General comments: This manuscript reported modeling impacts of nitrification inhibitor (NI) application on N2O emission. The authors incorporated new processes into the ecosys model and compared the simulations against field observations and some literature reports. In general, the work in this manuscript can contribute to the simulations of NI impacts on N2O production and emission. However, I think some changes can further improve this manuscript.

Firstly, the new contents in this manuscript are simulating NI impacts and a lot of descriptions in the section 2 (model development) are the introductions of the ecosys model, instead of the new model development. These introductions are not necessary for me since they have been well described in literatures. I suggest the authors delete unnecessary descriptions (or move them into supporting materials) and focus more on the new model improvement/new contents.

I have reworded sec. 2.1 to clarify the relationship between the description of earlier model components in sec. 2.2 to 2.8, and nitrification inhibition in sec. 2.9. However because readers’ understanding sec. 2.9 requires their understanding of sec. 2.2 to 2.8, I am reluctant to abbreviate them, as I frequently refer to specific steps in these sections to explain model behavior in the Discussion. I have removed Sec. 2.10 and 2.11, and all later references to them, to shorten the manuscript.

Secondly, I have noticed some discrepancies between simulations and observations in yields, mineral nitrogen, and N2O emission. However, some discrepancies were not fully discussed. I would like to see more discussions regarding what might be reasons for the discrepancies and how the discrepancies (and reasons) inform further improvement in simulating N2O emission following soil thaw and NI impacts.

I have added Sec. 6.5 to the Discussion in which I raise ongoing issues about modelling N2O emissions and NI effects on them. I have confined this section to these issues as they are the focus of this paper, rather than mineral N and crop yields.

Specific comments:

Lines 96 to 99: This sentence is not clear for me. Please rewrite.

Line 230: From this section, it seems that impacts of NI are not related to the application amount of NI. Is this reasonable? Does this need to be considered in further model developments.

I have not seen any experimental results in the literature in which different amounts of NI were evaluated from which such an impact could be parameterized. I have added a note to this effect in Sec. 6.4.

Line 235: “I(t)” in the right part should be “l(t-1)”?
Good point. Done

Line 311: So the measurement depths were shallower than the depth of slurry injection? Is this a potential reason for the discrepancies between the simulated and observed mineral nitrogen.

That could be, because the mineral N would have to diffuse upwards from the injection zone.

Line 324: "as soon as possible" may be not proper here.

Reworded in Sec. 3.2

Line 346: Could you clarify the source of the parameters in the Table 2? All from field records?

Ksat was derived from a pedotransfer function, as now noted in Table 2. All others are from field records.

Line 354: Could you provide the input parameters of the simulated crop?

That would require a lot more model explanation that has already been provided in earlier papers, and would be inconsistent with the first point about shortening the model description raised above. Also crop growth is not the key focus of this paper, but rather NI.

Line 372: Did you mean disturbance of the soil profile from surface to 0.5m or 0.8m? If so, is this setting accommodate to normal tillage practices? Is 0.8m too deep?

These values refer to soil mixing coefficients during tillage, not depth which was that of application (14 cm) as stated in Sec. 4.2.

Lines 421 to 422: This sentence is hard to follow. Could you rewrite into two short sentences?

This sentence is already less than 2 lines.

Line 469: RI should be NI? Please check other places of the manuscript.

Reworded in Sec. 5.4.1 to show that RI refers to rate constants for declining NI activity used for DMPP and nitrapyrin.

Line 473: Deleting "and measured" as these are modeled values.

This line refers to Table 5 that shows both modelled and measured values.

Line 534: Could you please discuss more about the discrepancies in simulating yields in this section, such as the reasons and implications for further model improvement.

That would be interesting, but the point most relevant to this paper is whether NI affected modelled and measured barley yields. In common with most NI studies, yields were not much affected. I mentioned that yields were reduced by lodging in the 2016 field experiment.

Line 567: How about N2O reduction to N2 during this period? Was the rate of this process low or high?
This process is modelled in ecosys, but no experimental data are available from this study to corroborate modelled values.

Line 606: Should be "Lin et al., 2018".

Corrected

Line 632: grammar error.

I split this sentence in Sec. 6.2.1 to simplify the grammar.

Line 693: more intensive tillage could accelerate O2 transfer from atmosphere to soils. Does the model consider this?

Yes, but I thought this was getting too detailed for a discussion of Ni effects.

Line 736: May be the offset need to considered not only in Tier 3 methodology but also other methodologies.

Perhaps, but measurements of this offset are limited.

Figure 3a, b: O2 were zero for about 10 days. Did the model simulate N2O reduction to N2 during this period?

Actually O2 was not zero, but very near zero. N2O reduction can be modelled, depending on demand for e- acceptors unmet by NO3-, NO2- and N2O. N2 emissions from N2O reduction are modelled in ecosys, but were not included in this paper.

Figures 4 to 7: Did you compare daily simulations against daily observations? It looks that the auto-chamber observations were sub-daily; if so, how many observations per day? It would be useful to clarify these points.

Observed fluxes were plotted at the same 3-h frequency as that at which they were measured as now stated in Sec. 3.2.

Anonymous Referee #2

The authors have modified the ecosystem model to simulate effects of nitrification inhibitors on N2O emissions. The subject is interesting and useful. However, there are several issues that need to be improved before it can be accepted. My detailed comments are listed below:

1. Ln 73-77 recent references for modelling of nitrification inhibitor should be included. For example, Y Li et al., 2020. Modelling nitrification inhibitor effects on emissions of nitrous oxide (N2O) in the UK, Science of The Total Environment, 709: 136156.
This paper, which had not been published when I submitted the manuscript last year, is now cited. I also contrast this model with ours in Sec. 6.5 which has been added to the manuscript.

2. Original model seems too long although most of them are putted in Supplementary materials. This distracts from the modified parts and novelties. It would be better if this paper can focus more on the modified parts of nitrification inhibitor. I would like to use a subsection to describe briefly the original model, such as oxidation reduction reaction. On the other hand, Section 2.9 should include more details, such as some equations related to the modification of nitrification inhibitor.

I have reworded sec. 2.1 to clarify the relationship between the description of earlier model components in sec. 2.2 to 2.8, and nitrification inhibition in sec. 2.9. However because readers’ understanding sec. 2.9 requires their understanding of sec. 2.2 to 2.8, I am reluctant to abbreviate them, as I frequently refer to these sections to explain model behavior in the Discussion. In fact, Sec. 2.9 includes all equations by which NI activity is modelled in this paper. I have removed Sec. 2.10 and 2.11, and all later references to them, to shorten the manuscript.

3. For the site description, it is better to add a figure to show the location of specific fields.

There was only 1 set of experimental plots located in only 1 field in this study. Further details about plot topography and size have been added to Sec. 3.1 with further details in an earlier paper by Lin et al. (2018)

4. Ln240, the Arrhenius equation of $f_{Ts}$ could be given.

I now cite the Arrhenius equation in sec. 2.9 as [A6] in S1 of the Supplementary material in which all parameters are given.

5. It is unclear what Fall and Spring in Fig. 2 are since Fig. 2 (a)-(d) were in 2014-2016.

I have added seasonal indicators to Fig. 2.

6. It may not be sufficient to examine the sensitivity of one parameter, $K_{NH4}$ (Table 9) because other parameters should be important, such as $R_I$, $K_{CO2}$ and temperature coefficients in $f_{Ts}$.

I examine the sensitivity to two parameters, $I_{t=0}$ and $K_{NH4}$ which could not be estimated from experimental studies. The other 2 parameters, $R_I$ and $f_{Ts}$ could at least be estimated from other studies, although I now discuss issues concerning this estimation in Sec. 6.5 which had been added to the paper.

7. What is $f_{tl}$ in Eq. (3)?

This has been corrected to $f_{tl}$ as in Eq. 1.

8. Other factors, such as soil moisture and pH, can also affect N2O emission with the nitrification inhibitor. The limitations should be discussed due to the neglect of these factors.
Anonymous Referee #3

Nitrification inhibitors (NI) have attracted much interest recently because retarding nitrification by NI can reduce the emission of N2O from farmland, thus reducing the climate forcing of food production. However, it is difficult to simulate effects of nitrification inhibitors on N2O emission from agriculture due to complex interaction among NI, nutrients, soils and weather. This paper modified Ecosystem model to incorporate NI processes and applied it to evaluate effects of NI on N2O emissions. Thus, the topic of the paper is highly relevant. However, it may require some changes before acceptance for publication.

Below is a list of major and minor comments.

Major comments

1. Many of the described methods in this study are already stated in their previous works. Some of them have included from their previously published works.

I have added a note to this effect in Sec. 6.4, but insufficient data are available for model parameterization.

2. In Section 3.1, more details are needed; for example, describe the vegetation, in terms of species, snow depth, drainage patterns of the fields, slope, .... This information will help for repeatability of this study. Also, this information can be used in a larger study for globalizing the model capability addressed in this study.

I have added a few further details about the experimental site in Sec. 3.1, noting that this experiment was already described in an earlier publication (Lin et al., 2018).

3. In Section 4, it is unclear what site boundaries were modelled. Ecosystem could be a 3D model for water and nutrient transports in S4. Did the authors simulate the 3D fluxes in soils in this study? More details should be provided for the site topology and slopes for a 3D simulation if yes.

Field plots were simulated as 1D soil profiles with a subsurface water table at 1.2 m as now described in Sec. 4.1.

4. In Section 5, though the paper stressed effects of snowmelt and freeze-thaw on NI and N2O emissions, no results were reported on the freeze-thaw processes, such as snowpack depths, and snowmelt water pools. For example, in Section 5.2.1, oxygen transfer and uptake are explained using snowmelt and drainage of meltwater. However, snowpack was not provided in both measurement and simulations. In Lines 439-441, the smaller rises and subsequent declines in N2O in Fig. 5 were attributed to effects of information of thawing and refreezing. However, Fig. 5 does not provide information of snow depth and freeze-thaw.

I have added further information in Sec. 5.2.1 about how snowmelt and freezing-thawing affect N2O fluxes modelled in ecosys. These effects are further described in Grant and Pattey (1999) as now cited in Sec. 5.2.1. To some extent freezing and thawing can be inferred from temperatures plotted in Figs 4
through 7. I have not added any further graphics about snowmelt and soil thawing because the focus of this paper is on NI effects on N2O emissions rather than the emissions themselves, and the paper is already rather long.

Minor comments

5. Lines 49-51, give references.
Done

6. Lines 74-77, a testing of modelled NI effects on N2O emissions has been performed in Science of The Total Environment recently.
This paper, which had not been published when I submitted the manuscript last year, is now cited. I also contrast this model with ours in Sec. 6.5 which has been added to the manuscript.

7. In Conclusions, it is better to include quantitative results of NI effects.
I have added a range of N2O emission reductions modelled with NI
Modelling Nitrification Inhibitor Effects on N₂O Emissions after Fall and Spring-Applied Slurry by Reducing Nitrifier NH₄⁺ Oxidation Rate

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ABSTRACT

Reductions in N₂O emissions from nitrification inhibitors (NI) are substantial, but remain uncertain because measurements of N₂O emissions are highly variable and discontinuous. Mathematical modelling may offer an opportunity to estimate these reductions if the processes causing variability in N₂O emissions can be accurately simulated. In this study, the effect of NI was simulated with a simple, time-dependent algorithm to slow NH₄⁺ oxidation in the ecosystem model ecosys. Slower nitrification modelled with NI caused increases in soil NH₄⁺ concentrations and reductions in soil NO₃⁻ concentrations and in N₂O fluxes that were consistent with those measured following fall and spring applications of slurry over two years from 2014 to 2016. The model was then used to estimate direct and indirect effects of NI on seasonal and annual emissions. After spring slurry applications, NI reduced N₂O emissions modelled and measured during the drier spring of 2015 (35% and 45%) less than during the wetter spring of 2016 (53% and 72%). After fall slurry applications, NI reduced modelled N₂O emissions by 58% and 56% during late fall in 2014 and 2015, and by 8% and 33% during subsequent spring thaw in 2015 and 2016. Modelled reductions were consistent with those from meta-analyses of other NI studies. Simulated NI activity declined over time, so that reductions in N₂O emissions modelled with NI at an annual time scale were relatively smaller than those during emission events. These
reductions were accompanied by increases in NH$_3$ emissions and reductions in NO$_3^-$ losses with
NI that caused changes in indirect N$_2$O emissions. With further parameter evaluation, the
addition of this algorithm for NI to ecosys may allow emission factors for different NI products
to be derived from annual N$_2$O emissions modelled under diverse site, soil, land use and weather.

