Evaluation of denitrification and decomposition from three biogeochemical models using laboratory measurements of N_2, N_2O and CO_2

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Abstract. Biogeochemical models are ~~useful~~essential for the prediction and management of nitrogen (N) cycling ~~processes~~in agroecosystems, but ~~accurate description~~the accuracy of the denitrification and decomposition sub-modules is critical. Current models were developed before suitable soil N_2 flux data were available~~; new~~, which may have led to inaccuracies in how denitrification was described. New measurement techniques, using gas chromatography and isotope-ratio mass spectrometry (IRMS) have enabled the collection of ~~improved~~more robust N_2, N_2O and CO_2 data. We ~~use measured data from two laboratory incubations to test the denitrification sub-modules of existing biogeochemical models. Two~~incubated two arable soils – a silt-loam and a sand – ~~were incubated~~ for 34 and 58 days, respectively~~. Fluxes of N_2, N_2O and CO_2 were quantified using gas chromatography and isotope-ratio mass spectrometry (IRMS).~~, with small field-relevant changes made to control factors during this period. For the ~~loamy~~silt-loam soil, seven treatments varying in moisture, bulk density and ~~three~~ NO_3^- contents were included, with temperature changing during the incubation. The sandy soil was incubated with and without incorporation of litter (ryegrass), with temperature, water content and NO_3^- content changing during the incubation. ~~Three common biogeochemical models (~~The denitrification and decomposition sub-modules of DeNi, Coup and, DNDC ~~and DeNi)~~ were tested using the data. No systematic calibration of the model parameters was conducted since our intention was to evaluate the general model structure or 'default' model runs. ~~As compared with~~

~~measured~~Measured fluxes~~,~~ generally responded as expected to control factors. We assessed the ~~average N_2+N_2O fluxes~~ direction of ~~the default runs for loamy soil were approximately 3 times higher for Deni, 105 times smaller for DNDC and 22 times smaller for Coup. For the sandy soils, default runs were 3 times higher for DeNi, 7 times smaller for DNDC and 12 times smaller for Coup. While measured fluxes were~~ modeled responses to control factors using three categories: no response, a response in the same direction as measurements or a response in the opposite direction to measurements. DNDC responses were: 14%, 52% and 34%, respectively. Coup responses were: 47%, 19% and 34%, respectively. DeNi responses were: 0%, 67% and 33%, respectively. The magnitude of the modeled fluxes were underestimated by Coup and DNDC and overestimated by DeNi ~~and underestimated by DNDC and Coup, the temporal patterns of the measured and~~ for the sandy soil, while there was no general trend for the ~~modeled emissions were similar for the different treatments.~~silt-loam soil. None of the models was able to determine litter-induced decomposition correctly. ~~The reason for the differences between the measured and modeled values can be traced back to model structure uncertainty and/or parameter uncertainty. Given the aim of our work - to assess existing model~~ To conclude, the currently used sub-modules are not able to consistently simulate the denitrification and decomposition processes ~~for further development and/or to identify~~. For better model evaluation and development, we need to design better experiments, take more frequent measurements, use new or updated measurement techniques, address model complexity, add missing processes ~~within~~to the models ~~- these results provide valuable insights into avenues for future research. We conclude that the predicting power of the models~~, calibrate denitrifer microbial dynamics and evaluate the anaerobic soil volume concept. Further development of the models ~~could be improved through future experiments that collect data~~to overcome the identified limitations ~~on denitrification activity with a concurrent focus on control parameter determination~~can largely improve the predicting power of the models. Models should then often be re-evaluated to keep them up-to-date with current research developments.

1 Introduction

Although our understanding of nitrous oxide (N_2O) fluxes~~, nitrogen (N) use efficiency and N leaching~~ in agricultural ecosystems has ~~steadily~~ increased in recent decades (Galloway et al., 2004; Singh 2011; Zaehle 2013), we still have ~~only~~ a limited understanding of soil denitrification and the complex interaction of factors controlling ~~denitrification processes.~~it. Addressing this knowledge gap is crucial for mitigating ~~nitrogen~~N fertilizer loss as well as for predicting and reducing N_2O emissions.

Denitrification is an anaerobic soil process by which microbes carry out the step-by-step reduction of nitrate (NO_3^-), to nitric oxide (NO), N_2O and finally dinitrogen (N_2) (Groffman et al., 2006). The production and consumption of N_2O via denitrification is affected by~~:~~ temperature (Rodrigo et al., 1997), O_2 concentration (Müller and Clough 2014), moisture (Grundmann and Rolston 1987; Groffman and Tiedje 1998), pH (Peterjohn 1991; Simek and Hopkins 1999; Simek and Cooper 2002), ~~substrate (N oxides and organic carbon) availability (Heinen 2006)~~ and gas diffusivity ~~(a function of water content)~~ of the soil (Leffelaar 1988; Leffelaar and Wessel, 1988; Li et al., ~~1992a~~1992; Del Grosso et al. 2000; Schurgers et al., 2006). Denitrification is also strongly dependent on substrate availability (N oxides and labile organic carbon) (Heinen 2006; Groffman et al., 2009). Denitrification processes positively correlated with soluble carbon (Bijay-Singh et al., 1988; Burford and Bremner, 1975; Cantazaro and Beauchamp, 1985; McCarty and Bremner, 1993). The representation of organic matter as source of electron donor in the root zone has a direct effect on the denitrification rate and indirectly also has an O_2 concentration decreasing effect by elevating the microbial activity (Philippot et al., 2007). Field measurements of denitrification that explore the interactions between these factors are challenging, due to the methodological issues surrounding the measurement of N_2 fluxes ~~(~~high background N_2 and low soil N_2 flux~~)~~ (Groffman et al., 2006). However, the impact of these different factors on denitrification can be assessed with properly designed laboratory experiments (Butterbach-Bahl et al., 2013; Cardenas et al., 2003).

