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1. Changes with respect to the DoA (Description of the Action)

No changes with respect to the DoA.

2. Dissemination and uptake

Studies that examine nitrous oxide (N_2O) production pathways in arable soil are needed across all geographic scales, and both the methodologies and the outputs that were developed for the PARIS project are useful to many stakeholders as they may improve mitigation strategies. The studies in this project used various methods to improve how N_2O pathways are estimated in biogeochemical models. Although state-of-the-art biogeochemical models simulate the dominant nitrous oxide production processes of nitrification and denitrification, data measuring their relative contributions have remained scarce. Consequently, model calibration activities frequently concentrate on optimising total N_2O emissions. However, inadequate allocation of N_2O production to its source processes may lead to erroneous N_2O emissions when biogeochemical models are used for up-scaling to regional or national level where combinations of management activities, soil properties and weather conditions occur that were not contained in the calibration datasets. This makes calibration approaches that explicitly consider the different production processes an important improvement in the context of model-based N_2O emission calculation.

In this part of the PARIS project, strategies for calibrating N_2O source processes were developed and the ability of two widely used biogeochemical models (DAYCENT and LandscapeDNDC) to simulate the relative contributions of nitrification and denitrification to total emissions was assessed. To this end, we used datasets based on the intra-molecular isotopic composition of nitrous oxide, which provides information on the source processes, including new, observations made as part of the PARIS project for milestone M19. The DayCent model study demonstrates how to enhance model simulations of N_2O emissions using a traditional and a new, observation-based approach. The LandscapeDNDC model study demonstrates the utility of isotopic measurements in model calibration and uncertainty reduction.

Dissemination pathways include open-access data repositories for measurements carried out within the project, peer-reviewed articles on calibration strategies and detailed procedures for the application of isotope-informed calibration. The target groups for uptake are the scientific community, authorities and practitioners. Other researchers can adopt and further develop the methodologies to improve N_2O estimations in biogeochemical models, authorities can include the results in the development of mitigation strategies, which are put into practice by farmers. Within the project, process-based bottom-up simulations of N_2O emissions can identify and resolve differences in spatial and seasonal emission patterns derived from the top-down nitrous oxide inversions.

3. Short Summary of results

The traditional calibration approach for process-based models like DayCent and LandscapeDNDC is to adjust model parameters in an iterative fashion and assess the fit of simulated total N_2O flux to measured observations. However, the contributions of individual production pathways, namely nitrification and denitrification, often remain unconstrained.

Here, N_2O emissions from the soil of sugar beet plots with control (Null) and mineral (NPK) fertilizer treatments were measured (PARIS milestone M19) and the isotopic composition of emitted N_2O was analyzed to identify the N_2O production pathways. The latter showed that denitrification was the predominant source of N_2O emissions at this site.

In the DayCent study, estimations of total N_2O using the model's default settings were compared to the traditional calibration approach and an "expert-informed" approach in which the parameters were manually adjusted to better represent the observation derived contributions of nitrification and denitrification. Although, this "expert-informed approach", showed a somewhat lower performance concerning the cumulative N_2O flux (Null: RMSE = 0.24 kg N ha^{-1} yr^{-1}, NPK: RMSE = 0.30 kg N ha^{-1} yr^{-1}) than the traditional calibration (Null: RMSE = 0.15 kg N ha^{-1} yr^{-1}, NPK: RMSE = 0.10 kg N ha^{-1} yr^{-1}), it may be considered as more representative and suitable.

In the LandscapeDNDC study, the model parameterisation and corresponding parameter uncertainties were improved upon through inclusion of isotopic composition in a new calibration and uncertainty analysis scheme which incorporates the isotope tracing model SIMONE.

4. Evidence of accomplishment

In this part of the PARIS project, one measurement campaign was carried out and two widely used biogeochemical models, DayCent and LandscapeDNDC were independently used. For the sake of simplicity, the different approaches taken by the two modeling groups are referred to as the DayCent study and the LandscapeDNDC study, respectively. The DayCent study, which is entitled "Coupling observational methods and the biogeochemical model DayCent for examinations of N_2O emissions from nitrification and denitrification in a temperate cropland" is currently in review in *Nutrient Cycling in Agroecosystems*.

The data from the field study was uploaded to the ICOS CP and (after embargo) will be publicly available after May 2026 (https://doi.org/10.18160/ANQW-32YY).

4.1 Introduction | Background of the deliverable | milestone

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) with a global warming potential 273 times that of CO_2 over a 100 years period and contributes approx. 6% to the total effective radiative forcing of the well mixed GHG (Forster et al., 2021). In addition to its role as a driver of global warming, N_2O is the single most-important substance in the context of stratospheric ozone depletion (Ravishankara et al., 2009).

Agriculture is the largest anthropogenic source of N_2O (Ciais et al., 2013) with the widespread application of synthetic fertilizers and manure on cropland and pasture stimulating microbial nitrogen (N) turnover in soils, eventually leading to increased N_2O production and emission. The global population growth and the associated increasing demand for food and fiber promotes agricultural intensification which - in a business-as-usual scenario - suggests a doubling of N_2O emissions by 2050 (Davidson and Kanter, 2014). Consequently, there is an urgent need for the development of mitigation strategies, which are usually based on field studies. However, quantification of N_2O source strength using field measurements is intense in cost and labor, so that not all soil types and climates can be covered. Simultaneously, climate change alters temperature and soil moisture regimes in ways that either amplify or suppress microbial N_2O production and consumption processes as well as plant production, adding an additional long-term dimension to mitigation research further complicating the situation.

Thus, direct measurements of N_2O emissions at sufficient temporal and spatial scale are unfeasible with current infrastructure and technology. For this reason, notable effort was spent on the development of process-based biogeochemical simulation models during the last decades. Such models use information on soil properties (e.g., bulk density, texture or soil organic carbon), meteorological information (e.g., global radiation, precipitation, temperature) and agricultural management activities (e.g., tilling, planting, fertilization) to calculate soil environmental conditions (e.g., soil moisture and soil temperature), plant growth, and the coupled soil carbon and nitrogen cycles, including relevant N_2O-producing and consuming microbial processes on temporal scales of days to months (Bell et al., 2012; Chirinda et al., 2010; Grosso et al., 2006; Gabrielle et al., 2006; Li 2000; Haas et al., 2013).

While first applications were proof-of-concept studies at site scale, increasing availability of GIS databases holding spatially explicit model input variables has fostered utilization of biogeochemical models to simulate fluxes at landscape and regional scale (Grosso et al., 2006; Werner et al., 2007; Zaehle et al., 2005; Sifounakis et al., 2024). This development is especially relevant as so far, national bottom-up N_2O emission inventories are predominately based on Tier 1 or Tier 2 approaches that relate activity data (e.g., fertilizer amount), with an emission factor, to obtain annual N_2O emissions. However, these approaches represent annual total emissions neglecting spatial and temporal variability of fluxes due to soil properties, soil environmental conditions, meteorology, and agricultural management (e.g., timing of fertilizer application). This limitation can be overcome by the presented process-based biogeochemical models, with model-based inventories of soil-derived GHG emissions being defined by the IPCC as Tier 3 method for national GHG reporting. Tier 3 methods are not widely adopted for national inventory reporting of N_2O emissions (one exception being the USA where the process model DayCent is applied) but some countries are moving toward this capability. However, for any simulation study to be admissible, the uncertainties of simulation results need to be included (IPCC 2006).

Uncertainty of simulation results can be attributed to four sources: (i) model inputs, i.e., information used to initialize and drive the model such as meteorologic information, soil properties and agricultural management (Vrugt et al., 2008), (ii) model parameters, for instance the rate constants for microbial processes, for instance ammonification of soil organic matter (Vrugt et al., 2003), (iii) model structure, i.e., inadequate modeling of relevant processes (Refsgaard et al., 2006) and (iv) accuracy of measurements based on which models were developed and calibrated such as soil-atmosphere greenhouse gas exchange (Van Oijen et al., 2005). So far, published work on modeling the soil-atmosphere exchange of trace gases has predominately focused on the assessment of input uncertainty (Li et al., 2004; Winiwarter and Rypdal 2001; Werner et al., 2007). The reason for that is that in many cases the way the model is programmed prohibits the determination of uncertainty due to model structure and that the computational demand of complex models is high (Ogle et al., 2010). This specifically applies to process-based biogeochemical models as they are highly parameterized, with the range of plausible parameter values constituting a major source of model uncertainty. However, studies investigating parameter uncertainty have remained scarce due to the high computational demand.

Several studies have shown that biogeochemical models can be improved through the calibration of model parameters that control the flow of N as it is transformed through the nitrification and denitrification pathways (dos Reis Martins et al., 2022; Necpalova et al., 2018). The traditional calibration approach entails the user manually adjusting individual model parameters in an iterative fashion. Biogeochemical models can also be coupled with advanced inverse modeling tools that accelerate the identification of parameter effects on model outputs (dos Reis Martins et al., 2022; Necpalova et al., 2015; Rafique et al., 2015). Both techniques use comparisons of the simulated total N_2O flux with measured observations to refine the model. While these approaches improve estimations of N_2O emissions, the contributions from nitrification and denitrification are still poorly understood (Berardi et al., 2020; Dueri et al., 2023). This is primarily due to the methodological difficulties involved in measuring the gaseous and soluble components of the nitrification and denitrification processes, which hinder direct comparisons to simulated N-gas production and emissions within process-based models (Friedl et al., 2020; Groffman et al., 2006).

Parameter values within biogeochemical models can also be adjusted using information derived from observational methods, which provide important insights into both ecosystem and model function (Del Grosso et al., 2020). For example, soil water-filled pore space (WFPS) is the characterization of the proportion of soil pore space that is filled with water and is a useful measure, which denotes soil water content and the availability of oxygen throughout the soil profile (Linn and Doran, 1984). Many studies have shown that soil water content is a key regulator of N_2O emissions, because it directly affects microbial activity and thus microbially mediated N transformation processes (Kuang et al., 2019; Liu et al., 2022; Wang et al., 2023). Given the importance of soil water content for N_2O production from nitrification and denitrification, this metric can be used to identify discrepancies between the simulated and the observed soil moisture environment on the field that may impact N_2O emission via each pathway (Bateman and Baggs, 2005).

