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Modeling Nitrogen and Carbon dynamics in wetland soils and water using a mechanistic wetland model

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Abstract

In this article, extension and application to variably-saturated wetland conditions of a process-based wetland model, namely WetQual is demonstrated. The new model described in this article is an improved version of an earlier model, which was only capable of capturing nutrient dynamics in continuously ponded wetlands. The upgraded model is capable of simulating nutrient cycling and biogeochemical reactions in both ponded and unsaturated zones of the wetland. To accomplish this goal, a comprehensive module for tracking water content in wetland soil was implemented in the model, and biogeochemical relationships were added to explain cycling of nitrogen (N) and carbon (C) in variably saturated zones of wetlands. The developed model was applied to a small, restored wetland receiving agricultural runoff, located on Kent Island, Maryland. On average, during the two year study period, the ponded compartment of the study wetland covered 65% of the total 1.2 ha area. Through mass balance analysis, it was revealed that the mass of nitrogen lost to denitrification at the variably saturated compartment of the study wetland was about 3 times higher than that of the ponded compartment (32.7 ± 29.3 kg vs. 9.5 ± 5.5 kg) whereas ammonia volatilization at the variably saturated compartment was a fraction of that of ponded compartment (1.2 ± 1.9 kg vs. 11.3 ± 11.8 kg). Sensitivity analysis showed that cycling of carbon related constituents in variably saturated compartment had high sensitivity to temperature and available soil moisture.

Keywords

Wetland modeling; nitrogen; carbon; process based

1. Introduction

In contrast to upland ecosystems, vast majority of biogeochemical properties of soil and wetland biota are governed by hydrology (Mitsch and Gosselink, 2007). Hydrology regulates oxygen availability in wetland soils, consequently governing nutrient availability, pH, greenhouse gas emissions and toxicity of wetland soil (Takater et al., 1999; Bai et al. 2004; Reddy and Delaune, 2008). In addition, soil water content controls microbial activity in wetland soil, and thus determines rates of microbial respiration (Orchard and Cook, 1983;

Davidson et al., 1998; Ise and Moorcroft, 2006; Sleutel et al., 2008; Cook and Orchard, 2008; Reddy and Delaune, 2008; Manzoni et al., 2011). Metabolic activity of most microorganisms is decreased as soil gets drier, resulting in lower respiration/mineralization rates (Griffin 1981, Schimel et al. 2007). In addition, soil matric potential increases exponentially as soil becomes drier, subsequently inhibiting enzyme mobility and substrate supply to decomposing organisms (Or et al., 2007; Manzoni et al., 2011).

There are two aspects of wetland hydrology that need special attention when it comes to wetland biogeochemical modeling. The first aspect is the effect of ground water (GW) fluctuations on wetland soil moisture. Many wetland nutrient cycling models use an internal, simple mass balance equation to simulate ground water levels based on precipitation and ET losses. In other words, as Fan and Miguez-Macho (2011) stated, in many large scale models “wetlands are only ‘wetted’ from above, but not from below by the high water table characteristic of wetland conditions”. This results in inadequacies representing the hydrologic cycle of groundwater fed wetlands that are ‘wetted from below’ by groundwater upwelling (Fan and Miguez-Macho, 2011).

Another aspect that requires special consideration in wetland modeling is the seasonal pattern of water level in wetlands and the rise and fall of wetland surface and subsurface water. Consider the hypothetical wetland in Figure 1. The presented wetland is seasonally flooded, meaning that it is flooded for extended periods during growing season. As water level falls and rises, the flooded section of the wetland will shrink and expand, respectively. A limitation of WetQual model (Hantush et al., 2013; Kalin et al., 2013; Sharifi et al., 2013a; Sharifi et al., 2015) and many other wetland models (e.g. Martin and Reddy, 1997; van Dam et al., 2007) is the inability to track the dynamics of geochemical reactions in un-inundated sections of the wetland. Consequently, these models are not capable of modeling nutrient dynamics in wetlands where standing water is rarely present.

In this article, we extend WetQual to unsaturated sections of wetland and demonstrate its application. The model described in this article is a modification of an earlier wetland model (Hantush et al., 2013; and Sharifi et al., 2013a), which was only capable of capturing nutrient dynamics in continuously ponded wetlands. The goal of this paper is therefore to present the development and evaluation of the wetland model to variably-saturated wetland conditions. To this end, it is necessary to implement a new modeling approach for tracking moisture in wetland soil. Once daily soil moisture profile of wetland soil is attained, model relationships are updated to simulate geochemical reactions and track concentrations of nitrogen (N) and carbon (C) related constituents in unsaturated wetland soil.

2. WetQual Model

WetQual is a field scale, process based, hydrologic and nutrient cycling model for wetlands (Hantush et al., 2013). The model was later modified for carbon cycling and methane gas emissions (Sharifi et al., 2013a). Previous versions of the model were exclusive to the flooded section of wetland environments (Kalin et al., 2013; Sharifi et al., 2013a). The new developments, presented in this paper, expand the scope of the model to the variably saturated areas surrounding the ponded soil. Within each compartment (flooded section and

surrounding unsaturated soil), the model lumps the mass of nutrients and carbon, and tracks the biogeochemical transformations and exchanges concerning various N and C pools on a subdaily basis.

In the ponded section, WetQual simulates oxygen dynamics and the impact of oxidizing and reducing conditions on nitrogen and carbon transformation and removal. The model separates rooted aquatic plants from free-floating plant biomass (e.g., phytoplankton), and uses a simple model to simulate plant productivity as a function of daily solar radiation and annual growth rates. Volatilization and denitrification, two major loss pathways of mineral nitrogen are explicitly accounted for in the model. In addition, WetQual reflects various biogeochemical feedbacks affecting carbon cycling, methane emissions, organic carbon export and retention. Readers are referred to earlier WetQual publications (Hantush et al., 2013; Kalin et al. 2013; and Sharifi et al., 2013b) for detailed information regarding governing equations and case study applications of the model.

2.1 Hydrologic routing of the ponded compartment

As appears in Figure 1, WetQual model allows for a ponded pool in the middle of the wetland landscape, surrounded by unsaturated wetland soils. The hydrology of the wetland is first solved over the entire simulation period by ignoring the exchange of water between the ponded pool and surrounding soil pool. Once the wetland depth, area, volume and outflow are determined over the simulation period, in the next step the exchange of water (and nutrients) between the two pools are simulated, which will be explained later.

As water level falls and rises, the flooded section of the wetland will shrink and expand, respectively. Inflow to the wetland should be provided to the model, either from field measurements, or as a result of running an upland hydrologic model. Outflows from the wetland, and the expansion/shrinkage of the ponded section, are estimated (if not provided from field measurements) using a flow routing module within the model. The routing module solves the continuity equation for the ponded compartment of the wetland:

$$\phi_w \frac{dV}{dt} = Q_{in} - Q_{out} - ET + P - I - Q_g \quad (1)$$

where V is flooded wetland volume (L^3); Q_{in} and Q_{out} represent inflows and outflows to/from the wetland (L^3T^{-1}); ET and I account for losses to evapotranspiration from open water and infiltration (L^3T^{-1}); Q_g is seepage losses (L^3T^{-1}); P accounts for direct precipitation input to the wetland (L^3T^{-1}); and ϕ_w is effective porosity of flooded wetland area (flow accessible fraction of wetland due to vegetation) (L^3L^{-3}). Storage-outflow relationship at the wetland outlet and the bathymetry containing storage-area curve have to be provided to the model. The routing module is equipped with a third order Runge-Kutta solver (Carnahan et al., 1969) for solving the continuity equation at each time step (~ 0.01 day to 0.1 day).

Evapotranspiration and seepage/subsurface discharge are estimated at a daily scale (if not provided from field measurements). In case the wetland surface water is hydraulically connected to subsurface water table, gravity drainage may be assumed and seepage from the

ponded compartment can be estimated as: $Q_g = K_s \times A_w$, where K_s is saturated hydraulic conductivity [LT^{-1}] and A_w is daily inundated area [L^2]. Q_g can be estimated from measured hydraulic head values or computed externally using any of the existing groundwater flow models (e.g., MODFLOW).

The Penman equation (Penman, 1948) is used to estimate daily evaporation rates from the open water:

$$E_o = \frac{H\Delta + \gamma E_a}{\Delta + \gamma} \quad (2)$$

where E_o is evaporation rate from open water (cm/day), H is evaporation rate due to net radiation (cm/day), Δ (mb/°C) is the slope of the curve relating saturation vapor pressure to temperature, γ is the psychrometric constant (0.66 mb/°C) and E_a is mass transfer evaporation rate. E_a is estimated as (Dunne and Leopold, 1978):

$$E_a = (0.013 + 0.00016u_2)(e_{sa} - e_a) \quad (3)$$

where u_2 is the wind speed (km/day) measured at height of 2 m above the ground, e_{sa} (millibars) is the saturation vapor pressure at the overlying air temperature, and e_a (millibars) is the atmospheric vapor pressure.

2.2 Conceptualization of ponded and variably saturated compartments

In the extended WetQual model, the wetland is divided into two compartments: ponded and variably saturated. The ponded compartment is conceptualized by a pool of standing water (W) at the top; a thin layer of aerobic soil in the middle (S_1) and a relatively thick column of reduced soil at the bottom (S_2) (Figure 2). The variably saturated compartment has three layers of soil standing on top of each other (Figure 2). At the top, there is a column of soil, which extends from soil surface down to the top of water table (S_0 in Figure 2). This column (S_0) is situated above the water table, unsaturated and assumed to be completely aerobic. Extending from the water table to some depth below, lays a thin aerobic layer (S_1). Below this depth, where oxygen is practically negligible, the soil is saturated but anaerobic, with thickness extending from the depth of zero oxygen concentration to the depth of the active sediment layer (S_2). Note that model is fully mixed in each layer, where constituent concentrations are represented with average values for each layer. For layer S_0 , soil moisture estimations are averaged over that layer's depth to yield an average moisture content to represent the whole layer.

3. Modeling moisture redistribution in wetland soil

Simulating soil moisture dynamics in wetland soils can be highly challenging (Fan and Miguez-Macho, 2011). The challenges that make this task highly uncertain stem from various sources of complexities, such as wetland soil heterogeneity, non-linearity of physical properties in wetland soil and non-uniform root water uptake of wetland plants. In fact, the

key to a successful model application in waterlogged environment, such as wetlands, is an accurate simulation of soil moisture content. Accordingly, a proper soil moisture model should consider different sources that provide water to wetland soil (precipitation, GW upwelling, etc.), and sinks that take moisture away (soil evaporation, water extraction by plant roots, and percolation). Having the ability to handle different boundary conditions at the top and the bottom of soil column is another characteristic of the model in mind.. To this end, we solved Richards equation (Richards, 1931) numerically over the expanding or retreating variably saturated zone of the wetland. Richards Equation has a clear physical basis; therefore it is generally applicable to soils of different characteristics. In addition, soil hydraulic data are becoming increasingly available (e.g. Leij, 1996) which enhance the pertinence of the Richards equation.

