

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

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**Abstract** Multi-year nitrogen (N) and phosphorus (P) budgets were developed for the Patuxent River estuary, a seasonally stratified and moderately eutrophic tributary of Chesapeake Bay. Major inputs (point, diffuse, septic, and direct atmospheric) were measured for 13 years during which, large reductions in P and then lesser reductions in N-loading occurred due to wastewater treatment plant improvements. Internal nutrient losses (denitrification and long-term burial of particulate N and P) were measured in tidal marshes and sub-tidal sediments throughout the estuary as were nutrient storage in the water column, sediments, and biota. Nutrient transport between the oligohaline and mesohaline zones and between the Patuxent and Chesapeake Bay was estimated using a salt and water balance model. Several major nutrient recycling terms were directly and indirectly evaluated and compared to new N and P inputs on seasonal and annual time-scales. Major

findings included: (1) average terrestrial and atmospheric inputs of N and P were very close to the sum of internal losses plus export, suggesting that dominant processes are captured in these budgets; (2) both N and P export were a small fraction (13% and 28%, respectively) of inputs, about half of that expected for N based on water residence times, and almost all exported N and P were in organic forms; (3) the tidal marsh-oligohaline estuary, which by area comprised ~27% of the full estuarine system, removed about 46% and 74% of total annual upland N and P inputs, respectively; (4) recycled N and P were much larger sources of inorganic nutrients than new inputs during warm seasons and were similar in magnitude even during cold seasons; (5) there was clear evidence that major estuarine processes responded rapidly to inter-annual nutrient input variations; (6) historical nutrient input data and nutrient budget data from drought periods indicated that diffuse nutrient sources were dominant and that N loads need to be reduced by about 50% to restore water quality conditions to pre-eutrophic levels.

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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) and estimates are now available concerning the magnitude of nutrient discharges

to estuarine and coastal ecosystems at global (Kroeze 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 (Conley 2000; Rabalais 2002). 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, much 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, and better understood at time and space scales relevant to systems ecology and estuarine management. Whole-system nutrient budgets have been used as quantitative frameworks to examine estuarine N and P inputs, transformations, transport, and fate. They have been useful as management tools (e.g. D'Elia et al. 2003) and have led to better understanding of estuarine nutrient dynamics (Nixon et al. 1996). Unfortunately, nutrient budgets are also relatively rare, probably because several of the required budget components are not commonly measured in estuarine monitoring programs (e.g., denitrification, burial of N and P, nutrient export) and budget development requires collaboration across scientific disciplines.

The Patuxent River estuary, a tributary of Chesapeake Bay, is a well-monitored and studied estuarine ecosystem. There is a substantial time series of nutrient inputs from point, diffuse, and atmospheric sources which includes years with above-average, average, and below-average rainfall. Measurements of water column nutrient stocks, phytoplankton primary production and biomass, zooplankton, and benthic invertebrate biomass and sediment nutrient releases have been made monthly or bi-monthly for two decades. Newer data sets include burial rates of N and P in sub-tidal areas and inter-tidal marshes and denitrification rates in these same habitats (Merrill 1999; Greene 2005a). A salt-and-water balance model was developed for estimating physical N and P transport between the oligohaline and mesohaline portions of the estuary and at the junction of the Patuxent estuary with Chesapeake Bay (Hagy et al. 2000); in most earlier nutrient budgets physical transport terms were obtained by subtracting internal nutrient losses from landside inputs (Boynton et al. 1995). Finally, a nutrient management plan, focused on point source nutrient reductions, was implemented in the Patuxent basin. Beginning in the mid-1980s, a phosphate detergent ban and phosphorus removal at all major sewage treatment plants was instituted

and by 1993 nitrogen was also being removed during warm seasons at all major treatment plants (D'Elia et al. 2003). Regional climate conditions also varied during this period of time. On average, conditions were drier during the early part of the record (1985–1990) and wetter later in the record (1993–2000).

The overall objective of this work was to produce well-constrained budgets for N and P for this estuarine system. More specifically, these budgets were used to examine the following: (1) inter-annual variability of nutrient inputs and estuarine responses to this variability; (2) regional differences in estuarine nutrient dynamics; (3) influences of tidal marshes on nutrient fate in the estuary and; (4) the effects of major nutrient management actions on this coastal plain estuary. These issues are not unique to the Patuxent system; lessons learned here have relevance to other temperate zone estuaries.

### Description of the Patuxent Basin and Estuary

The Patuxent River basin encompasses 2,256 km<sup>2</sup> of land, 143 km<sup>2</sup> of open tidal waters and 29 km<sup>2</sup> of tidal marshes; inter-tidal area is very small (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). 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; Fisher et al. 2006).

Human population in the Patuxent basin was about 30,000 (13 km<sup>-2</sup>) in 1900. The basin remained very rural until about 1960 when rapid population growth began, a trend that continues to the present (Table 1). During a recent 10-year period (1992–2001) population increased by 36, 14, and 50% in the upper, mid, and lower basins, respectively. Population density in 2001 was highest in the upper basin (356 km<sup>-2</sup>) and less than half that in the mid (154 km<sup>-2</sup>) and lower (157 km<sup>-2</sup>) basins. Population density in mid-Atlantic basins averaged 317 km<sup>-2</sup> in 1990, similar to the density of the upper Patuxent basin (Basta et al. 1990).

The dominant land use in the Patuxent basin as of 2001 (Homer et al. 2004) was forested lands (40%); the percentage decreased from the lower (47%) to upper basin (26%). Agricultural land uses accounted for 44% of the upper watershed and a smaller proportion in the middle and lower basins. Urban, suburban, and other developed land uses were highest in the upper basin (22%) and lower elsewhere. These data reflect ongoing conversion of forest and agricultural land to residential and urban uses.

The Patuxent River and estuary are about 170 km in total length; the lower 95 km are tidal (Fig. 1). The upper portion of the tidal estuary, from river kilometer (rkm) 40 to 95, is

**Table 1** Summary of 1992 (Pre-BNR) and 2001 (Post-BNR) land cover in the Patuxent River watershed by region and for the full watershed

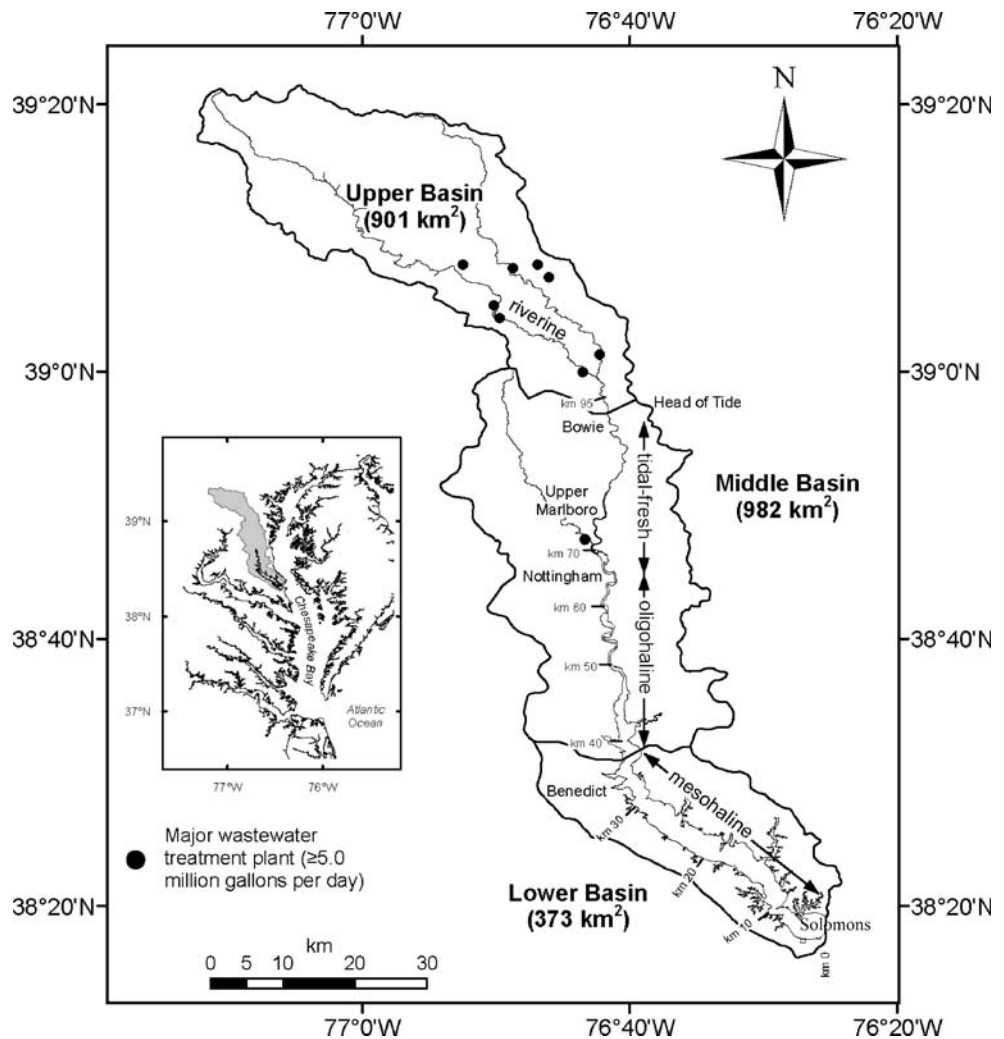
	1992 (Pre-BNR)				2001 (Post-BNR)			
	Upper	Mid	Lower	Whole	Upper	Mid	Lower	Whole
Population	261	135	104	181	356	154	157	235
Developed	14	10	6	11	22	15	7	17
Forest	38	43	49	42	30	46	47	40
Row crop	7	13	6	9	14	10	6	11
Pasture/hay	31	21	12	23	30	21	14	23
Other	10	13	27	15	4	8	26	9

Land cover (% of total) for both periods was obtained from the National Land Cover Database (Homer et al. 2004). Some differences in land cover may be attributable to methodological differences between the 1992 and 2001 assessments. Dates are nominal and represent the center of the period from which satellite imagery was obtained. Land-use categories are aggregations of reported land-use classifications. Developed land includes all densities of developed land, including land developed as open space. "Other" is largely open water, wetlands, and several other categories. Population data (density, km<sup>-2</sup>) is from Chesapeake Bay Watershed Model Land Use and Linkages to the Airshed and Estuarine Models (2000). Areas of Upper, Mid, Lower, and Whole Basin are 901, 982, 373, and 2,256 km<sup>2</sup>.

narrow (50–300 m wide), very turbid ( $K_d=3.0\text{ m}^{-1}$ ), vertically well-mixed, and has a tidal range of 0.5–1.0 m and an average depth of 1.1 m. In addition, this portion of the estuary is flanked by extensive tidal freshwater and salt marshes with the ratio of marsh area to river distance ranging from 0.4 to

0.8 km<sup>2</sup> km<sup>-1</sup> of river. The surface area of the upper estuary is  $26 \times 10^6\text{ m}^2$ . The lower estuary (rkm 40 to mouth at Chesapeake Bay) is much wider (1 to 5 km), deeper (mean depth=5.4 m), clearer ( $K_d=0.9\text{ m}^{-1}$ ) and seasonally stratified. The surface area of the lower estuary is  $117 \times 10^6\text{ m}^2$ .

