

Response to Dr. Niall Broekhuizen

General comments

The authors describe a new, explicit, first-order accurate numerical integration scheme that is designed to ensure that (elemental) masses are conserved and remain non-negative regardless of the magnitude of the projection time-step.

They present a brief summary of prior schemes that have aimed to achieve non-negativity (but, in some cases, sacrificed conservation). They highlight the (regrettable) fact that code authors have frequently resorted to arbitrary means:

- *Restricting the total quantity of substrate consumed during a time-step to be $<$ amount of substrate available at the start of the time-step (an unnecessarily restrictive approach if substrate is also produced during the time-step)*
- *Restricting the total quantity of substrate consumed during a time-step without also reducing the associated quantity of product material that arises from the substrate reactions (introducing mass conservation errors)*

Aside from the aforementioned disadvantages, the authors note that these ‘ad hoc’ schemes imply there is an undesirable coupling between the numerical integration scheme and the implementation of the model equations as computer code. As a result, the model implementation (i.e. the code) becomes difficult to extend and results can become sensitive to the order in which rates of change are calculated.

As the authors note, there are somewhat less arbitrary explicit-type, mass-and-positivity conserving integration schemes that better separate model implementation (specification of the model’s differential equations in code) and model solution algorithms (used to project the differential equations forward in time) in existence (Sandu 2001, Broekhuizen et al 2008). Unfortunately, these too have disadvantages in terms of one or both of run-time or accuracy-limitations.

Overall, I found the paper interesting. Subject to satisfactory responses to the comments below, I believe that it should be published.

Response: We sincerely appreciate Dr. Niall Broekhuizen’s positive comments on our paper. We address his concerns point by point in the following.

Comment 1: *The authors repeatedly refer to (and compare against) the BBKS scheme (citing Broekhuizen et al 2001). In that paper, BBKS was an acronym used to refer to a numerical integration scheme that was first described in an earlier paper (namely, Bruggeman et al 2007). The central point made in Broekhuizen et al (2008) is that the original BBKS scheme was not ‘scale independent’ (adding more state variables into the system of equations would change the numerical results – even if the new state variables merely ‘duplicated’ the original ones or, indeed, are entirely uncoupled from those belonging to the original system of equations). Broekhuizen et al (2008) proposed a modified version (dubbed mBBKS) of the original BBKS scheme that overcame the scaling issue for ‘duplicated equations or extended systems of coupled equations (though it would not entirely overcome the scaling-issue if a user were to endeavor to solve two or more entirely independent sets of coupled ODEs within the same code). I find it surprising that Tang & Riley would have adopted BBKS rather than mBBKS. I wonder whether all of their references to BBKS should really be to mBBKS? If they have genuinely used BBKS, they should properly attribute it to Bruggeman et al 2007 rather*

than to Broekhuizen et al (2008) [though it would be appropriate to acknowledge the existence of the mBBKS scheme developed in Broekhuizen et al 2008).

Response: We apologize for for this confusion. We clarified in the revision that the mBBKS scheme was used in all our numerical experiments.

Comment 2: *If Tang & Riley have used BBKS rather than mBBKS, then I believe that they should adopt mBBKS in its place for these comparisons. That said, mBBKS is also prone to yielding a global flux limiter that underflows to zero (such that the predicted net changes to all state-variables are falsely said to be zero for a time-step projection). That was the explanation for the mBBKS's ultimate failure in the Robertson test-case. I suspect that it is also the explanation for the failure of the "BBKS" (Tang & Riley notation) [Methods section lines 12-13 "BBKS failed to predict any organic matter composition after the first few time-steps"].*

Response: We used the mBBKS scheme in all our numerical experiments. The mBBKS scheme failed to predict any organic matter decomposition after the first few time-steps because it applied the same scaling modifier (i.e. m in the notation of Broekhuizen et al. (2008)) to all equations in the ODE system, which prevented the release of mineral nutrient from the decomposition of soil organic matter pools that are not nutrient limited. After first few time steps, all mineral nutrients were consumed, and the mBBKS predicted that all SOM decompositions were nutrient limited and could not proceed any further.

Comment 3: *(related to 2). Results section lines 12-13 I think it would be helpful if the authors explained why the (m)BBKS scheme predicted zero net change of organic matter: was it underflow of the flux limiter toward zero, or was it underflow of the product of the limiter and one or more of the raw rates of change? (I suspect, the former).*

Response: See response to comment 2.

Comment 4: *Writing the differential equations in reaction form (eq 4 and page 13409 line 19). Is Eq 4 conceptually equivalent to the Petersen matrix ODE-system notation used in the reports describing the IWA's anaerobic digester (Batstone et al 2002 Anaerobic Digester Model #1 IWA Scientific & Technical report) and river water quality model (Reichert et al 2001 River Water Quality Model No. 1; IWA Scientific & Technical report)? If so, I suggest citing the original Petersen work and/or the IWA reports so that people who are familiar with that approach can see the similarity. If not, I think the authors should explain how their notation differs from the Petersen matrix notation.*

Response: Yes and many thanks for your suggestions. We believe these two citations would make our method accessible to a wider community of readers.

Comment 5: *My main concerns about this manuscript relate to the pseudo-code (equation 6. Page 13405). I believe that it needs much more care and explanation:*

- a. p_m is the m^{th} element of the vector \mathbf{p} rather than being a single scalar? Similarly for q_n ? I believe that the subscripts m & n are being used to indicate vector elements and some of my comments/questions below are based upon that belief.

- b. M (first for-loop) denotes the total number of state-variables? Please clarify
- c. N (second for-loop) denotes the total number of reactions? Please clarify
- d. Incidentally, there are an awful lot of n s and q s (and, perhaps some other symbols) used to mean different things in different parts of the paper. N , N_{min} , $N_{min,sup}$, $N_{min,up}$, q_n , q_{Nmin} (& the related q_{Pmin}). In some cases (N_{min} , $N_{min,sup}$, $N_{min,up}$) the quantities are closely related (so similar notation is justified), but in others the quantities are unrelated (N and N_{min} ; q_n and q_{Nmin}). In these latter cases, I think it would be helpful to adopt a notation that does not imply (however weakly) that the quantities might be related.
- e. k (summation terms for $x_m(t+DT)$) denotes the k^{th} non-zero reaction influencing this state-var? Aside from the implied computational inefficiency of including zero-reaction terms, it might be clearer to replace k with n and explicitly sum over $1,N$ (or am I completely mis-understanding things)
- f. Rather than using unadorned end, I suggest using endif and endfor to aid 'bracket matching' when reading the code.
- g. Indent the expression for $x_m(t+DT)$ properly
- h. Indent the expression for pm properly in the first branch of the if-test.
- i. Should it be IF ($x_m(t+DT) \leq 0$) THEN rather than IF ($x_m(t+DT) < 0$) THEN?
- j. At entry to the IF ($lneg == 1$) THEN block, the subscript m will have value M and it will retain that value throughout the execution of the block. As written, I believe that q_n will only even be influenced by p_M and $v_{M,n}$. Is that really what is intended?
- k. I suggest inserting brackets around the terms that form the IF-condition(s)
- l. In the two "IF" conditions, be consistent in presence (or absence) of a comma following the condition. Also, a space is required between "1" and "then" in the second IF condition.
- m. Ultimately, how are the values q_n used? I think it would be useful to extend the pseudo-code such that it explicitly illustrates the manner in which the final value of $x_m(t+DT)$ is calculated. My guess is that the pseudo code for an entire time-step projection (rather than just the calculation of the flux-limiter terms) may be something like:

```

FOR n=1,N
  qn=1
ENDFOR
lneg=1
WHILE(1 == lneg)
  lneg=0
  FOR (m = 1,M)
     $X_m(t+DT) = x_m(t) + [\text{sum\_over\_k}(S_{m,k}^+ r_k q_k) - \text{sum\_over\_k}(S_{m,k}^- r_k q_k)] DT$ 
    IF( 0 >  $x_m(t+DT)$  ) {
      ...
    ELSE
      ...
    ENDIF
  ENDFOR
  IF (1 == lneg)

```

... (but bearing in mind my reservations about this bit of code (see (i), above)

```
ENDIF  
ENDWHILE
```

Response: Per your suggestion, we rewrote the pseudo-code as Fortran 90 and added detailed annotation for a better understanding and more straightforward use.

Comment 6: *Within the discussion, the authors should emphasize that the ‘interface’ for the function which returns the rates required by the integration scheme will differ from that required by most standard explicit method numerical schemes. Those require that the function, which returns the instantaneous rates of change, does so by means of a vector of net rates of change (one rate per state-variable). In contrast, this numerical integration scheme will require the corresponding ‘rate calculation function’ to return two matrices [respectively, containing $S^+_{m,k}r_k$ and $S^-_{m,k}r_k$]. Since the interface will differ, this makes it a bit more difficult to switch between integration methods by means of a run-time (at model initialization) switch.*

Response: We explained this technical nuance in our revision. See P7, Line 12-15.

Comment 7: *In discussion, mention that whilst an individual p_m may underflow to zero (causing the corresponding q_n values to be zero), other q_n need not underflow. Thus, in comparison with (m)BBKS, this scheme is less likely (I believe) to yield solutions in which all state-variables are falsely predicted to cease changing.*

Response: Per your suggestion, we added this explanation in our revision. P8, Line 31, P9, Line 1-2.

Comment 8: *Appendix A. I am not familiar with the Parton et al model. I did obtain a copy of the paper and read it but I think it would be helpful if Tang & Riley provided a table that lists the state-variables by notation-name and gives a verbal description of what each is.*

Response: Follow your suggestion, we provided a more transparent description of the century model by Parton et al. See revised appendix A in P11.

Response to reviewer 2

General comments:

The goal of the note is to document a method of solving nutrient dynamics in biogeochemical models. Specially it focuses on improving numerical solutions of biogeochemical models (specifically soil model) so that 1) negative nutrient concentrations are not simulated and 2) serial access (i.e. microbes have first access, then plants) to nutrients is not required by the different nutrient consumers. These issues are motivated by specifics to the Community Land Model but can apply to other Earth system models and ecosystem models. Overall, improving the numeric methods associated with simulating nutrient uptake and limitation is important for the field of biogeochemical modeling and the authors show that different methods can lead to different answers.

