

**Chesapeake Bay nitrogen fluxes derived from a land-estuarine ocean
biogeochemical modeling system: Model description, evaluation and nitrogen
budgets**

Submitted to the special issue of Journal of Geophysical Research – Biogeosciences
devoted to “Land-ocean Interactions in Coastal Margin Systems”

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24 **Abstract**

25 The Chesapeake Bay plays an important role in transforming riverine nutrients before
26 they are exported to the adjacent continental shelf. Although the mean nitrogen budget of
27 the Chesapeake Bay has been previously estimated from observations, uncertainties
28 associated with interannually varying hydrological conditions remain. In this study, a
29 land-estuarine-ocean biogeochemical modeling system is developed to quantify
30 Chesapeake riverine nitrogen inputs, within-estuary nitrogen transformation processes
31 and the ultimate export of nitrogen to the coastal ocean. Model skill was evaluated using
32 extensive in situ and satellite-derived data, and a simulation using environmental
33 conditions for 2001-2005 was conducted to quantify the Chesapeake Bay nitrogen
34 budget. The five-year simulation was characterized by large riverine inputs of nitrogen
35 ($154 \times 10^9 \text{ gN y}^{-1}$) split roughly 60:40 between inorganic:organic components. Much of
36 this was denitrified ($34 \times 10^9 \text{ gN y}^{-1}$) and buried ($46 \times 10^9 \text{ gN y}^{-1}$) within the estuarine
37 system. A positive net annual ecosystem production for the Bay further contributed to a
38 large advective export of organic nitrogen to the shelf ($91 \times 10^9 \text{ gN y}^{-1}$) and negligible
39 inorganic nitrogen export. Interannual variability was strong, particularly for the riverine
40 nitrogen fluxes. In years with higher than average riverine nitrogen inputs, most of this
41 excess nitrogen (50-60%) was exported from the Bay as organic nitrogen, with the
42 remaining split between burial, denitrification and inorganic export to the coastal ocean.
43 In comparison to previous simulations using generic shelf biogeochemical model
44 formulations inside the estuary, the estuarine biogeochemical model described here
45 produced more realistic and significantly greater exports of organic nitrogen and lower
46 exports of inorganic nitrogen to the shelf.

1. Introduction

Located at the intersection between land and ocean, estuaries play an important role in global carbon and biogeochemical cycles [Bauer *et al.*, 2013; Bianchi and Bauer, 2011, Canuel *et al.*, 2012]. Chesapeake Bay, the largest estuary in the United States, plays a particularly significant role in the transformation and burial of riverine terrestrial nitrogen [Bronk *et al.*, 1998; Glibert *et al.*, 1991; Horrigan *et al.*, 1990; Kemp, 2005]. As a result, it significantly impacts the form and amount of nitrogen that is exported from riverine sources to the adjacent continental shelf.

The fate of riverine nutrients has been intensely studied in the Chesapeake Bay where available water quality data extend back to 1950 [Flemer *et al.*, 1983]. Using five early years (1977-1982) of U.S. Environmental Protection Agency (EPA) data, Smullen *et al.* [1982] concluded that the Chesapeake Bay retained almost all the nutrients entering during this time period. Using the same data Nixon *et al.* [1987] reassessed the nitrogen budget and concluded that the Bay retained only a small amount (3-6%) of the nitrogen entering the system. In a third study, Fisher *et al.* [1988] developed a conceptual model suggesting roughly 50% of total nitrogen left the Bay, primarily through phytoplankton sinking. In these early studies the relative amount of riverine total nitrogen loss in the Bay and export to the open ocean were quite controversial, primarily because of the limited availability of observations and the different assumptions and approaches employed.

A more consistent Chesapeake Bay nitrogen budget came together in the 1990's, after additional measurements were available. Boynton *et al.* [1995] calculated that about 70% of the nitrogen entering the Bay was lost to denitrification, burial and fisheries

harvest, and the remaining 30% was exported to the open ocean. However, these calculations did not include a separation of nitrogen between inorganic and organic forms, and the nitrogen exchange between the Bay and the adjacent shelf was calculated from subtracting the Bay internal sinks from riverine and atmospheric sources, rather than from direct measurements or modeling results. A more detailed budget was described by *Kemp et al.* [1997], however this budget was limited to the main stem of the Bay (Fig. 1). In these calculations nitrogen was separated into dissolved inorganic and organic forms, and the nitrogen seaward transport was calculated from a model simulation. They concluded that roughly 75% of the nitrogen entering the mainstem of the Bay was exported to the open ocean. In addition, the ratio of dissolved inorganic nitrogen to total organic nitrogen at the Bay mouth (0.04) was much smaller than that at the head of the Bay (5.1). Overall the net ecosystem production in the main stem of the Bay was positive, leading *Kemp et al.* [1997] to conclude that this portion of the Bay is net autotrophic.

Although nitrogen budget estimates from observational studies such as those described above have been becoming more consistent in recent decades, they are still associated with considerable uncertainties, largely resulting from relatively low temporal and spatial sampling frequency as well as the interannual variability associated with the observations. One issue with these previous nitrogen budget estimates, for example, is that due to data limitations, asynchronous observations had to be combined. In *Kemp et al.* [1997] nitrogen exchanges at the Bay mouth were from the year 1986, but net ecosystem production (called net ecosystem metabolism in their paper) was from a multiple year average (1986-1993). In addition, to avoid variation of fluxes with different hydrological

conditions, *Kemp et al.* [1997] and *Boynton et al.* [1995] both remove years with extreme wet or dry conditions and use years with low to moderate river flow only.

In order to examine how interannually varying riverine inputs of nitrogen to Chesapeake Bay affect estuarine nitrogen fluxes, a land-estuarine-ocean biogeochemical modeling system is developed for this region. Riverine inputs of nitrogen to the Bay are computed from a terrestrial ecosystem model that resolves riverine discharge variability on scales of days to years. This temporally varying discharge is then used as input to the estuarine-biogeochemical model, which provides estimates of the nitrogen fluxes within the Bay as well as advective exports from the Bay to the adjacent Mid-Atlantic Bight shelf. This coupled modeling system calculates the nitrogen budget of the Chesapeake Bay for a continuous 5-year period (2001-2005), of which the first two years (2001 and 2002) were dry flow years, the third year (2003) was a wet flow year, and the last two years (2004 and 2005) were intermediate flow years.

The content of this paper is organized as follows. Section 2 and the associated supporting information S1 present a complete description of our land-estuarine-biogeochemistry modeling system and the configuration implemented here. In Section 3, model skill is evaluated relative to extensive data from the Chesapeake Bay Program as well as satellite ocean color data. In Section 4, a simulated nitrogen budget for the Bay is presented and compared to previous budgets derived using observational data as well as model results using a generic basin-scale continental shelf model. A summary of our results and potential future work is provided in Section 5.

2. Model Description

2.1 Hydrodynamic Model: ROMS

The physical component of the coupled model is based on the Regional Ocean Modeling System (ROMS) [*Shchepetkin and McWilliams, 2005*] version 3.6. The model domain and horizontal grid follows the Chesapeake Bay community implementation of the ROMS (ChesROMS) [*Brown et al., 2013; Xu et al., 2012*]. The domain spans the region from 77.2°W to 75.0°W and from 36°N to 40°N, covering the main stem and primary tributaries of the Chesapeake Bay, as well as part of the mid-Atlantic Bight (Fig. 1). The horizontal grid spacing varies with highest resolution (430 m) in the northern Bay near the Chesapeake and Delaware Canal, lowest resolution (~10 km) in the southern end of the mid-Atlantic Bight, and an average grid spacing within the Chesapeake Bay of 1.7 km. As in ChesROMS, the model has 20 terrain-following vertical layers with higher resolution near the surface and bottom boundaries. However, unlike ChesROMS, the vertical s-coordinate function follows *Shchepetkin and Williams [2009]*, and stretching parameters at the surface and bottom are set to 6.0 and 4.0, respectively. The bottom topography is also slightly smoothed as in *Scully [2013]* to avoid pressure gradient errors caused by steep bathymetry.

The model is forced with spatially uniform but temporally varying winds, measured every hour at the Thomas Point Light Buoy (-76.4°W, 38.9°N). These observed winds are used rather than other wind products such as those derived from the North American Regional Reanalysis (NARR), since the latter underestimates the observed summer winds by roughly 30%, and does not show the strong directional asymmetry that may play a key role in modulating the strength of vertical mixing [*Scully, 2013*]. Other atmospheric forcing, including air temperature, relative humidity, pressure, precipitation, long and shortwave radiation were obtained from NARR with 3-hr time resolution. The

NARR shortwave radiation was found to be systematically higher than adjacent buoy observations, and therefore it was reduced by 80% [Wang *et al.*, 2012]. At the open boundary, the model is forced by open ocean tides and non-tidal water levels as in ChesROMS [Xu *et al.*, 2012].

The model is configured to use the recursive MPDATA 3D advection scheme for tracers, 3rd-order upstream advection scheme for 3D horizontal momentum and 4th-order centered difference for 3D momentum in the vertical. The Generic Length-Scale vertical turbulent mixing scheme [Warner *et al.*, 2005b] is implemented with the stability functions of Kantha and Clayson [1994], and background mixing coefficients for both momentum and tracers are set to $10^{-5} \text{ m}^2 \text{ s}^{-1}$ as in Scully [2010].

2.2 Biogeochemical Model: ECB

The Estuarine-Carbon-Biogeochemistry (ECB) model implemented here includes a simplified nitrogen cycle with eleven state variables (Fig. 2b): nitrate ($[\text{NO}_3]$), ammonium ($[\text{NH}_4]$), phytoplankton (P), zooplankton (Z), small and large detritus (D_S and D_L), semi-labile and refractory dissolved organic nitrogen ($[\text{DON}]_{\text{SL}}$ and $[\text{DON}]_{\text{RF}}$), inorganic suspended solids ($[\text{ISS}]$), chlorophyll ($[\text{Chl}]$) and oxygen ($[\text{O}_2]$). Although analogous carbon state variables are included in the model as well (dissolved organic carbon, detrital carbon and dissolved inorganic carbon), these will be described and analyzed in a separate publication.

All state variables are horizontally and vertically advected and diffused along with the physical circulation variables. The biological source/sink terms, functions and parameter values are presented in supporting information S1. The model structure was based on Druon *et al.* [2010], which was originally derived from Fennel *et al.* [2006],

with modifications similar to those described by *Hofmann et al.* [2008, 2011]. However, these models were all designed for coastal applications. To adapt the model to an estuarine application in the Chesapeake Bay, a number of model formulations were modified, as described below.

2.2.1 Refractory and Semi-labile DON

Since dissolved organic nitrogen plays a critical role in estuarine nitrogen cycling processes [*Keller and Hood, 2011*], semi-labile and refractory DON components are included as separate state variables in the model. Although $[DON]_{RF}$ does not participate actively in any biological processes, it is input from the rivers, and transported via advection and diffusion throughout the model domain and reduces the light intensity. The $[DON]_{SL}$ is derived from phytoplankton exudation, sloppy feeding and detrital solubilization, and is remineralized into NH_4 (Supporting Information S1).

2.2.2 Inorganic Suspended Solids

As the refractory DON, inorganic suspended solids (ISS) do not participate in the nitrogen cycling directly, but play an important role in reducing the light intensity in the northern Chesapeake Bay. The ISS formulation and related parameters follow *Xu and Hood* [2006]. Specifically, ISS is introduced as an additional state variable, which is decreased by water column sinking and increased by bottom resuspension (Supporting Information S1).

