

1 **Modelling Nitrification Inhibitor Effects on N<sub>2</sub>O Emissions after**  
2 **Fall and Spring-Applied Slurry by Reducing Nitrifier NH<sub>4</sub><sup>+</sup>**  
3 **Oxidation Rate**

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7 **ABSTRACT**

8 Reductions in N<sub>2</sub>O emissions from nitrification inhibitors (NI) are substantial, but remain  
9 uncertain because measurements of N<sub>2</sub>O emissions are highly variable and discontinuous.  
10 Mathematical modelling may offer an opportunity to estimate these reductions if the processes  
11 causing variability in N<sub>2</sub>O emissions can be accurately simulated. In this study, the effect of NI  
12 was simulated with a simple, time-dependent algorithm to slow NH<sub>4</sub><sup>+</sup> oxidation in the ecosystem  
13 model *ecosys*. Slower nitrification modelled with NI caused increases in soil NH<sub>4</sub><sup>+</sup>  
14 concentrations and reductions in soil NO<sub>3</sub><sup>-</sup> concentrations and in N<sub>2</sub>O fluxes that were consistent  
15 with those measured following fall and spring applications of slurry over two years from 2014 to  
16 2016. The model was then used to estimate direct and indirect effects of NI on seasonal and  
17 annual emissions. After spring slurry applications, NI reduced N<sub>2</sub>O emissions modelled and  
18 measured during the drier spring of 2015 (35% and 45%) less than during the wetter spring of  
19 2016 (53% and 72%). After fall slurry applications, NI reduced modelled N<sub>2</sub>O emissions by 58%  
20 and 56% during late fall in 2014 and 2015, and by 8% and 33% during subsequent spring thaw in  
21 2015 and 2016. Modelled reductions were consistent with those from meta-analyses of other NI  
22 studies. Simulated NI activity declined over time, so that reductions in N<sub>2</sub>O emissions modelled  
23 with NI at an annual time scale were relatively smaller than those during emission events. These  
24 reductions were accompanied by increases in NH<sub>3</sub> emissions and reductions in NO<sub>3</sub><sup>-</sup> losses with  
25 NI that caused changes in indirect N<sub>2</sub>O emissions. With further parameter evaluation, the

26 addition of this algorithm for NI to *ecosys* may allow emission factors for different NI products  
27 to be derived from annual N<sub>2</sub>O emissions modelled under diverse site, soil, land use and weather.

28

## 29 **1. INTRODUCTION**

30 Nitrification inhibitors (NI) have frequently been found to reduce N<sub>2</sub>O emissions from  
31 fertilizer and slurry applications in agricultural fields. In a meta-analysis of field experiments  
32 conducted to 2008, Akiyama et al. (2010) found average reductions of  $38 \pm 6\%$  in N<sub>2</sub>O emissions  
33 from NI with some variation attributed to land use type and emission rates. Similar average  
34 reductions of 35 - 40% were reported in more recent meta-analyses by Ruser and Schulz (2015),  
35 Gilsanz et al. (2016) and Gao and Bian (2017). However the magnitudes of these reductions are  
36 uncertain because they vary with rate and timing of fertilizer or slurry application, with land use  
37 and ecosystem type (Akiyama et al., 2010) and with application method (Zhu et al., 2016).  
38 These magnitudes are also uncertain because measurements of the N<sub>2</sub>O emissions on which they  
39 are based are highly variable temporally and spatially, and difficult to sustain over the annual  
40 time periods needed to estimate NI reductions.

41 The effects of NI on N<sub>2</sub>O emissions are attributed to inhibition of ammonia  
42 monooxygenase which slows the oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup> during nitrification (Subbarao et al.,  
43 2006), and hence slows the reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O during nitrifier denitrification. The  
44 consequent slowing of NO<sub>2</sub><sup>-</sup> oxidation to NO<sub>3</sub><sup>-</sup> would also slow the reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>O  
45 during denitrification. The effectiveness of NI has been found to decline over time due to  
46 mineralization, adsorption and volatilization, depending on NI formulation. The rate of this  
47 decline varies among NI products and soil types, and increases with soil temperature (Guardia et  
48 al., 2018).

49 The great majority of the studies included in meta-analyses of NI effects on N<sub>2</sub>O  
50 emissions were conducted following fertilizer or slurry application on warm soils in spring or  
51 summer (e.g. Akiyama et al., 2010). The effectiveness of NIs with fall applications of fertilizer  
52 or slurry on cold soils has thus far received very limited attention (Ruser and Schulz, 2015),  
53 although in cold climates N<sub>2</sub>O emissions during the spring thaw following fall applications may

54 exceed those during later spring and summer following spring applications (Lin et al., 2018).  
55 Emissions during spring thaw were attributed by Wagner-Riddle and Thurtell (1998) to soil  
56  $\text{NO}_3\text{-N}$  concentrations exceeding  $20 \text{ mg kg}^{-1}$  generated by fall-applied slurry that contributed to  
57 total  $\text{N}_2\text{O}$  emissions exceeding  $0.2 \text{ g N m}^{-2}$  measured between January and April of the  
58 following year. Large  $\text{N}_2\text{O}$  emissions measured in late winter were attributed by Dungan et al.  
59 (2017) to labile N not used by soil microorganisms during the previous fall and winter that was  
60 actively metabolized when the soils began to warm in early March. Interannual differences in  
61 spring thaw emission events after fall slurry applications were related by Kariyapperuma et al.  
62 (2012) to those in total soil mineral N content in the upper 15 cm of the soil profile during spring  
63 thaw. The effects of NI on  $\text{N}_2\text{O}$  emissions during spring thaw will therefore depend on the  
64 persistence with which NI reduces nitrification in cold soils during fall and winter, and thereby  
65 alters mineral N concentrations during the following spring.

66         Reductions in  $\text{N}_2\text{O}$  emissions directly caused by slower nitrification with NI may be  
67 partially offset by increases in indirect  $\text{N}_2\text{O}$  emissions from increasing  $\text{NH}_3$  emissions caused by  
68 greater soil  $\text{NH}_4^+$  concentrations (Lam et al., 2017, Qiao et al., 2015). NI may also decrease  
69 indirect  $\text{N}_2\text{O}$  emissions by reducing  $\text{NO}_3^-$  concentrations and hence leaching. Both direct and  
70 indirect effects of NI on  $\text{N}_2\text{O}$  emissions must be considered when estimating effects of NI on  
71 total  $\text{N}_2\text{O}$  emissions.

72         IPCC Tier 3 methodology for estimating  $\text{N}_2\text{O}$  emissions under diverse climates, soils,  
73 fertilizers and land uses includes the use of comprehensive, process-based mathematical models  
74 of terrestrial C, N, water and energy cycling (IPCC, 2019). Although NI effects on nitrification  
75 have been added to some existing process models (Cui et al., 2014; Del Grosso et al., 2009, Li et  
76 al., 2020), testing of modelled NI effects on  $\text{N}_2\text{O}$  emissions against measurements remains  
77 limited to brief periods following soil N amendments (e.g. Giltrap et al., 2011). The  
78 mathematical model *ecosys* explicitly represents the key processes in nitrification (Grant, 1994),  
79 denitrification (Grant, 1991) and associated  $\text{N}_2\text{O}$  emissions (Grant, 1995), and has been tested  
80 against measurements of  $\text{N}_2\text{O}$  emissions using micrometeorological methods, and manual and  
81 automated chambers (Grant and Pattey, 1999, 2008; Grant et al., 2006, 2016; Metivier et al.,  
82 2009). In this study, we propose that applying a time-dependent reduction of  $\text{NH}_4^+$  oxidation  
83 rates during nitrification will enable *ecosys* to simulate the time course of reductions in  $\text{N}_2\text{O}$

84 emissions with NI measured after fall and spring applications of dairy slurry in a field  
85 experiment. The model is then used to estimate the direct and indirect effects of NI on annual  
86 N<sub>2</sub>O emissions with fall and spring slurry applications as required for IPCC Tier 3 methodology,  
87 and how these effects would change with alternative tillage practices and timings of slurry  
88 application.

89

## 90 **2. MODEL DEVELOPMENT**

91

### 92 **2.1. General Overview**

93 The hypotheses for oxidation-reduction reactions involving N<sub>2</sub>O, and the aqueous and  
94 gaseous transport of their substrates and products, are represented in Fig. 1 and described in  
95 further detail below. These hypotheses function within a comprehensive model of soil C, N and  
96 P transformations, which is coupled to models of soil water, heat and solute transport in surface  
97 litter and soil layers. These models function within the comprehensive ecosystem model *ecosys*.  
98 Key transformations that drive N<sub>2</sub>O emissions are described in Sections 2.2 to 2.8 below, and  
99 modifications of these transformations to simulate nitrification inhibition are described in  
100 Section 2.9. References to equations and definitions in Sections 2.2 to 2.8 and given in  
101 Supplements S1, S3, S4, S5 and S8 of the Supporting Information (Table 1) are provided for  
102 those interested in model methodology, but are not needed for a general understanding of model  
103 behaviour.

