# Modeling denitrification: can we report what we don't know?

Balázs Péter Grosz[1], Amanda Matson[2], Klaus Butterbach-Bah[3], Timothy Clough[4], Eric A. Davidson[5], Rene Dechow[6], Stephen DelGrosso[7], Efstathios Diamantopoulos[8], Peter Dörsch[9], Edwin Haas[10], Hongxing He[11], Christopher Vincent Henri[12], Dafeng Hui[13], Kristina Kleineidam[14], David Kraus[15], Matthias Kuhnert[16], Joël Léonard[17], Christoph Mueller[14], Søren O. Petersen[3], Debjani Sihi[18], Iris Vogeler[3], Reinhard Well[19], Jagadeesh Babu Yeluripati[20], Jie Zhang[3], and Clemens Scheer[21]

[1]Thünen Institute of Climate-Smart Agriculture
[2]Wageningen University & Researchne
[3]Aarhus University
[4]Lincoln University
[5]University of Maryland Center for Environmental Science
[6]Thünen Institute
[7]USDA-ARS
[8]University of Copenhagen
[9]Norwegian University of Life Sciences
[10]Institute for Meteorology and Climate Research (IMK-IFU)
[11]McGill University
[12]Geological Survey of Denmark and Greenland
[13]Tennessee State University
[14]Justus-Liebig University Giessen
[15]Institute of Meteorology and Climate Research, Atmospheric Environmental Research, Karlsruhe Research Centre
[16]Aberdeen University
[17]INRAE
[18]Oak Ridge National Laboratory
[19]Thünen-Institute
[20]The James Hutton Institute
[21]IMK-IFU, Karlsruhe Institute of Technology

May 25, 2023

**Abstract**

Biogeochemical models simulate soil nitrogen (N) turnover and are often used to assess N losses through denitrification. Though models simulate a complete N budget, only specific N pools/fluxes (i.e. N2O, NO3-, NH3, NOx) are usually published, because the full budget cannot be validated with measured data. Field studies rarely include full N balances, especially N2 fluxes, which are difficult to quantify. Limiting publication of modeling results based on available field data is a missed opportunity to improve the understanding of modeled processes. We suggest that the modeler community support publication of all simulated N pools and processes in future studies.

**Hosted file**

962971_0_art_file_10972072_rbdwbw.docx available at https://authorea.com/users/620451/articles/644452-modeling-denitrification-can-we-report-what-we-don-t-know

# Modeling denitrification: can we report what we don't know?

**B. Grosz[1], A. Matson[2], K. Butterbach-Bah[3,4], T. Clough[5], E. A. Davidson[6], R. Dechow[1], S. DelGrosso[7], E. Diamantopoulos[8], P. Dörsch[9], E. Haas[3], H. He[10], C. V. Henri[11], D. Hui[12], K. Kleineidam[13,14], D. Kraus[3], M. Kuhnert[15], J. Léonard[16], C. Müller[13,14,17], S. O. Petersen[18], D. Sihi[19], I. Vogeler[18,20], R. Well[1], J. Yeluripati[21], J. Zhang[18], C. Scheer[3]**

[1]Thünen Institute of Climate-Smart Agriculture, Braunschweig, Germany,

[2]Wageningen University & Research, Wageningen, Netherlands,

[3]Institute of Meteorology and Climate Research Atmospheric Environmental Research (IMK-IFU), Karlsruhe Institute of Technology (KIT), Garmisch-Partenkirchen, Germany,

[4]Department of Agroecology - Center for Landscape Research in Sustainable Agricultural Futures - Land-CRAFT, Aarhus University, Aarhus, Denmark,

[5]Department of Soil & Physical Sciences, Lincoln University, Lincoln 7647, Canterbury, New Zealand,

[6]University of Maryland Center for Environmental Science, MD, USA,

[7]Soil Management and Sugar beet Research Unit, USDA-ARS, CO, USA,

[8]Faculty for Biology, Chemistry, and Earth Science, University of Bayreuth, Bayreuth, Germany,

[9]Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Scinces, Ås, Norway,

[10]Department of Geography, McGill University, Quebec, Canada,

[11]Department of Hydrology, Geological Survey of Denmark and Greenland (GEUS), Copenhagen, Denmark,

[12]Department of Biological Sciences, Tennessee State University, Nashville, TN 37209, USA,

[13]Liebig Centre for Agroecology and Climate Impact Research, Justus Liebig University, Germany

[14]Institute of Plant Ecology, Justus Liebig University Giessen, Germany

[15]Institute of Biological and Environmental Sciences, University of Aberdeen, Aberdeen, AB24 3UU, UK,

[16]BioEcoAgro Joint Research Unit, INRAE, Université de Liège, Université de Lille, Université de Picardie Jules Verne, 02000, Barenton-Bugny, France,

[17]School of Biology and Environmental Science, University College Dublin, Ireland,

[18]Department of Agroecology, Aarhus University, Tjele, Denmark,

[19]Department of Environmental Sciences, Emory University, GA, USA,

[20]Grass Forage Science/Organic Agriculture, Christian Albrechts University, 24118 Kiel, Germany,

[21]Information and Computational Sciences Department, The James Hutton Institute, Craigiebuckler, Aberdeen, UK

Corresponding author: Balázs Grosz (balazs.grosz@thuenen.de)

**Key Points:**

- Biogeochemical models simulate soil denitrification through multiple pools/processes, but only incomplete N budgets are reported.
- Missing (unpublished) model outputs are important for model evaluation and benefit model intercomparison and model development.
- The ecosystem N modelers need to support and encourage the publication of all relevant N model outputs for denitrification modeling.