**Fig. 1** Map showing regional location (a) and spatial details (b) of the Patuxent basin and Patuxent River estuary

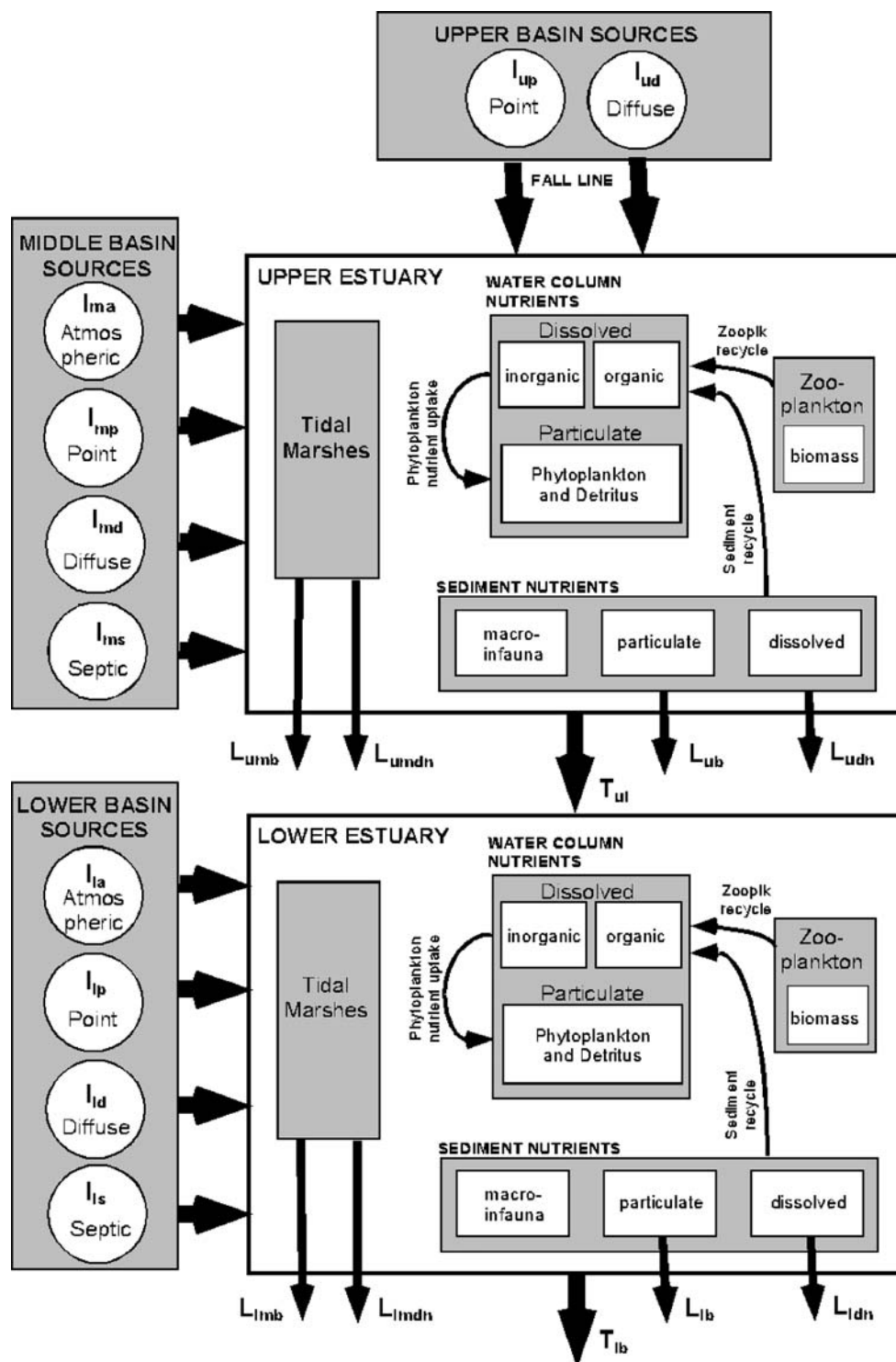


## Budget Framework, Data Sources, and Computational Issues

### Conceptual Model

A detailed nutrient budget conceptual model was developed for this analysis but it still represents a compromise

**Fig. 2** Conceptual model of the nutrient budgets evaluated for the Patuxent River estuary. Geographic boundaries are shown in Fig. 1. The model is described in the text. Abbreviations on the diagram are as follows:  $I$  inputs,  $L$  internal losses due to long-term burial or denitrification,  $T$  transport between estuarine regions or Chesapeake Bay. Subscripts  $u$ ,  $m$ , 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



between the current understanding of major nutrient processes and the temporal and spatial availability of data to evaluate model terms (Fig. 2). In this model the drainage basin was treated as three distinct units (upper, middle, and lower basins). The estuary was divided into upper and lower portions corresponding to the tidal fresh/oligohaline and mesohaline zones, respectively (Fig. 1). The conceptual

model includes four classes of nutrient inputs, four internal loss terms for N and two for P, eight storage categories, three nutrient cycling pathways and two net nutrient transport terms. Nutrient budget computations were conducted on several temporal scales including seasonal, annual, and before and after major sewage treatment plant modifications. The latter represent averaging over years prior to implementation of biological nitrogen removal (pre-BNR; 1985–1990) and after full implementation of BNR (post-BNR; 1993–1999). The years 1991 and 1992 were not included in this averaging scheme because some of the major sewage treatment plants were still in the process of adding BNR capabilities.

Four classes of nutrient inputs (left and top of Fig. 2) include point, diffuse, septic, and atmospheric sources. The atmospheric term includes only 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 monitoring of river flow and nutrient concentrations; diffuse sources from the middle and lower basins were estimated using a land-use model (septic sources not included in diffuse sources). Septic sources were estimated separately based on population living in homes not served by sewer systems. Nitrogen fixation was not directly evaluated in this budget but was probably a small source, as is the case for most nutrient-rich, temperate estuarine systems (Howarth et al. 1988; Marino et al. 2002). 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, and net transport of N and P at the downstream boundary of the two estuarine segments. Major nutrient pools and several nutrient cycling processes (net sediment N and P releases, zooplankton excretion, and phytoplankton nutrient demand) were included in this analysis to allow estimates of turnover times and evaluation of the relative importance of “new” versus “recycled” nutrients.

#### Data Sources and Computational Issues

All data sources used in this analysis are listed in Table 2; all variables shown in the conceptual model (Fig. 2) are listed there as well. Concise descriptions of variables, and information regarding measurement frequency, duration of record, measurement technique, are also provided. All primary data sources are contained in this table.

The magnitude and sources of uncertainty, the extent to which uncertainty from various sources propagates through the computations, and the possible impact of

uncertainty on the main conclusions was evaluated. The approach is necessarily incomplete, leaving significant work for the future. Where possible, quantitative estimates were developed, relying on Lehrter and Cebrian (2008), who develop and present mathematical approaches for quantifying uncertainty in a variety of ecological estimates commonly present in nutrient budgets. Their approach, which relies on well-accepted mathematical formulas, was used to compute the standard errors of sums, products, quotients, and multi-annual or other averages when reasonable estimates of the uncertainty of inputs to such operations could be made. We assumed that the errors associated with all the terms were independent, since we did not have an estimate of their covariance. Where errors are highly correlated, they tend to increase in sums, rather than decrease. We have considered this assumption in our interpretation of the results. Where a fully quantitative derivation of uncertainty could not be developed, uncertainty estimates were based on the expert opinion of scientists who generated the estimates. These uncertainty estimates were then propagated through subsequent computations utilizing the appropriate formulae. We have not attempted to quantify the uncertainty associated with estimates of tidal transport because it is beyond the present state of the science and not possible in this study.

The precision to which terms in the nutrient budgets are reported is based on either best professional judgment or, where possible, the quantitative analysis of uncertainty.

## Results and Discussion

### Nutrient Inputs

*Inter-Annual Variability* We begin by examining TN, TP, 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 4,300 to 8,600 kg N d<sup>-1</sup> and 3,200 to 6,000 kg N d<sup>-1</sup>, respectively, and averaged 6,200 and 4,300 kg N d<sup>-1</sup> (Fig. 3). Annually averaged DIN loads were correlated with TN loads ( $r^2=0.71$ ;  $p<0.01$ ) and averaged 69% of TN loads during the study period. TP and DIP loading rates ranged from 210 to 780 kg P d<sup>-1</sup> and 110 to 410 kg P d<sup>-1</sup>, respectively, and averaged 450 and 240 kg P d<sup>-1</sup> during the same period (Fig. 3). DIP loads also closely tracked TP loads ( $r^2=0.92$ ;  $p<0.01$ ) and averaged 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). The observed inter-annual variability exceeds the annual load reductions (~40%) that management agencies are trying to achieve in this estuary.

**Table 2** A description of nutrient budget variables, measurement frequency, duration of record, measurement techniques/computations and data sources

Specific variable	General description	Measurement frequency	Duration of records	Measurement technique
1 Point sources	Includes all major ( $>10^6$ gpd) point discharges of TN and TP	Discharge volume~continuous. Concentrations ~weekly to monthly	1985–1999	Standard flow gauges and wet chemical techniques
2 Diffuse sources	Includes diffuse TN and TP loads from all portions of the basin; DIN and DIP loads also estimate does not include septic loads	Discharge volume~continuous. Concentrations ~weekly to monthly. Modeling period 1985–1997	1978–present NA	Upper basin diffuse loads based on measurements of flow and nutrient concentration at head of tide. Other basin diffuse loads estimated from Ches. Bay Program HSPF model (monthly estimates)
3 Septic sources	Septic system DIN reaching streams draining basin: P loads assumed to be zero	Estimates based on literature values;	NA	Fraction of population served by septic, average N excreted per person per year; 40% of N reaches stream segment
4 Direct atmospheric deposition (wet and dry)	Wet deposition of $\text{NO}_3^- + \text{NH}_4^+$ + organic N and dry deposition of $\text{HNO}_3/\text{NO}_3^- + \text{NH}_3$ to surface water of estuary; P deposition from literature	Rainfall~continuous; nutrient concentrations during many rain events. Dry fall collections~9 days	1984–1999 1997–1999	Rain gauges and wet chemical techniques Acid impregnated glass fiber filters; honeycomb denuder/filter pack
5 Water column	Vertically averaged and spatial extrapolated concentrations of TN, TP, DIN, and DIP	16–20 times year <sup>-1</sup> ; 13 locations along estuarine axis	1985–1996	Shipboard sampling, filtering, and freezing; standard wet chemical techniques
6 Biota	Includes macrozooplankton and benthic infauna biomass in N and P equivalents	4–16 times year <sup>-1</sup> ; upper and lower estuary sites for zooplankton and 5–11 sites for infauna	1985–1999	Zooplankton sampled with 202u mesh paired bongo nets; infauna sampled with various grabs and sieved with 0.5 mm screen
7 Sediments	Mass of PN and PP in surface 2 cm of sediments	Occasional from ~30 locations	1985–1999	Sediments sampled with box corer; PN analyses via high temperature combustion; PP via combustion and acid extraction
8 Plankton uptake	Phytoplanktonic N and P demand estimated via Redfield C:N:P ratio (106:16:1)	10–16 times year <sup>-1</sup> ; upper and lower estuary sites	1986–1999	C fixation via <sup>14</sup> C incubations (4 hrs); short-term rates extrapolated to day periods and then to N and P uptake via Redfield ratios
9 Net Sediment releases	Sediment releases of dissolved N and P to the water column	4–6 times year <sup>-1</sup> ; 4 to 12 sites	1985–2000	Shipboard incubation (in the dark; 4 h) of intact sediment cores
10 Zooplankton excretion	Excretion rates of N for macrozooplankton community	4–16 times year <sup>-1</sup> ; upper and lower estuary sites	1985–1999	Abundances converted to dry weights and N excretion estimated using equation of Mauchline 1998
11 Transport between estuarine zones and Chesapeake Bay	Net transport of TN, TP, DIN, and DIP between upper and lower estuary and between lower estuary and Chesapeake Bay	Estimates computed on a monthly basis	1985–1999	Two layer salt-and-water balance model for advective and diffusive transport; nutrient concentrations coupled to model to obtain nutrient transport rates

Table 2 (continued)

Specific variable	General description	Measurement frequency	Duration of records	Measurement technique
<b>12 Sediment denitrification</b>	Tidal marsh and sub-tidal measurements of N loss via denitrification	4–10 times year <sup>-1</sup> at 6–18 sites	1999; 2000; 2004	Sediment core time course incubations of N <sub>2</sub> change based on N <sub>2</sub> :Ar ratio
<b>13 Sediment long-term burial</b>	Long-term burial of PN and PP in the accreting sediment column	29 marsh and 6 sub-tidal cores collected once; sediments PN and PP profiles from many sites and all cores	1999; 2004	Sedimentation rates via vertical <sup>210</sup> Pb profiles coupled with sediment PN and PP concentrations following the technique of Cornwell et al. 1996