Isotopic methods have been applied in numerous studies to evaluate the contribution of individual N_2O source processes and can be combined with process-based models to constrain model parameters. In this regard, singly substituted isotopologues of N_2O ($^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$) become critically important. These species differ from the most abundant N_2O isotopologue ($^{14}N^{14}N^{16}O$) by the substitution of one nitrogen atom at the central (α) or terminal (β) nitrogen position by ^{15}N, or the oxygen atom by the rare ^{18}O isotope (Toyoda and Yoshida, 1999). Their relative abundances are expressed using δ-notation, where $\delta^{15}N = (R(^{15}N/^{14}N)_{sample}/R(^{15}N/^{14}N)_{reference})-1$ denotes the relative difference in isotope ratio of the sample versus a reference material in per mil (‰). By extension, position-specific δ-values are defined as follows: $\delta^{15}N^{\alpha}$ for $^{14}N^{15}N^{16}O/^{14}N^{14}N^{16}O$, $\delta^{15}N^{\beta}$ for $^{15}N^{14}N^{16}O/^{14}N^{14}N^{16}O$. The term site preference (SP) of ^{15}N ($\delta^{15}N^{SP} = \delta^{15}N^{\alpha}-\delta^{15}N^{\beta}$) describes the preference of ^{15}N substitution in the central α-position as compared to the terminal β-position within the N_2O molecule. Likewise, bulk $\delta^{15}N$ ($\delta^{15}N^{bulk} = (\delta^{15}N^{\alpha}+\delta^{15}N^{\beta})/2$) represents the average N isotopic composition of the N_2O molecule. Specifically, the parameter $\delta^{15}N^{SP}$ offers a distinctive fingerprint independent of the isotopic composition of the substrates, with higher values (~+33 to +38 ‰) indicating nitrification and lower values (~ -5 to +5 ‰) being typical for denitrifying pathways (Denk et al., 2017; Yu et al., 2020). In contrast, $\delta^{15}N^{bulk}$ reflects the integrated isotope signature of the N substrate pool and fractionation processes during N_2O production, with broad, overlapping ranges in $\delta^{15}N^{bulk}$ possible for both nitrification and denitrification. In parallel, $\delta^{18}O$ traces the origin of the O atom, e.g., from soil water, oxidized N substrates or molecular O_2, and exchange processes, further aiding in the distinction between pathways. Isotopic information thus provides important pathway-specific fingerprints that enable improved source attributions of N_2O, thereby reducing uncertainties and enhancing predictions in model estimates (Yu et al., 2020).

Calibration methods typically employ a combination of strategies to constrain model parameters, including manual iterative adjustment in comparison with observational data and more recent automated Bayesian calibration techniques that rely on large numbers of model runs (Van Oijen et al., 2005; Houska et al., 2017; Sifounakis et al., 2024). The expert-informed strategy utilizes manual iterative parameter adjustment in combination with inference drawn from observational data and process-based understanding can be used to compensate for inaccurate representations of processes within biogeochemical models (Del Grosso, 2020). An early application of this combined approach coupled an N isotope model with DayCent to examine gaseous nitrogen losses from soils (Bai and Houlton, 2009). More recently, isotopic composition of N_2O measurements were paired with the stable isotope model SIMONE and used to parameterize and test the process-based model LandscapeDNDC in its identification of N_2O source processes (Denk et al., 2019; Ibraim et al., 2020).

The objectives of the DayCent study were to determine the primary source of N_2O emissions at the field scale based on isotopic analysis, to identify potential discrepancies between the DayCent model and the soil water environment at the site, and to evaluate the performance of DayCent to estimate N_2O emissions from nitrification and denitrification through different model parameterisations.

Similarly, the objectives of the LandscapeDNDC study were to use measurements of isotopic composition to identify systematic model biases and improve model parameter calibration. As the additional information on N_2O source processes provided by the isotope measurements suggests a reduction in parameter uncertainty, a Bayesian calibration-uncertainty estimation framework was developed to consider both N_2O flux and N_2O isotopic composition. To this end, we used the biogeochemical model LandscapeDNDC (Haas et al., 2013) in conjunction with the stable isotope model for nutrient cycles SIMONE (Denk et al., 2019).

4.2 Scope of the deliverable | milestone

This deliverable addresses the challenge of improving model-based estimates of soil N_2O emissions by calibrating the relative contributions of the modeled processes that produce nitrous oxide. This is important because process-specific calibrations are rare, but enable a more accurate representation of N_2O emissions, given that various factors such as tillage, fertilization, soil temperature, pH and soil moisture affect the underlying processes in different ways. This enables more reliable regional to national inventories to be achieved.

To expand the limited existing body of measurements including source process information, within the project PARIS an additional dataset was generated comprising soil N_2O emissions and the associated soil-emitted N_2O isotopic composition from a cropland site. The corresponding measurement campaign was carried out in 2024 on two sugar beet plots in the long-term Demo field trial in Switzerland.

Using the aforementioned dataset and existing datasets from the published literature, the following were assessed for two widely used biogeochemical process models, DayCent and LandscapeDNDC: (i) model bias due to default parameterisation or calibration using N_2O flux alone (traditional calibration); (ii) the implications of using N_2O flux and isotope information (flux and SP); and (iii) the ability to reflect measured source process contributions.

For DayCent, flux-based (traditional) calibration resulted in good agreement between the measured and modeled growing season N_2O emission. However, nitrification was the dominant source for N_2O, which contrasts with the isotope information. Calibrating the model using the isotope information showed that a similar level of agreement between the measured and modeled N_2O emissions could be achieved with denitrification playing a predominant role, as indicated by the isotope measurements. Similarly, LandscapeDNDC systematically overestimates nitrification in the default parameterisation. After calibration, the balance between nitrification and denitrification, as observed in the site-preference dynamics, improved significantly. This suggests that both models can reflect the interplay between nitrification and denitrification processes, as observed using isotope measurements, and that improving our understanding of N_2O source processes can enhance biogeochemical models.

4.3 Content of the deliverable | milestone

4.3.1 Field measurements

The field component of this study was conducted at the Demo87 (Demo) trial, which is located at the Agroscope-Reckenholz Research Station in Zürich, Switzerland (47°25′31″ N, 8°30′59″ E; 443 m asl). Mean annual temperature at the site is 9.4°C and mean annual precipitation is 1,031 mm. The topsoil is classified as an Eutric Cambisol (WRB), and it has a loam soil texture (20% clay, 33% silt, 47% sand), and an organic carbon content of 3%.

A detailed description of the management practices at the Demo site can be found in Frei et al. (2024). For the present study, measurements were performed in 2024 on the mineral fertilizer (NPK) and the non-fertilized (Null) treatment of the rotation with sugar beet in that year. The NPK treatment received ammonium sulfate (50 kg N ha-1) on 7 May 2024, and ammonium nitrate (50 kg N ha-1) on 21 May 2025.

Soil volumetric water content (VWC) was measured in 2023 using a TEROS 12 soil moisture sensor (METER Group, Pullman, WA, USA) that was installed in the NPK treatment of the sugar beet plot at the 5cm soil depth. The soil VWC was recorded at fifteen-minute intervals, and daily averages were determined for comparisons to the DayCent model. The WFPS was calculated as the quotient between VWC and total porosity (Linn and Doran, 1984), in which soil porosity was determined as a function of bulk density (BD, 1.39 g cm^{-3}) and a soil particle density (PD) of 2.65 g cm^{-3} (Minasny et al., 1999):

$$WFPS = 100 * \frac{VWC}{\left(1-\frac{BD}{PD}\right)} \quad \text{(Eq. 1)}$$

The data from the field study was uploaded to the ICOS carbon portal and, after embargo, will be publicly available after May 2026 (https://doi.org/10.18160/ANQW-32YY).

4.3.1.1 Nitrous oxide flux measurements and identification of N_2O production pathways using isotopologues

Gas concentrations (N_2O, CH_4, CO_2) and singly substituted isotopic composition of N_2O ($\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$) were analysed using commercial cavity ring-down spectroscopy (CRDS; Picarro Inc., USA). Measurements of CH_4 and CO_2 were performed with a G2401-m analyser (serial number: 2829-CFKADS2266), while N_2O, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ measurements were conducted on two G5131-*i* analysers (serial numbers: 5080-DAS-JDD S5089 and 5056-PPU-JDD S5065) at Empa, Dübendorf, Switzerland. The measured δ-values were derived from the isotopologue ratios in the sample and reference gases and are expressed relative to the atmospheric N_2 (AIR-N2) scale for nitrogen and the Vienna Standard Mean Ocean Water (VSMOW) scale for oxygen (Mohn et al., 2022; Ostrom et al., 2018). The raw data were corrected for spectral interferences, instrumental drift, and calibrated against the established reference scales, provided by the Global Atmosphere Watch (GAW) program for greenhouse gases from the World Meteorological Organization (WMO). Full details on the correction and calibration approach are provided in Havsteen et al. (2025).

This analytical workflow enabled the calculation of weekly mean fluxes of N_2O, CH_4 and CO_2 per chamber using a linear regression approach for gas concentration over time, with an imposed quality criterion of $R^2 \geq 0.7$ for data acceptance. The concentration-to-flux conversion considered dynamic molar volumes, calculated from the mean ambient temperature over the measurement period, recorded two meters above the ground at the Zürich-Affoltern weather station (REH; 47.4277° N, 8.5180° E; 444 m a.s.l.), which is part of the automatic monitoring network operated by MeteoSwiss (WIGOS ID: 0-20000-0-06664). The N_2O isotopic source signatures emitted from soil were derived using a two-endmember mixing model (Keeling plot) (Keeling, 1958), where each gas sample collected from a chamber represents a mixture of ambient atmospheric N_2O and N_2O from soil-derived microbial production. To determine the microbial source endmember for a specific time and chamber, isotopologue values were plotted against the inverse N_2O concentrations of the respective bags. The intercept of the regression line provides an estimate of the microbial N_2O source signature ($\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$). To assess the data quality, the regression-derived isotopic composition at ambient N_2O concentration was compared to actual values. Three quality classes were defined: Quality 1 (Q1) for agreement within 4 ‰, Q2 (4–6 ‰) and Q3 (6–8 ‰). Regression lines with deviations in ambient isotopic signatures from actual values of more than 8 ‰ were excluded from further analysis. If a sample sequence was measured on two G5131-*i* analysers, duplicate analysis provides two Keeling plot intercepts, which were averaged before further interpretation. To avoid false positive results under low flux scenarios, an additional criterion was applied, requiring a minimum N_2O flux threshold of 75 µg N_2O-N m^{-2} h^{-1} combined with a regression quality threshold of $R^2 \geq 0.7$.

