Simulation of N_2O emissions from a urine-affected pasture in New Zealand with the ecosystem model DayCent

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[1] We used the trace gas model DayCent to simulate emissions of nitrous oxide (N_2O) from a urine-affected pasture in New Zealand. The data set for this site contained year-round daily emissions of nitrification-N_2O (N_2O_{nit}) and denitrification-N_2O (N_2O_{den}), meteorological data, soil moisture, and at least weekly data on soil ammonium (NH_4^+) and nitrate (NO_3^-) content. Evapotranspiration, soil temperature, and most of the soil moisture data were reasonably well represented. Observed and simulated soil NH_4^+ concentrations agreed well, but DayCent underestimated the NO_3^- concentrations, due possibly to an insufficient nitrification rate. Modeled N_2O emissions (18.4 kg N_2O-N ha^{-1} yr^{-1}) showed a similar pattern but exceeded observed emissions (4.4 kg N_2O-N ha^{-1} yr^{-1}) by more than 3 times. Modeled and observed N_2O emissions were dominated by peaks following N-application and heavy rainfall events and were favored under high soil temperatures. The contribution of N_2O_{den} was simulated well except for a 4-week period when water-filled pore space was overestimated and caused high N_2O emissions which accounted for one third of the simulated annual N_2O emissions. N_2O_{nit} fluxes were overestimated with DayCent because they are calculated as a fixed proportion of NH_4^+ converted to NO_3^-, while the data suggest that significant rates of nitrification can occur without inducing significant N_2O emissions. The comprehensive data set made it possible to explain discrepancies between modeled and observed values. In-depth model validations with detailed data sets are essential for a better understanding of the internal model behavior and for deriving possible model improvements. *INDEX TERMS:* 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); 3337 Meteorology and Atmospheric Dynamics: Numerical modeling and data assimilation; *KEYWORDS:* nitrous oxide, N_2O, grassland, model, biosphere/atmosphere interactions, biogeochemical processes

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1. Introduction

[2] The trace gas nitrous oxide (N_2O) contributes to the greenhouse effect, is involved in stratospheric ozone depletion [*Crutzen*, 1970], and is currently increasing at a rate of 0.2–0.3% yr^{-1} [*Granli and Bøckman*, 1994]. Most N_2O is produced by the soil microbial processes nitrification and denitrification [*Wrage et al.*, 2001]. Research activities during the last decades have identified soil nitrate (NO_3^-) and ammonium (NH_4^+) content, soil moisture, or rather, water-filled pore space (WFPS), soil temperature, easily metabolizable carbon, soil pH, and their interactions as the main controllers for N_2O production and release from soils [*Parton et al.*, 2001]. This has led to the development of simulation models such as Century/DayCent [*Parton et al.*, 1988] or DNDC [*Li et al.*, 1992]. The models describe the processes related to N_2O production generally in more detail than what is usually available from data sets. To validate such ecosystem models, not only the total N_2O emissions (N_2O_{tot}) but also the process driven N_2O emissions from nitrification (N_2O_{nit}) and denitrification (N_2O_{den}) and the main driving variables are needed. While N_2O_{tot} emissions, soil moisture, and soil temperature may be quantified with high-resolution automatic techniques [*Stange et al.*, 2000], it is the dearth of N_2O_{nit} and N_2O_{den} and the soil mineral N data which often preclude a more rigorous model testing. Here we present such an in-depth evaluation of the DayCent model [*Parton et al.*, 1998] using a 1-year data set obtained from a urine-affected pasture in New Zealand which contains daily data on N_2O_{tot}, N_2O_{nit}, N_2O_{den} emissions, and all main driving variables.

