

Denitrification is the main nitrous oxide source-process in grassland soils according to quasi-continuous isotopocule analysis and biogeochemical modelling

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Key Points:

1. Spatial allocation and high instrumental sensitivity achieved with automated flux-chambers and laser spectroscopy with preconcentration
2. First quasi-continuous analysis of the intramolecular ¹⁵N distribution (known as *site preference*, *SP*) of soil-emitted N₂O over three months
3. Measurements and biogeochemical modelling revealed that denitrification was the dominant N₂O production pathway in the managed grassland

Abstract

Isotopic composition of soil-emitted nitrous oxide (N_2O), especially the intramolecular distribution of ^{15}N in N_2O known as site preference (SP), can be used to track the two major N_2O emitting soil-processes nitrification and denitrification. On-line analysis of SP in ambient air has been achieved recently, yet those approaches only allowed addressing large areas (footprints) on the basis of strong changes in surface atmospheric N_2O concentrations. Here, we combined laser spectroscopy with automated static flux-chambers to measure, for the first time, SP of low N_2O fluxes with high sensitivity and temporal resolution and to explore its spatial variability. The measurements were then used to test the N_2O isotope module SIMONE in combination with the biogeochemical model LandscapeDNDC to identify N_2O source processes.

End-member-mixing-analysis of the data revealed denitrification as the predominant N_2O source. This finding was independent of the soil water content close to the soil surface, suggesting that N_2O production in the subsoil under high water-filled pore space conditions outweighed the potential production of N_2O by nitrification closer to the surface. Applying the SIMONE-LandscapeDNDC model framework to our field site showed that the modelled SP was on average 4.2 ‰ lower than the observed values. This indicates that the model parameterization reflects the dominant N_2O production pathways but overestimates the contribution of denitrification by 6 ‰. Applying the stable isotope based model framework at other sites and comparing with other models will help identifying model shortcomings and improve our capability to support N_2O mitigation from agricultural ecosystems.

Plain Language Summary

Between August and December 2017 the concentration and isotopic composition of soil emitted nitrous oxide (N_2O) was measured above a grassland site in Central Switzerland. Automated flux-chambers were coupled to a custom-built preconcentration and laser spectroscopy based on-line measurement method. The obtained results were used to validate a recently developed isotope sub module (SIMONE) for a biogeochemical model (LandscapeDNDC), to simulate fluxes of trace gases. Our results show a clear predominance of denitrification as the primary N_2O emitting source process. In contrast to previous studies, this dominance led to stable N_2O site preference values throughout the measurement campaign, a feature that was also represented by SIMONE. These findings will bridge current shortcomings in our model understanding and thereby help developing targeted N_2O mitigation strategies.

1 Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) and accounts for 6 % of the total anthropogenic radiative forcing (Ravishankara et al., 2009). Furthermore, it is the main stratospheric ozone (O_3) depleting substance. The mean tropospheric abundance of N_2O has steadily increased from 270 ± 7 ppb (IPCC, 2013) during the pre-industrial era to 328.9 ± 0.1 ppb in 2016 (WMO & GAW, 2017) at an average rate of 0.73 ± 0.03 ppb yr^{-1} over the last three decades (IPCC, 2013). The main driver behind the observed increase of atmospheric N_2O is the use of fertilizer in agriculture, which fuels microbial N_2O production in soils (IPCC, 2013). N_2O emissions from soils are closely linked to the microbial processes nitrification, during which NH_4^+ is oxidized to NO_3^- , and denitrification, a process during which NO_3^- is reduced to N_2 . As any biological process, nitrification and denitrification depend on environmental conditions, which are known to vary significantly on small spatiotemporal scales. However, understanding how much of the two processes finally drives soil N_2O emissions is essential for developing targeted N_2O mitigation strategies. Although source attribution on sectorial level,

i.e. to categories like agriculture, industry or biomass burning is possible (Davidson & Kanter, 2014), the partitioning of soil N₂O emissions to the underlying processes (source partitioning) remains challenging, for instance because different N₂O producing processes do occur simultaneously.

More recently the intramolecular isotopic composition of soil emitted N₂O has been identified to be a powerful tool for disentangling source processes (Toyoda et al., 2005; Sutka et al., 2006; Decock & Six, 2013). The relative abundance of the four most abundant singly substituted N₂O isotopocules, ¹⁴N¹⁴N¹⁶O (99.03 %), ¹⁴N¹⁵N¹⁶O (0.36 %), ¹⁵N¹⁴N¹⁶O (0.36 %) and ¹⁴N¹⁴N¹⁸O (0.20 %), is expressed with respect to a standard reference material using the delta (δ) notation in permil (‰) according to equation Eq 1.

$$\delta X = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}} \quad \text{Eq 1}$$

In Eq 1, X denotes ¹⁵N^α, ¹⁵N^β or ¹⁸O, while R refers to the sample gas or standard gas isotope ratios ¹⁴N¹⁵N¹⁶O/¹⁴N¹⁴N¹⁶O (for ¹⁵N^α), ¹⁵N¹⁴N¹⁶O/¹⁴N¹⁴N¹⁶O (for ¹⁵N^β) or ¹⁴N¹⁴N¹⁸O/¹⁴N¹⁴N¹⁶O (for ¹⁸O), respectively (Toyoda & Yoshida, 1999). The ¹⁵N/¹⁴N ratio is referenced to the international isotope ratio scale atmospheric N₂ (AIR-N₂), while the ¹⁸O/¹⁶O ratio is referenced to Vienna Standard Mean Ocean Water (V-SMOW). While the total ¹⁵N content of N₂O is reported as bulk ¹⁵N content (δ¹⁵N^{bulk}, Eq 2), the predominance for ¹⁵N substitution in the central position is reported as site preference (SP, Eq 3) (Toyoda & Yoshida, 1999; Mohn et al., 2016).

$$\delta^{15}\text{N}^{\text{bulk}} = (\delta^{15}\text{N}^{\alpha} + \delta^{15}\text{N}^{\beta}) / 2 \quad \text{Eq 2}$$

$$\text{SP} = \delta^{15}\text{N}^{\alpha} - \delta^{15}\text{N}^{\beta} \quad \text{Eq 3}$$

Source partitioning between the process groups (i) (nitrifier) denitrification (N₂O_D) versus (ii) nitrification, abiotic N₂O production and fungal denitrification (N₂O_N) is possible as the site preference of the emitted N₂O is distinctly lower for the first (N₂O_D, -0.9 ± 4.1 ‰) as compared to the second category (N₂O_N, 32.8 ± 2.2 ‰) (Denk et al., 2017; Lewicka-Szczebak et al., 2017; Koba et al., 2009). Generally two end-member mixing maps, additionally accounting for isotopic fractionation due to N₂O reduction by denitrifying bacteria, are applied for data interpretation (Koba et al., 2009; Decock & Six, 2013; Wolf et al., 2015; Lewicka-Szczebak et al., 2017; Verhoeven et al., 2019; Ibraim et al., 2019). This approach has shown potential to source partition in laboratory experiments and in engineered systems under defined reaction conditions or microbial consortia (Wunderlin et al., 2012; Koster et al., 2013), while in natural systems such unequivocal distinction is impeded. The combination of analytical challenges and the complexity of data interpretation is the reason for the scarcity of studies interpreting N₂O isotope signatures from natural systems.

For many years, isotope ratio mass spectrometry (IRMS) was the only technique with sufficient sensitivity to trace natural abundances of N₂O isotopocules (Toyoda & Yoshida, 1999; Röckmann et al., 2003). More recently, laser spectroscopy-based methods were developed and are increasingly used to analyse the stable isotopes of atmospheric trace gases (Süess et al., 2016; Winther et al., 2018). The on-line analysis of N₂O isotopocules in ambient air, however, is complicated by the fact that variations in concentration and isotopocule abundances are small (Mohn et al., 2012; Yamamoto et al., 2014). Nevertheless, N₂O isotopic analysis in ambient air at sensitivities similar to those achieved by IRMS has been presented using a more sophisticated approach deploying quantum cascade laser absorption (QCLAS) spectrometers in combination with automated preconcentration (Mohn et al., 2010; Wolf et al., 2015; Harris et al., 2017). Using a more compact spectrometer and a more powerful preconcentration device (TRace gas EXtractor, or TREX), the TREX-QCLAS method was recently re-designed by Ibraim et al. (2018) and applied at a grassland site in southern Germany (Ibraim et al., 2019). The measurements reached a level of precision sufficient to resolve

changes in ambient N₂O isotopocule concentrations. Using an end-member-mixing analysis approach (Keeling, 1958, 1961), the isotopic composition of soil-emitted N₂O was determined from N₂O accumulations in the nocturnal boundary layer. This technique did, however, not allow explicit spatial mapping and could not be implemented during the daytime due to atmospheric mixing. Higher temperatures and evaporation during the day alter the soil environmental conditions, which in turn might favour either N₂O_N or N₂O_D. Consequently, short-term changes in the relative contributions of N₂O produced via N₂O_N and N₂O_D due to diurnal variation of soil conditions may be concealed if measurements are restricted to the night.

Biogeochemical models such as DNDC/ LandscapeDNDC (Li et al., 1992a, 1992b; Li et al., 2000), CERES (Gabrielle et al., 2006) and DAYCENT (Del Grosso et al., 2000; Parton et al., 2001) simulate relevant N cycling processes and their dependence on soil environmental conditions. These models are increasingly used to assess the fate of N species in the environment, to transfer observations at a specific site to different soils and climates and to evaluate agricultural management options to reduce the release of N₂O and other N losses (Kim et al., 2015; Molina-Herrera et al., 2016). The parameterization of biogeochemical models can be improved combining models with the process information contained in the N₂O isotopic composition. Despite this potential for improvements, the implementation of isotopes in biogeochemical models has lagged behind (Rastetter et al., 2005). First steps in this direction have been made for the CLM-CN model (Houlton et al., 2015), the DAYCENT model (Bai & Houlton, 2009) and the non-equilibrium stable isotope simulator NESIS (Rastetter et al., 2005). Recently, Denk et al. (2019) developed the “Stable Isotope Model for Nutrient cycles” model (SIMONE), which uses fluxes between ecosystem N pools (soil organic N, mineral N, plants, microbes) calculated by biogeochemical models, and literature isotope effects to calculate the isotopic composition of soil N pools and N₂O emissions.

