

Approaches and concepts of modelling denitrification: increased process understanding using observational data can reduce uncertainties[☆]

Stephen J Del Grosso¹, Ward Smith², David Kraus³,
Raia S Massad⁴, Iris Vogeler⁵ and Kathrin Fuchs³



Denitrification is a key but poorly quantified component of the N cycle. Because it is difficult to measure the gaseous (NO_x , N_2O , N_2) and soluble (NO_3) components of denitrification with sufficient intensity, models of varying scope and complexity have been developed and applied to estimate how vegetation cover, land management and environmental factors such as soil type and weather interact to control these variables. In this paper we assess the strengths and limitations of different modeling approaches, highlight major uncertainties, and suggest how different observational methods and process-based understanding can be combined to better quantify N cycling. Representation of how biogeochemical (e.g. org. C., pH) and physical (e.g. soil structure) factors influence denitrification rates and product ratios combined with ensemble approaches may increase accuracy without requiring additional site level model inputs.

Addresses

¹ USDA Agricultural Research Service, SMSBRU, Fort Collins, CO, USA

² Ottawa Research and Development Centre, Agriculture and Agri-Food Canada, ON, Canada

³ Karlsruhe Institute of Technology, Garmisch-Partenkirchen, Germany

⁴ Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 78850, Thiverval-Grignon, France

⁵ Aarhus University, Department of Agroecology, Tjele, Denmark

Corresponding author:

Del Grosso, Stephen J (steve.delgrosso@ars.usda.gov)

Current Opinion in Environmental Sustainability 2020, 47:37–45

This review comes from a themed issue on **Climate change, reactive nitrogen, food security and sustainable agriculture**

Edited by **Clemens Scheer**, **David E Pelster** and **Klaus Butterbach-Bahl**

For a complete overview see the [Issue](#) and the [Editorial](#)

Available online 12th August 2020

Received: 22 March 2020; Accepted: 16 July 2020

<https://doi.org/10.1016/j.cosust.2020.07.003>

1877-3435/© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

Denitrification partially closes the global nitrogen (N) cycle because it converts different species of biologically reactive N (Nr) to inert N_2 . In contrast to the amount of anthropogenic N_2 fixation to Nr which is fairly well constrained, the amount of Nr transformed back to N_2 by denitrification is more uncertain [1^{*}]. However, it is clear that since approximately 1970 the amount of N_2 returned to the atmosphere is less than the amount fixed because reactive forms of N are accumulating in the Earth's atmosphere, soils, and aquatic systems [2]. It is challenging to quantify denitrification rates because the reactants and products involved are difficult to measure and are influenced by other biogeochemical processes. Anthropogenically fixed Nr added to terrestrial systems from industrial N_2 fixation (mostly for fertilizer) and microbial N_2 fixation (mostly by legume cropping), currently exceeds natural N fixation [3]. As this Nr cascades through ecosystems it is transformed to various organic, soluble and gaseous components that contribute to air and water pollution, as well as global warming and stratospheric ozone depletion [3,4]. Initial fixation produces reduced N compounds, mainly ammonia (NH_3), which undergo various oxidation reactions. One of these, nitrification, results in formation of water-soluble nitrate (NO_3), which is a primary source of N for plants as well as the substrate for denitrification.

Denitrification is influenced directly and indirectly by various processes. A combination of observational and modeling approaches is used to quantify the rates of these processes and how much of the different species of Nr reside in various pools. For example, mineral and organic forms of Nr are routinely measured from soil and water samples extracted from research plots, particularly in agricultural systems because this informs N availability to plants and helps determine the amount of fertilizer and legume N recommended to optimize crop and forage production. Similarly, gaseous emissions of ammonia (NH_3) and N oxides (NO_x , N_2O) are occasionally measured for agricultural soils and livestock production systems. But because measurements provide only a snapshot

[☆] OECD Disclaimer: The opinions expressed and arguments employed in this publication are the sole responsibility of the authors and do not necessarily reflect those of the OECD or of the governments of its Member countries.

of limited spatial and temporal extent and often entail some degree of plant/soil system disturbance, modeling approaches are needed to more completely quantify the rates of processes responsible for N transformations and the quantities of reactants and products involved in these transformations. In particular, it is difficult and expensive to measure N_2 gas emitted from soils and water bodies due to its high atmospheric background concentration, so models are relied upon almost entirely to estimate these flux rates. Lack of measurements to constrain model derived estimates of this major flux of N lead to high uncertainty. In this paper we describe the major N transformation processes with a focus on denitrification, overview and compare/contrast the different modeling approaches, and suggest research priorities to improve estimates and reduce uncertainties.

Denitrification in context of N cycling

Denitrification is the biochemical reduction of NO_3^- , NO_2^- , NO , N_2O , and N_2 under O_2 limited conditions mostly by heterotrophic microbes [5]. In addition to the amount of NO_3^- in soil, other factors influencing the denitrification rate include water content, labile carbon (C) supply, temperature, gas diffusivity, pH, as well as microbial community structure and gene expression. Denitrification rates tend to be limited in well aerated soils and increase as soils become wetter and as soil gas exchange and O_2 concentration decrease. In addition to water content, bulk soil porosity, pore size distribution, and O_2 demand from auto and heterotrophic respiration influence O_2 supply. As conditions become more anoxic denitrification rates, as well as the portion of N lost as N_2 instead of NO_x or N_2O , tend to increase. For example, flooded rice systems often have high denitrification rates, but relatively low losses of N_2O because pervasive anaerobic conditions in these environments facilitate complete reduction to N_2 [6].

Denitrification is influenced by land management and interreacts with other biochemical processes. In cropped and grazed systems, the majority of external N input originates from synthetic fertilizers containing different formulations of NH_4 and NO_3^- , followed by biological N fixation associated with legume cropping and minor amounts from atmospheric deposition of N oxides, NO_3^- and NH_3/NH_4 . Nitrogen is also recycled internally within plant/soil/livestock systems from urine and dung deposition and decomposition of dead vegetation and soil organic matter which transforms N from organic to mineral forms (N mineralization). This added or recycled N can remain in soil, be taken up by plant roots, transformed by biochemical processes such as nitrification and denitrification, or lost from the system by volatilization, leaching, or erosion. Nitrification is the oxidation of NH_3 or NH_4 to NO_3^- by mainly autotrophic bacteria via the intermediate products NH_2OH and NO_2^- [7]. Although the majority of nitrified N is converted to NO_3^- ,

nitrification leads to substantial gaseous losses of N_2O and NO_x . The NO_3^- resulting from nitrification can be taken up by plants, leached from the system, or provide the substrate for denitrification. Besides ammonia oxidizing nitrification other processes such as heterotrophic nitrification [8], anaerobic ammonium oxidation [9], nitrifier denitrification [10] and dissimilatory nitrate reduction to ammonium [11] affect the reactants and products of denitrification. How well these interacting land management and biogeochemical processes are represented in ecosystem models limits the probability of denitrification modeling [12].

