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Key Points:

- N deposition continues to induce land C sequestration into the 21st century as N demand is sustained by CO_2 fertilization
- Phosphorus limitations cause nitrogen deposition to have net negative effects on plant growth in some temperate regions with excess N supply
- Current land surface model representations likely underestimate direct negative effects of excess N supply

Supporting Information:

- Supporting Information S1

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Nitrogen Deposition Maintains a Positive Effect on Terrestrial Carbon Sequestration in the 21st Century Despite Growing Phosphorus Limitation at Regional Scales

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Abstract Nitrogen (N) and phosphorus (P) are two dominant nutrients regulating the productivity of most terrestrial ecosystems. The growing imbalance of anthropogenic N and P inputs into the future is estimated to exacerbate P limitation on land and limit the land carbon (C) sink, so that we hypothesized that P limitation will increasingly reduce C sequestered per unit N deposited into the future. Using a global land surface model (CABLE), we simulated the effects of increased N deposition with and without P limitation on land C uptake and the fate of deposited N on land from 1901 to 2100. Contrary to our hypothesis, we found that N deposition continued to induce land C sequestration into the future, contributing to 15% of future C sequestration as opposed to 6% over the historical period. P limitation reduced the future land C uptake per unit N deposited only moderately at the global scale but P limitation increasingly caused N deposition to have net negative effects on the land C balance in the temperate zone. P limitation further increased the fraction of deposited N that is lost via leaching to aquatic ecosystems, globally from 38.5% over the historical period to 53% into the future, and up to 75% in tropical ecosystems. Our results suggest continued N demand for plant productivity but also indicate growing adverse N deposition effects in the future biosphere, not fully accounted for in global models, emphasizing the urgent need to elaborate on model representations of N and P dynamics.

Plain Language Summary Human activity has altered the cycling of the most essential nutrients for live, namely nitrogen and phosphorus. Due to the use of industrial fertilizers and the combustion of fossil fuels, nitrogen enters ecosystems via atmospheric deposition in much higher rates than phosphorus, creating a nutritional imbalance. We use a global land surface model to estimate the effect of nitrogen deposition on global ecosystems in the past and in the future. We speculated that due to the heightened availability of nitrogen in the future, limitations by phosphorus would become more pronounced. We find that nitrogen deposition continues to have fertilizing effects on plant growth that is otherwise limited by nitrogen supply. Phosphorus limitations become more prevalent in the future in our simulations but not as strong as we expected. Alarmingly, however, we find that an increasing amount of nitrogen is lost from terrestrial ecosystems and enters aquatic ecosystems with expected deleterious effects. Our results highlight one possible scenario of our future world, indicating that many uncertainties remain in regard to nutrient supply and interactions, all of which, however, need to be understood and quantified to predict global vegetation responses to and interactions with the future climate.

1. Introduction

The carbon (C) balance of most terrestrial ecosystems is strongly regulated by nitrogen (N) and/or phosphorus (P; Fernández-Martínez et al., 2014; Vitousek et al., 2010). Since the preindustrial revolution, atmospheric N deposition (both wet and dry) has been increasing steadily across most land regions, where it reached record levels in highly industrialized regions, such as Europe, and in intensely farmed regions, such as southern China and parts of India (Galloway et al., 2008; Lamarque et al., 2010). Globally, the input of anthropogenic N through atmospheric deposition increased from about 26 Tg N/year in 1900 to about 73 Tg N/year in 2010 (Lamarque et al., 2010). N deposition may stimulate photosynthesis and growth, inducing net C sequestration in biomass and soils when N limits productivity (Fleischer et al., 2013; Magnani et al., 2007; Thomas et al., 2010). Anthropogenic N deposition was estimated to have contributed about 8.8 Pg C, or 6% of total C accumulation on land due to CO_2 fertilization and climate from 1860 to 2010 (Zaehle, 2013). If N fertilizer use and N_2-fixing crops are considered, the increase in total anthropogenic N inputs and its effect on to the land biosphere will even be greater.

The rapid increase in N input to unmanaged land biosphere is not matched by the change in P input through dust deposition, which only increased from about 1.8 Tg P/year before 1960 to about 2.7 Tg P/year at present (Wang et al., 2015). As projected into the future under the representative concentration pathway (RCP) 8.5, atmospheric N deposition will continue to increase to 88 Tg N/year by 2100 (Lamarque et al., 2013), while little change of P deposition is anticipated. Field observations found that N:P plant stoichiometry was shifted toward higher N:P ratio in response to increased N deposition (Sardans et al., 2012). At the global scale, this disproportional human-induced supply of reactive N relative to P can cause a significant shift in nutrient balance and land C sequestration (Peñuelas et al., 2013), as well as a significant increase in N loss, adversely affecting water quality and increasing emissions of N_2O, a potent greenhouse gas in the atmosphere.

Based on mass balance accounting, the availability of N and P will limit the future productivity and land C storage (Wieder, Cleveland, et al., 2015), while the imbalance of N and P inputs is expected to further reduce future C storage by the land biosphere (Peñuelas et al., 2013). However, mass balance approaches do not consider significant spatial variations of N and P inputs on land, and the likely different responses and interactions of N and P cycles among different ecosystems. For example, boreal and temperate forests are generally N limited due to relatively young soils that have not yet undergone extensive built up of N through biological N fixation (Lambers et al., 2008; Vitousek et al., 2010). N deposition was estimated to induce C sequestration at rates of 15–40 kg C per kg N ha^{-1} in boreal and temperate ecosystems (Butterbach-Bahl et al., 2011; de Vries et al., 2009; Erisman et al., 2011). N deposition effects for tropical ecosystems are reported less frequently, although human-induced changes to the tropical N cycle are underway (Hietz et al., 2011; Huang et al., 2012). We do however expect the N deposition effect on C sequestration to be small in tropical ecosystems, generally characterized by highly weathered soils, low P availability and high rates of N cycling (Vitousek et al., 2010). Although generalizations of nutrient limitation across climate zones are useful, some nuance and refinement of this view is required as N and P limitation, as well as colimitation of N and P may occur in forests worldwide due to heterogeneity in soil pedogenesis and nutrient availability (Elser et al., 2007; Harpole et al., 2011).

Considering this natural complexity of nutrient dynamics, other factors may alter future N and P dynamics, such as N inputs from biological N fixation, which is a major natural source of N for terrestrial ecosystems (Cleveland et al., 2013; Vitousek et al., 2013). Biological N fixation is dynamically controlled by climate, nutrition and vegetation composition, and although regulating factors are not fully elucidated yet, a process-based model foresees a potential rise in biological N fixation due to climate warming and elevated atmospheric CO_2 concentrations (eCO_2) (Houlton et al., 2008; Wang & Houlton, 2009). Excess reactive N may further alter N and P dynamics as it continuously cascades in the biosphere, causing detrimental effects on ecosystem health and plant growth due to eutrophication and chemical imbalances, not only in terrestrial ecosystems, but also in aquatic ecosystems due to leaching or direct deposition (Erisman & de Vries, 2000; Galloway et al., 2003, 2008). It remains unclear to what degree the stimulatory effects of N deposition on land C storage will be counterbalanced by feedbacks from P limitation and N:P imbalances, by other N inputs to terrestrial ecosystems, such as biological N fixation, or to what degree direct negative effects on the C balance would occur due to excess N.

