Ecological Modelling 515 (2026) 111513

Contents lists available at ScienceDirect

Ecological Modelling

journal homepage: www.elsevier.com/locate/ecolmodel

Modeling impacts of N sources on N_2O emissions in long-term crop rotation system in Brazil's Cerrado using DNDCv.CAN

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A R T I C L E I N F O

Key words:
nitrous oxide
ammonia
mineral N
maize
irrigated common bean
Oxisols

A B S T R A C T

Predicting N_2O emissions can help identify crop production practices and environmental conditions for mitigation. The objectives were to calibrate and validate the DeNitrification-DeComposition (DNDCv.CAN) model to simulate N_2O emission in crop rotation (CR) systems in Brazil's Cerrado biome, using different N fertilizer sources. Field data were obtained from a CR experiment with maize and common beans cultivated under no-till for 10 years. Treatments were: Zero-N, calcium ammonium nitrate (CAN), urea (UR), and ammonium sulfate (AS), with 5 replicates. Measured data including N_2O fluxes, NH_3 volatilization, soil NH_4^+ and NO_3^-, water-filled pore space (WFPS), and grain yields were used to calibrate and validate the DNDCv.CAN. The model acceptably captured the daily N_2O emissions associated with different N sources, although episodic peaks were over or under-predicted. Correlation coefficient was 0.62 during calibration, with a mean absolute error of 17 g N_2O-N ha^{-1} day^{-1}, close to average measured (18 g ha^{-1} d^{-1}), and simulated (17 g ha^{-1} day^{-1}) emissions. Accumulated measured N_2O-N emissions were 1.19, 4.38, 3.17, and 2.56 kg N_2O-N ha^{-1} for Zero-N, CAN, UR, and AS, respectively, whereas the simulated were 1.13, 3.44, 2.24, and 3.32 kg N_2O-N ha^{-1}. The NH_3, NH_4^+, NO_3^-, WFPS, and yields were also fairly simulated. Soil hydrologic parameters were adjusted in the model using a built in pedotransfer function to improve the simulations, which should be further investigated. The DNDCv.CAN effectively simulated cumulative N_2O emissions from different N sources applied to CR under tropical conditions, making it valuable for evaluating potential emissions and mitigation strategies.

1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) with global warming potential of 273 (IPCC, 2021). Anthropogenic sources represent 43% of global nitrous oxide (N_2O) emissions, with most originating from the agriculture sector due in part to N fertilization (Tian et al., 2020). Over the period from 2000 to 2020, N_2O emissions increased beyond the worst-case IPCC scenario (Representative Concentration Pathway - RCP 8.5), which is the highest trajectory of projected GHG concentrations and resulting radiative forcing (Tian et al., 2020). The amount of N_2O-N emitted from N fertilizer is on average 1% of the N applied with fertilizers (IPCC, 2006). This emission factor (EF1) was further disaggregated into 0.5% in dry (uncertainty range: 0.0-1.1%), and 1.6% (1.3-1.9%) in wet climates for mineral N fertilizer inputs (IPCC, 2019).

Soil derived N_2O emissions occur via microbial and biochemical processes including nitrification, denitrification, nitrifier denitrification, dissimilatory reduction of nitrate to ammonium, chemo-denitrification, and co-denitrification (Hayatsu et al., 2008; Müller et al., 2014; Spott et al., 2011; Stevens and Laughlin, 1998). Soil N_2O emission due to N

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https://doi.org/10.1016/j.ecolmodel.2026.111513
Received 3 November 2025; Received in revised form 12 January 2026; Accepted 27 January 2026
Available online 4 February 2026

application is highly variable in time and space and is characterized by feature peak events that are influenced by N application, soil management, weather, and soil properties. In the Cerrado biome, most of the soils are Oxisols (Soil Survey Staff, 1999) that are often well drained, and various studies have measured lower emission factor (EF1) than the IPCC default in this region (IPCC, 2019). However, N_2O-N emissions can range from 0.01 to 4.6% of applied N depending upon soil, management and weather conditions (Carvalho et al., 2014, 2013; de Carvalho et al., 2024; Lessa et al., 2014; Martins et al., 2015; Mascarenhas et al., 2020; Sato et al., 2017; Silva et al., 2017). The Cerrado region is situated mainly in mid-west Brazil, where it contributes to more than 50% of the country's total grain production, corresponding to 322 Mt in 77 Mha (CONAB, 2024).

Using process-based models, such as DNDC or DayCent, is an effective means to examine the impacts of soil and crop management and scenarios on N_2O emissions, aiding in the development of strategies to mitigate GHG emissions on a larger scale (Brilli et al., 2017). Lugato et al. (2018) for example simulated N_2O emissions in 8,000 locations in Europe with the DayCent model and observed that conservation practices (no-till farming and legume cultivation in crop rotation) can increase N_2O emissions which would offset the beneficial effects of soil C sequestration. These simulations can help to define national targets to reduce GHG emissions, which can be useful at both national and international levels including to meet the aspirations of the Paris Agreement.

The DeNitrification-DeComposition model (DNDC) consists of two components and six sub-models. The first component includes soil and climate data, crop growth, and decomposition sub-models, which estimate soil temperature and moisture, pH, redox potential (Eh), and carbon and nitrogen substrates based on ecological guidelines (e.g., climate, soil, vegetation, and management). The second component includes nitrification, denitrification, and fermentation sub-models, estimating fluxes of NH_3, NO, N_2O, and CH_4 based on climate and soil variables (Gabbrielli et al., 2024; Gilhespy et al., 2014; Li et al., 2012; Li, 2000). The DNDC model is widely used since it can well simulate N cycle processes. Several modifications have been made to the model, leading to multiple versions that better capture location and treatment specific results, including simulations of N and C gas fluxes, crop and forest growth, soil C stock, soil NH_4^+, NO_3^- leaching, etc. (Gilhespy et al., 2014). For example, the Canadian version (DNDCv.CAN) has had several modifications to optimize the model performance for simulating crop biomass, evapotranspiration, soil temperature and soil hydrology (Dutta et al., 2018, 2016; Smith et al., 2020, 2019) and recent studies have focused on improving the simulation of N_2O emission and NH_3 volatilization (He et al., 2020; Kang et al., 2025; Mencaroni et al., 2021).

Although many simulations were published, results must be used with caution, as specific model versions could lead to unsatisfactory predictions for not-validated environments or regions. For example, the NZ-DNDC version, calibrated for N_2O emissions in New Zealand pasture (Saggar et al., 2004), did not simulate well the tropical and subtropical savanna conditions (Grote et al., 2009). Shirato (2020) showed that simulations of soil C stocks were not satisfactory in soils with low C content. Zimmermann et al. (2018) compared the Daycent, DNDC, and ECOSSE models for N_2O emissions in pasture and barley as a function of fertilizer sources and rates, but they found low correlation in all models and suggested calibrating the model for each local condition before it could be used.

In tropical conditions, Costa et al. (2021) calibrated the DNDC model to estimate N_2O emissions from varying N rates in maize-soybean production in Oxisols in the Southern part of the Amazon. They were able to obtain good simulations but concluded that more observed N_2O data and model calibration are needed. Discrepancies between observed and DNDC simulated data were reported when simulating the straw levels effects on N_2O emissions on sugarcane cultivation in Brazil (Dias de Oliveira and Moraes, 2017; Portela et al., 2018). However, there are very few N_2O simulations using the DNDC model for N management practices under tropical soil conditions; especially in regions with Oxisol soils, such as in Cerrado biome, which are well drained and exhibit a strong seasonality. Therefore, the objectives of the present study were to calibrate and validate the DNDCv.CAN model to simulate N_2O emissions, NH_3 volatilization, crop yields, soil inorganic N, and soil moisture from a long-term crop rotation in Brazil's Cerrado biome with different N sources.

