AGU PUBLICATIONS

Journal of Advances in Modeling Earth Systems

RESEARCH ARTICLE

10.1002/2015MS000573

Key Points:

- River N export is modeled prognostically with the coupled Community Land Model-River Transport Model
- Nitrogen loss parameterizations in CLM are uncertain, with implications for model C-N interactions
- Comparison of modeled and observed river N export can help provide constraints on CLM N loss

Correspondence to:
C. Nevison,
cynthia.nevison@colorado.edu

Citation:
Nevison, C., P. Hess, S. Riddick, and D. Ward (2016), Denitrification, leaching, and river nitrogen export in the Community Earth System Model, *J. Adv. Model. Earth Syst.*, *8*, 272–291, doi:10.1002/2015MS000573.

Received 27 OCT 2015
Accepted 3 FEB 2016
Accepted article online 6 FEB 2016
Published online 6 MAR 2016

Denitrification, leaching, and river nitrogen export in the Community Earth System Model

Cynthia Nevison[1], **Peter Hess**[2], **Stuart Riddick**[3], **and Dan Ward**[2,4]

[1]Institute for Arctic and Alpine Research, University of Colorado, Boulder, Colorado, USA, [2]Department of Biological Environmental Engineering, Cornell University, Ithaca, New York, USA, [3]Centre for Atmospheric Science, University of Cambridge, Cambridge, UK, [4]Now at Department of Atmospheric and Oceanic Sciences, Princeton University, Princeton, New Jersey, USA

Abstract River nitrogen export is simulated within the Community Earth System Model (CESM) by coupling nitrogen leaching and runoff fluxes from the Community Land Model (CLM) to the River Transport Model (RTM). The coupled CLM-RTM prognostically simulates the downstream impact of human N cycle perturbation on coastal areas. It also provides a framework for estimating denitrification fluxes of N_2 and associated trace gases like N_2O in soils and river sediments. An important limitation of the current model is that it only simulates dissolved inorganic nitrogen (DIN) river export, due to the lack of dissolved organic nitrogen (DON) and particulate nitrogen (PN) leaching fluxes in CLM. In addition, the partitioning of soil N loss in CLM between the primary loss pathways of denitrification and N leaching/runoff appears heavily skewed toward denitrification compared to other literature estimates, especially in nonagricultural regions, and also varies considerably among the four model configurations presented here. River N export is generally well predicted in the model configurations that include midlatitude crops, but tends to be underpredicted in rivers that are less perturbed by human agriculture. This is especially true in the tropics, where CLM likely underestimates leaching and runoff of all forms of nitrogen. River export of DIN is overpredicted in some relatively unperturbed Arctic rivers, which may result from excessive N inputs to those regions in CLM. Better representation of N loss in CLM can improve confidence in model results with respect to the core model objective of simulating nitrogen limitation of the carbon cycle.

1. Introduction

Nitrogen is a key limiting nutrient that strongly influences the carbon cycle through down regulation of gross primary production (GPP) and soil decomposition. Nitrogen is increasingly being incorporated into terrestrial ecosystem models (TEMs), with the goal of more accurately predicting the evolution of atmospheric CO_2 and also allowing the explicit calculation of the soil emissions of environmentally important reactive nitrogen species like N_2O. Carbon-only models that neglect nitrogen limitation have been criticized for predicting overly optimistic future land carbon uptake via the CO_2 fertilization effect, which cannot be supported by the limited available N [*Friedlingstein et al.*, 2006; *Hungate et al.*, 2003; *Wang and Houlton*, 2009]. Indeed, climate models coupled to TEMs that include nitrogen limitation tend to predict higher future atmospheric CO_2 concentrations, due to reduced CO_2 fertilization, than climate models coupled to carbon-only TEMs [*Sokolov et al.*, 2008; *Thornton et al.*, 2009; *Zaehle et al.*, 2014]. This is true despite the mitigating effect of climate change-induced enhancement of soil nitrogen mineralization, which promotes N availability to plants [*Shaver et al.*, 1992; *McGuire et al.*, 2007].

In the TEM framework, nitrogen controls GPP and soil decomposition via the soil inorganic nitrogen pool. This pool comprises only a small fraction of total ecosystem nitrogen ($<$1% in many TEMs), but exerts a disproportionately large effect on the model carbon cycle. The size of the soil inorganic N pool reflects a dynamic balance between inputs and outputs. External N inputs to TEMs include biological nitrogen fixation, atmospheric deposition and, in models that include human agriculture, the application of nitrogenous fertilizers to soils. All three processes, particularly N fertilizer application, have increased over the past century due to human activities, leading to large changes in both the geographic distribution and the overall magnitude of N inputs to terrestrial ecosystems [*Galloway et al.*, 2004, 2008]. Outputs include N leaching losses and volatilization of gaseous species like N_2, N_2O, NO, and NH_3. A net positive balance between N inputs and outputs leads to net ecosystem N retention, with associated carbon storage that is particularly important in forest ecosystems with wide C:N ratios in woody tissue [*Hungate et al*., 2003; *Wang and Houlton*, 2009].

N inputs from atmospheric deposition in TEMs typically are prescribed based on atmospheric chemistry transport model simulations, with careful attention to magnitude and geographic distribution [*Lamarque et al*., 2005; *Dentener et al*., 2006]. N inputs from biological nitrogen fixation (BNF) commonly are parameterized as functions of NPP or evapotranspiration [*Cleveland et al*., 1999]. These parameterizations involve substantial uncertainty and may tend to overestimate BNF in temperate and boreal ecosystems, but still capture broad-scale geographic patterns reasonably well [*Cleveland et al*., 1999; *Thomas et al*., 2013b].

In contrast, inorganic N losses in TEMs, including leaching and denitrification fluxes, are not always realistic biogeochemically and the ultimate fate of the N after it leaves the model generally is not specified. In earlier versions of CLM, N leaching fluxes were dramatically underestimated relative to available observations in forest and boreal ecosystems, while denitrification was prescribed as an ad hoc loss of a fixed fraction of excess mineral N that primarily served to prevent inorganic N buildup [*Thomas et al*., 2013a]. Inorganic N losses thus are one of the most uncertain fluxes in global carbon-nitrogen models but at the same time exert an important influence on how TEMs respond to increasing atmospheric CO_2, e.g., helping to determine to what extent future NPP is restricted by progressive N limitation [*Walker et al*., 2015]. The scarcity of suitable observations of N loss fluxes has been cited as a major impediment to developing and validating global coupled C-N models and improving confidence in their future predictions of carbon uptake [*Zaehle et al*., 2010].

Meanwhile, the growing anthropogenic perturbation to the global nitrogen cycle and the associated increases in inorganic N loss are important environmental concerns in their own right. The main product of denitrification, inert N_2 gas, is not itself a pollutant, but other gaseous N species lost from soil, including N_2O, NO_x, and NH_3, contribute to localized acidification and eutrophication, air pollution, modified radiative forcing, tropospheric O_3 production, and stratospheric O_3 loss [*Forster et al*., 2007; *Ravishankara et al*., 2009]. In addition, soil N leaching losses have led to increased nitrogen export in rivers, especially in agricultural areas receiving large fertilizer inputs. The growth in river N export has led to coastal eutrophication and the expansion of "dead zones" in coastal waters worldwide [*Rabalais*, 2002; *Seitzinger et al*., 2010; *Howarth et al*., 2012]. Further, denitrification of N in river and stream sediments and receiving coastal areas is increasingly recognized as an important source of N_2O to the atmosphere [*Beaulieu et al*., 2011; *Ivens et al*., 2011].

In principle, terrestrial ecosystem models (TEMs) with coupled carbon-nitrogen interactions are appropriate, prognostic tools for modeling the export of N in rivers to the coastal zone. TEMs can receive and process N inputs from BNF, atmospheric deposition, and agricultural manure and synthetic fertilizer application. They simulate soil hydrology and vegetation-dependent variations in primary production, decomposition, and C:N ratios of leaves and soil organic matter. All these variables combine to influence the amount of N leached from watersheds into groundwater, streams, and rivers. At present, however, TEMs are not widely used to simulate river N dynamics [*Lee et al*., 2014]. Rather, most current models of river N export are primarily diagnostic rather than prognostic [*Seitzinger and Kroeze*, 1998; *Green et al*., 2004; *Van Drecht et al*., 2005; *Wollheim et al*., 2008].

Diagnostic river models use correlations between a variety of N inputs to watersheds and observed river N export to estimate watershed-to-river "transfer coefficients," which describe the leached fraction of the N inputs. In many recent models, the prescribed N inputs are coupled to gridded global water balance/river routing models with the primary goal of modeling river N export to the coastal zone, and in some cases also tracking the evolution of N concentrations along the length of the river [*Wollheim et al*., 2008; *Seitzinger et al*., 2010]. River routing models use topological networks to calculate horizontal flows of water and dissolved constituents between neighboring grid cells, based on mass balance relationships. Denitrification loss within streams and rivers is parameterized a function of hydrological properties such flow volume, velocity, and length. In-stream denitrification occurs primarily within oxygen-depleted bottom sediments and typically removes about half of the original leached N input [*Seitzinger et al*., 2002; *Boyer et al*., 2006]. Fractional loss is greatest in small, slow moving streams, where long residence times and shallow depths allow for frequent contact of dissolved nitrogen with sediments [*Alexander et al*., 2002; *Seitzinger et al*., 2002; *Donner et al*., 2002; *Wollheim et al*., 2008].

An advantage of diagnostic models is that they reproduce observed river N export relatively accurately, with R^2 values typically in the 0.7–0.8 range [*Seitzinger and Kroeze*, 1998; *Van Drecht et al*., 2003]. The accuracy results in part from the empirically derived watershed-to-river N transfer coefficients and also from the water runoff inputs to the river routing model. Runoff in these diagnostic models commonly is derived from a water balance model driven by climatological precipitation and temperature inputs and is constrained to agree with observed climatological river discharge [*Fekete et al*., 2002]. Despite their relative accuracy in modeling current patterns of river N export, a disadvantage of diagnostic models is that they are bound by existing relationships among river N export, climate, and N inputs to watersheds, whereas TEMs in principle can model these relationships prognostically. This capability may be particularly important when diagnosing river N export in future scenarios with encompassing changes in climate, agriculture, and atmospheric N deposition.

In this paper, we present a preliminary effort to model river N export in a global TEM, the Community Land Model (CLM) coupled to the River Transport Model (RTM), both of which are modules within the Community Earth System Model (CESM). While current uncertainties in the CLM nitrogen leaching rates pose challenges, we explore these uncertainties by examining results from several alternative versions of CLM. The distribution and magnitude of N leaching and volatilization losses and resulting differences in river N export patterns among different model versions are evaluated. Our primary goal is to establish a framework for modeling N river export, which will lay the groundwork for more realistic simulations as the representation of the agricultural N cycle evolves in the model and the parameterization of denitrification and leaching rates improves.

A secondary goal is to examine the potential of the coupled CLM-river N transport model to serve as a constraint on N loss pathways in the CLM-CN, given the relative abundance of river N concentration data compared to the dearth of landscape denitrification data. The largest loss term for nitrogen from terrestrial ecosystems is thought to be denitrification to N_2 gas [*Gruber and Galloway*, 2008; *Schlesinger*, 2009], but measuring N_2 fluxes at regional or ecosystem scales is difficult given the large background burden in the atmosphere [*Groffman et al*., 2006]. In contrast, the concentration of N in rivers and streams resulting from leaching and runoff is relatively well documented in both observational and diagnostic river model databases. Further, the N discharge observed at the coastal outlet of rivers provides a large-scale, integrated measure of total N exported from the regional watershed [*Meybeck*, 1982; *Van Drecht et al*., 2003; *Seitzinger et al*., 2010]. Thus, coupled TEM-river routing models, such as the CLM-RTM presented here, potentially can serve as a constraint on N loss pathways in TEMs, while also permitting the representation of the increased export of N in rivers to the coastal zone, one of the major consequences of global N cycle perturbation.