## Abstract

Biogeochemical models simulate soil nitrogen (N) turnover and are often used to assess N losses through denitrification. Though models simulate a complete N budget, only specific N pools/fluxes (i.e. $N_2O$, $NO_3^-$, $NH_3$, NOx) are usually published, because the full budget cannot be validated with measured data. Field studies rarely include full N balances, especially $N_2$ fluxes, which are difficult to quantify. Limiting publication of modeling results based on available field data is a missed opportunity to improve the understanding of modeled processes. We suggest that the modeler community support publication of all simulated N pools and processes in future studies.



## Plain Language Summary

Biogeochemical models calculate the entire N balance to describe soil N turnover, but published results are generally limited to environmentally harmful N losses like $N_2O$ fluxes and $NO_3^-$ leaching. We argue that the publication and presentation of the full N cycle calculated by the model are crucial for model development, quality control, model intercomparison, and generating new hypothesis for empirical field studies. We therefore encourage ecosystem modelers to report all relevant results, even those that cannot be fully validated due to a lack of measurements. We particularly emphasize the importance of denitrification and reporting modeled $N_2$ fluxes.


## 1 The denitrification data deficit

### 1.1 Importance of denitrification ($N_2O$ and $N_2$)

Denitrification is an anaerobic metabolic process for energy production in soils driven by the soil microbial community. It describes the step-wise reduction of nitrate ($NO_3^-$) to nitrite ($NO_2^-$), nitric oxide (NO), nitrous oxide ($N_2O$), and finally, dinitrogen ($N_2$) as the end product (Groffman et al., 2009; Nömmik, 1956). Although our knowledge and understanding of denitrification in terrestrial ecosystems has increased in recent decades (Galloway et al., 2004; Singh et al., 2011; Zaehle, 2013), we still have limited knowledge of the complex interaction of the many controlling factors, especially with respect to $N_2$ production.

Denitrification is a key N transformation process in soil, with both positive and negative consequences. On the one hand, it is a source of $N_2O$, a strong greenhouse gas, and reactant in the destruction of stratospheric ozone (Canadell et al., 2021; Ravishankara et al., 2009; Robertson, 2000) and reduces ecosystem N availability and N use efficiency of agricultural crops. On the other hand, complete reduction to $N_2$ is a sink for $N_2O$, and N loss via this pathway decreases the possibility of $NO_3^-$ leaching, returning N to the atmosphere and closing the N cycle (Davidson & Seitzinger, 2006). Globally, denitrification rates are associated with large uncertainties, estimated to be in the range of 109-573 Tg $yr^{-1}$ (Groffman et al., 2006; Scheer et al., 2020; Schlesinger, 2009). The lack of data on total denitrification has long been recognized as one of the reasons that N balances can seldom be closed at the plot scale (Allison, 1955). Given the importance of this for the N balance of terrestrial ecosystems, it is vital that we reduce uncertainty through a better understanding of the denitrification process.

The $N_2O$ fluxes of agricultural soils are well documented and regularly measured, with intensive worldwide measurement campaigns over the last 20-30 years (Bouwman et al., 2002; Reay et al., 2012; Stehfest & Bouwman, 2006). These studies show that $N_2O$ emissions are event driven, with high variability both spatially and temporally, responding nonlinearly to environmental parameters, e.g., temperature, oxygen ($O_2$), organic carbon (SOC), pH, freeze/thaw, and $NO_3^-$ availability (Davidson & Swank, 1986; Firestone et al., 1979; Groffman et al., 2009; Mørkved et al., 2006; Nömmik, 1956; Thomas et al., 1994; Wagner-Riddle et al., 2017; Weier et al., 1993). This level of complexity is challenging to model. Laboratory studies under controlled conditions help to isolate the effects of specific controlling factors (Grosz et al., 2021; Müller & Clough, 2014; Weier et al., 1993), with both field and laboratory measurements being used to refine biogeochemical models to calculate $N_2O$ flux under differing conditions (Deng et al., 2016; Hergoualc'h et al., 2021). Much effort has been made to monitor, understand, and model $N_2O$ emissions, but $N_2O$ is neither the final product, nor in many cases the main product, of denitrification (Scheer et al., 2020). The end product of denitrification is $N_2$. Unlike $N_2O$ fluxes, measuring $N_2$ fluxes from the soil is fraught with difficulties due to the relatively small production from denitrification compared to the high atmospheric background. While several methods exist for measuring $N_2$ fluxes, each has its own shortcomings, and there is no simple field-appropriate method (Friedl et al., 2020). Therefore, very few *in-situ* measurements of $N_2$ fluxes are available (Buchen et al., 2016; Ding et al., 2022; Liu et al., 2022; Scheer et al., 2020; Sgouridis et al., 2016; Zistl-Schlingmann et al., 2019).