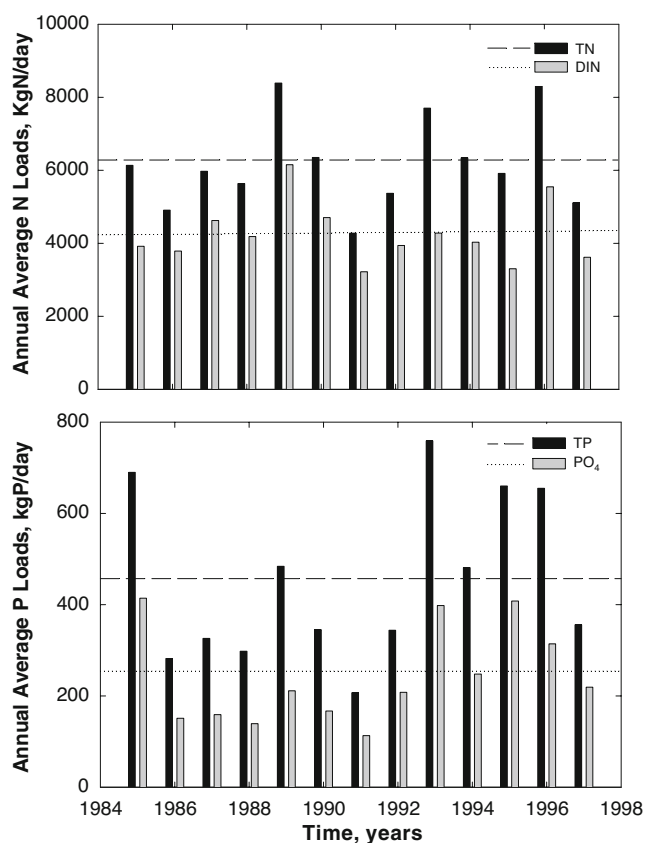
All variables listed here are also indicated in Fig. 2. Further details concerning nutrient budget variables are contained in legends and footnotes of tables and figures. Field and modeling data specific to this budget computation are in bold italics in the Specific variable column. (1) Wiedeman and Cosgrove 1998; Chesapeake Bay Program 2001 (2) Donigian et al. 1994; Linker et al. 1999; Langland et al. 2001; Shenk and Linker 2001 (3) Maizel et al. 1997 (4) Smullen et al. 1982; Wies and O'Melia 1989; Jordan et al. 1995; Hu et al. 1998; Larsen et al. 2001; NADP 2001 (5) Chesapeake Bay water Quality Monitoring Program 2001 (6) Jorgensen et al. 1991; Waive and Larsson 1999; Chesapeake Bay Benthic monitoring Program 2001; Chesapeake Bay Zooplankton Monitoring Program 2001 (7) Boynton and Rohland 2001; Keefe et al. 2004 (8) Chesapeake Bay Phytoplankton Monitoring Program 2001 (9) Boynton et al. 1982a; Boynton and Rohland 2001 (10) Heinle 1966; Jorgensen et al. 1991; Mauchline 1998; Chesapeake Bay Zooplankton Monitoring Program (11) Hagy et al. 2000; Chesapeake Bay Water Quality Monitoring Program 2001 (12) Jenkins and Kemp 1984; Twilley and Kemp 1987; Kana et al. 1994; Merrill 1999; Merrill and Cornwell 2000; Greene 2005a (13) Boynton and Kemp 1985; Boynton et al. 1995; Cornwell et al. 1996; Merrill 1999; Merrill and Cornwell 2000; Greene 2005a

*Relationships to Regional Climate Conditions* A portion of the variability in nutrient loading rates was associated with variability in local weather conditions. Annual average river flow at the head of tide (HoT) ranged from 5.5 to 17.5 m<sup>3</sup> s<sup>-1</sup> and averaged 10.3 m<sup>3</sup> s<sup>-1</sup> during 1978–2003. River flow was generally highest during the winter and spring and lowest during summer and fall. However, there were several exceptions to this pattern. During two drought years (1992 and 1995), river flow was low all year, whereas flow remained relatively high all year during 1996, and peak flow in 1989 was delayed until late spring.

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<sup>-1</sup>/m<sup>3</sup> s<sup>-1</sup> and 65 kg P d<sup>-1</sup>/m<sup>3</sup> s<sup>-1</sup>, 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 implement BNR was initiated in the early 1990s 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 m<sup>3</sup> s<sup>-1</sup>), whereas wetter conditions prevailed for 4 of the 5 years of the post-BNR period (average river flow=13.0 m<sup>3</sup> s<sup>-1</sup>).

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. 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 nutrients occurred during 1991, a dry year (TN=4,300 kg N day<sup>-1</sup>; TP=210 kg P day<sup>-1</sup>). The highest loads for all nutrients, other than DIP, occurred during wet years (1989, 1993, and 1996; TN=8,600 kg N day<sup>-1</sup>; TP=760 kg P day<sup>-1</sup>). Highest DIP loads occurred during 1985 (a dry year) before P was removed from major sewage discharges throughout the basin. Management actions to reduce P at sewage treatment plants were evident at the whole watershed scale. In contrast, highest TN loading occurred after implementation of BNR and the lowest TN loading



**Fig. 3** Annual average TN, DIN, TP, and PO<sub>4</sub> loading rates (kg N or P day<sup>-1</sup>) 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

occurred before implementation. Thus, at the whole watershed scale, changes in diffuse sources associated with rainfall overwhelmed improvements in wastewater treatment. Nonetheless, nutrient removal at treatment plants clearly reduced both P and N loads from the upper basin (above HoT), where eight of the nine major sewage treatment plants are located. At a sub-basin scale, load reductions for both nutrient groups were evident.

#### Loading Rates Relative to Other Estuarine Systems

Among 34 estuarine systems, annual nutrient loading rates from adjacent watersheds ranged over several orders of magnitude, from 1.1 to 190 g N m<sup>-2</sup> year<sup>-1</sup> and from 0.1 to 32 g P m<sup>-2</sup> year<sup>-1</sup> (Fig. 4). The 1985–1997 average loads of TN and TP to the Patuxent River estuary were 15.8 g N m<sup>-2</sup> year<sup>-1</sup> and 1.2 g P m<sup>-2</sup> year<sup>-1</sup>, moderate compared to many other sites. Multi-year TN and TP input data for a few estuaries indicate that inter-annual variability can be

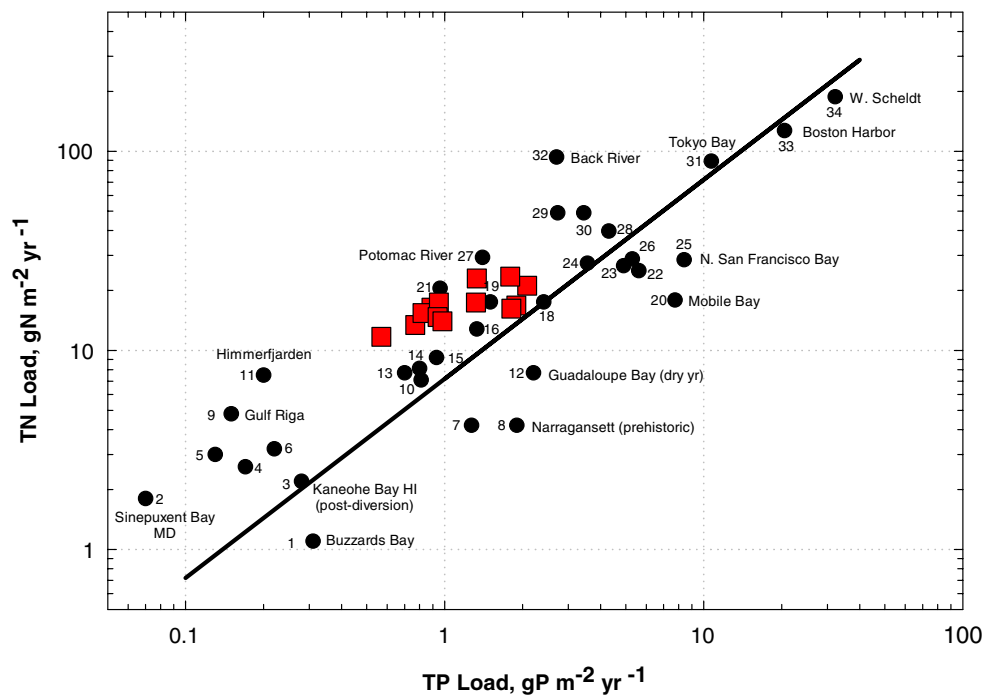
large, but is not as large as the variability among systems. For example, TN and TP load to the Guadalupe estuary varied by factors of 3.7 and 2.5, respectively. In comparison, TN and TP loading to the Patuxent varied by 2.0 and 2.6, respectively. Kaneohe Bay, HI is an example of significant loading reductions resulting from a diversion of wastewater out of the Bay; TN and TP loads were reduced 2.0 and 4.5-fold respectively.

Among the same 34 estuaries, N:P ratios (mass basis) of inputs ranged from 2 to 38, bracketing the Redfield ratio (N:P=7.2:1 mass ratio). About a quarter of these locations (9 of 34) had load ratios that were considerably lower (<5) than the Redfield ratio while 50% (18 of 34) had ratios equal to or higher than 9. The ratio for Patuxent River was 14. Although point source dominated systems tend to have lower load ratios (Boynton et al. 1995) this is not always the case. For example, several systems (Himmerfjarden, Back, and Potomac River estuaries) had very high load ratios (38) even though point sources were the dominant nutrient source because P (and not N) was removed from sewage treatment plant effluent.

#### Components of Nitrogen and Phosphorus Loads

**Atmospheric Deposition** An annual time series of total atmospheric nitrogen deposition was constructed for the Patuxent from 1985 to 1999 (NADP 2001). In this time series, TN was composed of wet deposition of NH<sub>3</sub> and NO<sub>3</sub>, dry deposition of HNO<sub>3</sub> and NO<sub>3</sub>, and net dry exchange of NH<sub>3</sub>/NH<sub>4</sub>. Atmospheric deposition ranged from 580 to 1130 mg N m<sup>-2</sup> year<sup>-1</sup>, averaged 810 mg N m<sup>-2</sup> year<sup>-1</sup>, and was generally higher in wet years (e.g., 1989, 1994) than in dry years (e.g., 1985, 1987, 1992). 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 ranged from about 30 to 120 mg N m<sup>-2</sup> month<sup>-1</sup> and was higher during late spring and summer than during fall and winter (Fig. 5). Consequently, direct atmospheric TN deposition to the estuary contributed a larger proportion of the overall TN load during summer, when diffuse sources are at a seasonal minimum. The impact on phytoplankton production is likely more direct because much of the atmospheric N deposition to the surface waters is in a chemical form directly available to phytoplankton (Paerl 1997). The dominant form of N deposition was wet fall NH<sub>x</sub>+NO<sub>3</sub>, comprising about 67% of the total followed by organic N (17%) and all measured forms of dry fall N (15%; NADP 2001). Direct N deposition to the surface waters of the estuary was largest in the lower estuary, where estuarine surface area was large, and minor in the upper estuary. In the lower estuary, annual N loads from atmospheric deposition averaged 360 kg N day<sup>-1</sup> and were larger in



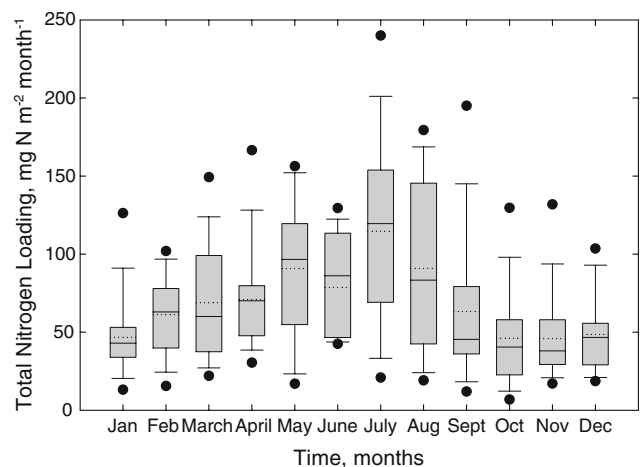


**Fig. 4** A scatter diagram showing annual TN and TP loading rate to a selection of coastal, estuarine, and lagoon ecosystems. Systems are coded by number as follows: 1 Buzzards Bay MA (NOAA/EPA 1989), 2 Sinepuxent Bay MD (Boynton et al. 1996), 3 Kaneohe Bay HI, post-diversion (Smith 1981), 4 Isle of 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 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 Himmerfjarden 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 (1×) 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 Patapsco River Estuary MD (Stammerjohn et al. 1991), 31 Tokyo Bay Japan (Nixon et al. 1986b), 32 Back River MD (Boynton et al. 1998), 33 Boston Harbor, pre-sewage diversion (Nixon et al. 1996), 34 Western Scheldt Netherlands (Nixon et al. 1996). Loads to the Patuxent River estuary for the years 1985–1997 are shown as *solid squares*. The *solid diagonal line* represents the Redfield ratio of TN:TP inputs (mass basis)

spring and summer than in fall and winter. The available data concerning atmospheric P deposition in this region indicated that atmospheric P loading rate was a small fraction (<10%) of total P inputs to the estuary on both seasonal and annual time scales (Boynton et al. 1995).