Models are an important tool to explore complex interactions and develop climate-smart strategies for agriculture (Butterbach-Bahl et al., 2013). Although numerous models exist, which predict denitrification in varying environments and at different scales (Heinen 2006), it has always been challenging to evaluate the accuracy of modeled denitrification due to the paucity of suitable measured data (Sgouridis et al., 2016, Scheer et al., 2020). ~~Simplified process descriptions, inaccurate model parameters and/or inadequately collected input data result in poor predictions of N_2 and N_2O fluxes (Parton et al., 1996).~~ While in many studies N_2O emissions alone are used to develop and train models (Chen et al., 2008), measurements of both N_2O and N_2 fluxes~~, under varying soil conditions,~~ are necessary to develop and/or test ~~model~~ algorithms (~~Li et al., 1992~~Leffelaar and Wessel, 1988; Parton et al., 1996; Del Grosso et al., 2000). Simplified process descriptions, inaccurate model parameters and/or inadequately collected input data may result in poor predictions of N_2 and N_2O fluxes (Parton et al., 1996). ~~Data suitable~~While models are intended for use in the field, and ultimately the goal is for them to ~~validate N_2O and N_2 flux calculations within denitrification~~be accurate under field conditions, in order to describe processes accurately, it is often necessary to test and develop the sub-modules ~~are still scarce, yet these~~under controlled conditions, using targeted laboratory experiments (i.e. DNDC Scientific Basis and Processes, 2017). However, even targeted experiments often focus on large ~~datasets are needed~~differences in control factors (Li et al., 1996; Jiang et al., 2021); in order to validate models and improve their accuracy with respect to denitrification~~ processes.~~, datasets of small, field-relevant changes in control factors are also necessary.

Three robust, well-used models for describing denitrification processes are~~:~~ Coup (~~Jansson and Moon, 2001~~Jansson and Moon, 2001), DNDC (Li et al., 1992) and DeNi (based on the approach of the NGAS and DailyDayCent; Parton et al., 1996 and Del Grosso et al., 2000). These models were developed between 20 and 30 years ago and, with minor modifications, are still used today. DNDC has been extensively tested globally and has shown reasonable agreements between measured and modeled N_2O emissions for many different ecosystems (e.g. Li, 2007; Kurbatova et al., 2009; Giltrap et al., 2010; Khalil et al., 2016; 2018; 2019). ~~Within each of the three models (Coup, DNDC, DeNi),~~ Within each of the three models, the denitrification sub-modules use different approaches to address the complexity of denitrification, including how they consider controlling factors (e.g. soil moisture, heat transfer, nitrification, decomposition, growth/death of the denitrifiers) as well as how they simulate temporal and spatial dynamics. ~~Despite~~ However, to our knowledge evaluation of the ~~success with which each~~denitrification sub-modules of these models ~~has been used,~~was limited due to the ~~incorporation of recent advancements in our understanding~~lack of ~~denitrification may be able to improve~~ proper N_2 datasets. There is a difficulty measuring the N_2 flux in the field and the very few laboratory experiments (^{15}N or He/O_2 gas flux method) are so far the only option to validate N_2 fluxes and use the data for model ~~estimates. For example, the~~ evaluation. The development and/or testing of the NGAS and DailyDayCent models (Parton et al., 1996 and Del Grosso et al., 2000) used measured denitrification data based on the acetylene inhibition technique (Weier et al., 1993~~; Parton et al.,~~). This method~~1996 and Del Grosso et al., 2000), which~~ is no longer considered suitable for ~~many applications~~quantifying soil denitrification (Bollmann and Conrad, 1997; Nadeem et al., 2013; Sgouridis et al., 2016). Therefore, it is questionable whether past evaluations of N_2 flux modeling were valid. The lack of the proper N_2 datasets, and new research not being integrated into existing models, has developed into an urgent need for focused model development using newly developed and/or more precise data collection techniques.

In this study~~,~~ we ~~use newly measured data to test the denitrification products simulated by existing biogeochemical models as a pre-requisite for the development of new or improved approaches to denitrification modelling. Our aim in this study was not to fit the magnitude of the modeled fluxes to the measured values and rate the performance of the models. Instead, we aim to~~ identify missing processes ~~and~~or limitations in the denitrification and decomposition sub-modules ~~and determine the best next step for model development. Therefore, the denitrification~~ that interfere with process description. We use newly measured data to test the sub-modules of ~~the models were not calibrated, since the~~existing biogeochemical models under field-relevant ranges in control factors. No systematic calibration ~~would have been different for the different experimental settings and the results of the~~of the model parameters was conducted since our intention was to evaluate the general model structure or 'default' model runs~~would not have been comparable for the different measurements~~. Without calibration, we can compare the performance of the sub-modules with the same (factory) settings for the different experimental treatments. Specifically, our aims were to: (i) compile and present unpublished N_2, N_2O and ~~N_2O~~CO_2 results from two laboratory incubations (Ziehmer, 2006, Merl, 2018) (ii) simulate denitrification ~~products~~and decomposition using the three models (Coup, DNDC, DeNi) (iii) compare the measured and modeled ~~values~~temporal dynamics, (iv~~) identify soil conditions when models could or could not predict N_2 and N_2O fluxes, and (v~~) make suggestions for model improvement.