2.2.3 Light Attenuation

The photosynthetic available radiation decreases exponentially with water depth:

$$I(z) = I_0 \cdot PARfrac \cdot e^{-zK_D}$$

where I_0 is the light just below the sea surface, PAR_{frac} is the fraction of light that is available for photosynthesis, K_D is the diffuse attenuation coefficient, and z is depth. *Xu et al.* [2005] used chlorophyll, total suspended solids (TSS), and surface salinity to specify K_D for the Chesapeake Bay, where salinity was used as a proxy for chromophoric dissolved organic matter (CDOM), since CDOM is generally inversely related to salinity. To avoid K_D becoming negative in high salinity regimes, *Xu et al.* [2005] identified empirical relations for high (≥ 15 psu) and low (≤ 15 psu) salinity regimes, respectively. They found that their model successfully explained 70% of the observed K_D variability in the Chesapeake Bay. However, their empirical relationship was based on Chesapeake Bay Program observations from 1995 and 1996, which is outside the more recent study period used in this analysis. Therefore, as a part of this analysis their method was repeated using observations from 2000-2005, and resulted in the following empirical relationship:

$$K_D = 1.4 + 0.063[TSS] - 0.057S$$

where TSS [in mg L^{-1}] represents total suspended solids, including both the inorganic suspended solids (section 2.1.2.1) and organic suspended solids (defined here as particulate organic nitrogen (PON) including P, Z, D_s , and D_L). This relationship was found to explain 76% of the observed variability in K_D . Chlorophyll was excluded from the relationship, as it did not successfully explain any significant additional variability [*Feng et al.*, in prep.]. With this single relationship, K_D is positive when salinity is less than ~ 24 PSU, which covers almost the entire Chesapeake Bay. In high salinity regions of the model domain (close to the Bay mouth and on the Mid-Atlantic Bight shelf) it is possible for the right hand side of the above equation to become negative. To prevent

this, the configuration of K_D used for the U.S East Coast shelf model [*Friedrichs et al.*, in prep. for this issue], is used in high salinity regimes:

If $1.4 + 0.063[TSS] - 0.057S < 0$, then

$$K_D = 0.04 + 0.02486[Chl] + 0.003786\{0, 6.625[DON] - 70.819\}_{\max}$$

where [DON] represents total DON, i.e. the sum of both refractory and semi-labile components.

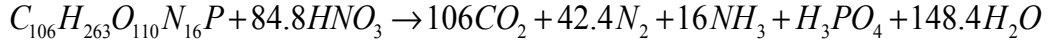
2.2.4 Phytoplankton Specific Growth Rate

Druon et al. [2010] found that using a temperature-independent maximum specific growth rate ($\mu_{\max} = 1.6 \text{ d}^{-1}$) substantially improved their model results in the Mid-Atlantic Bight (their Supporting Information S1, Table S2). In their Chesapeake Bay biogeochemical model, *Xu and Hood* [2006] also used constant (temperature-independent) specific growth rates for phytoplankton species, but imposed different values for phytoplankton adapted to low salinity ($\mu_{\max} = 0.96 \text{ d}^{-1}$) versus high salinity ($\mu_{\max} = 3.22 \text{ d}^{-1}$) regions. Here, a constant maximum specific growth rate (2.15 d^{-1}) is used for our single phytoplankton state variable, based on information provided by *Li et al.* [2009] for the Chesapeake Bay.

2.2.5 Water Column Denitrification

One of the most significant differences between the ECB model and model implementations for the continental shelf results from the fact that hypoxia can occur in estuarine sub-pycnocline waters when water column stratification prevents re-aeration of deeper waters [*Hagy et al.*, 2004; *Bever et al.*, 2013]. During such periods, remineralization of organic matter in the water column transitions from an aerobic to an anaerobic process via facultative anaerobes that shift to suitable alternative electron

acceptors such as nitrate or nitrite [King, 2005]. Water column denitrification has previously been considered in marine ecosystem models of other hypoxic systems, such as the Black Sea and Arabian Sea [Oguz, 2002; Resplandy et al., 2012]. The stoichiometric equation for oceanic denitrification first proposed by Richards [1965] follows:



where organic matter is reduced and dinitrogen gas is released to the atmosphere, a process that has global N-cycle implications [e.g., Codispoti et al., 2001].

Within the ROMS-ECB implementation, onset of water column denitrification is associated with decreasing dissolved oxygen concentration, which reflects the known oxidic repression of nitrogen oxide reductases that are needed to catalyze denitrification reactions [Hood et al., 2006]. With these issues in mind and following Oguz [2002], nitrate loss during water column denitrification is modeled as:

$$\left. \frac{\partial [NO_3]}{\partial t} \right|_{WC-DNF} = -\eta_{DNF} [f_{DNF}, f_{WC}]_{\min} \{ (1 - \delta_N) (r_{D_S} D_S + r_{D_L} D_L) + r_{[DON]} e^{\kappa_{[DON]}^T} [DON] \}$$

where $f_{DNF} = \frac{K_{DNF}}{O_2 + K_{DNF}}$ and $f_{WC} = \frac{[NO_3]}{[NO_3] + K_{WNO_3}}$ are the oxygen and nitrate limitation terms, respectively, for denitrification. The latter limitation is imposed to prevent generation of negative nitrate concentrations. In this way, water column denitrification depends on the stoichiometry for remineralization via denitrification (η_{DNF}), the half-saturation constant for water column denitrification (K_{DNF}), as well as the half-saturation constant for water column NO_3 uptake shutting down (K_{WNO_3}).

2.2.6 Oxygen Limitation of Remineralization

In the water column, oxygen concentration also regulates the rate of nitrification, but in an inverse fashion as compared to its influence on denitrification: as denitrification is enhanced, nitrification is diminished. Thus the nitrification limitation term in the ECB model takes the form:

$$f_{NTR} = \frac{O_2}{O_2 + K_{NTR}}$$

where K_{NTR} is the half-saturation constant for water column nitrification. The remineralization rate of organic matter is regulated by the combined rates of nitrification and denitrification; therefore, the summation of f_{NTR} and f_{DNF} is included for all terms associated with remineralization. The factors f_{NTR} and f_{DNF} are then used to partition aerobic and anaerobic bacterial processing of organic matter between consumption of oxygen and nitrate, respectively.

2.3 Riverine Inputs

In this implementation, ROMS-ECB is forced with daily riverine nutrient input derived from the Dynamic Land Ecosystem Model (DLEM), including NO_3 , NH_4 , DON and PON as well as daily freshwater discharge (Fig. 2a). DLEM is a grid-based fully distributed model which couples major biogeochemical cycles, the water cycle, and vegetation dynamics to derive temporally and spatially explicit estimates of fluxes of water, greenhouse gases and carbon and nitrogen storage in terrestrial ecosystems (Tian *et al.*, 2010, 2014; Liu *et al.*, 2013]. DLEM has been used to hindcast riverine discharge of freshwater, nutrients and organic matter to the U.S. eastern continental shelf over the past century [Yang *et al.*, 2014a,b] and forecast these fluxes over the 21st century [Tao *et al.*, 2014]. The model incorporates hydrological components to simulate lateral water flux from terrestrial ecosystems to river networks. Export of freshwater from land surface to

coastal areas is simulated through three major processes: generation of surface runoff after rainfall events, the leaching of water from land to river networks in the form of overland flow and base flow, and the flow routing process along river channels from upstream areas to coastal regions. For ease of computing in the estuarine model, the total export to the Chesapeake Bay computed by DLEM, including groundwater discharge, was apportioned to ten tributaries, and entered the model domain at these ten locations (Fig. 1a). Because DON provided by DLEM was not separated into semi-labile and refractory components, assumptions had to be made regarding the relative proportions of each component. Of the total DON entering the Bay, 50% was assumed to be semi-labile, and 20% was assumed to be refractory. The remaining 30% of the DON leaving the rivers was assumed to flocculate and be buried before reaching the 5 psu isohaline [Bronk *et al.*, 1998]. The PON provided by DLEM was assumed to enter the Bay entirely as small detritus.

In addition to the above nitrogen components, the river forcing of the model requires temperature and salinity, which was calculated from climatological USGS data (1980 to 2011), and oxygen, which was assumed to be at saturation and computed as a function of temperature and salinity [Weiss, 1970]. The concentration of other river variables, including phytoplankton ($1.8 \text{ mmole-N m}^{-3}$), zooplankton ($0.06 \text{ mmole-N m}^{-3}$) and chlorophyll ($6.0 \text{ mg-Chl m}^{-3}$), were input to the model domain as uniform concentrations.

2.4 Model Implementation

At the open boundary, the *Chapman* [1985] condition is used for the free surface, the radiation condition is used for tracers and baroclinic 3D velocities and the *Flather*

[1976] condition is used for barotropic 2D velocities. Temperature and salinity are nudged in and out of the model domain to climatological data fields generated from the 2001 World Ocean Atlas with time scales of 2-hr and 2 day, respectively [Marchesiello *et al.*, 2001]. The model is initialized with temperature and salinity fields that varied meridionally as in Xu *et al.* [2012]. The initial NO₃ field is derived from fitting winter data from main stem stations with a power function [Xu and Hood, 2006]. The remaining biological variables are set to the following horizontally uniform values: [NH₄] = 0.1 mmole-N m⁻³; P = 6 mmole-N m⁻³; Z = 1 mmole-N m⁻³; D_S = 6.66 mmole-N m⁻³; D_L = 3.33 mmole-N m⁻³; [DON]_{SL} = 13 mmole-N m⁻³; [DON]_R = 23 mmole-N m⁻³, [Chl] = 15 mg-Chl m⁻³, [O₂] = 281.25 mmole-O₂ m⁻³ and ISS = 7 mg L⁻¹. All initial fields are vertically uniform.

The model was first run starting with the above initial conditions from 1 January 2000 until 31 December 2005. The simulated distributions from 31 December 2005 were then used to restart the model on 1 January 2000 and the model was run until 31 December 2005 again. In total, this six-year run was conducted five times to ensure the model was spun up adequately, i.e, there was no clear linear trend for any physical or biological variables and the fluctuations of each of the variables were nearly identical between the fourth and fifth simulations. The last 5-years of this simulation was used for analysis (2001-2005).

3. Model Skill Assessment

Quantitative model-data comparisons using multiple skill metrics [Jolliff *et al.*, 2009; Stow *et al.*, 2009] are critical, as they reveal the advantages and potential limitations of a particular model, which must be carefully considered before using such a

model as a tool for scientific study or decision-making. Using the skill metrics described in supporting information S2, the simulated physical fields (including temperature and salinity) and biogeochemical fields (including NO_3 , NH_4 , DON, PON, chlorophyll and oxygen) were compared with EPA Chesapeake Bay Program Water Quality Monitoring Data.

The Chesapeake Bay Program has been routinely monitoring the main stem of the Chesapeake Bay since June 1984. Specifically, throughout our analysis time period (2001-2005) many water quality parameters, including various forms of nitrogen as well as water temperature, salinity, and dissolved oxygen, were measured once each month during the colder late fall/winter/spring months, and twice each month during the warmer months. At each station (Fig. 1b), vertical profiles of water temperature, salinity and dissolved oxygen were measured at approximately 1- to 2- m intervals through the water column. Data on other variables such as NO_3 , NH_4 , DON, PON, and chlorophyll were collected in the surface and bottom layers, and at depths representing upper (above pycnocline) and lower (below pycnocline) layers in the deeper main-stem stations where salinity stratification occurs.

In addition to comparing simulated fields with these in situ data, simulated surface chlorophyll fields were also compared with satellite-derived surface chlorophyll concentrations from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS). For this purpose, monthly SeaWiFS data for the Chesapeake Bay were processed at a spatial resolution of 2 km using the OC4v6 chlorophyll algorithm.

3.1 Evaluation of Hydrodynamic Fields

Although the focus of this analysis is on the nitrogen budget of the Chesapeake Bay, reasonable nutrient distributions cannot be obtained without an adequate simulation of the observed hydrodynamic fields. Thus simulated temperature and salinity fields were extensively compared to CBP observations.

3.1.1 Temperature

Seasonally averaged simulated temperature distributions are in very good agreement with CBP observations throughout the water column (Fig. 3). Monthly depth-averaged temperature in three Bay subareas, the upper, middle and lower Bay (Fig. 1), show comparable magnitude and fluctuations in both model and observations (Fig. 4). Although the temperature field shows significant temporal variability, increasing from 0°C to 30°C between winter and summer (Fig. 4), there is little horizontal or vertical variability within any given season, with average temperatures being nearly uniform throughout the water column and throughout the main stem of the Bay (Fig. 3). Model skill statistics for temperature (presented in Table 1, and summarized in Taylor and target diagrams (Fig. 5)), indicate that correlations between the simulated and observed temperature fields are very high (> 0.99) and the normalized unbiased RMSD (≤ 0.2) and Bias (≤ 0.1) are both very small. Both temporal and spatial Willmott skill is close to 1.0, further demonstrating that the model has significant skill in reproducing the observed temperature field.