Compare and contrast different modeling approaches

Models used to quantify N budgets and cycling range from simple empirical equations to complex simulation models. In the context of greenhouse gas (GHG) inventories [13] partitions methods into three categories: Tier 1 emission factors based on analysis of global data sets, Tier 2 factors based on regional data, and Tier 3 methods which include use of process-based models. For example, the IPCC Tier 1 factor for direct soil N_2O emission assumes that 1% of N from fertilizer additions and residue inputs is emitted as N_2O . In contrast, simulation models such as DNDC [14], DayCent [15], APSIM [16], and CERES-EGC [17] represent the processes (nitrification, denitrification, plant N uptake, soil water and nutrient movement, etc.) that interact to control N_2O emissions. Tier 1 methods are transparent and easy to apply, but process-based simulation models are typically more accurate than emission factor approaches when compared with site level observations (e.g. Ref. [18]) and estimates using different methods can vary by a factor of 3 or more [19]. However, there is considerable disparity among simulation models regarding the detail in which processes are represented, degree of spatial and temporal resolution, and if processes such as microbial dynamics are implicitly or explicitly represented [20]. The following sections compare and contrast how factors and processes controlling denitrification are represented in some currently available models.

Temporal and spatial scaling

The degree of spatial and temporal resolution among approaches varies widely. At one extreme, Tier 1 emission factor methods assume uniformity in soil properties, weather, vegetation cover, and management at landscape, regional, and greater spatial scales and estimate important denitrification products/reactants (N_2O emissions, NO_3^- leaching) at annual temporal scale. At the other extreme, detailed mechanistic models (e.g. Ref. [21*]) attempt to represent the 3-D soil structure and properties such as pore space and aggregate size distribution at highly resolved (\sim mm) spatial resolution and processes such as microbial activity and O_2 flow at highly resolved (hourly or less) temporal resolution. In the middle, many

widely used models (e.g. APSIM, DayCent) represent soil properties at moderate (e.g. plot/field scale, i.e. m^2 to ha) spatial resolution and processes at daily temporal resolution. Both models and observations are limited because they integrate quantities to discrete spatial and temporal scales that are much less resolved than the scales at which the processes actually occur. Because denitrification rates often respond non-linearly to important drivers and the quantities of reactants and products involved are characterized by high spatial and temporal variability (hot spots/moments), highly resolved models are expected to perform better than more coarse methods. However, limited availability of highly resolved driver data constrains the applicability of models that rely on detailed information regarding soil physical, chemical and biological properties that control denitrification rates.

As an anaerobic process, maximum denitrification rates often occur when soils are at, or close to saturation. However, it is well established that substantial denitrification can occur in soil microsites even when bulk soil is at moderate water content. For example, O_2 concentration tends to be low within aggregate centers due to physical diffusion constraints [22,23]. Anaerobic conditions also occur under surface water films surrounding labile particulate organic matter where high respiration rates can deplete O_2 faster than it can be supplied [24]. These observations suggest that it is insufficient to only include bulk soil anaerobic space, but the distribution of hotspots of microbial activity and anaerobic pockets must be represented as well. Consequently, explicit representation of the soil matrix and how distances between hot spots and air-filled pores regulate activity of aerobic versus anaerobic microbes has been suggested to improve model outcomes [25]. The DNDC model accounts for this to some extent in that aerobic and anaerobic soil volumes are represented, versus DayCent and APSIM only model bulk soil properties. In addition to spatial variability, soil properties such as porosity vary through time, for example, in response to water inputs, but most models assume static soil properties. One exception is that DNDCv.CAN [26^{*}] recalculates soil water holding capacity based on changes in organic matter.