4.3.1.2 Results

Fluxes and sources of N_2O emissions at the Demo site

Across the sampling period (05.03.2024 to 11.12.2024), the integrated weekly average N_2O flux was generally small and typically below the 75 µg N_2O-N m^{-2} h^{-1} threshold required for isotopic source member determination (Fig. 1b, dashed line). For the NPK treatment, two larger emission pulses occurred in late spring to mid-summer peaking at ~350–400 µg N_2O-N m^{-2} h^{-1} (Fig. 1b). The emission pulses coincided with periods of increased precipitation and followed the two fertilization events (50 kg N ha^{-1} each) applied at the beginning and the end of May (07.05.2024 and 21.05.2024), expressed by the vertical grey stippled lines in Fig. 1. Isotopic source signatures were only measurable during the high flux periods, while the remaining dataset did not offer sufficiently high N_2O fluxes to pass the quality criteria and threshold values ($R^2_{[N2O]} > 0.7$, $flux_{[N2O]} > 75$ µg N_2O-N m^{-2} h^{-1} and Keeling line within ±8 ‰ of ambient air endmember). For periods with sufficiently high fluxes for isotopic analysis, the dataset indicates that bacterial denitrification is the predominant pathway of N_2O production in the soils at the Demo site, with most source signatures clustering within or close to $\delta^{15}N^{SP}$ values reported for denitrification in literature (Yu et al., 2020). This is visualized by the majority of the determined source signatures falling close to or within the red box, signifying denitrification in Fig. 2.

To contextualize these findings, the colour gradient in Fig. 2 encodes the seven-day accumulated rainfall prior to sampling, while the symbol size scales with the weekly mean N_2O flux, thereby linking the isotopic source signatures to both the magnitude of the emissions and precipitation. Across the period characterized by largest emissions in late spring to mid-summer (May – July 2024), $\delta^{15}N^{SP}$ and $\delta^{15}N^{bulk}$ showed an overall increasing trend, a pattern most consistent with a progressive share of N_2O reduced to N_2 via denitrification or, alternatively, an increasing contribution of nitrification (i.e., see dates next to round symbols in Fig. 2). This is most notable during the week with the highest seven-day accumulated precipitation (17.07.2024), where both $\delta^{15}N^{SP}$ and $\delta^{15}N^{bulk}$ are shifted towards higher values (Fig. 2). However, this linkage remains weak to moderate in the dataset, likely because shifts in isotopic source signatures are not only governed by wetting, but also other factors such as sub-weekly variability in labile carbon and ammonium or nitrate availability, the extent of N_2O reduction and mixing of different N_2O production pathways typical for agricultural soils (Butterbach-Bahl et al., 2013; Yu et al., 2020). To get a quantitative estimate of process contributions, a Monte Carlo simulation was performed on the N_2O isotopic source signatures measured at the Demo trial site using the FRAME model. The FRAME model relates measured N_2O source signatures and in addition accounts for isotopic fractionation during partial N_2O reduction (Lewicki et al., 2022). Likewise, the majority of N_2O emissions for the high flux period was attributed to denitrification and nitrifier denitrification (79–96 %), whereas nitrification contributed only 4–21 % (Table 2). Temporal trends in model results display an increasing share of nitrification derived N_2O from mid-May to early-July in parallel with drier and better aerated conditions (Table 1, Fig. 1).

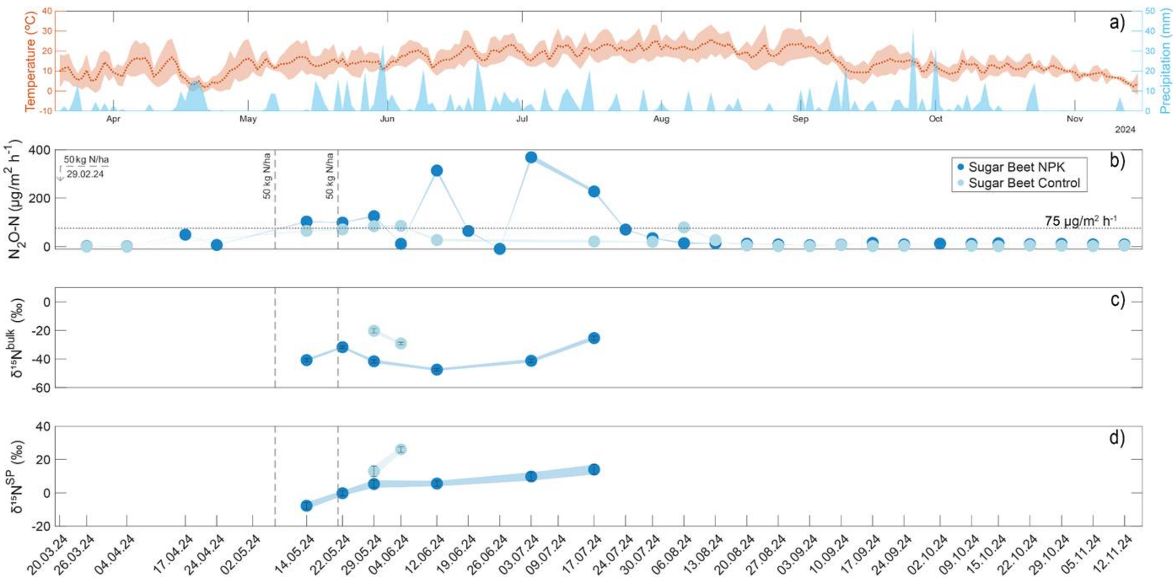


Fig. 1: Seasonal course of N_2O fluxes and isotopic composition for sugar beet under NPK fertilization vs. control of the Demo experiment: (a) daily air temperature and precipitation, (b) N_2O flux (µg N_2O-N m^{-2} h^{-1}), (c) $\delta^{18}O$, $\delta^{15}N^{bulk}$ and (d) site preference ($\delta^{15}N^{SP}$). The stippled line in the N_2O flux graph represents the 75 µg m^{-2} h^{-1} threshold for isotope flux analysis.

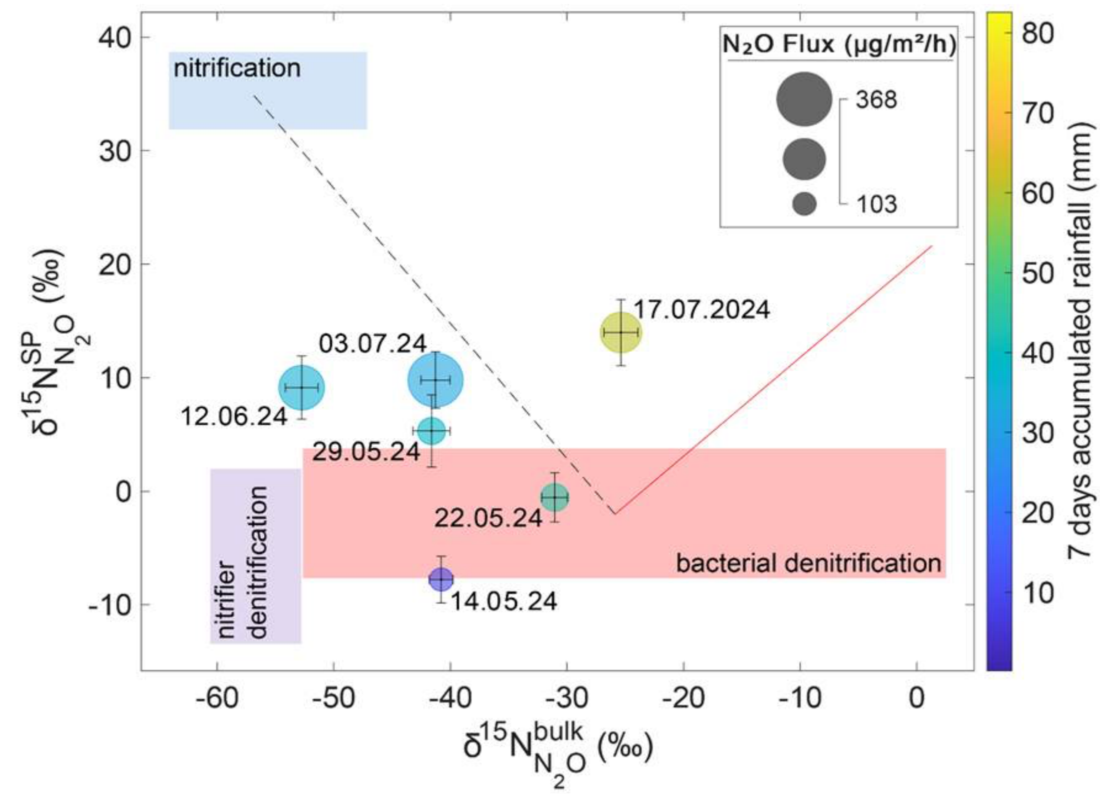


Fig. 2: Dual isotope plot of site preference $\delta^{15}N^{SP}$ versus $\delta^{15}N^{bulk}$ for N_2O emitted from the NPK-fertilized sugar beet plot. The points are color-coded by 7-day accumulated rainfall (mm) and scaled by N_2O flux (µg N/m² h^{-1}). The colored boxes indicate ranges of isotopic signatures reported for prominent microbial N_2O production pathways in literature (Yu et al., 2020).

Table 1: Estimated source contributions of N_2O emissions from the mineral fertilized sugar beet plot (mean and 95% CI) for bacterial denitrification (bD) + nitrifier denitrification (nD) and nitrification (Ni).

Date	N_2O flux (µg N_2O-N m^{-2} h^{-1}) ± SE	Fraction of bD + nD	Fraction of Ni
14.05.2024	103 ± 2	0.96 [0.26-1.68]	0.04 [0.001-0.13]
22.05.2024	128 ± 43	0.88 [0.17-1.65]	0.12 [0.004-0.29]
29.05.2024	125 ± 3	0.84 [0.07-1.74]	0.16 [0.005-0.39]
12.06.2024	265 ± 103	0.84 [0.07-1.73]	0.16 [0.010-0.36]
03.07.2024	368 ± 11	0.79 [0.07-1.64]	0.21 [0.014-0.45]
17.07.2024	227 ± 6	0.86 [0.13-1.64]	0.14 [0.004-0.35]

Note: Results include a correction for isotopic enrichment due to microbial N_2O reduction. Sources bD (bacterial denitrification) and nD (nitrifier denitrification) are combined.

Flux values represent the mean across replicate chambers and analyzers, while the uncertainty (SE), incorporates errors of both the regression fit error and variation among chambers.