The objectives of this study were to i) quantify fluxes¹ and isotopic composition of N₂O emitted from a grassland site in central Switzerland, ii) map emissions explicitly in space and time by using flux-chambers to repeatedly determine the isotopic composition of N₂O emitted from soil during the day, iii) use the obtained data to source partition major soil microbial processes by carrying out end-member mixing model analysis and iv) assess the process parameterization of the biogeochemical model LandscapeDNDC by comparing measured fluxes and isotopic signatures of N₂O with results obtained using the LandscapeDNDC-SIMONE modelling framework.

2 Material and Methods

2.1. Characterization of the research site Beromünster

2.1.1. Study site

The study site is located on top of a hill at 797 m a.s.l in the vicinity of the decommissioned radio tall-tower of Beromünster (BRM; N: 47°11'22" E: 8°10'32") in central Switzerland. BRM was established as a measurement station for GHG monitoring within the SNF Sinergia project CarboCount (Oney et al., 2015) and in 2016 integrated to the Swiss National Air Pollution Monitoring Network (NABEL). In 2017, the mean annual precipitation and temperature were 1142 mm and 9.1 °C, respectively. The experimental site was a 10 m × 30 m area, which is part of a 3-ha grassland west of the tall-tower (Figure S1). The grasslands surrounding the Beromünster tower were grazed by cattle during the study-period. Soil properties at the BRM study site are given in Table 1.

¹ We use the term flux to describe the “emission of gas per unit area per unit time”

Table 1 Soil properties within the perimeter of the experimental site Beromünster

Depth (cm)	Bulk density (g cm ⁻³)	C _{org} (%)	N _{tot} (%)	pH (a.u.)	Clay (%)	Silt (%)	Sand (%)
7	1.3 ± 0.1	3.5 ± 0.5	0.6 ± 0.3	5.5	24.6 ± 0.5	42.9 ± 0.2	32.5 ± 0.6
14	1.4 ± 0.0	1.8 ± 0.2	0.2 ± 0.0	5.3	22.9 ± 0.4	40.1 ± 1.5	37.0 ± 1.4
32	1.4 ± 0.1	0.9 ± 0.3	0.1 ± 0.0	5.5	25.8 ± 1.4	39.2 ± 2.0	35.0 ± 1.2
50	1.5 ± 0.1	0.5 ± 0.1	0.1 ± 0.0	5.6	26.9 ± 0.5	40.6 ± 0.7	32.5 ± 1.1

As indicated in Figure S1, the study site was sub-divided into the sections B1, B2 and BF. Both B1 and B2 were equipped with three automated static chambers that were opened and closed by means of pneumatic actuators to determine N₂O fluxes during chamber closure. While B1 chambers were exclusively used for N₂O flux measurements, headspace air from the B2 chambers was preconcentrated for determination of N₂O isotopic composition. BF represents a 1 m × 1 m section that was treated identically to the B1 and B2 chambers' area regarding fertilizer addition and was used for soil sampling after fertilization in order to keep the ongoing measurements in the sections B1 and B2 undisturbed. When no recent fertilizer application had occurred, bi-weekly soil sampling was conducted at B1 and B2 (see section 2.1.3).

2.1.2. Environmental conditions and agricultural management

A wide range of meteorological and air quality related data are available from 15 March 2017 onwards, including air temperature and precipitation. In addition, a soil temperature profile (depths of 5, 10 and 15 cm) was installed between sites B1 and B2 using three PT100 sensors (IMKO, Ettlingen, Germany) and soil temperature in 5 cm depth was measured at B1 and B2 using the same type of sensors. A precipitation sensor (Campbell ARG100, Campbell Scientific, USA) was used to open the chambers upon rainfall. Soil volumetric water content (VWC) was determined with four ThetaML2x probes (Delta-T Devices, Cambridge, UK) distributed across the experimental site. While the probes integrate the VWC over a soil depth of 0 – 6 cm, water-filled pore space (WFPS) was calculated according to measured VWC by taking into account the observed soil characteristics (Wu et al., 2010).

Agricultural management comprised mowing (17 May, 19 June, 29 August and 24 October 2017) and fertilization. While the surrounding grassland site received two loads of manure on 27 May and 18 November, the perimeter of the experimental site was not manured to avoid cross-interference with own fertilizer-addition experiments.

2.1.3. N₂O fluxes, concentration of soil extracted NH₄⁺ and NO₃⁻, and δ¹⁵N of NH₄⁺ and NO₃⁻

Two sets of three chamber frames were inserted into the soil for each of the blocks (B1 and B2) a week before the measurements began. Adverse effects on the vegetation arising from shadowing were minimized by regularly mounting the chambers to the alternative frames. Fluxes of soil-emitted N₂O (f_{N₂O}) were measured between 23 August and 1 December 2017 using three opaque static chambers (hereafter referred to as 'chambers'; 0.5 x 0.5 x 0.5m) in combination with a field-deployable gas chromatograph with an electron capture detector (GC-ECD, GC-17A, Shimadzu) contained in a trailer. The chambers automatically closed for 48 minutes during which each chamber was consecutively sampled for three minutes. At the end of the three minutes period, 3 ml air were automatically injected into the GC-ECD for determination of N₂O mixing ratio, yielding four N₂O concentration measurements per chamber and closure cycle. In addition, calibration gas was injected twice every 24 minutes. Between flux measurements, the three chambers remained open for 48 minutes. Fluxes were calculated based on the increase of N₂O mixing ratios. Details of the method were previously presented by Butterbach-Bahl et al. (1997) and Rosenkranz et al. (2006).

Soil samples were collected bi-weekly between 23 August and 29 November, with increased sampling frequency during the fertilization experiments. In total, 116 soil samples of approx. 150 g (0-6 cm depth) were taken from the surroundings of the flux-chambers (prior to the fertilizer addition experiments) and from the section BF (during the fertilizer addition experiments as described in section 2.4). Soil (100 g) of soil were extracted with 150 ml 1 M potassium chloride (KCl, Merck KGaA, Germany), filtered (GE Healthcare Life Sciences, Whatman GF/A, United Kingdom) and the soil-extracts were stored at -20 °C. Subsequently, NH_4^+ and NO_3^- concentrations were determined colorimetrically with a spectrophotometer (AGROLAB Agrarzentrum GmbH, Germany).

In addition, all soil extracts were analysed for $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NH}_4^+$ using chemical methods (Zhang et al., 2015; Lachouani et al., 2010). $\delta^{15}\text{N-NH}_4^+$ signatures were determined with the same method as $\delta^{15}\text{N-NO}_3^-$ signatures after microdiffusion of NH_4^+ and alkaline persulfate oxidation of NH_4^+ to NO_3^- . NO_3^- was subsequently converted via NO_2^- to N_2O by acidic VCl_3 reduction and sodium azide reaction (Lachouani et al., 2010). Isotopic composition of N_2O was then measured by purge-and-trap isotope ratio mass spectrometry (cryotrap Gasbench - Delta V Advantage, Thermo Fisher, Vienna, Austria) and calibrated using appropriate natural ^{15}N abundance standards (Lachouani et al., 2010). The standard deviation of repeated measurements of a reference material was $< 0.2 \text{ ‰}$. The analytical work was carried out between 12 February and 2 March 2018 in the SILVER stable isotope laboratory at the Division of Terrestrial Ecosystem Research, University of Vienna.

2.2. N_2O isotopocule analysis

Between 29 August and 4 December, 610 and 828 measurements were obtained from the 2 m inlet and from the headspaces of the three B2 chambers, respectively, all being analysed with the TREX-QCLAS for concentration and isotopic composition of N_2O (Figure S2). A pressurized air tank (T) with an N_2O concentration and isotopic composition similar to that of ambient air was measured 542 times along with the ambient air measurements (Figure S3 – Figure S6). According to those 542 T measurements, the long-term analytical repeatability of the measurements spanning the whole measurement period was 0.61 ‰, 0.55 ‰, 0.47 ‰, and 3.3 ppb for $\delta^{15}\text{N}^\alpha$, $\delta^{15}\text{N}^\beta$, $\delta^{18}\text{O}$, and N_2O concentration measurements, respectively. The accuracy of the applied technique was additionally assessed by triplicate *in-situ* measurements of T, T1 and T2 undergoing identical treatment as the sample measurements by TREX-QCLAS and IRMS at ETH and at the Tokyo Institute of Technology (Tokyo Tech; Figure S7, Table S1 and Table S2). Average deviations of TREX-QCLAS to IRMS measurements are in the range 0.21 – 0.35 ‰ (IRMS ETH) and 0.03 – 0.48 ‰ (IRMS Tokyo Tech) for all isotope deltas ($\delta^{15}\text{N}^\alpha$, $\delta^{15}\text{N}^\beta$ and $\delta^{18}\text{O}$), indicating an excellent degree of accuracy.

2.2.1. N_2O isotopocule analysis with IRMS

For an independent validation, the target gases T, T1 and T2 as well as the sample gases from the chamber headspace of 26 September were analysed with IRMS at the Department of Environmental Systems Science, ETH Zurich (Verhoeven et al., 2019). To this end, discrete air samples were collected from the chamber headspace through a sample port using a 60 mL syringe at 0, 20, 40, 60, 80, 110 and 130 min time intervals after chamber closure. Subsamples from each time point were immediately injected in pre-evacuated 12 mL Labco exetainer and 110 mL serum crimp vials for GC (456-GC, Scion Instruments, Livingston, UK) and IRMS (IsoPrime100, Elementar, UK) analysis, respectively. Sampling was conducted for all three chambers, leading to a total of 21 samples. Sampling from tank T, T1 and T2 was done in a similar fashion, using a sampling port at the pressure valve (Table S1).

