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# Using Reactive Transport Codes to Provide Mechanistic Biogeochemistry Representations in Global Land Surface Models

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**Abstract.** We explore a flexible and extensible approach to biogeochemistry in land surface models: coupling to a configurable subsurface reactive transport code, to facilitate testing of alternative models and incorporation of new understanding. A reaction network with the CLM-CN decomposition, nitrification, denitrification, and plant uptake is used as an example. We implement the reactions in the open source PFLOTRAN code, couple to CLM, and test at arctic, temperate, and tropical sites. To make the reaction network designed for use in explicit time-stepping in CLM compatible with implicit time-stepping, the Monod substrate rate-limiting function with a residual concentration is used to represent the limitation of nitrogen availability on plant uptake and immobilization. To achieve accurate, efficient, and robust numerical solutions, care needs to be taken to using scaling, clipping, or log transformation to avoid negative concentrations during the Newton iterations. With a tight relative update tolerance (STOL, e.g.,  $10^{-12}$ ) to avoid false convergence, accurate solution can be achieved with about 50% more computing time than CLM in point mode site simulations using either the scaling or the clipping methods. Log transformation takes 60% to 100% more computing time than CLM. The computing time increases slightly for clipping and scaling, substantially for log transformation for half saturation decrease from  $10^{-3}$ ,  $10^{-6}$ , to  $10^{-9} \text{ mol m}^{-3}$ , which normally results in decreasing nitrogen concentrations. Frequent occurrence of very low concentrations (e.g. below nM) can increase the computing time for clipping by about 20%, and double for log transformation. Caution needs to be taken for the scaling method as a small scaling factor caused by a positive update to a small concentration may diminish the update and result in false convergence even with very tight STOL. As methane and nitrous oxide production and consumption involve very low half saturation and threshold concentrations, this work provides insights for addressing nonnegativity issue and facilitates mechanistic biogeochemistry representation in earth system models to reduce climate prediction uncertainty.

## 1 Introduction

Land surface (terrestrial ecosystem) models (LSM) calculate the fluxes of energy, water, and green house gases across the land-atmosphere interface for the atmospheric general circulation models for climate simulation and weather forecasting (Sellers et al., 1997). Evolving from the first generation 35 “bucket”, second generation “biophysical”, and third generation “physiological” models (Seneviratne et al., 2010), current LSMs, e.g., the Community Land Model (CLM), implement comprehensive thermal, hydrological, and biogeochemical processes (Oleson et al., 2013). The important role of soil biogeochemistry is suggested by the confirmation that the increase of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) in the atmosphere since the preindustrial time is 40 the main driving cause of climate change, and interdependent water, carbon and nitrogen cycles in terrestrial ecosystems are very sensitive to climate changes (IPCC, 2013). In addition to ~250 soil biogeochemical models developed in the past ~80 years (Manzoni and Porporato, 2009), increasingly mechanistic models continue to be developed to increase the fidelity of process representation 45 for improving climate prediction (e.g., Riley et al., 2014).

As LSMs usually hardcode the reaction network (pools/species, reactions, rate formulae), substantial effort is often required to modify the source code for testing alternative biogeochemical models, and incorporating new process understanding. Fang et al. (2013) demonstrated use of a reaction-based approach to facilitate implementation of CLM-CN and CENTURY models, and incorporation 50 of phosphorus cycle. Tang et al. (2013b) solved the advection diffusion equation in CLM using operator splitting. In contrast, TOUGH-REACT, a reactive transport modeling (RTM) code, was used to develop multi-phase mechanistic carbon and nitrogen models with many speciation and microbial reactions (Maggi et al., 2008; Gu and Riley, 2010; Riley et al., 2014). PHREEQC was coupled with DayCent to describe soil and stream water equilibrium chemistry (Hartman et al., 2007). Coupling 55 a RTM code with CLM will facilitate testing of increasingly mechanistic biogeochemical models in LSMs.

An essential aspect of LSMs is to simulate competition for nutrients (e.g., mineral nitrogen, phosphorus, etc.) among plants and microbes. In CLM, plant and immobilization nitrogen demands are calculated independent of soil mineral nitrogen. The limitation of nitrogen availability on plant uptake and immobilization is simulated by a demand based competition: demands are downregulated 60 by soil nitrogen concentration (Oleson et al., 2013; Thornton and Rosenbloom, 2005). This avoids negative concentrations and does not introduce numerical errors (Tang and Riley, 2015) as CLM uses explicit time stepping.

RTM model often accounts for the limitation of reactant availability on the reaction rates for each individual reaction for mechanistic representations and flexibility in adding reactions. RTM codes 65 generally use implicit time stepping and the Newton-Raphson method. Negative concentration can be introduced during iterations, which is not physical, and can cause numerical instability and errors (Shampine et al., 2005). This is expected to worsen when we implement microbial reactions for

methane and nitrous oxide consumption and production as the threshold and half saturation are at or below nM ( $10^{-9}$  M) level (Conrad, 1996). The redox potential Eh needs to be decreased to  $-0.35$   
70 V (oxygen concentration  $< 10^{-22}$  M Hungate, 1975) for methanogens to grow (Jarrell, 1985).

Three methods are used to avoid negative concentration in geochemical codes. One is to use  
the logarithm concentration as the primary variable (Bethke, 2007; Hammond, 2003; Parkhurst and  
Appelo, 1999). The other two either scale back the update vector (Bethke, 2007; Hammond, 2003) or  
clip the concentrations for the species that are going negative (Yeh et al., 2004; White and McGrail,  
75 2005; Sonnenthal et al., 2014) in each iteration. Except that log transformation poses some efficiency  
issues (Hammond, 2003), few implications in accuracy and efficiency are reported for these methods.

As LSMs need to run under varies conditions at the globe scale for simulation duration of cen-  
turies, it is necessary to resolve accuracy and efficiency issues to use RTM codes for LSMs. The  
objective of this work is to obtain accurate, efficient, and robust solutions for CLM subsurface bio-  
80 geochemical reactions in CLM-PFLOTRAN. To this end, we implement a CLM biogeochemical  
reaction network, test the implementation at arctic, temperate, and tropical sites, and examine the  
implication of using scaling, clipping, and log transformation for avoiding negative concentrations.  
Comprehensive CLM-PFLOTRAN coupling in heat transfer (including freeze and thaw), hydrology,  
and biogeochemistry will be presented in future publications.

## 85 2 Methods

LSMs generally include biogeochemical reactions for carbon and nitrogen cycles, in particular, the  
organic matter decomposition, nitrification, denitrification, plant nitrogen uptake, and methane pro-  
duction and oxidation. The kinetics are usually described by a first-order rate modified by response  
functions for environmental variables (temperature, moisture, pH, etc.) (Bonan et al., 2012; Boyer  
90 et al., 2006; Schmidt et al., 2011). In this work, we use the CLM-CN decomposition (Bonan et al.,  
2012; Oleson et al., 2013; Thornton and Rosenbloom, 2005), nitrification, denitrification (Dickinson  
et al., 2002; Parton et al., 2001, 1996), and plant nitrogen uptake reactions (Fig. 1) as an example.  
The reactions and rate formulae are detailed in Appendix A.

### 2.1 CLM-PFLOTRAN biogeochemistry coupling

95 In CLM-PFLOTRAN, CLM instructs PFLOTRAN to solve the partial differential equations for en-  
ergy (including freezing and thawing), water flow, and reaction and transport in the surface and  
subsurface. This work focuses on the biogeochemistry as CLM solves the energy and water flow  
equations and handles the solute transport (mixing, advection, diffusion, and leaching). In each CLM  
time step, CLM provides production rates for Lit1C, Lit1N, Lit2C, Lit2N, Lit3C, Lit3N for litter  
100 fall; CWDC, and CWDN for coarse woody debris production, ammonium and nitrate for nitrogen  
deposition and fixation; and plant nitrogen demand; and specifies liquid water content, matrix po-

tential and temperature for PFLOTRAN; PFLOTRAN solves the ordinary differential equations for the kinetic reactions, the mass action equations for the equilibrium reactions, and provides the final concentrations back to CLM.

105 The reactions and rates are implemented using the “reaction sandbox” concept in PFLOTRAN (Lichtner et al., 2015). For each reaction, we specify a rate and a derivative of the rate with respect to any components in the rate formula, given concentrations, temperature, moisture content, and other environmental variables (see reaction\_clm.F90 in pflotran-dev source code for details). PFLOTRAN accumulates these rates and derivatives into a residual vector and a Jacobian matrix, and the global  
110 equation is discretized in time using the backward Euler method and solved using the Newton-Raphson method (Appendix B).

Unlike the explicit time stepping in CLM where only reaction rates need to be calculated, implicit time stepping requires derivatives. While PFLOTRAN provides an option to calculate derivatives numerically, analytical derivative calculation is generally preferred (e.g., Xu et al., 2006) because  
115 numerical calculation for accurate Jacobian is a notoriously difficult task (Shampine et al., 2005).

Many reactions can be specified in an input file, providing flexibility in adding various reactions with user-defined rate formulae. As typical rate formulae consist of first order, Monod, and inhibition terms, a general rate formula with flexible number of terms and typical moisture, temperature, and pH response functions are coded in PFLOTRAN. Most of the biogeochemical reactions can be  
120 specified in an input file, with flexible number of reactions, species, rate terms, and various response functions without source code modification. Code modification is necessary only when different rate formulae, or response functions are introduced. In contrast, the number of pools and reactions are traditionally hard-coded in CLM. Consequently, any change of the pools, reactions, or rate formula may require source code modification. Therefore, this new approach facilitates implementation of  
125 increasingly mechanistic reactions and tests of various representations with less code modifications.

## 2.2 Mechanistic representation of rate-limiting processes

To use RTMs in LSMs, we need to make reaction networks designed for use in explicit time-stepping LSMs compatible with implicit time-stepping RTMs. The limitation of reactant availability on reaction rate is well represented by the first-order rate (Eqs. A1, A2, A5, A7): the rate decreases to  
130 zero as the concentration decreases to zero. A residual concentration is often added to represent a threshold below which a reaction stops. For example the decomposition rate, Eq. (A1) becomes

$$\frac{d[\text{CN}_u]}{dt} = -k_d f_T f_w ([\text{CN}_u] - [\text{CN}_u]_r). \quad (1)$$

Where  $\text{CN}_u$  is the upstream pool with 1:u as the CN ratio in mole; [] denotes concentration;  $k_d$ ,  $f_T$ , and  $f_w$  is the rate coefficient, temperature and moisture response function. When  $\text{CN}_u$  goes below  
135  $[\text{CN}_u]_r$  in an iteration, Eq. (1) implies a hypothetical reverse reaction to bring it back to  $[\text{CN}_u]_r$ . The residual concentration can be set to zero to nullify the effect.

