Revision of Global soil nitrous oxide emissions in a dynamic carbon-nitrogen model

Dear Soenke,

Thank you very much for providing us with the opportunity to further strengthen our manuscript. Based on your assessment and based on the reviews, the two most distinct changes in this new submission are

- We found for 2 sites, where we show temporal trends of N2O emission some, but limited information on soil moisture. While we did not incorporate them in a graph, we characterize the soil moisture measurements in the text.
- We rearranged the discussion (and the conclusion) to better highlight the implication of our work, where we find a) strong sensitivity to soil moisture, b) the global N2O emission and response to environmental forcing is mostly determined by tropics, where few measurements exist, c) A discussion how the response to CO2 and temperature perturbation differs across models.

We detail our changes below. Thank you very much for considering our manuscript for potential publication and are ready, to make further modification, if needed.

Best regards,

Stefan

Editor and Reviewer comments

Editor comments

many thanks for your revised manuscript. Your revision has been assessed by two reviewers, which have varying opinions on the quality of the revision (see below). I disagree with reviewer #1 that the ms would not be suitable for Biogeoscience (although I also agree that this ms could also be published as part of Geophysical Model Development), however, I agree that the discussion of the implications of this research for our understanding of the terrestrial N2O budget can be further strengthened. For instance, in the introduction you discuss different models. These have been used to make future projections - based on the sensitivity study, would you expect similar changes (in particular in sign and magnitude) as these studies (knowing how other parts of your model respond to changing temperature and CO2)?

We expand the discussion and compare our results of temperature and CO2 fertilization against other models. We note now, that we do not find the synergistic effects between CO2 and climate that Stocker et al., (2013) and Xu-Ri et al., (2012) found. We further compared our changes to Zaehle et al., (2011), where we found that our short-term response is similar. We further now elaborate, that this initial effect ultimately transitions over time into a positive CO2 response, while the temperature effect disappears. We speculate, that this transition may occur faster in LM3V, where N2 fixation up-regulates when N demand increases, particularly in the tropics. We note however, that this is not an "apple-to-apple" comparison, as we compare step changes

against transient changes in other models that also includes other factors (precipitation, CO2, nitrogen deposition).

I think that the study does provide a sufficient level of comparison to other studies, although more could have been done. However, I think for Biogeosciences it would be good to highlight the relevance of the sensitivities and the comparison to the observations in discussion and (more importantly) the conclusions somewhat. Currently, much of this comparison is hidden in the results section.

We changed our discussion in that we added how analysis against field scale data may be interpreted. We keep the caveat on field scale mismatches, but add that our different soil moisture representations (with 2 data-derived products), do not reproduce the measured values (for the sites where we could obtain data). We interpret this as an impediment to more accurate predictions. We further discuss, that at specific sites, there are large differences across plots, which poses an additional challenge for modelers. We reiterate our point that much of the simulated N2O emissions occur in the tropics, where few measurements and experimental manipulations have been carried out. We specifically add to our conclusion, that both the sensitivity to parameters that address the larger plant-soil N cycle, as well as the comparison against other models show that the similar nitrification-denitrification modules in different models yield distinct and different responses.

Referee 3

I thank the authors for their constructive responses and the efforts put into revising their original manuscript. Several major concerns were raised by the reviewers (see below), most of them by more than one reviewer, which underlines their significance. The authors took on the task of addressing these issues, but didn't "re-invent the study". As a general impression, the limited modifications made in the revised manuscript contrast with the authors' acknowledgment of the weaknesses of their initial submission. However, I also acknowledge that model evaluation w.r.t. N2O emissions remains a particulary challenging task, which shouldn't prevent incremental progress (by studies like this one) before "all problems are solved".

In the following, I'm trying to list what were in my view some key points of criticism raised by the different reviewers, and how I judge the authors' respective responses.

Novelty and scope

Regarding this aspect, the authors write "Since we build largely on existing parameterization of nitrification-denitrification processes, our focus relies on the evaluation of these processes if transferred to a different model." (p.34,l.14/15). The aspect of how a similar implementation of one module (inorganic N dynamics following a DNDC-type model) yields different results when integrated within different coupled C-N cycling models (comparison to DyN-LPJ and O-CN), could be strengthened. This leaves model evaluation as the most important aspect of this paper.

We attempted to strengthen this by comparing specifically the response to temperature and CO2 with other models. We show, that particularly the interactive effects play out differently across models, but also find that these responses change over time. We were cautious, though, as the model-to-model comparison is not direct, since the experiments were carried out differently (E.g. Nr is included, transient increases vs. step changes).

I like the track of evaluating sensitivity to WFPS, also considering the interesting model parametrisations of the N2O yield factor as a function of WFPS (which is an innovation, considering that other models use a constant factor). I find this aspect of the paper particularly interesting as the authors use empirical parametrisations to calculate the N2O yield factor from nitrification and denitrification (section 2.1.2.2) and provide insights of N2O sensitivity to soil moisture. However, WFPS itself is not benchmarked and observed soil moisture at the measurement sites (I assume/hope this is measured along with N2O) was not used in the model for the scale evaluation across the season (Fig. 5). Therefore, we still don't know if the relationship of N2O to WFPS is correct. I consider the seasonal analysis provided by Fig. 5 as a valuable addition. It may even provide more insights if the analysis of N2O and WFPS is coupled.

Surprisingly, WFPS is sparingly reported. We add in the result section the characteristics of the WFPS in text form for two sites, where we could find some reporting on soil moisture and soil properties to derive WFPS. This sheds additional light on site-level N2O emission. We discuss this also in light of field-scale mismatches, where global models integrate over large swaths at the landscape, whereas plot-to-plot differences highlight the characteristics of N2O production being caused by small-scale processes (Figure 6).

Suitability for BG (vs. GMD)

The authors' responses to this point do not convince me, but it is not my task to make a final judgment. The authors agree that the main scope of this paper is model evaluation (see above "novely and scope"). I think the revisions even reinfoce this aspect (model description moved from appendix into main text).

We added the model description into the main text per request of an earlier review, and think this is helpful for the reader. We include now a broader discussion of the CO2 and temperature response and comparison against other models, as well as reinforcing in the conclusion, that the tight cycling as set up in LM3V-N renders makes N2O emissions very sensitive that affect the "openness", such as fire, BNF, and DON losses – with the goal to convey to the reader that this manuscript, while containing technical description, provide insights into the mechanisms of N2O emissions of not only LM3V-N but also other models.

Subject to model performance of entire C-N cycling and sensitivity analysis

I appreciated the added description of general characteristics and key processes in LM3V-N. This section is now rather technical with a few equations provided. This could be improved by providing a more general description of the model characteristics. For example, in the responses the authors note that LM3V-N simulates very tight N cycling as opposed to other models, and

correspondingly small BNF ("empirical" BNF rate of 108 TgN/yr: what reference?). Chosen yield factors of N2O from nitrification/denitrification are rather high, probably necessary due to the tight N cycling.

We tried to ease the technical description a bit by providing a sentence in each subsection to make a link to the larger N cycle, thereby offering broader insight into model characteristics. The formulation of LM3V-N's biological N fixation yields 72 Tg N yr-1 for pre-industrial rates, which is considered a low rate. Although simulated post-industrial BNF increases with time, the rate is still lower than the empirical estimates for the pre-industrial rate. We use empirical estimates based on Green et al., (2004) and regridded to LM3V-N's grid. The empirical estimated preindustrial BNF rate is 108 Tg N yr-1 (or 107 Tg N yr-1 after regridding), which is critically smaller than Cleveland et al. (1999) but is comparable with 104 Tg N yr-1 reported in O-CN (Zaehle et al., 2010).

The sensitivity analysis to other model parts (BNF, fire, DON, and gaseous losses, N uptake rate, and N2O yield factors) underlines what may be expected anyway. The resulting changes in N2O emissions from varying parameters by factor 10 are on the same order of magnitude as the absolute value using "standard" values. The analysis is not used in the light of observational constraints and therefore provide limited new insights. I acknowledge that this point is a challenge for all C-N models attempting to simulate N2O emissions. However, this manuscript doesn't offer a clear way forward, leaving this as a weakness of the paper.

We conducted two types of sensitivity analyses, one that is "subject to model performance of entire C-N cycling" and a test to the nitrification/denitrification parameterization itself. We agree, that none of the results were surprising except that increased plant uptake strength resulted in higher N2O emissions. Our findings nevertheless show that N2O emissions are subject to model performance, as pointed out by Beni Stocker initially, particularly in the response to climate and CO2 perturbation. Overall, we sought to strengthen the discussion by our comparison to with models, and by portraying potential mechanisms that accompany the responses.

Poorly documented equations and parameter values and placement of model description in Appendix

This has been improved and the equations are moved into the main text. However, in some instances, it was still not clear where exactly the equations and parameter values were drawn from (e.g., Section 2.1.2.2: Gaseous partitions from nitrification-denitrification).

Another aspect that confused me: How do these empirical functions fit in with the statement that single constant factor of 0.4% is for the N2O yield from nitrification? This number doesn't appear in Eq. 14, 15, 16 - I must have misunderstood something...

The gaseous partition are based entirely on CENTURY (or its daily version DayCent). We listed the reference from where the equations and parameter are taken from, so that the reader can make the link to these earlier publications.

We now also realize the source of confusion about the partitioning of the gas emissions. We changed the first paragraph in that particular subsection, such that we clearly mention that a) a constant fraction of nitrification leaves as N2O gas. Further the ratio of NOx:N2O indicates how much additional loss occurs during nitrification via NOx production and emission. In the following paragraph we then discuss the implementation of the partitioning for denitrification which creates N2O and N2.

Referee 1

I like how the authors revised the paper and I find this to be of value to readers of Biogeosciences, after the authors correct the following typos in the manuscript:

L. 11, P. 12 – "available water capacity smaller" to "available water capacity is smaller"

L. 24, p. 14 – "addtion" to "addition"

L. 2, p. 23 – "impromvent" to "improvement"

L. 3, p. 23 – "Similar" to "Similarly"

L. 24, p. 24 – "which are be" to "which are"

L. 8, p. 24 – "in need" to "needed"

L. 22, p. 24 – "model suggest" to "model suggests"

We thank the reviewer for taking the time to evaluate our ms and pointing out these typos/mistakes, which we have now corrected.

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The following pages contains the changes compared to our earlier submission, using Microsoft Word mark up.

1 Global soil nitrous oxide emissions in a dynamic carbon-

2 nitrogen model

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Abstract

Nitrous oxide (N₂O) is an important greenhouse gas that also contributes to the depletion of stratospheric ozone. Due to its high temporal and spatial heterogeneity, a quantitative understanding of terrestrial N₂O emission, its variabilities and responses to climate change is challenging. We added a soil N₂O emission module to the dynamic global land model LM3V-N, and tested its sensitivity to mechanisms that affect the level of mineral N in soil such as plant N uptake, biological N fixation, amount of volatilzed N redeposited after fire, and nitrification. denitrification. We further tested the relationship between N₂O emission and soil moisture, and finally assessed responses to elevated CO₂ and temperature. Results extracted from the corresponding gridcell (without site-specific forcing data) were comparable with the average of cross-site observed annual mean emissions, although differences remained across individual sites if stand-level measurements were representative of gridcell emissions. Processes, such as plant N uptake and N loss through fire volatilization, that regulate N availability for nitrification-denitrification have strong controls on N2O fluxes in addition to the parameterization of N₂O loss through nitrification and denitrification. Modelled N₂O fluxes were highly sensitive to water filled pore space (WFPS), with a global sensitivity of approximately 0.25 TgN per year per 0.01 change in WFPS. We found that the global response of N₂O emission to CO₂ fertilization was largely determined by the response of tropical emissions with reduced N2O fluxes in the first few decades and increases afterwards. The initial reduction was linked to N limitation under higher CO₂ level, and was alleviated through feedbacks such as biological N fixation. The extratropical response was weaker and generally positive, highlighting the need to expand field studies in tropical ecosystems. We did not find synergistic effects betwen warming and CO₂ increase as reported in analyses with different

- 1 models. Warming generally enhanced N₂O efflux, and the enhancement was greatly dampened
- when combined with elevated CO₂, although CO₂ alone had a small effect. Our analysisThe
- 3 differential response in the tropics compared to extratropics with respect to magnitude and sign
- 4 suggests caution when extrapolation from current field CO₂ enrichment and warming studies
- 5 to the global scale.