2.3. N addition experiments

To investigate the response of the N₂O isotopic composition to changes in substrate availability and environmental conditions, a set of experiments was designed aiming to trigger (i) nitrification and (ii) complete denitrification (i.e., N₂O reduction). For this purpose, 70 kg N ha⁻¹, either in the form of ammonium sulfate ((NH₄)₂SO₄, ≥ 99 % purity, Sigma-Aldrich Chemie GmbH, Switzerland) or potassium nitrate (KNO₃, ≥ 99 % purity, Sigma-Aldrich Chemie GmbH, Switzerland) was added following the procedure described below. As shadowing effects were negligible in November, only one frame set, i.e. three frames, of both B1 and B2 were supplied with fertilizer. This approach had the advantage, that we could compare the fertilized plots with non-fertilized plots. Hereafter, the framesets that have received fertilizer will be referred to as *treatment* framesets, while the framesets that have not received fertilizer will be referred to as *reference* framesets. After the fertilizer addition, the position of the B2 chambers was alternated daily between the treatment and reference frameset to test effects caused by the fertilizer addition. At B1, chambers remained on the treatment frameset. Details on the fertilizer addition can be found in the supplementary materials.

As mentioned in section 2.1.1 and 2.1.2, typical management practices at BRM include cattle grazing, manure application and mowing. Within the presented NH₄⁺ and NO₃⁻ application treatments, we used mineral fertilizers to stimulate specific microbial pathways, partly at the expense of representing typical grassland management practices. At the same time, the presented approach is a clear step forward in source partitioning N₂O fluxes to microbial processes within the framework of an open grassland ecosystem.

2.3.1. Isotopic characterization of fertilizers

The fertilizers ((NH₄)₂SO₄ and KNO₃) were analysed for their δ¹⁵N signature at the Department for Environmental Systems Science, ETH Zurich using IRMS. The instrumentation consisted of an elemental analyser (Flash EA, Thermo Fisher Scientific, MA, USA) coupled to a Delta^{Plus} XP Isotope Ratio Mass Spectrometer with a 6-port valve and a ConFlo III interface (Finnigan MAT, HB, Germany). Details of this method are presented by Werner et al. (1999). Obtained δ¹⁵N^{bulk} values of (NH₄)₂SO₄ and KNO₃ corresponded to 16.11 ± 0.04 ‰ and 3.25 ± 0.01 ‰, respectively.

2.4. Keeling plot analysis and daily mean source signatures

Source signatures of soil-emitted N₂O were derived using the Keeling plot approach (Keeling, 1958, 1961). The measurement routine allowed for one Keeling plot analysis for each B2 chamber per day. Retrieved signatures were only interpreted further if the Keeling plots' linear model was statistically significant, which was the case in 264 of 276 Keeling plots. To account for spatial heterogeneity, the source signatures derived for the three chambers were then pooled into daily mean values, weighing signatures of individual chamber measurements with the observed N₂O fluxes. δ¹⁵N^{bulk} signatures of N₂O prior to fertilizer application were corrected for the substrate δ¹⁵N^{bulk}-NO₃⁻ and δ¹⁵N^{bulk}-NH₄⁺ values as suggested by Koba et al. (2009), while for the period after the fertilizer addition also the δ¹⁵N^{bulk} values of applied (NH₄)₂SO₄ or KNO₃ were used. Statistical analysis was carried out using Matlab (MathWorks, Inc., MA, USA) and p < 0.05 was chosen as significance threshold unless stated otherwise.

2.5. Biogeochemical and isotope modelling using LandscapeDNDC and SIMONE

LandscapeDNDC (Grote et al., 2009; Haas et al., 2013) is a biogeochemical model simulation framework for terrestrial ecosystems to simulate carbon (C) and N cycling in agricultural and forest ecosystems (Kim et al., 2015; Kraus et al., 2015; Molina-Herrera et al., 2015). In this study, biogeochemistry, soil hydrology and vegetation growth were modelled

using the modules DNDC, WatercycleDNDC (Kiese et al., 2011) and GrasslandDNDC (Li et al., 2000; Molina-Herrera et al., 2016), respectively. The model setup requires input data on precipitation, temperature, vegetation, soil characteristics and agricultural management. Soil characteristics comprise depth profiles of soil texture, soil organic carbon, total nitrogen, bulk density and soil hydraulic properties. In this study, the soil profile was divided into 40 layers. Layers in the topsoil and subsoil were 1 cm and 1.8 cm thick, respectively.

The Stable Isotope MOdel for Nutrient cyclEs (SIMONE; Denk et al. (2019)) calculates the isotopic composition of the N pools simulated by a parent biogeochemical model (here LandscapeDNDC). To this end, SIMONE uses the pool sizes and fluxes from a given simulation to calculate the isotopic composition of soil N pools such as NH_4^+ , NO_3^- , and N_2O . This is based on the fraction of substrate converted to the product and the corresponding isotope fractionation factor of each transformation process (Denk et al., 2017) and applies the closed-system Rayleigh isotope fractionation equations (Mariotti et al., 1981). SIMONE follows the sequence of the process calculations dictated by the parent model, i.e. the cumulative product of a preceding reaction becomes the initial product of the following reaction in the sequence. The SIMONE model was previously presented in detail by (Denk et al., 2019), while a brief description can also be found in Figure S10.

3 Results

3.1. Environmental conditions and rates of soil emitted N_2O

Between 23 and 28 August 2017 the ambient air temperature was between 14.5 and 24.9 °C, and since only little precipitation occurred during that period, the water filled pore space (WFPS) steadily decreased from approx. 70 % to 50 %. The experimental site was mown on 29 August. Between 31 August and 3 September, continuing rainfall of around 15 mm day⁻¹ was observed, driving WFPS to values beyond 90 % (Figure 1). At the same time, the soil temperature dropped by approximately 7 °C. Thereafter, the rainfall ceased while the temperatures steadily increased again.

Between 6 November and 1 December, which corresponds to the period of the fertilizer addition experiments, ambient and soil temperatures steadily decreased reaching soil temperatures close to 0 °C at 5 cm depth. On 6 November, in parallel with the initialization of the fertilizer addition experiments, the first snowfall of the season was observed at BRM.

The NH_4^+ concentrations prior to the fertilizer addition, i.e. between 23 August and 5 November, were 3.5 ± 0.9 and 4.6 ± 1.0 $\mu\text{g NH}_4^+ \text{g}^{-1}$ soil at B1 and B2, respectively. The NO_3^- concentrations during the same time were 5.2 ± 2.9 and 3.3 ± 1.7 $\mu\text{g NO}_3^- \text{g}^{-1}$ soil at B1 and B2, respectively (Figure 1g and Figure S8). While NO_3^- concentrations did not systematically change from August to October, NH_4^+ values showed a slight positive trend, reaching values of 5.1 and 6.6 $\mu\text{g NH}_4^+ \text{g}^{-1}$ soil at B1 and B2 by 17 October. NH_4^+ fertilization on 6 November led to an increase of both NH_4^+ and NO_3^- concentrations, while NO_3^- fertilization led to increased NO_3^- concentrations only.

N_2O fluxes were highest between 29 August and 7 September on both sections (B1 and B2) of the experimental site with peak emission rates between 500 and 1000 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ (Figure 1a). After 12 September, the N_2O fluxes were relatively stable and resulted in an average rate of 120 ± 50 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$. Fluxes higher than 500 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ were associated with soil temperatures greater than 20 °C and WFPS values of 80 to 95 % (Figure 3). N_2O emission rates slightly increased in the B2 treatment frameset immediately after the mineral fertilizer (NH_4^+) addition on 6 November. After the NO_3^- addition on 20 November, no increase of the N_2O fluxes was observed.

