Ecological Controls on N$_2$O Emission in Surface Litter and Near-surface Soil of a Managed Grassland: Modelling and Measurements

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ABSTRACT

Large variability in N$_2$O emissions from managed grasslands may occur because most emissions originate in surface litter or near-surface soil where variability in soil water content ($\theta$) and temperature ($T_s$) is greatest. To determine whether temporal variability in $\theta$ and $T_s$ of surface litter and near-surface soil could explain that in N$_2$O emissions, a simulation experiment was conducted with ecosys, a comprehensive mathematical model of terrestrial ecosystems in which processes governing N$_2$O emissions were represented at high temporal and spatial resolution. Model performance was verified by comparing N$_2$O emissions, CO$_2$ and energy exchange, and $\theta$ and $T_s$ modelled by ecosys with those measured by automated chambers, eddy covariance (EC) and soil sensors at an hourly time-scale during several emission events from 2004 to 2009 in an intensively managed pasture at Oensingen, Switzerland. Both modelled and measured events were induced by precipitation following harvesting and subsequent fertilizing or manuring. These events were brief (2 – 5 days) with maximum N$_2$O effluxes that varied from < 1 mg N m$^{-2}$ h$^{-1}$ in early spring and autumn to > 3 mg N m$^{-2}$ h$^{-1}$ in summer. Only very small emissions were modelled or measured outside these events. In the model, emissions were generated almost entirely in surface litter or near-surface (0 – 2 cm) soil, at rates driven by N availability with fertilization vs. N uptake with grassland regrowth, and by O$_2$ supply controlled by litter and soil wetting relative to O$_2$ demand from microbial respiration. In the model, NOx availability relative to O$_2$ limitation governed both the reduction of more oxidized electron acceptors to N$_2$O and the reduction of N$_2$O to N$_2$, so that the magnitude of N$_2$O emissions was not simply related to surface and...
near-surface $\theta$ and $T_s$. Modelled $\text{N}_2\text{O}$ emissions were found to be sensitive to defoliation intensity and timing which controlled plant N uptake and soil $\theta$ and $T_s$ prior to and during emission events. Reducing LAI remaining after defoliation to one-half that under current practice and delaying harvesting by 5 days raised modelled $\text{N}_2\text{O}$ emissions by as much as 80% during subsequent events and by an average of 43% annually. Modelled $\text{N}_2\text{O}$ emissions were also found to be sensitive to surface soil properties. Increasing near-surface bulk density by 10% raised $\text{N}_2\text{O}$ emissions by as much as 100% during emission events and by an average of 23% annually. Relatively small spatial variation in management practices and soil surface properties could therefore cause the large spatial variation in $\text{N}_2\text{O}$ emissions commonly found in field studies. The global warming potential from annual $\text{N}_2\text{O}$ emissions in this intensively managed grassland largely offset those from net C uptake in both modelled and field experiments. However model results indicated that this offset could be adversely affected by suboptimal land management and soil properties.

INTRODUCTION

The contribution of managed grasslands to reducing atmospheric greenhouse gas (GHG) concentrations through net uptake of CO$_2$ (Ammann et al., 2005) may be at least partially offset by net emissions of $\text{N}_2\text{O}$ (Conant et al., 2005, Fléchard et al., 2005). These emissions may be substantial, with $\text{N}_2\text{O}$ emission factors of as large as 3% measured in intensively managed grasslands with fertilizer rates of 25 - 30 g N m$^{-2}$ y$^{-1}$ (Imer et al., 2013; Rafique et al., 2011) These emissions are highly variable temporally and spatially because they are determined by complex interactions among short-term weather events (warming, precipitation), land management practices (N amendments, defoliation), and soil properties (e.g. bulk density, water retention). The $\text{N}_2\text{O}$ driving these emissions in managed grasslands is thought to be generated within the upper 2 cm of the soil profile (van der Weerden et al., 2013) and in surface litter left by grazing or harvesting (Pal et al., 2013) so that diurnal heating and precipitation events that cause rapid warming and wetting of the litter and soil surface may cause large but brief emission events. These events are thought to be driven by increased demand for electron acceptors by nitrification and denitrification, and reduced supply of $\text{O}_2$ by which these demands are preferentially met, and therefore increased demand for alternative acceptors $\text{NO}_3^-$, $\text{NO}_2^-$ and $\text{N}_2\text{O}$ by autotrophic nitrifiers and heterotrophic denitrifiers.
The magnitude of N$_2$O emission events in managed grasslands generally increases with the
amount of N added as urine, manure or fertilizer, and with the intensity of defoliation by grazing or
cutting (Ruzjerez et al. 1994). Thus Imer et al. (2013) found a negative correlation between LAI and
N$_2$O emissions at intensively managed grasslands in Switzerland. The increase in emissions with
defoliation has been attributed to increased urine and manure deposition and soil compaction with
defoliation by grazing, and to slower uptake of N and water by slower-growing plants with defoliation
by harvesting (Jackson et al., 2015). Both N additions and defoliation are thought to raise these
emissions by increasing the supply of NH$_4^+$ and NO$_3^-$ to autotrophic nitrifiers and heterotrophic
denitrifiers. This increase raises the demand for alternative e$^-$ acceptors by these microbial populations if
the supply of O$_2$, the preferred e$^-$ acceptor, fails to meet demand, as may occur when soil water content
($\theta$) after defoliation rises with precipitation or reduced transpiration. This supply is governed by physical
and hydrological properties (porosity, water retention) of the near-surface soil. Consequently land use
practices and soil properties must be considered when estimating N$_2$O emissions from managed
grasslands.

Recognition of the effects of precipitation events, N amendments and soil properties on N$_2$O
emissions has led to empirical models in which annual emission inventories are calculated directly from
annual precipitation and N inputs (Lu et al., 2006), or monthly emission events are calculated from
monthly precipitation, air temperature $T_a$, and $\theta$ (Fléchard et al., 2007). However the soil depth at which
most emitted N$_2$O is generated (0 – 2 cm) is much shallower than that at which $\theta$ used in these models is
measured (5 – 10 cm) (Fléchard et al., 2007), and the soil temperature $T_s$ at this depth may differ from $T_a$
This is particularly so for grasslands in which N additions are necessarily left on the soil surface without
incorporation. Thus large N$_2$O emissions may be caused by surface wetting from precipitation on dry
soils following fertilizer application, so that deeper $\theta$ is sometimes found to be of little explanatory value
in empirical models (Fléchard et al., 2007). Furthermore the response of denitrification to $\theta$ has been
found in experimental studies to rise sharply with $T_s$, likely through the combined effects of $T_s$ on
increasing demand and reducing supply of O$_2$ at microbial microsites (Craswell, 1978). The interaction
between $T_s$ and $\theta$ on N$_2$O emissions is clearly apparent in the meta-analysis of N$_2$O emissions from
European grasslands by Fléchard et al. (2007). This interaction has been represented in empirical models
by fitting interdependent threshold values of $T_s$ and $\theta$ above which emissions have been measured in
field experiments (Smith and Massheder, 2014). However a more robust simulation of this interaction on
N₂O emissions should be built from basic biological and physical processes that are independent of site-specific measurements.

Process models used to simulate N₂O emissions from managed grasslands must therefore explicitly represent the effects of short-term weather events on near-surface $T_s$ and $\theta$, as well as the effects of N additions and defoliation on near-surface NH₄⁺ and NO₃⁻. These models must also explicitly represent the effects of mineral N, $T_s$ and $\theta$, and of soil physical and hydrological properties, on the demand for vs. supply of O₂ and alternative e⁻ acceptors NO₃⁻, NO₂⁻ and N₂O, and on the oxidation-reduction reactions by which these e⁻ acceptors are reduced. However earlier process models have usually simulated N₂O emissions as $T_s$-dependent functions of nitrification and denitrification rates, modified by texture-dependent functions of water-filled pore space (WFPS) (e.g. Li et al., 2005). In some models additional empirical functions of $T_s$ (Chatskikh et al., 2005), or of $T_s$ and WFPS (Schmid et al., 2001), are used to calculate the fraction of nitrification that generates N₂O, and the fraction of heterotrophic respiration $R_h$ that drives denitrification (Schmid et al., 2001), thereby avoiding the explicit simulation of O₂ and its control on N₂O emissions. A more detailed summary of functions of mineral N, $T_s$ and WFPS currently used to model N₂O emissions is given in Fang et al. (2015). These functions have many model-dependent parameters and function independently of each other, so that key interactions among reduced C and N substrates, $T_s$ and $\theta$ on N₂O production may not be simulated. In none of these approaches are the oxidation-reduction reactions by which N₂O is generated or consumed explicitly represented. Furthermore the effects of defoliation and surface litter on N₂O emissions have not been considered in earlier process models.

Process models used to simulate N₂O emissions must also accurately represent the key processes of C cycling that drive those of N cycling from which N₂O is generated and consumed. These include gross and net primary productivity (GPP and NPP) which drive mineral N uptake and assimilation with plant growth. GPP and consequent plant growth also drive autotrophic respiration ($R_a$), the below-ground component of which contributes to soil O₂ demand. NPP drives litterfall and root exudation, which in turn drive heterotrophic respiration ($R_h$) that also contributes to litter and soil O₂ demand, and thereby to demand for alternative e⁻ acceptors which drive N₂O generation. Heterotrophic respiration also drives key N transformations such as mineralization/immobilization, thereby controlling availability of these alternative e⁻ acceptors. Land use practices such as defoliation from grazing or harvesting, and
soil properties such as porosity and water retention, alter these key C cycling processes, and thereby N₂O emissions. Therefore these emissions are best simulated by comprehensive ecosystem models.

In the mathematical model *ecosys*, the effects of weather and N amendments on $T_s$, $\theta$, and mineral N, and hence on the demand for vs. supply of O₂, NO₃⁻, NO₂⁻ and N₂O, and thereby on N₂O emissions, are simulated by explicitly coupling the transport processes with the oxidation – reduction reactions by which these e⁻ acceptors are known to be generated, transported and consumed in soils (Grant and Pattey, 1999, 2003, 2008; Grant et al., 2006; Metivier et al., 2009). The development of model algorithms for these processes was guided by two key principles:

1. all algorithms in the model must represent physical, biochemical and biological processes studied in basic research programs (e.g. convective-diffusive transport, oxidation-reduction reactions) so that these algorithms can be parameterized independently of the model

2. this parameterization must be conducted at spatial and temporal scales smaller than those of prediction (in this case seasonal N₂O fluxes) so that site-specific effects on predicted values are not incorporated into the algorithms, limiting their robustness.

These principles are designed to avoid as much as possible the use of site- and model-specific algorithms that may lack application in sites and models other than those for which they were developed. Although models based on these principles appear complex, they can be better constrained than simpler models because they are parameterized from independent experiments. The resulting detail that application of these principles brings to the model enables better constrained tests of model output against more comprehensive and diverse site data than are possible with simpler models.