2 Materials and methods

2.1 Denitrification and decomposition data collection

2.1.1 Hattorf field site (silt-loam soil)

Soil samples were taken in October 2005 from an arable soil near Hattorf (hereafter referred to as the silt-loam soil), Lower Saxony, Germany, in the loess-covered Pöhlde basin near the Harz mountains (51°39.35868' N, 10°14.71872' E, 215 m a.s.l.). The site is in the transition zone of the cool continental/subarctic climate and warm-summer humid continental climate, where the mean annual temperature is between 7 and 8.5°C and the average yearly precipitation is 700 mm. The cropping rotation of the site was winter rape – winter wheat – winter barley, and sampling was conducted when the vegetation was winter rape. The Haplic Luvisol (IUSS Working Group WRB. 2015.) soil had a silt-loam texture with relatively low organic ~~matter~~carbon content (Table 1). In the field, a 4 m^2 area was marked out for sampling. In this area, plants (winter rape) were first removed and then surface soil (0 to 10 cm depth) was collected with spades and shovels in large, plastic boxes. Soil was returned to the lab, where it was sieved to 10 mm, homogenized, subsamples sieved for 2 mm and analyzed for physical and chemical properties (Table 1), and remaining field moist soil stored at 4ºC until use.

Table 1: Physical and chemical data of surface soil from Hattorf (silt-loam, 0 to 10 cm depth) and Fuhrberg (sand, 5 to 20 cm depth), Germany~~y~~

	Clay	Silt	Sand	Bulk density	pH ($CaCl_2$)	Total N	Organic C	C/N ratio
	[%]	[%]	[%]	[g cm^{-3}]		[%]	[%]	
Hattorf	15.2	77.6	7.2	1.4	6	0.1	1.1	10
Fuhrberg	3.1	5.9	91.0	1.5	4.8	0.1	2.1	16

	~~Clay~~	~~Silt~~	~~Sand~~	~~Bulk density~~	~~pH~~	~~Total N~~	~~Organic C~~	~~C/N ratio~~	
	~~[%]~~	~~[%]~~	~~[%]~~	~~[g/cm³]~~		~~[mg N kg-1]~~	~~[mg N kg-1]~~	~~(CaCl2)~~	~~[%]~~
~~Hattorf~~	~~15.2~~	~~77.6~~	~~7.2~~	~~1.4~~	~~6~~	~~0.1~~	~~1.05~~	~~10~~	
~~Fuhrberg~~	~~3.1~~	~~5.9~~	~~91.0~~	~~1.5~~	~~4.8~~	~~0.1~~	~~2.1~~	~~15.5~~	

2.1.2 Fuhrberg field site (sand soil)

Soil samples were taken in August 2016 from an arable soil near Fuhrberg (hereafter referred to as the sand soil), Lower Saxony, Germany (52°33.17622' N, 9°50.85816' E, 40 m asl). The site is in the transition zone of the temperate oceanic climate and warm-summer humid continental climate, where the mean annual temperature is 8.2°C and the average yearly precipitation is 680 mm. Typical crops during the preceding decades were winter cereals, potatoes, sugar beet and maize. The soil is a Gleyic Podzol (IUSS Working Group WRB. 2015.) developed in glacifluvial sand (Böttcher et al., 1999; Well et al., 2005). The first 5 cm of soil contained incorporated winter wheat straw residuals. To avoid inaccuracy in the measurement of soil parameters~~,~~ (Table 1), this 5 cm layer was removed by hand in a 100 m^2 area followed by the collection of soil from a depth of 5 to 20 cm. After field collection with spades and shovels, soil was transported to the lab, air dried, sieved to 10 mm, homogenized and stored in plastic boxes at 4°C until use. ~~The measured physical and chemical properties of the soil are shown in Table 1.~~The soil samples for the laboratory analyses were sieved to 2 mm.

2.1.3 Silt-loam laboratory incubation

To avoid measuring the effect of rewetting (increased respiration and mineralization) during the incubation, soil was pre-incubated at room temperature for 2 weeks at 50% of maximum water holding capacity. ~~After the pre-incubation period~~Then, ^{15}N-KNO_3 solutions (see Tables 2 and 3 for concentrations) were added ~~to subsets of soil~~ and thoroughly mixed. Three replicates of each treatments were prepared. Soils were then packed into plexiglass cylinders (14.4 cm inner diameter) at typical field bulk density (1.4-1.5 g cm^{-3}) and a soil depth of 25 cm. Distilled water was ~~then~~ added to each cylinder to bring the water-filled pore space (WFPS) up to ~~the target~~73-90% for each treatment (Table 2). The soil cylinders were incubated for 34 days, during which the headspace was continuously flushed with ambient air at a flow rate of 6 ml min^{-1}. During the incubation, only temperature was changed (~~Fig. S.~~Table 3), while the initial settings of water content were not changed and loss of soil water by evaporation was minimized because the mesocosms were kept ~~constant~~closed. Temperatures were selected to mimic winter conditions, to assess whether previously observed NO_3^--N losses during winter could be explained by denitrification (~~Ziemer~~Ziehmer, 2006). Gas samples were collected manually once a day and analyzed by gas chromatography (GC) (Well et al., 2009) to determine N_2O and CO_2 fluxes, and by isotope ratio mass spectrometry (IRMS) to determine the flux of N_2+N_2O originating from the ^{15}N–labeled NO_3^- (Well et al., 1998; Lewicka-Szczebak et al., 2013). Soil samples were collected after pre-incubation immediately before packing of the mesocosm as well as at the ~~beginning and~~ end of the ~~incubations~~incubation and analyzed for NO_3^-, NH_4^+ and water content as described in Buchen et al. (2016).