104

### 105 **2.2. Mineralization and Immobilization of Ammonium by Microbial Functional Types**

106 Heterotrophic microbial functional types (MFTs) *m* (obligately aerobic bacteria,  
107 obligately aerobic fungi, facultatively anaerobic denitrifiers, anaerobic fermenters, acetotrophic  
108 methanogens, and obligately aerobic and anaerobic non-symbiotic diazotrophs) are associated  
109 with each organic substrate *i* (*i* = manure, coarse woody plant residue, fine non-woody plant  
110 residue, particulate organic matter, or humus). Autotrophic MFTs *n* (aerobic NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup>  
111 oxidizers, aerobic methanotrophs and hydrogenotrophic methanogens) are associated with  
112 inorganic substrates. These MFTs grow [A25] with energy generated from oxidation of dissolved

113 organic C (DOC) by heterotrophs [H2, H10], of acetate by acetotrophic methanogens, of mineral  
 114 N ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ) [H11, H15] by nitrifiers, of  $\text{CH}_4$  by methanotrophs [G7], or of  $\text{H}_2$  by  
 115 hydrogenotrophic methanogens [G12], coupled with reduction of  $e^-$  acceptors  $\text{O}_2$  [H4, G22],  
 116 acetate [G8],  $\text{NO}_x$  [H7 – H9], and  $\text{CO}_2$  [G13]. These MFTs decay according to first-order rate  
 117 constants [A23] with internal recycling of resources (C, N, P) from structural to nonstructural  
 118 components  $j$  ( $j = \text{labile, recalcitrant, nonstructural}$ ) varying with nonstructural C:N:P ratios  
 119 [A24], the decay products of which form humus C, N and P [A35, A36]. Each MFT seeks to  
 120 maintain a set nonstructural C:N:P ratio by mineralizing  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  [H1a] from, or by  
 121 immobilizing  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  [H1b, H1c] into, its nonstructural N and P components.  
 122 These transformations control the exchange of N and P between organic and inorganic states,  
 123 and of  $\text{O}_2$  between aqueous and gaseous states, and hence affect the availability of substrates and  
 124  $e^-$  acceptors for nitrification and denitrification.

125

### 126 **2.3. Oxidation of DOC and Reduction of Oxygen by Heterotrophs**

127  $\text{N}_2\text{O}$  is generated when demand for  $e^-$  acceptors from oxidation by aerobic heterotrophs  
 128 and autotrophs (Sec. 2.2) exceeds supply from  $\text{O}_2$ , requiring explicit modelling of  $\text{O}_2$  transport  
 129 and uptake, and consequent  $\text{O}_2$  constraints to oxidation-reduction reactions (Fig. 1). Constraints  
 130 on heterotrophic oxidation of DOC imposed by  $\text{O}_2$  uptake are solved in four steps:

- 131 1) DOC oxidation by heterotrophs under non-limiting  $\text{O}_2$  is calculated from specific oxidation  
 132 rates multiplied by active biomasses and an Arrhenius function of  $T_s$  [A6] used for all  
 133 microbial transformations, constrained by DOC concentration [H2],
- 134 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  
 135 from step 1 using a set respiratory quotient [H3],
- 136 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  
 137 films with thicknesses determined by soil water potential [H4a] coupled with active uptake at  
 138 heterotroph surfaces driven by step 2 [H4b]. Diffusion and uptake are sustained by  $\text{O}_2$  transfer  
 139 through soil aqueous and gaseous phases controlled by soil water- and air-filled porosity  
 140 governed by freezing, thawing and transfer of soil water [D14 – D20].  $\text{O}_2$  diffusion and active  
 141 uptake are calculated for each heterotrophic population associated with each organic substrate,  
 142 allowing [H4] to calculate lower  $\text{O}_2$  concentrations at microbial surfaces ( $\text{O}_{2m}$ ) associated with  
 143 more biologically active substrates (e.g. manure, litter). Localized zones of low  $\text{O}_2$

144 concentration (hotspots) are thereby simulated when O<sub>2</sub> uptake by any aerobic MFT is  
 145 constrained by O<sub>2</sub> diffusion to that functional type. O<sub>2</sub> uptake by each heterotrophic MFT is  
 146 affected by competition for O<sub>2</sub> uptake with other heterotrophs, nitrifiers, roots and  
 147 mycorrhizae, calculated from its biological O<sub>2</sub> demand relative to those of other aerobic  
 148 functional types.

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

155

#### 156 **2.4.Oxidation of DOC and Reduction of Nitrate, Nitrite and Nitrous Oxide by** 157 **Denitrifiers**

158 N<sub>2</sub>O may be both product and substrate of NO<sub>x</sub> reduction coupled with DOC oxidation by  
 159 denitrifiers. Constraints imposed by NO<sub>3</sub><sup>-</sup> availability on denitrifier DOC oxidation are solved  
 160 in five steps:

- 161 1) NO<sub>3</sub><sup>-</sup> reduction to NO<sub>2</sub><sup>-</sup> by heterotrophic denitrifiers under non-limiting NO<sub>3</sub><sup>-</sup> is calculated  
 162 from demand for e<sup>-</sup> acceptors by denitrifiers for DOC oxidation to CO<sub>2</sub>, but not met from O<sub>2</sub>  
 163 reduction to H<sub>2</sub>O because of diffusion limitations to O<sub>2</sub> supply (Sec. 2.3 step 3). This unmet  
 164 demand is transferred to NO<sub>3</sub><sup>-</sup> [H6],
- 165 2) NO<sub>3</sub><sup>-</sup> reduction to NO<sub>2</sub><sup>-</sup> under ambient NO<sub>3</sub><sup>-</sup> is calculated from step 1, accounting for relative  
 166 concentrations and affinities of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> [H7],
- 167 3) NO<sub>2</sub><sup>-</sup> reduction to N<sub>2</sub>O under ambient NO<sub>2</sub><sup>-</sup> is calculated from demand for e<sup>-</sup> acceptors not met  
 168 by NO<sub>3</sub><sup>-</sup> reduction in step 2, accounting for relative concentrations and affinities of NO<sub>2</sub><sup>-</sup> and  
 169 N<sub>2</sub>O. This unmet demand is transferred to NO<sub>2</sub><sup>-</sup> [H8].
- 170 4) N<sub>2</sub>O reduction to N<sub>2</sub> under ambient N<sub>2</sub>O is calculated from demand for e<sup>-</sup> acceptors not met by  
 171 NO<sub>2</sub><sup>-</sup> reduction in step 3, and hence transferred to N<sub>2</sub>O [H9].
- 172 5) additional energy yield from DOC oxidation to CO<sub>2</sub> enabled by NO<sub>x</sub> reduction in steps 2, 3  
 173 and 4 is added to that enabled by O<sub>2</sub> reduction from [H5], which drives additional DOC

174 uptake for construction of  $M_{i,n}$ . This additional uptake offsets the disadvantage incurred by the  
 175 larger construction energy costs of denitrifiers (Sec. 2.3 step 4).

176

## 177 **2.5. Oxidation of Ammonium and Reduction of Oxygen by Nitrifiers**

178  $N_2O$  may also be generated by reduction of  $NO_2^-$  coupled with oxidation of  $NH_4^+$  by  
 179 autotrophic nitrifiers. Constraints on nitrifier oxidation of  $NH_4^+$  imposed by  $O_2$  uptake are solved  
 180 in four steps:

- 181 1) Oxidation of  $NH_4^+$  (in dynamic equilibrium with  $NH_3$  [E24]) under non-limiting  $O_2$  is  
 182 calculated from a specific oxidation rate multiplied by active biomass and an Arrhenius  
 183 function of  $T_s$ , and constrained by  $NH_4^+$  and  $CO_2$  concentrations [H11],
- 184 2)  $O_2$  reduction to  $H_2O$  under non-limiting  $O_2$  ( $O_2$  demand) is calculated from step 1 using set  
 185 respiratory quotients [H12],
- 186 3)  $O_2$  reduction to  $H_2O$  under ambient  $O_2$  is calculated from radial  $O_2$  diffusion through water  
 187 films of thickness determined by soil water potential [H13a] coupled with active uptake at  
 188 nitrifier surfaces driven by step 2 [H13b].  $O_2$  uptake by nitrifiers is affected by competition  
 189 for  $O_2$  uptake with heterotrophic DOC oxidizers, roots and mycorrhizae, calculated from its  
 190 biological  $O_2$  demand relative to those of other aerobic functional types.
- 191 4)  $NH_4^+$  oxidation to  $NO_2^-$  under ambient  $O_2$  is calculated from steps 2 and 3 [H14]. The energy  
 192 yield of  $NH_4^+$  oxidation drives the fixation of  $CO_2$  for construction of microbial biomass  $M_{i,n}$   
 193 according to nitrifier construction energy costs.

194

## 195 **2.6. Oxidation of Nitrite and Reduction of Oxygen by Nitrifiers**

196 Constraints on nitrifier oxidation of  $NO_2^-$  to  $NO_3^-$  imposed by  $O_2$  uptake [H15 - H18] are  
 197 solved in the same way as are those of  $NH_4^+$  to  $NO_2^-$  [H11 - H14]. The energy yield of  $NO_2^-$   
 198 oxidation drives the fixation of  $CO_2$  for construction of microbial biomass  $M_{i,o}$  according to  
 199 nitrifier construction energy costs.

200

## 201 **2.7. Oxidation of Ammonium and Reduction of Nitrite by Nitrifiers**

202 In both nitrifier and denitrifier processes,  $N_2O$  is generated from reduction of  $NO_2^-$ , the  
 203 availability of which is controlled by  $NO_2^-$  oxidation (Sec. 2.6). Under low  $O_2$  concentrations

204  $\text{NO}_2^-$  oxidation is suppressed [H18], favoring  $\text{NO}_2^-$  reduction. Constraints on nitrifier oxidation  
 205 of  $\text{NH}_4^+$  imposed by  $\text{NO}_2^-$  availability are solved in three steps:

- 206 1)  $\text{NO}_2^-$  reduction to  $\text{N}_2\text{O}$  under non-limiting  $\text{NO}_2^-$  is calculated from  $e^-$  acceptors demanded by  
 207  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$  but not met by  $\text{O}_2$  for reduction to  $\text{H}_2\text{O}$  because of diffusion  
 208 limitations to  $\text{O}_2$  supply, and hence transferred to  $\text{NO}_2^-$  [H19],
- 209 2)  $\text{NO}_2^-$  reduction to  $\text{N}_2\text{O}$  under ambient  $\text{NO}_2^-$  and  $\text{CO}_2$  is calculated from step 1 [H20],  
 210 competing for  $\text{NO}_2^-$  with denitrifiers [H8] and nitrifiers [H18],
- 211 3) energy yield from additional  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$  enabled by  $\text{NO}_2^-$  reduction in step 2  
 212 [H21] is added to that enabled by  $\text{O}_2$  reduction from Sec. 2.5 step 4 [H14] which drives the  
 213 fixation of additional  $\text{CO}_2$  for construction of  $M_{i,n}$ .