In an extension of earlier work with *ecosys*, we propose that temporal and spatial variation in N₂O emissions from an intensively managed grassland can be largely explained from the modelled effects of N amendments (fertilizer, manure), plant management (e.g. harvest intensity and timing), soil properties (e.g. bulk density) and weather ($T_s$, precipitation events) on the demand for vs. supply of O₂, NO₃⁻, NO₂⁻ and N₂O in surface litter and near-surface soil (0 – 2 cm). Testing this explanation requires frequent measurements to characterize the large temporal variation in N₂O emissions found in managed ecosystems. Such measurements were recorded from 2004 to 2009 using automated chambers in
intensively managed grass-clover grassland at Oensingen, Switzerland, and used here to test our
modelled explanation of these fluxes.

MODEL DEVELOPMENT

General Overview

The hypotheses for N$_2$O oxidation-reduction reactions and their coupling with gas transport in
ecosys are represented in Fig. 1 and described further below with reference to equations and definitions
listed in Appendices A, C, D, E, H of the Supplement (indicated by square brackets in the text below,
e.g. [H1] refers to Eq. 1 in Appendix H), as well as in earlier papers (Grant and Pattey, 1999, 2003,
2008; Grant et al., 2006; Metivier et al., 2009). These hypotheses are part of a larger model of soil C, N
and P transformations (Grant et al., 1993a,b), coupled to one of soil water, heat and solute transport in
surface litter and soil layers, which are in turn components of the comprehensive ecosystem model
ecosys (Grant, 2001).

Mineralization and Immobilization of Ammonium by All Microbial Populations

Heterotrophic microbial populations $m$ (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 $i$ ($i =$
aminal manure, coarse woody plant residue, fine non-woody plant residue, particulate organic matter, or
humus). Autotrophic microbial populations $n$ (aerobic NH$_4^+$ and NO$_2^-$ oxidizers, hydrogenotrophic
methanogens and methanotrophs) are associated with inorganic substrates. These populations grow with
energy generated from coupled oxidation of reduced dissolved C (DOC) by heterotrophs, or of mineral
N (NH$_4^+$ and NO$_2^-$) by nitrifiers, and reduction of e- acceptors O$_2$ and NO$_x$. These populations decay
according to first-order rate constants with provision for internal recycling of limiting nutrients (N, P).
During growth, each functional component $j$ ($j =$ nonstructural, labile, resistant) of these populations
seeks to maintain a set C:N ratio by mineralizing NH$_4^+$ ([H1a]) from, or by immobilizing NH$_4^+$ ([H1b])
or NO$_3^-$ ([H1c]) to, microbial nonstructural N. Nitrogen limitations during growth may cause C:N ratios
to rise above set values, and greater recovery of microbial N from structural to nonstructural forms to
reduce N loss during decay, but at a cost to microbial function. These transformations control the
exchange of N between organic and inorganic states, and hence affect the availability of alternative e⁻
acceptors for nitrification and denitrification.

Oxidation of DOC and Reduction of Oxygen by Heterotrophs

Constraints on heterotrophic oxidation of DOC imposed by O₂ uptake are solved in four steps:
1) DOC oxidation under non-limiting O₂ is calculated from active biomass, DOC concentration, and an
   Arrhenius function of \( T_s \) [H₂],
2) O₂ reduction to H₂O under non-limiting O₂ (O₂ demand) is calculated from 1) using a set respiratory
   quotient [H₃],
3) O₂ reduction to H₂O under ambient O₂ is calculated from radial O₂ diffusion through water films of
   thickness determined by soil water potential [H₄a] coupled with active uptake at heterotroph surfaces
   driven by 2) [H₄b]. O₂ diffusion and active uptake is calculated for each heterotrophic population
   associated with each organic substrate, allowing [H₄] to calculate lower O₂ concentrations at
   microbial surfaces 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
   population is constrained by O₂ diffusion to that population. O₂ uptake by each heterotrophic
   population also accounts for competition for O₂ uptake with other heterotrophs, nitrifiers, roots and
   mycorrhizae, calculated from its O₂ demand relative to those of other aerobic populations.
4) DOC oxidation to CO₂ under ambient O₂ is calculated from 2) and 3) [H₅]. The energy yield of DOC
   oxidation drives the uptake of additional DOC for construction of microbial biomass \( M_{i,k} \) according to
   construction energy costs of each heterotrophic population [A21]. Energy costs of denitrifiers are
   larger than those of obligately aerobic heterotrophs, placing denitrifiers at a competitive disadvantage
   for growth and hence DOC oxidation that declines with greater use of e⁻ acceptors other than O₂.

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

Constraints imposed by NO₃⁻ availability on DOC oxidation by denitrifiers are solved in five
steps:
1) NO₃⁻ reduction to NO₂⁻ under non-limiting NO₃⁻ is calculated from electrons demanded by DOC
   oxidation to CO₂ but met by O₂ reduction to H₂O because of diffusion limitations to O₂ supply, and
   hence transferred to NO₃⁻ [H₆],
2) NO$_3^-$ reduction to NO$_2^-$ under ambient NO$_3^-$ is calculated from 1), accounting for relative concentrations and affinities of NO$_3^-$ and NO$_2^-$ [H7],

3) NO$_2^-$ reduction to N$_2$O under ambient NO$_2^-$ is calculated from demand for electrons not met by NO$_3^-$ reduction in 2), accounting for relative concentrations and affinities of NO$_2^-$ and N$_2$O [H8],

4) N$_2$O reduction to N$_2$ under ambient N$_2$O is calculated from demand for electrons not met by NO$_2^-$ reduction in 3) [H9],

5) additional DOC oxidation to CO$_2$ enabled by NO$_x$ reduction in 2), 3) and 4) is added to that enabled by O$_2$ reduction from [H5], the energy yield of which drives additional DOC uptake for construction of $M_{i,n}$. This additional uptake offsets the disadvantage incurred by the larger construction energy costs of denitrifiers.

Oxidation of Ammonia and Reduction of Oxygen by Nitrifiers

Constraints on nitrifier oxidation of NH$_3$ imposed by O$_2$ uptake are solved in four steps:

1) substrate (NH$_3$) oxidation under non-limiting O$_2$ is calculated from active biomass, NH$_3$ and CO$_2$ concentrations, and an Arrhenius function of $T_s$ [H11],

2) O$_2$ reduction to H$_2$O under non-limiting O$_2$ is calculated from 1) using set respiratory quotients [H12],

3) O$_2$ reduction to H$_2$O under ambient O$_2$ is calculated from radial O$_2$ diffusion through water films of thickness determined by soil water potential [H13a] coupled with active uptake at nitrifier surfaces driven by 2) [H13b]. O$_2$ uptake by nitrifiers also accounts for competition for O$_2$ uptake with heterotrophic DOC oxidizers, roots and mycorrhizae,

4) NH$_3$ oxidation to NO$_2^-$ under ambient O$_2$ is calculated from 2) and 3) [H14]. The energy yield of NH$_3$ oxidation drives the fixation of CO$_2$ for construction of microbial biomass $M_{i,o}$ according to construction energy costs of nitrifier populations.

Oxidation of Nitrite and Reduction of Oxygen by Nitrifiers

Constraints on nitrifier oxidation of NO$_2^-$ to NO$_3^-$ imposed by O$_2$ uptake [H15 - H18] are solved in the same way as are those of NH$_3$ [H11 - H14]. The energy yield of NO$_2^-$ oxidation drives the fixation of CO$_2$ for construction of microbial biomass $M_{i,o}$ according to construction energy costs of each nitrifier population.
Oxidation of Ammonia and Reduction of Nitrite by Nitrifiers

Constraints on nitrifier oxidation of NH₃ imposed by NO₂⁻ availability are solved in three steps:

1) NO₂⁻ reduction to N₂O under non-limiting NO₂⁻ is calculated from electrons demanded by NH₃ oxidation but not accepted for O₂ 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 1) [H20], competing for NO₂⁻ with denitrifiers [H8] and nitrifiers [H18],

3) additional NH₃ oxidation to NO₂⁻ enabled by NO₂⁻ reduction in 2) [H21] is added to that enabled by O₂ reduction from [H14]. The energy yield from this oxidation drives the fixation of additional CO₂ for construction of \( M_{l,n} \).

Uptake of Ammonium and Reduction of Oxygen 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 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 is calculated from 1) plus oxidation of root and mycorrhizal nonstructural C under non-limiting O₂ 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 2) [C14c]. O₂ uptake by roots and mycorrhizae also accounts for competition with O₂ uptake by heterotrophic DOC oxidizers, and autotrophic nitrifiers, calculated from their O₂ demands relative to those of other populations.

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

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

Cation Exchange and Ion Pairing of Ammonium

Soil Transport and Surface - Atmosphere Exchange of Gaseous Substrates and Products

Exchange of all modelled gases $\gamma$ ($\gamma =$ O$_2$, CO$_2$, CH$_4$, N$_2$, N$_2$O, NH$_3$ and H$_2$) between aqueous and gaseous states is driven by disequilibrium between aqueous and gaseous concentrations according to a $T_s$-dependent solubility coefficient, constrained by a transfer coefficient based on air-water interfacial area that depends on air-filled porosity [D14 – D15] (Fig. 1). These gases undergo 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 gas- and water-filled porosity. Exchange 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 structure of vegetation and surface litter [D15].

FIELD EXPERIMENT

Site description

The Oensingen field site is located in the central Swiss lowlands (7° 44′E, 47° 17′N) at an altitude of 450 m. The climate is temperate with an average annual rainfall of about 1100 mm and a mean air temperature of 9.5 °C. The soil is classified as a Eutri-Stagnic Cambisol developed on clayey alluvial deposits, key properties of which are given in Table 1. Prior to the experiment, the field site was managed as a ley-arable rotation. In December 2000, the field was ploughed and left in fallow until 11 May 2001. The field was then sown with a grass-clover mixture typical for permanent grassland under intensive management. The field was ploughed again on 19 December 2007, left in fallow until 5 May 2008, when it was tilled and re-sown with the same grass-clover mix as in 2001. The period of study extended from sowing in 2001 to the end of 2009, during which the field was cut between three and five times per year and harvested as hay, silage or fresh grass, fertilized two to three times per year with manure as liquid cattle slurry and two to three times per year with mineral fertilizer as
ammonium nitrate (NH₄NO₃) pellets, for an average annual N application of 23 g N m⁻². All key
management operations during this period are summarized in Table 2.

**Soil, plant and meteorological measurements**

Soil θ and Tₛ were recorded continuously using TDR (Time Domain Reflectometry, ThetaProbe
ML2x, Delta-T Devices, Cambridge, UK) and thermocouples at 5, 10, 30 and 50 cm for θ and at 2, 5,
10, 30 and 50 cm for Tₛ. Leaf area index (LAI) was measured weekly with an optical leaf area meter
(LI-2000, Li-Cor, Lincoln, NB, USA). Plants were collected every 2 to 4 weeks and the samples were dried
for 48 h at 80°C, weighed and analyzed for C, N, P and K by using an elemental analyzer. Hourly
climatic data were recorded continuously with an automated meteorological station, including air
temperature (°C), rainfall (mm), relative humidity (%), global radiation (W m⁻²) and windspeed (m
s⁻¹).

