6	317183	69780		
							total	391676	83037	
System Total								892001	210145	

^a Deposition rate estimates for the tidal marshes were from Pb²¹⁰-based measurements made by Merrill (1999) and Greene (2005); lower estuary sub-tidal deposition rates were from Pb²¹⁰-based measurements by Cornwell (unpublished data); upper estuary sub-tidal deposition rates were based on riverine plus diffuse source sediment inputs corrected for sediment deposition in adjacent tidal marshes and assuming no sediment transport into the lower estuary.

^b Sediment composition data were from Merrill (1999) and Greene (2005) for tidal marsh habitats; upper estuary sub-tidal sediment PN and PP concentrations were from Boynton et al (1995) and lower estuary data were from Cornwell (unpublished data) and Boynton et al (1995).

^c Annual areal burial rates were estimated as the product of deposition rate times PN or PP concentration at sediment depth where nutrient concentration change with further depth in the sediment column approached zero. In the tidal marshes this depth was about 20-30 cm and in the sub-tidal estuary about 5-10 cm.

^d Total burial rates were estimated as the product of areal annual rates times the area of tidal marsh and sub-tidal estuary.

Table 17. Estimates of vertical accretion rates and long-term PN and PP burial rates measured in a variety of wetlands using radiotracer techniques. This table was adapted from Greene (2005a).

Wetland Type	Tracer Technique	Vertical Accretion (mm yr ⁻¹)	N Burial	P Burial	References
Brackish					
Barataria Bay, LA	¹³⁷ Cs				Hatton et al. 1982
levee		14.0	25.0	2.4	
backmarsh		5.9	10.0	0.5	
Barataria Basin, LA	¹³⁷ Cs				DeLaune et al. 1981
7 m inland		13.5	21.0	—	
45 m inland		7.5	13.4	—	
Choptank Estuary, MD	²¹⁰ Pb	9.2	23.0	2.0	Merrill 1999
Monte Bay, MD	²¹⁰ Pb	5.5	11.1	0.3	Merrill 1999
Tidal Freshwater					
Patuxent Estuary, MD	²¹⁰ Pb	8.5	12.6	2.2	Greene 2005a
Otter Creek, MD	²¹⁰ Pb	5.0	8.8	1.2	Merrill 1999
Freshwater					
Riparian Forest, WI	¹³⁷ Cs	5 to 13	12.8	2.6	Johnston et al. 1984
Barataria Bay, LA	¹³⁷ Cs				Hatton et al. 1982
levee		10.6	16.0	1.0	
backmarsh		6.5	9.0	0.5	
Everglades, FL	¹³⁷ Cs	0.3 - 6.6	6.3 - 14.1	0.11 - 0.7	Craft and Richardson 1993

Table 18. A comparison of earlier (Boynton et al. 1995) and current TN and TP nutrient budgets for the Patuxent River estuary. In the earlier budget marshes were considered to be neutral regarding TN and TP inputs and losses, export to Chesapeake Bay was computed by subtracting internal losses from all external inputs and septic inputs were included in the diffuse term. Areal loads have units of g N or P m⁻² yr⁻¹.

Nutrient Source	(kg N or P x 10 ⁶ yr ⁻¹)			
	Old Budget		New Budget	
	TN	TP	TN	TP
Atmospheric	0.22	0.009	0.16	0.009
Point	0.83	0.116	0.44	0.039
Diffuse	0.68	0.070	1.69	0.124
Septic	0.00	0.000	0.13	0
<i>Total</i>	<u>1.73</u>	<u>0.195</u>	<u>2.42</u>	<u>0.172</u>
<i>Areal Load</i>	13.0	1.5	18.2	1.3
Internal Losses				
Burial				
Marshes	0.00	0.000	0.38	0.060
Sub-tidal	0.92	0.250	0.70	0.207
Denitification				
Marshes	0.00		0.37	
Sub-tidal	0.54		0.62	
<i>Total</i>	<u>1.46</u>	<u>0.250</u>	<u>2.05</u>	<u>0.267</u>
Fisheries Yields	0.06	0.002	0.06	0.002

List of Figures

Figure 1. A map showing regional location (a) and spatial details (b) of the Patuxent basin and Patuxent River estuary.

Figure 2. Conceptual model of the nutrient budgets evaluated for the Patuxent River estuary. Geographic boundaries are shown in Figure 1. The model is described in the text. Abbreviations on the diagram are as follow: I = inputs, L = internal losses due to long-term burial or denitrification, T = transport between estuarine regions or Chesapeake Bay. Superscripts u, m and l indicate upper, middle or lower basin; subscripts a = direct atmospheric deposition of N or P to surface waters of the estuary, p = point source, d = diffuse source and s = septic source; dn and b refer to denitrification and long-term burial, respectively; m and l indicate processes occurring in tidal marshes and sub-tidal estuarine sediments, respectively.

Figure 3. Annual average TN, DIN, TP and PO₄ loading rates (kg N or P day⁻¹) for the full Patuxent River estuarine system. Loads include combined sources from above the head of tide (HoT) and all diffuse, point, septic and direct atmospheric deposition to tidal waters of the upper and lower estuary. Dashed and dotted lines indicate average values of total and inorganic loads for the years 1985-1997.

Figure 4. River flow at the head of tide (Bowie, MD gage; USGS 2004) averaged by season (vertical bars) and year (bold dots) for the period 1985-1997. The letters w, sp, su, and f refer to winter, spring, summer, and fall, respectively. The dashed line is the long-term (1978-2002) average river flow. The dotted lines are average flows for the pre (1985-1990) and post (1993-1997) BNR periods.