214

## 215 **2.8. Uptake of Ammonium and Reduction of Oxygen by Roots and Mycorrhizae**

216  $\text{NH}_4^+$  oxidation and  $\text{O}_2$  reduction by nitrifiers compete for substrates with  $\text{NH}_4^+$  uptake  
 217 and  $\text{O}_2$  reduction by other MFTs, and by roots and mycorrhizae.

- 218 1)  $\text{NH}_4^+$  uptake by roots and mycorrhizae under non-limiting  $\text{O}_2$  is calculated from mass flow  
 219 and radial diffusion between adjacent roots and mycorrhizae [C23a] coupled with active  
 220 uptake at root and mycorrhizal surfaces [C23b]. Active uptake is subject to product inhibition  
 221 by root nonstructural N:C ratios [C23g] where nonstructural N is the active uptake product,  
 222 and nonstructural C is the  $\text{CO}_2$  fixation product transferred to roots and mycorrhizae from the  
 223 canopy.
- 224 2)  $\text{O}_2$  reduction to  $\text{H}_2\text{O}$  under non-limiting  $\text{O}_2$  is calculated from  $\text{O}_2$  demands for  $\text{NH}_4^+$  uptake in  
 225 step 1, and for oxidation of root and mycorrhizal nonstructural C for root maintenance and  
 226 growth using a set respiratory quotient [C14e],
- 227 3)  $\text{O}_2$  reduction to  $\text{H}_2\text{O}$  under ambient  $\text{O}_2$  is calculated from mass flow and radial diffusion  
 228 between adjacent roots and mycorrhizae [C14d] coupled with active uptake at root and  
 229 mycorrhizal surfaces driven by step 2 [C14c].  $\text{O}_2$  uptake by roots and mycorrhizae is also  
 230 affected by competition with  $\text{O}_2$  uptake by heterotrophic DOC oxidizers, and autotrophic  
 231 nitrifiers, calculated from their biological  $\text{O}_2$  demands relative to those of other populations.
- 232 4) oxidation of root and mycorrhizal nonstructural C to  $\text{CO}_2$  under ambient  $\text{O}_2$  is calculated from  
 233 steps 2 and 3 [C14b],



234 5)  $\text{NH}_4^+$  uptake by roots and mycorrhizae under ambient  $\text{O}_2$  is calculated from steps 1, 2, 3 and 4  
235 [C23b].

236

## 237 **2.9. Nitrification Inhibition**

238 For this study, NIs were assumed to reduce specific rates of  $\text{NH}_4^+$  oxidation by nitrifiers  
239 in Sec. 2.5 step 1, thereby simulating inhibition of ammonia monooxygenase (Subbarao et al.,  
240 2006). This reduction was represented by a time-dependent scalar  $I$ :

241

$$242 \quad I_t = I_{t-1} - I_{t-1} * R_I * f_{T_s} \quad [1]$$

243

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

253

254 Specific rates of  $\text{NH}_4^+$  oxidation (Sec. 2.5 step 1) with NI was calculated as:

255

$$256 \quad X'_{\text{NH}_4} = X''_{\text{NH}_4} * (1.0 - I_t / (1.0 + [\text{NH}_4^+] / K_{\text{INH}_4})) \quad [2]$$

257

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

262

$$263 \quad X_{\text{NH}_4} = X'_{\text{NH}_4} M_n f_{T_s} \{ [\text{NH}_4^+] / ([\text{NH}_4^+] + K_{\text{NH}_4}) \} \{ [\text{CO}_2\text{S}] / ([\text{CO}_2\text{S}] + K_{\text{CO}_2}) \} [3]$$

264

265 where  $X_{\text{NH}_4\text{t}}$  is the nitrification rate ( $\text{g N m}^{-2} \text{h}^{-1}$ ),  $M_n$  is the nitrifier biomass ( $\text{g C m}^{-2}$ ) and  $K_{\text{NH}_4}$   
266 and  $K_{\text{CO}_2}$  are half-saturation constants for aqueous  $\text{NH}_4^+$  and  $\text{CO}_2$  ( $\text{g N}$  and  $\text{C m}^{-3}$ ). NI in Eq. 1  
267 slows  $X'_{\text{NH}_4\text{t}}$  in Eq. 2 and thereby  $X_{\text{NH}_4\text{t}}$  in Eq. 3, and hence slows  $\text{NO}_2^-$  production from  
268 nitrification (Sec. 2.5 step 4), and thereby  $\text{N}_2\text{O}$  production from nitrification (Sec. 2.7 step 2) and  
269 denitrification (Sec. 2.4 step 3). By slowing  $X_{\text{NH}_4\text{t}}$  in Eq. 3, NI also reduces nitrification energy  
270 yield and hence  $M_n$  growth, biomass [A25] and  $\text{O}_2$  uptake [H13], thereby further reducing  $\text{N}_2\text{O}$   
271 production.

272

273

### 274 3. FIELD EXPERIMENT

275

#### 276 3.1. Site Description and Experimental Design

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

290

291 Weather data (radiation, air temperature ( $T_a$ ), humidity, windspeed and precipitation)  
292 were recorded hourly from 2012 through 2016 at the South Campus Farm. During the first  
293 experimental year (16 Sep. 2014 to 15 Sep. 2015)  $T_a$  remained 1 – 2 °C higher than historical  
294 (1981 – 2010) averages (Lin et al., 2018) (Table 4). Precipitation was slightly higher than  
295 historical averages during autumn and winter, but was about one-half those during spring and

296 summer. During the second experimental year (16 Sep. 2015 to 15 Sep. 2016),  $T_a$  was higher  
297 than that of the first year during winter and early spring, and similar during late spring and  
298 summer. However precipitation during the second year was lower from autumn to early spring  
299 and much higher during late spring and summer.

300

### 301 **3.2. N<sub>2</sub>O Flux Measurements**

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

313

314 N<sub>2</sub>O emissions were also measured once or twice per week from spring thaw to autumn  
315 freezing during both experimental years with manually operated chambers as described in Lin et  
316 al. (2018). The time required for installation of the automated chambers after snowmelt limited  
317 their ability to measure N<sub>2</sub>O emissions during spring thaw, so that measurements from the  
318 manually operated chambers were used to evaluate emissions during these periods.

319

## 320 **4. MODEL EXPERIMENT**

321

### 322 **4.1. Model Spinup**

323 To simulate site conditions prior to the experiment, *ecosys* was initialized with the properties  
324 of the Black Chernozem, simulated as a one-dimensional profile (Table 2) with surface water  
325 runoff and subsurface water exchange with a water table at 1.2 m depth. The model was run  
326 from model dates 1 Jan. 1992 to 31 Dec. 2013 under a repeating 5-year sequence of weather

327 data (radiation, air temperature ( $T_a$ ), humidity, windspeed and precipitation recorded hourly  
328 from 2012 through 2016 at the South Campus Farm. The soil was During each year of the  
329 spinup run, barley was planted, fertilized and harvested as silage to reproduce land use practices  
330 reported from the field site.

331

## 332 **4.2. Model Runs**

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

345

346 There is some flexibility in the timing of fall slurry application between crop harvest in late  
347 summer and soil freezing in early November. To examine how timing of fall slurry application  
348 would affect subsequent  $\text{N}_2\text{O}$  emissions with and without NI, fall slurry application dates were  
349 advanced or delayed by 2 weeks from those in Table 3, and effects on spring and annual  $\text{N}_2\text{O}$   
350 emissions were evaluated. To examine how increased tillage during slurry application would  
351 affect subsequent  $\text{N}_2\text{O}$  emissions with and without NI, coefficients for surface litter  
352 incorporation and soil mixing to the depth of slurry application were raised from 0.2 to 0.5 and  
353 0.8 for fall and spring applications.

354

## 355 **5. RESULTS**

356

### 357 **5.1. NI and Soil $\text{NH}_4^+$ and $\text{NO}_3^-$ Concentrations**

### 358 **5.1.1. Fall Slurry Applications**

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

370

### 371 **5.1.2. Spring Slurry Applications**

372 Declines in  $\text{NH}_4^+$  concentrations modelled after slurry applications with NI in spring 2015  
373 and 2016 were also slower than after those without NI (Fig. 2b), consistent with higher  $\text{NH}_4^+$   
374 concentrations measured after spring application with DMPP in both years (Fig. 2b). These  
375 slower declines caused slower rises in  $\text{NO}_3^-$  concentrations to be modelled following spring  
376 slurry applications with NI (Fig. 2d).

377

## 378 **5.2. NI and Soil Gas Concentrations**

### 379 **5.2.1. Fall Slurry Applications**

380 In the model, soil ice impeded drainage during spring snowmelt and soil thaw, raising  $\theta_w$  and  
381 lowering  $\theta_g$ , and thereby slowing gas transfers in gaseous phases and gas exchanges between  
382 gaseous and aqueous phases (Sec. 2.3 step 3; Fig. 1). Freeze-thaw effects on  $\text{N}_2\text{O}$  emissions  
383 modelled during early spring are further described in Grant and Pattey (1999). Slower  $\text{O}_2$   
384 transfers relative to  $\text{O}_2$  uptake (Sec. 2.3, 2.5 and 2.6) forced reductions in aqueous  $\text{O}_2$   
385 concentrations ( $\text{O}_{2s}$ ) to be modelled during early spring in 2015 (Fig. 3a,b) and 2016 (Fig. 3c,d)  
386 following fall slurry applications in 2014 and 2015. Declines in aqueous  $\text{O}_2$  ( $\text{O}_{2s}$ ) were later but  
387 more rapid in 2015 than in 2016, following greater winter precipitation and hence greater

388 snowmelt in 2014/2015 (Table 4). Earlier and more persistent declines in  $O_{2s}$  were modelled in  
389 2016 because greater  $\theta_t$  modelled with less thermal insulation under a shallower snowpack  
390 reduced or eliminated  $\theta_g$  during much of the winter. Drainage of meltwater after snowmelt  
391 eventually lowered  $\theta_w$  and raised  $\theta_g$ , allowing  $O_{2s}$  to return to atmospheric equivalent  
392 concentrations.