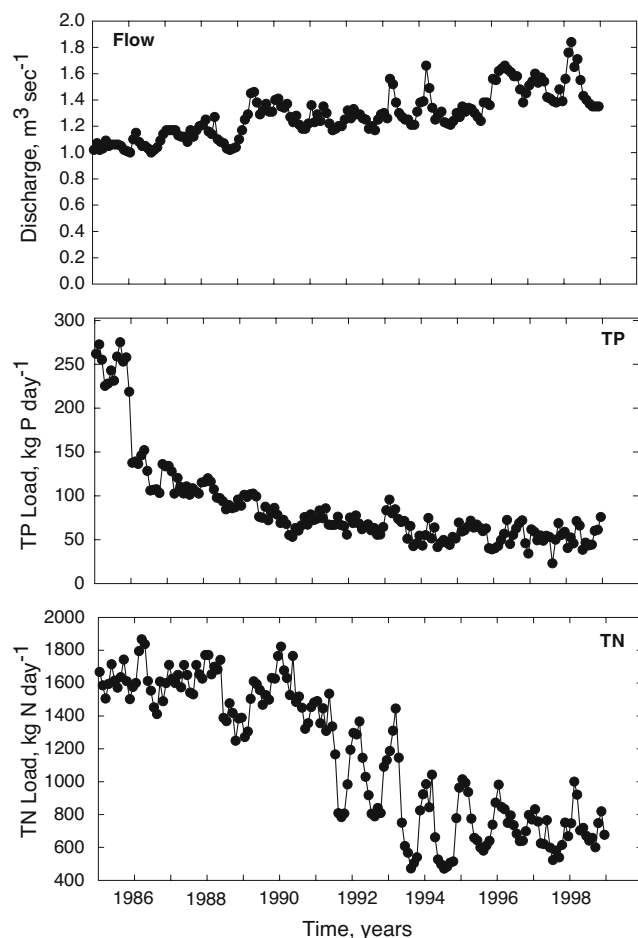
The impact of atmospheric N deposition to estuaries is underestimated when only direct deposition to the surface waters is considered. Regional assessments of nitrogen additions and losses from landscapes have become more common and some have focused on estimating the portion of N export from landscapes resulting from atmospheric deposition of N (Howarth et al. 1996). In the case of the Chesapeake Bay basin Fisher and Oppenheimer (1991) and more recently Castro et al. (2003) estimated that about 25% and 22%, respectively, of atmospheric N deposition to the landscape is exported 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,



**Fig. 5** Box and whisker plot of monthly atmospheric TN deposition rate. Data were collected at the NADP site at Wye, MD (NADP 2001) and were averaged from 1985–1999. See text for components of TN wet deposition

about  $990 \text{ kg N day}^{-1}$  would reach estuarine waters as a component of diffuse source loading, or about 16% of the total diffuse source load.

**Point Sources** Point sources of N and P were substantially reduced during the past two decades by improvements to wastewater treatment, with first a P-ban in detergents followed by P removal (1986) and then seasonal N removal (1993). Seasonal biological N removal reduced TN concentrations in effluents from  $\sim 18 \text{ mg l}^{-1}$  to  $4 \text{ mg l}^{-1}$  during summer and fall seasons. Point source loads of TP declined from about  $250 \text{ kg P day}^{-1}$  before upgrades to about  $60 \text{ kg day}^{-1}$  following upgrades (Fig. 6). TN loads from wastewater prior to seasonal N removal did not vary seasonally but varied between  $1,200\text{--}1,900 \text{ kg day}^{-1}$  among years. Seasonal N removal resulted in summer and fall loads about 30% lower (summer loads  $\sim 500\text{--}600 \text{ kg N day}^{-1}$ ) than in cooler seasons (winter loads  $\sim 900\text{--}1000 \text{ kg N day}^{-1}$ ). Because efficiency of P removal is not temperature-



**Fig. 6** Time-series plot of average monthly sewage treatment plant discharge, TP and TN loads from above HoT in the Patuxent River basin. The distinct oscillation in TN load is due to seasonal removal of N via denitrification at these facilities. Data were from Chesapeake Bay Program (2001) and Wiedeman and Cosgrove (1998)

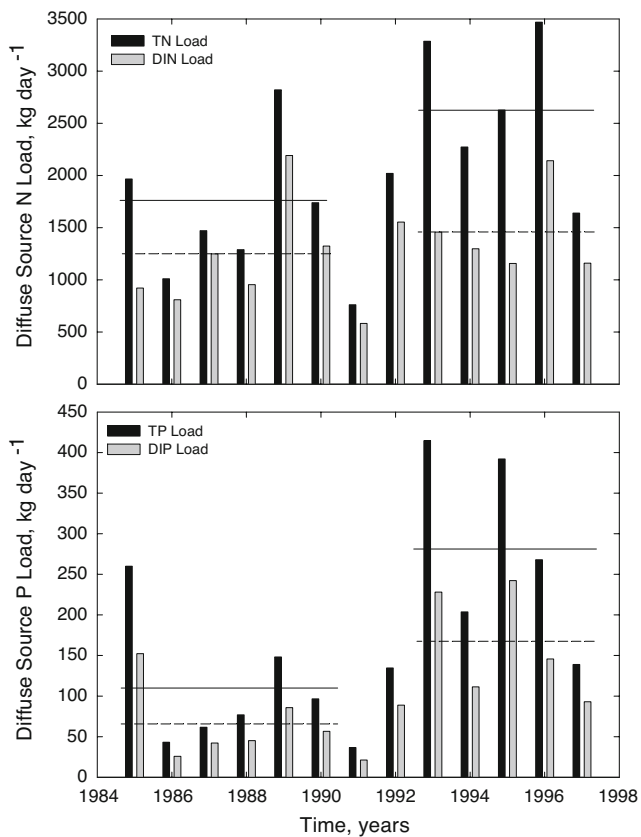
sensitive, there were very small seasonal variations in P loads (Wiedeman and Cosgrove 1998; Chesapeake Bay Program 2001).

One important aspect of point source N and P loads is that it is predominantly in dissolved inorganic forms, with the remainder in dissolved organic form. For sewage N, 92% and 82% of the load was DIN during the pre- and post-BNR periods, respectively. 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 total N or P to the estuary, the fact that most was in chemical forms directly available for algal assimilation increases the importance of this source (Chesapeake Bay Program 2001).

**Diffuse Sources** Diffuse nutrient loading rates varied markedly from year to year, generally in association with wet or dry years (Fig. 3). For TN, annual average diffuse loads from the middle basin ranged from 760 to  $3,500 \text{ kg N day}^{-1}$  and averaged  $1,700$  and  $2,700 \text{ kg N day}^{-1}$  for the pre- and post-BNR periods, respectively. For the same region, P loads ranged from 40 to  $420 \text{ kg P day}^{-1}$  and averaged 110 and  $280 \text{ kg P day}^{-1}$  during the pre- and post-BNR periods, respectively (Fig. 7). Diffuse source loads of N were the largest single source category both before and after BNR implementation; diffuse sources of P were slightly smaller than point sources before P removal at sewage treatment plants was implemented. The proportion of diffuse TN loads as DIN varied from 44 to 85% of TN (average=67%), 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 that correlated with river flow. During the pre-BNR years, TN loads at HoT averaged about  $2300 \text{ kg N day}^{-1}$  during winter–spring and about  $1,450 \text{ kg N day}^{-1}$  during summer–fall. During the generally wetter post-BNR years these averages were  $2,700 \text{ kg N day}^{-1}$  and  $1,200 \text{ kg N day}^{-1}$ , for winter–spring and summer–fall, respectively.

**Septic Sources** At the basin level, N estimated to come from septic systems was relatively small (<5% of total N inputs to the middle basin and <2% of total N loads to the lower basin). Total septic inputs were 300 and  $340 \text{ kg N day}^{-1}$  in pre- and post-BNR periods, respectively. However, in a few heavily developed, but un-sewered, residential areas adjacent to tidal creeks, septic system N appeared to be a dominant local source (Barnes et al. 2004). Septic system P was assumed to be effectively bound to sub-surface soils and to 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. 8), illustrating several important find-



**Fig. 7** Time-series plots of diffuse source *TN*, *DIN*, *TP*, and *DIP* loads from the middle basin of the Patuxent River estuary. *Horizontal lines* represent average inputs of *TN* and *TP* (*solid lines*) and *DIN* and *DIP* (*dashed lines*) for the pre (1985–1990) and post-BNR periods (1993–1997). These model-generated estimates were from Shenk and Linker (2001)

ings. 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. TN and TP loads from point sources in the upper basin decreased from 1600 to 740 kg N day<sup>-1</sup> and from 120 to 60 kg P day<sup>-1</sup>, respectively. Smaller reductions were also observed in the middle basin where point sources of TN and TP decreased from 740 to 450 kg N day<sup>-1</sup> and from 60 to 50 kg P day<sup>-1</sup>, 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, improved wastewater treatment substantially changed the relative importance of nutrient sources. Secondly, direct atmospheric deposition of N and P to the surface waters of the estuary was relatively small (TN~7%; TP~4%) 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, emphasizing the importance of diffuse sources in this system and the impact of climate variability.

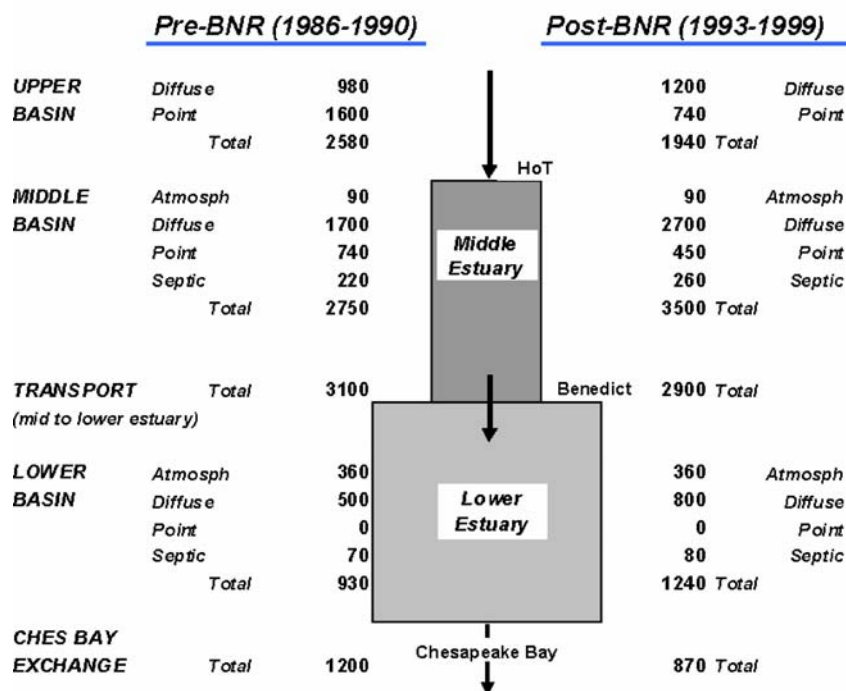
*Uncertainty in Nutrient Inputs* Although nutrient inputs were often highly variable, for example on an annual basis, the estimated uncertainty (error) associated with the inputs was often quite low. USGS (2004) reported that standard errors for the estimates of annual fall line TN and TP inputs were 2% and 4–5% of the mean, respectively. The standard errors for multi-annual means of these values are even lower. Similarly, estimates of the standard error for point source inputs are 2% and 5% for the annual TN and TP inputs, respectively, and about half that for means of several annual inputs. The uncertainty associated with loading measured at the fall line or from point sources is effectively insignificant compared to the much larger uncertainty associated with estimates based on watershed models. Standard errors for these estimates were estimated to be on the order of 15% for TN and 40% for TP. Of the atmospheric and septic inputs, the only significant sources of uncertainty were atmospheric N inputs to the lower basin, which contributed ~20% of the standard error for N inputs to that portion of the estuary. The magnitude of the other inputs was too small to impact overall uncertainty.

Propagated errors were computed for sums of all inputs averaged over the multi-annual pre-BNR and post-BNR periods. For the middle basin, the estimated standard error for TN inputs from all sources is 5% of the mean prior to BNR and 7% of the mean after BNR. The sum of TP inputs from all sources estimated with less precision, with relative standard errors of 13% for the pre-BNR period and 24% for the post-BNR period. Uncertainty is larger for both TN and TP for the post-BNR period because the relative contribution of diffuse inputs computed from the less precise watershed model was larger.

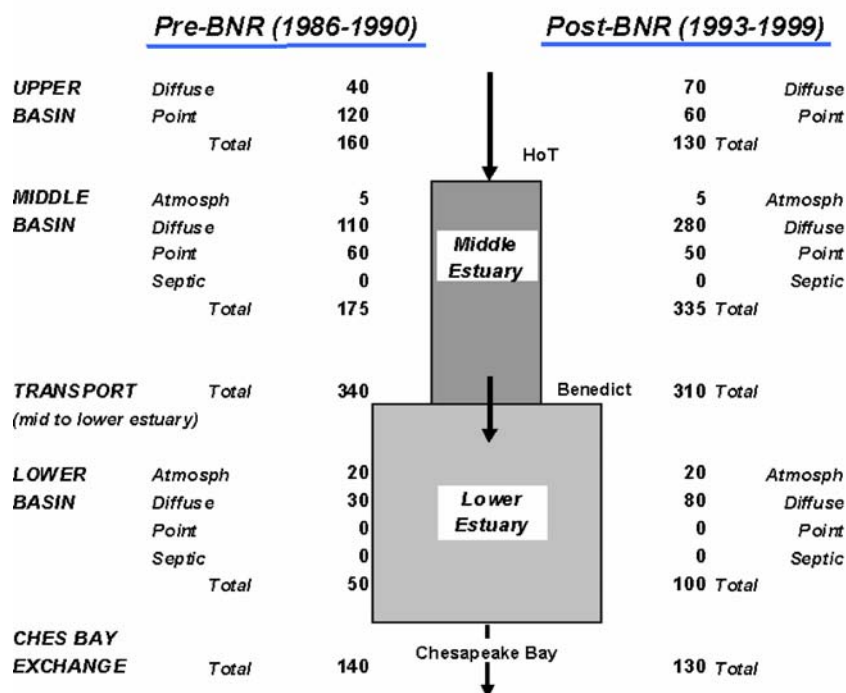
The standard error of TN inputs to the lower basin from all watershed sources (i.e., excluding tidal transport) is about 10% of the mean, greater than for the middle estuary because there is no contribution from either point sources or loads measured at a fall line. The standard error for TP loading is about 30% of the mean and was approximately the same for the pre-BNR and post-BNR periods. The much greater uncertainty associated with estimates of TP loading likely reflects the mode of transport. To a greater extent than for N, P transport in watersheds involves erosion and transport of particulates, often at the event scale. Quantifying these processes, either by measurements or models, is very challenging (Jordan et al. 2003; Williams et al. 2005).

