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Nitrification and denitrification in the Community Land Model compared to observations at Hubbard Brook Forest

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Abstract

Models of terrestrial system dynamics often include nitrogen (N) cycles to better represent N limitation of terrestrial carbon (C) uptake but simulating the fate of N in ecosystems has proven challenging. Here, key soil N fluxes and flux ratios from the Community Land Model version 5.0 (CLM5.0) are compared to an extensive set of observations from the Hubbard Brook Forest Long-Term Ecological Research (LTER) site in New Hampshire. Simulated fluxes include microbial immobilization and plant uptake, which compete with nitrification and denitrification, respectively, for available soil ammonium (NH_4^+) and nitrate (NO_3^-). In its default configuration, CLM5.0 predicts that both plant uptake and immobilization are strongly dominated by NH_4^+ over NO_3^- , and that the model ratio of nitrification:denitrification is approximately 1:1. In contrast, Hubbard Brook observations suggest that NO_3^- plays a more significant role in plant uptake and that nitrification could exceed denitrification by an order of magnitude. Modifications to the standard CLM5.0 at Hubbard Brook indicate that a simultaneous increase in the competitiveness of nitrifying microbes for NH_4^+ and reduction in the competitiveness of denitrifying bacteria for NO_3^- are needed to bring soil N flux ratios into better agreement with observations. Such adjustments, combined with evaluation against observations, may help improve confidence in present and future simulations of N limitation on the C cycle, although C fluxes such as gross primary productivity (GPP) and net primary productivity (NPP) are less sensitive to the model modifications than soil N fluxes.

Key Words

Nitrogen cycle, nitrogen limitation, Community Land Model, CLM5.0, nitrification, denitrification

Introduction

Land models that neglect N limitation of net primary production (NPP) may project future rates of land C uptake that are unsustainable under realistic scenarios of soil nutrient availability [e.g., *Hungate et al.*, 2003; *Zaehle et al.* 2014; *Wieder et al.* 2015]. Studies based on the National Center for Atmospheric Research (NCAR) Community Land Model (CLM) and other land models suggest that N limitation reduces the terrestrial biosphere's ability to sequester C under increasing atmospheric CO₂, although the extent of the reduction has varied among models [e.g., *Thornton et al.*, 2009; *Jain et al.*, 2009; *Zaehle et al.*, 2010]. The introduction of N limitation into land models has been challenging due to the complexity of C-N interactions, the multiple oxidation states of N in soil, and the limited understanding of plant-soil-microbial competition for N [e.g., *Thomas et al.*, 2015; *Zhu et al.*, 2017; *Sulman et al.*, 2019]. In addition, N loss fluxes from soil, including denitrification and leaching, help determine N availability but have been prescribed in land models with uncertain or ad hoc parameterizations that can yield poor agreement with available observations [e.g., *Thomas et al.*, 2013a; *Houlton et al.*, 2015; *Nevison et al.*, 2016].

The current CLM5.0 carbon cycle model is generally in good agreement with available observations, e.g., it captures well the historical evolution of terrestrial C sources and sinks over the historical period [*Lawrence et al.*, 2019]. However, its ability to simulate

CO₂ sinks in the future will depend in part on how well it represents N limitation [Hungate *et al.*, 2003; Wieder *et al.* 2019]. Nevison *et al.* [2020] evaluated the N fluxes in two land models, including CLM5.0, with a focus on the models' representation of separate pools of NH₄⁺ and NO₃⁻, the two most important forms of reactive N in soils. They found some large discrepancies between the models and observations, particularly for fluxes involving NO₃⁻, raising concerns that these might reduce the credibility of CLM5.0 future projections. However, a competing concern and challenge is that improvements in the representation of soil N transformations and fluxes may feed back on the carbon, water, and energy cycles, potentially degrading how well those are represented by the present-day model [Wieder *et al.* 2015].

The N cycle is complex. Even simplified consideration of the cycle includes multiple N forms and often-competing processes. The two primary forms of soil inorganic N, NH₄⁺ and NO₃⁻, are connected through the process of nitrification, in which chemoautotrophic bacteria gain energy by oxidizing NH₄⁺ to NO₃⁻. Plants can assimilate either form of inorganic N and incorporate it into above and below-ground tissue [Wang and Macko, 2011; Zhang *et al.*, 2018]. Microbes also can assimilate both NH₄⁺ and NO₃⁻ as they decompose C-rich and relatively N-poor plant litter in the process of N immobilization. Later stages of microbial decomposition release NH₄⁺ back to soil solution in the process of mineralization [Schimel & Bennett, 2004]. In addition to plant uptake or immobilization, other fates for NO₃⁻ include loss from soil through leaching or through dissimilatory respiratory processes, e.g., denitrification, a heterotrophic microbial process in which NO₃⁻ is reduced to inert N₂ or N₂O gas under low-oxygen conditions

[Butterbach-Bahl *et al.*, 2002; Seitzinger *et al.*, 2006; Burgin and Groffman, 2012; Ibraim *et al.*, 2020]. Denitrification is difficult to quantify due to its extraordinary spatiotemporal heterogeneity and the difficulty in discerning the end product, N_2 , which composes most of the atmosphere [Groffman *et al.*, 2006a; Kulkarni *et al.* 2014].

In principle, the implementation of distinct NH_4^+ and NO_3^- pools into land models has improved the sophistication of their representation of coupled C-N interactions and allowed for a more mechanistically based parameterization of denitrification [Del Grosso *et al.*, 2000; Koven *et al.*, 2013]. However, it also has yielded a new set of fluxes that invite scrutiny, such as nitrification, denitrification and NH_4^+ and NO_3^- -specific plant uptake and immobilization. A number of previous studies have pointed out that the high rate of denitrification in CLM, and the corresponding low rate of NO_3^- leaching, is incompatible with available observations [Thomas *et al.*, 2013a; Houlton *et al.*, 2015; Nevison *et al.*, 2016]. However, the denitrification:leaching ratio may not be critical to the model representation of plant-microbe competition [Gerber *et al.*, 2010]. Leaching occurs in CLM5.0 only after the respective competitions for NH_4^+ and NO_3^- have taken place, and only then if there is excess NO_3^- left over. In contrast, CLM5.0's low 1:1 nitrification:denitrification ratio in many ecosystems, identified by Nevison *et al.* [2020], may be more relevant to the credibility of the NH_4^+ and NO_3^- plant-microbe competition algorithms. This is true because nitrifier and denitrifier demand for available inorganic N competes directly with plant demand and can lead to down-regulation of plant growth due to N limitation.

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In this paper, we evaluate CLM5.0 N fluxes and flux ratios at the Hubbard Brook Experimental Forest, an LTER site in New Hampshire. We compile results from the wide range of field and laboratory measurements at Hubbard Brook of N fluxes and their ratios, including nitrification, denitrification, N mineralization, leaching, immobilization, and plant N uptake, with the two latter partitioned between NO_3^- and NH_4^+ . Finally, we make a variety of modifications to CLM5.0 focused on improving the parameterizations of nitrification and denitrification, which we identify as key fluxes creating some of the discrepancies with observations. We examine how these modifications change soil N fluxes in the model, as well as their repercussions for model C fluxes.