2. Material and Methods

2.1. Field experiment

The experimental area is situated in Capivara Farm of the Brazilian Agricultural Research Corporation's National Rice and Beans Research Center (Embrapa Rice and Beans), in Santo Antonio de Goiás, Goiás State (16°28S, 49°17W, 823 m). The soil was classified as Typic Acrustox (Soil Survey Staff, 1999) and Latossolo Vermelho Ácrico típico (Santos et al., 2025). Kaolinite and iron and aluminum oxides (Fe_2O_3: 10-14%) predominate the clay fraction. The relief is flat or smoothly undulated with 2-7 % slope. The original vegetation was semideciduous tropical forest. The chemical and physical soil properties are described in Table 1. The climate is tropical savanna (Aw), according to Köppen's classification, with clear separation of a rainy (November – April) and a dry (May – October) season (Alvares et al., 2013), where the historical (30 yr) average annual precipitation is 1,490 mm (Agritempo, 2017). Common beans were grown in the dry season and irrigated with a center-pivot system according to water demand, giving a total water amount of 340-390 mm per season.

Data from a long-term crop rotation experiment (CR) was used in the study. It consisted of maize (*Zea mays* L.) in the rainy season and common beans (*Phaseolus vulgaris* L.) in the dry season, in no-tillage system for 10 years (Supplementary Table S1). The one exception was soybean (*Glycine max* L.) in the rainy season of 2014/15 that was followed by maize as a second crop immediately after soy harvest. The site history included the conversion from native forest to agriculture between 1950-1970 (Oliveira et al., 2022). The area has a history of at least 5 years of perennial pasture (*Urochloa* spp.) before the implementation of the current experiment in 2013. The pasture was not managed and there was no livestock grazing. In the CR, lime was applied two or three months before sowing maize every 3 years following soil analysis and regional recommendation. The experiment consisted of the following treatments: Zero-N, calcium ammonium nitrate (CAN), urea (UR) and ammonium sulfate (AS). The experiment has a randomized block design with 5 replicates of the treatments. Each plot occupies 28 m^2 (7 m x 4 m). Nitrogen fertilizer was applied at the recommended rate for each crop, following regional farmer guidance (Sousa and Lobato, 2004). The three N sources were applied at the same N rate, and they were broadcast when the maize and common bean were at the V1 – V5 stages of physiological development (Supplementary Table S1). Other macronutrients were applied at sowing, either mechanically in-furrow near the seeds or manually broadcasted (Supplementary Table S1), and micronutrients were delivered via foliar application. Pesticides and herbicides were used for each crop according to local guidelines.

2.2. Experimental variables

N_2O fluxes were measured using static dark steel chambers (40×60 cm) installed in each plot (5 replicates) (Davidson et al., 2002). Gas samples were collected every 1–3 days during the first month after N fertilization, then every 7–15 days, always in the morning (Alves et al., 2012). Gas samples (60 ml) were collected at 0, 15, and 30 minutes after chamber closure, transferred to pre-evacuated 12 ml Exetainers®, and analyzed for N_2O concentration by gas chromatography with an electron capture detector (ECD). Daily N_2O fluxes were calculated by linear interpolation of the three sampling times (Soares et al., 2016). Cumulative N_2O emissions were calculated by summing the measured daily emissions.

Table 1
Chemical and physical properties of the Typic Acrustox, Fazenda Capivara, Embrapa Rice and Beans, Santo Antônio de Goiás, Goiás State.

Soil depth	OC	pH ($CaCl_2$)	NH_4^+	NO_3^-	P	K	Ca	Mg	Al	H+Al	CEC	Sand	Silt	Clay	FC	WP	BD	TP	HC
cm	g kg^{-1}		mg N kg^{-1}		mg dm^{-3}		mmol$_c$ dm^{-3}					g kg^{-1}			WFPS (%)		g cm^{-3}	%	cm h^{-1}
0-10	20.0	6.4	0.4	1.2	20	113	19.9	15.8	0	9.5	48.1	416	40	544	78	61	1.41	47	3.5
10-20	15.5	6.5	0.4	1.7	18	112	12.6	8.2	0	19	42.6	426	20	554	83	69	1.49	42	0.8
20-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	73	61	1.41	44	0.5
30-40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	66	54	1.32	47	1.0
40-60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	69	55	1.33	46	1.6
60-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	62	50	1.26	48	4.4
80-100	-	-	-	-	-	-	-	-	-	-	-	-	-	-	59	47	1.21	49	4.7

OC: organic carbon determined by dichromat oxidation; pH in 0.01 mol L^{-1} $CaCl_2$ (soil: suspension 1:2,5); Phosphorus (P), and potassium (K), were extracted by melich1 solution; ammonium (NH_4^+), nitrate (NO_3^-), calcium (Ca), magnesium (Mg), and aluminum (Al) was extracted in a 1 mol L^{-1} KCl; Hydrogen plus aluminum (H+Al) was determined by the SMP Buffer Solution method (pH 7,0); CEC: cation exchange. FC: field capacity; WP: wilting point; BD: Bulk density; TP: Total porosity; HC: Hydraulic conductivity. Methodology of soil analysis by Donagema et al. (2011).
OC to Clay: Measured in 2013 after lime application as part of the implementation protocol of the experiment.
FC to HC: Measured in 2024.

NH_3 volatilization was measured during the first month after N application using semi-open chambers (10 cm diameter) installed in each plot (5 replicates) (Nômmik, 1973). In the field NH_3 was trapped in a foam containing a mixture of sulfuric acid and glycerin, followed by the determination of NH_4^+ in the laboratory (Cantarella and Trivelin, 2001).

Ammonium (NH_4^+), nitrate (NO_3^-) (Miranda et al., 2002) and gravimetric water were determined from soil samples collected adjacent to the static chambers, on the same of the GHG sampling in each plot (5 replicates). Water-filled pore space (WFPS) was obtained from gravimetric water content (θg), bulk density, and particle density (Linn and Doran, 1984). Soil physical and chemical data were obtained from soil cores collected from 0-20 and 0-100 cm layers (Table 1).

Grain yields were measured by harvesting three central crop rows (5 meters each), assessing moisture content, and adjusting it to 130 g kg^{-1} (Silveira et al., 2022).

The climate data was obtained from the meteorological station close to the experiment (100 m), which includes air temperature, precipitation, and radiation. The wind speed and humidity data were obtained from the NASA Langley Research Center (LaRC) POWER Project funded through the NASA Earth Science/Applied Science Program (available at https://power.larc.nasa.gov/).

2.3. Model development, calibration, and validation

N_2O fluxes, NH_3 volatilization, extractable soil NH_4^+ and NO_3^-, WFPS, and grain yield were simulated in the 10 growing seasons from the field experiment using the DNDC model (Li et al., 1992). The Canadian DNDC (DNDCv.CAN) version 9.6.0 (Jan 2025), available at https://github.com/BrianBGrant/DNDCv.CAN, was chosen for this study because it demonstrated good performance in several model ensemble studies conducted in multiple countries globally (Couëdel et al., 2024; Ehrhardt et al., 2018; Falconnier et al., 2020; Farina et al., 2021; Kothari et al., 2024; Sándor et al., 2023; Wang et al., 2022). This model version has had several modifications from the original DNDC version 9.5.0 (available at https://www.dndc.sr.unh.edu/), showing effective simulation of N_2O emissions in diverse field and N management conditions (Dutta et al., 2018, 2016; He et al., 2020; Kang et al., 2025; Mencaroni et al., 2021; Smith et al., 2020, 2019).

In this study, the model was adjusted to improve the effect of pH on modeled NH_3 volatilization. The model uses an acid-base equilibrium to determine the concentrations of aqueous ammonium and NH_3, with these concentrations being governed by dissociation constants (Kb and Kw). The model's accuracy was initially validated through a series of experiments conducted in Eastern Canada, which focused on the effects of swine slurry application on ammonia volatilization (Congreves et al., 2016). However, an initial assessment of NH_3 volatilization rates following the application of three mineral fertilizers revealed that the DNDCv.CAN model was unable to accurately capture the low NH_3 volatilization from AS and the corresponding high losses from UR fertilizer applied to acidic tropical soils. We revisited the model's expression of the NH_4:NH_3 equilibrium. To improve its performance, we adapted equation (2) from Potter et al. (2003) to better reflect the influence of soil temperature and pH on this equilibrium. The modified ammonia flux scalar is defined as follows:

$$\textit{Ammonia flux scalar} = \frac{1}{\left[1 + 10^{\frac{0.09018+2729.92}{273.16+T_s} - pH}\right]}$$

Where T_s represents the hourly soil temperature, and pH is the soil pH. This flux scalar was subsequently applied to adjust the molar concentration equilibrium of NH_4^+ and NH_3 within the model.