4.3.2 The DayCent study

4.3.2.1 Methods

DayCent Model description

DayCent is a process-based ecosystem model that simulates carbon, nitrogen, phosphorus, and sulfur dynamics in plant-soil systems (Del Grosso et al., 2000). The main inputs of the DayCent model include soils data (soil texture, bulk density, pH), field management data (crop type, fertilization, tillage, harvest), and daily weather data (minimum and maximum temperature and precipitation).

The N-gas sub-model in DayCent is based on the "leaky pipe" concept (Firestone and Davidson, 1989), in which total N gas emissions are proportional to N cycling and soil diffusivity. Within the N-gas sub-model, the nitrification and denitrification processes represent the figurative "pipes" which facilitate the transformation of N, wherein nitrate and dinitrogen are the respective end products of each process. Nitrous oxide emissions from nitrification are a function of the soil ammonium concentration, WFPS, soil temperature, pH, and soil texture. Modelled N_2O flux from denitrification is driven by the soil NO3- concentration, the heterotrophic CO2 respiration rate (which is representative of labile C availability), WFPS, and soil physical properties that impact gas diffusivity (such as soil texture and bulk density). The pipe is said to be "leaky" because N_2O and nitric oxide (NO) are by-products of nitrification and denitrification and the amount of N_2O and NO that is produced is determined by soil water content, soil temperature, and soil physical properties that impact gas diffusivity (the size of the holes in the pipe) during intermediate steps.

Within DayCent, N cycling is controlled by several adjustable model parameters (Del Grosso et al., 2000). While the value of these parameters ranges between sites, sensitivity analyses have found that parameter estimation improves the model's ability to simulate

N_2O emissions (Necpálová et al., 2015; Rafique et al., 2013). In a study that used approximately 24,000 daily N_2O flux observations from six cropland sites located in Western Europe, including sites in Switzerland, dos Reis Martins et al. (2022) found that improvements to N_2O predictions were associated with seven N-cycle related parameters within DayCent (Table 2). Here, we focus on the three parameters that influence the effect of soil water content on the nitrification and denitrification processes within the model. Specifically, the N2Oadjust_fc and N2Oadjust_wp parameters, respectively, that control the maximum and minimum proportions of nitrified N lost as N_2O when soil conditions are at field capacity and wilting point. N_2O emissions are also directly impacted by the wfpsdnitadj parameter, which controls the inflection point for the effect of WFPS on denitrification, wherein values less than one permit denitrification to occur at lower soil water content and values greater than one require wetter conditions for denitrification to occur.

Table 2: Three different sets of DayCent parameter values which are relevant for soil nitrogen cycling. The default parameters are described in Hartman et al. (2018). The optimized parameter values from dos Reis Martins et al. (2022) and the values for the traditional calibration and the expert-informed approaches were used for simulations in DayCent. The N2Oadjust_fc, N2Oadjust_wp, and wfpsdnitadj model parameters are the focus of this study.

DayCent Parameter	Default	Traditional	Expert-informed
Ncoeff	0.030	0.027	0. 027
N2Oadjust_fc	0.025	0.000	0.000
N2Oadjust_wp	0.020	0.004	0.000
MaxNitAmt	1.500	3.690	3.690
Netmn_to_no3	0.200	0.359	0.359
wfpsdnitadj	1.000	1.400	1.0
N2N2Oadj	1.000	1.159	1.0

Model parameterization and calibration

Model simulations were conducted for the plots with Null and NPK treatments on which sugar beet was cultivated in 2024. Spin up (5,000 yrs) and base (1,989 yrs) simulations were performed to bring the soils to equilibrium and to reflect the management histories of the different land use types. In 2024, mineral fertilizers (50 kg N ha-1, ammonium sulfate on 7 May, and 50 kg N ha-1, ammonium nitrate on 21 May) were applied to the NPK treatment of the Demo trial, providing a total of 100 kg N ha-1 to the sugar beet plot.

For this study, the DayCent parameters characterised by the maximum proportion of nitrified N lost as N_2O at field capacity (N2Oadjust_fc), the minimum proportion of nitrified N lost as N_2O at wilting point (N2Oadjust_wp), and the inflection point for the effect of WFPS on denitrification (wfpsdnitadj) were manually calibrated using the "traditional" (N_2O-flux based) and "expert-informed" (considering N_2O flux and SP) approaches, respectively. Both approaches used values of the other N cycle related parameters based on the multi-site calibration by dos Reis Martins et al. (2022) and were performed by adjusting one parameter at a time while keeping the others constant. For the traditional approach, the three parameters were modified iteratively between a range of values, and parameter values were adjusted based on how well the simulated total N_2O outputs reflected observations. This classical approach avoided heuristic judgement made on behalf of the user and considers field observations of total N_2O fluxes. The expert-informed approach assigned specific values for each parameter based on information gathered from the results of the WFPS and the isotopic composition of N_2O observations. Specifically, the WFPS data from 2023 was used to identify potential discrepancies between the observed and simulated soil moisture content, and the isotopic composition of the soil N_2O endmember was determined using the Keeling plot approach to identify the primary N_2O production pathway in the soils at the Demo site. In DayCent, the N2Oadjust_fc and N2Oadjust_wp parameters control the impact of WFPS on N_2O emissions via nitrification and the wfpsdnitadj parameter directs the soil moisture conditions under which N_2O emissions via denitrification can occur. Within the model, lower values of the N2Oadjust_fc and N2Oadjust_wp parameters limit the release of N_2O emissions via nitrification, and the wfpsdnitadj parameter facilitates the occurrence of N_2O emissions from denitrification under dry or wet soil moisture conditions. Therefore, parameter values in the expert-informed approach were selected to account for discrepancies in the model's interpretation of the effect of soil moisture content on N_2O emissions from nitrification and denitrification at the Demo site.

The simulations were calibrated based on the relationship between the simulated total N_2O flux and the measured N_2O flux observations throughout the year. We compared the cumulative total N_2O flux, as well as the cumulative N_2O emissions from nitrification and denitrification from DayCent simulations using parameter values from the model's default settings, the traditional calibration, and the expert-informed approach (Table 1).

Statistical analysis

Water-filled pore space measurements were unavailable for 2024 due to unforeseen complications with fieldwork. Therefore, the coefficient of determination (r^2) was calculated to measure how well WFPS measurements collected during 2023 were replicated by the model. As the same input data such as soil bulk density was used to determine the WFPS at this site in both years, differences in the simulation of WFPS within DayCent between 2023 and 2024 would result from interannual variability in weather conditions, namely the amount of precipitation that occurs throughout the year (Hartman et al., 2018). To ensure that there were no substantial differences in weather conditions between 2023 and 2024, we evaluated the means of the monthly minimum and maximum temperature and precipitation for each year using the Welch Two Sample t-test. Model calibration was evaluated by calculating the root mean squared error (RMSE) between the model outputs and the corresponding field measurements using the following equation:

$$RMSE = \sqrt{\sum_{i=1}^{n}(S_i - O_i)^2 / n} \quad \text{(Eq. 2)}$$

where O_i and S_i represent the observed and simulated values at point in time i and n denotes the number of observations. All statistical analyses were performed using R version 4.4.2 (R Core Team, 2024). P-values less than 0.05 were considered statistically significant.

4.3.2.2 Results

Comparison of soil moisture content

The correlation between the observed vs. simulated WFPS (Fig. 3) was moderate at the Demo site in 2023 (r^2 = 0.64; Fig. 3), and several inconsistencies were observed. A discrepancy between the measured and simulated WFPS occurred between January and mid-February, and again in December when DayCent over-represented WFPS when the soil water content was at or above field capacity. For example, the model predicted that the soil water content was at or above field capacity at the 5 cm soil depth (i.e., at or above upper dashed line) 74 days or roughly 20% of the days throughout the year, while the measured observations show that the soil experienced field capacity only 17 days during the year (Fig. 3). DayCent also estimated that the soil water content was at or below the site's wilting point more frequently than was measured on the field (i.e., at or below the lower dashed line). This discrepancy was most prominent in April and throughout the growing season (early June – late October), during which DayCent simulated drier soil conditions 48 more days at 5 cm than found in the measured observations. During this time, there were distinct periods during which DayCent consistently simulated WFPS to be under the site's wilting point in each of the measured soil depths (mid-June – mid-July, late-August, and late-October).

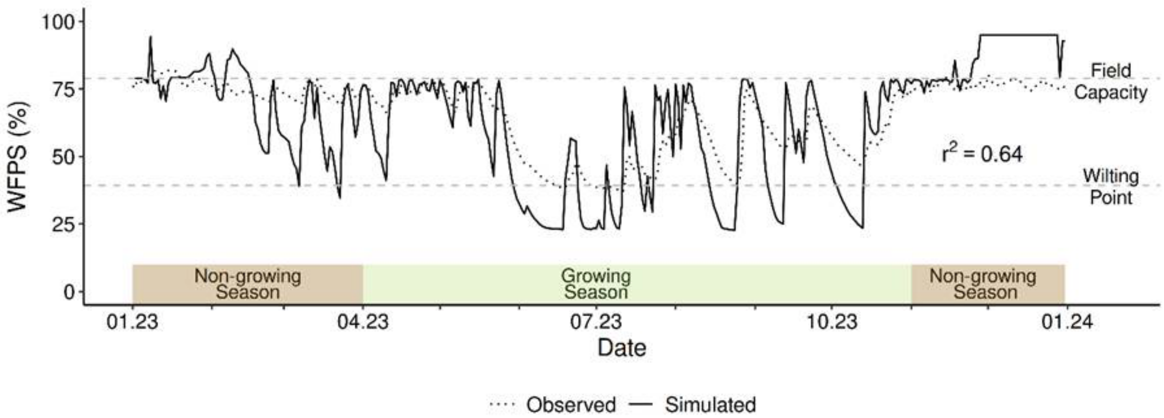


Fig. 3: Water-filled pore space (WFPS) measurements from the 5 cm soil depth at the Demo site in Switzerland. The observed and simulated values during the growing season (April – October) and non-growing season (January – March and November – December) of 2023 are represented by the dotted and solid black lines, respectively. The dashed grey lines indicate the field capacity (78.87 %) and wilting point (39.33 %) of the Demo site.