2. Methods

2.1. Community Land Model

The Community Land Model with coupled Carbon and Nitrogen cycles (CLM-CN) is the terrestrial component of the Community Earth System Model [*Thornton and Rosenbloom*, 2005; *Thornton et al*., 2007; *Thornton et al*., 2009]. A more recent version of the model, CLM-BGC (biogeochemistry) v4.5, differs from CLM-CN in that it includes vertically resolved soil biogeochemistry and explicitly resolves soil mineral NH_4^+ and NO_3^- pools [*Koven et al*., 2013]. The current study uses several different variants of CLM-BGC, run offline (i.e., uncoupled to all other CESM components except for the River Transport Model (RTM) described below) on a $1.9^\circ \times 2.5^\circ$ finite volume grid. External N inputs to CLM include BNF and atmospheric N deposition. BNF is estimated using an NPP-scaled algorithm based on *Cleveland et al*. [1999]. Atmospheric N deposition is based on an offline atmospheric transport model (ATM) simulation [*Lamarque et al*., 2005]. While the original ATM simulation distinguishes reduced (NH_x) and oxidized (NO_y) forms of reactive N, CLM assumes that both forms go into the soil NH_4^+ pool upon deposition.

The CLM hydrology module simulates surface and subsurface fluxes of water, which are used as one-way inputs to the River Transport Model (RTM) described below [*Oleson et al*., 2008]. The CLM biogeochemistry module includes litter and soil organic matter dynamics and explicit competition between plants and soil biota for soil mineral nitrogen resources. The soil biogeochemistry parameterizations are linked to the model hydrology to calculate dissolved inorganic nitrogen (DIN) fluxes associated with both surface runoff and subsurface leaching (the sum is referred to here as the leaching/runoff flux). At present, the model does not simulate dissolved organic N (DON) fluxes such as leaching losses or uptake by plants and mycorrhizae, nor does it simulate leaching of particulate nitrogen (PN), although both DON and PN are important components of the total N flux in many rivers [*Seitzinger et al*., 2005].

CLM includes a crop model option, which is based on the Agro-IBIS agroecosystems model [*Kucharik and Brye*, 2003; *Kucharik and Twine*, 2007], as described in *Levis et al*. [2012]. Agro-IBIS is a process-based ecosystem model capable of simulating managed ecosystem dynamics to explicitly model corn, soybean, and wheat crop systems. Global cropland distribution is prescribed for circa 2000 conditions based on the 0.5° × 0.5° data set described in *Ramankutty and Foley* [1999], which is derived from a combination of remote sensing and atlas data. Synthetic nitrogen fertilizer inputs are prescribed based on the above crop distribution and crop-specific fertilization rates. Uniform fertilization rates are assumed for each crop type, generally based on information from North American crops, and the prescribed fertilizer input is directed into the soil NH_4^+ pool. In CLM v4.5, the crop model is constrained to run under perpetual year 2000 conditions.

In this paper, we present results from four different variants of CLM v 4.5, differing in their spin-up as well as their incorporation of nitrogen inputs. These versions allow us to analyze the impact of crops on nitrogen losses with and without the use of fertilizer vis-à-vis a control simulation with no crops. In addition, we evaluate a simulation where the explicit surface cycling of nitrogen from fertilizer and manure application is modeled. In the first three cases, the models are analyzed when the net ecosystem nitrogen exchange has achieved a near equilibrium. This allows the model results to be compared against each other. An alternative framework would have been to run transient simulations from the preindustrial to the present day, as the present-day nitrogen cycle is most likely not in balance due to increases in nitrogen inputs and land use change. However, the mechanisms to input transient cropland from the preindustrial had not yet been developed for these simulations. Further, errors in comparing spun-up simulations to measurements are likely small in comparison to other model uncertainties.

A goal for the future is to develop a more sophisticated coupled C-N agricultural crop model that is fully spun-up to the preindustrial and then forced with changing agricultural practices and land-use. For the current study, we believe the four variants described below are sufficient to establish: (i) a framework for modeling N river export and (ii) the potential of the coupled CLM-river N transport model to serve as a constraint on N loss pathways in the CLM-CN.

1. The standard CLM-BGC v4.5 release with crop model option (*Temperate Crop*), which simulates managed crops in the temperate zone north or south of 30° latitude and also includes a generic unmanaged crop plant functional type (PFT) in the tropics [*Levis et al*., 2012]. Only managed crops receive N fertilizer inputs. The Temperate Crop model was forced by a repeating 33 year NCEP atmospheric reanalysis data set (1972–2004) [*Qian et al*., 2006] and run with CO_2 fixed at 367 ppm and constant 2000 N deposition. For the results presented here, the simulation was started from a nominally spun-up initial file and run an additional 175 years, at which time the nitrogen loss fluxes and the net ecosystem nitrogen exchange had achieved a near equilibrium (Table 1). (The "nominally spun-up" initial file had branched off of a spun-up no-crop version of CLM4.5 and run for 300 years (S. Levis, personal communication, 2015), but was not yet in equilibrium with respect to net ecosystem N exchange.)
2. A version of the temperate crop model identical to that described above, except that the N fertilizer input was set to zero (*Temperate Crop NF*). This simulation was started from the same nominally spun-up initial file described above and run an additional 307 years (i.e., through four additional cycles of the 33 year NCEP atmospheric reanalysis data set compared to the standard Temperate Crop simulation), to achieve a near equilibrium in the net ecosystem nitrogen exchange and N loss fluxes (Table 1).
3. The standard CLM-BGC v4.5 release without crops (*No Crop*), which includes N inputs from atmospheric deposition and BNF but not fertilizer [*Koven et al*., 2013]. The no-crop model used the same meteorological drivers and atmospheric N deposition and CO_2 forcing of the Temperate Crop simulations. This version was initialized from a cold start, with a 1000 year accelerated decomposition spin-up, followed by a 200 year final spin-up and an additional 50 years simulation, at which point the nitrogen fluxes had achieved a near equilibrium (Table 1).
4. A version of CLM-BGC v4.5 was developed to model the global NH_x cycle following manure and fertilizer input (*Mechanistic NH_x*). This model estimates NH_3 volatilization, reactive nitrogen (N) run-off, and formation of soil mineral and organic N from sources of animal manure and synthetic fertilizer [*Riddick et al*., 2015]. The nitrogen runoff is based on the runoff of rain water (as calculated in CLM4.5) and the

Table 1. Soil Inorganic N Budgets for 3 Versions of CLM[a]

	No Crop	Temperate Crop NF No N Fertilizer	Temperate Crop Standard Case
N Inputs			
Biological N fixation	106 ± 1	88 ± 0.9	88 ± 0.9
Atmospheric deposition	65 ± 0	65 ± 0	65 ± 0
Synthetic fertilizer	0	0	36 ± 0
N Outputs			
Leaching	0.6 ± 0.02	9 ± 0.4	12 ± 0.6
Runoff	10 ± 0.5	19 ± 0.7	24 ± 0.9
Denitrification	91 ± 6	83 ± 4	105 ± 4
[b]Fire (Pyrodenitrification)	**61** ± 6	**42** ± 4	**42** ± 4
[c]N_2O emissions	4.0 ± 0.2	3.9 ± 0.2	5.5 ± 0.2
Net Ecosystem N Change	−3 ± 11	0 ± 7	−5 ± 7

[a] Table values are in Tg N yr^{-1} and show the average and standard deviation of the last 10 simulation years.

[b] Pyrodenitrification via biomass burning is shown in grey background because it is not lost directly from the soil inorganic N pool.

[c] N_2O loss is encompassed within the denitrification flux and thus is not included in the net ecosystem N change summation.

concentration of nitrogen in the total ammoniacal nitrogen (TAN) synthetic fertilizer and manure pools, as calculated in the new NH_x module. The simulation is effectively a "one-way" version of CLM in which the NH_x module receives hydrology, soil, and climate inputs from CLM but does not feedback on the carbon cycle. This model configuration therefore did not require fully spun-up carbon and nitrogen pools within CLM and for that reason is not included in Table 1 below. Instead of the crop PFT-based approach for specifying N fertilizer inputs, the Mechanistic NH_x model uses prescribed manure inputs circa 2007 of 128 TgN/yr and synthetic fertilizer inputs circa 2000 of 70 TgN/yr from *Potter et al*. [2010]. The model was run for 20 years beginning in 1990 with cycled CRUNCEP meteorology [*Viovy and Ciais*, 2009] with transient N deposition through 2005 and CO_2 fixed at 367 ppm. Only fluxes calculated directly from the Mechanistic NH_x model from input manure and fertilizer (and not CLM) fluxes, from the last 10 years of the simulation, are presented here.

2.2. River Transport Model With N Added as Tracer

The River Transport Model (RTM) [*Dai and Trenberth*, 2002; *Branstetter and Erickson*, 2003] is a river routing scheme that is a stand-alone module within CESM. RTM receives surface and subsurface runoff from the CLM hydrology module and routes the water among cells to their downstream neighbors using elevational gradients and a mass balance between horizontal water inflows and outflows. The horizontal inflows represent the sum of the inflows from adjacent upstream cells. The downstream flow direction for each cell is determined based on the steepest downhill slope. Since RTM is typically run at finer resolution ($0.5° \times 0.5°$) than CLM, the CLM runoff is interpolated to the RTM grid. For this study, the combined dissolved inorganic N runoff and leaching fluxes calculated by CLM were used as a new input to RTM, and DIN was added as a new transported variable (in addition to water and ice) within RTM. Here, "runoff" is defined as the dissolved nitrate in surface runoff, while leaching refers to subsurface loss of nitrate dissolved in soil water. Although an optional flooding module exists in CLM, the CLM fluxes were input to RTM in one-way mode. Thus, RTM does not represent long-term storage and release of groundwater or its dissolved N constituents to rivers and streams.

Nitrogen is lost to denitrification during its course downstream and may also be subject to other transformations such as assimilatory N uptake and nitrification. For the current study, we focus on denitrification as the first order control on N removal in river networks, consistent with other global-scale efforts that omit the higher order processes [*Wollheim et al*., 2008; *Seitzinger et al*., 2002, 2010]. Our treatment of N contrasts with that of water, which is transported conservatively to the ocean by RTM. We simulate in-stream denitrification using the relationship described in *Wollheim et al*. [2008],

$$f = 1 - \exp(-v_f \tau / d), \qquad (1)$$

where f is the steady state fraction denitrified, d is depth (m) estimated as an empirical function of flow as per *Leopold and Maddock* [1953], v_f (m/yr) represents a biological activity coefficient for denitrifiers which is set to a constant value of 35 m/yr. τ is the residence time within the river in years, estimated as the distance of each 0.5° river segment divided by the assumed RTM constant flow rate of 0.35 m/s. The river segment distance in RTM is based on grid cell length and does not account for sinuous or meandering rivers. The steady state removal fractions from equation (1) are too large for a discrete time step model with a relatively frequent 30 min time step, so they are transformed to appropriate values following *Olson* [1963],

$$f' = 1 - \exp[(-\ln(1-f)\Delta t/\tau], \tag{2}$$

where Δt and τ are both expressed in seconds.

N removal from streams and rivers increases proportionally to the dissolved concentration of reactive N. Therefore, removal can be modeled as a first-order reaction rate.

$$Sed\_Denit(\mathrm{gN/s}) \;= f'M/\Delta t, \tag{3}$$

where *Sed_Denit* is the rate of sediment denitrification in gN/s and *M* is the mass of nitrogen in the river in grams N.

Because equation (1) and its implementation in RTM are uncertain, we experimented with several modifications to test the sensitivity of RTM results to the sediment denitrification parameterization. The sensitivity experiments were all conducted with 10 year simulations (years 166–175) using CLM leaching inputs from the standard Temperate Crop model. The modifications were: (1) Doubling the residence time τ, with the rationale that the RTM likely underestimates the residence time of river water due to a variety of factors, including neglecting to represent meandering rivers. (2) Raising the power of the depth variable in equation (1) from the standard d^{-1} to $d^{-1.5}$. The rationale for this test was that the RTM represents all water flow in a given grid cell as a single stream or river, when in reality it is often a group of smaller, shallower streams. This modification allows for higher rates of denitrification in grids with relatively low flow and shallow streams ($d < 1$m) and tends to reduce denitrification in large rivers ($d > 1$m) with less opportunity for contact with bottom sediments. (3) As a final sensitivity test, we imposed both (1) and (2) simultaneously.