Global ecosystem models are progressively incorporating dynamic N and P cycles to test their control on the global C balance (Buendía et al., 2014; Goll et al., 2012, 2017; Yang et al., 2014). The land surface model CABLE considers C, N, and P dynamics and has previously been employed to estimate the control of N and P limitation on the historical and future global C balance (Y.-P. Wang et al., 2010). Simulations with

Table 1
List of Model Experiments Including Biogeochemical Interactions Considered (CN or CNP), the Forcing Used (Climate, Atmospheric CO_2, N Deposition, N Fixation, and Land Cover), and Their Application in This Study

Experiment	CABLE	Climate	Atm. CO_2	N deposition	N fixation	Land Cover	Application
CN_0	CN	1900–2100	1900–2100	1900	Original	1900	Effect of N deposition rise considering C-N interactions
CN_1	CN	1900–2100	1900–2100	1900–2100	Original	1900	
CNP_0	CNP	1900–2100	1900–2100	1900	Original	1900	Effect of N deposition rise considering C-N-P interactions
CNP_1	CNP	1900–2100	1900–2100	1900–2100	Original	1900	
CN_{0BNF+}	CN	1900–2100	1900–2100	1900	+100%	1900	Effect of N deposition rise considering C-N interactions and high N fixation
CN_{1BNF+}	CN	1900–2100	1900–2100	1900–2100	+100%	1900	
CNP_{0BNF+}	CNP	1900–2100	1900–2100	1900	+100%	1900	Effect of N deposition rise considering C-N-P interactions and high N fixation
CNP_{1BNF+}	CNP	1900–2100	1900–2100	1900–2100	+100%	1900	

Note. Transient changes of forcing indicated as “1900–2100” and stagnant forcing as “1900,” representing conditions of 1900.

CABLE indicated that P effects are moderate at the global scale but significant at the regional scale (Wang et al., 2010; Zhang et al., 2011, 2014). These simulations did however not consider the transient nature of N deposition and the potential control of elevated biological N fixation inputs in the future, nor were consequences on N leaching examined.

We therefore extended these analyses with a set of global simulations with CABLE to estimate the effect of transient N deposition on land C storage and N losses, considering P feedbacks from 1900 to 2100. We focused on the effects of P limitation on total C sequestration, the net C uptake per unit N deposited, and the different pathways of deposited N (accumulation in plant, litter, or soil pools, leaching, and gaseous loss) among different ecosystem types, and considered different scenarios of future biological N fixation to estimate its potential counterbalancing effect (Table 1). We tested the hypothesis that N deposition induced significant C sequestration over the historical period (1900–2010) but that its positive effect on the C balance would be reduced in the future (2011–2100) due to growing N:P imbalances, or P limitation. We further expected that increasing N deposition and N:P imbalances would augment N leaching into the future.

2. Methods

2.1. Land Surface Model: CABLE

The land surface model CABLE (version 2.0 released in 2012, revision 1721 for this study) simulates land-atmosphere exchange of water, energy, and gas, including the biogeochemical cycles of C, N, and P. Detailed descriptions and evaluation of CABLE and its biogeochemistry are described elsewhere (Wang et al., 2007, 2010; Zhang et al., 2013). Ecosystem N inputs occur from deposition, prescribed from atmospheric transport models (Lamarque et al., 2010, 2011) and from biological N fixation (Wang & Houlton, 2009). Plant N uptake is a function of plant N demand and the plant available soil mineral N pool, while plant N demand in turn is a function of maximum N:C ratio and net primary productivity (NPP) for each plant pool. N is lost via gaseous losses, proportional to the net N mineralization rate, and via leaching, proportional to the soil mineral N pool (Wang et al., 2010). Nitrification and denitrification were not modeled explicitly, and ammonia volatilization or organic N and P uptake were not considered in CABLE.

In addition to three soil organic matter P pools as in the C and N cycles, the microbial, slow and fast pool, three secondary P pools are considered: the labile, sorbed, and strongly sorbed, of which only the labile P pool is available for plant uptake (Wang et al., 2010). Labile P is derived from biological and biochemical P mineralization. Biological P mineralization depends on soil C mineralization and the C:P ratio of soil organic matter. Biochemical P mineralization of the slow and passive soil pool is modeled as a function of the size and the N:P ratio of these pools, the maximal specific biochemical P mineralization rate and the fixed N cost for P uptake and phosphatase production (Wang et al., 2007). P enters the ecosystem through weathering and atmospheric deposition. Outputs of the P cycle are leaching loss of labile P, a function of the labile P pool size (Wang et al., 2010).

The N and P cycles are coupled to the C cycle via controls on gross primary productivity (GPP), autotrophic respiration (R_a), and stoichiometric requirements for NPP (NPP = GPP − R_a). GPP is determined by plant functional type (PFT) specific leaf C:N and N:P ratios (Kattge et al., 2009; Reich et al., 2009; Zhang et al., 2013). Plant available soil N and P limit NPP when the respective plant N or P demand is not met (Wang et al., 2010). R_a increases with lowering C:N and N:P ratios in plant tissue, where leaf R_a increases faster than photosynthesis at the high end of leaf N (Kattge et al., 2009; Wang et al., 2010). Heterotrophic respiration (R_h) is limited by the mineral N pool required for microbial soil C decomposition (Wang et al., 2010). Net ecosystem exchange ($-\text{NEE} = \text{GPP} - R_a - R_h$) is the amount of C sequestered or lost from terrestrial ecosystems, neglecting lateral fluxes, and is controlled by N and P availability via abovementioned C-N-P interactions.