3.1 Richards Equation

Richards (1931) applied Buckingham's continuity equation to Darcy's law and introduced a differential equation for describing water movement in unsaturated non-swelling soil. One-dimensional Richards equation could be written as:

$$\frac{\partial \theta}{\partial t} = C(h) \frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] - S(z) \quad (4)$$

where θ is the volumetric water content (dimensionless), K is the hydraulic conductivity (LT^{-1}), h is soil water pressure head (L), z is the vertical coordinate (L, positively upward), t is the time (T), S is the collective term for soil water extraction rate by plant roots and drain discharge (T^{-1}) and C is the specific water content capacity (given by $= \frac{d\theta}{dh}$) (L^{-1}). Soil hydraulic functions of $\theta(h)$, $K(\theta)$ and $C(h)$ could be described by Mualem- van Genuchten model (van Genuchten, 1980):

$$\theta(h) = \theta_{res} + \frac{\theta_{sat} - \theta_{res}}{(1 + |\alpha h|^n)^m} \quad (5)$$

$$C(h) = \frac{d\theta}{dh} = \alpha m n |\alpha h|^{n-1} (\theta_{sat} - \theta_{res}) (1 + |\alpha h|^n)^{-(m+1)} \quad (6)$$

$$K(\theta) = K_{sat} \left(\frac{\theta - \theta_{res}}{\theta_{sat} - \theta_{res}} \right)^\lambda \left[1 - \left(\frac{\theta - \theta_{res}}{\theta_{sat} - \theta_{res}} \right)^{\frac{1}{m}} \right]^{m^2} \quad (7)$$

where, θ_{sat} and θ_{res} are, respectively, saturated and residual water content (dimensionless), K_{sat} is the saturated hydraulic conductivity (LT^{-1}) and α (L^{-1}), n (dimensionless) and λ

(dimensionless) are fitting parameters, which can be extracted from soil databases (e.g. Kroes et al., 2008). The parameter m is related to n by $m = 1 - 1/n$ (van Genuchten, 1980).

3.2 Finite difference solution to Richards equation

The methodology presented in van Dam and Feddes (2000) was adapted in this study with slight modifications to solve the 1-D Richards equation. This methodology is similar to what is applied in the SWAP model, a field scale model for water, solutes and heat transport in the vadose zone (Kroes et al., 2008). Following van Dam and Feddes (2000), for an implicit backward finite difference solution to Richards equation, the active soil layer is divided into compartments with thickness of Δz with each compartment containing a node in the middle (Figure 3). Equation (4) is discretized to the following form (van Dam and Feddes, 2000):

$$C_i^{j+1,p-1}(h_i^{j+1,p} - h_i^{j+1,p-1}) + \theta_i^{j+1,p-1} - \theta_i^j = \frac{\Delta t}{\Delta z} \left[K_{i-0.5}^j \left(\frac{h_{i-1}^{j+1,p} - h_i^{j+1,p}}{\Delta z} \right) + K_{i-0.5}^j - K_{i+0.5}^j \left(\frac{h_i^{j+1,p} - h_{i+1}^{j+1,p}}{\Delta z} \right) - K_{i+0.5}^j \right] - \Delta t S_i^j \quad (8)$$

where subscript i is the node number, superscript j is the time step, Δt is length of each time step and Δz is compartment thickness (see Figure 3). Superscript p is the Picard iteration level, thus $C_i^{j+1,p-1}$ is the specific water content capacity evaluated at the pressure head value of the last Picard iteration, $h_i^{j+1,p-1}$. $K_{i-0.5}^j$ and $K_{i+0.5}^j$ are internodal hydraulic conductivity for i^{th} node. Hydraulic conductivity (K) and root water extractions (S) are evaluated at the old time level j , which according to van Dam and Feddes (2000), gives a good approximation at time steps of $10^{-6} < t < 0.2$ days. Once Equation (8) is written for all nodes, the series on n equations (n =number of nodal points) could be re-arranged to form a tri-diagonal system which can be solved efficiently at each Picard iteration.

In the finite difference method adapted from van Dam and Feddes (2000), special attention is paid to the procedure of selecting the right top and bottom boundary conditions. The right conditions for top and bottom boundaries become very important for situations with intense rainfall (specifically where rainfall intensity is greater than soil infiltration capacity) or with fluctuating groundwater levels close to the soil surface. The top boundary condition could be flux-controlled or head-controlled (Figure 4). In case of excessive wet conditions that lead to ponding above the soil column, the top boundary condition becomes head controlled. On the other hand, in case of saturated soil with no ponding at the top, a flux controlled top boundary condition is imposed. When the top soil is not saturated, the boundary condition problem becomes more complex. The procedure for selecting the top boundary condition is demonstrated in Figure 4.

The bottom boundary conditions vary depending on presence of GW table at the bottom of soil column. If there is an existing GW table, the bottom boundary is head controlled, with

$h=0$ at the water table. When GW table is non-existent, or is very deep, the bottom flux controls the bottom boundary conditions. In such circumstances, the head pressure gradient equals zero and bottom flux is only controlled by gravity; thus $q_{bot} = -K^{j+\frac{1}{n+2}}$.

For the variably saturated compartment, ET loss is embedded in the Richards solution. The user provides PET to the model (from Eq. (2)). Given available soil moisture at the top nodes and prevailing air relative humidity (top node boundary conditions), the finite difference solution to Richards equation determines actual ET (see Figure 4).

4. Governing relationships for N and C cycling

4.1 Ponded compartment

The ponded compartment is conceptualized by a pool of standing water (W) at the top; a thin layer of aerobic soil in the middle (S_1) and a relatively thick column of reduced soil at the bottom (S_2) (see Figure 2). For each constituent in C and N cycles, three ordinary differential equations (one for each layer) are solved to explain the variation of concentration in the water and sediment layers. It is assumed that constituent concentrations are spatially uniform throughout each layer within the ponded compartment (model is fully mixed in each layer and constituent concentrations are represented with average values for each layer). For a generic dissolved constituent (such as NO_3) in the water column, the ODE (ordinary differential equation) portraying mass balance is given by:

$$\phi_w \frac{dV_w C_w}{dt} = Q_{in} C_{in} - Q_{out} C_w - S^* + \beta_1 A (C_s - C_w) + F_{C_{Dg}}^w \quad (9)$$

The left hand side of Eq. (9) describes variation of concentration (C_w) over time in the water column (V_w is the volume of standing water pool [L^3], and C_w is concentration of dissolved constituent [ML^{-3}]). The terms on the right-hand-side, respectively, explain loading gains via inflows, losses via hydrologic outflows, losses through biogeochemical reactions (decay), and exchanges between water and sediment columns through: 1) diffusive transport and 2) advective groundwater exchange (recharge or discharge) (Q_{in} is volumetric inflow rate [L^3T^{-1}], C_{in} is constituent concentrations in incoming water [ML^{-3}], Q_{out} is wetland discharge (outflow) rate [L^3T^{-1}], $F_{C_{Dg}}^w$ represents groundwater recharge/discharge, S^* is net mass

removal by aerobic and anaerobic respiration [MT^{-1}], β_1 is the diffusive mass-transfer rate of dissolved constituent between wetland water and aerobic soil layer [LT^{-1}], A is wetland surface area [L^2] and C_s is the pore water constituent concentrations in aerobic sediment layer [ML^{-3}]). Model relationships for C and N related constituents are thoroughly described in Hantush et al. (2013) and Sharifi et al. (2013b).

4.2 Variably saturated compartment

Model relationships for N and C related constituents described by Hantush et al. (2013) and Sharifi et al. (2013b) were adjusted to reflect physical and geochemical dynamics under unsaturated soil conditions. Most biogeochemical reaction rates were adjusted for available

soil moisture in the unsaturated soil layer. Many studies have shown that moisture deficiency slows soil respiration reactions (Davidson et al., 1998; Ise and Moorcroft, 2006; Reddy and Delaune, 2008). The common practice in ecological models is to adjust reaction rates based on the ratio of soil water content to soil moisture at field capacity or at wilting point. For instance, SWAT model (Neitsch et al., 2005) adjusts mineralization rate in agricultural soil by multiplying by the following adjustment factor (Neitsch et al., 2005):

$$\eta_{sw} = \frac{SW}{FC} \quad (10)$$

where η_{sw} is mineralization adjustment factor for soil moisture, SW is soil water content on a given day (mm), and FC is amount of water held in soil at field capacity water content (mm). In SWAT model, η_{sw} is never allowed to fall below 0.05.

For the case of this study, a generic correction factor was employed to adjust reaction rates according to available soil moisture in the unsaturated soil layer. Since θ_{sat} and θ_{res} (saturation and residual moisture content) were already employed in model, they were used to form the following relationship:

$$\eta_{sw,x} = \left(\frac{\theta}{\theta_{sat}}\right)^{\xi_x} \quad (11)$$

where $\eta_{sw,x}$ is reaction x adjustment factor for soil moisture, θ is available soil moisture in unsaturated soil and ξ_x is a calibration parameter ($0.01 < \xi_x < 1$) which adjusts the shape of the correction factor. Adjusted model relationships for unsaturated soil layer are presented later in this section. In those relationships, reaction rates that are adjusted for soil moisture have been marked with (θ) sign.

The thickness of aerobic layer in variably saturated compartment ($S_{1,u}$) was calculated using a formula derived by solving a boundary-value problem similar to that reported by (Hantush and Kalin, 2014, Kalin and Hantush, 2007) but modified here for gaseous phase transfer across the soil-air interface:

$$l_{1,u} = -\pi\tau\delta + \sqrt{(\pi\tau\delta)^2 + \frac{2\theta\tau(D_0^* + \frac{\pi}{\theta}K_{H,O}D^*)O_a}{K_{H,O}\Omega}} \quad (12a)$$

$$\Omega = r_{on,n}\phi f_N k_{ns}(\theta)N_{a1} + r_{on,m}(k_{ms}(\theta)N_{os} + k_{mr}(\theta)N_{or}) + S_s \quad (12b)$$

where $l_{1,u}$ is the thickness of the top oxic soil layer of variably saturated compartment [L], O_a is oxygen concentration in the air [ML^{-3}], δ is thickness of the resistive air boundary layer at the soil-air interface [L]; π is portion of soil volume that is filled with air ($\pi = \phi -$

θ ; θ is soil water content; τ is the wetland soil tortuosity factor; D_o^* is free-water oxygen diffusion coefficient [L^2T^{-1}]; D^* is free-air oxygen diffusion coefficient [L^2T^{-1}], Ω is oxygen removal rate per unit volume [$ML^{-3}T^{-1}$]; and $K_{H,O}$ is Oxygen dimensionless Henry's constant, $r_{on,n}$ is gram of oxygen consumed per gram of total ammonium nitrogen oxidized by nitrification ($= 4.57$), fN is fraction of total ammonia nitrogen in ionized form, $k_{ns}(\theta)$ is first-order nitrification rate in aerobic soil layer [T^{-1}] (adjusted for soil moisture), N_{a1} is total ammonia-nitrogen pore-water concentration in the saturated aerobic layer [ML^{-3}], $r_{on,m}$ is gram of oxygen consumed per gram of organic nitrogen mineralized ($= 15.29$), $k_{ms}(\theta)$ is moisture adjusted first-order slow mineralization rate in wetland soil [T^{-1}], N_{os} is concentration of refractory organic nitrogen in wetland soil [ML^{-3}], $k_{mr}(\theta)$ is moisture adjusted first-order rapid mineralization rate in wetland soil [T^{-1}], N_{or} is concentration of labile organic nitrogen in wetland soil [ML^{-3}] and S_s is oxygen removal rate per unit volume of aerobic layer by other processes [MT^{-1}]. In this analysis we assume zero-resistance to diffusive mass transfer at the soil-air interface ($\delta = 0$); and 2) dissolved oxygen concentration in soil moisture is at equilibrium with the gaseous phase.