Response: We thank the reviewer’s appreciation of our effort. We address your

comments point by point in the following.

Comment: *It would be valuable to discuss model forms where the methods described are necessary and where they might not be as important. The Century model used in the manuscript is an example of a model without rate limitation kinetics (i.e. Michaelis–Menten kinetics) where the efficiency of N uptake does not scale with the inorganic N concentration. In this case method introduced in the manuscript is clearly important. In contrast, some ESMs and ecosystem models use rate limitation (i.e. Michaelis–Menten kinetics) to adjust the efficiency of N uptake rates so that as inorganic N concentrations get smaller the efficiency of N uptake rate declines. In this case, the methods described may not be as important because it is very rare that inorganic N concentration become negative (especially with an adaptive-time step ODE solver) and the competition between consumers is represented in the Michaelis-Menten parameters. See the LM3V (Gerber et al. 2010) and MEL (Rastetter et al. 2013) as examples.*

Response: We thank the reviewer to point out the difference between CENTURY's formulation and the MM based formulation. However, according to our experience with biogeochemical modeling, even MM based formulation will suffer from the same problem, especially when there are more than one substrates can limit the reaction rates. Essentially, when a certain substrate is of a small amount, its consumption rate as calculated from MM kinetics is a linear function of the substrate amount. When there are several reactions demanding the same substrate, for instance O₂ by all aerobic processes, negative substrate concentration will still occur if reaction rates are not limited or unless the time step used is unrealistically small. We therefore suggest the non-negativity issue is common to all sorts of biogeochemical models. We added this discussion in our revised manuscript. See P5, Line 19-25.

Other minor comments

Overall, the main message of the manuscript is clear but it is challenging to understand the specifics and to visualize how to apply the concepts because there are ambiguous subscripts and undefined concepts (see below)

Page 13401, Line 18: Define 'standard operator splitting approach'.

Greater detail in the use of subscripts and variables is needed. In particular:

- Page 13403: subscript i and m are not defined

- Page 13405: The pseudo code describes how q_n is calculated but the text does not describe how q_n is used or defines q_n . Please clarify. (note that q_n is also used in Appendix A for the loss rate – which is confusing)

- Page 13405: What does the k index refer to in the first for loop? Why use the n variable in the second for loop when the nomenclature in the text uses j ?

Page 13404, Line 18: This is the first time the term 'flux limiter' is used in the main text. Please define. Mechanistically how is the flux limiter used in the equations?

Page 13404, Line 24: Greater explanation is needed for why the S - is used to control the flux limitation. The current explanation is not clear.

Response: Per your suggestion, in the revised manuscript, we clarified the above issues and rewrote our pseudo-code as F90 code with detailed comments for a better understanding to readers.

1 **Technique Note: A generic law-of-the-minimum flux limiter**
2 **for simulating substrate limitation in biogeochemical**
3 **models**

4

5 **J. Y. Tang and W. J. Riley**

6 Department of Climate and Carbon Sciences, Lawrence Berkeley National Laboratory

7 Correspondence to: J. Y. Tang (jinyuntang@lbl.gov)

8

9 **Abstract**

10 We present a generic flux limiter to account for mass limitations from an arbitrary
11 number of substrates in a biogeochemical reaction network. The flux limiter is based on the
12 observation that substrate (e.g., nitrogen, phosphorus) limitation in biogeochemical models
13 can be represented as to ensure mass conservative and non-negative numerical solutions to the
14 governing ordinary differential equations. Application of the flux limiter includes two steps:
15 (1) formulate the biogeochemical processes with a matrix of stoichiometric coefficients and
16 (2) apply Liebig's law of the minimum using the dynamic stoichiometric relationship of the
17 reactants. This approach contrasts with the ad hoc down-regulation approaches that are
18 implemented in many existing models (such as CLM4.5 and the ACME (Accelerated Climate
19 Modeling for Energy) Land Model (ALM)) of carbon and nutrient interactions, which are
20 error prone when adding new processes, even for experienced modelers. Through an example
21 implementation with a CENTURY-like decomposition model that includes carbon, nitrogen,
22 and phosphorus, we show that our approach (1) produced almost identical results to that from
23 the ad hoc down-regulation approaches under non-limiting nutrient conditions; and (2)
24 properly resolved the negative solutions under substrate-limited conditions where the simple
25 clipping approach failed; and (3) successfully avoided the potential conceptual ambiguities
26 that are implied by those ad hoc down-regulation approaches. We expect our approach will
27 make future biogeochemical models easier to improve and more robust.

28

Jinyun Tang 11/16/2015 10:33 AM

Deleted: Century

1 Introduction

Biogeochemical modeling has been one of the major themes in developing earth system models (Hurrell et al., 2013), yet developing numerically robust and mathematically consistent biogeochemical models has been challenging (Broekhuizen et al., 2008). In biogeochemical modeling, the systems of interest, such as terrestrial ecosystems, are often nutrient limited under a wide range of conditions (Vitousek and Howarth, 1991; Vitousek et al., 2010). Therefore, proper modeling of nutrient limitation is a prerequisite for credible predictions of carbon-climate feedbacks (Bouskill et al., 2014; Thomas et al., 2015). In the Earth System Models (ESMs) joining phase 5 of the Coupled Model Intercomparison Project (CMIP5), only CLM-CN (Thornton et al., 2007) considered carbon and nitrogen interactions, although observations indicate nitrogen has significantly limited the terrestrial carbon sink (Arora et al., 2013). Further, many analyses indicate phosphorus is critical for improving carbon-climate feedback predictions (Vitousek et al., 2010; Yang et al., 2014; Wieder et al., 2015), and other nutrients (e.g., sulfur, potassium, molybdenum) may also be important (Schmidt et al., 2013; Moro et al., 2014). Therefore, we expect that as more processes are included in future biogeochemical models, more substrates will limit different biogeochemical processes under different conditions.

To develop numerically accurate biogeochemical models, it is important to develop a robust formulation of the biogeochemical processes, such that modelers can safely add or remove biogeochemical processes without degrading the numerical solution. This capability would allow users to focus only on deriving the governing ordinary differential equations (ODEs) of the biogeochemical processes. If the model uses a standard operator splitting approach (as is common, e.g., Tang et al., 2013), which solves the transport and chemistry separately, then the numerical solver could resolve the numerical details, such as maintaining mass conservation and avoiding nonphysical values, without knowing the details of the ODEs.

Existing terrestrial biogeochemical models often describe substrate limitation as occurring when the total available substrate cannot satisfy the demand from all consuming fluxes over a particular time step. For nitrogen limitation, many BGC models impose substrate limitation when the total potential ecosystem nitrogen demand (i.e., demand in the absence of nitrogen limitation; Thornton et al., 2007; Wang et al., 2010; Thomas et al., 2015) exceeds the total available mineral nitrogen, provided nitrogen from nitrogen fixers is

Jinyun Tang 11/16/2015 11:54 AM
Deleted: and the ODEs represent biogeochemical processes in a numerical cell.

Jinyun Tang 11/16/2015 11:51 AM
Deleted: then

Jinyun Tang 12/9/2015 12:19 PM
Deleted: exceeds the total available mineral nitrogen

1 supplied in mineral form over that time step and contributions from organic nitrogen are
2 assumed negligible (the latter of which could be incorrect, see Chapin et al., 1993). However,
3 this conceptual model (which served as the basis for those ad hoc down-regulation
4 approaches) is not mathematically consistent with the ODE that governs nitrogen limitation:

$$\frac{dN_{\min}}{dt} = N_{\min,\text{sup}} - N_{\min,\text{up}} \quad (1)$$

5 where N_{\min} (gN), $N_{\min,\text{sup}}$ (gN s⁻¹), and $N_{\min,\text{up}}$ (gN s⁻¹) represent mineral nitrogen, [mineral](#)
6 nitrogen supply (e.g., fixation, deposition), and [mineral](#) nitrogen uptake, respectively.
7 Mathematically, Eq. (1) implies that nitrogen limitation occurs only when the numerical
8 approximation to $N_{\min}(t + \Delta t)$ is negative after accounting for mineral nitrogen supply and
9 demand over the numerical time step Δt . Therefore, considering that negative mineral
10 nitrogen concentration is unphysical, imposing nitrogen limitation should be mathematically
11 interpreted as a means to ensure $N_{\min}(t + \Delta t) = (N_{\min,\text{sup}} - N_{\min,\text{up}})\Delta t + N_{\min}(t) \geq 0$, rather than
12 imposing the constraint $N_{\min,\text{up}}\Delta t \leq N_{\min}(t)$ as it is often done in current BGC models. Another
13 requirement to ensure correct numerical solutions to the ODEs of the biogeochemical model
14 is to maintain mass conservation for different chemical elements involved in the
15 biogeochemical processes. The mass conservation could be violated if one uses the popular
16 clipping method (e.g. Sandu, 2001) to reset negative solutions or by setting the derivative of
17 the negative to-be variable to zero, as is done for some explicit ODE solvers. For example, the
18 MATLAB function `odenonnegative`, which is used in the explicit solver ODE45 to avoid
19 negative solutions, resets the derivative for a negative to-be variable to zero. In either
20 implementation, clipping will artificially introduce new mass into the model and such mass
21 will accumulate and grow throughout the model integration, resulting in incorrect model
22 predictions (Sandu et al., 2001).

23 In this note, we show that by ensuring mass conservation and non-negative solutions
24 to the governing equations of a given biogeochemical model, it is possible to obtain a
25 universal solution to the mass limitation for an arbitrary number of substrates. We organize
26 the remaining of this paper as follows: section 2 describes the technical details of our method;
27 section 3 presents an evaluation of the method based on a [CENUTRY](#)-like organic matter
28 decomposition model (Parton et al., 1988; Appendix A, [Table 1](#), and [Table 2](#)); and section 4

Jinyun Tang 11/16/2015 3:06 PM

Deleted: (1)

Jinyun Tang 11/16/2015 1:10 PM

Deleted: Century

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Table 1

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Table 2

1 summarizes our findings. Note that, even though our evaluation of the approach is based on a
2 soil biogeochemical model, the approach is generic and could be applied to any
3 biogeochemical models.