N_2O emissions and DayCent simulations

The measured, cumulative total N_2O emission for the NPK fertilizer treatment (0.63 kg N ha^{-1} yr^{-1}) at the Demo site was three times higher than that of the Null treatment (0.20 kg N ha^{-1} yr^{-1}; Fig. 4). Total N_2O emissions increased throughout the growing season, together with increased precipitation and fertilization events, between spring and early autumn. DayCent simulations with the default parameter values indicated N_2O was emitted from the nitrification and denitrification processes, but the total cumulative N_2O emissions for both the Null and NPK treatments were strongly overestimated (RMSE = 1.58 kg N ha^{-1} yr^{-1} for the Null treatment and 2.49 kg N ha^{-1} yr^{-1} for the NPK treatment) (Fig. 4 a and b). Model fit improved for simulations that were performed with parameter values from the traditional calibration (RMSE = 0.15 for the Null treatment and RMSE = 0.10 kg N ha^{-1} yr^{-1} for the NPK treatment, Fig. 4 c and d). However, these simulations attributed all N_2O emissions to the nitrification process, which is not in line with isotope measurements. The RMSE was slightly greater for the simulations that used the expert-informed parameter values (RMSE = 0.24 kg N ha^{-1} yr^{-1} for the Null treatment and RMSE = 0.30 kg N ha^{-1} yr^{-1} for the NPK treatment, Fig. 4 e and f), and these simulations improved estimations of the cumulative total N_2O flux by limiting all N_2O emissions from nitrification and allocating N_2O emissions to denitrification in agreement with isotope measurement.

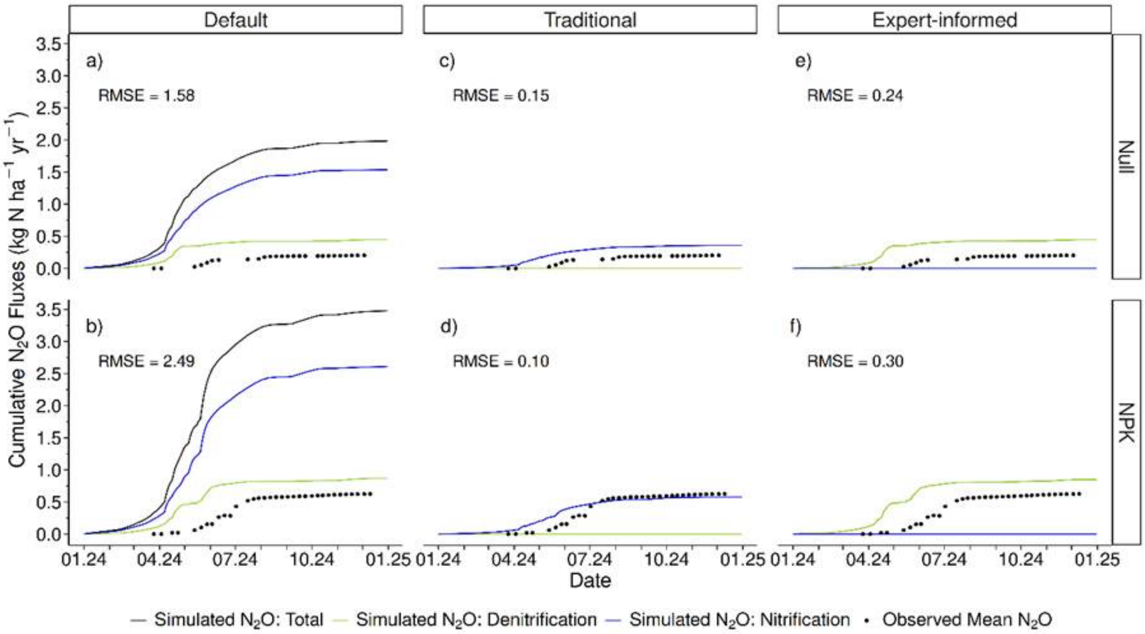


Fig. 4 DayCent simulations of the cumulative N_2O fluxes for the Null and NPK treatments of the sugar beet crop at the Demo site in Switzerland using the default (a-b), traditional calibration (c-d), and expert-informed (e-f) parameter values. Total cumulative N_2O emission (black) and N_2O production from denitrification (green) and nitrification (blue) are represented by the solid lines, and the observed mean cumulative N_2O flux measurements are represented by the black dots. The root mean square error (RMSE) represents the deviation between simulated and measured cumulative total N_2O flux values.

4.3.2.2 Discussion

This study focuses on the parameters that influence the effect of soil water content on the nitrification and denitrification processes in the DayCent model because there were noted discrepancies in the simulated and measured soil water content at this site. These inconsistencies were unaddressed by the model's default settings and unaccounted for by the traditional calibration. Consequently, predictions of total N_2O flux using the default settings had the highest error and predictions of N_2O contributions from nitrification and denitrification were wrong, as compared to source attribution by isotope measurements. While the traditional calibration provided the best model fit for total N_2O flux, the expert-informed approach better represented N_2O emissions from nitrification and denitrification at the Demo trial. Inconsistencies in DayCent's simulations of soil water content have been observed in other studies (Brilli et al., 2017; Gaillard et al., 2018; Guest et al., 2017; Stehfest and Müller, 2004). Overall, factors such as errors in the site input data and limitations in the modelling of soil processes that may impact water flow may account for these variabilities (Del Grosso et al., 2019; Scheer et al., 2014; Wagner-Riddle et al., 2017). Modifying general soil properties could potentially improve DayCent's prediction of soil water content (Smith et al., 2008). However, N_2O flux for this region has already undergone extensive calibrations (dos Reis Martins et al. 2022), and maintaining the site-specific soil parameters was preferable to reflect actual soil conditions at the Demo site, as altering them could affect other model outputs such as crop yields, which were well predicted by the regional study (Del Grosso et al., 2011; Fitton et al., 2014). Therefore, only adjustments to parameters that influence the effect of soil water content on the nitrification and denitrification processes in DayCent were performed at the Demo site because they directly addressed discrepancies in the model's depiction of the soil moisture environment and its impact on key underlying processes that affect model results.

Unfortunately, measured WFPS values from 2024 were unavailable because of complications with fieldwork. As daily temperature and precipitation events differ annually, and water flow is simulated on a daily time step within the model, it is not expected that WFPS simulations would be the same for each year (Del Grosso et al., 2011). However, it was important to compare the temperature and precipitation data from 2023 and 2024 to confirm that the weather at the site was consistent. Since the model used the same input data (site details and soil properties) and the monthly rainfall was not significantly different between 2023 and 2024, it is presumed that DayCent simulated discrepancies in soil moisture levels similarly for both years.

In this study, the model's overestimation of WFPS at field capacity and underestimation at wilting point at different times of the year may appear contradictory, but these discrepancies stem from distinct sources. For example, at this site the overestimation of WFPS at field capacity was prompted by precipitation events which increased the WFPS more within the model than on the field. This indicates insufficient water movement in the model, possibly because DayCent is unable to represent certain soil hydrological processes, such as preferential macropore flow, which was shown to improve drainage. In a study of soil water and N dynamics in eastern Canada, Guest et al. (2017) reported similar inconsistencies between DayCent-simulated and observed volumetric soil water content at different cropland sites during winter and early spring. The observation that DayCent overrepresented the frequency at which WFPS was at or below the site's wilting point during late spring and summer aligns with established patterns of WFPS simulations during the growing season (Guest et al., 2017; Jarecki et al., 2008, Smith et al., 2008). Lower precipitation and higher crop transpiration rates during this period resulted in DayCent simulating drier conditions than those measured in the field. Despite being a reasonable representation of soil water flow, the model's one-dimensional simplification, coupled with DayCent's lack of consideration of factors like lateral flow, limits its accuracy.

Subsequently, inconsistencies in DayCent's soil water content most likely led to overestimations of N_2O production from nitrification in the simulations that were performed using the parameters values from the default model settings and the traditional calibration. Within the model, nitrification is the dominant source of N_2O emissions under aerobic conditions (WFPS between 35-60%) (Bateman and Baggs, 2005), and N_2O can also be emitted via nitrification at field capacity depending on the value of the N2Oadjust_fc parameter (as higher values permit increased emissions). Denitrification is regarded as the main pathway that contributes to N_2O emissions under high soil moisture conditions, which is defined by a specific threshold (WFPS > 60%) (Wang et al., 2021). The default and traditional calibration parameterisations overestimated N_2O production via nitrification because non-zero values of the N2Oadjust_fc and N2Oadjust_wp parameters permitted N_2O emissions via this process at these particular points on the soil moisture regime. As denitrification is the primary source of N_2O emissions, these parameterisations do not align with the isotopic composition results since N_2O emissions are not emitted via nitrification under either soil moisture condition at this site.

Modifying the N2Oadjust_fc, N2Oadjust_wp, and wfpsdnitadj parameters were required to reconcile the inconsistencies between DayCent's simulations of WFPS and process-based understanding gathered from the observational methods. Namely, most of the N_2O emissions for both the Null and NPK treatments occurred between April and August, which suggests that denitrification occurs across a broad spectrum of soil moisture conditions. Model fit improved for simulations with the traditional and expert-informed parameters because the values of the N2Oadjust_fc and N2Oadjust_wp parameters were lowered, which reduced N_2O emissions via nitrification and better reflected field conditions at the Demo site. The value of the wfpsdnitadj parameter also needed to be refined in the expert-informed approach to reflect the N_2O emissions from denitrification. This was achieved by shifting the threshold, and thus the range within which denitrification could occur along the soil moisture gradient within the model (Xing et al., 2023). At this site, the wfpsdnitadj parameter needed to be adjusted to allow denitrification to occur under drier soil moisture conditions because DayCent continuously simulated lower WFPS levels during the growing season than was measured on the field. DayCent simulations with the traditional parameterisation did not accurately represent the primary source of N_2O emissions at the Demo site because the wfpsdnitadj value was greater than one, which required wetter soil conditions to facilitate N_2O emissions through denitrification. When the wfpsdnitadj parameter was reduced to one, as in the simulations with the default and expert-informed parameterisations, the threshold is lowered and denitrification could occur under drier conditions within the model (Xing et al., 2023).

4.3.3 The LandscapeDNDC study

The overall aim of this study is to improve the ability of the biogeochemical model Landscape DNDC to calculate the relative contributions of the main microbial production processes nitrification and denitrification to the total N_2O emission using source process information provided by isotope measurements. LandscapeDNDC is a simulation framework for terrestrial ecosystem models with a focus on the coupled carbon (C) and N cycling and associated N losses from agricultural and forest ecosystems. The model setup that has been used in this study includes the soil biogeochemical model METRX and the hydrology model WatercycleDNDC (Kiese et al. 2011, Kraus et al. 2015). As this configuration does not allow calculation of isotopic compositions, LandscapeDNDC was used in combination with the Stable Isotope Model for nutrient cycles (SIMONE) model. To calculate N-compound isotopic composition, SIMONE uses the Rayleigh equations of isotopic distillation (Mariotti et al., 1981). While one central quantity of the aforementioned approach is the residual fraction of the substrate, the other is the isotope effect, i.e., the constant that describes the difference in reactivity between the light and heavy isotope. The residual fraction is provided by LandscapeDNDC's soilchemistry module METRX to SIMONE, and the isotope effects originate from literature resources.