Methods

Hubbard Brook Observations

The Hubbard Brook Experimental Forest LTER site is dominated by northern hardwood forest vegetation in the White Mountain National Forest in New Hampshire USA ($43^\circ 56' \text{N}$, $71^\circ 45' \text{W}$). The N budget of Hubbard Brook has been documented since the 1960s [e.g., *Likens et al.*, 1969; 1978; *Bormann et al.*, 1977; *Whittaker et al.*, 1979; *Likens*, 2013; *Yanai et al.*, 2013; *Lovett et al.*, 2018]. For the current study, we compiled measurements of plant and soil N and C fluxes from Hubbard Brook and C fluxes at a nearby site to evaluate CLM5.0 output (Table 1). Our analysis includes absolute fluxes but focuses primarily on the ratios of relevant N fluxes, since the latter are useful for evaluating the relative importance of various N transformations and losses relative to one another. The ratios examined include gross nitrification:gross mineralization, gross

nitrification:denitrification, and denitrification:stream NO_3^- loss, as well as estimates of relative plant uptake and microbial immobilization of NO_3^- vs. NH_4^+ .

Gross rates of N mineralization, immobilization, and nitrification are quantified with short-term (typically 24-hour) ^{15}N pool dilution measurements in the lab, while net rates of mineralization (the balance of gross mineralization and NH_4^+ immobilization) and nitrification (the balance of gross nitrification and NO_3^- immobilization) are measured with lab assays or with field-based “buried bag” incubations over weeks to months [Davidson *et al.* 1992, Hart *et al.* 1994; Schimel and Bennett, 2004]. We combined 3 different studies to estimate annual gross nitrification, denitrification, and their ratio at Hubbard Brook. First, we used sequential buried bag measurements of *in situ* annual mean net nitrification over the top 15 cm of combined forest floor and mineral soil from Durán *et al.* [2016], which averaged 3.0 (range = 0.5-7.2) $\text{gN/m}^2/\text{yr}$ over 2010-2012. Second, we used ^{15}N pool dilution column-integrated gross and net nitrification rates of 3.9 (std. dev. 3.6) $\text{kg N ha}^{-1} \text{ day}^{-1}$ and 2.1 (std dev 2.1) $\text{kg N ha}^{-1} \text{ day}^{-1}$, respectively, from Darby *et al.* [2020] to estimate a gross:net nitrification ratio of 1.8 (std. dev. = 0.6). We assumed that this ratio could be applied annually and used it to scale the annual net nitrification rates from Durán *et al.* [2016] to estimate an annual gross nitrification rate of 5.5 (range = 0.9-13.3) $\text{gN/m}^2/\text{yr}$.

Our third step involved pairing the above gross annual nitrification rate with the estimated annual mean rate of denitrification over the top 10-12 cm of forest floor and mineral soil of 0.4 (range = 0.2-1.8) $\text{gN/m}^2/\text{yr}$ from Hubbard Brook [Morse *et al.* 2015]. The Morse *et al.* study combined lab-based measurements of N_2O and N_2 fluxes from soil

cores with field measurement of N_2O fluxes and *in situ* continuous measurements of temperature, moisture and oxygen concentrations. The N_2O and N_2 fluxes were from a system that replaced the natural N_2/O_2 atmosphere with a He/O_2 atmosphere, making possible direct detection of the resulting small increases in N_2 concentrations.

Combining the results from all three steps yields a gross nitrification:denitrification ratio of approximately 14 (1-76). The wide range of uncertainty is due in particular to denitrification, which can be highly variable in space and time.

We used the Morse *et al.* data in a separate calculation to estimate the ratio of denitrification to NO_3^- leaching. Leaching rates have been extensively documented at Hubbard Brook based on measured streamflow and NO_3^- concentrations [e.g., Likens, 2013; Yanai *et al.*, 2013; Groffman *et al.* 2018]. We used NO_3^- leaching rates of 0.11 ± 0.05 $\text{gN}/\text{m}^2/\text{yr}$ from data collected between 1992-2007 (note: leaching rates were higher in earlier decades for reasons that aren't fully understood Yanai *et al.* [2013]). Pairing this with the denitrification rate of 0.4 $\text{gN}/\text{m}^2/\text{yr}$, we estimate a denitrification:leaching ratio of ~ 4 at Hubbard Brook.

We used isotope dilution data from Darby *et al.* 2020] to estimate 3 additional N flux ratios, including gross nitrification:gross mineralization (0.45 ± 0.21), NO_3^- immobilization:total N immobilization (0.31 ± 0.08) and NH_4^+ immobilization:gross mineralization (0.82 ± 0.17). These estimates were based on the slopes of scatterplots of the individual fluxes measured down to 50 cm (Table 1; Appendix S1: Fig. S1). The gross nitrification:gross mineralization result of 0.45 ± 0.21 from Darby *et al.* [2020] was

supported by additional gross N cycling measurements from *Groffman et al.* [2006b] and *Weitzman et al.* [2020].

We also used paired measurements of potential annual net mineralization and nitrification from *Groffman et al.* [2018] in a scatterplot to assess the linearity of the nitrification vs. mineralization relationship, which had a tightly correlated slope of 0.40 ± 0.02 ($R=1.0$), despite declines in the absolute fluxes over time.

Aboveground plant N uptake at Hubbard Brook of 7.5 ± 2.5 gN/m²/yr was estimated from our update of *Whittaker et al.* [1979], in which measured NPP was combined with measured C:N ratios in various plant components. Additional information on the partitioning of plant uptake into NO₃⁻ and NH₄⁺ was based on *Socci and Templer* [2011], who measured N uptake using both an *in situ* depletion method with intact roots and an *ex situ* ¹⁵N tracer method with excised roots from mature sugar maple and red spruce trees. Their data suggest that NH₄⁺ accounts for ~94% of plant uptake in September, but only 57-82% in July. These measurements of plant preference have high uncertainty and are limited in scope, spatially, temporally and with respect to tree species.

Finally, we compiled data on several key C cycle fluxes from the nearby Bartlett Experimental Forest (44°06'N, 71°3'W), which shares a similar climate, forest composition and stand age with Hubbard Brook [*Ouimette et al.*, 2018]. The C flux data spanned 2004-2016 and were based on eddy covariance, biometric tracking of tree growth and soil respiration measurements. They yielded the following estimates: gross primary production (GPP) = 1285 ± 62 gC/m²/yr, net primary production (NPP) = $615 \pm$

118 gC/m²/yr and soil heterotrophic respiration = 434 ± 101 gC/m²/yr. *Fahey et al.*

[2005] estimate very similar values for these fluxes at Hubbard Brook using a combination of late 1990s field data and the PnET-II model [*Aber et al.*, 1995].