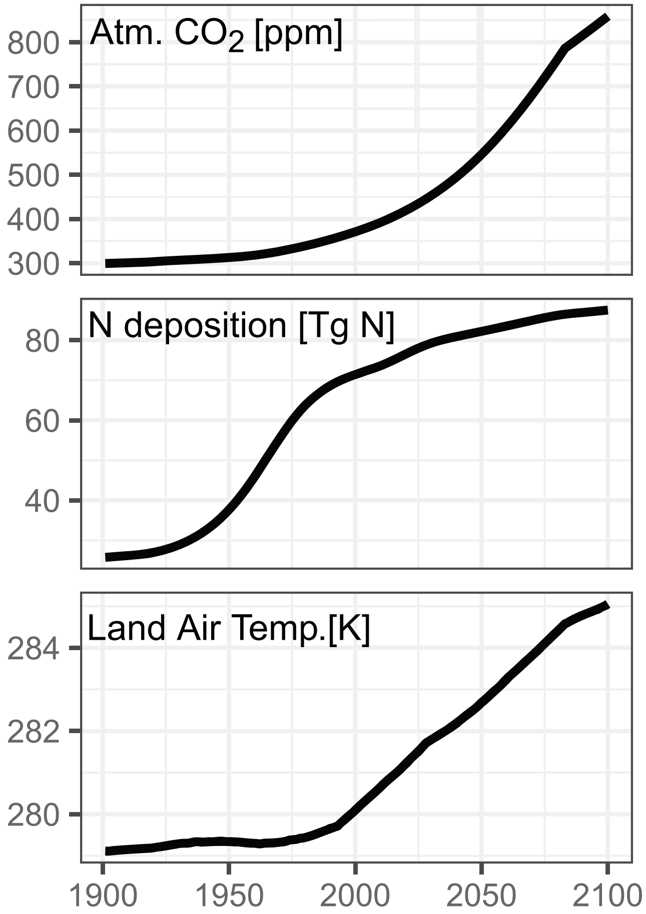

Figure 1. Trajectories of transient forcing data for historical and future simulation period (1901–2100), from top to bottom; atmospheric CO_2 (ppm), global total N deposition (Tg N), and air temperature over all land grids (K).

2.2. Input Data Sets

CABLE requires input of meteorological conditions, atmospheric CO_2 concentrations, and vegetation distribution; additional inputs of N and P deposition, biological N fixation, and P weathering are required for simulating the N and P cycles. The climatic forcing data, that is, air temperature, humidity, wind speed, air pressure, precipitation, and long-wave and short-wave radiation, were taken from simulations by the Community Climate System Model with a 1.9° × 2.5° spatial resolution and hourly time steps from the historical period (1900–2005) and the RCP 8.5 scenario (Representative Concentration Pathway 8.5) from 2006 to 2100 (G. Bonan, personal communication, May 2014). Atmospheric CO_2 concentrations from 1900 to 2100 are taken from the CMIP5 data set, including the RCP 8.5 scenario after 2005 (Etheridge et al., 1996; MacFarling Meure et al., 2006).

Annual N deposition estimates were linearly interpolated from decadal time slices of global N deposition from the atmospheric chemistry model CAM-Chem (Lamarque et al., 2012) at a spatial resolution of 1.9° × 2.5°. Historical estimates served for 1900–1999 and the RCP8.5 scenario for 2000–2100 (Lamarque et al., 2010, 2011; see Figure S1). J. F. Lamarque provided both data sets, which are available upon request (lamar@ucar.edu). N fertilizer applications on croplands were not considered in our simulations. Biological N fixation was derived from an independent process-based model, as a function of temperature and competition between fixers and nonfixers for light, soil N and P (Houlton et al., 2008; Wang et al., 2007; Wang & Houlton, 2009), so it was prescribed spatially explicit but constant in time, see Figure S1. P weathering rates are calculated as a function of soil order (Wang et al., 2010) and P atmospheric deposition are taken from (Mahowald et al., 2008).

We employed a land cover map from 1900 for the entire simulation, derived from fractional PFT distributions for the Community Land Model version 4.0 (CLM 4.0) at 0.5° × 0.5° spatial resolutions, including 12 PFT classes and their percentile coverage per grid cell (Lawrence et al., 2012). PFT distributions from CLM 4.0 were upscaled to 1.9°× 2.5° and translated to the 13 CABLE PFTs with additional ice, lake, and wetland fractions for each land cell (Figure S2).

2.3. Modeling Protocol

CABLE was applied at a 1.9° × 2.5° spatial resolution (latitude vs longitude) in two different configurations of the biogeochemical cycling component (CN and CNP mode) and was brought into steady-state conditions of biogeochemical fluxes and pools in 1900. The spin-up phase consisted of two times 100 years with repeated meteorological forcing from 1901–1910, N deposition levels, and CO_2 concentrations of 1900, intermitted with an accelerated spin-up routine (Xia et al., 2012), and resulted in all pools and fluxes being in steady-state.

We performed eight model experiments from 1901–2100 to discern the effect of N deposition on land C storage, considering P cycle feedbacks and increasing N inputs from biological N fixation. The base set of simulations represent a low and high N deposition scenario including the C and N cycles (CN_0 and CN_1), and the C, N, and P cycles (CNP_0 and CNP_1). These four simulations were repeated with a high future biological N fixation scenario (denoted with the subscript "BNF+"; Table 1). We considered historical estimates and future projections of transient changes in global drivers, assuming the "business-as-usual" scenario (RCP8.5) for future projections (Figure 1). Based on these, atmospheric CO_2 concentrations rose from 296 ppm in 1901, to 389 ppm in 2010 and was expected to reach 881 ppm in 2100. Global terrestrial N deposition increased exponentially from 26 to 73 Tg N/year between 1901 and 2010 with a projected further rise to 88 Tg N/year in 2100. Global mean land temperatures were projected to rise another 5 K over the 21st century. The high biological N fixation scenario considered a rise of 100% from 2011 onward, from 169.4 to 338.8 Tg N/year globally (Table 1 and Figure S1). The approximation of a 100% rise is based on the process-based projections (Wang & Houlton, 2009), roughly corresponding to the global change scenario considered in this study.

3. Results

3.1. Evaluation of the Global Carbon Balance and the Historical N Deposition Effect

We evaluated CABLE's performance in simulating the current and historical land C balance based on our baseline simulation (CNP_1), including C-N-P dynamics as well as the rise in N deposition (Table 2). CNP_1 resulted in a global GPP of 129.9 Pg C/year and a net C uptake of 2.3 Pg C/year in the 2000s. Our estimate is within reported ranges for the residual land C sink from the Global Carbon Project (Le Quéré et al., 2018), which is a fair comparison as we do not consider C fluxes from land use and land cover changes in our simulations. NPP of 59.8 Pg C/year in the 2000s agreed well with a synthesis of observations (Ito, 2011). Current global biomass and soil C estimates were also close to or within observed ranges, although associated to considerable uncertainties, in particular for soil C (Tifafi et al., 2018). Terrestrial ecosystems have sequestered ~200 Pg C from 1901 to 2010 (CNP_1) in our simulations, for which the latest Intergovernmental Panel on Climate Change assessment reports a potential range of 160 ± 90 Pg C (Ciais et al., 2013).

N deposition was responsible for ~6% of total C accumulation, or 10.9 Pg C (CNP_1-CNP_0) from 1901 to 2010 and induced 0.3 Pg C sequestration per year in the 2000s (Table 2). The difference in N deposition input between the low and high N deposition scenario amounted to 2253 Tg N between 1901 and 2010. N deposition thus induced land C uptake of 4.8 kg C per kg N globally and up to 12.9 kg C per kg N in boreal ecosystems in the CNP simulations (Table 3). Our simulations suggest that temperate ecosystems sequestered the bulk of the N deposition induced C uptake (5.5 Pg C), followed by boreal (2.8 Pg C), tropical (1.5 Pg C), and subtropical ecosystems (1.0 Pg C; Figure 3 and Table 3).

