






Assessing nitrous oxide emissions from grass-clover ley within a crop rotation using measurements and modeling

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ABSTRACT

Nitrous oxide (N₂O) is a significant greenhouse gas that contributes to climate change, with one of the major anthropogenic sources being agricultural fertilizer application. In Europe, a substantial fraction of nitrogen (N) fertilizers is applied in grass-based systems, including leys, which generate N₂O emissions. The contribution of grass-clover leys to N₂O emissions and the specific emission factors (EFs) are not well-documented. Therefore, we monitored N₂O emissions in grass-clover ley over three full years (2021 – 2023) and assessed the feasibility of using the process-based model DayCent with a previously published multi-site calibration for Western European cropland to simulate N₂O emissions. The monitoring was undertaken using an automatic time integrating chamber system in three treatments of a long-term fertilization experiment on a ley–arable rotation in Switzerland, including organic fertilization (slurry), mineral fertilization (ammonium nitrate and ammonium sulphate) and a control (unfertilized). The results showed mean annual N₂O emissions of $0.51 \pm 0.26 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, $0.53 \pm 0.08 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $0.02 \pm 0.03 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from organic, mineral and control treatments, respectively, over the three study years. We found that the EF values, which were determined from measured emissions of the fertilized treatments after subtracting the control treatment, were 0.23 % for organic and 0.41 % for mineral fertilizer, which are much lower than the IPCC wet climate default EF values of 0.6 % and 1.6 %, respectively. For DayCent simulations, we used aboveground N yield to adjust for model parameters associated to plant C/N ratio and the biological N₂ fixation of the specific grass-clover mixture ley. The model yielded mean EFs of 0.26 % and 0.29 % for organic and mineral fertilizer, respectively, showing no significant difference ($p > 0.05$) to the corresponding measured EF values. The modeling results suggest that grass-clover ley under these conditions tends to have lower N₂O emissions than the arable crops in the rotation. Our results indicate that using IPCC default EFs may overestimate the N₂O emission from grass-clover ley under the studied soil conditions, and that DayCent with an average multi-site calibration with adjustment of few crop N parameters is able to reproduce the comparatively low N₂O emissions and EFs for ley.

1. Introduction

Nitrous oxide (N₂O) is a potent and long-lasting greenhouse gas (GHG). In comparison to CO₂, it has a 273 times greater global warming potential on average over 100 years (IPCC, 2023). Soil N₂O emission from the agricultural sector represents a dominant fraction of anthropogenic GHG emissions, and it is mostly derived from the application of synthetic fertilizers and organic manure (Davidson, 2009; Tian et al., 2020). Soil N₂O emissions from agriculture tend to increase along with the growing population and the rising demands for food and feed

production to meet human nutritional needs. Thus urgent action is required to mitigate N₂O emissions from the agricultural sector, particularly in feed production.

In Europe, dairy cattle farming is based significantly on ley-arable rotations (Vertès et al., 2007), representing the regular cultivation of grass-clover mixtures every few years in alternation with arable crops (Biernat et al., 2020b; Krauss et al., 2017; Poulton et al., 2023; Vertès et al., 2007). In Switzerland, for example, ley for intensive forage production covers 30 % of the arable cropland area and is an important part of Swiss agriculture (Gilgen et al., 2023; Lüscher et al., 2019). It has been

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suggested that the introduction of ley in arable rotations has multi-functional benefits, such as sequestering soil carbon, preventing soil erosion, and reducing the environmental footprint of agricultural production, while also capturing atmospheric N_2 (Hu and Chabbi, 2022; Smit et al., 2021; Zani et al., 2020). When compared to permanent grasslands and croplands only based on annual arable crops, grass-clover leys in an arable rotation can result in lower N_2O emissions (Biernat et al., 2020a; Petersen et al., 2006). The use of clover in ley increases the biological N_2 fixation (BNF), which may lead to a lower fertilizer N demand for ley and therefore a N_2O reduction in ley compared with arable crops (Hu and Chabbi, 2022; Petersen et al., 2006). Moreover, the lower soil organic matter (SOM) content in ley compared with permanent grassland, attributed to soil disturbance from the management of previous crops, may result in reduced inputs of C and N substrates for N_2O production in ley. However, defining the effective contribution of ley within arable rotations on N_2O emissions depends on reliable field emission measurements, which are still limited. According to the IPCC (2019) concept, N_2O emissions are often described as emission factors (EF) relative to the applied N fertilizer amount. IPCC also specified global average (default) EF values either for mineral and organic fertilizers combined (1.0 %) or as disaggregated values e.g. for mineral (1.6 %) and organic fertilizers (0.6 %) in wet climate. Whether to use the same or separate EF values for different fertilizer types in national inventories is still under debate and depends on experimental evidence in the individual countries. In Switzerland, the combined EF value of 1.0 % is presently in use, but broadly based experimental evidence is still lacking.

In addition to field measurements, another useful complementary approach to understanding N_2O emission dynamics is process-based modeling. A major advantage of using such models is that, when calibrated on the basis of reliable field observations, they allow the assessment of factors driving N_2O emissions and possible mitigation options in a cost- and time-effective way. The process-based model DayCent has been widely employed to simulate N_2O emissions from various ecosystems worldwide. Its good performance has been confirmed by numerous N_2O emission datasets from cropland and grassland with diverse field management practices (Abdalla et al., 2010; Alvaro-Fuentes et al., 2017; Del Grosso et al., 2005; Zhang et al., 2013). The successful simulation of N_2O emissions highly depends on the calibration of the model by using field data, in particular the calibration of parameters related to the N cycle. Although, studies have been carried out to improve the performance of the model for simulating the GHG emissions in cropland and grassland (dos Reis Martins et al., 2022; Senapati et al., 2016), there is still a lack of information about using DayCent to simulate N_2O emissions from grass-clover ley within the arable rotation. For instance, the BNF associated with the clover fraction is a challenging aspect for modeling N cycling and, consequently, the N_2O emissions in grass-clover leys. Thus, modeling N_2O emissions from ley may need special calibration compared to the arable crops within the same rotation. Therefore, we conducted field measurements of N_2O emissions from grass-clover ley with different fertilizer treatments over three years and assessed the performance of the DayCent model to simulate the emissions. The first hypothesis of the study was that DayCent with the existing multi-site calibration of soil parameters for Western European cropland (dos Reis Martins et al., 2022) is able to simulate the magnitude of the annual N_2O emission from fertilized ley and the corresponding EF with reasonable agreement. However, since ley is treated in DayCent as one single crop, it was expected that an adjustment of the ley plant parameters is necessary to get the appropriate N yield for the specific grass-clover mixture in the field experiment. The second hypothesis was that the N_2O EF for mineral fertilizer is equal to that for organic fertilizer.