2.3. STN-30p and Global NEWS

For this study, we replaced the standard RTM flow direction data set with an external database of river topology to aid in the analysis of RTM results. The Simulated Topological Network (STN-30p) data set provides an accurate representation of the global river system at 30 min (0.5°) spatial resolution, coinciding with the standard RTM resolution. STN-30p comes with supporting metadata for basin-wide or subbasin characteristics such as Strahler stream order, main stem length and catchment area, which are useful for grouping grid cells into common watershed basins for comparison to observations and diagnostic model results [*Vörösmarty et al.*, 2000; *Fekete et al.*, 2001]. While the STN-30p and standard RTM flow direction data sets are similar, the correspondence of the resulting river network is not always exact. For, example, the longest main stem length assigned to the Amazon, representing its site of discharge to the ocean, is displaced 1 grid cell to the north in RTM relative to STN-30p.

Another advantage of STN-30p is that it has been widely used in diagnostic models of river N export, including the Global Nutrient Export from Watersheds (NEWS) model [*Van Drecht et al.*, 2003; *Seitzinger et al.*, 2010]. Global NEWS estimates the export of important nutrients, including N, P, and Si, to the ocean from more than 6000 global rivers, using prescribed nutrient inputs to the corresponding watersheds. Global NEWS provides metadata on these watersheds, along with model estimates of total N (TN) export, partitioned into DIN, DON, and particulate nitrogen (PN) [*Mayorga et al.*, 2010]. Although the N export estimates are model based, they are useful as reference values in cases where observations are not available. Here, for example, the NEWS DIN:TN ratio is used to identify rivers that are most strongly affected by human activity, with the assumption that rivers dominated by DON or PN are likely to be in a more natural condition than rivers dominated by DIN [*Wollheim et al.*, 2008; *Tank et al.*, 2012].

STN-30p and the standard RTM flow direction data set yield similar values for global river N export. This is true despite the fact that the substitution of STN-30p restores 164 endorheic basins that were edited out of the RTM data set to ensure mass balance between global runoff inputs to rivers and outputs to the ocean. In practice, this endorheic flow accounts for only ~1% of the RTM water budget and close to 0% of the N export and thus is not discussed in the results below.

2.4. Observational Data

Observed values of annual mean TN export in 31 world rivers were taken from Table 4 of *Van Drecht et al*. [2003]. These values were based on total N concentrations from *Meybeck and Ragu* [1997] multiplied by volume discharge from *Fekete et al*. [2002]. Observed annual mean DIN export from 19 of these rivers was taken from Table A1 of *Dumont et al*. [2005]. For the remaining 12 rivers, the Global NEWS DIN:TN ratio was used to scale observed TN to estimate observed DIN export. Additional data from the United States Geological Survey (USGS) National Water Information System (NWIS) (http://waterdata.usgs.gov/nwis/qw) were used to evaluate seasonality in volume discharge and dissolved NO_3^- and total (unfiltered) N concentrations at the mouth of the Mississippi River. (For the Mississippi data set, $[NO_3^-]$ was directly measured, rather than estimated based on Global NEWS DIN/TN ratios, as described above for the global data set.) The USGS NWIS observations are from the station at St. Francisville, LA (30.8°N, 91.4°W) over the period 1974–2014, with substantially greater data density in the latter half of the record. Interannual variability in NO_3^- and TN export at this station (calculated as the product of discharge and N concentration) was estimated by interpolating the observed data over a complete annual cycle and integrating the interpolated data annually. Only years with a minimum of at least five observation times, spanning a range of seasons, were included in this calculation. Most of the CLM-RTM simulations presented below were forced with repeated 1972–2004 cycles of NCEP atmospheric reanalysis data [*Qian et al*., 2006], which allowed model results to be lined up to match the USGS NWIS observation years for the overlapping period 1974–2004.

3. Results

The three spun-up versions of CLM (No Crop, Temperate Crop NF, Temperate Crop) all have a near zero change in net ecosystem N, suggesting that the model mineral nitrogen budget is roughly in balance. The three models have identical atmospheric deposition inputs and similar biological nitrogen fixation inputs. BNF decreases by 18 Tg N/yr from the No Crop case to the two crop cases, but the synthetic N fertilizer input is double that amount (36 Tg N/yr) in the standard Temperate Crop case (Table 1).

The N loss terms are variable across the models, with particularly large differences in nitrate leaching and runoff. These fluxes increase from 0.6 Tg N/yr and 10 Tg N/yr, respectively, in the No Crop model to 12 Tg N/yr and 24 Tg N/yr, respectively, in the Temperate Crop model. Leaching and runoff are about 20–25% lower in the Temperate Crop NF model compared to the standard Temperate Crop model, but are still substantially larger than in the No Crop case. All three models have large soil denitrification losses, ranging from 83 to 105 Tg N/yr, and in all cases the partitioning of inorganic N loss is heavily weighted toward denitrification over leaching/runoff. The denitrification:leaching/runoff ratio is 75:25% in both crop model versions and as high as 90:10% in the No Crop model. Nitrogen losses from N_2O emissions, which are estimated as a fraction of denitrification, follow similar patterns as the denitrification losses. Pyrodenitrification, which occurs via burning of organic N bound in vegetation and litter rather than microbial processing of mineral N, is a notably large term (42–61 Tg N/yr) in the N budget of all three models.

The spatial distribution of the N loss fluxes varies substantially among model versions, particularly for leaching/runoff (Figure 1). In the No Crop model, the leaching/runoff fluxes are concentrated in certain arid or mountainous regions and are small elsewhere (Figure 1e). In contrast, the Temperate Crop model predicts larger and more widespread leaching/runoff fluxes that occur mainly in agricultural areas. The Temperate Crop NF leaching/runoff fluxes show similar patterns, but are $\sim$25% lower relative to the standard Temperate Crop case. Compared to leaching/runoff, the denitrification fluxes are more widely distributed across the globe, with hot spots in the tropics, in temperate agricultural regions, and at northern high latitudes. In the two crop model variants, the magnitude of denitrification intensifies in temperate agricultural regions from the no fertilizer (NF) to the standard case. The pattern of fluxes for the Mechanistic NH_X model are similar to those for the Temperate Crop case [see *Riddick et al*., 2015], although the former model shows a greater signal due to manure application in South America and Africa.

Coupling the CLM leaching/runoff fluxes to the RTM river N transport model yields lateral DIN fluxes that trace the flow pathways of the world's major rivers (Figure 2). RTM gridded land-to-ocean fluxes permit global accounting of DIN export in rivers, while watershed metadata available from STN-30p and Global NEWS allow these fluxes to be assigned to the coastal outlets of specific rivers. Figure 2 highlights results for four selected rivers, using the Temperate Crop version of CLM coupled to RTM. This figure shows that

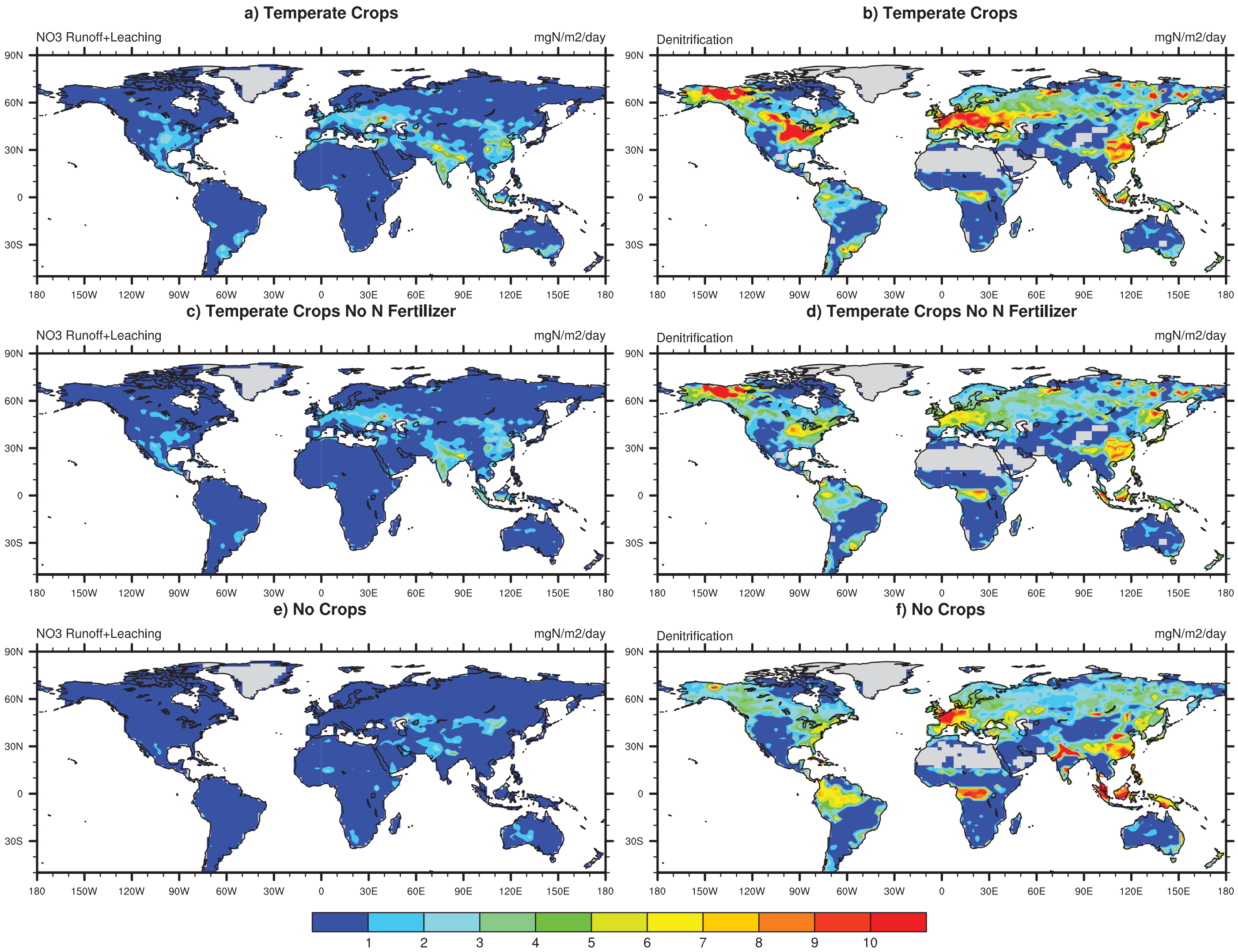

Figure 1. Annual mean soil mineral N loss fluxes (mgN m^{-2} d^{-1}), comparing (left column) NO_3^- leaching + runoff and (right column) soil denitrification fluxes from three versions of CLM: (a, b) Temperate Crops, (c, d) Temperate Crops NF (with no N fertilizer), and (e, f) No Crops.

DIN export in the Mississippi and Danube is somewhat underestimated relative to observed total N export (which also include DON and PN), while export in the Amazon and Lena, watersheds less heavily impacted by human agriculture, is more strongly underestimated.

The globally summed model river DIN budgets vary considerably, depending on which version of CLM is used to provide nitrogen leaching/runoff inputs to RTM (Table 2). In the No Crop model, the relatively small global DIN leaching/runoff input is more or less evenly distributed between export to the ocean and sediment denitrification loss. In the Temperate Crop NF, Temperate Crop, and Mechanistic NH_x model variants, most DIN is exported to the ocean with ~30–40% of the leaching/runoff input lost to sediment denitrification. Total river DIN export to the ocean ranges from about 6 Tg N/yr in the No Crop cases to 21 Tg N/yr in the Temperate Crop model.

The partitioning of the fate of the river N input, however, is sensitive to the parameterization of sediment denitrification. Using the Temperate Crop model as the CLM leaching/runoff input, the standard sediment denitrification parameterization yields a loss fraction of 40% (with 60% exported to the ocean). Relative to this standard case, doubling the residence time of DIN in the river increases the loss fraction to 54%, increasing the sensitivity to depth decreases it to 33%, and applying both changes increases it to 45% (Table 3).