N deposition accumulated predominantly in soils (56.5%) and only small fractions (3.4%) in vegetation biomass over the historical period, while the second largest fraction (38.5%) of N deposition was lost via leaching (Table 3). The bulk of N deposition from 1901 to 2010 occurred over temperate and tropical ecosystems, less over subtropical and boreal ecosystems (Table 3 and Figure S1). N deposition's fate differed accordingly, so that in the tropics, N deposition was predominantly lost (63.3%) and this fraction decreased poleward to only small fractions being lost in the boreal zone (9.1%). In boreal ecosystems, N deposition accumulated predominantly in soils (79.0%), while this fraction decreased toward the tropics (33.0%; Table 3).

3.2. N Deposition Induces Significant C Storage and N Losses Into the Future

N deposition increased its fertilizing effect on global land C uptake in the 21st century in both CN and CNP simulations, contrary to our expectation of a reduced positive effect in the future (Figure 2). Over the period from 2010 to 2100, N deposition induced an additional 26.8 Pg C storage on land in the CNP simulations, which accounted for 15% of total land C accumulation (Table 2). In the temperate zone N deposition sustained ~36% of total future C accumulation, and 23% and 18% in the subtropical and boreal zone, respectively for the CNP simulation (Figure 3). Future land C accumulation occurred at rates of 5.2 kg C per kg N globally, ranging from 18.2 kg C per kg N in boreal ecosystems to 0.5 kg C per kg N in tropical ecosystems in the CNP simulations (Table 4). Rates of land C accumulation per unit N deposition thus increased in all climate zones over the future period, except the tropics, where P limitations halted the fertilizing effect of N deposition.

Table 2

Global C Fluxes, Pools, and C Sequestration Rates per Model Run (as in Table 1), Compared to Observational Based Estimates, Including Mean C Fluxes in the 2000s and 2090s, C Pools in 2010, and Historical and Future C Sequestration

Variable	CN$_0$	CN$_1$	CNP$_0$	CNP$_1$	Observations
Current C fluxes (Pg C/year; 2000–2010)					
GPP	134.3	135.8	128.6	129.9	123 ± 8[a] 150–175[b]
NPP	63.0	64.0	59.0	59.8	59.5[c] 56.6[d]
NEE	−2.4	−2.7	−2.0	−2.3	−2.7 ± 0.7[e] −2.3 ± 0.5[f]
Current C pools (Pg C; 2010)					
Vegetation C	731	738	693	699	450–650[e]
Soil C	935	939	897	901	1,416 (504–3,000)[g] 1,520 ± 770[h]
Historical terrestrial C sequestration (Pg C; 1901–2010)					
Cumulative NEE^{-1}	200.0	212.5	190.6	201.5	160 ± 90[i]
Future C fluxes in (Pg C/year; 2090–2100)					
GPP	169.6	174.6	164.1	168.4	
NPP	73.1	75.8	69.3	71.6	
NEE	0.8	0.5	0.7	0.4	
Future terrestrial C sequestration (Pg C; 2011–2100)					
cumulative NEE^{-1}	153.1	185.1	152.1	178.9	

Note. C fluxes are gross primary productivity (GPP), net primary productivity (NPP), and net ecosystem productivity (NEE), with negative NEE representing a terrestrial net C uptake (C sink). Carbon pools shown for vegetation C (i.e., sum of root, wood and leaf pool), and soil C. Note that terrestrial C sequestration rates are denoted as cumulative NEE^{-1}, so that positive values indicate net terrestrial gain of C.
[a] Beer et al. (2010): Upscaling of C flux measurements. [b] Welp et al. (2011): Oxygen isotope analysis of atmospheric CO$_2$. [c] Ito (2011): Synthesis of published estimates. [d] Running et al. (2004): Satellite-derived product (Moderate-resolution Imaging Spectroradiometer (MODIS)), mean of 2001 and 2002. [e] Le Quéré et al. (2018): Global Carbon Project: Booking method, residual terrestrial land sink 2000–2009. [f] Pan et al. (2011): Forest inventories, forests only, 2000–2007. [g] Scharlemann et al. (2014): Median and range from summary of 27 studies. [h] Todd-Brown et al. (2013): Mean ± standard error from 11 ecosystem model predictions. [i] Ciais et al. (2013): Residual land C sink without land use change emissions (fifth Intergovernmental Panel on Climate Change report).

N deposition was increasingly lost via leaching over the 21st century. The total N deposited over the future period (compared to the low N deposition scenario) amounted to 5169 Tg N, of which 53.0% leached to aquatic ecosystems in the CNP simulations, representing a threefold increase of total N leaching compared to the historical period (Table 4). Soil accumulation of deposited N reduced to 38.9%, although in absolute terms

Table 3

Historical Effect of N Deposition on C Sequestration and N Leaching (1901–2010) per Climate Zone in CN and CNP Model Simulations, From Left to Right: Total Ecosystem C Sequestration in the High N Deposition Scenario, Cumulative Sum of N Deposition, Total and Relative C Sequestration From N Deposition, Cumulative Sum of N Leached Due To N Deposition and the Fraction of N Deposition That Is Leached and That Is Accumulated in Soil and Biomass

Historical: 1901–2010								
			N deposition effect on C sequestration			Fate of N deposition (%)		
Climate zone	Pg C sequestered	Tg N deposited[a]	Pg C sequestered due to N deposition	kg C sequestered per kg N deposited	Tg N leached	Leaching	Soil accumulation	Biomass accumulation
	CN$_1$	CN$_1$-CN$_0$	CN$_1$-CN$_0$		CN$_1$-CN$_0$			
Boreal	20.9	219	2.8	12.7	20	9.0	79.4	5.2
Temp.	61.4	893	6.6	7.4	171	19.2	75.1	3.9
Subtrop.	26.6	372	1.6	4.4	153	41.1	56.7	3.1
Tropical	103.6	768	1.5	2.0	484	63.0	33.1	3.3
Global	212.5	2253	12.5	5.6	827	36.7	58.1	3.7
	CNP$_1$		CNP$_1$-CNP$_0$	CNP$_1$-CNP$_0$	CNP$_1$-CNP$_0$			
Boreal	20.8	219	2.8	12.9	20	9.1	79.0	5.4
Temp.	57.5	893	5.5	6.1	194	21.7	72.8	3.5
Subtrop.	21.3	372	1.0	2.8	168	45.2	52.4	2.4
Tropical	101.9	768	1.5	2.0	486	63.3	33.0	3.2
Global	201.5	2253	10.9	4.8	868	38.5	56.5	3.4

[a] Additional N deposition in high N deposition scenario (CN$_1$-CN$_0$ and CNP$_1$-CNP$_0$).