3.1.2 Salinity

Stratification is typically dominated by the salinity signal in the Chesapeake Bay, and thus it is critical for the model to accurately represent the salinity field. Seasonally

averaged simulated salinity distributions are in very good agreement with CBP observations throughout the water column (Fig. 6), successfully capturing both the horizontal and vertical gradients in salinity concentrations. In contrast to that of the temperature field, the spatial variability of the salinity field is much stronger than that of the temporal variability. Observed and simulated salinities vary from ≤ 5 PSU in the upper Bay to ≥ 25 PSU in the lower Bay where seawater intrudes into the Bay mouth. Specifically, over this time period the observed (simulated) averaged salinity \pm standard deviation in the upper Bay is 3.5 ± 4.2 (4.1 ± 4.4), in the middle Bay is 15 ± 3.5 (14 ± 3.8), and in the lower Bay is 22 ± 3.7 (22 ± 4.3). The simulated and observed salinity distributions also show significant interannual variability (Fig. 7), which is strongly influenced by the variable riverine inputs. For example, average salinity was particularly low in 2004, which was an unusually wet year characterized by strong riverine inputs. Although the temporal model skill for salinity is not quite as high as for temperature (Fig. 5, Table 1), correlations between modeled and observed salinity are greater than 0.7 and Willmott skill is greater than 0.85.

3.2 Evaluation of Biogeochemical Fields

Simulated nitrogen (NO_3 , NH_4 , PON and DON), chlorophyll and oxygen fields were also compared with CBP observations. A quantitative skill assessment analysis was performed on both the temporally averaged distributions and the spatially averaged distributions, in order to quantify how well the model captures both the spatial and the temporal (monthly) variability. Finally, the simulated surface chlorophyll concentrations were compared with those derived from SeaWiFS, in which case skill was assessed at each pixel.

3.2.1 NO₃

The simulated NO₃ field successfully captures the horizontal gradient of the observed CBP NO₃ + NO₂ field (Fig. 8a, b). Nitrate concentration is about 60 mmole-N m⁻³ in the upper Bay throughout the water column, decreases rapidly to <15 mmole-N m⁻³ in the middle Bay, and is routinely lower than 5 mmole-N m⁻³ in the lower Bay. The observed and simulated nitrate fields show little vertical gradient throughout most of the Bay, with the exception of the transition zone between the upper and middle Bay (CBP station CB3.2, CB3.3C and CB4.1C). The vertically integrated, simulated NO₂ + NO₃ field reproduces both the magnitude and seasonal cycle of the observations in the upper Bay (Fig. 9a): the observed (simulated) values reach 1.3 ± 0.6 (1.5 ± 0.5) mole-N m⁻² in January, gradually decrease to 0.6 ± 0.5 (0.6 ± 0.3) mole-N m⁻² in August, and increase to 1.1 ± 0.5 (1.4 ± 0.7) mole-N m⁻² again in December. In the middle and lower Bay, the model has more difficulty reproducing the observed seasonal variability: the simulated nitrate is in agreement with the observations for most of the year, but over-estimates the observations in winter, though the observational variability is particularly large in these winter months. As a result, Wilmott skill of NO₂ + NO₃ is higher in the upper Bay (0.84) than in the middle (0.74) or lower Bay (0.34), since concentrations in the upper Bay are primarily dependent on the riverine inputs and physical (advective/diffusive) processes which are well prescribed in this modeling system. Overall, as was the case for salinity and almost all biogeochemical variables, the model demonstrates a greater skill in reproducing the observed spatial mean and variability along the main stem of the Bay, than the interannual mean and monthly variability. Correlations between the simulated and observed distributions are 0.98 (0.64) for the space (time) series. Similarly, the

spatial model skill for NO_3 was as high as 0.99, whereas the temporal model skill was somewhat lower (0.77).

3.2.2 NH_4

Although the model reproduces the spatial variability of the ammonium field relatively well, the magnitude is overestimated, particularly in the upper and middle Bay (Fig. 8c, d). The depth of the strong vertical gradient of NH_4 apparent in the observations (~10-15m) was considerably deeper than that of the simulated NH_4 fields (5-10m). The bottom regeneration causing this vertical gradient may be overly strong in the model. Close to the mouth of the estuary (CBP station CB7.3 and CB7.4), the model successfully reproduces low ammonium concentrations throughout the water column. The model also reproduces the observed pattern of higher NH_4 in the middle Bay compared to other regions of the Bay (Fig. 9b, h, n), but the model somewhat underestimates the magnitude of the seasonal cycle in this region, regenerating too much organic matter in the fall and winter months in this region (Fig. 9h). The depth integrated annual average observed (modeled) NH_4 concentrations in the upper Bay are 0.12 ± 0.13 (0.18 ± 0.12) moleN m^{-2} , in the middle Bay are 0.25 ± 0.3 (0.43 ± 0.33) moleN m^{-2} , and in the lower Bay are 0.068 ± 0.064 (0.074 ± 0.083) moleN m^{-2} , respectively. The quantitative skill of the simulated ammonium distributions are summarized in the Taylor and target diagrams (Fig. 5). As is the case for NO_3 , the model has more skill in repeating the observed spatial variability than the temporal variability. Correlations between the simulated and observed distributions are 0.94 (0.74) for the space (time) series. Overall, the spatial model skill was 0.87, whereas the temporal model skill was again somewhat lower (0.65).

3.2.3 PON

The model reproduced the structure of the observed PON field throughout most of the upper and middle Bay (stations CB2.1 to CB5.3), but overestimated PON in the lower portions of the Bay (stations CB5.4 to CB7.4) (Fig. 7e, f). At the upper Bay stations, the observed (modeled) PON concentration was as low as $15 \pm 8 \text{ mmole-N m}^{-3}$ ($14 \pm 10 \text{ mmole-N m}^{-3}$) throughout the water column. In the middle Bay, the observed (modeled) PON was as high as $21 \pm 9 \text{ mmole-N m}^{-3}$ ($16 \pm 8 \text{ mmole-N m}^{-3}$) above 10 m, but as low as $15 \pm 6 \text{ mmole-N m}^{-3}$ ($12 \pm 9 \text{ mmole-N m}^{-3}$) below 10 m. This structure resulted from the fact that phytoplankton growth was not as light limited in the surface middle Bay waters, as it was nearer the Susquehanna River, where high ISS and CDOM concentrations significantly decreased phytoplankton growth rates. The annual cycle of depth-integrated PON (Fig 9. c, i, o) illustrates that the PON in the middle Bay is overestimated in the summer, primarily from May to September, when phytoplankton growth is overestimated. In the upper Bay, observed PON shows a peak in March, however this peak is associated with large interannual variability ($0.72 \pm 0.70 \text{ mole-N m}^{-2}$) and the modeled concentrations are within this range ($0.25 \pm 0.11 \text{ mole-N m}^{-2}$). Correlations between simulated and observed PON concentrations were 0.93 (0.25) for spatial (time) series (Fig. 5). Overall PON spatial model skill (Table 1) was as high as 0.88, whereas temporal model skill was somewhat lower (0.52).

3.2.4 DON

As is the case for ammonium, observed DON concentrations are highest in the middle Bay, and somewhat lower in the upper and lower Bay. The modeled DON concentrations are generally in agreement with the mean observed DON concentrations, but the model tends to overestimate DON in the upper Bay and at some stations near the

division between the middle and lower Bay (Fig. 8g, h). The mean observed (simulated) DON concentration in the upper Bay is 21 ± 6 (17 ± 4) mmole-N m⁻³; in the middle Bay is 22 ± 4 (20 ± 4) mmole-N m⁻³; and in the lower Bay is 19 ± 4 (14 ± 3) mmole-N m⁻³. The observed DON concentrations show only a slight seasonal signal, with higher concentrations from October through January; this is not well represented in the simulated distributions, which show relatively high concentrations from March to June in both the middle and lower Bay (Fig. 9, d, j, p). Because the model reverses the observed temporal DON pattern, the temporal correlation between modeled and observed DON is negative (-0.17; Fig. 5) and the temporal model skill is low (0.38; Table 1); however, the model has a high skill in reproducing the spatial variability (correlation = 0.98; spatial model skill = 0.96).

3.2.5 Dissolved Oxygen Field

The model reproduces the observed oxygen distributions in the Bay very well. In the upper and lower Bay, both simulated and observed oxygen concentrations are consistently high throughout the water column, whereas in the middle Bay, both simulated and observed oxygen concentrations show a strong vertical gradient (Fig. 8k, l). The model also successfully reproduces the observed vertically integrated dissolved oxygen seasonal cycle (Fig. 9f, l, and r), which closely follows the seasonal cycle of temperature, largely due to the solubility effect of oxygen. Quantitatively, both spatial and temporal model skill are high for dissolved oxygen, with correlations between the simulated and observed fields reaching 0.98 in terms of both space and time (Fig. 5) and overall spatial and temporal model skill both as high as 0.97.

3.2.6 Chlorophyll

The model reproduces the structure of the observed chlorophyll field throughout most of the upper and lower Bay. However, in the middle Bay, the model is in agreement with the observations above 10 m, but underestimates them in deeper waters (Fig. 8 i, j). Not surprisingly, the annual cycle of chlorophyll (Fig. 8 e, k, q) shows a pattern similar to that of PON in the upper and middle Bay for both model and observations, since a significant component of PON is phytoplankton. As is the case for PON, the model overestimates chlorophyll in the middle and upper Bay primarily from May to September when phytoplankton growth is too high, and underestimates chlorophyll in the winter when phytoplankton growth is too low. In addition, observed chlorophyll also shows a peak in March in the upper Bay, however, this peak is associated with large interannual variability ($0.35 \pm 0.43 \text{ g-Chl m}^{-2}$) and the modeled concentrations are within this range ($0.11 \pm 0.07 \text{ g-Chl m}^{-2}$). Overall correlation between model and observations was 0.92 (0.33) for spatial (time) series (Fig. 5). Overall spatial model skill for chlorophyll was as high as 0.94, whereas the temporal model skill was 0.49.

The averaged simulated surface chlorophyll fields were also compared with SeaWiFS-derived chlorophyll concentrations (Fig. 10). The model successfully captures the spatial along-Bay gradient of surface chlorophyll with an overestimation of the satellite-derived estimates in the middle and lower Bay. The five-year mean surface chlorophyll distributions show very low RMSD and high Wilmott skill in the northern half of the Bay, but show some positive bias in the southern half of the Bay. The median value of temporal model skill throughout the Bay is 0.49 (Fig. 10f). The five-year mean vertically integrated primary production was also computed as $1321 \text{ mg-C m}^{-2} \text{ d}^{-1}$, which

is comparable to the mean net primary production ($1357 \text{ mg-C m}^{-2} \text{ d}^{-1}$) derived from MODIS-Aqua [Son *et al.*, 2014].

4. Results and Discussion

4.1 Mean nitrogen fluxes

A mean nitrogen budget for the Chesapeake Bay covering the time period 2001-2005 was computed from the simulated fields described above (Fig. 11). The average total riverine nitrogen (inorganic + organic) entering the Chesapeake Bay as computed from DLEM was $154 \times 10^9 \text{ g-N y}^{-1}$, with roughly 60% of this being present in the inorganic form ($\text{NO}_3 + \text{NH}_4$). Burial removed about 30% of the riverine nitrogen entering the Bay ($46 \pm 10 \times 10^9 \text{ g-N y}^{-1}$), with less than half of this occurring in the main stem (Table 2). Together, water-column denitrification and sediment denitrification removed roughly 20% of the riverine nitrogen entering the Bay ($34 \pm 10 \times 10^9 \text{ g-N y}^{-1}$; Fig. 11), with more than half of this occurring in the main stem. The largest term representing loss of total nitrogen was advective export to the coastal ocean. Although ocean export of inorganic nitrogen was essentially negligible, the export of organic nitrogen was the largest of the nitrogen loss terms ($91 \pm 36 \times 10^9 \text{ g-N y}^{-1}$). Together, the large amount of inorganic nitrogen entering the Bay from the rivers coupled with the large amount of organic nitrogen exiting the Bay through the Bay mouth is indicative of a system characterized by a positive net ecosystem production ($\text{NEP} = 74 \pm 23 \times 10^9 \text{ g-N y}^{-1}$). This is consistent with other studies, which have similarly reported that the Chesapeake Bay acts as a net autotrophic estuary with production of organic nitrogen exceeding the loss of organic nitrogen due to remineralization processes [Fisher *et al.*, 1988; Kemp *et al.*, 1997; 2005].