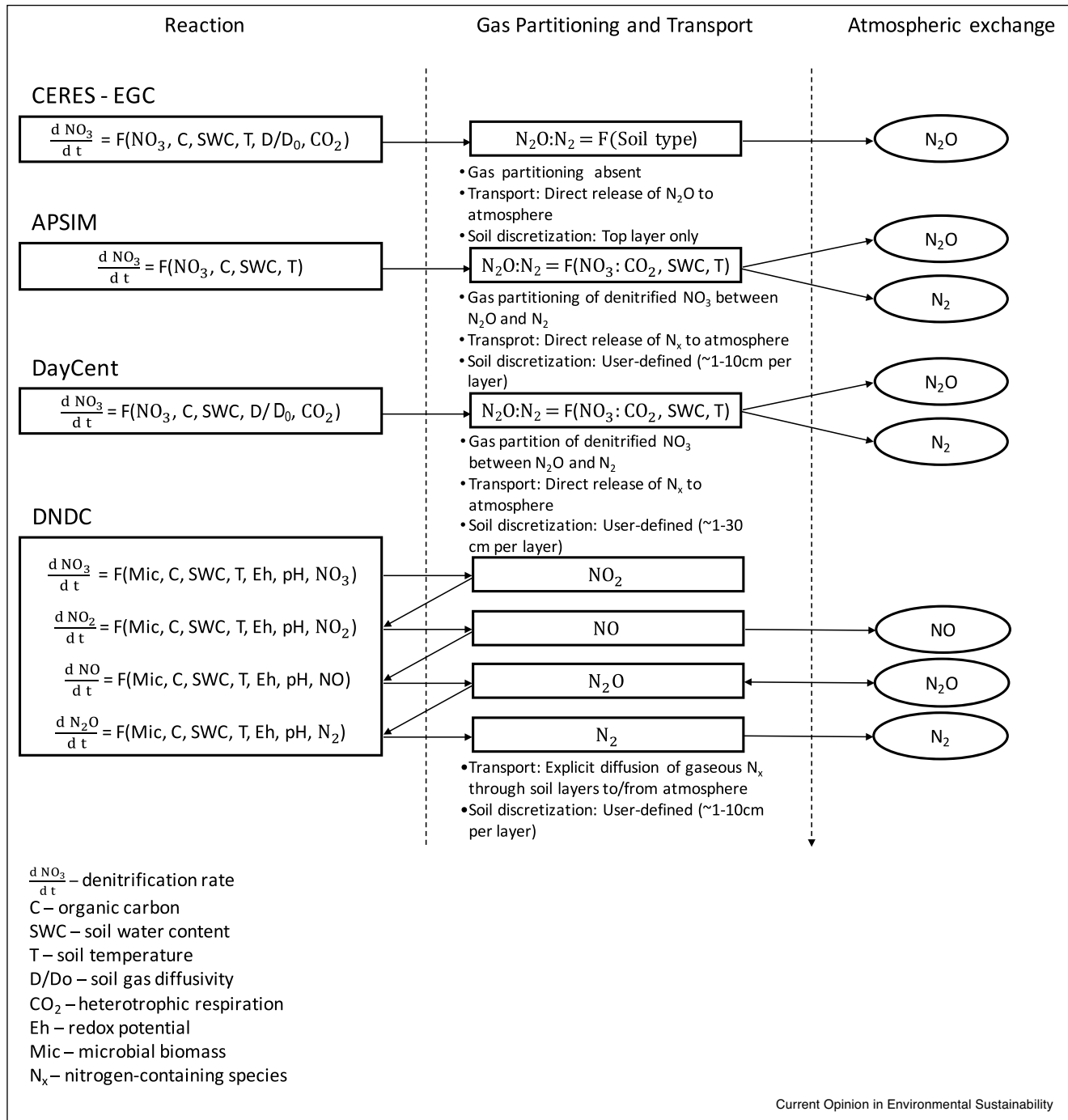
In addition to the direct controls (e.g. current soil NO_3 , labile C and O_2 availability, water content, temperature), hysteresis (legacy effects) can affect hot moments of high denitrification rates [27]. For example, N_2O production has been observed to be higher during drying compared to wetting events at similar water filled pore space implying hysteresis effects [27]. In addition to wet/drying events, spring melting of snowpack/frozen soil in northern regions often leads to pulses of N_2O emissions which are thought to be mainly driven by denitrification. Pulse magnitude is correlated with accumulated winter season freezing degree days [28^{*}] which also implies hysteresis effects. The mechanisms responsible are not entirely

clear but are thought to be related to release of substrates from aggregate destruction during freeze/thaw cycles, impacts on soil gas diffusivity and O_2 availability in pores during freeze-thaw events that influence denitrification rates, and differing temperature sensitivities of the enzymatic processes that control the amounts of N_2 and N_2O gases released during denitrification [27]. Some of these factors (e.g. freeze/thaw impacts on gas diffusion) are represented in some of the field scale models (e.g. Ref. [29,30^{*}]) but not all of them (e.g. aggregate disruption) are. One approach would be to model temporal changes in soil properties such as porosity and aggregate formation/destruction but these dynamics are difficult to represent and are not currently included in any ecosystem models we are aware of. Instead of trying to model all the potential mechanisms, an alternative approach is to account for the effect of cumulative freezing degree days (CFD; [28^{*}]) because this relationship is easy to calculate and avoids the challenge of trying to model short term soil processes such as aggregate dynamics. It is not entirely clear why CFD are correlated with freeze/thaw pulse magnitude, but it is likely that CFD integrates various controls such as the stable but slow mineralization of organic matter that can occur under sustained frozen temperatures [31] as well as the buildup of N_2O entrapped under frozen layers which is suddenly released upon thaw [32].

Microbial community dynamics

The representation of microbial dynamics varies widely among approaches. DayCent [15], CERES-EGC [17] and APSIM [16], for example, do not explicitly represent microbial dynamics, but microbial impacts are implicitly represented in these models by assuming that denitrifier activity is correlated with environmental conditions (e.g. soil NO_3 concentration, water content, and so on, see Figure 1). More complex models such as DNDC [25^{*},33], and ecosys [34], explicitly represent biomass of important microbial functional groups (e.g. facultatively anaerobic denitrifiers, aerobic nitrifiers, anaerobic fermenters, etc.). The degree to which explicit representation of microbial dynamics is needed to produce reliable model estimates of soil N and C flows is debatable with some asserting that explicit representation leads to improved model performance (e.g. Ref. [35]) while others (e.g. Ref. [36^{*}]) emphasize that comparisons with field observations are limited and inconclusive. Incubation studies provide some evidence to support explicit representation, for example, a model that explicitly represents microbial dynamics more accurately represented measured soil organic matter decomposition patterns compared to models that only implicitly include microbes [37]. Similarly, microbial enzyme kinetic models have been shown to represent soil N dynamics very well for incubation (e.g. Ref. [38]) and some field studies (e.g. Ref. [39]). However, there are very few studies that have rigorously compared different classes of models with field

Figure 1



Conceptual representation of denitrification in four widely used ecosystem models. All models use substrate (C and N) and environmental controls to calculate denitrification for different soil depths but vary in level of detail and extent to which processes are implicitly versus explicitly represented. CERES – EGC, APSIM and DayCent calculate only denitrification of NO₃ explicitly. The intermediate products NO₂ and NO are neglected. Denitrification of N₂O is determined by the calculation of N₂O:N₂ ratios. Though denitrification products are directly released to the atmosphere, transport is implicitly accounted for by changing N₂O:N₂ ratios depending on, for example, soil diffusivity. DNDC explicitly calculates denitrification NO₃, NO₂, NO and N₂O. All intermediate products are subject to explicit calculation of soil diffusion and can be subject to different denitrification steps in varying soil depth.

observations of C or N fluxes across sites. In one such study, no conclusions regarding model performance could be affirmed when comparing a suite of models of varying complexity and implicit versus explicit representation of microbes with CO₂ emission and soil organic matter observations from field studies that manipulated soil warming and litter inputs [40]. Explicit representation of microbial dynamics has potential to improve model performance because, for example, microbial diversity is correlated with organic matter mineralization [41] but the accompanying increase in complexity can increase uncertainties in model outputs because microbial related model parameters are usually not well constrained [42^{*}]. Partially because of these reasons, most field and larger scale models do not include microbial community dynamics or gene expressions. However, increasing insights into microbial system dynamics may provide the basis for future considerations [43].