While SIMONE calculates the isotopic composition of all N-compounds that appear in LandscapeDNDC, not all isotopic quantities are equally suitable for obtaining source process information. Some isotopic quantities, such as soil $\delta^{15}N$, represent N cycling over long time periods, i.e., decades, or $\delta^{15}N$-N_2O depend on the isotopic composition of different precursor materials such as ammonium or nitrate. However, site preference (SP), introduced in section 4.1, does provide information on the relative contribution of different N_2O producing microbial processes (Toyoda et al., 2002; Sutka et al., 2006; Heil et al., 2014), and was therefore included in this study as a second calibration variable. Thus, off-line coupling of LandscapeDNDC and SIMONE allows modeling the dynamics of N-isotopic composition in biogeochemical nitrogen cycling (Denk et al., 2019, 2017), which is the basis for a seamless integration in automated calibration setups considering both N_2O flux and isotopic composition.

4.3.3.1 Methods

To achieve a seamless, automated approach to assess the benefit of isotope information on model calibration, a novel calibration and validation framework was developed. This framework is schematically represented in Fig. 5. In brief, most influential parameters of LandscapeDNDC for N_2O emissions are identified by means of a global sensitivity analysis. Subsequently, parameters are calibrated using measurements and likelihood estimation, which leads to a posterior distribution of parameter vectors.

Since it was expected that the additional information on source processes provided by the isotope measurements constrains the plausible parameter sets, the posterior distributions are used to estimate the model parameter uncertainty based on a Monte Carlo resampling approach, specifically a Sampling-Importance-Resampling approach (e.g., Gurung et al., 2020). The calibration-uncertainty estimation was carried out in two stages: following the left branch in Fig. 5, we evaluate a reference model uncertainty which makes use of N_2O flux measurements alone; second we apply a combined scheme involving both branches simultaneously to determine the model parameter uncertainty, taking both the N_2O flux measurements and isotopic composition measurements into account. More specifically, the global sensitivity analysis led to a list of 17 selected model parameters, which are highly influential on production of N_2O, including through adjustment of denitrification and nitrification pathways. The values of these 17 parameters were sampled from a uniform distribution over the allowed ranges in the model. In total, over 16000 parameter vectors were sampled as model inputs and

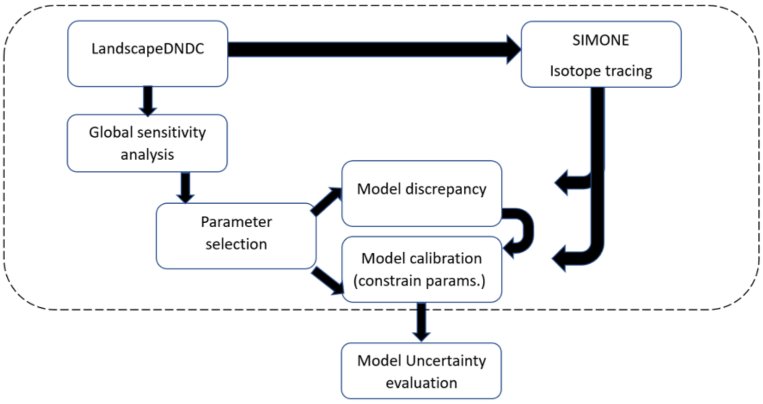


Fig. 5: Schematic flowchart showing the key steps that we use to arrive at estimates of model parameter uncertainty.

these were used to run corresponding LandscapeDNDC and SIMONE model iterations for each site. The statistics regarding the plausibility of parameter vectors are subsequently obtained by estimating the likelihood of a given parameter vector occurring, combined with the knowledge of the prior distributions from which the vectors were sampled which in this case are all uniform. We resample from the new posterior distribution of parameter vectors, weighted by the corresponding probability based on the likelihood of each vector, and then extract the mean and standard deviation on the corresponding daily simulation outputs for N_2O and site preference. We evaluate the goodness of fit for each calibration be evaluating the RMSE of the measured data points against the default and calibrated simulations.

4.3.3.2 Datsets used

In addition to the new field site at Zürich (Demo site, section 4.3.1) established as part of the PARIS project, a Swiss grassland site located at Chamau was used for LandscapeDNDC isotopic calibration. The Chamau site was included with a view to improving general model parameterisation for regional to national up-scaling as it is important to distinguish between arable and grassland sites for calibration purposes, due to the distinct differences in respective soil properties. The site at Chamau is an intensively managed grassland at an elevation of 398m, with anoxic gleysol with a soil organic carbon content of 4.23%, for which N_2O fluxes and corresponding isotopic composition measurements are available at daily resolution from a summer campaign running from June to September 2013 (Wolf et al., 2015).

The measurement techniques applied to the Demo site in Zürich led to different measurement frequency than Chamau, with each measurement corresponding to an average over the preceding seven days. This led to a sparser measurement dataset, with a larger potential for the calibration results to be impacted by individual outlier measurements and for the model to become incorrectly constrained. To maximize data quality, we retain only measurements in which, outside of the four weeks following fertilization, the data either agrees within uncertainty with the control treatment or for which at least two chambers were operational. Observed site preference values less than -1.6‰ are assumed for the purpose of model calibration to be -1.6‰, as this is the lowest possible value reachable by the model, and is only reached in the case where 100% of the N_2O flux is simulated to arise from denitrification.

4.3.3.3 Results and discussion for the LDNDC study

The default simulations for the Demo site shows dynamics with high values of site preference relative to the corresponding observations, and for the Chamau site, modeled SP values are also overestimated during one extended period in summer when soils were relatively dry. This suggests that LandscapeDNDC simulations are systematically overestimating the contribution of nitrification, shown in Fig.6. It is noteworthy that both investigated biogeochemical models, LandscapeDNDC and DayCent, overestimate nitrification despite model structural differences. To address this, a calibration focusing first on the three nitrification parameters out of the 17 most influential parameters was carried out for the arable Demo and grassland Chamau sites, and then using the 17 most influential parameters on N_2O emissions, including both nitrification and denitrification parameters. The results are collected respectively in Figs. 7-8 and Figs. 9-10.

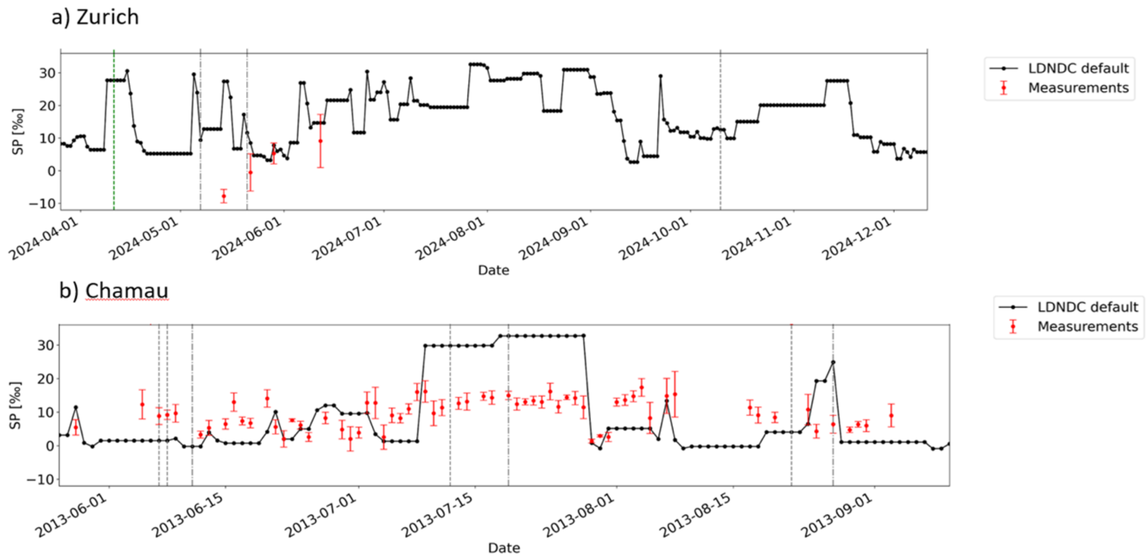
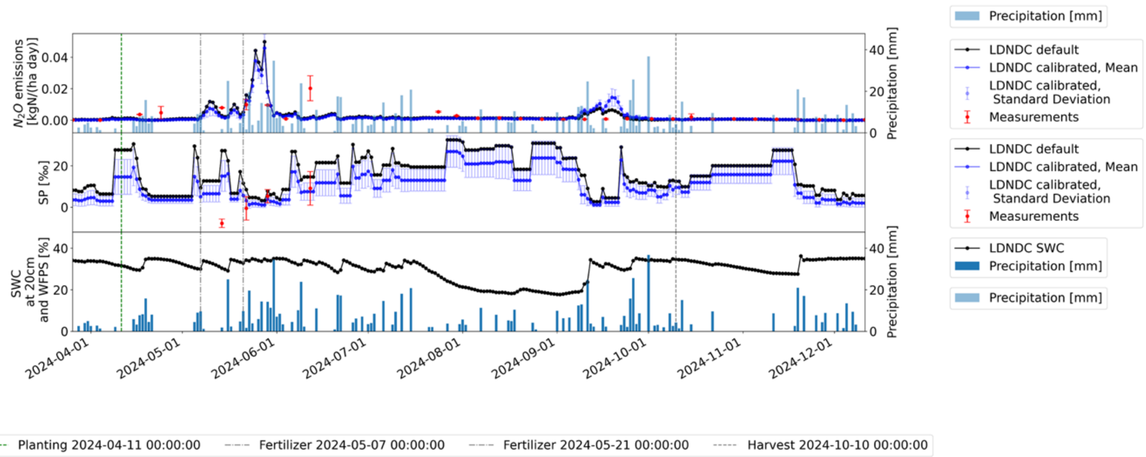


Fig. 6: Simulated and measured site preference results, in which during periods of dry soils the effects of modeled nitrification are overestimated.

The resulting calibration for the Demo site is shown in Fig. 7, which shows that the calibration based on N_2O data alone does already favour parameter vectors that reduce nitrification, but does not significantly change the profile of simulated emissions. A simulated rewetting event is observed at the end of September, both before and after calibration, which was not observed in the measurements. In the absence of soil water content data for the year 2024, it is not possible to comment further on the discrepancy. The corresponding isotopic calibration, including in addition the site preference as a calibrated output variable, drives the site preference down over the whole campaign period, and changes the N_2O flux dynamics.