Our simulated nitrogen budget for 2001-2005 is surprisingly comparable to earlier budgets derived from observations for both the whole Bay [Boynton *et al.*, 1995] and the main stem [Kemp *et al.*, 1997], especially when considering that these estimates were based on different time periods. The observationally based estimates were made using data from 1975-1990, whereas the model was implemented for 2001-2005. Despite these differing time periods of analysis, burial and denitrification rate estimates were very similar, with the data derived estimates falling within the standard deviation of the simulated estimates (Table 2) again for both the main stem [Kemp *et al.*, 1997] and the Bay as a whole [Boynton *et al.*, 1995.] The advective ocean export fluxes calculated using the two different methods were also surprisingly comparable, again especially when considering the significant interannual variability (standard deviations) in the simulated fluxes (Table 2). Finally, the net ecosystem production derived from our ROMS-ECB simulation was calculated to be 5% - 9% of total annual primary production, again in good agreement with the 8% reported by Kemp *et al.* [1997].

4.2 Interannual variability of annual mean nitrogen fluxes

The simulated nitrogen fluxes in the Bay vary considerably on interannual time scales, as quantified by the high standard deviations associated with the individual annual mean fluxes discussed above (Fig. 11). Although some interannual variability exists in the wind, precipitation and radiative forcing, the primary source of this variability is river discharge. For the five years analyzed, the DLEM freshwater river discharge varied by more than a factor of two, from a mean of roughly $50 \text{ km}^3 \text{ y}^{-1}$ over the two lowest flow years (2001-2002) to a mean of nearly $128 \text{ km}^3 \text{ y}^{-1}$ over the two highest flow years (2003-2004; Fig. 12a.) This strong interannual variability in freshwater discharge estimated by

DLEM [Yang *et al.*, 2014a] closely matches (Table 3) that estimated by the regulatory EPA Chesapeake Bay Watershed Model (CBP WM), which has been well tuned to observations from USGS gauging stations [Shenk and Linker, 2013]: 2001-2002 = 56 km³ y⁻¹ and 2003-2004 = 122 km³ y⁻¹ (Shenk and Hinson, pers. comm.)

The strong interannual variability in freshwater discharge entering the Bay leads to a similarly strong interannual variability in DIN and TON inputs into the Bay (Fig. 12b). Specifically, riverine inputs of TON for the high flow years of 2003-2004 (DLEM: 81 x10⁹ kg y⁻¹; CBP WM: 75 x10⁹ kg y⁻¹) are more than twice those of 2001-2002 (DLEM: 38 x10⁹ kg y⁻¹; CBP WM: 32 x10⁹ kg y⁻¹), with once again a similar magnitude for both the DLEM and CBP WM estimates (Table 3). Both the DLEM and CBP WM also indicate that the interannual variability of riverine DIN inputs is strong as well, though this interannual variability estimated by DLEM is somewhat stronger than that of the CBP WM (Table 3). Between 2001-2002 and 2003-2004, DLEM estimates a factor of ~2.5 increase in riverine DIN input, while the CBP WM estimates an increase by a factor of closer to 1.5 (Fig 12b).

The impact of interannual variability of nitrogen inputs on nitrogen fluxes within the Bay is strong. Although the magnitude of NEP, denitrification, burial and ocean export fluxes were higher in high flow years and lower in low flow years, the magnitude of this interannual variability does not vary linearly with freshwater discharge. For example, DLEM estimated that the freshwater discharge increased 160% from the two lowest to the two highest flow years and was associated with a similarly large (150%) increase in riverine input of DIN; however, the resulting variability in the estuarine biogeochemical fluxes was considerably smaller. Burial, and denitrification increased by

only about 50% ($19 \times 10^9 \text{ kg y}^{-1}$) and 70% ($18 \times 10^9 \text{ kg y}^{-1}$) respectively, between these pairs of years.

Interannually varying riverine inputs also impact the advective export of DIN and TON to the coastal ocean. The increase in TON export for the high flow vs. low flow years was even greater in magnitude ($69 \times 10^9 \text{ kg y}^{-1}$) than the increase in TON riverine input ($43 \times 10^9 \text{ kg y}^{-1}$). This result, i.e. the fact that the export of TON increased more than the input of TON, can be explained by examining the inorganic nitrogen fluxes. Specifically, the increase in DIN export for the high flow vs. low flow years was considerably smaller in magnitude ($14 \times 10^9 \text{ kg y}^{-1}$) than the increase in DIN riverine input ($86 \times 10^9 \text{ kg y}^{-1}$). The remaining excess DIN entering the estuary that was not exported to the coastal ocean was either denitrified, or transformed into organic nitrogen prior to export to the continental shelf.

4.3 Comparison of simulated fluxes with those from a continental shelf biogeochemical model

The Chesapeake Bay nitrogen fluxes computed using the ROMS-ECB estuarine model are significantly different (Table 3) from those computed using a regional biogeochemical shelf model configured for the mid-Atlantic Bight [*Druon et al.*, 2010; *Hofmann et al.*, 2011; *Xiao and Friedrichs*, 2014a,b; *Friedrichs et al.*, in prep for this issue]. The version of the regional shelf model used here for comparison (Table 4) did not include the estuarine specific processes developed for ROMS-ECB (Section 2.2) such as light attenuation due to inorganic suspended solids, estuarine specific phytoplankton growth rates, water column denitrification and oxygen limitation of remineralization. Although the riverine fluxes to the Chesapeake Bay are generally comparable for the two

models over the various years examined, the burial and denitrification fluxes computed from the estuarine model removed nearly an order of magnitude more nitrogen from the Bay than did the coastal model (Table 4). In addition, although the total ocean export of nitrogen was similar for the two models, the estuarine model exported almost entirely TON and very little DIN. In contrast, the regional shelf model exported nearly equal amounts of TON and DIN. The critical nitrogen transformations that occur within the estuary were not successfully represented in the regional model, and thus this model overestimated the transport of riverine DIN to the coastal ocean.

The above results demonstrate the importance of resolving estuarine-specific processes in larger scale regional models that include estuarine domains. This is specifically critical for regions receiving considerable amounts of inorganic nutrients and organic matter from estuaries, such as the Mid-Atlantic Bight [Nixon, 1987] and the Louisiana Shelf [Feng *et al.*, 2012; 2014]. In these regions it will likely be necessary and will certainly be most efficient to have relatively high-resolution models specifically developed for estuaries nested inside potentially coarser resolution regional shelf models. Fortunately, many of the critical estuarine biogeochemical formulations in ROMS-ECB are active only in regions of low dissolved oxygen concentrations and high inorganic suspended solids. Since these conditions are not generally present in the mid-Atlantic Bight shelf adjacent to the Chesapeake Bay, the ECB model is likely to successfully reproduce biogeochemical processes on the outer shelf as well as in the Chesapeake Bay. Research devoted to testing this hypothesis is currently underway.

5. Summary

In this study the interannual variability associated with physical and biogeochemical nitrogen fluxes in the Chesapeake Bay has been quantified by means of an estuarine-biogeochemical model (ECB) coupled to a three-dimensional hydrodynamic model (ROMS) and forced by a terrestrial ecosystem model (DLEM). The estuarine model was based on previous mid-Atlantic Bight models [*Druon et al.*, 2010; *Hofmann et al.*, 2008; 2011], but was modified to include key estuarine processes including light attenuation due to inorganic suspended solids, estuarine specific phytoplankton growth rates, water column denitrification and oxygen limitation of remineralization. The ROMS-ECB-DLEM implementation described here shows significant skill in reproducing the variability of both physical and biogeochemical fields of the Bay when evaluating with in-situ and satellite-derived data for a contemporary period (2001-2005). In addition, the nitrogen fluxes computed with this modeling system closely match mean fluxes derived from historical Chesapeake Bay observations, which is particularly surprising given the strong interannual variability associated with these fluxes. Although a number of 3D coupled estuarine models have been previously implemented in the Chesapeake Bay [*Cerco*, 2002; *Li et al.*, 2009; *Testa et al.*, 2014; *Xu and Hood* 2006; *Scully*, 2010; 2013], these previous efforts have been limited to examining one or two specific aspects of estuarine biogeochemistry associated with nitrogen cycling, such as phytoplankton biomass, dissolved inorganic nutrients, or dissolved oxygen concentrations. To our knowledge, this is the first time both physical and biogeochemical components of the complete Chesapeake Bay nitrogen cycle have been investigated using a coupled hydrodynamic-biogeochemical model.

The continuous 5-year period selected for analysis incorporated very different hydrological conditions: dry (2001 and 2002), wet (2003 and 2004) and intermediate (2005). The comparison of nitrogen fluxes obtained for these different hydrological conditions shows that although the magnitude of total nitrogen input from rivers is approximately proportional to river freshwater discharge, the estuarine biogeochemical fluxes, i.e. burial, denitrification and net ecosystem production, are not. An increase of total nitrogen into the Bay of $100 \times 10^9 \text{ kg y}^{-1}$ (including $40 \times 10^9 \text{ kg y}^{-1}$ of TON and $60 \times 10^9 \text{ kg y}^{-1}$ of DIN), which is similar to the difference between the high flow year of 2004 and the low flow year of 2001, results in relatively small increases in denitrification, burial and DIN export to the coastal ocean ($10\text{-}15 \times 10^9 \text{ kg y}^{-1}$). In contrast, such an increase in total nitrogen into the Bay results in nearly a $50\text{-}60 \times 10^9 \text{ kg y}^{-1}$ input of TON to the coastal ocean. Thus increased DIN input to the Bay is not exported directly as DIN to the coastal ocean, but rather is primarily denitrified, or converted to TON before advected out of the Bay.

Three-dimensional (3D) coupled hydrodynamic-biogeochemical models have been widely used in recent years for the study of marine biogeochemical cycling within ocean margins, and provide a useful tool for examining the transformation of nutrients in coastal regions [Banas *et al.*, 2009; Druon *et al.*, 2010; Feng *et al.*, 2014; Fennel *et al.*, 2006; 2011; Friedland *et al.*, 2012; Wakelin *et al.*, 2012; Xue *et al.*, 2013]. However estuaries, which play an important role in global nutrient cycling, are often poorly represented in these types of models. Regional and basin-scale models typically either export riverine nutrients to coastal waters directly omitting the estuaries altogether, or include estuarine regions but apply biogeochemical models derived for continental

shelves to the estuarine domains (e.g., *Fennel et al.* [2006], *Druon et al.* [2010], *Hofmann et al.*, [2008; 2011]). Here nitrogen exported from the Chesapeake Bay computed from the estuarine-specific ECB model was compared with a model developed for the U.S. eastern continental shelf. The significant resulting differences in DIN export ($49 \pm 10 \times 10^9$ gN yr⁻¹ for the coastal model vs. $8 \pm 8 \times 10^9$ gN yr⁻¹ for the estuarine model) highlight the importance of carefully resolving estuarine physical and biogeochemical processes in regional and basin scale models.

Although the ROMS-ECB-DLEM simulations documented here closely replicated nitrogen fluxes derived from observations in the Chesapeake Bay, future efforts will be devoted to further improving the Chesapeake Bay model implementation. First, atmospheric nitrogen deposition, estimated to contribute 12% of the total nitrogen input to the Bay, and commercial fisheries harvest, estimated to only contribute ~3% error [*Boynton et al.*, 1995] have not been included in our budget analysis. These terms will be estimated in future analyses. Secondly, our NPZD-structured model includes a very simplified ecosystem, with only one type of phytoplankton and zooplankton, whereas in reality multiple distinct phytoplankton species are present in the Bay [*Marshall and Nesius*, 1996]. Although efforts are currently underway to expand the model to include multiple phytoplankton and zooplankton components [*Xiao and Friedrichs*, 2014a; 2014b], this will still represent a dramatic over-simplification of the Chesapeake Bay ecosystem, which includes other producers such as submerged plants and benthic algae. These primary producers do contribute to nitrogen fluxes, however it is likely that our simulated nitrogen budgets are still quite robust, as the primary producers within the main stem are dominated by phytoplankton. Possible further

improvements to ROMS-ECB include the incorporation of other nutrient limitation effects such as phosphate and silicate [Fisher *et al.*, 1992] and refining our representation of pelagic-benthic coupling processes. Finally, although ROMS-ECB includes a full carbon cycle (not described here), many of the carbon formulations are more similar to those described in the continental shelf models of Fennel *et al.* [2008] and Druon *et al.* [2010]. These formulations and parameterizations need to be updated so that they are more representative of estuarine systems.