For the litter decomposition reactions (R7, R8, R9) that immobilize nitrogen (N), the nitrification reaction (R11) associated with decomposition to produce nitrous oxide, and the plant nitrogen uptake reactions (R13,R14), the rate formulae do not account for the limitation of the reaction rate by nitrogen availability. Mechanistically, a nitrogen limiting function needs to be added. For example, using the widely used Monod substrate limitation function (Hammond, 2003), Eq. (1) becomes

$$\frac{d[\text{CN}_u]}{dt} = -k_d f_T f_w ([\text{CN}_u] - [\text{CN}_u]_r) \frac{[N] - [N]_r}{[N] - [N]_r + k_m}, \quad (2)$$

with half saturation  $k_m$  and a mineral nitrogen residual concentration  $[N]_r$ . In the case of  $[N] - [N]_r = k_m$ , the rate is decreased by half. For  $[N] \gg k_m$ , Eq. (2) approximates zero order with respect to  $[N]$ . For  $[N] \ll k_m$ , Eq. (2) approximates first order with respect to  $[N]$ . The derivative of the Monod term,  $k_N([N] + k_m)^{-2}$ , increases to about  $k_m^{-1}$  as the concentration decreases to below  $k_m$ . This represents a steep transition when  $k_m$  is small. The half saturation is expected to be greater than the residual concentration. When both are zero, the rate is not limited by the substrate availability.

To separate mineral nitrogen into ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ), we need to distribute the demands between ammonium and nitrate for plant uptake and immobilization. If we simulate the ammonium limitation on plant uptake with

$$R_a = R_p \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + k_m}, \quad (3)$$

the plant nitrate uptake can be represented by

$$R_n = (R_p - R_a) \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + k_m} = R_p \frac{k_m}{[\text{NH}_4^+] + k_m} \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + k_m}. \quad (4)$$

Where  $R_p$ ,  $R_a$ , and  $R_n$  are the plant uptake rate for nitrogen, ammonium, and nitrate. This essentially assumes an inhibition of ammonium on nitrate uptake, which is consistent with the observation that plant nitrate uptake rate remained low until ammonium concentrations dropped below a threshold (Eltrop and Marschner, 1996). However, the preference differs for different plants (Pfautsch et al., 2009; Warren and Adams, 2007; Nordin et al., 2001; Falkengren-Grerup, 1995; Gherardi et al., 2013), which require different representations in future developments.

CLM uses a demand based competition approach (Appendix A5) to represent the limitation of available nitrogen on plant uptake and immobilization. It is similar to the Monod function except that it introduces a discontinuity during the transition between the zero and first order rate. Implementation of the demand based competition in a RTM involves separating the supply and consumption rates for each species in each reaction, and conducting downregulation when necessary after contributions from all of the reactions are accumulated. It involves not only the rate terms for the residual but also the derivative terms for the Jacobian. The complexity increases quickly when more species need to be downregulated (e.g., ammonium, nitrate, and organic nitrogen) and there are transformation processes among these species. It becomes challenging to separate, track, and downregulate consumption and production rates for an indefinite number of species, and calculation of the Ja-

cobian becomes convoluted. In contrast, use of Monod function with a residual concentration for individual reactions is easier to implement, and allows more flexibility in adding reactions..

### 2.3 Scaling, clipping and log transformation for avoiding negative concentration

The concentration update for iteration  $p$  from time step  $k$  to  $k + 1$ ,  $\delta\mathbf{c}^{k+1,p}$ , in a Newton-Raphson iteration can be greater than the concentration  $\mathbf{c}^{k+1,p}$  in some entries (Eq. B6), which can result in nonphysical negative concentrations. One approach to avoid negative concentration is to scale back the update with a scaling factor  $\lambda$  (Bethke, 2007; Hammond, 2003) such that

$$\mathbf{c}^{k+1,p+1} = \mathbf{c}^{k+1,p} - \lambda\delta\mathbf{c}^{k+1,p} > 0, \quad (5)$$

where

$$180 \quad \lambda = \min_{i=0,m} [1, \alpha\mathbf{c}^{k+1,p}(i)/\delta\mathbf{c}^{k+1,p}(i)] \quad (6)$$

for positive  $\delta\mathbf{c}^{k+1,p}(i)$  with  $m$  as the number of species times the number of numerical grid cells. RTM codes STOMP, HYDROGEOCHEM 5.0, and TOUGH-REACT using clipping, i.e., for any  $\delta\mathbf{c}^{k+1,p}(i) \geq \mathbf{c}^{k+1,p}(i)$ ,  $\delta\mathbf{c}^{k+1,p}(i) = \mathbf{c}^{k+1,p}(i) - \epsilon$  with  $\epsilon$  as a small number (e.g.,  $10^{-20}$ ).

Log transformation also ensures positive solution (Bethke, 2007; Hammond, 2003; Parkhurst and Appelo, 1999). It is widely used in geochemical codes for describing highly variable concentrations for primary species such as  $H^+$  or  $O_2$  that can vary over many orders of magnitude as pH or redox state changes without the need to use variable switching. Instead of solving Eq. (B3) for  $\mathbf{c}^{k+1}$  using Eqs. (B4,B5,B6), this method solves for  $(\ln \mathbf{c}^{k+1})$  (Hammond, 2003) with

$$\mathbf{J}_{\ln}(i,j) = \frac{\partial \mathbf{f}(i)}{\partial \ln(\mathbf{c}(j))} = \mathbf{c}(j) \frac{\partial \mathbf{f}(i)}{\partial \mathbf{c}(j)} = \mathbf{c}(j) \mathbf{J}(i,j), \quad (7)$$

190

$$\delta \ln \mathbf{c}^{k+1,p} = \mathbf{J}_{\ln}^{-1} \mathbf{f}(\mathbf{c}^{k+1,p}), \quad (8)$$

and

$$\mathbf{c}^{k+1,p+1} = \mathbf{c}^{k+1,p} \exp[-\delta \ln(\mathbf{c}^{k+1,p})]. \quad (9)$$

### 3 Tests, results, and discussions

195 The Newton-Raphson method and scaling, clipping, and log transformation are widely used and extensively tested for RTM, but not for LSM simulations. CLM describes biogeochemical dynamics within daily cycles for simulation durations of hundreds of years; the nitrogen concentration can be very low (mM to nM) while the carbon concentrations can be very high (e.g., thousands mol m<sup>-3</sup> carbon in organic layer); the concentrations and dynamics can vary dramatically in different locations around the globe. It is not surprising that the complex biogeochemical dynamics in a wide

range of temporal and spatial scales in CLM poses numerical challenges for the RTM methods. Our simulations reveal some numerical issues (numerical errors, divergence, and small time step sizes) that were not widely reported. We identify the issues from coupled simulations, and reproduce them in simple test problems. We examine remedies in the simple test problems, and test them in the coupled simulations. For convenience of presentation in this paper, we examine the reaction network and illustrate the numerical issues and remedies using simple test problems, and then test them in the coupled simulations.

For Test 1, we start with plant ammonium uptake to examine numerical solution for Monod function, and then add nitrification and denitrification incrementally to assess the implication of adding reactions. For Test 2, We check the implementation of mineralization and immobilization in the decomposition reactions. Thirdly, we compare the nitrogen demand distribution into ammonium and nitrate between CLM and PFLOTRAN. With coupled CLM-PFLOTRAN spinup simulations for arctic, temperate, and tropical sites, we assess the application of scaling, clipping and log transformation to achieve accurate, efficient, and robust simulations. Spreadsheet and PFLOTRAN input files are provided as supplemental information (SI).

Our implementation of CLM biogeochemistry introduces mainly two parameters: half saturation  $k_m$  and residual concentration. A wide range of  $k_m$  values were reported for ammonium, nitrate, and organic nitrogen for microbes and plants. The median, mean, and standard deviations range from 10~100, 50~500, and 10~200  $\mu\text{M}$ , respectively (Kuzyakov and Xu, 2013). Reported residual concentrations are limited and are considered to be zero (e.g., HØGh-Jensen et al., 1997), likely because of the detection limits of the analytical methods. The detection limits are usually at  $\mu\text{M}$  level, while up to nM level was reported (Nollet and De Gelder, 2013). In Ecosys, the  $k_m$  is 0.40 and 0.35  $\text{gN m}^{-3}$ , and the residual concentration is 0.0125 and 0.03  $\text{gN m}^{-3}$  (Grant, 2013) for ammonium and nitrate for microbes. We start with  $k_m = 10^{-6} \text{ M}$  or  $\text{mol m}^{-3}$ , and residual concentration  $10^{-15} \text{ M}$  or  $\text{mol m}^{-3}$  for plants and microbes. To further investigate the nonphysical solution negativity for the current study and for future application for other nutrients (e.g.,  $\text{H}_2$  and  $\text{O}_2$ ) where the concentrations can be much lower, we examine  $k_m$  from  $10^{-3}$  to  $10^{-9}$  in our test problems. The  $k_m$  is expected to be different for different plants, microbes, and for ammonium and nitrate. We do not differentiate them in this work as we focus on numerical issues.

### 230 3.1 Plant nitrogen uptake, nitrification, and denitrification

It was observed that plants can decrease nitrogen concentration to below detection limit in hours (Kamer et al., 2001). In CLM, the total plant nitrogen demand is calculated based on photosynthesized carbon allocated for new growth and the C:N stoichiometry for new growth allocation, and the plant nitrogen demand from the soil is equal to the total nitrogen demand minus retranslocated nitrogen stored in the plants (Oleson et al., 2013). The demand is provided as an input to PFLOTRAN. We use the Monod function to represent the limitation of nitrogen availability on uptake.

We examine the numerical solutions for the Monod equation. Incrementally, we add first order reactions (e.g., nitrification, denitrification, and plant nitrate uptake) to look into the numerical issues in increasingly complex reaction networks.

240 **3.1.1 Plant ammonium uptake (Test 1)**

We consider the plant ammonium uptake reaction (R13) with a rate  $R_a$

$$\frac{d[\text{NH}_4^+]}{dt} = -R_a \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + k_m} = -R_{at}. \quad (10)$$

Discretizing it in time using the backward Euler method for a time step size  $\Delta t$ , a solution is

$$[\text{NH}_4^+]^{k+1} = 0.5 \left[ [\text{NH}_4^+]^k - k_m - R_a \Delta t \pm \sqrt{([\text{NH}_4^+]^k - k_m - R_a \Delta t)^2 + 4k_m [\text{NH}_4^+]^k} \right]. \quad (11)$$

- 245 Ignoring the negative root,  $[\text{NH}_4^+]^{k+1} \geq 0$ . Adding a residual concentration by replacing  $[\text{NH}_4^+]$  with  $[\text{NH}_4^+] - [\text{NH}_4^+]_r$ ,  $[\text{NH}_4^+] \geq [\text{NH}_4^+]_r$ . Namely, the representation of plant ammonium uptake with the Monod function mathematically ensures  $[\text{NH}_4^+]^{k+1} \geq [\text{NH}_4^+]_r$ .