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2. Materials and Methods

2.1. Data Set

[3] The data used in this paper were obtained from two field experiments located near Lincoln University on the

South Island, New Zealand (43°6′S), receiving an annual precipitation of 657 mm. The soil at the experimental site is a Templeton silt loam (Udic Ustochrept; U.S. Department of Agriculture Soil Taxonomy) and had been under a ryegrass (*Lolium perenne*)-white clover (*Trifolium repens*) pasture for 4 years. The effect of sheep urination events was simulated by applying synthetic urine at four times during 1 year on separate plots each at rates of 500 kg N ha^{-1}. The full data set is published elsewhere [*Müller et al.*, 1997; *Müller and Sherlock*, 2004].

[4] During the 1-year study, N_2O_{tot} emissions were determined on 235 days and soil variables including soil NO_3^- and soil NH_4^+ were measured on 51 days. All other variables such as soil moisture, soil temperature, and rainfall were determined on a daily basis with an automatic weather station. In a separate field experiment the relative importance of nitrification and denitrification to N_2O_{tot} emissions was quantified. The soil and urine application rates were identical to the ones used in the first experiment. The N_2O_{den} fraction was determined by incubating the soil at 0 and 5 Pa acetylene (C_2H_2) [*Müller et al.*, 1998]. Assuming that other N_2O production processes were negligible, N_2O_{nit} was calculated by difference (i.e., $N_2O_{nit} = N_2O_{tot} - N_2O_{den}$). Relationships between N_2O_{den}/N_2O_{tot} and mineral N, soil moisture, and soil temperature were developed and used to partition the N_2O_{tot} emissions of the full data set into N_2O_{nit} and N_2O_{den} emissions [*Müller et al.*, 1998; *Müller and Sherlock*, 2004].

2.2. The DayCent Model

[5] The DayCent model, the daily version of the Century model [*Parton et al.*, 1988], is a terrestrial ecosystem model that can be used to simulate C, N, P, and S dynamics of agricultural and natural systems [*Del Grosso et al.*, 2001; *Parton et al.*, 1998]. The main changes compared with Century are the finer timescale, a higher spatial resolution of the soil processes, and the new N trace gas model; daily precipitation, maximum and minimum temperature, and optionally wind speed, radiation, and humidity drive the model. The land surface submodel [*Parton et al.*, 1998] simulates water content and temperature for various soil layers and evapotranspiration. Plant production is modeled with a maximal production function limited by temperature, available water, and nutrients. The assimilated carbon is allocated to five biomass pools which are characterized by nominal C/N ratios and death rates that can further be affected by water and temperature stress. Dead plant material, which is entering the soil organic matter (SOM) submodel, is divided into structural and metabolic pools (depending on their N and lignin content) and decomposes to three SOM pools with different turnover times. Soil organic matter decomposition is restricted to the top 20 cm of the soil.

[6] The N trace gas model contains a denitrification and nitrification submodel. The denitrification submodel relates soil NO_3^- and CO_2 concentrations to maximal total N_2O_{den} and N_2 emissions (D_t), and the effect of WFPS on soil gas diffusivity is included by a dimensionless multiplier [*Del Grosso et al.*, 2000].

$$D_t = \min[F_d(NO_3), F_d(CO_2)] \times F_d(\mathrm{WFPS}) \quad (1)$$

$$F_d(NO_3) : y = 1.15x^{0.57} \quad (2)$$

$$F_d(CO_2) : y = 0.1x^{1.3} \quad (3)$$

$$F_d(\mathrm{WFPS}) : y = 0.45 + \arctan(0.6\pi(0.1x - a))/\pi$$
$$a = F(D_{fc}, CO_2) \quad (4)$$

[7] After calculating $N_2 + N_2O$ emissions from denitrification, the ratio of N_2 to N_2O ($R_{N2/N2O}$) emissions is calculated as a function of WFPS, NO_3/CO_2 ratio, and gas diffusivity at field capacity (D_{fc}) [*Del Grosso et al.*, 2000; *Weier et al.*, 1993].