As an example of how the new methodology was implemented, we present the governing relationships for NH_4 fate and transport for the top layers of ponded and variably saturated compartments (W_p and $S_{0,u}$ in Figure 2). The relationship of the ponded compartment conforms to that of the original model (Hantush et al., 2013). For the water layer of ponded compartment, the governing for NH_4 fate and transport are written as:

$$\begin{aligned} \phi_w \frac{d(V_w N_{aw})}{dt} = & Q_i N_{aw\ in} + i_p A_w N_{ap} - \phi_w V_w f_N k_{nw} N_{aw} + \beta_{a1} A_w (N_{a1} - N_{aw}) \quad (13) \\ & + F_{N_{ag}}^w - k_v \phi_w A_w (1 - f_N) N_{aw} + \phi_w V_w k_{mw} N_{ow} - Q_o N_{aw} \\ & - f_{aw} a_{na} k_{ga} a + A_w q_a \end{aligned}$$

where N_{aw} and N_{a1} are concentration of NH_4 in free water and aerobic sediment of the ponded compartment [ML^{-3}], N_{ap} and $N_{aw\ in}$ are concentration of NH_4 in rainfall and inflow [ML^{-3}], A_w is the inundated area of the wetland [L^2], V_w is the volume of water in the ponded compartment [L^3], k_v is the volatilization mass transfer velocity [LT^{-1}], f_N is fraction of total ammonia nitrogen in ionized form, $F_{N_{ag}}^w$ is groundwater source/loss for NH_4 [MT^{-1}], q_a is dry deposition rate of NH_4 [$ML^{-2}T^{-1}$], and a is mass of free floating plants [$M\ Chl\ a$]. The definition of the rest of the terms used in the above equation can be found in Table 1. In brief, the left hand side of Eq. (13) tracks change of mass of NH_4 in water layer of the ponded compartment (N_{aw}) over time, and the right hand side of the equation explains the gains/losses of NH_4 mass to various reactions/processes (flow influx, wet deposition, nitrification, diffusion, groundwater exchanges, volatilization, ammonification, outflow, plant uptake and dry deposition, respectively). For the top layer of variably saturated compartment, the equivalent equation is written as:

$$\begin{aligned}
& K_h \left(1 - f_N \right) \frac{d\pi V_0 N_{a0}}{dt} + R_s \frac{d\theta V_0 N_{a0}}{dt} \\
& = -A_0 \phi k_v \left(K_h (1 - f_N) N_{a0} - N^* \right) + F_{N_{ag}}^0 - f_{a0} a_{na} k_{gb.i}(\theta) f_0 b \\
& + V_0 k_{mr} \left(\theta \right) N_{or} + V_0 k_{ms} \left(\theta \right) N_{os} - \theta V_0 f_N k_{ns} \left(\theta \right) N_{a0} + A_0 \beta_{ax} \left(N_{a1} - N_{a0} \right)
\end{aligned} \tag{14}$$

where N_{a0} is concentration of dissolved NH_4 in the top (aerobic) layer of variably saturated compartment, N^* is equilibrium concentration of NH_4 in atmosphere [ML^{-3}], N_{or} and N_{os} are concentration of rapidly mineralizing and slowly mineralizing organic nitrogen in wetland soil [ML^{-3}], $F_{N_{ag}}^0$ is groundwater source/loss of NH_4 in the unsaturated soil layer

[MT^{-1} , β_{ax} is diffusive mass-transfer rates of NH_4 between unsaturated wetland soil and saturated aerobic soil layer [LT^{-1}], A_0 is the area of variably saturated compartment ($A_0 = \text{total area} - A_w$), V_0 is volume of unsaturated soil layer [L^3] ($V_0 = A_0 \times \text{depth of unsaturated soil}$) and $R_s = 1 + m_s K_d f_N / \phi$ is total ammonia retardation factor in wetland soil, where, m_s is wetland soil bulk density (ML^{-3}); K_d is total ammonia distribution coefficient ($\text{L}^3 \text{M}^{-1}$); and ϕ is soil porosity ($\text{L}^3 \text{L}^{-3}$), K_h is Ratio of NH_3 in gas form to NH_3 in liquid form, θ is soil water content (L^0), f_N is fraction of total ammonia in ionized form and k_v is volatilization mass transfer velocity [LT^{-1}]. The definition of the rest of the biogeochemical reaction and plant uptake terms used in the above equation can be found in Table 1. Similar to Eq. (14), the left hand side depicts change of mass of total ammonia in unsaturated soil (N_{a0}) over time. Note that in the case of unsaturated soil, total ammonia exists in the form of unionized ammonia (NH_3 – gas or liquid) and ionized ammonium (NH_4^+ - liquid). Hence, the left-hand side of the equation is comprised of two terms, where the first term traces variation in mass of total ammonia in gas form over time – found in the soil voids filled with gas, and the second term depicts change of mass of total ammonia in liquid form. The right hand side of the equation explains the gains/losses of total ammonia to various reactions/processes in unsaturated soil layer (volatilization, groundwater exchanges, plant uptake, ammonification from labile plant material, ammonification from refractory plant material, nitrification and diffusion to/from lower layer, respectively). Note that reaction rates marked by (θ) are a function of available soil water content (refer to Eq. (11)). In contrast to the two-resistive layers gaseous transfer in open water surfaces, net transfer velocity of any gas across the air-partially saturated porous media interface occurs through one resistive gaseous layer at the soil surface. A similar approach of that reported in Hantush et al (2013) can be implemented to yield this formula relating mass transfer velocity to wind speed:

$$k_v = 170.4 U_w^\beta \tag{15}$$

where U_w is wind speed (m s^{-1}) and η is an empirical parameter.

The updated relationships and parameter definition for constituents in the non-ponded areas of the wetland can be found below (Eqs. (16) to (35)). Please refer to Table 1 for definition of model parameters.

Organic Nitrogen

$$V_s \frac{dN_{or}}{dt} = f_r a_{na} k_{db}(\theta) f_{bs} b - V_s k_{mr}(\theta) N_{or} + f_r (1 - f_{sw}) AS \quad (16)$$

$$V_s \frac{dN_{os}}{dt} = f_s a_{na} k_{db}(\theta) f_{bs} b - V_s k_{ms}(\theta) N_{os} + f_s (1 - f_{sw}) AS \quad (17)$$

Ammonia-N

$$K_h(1 - f_N) \frac{d\pi V_0 N_{a0}}{dt} + R_{s.i} \frac{d\theta V_0 N_{a0}}{dt} \quad (18)$$

$$= -A\phi k_v(K_h(1 - f_N)N_{a0} - N^*) + F_{N_{ag}}^0 - f_{a0} a_{na} k_{gb}(\theta) f_0 b \\ + V_0 k_{mr}(\theta) N_{or} + V_0 k_{ms}(\theta) N_{os} - \theta V_0 f_N(\theta) N_{a0} + A\beta_{ax}(N_{a1} - N_{a0})$$

$$\phi R_s \frac{dV_1 N_{a1}}{dt} = F_{N_{ag}}^1 - f_{a1} a_{na} k_{gb}(\theta) f_1 b + V_1 k_{mr}(\theta) N_{or} + V_1 k_{ms}(\theta) N_{os} \quad (19) \\ + A_i \beta_{ax}(N_{a0} - N_{a1}) - \phi V_1 f_N k_{ns} N_{a1} + A_i \beta_{n2}(N_{a2} - N_{a1})$$

$$\phi R_s \frac{dV_2 N_{a2}}{dt} = F_{N_{ag}}^2 - f_{a2} a_{na} k_{gb}(\theta) f_2 b + V_2 k_{mr}(\theta) N_{or} + V_2 k_{ms}(\theta) N_{os} \quad (20) \\ + A\beta_{n2}(N_{a1} - N_{a2})$$

NO₃-N

$$V_0 \frac{d\theta_i N_{n0}}{dt} = F_{N_{ng}}^0 + \phi V_0 f_N k_{ns}(\theta) N_{a0} - A\beta_{nx}(N_{n0} - N_{n1}) - f_{n1} a_{na} k_{gb}(\theta) f_1 b \quad (21)$$

$$\phi_i V_1 \frac{dN_{n1}}{dt} = A\beta_{nx}(N_{n0} - N_{n1}) - A\beta_{n2}(N_{n1} - N_{n2}) + \phi V_1 f_N k_{ns} N_{a1} + F_{N_{ng}}^1 - f_{n1} a_{na} k_{gb}(\theta) f_1 b \quad (22)$$

$$\phi_i V_2 \frac{dN_{n2}}{dt} = A\beta_{n2}(N_{n1} - N_{n2}) - \phi V_2 k_{dn} N_{n2} + F_{N_{ng}}^2 - f_{n2} a_{na} k_{gb}(\theta) f_2 b \quad (23)$$

Labile particulate organic carbon

$$V_0 \frac{dC_{L0}}{dt} = a_{ca} k_{db}(\theta) f_0 f_{bs} f_{bL} b - V_0 k_L(\theta) C_{L0} \quad (24)$$

$$V_1 \frac{dC_L}{dt} = a_{ca} k_{db}(\theta) f_1 f_{bs} f_{bL} b - V_1 k_L C_{L1} \quad (25)$$

$$V_2 \frac{dC_{L2}}{dt} = a_{ca} k_{db}(\theta) f_2 f_{bs} f_{bL} b - V_2 k_L C_{L2} \quad (26)$$

Refractory particulate organic carbon

$$V_0 \frac{dC_{R0}}{dt} = a_{ca} k_{db}(\theta) f_0 f_{bs} f_{bR} b - V_0 k_R(\theta) C_{R0} \quad (27)$$

$$V_1 \frac{dC_{R1}}{dt} = a_{ca} k_{db}(\theta) f_1 f_{bs} f_{bR} b - V_1 k_R C_{R1} \quad (28)$$

$$V_2 \frac{dC_{R2}}{dt} = a_{ca} k_{db}(\theta) f_2 f_{bs} f_{bR} b - V_2 k_R C_{R2} \quad (29)$$

Dissolved organic carbon

$$V_0 \frac{d\theta C_{D0}}{dt} = a_{ca} k_{db}(\theta) f_0 f_{bs} F_{bD} b + V_0 k_L(\theta) C_{L0} + V_0 k_R(\theta) C_{R0} \quad (30)$$

$$- \beta_{Dx} A(C_{D0} - C_{D1}) + F_{C_{Dg}}^0 - \phi V_0 k_D^1(\theta) C_{D0}$$

$$\phi V_1 \frac{dC_{D1}}{dt} = a_{ca} k_{ab}(\theta) f_1 f_{bs} F_{bD} b + V_{1,i} k_L C_{L1} + V_1 k_R C_{R1} \quad (31)$$

$$- \beta_{D2} A(C_{D1} - C_{D2}) + F_{C_{Dg}}^1 - \beta_{Dx} A(C_{D1} - C_{D0}) - \phi V_1 \frac{O_{s1}}{O_{s1} + K_O} k_D^1 C_{D1}$$

$$\phi V_2 \frac{dC_{D2}}{dt} = a_{ca} k_{db}(\theta) f_2 f_{bs} f_{bD} b + V_2 k_L C_{L2} + V_2 k_R C_{R2} - \beta_{D2} A(C_{D2} - C_{D1}) + F_{C_{Dg}}^2 \quad (32)$$

$$- \phi V_2 \frac{N_{n2}}{N_{n2} + K_N} k_D^2 C_{D2} - \phi V_2 \frac{K_N^{in}}{N_{n2} + K_N^{in}} k_D^3 C_{D2}$$

CH₄

$$K_h \frac{d\pi V_0 C_{M0}}{dt} + \frac{d\theta V_0 C_{M0}}{dt} \quad (33)$$

$$= -A\phi k_v \left(K_H C_{M0} - C_M^* \right) + \beta_{Mx} A \left(C_{M1} - C_{M0} \right) - \theta V_0 k_M^1(\theta) C_{M0} + F_{C_{Mg}}^0$$

$$+ \lambda_r f_0 f_{bs} b_i R_v D^o \left(C^* - C_{M0} \right)$$

$$\phi V_1 \frac{dC_{M1}}{dt} = -\beta_{M2} A \left(C_{M1} - C_{M2} \right) - \phi V_1 \frac{O_{s1}}{O_{s1} + K_O} k_M^1 C_{M1} + F_{C_{Mg}}^1 \quad (34)$$

$$+ \lambda_r f_1 f_{bs} b_i R_v D^o \left(C^* - C_{M1} \right) + \beta_{Mx} A \left(C_{M1} - C_{M0} \right)$$

$$\begin{aligned} \phi V_2 \frac{dC_{M2}}{dt} = & \phi V_2 \frac{K_N^{in}}{N_{n2} + K_N^{in}} k_D^3 C_{D2} + \beta_{M2} A \left(C_{M1} - C_{M2} \right) - \phi V_2 \frac{N_{n2}}{N_{n2} + K_N} k_M^2 C_{M2} + F_{C_{Mg}}^2 \\ & + \lambda_r f_2 f_{bs} b R_v D^a \left(C^* - C_{M2} \right) \end{aligned} \quad (35)$$

5. Exchanges between ponded and variably saturated compartments

In this study a compartmentalization scheme has been employed that keeps track of constituents mass in wetland soil and water accurately, thus reducing the overall mass balance error.