Community Land Model v. 5.0

The Community Land Model (CLM) is the terrestrial component of the Community Earth System Model version 2 (CESM2) [*Danabasoglu et al.*, 2020]. The coupled C-N cycle was introduced into CLM by *Thornton et al.*, [2002] with various updates over the years [*Thornton and Rosenbloom*, 2005; *Thornton et al.*, 2009]. The updates include a major revision by *Koven et al.* [2013] to create CLM-BGC (biogeochemistry) v4.5, which resolves soil biogeochemistry vertically and separates soil mineral N into explicit NH₄⁺ and NO₃⁻ pools. CLM version 5.0 was further updated from CLM4.5 in multiple ways, including with respect to its representation of soil and plant hydrology, agriculture, and coupled C-N dynamics [*Swenson and Lawrence*, 2015; *Badger and Dirmeyer*, 2015; *Levis et al.*, 2016; *Lawrence et al.*, 2019; *Lombardozzi et al.*, 2020;].

CLM5.0 also was modified to replace formerly fixed foliar nitrogen concentrations (leaf C:N ratios) with more flexible stoichiometry to allow plants to respond to environmental change [*Wieder et al.*, 2019]. A related update was made to treat biological N fixation based on the Fixation and Uptake of Nitrogen (FUN) model, which calculates the carbon costs of various nitrogen acquisition strategies and adjusts carbon expenditure accordingly [*Fisher et al.*, 2010; *Shi et al.*, 2016]. However, for this study we use an older

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representation of N₂ fixation as a function of evapotranspiration, which is added to the soil NH₄⁺ pool [Cleveland *et al.*, 1999]. The fallback to this older treatment of N₂ fixation was necessary to resolve soil NH₄⁺ and NO₃⁻ fluxes, since some relevant variables are not available when FUN is active. We note that turning FUN off led to a 15% decrease in GPP (i.e., from ~980 to 830 gC/m²/yr) and soil N fluxes relative to the FUN-on case in the default code.

Soil C and N decomposition processes in CLM5.0 use a plant/microbe equal competition scheme, in which potential rates of nitrification, plant uptake and microbial immobilization of NH₄⁺ at each soil depth are computed and then reduced proportionally to match available mineral NH₄⁺ [Zhu *et al.*, 2017]. Next, in a sequential algorithm, the potential rates of denitrification, plant uptake and microbial immobilization of NO₃⁻ are computed and reduced proportionally to match available NO₃⁻. Finally, any remaining residual NO₃⁻ becomes available for leaching, in an algorithm dependent on soil dissolved NO₃⁻ concentration, surface runoff and subsurface drainage.

Modifications to CLM5.0 at Hubbard Brook LTER

We modified CLM5.0 at a grid cell corresponding to the Hubbard Brook Experimental Forest to test alternative parameterizations for nitrification and denitrification, which our analysis of global model output identified as likely key contributors to unrealistic soil N flux ratios [Nevison *et al.*, 2020]. Following previous CLM work in single grid mode (where the model is run in one particular location) [e.g., Thomas *et al.*, 2013b; Cheng *et al.*, 2019], we created site-level present day meteorological (from GSWP3 v. 1) and N

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deposition inputs by extracting the single grid cell values from the global gridded forcing data for CLM5.0 [Lawrence *et al.*, 2019]. These were written to computationally-efficient site-specific forcing files, allowing the model to reach a state of statistical equilibrium (spin-up) in just 2% of the time required for the full model. Atmospheric CO₂ concentration (= 367 ppm), land use and N deposition (= 0.7 gN/m²/yr) were fixed at year 2000 conditions throughout the simulations, while meteorological forcings were cycled over 1991-2010. The plant functional type of the grid cell was prescribed as 100% broadleaf deciduous temperate forest. Spin-up for each simulation was run in accelerated decomposition mode [Thornton and Rosenbloom, 2005] for 400 years, followed by a final spin-up for 200 years, of which the last 20 years were sampled for the results presented here. The N fluxes varied interannually but displayed no obvious drift or trends over these 20 years.

We tested a variety of new parameterizations, described in more detail below, in which model nitrification and/or denitrification was revised based on observed empirical relationships. We extracted gross mineralization, gross nitrification, leaching and denitrification rates as well as rates of immobilization and plant uptake (for each of NH₄⁺ and NO₃⁻), both vertically resolved and integrated over the soil column. For the results presented here, the large majority of the fluxes occurred within the top 20-30 cm, but we integrated down to 60 cm, the depth where most fluxes had decreased to ~ zero.

We compared absolute fluxes to Hubbard Brook observations and also computed flux ratios described above. We calculated the latter as the ratios of the total column-

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integrated annual fluxes spanning 20 years of model output (Table 1). Alternatively, we used scatterplots and Deming regressions to derive the relationship between N fluxes [Nagy, 2020]. This approach assigns the same uncertainty to the X and Y axis variables, rather than assuming all error is in the Y variable, as in a standard least squares regression. Our scatterplots contained 20 years of annual mean fluxes, column-integrated from 1-60 cm, plotted one against another (Figure 1). We calculated flux ratios based on the slope of the Deming regression (when a linear relationship existed). In addition to the annual mean fluxes, Figure 1 also shows the monthly mean model results, which provide a sense of the largely temperature-driven seasonal variation in the flux relationships. By taking the ratio of fluxes, we sought to normalize differences in absolute rates and their depth sampling to the relative rates of fluxes that are modeled and observed.

The modifications made to CLM5.0 at Hubbard Brook are summarized below:

1a) Increased nitrification (Parton)

We added an NH_4^+ mineralization-based term to the CLM5.0 formula for potential nitrification in accord with the *Parton et al.* [2001] equation, from which the formula is derived. The original Parton *et al.* nitrification formula is based on empirical data from Great Plains grassland and has two component terms, proportional to a) the amount of excess NH_4^+ in the inorganic N pool and b) the soil N turnover rate, represented by the NH_4^+ mineralization flux multiplied by an assumed scalar [Parton *et al.*, 2001]. This second term is not included in the default CLM5.0, an omission that puts nitrifiers at a competitive disadvantage for NH_4^+ in grid cells like Hubbard Brook, where soil

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heterotrophs and plants quickly consume most of the mineralized NH_4^+ , leaving little to no excess ammonium for nitrification. We hypothesized that restoring the turnover rate-based term from the original Parton *et al.* equation would make nitrifiers more competitive with heterotrophs and plants.

