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Supporting Information for

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

Yang Feng[1], Marjorie A. M. Friedrichs[1], John Wilkin[2], Hanqin Tian[3], Qichun Yang[3], Eileen E. Hofmann[4], Jerry D. Wiggert[5] and Raleigh R. Hood[6]

[1]Virginia Institute of Marine Science, College of William and Mary, Gloucester Point, Virginia

[2]Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, New Jersey

[3]International Center for Climate and Global Change Research and School of Forestry and Wildlife Sciences, Auburn University, Auburn, Alabama

[4]Center for Coastal Physical Oceanography, Old Dominion University, Norfolk, Virginia

[5]Department of Marine Science, University of Southern Mississippi, Stennis Space Center, Mississippi

[6]Horn Point Laboratory, University of Maryland Center for Environmental Science, Cambridge, Maryland

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Additional Supporting Information (Files uploaded separately)

Model Equations for Biogeochemistry

The biogeochemical source/sink equations for the estuarine biogeochemical model state variables that specifically pertain to the nitrogen cycle are described in the below text as well as summarized in Tables A1 and A2. Model function symbols are defined in Table A3, and parameter definitions and values are provided in Table A4 (see appendix in the text).

Phytoplankton

Phytoplankton are increased by primary production and decreased by grazing, mortality, aggregation and sinking. Two additional processes, exudation to semi-labile DON and ammonium were added. The exudation to ammonium pool was limited by coupled water column nitrification/denitrification through the low oxygen condition. Changes in phytoplankton due to those biological processes are finally determined as:

$$\frac{\partial P}{\partial t} = \left[1-\gamma-(f_{NTR}+f_{DNF})\omega\right]\mu_0 L_I (L_{NO_3}+L_{NH_4})P - gZ - m_P P - \tau(D_S+P)P - w_P\frac{\partial P}{\partial t} \tag{1}$$

Chlorophyll

The sources and sinks of chlorophyll are consistent with those for phytoplankton:

$$\begin{aligned}\frac{\partial[Chl]}{\partial t} &= \rho_{[Chl]}\left[1-\gamma-(f_{NTR}+f_{DNF})\omega\right]\mu_0 L_I (L_{NO_3}+L_{NH_4})[Chl] \\ &-g\frac{Z}{P}[Chl] - m_P[Chl] - \tau(D_S+P)[Chl] - w_P\frac{\partial[Chl]}{\partial z}\end{aligned} \tag{2}$$

Zooplankton, Small and large detritus

The zooplankton source term is the assimilation of phytoplankton. The loss terms represent excretion and mortality. The efficiency of the assimilation is β, and the remainder *(1- β)Z* is lost to semi-labile DON and ammonium through sloppy feeding and to large detritus by fecal pellet production.

$$\frac{\partial Z}{\partial t} = \beta g Z - \left(l_{BM} + l_E \beta \frac{P^2}{K_P + P^2} \right) Z - m_Z Z^2 \tag{3}$$

Small and large detritus

Phytoplankton and zooplankton mortality is transferred into the small and large detritus pools, respectively. Phytoplankton and small detritus aggregate to large detritus. Following *Druon et al.* [2010], part of the small and large detritus pools are transferred to semi-labile DON by bacterial solubilization with an efficiency of δ_N. The remaining detrital material is remineralized. The remineralization rate is limited by water column nitrification and denitrification processes.

$$\frac{\partial D_S}{\partial t} = m_P P - \tau (D_S + P) D_S - \left[\delta_N + (1 - \delta_N) \left(f_{NTR} + f_{DNF} \right) \right] r_{D_S} D_S - w_S \frac{\partial D_S}{\partial z} \tag{4}$$

$$\frac{\partial D_L}{\partial t} = (1 - \beta)(1 - \lambda) g Z + m_Z Z^2 + \tau (D_S + P)^2 - \left[\delta_N + (1 - \delta_N) \left(f_{NTR} + f_{DNF} \right) \right] r_{D_L} D_L - w_L \frac{\partial D_L}{\partial z} \tag{5}$$

Semi-labile and refractory DON

Semilabile DON may be gained through phytoplankton exudation, sloppy feeding, bacterial solubilization, and lost through remineralization. The rate of remineralization is limited by temperature as well as nitrification/denitrification.

$$\begin{aligned} \frac{\partial [DON]_{SL}}{\partial t} &= \gamma \mu_0 L_I (L_{NO_3} + L_{NH_4}) P + (1 - \beta) \lambda \varepsilon g Z + \delta_N (r_{D_S} D_S + r_{D_L} D_L) \\ &- r_{[DON]_{SL}} e^{\kappa_{[DON]_{SL}} T} (f_{NTR} + f_{DNF}) [DON]_{SL} \end{aligned} \tag{6}$$

The refractory DON does not participate directly in the biogeochemical cycling, however it does affect light attenuation.