Table 2: Initial settings of laboratory incubations of soil from Fuhrberg (Sand) and Hattorf (silt-loam; treatments I to VII), Germany.

	Silt-loam							Sand
	I	II	III	IV	V	VI	VII	
Added N (KNO_3) [mg N kg^{-1} dry soil]	20	10	40	20	20	20	20	50
atom % ^{15}N in KNO_3	60	98	60	60	60	60	60	60
Calculated ^{15}N enrichment [at%] of the NO_3^- in the soil	35	41	45	35	35	35	35	60
NO_3^--N + NH_4^+-N in the unfertilized soil [mg N kg^{-1} dry soil]	14	14	14	14	14	14	14	16
Thickness of soil layer ~~(~~[cm~~)~~]	25	25	25	25	25	25	25	10
Bulk density [g cm^{-1}]	1.4	1.4	1.4	1.46	1.52	1.4	1.4	1.5
grav. water content [g g^{-1}]	0.25	0.27	0.27	0.25	0.25	0.27	0.30	0.~~231~~*23
WFPS ~~(%)~~[%]	73~~.0~~	80~~.0~~	80~~.0~~	80	88	80~~.0~~	90~~.0~~	80~~.0~~*

~~Table 3: Initial extractable N content, N fertilization and calculated ^{15}N enrichment after fertilization in laboratory incubations from Fuhrgerg (sand) and Hattorf (silt-loam), Germany. The Hattorf incubation had 7 different treatments (Roman numbers) with 3 different added N values.~~

~~Experiment (variants)~~	~~NO_3^--N + NH_4^+-N in the unfertilized soil [mg N kg^{-1} dry soil]~~	~~Added N (KNO_3) [mg N kg^{-1} dry soil]~~	~~Calculated ^{15}N enrichment (at%) of the NO_3^- in the soil~~
~~Silt-loam (II)~~	~~14~~	~~10~~	~~41~~
~~Silt-loam (I, IV, V, VI, VII)~~	~~14~~	~~20~~	~~35~~
~~Silt-loam (III)~~	~~14~~	~~40~~	~~45~~
~~Sand~~	~~16~~	~~50~~	~~60~~

2.1.4 Sand laboratory incubation

~~To exclude~~Similar to the ~~phase of intensive respiration and mineralization typically following rewetting, soils were~~silt-loam soil, the sandy soil was pre-incubated at 50% of maximum water holding capacity (determined from the measured water retention curve) for 3 weeks (at room temperature). After pre-incubation, ^{15}N-labelled KNO_3 solution (50 mg N kg^{-1} dry soil) was added ~~to the soil,~~ and thoroughly mixed (Table 2 ~~and Table 3~~). After addition of NO_3^-~~,~~, the soil was divided, and in half of it, ground ryegrass (sieved with 1 mm mesh; added at a rate of 2.2 g kg^{-1} dry soil) was also homogenously incorporated.

The ryegrass had a C~~-to-~~/N ratio of 25, and ~~nitrogen~~N, carbon and sulphur content of: 1.3%, 32.2% and 0.4%, respectively. Four replicates of soil from each of the two treatments (with and without ryegrass) were then packed into plexiglass cylinders ~~(14.4 cm inner diameter)~~ at typical field bulk density (1.5 g cm^{-3}) and a soil depth of 10 cm (Table 2). The~~ soil~~ cylinders were incubated for 58 days~~, during which the headspace was continuously flushed with an artificial gas mixture (2% N_2 and 20% O_2 in He) at a flow rate of 20 ml min^{-1}. The low N_2 concentration was established to increase the sensitivity of N_2 flux detection (Lewicka-Szczebak et al., 2017).~~

~~The cylinders were incubated using an~~. An automated incubation system was used, including gas analysis by GC, suction plates at the bottom of the cylinders to control water potential and collect leachate, and an irrigation device to mimic precipitation and/or fertilization~~. Using the GC, N_2O, CH_4, N_2 and CO_2 (Säurich et al., 2019) were continuously measured throughout the incubation. Gas samples were also collected~~ (Lewicka-Szczebak et al., 2017; Kemmann et al., 2021; Säurich et al., 2019). Gas samples were also collected every third day manually for IRMS analysis, to determine fluxes of N_2 and N_2O originating from the ^{15}N labeled NO_3^- (Well et al., 1998; Lewicka-Szczebak et al., 2013~~). The pressure head at the suction plates was controlled by connecting the bottles for seepage collection to a gas reservoir, which was maintained at the target pressure (±0.5 kPa). Water potential in the soil column resulted from the difference in the pressure head between the soil cylinder headspace and suction plate. Headspace pressure was positive due to the continuous headspace flow and flow restriction in the exhaust line of the gas sampling system.~~).

Instability in the headspace pressure (values between 1 and 3 kPa) occurred near the end of the experiment, due to partial clogging of the hypodermic needles that were used to lead the exhaust gas through sampling vials (Well et al., 2006). Therefore, pressure head in the soil columns was associated with an uncertainty of about 2.5 kPa.