4 2 Methods

5 Our approach makes use of the reaction-based formulation of a biogeochemical model
6 (e.g., [Reichert et al., 2001](#); [Batstone et al., 2002](#); Fang et al., 2013). Mathematically, for the j -
7 th reaction, we have

$$\sum_i v_{i,j}^- A_{i,j} \rightarrow \sum_m v_{m,j}^+ B_{m,j} \quad (2)$$

8 where $v_{i,j}^-$ and $v_{m,j}^+$ are stoichiometric coefficients for the i -th reactant $A_{i,j}$ and m -th product
9 $B_{m,j}$, respectively. Hereforth we assume the units of all chemical species are consistently
10 defined depending on the specific problem.

11 By defining reaction rate r_j of the j -th reaction as the consumption rate of the master
12 species in Eq. (2), for instance, $A_{1,j}$, whose stoichiometric coefficient is one, we calculate the
13 temporal variation of any chemical species due to the j -th reaction as

$$\left(\frac{dx_i}{dt} \right)_j = v_{i,j} r_j \quad (3)$$

14 where $v_{i,j}$ is the stoichiometric coefficient for chemical x_i in the j -th reaction. For reactants,
15 $v_{i,j}$ is negative, for products $v_{i,j}$ is positive, and $v_{i,j}$ is zero when a chemical species is not
16 involved in the reaction.

17 We describe the generic model structure [using the Peterson matrix form \(e.g. Russell,](#)
18 [2006\)](#) as:

$$\frac{d\mathbf{x}}{dt} = \mathbf{S}\mathbf{r} \quad (4)$$

19 where $\mathbf{S} = \{v_{i,j}\}$ is the matrix of stoichiometric coefficients and \mathbf{x} and \mathbf{r} are vectors of the
20 state variables and reaction rates, respectively.

Jinyun Tang 11/16/2015 1:15 PM

Deleted: s

Jinyun Tang 11/16/2015 1:16 PM

Formatted: Font:Italic

Jinyun Tang 11/16/2015 1:16 PM

Deleted: s

Jinyun Tang 11/16/2015 1:16 PM

Formatted: Font:Italic

Jinyun Tang 11/16/2015 3:06 PM

Deleted: (2)

1 We now separate \mathbf{S} into two parts, \mathbf{S}^+ and \mathbf{S}^- , which, respectively, contain product
2 ($v_{i,j}^+ > 0$) and reactant ($v_{i,j}^- \geq 0$) stoichiometric coefficients, such that

$$\frac{dx}{dt} = (\mathbf{S}^+ - \mathbf{S}^-)\mathbf{r} \quad (5)$$

3 In finding the numerical solution to Eq. (5) over a certain number time step, if some reaction
4 rates are too high, certain state variables will become negative unless those reaction rates are
5 reduced.

6 Several approaches (other than clipping) have been proposed to ensure non-negative
7 and mass conservative solutions to equations such as Eq. (5). For instance, Sandu (2001)
8 proposed two projection-based approaches to post-correct the negative solution using the null
9 space of \mathbf{S}^T (here T denotes transpose). Although his approaches overcome the barriers that
10 non-negativity either restricts the order of the method to one or restricts the step size to
11 impractically small values (Bolley and Crouzeix, 1978), they require matrix inversion, which
12 may become computationally intensive as the problem size increases or impractical because
13 not every model formulation allows negative state variables in the intermediate step when a
14 high order scheme is employed. Broekhuizen et al. (2008) ensured the solution non-negativity
15 of Eq. (5) by applying a single flux limiter (i.e., a scalar modifier that reduces the reaction
16 rate) to all reaction rates in the governing equations (aka, the mBBKS scheme). However, as
17 we will show below, the mBBKS approach will fail for models such as CENTURY-like
18 organic matter decomposition models (Parton et al., 1988; Appendix A, Table 1) when
19 multiple substrates are limiting under different conditions. We also note that the occurrence of
20 negative-solution is not unique to the CENTURY-like model that calculates the reaction rates
21 using the linear kinetics. Michaelis-Menten kinetics based soil biogeochemical models (e.g.,
22 Gerber et al., 2010; Bouskill et al., 2012) would similarly suffer from the negative solution
23 problem when many substrates could limit the reaction rates, and such problem cannot be
24 easily solved by simply resorting to adaptive time stepping algorithms, therefore the solution
25 strategy proposed below resolves a common issue for any biogeochemical models.

26 To propose a simple solution to ensure non-negative numerical solutions to Eq. (5), we
27 restrict our ODE integrator to the first order and apply a vector of flux limiters that are
28 dependent on the reactant stoichiometry \mathbf{S}^- , which controls the total substrate demand.
29 Forcing the flux limiter solution to depend linearly on \mathbf{S}^- maintains the stoichiometric

Jinyun Tang 11/16/2015 3:06 PM
Deleted: (5)

Jinyun Tang 11/16/2015 3:06 PM
Deleted: (5)

Jinyun Tang 11/16/2015 1:51 PM
Deleted: (BBKS scheme)

Jinyun Tang 11/16/2015 1:52 PM
Deleted: Century

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 1

Jinyun Tang 11/16/2015 2:49 PM
Deleted: negativity of the

Jinyun Tang 11/16/2015 3:06 PM
Deleted: (5)

Jinyun Tang 11/16/2015 2:49 PM
Deleted: is

1 | relationship for all reactions, and thus, mass balance over the time step. Specifically, we
 2 | calculate and apply the flux limiter for each reaction according to the Fortran 90 code:

!M1 is number of state variables.
 !N1 is number of reactions.
 !xt is vector of state variables at current time step.
 !xtnew is vector of temporary state variables for next time step.
 !q is vector of flux limiters for all reactions.
 !dt is time step size.

lneg = .false. !Initialize negative state variable indicator to zero
 do m = 1, M1 !Loop over all state variables

xtnew(m) = xt(m)

Fp = 0.0 !Initialize production flux accumulator to zero

Fm = 0.0 !Initialize consumption flux accumulator to zero

do n = 1, N1 !Loop over all reactions

xtnew(m) = xtnew(m) + (sp(m,n) - sm(m,n)) * r(n) * dt

Fp = Fp + sp(m,n) * r(n)

3 | Fm = Fm + sm(m,n) * r(n) (6)

enddo

if(xtnew(m) < 0) then !The state variable tends to be negative

!Calculate the limiting factor

p(m) = (xt(m) + Fp * dt) / (dt * Fm)

lneg = .true.

endif

enddo

!Now compute and apply the flux limiter

!when there is any negative state variable

if(lneg) then

do n = 1, N1

!minp finds the minimum of p,

!where the corresponding entry in sm is > 0.

q(n) = min(p(1:M1), sm(1:M1,n))

r(n) = r(n) * q(n)

enddo

endif

Jinyun Tang 11/16/2015 2:50 PM

Deleted: ,

Jinyun Tang 11/16/2015 2:50 PM

Deleted: thus ensuring

Jinyun Tang 11/16/2015 2:50 PM

Deleted: conservation

Jinyun Tang 11/16/2015 2:51 PM

Deleted: following

1 where the function \min_p is defined in Appendix B. In rare situations, one has to apply the
 2 above flux limiting procedure several times to ensure solution non-negativity, but the
 3 computation is much quicker and simpler than the matrix inversion required in Sandu's
 4 projection methods (2001), and can be paralleled easily. In addition, for a single
 5 biogeochemical reaction, one can verify that our approach is equivalent to Liebig's law of the
 6 minimum as applied to a generic biogeochemical reaction, which can be re-stated for a high-
 7 frequency BGC model to imply that the mean reaction rate during a numerical time step is
 8 controlled by the most limiting substrate. It is also noted that our approach avoids the explicit
 9 formulation of the law of the minimum in calculating the reaction rates, as is often done in
 10 many existing biogeochemical models (e.g. CLM-CNP, Yang et al., 2014), which when
 11 combined with their ad hoc down-regulation method leads to double counting of substrate
 12 limitation. We further note that traditional ODE solvers only require the temporal derivatives
 13 of the state variables from the biogeochemical model. To apply our approach in an ODE
 14 solver, however, requires the biogeochemical model to return the reaction rates, and the
 15 positive and negative parts of the stoichiometry matrix S .

16 In our evaluation, we compared the performance of our new approach to the mBBKS
 17 approach (Broekhuizen et al., 2008) and two ad hoc down-regulation formulations derived
 18 based on the nitrogen limitation scheme in CLM4.5 (CLM-1 and CLM-2). During a particular
 19 numerical time step, CLM-1 assumes complete independence between nutrient mobilizers and
 20 immobilizers, while CLM-2 assumes complete coupling between nutrient mobilizers and
 21 immobilizers (see details in Appendix C). We analyzed scenarios where the organic matter
 22 decomposition is (1) not nutrient limited (Case-1) and (2) nitrogen and phosphorus limited
 23 (Case-2 and Case-3); the latter situations are where a direct solution (without flux limitation)
 24 to Eq. (5) may produce negative values, and clipping will be triggered in methods like
 25 ODE45. We evaluated the difference between simulations for predicted mineral nitrogen
 26 N_{\min} , mineral phosphorus P_{\min} , total litter carbon, and total soil organic carbon. We note that
 27 all litter-decomposing reactions in the CENTURY-like model immobilize nitrogen and
 28 phosphorus; therefore, when SOM pools (SOM1, SOM2, and SOM3) are nil, a non-zero pool
 29 size must be assigned to both soil mineral nitrogen and mineral phosphorus to initialize litter
 30 decomposition (such as for Case-2 and Case-3; Table 3). We describe the initial conditions
 31 for our model runs in Table 3; Case-1 represents nutrient non-limiting decomposition; Case-2
 32 represents nutrient limited decomposition with zero initial SOM pools; and Case-3 represents