Nitrate

Nitrate is taken up by phytoplankton during photosynthesis and produced through nitrification. In addition, nitrate is lost to the atmosphere as nitrogen gas through water column denitrification, the rate of which is limited by the availability of oxygen. The time rate of change due to biological process for nitrate is:

$$\frac{\partial[NO_3]}{\partial t} = -\mu_0 L_I L_{NO_3} P - \eta_{DNF}\left[f_{DNF}, f_{WC}\right]_{\min}\left\{(1-\delta_N)\left(r_{D_S} D_S + r_{D_L} D_L\right) + r_{[DON]_{SL}} e^{\kappa_{[DON]_{SL}} T}[DON]_{SL}\right\} \\ + n f_{NTR}[NH_4] \tag{7}$$

Ammonium

The sources of ammonium include phytoplankton exudation and sloppy feeding, zooplankton excretion, and remineralization of small detritus, large detritus and semi-labile organic nitrogen. The sinks of ammonium include nitrification and uptake by phytoplankton. The time rate of change due to biological processes for ammonium is:

$$\frac{\partial[NH_4]}{\partial t} = \mu_0\left[-L_{NH_4} + (f_{NTR} + f_{DNF})(L_{NO_3} + L_{NH_4})\omega\right] L_I P + \left[(1-\beta)\lambda(1-\varepsilon)g + \left(l_{BM} + l_E \beta \frac{P^2}{K_P + P^2}\right)\right] Z \\ + (f_{NTR} + f_{DNF})\left\{(1-\delta_N)\left(r_{D_S} D_S + r_{D_L} D_L\right) + r_{[DON]_{SL}} e^{\kappa_{[DON]_{SL}} T}[DON]_{SL}\right\} - n f_{NTR}[NH_4] \tag{8}$$

Inorganic Suspended Solids

Inorganic suspended solids do not participate in the water column biogeochemical cycle, however they do affect light attenuation. Concentrations of ISS are reduced by sinking and increased by seabed resuspension.

$$\frac{\partial[ISS]}{\partial t} = -w_{ISS}\frac{\partial[ISS]}{\partial z} \tag{9}$$

Dissolved Oxygen

The oxygen increased or decreased due to the above biological processes with the stoichiometry $\eta_{O_2:NO_3}=138:16$ and $\eta_{O_2:NH_4}=106:16$ when consuming 1 mole of nitrate or ammonium. The phytoplankton exudated semi-labile DOC during photosynthesis. The semi-labile DOC exudation process does not follow the Redfield ratio. *Druon et al.* [2010] describe a carbon excess-based semi-labile DOC exudation process, which is the carbohydrate production over the nutrient-based part. The oxygen produced by the synthesis of carbohydrates (carbon excess uptake) has a one to one molar ratio following the equation: CO_2 +H_20 + energy -> (CH_2O) + O_2. The oxygen uptake from oxidation of DON with a C to N ratio of $\eta_{C:N}$= 6.6, therefore, the oxygen production by this part is $\gamma_C\eta_{C:N}\mu_0 L_I(1-L_{NH_4}-L_{NO_3})P$.

In addition to the biochemical sources and sinks of oxygen, there is gas exchange across the air-sea interface, which modified the oxygen concentration in the top layer. The air-sea oxygen exchange was calculated as $vk_{O_2}/\Delta z([O_2]_{sat}-[O_2])$ as in *Fennel et al.* [2013], where vk_{O_2} is the gas exchange coefficient for oxygen, and $[O_2]_{sat}$ is the oxygen saturation calculated from *Garcia and Gordon* [1992].

$$\begin{aligned}\frac{\partial[O_2]}{\partial t}=&+\mu_0\left[\eta_{O_2:NO_3}L_{NO_3}+\eta_{O_2:NH_4}L_{NH_4}-\eta_{O_2:NH_4}f_{NTR}\omega(L_{NO_3}+L_{NH_4})\right]L_I P\\&-\eta_{O_2:NH_4}\left[(1-\beta)\lambda(1-\varepsilon)g+\left(l_{BM}+l_E\beta\frac{P^2}{K_P+P^2}\right)\right]Z\\&-\eta_{O_2:NH_4}f_{NTR}\left\{(1-\delta_N)\left(r_{D_S}D_S+r_{D_L}D_L\right)+r_{[DON]_{SL}}e^{\kappa_{[DON]_{SL}}T}[DON]_{SL}\right\}\\&-2f_{NTR}n[NH_4]\\&+\gamma_C\eta_{C:N}\mu_0 L_I(1-L_{NH_4}-L_{NO_3})P\\&+v\frac{K_{O_2}}{\Delta z}\left([O_2]_{sat}-[O_2]\right)\end{aligned} \quad (10)$$

