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Phytoplankton response to nutrient enrichment in an urbanized estuary: Apparent inhibition of primary production by overeutrophication

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Abstract

Phytoplankton response to nutrients was examined with a 26-yr database from the Delaware Estuary. Biomass-normalized primary production did not increase linearly with increasing nutrient concentrations and instead showed saturation at comparatively low nutrient concentrations and decreased at high concentrations. To separate the effects of light availability and temperature on primary production from those of other environmental variables, we developed an empirical model of areal primary production. The model equation was obtained for the entire dataset and the effect of the residual variables was expressed as correction factors of observed primary production to the model estimates. The model accounted for 67% of variability of observed primary production overall, indicating that production of the estuary was mainly controlled by light availability and temperature. In contrast, a similar model applied to a Chesapeake Bay database had shown a poorer fit, indicating consistent light limitation in the Delaware Estuary and varying strengths of light and nutrient limitation in the Chesapeake Bay. The relationships between nutrients and correction factors for the Delaware Estuary showed that the model underestimates primary production at low and mid nutrient concentrations and overestimates it at high concentrations. The model fit and correction factors for five regions of the estuary indicate a high-nutrient, low-growth situation in the Delaware Estuary because of varying influences of light limitation, proportions of nutrients, and probably toxic contaminants in areas with large anthropogenic inputs—including high nutrients.

Much of the classical thinking about eutrophication has arisen from lake studies. In lake systems, a relatively simple model appeared to successfully describe phytoplankton response to the effect of a single limiting nutrient, phosphate (Hutchinson 1969). In estuaries, early evaluation of eutrophication was made by Ketchum (1969) and was popularized by Jaworski in the Potomac River (Jaworski et al. 1972). During the evolution of conceptual models of estuarine eutrophication, cautions about oversimplification of this problem have been made for a number of years (e.g., Schindler 1981; Nixon and Pilson 1983; Vollenweider et al. 1992). However, there is still a tendency to think of eutrophication in estuarine waters in terms of a simple linear response to a single limiting nutrient: what Cloern (2001) has described as a Phase I model. To construct more complex models, Cloern addresses system-specific responses; complex geometry and physical forces generate diverse environments that respond to nutrient loading differently. He also emphasizes the influence of multiple stressors in waters with multiple anthropogenic influences (Cloern 2001).

Nutrient enrichment is a common feature in estuarine and coastal waters worldwide (Smith 2003) and has been attributed as the primary cause of eutrophication from excess algal growth. The most prominent symptoms of this eutrophication are oxygen depletion in bottom waters and harmful algal blooms (Richardson and Jorgensen 1996). Although severe nutrient enrichment is seen in many urbanized estuaries, those eutrophication symptoms are not found in some estuaries (e.g., Alpine and Cloern 1992; Monbet 1992; Le Pape et al. 1996). A partial explanation is that the balance of competing limitation by light and nutrients is different in each estuary (Cloern 1999). If a system is nutrient limited, an increase in nutrient concentrations leads to an increase in primary production; if a system is light limited, an increase in nutrient concentration has less effect on primary production.

An estuarine system that does not show a direct linear response to increased nutrient loading will instead accumulate elevated nutrient concentrations. Such a situation has been discussed recently (Borum 1996; Cloern 2001) and is considered analogous to the oceanic high-nutrient, low-chlorophyll condition (Martin et al. 1990). Sharp (2001) called this situation a high-nutrient, low-growth (HNLG) condition, and it is characterized in the estuary by (1) a high concentration of nutrients, (2) moderate to high phytoplankton biomass, and (3) low phytoplankton production relative to its biomass. High nutrient concentrations in estuaries should, in themselves, be considered another indicator of eutrophication, and the question that should be asked in such a situation is: Why is primary production not greater?

Here, we evaluate phytoplankton response to overenrich-

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ment of nutrients in a highly urbanized estuary. We have used our 26-yr database built on consistent measurements of ambient chemical concentrations and estimates of primary production made along the full length of the Delaware River and Bay estuary. With this database, we examine empirical relationships between nutrient concentrations and both algal biomass and primary production.

We have also evaluated the effects of environmental variables on primary production with a series of depth-integrated models (Behrenfeld and Falkowski 1997*b*). We modeled ^{14}C-based areal primary production as a function of surface chlorophyll *a* (Chl *a*) concentration, daily irradiance, photic zone depth, day length, and temperature. The model allows evaluation of effects of these variables on control of the areal primary production and, thus, separation of these effects from those of nutrients and other environmental factors. The influence of the residual factors was expressed as a correction factor of the observed production to the model estimate.

Study area and methods

The Delaware Estuary—The estuary of the Delaware River and Bay is a coastal plain estuary in the Middle Atlantic States of the United States. It is heavily urbanized with extremely high nutrient concentrations (Sharp et al. 1982; Sharp 1988) but is not accompanied by extremely high phytoplankton biomass or primary production (Pennock 1985; Pennock and Sharp 1986, 1994). The circulation of the estuary is dominated by a single river discharge, and it does not have summer stratification (Sharp et al. 1986). There have been major changes in the water quality of the estuary over the past several decades, including changes in nutrient concentrations and speciation (Sharp 1988; Sharp and Yoshiyama unpubl.).

Database—Since 1978, a number of cruises have been carried out through a variety of research projects in the Delaware Estuary, and samples were taken along the longitudinal transect of the estuary from the mouth of the bay (0 km) to the head of the tide (215 km). Data from earlier cruises were included in reports, and the entire 26-yr dataset of 2,068 sampling stations from 101 cruises are compiled in a database. The database includes temperature, salinity, dissolved oxygen, dissolved inorganic carbon, total suspended sediments, dissolved organic carbon, nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), particulate carbon and nitrogen, light attenuation coefficient, secchi depth, Chl *a*, and ^{14}C-based areal and maximum volumetric primary production. Primary production measurements were conducted from 1980 to the present. A complete description of methods used for those measurements can be found in earlier publications (Sharp et al. 1982; Pennock and Sharp 1986; Fogel et al. 1992). On the basis of Chl *a* and nutrient concentrations and the light attenuation coefficient, the estuary was separated into five geographic regions. The five regions, shown in Fig. 1, are: lower bay (0–25 km), midbay (25–70 km), turbidity maximum (70–115 km), urban river (115–175 km), and upper river (175–215 km).