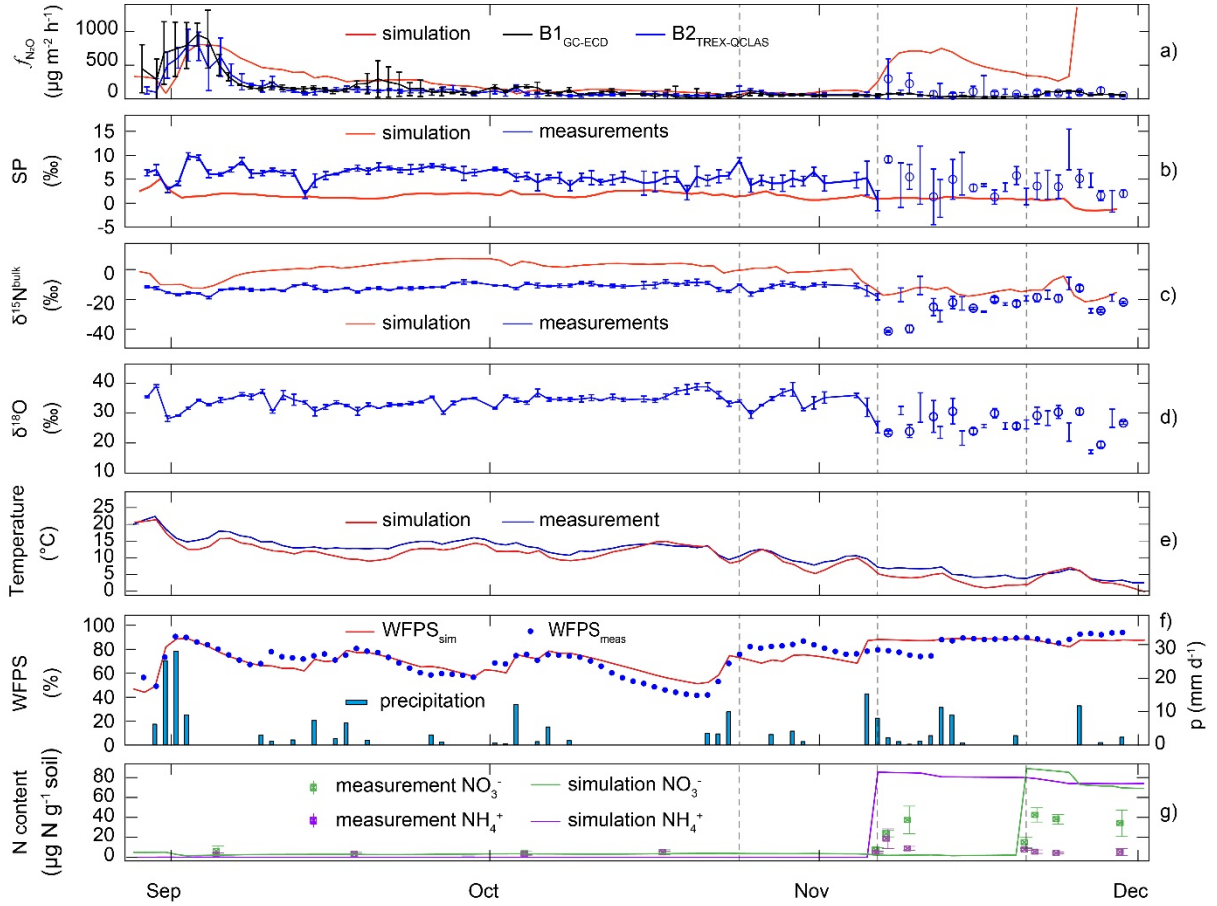


Figure 1 a) N_2O fluxes obtained by measurements with GC-ECD and TREX-QCLAS at the sections B1 and B2 of the experimental site and by simulation with SIMONE. Error bars indicate observed variation (1σ). b), c) and d) depict the observed and simulated source signatures SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$, where consigned circles after 6 November indicate measurements from chamber frames that received fertilizer, while absence of circles refers to reference frameset measurements (no fertilizer received). Indicated error bars refer to 1σ variation according to a Monte Carlo simulation ($n=200$) in b) and to 1σ variation of obtained data in c) and d). e) Observed and simulated soil temperature at 5 cm soil depth. f) Observed and simulated water filled pore space (WFPS) and observed precipitation. g) Measured (squares with 1σ variation error bars) and simulated NH_4^+ and NO_3^- concentrations in $\mu\text{g g}^{-1}$ soil. Dashed vertical lines indicate mowing of the experimental site (24 October) and addition of 70 kg N ha^{-1} $(\text{NH}_4)_2\text{SO}_4$ and KNO_3 on 6 November and 20 November 2017, respectively.

3.2. Source signatures of soil-emitted N_2O

The $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ values obtained from open chambers, thus representing atmospheric background values, were $15.45 \pm 0.82\text{‰}$, $-3.07 \pm 0.59\text{‰}$ and $44.69 \pm 0.52\text{‰}$, respectively. In the period before fertilizer addition, the daily mean SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ values of soil-emitted N_2O , i.e. the flux weighed Keeling plot derived source signatures, were $5.8 \pm 1.6\text{‰}$, $-11.8 \pm 2.3\text{‰}$ and $34.8 \pm 2.3\text{‰}$, respectively (Figure 1 b – d). The $(\text{NH}_4)_2\text{SO}_4$ addition on 6 November caused a decrease in mean SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ values of N_2O , leading to $4.5 \pm 2.8\text{‰}$, $-28.1 \pm 8.6\text{‰}$ and $30.5 \pm 4.3\text{‰}$, respectively. Finally, after the KNO_3 addition on 20 November mean SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ values resulted in $3.1 \pm 1.4\text{‰}$, $-20.0 \pm 5.5\text{‰}$ and $35.0 \pm 4.4\text{‰}$, respectively.

The TREX-QCLAS derived measurements were cross-validated on 26 September by parallel GC/IRMS measurements and Keeling plot analysis. Source signatures determined by GC/IRMS of $4.94 \pm 2.69\text{‰}$, $-10.64 \pm 2.96\text{‰}$ and $29.31 \pm 3.01\text{‰}$ for SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$ (mean ± 1 SD, $n = 3$ chambers), agreed with TREX-QCLAS results of $7.54 \pm 1.60\text{‰}$, $-11.70 \pm 4.62\text{‰}$ and $30.06 \pm 3.24\text{‰}$ (SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$) within one standard deviation.

3.2.1. Correlation of $\delta^{18}\text{O}$ - N_2O with WFPS

During the campaign, WFPS ranged from 40 to 90 %. Over this WFPS range, $\delta^{18}\text{O}$ - N_2O decreased from approx. 45 ‰ to 25 ‰, and showed a significant negative correlation to WFPS ($p < 0.001$). The relationship of the $\delta^{18}\text{O}$ values in dependence of the WFPS values was best explained with the exponential model $y = -5.51\text{e-}10 \times \exp(0.24 \times \text{WFPS}) + 50.84 \times \exp(-2.91\text{e-}03 \times \text{WFPS})$ shown in Figure 3.

3.3. Biogeochemical modelling

Soil environmental conditions simulated by LandscapeDNDC agreed well with the measured conditions (Figure 1e – f). For soil water content, this is reflected by the high coefficient of correlation (R) of 0.86, and the low root mean square error (RMSE) of 6.7 % (average simulated = 76.2 %, measured = 75.2 % from 29 August to 30 November 2017). The high R and low RMSE of soil temperature (0.97 and 1.92K, respectively) indicate a good representation of soil temperature dynamics and accuracy. With moderate baseline emissions of 60 to 150 $\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$, one major (start of September) and two minor emission events (mid-September and mid-October), the measured and simulated N_2O emissions showed the same features. However, timing of the simulated, rainfall induced N_2O emission peaks was biased as well as the decline in emissions following the peak emission periods. This as well as the too high baseline emission rates at the start of the measurements resulted in R and high RMSE values of 0.51 and 260 $\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$, respectively. Prior to fertilizer addition, simulated soil NH_4^+ concentrations (0.11 $\mu\text{g g soil}^{-1}$) were lower than the measured concentrations (3.5 $\mu\text{g g soil}^{-1}$), while NO_3^- concentrations were also underestimated, but to a lower degree, with 2.8 $\mu\text{g g soil}^{-1}$ (simulated) and 5.2 $\mu\text{g g soil}^{-1}$ (measured), respectively.

3.3.1. Isotope modelling

Based on the LandscapeDNDC output, SIMONE was used to calculate $\delta^{15}\text{N}^{\text{bulk}}$ and SP. While simulated $\delta^{15}\text{N}^{\text{bulk}}$ values were higher compared to the measurements (RMSE of 12.3‰), the low variability of $\delta^{15}\text{N}^{\text{bulk}}$ before fertilizer addition agreed well with the measurements. After ammonium fertilization, the depletion of $\delta^{15}\text{N}^{\text{bulk}}$ was lower in the LandscapeDNDC-SIMONE simulations as compared to the measurements, which, however, showed a large variability. In contrast, for the KNO_3 fertilization simulated and measured $\delta^{15}\text{N}^{\text{bulk}}$ agreed well, and the decline in soil NO_3^- concentration following peak concentrations immediately after KNO_3 application coincided with a decline in $\delta^{15}\text{N}^{\text{bulk}}$ (Figure 1c). With regard to SP, the LandscapeDNDC-SIMONE simulations produced lower values as compared to measurements throughout the campaign, only showing a slight increase in SP of approx. 3 ‰ on 31 August. While the observations showed slightly larger variability throughout the measurement campaign, the simulated SP values were very stable at 1.43 ± 0.96 ‰ (Figure 1b).

4 Discussion

4.1. Methodological considerations

To determine the isotopic composition of N_2O emitted from soils in-situ, previous studies have relied on Keeling plots (Wolf et al., 2015; Ibraim et al., 2019). This approach presumes mixing of the atmospheric background with soil air at a higher N_2O concentration, and, thus, a change of N_2O concentration. For this reason, the named studies used measurements taken at overnight periods since N_2O concentration increases in the nocturnal boundary layer due to a decrease of the mixing layer height under stable atmospheric conditions. A major constraint of this approach is the fact that N_2O accumulation in the NBL hardly results in N_2O concentrations beyond 400 ppb, while at most of the night hours maximum N_2O concentrations of 350 ppb could be observed. Furthermore, a stable NBL is only present if advantageous

conditions regarding meteorology and topography are provided (Garratt, 1994), otherwise no N₂O concentration increase may be observed, obviating Keeling plot analysis of the isotope signatures of soil N₂O. Therefore, in a recent study out of 30 days of measurements comprising close to 600 measurements only 12 Keeling plot derived source signatures could be retrieved (Ibraim et al., 2019).

Within the present study, for the first time a combined approach of automated flux-chambers and TREX-QCLAS was achieved. Accumulating soil-emitted N₂O in the chamber headspaces allowed determination of N₂O isotopic composition even at day time. Obtained N₂O isotope δ -values were lower by 4 – 9 ‰ compared to background N₂O isotope δ -values, thus, a factor 10 – 20 higher than the analytical precision of TREX-QCLAS. Accordingly, with respect to instrumental sensitivity, the technique presented here is distinctly superior to previous approaches (Wolf et al., 2015; Harris et al., 2017; Ibraim et al., 2019), yielding clearly more precise and accurate N₂O source signatures. In addition, using flux-chambers allowed allocating obtained N₂O source processes in space and time, which can be interpreted more closely with respect to soil characteristics (e.g. WFPS) and nutrient availability (NH₄⁺, NO₃⁻).

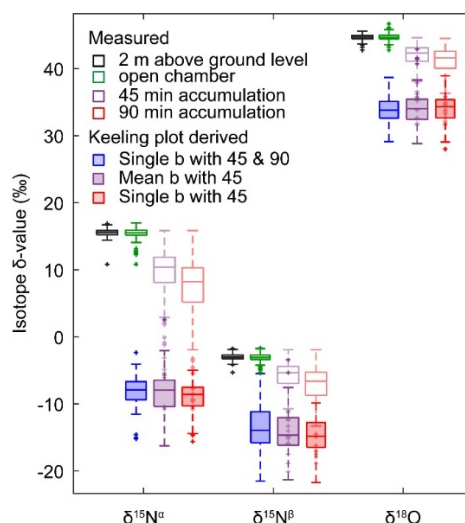


Figure 2 Variability of $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ values in background air at daytime (green), after 45 minutes chamber closure (empty pale purple boxplots) and after 90 minutes chamber closure (empty pale red boxplots). Black boxplots represent the isotope δ -values obtained at night from the 2 m above ground level sample inlet. Filled boxplots illustrate Keeling plot derived isotope δ -values as obtained from individual background (i.e. open chamber) measurements in conjunction with 45 and 90 min chamber closure measurements (blue), daily mean background measurements in conjunction with 45 minutes chamber closure (purple), and individual background measurements in conjunction with 45 minutes chamber closure measurements (red).