$$R_{N2/N2O} = F_r(NO_3/CO_2) \times F_r(\mathrm{WFPS}) \quad (5)$$

$$F_r(\mathrm{WFPS}) : y = \max[0.1; 1.5x - 0.32] \quad (6)$$

$$F_r(NO_3/CO_2) : y = \max\left[0.16; e^{-0.8(NO_3/CO_2)}\right] \times \max[1.7; 38.4 - 350\ D_{fc}] \quad (7)$$

then

$$N_2O_{den} = D_t/\left(1 + R_{N2/N2O}\right) \quad (8)$$

[8] In the nitrification submodel a fixed proportion (2%) of the nitrification rate (F_{NO3}) is assumed to be lost as N_2O_{nit}. Nitrification rate itself is influenced by soil NH_4^+ concentrations, soil temperature (t), pH, and WFPS [*Parton et al.*, 2001, 1996].

$$F_{NO3} = \mathrm{baseflow} + 0.1 \times NH_4 \times F(t) \times F(\mathrm{pH}) \times F(\mathrm{WFPS}) \quad (9)$$

$$N_2O_{nit} = F_{NO3} \times 0.02 \quad (10)$$

[9] NO_x emissions are calculated as a fraction of N_2O_{tot} depending on soil gas diffusivity (D/D_0) and an additional factor P to account for pulses in NO_x emissions initiated by precipitation on dry soils [*Parton et al.*, 2001; *Yienger and Levy* [1995].

$$NO_x = R_{NOx} \times N_2O_{den} + R_{NOx} \times N_2O_{nit} \times P \quad (11)$$

$$R_{NOx} = 15.2 + (35.5 \arctan(0.68\pi(10D/D_0 - 1.86)))/\pi \quad (12)$$

2.3. Running the Model

[10] DayCent requires initial variables and parameters for site and soil properties, organic soil and biomass pools, mineral pools, water content, and N deposition (Table 1). Additionally, daily climate (minimum and maximum temperature and precipitation) and information on land use is needed. Land management was simulated as a grass-clover vegetation, with monthly mowing removing 75% of the aboveground biomass. Ammonia volatilization after synthetic urine application is not considered in the model but was assumed to amount to 30% of applied N. One important constraint of the version of DayCent used in these simu-

Table 1. Initial Driving Variables for the DayCent Model Run

Parameter	(Initial) Values
Bulk density, g m^{-3}	1.2
Clay, %	20
Silt, %	60
Sand, %	20
pH	6
Organic N, %	0.7
Organic C, %	7
Wilting point, volume fraction	0.15
Field capacity, volume fraction	0.45
Saturated hydraulic conductivity, cm s^{-1}	0.00403
Land use	grass-clover pasture, harvested monthly except for the winter months of June and July

lations is that management events can only be scheduled on a monthly basis. To match the actual with the modeled fertilizer events, the climate data were shifted by 8 days, which resulted in the smallest possible shift with negligible errors in incoming solar radiation. No further correction or "model fitting" was needed. We decided not to do an equilibrium run but calculated 1.5 years before the actual simulation period to account for pool changes that occurred in the first year.

2.4. Presentation of Results

[11] Some of the processes in DayCent are calculated and updated only weekly; therefore some model outputs show 7-day steps (e.g., N plant growth). The output of DayCent (lines) is presented in our figures versus the observed mean value of the data (dots or dotted lines).

3. Results

3.1. Nitrous Oxide

[12] The general pattern of simulated N_2O emissions agreed reasonably well with the observed dynamics (Figure 1). During the experimental period the total measured N_2O_{tot} emissions amounted to 4.4 kg N_2O-N ha^{-1}, while total simulated emissions were 18.4 N_2O-N ha^{-1}. Highest N_2O emissions were observed shortly after urine applications and after the heavy rainfall event at day 154 (Figure 2). After this rainfall event and after the first urine application the model strongly overestimated the N_2O emissions, while for the other periods simulated and observed values agreed reasonably well (Figure 1). The modeled and observed N_2O_{nit} were on average 48 and 32% and the N_2O_{den} were on average 52 and 68% of total N_2O_{tot} emissions. Hence the model overestimated the contribution of nitrification related N_2O emissions to the overall flux (Figure 1).