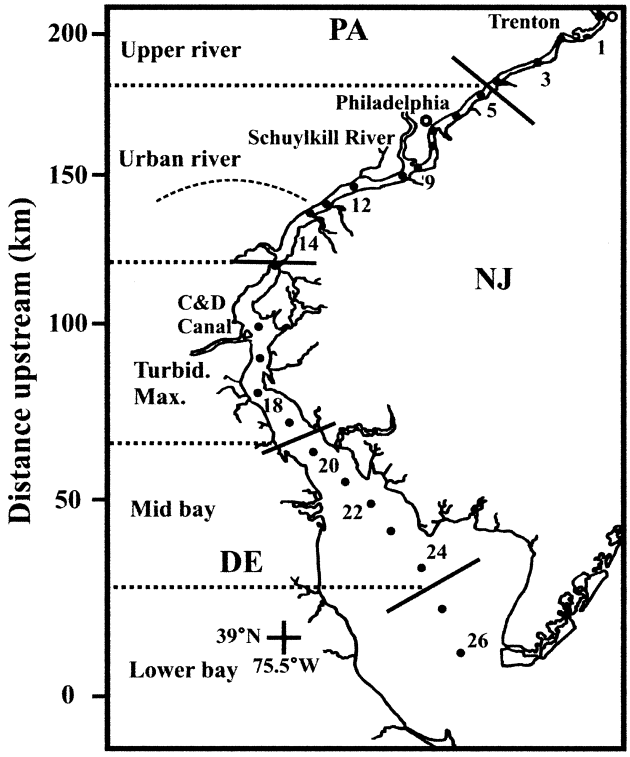

Fig. 1. The Delaware Estuary with sampling station locations (1–26) along the longitudinal transect. Thick solid bars separate the estuary into five regions: upper river, urban river, turbidity maximum, midbay, and lower bay.

Algal response to nutrient enrichment—empirical relationships—The effect of nutrient enrichment on algal response was examined from the database. Depth-integrated areal production (mg C m^{-2} d^{-1}), Chl *a* concentration (μg L^{-1}), and the ratio of maximum volumetric primary production to Chl *a* concentration, the P : B ratio (μg C [μg Chl]$^{-1}$ d^{-1}) were plotted against nutrient concentrations. Examining plots of these three parameters for both spring and summer (Sharp and Yoshiyama unpubl.), it was seen that chlorophyll was a poor indicator of algal response to eutrophication; algal biomass was high during spring blooms in mid- and lower bay regions when primary production was not extremely high and was moderately high in the urban river region when primary production was relatively low. In a similar fashion, the areal primary production showed less differentiation between regions of the estuary and seasons when considered alone. The P : B ratio normalizes production across the range of phytoplankton biomass and represents algal response (carbon uptake rate) to the ambient nutrient condition, a physiological indicator. To minimize the effect of temperature and daily irradiance, we separated the data by seasons: spring (days 60–130), summer (days 131–255), fall (days 256–320), and winter (days 321–59).

Depth-integrated models—We constructed empirical models of observed areal primary production ($APROD_{obs}$, mg C m^{-2} d^{-1}) to evaluate effects of environmental variables. $APROD_{obs}$ was calculated with the light attenuation coefficient (*k*, m^{-1}) measured by submersible quantum probes and

^{14}C uptake values measured in a deck incubator by 24-h incubation at six light levels: 100%, 60%, 30%, 12%, 3.3%, and 1.1% of incident photosynthetically active radiation (PAR; Pennock and Sharp 1986). For the light measurements from 1978 to 1988, a hand-held unit (QSR-100, Biospherical Instruments) measuring PAR energy was used with manual estimates of depth from cable out; for the later measurements, a computerized multichannel instrument (PRR-600, Biospherical Instruments) was used, but only the downward PAR energy was used for the calculation. Comparison of light attenuation coefficient to suspended sediment concentration for the entire dataset verifies that the two measurement methods give identical estimates of light attenuation coefficient. Five variables were used for modeled primary production.

1. Surface Chl *a* concentration (Chl_{surf}, mg m^{-3}) via fluorometry (Strickland and Parsons 1972).
2. Daily irradiance (E_0, mol quanta m^{-2} d^{-1}) via a QSR-250 integrating quantum meter.
3. Photic zone depth (Z_{eu}, m) calculated from light attenuation coefficient as $Z_{eu} = -\ln(0.01)/k$.
4. Water temperature (T, °C).
5. Day length (DL, h).

The daily irradiance and day length data were not in the database but were retrieved from individual data sheets of the primary production measurements.

We first employed a simplest version of the depth-integrated model, the Ψ model (Platt 1986). The model (hereafter, Type I model) is formulated as a product of a constant (Ψ), Chl_{surf}, Z_{eu}, and a function (f) of E_0.

$$\text{APROD}_{\text{I}} = \Psi \times \text{Chl}_{\text{surf}} \times Z_{\text{eu}} \times f(E_0) \quad (1)$$

APROD_{I} is the estimated areal primary production by the Type I model. In most Ψ models, $f(E_0) = E_0$ (Cole and Cloern 1984, 1987; Platt 1986). Behrenfeld and Falkowski (1997*a*,*b*) suggested several forms of the function $f(E_0)$ that are based on empirical photosynthesis–irradiance curves. We simply used a third-order polynomial with the intercept forced through zero rather than a specific function.

$$f(E_0) = E_0 + \sum_{i=2,3} a_i E_0^i \quad (2)$$

Coefficients of the polynomial are a_2 and a_3.

In the Type I model, Ψ is considered to be a constant, although it will vary according to species composition, the physiological state of the phytoplankton community, and other environmental factors such as temperature, ambient nutrient concentrations, and day length. It was determined by a nonlinear fit between $\text{APROD}_{\text{obs}}$ and APROD_{I} for the entire dataset, forcing the slope to unity.