Model selection and complexity

Although defining optimum model complexity remains debatable, some generalities can be drawn. The spatial/temporal resolution of available input data and purpose of model application are primary drivers of model selection. When data are limited or for purposes of national GHG inventories, simple Tier 1 or Tier 2 methods are often acceptable especially if outcomes (e.g. N₂O emissions) are reported at highly aggregated spatial and temporal scales so errors tend to cancel [44]. But for smaller spatial and temporal scales and to accurately estimate mitigation potentials more complex models are needed. Models of intermediate (e.g. DayCent, APSIM, CERES-EGC) or greater (e.g. DNDC) complexity typically match observations of N₂O emissions more closely than simpler emission factor-based methods (e.g. Refs. [18,45]). However, optimal complexity for field level application has not been thoroughly addressed and current evidence is mixed. For example, a comparison of 24 process-based biogeochemical models of varying complexity, most of which represent nitrification and denitrification, with observations of crop or grassland growth and N₂O emissions showed that no single model outperformed the model ensemble [46^{*}]. Highlighting DayCent and DNDC is instructive in this context because the models have virtually identical input requirements but substantially different algorithms. For example, DayCent does not explicitly represent diffusion of gases in soil or the microbial community responsible for denitrification reactions but implicitly accounts for these processes by assuming that diffusivity decreases as water content and field capacity increase and that denitrifier activity is correlated with NO₃ and labile C availability. In contrast, the DNDC model explicitly represents diffusive gas transport as well as separate microbial growth dynamics in aerobic and anaerobic soil compartments. The share between aerobic and anaerobic soil compartments is determined from depth-specific oxygen concentration

depending on respiratory processes. Nr species such as N₂O can be produced in deeper soil layers and further denitrified to N₂ in upper soil layers before they are released to the atmosphere. Despite these clear differences in model complexity, comparisons with field observations of N dynamics are mixed with DayCent performing better in some cases (e.g. Ref. [47] and DNDC better in others (e.g. Ref. [48])).

Models such as DayCent, APSIM and DNDC are 1-D in that lateral flow of water and nutrients are not included. This likely contributes to poor representation of soil water contents in some cases and compromises the ability to address N cycling and NO₃ mitigation. To account for lateral transport processes, biogeochemical models can be externally coupled [49–51] or internally implemented to spatially distributed hydrology models such as SWAT [52]. In the case of DNDCv.CAN [26^{*}], the inclusion of quasi-2D tile flow, revised root density functions and simulation of soil C and N processes to 2 m depth greatly improved the performance of the model for simulating soil water content, and the timing of water and N transport to tile drains. These modifications were responsible for improved simulation of N₂O emissions presumably due to better representation of soil water, C and N dynamics [53].

One constraint on complexity is availability of required model inputs especially at large spatial scales. Most earth system models use simple equations based on soil texture to estimate hydraulic properties and gas diffusion rates. However, soil structure and aggregation also impact flows of water and gases. A simple way to partially account for this is to assume that soil biological activity increases with plant productivity and SOC which improves soil structure and increases hydraulic conductivity [54,55]. In addition, soil structure and aggregate size distribution affect gas diffusion and N₂O emissions tend to increase with aggregate size [56^{*}]. Accounting for impacts of plant growth and SOC on soil aggregation and structure may provide a way to increase complexity and potentially improve model performance without increasing data required for model inputs or calibration because models already simulate plant growth and SOC. For example, Jarecki *et al.* [57] incorporated a pedo-transfer function in DNDCv.CAN to recalculate changes in soil water holding capacities based on changes in SOC, however, the impacts on other soil hydraulic properties and aggregate stability was not considered. In contrast, explicitly accounting for how biological activity and physical/chemical processes affect soil structure, aggregate dynamics and C and N flows likely would require more site level data to inform model inputs.

Research priorities and ways forward

There is opportunity to improve models because not all relevant environmental and biochemical drivers and processes are currently represented in widely used models.

For example, the impacts of soil pH on both denitrification rates and the N_2/N_2O product ratio are well established [58] but are only included in a few models such as DNDC [59] and recently in DayCent [60] and NOE [61]. Some emergent processes such as heterotrophic nitrification, which was observed to be the dominant process resulting in increased N_2O under elevated CO_2 [8], anaerobic ammonium oxidation [9] and dissimilatory nitrate reduction to ammonium [11] could be implemented. The benefits of including additional processes should be compared to the costs of additional complexity and associated model input burdens. In the case of pH, representing these impacts does not necessarily increase the need for additional site level inputs but representing all of the biochemical pathways that contribute to the products and reactants involved in denitrification may entail detailed measurements that are not routinely performed.

More complete exploitation of established and emerging observational data provides further opportunity to inform model selection, optimal complexity, and improvement. Ensemble models have been used more extensively for crop than N_2O and denitrification modeling [62], but recent evaluations suggests that this approach could be promising [12,63] especially when comparing results with global databases derived from rigorous field studies (e.g. Ref. [64]). While the vast majority of field studies reporting N_2O emissions used soil surface based bottom up measurements, N_2O fluxes from tower based top down methods are becoming increasingly available and have the advantage of integrating fluxes over large time scales and spatial scales ranging from field (e.g. Ref. [28*]) to continental scales [65*]. Running models at landscape and larger scales for comparing with top down data relies on availability of spatially and temporally resolved model input databases. Fortunately, land cover, soils, and weather data required for model inputs are available at near complete spatial coverage for countries such as the USA [66], Canada [67] or at the European level [68].

Although extensive N_2O data are valuable for model comparisons, they are limited because other processes such as nitrification directly contribute to observed N_2O fluxes while various Nr transformation indirectly contribute to observed N_2O . Measurements of isotopic composition and intramolecular distribution of ^{15}N in the N_2O molecule can be used to constrain Nr turnover [69]. Recently, Denk *et al.* [70*] developed the stable isotope model SIMONE, which is an offline model that uses predicted process rates (e.g. mineralization, nitrification, denitrification, etc.) of parent biogeochemical models to simulate the corresponding isotopic signature of Nr. The model has been applied to the LandscapeDNDC model to evaluate simulated process rates

and attribute N_2O production to either nitrification or denitrification.