The DNDC model can run at field scale (Costa et al., 2021) or at a regional level (Dias de Oliveira and Moraes, 2017). At field scale, the DNDCv.CAN model requires the site latitude and longitude, daily climate data (maximum and minimum air temperature, precipitation, radiation, wind speed, and humidity), soil properties (texture, field capacity, wilting point, soil bulk density, organic carbon, pH, and hydraulic conductivity), yearly cropping management history (crops, cultivation system, fertilization, manure, irrigation, mulching, and grazing), tile drainage if applicable, and adjustable nitrogen cycling-related parameters (urea hydrolysis, urea diffusion, N retention, NO_3^- movement, NO_3^- leaching, runoff N, denitrifier growth rate, nitrifier growth rate, nitrification factor, N_2:N_2O ratio, NH_3 wind factor, and NH_3 soil depth factor) and there is also an option for soil water preferential flow.

A simulation of 5 years of unmanaged perennial pasture was included in the model simulation as “spin-up”, before the 10 years of crop rotation to stabilize soil carbon, litter pools, nitrogen pools, and water status. It is important to stabilize soil litter pools, as default model values are not crop-specific. The model was initialized using observed weather, soil and crop management information and was then calibrated and validated using observed N_2O flux, NH_3 volatilization, soil NH_4^+ and NO_3^-, WFPS, and grain yield data. Model calibration used data from 2013-2016; validation employed data from 2017-2022. All variables were measured in all seasons, except in the period of 2017-2020, when only crop grain yield was obtained due to operational issues. As DNDC crop yields output is in C units, it was assumed that C content corresponds to 43% of dry biomass (Latesha and Muller, 1924). Overall, 788 observations of daily N_2O, 560 observations of daily NH_3, 1,232 observations of daily NH_4^+ and NO_3^-, 148 observations of daily WFPS, and 68 observations of yield were used to calibrate and validate the DNDCv.CAN model.

During the calibration process, some parameters were adjusted to better fit the model outcomes with the observed data (Supplementary

Table S2). The field capacity and wilting point were generated using an internal pedotransfer function in DNDC based on the Saxton method (Saxton et al., 1986). Field capacity was modified from 0.78 to 0.62 WFPS and wilting point from 0.61 and 0.31 WFPS (Supplementary Table S2). This greatly improved the model performance for simulating soil moisture (WFPS).

The model performance was evaluated using mean absolute error (MAE), root mean squared error (RMSE), and Pearson linear correlation (r) during calibration and validation processes (Li et al., 2020), according to the equations:

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|X_i - Y_i|$$

$$RMSE = \left(\frac{1}{n}\sum_{i=1}^{n}(X_i - Y_i)^2\right)^{0.5}$$

$$r = \frac{\sum_{i=0}^{n}(X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\sum_{i=0}^{n}(X_i - \overline{X})^2}.\sqrt{\sum_{i=0}^{n}(Y_i - \overline{Y})^2}}$$

where, *Xi* is the simulated data in point i, $\overline{X}$ is the average simulated data, *Yi* is the observed data in point i, $\overline{Y}$ is the average observed data, and *n* is the number of observations.

3. Results

The DNDCv.CAN model demonstrated acceptable performance in simulating N_2O emissions and was responsive to N fertilization in the maize phase of the rotation (Fig. 1 and 2). For example, in the maize season 2013/14, the N_2O peak reached 360 g N_2O-N ha^{-1} day^{-1} after 20 days of CAN application, in which the model simulated a peak of 330 g N_2O-N ha^{-1} day^{-1}, while in Zero-N the N_2O peaks were 110 and 170 g N_2O-N ha^{-1} day^{-1} for observed and simulated, respectively (Fig. 1). The model correctly predicted the timing of the initial N_2O emission peaks for AS, UR, and CAN; however, it overestimated the magnitude for the Zero-N, UR and AS. Overall, similar N_2O patterns occurred in both modeled and measured values throughout all seasons for both control (Zero-N) and N-treated plots. However, the magnitude of individual peaks was often over or under-predicted for any one event (Fig.s 1 and 2). For example, during the maize season in 2015, the observed N_2O maximum peaks following UR application reached around 150 g N_2O-N ha^{-1} day^{-1}, while the model simulated around 50 g N_2O-N ha^{-1} day^{-1} (Fig. 1).

The model provided a fair simulation of N_2O emissions. The RMSE and MAE of N_2O emission in the calibration were 35 and 17 g N_2O-N ha^{-1}, respectively, which corresponded to 194% and 94% compared to the general average observed N_2O-N emission (18 g N_2O-N ha^{-1} day^{-1}), resulting in a r value of 0.62 (Table 2 and Supplementary Fig. S1). The general average simulated N_2O emission was 17 g N_2O-N ha^{-1} day^{-1}. In the validation process, the RMSE and MAE were lower, 22 and 7.5, respectively, and r was 0.26 (Table 2 and Supplementary Fig. S1). In the validation, the average daily observed N_2O-N emission was 10 g N_2O-N ha^{-1} day^{-1} and the simulated was 7 g N_2O-N ha^{-1} day^{-1}.

The DNDCv.CAN model effectively simulated ammonia volatilization, showing higher peaks with UR application compared to other N sources and Zero-N treatments, consistent with observed data except for the calibration phase in February 2015, where it underestimated ammonia losses for UR (Fig. 3). In 2015, the measured ammonia loss for the UR treatment was 12.4 kg NH_3-N ha^{-1} day^{-1}, whereas the model

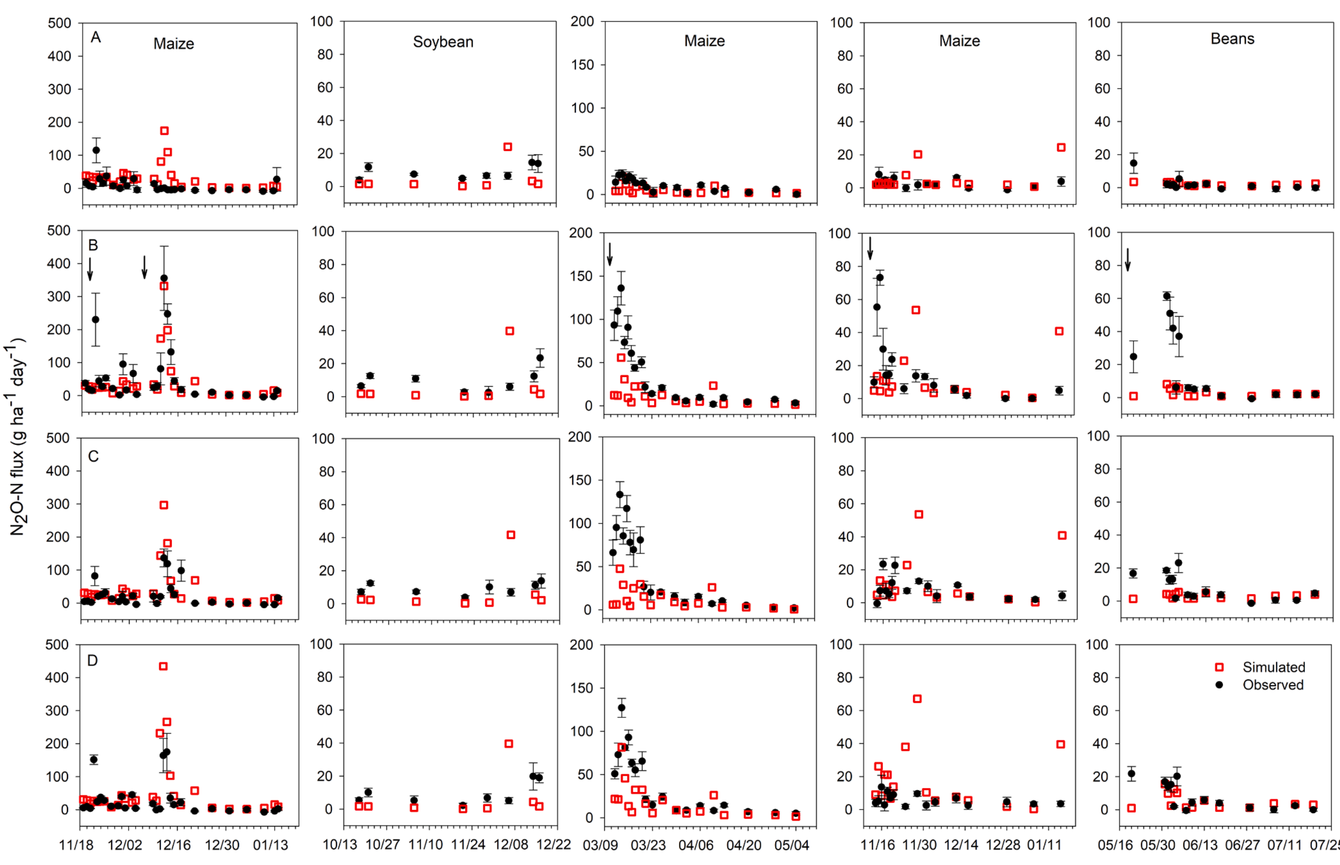

Fig. 1. Daily nitrous oxide fluxes (observed and simulated) during first months after N application (A: Zero-N; B: calcium ammonium nitrate (CAN); C: urea (UR); D: ammonium sulfate (AS)) in crop rotation system (five crop seasons) in Cerrado - Brazil using DNDCv.CAN model (calibration process). Arrows indicate N fertilizer application time.