1. INTRODUCTION

Nitrification inhibitors (NI) have frequently been found to reduce N$_2$O emissions from
fertilizer and slurry applications in agricultural fields. In a meta-analysis of field experiments
conducted to 2008, Akiyama et al. (2010) found average reductions of 38 ± 6% in N$_2$O emissions
from NI with some variation attributed to land use type and emission rates. Similar average
reductions of 35 - 40% were reported in more recent meta-analyses by Ruser and Schulz (2015),
Gilsanz et al. (2016) and Gao and Bian (2017). However the magnitudes of these reductions are
uncertain because they vary with rate and timing of fertilizer or slurry application, with land use
and ecosystem type (Akiyama et al., 2010) and with application method (Zhu et al., 2016).
These magnitudes are also uncertain because measurements of the N$_2$O emissions on which they
are based are highly variable temporally and spatially, and difficult to sustain over the annual
time periods needed to estimate NI reductions.

The effects of NI on N$_2$O emissions are attributed to inhibition of ammonia
monooxygenase which slows the oxidation of NH$_4^+$ to NO$_2^-$ during nitrification (Subbarao et al.,
2006), and hence slows the reduction of NO$_2^-$ to N$_2$O during nitrifier denitrification. The
consequent slowing of NO$_2^-$ oxidation to NO$_3^-$ would also slow the reduction of NO$_3^-$ to N$_2$O
during denitrification. The effectiveness of NI has been found to decline over time due to
mineralization, adsorption and volatilization, depending on NI formulation. The rate of this
decline varies among NI products and soil types, and increases with soil temperature (Guardia et
al., 2018).

The great majority of the studies included in meta-analyses of NI effects on N$_2$O
emissions were conducted following fertilizer or slurry application on warm soils in spring or
summer (e.g. Akiyama et al., 2010). The effectiveness of NIs with fall applications of fertilizer
or slurry on cold soils has thus far received very limited attention (Ruser and Schulz, 2015), although in cold climates N₂O emissions during the spring thaw following fall applications may exceed those during later spring and summer following spring applications (Lin et al., 2018). Emissions during spring thaw were attributed by Wagner-Riddle and Thurtell (1998) to soil NO₃–N concentrations exceeding 20 mg kg⁻¹ generated by fall-applied slurry that contributed to total N₂O emissions exceeding 0.2 g N m⁻² measured between January and April of the following year. Large N₂O emissions measured in late winter were attributed by Dungan et al. (2017) to labile N not used by soil microorganisms during the previous fall and winter that was actively metabolized when the soils began to warm in early March. Interannual differences in spring thaw emission events after fall slurry applications were related by Kariyapperuma et al. (2012) to those in total soil mineral N content in the upper 15 cm of the soil profile during spring thaw. The effects of NI on N₂O emissions during spring thaw will therefore depend on the persistence with which NI reduces nitrification in cold soils during fall and winter, and thereby alters mineral N concentrations during the following spring.

Reductions in N₂O emissions directly caused by slower nitrification with NI may be partially offset by increases in indirect N₂O emissions from increasing NH₃ emissions caused by greater soil NH₄⁺ concentrations (Lam et al., 2017, Qiao et al., 2015). NI may also decrease indirect N₂O emissions by reducing NO₃⁻ concentrations and hence leaching. Both direct and indirect effects of NI on N₂O emissions must be considered when estimating effects of NI on total N₂O emissions.

IPCC Tier 3 methodology for estimating N₂O emissions under diverse climates, soils, fertilizers and land uses includes the use of comprehensive, process-based mathematical models of terrestrial C, N, water and energy cycling (IPCC, 2019). Although NI effects on nitrification have been added to some existing process models (Cui et al., 2014; Del Grosso et al., 2009, Li et al., 2020), testing of modelled NI effects on N₂O emissions against measurements remains limited to brief periods following soil N amendments (e.g. Giltrap et al., 2011). The mathematical model ecosys explicitly represents the key processes in nitrification (Grant, 1994), denitrification (Grant, 1991) and associated N₂O emissions (Grant, 1995), and has been tested against measurements of N₂O emissions using micrometeorological methods, and manual and automated chambers (Grant and Pattey, 1999, 2008; Grant et al., 2006, 2016; Metivier et al.,
In this study, we propose that applying a time-dependent reduction of NH$_4^+$ oxidation rates during nitrification will enable ecosys to simulate the time course of reductions in N$_2$O emissions with NI measured after fall and spring applications of dairy slurry in a field experiment. The model is then used to estimate the direct and indirect effects of NI on annual N$_2$O emissions with fall and spring slurry applications as required for IPCC Tier 3 methodology, and how these effects would change with alternative tillage practices and timings of slurry application.

2. MODEL DEVELOPMENT

2.1. General Overview

The hypotheses for oxidation-reduction reactions involving N$_2$O, and the aqueous and gaseous transport of their substrates and products, are represented in Fig. 1 and described in further detail below. References to equations and definitions listed in Supplements S1, S3, S4, S5 and S8 of the Supporting Information (Table 1) are provided for those interested in model methodology, but are not needed for a general understanding of model behaviour. These hypotheses function within a comprehensive model of soil C, N and P transformations, which is coupled to one models of soil water, heat and solute transport in surface litter and soil layers, which These models are in turn components of the function within the comprehensive ecosystem model ecosys. Key transformations that drive N$_2$O emissions are described in Sections 2.2 to 2.8 below, and modifications of these transformations to simulate nitrification inhibition are described in Section 2.9. References to equations and definitions listed in Sections 2.2 to 2.8 and given in Supplements S1, S3, S4, S5 and S8 of the Supporting Information (Table 1) are provided for those interested in model methodology, but are not needed for a general understanding of model behaviour.

2.2. Mineralization and Immobilization of Ammonium by Microbial Functional Types

Heterotrophic microbial functional types (MFTs) m (obligately aerobic bacteria, obligately aerobic fungi, facultatively anaerobic denitrifiers, anaerobic fermenters, acetotrophic
methanogens, and obligately aerobic and anaerobic non-symbiotic diazotrophs) are associated
with each organic substrate \( i \) (\( i = \) manure, coarse woody plant residue, fine non-woody plant
residue, particulate organic matter, or humus). Autotrophic MFTs \( n \) (aerobic \( \text{NH}_4^+ \) and \( \text{NO}_2^- \)
oxidizers, aerobic methanotrophs and hydrogenotrophic methanogens) are associated with
inorganic substrates. These MFTs grow \( \text{A25} \) with energy generated from oxidation of dissolved
organic C (DOC) by heterotrophs \( \text{H2, H10} \), of acetate by acetotrophic methanogens, of mineral
\( \text{N} (\text{NH}_4^+ \) and \( \text{NO}_2^- ) \) \( \text{H11, H15} \) by nitrifiers, of \( \text{CH}_4 \) by methanotrophs \( \text{G7} \), or of \( \text{H}_2 \) by
hydrogenotrophic methanogens \( \text{G12} \), coupled with reduction of \( e^- \) acceptors \( \text{O}_2 \) \( \text{H4, G22} \),
acetate \( \text{G8} \), \( \text{NO}_x \) \( \text{H7 – H9} \), and \( \text{CO}_2 \) \( \text{G13} \). These MFTs decay according to first-order rate
constants \( \text{A23} \) with internal recycling of resources (\( \text{C, N, P} \)) from structural to nonstructural
components \( j \) (\( j = \) labile, recalcitrant, nonstructural) varying with nonstructural C:N:P ratios
\( \text{A24} \), the decay products of which form humus \( \text{C, N and P} \) \( \text{A35, A36} \). Each MFT seeks to
maintain a set nonstructural C:N:P ratio by mineralizing \( \text{NH}_4^+ \) and \( \text{H}_2\text{PO}_4^- \) \( \text{H1a} \) from, or by
immobilizing \( \text{NH}_4^+ \), \( \text{NO}_x^- \) and \( \text{H}_2\text{PO}_4^- \) \( \text{H1b, H1c} \) into, its nonstructural N and P components.
These transformations control the exchange of N and P between organic and inorganic states,
and of \( \text{O}_2 \) between aqueous and gaseous states, and hence affect the availability of substrates and
\( e^- \) acceptors for nitrification and denitrification.

2.3. Oxidation of DOC and Reduction of Oxygen by Heterotrophs

\( \text{N}_2\text{O} \) is generated when demand for \( e^- \) acceptors from oxidation by aerobic heterotrophs
and autotrophs (Sec. 2.2) exceeds supply from \( \text{O}_2 \), requiring explicit modelling of \( \text{O}_2 \) transport
and uptake, and consequent \( \text{O}_2 \) constraints to oxidation-reduction reactions (Sec. 2.11 below)
(Fig. 1). Constraints on heterotrophic oxidation of DOC imposed by \( \text{O}_2 \) uptake are solved in four
steps:
1) DOC oxidation by heterotrophs under non-limiting \( \text{O}_2 \) is calculated from specific oxidation
rates multiplied by active biomasses and an Arrhenius function of \( T_{\text{act}} \) \( \text{A6} \) used for all
microbial transformations, constrained by DOC concentration \( \text{H2} \),
2) \( \text{O}_2 \) reduction to \( \text{H}_2\text{O} \) under non-limiting \( \text{O}_2 \) (\( \text{O}_2 \) demand) by aerobic heterotrophs is calculated
from step 1 using a set respiratory quotient \( \text{H3} \),
3) \( \text{O}_2 \) reduction to \( \text{H}_2\text{O} \) under ambient \( \text{O}_2 \) is calculated from radial \( \text{O}_2 \) diffusion through water
films with thicknesses determined by soil water potential \( \text{H4a} \) coupled with active uptake at
heterotroph surfaces driven by step 2 [H4b]. Diffusion and uptake are sustained by O₂ transfer through soil aqueous and gaseous phases controlled by soil water- and air-filled porosity governed by freezing, thawing and transfer of soil water [D14 – D20]. O₂ diffusion and active uptake are calculated for each heterotrophic population associated with each organic substrate, allowing [H4] to calculate lower O₂ concentrations at microbial surfaces (O₂m) associated with more biologically active substrates (e.g. manure, litter). Localized zones of low O₂ concentration (hotspots) are thereby simulated when O₂ uptake by any aerobic MFT is constrained by O₂ diffusion to that functional type. O₂ uptake by each heterotrophic MFT is affected by competition for O₂ uptake with other heterotrophs, nitrifiers, roots and mycorrhizae, calculated from its biological O₂ demand relative to those of other aerobic functional types.

4) DOC oxidation to CO₂ under ambient O₂ is calculated from steps 2 and 3 [H5]. The energy yield of DOC oxidation with O₂ reduction drives the uptake of additional DOC for construction of microbial biomass $M_{i,h}$ according to construction energy costs of each heterotrophic functional type [A21]. Energy costs of denitrifiers are slightly larger than those of obligately aerobic heterotrophs, placing denitrifiers at a small competitive disadvantage for growth and hence DOC oxidation under non-limiting O₂.