A significant difference between previous Chesapeake Bay model implementations and the modeling effort described here, is that our river forcing is provided by a process based terrestrial ecosystem model. An advantage of linking our estuarine biogeochemistry model directly to such a terrestrial ecosystem model is that the impacts on estuarine nutrient cycling processes of past and future changes in climate, land use and land cover can be examined. Such past and future scenario simulations are currently being conducted and will be described in follow-up studies. As a result, our linked modeling system will likely not only benefit future estuarine scientific studies, but also support management applications and future high stakes decision-making.

702 **Acknowledgments**

703 This work was supported by the NASA Interdisciplinary Science Program
704 (NNX11AD47G). The authors are grateful to the NASA U.S. Eastern Continental Shelf
705 Carbon Cycling (USECoS) team for their useful comments. We thank Jeremy Werdell
706 for providing the high-resolution SeaWiFS chlorophyll level3 data, and Kyle Hinson and
707 Gary Shenk for providing us with Phase 5.3.2 output from the Chesapeake Bay Program
708 Wateshed Model. This is VIMS contribution # xxxx.

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1046

1047 **Table 1:** Willmott Skill of Model Temperature, Salinity, NO₃, NH₄, PON, DON,
1048 Chlorophyll and Dissolved Oxygen
1049

	Upper Bay	Middle Bay	Lower Bay	All (temporal)	All (spatial)
Temperature	0.99	0.99	1.00	1.00	1.00
Salinity	0.87	0.94	0.92	0.99	1.00
NO ₃	0.84	0.74	0.40	0.77	0.99
NH ₄	0.46	0.64	0.71	0.65	0.87
PON	0.32	0.39	0.54	0.52	0.88
DON	0.36	0.40	0.41	0.36	0.96
Chlorophyll	0.36	0.43	0.54	0.49	0.94
DO	0.93	0.98	0.96	0.97	0.97

1050

1051 **Table 2:** Comparison of Chesapeake Bay Nitrogen Fluxes (10^9 g-N y^{-1})
 1052

		Historical estimates (1975-1990)	DLEM-ROMS-ECB Model ¹ (2001-2005)
Total Nitrogen input from river		134 ²	
	DIN	-	96 ± 49
	TON	-	58 ± 22
Burial	Stem + Trib	53 ²	46 ± 10
	Stem	21 ³	22 ± 4
Denitrification ⁴	Stem + Trib	40 ²	34 ± 10
	Stem	23 ³	22 ± 9
Net ecosystem productivity		54 ³	74 ± 23
Total Nitrogen export to ocean			
	DIN	3 ³	8 ± 8
	TON	78 ³	91 ± 36

1053 ¹From this study

1054 ²From data derived estimates of *Boynton et al.* [1995]

1055 ³From data derived estimates of *Kemp et al.* [1997]

1056 ⁴Includes both water column and sediment denitrification

1057 ⁵Calculated from TON budget

Table 3: Comparison of Freshwater Discharge (km^3y^{-1}), DIN flux (10^9g-N y^{-1}) and TON flux (10^9g-N y^{-1}) to Chesapeake Bay

	DLEM <i>Yang et al. [2014a]</i>	CBP WM* <i>Shenk and Linker [2013]</i>
<i>Freshwater discharge:</i>		
2001	48	55
2002	50	57
2003	144	138
2004	112	106
2005	76	81
mean 2001-2005	86 ± 41	87 ± 35
mean 1985-2005	63 ± 22	75
<i>DIN flux:</i>		
2001	55	65
2002	61	73
2003	176	120
2004	112	88
2005	80	84
mean 2001-2005	96 ± 49	86 ± 21
<i>TON flux:</i>		
2001		32
2002	37	33
2003	40	84
2004	87	67
2005	75	49
mean 2001-2005	52	53 ± 21

*Shenk and Hinson, pers. comm.

Table 4: Comparison of Chesapeake Bay Nitrogen Fluxes and Standard Deviations (10^9g-N y^{-1}) Obtained Using Estuarine Biogeochemical Model (ROMS-ECB; this study) and Regional Shelf Biogeochemical Model (USECoS; *Friedrichs et al., in prep. for this issue*).

	ROMS-ECB (2001-2005)	USECoS (2004-2008)
river input DIN	96 ± 50	82 ± 16
river input TON	58 ± 22	75 ± 16
Burial	46 ± 10	5 ± 1
Denitrification ³	34 ± 10	6 ± 1
DIN export to ocean	8 ± 8	49 ± 10
TON export to ocean	91 ± 36	56 ± 11

Figure Captions

Figure 1: Chesapeake Bay (a) model grid and bathymetry, and (b) map illustrating location of riverine inputs (magenta dots), Thomas Point Light Buoy used for wind forcing (yellow triangle) and EPA Chesapeake Bay Program Water Quality Monitoring Stations in the upper (red circles), middle (green circles), and lower (blue circles) Bay. The black line in (a) denotes the edge of the Bay interior, over which the Bay-wide budget numbers are computed. The black line in (b) shows the stations along the trench of the Bay used in Figs. 3, 6, 8.

Figure 2: Schematic of the land-estuarine ocean biogeochemical modeling system. The nitrogen cycle of the estuarine model was detailed illustrated.

Figure 1: Observed and simulated seasonal temperature from 2001-2005. Left panels: temperature along the trench with background color representing the simulation and circles showing the observations. Right panels: modeled vs. observed temperature at coincident times and locations. Panels from top to bottom: winter (Dec-Feb); spring (Mar-May); summer (Jun-Aug) and fall (Sep-Nov). Gray dashed lines in (a) denote the boundaries of the upper, middle and lower Bay. Stations from upper Bay to lower Bay are: CB2.1, CB2.2, CB3.1, CB3.2, CB3.3C, CB4.1C, CB4.2C, CB4.3C, CB5.1, CB5.2, CB5.3, CB5.4, CB5.5, CB6.1, CB6.2, CB6.3, CB7.3, CB7.4.

Figure 2: Observed and simulated mean monthly depth-averaged temperature from 2001-2005 in the upper (a), middle (b), and lower (c) Bay. Vertical bars represent ± 1 standard deviation.

Figure 5: Taylor (a) and Target (b) diagrams illustrating model skill for hydrodynamic and biogeochemical fields. Squares represent temporal model skill and circles represent spatial model skill.

Figure 6: As in Figure 3, except for salinity.

Figure 7: Observed and simulated monthly salinity from 2001-2005 in the upper (a), middle (b), and lower (c) Bay. Error bars are ± 1 standard deviations.

Figure 8: Observed and simulated climatological (average over five years) biogeochemical fields from 2001-2005. Panels from top to bottom: $\text{NO}_2 + \text{NO}_3$, NH_4 , PON, DON, chlorophyll, and oxygen. Left panels: concentrations along the trench with background color representing the simulation and circles showing the observations. Right panels: vertically integrated observed and simulated concentrations at stations shown in Figure 1b with error bars showing ± 1 standard deviation relative to the 5-year mean.

Gray dashed lines in (a) denote the boundaries of the upper, middle and lower Bay.

Figure 9: Observed and simulated vertically integrated monthly biogeochemical fields averaged over 2001-2005. Error bars are ± 1 standard deviations. Panels from left to right:

NO₂ + NO₃, NH₄, PON, DON, chlorophyll and oxygen. Panels from top to bottom:
upper, middle and lower Bay.

Figure 10: Comparison between five-year (2001-2005) averaged sea surface chlorophyll from (a) SeaWiFS and (b) model simulation. Skill assessment is illustrated by (c) unbiased RMSD, and (d) Willmott skill together with histograms of (e) unbiased RMSD and (f) Willmott skill.

Figure 11: The nitrogen budget for 2001-2005 in the Chesapeake Bay from our modeling system (unit: 1×10^9 g-N y⁻¹). The exchange of DIN/PON between the internal Bay and exterior ocean was estimated using the mean velocity and DIN/PON concentration fields averaged daily at a cross section of Bay mouth (red line in Figure 1a). Net ecosystem productivity (NEP) was estimated from the TON budget as in *Kemp et al.* [1997].

Figure 12: (a) Freshwater discharge for the 2001-2005 period. Multiple years average (1980-2008) with the standard deviation was shown (grey solid and dashline); (b) Interannual variability of nitrogen fluxes computed for the 2001-2005 analysis period.

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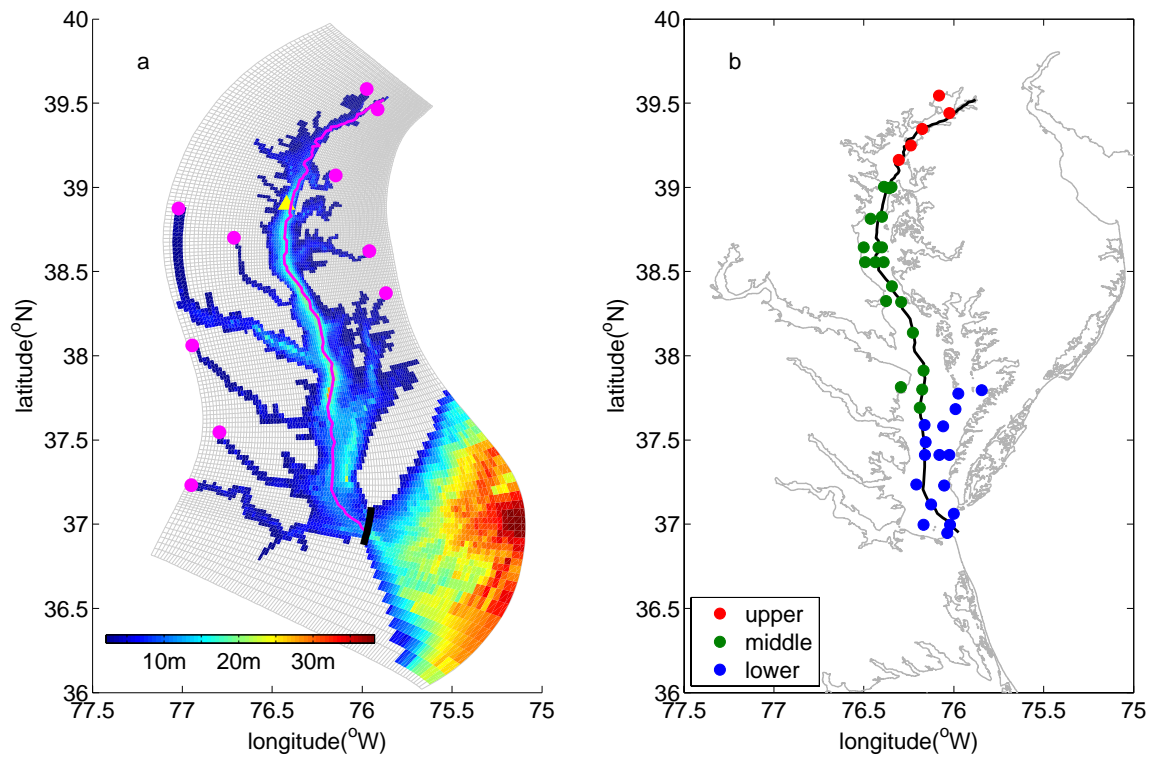


Figure 1: Chesapeake Bay (a) model grid and bathymetry, and (b) map illustrating location of riverine inputs (magenta dots), Thomas Point Light Buoy used for wind forcing (yellow triangle) and EPA Chesapeake Bay Program Water Quality Monitoring Stations in the upper (red circles), middle (green circles), and lower (blue circles) Bay. The black line in (a) denotes the edge of the Bay interior, over which the Bay-wide budget numbers are computed. The black line in (b) shows the stations along the trench of the Bay used in Figs. 3, 6, 8.