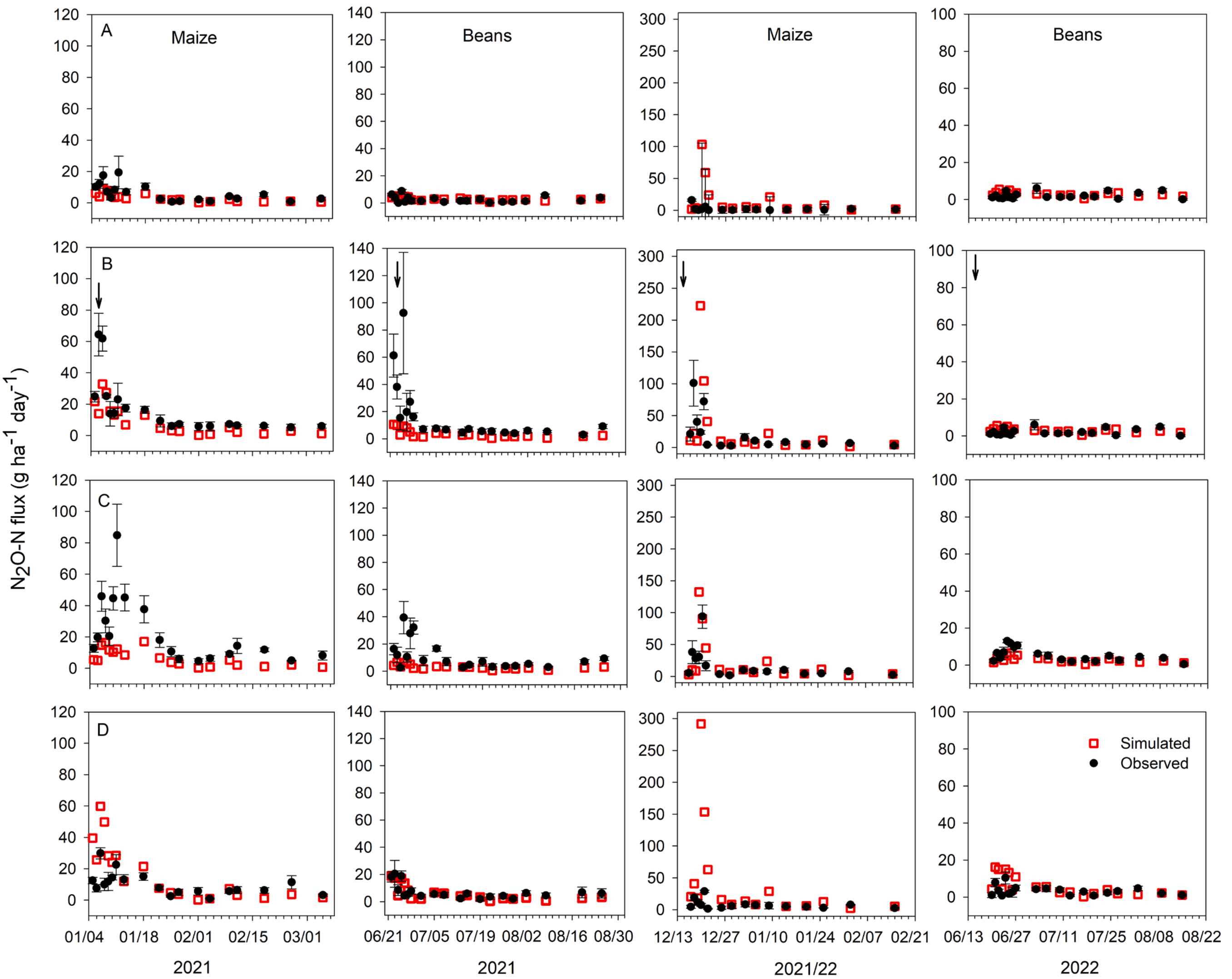

Fig. 2. Daily nitrous oxide fluxes (observed and simulated) during first months after N application (A: Zero-N; B: calcium ammonium nitrate; C: urea; D: ammonium sulfate) in crop rotation system (four crop seasons) in Cerrado - Brazil using DNDCv.CAN model (validation process). Arrows indicate N fertilizer application time.

estimated a value of 3.88 kg NH_3-N ha^{-1} day^{-1}. However, emission levels were fairly simulated following most fertilizer applications. The RMSE and MAE of NH_3 during calibration across all treatments were 1.32 and 0.39, respectively, which correspond to 330% and 97% compared to the observed mean (0.40 kg NH_3-N ha^{-1} day^{-1}). The correlation coefficient (r) was 0.54 (Table 2).

In the validation phase, the NH_3 peak observed for maize 2020/21 with UR was 4.53 kg NH_3-N ha^{-1} day^{-1}, and the simulated was 4.89 kg NH_3-N ha^{-1} day^{-1}; for bean 2022, the observed and simulated NH_3 peaks were 4.41 and 6.48 kg NH_3-N ha^{-1} day^{-1}, respectively (Fig. 4).

The observed and simulated WFPS data was correlated over the rain events as well as in the dry seasons (Fig. 5), with an r value of 0.59, RMSE of 0.07 (12%), and MAE of 0.06 (10%) during calibration (Table 2). However, in irrigated beans in 2021 and 2022 cycles, simulated WFPS demonstrated discrepancies compared to observed data, likely because the model was not able to simulate the very high drainage under Cerrado soils under irrigated conditions. Soil NH_4^+ content was also effectively simulated by the model, showing an RMSE and MAE of 19.1 (107%) and 11.9 (66%), respectively, and an r of 0.69 in calibration (Table 2). The NO_3^- was also fairly simulated by DNDCv.CAN, showing a coefficient (r) of 0.48 and RSME of 17.3 (140%) and MAE of 11.4 (92%) in the calibration process (Table 2).

The cumulative N_2O emissions measured over 6 seasons were always higher with N application compared to Zero-N, except for soybean in 2014 since it did not received mineral N (Fig. 6). The model effectively simulated cumulative N_2O for each N treatment per season, capturing both high emissions in maize 2013/14 (>1.5 kg N_2O-N ha^{-1}) and low emissions in beans 2022 (<0.15 kg N_2O-N ha^{-1}) (Fig. 6). However, discrepancies occurred in some seasons, such as maize 2015, where the model underestimated cumulative N_2O emissions, and in maize 2022, where the model overestimated N_2O emission from AS (Fig. 6). The total cumulative N_2O emissions were 1.19, 4.38, 3.17, and 2.56 kg N_2O-N ha^{-1} for Zero-N, CAN, UR, and AS, while the simulated N_2O emissions using the DNDC model were 1.13, 3.44, 2.24, and 3.32 kg N_2O-N ha^{-1} (Fig. 6).