3.2. Precipitation, Soil Moisture, and Soil Temperature

[13] Rain events >45 mm d^{-1} caused large observed N_2O_{tot} emission peaks at days 154 and 285 (Figure 2). The second peak, which coincided with the fertilizer-induced peak after the fourth urine application, was modeled reasonably well, while the first peak which occurred 59 days after N application was largely overestimated in the simulation. The rain at day 59 fell on relatively dry soil and caused the model to predict a short-term emission peak that was not measured. However, as measurements were not carried out daily during this period, this short-term emission peak may have been missed.

[14] Soil temperatures in the top 1 cm of the soil profile were simulated well with DayCent, due to its close connection to observed air temperatures (Figure 2). DayCent seems to overestimate soil temperature in summer and underestimate it in winter. After the third N application, no large

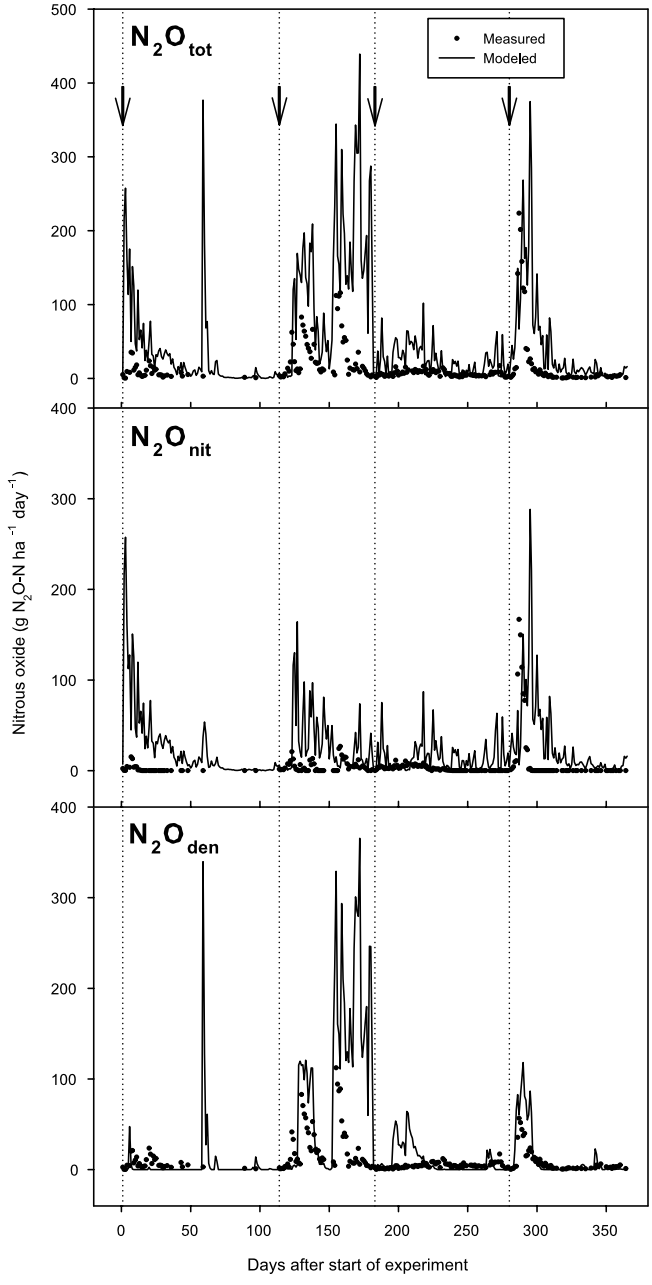

Figure 1. Simulated and measured N_2O_{tot}, N_2O_{nit}, and N_2O_{den} emissions for the experimental period (arrows indicate the times of synthetic urine applications on separate plots, i.e., between the dotted vertical lines; "measured" N_2O_{nit} and N_2O_{den} were calculated according to *Müller et al.* [1998]).