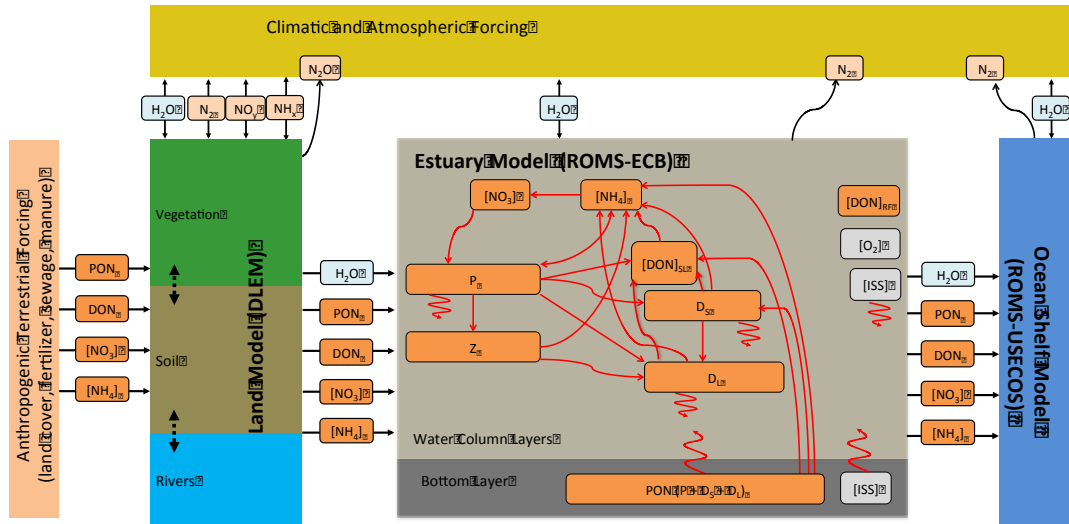


Figure 2: Schematic of the nitrogen components of the land-estuarine-ocean biogeochemical modeling system (ROMS-ECB-DLEM).

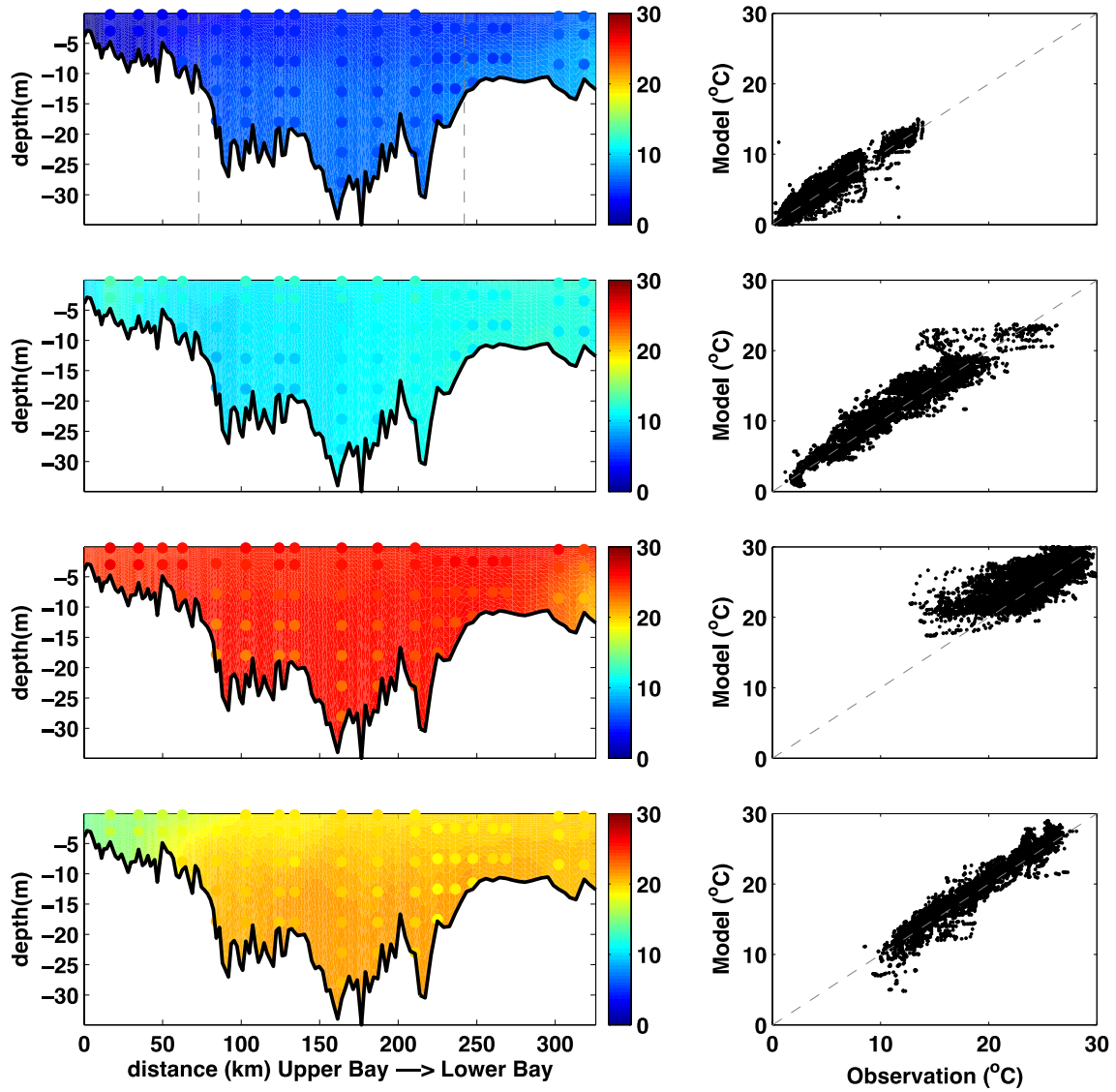


Figure 3: Observed and simulated seasonal temperature from 2001-2005. Left panels: temperature along the trench with background color representing the simulation and circles showing the observations. Right panels: modeled vs. observed temperature at coincident times and locations. Panels from top to bottom: winter (Dec-Feb); spring (Mar-May); summer (Jun-Aug) and fall (Sep-Nov). Gray dashed lines in (a) denote the boundaries of the upper, middle and lower Bay. Stations from upper Bay to lower Bay are: CB2.1, CB2.2, CB3.1, CB3.2, CB3.3C, CB4.1C, CB4.2C, CB4.3C, CB5.1, CB5.2, CB5.3, CB5.4, CB5.5, CB6.1, CB6.2, CB6.3, CB7.3, CB7.4.

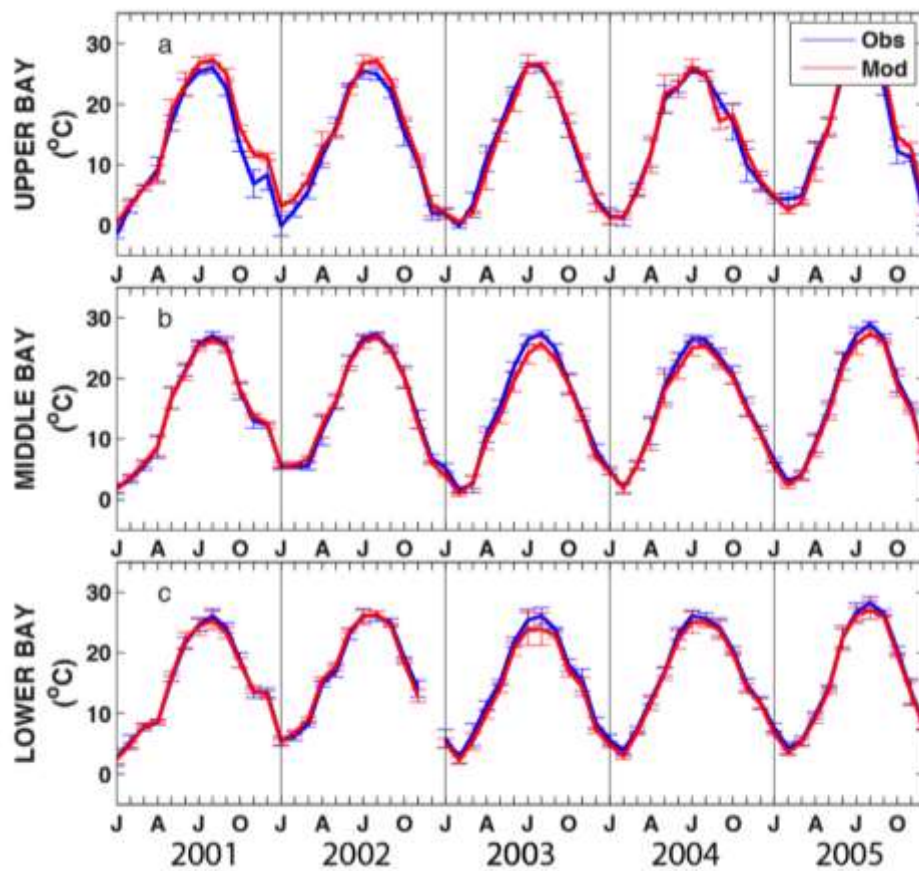


Figure 4: Observed and simulated mean monthly depth-averaged temperature from 2001-2005 in the upper (a), middle (b), and lower (c) Bay. Vertical bars represent ± 1 standard deviation.

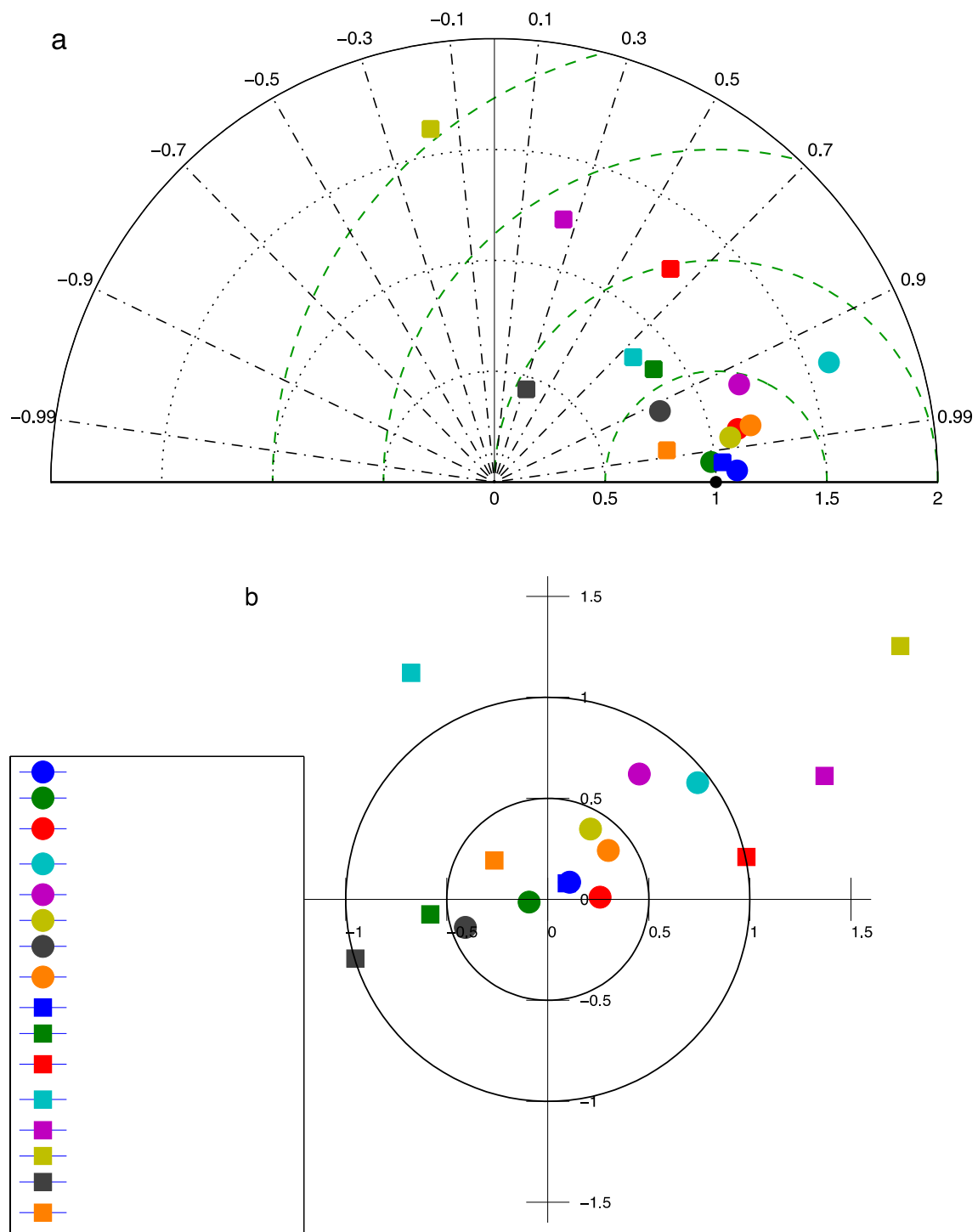


Figure 5: Taylor (a) and Target (b) diagrams illustrating model skill for hydrodynamic and biogeochemical fields. Squares represent temporal model skill and circles represent spatial model skill.