### 1.2 Considering $N_2$ fluxes in models

Models are tested and calibrated using measured data, so access to measured $N_2$ fluxes is important for model developers. But those data are simply not yet available in sufficient quantity. Biogeochemical models have nevertheless been developed for describing the N cycle of agricultural soils and predicting $N_2O$ and $N_2$ emissions (Del Grosso et al., 2000; Li et al., 1992; Nylinder et al., 2011; Parton et al., 1996; Sihi et al., 2020). Some models (Del Grosso et al., 2000; Parton et al., 1996) have been partly parameterized with data that are no longer considered reliable (e.g., $N_2$ loss estimation on basis of the acetylene inhibition technique (Weier et al., 1993)) and other model calibrations are simply incomplete.

Given the lack of data to generate empirical models, approaches to describe the production and transport of $N_2$ are mostly process-oriented. Denitrification models are highly diverse with regard to their complexity, but the sensitivity of both $N_2$ and $N_2O$ to controlling factors (e.g. temperature, $pO_2$, SOC, pH, freeze/thaw and $NO_3^-$ availability) is commonly constrained solely based on $N_2O$ data (Grosz et al., 2021; Zhang et al., 2022). Yet it is notable that even given the extensive $N_2O$ data available, no statistical or process-based model has been found that can consistently and satisfactorily predict daily $N_2O$ emissions. Some models can simulate the cumulative annual emissions, but these approaches often fail to capture the timing and magnitude of observed emission peaks (Frolking et al., 1998). The inaccuracy of predicted daily $N_2O$ fluxes by biogeochemical models is a well-known problem (Butterbach-Bahl et al., 2013; Zimmermann et al., 2018), and partly due to the incomplete understanding of the $N_2/N_2O$ product ratio of denitrification.

Since the calibration data and approaches of different models vary, they may produce contrasting results regarding $N_2$ emissions, while still creating similar $N_2O$ emissions. Grosz et al. (2021) compared measured $N_2$ and $N_2O$ emissions from a laboratory experiment with modeled results from the process-based models DNDC and DeNi. It is important to note that the models were not calibrated and DNDC – without the possibility to manipulate the source code –

is not ideal for modeling laboratory experiments. Nevertheless, as shown in Table 1, the modeled $N_2O$ fluxes from both models were acceptable, with DNDC producing results of the same magnitude as measured fluxes, while DeNi produced fluxes four times higher, but not implausible. In contrast, the modeled $N_2$ fluxes by DNDC were almost 3000 times smaller than the measured data, while those from DeNi were overestimated by a factor of more than 100. While model calibration would clearly have improved those results, this example shows that the additional $N_2$ flux information is critical for understanding model outputs and identifying implausible model estimates of denitrification.

**Table 1.** The measured (laboratory experiment with $^{15}N$ labeling) and modeled (DNDC and DeNi) average, cumulative $N_2$, $N_2O$ fluxes (g N $ha^{-1}$), for arable sandy soil from Fuhrberg, Germany (Grosz et al., 2021).

| | **Measured** | **DNDC** | **DeNi** |
|---|---|---|---|
| **$N_2$ [g N $ha^{-1}$]** | 56.63 | 0.019 | 7067 |
| **$N_2O$ [g N $ha^{-1}$]** | 638.5 | 345.4 | 2460 |

Unfortunately, although many models estimate $N_2$ fluxes, there are only a few publications presenting modeled $N_2$ flux results (Del Grosso et al., 2000; Grosz et al., 2021; Leip et al., 2008; Parton et al., 1996). We argue that the publication of total denitrification rates (both $N_2$ and $N_2O$, reported on the same time scale), even if $N_2$ fluxes are not validated, would significantly improve our understanding of different model approaches and aid model development. Models are often used under soil, climate or management conditions that are not fully covered by data sets used for model training and evaluation. Especially in these cases, publishing modeled $N_2$ fluxes would help to assess the quality and improve the comparability of process descriptions. Presenting only one metabolic intermediate of denitrification, namely $N_2O$ flux, while neglecting $N_2$ flux, compromises data reliability. Moreover, in the future, as more measured $N_2$ and $N_2O$ fluxes from field experiments become available, already published simulations of $N_2$ fluxes will facilitate the uptake and incorporation of new insights.

## 2 Additional uncertainties in denitrification modeling

### 2.1 Unknown N-balances

The inaccuracy of predicted daily $N_2O$ fluxes by biogeochemical models (Butterbach-Bahl et al., 2013; Zimmermann et al., 2018) is not only due to uncertainties in $N_2$ fluxes, but also due to a lack of comprehensive understanding of other processes within the N cycle. $N_2O$ fluxes are an integral part of the N cycle, but only represent 0.1-3.1% of N losses during ecosystem N cycling (Bolan et al., 2004; Bouwman, 1996; Bouwman et al., 1993; Bremner, 1997; Cameron et al., 2013; Clough et al., 2005; de Klein et al., 2001; Firestone, 1982; Freney, 1997; Haynes & Sherlock, 1986; Mosier et al., 1998; Saggar et al., 2009; Thomson et al., 2012). Therefore, they are highly sensitive to other components of the N cycle, including N pools ($NH_4^+$, $NO_3^-$ or organic N), plant and microbial N immobilization, decomposition, and related N losses like $NH_3$, NOx, and $NO_3^-$ leaching. Without going into extensive detail, we emphasize here the importance of publishing the full modeled N balance in denitrification studies.