393

394 Declines in  $O_{2s}$  in slurry-amended treatments drove increases in aqueous  $N_2O$  concentrations  
395 ( $N_2O_s$ ) (Fig. 3b,d) during winter and early spring (Sec. 2.7, step 1). These rises were similar with  
396 and without NI, in spite of higher  $NH_4^+$  concentrations without NI (Fig. 2a). Rises in  $\theta_g$   
397 following spring drainage allowed volatilization of  $N_2O$  from aqueous to gaseous phases,  
398 reducing  $N_2O_s$  and driving  $N_2O$  emissions modelled during spring thaw.

399

#### 400 **5.2.2. Spring Slurry Applications**

401 Declines in  $O_{2s}$  modelled after spring slurry application were small during the drier spring of  
402 2015 (Table 4) (Fig. 3e), but were greater with lower  $\theta_g$  during the wetter spring of 2016 (Fig.  
403 3g). During both years, these declines were more rapid with slurry than without, but less rapid  
404 with NI-amended slurry than with unamended slurry. Greater declines in  $O_{2s}$  modelled in 2016  
405 vs. 2015 drove greater increases in  $N_2O_s$  (Sec. 2.7), particularly without NI, and hence greater  
406 emissions of  $N_2O$  during subsequent declines in  $N_2O_s$ .

407

### 408 **5.3. NI and $N_2O$ Fluxes**

#### 409 **5.3.1. Fall Slurry Applications**

410 Smaller rises and subsequent declines in  $N_2O_s$  modelled with NI than without (Fig. 3b) drove  
411 smaller  $N_2O$  emission events modelled during spring thaw in 2015 (Fig. 4a) following slurry  
412 application in fall 2014 (Fig. 4b). These events were driven by increases in  $\theta_g$  during  
413 midafternoon thawing of near-surface soil, but were terminated by loss of  $\theta_g$  during nighttime  
414 refreezing. These events preceded the start of the automated chamber measurements on DOY  
415 102 and so could not be corroborated by them. However measurements with manual chambers  
416 earlier in spring 2015 by Lin et al. (2018) indicated that  $N_2O$  emission events occurred from  
417 DOY 85 to 100 that were similar in magnitude although not always in timing with those

418 modelled (Fig. 4b). These measured emissions were smaller with NI than without, consistent  
419 with modelled emissions.

420

421 The smaller rises and subsequent declines in  $N_2O_s$  modelled with NI than without in the  
422 winter of 2016 (Fig. 3d) drove smaller emission events during thawing and refreezing of near-  
423 surface soil in spring 2016 (Fig. 5a) following slurry application in fall 2015 (Fig. 5b). These  
424 modelled events preceded the start of automated chamber measurements on DOY 91, but earlier  
425 measurements with manual chambers indicated  $N_2O$  emission events occurred from DOY 74 to  
426 93. The smaller emission events modelled with NI were consistent with those measured using the  
427 manual chambers, although some larger emissions measured with DMPP using the automated  
428 chambers from DOY 91 to 102 were not modelled (Fig. 5b). In both years, emissions modelled  
429 and measured without slurry remained very small, consistent with low  $N_2O_s$  (Fig. 3b,f).

430

### 431 **5.3.2. Spring Slurry Applications**

432 Modelled  $N_2O$  emissions closely followed measured values during a brief emission event  
433 following slurry application in the drier spring of 2015 (Fig. 6a,b), driven by small rises and  
434 declines in  $N_2O_s$  (Fig. 3f). The smaller rise and decline in  $N_2O_s$  modelled with NI than without  
435 drove smaller  $N_2O$  emissions which declined more rapidly after application than did emissions  
436 measured with DMPP (Fig. 6b).

437

438 Emissions modelled without NI in the wetter spring of 2016 were larger than those in the  
439 drier spring of 2015 (Fig. 7a,b), driven by a larger rise and decline in  $N_2O_s$  with lower  $\theta_g$  (Fig.  
440 3h). These emissions were suppressed by low  $\theta_g$  with soil wetting during heavy rainfall on DOY  
441 141 – 143 shortly after slurry application (Fig. 7a,b), but resumed when  $\theta_g$  rose with soil  
442 drainage thereafter (Fig. 7b). Emissions modelled without NI remained greater than those  
443 measured until DOY 150, after which modelled values declined with soil drying while measured  
444 value rose (Fig. 7b). Greater reductions in  $N_2O_s$  (Fig. 3h) and hence in  $N_2O$  emissions were  
445 modelled with NI after slurry application in the wetter spring of 2016 (Fig. 7b) than in the drier  
446 spring of 2015 (Fig. 6b). In both years, emissions modelled and measured without slurry  
447 remained very small, consistent with low  $N_2O_s$  (Fig. 3f,h).

448

## 5.4. NI Effects on Seasonal and Annual N<sub>2</sub>O Emissions

### 5.4.1. Modelled vs. Measured N<sub>2</sub>O Emissions after Spring Slurry Applications

Total N<sub>2</sub>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 N<sub>2</sub>O Emissions Modelled After Fall and Spring Slurry Applications

#### 5.4.2.1. Fall Slurry Applications

NI greatly reduced N<sub>2</sub>O emissions modelled from fall applications during autumn (16 Sep. – 31 Dec. in Table 6) in 2014 and 2015, slightly reduced N<sub>2</sub>O emissions modelled during the following winter and early spring (1 Jan. – 30 Apr.), but slightly raised N<sub>2</sub>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 N<sub>2</sub>O 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



480 2015/2016 respectively (Table 6). The reduction modelled with NI in 2014/2015 was greater  
481 than one of 0% for DMPP estimated from manual chamber measurements from 1 Oct. 2014 to  
482 30 Sep. 2015 by Lin et al. (2018), although the reduction modelled in 2015/2016 was similar to  
483 one of 38% estimated from manual chamber measurements from 1 Oct. 2015 to 30 Sep. 2016.

#### 485 **5.5. Effects of Management on Seasonal and Annual N<sub>2</sub>O Emissions Modelled After** 486 **Fall and Spring Slurry Applications**

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

498  
499 Increasing surface litter incorporation and soil mixing during fall slurry application raised  
500 N<sub>2</sub>O emissions modelled without NI only slightly during 2014/2015, but substantially during  
501 2015/2016, particularly during spring thaw (F 0.5 and F 0.8 vs. F in Table 6). Increasing surface  
502 litter incorporation and soil mixing during spring slurry application had limited effects on  
503 emissions (S 0.5 and S 0.8 vs. S in Table 6). Greater mixing caused reductions in N<sub>2</sub>O emissions  
504 modelled with NI to be smaller relative to those without NI.

#### 505 506 **5.6. NI Effects on Annual Mineral N Losses and NH<sub>3</sub> Emissions**

507 Injecting the slurry to 14 cm in the model suppressed NH<sub>3</sub> emissions with limited soil mixing,  
508 and caused only very small emissions with greater mixing (Table 7). Higher NH<sub>4</sub><sup>+</sup> concentrations  
509 modelled with NI (Fig. 2a,b) increased net NH<sub>3</sub> emission, particularly if fall slurry application  
510 was delayed or soil mixing was increased in 2014/2015.

511

512 The subhumid climate at Edmonton (Table 4) caused modelled  $\text{NO}_3^-$  losses to remain small.  
513 For both fall and spring applications, lower  $\text{NO}_3^-$  concentrations modelled with NI (Fig. 2c,d)  
514 caused small reductions in  $\text{NO}_3^-$  losses.

515

### 516 **5.7. NI Effects on Barley Silage Yields**

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

524

## 525 **6. DISCUSSION**

### 526 **6.1. Process Modelling of $\text{N}_2\text{O}$ Emissions**

527  $\text{N}_2\text{O}$  emissions were driven by declines in gaseous  $\text{O}_2$  ( $\text{O}_{2g}$ ) and  $\text{O}_{2s}$  modelled by  
528 equilibrating  $\text{O}_2$  active uptake by autotrophic and heterotrophic oxidation (Sec. 2.5 step 3 and  
529 Sec. 2.3 step 3) with  $\text{O}_2$  diffusion and dissolution through gaseous and aqueous phases, and  
530 dissolution from gaseous to aqueous phases, largely controlled by  $\theta_g$  (Fig. 1). These  $\text{O}_2$  transfers  
531 were sustained by concentration gradients from  $\text{O}_{2g}$  to  $\text{O}_{2s}$  and from  $\text{O}_{2s}$  to  $\text{O}_2$  at microbial  
532 surfaces ( $\text{O}_{2m}$ ), so that declines in  $\text{O}_{2s}$  (Fig. 3) and  $\text{O}_{2m}$  were relatively larger than those in  $\text{O}_{2g}$ .  
533 These greater declines enabled  $\text{N}_2\text{O}$  emissions to be modelled from  $\text{O}_2$  deficits while  $\text{O}_{2g}$   
534 remained above one-half of atmospheric concentration, consistent with observations of  $\text{O}_{2g}$   
535 during  $\text{N}_2\text{O}$  emissions from incubation and field experiments (Nguyen et al., 2017; Owens et al.,  
536 2017). These  $\text{O}_2$  deficits were modelled using a  $K_m$  for  $\text{O}_{2m}$  of 10  $\mu\text{M}$  by nitrifiers (Sec. 2.5 step  
537 3) and 2  $\mu\text{M}$  by denitrifiers (Sec. 2.3 step 3) derived from biochemical studies by Focht and  
538 Verstraete (1977). These  $K_m$  are less than 5% and 1% of atmospheric equivalent concentration,  
539 indicating the importance of explicitly simulating gaseous and aqueous transport processes when  
540 modelling  $\text{N}_2\text{O}$  emissions.