2. Material and methods

2.1. Study site

The field study was conducted at the Reckenholz Research Station, Zurich (47°25'32''N, 8°30'59''E, 443 m a.s.l.), within the long-term DEMO trial established in 1987 to test the effect of primary macronutrient deficiency in crops (Frei et al., 2024). The soil at this site was characterized in Keel et al. (2019) and consists of Eutric Cambisol by the definition of World Reference Base for Soil Resources (FAO-WRB, 2014) with a loamy texture (20 % clay, 33 % silt, 47 % sand) and an approximately 2 % organic C content. Soil pH was between 7.0 and 7.5 depending on treatment. The annual mean precipitation was 1050 mm and the annual mean temperature 9.4°C. The management of the field experiment is based on a seven-year crop rotation with a sequence of grass-clover ley (biennial), summer wheat, sugar beet, grain maize, potatoes, and winter barley (Fig. 1). The ley and winter barley are sown in late summer or autumn of the preceding year, shortly after the harvest of the previous crop. The rotation sequence is replicated seven times in the experiment but with a temporal shift of one to six years corresponding to a staggered-start design with seven blocks (Loughin, 2006). Therefore, each individual crop grows in parallel every year. In addition, each crop sequence (block) comprises various mineral and organic fertilizer treatments (one 5 × 6 m plot each; for details see Frei et al., 2024).

For the present study, N_2O observations were carried out on 2nd year ley during the consecutive years 2021–2023 (Fig. 1) for three selected fertilizer treatments: (i) mineral fertilizer, (ii) organic fertilizer, and (iii) control treatment without any fertilizer application. Each fertilizer treatment has been applied consistently in all years (for all crops in the rotation) on the respective plots since the beginning of the experiment in 1987. The mineral fertilizer containing N, P, K, and S was applied at rates according to the official Swiss (best practice) fertilizer recommendations for each crop (Richner et al., 2017). The organic fertilizer was always applied in the form of cattle slurry and the application rate was adjusted to provide the same amount of plant available (water soluble ammonium) N as for the mineral fertilizer treatment. For this purpose, the slurry was taken from the same batch throughout individual years with an initial lab analysis of the slurry composition. Thus, the organic fertilizer treatment included an additional and somewhat varying amount of organic N compared to the mineral fertilizer treatment, resulting in a total N input about double that of the mineral fertilizer treatment (see Table A1). The application rates of other nutrients in the different fertilizer treatments are reported by Frei et al. (2024).

Except for fertilization, the management of the ley was identical for the three treatments. The ley was harvested four to five times per year, depending on weather conditions, and had the same number of fertilizer applications annually, which were timed with the beginning of each (re-)growth phase. For the mineral fertilizer treatment, the first application within each year was 30 kg N ha⁻¹ as ammonium sulphate, with all subsequent application being 25 kg N ha⁻¹ as ammonium nitrate. This resulted in an annual maximum of 130 kg N ha⁻¹. However, in year 2022, one fertilization event was skipped due to the dry summer, resulting in an annual N input of 105 kg N ha⁻¹ (Table A1). The grass-clover ley was a commercial mixture (UFA 330 M, UFA AG, Winterthur, Switzerland) of English ryegrass (*Lolium perenne* L.), meadow fescue (*Festuca pratensis* Huds.), cocksfoot (*Dactylis glomerata* L.), timothy grass (*Phleum pratense* L.), red clover (*Trifolium pratense* L.) and white clover (*Trifolium repens* L.).

2.2. N_2O flux measurements

The N_2O emission from ley was monitored using automatic time integrating chamber (ATIC) systems from January 2021 to December 2023. Due to the limited available number of ATIC units (6 in the first year and 9 in the second and third year), we focused the measurements on the 2nd-year-ley. On each investigated plot (one per treatment per

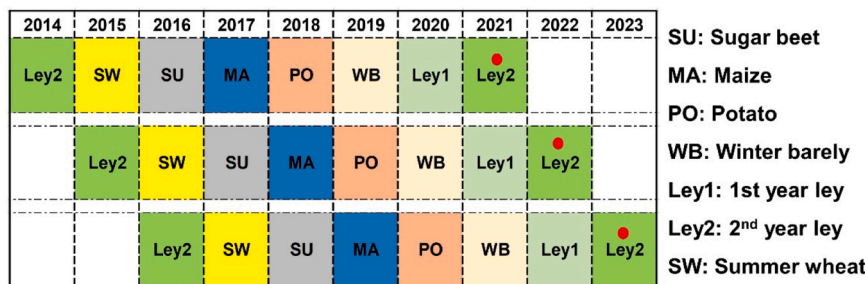


Fig. 1. Schematic illustration of the crop sequences in the DEMO experiment showing three out of total seven parallel ley-arable rotations (staggered-start design). These three rotations were chosen for chamber N_2O flux measurements because they had 2nd year ley in the study period 2021–2023 (years/crops marked with red dots). Each crop sequence comprises plots with different fertilizer treatments (not shown here).

year), three ATICs were applied (except for the unfertilized control that was only measured in the 2nd and 3rd year) in parallel. They covered the small-scale variability on the 5×6 m plots, but cannot be considered as true replicates. Detailed information about the ATICs can be found in Wang et al. (2022). Briefly, the system provides multiday integration measurements of multiple measurement cycles for each chamber (size $300 \times 300 \times 220$ mm). Here, we define a measurement cycle as a lid-closing phase of 15 min. Within this time, chamber air was sampled sequentially into four different foil gas bags (Supelco, Germany) per chamber at intervals of 3.5 min to account for the concentration increase during closure. Measurement cycles were repeated about 30–40 times (every 2–9 h) and the air samples were accumulated in the four bags. As a result, the bags were filled and collected at time intervals T_j ranging from 3 to 14 days (referred to hereafter as “sampling period”). The standard sampling period was 7 days, with shorter sampling periods around fertilizer applications and longer ones during the non-growing season. At each collection, the air mixture in each filled bag represented an average pooled sample over the corresponding sampling period. The 30–40 measurement cycles per sampling period were constrained by the volume of the bag (5 L) and the flow rate of the pump (0.5 L min^{-1}). At the end of each sampling period, the filled bags were replaced with empty ones and were transferred to the lab to determine their GHG concentration using a cavity ring down spectroscopy analyzer (G2308, Picarro, USA).