Figure 5. A scatter diagram showing annual TN and TP loading rate to a selection of coastal, estuarine and lagoon ecosystems. Systems are coded by number as follows: 1 Buzzards Bay MA (NOAA/EPA 1989), 2 Sinepuxent Bay MD (Boynton et al 1996), 3 Kaneohe Bay HI, post-diversion (Smith et al 1981), 4 Isle of Wight Bay MD (Boynton et al 1996), 5 Baltic Sea (Nixon et al 1996), 6 Chincoteague Bay MD (Boynton et al 1982b, 1996), 7 Kaneohe Bay HI, pre-diversion (Smith et al 1981), 8 Narragansett Bay RI, prehistoric (Nixon 1997), 9 Gulf of Riga (Yurkovskis et al 1993), 10 Albemarle Sound NC (Nixon et al 1986b), 11 Himmerfjorden Estuary Sweden (Engqvist 1996), 12 Guadalupe Bay TX, dry year (Nixon et al 1996), 13 Buttermilk Bay MA (Valiela and Costa 1988), 14 Moreton Bay Australia (Eyre and McKee 2002), 15 Seto Inland Sea Japan (Nixon et al 1986b), 16 Taylorville Creek MD (Boynton et al 1996), 17 Nanaimo River estuary, BC (Naiman and Sibert 1978), 18 Newport Bay MD (Boynton et al 1996), 19 N. Adriatic Sea (Degobbis and Gilmartin 1990), 20 Mobile Bay AL (NOAA/EPA 1989), 21 Chesapeake Bay MD (Boynton et al 1995), 22 MERL (1x) RI (Nixon et al 1986b), 23 Delaware Bay DE (Nixon et al 1996), 24 Narragansett Bay RI, current (Nixon et al 1995), 25 N. San Francisco Bay CA (Hager and Schemel 1992), 26 Guadalupe Bay TX, wet year (Nixon et al 1996), 27 Potomac River Estuary MD (Boynton et al 1995), 28 St Martins River MD (Boynton et al 1996), 29 Apalachicola Bay FL (Mortazavi et al 2000), 30 Patuxent River Estuary MD (Stammerjohn et al 1991), 31 Tokyo Bay Japan

Figure 1.

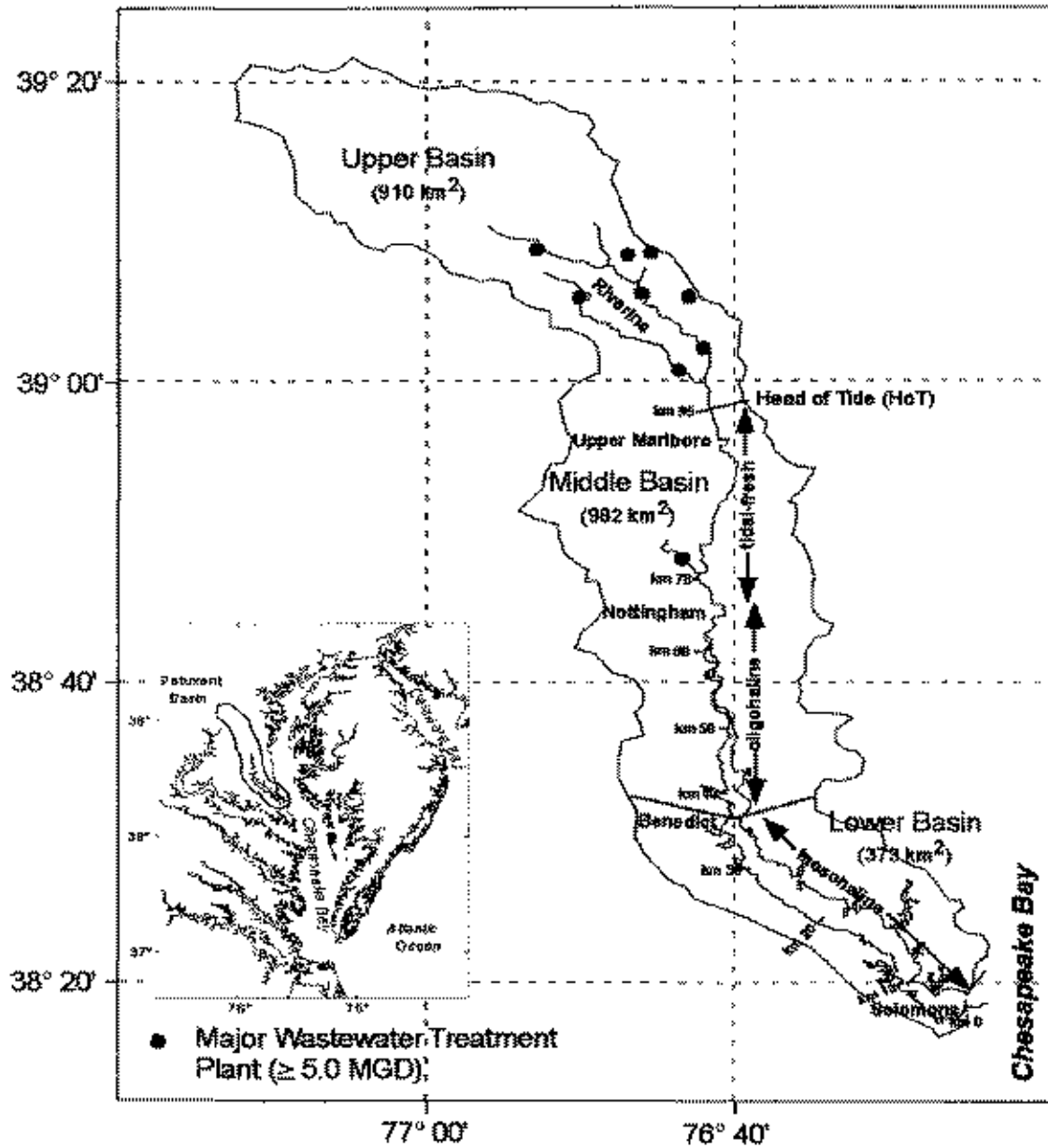


Figure 2.