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1 Introduction

- 8 Nitrous oxide (N₂O) is a major reactant in depleting stratospheric ozone as well as an important
- 9 greenhouse gas (Ravishankara et al., 2009;Butterbach-Bahl et al., 2013;Ciais et al., 2013). With
- a global warming potential of 298 times more (per unit mass) than that of carbon dioxide (CO₂)
- over a 100-year period (Forster et al., 2007), the contributions of N₂O emissions to global
- radiative forcing and climate change are of critical concern (Zaehle and Dalmonech, 2011). The
- concentration of atmospheric N₂O has been increasing considerably since the industrial
- revolution with a linear rate of 0.73 ± 0.03 ppb yr⁻¹ over the last three decades (Ciais et al., 2013).
- 15 Although applications of synthetic fertilizer and manure during agriculture intensification have
- been identified as the major causes of this increase which has resulted in an increase of the
- 17 radiative forcing by 0.125W m⁻² (Davidson, 2009; Zaehle and Dalmonech, 2011; Zaehle et al.,
- 18 2011), nonagricultural (natural) soil is still an important N₂O source (Ciais et al., 2013;Syakila
- and Kroeze, 2011). N₂O fluxes from nonagricultural soils are highly heterogeneous, which
- 20 limits our ability to estimate and predict global scale budget, and quantify its response to global
- 21 environmental changes (Butterbach-Bahl et al., 2013; Ciais et al., 2013).
- 22 Most of the N₂O fluxes from soil are produced by microbial nitrification and denitrification
- 23 (Braker and Conrad, 2011; Syakila and Kroeze, 2011). Nitrification is an aerobic process that
- 24 oxidizes ammonium (NH₄⁺) to nitrate (NO₃⁻), during which some N is lost as N₂O.
- Denitrification reduces nitrate or nitrite to gaseous N (i.e. NO_x, N₂O and N₂), a process that is
- fostered under anaerobic conditions. <u>During denitrification</u> N₂O is generated in intermediary
- 27 steps during denitrification and where a small portion can escape from soil before further
- 28 reduction to N₂ takes place. Soil texture, soil NH₄⁺, soil water filled pore space (WFPS),
- 29 mineralization rate, soil pH, and soil temperature are well-known regulators of nitrification N₂O
- 30 fluxes (Parton et al., 1996;Li et al., 2000;Parton et al., 2001). Denitrification and associated
- N₂O emissions depend primarily on carbon supply, the redox potential and soil NO₃⁻ (Firestone

1 and Davidson, 1989; Parton et al., 1996). Soil moisture has a particularly strong impact 2 (Galloway et al., 2003; Schlesinger, 2009) as it influences nitrification and denitrification rates 3 through its regulations on substrate availability and soil redox potential (as oxgyen diffusion 4 proceeds at much slower rate in water filled than in air filled pore space), thereby also 5 controlling the partitioning among various denitrification products (i.e. NO_x, N₂O and N₂) (Firestone and Davidson, 1989; Parton et al., 2001). Although emissions are known to be 6 7 sensitive to soil moisture, quantitative understanding of its role in terrestrial N2O fluxes and 8 variability is limited (Ciais et al., 2013). 9 At regional to global scale, the application of the "hole-in-pipe" concept (Firestone and Davidson, 1989) in the CASA biosphere model pioneered one of the earliest process-based 10 11 estimation of natural soil N₂O fluxes. The model calculated the sum of NO, N₂O and N₂ fluxes as a constant portion of gross mineralized N, and the relative ratios of N trace gases 12 (NO_x:N₂O:N₂) as a function of soil moisture (Potter et al., 1996). While the early models of 13 14 nitrification and denitrification are primarily conceptual driven, recent global N2O models 15 combine advancements in global dynamic land models with more detailed processes, including 16 microbial dynamics. Xu-Ri and Prentice (2008) simplified nitrification and denitrification 17 modules from DNDC (i.e., DeNitrification-DeComposition) (Li et al., 1992; Li et al., 2000) in 18 their global scale dynamic N scheme (DyN) and incorporated DyN into the LPJ dynamic global vegetation model. In the DNDC approach, nitrification and denitrification were allowed to 19 20 happenoccur simultaneously in aerobic and anaerobic microsites. Zaehle et al. (2011) incorporated a nitrification-denitrification scheme into the O-CN land model following largely 21 22 the LPJ-DyN with minor modifications and additions of the effects of soil pH and chemo-23 denitrification that originated from DNDC (Li et al., 2000). Stocker et al. (2013) 24 embededembedded the LPJ-DyN approach into an Earth System Model and investigated the 25 feedbacks of N₂O emissions, together with CO₂ and CH₄, to climate. Compared to LPJ-DyN 26 approach, Saikawa et al. (2013) retained the explicit simulation of nitrifying and denitrifying 27 bacteria from DNDC in their CLMCN-N2O module based on CLM V3.5 land model. 28 Simulations with O-CN demonstrated a positive response of N₂O emissions to historical 29 warming and a negative response to historical CO₂ increase, globally. While CO₂ and 30 interaction with climate change resulted in an increase in historical and future N₂O emissions fromin LPJ-DyN (Xu-Ri et al., 2012) and its application in LPX-Bern (Stocker et al., 2013), 31 32 respectively, historical CO₂ change alone, i.e. single factor of Xu-Ri et al., (2012), caused a

- slight decrease in historical N₂O emissions. The negative CO₂ response seems to be in
- 2 disagreement with one meta-analysis of manipulative field experiments showing an increase in
- 3 N₂O emissions at elevated levels of CO₂ (Zaehle et al., 2011;Xu-Ri et al., 2012;van Groenigen
- 4 et al., 2011). The discrepancy in response to global change factors needs to be addressed both
- 5 in models and in the interpretation of manipulative field experiments.
- 6 Here we add a N₂O gas emission module to LM3V-N, a land model developed at the Gephysical
- 7 Fluid Dynamics Laboratory (GFDL). In this paper, we will first briefly introduce LM3V-N and
- 8 describe the added N_2O emission module. We then subject the model to historic changes in CO_2 ,
- 9 N deposition, and recent climate change to infer natural N₂O emissions in the past few decades.
- We test the model's sensitivity to soil water regime, by addressing the parameterization of soil
- WFPS, and by replacing the model soil moisture with two different soil moisture reanalysis
- 12 products. We also conduct sensitivity tests with regard to the general N cycling and
- parameterization of N₂O emissions. Since we build largely on existing parameterization of
- 14 nitrification-denitrification processes, our focus relies on the evaluation of these processes if
- 15 tranferred to a different model. Finally, we'We then subject the model to step changes in
- atmospheric CO₂ and temperature to understand modelled reponses to CO₂ fertilization/climate
- 17 change. Since we build largely on existing parameterization of nitrification-denitrification
- processes, we will briefly discuss implications from transferring process formulations to
- 19 LM3V-N where other aspects of the N cycle are treated differently.

20 2 Methods

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2.1 Model description

- 22 LM3V is capable of simulating ecosystem dynamics and exchange of CO₂, water and energy
- between land and atmosphere with the fastest time step of 30 minutes (Shevliakova et al., 2009).
- 24 LM3V-N expands the LM3V land model with a prognostic N cycle (Gerber et al., 2010), and
- 25 includes five plant functional types (PFTs):C3 and C4 grasses, tropical, temperate deciduous
- and cold evergreen trees. Each PFT has five vegetation C pools (leaf, fine root, sapwood, labile,
- and wood), two litter and two soil organic C pools and their corresponding N pools based on
- 28 the specific C:N ratios. Photosynthesis is coupled with stomatal conductance on the basis of the
- Collatz et al., 's (1991,1992) simplification of the Farquhar scheme (Farquhar et al., 1980). Soil
- 30 hydrology in LM3V follows partly on Land Dynamics (LaD) with further improvements
- 31 (Shevliakova et al., 2009; Milly and Shmakin, 2002; Milly et al., 2014). N enters the ecosystem

- through atmospheric N deposition and biological N fixation (BNF), losses via fire and leaching
- of dissolved organic N (DON) as well as mineral N. MajorWe briefly describe the major
- 3 characteristics of LM3V-N include in the following 5 aspects, next subsection (2.1.1), and details
- 4 are available in Gerber et al. (2010).

5 2.1.1 Main characteristic of LM3V-N

6 2.1.1.1 C-N coupling in vegetation

- 7 We briefly describe the larger plant-soil N cycle and how it links to mineral N (ammonium and
- 8 nitrate). Details are described in Gerber et al. (2010). Plants adjust their uptake of C and N to
- 9 maintain their tissue specific C:N ratios, which are PFT-dependent constants. Instead of varying
- 10 C:N ratios in tissues, short-term asynchronies in C and N assimilations or temporary imbalances
- in stoichiometry are buffered by additional N storage pool (S) in which N is allowed to
- 12 accumulate once plant N demand is satisfied. The optimum storage size S_{target} is based on tissue
- 13 turnover $Q_{N,liv}$,

$$14 S_{target} = t_h Q_{N,liv} (1)$$

- where t_h is the time span that buffer plant N losses (currently set as 1 year). Plant N status (x)
- is defined as the fraction of the actual N storage compared to the target storage: $x = S/S_{target}$.
- 17 Consequently, N constraints on photosynthesis and soil N assimilation are based on plant N
- 18 status:

19
$$A_{g,N} = A_{g,pot}(1 - e^{-x\varphi})$$
 (2)

$$20 U_{N,P} = U_{N,P,pot} * \begin{cases} 1 & if \ S < S_{target} \\ 0 & else \end{cases}$$
 (3)

- where $A_{g,N}$ indicates N constrained rate of gross photosynthesis (µmolC m⁻² s⁻¹) and $A_{g,pot}$
- corresponds to the potential photosynthetic rate without N limitation. The parameter φ mimics
- 23 the metabolic deficiency as plant N decreases. $U_{N,P,pot}$ is the potential inorganic N uptake rate
- from soil available ammonium and nitrate pools. The actual inorganic N uptake rate $(U_{N,P})$
- 25 operates at its potential if plants are N limited and drops to zero when N storage (S) reaches its
- 26 target size. Overall this set-up intends to overcome short-term asynchronies between C and N
- 27 <u>supply.</u>

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2.1.1.2 Soil C-N interactions in organic matter decomposition

1 Organic matter decomposition is based on a modified CENTURY approach (Bolker et al.,

1998), and amended with formulations of N dependent C and N mineralization rates. Here,

we use a 3 pool model where the pools broadly represent labile and structural litter, and

processed soil organic matter. Decomposition is the main source of available N for nitrification

and denitrification. In turn, NO₃ and NH₄ can both trigger the decomposition of "light" organic

matter and stabilize C in "heavy" organic matter in LM3V-N. Sustained positive effect of

available N on litter decomposition relies on the persistence of microbial N limitation during

decomposition, which is implemented through the combination of available N supply to

microbial organisms and their respiration rate. Further, LM3V-N incorporates the negative

effects of N on recalcitrant organic matter decomposition through increasing the fraction of C

and N fluxes into the recalcitrant pool. Formation of a slow decomposable organic matter pool

leads to immobilization of ammonium and nitrate to satisfy the fixed carbon to nitrogen ratio

of this pool.

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2.1.1.3 Competing sinks of available N

15 The fate of soil mineral N (i.e. ammonium and nitrate) depends on the relative strength of the

competing sinks, with the broad hierarchy of sorption > soil immobilization > plant uptake >

17 leaching/denitrification. This creates a tight N cycle, since internal (plant and soil) sinks

dominate over N losses. Denitrification thus far has been lumped with leaching losses and

summed into a generic N loss term. Sorption/desorption buffers available N and is assumed to

have the highest priority and be at steady state in each model time step. N immobilization into

organic matter occurs during transfers among litter and soil organic matter pools. Leaching

losses of available N are simulated on the basis of drainage rate. Plant uptake of mineral N is a

combination of both active and passive processes. The active uptake is modeled as a Monod

function, and the passive transport is a function of available N and plant transpiration.

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$$U_{N,P,pot,i} = \frac{v_{max}c_rN_{i,av}}{h_s(k_{p,1/2} + [N_{av}])} + \frac{[N_{av}][N_{i,av}]Q_{W,T}$$

26 (4)

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where $v_{max}(yr^{-1} kgC^{-1})$ stands for the maximum uptake rate per unit root mass C_r , h_s is soil depth,

28 $k_{p,1/2}$ is the half saturation constant, and $Q_{W,T}$ represents the transpiration flux of water. Te

subscript i refers to either ammonium or nitrate, while $[N_{av}]$ is the concentration of the combined

dissolved ammonium nitrate pool. Potential uptake and thus effective removal of available N

occurs if plants are N limited (see Equation 3).

2.1.1.4 N losses from organic pools

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- 2 With the implementation of high ecosystem N retention under limiting condition where internal
- 3 N sinks outcompeting losses from the ammonium/nitrate pools, losses via organic pathways
- 4 <u>become important (Gerber et al., 2010; Thomas et al., 2015).</u> Over the long term, N losses via
- 5 fire and DON are thus critical factors limiting ecosystem N accumulation and maintaining N
- 6 limitation in LM3V-N-(Gerber et al., 2010; Thomas et al., 2015). N volatilized from via fire is
- 7 approximated as a function of C released from CO₂ produced in a fire, stoichiometric ratio of
- 8 burned tissues and but reduced by a global retention factor representing the fraction of N that is
- 9 retained as ash (ash fraction, currently set as 0.45). DON leaching is linked to hydrologic losses
- of dissolved organic matter (L_{DOM}) and its C:N ratio. In turn L_{DOM} is based on drainage rate (Q_W)
- 11 D) and a buffer or sorption parameter b_{DOM} (currently set as 20).

$$12 L_{DOM} = \frac{Q_{W,D}}{h_S b_{DOM}} DOM (5)$$

- where DOM is the amount of dissolve organic matter in the soil column. Soil depth (h_s) is used
- 14 to convert DOM unit to concentration (in unit of kgC m⁻³). Production of DOM (in unit of kgC
- 15 m⁻²) is assumed to be proportional to the decomposition flux of the structural litter and soil
- water content. Both, losses via fire and via DOM are losses from a plant-unavailable pool
- 17 (Thomas et al., 2015), and have the potential to increase or maintain N limitation over longer
- 18 timescales, and consequently reduce N available availability for N₂O production through
- sustained and strong plant N uptake (see Equations 2-4).