As a result of BRM's topography (the site is on top of a small hill, see section 2.1.1), unlike in the aforementioned studies, N₂O did not accumulate in the NBL during the period of this study. Therefore, variability in N₂O concentrations and N₂O δ -values from the 2 m inlet were not significantly different from background conditions (black and green boxplots in Figure 2) and did not allow for reliable Keeling plot analysis.

In this study Keeling plot analysis used an individual background (time 0) and two consecutive (45, 90 min after chamber closure) chamber headspace measurements. To evaluate the potential for a further increase in temporal resolution of the sampling technique, we investigated the following scenarios: (i) the use of mean background measurement-values instead of using individual background values and (ii) use of one analysis of chamber headspace air (45 min) in combination with individual / mean background air measurements. Due to the excellent signal-to-noise ratios none of the investigated scenarios was statistically different (Figure 2).

Therefore, the measurement frequency can be substantially increased in future studies by carrying out the Keeling plot analysis based on one single background measurement per day combined with individual analyses 45 minutes after chamber closure. With this adaptation, a frequency of approx. one source signature measurement per hour will be achieved, which is a clear step forward in monitoring and understanding short-term dynamics of the soil processes involved in N₂O emissions.

4.2. Environmental controls on N₂O fluxes and isotope signatures

Between end of August and end of September, N₂O emission rates obtained at BRM were comparable to those found in previous grassland related studies in Switzerland and Germany (Merbold et al., 2014; Wolf et al., 2015; Hörtnagl et al., 2018; Ibraim et al., 2019). As also observed previously, N₂O emission rates significantly correlated with WFPS values at BRM (Figure 3), with a positive correlation between 40 and 90 % WFPS and decreasing N₂O fluxes beyond 90 % WFPS (Lewicka-Szczebak et al., 2017; Ibraim et al., 2019). High WFPS favours anoxic conditions and thereby bacterial denitrification, thus high N₂O fluxes (Schindlbacher et al., 2004; Toyoda et al., 2011). However, at WFPS values close to saturation (i.e. > 90 %), diffusion of N₂O from soil to atmosphere is suppressed. Moreover, under such conditions, the share of complete denitrification is higher due to low oxygen availability, ultimately leading to higher N₂ production and lower N₂O emissions. N₂O emissions were further affected by the soil temperature (p-value < 0.001), which is due to the temperature-dependent rates of microbial N₂O production (Butterbach-Bahl et al., 2013; Schindlbacher et al., 2004).

SP values of N₂O emitted from grassland soils observed in previous studies ranged from 0 – 35 ‰ (Wolf et al., 2015; Ibraim et al., 2019). In contrast, in the present study the SP values were between 1.8 and 9.8 ‰, resulting in a mean value of 5.8 ‰ ± 1.6 (Figure 4 and Figure 5). As discussed in detail in section 4.3, low SP values are a strong indication that the N₂O_D domain has predominantly contributed to the observed N₂O emissions (Decock & Six, 2013). Occasional increases in SP may be explained as an initialization of complete denitrification (Lewicka-Szczebak et al., 2017; Friedl et al., 2016), or as a temporal increase in the relative contribution of nitrification to total N₂O emission. In the first week of September, after heavy rainfalls between 30 August and 2 September, an increase of WFPS values beyond 90 % was observed. In this case, an initialization of complete denitrification is most likely.

Environmental controls on $\delta^{18}\text{O}$ -N₂O are especially important, since SP versus $\delta^{18}\text{O}$ -N₂O mapping has been proposed as a means for calculating the share of N₂O that has been reduced to N₂, which is a prerequisite for source partitioning to the process groups N₂O_N and N₂O_D. The final step of denitrification, i.e., N₂O reduction to N₂, leads to an enrichment of both $\delta^{18}\text{O}$ -N₂O and SP. For this reason, the shift in N₂O isotopic composition due to N₂O reduction to N₂ has to be considered when partitioning total N₂O emission to the process groups N₂O_N and N₂O_D. To deduce the share of N₂O that was produced in the soil, then reduced to N₂ and subsequently emitted to the atmosphere, isotopomer maps have been suggested (Koba et al., 2009; Lewicka-Szczebak et al., 2017; Verhoeven et al., 2019) that show the relation of $\delta^{18}\text{O}$ to SP. This approach assumes a stable isotopic composition of N₂O originating from process group N₂O_D with regard to SP and $\delta^{18}\text{O}$, and interprets deviations from this composition with respect to N₂O reduction. This might be a robust assumption as the associated N-intermediates of the N₂O precursor, NO₃⁻, exchange oxygen with soil water, which stabilizes the precursor isotopic composition against fractionation due to nitrification (production), denitrification (consumption), and other fractionating processes such as microbial immobilization, or plant uptake. For this reason, however, systematic effects on $\delta^{18}\text{O}$ -N₂O other than N₂O reduction need to be identified. During the campaign, WFPS ranged from 40 to 95 %. Over this WFPS

range, $\delta^{18}\text{O}-\text{N}_2\text{O}$ decreased from approx. 45 ‰ to 30 ‰ (Figure 3), and showed a significant negative correlation ($p < 0.001$). Since high WFPS is caused by precipitation, and $\delta^{18}\text{O}$ of precipitation is depleted compared to $\delta^{18}\text{O}-\text{N}_2\text{O}$ ($\delta^{18}\text{O}-\text{H}_2\text{O}_{\text{precip}}$ varies between -10 to -3 ‰ according to Mook (2001)), this correlation indicates a high oxygen exchange rate between soil water and NO_3^- . This phenomenon, also known from previous laboratory scale studies, is indicated by replacing $\delta^{18}\text{O}-\text{N}_2\text{O}$ by $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ as the difference of $\delta^{18}\text{O}$ values between the soil water ($\delta^{18}\text{O}-\text{H}_2\text{O}$) and the product ($\delta^{18}\text{O}-\text{N}_2\text{O}$). (Well et al., 2008; Zhu et al., 2013; Lewicka-Szczebak et al., 2014; Lewicka-Szczebak et al., 2016). The enrichment of $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ during drying or dry periods (Figure 3 and Figure S9) supports the notion that besides N_2O reduction, evaporative ^{18}O -enrichment of $\delta^{18}\text{O}-\text{H}_2\text{O}_{\text{soil water}}$ affects $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values, which is also in accordance with previous observations (Sprenger et al., 2017; Kayler et al., 2018; Benettin et al., 2018). This indicates that, in summary, the variability of $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ can be explained by the effects of i) mixing of precipitation water and soil water with subsequent oxygen exchange between soil water and NO_3^- , ii) evaporative ^{18}O -enrichment of soil water and propagation of ^{18}O enriched water to NO_3^- , and iii) N_2O reduction on $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$.

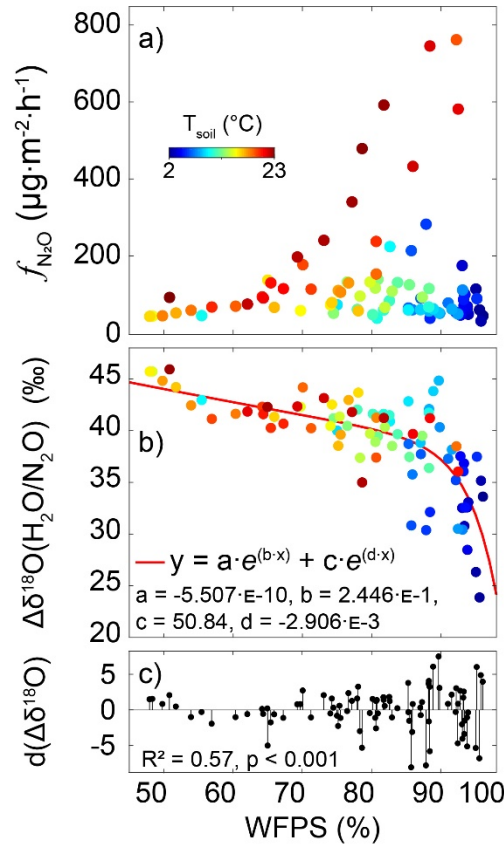


Figure 3 (a) Observed daily mean N_2O fluxes vs. water filled pore space (WFPS), (b) $\Delta\delta^{18}\text{O}-\text{N}_2\text{O}$ vs. WFPS and the related nonlinear fit (red curve) with the given model parameters and (c) deviations of observed $\Delta\delta^{18}\text{O}$ values from the derived function. In (a) and (b) the color code refer to the corresponding soil temperature according to the legend given in (a).

4.3. Source signatures of soil emitted N_2O and implicated processes

Two end-member mapping approaches were proposed based on (i) SP vs. $\delta^{15}\text{N}^{\text{bulk}}-\text{N}_2\text{O}$ and (ii) SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ as a means for identifying N_2O emitting source processes (Toyoda et al., 2005; Sutka et al., 2006; Sutka et al., 2008; Koba et al., 2009). Because SP is thought to be independent of the isotopic composition of the precursors NH_4^+ and NO_3^- it is considered to be more robust in this regard than $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$. However, due to the overlap

of SP from different processes, only the process groups N_2O_D and N_2O_N can be distinguished with this parameter. In addition, source partitioning based on a single isotopic quantity (SP) does not allow a unique mathematical solution if a third process is involved. Therefore, the impact of the final process step of denitrification, N_2O reduction to N_2 , which increases SP, needs to be considered while partitioning N_2O_D and N_2O_N source contributions. To this end, isotope maps as shown in Figure 4 and Figure 5 have been proposed (Koba et al., 2009; Lewicka-Szczepak et al., 2017). The basic assumption of these approaches is that there are characteristic isotopic compositions for the process groups N_2O_N and N_2O_D , and N_2O to N_2 reduction displays a constant SP / $\delta^{15}N^{bulk}$ or SP / $\delta^{18}O$ ratio (derivation of the black boxes from literature as explained by Ibraim et al. (2019)). The N_2O_N and N_2O_D source signatures' $\delta^{15}N^{bulk}$ values are calculated the difference between the precursors' and N_2O 's $\delta^{15}N$ values, i.e. between $\delta^{15}N-NO_3^-$, $\delta^{15}N-NH_4^+$ and $\delta^{15}N^{bulk}-N_2O$. The implementation of this procedure is indicated by replacing $\delta^{15}N^{bulk}$ by either $\Delta\delta^{15}N^{bulk}(NO_3^-/N_2O)$ or $\Delta\delta^{15}N^{bulk}(NH_4^+/N_2O)$, depending on the anticipated dominant precursor.