N_2O fluxes were determined following Wang et al. (2022):

$$F = \frac{V}{A} \times \frac{\partial \bar{C}}{\partial t} \quad (1)$$

where $V = 0.02 \text{ m}^3$ and $A = 0.09 \text{ m}^2$ are the volume and the soil surface covered by the static chamber. $\frac{\partial \bar{C}}{\partial t}$ represents the average rate of concentration increase between the four bags of a sampling period. Since each average bag concentration \bar{C}_i ($i = 1, 2, 3, 4$) is the arithmetic average of the respective concentrations in each chamber closing cycle, the average slope $\frac{\partial \bar{C}}{\partial t}$ also represents the average of the individual increase rates in N_2O concentration of each cycle $\left(\frac{\partial C}{\partial t}\right)$ during the sampling period. Therefore, F in Eq. 1 represents the average gas flux over the sampling period. The fluxes of the individual sampling periods were checked for quality, gap-filled (see Sect. 2.3), and accumulated to total annual fluxes (full calendar year) for each chamber:

$$F_{\text{cum}} = \sum_j (F_j \times T_j) \quad (2)$$

F_j is the gas flux (according to Eq. 1) for the sampling period j . Subsequently, the results of the three chambers per treatment were averaged to a mean N_2O emission per treatment and year. Its uncertainty was estimated from the spatial variability among the three chambers. The corresponding annual N_2O emission factors (%) for the two fertilizer treatments were calculated as:

$$EF = \frac{F_{\text{cum, fert}} - F_{\text{cum, control}}}{N_{\text{fert}}} \times 100\% \quad (3)$$

Here, $F_{\text{cum, fert}}$ is the annual N_2O emission from plots with either organic or mineral fertilizer, $F_{\text{cum, control}}$ is the annual N_2O emission from the control plot without fertilizer application, and N_{fert} is the total N fertilizer input on the plot with fertilization (all three quantities in $\text{kg N ha}^{-1} \text{ yr}^{-1}$). Finally, the three annual EF values, considered as true replicates in this study, were averaged to a 3-year mean EF for the two fertilizer treatments. The corresponding uncertainty was estimated from the variability of the annual values, and the significance of the differences between treatments were determined by a simple t -test.

2.3. N_2O flux quality control and gap-filling

The individual flux data were subject to quality control according to the procedure described in Wang et al. (2022) for the same measurement system. Data were generally rejected if the linear regression of the CO_2 concentration as a function of chamber closure time showed an $R^2 < 0.9$. In addition, the linear regression for N_2O also had to show a $R^2 > 0.9$ for fluxes beyond the detection limit ($\pm 0.5 \text{ mg N}_2\text{O-N m}^{-2} \text{ day}^{-1}$) for being acceptable. For any missing N_2O flux values during the experimental period due to a failure of the ATIC chamber or a rejection of the data because of low quality, the gaps were filled by a random forest model with the “caret” package in R. The model was set up using eight predictors including: (i) information about the previous fertilization event: days after last fertilization, mineral N input, organic N input, and (ii) environmental conditions during the sampling period: mean rainfall, mean and range of water filled pore space (WFPS), as well as mean and range of soil temperature. Two random forest models were trained, one for the control treatment (without the fertilizer related predictors) and the other for the two fertilizer treatments combined. For the two fertilizer treatments, only 14 % of the sampling period had to be gap-filled (RMSE = $0.19 \text{ mg N m}^{-2} \text{ day}^{-1}$, nRMSE = 2 %, $R^2 = 0.76$). Since no data were available for the first year for the control treatment, the random forest model was also used to make an estimation of this period using the measured predictor variables. The model validation based on bootstrapping (80 % of data for training and 20 % for validation) for the years 2022 and 2023 showed a reasonable performance (RMSE = $0.04 \text{ mg N m}^{-2} \text{ day}^{-1}$, nRMSE = 4 %, $R^2 = 0.86$).

2.4. Ancillary measurements

Meteorological data were available from the nearby meteorological station (200 m away) operated by the national weather service MeteoSwiss (<https://www.meteoswiss.admin.ch>). These data included air temperature, precipitation, solar radiation, and wind speed. During the present study, soil temperature and soil volumetric water content were recorded every 15 min using TEROS 12 sensors (METER Group, Pullman, USA) at two separate locations (40 m apart) in 5 cm depth.

Gaps in soil temperature data – due to a failure of a data logger between 16 February and 2 March 2021 (around 1 % of the sampling period) – were filled using linear regression between air temperature and soil temperature (RMSE = 1.9 °C, nRMSE = 7 %, $R^2 = 0.93$). Gaps in soil water content data during the same period were filled using regression with air temperature and precipitation (RMSE = 9.9 %, nRMSE = 18 %, $R^2 = 0.44$).

2.5. Ley production

Harvested yield of the investigated ley plots was measured at each mowing event for an area of 1.5×6 m, that was not occupied by the chamber systems. After each cut, harvested biomass samples were oven-dried at 60°C for 72 h and milled to quantify the C and N contents and calculate the N yield. Therefore, we could use the total annual ley N yields to evaluate the model performance over multiple years. On five occasions during the measurement period, the clover fraction of the measured ley plots was determined. For this purpose, the harvest samples from three randomly selected $0.5 \text{ m} \times 0.5 \text{ m}$ subplots per plot were collected for separation of grass and clover species and then oven-dried at 60°C for 72 h to measure the dry matter yield and the proportion of clover in the dry matter. For the other arable crops, the yield was determined in the same way as for ley, but only once per year before harvest (Frei et al., 2024).

2.6. DayCent model

2.6.1. Model description

DayCent is a process-based biogeochemical model. The model concept and mechanism are described by Del Grosso et al. (2005). Briefly, DayCent simulates plant-soil system C and N dynamics by integrating sub-models for plant production, SOM decomposition, soil water and temperature by soil layer, nitrification and denitrification, methanogenesis and CH₄ oxidation. Data on daily weather, soil, plant, and field management, including fertilizer input, irrigation, and tillage are needed as model inputs.

For the initialization of the model, we had to approximate the regional land-use history. Since drainage pipes were found at the site, we assume that it was relatively wet till the 1960s. The land-use history was set up with three periods: 1) wet grassland without fertilization for bringing the model to equilibrium and also for a first part of a base pre-experimental phase (1801–1969); 2) a post-drainage period (1970–1988) with a first transitional year as grassland followed by a three-year arable rotation (potato, winter wheat, and sugar beet) fertilized with manure. 3) The DEMO trial phase (1989–2023), which was set up with a ley – arable rotation and with the different parallel fertilization treatments described in Section 2.1.

Concerning N fertilizer input, DayCent allows to specify the amounts of ammonium N and nitrate N for mineral fertilizer, and total amounts of C together with the corresponding C/N ratios in organic fertilizer. For the present study, we tested an alternative way for the specification of the organic fertilizer inputs: we split the slurry N input into two individual parts: 1) the dissolved ammonium N was specified as mineral fertilizer addition, and 2) the organic N in the slurry was specified as organic matter addition. We found that this modification had only a very small effect on the resulting cumulative N₂O emissions. However, it allowed to account for the ammonia volatilization after slurry application. This was estimated using the ALFAM2 (version 3.2) model (Hafner et al., 2019), and the ammonium input to the model was reduced accordingly.