Publishing modeled N sources for $N_2O$ fluxes provides information on what pathways the model is simulating (e.g., nitrification or denitrification). Under certain environmental conditions, a model may provide accurate $N_2O$ fluxes, even though the underlying processes are incorrect (i.e. be right for the wrong reason); a high degree of equifinality has been shown in previous studies (He et al., 2016). Nitrification is particularly important in this context because in addition to being a source of $N_2O$, it provides substrate ($NO_2^-$ and $NO_3^-$) for denitrification. David et al. (2009) simulated an intensively cropped watershed in Illinois using measured water drainage and $NO_3^-$ concentration and compared denitrification from six different models (David et al., 2009). Most of the models accurately simulated the measured $NO_3^-$ leaching, but the denitrification rates varied widely among the models. This high variation in $NO_3^-$ lost through denitrification would then impact each model's availability of soil $NO_3^-$ for plant and microbial uptake, leaching, and later denitrification. These key difference between models do not become visible without publishing the complete N balance. Finally, having a complete picture of N pools and processes within a model exercise makes it possible to recognize knowledge gaps. In Giltrap et al. (2014), the APSIM and NZ-DNDC models were used for estimating water drainage, $NO_3^-$ leaching, and plant N-uptake from a lysimeter experiment (Giltrap et al., 2014). An important conclusion of their work was that $NO_3^-$ adsorption, a process that was not captured by the models, could influence the whole N-cycle and the calculated N balance.

Unlike $N_2$, there are available methods for the measurement of the other N pools and processes mentioned here. However, given the cost and time that would be necessary to include such a wide array of supporting measurements, few studies (Delon et al., 2017; Janz et al., 2022 are exceptions) can realistically measure all N fluxes in parallel, instead focusing on specific N pools and processes of interest. This makes it difficult to compare different studies and to use them for model calibration and validation. We argue here, as we argued above for $N_2$ fluxes, that publishing unvalidated model output may provide valuable insights into model processes and support the development of models or sub-processes for N cycling.

### 2.2 Additional soil information and sources of uncertainty

Ecosystem N cycling does not exist in isolation. Other factors, such as the soil oxygen availability and distribution (Zhang et al., 2022) and labile organic carbon (Philippot et al., 2007), also affect the success of modeling $N_2O$ and $N_2$ production. For example, whether a model relates transport functions to water-filled pore space or soil gas diffusivity in order to understand and model soil aeration, can have a significant effect on the simulated $N_2O$ and $N_2$ production (Balaine et al., 2013, 2016). Similarly, soil gas diffusivity may be used by the model to predict when $N_2O$ and $N_2$ become entrapped in the soil, rather than released (Clough et al., 2000, 2001; Ding et al., 2022). Studies show that available C can strongly influence losses of N and $N_2O$ emissions (Philippot et al., 2007), but accounting for labile C is still a knowledge gap and needs to be better addressed in denitrification modeling (Grosz et al., 2021). Therefore, reporting both model carbon dioxide ($CO_2$) simulations as well as soil aeration in addition to N cycling simulation results would considerably improve understanding of model outputs.

## 3 Recommendations

Although our main focus here is on the importance of reporting both $N_2$ and $N_2O$ fluxes when modeling denitrification, we argue that including the entire N balance and related parameters should become standard when publishing the results of N model studies. Based on what we outlined above, this would: 1) enhance future model development, 2) allow to assess the robustness of modelled N balances, 3) illustrate the diversity and uncertainty of the different approaches for modeling denitrification processes in soils, and 4) identify data gaps that should be addressed in future studies.

We assume that the scarcity of "complete" (i.e. including $N_2$ fluxes and other N pools/pathways) modeled N balances in the soil denitrification literature stems from the reluctance of the scientific community to support the publication of unvalidated modeled output, especially given that the simulation results of these 'neglected' N pools may be unrealistic. But this self-censorship of authors has resulted in a missed opportunity to share knowledge and improve our understanding of modeled processes. We recommend that future studies exercise transparency in publishing model outputs. We ask authors to focus on the aspects of their model that were of particular interest (i.e. validated model developments), but, while clearly stating which variables were not validated by measurements, to include all related pools and parameters to the fullest extent possible (e.g. all modeled N pools/pathways, soil aeration and $CO_2$ flux). Presenting such results does put additional pressure on the authors, as the presented model outputs have to be sufficiently robust and coherent for publication. However, the publication of the modeled N-balance simulations is crucial for future model development; it would fundamentally improve the robustness of models, speed up fine-tuning and ultimately advance our understanding of the N cycle.

## Acknowledgments

The authors declare no conflicts of interest to this study.

This study is the products of a workshop funded by the Deutsche Forschungsgemeinschaft through the research unit DFG-FOR 2337: Denitrification in Agricultural Soils: Integrated Control and Modelling at Various Scales (DASIM), and by the German Federal Ministry of Education and Research (BMBF) under the "Make our Planet Great Again – German Research Initiative", grant number 306060, implemented by the German Academic Exchange Service (DAAD). This work was supported by the European Union's Horizon 2020 research and innovation programme project VERIFY [grant agreement No 776810]. We would like to thank the contribution of all workshop participants of the II. DASIM Modeler Workshop.