541

542  $O_2$  deficits were modelled in spring thaw 2015 (Fig. 3a), when diffusion was sharply reduced  
543 by soil saturation because drainage from snowmelt and soil thaw was impeded by underlying ice  
544 layers. These declines drove  $N_2O$  generation (Fig. 3b) and emission (Fig. 4b) almost entirely  
545 from  $NO_2^-$  reduced during spring thaw.  $O_2$  deficits were also modelled during winter 2016 when  
546 increased  $\theta_l$  from soil freezing with lower  $T_s$  under a shallower snowpack caused near-surface  
547 soil porosity to be fully occupied by ice and water. Consequent loss of  $\theta_g$  greatly reduced  
548 surface gas exchange and hence gradually reduced soil  $O_2$  concentrations, particularly with  
549 increased  $O_2$  demand from fall slurry application (Fig. 3c). The extended period of low  $O_{2s}$   
550 prolonged overwinter accumulation of  $N_2O_s$  after fall slurry application (Fig. 3d). Transient  
551 increases in  $\theta_g$  during soil freeze-thaw cycles caused several  $N_2O$  emission events to be modelled  
552 during spring thaw in 2016, mostly from degassing through volatilization of overwinter  $N_2O_s$   
553 (Fig. 5b). Degassing events in the model were consistent with field observations by Chantigny et  
554 al. (2017) that passive degassing of accumulated gases made a significant contribution to spring  
555 thaw emissions during which two or more consecutive emission peaks were often observed. In  
556 the model, the contribution by degassing of overwinter  $N_2O_s$  to spring thaw emissions increased  
557 with intensity and duration of soil freezing during the previous winter.  $N_2O$  emissions simulated  
558 during spring thaw were thus driven by concurrent  $NO_2^-$  reduction during spring thaw (2015)  
559 and by earlier  $NO_2^-$  reduction accumulated over the previous winter (2015/2016), as has been  
560 proposed from experimental observations (Teepe et al., 2004).

561  
562  $O_2$  deficits were also caused by rapid increases in  $O_2$  active uptake with addition of labile C  
563 in slurry, the rapid decomposition and oxidation of which (Sec. 2.3 step 1) caused transient  
564 declines in  $O_{2s}$  with soil wetting from slurry application and precipitation (Fig. 3e,g). After slurry  
565 application in the wetter spring of 2016, modelled  $O_{2g}$  declined to *ca.* one-half of atmospheric  
566 concentration, driving the sharp declines in  $O_{2s}$  shown in Fig. 3g. The modelled declines in  $O_{2g}$   
567 were consistent with results from an incubation of wetted soil amended with cattle slurry by  
568 Nguyen et al. (2017) in which  $O_{2g}$  declined below one-half of atmospheric concentration within  
569 one day of slurry application and gradually rose again after two days, while no decline occurred  
570 in an unamended soil. The period of low  $O_{2s}$  in this incubation study co-occurred with peak  
571 emissions of  $CO_2$  and  $N_2O$  from the amended soil, as was modelled here in Fig. 3f,h and Fig. 6b  
572 and 7b. This co-occurrence indicated that  $NH_4^+$  and DOC oxidation drove  $O_2$  deficits from

573 demand for O<sub>2</sub> from oxidation vs. supply of O<sub>2</sub> through convection – dispersion, which caused  
574 NO<sub>2</sub><sup>-</sup> reduction as represented in the model, again demonstrating the importance of simulating  
575 aqueous and gaseous O<sub>2</sub> transfers when modelling N<sub>2</sub>O emissions.

576

## 577 **6.2. Process Modelling of NI Effects on N<sub>2</sub>O Emissions**

### 578 **6.2.1. Fall Slurry Application**

579 NH<sub>4</sub><sup>+</sup> oxidation in the model (Sec. 2.5 step 4) proceeded rapidly after fall slurry application  
580 without NI as indicated by rapid declines in NH<sub>4</sub><sup>+</sup> (Fig. 2a), consistent with observations in other  
581 studies that soil NH<sub>4</sub><sup>+</sup> concentrations returned to background levels 30 d after fall slurry  
582 application (Rochette et al., 2004). Slower NH<sub>4</sub><sup>+</sup> oxidation modelled with NI (Eq. 3) during fall  
583 caused slower declines of soil NH<sub>4</sub><sup>+</sup> before and during freezing and hence larger NH<sub>4</sub><sup>+</sup>  
584 concentrations during spring thaw (Fig. 2a). These slower declines were modelled from slower  
585 decline of  $I_t$  with low  $f_{Ts}$  in cold soils (Eq. 1) which slowed NH<sub>4</sub><sup>+</sup> oxidation and thereby reduced  
586 N<sub>2</sub>O emissions simulated during late autumn and spring thaw (Figs. 4b and 5b), despite increased  
587 NH<sub>4</sub><sup>+</sup> concentrations (Fig. 2). These reductions were consistent with those from chamber  
588 measurements at the Edmonton South Farm (Lin et al., 2018), and with those from a limited  
589 number of studies elsewhere in which persistent effects of NI in reducing overwinter N<sub>2</sub>O  
590 emissions have been found (e.g. Pfab et al., 2012), indicating the importance of  $f_{Ts}$  in Eq. 1.

591

592 The slower decline of  $I_t$  from low  $f_{Ts}$  enabled *ecosys* to simulate larger reductions in N<sub>2</sub>O  
593 emissions with NI after fall slurry applications in cooler soil vs. spring slurry applications in  
594 warmer soil during both years (F during autumn vs. S during late spring-summer in Table 6).  
595 Reductions in N<sub>2</sub>O emissions modelled with NI after fall slurry applications became greater  
596 when fall applications were delayed (F +2 in Table 6), further reducing  $T_s$  and  $f_{Ts}$  during  
597 subsequent nitrification. The greater reductions modelled with fall applications were consistent  
598 with experimental observations by Merino et al. (2005) who attributed larger reductions in N<sub>2</sub>O  
599 emissions measured with NI from fall- vs. spring-applied cattle slurry to slower NI degradation  
600 in cooler soil. These modelled and experimental results indicated that NI effectiveness in  
601 reducing N<sub>2</sub>O emissions varies with the effect of fall slurry timing on  $f_{Ts}$ .

602

603 The greater reductions in N<sub>2</sub>O emissions modelled from delayed fall applications with NI  
604 were associated with much greater N<sub>2</sub>O emissions modelled from delayed fall applications  
605 without NI (F+2 in Table 6). These greater emissions were attributed to less NH<sub>4</sub><sup>+</sup> oxidation  
606 before freeze up in fall, resulting in more NH<sub>4</sub><sup>+</sup> remaining to drive NH<sub>4</sub><sup>+</sup> oxidation and hence  
607 N<sub>2</sub>O emissions during spring thaw. These model findings were consistent with field results from  
608 Chantigny et al. (2017) in Quebec, and Kariyapperuma et al. (2012) in Ontario, where greater  
609 spring N<sub>2</sub>O emissions were measured when fall slurry was applied in late November than in  
610 early November. These greater spring thaw N<sub>2</sub>O emissions were attributed by Kariyapperuma et  
611 al. (2012) to greater mineral N concentrations during spring thaw caused by less nitrification  
612 before freeze up during the previous fall, as modelled here. The greater N<sub>2</sub>O emissions modelled  
613 with later slurry application were also driven by more rapid DOC oxidation from more labile  
614 manure C remaining during spring thaw. This more labile manure C reduced [O<sub>2s</sub>] below that  
615 simulated after earlier fall applications (Fig. 3d). NI may therefore be particularly effective in  
616 reducing N<sub>2</sub>O emissions during spring thaw following late fall slurry applications.

617

618 The decreases in N<sub>2</sub>O emissions modelled with NI from greater soil mixing (F 0.5 and F 0.8  
619 vs. F in Table 6) were affected by how the redistribution of NI activity with soil mixing was  
620 modelled. Simulating this redistribution during tillage requires further consideration and  
621 corroboration from observations. These decreases in N<sub>2</sub>O emissions with NI were associated  
622 with greater N<sub>2</sub>O emissions modelled from greater soil mixing without NI in 2016 (F 0.5 and F  
623 0.8 in Table 6). These greater emissions were attributed in the model to longer periods with high  
624  $\theta_l$  and low  $\theta_g$  in the upper soil profile caused by greater heat loss through reduced insulation  
625 from less surface litter under a shallow snow pack [D12, D13]. This longer period further  
626 reduced overwinter [O<sub>2s</sub>] from that modelled in F (Fig. 3c), causing greater accumulation of  
627 N<sub>2</sub>O<sub>s</sub> and hence greater emissions during thaw. These model findings were consistent with field  
628 observations by Congreves et al. (2017) and Wagner-Riddle et al. (2010) that overwinter N<sub>2</sub>O  
629 emissions increased with greater freezing under conventional vs. no tillage, particularly with  
630 surface residue removal. Model findings were also consistent with observations by Teepe et al.  
631 (2004) that N<sub>2</sub>O emissions during soil thawing rose sharply with increased duration of soil  
632 freezing. Consequent changes in  $T_s$  with freezing may alter NI effectiveness with tillage.

633

### 6.2.2. Spring Slurry Application

Annual N<sub>2</sub>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 N<sub>2</sub>O emissions from fall applications relative to those from spring (e.g. Cambareri et al., 2017). These model results indicate that effects of spring vs. fall slurry applications on annual N<sub>2</sub>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 NH<sub>4</sub><sup>+</sup> modelled after spring applications comparably to those measured (Fig. 2b). These slower declines were caused by slower NH<sub>4</sub><sup>+</sup> oxidation that reduced nitrifier growth (Sec. 2.9 Eq. 3) and active O<sub>2</sub> uptake (Sec. 2.5 step 3). Consequently smaller nitrifier biomass and greater [O<sub>2s</sub>] 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. (2013) that DMPP reduced populations of ammonia oxidizing bacteria in soil incubations. Greater [O<sub>2s</sub>] modelled with NI was consistent with greater [O<sub>2g</sub>] measured in an incubation of wetted soil amended with cattle slurry with vs. without DMPP by Nguyen et al. (2017). Slower nitrifier growth and greater [O<sub>2s</sub>] both contributed to reductions in N<sub>2</sub>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<sub>2</sub>O emissions that should be considered in NI models.