2.4. Oxidation of DOC and Reduction of Nitrate, Nitrite and Nitrous Oxide by Denitrifiers

N₂O may be both product and substrate of NO₃⁻ reduction coupled with DOC oxidation by denitrifiers. Constraints imposed by NO₃⁻ availability on denitrifier DOC oxidation are solved in five steps:

1) NO₃⁻ reduction to NO₂⁻ by heterotrophic denitrifiers under non-limiting NO₃⁻ is calculated from demand for $e^-$ acceptors by denitrifiers for DOC oxidation to CO₂, but not met from O₂ reduction to H₂O because of diffusion limitations to O₂ supply (Sec. 2.3 step 3). This unmet demand is transferred to NO₃⁻ [H6],

2) NO₃⁻ reduction to NO₂⁻ under ambient NO₃⁻ is calculated from step 1, accounting for relative concentrations and affinities of NO₃⁻ and NO₂⁻ [H7],
3) NO\textsuperscript{2-} reduction to N\textsubscript{2}O under ambient NO\textsubscript{2} is calculated from demand for e\textsuperscript{-} acceptors not met by NO\textsuperscript{3-} reduction in step 2, accounting for relative concentrations and affinities of NO\textsuperscript{2-} and N\textsubscript{2}O. This unmet demand is transferred to NO\textsuperscript{2-} [H8].

4) N\textsubscript{2}O reduction to N\textsubscript{2} under ambient N\textsubscript{2}O is calculated from demand for e\textsuperscript{-} acceptors not met by NO\textsuperscript{2-} reduction in step 3, and hence transferred to N\textsubscript{2}O [H9].

5) additional energy yield from DOC oxidation to CO\textsubscript{2} enabled by NO\textsubscript{x} reduction in steps 2, 3 and 4 is added to that enabled by O\textsubscript{2} reduction from [H5], which drives additional DOC uptake for construction of M\textsubscript{i,n}. This additional uptake offsets the disadvantage incurred by the larger construction energy costs of denitrifiers (Sec. 2.3 step 4).

2.5. Oxidation of Ammonium and Reduction of Oxygen by Nitrifiers

N\textsubscript{2}O may also be generated by reduction of NO\textsuperscript{2-} coupled with oxidation of NH\textsubscript{4}\textsuperscript{+} by autotrophic nitrifiers. Constraints on nitrifier oxidation of NH\textsubscript{4}\textsuperscript{+} imposed by O\textsubscript{2} uptake are solved in four steps:

1) Oxidation of NH\textsubscript{4}\textsuperscript{+} (in dynamic equilibrium with NH\textsubscript{3} [E24]) under non-limiting O\textsubscript{2} is calculated from a specific oxidation rate multiplied by active biomass and an Arrhenius function of T\textsubscript{s} and constrained by NH\textsubscript{4}\textsuperscript{+} and CO\textsubscript{2} concentrations [H11],

2) O\textsubscript{2} reduction to H\textsubscript{2}O under non-limiting O\textsubscript{2} (O\textsubscript{2} demand) is calculated from step 1 using set respiratory quotients [H12],

3) O\textsubscript{2} reduction to H\textsubscript{2}O under ambient O\textsubscript{2} is calculated from radial O\textsubscript{2} diffusion through water films of thickness determined by soil water potential [H13a] coupled with active uptake at nitrifier surfaces driven by step 2 [H13b]. O\textsubscript{2} uptake by nitrifiers is affected by competition for O\textsubscript{2} uptake with heterotrophic DOC oxidizers, roots and mycorrhizae, calculated from its biological O\textsubscript{2} demand relative to those of other aerobic functional types.

4) NH\textsubscript{4}\textsuperscript{+} oxidation to NO\textsubscript{2-} under ambient O\textsubscript{2} is calculated from steps 2 and 3 [H14]. The energy yield of NH\textsubscript{4}\textsuperscript{+} oxidation drives the fixation of CO\textsubscript{2} for construction of microbial biomass M\textsubscript{i,n} according to nitrifier construction energy costs.

2.6. Oxidation of Nitrite and Reduction of Oxygen by Nitrifiers

Constraints on nitrifier oxidation of NO\textsubscript{2-} to NO\textsubscript{3-} imposed by O\textsubscript{2} uptake [H15 - H18] are solved in the same way as are those of NH\textsubscript{4}\textsuperscript{+} to NO\textsubscript{2-} [H11 - H14]. The energy yield of NO\textsubscript{2-}
oxidation drives the fixation of CO₂ for construction of microbial biomass $M_{\text{i,o}}$ according to nitrifier construction energy costs.

2.7. Oxidation of Ammonium and Reduction of Nitrite by Nitrifiers

In both nitrifier and denitrifier processes, N₂O is generated from reduction of NO₂⁻, the availability of which is controlled by NO₂⁻ oxidation (Sec. 2.6). Under low O₂ concentrations NO₂⁻ oxidation is suppressed [H18], favoring NO₂⁻ reduction. Constraints on nitrifier oxidation of NH₄⁺ imposed by NO₂⁻ availability are solved in three steps:

1) NO₂⁻ reduction to N₂O under non-limiting NO₂⁻ is calculated from e⁻ acceptors demanded by NH₄⁺ oxidation to NO₂⁻ but not met by O₂ for reduction to H₂O because of diffusion limitations to O₂ supply, and hence transferred to NO₂⁻ [H19],

2) NO₂⁻ reduction to N₂O under ambient NO₂⁻ and CO₂ is calculated from step 1 [H20], competing for NO₂⁻ with denitrifiers [H8] and nitrifiers [H18],

3) energy yield from additional NH₄⁺ oxidation to NO₂⁻ enabled by NO₂⁻ reduction in step 2 [H21] is added to that enabled by O₂ reduction from Sec. 2.5 step 4 [H14] which drives the fixation of additional CO₂ for construction of $M_{\text{i,n}}$.

2.8. Uptake of Ammonium and Reduction of Oxygen by Roots and Mycorrhizae

NH₄⁺ oxidation and O₂ reduction by nitrifiers compete for substrates with NH₄⁺ uptake and O₂ reduction by other MFTs, and by roots and mycorrhizae.

1) NH₄⁺ uptake by roots and mycorrhizae under non-limiting O₂ is calculated from mass flow and radial diffusion between adjacent roots and mycorrhizae [C23a] coupled with active uptake at root and mycorrhizal surfaces [C23b]. Active uptake is subject to product inhibition by root nonstructural N:C ratios [C23g] where nonstructural N is the active uptake product, and nonstructural C is the CO₂ fixation product transferred to roots and mycorrhizae from the canopy.

2) O₂ reduction to H₂O under non-limiting O₂ is calculated from O₂ demands for NH₄⁺ uptake in step 1, and for oxidation of root and mycorrhizal nonstructural C for root maintenance and growth using a set respiratory quotient [C14e],
3) O₂ reduction to H₂O under ambient O₂ is calculated from mass flow and radial diffusion between adjacent roots and mycorrhizae [C14d] coupled with active uptake at root and mycorrhizal surfaces driven by step 2 [C14c]. O₂ uptake by roots and mycorrhizae is also affected by competition with O₂ uptake by heterotrophic DOC oxidizers, and autotrophic nitrifiers, calculated from their biological O₂ demands relative to those of other populations.

4) oxidation of root and mycorrhizal nonstructural C to CO₂ under ambient O₂ is calculated from steps 2 and 3 [C14b],

5) NH₄⁺ uptake by roots and mycorrhizae under ambient O₂ is calculated from steps 1, 2, 3 and 4 [C23b].

2.9. Nitrification Inhibition

For this study, NIs were assumed to reduce specific rates of NH₄⁺ oxidation by nitrifiers in Sec. 2.5 step 1, thereby simulating inhibition of ammonia monoxygenase (Subbarao et al., 2006). This reduction was represented by a time-dependent scalar \( I \):

\[
I_t = I_{t-1} - \frac{I_{t-1} \cdot f_{Ts_l} \cdot R_I \cdot f_{Ts_l}}{1.0 + \frac{[NH_4^+]_{l}}{K_{NH4}}}
\]  

[1]

where \( t \) is the current time step (h), \( t-1 \) is the previous time step (h), \( I \) is the inhibition (initialized to 1.0 at \( t = 0 \) at the time of application), \( R_I \) is the rate constant for decline of \( I \) representing NI degradation (set to 2.0 \( \times \) 10⁻⁴ h⁻¹ for more persistent NIs such as DMPP and to 1.0 \( \times \) 10⁻³ h⁻¹ for less persistent NIs such as nitrapyrin (Ruser and Schulz, 2015)), \( f_{Ts} \) is an Arrhenius function of soil temperature \( (T_s) \) used to simulate \( T_s \) effects on microbial activity ([A6] in Sec. 2.3 step 1), and \( l \) is the soil layer in which NI is present. The values of \( R_I \) and \( f_{Ts} \) for DMPP were selected to give time and temperature dependencies of DMPP activity following application inferred from incubation studies by Guardia et al. (2018). Model results for NI presented below are those using the smaller \( R_I \) for DMPP unless stated as those using the larger \( R_I \) for nitrapyrin.

Specific rates of NH₄⁺ oxidation (Sec. 2.5 step 1) with NI was calculated as:

\[
\chi'_{NH4} = \chi'_{NH4} \cdot (1.0 - I_t / (1.0 + [NH4^+] / K_{NH4}))
\]  

[2]
where \( X'_{\text{NH}_4} \) and \( X''_{\text{NH}_4} \) are specific NH\(_4^+\) oxidation rates with and without NI (g N g nitrifier C\(^{-1}\) h\(^{-1}\)), [NH\(_4^+\)] is the aqueous NH\(_4^+\) concentration (g N m\(^{-3}\) in dynamic equilibrium with [NH\(_3\)]), and \( K_{\text{NH}_4} \) is an inhibition constant set at 7000 g N m\(^{-3}\) to reduce inhibition at very large [NH\(_4^+\)] as suggested in Janke et al. (2019). These rates were used to calculate nitrification rates \([H11]\):

\[
X_{\text{NH}_4t} = X'_{\text{NH}_4t} M_n \frac{[\text{NH}_4^+]}{([\text{NH}_4^+] + K_{\text{NH}_4})} \frac{[\text{CO}_2]}{([\text{CO}_2] + K_{\text{CO}_2})} [3]
\]

where \( X_{\text{NH}_4t} \) is the nitrification rate (g N m\(^{-2}\) h\(^{-1}\)), \( M_n \) is the nitrifier biomass (g C m\(^{-2}\)) and \( K_{\text{NH}_4} \) and \( K_{\text{CO}_2} \) are half-saturation constants for aqueous NH\(_4^+\) and CO\(_2\) (g N and C m\(^{-3}\)). NI in Eq. 1 slows \( X'_{\text{NH}_4t} \) in Eq. 2 and thereby \( X_{\text{NH}_4t} \) in Eq. 3, and hence slows NO\(_2^-\) production from nitrification (Sec. 2.5 step 4) and thereby N\(_2\)O production from nitrification (Sec. 2.7 step 2) and denitrification (Sec. 2.4 step 3). By slowing \( X_{\text{NH}_4t} \) in Eq. 3, NI also reduces nitrification energy yield and hence \( M_n \) growth, biomass \([A25]\) and O\(_2\) uptake \([H13]\), thereby further reducing N\(_2\)O production.

### 2.10. Cation Exchange and Ion Pairing of Ammonium

Availability of NH\(_4^+\) to nitrifiers is also controlled by NH\(_4^+\) adsorption. A Gapon selectivity coefficient is used to solve cation exchange of NH\(_4^+\) vs. Ca\(^{2+}\) \([E10]\) as affected by other cations \([E11]–[E15]\) and CEC \([E16]\). A solubility product is used to equilibrate soluble NH\(_4^+\) and NH\(_3\) \([E24]\) as affected by pH \([E25]\) and other solutes \([E26]–[E57]\). Equilibrium NH\(_4^+\) concentrations drive NH\(_4^+\) oxidation (Sec. 2.5 step 1) and NH\(_3\) volatilization (Sec. 2.11 below).

### 2.11. Soil Transport and Surface—Atmosphere Exchange of Aqueous and Gaseous Substrates and Products

O\(_2\)-uptake and N\(_2\)O emissions in Sec. 2.3 to 2.8 above are governed by aqueous and gaseous transport processes in vertical and lateral directions:

1) Exchanges of all modelled gases \( \gamma (\gamma = \text{O}_2, \text{CO}_2, \text{CH}_4, \text{N}_2, \text{N}_2\text{O}, \text{NH}_3\text{, and H}_2) \) between aqueous and gaseous states within each soil layer are driven by disequilibrium between aqueous and gaseous concentrations according to a \( T \), dependent solubility coefficient,
constrained by an interphase transfer coefficient based on air-water interfacial area that depends on air-filled porosity ($\theta_g$) [D14–D15] (Fig. 1).