20 **2.1.1.5** Biological nitrogen fixation (BNF)

- 21 BNF in LM3V-N is dynamically simulated on the basis of plant N availability, N demand and
- 22 light condition. BNF increases if plant N requirements are not met by uptake. The rate of up-
- 23 regulation is swift for tropical trees but constrained by light penetrating the canopy for other
- 24 PFTs, mimicking the higher light requirements for new recruits that possibly can convert
- 25 atmospheric N₂ into plant available forms. In turn, sufficient N uptake reduces BNF. The BNF
- parameterization thus creates a negative feedback, where high plant available N and thus the
- 27 potential for denitrification is counteracted with reduction of N input into the plant-soil system.
- 28 This explicit negative feedback is different to other models where BNF is parameterized based
- on NPP (Thornton et al., 2007), or transpiration (Zaehle and Friend, 2010). The inclusion of

- 1 BNF as a negative feedback contributes to a rather tight cycling within LM3V-N, with low
- 2 overall rates of BNF under unperturbed conditions (Gerber et al., 2013).

2.1.2 Soil N₂O emission

3

13

- 4 LM3V-N assumes that nitrification is linearly scaled to ammonium content, and modified by
- 5 soil temperature and soil moisture. Gaseous losses so far were not differentiated from
- 6 hydrological leaching. We add a soil nitrification-denitrification module which accounts for N
- 7 gaseous losses from NH₃ volatilization, nitrification and denitrification. The nitrification-
- 8 denitrification scheme implemented here combines features from both the DNDC model (Li et
- 9 al., 1992;Li et al., 2000) and the CENTURY/DAYCENT (Parton et al., 1996;Parton et al.,
- 10 2001;Del Grosso et al., 2000). In this partsubsection, we provide details on the nitrification-
- denitrification module which explicitly simulates N gaseous losses from nitrification and
- denitrification, as well as other process modifications compared to the original LM3V-N.

2.1.2.1 Nitrification-Denitrification

- 14 Transformation among mineral N species (ammonium and nitrate) occurs mainly through two
- microbial pathways: nitrification and denitrification. Although ongoing debate exists in whether
- 16 nitrification rates may be well described by bulk soil ammonium concentration or soil N
- turnover rate (Parton et al., 1996; Zaehle and Dalmonech, 2011), we adopt the donor controlled
- scheme (ammonium concentration). In addition to substrate, soil texture, soil water filled pore
- space (WFPS, the fraction of soil pore space filled with water), and soil temperature are all well
- 20 known regulators of nitrification. As a first order approximation, nitrification rate (N, in unit,
- 21 kgN m⁻² year⁻¹) is simulated as a function of soil temperature, NH₄⁺ availability and WFPS,

22
$$N = k_n f_n(T) f_n(WFPS) \frac{N_{NH_4^+}}{b_{N,NH_4^+}}$$

- 23 (6)
- 24 where k_n is the optimumbase nitrification rate (11000 year⁻¹, the same as in LM3V-N) (Gerber
- et al., 2010); $N_{NH_4^+}$ is ammonium content (in unit, kgN m⁻²); b_{N,NH_4^+} is the buffer or sorption
- parameter for NH₄⁺ (unitless, 10 in LM3V-N) (Gerber et al., 2010); $f_n(T)$ is the temperature
- 27 response function following Li et al. (2000), with an optimum temperature for nitrification at
- 28 35°C; and $f_n(WFPS)$ is the soil water response function. The effect of WFPS on nitrification is
- texture dependent, with most of the reported optimum value around 0.6 (Parton et al., 1996;Linn

- and Doran, 1984). We adopt the empirical WFPS response function from Parton et al. (1996)
- 2 with medium soil texture.

$$3 f_n(T) = \left(\frac{60 - Tsoil}{25.78}\right)^{3.503} \times e^{\frac{3.503 \times (Tsoil - 34.22)}{25.78}} (7)$$

$$4 f_n(WFPS) = \left(\frac{WFPS - 1.27}{-0.67}\right)^{\frac{1.9028}{0.59988}} \times \left(\frac{WFPS - 0.0012}{0.59988}\right)^{2.84}$$
 (8)

- 5 where *Tsoil* is the soil temperature in degree Celsius.
- 6 Denitrification is controlled by substrate NO₃ (electron acceptor), labile C availability (electron
- 7 donor), soil moisture and temperature. Labile C availability is estimated by soil heterotrophic
- 8 respiration (HR). Following LPJ-DyN (Xu-Ri and Prentice, 2008), denitrification is assumed
- 9 to have a Q₁₀ value of 2 when the soil temperature is between 15 and 25 °C. The soil moisture
- 10 response function is adopted from Parton et al. (1996). Soil pH is reported to be an important
- indicator of chemodenitrification which occurs predominantly in acidic soils (pH<5) under
- 12 conditions of high nitrite concentration (Li et al., 2000). However, its role for N₂O production
- is not well studied (Li et al., 2000) and we do not model the chemodenitrification explicitly.

$$14 D = k_d f_d(T) f_d(WFPS) f_q NO_3^- (9)$$

15 And
$$f_g = \frac{HR}{HR + K_c} \frac{HR}{HR + K_c} \frac{NO_3^-}{NO_3^- + K_n}$$
 (10)

$$NO_3^- = \frac{N_{NO_3^-}}{b_{NO_3^-}} \tag{11}$$

- where D is the denitrification rate (in unit, kgN m⁻² year⁻¹); k_d is the optimumbase denitrification
- rate (8750 year⁻¹); f_g mimics the impact of labile C availability and substrate (nitrate) on the
- growth of denitrifiers, adapted from Li et al. (2000); K_c and K_n are half-saturation constants
- taken from Li et al. (2000) (0.0017 and 0.0083 kgN m⁻² respectively, assuming an effective soil
- depth of 0.1m); $b_{NO_3^-}$ is the buffer or sorption parameter for NO_3^- (unitless, 1 in LM3V-N)
- (Gerber et al., 2010); $N_{NO_3^-}$ and NO_3^- are nitrate content before and after being buffered (in unit,
- kgN m⁻²), respectively; and $f_d(T)$ and $f_d(WFPS)$ are empirical soil temperature and water reponse
- function for denitrification, adopted from Xu-Ri and Prentice (2008) and Parton et al. (1996),
- 25 respectively.

26
$$f_d(T) = e^{\frac{308.56 \times (\frac{1}{68.02} + \frac{1}{Tsoil + 16.02})}{68.02}} e^{308.56 \times (\frac{1}{68.02} - \frac{1}{Tsoil + 46.02})}$$
 (12)

$$1 f_d(WFPS) = \frac{1.56}{12.0^{(\frac{16.0}{12.0(2.01 \times WFPS)})}} (13)$$

2 2.1.2.2 Gaseous partitions from nitrification-denitrification

- 3 N₂O is released as a byproduct from during both nitrification and denitrification. The fraction
- 4 of N₂O lost fromduring net nitrification is uncertain (Li et al., 2000;Xu-Ri and Prentice, 2008).
- 5 Here we set this fraction to be 0.4%, which is higher than Goodroad and Keeney (1984), but at
- 6 the low end provided by Khalil et al. (2004). <u>Nitrification also generate NO_x gas, in addition to</u>
- 7 N₂O-and. N losses as NO_x emissions from during nitrification are based on scaled to the NO_x:
- 8 N2O release using a variable NO_x:N₂O ratio (R_{NOx:N2O}) which is updated at every time step and
- 9 for each grid cell.). $R_{NOx:N2O}$ varies with relative gas diffusivity (D_r , the relative gas diffusivity
- in soil compared to air) (Parton et al., 2001), which is calculated from air filled porosity (AFPS,
- i.e., the portion of soil pore space that is filled by air) (Davidson and Trumbore, 1995)

12
$$R_{NOx:N2O} = 15.2 + \frac{35.5 \times ATAN(0.68 \times \pi \times (10 \times D_r - 1.68))}{\pi}$$
 (14)

13
$$D_r = 0.209 \times AFPS^{\frac{4}{3}}$$
 (15)

- where ATAN stands for the trigonometric arctangent function; AFPS is the air filled porosity
- 15 (1-WFPS), and π is the mathematical constant, approximately 3.14159.
- During denitrification, the gaseous ratio between N_2 and N_2O ($R_{N2:N2O}$) is calculated following
- the empirical function derived by Del Grosso et al. (2000), which combines the effects of
- substrate (NO₃⁻) to electron donor (HR, the proxy for labile C) ratio and WFPS. $R_{N2:N2O}$ is
- 19 updated at every time step and for each grid cell.

$$20 R_{N2:N2O} = Fr(\frac{NO_3^-}{HR}) \cdot Fr(WFPS) (16)$$

21 With

22
$$Fr\left(\frac{NO_3^-}{HR}\right) = \max(0.16 \times k, k \times e^{(-0.8 \times \frac{NO_3^-}{HR})})$$
 (17)

23
$$Fr(WFPS) = \max(0.1, 0.015 \times WFPS - 0.32)$$
 (18)

- 24 where k is a texture dependent parameter- (Table 1) estimated from Del Grosso et al. (2000). k
- 25 controls the maximum value of the function $Fr\left(\frac{NO_3^-}{HR}\right)$.

26 **2.1.2.3 Other modified processes**

- 1 To complete the N loss scheme in LM3V-N, we also added NH₃ volatilization into LM3V-N.
- 2 NH₃ volatilization in soil results from the difference between the equilibrium NH₃ partial
- 3 pressure in soil solution and that in the air. Dissolved NH₃ is regulated by ammonium
- 4 concentration and pH. The net flux of NH₃ from soil to the atmosphere varies with soil NH₃,
- 5 moisture, temperature, therefore

6
$$NH_3 = k_{nh}f(pH)f_{NH3}(T)(1 - WFPS)\frac{N_{NH_4^+}}{b_{N,NH_4^+}}$$
 (19)

- 7 where NH_3 is the net ammonia volatilization flux (in unit, kgN m⁻² year⁻¹); k_{nh} is the
- 8 optimumbase ammonia volatilization rate (365 year⁻¹); f(pH) is the pH factor and f(T) is the
- 9 temperature factor which are given by the following two equations:

10
$$f(pH) = e^{2 \times (pH_{soil} - 10)}$$
 (20)

11
$$f_{NH3}(T) = \min(1, e^{308.56 \times (\frac{1}{71.02} - \frac{1}{Tsoil + 46.02})})$$
 (21)

- where pH_{soil} is the soil pH which is prescribed instead of simulated dynamically. f(pH) and f(T)
- 13 follow largely on the NH₃ volatilization scheme implemented in the dynamic global vegetation
- model LPJ-DyN (Xu-Ri and Prentice, 2008).

15 **2.2 Model experiments**

16

2.2.1 Global hindcast with potential vegetation

- 17 To understand the model performance and compare with other models and observations, we
- conducted a hindcast simulation with potential vegetation. The model resolution was set to 3.75
- degrees longitude by 2.5 degrees latitude. We forced the model with 3 hourly reanalysis weather
- data based on Sheffield et al. (2006). We used a 17 year recycled climate of 1948-1964 for the
- 21 spin-up and simulation years prior to 1948. Atmospheric CO₂ concentration was prescribed
- 22 with 284 ppm for model spin-up and based on ice core and atmospheric measurements for
- transient simulations (Keeling et al., 2009). N deposition was set as natural background for
- simulations before 1850 (Dentener and Crutzen, 1994), and interpolated linearly between the
- 25 natural background and a snapshot of contemporary (1995) deposition (Dentener et al., 2006)
- 26 for simulations after 1850. Soil pH was prescribed and derived from the Harmonized World
- 27 Soil Database (HWSD) version 1.1, the same as NACP model driver data (Wei et al., 2014).

- 1 The model was spun up from bare ground without C-N interactions for the first 68 years and
- with C-N interactions for the following 1200 years to develop and equilibrate C and N stocks.
- 3 To speedupaccelerate the spin-up process, slow litter and soil C and N pools were set to the
- 4 equilibrium values based on litterfall inputs and decomposition/leaching rates every 17 years.
- 5 We determined the model to reach a quasi-equlibrium state by confirming the drift to be less
- 6 than 0.03 PgC yr⁻¹ for global C storage and 0.2 TgN yr⁻¹ for global N storage. From this quasi
- 7 equilibrium state, we initialized the global hindcast experiment starting from 1850 using the
- 8 corresponding climatic forcings, CO₂ and N deposition data. In the following analysis, we will
- 9 focus mostly on the last three decades (1970-2005).