Cumulative NH_3 volatilization was consistently greater in the UR treatment compared to all other treatments across each season, as anticipated (Fig. 7). The model simulated total NH_3 emissions effectively across eight seasons, though differences were noted. In the 2022 season for beans, simulation results aligned with observations, while the model overestimated NH_3 emissions from UR application in maize during the 2013/14 season and in beans during 2016. Conversely, it underestimated emissions in maize in the 2015/16 and 2021/22 seasons (Fig. 7). The total measured NH_3 losses were 8.7, 15.3, 119.3, and 23.5 kg NH_3-N ha^{-1} for Zero-N, CAN, UR, and AS, while the modeled values were 0.8, 8.9, 106.0, 24.8 kg NH_3-N ha^{-1} (Fig. 7). The observed NH_3-N losses corresponded to 0.9%, 13.3%, and 1.8% of N applied for CAN, UR,

Table 2
Correlation between observed and simulated NH_3-N volatilization, soil contents of NH_4^+-N and NO_3^--N, water-filled pore space (WFPS) and maize yield in crop rotation system in Cerrado - Brazil using DNDCv.CAN model.

Variable	Mean		RSME	MAE	r	P value	n
	observed	simulated					
Calibration							
N_2O-N (g ha^{-1})	18	17	35	17	0.62	< 0.001	436
NH_3-N (kg ha^{-1})	0.40	0.26	1.32	0.39	0.54	< 0.001	264
NH_4^+-N (kg ha^{-1})	17.9	17.7	19.1	11.9	0.69	< 0.001	268
NO_3^--N (kg ha^{-1})	12.4	10.6	17.3	11.4	0.48	< 0.001	268
WFPS (decimal)	0.59	0.58	0.07	0.06	0.59	< 0.001	61
Yield (kg ha^{-1})	7,030	7,496	1284	796	0.99	< 0.001	20
Validation							
N_2O-N (g ha^{-1})	10	8	22	7.5	0.26	< 0.001	352
NH_3-N (kg ha^{-1})	0.21	0.28	0.78	0.24	0.68	< 0.001	296
NH_4^+-N (kg ha^{-1})	23.3	24.6	22.8	13.7	0.75	< 0.001	348
NO_3^--N (kg ha^{-1})	17.5	21.1	24.2	13.2	0.61	< 0.001	348
WFPS (decimal)	0.50	0.58	0.11	0.09	0.41	< 0.001	87
Yield (kg ha^{-1})	5,609	5,443	1093	776	0.95	< 0.001	48

r: correlation coefficient. RMSE: root mean square error. MAE: mean absolute error. n: number of observations

and AS, respectively.

Crop grain yield was effectively simulated by the model, showing an RMSE of 1284 kg ha^{-1} (18%) and MAE of 796 kg ha^{-1} (11%) during calibration, and r of 0.99 (Table 2). The average yield was 7,030 kg ha^{-1} and the simulated 7,496 kg ha^{-1}. In the validation stage, the r was 0.95, and RMSE and MAE were 1,093 and 776 kg ha^{-1}, respectively (Table 2). In general, grain yields simulated by DNDCv.CAN closely corresponded with the observed data across all crop seasons and nitrogen sources. The observed maize yields ranged from 4,798 to 12,402 kg ha^{-1}, and the simulated yields fell between 4,708 and 11,740 kg ha^{-1}. In 2014/15, observed soybean yields across four treatments ranged from 4,045 to 4,639 kg ha^{-1}, while simulated yields were between 4,044 and 4,092 kg ha^{-1} (Supplementary Table S3). Observed grain yield for common beans was 1,356–3,899 kg ha^{-1}, while modeled yield was 1,695–3,008 kg ha^{-1}. The model showed higher accuracy when simulating maize yields compared to bean yields (Supplementary Table S3).

4. Discussion

Irrigation during the dry season in the Cerrado enables intensive crop production with at least two harvests. The maize – irrigated common beans rotation is one of the most frequently used rotations. Models, such as the DNDC, can be effective tools to study these systems to identify management solutions to minimize their negative impacts.

The DNDCv.CAN model satisfactorily simulated daily N_2O and NH_3 losses in comparison to previous studies (Kang et al., 2025; Uzoma et al., 2015), but demonstrated discrepancies in simulating emission peaks. On the other hand, the effects of the N sources and seasonality were well captured by the model. For daily N_2O fluxes, the model exhibited errors (RMSE) of 35 g N_2O-N ha^{-1}d^{-1} or 194% with an r of 0.62 during calibration. Several studies reported good simulation of N_2O emission in grain crops. Kang et al. (2025) adapted DNDCv.CAN for maize in Canada to assess the impact of nitrogen application timing on N_2O emissions. The model simulated daily N_2O emissions reasonably well, with RMSEs of 266% during calibration and 310% during validation over three years. It is common for models to estimate high RMSE for daily N_2O, since specific soil N_2O diffusion timing and daily production and consumption is difficult to simulate (He et al., 2020). However, DNDC often has improved estimates of cumulative emissions over longer time periods which is the case in our study.

The measured N_2O emissions following nitrogen application demonstrated pronounced daily peaks shortly after fertilizer was applied, particularly during the initial month, with values reaching approximately 300 g N_2O-N ha^{-1}. These findings are consistent with previous research (Soares et al., 2016) and were accurately replicated by the DNDC model. The cumulative observed N_2O emissions from CAN, UR and AS were 4.38, 3.17 and 2.56 kg N_2O-N ha^{-1}, and the DNDC model produced similar patterns, with simulated N_2O emissions of 3.44, 2.24, and 3.32 kg N_2O-N ha^{-1} for CAN, UR, and AS, respectively. Simulated N_2O emissions were slightly higher for AS and CAN compared to UR, while observed data indicated higher N_2O emission from CAN compared to UR and AS, likely due to lower NH_3 losses thus more available soil N. According to the "Pipes & Valves" concept (Drury et al., 2024b), increased NH_3 volatilization can reduce N_2O emissions, which may explain the lower observed and simulated emissions for UR relative to CAN. However, the observed NH_3 losses from UR in the present study reached 13% of N applied, which was not very high, considering that losses can reach more than 50% (Cantarella et al., 2018; Drury et al., 2017; Silva et al., 2017), and may not fully explain the modeled N_2O emission results.

The effects of N fertilizer sources on N_2O emissions depends on soil and climate conditions, with no consistent differences reported in various studies reviewed by Snyder et al. (2009). For example, Harty et al. (2016) reported higher N_2O emissions from CAN (1.49%) than from UR (0.25%) in a temperate permanent grassland in Ireland, likely due to higher contribution of the denitrification process than other N_2O pathways. Whereas, in an Oxisol in Brazil, Degaspari et al. (2020) observed higher N_2O emissions from UR than CAN, which was attributed to a higher contribution of the nitrification process over denitrification; since 50% of the applied N in CAN (NH_4^+) undergoes nitrification, whereas all N from UR is subject to nitrification (Soares et al., 2016). Other studies reported no differences between CAN, AS and UR in N_2O emissions (Luo et al., 2023; Martins et al., 2015; Roche et al., 2016). The microbiota in soil and the climate conditions during these field trials likely influenced the impact of N sources on N_2O emissions and the model may require additional adjustments to capture these effects. Gene abundance data targeting the N cycle including *amoA* for nitrification, *nirK/nirS*, and *norB* for denitrification, may help to better distinguish N_2O emissions from N sources and these parameters could be considered in future model updates, such as microbial functions.

Comparisons between different N sources using DNDC were reported in temperate soil conditions. Zhou et al. (2023) calibrated DNDC and simulated 36 years of maize cultivation in China, where organic fertilizer can increase maize yield and decrease N_2O emissions by 50% compared to common urea. Nasielski et al. (2020) compared different N sources (urea and urea ammonium nitrate), N rates, placement, and timing in maize cultivation in Canada, where no differences occurred for both observed and modeled N_2O emissions between the different N sources at the economically optimum N rate. Studies using DNDCv.CAN reported reductions in both observed and simulated NH_3 and N_2O losses from enhanced-efficiency fertilizers and improved N placement compared to conventional sources (Banger et al., 2020; Drury et al., 2024a; Jiang et al., 2023).