Jinyun Tang 11/16/2015 10:21 AM

Deleted: $\min\{p_m | v_{m,n}^- > 0\}$

Jinyun Tang 11/16/2015 10:21 AM

Formatted: Font:Italic

Jinyun Tang 11/16/2015 10:21 AM

Deleted: means to find the minimum among the elements of the vector whose corresponding stoichiometric coefficient $v_{m,n}^-$ is positive

Jinyun Tang 11/16/2015 10:21 AM

Deleted: (

Jinyun Tang 11/16/2015 10:21 AM

Deleted:)

Jinyun Tang 11/16/2015 2:12 PM

Deleted: limiter

Jinyun Tang 11/16/2015 2:21 PM

Deleted: (

Jinyun Tang 11/16/2015 2:21 PM

Deleted:)

Jinyun Tang 11/16/2015 3:06 PM

Deleted: (5)

Jinyun Tang 11/16/2015 2:21 PM

Deleted: Century

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Table 3

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Table 3

1 nutrient limited decomposition with non-zero initial SOM pools. We also conducted Case-4 to
2 reveal that the conceptual ambiguity in those ad hoc down-regulation approaches will result in
3 model uncertainties that could be avoided in our new approach. Case-4 differs from Case-3
4 with the addition of a first order loss term for both mineral nitrogen and mineral phosphorus
5 and a continuous litter input for the first 1500 days of the 3000-day integration (Table 3).
6 These mineral nutrient loss terms are used to mimic nutrient demand from other processes as
7 would occur in a BGC model in ESMs. Because there are no analytical solutions to the
8 CENTURY-like model, Case-1 also serves as a benchmark for our implementation of
9 different numerical solution strategies with respect to ODE45, which has been very well
10 tested by the MATLAB developers for problems that have no non-negativity constraint on
11 their solutions. We coded all our methods as MATLAB scripts and all ODE integrations are
12 carried out using an adaptive time stepping strategy (Appendix D) with a relative error 10^{-4} .

13 3 Results and discussions

14 3.1 Method evaluation

15 In simulations for the decomposition of nutrient-sufficient organic matter (i.e., no
16 nutrient limitation; Figure 1), we found our new approach (Fortran 90 code (6)), mBBKS,
17 CLM-1 and CLM-2 predicted almost identical time series for the various pools when
18 compared to that from ODE45, indicating the four approaches are implemented correctly as
19 benchmarked with ODE45.

20 However, for Case-2 (Figure 2, Table 3) where both nitrogen and phosphorus are
21 insufficient to support decomposition (because it has even less mineral nutrients available
22 than the nutrient-limited Case-3), mBBKS failed to predict any organic matter decomposition
23 after the mineral nutrients are consumed in the first few time steps and predicted that all
24 decomposition pathways were phosphorus limited thereafter (cyan line in Figure 2b). In
25 contrast, the two ad hoc down-regulation approaches, CLM-1 and CLM-2, and our new
26 approach all predicted visually identical time series of the different pools and correctly
27 indicated that the decomposition of SOM pools (SOM1, SOM2, and SOM3 as derived from
28 litter decomposition using the non-zero initial pools of mineral nutrients) released small
29 amounts of mineral nutrients to support further litter organic matter decomposition (as can be
30 inferred from Table 2, which shows that the decomposition of litter pools are all nutrient
31 limited by stoichiometry). This response was missed by mBBKS, because it applied a single

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 3

Jinyun Tang 11/16/2015 2:22 PM
Deleted: Century

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Figure 1

Jinyun Tang 11/16/2015 2:34 PM
Deleted: pseudo

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Figure 2

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 3

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Figure 2

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 2

1 [flux limiter to all decomposition pathways, preventing the release of nutrients from](#)
2 [mineralizing pathways to support further decomposition](#). Besides [mBBKS](#), ODE45 also failed
3 to predict meaningful decomposition dynamics, because by clipping the derivatives of the
4 negative to-be state variables to zero it introduced artificial mass into some state variables
5 during the integration. Specifically, ODE45 predicted the final total nitrogen and total
6 phosphorus (including both mineral and organic pools) as 0.8066 gN and 0.0511 gP, as
7 compared to the correct values 0.4445 gN and 0.0175 gP, whereas CLM-1, CLM-2, and our
8 new approach all conserved carbon, nitrogen, and phosphorus mass within the machine round
9 off error.

10 For Case-3 ([Figure 3](#), [Table 3](#)), where non-zero SOM pools were introduced to release
11 nitrogen and phosphorus to support litter decomposition, [mBBKS](#) again predicted no visible
12 decomposition because [of its use of a single flux limiter to all fluxes \(based on the nutrient](#)
13 [limited litter decomposition\)](#), even though the SOM decomposition should not be nutrient
14 limited. ODE45 also failed for Case-3, and predicted very different time series for the various
15 pools as compared to CLM-1, CLM-2, and our new approach. By day 300, ODE45 predicted
16 the total nitrogen and total phosphorus (including both mineral and organic pools) as 3.2164
17 gN and 0.2338 gP as compared to their correct values 3.1046 gN and 0.2273 gP, respectively.

18 3.2 The conceptual ambiguity of implementing nutrient limitation

19 Although we found little differences between our new method, CLM-1, and CLM-2 in
20 predicted decomposition dynamics for the three simple cases analyzed ([Figure 1](#), [Figure 2](#),
21 and [Figure 3](#)), we acknowledge that differences should be expected when applying our new
22 method and the two ad hoc down-regulation approaches CLM-1 and CLM-2 for modeling
23 ecosystem dynamics because they define nutrient limitation differently ([Fortran 90 code \(6\)](#)
24 and Appendix C; Figure 4 and [Figure 5](#)). As one would infer from Eq. [\(1\)](#), mathematically,
25 nutrient limitation occurs only when the state variable that represents a certain nutrient
26 becomes negative if the reaction rates are not limited during a given numerical integration
27 time step. However, (as we implemented in [the Fortran 90 code \(6\)](#)), this situation is
28 equivalent to assuming that a released mineral nutrient from the mobilizers will be
29 instantaneously available to all immobilizers that demand this nutrient. Although the existing
30 mineral nutrient pool and the newly released mineral nutrients will be tapped proportionally
31 by the immobilizers, this assumption may still be too strong if a given grid cell covers a too
32 large spatial domain to support this assumption of homogeneity (Manzoni et al., 2008). CLM-

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 3

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Table 3

Jinyun Tang 12/9/2015 12:38 PM

Deleted: it imposed

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 1

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 2

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 3

Jinyun Tang 11/16/2015 3:03 PM

Deleted: pseudo

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 5

Jinyun Tang 11/16/2015 3:06 PM

Deleted: (1

Jinyun Tang 11/16/2015 3:04 PM

Deleted: pseudo

1 1 and CLM-2 represent the two extremes of this coupling between mineral nutrient mobilizers
2 (who release nutrients) and mineral nutrient immobilizers (who take up nutrients) in that
3 CLM-1 assumes the mobilizers and immobilizers are completely independent during the
4 calculation of mineral nutrient uptake, whereas CLM-2 assumes the nutrients released by
5 mobilizers are first assimilated by immobilizers and if there is additional demand, the
6 remaining comes from the mineral nutrient pool (thus CLM-2 adopts an even stronger
7 mobilizer and immobilizer coupling than our new approach). Indeed the difference between
8 CLM-1 and CLM-2 is already discernible for Case-3 (Figure 4), and when the decomposition
9 model is coupled with other nutrient consumers in an ecosystem model, one would potentially
10 find very different predictions of carbon dynamics (see Case-4 in Figure 5 as a model with
11 slightly more complicated dynamics than Case-3). With slight modification, our new
12 approach will allow a consistent representation of the coupling between mobilizers and
13 immobilizers, including both the CLM-1 and CLM-2 assumptions regarding nutrient
14 competition. This approach will provide a new tool to analyze prediction uncertainty from the
15 ambiguity of defining the coupling strength between nutrient mobilizers and immobilizers.

16 Another advantage of our new approach, compared to the ad hoc down-regulation
17 approaches (e.g. CLM-1 and CLM-2 discussed above), is that it can handle limitation from an
18 arbitrary number of substrates, as long as the matrix of stoichiometric coefficients is
19 formulated. In principle, any biogeochemical reaction can be formulated into reaction form
20 (e.g. Fang et al., 2013), thus our approach will avoid the ordering problem often encountered
21 in those ad hoc approaches. In this context, the “ordering problem” refers to the situation that
22 different answers are calculated depending on the order of nutrient limitation (e.g., resolving
23 nitrogen limitation first, and then phosphorus limitation). For example, following the nutrient
24 limitation definition in CLM-1, when nitrogen and phosphorus limitation are treated
25 sequentially, the predicted decomposition dynamics differ significantly from when the
26 opposite order is applied (CLM-INP vs CLM-IPN in Figure 5). The implementation where
27 nitrogen limitation occurs before phosphorus limitation (CLM-INP, cyan circles in Figure 5)
28 predicted stronger litter decomposition than when phosphorus limitation is applied before
29 nitrogen limitation (CLM-IPN, black dots that overlap with blue line in Figure 5c).
30 Analogously, in the current CLM4.5 soil biogeochemical formulation (Oleson et al., 2013),
31 organic matter decomposition and methane oxidation are often limited by oxygen (Riley et al.
32 2011), and nitrogen limitation is imposed after accounting for oxygen limitation, which
33 potentially would result in different predictions were nitrogen limitation imposed before

Jinyun Tang 11/16/2015 3:05 PM

Deleted: up

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 5

Jinyun Tang 12/9/2015 12:41 PM

Deleted: than

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 5

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 5

Jinyun Tang 11/16/2015 3:06 PM

Deleted: Figure 5

1 oxygen limitation. This ordering issue can become more severe if more nutrients (e.g.,
2 phosphorus, sulfur) are to be introduced in future biogeochemical formulations, and our
3 approach relieves numerical inaccuracies associated with this ordering ambiguity.