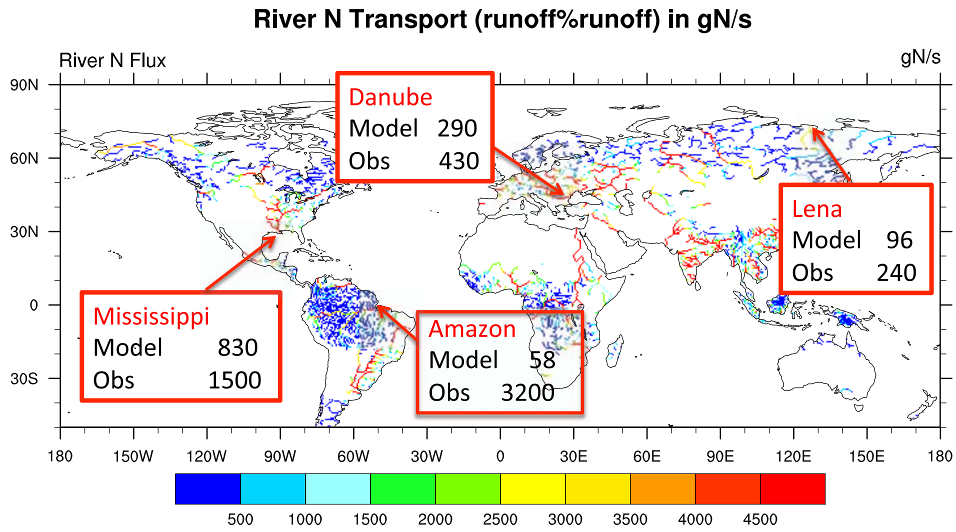

Figure 2. DIN export to the ocean (in GgN yr^{-1}) from major world rivers using the Temperate Crop version of CLM coupled to RTM. Red inset boxes compare modeled DIN export in three selected rivers to observed total N (TN) export from *Van Drecht et al.* [2003].

When the modeled DIN export to the ocean from 31 world rivers is compared to observed DIN export, most versions of CLM-RTM capture some of the observed variability (Figure 3), but with substantial mean biases and differences in modeled versus observed export among individual rivers in the subset of 11 of the 31 rivers examined in Table 4. The model versus observed correlation coefficients range from R = 0.4 in the No Crop case to R = 0.7 in the Temperate Crop and Temperate Crop NF cases and R = 0.8 in the Mechanistic NH$_x$ case. These results are in large part due to the RTM's skill in capturing the observed volume discharge in the rivers (R~0.95 for all versions). Plots of modeled versus observed [N] concentration at the mouths of the rivers give a lower correlation coefficient that is generally not statistically significant.

Table 4 shows that the No Crop model strongly underestimates N export, by many orders of magnitude, in rivers with high human impact. In contrast, the crop models capture observed DIN export reasonably well in human-impacted rivers, with a slight negative bias for the standard Temperate Crop model and a more substantial negative bias for the Temperate Crop NF model. In more natural watersheds, all models all strongly underestimate export in tropical rivers like the Amazon and Orinoco, while the crop models tend to overestimate DIN export in Arctic rivers like the Lena and Kolyma. However, DIN accounts for a relatively small fraction of TN export in these natural rivers. When the Temperate Crop model results are compared to observed TN, they underestimate TN export in all cases, even in the Arctic rivers (Figure 2). The Mechanistic NH$_x$ version of CLM, with prescribed N fertilizer and manure inputs, captures observed DIN export well in rivers impacted heavily by human activity (Figure 3b, red circles), and shows less overall bias and better overall correlation with the selected rivers in Table 4 than the Temperate Crop model. At the same time, the Mechanistic NH$_x$ model tends to strongly underestimate N export in more natural rivers, including Arctic rivers (Table 4, Figure 3b, blue triangles). This is because the N export in the Mechanistic NH$_x$ is only due to direct applied fertilizer and manure application and does not capture the export from the natural soils.

Using the Mississippi River watershed as an example, Figure 4 shows the partitioning of CLM soil N losses in the Temperate Crop model, with denitrification dominating over leaching/runoff. Figure 4 also compares the relative spatial pattern of CLM soil denitrification and CLM-RTM river sediment denitrification. The

Table 2. River DIN Budgets for Four Different Versions of CLM[a]

	No Crop	Temperate Crop NF No N Fertilizer	Temperate Crop Standard Case	Mechanistic NHx
N Input to river	10.8 ± 0.5	28.2 ± 0.9	35.4 ± 1.1	17.5 ± 1
Export to ocean	5.6 ± 0.3	17.2 ± 0.5	21.4 ± 0.7	12.5 ± 0.7
Sediment denitrification	5.1 ± 0.2	11.0 ± 0.4	14.1 ± 0.5	5.0 ± 0.3

[a] All values are in Tg NO$_3$-N yr^{-1} and show the average and standard deviation of the last 10 simulation years.

Table 3. River DIN Budgets: Sensitivity to Sediment Denitrification[a]

	Standard Parameters $1-\exp(-v_f\,\tau/d)$	Double Residence Time $1-\exp(-v_f\,2\tau/d)$	Increase Sensitivity to Depth $1-\exp(-v_f\,\tau/d^{1.5})$	Modify Residence Time and Depth Sensitivity $1-\exp(-v_f\,2\tau/d^{1.5})$
N Input to river	35.4 ± 1.1	35.4 ± 1.1	35.4 ± 1.1	35.4 ± 1.1
Export to ocean	21.4 ± 0.7	16.2 ± 0.6	23.8 ± 0.8	19.5 ± 0.7
Sediment denitrification	14.1 ± 0.5	19.3 ± 0.7	11.6 ± 0.4	16.0 ± 0.6

[a] All values are in Tg NO_3-N yr^{-1} and show the average and standard deviation of the last 10 simulation years. All simulations are based on the same CLM4.5 Temperate Crop simulation with N fertilizer, but use different parameterizations for sediment denitrification. The standard parameterization is $f = 1-\exp(-v_f\,\tau/d)$, where f is the fraction denitrified, d is depth, τ is residence time, and v_f is the biological activity coefficient for denitrifiers.

coupled model predicts that soil denitrification dominates sediment denitrification by a factor of 10 (9.8 Tg N/yr versus 0.75 ± 0.25 Tg N/yr integrated across the Mississippi basin). While soil denitrification closely follows the spatial pattern of fertilizer N input, the pattern of sediment N loss shows substantial redistribution along aquatic pathways, with highest sediment loss along the main stem of the Mississippi River. The spatial distribution of sediment denitrification in turn is sensitive to the parameterization of that process in RTM. Changing the sensitivity to depth, particularly in combination with an increase in river residence time, shifts sediment denitrification out of the main stem and into smaller tributary regions (Figure 4f).

The seasonal pattern of N flow in rivers was investigated by comparing [NO_3^-] concentration and flow volume observed by the USGS at the mouth of the Mississippi River to results from the Temperate Crop model and the Mechanistic NH_x model (Figure 5). Note that the interannual variability of the runoff here is not directly comparable to the observations as simulated meteorological input does not directly correspond to the measured years. Measured peak flow shows considerably interannual variability but generally occurs from the spring

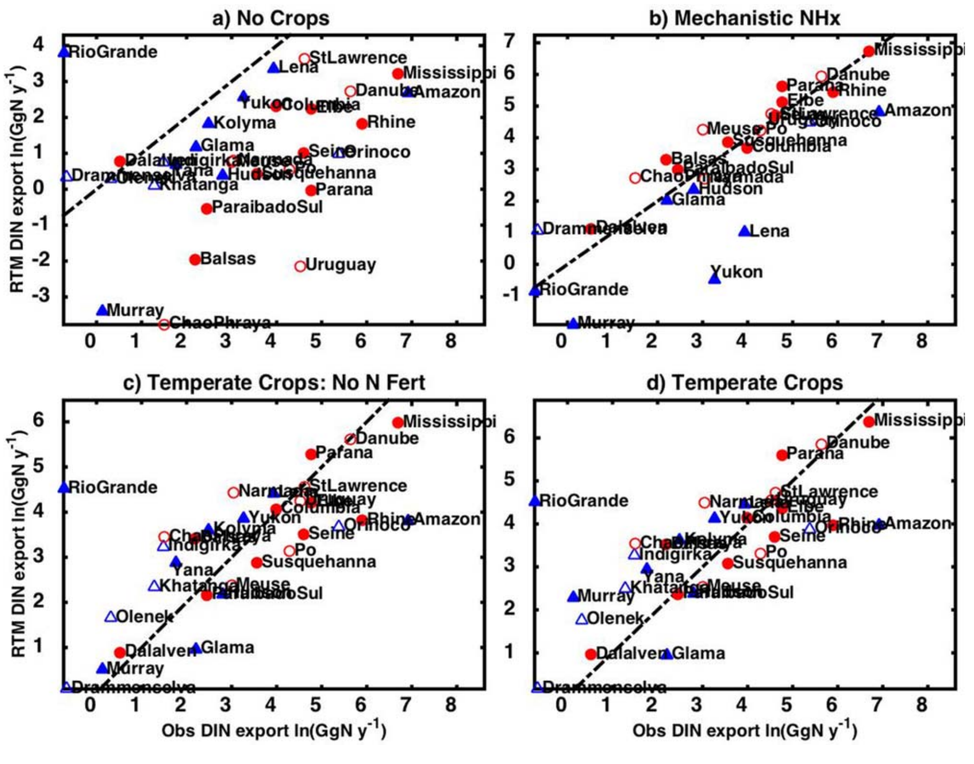

Figure 3. Annual modeled DIN versus observed DIN export in GgN y^{-1} (natural log scale) for 31 global rivers. Observed DIN is taken either directly from observed DIN values in Table A5 of *Dumont et al*. [2005] (solid symbols) or calculated from observed TN values taken from Table 4 of *Van Drecht et al*. [2003] and scaled by the Global NEWS model DIN/TN ratio (open symbols). Plots compare four different versions of CLM: (a) No Crop, (b) Mechanistic NHx model, (c) Temperate Crop with no N fertilizer, (d) Temperate Crop standard case. Red circles are used for rivers that are most heavily impacted by human activity, as defined based on a Global NEWS DIN/TN ratio of >0.4. Blue triangles are used for rivers in which N export is dominated by DON and/or PN. Black dot-dash line is the 1:1 line.

Table 4. Modeled DIN Export Compared to Observed DIN Export in 11 Rivers

	Observed	No Crop	Temperate Crop: No N Fertilizer	Temperate Crop	Mechanistic NHx 2005
Tropical rivers with lower human impact[a]					
Leaching GgN/yr	NA	63	220	258	458
Export GgN/yr	1220	17	85	102	212
% Bias[b]	NA	−99%	−89%	−86%	−74%
Arctic rivers with lower human impact[c]					
Leaching GgN/yr	NA	75	252	285	6
Export GgN/yr	89	48	167	185	3
% Bias[b]	NA	−47%	+116%	+139%	−97%
Rivers with high human impact[d]					
Leaching GgN/yr	NA	166	1680	2320	2840
Export GgN/yr	1700	94	935	1260	1730
% Bias[b]	NA	−89%	−28%	−10%	+2%
Combined lower and high human impact rivers					
Export GgN/yr	3000	159	1187	1547	1945

[a] Amazon, Orinoco.

[b] Calculate bias for each river as (obs-model)/obs*100, then take mean for each category.

[c] Kolyma, Lena, Yukon.

[d] Columbia, Danube, Mississippi, Rhine, Saint Lawrence, Uruguay.

[a, c, d] Note: these rivers were chosen because, for each category in Table 3, because they had the largest annual mean flow volumes among the 31 rivers in Figure 3.

months until about June. The measurements also display considerable variability in the interannual and intranual $[NO_3^-]$ and TN concentrations. Peak $[NO_3^-]$ tends to be slightly lagged and occurs in late spring to early summer. Temporal patterns in TN concentrations closely follow those in $[NO_3^-]$, with an average $[NO_3^-]$:TN ratio of 0.67 in the USGS data set. The Temperate Crop and Mechanistic NH_x models generally reproduce the observed relationship between flow and $[NO_3^-]$. The fall minimum in the measured $[NO_3^-]$ appears to be well captured in the Mechanistic NH_x model. Interannual variability in the springtime maximum obfuscates a straightforward comparison of the springtime maximum. As currently configured, fertilization in the Mechanistic NH_x model is assumed to coincide with spring planting, while manure is spread constantly throughout the year. More realistic fertilizer and manure application schedules would be expected to modify the seasonality. RTM volume flow in both model versions tends to exceed observed flow, especially in spring, for reasons that are not clear but may in part reflect natural interannual variability in the specific years sampled.