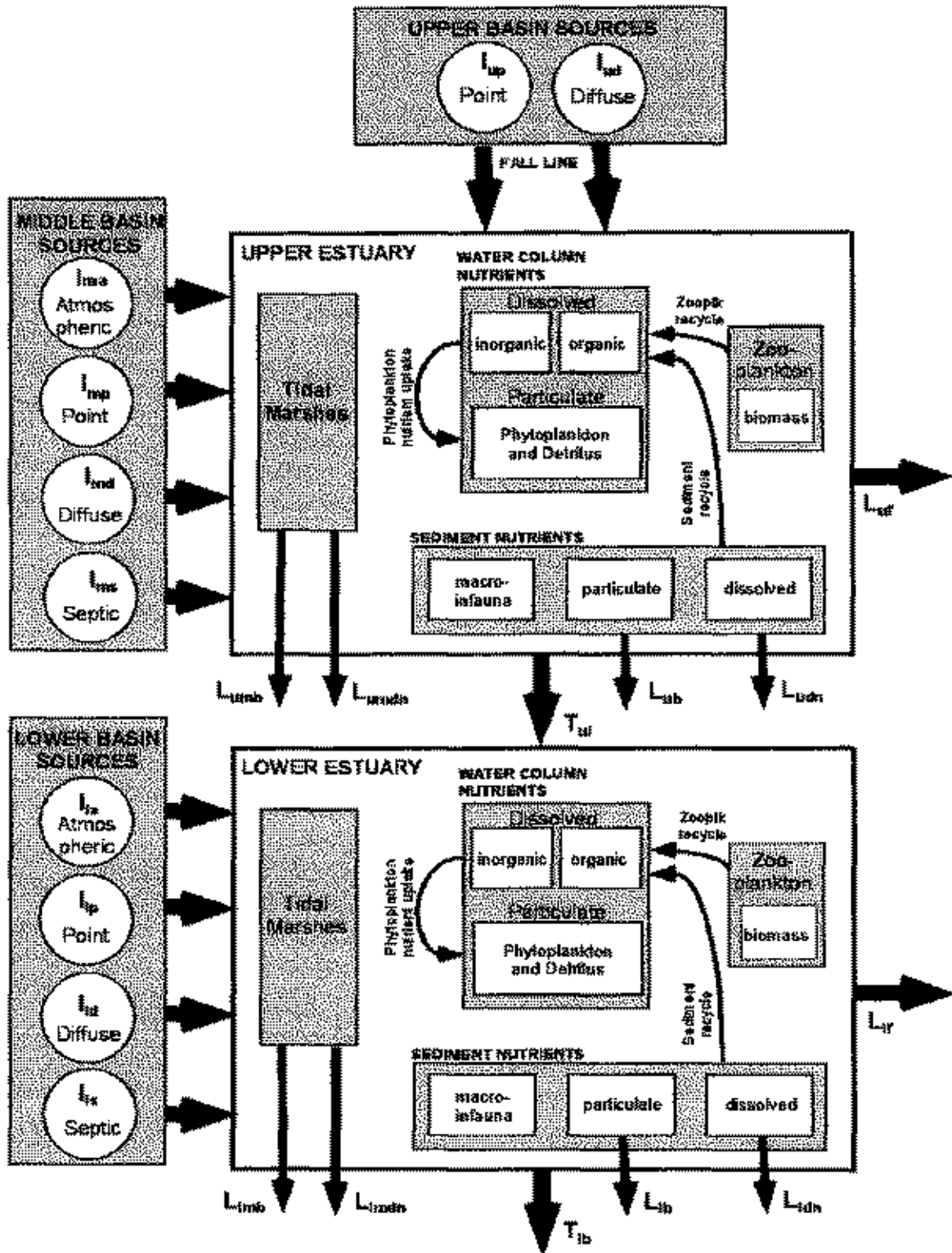


Figure 3.

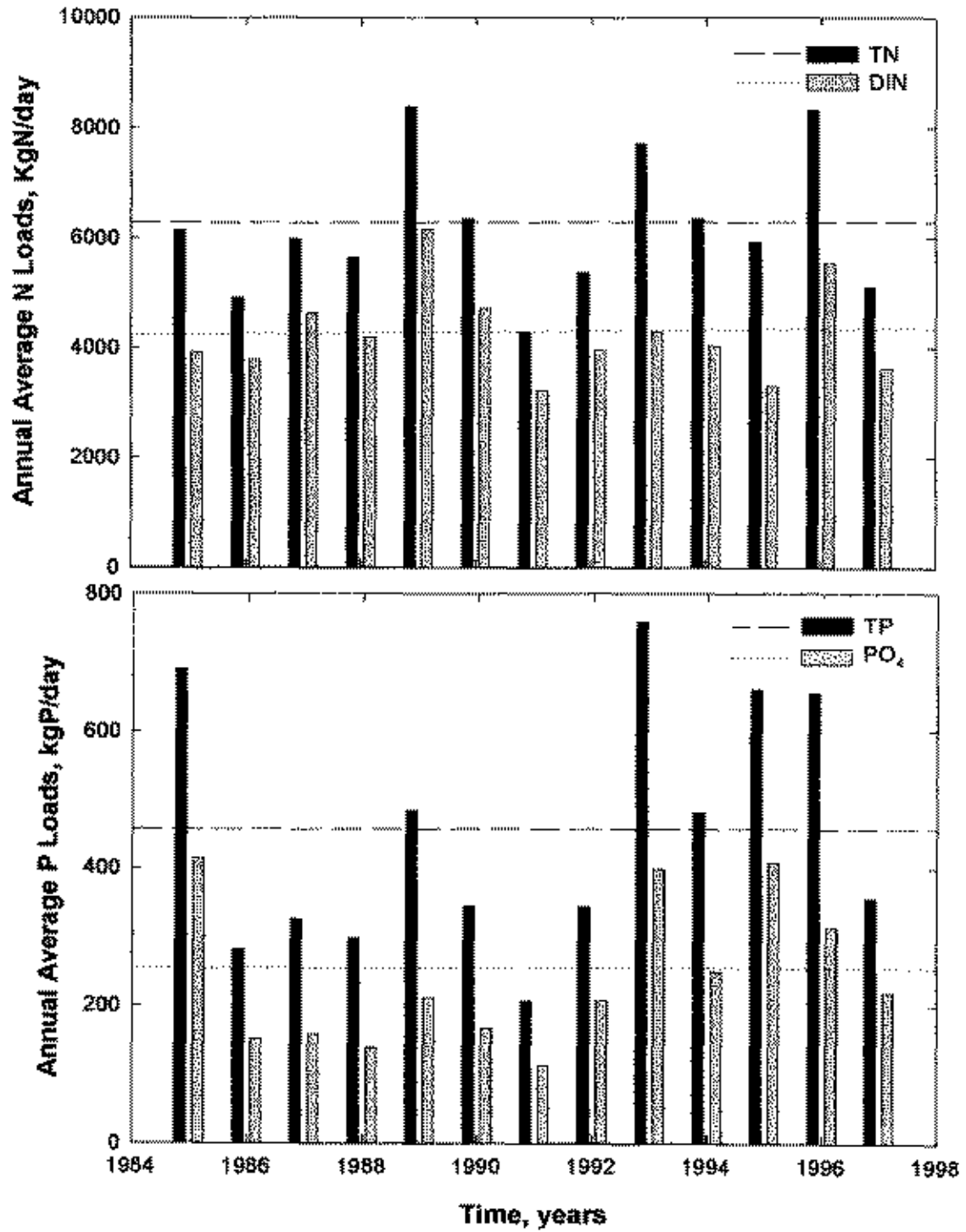


Figure 4.