4 4 Conclusions

5 In this study, we proposed a generic law of the minimum based flux limiter to handle
6 substrate limitation in biogeochemical models. Evaluations indicate our method could
7 produce as accurate results as those ad hoc down-regulation approaches implemented in
8 existing biogeochemical models for simple decomposition dynamics that only include
9 decomposers. Additionally, our new approach provides a way to resolve some conceptual
10 ambiguities implied in those ad hoc down-regulation approaches. We expect our new
11 approach to help the community to develop more robust and easier to maintain
12 biogeochemical codes to better predict carbon-climate feedbacks.

13

14 Appendix A: Governing equations for the CENTURY-like decomposition model

15 The soil biogeochemical model used in this study adopts the form from the
16 CENTURY-model, which uses a turnover pool based formulation of soil organic matter
17 decomposition (Parton et al., 1988). The model includes three pools of litter, one pool of
18 coarse wood debris (CWD) and three pools of SOM. The model calculates the non-nutrient
19 limited decomposition of a given organic matter pool X using the first order kinetics,
20 $r_x = -k_x X$, where k_x (yr^{-1}) is the decay parameter (and is equal to the reciprocal of the
21 turnover time). In most applications k_x is a function of temperature and moisture, however, it
22 is taken as constant in this study. Following CLM4.5 BGC (Oleson et al., 2013), the turnover
23 times are 0.066 yr, 0.25 yr and 0.25 yr, respectively, for the three litter pools $LIT1$, $LIT2$ and
24 $LIT3$. For the three SOM pools, the turnover times are 0.17 yr, 6.1 yr and 270 yr, respectively,
25 for $SOM1$, $SOM2$ and $SOM3$. CWD has a turnover time of 4.1 yr. The decomposed organic
26 matter released from linear decay is redistributed through the seven organic matter pools
27 according to the reaction stoichiometry in Table 1. Mathematically, the CENTURY-like
28 decomposition model is summarized with the following governing equations,

$$29 \quad \frac{dLIT1}{dt} = -r_{LIT1} + I_{LIT1} \quad (\text{A-1})$$

Jinyun Tang 11/16/2015 11:37 AM
Deleted: Century

Jinyun Tang 11/16/2015 11:41 AM
Formatted: Lowered by 7 pt

Jinyun Tang 11/16/2015 11:42 AM
Formatted: Lowered by 7 pt

Jinyun Tang 11/16/2015 11:43 AM
Formatted: Superscript

Jinyun Tang 11/16/2015 4:00 PM
Formatted: Font:Italic

Jinyun Tang 11/16/2015 11:47 AM
Deleted: . By following the reactions in Table 1, the governing equations for the Century-like decomposition model are

$$1 \quad \frac{dLIT2}{dt} = -r_{LIT2} + 0.76r_{cwd} + I_{LIT2} \quad (A-2)$$

$$2 \quad \frac{dLIT3}{dt} = -r_{LIT3} + 0.24r_{cwd} + I_{LIT3} \quad (A-3)$$

$$3 \quad \frac{dCWD}{dt} = -r_{CWD} + I_{CWD} \quad (A-4)$$

$$4 \quad \frac{dSOM1}{dt} = -r_{SOM1} + 0.45r_{LIT1} + 0.5r_{LIT2} + 0.42r_{SOM2} + 0.45r_{SOM3} + I_{SOM1} \quad (A-5)$$

$$5 \quad \frac{dSOM2}{dt} = -r_{SOM2} + 0.5r_{LIT3} + f_1r_{SOM1} + I_{SOM2} \quad (A-6)$$

$$6 \quad \frac{dSOM3}{dt} = -r_{SOM3} + 0.03r_{SOM2} + f_2r_{SOM1} + I_{SOM3} \quad (A-7)$$

$$7 \quad \begin{aligned} \frac{dN_{min}}{dt} = & \left(\frac{1}{CN_{LIT1}} - \frac{0.45}{CN_{SOM1}} \right) r_{LIT1} + \left(\frac{1}{CN_{LIT2}} - \frac{0.5}{CN_{SOM1}} \right) r_{LIT2} + \left(\frac{1}{CN_{LIT3}} - \frac{0.5}{CN_{SOM2}} \right) r_{LIT3} \\ & + \left(\frac{1}{CN_{CWD}} - \frac{0.76}{CN_{LIT2}} - \frac{0.24}{CN_{LIT3}} \right) r_{CWD} + \left(\frac{1}{CN_{SOM1}} - \frac{f_1}{CN_{SOM2}} - \frac{f_2}{CN_{SOM3}} \right) r_{SOM1} \\ & + \left(\frac{1}{CN_{SOM2}} - \frac{0.42}{CN_{SOM2}} - \frac{0.03}{CN_{SOM3}} \right) r_{SOM2} + \left(\frac{1}{CN_{SOM3}} - \frac{0.45}{CN_{SOM1}} \right) r_{SOM3} - q_{Nmin} N_{min} \end{aligned} \quad (A-8)$$

$$8 \quad \begin{aligned} \frac{dP_{min}}{dt} = & \left(\frac{1}{CP_{LIT1}} - \frac{0.45}{CP_{SOM1}} \right) r_{LIT1} + \left(\frac{1}{CP_{LIT2}} - \frac{0.5}{CP_{SOM1}} \right) r_{LIT2} + \left(\frac{1}{CP_{LIT3}} - \frac{0.5}{CP_{SOM2}} \right) r_{LIT3} \\ & + \left(\frac{1}{CP_{CWD}} - \frac{0.76}{CP_{LIT2}} - \frac{0.24}{CP_{LIT3}} \right) r_{CWD} + \left(\frac{1}{CP_{SOM1}} - \frac{f_1}{CP_{SOM2}} - \frac{f_2}{CP_{SOM3}} \right) r_{SOM1} \\ & + \left(\frac{1}{CP_{SOM2}} - \frac{0.42}{CP_{SOM2}} - \frac{0.03}{CP_{SOM3}} \right) r_{SOM2} + \left(\frac{1}{CP_{SOM3}} - \frac{0.45}{CP_{SOM1}} \right) r_{SOM3} - q_{Pmin} P_{min} \end{aligned} \quad (A-9)$$

9 where q_{Nmin} (s^{-1}) and q_{Pmin} (s^{-1}) are, respectively, the loss rates for mineral nitrogen and
10 mineral phosphorus; $I_{(x)}$ ($gC s^{-1}$) designates the input rate for organic matter X ; all other
11 symbols are explained in Table 1.

12 **Appendix B: Pseudo code for *minp***

13 For two vectors x and y of size n , $p = minp(x, y)$ (assuming $p \leq 1$) is calculated as

```

p=1
do i=1, n
  if(y(i)>0)then
    p=min(x(i),p)
  endif
enddo

```

(B1)

Jinyun Tang 12/9/2015 12:48 PM
Deleted: A1

Appendix C: Two ad hoc down-regulation formulations of nutrient limitation

The first ad hoc down-regulation approach (CLM-1) follows the implementation of nitrogen down regulation in CLM4.5 (Oleson et al., 2013), where all nitrogen immobilization fluxes N_{immob} within the time step Δt are summed and compared to available nitrogen (N_{min}).

The flux limiter from mineral nitrogen is:

$$\gamma_N = \min\left(\frac{N_{min}}{N_{immob}\Delta t}, 1\right)$$

(C1)

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B1

Similarly for mineral phosphorus:

$$\gamma_P = \min\left(\frac{P_{min}}{P_{immob}\Delta t}, 1\right)$$

(C2)

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B2

Then for reactions (Table 1) that are only nitrogen limited, we multiply their reaction rates with γ_N , for reactions that are only phosphorus limited, we multiply their reaction rates with γ_P , and for reactions that are both nitrogen and phosphorus limited, we multiply their reaction rates with $\min(\gamma_N, \gamma_P)$.

The second ad hoc down-regulation approach (CLM-2) is similar to the first one, except that it first subtracts the mobilizing fluxes from the immobilizing fluxes, such that

$$\gamma_N = \min\left(\max\left(\frac{N_{min}}{(N_{immob} - N_{mob})\Delta t}, 0\right), 1\right)$$

(C3)

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B3

$$\gamma_P = \min\left(\max\left(\frac{P_{min}}{(P_{immob} - P_{mob})\Delta t}, 0\right), 1\right)$$

(C4)

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B4

1 Therefore, it can be inferred that (under similar conditions) nutrient limitation would
2 (theoretically) occur more frequently in the first (CLM-1) than in the second (CLM-2) ad hoc
3 down-regulation approach.

4 One can further define

5
$$\gamma_N = \min \left(\max \left(\frac{N_{\min} + N_{\text{mob}} \Delta t}{N_{\text{immob}} \Delta t}, 0 \right), 1 \right) \quad (\text{C5})$$

6
$$\gamma_P = \min \left(\max \left(\frac{P_{\min} + P_{\text{mob}} \Delta t}{P_{\text{immob}} \Delta t}, 0 \right), 1 \right) \quad (\text{C6})$$

7 which can be verified to be identical to that calculated in the pseudo code (6) in the main text
8 when only one nutrient is limiting. Because this last definition does not change the conclusion
9 of our study, we only analyzed the first two ad hoc down-regulation approaches (CLM-1 and
10 CLM-2) in our comparison.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B5

Jinyun Tang 12/9/2015 12:48 PM
Deleted: B6

Jinyun Tang 11/16/2015 4:07 PM
Deleted: -

Jinyun Tang 11/16/2015 4:07 PM
Deleted: -

Jinyun Tang 11/16/2015 4:07 PM
Formatted: Left

1 **Appendix D: MATLAB pseudo code for the adaptive time stepping integration**

2 For a certain time step

```
%hscal is the time step scaling factor.  
%xold is the state variable at current time step.  
%t is current time, and Δt is time step.  
xnew = ode(xold, Δt, t)  
xnew* = ode(xold, Δt / 2, t)  
xnew* = ode(xnew*, Δt / 2, t + Δt / 2)  
%Find the maximum relative error across all state variables.
```

$$rerr = \max_i \left\{ \frac{|x_{new}^*(i) - x_{new}(i)|}{|x_{new}^*(i)| + eps} \right\}$$

3 if $rerr < 0.5 * rerr_{tol}$

```
hscal = 2; accept = 1
```

```
elseif  $rerr < rerr_{tol}$ 
```

```
hscal = 1; accept = 1
```

```
elseif  $rerr < 2 * rerr_{tol}$ 
```

```
hscal = 0.5; accept = 1
```

```
else
```

```
hscal = 0.5; accept = 0
```

```
end
```

```
xold = (1 - accept)xold + accept * xnew*
```

```
t = t + accept * Δt; Δt = max(Δt * hscal, Δtmin)
```

```
loop
```

4 where $ode(\cdot)$ represents the numerical solver of the ODEs, eps represents the floating-point

5 relative accuracy in MATLAB, the relative error tolerance $rerr_{tol}$ is 10^{-4} in all simulations in

6 this study. Other symbols in (D1) should be self-explanatory.