## References

Allison, F. E. (1955). The Enigma of Soil Nitrogen Balance Sheets. In *Advances in Agronomy* (Vol. 7, pp. 213–250). Elsevier. https://doi.org/10.1016/S0065-2113(08)60339-9

Balaine, N., Clough, T. J., Beare, M. H., Thomas, S. M., & Meenken, E. D. (2016). Soil Gas Diffusivity Controls $N_2O$ and $N_2$ Emissions and their Ratio. *Soil Science Society of America Journal*, *80*(3), 529–540. https://doi.org/10.2136/sssaj2015.09.0350

Balaine, N., Clough, T. J., Beare, M. H., Thomas, S. M., Meenken, E. D., & Ross, J. G. (2013). Changes in Relative Gas Diffusivity Explain Soil Nitrous Oxide Flux Dynamics. *Soil Science Society of America Journal*, *77*(5), 1496–1505. https://doi.org/10.2136/sssaj2013.04.0141

Bolan, N. S., Saggar, S., Luo, J., Bhandral, R., & Singh, J. (2004). Gaseous Emissions of Nitrogen from Grazed Pastures: Processes, Measurements and Modelling, Environmental Implications, and Mitigation. In *Advances in Agronomy* (Vol. 84, pp. 37–120). Elsevier. https://doi.org/10.1016/S0065-2113(04)84002-1

Bouwman, A. F. (1996). Direct emission of nitrous oxide from agricultural soils. *Nutrient Cycling in Agroecosystems*, *46*(1), 53–70. https://doi.org/10.1007/BF00210224

Bouwman, A. F., Boumans, L. J. M., & Batjes, N. H. (2002). Emissions of $N_2O$ and NO from fertilized fields: Summary of available measurement data: Summary of NO and $N_2O$ measurement data. *Global Biogeochemical Cycles*, *16*(4), 6-1-6–13. https://doi.org/10.1029/2001GB001811

Bouwman, A. F., Fung, I., Matthews, E., & John, J. (1993). Global analysis of the potential for $N_2O$ production in natural soils. *Global Biogeochemical Cycles*, *7*(3), 557–597. https://doi.org/10.1029/93GB01186

Bremner, J. M. (1997). Sources of nitrous oxide in soils. *Nutrient Cycling in Agroecosystems*, *49*(1/3), 7–16. https://doi.org/10.1023/A:1009798022569

Buchen, C., Lewicka-Szczebak, D., Fuß, R., Helfrich, M., Flessa, H., & Well, R. (2016). Fluxes of $N_2$ and $N_2O$ and contributing processes in summer after grassland renewal and grassland conversion to maize cropping on a Plaggic Anthrosol and a Histic Gleysol. *Soil Biology and Biochemistry*, *101*, 6–19. https://doi.org/10.1016/j.soilbio.2016.06.028

Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., & Zechmeister-Boltenstern, S. (2013). Nitrous oxide emissions from soils: How well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society B: Biological Sciences*, *368*(1621), 20130122. https://doi.org/10.1098/rstb.2013.0122

Cameron, K. C., Di, H. J., & Moir, J. L. (2013). Nitrogen losses from the soil/plant system: A review: Nitrogen losses. *Annals of Applied Biology*, *162*(2), 145–173. https://doi.org/10.1111/aab.12014

Canadell, J. G., Monteiro, P. M. S., Costa, M. H., Cotrim da Cunha, L., Cox, P. M., Eliseev, A. V., Henson, S., Ishii, M., Jaccard, S., Koven, C., Lohila, A., Patra, P. K., Piao, S., Rogelj, J., Syampungani, S., Zaehle, S., & Zickfeld, K. (2021). Global Carbon and other Biogeochemical Cycles and Feedbacks. In V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B. R. Matthews, T. K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, & B. Zhou (Eds.), *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change* (pp. 673–816). Cambridge University Press. https://doi.org/10.1017/9781009157896.007

Clough, T. J., Sherlock, R. R., & Cameron, K. C. (2000). Entrapment and displacement of nitrous oxide in a drained pasture soil. *Nutrient Cycling in Agroecosystems*, *57*(2), 191–193. https://doi.org/10.1023/A:1009891717386

Clough, T. J., Sherlock, R. R., Cameron, K. C., Stevens, R. J., Laughlin, R. J., & Müller, C. (2001). Resolution of the $^{15}N$ balance enigma? *Soil Research*, *39*(6), 1419. https://doi.org/10.1071/SR00092

Clough, T. J., Sherlock, R. R., & Rolston, D. E. (2005). A Review of the Movement and Fate of $N_2O$ in the Subsoil. *Nutrient Cycling in Agroecosystems*, *72*(1), 3–11. https://doi.org/10.1007/s10705-004-7349-z

David, M. B., Del Grosso, S. J., Hu, X., Marshall, E. P., McIsaac, G. F., Parton, W. J., Tonitto, C., & Youssef, M. A. (2009). Modeling denitrification in a tile-drained, corn and soybean agroecosystem of Illinois, USA. *Biogeochemistry*, *93*(1–2), 7–30. https://doi.org/10.1007/s10533-008-9273-9

Davidson, E. A., & Seitzinger, S. (2006). The enigma of progress in denitrification research. *Ecological Applications*, *16*(6), 2057–2063. https://doi.org/10.1890/1051-0761(2006)016[2057:TEOPID]2.0.CO;2