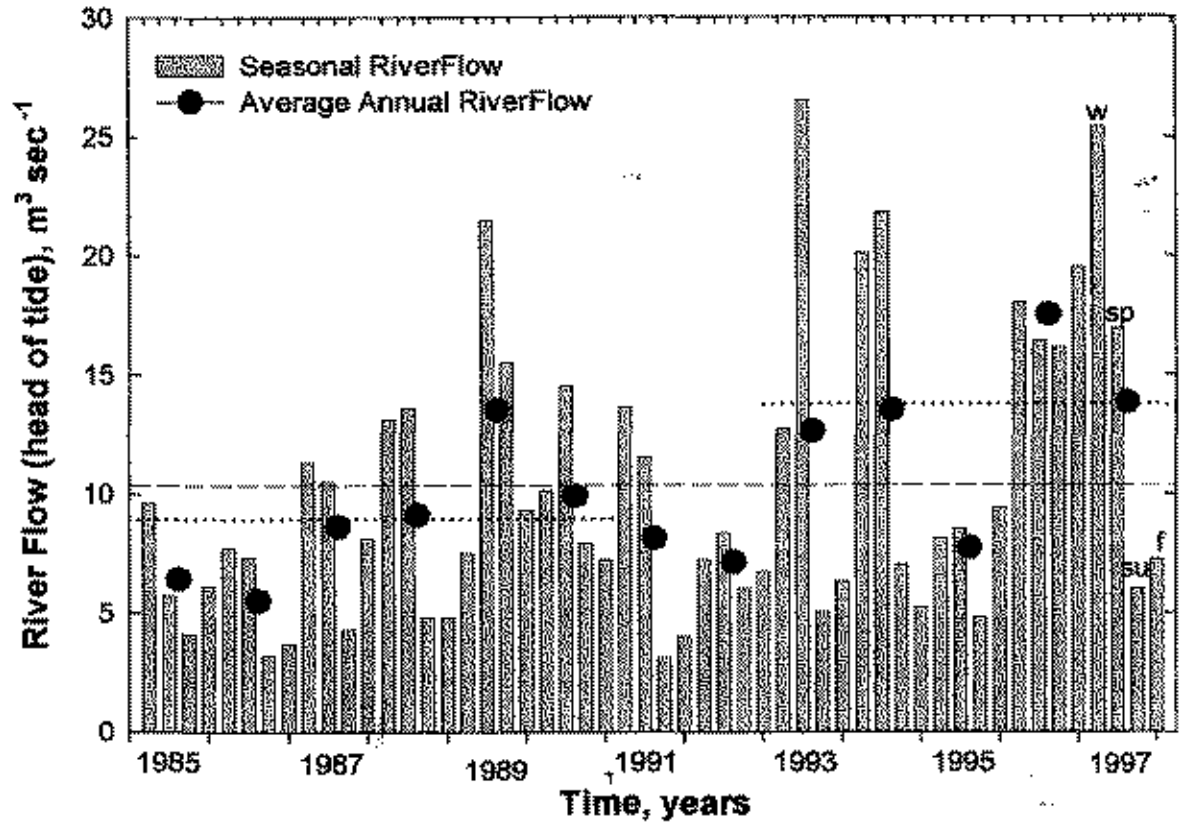


Figure 6

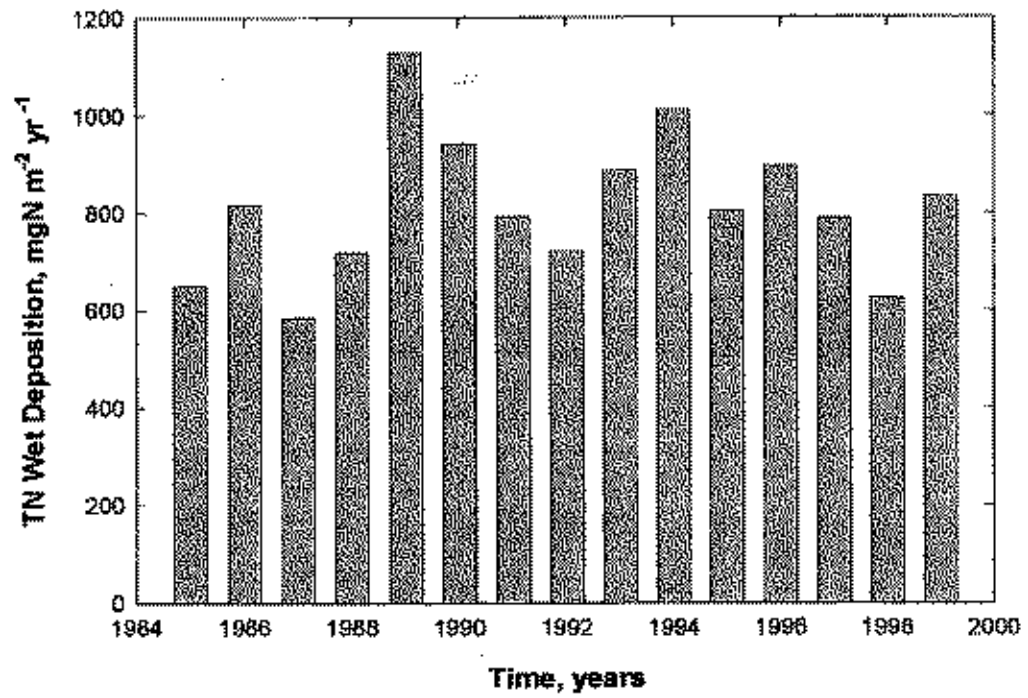


Figure 7