2a) Increased nitrification (Zhang)

In an alternative approach to boosting nitrifier competitiveness, we implemented a parameterization of potential nitrification suggested by Zhang *et al.* [2018], who concluded, based on a compilation of empirical data, that nitrification is closely related to gross mineralization and is modulated by pH. Zhang *et al.* found a linear increase in the gross nitrification:gross mineralization ratio with increasing pH, climbing from 0 at pH 4 to > 1 at alkaline pH (see their Figure 2b). (Note: ratios > 1 occur when nitrification consumes both newly mineralized NH_4^+ as well as NH_4^+ already present in the soil solution at the start of the assay.) In our Zhang experiment, we parameterized potential nitrification as a direct linear function of gross mineralization multiplied by a scalar computed as $\frac{(pH-4)}{6}$, reflecting the empirical linear relationship found by Zhang *et al.* Since CLM5.0 has a uniform default pH of 6.5, this scalar was effectively 0.42. In reality, soil pH at Hubbard Brook is closer to pH 4 [Groffman *et al.*, 2006b], but we used the CLM5.0 default pH=6.5, since pH=4 would have yielded zero nitrification in our scalar equation. We note that the Parton potential nitrification parameterization in both the default CLM5.0 and modification 1 also includes a pH dependent scalar, but it modifies the excess NH_4^+ term rather than the mineralization term. Unlike modification 1a, modification 2a does not include an excess soil NH_4^+ concentration term in the

nitrification parameterization.

1b and 2b) Reduced denitrification (Reduced Denit)

As described below, modifications 1a and 2a succeeded in raising nitrification rates, but nitrification:denitrification ratios remained unrealistically low in model output, implying that denitrification consumes nearly all NO_3^- generated by nitrification. We therefore turned our attention to the CLM5.0 algorithm for potential denitrification, which is based on a laboratory study of 120 soil cores with manipulated levels of 3 primary input variables, nitrate concentration $[\text{NO}_3^-]$, glucose (i.e., C substrate) and water-filled pore space (WFPS), across a range of values [Del Grosso *et al.*, 2000]. The cores were collected from 4 different soils with a history of agricultural use ranging from barley and wheat cultivation to moderate grazing. In the full dataset, the 3 input variables had only weak effects on the measured denitrification rate. To better isolate the effect of each variable, Del Grosso *et al.* defined thresholds for WFPS, $[\text{NO}_3^-]$ and measured soil CO_2 emission (a proxy for soil C availability, which provides the energy source for denitrifiers). They used those thresholds to sort the data into two subsets in which $[\text{NO}_3^-]$ and soil C, respectively, were assumed to be the limiting factors (with WFPS non-limiting in either subset). Power equations of the form $y=ax^b$ were empirically fit to each subset of data to define the potential rate of denitrification (y) as a function of x , where x was either $[\text{NO}_3^-]$ or CO_2 respiration rate. CLM5.0 takes the minimum of these $[\text{NO}_3^-]$ and C-based power equations and then further scales down that minimum by the calculated anaerobic fraction of the grid cell to determine the potential denitrification rate.

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In practice, the functional ranges of soil $[\text{NO}_3^-]$ and CO_2 respiration rate in global CLM5.0 output correspond to about the lowest 10% of the Del Grosso *et al.* input data (Appendix S1: Fig. S2). Even within this lowest 10% range, the global $[\text{NO}_3^-]$ -limited and C-limited potential denitrification rates from these functions, extrapolated over the top 20 cm of soil, are as high as $\sim 700 \text{ gN/m}^2/\text{yr}$ and $\sim 150 \text{ gN/m}^2/\text{yr}$. Furthermore, the $[\text{NO}_3^-]$ term in CLM5.0 is generally substantially larger than the CO_2 respiration term, such that C availability is typically the limiting factor governing potential model denitrification. In contrast, empirical evidence suggests that NO_3^- availability typically limits denitrification in natural ecosystems [e.g., Seitzinger *et al.*, 2006]. These results suggest that the power functions used in the potential denitrification algorithm, particularly the $[\text{NO}_3^-]$ term, may be more suitable for manipulated laboratory conditions than typical CLM5.0 conditions and probably tend to overestimate potential denitrification.

In our CLM5.0 modifications, we reduced the $[\text{NO}_3^-]$ -limited and CO_2 respiration-limited equations for potential denitrification by a factor of 100 and 10, respectively. These reductions were tailored to bring model potential denitrification into a reasonable range at Hubbard Brook, taking into account the soil anaerobic fraction in the model, which is typically 0.1-0.25 over most of the year, peaking at 0.8 in April following snowmelt. We ran two reduced denitrification modifications: 1b) Reduced Denitrification with Parton nitrification scheme (from modification 1a) and 2b) Reduced Denitrification with Zhang nitrification scheme (from modification 2a).

1c) Denitrification scaled to Nitrification (Denit=Nitrif/10)

We tested an alternative parameterization, building off modification 1a), to reduce the rate of denitrification. In this alternative approach, we bypassed the *Del Grosso et al.* [2000] algorithm altogether and instead set potential denitrification equal to potential nitrification divided by 10. This formulation was predicated on the general understanding that nitrification, which produces NO_3^- , is a necessary precursor to denitrification [Seitzinger *et al.*, 2006], combined with our own analysis of Hubbard Brook observational data described above, which indicates that denitrification rates are about an order of magnitude lower than nitrification rates.

We made two additional modifications designed to evaluate model sensitivities. These included:

1bx) No N_2 fixation

We turned off N_2 fixation (beginning from year 1 in the spin-up phase) due to concern that CLM adds an excessive amount of N to northern temperate ecosystems such as Hubbard Brook that lack symbiotic N_2 fixers and where heterotrophic N fixation rates are low [Thomas *et al.*, 2013b]. N deposition was left turned on in this experiment. N deposition and N_2 fixation in the default version of CLM5.0 are of similar magnitude at Hubbard Brook, at about $0.7 \text{ gN/m}^2/\text{yr}$ and $1.0 \text{ gN/m}^2/\text{yr}$, respectively. While the model N deposition flux matches observations for recent decades [Yanai *et al.*, 2013], model N fixation rates are roughly an order of magnitude larger than available measurements

[Roskowski 1980; Yanai *et al.*, 2013; Lovett *et al.*, 2018]. Modification 1bx was performed with the 1b) modifications (Parton increased nitrification and Reduced Denitrification adjustments) also turned on.

3) Swap NO_3^-

The order of competition for mineral N between plants and soil microbes was switched such that they competed first for NO_3^- and second for NH_4^+ . This was a swap in the sense that the default CLM5.0 competition occurs in the opposite order, i.e., first for NH_4^+ then for NO_3^- . Unlike the Parton and Zhang parameterizations, there was no empirical justification in the literature for the Swap NO_3^- modification. However, we conducted the exercise based on the hypothesis that the low rate of NO_3^- consumption by plants and immobilizers (discussed below) was related to the order of competition among mineral N species. Aside from reversing that order, we made no other adjustments to the algorithms for potential nitrification and denitrification in modification 3.

Results and Discussion

Below we discuss the results of the default CLM5.0 at Hubbard Brook, focusing first on the overall C-N cycle and on the possible fates of NH_4^+ produced by gross N mineralization, including plant uptake, immobilization and nitrification. We next discuss the role of NO_3^- in the default model, some important discrepancies with respect to Hubbard Brook observations and the results of our model modifications to address those discrepancies. Finally, we discuss the significance of our findings in the context of previous studies in the literature.