**Nitrous oxide flux measurements**

N₂O fluxes were measured with a fully automated system consisting of up to eight stainless steel
chambers (30 cm × 30 cm × 25 cm) (Flechard et al., 2005, Felber et al., 2014) fixed on PVC frames
permanently inserted 10-cm deep into the soil. The positions of the chambers were changed about every
two months. During measurements, the lids of the chambers were sequentially closed for 15 min. every
2 hours to allow N₂O accumulation in the chamber headspace. During closure the chamber atmosphere
was recirculated at a rate of 1000 ml min⁻¹ through polyamide tube lines (4-mm ID) to analytical
instruments installed in a temperature-controlled field cabin adjacent to the field plots (10 m) and then
back to the chamber headspace. Until autumn 2006 concentrations of N₂O, CO₂ and H₂O in the head
space were measured once per minute with an INNOVA 1312 photoacoustic multi-gas analyzer
(INNOVA Air Tech Instruments, Ballerup, Denmark; www.innova.dk). Interferences in the
measurements caused by overlaps in the absorption spectra of the different gases and by temperature
effects were corrected with a calibration algorithm described in detail by Flechard et al (2005). In
autumn 2006 the system was changed to the gas filter correlation technique for N₂O (Model 46C,
Thermo 279 Environmental Instruments Inc., Sunnyvale, CA, USA). This system was calibrated every 8
hours using certified standard gas mixtures (Messer Schweiz AG, Lenzburg, Switzerland) (Felber et al.
2014).
These measurements were used to calculate N\textsubscript{2}O fluxes from the rate of change in concentration by using a linear or non-linear approach determined by the HMR R-package (Pedersen et al., 2010). The first three of the fifteen 1-min. measurements were omitted from the flux calculation to exclude gas exchange during closing that did not result from changes in emission/production in the soil. This procedure caused a mean increase of about 30% in the fluxes compared to values published in Fléchard et al. (2005) and Ammann et al. (2009), which were evaluated using linear regression. Fluxes from all chambers were averaged over 4-hourly intervals and resulting values attributed to the mid-points of the intervals. Standard errors of these averages were calculated from all fluxes measured during each interval, and thus included both spatial and temporal variation. The fluxes measured from 2002 to 2003 were summarized in Fléchard et al. (2005). Those from 2004 to 2007 were re-evaluated from values described in Ammann et al. (2009). Those from 2008 and 2009 were reprocessed from the EU-Project NitroEurope-IP database using the HMR algorithm.

**CO\textsubscript{2} and Energy Flux Measurements**

CO\textsubscript{2} and energy fluxes were measured by an eddy covariance (EC) system consisting of three-axis sonic anemometers (models R2 and HS, Gill instruments, Lymington, UK) and an open-path infrared CO\textsubscript{2}/H\textsubscript{2}O gas analyzer (model LI-7500, Li-Cor, Lincoln, USA). The EC system used in this study is described in Ammann et al. (2007). The EC tower was located in the centre of the field (52m x 146m), whereas the chambers were located in the south east corner. For most meteorological conditions, the chambers were not within the footprint of the EC towers, although for the main wind directions 80% or more of the footprint was within the field (Neftel et al. 2008). The management of the entire field was uniform throughout the experiment.

**MODEL EXPERIMENT**

*Ecosys* was initialized with the biological properties of plant functional types (PFTs) representing the ryegrass and clover planted at Oensingen. These properties were identical to those in an earlier study (Grant et al., 2012) except for a perennial rather than annual growth habit. These PFTs competed for common resources of radiation, water and nutrients, based on their vertical distributions of leaf area and root length driven by uptake and allocation of C, N and P in each PFT. *Ecosys* was also initialized with the physical and chemical properties of the Eutri-Stagnic Cambisol at Oensingen (Table...
The model was then run from model dates 1 Jan. 1931 to 31 Dec. 2000 under repeating sequences of land management practices and continuous hourly weather data (radiation, $T_a$, RH, wind speed and precipitation) recorded at Oensingen from 1 Jan. 2001 to 31 Dec. 2007 (i.e. 10 cycles of 7 years). This run was long enough for C, N and energy cycles in the model to attain equilibrium under the Oensingen site conditions well before the end of the spinup run. The modelled site was plowed on 19 Dec. 2000, terminating all PFTs.

The model run was then continued from model dates 1 Jan. 2001 to 31 Dec. 2009 under continuous hourly weather data recorded at Oensingen from 1 Jan. 2001 to 31 Dec. 2009 with the same PFTs and land management practices as those at the field site listed in Table 2. For each manure application in the model, an irrigation of 4 mm was added to account for the water in the slurry. For each harvest in the model, the fraction of canopy LAI to be cut (usually 0.85 – 0.95) was calculated from measurements of LAI before and after the corresponding harvest in the field. In ecosys, leaves of each PFT are aggregated into a common canopy which is dynamically resolved into a selected number of layers (10 in this case) of equal LAI for calculating irradiance interception. The leaf fraction to be cut was removed from successive leaf layers from the top of the combined canopy downwards until the cumulative removal attained the set fraction, so that the LAI cut from each PFT depended on the leaf area of the PFT in these layers. Of the phytomass cut with the LAI, 0.76 was removed as harvest and the remainder was added to surface litter, as determined in the intensively managed grassland at Oensingen by Amman et al. (2009). N$_2$O emissions modelled from 2004 through 2009 were compared with those measured by the automated chambers by regressing log-transformed 4-hour averages of modelled on measured values during each year of the study. These comparisons were supported by ones with thermistor and TDR measurements of $T_s$, $\theta$, and with EC measurements of CO$_2$ and energy exchange.

**Model Sensitivity Studies**

Modelled N$_2$O emissions may be affected by three general sources of uncertainty in model inputs: land management practices, soil properties and model parameters. To examine the possible effects of some different land management practices on N$_2$O emissions, the model run from 2001 to 2009 (field) was repeated with (1) increased harvest intensity in which canopy LAI remaining after each harvest was reduced to one-half of those in the first run (1/2), and (2) increased harvest intensity with each harvest delayed by 5 days (1/2 + 5d). These alternative practices caused canopy regrowth
and hence N uptake to be slower during emission events following subsequent manure and fertilizer
applications.

To examine the possible effects of spatial variability in soil properties on N₂O emissions, the
model run from 2001 to 2009 (field) was repeated with bulk density (BD) of the upper 3 cm in the soil
profile (Table 1) increased by 5% or 10%. These larger BDs reduced soil porosity in the upper 3 cm
of the soil, thereby slowing gas exchange with the atmosphere, particularly when the soil was wet
(Fig. 1). All other soil properties used in the model remained unchanged (Table 1).

To examine an effect of uncertainty in model parameterization, the model run from 2001 to
2009 (field) was repeated with the values of two key parameters governing N₂O emissions, the
Michaelis-Menten constants for reduction of O₂ (\(K_{O2}\) in [H4]) or of NO₃⁻ and NO₂⁻ (\(K_{NOx}\) in [H7],
[H8] and [H20]), halved or doubled from those used in the model. Halving or doubling \(K_{O2}\) hastened
or slowed the reduction of O₂ by nitrifiers and denitrifiers and hence slowed or hastened the transfer
of electrons to reduce NO₂⁻ and NO₃⁻ during nitrification and denitrification. Halving or doubling
\(K_{NOx}\) hastened or slowed the reduction of NO₂⁻ by nitrifiers and of NO₃⁻ and NO₂⁻ by denitrifiers All
other parameters in the model remained unchanged.

RESULTS

LAI Modelled vs. Measured from 2002 to 2009

Accurate modelling of ecosystem C cycling and hence N₂O emissions requires accurate
modelling of plant growth as determined by land management practices. LAI modelled and measured
from 2002 to 2009 rose rapidly from low values remaining in spring and after each harvest (Table 1)
to 4 – 6 m² m⁻² before the next harvest, except during 2003 (Fig. 2). Regrowth of LAI in ecosys was
driven by plant nonstructural C, N and P pools replenished from storage reserves remobilized after
harvests, and from products of current C, N and P uptake, those of C being governed by irradiance
interception calculated from regrowing LAI. Regrowth in the model was less rapid than that measured
in 2009 (Fig. 2) because more frequent cutting forced more frequent replenishment of plant
nonstructural C, N and P pools which gradually depleted storage reserves and hence slowed
subsequent regrowth. Hence rates of regrowth modelled after harvests were affected by harvest timing and intensity, as represented by the fractions of LAI removed at harvest.

**N2O Fluxes Modelled vs. Measured from 2004 to 2009**

During peak emissions, standard deviations of N₂O fluxes measured within each 4-hourly interval were found to be as much as 85% relative to mean values. These deviations were largely attributed to small-scale spatial variation in land management (manure and fertilizer application, surface litter from harvesting) and in soil properties (bulk density, water retention), which was not represented in the model run, rather than to temporal variation in environmental conditions (θ, Tₛ) which was represented in the model run. Therefore only a limited fraction of variation in the measured values was amenable to correlation with modelled values. Consequently slopes and coefficients of determination (R²) from regressions of modelled on measured log-transformed fluxes varied from 0.5 to 1.0 and from 0.1 to 0.5 respectively, while intercepts remained close to zero (Table 3). However ratios of mean squares for regression vs. error (F) were highly significant (P < 0.001) in all years of the study, indicating some agreement in the timing and magnitude of modelled and measured emission events. Improved agreement would require that more detailed information about land management and soil properties at each chamber site be provided to the model.

**Daily-Aggregated N₂O Fluxes Modelled vs. Measured from 2004 to 2009**

Daily aggregations of both measured and modelled N₂O emissions indicated that emission events during the study period were confined to intervals of no longer than 5 days when precipitation followed manure or fertilizer applications (Fig. 3). Outside of these intervals emissions remained very small except for a period of emissions modelled, but not measured, after manure application in autumn 2006 (Fig. 3c) and measured, but not modelled, before fertilizer application in spring 2008 (Fig. 3e).

The largest emissions followed manure applications in July and August, but their magnitudes did not vary with the amount of manure N applied. For example, emissions during an event in August 2009 (244 vs. 185 mg N m⁻² measured vs. modelled in Fig. 3f) were greater than those during an event in July 2007 (86 vs. 112 mg N m⁻² measured vs. modelled in Fig. 3d) which in turn were greater than those during an event in July 2005 (54 vs. 96 mg N m⁻² measured vs. modelled in Fig.2b).
However manure N application preceding the event in August 2009 (4.5 g N m$^{-2}$) was less than that in July 2007 (6.7 g N m$^{-2}$) which in turn was less than that in July 2005 (8.5 g N m$^{-2}$) (Table 2), so that smaller applications were followed by greater emissions, precluding a simple emission factor for manure N application.