Even though N_2 is a major product of denitrification, modeling studies rarely evaluate simulated N_2 emissions because few observations are available. When models fail to accurately represent N_2O emissions it cannot be determined if total denitrification rates were incorrect, or if the stoichiometry of denitrification products was incorrect. Studies reporting N_2 emissions measured using advanced methods such as helium enclosed chambers [71], ^{15}N labeled NO_3^- [72], and isotope ratios [1*] should be prioritized for model evaluation. When N_2 measurements are not available, emissions for different models could at least be compared (e.g. Ref. [73]). The scarcity of accessible measurements as compared to the extent of simulated processes is a general problem for the calibration and validation of complex biogeochemical models.

In many studies it remains unclear if model algorithms for soil N transformations are incomplete, or if inaccurate representations of other processes such as soil water flows (e.g. Ref. [26*]), ammonia volatilization (e.g. Ref. [74]) and plant N uptake (e.g. Ref. [75]) are responsible for model inaccuracies. Houska *et al.* [76] showed for the LandscapeDNDC model that it is not easy to accurately represent multiple outputs at the same time (0.01% of model runs sampled by Latin Hypercube Sampling) while a single output quantity could be well represented (40–70% of runs) thus providing evidence that models are often right for the wrong reasons. A recent study showed that using measured instead of model generated values for soil water content resulted in worse model performance for crop yields and highlights the risk of compensating effects when calibrating model parameters [77]. Systematic evaluation of the sensitivity of denitrification rates and product ratios to key drivers and comparisons with measurements would address these issues and isolate which model algorithms and parameter values are most responsible for inaccurate representation of N_2O emissions and other variables related to denitrification. We conclude that current levels of process understanding and available observational data sets could be readily exploited to improve models and to quantify how complexity and burden of required model inputs interact to determine uncertainty in model outputs.

Conflict of interest statement

Nothing declared.