10

2.2.2 Sensitivity to soil water filled pore space (WFPS)

- While LM3V-N carries a simplified hydrology, we bracketed effects of soil moisture by
- exploring the paremeterization of WFPS and by substituting the predicted soil moisture with 3-
- hourly re-analysis data. Levels of soil water (in unit kg m⁻²) therefore stem from: (1) the
- simulated water content based on LM3V-N soil water module, hereafter LM3V-SM (2) the
- 15 Global Land Data Assimilation System Version 2 with the land surface model NOAH 3.3
- 16 (Rodell et al., 2004), hereafter NOAH-SM, and (3) the ERA Interim reanalysis dataset from
- 17 European Center for Medium range Weather Forecasting (ECMWF) (Dee et al., 2011),
- hereafter ERA-SM. The latter two datasets integrate satellite and ground based obervations with
- 19 land surface models. When overriding soil moisture, we linearly interpolated the 3 hourly data
- 20 onto the 30 minutes model time step. In these simulations, we allowed soil C and N dynamics
- 21 to vary according to different soil moisture datasets, but kept the model prediction of soil water
- 22 to use for plant productivity and evapotranspiration.
- 23 Parameterization of the soil moisture effect on nitrification and denitrification are based on
- 24 WFPS. LM3V-N uses the concept of plant available water, where water that is available to
- 25 plants varies between the wilting point and field capacity. Water content above the available
- 26 water capacity (i.e., the difference between field capacity and wilting point) leaves the soil
- immediately (Milly and Shmakin, 2002), and thus WFPS does not attain high values typically
- observed during denitrification. To explore the effect of WFPS soil moisture relationship on
- 29 N₂O emissions, we calcuated WFPS using three methods. Method 1 assumes WFPS is the ratio
- of available water and the available water capacity in the rooting zone. In Method 2 we
- 31 assume assumed, WFPS is the ratio of the water filled porosity and total porosity which is

- derived from bulk density (BD, in unit g cm⁻³). BD was obtained from the Harmonized World
- 2 Soil Database (HWSD) version 1.1 (Wei et al., 2014). The calculation is given by

$$3 WFPS = \frac{\frac{\theta}{\rho h_r}}{1 - \frac{BD}{PD}}$$
(22)

- 4 where θ (kg m⁻²) is the root zone soil water; h_r (m) is the effective rooting depth of vegetation;
- 5 ρ is the density of water (1000 kg m⁻³); and PD is the particle density of soil (2650 kg m⁻³).
- 6 Method 1 geerally leads to an overestimation of WFPS because the available water
- 7 capacity is smaller than total pore space. In contrast, the use of Method 2 with LM3V-SM
- 8 creates an underestimation since water is not allowed to accumulate beyond field capacity and
- 9 misses high WFPS to which nitrification and denitrification are sensitive. Meanwhile, for
- 10 NOAH-SM and ERA-SM data, Methods 2 is more close to the "real" WFPS and is the default
- method when using these data sets. In a The third approach, which is also the default method
- with LM3V-SM that is applied in the global hindcast experiment, the subsequent elevated CO₂
- and temperature responses experiment, and sensitivity tests with regard to N cycling, calculates
- 14 WFPS as the average of the previous two methods.

24

- 15 For each soil moisture dataset (3 in total, 2 replacements and 1 simulated by LM3V-N), we
- 16 calculated WFPS using three methods mentioned above. We conducted transient simulations
- with the nine different WFPSs (3 datasets × 3 methods) starting from the near equilibrium state
- obtained in the global hindcast experiment in 2.2.1. The use of less realistic Method for WFPS
- 19 for each soil moisture driver (LM3V-SM, NOAH-SM and ERA-SM) offers insights of the
- sensitivity of N₂O emissions to soil moisture. –The simulation procedure was the same as that
- 21 in global hindcast experiment except for the WFPS. ERA-SM is only availabe starting from
- 22 1979, prior to which simulations were conducted with model default soil moisture (LM3V-SM).
- 23 Results from ERA-SM were analyzed starting from 1982, leaving a short period for adjustment.

2.2.3 Sensitivity to N cycling processes and parameterization

- 25 N₂O emission is constrained by ecosystem availability of mineral N, which is linked
- 26 to different N cycling processes in addition to nitrification and denitrification processes.
- 27 To test the sensitivity of modelled N₂O emission to the larger plant-soil N cycle, we conducted
- 28 the following sensitivity analyses, in form of a one at a time perturbation. We replaced the
- 29 dynamic BNF scheme with empirically reconstructed preindustrial fixation rates (Cleveland et

1 al., 1999; Green et al., 2004), removing the negative feedback between BNF and plant N 2 availability. We further shut off N loss pathways through DON leaching and fire volatilization 3 (with ash fraction =1). We expect that these three modifications alleviate N limitation: 4 Prescribed BNF may continuously add N beyond plant N demand. Further eliminating fire and 5 DOM N losses leave loss pathways that have to pass the available N pool thereby opening the 6 possibility of increasing gaseous losses. Further, removing these plant-unvailable unavailable pathways (Thomas et al., 2015) increases N retention and opens the possibility of alleviating N 7 8 limitation. In addition, we modified key parameters related to general N cycling and N₂O 9 emissions one-at-a-time. We multiplied several parameters that directly affect ammonium and 10 nitrate concentration or N₂O fluxes by 10 (x10) or 0.1 (x0.1), while kept other parameters as 11 defaults. Those parameters control the active root N uptake rates (v_{max}) , nitrification rate (k_n) , 12 denitrification rate (k_d, K_c, K_n) and the fraction of net nitrification lost as N_2O (frac),

2.2.4 Responses to elevated CO₂ and temperature

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14 Respones of N₂O emissions to atmospheric CO₂ and global warming have been reported at field 15 scale (Dijkstra et al., 2012; van Groenigen et al., 2011). Here, we evaluate the model's response to step changes in form of a doubling of preindustrial CO₂ level (284 ppm to 568 ppm) and a 16 17 2K increase in atmospheric temperature. Starting from the same quasi-equilibrium state with 18 potential vegetation as in the global hindcast experiment in 2.2.1, we conducted four transient 19 model runs: (1) the CONTROL run with the same drivers as spin-up; (2) the CO2_FERT run 20 with the same drivers as the CONTROL except a doubling of atmospheric CO₂ level; (3) the 21 TEMP run with the same drivers as the CONTROL except a 2K rise in atmospheric temperature; 22 and (4) the CO₂ FERT×TEMP run with both the doubling of CO₂ and 2K rise in temperature. 23 For each experiment, we ran the model for 100 years and evaluated the corresponding results.

2.3 Comparisons with observations

We compared our model results for annual N_2O gas loss with field data: We compiled annual N_2O emissions from peer-reviewed literature (see Appendix A for more information). To increase the representativeness of the measurements, we included only sites with more than 3 months or 100 days experimental span. We limited our datasets where there was no reference to a disturbance of any kind. Only locations with at least 50 years non-disturbance history for forests and 10 years for vegetation other than forests were included. The compiled 61

- 1 measurements cover a variety of spatial ranges with vegetation types including tropical 2 rainforest, temperate forest, boreal forest, tundra, savanna, perennial grass, steppe, alpine grass 3 and desert vegetation. Multiple measurements falling into the same model grid cell were 4 averaged. If the authors had indicated the dominant vegetation or soil type, we used the values 5 reported for the dominant type instead of the averaged. For multiyear measurements, even if 6 the authors gave the individual year's data, we averaged the data to avoid overweighting of long 7 term studies. If the location was between borders of different model grid cells, we averaged 8 across the neighboring grid cells. 9 We also compared monthly N₂O fluxes at a group of sites: (a) the Tapajós National Forest in 10 Amazonia (3°S, 55°W), taken from Davidson et al. (2008); (b) the Hubbard Brook Experimental Forest in New Hampshire, USA (44°N, 72°W), as described in Groffman et al. 11
- 12 (2006); (c) the cedar forest from Oita, Japan (33°N, 131°E), as described in Morishita et al.
- 13 (2007); (d) the Leymus chinensis (LC) and Stipa grandis (SG) steppe in Inner Mongolia, China
- 14 (44°N, 117°E), taken from Xu-Ri et al. (2003); (e) the cedar forest in Fukushima, Japan (37°N,
- 15 140°E), taken from Morishita et al. (2007); and (f) the primary (P1 and P2) and secondary (L1
- and L2) forests located at the Pasir Mayang Research Site (1°S, 102°E), IndonsiaIndonesia,
- taken from Ishizuka et al. (2002). In addition, daily measurements of soil temperature,
- soil moisture and N₂O emissions were compared at four German forest sites located in the same
- 19 grid cell (50°N, 8°E), as described in Schmidt et al. (19861988).

20 3 Results

21

3.1 Global budget, seasonal and inter-annual variability

- Our modelled global soil N₂O flux is 6.69±0.32 TgN yr⁻¹ (1970-2005 mean and standard
- 23 deviation among different years) (Fig.1) with LM3V-SM (Method 3, default method for
- 24 LM3V-N calculated soil moisture), 5.61±0.32 TgN yr⁻¹ with NOAH-SM (Method 2) and
- 25 7.47±0.30 TgN yr⁻¹ with ERA-SM (1982-2005, Method 2) which is within the range of reported
- values: The central estimation estimate of N₂O emission from soils under natural vegetation is
- 27 6.6 TgN yr⁻¹ based on the Intergovernmental Panel on Climate Change (IPCC) AR5 (Ciais et
- al., 2013) (range, 3.3–9.0 TgN yr⁻¹) for the mid-1990s. Mean estimation for the period of 1975-
- 29 2000 ranged from 7.4 to 10.6 TgN yr⁻¹ with different precipitation forcing data (Saikawa et al.,
- 30 2013). Xu-Ri et al. (2012) reported the decadal-average to be 8.3-10.3 TgN yr⁻¹ for the 20th

- 1 century. Potter and Klooster (1998) reported a global mean emission rate of 9.7 TgN yr⁻¹ over
- 2 1983-1988, which is higher than the earlier version of their model (6.1 TgN yr⁻¹) (Potter et al.,
- 3 1996). Other estimates includes include 6-7 TgN yr⁻¹ (Syakila and Kroeze, 2011), 6.8 TgN yr⁻¹
- 4 based on the O-CN model (Zaehle et al., 2011), 3.9-6.5 TgN yr⁻¹ for preindustrial periods from
- 5 a top-down inversion study (Hirsch et al., 2006), 1.96-4.56 TgN yr⁻¹ in 2000 extrapolated from
- 6 field measurements by an artificial neural network approach (Zhuang et al., 2012), 6.6-7.0 TgN
- 7 yr⁻¹ for 1990 (Bouwman et al., 1995), and 7-16 TgN yr⁻¹ (Bowden, 1986) as well as 3-25 TgN
- 8 yr⁻¹ (Banin, 1986) from two earlier studies.
- 9 Following Thompson et al. (2014), El Niño years are set to the years with the annual
- 10 multivariate ENSO index (MEI) greater than 0.6. 1972, 1977, 1982, 1983, 1987, 1991, 1992,
- 11 1993, 1994, 1997 and 1998 were chosen as El Niño years. We detected reduced emissions
- during El Niño years (Fig. 1), in line with the global atmospheric inversion study of Thompson
- et al. (2014) and the process based modelling study from Saikawa et al. (2013).
- 14 Figure 2 shows the simulated global natural soil N₂O emissions in 4 seasons averaged over the
- period of 1970-2005 based on LM3V-SM (Method 3). The northern hemisphere displays a large
- seasonal variability, with the highest emissions in the northern summer (JJA, June to August)
- 17 and lowest in winter (DJF, December to February). Globally, northern spring (MAM, March to
- 18 May) has the highest emission rate (2.07 TgN) followed by summer (1.89 TgN). The smaller
- 19 emissions in summer compared to spring stems from a reduced contribution of the southern
- 20 hemisphere during northern summer.
- As expected, a large portion (more than 60%) of the soil N₂O fluxes have tropical origin (23.5
- S to 23.5N), while emissions from cooler regions are limited by temperature and arid/semi-arid
- regions by soil water. Our modelling results <u>suggestedsuggest</u> year-round high emission rates
- 24 from humid zones of Amazonia, east central Africa, and throughout the islands of Southeast
- Asia, with small seasonal variations (Fig. 2). Emissions from tropical savannah are highly
- variable, with locations of both high fluxes (seasonal mean > 30 mgN m⁻² month⁻¹ or 3.6 kg ha⁻¹
- 1 yr⁻¹) and low fluxes (seasonal mean < 1.3 mgN m⁻² month⁻¹ or 0.16 kg ha⁻¹ yr⁻¹). The simulated
- average tropical emission rate is 0.78 kgN ha⁻¹ yr⁻¹ (1970-2005), within the range of estimates
- 29 (0.2-1.4 kgN ha⁻¹ yr⁻¹) based on site-level observations from the database of Stehfest and
- Bouwman (2006), but smaller than a more detailed simulation study (1.2 kgN ha⁻¹ yr⁻¹) carried
- out by Werner et al. (2007). Our analysis here excluded land cover, land use changes and human

- 1 management impacts, while most of the observation-based or regional modelling studies did
- 2 not factor out those impacts. Our modelling result in natural tropics is comparable with another
- 3 global modelling study (average emission rate, 0.7 kgN ha⁻¹ yr⁻¹) (Zaehle et al., 2010), in which
- 4 the authors claimed they may underestimate the tropical N₂O sources compared to the inversion
- 5 estimates from the atmospheric transport model TM3 (Hirsch et al., 2006).