To improve the Type I model, we considered DL and T as additional variables. As previous studies suggested (Behrenfeld and Falkowski 1997*a*,*b*; Harding et al. 2002), Ψ can be formulated as a product of DL and a function of T. We used a second-order polynomial of T (Eq. 3).

$$\Psi = \sum_{0 \le i \le 2} b_i T^i \times \text{DL} \quad (3)$$

Coefficients of the polynomial are b_0, b_1, and b_2. Thus, the Type II model is formulated as Eq. 4:

$$\text{APROD}_{\text{II}} = \sum_{0 \le i \le 2} b_i T^i \times \text{DL} \times \text{Chl}_{\text{surf}} \times Z_{\text{eu}} \times \left(E_0 + \sum_{i=2,3} a_i E_0^i \right) \quad (4)$$

APROD_{II} is the estimated areal primary production by the Type II model. For the Type II model, we determined a_i and b_i by a nonlinear fit between $\text{APROD}_{\text{obs}}$ and APROD_{II} for the entire dataset, forcing the slope to unity; coefficients in the polynomials were neglected unless there were significant departures from zero ($p < 0.05$). These models were evaluated by both coefficient of determination (r^2; Cole and Cloern 1984) adjusted for the degree of freedom of each model and root mean square error (RMSE, %; Harding et al. 2002). All r^2 values shown here were statistically significant ($p < 0.001$). Throughout this paper, we used the computer program **R** (http://cran.r-project.org) for statistical analyses.

Correction factor for the model estimate—To evaluate the Type II model fit for subsets of data, a correction factor (c) is defined as the slope of linear regression of $\text{APROD}_{\text{obs}}$ to APROD_{II}, with the intercept forced through zero for a subset of the dataset. For an individual subset, the calibrated model equation is shown in Eq. 5.

$$\text{APROD}_{\text{obs}} = \text{c} \times \text{APROD}_{\text{II}} \quad (5)$$

The model underestimates primary production if $c > 1$ and overestimates if $c < 1$ for that subset of the full dataset. Specifically, the correction factor for a single data point is the ratio of $\text{APROD}_{\text{obs}}$ to APROD_{II} for that point.

Results

Response to nutrient enrichment: Empirical relationships—Environmental parameters and algal responses were averaged for the five estuarine regions; results for the spring and summer seasons are shown in Table 1. The general seasonal and spatial patterns of Chl *a*, primary production, and inorganic nutrients during the 26-yr period were consistent with the patterns shown previously for the 1980s (Pennock and Sharp 1994). Winter production is generally very low; during the fall, production is lower than summer, grading into low winter conditions. Thus, emphasis here is on the spring and summer seasons in which production and chlorophyll are comparatively high. Details of historical changes in nutrients and dissolved oxygen over a longer time period (1967–present) have been illustrated elsewhere (Sharp 1988). Changes in nutrients from the early 1980s to the present were comparatively small, and we could not demonstrate any systematic change in production or chlorophyll for this period. Therefore, averaging was appropriate even though there were some slight changes in the 26-yr period.

With an orientation starting at the head of the tides (215 km from the mouth of the bay, Fig. 1), nutrient concentrations in the upper river are high from cumulative terrestrial inputs. Nitrogen and phosphorus nutrients show large additional elevations in the urban region (175–115 km); there is a downstream dilution of all nutrients from the beginning of

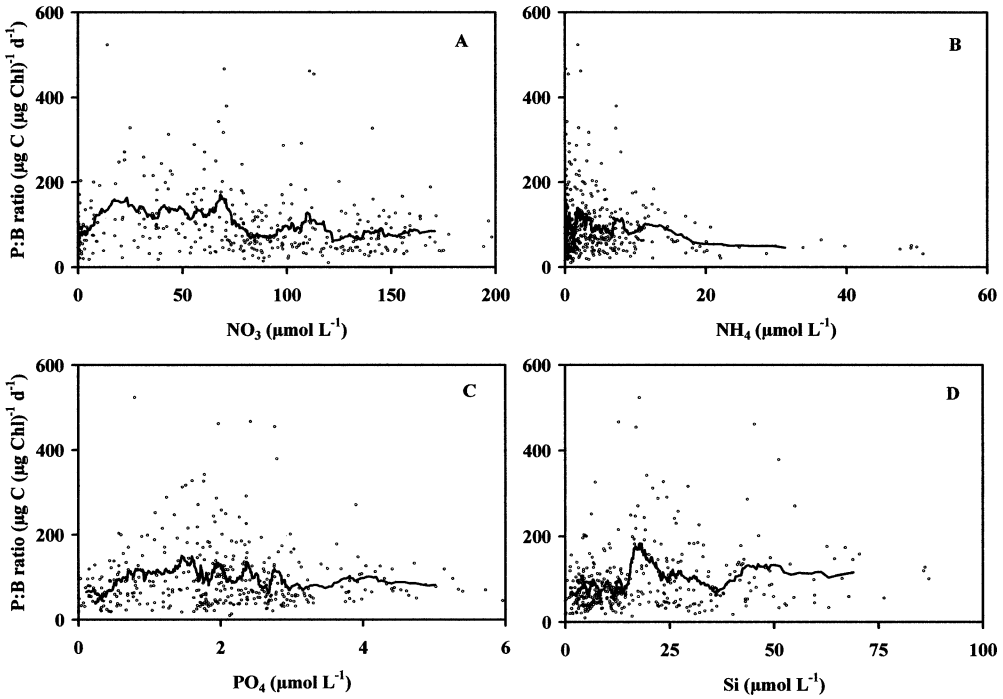

Fig. 2. Maximum volumetric primary production per unit Chl *a* (P : B ratio) versus nutrients in summer (days 131–255): (A) nitrate, (B) ammonium, (C) phosphate, and (D) silicate. The lines on each panel indicate 20-term moving averages of the P : B ratio.