The reductions in N<sub>2</sub>O emissions modelled for 30 d after spring slurry applications with  $R_1$  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<sub>2</sub>O emissions from a given land use when emissions were greater. These greater

665 reductions were attributed in the model to heavy rainfall several days after application in 2016  
666 (Fig. 7a) that extended the N<sub>2</sub>O emission period (Fig. 7b). During this extension  $I_t$  remained high  
667 because [NH<sub>4</sub><sup>+</sup>] had declined from the large values modelled immediately after application (Eq.  
668 3).

669  
670 The effects of NI on N<sub>2</sub>O emissions modelled with greater soil mixing during spring  
671 applications (S 0.5 and S 0.8 vs. S in Table 6) were affected by how the redistribution of NI  
672 activity with soil mixing was modelled, as were those during fall applications. The effects of soil  
673 mixing on N<sub>2</sub>O emissions without NI modelled from slurry applications in spring were smaller  
674 than those in fall in the absence of soil freezing effects on O<sub>2s</sub>. These smaller effects were  
675 modelled because tillage in this study involved mixing of injected manure rather than  
676 incorporation of surface-applied manure. These small effects were consistent with an observation  
677 by VanderZaag et al. (2011) that tillage was less important than timing and placement for N<sub>2</sub>O  
678 emissions from slurry applications.

679  
680 The reductions in annual N<sub>2</sub>O emissions modelled after spring slurry applications with  $R_t$  for  
681 DMPP and nitrapyrin in 2015 (22% and 17%) and 2016 (40% and 27%) (Table 6) were smaller  
682 than those modelled after 30 d (Table 5) due to gradual degradation of NI effectiveness modelled  
683 with time since application (Eq. 1), indicating the importance of year-round modelling and  
684 measurements to fully assess NI effects on N<sub>2</sub>O emission factors for IPCC Tier 3 methodology.  
685 However most of the datasets used in meta-analyses of these assessments did not include  
686 emissions during autumn, winter and spring thaw (Ruser and Schulz, 2015) which are  
687 particularly important for estimating emission factors for NI effects from fall slurry applications  
688 in cold climates (Table 6). Ecosystem modelled with well tested simulation of NI effects may  
689 make a valuable contribution to these assessments.

690

### 691 **6.3. Modelling NI Effects on NH<sub>3</sub> Emissions and Mineral N Losses**

692 The small NH<sub>3</sub> emissions modelled from slurry injection with limited soil mixing (Table 7)  
693 were consistent with observations of almost no NH<sub>3</sub> volatilization from closed-slot injection of  
694 slurry by Rodhe et al. (2006). In the model, NH<sub>3</sub> emissions with or without NI were sharply  
695 reduced by NH<sub>4</sub><sup>+</sup> adsorption with diffusion of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> from the injection site. Greater soil

696 mixing brought more  $\text{NH}_4^+$  closer to the surface, reducing  $\text{NH}_4^+$  adsorption and thereby  
697 increasing  $\text{NH}_3$  emission, particularly from fall applications with NI (Table 7). Consequently  
698 only small net increases in  $\text{NH}_3$  emissions (Table 7) were modelled with NI from increased  
699 volatilization of aqueous  $\text{NH}_3$  in equilibrium with increased  $\text{NH}_4^+$  concentrations (Fig. 2).  
700 However these increases were large in relative terms particularly following fall applications,  
701 consistent with increases of 33 – 67% and 3 – 65% relative to emissions without NI derived from  
702 meta-analyses of field experiments by Qiao et al. (2015) and Lam et al. (2017) respectively.  
703 Increases in  $\text{NH}_3$  emissions with NI will thus depend on soil adsorptive properties and depth of  
704 slurry incorporation.

705

706 The small losses of  $\text{NO}_3^-$ , and consequently the small reductions in these losses with NI,  
707 modelled in the subhumid climate at the Edmonton South Farm (Table 7) conform to the  
708 assumption by De Klein et al. (2006) that  $\text{NO}_3^-$  leaching is an insignificant source of indirect  
709  $\text{N}_2\text{O}$  emission from dryland cropping systems in subhumid climates. Consequently reductions in  
710 leaching have minimal impact on the overall effect of NI on  $\text{N}_2\text{O}$  emission in these climates  
711 (Lam et al., 2017). Reductions in  $\text{NO}_3^-$  losses modelled with NI would be larger at sites with  
712 better drainage and more excess precipitation, although even under these conditions such  
713 reductions may be small and inconsistent (Smith et al., 2002).

714

715 The increases in  $\text{NH}_3$  emissions modelled with NI were larger than reductions in  $\text{NO}_3^-$   
716 leaching (Table 7), indicating that net increases in  $\text{N}_2\text{O}$  emissions from indirect effects of NI will  
717 partially offset decreases in  $\text{N}_2\text{O}$  emissions from direct effects. This offset must be included  
718 when estimating changes in  $\text{N}_2\text{O}$  emission factors attributed to NI in IPCC Tier 3 methodology.

719

#### 720 **6.4. Modelling NI Effects on $\text{N}_2\text{O}$ Emissions: Parameter Evaluation**

721 The simulation of  $\text{N}_2\text{O}$  emissions from nitrification and denitrification in *ecosys* is based on a  
722 comprehensive representation of biological and physical processes governing production and  
723 transport of  $\text{N}_2\text{O}$ . Parameters used in these processes are well constrained from basic research so  
724 that the model may provide a robust means to predict emissions under diverse climates, soils and  
725 land use practices. These processes in *ecosys* were not changed when adding the algorithm for  
726 inhibiting  $\text{NH}_4^+$  oxidation by nitrifiers proposed in Eqs. 1 and 2 (Sec. 2.9). This algorithm used



727 only three parameters,  $I_{t=0}$  and  $R_1$  in Eq. [1] and  $K_{\text{INH4}}$  in Eq. [2] with values of 1.0,  $2.0 \times 10^{-4} \text{ h}^{-1}$ ,  
 728 and  $7000 \text{ g N m}^{-3}$  to simulate the time course of NI activity following slurry application. The  
 729 first two parameters correspond to ones in earlier models of NI for inhibition effectiveness (0.5 –  
 730 0.9) and duration (30 – 60 days) (Cui et al., 2014; Del Grosso et al., 2009). These models have  
 731 given reductions in  $\text{N}_2\text{O}$  emissions with NI in agricultural crops of *ca.* 25% (Cui et al., 2014),  
 732 10% (Del Grosso et al., 2009) or less (Abalos et al., 2016), that are frequently smaller than  
 733 reductions of 26% – 43% and 24% – 46% derived from meta-analyses of NI effects in  
 734 agricultural crops by Akiyama et al. (2010) and Gilsanz et al. (2016) respectively. Direct effects  
 735 on NI of soil water content and pH were not modelled here due to uncertainty in  
 736 parameterization, although both affect nitrification and hence the magnitude of NI activity.

737  
 738 Each of the parameters used to model NI in *ecosys* requires further evaluation. A larger  $R_1$ ,  
 739 such as that used for nitrapyrin *vs.* DMPP (Sec. 2.9), caused a more rapid decline of NI activity  
 740 in soil, and hence greater  $\text{N}_2\text{O}$  emissions with time after slurry application that were consistent  
 741 with measurements (Tables 5 and 6; Lin et al., 2018). This larger value might represent more  
 742 rapid degradation of nitrapyrin through volatilization (Ruser and Schulz, 2015), although meta-  
 743 analyses of  $\text{N}_2\text{O}$  reductions with NI indicate that those with nitrapyrin are similar to those with  
 744 DMPP. The value of  $R_1$  used for NI in the model will thus likely be product specific. The effect  
 745 of  $T_s$  on  $R_1$  might reasonably be represented by  $f_{T_s}$  as is the effect of  $T_s$  on all other biological  
 746 reactions in the model. This function allowed modelled NI activity to persist overwinter (Fig. 2)  
 747 and hence reduce  $\text{N}_2\text{O}$  emissions modelled during spring thaw (Fig. 6 and Fig. 7). However the  
 748 effects of temperature on reductions in  $\text{N}_2\text{O}$  emission with NI over time are sometimes unclear in  
 749 controlled studies (Kelliher et al., 2008).

750  
 751 The value of  $I_{t=0}$  set the value of  $I_t$  at the time of slurry application, after which  $I_t$   
 752 underwent first order decline over time according to Eq. 1 (Sec. 2.9). The current value of 1.0  
 753 indicates complete inhibition at the time of application, but might be reduced if the amount of NI  
 754 at application is less than that required for complete inhibition. However  $I_t$  had to remain large  
 755 enough to reduce  $\text{N}_2\text{O}$  emissions from nitrification for several weeks after application (Figs. 6  
 756 and 7) even with higher soil  $\text{NH}_4^+$  concentrations (Fig. 2). Lowering  $I_{t=0}$  from 1.0 to 0.8, similar

757 to that in earlier NI models in which  $I_t$  decline was not simulated, increased N<sub>2</sub>O emissions  
758 modelled over 30 days after spring slurry applications by 7% in 2015 and 25% in 2016 (Table 9).