Variable pressure resulted in differing water content within and between treatments, so results are shown for individual replicates of both treatments (Fig. S.1 and Fig. S.2). The water content of the soil was initially set to 0.231 g g^{-1} (equivalent to 80 % WFPS) and was subsequently changed by establishing defined water potential at the suction plates (Table ~~4~~3) and by adding water and/or KNO_3 solution from the top of the columns as irrigation/fertilization events. Phases with defined temperature were set as shown (~~Fig. S.3 and Table 4). Soil samples were collected at the beginning and end of the incubations and analyzed for NO_3^-, NO_2^-, NH_4^+, DOC, pH and water content as described in Buchen et al. (2016~~Table 3).

Table ~~4~~3: Experimental settings during ~~an~~ a 5-8~~-~~ week laboratory incubation of re-packed soil cores from Fuhrberg, Germany~~.~~ (sand) and Hattorf, Germany (silt-loam)

Soil	Week of Experiment	1	2	3	4	5	6	7	8
Sand	Bottom water potential ~~(~~[kPa~~)~~]	-10	-20	-60	-60	-10	-10	-10	-10
	~~Temp.~~ Temperature [°C]	20	20	20	20	20	10	5	10
	Irrigation with water ~~(~~[mm~~)~~]	-	-	-	-	10	-	-	-
	Irrigation with NO_3^- solution [mm / mg N kg^{-1}]	-	-	-	-	30 / 30	-	-	-

Silt-loam	Temperature [ºC]	10	6	2	6	10	-	-	-

2.2 Model ~~choice and~~ description and setup

Using the denitrification data collected in the incubations described above, we tested the denitrification and decomposition sub-modules of three biogeochemical models: Coup (Jansson and Moon, 2001), DNDC (Li et al., 1992) and DeNi (based on the approach of the NGAS and DailyDayCent; Parton et al., 1996 and Del Grosso et al., 2000). Selected experimental data for model evaluation included denitrification (N_2 and N_2O fluxes produced from soil NO_3^-) and decomposition (CO_2 fluxes) and "proximal" and "distal" controls (according to the definition by Groffman and Tiedje 1998). Proximal controls were temperature, NO_3^-, pH and organic C. Distal controls were soil moisture, texture, NH_4^+-N, bulk density and respiration (as a proxy for O_2 consumption). Models were set up according to the initial experimental setups of the two incubations (i.e. 7 initial model set-ups for silt-loam and 2 set-ups for sand; Table 2). For the silt-loam soil, only soil temperature was changed during the experiment, while for the sand soil temperature, soil water status (change of the water potential and irrigation) and NO_3^- content (by irrigation with KNO_3 solution) were changed~~Our first criterion of denitrification sub-modules evaluation was the agreement of measured and modeled results with respect to directional changes of N2 and N2O (i.e. fluxes increasing or decreasing) in response to the relevant control factors. Comparing the magnitude of measured and modeled fluxes was not considered as a criterion. We note that individual control factors were tested only to a limited extent, and were otherwise affected by interactions with other control factors (see description of experimental design in 2.12.1). Nevertheless, comparing the temporal dynamics of fluxes measured in the experiments and given by the models, reveals the suitability and deficiencies of both, which can pave the way for planning better model evaluation experiments and for developing model routines to fill the gaps of the current approaches~~.

In the two experimental setups, variation of individual control factors was only tested to a limited extent, but measurements reflected the interaction of multiple control factors (see 2.1.3 and 2.1.4). Those interactions presented additional complexity, which provided valuable data on the temporal dynamics of measured vs modeled fluxes. Comparing the magnitude of measured and modeled fluxes was considered in the evaluation process but it was not our primary criterion. Our first criterion of model evaluation was the agreement of measured and modeled results with respect to directional changes of N_2, N_2O and CO_2 (i.e. fluxes increasing or decreasing) in response to the relevant control factors.

2.2.1 Coup

Coup (coupled heat and mass transfer model for soil–plant–atmosphere systems) is a complex, adjustable process-oriented model that uses a modified approach of PnET-N-DNDC to simulate nitrification and denitrification (Norman et al., 2008). Coup gives users the option to choose between different algorithms, each representing the functionality of a sub-module, with each sub-module addressing a different aspect of the soil-atmosphere-vegetation system (Senapati et al., 2016; He et al., 2016; Norman et al., 2008; Nylinder et al., 2011; Conrad and Fohrer, 2009). ~~It is a developed version of the SOIL and SOILN models (Jansson and Moon, 2001). The main model structure is a vertical layered, 1-D soil profile. Coup includes all main heat and water flow processes in the soil profile as well as exchange with the atmosphere.~~This complex modular structure allowed us considerable freedom in adapting the model structure to our experimental setup and the available data (Table S.1).

In the model, soil columns of sand were divided into 5 layers (we are assuming equilibrium, and it was calculated based on the water retention curve and layer depth) with layer extents of 2 cm. The water retention curve was not available for the silt-loam soil. The soil columns were thus modeled as a 25 cm unified, single soil layer. Daily water content and soil temperature were set up in the model as dynamic input parameters coming from water balances and measurements, respectively. The initial contents of organic carbon, total N, NO_3^--N and NH_4^+-N of the silt-loam and sand were used in the model (Table S.2). A first order kinetics approach for two pools (litter and humus) governed by response functions of soil moisture and temperature is used to simulate soil organic carbon dynamics. ~~In Coup, soil~~Soil litter represents the rapidly decomposable organic material (e.g. fresh plant litter) and the humus pool represents the more resistant fraction. ~~Fluxes of NO, N_2O and N_2 are modeled via nitrification and denitrification, which in turn are obtained from modeled parameters including respiration, mineral N, and dissolved organic C (DOC).~~The initial amount of soil organic carbon (SOC) allocated into the labile pool was based on default SOC allocation fractions. For the sand soil cores with application of ryegrass, the C and N of ryegrass were exclusively added to the labile pool. Since the basic settings resulted in overestimation of CO_2 production, first order decomposition rate coefficients for litter and humus were changed to modify decomposition and mineralization to fit measured rates. From the two available algorithms to describe denitrification, the algorithm with explicit consideration of denitrifiers was chosen (Table S.1), which includes the microbial approach for the denitrification sub-model. The applied settings and parameters are in Tables S.1, S.2 and S.3. Parameters were adjusted separately for each experiment (silt-loam and sand) but were identical between treatments. The soil anaerobic fraction is defined by the approach of the anaerobic balloon concept of DNDC (Norman et al., 2008).