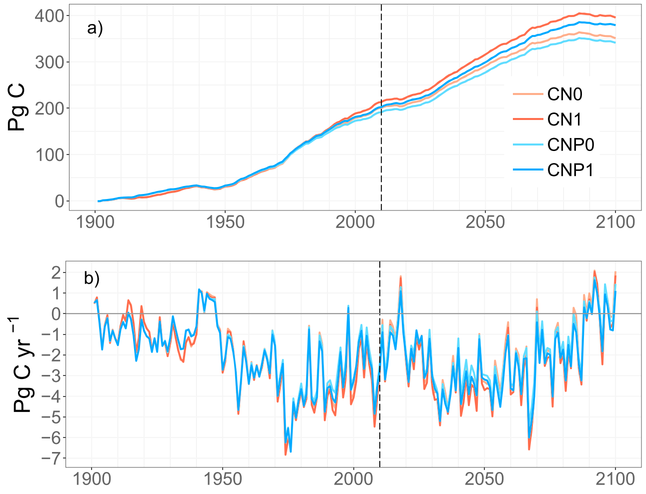

Figure 2. Cumulative NEE (= GPP − R_{eco}) from 1901–2100 for the CN and CNP simulation runs (Pg C), with positive values for net terrestrial C uptake, that is, Σ (NEE * −1) (a), and annual NEE (Pg C per year), with negative values indicating a net terrestrial C uptake (b). NEE = et ecosystem exchange; GPP = gross primary productivity; R_{eco} = ecosystem respiration.

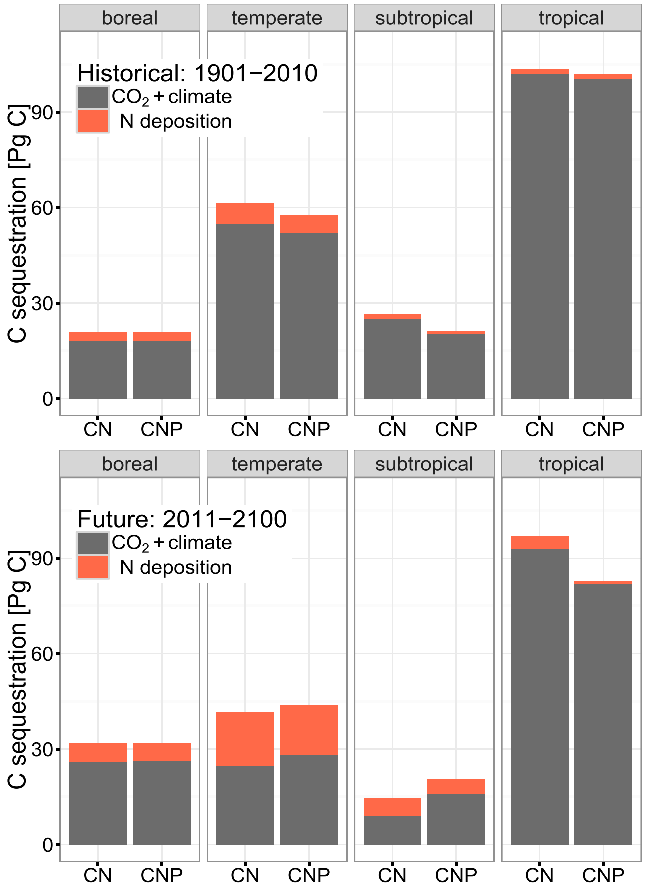

Figure 3. Total land C sequestration and contribution of N deposition from 1901 to 2010 (left) and from 2011–2100 (right) per climate zone in CN simulations (CO_2 + climate = CN_0; N deposition = $CN_1 - CN_0$) and CNP simulations (CO_2 + climate = CN_0; N deposition = $CN_1 - CN_0$; unit: Pg C).

soil N accumulation more than doubled compared to the historical period (Table 3). In the tropics, 75.1% of N deposition was lost via leaching and this fraction decreased poleward to 59.1% in the subtropics and to 14.8% in the boreal zone. Soil N accumulation of deposited N was highest in boreal soils (72.5%) and lowest in tropical soils (20.0%; Table 4).

The global land C sink gradually declined after ~2050 in our simulations and the terrestrial biosphere acts as a net C source of 0.4–0.8 Pg C/year by the end of the 21st century, equivalent to 0.2–0.4 ppm of atmospheric CO_2 (Figure 2b; Table 2). The CO_2 fertilization effect on GPP slowly declined after 2050 and saturated ~2070 from which point onward the stimulation of heterotrophic respiration due to rising temperatures outweighs terrestrial C gains (not shown). The total land C sink was thus lower in the future period (Figure 3) due to the combined effects of saturating CO_2 fertilization of plant productivity and climate warming, while the relative contribution of N deposition on the land C sink was greater (Figure 3).

Higher biological N fixation rates did not notably alter our simulated effects of N deposition over the 21st century (Table 5). N deposition induced land C uptake reduced by 2.0 Pg C and increased by 1.0 Pg C in the CN and CNP simulations, respectively (Table 5). Total C accumulation, in fact, reduced with higher biological N fixation and slightly increased the C source strength of the terrestrial biosphere in the 2090s.

3.3. P Limitation on C Accumulation Minor at Global Scale but P Feedbacks Occur at Regional Scale

P cycle feedbacks reduced global land C accumulation only slightly by 5% and the fertilizing effect of N deposition on C sequestration was reduced moderately by 13% from 1900–2010 (CNP-CN; Table 3). P limitation occurred mainly in the temperate and subtropical ecosystems, while boreal and tropical ecosystems experienced hardly any P limitation in our simulations over the historical period (Figure 3). Over the future period, from 2011 to 2100, P feedbacks reduced land C uptake by 3% and the fertilizing effect of N deposition by 16%. Contrary to our expectation, P limitation at the global scale was subtle and did not increase into the future. In tropical ecosystems, however, P limitation reduced the land C uptake by 15% and the fertilizing effect of N deposition on the land C uptake by 77% over the future period (Figure 3).

Growing adverse effects of N deposition due to excess N and increasing N:P imbalances occurred at the regional scales. N deposition induced net negative effects on the C balance in both CN and CNP (Figures 4c and 4d), which occurred when N supply exceeded its demands, so that maintenance respiration costs of N in tissues were higher than the associated increase in V_{cmax} and GPP (Wang et al., 2010). Considering P limitation on V_{cmax} and GPP aggravated this feedback, mainly in the temperate zone, where frequencies of N deposition inducing net negative effects on the C balance increased and frequencies of net positive effects reduced due to P feedbacks (Figures 4d and S3). P cycle feedbacks further induced net negative effects on the terrestrial N balance by increasing N leaching moderately, by ~10% over the future period (Table 4). P limitation slightly shifted the predominant fate of deposited N toward leaching (53.0%) and reduced the amount of N accumulating in soil (38.9%) and biomass (2.4%; Table 4). This shift was strongest in tropical ecosystems, where 75.1% of deposited N was lost via leaching.