4.3.1. Interpretation of obtained source signatures with the SP vs. $\Delta\delta^{15}N^{bulk}$ approach

The SP vs. $\Delta\delta^{15}N^{bulk}$ dual-isotope maps are interpreted with respect to the mixing line between the characteristic SP and $\Delta\delta^{15}N^{bulk}$ domains of N_2O_N and N_2O_D . Deviations from this line towards higher SP and lower $\Delta\delta^{15}N^{bulk}$ values (red arrow in Figure 4) indicate a shift in isotopic composition due to N_2O reduction.

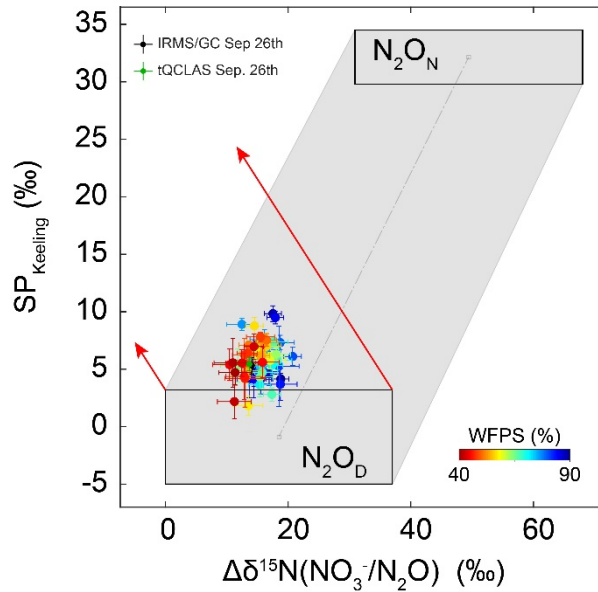


Figure 4 SP vs. $\Delta\delta^{15}N^{bulk}(NO_3^-/N_2O)$ source signature map for the period before fertilizer addition (29 August to 5 November 2017). The N_2O_D (nitrifier-denitrification, denitrification) and N_2O_N (nitrification, abiotic N_2O production and fungal denitrification) boxes indicate the region of N_2O source signatures from the related processes. The grey shaded area represents the region of source signatures expected for a mix of N_2O_N and N_2O_D , while red arrows indicate changes in the source signatures due to partial N_2O reduction. Indicated values correspond to obtained mean ± 1 SD values and the colour-trend indicates the corresponding water filled pore space (WFPS) values.

The slope of the line connecting the mixing line and product N_2O is defined by the ratio of the fractionation factors for SP and $\Delta\delta^{15}N^{bulk}$ during N_2O reduction as introduced by Koba et al. (2009). The mean $\Delta\delta^{15}N^{bulk}(NO_3^-/N_2O)$ source signature determined in this study corresponds to 15.2 ± 2.1 ‰ (Figure 4), which is in agreement with $\Delta\delta^{15}N^{bulk}(NO_3^-/N_2O)$ values presented by Ibraim et al. (2019) for an intensively managed grassland site in Southern Germany. Interestingly, the values also agree with those found in a groundwater study by Koba et al. (2009), where $\Delta\delta^{15}N^{bulk}(NO_3^-/N_2O)$ values between 0 and 22 ‰ were observed. Compared

to the $\Delta\delta^{15}\text{N}^{\text{bulk}}(\text{NO}_3^-/\text{N}_2\text{O})$ values, the $\Delta\delta^{15}\text{N}^{\text{bulk}}(\text{NH}_4^+/\text{N}_2\text{O})$ values (not shown) were offset by +4.8 ‰. They are not discussed further due to the observed predominance of denitrification derived N_2O .

In contrast to $\Delta\delta^{15}\text{N}^{\text{bulk}}$ values, the observed SP values were distinctly more confined, clustering close to the $\text{N}_2\text{O}_\text{D}$ domain at 1.8 to 9.8 ‰, than SP signatures presented in the aforementioned surveys (Wolf et al., 2015; Ibraim et al., 2019), where SP values ranged between 0 and 35 ‰. The average SP source signature of 5.8 ± 1.6 ‰ is around 7 ‰ higher than that expected from pure bacterial denitrification (Sutka et al., 2006). Based on the graphical approach presented in Figure 4 we found that 30 – 55% of produced N_2O was reduced to N_2 . The share of $\text{N}_2\text{O}_\text{N}$ derived N_2O amounted to 3 – 18%. Related values are given in Table S3 in more detail.

4.3.2. Interpretation of obtained source signatures with the SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ approach

To further confine the share of N_2O reduction, Lewicka-Szczebak et al. (2017) introduced the approach based on SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$. In this approach, $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ is calculated as the difference of $\delta^{18}\text{O}$ values between the product (N_2O) and soil water (H_2O). Since no measurements for the $\delta^{18}\text{O}$ - H_2O values of soil water were available, we used an average $\delta^{18}\text{O}$ - H_2O value of -7 ‰ as reported by Feng et al. (2009). An advantage of the Lewicka-Szczebak et al. (2017) approach is that the range of $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values is distinctly smaller, reducing the size of the $\text{N}_2\text{O}_\text{D}$ box in Figure 5. There are two scenarios that could lead to the final observed N_2O isotopic composition. The first scenario assumes partial reduction of $\text{N}_2\text{O}_\text{D}$ followed by mixing with $\text{N}_2\text{O}_\text{N}$, while the second pathway assumes mixing of $\text{N}_2\text{O}_\text{D}$ and $\text{N}_2\text{O}_\text{N}$, followed by N_2O reduction. Although it is not possible to identify which scenario is more appropriate, this approach constrained the share of N_2O originating from $\text{N}_2\text{O}_\text{N}$ to a range of 2 – 20 %. The share of the produced N_2O further reduced to N_2 , was 30 – 70 % according to the Rayleigh equation $\text{SP} = \text{SP}_0 + \varepsilon_{\text{SP}} * \ln(r\text{N}_2\text{O})$ (Mariotti et al., 1981; Lewicka-Szczebak et al., 2017) with $r\text{N}_2\text{O}$ being the residual fraction of N_2O and using an average enrichment factor, $\varepsilon_{\text{SP}} = -5.9$ ‰, in accordance with Ostrom et al. (2007). Therefore, we conclude that, at BRM the observed SP shift was caused by N_2O reduction to N_2 rather than by a contribution of $\text{N}_2\text{O}_\text{N}$.

Based on the SP vs. $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ method the share of $\text{N}_2\text{O}_\text{D}$ and $\text{N}_2\text{O}_\text{N}$ can be derived as explained. However, this method was developed for studies under controlled conditions, implying complete O-exchange between soil water and N-precursors (NO_3^-) of denitrification. Hence, the two process domains $\text{N}_2\text{O}_\text{D}$ and $\text{N}_2\text{O}_\text{N}$ together with N_2O reduction to N_2 are assumed to be the only parameters influencing the final observed SP and $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values. In contrast, as outlined in section 4.2, evaporative ^{18}O -enrichment (Sprenger et al., 2017; Benettin et al., 2018; Kayler et al., 2018) and the extent of O-exchange between soil water and precipitation (Well et al., 2008; Zhu et al., 2013; Lewicka-Szczebak et al., 2014; Lewicka-Szczebak et al., 2016) may have systematically influenced the observed $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values in this study, because we observed a wide range of WFPS values during the measurement campaign. This is based on the notion that nitrification played a minor role during the measurement campaign and that increases in WFPS should be accompanied with enrichment in $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ due to an increasing share of N_2O reduction to N_2 , which however was in contrast to observations. Consequently, the share of $\text{N}_2\text{O}_\text{N}$ and the rate of N_2O reduction to N_2 presented above may be biased due to low $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ end-member-values (actual $\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ end-member-values are assumed to be higher due to evaporative ^{18}O enrichment in soil water and incomplete ^{18}O exchange with NO_3^-). To deduce the influence of evaporative ^{18}O -enrichment and O-exchange, we applied a statistical correction following equation 4 (Eq 4):

$$\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})_{\text{corr}} = \Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O}_{\text{Keeling}}) - \Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})_{\text{Fit}} + \Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})_{90\%\text{WFPS}} \quad \text{Eq 4}$$

In Eq 4, $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O}_{\text{Keeling}})$ corresponds to the Keeling plot derived $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values. The term $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})_{\text{Fit}}$ depicts the fitted values at given WFPS as following the two-term exponential fit introduced in section 3.2.1. The term $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})_{90\%\text{WFPS}}$ equals 37.1 ‰ and represents the fitted $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ value at 90 % WFPS, thus depicting the characteristic bacterial denitrification derived $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ value at BRM.

Thus, the corrected $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values may be less vulnerable towards systematic influences of evaporative ^{18}O -enrichment or incomplete O-exchange, and isolate the effect of N_2O reduction to N_2 . The average $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ values were 34.0 ± 2.4 ‰ and 30.7 ± 2.2 ‰ before and after the correction. Using the corrected $\delta^{18}\text{O}$ - N_2O values, the share of $\text{N}_2\text{O}_\text{N}$ derived N_2O corresponded to 6 – 14 % (Table S3). This is well within the range of values (3 – 18 %) obtained without correction. The share of N_2O reduction to N_2 based on the corrected values amounts to 30 – 55 % which is 9 to 10 % lower than prior to the correction. Since the standard deviation of the Keeling plot derived $\delta^{18}\text{O}$ -values are around 2 ‰, half of the average correction, the influence of evaporative enrichment or efficiency of exchange with water, on the share of N_2O reduced to N_2 , is rather moderate.