2) These gases undergo vertical and lateral convective-dispersive transport through soil in gaseous [D16] and aqueous [D19] states driven by soil water flux and by gas concentration gradients. Dispersive transport is controlled by gaseous diffusion [D17] and aqueous dispersion [D20] coefficients calculated from $\theta_g$ and water-filled porosity ($\theta_w$). Both $\theta_g$ and $\theta_w$ are affected by ice-filled porosity ($\theta_i$) from freezing and thawing driven by soil heat fluxes [D13].

3) Vertical exchanges of all gases between the atmosphere and both gaseous and aqueous states at the soil surface are driven by atmosphere–surface gas concentration differences and by boundary layer conductance above the soil surface, calculated from wind speed and from vegetation density and surface litter [D15]. These exchanges give modelled surface fluxes used in tests against surface fluxes measured in field experiments.

4) All solutes can be lost/gained by lateral surface runoff/runon, modelled from Manning’s equation [D1a] with surface water depth [D2] calculated from surface water balance [D4] using kinematic wave theory, and by lateral subsurface discharge/recharge modelled from convective exchange through subsurface boundaries with an external water table.

3. FIELD EXPERIMENT

3.1. Site Description and Experimental Design

An experiment was established on a Black Chernozem (Table 2) under barley (*Hordeum vulgare* L.) silage from 2014 to 2016 on a level site at the South Campus Farm in Edmonton, AB, Canada (53°29′30″N, 113°31′53″W). The experimental design was an incomplete split-plot design (main plot: fall vs. spring application of dairy slurry; split plot: control vs. NI treatments) on plots 2.4 m in width and 6.1 m in length with three replicates (Lin et al., 2018). The NI products ENTEC (Eurochem Agro, Mannheim, Germany) and eNtrench Nitrogen Stabilizer (Dow Chemical Company, Dow AgroSciences, Calgary, AB, Canada) were mixed with the slurry immediately before application to provide 0.4 kg ha$^{-1}$ active ingredient with slurry injection of 56.17 m$^3$ ha$^{-1}$ at 12.7 to 15.2 cm (average 14 cm) depth and 28 cm spacing. Measured concentrations of NH$_4^+$ and of organic N and C in each slurry application were used to
calculate rates of $\mathrm{NH}_4^+$, organic N and organic C amendments (Table 3). Soil $\mathrm{NH}_4^+$
concentrations were measured from 0 to 10 cm every 2 – 3 weeks between spring thaw and
autumn freezing in 2014, 2015 and 2016. Further details of this field experiment are given in Lin

Weather data (radiation, air temperature ($T_a$), humidity, windspeed and precipitation)
were recorded hourly from 2012 through 2016 at the South Campus Farm. During the first
experimental year (16 Sep. 2014 to 15 Sep. 2015) $T_a$ remained 1 – 2 °C higher than historical
(1981 – 2010) averages (Lin et al., 2018) (Table 4). Precipitation was slightly higher than
historical averages during autumn and winter, but was about one-half those during spring and
summer. During the second experimental year (16 Sep. 2015 to 15 Sep. 2016), $T_a$ was higher
than that of the first year during winter and early spring, and similar during late spring and
summer. However precipitation during the second year was lower from autumn to early spring
and much higher during late spring and summer.

3.2. $\mathrm{N}_2\mathrm{O}$ Flux Measurements

$\mathrm{N}_2\mathrm{O}$ fluxes were measured at 3-h intervals from as soon as possible field conditions allowed
after spring thaw to late summer during both experimental years with automated chambers
(height 26 cm, area 0.216 m$^2$) connected by 0.5 cm i.d. tubes to a FTIR gas analyzer (GASMET
model CX4025, Temet Instruments, Finland) through which air flow was maintained at 5.1 L
min$^{-1}$. During each 20 minute measurement period, the chambers remained open for the first 5
minutes to restore ambient $\mathrm{N}_2\mathrm{O}$ concentrations in the gas analyzer, after which chambers were
closed and $\mathrm{N}_2\mathrm{O}$ concentrations were measured at 10 Hz and averages recorded at 1 minute
intervals. Concentrations during the first minute after closure were discarded and those during
the following 14 minutes were used to calculate fluxes using linear regression with an acceptance
criterion of $R^2 \geq 0.85$. Based on the analytical precision of the gas analyzer, the $\mathrm{N}_2\mathrm{O}$ flux
detection limit was determined to be +/- 0.03 mg N m$^{-2}$ h$^{-1}$.

$\mathrm{N}_2\mathrm{O}$ emissions were also measured once or twice per week from spring thaw to autumn
freezing during both experimental years with manually operated chambers as described in Lin et
al. (2018). The time required for installation of the automated chambers after snowmelt limited
their ability to measure N$_2$O emissions during spring thaw, so that measurements from the manually operated chambers were used to evaluate emissions during these periods.

4. MODEL EXPERIMENT

4.1. Model Spinup

To simulate site conditions prior to the experiment, ecosys was initialized with the properties of the Black Chernozem, simulated as a one-dimensional profile (Table 2) with surface water runoff and subsurface water exchange with a water table at 1.2 m depth, and the model was run from model dates 1 Jan. 1992 to 31 Dec. 2013 under a repeating 5-year sequence of weather data (radiation, air temperature ($T_a$), humidity, windspeed and precipitation recorded hourly from 2012 through 2016 at the South Campus Farm. The soil was During each year of the spinup run, barley was planted, fertilized and harvested as silage to reproduce land use practices reported from the field site.

4.2. Model Runs

The spinup run was extended from 1 Jan. 2014 to 31 Dec. 2016 under weather data recorded from 2014 to 2016 with the land use schedules and practices from the field site (Table 3). Each modelled slurry application was added to the soil layer the depth of which corresponded to that of slurry injection in the field experiment (14 cm). Modelled applications were accompanied by addition of water corresponding to the volume and depth of the application (5.6 mm from 56.17 m$^3$ ha$^{-1}$ at 14 cm in Sec. 3.1), and by tillage using a coefficient for surface litter incorporation and soil mixing of 0.2 to the depth of application (14 cm), based on field observations. A control run was also conducted in which no slurry applications were modelled. For all silage harvests, cutting height and harvest efficiency were set to 0.15 m and 0.9, so that 0.9 of all plant material above 0.15 m was removed as yield. Concentrations of NH$_4^+$ and NO$_3^-$, and N$_2$O emissions modelled during key emission events, were compared with measured values (Sec. 3.1 and 3.2), and modelled emissions were then aggregated into seasonal and annual values.

There is some flexibility in the timing of fall slurry application between crop harvest in late summer and soil freezing in early November. To examine how timing of fall slurry application
would affect subsequent N$_2$O emissions with and without NI, fall slurry application dates were advanced or delayed by 2 weeks from those in Table 3, and effects on spring and annual N$_2$O emissions were evaluated. To examine how increased tillage during slurry application would affect subsequent N$_2$O emissions with and without NI, coefficients for surface litter incorporation and soil mixing to the depth of slurry application were raised from 0.2 to 0.5 and 0.8 for fall and spring applications.

5. RESULTS

5.1. NI and Soil NH$_4^+$ and NO$_3^-$ Concentrations

5.1.1. Fall Slurry Applications

In the model, NI slowed NH$_4^+$ oxidation (Sec. 2.9, Eq. 3) so that declines in NH$_4^+$ concentrations modelled and measured after fall and spring slurry applications with NI were slower than those without NI (Fig. 2a), particularly during winter when declines in inhibition were slowed by low $T_s$ (Sec. 2.9, Eq. 1) following the onset of soil freezing modelled at the depth of slurry injection (DOY 313 in 2014 and DOY 318 in 2015 in Fig. 2a). Overwinter declines in NH$_4^+$ concentrations were slower during the winter of 2015/2016 with lower $T_s$ modelled under less winter precipitation and hence shallower snowpack (Table 4). These slower declines caused larger NH$_4^+$ concentrations to be modelled during the following spring, consistent with measurements (Fig. 2a). The slower declines in NH$_4^+$ concentrations modelled with NI caused slower rises in NO$_3^-$ concentrations following fall slurry applications (Fig. 2c). However slower rises with NI were not always apparent in the measured NO$_3^-$ concentrations.

5.1.2. Spring Slurry Applications

Declines in NH$_4^+$ concentrations modelled after slurry applications with NI in spring 2015 and 2016 were also slower than after those without NI (Fig. 2b), consistent with higher NH$_4^+$ concentrations measured after spring application with DMPP in both years (Fig. 2b). These slower declines caused slower rises in NO$_3^-$ concentrations to be modelled following spring slurry applications with NI (Fig. 2d).
5.2. NI and Soil Gas Concentrations

5.2.1. Fall Slurry Applications

In the model, soil ice impeded drainage during spring snowmelt and soil thaw, raising \( \theta_w \) and lowering \( \theta_g \), and thereby slowing gas transfers in gaseous phases and gas exchanges between gaseous and aqueous phases (Sec. 2.11 step 1, 2) (Sec. 2.3 step 3; Fig. 1).

Freeze-thaw effects on \( \text{N}_2\text{O} \) emissions modelled during early spring are further described in Grant and Pattey (1999). Slower \text{O}_2 transfers relative to \text{O}_2 uptake (Sec. 2.3, 2.5 and 2.6) forced reductions in aqueous \text{O}_2 concentrations (\( \text{O}_2s \)) to be modelled during early spring in 2015 (Fig. 3a,b) and 2016 (Fig. 3c,d) following fall slurry applications in 2014 and 2015. Declines in aqueous \( \text{O}_2 \) (\( \text{O}_2s \)) were later but more rapid in 2015 than in 2016, following greater winter precipitation and hence greater snowmelt in 2014/2015 (Table 4). Earlier and more persistent declines in \( \text{O}_2s \) were modelled in 2016 because greater \( \theta_i \) modelled with less thermal insulation under a shallower snowpack (Sec. 2.11 step 2) reduced or eliminated \( \theta_g \) during much of the winter. Drainage of meltwater after snowmelt eventually lowered \( \theta_w \) and raised \( \theta_g \), allowing \( \text{O}_2s \) to return to atmospheric equivalent concentrations.

Declines in \( \text{O}_2s \) in slurry-amended treatments drove increases in aqueous \( \text{N}_2\text{O} \) concentrations (\( \text{N}_2\text{O}_s \)) (Fig. 3b,d) during winter and early spring (Sec. 2.7, step 1). These rises were similar with and without NI, in spite of higher \( \text{NH}_4^+ \) concentrations without NI (Fig. 2a). Rises in \( \theta_g \) following spring drainage allowed volatilization of \( \text{N}_2\text{O} \) from aqueous to gaseous phases (Sec. 2.11 step 1), reducing \( \text{N}_2\text{O}_s \) and driving \( \text{N}_2\text{O} \) emissions modelled during spring thaw.

5.2.2. Spring Slurry Applications

Declines in \( \text{O}_2s \) modelled after spring slurry application were small during the drier spring of 2015 (Table 4) (Fig. 3e), but were greater with lower \( \theta_g \) during the wetter spring of 2016 (Fig. 3g) (Sec. 2.11). During both years, these declines were more rapid with slurry than without, but less rapid with NI-amended slurry than with unamended slurry. Greater declines in \( \text{O}_2s \) modelled in 2016 vs. 2015 drove greater increases in \( \text{N}_2\text{O} \) (Sec. 2.7), particularly without NI, and hence greater emissions of \( \text{N}_2\text{O} \) (Sec. 2.11) during subsequent declines in \( \text{N}_2\text{O}_s \).