The observed NH_3 volatilization was higher with UR (13% of N applied) than CAN and AS (< 2%), which was well simulated by the DNDC model. In acidic soils, the NH_3 loss from N fertilizer in ammonium or nitrate form, such as AS and CAN, is usually very low, due to high H^+ content maintaining N in NH_4^+ over NH_3 form in the chemical equilibrium (Cantarella et al., 2018, 2008). On the other hand, UR has been shown to have high NH_3 losses due to soil pH increases during urea

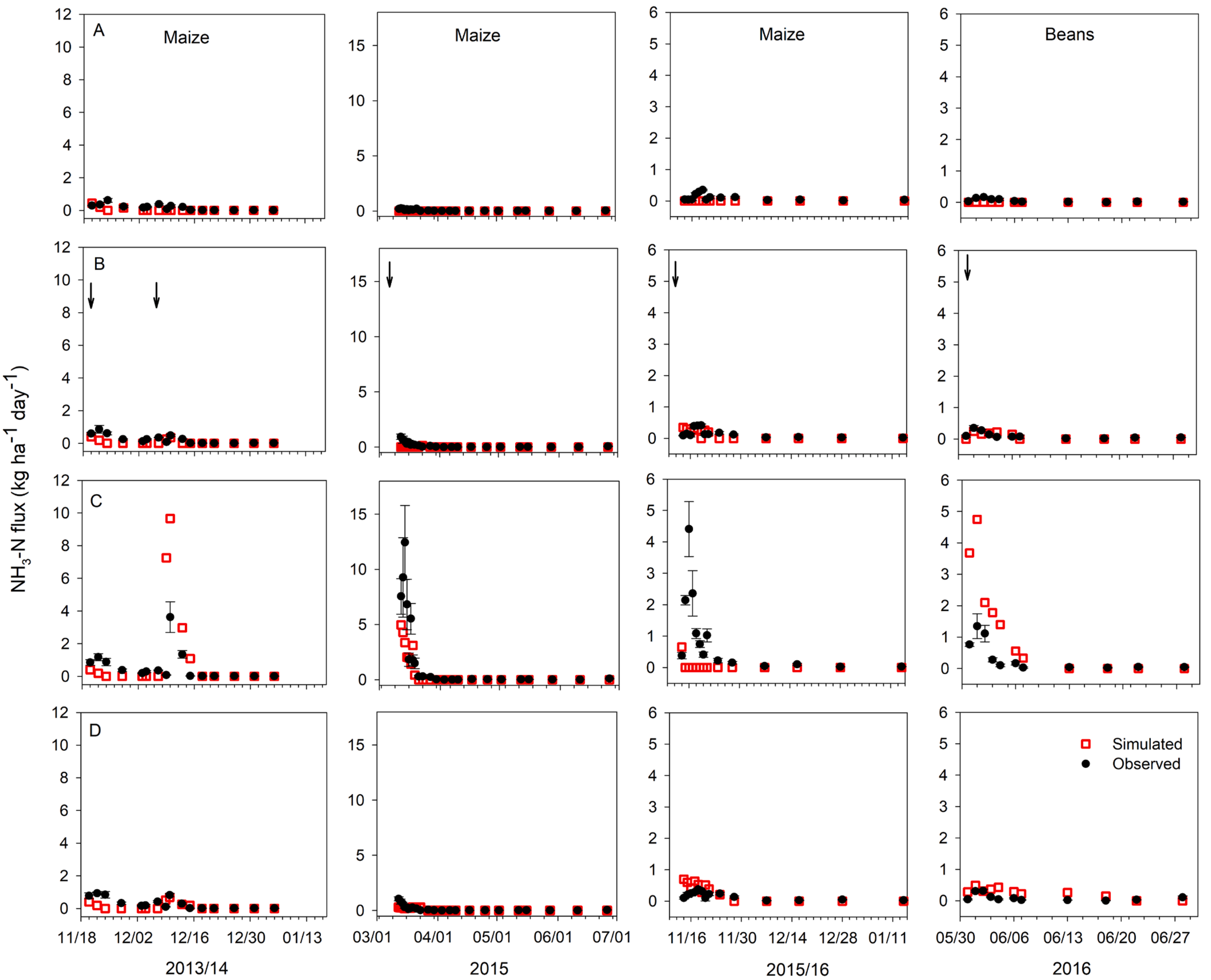

Fig. 3. Daily ammonia volatilization (observed and simulated) during first months after N application (A: Zero-N; B: calcium ammonium nitrate; C: urea; D: ammonium sulfate) in crop rotation system (four crop seasons) in Cerrado - Brazil using DNDCv.CAN model (calibration process). Arrows indicate N fertilizer application time.

hydrolysis (Cantarella et al., 2018).

Various parameters of the DNDC model were adjusted to enhance the simulations, including field capacity, wilting point, nitrification, and crop-related factors. Other crop growth and GHG emission modeling studies modified parameters to improve simulations, such as in Oxisols in Brazil, where Costa et al. (2021) calibrated the DNDC model for N_2O emission in cropping and double cropping maize and soybean. The authors changed hydraulic properties of the model using pedotransfer equations for WFPS and wilting point. The change improved the model, which had overestimated WFPS before calibration. However, some discrepancies were still recorded in irrigated beans during the 2021 and 2022 seasons, in which the model overestimated WFPS. This was likely because the model could not adequately represent the rapid drainage typical of Oxisols under irrigation. Despite their high clay content Oxisols may drain quickly probably because Oxisols are usually well drained–even with high clay content–due to micro-aggregate structure (Costa et al., 2021). In this present study, the simulated drainage and resulting WFPS was improved using a recently built-in pedotransfer function albeit still lacking under irrigation. This highlights the importance of accurately representing water dynamics in tropical soils to adapt the model for soils dominated by kaolinitic – oxidic clay minerals.

Various studies reported discrepancies between observed data and DNDC simulations, creating new versions to improve the model results (Gilhespy et al., 2014). Saggar et al. (2004) calibrated the DNDC, version 6.7, for New Zealand grassland conditions, creating the NZ-DNDC version. The authors altered parameters to reflect the seasonality of the grassland; soil drainage to reflect saturated conditions, the relationship between air and soil temperatures, the soil moisture point (WFPS) that influences N_2O losses, and an increase in the rate of animal manure addition (input). Later, Saggar et al. (2007) modified the NZ-DNDC version to better account for grassland growth, N availability from animal manure, evapotranspiration, and soil water regime which would influence N_2O emissions. However, as expected, the NZ-DNDC model did not simulate tropical and subtropical savanna growth conditions very well. Grote et al. (2009) created the Mobile-DNDC version, which has six modules with different integrated models; they used the OSU model for water balance and physical conditions, PSIM for plant growth and photosynthesis, and DNDC for soil C and N dynamics. The DNDCv.CAN model is continuing to be developed to simulate cropping systems in diverse environments globally through several Global Research Alliance and Agricultural Model Intercomparison and Improvement Projects (Couëdel et al., 2024; Ehrhardt et al., 2018; Falconnier et al., 2020; Kothari et al., 2024; Sándor et al., 2023; Wang et al., 2022). Comparisons and developments across diverse environments are