In the earlier wetland model only the ponded areas were modeled and the processes within the surrounding unsaturated soils were ignored. The ponded section was allowed to dynamically expand and shrink, however, the exchanges between the ponded pool and the surrounding areas were ignored. In the new compartmentalization scheme, the total area of the wetland is kept constant, and dynamically distributed between ponded and variably saturated compartments. The area of ponded compartment is allowed to shrink and expand dynamically, with fall and rise of water level. Areal extent of each compartment is determined by the area-depth relationship for the wetland. Since the total area of the wetland is fixed, this shrinking and expanding will be at the expense of variably saturated compartment, meaning that when the ponded compartment expands, the variably saturated compartment shrinks, and vice versa. In order to track the mass exchange between the two compartments, it was necessary to introduce a transitional compartment. At each time step, the transitional compartment will form and will adopt the concentrations of either ponded or variably saturated compartments (depending on whether water level is falling or rising). This was a necessary invention because neither horizontal nor associated inter-compartmental advective transport can be simulated by an inherently lumped-modeling approach. The constituent concentrations of ponded or variably saturated compartments will be updated at the end of the time step as one or the other incorporates the transitional compartment. Figure 2 presents schematics of a case where water level of the ponded compartment (on the left) has risen over one time step, i.e. $h(t + \Delta t) > h(t)$. Consequently, ponded compartment has taken over an area, which previously belonged to the variably saturated compartment. In such case, the transitional compartment in the middle initially has the concentration of the variably saturated compartment. However, because of rise in water level, the empty pore spaces of soil in transitional compartment have been filled with water that has concentration of the ponded compartment. Thus, the constituent concentration in transitional compartment soil could be approximated through volumetric averaging between the two concentrations (concentration in water pool of ponded compartment and concentration of variably saturated compartment soil). For a generic constituent (C) we have:

$$C_{1,t} = \frac{\theta_u^{j+1} C_{1,u}^{j+1} + (\phi_u - \theta_u^{j+1}) C_{w,p}^{j+1}}{\phi_u} \quad (36)$$

$$C_{2,t} = \frac{\theta_u^{j+1} C_{1,u}^{j+1} + (\phi_u - \theta_u^{j+1}) C_{w,p}^{j+1}}{\phi_u}$$

where $C_{1,t}$ and $C_{2,t}$ represent constituent concentration in aerobic and anaerobic soil of the transitional compartment and j denotes time. Subscript p and u , respectively, refer to ponded and variably saturated compartments, thus ϕ_u and θ_u are porosity and water content of the variably saturated compartment (θ_u^{j+1} is obtained by solving Richards equation), and $C_{w,p}$ is constituent concentration in water column of ponded compartment. Accordingly, at the end of time step, the transitional compartment is incorporated into the ponded compartment. In other words, mass of constituents in transitional compartment is transferred to the ponded compartment, and the concentrations in aerobic and anaerobic soil of ponded compartment are updated such that:

$$\bar{C}_{1,p} = \frac{C_{1,p}^{j+1} \times A_p^j + C_{1,t} \times (A_p^{j+1} - A_p^j)}{A_p^{j+1}} \quad (37)$$

$$\bar{C}_{2,p} = \frac{C_{2,p}^{j+1} \times A_p^j + C_{2,t} \times (A_p^{j+1} - A_p^j)}{A_p^{j+1}}$$

where A_p is area of ponded compartment and $\bar{C}_{1,p}$ and $\bar{C}_{2,p}$ are the updated concentrations in ponded compartment's aerobic and anaerobic soil layers respectively ($\bar{C}_{1,p}$ and $\bar{C}_{2,p}$ will replace $C_{1,p}^{j+1}$ and $C_{2,p}^{j+1}$).

Similarly, in case of falling water level in the ponded compartment, i.e. $h(t+\Delta t) < h(t)$, the variably saturated compartment will take over an area which previously belonged to the ponded compartment. In such case, the transitional compartment (in the middle) adopts the concentration of the ponded compartment, thus:

$$C_{1,t} = C_{1,p}^{j+1} \quad (38)$$

$$C_{2,t} = C_{2,p}^{j+1}$$

And at the end of time step, the transitional compartment is incorporated into the variably saturated compartment. The concentrations in the variably saturated soil compartment are updated such that:

$$\begin{aligned}\bar{C}_{0,u} &= \frac{\phi_p(A_p^j - A_p^{j+1})\Delta h_p C_{1,t} + L_{0,u}\theta_u A_u^j C_{0,u}^{j+1}}{A_u^{j+1} L_{0,u} \theta_u^j} \quad (39) \\ \bar{C}_{1,u} &= \frac{\phi_p(A_p^j - A_p^{j+1})C_{1,t} + \phi_u A_u^j C_{1,u}^{j+1}}{A_u^{j+1} \phi_u} \\ \bar{C}_{2,u} &= \frac{\phi_p(A_p^j - A_p^{j+1})C_{2,t} + \phi_u A_u^j C_{2,u}^{j+1}}{A_u^{j+1} \phi_u}\end{aligned}$$

where $\bar{C}_{0,u}$, $\bar{C}_{1,u}$ and $\bar{C}_{2,u}$ are the updated concentrations in variably saturated compartment ($\bar{C}_{0,u}$, $\bar{C}_{1,u}$ and $\bar{C}_{2,u}$ will replace $C_{0,u}^{j+1}$, $C_{1,u}^{j+1}$ and $C_{2,u}^{j+1}$ respectively), $L_{0,u}$ represents depth of layer S_0 of variably saturated compartment, θ_u stands for average moisture content of column S_0 , and h_p is variation of water depth in ponded compartment during time step j . In addition to concentrations, moisture content of column S_0 requires updating:

$$\bar{\theta}_{0,u} = \frac{\phi_p \Delta A_p \Delta h_p + L_{0,u} \theta_u^{j+1} A_u^j}{A_u^{j+1} L_{0,u}} \quad (40)$$

where $\bar{\theta}_{0,u}$ is the updated moisture content of S_0 ($\bar{\theta}_{0,u}$ will replace θ_u^{j+1}).

In essence, the transitional compartment is formed at every time step to redistribute mass between the ponded and variably saturated compartments. In summary, in each simulation time step, the solution of Eq. (1) and the area-depth relationship were used to estimate the areal extent of the ponded compartment (depicted in Figure 1). Next, the areal extent of the variably saturated compartment is updated to its value at the end of the time step. The corresponding incremental increase or decrease in the area of the ponded area corresponds to the transitional compartment (shown in Figure 2). The variably saturated compartment-averaged volumetric moisture content is obtained by depth-averaging of the solution of Richards equation over each of the unsaturated layer (Figure 2). This information, along with the areas of the ponded and variably saturated compartments at the beginning and end of the time step are used to evaluate constituent concentrations in the transition compartment (Eqs. (36) and (38)). Ultimately, concentrations in variably saturated and ponded compartments are updated at the end of the time step (Eqs. (39) and (37)).

6. Case study application

The developed model was applied to a study wetland, previously introduced in Sharif et al. (2013) and Kalin et al. (2013). The study wetland, described thoroughly by Jordan et al. (2003), is a small restored wetland located on Kent Island, Maryland (Figure 5) which was monitored for flow and water quality data for approximately 2 years from May 1995 - May 1997. The study wetland, called Barnstable wetland, was restored from an artificially drained cropland by the Chesapeake Wildlife Heritage with the intention to provide wildlife

habitat and improve the quality of runoff from surrounding crop fields. During the study period, a maximum 90% of the wetland surface was covered by emergent vegetation through growing season; this portion dropped to a minimum of 10% during non-growing season. Much of the 14-ha watershed draining to the wetland land was farmlands (82%), cultivated primarily for corn and soybean production, and the rest (18%) was covered by forest. Soils of the area have moderate to moderately low permeability, hence most croplands in the study area are artificially drained by ditches or by plowed channels. Water entered the wetland through ditches draining surface runoff from the surrounding catchment. The entire 1.3-ha area of the wetland was submerged and lacked well-defined flow channels when the water was deep enough to flow out of a 120° V-notch weir. An impermeable layer of clay, at shallow depth below the soil surface (0.50 m below soil surface) blocked groundwater exchanges and seepage losses. Automated instruments were used to measure unregulated water inflows and to sample water entering and leaving the wetland from 8 May 1995 through 12 May 1997. Weekly (typically 5 to 8 days) flow averaged nitrate N, total ammonia N, organic N, inorganic P, and TSS and TOC (total organic carbon) concentrations of the inflow and outflow were available from Jordan et al. (2003). Figure 6 exhibits the inflow, outflow and average water depth in ponded compartment of the study wetland in addition to inflow concentrations of TOC, NH₄, NO₃, TSS and inorganic phosphorus to the study wetland. Further information on the data collection and analysis can be found in Jordan et al. (2003). Sources for other model input data (precipitation, temperature, etc.) can be found in Kalin et al. (2013) where the nitrogen and phosphorus cycles of WetQual model were validated on the same study wetland. Later in the results section, we will compare findings of Kalin et al. (2013) (original model for ponded wetlands) to the results obtained from the updated model, presented in this study to demonstrate how the extension of WetQual to include ponded and unponded conditions would impact the results.

As mentioned earlier, the main objective of this study was to extend WetQual's capabilities to simulate geochemical reactions in unsaturated wetland soil and to track constituent concentrations in parts of the wetland which are not flooded. A proper validation procedure for the developed model requires field measurements of soil moisture and constituent concentration in unsaturated soil for a period of time. Finding such dataset was not easy to come by; consequently, the only available dataset was exploited for model evaluation purposes. Applying the newly developed model to Barnstable wetland, which is missing the desired level of detailed data, will not allow for validating all the new developments in the model. However, the newly developed model can still provide insight on the mass exchanges through microbial activities in the unsaturated banks of the study wetland.

The model applied to Barnstable wetland was divided into two compartments, a ponded compartment in the middle, surrounded by a variably saturated compartment (similar to Figure 1). As mentioned earlier the total area of the wetland was kept constant. The area of ponded compartment was allowed to shrink and expand dynamically at the expense of the variably saturated compartment, meaning that when the ponded compartment expanded, the variably saturated compartment contracted, and vice versa. On average, the ponded compartment covered 65% of the total 1.2 ha area of the wetland. Figure 7 shows the percentage of total wetland area covered by ponded compartment over the two year study period.