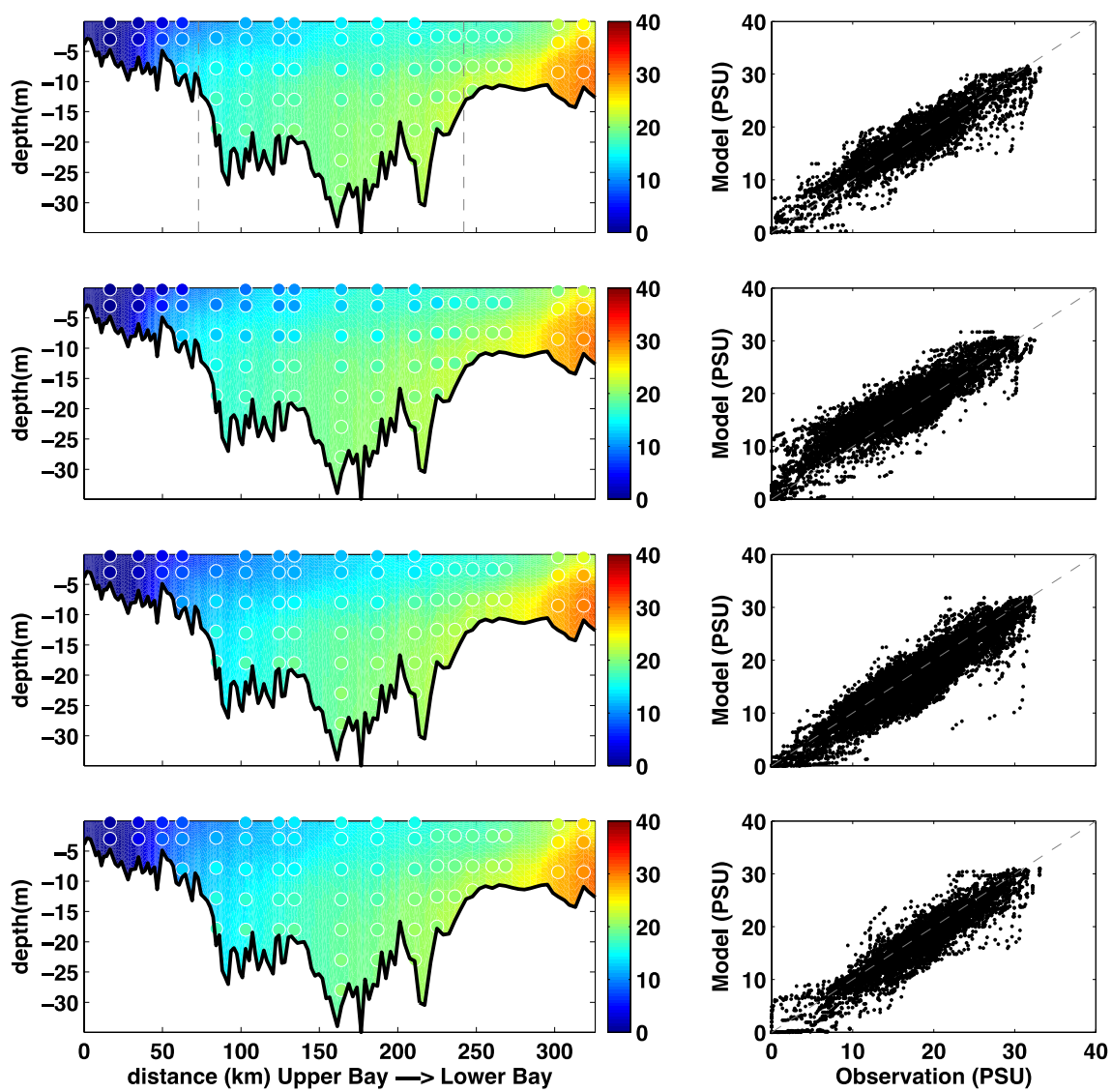


Figure 6: As in Figure 3, except for salinity.

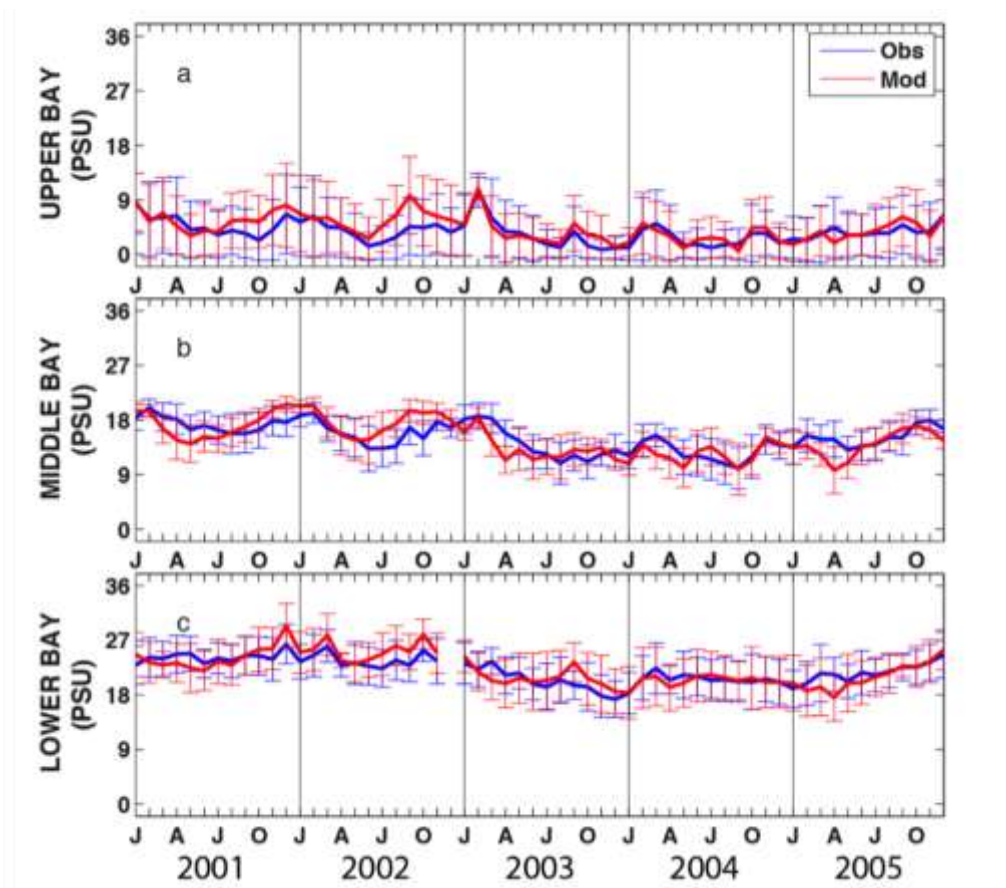


Figure 7: Observed and simulated monthly salinity from 2001-2005 in the upper (a), middle (b), and lower (c) Bay. Error bars are ± 1 standard deviations.

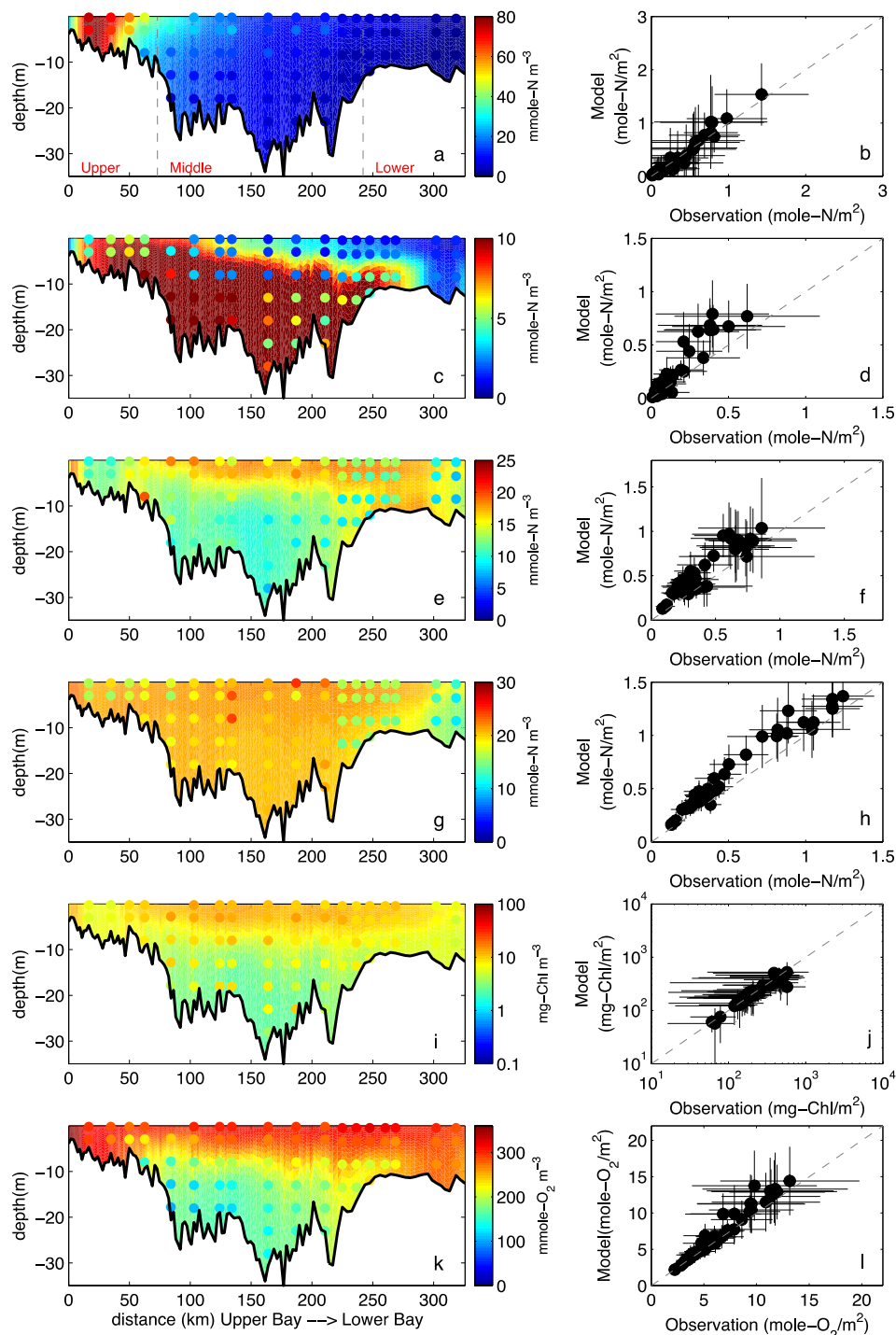


Figure 8: Observed and simulated climatological (average over five years) biogeochemical fields from 2001-2005. Panels from top to bottom: $\text{NO}_2 + \text{NO}_3$, NH_4 , PON, DON, chlorophyll, and oxygen. Left panels: concentrations along the trench with background color representing the simulation and circles showing the observations. Right panels: vertically integrated observed and simulated concentrations at stations shown in Figure 1b with error bars showing ± 1 standard deviation relative to the 5-year mean. Gray dashed lines in (a) denote the boundaries of the upper, middle and lower Bay.