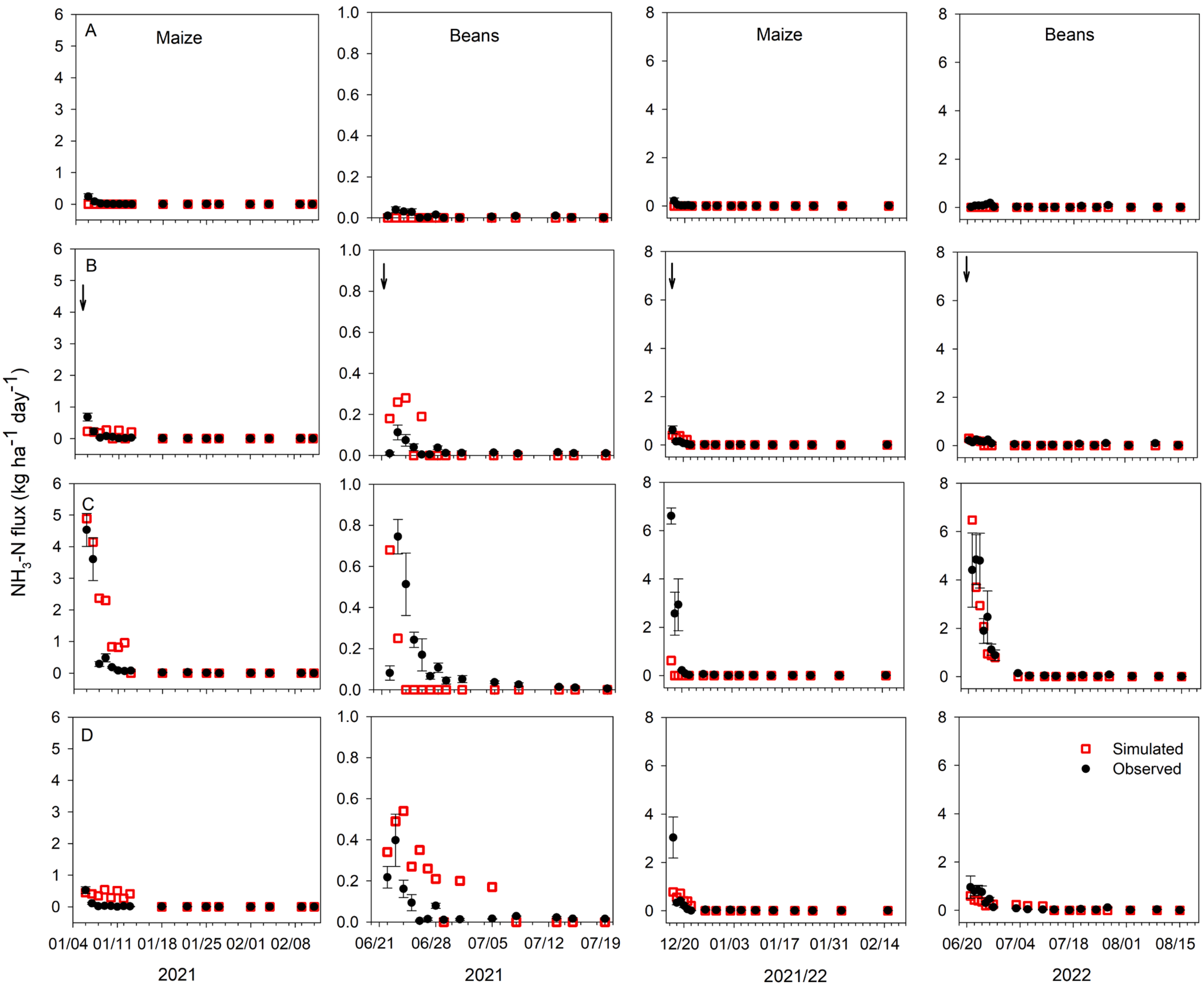

Fig. 4. Daily ammonia volatilization (observed and simulated) during first months after N application (A: Zero-N; B: calcium ammonium nitrate; C: urea; D: ammonium sulfate) in crop rotation system (four crop seasons) in Cerrado - Brazil using DNDCv.CAN model (validation process). Arrows indicate N fertilizer application time.

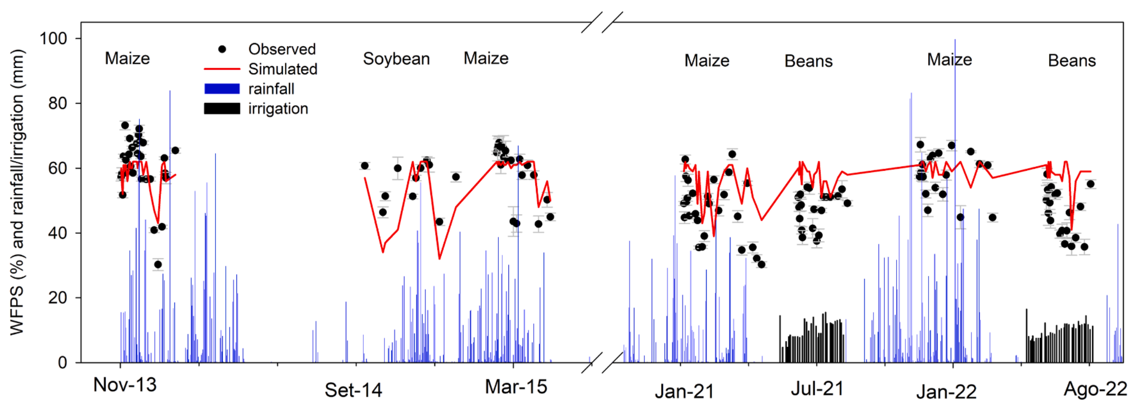

Fig. 5. Rainfall/irrigation in the field experiment, and soil water-filled pore space (WFPS) observed and simulated in the crop rotation system in Cerrado - Brazil using DNDCv.CAN model.

essential to ensure the model's applicability under varying conditions.

In many cases, the DNDC model requires recalibration when applied to new regions beyond its original calibration and validation, in order to account for soil and site-specific conditions, ensuring accurate predictions (Costa et al., 2021; Gabbrielli et al., 2024; Gilhespy et al., 2014; Zimmermann et al., 2018). Therefore, the newly calibrated and

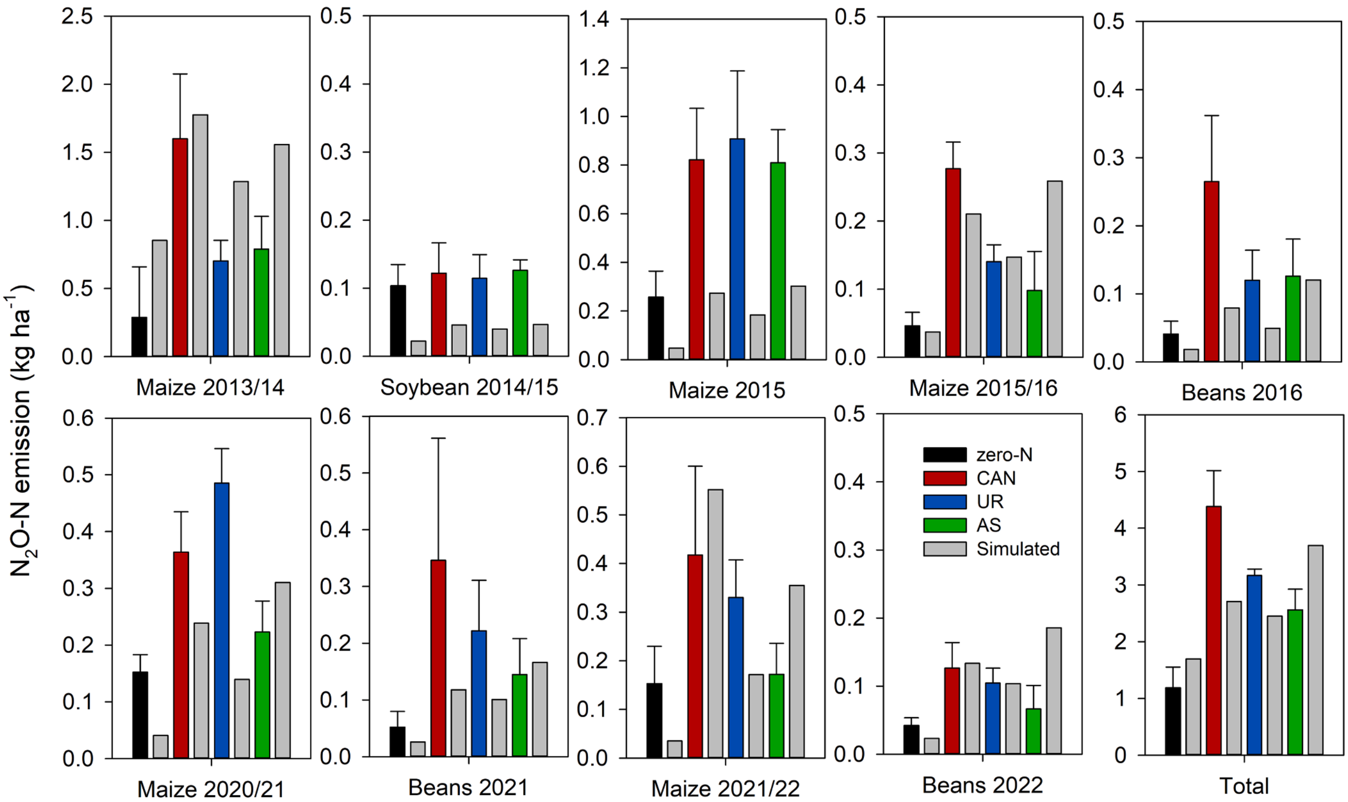

Fig. 6. Cumulative emission of N_2O (observed and simulated) in each season and total (measured points), according to N source applied (Zero-N; calcium ammonium nitrate; urea; ammonium sulfate) in crop rotation system in Cerrado – Brazil. Error bars in observed data correspond to standard deviations.