Davidson, E. A., & Swank, W. T. (1986). Environmental Parameters Regulating Gaseous Nitrogen Losses from Two Forested Ecosystems via Nitrification and Denitrification. *Applied and Environmental Microbiology*, *52*(6), 1287–1292. https://doi.org/10.1128/aem.52.6.1287-1292.1986

de Klein, C. A. M., Sherlock, R. R., Cameron, K. C., & van der Weerden, T. J. (2001). Nitrous oxide emissions from agricultural soils in New Zealand—A review of current knowledge and directions for future research. *Journal of the Royal Society of New Zealand*, *31*(3), 543–574. https://doi.org/10.1080/03014223.2001.9517667

Del Grosso, S. J., Parton, W. J., Mosier, A. R., Ojima, D. S., Kulmala, A. E., & Phongpan, S. (2000). General model for $N_2O$ and $N_2$ gas emissions from soils due to dentrification. *Global Biogeochemical Cycles*, *14*(4), 1045–1060. https://doi.org/10.1029/1999GB001225

Delon, C., Galy-Lacaux, C., Serça, D., Loubet, B., Camara, N., Gardrat, E., Saneh, I., Fensholt, R., Tagesson, T., Le Dantec, V., Sambou, B., Diop, C., & Mougin, E. (2017). Soil and vegetation-atmosphere exchange of NO, $NH_3$ , and $N_2O$ from field measurements in a semi arid grazed ecosystem in Senegal. *Atmospheric Environment*, *156*, 36–51. https://doi.org/10.1016/j.atmosenv.2017.02.024

Deng, Q., Hui, D., Wang, J., Yu, C.-L., Li, C., Reddy, K. C., & Dennis, S. (2016). Assessing the impacts of tillage and fertilization management on nitrous oxide emissions in a cornfield using the DNDC model: Modeling $N_2O$ emission in a cornfiled. *Journal of Geophysical Research: Biogeosciences*, *121*(2), 337–349. https://doi.org/10.1002/2015JG003239

Ding, K., Luo, J., Clough, T. J., Ledgard, S., Lindsey, S., & Di, H. J. (2022). In situ nitrous oxide and dinitrogen fluxes from a grazed pasture soil following cow urine application at two nitrogen rates. *Science of The Total Environment*, *838*, 156473. https://doi.org/10.1016/j.scitotenv.2022.156473

Firestone, M. K. (1982). Biological Denitrification. In F. J. Stevenson (Ed.), *Nitrogen in Agricultural Soils* (Vol. 1–22, pp. 289–326). American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. https://doi.org/10.2134/agronmonogr22.c8

Firestone, M. K., Smith, M. S., Firestone, R. B., & Tiedje, J. M. (1979). The Influence of Nitrate, Nitrite, and Oxygen on the Composition of the Gaseous Products of Denitrification in Soil. *Soil Science Society of America Journal*, *43*(6), 1140–1144. https://doi.org/10.2136/sssaj1979.03615995004300060016x

Freney, J. R. (1997). Emission of nitrous oxide from soils used for agriculture. *Nutrient Cycling in Agroecosystems*, *49*(1/3), 1–6. https://doi.org/10.1023/A:1009702832489

Friedl, J., Cardenas, L. M., Clough, T. J., Dannenmann, M., Hu, C., & Scheer, C. (2020). Measuring denitrification and the $N_2O$:($N_2O$ + $N_2$) emission ratio from terrestrial soils. *Current Opinion in Environmental Sustainability*, *47*, 61–71. https://doi.org/10.1016/j.cosust.2020.08.006

Frolking, S. E., Mosier, A. R., Ojima, D. S., Li, C., Parton, W. J., Potter, C. S., Priesack, E., Stenger, R., Haberbosch, C., Dörsch, P., Flessa, H., & Smith, K. A. (1998). Comparison of $N_2O$ emissions from soils at three temperate agricultural sites: Simulations of year-round measurements by four models. *Nutrient Cycling in Agroecosystems*, *52*(2/3), 77–105. https://doi.org/10.1023/A:1009780109748

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., & Vörösmarty, C. J. (2004). Nitrogen Cycles: Past, Present, and Future. *Biogeochemistry*, *70*(2), 153–226. https://doi.org/10.1007/s10533-004-0370-0

Giltrap, D. L., Cichota, R., Vogeler, I., & Shepherd, M. (2014). Comparison of APSIM and NZ-DNDC models with plant n uptake and water and nitrate leaching data. *In: Nutrient Management for the Farm, Catchment and Community. (Eds L.D. Currie and C L. Christensen).* Occasional Report No. 27., Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. http://tur-www1.massey.ac.nz/~flrc/workshops/14/Manuscripts/Paper_Giltrap_2014.pdf

Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone, M. K., Giblin, A. E., Kana, T. M., Nielsen, L. P., & Voytek, M. A. (2006). Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecological Applications*, *16*(6), 2091–2122. https://doi.org/10.1890/1051-0761(2006)016[2091:MFMDDA]2.0.CO;2

Groffman, P. M., Butterbach-Bahl, K., Fulweiler, R. W., Gold, A. J., Morse, J. L., Stander, E. K., Tague, C., Tonitto, C., & Vidon, P. (2009). Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry*, *93*(1–2), 49–77. https://doi.org/10.1007/s10533-008-9277-5

Grosz, B., Well, R., Dechow, R., Köster, J. R., Khalil, M. I., Merl, S., Rode, A., Ziehmer, B., Matson, A., & He, H. (2021). Evaluation of denitrification and decomposition from three biogeochemical models using laboratory measurements of $N_2$, $N_2O$ and $CO_2$. *Biogeosciences*, *18*(20), 5681–5697. https://doi.org/10.5194/bg-18-5681-2021

Haynes, R. J., & Sherlock, R. R. (1986). Gaseous losses of nitrogen. In R. J. Haynes (Ed.), *Mineral nitrogen in the plant-soil system*. Academic press.