According to Jordan et al. (2003), the study wetland was underlain by a silty clay loam subsurface horizon which formed an extensive and continuous aquiclude. Given this information, it was safe to assume presence of a perched water table below wetland surface, sustaining the study wetland during dry periods. Since there were no records on the depth of such perched water table, it was assumed that the water table resided at a depth equivalent to the bottom of ponded compartment.

As mentioned earlier, inflow and outflow were measured at the study wetland. Precipitation was measured onsite using a standard rain gauge, and infiltration was assumed negligible since an impermeable layer of clay blocked groundwater exchanges and seepage losses. ET data was acquired from the Wye Research Center (WRC), located 13 km away from the study wetland. The volume-area relationship of the study wetland was extracted from the topography map of the study wetland, and used to estimate inundated area at each time step. The transitional zone during a simulation time increment corresponds to incremental ponded/drained outer area of the wetland.

To investigate the effectiveness of new additions to the model, in sections to follow, we compare the results of this effort to the past results of earlier version of WetQual model (reflected in Sharifi et al. (2013) and Kalin et al (2013)). To avoid confusion, the former model will be referred to as “Original model”, whereas the newly developed model presented in this paper will be referenced as “Expanded model”.

7. Model Assessment

Model assessment performed in this study is similar to the methodology described by Sharifi et al. (2013) and Kalin et al. (2013). A combination of both GLUE and GSA methods (Beven and Binley, 1992; Spear and Hornberger, 1980) were employed to assess model prediction uncertainty and quantitative sensitivity to model parameters. Readers may refer to Sharifi et al. (2013) for a complete description of the GSA/GLUE methodology as applied in this article. In brief, 100,000 statistically independent parameter sets were generated for each compartment (ponded and variably saturated compartments), sampled randomly from previously defined distributions, which were extracted from literature values/tabulations. To perform Monte Carlo (MC) simulations, the model was run 100,000 times, each time with one set of parameters to yield an ensemble of 100,000 time series for constituent concentrations (this number was selected to be consistent with previous WetQual studies, i.e. Sharifi et al., (2013) and Kalin et al., (2013)). Two performance criteria, Mass balance error (MBE) and Nash-Sutcliffe efficiency (E_{ns}) were used to construct a goodness of fit function that evaluates the efficiency of model-predicted concentrations against observed data for each MC simulation (Sharifi et al., 2013):

$$L_k = 0.5 \times (E_{ns} + \exp(\frac{-|MBE|}{100})) \quad (41)$$

where L_k represents the goodness of fit measure. For each compartment, parameter sets were sorted based on their likelihoods and the top 1% datasets with the highest likelihoods were separated as behavioral dataset (B) from the rest of the parameter sets (non-behavioral

datasets, B'). Subsequently, quantitative sensitivity analysis was performed using Kolmogorov-Smirnov test (Massey Jr, 1951) to reveal the most sensitive parameters. Kolmogorov-Smirnov test is a nonparametric test that is used to quantify the maximum distance between the reference cumulative distribution function (CDF) – generated from non-behavioral parameter values or B' – and posterior CDF of a parameter generated from behavioral datasets (or B). If such distance – referred to as D_{max} – is significant at a certain confidence level (α), the parameter is declared sensitive. Prior and posterior prediction uncertainty were next obtained by using model predictions generated respectively from the whole spectrum of model parameter distributions ($B \cup B'$), and from behavioral parameters only (B). The Reader is referred to Sharifi et al (2013) and Kalin et al. (2013) for a complete list of model parameters and their respective min/max bounds (quantities) and distributions.

8. Results and discussion

Model fitness was gauged by comparing simulated loading (export) of TSS, TN, NO_3 , ON, NH_4 , and TOC with observed data collected at the outlet using two performance criteria of Mass Balance Error (MBE) and Nash-Sutcliffe efficiency (E_{ns}). Table 2 exhibits average model performances (E_{ns} , MBE and L_k) for behavioral simulations (top 1%).

As shown in Table 2, the model had good skill in capturing dynamics of TOC, NO_3 and NH_4 loadings (mass export) from the study wetland with small mass balance error (except for NO_3) and large E_{ns} ($E_{ns} > 0.88$). Model performance was acceptable in predicting TN and TSS exports from the study wetland, with E_{ns} ranging from 0.58 to 0.61. However, MBE was relatively large for TSS. Despite increased complexity, model performance of the Expanded model is very close to that of the simpler Original model (refer to Sharifi et al., 2013b and Kalin et al., 2013). Note that in this study, 100,000 Monte Carlo simulations were performed, similar to that of the Original model studies (Sharifi et al., 2013b and Kalin et al. 2013). Given that the expanded model has more parameters (compared to the lumped version), it could be argued that more consistent observed hydrologic and water quality data and more MC simulations are required to achieve improved results compared to the Original model. In other words, finding the optimal combination of parameters in GLUE/GSA method requires more number of MC simulations when dealing with increased model complexity. Unfortunately, lack of sufficient data commensurate with the added level of complexity precludes full evaluation of the expanded model. Never the less, valuable insights could be learned from the application of the Expanded model, especially impact of interactions between wet/dry hydrologic conditions and physical and biogeochemical processes on wetland nutrient and carbon function.

8.1 Soil moisture redistribution in Barnstable wetland

Fixed parameters used in Mualem- van Genuchten model (θ_{sat} , θ_{res} , K_{sat} , λ , α and n) were extracted from literature (Kroes et al., 2008) for soils thought to be close to Jordan et al.'s (2003) description of soil in the study site - Typic Endoaquults of the Othello soil series (fine-silty, mixed, active, mesic Typic Endoaquult)(Table 3). Although assessing model sensitivity to parameters embedded in Richard equation was considered, multiple crashes of the numerical model forced the authors to run the soil moisture model deterministically.

Figure 8 exhibits model simulated soil moisture content in the variably saturated compartment of Barnstable wetland, averaged vertically over the whole soil column. Barnstable wetland has no records of soil moisture during the study period, thus the simulated results cannot be validated directly. However, the general trends in soil moisture of variably saturated compartment could be verified with side by side comparison of two graphs: 1) soil moisture time series in banks of wetland, and 2) depth of ponding in the center. Depth of standing water is a representative of wetland hydroperiod, and a direct function of rainfall. Similarly, soil moisture in the banks is directly a function of precipitation, thus one could expect that the local minima and maxima of the two graphs to coincide. The explained logic is evident in Figure 8, specifically during the long dry period between days 100 to 160 where depth of ponding is at its minimum. The only discrepancy between the two graphs occurs during days 10 to 80, where despite precipitation episodes and steady increase in soil moisture, a fall in the pool water level is observed. This observation can be explained if during such period, the precipitation was merely enough to fill pore spaces of the initially dry watershed soils and not enough to generate enough runoff to fill the pond. During the two year simulation period, soil moisture in the banks of the wetland had an average moisture content (θ) of 0.41 which is close to soil saturated water content ($\theta_{sat} = \phi = 0.43$).

To further explore validity of the employed numerical scheme, soil moisture profiles were drawn for the first two weeks of simulation period (Figure 9). As shown in Figure 9, the bottom node that coincides with perched water table (depth = -50 cm) (Jordan et al., 2003) remains saturated during simulation period due to defined bottom boundary conditions (head controlled, with $h=0$ at GW level). During the first 5 days, where there is no record of precipitation, soil becomes drier at the top few centimeters. Between days 5 to 10, where a sum of 3.75 cm of rainfall occurs, soil becomes saturated at the top; and afterwards, soil moisture starts to redistribute downwards. In general, due to existence of a shallow perched water table and excessive rainfall, soil moisture at banks of Barnstable wetland remains close to saturation. At driest conditions ($t=130$ days), the average soil moisture does not drop below 0.39 (Figure 8).

8.2 Sensitivity analysis

The Kolmogorov-Smirnov (K-S) test was applied to the behavioral (**B**) and non-behavioral (**B'**) datasets of each compartment, to statistically quantify the sensitive and insensitive parameters. Figure 10 to Figure 12 summarize the most sensitive parameters for ponded and variably saturated compartments of the study wetland in order of sensitivity based on NH_4 , NO_3 and TOC loading respectively. On the vertical axes of the presented graphs is D_{max} resulted from K-S test, and sensitive parameters are listed on horizontal axis in order of sensitivity. For the ponded compartment, the sensitivity was gauged at 5% significance level, whereas for the variably saturated compartment, significance level was set to 20%, simply because not too many parameters showed sensitive at 5% level. The reason behind this lack of sensitivity at 5% level stems from the fact that there are no observations available for direct validation of variably saturated compartment. Bottom panels of Figure 10 to Figure 12 displays the sensitive parameters of the Original model for the represented constituent.

These extra panels were borrowed from Sharifi et al. (2013) and from Kalin et al. (2013) for comparison purposes.

Comparing top and bottom panels of Figure 10, it is observed that the parameters for NH_4 that appear sensitive for ponded compartment more or less conform to the sensitive parameters of the Original model. However, the order of sensitivity is not necessarily the same. Another observation is that the total number of sensitive parameters for the ponded compartment of the Expanded model is more or less equal to that of the Original model (13 vs. 11). The same observations could be made for NO_3 in Figure 11.

Looking at top panels of Figure 10, in both ponded and variably saturated compartments, parameter f_N which captures the effects of pH and temperature on the fraction of total ammonia in ionized form (Hantush et al., 2013) appears as the most sensitive parameter. Depth of active sediment layer (H) also appears sensitive for both compartments. Parameter k_{ns} (nitrification rate in aerobic soil) followed by R_s (ammonia retardation factor in wetland soil) represent the second and third sensitive parameters for variably saturated compartment. Judging from the sensitive parameter, it appears that loss of ammonia to nitrification is the most important process in the variably saturated compartment, which is not unexpected due to abundance of oxygen in the top soil layer. The relatively high sensitivity of ammonia retardation factor in wetland soil, R_s indicates the importance of adsorption of ammonium ions onto negatively charged particles in variably saturated compartment.

From top right panel of Figure 11, with appearance of k_{dn} and H (denitrification rate and depth of active sediment layer) as top sensitive parameters, one could conclude that denitrification is the most important loss pathway of nitrate in variably saturated compartment. An explanation for this phenomenon could be that soil aeration in the variably saturated compartment promotes more nitrification. Once nitrate is diffused into lower soil layers, denitrification is promoted in reduced soil column- a statement supported by appearance of β_{nl} as the second most sensitive parameter in variably saturated compartment. A similar trend is observed in the ponded compartment, where β_{nl} is followed by k_{dn} at top of the sensitivity list. This appearance supports importance of denitrification in the ponded compartment, a phenomenon reflected by the Original model as well, although not as firmly.

From top right panel of Figure 12, an interesting observation that could be made is the appearance of ξ_D as second most sensitive parameter for TOC. Parameter ξ_D is the adjustment factor for aerobic respiration of DOC in reference to available soil moisture. Appearance of ξ_D in a sequence with θ_T° reveals that cycling of carbon related constituents in wetland banks (unsaturated soil) has high sensitivity to temperature and available soil moisture (θ_T° reflects the temperature dependence of reaction rates). Parameter a_{ca} (ratio of carbon to chlorophyll a in plants) appears as most sensitive parameter for carbon cycling of variably saturated compartment, indicating important effect of plant decomposition on C cycling in wetland banks.