2.6.2. Ley crop parameter calibration

The soil N processing parameters and the plant parameter for the arable crops were adopted from the multi-site data-driven calibration for Western Europe by dos Reis Martins et al. (2022) (Table 1). However, they did not consider observed N yield data for ley to calibrate the

Table 1

Parameter values of the DayCent model for soil N cycling and plant production for ley as used in this study. The listed values of the parameter file 'sitepar.in' have been adopted from dos Reis Martins et al. (2022); the listed values for ley in the plant parameter file 'crop.100' (see Necpalova et al., 2018) were adjusted as described in this study.

File name	Parameter	Description	Unit	Value
sitepar.in	Ncoeff	Minimum water/temperature reduction on nitrification	Scaling factor	0.027
	N2Oadjust_fc	Maximum proportion of nitrified N lost as N ₂ O at field capacity	Fraction (0–1)	0.072
	N2Oadjust_wp	Minimum proportion of nitrified N lost as N ₂ O at wilting point	Fraction (0–1)	0.0063
	MaxNitAmt	Maximum daily nitrification amount	g N m ⁻²	3.69
	netmn_to_no3	Fraction of new net mineralization that goes to NO ₃	Fraction (0–1)	0.36
	wfspdntadj	Adjustment on inflection point for the water filled pore space effect on denitrification curve	-	1.30
crop.100	N2N2Oadj	N ₂ /N ₂ O ratio adjustment coefficient	-	1.16
	pramn (1,1) ^a	Minimum aboveground C/N ratio at the beginning of the growth curve	C/N ratio	5
	pramn (1,2) ^a	Minimum aboveground C/N ratio for biomass > 400 g m ⁻²	C/N ratio	15
	pramx (1,1) ^a	Maximum aboveground C/N ratio at the beginning of the growth curve	C/N ratio	30
	pramx (1,2) ^a	Maximum aboveground C/N ratio for biomass > 400 g m ⁻²	C/N ratio	130
	snfxmx ^a	Maximum symbiotic N ₂ fixation	g N fixed/g C new growth	0.02

^a The tested value range for the calibration was chosen as follows: pramn (1,1) 5–15; pramn (1,2) 10–20; pramx (1,1) 20–40; pramx (1,2) 120–140; snfxmx 0–0.06.

respective plant N parameter values. Using the default values for ley led to a considerable underestimation of the aboveground N yield in the long-term. Therefore, we calibrated five ley-related plant N parameters in the *crop.100* file (Table 1), including the symbiotic N₂ fixation parameter *snfxmx*, based on the observed N yield data between 1989 and 2020 (before the start of the present study). To perform the partial calibration, we used a sensitivity analysis and varied the value of each of these parameters in a systematic way, while keeping the others constant at the default value. The plant N output of the model runs was compared with the corresponding field observations to search for the parameter setting with the best agreement (minimum RMSE).

With these adjustments, the DayCent model reproduced the observed long-term average N yield values (Fig. 2) much better than before with RMSE over all treatments improving from 8.8 to 2.4 g N m⁻² (rRMSE improving from 29 % to 8 %). The modeled values for the control treatment were somewhat higher than the observed values, while the deviation before calibration was much larger. For the treatments with mineral and organic fertilization, the observed N yields were not significantly different from each other ($p > 0.05$), which was also reproduced by the model. Here, the combined effect of the plant parameter calibration was less pronounced.

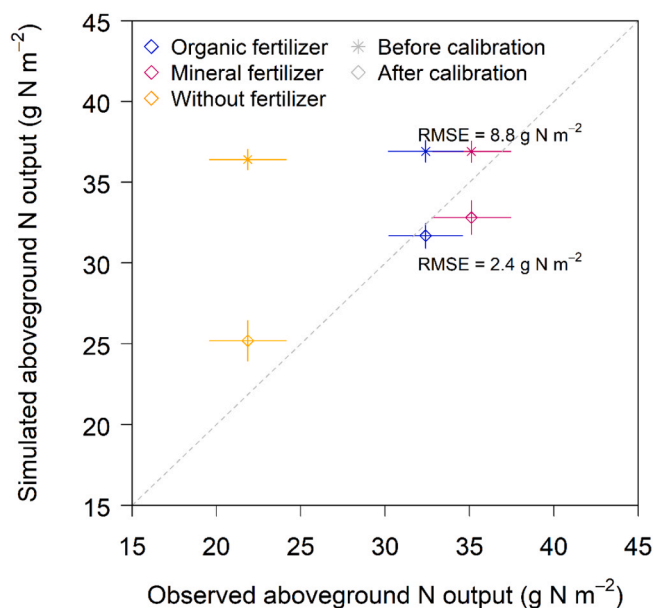


Fig. 2. Comparison of annual DayCent simulated with measured aboveground plant N yield for second year ley during 1989–2020. The dashed line indicates the 1:1 line. Symbols indicate mean values of the observed aboveground N output and error bars the $2 \times \text{SE}$ uncertainty. The plant parameter values before calibration were the model default values. The displayed RMSE values relate to all three treatments before and after calibration, respectively.

2.6.3. Evaluation of model performance

To compare modelled and measured N_2O emissions, the daily N_2O emission output of the DayCent model was cumulated to annual emissions, from which corresponding EF values were derived similarly as described for the field measurements in Section 2.2. Since for the field measurements, the uncertainty from true replicates only could be determined for the 3-year mean EF, the latter was also calculated for the modelled EF values, and the agreement between model results and

observations was tested using a *t*-test.

3. Results

3.1. Environmental conditions and ley yield

The environmental conditions within the three sampling years showed similar annual rainfall but slightly higher air temperature (Fig. 3a) compared to the long-term means of the DEMO field experiment (939 mm and 10.8°C). The annual precipitation was higher in 2021 (1056 mm) than in 2022 (836 mm) and 2023 (926 mm). The soil water filled pore space (WFPS) ranged from 35 % to 90 % over the three experimental years and with generally high values in winter and lower values in summer (Fig. 3b). In summer 2021 (May till mid August) the WFPS was higher than in the other years due to unusually wet weather conditions. Despite frequent winter frosts, as shown by the intermittent sub-zero air temperature (Fig. 3a), soil temperature at 5 cm depth remained consistently above 0°C during the three sampling years. The average soil temperature was higher in 2023 (18.2°C) than in 2022 (17.9°C) and 2021 (16.5°C).

The observed annual N harvest yields for the different treatments are listed in Table A1. Mean values ($\pm \text{sd}$) over the entire study period were 10 ± 3 , 32 ± 5 , and $28 \pm 5 \text{ g N m}^{-2} \text{ yr}^{-1}$ for control, mineral fertilization, and organic fertilization, respectively. The corresponding dry matter ley yield was 3.7 ± 1.2 , 11.7 ± 1.9 , and $10.3 \pm 1.4 \text{ tons ha}^{-1} \text{ yr}^{-1}$. The average clover fractions ($\pm 2 \times \text{SE}$) in the harvest were $62 \pm 4 \%$, $43 \pm 10 \%$, and $45 \pm 10 \%$ for the control, mineral, and organic fertilizer treatments, respectively.