the salinity gradient (115 km). The dissolved inorganic nitrogen (DIN, $NO_3 + NO_2 + NH_4$) and PO_4 reach maxima in the urban river region and then decrease by dilution going down to the estuary (Table 1). In upper and urban river regions, DIN was never depleted (>20 μmol L^{-1}) and PO_4 and Si were seldom below 1 μmol L^{-1} and 5 μmol L^{-1}, respectively (Table 1). This indicates that there is no obvious nutrient limitation in the river regions. NH_4 concentration exceeded 2 μmol L^{-1} in more than 90% of samples in the river regions, indicating NH_4 should be the primary source of nitrogen for phytoplankton and little NO_3 should be utilized in those regions, according to previous N uptake measurements (Pennock 1987; Pennock and Sharp 1994). Because of spring blooms in both the midbay and lower bay regions, nutrient concentrations in this season were pronouncedly depleted below limits of detection by colorimetric methods (i.e., <0.05 μmol L^{-1} for NH_4, PO_4, and Si), which is consistent with previous observations. In the summer, when nutrient regeneration matches phytoplankton use (Cifuentes et al. 1989), nutrient concentrations in the lower bay were low, but detectable (usually >0.1–0.2 μmol L^{-1} for N, P, and Si).

Light attenuation coefficients were low in the lower bay region, giving 1% light depth equivalent to ~6 m, and high in the turbidity maximum region, with 1% light depth to ~1 m (Table 1). In the spring, the average light attenuation in the midbay, urban river, and upper river were similar, with the lower bay and turbidity maximum regions being significantly lower and higher, respectively ($p < 0.05$). In the summer, the average light attenuation coefficients were also significantly lower in the lower bay and higher in the turbidity maximum compared with the other three regions; in this season, the urban river region had a significantly higher coefficient than the midbay region ($p < 0.05$).

For the entire year, the highest average Chl *a* concentrations were found in the midbay region in the spring, and the highest average areal production was found in the midbay in the summer. In the spring, the P : B ratio was relatively uniform throughout the estuary, with a slightly higher average value in the midbay than in the other regions (Table 1). The P : B ratio in each region was considerably higher in the summer than in the spring. Although not shown, the average P : B ratios were lower in the fall and winter than in the spring. In the summer, the average P : B ratio was the highest in the midbay—statistically higher than in the lower bay or urban river ($p < 0.05$). In the urban river, the average P : B ratio was the lowest—statistically lower than in the upper river, turbidity maximum, or midbay ($p < 0.05$). The P : B ratio was plotted against nutrient concentrations in Fig. 2 for summer data only. For NO_3, PO_4, and Si, the maximum P : B ratio was observed at the low to mid range of nutrient concentration. With NH_4, the maximum P : B ratio was achieved at a low concentration, and all of the high P : B values (>200 μg C [μg Chl]$^{-1}$ d^{-1}) occurred at low NH_4 concentrations (<10 μmol L^{-1}). The 20-term moving average lines in Fig. 2 also had their peaks at the low to mid range of nutrient concentration; in all cases, it appeared that there were no prolonged simple linear responses of production to increasing concentrations of any of the nutrients.

Because the response to NH_4 indicated decreased production beyond a comparatively low concentration, this relationship was further evaluated by plotting P : B ratio versus

Table 1. Twenty-six-year averages and standard deviations of environmental and algal response variables in five regions of the Delaware Estuary in spring and summer: nutrient concentrations, light attenuation coefficient (k), Chl *a* concentration, areal primary production (APROD), maximum volumetric primary production (VPROD), and maximum volumetric primary production per unit of Chl *a* (P : B ratio).

	Spring				
Variable	Lower bay	Midbay	Turbidity maximum	Urban river	Upper river
NO_3 (μmol N L^{-1})	3.4(±4.7)	41.1(±24.2)	93.1(±19.3)	80.9(±20.1)	62.0(±16.5)
NH_4 (μmol N L^{-1})	1.0(±1.6)	7.0(±10.0)	29.3(±18.9)	35.1(±17.4)	11.9(±6.7)
PO_4 (μmol P L^{-1})	0.2(±0.1)	0.3(±0.4)	1.5(±0.7)	2.3(±1.0)	1.5(±0.6)
Si (μmol Si L^{-1})	1.2(±1.2)	16.9(±19.3)	57.7(±25.4)	64.3(±26.5)	56.8(±21.5)
k (m^{-1})	0.77(±0.26)	2.01(±1.14)	4.09(±1.32)	2.04(±1.02)	1.46(±0.98)
Chl *a* (μg L^{-1})	10.4(±12.4)	28.5(±19.8)	18.8(±18.4)	9.9(±9.5)	4.7(±2.4)
APROD (mg C m^{-2} d^{-1})	672(±549)	1,256(±994)	273(±315)	305(±316)	206(±197)
VPROD (mg C m^{-3} d^{-1})	206(±192)	865(±620)	440(±459)	254(±239)	120(±116)
P : B (μg C [μg Chl]$^{-1}$ d^{-1})	30.0(±30.4)	41.0(±33.3)	26.7(±19.4)	28.2(±24.5)	21.7(±15.3)

NH_4 for each of five regions of the estuary with data for all four seasons together (Fig. 3). High P : B ratio was never found at elevated NH_4 concentrations in any of the regions any time of the year. With the minor exception of the upper river samples (Fig. 3E), there were almost no P : B values higher than 100 μg C (μg Chl)$^{-1}$ d^{-1} for samples with NH_4 > 10 μmol L^{-1}. Essentially all the P : B values greater than 100 μg C (μg Chl)$^{-1}$ d^{-1} were from the spring and summer, and the highest values were found in the midbay region and the lower edge of the turbidity maximum region. The occasional elevated production in the turbidity maximum region probably indicates algal populations advected in from the upper edge of the midbay region, which then gave higher measured production because the incubation bottles had higher daily irradiance than the cells would experience in the more turbid waters. The lower and midbay samples with $NH_4 > 2.5$ or 5 μmol L^{-1}, respectively, had >0.2 μmol L^{-1} PO_4 in 90% of cases. In the other three regions, samples with $NH_4 > 10$ μmol L^{-1} had >1 μmol L^{-1} PO_4. Half-saturation constants for the uptake of PO_4 that range from 0.02 (oligotrophic waters) to 0.5 μmol L^{-1} (eutrophic waters; Cembella et al. 1984; Lebo 1990) indicate that the low production in the higher N samples is probably not due to P limitation.