**Fig. 8** A summary of annual TN and TP loads by source to the upper and lower Patuxent River estuary during the pre and post-BNR periods. Data sources are provided in Table 2

### TN Loading: Annual ( $\text{kg N d}^{-1}$ )



### TP Loading: Annual ( $\text{kg P d}^{-1}$ )



#### Major Storages of N and P

Water column TN concentrations were higher in both the upper and lower estuary during winter–spring than sum-

mer–fall and were 20–30% higher in the upper than lower estuary during all seasons. 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 (Table 3). 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 whole-estuary scale the annual average total mass of TN in the water column was about 580 and  $520 \times 10^3$  kg N during the pre- and post-BNR periods, respectively. Water column 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, DIP was a smaller fraction of TP than in the analogous case for N, comprising about 20% and 30% of TP in the upper and lower estuary, respectively. At the whole-estuary scale the total mass of TP in the water column was about 48 and  $36 \times 10^3$  kg P during the pre- and post-BNR periods, respectively, a decrease of about 25% following implementation of BNR technology.

Monthly estimates of benthic invertebrate biomass ranged from 4 to 19 g AFDW  $m^{-2}$  in the upper estuary and from about 1 to 10 g AFDW  $m^{-2}$  in the lower estuary. Average biomass was 13 and 4 g AFDW  $m^{-2}$ , respectively. In both the upper and lower estuary, biomass was highest during spring and lowest during fall and winter. Macrobenthic N and P biomass was  $120 \times 10^3$  kg N and  $5 \times 10^3$  kg P, representing 4.4% and 0.7% of the N and P in the system (Table 3). Thus, zooplankton represented a very small fraction of the N and P stock. Annual average N and P biomass in zooplankton was even smaller, amounting to  $5 \times$

$10^3$  kg N and  $0.8 \times 10^3$  kg P, or about 0.2 and 0.1% of the total N and P stock, respectively (Table 3).

Most of the N and even more of the P in this system were contained in the sediments. Somewhat arbitrarily, only the upper 2 cm of the sediment column was used in this analysis, so as to include only the N and P that was deposited relatively recently and still readily available to ecological processes. About 75% of TN and about 93% of TP in the system were in sediments (Table 3). We did not have a time series of sediment composition data sufficient to consider either seasonal or pre- and post-BNR changes in these values.

If all nutrient storages are combined (Table 3) 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 readily available nutrients in the system compared to new inputs of N and P. If we delete sediment storage of TN and TP from turnover computations, much shorter water column 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; Fisher et al. 2006). Thus, it also seems reasonable to expect rapid responses of such processes as those indicated above to

**Table 3** 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

Nutrient stock	Nutrient type	Upper estuary	Lower estuary	Total
Water column	TN	89	470	560
	TP	10	33	43
	DIN	46	120	170
	DIP	2	9	11
Sediments <sup>a</sup>	TN	460	1,580	2,000
	TP	160	470	630
Benthic infauna <sup>b</sup>	TN	50	70	120
	TP	2	3	5
Macro-zooplankton <sup>c</sup>	TN	1	4	5
	TP	<1	1	1
Totals	TN			2,700
	TP			680

Pre and post-BNR data have been averaged; details concerning pre and post-BNR stocks, where available, are provided in the footnotes. All values are as kilogram N or P  $\times 10^3$

<sup>a</sup> Sediment PN concentrations were 0.31 and 0.35% dry weight in the lower and upper estuary, respectively; PP values were 0.093 and 0.13% in the lower and upper estuary, respectively; sediment bulk density was 0.23 and 0.25 g  $cm^{-3}$  in the lower and upper estuary, respectively.

<sup>b</sup> N and P content of ash-free dry weight was 15 and 0.62%, respectively. There were not sufficient data to estimate differences between pre and post-BNR periods.

<sup>c</sup> Zooplankton N and P content were estimated to be 11 and 1.3%, respectively (Walve and Larsson 1999). Zooplankton dry weights ( $\mu g$ /individual) were: *Acartia* spp. adults (7.0), copepodites (3.0) from Heinle (1966); *Eurytemora affinis* adults (10.0), copepodites (5.5) from Chesapeake Bay Zooplankton Monitoring Program (2001); *Bosmina longirostris* adults and juveniles (1.6) from Jorgensen et al. (1991).

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 historically higher 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 are now largely absent. Compared to benthic biomass estimates assembled by Herman et al. (1999), Patuxent values were two to three times lower than those observed at similar levels of primary production in other estuarine systems. Second, Stankelis et al. (2003) assembled data concerning seagrass communities in the Patuxent from the late 1930s to the present. Seagrasses were once 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 that these autotrophs have largely been lost in recent decades. The status of fish stocks, both commercial and forage, is far less clear, although long-term residents uniformly insist that fish were far more abundant prior to the 1970s. 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, 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 (i.e., phytoplanktonic debris) observed under present conditions.

### Nutrient Transport

An existing box model (Hagy et al. 2000) was used to compute monthly average transport of nitrate plus nitrite, ammonium, total dissolved N (TDN), TN, DIP, total dissolved P (TDP) and TP for the pre- and post-BNR periods (Fig. 9). For our budget computations, the particulate fraction of TN and TP was assumed to be transported as if it were dissolved. However, by separately computing TDN and TDP fluxes, we were able to evaluate the possible impact that violations of this assumption could have on our conclusions. Nutrient transport rates were calculated between the upper and lower estuary and between the Patuxent estuary and the Chesapeake Bay.

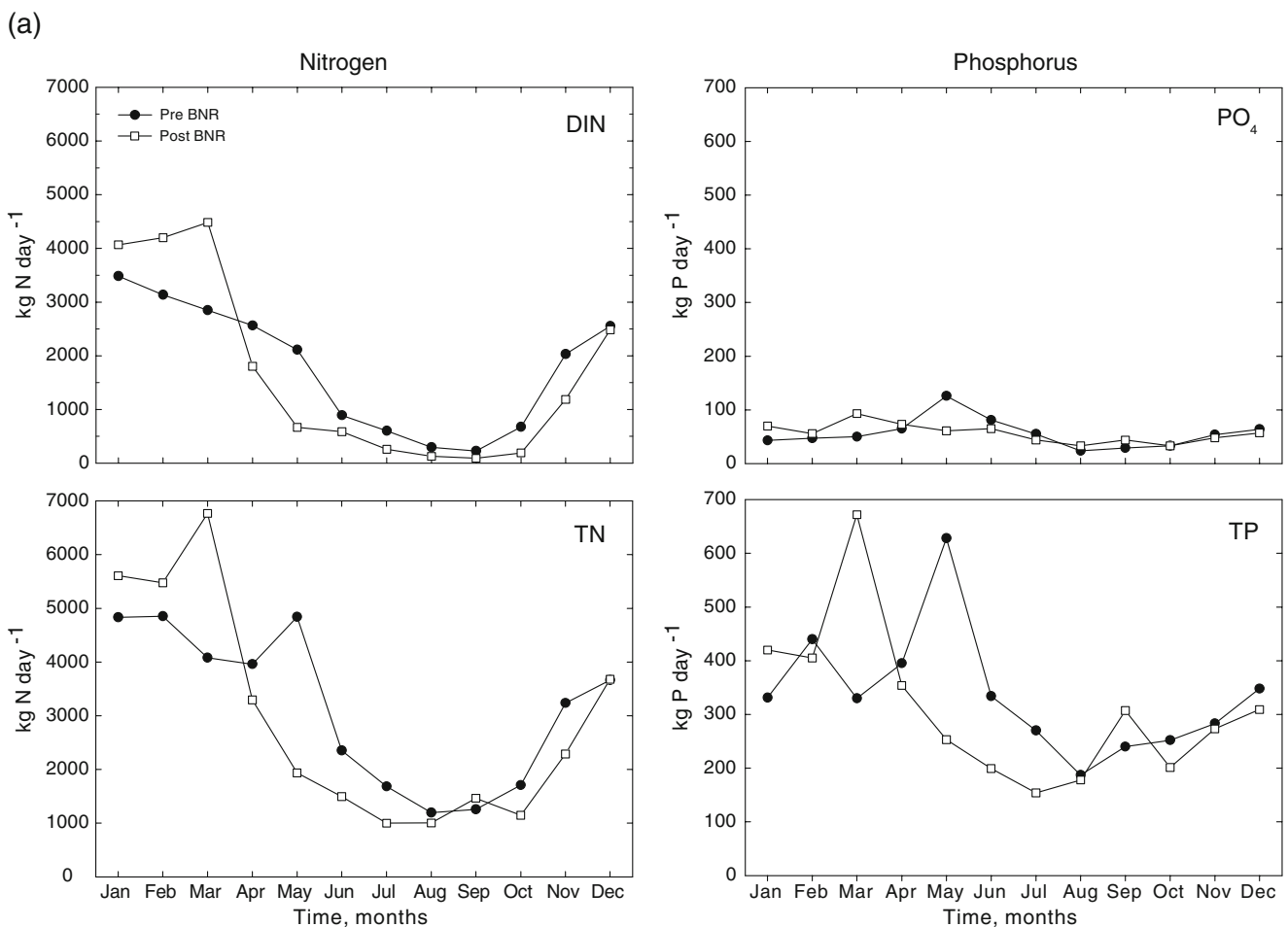
*Transport from Upper to Lower Estuary* During both the pre- and post-BNR periods there were very strong seasonal patterns in DIN and TN transport between the upper and lower estuary (Fig. 9a). Transport was highest during winter and early spring, intermediate during fall and early winter and lowest during summer, following seasonal patterns in river flow and ambient nutrient concentrations. Both TN and DIN transport estimates were higher during the post-BNR winter seasons than during pre-BNR winters, reflecting the higher river flow in many post-BNR years (1993, 94, 96, 98). In contrast, flow was below average during much of the pre-BNR period. In addition, BNR did not reduce N loading from sewage treatment plants during cold seasons. During summer, when BNR was active and river flow differences 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. Particulate N (PN) was estimated to account for approximately 25% of the annual TN flux to the lower estuary, assuming that PN is transported as if it were dissolved. Observations of the vertical distribution of PN indicate that at the boundary between the upper and lower basin, it is concentrated near the surface in summer and well-distributed in the water column, as chlorophyll-a, during winter. These distributions are consistent with PN being of a relatively fresh planktonic origin. Although one cannot rule out that some fraction of the particulate fraction is not transported seaward, it seems unlikely that all the PN (25% of TN) is retained.

There were also clear seasonal patterns evident for P transport between the upper and lower estuary. As with N, rates were highest during winter and spring and lowest during summer and fall. For the most part, pre-BNR transport was lower than post-BNR transport, 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. On an annual basis, transport of particulate P was estimated to account for about two-thirds of TP transport. Near the boundary between the upper and lower basin, TP had a bi-modal distribution, with elevated concentrations near the surface, likely due to plankton, and elevated concentrations near the bottom, likely due to sediment resuspension. In this case, the box model is probably not fully adequate to compute the transport of P, but it is difficult to ascertain the direction or magnitude of error. Deposition and landward advection could well promote retention of particulate P, as is common in two-layer circulation. However, the seaward transport in this

region of the estuary is approximately five times the landward transport (Hagy et al. 2000). One may hypothesize that episodic or tidal resuspension of sediments in the broad surface layer (ten-fold wider than the bottom layer) could at times transport more PP seaward than the box model computes. Particulate P transport must simply be acknowledged as a source of uncertainty.

*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. 9b). This reflects the fact that the net direction of this transport depends on small differences between the N concentration in the seaward (outward) flowing surface water and the landward (inward) flowing bottom water. The relatively small vertical gradient can easily change. Similarly, the two-layer gravitational circulation, which dominates water exchange at time scales longer than that of tides, can change substantially (Hagy et al. 2000).