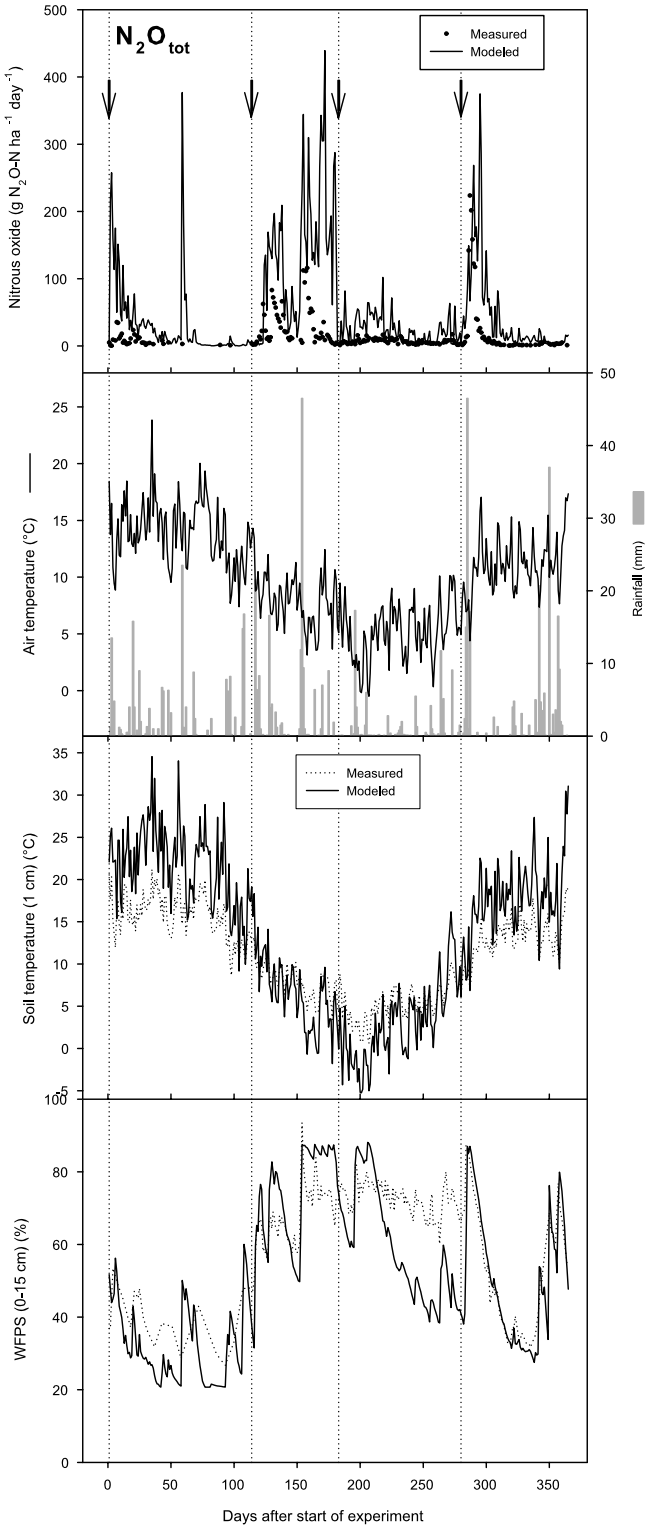

Figure 2. Simulated and measured N_2O_{tot}, soil and air temperature, precipitation, and WFPS for the experimental period (arrows indicate the times of synthetic urine applications on separate plots, i.e., between the dotted vertical lines).

N_2O_{tot} increase occurred despite high mineral N values, probably because soil temperatures were <5°C. Simulated emissions during this period were higher than observed ones, but stayed on a relatively low level due to the temperature effect.

[15] Modeled and observed WFPS values show in general a similar pattern (Figure 2). However, while the wetting-up periods agreed well with the observations, there were discrepancies during times of soil drying. The largest discrepancy occurred after the third urine application when the soil temperatures were low (Figure 2).