8.3 Mass balance analysis

Table 4 and Table 5 summarize the N and C budgets and the major retention and removal pathways for ponded and variably saturated compartments during the study period. Last

columns of the two tables represent earlier findings from the Original model (borrowed from Sharifi et al., 2013 and Kalin et al., 2013). For the last two columns of both tables, all the numbers are normalized with the incoming load (shown in parentheses) to demonstrate a better picture of all the sources and sinks relative to loading. Values shown are the means $\pm$ one standard deviation obtained from the behavioral set simulations.

It is evident from Table 4 that Original and Expanded models have some differences in their nitrogen budget, particularly in denitrification and net deposition (settling – resuspension). The most notable difference is in the mass of denitrification, where the Expanded model reports almost three times as much denitrification as the Original model (79.4 ± 72.2 kg vs. 27.9 ± 5.8 kg). It is also notable that the uncertainty related to denitrification in the Expanded model is much higher than that of the Original model, with the large uncertainty stemming from the variably saturated compartment. Denitrification in variably saturated compartment is reported around 7 times higher than that of the ponded compartment (69.1 ± 67.2 kg-N vs. 10.3 ± 5.5 kg-N), whereas ammonia volatilization in variably saturated compartment was a fraction of that of ponded compartment (2.4 ± 4.6 kg-N vs. 11.9 ± 8.5 kg-N). The latter observation could be a result of higher nitrification activity in aerobic wetland soil and less availability of ammonia. In general, the Expanded model has a higher uncertainty compared to Original model. This was not unexpected given that the unsaturated model has a larger number of parameters, and lack of field observations for direct validation of the variably saturated compartment results. Another observation is that the Expanded model reports about 26% more losses in net deposition compared to the Lumped model (81.5 ± 18.4 kg-N vs. 64.6 ± 31.3 kg-N).

Table 5 presents the carbon mass exchanges and exports for the study wetland, averaged over behavioral model outputs over the simulation period. During the study period, 3849 kg of organic carbon was washed into the wetland through inflow and 360.1 ± 177.6 kg of atmospheric C was fixed by plants. Over the two year period, 1419.2 ± 403.4 kg of OC ($36.9 \pm 10.5\%$ of OC loading) was removed via microbial decomposition processes and eventually emitted to the atmosphere in inorganic form ($\text{CO}_2 + \text{CH}_4$). Diffusion of DOC to soil layers retained 260.7 ± 117.2 kg ($6.8 \pm 3.0\%$) and a minimal amount (162.5 ± 94.0 kg, equivalent to $4.2 \pm 2.4\%$ of OC load) was retained in the soil as a result of settling.

Similar to earlier findings, the Original and Expanded models are in agreement and report close numbers for carbon budget in the study wetland. It remains inconclusive, however, if lack of sufficient data and the relatively small unponded area of the wetland (30% at most) have contributed to less than significant differences between the Original and the Expanded models. The most prominent difference is in the mass of accumulated biomass where the Expanded model reports twice as much biomass accumulation compared to the Original model. This difference lies in the structural difference between the two models. As explained earlier in the design scheme of Expanded model, the total area of the wetland is modeled (ponded + variably saturated compartments), as opposed to the Original model where the area of the wetland shrinks and expands with rise and fall of water level in ponded sections of the wetland. In other words, the Original model ignores plants that grow out of the ponded boundary whereas the Expanded model considers both ponded and unsaturated

areas. The model reports minimal gaseous losses ($\text{CO}_2 + \text{CH}_4$) from variably saturated compartments, which might be due to low availability of labile OC in those areas.

9. Summary and Conclusion

In this study, a biogeochemical model for wetland nutrient cycling, was extended to also simulate geochemical reactions in parts of the wetland that are variably saturated. A comprehensive module was implemented for tracking moisture in wetland soil. The rapidly converging finite difference solution to Richards equation, introduced by van Dam and Feddes (2000), was coded in the model to trace soil moisture in unsaturated wetland soil. Once daily soil moisture profile of wetland soil were attained, model relationships were updated to simulate geochemical reactions and track concentrations of N and C related constituents in wetland soil. The developed model was applied to a small restored wetland located on Kent Island, Maryland which was monitored flow and water quality data for approximately 2 years. This wetland study provides inflow and outflow data for the ponded component for validation, but no studies including this one provide similar data for modeling the unponded component of a wetland. Although the new developments in the model were not completely validated, we were able to quantify mass exchanges through microbial activities in the unsaturated banks of the study wetland, a task that was not possible before.

Comparison of simulated soil moisture time series (in banks of wetland) with depth of ponding (at the center) showed that local minima and maxima of the two graphs coincide, indicating the validity of soil moisture module.

The parameters that appeared sensitive for ponded compartment (through KS test) more or less conformed to the sensitive parameters of the Original model; however, the order of sensitivity was not necessarily the same. KS test also revealed that carbon cycling in the unsaturated zone has high sensitivity to temperature and available soil moisture. Mass balance analysis revealed that Original and Expanded models have differences in their nitrogen and carbon budget. For N budget, the most notable difference appeared in the mass of denitrification, where the Expanded model reported almost three times more denitrification than the Original model. Denitrification in variably saturated compartment was reported around 3 times higher than that of the ponded compartment, whereas ammonia volatilization in variably saturated compartment was a fraction of that of ponded compartment. Regarding carbon mass balance, model reported minimal gaseous losses ($\text{CO}_2 + \text{CH}_4$) from variably saturated compartments which could have been due to low availability of labile OC in those areas. Expanded model reported twice as much biomass accumulation in the study wetland compared to the Original model.

A unique approach implemented in this study is the use of a transient compartment to estimate exchanges between ponded and variably saturated compartments. This approach eliminates the need for complex simulation of horizontal inter-compartmental advective transport in the model.

Due to a relatively large number of parameters, utility of the wetland model may not be fully realized and limited by availability of observed concentrations and fluxes of various constituents. Simplifying assumptions and overlooking important processes may limit the utility of the model and the relatively large number of parameters may contribute to the model predictive uncertainty. In general, application of any complex environmental model should be accompanied with some field collected data to constraint model parameters and reduce the inherent uncertainty in model predictions. When field data is not available, models should be used with caution, as the embedded uncertainty can lead to significant prediction errors, overshadowing the benefits that models provide. One limitation of WetQual model is partial representation for microbial competition over resources (i.e. oxygen and other electron acceptors) in wetland soil and water. Another limitation of the model is ignoring some of the minor processes of the N cycle such as anammox (Anaerobic ammonium oxidation) and DRNA (dissimilatory nitrate reduction to ammonium). Adding the aforementioned processes might improve the model as a whole, however, adding complexity without the support of field observed data can lead to more uncertainty in model predictions.

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10. References

- Bai J, Deng W, Zhu Y, and Wang Q (2004), Spatial variability of nitrogen in soils from land/inland water ecotones, *Communications in soil science and plant analysis*, 35(5–6), 735–749.
- Beven K, and Binley A (1992), The future of distributed models: model calibration and uncertainty prediction, *Hydrological processes*, 6(3), 279–298.
- Carnahan B, Luther HA, and Wilkes JO (1969). *Applied numerical methods*, Wiley New York.
- Cook FJ, and Orchard VA (2008), Relationships between soil respiration and soil moisture, *Soil Biology and Biochemistry*, 40(5), 1013–1018.
- Davidson E, Belk E, and Boone RD (1998), Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest, *Global change biology*, 4(2), 217–227.
- Dunne T (1978). *Water in environmental planning*, Macmillan.
- Fan Y, and Miguez-Macho G (2011), A simple hydrologic framework for simulating wetlands in climate and earth system models, *Climate dynamics*, 37(1–2), 253–278.
- Griffin D (1981), Water and microbial stress, in *Advances in microbial ecology*, edited, pp. 91–136, Springer.
- Hantush M, and Kalin L (2014), Modeling Nitrogen Fate and Transport at the Sediment-Water Interface, in *Modelling and Simulation of Diffusive Processes*, edited, pp. 161–185, Springer.
- Hantush M, Kalin L, Isik S, and Yucekaya A (2013), Nutrient dynamics in flooded wetlands. I: model development, *Journal of Hydrologic Engineering*, 18(12), 1709–1723.
- Ise T, and Moorcroft PR (2006), The global-scale temperature and moisture dependencies of soil organic carbon decomposition: an analysis using a mechanistic decomposition model, *Biogeochemistry*, 80(3), 217–231.
- Jordan TE, Whigham DF, Hofmockel KH, and Pittek MA (2003), Nutrient and sediment removal by a restored wetland receiving agricultural runoff, *Journal of Environmental Quality*, 32(4), 1534–1547. [PubMed: 12931911]

- Kalin L, and Hantush M (2007), Predictive Uncertainty and Parameter Sensitivity of a Sediment-Flux Model: Nitrogen Flux and Sediment Oxygen Demand, in World Environmental and Water Resources Congress 2007: Restoring Our Natural Habitat. Tampa, 5 15–19, edited, pp. 1–10.
- Kalin L, Hantush M, Isik S, Yucekaya A, and Jordan T (2013), Nutrient dynamics in flooded wetlands. II: Model application, *Journal of Hydrologic Engineering*, 18(12), 1724–1738.
- Kroes J, Van Dam J, Groenendijk P, Hendriks R, and Jacobs C (2008), SWAP version 3.2: Theory description and user manual, Alterra Wageningen, The Netherlands.
- Leij FJ (1996), UNSODA unsaturated soil hydraulic database.
- Manzoni S, Schimel JP, and Porporato A (2011), Responses of soil microbial communities to water stress: results from a meta-analysis, *Ecology*, 93(4), 930–938.
- Martin JF, Reddy KR, 1997 Interaction and spatial distribution of wetland nitrogen processes. *Ecological modelling* 105, 1–21. Doi 10.1016/S0304-3800(97)00122-1
- Massey FJ, Jr (1951), The Kolmogorov-Smirnov test for goodness of fit, *Journal of the American statistical Association*, 46(253), 68–78.
- Mitsch WJ, and Gosselink JG (2007), *Wetlands*. Hoboken, edited, NJ: Wiley.
- Neitsch S, Arnold J, Kiniry J, Williams J, and King K (2005), *Soil and water assessment tool: theoretical documentation*, version 2005, Texas, USA.
- Or D, Smets BF, Wraith J, Dechesne A, and Friedman S (2007), Physical constraints affecting bacterial habitats and activity in unsaturated porous media—a review, *Advances in Water Resources*, 30(6), 1505–1527.
- Orchard VA, and Cook FJ (1983), Relationship between soil respiration and soil moisture, *Soil Biology and Biochemistry*, 15(4), 447–453.
- Penman HL (1948). “Natural evaporation from open water, bare soil and grass.” *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 193(1032), 120–145.
- Reddy K, and DeLaune R (2008), *Biogeochemistry of wetlands: science and applications*, Biogeochemistry of wetlands: science and applications.
- Richards LA (1931), Capillary conduction of liquids through porous mediums, *Physics*, 1(5), 318–333.
- Schimel J, Balser TC, and Wallenstein M (2007), Microbial stress-response physiology and its implications for ecosystem function, *Ecology*, 88(6), 1386–1394. [PubMed: 17601131]
- Sharifi A (2013a), Development and application of WetQual-C, a mechanistic model for simulating carbon dynamics, GHG gas emissions and carbon export from wetlands, Auburn University.
- Sharifi A, Kalin L, Hantush MM, Isik S, and Jordan TE (2013b), Carbon dynamics and export from flooded wetlands: A modeling approach, *Ecological Modelling*, 263, 196–210.
- Sharifi A, Kalin L, Hantush M, Dahlgren R, O’Geen A, and Maynard J (2015). “Capturing Spatial Variability of Biogeochemical Mass Exchanges and Reaction Rates in Wetland Water and Soil through Model Compartmentalization.” *Journal of Hydrologic Engineering*, D4015001.
- Sleutel S, Moeskops B, Huybrechts W, Vandenbossche A, Salomez J, De Bolle S, Buchan D, and De Neve S (2008), Modeling soil moisture effects on net nitrogen mineralization in loamy wetland soils, *Wetlands*, 28(3), 724–734.
- Spear R, and Hornberger G (1980), Eutrophication in Peel Inlet—II. Identification of critical uncertainties via generalized sensitivity analysis, *Water Research*, 14(1), 43–49.
- Takatert N, Sanchez-Pérez JM, and Trémolières M (1999), Spatial and temporal variations of nutrient concentration in the groundwater of a floodplain: effect of hydrology, vegetation and substrate, *Hydrological Processes*, 13(10), 1511–1526.
- Van Dam JC, and Feddes RA (2000), Numerical simulation of infiltration, evaporation and shallow groundwater levels with the Richards equation, *Journal of Hydrology*, 233(1), 72–85.
- van Dam A, Dardona A, Kelderman P, Kansime F, 2007 A simulation model for nitrogen retention in a papyrus wetland near Lake Victoria, Uganda (East Africa). *Wetlands ecology and management* 15, 469–480
- Van Genuchten MT (1980), A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil science society of America journal*, 44(5), 892–898.