To examine more closely the interannual variability in RTM output and its relationship to climate, Figure 6 plots a 50 year time series of annual DIN export at the mouth of four major world rivers, juxtaposed against the corresponding time series in annual mean NCEP rainfall integrated over the river watershed. The plot covers the last 50 years of the 150 year Temperate Crop simulation. Crop distribution is held constant over the course of the simulation, with the result that fertilizer N input is relatively unchanging and the variability is driven primarily by climate, i.e., the simulation represents model variability in DIN export over a 50 year period as it responds to variability in the cycled NCEP meteorological forcing. In general, a positive correlation between interannual variability in model river N export and mean watershed rainfall is found, although the strength of the relationship varies substantially among watersheds. Rainfall and N export correlate well at $R = 0.75$ in the Yangtze (Chiang Jiang), which has the highest mean rainfall of the four rivers shown, and more weakly at $R = 0.22$ in the Mississsippi river. Two European rivers, the Rhine and Danube show intermediate strength correlations of 0.47 and 0.35, respectively. A corresponding analysis of the CLM leaching/runoff fluxes versus mean rainfall shows slightly weaker correlations, but very similar patterns, suggesting that increased N leaching and runoff in wet years are the main drivers of the positive correlation between river DIN export and mean rainfall. Similar calculations were performed with mean watershed surface air temperature, but temperature was found to be a less reliable predictor of DIN export than rainfall.

The observed interannual variability in N export in the Mississippi River in USGS NWIS data from 1974 to 2004 is significantly correlated to mean annual NCEP rainfall integrated over the Mississippi basin for both DIN ($R = 0.87$) and TN ($R = 0.64$). The corresponding CLM-RTM results (corresponding to model years 3–23 in Figure 6) are comparable in mean value but substantially underestimate the interannual variability and the strength of the correlation to mean rainfall (Figure 7).

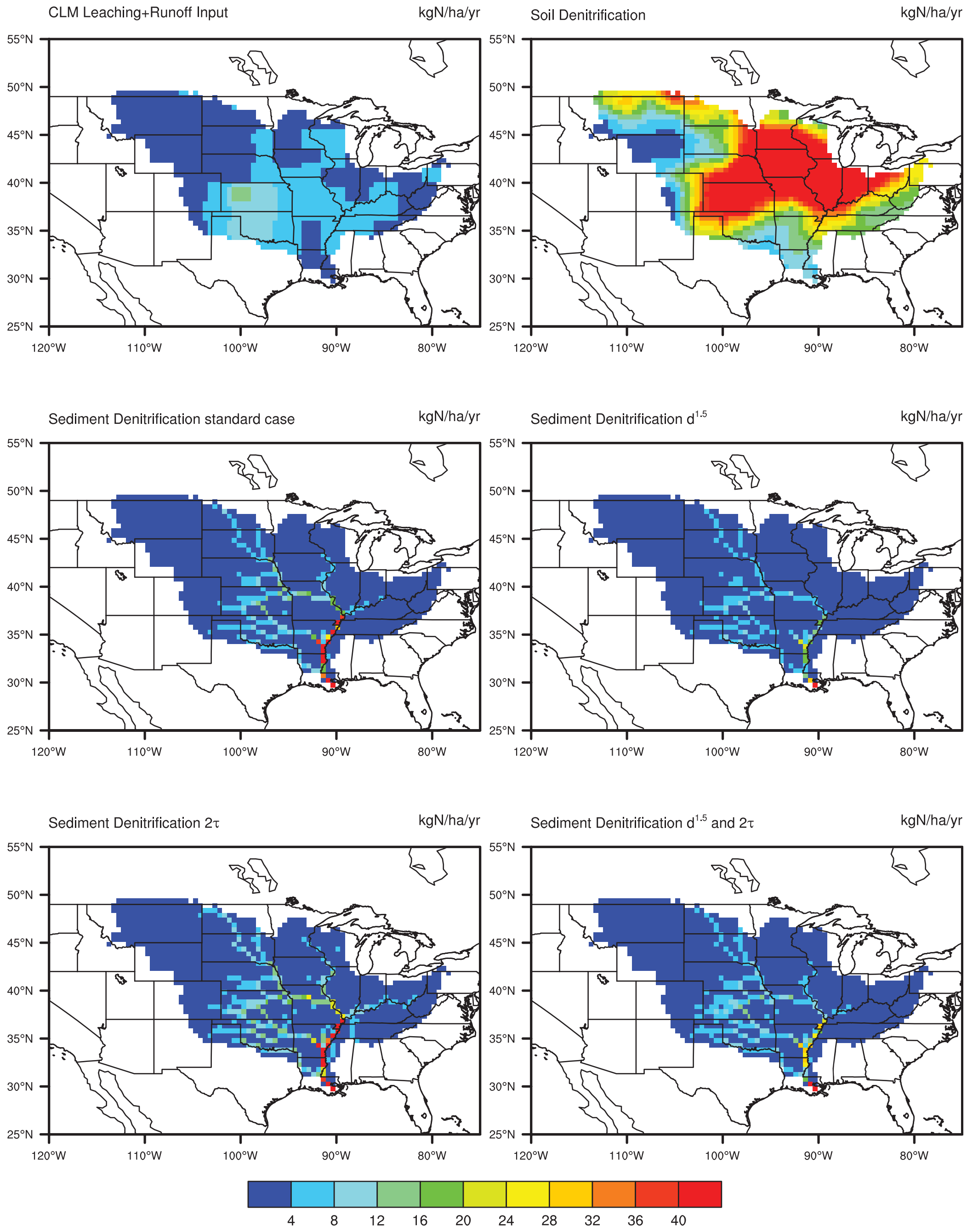

Figure 4. Watershed-scale results of the Temperate Crop CLM coupled to the RTM for the Mississippi River basin. (a) CLM DIN leaching + runoff input to RTM, (b) CLM soil denitrification. The bottom four plots show RTM sediment denitrification with the (c) standard $1-\exp(-v_f\,\tau/d)$, (d) $1-\exp(-v_f\,\tau/d^{1.5})$, (e) $1-\exp(-v_f\,2\tau/d)$, and (f) $1-\exp(-v_f\,2\tau/d^{1.5})$ parameterizations.

4. Discussion

The results presented above illustrate the potential of the coupled CLM-RTM to simulate key biogeochemical fluxes pertaining to human N cycle perturbation and its downstream impact on coastal areas. Compared to diagnostic models of river N export with tuned water balance and leaching inputs, CLM-RTM is a prognostic model that offers greater flexibility for investigating the influence of climate on these fluxes and their spatial and temporal variability. However, current model results vary considerably among different versions of CLM and are sensitive to parameterizations that are not well constrained and processes, e.g., DON and PN leaching, that are not represented.

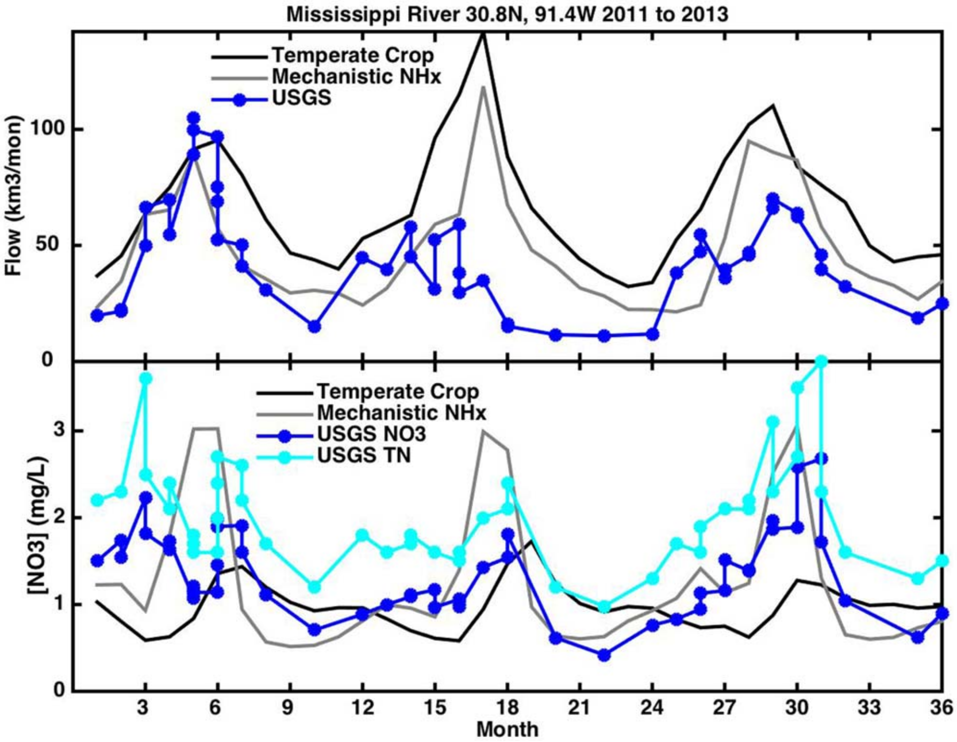

Figure 5. Seasonality of total N (TN) and [NO$_3^-$] concentrations (mg/L) and flow (km^3/mon) observed at the mouth of the Mississippi River at USGS NWIS station 30.8N, 91.4W in 2011–2013, compared to results (flow and [NO$_3^-$] only) over 3 year period from two different versions of CLM coupled to the RTM. The CLM years reflect interannual climate variability but do not correspond directly to real years.

Many of the differences in river DIN export among the model versions presented here arise due to the inclusion or exclusion of crops per se and to a lesser extent due to the influence of synthetic fertilizer N inputs. The introduction of cropping alone dramatically increases the CLM subsurface leaching loss by an order of

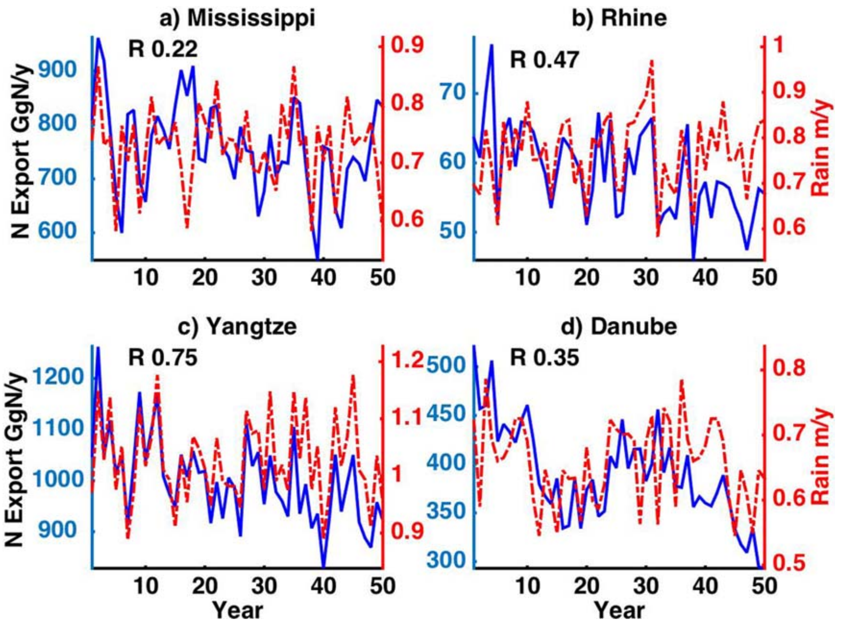

Figure 6. Annual mean N export at the river mouth of four major world rivers from the last 50 years of the coupled RTM-Temperate Crop CLM simulation, juxtaposed against mean annual rainfall from the NCEP reanalysis data used to force the simulation, integrated over the watershed. (a) Mississippi, (b) Rhine, (c) Yangtze (Chiang Jiang), and (d) Danube.

magnitude and nearly doubles the surface runoff loss of nitrate (Table 1). Without crops, leaching/runoff fluxes are narrowly and probably unrealistically confined to arid or mountainous regions (Figure 1). The input of synthetic N fertilizer to the cropped areas leads to ∼25–30% incremental enhancements in denitrification and leaching/runoff, without fundamentally altering its spatial distribution. The reasons for these differences among model versions are beyond the scope of this paper but likely are related in part to changes in aboveground biomass when natural ecosystems are replaced with crops [*Levis et al*., 2012; *Ward and Mahowald*, 2015].