3.3. Mineral N

[16] N fertilization events in DayCent can only occur as NH_4^+ and NO_3^- but not as urea-N, and therefore the applied urine N was considered to be NH_4^+. Both observed and modeled results show a sharp increase of NH_4^+ after N application, followed by a gradual decrease (Figure 3). While the course of the NH_4^+ content agreed reasonably well after the first and the fourth urea applications, simulated NH_4^+ concentrations decreased much slower after the second and the third applications (Figure 3). This discrepancy can only partly be caused by different plant N uptake, which was 80 kg N ha^{-1} observed and 45 kg N ha^{-1} modeled during this 3-month period. Over the entire year, modeled (573 kg N ha^{-1}) and observed plant N uptake (572 kg N ha^{-1}) were the same. Soil NO_3^- concentrations were systematically underestimated by DayCent. After the first and the fourth urine applications, when NH_4^+ content was simulated well, the NO_3^- concentrations were underestimated by a factor of 2, while after the second and the third applications, when NH_4^+ content decreased much slower, it was underestimated by a factor of approximately 4 (Figure 3).

[17] The four urine applications were carried out on separate plots, and therefore it was assumed that the N-content was zero before the next fertilizer application. Hence annual sums will not be true annual sums of emissions because of the exclusion of the long-term effect of the fertilization.

3.4. Total N Gas Loss

[18] The combined N gas (N_2O_{tot} + NO + N_2) loss estimated via DayCent over the entire observation period was 116 kg N ha^{-1} yr^{-1} (18.4 kg N_2O-N; 64.7 kg NO-N; 33.3 kg N_2-N) or 5.8% of the applied N. The simulated NO and N_2 emission were 3.5 and 1.8 times higher than simulated N_2O_{tot} emissions. No validation data existed for NO emissions. Dinitrogen emissions were determined with the acetylene technique (10 kPa) which may produce erroneous results when applied to aerobic soils [*Bollmann and Conrad*, 1997]. Therefore we decided not to validate the simulated N_2 data.

4. Discussion

4.1. Simulated N_2O Emissions

[19] For the 1-year observation period, DayCent overestimated observed N_2O_{tot} by 318%. One reason for this relatively large discrepancy is the period after the strong rainfall event at day 154, where one third of the total simulated annual N_2O flux was emitted within only 4 weeks