Depth-integrated models for Delaware Estuary primary production—The parameter values of the Type I model (Eq. 1) were obtained for all data points ($n = 678$). Coefficients of the polynomial, a_2 and a_3, were not significantly different from zero and hence were neglected. We obtained the Type I model shown in Eq. 6 ($r^2 = 0.56$, RMSE = 104%; Fig. 4A).

$$\text{APROD}_\text{I} = 0.244 \times \text{Chl}_\text{surf} \times Z_\text{eu} \times E_0 \qquad (6)$$

The Type I model had varied results in different regions of the estuary (Table 2). The model accounted for 74% and 69% of the observed variability in the urban and upper river regions, respectively. In contrast, the model fit less well in the midbay ($r^2 = 0.39$) and the turbidity maximum ($r^2 = 0.43$).

For the Type II model (Eq. 4), coefficients of the polynomials a_3 and b_1 were not significantly different from zero and were neglected. We obtained the Type II model equation shown in Eq. 7 ($r^2 = 0.67$, RMSE = 67%; Fig. 4B).

$$\text{APROD}_\text{II} = (1.846 \times 10^{-2} + 2.769 \times 10^{-5} T^2) \times \text{DL} \times \text{Chl}_\text{surf} \times Z_\text{eu} \times (E_0 - 4.266 \times 10^{-3} E_0^2) \qquad (7)$$

For individual regions, both r^2 and RMSE were improved over the Type I model, with $r^2 > 0.75$ except in the midbay and turbidity maximum (Table 2; Fig. 5).

Correction factor of the Type II model—For each region, the correction factor for the Type II model was obtained (Table 2). The correction factor for the midbay was significantly above unity ($p < 0.001$). In contrast, the correction factors were significantly lower than unity for the lower bay and urban river ($p < 0.001$); for the upper river and turbidity maximum regions, they were not different from unity ($p > 0.05$). These indicate that the Type II model underestimates areal primary production in the midbay and overestimates in the lower bay and urban river.

Correlation coefficients were obtained between parameter values used in the Type II model (Eq. 4) and correction factors for individual data points from all seasons and regions: -0.10 for Chl_surf, 0.15 for T, 0.16 for DL, 0.11 for Z_eu, and no significant correlation for E_0. Although there are significant correlations because of the large amount of data, we consider the influence to be small, especially when compared with the absolute magnitude of the correlation coefficients between nutrient concentrations and correction factors. Nutrient concentrations correlate negatively with correction factors for individual data points: -0.26 for nitrate, -0.30 for ammonium, -0.22 for phosphate, and -0.26 for silicate.

Figure 6 shows correction factors for five ranges of nutrient concentrations. Nutrient concentrations were divided into five ranges, with approximately even numbers of data points ($n = 110$–150). Correction factors were significantly above unity for low to mid ranges of NO_3 (Fig. 6A; 25–65 μmol L^{-1}), NH_4 (Fig. 6B; 1–3.5 μmol L^{-1}), and Si (Fig. 6D; 18–35 and 35–70 μmol L^{-1}), indicating underestimation of areal primary production with the Type II model. In contrast, correction factors were significantly below unity for high

Table 1. Extended.

Summer				
Lower bay	Midbay	Turbidity maximum	Urban river	Upper river
1.4(±2.8)	35.3(±26.6)	112.2(±31.0)	118.4(±36.7)	73.3(±15.4)
1.4(±1.8)	3.0(±3.9)	3.2(±5.6)	10.8(±14.1)	8.9(±5.4)
0.4(±0.3)	1.3(±0.8)	2.1(±0.7)	3.1(±1.2)	2.5(±0.9)
5.3(±3.5)	16.2(±11.1)	22.7(±12.5)	13.7(±16.2)	45.2(±25.9)
0.80(±0.28)	1.33(±0.56)	3.54(±1.47)	1.86(±0.64)	1.72(±0.40)
8.6(±8.9)	9.7(±9.3)	10.1(±5.9)	17.0(±11.0)	18.2(±17.2)
1,454(±1,361)	1,475(±1,322)	431(±275)	1,013(±685)	1,302(±1,329)
579(±433)	1,143(±1,101)	876(±602)	1,107(±888)	1,584(±1,772)
72.8(±40.2)	127.0(±89.4)	108.5(±90.2)	69.4(±32.5)	112.0(±85.9)