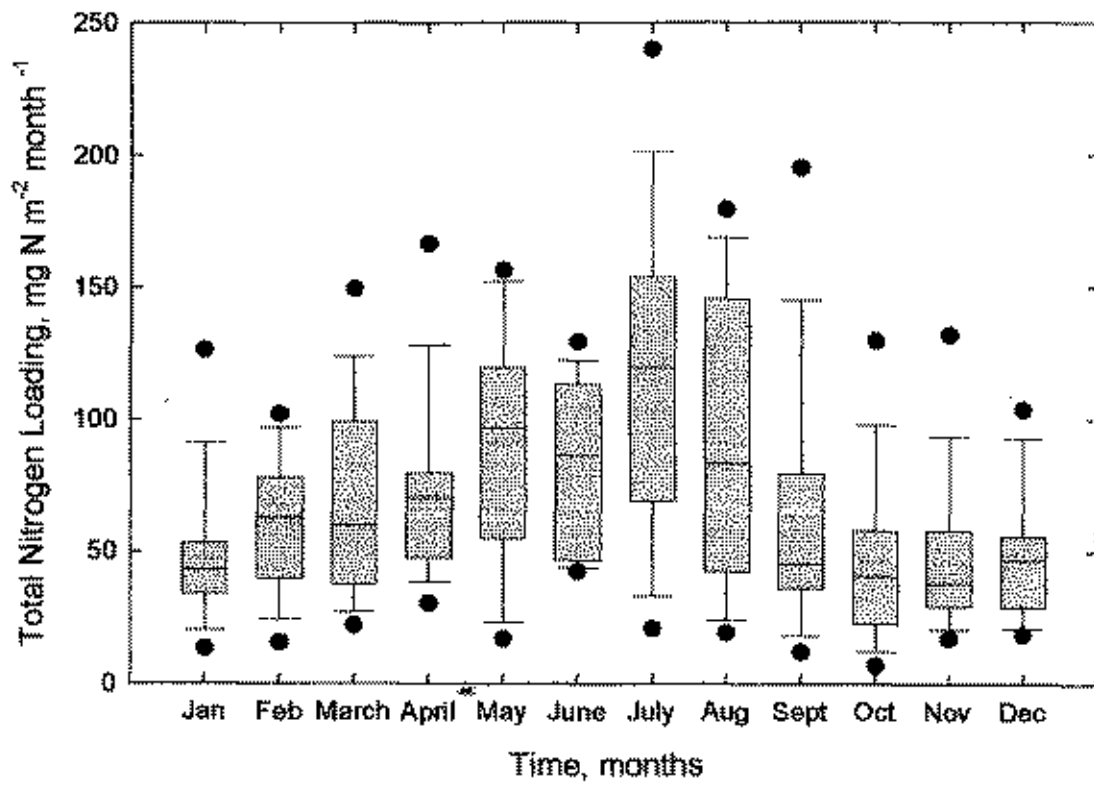


Figure 8

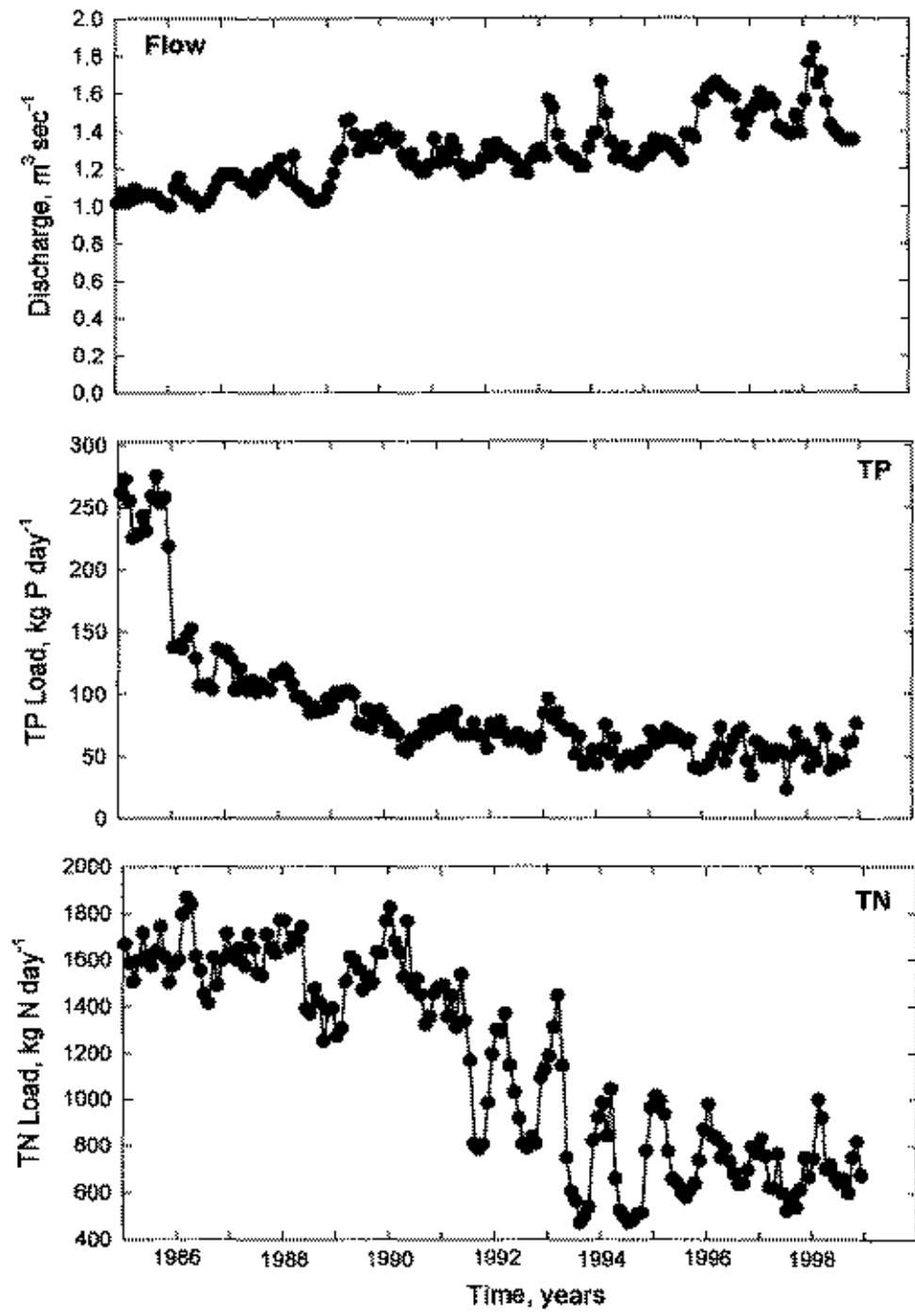


Fig. 9

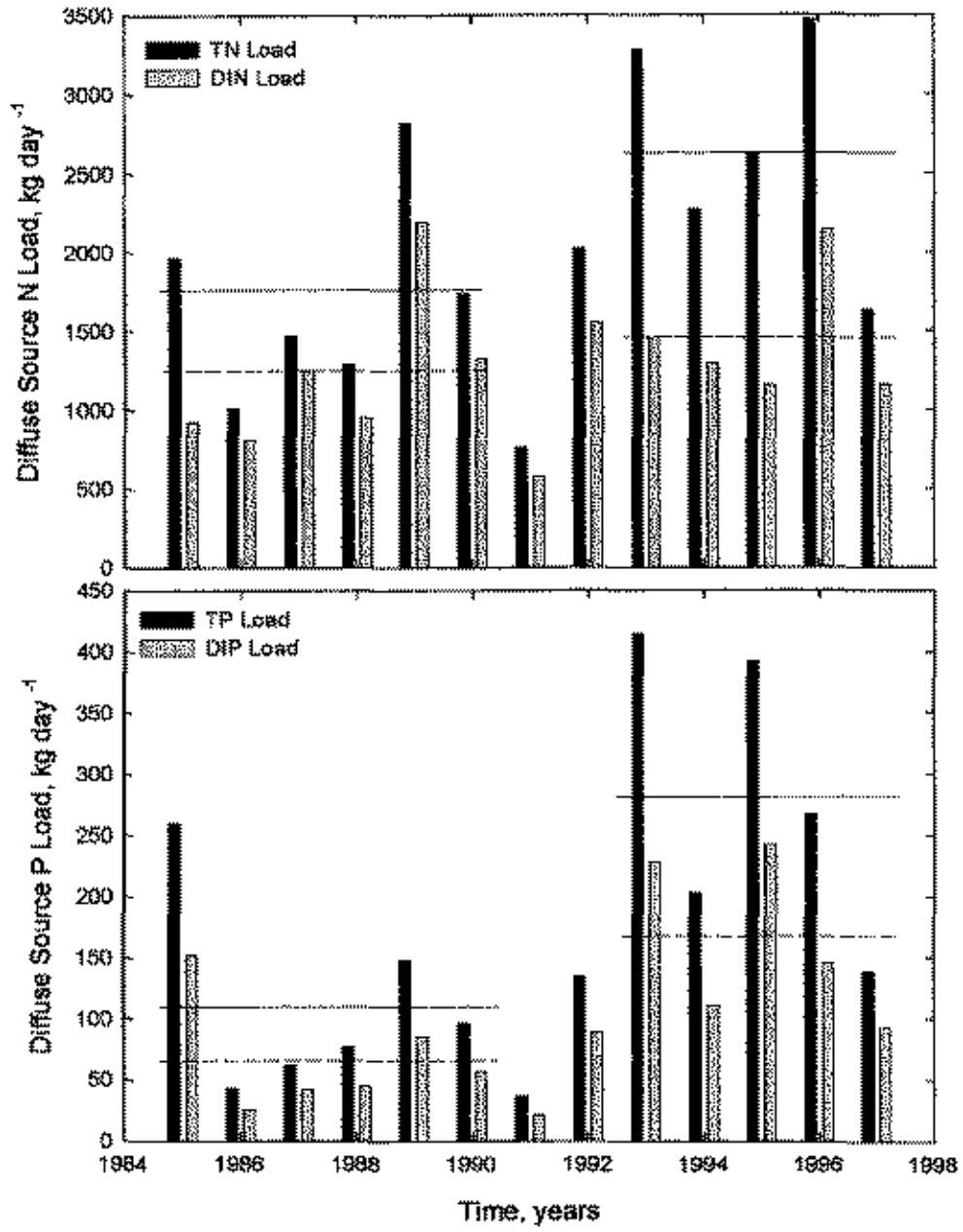