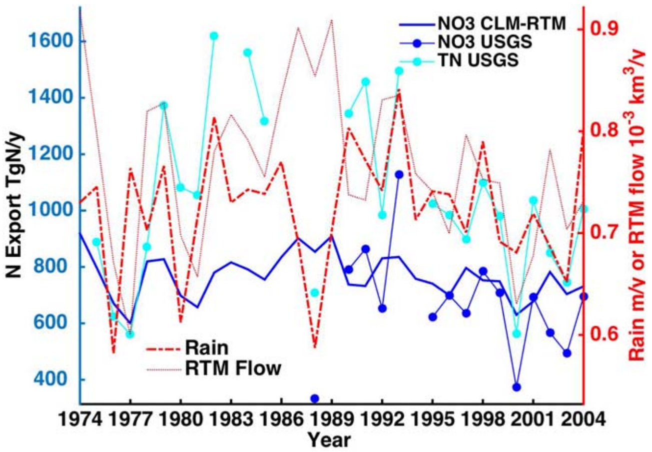

Figure 7. Annual mean N export at the river mouth of the Mississippi from 1974 to 2004 of the coupled RTM-Temperate Crop CLM simulation, juxtaposed against mean annual rainfall integrated over the watershed from the NCEP reanalysis data, as in Figure 6. For reference, RTM volume flow (10^{-3} km^3/yr) at the river mouth is also plotted on the right *y* axis. Model results are compared to observed NO_3^- and TN export from the USGS-NWIS.

The differences in leaching/runoff in different CLM configurations occur against the backdrop of the historical role of inorganic N loss fluxes, which have functioned within CLM more as ad hoc terms that keep the inorganic N pool in check than as realistic biogeochemical fluxes. Since the inorganic N pool exerts key controls on the CLM carbon cycle, better constraints on the N loss fluxes that govern the size of this pool are important for improving confidence in CLM results. Below we discuss the terms that determine the terrestrial N budget and their accuracy so as to better understand the constraints that leaching and runoff place on the overall budget.

4.1. DIN Versus Total N Export

Comparison of simulated and observed N export to the ocean can provide some basic constraints on CLM N leaching/runoff fluxes, although these constraints must be regarded with caution for several reasons. First, the coupled CLM-RTM at present can only simulate DIN export to the coastal zone, and thus cannot provide complete information about TN export, which consists mainly of PN and DON in many watersheds. Literature estimates of global export under present day conditions are typically about 40–60 Tg N/yr for TN, with over 40% of the export (about 20 TgN/yr) attributed to DIN and the remainder split more or less evenly between DON and PN [*Green et al*., 2004; *Galloway et al*., 2004; *Kroeze et al*., 2012]. These global estimates are based on diagnostic models of river N export and thus are to some extent modeled values themselves. Nonetheless, the estimates are probably reasonably accurate, because the diagnostic models have been tuned to agree with observed N export data in available rivers. Compared to the ∼20 Tg N/yr yardstick, modeled DIN export is far too low in the No Crop version of CLM, not surprisingly, given its lack of agricultural perturbation. Export of DIN is better represented in the CLM versions with explicit application of fertilizer (Temperate Crops: 21 Tg N/yr) or fertilizer and manure (Mechanistic NH_x model: 12 Tg N/yr). Interestingly, it is also represented reasonably well in the CLM version with crops but lacking synthetic N fertilizer (Temperate Crop NF: 17 Tg N/yr). The Temperate Crop global DIN export of 21 TgN/yr, agrees best with the diagnostic model-based estimates, although this agreement on a global-scale reflects some cancellation of errors among individual rivers (Figure 3). Evaluation of a selected set of individual rivers with high human impact (in which DIN comprises most of TN) shows relatively low mean biases in the Temperate Crop and the Mechanistic NH_x model of -10% and $+2\%$, respectively (Table 4).

In contrast, DIN export in low human impact rivers (i.e., in watersheds that have not been heavily polluted by anthropogenic N) is poorly simulated in all versions of CLM examined. Furthermore, distinct patterns emerge across characteristic tropical and Arctic rivers (Table 3). In tropical rivers, modeled export strongly underestimates observed export, with large negative mean biases in all versions of CLM examined (Table 4). However, DIN export in Arctic rivers is overestimated in many model versions (Figure 3, Table 4), with a strong exception in the case of the Mechanistic NH_X model. The latter only includes the direct N runoff from manure and fertilizer inputs, which are low in Arctic watersheds, and not the leaching or runoff from the CLM nitrogen pools. It also should be noted that all versions of CLM underestimate total N (TN) export in Arctic rivers. Collectively, these results suggest that CLM-RTM tends to overestimate DIN leaching/runoff in Arctic watersheds (while underestimating TN leaching/runoff), can represent DIN leaching and runoff reasonably well in temperate agricultural areas, and strongly underestimates all forms of nitrogen leaching and runoff in the tropics. This last result is consistent with the very small leaching/runoff fluxes in tropical Africa and South America shown in Figure 1.

In low human impact rivers in both the tropics and the Arctic, dissolved organic and particulate N (DON and PN) are the dominant forms of N observed [*Wollheim et al*., 2008; *Tank et al*., 2012]. In contrast, DIN tends to dominate N export in anthropogenically perturbed rivers. The current CLM-RTM only simulates the leaching, runoff, and river export of DIN, although direct observations of DIN and TN in the Mississippi River suggests that the seasonal and interannual variability in these species are closely related (Figures 5 and 7). In these observations, DIN accounts for about 2/3 of observed TN. Placeholder fluxes for both organic N and C leaching exist in CLM, but these are not currently active variables. Other TEMs have parameterized DON and DOC leaching as a small fraction of soil organic matter turnover [*Gerber et al*., 2010] and this approach has been introduced to CLM-CN v4.0 in single grid simulations [*Thomas et al*., 2013b]. Introducing organic N and C leaching into the full CLM potentially may have substantial feedbacks on soil organic matter, with repercussions throughout the model. Particulate N is also an important component of river N export, especially in less perturbed rivers. PN, which consists mainly of organic N sorbed on mineral surfaces, is typically is modeled based on physical erosion and sediment transport [*Beusen et al*., 2005]. Neither process currently is considered in CLM (N. Rosenbloom, personal communication, 2015). Further, sediment retention in dams and reservoirs, which is an important sink for PN in the river network, is not currently included in RTM [*Syvitski et al*., 2003]. A more realistic accounting of DON and PN export thus would require incorporating a variety of new processes into CLM-RTM, but may be a needed step to represent the coupled carbon-nitrogen cycle more fully.

4.2. Sediment Denitrification

A second issue that limits the use of observed river N export for constraining the CLM leaching/runoff fluxes is that sediment denitrification loss of N within rivers and streams is not well quantified. It is possible, for example, that CLM could underestimate the total DIN leaching/runoff input to RTM, but that RTM might underestimate sediment denitrification loss within rivers and thus simulate an apparently reasonable total N export to the ocean. Indeed, the fraction of the total DIN leaching/runoff input in the Temperate Crop and Mechanistic NH_x models that is denitrified in sediments, using the standard parameterization in RTM, is only about 30–40%. This fraction falls on the low side of the $\sim$50% removal rate reported in other model studies [*Seitzinger et al*., 2002; *Wollheim et al*., 2008], and may reflect the lack of representation in RTM of dams and reservoirs, which lead to increased retention time and removal by sediment denitrification [*Van Drecht et al*., 2003]. Slightly more than half of the leaching/runoff input is denitrified before reaching the ocean in the No Crop model, but this is likely because the input is small overall and much of it occurs in arid regions. Such regions tend to have shallow rivers with low flow volume, which leads to a relatively large sediment removal fraction of N input.

The sensitivity tests shown in Table 3 and Figure 4, using the Temperate Crop model, show that varying the sediment denitrification parameters can increase the in-river loss fraction to up to 54% and lead to global DIN export values that vary by $\pm\sim$25% (ranging from 16 to 24 Tg N/yr). While these values vary considerably, the observational constraints at present are too limited, both globally and with respect to individual rivers, to distinguish which if any of the parameterization is the best. Within the scope of the current study, given the other uncertainties, the sediment denitrification parameterization is probably a second order issue, although one that merits more scrutiny in future work.

4.3. N Inputs

Biological nitrogen fixation (BNF) is an uncertain N input to CLM that can be constrained to some extent by evaluating CLM-RTM river N export against observations. Other N inputs, including atmospheric N deposition and anthropogenic fertilizer, are relatively well known compared to N losses. Most global estimates of fertilizer and manure application are within approximately 20% of each other [*Potter et al*., 2010], while atmospheric deposition of nitrate and ammonium are also fairly well constrained by atmospheric measurements. For example, *Dentener et al*. [2006] show that for the most part the mean modeled deposition from a multimembered model ensemble is within 50% of the measurements over a range of measurement stations. In contrast, the commonly used algorithms that scale BNF inputs as a function of NPP or evapotranspiration are not well validated against observations and probably tend to overestimate BNF in temperate and boreal ecosystems [*Cleveland et al*., 1999; *Thomas et al*., 2013b]. Excess BNF inputs in turn can translate into exaggerated N losses from these ecosystems as models attempt to rid themselves of excess N through unrealistically high leaching and/or denitrification rates [*Thomas et al*., 2013a]. In CLM, most high latitude N loss occurs through denitrification. Indeed Figure 1 shows that the denitrification rates in the Arctic are higher than in any other global region, with the exception of temperate agricultural areas. However, N leaching/runoff losses, even though only a small fraction of total N loss, may still be sufficiently large to contribute to the overestimate of DIN export in Arctic rivers. Thus, the overestimate of DIN export in the Arctic (Figure 3, Table 4) may be more a response to excessive N inputs to the model, serving to keep the inorganic N pool in check, rather than a reflection of problems in the N loss parameterizations per se.

4.4. Partitioning of Denitrification Versus Leaching/Runoff

The underestimate of N leaching/runoff in the tropics suggests other loss pathways for nitrogen in CLM are excessive. Denitrification dominates over leaching/runoff more or less everywhere in CLM, accounting for 75% of inorganic N loss in the Temperate Crop standard and NF models and about 90% of loss in the No Crop model. Previous versions of CLM, such as CLM-CN v 4.0, had an even greater imbalance between the two loss pathways, with negligible leaching and essentially 100% of inorganic N loss attributed to soil denitrification [*Koven et al*., 2013]. The 75–90% denitrification loss fraction in the current CLM contrasts with other estimates reported in the literature, which are highly uncertain themselves and range from 28%, based on global isotopic mass balance calculations [*Houlton et al*., 2009, 2015], to about 60%, based on a series of scalars representing the effects of climate and soil texture, drainage, and organic carbon content on denitrification [*Van Drecht et al*., 2003].

Some have argued that it is not necessary to distinguish leaching and denitrification to accurately model carbon-nitrogen interactions, since the functional influence of nitrogen on the model terrestrial carbon cycle is the same regardless of the details of how it is lost from soil [*Gerber et al*., 2010]. Some models avoid uncertainties in inorganic N loss fluxes altogether, because they by design are conservative with respect to N inputs and outputs and consider only the internal recycling of N among soil and vegetation [*Sokolov et al*., 2008]. In practice, this conservation of mass is not realistic in the face of global change scenarios, which almost certainly will involve large N inputs to and losses from terrestrial ecosystems, with transient imbalances in net retention [*Galloway et al*., 2004]. (Here, we note that the variability in N leaching/runoff and denitrification among the model configurations presented in this paper was downplayed by the use of No Crop and Temperate Crop cases in near-equilibrium with respect to net N balance, and would have been larger if we had presented transient simulation results.)

In a relevant study, *Thomas et al*. [2013a] found that an earlier version of the model used here (CLM-CN v 4.0) tended to substantially underestimate the retention of atmospherically deposited N relative to field ^{15}N tracer experiments (losing 55% of added N compared to the measured 27%), and suggested that model performance might be improved by requiring N to cycle through organic matter before being denitrified. In follow-up work, *Thomas et al*. [2013b] showed that the retention of N from long-term anthropogenic increases in atmospheric N deposition was highly sensitive to the parameterization and assumed processes of N losses. They found improved model simulation of the response to N deposition when denitrification loss was parameterized as a function of N turnover in soil organic matter, rather than as a function of soil inorganic N concentration (as in the current CLM v 4.5). They also found that their modified parameterization tended to bring denitrification and leaching losses more into balance.