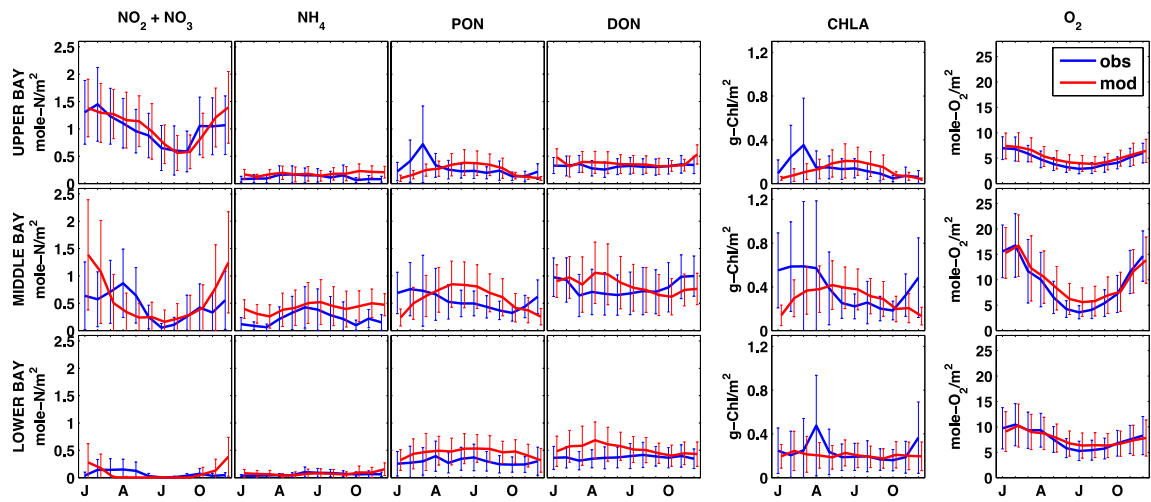


Figure 9: Observed and simulated vertically integrated monthly biogeochemical fields averaged over 2001-2005. Error bars are ± 1 standard deviations. Panels from left to right: NO₂ + NO₃, NH₄, PON, DON, chlorophyll and oxygen. Panels from top to bottom: upper, middle and lower Bay.

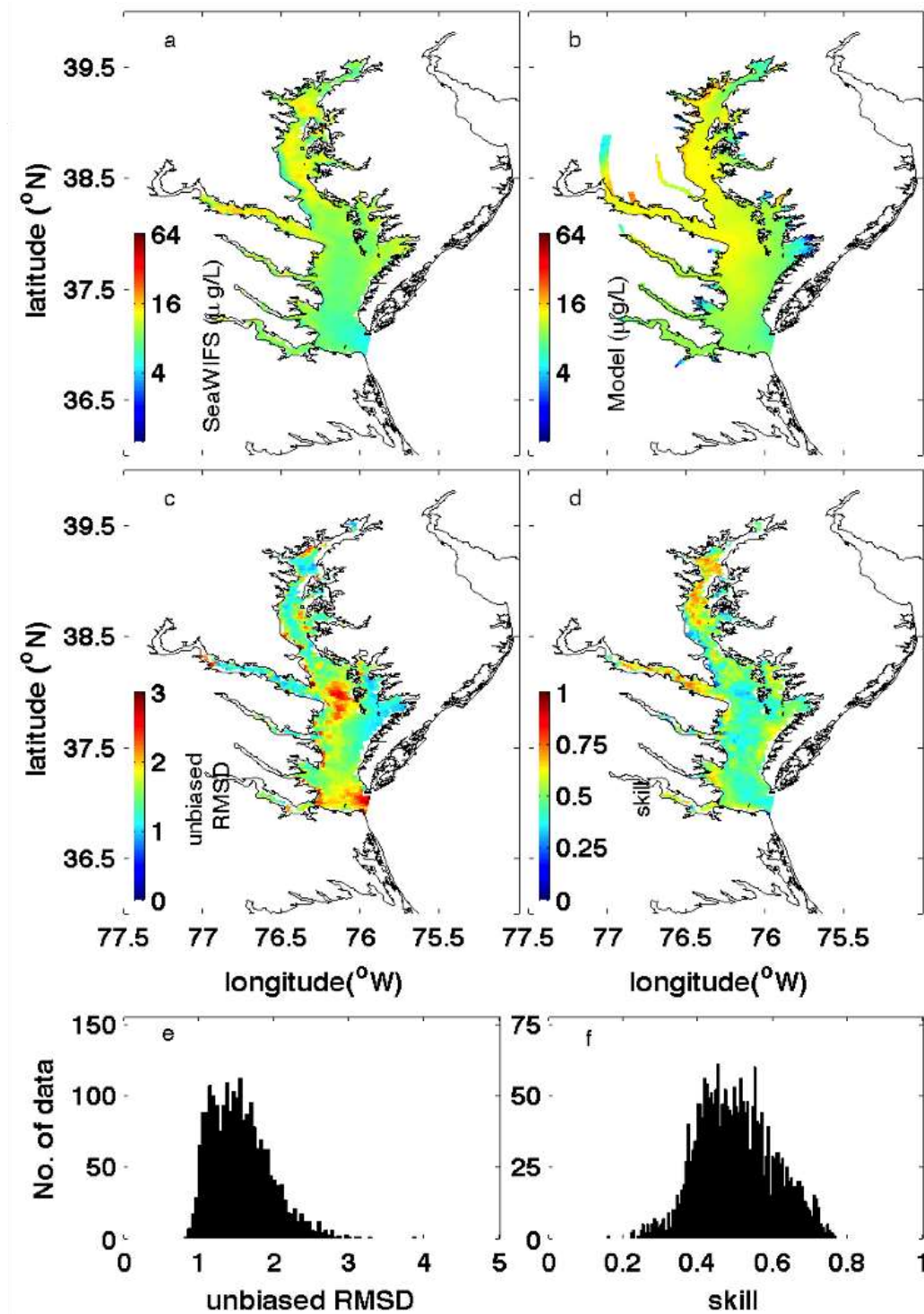


Figure 10: Comparison between five-year (2001-2005) averaged sea surface chlorophyll from (a) SeaWiFS and (b) model simulation. Skill assessment is illustrated by (c) unbiased RMSD, and (d) Willmott skill together with histograms of (e) unbiased RMSD and (f) Willmott skill.

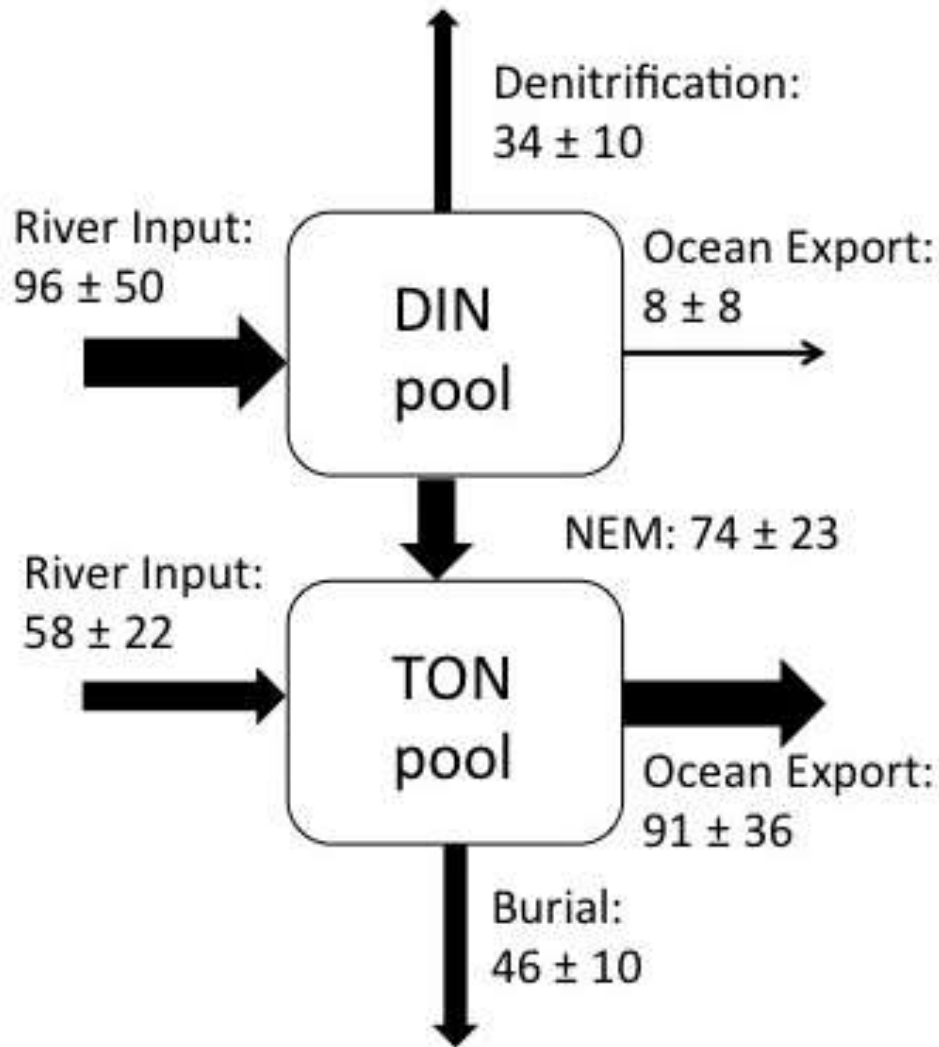


Figure 11: The nitrogen budget for 2001-2005 in the Chesapeake Bay from our modeling system (unit: 1×10^9 g-N y^{-1}). The exchange of DIN/PON between the internal Bay and exterior ocean was estimated using the mean velocity and DIN/PON concentration fields averaged daily at a cross section of Bay mouth (red line in Figure 1a). Net ecosystem productivity (NEP) was estimated from the TON budget as in *Kemp et al.* [1997].

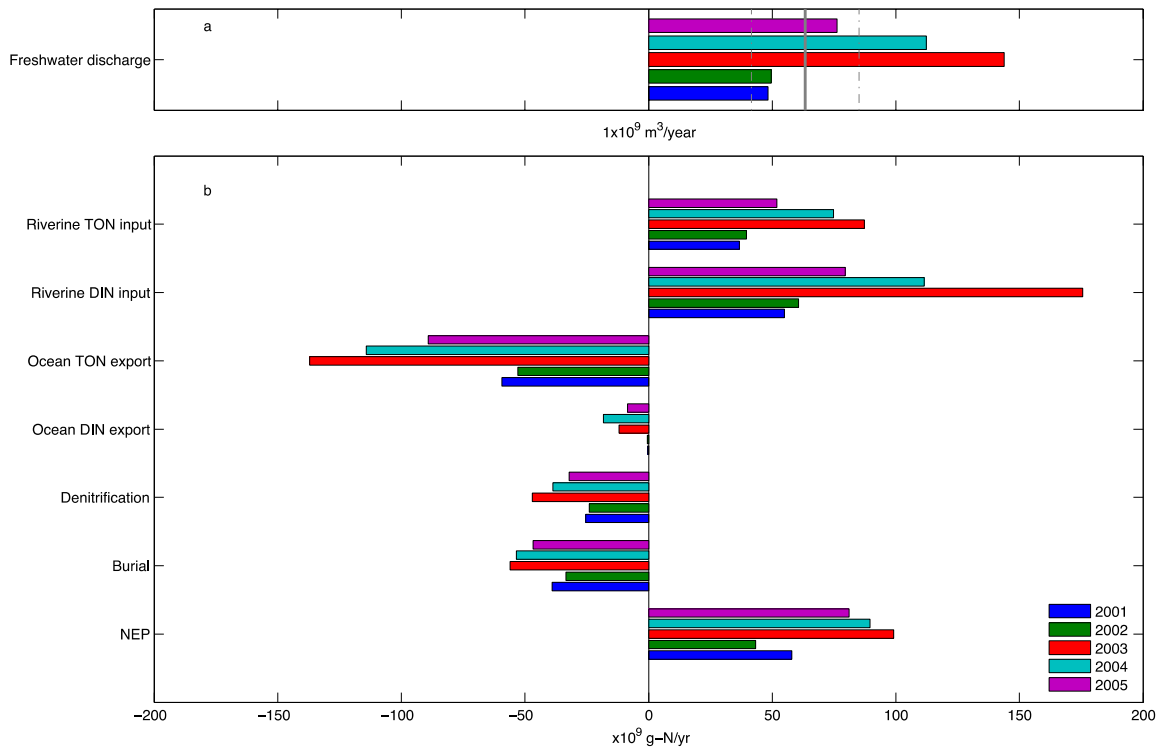


Figure 12: (a) Mean freshwater discharge for each simulation year, with the long-term DLEM mean discharge (1980-2008; grey solid line) and standard deviation (gray dashed line) included for reference; (b) Interannual variability of nitrogen fluxes computed for each of the simulation years.