~~The simulation of nitrification is calculated by the response functions of soil temperature and moisture, pH and NH_3 concentration (Norman et al., 2008) Denitrification processes are simulated by soil temperature, pH and the N concentration of the microbial pool and the anaerobic fraction of the soil (Jansson and Karlberg, 2011) (see Table S.6). The model can simulate C, N and water fluxes in hourly resolution. The complex modular structure gives flexibility to users for planning a step-by-step increase in the complexity of simulations. This option is ideal for the simulation of laboratory~~

~~experiments. Users can freely define the thickness and the number of soil layers and the setup of the initial conditions of each layer. The model can also simulate changes of the parameters between soil layers.~~

2.2.2 DeNi

DeNi was programmed based on the nitrification and denitrification approach of the NGAS model (an early stage of the ~~DayCent~~DailyDayCent model) (Parton et al., 1996) (see Table S.~~6~~3). The approach of the DailyDayCent (and therefore DeNi) model for the description of denitrification is a hybrid between detailed process-oriented models and simpler nutrient cycling models (Parton et al., 1996). It allows users to separately test the nitrification and denitrification sub-modules. The model runs on daily time steps. The main difference between DailyDayCent and Coup is that Coup~~, like other more complex process-oriented models,~~ explicitly models denitrifier dynamics. In contrast, the ~~DailyDaycent~~DailyDayCent/NGAS model is a relatively simple, semi-empirical model to simulate the N_2+N_2O production without directly considering microbes.~~ It uses empirical parameters and functions that have no direct physical, chemical or biological explanation and were developed from experimental observations. Therefore, it is the combination of a simplistic nutrient cycle model and a more detailed process-based model (Parton et al., 1996).~~

~~The N_2O flux from nitrification is modeled using: soil pH, soil temperature, soil moisture, soil NH_4^+ concentration (available NH_4^+ is then computed as a function of NH_4^+ concentration), and the N turnover coefficient, which is a soil-specific parameter.~~

~~The denitrification sub-module calculates the fluxes of N_2 and N_2O. The soil heterotrophic respiration rate (depending on the available carbon), soil NO_3^- concentration and soil moisture (WFPS) control total denitrification. The N_2/N_2O ratio is calculated as a function (F(NO_3/CO_2)) of electron donor (NO_3^-) to substrate and soil water content (Del Grosso et al., 2000).~~Parameter adjustment and data input were accomplished using the DeNi source code. Measured soil texture, bulk density, initial NO_3^-, NH_4^+ and C/N ratio were used to initialize the model. For the silt-loam soil we ran the model calculated with one soil layer because water content was assumed homogenous. For the sand soil, five, 2 cm thick soil layers with differing water contents were simulated because significant differences in water content were evident/expected. We used the measured daily temperature and the theoretical (calculated) water content of each of the 5 layers. Irrigation, seepage and fertilization events were included, and the model was modified with calculated changes in NO_3^--N and water content, which were calculated based on the irrigation, seepage and fertilization events. The ryegrass treatment as extra labile organic carbon was added as a higher C/N ratio. The theoretical NH_4^+ and NO_3^- concentrations (Table S.4) were changed (modeled production and consumption) by mineralization, nitrification, denitrification, leaching and the added fertilizer (Table S.5) during the simulations. For the calculation of missing soil physical parameters (e.g the soil gas diffusion coefficients) the respective pedotransfer functions were applied (Saxton and Rawls, 2000).

2.2.3 DNDC

The Denitrification-Decomposition model (DNDC) is a complex, widely used process-based model of C and N biogeochemistry in agricultural ecosystems (e.g. Li et al. 1994). ~~It has been extensively tested globally and has shown reasonable agreements between measured and modeled N_2O emissions for many different ecosystems (e.g. Li, 2007; Kurbatova et al., 2009; Giltrap et al., 2010; Khalil et al., 2016; 2018; 2019). Several modifications/versions have been developed to fit different ecosystems and those provide variable estimates depending on the model versions used.~~ DNDC contains six sub-modules: soil climate, crop growth, decomposition, denitrification (see Table S.~~6~~3), nitrification and fermentation. ~~It additionally includes subroutines for cropping practices (fertilization, irrigation, tillage, crop rotation and manure addition).~~ The model joins denitrification and decomposition processes together to predict emissions of C and N from agricultural soils, based on various soil, climate and environmental factors. ~~It considers the soil as a series of discrete horizontal layers with uniform soil properties within each layer, except for some soil physical properties that are anticipated as being constant across all layers. However, time~~Time-dependent variations in soil moisture, temperature, pH, C and N pools are considered ~~for a reliable estimate of C and N fluxes~~ by calculating them for each soil layer for each time step. Like in Coup, denitrifiers are explicitly modeled.