4.4.1. Regional Mass Balance Studies

On a regional scale, N mass balance studies in individual watersheds have also addressed the partitioning of denitrification and leaching. These studies have typically found that about 20% (range 15–30%) of the N input to the watershed is exported to the coast [*Van Bremen et al*., 2002; *Swaney et al*., 2012]. Assuming (as per the discussion above) that the measured river N export at the coast is about half the original leaching/runoff input, this suggests that ~40% of N input to the watershed is leached. Some apples to oranges issues arise when trying to compare the regional mass balance studies to global CLM-RTM results. First, unlike CLM, the regional studies explicitly account for N inputs via feed and food imports and N exports via crops, livestock, and humans, without defining the ultimate fate (e.g., denitrification or leaching) of those exports, even though they are large terms in the budget. Second, the regional studies infer the fraction denitrified as a residual of the better-known terms (coastal N export, agricultural import/export), typically concluding that a large fraction, on the order of 50% or more, of N inputs to the watershed is lost to denitrification somewhere in the landscape. However, whereas CLM-RTM distinguishes between soil and river sediment denitrification, the regional studies define the "landscape" broadly to include denitrification in both soils and sediments as well as in domains not explicitly represented in CLM-RTM, such as groundwater and riparian zones. Collectively, these apples to oranges issues make it difficult within the current model framework to directly compare CLM-RTM results to the regional mass balance studies.

4.4.2. Pyrodenitrification

An additional consideration with respect to the partitioning between leaching/runoff and denitrification is that a large fraction of the net total N input to CLM-CN is lost through pyrodenitrification, i.e., biomass burning of organic N resulting in pyrolytic conversion to N_2. This is especially true in the No Crop model, in which cropped regions, where CLM does not permit agricultural fires, are replaced by frequent-burning natural vegetation [*Ward and Mahowald*, 2015]. Pyrodenitrification is a term that is not explicitly considered in many global and regional N budgets in the literature, but removes about 20–35% of annual N inputs in various configurations of CLM (Table 1). The CLM pyrodenitrification total of 42–61 Tg N/yr exceeds the global estimate of *Andreae and Merlet* [2001] of 26 Tg N/yr. Since CLM uses Andreae and Merlet's N_2:biomass conversion factor, the source of the discrepancy with their estimate likely lies in the larger amount of nitrogen biomass burned in CLM. If the soil denitrification and pyrodenitrification fluxes are combined, the total denitrification fraction of N loss in CLM increases to 94% in the No Crop version and just over 80% in the crop model versions.

In considering the above results, we note that denitrification currently has a competitive advantage over leaching in CLM; pyrodenitrification of organic N is represented explicitly while leaching of organic nitrogen as DON or PN is not. Diagnostic river models have estimated total DON and PN export to the ocean at $\sim$40 Tg N/yr [*Beusen et al*., 2005; *Harrison et al*., 2005]. The original leached amount may be substantially larger, given the likelihood of in-river processing and additional loss of PN to sedimentation. In future work, incorporation of the DON and PN leaching and downstream processing into CLM-RTM could help to achieve a more appropriate balance between denitrification and leaching and a more complete accounting of the global N cycle.

To summarize, the partitioning of N loss in the current CLM appears heavily skewed toward denitrification at the expense of leaching/runoff relative to other literature estimates. This lopsided partitioning is most evident in the tropics, which is a region where model representation of mineral nutrient limitation is particularly important for the future evolution of atmospheric CO_2 [*Thornton et al*., 2009]. N loss in the Arctic also appears skewed toward denitrification, but this point is obscured by the fact that CLM-RTM in some configurations actually tends to overestimate DIN export in Arctic rivers, which may be the result of excessive BNF inputs to high latitude regions. In temperate agricultural regions, N loss partitioning appears reasonable, based on the relatively good representation by CLM-RTM of DIN export in rivers draining those regions. Altogether, these results suggest the need for improved treatment of both BNF and N loss in CLM and illustrate how the evaluation of model river N export against observations can help in constraining the CLM N cycle. In addition, regional differences in river N export can provide clues to region-specific needs for improvement in biological nitrogen fixation, leaching, and denitrification. Ultimately, improvements in model BNF and N loss will help increase confidence in CLM's representation of the response of the land biosphere to climate change and increasing atmospheric CO_2 and N deposition, which is the core goal of the coupled carbon-nitrogen model.

4.5. Influence of Climate on River N Export

Despite the many uncertainties discussed above, CLM-RTM shows promise in its ability to represent the influence of climate on seasonal and interannual variability in river N export. In the Mississippi River, the Temperate Crop model captures the observed late spring peak in flow and the slightly delayed early summer peak in N concentration. Further, the model predicts that interannual variability in N export is positively correlated to mean annual watershed rainfall, and that this relationship is driven largely by increased N leaching in wet years. While CLM-RTM underestimates the strength of the correlation in the Mississippi River, where USGS NWIS observations provide strong evidence for such a relationship, it captures the relationship more robustly in other world rivers such as the Yantgze and Rhine.

5. Conclusions

Preliminary efforts to model river N export in the coupled CLM-RTM reveal both benefits and challenges. Benefits include the simulation of a key Earth system process that has accompanied human agricultural expansion: the increased export of N to the coastal zone. The CLM-RTM differs from diagnostic models of rivers in its ability to prognostically represent the influence of changing climate on river N export. The coupled CLM-RTM simulation also helps provide first-order constraints on CLM soil N loss processes, which hitherto have received little attention. Among the challenges revealed by the preliminary modeling exercise, at least two dominant needs arise. The first is the need to simulate particulate and dissolved organic N leaching fluxes in CLM. The current lack of organic N leaching in CLM hinders comparison of modeled and observed TN export, especially in the relatively unperturbed watersheds of the Amazon and Arctic. The second challenge involves the need to scrutinize the model partitioning between the primary inorganic N loss fluxes of denitrification and leaching/runoff. The current CLM N loss partitioning appears heavily weighted toward denitrification at the expense of leaching/runoff compared to other literature estimates. Since inorganic N loss fluxes help control soil N availability, a key regulator of the carbon cycle, a more realistic simulation of the partitioning of denitrification versus leaching/runoff can help improve model credibility with respect to coupled C-N interactions.

Acknowledgments
This work was carried out with support from NSF ETBC award 1021070. We are grateful to Todd Walter for providing USGS NWIS data and to Christine Goodale for helpful discussions. Computing resources were provided by the Climate Simulation Laboratory at the National Center for Atmospheric Research (NCAR) Computational and Information Systems Laboratory (CISL). NCAR is sponsored by the National Science Foundation (NSF). We gratefully acknowledge Sam Levis, who was at NCAR at the time, for help with the CLM crop model. The source code for the CLM and RTM modules of CESM used in this study is freely available at http://www2.cesm.ucar.edu. The code modifications necessary to reproduce the experiments with CLM-RTM are available from the authors upon request (Cynthia.Nevison@colorado.edu). The model output is archived at NCAR. Supporting USGS NWIS data used in the study are available from (http://waterdata.usgs.gov/nwis/qw). The STN-30p topological network is available through the ORNL DAAC, and the Global NEWS data set is available at http://marine.rutgers.edu/globalnews/documents.htm.

References

Alexander, R. B., P. J. Johnes, E. W. Boyer, and R. A. Smith (2002), A comparison of models for estimating the riverine export of nitrogen from large watersheds, *Biogeochemistry*, *57/58*, 295–339.

Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, *15*, 955–966.

Beaulieu, J. J., et al. (2011), Nitrous oxide emissions from denitrification in stream and river networks. *Proc. Natl. Acad. Sci., U. S. A.*, *108*, 214–219.

Beusen, A. H. W., A. L. M. Dekkers, A. F. Bouwman, W. Ludwig, and J. Harrison (2005), Estimation of global river transport of sediments and associated particulate C, N, and P, *Global Biogeochem. Cycles*, *19*, GB4S05, doi:10.1029/2005GB002453.

Boyer, E. W., R. W. Howarth, J. N. Galloway, F. J. Dentener, P. A. Green, and C. J. Vorosmarty (2006), Riverine nitrogen export from the continents to the coasts, *Global Biogeochem. Cycles*, *20*, GB1S91, doi:10.1029/2005GB002537.

Branstetter, M. L., and D. J. Erickson, III (2003), Continental runoff dynamics in the Community Climate System Model 2 (CCSM2) control simulation. *J. Geophys. Res.*, *108*(D17), 4550, doi:10.1029/2002JD003212.

Cleveland, C. C., et al. (1999), Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems, *Global Biogeochem. Cycles*, *13*, 623–645.

Dai, A., and K. E. Trenberth (2002), Estimates of freshwater discharge from continents: Latitudinal and seasonal variations, *J. Hydrometeorol.* *3*, 660–687.

Dentener, F., et al. (2006), Nitrogen and sulfur deposition on regional and global scales: A multi-model evaluation, *Global Biogeochem. Cycles*, *20*, GB4003, doi:10.1029/2005GB002672.

Donner, S. D., M. T. Coe, J. D. Lenters, T. E. Twine, and J. A. Foley (2002), Modeling the impact of hydrological changes on nitrate transport in the Mississippi River basin from 1955 to 1994, *Global Biogeochem. Cycles*, *16*(3), 1043, 10.1029/2001GB001396.

Dumont, E., J. A. Harrison, C. Kroeze, E. J. Bakker, and S. P. Seitzinger (2005), Global distribution and sources of DIN export to the coastal zone, *Global Biogeochem. Cycles*, *19*, GB4S02, doi:10.1029/2005GB002488.

Fekete, B. M., C. J. Vörösmarty, and R. B. Lammers (2001), Scaling gridded river networks for macroscale hydrology: Development, analysis and control of error, *Water Resour. Res.*, *3*, 1955–1967.

Fekete, B. M., C. J. Vörösmarty, and W. Grabs (2002), High-resolution fields of global runoff combining observed river discharge and simulated water balances, *Global Biogeochem. Cycles*, *16*(3), 1042, doi:10.1029/1999GB001254.

Forster, P., et al. (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon, D. Qin and M. Manning, Cambridge Univ. Press, Cambridge, U. K.

Friedlingstein, P., et al. (2006), Climate-carbon cycle feedback analysis: Results from the C4MIP model intercomparison, *J. Clim.*, *19*(14), 3337–3353.

Galloway, J. N., et al. (2004), Nitrogen cycles: Past, present, and future, *Biogeochemistry*, *70*(2), 153–226.

Galloway, J. N., A. R. Townsend, J. Erisoman, M. Bekunda, Z. Cai, J. Freney, L. Martinelli, S. Seitzinger, and M. Sutton (2008), Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions, *Science*, *320*, 889–892.

Gerber, S., L. O. Hedin, M. Oppenheimer, S. W. Pacala, and E. Shevliakova (2010), Nitrogen cycling and feedbacks in a global dynamic land model, *Global Biogeochem. Cycles*, *24*, GB1001, doi:10.1029/2008GB003336.

Green, P., C. J. Vorosmarty, M. Meybeck, J. N. Galloway, B. J. Peterson, and E. W. Boyer (2004), Pre-industrial and contemporary fluxes of nitrogen through rivers: A global assessment based on typology, *Biogeochem.*, *68*, 71–105.

Groffman, P. M., M. A. Altabet, J. K. Böhlke, K. Butterbach-Bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, and M. A. Voytek (2006), Methods for measuring denitrification: Diverse approaches to a difficult problem, *Ecol. Appl.*, *16*, 2091–2122.

Gruber, N., and J. Galloway (2008), An Earth-system perspective of the global nitrogen cycle, *Nature*, *451*, 293–296.

Harrison, J. A., N. Caraco, and S. P. Seitzinger (2005), Global patterns and sources of dissolved organic matter export to the coastal zone: Results from a spatially explicit, global model, *Global Biogeochem. Cycles*, *19*, GB4S04, doi:10.1029/2005GB002480.

Houlton, B. Z., E. Bai, and W. H. Schlesinger (2009), Imprint of denitrifying bacteria on the global terrestrial biosphere, *Proc. Natl. Acad. Sci. U. S. A.*, *106*, 21,713–21,716, doi:10.1073/pnas.0912111106.