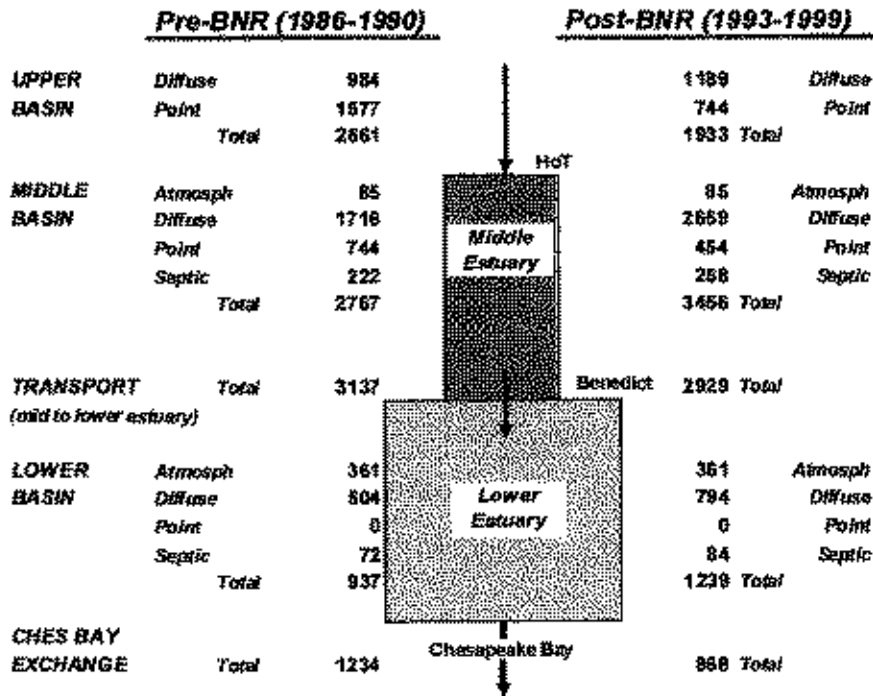


Figure 10

TN Loading: Annual (kg N d^{-1})



TP Loading: Annual (kg P d^{-1})