6 3.2 Sensitivity to WFPS

- 7 The different parameterization of WFPS and the use of different soil moisture modeling and
- 8 data allows to test the sensitivity of soil N₂O emissions to variable WFPS. Globally, emissions
- 9 generally increase with WFPS (Fig. 3). WFPS derived from Method 1 is higher than that based
- on Method 2. Data-derived soil moisture datasets combined with different calculation methods
- together produced a range of 0.15-0.72 for the global mean WFPS (1982-2005). While mean
- values greater than 0.6 (approximately field capacity) are less realistic, these high WFPS values
- provide the opportunity to test the model's response to the soil moisture-based parameterization
- of redox conditions in soils. Global soil N₂O emissions are highly sensitive to WFPS, with
- approximately 0.25 TgN per year per 0.01 change in global mean WFPS in the range 0 to 0.6.
- 16 The spatial and temporal characteristic of WFPS also matters. Emission rate from LM3V-SM
- 17 (Fig. 3 green cycle) is 1.13 TgN yr⁻¹ higher than that from NOAH-SM (Fig. 3 blue triangle),
- while both model configuration have the same mean WFPS (ca. 0.21), highlighting effects of
- regional and temporal differences between the soil moisture products.

3.3 Model-observation comparisons

- 21 Modelled N₂O emissions capture the average of cross-site observed annual mean emissions
- 22 (0.54 vs. 0.53 kgN ha⁻¹ yr⁻¹ based on LM3V-SM) reasonably (Appendix A and Fig. 4a), but
- 23 spread considerably along the 1:1 line. The points deviating the most are from tropical forests,
- 24 with overestimations from montane tropical forest and underestimations from lowland tropical
- 25 forests if those measurements are representative of gridcell emissions. These patterns are
- similar as results from NOAH-SM (Appendix A and Fig. 4b) and ERA-SM (Appendix A and
- 27 Fig. 4c), except that the application of WFPS from NOAH-SM slightly underestimates the
- observed global mean (0.54 vs. 0.47 kgN ha⁻¹ yr⁻¹ from NOAH-SM with WFPS based on
- 29 Method 2).

20

1 At the Tapajós National Forest, results from LM3V-SM capture some of the variations in N₂O 2 fluxes, but the model is not able to reproduce the high emissions observed during spring (Panel 3 (a), Fig. 5). At the Hubbard Brook Experimental Forest, the correlation 5), which might be 4 caused by the underestimation of WFPS from models. We used a total porosity of 0.62 5 (Davidson et al., 2004) to estimate root zone WFPS based on the reported soil water content 6 (Davidson et al., 2008). The average WFPS from observation is estimated to be 0.49, which is 7 higher than the modelled average of root zone WFPS for all 3 model configurations (LM3V-8 SM, 0.27, NOAH-SM 0.30, and ERA-SM 0.37). WFPS varies between < 0.05 and 0.45 in 9 LM3V-SM (range from 0.20 to 0.36 in NOAH-SM and 0.30 to 0.41 in ERA-SM), and contrasts 10 with observation that show seasonal variations with WFPS in the range of 0.37 to 0.58. At the 11 Hubbard Brook Experimental Forest, the correlations between model results and observations 12 are 0.51 (LM3V-SM), 0.56 (NOAH-SM) and 0.62 (ERA-SM) for yellow birch, 0.66 (LM3V-13 SM), 0.68 (NOAH-SM) and 0.70 (ERA-SM) for sugar maple, However, the model is less robust 14 in reproducing the magnitude of emission peaks. Groffman et al. (2006) suggested high 15 emissions of N₂O in winter were associated with soil freezing. However, the model assumes little emissions when soil temperature is under 0 °C. In addition, observations suggested N₂O 16 17 uptake (negative values in Panel (b), Fig. 5) while the model does not incorporate mechanisms 18 to represent N₂O uptake. At the Oita cedar forest, modelLM3V-N reproduces the seasonality of N₂O emissions accurately (Panel (c), Fig. 5). ERA-SM overestimates the magnitude of N₂O 19 20 fluxes from Inner Mongolia grassland, while the magnitudes produced from LM3V-SM and 21 NOAH-SM are comparable with observations. However, the timing of the emission peaks are 22 one or two month in advance from model output compared to observations (Panel (d), Fig. 5).in 23 the model compared to observations (Panel (d), Fig. 5). WFPS at a nearby meterological station 24 fluctuated between 0 and 0.5 for 0-20cm depth (Xu-Ri et al., 2003) which agrees with our values 25 based on LM3V-SM and ERA-SM, but the range is lower for NOAH-SM (0.05 to 0.35). At the 26 specific plots, Xu-Ri et al. (2003) reported a mean WFPS of 0.32 in one plot (LC) and 0.20 27 from in the other plot (SG) for the 0 to 0.1 m depth interval which are close to ERA-SM and 28 NOAH-SM (LM3V-SM 0.14, NOAH-SM 0.19, ERA-SM 0.30), however, no temporal 29 information was provided for the specific sites. At the Fukushima cedar forest, similar as at the 30 Oita cedar forest, models are less robust at capturing the magnitude of high peaks despiteof 31 N₂O emissions althoug the seasonality produced by the model are good (Panel (e), Fig. 5). 32 Emissions fromin the primary and secondary tropical rainforest at the Pasir Mayang Research

- 1 Site are highly variable, which makes the comparison difficult (Panel (f), Fig. 5). LM3V-SM
- 2 (but not ERA-SM and NOAH-SM) reproduces the low emissions in September-November
- 3 1997 and the increase of emissions from secondary forests in December, 1997. Overall,
- 4 modeled variability is smaller compared to observation across these sites.
- 5 The strong variability of measured N₂O emissions is further illustrated in Fig. 6.
- 6 Difference Differences in measured N2O fluxes between different forest sites within one grid
- 7 cell is are large, reflecting the heterogeneity that is not captured within one model grid cell. In
- 8 addition, the error bars, which represent the standard deviation of measured N₂O fluxes at three
- 9 different plots of the same forest, are large. The standard deviation is as high as 49.27 µgN m⁻
- 10 ²h⁻¹, indicating the strong variability of measured N₂O fluxes at the plot scale. Modeled N₂O
- 11 fluxes are generally within the range of measured N₂O emissions. Model outputs slightly
- 12 underestimate N₂O emissions largely due to the underestimation of soil water content (Panel
- 13 (b) Fig. 6).

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3.4 Sensitivity to N cycling processes and parameterization

- 15 Disallowing of N losses through DON and fire volatilization enhance ecosystem N
- accumulation and availability to plants and microbes, and therefore increases N₂O emissions
- 17 (Panel (a), Fig.7). The gain in N₂O emissions from disallowing DON loss is small (0.12 TgN
- 18 yr⁻¹). However, N₂O emission is on average (1950-2005) increased by 3.63 TgN yr⁻¹ in the
- 19 absence of fire volatilization N loss (we note, that fires do occur, but N is retained as ash in the
- 20 litter). The gain is most evident in tropical regions (not shown), indicating the importance of
- 21 fire in regulating ecosystem N status. Simulated preindustrial BNF is smaller than the empirical
- reconstructed BNF (72 in LM3V-N vs. 108 TgN yr⁻¹ from empirical based data). Green et al.,
- 23 2004). However, BNF in LM3V-N increases with time under historical varying climate,
- 24 increasing atmospheric CO₂ level and N deposition. The global average BNF during 1950-2005
- 25 is 100 TgN yr⁻¹, close to the empirical value. Neverthless, substitution of BNF in LM3V-N by
- empirical preindustrial value increased N₂O flux by 1.2 TgN yr⁻¹(Panel (a), Fig.7).
- 27 Among the specific parameters tested, N₂O emission is most sensitive to the 10 times change
- 28 (x10) of the fraction of net nitrification lost as N₂O gas. The relative magnitude of N₂O flux on
- average (1950-2005) reaches 6.5 times of the default (Panel (b), Fig.7). Reduction (x0.1) of
- maximum active plant N uptake strength (v_{max}) strongly increases N₂O emissions (ca. by 3 times
- of the default). Meanwhile, enhancement of v_{max} also increases N₂O fluxes, reflecting the non-

- linear response of N₂O emissions to v_{max} . x10 in the maximum nitrification rate k_n and
- denitrification rate k_d increase N₂O emissions, while x0.1 decrease N₂O flux. N₂O increases
- 3 more with increasing k_d than with increasing k_n , whereas reduction of k_n (x0.1) produces a
- 4 stronger response than reduction of k_d . The half-saturation constant that represents the
- 5 regulation of labile carbon availability on denitrification rate, *Kc*, is the least sensitive parameter.
- 6 Meanwhile, reduction (x0.1) of the half-saturation constant Kn that represents the regulation of
- substrate availability on denitrification rate on average increased N₂O fluxes by 4.5 TgN yr⁻¹
- 8 (Panel (b), Fig.7).

9 3.5 CO₂ and temperature responses

- 10 Globally, N₂O emissions respond to a step CO₂ increase first with a decline to ultimately
- increased levels after approximately 40 years (Fig. 8a, black line). The simulated global
- response follows largely the behaviour as simulated for tropical forests (Fig. 8a, yellow line).
- 13 The shift from a negative to a positive response indicates possible competing mechanisms
- operating on different time scales. Field level experiments revealed the highly variable effects
- of CO₂ fertilization on N₂O emissions. Based on a meta-analysis, van Groenigen et al. (2011)
- suggested that elevated CO₂ significantly increased N₂O emission by 18.8%, while Dijkstra et
- 17 al. (2012) argued for a non-significant response in non-N-fertilized studies. In contrast to
- observation studies, the global C-N cycle model analyses from O-CN suggested negative CO₂
- 19 fertilization effects on N₂O emissions (Zaehle et al., 2011). The negative impacts (reduced N₂O
- 20 flux), which are also reported in manipulative experiments, are likely from increased plant N
- 21 and immobilization demand under CO₂ fertilization, reducing N availability for nitrifiers and
- denitrifiers (Dijkstra et al., 2012). CO₂ fertilization on average (over 100 years) increased the
- 23 global mean plant nitrogen uptake rate by 10.02 kgN ha⁻¹ yr⁻¹, as shown in Fig. 9 (Panel (b)).
- 24 Modelled soil inorganic N content (ammonium and nitrate) is reduced at first, but the reduction
- 25 is not sustained. One mechanism to alleviate CO₂ fertilization caused induced N limitation is
- 26 through BNF, which is on average (over 100 years) more than doubled (Fig. 9 Panel (e)).
- 27 Similar asto manipulative field experiments (Dijkstra et al., 2012), positive effects (increase
- N₂O fluxes) can result from the impacts of elevated CO₂ level to increase litter production (Fig.
- 9 Panel (a)) and consequently C sources for denitrifiers, and to increase soil moisture (Fig. 9
- Panel (d)) from reduced stomatal conductance and leaf transpiration (Fig. 9 Panel (c)). With

- both positive and negative mechanisms embedded in our model, the net effects depend on the
- 2 relative strength of the opposing forces.
- 3 Temperate deciduous forests, where most of the forest CO₂ fertilization experiments are
- 4 conducted, respond positively to elevated CO₂ level (Fig. 8a, green line). The slight increase in
- 5 modelled N₂O emission are comparable with the mean response of field data compiled for
- 6 temperate forests (ca. 0.01-0.03 kgN yr⁻¹ ha⁻¹) (Dijkstra et al., 2012). A similar positive response
- 7 was detected for cold evergreen forests (Fig. 8a, pink line) with stronger magnitude compared
- 8 to temperate deciduous forests. For grasslands, Dijkstra et al. (2012) reported small negative
- 9 mean response from northern mixed prairie (ΔN_2O , ca. -0.01 to -0.03 kgN yr⁻¹ ha⁻¹), zero mean
- response from shortgrass steppe and positive mean response from annual grassland (ca. 0.03-
- 11 0.06 kgN yr⁻¹ ha⁻¹). Our model shows a small negative mean response from C4 grassland (Fig.
- 8a, cyan line) with the similar magnitude of that reported for the Northern mixed prairie, where
- the composition of C4 grass varies (Dijkstra et al., 2012). A CO₂ increase in C3 grassland
- initially reduces N₂O emission (Fig. 8a, blue line). However, this slight negative response turns
- into a small positive within one decade.
- 16 Elevated temperature generally increases N₂O emissions except for the slight negative effect in
- 17 C4 grass (Fig. 8b). Overall the response to a 2 degree warming is bigger than that of doubling
- of CO₂. The simulated temperature effects are more pronounced in the first decade and decrease
- 19 over time in tropical forests (Fig. 8b, yellow line), while for the temperate deciduous forests
- 20 (Fig. 8b, green line) and boreal forests (Fig. 8b pink line), the temperature effects become more
- 21 pronounced over time. Simulated temperate forest response (in the first decade) is close to that
- of observed mean (ca. 0.2-0.5 kgN yr⁻¹ ha⁻¹) (Dijkstra et al., 2012). Our modelled slight negative
- 23 response in C4 grass and positive in C3 grass are in alignment with data compiled by Dijkstra
- et al. (2012) who reported both positive and negative responses in grasslands.
- 25 The results of combining CO₂ and temperature are similar to the CO₂ effect alone (Fig. 8c),
- 26 despite the fact, that the individual effect of temperature is much stronger than that of CO₂. This
- 27 antagonistic interaction (i.e. the combined enhancement in N₂O flux from elevated CO₂ and
- temperature are smaller than the summary of their individual effects) is also evident for C3
- 29 grass (first 50 years), temperate deciduous tree and cold evergreen forests (Fig. 8d).