Default Model

The overall C-N cycle in CLM5.0 agrees reasonably well with observations at Hubbard Brook. The modeled total plant N uptake:gross N mineralization ratio, 0.16 ± 0.01 , is similar to the observed ~ 0.2 ratio at Hubbard Brook (Table 1). The gross NH_4^+ immobilization:gross N mineralization ratio, 0.84 ± 0.01 , is in good agreement with the observed range (0.82 ± 0.17 ; Figure 1, Table 1) [Darby *et al.*, 2020]. The absolute value of CLM5.0 gross mineralization (Figure 1, Table 1) is generally in the same range as the observations, while total plant N uptake and GPP in CLM5.0 are about 35% lower than observed, at 4.7 vs. 7.5 ± 2.5 $\text{gN/m}^2/\text{yr}$ and 830 vs. 1285 ± 62 $\text{gC/m}^2/\text{yr}$, for the model and observations, respectively (Table 1, Figure 2) [Whittaker *et al.*, 1979; Groffman *et al.*, 2018].

Despite the model's relative success in simulating the overall C-N cycle, a number of CLM5.0 N fluxes and flux ratios, particularly those involving NO_3^- , are strongly inconsistent with Hubbard Brook observations. Most notably, CLM5.0 NO_3^- immobilization is near negligible and its contribution to total N immobilization is approximately zero. In contrast, observations at Hubbard Brook suggest that NO_3^- accounts for 20-44% of total N immobilization (Table 1) [Darby *et al.*, 2020]. NO_3^- uptake by plants in CLM5.0 is also near negligible such that NH_4^+ accounts for $\sim 100\%$ of annual plant uptake. The available observations apportioning plant N uptake at Hubbard Brook support up to 94% dominance of NH_4^+ late in the growing season in September but suggest that 20% or more occurs via NO_3^- in July (Table 1, Figure 3) [Socci and Templer, 2011].

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An additional discrepancy between the model and observations is that the gross nitrification: gross mineralization ratio of 0.07 in the default CLM5.0 is considerably below the mean observed ratio of 0.45 ± 0.21 at Hubbard Brook [Groffman *et al.*, 2006b; Weitzman *et al.*, 2020; Darby *et al.*, 2020]. The model mineralization fluxes themselves are generally in a similar range as the observations, but the nitrification fluxes are too low. Accordingly, the slope of the nitrification vs. mineralization scatterplot is too shallow (Figure 1) [Groffman *et al.*, 2018].

CLM5.0 denitrification rates peak sharply in springtime, consistent with the timing of denitrification observed by Morse *et al.* [2015] and likely driven by the spring increase in the model soil anaerobic fraction. However, the 1:1 ratio of nitrification:denitrification simulated by CLM5.0 at Hubbard Brook is an order of magnitude lower than the observed ratio of 14 (range 1-76) (Table 1, Figure 3). It is not clear how extrapolatable this observed value is to other sites [Fahey *et al.*, 2015], particularly since estimates of the nitrification:denitrification ratio are generally not available in the literature. However, our best estimate of 14 is conceptually consistent with the idea that nitrification fluxes, which recycle soil N, are substantially larger than denitrification fluxes, which drive ecosystem N losses. The CLM5.0 denitrification:leaching ratio of 231 also greatly exceeds the observed ratio of ~ 4 (Table 1) and, in the underlying component fluxes, reflects a combination of large denitrification and small leaching rates in CLM5.0 relative to observations.

Model Modifications

The Parton and Zhang model modifications (1a and 2a) are both alternative parameterizations of nitrification that are linked to soil organic matter turnover rather than solely to excess NH_4^+ concentration, as in the default model. Both modifications were generally successful in boosting the ratio of gross nitrification:gross mineralization from 0.07 into ranges (0.18-0.30) more compatible with observations 0.45 ± 0.21 at Hubbard Brook (Table 1, Figure 1). Both modifications also increased the ratio of NO_3^- immobilization:total immobilization to values that were no longer negligible although still low compared to observations (Table 1).

However, model modifications 1a and 2a only raised the ratio of nitrification:denitrification slightly from 1.0 in the default model to values that were still quite low (1.5 and 2.2, respectively) (Table 1). Both modifications also sharply reduced absolute gross mineralization and plant uptake to values that were lower than observations by a factor of 3 and 5, respectively (Table 1, Figure 1). Further, they reduced GPP, NPP and soil heterotrophic respiration by more than a factor of 2, relative to the default case (Figure 2). The tendency of these increased nitrification modifications to reduce the overall rate of soil N cycling, with negative repercussions for the C cycle, indicates that too much NO_3^- and thus N overall is being lost to denitrification. This result suggests that boosting the competitiveness of nitrifiers for NH_4^+ is an insufficient step on its own to correct the model N cycle imbalances; the demand for NO_3^- of denitrifiers and their competitiveness relative to plants and immobilizers must also be reduced.

Accordingly, two additional modifications, Parton+Reduced Denit (1b) and Zhang+Reduced Denit (2b), attempted to increase the competitiveness of nitrifiers while at the same time decreasing the loss of NO_3^- to denitrification. Both modifications succeeded in simultaneously raising the fraction of gross mineralization nitrified (to 0.14 and 0.23, in 1b and 2b, respectively) and raising the nitrification:denitrification ratio (to 5.4 and 8.8), values more in line with observations. Modification (1c), in which potential denitrification was fixed at 10% of potential nitrification, also succeeded in raising both ratios, to 0.18 and ~ 10 (by design), respectively (Table 1, Figures 1 and 3).

Modifications 1b, 1c and 2b all avoided the sharp reduction of overall soil N turnover that occurred in modifications 1a and 2a. All three yielded very similar GPP, NPP and soil heterotrophic respiration fluxes, which were modestly larger than the default model C fluxes and in good agreement with observations (Figure 2).

Modifications 1b, 1c and 2b also succeeded in lowering the excessively large default CLM5.0 denitrification:leaching ratio of 231. However, the lower denitrification:leaching ratios masked unresolved issues with the underlying absolute fluxes, particularly the leaching flux. The leaching flux increased from negligible values in the default model to 0.85 gN/m²/yr for modifications 1b and 2b and to 1 gN/m²/yr for modification 1c, values substantially larger than the well-documented observed value of about 0.1 gN/m²/yr [Likens, 2013; Yanai *et al.*, 2013]. This was due primarily to a large buildup of soil NO_3^- between 5-20 cm depth. Meanwhile, the absolute denitrification

flux simulated by CLM5.0 was reduced substantially from the default model, especially for modification 1c, but fell generally within the (large) range of observations at Hubbard Brook (Table 1).

The higher-than-observed N losses in the model, from both leaching and denitrification, may reflect steady state assumptions inherent to our simulations in which soil losses are balanced by inputs from deposition and N fixation, while observational studies have shown that N inputs from deposition alone exceed losses over the last several decades [e.g., *Bernal et al.* 2012, *Yanai et al.* 2013, *Groffman et al.* 2018, *Lovett et al.* 2018]. Modification 1bx addressed the possibility that excess N loss in part may reflect excessive N input through biological N₂ fixation, a concern noted previously for CLM in northern temperate forests [*Thomas et al.*, 2013b, *Cheng et al.*, 2019]. This modification was successful in reducing denitrification and leaching losses, although the leaching losses were still high compared to observations (Table 1), while having little impact on model C fluxes (Figure 2). Effectively the N deposition input flux on its own, even without the N₂ fixation input, appears large enough to launch an internal recycling of soil N that fully covers plant and microbial N needs. Notably, N deposition is treated as a completely external input in CLM5.0 even though in the real world it is derived partly from soil NO_x and NH₃ emissions [*Riddick et al.*, 2016; *Lawrence et al.*, 2019; *Donagoboslu et al.*, 2020].