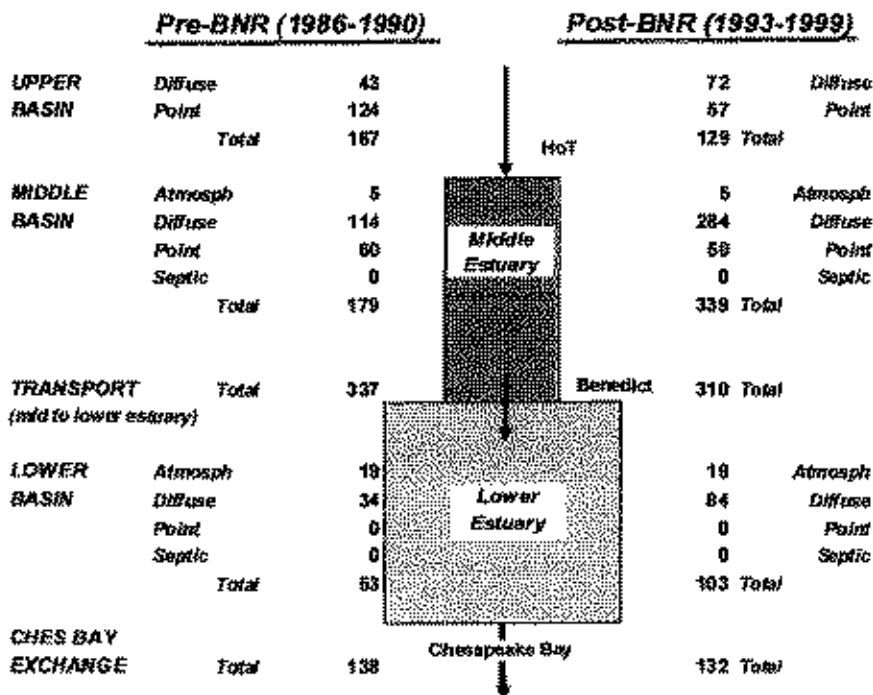
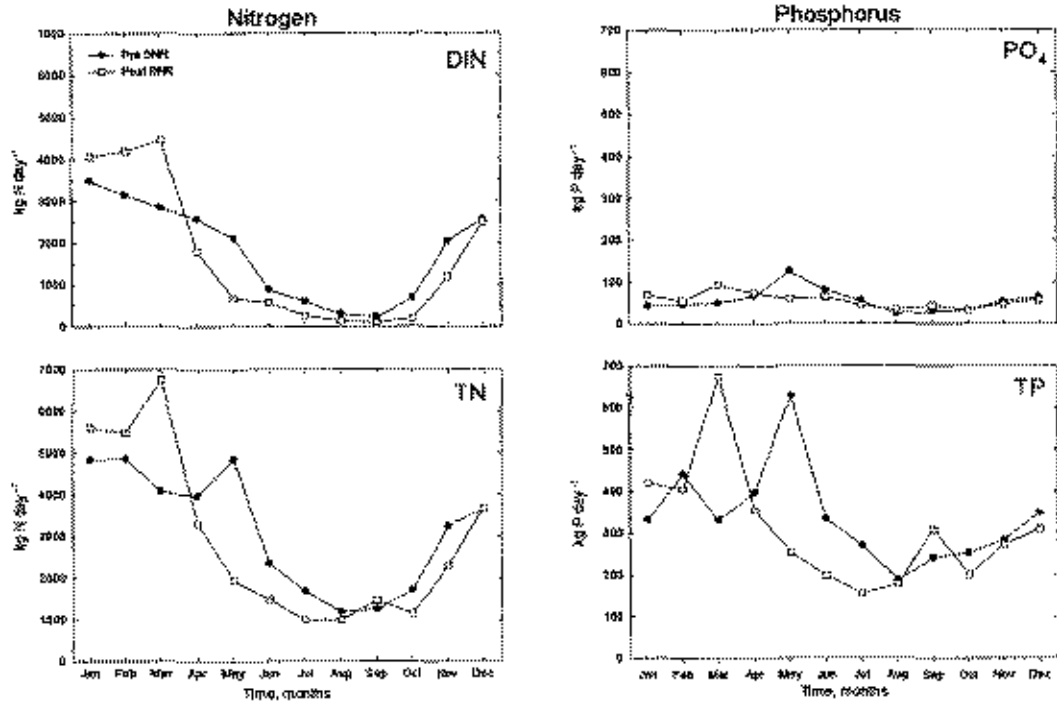