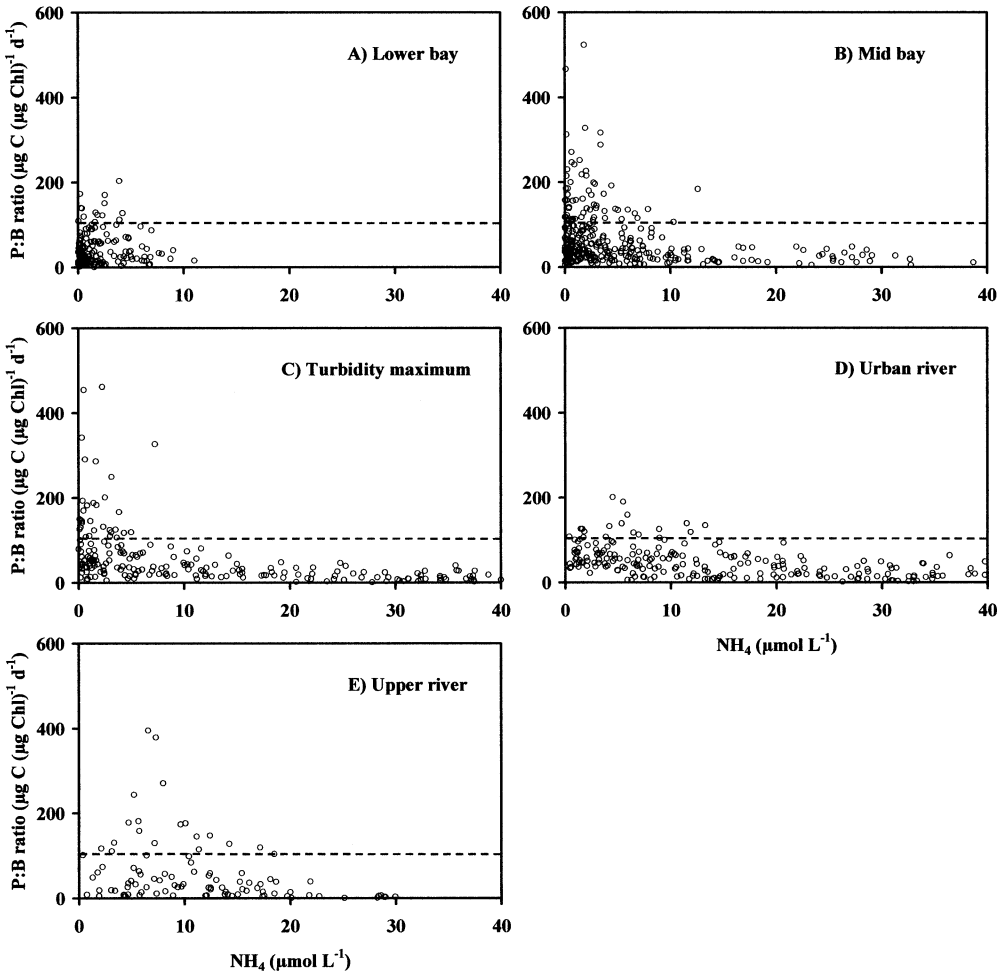

Fig. 3. Maximum volumetric primary production per unit Chl *a* (P : B ratio) versus ammonium for the five regions of the estuary. All data for all seasons for the period 1980–2003 are used for the plots. We consider a P : B ratio >100 μg C (μg Chl)$^{-1}$ d^{-1} to be high production (dashed line on each panel). The highest recorded NH_4 concentrations for the lower bay, midbay, and upper river regions were <40 μmol L^{-1}. In the urban river and turbidity maximum, a number of NH_4 values were recorded up to 100 μmol L^{-1}; no samples with NH_4 >40 μmol L^{-1} had a P : B ratio >50 μg C (μg Chl)$^{-1}$ d^{-1}.

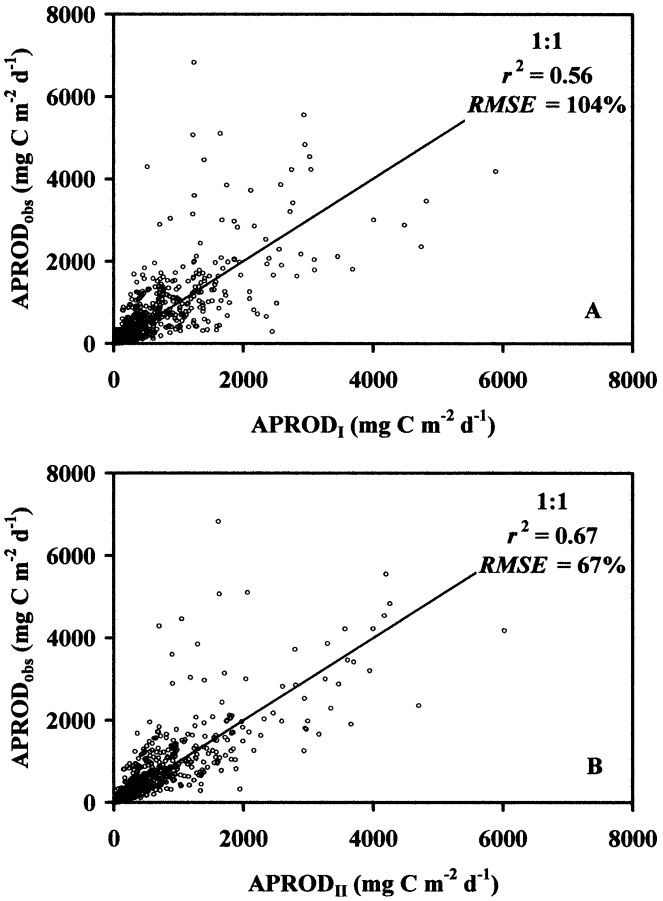

Fig. 4. Observed areal primary production ($APROD_{obs}$) versus estimated areal primary production by (A) the Type I model ($APROD_I$) and (B) the Type II model ($APROD_{II}$).

concentrations of all nutrients except $PO_4 > 2.8$ μmol L^{-1}, indicating overestimation of areal primary production at elevated nutrient levels.

Discussion

In urbanized estuaries, nutrients will accumulate when primary producers cannot effectively utilize them. Borum (1996) has plotted primary production for a number of estuarine and coastal waters versus nitrogen loading. The plot (*see* fig. 9.11 in Borum 1996) shows a maximal increase in primary production at relatively low N with a general decrease at higher N. This type of pattern fits what we are calling a HNLG situation; often a major contributing factor is light limitation. In the Delaware Estuary, light availability is considered to be the central limiting factor; nutrient limitation is only documented in the lower bay region and occasionally in the midbay region (Pennock and Sharp 1994). Our 26-yr dataset strongly indicates a HNLG situation in the Delaware Estuary, as seen in Fig. 2. This empirical observation leads to the question: Why is primary production in nutrient-enriched waters not only saturated but apparently suppressed? Figure 6 shows higher correction factors in low- to mid-nutrient waters and lower correction factors in high-nutrient waters, indicating that any positive nutrient influence is only at relatively low concentration; the correction factors were consistently at or below unity for high NO_3, NH_4, PO_4, and Si (Fig. 6).