Figure 1:
Schematics of a hypothetical seasonally flooded wetland

Figure 2:
Schematic representation of the wetland compartmentalization into ponded and variably saturated compartments. Subscripts p and u , respectively, refer to ponded and variably saturated compartments. $h(t)$ and $h(t+\Delta t)$ respectively represent water level in the ponded compartment at times t and $t+\Delta t$.

Figure 3:
Spatial and temporal discretization of Richards Equation

Figure 4:

Procedure for selecting head controlled (h_{sur}) or flux controlled (q_{sur}) top boundary condition. This Diagram is adopted from van Dam and Feddes (2000) with permission. In the diagram, Q_{in} is inflow to the soil column (LT^{-1}), q_{bot} is the potential flux at the soil bottom (LT^{-1}), q_{eva} is potential ET flux (LT^{-1}), q_{root} the total water flux extracted by roots (LT^{-1}), q_{drain} is the total lateral flux to drains or ditches (LT^{-1}), q_{top} is the potential flux at the soil surface (LT^{-1}), q_{prec} is the precipitation rate at the soil surface (LT^{-1}), q_{irrig} is the applied irrigation flux (LT^{-1}), h_{pond} is the height of water ponding on the soil surface (L), $I_{\max}$ is the maximum soil water flux at the soil surface (LT^{-1}), h_{atm} the soil water pressure head in equilibrium with the prevailing air relative humidity (L), $E_{\max}$ is the maximum evaporation flux (LT^{-1}), K_{sat} is saturated hydraulic conductivity (LT^{-1}) and V_{air} denotes the pore volume in the soil profile which is filled with air (L), z_1 is thickness of the top soil compartment containing the first node, $K_{(1/2)}$ is saturated hydraulic conductivity of the top soil compartment containing the first node and $h_1^{j+1,p-1}$ is soil water pressure head at the top node evaluated at the last Picard iteration. Note that q_{eva} is estimated using the Penman equation (Eq. (2)).

¥ Outflow structure consisted of a standpipe connected to a 120° V-notch weir.

§ Automated samplers were installed to sample water entering and leaving the wetland.

Figure 5:
Study wetland and its watershed outlined by dashed lines (redrawn from Sharifi et al., 2013b).

Figure 6:

Hydrology of the study wetland (inflow, outflow and average water depth in ponded compartment) in addition to inflow concentrations of TOC (total organic C), NH_4 and NO_3 from May 1995 to May 1997. Q_{out} is outflow volume, P represents rainfall volume falling on the wetland and Q_{in} is inflow volume.

Figure 7:
Percent Area covered by ponded compartment in Barnstable wetland over study period

Figure 8:

Average volumetric water content in variably saturated compartment of Barnstable wetland (simulated) + daily precipitation records (top) along with average depth of water in the ponded compartment (bottom)

Figure 9: Simulated soil moisture profile in the banks of Barnstable wetland (top) in addition to evapotranspiration rate and precipitation records (bottom) during first two weeks of study period.

Figure 10:

Summary of the K-S test and order of sensitivities based on NH_4 loading for ponded and variably saturated compartments (top) and Original model (bottom, reproduced from Kalin et al., 2013). Note that $\%p$ indicates p value yielded from K-S test.

Figure 11: Summary of the K-S test and order of sensitivities based on NO_3 loading for ponded and variably saturated compartments (top) and Original model (bottom, borrowed from Kalin et al., 2013). Note that %p indicates p value yielded from K-S test.

Figure 12:

Summary of the K-S test and order of sensitivities based on TOC loading for ponded and variably saturated compartments (top) and Original model

Table 1:

Definitions and dimensions of model parameters

Symbol	Definition & Dimension
A	wetland surface area [L^2]
a	mass of free floating plant [$M\ Chl\ a$]
a_{na}	<i>gram of nitrogen per gram of chlorophyll-a in plant/algae</i>
a_{oc}	<i>gram of oxygen produced per gram of organic carbon synthesized (= 2.67)</i>
a_{ca}	ratio of carbon to chlorophyll-a in algae [MM^{-1}]
a_{mc}	the stoichiometric yield of Methane from the anaerobic decomposition of gram of organic carbon during methanogenesis [MM^{-1}]
B	mass of rooted plants [$M\ Chl\ a$]
C^*	equilibrium concentration of CH_4 in atmosphere [ML^{-3}]
C_{L0}	concentrations of labile (fast reacting) particulate organic C in unsaturated soil [ML^{-3}]
C_{R0}	concentrations of refractory (slow reacting) particulate organic C in unsaturated soil [ML^{-3}]
C_{D0}	concentrations of dissolved organic C in unsaturated soil [ML^{-3}]
C_{M0}	methane concentration in anaerobic sediment, aerobic sediment layer and water respectively [ML^{-3}]
C_{Lw}	concentrations of labile (fast reacting) particulate organic C in free water [ML^{-3}]
C_{Rw}	concentrations of refractory (slow reacting) particulate organic C in free water [ML^{-3}]
C_{Dw}	concentrations of dissolved organic C in free water [ML^{-3}]
C_{L1}, C_{R1}, C_{D1}	pore water concentrations of LPOC, RPOC and DOC in aerobic sediment layer [ML^{-3}]
C_{L2}, C_{R2}, C_{D2}	pore water concentrations of LPOC, RPOC and DOC in lower anaerobic sediment layer respectively [ML^{-3}]
C_{M2}, C_{M1}, C_{Mw}	methane concentration in anaerobic sediment, aerobic sediment layer and water respectively [ML^{-3}]
$C_{Lin}, C_{Rin}, C_{Din}$	concentrations of LPOC, RPOC and DOC in incoming flow [ML^{-3}]
D_o^*	free-water oxygen diffusion coefficient [L^2T^{-1}]
D^o	Diffusivity of Methane in air [L^2T^{-1}]
D_M^*, D_D^*	diffusivity of methane and DOC in water, respectively [L^2T^{-1}]
E_T	evapotranspiration rate [$L^3T^{-1}L^{-2}$]
$F_{N_{ag}}^w, F_{N_{ng}}^w$	groundwater source/loss for total ammonia nitrogen and nitrate nitrogen [MT^{-1}]
$F_{N_{ag}}^1, F_{N_{ng}}^1$	groundwater source/loss of total ammonia nitrogen and nitrate in the aerobic layer [MT^{-1}]
$F_{N_{ag}}^2, F_{N_{ng}}^2$	groundwater source/loss of total ammonia nitrogen and nitrate in the anaerobic layer [MT^{-1}].
$F_{C_{Dg}}^w$	groundwater source/loss for DOC
$F_{C_{Dg}}^1$	groundwater source/loss of DOC from aerobic sediment layer [MT^{-1}]
$F_{C_{Dg}}^2$	groundwater source/loss of DOC from anaerobic sediment layer [MT^{-1}].

Symbol	Definition & Dimension
$F_{C_{Mg}}^0, F_{C_{Dg}}^0, F_{N_{ng}}^0, F_{N_{ag}}^0$	groundwater source/loss of methane, DOC, nitrate and total ammonia nitrogen in the unsaturated soil layer [MT ⁻¹]
$F_{C_{Mg}}^1, F_{C_{Mg}}^2$	groundwater source/loss for methane [MT ⁻¹]
f_{act}	Vertical diffusion magnification factor
f_1	volumetric fraction of the active soil layer that is aerobic
f_2	volumetric fraction of the active soil layer that is anaerobic
f_{a1}	fraction of mineral nitrogen plant uptake as ammonia-N in the soil aerobic layer.
f_{a2}	fraction of mineral nitrogen plant uptake as ammonia-N in the soil anaerobic layer.
f_{aw}	fraction of mineral nitrogen plant uptake as ammonia-N in free water
f_{bs}	fraction of rooted plant biomass below soil-water interface (within soil layer)
f_{bw}	fraction of rooted plant biomass above soil-water interface
f_{nw}	fraction of mineral nitrogen plant uptake as nitrate-N in free water
f_{n1}	fraction of mineral nitrogen plant uptake as nitrate-N in the aerobic layer
f_{n2}	fraction of mineral nitrogen plant uptake as nitrate-N in the anaerobic layer
f_N	fraction of total ammonia nitrogen in ionized form
f_r	fraction of rapidly mineralizing particulate organic matter
f_s	fraction of slowly mineralizing particulate organic matter
f_{Sw}	fraction of nitrogen fixation in water
f_{aL}, f_{aR}, f_{aD}	fraction of, respectively, labile particulate, refractory particulate and dissolved organic C produced by death/loss of free floating plants and attached algae ($f_{aL}+f_{aR}+f_{aD}=1$)
f_{bL}, f_{bR}, f_{bD}	fraction of, respectively, labile particulate, refractory particulate and dissolved organic C produced by death/loss of rooted and benthic plants ($f_{bL}+f_{bR}+f_{bD}=1$)
f_{bw}, f_{bs}	fraction of rooted plant biomass, respectively, above and under soil-water interface
f_1, f_2	volumetric fraction of aerobic and reduced soil layers
f_N	fraction of total ammonia in ionized form
H	thickness of active soil layer
h	average depth of water in wetland [L]
i_p	precipitation rate [LT ⁻¹]
J_M	methane mass exchange coefficient between water and atmosphere [LT ⁻¹]
K_{s1}	distribution coefficient in aerobic layer [L ³ M ⁻¹]
K_{s2}	distribution coefficient in reduced wetland soil [L ³ M ⁻¹].
K_o	oxygen mass-transfer coefficient [LT ⁻¹]
K_d	ammonium ion distribution coefficient [L ³ M ⁻¹]
K_o	oxygen reaeration mass-transfer velocity [LT ⁻¹]
K_O^{in}	Michaelis–Menten oxygen inhabitation coefficient [ML ⁻³]
K_N^{in}	Michaelis–Menten nitrate-N inhibition coefficient [ML ⁻³]
K_N	Michaelis–Menten nitrate N half saturation concentration required for denitrification [ML ⁻³]
K_O	Michaelis–Menten half saturation concentration of dissolved oxygen required for oxic respiration [ML ⁻³]