Table 4

Future Effect of N Deposition on C Sequestration and N Leaching (2011–2100) per Climate Zone in CN and CNP Model Simulations, From Left to Right: Total Ecosystem C Sequestration in the High N Deposition Scenario, Cumulative Sum of N Deposition, Total and Relative C Sequestration From N Deposition, Cumulative Sum of N Leached Due To N Deposition and the Fraction of N Deposition That Is Leached and That Is Accumulated in Soil and Biomass

Future: 2011–2100								
			N deposition effect on C sequestration			Fate of N deposition (%)		
Climate zone	Pg C sequestered	Tg N deposited[a]	Pg C sequestered due to N deposition	kg C sequestered per kg N deposited	Tg N leached	Leaching	Soil accumulation	Biomass accumulation
	CN_1	CN_1-CN_0	CN_1-CN_0		CN_1-CN_0			
Boreal	31.9	310	5.7	18.4	46	14.8	72.8	5.2
Temp.	41.6	1882	16.8	8.9	594	31.6	57.2	3.4
Subtrop.	14.6	1148	5.6	4.9	647	56.3	36.8	2.3
Tropical	96.9	1828	3.9	2.1	1208	66.1	27.3	1.6
Global	185.1	5169	32	6.2	2495	48.3	43.0	2.6
	CNP_1		CNP_1-CNP_0	CNP_1-CNP_0	CNP_1-CNP_0			
Boreal	31.8	310	5.6	18.2	46	14.8	72.5	5.2
Temp.	43.8	1882	15.6	8.3	643	34.1	54.5	3.3
Subtrop.	20.6	1148	4.7	4.1	678	59.1	34.2	2.2
Tropical	82.7	1828	0.9	0.5	1374	75.1	20.0	1.0
Global	178.9	5169	26.8	5.2	2741	53.0	38.9	2.4

[a] Additional N deposition in high N deposition scenario (CN_1-CN_0 and CNP_1-CNP_0).

3.4. N Deposition Induces C Sequestration Due To Higher N Uptake and Shifts From Biomass to Soil C Sink Into the Future

Higher N uptake with N deposition, and thus alleviation from N limitation, was the dominant mechanism in CABLE to induce land C storage (Figure 5). Alleviation from N limitation caused stimulation of NPP and higher growth efficiency (NPP / leaf area index (LAI)). Elevated atmospheric CO_2 stimulated GPP via increased photosynthetic rate per unit of LAI, and via higher LAI until reaching its maximum (not shown). Leaf stoichiometric changes were minimal due to constrained stoichiometry, as were changes in C allocation fractions, so that nitrogen use efficiency (NUE = NPP / N uptake) increased only slightly with N deposition.

N deposition induced C storage mainly in biomass over the historical period, which shifted toward a dominant soil C sink in the future period due to sustained litter C inputs, in both CN and CNP simulations. For the CNP simulations, for example, the biomass and soil C sink represented 54% and 36% of total historical land C accumulation, respectively, which reversed to 38% and 54% over the future period (Figure 6). P limitation did not markedly alter these shifts in dominating N induced C sinks.

4. Discussion

4.1. N Deposition Effect on Land C Sequestration

N deposition had a fertilizing effect on plant productivity and induced land C sequestration, although moderate with an additional 5–6% from 1901 to 2010, confirming the first part of our hypothesis. During the 2000s, N deposition added 0.3 Pg C/year to the global land C sink, equivalent to 11–13%, and within previously reported ranges of 0.2–0.6 Pg C/year based on other CN models and observations (Zaehle et al., 2010). Our historical N deposition effect is somewhat low compared to the reported range of 15–40 kg C per kg N for temperate and boreal ecosystems (Butterbach-Bahl et al., 2011). Land C sequestration responded most in the temperate and boreal regions to N deposition, while the tropics showed little response, which is in agreement with previous findings (Fleischer et al., 2013; Jain et al., 2009; Zaehle, 2013). Despite the high sensitivity to N deposition in boreal regions, total induced C sequestration remained below 3 Pg C due to relatively low N deposition. Similar low responses in total C sink to N deposition in the boreal zone have been observed (Gundale et al., 2014) and estimated with the ecosystem model

Table 5

Future Global C Fluxes and Sequestration Rates for the High Biological N Fixation Scenarios (Denoted as "BNF+"; See Table 1) With Changes to Original Biological N Fixation Simulation (See Table 2) in Brackets

Future terrestrial C sequestration (Pg C)				
Time period	CN_0_BNF+	CN_1_BNF+	CNP_0_BNF+	CNP_1_BNF+
2011–2100	154.0 (+0.9)	184.0 (−1.1)	146.2 (−5.9)	173.8 (−5.1)
2051–2100	60.5 (−4.8)	79.4 (−5.5)	63.0 (−5.4)	80.3 (−4.0)

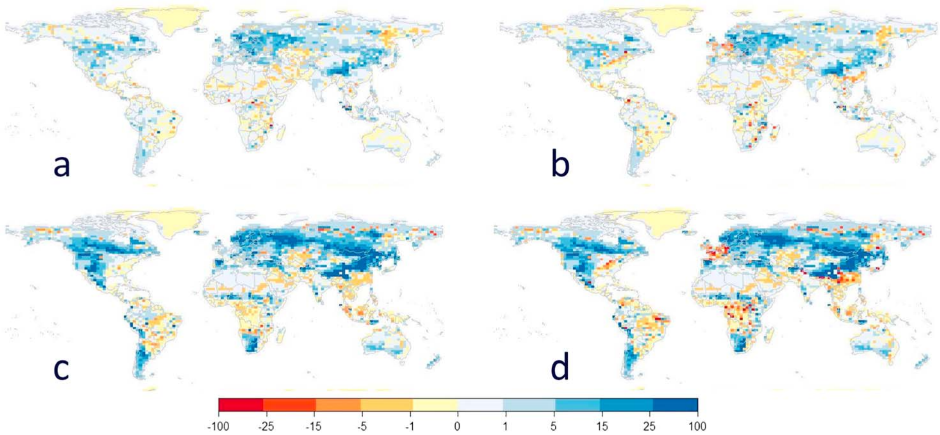

Figure 4. Change in land C sequestration due to N deposition from 1961–2010 (g C·m^{-2}·year^{-1}) for CN and CNP simulations (a, b), and for 2051–2100 for CN and CNP simulations (c, d); blue indicates a positive and red a negative effect on terrestrial C uptake from the atmosphere.

LPJ-GUESS (Fleischer et al., 2015). Tropical and subtropical ecosystems gained <2 Pg C due to N deposition in our simulations, which is due to higher BNF rates covering plant N demand in the tropics.