759 The value of  $K_{iNH_4}$  in Eq. 2 reduced  $I_t$  with the very large NH<sub>4</sub><sup>+</sup> concentrations modelled  
760 immediately after injecting slurry with large NH<sub>4</sub><sup>+</sup> content (Table 3) into small bands (Sec. 3.1).  
761 The use of  $K_{iNH_4}$  was suggested by the findings of Janke et al. (2019) that NI may not have the  
762 expected impacts on N transformations and availability when applied in a concentrated band  
763 with large NH<sub>4</sub><sup>+</sup> concentrations (up to 12 kg N Mg<sup>-1</sup>), similar to those modelled immediately  
764 after slurry application in this study. The modelled NH<sub>4</sub><sup>+</sup> concentrations declined rapidly after  
765 application through diffusion, adsorption and nitrification (Sec. 2.5), and thus so did  $K_{iNH_4}$   
766 effects on inhibition. The value of  $K_{iNH_4}$  in Eq. 2 therefore governed NI effects modelled during  
767 the brief periods of rapid N<sub>2</sub>O emissions following application (*ca.* 3 days in Figs. 6 and 7), but  
768 had sharply diminishing impacts on NI effects modelled thereafter. An alternative hypothesis for  
769 reduced inhibition by NI immediately after application might be more rapid diffusion of NH<sub>4</sub><sup>+</sup>  
770 than NI from the band, leading to spatial separation (Ruser and Schulz, 2015), although  
771 parameterization of this hypothesis is uncertain. Halving or doubling  $K_{iNH_4}$  from the value set in  
772 Sec. 2.9 raised or lowered N<sub>2</sub>O emissions modelled over 30 days after spring slurry applications  
773 by 7 – 8% in 2015 and 2016 (Table 9), indicating some latitude in evaluating this parameter.

774 Reductions in N<sub>2</sub>O emissions modelled with all proposed values of  $I_{t=0}$  and  $K_{iNH_4}$  varied from  
775 27% to 41% in 2015, and from 38% to 57% in 2016 (Table 9), close to the range of 42.6% ±  
776 5.5% derived from meta-analyses of NI effects with cattle slurry by Gilsanz et al. (2016). Further  
777 evaluation of these parameters should be undertaken in future studies in which measurements are  
778 taken at higher frequencies (e.g. Figs. 6 and 7) required to assess N<sub>2</sub>O emissions and NI effects  
779 on them.

780

## 781 **6.5. Modelling NI Effects on N<sub>2</sub>O Emissions: Outstanding Issues**

782 Several issues remain to be addressed in modelling N<sub>2</sub>O emissions and NI effects on these  
783 emissions. Accurately modelling emissions during spring thaw depended upon accurately  
784 modelling soil freezing and thawing following snow melt, and their effects on soil O<sub>2</sub> transfer. A  
785 small delay of 2 – 3 days in modelled thawing caused some small emission events measured in  
786 early spring of 2015 to be missed (Fig. 4b). However because modelled emissions were driven

787 by overwinter accumulation of N<sub>2</sub>O (Fig. 3), seasonal emissions were less affected by such  
788 delays than were emissions from individual events. Algorithms for modelling snowpack  
789 accumulation and ablation in *ecosys* are being further refined to improve simulation of soil  
790 freezing and thawing. Accurately modelling emissions during later spring depended upon  
791 accurately modelling soil wetting and drying following rainfall, and their effects on soil O<sub>2</sub>  
792 transfer. Soil wetting from heavy precipitation typically drives N<sub>2</sub>O emission events following  
793 soil N additions, as modelled here during DOY 143 – 146 in 2016, although such events were  
794 not always measured (Fig. 7b). Such wetting caused sharp declines in O<sub>2s</sub> when soil water  
795 content rose above a critical threshold, driving N<sub>2</sub>O generation and subsequent emission (Fig. 3).  
796 However modelling these thresholds depends on soil hydrological properties used in the model  
797 (Table 2) which may not be known with sufficient accuracy.

798 Modelling NI effects on N<sub>2</sub>O emissions depended upon  $I_{t=0}$  (Eq. 1) and  $K_{iNH_4}$  (Eq. 2) as  
799 evaluated in Sec. 6.4 and Table 9, but also on the time course for declining NI activity governed  
800 by the first order rate constant  $R_I$  and its temperature dependence  $f_{T_{s_I}}$  (Eq. 1). NI activity  
801 modelled with  $R_I$  and  $f_{T_{s_I}}$  in this study reduced nitrification alone (Sec. 2.9), which enabled  
802 higher [NH<sub>4</sub><sup>+</sup>] and lower [NO<sub>3</sub><sup>-</sup>], and hence greater NH<sub>3</sub> emissions, to be simulated with NI after  
803 amendment as has been found in field studies (Fig. 2). These higher [NH<sub>4</sub><sup>+</sup>] required a low value  
804 of  $R_I$  so that NI activity would persist in reducing nitrification and hence N<sub>2</sub>O emissions after soil  
805 amendment. This model of NI activity contrasted with that in a more complex model in which NI  
806 reduced N<sub>2</sub>O emissions directly, rather than through nitrification (Li et al., 2020). In such a  
807 model, NI would not directly affect [NH<sub>4</sub><sup>+</sup>] and [NO<sub>3</sub><sup>-</sup>] so that greater values of  $R_I$  could be used  
808 to get similar reductions in N<sub>2</sub>O emissions. The values of  $R_I$  and  $f_{T_{s_I}}$  used in our model caused  
809 N<sub>2</sub>O emissions modelled with NI to decline more rapidly than those measured following spring  
810 applications (Fig. 6b and Fig. 7b). These values need to be constrained by further studies with  
811 more frequent measurements of declines in NI activity following amendment to determine if  
812 alternative models for the time course of these declines might be considered.

813

## 814 7. CONCLUSIONS

- 815 (a) A simple, time-dependent algorithm for adding NI effects on N<sub>2</sub>O emissions into the  
816 existing model *ecosys* has been presented.
- 817 (b) The direct effect of NI on N<sub>2</sub>O emissions in the model was confined to the inhibition  
818 of NH<sub>4</sub><sup>+</sup> oxidation
- 819 (c) Additional effects of NI on N<sub>2</sub>O emissions were caused by slower nitrifier growth and  
820 O<sub>2</sub> uptake. The combined effects in (b) and (c) reduced N<sub>2</sub>O emissions by 35% - 58%  
821 depending on seasonal weather and time of manure application.
- 822 (d) Slower nitrification modelled with this algorithm caused increases in soil NH<sub>4</sub><sup>+</sup>  
823 concentrations and reductions in soil NO<sub>3</sub><sup>-</sup> concentrations and N<sub>2</sub>O fluxes that were  
824 consistent with those measured following fall and spring applications of slurry over  
825 two years.
- 826 (e) NI in the model remained effective in reducing N<sub>2</sub>O emissions modelled during  
827 spring thaw, particularly when these emissions were increased by delaying fall slurry  
828 applications or increasing fall tillage intensity
- 829 (f) NI in the model increased NH<sub>3</sub> emissions more than it reduced NO<sub>3</sub><sup>-</sup> leaching, causing  
830 indirect effects on N<sub>2</sub>O emissions that partially offset direct effects.
- 831 (g) NI had no significant effect on modelled or measured barley silage yields.
- 832 (h) Some further work is needed to corroborate parameters in the NI algorithm under a  
833 wider range of site conditions.
- 834 (i) The addition of NI to *ecosys* may allow emission factors for different NI products to  
835 be derived from annual N<sub>2</sub>O emissions modelled under diverse site, soil, land use and  
836 weather as required in IPCC Tier 3 methodology.

837

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844

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**Table 1:** List of supplements in the Supporting Material

<b>Supplement</b>	<b>Title</b>	<b>Equations</b>
S1	Microbial C, N and P Transformations	[A1] – [A39]
S2	Soil-Plant Water Relations	[B1] – [B14]
S3	Gross Primary Productivity, Autotrophic Respiration, Growth and Litterfall	[C1] – [C53]
S4	Soil Water, Heat, Gas and Solute Fluxes	[D1] – [D21]
S5	Solute Transformations	[E1] – [E57]
S6	Symbiotic N <sub>2</sub> Fixation	[F1] – [F26]
S7	CH <sub>4</sub> Production and Consumption	[G1] – [G27]
S8	Inorganic N Transformations	[H1] – [H21]

985 **Table 2:** Key soil properties of the Black Chernozem soil at the South Edmonton Farm used in  
 986 *ecosys*.

Depth	BD	FC	WP	Ksat <sup>†</sup>	Sand	Silt	Clay	pH	SOC	SON
m to bottom	Mg m <sup>-3</sup>	m <sup>3</sup> m <sup>-3</sup>		mm h <sup>-1</sup>	g kg <sup>-1</sup> mineral soil				g kg <sup>-1</sup> soil	
0.01	1.15	0.34	0.15	18.0	280	450	270	6.3	57.1	5.74
0.025	1.15	0.34	0.15	18.0	280	450	270	6.3	57.1	5.74
0.05	1.15	0.34	0.15	18.0	280	450	270	6.3	57.1	5.74
0.10	1.15	0.34	0.15	18.0	280	450	270	6.3	57.1	5.74
0.15	1.35	0.34	0.15	18.0	280	450	270	6.3	40.7	3.80
0.30	1.40	0.34	0.15	7.5	250	470	280	6.3	40.7	3.80
0.60	1.50	0.35	0.17	2.5	270	420	310	7.1	3.2	0.3
0.90	1.50	0.35	0.17	2.5	270	420	310	7.1	3.2	0.3
1.20	1.50	0.35	0.17	2.5	270	420	310	7.1	3.2	0.3
1.50	1.50	0.35	0.17	2.5	270	420	310	7.1	3.2	0.3

987 <sup>†</sup> from Saxton et al. (1986)

988

989 **Table 3.** Plant and soil management schedule at the Edmonton South Campus Farm

990

Year	Date	Management	Amount			
			----- g N m <sup>-2</sup> -----			g C m <sup>-2</sup>
			Urea	NH <sub>4</sub> <sup>+</sup>	Organic N	Organic C
2014	15 May	fertilizer	7.2			
	15 May	planting				
	21 Aug.	harvest				
	30 Sep.	fall slurry		21.7	16.4	229.4
2015	11 May	planting				
	12 May	spring slurry		19.4	20.5	176.9
	28 Jul.	harvest				
	07 Oct.	fall slurry		21.3	19.0	198.5
2016	14 May	planting				
	16 May	spring slurry		27.2	18.6	227.5
	15 Aug.	harvest				

991

992

993 **Table 4.** Average temperatures and total precipitation measured at the Edmonton South Farm  
 994 during autumn/winter, winter/spring and spring/summer in 2014/2015 and 2015/2016.