We used a series of depth-integrated models to evaluate the effect of environmental variables on primary production in the Delaware Estuary. To our knowledge, a comparable long-term dataset from a single estuary can be found only in the Chesapeake Bay ($n = 585$; Harding et al. 2002). The Ψ model in the Chesapeake Bay gave RMSE = 214%; a model comparable to our Type II model gave RMSE = 120%. These models showed better fit in the Delaware Estuary; RMSE values were 104% and 67%, respectively. The comparison of model results in these two estuaries clarified the controlling factors of their primary productivities. Because estuarine environments show considerable spatial and temporal variability among seasons and years, analysis of a large dataset can aid in a better understanding of primary production in estuaries. Although there are general impressions of differences in primary production between the neighboring Chesapeake and Delaware Bays, it was difficult to quantify these before this comparison. With the Type II model, it is clear that the Delaware Estuary is more controlled by light and temperature and that the Chesapeake Bay, with lower nutrients overall, has a greater dependence on nutrients for control of primary production, although it is still controlled by light availability in the oligohaline and mesohaline regions (Harding et al. 2002).

In addition to the general comparison between estuaries, the difference in the model fit in each region of the Delaware Estuary also is informative. The model fit was better in the

Table 2. Coefficient of determination (r^2) and root mean square percent error (RMSE) values for Type I and Type II model and correction factors (c) for Type II model for five regions of the Delaware Estuary. Correction factors marked with asterisks are significantly above/below unity ($p < 0.001$).

	Type I model		Type II model			No. of samples
	r^2	RMSE	r^2	RMSE	c	
Lower bay	0.63	81%	0.76	70%	0.86*	83
Midbay	0.39	188%	0.57	134%	1.24*	174
Turbidity maximum	0.43	88%	0.61	42%	1.08	134
Urban river	0.74	46%	0.80	31%	0.82*	205
Upper river	0.69	119%	0.77	55%	1.01	82
Total	0.56	104%	0.67	67%	1.00	678

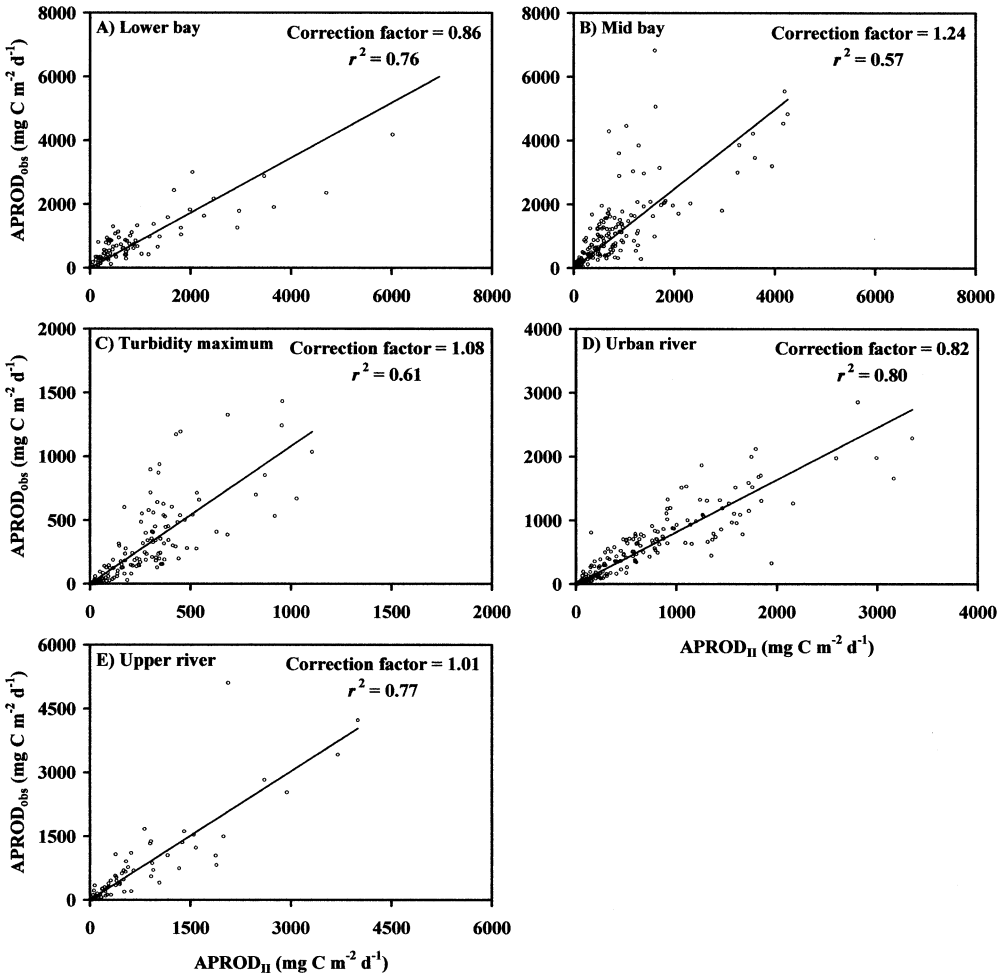

Fig. 5. Observed areal primary production ($APROD_{obs}$) versus estimated areal primary production by the Type II model ($APROD_{II}$) for five regions of the Delaware Estuary.

lower bay and two river regions and worse in the midbay and turbidity maximum. In the river regions, nutrients were never depleted, and primary production was strongly influenced by light availability and temperature; in the lower bay region, the nutrient levels were consistently low throughout the year. These contrasting mechanisms explain the good model fit in these regions. In the midbay, environmental conditions are quite variable; nutrients are depleted during spring blooms when fresh water inflow generates water stratification and degree of light limitation varies with tidal and flow conditions (Pennock 1985). The environmental conditions in the turbidity maximum are also highly variable because it is influenced both by the urban river and midbay via tidal mixing (Sharp et al. 1986).

The actual correction factors for the different regions of the estuary also convey information. In the lower bay, the model overestimates production on average probably because it does not include nutrients and there is considerable nutrient limitation. In the urban river region, the model also overestimates production. Here, both light and nutrients are probably always sufficient, so limitation of production is probably caused by other factors, as is discussed later. In the midbay, the model underestimates production. The reason for this is less clear but is probably related to the fact that light limitation can vary sharply over tidal cycles in some part of this region. The observed production is based on 24-h incubations that do not have the same variation in light level and in which settling of particles can give a greater light field than might be expected from ambient light parameters. The turbidity maximum region with poor correlation does have a correction factor close to unity, indicating that, on average, the model does predict production fairly well. Also, the correction factor for the upper river is close to unity, again indicating that the model variables fairly well characterize the controls on the production.