The magnitude of emission events following fertilizer application also varied. For example, emissions during an event in late August 2007 (105 vs. 82 mg N m$^{-2}$ measured vs. modelled in Fig. 3d) were greater than those during events in September 2004 (24 vs. 2 mg N m$^{-2}$ measured vs. modelled in Fig 2a) and 2005 (6 vs. 11 mg N m$^{-2}$ measured vs. modelled in Fig. 3b), although the fertilizer N applications of 3.0 g N m$^{-2}$ preceding each event were the same (Table 2). These differences in emissions indicated important differences in ecological controls imposed by environmental conditions ($\theta$ and $T_s$) and plant management during each event.

The standard deviations of ~85% relative to the mean values of fluxes measured within each 4-hourly interval during emission events was used to estimate an uncertainty in daily-aggregated fluxes of ca. 30%. Uncertainty in daily fluxes measured during emission events was smaller than the several-fold differences among the events indicating that the magnitude of these events likely differed significantly.

**Relationships between N$_2$O Fluxes and Environmental Conditions during Selected Emission Events**

Environmental conditions measured and modelled from harvest to the end of the two largest emission events following manure applications in July 2007 (Fig. 3d) and August 2009 (Fig. 3f) were examined in greater detail to investigate relationships among near-surface $T_s$, $\theta$, aqueous gas concentrations, and surface fluxes of energy, CO$_2$ and N$_2$O (Figs. 4 and 5). In July 2007, several small precipitation events wetted and cooled the soil between harvesting on DOY 187 and manure application on DOY 194 (Fig. 4a,b). The soil then dried during several days without precipitation and warmed with reduced shading from defoliation (Fig. 2) until DOY 200, after which the soil wetted with further precipitation and cooled with increased shading from plant regrowth (Fig. 4a,b). The higher $\theta$ measured during this period (Fig. 4b) may have been caused by difficulties in maintaining calibration of the TDR probes over long periods in the high-clay soil at Oensingen (Table 1).
higher $\theta$ was not likely caused by overestimated evapotranspiration because modelled LE fluxes, reduced by low LAI after harvesting but increasing with subsequent regrowth, were close to those measured (Fig. 4c), suggesting that total water uptake was accurately modelled. Comparison of modelled and measured $\theta$ was further complicated by soil cracking which altered infiltration at low $\theta$. The effects of $\theta$-dependent macroporosity on preferential flow are explicitly modelled in ecosys, but have not yet been tested in detail.

CO$_2$ influxes were also reduced by low LAI after cutting, but recovered to pre-cut levels by the end of the emission event (Fig. 4d), driving rapid regrowth of LAI (Fig. 2). Large CO$_2$ effluxes measured and modelled after manure application indicated rapid $R_h$ and hence O$_2$ demand that persisted for several days. Influxes measured in the field were reduced from those in the model for several days after manure application, suggesting temporary interference of CO$_2$ fixation by the manure application which was not accounted for in the model.

Litterfall from plant growth [C18, C19] and cutting, as well as from manure application caused a litter layer of 1 – 2 cm to develop on the soil surface in the model. During the N$_2$O emission event from DOY 200 to DOY 205 in 2007 (Fig. 3d), several precipitation events (Fig. 4a) wetted the modelled surface litter and near-surface soil (layers 1 and 2 in Table 1) (Fig. 4e) without increasing $\theta$ at 5 cm (Fig. 4b). This surface wetting slowed gas exchange with the atmosphere, sharply reducing aqueous O$_2$ concentrations [O$_2(s)$] (Fig. 4f) and thereby raising aqueous N$_2$O concentrations [N$_2$O$_{(s)}$] (Fig. 4g). Between precipitation events, drying of the surface litter and near-surface soil in the model allowed recovery of [O$_2(s)$] and forced declines in [N$_2$O$_{(s)}$]. These rises and declines in [N$_2$O$_{(s)}$] drove rises and declines in N$_2$O emissions that tracked those measured in the chambers (Fig. 4h). These emissions rose immediately with the onset of precipitation on DOY 200 (Fig. 4a) before wetting occurred at 5 cm (Fig. 4b), indicating that emissions were driven by surface wetting (Fig. 4e) combined with rapid O$_2$ demand (Fig. 4d). The net generation of N$_2$O modelled in each soil zone, calculated from [H8] + [H20] – [H9], indicated that 0.21 of surface emissions originated in the surface litter and the remainder in the 0 – 1 cm soil layer as indicated by higher [N$_2$O$_{(s)}$] (Fig. 4g), while the deeper soil layers were a very small net sink of N$_2$O. Rises and declines in [N$_2$O$_{(s)}$] also drove rises and declines in N$_2$ emissions that persisted until DOY 205, after which more rapid mineral N uptake
with recovering plant growth, driven by rising LAI (Fig. 2) and hence CO$_2$ influxes (Fig. 4d), caused
both emissions to return to background levels (Fig. 4h).

In 2009, a period of low precipitation with soil drying and warming occurred between
harvesting in late July and manure application on DOY 218 in early August, followed by heavy
precipitation with soil wetting and cooling on DOY 220 (Fig. 5a,b). LE effluxes and CO$_2$ influxes
declined sharply with LAI after cutting, and did not recover to pre-cut levels by the end of the
subsequent emission event on DOY 224 (Fig. 5c,d), indicating a slow recovery of plant growth.
Slurry application caused brief surface wetting on DOY 218 (Fig. 5e) and heavy precipitation on
DOY 220 caused prolonged soil wetting at the surface (Fig. 5e) and at 5 cm (Fig. 5b). Wetting caused
declines in [O$_2$(s)] (Fig. 5f) and thereby rises in [N$_2$O(s)] (Fig. 5g) that were sustained over 3 days.
These rises drove particularly rapid N$_2$O emissions in the model which were consistent in magnitude
with those measured in the chambers (Fig. 5h). Diurnal variation modelled with soil warming and
cooling (Fig. 5a) was not apparent in the measurements, although modelled values remained within
the large uncertainty of the measured values during the emission event. These large emissions were
enabled in the model by slow plant uptake of manure N (Table 2) caused by the slow recovery of
plant CO$_2$ uptake and hence growth after cutting (Fig. 5d). The rises in [N$_2$O(s)] also drove rises in
modelled N$_2$ emissions (Fig. 5h). Emissions declined with surface litter drying on DOY 223 (Fig. 5e)
which allowed surface [O$_2$(s)] to rise (Fig. 5f) and [N$_2$O(s)] to fall (Fig. 5g) while $\theta$ at 5 cm remained
high (Fig. 5b), again indicating that N$_2$O emissions were largely determined by ecological controls in
the surface litter and soil. The net generation of N$_2$O modelled in each soil zone indicated that 0.48 of
surface emissions originated in the surface litter, 0.48 in the 0 – 1 cm soil layer and 0.05 in the 1 – 3
cm soil layer, while the deeper soil layers were a very small net sink of N$_2$O, as indicated by near-
surface gradients of [N$_2$O(s)] (Fig. 5g).

Greater N$_2$O emissions were modelled and measured during the event in August 2009 than in
July 2007 (Fig. 5h vs. Fig. 4h), in spite of smaller N addition (Fig. 3f vs. Fig. 3d; Table 2) and similar
$\theta$ and $T_s$ modelled and measured at 5 cm (Fig. 5a,b vs. Fig. 4a,b). These greater emissions were
attributed in the model to (1) earlier and heavier precipitation after manure application (2 days after
application in Fig. 5a vs. 6 days in Fig. 4a), and (2) slower recovery of CO$_2$ fixation after defoliation,
indicated by slower rises in diurnal amplitude of CO$_2$ fluxes (Fig. 5d vs. Fig. 4d). Heavier
precipitation in 2009 vs. 2007 drove sustained vs. intermittent surface and near-surface wetting (Fig. 5e vs. Fig. 4e) and hence sustained vs. intermittent declines in [O$_2$(s)] and rises in [N$_2$O$_{(s)}$] (Fig. 5f,g vs. Fig. 4f,g). Slower recovery of CO$_2$ fixation after cutting in 2009 vs. 2007 slowed removal of added NH$_4^+$ and NO$_3^-$ from soil. This slower removal, combined with the shorter period between manure application and precipitation, left larger NO$_3^-$ concentrations ([NO$_3^-$]) in litter and surface soil to drive N$_2$O production following precipitation [H7]. These model findings indicated the importance to N$_2$O emissions of surface and near-surface $\theta$ after precipitation, and of plant management (intensity and timing of defoliation in relation to N application) and its effect on subsequent plant CO$_2$ fixation and N uptake.

**Effects of Intensity and Timing of Defoliation on N$_2$O Emission Events**

Increasing harvest intensity and delaying harvest dates slowed LAI regrowth modelled after harvests (Fig. 6). The effects of this slowing on N$_2$O emissions during selected events modelled after subsequent fertilizer and manure applications were examined under diverse $\theta$ and $T_s$ (Figs. 7, 8).

Following manure application on DOY 194 in 2006 (Table 2), slower LAI regrowth from increasing and delaying defoliation slowed the recovery of CO$_2$ fixation (Fig. 7a) and of NH$_4^+$ uptake (Fig. 7b), allowing more nitrification of manure N and hence greater surface [NO$_3^-$] (Fig. 7c). Slower LAI regrowth (Fig. 6) also reduced shading and ET, raising $T_s$ (Fig. 7d) and $\theta$ (Fig. 7e). N$_2$O emissions modelled under field management remained small because of soil drying, in spite of high $T_s$, consistent with measurements (Fig. 3c, Fig. 7f). Increases in emissions modelled with slower LAI regrowth, particularly from delayed harvesting (Fig. 7f), were attributed to slower N uptake (Fig. 7b) and hence larger [NO$_3^-$] in litter and surface soil (Fig. 7c), and to warmer and wetter soil (Fig. 7d,e) which increased O$_2$ demand while reducing O$_2$ supply.

Following a similar manure application on DOY 194 in 2007 (Table 2; Fig. 6), slower LAI regrowth from increasing and delaying defoliation also caused reductions in CO$_2$ fixation (Fig. 7g), which slowed NH$_4^+$ and NO$_3^-$ uptake (Fig. 7h), allowing more nitrification of manure N and hence greater [NO$_3^-$] (Fig. 7i). Lower LAI also caused increases in $T_s$ (Fig. 7j) and $\theta$ (Fig. 7k). Emissions modelled and measured under field management in 2007 (Fig. 7l) were greater than those in 2006 (Fig. 7f), in spite of lower $T_s$ (Fig. 7j vs. Fig. 7d), because near-surface wetting from several precipitation events (Fig. 4a,e) reduced [O$_2$(s)] and increased [N$_2$O$_{(s)}$] (Fig. 4f,g). Emissions modelled
with increased and delayed harvesting rose from those with field harvesting as the emission event progressed (Fig. 7I) because elevated [NO₃⁻] from the manure application persisted longer during the event (Fig. 7I).