However, over the course of the whole season, the change in the RMSE before and after calibrations is negligible (see Table 3). A key result can already be observed from these calibrations, namely that the calibration, which additionally includes site preference, leads to a visible reduction in the error bars corresponding to the model parameter uncertainty around high flux events. Additionally however, in this case, the magnitude of the peak reduction obtained from the calibration including isotopic composition overshadows the percentage variation in model parameter uncertainty, and in fact on the annual scale, the uncertainty on the N_2O emissions for this case has marginally increased from the addition on isotopic composition (Table 4, 2nd column).

a) Reference uncertainty



b) Uncertainty evaluated using isotopic composition

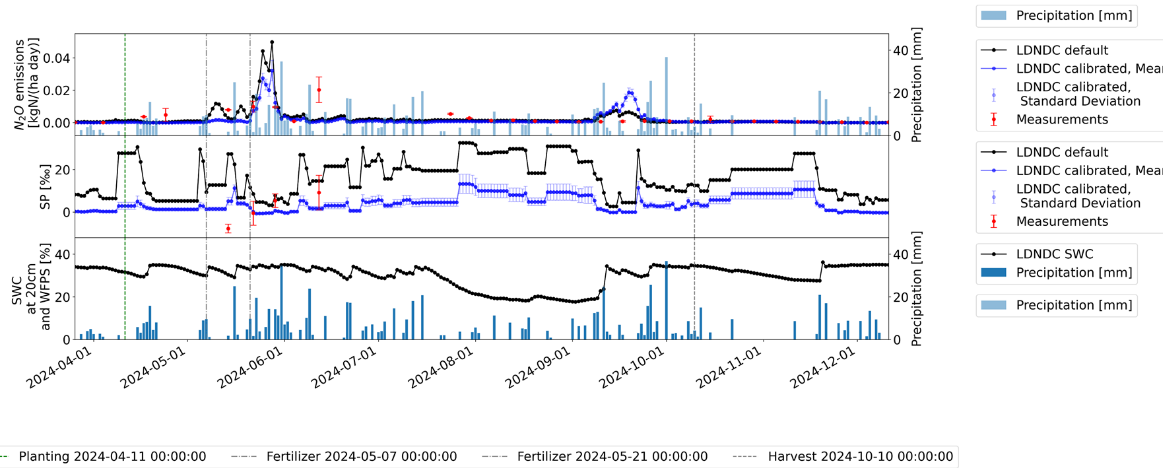


Fig. 7: results of nitrification calibration and model parameter uncertainty evaluation on the Demo site using a) N_2O flux measurements and b) both N_2O flux and site preference observations.

Table 3: RMSE values from all attempted calibration strategies for the grassland (Chamau) and arable (Zürich) sites.

LDNDC simulations	Default	N_2O calibrated	N_2O + SP calibrated	Default	N_2O calibrated	N_2O + SP calibrated
	RMSE N_2O [kg N ha^{-1} day^{-1}]			RMSE SP [‰]		
Zürich (nit. parameters)	0.007	0.007	0.007	15.0	11.0	8.1
Zürich (17 parameters)	0.007	0.005	0.005	15.0	9.6	6.7
Chamau (nit. parameters)	0.039	0.039	0.038	11.5	6.9	6.3
Chamau (17 parameters)	0.039	0.040	0.041	11.5	8.2	5.0

The results of the calibration for the site Chamau using the three nitrification parameters are shown in Fig. 8. The dynamics between both calibrations and the default do not vary greatly in this case, since adjusting nitrification alone cannot account for the N_2O flux observed following rewetting at the end of July 2013, as the site preference indicates that following the rewetting peak the default model does not achieve the rebound in site preference, and this behavior requires additional calibration of other relevant parameters, including denitrification parameters. This also explains the low reduction of uncertainty for the runs exclusively including nitrifcation parameter (Table 4, column 4).

Next, we examine the results of a more comprehensive parameter calibration on the two candidate sites. The results for Chamau are collected in Fig. 9, and the calibration results for the Demo site are shown in Fig. 10.

In the case of Chamau, after both the reference and isotope calibrations using 17 parameters, the simulated emissions show a much stronger response to management and rewetting events and perform better than the default parameterization when compared to the observations, see Fig. 9. The uncertainty associated to the simulated peak emissions is visibly decreased from the reference to the isotopic calibration scheme (Table 4, column 5). This showcases the potential value of isotopic composition measurements of N_2O fluxes, specifically site preference, as a tool to help constrain model parameter uncertainty. In addition, the site preference results reveal a strong model bias towards nitrification in the second half of July that persists following the calibration. This was the driest part of the measured period (Wolf et al., 2015). Following the rewetting event at the end of July, LandscapeDNDC is slow to respond (if at all) with a recovery of nitrification processes. This additionally showcases the potential for isotopic measurements to identify systematic model biases. Addressing the source of this bias will be the subject of future work.

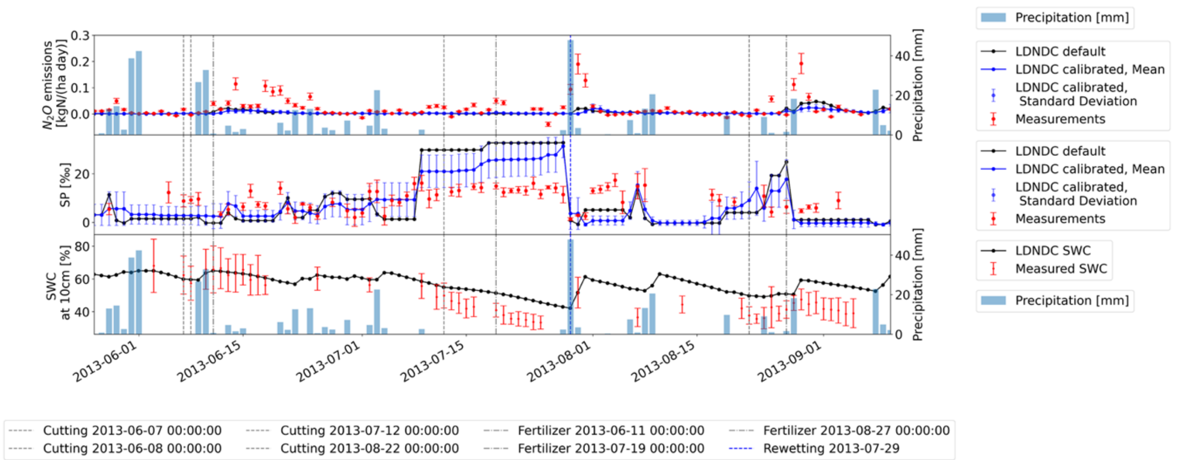
For the Demo site, the 17 parameter calibration on N_2O only was successful in partly reducing the height of the post fertilizer emissions peak towards the values expected from the measurements. Due to the scarcity of site preference measurements, the calibration strategy including site preference led to less plausible N_2O simulation results in both the previously discussed cases, with an artificially raised background baseline. The reintroduction of denitrification parameters into this calibration under conditions of data scarcity was not successful in returning a plausible calibration, see Fig. 10. For both the arable and grassland sites, we do consistently observe that the inclusion of site preference as a second calibration variable leads to a significant reduction in the model parameter uncertainties by on average 39.5%, as summarized in Tab. 4. RMSE values are collected comparing the default LDNDC results to the calibrated model results in Tab. 3.

To understand how different the calibrated parameter sets for each site are with respect to the default, we evaluated the average parameter vectors obtained from both reference and isotopic calibrations in the 17 parameter calibrations. We used these values to examine the distance between the average calibrated and default parameter vectors, by considering their difference from the default vector component-wise. To represent the share of the changes attributable to denitrification and nitrification parameters respectively, we tally the absolute magnitude of the percentage changes to all individual parameters and calculate what share of this corresponds to changes in denitrification and nitrification parameters. The calibrations using isotopic composition show a clear reduction in the amount that nitrification related parameters are adjusted relative to the default. This is consistent with the fact that the nitrification parameters are strong drivers of N_2O flux emissions and that without the additional information supplied by isotopic calibration, nitrification parameterisations that achieve the right results for wrong reasons can be favoured. Hence isotopic composition measurements assist in constraining model nitrification parameterisations.

Table 4: Summary of annual N_2O emissions per site following the two calibration schemes using 17 parameters and corresponding N_2O uncertainty reduction from inclusion of isotopic composition.

	Zürich (nit. parameters)	Zürich (17 parameter)	Chamau (nit. parameters)	Chamau (17 parameter)
Reference calibration N_2O emissions [kgN/(ha yr)]	0.69±0.11	0.32±0.33	1.11±0.32	3.21±3.85
Isotope calibration N_2O emissions [kgN/(ha yr)]	0.43±0.08	1.90±0.51	1.41±0.15	2.30±1.24
Percentage uncertainty reduction on N_2O emissions	-2.66%	76.3%	18.2%	66.0%