We use spreadsheet to examine the Newton-Raphson iteration process for solving Eq. (10) and the application of clipping, scaling, and log transformation (SI test1.xlsx). When an overshoot gets  
250 the concentration closer to the negative than the positive root (Eq. 11), the iterations converge to the nonphysical negative semi-analytical solution (sheet case3). This can be avoided by using clipping, scaling, or log transformation (sheet case4, case8, case9).

While clipping avoids convergence to the negative solution, a mass balance error is introduced as the ammonium consumption is clipped but the PlantA production is not in the clipping iteration  
255 (sheet case5). The convergence tolerances typically are not satisfied in the iteration, and subsequent iterations eliminate the error. This is different from (Tang and Riley, 2015) in that the explicit method does not have subsequent iterations to correct mass balance error. However, if a nonreactive species is added with a concentration of 1000 mol m<sup>-3</sup> (e.g., SOM4 in organic layer), the relative update rtol =  $\|\delta\mathbf{c}^{k+1,p}\|_2 / \|\mathbf{c}^{k+1,p}\|_2$  decreases to  $1.9 \times 10^{-9}$  in the iteration (sheet case5a). With STOL =  $10^{-8}$ ,  
260 the iteration would be deemed converged with the mass balance error. Satisfying the relative update tolerance criteria does not guarantee that the residual equations are satisfied (Lichtner et al., 2015). For this reason, we need to a tight STOL to avoid this false convergence so that additional iterations can be taken to resolve the mass balance error.

In contrast to clipping, scaling applies the same scaling factor to dampen both ammonium consumption and PlantA production following the stoichiometry of the reaction to maintain mass balance (sheet case6). However, if we add a production reaction that is independent of plant ammonium uptake, say nitrate deposition, then the nitrate increases due to deposition will be damped by the same scaling factor, introducing numerical error in the iteration (sheet case7). Like clipping, the error can be eliminated in the subsequent iterations, and a loose STOL may lead to false convergence.  
270

Small to zero concentration for ammonium and PlantA has no impact on the iterations for the clipping or scaling methods in this test. In contrast, a small initial PlantA concentration can cause

challenge for log transformation even though PlantA is only a product. When it is zero, the Jacobian matrix is singular because zero is multiplied to the column corresponding to PlantA (Eq. 7). An initial PlantA concentration of  $10^{-9}$  can result in overflow of the exponential function (sheet casea, as  
275 a 64-bit real number, which corresponds to double precision, is precise to 15 significant digits and has a range of  $e^{-709}$  to  $e^{709}$ , Lemmon and Schafer,2005). Clipping the update (say to be between -5 and 5) is needed to prevent numerical overflow or excessively large update. Like the cases with clipping without log transformation, mass balance error is introduced, and can be resolved in subsequent iterations (sheet caseb).

280 This simple test for the Monod function indicates that 1) Newton-Raphson iterations may converge to a negative concentration; 2) scaling, clipping, and log transformation can be used to avoid convergence to negative concentration; 3) small or zero concentration makes the Jacobian matrix stiff or singular when log transformation is used, and clipping is needed to guard against overflow of the exponential function; 4) mass balance error is introduced in the iterations when clipping is applied as  
285 it dampens only the consumption, but not the corresponding production; 5) independent reactions is numerically inhibited in the iterations when scaling is applied; 6) the errors due to clipping or scaling can be eliminated with subsequent iterations; and 7) loose update tolerance convergence criteria may cause false convergence.

### 3.1.2 Plant ammonium uptake and nitrification (Test 2)

290 Adding a nitrification reaction (R10) with a first-order rate, Eq. (10) becomes

$$\frac{d[\text{NH}_4^+]}{dt} = -R_a \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + k_m} - k_{nitr} [\text{NH}_4^+] = -R_{at} - R_{nitr}. \quad (12)$$

A semi-analytical solution similar to Eq. (11) can be derived. With  $J_{at} = dR_{at}/d[\text{NH}_4^+] = R_a k_m ([\text{NH}_4^+] + k_m)^{-2}$ , and  $J_{nitr} = dR_{nitr}/d[\text{NH}_4^+] = k_{nitr}$ , the matrix equation Eq. (B5), becomes

$$\begin{bmatrix} 1/\Delta t + J_{at} + J_{nitr} & 0 & 0 \\ -J_{at} & 1/\Delta t & 0 \\ -J_{nitr} & 0 & 1/\Delta t \end{bmatrix} \begin{pmatrix} \delta[\text{NH}_4^+]^{k+1,1} \\ \delta[\text{PlantA}]^{k+1,1} \\ \delta[\text{NO}_3^-]^{k+1,1} \end{pmatrix} = \begin{pmatrix} R_{at} + R_{nitr} \\ -R_{at} \\ -R_{nitr} \end{pmatrix}, \quad (13)$$

295 for the first iteration. As  $R_{at} + R_{nitr} \geq 0$ , the ammonium update is positive even when ammonium concentration is not very low. The off-diagonal terms for PlantA and nitrate in the Jacobian matrix bring the positive ammonium update into the updates for PlantA and nitrate even though there is no reaction that consumes them. Specifically,

$$\frac{\delta[\text{PlantA}]^{k+1,1}}{\Delta t} = -\frac{\frac{1}{\Delta t} + J_{nitr}}{\frac{1}{\Delta t} + J_{at} + J_{nitr}} R_{at} + \frac{J_{at}}{\frac{1}{\Delta t} + J_{at} + J_{nitr}} R_{nitr}, \quad (14)$$

300

$$\frac{\delta[\text{NO}_3^-]^{k+1,1}}{\Delta t} = \frac{J_{nitr}}{\frac{1}{\Delta t} + J_{at} + J_{nitr}} R_{at} - \frac{\frac{1}{\Delta t} + J_{at}}{\frac{1}{\Delta t} + J_{at} + J_{nitr}} R_{nitr}. \quad (15)$$

Depending on the rates ( $R_{at}$ ,  $R_{nitr}$ ), derivatives ( $J_{at}$ ,  $J_{nitr}$ ), and time step size  $\Delta t$ , the update can be positive for PlantA and nitrate, producing a zero order "numerical consumption" for PlantA or nitrate, in which the limitation of PlantA or nitrate availability is not explicitly represented. This  
305 has important implications for the scaling method.

The scaling factor ( $\lambda$ ) is not only a function of the update, but also of the concentration (Eq. 6). If a positive update is produced for a zero concentration, the scaling factor is zero, decreasing the scaled update to zero. The iteration converges without any change to the concentrations, numerically stop all of the reactions in the time step unless STOL is negative. We add the denitrification reaction with  
310  $R_{nitr} = 10^{-6} \text{ s}^{-1}$  to SI test1.xlsx case6 to create SI test2.xlsx to demonstrate that a small enough initial concentration relative to the positive update may numerically inhibit all of the reactions as well. An update of  $6.6 \times 10^{-6} \text{ M}$  is produced for nitrate (sheet scale1). When the initial nitrate concentration  $[\text{NO}_3^-]_0$  is not too small, say  $10^{-6} \text{ M}$ , the solution converges to the semi-analytical solution in six iterations. With decreasing  $[\text{NO}_3^-]_0$  to  $10^{-9} \text{ M}$ , the relative update stol is  $9.2 \times$   
315  $10^{-10}$ . If  $\text{STOL} = 10^{-9}$ , the solution is deemed converged as Eq. (B9) is met, but not to the semi-analytical solution. The ammonium uptake and nitrification reactions are numerically "inhibited" because the small scaling factor and a high concentration of a nonreactive species decreases the update to below STOL to reach false convergence. If we tighten STOL to  $10^{-30}$ , the iterations continues, with decreasing nitrate concentration,  $\lambda$ , and stol by two orders of magnitude (1- $\alpha$  as  
320 default  $\alpha = 0.99$ ) in each iteration, until stol reaches  $10^{-30}$  (sheet scale2). Unless the STOL is sufficient small, or MAXIT is small (Appendix B), false convergence will occur before the time stepping routine continues with time step cut for the scaling method. The impact of "numerical consumption" on clipping and log transformation is much less dramatic than the scaling method as the latter applies the same scaling factor to the whole update vector following stoichiometric  
325 relationships of the reactions to maintain mass balance, and the limiting concentration decreases by  $(1 - \alpha)$  times in each iteration, with the possibility of resulting in less than STOL relative update in MAXIT iterations.

In summary, this test problem demonstrates that 1) positive update can be produced even for products during Newton-Raphson iteration; 2) when a positive update is produced for a very low  
330 concentration, a very small scaling factor may numerically inhibits all of the reactions even with very tight STOL.

### 3.1.3 Plant uptake, nitrification, and denitrification (Test 3)

The matrix and update equations with added plant nitrate uptake and denitrification are available in Appendix C. In addition to nitrate and PlantA, PlantN and the denitrification product nitrogen  
335 gas may have positive updates. In addition to the off-diagonal terms due to the derivative of plant uptake with respect to ammonium concentration, the derivative of plant uptake with respect to nitrate concentration is added in the Jacobian matrix for PlantN (Eq. C1). As a result, positive update

for both ammonium and nitrate will contribute to positive PlantN update through the two nonzero off-diagonal terms. Therefore, the likelihood for a positive update to PlantN is greater than PlantA  
340 as the former are influenced by more rates and derivatives. We add plant nitrate uptake, and denitrification into SI test2.xlsx and assess the implications of increased reactions and complexity in SI test3.xlsx. In addition to nitrate, this introduces a positive update for nitrogen gas in the first iteration (sheet scale1). As the iterations resolve the balance between nitrite production from nitrification, and consumption due to plant uptake and denitrification, update to PlantN becomes positive, and  
345 eventually leads to false convergence. The time step size needs to be decreased from 1800 to 15 s to resolve the false convergence (sheet scale2). In contrast, the added reactions have less impact on clipping and log transformation.