~~2.3 Model initialization~~

~~Selected experimental data for model evaluation included denitrification (N_2 and N_2O fluxes produced from soil NO_3^-) and "proximal" and "distal" controls (according to the definition by Groffman et al., 1988). Proximal controls were temperature, NO_3^-, pH and organic C. Distal controls were soil moisture, texture, NH_4^+-N, bulk density and respiration (as a proxy for O_2 consumption).~~

~~Our first criterion of model evaluation was the agreement of measured and modeled results with respect to directional changes of N_2 and N_2O (i.e. fluxes increasing or decreasing) in response to the relevant control factors. Comparing the magnitude of measured and modeled fluxes was considered a secondary criterion. In the two experimental setups, individual control factors were only tested to a limited extent, while the remaining measurements reflected the interaction of multiple control factors (see 2.1.3 and 2.1.4). Those interactions presented additional complexity, which would not classically be used for model evaluation, yet provided valuable data on the temporal dynamics of measured vs modeled fluxes (see discussion for details).~~

~~Models were set up according to the initial experimental setups of the two incubations (i.e. 7 initial model set-ups for silt-loam and 2 set-ups for sand; Table 2). For the silt-loam soil, only soil temperature was changed during the experiment, while for the sand soil temperature, soil water status (change of the water potential and irrigation) and NO_3^- content (by irrigation with KNO_3 solution) were changed. We first compare to which extent the models fit the magnitude of fluxes in general, and subsequently, whether the models reflect the observed differences between the experimental treatments.~~

~~2.3.1 Coup~~

~~Coup gives users the option to choose between different algorithms, each representing the functionality of a sub-module, with each sub-module addressing a different aspect of the soil-atmosphere-vegetation system (Senapati et al., 2016; He et al., 2016; Norman et al., 2008; Nylinder et al., 2011; Conrad and Fohrer, 2009). This feature was used to adapt the model structure to the experimental setup and the available data (Table S.7).~~

~~In the model, soil columns of sand were divided into 5 layers (we are assuming equilibrium, and it was calculated based on the water retention curve and layer depth) with layer extents of 2 cm. The water retention curve was not available for the silt-loam soil. The soil columns were thus modeled as a 25 cm unified, single soil layer. Daily water content and soil temperature were set up in the model as dynamic input parameters coming from water balances and measurements, respectively. The initial contents of organic carbon, total N, NO_3^--N and NH_4^+-N of the silt-loam and sand were set up in the model (Table S.8). The initial amount of SOC allocated into the labile pool was based on default SOC allocation fractions. For sand treatments with application of ryegrass, the C and N of ryegrass were exclusively added to the labile pool. Since the basic settings resulted in overestimation of CO_2 production, first order decomposition rate coefficients for litter and humus were changed to modify decomposition and mineralization to fit measured respiration rates.~~

~~From the two available algorithms to describe denitrification, the algorithm with explicit consideration of denitrifiers was chosen (Table S.7), because we wanted to test a model which includes the microbial approach for the denitrification sub-model. The structure and the complexity of Coup made it necessary to modify some model parameters and settings to improve the fit between modeled and measured N_2O and N_2 fluxes. The applied settings and parameters are in Tables S.6, S.7 and S.8. Parameters were adjusted separately for each experiment (silt-loam and sand) but were identical between treatments.~~

~~2.3.2 DeNi~~

~~Parameter adjustment and data input were accomplished using the DeNi source code. Measured soil texture, bulk density, initial NO_3^-, NH_4^+ and SOC were used to initialize the model. We ran the model calculated with one soil layer for the silt-loam soil and with five, 2 cm thick soil layers for the sand soil, with differing water contents. We used the measured daily temperature and the theoretical (calculated) water content of each of the 5 layers (see 2.3.1). Irrigation, seepage and fertilization events were included, and the model was modified with calculated changes in NO_3^--N and water content, which were calculated based on the irrigation, seepage and fertilization events. The theoretical NH_4^+ and NO_3^- concentrations (Table S.2) were changed (modeled production and consumption) by mineralization, nitrification, denitrification, leaching and the added fertilizer (Table S.1) during the simulations. For the calculation of missing soil physical parameters (e.g the soil gas diffusion coefficients) the respective pedotransfer functions were applied (Saxton and Rawls, 2000). Besides N_2O and N_2, the model also calculated the soil fluxes of CO_2.~~

~~2.3.3 DNDC~~

~~The latest version of DNDC (DNDC95) was used to simulate N_2O, N_2 and soil CO_2 emissions. The model was originally designed for field and regional scales. Therefore, certain adjustments had to be made to establish suitable model inputs to represent the conditions of the laboratory incubations.~~ Based on the experimental setup for the sand soil, the irrigation with KNO_3 solution ~~had to be~~was simulated as rainfall containing NO_3^- and the atmospheric background of NH_3 and CO_2 was considered zero and negligible, respectively, since the incubation was in an artificial atmosphere. Minimum and maximum temperatures were set according to the actual experimental values. ~~Measured soil inputs were included with microbial activity index (factor to modify the denitrification process) of 1.~~ The mixing of the experimental soil prior to incubation was applied as litter-burying till with no crop and coupled with water and NO_3^- fertilizer addition. Nitrate fertilizer was added twice with ryegrass residue as straw either mixed or omitted. Water was added once in the beginning and twice in the middle of the experiment as per treatments in the form of irrigation following comparative tests with rainfall as well as rainfall and irrigation options.