3.2. Observed N_2O emissions

The measured N_2O emissions in the unfertilized control treatment (2022–2023) were consistently low without any obvious peak and emissions ranging between -0.24 and $0.85 \text{ mg N m}^{-2} \text{ day}^{-1}$ (Fig. 4). Fertilizer applications significantly increased N_2O emissions from grass-clover ley, with N_2O fluxes peaking over about 2–3 weeks following fertilizer application during all three experimental years. N_2O emissions

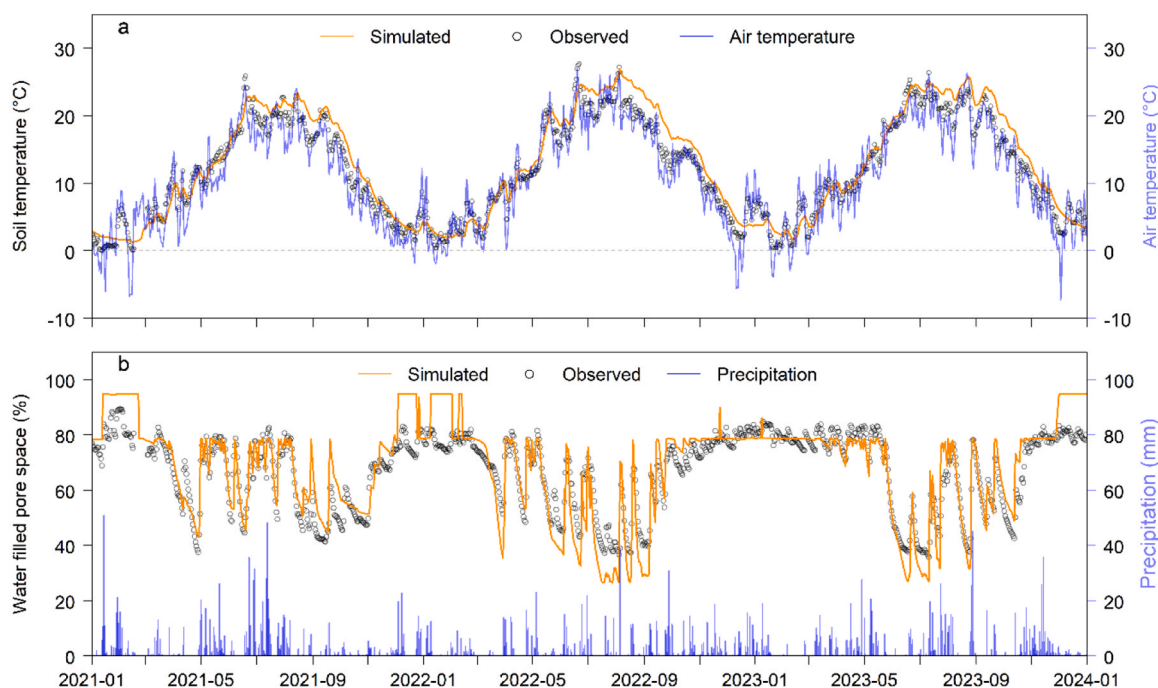


Fig. 3. Temporal variations in simulated (DayCent) and observed 5 cm daily soil temperature and air temperature (a) and 5 cm daily soil water filled pore space (WFPS) and precipitation (b), during January 2021 to December 2023.