### **3.2 Nitrogen immobilization and mineralization during decomposition (Test 4)**

We examine another part of the reaction network: decomposition, nitrogen immobilization, and mineralization (Fig. 1). We consider a case of decomposing 0.2 M Lit1C + 0.005 M Lit1N to produce SOM1 with initial 4  $\mu$  M ammonium using the reactions (R2 and R7) in the CLM-CN reaction network (Fig. 1). We use PFLOTRAN with a saturated grid cell with porosity of 0.25. At the beginning, Lit1 decreases and SOM1 increases sharply because the rate coefficient for Lit1 is 16 times that for SOM1 ((Figs. 3a,b)). As ammonium concentration decreases by orders of magnitude because of  
350 the faster immobilization than mineralization rate (Fig. 3c,d), Lit1 decomposition rate slows down to the level such that the immobilization rate is less than the mineralization rate. Namely, SOM1 decomposition controls Lit1 decomposition through limitation of mineralization on immobilization.  
355 As the immobilization rate decreases with decreasing Lit1, ammonium concentration rebounds after Lit1 is depleted. For  $k_m$  of  $10^{-6}$ ,  $10^{-9}$ , and  $10^{-12}$  M, Lit1 and SOM1 dynamics are similar except slight difference in the early transit periods, but the ammonium values are decreased to  $\sim 10^{-8}$ ,  
360  $10^{-11}$ , and  $10^{-14}$  M, respectively. Smaller  $k_m$  results in lower ammonium concentration, which has implications for the clipping, scaling and log transformation methods.

### **3.3 Nitrogen demand distribution between ammonium and nitrate**

For comparison with CLM, we examine the uptake rate as a function of demands and available concentrations  $f_{pi} = (R_a + R_n)/R_p$  as implemented in Eqs. (3,4). As an example, we consider uptake  
365  $R_p = 10^{-9}$  M s<sup>-1</sup> from a solution with various  $[NH_4^+]$  and  $[NO_3^-]$  for a 0.5 h time step. With CLM,  $f_{pi} = 1$  when  $[NH_4^+] + [NO_3^-] \geq R_p\Delta t$ ; otherwise, it decreases with decreasing  $[NH_4^+] + [NO_3^-]$  (Fig. 2). The new representation (Eqs. 3, 4) is generally similar, with  $f_{pi} = 1$  or 0 when  $[NH_4^+]$  or  $[NO_3^-]$   $\gg$  or  $\ll k_m$ . For the intermediate concentrations,  $f_{pi}$  in the new scheme is less than or equal to  
370 that in CLM because  $NH_4^+$  “inhibits”  $NO_3^-$  uptake. The difference decreases with decreasing  $k_m$ , apparently disappearing at  $k_m = 10^{-10}$ . Various level of preferences of ammonium over nitrate uptake were observed for plants (Pfautsch et al., 2009; Warren and Adams, 2007; Nordin et al., 2001;

Falkengren-Grerup, 1995; Gherardi et al., 2013). The microbial uptake of inorganic and organic nitrogen species is similar (Fouilland et al., 2007; Kirchman, 1994; Kirchman and Wheeler, 1998; 375 Middelburg and Nieuwenhuize, 2000; Veuger et al., 2004). CLM implies a strong preference for ammonium over nitrate. For example, if ammonium is abundantly sufficient, nitrate will not be taken. The new scheme allows the level of preference to be adjusted by varying  $k_m$ .

### 3.4 CLM-PFLOTRAN simulations

We test the implementation by running CLM-PFLOTRAN simulations for arctic (US-Brw), temperate (US-WBW), and tropical (BR-Cax) AmeriFlux sites. The CLM-PFLOTRAN simulations are run in the mode that PFLOTRAN only handles subsurface chemistry (decomposition, nitrification, denitrification, plant nitrogen uptake). For comparison with CLM, 1) depth and O<sub>2</sub> availability impact on decomposition, 2) cryoturbation, 3) SOM transport, and 4) nitrogen leaching are ignored by setting 1) decomp\_depth\_efolding to 10<sup>6</sup> m, o\_scalar to 1, 2) cryoturb\_diffusion, 3) som\_diffusion, 385 and 4) sf\_no3 and sf\_sminn to 0 (Oleson et al., 2013). Spin-up simulations are used because they are numerically more challenging as the simulations start far away from equilibrium. In these site simulations, PFLOTRAN uses the same 10 layer grid for the 3.8 m one-dimensional column as CLM. The simulation duration is 1000, 600, and 600 year for the arctic, temperate, and tropical site, respectively. In the base case,  $k_m = 10^{-6}$  mol m<sup>-3</sup> and residual concentration 10<sup>-15</sup> mol m<sup>-3</sup>. To 390 assess the sensitivity of various preference levels for ammonium and nitrate uptake, and downregulation levels, we examine  $k_m = 10^{-3}$  to 10<sup>-9</sup> mol m<sup>-3</sup>. We evaluate how scaling, clipping, and log transformation for avoiding negative concentrations influence accuracy and efficiency.

#### 3.4.1 Site descriptions

The US-Brw site (71.35N,156.62W) is located near Barrow, Alaska. The mean annual temperature, 395 precipitation, and snowfall are -12 °C, 11 cm, and 69 cm, respectively (1971~2000) (Lara et al., 2012). The landscape is poorly drained polygonized tundra. The maximum thaw depth ranges from 30 to 40 cm, and the snow free-period is variable in length but generally begins in early June and lasts until early September (Hinkel and Nelson, 2003). The area is composed of several different representative wet-moist coastal sedge tundra types, including wet sedges, grasses, moss, and assorted 400 lichens. The leaf area index (LAI) is ~1.1 (AmeriFlux data).

The US-WBW site (35.96N, 84.29W) is located in the Walker Branch Watershed in Oak Ridge, Tennessee (Hanson and Wullschleger, 2003). The climate is typical of the humid southern Appalachian region. The mean annual precipitation is ~139 cm, and the mean median temperature is 14.5 °C. The soil is primarily Ultisols that developed in humid climates in the temperate zone 405 on old or highly weathered material under forest. The temperate deciduous broadleaf forest was regenerated from agriculture land 50 years ago. LAI is ~ 6.2(Hanson et al., 2004).

The BR-Cax site (-1.72N, -51.46W) is located in the eastern Amazon tropical rainforest. The mean annual rainfall is between 2000 and 2500 mm, with a pronounced dry season between June and November. The soil is a yellow oxisol (Brazilian classification latossolo amarelo) with a thick stony laterite layer at 3~4 m depth (da Costa et al., 2010). The vegetation is evergreen broadleaf forest. The LAI is 4~6 (Powell et al., 2013).

### 3.4.2 CLM-PFLOTRAN site simulation results

The site climate data from 1998 to 2006, 2002 to 2010, and 2001 to 2006 are used to drive the spin-up simulation for the arctic (US-Brw), temperate (US-WBW), and tropical (BR-Cax) sites, respectively. This introduces a multi-year cycle in addition to the annual cycle (Figs. 4, 5, 6). Overall, CLM-PFLOTRAN is close to CLM4.5 in predicting LAI and nitrogen distribution among vegetation, litter, SOM, ammonium and nitrate pools for the arctic (Fig. 4), temperate (Fig. 5), and tropical (Fig. 6) sites . CLM4.5 does reach equilibrium earlier than CLM-PFLOTRAN. The maximum differences occur during the transient (200-400 year for the arctic, and 50-70 year for the temperate and tropical sites) for SOMN, ammonium, and nitrate. This is expected as the nitrogen demand competition scheme implemented in CLM-PFLOTRAN is different from that in CLM4.5 (Fig. 2), the former solves the reaction network simultaneously while latter sequentially (resolve the plant uptake and decomposition at first, and then nitrification, and denitrification) , and the carbon nitrogen cycle is very sensitive to the nitrogen competition representation.

The arctic site shows a distinct summer growing season (Fig. 4): LAI and VEGN jump up at the beginning, then level off, and drop down at the end of the growing season when LITN jumps up due to litter fall. Ammonium and nitrate concentration drop to very low level at the beginning of growing season and accumulate at the other times. In addition to a longer growing season than the arctic site, the temperate site shows more litter fall by the end of the growing season as it is a temperate deciduous forest, which introduces immobilization demand that further lowers ammonium and nitrate concentrations (Fig. 5e inset). The seasonality is much less apparent in the tropical site than in the arctic and temperate sites. LAI, VEGN, LITN, and SOMN accumulate with less seasonal variations to reach equilibrium.

Except for the tropical site where the higher  $k_m$  of  $10^{-3}$  mol m $^{-3}$  results in lower immobilization, higher accumulation of LITN, and higher ammonium and nitrate concentrations during the spinup (Fig. 6), the range of  $k_m$  values ( $10^{-3}$ ,  $10^{-6}$ , and  $10^{-9}$  mol m $^{-3}$ ) generally has limited impact on the overall calculations except that the nitrogen concentrations drop lower with lower  $k_m$  values (e.g., inset in Figs. 4e,f, 5e). The lack of sensitivity is because these very low concentrations do not make up a mass of nitrogen that is significant enough to influence the carbon and nitrogen cycle. However, as a small  $k_m$  means weak downregulation and steep transition between zero order and first order, it has implications on accuracy, and efficiency of the numerical solutions.

### 3.4.3 Accuracy and efficiency

Numerical errors introducing in clipping, scaling or log transformation are captured in CLM when it checks carbon and nitrogen mass balance for every time step for each column, and report  $\geq 10^{-8}$  g m<sup>-2</sup> errors. When log transformation is used, mass balance errors are not recorded for the arctic, temperate, and tropical sites with  $k_m$  values  $10^{-3}$ ,  $10^{-6}$ , and  $10^{-9}$  mol m<sup>-3</sup>. The computing time for CLM-PFLOTRAN is about 60% to 100% more than that of CLM (Table 1). This is not unreasonably high as the implicit method involves matrix inversion, and log transformation converts the linear problem into nonlinear problem. The computational cost increases substantially with decreasing half saturation, which is expected as a smaller half saturation requires smaller time step sizes to march through steeper transition between the zero and first order rate in Monod function. Overall, log transformation is accurate, robust, and reasonably efficient.

Mass balance errors are reported for  $k_m$  values of  $10^{-6}$ , and  $10^{-9}$  but not for  $10^{-3}$  mol m<sup>-3</sup> when clipping is applied. With  $k_m = 10^{-3}$  mol m<sup>-3</sup>, the plant uptake and immobilization are inhibited at relatively high concentration so that nitrogen concentrations are high. With decreasing from  $k_m = 10^{-6}$  to  $10^{-9}$  mol m<sup>-3</sup>, nitrogen concentrations are lowered to much lower level (Figs. 4, 5, 6, similar to Fig. 3c), increasing the likelihood of overshoot. Mass balance errors are recorded when the relative update is below STOL to preventing further iterations to resolve the mass balance errors introduced by clipping. The frequency of mass balance errors decreases with increasing  $k_m$ , and decreasing STOL. Tightening STOL from  $10^{-8}$  to  $10^{-12}$ , the reported greater than  $10^{-8}$  g m<sup>-3</sup> mass balance errors are eliminated. The computing time is about 50% more than CLM, which is more efficient than log transformation (Table 1), particularly for  $k_m = 10^{-9}$  mol m<sup>-3</sup>. Tightening STOL only slightly increases the computing time. Because clipping often occurs at very low concentrations, the reported mass balance errors are usually small (mostly  $\sim 10^{-8}$  gN m<sup>-3</sup> and some  $\sim 10^{-7}$  gN m<sup>-3</sup> ), and do not have substantial impact on the final simulation results.