Here we note that by running CLM5.0 in perpetual 2000 conditions, our study does not address transient effects, such as net accumulation of fixed N (and associated carbon) in

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soils and vegetation. We used a steady state protocol because we wanted to isolate the effects of our modifications to CLM5.0 on simulated N fluxes from the model's inherent tendency to return to steady state.

In the default CLM5.0, the nearly complete dominance by NH_4^+ of plant uptake and immobilization appears to result from the combination of low model nitrification rates, which produce little NO_3^- , and the related fact that NH_4^+ alone is generally sufficient to meet ecosystem N requirements, such that there is no residual demand for NO_3^- (Figure 3). Due to the sequential nature of the simulated competition first for NH_4^+ and then for NO_3^- , potential NH_4^+ immobilization is set equal to the total N immobilization demand, while potential NO_3^- immobilization is set equal to the total N immobilization demand minus actual NH_4^+ immobilization, where that difference is effectively zero. Similar results hold for plant N uptake. The Parton and Zhang modifications (1a and 2a), with or without accompanying reductions in denitrification, have the effect of diverting some NH_4^+ toward nitrification, such that a residual demand for NO_3^- plant uptake and immobilization remains (Figure 3).

The Swap NO_3^- modification greatly increased the NO_3^- :total immobilization ratio from ~ 0 in the default CLM to 0.46, slightly in excess of the observed ratio of 0.2-0.44. (Table 1). The modification effectively shifted plant uptake from ~100% dominance by NH_4^+ to 71% dominance by NO_3^- . Neither result is consistent with available observations, which suggest moderate contributions from NO_3^- uptake (Table 1) [Socci and Templer, 2011]. Interestingly, however, the Swap NO_3^- C fluxes were similar to those of most of the other

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modifications (Figure 2). Other outcomes relative to the default case were that the gross nitrification:gross mineralization ratio increased from 0.07 to 0.55, while the NH_4^+ immobilization:gross mineralization ratio was halved from 0.84 to 0.42. These ratios represent a dramatic reversal in the fate of NH_4^+ compared to the default CLM5.0 and are generally incompatible with observations at Hubbard Brook (Table 1, Figure 3). Overall, the Swap NO_3^- modification suggests that the sequential competition among plants and microbes for one mineral N form and then the other may be inherently problematic, regardless of which competition occurs first.

Relevance to previous research

Similar to our current results with CLM5.0, other studies have shown that earlier versions of CLM simulated excessively large losses of N by gaseous instead of leaching pathways when compared to observations in the northeastern U.S. [Thomas *et al.*, 2013a] as well as globally [Houlton *et al.* 2015]. Both of these studies used CLM4.0 (Houlton *et al.* also examined CLM4.5), which did not treat soil NO_3^- and NH_4^+ as separate pools and used an ad hoc parameterization that assumed half of any excess soil inorganic N at any given time step was lost to denitrification.

The introduction of explicit NO_3^- and NH_4^+ pools in CLM4.5 and subsequent model versions and the use of the Del Grosso *et al.* [2000] parameterization, which is based on empirical data, was part of an effort to simulate denitrification in a more defensible, mechanistic manner [Koven *et al.*, 2013]. However, the representation of NH_4^+ and NO_3^- pools has created a new set of concerns related to the production, uptake and loss of NO_3^-

from terrestrial ecosystems. Our companion paper on global CLM5.0 simulations shows that the unrealistic results identified at Hubbard Brook, e.g., the 1:1 nitrification:denitrification ratio and the dominance of denitrification over other fates of NO_3^- , such as plant uptake, immobilization and leaching, are not unique to northern temperate forest grid cells but rather are widespread in the model [Nevison *et al.*, 2020].

A study with CLM4.0 found that the model overestimated the responsiveness of aboveground NPP to N additions, compared to a meta-analysis of ^{15}N tracer field experiments [Thomas *et al.*, 2013b]. A more recent N fertilization study with CLM5.0 also found that model recovery of N by plants was higher than that observed in ^{15}N tracer addition experiments by a factor of 2 [Cheng *et al.*, 2019]. At the same time, model recovery of N in soil was underestimated compared to field data and furthermore was not due to direct immobilization of added N, as observed, but rather proceeded indirectly via the cycling of N through plants. This latter result seems consistent with our finding of negligible NO_3^- immobilization in CLM5.0, which can be an important pathway for NO_3^- retention in many ecosystems [Nadelhoffer *et al.*, 2004; Goodale 2017].

Modification (1b) might be regarded as this study's best recommendation for simple adjustments to the CLM5.0 nitrification and denitrification algorithms that are faithful to the original parameterizations upon which they are based [Parton *et al.*, 2001; Del Grosso *et al.*, 2000] and succeed in promoting NO_3^- to a more significant (i.e., nonnegligible) role in the soil N cycle. However, a more thorough revision of the CLM5.0 denitrification scheme as well as a sensitivity study across the full nitrification

and denitrification parameter space would be useful goals for future work. Modification 1c, which constrained denitrification to be only about 10% of nitrification, yielded generally better agreement with observed N fluxes and flux ratios than modification 1b, but the nitrification:denitrification ratio is highly unlikely to be constant over the wide range of varying field conditions controlling soil oxygen levels and N- and C availability. In general, empirical parameterizations likely need to be evaluated over a range of soil types and ecosystems before they are applied as one-size-fits-all algorithms in global scale models like CLM5.0.

Conclusion

CLM5.0, while capturing observed C fluxes relatively well at the Hubbard Brook LTER site, has some notable discrepancies with observations in its simulation of soil N fluxes. These include near negligible NO_3^- plant uptake, NO_3^- immobilization and leaching rates, low nitrification:gross mineralization ratios, and 1:1 nitrification:denitrification ratios that are likely an order of magnitude too small. Similar results appear in global CLM5.0 output, suggesting such discrepancies with observations are widespread. These discrepancies raise concerns about how reliably CLM5.0 can project future changes in the coupled C-N cycle, e.g., in response to increasing CO_2 concentrations or fertilization or changing N deposition.

Modifications to CLM5.0 that simultaneously increase nitrification while decreasing denitrification succeed in raising NO_3^- immobilization and NO_3^- plant uptake rates while

yielding a more realistic balance between recycling of N via nitrification vs. loss via denitrification. The modifications to nitrification are relatively straightforward and grounded in empirical data, while the CLM5.0 denitrification parameterization likely requires a more thorough revision than the simple fixes applied here. Another concern is that the reduction in denitrification leads to a buildup of subsurface NO_3^- and accompanying large leaching rates. This result could be linked to an excessive biological N_2 fixation input to the model and to the steady state protocol of the simulations conducted here, which didn't allow for accumulation or loss of fixed N. Additional work is needed to evaluate the impact of modifications to nitrification and denitrification on terrestrial C and N cycles globally and in transient simulations.