7

8

9

10

(D1)

Jinyun Tang 11/16/2015 11:36 AM

Deleted: -

... [2]

Jinyun Tang 11/16/2015 4:05 PM

Deleted: Pseudo

Jinyun Tang 11/16/2015 4:06 PM

Deleted:

Jinyun Tang 11/16/2015 4:06 PM

Deleted:

Jinyun Tang 12/9/2015 12:49 PM

Deleted:

Jinyun Tang 11/16/2015 4:06 PM

Formatted: Left

Jinyun Tang 12/9/2015 12:49 PM

Deleted: C1

Jinyun Tang 12/9/2015 12:49 PM

Deleted: C1

1 **Author contributions**

2 JYT developed the theory, conducted the analyses, and wrote the paper. WJR discussed the
3 analyses and wrote the paper.

4 **Acknowledgements**

5 This research is supported by the Director, Office of Science, Office of Biological and
6 Environmental Research of the US Department of Energy under contract no. DE-AC02-
7 05CH11231 as part of the Next-Generation Ecosystem Experiments (NGEE-Arctic) and the
8 Accelerated Climate Model for Energy project in the Earth System Modeling program. We
9 thank Dr. Niall Broekhuizen and an anonymous reviewer for their constructive comments,
10 which improved the paper significantly.
11

1 References

2 Arora, V. K., Boer, G. J., Friedlingstein, P., Eby, M., Jones, C. D., Christian, J. R., Bonan, G.,
3 Bopp, L., Brovkin, V., Cadule, P., Hajima, T., Ilyina, T., Lindsay, K., Tjiputra, J. F., and Wu,
4 T.: Carbon-Concentration and Carbon-Climate Feedbacks in CMIP5 Earth System Models, J
5 Climate, 26, 5289-5314, 2013.

6 [Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A.,
7 Sanders, W. T. M., Siegrist, H., and Vavilin, V. A.: The IWA Anaerobic Digestion Model No
8 1 \(ADM1\), Water Sci Technol, 45, 65-73, 2002.](#)

9 Bolley, C. and Crouzeix, M.: Conservation de la positivite lors de la discretization des
10 problemes d'evolution parabolique, R.A.I.R.O. Numer. Anal. 12(3), 237 (1978).

11 [Bouskill, N. J., Tang, J.Y., Riley, W. J., and Brodie, E. L.: Trait-based representation of
12 biological nitrification: model development testing, and predicted community composition,
13 Front Microbiol, 3, 2012.](#)

14 Bouskill, N. J., Riley, W. J., and Tang, J. Y.: Meta-analysis of high-latitude nitrogen-addition
15 and warming studies implies ecological mechanisms overlooked by land models,
16 Biogeosciences, 11, 6969-6983, 2014.

17 Broekhuizen, N., Rickard, G. J., Bruggeman, J., and Meister, A.: An improved and
18 generalized second order, unconditionally positive, mass conserving integration scheme for
19 biochemical systems, Appl Numer Math, 58, 319-340, 2008.

20 Chapin, F. S., Moilanen, L., and Kielland, K.: Preferential Use of Organic Nitrogen for
21 Growth by a Nonmycorrhizal Arctic Sedge, Nature, 361, 150-153, 1993.

22 Fang, Y., Huang, M., Liu, C., Li, H., and Leung, L. R.: A generic biogeochemical module for
23 Earth system models: Next Generation BioGeoChemical Module (NGBGC), version 1.0,
24 Geosci Model Dev, 6, 1977-1988, 2013.

25 [Gerber, S., Hedin, L. O., Oppenheimer, M., Pacala, S. W., and Shevliakova, E.: Nitrogen
26 cycling and feedbacks in a global dynamic land model, Global Biogeochem Cy, 24, 2010.](#)

27 Hurrell, J. W., Holland, M. M., Gent, P. R., Ghan, S., Kay, J. E., Kushner, P. J., Lamarque, J.
28 F., Large, W. G., Lawrence, D., Lindsay, K., Lipscomb, W. H., Long, M. C., Mahowald, N.,
29 Marsh, D. R., Neale, R. B., Rasch, P., Vavrus, S., Vertenstein, M., Bader, D., Collins, W. D.,

Jinyun Tang 11/16/2015 1:45 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

Jinyun Tang 11/16/2015 2:09 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

Jinyun Tang 11/16/2015 2:09 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

Jinyun Tang 11/16/2015 2:09 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

Jinyun Tang 11/16/2015 2:08 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

- 1 Hack, J. J., Kiehl, J., and Marshall, S.: The Community Earth System Model A Framework
2 for Collaborative Research, *B Am Meteorol Soc*, 94, 1339-1360, 2013.
- 3 Manzoni, S., Porporato, A., and Schimel, J. P.: Soil heterogeneity in lumped mineralization-
4 immobilization models, *Soil Biol Biochem*, 40, 1137-1148, 2008.
- 5 Moro, H., Kunito, T., Saito, T., Yaguchi, N., and Sato, T.: Soil microorganisms are less
6 susceptible than crop plants to potassium deficiency, *Arch Agron Soil Sci*, 60, 1807-1813,
7 2014.
- 8 Oleson, K., Lawrence, D. M., Bonan, G. B., Drewniak, B., Huang, M., Koven, C. D., Levis,
9 S., Li, F., Riley, W. J., Subin, Z. M., Swenson, S., Thornton, P. E., Bozbiyik, A., Fisher, R.,
10 Heald, C. L., Kluzek, E., Lamarque, J.-F., Lawrence, P. J., Leung, L. R., Lipscomb, W.,
11 Muszala, S. P., Ricciuto, D. M., Sacks, W. J., Sun, Y., Tang, J., and Yang, Z.-L.: Technical
12 description of version 4.5 of the Community Land Model (CLM), NCAR Technical Note
13 NCAR/TN-503+STR, 420 pp., doi:10.5065/D6RR1W7M, 2013.
- 14 Parton, W. J., Stewart, J. W. B., and Cole, C. V.: Dynamics of C, N, P and S in Grassland
15 Soils - a Model, *Biogeochemistry*, 5, 109-131, 1988.
- 16 [Reichert, P., Borchardt, D., Henze, M., Rauch, W., Shanahan, P., Somlyódy, L., and
17 Vanrolleghem, P.: River water quality model no. 1 \(RWQM1\): II. Biochemical process
18 equations, *Water Sci Technol*, 43, 11-30, 2001.](#)
- 19 Riley, W. J., Subin, Z. M., Lawrence, D. M., Swenson, S. C., Torn, M. S., Meng, L.,
20 Mahowald, N. M., and Hess, P.: Barriers to predicting changes in global terrestrial methane
21 fluxes: analyses using CLM4Me, a methane biogeochemistry model integrated in CESM,
22 *Biogeosciences*, 8, 1925-1953, 2011.
- 23 [Russell: Practical wastewater treatment, John Wiley & Sons, Inc. ISBN: 978-471-78044-1,
24 2006.](#)
- 25 Schmidt, F., De Bona, F. D., and Monteiro, F. A.: Sulfur limitation increases nitrate and
26 amino acid pools in tropical forages, *Crop Pasture Sci*, 64, 51-60, 2013.
- 27 Sandu, A.: Positive numerical integration methods for chemical kinetic systems, *J Comput
28 Phys*, 170, 589-602, 2001.

Jinyun Tang 11/16/2015 1:46 PM

Formatted: Font:(Default) Times New Roman, Font color: Auto

Jinyun Tang 12/9/2015 1:33 PM

Formatted: Font:12 pt, Font color: Auto

1 Tang, J. Y., Riley, W. J., Koven, C. D., and Subin, Z. M.: CLM4-BeTR, a generic
2 biogeochemical transport and reaction module for CLM4: model development, evaluation,
3 and application, *Geosci Model Dev*, 6, 127-140, 2013.

4 Thomas, R. Q., Brookshire, E. N. J., and Gerber, S.: Nitrogen limitation on land: how can it
5 occur in Earth system models?, *Global Change Biol*, 21, 1777-1793, 2015.

6 Thornton, P. E., Lamarque, J. F., Rosenbloom, N. A., and Mahowald, N. M.: Influence of
7 carbon-nitrogen cycle coupling on land model response to CO₂ fertilization and climate
8 variability, *Global Biogeochem Cy*, 21, 2007.

9 Vitousek, P. M. and Howarth, R. W.: Nitrogen Limitation on Land and in the Sea - How Can
10 It Occur, *Biogeochemistry*, 13, 87-115, 1991.

11 Vitousek, P. M., Porder, S., Houlton, B. Z., and Chadwick, O. A.: Terrestrial phosphorus
12 limitation: mechanisms, implications, and nitrogen-phosphorus interactions, *Ecol Appl*, 20, 5-
13 15, 2010.

14 Wang, Y. P., Law, R. M., and Pak, B.: A global model of carbon, nitrogen and phosphorus
15 cycles for the terrestrial biosphere, *Biogeosciences*, 7, 2261-2282, 2010.

16 Wieder, W. R., Cleveland, C. C., Smith, W. K., and Todd-Brown, K.: Future productivity and
17 carbon storage limited by terrestrial nutrient availability, *Nat Geosci*, 8, 441-U435, 2015

18 Yang, X., Thornton, P. E., Ricciuto, D. M., and Post, W. M.: The role of phosphorus
19 dynamics in tropical forests - a modeling study using CLM-CNP, *Biogeosciences*, 11, 1667-
20 1681, 2014.