The results for scaling is similar to clipping: mass balance errors are recorded for  $k_m$  values of  $10^{-6}$  and  $10^{-9}$  but not for  $10^{-3}$  mol m<sup>-3</sup>; tightening STOL to  $10^{-12}$  resolves the error; it takes about 50% more computing time than CLM. To examine the influence of low concentrations on the accuracy and efficiency of the scaling method, we conduct numerical experiments in which we reset the nitrous oxide concentration produced from decomposition (reaction R11, rate Eq. A3) to  $10^{-12}$ ,  $10^{-10}$ , or  $10^{-8}$  mol m<sup>-3</sup> in each CLM half hour time step for the tropical site for the first year. This can be used to calculate the nitrous oxide production rate from decomposition and feed back to CLM without saving the concentration for the previous time step. Overall, nitrogen is abundant in the first half year, and then becomes limiting in the last five months (Fig. 6e,f, inset). We look into the daily ammonium cycles as an example during the nitrogen limiting period (day 250 to 260, Fig. 7a). Every day the ammonium concentration increases with time due to deposition, but drops when the plant nitrogen demand shots up. With reset concentration of  $10^{-8}$  mol m<sup>-3</sup>, the minimum nitrous oxide concentration for the ten layers is  $10^{-8}$  mol m<sup>-3</sup>, and ammonium concentrations show

two peaks followed by two drops due to the two plant uptake peaks every day. Decreasing the reset  
480 concentration to  $10^{-10}$  mol m $^{-3}$ , the minimum concentration drops to  $10^{-12}$ ,  $10^{-14}$ , and  $10^{-16}$   
mol m $^{-3}$ , corresponding to 1, 2, and 3 iterations with overshoot for nitrous oxide. These result  
in numerical "inhibition" of ammonium rebound everyday. It worsens with further decreasing the  
reset concentration to  $10^{-12}$  mol m $^{-3}$ . This introduces mass balance errors as reported in CLM  
because the false convergence numerically inhibits all of the reactions including nitrogen deposition,  
485 litter input from CLM to PFLOTRAN. Unlike clipping, these false convergences introduce excessive  
numerical errors.

The frequent positive update to nitrous oxide is produced because the rate for the nitrification  
reaction (R11) is parameterized as a fraction of net mineralization rate to reflect the relationship  
between labile carbon content and nitrous oxides production (Parton et al., 1996). A Monod func-  
490 tion is added to describe the limitation of ammonium concentration on nitrification. Calculation of  
the net mineralization rate involves all of the decomposition reactions, and the litter decomposition  
reactions bring in ammonium and nitrate limitation, and ammonium inhibition on nitrate immobi-  
lization. As a result, the off-diagonal terms for nitrous oxide in the Jacobian matrix corresponding  
to Lit1C, Lit1N, Lit2C, Lit2N, Lit3C, Lit3N, SOM1, SOM2, SOM3, SOM4, ammonium, and  
495 nitrate are nonzero. Positive updates to all of these species are expected to contribute to positive  
update to nitrous oxide. While the empirical parameterization of nitrification rate as a function of net  
mineralization rate is conceptually convenient, it increases the complexity of the reaction network  
and numerical challenges due to the less sparse Jacobian matrix. While we use nitrous oxide as an  
example here, similar results can be obtained for PlantN, PlantA, and nitrogen gas produced from  
500 denitrification, etc. Theoretically, the numerical "inhibition" of all reaction can be caused by positive  
update to very low concentrations for any species.

The numerical errors can be decreased and eliminated by decreasing STOL. Similar to the Test 2  
(SI test2.xlsx sheet scale2), a small STOL can result in small stol, then a very small STOL is needed.  
For the case of reset concentration  $10^{-10}$  for the one year tropical site simulation, the numerical  
505 "inhibition" decreases with decreasing STOL and vanishes for the observed time window when  
STOL =  $10^{-50}$  (Fig. 8), indicating the need for very small, zero or even negative STOL to avoid  
false convergence. We test STOL =  $10^{-200}$  and find that the temperate site simulations involve  
extensive time step cutting with default maximum number of iterations of 16 (MAXIT, Appendix  
B). The impact of resetting nitrous oxide concentration on clipping and log transformation is less  
510 dramatic. Nevertheless, the computing time increases about 10% for clipping, and double for the log  
transformation.

## 4 Summary and Conclusions

Global land surface models have traditionally represented subsurface biogeochemical processes using preconfigured reaction networks. This hardcoded approach makes it necessary to revise source code to test alternative models or to incorporate improved process understanding. We couple PFLO-TRAN with CLM to facilitate testing of alternative models and incorporation of new understanding. We implement CLM-CN decomposition cascade, nitrification, denitrification, and plant nitrogen uptake reactions in CLM-PFLOTTRAN. We illustrate that the concentration can become negative even for species that has no consumption with implicit time stepping and Newton-Raphson method, which is not physical, and may introduce numerical error.

Clipping, scaling and log transformation can all prevent negative concentration. However, our results reveal implications when the relative update tolerance is used as one of the convergence criteria (STOL). While use of STOL improves efficiency, satisfying STOL does not guarantee satisfying the residual equation, therefore, may introduce false convergence. Clipping reduces the consumption but not the production in some reactions, introducing mass balance errors. A tight STOL is needed to avoid false convergence and prevent mass balance errors. While the scaling method dampens the whole update vector following the stoichiometry of the reactions to keep mass balance, a small scaling factor caused by a positive update to a small concentration may diminish the update and result in false convergence, numerically inhibiting all reactions. For accuracy and efficiency, a very tight STOL is needed when the concentration can be very low. Log transformation is accurate and robust, but requires more computing time. The computational cost increases with decreasing concentrations, most substantially for log transformation.

Our CLM-PFLOTTRAN spin-up simulation at an arctic, temperate, and tropical site indicates that accurate and robust solution can be achieved with clipping, scaling or log transformation with 50% to 100% more computing time than CLM4.5 for a range of half saturation values from  $10^{-3}$  to  $10^{-9}$  and a residual concentration of  $10^{-15}$  for nitrogen. As physical half saturation ranges from  $10^{-5}$  to  $10^{-6}$  M for nitrogen, and the detection limits are often above  $10^{-9}$  M, these methods are expected to provide an accurate, efficient, and robust solution for CLM-PFLOTTRAN implementation for current CLM biogeochemistry. As more substrate limiting processes, such as labile C, P, O<sub>2</sub>, and H<sub>2</sub>, are implemented with lower half saturation and residual concentration, and more complicated rate relationship, the maximum allowable time step cut may need to be increased, and the computing time is expected to increase.

## 5 Code availability

PFLOTTRAN is an open-source software. It is distributed under the terms of the GNU Lesser General Public License as published by the Free Software Foundation either version 2.1 of the License, or any

later version. It is available at <https://bitbucket.org/pfotran>. CLM-PFOTRAN is under development and will be available subject to guidelines of NGEE-Arctic and ACME projects.

## 6 Author contribution

G. B., B. A., R. M., J. K., and F. H. developed the CLM-PFOTRAN framework that this work  
550 built upon. F.Y., G.T., G. B., and X.X. added biogeochemistry to the CLM-PFOTRAN interface. F. Y. proposed the nitrification and denitrification reactions and rate formulae. G. T., F. Y., and X. X. implemented the CLM biogeochemistry in PFOTRAN under guidance of G. H., P. L., S. P., and P.T. G.T. prepared the manuscript with contributions from all co-authors. G. T., F. Y., G. B., and G.H. contributed equally to the work.