4 Discussion

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2 Our model combines two of the most widely applied biogeochemical models (DNDC and 3 CENTURY) with current advancements in field level studies. The model iswas capable of reproducing the global mean natural N₂O emissions fromin other modeling and inverse methods, 4 5 and the average of observed cross-site annual mean behavior. By focusing on the role of soil 6 moisture in N₂O emissions, we find found on a global scale a high dependence of simulated N₂O 7 emissions on soil moisture (WFPS), mainly driven by emissions from tropical regions. The 8 model broadly reproduces reproduced the magnitude and direction of responses to elevated CO₂ 9 and temperature from manipulative field experiments where data is avilable. The Both the global responses total emission as well as the global response to elevated CO2 and temperature 10 11 followand CO₂ increase followed largely the response of tropical forests, where a noted absence 12 of field experiments are rare and no evaluation of CO₂ responses exist. 13 Evaluation of global simulations agaist field measurements is susceptible to scale mismatches. 14 The complexity of microscale interactions for N₂O production creates notorious large spatial 15 and temporal variabilities which are undoubtedly difficult to constraint even at the stand level 16 (Butterbach Bahl et al., 2013). Daily measurements from the German forest sites (Fig.6) 17 illustrate the large variability in N2O emissions. Further improvement in soil moisture 18 simulation will improve our estimation of N2O fluxes at the German forest sites. However, the 19 homogeneous representation of environmental drivers within model grid cells easts doubt on 20 site-specific model-observation comparison in global simulations. For example, N2O emissions vary with topography which are not treated explicitly in most of the global C-N models. 3.8 21 22 times difference was detected in a montane forest (Central Sulawesi, Indonesia) moving from 1190 m to 1800m (Purbopuspito et al., 2006), and 4.3 times difference was found from a tropical 23 moist forest (Brazilian Atlantic Forest) with the altitude change from 100m to 1000m (Sousa 24 25 Neto et al., 2011). However, comparison against field data revealed, that the model's varibility is smaller compared to observation for both across field sites (Fig. 4), and at different sites (Figs. 26 27 5 and 6). One of the reason for this shortcoming may be that fast transitions, such as freeze-28 thaw eyele (Groffman et al., 2006) and pulsing (Yienger and Levy, 1995) are not sufficiently 29 captured. 30 Soil moisture is a key variable in climate system but difficult to derive or measure at the global

scale (Seneviratne et al., 2010). Our modelled fluxes arewere highly sensitive to WFPS, which

1 is in agreement with observation and model synthesis studies (Heinen, 2006;Butterbach-Bahl 2 et al., 2013). The large range when calculating WFPS from different methods resulted in a 3 difference of more than 5 TgN yr⁻¹ in global soil N₂O fluxes. Saikawa et al. (2013) found an up to 3.5 TgN yr⁻¹ gap induced by different precipitation forcing data from CLMCN-N2O. It is 4 difficult to single out the difference caused by soil moisture alone from their results. 5 6 Nevertherless, those two studies did suggest the importance of improving the dynamics of soil 7 water and representation of WFPS for the purpose of predicting soil N₂O emission and climate 8 feedbacks. 9 The root zone soil water in LM3V-N is based on a single layer bucket model. This simplified treatment of soil water dynamics may increase the difficulty in reproducing the temporal and 10 11 spatial dynamics of WFPS. As a first step, we used the average between the original analog in 12 LM3V-N and a formulation that was derived from soil total porosity to account for actual soil moisture and the possibility of soil water above field capacity. Meanwhile, overriding soil 13 moisture with data-derived products (NOAH-SM and ERA-SM) suggests that the most realistic 14 average (1970-2005) soil N₂O emission is in the range of 5.61-7.47 TgN yr⁻¹. However, despite 15 using data-derived soil moisture, it appears that the prediction of soil moisture is an impediment 16 17 towards validating N₂O emissions at field scale. If evaluated against field data, the model was 18 capable of representing the mean across sites and to a certain degree also compared adequately 19 with site-specific time series. However, there are differences between sites (Fig. 4) and also 20 peak emissions were poorly represented in the model (Fig. 5), and they can at least partly be 21 attributed to mismatches in WFPS. Overall, comparison against field data revealed that the model's variability is smaller compared to observation for both across field sites (Fig. 4) and at 22 23 different sites (Figs. 5 and 6). One of the reason for this shortcoming may be that fast transitions, such as freeze-thaw cycle (Groffman et al., 2006) and pulsing (Yienger and Levy, 1995) are not 24 25 sufficiently captured. As a first step, we used the average between the original analog in LM3V-N and thatis derived from soil total porosity to account for actual soil moisture and the 26 27 possibility of soil water above field capacity. Meanwhile, overriding soil moisture with dataderived products (NOAH-SM and ERA-SM), suggests that the most realistic average (1970-28 29 2005) soil N₂O emission is in the range of 5.61-7.47 TgN yr⁻¹. A more realistic root zone water 30 module, such as multilayer representations of biogeochemistry and soil water dynamics, would 31 refine models of soil N2O emissions. El Niño events trigger reduced soil emissions in our results

similar as proposed by Saikawa et al. (2013) and Thompson et al. (2014). El Niño events are

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known to have induced several of the most well known large scale droughts and alters soil 2 moisture dynamics (Schwalm et al., 2011). Tropical forests N₂O emissions are highly correlated 3 with root zone soil water content and contribute strongly to the global scale fluxes of N2O in 4 our model. Whether there is a strong link between soil N2O emission anomalies and El Niño 5 induced soil moisture deviations needs further investigation with improved soil hydrology. Perhaps equally important to address in future analysis, is the tremendous variability of N₂O 6 7 emissions from site to site within the same region (see Fig. 6) This field-scale variability 8 highlights the complexity of microscale interactions for N2O production, which creates 9 notorious large spatial and temporal variabilities and are undoubtedly difficult to constrain even 10 at the stand level (Butterbach-Bahl et al., 2013). The homogeneous representation of 11 environmental drivers within model grid cells casts doubt on site-specific model-observation 12 comparison in global simulations. For example, N2O emissions vary with topography which 13 are not treated explicitly in most of the global C-N models. 3.8 times difference was detected 14 in a montane forest (Central Sulawesi, Indonesia) moving from 1190 m to 1800m (Purbopuspito 15 et al., 2006), and 4.3 times difference was found from a tropical moist forest (Brazilian Atlantic Forest) with the altitude Globally, the tropical fluxes contribute with more than 60% to the 16 17 global soil N2O fluxes. Also, global responses to elevated CO2 and temperature are dominated 18 by the tropical response. In contrast to temperate and boreal forests, tropical forests respond 19 negatively to elevated CO2 in the first few decades. Our results therefore suggest caution when 20 extrapolating from current manipulative field studies to the globe: The postive response to CO₂ 21 enrichment as obtained from (mostly) extratropical field study may be overestimated, when the 22 studies' fluxes are scaled up to the globe. Moreover, we found strong interaction of elevated 23 CO₂ and temperature, acting to reduce soil N₂O emission compared to the sum of individual 24 responses, highlighting the non-linear impacts of CO₂ and temperature on N₂O emissions. Our 25 results from step increases of CO2 and temperature is different from Xu-Ri et al. (2012) in 26 which CO₂ and climate change act synergistically to increase historical N₂O emissions, 27 especially in tropical regions. CO₂ fertilization plus interaction with temperature rise reduce tropical N₂O fluxes in the first several decades from our model. We realize that this interaction 28 29 is likely to be different when incorporating other factors (Brown et al., 2012), such as N 30 depostion, precipitation and land use change (disturbance). In addition, step changes in 31 atmospheric CO2 and temperature compared to gradual and sustained increases may also lead 32 to differences, and may explain the discrepancy between the previous modeling study and meta-

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- 1 analysis of manipulative field experiments with regard to CO₂ fertilization responses (Zaehle
- 2 et al., 2011; van Groenigen et al., 2011). However, step changes mimic most closely
- 3 manipulative experiments. Nevertheless, the largest uncertainties lie in the tropical region
- 4 where our model indicated strongest responses and strongest nonlinear interactions of elevated
- 5 CO₂ and temperature.
- 6 Globally, N₂O emissions from nitrification-denitrification are changing from 100m to 1000m
- 7 (Sousa Neto et al., 2011).
- 8 Globally, N₂O emissions from nitrification-denitrification were similar to O-CN and LPJ-DyN
- 9 as they are all derived from DNDC's formulation. Embedding an established N₂O emission
- module into LM3V-N enables evaluation of the response of N₂O emissions under different
- assumptions across models with respect to the dynamics of the larger plant-soil N cycle.
- Generally higher inputs from BNF or constraints on restriction of losses through organic N (fire,
- 13 DON) enhance N₂O emissions. The representation of of BNF in models requires
- 14 <u>impromventimprovement</u> but we <u>showshowed</u> here that different implementations are globally
- 15 important for N₂O emissions. Similar Similarly, the magnitude of N lost through fire
- 16 <u>impactsimpacted</u> N₂O emissions in fire prone regions, while N emission factors are poorly
- 17 constrained globally (Andreae and Merlet, 2001). The strength of plant uptake of N posesposed
- a strong constraint on the avaiability availability of N for nitrification-denitrification losses as it
- can draw down N substantially (Gerber and Brookshire, 2014). A reduction of plant uptake
- strength allows for relatively more N allocated for denitrification. More surprising was the
- 21 positive effect of a stronger plant uptake capacity on N₂O emissions: Enhanced plant uptake
- 22 allow increased vegetation production, and anN throughput through litterfall and mineralization
- 23 in the long run, which ultimately may allow higher N₂O losses in lieu of other export pathways.
- 24 In addition to those N cycling processes, N₂O emission isemissions were highly sensitive to the
- 25 fraction of N lost as N₂O fromduring net nitrification. The fraction of -N₂O lost fromduring net
- 26 nitrification is uncertain. Goodroad and Keeney (1984) suggested a value of 0.1-0.2%, while
- 27 Khalil et al. (2004) reported a range of 0.16%-1.48% depending on the O₂ concentration. We
- applied a global constant of 0.4% in our default simulation, bearing in mind the large
- 29 uncertainties associated with this parameter. We also note that this value has
- 30 significant impact on global N2O emissions.

1 The response to increases in temperature and CO2 is a consequence of both the direct effect of 2 temperature on nitrification and denitrification, and indirect effects via water and mineral N 3 availability. The inital negative response of N2O emissions to CO2 fertilization from tropical 4 forests produced by LM3V-N stems largely from the Our results showed that tropical forests 5 play a major role in both rates of emission and responses to perturbations. Tropical forests contributed with more than 60% to the global soil N₂O fluxes. El Niño events triggered reduced 6 7 soil N₂O emissions that are in our simulations similar to earlier estimates (Saikawa et al., 2013; 8 Thompson et al., 2014). El Niño events are known to have induced several of the most well 9 known large scale droughts and altered soil moisture dynamics (Schwalm et al., 2011) in the 10 tropics. Tropical forest N₂O emissions were highly correlated with root zone soil water content 11 and contributed strongly to the global-scale fluxes of N₂O in our model. Similarly, global 12 responses to elevated CO₂ and temperature were dominated by the tropical response. In contrast to temperate and boreal forests, tropical forests responded negatively to elevated CO₂ in the 13 14 first few decades. The inital negative response of N₂O emissions to CO₂ fertilization in tropical 15 forests produced by LM3V-N stemmed largely from increased demand and uptake of mineral 16 N due to enhanced vegetation growth under elevated atmospheric CO₂ level. Despite soil N 17 availability has been reported to decrease, unchanged or increase from manipulative CO2 18 enrichment experiments across extrotropical ecosystems (Reich et al., 2006; Drake et al., 2011; 19 Reich and Hobbie, 2013), no empirical evidence is available in tropical forests. LM3V-N 20 produced, on average, a reduced soil mineral N concentration in tropical forests initially. 21 Consequencely, less N is available for gaseous losses. Consequencely, less N is available for 22 gaseous losses as the N cycle tightens. If gross mineralization is used as an indicator of the rate 23 of N flow in the "hole-in-the-pipe" concept and gaseous losses are proportional to mineralization, 24 the inital negative response is unlikely to be detected. We found increased mineralization rate with increased litterfall under elevated CO₂, while N availability is reduced from LM3V-N. The 25 26 mineralization based approach is likely to predict an inrease of losses regardless of N limitation. 27 In LM3V-N, N availability recovers as N cycling processes adjust to CO2 fertilization, 28 especially from BNF, but also via higher transient retention of N from deposition. 29 In addition to the uncertainties mentioned above, we simplified N₂O sources and processes, 30 ignoring other microbial metabolic pathways and abiotic processes that produce or consume 31 N₂O. The global magnitude of those ignored process remains largely unexplored. We do not 32 incorporate explicit mechanisms for N2O emissions from freeze-thaw cycle or poorly drained