Following fertilizer application on DOY 259 in 2005 (Table 2), modelled and measured emissions remained small after soil wetting (Fig. 8f) because lower \( T_s \) (Fig. 8d) slowed soil respiration after wetting, manifested as smaller measured and modelled CO₂ effluxes (Fig. 8a), and so slowed demand for e⁻ acceptors. Under these conditions, increasing and delaying defoliation had little effect on modelled N₂O emissions (Fig. 8f), while CO₂ fixation (Fig. 8a) and N uptake (Fig. 8b) were only slightly reduced and surface NO₃⁻ only slightly increased (Fig. 8c). Following the same fertilizer application on DOY 240 in 2007, modelled and measured emissions were greater than those in 2005 (Fig. 8I) because soils were warmer (Fig. 8j) with more rapid respiration (Fig. 8g), and because fertilizer application and subsequent wetting occurred sooner after cutting (Table 2). Consequently recovery of CO₂ fixation was less advanced (Fig. 8g), reducing cumulative N uptake (Fig. 8h) and leaving larger [NO₃⁻] to drive N₂O generation during the event (Fig. 8h). However reducing LAI remaining after each harvest did not raise N₂O emissions after this application (Fig. 8I), because slower LAI regrowth from earlier harvests had reduced primary productivity and consequently litterfall and hence the mass of the surface litter from which much of the emitted N₂O was generated. Consequently more intense harvests could cause surface litter later in the year to decline to levels at which N₂O generation modelled in the litter was reduced.

**Annual Productivity, N₂O Emissions and the Effects of Defoliation Intensity and Timing**

In the model, plant management practices affected LAI regrowth (Fig. 6), CO₂ fixation, N uptake, and hence soil [NO₃⁻] and N₂O emissions (Figs. 7,8). These effects were summarized at an annual time scale in Table 4. Modelled and EC-derived gross primary productivity (GPP) remained close to 2000 g C m⁻² y⁻¹ during most years except with low precipitation in 2003 and replanting in 2008, indicating a highly productive ecosystem with rapid C cycling and hence rapid demand for e⁻ acceptors (Table 4). Larger modelled vs. measured GPP caused larger modelled vs. measured NEP in 2003, 2005 and 2007. Harvest removals in the model varied with NEP except during replanting in 2008, but tended to exceed those recorded in the field, particularly with low EC-derived NEP in 2005 and 2006. Modelled values were determined in part by the assumed constant harvest efficiency of
Including C inputs from manure applications, modelled and estimated net biome productivity (NBP) were positive except during replanting in 2008, indicating that this intensively managed grassland was a C sink unless replanted. Average annual NBP modelled vs. measured from 2002 to 2009 was 30 vs. 58 g C m\(^{-2}\), with the lower modelled value attributed to greater modelled harvest removals, particularly in 2006.

Slower LAI regrowth from increasing and delaying defoliation (Fig. 6) reduced modelled GPP, \(R_e\) and hence NEP by 5 - 10% during years with greater productivity. However increasing and delaying defoliation did not much affect harvest removals because reduced NEP was offset by greater harvest intensity, so that NBP was reduced except with replanting in 2008.

Annual \(N_2O\) emissions were estimated from chamber measurements for each year of the study by scaling the mean measured fluxes to annual values. These values are presented in Table 4 as upper boundaries for annual emissions because flux measurements from which means were calculated were more frequent during emission events. A lower boundary for annual emissions was also estimated in Table 4 by replacing missing flux measurements with zero. Average lower and upper boundaries for annual emissions estimated from 2002 to 2009 were 0.220 and 0.355 g N m\(^{-2}\) respectively vs. an average annual emission in the model of 0.260 g N m\(^{-2}\) (Table 4). Modelled emissions were nearer to upper boundaries during years with lower measured emissions (2003, 2004, 2006), and to lower boundaries during years with higher measured emissions (2007, 2008, 2009). There was no significant correlation between annual N inputs and measured or modelled emissions. Although annual emissions in the model were close to 1% of annual N inputs during most years, they were greater in 2008 and 2009 in spite of smaller N inputs because of the large emission events modelled after summer applications of fertilizer and manure (Fig. 3e,f; Fig. 5h). Annual N inputs (Table 4), supplemented by 3 – 6 g N m\(^{-2}\) y\(^{-1}\) modelled from symbiotic fixation by clover [F1 – F26]), were only slightly larger than annual N removals with harvesting, supplemented by losses of 2 – 3 g N m\(^{-2}\) y\(^{-1}\) from all other gaseous and aqueous emissions (\(N_2\) from denitrification, \(NH_3\) from volatilization, \(NO_3^-\) from leaching). Consequently residual soil \(NO_3^-\), while present in the model, did not accumulate during the study period, and so did not drive increasing \(N_2O\) emissions with sustained N applications. Modelled and measured annual \(N_2O\) emissions, if expressed in C equivalents (~130 g C g N\(^{-1}\)), largely offset net C uptake expressed as NBP (Table 4).
Increasing harvest intensity and delaying harvest dates had little effect on annual N₂O emissions modelled during the first two years after planting in 2001 and 2008, but raised them substantially thereafter (2003 – 2007) (Table 4). During this period, annual emissions rose by an average of 24% with increased harvest intensity, and by an average of 43% with increased harvest intensity combined with delayed harvest dates. These increases were attributed to reduced N uptake, and to increased $T_s$ and $\theta$ (Figs. 7, 8).

**Effects of increased bulk density on N₂O emissions**

Increasing near-surface (0 – 3 cm) soil BD by 5% or 10% at the beginning of 2001 in the model reduced $[O_{2(s)}]$ after rainfall events and slowed recovery of $[O_{2(s)}]$ during subsequent drying as shown following the manure application in July 2007 (Fig. 9a) and the fertilizer application in late August 2007 (Fig. 9c). These reductions caused increases in modelled N₂O effluxes that varied during emission events (Fig. 9b,d). Effluxes modelled with increases of 10% in near-surface BD were at times double those modelled without (e.g. DOY 201 and 240 in Fig. 9), indicating that relatively small changes in soil surface properties could at times cause large changes in emissions. The effects of increased BD on modelled $T_s$, $\theta$, CO₂ exchange, crop production and N uptake during these events were small (results not shown). Increasing near-surface BD by 10% raised annual N₂O emissions by amounts that increased with annual precipitation from ca. 10% in drier years (e.g. 2003) to ca. 50% in wetter (e.g. 2006) (Table 5).

**Effects of Changes in $K_{O_2}$ and $K_{NO_x}$ on N₂O emissions**

Lowering $K_{O_2}$ to one-half that used in ecosys reduced annual N₂O emissions modelled from 2004 to 2009 by 16% to an average of 0.218 g N m⁻² y⁻¹, near the average lower boundary of the measured values (Table 5). Raising $K_{O_2h}$ to double that used ecosys increased these emissions by 28% to an average of 0.334 g N m⁻² y⁻¹, near the average upper boundary of the measured values. Lowering $K_{NO_x}$ to one-half that used in ecosys increased annual N₂O emissions modelled from 2004 to 2009 by 30% to an average of 0.338 g N m⁻² y⁻¹, near the average upper boundary of the measured values (Table 5). Raising $K_{NO_x}$ to double that used ecosys reduced these emissions by 27% to an average of 0.189 g N m⁻² y⁻¹, near the average lower boundary of the measured values. In years with lower annual
emissions (2003, 2004, 2006 in Table 4), the lower $K_{O_2}$ or higher $K_{NO_x}$ gave modelled values that were closer to measured values. However in years with higher annual emissions (2008 and 2009 in Table 4), the higher $K_{O_2}$ or lower $K_{NO_x}$ gave modelled values that were closer.

DISCUSSION

Modelled vs. Measured N$_2$O Emissions

Most N$_2$O emission events measured from 2004 to 2009 were simulated within the range of measurement uncertainty, estimated to be about 30% of mean daily values (Fig. 3). However some deviations between modelled and measured N$_2$O emissions were apparent, such as the larger emissions modelled in autumn 2006 (Fig. 3c) and the smaller emissions modelled in spring 2008 (Fig. 3e). These deviations may be attributed to uncertainties in both the measurements and the model. In the automated measurement system, the static chambers were rotated about every two months among fixed positions in a corner of the field. During these periods, surface conditions in the chamber could deviate from the mean field conditions represented in the model. However we do not have an explanation for the very small emissions measured after the three manure slurry applications 2006. The chambers had been removed before the applications and were reinstalled within two hours, during which the cut grass was removed so that the surface litter in the chambers may have been reduced from that outside. In the model, emissions following manure or fertilizer applications were sensitive to the amount of surface litter as noted earlier. The absence of emission events measured after slurry applications in 2006 was unusual (Fig. 3) given the large precipitation that year (Table 4), demonstrating that large variability at small spatial scales inevitably affects these measurements. Such variability adversely affects agreement between modelled and measured emissions (Table 3).

During spring 2008 sustained emissions of about 5 mg N m$^{-2}$ d$^{-1}$ were measured by the chambers in the absence of any manure or fertilizer applications (Fig. 3e). These emissions were related to the ploughing of the field to a depth of 25cm in December 2007 (Table 2) which hastened soil organic matter decomposition, and hence N mineralization that increased mineral N substrate for nitrification and denitrification, and possibly microbial nitrifier and denitrifier populations. These increases must remain conjectural as the Oensingen study did not include stratified analysis of N$_2$O.
production factors (e.g. microbial biomass, potential denitrification) within the chamber soils.

Although *ecosys* simulates hastened SOM decomposition with tillage (Grant et al., 1998), large amounts of above- and below-ground plant litter with relatively high C:N ratios were incorporated in the model with tillage in December 2007 which slowed net N mineralization and hence accumulation of mineral N products in the model during spring 2008. Consequently modelled N$_2$O emissions remained small until mineral N was raised by fertilizer applications in July (Fig. 3c).

**Modelling Controls on N$_2$O Emissions by Litter and Near-Surface $\theta$ and $T_s$**

In the model, almost all the N$_2$O emissions originated in the surface litter and in the near-surface (0 – 1 cm) soil layer, so that emissions were strongly controlled by litter and near-surface $\theta$ and $T_s$ (Figs. 3 – 4). This model finding is consistent with the experimental finding of Pal et al. (2013) from $^{15}$N enrichment studies that approximately 70% of N$_2$O measured during emission events in a managed grassland originated in the surface litter. Similarly van der Weerden et al. (2013) inferred from diurnal variation in $T_s$ and N$_2$O emissions measured after urine amendments on a managed grassland that N$_2$O production was at or near the soil surface (0 - 2 cm). Also Fléchard et al. (2007) inferred in a meta-analysis of N$_2$O emissions from grasslands in Europe that $\theta$ measured at 5 cm was not in some cases an adequate scaling factor for N$_2$O source strength because N$_2$O production and emission took place at or near the soil surface. *Ecosys* simulated little net production, and even a small net consumption, of N$_2$O in soil below 2 cm during emission events, as may be inferred from peak [N$_2$O(s)] modelled in the 0 – 1 cm soil layer and much lower [N$_2$O(s)] modelled in the 1 – 3 cm soil layer below (Figs. 3g and 4g). This model finding was consistent with the experimental finding of Neftel et al. (2000) that N$_2$O concentrations below near-surface soil layers in a managed grassland remained below atmospheric values during emission events, from which they inferred that any N$_2$O generated at depths greater than ~3 cm would not likely reach the soil surface. Thus attempts to relate N$_2$O emissions to $T_s$ and $\theta$ measured at greater depths than 3 cm in grasslands are unlikely to be informative if these differ from near-surface values. These emissions should rather be related to conditions in the litter and near-surface soil, which need to be better characterized in future studies.