21 Zhu, Q., Riley, W. J., Tang, J., and Koven, C. D.: Multiple soil nutrient competition between
22 plants, microbes, and mineral surfaces: model development, parameterization, and example
23 applications in several tropical forests, *Biogeosciences Discuss.*, 12, 4057-4106,
24 doi:10.5194/bgd-12-4057-2015, 2015.

25
26
27
28
29

1 Table 1. A list of biogeochemical reactions as represented in the century-like organic matter
 2 decomposition model (Appendix A). The decomposition is calculated as in Parton et al.
 3 (1988). Here we use CN to represent carbon to nitrogen ratio, and CP to represent carbon to
 4 phosphorus ration. The subscript “min” designates mineral pool for a nutrient, such as
 5 nitrogen (N) and phosphorus (P). The three litter pools are $LIT1$, $LIT2$ and $LIT3$. The three
 6 SOM pools are $SOM1$, $SOM2$ and $SOM3$. CWD is the pool of coarse wood debris.

 ID Reactions

$$1 \quad LIT1 \rightarrow 0.45SOM1 + 0.55CO_2 + \left(\frac{1}{CN_{LIT1}} - \frac{0.45}{CN_{SOM1}} \right) N_{\min} + \left(\frac{1}{CP_{LIT1}} - \frac{0.45}{CP_{SOM1}} \right) P_{\min}$$

$$2 \quad LIT2 \rightarrow 0.5SOM1 + 0.5CO_2 + \left(\frac{1}{CN_{LIT2}} - \frac{0.5}{CN_{SOM1}} \right) N_{\min} + \left(\frac{1}{CP_{LIT2}} - \frac{0.5}{CP_{SOM1}} \right) P_{\min}$$

$$3 \quad LIT3 \rightarrow 0.5SOM2 + 0.5CO_2 + \left(\frac{1}{CN_{LIT3}} - \frac{0.5}{CN_{SOM2}} \right) N_{\min} + \left(\frac{1}{CP_{LIT3}} - \frac{0.5}{CP_{SOM2}} \right) P_{\min}$$

$$4 \quad CWD \rightarrow 0.76LIT2 + 0.24LIT3 + \left(\frac{1}{CN_{CWD}} - \frac{0.76}{CN_{LIT2}} - \frac{0.24}{CN_{LIT3}} \right) N_{\min} + \left(\frac{1}{CP_{CWD}} - \frac{0.76}{CP_{LIT2}} - \frac{0.24}{CP_{LIT3}} \right) P_{\min}$$

$$5^* \quad SOM1 \rightarrow f_1SOM2 + f_2SOM3 + (1 - f_1 - f_2)CO_2 \\ + \left(\frac{1}{CN_{SOM1}} - \frac{f_1}{CN_{SOM2}} - \frac{f_2}{CN_{SOM3}} \right) N_{\min} + \left(\frac{1}{CP_{SOM1}} - \frac{f_1}{CP_{SOM2}} - \frac{f_2}{CP_{SOM3}} \right) P_{\min}$$

$$6 \quad SOM2 \rightarrow 0.42SOM1 + 0.03SOM3 + 0.55CO_2 \\ + \left(\frac{1}{CN_{SOM2}} - \frac{0.42}{CN_{SOM1}} - \frac{0.03}{CN_{SOM3}} \right) N_{\min} + \left(\frac{1}{CP_{SOM2}} - \frac{0.42}{CP_{SOM1}} - \frac{0.03}{CP_{SOM3}} \right) P_{\min}$$

$$7 \quad SOM3 \rightarrow 0.45SOM1 + 0.55CO_2 + \left(\frac{1}{CN_{SOM3}} - \frac{0.45}{CN_{SOM1}} \right) N_{\min} + \left(\frac{1}{CP_{SOM3}} - \frac{0.45}{CP_{SOM1}} \right) P_{\min}$$

7 * In this study, we set $f_1 = 0.6235$ and $f_2 = 0.0025$.

8

9

10

11

1 Table 2. Parameter values used in this study. These values are based on syntheses from Parton
2 et al. (1988), Yang et al. (2014) and Zhu et al. (2015).

Jinyun Tang 11/16/2015 3:55 PM
Deleted: - ... [4]

Parameters	Values
(CN_{LIT1}, CP_{LIT1})	(90, 1600)
(CN_{LIT2}, CP_{LIT2})	(90, 2000)
(CN_{LIT3}, CP_{LIT3})	(90, 2500)
(CN_{CWD}, CP_{CWD})	(90, 4500)
(CN_{SOM1}, CP_{SOM1})	(13, 110)
(CN_{SOM2}, CP_{SOM2})	(16, 320)
(CN_{SOM3}, CP_{SOM3})	(7.9, 114)

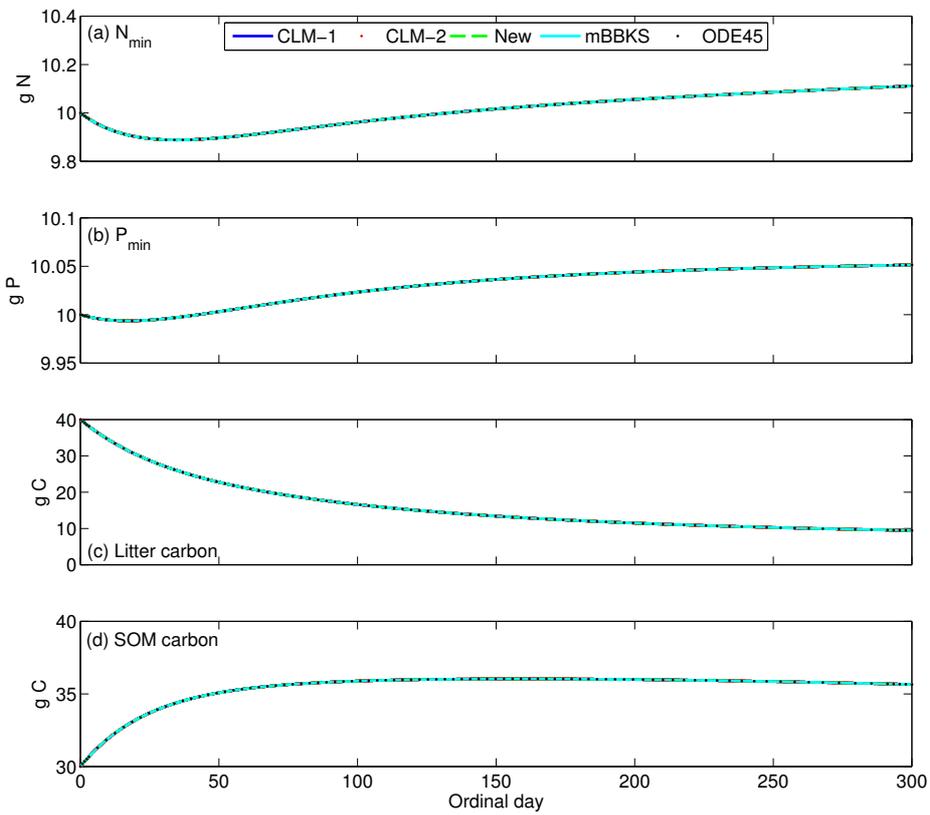
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

1 Table 3. Initial conditions and integration length (#days) for the analyzed model simulations.

Variables	Case-1	Case-2	Case-3	Case-4*
<i>LIT1</i>	10 gC	10 gC	10 gC	10 gC
<i>LIT2</i>	10 gC	10 gC	10 gC	10 gC
<i>LIT3</i>	10 gC	10 gC	10 gC	10 gC
<i>CWD</i>	10 gC	10 gC	10 gC	10 gC
<i>SOM1</i>	10 gC	0 gC	10 gC	10 gC
<i>SOM2</i>	10 gC	0 gC	10 gC	10 gC
<i>SOM3</i>	10 gC	0 gC	10 gC	10 gC
N_{\min}	10 g N	10^{-4} gN	10^{-4} gN	10^{-3} gN
P_{\min}	10 g P	10^{-8} gP	10^{-8} gP	10^{-7} gP
$q_{N_{\min}}$	0 s^{-1}	0 s^{-1}	0 s^{-1}	10^{-6} s^{-1}
$q_{P_{\min}}$	0 s^{-1}	0 s^{-1}	0 s^{-1}	10^{-6} s^{-1}
#days	300 days	300 days	300 days	3000 days

2 *For Case-4, there were rates of 0.04 gC day^{-1} , 0.04 gC day^{-1} and 0.02 gC day^{-1} input for

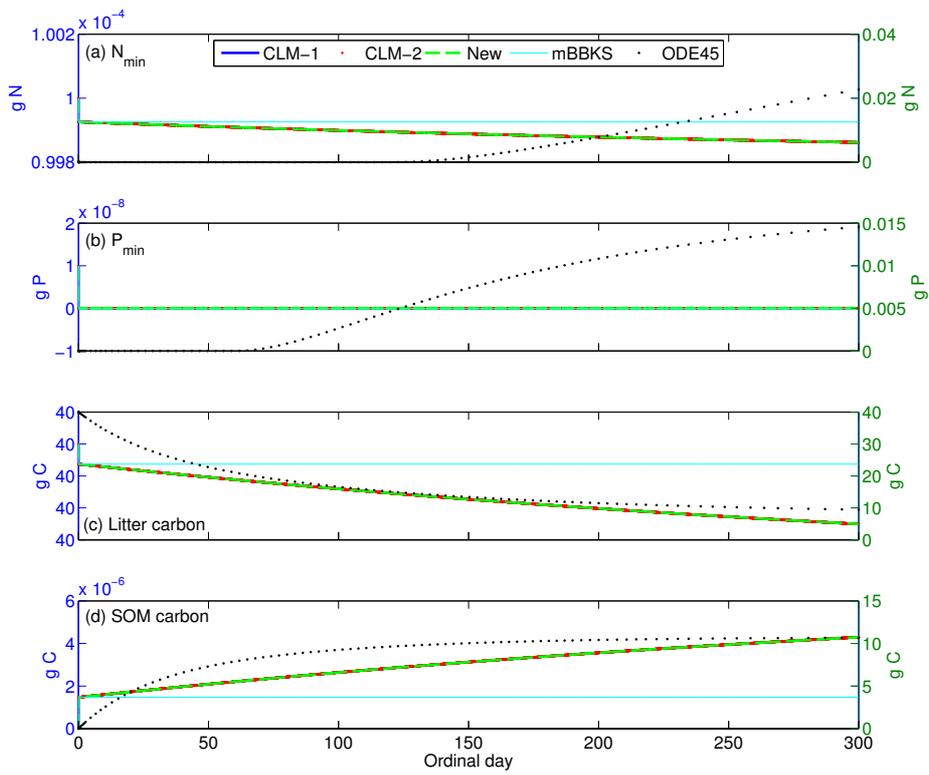
3 *LIT1*, *LIT2* and *LIT3* in the first 1500 days.