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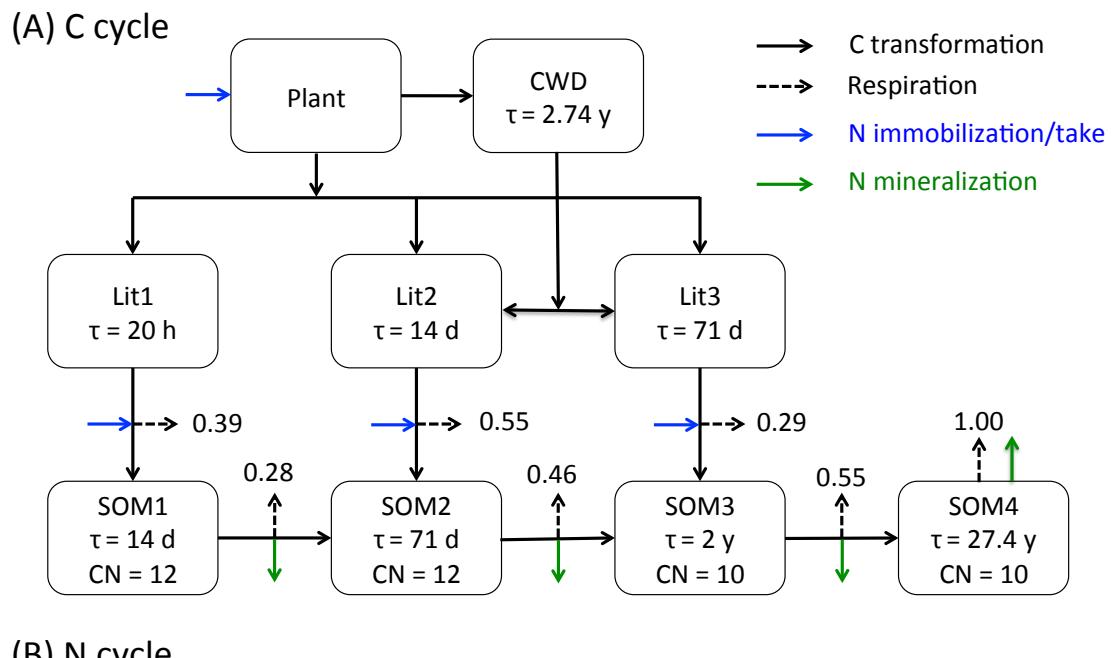
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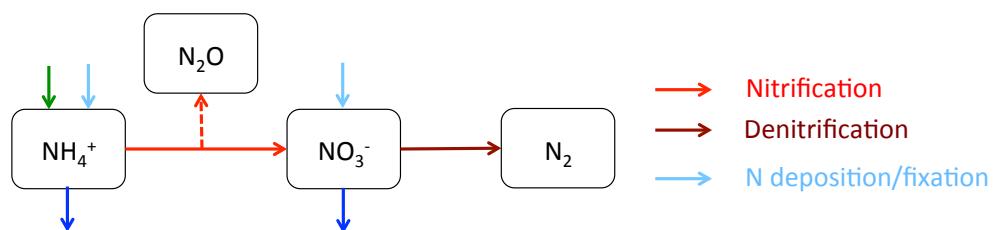
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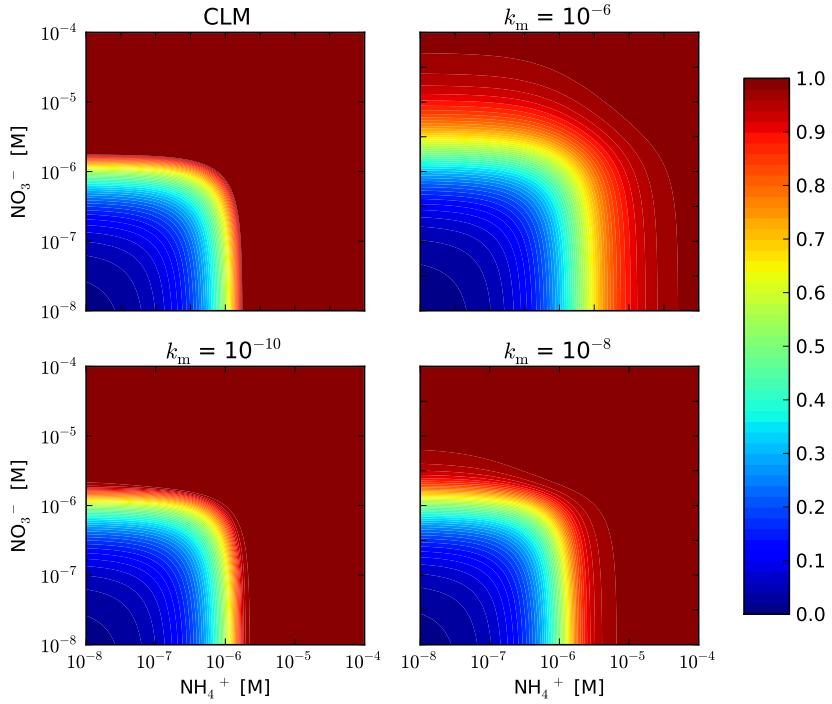
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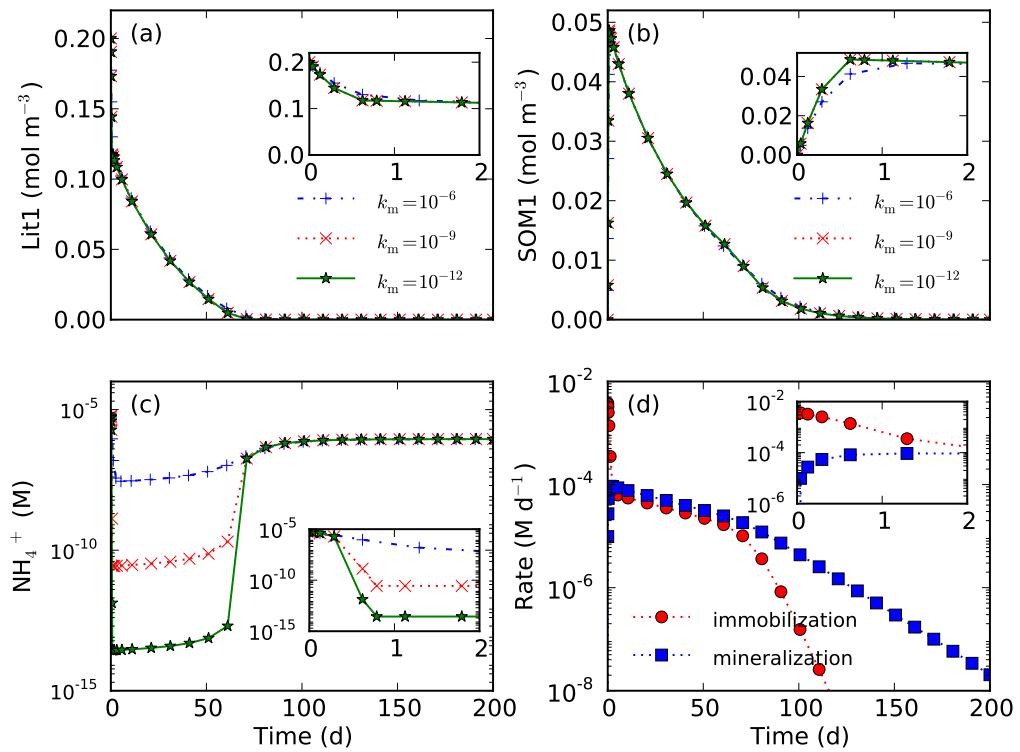
(B) N cycle



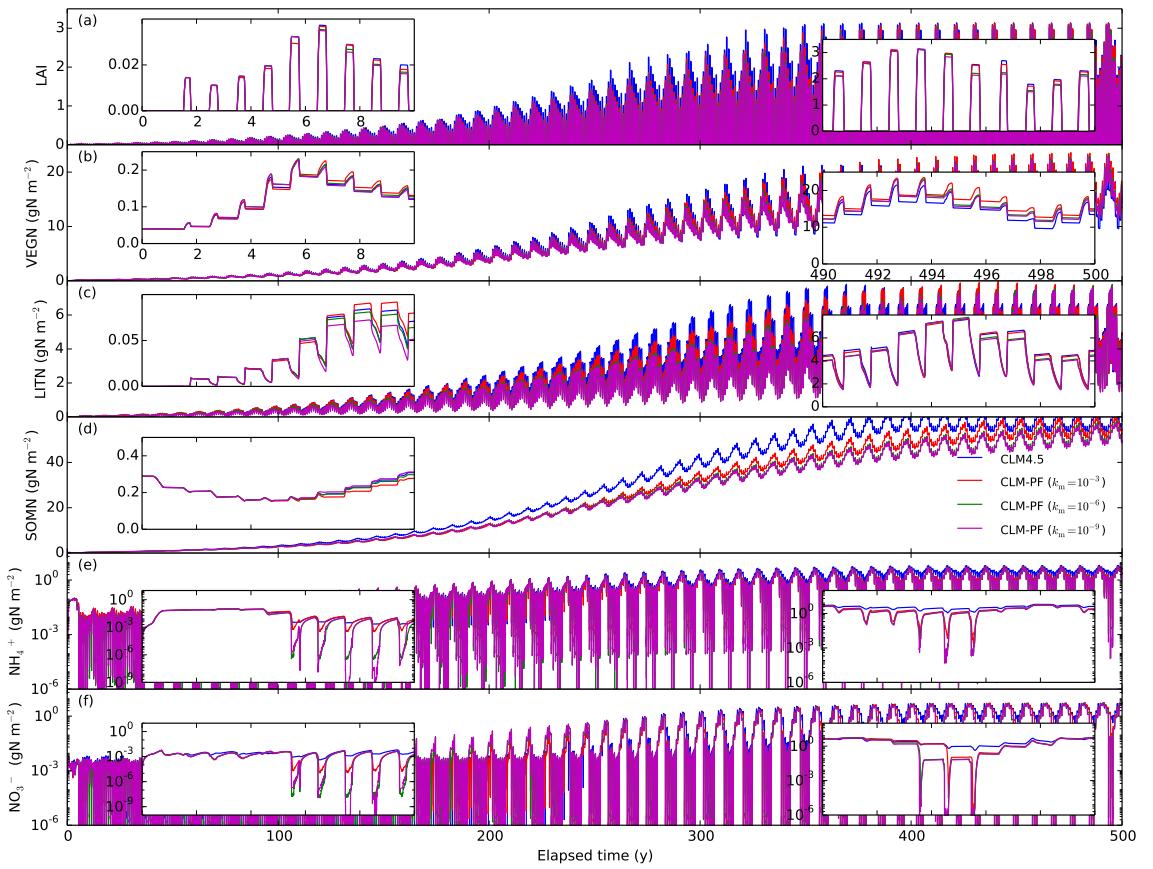
**Figure 1.** The reaction network for the carbon (A) and nitrogen (B) cycles implemented in this work. The carbon cycle is modified from Thornton and Rosenbloom (2005) and Bonan et al. (2012).  $\tau$  is the turnover time, and CN is the CN ratio in gC over gN.



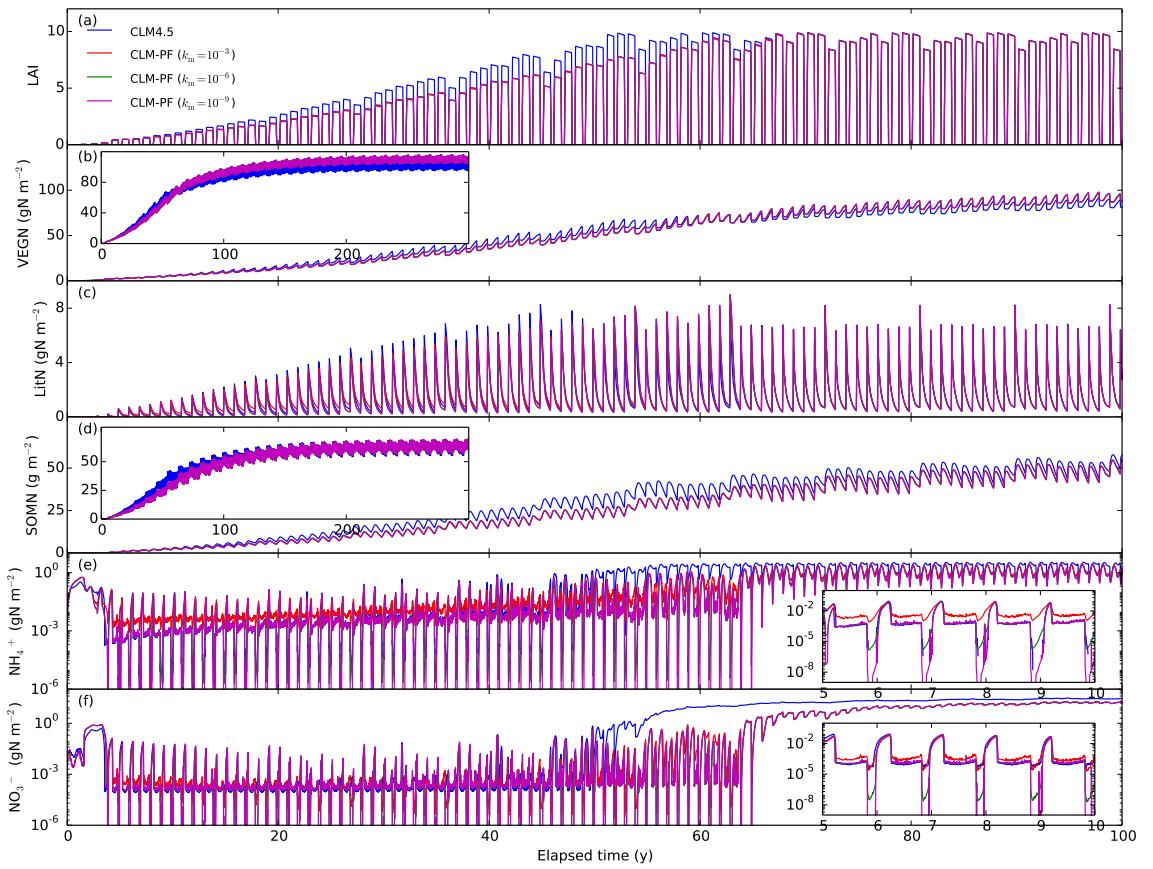
**Figure 2.** The ratio of uptake and demand ( $f_{pi}$ ) as a function of concentrations with CLM and representation by Eqs. (3) and (4) in a 0.5 h time step with an uptake rate of  $10^{-9} \text{ M s}^{-1}$ .  $f_{pi}$  for the new representation is less than or equal to that for CLM. The difference decreases with decreasing half saturation  $k_m$ .