Consequently modelled N$_2$O emissions were highly sensitive to surface wetting and drying (e.g. Fig. 4e,h) modelled from precipitation vs. ET (e.g. Fig. 4a,c), or to surface warming and cooling (e.g. Fig. 8j,l) modelled from surface energy balance (e.g. Fig. 4c). The sensitivity to surface wetting and
drying was modelled from the effects of $\theta$ on air- vs. water-filled porosity and hence on diffusivity of
gases in gaseous [D17] and aqueous [D20] phases, and on gaseous volatilization - dissolution transfer
coefficients and hence gas exchange between gaseous and aqueous phases [D14, D15]. These
transfers controlled $O_2$ supply, and hence demand for alternative e$^{-}$ acceptors as the $O_2$ supply fell
below $O_2$ demand, which drove $N_2O$ generation from denitrification [H6 – H8] and nitrification
[H19]. The control of $O_2$ supply on e$^{-}$ acceptors used in nitrification thereby simulated the effect of
WFPS on the fraction of $N_2O$ generated during nitrification identified by Fang et al. (2015) as
necessary to modelling $N_2O$ emissions, while avoiding the model-specific parameterization needed in
simpler models. The sensitivity to surface wetting in ecosys enabled sharp rises in $N_2O$ emissions to
be modelled from surface litter and near-surface soil after small precipitation events during DOY 200
- 201 in 2007 (Fig. 4a,h), and after slurry application during DOY 218 in 2009 (Fig. 5a,h), even when
the soil at 5 cm remained dry (Fig. 4b; Fig. 5b). Such rises were consistent with the experimental
findings of Fléchard et al. (2007) that precipitation on dry soil can cause substantial $N_2O$ emissions
after fertilizer application in grasslands.

The sensitivity to surface warming and cooling was modelled from the effects of $T_s$ on
diffusivity of gases in gaseous [D17] and aqueous [D20] phases, and on solubility of gases and hence
exchange of gases between gaseous and aqueous phases [D14, D15], both parameterized from basic
physical relationships independently from the model. These transfers controlled [$O_2(g)$] in the surface
litter and soil (Figs. 3f and 4f), and hence $O_2$ uptake by aerobic heterotrophs [H4] and autotrophs
[H13] through a Michaelis-Menten constant [H4b, H13b]. The sensitivity to surface warming and
cooling was also modelled from the effects of $T_s$ on SOC oxidation [H2] and hence $O_2$ demand by
aerobic heterotrophs [H3], and on $NH_4^+$ and $NO_2^-$ oxidation [H11, H15] and hence $O_2$ demand by
aerobic autotrophs [H12, H16]. These effects were driven by a single Arrhenius function used for all
biological transformations [A6] parameterized from basic research conducted independently from the
model. Under sustained high surface $\theta$, this combination of physical and biological processes drove
large diurnal variation in $N_2O$ emissions modelled with diurnal surface warming and cooling during
emission events (e.g. DOY 221 in Fig. 5h, DOY 243 in Fig. 8l), as observed experimentally by van
der Weerden et al. (2013). By explicitly simulating the diverse processes that determine $N_2O$
emissions, ecosys could model the large sensitivity of emissions to $T_s$ without the use of
unrealistically large parameters for temperature sensitivity inferred from controlled temperature
studies of N$_2$O emissions (e.g. Dobbie and Smith, 2001). This large sensitivity to $T_s$ has been inadequately represented in simpler models, causing underestimation of large emissions measured from warm soils (e.g. Saggar et al., 2004). At a seasonal time scale, higher $T_s$ could cause large increases in N$_2$O emissions modelled with comparable $\theta$ after the same fertilizer application (Fig. 8l vs. Fig. 8f). However the effects of $T_s$ on N$_2$O emissions were dominated by those of $\theta$ during surface wetting and drying (e.g. Figs. 4h, 7l).

Values of both $\theta$ and $T_s$ thus determined O$_2$ demand not met by O$_2$ uptake which drove demand for alternative e$^-$ acceptors by heterotrophic denitrifiers [H6] and autotrophic nitrifiers [H19]. This demand drove the sequential reduction of NO$_3^-$, NO$_2^-$ and N$_2$O to NO$_2^-$, N$_2$O and N$_2$ respectively by heterotrophic denitrifiers [H7, H8, H9], and the reduction of NO$_2^-$ to N$_2$O by autotrophic nitrifiers [H20]. The consequent production of N$_2$O (Fig. 4g, Fig. 5g) and N$_2$ drove emissions of both N$_2$O and N$_2$ (Fig. 4h, Fig. 5h) through volatilization [D14, D15] and through gaseous and aqueous diffusion [D16, D19]. Ratios of N$_2$O and N$_2$ emissions in ecosys (Fig. 4h, Fig. 5h) were not parameterized as done in other models, but rather were determined by relative affinities determined from basic research [H8, H9], and by environmental conditions. When demand from heterotrophic denitrifiers for alternative e$^-$ acceptors was small relative to their availability, the preferential reduction of more oxidized e$^-$ acceptors generated larger emissions of N$_2$O [H7, H8] relative to N$_2$ [H9]. Such conditions occurred during the early part of an emission event when surface [NO$_3^-$] rose with nitrification of fertilizer or manure NH$_4^+$ after application (e.g. DOY 200 – 201 in Fig. 4h). However when demand for alternative e$^-$ acceptors was large relative to their availability, this same reduction sequence forced more rapid reduction of N$_2$O to N$_2$ and hence smaller emissions of N$_2$O relative to N$_2$. Such conditions occurred during the later part of emission events when surface [NO$_3^-$] declined with plant uptake (e.g. DOY 202 – 205 in Fig. 4h and DOY 222 in Fig. 5h), or when greater surface wetting reduced O$_2$ supply (e.g. DOY 220 in Fig. 5h). This greater demand for alternative e$^-$ acceptors with wetting provided a process-based explanation for declines in N$_2$O emissions frequently found at higher $\theta$ in field studies (e.g. Rafique et al., 2011) without explicit parameterization of N$_2$O:N$_2$ ratios.

Nitrification and denitrification were also driven by the concentrations of NH$_4^+$ [H11], NO$_3^-$ [H7], NO$_2^-$ [H8, H15, H20] and N$_2$O [H9] relative to Michaelis-Menten constants evaluated from basic research. The concentrations of NH$_4^+$ and NO$_3^-$ in ecosys were increased by N additions from
manure and fertilizer N applications (Table 2), and by net mineralization soil organic N from oxidation of litterfall, manure and SOM [A26] as indicated by soil CO2 effluxes. These concentrations were reduced by root uptake of NH4+ and NO3− [C23] and consequent plant N assimilation with growth, indicated by more rapid CO2 fixation with time after cutting (Figs 3 – 4 and Figs. 6 - 7). In the model, more rapid CO2 fixation drove more rapid production of nonstructural C, and hence more rapid exchange of nonstructural C and N between canopy and roots [C50], and so hastened root active N uptake by increasing $R_a$ driving root growth [C14b], and by hastening removal of N uptake products and hence reducing their inhibition of active uptake [C23g]. The diversity of controls on key substrates for N2O generation suggests that robust simulations of N2O emissions require comprehensive ecosystem models in which these controls are fully represented.

Modelling Effects of Defoliation Intensity and Timing on N2O Emissions

The control of NH4+ and NO3− availability by root N uptake indicated that plant management practices determining uptake would thereby affect N2O emissions. In the model, increasing harvest intensity and delaying harvest dates both slowed N uptake (Fig. 7b,h and Fig. 8b,h) by slowing the recovery of LAI (Fig. 6) and CO2 fixation (Fig. 7a,g and Fig. 8a,g). Both thereby increased [NO3−] (Fig. 7c,i and Fig. 8c,i), $T_s$ (Fig. 7d,j and Fig. 8d,j) and $\theta$ (Fig. 7e,k and Fig. 8e,k), raising N2O effluxes modelled during most emission events (Fig. 7f,l and Fig. 8f,l), and hence annually (Table 4). This model finding was consistent with the field observations of Jackson et al. (2015) that increased N2O emissions after defoliation in grasslands were caused by reduced uptake of N and water by slower-growing plants.

The effects of defoliation on N2O emissions during modelled emission events were similar to, or greater than, those of $T_s$ and $\theta$ (e.g. Fig. 7f,l), consistent with the experimental finding of Imer et al. (2013) that plant management, as represented by its effects on LAI, had a larger effect on N2O fluxes than did the environment, as represented by $T_a$, at an intensively managed grassland in Switzerland. Reducing LAI remaining after harvest by one-half and delaying harvest by 5 days had little effect on modelled harvest removals (Table 4), suggesting that N2O emissions from managed grasslands are more sensitive to plant management practices than are yields. Intensity and timing of harvests should therefore be selected to avoid slow regrowth of LAI following N additions by avoiding excessive defoliation and by allowing as much time as possible between defoliation and subsequent fertilizer or
manure application. Neftel et al. (2010) reported enhanced N$_2$O emissions after cuts in managed
grassland and hypothesized that a simple mitigation option would be to optimize the timing of the
fertilizer applications. To our knowledge this option has not been systematically investigated.

**Modelling Effects of Soil Bulk Density on N$_2$O Emissions**

The small increases in near-surface BD included in this study were typical of those arising from
natural variation in soil properties or from compaction by vehicular traffic during field management
operations. In the model, these increases reduced soil porosity and hence gaseous diffusivity [D17]
which slowed O$_2$ uptake from the atmosphere [D15] and O$_2$ transfer through the soil profile [D16].
Consequent reductions in near-surface [O$_2$(s)] (Fig. 9a,c) slowed O$_2$ reduction by denitrifiers [H4] and
nitrifiers [H13], forcing more rapid e$^-$ transfer to NO$_3^-$ by denitrifiers [H6] and to NO$_2^-$ by nitrifiers
[H19] and hence more rapid emissions of N$_2$O following applications of manure (Fig. 9b) and fertilizer
(Fig. 9d).