He, H., Jansson, P.-E., Svensson, M., Meyer, A., Klemedtsson, L., & Kasimir, Å. (2016). Factors controlling Nitrous Oxide emission from a spruce forest ecosystem on drained organic soil, derived using the CoupModel. *Ecological Modelling*, *321*, 46–63. https://doi.org/10.1016/j.ecolmodel.2015.10.030

Hergoualc'h, K., Mueller, N., Bernoux, M., Kasimir, Ä., Weerden, T. J., & Ogle, S. M. (2021). Improved accuracy and reduced uncertainty in greenhouse gas inventories by refining the IPCC emission factor for direct $N_2O$ emissions from nitrogen inputs to managed soils. *Global Change Biology*, *27*(24), 6536–6550. https://doi.org/10.1111/gcb.15884

Janz, B., Havermann, F., Lashermes, G., Zuazo, P., Engelsberger, F., Torabi, S. M., & Butterbach-Bahl, K. (2022). Effects of crop residue incorporation and properties on combined soil gaseous $N_2O$, NO, and $NH_3$ emissions—A laboratory-based measurement approach. *Science of The Total Environment*, *807*, 151051. https://doi.org/10.1016/j.scitotenv.2021.151051

Leip, A., Marchi, G., Koeble, R., Kempen, M., Britz, W., & Li, C. (2008). Linking an economic model for European agriculture with a mechanistic model to estimate nitrogen and carbon losses from arable soils in Europe. *Biogeosciences*, *5*(1), 73–94. https://doi.org/10.5194/bg-5-73-2008

Li, C., Frolking, S., & Frolking, T. A. (1992). A model of nitrous oxide evolution from soil driven by rainfall events: 2. Model applications. *Journal of Geophysical Research: Atmospheres*, *97*(D9), 9777–9783. https://doi.org/10.1029/92JD00510

Liu, Y., Wang, R., Pan, Z., Zheng, X., Wei, H., Zhang, H., Mei, B., Quan, Z., Fang, Y., & Ju, X. (2022). Quantifying in situ $N_2$ fluxes from an intensively managed calcareous soil using the $^{15}N$ gas-flux method. *Journal of Integrative Agriculture*, *21*(9), 2750–2766. https://doi.org/10.1016/j.jia.2022.07.016

Mørkved, P. T., Dörsch, P., Henriksen, T. M., & Bakken, L. R. (2006). $N_2O$ emissions and product ratios of nitrification and denitrification as affected by freezing and thawing. *Soil Biology and Biochemistry*, *38*(12), 3411–3420. https://doi.org/10.1016/j.soilbio.2006.05.015

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., & van Cleemput, O. (1998). Closing the global $N_2O$ budget: Nitrous oxide emissions through the agricultural nitrogen cycle: OECD/IPCC/IEA phase II development of IPCC guidelines for national greenhouse gas inventory methodology. *Nutrient Cycling in Agroecosystems*, *52*(2/3), 225–248. https://doi.org/10.1023/A:1009740530221

Müller, C., & Clough, T. J. (2014). Advances in understanding nitrogen flows and transformations: Gaps and research pathways. *The Journal of Agricultural Science*, *152*(S1), 34–44. https://doi.org/10.1017/S0021859613000610

Nömmik, H. (1956). Investigations on Denitrification in Soil. *Acta Agriculturae Scandinavica*, *6*(2), 195–228. https://doi.org/10.1080/00015125609433269

Nylinder, J., Stenberg, M., Jansson, P.-E., Klemedtsson, Å. K., Weslien, P., & Klemedtsson, L. (2011). Modelling uncertainty for nitrate leaching and nitrous oxide emissions based on a Swedish field experiment with organic crop rotation. *Agriculture, Ecosystems & Environment*, *141*(1), 167–183. https://doi.org/10.1016/j.agee.2011.02.027

Parton, W. J., Mosier, A. R., Ojima, D. S., Valentine, D. W., Schimel, D. S., Weier, K., & Kulmala, A. E. (1996). Generalized model for $N_2$ and $N_2O$ production from nitrification and denitrification. *Global Biogeochemical Cycles*, *10*(3), 401–412. https://doi.org/10.1029/96GB01455

Philippot, L., Hallin, S., & Schloter, M. (2007). *Ecology of Denitrifying Prokaryotes in Agricultural Soil*. 249–305. https://doi.org/10.1016/S0065-2113(07)96003-4

Ravishankara, A. R., Daniel, J. S., & Portmann, R. W. (2009). Nitrous Oxide ($N_2O$): The Dominant Ozone-Depleting Substance Emitted in the 21st Century. *Science*, *326*(5949), 123–125. https://doi.org/10.1126/science.1176985

Reay, D. S., Davidson, E. A., Smith, K. A., Smith, P., Melillo, J. M., Dentener, F., & Crutzen, P. J. (2012). Global agriculture and nitrous oxide emissions. *Nature Climate Change*, *2*(6), 410–416. https://doi.org/10.1038/nclimate1458

Robertson, G. P. (2000). Denitrification. In M. E. Sumner (Ed.), *Handbook of Soil Science* (pp. 181–190). CRC Press.