Bottom boundary conditions

The fate of organic matter reaching the benthos includes: (1) resuspension; (2) remineralization; (3) burial. The resuspension of the organic matter is back to the water column as D_S. The fraction of resuspension is ϕ_1, which is a function of the bottom stress [*Druon et al.* 2010]: $\phi_1 = \Gamma / \Gamma_c$, where $\Gamma = \sqrt{\tau_{b_x}^2 + \tau_{b_y}^2}$ is the bottom shear stress, $\Gamma_c = 0.05$Pa is the critical shear stress [*Xu and Hood*, 2006]. Therefore, the time rate of change of small detritus in the model's bottom layer is:

$$\left.\frac{\partial D_S}{\partial t}\right|_{z=H} = \frac{\phi_1}{\Delta z} F_{TON} \tag{11}$$

where $F_{TON} = w_P P\big|_{z=H} + w_{D_S} D_S\big|_{z=H} + w_{D_L} D_L\big|_{z=H}$. The fraction of the buried organic matter is $\phi_2 = 0.092 F_{BC}^{0.5797}$, where a maximum of 75% of carbon burial efficiency is applied [*Druon et al. 2010*] and F_{BC} is the flux of total organic carbon in the sediment, which is $\eta_{C:N} w_P P\big|_{z=H} + \eta_{C_B:N_B}(w_{D_S} D_S\big|_{z=H} + w_{D_L} D_L\big|_{z=H})$. $\eta_{C:N} = 106/16$ is the carbon to nitrogen ratio in phytoplankton. $\eta_{C_B:N_B} = 9.3$ is the carbon to nitrogen ratio in bottom small and large detritus. The rest (1- ϕ_1)(1- ϕ_2) is remineralized through coupled nitrification and denitrification processes in the benthos. The regeneration of the organic matter includes the ammonium form and semi-labile DON form, and follows the implementation for sediments below normal oxic waters described in *Fennel et al*. [2006, see their eq. 15]. To account for the observed shift in benthic influx and efflux rates that occurs below hypoxic to anoxic overlying waters [*Rysgaard et al.,* 1994], an additional term is included to regulate these benthic regeneration rates in response to the seasonal transition to hypoxic in the overlying waters. i.e., as hypoxia in the overlying water column intensifies, the benthic nitrification-denitrification balance will shift toward the latter.

The amount of NH_4 regenerated is:

$$\left.\frac{\partial[NH_4]}{\partial t}\right|_{z=H} = \eta_{NF/DNF}\frac{(1-\phi_1)(1-\phi_2)}{\Delta z}F_{TON}(1+3L_{BO_2}) \qquad (12)$$

Where $L_{BO_2} = \frac{f_B(O_2)-f_B(O_2^{\max})}{1-f_B(O_2^{\max})}$, $f_B(O_2) = \frac{K_{BO_2}}{O_2|_{z=H}+K_{BO_2}}$, K_{BO_2} is the half-saturation coefficient for sediment denitrification, and equals 26.5 mmole-O m^{-3}.

The amount of semi-labile DON regenerated is:

$$\left.\frac{\partial[DON]_{SL}}{\partial t}\right|_{z=H} = \gamma_{[BDON]_{SL}}\frac{(1-\phi_1)(1-\phi_2)}{\Delta z}F_{TON}(1+3L_{BO_2}) \qquad (13)$$

Where, $\gamma_{[BDON]_{SL}} = 0.01$ is the fraction of bottom semilabile DON produced through coupled nitrification and denitrification.

The oxygen consumption during this process is:

$$\left.\frac{\partial[O]_2}{\partial t}\right|_{z=H} = -\eta_{O_2:NF/DNF}\frac{(1-\phi_1)(1-\phi_2)}{\Delta z}F_{TON}(1-L_{BO_2}) \qquad (14)$$

The terms $\eta_{NF/DNF}$ and $\eta_{O_2:NF/DNF}$ are stoichiometric relations drawn from *Fennel et al.* [2006].

The term $\eta_{[BDON]}$ is the fraction of bottom semilabile DON produced through coupled nitrification and denitrification.

At the bottom, particles that hit the bottom are resuspended when bottom stress exceeds critical shear stress, which is calculated by [*Xu and Hood*, 2006] $\xi\left(\Gamma-\Gamma_c\right)$, where ξ = 4320 $gm^{-2}d^{-1}Pa^{-1}$ is the resuspension rate.