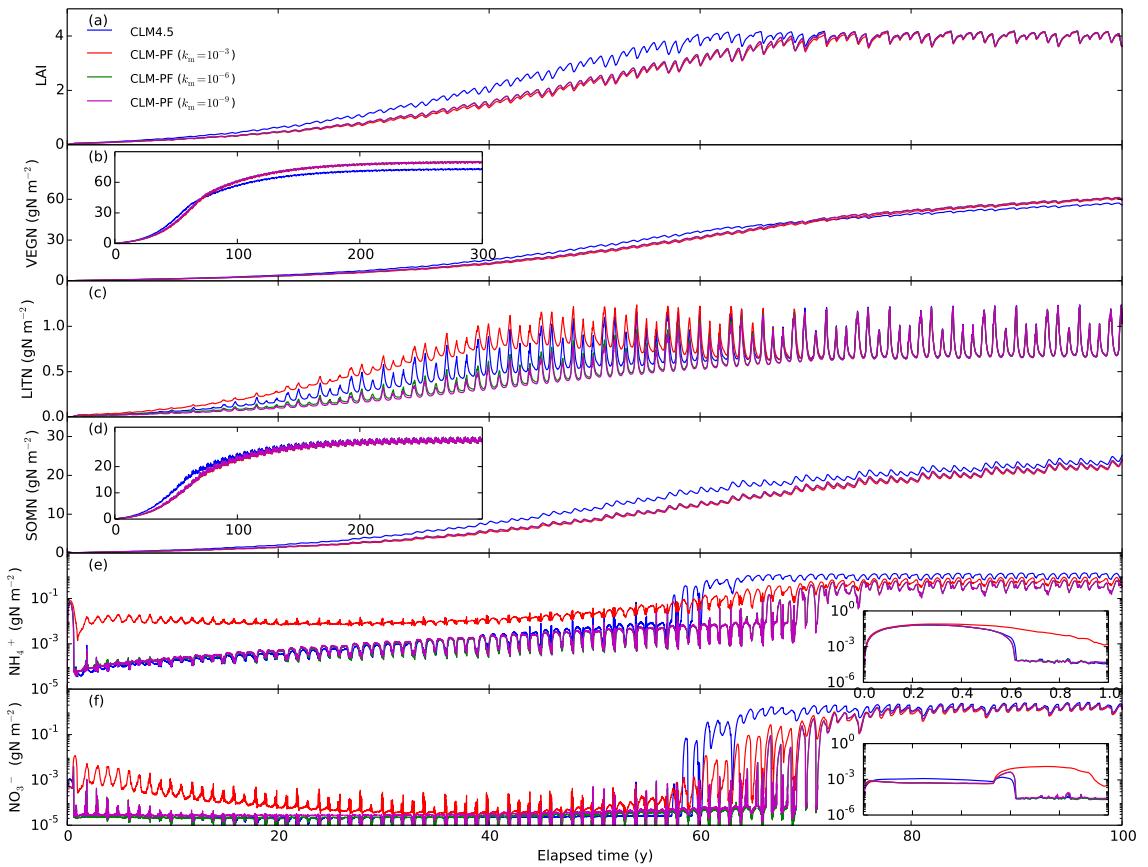
**Figure 3.** Influence of half saturation  $k_m$  on decomposition that involves both nitrogen immobilization and mineralization. Smaller half saturation can result in lower nitrogen concentration (c) but does not substantially impact the calculated concentrations other than ammonium (a,b).



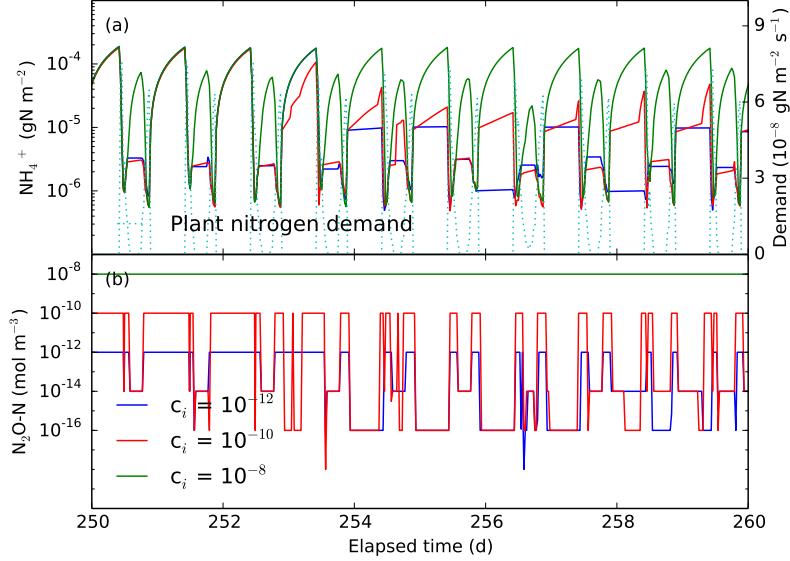
**Figure 4.** Calculated LAI and nitrogen distribution among vegetation, litter, SOM,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  pools in spin-up simulations for the US-Brw site.



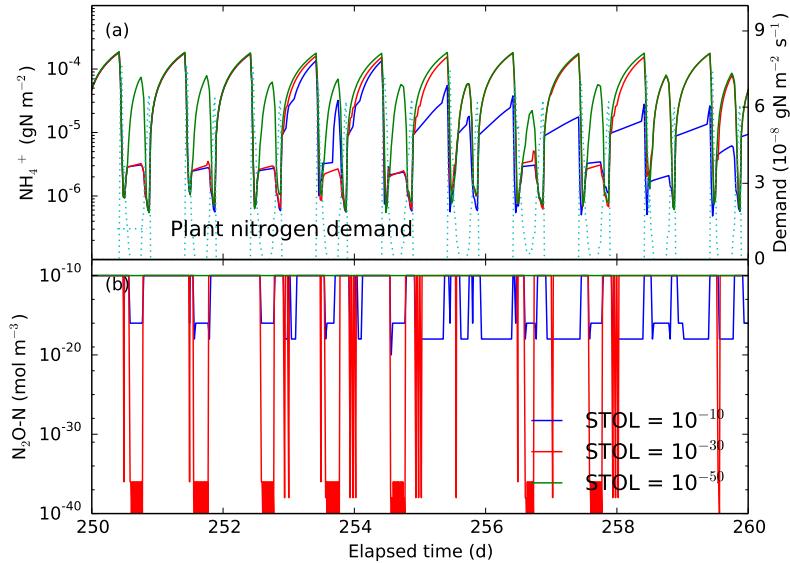
**Figure 5.** Calculated LAI and nitrogen distribution among vegetation, litter, SOM,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  pools in spin-up simulations for US-WBW site.



**Figure 6.** Calculated LAI and nitrogen distribution among vegetation, litter, SOM,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  pools in spin-up simulations for BR-Cax site.



**Figure 7.** Resetting nitrous oxide concentration to  $10^{-8}$ ,  $10^{-10}$ , and  $12^{-10}$   $\text{mol m}^{-3}$  in every CLM 0.5 h time step results in no inhibition to increasing inhibition of reactions when the scaling method is used with  $\text{STOL} = 10^{-8}$ . Numerical experiments are conducted for the tropical site for the first year with  $k_m = 10^{-6} \text{ mol m}^{-3}$ . See inset in Fig. (6e) for ammonium concentration in the first year with daily data points.



**Figure 8.** Decreasing STOL can decrease and eliminate the numerical inhibition in the case of  $10^{-10} \text{ mol m}^{-3}$  in Fig. (7).  $\text{N}_2\text{O}-\text{N}$  concentration in taxis in (b) is the minimum of the 10 soil layers.

**Table 1.** Wall time for CLM-PFLOTRAN relative to CLM for spinup simulation on OIC (ORNL Institutional Cluster Phase5)

Site	Clipping			Scaling			Log transformation			
	$k_m$	$10^{-3}$	$10^{-6}$	$10^{-9}$	$10^{-3}$	$10^{-6}$	$10^{-9}$	$10^{-3}$	$10^{-6}$	$10^{-9}$
US-Brw		1.28	1.30	1.30	1.29	1.29	1.32	1.45	1.49	1.72
US-Pit		1.45	1.47	1.47	1.45	1.45	1.47	1.64	1.68	1.89
BR-Cax		1.43	1.49	1.55	1.44	1.48	1.52	1.62	1.66	1.99

CLM wall time is 29.3, 17.7, and 17.1 hour for the arctic, temperate, and tropical sites for a simulation duration of 1000, 600, and 600 year.

## Appendix A: CLM biogeochemical reactions and rates

### A1 CLM-CN decomposition

The CLM-CN decomposition cascade consists of three litter pools with variable CN ratios, four soil  
745 organic matter (SOM) pools with constant CN ratios, and seven reactions (Bonan et al., 2012; Oleson  
et al., 2013; Thornton and Rosenbloom, 2005). The reaction can be described by



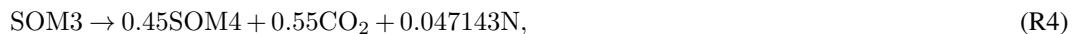
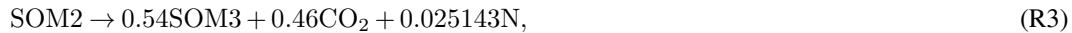
with  $\text{CN}_u$  and  $\text{CN}_d$  as the upstream and downstream pool (molecular formula, for 1 mol upstream  
and downstream pool, there is  $u$  and  $d$  mol N), N as either  $\text{NH}_4^+$  or  $\text{NO}_3^-$ ,  $f$  as the respiration fraction,  
750 and  $n = u - (1 - f)d$ . The rate is

$$\frac{d[\text{CN}_u]}{dt} = -k_d f_T f_w [\text{CN}_u], \quad (\text{A1})$$

with  $k_d$  as the rate coefficient and  $f_T$  and  $f_w$  as the temperature and moisture response functions. With  
a constant CN ratio, the decomposition reactions for the four SOM pools are



755



and



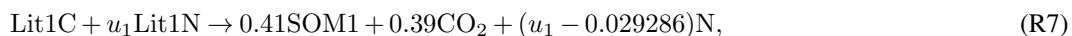
The exact stoichiometric coefficients are calculated in the code using values for respiration factor,  
CN ratio, and molecular weight specified in the input file.