Simulations of the 21st century however did not agree with our expectation, and the N deposition effect on global C sequestration did not saturate but gained in significance. This is because C sequestered per unit N deposited decreased with P limitation and increased with increasing CO_2 concentration. As a result, the C sequestered per unit N deposited over the historical period was quite similar to that in the future by 2100 at the global scale. Among the four different regions, C sequestered per unit N deposited increased for all nontropical but decreased for tropical regions from the past into the future. P limitation reduced C sequestered per unit N deposited in the temperate and subtropical regions over the historical period and significantly only in the tropical regions in the future period. Our simulations imply that N increasingly limits future C sequestration, in part due to N increasingly accumulating in soil organic matter and an increasing N demand from greater CO_2 fertilization in all three nontropical regions.

4.2. Direct Negative Effects of N Deposition

N deposition had negative effects on C sequestration in our simulations when maintenance respiration costs of acquired N exceeded the associated gain in productivity and growth (Wang et al., 2010; Zhang et al., 2013).

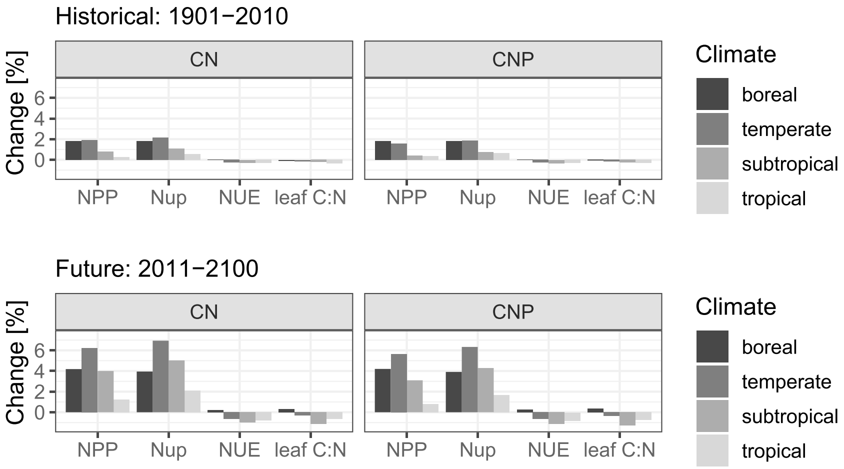

Figure 5. Mean N deposition induced change (%) for key C-N-P cycling variables (NPP, N uptake, NUE, leaf C:N) per climate zone for the historical period (1901–2010, top row) and future period (mean of 2011–2100, bottom row), separated for CN simulation (left panel) and in CNP simulations (right panel). NPP = net primary productivity; NUE = nitrogen use efficiency (NPP / Nuptake).

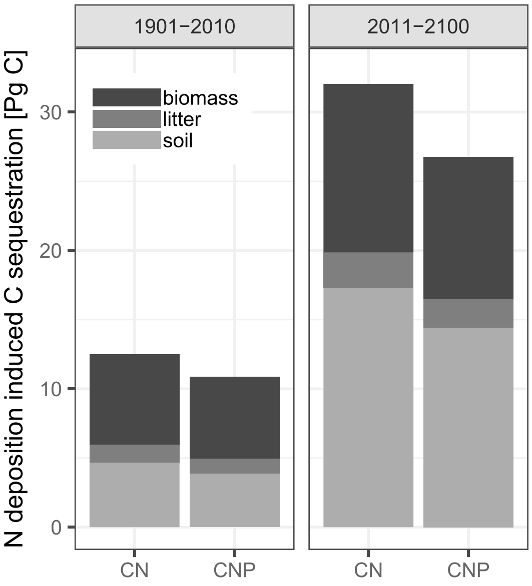

Figure 6. N deposition induced land C sequestration from 1901–2010 (left) and 2011–2100 (right) into biomass, soil, and litter C pools, separated for CN and CN simulations (Pg C).

This process-level representation is based on observations (Kattge et al., 2009; Kerkhoff et al., 2005; Reich et al., 2009) but may not be a universal plant response to high N supply. However, this modeled feedback may have partially represented and indicated conditions of excess N supply, under which other direct negative effects on plant growth and ecosystem health would occur due to chemical imbalances, not accounted for in our model (Bowman et al., 2008; Erisman & de Vries, 2000; Galloway et al., 2003; Gao et al., 2014). Net negative effects of N deposition aggravated into the future and occurred predominantly in the temperate zone due to excess N supply. N saturation often occurs locally and involves a biochemical complexity not represented in most ecosystem models. We therefore believe that we have rather underestimated the deleterious effects of N deposition on plant growth at local and regional scales and the degree to which these would alter global N deposition effects on C sequestration rates remains unexplored.

One possibility to address the shortcoming in ecosystem models to represent direct negative N effects on plant functioning is by improving root and soil C dynamics. The separation of functional and transport fine roots, and the consideration of the root environment on root dynamics should facilitate to simulate consequences of excess N on plant functionality (Smithwick et al., 2013, 2014). Soil mineral N availability may limit soil C decomposition rates in CABLE and many other ecosystem models, while a meta-analysis indicated a large range of potential soil C efflux responses to N deposition, from retardation to stimulation (Janssens et al., 2010). The consideration of microbial dynamics and their demands for substrate and nutrients, when modeling soil and litter decomposition could facilitate the more realistic representation of N addition on decomposition processes (Wieder, Allison, et al., 2015).

4.3. P Limitation on C Sequestration and Increasing N Losses

P limitation reduced historical C sequestration by 5% in our simulations (Table 2), supported by another ecosystem model pointing to an equally low reduction of NPP due to P limitation of 3 % (Goll et al., 2012). P limitation and N:P imbalances did however not intensify with rising N deposition in the future to the degree that would cause severe global P limitation of C sequestration, as we hypothesized. At regional scales, P limitation was significant in the tropical zone and N deposition intensified N:P imbalances in the temperate zone, both leading to net negative effects of N deposition on the C balance and aggravating N losses in the future. This occurred mainly in areas with coinciding low soil P availability and high N deposition, where the higher N availability stimulated plant growth, leading to higher plant P demand and uptake, and in turn progressive soil P limitation of plant growth. With plant growth being P limited, N uptake subsequently reduced and N deposition was increasingly lost via leaching, that is, ecosystems reached the point where N lost its fertilizing effect at an earlier stage due to P limitation (Peñuelas et al., 2013).

P limitations significantly increased the percentage of deposited N leaching into aquatic ecosystems, despite the moderate rates of P limitation in our simulations. The ecological consequences of N deposition being increasingly lost to aquatic ecosystems, and the associated atmospheric feedbacks, could not all be considered here, but our results indicate an alarming ongoing and intensifying rate at which N accumulates and circulates in our biosphere (Erisman et al., 2011; Galloway et al., 2003; Gao et al., 2014; Lamarque et al., 2013).