On an annual average basis, DIN was imported from the Bay to the Patuxent during both pre- and post-BNR periods, while TN was almost always exported to the Bay. Inflow of DIN was greater in the post-BNR period by  $580 \text{ kg d}^{-1}$ , increasing from an annual average of  $140$  to  $720 \text{ kg d}^{-1}$ . This increase was about half the size of the decrease in DIN input ( $1,100 \text{ kg d}^{-1}$ ) from point sources due to BNR implementation, leading to a smaller reduction in overall DIN input to the lower Patuxent estuary. TN export from the estuary during the pre-BNR and post-BNR period averaged  $1,300$  and  $870 \text{ kg d}^{-1}$ , 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 there were months during spring and fall when TN was imported into the estuary. Total dissolved N (TDN) was exported to the Bay during the Pre-BNR period, indicating that even if a fraction of PN was retained in the Bay, rather than transported as the box model indicates, the



**Fig. 9** Estimated N and P transport between the upper and lower portions of the Patuxent River estuary (a) and transport between the Patuxent River estuary and Chesapeake Bay (b). Transport was

estimated using the box model developed by Hagy et al. (2000) and nutrient concentration data from Chesapeake Bay Water Quality Monitoring Program (2001)

(b)

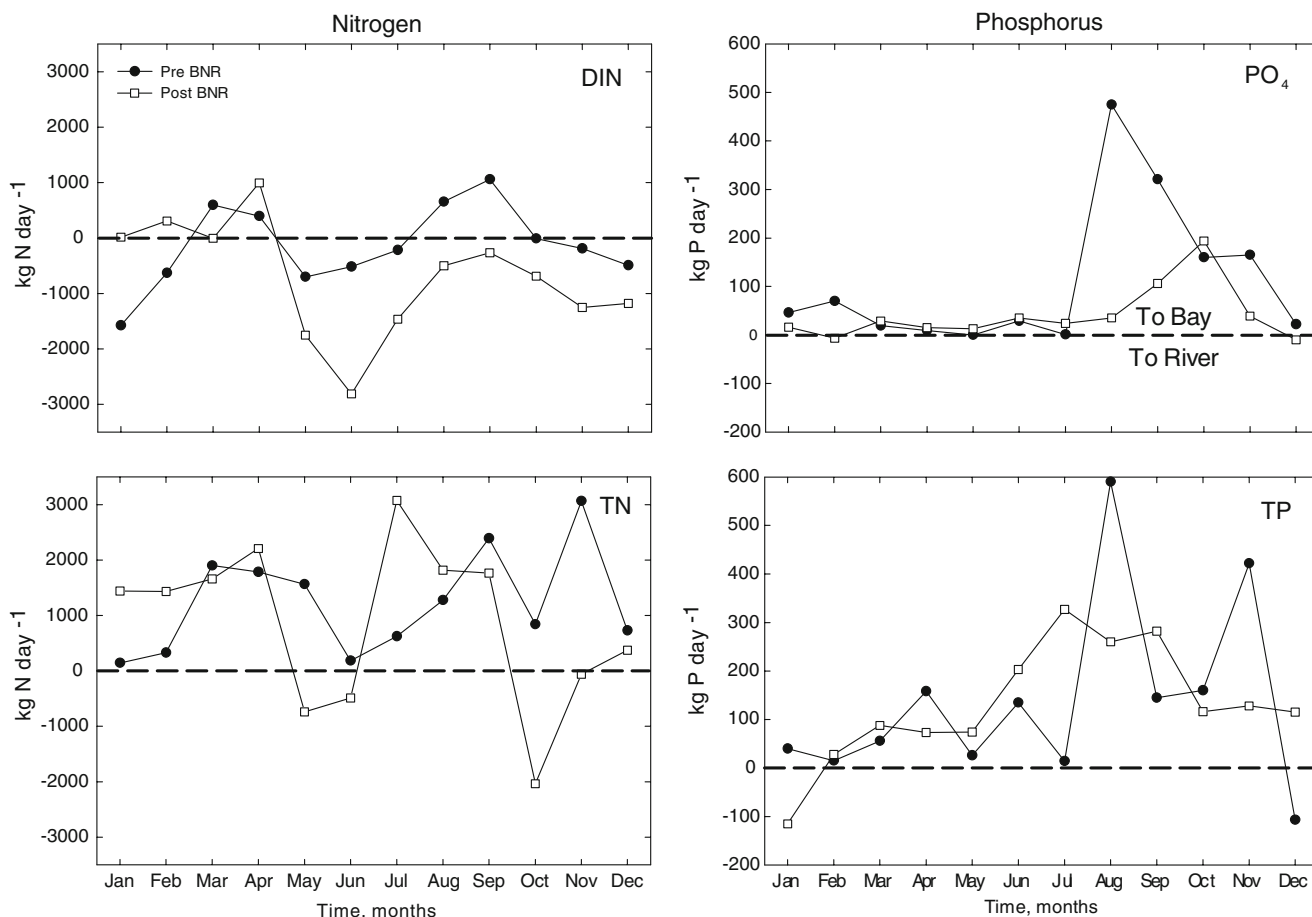


Fig. 9 (continued)

net TN flux would remain seaward. In the post-BNR period, however, the computed TDN flux was directed landward at 500 kg d<sup>-1</sup>. Thus, if as much as half of the computed PN flux in the post-BNR period was actually retained in the estuary, the TN exchange with Chesapeake Bay would be approximately balanced.

Both TP and DIP were exported from the estuary during almost all months of the year. Annual DIP export averaged 110 and 40 kg P d<sup>-1</sup> during the pre-BNR and post-BNR periods, respectively. During both periods, exports were highest during late summer and fall. TP exports averaged about 130 kg P d<sup>-1</sup> during both pre-BNR and post-BNR periods. However, seasonal patterns were quite different. Exchanges were variable during the pre-BNR period, but a clear summer maximum was present during the post-BNR period. Total dissolved P (TDP) fluxes accounted for a variable fraction of the computed TP flux, averaging 20 to 30% for the year. If the computed particulate P flux to the Bay was actually fully retained, the TP flux would decrease proportionately, but would not change direction.

There are currently three estimates available of nutrient exchanges at the mouth of the Patuxent River estuary. The first was generated by subtraction of internal losses of TN and TP from all terrestrial plus direct atmospheric inputs of N and P (Boydton et al. 1995), the second was computed from a coupled hydrodynamic/water quality model Cerco and Cole 1992) and the third was based on the box model computations described above. Estimates of TN export to the Bay were remarkably similar, with values between 0.2 to 0.5 kg N × 10<sup>6</sup> year<sup>-1</sup>. The range in estimates of TP exchange was from -0.6 to 0.5 kg P × 10<sup>5</sup> year<sup>-1</sup>, bracketing a balanced exchange. 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. These estimates indicate remarkable coherence since dependable estimates of net nutrient exchange at the mouths of estuaries are often difficult to obtain due to the large bi-directional water flow and small and variable nutrient concentration gradients associated with these water flows (Nixon et al. 1986a).



**Ecosystem-Level Export Comparisons** Current estimates of nutrient export from the Patuxent can be compared to total nutrient inputs from all external sources to evaluate nutrient retention versus export. 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. Nixon et al. (1996) reported an inverse relationship between percent of nutrient inputs exported and the log mean of estuarine water residence time, indicating that estuarine communities reduce the exported portion of input nutrients as a function of the time available for processing via uptake, sinking, and burial or denitrification. Relative to the Nixon et al. (1996) relationship, however, the Patuxent removes substantially more nutrients than expected based on water residence times. Perhaps, its sediment-rich and eutrophic status tends to facilitate nutrient 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 time. In addition, the Patuxent has substantial areas of tidal marshes in the upper estuary that sequester both N and P (Merrill 1999; Greene 2005a). Thus, it's possible that some estuarine features, such as tidal marshes, large sediment inputs or extensive seagrass communities,

may further modify nutrient export characteristics (Valiela et al. 2001).

#### Nutrient Recycling and Nutrient Demand

Recycling rates for N and P were organized by seasons (summer, winter, annual), locations (upper and lower estuary) and time periods (pre- and post-BNR) to compare the magnitude of new versus recycled nutrients (Dugdale and Goering 1967) with phytoplanktonic nutrient demand (Table 4).

Inputs of new DIN were highest during winter, associated with high river flows, and lowest during summer; seasonal differences in new DIN inputs were larger for the lower than upper estuary. New inputs of DIN to the estuary were slightly lower during the post-BNR period, whereas new inputs of  $\text{PO}_4^{3-}$  were larger (30–80%) during the post-BNR period.

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 winter, both DIN and DIP recycling rates were higher during the post-BNR period. Experimental evidence is not available to explain these differences, but it seems likely that higher river flow during the post-BNR

**Table 4** Upper and lower estuary estimates of nitrogen and phosphorus inputs, recycle, and phytoplankton nutrient uptake rates

Input/recycle/ uptake component <sup>a</sup>	Upper estuary, kg day <sup>-1</sup>						Lower estuary, kg day <sup>-1</sup>					
	Annual		Summer		Winter		Annual		Summer		Winter	
	NH <sub>4</sub> /DIN	DIP	NH <sub>4</sub> /DIN	DIP	NH <sub>4</sub> /DIN	DIP	NH <sub>4</sub> /DIN	DIP	NH <sub>4</sub> /DIN	DIP	NH <sub>4</sub> /DIN	DIP
Pre-BNR (1986–1990)												
New inputs <sup>b</sup>	4,100	130	3,600	130	4,200	130	2,500	80	1,300	70	3,700	70
Recycle <sup>c</sup>												
Sediments	2,500	210	2,700	790	660	40	4,600	970	9,100	1,900	910	190
Macrozooplankton	180	20	290	40	50	nd	270	40	300	40	110	nd
Total	2,680	230	2,990	830	710	40	4,870	1,010	9,400	1,940	1,020	190
Uptake by phytoplankton	-3,350	-460	-6,480	-880	-1,260	-180	-35,000	-4,810	-54,000	-7,530	-22,000	-3,020
Post-BNR (1993–1999)												
New inputs	3,600	240	2,500	160	4,200	190	2,500	110	1,100	80	4,200	100
Recycle												
Sediments	1,900	310	3,700	820	370	80	5,900	1,400	12,000	2,800	1,200	280
Macrozooplankton	1,400	190	2,600	360	410	nd	320	50	320	40	140	nd
Total	3,300	500	6,300	1,180	780	80	6,220	1,450	12,320	2,840	1,340	280
Uptake by Phytoplankton	-2,900	-400	-5,500	-770	-250	-40	-27,000	-3,800	-38,000	-5,300	-14,000	-1,980

Rates were computed for annual, winter, and summer seasons and for pre and post-BNR periods. All entries are as kg N or P day<sup>-1</sup>. Inputs and recycle rates are shown as positive values; phytoplankton uptake is indicated by negative values

<sup>a</sup> Details concerning data sources and calculations are provided in Table 2.

<sup>b</sup> New inputs include only DIN ( $\text{NO}_2 + \text{NO}_3 + \text{NH}_4$ ) and DIP (Dissolved Inorganic Phosphorus) because these are the N and P forms directly available to phytoplankton and are similar in form to those associated with recycle processes.

<sup>c</sup> Nutrient releases from sediments are for  $\text{NH}_4$  and DIP; sediment release or uptake of other forms of N and P were usually small. Nitrogen releases by macrozooplankton in the upper estuary were based on samples collected in the tidal freshwater zone of the estuary.

period lead to larger inputs of new nutrients, larger phytoplankton crops, and ultimately, more organic matter available for recycling from sediments (Cowan and Boynton 1996). Finally, estimated phytoplankton nutrient demand in the upper estuary was similar to nutrient recycle rates and always smaller than the combined rates of new inputs plus nutrients supplied via recycling. Phytoplankton growth rates were almost never limited by nutrients in this zone of the estuary, but were often light-limited (Fisher et al. 1999).

In the lower estuary, recycle of DIN was larger than new inputs, in contrast to the upper estuary. Winter was an exception, when new inputs were larger than recycle. 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. The reason is probably the same as suggested above for the upper estuary. 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 about 30% and 40% of phytoplankton demand, respectively.

The large discrepancy between phytoplankton nutrient demand in the lower estuary and the supplies of nutrients most likely reflects the omission of nutrient recycling in the water column by bacteria and other microheterotrophs, which we could not evaluate directly. As an approximation, we estimated water column recycle using water column respiration measurements and an assumed C:N:P for the respired material. 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 to rates for the mesohaline portion of Chesapeake Bay (Smith 2000). If typical summer respiration rates are converted to nitrogen and phosphorus equivalents (C:N:P=106:16:1) and extrapolated to the area of the estuary, this implies 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 the computed discrepancy between phytoplanktonic nutrient demand and nutrient supply when coupled with smaller, but still significant, sediment nutrient releases.

Several points emerge from these whole-estuary computations. First, new inputs of N and P never approach phytoplanktonic nutrient demand in the lower estuary. Even during winter, when inputs of new N and P are highest and demand lowest, only 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. Water column nutrient recycling is even more important. Kemp et al. (1992) showed that across estuaries one expects the importance of sediment processes to decline sharply with increasing depth. Using their relationship, and the 6-m average depth of the Patuxent, sediments are expected to contribute about 30% of total community respiration, similar to the percentage of N and P recycled by sediments found in this evaluation (Table 4). Thus, even in relatively shallow estuaries such as the Patuxent, water column nutrient recycling dominates N and P recycling.