- soils (e.g. wetlands), the uptake of organic N etc., which are be globally important, especially
- 2 with future climate changes. Considering those uncertainties and gaps, more studies are in need
- 3 in order to undstand the terretrial N₂O emissions.
- 4 The marked decrease in our simulation for the tropcial forests also contrasts somewhat findings
- 5 from manipulative field experiments where CO₂ enrichment caused decrease, unchanged or
- 6 increase across extratropical ecosystems (Dijkstra et al., 2012; van Groenigen et al., 2011),
- 7 whereas no empirical evidence is available in tropical forests. Overall, the marked differences
- 8 between tropics and extratropics in the response to environmental forcing, and the large
- 9 contribution of tropical forests to global N₂O emissions suggests caution when extrapolating
- 10 <u>field studies mostly carried out in extraropical regions to the globe.</u>
- 11 Based on single factor analysis with LM3V-N, the initial response of N₂O emission to a
- 12 temperature increase was much larger than the response to increase atmospheric CO₂ (Fig. 8).
- 13 However, we found large interactions between warming and CO₂ fertilization, in that the
- 14 combined effect much more resembled the CO₂ effect alone. This interaction is the result of
- 15 two antagonistic responses where a warming lead to increased N mineralization and potential
- 16 N surplus, whereas a CO₂ increase fostered plant N demand that competed with microbial N₂O
- 17 production. While these mechanisms are part of most models, both comparison against different
- 18 models show notable differences when analyzing these two opposing effects. For example,
- 19 Stocker et al. (2013) found that under future climate change scenarios, CO₂ and climate effects
- are amplifying each other, in accordance with earlier model experiments (Xu-Ri et al., 2012).
- 21 In LM3V-N we find that these interactions are negative. On the other hand, simulations with
- 22 O-CN (Zaehle et al., 2011) showed the marginal effects of CO₂ and climate to be approximately
- equal and opposite. The marginal effects in the modeling setup of Zaehle et al. (2011) compare
- 24 best with our single effect for CO₂, while for climate, it is the combination of temperature and
- 25 interaction (Fig. 8). Analyzed in their fashion, LM3V-N's are congruent with those of Zaehle
- 26 et al. (2011), albeit we found a slightly weaker temperature effect compared to CO₂. This initial
- 27 response then transitions into a much larger CO₂ effect, while the response to temperature
- diminishes. This long-term response of a positive CO₂ effect can be expected in a model that
- 29 strongly retains N under limiting conditions such as LM3V-N. Retention ultimately allows
- 30 <u>build-up of N stocks</u>, thereby alleviating limitation and increasing the substrate for nitrifiers
- and denitrifiers. This transition into a positive CO₂ response was likely facilitated by up-
- 32 regualtion of BNF (Figure 9), which acts to reduce ecosystem N deficits and plant N demand

1 in medium- to long-term. Up-regulation is expected to be much weaker or absent in models 2 where BNF is parameterized based on evapotranspiration (Thomas et al., 2015). We realize that 3 strong interactions as found here and elsewhere (Xu-Ri et al., 2012; Stocker et al., 2013) may 4 also play out when other factors are considered (Brown et al., 2012), including N deposition, 5 precipitation and land use change (disturbance). Therefore some of the discrepancy with other 6 models may be caused by differences in the modeling setup. In addition, step changes in 7 atmospheric CO₂ and temperature compared to gradual and sustained increases may also lead 8 to differences. Yet applying step changes is useful to test our conceptual understanding and 9 may help explain the discrepancy between the previous modeling study and meta-analysis of 10 manipulative field experiments with regard to CO₂ fertilization responses (Zaehle et al., 2011; van Groenigen et al., 2011) 11

5 Conclusions

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13 We present estimates of terrestrial soil N₂O fluxes under natural vegetation (1970 to 2005) 14 based on existing N₂O emission formulations embedded into the global C-N cycle model LM3V-N. To determine the sensitivity of the modelling result to soil water (WFPS), we 15 16 replaced the root zone soil water with two other derived datasets and altered the way in which WFPS is calculated. Our best estimate of modelled global soil N₂O flux is 5.61-7.47 TgN yr⁻¹ 17 (1970-2005 mean and interannual variability), within the range of current understanding of soil 18 19 N₂O emissions, but highly sensitive to WFPS, general N cycling and parameterization of N₂O losses through nitrification and denitrification. Improvement of soil hydrology is likely to 20 significantly reduce the large uncertainties associated with soil N2O emission estimates. 21 22 Although the simulated mean responses are in agreement with manipulative field studies where 23 effects of elevated CO2 and temperature were investigated, we found that the global response 24 was dominated by tropical forest, where our model suggest a different response than the field 25 studies carried out in temperate ecosystems Comparison against field experiments suggests that LM3V-N was able to capture mean values, although site-to-site and temporal mismatches 26 27 remained. Given the sensitivity of N₂O emissions to WFPS, improvements in soil hydrology are likely to improve soil N₂O emission estimates. As expected, we found that processes in the 28 29 model that alleviate ecosystem N limitation, such as reduced N losses through fire volatilization 30 and increased N inputs through higher biological nitrogen fixation (BNF) rate, enhance N2O emissions. Responses to CO₂ and temperature perturbations showed differences compared to 31 other models. In particular elevated CO₂ curbs N₂O emissions sharply initially, but this negative 32

response is alleviated after a few decades, likely in conjunction with fast N replenishment from up-regulated BNF. Our sensitivity analysis and the comparison with other models showed that existing parameterizations of fast N cycle processes such as nitrification-denitrification lead to distinct and new results if the larger plant-soil N cycle is treated differently. More importantly, our work suggests a strong response to warming and CO₂ in tropical forests, where few manipulative field studies have been carried out.

1 Appendix A: Observed annual N₂O fluxes data

- 2 Annual N₂O fluxes data were compiled from peer-reviewed literature. We applied simple
- 3 selection criteria (see the main text) to reduce the mismatches between model outputs and field
- 4 measurements, bearing in mind the gaps between complex field conditions and idealized model
- 5 forcings. Latitutes (Lat) and longitudes (Lon) in Table A1 are based on model grids.

6 Table A1 Observed annual N₂O emission data for model comparison

No	Country	Lon	Lat	Location	Veg Type	$N_2O~kgN~ha^{-1}yr^{-1}$			
						OBS	LM3V-N	NOAH	ERA
1	Australia	133.1	-12.3	Douglas Daly region	Savanna	0.02	0.15	0.25	
2	Australia	148.1	-37.3	Moe	Temperate forest	0.11	0.58	0.74	0.72
3	Australia	151.9	-27.3	South-east Queensland	Tropical forest	0.52	0.01	0.03	
4	Austria	16.9	47.8	Klausenleopoldsdorf	Temperate forest	0.62	0.64	0.52	0.53
5	Austria	9.4	47.8	Achenkirch	Temperate forest	0.35	0.54	0.48	0.47
6	Austria	13.1	47.8	Innsbruck	Temperate forest	0.08	0.42	0.36	0.31
7	Austria	16.3	48.2	Schottenwald and	Temperate forest	0.76	0.61	0.54	0.52
				Klausenleopoldsdorf	•	0.76	0.61	0.54	0.53
8	Brazil	-61.9	-2.3	Manaus	Tropical rain forest	1.9	1.6	1.68	1.56
9	Brazil	-61.9	-2.3	Manaus	Tropical rain forest	1.930	1.71	1.74	1.55
10	Brazil	-54.4	-4.8	East-central Amazonia	Tropical rain forest	2.1	1.34	2.19	1.57
11	Brazil	-46.9	-2.3	Paragominas	Rainforest	2.430	1.22	1.19	1.11
12	Burkina Faso	-1.9	10.3	Ioba	Savanna	0.6	0.03	1.32	
13	Canada	-80.6	50.3	Ontario	Boreal forest	0.04	0.11	0.14	0.12
14	Canada	-106.9	52.8	Saskatchewan	Boreal forest	0.28	0.01	0.01	0.01
15	Canada	-103.1	52.8	Saskatchewan	Boreal forest	0.07	0.21	0.17	
16	Canada	-106.9	52.8	Saskatchewan	Boreal forest	0.09	0.01	0.01	
17	Canada	-73.1	45.3	Mont St. Hilaire	Temperate forest	0.42	0.54	0.46	
18	China	91.9	35.3	Tibet	Alpine grassland	0.07	0	0	0
					Alpine tundra, temperate				
19	China	125.6	40.3	Changbai mountain	forest	0.56	0.73	0.64	0.45
20	China	114.4	42.8	Inner mongolia	Temperate forest	0.73	0.1	0.14	0.71
				Sanjiang Experimental					
22	China	133.1	47.8	Station	Freshwater marshes	0.21	0.34	0.35	0.34
23	Denmark	13.1	55.3	Solo	Temperate forest	0.29	0.27	0.42	0.06

24	Denmark	13.1	55.3	Denmark	Temperate forest	0.52	0.28	0.37	0.05
25	Ecuador	-80.6	-4.8	Bombuscaro	Tropical forest	0.3	1.02	0	
26	Finland	24.4	60.3	Southern	Boreal forest	0.78	0.62	0.35	0.17
27	Germany	9.4	50.3	Average	Temperate forest	0.57	0.6	0.53	0.5
28	Germany	9.4	52.8	Kiel	Temperate forest	0.4	0.48	0.53	0.52
29	Germany	9.4	47.8	Southwest	Temperate forest	0.93	0.56	0.51	0.49
30	Germany	13.1	47.8	Höglwald	Temperate forest	0.41	0.47	0.4	0.39
31	Germany	9.4	52.8	Average	Temperate forest	0.66	0.44	0.5	0.5
32	Germany	9.4	52.8	Harz mountains	Mire	0.25	0.48	0.56	0.52
34	Indonesia	103.1	-2.3	Jambi	Lowland tropical rainforest	0.260	0.44		
35	Indonesia	121.9	-2.3	Central Sulawesi	Tropical seasonal rain forest	0.800	1.73	2.31	1.7
36	Indonesia	114.4	-2.3	Central Kalimantan	Tropical forest	2.51	2	2.45	1.73
37	Italy	9.4	45.3	P.Ticino BoscoNegri	Temperate forest	0.18	1.38	2.8	1.82
38	Malaysia	110.6	-2.3	Sarawak	Mixed peat swamp forest	0.7	0.66	0.65	0.57
39	New Zealand	170.6	-44.8	New Zealand	Temperate forest	0.01	1.24	2.84	1.24
40	Norway	9.4	60.3	Norway	Temperate forest	0.73	0.52	0.52	0.38
41	Panama	-80.6	7.8	Gigante Peninsula	Tropical forests	1.6	0.2	0.39	0.39
42	Sweden	13.1	57.8	Southwestern	Temperate forest	0.07	1.86	1.67	
43	Sweden	13.1	57.8	Asa experimental forest	Undrained bog	0.65	0.36	0.45	0.36
44	UK	-1.9	55.3	Northumberland	Grassland	0.3	0.4	0.5	0.41
45	USA	-73.1	42.8	Harvard forest	Mixed hardwood	0.04	0.56	0.54	0.48
46	USA	-73.1	40.3	New York	Temperate forest	0.9	0.4	0.49	0.41
47	USA	-80.6	25.3	Florida	Marsh	1	0.45	0	
48	USA	-73.1	42.8	New Hampshire	Temperate forest	0.070	0.64	2.15	
49	USA	-106.9	35.3	New mexico	Temperate forest	0.06	0.41	0.51	0.43
50	USA	-118.1	45.3	Washington	Temperate shrub-steppe	0.15	0.02	0.02	0.02
51	USA	-114.4	37.8	Mojave desert	Perennial grasses	0.11	0.02	0.02	0.02
52	USA	-106.9	40.3	Wyoming	Sagebrush steppe	0.21	0.01	0.02	0.03
53	USA	-73.1	45.3	Northeastern	Temperate forest	0.18	0.05	0.04	0.05
54	USA	-69.4	45.3	Northeastern	Temperate forest	0.03	0.53	0.46	0.44
55	USA	-103.1	40.3	Colorado	Temperate steppe	0.14	0.37	0.53	0.4
56	USA	-88.1	42.8	Wisconsin	Grass	0.040	0.03	0.05	0.05
57	USA	-114.4	37.8	Nevada	Mojave desert	0.11	0.45	0.45	

58	USA	-110.6	32.8	Arizona	Sonoran desert	0.4	0.04	0.04	0.05
59	USA	-118.1	45.3	Ft. Collins, Colorado	Temperate grassland	0.12	0.01	0.03	0.03
60	Venezuela	-61.9	10.3	Venezuela	Savana	0.73	0.06	0.07	0.07
61	Zimbabwe	31.9	-17.3	Harare	Miombo woodland savanna	0.51	0.83	1.61	0.57

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Figures and Tables

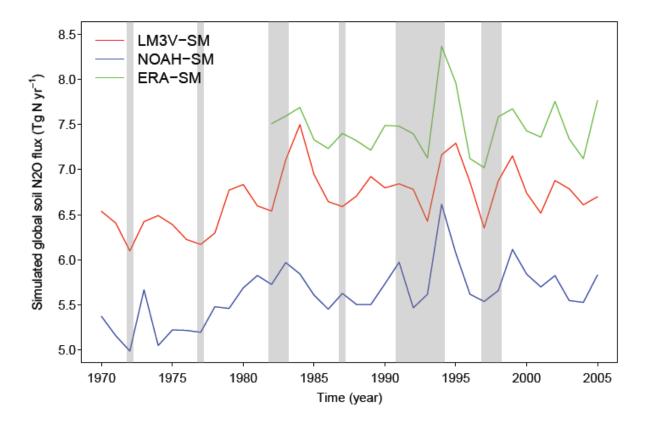


Figure 1. Simulated annual global soil N_2O emissions based on potential vegetation (1970-2005). Shaded grey area indicates El Niño years with the annual multivariate ENSO index (MEI) greater than 0.6. Colours refer to different soil moisture dataset used in the estimation: red for LM3V-SM (with WFPS calculated by Method 3); blue for NOAH-SM (Method 2) and green for ERA-SM (Method 2). Details for these soil moisture dataset and WFPS calculating methods is available in the main text.