Our study highlights the need for more field studies of soil N fluxes and flux ratios. Such observational data would be useful for model evaluation and for improving confidence in model simulation of N limitation on the C cycle. Measurements that provide insight into the empirical controls on denitrification, and how these can be translated into a land model algorithm, would be especially useful. LTER sites like Hubbard Brook, with a long history and variety of N cycle studies, can help provide such observations.

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Supporting Information

Additional supporting information may be found online at: [link to be added in production]

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NO_3^-	^a 0.31	0.0005	0.05	0.07	0.08	0.08	0.15 (.01)	0.16	0.46
Immobilization:	(0.23-0.4)	(.0003)	(.006)	(.03)	(.01)	(.06)		(.03)	(.07)
Total									
Immobilization									
NH_4^+ plant	^c 0.57-0.82	1.0	0.95 (.02)	0.88	0.86	0.86	0.82 (.02)	0.77	0.29
uptake:	July; 0.93-	(.002)		(.08)	(.02)	(.15)		(.06)	(.16)
Total plant	0.95 Sept.								
uptake									
Nitrification:	^a 0.45	0.065	0.18	0.14	0.13	0.18	0.30	0.23	0.55
Gross	(0.24-	(.007)	(.004)	(.01)	(.01)	(.04)	(.003)	(.01)	(.07)
Mineralization	0.66) ^d								
Nitrification:	^e 14 (1-76)	1.0	1.5 (.1)	5.4 (1.0)	7.1	9.9 (0.8)	2.2 (0.3)	8.8 (1.9)	11 (3)
Nitrification	(.02)				(1.7)				
D nitrification:	^f ~ 4	231	22 (6)	1.4 (1.4)	1.9	0.55	14 (3.5)	1.4 (1.3)	99

NO_3^- Leaching	0.4:0.1	(209)	1.5:0.07	0.85:0.8	(1.1)	0.55:1.0	1.4:0.10	0.85:0.8	(83)
		1.7:0.0		1	0.55:0.			1	1.7:0.0
		1			4				3

^a Darby et al., 2020.

^b Total plant uptake based on update of *Whittaker et al.* [1979] in which measured NPP is combined with measured C:N ratios in various plant components. Absolute values of the individual fluxes in $\text{gN/m}^2/\text{yr}$ are shown in italics.

^c *Socci and Templer*, 2011 studies with sugar maple and red spruce.

^d Range also supported by *Groffman et al.*, 2006b and *Weitzman et al.*, 2020.

^e Estimated based on *Morse et al.*, 2015 denitrification flux of 0.4 (0.2-1.8) $\text{gN/m}^2/\text{yr}$ and *Durán et al.*, 2016 in situ net nitrification ratio of 3.0 (0.5-7.2) $\text{gN/m}^2/\text{yr}$, scaled by *Darby et al.*, 2020 gross:net nitrification ratio of 3.9:2.1.

^f *Morse et al.*, 2015 denitrification flux divided by *Yanai et al.* [2013] leaching estimate of ~0.1 $\text{gN/m}^2/\text{yr}$. Absolute values of the individual fluxes in $\text{gN/m}^2/\text{yr}$ are shown in italics.

^g The Parton and Reduced Denitrification parameterizations were also turned on.

Figure Captions

Figure 1. Scatterplot of NH_4^+ immobilization vs. gross mineralization (blue squares) and gross nitrification vs. gross mineralization (red circles) for CLM5.0 at Hubbard Brook, both in the default configuration and for 7 experiments. Annual mean output is plotted over 20 model years as large symbols while the range of the monthly mean output is shown as small dots. Fit lines and text show Deming regression slopes to the annual mean output. Open red squares reflect observations of annual potential nitrification and gross mineralization measured at Hubbard Brook over 2007-2012, which have a linear regression slope (dotted red line) of 0.4 ± 0.02 ($R=1.0$) [Groffman *et al.*, 2018]. The observed range of the NH_4^+ immobilization:gross mineralization ratio (not shown) is 0.82 ± 0.17 .

Figure 2. Annual mean GPP, NPP and soil heterotrophic respiration fluxes for observations and simulations with CLM5.0 at Hubbard Brook, both in the default configuration and for 7 model modifications. Gray bars show observations and estimated uncertainties from Ouimette *et al.* [2018]. Model values and error bars reflect 20 year means and standard deviations.

Figure 3. Annual mean a) NO_3^- immobilization: immobilization, b) NO_3^- uptake:total plant uptake, c) gross nitrification:gross mineralization, d) gross nitrification:denitrification, and e) denitrification: NO_3^- leaching ratios (note: log scale for the latter) for observations and simulations with CLM5.0 at Hubbard Brook, both in the default configuration and for 7 model modifications. Gray bars show observations and estimated uncertainties as described in Table 1. Model values and error bars reflect 20 year means and standard deviations.