	2014	2015		2014/5		2015	2016		2015/6
from	16 Sep	1 Jan	1 May	Average		16 Sep	1 Jan	1 May	Average
to	31 Dec	30 Apr	15 Sep	or Total		31 Dec	30 Apr	15 Sep	or Total
Temp. (°C)	0.4	-1.8	16.0	<b>5.6</b>		0.8	0.1	15.8	<b>6.3</b>
Precip. (mm)	50	75	195	<b>320</b>		41	38	402	<b>481</b>

995

996 **Table 5:** Seasonal N<sub>2</sub>O emissions measured and modelled during late spring in 2015 and 2016  
 997 without slurry (C) or with slurry applied in spring (S) without NI, with nitrapyrin or with DMPP  
 998 on dates in the field study (Table 3). Negative values denote emissions, positive values uptake.

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999

	Year	2015		2016	
	Period	12 May – 11 June		17 May – 16 June	
		Measured	Modelled	Measured	Modelled
Treat.	Amend.	----- mg N m <sup>-2</sup> -----			
C		+3	-1	+14	-5
S	none	-88	-89	-160	-153
S	DMPP	-48	-58	-45	-72
S	nitrapyrin	-56	-62	-57	-91

1000

1001

1002 **Table 6:** Seasonal and annual N<sub>2</sub>O emissions modelled during autumn/winter, winter/spring and  
 1003 spring/summer in 2014/2015 and 2015/2016 without slurry (C) or with slurry applied in fall (F)  
 1004 or spring (S) without NI or with R<sub>I</sub> for DMPP on dates in the field study (Table 3), and in fall on  
 1005 dates 2 weeks before (F-2) or after (F+2) those in the field study, and with soil mixing during  
 1006 slurry application (M) increased to 0.4 and 0.6 from 0.2 in the field study. Negative values  
 1007 denote emissions.

1008

	Year	2014	2015		2014/5	2015	2016		2015/6
	from	16 Sep	1 Jan	1 May	Total	16 Sep	1 Jan	1 May	Total
	to	31 Dec	30 Apr	15 Sep		31 Dec	30 Apr	15 Sep	
Treat.	Amend.	----- mg N m <sup>2</sup> -----							
C		-2	-10	-14	<b>-26</b>	-2	-11	-13	<b>-26</b>
F	none	-93	-74	-17	<b>-184</b>	-93	-74	-27	<b>-194</b>
F	DMPP	-39	-68	-29	<b>-136</b>	-41	-50	-30	<b>-121</b>
F	nitrapyrin	-50	-101	-20	<b>-171</b>	-48	-61	-29	<b>-136</b>
S	none	-2	-10	-119	<b>-131</b>	-3	-25	-182	<b>-210</b>
S	DMPP	-2	-10	-90	<b>-102</b>	-3	-18	-106	<b>-127</b>
S	nitrapyrin	-2	-10	97	<b>-109</b>	-3	-24	-126	<b>-153</b>
F -2	none	-102	-64	-17	<b>-183</b>	-137	-47	-26	<b>-210</b>
F -2	DMPP	-56	-63	-19	<b>-138</b>	-55	-34	-23	<b>-112</b>
F +2	none	-92	-111	-17	<b>-220</b>	-84	-189	-52	<b>-325</b>
F +2	DMPP	-28	-78	-39	<b>-145</b>	-29	-99	-43	<b>-171</b>
F 0.5	none	-97	-71	-16	<b>-184</b>	-93	-168	-22	<b>-283</b>
F 0.5	DMPP	-58	-77	-17	<b>-152</b>	-59	-111	-20	<b>-190</b>
F 0.8	none	-102	-81	-21	<b>-204</b>	-98	-184	-19	<b>-301</b>
F 0.8	DMPP	-65	-76	-18	<b>-159</b>	-69	-138	-18	<b>-225</b>
S 0.5	none	-2	-10	-129	<b>-141</b>	-3	-27	-168	<b>-198</b>
S 0.5	DMPP	-2	-10	-98	<b>-110</b>	-3	-21	-124	<b>-147</b>
S 0.8	none	-2	-10	-138	<b>-150</b>	-3	-25	-168	<b>-196</b>
S 0.8	DMPP	-2	-10	-102	<b>-114</b>	-3	-19	-123	<b>-145</b>

1009

1010

1011 **Table 7:** Annual  $\text{NO}_3^-$  discharge and  $\text{NH}_3$  emissions modelled from 16 Sep. to 15 Sep. in  
 1012 2014/2015 and 2015/2016 without slurry (C) or with slurry applied in fall (F) or spring (S)  
 1013 without NI and with DMPP on dates in the field study (Table 3), and in fall on dates 2 weeks  
 1014 before (F-2) or after (F+2) those in the field study, and with soil mixing during slurry application  
 1015 (M) increased to 0.5 and 0.8 from 0.2 in the field study. For  $\text{NH}_3$  positive values indicate  
 1016 deposition, negative values emission.

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1017

	Year	2014/5		2015/6	
Treat.	Amend.				
		$\text{NH}_3$	$\text{NO}_3^-$	$\text{NH}_3$	$\text{NO}_3^-$
		----- mg N m <sup>-2</sup> -----			
C		+14	277	+34	421
F	none	+7	330	+29	691
F	DMPP	-147	317	+13	662
S	none	+8	279	+21	617
S	DMPP	+4	279	+14	598
F -2	none	+4	336	+26	678
F -2	DMPP	-9	326	+12	658
F +2	none	+3	336	+28	697
F +2	DMPP	-194	321	+10	662
F 0.5	none	-9	321	+17	558
F 0.5	DMPP	-79	314	-3	554
F 0.8	none	-34	500	+1	368
F 0.8	DMPP	-101	473	-29	370
S 0.5	none	-3	279	+1	490
S 0.5	DMPP	-7	279	-8	493
S 0.8	none	-15	279	-15	361
S 0.8	DMPP	-21	279	-26	365

1018

1019



1020 **Table 8:** Barley silage yields modelled and measured without slurry (C) or with slurry applied in  
 1021 fall (F) or spring (S) with and without NI applied on dates in the field study (Table 3)

	Year	2015		2016	
Treat.	Amend.	Mod.	Mes. <sup>†</sup>	Mod.	Mes. <sup>††</sup>
----- g C m <sup>-2</sup> -----					
C		154	198 ± 24	128	124 ± 9
F	none	284	355 ± 4	344	242 ± 45
F	DMPP	283	360 ± 25	343	255 ± 15
S	none	293	267 ± 12	334	195 ± 33
S	DMPP	297	317 ± 17	344	189 ± 32

1022 <sup>†</sup> calculated as 45% DM

1023 <sup>††</sup> measured yields reduced by lodging

1024

1025

1026 **Table 9:** Sensitivity of seasonal N<sub>2</sub>O emissions modelled during late spring in 2015 and 2016 to  
 1027 changes in initial inhibition ( $I_{t=0}$  in Eq. 1) and inhibition constant ( $K_{iNH_4}$  in Eq. 2) following  
 1028 spring slurry application on dates in the field study (Table 3). Negative values denote emissions.

---

1029

Year		2015	2016
Period		12 May – 11 June	17 May – 16 June
		----- mg N m <sup>-2</sup> -----	
No NI		-89 <sup>†</sup>	-153 <sup>†</sup>
$I_{t=0}$	$K_{iNH_4}$		
1.0	7000	-58 <sup>†</sup>	-72 <sup>†</sup>
0.9	7000	-60	-80
0.8	7000	-62	-90
1.0	3500	-62	-78
0.9	3500	-64	-86
0.8	3500	-65	-95
1.0	14000	-54	-66
0.9	14000	-57	-75
0.8	14000	-59	-85

1030 <sup>†</sup> from Table 5

1031

1032

**LIST OF FIGURES**

1033

1034 **Fig. 1.** Key transformations governing N<sub>2</sub>O emissions as represented in *ecosys*. Expressions in  
1035 square brackets refer to equations in the Supplement as described in Sec. 2.

1036 **Fig. 2.** Soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations measured (symbols) and modelled (lines) at 0 – 10 cm  
1037 depth following applications of dairy slurry without and with DMPP. Arrows indicate dates of  
1038 application.

1039 **Fig. 3.** Aqueous concentrations of O<sub>2</sub> and N<sub>2</sub>O modelled at depth of slurry injection (14 cm)  
1040 during emission events in early spring of (a,b) 2015 and (c,d) 2016 after fall slurry applications  
1041 with or without DMPP on DOY 273 in 2014 and DOY 280 in 2015, and in later spring of (e,f)  
1042 2015 and (g,h) 2016 after spring slurry applications on DOY 132 in 2015 and DOY 137 in 2016.

1043 **Fig. 4.** (a) Air temperature and precipitation, and (b) N<sub>2</sub>O fluxes measured (symbols) and  
1044 modelled (lines) during early spring 2015 with no slurry (control), and following slurry  
1045 application on DOY 273 in 2014 with or without DMPP. Filled symbols represent manual  
1046 chamber measurements by Lin et al. (2018). Negative values denote emissions.

1047 **Fig. 5.** (a) Air temperature and precipitation, and (b) N<sub>2</sub>O fluxes measured (symbols) and  
1048 modelled (lines) during early spring 2016 with no slurry (control), and following slurry  
1049 application on DOY 280 in 2015 with or without DMPP. Filled symbols represent manual  
1050 chamber measurements. Negative values denote emissions.

1051 **Fig. 6.** (a) Air temperature and precipitation, and (b) N<sub>2</sub>O fluxes measured (symbols) and  
1052 modelled (lines) during spring 2015 with no slurry (control), and following slurry application on  
1053 DOY 132 in 2015 with or without DMPP. Negative values denote emissions.

1054 **Fig. 7.** (a) Air temperature and precipitation, and (b) N<sub>2</sub>O fluxes measured (symbols) and  
1055 modelled (lines) during spring 2016 with no slurry (control), and following slurry application on  
1056 DOY 137 in 2016 with or without DMPP. Negative values denote emissions.

1057