Saggar, S., Luo, J., Giltrap, D., & Maddena, M. (2009). Nitrous oxide emissions from temperate grasslands: Processes, measurements, modeling and mitigation. In A. I. Sheldon & E. P. Barnhart (Eds.), *Nitrous Oxide Emissions Research Progress* (pp. 1–66). Nova Science Publishers Inc.

Scheer, C., Fuchs, K., Pelster, D. E., & Butterbach-Bahl, K. (2020). Estimating global terrestrial denitrification from measured $N_2O$:($N_2O$ + $N_2$) product ratios. *Current Opinion in Environmental Sustainability*, *47*, 72–80. https://doi.org/10.1016/j.cosust.2020.07.005

Schlesinger, W. H. (2009). On the fate of anthropogenic nitrogen. *Proceedings of the National Academy of Sciences*, *106*(1), 203–208. https://doi.org/10.1073/pnas.0810193105

Sgouridis, F., Stott, A., & Ullah, S. (2016). Application of the $^{15}N$ gas-flux method for measuring in situ $N_2$ and $N_2O$ fluxes due to denitrification in natural and semi-natural terrestrial ecosystems and comparison with the acetylene inhibition technique. *Biogeosciences*, *13*(6), 1821–1835. https://doi.org/10.5194/bg-13-1821-2016

Sihi, D., Davidson, E. A., Savage, K. E., & Liang, D. (2020). Simultaneous numerical representation of soil microsite production and consumption of carbon dioxide, methane, and nitrous oxide using probability distribution functions. *Global Change Biology*, *26*(1), 200–218. https://doi.org/10.1111/gcb.14855

Singh, N., Pal, N., Mahajan, G., Singh, S., & Shevkani, K. (2011). Rice grain and starch properties: Effects of nitrogen fertilizer application. *Carbohydrate Polymers*, *86*(1), 219–225. https://doi.org/10.1016/j.carbpol.2011.04.039

Stehfest, E., & Bouwman, L. (2006). $N_2O$ and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. *Nutrient Cycling in Agroecosystems*, *74*(3), 207–228. https://doi.org/10.1007/s10705-006-9000-7

Thomas, K. L., Lloyd, D., & Boddy, L. (1994). Effects of oxygen, pH and nitrate concentration on denitrification by *Pseudomonas* species. *FEMS Microbiology Letters*, *118*(1–2), 181–186. https://doi.org/10.1111/j.1574-6968.1994.tb06823.x

Thomson, A. J., Giannopoulos, G., Pretty, J., Baggs, E. M., & Richardson, D. J. (2012). Biological sources and sinks of nitrous oxide and strategies to mitigate emissions. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *367*(1593), 1157–1168. https://doi.org/10.1098/rstb.2011.0415

Wagner-Riddle, C., Congreves, K. A., Abalos, D., Berg, A. A., Brown, S. E., Ambadan, J. T., Gao, X., & Tenuta, M. (2017). Globally important nitrous oxide emissions from croplands induced by freeze–thaw cycles. *Nature Geoscience*, *10*(4), 279–283. https://doi.org/10.1038/ngeo2907

Weier, K. L., Doran, J. W., Power, J. F., & Walters, D. T. (1993). Denitrification and the Dinitrogen/Nitrous Oxide Ratio as Affected by Soil Water, Available Carbon, and Nitrate. *Soil Science Society of America Journal*, *57*(1), 66–72. https://doi.org/10.2136/sssaj1993.03615995005700010013x

Zaehle, S. (2013). Terrestrial nitrogen–carbon cycle interactions at the global scale. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *368*(1621), 20130125. https://doi.org/10.1098/rstb.2013.0125

Zhang, J., Zhang, W., Jansson, P.-E., & Petersen, S. O. (2022). Modeling nitrous oxide emissions from agricultural soil incubation experiments using CoupModel. *Biogeosciences*, *19*(19), 4811–4832. https://doi.org/10.5194/bg-19-4811-2022

Zimmermann, J., Carolan, R., Forrestal, P., Harty, M., Lanigan, G., Richards, K. G., Roche, L., Whitfield, M. G., & Jones, M. B. (2018). Assessing the performance of three frequently used biogeochemical models when simulating $N_2O$ emissions from a range of soil types and fertiliser treatments. *Geoderma*, *331*, 53–69. https://doi.org/10.1016/j.geoderma.2018.06.004

Zistl-Schlingmann, M., Feng, J., Kiese, R., Stephan, R., Zuazo, P., Willibald, G., Wang, C., Butterbach-Bahl, K., & Dannenmann, M. (2019). Dinitrogen emissions: An overlooked key component of the N balance of montane grasslands. *Biogeochemistry*, *143*(1), 15–30. https://doi.org/10.1007/s10533-019-00547-8