#### Internal Nutrient Losses

Internal nutrient losses considered here include 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 of the lower estuary ranged from about 6 to  $50 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  during spring and from about 0.0 to  $100 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  during late fall. Summer rates in the lower estuary were not detectable, probably because of low oxygen conditions and resulting lack of sediment nitrification activity (Rysgaard et al. 1994). Annual average rates for the upper and lower estuary were about 38 and  $32 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ , respectively (Table 5).

Rates of denitrification for tidal marsh areas ranged from non-detectable during late winter to over  $500 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  in the high marsh during spring. Rates decreased from the high to low marsh and from early spring through fall. Annual average rates computed using both temporal and spatial weightings based on season and marsh type (e.g., extent of high, mid, or low marsh areas) were  $\sim 110 \mu\text{mol N m}^{-2} \text{ h}^{-1}$  (Table 5). When rates were extrapolated to include all sub-tidal and marsh areas, denitrification removed about  $0.9 \times 10^6 \text{ kg N year}^{-1}$  from the system; sub-tidal sediments removed about 60% and tidal marshes the remaining 40%.

Sediment deposition rates were calculated for both sub-tidal areas and tidal marshes. Deposition rates were largest in the sub-tidal upper estuary ( $2,700 \text{ g dry sediment m}^{-2} \text{ year}^{-1}$ ) and smallest in the lower estuary ( $1,100 \text{ g dry sediment m}^{-2} \text{ year}^{-1}$ ; Table 6). Rates were variable in tidal marshes and averaged  $2,100 \text{ g dry sediment m}^{-2} \text{ year}^{-1}$  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

**Table 5** 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 <sup>2</sup> ×10 <sup>6</sup> )	Annual average denitrification rate (μmol N m <sup>-2</sup> h <sup>-1</sup> ) <sup>a</sup>	Total denitrification (kg N year <sup>-1</sup> ) <sup>b</sup>
Sub-tidal estuarine sediments			
Upper estuary	22	38	104,000
Lower estuary	110	32	436,000
Total			540,000
Tidal marshes			
Upper estuary	23	110	310,000
Lower estuary	6	80	58,000
Total			368,000
System total			908,000

<sup>a</sup> Tidal marsh rates of denitrification (Greene 2005a) were spatially weighted (high, mid, and low marshes) for upper estuary marshes but not weighted for the much smaller lower estuary marshes.

<sup>b</sup> System denitrification was estimated as the product of marsh or estuarine area and annual average denitrification rate.

sediment depths of 10–15 cm) were higher in the upper than lower estuary, especially for PP. Marsh values for PP were similar to values for sub-tidal areas of the upper estuary. In contrast, sediment PN values in tidal marsh sediments were about twice those in sub-tidal areas (Table 6). Estimates of PN burial ranged from about 3 to 12 g N m<sup>-2</sup> year<sup>-1</sup>, with the highest burial rates in the upper and lower rates in the lower estuary. Burial rates of PP ranged from 0.7 to 3.5 g P m<sup>-2</sup> year<sup>-1</sup> 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 0.9×10<sup>6</sup> kg N year<sup>-1</sup> and 0.2×10<sup>6</sup> kg P year<sup>-1</sup> from the system; 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 Chesapeake Bay nutrient budget analyses (Boynton et al. 1995) whole-system denitrification and burial remain relatively uncertain components of the nutrient budget. Until far more measurements of both processes are made, rigorous estimates of error are not possible. We can, however, compare our estimates to values for other estuarine and tidal marsh ecosystems to obtain a qualitative sense of whether our estimates are within the expected range. Greene (2005b) assembled a large number of denitrification rate measurements from coastal habitats. Sixty six percent of measured rates were less than 100 μmol N m<sup>-2</sup> h<sup>-1</sup>. The median rates for coastal wetlands and estuaries were 54 and 40 μmol N m<sup>-2</sup> h<sup>-1</sup>, 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 measured rates in an expected range.

A similar situation exists regarding burial rates. We examined burial rates observed in other coastal systems and found rates for PN and PP burial to range from 6 to 25 g N m<sup>-2</sup> year<sup>-1</sup> and from 0.1 to 3 g P m<sup>-2</sup> year<sup>-1</sup>, respectively. Thus, burial rates used in this analysis were comparable to those observed elsewhere. An additional step we took to evaluate the adequacy of our measurements was to organize

**Table 6** 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 <sup>2</sup> )	Sediment deposition rate <sup>a</sup> (g dry sediment m <sup>-2</sup> year <sup>-1</sup> )	Sediment Composition		Annual burial rate <sup>b</sup>		Total burial rate <sup>c</sup>	
			PN (mgN g dry sediment <sup>-1</sup> )	PP (mgP g dry sediment <sup>-1</sup> )	PN (g N m <sup>-2</sup> year <sup>-1</sup> )	PP (g P m <sup>-2</sup> year <sup>-1</sup> )	PN (kg N year <sup>-1</sup> )	PP (kg P year <sup>-1</sup> )
Upper estuary								
Tidal marsh	23	2,100	5.9	1.1	12.4	2.3	285,000	53,000
Sub-tidal estuary	22	2,700	3.5	1.3	9.5	3.5	208,000	77,000
Total							493,000	130,000
Lower Estuary								
Tidal marsh	6	2,100	5.9	1.1	12.4	2.3	74,000	14,000
Sub-tidal estuary	110	1,100	2.5	0.6	2.8	0.7	303,000	73,000
Total							377,000	87,000
System total							870,000	217,000

<sup>a</sup> Deposition rate estimates for the tidal marshes were from <sup>210</sup>Pb-based measurements; lower estuary sub-tidal deposition rates were from <sup>210</sup>Pb-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.

<sup>b</sup> Annual areal burial rates were estimated as the product of deposition rate and 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.

<sup>c</sup> Total burial rates were estimated as the product of areal annual rates and the area of tidal marsh and sub-tidal estuary.

data concerning sediment sources to evaluate if there was enough sediment entering the system to support the computed accretion rates. In the lower Patuxent estuary, like other mesohaline regions of Chesapeake Bay, shoreline erosion is a primary source of fine sediments (Hobbs et al. 1992). In the case of the lower Patuxent, Halka (personal communication) estimated that shoreline erosion yielded sufficient fine-grained sediments to support an average annual deposition rate of about 750 g (dry sediment)  $\text{m}^{-2}$   $\text{year}^{-1}$ , close to the estimate based on  $^{210}\text{Pb}$ . For 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 2,900 g (dry sediment)  $\text{m}^{-2}$   $\text{year}^{-1}$ , similar to our computed rates for that region (Table 6). These considerations suggest that our estimates of deposition are reasonable.

We do not have time series of burial or denitrification rates to evaluate inter-annual variability; an unfortunate situation because we do have such information for nutrient inputs. It would be very instructive to see how these important losses change in relation to inputs. Intuition suggests 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. 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. We suspect that inter-annual variability in denitrification rates is also substantial. 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 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 higher during wet than dry years. However, hypoxia is also more extensive in wet years (Fisher et al. 2006), impeding coupled nitrification–denitrification during summer in affected areas (Rysgaard et al. 1994). Hagy and Kemp (2002) developed a 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 minus N fixation) denitrification that ranged from about 20 to 80  $\mu\text{mol m}^{-2} \text{h}^{-1}$ , spanning the range of rates used in the current budget analysis. During the period of time analyzed with the LOICZ approach, the highest denitrification rates were associated with wet years and the lowest rates with drought years. Thus, indirect evidence indicates that internal loss rates (burial and denitrification) are proportional to external loading rates.

#### Uncertainty of Nutrient Losses

Estimates of nutrient losses were most likely not as well-constrained as the estimated input rates. Similarly, the uncertainty is also less certain. Whereas fairly rigorous quantitative estimates of uncertainty could be developed for some of the inputs, the uncertainty associated with the loss terms was based to a greater degree on professional opinion. We suggested that the denitrification rates for sub-tidal sediments and marshes were accurate within 15%. Assuming that the area to which these rates apply is known to within 5%, we compute that the uncertainty of the product, namely the total denitrification rate, is 16%, similar to the uncertainty for the estimate of the rate. Estimated uncertainty for particulate N and P burial in marshes and sub-tidal sediments was about 20%, except for burial in lower estuary marshes, for which some additional uncertainty must be assumed because the rates for these marshes were assumed to be the same as for the upper estuary marshes. Based on standard errors for loss terms for N and P ranging from 16% to 35%, the computed standard error for the sum of all losses for the middle basin is 10% for N and 12% for P. For the lower estuary, the standard error is 12% for N and 18% for P. If some of the errors were in fact correlated, the uncertainty for the sum would be more similar to that of the individual terms. In a broad sense, one may conclude that the N and P losses are estimated with less precision than the N and P inputs and that estimates of N losses are slightly better constrained than those for P.

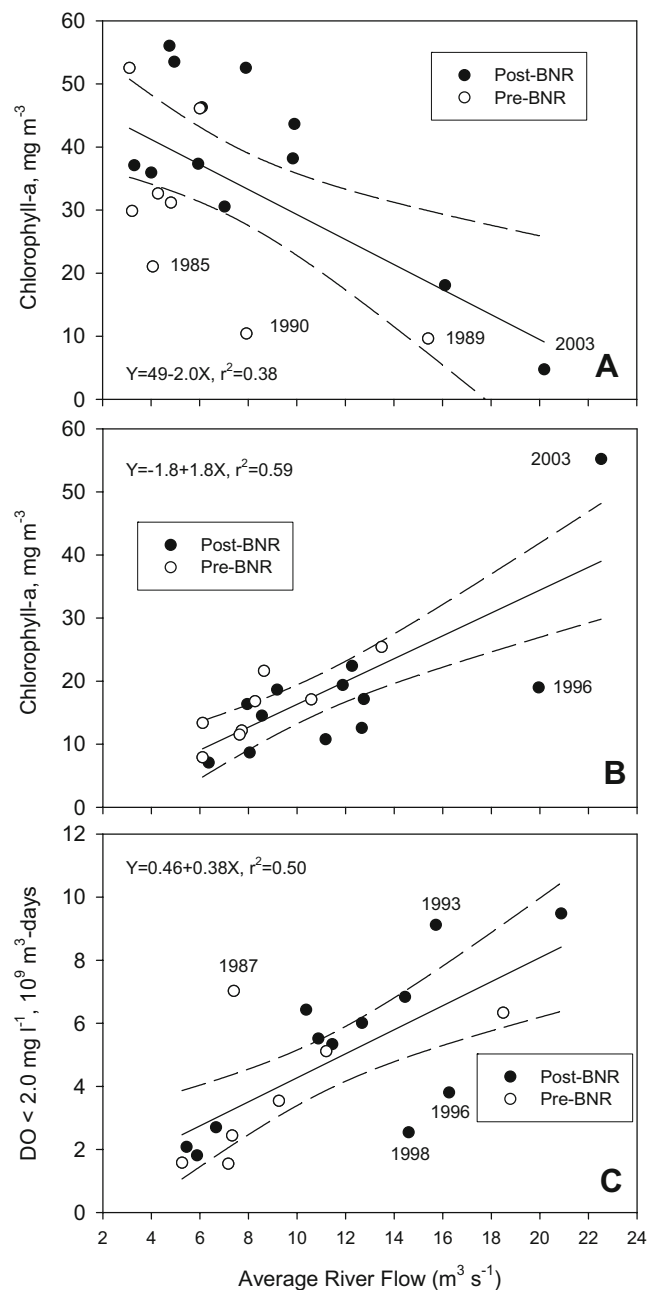
#### Estuary Responses to Nutrient Loading Rates

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 inter-annual basis in response to external forcing of the system by nutrient loading and freshwater inflow. Earlier research on Patuxent estuary water quality (Hagy 1996) also reported that different regions of the estuary had different seasonal patterns of water quality and responded differently to external forcing. A qualitative understanding of the eco-

logical processes controlling water quality patterns was used to inform the development and interpretation of simple regression models of ecosystem response (Fig. 10). These relationships are similar to those observed by Hagy (1996), but have reduced uncertainty because an additional 10 years of data are included.

Summer algal biomass (chlorophyll-a) in tidal fresh surface waters varied from 30–60  $\mu\text{g l}^{-1}$  during periods of normal summertime freshwater inflow. During periods with above average summer (June–August) freshwater inflow, algal biomass tended to be much lower, approximately 10  $\mu\text{g l}^{-1}$  (Fig. 10a). This pattern likely reflects the large increase in flushing of this region as flow increases (Hagy et al. 2000). Consistently low biomass in winter may reflect the combination of slow, light-limited algal growth and rapid flushing, 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 that occurred in the early 1990s. These responses implicate residence time in the upper estuary as the dominant control on algal biomass rather than nutrient (particularly N) limitation.