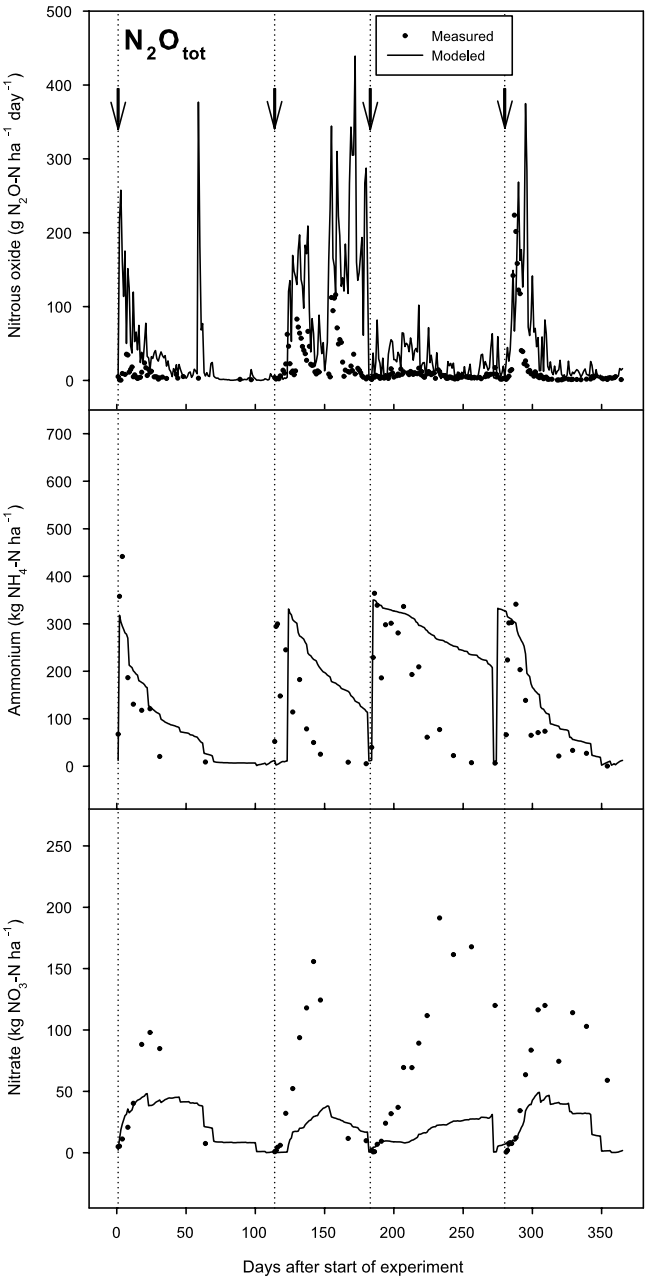

Figure 3. Simulated and measured N_2O_{tot}, NH_4^+ and NO_3^- concentrations of the upper 15 cm of the soil (arrows indicate the times of synthetic urine applications on separate plots, i.e., between the dotted vertical lines).

(Figure 2). During this time the simulated WFPS was almost 90%, while the observed WFPS was about 70%. Because of the functional relationship between N_2O_{den} and WFPS the N_2O emissions were overestimated. This highlights that periods after extreme events where many of the driving variables for N_2O emissions may be in optimum have to be simulated well because of their importance for the annual balance of N_2O emissions [*Priemé and Christensen*, 2001].

[20] Nitrification contributed significantly to the observed emissions only after the fourth urine application, while DayCent also simulated relevant N_2O_{nit} after the first and the second applications. Furthermore, between days 180 and 280 no emissions were observed but simulated N_2O_{nit} were still relatively high. In DayCent, N_2O_{nit} emissions are functionally related to the nitrification rate and the soil NH_4^+ concentrations (equations (9) and (10); Figures 1 and 3). Instead of relating the N_2O_{nit} to the simulated nitrification rate by a fixed factor, it may be more accurate to relate it to the buildup of nitrification-related nitrite (NO_2^-) which does not occur under conditions which favor quick NO_2^- oxidation [*Venterea and Rolston*, 2000; *Wrage et al.*, 2001].

[21] Simulated N_2O_{den} showed better agreement with observations, apart for the peaks around days 59 and 154 that were discussed above. However, as N_2O_{den} depends on soil NO_3^- concentrations, which are underestimated systematically by a factor of 2–4 during the simulation period, it can be concluded that the simulation procedure is overestimating N_2O_{den}.

[22] Though N_2O_{nit} and N_2O_{den} are considered separately in DayCent, their comparison with observed N_2O_{nit} and N_2O_{den} is not as predicative as for N_2O_{tot} because the acetylene technique used and the application of a relationship observed during a separate field experiment to the entire data set may have produced inaccuracies [*Müller et al.*, 1998]. However, subsequent measurements of the N_2O_{nit} and N_2O_{den} fractions during another field experiment on temperate grassland soil, using in situ ^{15}N-labeling techniques, showed that the N_2O_{nit} fractions were most likely even lower compared to the one presented here [*Müller et al.*, 2004].

4.2. WFPS Modeling

[23] The overestimation of WFPS between days 154 and 220 that has been discussed above may be explained by an overestimated WFPS at field capacity, as the maximal observed WFPS after rainfall events apparently was short-lived and probably related to a water content exceeding field capacity. Reducing the input value for field capacity led to a better simulation of WFPS and significantly reduced the overestimation of N_2O_{den} but was regarded as an illegitimate model tuning (data not shown).