5.3. NI and \( \text{N}_2\text{O} \) Fluxes
5.3.1. Fall Slurry Applications

Smaller rises and subsequent declines in N$_2$O modelled with NI than without (Fig. 3b) drove smaller N$_2$O emission events modelled during spring thaw in 2015 (Fig. 4a) following slurry application in fall 2014 (Fig. 4b). These events were driven by increases in $\theta_g$ during midafternoon thawing of near-surface soil (Sec. 2.11 step 1), but were terminated by loss of $\theta_g$ during nighttime refreezing. These events preceded the start of the automated chamber measurements on DOY 102 and so could not be corroborated by them. However measurements with manual chambers earlier in spring 2015 by Lin et al. (2018) indicated that N$_2$O emission events occurred from DOY 85 to 100 that were similar in magnitude although not always in timing with those modelled (Fig. 4b). These measured emissions were smaller with NI than without, consistent with modelled emissions.

The smaller rises and subsequent declines in N$_2$O modelled with NI than without in the winter of 2016 (Fig. 3d) drove smaller emission events during thawing and refreezing of near-surface soil in spring 2016 (Fig. 5a) following slurry application in fall 2015 (Fig. 5b). These modelled events preceded the start of automated chamber measurements on DOY 91, but earlier measurements with manual chambers indicated N$_2$O emission events occurred from DOY 74 to 93. The smaller emission events modelled with NI were consistent with those measured using the manual chambers, although some larger emissions measured with DMPP using the automated chambers from DOY 91 to 102 were not modelled (Fig. 5b). In both years, emissions modelled and measured without slurry remained very small, consistent with low N$_2$O (Fig. 3b,f).

5.3.2. Spring Slurry Applications

Modelled N$_2$O emissions closely followed measured values during a brief emission event following slurry application in the drier spring of 2015 (Fig. 6a,b), driven by small rises and declines in N$_2$O (Fig. 3f). The smaller rise and decline in N$_2$O modelled with NI than without drove smaller N$_2$O emissions which declined more rapidly after application than did emissions measured with DMPP (Fig. 6b).

Emissions modelled without NI in the wetter spring of 2016 were larger than those in the drier spring of 2015 (Fig. 7a,b), driven by a larger rise and decline in N$_2$O with lower $\theta_g$ (Fig.
These emissions were suppressed by low $\theta$ with soil wetting during heavy rainfall on DOY 141 – 143 shortly after slurry application (Fig. 7a,b), but resumed when $\theta$ rose with soil drainage thereafter (Fig. 7b). Emissions modelled without NI remained greater than those measured until DOY 150, after which modelled values declined with soil drying while measured value rose (Fig. 7b). Greater reductions in $\text{N}_2\text{O}$ after slurry application in the wetter spring of 2016 (Fig. 7b) than in the drier spring of 2015 (Fig. 6b). In both years, emissions modelled and measured without slurry remained very small, consistent with low $\text{N}_2\text{O}$ (Fig. 3f,h).

### 5.4. NI Effects on Seasonal and Annual $\text{N}_2\text{O}$ Emissions

#### 5.4.1. Modelled vs. Measured $\text{N}_2\text{O}$ Emissions after Spring Slurry Applications

Total $\text{N}_2\text{O}$ emissions modelled without NI and with NI using $R_1$ for DMPP or nitrapyrin (Sec. 2.9) were compared with those aggregated from automated chamber measurements over 30-day periods after spring slurry applications in 2015 and 2016 (Table 5). Total emissions modelled and measured without NI were greater during the wetter spring of 2016 than during the drier spring of 2015. Reductions in 30 d emissions modelled and measured with $R_1$ for DMPP and nitrapyrin were greater during the wetter spring in 2016 (53% and 41%) than during the drier spring in 2015 (35% and 30%). These reductions were somewhat smaller than those measured with DMPP and nitrapyrin in 2016 (72% and 64%) and 2015 (45% and 36%). Emissions were not measured with automated chambers after fall slurry applications, preventing comparisons with modelled values.

#### 5.4.2. Seasonal and Annual $\text{N}_2\text{O}$ Emissions Modelled After Fall and Spring Slurry Applications

##### 5.4.2.1. Fall Slurry Applications

NI greatly reduced $\text{N}_2\text{O}$ emissions modelled from fall applications during autumn (16 Sep. – 31 Dec. in Table 6) in 2014 and 2015, slightly reduced $\text{N}_2\text{O}$ emissions modelled during the following winter and early spring (1 Jan. – 30 Apr.), but slightly raised $\text{N}_2\text{O}$ emissions modelled during the following summer (1 May – 15 Sep.) in both 2015 and 2016. Annual emissions modelled with NI were reduced from those without NI by 26% and 38% in 2014/2015 and 2015/2016 respectively (Table 6). The reduction modelled in 2014/2015 was similar to one of
23% estimated for DMPP from manual chamber measurements from 1 Oct. 2014 to 30 Sep. 2015 by Lin et al. (2018), although the reduction with NI modelled in 2015/2016 was greater than one of 15% estimated from manual chamber measurements from 1 Oct. 2015 to 30 Sep. 2016.

5.4.2.2. Spring Slurry Applications

Reductions in annual N₂O emissions modelled from spring slurry applications with DMPP and nitrapyrin occurred almost entirely during late spring and summer (1 May – 15 Sep. in Table 6). These reductions were 22% and 40% from those modelled without NI in 2014/2015 and 2015/2016 respectively (Table 6). The reduction modelled with NI in 2014/2015 was greater than one of 0% for DMPP estimated from manual chamber measurements from 1 Oct. 2014 to 30 Sep. 2015 by Lin et al. (2018), although the reduction modelled in 2015/2016 was similar to one of 38% estimated from manual chamber measurements from 1 Oct. 2015 to 30 Sep. 2016.

5.5. Effects of Management on Seasonal and Annual N₂O Emissions Modelled After Fall and Spring Slurry Applications

Advancing fall slurry application by 2 weeks increased N₂O emissions modelled with and without NI during autumn but reduced those during subsequent spring thaw (F -2 in Table 6) so that annual emissions modelled with and without NI were similar to those in F with the application dates in the experiment (Table 3). Delaying fall slurry application by 2 weeks reduced N₂O emissions modelled with and without NI only slightly during autumn, but greatly increased emissions modelled during subsequent spring thaw (F +2 in Table 6), particularly with the later fall application in 2016 (Table 3). Consequently delaying fall slurry application by 2 weeks caused substantial increases in annual N₂O emissions. However reductions in N₂O emissions modelled with NI in F +2 in 2015 and 2016 (34% and 47%) were greater than those in F (26% and 38%), because inhibition declined more slowly in colder soil (Eq. 1), particularly with later application in 2016.

Increasing surface litter incorporation and soil mixing during fall slurry application raised N₂O emissions modelled without NI only slightly during 2014/2015, but substantially during 2015/2016, particularly during spring thaw (F 0.5 and F 0.8 vs. F in Table 6). Increasing surface
litter incorporation and soil mixing during spring slurry application had limited effects on emissions (S 0.5 and S 0.8 vs. S in Table 6). Greater mixing caused reduced N\textsubscript{2}O emissions modelled with NI to be smaller relative to those without NI.

5.6. NI Effects on Annual Mineral N Losses and NH\textsubscript{3} Emissions

Injecting the slurry to 14 cm in the model suppressed NH\textsubscript{3} emissions with limited soil mixing, and caused only very small emissions with greater mixing (Table 7). Higher NH\textsubscript{4}\textsuperscript{+} concentrations modelled with NI (Fig. 2a,b) increased net NH\textsubscript{3} emission, particularly if fall slurry application was delayed or soil mixing was increased in 2014/2015.

The subhumid climate at Edmonton (Table 4) caused modelled NO\textsubscript{3} losses to remain small. For both fall and spring applications, lower NO\textsubscript{3} concentrations modelled with NI (Fig. 2c,d) caused small reductions in NO\textsubscript{3} losses.

5.7. NI Effects on Barley Silage Yields

Silage yields modelled with fall slurry application were smaller than those measured in the drier year 2015, but those modelled with both applications were greater than those measured in the wetter year 2016, likely because of lodging observed in the field plots following the second year of heavy manure use (Table 8). Modelled yields were unaffected by NI for fall and spring applications in both years, although measured yields were raised by NI with spring application in 2015. Modelled yields were affected by the cutting height and harvest efficiency set in the model runs (Sec. 4.2).

6. DISCUSSION

6.1. Process Modelling of N\textsubscript{2}O Emissions

N\textsubscript{2}O emissions were driven by declines in gaseous O\textsubscript{2} (O\textsubscript{2g}) and O\textsubscript{2s} modelled by equilibrating O\textsubscript{2} active uptake by autotrophic and heterotrophic oxidation (Sec. 2.5 step 3 and Sec. 2.3 step 3) with O\textsubscript{2} diffusion and dissolution through gaseous and aqueous phases, and dissolution from gaseous to aqueous phases, largely controlled by $\theta_g$ (Sec. 2.11 steps 1–3) (Fig. 1). These O\textsubscript{2} transfers were sustained by concentration gradients from O\textsubscript{2g} to O\textsubscript{2s} and from O\textsubscript{2s} to O\textsubscript{2 at microbial surfaces} (O\textsubscript{2ms}), so that declines in O\textsubscript{2s} (Fig. 3) and O\textsubscript{2ms} were relatively larger.
than those in O$_2$g. These greater declines enabled N$_2$O emissions to be modelled from O$_2$ deficits while O$_2$g remained above one-half of atmospheric concentration, consistent with observations of O$_2$g during N$_2$O emissions from incubation and field experiments (Nguyen et al., 2017; Owens et al., 2017). These O$_2$ deficits were modelled using a $K_m$ for O$_2$m of 10 μM by nitrifiers (Sec. 2.5 step 3) and 2 μM by denitrifiers (Sec. 2.3 step 3) derived from biochemical studies by Focht and Verstraete (1977). These $K_m$ are less than 5% and 1% of atmospheric equivalent concentration, indicating the importance of explicitly simulating gaseous and aqueous transport processes (Sec. 2.11) when modelling N$_2$O emissions.

O$_2$ deficits were modelled in spring thaw 2015 (Fig. 3a), when diffusion was sharply reduced by soil saturation because drainage from snowmelt and soil thaw was impeded by underlying ice layers. These declines drove N$_2$O generation (Fig. 3b) and emission (Fig. 4b) almost entirely from NO$_2^-$ reduced during spring thaw. O$_2$ deficits were also modelled during winter 2016 when increased $\theta_i$ from soil freezing with lower $T_s$ under a shallower snowpack caused near-surface soil porosity to be fully occupied by ice and water. Consequent loss of $\theta_g$ greatly reduced surface gas exchange (Sec. 2.11) and hence gradually reduced soil O$_2$ concentrations, particularly with increased O$_2$ demand from fall slurry application (Fig. 3c). The extended period of low O$_2$s prolonged overwinter accumulation of N$_2$O$_s$ after fall slurry application (Fig. 3d).

Transient increases in $\theta_g$ during soil freeze-thaw cycles caused several N$_2$O emission events to be modelled during spring thaw in 2016, mostly from degassing through volatilization of overwinter N$_2$O$_s$ (Fig. 5b) (Sec. 2.11 step 4). Degassing events in the model were consistent with field observations by Chantigny et al. (2017) that passive degassing of accumulated gases made a significant contribution to spring thaw emissions during which two or more consecutive emission peaks were often observed. In the model, the contribution by degassing of overwinter N$_2$O$_s$ to spring thaw emissions increased with intensity and duration of soil freezing during the previous winter. N$_2$O emissions simulated during spring thaw were thus driven by concurrent NO$_2^-$ reduction during spring thaw (2015) and by earlier NO$_2^-$ reduction accumulated over the previous winter (2015/2016), as has been proposed from experimental observations (Teepe et al., 2004).
O₂ deficits were also caused by rapid increases in O₂ active uptake with addition of labile C in slurry, the rapid decomposition and oxidation of which (Sec. 2.3 step 1) caused transient declines in O₂, with soil wetting from slurry application and precipitation (Fig. 3c,g). After slurry application in the wetter spring of 2016, modelled O₂ declined to ca. one-half of atmospheric concentration, driving the sharp declines in O₂ shown in Fig. 3g. The modelled declines in O₂ were consistent with results from an incubation of wetted soil amended with cattle slurry by Nguyen et al. (2017) in which O₂ declined below one-half of atmospheric concentration within one day of slurry application and gradually rose again after two days, while no decline occurred in an unamended soil. The period of low O₂ in this incubation study coincided with peak emissions of CO₂ and N₂O from the amended soil, as was modelled here in Fig. 3f,h and Fig. 6b and 7b. This co-incidence indicated that NH₄⁺ and DOC oxidation drove O₂ deficits from demand for O₂ from oxidation vs. supply of O₂ through convection – dispersion, which caused NO₂⁻ reduction as represented in the model, again demonstrating the importance of simulating aqueous and gaseous O₂ transfers when modelling N₂O emissions.