Acknowledgements

This article evolved from a workshop titled 'Climate Change, Reactive Nitrogen, Food Security and Sustainable Agriculture' held at the Karlsruhe Institute of Technology in Garmisch-Partenkirchen, Germany, on 15–16 April 2019, and which was sponsored by the OECD Co-operative Research Programme: Biological Resource Management for Sustainable Agricultural Systems whose financial support made it possible for the authors to participate in the workshop.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
1. Warner DI, Scheer C, Friedl J, Rowlings DW, Brunk C, Grace PR: **Mobile continuous-flow isotope-ratio mass spectrometer system for automated measurements of N₂ and N₂O fluxes in fertilized cropping systems.** *Sci Rep* 2019, **9**:1-10.
 - Describes a new method to quantify in field N₂ emissions, which could be used to generate much needed data to evaluate model outputs of this important denitrification product.
 2. Erisman JW, Galloway JN, Dice NB, Sutton MA, Bleeker A, Grizzetti B, Leach AM, de Vries W: **Nitrogen: too much of a vital resource.** *Science Brief.* Netherlands, Zeist, The Netherlands: WWF; 2015.
 3. Fowler D, Coyle M, Skiba U, Sutton MA, Cape JN, Reis S, Sheppard LJ, Jenkins A, Grizzetti B, Galloway JN, Vitousek P: **The global nitrogen cycle in the twenty-first century.** *Philos Trans R Soc B Biol Sci* 2013, **368** p.20130164.
 4. Galloway JN, Aber JD, Erisman JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby BJ: **The nitrogen cascade.** *Bioscience* 2003, **53**:341-356.
 5. Wang J, Chadwick DR, Cheng Y, Yan X: **Global analysis of agricultural soil denitrification in response to fertilizer nitrogen.** *Sci Total Environ* 2018, **616**:908-917.
 6. Xia L, Li X, Ma Q, Lam SK, Wolf B, Kiese R, Butterbach-Bahl K, Chen D, Li Z, Yan X: **Simultaneous quantification of N₂, NH₃ and N₂O emissions from a flooded paddy field under different N fertilization regimes.** *Global Change Biol* 2019, **26**:2292-2303 <http://dx.doi.org/10.1111/gcb.14958>.
 7. Kuypers MM, Marchant HK, Kartal B: **The microbial nitrogen-cycling network.** *Nat Rev Microbiol* 2018, **16**:263.
 8. Moser G, Gorenflo A, Brenzinger K, Keidel L, Braker G, Marhan S, Clough TJ, Müller C: **Explaining the doubling of N₂O emissions under elevated CO₂ in the Giessen FACE via in-field 15N tracing.** *Global Change Biol* 2018, **24**:3897-3910.
 9. Zhu GB, Singh B, Zhu YG: **Anaerobic ammonium oxidation in agricultural soils-synthesis and prospective.** *Environ Pollut* 2019, **244**:127-134.
 10. Wrage-Mönnig N, Horn MA, Well R, Müller C, Velthof G, Oenema O: **The role of nitrifier denitrification in the production of nitrous oxide revisited.** *Soil Biol Biochem* 2018, **23**:3-16.
 11. Friedl J, De Rosa D, Rowlings DW, Grace PR, Müller C, Scheer C: **Dissimilatory nitrate reduction to ammonium (DNRA), not denitrification dominates nitrate reduction in subtropical pasture soils upon rewetting.** *Soil Biol Biochem* 2018, **125**:340-349.
 12. Tian H, Yang J, Xu R, Lu C, Canadell JG, Davidson EA, Jackson RB, Arneeth A, Chang J, Ciais P, Gerber S: **Global soil nitrous oxide emissions since the preindustrial era estimated by an ensemble of terrestrial biosphere models: magnitude, attribution, and uncertainty.** *Global Change Biol* 2019, **25**:640-659.
 13. IPCC: In *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.* Edited by Calvo Buendia E, Tanabe K, Kranjc A, Baasansuren J, Fukuda M, Ngarize S, Osako A, Pyrozhenko Y, Sherman P, Federici S. Switzerland: IPCC; 2019.
 14. Li C, Aber J, Stange F, Butterbach-Bahl K, Papen H: **A process-oriented model of N₂O and NO emissions from forest soils: 1. Model development.** *J Geophys Res Atmos* 2000, **105**:4369-4384.
 15. Necpálová M, Anex RP, Fienen MN, Del Grosso SJ, Castellano MJ, Sawyer JE, Iqbal J, Pantoja JL, Barker DW: **Understanding the DayCent model: calibration, sensitivity, and identifiability through inverse modeling.** *Environ Modell Softw* 2015, **66**:110-130.
 16. Thorburn PJ, Biggs JS, Collins K, Probert ME: **Using the APSIM model to estimate nitrous oxide emissions from diverse Australian sugarcane production systems.** *Agric Ecosyst Environ* 2010, **136**:343-350 <http://dx.doi.org/10.1016/j.agee.2009.12.014>.
 17. Gabrielle B, Gagnaire N, Massad RS, Dufossé K, Bessou C: **Environmental assessment of biofuel pathways in Ile de France based on ecosystem modeling.** *Bioresour Technol* 2013, **152**:511-518 <http://dx.doi.org/10.1016/j.biortech.2013.10.104>.
 18. Goglio P, Smith WN, Grant BB, Desjardins RL, Gao X, Hanis K, Tenuta M, Campbell CA, McConkey BG, Nemecek T et al.: **A comparison of methods to quantify greenhouse gas emissions of cropping systems in LCA.** *J Clean Prod* 2018, **172**:4010-4017.
 19. Del Grosso SJ, Wirth T, Ogle SM, Parton WJ: **Estimating agricultural nitrous oxide emissions.** *EOS Trans Am Geophys Union* 2008, **89** pp.529-529.
 20. Brilli L, Bechini L, Bindi M, Carozzi M, Cavalli D, Conant R, Dorich CD, Doro L, Ehrhardt F, Farina R, Ferrise R: **Review and analysis of strengths and weaknesses of agro-ecosystem models for simulating C and N fluxes.** *Sci Total Environ* 2017, **98**:445-470.
 21. Ebrahimi A, Or D: **On upscaling of soil microbial processes and biogeochemical fluxes from aggregates to landscapes.** *J Geophys Res Biogeosci* 2018, **123**:1526-1547.
 - Demonstrates that a highly mechanistic model representing fine spatial/temporal resolution soil physical properties and microbial dynamics compared favorably with various field observations.
 22. Sexstone AJ, Revsbech NP, Parkin TB, Tiedje JM: **Direct measurement of oxygen profiles and denitrification rates in soil aggregates 1.** *Soil Sci Soc Am J* 1985, **49**:645-651.
 23. Rabot E, Cousin I, Hénault C: **A modeling approach of the relationship between nitrous oxide fluxes from soils and the water-filled pore space.** *Biogeochemistry* 2015, **122**:395-408 <http://dx.doi.org/10.1007/s10533-014-0048-1>.
 24. Parkin TB: **Soil microsites as a source of denitrification variability.** *Soil Sci Soc Am J* 1987, **51**:1194-1199.
 25. Schlüter S, Zawallich J, Vogel HJ, Dörsch P: **Physical constraints for respiration in microbial hotspots in soil and their importance for denitrification.** *Biogeosciences* 2019, **16**:3665-3678 <http://dx.doi.org/10.5194/bg-16-3665-2019>.
 26. Smith W, Grant B, Qi Z, He W, VanderZaag A, Drury CF, Helmers M: **Development of the DNDC model to improve soil hydrology and incorporate mechanistic tile drainage: a comparative analysis with RZWQM2.** *Environ Modell Softw* 2020, **123** p.104577.
 - Shows that representation of N cycling in models can be improved by addressing limitations in hydrological algorithms.
 27. Congreves KA, Wagner-Riddle C, Si BC, Clough TJ: **Nitrous oxide emissions and biogeochemical responses to soil freezing-thawing and drying-wetting.** *Soil Biol Biochem* 2018, **117**:5-15.
 28. Wagner-Riddle C, Congreves KA, Abalos D, Berg AA, Brown SE, Ambadan JT, Gao X, Tenuta M: **Globally important nitrous oxide emissions from croplands induced by freeze-thaw cycles.** *Nat Geosci* 2017, **10**:279.
 - Used high frequency measurements from flux towers to show the importance of spring thaw induced N₂O pulses and drove model development to represent the relevant processes.
 29. De Bruijn AMG, Butterbach-Bahl K, Blagodatsky S, Grote R: **Model evaluation of different mechanisms driving freeze-thaw N₂O emissions.** *Agric Ecosyst Environ* 2009, **133**:196-207.
 30. Dutta B, Grant BB, Congreves KA, Smith WN, Wagner-Riddle C, VanderZaag AC, Tenuta M, Desjardins RL: **Characterising effects of management practices, snow cover, and soil texture on soil temperature: model development in DNDC.** *Biosyst Eng* 2018, **168**:54-72.
 - The paper describes one of the first attempts to improve a widely used agroecosystem model to represent spring thaw induced N₂O pulses.
 31. Segura JH, Nilsson MB, Haei M, Sparrman T, Mikkola JP, Gråsvik J, Schleucher J, Öquist MG: **Microbial mineralization of cellulose in frozen soils.** *Nat Commun* 2017, **8**:1-8.