In a study of soil compaction effects on N$_2$O emissions from a fertilized agricultural field in a
climate similar to that at Oensingen, Bessou et al. (2010) found that increasing the BD of the upper 30
cm of the soil profile by ca. 15% raised annual N$_2$O emissions measured with automated chambers by
at least 50% during each of two growing seasons. This rises were similar to that modelled with a
smaller increase in BD of the upper 3 cm during the wettest year of this study (Table 5). During
emission events, Bessou et al. (2010) measured peak fluxes from compacted soil that were double
those from uncompacted, as also modelled here (Fig. 9b,d).

The detailed algorithms from which ecosys was constructed enabled increases in N$_2$O
emissions from surface compaction to be simulated from specified changes to surface BD, a
measureable site characteristic, without further model parameterization. The marked increases in N$_2$O
emissions modelled with these increases in BD (Table 5) indicated that some of the large spatial
variation in these emissions commonly found in field measurements could arise from relatively small
variation in physical properties of near-surface soil. In future studies of N$_2$O emissions, near-surface
soil properties could be determined at each measurement site to establish the extent to which variation
in these properties are associated with those in emissions.
Modelling Effects of $K_{O_2}$ and $K_{NO_x}$ on N$_2$O Emissions

The value of $K_{O_2}$ used in ecosys ($=2 \mu M$) was taken from the upper range of values determined experimentally for intact cells of heterotrophic bacteria by Longmuir (1954). Halving or doubling $K_{O_2}$ changed modelled N$_2$O emissions (Table 5) by amounts similar to uncertainty in measured emissions expressed as lower and upper boundaries of likely values (Table 4), although the doubled value of $K_{O_2}$ was larger than those derived from experiments. The value of $K_{NO_x}$ used in ecosys ($=100 \mu M$) was within the range of values determined experimentally by Yoshinari et al. (1977). As for $K_{O_2}$, halving or doubling $K_{NO_x}$ changed modelled N$_2$O emissions (Table 5) by amounts similar to uncertainty in measured emissions expressed as lower and upper boundaries of likely values (Table 4). The halved value of $K_{NO_x}$ was closer to those measured by Betlach and Tiedje (1981) and Khalil et al. (2007) while the doubled value was closer to that measured by Klemedtsson et al. (1977). These changes indicate that key parameters used in process models must be capable of being constrained by accurate evaluation in independent experiments.

CONCLUSIONS

N$_2$O emissions modelled in this managed grassland originated in the surface litter and upper 2 cm of the soil profile. The shallow origin of these emissions enabled ecosys to simulate the response of measured emissions to changes in near-surface $\theta$ and $T_s$ during brief emission events when rainfall followed manure or mineral fertilizer applications. Measurements of $\theta$ and $T_s$ used to estimate N$_2$O emissions from managed grasslands should therefore be taken in surface litter and near-surface soil (0 – 2 cm), rather than deeper in the soil profile (5 – 10 cm) as is currently done.

N$_2$O fluxes modelled during emission events were greater when grassland regrowth and hence mineral N uptake was slower following harvest and subsequent N application. The control of N$_2$O emissions by grassland N uptake indicated that N$_2$O emissions from managed grassland could be increased by harvesting practices and fertilizer timing that resulted in slower regrowth during periods when emission events are most likely to occur. N$_2$O fluxes modelled during emission events rose
sharply with small increases in surface BD, indicating the importance of avoiding surface compaction in fields to which large amounts of N are applied.

The basic and comprehensive approach to model development in *ecosys* allowed diverse responses of N$_2$O emissions to changes in weather ($T_s$, $\theta$), land management and soil properties to be modelled from specified changes to readily measured inputs with parameters constrained by basic experiments conducted independently of the model rather than derived from site-specific observations. This approach enabled concurrent, well-constrained tests of model performance against a diverse set of field measurements, and so is expected to confer robustness to the modelling of these emissions under different climates, soils and land uses in future studies.

**ACKNOWLEDGEMENTS**

Computational facilities for *ecosys* were provided by the University of Alberta and by the Compute Canada high performance computing infrastructure. A PC version of *ecosys* with GUI can be obtained by contacting the corresponding author at rgrant@ualberta.ca. The authors also acknowledge contributions from valuable discussions with Christoph Amman concerning measurement methodology.
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Evaluating four nitrous oxide emission algorithms in response to N rate on an irrigated corn

Felber, R., Leifeld, J., Horak J and Neftel, A.: Nitrous oxide emission reduction with greenwaste
biochar: comparison of laboratory and field experiments Euro. J. Soil Sci. 65, 128–138 doi:

exchange over two mown grassland systems with contrasting management practices. Glob


Table 1. Key soil properties of the Eutri-Stagnic Cambisol at Oensingen as used in *ecosys*.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>BD (Mg m$^{-3}$)</th>
<th>TOC (g kg$^{-1}$)</th>
<th>TON (g kg$^{-1}$)</th>
<th>FC (m$^3$ m$^{-3}$)</th>
<th>WP (mm h$^{-1}$)</th>
<th>K$_{sat}$ (mm h$^{-1}$)</th>
<th>pH</th>
<th>Sand (g kg$^{-1}$)</th>
<th>Silt (g kg$^{-1}$)</th>
<th>Clay (g kg$^{-1}$)</th>
<th>CF (m$^3$ m$^{-3}$)</th>
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<tbody>
<tr>
<td>0.01</td>
<td>1.21</td>
<td>27.2</td>
<td>2.9</td>
<td>0.38</td>
<td>0.22</td>
<td>3.4</td>
<td>7</td>
<td>240</td>
<td>330</td>
<td>430</td>
<td>0</td>
</tr>
<tr>
<td>0.03</td>
<td>1.21</td>
<td>27.2</td>
<td>2.9</td>
<td>0.38</td>
<td>0.22</td>
<td>3.4</td>
<td>7</td>
<td>240</td>
<td>330</td>
<td>430</td>
<td>0</td>
</tr>
<tr>
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<td>27.2</td>
<td>2.9</td>
<td>0.38</td>
<td>0.22</td>
<td>3.4</td>
<td>7</td>
<td>240</td>
<td>330</td>
<td>430</td>
<td>0</td>
</tr>
<tr>
<td>0.13</td>
<td>1.24</td>
<td>27.2</td>
<td>2.9</td>
<td>0.39</td>
<td>0.23</td>
<td>3.4</td>
<td>7</td>
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<td>330</td>
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<td>7</td>
<td>180</td>
<td>380</td>
<td>440</td>
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</tr>
<tr>
<td>0.6</td>
<td>1.28</td>
<td>11.6</td>
<td>1.1</td>
<td>0.40</td>
<td>0.24</td>
<td>1.4</td>
<td>7</td>
<td>180</td>
<td>380</td>
<td>440</td>
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<td>11.6</td>
<td>1.1</td>
<td>0.40</td>
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<td>6</td>
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<td>0.40</td>
<td>0.24</td>
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<td>7</td>
<td>180</td>
<td>380</td>
<td>440</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Abbreviations: BD: bulk density, TOC and TON: total organic C and N, FC: field capacity, WP: wilting point, K$_{sat}$: saturated hydraulic conductivity, CF: coarse fragments.

BD, TOC and texture were determined from soil cores taken in 2001 and 2006. Details are given in Leifeld et al. (2011).

FC, WP and K$_{sat}$ were estimated from BD, TOC and texture according to Saxton et al. (1996) and Saxton and Rawls (2006).
Table 2. Plant and soil management operations at the Oensingen intensively managed grassland from 2001 to 2009.

<table>
<thead>
<tr>
<th>Year</th>
<th>Plant Management</th>
<th>Soil Management</th>
<th>Amount (g m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Date</td>
<td>Date</td>
<td>NH$_4^+$</td>
</tr>
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<td>2001</td>
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<td>tillage</td>
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</tr>
<tr>
<td></td>
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<td>planting</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>tillage</td>
<td></td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>8 Aug.</td>
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<tr>
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<td>12 Sep.</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>31 Oct.</td>
<td>harvest</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>15 May</td>
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<tr>
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Table 3: Intercepts ($a$), slopes ($b$) coefficients of determination ($R^2$), ratios of mean squares for regression vs. error (F) and number of data pairs from regressions of log-transformed 4-hour averages of N$_2$O fluxes modelled vs. measured at the Oensingen intensively managed grassland from 2004 to 2009.

<table>
<thead>
<tr>
<th>Year</th>
<th>$a$</th>
<th>$b$</th>
<th>$R^2$</th>
<th>F$^\dagger$</th>
<th>n</th>
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</thead>
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<tr>
<td>2004</td>
<td>$1.25 \pm 0.88 \times 10^{-5}$</td>
<td>$0.49 \pm 0.06$</td>
<td>0.08</td>
<td>69</td>
<td>818</td>
</tr>
<tr>
<td>2005</td>
<td>$1.63 \pm 0.43 \times 10^{-5}$</td>
<td>$0.59 \pm 0.03$</td>
<td>0.24</td>
<td>368</td>
<td>1173</td>
</tr>
<tr>
<td>2006</td>
<td>$4.28 \pm 0.44 \times 10^{-5}$</td>
<td>1.04 $\pm 0.08$</td>
<td>0.14</td>
<td>155</td>
<td>948</td>
</tr>
<tr>
<td>2007</td>
<td>$1.21 \pm 0.33 \times 10^{-5}$</td>
<td>$0.67 \pm 0.02$</td>
<td>0.35</td>
<td>989</td>
<td>1794</td>
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<tr>
<td>2008</td>
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<td>$0.44 \pm 0.03$</td>
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<td>$0.71 \pm 0.02$</td>
<td>0.49</td>
<td>1574</td>
<td>1614</td>
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</table>

$^\dagger$ All values of F were highly significant ($P < 0.001$).
Table 4. Annual gross primary productivity (GPP), ecosystem respiration \( (R_e) \), net ecosystem productivity \( (\text{NEP} = \text{GPP} - R_e) \), harvest, net biome productivity (NBP) and N\textsubscript{2}O emissions derived from EC or chambers and modelled (M) with current land management (Table 2), and with defoliation increased so that LAI remaining after harvesting was reduced by one-half \((1/2)\), with defoliation increased and delayed by 5 days \((1/2 + 5d)\). Positive values indicate uptake, negative values emissions.