a) Reference uncertainty



b) Uncertainty evaluated using isotopic composition

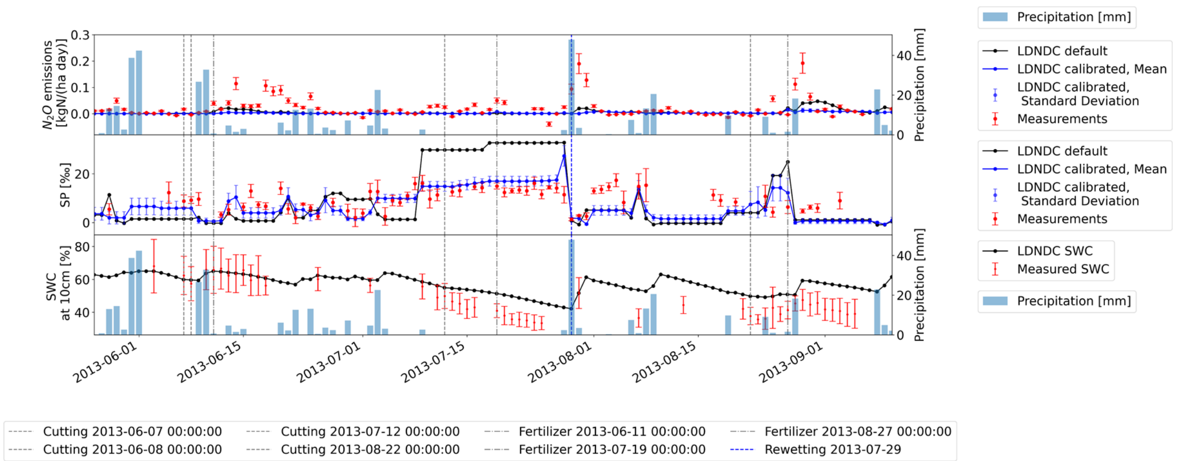
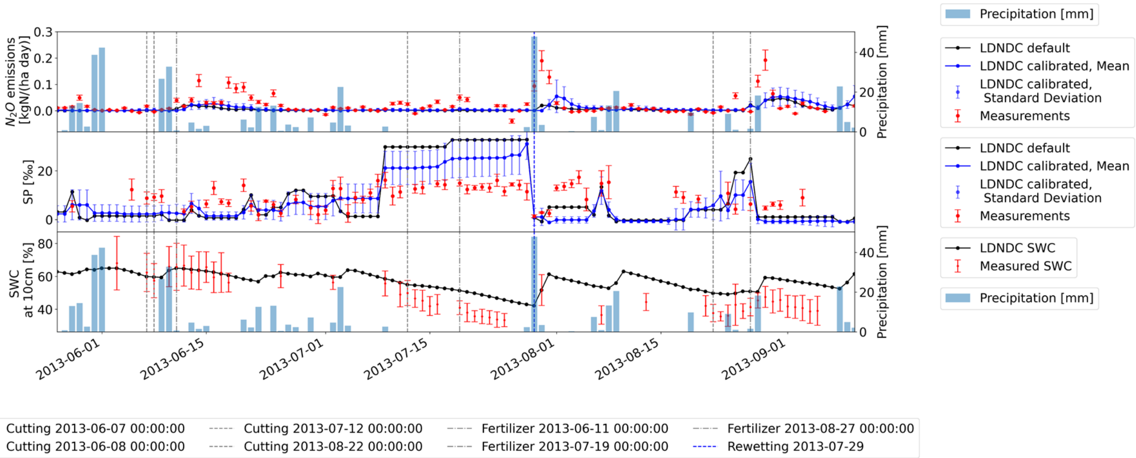


Fig. 8: results of nitrification calibration and model parameter uncertainty evaluation on the site Chamau using a) N_2O flux measurements and b) both N_2O flux and site preference observations.

a) Reference uncertainty



b) Uncertainty evaluated using isotopic composition

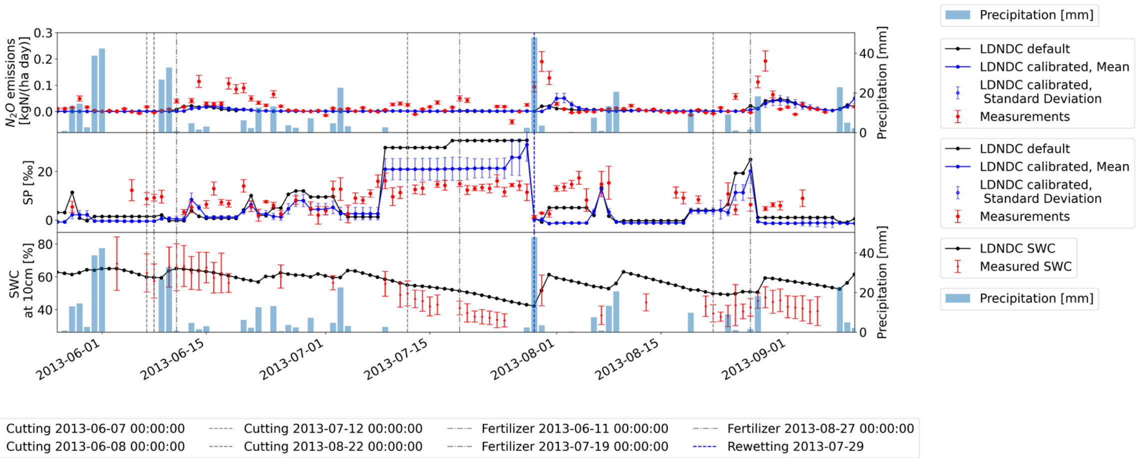
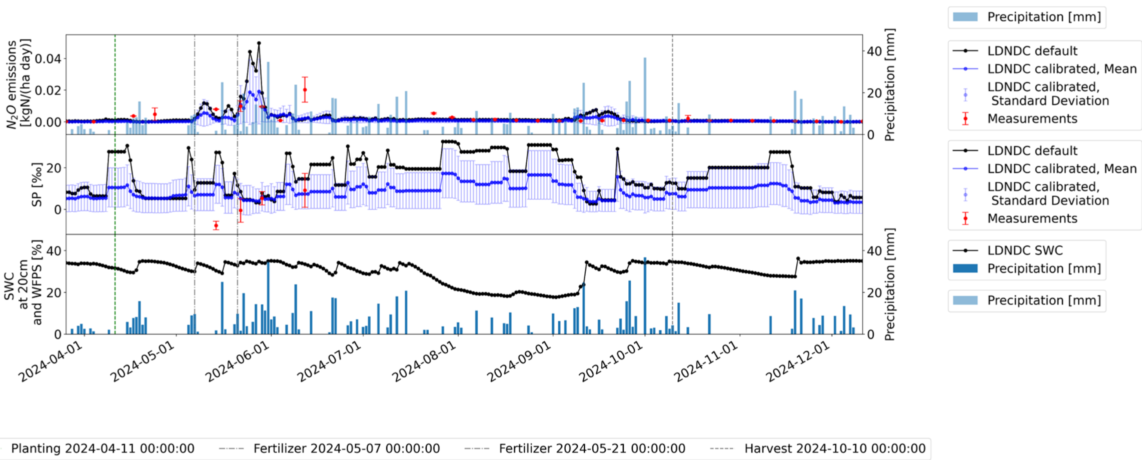


Fig. 9: results of 17 parameter calibration and model parameter uncertainty evaluation on the site Chamau using a) N_2O flux measurements and b) both N_2O flux and site preference observations

a) Reference uncertainty



b) Uncertainty evaluated using isotopic composition

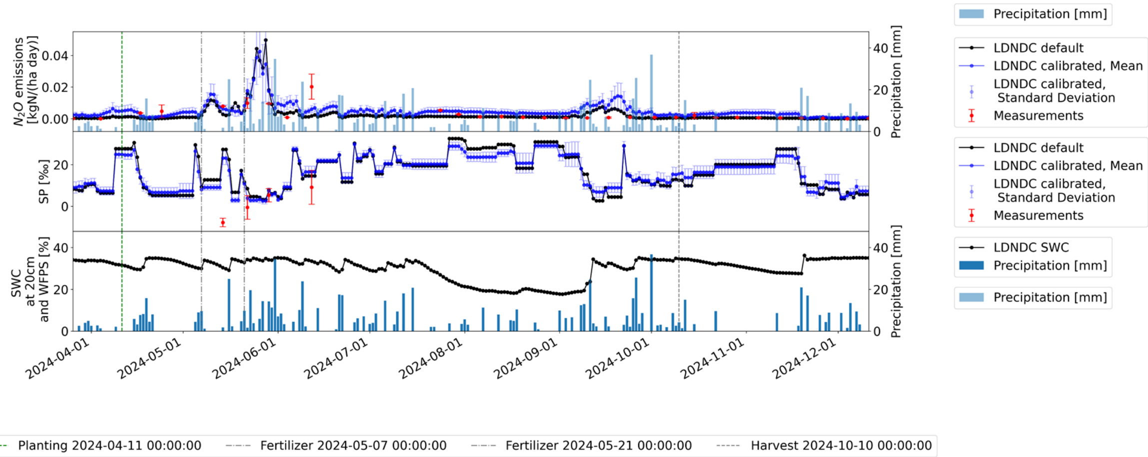


Fig. 10: Zürich site, results of 17 parameter calibration and model parameter uncertainty evaluation on the site Chamau using a) N_2O flux measurements and b) both N_2O flux and site preference observations.

4.4 Conclusion and possible impact

This part of the PARIS project focused on creating new field data and calibration frameworks that account for the different N_2O production pathways within the soil, through measurement of isotopic composition. Two biogeochemical models, DayCent and LDNDC, were studied, respectively, and found to overestimate the role of nitrification in the production of N_2O fluxes, especially in situations with dry soils for LandscapeDNDC.

For the study with the biogeochemical model DayCent, we started with a well-calibrated version in terms of total N_2O emissions. A comparison of the contributions of the two dominant processes that lead to N_2O production in soils (nitrification, denitrification) of the model versus estimates using stable isotope analysis clearly showed a strong disagreement. Additionally, comparisons of soil moisture measurements indicated that soil water processes were not well parameterized. Based on these discrepancies, an expert informed calibration was performed which clearly improved the performance of DayCent for the study site in Switzerland, while total N_2O emissions remained similar. This study showed that the special stable isotope analysis that were performed as part of milestone M19 was very useful to critically evaluate N cycling processes in soils that lead to N_2O emissions. However, since the model-observation comparison was restricted to a single site, we decided to keep the initial parametrisation for the national-scale simulations within the PARIS project (i.e., for the comparisons against the atmospheric inverse modelling), as earlier studies performed at Agroscope have shown good agreement with N_2O fluxes from all available long-term experiments in Switzerland (dos Reis et al. 2022; dos Reis et al. 2024).

The LDNDC study combined simulated results with isotope tracing results from the model SIMONE, allowing information about the ratio of nitrification to denitrification, contained in the site preference, to further guide the calibrations. Data from the new arable field site generated as part of the PARIS project were used in addition to published data from a Swiss grassland site (Denk et al., 2019). The calibration framework developed which combines LDNDC with SIMONE was shown to be capable of adjusting the balance and improving the fit for site preference. A second key result of this study was the reduction in model parameter uncertainty obtained by including measurements of isotopic composition. This is a consequence of the fact that complex biogeochemical models often have parameterisations that successfully describe observed dynamics but are incorrect at the level of production processes. Thus, we were able to demonstrate that the inclusion of isotopic composition measurements is a critical tool for further constraining process-based biogeochemical models.

Comparison to observations showed that both the default LDNDC and DayCent parameterizations are systematically overestimating the role of nitrification and suggests that researchers employing process-based biogeochemical modeling can benefit strongly from use of data that allows process attribution, such as isotopic composition. On the basis of added value demonstrated here for process-based modeling, it is expected to be of value for the experimental community to consider the inclusion of isotopic composition measurements at the time of experiment/campaign design.

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5. History of the document

Version	Author(s)	Date	Changes
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