32. Risk N, Snider D, Wagner-Riddle C: **Mechanisms leading to enhanced soil nitrous oxide fluxes induced by freeze-thaw cycles.** *Can J Soil Sci* 2013, **93**:401-414.
33. Haas E, Klatt S, Fröhlich A, Kraft P, Werner C, Kiese R, Grote R, Breuer L, Butterbach-Bahl K: **LandscapeDNDC: a process model for simulation of biosphere-atmosphere-hydrosphere exchange processes at site and regional scale.** *Landsc Ecol* 2013, **28**:615-636.
34. Grant RF, Neftel A, Calanca P: **Ecological controls on N₂O emission in surface litter and near-surface soil of a managed grassland: modelling and measurements.** *Biogeosciences* 2016, **13**:3549-3571.
35. Grandy AS, Wieder WR, Wickings K, Kyker-Snowman E: **Beyond microbes: are fauna the next frontier in soil biogeochemical models?** *Soil Biol Biochem* 2016, **102**:40-44.
36. Parton WJ, Del Grosso SJ, Campbell EE, Hartman MD, Hobbs NT, Moore J, Swift D, Schimel DS, Ojima DS, Coughenour M *et al.*: **Five Decades of Modeling Supporting the Systems Ecology Paradigm.** 2020.
- Comprehensive review of the advantages and limitations of different approaches used to model denitrification and other plant-soil system processes.
37. Huang Y, Guenet B, Ciaï P, Janssens IA, Soong JL, Wang Y, Goll DS, Blagodatskaya E, Huang Y: **ORCHIMIC (v1. 0), a microbe-mediated model for soil organic matter decomposition.** *Geosci Model Dev* 2018, **11**:2111-2138 <http://dx.doi.org/10.5194/gmd-11-2111-2018>.
38. Li M, Qian WJ, Gao Y, Shi L, Liu C: **Functional enzyme-based approach for linking microbial community functions with biogeochemical process kinetics.** *Environ Sci Technol* 2017, **51**:11848-11857.
39. Bhanja SN, Wang J, Shrestha NK, Zhang X: **Microbial kinetics and thermodynamic (MKT) processes for soil organic matter decomposition and dynamic oxidation-reduction potential: model descriptions and applications to soil N₂O emissions.** *Environ Pollut* 2019, **247**:812-823.
40. Sulman BN, Moore JA, Abramoff R, Averill C, Kivlin S, Georgiou K, Sridhar B, Hartman MD, Wang G, Wieder WR, Bradford MA: **Multiple models and experiments underscore large uncertainty in soil carbon dynamics.** *Biogeochemistry* 2018, **141**:109-123.
41. Louis BP, Maron PA, Viaud V, Leterme P, Menasseri-Aubry S: **Soil C and N models that integrate microbial diversity.** *Environ Chem Lett* 2016, **14**:331-344.
42. Crowther TW, Van den Hoogen J, Wan J, Mayes MA, Keiser AD, Mo L, Averill C, Maynard DS: **The global soil community and its influence on biogeochemistry.** *Science* 2019, **365** p.eaav0550.
- Describes the importance of microbial community heterogeneity on soil biogeochemical processes and the opportunities as well as limitations for ecosystem modeling.
43. Otwell AE, López García de Lomana A, Gibbons SM, Orellana MV, Baliga NS: **Systems biology approaches towards predictive microbial ecology.** *Environ Microbiol* 2018, **20**:4197-4209.
44. Davidson EA, Kanter D: **Inventories and scenarios of nitrous oxide emissions.** *Environ Res Lett* 2014, **9** p.105012.
45. Fitton N, Datta A, Hastings A, Kuhnert M, Topp CFE, Cloy JM, Rees RM, Cardenas LM, Williams JR, Smith K, Chadwick D: **The challenge of modelling nitrogen management at the field scale: simulation and sensitivity analysis of N₂O fluxes across nine experimental sites using DailyDayCent.** *Environ Res Lett* 2014, **9** p.095003.
46. Ehrhardt F, Soussana JF, Bellocchi G, Grace P, McAuliffe R, Recous S, Sándor R, Smith P, Snow V, de Antoni Migliorati M, Basso B: **Assessing uncertainties in crop and pasture ensemble model simulations of productivity and N₂O emissions.** *Global Change Biol* 2018, **24**:e603-e616.
- Reports the first ensemble comparison of N₂O emissions from 24 models with observations from 9 field sites.
47. Zimmermann J, Carolan R, Forrestal P, Harty M, Lanigan G, Richards KG, Roche L, Whitfield MG, Jones MB: **Assessing the performance of three frequently used biogeochemical models when simulating N₂O emissions from a range of soil types and fertilizer treatments.** *Geoderma* 2018, **331**:53-69 <http://dx.doi.org/10.1016/j.geoderma.2018.06.004>.
48. Dutta B, Grant BB, Campbell CA, Lemke RL, Desjardins RL, Smith WN: **A multi model evaluation of long-term effects of crop management and cropping systems on nitrogen dynamics in the Canadian semi-arid prairie.** *Agric Syst* 2017, **151**:136-147 <http://dx.doi.org/10.1016/j.agry.2016.12.003>.
49. Duret S, Drouet JL, Durand P *et al.*: **NitroScape: a model to integrate nitrogen transfers and transformations in rural landscapes.** *Environ Pollut* 2011, **159**:3162-3170 <http://dx.doi.org/10.1016/j.envpol.2011.05.005>.
50. Klatt S, Kraus D, Kraft P, Breuer L, Wlotzka M, Heuveline V, Haas E, Kiese R, Butterbach-Bahl K: **Exploring impacts of vegetated buffer strips on nitrogen cycling using a spatially explicit hydro-biogeochemical modeling approach.** *Environ Modell Softw* 2017, **90**:55-67.
51. Zhang W, Li Y, Zhu B, Zheng X, Liu C, Tang J, Su F, Zhang C, Ju X, Deng J: **A process-oriented hydro-biogeochemical model enabling simulation of gaseous carbon and nitrogen emissions and hydrologic nitrogen losses from a subtropical catchment.** *Sci Total Environ* 2018, **616**:305-317.
52. Melaku ND, Shrestha NK, Wang J, Thorman RE: **Predicting nitrous oxide emissions following the application of solid manure to grassland in the United Kingdom.** *J Environ Qual* 2020, **49**:1-13 <http://dx.doi.org/10.1002/jeq2.20002>.
53. He W, Smith WN, Grant BB, VanderZaag AC, Schwager EA, Qi Z, Reynolds D, Wagner-Riddle C: **Understanding the fertilizer management impacts on water and nitrogen dynamics for a corn silage tile-drained system in Canada.** *J Environ Qual* 2019, **48**:1016-1028.
54. Fatichi S, Or D, Walko R, Vereecken H, Young MH, Ghezzehei TA, Hengl T, Kollet S, Agam N, Avissar R: **Soil structure is an important omission in earth system models.** *Nat Commun* 2020, **11**:1-11.
55. Woodley AL, Drury CF, Reynolds WD, Tan CS, Yang XM, Oloya TO: **Long-term cropping effects on partitioning of water flow and nitrate loss between surface runoff and tile drainage.** *J Environ Qual* 2018, **47**:820-829.
56. Wang B, Brewer PE, Shugart HH, Lerdau MT, Allison SD: **Soil aggregates as biogeochemical reactors and implications for soil-atmosphere exchange of greenhouse gases—a concept.** *Global Change Biol* 2019, **25**:373-385.
- Shows that in addition to bulk soil properties, small scale soil physical heterogeneity influences processes such as denitrification and should be represented to improve models.
57. Jarecki M, Grant B, Smith W, Deen B, Drury C, VanderZaag A, Qian B, Yang J, Wagner-Riddle C: **Long-term trends in corn yields and soil carbon under diversified crop rotations.** *J Environ Qual* 2018, **47**:635-643.
58. Bakken LR, Frostegård Å: **Sources and sinks for N₂O, can microbiologist help to mitigate N₂O emissions.** *Environ Microbiol* 2017, **19**:4801-4805.
59. Li C, Salas W, Zhang R, Krauter C, Rotz A, Mitloehner F: **Manure-DNDC: a biogeochemical process model for quantifying greenhouse gas and ammonia emissions from livestock manure systems.** *Nutr Cycl Agroecosyst* 2012, **93**:163-200.
60. Del Grosso SJ, Ogle SM, Parton WJ, Nevison C, Smith W, Gran B, Wagner-Riddle C, Tenuta M, Hartman MD, Blanc-Betes E, DeLucia EH: **Modelling denitrification and N₂O emissions from fertilised cropping systems using Daycent.** In *Proceedings of the Workshop on "Climate Change, Reactive Nitrogen, Food Security and Sustainable Agriculture" 15-16 April, 2019; Garmisch-Partenkirchen, Germany: 2019.*
61. Hénault C, Bourennane H, Ayzac A, Ratié C, Saby NP, Cohan JP, Eglin T, Le Gall C: **Management of soil pH promotes nitrous oxide reduction and thus mitigates soil emissions of this greenhouse gas.** *Sci Rep* 2019, **9** <http://dx.doi.org/10.1038/s41598-019-56694-3> p. 20182.
62. Wallach D, Thorburn PJ: **Estimating uncertainty in crop model predictions: current situation and future prospects.** *Eur J*