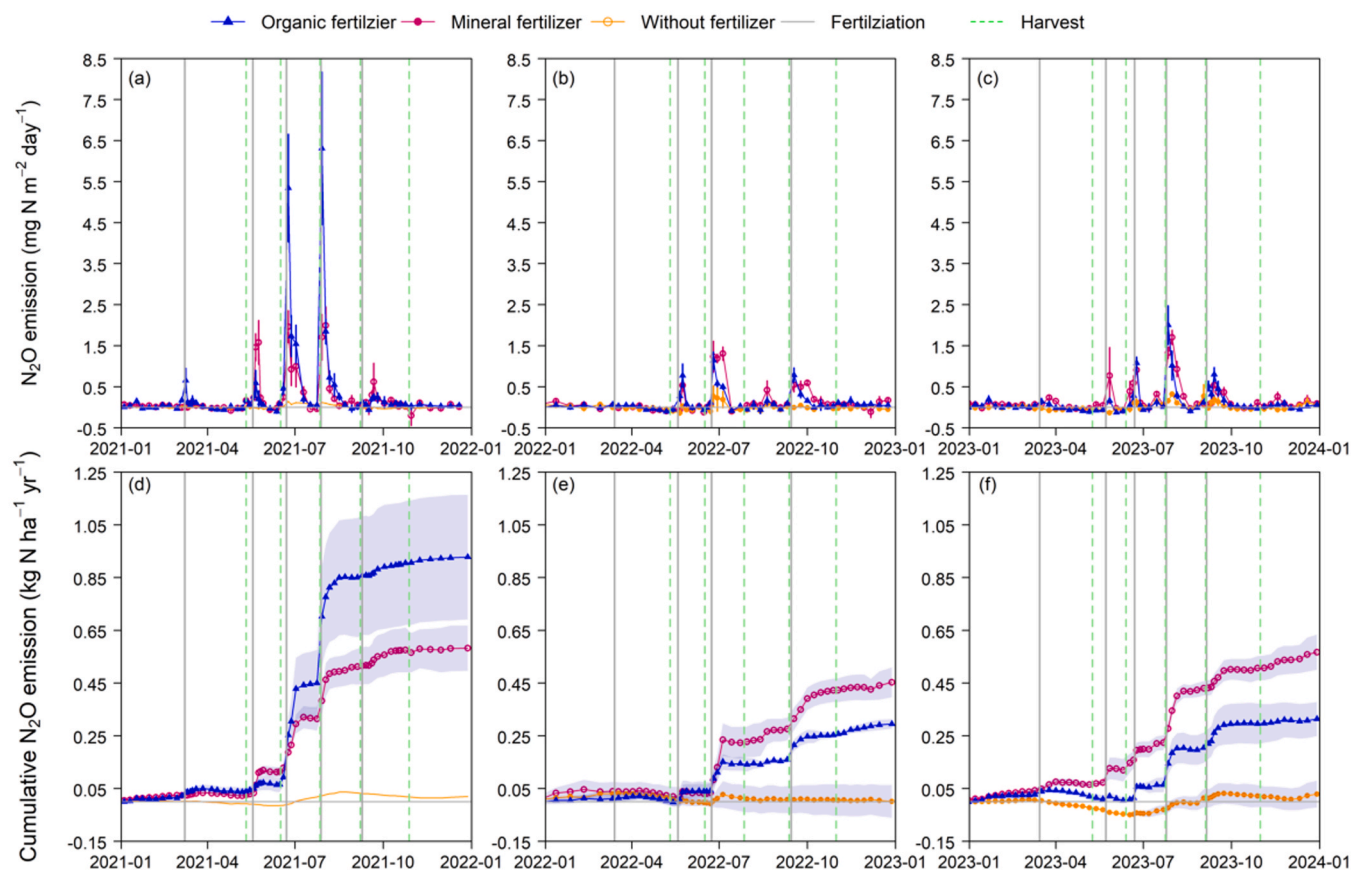


Fig. 4. Observed (a,b,c) and cumulative (d,e,f) gap-filled N_2O emissions (mean \pm SE of three chambers per treatment plot per year) for organic fertilization, mineral fertilization, and unfertilized control treatments. The vertical grey lines indicate the fertilizer application dates, and the green dashed lines indicate the harvest dates for all treatments. The horizontal grey line indicates the zero line in each panel. In panels (a), (b), and (c), each data point indicates the average N_2O flux during a sampling period (varies between 3 – 12 days). It needs to be noted that the N_2O emissions and cumulative emissions from the control treatment in year 2021 were simulated by a random forest model and are represented by a line without dots in panels (a) and (d).

ranged between -0.21 and $9.69 \text{ mg N m}^{-2} \text{ day}^{-1}$ in the organic fertilization treatment and between -0.68 and 2.81 mg N m^{-2} in the mineral fertilization treatment (Fig. 4a – c). Small negative fluxes (indicating uptake of N_2O) were frequently observed at all three treatments (account for 55 % of data of the control treatment, 27 % of the mineral fertilization treatment, and 29 % of the organic fertilization treatment), which was especially consistent during the first half of the sampling years (Fig. 4a – c). The mean cumulative annual N_2O emissions (Fig. 4d – f) of the organic and mineral fertilizer treatments were always much higher than for the control treatment. The annual emissions of the two fertilizer treatments, as well as the difference between them, showed a considerable variation among the three study years. The organic fertilizer treatment exhibited a larger variability (between 0.29 and $0.93 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) than the mineral fertilizer treatment (between 0.45 and $0.58 \text{ kg N ha}^{-1} \text{ yr}^{-1}$). However, mean annual N_2O emissions ($\pm 2 \times \text{SE}$) over all three study years were not significantly different with values of $0.53 \pm 0.08 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $0.51 \pm 0.26 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for the mineral and organic fertilizer treatment, respectively. It needs to be noted that although the available N in the mineral and organic fertilizer treatment was the same, the total N applied in the organic fertilizer treatment was larger (by roughly a factor of two, see Sect. 2.1 and Table A1) than in the mineral fertilizer treatment. However, the N_2O losses showed no significant difference between the two treatments, despite the higher total N application rate at the organic fertilizer treatment. This resulted in a significantly higher mean N_2O EF ($0.43 \% \pm 0.06 \%$) for mineral fertilizer compared to organic fertilizer application ($0.22 \% \pm 0.10 \%$) at the experimental site. The EF for mineral fertilizer remained relatively constant over the three measurement years

with annual values of 0.43% , 0.43% , and 0.41% , while for organic fertilizer the EF was 0.38% in 2021, which was 2.5-fold higher than in 2022 (0.14%) and 2.2-fold higher than in 2023 (0.13%).

3.3. Performance of DayCent model

During the three-year study period 2021–2023, a good agreement of modeled (Table A2) with observed annual N harvest yields (Table A1) was found with rRMSE values $< 22 \%$ and mean recovery rates of 98% for the mineral and 111% for the organic fertilizer treatments. However, for the unfertilized control treatment the observed N yield had exhibited a declining trend over the three decades before the start of the present study, which was not reproduced by the model. Therefore, the observed N yield for the control treatment in 2021–2023 was about 50% lower than the corresponding simulations (Tables A1 and A2).

The fertilizer related EFs for the observed and simulated results were determined from the N_2O emissions of the fertilized treatment with subtraction of the N_2O emissions from the control treatment (Eq. 3). As shown in Fig. 5, the 3-year mean EF for the organic fertilizer resulting from the DayCent simulations (*i.e.* $0.26 \% \pm 0.08 \%$) showed no significant difference to the corresponding observed EF ($p > 0.05$). For mineral fertilizer, the mean simulated EF ($0.29 \% \pm 0.12 \%$) was lower by one third compared to the observed EF, although the difference was not statistically significant ($p > 0.05$). However, DayCent did not reproduce the inter-annual variability of the observed EF values. For the organic fertilizer treatment, the model agreed well with observations in 2022, but underestimated the EF for mineral fertilization in 2021 and 2023. The year 2021 showed an exceptionally wet period from May to

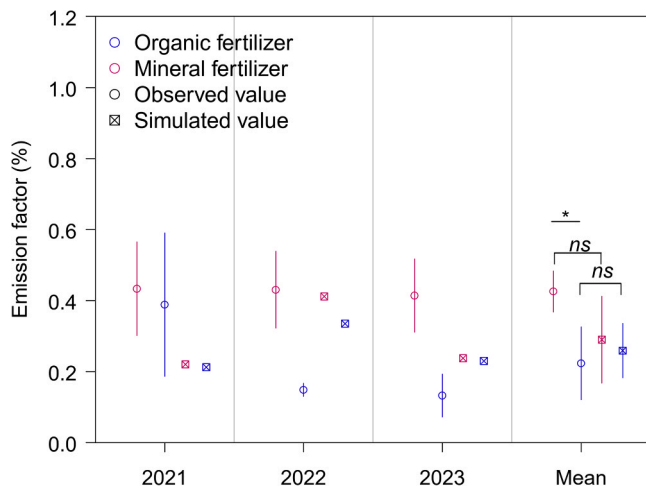


Fig. 5. Comparison of DayCent simulated and measured ley-specific N_2O emission factors (mean $\pm 2 \times SE$) for mineral and organic fertilizer application treatments during the three-year experimental period. Emission factors were determined according to Eq. 3. Significance of the difference between the mean measured emission factor of mineral and organic fertilization and between the mean simulated and measured emission factors are based on t-tests and indicated with an asterisk ($p < 0.05$) or with “ns” (no significant difference).

mid August (Fig. 3b) that is probably responsible for the high observed EF for the organic fertilizer treatment. Why the effect was different between the two fertilizer types may be related to the different dissolving and infiltration effects under varying soil moisture conditions, which is not mirrored in the model simulations.