<table>
<thead>
<tr>
<th>Year</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precip.(mm)</td>
<td>1478</td>
<td>817</td>
<td>1158</td>
<td>966</td>
<td>1566</td>
<td>1328</td>
<td>1188</td>
<td>1004</td>
</tr>
<tr>
<td>MAT (°C)</td>
<td>9.56</td>
<td>9.58</td>
<td>8.92</td>
<td>8.67</td>
<td>9.30</td>
<td>9.59</td>
<td>9.30</td>
<td>9.48</td>
</tr>
<tr>
<td>GPP ((g \text{ C m}^{-2} \text{ y}^{-1}))</td>
<td>EC</td>
<td>2159</td>
<td>1773</td>
<td>2058</td>
<td>1766</td>
<td>1817</td>
<td>2102</td>
<td>1455</td>
</tr>
<tr>
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<td>2214</td>
<td>1836</td>
<td>2220</td>
<td>2111</td>
<td>1953</td>
<td>2539</td>
<td>1419</td>
<td>1852</td>
</tr>
<tr>
<td>: 1/2</td>
<td>2064</td>
<td>1764</td>
<td>2054</td>
<td>1969</td>
<td>1865</td>
<td>2285</td>
<td>1305</td>
<td>1705</td>
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<td>1774</td>
<td>2076</td>
<td>1966</td>
<td>1771</td>
<td>2277</td>
<td>1225</td>
<td>1686</td>
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<td>(R_e) ((g \text{ C m}^{-2} \text{ y}^{-1}))</td>
<td>EC</td>
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<td>-1541</td>
<td>-1565</td>
<td>-1577</td>
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<td>-1450</td>
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<tr>
<td>: 1/2</td>
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<td>: 1/2 + 5d</td>
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<td>-1519</td>
<td>-1679</td>
<td>-1183</td>
<td>-1235</td>
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<td>215</td>
<td>517</td>
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<td>240</td>
<td>418</td>
<td>5</td>
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<td>415</td>
<td>516</td>
<td>432</td>
<td>273</td>
<td>604</td>
<td>53</td>
<td>479</td>
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<tr>
<td>: 1/2</td>
<td>607</td>
<td>419</td>
<td>485</td>
<td>397</td>
<td>286</td>
<td>571</td>
<td>93</td>
<td>446</td>
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<tr>
<td>: 1/2 + 5d</td>
<td>556</td>
<td>414</td>
<td>535</td>
<td>449</td>
<td>252</td>
<td>598</td>
<td>42</td>
<td>451</td>
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<tr>
<td>Harvest ((g \text{ C m}^{-2} \text{ y}^{-1}))</td>
<td>field</td>
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<td>401</td>
<td>247</td>
<td>232</td>
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<td>314</td>
<td>525</td>
<td>460</td>
<td>421</td>
<td>690</td>
<td>308</td>
<td>487</td>
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<tr>
<td>: 1/2</td>
<td>561</td>
<td>360</td>
<td>465</td>
<td>497</td>
<td>455</td>
<td>678</td>
<td>314</td>
<td>484</td>
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<td>: 1/2 + 5d</td>
<td>537</td>
<td>353</td>
<td>579</td>
<td>513</td>
<td>446</td>
<td>686</td>
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<td>473</td>
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<td>80</td>
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<td>102</td>
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<td>160</td>
<td>9</td>
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<td>54</td>
<td>145</td>
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<tr>
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<td>20</td>
<td>74</td>
<td>-64</td>
<td>74</td>
<td>-246</td>
<td>37</td>
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<tr>
<td>: 1/2</td>
<td>127</td>
<td>139</td>
<td>49</td>
<td>2</td>
<td>-85</td>
<td>53</td>
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<tr>
<td>: 1/2 + 5d</td>
<td>101</td>
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<td>-15</td>
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<td>18.5</td>
<td>24.3</td>
<td>21.4</td>
<td>30.1</td>
<td>9.4</td>
<td>20.0</td>
</tr>
<tr>
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<td>upper bound</td>
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<td>-0.060</td>
<td>-0.230</td>
<td>-0.020</td>
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<td>-0.180</td>
<td>-0.320</td>
<td>-0.060</td>
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<td>-0.620</td>
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<tr>
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<td>-0.209</td>
<td>-0.183</td>
<td>-0.193</td>
<td>-0.220</td>
<td>-0.281</td>
<td>-0.326</td>
<td>-0.366</td>
</tr>
<tr>
<td>: 1/2</td>
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<td>-0.215</td>
<td>-0.250</td>
<td>-0.249</td>
<td>-0.318</td>
<td>-0.312</td>
<td>-0.335</td>
<td>-0.318</td>
</tr>
<tr>
<td>: 1/2 + 5d</td>
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<td>-0.234</td>
<td>-0.347</td>
<td>-0.352</td>
<td>-0.273</td>
<td>-0.348</td>
<td>-0.327</td>
<td>-0.395</td>
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</tbody>
</table>
Table 5. Annual N₂O emissions modelled with current field management (Table 2) and soil properties (Table 1) (current), with soil bulk density (BD) increased by 5% and 10% to a depth of 3 cm, and with the Michaelis-Menten constants for reduction of O₂ ($K_{O2}$) and of NO₃⁻ and NO₂⁻ ($K_{NOx}$) halved or doubled from those used in the model.

<table>
<thead>
<tr>
<th>Year</th>
<th>Precip.(mm)</th>
<th>MAT (°C)</th>
<th>N₂O (g N m⁻² y⁻¹)</th>
<th>BD + 5%</th>
<th>BD + 10%</th>
<th>$K_{O2}$ x 0.5</th>
<th>$K_{O2}$ x 2.0</th>
<th>$K_{NOx}$ x 0.5</th>
<th>$K_{NOx}$ x 2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precip.(mm)</td>
<td>1478</td>
<td>817</td>
<td>1158</td>
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<td>1328</td>
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<tr>
<td>MAT (°C)</td>
<td>9.56</td>
<td>9.58</td>
<td>8.92</td>
<td>8.67</td>
<td>9.30</td>
<td>9.59</td>
<td>9.30</td>
<td>9.48</td>
<td></td>
</tr>
<tr>
<td>N₂O (g N m⁻² y⁻¹)</td>
<td>current</td>
<td>-0.302</td>
<td>-0.209</td>
<td>-0.183</td>
<td>-0.193</td>
<td>-0.220</td>
<td>-0.281</td>
<td>-0.326</td>
<td>-0.366</td>
</tr>
<tr>
<td></td>
<td>BD + 5%</td>
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<td>-0.213</td>
<td>-0.218</td>
<td>-0.199</td>
<td>-0.309</td>
<td>-0.332</td>
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<td>BD + 10%</td>
<td>-0.334</td>
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<td>-0.231</td>
<td>-0.236</td>
<td>-0.336</td>
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<tr>
<td>K₉O₂ x 0.5</td>
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<td>-0.154</td>
<td>-0.159</td>
<td>-0.160</td>
<td>-0.216</td>
<td>-0.276</td>
<td>-0.349</td>
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<tr>
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<td>-0.385</td>
<td>-0.381</td>
<td>-0.468</td>
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<tr>
<td>K₉NO₂ x 0.5</td>
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<td>-0.261</td>
<td>-0.265</td>
<td>-0.267</td>
<td>-0.262</td>
<td>-0.378</td>
<td>-0.432</td>
<td>-0.457</td>
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</tr>
<tr>
<td>K₉NO₂ x 2.0</td>
<td>-0.234</td>
<td>-0.163</td>
<td>-0.126</td>
<td>-0.132</td>
<td>-0.126</td>
<td>-0.208</td>
<td>-0.232</td>
<td>-0.288</td>
<td></td>
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</table>
Fig. 1: Summary of key processes governing generation and emission of N₂O as represented in ecosys.
Fig. 2. LAI measured (symbols) and modelled (lines) from 2002 through 2009 at the Oensingen intensively managed grassland.
Fig. 3. Daily-aggregated N$_2$O emissions measured (symbols) and N$_2$O and N$_2$ emissions modelled (lines) from 2004 through 2009 at the Oensingen intensively managed grassland. Numbers above and beside each fertilizer or manure addition indicate total measured/modelled N$_2$O-N emitted during emission events (mg N m$^{-2}$), and total N applied (g N m$^{-2}$). Negative values indicate effluxes to the atmosphere.
Fig. 4. (a) Precipitation and soil temperature at 0.05 m, (b) soil water content ($\theta$) at 0.05, 0.10, 0.30 and 0.50 m, (c) energy and (d) CO$_2$ fluxes measured (closed symbols), gap-filled (open symbols) and modelled (lines) during 20 days from harvest (cut) to the end of the emission event following manure application (manure) in July 2007. (e) $\theta$, (f and g) aqueous concentrations of O$_2$ and N$_2$O modelled in the surface litter and at 0.01 and 0.02 m in the soil, and (h) N$_2$O and N$_2$ fluxes measured (symbols) and modelled (lines) during the last 10 days of this period when the emission event occurred. For fluxes, positive values represent influxes to the soil, negative values effluxes to the atmosphere.
Fig. 5. (a) Precipitation and soil temperature at 0.05 m, (b) soil water content ($\theta$) at 0.05, 0.10, 0.30 and 0.50 m, (c) energy and (d) CO$_2$ fluxes measured (closed symbols), gap-filled (open symbols) and modelled (lines) during 20 days from harvest (cut) to the end of the emission event following manure application (manure) in August 2008. (e) $\theta$, (f and g) aqueous concentrations of O$_2$ and N$_2$O modelled in the surface litter and at 0.01 and 0.02 m in the soil, and (h) N$_2$O and N$_2$ fluxes measured (symbols) and modelled (lines) during the last 10 days of this period when the emission event occurred. Positive flux values represent influxes to the soil, negative values effluxes to the atmosphere.
Fig. 6. LAI modelled from 2002 through 2009, with LAI after each cut reduced to one-half of that estimated from the field experiment without or with a delay of 5 days at the Oensingen intensively managed grassland.
Fig. 7. (a,g) CO₂ fluxes, (b,h) cumulative NH₄⁺ (dashed) and NO₃⁻ (solid) uptake since manure application, (c,i) aqueous NO₃⁻ concentrations at 0 – 1 cm, (d,j) $T_s$ and (e,k) $\theta$ at 5 cm, and (f,l) N₂O fluxes measured (symbols) and modelled (lines) with LAI after each cut reduced to one-half of that estimated from the field experiment without or with a delay of 5 days during emission events following manure applications on DOY 194 in (a-f) 2006 and (g-l) 2007 (see Table 2). For fluxes, positive values represent influxes to the soil, negative values effluxes to the atmosphere.
Fig. 8 (a,g) CO₂ fluxes, (b,h) cumulative NH₄⁺ (dashed) and NO₃⁻ (solid) uptake since fertilizer application, (c,i) aqueous NO₃⁻ concentrations at 0 – 1 cm, (d,j) Tₛ and (e,k) θ at 5 cm, and (f,l) N₂O fluxes measured (symbols) and modelled (lines) with LAI after each cut reduced to one-half of that estimated from the field experiment without or with a delay of 5 days during emission events following fertilizer applications on DOY 259 in 2005 (a-f) and DOY 240 in 2007 (g-l) (see Table 2). For fluxes, positive values represent influxes to the soil, negative values effluxes to the atmosphere.
Fig. 9. (a,c) Aqueous O$_2$ concentrations, and (b,d) N$_2$O fluxes measured (symbols) and modelled (lines) with bulk density (BD) from field measurements, and with BD raised by 5% or 10% following (a,b) manure application on DOY 194 and (c,d) fertilizer application on DOY 240 in 2007 (see Table 2). For fluxes, positive values represent influxes to the soil, negative values effluxes to the atmosphere.