Houlton, B. Z., A. R. Marklein, and E. Bai (2015), Representation of nitrogen in climate change forecasts, *Nat. Clim. Change*, *5*, 398–401.

Howarth, R. W., F. Chan, D. J. Conley, J. Garnier, S. C. Doney, R. Marino, and G. Billen (2012), Coupled biogeochemical cycles: Eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems, *Front. Ecol. Environ.*, *9*, 18–26.

Hungate, B., J. S. Dukes, M. R. Shaw, Y. Luo, and C. B Field (2003), Nitrogen and climate change, *Science*, *302*, 1512–1513.

Ivens, W., D. Tysmans, C. Kroeze, A. Loehr, and J. van Wijnen (2011), Modeling global N_2O emissions from aquatic systems, *Curr. Opin. Environ. Sustain.*, *3*, 350–358.

Koven, C. D., W. J. Riley, Z. M. Subin, J. Y. Tang, M. S. Torn, W. D. Collins, G. B. Bonan, D. M. Lawrence, and S. C. Swenson (2013), The effect of vertically resolved soil biogeochemistry and alternate soil C and N models on C dynamics of CLM4, *Biogeosciences*, *10*, 7109–7131, doi:10.5194/bg-10-7109-2013.

Kroeze, C., L. Bouwman, and S. Seitzinger (2012), Global nutrient export from watersheds, *Curr. Opin. Environ. Sustain.*, *4*, 195–202.

Kucharik, C. J., and K. R. Brye (2003), Integrated BIosphere Simulator (IBIS) Yield and Nitrate Loss Predictions for Wisconsin Maize Receiving Varied Amounts of Nitrogen Fertilizer, *J. Environ. Qual.*, *32*, 247–268.

Kucharik, C. J., and T. E. Twine (2007), Residue, respiration, and residuals: Evaluation of a dynamic agroecosystem model using eddy flux measurements and biometric data, *Agric. For. Meteorol.*, doi:10.1016/j.agrformet. 2007.05.011.

Lamarque, J. F., et al. (2005), Assessing future nitrogen deposition and carbon cycle feedbacks using a multimodel approach: Analysis of nitrogen deposition, *J. Geophys. Res.*, *110*, D19303, doi:10.1029/2005JD005825.

Lee, M., S. Malyshev, E. Shevliakova, P. C. D. Milly, and P. R. Jaffe (2014), Capturing interactions between nitrogen and hydrological cycles under historical climate and land use: Susquehanna watershed analysis with the GFDL land model LM3-TAN, *Biogeosciences*, *11*, 5809–5826, doi:10.5194/bg-11-5809-2014.

Levis, S., G. B. Bonan, and E. Kluzek (2012), Interactive crop management in the community earth system model (CESM1): Seasonal influences on land-atmosphere fluxes, *J. Clim.*, *25*, 4839–4859, doi:10.1175/JCLI-D-11-00446.1.

Mayorga, E., S. P. Seitzinger, J. A. Harrison, E. Dumont, A. H. W. Beusen, A. F. Bouwman, B. M. Fekete, C. Kroeze, and G. Van Drecht (2010), Global Nutrient Export from WaterSheds 2 (NEWS 2): Model development and implementation, *Environ. Modell. Software 25*(7), 837–853, doi:10.1016/j.envsoft.2010.01.007.

McGuire, A. D., et al. (2007), Responses of high latitude ecosystems to global change: Potential consequences for the climate system, in *Terrestrial Ecosystems in a Changing World, IGBP Series*, edited by J. G. Canadell, D. E., Pataki, and L. F. Pitelka, pp. 297–310, Springer, Berlin.

Meybeck, M. (1982), Carbon, nitrogen and phosphorous transport by world rivers, *Am. J. Sci.*, *282*, 401–450.

Meybeck, M. and A. Ragu (1997), Presenting the GEMS-GLORI, a compendium for world river discharge to the oceans, *IAHS Publ.*, *243*, 3–14.

Oleson, K.W., et al. (2008), Improvements to the Community Land Model and their impact on the hydrological cycle. *J. Geophys. Res.*, *113*, G01021, doi:10.1029/2007JG000563.

Olson, J. S. (1963), Energy stores and the balance of producers and decomposers in ecological systems, *Ecology*, *44*, 322–331.

Potter, P., N. Ramankutty, E. M. Bennett, and S. D. Donner (2010), Characterizing the spatial patterns of global fertilizer application and manure production, *Earth Interact.*, *14*, pp. 2, doi:10.1175/2009EI288.1.

Qian T, A. Dai, K. E. Trenberth, and K. W. Oleson (2006), Simulation of global land surface conditions from 1948 to 2004. Part I: Forcing data and evaluations, *J. Hydrometeorol.*, *7*, 953–975.

Rabalais, N. N. (2002), Nitrogen in aquatic ecosystems, *Ambio*, *31*, 102–112.

Ramankutty, N., and J. A. Foley (1999), Estimating historical changes in global land cover: Croplands from 1700 to 1992, *Global Biogeochem. Cycles*, *13*, 997–1027.

Ravishankara, A., J. Daniel, and R. Portmann (2009), The dominant ozone-depleting substance emitted in the 21st century. *Science*, *326*, 123–125.

Riddick, S. N., D. S. Ward, P. Hess, N. Mahowald, R. S. Massad, and E. A. Holland (2015), Estimate of changes in agricultural terrestrial nitrogen pathways and ammonia emissions from 1850 to present in the Community Earth System Model, *Biogeosci. Discuss.*, *12*(18), 15,947–16,018, doi:10.5194/bgd-12-15947-2015.

Schlesinger, W. H. (2009), On the fate of anthropogenic nitrogen, *Proc. Natl. Acad. Sci. U. S. A.*, *106*, 203–208, doi:10.1073/pnas.0810193105.

Seitzinger, S. P., and C. Kroeze (1998), Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems, *Global Biogeochem. Cycles*, *12*, 93–113.

Seitzinger, S. P., R. V. Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. Van Breemen (2002), Nitrogen retention in rivers: Model development and application to watersheds in the northeastern U.S.A., *Biogeochemistry*, *57/58*, 199–237.

Seitzinger, S. P., J. A. Harrison, E. Dumont, A. H. W. Beusen, and A. F. Bouwman (2005), Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, *Global Biogeochem. Cycles*, *19*, GB4S01, doi:10.1029/2005GB002606.

Seitzinger, S. P., et al. (2010), Global river nutrient export: A scenario analysis of past and future trends, *Global Biogeochem. Cycles*, *24*, GB0A08, doi:10.1029/2009GB003587.

Shaver, G. R., W. D. Billings, F. S. Chapin, A. E. Giblin, K. J. Nadlehoffer, W. C. Oechel, and E. B. Rastetter (1992), Global change and the carbon balance of arctic ecosystems, *BioScience*, *42*, 433–441, doi:10.2307/1311862.

Sokolov, A. P., D. W. Kicklighter, J. M. Melillo, B. S. Felzer, C. A. Schlosser, and T. W. Cronin (2008), Consequences of considering carbon-nitrogen interactions on the feedbacks between climate and the terrestrial carbon cycle, *J. Clim.*, *21*, 3776–3796, doi:10.1175/2008JCLI2038.1.

Swaney, D.P., Hong, B., Ti, C., Howarth, R.W. and Humborg, C. (2012), Net anthropogenic nitrogen inputs to watersheds and riverine N export to coastal waters: A brief overview, *Curr. Opin. Environ. Sustain.*, *4*, 203–212.

Syvitski, J. P. M., S. D. Peckham, R. Hilberman, and T. Mulder (2003), Predicting the terrestrial flux of sediment to the global ocean: A planetary perspective, *Sediment Geol.*, *162*, 5–24.

Tank, S. E., M. Manizza, R. M. Holmes, J. W. McClelland, and B. J. Peterson, (2012), The Processing and Impact of Dissolved Riverine Nitrogen in the Arctic Ocean, *Estuaries Coasts*, *35*, 401–415.

Thomas, R. Q., S. Zaehle, P. H. Templer, and C. L. Goodale (2013a), Global patterns of nitrogen limitation: Confronting two global biogeochemical models with observations, *Global Change Biol.*, *19*, 2986–2998.

Thomas, R. Q., G. B. Bonan, and C. L. Goodale (2013b), Insights into mechanisms governing forest carbon response to nitrogen deposition: A model-data comparison using observed responses to nitrogen addition, *Biogeosciences*, *10*, 3869–3887.

Thornton, P. E., and N. A. Rosenbloom (2005), Ecosystem model spin-up: Estimating steady state conditions in a coupled terrestrial carbon and nitrogen cycle model, *Ecol. Modell.*, *189*, 25–48.

Thornton, P. E., J.-F. Lamarque, N. A. Rosenbloom, and N. M. Mahowald (2007), Influence of carbon-nitrogen cycle coupling on land model response to CO2 fertilization and climate variability, *Global Biogeochem. Cycles*, *21*, GB4018, doi:10.1029/2006GB002868.

Thornton, P., S. C. Doney, K. Lindsay, J. K. Moore, N. Mahowald, J. T. Randerson, I. Fung, J.-F. Lamarque, J. J. Feddema, and Y.-H. Lee (2009), Carbon-nitrogen interactions regulate climate-carbon cycle feedbacks: Results from an atmosphere-ocean general circulation model, *Biogeosciences*, *6*, 2099–2120.

Van Bremen, N., et al. (2002), Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A., *Biogeochemistry*, *57/58*, 267–293.

Van Drecht, G., A. F. Bouwman, J. M. Knoop, A. H. W. Beusen, and C. R. Meinardi (2003), Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water, *Global Biogeochem. Cycles*, *17*(4), 1115, doi:10.1029/2003GB002060.

Van Drecht, G., A. F. Bouwman, E. W. Boyer, P. Green, and S. Siebert (2005), A comparison of global spatial distributions of nitrogen inputs for nonpoint sources and effects on river nitrogen export, *Global Biogeochem. Cycles*, *19*, GB4S06, doi:10.1029/2005GB002454.

Viovy, N., and P. Ciais (2009), *A Combined Dataset for Ecosystem Modelling*. [Available at http://dods.extra.cea.fr/data/p529viov/cruncep/readme.htm.]

Vörösmarty, C. J., B. M. Fekete, M. Meybeck, and R. Lammers (2000), A simulated topological network representing the global system of rivers at 30-minute spatial resolution (STN-30), *Global Biogeochem. Cycles*, *14*, 599–621.

Walker, A. P., et al. (2015), Predicting long-term carbon sequestration in response to CO_2 enrichment: How and why do current ecosystem models differ?, *Global Biogeochem. Cycles*, *29*, 476–495, doi:10.1002/2014GB004995.

Wang, Y.-P., and B. Z. Houlton (2009), Nitrogen constraints on terrestrial carbon uptake: Implications for the global carbon-climate feedback, *Geophys. Res. Lett.*, *36*, L24403, doi:10.1029/2009GL041009.

Ward, D. S., and N. M. Mahowald (2015), Local sources of global climate forcing from different categories of land use activities, *Earth Syst. Dyn.*, *6*, 175–194, doi:10.5194/esd-6-175-2015.

Wollheim, W. M., C. J. Vorosmarty, A. F. Bouwman, P. Green, J. Harrison, E. Linder, B. J. Peterson, S. P. Seitzinger, and J. P. M. Syvitski (2008), Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach, *Global Biogeochem. Cycles*, *22*, GB2026, doi:10.1029/2007GB002963.

Zaehle, S., A. D. Friend, P. Friedlingstein, F. Dentener, P. Peylin, and M. Schulz (2010), Carbon and nitrogen cycle dynamics in the O-CN land surface model: 2. Role of the nitrogen cycle in the historical terrestrial carbon balance, *Global Biogeochem*. *Cycles*, *24*, GB1006, doi:10.1029/2009GB003522.[10.1029/2009GB003522]

Zaehle, S., C. D. Jones, B. Houlton, J.-F. Lamarque, and E. Robertson (2014), Nitrogen availability reduces CMIP5 projections of twenty-first-century land carbon uptake, *J. Clim.*, *28*, 2494–2511, doi:10.1175/JCLI-D-13-00776.1.