6.2. Process Modelling of NI Effects on N₂O Emissions

6.2.1. Fall Slurry Application

NH₄⁺ oxidation in the model (Sec. 2.5 step 4) proceeded rapidly after fall slurry application without NI as indicated by rapid declines in NH₄⁺ (Fig. 2a), consistent with observations in other studies that soil NH₄⁺ concentrations returned to background levels 30 d after fall slurry application (Rochette et al., 2004). Slower NH₄⁺ oxidation modelled with NI (Eq. 3) during fall caused slower declines of soil NH₄⁺ before and during freezing and hence larger NH₄⁺ concentrations during spring thaw (Fig. 2a). These slower declines were modelled from slower decline of I_l with low f_Ts in cold soils (Eq. 1) which slowed NH₄⁺ oxidation and thereby reduced N₂O emissions simulated during late autumn and spring thaw (Figs. 4b and 5b), despite increased NH₄⁺ concentrations (Fig. 32). These reductions were consistent with those from chamber measurements at the Edmonton South Farm (Lin et al., 20172018), and with those from a limited number of studies elsewhere in which persistent effects of NI in reducing overwinter N₂O emissions have been found (e.g. Pfab et al., 2012), indicating the importance of f_Ts in Eq. 1.
The slower decline of \( f_s \) from low \( f_{ts} \) enabled *ecosys* to simulate larger reductions in \( \text{N}_2\text{O} \) emissions with NI after fall slurry applications in cooler soil vs. spring slurry applications in warmer soil during both years (F during autumn vs. S during late spring-summer in Table 6). Reductions in \( \text{N}_2\text{O} \) emissions modelled with NI after fall slurry applications became greater when fall applications were delayed (F+2 in Table 6), further reducing \( T_s \) and \( f_{ts} \) during subsequent nitrification. The greater reductions modelled with fall applications were consistent with experimental observations by Merino et al. (2005) who attributed larger reductions in \( \text{N}_2\text{O} \) emissions measured with NI from fall- vs. spring-applied cattle slurry to slower NI degradation in cooler soil. These modelled and experimental results indicated that NI effectiveness in reducing \( \text{N}_2\text{O} \) emissions varies with the effect of fall slurry timing on \( f_{ts} \).

The greater reductions in \( \text{N}_2\text{O} \) emissions modelled from delayed fall applications with NI were associated with much greater \( \text{N}_2\text{O} \) emissions modelled from delayed fall applications without NI (F+2 in Table 6). These greater emissions were attributed to less \( \text{NH}_4^+ \) oxidation before freeze up in fall, resulting in more \( \text{NH}_4^+ \) remaining to drive \( \text{NH}_4^+ \) oxidation and hence \( \text{N}_2\text{O} \) emissions during spring thaw. These model findings were consistent with field results from Chantigny et al. (2017) in Quebec, and Kariyapperuma et al. (2012) in Ontario, where greater spring \( \text{N}_2\text{O} \) emissions were measured when fall slurry was applied in late November than in early November. These greater spring thaw \( \text{N}_2\text{O} \) emissions were attributed by Kariyapperuma et al. (2012) to greater mineral N concentrations during spring thaw caused by less nitrification before freeze up during the previous fall, as modelled here. The greater \( \text{N}_2\text{O} \) emissions modelled with later slurry application were also driven by more rapid DOC oxidation from more labile manure C remaining during spring thaw. This more labile manure C reduced \([\text{O}_2]\) below that simulated after earlier fall applications (Fig. 3d). NI may therefore be particularly effective in reducing \( \text{N}_2\text{O} \) emissions during spring thaw following late fall slurry applications.

The decreases in \( \text{N}_2\text{O} \) emissions modelled with NI from greater soil mixing (F 0.5 and F 0.8 vs. F in Table 6) were affected by how the redistribution of NI activity with soil mixing was modelled. Simulating this redistribution during tillage requires further consideration and corroboration from observations. These decreases in \( \text{N}_2\text{O} \) emissions with NI were associated with greater \( \text{N}_2\text{O} \) emissions modelled from greater soil mixing without NI in 2016 (F 0.5 and F...
These greater emissions were attributed in the model to longer periods with high $\theta$ and low $\theta_g$ in the upper soil profile caused by greater heat loss through reduced insulation from less surface litter under a shallow snow pack \cite{D12, D13}. This longer period further reduced overwinter $[\text{O}_2\text{s}]$ from that modelled in F (Fig. 3c), causing greater accumulation of $\text{N}_2\text{O}$, and hence greater emissions during thaw. These model findings were consistent with field observations by Congreves et al. \cite{2017} and Wagner-Riddle et al. \cite{2010} that overwinter $\text{N}_2\text{O}$ emissions increased with greater freezing under conventional vs. no tillage, particularly with surface residue removal. Model findings were also consistent with observations by Teepe et al. \cite{2004} that $\text{N}_2\text{O}$ emissions during soil thawing rose sharply with increased duration of soil freezing. Consequent changes in $T_s$ with freezing may alter NI effectiveness with tillage.

### 6.2.2. Spring Slurry Application

Annual $\text{N}_2\text{O}$ emissions modelled without NI from spring applications were smaller than those from fall applications in 2014/2015 with a wetter early spring and drier late spring, and slightly greater in 2015/2016 with a drier early spring and wetter late spring (Table 4), except when fall application was delayed (e.g. F +2 in Table 6). These modelled differences in emissions were consistent with experimental findings that drier springs reduce $\text{N}_2\text{O}$ emissions from fall applications relative to those from spring \cite{2017}. These model results indicate that effects of spring vs. fall slurry applications on annual $\text{N}_2\text{O}$ emissions may not be consistent, but rather will depend on the timing of fall application relative to freeze up, and on precipitation during the following winter and spring.

Amendment of slurry with NI slowed declines in $\text{NH}_4^+$ modelled after spring applications comparably to those measured (Fig. 2b). These slower declines were caused by slower $\text{NH}_4^+$ oxidation that reduced nitrifier growth (Sec. 2.9 Eq. 3) and active $\text{O}_2$ uptake (Sec. 2.5 step 3). Consequently smaller nitrifier biomass and greater $[\text{O}_2\text{s}]$ were modelled with vs. without NI (Fig. 3e,g), particularly with rainfall after spring application in 2016 (Fig. 7a). The smaller nitrifier biomass modelled with NI was consistent with the findings of Dong et al. \cite{2013} that DMPP reduced populations of ammonia oxidizing bacteria in soil incubations. Greater $[\text{O}_2\text{s}]$ modelled with NI was consistent with greater $[\text{O}_2\text{s}]$ measured in an incubation of wetted soil amended with cattle slurry with vs. without DMPP by Nguyen et al. \cite{2017}. Slower nitrifier growth and greater...
both contributed to reductions in N$_2$O emissions modelled with NI beyond those from the
direct effects of $I_t$ on nitrification in Eq. 1, indicating additional effects of NI on N$_2$O emissions
that should be considered in NI models.

The reductions in N$_2$O emissions modelled for 30 d after spring slurry applications with $R_i$
for DMPP and nitrapyrin in 2015 (35% and 30%) and 2016 (53% and 41%) were less than those
measured with automated chambers (Table 5), but within the range of 31% to 44% in meta-
analyses of NI research by Akiyama et al. (2010) and Ruser and Schultz (2015). The greater
reductions modelled in 2016 vs. 2015 (Fig. 7 vs. Fig. 6) were consistent with findings in meta-
analyses by Akiyama et al. (2010) and Gilsanz et al. (2016) that NI was more effective in
reducing N$_2$O emissions from a given land use when emissions were greater. These greater
reductions were attributed in the model to heavy rainfall several days after application in 2016
(Fig. 7a) that extended the N$_2$O emission period (Fig. 7b). During this extension $I_t$ remained high
because [NH$_4^+$] had declined from the large values modelled immediately after application (Eq.
3).

The effects of NI on N$_2$O emissions modelled with greater soil mixing during spring
applications (S 0.5 and S 0.8 vs. S in Table 6) were affected by how the redistribution of NI
activity with soil mixing was modelled, as were those during fall applications. The effects of soil
mixing on N$_2$O emissions without NI modelled from slurry applications in spring were smaller
than those in fall in the absence of soil freezing effects on O$_2$s. These smaller effects were
modelled because tillage in this study involved mixing of injected manure rather than
incorporation of surface-applied manure. These small effects were consistent with an observation
by VanderZaag et al. (2011) that tillage was less important than timing and placement for N$_2$O
emissions from slurry applications.

The reductions in annual N$_2$O emissions modelled after spring slurry applications with $R_i$ for
DMPP and nitrapyrin in 2015 (22% and 17%) and 2016 (40% and 27%) (Table 6) were smaller
than those modelled after 30 d (Table 5) due to gradual degradation of NI effectiveness modelled
with time since application (Eq. 1), indicating the importance of year-round modelling and
measurements to fully assess NI effects on N$_2$O emission factors for IPCC Tier 3 methodology.
However most of the datasets used in meta-analyses of these assessments did not include emissions during autumn, winter and spring thaw (Ruser and Schulz, 2015) which are particularly important for estimating emission factors for NI effects from fall slurry applications in cold climates (Table 6). Ecosystem modelled with well tested simulation of NI effects may make a valuable contribution to these assessments.

6.3. Modelling NI Effects on NH₃ Emissions and Mineral N Losses

The small NH₃ emissions modelled from slurry injection with limited soil mixing (Table 7) were consistent with observations of almost no NH₃ volatilization from closed-slot injection of slurry by Rodhe et al. (2006). In the model, NH₃ emissions with or without NI were sharply reduced by NH₄⁺ adsorption (Sec. 2.10) with diffusion of NH₃ and NH₄⁺ from the injection site (Sec. 2.11). Greater soil mixing brought more NH₄⁺ closer to the surface, reducing NH₄⁺ adsorption and thereby increasing NH₃ emission, particularly from fall applications with NI (Table 7). Consequently only small net increases in NH₃ emissions (Table 7) were modelled with NI from increased volatilization of aqueous NH₃ (Sec. 2.11 step 1) in equilibrium with increased NH₄⁺ concentrations (Fig. 2). However these increases were large in relative terms particularly following fall applications, consistent with increases of 33 – 67% and 3 – 65% relative to emissions without NI derived from meta-analyses of field experiments by Qiao et al. (2015) and Lam et al. (2017) respectively. Increases in NH₃ emissions with NI will thus depend on soil adsorptive properties and depth of slurry incorporation.

The small losses of NO₃⁻, and consequently the small reductions in these losses with NI, modelled in the subhumid climate at the Edmonton South Farm (Table 7) conform to the assumption by De Klein et al. (2006) that NO₃⁻ leaching is an insignificant source of indirect N₂O emission from dryland cropping systems in subhumid climates. Consequently reductions in leaching have minimal impact on the overall effect of NI on N₂O emission in these climates (Lam et al., 2017). Reductions in NO₃⁻ losses modelled with NI would be larger at sites with better drainage and more excess precipitation, although even under these conditions such reductions may be small and inconsistent (Smith et al., 2002).
The increases in NH₃ emissions modelled with NI were larger than reductions in NO₃⁻ leaching (Table 7), indicating that net increases in N₂O emissions from indirect effects of NI will partially offset decreases in N₂O emissions from direct effects. This offset must be included when estimating changes in N₂O emission factors attributed to NI in IPCC Tier 3 methodology.