The striking decline in production at NH_4 levels above a low threshold (around 10 μ mol N L^{-1}) suggests a strongly negative influence of NH_4 itself, of something that accompanies high NH_4 concentrations, or both. Dugdale (unpubl.) has recently suggested that elevated NH_4 reduces primary production in the San Francisco Bay estuary. Figure 3 shows this apparent low production at elevated NH_4 concentrations for all five regions of the Delaware Estuary. In Table 1 and Fig. 2, spring and summer or summer-only data were used to avoid variations caused by temperature and daily irradiance. In Fig. 3, the highest NH_4 concentrations were found

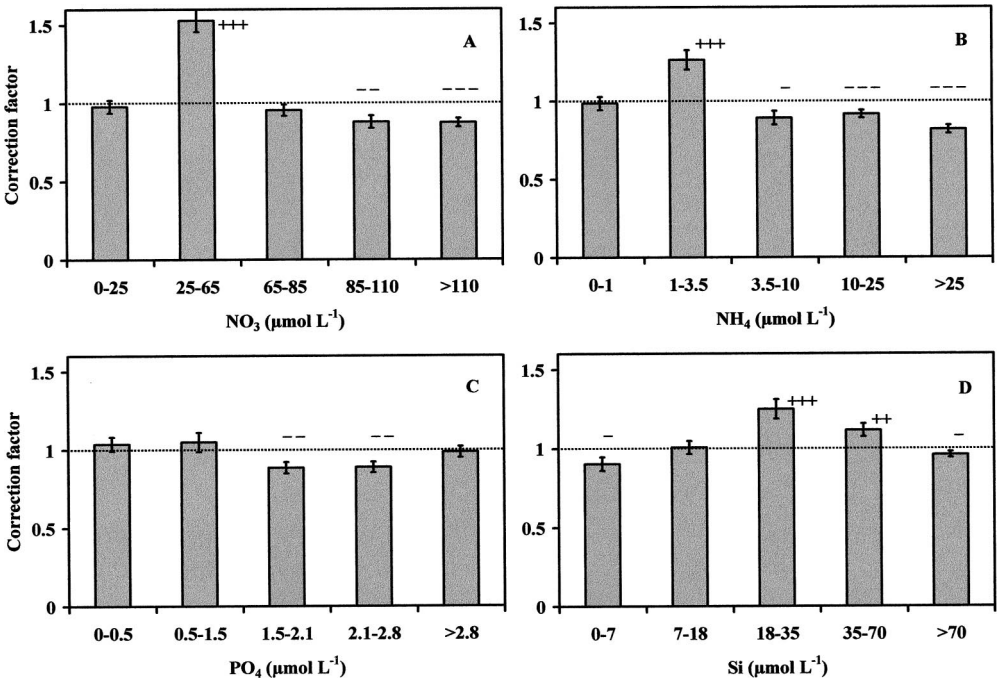

Fig. 6. Correction factors and their standard deviations for five concentration ranges of (A) nitrate, (B) ammonium, (C) phosphate, and (D) silicate. Correction factors are marked when they are significantly different from unity: above unity with $+++$ ($p < 0.001$), $++$ ($p < 0.01$), and $+$ ($p < 0.05$); below unity with $---$ ($p < 0.001$), $--$ ($p < 0.01$), and $-$ ($p < 0.05$).

in the colder months when temperature and daily irradiance were lower. However, the striking decline in production with increasing NH_4 demonstrates the necessity of not using a simple linear relationship between nutrient concentration and primary production. Some of the low production with high NH_4 concentrations occurs when low temperature and daily irradiance might be influential. However, PO_4 does not appear to be limiting at stations with high NH_4. This interesting phenomenon clearly needs further evaluation because it seemingly contradicts the advantage to phytoplankton of preference for NH_4 over NO_3 (Dortch 1990; Flynn et al. 1997). We have confirmed this with a paired mesocosm study in the Delaware Estuary in which identical communities were supported by NO_3 or NH_4 and showed greater production with NO_3 (Parker 2004). This subject is being evaluated further in our laboratory and by R. C. Dugdale (pers. comm.).

In the urban river, where the nutrients are highest, the P : B ratio was significantly lower than in the other parts of the estuary. The correction factor for the urban river region was significantly lower than unity—even lower than for the lower bay. Because this region of the estuary is not strongly light limited, these results suggest that the phytoplankton physiological response in these nutrient-rich waters is diminished by something else. Sanders and Riedel (1992) tried to explore the limiting factors of primary production in the Delaware River and addressed limitation by micronutrients and toxic contaminants. They could not show strong direct evidence of phytoplankton growth inhibition from their experiments but speculated that toxic influences were probable. Although we do not have any direct evidence, negative effects of toxic contaminants should be suspected in this urban region where a number of contaminants are documented as being detrimental to aquatic life (Sheldon and Hites 1978; Delaware River Basin Commission 1991; Fikslin 1991). The major source of anthropogenic inputs is from municipal and industrial discharges around Philadelphia (160 km from the mouth of the bay). We hypothesize that toxic contaminants (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, chlorine by-products, or a combination of toxins) affect the river biota and inhibit primary production. Toxic contaminants are diluted because of the exponential increase in cross-sectional area of the estuary and removed through flocculation of organic matter in the turbidity maximum (Burton 1976). High particulate concentration in the turbidity maximum works as a biogeochemical filter, and the toxicity can be effectively removed (Sharp et al. 1984), resulting in better algal response in the midbay.

The empirical relationships and modeling based on our 26-yr dataset have shown the HNLG situation in the Delaware Estuary. Decreased phytoplankton responses were found in overenriched waters; in particular, primary production was depressed in the urban river where anthropogenic influences were strongest. These findings indicate that high nutrient concentrations do not stimulate primary production; in contrast, it appears that high nutrients are indicative of inhibition. Light was shown to limit primary production in parts of the estuary, and toxic contaminants are suspected of having a negative influence on production in areas with large anthropogenic inputs. The HNLG phe-

nomenon should be considered further in relation to estuarine eutrophication.

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