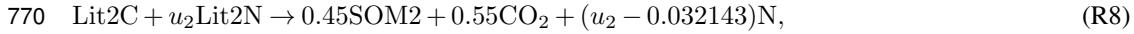
CLM4.5 has an option to separate N into  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . The N mineralization product is  $\text{NH}_4^+$ .

As the CN ratio is variable for the three litter pools, litter N pools need to be tracked such that  
765 reaction (R1) becomes

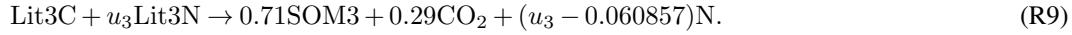


with  $u = [\text{LitN}]/[\text{LitC}]$ . The three litter decomposition reactions are





and



As the CN ratio of the litter pools is generally high,  $u_1$ ,  $u_2$ , and  $u_3$  are usually small, and  $n$  in these reactions (e.g.,  $n_1 = u_1 - 0.029286$  for Lit1) is normally negative. Namely, these reactions consume  
775 (immobilize) N, which can be  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , or both.

## A2 Nitrification

The nitrification reaction to produce  $\text{NO}_3^-$  is



with  $\dots$  for additional reactants and products to balance the reaction. The rate is (Dickinson et al.,  
780 2002)

$$\frac{d[\text{NH}_4^+]}{dt} = -\frac{d[\text{NO}_3^-]}{dt} = -k_n f_T f_w [\text{NH}_4^+]. \quad (\text{A2})$$

The nitrification reaction to produce  $\text{N}_2\text{O}$  is



with one component related to decomposition as

$$785 \quad \frac{d[\text{NH}_4^+]}{dt} = -2 \frac{d[\text{N}_2\text{O}]}{dt} = -f_{nm} f_T f_w f_{pH} \max(R_{nm}, 0) \quad (\text{A3})$$

with  $f_{nm}$  as a fraction (Parton et al., 1996) and  $R_{nm}$  as the net N mineralization rate,

$$R_{nm} = \sum_i n_i R_i, \quad (\text{A4})$$

where  $R_i$  denotes the rate of reaction (R2, R3, R4, R5, R7, R8, R9). The second component is (Parton et al., 1996)

$$790 \quad \frac{d[\text{NH}_4^+]}{dt} = -2 \frac{d[\text{N}_2\text{O}]}{dt} = -k_{n2o} f_T f_w f_{pH} (1 - e^{-0.0105[\text{NH}_4^+]}). \quad (\text{A5})$$

Ignoring the high-order terms and moving the unit conversion factor into  $k_{n2o}$ , it can be simplified as a first-order rate as

$$\frac{d[\text{NH}_4^+]}{dt} = -2 \frac{d[\text{N}_2\text{O}]}{dt} = -k_{n2o} f_T f_w f_{pH} [\text{NH}_4^+]. \quad (\text{A6})$$

### A3 Denitrification

795 The denitrification reaction is



with rate (Dickinson et al., 2002)

$$\frac{d[\text{NO}_3^-]}{dt} = -2\frac{d[\text{N}_2]}{dt} = -k_{\text{deni}} f_T f_w f_{\text{pH}} [\text{NO}_3^-]. \quad (\text{A7})$$

### A4 Plant nitrogen uptake

800 The plant nitrogen uptake reaction can be written as



and



The rate is specified by CLM (plant nitrogen demand) and assumed to be constant in each half-hour  
805 time step.

### A5 Demand-based competition and demand distribution between ammonium and nitrate

Denote  $R_{d,p}$  and  $R_{d,i}$  as the potential plant, immobilization, nitrification, and denitrification demand  
810 (rate);  $R_{a,tot} = R_{d,p} + R_{d,i}$  as the total  $\text{NH}_4^+$  demand; and  $R_{n,tot}$  as the total  $\text{NO}_3^-$  demand. CLM  
uses a demand-based competition approach to split the available sources in proportion to the demand  
rates to meet the demands (Oleson et al., 2013; Thornton and Rosenbloom, 2005). Specifically, for  
each time step, if  $R_{a,tot}\Delta t \leq [\text{NH}_4^+]$ , the uptakes are equal to potential demands, and  $R_{n,tot} = 0$ ;  
otherwise, the uptakes for  $\text{NH}_4^+$  are  $[\text{NH}_4^+]R_{d,p}/R_{a,tot}\Delta t$  and  $[\text{NH}_4^+]R_{d,i}/R_{a,tot}\Delta t$  for plants and  
immobilization;  $R_{n,tot} = R_{a,tot} - [\text{NH}_4^+]/\Delta t$ . If  $R_{n,tot}\Delta t < [\text{NO}_3^-]$ , all of the remaining demand  
 $R_{n,tot}$  is met with available  $\text{NO}_3^-$ . Otherwise, available  $\text{NO}_3^-$  is split to meet the remaining plant,  
815 immobilization, and denitrification demands in proportion to their rates.

## Appendix B: Implicit time stepping and Newton-Raphson iteration

Ignoring equilibrium reactions and transport for simplicity of discussion in this work, PFLOTRAN  
solves the ordinary differential equation,

$$dc/dt = \mathbf{R}(\mathbf{c}), \quad (\text{B1})$$

820 with  $\mathbf{c}$  as the concentration vector and  $\mathbf{R}$  as the kinetic reaction rate. Discretizing Eq. (B1) in time  
using the backward Euler method,

$$(\mathbf{c}^{k+1} - \mathbf{c}^k)/\Delta t = \mathbf{R}(\mathbf{c}^{k+1}). \quad (\text{B2})$$

Solving the equation using the Newton-Raphson method, we denote the residual as

$$\mathbf{f}(\mathbf{c}^{k+1,p}) = (\mathbf{c}^{k+1,p} - \mathbf{c}^k)/\Delta t - \mathbf{R}(\mathbf{c}^{k+1,p}), \quad (\text{B3})$$

825 and Jacobian as

$$\mathbf{J} = \frac{\partial \mathbf{f}(\mathbf{c}^{k+1,p})}{\partial \mathbf{c}^{k+1,p}}, \quad (\text{B4})$$

the update is

$$\delta \mathbf{c}^{k+1,p} = \mathbf{J}^{-1} \mathbf{f}(\mathbf{c}^{k+1,p}), \quad (\text{B5})$$

and the iteration equation is

$$830 \quad \mathbf{c}^{k+1,p+1} = \mathbf{c}^{k+1,p} - \delta \mathbf{c}^{k+1,p}. \quad (\text{B6})$$

The iteration continues until either the residual  $\mathbf{f}(\mathbf{c}^{k+1,p})$  or the update  $\delta \mathbf{c}^{k+1,p}$  is less than a specified tolerance. Specifically,

$$\|\mathbf{f}(\mathbf{c}^{k+1,p})\|_2 < \text{ATOL}, \quad (\text{B7})$$

$$835 \quad \frac{\|\mathbf{f}(\mathbf{c}^{k+1,p})\|_2}{\|\mathbf{f}(\mathbf{c}^{k+1,0})\|_2} < \text{RTOL}, \quad (\text{B8})$$

or

$$\frac{\|\delta \mathbf{c}^{k+1,p}\|_2}{\|\mathbf{c}^{k+1,p}\|_2} < \text{STOL}. \quad (\text{B9})$$

If none of these tolerances are met in MAXIT iterations or MAXF function evaluations, the iteration is considered to diverge, and PFLOTRAN decreases the time step size for MAX\_CUT times.

840 The default values in PFLOTRAN are  $\text{ATOL} = 10^{-50}$ ,  $\text{RTOL} = 10^{-8}$ ,  $\text{STOL} = 10^{-8}$ ,  $\text{MAXIT} = 50$ ,  $\text{MAXF} = 10^4$ , and  $\text{MAX\_CUT} = 16$ .

## Appendix C: Matrix equation for example Test 3

Adding plant  $\text{NO}_3^-$  uptake reaction (R14) with rate  $R_{nt} = R_p \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + k_m} \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + k_m}$ ,  $J_{nt,n} = \frac{dR_{nt}}{d[\text{NO}_3^-]} =$

$R_p \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + k_m} \frac{k_m}{([\text{NO}_3^-] + k_m)^2}$ , and  $J_{nt,a} = \frac{dR_{nt}}{d[\text{NH}_4^+]} = \frac{dR_n}{d[\text{NH}_4^+]} \frac{k_m}{([\text{NH}_4^+] + k_m)^2} \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + k_m}$ , and denitrification

845 reaction (R12) with rate  $R_{deni} = k_{deni} [\text{NO}_3^-]$ , and  $J_{deni} = \frac{dR_{deni}}{d[\text{NO}_3^-]} = k_{deni}$ , the matrix equation (Eq. B5) becomes Eq. (C1),

$$\begin{bmatrix} \frac{1}{\Delta t} + J_{at} + J_{nitr} & 0 & 0 & 0 \\ -J_{at} & \frac{1}{\Delta t} & 0 & 0 \\ -J_{nitr} + J_{nt,a} & 0 & \frac{1}{\Delta t} + J_{nt} + J_{deni} & 0 \\ -J_{nt,a} & 0 & -J_{nt,n} & 1/\Delta t \\ 0 & 0 & -0.5J_{deni} & 0 \end{bmatrix} \begin{pmatrix} \delta[\text{NH}_4^+]^{k+1,1} \\ \delta[\text{PlantA}]^{k+1,1} \\ \delta[\text{NO}_3^-]^{k+1,1} \\ \delta[\text{PlantN}]^{k+1,1} \\ \delta[\text{N}_2]^{k+1,1} \end{pmatrix} = \begin{pmatrix} R_{at} + R_{nitr} \\ -R_{at} \\ -R_{nitr} + R_{nt} + R_{deni} \\ -R_{nt} \\ -0.5R_{deni} \end{pmatrix}. \quad (\text{C1})$$