The simulation of N₂O emissions from nitrification and denitrification in ecosys is based on a comprehensive representation of biological and physical processes governing production and transport of N₂O. Parameters used in these processes are well constrained from basic research so that the model may provide a robust means to predict emissions under diverse climates, soils and land use practices. These processes in ecosys were not changed when adding the algorithm for inhibiting NH₄⁺ oxidation by nitrifiers proposed in Eqs. 1 and 2 (Sec. 2.9). This algorithm used only three parameters, Iₜ₀ and Rᵢ in Eq. [1] and KᵦNH₄ in Eq. [2] with values of 1.0, 2.0 x 10⁻⁴ h⁻¹, and 7000 g N m⁻³ to simulate the time course of NI activity following slurry application. The first two parameters correspond to ones in earlier models of NI for inhibition effectiveness (0.5 – 0.9) and duration (30 – 60 days) (Cui et al., 2014; Del Grosso et al., 2009). These models have given reductions in N₂O emissions with NI in agricultural crops of ca. 25% (Cui et al., 2014), 10% (Del Grosso et al., 2009) or less (Abalos et al., 2016), that are frequently smaller than reductions of 26% – 43% and 24% – 46% derived from meta-analyses of NI effects in agricultural crops by Akiyama et al. (2010) and Gilsanz et al. (2016) respectively. Direct effects on NI of soil water content and pH were not modelled here due to uncertainty in parameterization, although both affect nitrification and hence the magnitude of NI activity.

Each of the parameters used to model NI in ecosys requires further evaluation. A larger Rᵢ, such as that used for nitrapyrin vs. DMPP (Sec. 2.9), caused a more rapid decline of NI activity in soil, and hence greater N₂O emissions with time after slurry application that were consistent with measurements (Tables 5 and 6; Lin et al., 2018). This larger value might represent more rapid degradation of nitrapyrin through volatilization (Ruser and Schulz, 2015), although meta-analyses of N₂O reductions with NI indicate that those with nitrapyrin are similar to those with DMPP. The value of Rᵢ used for NI in the model will thus likely be product specific. The effect of Tₛ on Rᵢ might reasonably be represented by fᵣᵢ as is the effect of Tₛ on all other biological
reactions in the model. This function allowed modelled NI activity to persist overwinter (Fig. 2) and hence reduce N_{2}O emissions modelled during spring thaw (Fig. 6 and Fig. 7). However the effects of temperature on reductions in N_{2}O emission with NI over time are sometimes unclear in controlled studies (Kelliher et al., 2008).

The value of \( I_{t=0} \) set the value of \( I_t \) at the time of slurry application, after which \( I_t \) underwent first order decline over time according to Eq. 1 (Sec. 2.9). The current value of 1.0 indicates complete inhibition at the time of application, but might be reduced if the amount of NI at application is less than that required for complete inhibition. However \( I_t \) had to remain large enough to reduce N_{2}O emissions from nitrification for several weeks after application (Figs. 6 and 7) even with higher soil NH_{4}^{+} concentrations (Fig. 2). Lowering \( I_{t=0} \) from 1.0 to 0.8, similar to that in earlier NI models in which \( I_t \) decline was not simulated, increased N_{2}O emissions modelled over 30 days after spring slurry applications by 7\% in 2015 and 25\% in 2016 (Table 9).

The value of \( K_{NH4} \) in Eq. 2 reduced \( I_t \) with the very large NH_{4}^{+} concentrations modelled immediately after injecting slurry with large NH_{4}^{+} content (Table 3) into small bands (Sec. 3.1). The use of \( K_{NH4} \) was suggested by the findings of Janke et al. (2019) that NI may not have the expected impacts on N transformations and availability when applied in a concentrated band with large NH_{4}^{+} concentrations (up to 12 kg N Mg^{-1}), similar to those modelled immediately after slurry application in this study. The modelled NH_{4}^{+} concentrations declined rapidly after application through diffusion (Sec. 2.11), adsorption (Sec. 2.10) and nitrification (Sec. 2.5), and thus so did \( K_{NH4} \) effects on inhibition. The value of \( K_{NH4} \) in Eq. 2 therefore governed NI effects modelled during the brief periods of rapid N_{2}O emissions following application (ca. 3 days in Figs. 6 and 7), but had sharply diminishing impacts on NI effects modelled thereafter. An alternative hypothesis for reduced inhibition by NI immediately after application might be more rapid diffusion of NH_{4}^{+} than NI from the band, leading to spatial separation (Ruser and Schulz, 2015), although parameterization of this hypothesis is uncertain. Halving or doubling \( K_{NH4} \) from the value set in Sec. 2.9 raised or lowered N_{2}O emissions modelled over 30 days after spring slurry applications by 7 – 8\% in 2015 and 2016 (Table 9), indicating some latitude in evaluating this parameter.
Reductions in \( \text{N}_2\text{O} \) emissions modelled with all proposed values of \( I_{t=0} \) and \( K_{\text{NH}_4} \) varied from 27% to 41% in 2015, and from 38% to 57% in 2016 (Table 9), close to the range of 42.6% \( \pm \) 5.5% derived from meta-analyses of NI effects with cattle slurry by Gilsanz et al. (2016). Further evaluation of these parameters should be undertaken in future studies in which measurements are taken at higher frequencies (e.g. Figs. 6 and 7) required to assess \( \text{N}_2\text{O} \) emissions and NI effects on them.

6.5. Modelling NI Effects on \( \text{N}_2\text{O} \) Emissions: Outstanding Issues

Several issues remain to be addressed in modelling \( \text{N}_2\text{O} \) emissions and NI effects on these emissions. Accurately modelling emissions during spring thaw depended upon accurately modelling soil freezing and thawing following snow melt, and their effects on soil O\(_2\) transfer. A small delay of 2–3 days in modelled thawing caused some small emission events measured in early spring of 2015 to be missed (Fig. 4b). However because modelled emissions were driven by overwinter accumulation of \( \text{N}_2\text{O} \) (Fig. 3), seasonal emissions were less affected by such delays than were emissions from individual events. Algorithms for modelling snowpack accumulation and ablation in *ecosys* are being further refined to improve simulation of soil freezing and thawing. Accurately modelling emissions during later spring depended upon accurately modelling soil wetting and drying following rainfall, and their effects on soil O\(_2\) transfer. Soil wetting from heavy precipitation typically drives \( \text{N}_2\text{O} \) emission events following soil N additions, as modelled here during DOY 143–146 in 2016, although such events were not always measured (Fig. 7b). Such wetting caused sharp declines in O\(_2\) when soil water content rose above a critical threshold, driving \( \text{N}_2\text{O} \) generation and subsequent emission (Fig. 3). However modelling these thresholds depends on soil hydrological properties used in the model (Table 2) which may not be known with sufficient accuracy.

Modelling NI effects on \( \text{N}_2\text{O} \) emissions depended upon \( I_{t=0} \) (Eq. 1) and \( K_{\text{NH}_4} \) (Eq. 2) as evaluated in Sec. 6.4 and Table 9, but also on the time course for declining NI activity governed by the first order rate constant \( R_I \) and its temperature dependence \( f_{Ts} \) (Eq. 1). NI activity modelled with \( R_I \) and \( f_{Ts} \) in this study reduced nitrification alone (Sec. 2.9), which enabled higher \([\text{NH}_4^+]\) and lower \([\text{NO}_3^-]\), and hence greater \( \text{NH}_3 \) emissions, to be simulated with NI after amendment as has been found in field studies (Fig. 2). These higher \([\text{NH}_4^+]\) required a low value
of $R_I$ so that NI activity would persist in reducing nitrification and hence $N_2O$ emissions after soil amendment. This model of NI activity contrasted with that in a more complex model in which NI reduced $N_2O$ emissions directly, rather than through nitrification (Li et al., 2020). In such a model, NI would not directly affect $[NH_4^+]$ and $[NO_3^-]$ so that greater values of $R_I$ could be used to get similar reductions in $N_2O$ emissions. The values of $R_I$ and $f_{Ts}$ used in our model caused $N_2O$ emissions modelled with NI to decline more rapidly than those measured following spring applications (Fig. 6b and Fig. 7b). These values need to be constrained by further studies with more frequent measurements of declines in NI activity following amendment to determine if alternative models for the time course of these declines might be considered.

7. CONCLUSIONS

(a) A simple, time-dependent algorithm for adding NI effects on $N_2O$ emissions into the existing model ecosys has been presented.

(b) The direct effect of NI on $N_2O$ emissions in the model was confined to the inhibition of $NH_4^+$ oxidation

(c) Additional effects of NI on $N_2O$ emissions were caused by slower nitrifier growth and $O_2$ uptake. The combined effects in (b) and (c) reduced $N_2O$ emissions by 35% - 58% depending on seasonal weather and time of manure application.

(d) Slower nitrification modelled with this algorithm caused increases in soil $NH_4^+$ concentrations and reductions in soil $NO_3^-$ concentrations and $N_2O$ fluxes that were consistent with those measured following fall and spring applications of slurry over two years.

(e) NI in the model remained effective in reducing $N_2O$ emissions modelled during spring thaw, particularly when these emissions were increased by delaying fall slurry applications or increasing fall tillage intensity

(f) NI in the model increased $NH_3$ emissions more than it reduced $NO_3^-$ leaching, causing indirect effects on $N_2O$ emissions that partially offset direct effects.

(g) NI had no significant effect on modelled or measured barley silage yields.

(h) Some further work is needed to corroborate parameters in the NI algorithm under a wider range of site conditions.
(i) The addition of NI to *ecosys* may allow emission factors for different NI products to be derived from annual N₂O emissions modelled under diverse site, soil, land use and weather as required in IPCC Tier 3 methodology.

**ACKNOWLEDGEMENTS**

High performance computing facilities for *ecosys* were provided by Compute Canada ([www.computecanada.ca](https://www.computecanada.ca)) through the WestGrid computing network ([https://www.westgrid.ca](https://www.westgrid.ca)). Field measurements were supported by the Alberta Livestock and Meat Agency Ltd. (2014E017R), Climate Change and Emissions Management Corporation (0019083), Dow AgroSciences (0022950), and Eurochem Agro (0027592).

**LIST OF REFERENCES**


Table 1: List of supplements in the Supporting Material

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<th>Supplement</th>
<th>Title</th>
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<td>S8</td>
<td>Inorganic N Transformations</td>
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Table 2: Key soil properties of the Black Chernozem soil at the South Edmonton Farm used in *ecosys*.

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*from Saxton et al. (1986)*
Table 3. Plant and soil management schedule at the Edmonton South Campus Farm

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<td>fall slurry</td>
<td>21.7</td>
<td>16.4</td>
<td></td>
<td></td>
<td>229.4</td>
</tr>
<tr>
<td>2015</td>
<td>11 May</td>
<td>planting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12 May</td>
<td>spring slurry</td>
<td>19.4</td>
<td>20.5</td>
<td></td>
<td></td>
<td>176.9</td>
</tr>
<tr>
<td></td>
<td>28 Jul.</td>
<td>harvest</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>07 Oct.</td>
<td>fall slurry</td>
<td>21.3</td>
<td>19.0</td>
<td></td>
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</tr>
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<td>2016</td>
<td>14 May</td>
<td>planting</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>16 May</td>
<td>spring slurry</td>
<td>27.2</td>
<td>18.6</td>
<td></td>
<td></td>
<td>227.5</td>
</tr>
<tr>
<td></td>
<td>15 Aug.</td>
<td>harvest</td>
<td></td>
<td></td>
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Table 4. Average temperatures and total precipitation measured at the Edmonton South Farm during autumn/winter, winter/spring and spring/summer in 2014/2015 and 2015/2016.

<table>
<thead>
<tr>
<th></th>
<th>2014 Average</th>
<th>2015 Average</th>
<th>2014/5 Total</th>
<th>2015 Average</th>
<th>2016 Average</th>
<th>2015/6 Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>from</td>
<td>16 Sep</td>
<td>1 Jan</td>
<td>1 May Average</td>
<td>16 Sep</td>
<td>1 Jan</td>
<td>1 May Average</td>
</tr>
<tr>
<td>to</td>
<td>31 Dec</td>
<td>30 Apr</td>
<td>15 Sep Total</td>
<td>31 Dec</td>
<td>30 Apr</td>
<td>15 Sep Total</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>0.4</td>
<td>-1.8</td>
<td>16.0</td>
<td>5.6</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Precip. (mm)</td>
<td>50</td>
<td>75</td>
<td>195</td>
<td>320</td>
<td>41</td>
<td>38</td>
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</table>
Table 5: Seasonal N₂O emissions measured and modelled during late spring in 2015 and 2016 without slurry (C) or with slurry applied in spring (S) without NI, with nitrapyrin or with DMPP on dates in the field study (Table 3). Negative values denote emissions, positive values uptake.