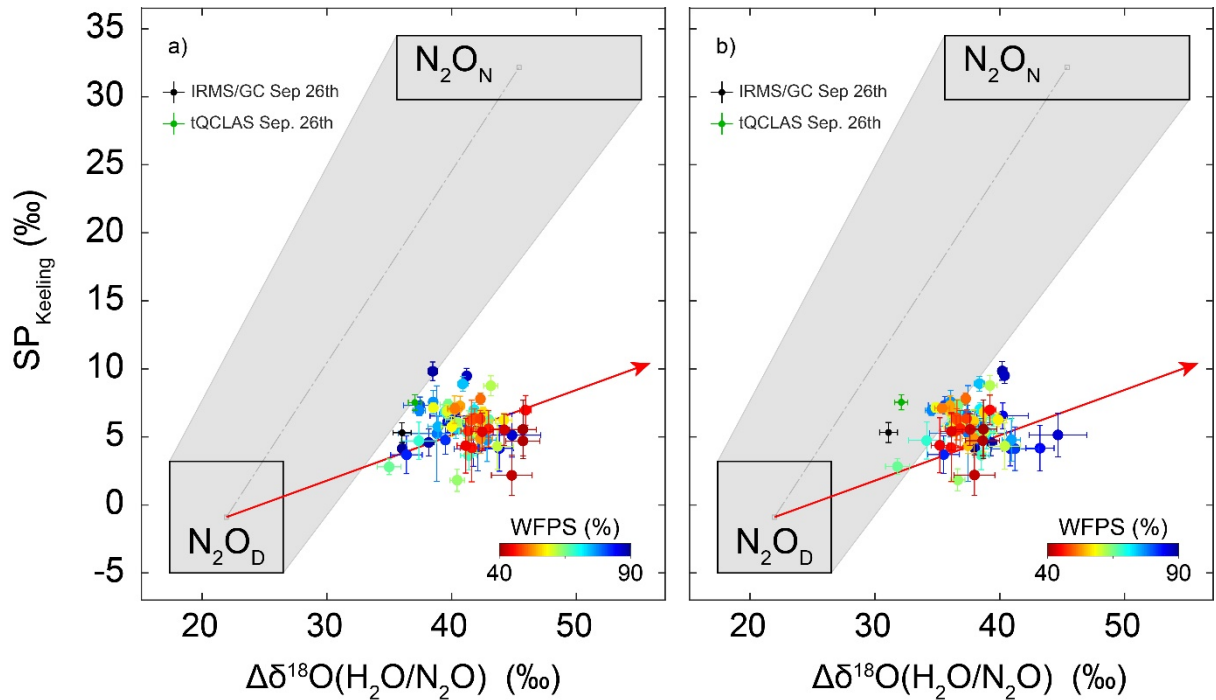


Figure 5 Source signature maps for the period before fertilizer addition (29 August to 5 November 2017) with the $\Delta\delta^{18}\text{O}$ approach according to Lewicka-Szczepak et al. (2017). The $\text{N}_2\text{O}_\text{D}$ (nitrifier-denitrification, denitrification) and $\text{N}_2\text{O}_\text{N}$ (nitrification, abiotic N_2O production and fungal denitrification) boxes indicate the region of N_2O source signatures from the related processes (a compilation of literature values can be found in Ibraim et al. (2019)). The grey shaded area represents the region of source signatures expected for a mix of $\text{N}_2\text{O}_\text{N}$ and $\text{N}_2\text{O}_\text{D}$, while red arrows indicate changes in the source signatures due to partial N_2O reduction. a) Before correction of $\delta^{18}\text{O}$ - N_2O values for WFPS and b) after correction for WFPS according to equation Eq 4. The colour-trend refers to observed water filled pore space (WFPS) as indicated. For the 26th of September, IRMS results are given in addition to the TREX-QCLAS results.

Even though the presented approach represents current best practice, assuming constant fractionation factors might be an over-simplification, as it has been previously shown that fractionation factors change over time (Jinuntuya-Nortman et al., 2008). Furthermore, additional N_2O source processes, e.g. fungal denitrification and chemodenitrification (implying

increased SP values) could not be specifically addressed here (Denk et al., 2017; Wei et al., 2019). Nevertheless source signatures at BRM are consistent with previous findings from open system studies (Wolf et al., 2015; Ibraim et al., 2019; Mohn et al., 2012; Mohn et al., 2013; Verhoeven et al., 2019; Yamamoto et al., 2014) revealing that N₂O reduction to N₂ was the main factor determining observed N₂O source signatures. Depending on WFPS, 30 – 70 % of produced N₂O was reduced to N₂ before emission of remaining N₂O to the atmosphere.

4.3.3. Interpretation of obtained source signatures after (NH₄)₂SO₄ and KNO₃ addition

Fertilization with 70 kg N ha⁻¹ (NH₄)₂SO₄ should promote N₂O production via nitrification due to the enhanced NH₄⁺ availability, ultimately leading to a shift of the N₂O source signatures towards the N₂O_N domain (Robertson & Groffman, 2015; Decock & Six, 2013). Indeed, on the first day after the fertilizer addition an increase in SP (pointing towards the N₂O_N domain) together with a strong increase of the $\Delta\delta^{15}\text{N}^{\text{bulk}}$ values was observed indicating that the applied (NH₄)₂SO₄ effectively enhanced N₂O production by the nitrification pathway. The fertilization effect was still visible on day three after (NH₄)₂SO₄ addition, but decreased over time and the difference between treatment and reference chambers disappeared at days 5, 7, 9, 11, and 13 (Figure 6). Thus, we conclude that the addition of (NH₄)₂SO₄ caused a shift of the N₂O emitting soil processes towards the N₂O_N domain, while it leaves open whether nitrification or fungal denitrification was primarily causing the shift. Nevertheless, the highest N₂O emission was observed on day one after fertilization, when NH₄⁺ concentrations were also at their climax. On days 3 and 5 after fertilization, both N₂O emission and NH₄⁺ concentrations in the soil decreased while NO₃⁻ concentrations reached their maximum, which suggests that the observed emissions may have been rather due to substrate induced nitrification than fungal denitrification. This notion is supported by the decrease of N₂O emission at increasing NO₃⁻ availability as most fungi are not capable to reduce N₂O to N₂ (Shoun et al., 1992). After the emission pulse, i.e., from day 5 after (NH₄)₂SO₄ addition, the N₂O source signatures suggest that denitrification was the dominating N₂O producing process with regard to background emission. As indicated in Figure 6, they were falling on lines with the slopes 0.23 and -0.53 in the SP vs. $\Delta\delta^{15}\text{N}^{\text{bulk}}$ and SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ end-member-mixing maps, respectively.

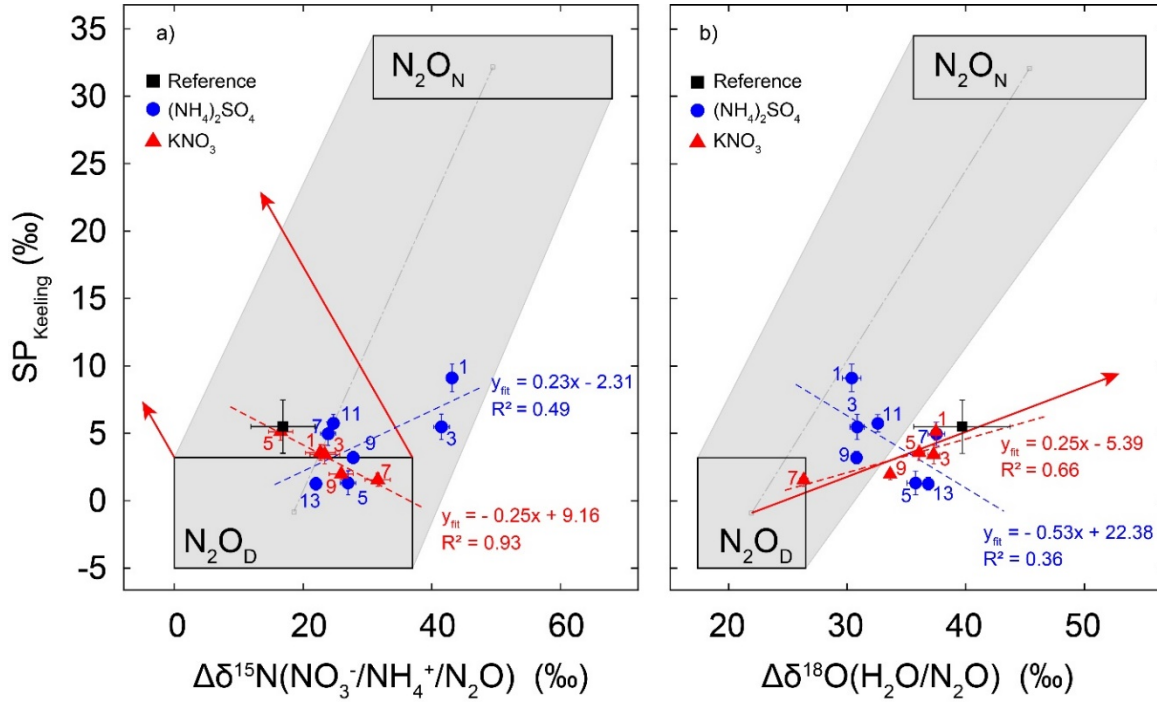


Figure 6 Source signature maps for the period after fertilizer addition (6 to 20 November 2017). The N₂O_D (nitrifier-denitrification, denitrification) and N₂O_N (nitrification, abiotic N₂O production and fungal denitrification) boxes indicate the region of N₂O source signatures from the related processes (a compilation of literature values can be found in Ibraim et al. (2019)). The grey shaded area represents the region of source signatures expected for a mix of N₂O_N and N₂O_D, while red arrows indicate direction of changes in the source signatures due to partial N₂O reduction. Blue dots represent measurements during (NH₄)₂SO₄-addition experiments, while red triangles depict measurements during KNO₃ addition experiments. Given numbers refer to number of days after fertilizer addition. Blue and red dashed lines represent linear fits of obtained source signatures. a) SP vs. $\Delta\delta^{15}\text{N}^{\text{bulk}}(\text{NO}_3^-/\text{NH}_4^+/\text{N}_2\text{O})$ map, where fertilizer $\delta^{15}\text{N}^{\text{bulk}}\text{-NO}_3^-$ and $\delta^{15}\text{N}^{\text{bulk}}\text{-NH}_4^+$ values were included to determine net isotope effects and b) SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ map as introduced earlier.