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 ( $r^2=0.59$ ). The facts that average chlorophyll-a for the mesohaline estuary was better correlated with freshwater flow (Fig. 10b) than TN loading may reflect the fact 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 into 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



**Fig. 10** Responses of Patuxent River estuary water quality to inter-annual variations in freshwater inflow at Bowie, MD. **a** The relationship between summer (June–August) average surface water chlorophyll-a at a tidal freshwater station and summer average freshwater inflow. **b** The relationship between annual average surface water chlorophyll-a and annual mean freshwater flow at a mesohaline station. **c** The relationship between March–August average freshwater inflow and the temporal and spatial extent of hypoxia ( $\text{DO} < 2.0 \text{ mg l}^{-1}$ ). Regression lines are least squares regressions with 95% confidence bands for the mean. All regression slopes are statistically significant ( $p < 0.01$ )

increased the volume of discharge (Fisher et al. 2006). Thus, it appears that freshwater flow may track N availability to phytoplankton in the lower estuary better than TN loading at HoT.

Hypoxia and anoxia occur annually in mesohaline bottom waters of the Patuxent estuary, affecting nearly all of the below-pycnocline volume at times, but usually only a smaller fraction. Hagy (1996) observed that hypoxia usually occurs within a 20-km portion 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. 2006). 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. 10c), whereas a 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 river 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 makes 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.

### Nutrient Budget Synthesis

In the previous sections we described 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 was well balanced with inputs closely approximating internal losses plus export (Fig. 11a and b). 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. The net TN imbalance was within a single standard error of zero, indicating that it could easily result from uncertainty alone. In addition to finding a reasonably balanced budget for N, there are other important aspects that emerged from this evaluation. In the case of the Patuxent, most of the TN input is to the upper estuary

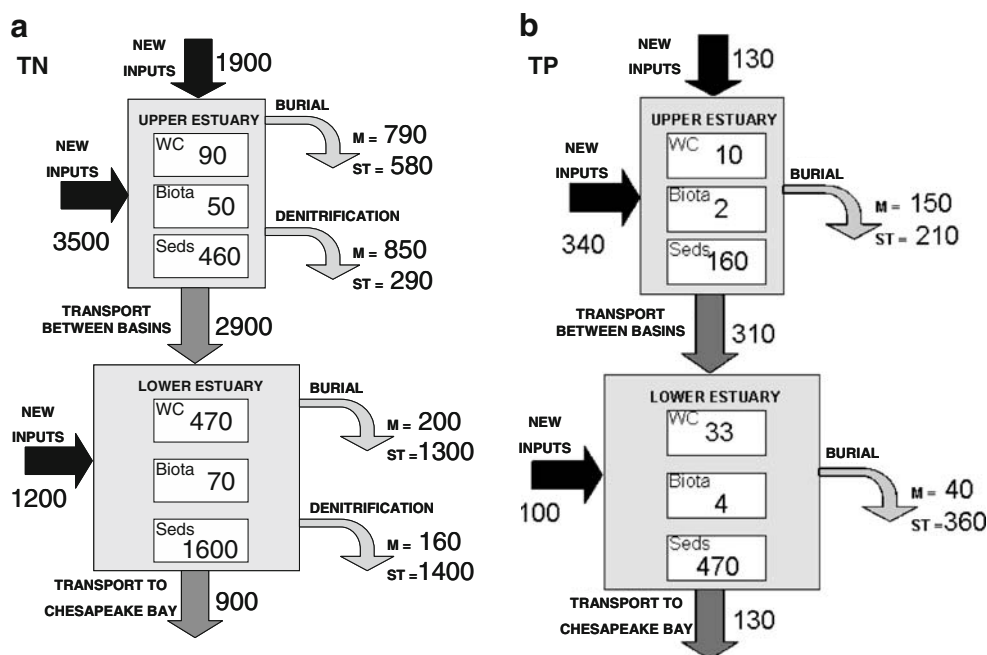
(5,400 kg N day<sup>-1</sup>; ~80% of total; Fig. 11a). In this portion of the system about 47% of these inputs were lost via long-term burial and denitrification. Loss processes occurring in the adjacent tidal marshes accounted for 64% of all losses in this region of the estuary. In the upper estuary, 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. Denitrification and long-term burial in sub-tidal estuarine sediments were 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. Clearly, this estuary does not simply convey nitrogen from its drainage basin to Chesapeake Bay.

The annual TP budget was less well balanced (Fig. 11b). We estimate that the computed imbalance for the upper basin is several times larger than our estimated standard error. 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 TP 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<sup>-1</sup>) 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. The estimated imbalance for the lower estuary TP budget is about equal to its estimated standard error. However, if the transport from the upper estuary was lower than estimated, this would exacerbate the imbalance.

It is difficult to identify the most probable source of error leading to the discrepancies in the TP budget. 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 varies with rain and wind events and is very transitory; it is quite possible to miss quantitatively important but very short-lived runoff events.

### Management Issues and Ecosystem-Scale Experiment

Considerable effort has been expended to reduce nutrient inputs to the Patuxent estuary, mainly from point sources,



**Fig. 11** A synthesis of annual TN (a) and TP (b) inputs, transport between estuarine regions, internal losses and stocks for the Patuxent River estuary. Inputs are multi-year averages of combined point, diffuse, direct atmospheric deposition to tidal waters, and septic for the post-BNR period. Spatial locations of inputs (from top to bottom of the diagram) are at the head of 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. N and P burial and denitrification values for the lower sub-tidal estuary include rates estimated for the small tributaries of the lower Patuxent (area =  $18 \times 10^6 \text{ m}^2$ ) using areal rates from Tables 5 and 6. All flows have units of kg N or P  $\text{day}^{-1}$  and all stocks have units of kg N or P  $\times 10^3$

and thereby restore the 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 points derived from this budgeting effort.

**Effects of Management Actions** There is clear evidence at the head of the estuary of nutrient load reductions resulting from point source N loading reductions (Fig. 6). These load reductions have been touted broadly as evidence of progress towards meeting Chesapeake Bay restoration goals. However, there is no evidence that at the 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. 9). Thus, diffuse sources, particularly those from the middle portion of the drainage basin, dominate the nutrient input signature for this estuary. Water quality improvements in the lower estuary 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 could reduce N loads to the upper estuary by an additional 20–25% and all N sources to the full estuarine system by an additional 9%.

**Interactions with Chesapeake Bay** A prolonged debate has focused on 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). A concern is that nutrient reductions from the Patuxent watershed would be ineffective because N and P are imported from the nutrient-enriched Chesapeake Bay. 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. In addition, regression models relating nutrient loading rates from the watershed to algal biomass accumulation and hypoxic volumes account for much of the variability, suggesting that nutrients derived from the Patuxent basin are centrally involved (Hagy 1996; Fig. 10). Finally, spring algal blooms and hypoxic waters develop within the Patuxent estuary before adjacent Chesapeake Bay waters. Thus, nutrient load reductions in the Patuxent should, if of sufficient size, contribute to a lessening of eutrophic characteristics. However, there are some features of DIN flux at the mouth of the Patuxent that

warrant continued attention (Fig. 9b). During the pre-BNR period there was some importation of DIN from the Bay to the Patuxent ( $\sim 140 \text{ kg N day}^{-1}$ ). During the wetter post-BNR period this importation of DIN increased to about  $720 \text{ kg N day}^{-1}$ . Testa (2006), using the same box-model approach used here, re-computed net DIN flux at the mouth of the Patuxent for a longer time period (1985–2004) and found a statistically significant trend of increasing DIN importation with import rates of about  $500 \text{ kg day}^{-1}$  during the last 5 years. These rates are still a relatively small portion of the TN input budget ( $\sim 10\%$ ) but if they continue to increase they will off-set future reductions in nutrient loads coming from the basin.

A related issue is the potential contribution of N and P export from the Patuxent estuary to eutrophication of Chesapeake Bay. This study showed that the Patuxent exported a very small fraction of N and P inputs. Although this result can be expected because systems with relatively long residence times generally process rather than export N and P inputs (Nixon et al. 1996), the Patuxent exported an even smaller fraction than expected. Moreover, most of the TN and TP exports were dissolved or particulate organic compounds, indicating that they have been transformed during transit through the estuary from highly reactive dissolved inorganic forms to forms not immediately utilizable by phytoplankton. Thus, the Patuxent contributes little to the eutrophication of Chesapeake Bay.

*Role of Tidal Marshes* This budget analysis also illustrated the quantitatively important role of tidal marshes as sinks for both N and P. Investigations elsewhere have reached similar conclusions (e.g., Bricker and Stevenson 1996; Stevenson et al. 2002). In the Patuxent, marshes removed about 70% more TN (30%) and TP (31%) than expected from their contribution to the estuarine/marsh system (18%). Thus, accreting marshes, such as those in the Patuxent, act as an efficient “ecosystem-scale kidney” and should continue to be protected for the ecosystem services that 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 removal associated with marshes would be lost; further still, eroding marshes could serve as a source of organic matter and nutrients, reversing the current beneficial role of marshes (Stevenson et al. 2002).

*New versus Recycled Nutrients* 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, cannot support increases in algal biomass, but rather can 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 by losses associated with coupled nitrification–denitrification. Thus, nutrient input reductions sufficient to relieve seasonal hypoxic/anoxic conditions might lead to larger improvements in water quality. The quantitative impact of a drop in sediment nutrient recycling efficiency is not available at this time. However, this mechanism suggests that we might expect the trajectory of water quality improvements to be more than proportional to loading reductions, possibly similar to the more complex hysteresis in ecosystem response observed in the Potomac River estuary (Jones 2000).

*Water Quality Responses to Load Variations* Our analyses indicate that major features of water quality in the estuary can be related to nutrient load changes on annual or multi-seasonal (e.g., winter+spring) time scales. For example, the volume of hypoxic water and the size of algal standing crop were proportional to annual and smaller time-scale nutrient loading rates. In addition, time-series measurements of community metabolism and sediment releases of N also appear to be related to annual time-scale 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, responded to short-term changes in nutrient inputs. There was no evidence of a residual pool of bioavailable nutrients embedded in the sediments or water column of the Patuxent or other portions of Chesapeake Bay (Boynton and Kemp 2000). Thus, should substantial nutrient reductions occur, we would predict measurable improvements in water quality conditions within a year or a slightly longer period.

*Estimates of Needed Load Reductions* A central water quality management issue concerning the Patuxent is how much nutrient load reduction is needed to remedy existing water quality problems such as hypoxia. The Patuxent is currently among the water bodies in Maryland listed as having impaired water quality; a Total Maximum Daily Load (TMDL) computation is currently being developed for nutrients in the Patuxent. Much of the TMDL result will be based on coupled land-use and water quality models and will thus depend on how well those models capture the



relevant ecological processes in the watershed and estuary. There are several additional approaches to estimating needed load reductions based on field measurements; in the long run, use of both types of approaches would be useful. Fisher et al. (2006) examined deep water dissolved oxygen concentrations in the Patuxent for an 18-year period (1986–2004). During summer, average oxygen concentrations were below  $1 \text{ mg l}^{-1}$  for six of those years and below  $2 \text{ mg l}^{-1}$  for ten additional years. During two drought years (1986 and 1992) summer dissolved oxygen concentrations were at or slightly above  $2 \text{ mg l}^{-1}$ . Whole-system TN and TP loads during those years averaged 5,100 and 310  $\text{kg N}$  and  $\text{P day}^{-1}$ , 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 1,500 to 2,500  $\text{kg N day}^{-1}$  and TP reductions on the order of 100  $\text{kg P day}^{-1}$  would be needed to return N and P loading to levels historically associated with deep water dissolved oxygen concentrations above  $2 \text{ mg l}^{-1}$ . 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 first approximations rather than as final targets. An alternative approach is to base reduction targets on nutrient loading rates during a period 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 1,200  $\text{kg N day}^{-1}$  and 220  $\text{kg P day}^{-1}$  during the 1960s. TP loads at the head of tide are now lower than during the 1960s by almost a factor of two. However, TN loads at the same location are still 60% greater than the earlier loads, despite BNR technology at the sewage treatment plants located above HoT. This comparison suggests the need for significant additional reductions in TN inputs. 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 coefficient for the basin area below HoT (areal rate =  $5 \text{ kg N ha year}^{-1}$ ) to represent inputs for the 1960s, the resulting TN load to the estuary is 3,100  $\text{kg N day}^{-1}$ . 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 similar to the previous one; TN loads need to be decreased on the order of 2,500–3,000  $\text{kg N day}^{-1}$  to be comparable to loads associated with far less eutrophic conditions of the 1960s. The second estimate is larger than the first, perhaps reflecting the fact

that the first only required deep water dissolved oxygen conditions to be above  $2 \text{ mg l}^{-1}$  in summer, while the latter estimate was associated with an ecosystem having a vibrant seagrass community, well-developed benthos with oyster reefs as well as higher deep water oxygen conditions.

Whatever nutrient input reductions are eventually agreed to during the TMDL process, two conclusions seem clear. First, TN reductions will need to be substantial to reduce hypoxic conditions during normal and wet years and larger still to also restore other community components (SAV, benthos) to the ecosystem. Second, further reductions in point source discharges are technically possible and, if instituted, will measurably reduce loads. Unfortunately, most of the needed reductions will necessarily involve diffuse sources and to date there appears to have been little progress in dealing with these sources of nutrients.

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