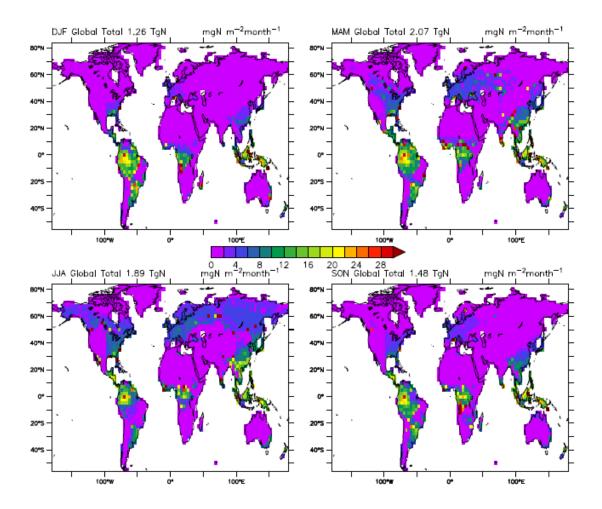


Figure 2. Global seasonal mean soil N₂O emissions (with potential vegetation) averaged over the years 1970-2005. DJF (December, January and February), stands for Northern Hemisphere Winter; MAM (March, April and May) for Spring; JJA (June, July and August) for Summer; and SON (September, October and November) for Autumn.

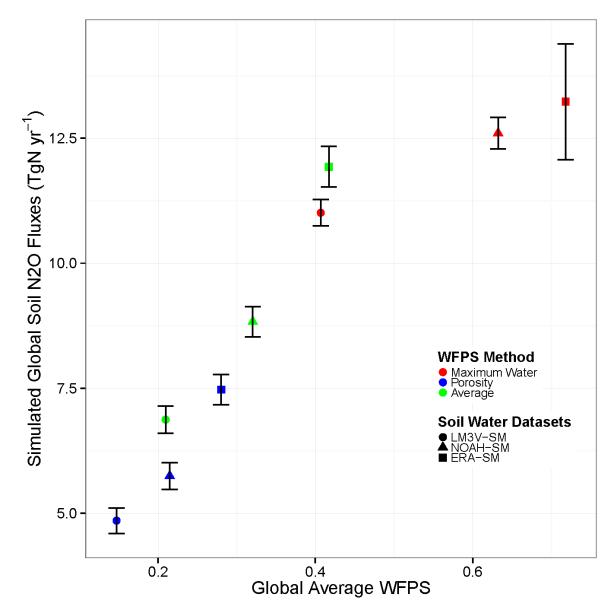


Figure 3. Sensitivity of simulated global soil N₂O emissions (with potential vegetation) to water filled pore space (WFPS). The x-axis is the WFPS averaged globally over 1982-2005; the y-axis represents the corresponding global total N₂O fluxes. A total of nine sets of WFPS are obtained through either different soil water datasets (colours) or varied calculation methods (symbols). Maximum water, porosity and average correspond to method 1, method 2 and method 3 in the main text, respectively. Coloured symbols represent interannual means and error bars indicate interannual standard deviations.

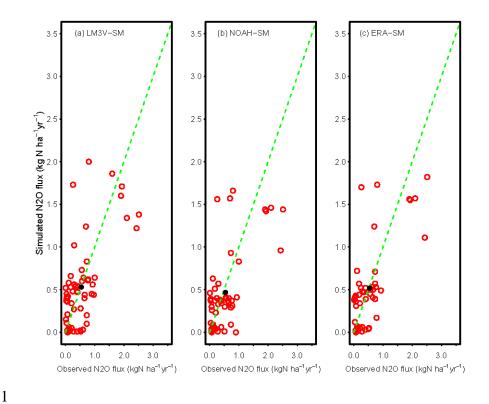


Figure 4. Observed vs. simulated annual N₂O emissions from natural soils. Dashed green lines are the 1:1 lines. The solid circles represent the overall means. Different panels represent simulations with different soil moisture data: (a) LM3V-SM (simulated by LM3V-N); (b) NOAH-SM (based on land surface model NOAH 3.3 in Global Land Data Assimilation System Version 2); and (c) ERA-SM (reanalysis data from ECMWF). Water filled pore space (WFPS) is calculated using the average of the one based on available water capacity and the one based on the total porosity (Method 3, see the main text for detailed description) for panel (a); and using the total porosity (Method 2) for panel (b) and (c).

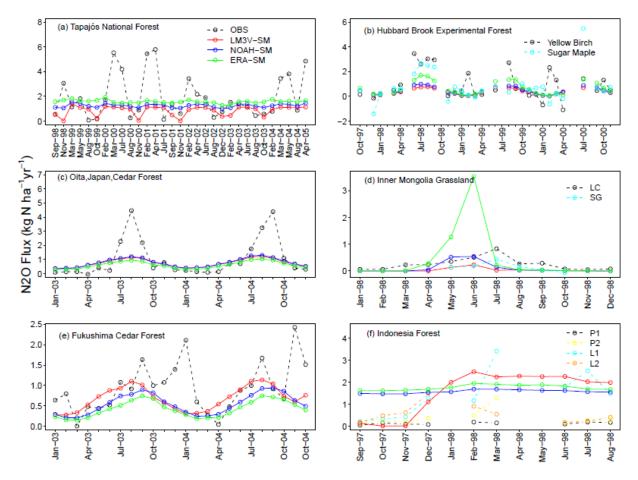


Figure 5. Observed vs. simulated monthly N₂O emissions at (a), the Tapajós National Forest in east-central Amazonia (3°S, 55°W), taken from Davidson et al. (2008); (b), the Hubbard Brook Experimental Forest in New Hampshire, USA (44°N, 72°W), taken from Groffman et al. (2006); (c), a cedar forest at Oita, Japan (33°N, 131°E), taken from Morishita et al. (2007); (d), the *Leymus chinensis* (LC)and *Stipa grandis* (SG) steppe in Inner Mongolia, China (44°N, 117°E), taken from Xu-Ri et al. (2003); (e), a cedar forest in Fukushima, Japan (37°N, 140°E), taken from Morishita et al. (2007); and (f), the primary (P1 and P2) and secondary (L1 and L2) forests located at the Pasir Mayang Research Site, IndonsiaIndonesia, taken from Ishizuka et al. (2002) (1°S, 102°E). Shown are modeled results from three WFPS schemes (LM3V-SM, NOAH-SM and ERA-SM) the same as in Figure 4.

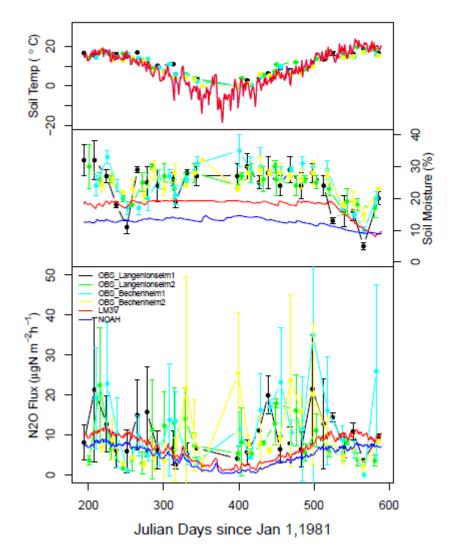


Figure 6. Comparison of (a) soil temperature (2cm from observation and 1 cm from model) in °C; (b) soil moisture (2cm from observation and root zone from model) in % and (c) soil N₂O emissions in μgN m⁻² h⁻¹ from observations and model outputs at four forest sites from GermanGermany (50°N, 8°E), taken from Schmidt et al. (19861988). Shown are modeled results from two WFPS schemes (LM3V-SM and NOAH-SM) similar as in Figure 4.

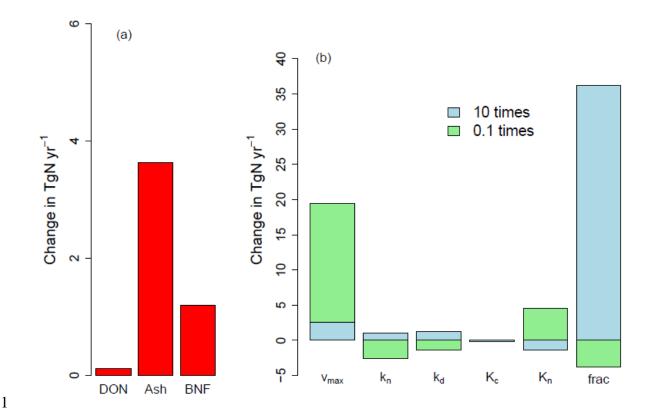


Figure 7. Changes in simulated global average N_2O (1950-2005) emissions from modifying general N cycling processes (a) and model parameters one-at-a-time (b). Altered processes include disallowing N losses through dissolved organic matter (DON in (a)) and fire volatilization (Ash in (a)), and replacing simulated biological N fixation with preindustrial N fixation rate (BNF in (a)). Parameters include: v_{max} , the maximum active N uptake rate per unit root biomass; k_n , the optimum nitrification rate; k_d , the optimum denitrification rate; k_c and k_n , the half saturation constants for labile C availability and nitrate respectively; and frac is the fraction of net nitrification lost as N_2O . Parameters are either increased by multiplying 10 (lightblue) or reduced by multiplying 0.1 (lightgreen) relative to the defaults.

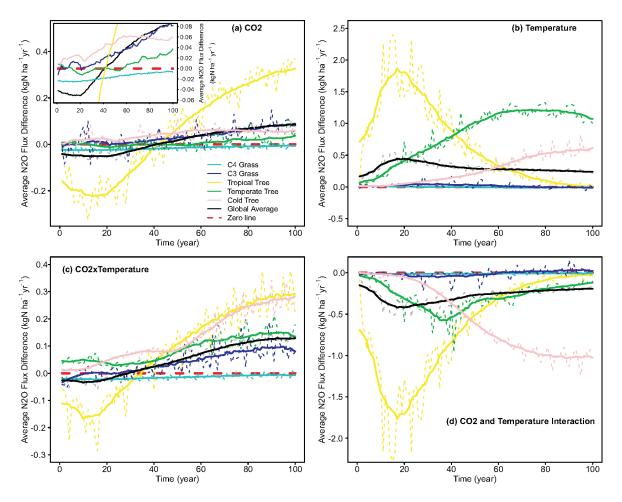


Figure 8. Soil N₂O emissions in response to step increases in atmospheric CO₂ and temperature. Panel (a) is the response to CO₂ fertilization alone, expressed as the difference between CO₂ increased run and the control run (CO2_FERT - CONTROL), the inset zooms into the y axis (flux difference) around zero; Panel (b) is the response to temperature increase alone (TEMP-CONTROL); Panel (c) is the combined response to both CO₂ enrichment and temperature rise (CO2_FERT*TEMP-CONTROL); and Panel (d) is the interactive effect of CO₂ and temperature responses, which is the difference between the combined (results from Panel (c)) and minus the individual responses (results from Panel (a) and (b)). Results are shown as annual values (thin dashed lines) and as running average with a moving window of 17 years (period of recycled climate forcing, thick solid lines)—1. The black lines represent the global average response. Coloured lines indicate responses for biome as represented by each plant functional type (PFT) considered in LM3V-N: C4 grass (cyan), C3 grass (blue), tropical forest (yellow), temperate deciduous forest (green) and cold evergreen forest (pink). Dashed red line represents the zero line.

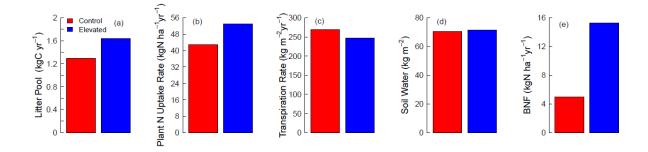


Figure 9. CO₂ fertilization effects (no temperature change) on litter pool size (Panel (a)), plant nitrogen uptake rate (Panel (b)), canopy transpiration rate (Panel (c)), soil water content in the root zone (Panel (d)) and biological nitrogen fixation (BNF) rate (Panel (e)). Shown are the 100-year average of global means (spatial) for control (284 ppm, red) and with elevated CO₂ (568 ppm, blue).

Table 1 Texture dependent parameter k, which partitions N2O/N2 gas fractions during dentirification, estimated from Del Grosso et al. (2000)

Soil	Coarse	Medium	Fine	Coarse	Coarse/		Coarse/ medium/	Organic
Texture				medium	fine	fine	fine	
k	2	10	22	6	12	16	11	2