Symbol	Definition & Dimension
K_h	Ratio of NH_3 in gas form to NH_3 in liquid form
k_D^1, k_D^2, k_D^3	maximum dissolved organic C utilization rate for, respectively, aerobic respiration, denitrification and methanogenesis [T^{-1}]
k_M^1, k_M^2	maximum methane utilization rate for, respectively, aerobic respiration and denitrification [T^{-1}]
k_{da}	death rate of free floating plants [T^{-1}]
k_{db}	death rate of rooted and benthic plants [T^{-1}]
k_L, k_R	first order hydrolysis rate of labile particulate organic carbon and refractory particulate organic carbon, respectively [T^{-1}]
k_{da}	death rate of free-floating plants [T^{-1}]
k_{db}	death rate of benthic and rooted plants [T^{-1}]
k_{dn}	denitrification rate in anaerobic soil layer [T^{-1}]
k_{ga}	growth rate of free-floating plant [T^{-1}]
k_{gb}	growth rate of benthic and rooted plant [T^{-1}]
k_{mr}	first-order rapid mineralization rate in wetland soil [T^{-1}]
k_{ms}	first-order slow mineralization rate in wetland soil [T^{-1}]
k_{mw}	first-order mineralization rate in wetland free water [T^{-1}]
k_{ns}	first-order nitrification rate in aerobic soil layer [T^{-1}]
k_{nw}	first-order nitrification rate in wetland free water [T^{-1}]
k_s^*	maximum first-order nitrification rate in wetland soil [T^{-1}]
k_v	volatilization mass transfer velocity [LT^{-1}]
l_1	thickness of aerobic soil layer [L]
l_2	thickness of anaerobic soil layer [L]
$m_{w\text{ in}}$	sediment concentration in incoming flow [ML^{-3}]
m_w	sediment concentration in free water [ML^{-3}]
m_s	wetland soil bulk density [ML^{-3}]
N^*	equilibrium concentration of NH_4 in atmosphere [ML^{-3}]
N_{ow}	particulate organic nitrogen concentration in free water [ML^{-3}]
N_{aw}	$[\text{NH}_4^+] + [\text{NH}_3]$ total ammonia-nitrogen concentration in free water [ML^{-3}]
N_{nw}	nitrate-nitrogen concentration in free water [ML^{-3}]
N_{or}	concentration of labile organic nitrogen in wetland soil [ML^{-3}]
N_{os}	concentration of refractory organic nitrogen in wetland soil [ML^{-3}]
N_{a2}	total ammonia-nitrogen pore-water concentration in lower anaerobic layer [ML^{-3}]
N_{n2}	nitrate-nitrogen pore-water concentration in lower anaerobic layer [ML^{-3}]
$N_{ow\text{ in}}, N_{aw\text{ in}}, N_{nw\text{ in}}$	concentrations of organic nitrogen, total ammonia nitrogen and nitrate nitrogen in incoming inflow [ML^{-3}]
N_{ap}, N_{np}	concentrations of total ammonia nitrogen and nitrate nitrogen in precipitation [ML^{-3}]
N_{u0}	$[\text{NH}_4^+] + [\text{NH}_3]$ total ammonia-nitrogen concentration in unsaturated soil [ML^{-3}]
N_{n0}	nitrate-nitrogen concentration in unsaturated soil [ML^{-3}]
N_{aG}, N_{nG}	total ammonia-nitrogen and nitrate-nitrogen concentration in ground water [ML^{-3}]
$O_{w\text{ in}}, O_p$	concentrations of oxygen in incoming water and precipitation [ML^{-3}]

Symbol	Definition & Dimension
O_w	oxygen concentration in free water [ML^{-3}]
O_{sl}	oxygen concentration in aerobic sediment [ML^{-3}]
O^*	oxygen concentration in the air (assumed at saturation) [ML^{-3}]
Q_{in}	volumetric inflow rate [L^3T^{-1}]
Q_g	groundwater discharge (negative for infiltration) [L^3T^{-1}]
Q_o	wetland discharge (outflow) rate [L^3T^{-1}]
q_d, q_n	dry depositional rates of total ammonia nitrogen and nitrate [$\text{ML}^{-2}\text{T}^{-1}$]
$R_0(i)$	solar radiation on day i
R_s	total ammonia retardation factor in wetland soil
$r_{c,chl}$	carbon mass ration in <i>chlorophyll a</i>
$r_{on,m}$	gram of oxygen consumed per gram of organic nitrogen mineralized (= 15.29)
$r_{on,n}$	gram of oxygen consumed per gram of total ammonium nitrogen oxidized by nitrification (= 4.57)
$r(i)$	earth's eccentricity correction factor for day i
S	rate of nitrogen fixation by microorganisms [$\text{ML}^{-2}\text{T}^{-1}$]
S_O	wetland soil oxygen depletion rate per unit area [$\text{ML}^{-2}\text{T}^{-1}$]
S_w	volumetric oxygen consumption rate in water by other processes [$\text{ML}^{-3}\text{T}^{-1}$]
S_B	Bunsen solubility coefficient for methane
Sc_M	Schmidt number of methane in a given temperature
S_s	oxygen removal rate per unit volume of aerobic layer by other processes
$T_d(i)$	total day length on day i
V_w	water volume of wetland surface water [L^3]
V_0	Volume of unsaturated soil column [L^3]
V_s	volume of active sediment layer [L^3]
V_1, V_2	volume of aerobic and anaerobic soil [L^3]
v_s	effective settling velocity [LT^{-1}]
v_r	resuspension rate [LT^{-1}]
v_b	burial velocity [LT^{-1}]
α	empirical parameter in the relationship relating oxygen liquid-film transfer velocity to wind speed
α_M	methane gas transfer velocity between water and atmosphere [LT^{-1}]
β_{a1}, β_{n1}	diffusive mass-transfer rates, respectively, of total ammonia nitrogen and nitrate between wetland water and aerobic soil layer [LT^{-1}]
β_{a2}, β_{n2}	diffusive mass-transfer rates, respectively, of total ammonia nitrogen and nitrate between oxygenated soil layer and lower anaerobic layer [LT^{-1}]
β_{D1}, β_{M1}	diffusive mass-transfer rates, respectively, of DOC and CH_4 between wetland water and aerobic soil layer [LT^{-1}]
β_{D2}, β_{M2}	diffusive mass-transfer rates, respectively, of DOC and CH_4 between wetland water and lower anaerobic soil layer [LT^{-1}]
β_{M1}	methane mass exchange coefficient between aerobic sediment and water [LT^{-1}]
β_{M2}	methane mass exchange coefficient between aerobic and anaerobic sediment [LT^{-1}]
$\beta_{nx}, \beta_{ax}, \beta_{Dx}, \beta_{Mx}$	diffusive mass-transfer rates, respectively, of total ammonia, nitrate, DOC and methane between unsaturated wetland soil and saturated aerobic soil layer [LT^{-1}]

Symbol	Definition & Dimension
δ	thickness of a laminar (diffusive) boundary layer situated on top of the soil-water interface [L]
ξ_D	adjustment factor for aerobic respiration of DOC in reference to available soil moisture
η	empirical parameter in the relationship relating oxygen liquid-film transfer velocity to wind speed
θ_{T^0}	Temperature coefficient in Arrhenius equation.
θ	Soil water content (L^0)
θ_{sat} θ_{res}	Soil saturated and residual water content
λ_r	specific conductivity of root system [LL^{-1}]
λ_σ λ_ω	empirical coefficients in the relationships limiting nitrification, respectively, in soil and free water to oxygen concentration in wetland water
π	Portion of soil volume that is filled with air ($\pi = \phi - \theta$)
ρ_s	wetland soil particle density [ML^{-3}]
τ_w	effective tortuosity of the flooded area above soil
τ	wetland soil tortuosity factor
ϕ	wetland soil porosity
ϕ_w	effective porosity of wetland surface water

Table 2:

Average model performances (MBE , Ens and L_k) for behavioral simulations based on observed and simulated loadings (mass of export)

	TN	Onw	NH ₄	NO ₃	TSS	TOC
MBE (%)	-8.2	-13.7	-0.3	29.1	-46.3	-4.1
E_{ns}	0.61	0.46	0.91	0.96	0.58	0.88
L_k	0.77	0.67	0.95	0.85	0.60	0.92

Table 3:

Adapted parameter values for Richards equation (extracted from Kroes et al., 2008)

θ_{sat}	θ_{res}	$K_{\text{sat}} \text{ (cm.sec}^{-1}\text{)}$	λ	$\alpha \text{ (cm}^{-1}\text{)}$	n
0.43	0.001	2.02×10^{-5}	-0.14	0.0249	1.507

Table 4:Nitrogen budget in the study wetland^χ

	Ponded compartment	Variably saturated Compartment	Total	Original model ^τ
<i>Run off</i>	336.3	N.A.	336.3 (95.8%)	336.3 (95.8%) [¥]
<i>Atmospheric Deposition</i>	14.6	N.A.	14.6 (4.2%)	14.6 (4.2%)
<i>Outflow</i>	260.5 ± 30.4	N.A.	262.3 ± 55.9 (74.17 ± 8.7%)	269.2 ± 36.7 (76.7 ± 10.5%)
<i>Net Deposition</i> [#]	81.5 ± 18.4	N.A.	81.5 ± 18.4 (23.21 ± 5.24%)	64.6 ± 31.3 (18.4 ± 8.9%)
<i>Volatilization</i>	11.9 ± 8.5	2.4 ± 4.6	14.3 ± 13.1 (4.07 ± 3.73%)	8.1 ± 6.8 (2.3 ± 1.9%)
<i>Denitrification</i>	10.3 ± 5.5	69.1 ± 67.2	79.4 ± 72.2 (22.61 ± 20.56%)	27.9 ± 5.8 (7.9 ± 1.6%)
<i>NH₄ diffusion</i>	0.6 ± 3.7	N.A.	0.6 ± 3.7 (0.17 ± 1.05%)	-1.1 ± 2.8 (-0.3 ± 0.8%)
<i>NO₃ diffusion</i>	12.2 ± 3.5	N.A.	12.2 ± 3.5 (3.47 ± 1%)	31.6 ± 5.0 (9.0 ± 1.4%)

^χ All Units are in kg^τ Results of the Lumped model are borrowed from Kalin et al. (2013)[¥] Numbers in parentheses are values normalized with runoff loading+atmospheric deposition[#] Net deposition is equivalent to settling - resuspension

Table 5:Carbon budgets in the study wetland^χ

	Ponded compartment	Variably saturated Compartment	Total	Original model ^τ
<i>Run off</i>	3849	N.A.	3849(100%)	3849 (100%)
<i>Outflow</i>	2429.4 ± 148.5	N.A.	2338.1 ± 173.4(63.1 ± 3.9%)	2430±152 (63.1 ± 4.0%)
<i>Gaseous losses</i>	1308.2 ± 257.6	111.0 ± 145.8	1419.2 ± 403.4(36.9 ± 10.5%)	1350± 269(35.1 ± 7.0%)
<i>Deposition</i> [Ⓜ]	162.5 ± 94	N.A.	162.5 ± 94.0 (4.2 ± 2.4%)	172±79 (4.5 ± 2.1%)
<i>Biomass accumulation</i> ^ξ	180.6 ± 88.3	179.7 ± 87.9	360.1 ± 176.2(9.4 ± 4.6%)	176±88 (4.6 ± 2.3%)
<i>Diffusion</i>	260.7 ± 117.2	N.A.	260.7 ± 117.2 (6.8 ± 3.0%)	269 122(7.0 ± 3.2%)

^χAll Units are in kg^τResults of the Original model are borrowed from Sharifi et al. (2013)[Ⓜ]Numbers in parentheses are values normalized with runoff loading^ξBiomass accumulation is equivalent to net primary productivity multiplied by area[Ⓜ]Net deposition is equivalent to settling - resuspension