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>C</td>
<td>none</td>
<td>+3</td>
<td>-1</td>
<td>+14</td>
<td>-5</td>
</tr>
<tr>
<td>2016</td>
<td>S</td>
<td>none</td>
<td>-88</td>
<td>-89</td>
<td>-160</td>
<td>-153</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>DMPP</td>
<td>-48</td>
<td>-58</td>
<td>-45</td>
<td>-72</td>
</tr>
<tr>
<td></td>
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<td>nitrapyrin</td>
<td>-56</td>
<td>-62</td>
<td>-57</td>
<td>-91</td>
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</table>
Table 6: Seasonal and annual N₂O emissions modelled during autumn/winter, winter/spring and spring/summer in 2014/2015 and 2015/2016 without slurry (C) or with slurry applied in fall (F) or spring (S) without NI or with R for DMPP on dates in the field study (Table 3), and in fall on dates 2 weeks before (F-2) or after (F+2) those in the field study, and with soil mixing during slurry application (M) increased to 0.4 and 0.6 from 0.2 in the field study. Negative values denote emissions.

<table>
<thead>
<tr>
<th>Year to</th>
<th>Treat.</th>
<th>Amend.</th>
<th>2014</th>
<th>2015</th>
<th>2014/5</th>
<th>2015</th>
<th>2016</th>
<th>2015/6</th>
</tr>
</thead>
<tbody>
<tr>
<td>from</td>
<td>16 Sep</td>
<td>1 Jan</td>
<td>1 May</td>
<td>Total</td>
<td>16 Sep</td>
<td>1 Jan</td>
<td>1 May</td>
<td>Total</td>
</tr>
<tr>
<td>31 Dec</td>
<td>30 Apr</td>
<td>15 Sep</td>
<td></td>
<td></td>
<td>31 Dec</td>
<td>30 Apr</td>
<td>15 Sep</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-2</td>
<td>-10</td>
<td>-14</td>
<td>-26</td>
<td>-2</td>
<td>-11</td>
<td>-13</td>
<td>-26</td>
</tr>
<tr>
<td>F</td>
<td>DMPP</td>
<td>-39</td>
<td>-68</td>
<td>-29</td>
<td>-136</td>
<td>-41</td>
<td>-50</td>
<td>-30</td>
</tr>
<tr>
<td>F</td>
<td>nitrapyrin</td>
<td>-50</td>
<td>-101</td>
<td>-20</td>
<td>-171</td>
<td>-48</td>
<td>-61</td>
<td>-29</td>
</tr>
<tr>
<td>S</td>
<td>none</td>
<td>-2</td>
<td>-10</td>
<td>-119</td>
<td>-131</td>
<td>-3</td>
<td>-25</td>
<td>-182</td>
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<tr>
<td>S</td>
<td>DMPP</td>
<td>-2</td>
<td>-10</td>
<td>-90</td>
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<td>-3</td>
<td>-18</td>
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</tr>
<tr>
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<td>nitrapyrin</td>
<td>-2</td>
<td>-10</td>
<td>97</td>
<td>-109</td>
<td>-3</td>
<td>-24</td>
<td>-126</td>
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<tr>
<td>F-2</td>
<td>none</td>
<td>-102</td>
<td>-64</td>
<td>-17</td>
<td>-183</td>
<td>-137</td>
<td>-47</td>
<td>-26</td>
</tr>
<tr>
<td>F+2</td>
<td>none</td>
<td>-92</td>
<td>-111</td>
<td>-17</td>
<td>-220</td>
<td>-84</td>
<td>-189</td>
<td>-52</td>
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<td>F 0.5</td>
<td>none</td>
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<td>-71</td>
<td>-16</td>
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<td>-22</td>
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<tr>
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<td>DMPP</td>
<td>-58</td>
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<td>-17</td>
<td>-152</td>
<td>-59</td>
<td>-111</td>
<td>-20</td>
</tr>
<tr>
<td>F 0.8</td>
<td>none</td>
<td>-102</td>
<td>-81</td>
<td>-21</td>
<td>-204</td>
<td>-98</td>
<td>-184</td>
<td>-19</td>
</tr>
<tr>
<td>F 0.8</td>
<td>DMPP</td>
<td>-65</td>
<td>-76</td>
<td>-18</td>
<td>-159</td>
<td>-69</td>
<td>-138</td>
<td>-18</td>
</tr>
<tr>
<td>S 0.5</td>
<td>none</td>
<td>-2</td>
<td>-10</td>
<td>-129</td>
<td>-141</td>
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<td>-27</td>
<td>-168</td>
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<tr>
<td>S 0.5</td>
<td>DMPP</td>
<td>-2</td>
<td>-10</td>
<td>-98</td>
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<td>-3</td>
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<td>-124</td>
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<tr>
<td>S 0.8</td>
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<td>-2</td>
<td>-10</td>
<td>-138</td>
<td>-150</td>
<td>-3</td>
<td>-25</td>
<td>-168</td>
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<tr>
<td>S 0.8</td>
<td>DMPP</td>
<td>-2</td>
<td>-10</td>
<td>-102</td>
<td>-114</td>
<td>-3</td>
<td>-19</td>
<td>-123</td>
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</table>
Table 7: Annual NO$_3^-$ discharge and NH$_3$ emissions modelled from 16 Sep. to 15 Sep. in 2014/2015 and 2015/2016 without slurry (C) or with slurry applied in fall (F) or spring (S) without NI and with DMPP on dates in the field study (Table 3), and in fall on dates 2 weeks before (F-2) or after (F+2) those in the field study, and with soil mixing during slurry application (M) increased to 0.5 and 0.8 from 0.2 in the field study. For NH$_3$ positive values indicate deposition, negative values emission.

<table>
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<tr>
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<th>NH$_3$</th>
<th>NO$_3^-$</th>
<th>NH$_3$</th>
<th>NO$_3^-$</th>
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<td>C</td>
<td>+14</td>
<td>277</td>
<td>+34</td>
<td>421</td>
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<td>F none</td>
<td>+7</td>
<td>330</td>
<td>+29</td>
<td>691</td>
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<td>F DMPP</td>
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<td>317</td>
<td>+13</td>
<td>662</td>
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<tr>
<td>S none</td>
<td>+8</td>
<td>279</td>
<td>+21</td>
<td>617</td>
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<td>S DMPP</td>
<td>+4</td>
<td>279</td>
<td>+14</td>
<td>598</td>
</tr>
<tr>
<td>F-2 none</td>
<td>+4</td>
<td>336</td>
<td>+26</td>
<td>678</td>
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<td>F-2 DMPP</td>
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<td>326</td>
<td>+12</td>
<td>658</td>
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<td>F+2 none</td>
<td>+3</td>
<td>336</td>
<td>+28</td>
<td>697</td>
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<td>F+2 DMPP</td>
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<td>+10</td>
<td>662</td>
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<tr>
<td>F 0.5 none</td>
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<td>321</td>
<td>+17</td>
<td>558</td>
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<td>F 0.5 DMPP</td>
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<td>314</td>
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<td>554</td>
</tr>
<tr>
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<td>+1</td>
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<td>370</td>
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<td>+1</td>
<td>490</td>
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<td>-8</td>
<td>493</td>
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<tr>
<td>S 0.8 none</td>
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<td>279</td>
<td>-15</td>
<td>361</td>
</tr>
<tr>
<td>S 0.8 DMPP</td>
<td>-21</td>
<td>279</td>
<td>-26</td>
<td>365</td>
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Table 8: Barley silage yields modelled and measured without slurry (C) or with slurry applied in fall (F) or spring (S) with and without NI applied on dates in the field study (Table 3)

<table>
<thead>
<tr>
<th>Year</th>
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<th>Amend.</th>
<th>2015</th>
<th>2016</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Mod.</td>
<td>Mes.†</td>
</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>154</td>
<td>198 ± 24</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>none</td>
<td></td>
<td>284</td>
<td>355 ± 4</td>
</tr>
<tr>
<td>F</td>
<td>DMPP</td>
<td></td>
<td>283</td>
<td>360 ± 25</td>
</tr>
<tr>
<td>S</td>
<td>none</td>
<td></td>
<td>293</td>
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</tr>
<tr>
<td>S</td>
<td>DMPP</td>
<td></td>
<td>297</td>
<td>317 ± 17</td>
</tr>
</tbody>
</table>

† calculated as 45% DM

†† measured yields reduced by lodging
Table 9: Sensitivity of seasonal N$_2$O emissions modelled during late spring in 2015 and 2016 to changes in initial inhibition ($I_{t=0}$ in Eq. 1) and inhibition constant ($K_{\text{NH}_4}$ in Eq. 2) following spring slurry application on dates in the field study (Table 3). Negative values denote emissions.

<table>
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<tr>
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<th>2016</th>
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<tr>
<td></td>
<td>12 May –</td>
<td>17 May –</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11 June</td>
<td>16 June</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No NI</td>
<td>mg N m$^{-2}$</td>
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</tr>
<tr>
<td>$I_{t=0}$</td>
<td>$K_{\text{NH}_4}$</td>
<td>-89$^a$</td>
<td>-153$^b$</td>
</tr>
<tr>
<td>1.0</td>
<td>7000</td>
<td>-58$^a$</td>
<td>-72$^a$</td>
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<tr>
<td>0.9</td>
<td>7000</td>
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<tr>
<td>0.8</td>
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<td>-90</td>
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<td>-95</td>
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<td>-66</td>
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<td>-75</td>
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<td>0.8</td>
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<td>-85</td>
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</table>

$^a$ from Table 5
Fig. 1. Key transformations governing N$_2$O emissions as represented in ecosys. Expressions in square brackets refer to equations in the Supplement as described in Sec. 2.
(a) fall

(b) spring

(c) fall

(d) spring

NH$_4^+$ (g N Mg$^{-1}$)

NO$_3^-$ (g N Mg$^{-1}$)

DOY since 1 Jan. 2014
Fig. 2. Soil NH$_4^+$ and NO$_3^-$ concentrations measured (symbols) and modelled (lines) at 0 – 10 cm depth following applications of dairy slurry without and with DMPP. Arrows indicate dates of application.

Fig. 3. Aqueous concentrations of O$_2$ and N$_2$O modelled at depth of slurry injection (14 cm) during emission events in early spring of (a,b) 2015 and (c,d) 2016 after fall slurry applications with or without DMPP on DOY 273 in 2014 and DOY 280 in 2015, and in later spring of (e,f) 2015 and (g,h) 2016 after spring slurry applications on DOY 132 in 2015 and DOY 137 in 2016.
Fig. 4. (a) Air temperature and precipitation, and (b) N\textsubscript{2}O fluxes measured (symbols) and modelled (lines) during early spring 2015 with no slurry (control), and following slurry application on DOY 273 in 2014 with or without DMPP. Filled symbols represent manual chamber measurements by Lin et al. (2018). Negative values denote emissions.
Fig. 5. (a) Air temperature and precipitation, and (b) N₂O fluxes measured (symbols) and modelled (lines) during early spring 2016 with no slurry (control), and following slurry application on DOY 280 in 2015 with or without DMPP. Filled symbols represent manual chamber measurements. Negative values denote emissions.
Fig. 6. (a) Air temperature and precipitation, and (b) N\textsubscript{2}O fluxes measured (symbols) and modelled (lines) during spring 2015 with no slurry (control), and following slurry application on DOY 132 in 2015 with or without DMPP. Negative values denote emissions.
Fig. 7. (a) Air temperature and precipitation, and (b) N₂O fluxes measured (symbols) and modelled (lines) during spring 2016 with no slurry (control), and following slurry application on DOY 137 in 2016 with or without DMPP. Negative values denote emissions.