[24] One reason for the discrepancies in WFPS during soil drying especially during times when the soil temperature was low may be the formation of dew, which is not accounted for in the precipitation data. When calculating daily soil water content from precipitation, evapotranspiration, and soil water content of the previous day, a curve very similar to the one modeled in DayCent emerged. This strongly indicates that measured soil water content is higher than could be expected from rain and evapotranspiration (ET), and dew is very likely to be the reason for this. On the other hand, ET might be overestimated, but the Linacre method used in DayCent and the Penman-Monteith method applied to the data gave almost the same results. Another reason for differing WFPS might be the way in which internal drainage and hysteresis effects are modeled in DayCent. The pedotransfer functions which are used to characterize hydraulic conductivity and drainage may have overestimated internal water flow and redistribution in this soil, but irrespective of the internal flows DayCent simulated no water flowing out

of the soil profile during the simulation period (data not shown).

4.3. Mineral N

[25] Soil NH_4^+ concentrations are modeled reasonably well after the first and fourth N application. However, after the second and the third applications the concentrations were too high, which coincided with times of low soil temperature. In the DayCent simulation the main sink for NH_4^+ is immobilization into microbial biomass, followed by plant N uptake, nitrification, and gaseous N losses. The DayCent version used for this validation study did not allow application of N in form of urea. Urea hydrolyzes quickly to NH_4^+ and in the process increases the soil pH. This can cause high ammonia (NH_3) emissions from soil and can inhibit the activity of microbial transformations [*Brady and Weil*, 2002]. Simulated N leaching was insignificant, although data suggest that it also contributed to N removal from the soil. The underestimation of leaching is known to the Century group and has been fixed in the latest version of the model (B. Parton, personal communication, 2003). Since modeled and observed plant N uptake agreed well, the main reason for the discrepancy in NH_4^+ and NO_3^- concentrations and N_2O emissions is related to the magnitude and interactions of nitrification, leaching, and immobilization. In grassland soils, in addition to autotrophic nitrification, also heterotrophic nitrification, which is carried out by fungi, may contribute considerably to the NO_3^- buildup [*McGill et al.*, 1981]. The speed and interactions of the gross N transformation rates will finally determine the magnitude of N_2O production and emissions from soils [*Azam et al.*, 2002; *Müller and Sherlock*, 2004].

5. Conclusions

[26] The pattern of modeled and observed N_2O emissions agreed reasonably well, but DayCent overestimated annual emissions by 318%. Analysis of driving variables showed that this was caused mainly by two reasons: (1) an overestimation of N_2O_{nit} while NH_4^+ content was modeled accurately and nitrification was underestimated and (2) an overestimation of soil WFPS during a period of only 4 weeks which caused higher than observed N_2O_{den} emissions (30% of total annual emissions) though NO_3^- concentrations were underestimated during this period. Our analysis highlighted the following areas where further model development is needed in DayCent:

[27] 1. The inaccuracies in the simulation of NH_4^+ and NO_3^- appear to be related to problems associated with the nitrification submodel and interactions with other processes such as immobilization and leaching.

[28] 2. The fixed correlation of the nitrification rate and the N_2O_{nit} emissions to NH_4^+ concentrations may lead to erroneous results because the data suggest that significant rates of nitrification can occur without inducing significant N_2O emissions.

[29] 3. Accurate simulation of WFPS is required because of its direct functional relationship to N_2O_{den} and N_2O_{nit} emissions.

[30] 4. The addition of different fertilizer types and a finer scheduling of management events are essential for more accurate testing with detailed data sets.

[31] As far as we know there are only a few published N_2O model validations that distinguish N_2O_{nit} from N_2O_{den}. Moreover, DayCent tests of N_2O emissions have rarely included comparisons with observations of the primary drivers of N_2O emissions [e.g., *Frolking et al.*, 1998]. Therefore validation studies such as the one presented here are valuable and should be carried out with other detailed data sets from other ecosystems because they highlight the directions in which ecosystem models such as DayCent should be developed.

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