4. Discussion

4.1. N_2O emissions and emission factors for ley

The observed annual N_2O emissions from the control plots without fertilization were nearly zero. The results are at the lower end of grassland/cropland emissions without fertilizer input reported in the literature with a range between -0.16 and 0.66 kg N_2O-N ha $^{-1}$ yr $^{-1}$ (Flecharde et al., 2005; Schils et al., 2008; Van Groenigen et al., 2004). We interpret that the low annual N_2O emissions from the control treatment in our study – and the considerable share of (small) negative fluxes contributing to them – may be due to the relatively N poor soil conditions (Chapuis-Lardy et al., 2007). The control plots have been conventionally managed for agricultural production since the year 1989 but without fertilizer application; this may lead to plant and soil system N deficiency as indicated by the declining ley N yield (Sect. 3.3), and further decrease the soil N availability for N_2O production. It has been reported that the mineralization of SOM must constitute an important N source in the system, as evidenced by the C loss from the study site (Keel et al., 2019). However, with the assumption that most of the N mineralization happened in the root layer at 0–30 cm depth, the mineralized N is taken up efficiently by the ley plants during the entire growing season. The increased N use efficiency of this unfertilized system is further evident from the higher clover fraction in the control treatments.

The observed annual N_2O emissions for organic/mineral fertilizer application (0.29 – 0.89 kg N ha $^{-1}$ yr $^{-1}$) were also at the lower end of reported N_2O emissions (0.5 – 3 kg N ha $^{-1}$ yr $^{-1}$) from grass-clover ley in Europe (Ball et al., 2002; Brozyna et al., 2013; Flecharde et al., 2005; Krauss et al., 2017; Nadeem et al., 2012). When looking at EF results normalized for the fertilizer N inputs, the organic fertilizer treatment showed lower values compared to the mineral fertilizer treatment, which is in agreement with the results of some previous studies (Aguilera et al., 2013; Charles et al., 2017; Pelster et al., 2012) but not with, e.g., the meta-analysis of Mathivanan et al. (2021) for Germany.

Yet, both the measured and the modelled ley EFs for organic fertilizer at our experimental site were at the lower end of the IPCC (2019) default EF (with 95 % of the confidence interval) for organic fertilizer in wet climates of $0.6 \% \pm 0.5 \%$. For mineral fertilizer, the difference was even higher due to the much larger corresponding IPCC default EF of $1.6 \% \pm 0.3 \%$. Besides, we also found that the ley-specific EFs simulated by DayCent were significantly lower than for most of the arable crops at the same site under both mineral and organic fertilizer application, except for winter barley (Table A3). According to the modelled ley N budget (Table A2), the harvest N export was considerably larger than the fertilizer N import, which was mainly balanced by BNF. This indicates a high fertilizer N use efficiency of the ley system with a permanent N uptake throughout the season, preventing temporarily large mineral N surplus that is susceptible to denitrification and other loss processes.

Since the modeled arable crop EF values (Table A3) were also significantly lower than the global IPCC values, the observed low emissions for ley in this study cannot be exclusively attributed to the ley *per se* but may partly be related to specific site conditions. The first possible effect is the relatively low WFPS during the growing season. Previous studies showed that soil moisture is a main driver of N_2O emissions, and that the optimum WFPS range for N_2O emissions are 70 %–80 % (Butterbach-Bahl et al., 2013). However, during the experimental period, the WFPS reached this threshold only for 135 days yr $^{-1}$, mostly during the non-growing season (Fig. 3b). The second reason for low emissions may be the high soil pH at the study site, ranging from 7.0 to 7.5. It is at the higher end of soil pH values for cropland areas in Switzerland (Meuli et al., 2017). A negative relationship with soil pH has been shown to be a significant predictor for the soil N_2O emissions (Stehfest and Bouwman, 2006; Wang et al., 2017). This may be due to the increase of the activity of the N_2O reductase enzyme under high soil pH conditions, resulting in a more complete denitrification and thus higher share of N_2 production (Samad et al., 2016; Žurovec et al., 2021). Hence, the relative high soil pH of the study site might also contribute to the low N_2O emissions.

4.2. Evaluation of the DayCent model

DayCent has been widely used for simulating N_2O emissions and crop productivity in a range of different regions and climate systems under different management conditions (Del Grosso et al., 2022; Del Grosso et al., 2009; Fitton et al., 2019; Fitton et al., 2014). However, the performance of DayCent in simulating N_2O emissions from ley has not been fully validated before, due to missing plant N parameter calibration in dos Reis Martins et al. (2022) and more generally due to limited field N_2O observations. After adjustment of the DayCent plant N parameters for the specific grass-clover mixture used in the investigated ley (based on harvest N yields observed before the beginning of this study), the model yielded N_2O EF values of similar magnitude like the observed ones. The clover proportion within ley typically surpasses that within permanent grassland, partly due to the decline in legume proportion within 3–4 years after reseeding (Karin et al., 2019). Increasing clover percentage within the ley enhanced the apparent N transfer of symbiotically fixed N_2 from the clover to the grasses (Oberson et al., 2013). Therefore, the successful application of the model in ley required an investigation of the BNF parameter (*snfxmx*). It has been reported that BNF decreased with the increase of the fertilizer N input (Nyfeler et al., 2011). However, the *snfxmx* parameter in DayCent (Table 1) is not determining the actual N_2 fixation rate but the potential maximum fixation rate, if other N sources are not sufficiently available (dos Reis Martins et al., 2024). Therefore, it is supposed to be independent of fertilizer treatment and yield. According to simulations of grass-clover BNF by Fitton et al. (2019), the effect of the fertilization rate on BNF was small for clover fractions below 65 % corresponding to *snfxmx* parameter values smaller than 0.03, which is the case in our study with average clover fractions below this value (see Sect. 3.1). Due to these

reasons a uniform value of 0.02 for the *snfxmx* parameter was used across all three treatments, although a separate adjustment of the *snfxmx* value for the control treatment could have corrected the overestimation of the simulated yields. Besides, it was found that the value of the *snfxmx* parameters had only a minor effect on the simulated N₂O emissions of the control treatment. For permanent grasslands, which typically have lower clover fractions than the ley in the present study, [dos Reis Martins et al. \(2024\)](#) adjusted a lower *snfxmx* value of 0.012.

Observed harvest N yields were similar in magnitude for mineral and organic fertilizer treatments, which was reproduced by the model simulations as illustrated in [Fig. 2](#). A key aspect to consider in the present experiment is that the total N input through organic fertilizer, *i.e.* slurry, was higher (almost double, see [Table A1](#)) than that of mineral fertilizer while both contained the same amount of plant available N, *i.e.* as ammonium or nitrate. For the cattle slurry used in this study, around half of the total N was present in the form of organic matter and thus was not readily available for plant growth, *i.e.* its N availability depends on relatively slow microbial mineralization. On the other hand, the ammonium-N in the slurry was prone to NH₃ volatilization directly after application. NH₃ volatilization has been reported to result in the loss of 10–47 % of available N ([Häni et al., 2016](#)). However, the DayCent model version used did not account for this loss and slurry applications were generally specified as organic matter input with a given C/N ratio. In the present study, we split the slurry application into two parts and treated them as separate inputs to the model (mineral and organic), which also allowed to account for the NH₃ volatilization in a pre-processing step. Hence, we suggest that when using DayCent to simulate N₂O emissions of organic fertilizers, it is crucial to consider the type of organic fertilizer and its N pool types. For liquid slurry, the organic and the mineral fractions of N should be treated separately before being fed into the model.