1
2
3
4
5

Figure 1 Simulated decomposition dynamics for Case-1 in [Table 3](#). In all panels, all results overlap each other.

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 3



1

2 Figure 2 Simulated decomposition dynamics for Case-2 in [Table 3](#). Note that the ODE45
 3 scheme (shown on the right hand y-axes) predicted wrong results that are of much large
 4 magnitude than the other methods.

Jinyun Tang 11/16/2015 3:06 PM
 Deleted: Table 3

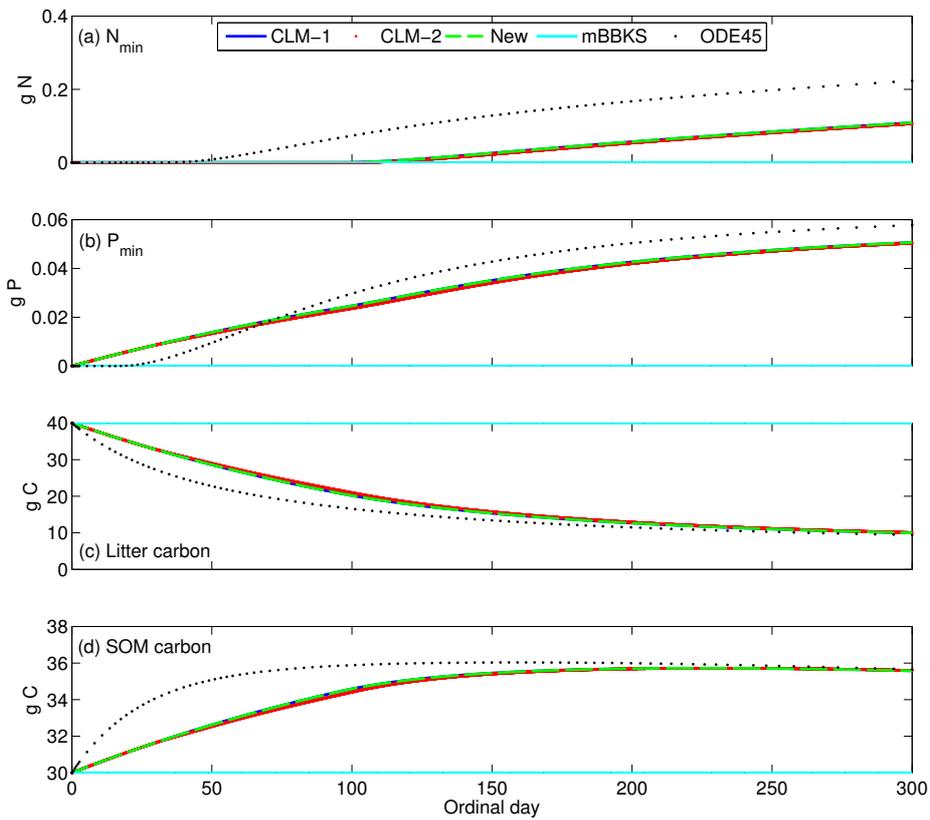
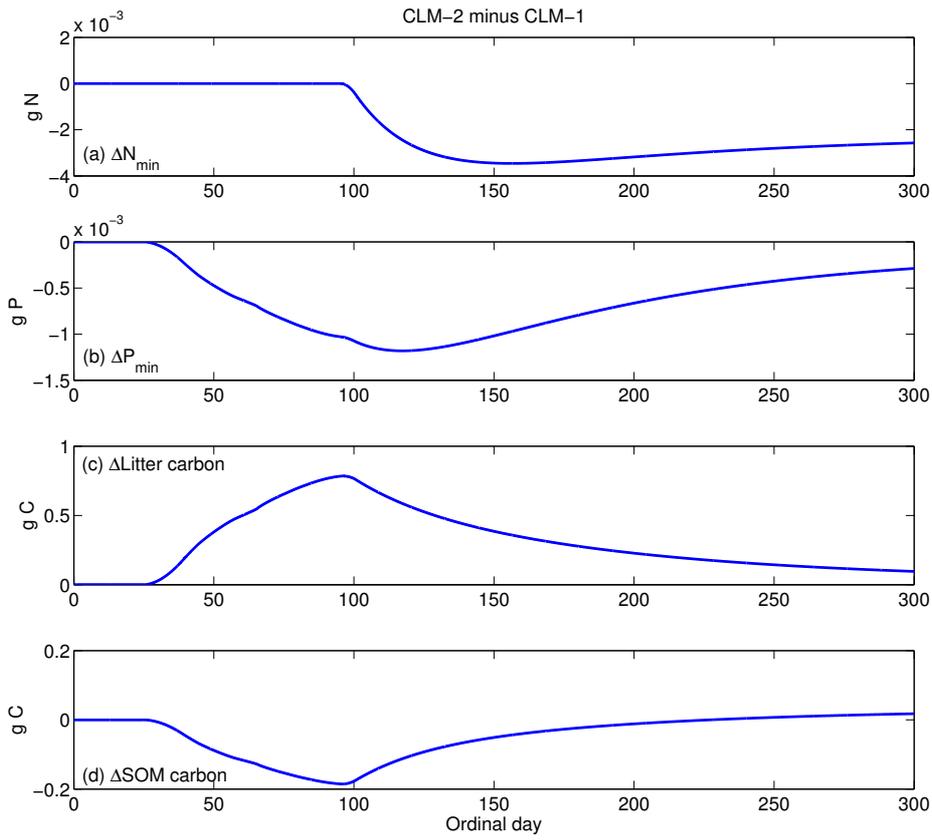


Figure 3 Simulated decomposition dynamics for Case-3 in [Table 3](#). In all panels, the result from CLM-1 overlaps with that from our new method.

Jinyun Tang 11/16/2015 3:06 PM
 Deleted: Table 3

1
 2
 3
 4
 5
 6
 7
 8
 9
 10
 11

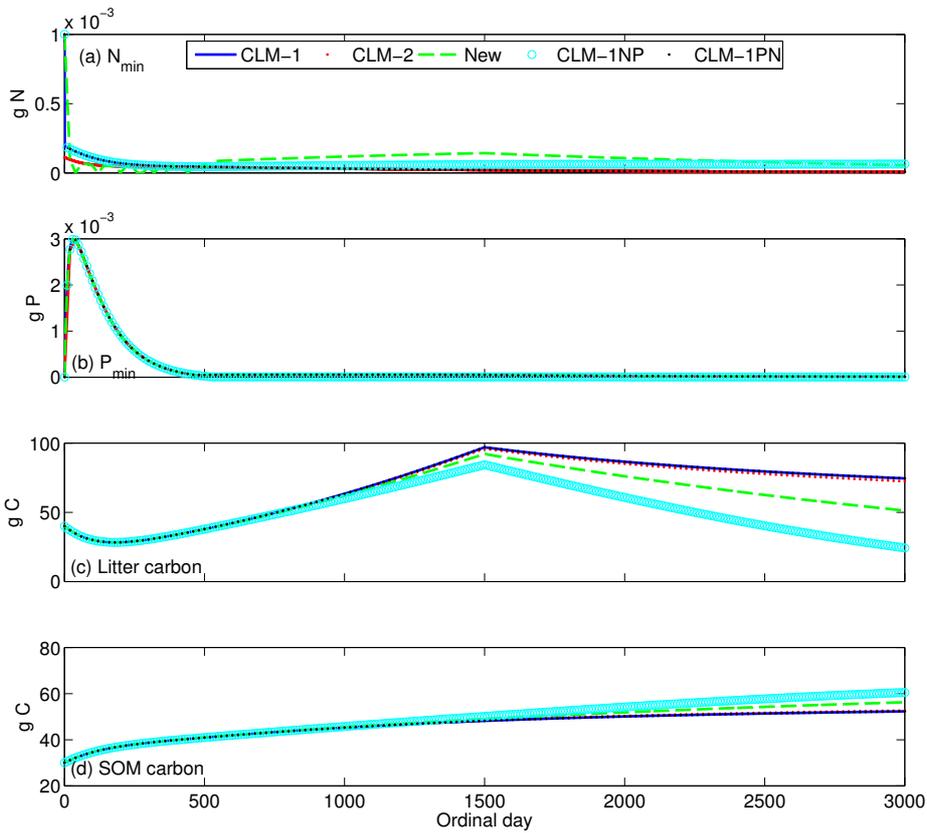
1



2

3 Figure 4 Differences between simulated decomposition dynamics by CLM-1 and CLM-2 for
4 Case-3.

5



1
2
3
4
5
6
7
8
9
10
11
12

Figure 5. Simulated decomposition dynamics for Case-4 in Table 3. CLM-1NP performs nitrogen down-regulation before phosphorus down-regulation, whereas CLM-1PN reverses the order. Similarly to CLM-1 (Appendix C), both CLM-1NP and CLM-1PN assume the nutrient mobilizer and immobilizer are independent within a numerical time step. In all panels, CLM-1PN predictions overlap with CLM-1 predictions.

Jinyun Tang 11/16/2015 3:06 PM
Deleted: Table 3