Addition of KNO₃ led to source signatures falling on a line that connects the average source signatures from the reference chambers with the N₂O_D domain, indicating that the high share of denitrification derived N₂O was increased even further. The related R² values of 0.93 and 0.66 with the two mapping approaches indicate a high degree of consistency in the represented processes. The slope of 0.25 in the SP vs. $\Delta\delta^{18}\text{O}(\text{H}_2\text{O}/\text{N}_2\text{O})$ map is very close to the slope derived with incubation studies by Lewicka-Szczebak et al. (2017). Addition of KNO₃ (i.e. inducing conditions that favour pure bacterial denitrification) led to slightly lower SP values compared to the SP values obtained prior to the KNO₃ addition. This seems plausible because the reference SP value was already very close to that expected from pure bacterial denitrification. Since the KNO₃ was applied with 22 mm water, in the first days after the KNO₃ application, the oxygen availability was limited due to high soil water content. Accordingly, obtained source signatures indicate a higher rate of N₂O reduction to N₂ in the first days after KNO₃ addition. At days 7 and 9, the oxygen availability slightly increased as a result of decreasing WFPS, ultimately leading to SP values that are very close to those of bacterial denitrification in the absence of N₂O reduction.

4.4. Biogeochemical and isotopic modelling

Comparing the measurements to the modelled results the coefficients of determination (R²) of WFPS and soil temperature were high (0.86 and 0.92, respectively) and the average deviations of the observed WFPS and soil temperature were low (2.2 % and 1.5 K, respectively), indicating that the LandscapedDNDC model produces a realistic representation of

the soil environmental conditions. As in model-data comparisons from other studies, R^2 values of 0.08-0.85 and 0.85-0.93 for WFPS and soil temperature as well as average deviations of 0.1-2.8 % and 0.2-1.7 K were reported (Gaillard et al., 2018; Molina-Herrera et al., 2016; Wolf et al., 2012). Therefore, the quality of the presented simulated soil environmental conditions can be classified as high. High R^2 values for measured versus simulated soil NH_4^+ (0.33) and NO_3^- (0.41) concentrations are also well within the reported ranges of 0.01 to 0.98 (NH_4^+) and 0.03 to 0.47 (NO_3^-) for grasslands and arable sites (Molina-Herrera et al., 2016). The R^2 of daily modelled vs. measured N_2O emissions during the growing season was 0.26 in this study, which is well within the range of reported values (0.01-0.68) obtained in LandscapeDNDC simulations and in a model intercomparison study (Gaillard et al., 2018; Molina-Herrera et al., 2016; Wolf et al., 2012). Low R^2 values for N_2O emissions are generally (including in this study) due to the bias in the timing of emission peaks and the delayed decay of peak emissions. Particularly high bulk densities were measured in the subsoil at BRM, which are associated with lower soil porosity and more meso- and micro-pores (Balaine et al., 2016). Meso- and micro-pores retain more water against a given suction head, so that anaerobic conditions occur more frequently in deeper soil layers. Anaerobic conditions stimulate denitrification which produces N_2O as an obligate intermediate (see Butterbach-Bahl et al. (2013) and references therein). As denitrification was the predominant source of N_2O in our simulations, and anaerobic conditions occurred frequently in the subsoil of the BRM site, the slow decrease of emissions and also the overestimation of N_2O emission were likely the result of the high bulk density in the sub-soil observed at BRM.

Following LandscapeDNDC application to the site, we used the simulation results on N turnover and N_2O production / emission to drive the SIMONE model. With regard to the $\delta^{15}\text{N}^{\text{bulk}}$ measurements, LandscapeDNDC-SIMONE simulations showed a higher ^{15}N -enrichment of N_2O as compared to the measurements. Since $\delta^{15}\text{N}^{\text{bulk}}$ directly depends on the isotopic composition of the precursors and NO_3^- was the predominant substrate for N_2O formation in the model, over estimation of ^{15}N -enrichment in NO_3^- could explain the difference. However, the comparison of measured and modelled $\delta^{15}\text{N}\text{-NO}_3^-$ showed only small deviations before the fertilization experiments, so that the isotope effect for denitrification used within SIMONE may be too weak. The enrichment of the NH_4^+ pool was distinctly overestimated by the model (Figure S11), which may have added to the too high enrichment in $\delta^{15}\text{N}^{\text{bulk}}$, though NH_4^+ was only a minor source of N_2O . The strong enrichment of the NH_4^+ pool suggests that mineralization may be underestimated compared to the nitrification rate.

The less pronounced decrease of $\delta^{15}\text{N}\text{-N}_2\text{O}$ after the first fertilizer application indicates that the amount of N transformed by microorganisms was underestimated, which is in line with the missing reduction in soil NH_4^+ , and indicates that the temperature limitation of microbial N turnover and plant growth in LandscapeDNDC needs to be revisited.

4.4.1. Source partitioning by isotope analysis and LandscapeDNDC-SIMONE

Although other recent studies including *in-situ* measurements of SP from grassland and agricultural systems based on QCLAS (Wolf et al., 2015; Harris et al., 2015; Ibraim et al., 2019) or flask sampling with subsequent IRMS analysis (Toyoda et al., 2011) showed pronounced variability of SP over time, we observed limited variability of SP. Since the variability in SP reported in the literature could be explained by changing contributions of N_2O producing processes, or changing degrees of N_2O reduction (Lewicka-Szczebak et al., 2017; Toyoda et al., 2011; Ibraim et al., 2019; Verhoeven et al., 2019), the lack of variability in our measurements and simulations indicates that there was a dominant combination of processes that prevailed throughout the campaign. The consistently low SP suggests that the main source of N_2O was denitrification or nitrifier denitrification, as a SP of approx. -0.9 ‰ has been observed for this process group. Though nitrifier denitrification cannot be ruled out entirely,

the high soil bulk densities and the associated higher probability of anaerobic conditions in the soil indicate that bacterial denitrification was more likely the dominant N₂O-producing process. The location of the measurements in SP- $\Delta\delta^{18}\text{O}$ space (Figure 5 a) relative to a simple mixing of N₂O produced by the process groups N₂O_D/ N₂O_N can be used to estimate the contribution of N₂O reduction and nitrification to the observed isotopic composition (Lewicka-Szczebak et al., 2017). According to this approach, the process group N₂O_N contributed on average 3 ± 4 % assuming scenario 1 (first reduction, then mixing of the N₂O derived from the domains N₂O_N and N₂O_D) and 18 ± 3 % assuming scenario 2 (first mixing, then reduction), accordingly leading to a N₂O_D contribution of approximately 82 – 97 %.

This is in general agreement with the calculated percentages of i) 72 % N₂O reduction for a scenario in which exclusively N₂O reduction with an isotope effect of -5.9 ‰ shifts SP from the - 0.9 ‰ of process group N₂O_D to the observed average SP of 5.8 ‰ and ii) a maximum contribution of 20 % for nitrification, assuming no N₂O reduction and endmembers of -0.9 ‰ and 32.8 ‰ for the process groups N₂O_D and N₂O_N, respectively. In the LandscapeDNDC simulations, 7 % of N₂O was produced on average during nitrification (range of 1.8 to 17 %), and an average of 30 % (range 18 - 47 %) of the produced N₂O was reduced to N₂ (Figure S12). While the low modelled contribution of nitrification together with the lower modelled share of N₂O reduction explain the underestimation of SP by 4.2 ‰, the total N₂O emission has to be taken into account as well. The modelled N₂O emissions were on average $190 \mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$ larger than the measured emissions. This might be due to an overestimation of N₂O production by denitrification or an underestimation of N₂O to N₂ reduction by the model. A reduction of N₂O production during denitrification by 50 % results in a contribution of nitrification of 13 %, and still produces an underestimation of the average SP by approx. 3 ‰. Consequently, such a large discrepancy cannot be explained by the too high source strength of denitrification alone. Since the location of the measurements in SP- $\Delta\delta^{18}\text{O}$ space suggests a substantial contribution of N₂O reduction, LandscapeDNDC most likely underestimates the amount of N₂O reduced to N₂.

5 Conclusions

To the best of our knowledge this study reports the first *in-situ* time-series of N₂O source signatures (SP, $\delta^{15}\text{N}^{\text{bulk}}$ and $\delta^{18}\text{O}$) emitted from an intensively managed grassland at daily resolution. This was possible by combining automated chamber measurements, laser spectroscopy and preconcentration with concurrent measurements of the isotopic composition of N₂O and its precursors.

We observed that N₂O fluxes were highly correlated with soil water filled pore space (WFPS) and with ambient temperatures. Based on the combined analysis of N₂O isotopic composition and ¹⁵N abundance of the N₂O precursors NO₃⁻ and NH₄⁺, we found that bacterial denitrification was the main N₂O-emitting process over the three-month measurement period. Even when (NH₄)₂SO₄ was added the share of nitrification-derived N₂O remained small (< 20 %) and occurred only in the first three days after addition. This dominance of denitrification was likely due to the subsequent use of nitrification derived NO₃⁻ as substrate for N₂O production via denitrification.

The comparison of modelled and measured N₂O isotopic composition demonstrated the high quality of the process parameterization in LandscapeDNDC since the simulations generally reflected the temporal dynamics and features of the measurements. Nevertheless, the juxtaposition of observed and modelled N₂O and NH₄⁺ signatures in combination with the observed and modelled N₂O fluxes suggests that LandscapeDNDC i) overestimates nitrification and N₂O production during denitrification in heavily textured soils, ii) underestimates N₂O

reduction to N₂ and iii) underestimates rates of tightly linked mineralization and microbial immobilization. Hence, future research aiming at improving process-based biogeochemical models will benefit from co-locating the presented in-situ determination of (natural abundance) N₂O isotopic composition with ¹⁵N-tracing approaches that are capable of providing information on gross rates of N cycling. In addition, the model results at the end of the growing season revealed weaknesses in plant and microbial activity parameterization at low temperatures calling for extending observation periods beyond the growing season.

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