- Agron* 2017, **88**:A1-A7 <http://dx.doi.org/10.1016/j.eja.2017.06.001>.
63. Fuchs K, Merbold L, Buchmann N, Bretscher D, Brilli L, Fitton N, Topp CFE, Klumpp K, Lieffering M, Martin R *et al.*: **Multimodel evaluation of nitrous oxide emissions from an intensively managed grassland.** *J Geophys Res Biogeosci* 2020, **125** <http://dx.doi.org/10.1029/2019JG005261> e2019JG005261.
 64. Dorich CD, Conant RT, Albanito F, Butterbach-Bahl K, Grace P, Scheer C, Snow VO, Vogeler I, van der Weerden TJ: **Improving N₂O emission estimates with the global N₂O database.** *Curr Opin Environ Sustain* 2020, **47**:13-20 <http://dx.doi.org/10.1016/j.cosust.2020.04.006>.
 65. Nevison C, Andrews A, Thoning K, Dlugokencky E, Sweeney C, Miller S, Saikawa E, Benmergui J, Fischer M, Mountain M, Nehrkorn T: **Nitrous oxide emissions estimated with the CarbonTracker-Lagrange North American regional inversion framework.** *Global Biogeochem Cycles* 2018, **32**:463-485.
 Presents continental scale estimates of N₂O emissions during 2008–2014 based on atmospheric concentration measurements that can be used to evaluate emission generated by models based on ground level observations.
 66. EPA: *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2018. Office of Atmospheric Programs.* Available online at: U.S. Environmental Protection Agency (EPA Publication No. 430-R-20-002); 2020 <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2018>.
 67. Liang C, MacDonald D, Thiagarajan A, Flemming C, Cerkowniak D, Desjardins R: **Developing a country specific method for estimating nitrous oxide emissions from agricultural soils in Canada.** *Nutr Cycl Agroecosyst* 2020, **117**:145-167.
 68. Lugato E, Paniagua L, Jones A, de Vries W, Leip A: **Complementing the topsoil information of the Land Use/Land Cover Area Frame Survey (LUCAS) with modelled N₂O emissions.** *PLoS One* 2017, **12**:e0176111 <http://dx.doi.org/10.1371/journal.pone.0176111>.
 69. Denk TR, Mohn J, Decock C, Lewicka-Szczębak D, Harris E, Butterbach-Bahl K, Kiese R, Wolf B: **The nitrogen cycle: a review of isotope effects and isotope modeling approaches.** *Soil Biol Biochem* 2017, **105**:121-137.
 70. Denk TR, Kraus D, Kiese R, Butterbach-Bahl K, Wolf B: **Constraining N cycling in the ecosystem model LandscapeDNDC with the stable isotope model SIMONE.** *Ecology* 2019, **100** p.e02675.
 Combines N isotope modeling with high frequency measurements of the N₂O to address weaknesses in N cycling models.
 71. Chen T, Oenema O, Li J, Misselbrook T, Dong W, Qin S, Yuan H, Li X, Hu C: **Seasonal variations in N₂ and N₂O emissions from a wheat-maize cropping system.** *Biol Fertil Soils* 2019, **55**:539-551.
 72. Well R, Burkart S, Giesemann A, Grosz B, Köster JR, Lewicka-Szczębak D: **Improvement of the 15N gas flux method for in situ measurement of soil denitrification and its product stoichiometry.** *Rapid Commun Mass Spectrom* 2019, **33**:437-448.
 73. David MB, Del Grosso SJ, Hu X, Marshall EP, McIsaac GF, Parton WJ, Tonitto C, Youssef MA: **Modeling denitrification in a tile-drained, corn and soybean agroecosystem of Illinois, USA.** *Biogeochemistry* 2009, **93**:7-30.
 74. Congreves KA, Grant BB, Dutta B, Smith WN, Chantigny MH, Rochette P, Desjardins RL: **Predicting ammonia volatilization from swine slurry application using DNDC: model development.** *Agric Ecosyst Environ* 2016, **219**:179-189 <http://dx.doi.org/10.1016/j.agee.2015.10.028>.
 75. Nasielski J, Grant B, Smith W, Niemeyera C, Janoviceka K, Deen B: **Effect of nitrogen source, placement and timing on the environmental performance of economically optimum nitrogen rates in maize.** *Field Crops Res* 2019, **246**:107686 <http://dx.doi.org/10.1016/j.fcr.2019.107686>.
 76. Houska T, Kraft P, Liebermann R, Klatt S, Kraus D, Haas E, Santabarbara I, Kiese R, Butterbach-Bahl K, Müller C, Breuer L: **Rejecting hydro-biogeochemical model structures by multi-criteria evaluation.** *Environ Modell Softw* 2017, **93**:1-12.
 77. Sima MW, Fang QX, Qi Z, Yu Q: **Direct assimilation of measured soil water content in RZWQM calibration for deficit-irrigated maize.** *Agron J* 2020, **112**:844-860 <http://dx.doi.org/10.1002/agj2.20088>.