4.3. N budget of ley

Our field observations indicated that ley within the crop rotation may have beneficial effects on N₂O emissions. Moreover, soil N accumulation is likely to occur during the ley season, due to the plant residue input and the BNF by clover. The average BNF at the study site was estimated to be 236, 231 and 237 kg N ha⁻¹ yr⁻¹ for the plots with mineral fertilizer, organic fertilizer, and control treatment, respectively ([Table A2](#)), according to DayCent simulations. These high numbers are consistent with the simulated yields and the observed high clover fractions in all treatments (see [Section 3.1](#)). Although, most of the above-ground biomass N was removed during harvests, the dead clover roots and nodules have been shown to be an important N source for subsequent plant growth ([Oberson et al., 2013](#); [Trannin et al., 2000](#)). This is also supported by the net positive N balance ([Table A2](#)) and an increased soil organic carbon content during the ley season (data not shown). The net N input to the soil during the ley season could be released during the following soil disturbance *e.g.* ploughing for the following arable crop (summer wheat in our study) and may reduce the mineral fertilizer N input for the next crop, as well as improve the N use efficiency for the whole rotation ([Ball et al., 2002](#); [Krauss et al., 2017](#)). However, it may also lead to enhanced N₂O emissions after ploughing of the ley and seeding of the following crop (often done in direct combination), and those emissions are then attributed to the following crop. Such an effect was found, *e.g.*, by [Efosa et al. \(2023\)](#). Unfortunately our dataset does not cover the crop phase following the ley. Yet, it was shown by [dos Reis Martins et al. \(2022\)](#) that DayCent is able to reproduce observed N₂O emission after ploughing of ley (see their supplementary material) with a reasonable agreement. For the present study, the DayCent results for

the summer wheat following the ley in the rotation ([Table A3](#)) does not show a considerably enhanced N₂O emission factor, which would be indicative of a strong legacy effect.

Globally, agricultural production is highly dependent on intensive fertilizer inputs, leading to high environmental impacts, calling for more sustainable agricultural practices. Based on our simulated results, including ley within the arable rotation has the benefit of sequestering soil N, and may therefore contribute to an optimal agricultural management strategy for achieving the environmental goal of agricultural production in Switzerland as well as in other European countries. However, further experimental and modeling studies of the N budget of the entire ley-arable rotation are required to support this interpretation.

5. Conclusions

Our study has provided insights into N₂O emissions and EFs of different types of fertilizer input in grass-clover ley as part of the arable rotation and assessed the suitability of the model DayCent to simulate observed N₂O emissions and the fertilizer related EFs. Over the 3-year experiment, no significant difference of absolute N₂O emissions was observed between the two fertilization treatments. However in contrast to the initial hypothesis, the mineral fertilization treatment exhibited a higher mean EF (0.41 %) compared to the organic fertilization treatment (0.23 %) mainly due to the different total N input amounts used for organic fertilizer applications. The EF of both fertilizers for ley in our study were considerably lower than the IPCC default values, potentially attributable to the specific soil conditions with relatively high soil pH and low WFPS at the study site. In agreement with the initial hypothesis, DayCent with a previously published multi-site calibration for Western European cropland was able to satisfyingly simulate the low observed N₂O EF on average over all three study years. Yet, because ley is simulated in the model as a single plant type, an adjustment of some plant parameters was necessary to account for the effect of the specific grass-clover mixture on the plant N content and the biological N₂ fixation. Thus, further tests with measurement data from other ley and soil types are necessary for a thorough assessment of the model performance and the N₂O EF of ley relative to other crops.

CRediT authorship contribution statement

Marcio dos Reis Martins: Writing – review & editing, Methodology, Investigation, Data curation. **Yuqiao Wang:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Alex Valach:** Writing – review & editing, Methodology, Investigation, Data curation. **Christof Ammann:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

Table A1

Amount of applied N fertilizer and observed N harvest yield for the different fertilizer treatments (Min = mineral, Org = organic, None = without fertilization) in the three study years. All values are in units g N m^{-2}

		2021			2022			2023		
		Min	Org	None	Min	Org	None	Min	Org	None
N input:	Fertilizer	13	23.4	0	10.5	19.8	0	13	21.5	0
N output:	Harvest	25.7	23.8	6.6	35.5	29.0	12.6	33.5	31.1	10.8

Table A2

Modelled nitrogen balance of ley for the different fertilizer treatments (Min = mineral, Org = organic, None = without fertilization) in the three study years. All values are in units g N m^{-2}

		2021			2022			2023		
Fertilizer type		Min	Org	None	Min	Org	None	Min	Org	None
N input	Fertilizer	13	23.4	0	10.5	19.8	0	13	21.5	0
	N fixation ^b	26.4	22.5	25.0	22.0	23.1	21.3	22.8	23.6	24.6
	N deposition ^a	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
	Total	41.9	48.4	27.5	35	45.4	23.8	38.3	47.6	27.1
N output	Gaseous N ^b	1.3	1.8	0.9	1.5	1.8	0.9	1.4	1.8	1.0
	NH ₃ volatilization ^c	0.0	7.9	0.0	0.0	6.3	0.0	0.0	7.4	0.0
	Harvest ^b	33.8	34.2	22.4	28.2	28.1	19.6	30.8	30.4	20.3
	N leaching ^b	0.0	0.9	0.0	0.0	1.1	0.0	0.0	3.4	0.0
	Total	35.2	44.8	23.4	29.7	37.3	20.5	32.2	43.0	21.2
N balance		6.7	3.6	4.1	5.3	8.1	3.3	6.1	4.6	5.9

^a N deposition was determined from Rihm and Künzle (2019).

^b Gaseous N, N fixation and N leaching were determined by DayCent. Gaseous N was calculated as sum of the gases N₂O, N₂, and NO.

^c NH₃ volatilization was determined during slurry application using the model ALFAM2 (Hafner et al., 2019).

Table A3

Modeled N₂O emission factors (mean \pm 2 \times SE) from mineral and organic fertilizer application treatment for each individual crop within the ley-arable rotation during 2000–2022

Crop	Organic fertilizer EF (%)	Mineral fertilizer EF (%)
Potato	0.67 \pm 0.18	0.50 \pm 0.10
Maize	0.48 \pm 0.10	0.36 \pm 0.06
1st year ley	0.19 \pm 0.04	0.18 \pm 0.02
2nd year ley	0.18 \pm 0.04	0.22 \pm 0.02
Summer wheat	0.45 \pm 0.06	0.50 \pm 0.06
Winter barley	0.26 \pm 0.06	0.28 \pm 0.02
Sugar beet	0.52 \pm 0.10	0.45 \pm 0.06

Data availability

Data will be made available on request.

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