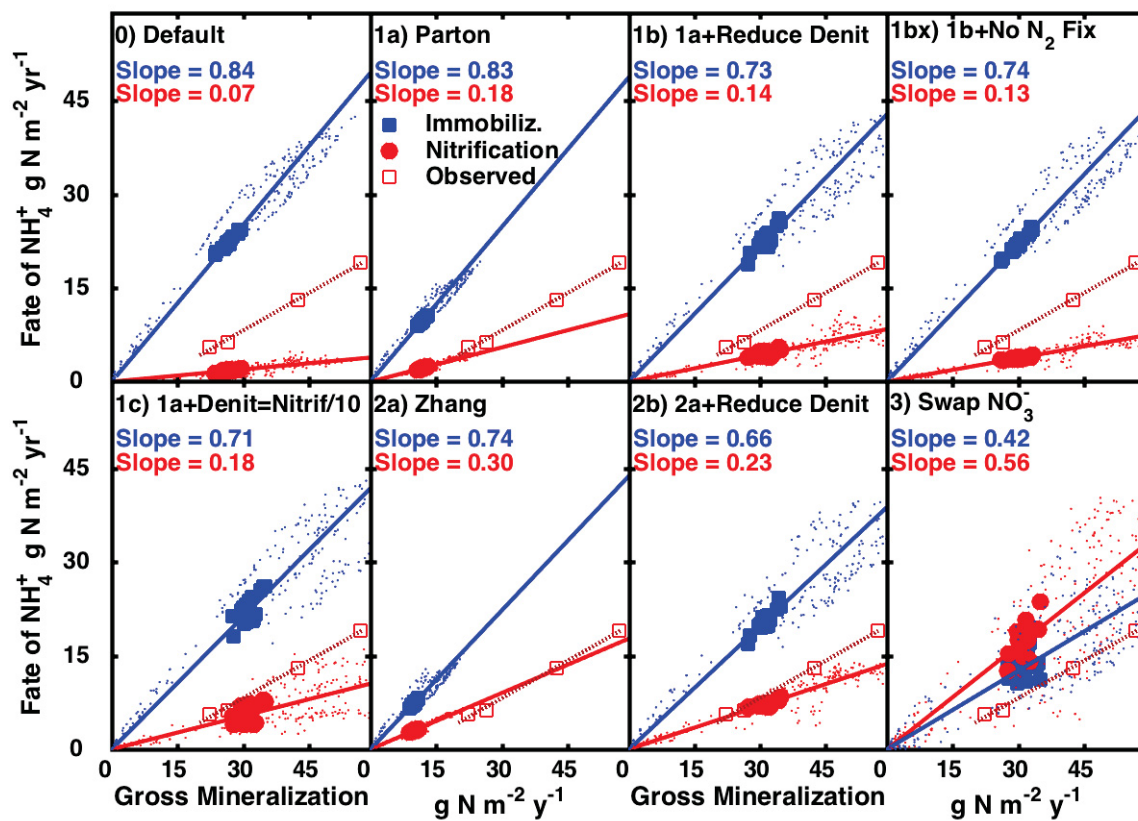


Figure 1.

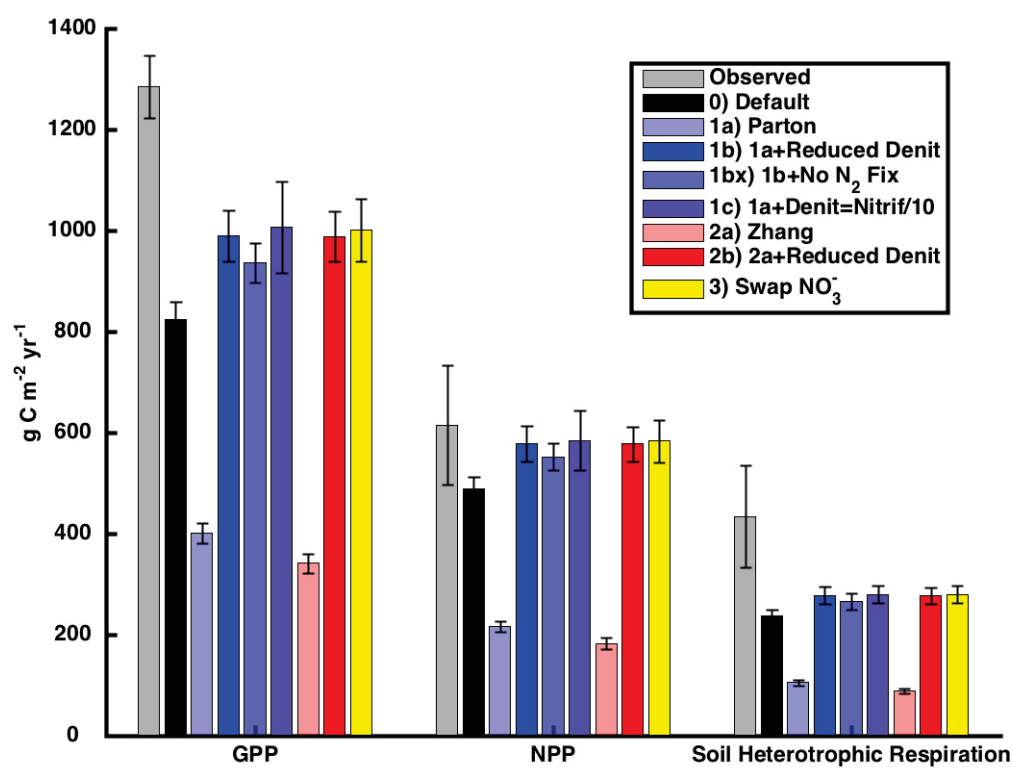


Figure 2.

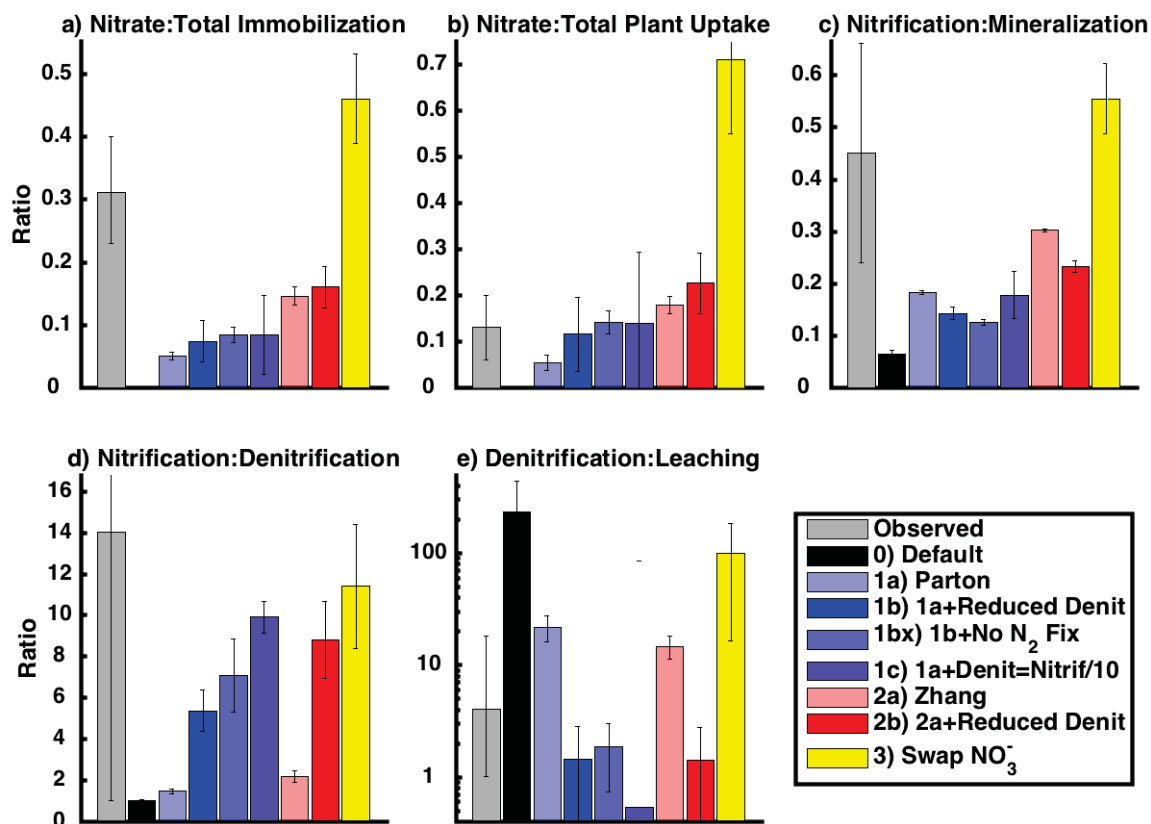


Figure 3.