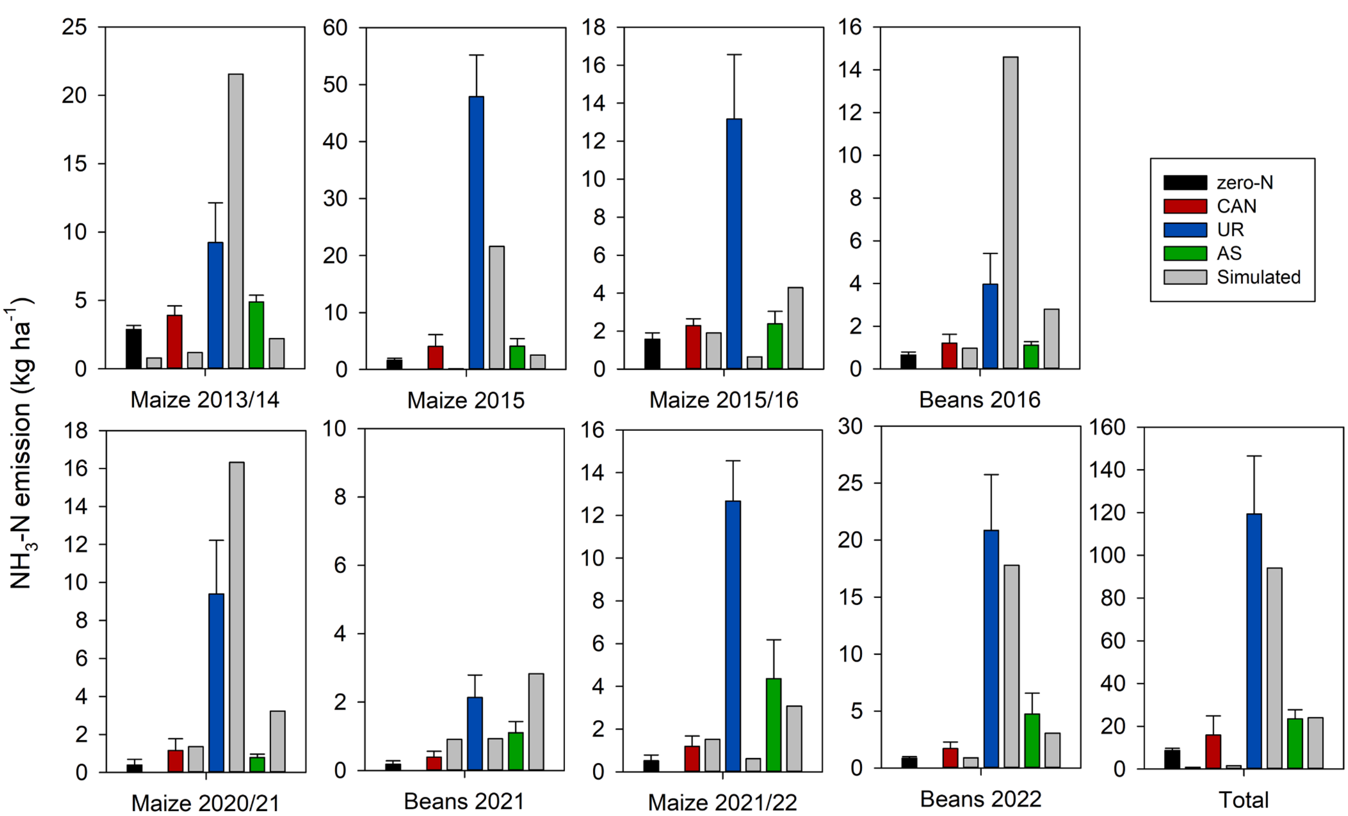

Fig. 7. Cumulative emission of NH_3 (observed and simulated) in each season and total, according to N source applied (Zero-N; calcium ammonium nitrate; urea; ammonium sulfate) in crop rotation system in Cerrado – Brazil. Error bars in observed data correspond to standard deviations.

validated DNDCv.CAN version used in the present study can now be more easily used for other studies conducted in tropical soils, such as Oxisols in Brazil's Cerrado. However, adjustments to accommodate different crop and soil types within this same biome may be necessary.

5. Conclusions

The DNDCv.CAN model demonstrated acceptable simulation of daily N_2O emissions in a 10-year crop rotation study in Brazil's Cerrado biome. The model performance for daily N_2O resulted in an r value of 0.62, an MAE of 17 (94% of the average N_2O), and an RMSE of 34 g N_2O-N ha^{-1} day^{-1} (194%) after calibration. However, the emission peaks were often over or under-predicted.

Nitrogen fertilizer application resulted in higher cumulative observed N_2O emissions compared to the control plots (Zero-N) a pattern which was well captured by the model. The total cumulative NH_3 volatilization was higher from UR than other treatments as expected, and it was effectively simulated by the model, but discrepancies were observed in some seasons. Although the model well simulated the cumulative N_2O emissions by N fertilizer sources, further model updates should be considered to better distinguish N_2O pathways according to N addition. In particular, the use of new observational data, such as microbiology gene abundance related to nitrification, denitrification and other microbial C and N processes, could be used to improve the simulation of microbial functions in DNDC.

The soil extractable NH_4^+, NO_3^-, and grain yield were adequately simulated by DNDC. Soil moisture (WFPS) simulations improved after modifying soil hydrologic parameters in the built-in pedotransfer function. The modification in the hydrologic parameters was necessary due to the distinct characteristics of clay minerals in Oxisols, that lead to distinct hydraulic behavior compared to most soils under temperate climate. This is an important adaptation in the model that also affects the simulation of N_2O and mineral N. Eventually, the DNDCv.CAN model could effectively simulate cumulative N_2O and NH_3 emissions from various N sources applied in a long-term maize – irrigated common bean rotation under tropical climate in an Oxisol, which makes it a valuable tool for identifying emission mitigation practices.

CRediT authorship contribution statement

Johnny Rodrigues Soares: Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation, Conceptualization. **Antônio Carlos Reis de Freitas:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Formal analysis. **Bruno José Rodrigues Alves:** Writing – review & editing, Validation, Methodology, Conceptualization. **Ward Smith:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Data curation. **Brian Grant:** Writing – review & editing, Visualization, Validation, Software. **Craig F. Drury:** Writing – review & editing, Visualization, Validation. **Claudia Pozzi Jantalia:** Writing – original draft, Visualization, Project administration, Funding acquisition. **Maria da Conceição Santana Carvalho:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Beata Emoke Madari:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, 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.

Acknowledgements

This study was financed by the Brazilian Agricultural Research Corporation (Embrapa), Yara (Cooperation Agreement N. 20200.21/0111-6), and Funding Authority for Studies and Projects (FINEP/CT – AGRO/FNDCT, Cooperation Agreement N. 01.22.0080.00, Ref. 1219/21). Besides, the authors acknowledge the financial support provided for the SENSE project (ID 109) through the partners of the 2021 Joint Call of the Cofund ERA-Net SusCrop (Grant N° 771134), FACCE ERA-GAS (Grant N° 696356), ICT-AGRI-FOOD (Grant N° 862665) and SusAn (Grant N° 696231) and by the New Zealand Government to support the objectives of the Global Research Alliance on Agricultural Greenhouse Gases. Furthermore, we acknowledge the support by the National Institute of Science and Technology in Low Carbon Emission in Agriculture (INCT-ABC) sponsored by CNPq (Grant N° 406635/2022-6). JRS received a fellowship from the Sustainable "Rural Sustentável—Cerrado" Project in partnership with the Inter-American Development Bank (IDB), the U.K. Government, the Brazilian Ministry of Agriculture, the Brazilian Institute for Development and Sustainability (IABS), and the ICLF Network Association. BJRA and BEM received fellowships by CNPq (Grant N° 315503/2023-8 and 307807/2022-3, respectively). The work was partly supported by the Science and Technology Branch of Agriculture and Agri-Food Canada.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ecolmodel.2026.111513.

Data availability

Data will be made available on request.

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