Several assumptions in our model simulations may have prevented a more intense P limitation and N:P feedbacks on the terrestrial C balance. First, we have assumed a trajectory with relatively high P weathering rates. Global P weathering rates in our simulations are 2.3 Tg P/year (based on Wang et al., 2010), while a recent model-based estimate points toward a much lower value of 1.1 Tg P/year (Hartmann et al., 2014). The degree of P limitation on the N deposition effect and C sequestration hinges on P inputs and its recycling, which are however associated to considerable uncertainties. Second, mild P limitations in our simulations benefitted the overall plant C balance due to the shifted balance between autotrophic respiration and photosynthesis at high tissue N levels discussed above (Wang et al., 2010; Zhang et al., 2013). Mild P limitation caused small reduction in P uptake and subsequently in N uptake, after which lower tissue N resulted in a plant C benefit that outweighed P limitation induced reductions in photosynthesis and growth. In the temperate and subtropical climate zone, for example, P limitation on C sequestration was evident only in the high N deposition scenario.

We expect no plant C gain due to mild P limitation but rather that plants invest C in additional P acquisition to overcome P limitation, which would reduce plant C gain per unit photosynthesis (Vicca et al., 2012). Plants may be able to tap into less available forms of P, for example, via mycorrhizal associations, root exudation or other rhizosphere interactions (Hoosbeek, 2016). Plant-induced mechanisms may increase P supply to counteract progressive P limitation, not accounted for in our simulations yet but shown to control the degree of nutrient limitation in other ecosystem models (Buendía et al., 2014; Goll et al., 2012, 2017; Yang et al., 2016). How much additional P can be acquired by plants via these mechanisms, the involved C costs and over which time frame such mechanisms can lift P limitation remains to be solved (Reed et al., 2015).

4.4. Future Biological N Fixation Control on N Deposition Effect

The assumption that biological N fixation would increase by 100% in the future did not alter our findings on the estimated future N deposition effect notably. Higher biological N fixation only marginally affected C sequestration rates, inducing net C losses in the tropics by adding to the N oversupply and stimulating C sequestration in the nontropics. N deposition induced land C sequestration in areas with very low prescribed biological N fixation rates, so that there was a geographical separation of N entering the system via deposition and fixation (Figure S1). Our simulations indicate that a 100% increase in biological N fixation in the temperate and boreal zone, presumably due to a warming climate, would not suffice to meet N demand and diminish the fertilizing effect of N deposition on C sequestration. The integration of dynamic biological N fixation in CABLE by considering N fixer-PFTs will allow elaborating on this first approximation made here and probe interactions with N deposition and P limitation (Dynarski & Houlton, 2018; Wang & Houlton, 2009).

4.5. Effects of Land Use and Land Cover Change

For the sake of simplicity, we ignored land use and land cover changes from 1901 to 2100 in this study. In the temperate and boreal regions, forest clearing, wood harvest, or fires generally increase ecosystem N loss, at least during the initial years after disturbance, so that these ecosystems become more N limited and biological N fixation becomes more active (Perakis et al., 2015), albeit at much lower rate than in disturbed tropical forests. Therefore, including land use change and other disturbances in our model will likely increase the estimated land C sequestration per unit N deposition, particularly in boreal and temperate forests. Field observations in the secondary tropical forests showed that biological N fixation increased after forest disturbance, and decreased over time as forests recovered (Batterman et al., 2013). Therefore, increase in N fixation after disturbance significantly contributed to ecosystem C accumulation, while also lower N demand in a recovering forest may contribute to recovery from N limitation (Yang et al., 2011). However, the increase in biological N fixation after disturbance also depends on availability of other resources, such as light, water and soil P. A meta-analysis of observations from 220 sampling sites found that afforestation substantially reduced total soil P but did not significantly change available P, depending on prior land use history (Deng et al., 2017). Because biological N fixation is often P limited (Dynarski & Houlton, 2018), stimulation of biological N fixation and ecosystem C accumulation after land use change will depend on prior land use history and other factors. A model simulation found that increasing nitrogen limitation on secondary tropical forest productivity after disturbance was alleviated by an increase in biological N fixation; however, this study did not include P limitation (Gerber et al., 2013). Therefore, how biological N fixation, P limitation vary with land use change is yet to be explored, and will be a high priority for future studies.

4.6. Stoichiometric Flexibility

Nitrogen's fertilizing effect on C sequestration arose due to increased N uptake in the model, less by improved NUE due to shifts in plant stoichiometry. N:P imbalances due to N deposition occurred mainly in soil organic matter in our simulations, while plant stoichiometric imbalances were constrained to ±10% of their PFT-specific mean C:N and N:P ratios. Plant tissue N:P ratios may increase substantially in response to N deposition (Güsewell, 2004; Peñuelas et al., 2013; Sardans et al., 2012; Yuan & Chen, 2015) but defining ranges of PFT-specific flexibility in plant tissue N:P and moreover their consequences on plant functioning and C cycling remains challenging (Meyerholt & Zaehle, 2015; Reed et al., 2015). The quasi-fixed plant stoichiometry scheme we have adopted may have overestimated the degree of N and P limitation in our simulations, since plants may exhibit some plasticity in their use of nutrients, thus theoretically allowing biomass C sequestration despite low availability of nutrients. Additionally, we expect a nonhomogenous response across species and environments, as phylogeny controls nutrients status and adaptive mechanisms differ among species and functional groups of plants to determine the response at the community level (Asner et al., 2014; Condit et al., 2013; Turner et al., 2018). Representing such variation in meaningful ways is a prioritized challenge for ecosystem models.

5. Conclusions

Our model experiments suggest a growing contribution of N deposition to future land C sequestration, in concert with sustained CO_2 fertilization of primary productivity and subsequent demand for N. Half of all deposited N over land was leached to aquatic ecosystems over the 21st century, indicating an alarming development of reactive N cascading in the biosphere. P limitation on the C balance remained moderate at the global scale but supported the notion of growing N:P imbalances and adverse effects of N deposition on the land C balance. We assumed optimistic rates of new P input and do not consider direct negative effects of soil chemical imbalances on plant growth in our simulations, so that the full scope of adverse N deposition effects on the future terrestrial biosphere may have been underestimated by our simulations. Given that only 2 of the 11 models in CMIP5 have included N dynamics and none have considered P dynamics (Ciais et al., 2013), our simulations demonstrate the need to advance representations of N and P dynamics in global models.

Acknowledgments
The model input and evaluation data used in this study are available via the referenced sources and the model output upon request. The source codes for CABLE are obtainable via the open source control system NCI, for more information see https://trac.nci.org.au/trac/cable/wiki website. We acknowledge NWO for providing a PhD grant (NWO 829.09.006) and enabling the research to be carried out by K. F. We further acknowledge the DFG grant (RA 2060/5-1) that supported the finalization of the study. We thank CSIRO for supporting a guest research stay for K. F. in Aspendale, Australia. We also thank all the scientists and technicians involved in the development, maintenance, and distribution of CABLE. We are further very grateful to Gordon Bonan, Sam Levis, and Jean François Lamarque from NCAR, for generating and providing input data.

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