Figure 11

(a) Transport between Upper and Lower Portions of Patuxent River Estuary



(b) Transport between Patuxent River Estuary and Chesapeake Bay

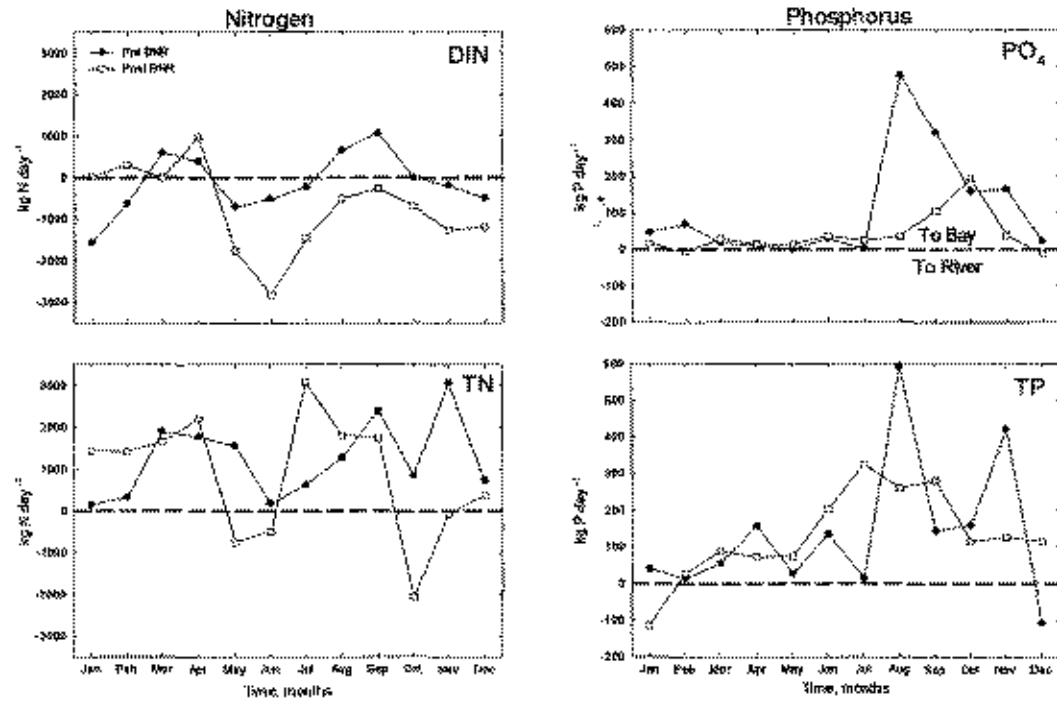


Figure 12

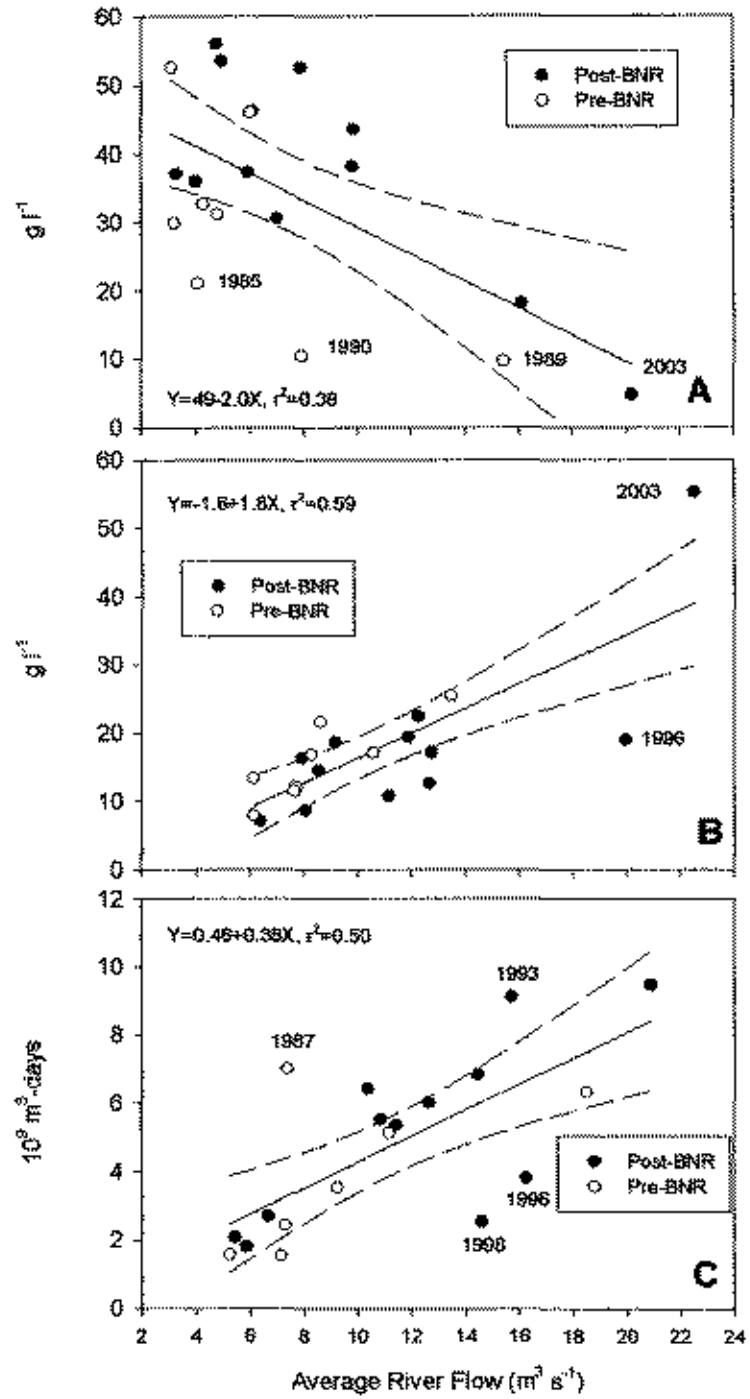


Figure 13a

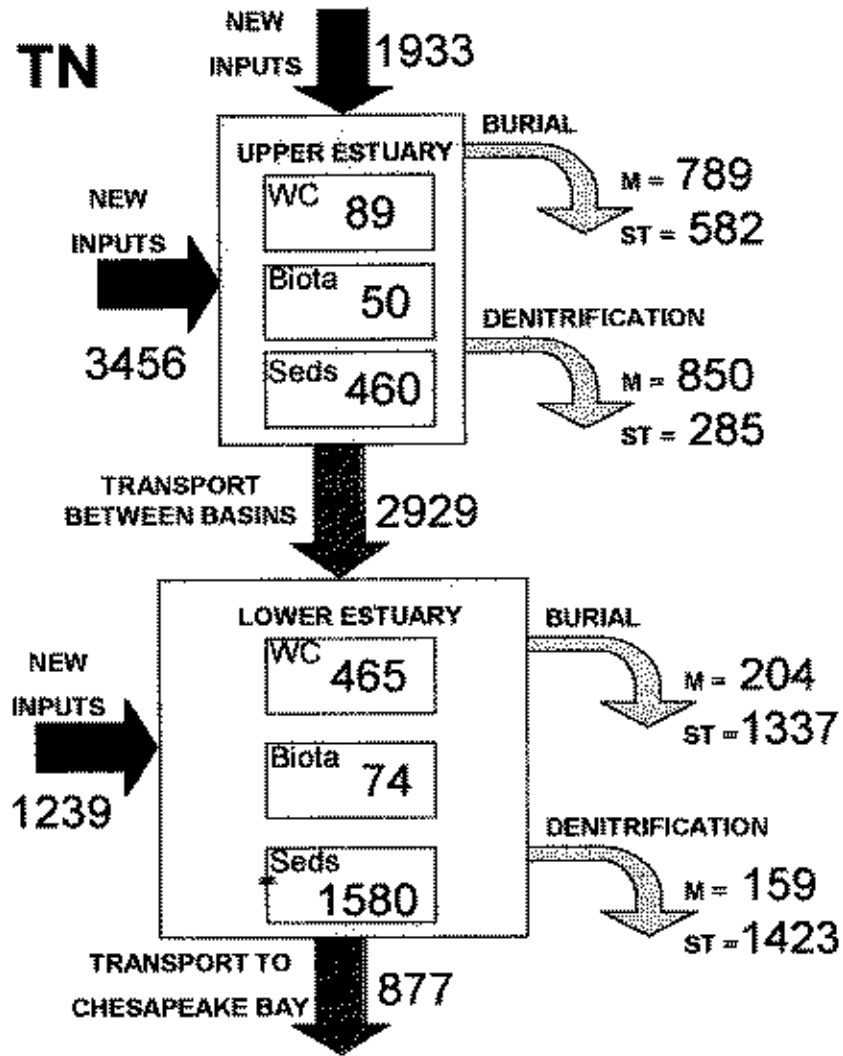


Figure 13b