To run the model using inputs from the silt-loam incubation, the microbial activity index, temperature setting and mixing of soil with water as irrigation and fertilizer were simulated as in the sand incubation but irrigation and fertilization were assumed to occur only once in the beginning and rainfall was considered zero.

2.~~4~~3 Statistics and calculations

Statistical calculations were done using the Python 3 (Van Rossum and Drake, 2009) and the R (R Core Team, 2013) programming languages and GNUPlot (Williams and Kelley, 2011) interactive plotting program. A multiple comparison of means (Tukey HSD, $p<0.05$) was performed on the N_2+N_2O and CO_2 data of the silt-loam soil. The N_2+N_2O data of the sand soil was not normally distributed. Therefore, the Wilcoxon signed-rank test was used for these data to test the effect of the ryegrass application~~.~~ ($p<0.05$).

Responses to control factors were assessed using the ratio of treatment differences between modeled and measured values, e.g. $((I_{Mod} - II_{Mod})/I_{Mod})/((I_{Meas}-II_{Meas})/I_{Meas})$. The ratio between relative treatment differences of measured and modeled values is 1, if the measured and the modeled values changed with the same magnitude in the same direction. If the ratio is bigger than 1, the direction of measured and modeled values is the same, but the magnitude of the response is bigger in the model than was seen in the measured values. If the value is between 0 and 1, the direction is the same, but the magnitude of the response is smaller in the model than was seen in the measured values. If the ratio is negative, the direction of the response is opposite in the model as compared to the measurements. For ratios of 0, there was no model response to differences between treatments.

3 Results

3.1 Silt-loam soil

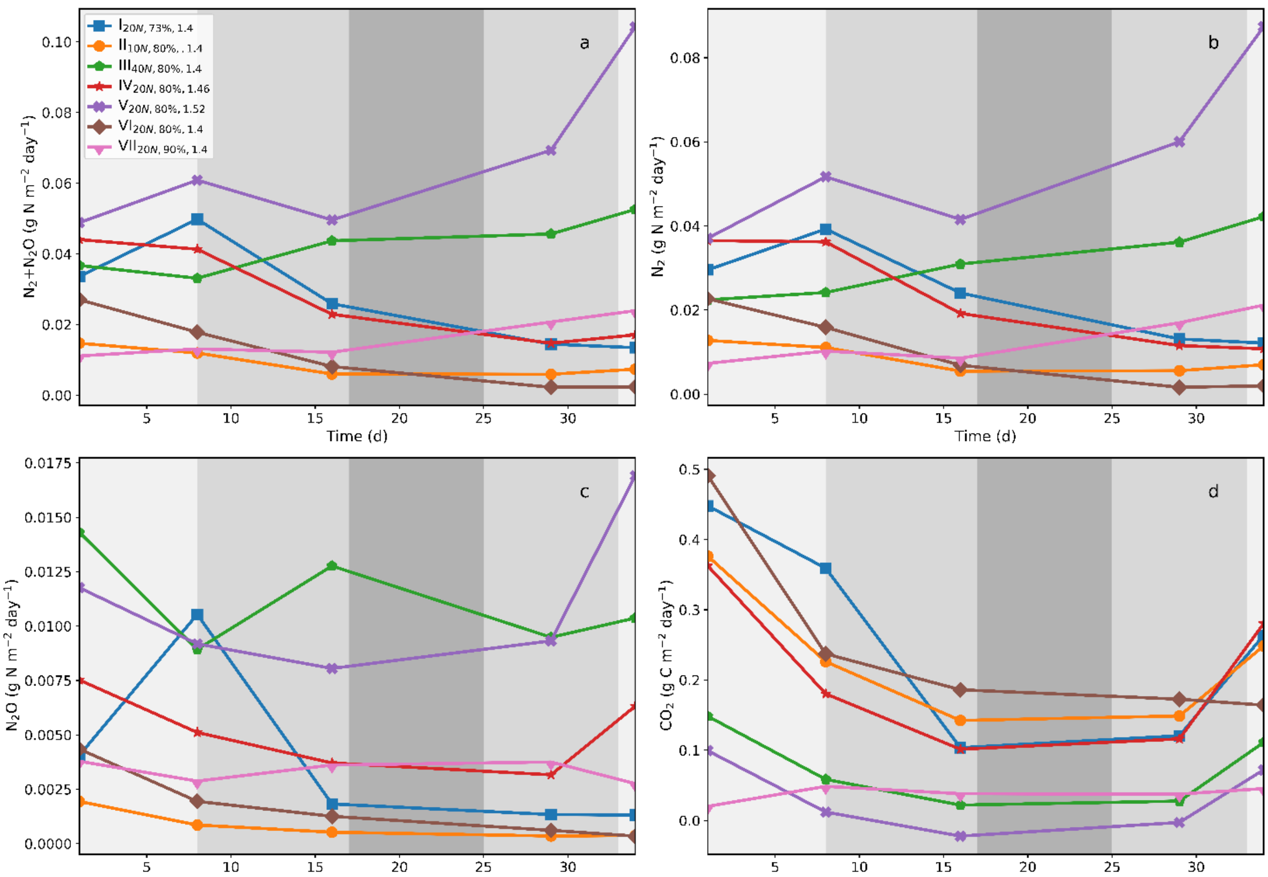
In the summary of the results, we discuss general trends seen in the data, with statistical differences specified when relevant. Results of the seven silt-loam treatments are shown in Table ~~5~~4. CO_2 fluxes were ~~positively correlated~~increased with temperature (Fig. S.3d, Table 3). Cumulative CO_2 fluxes were ~~generally~~ highest in the treatments with low WFPS and lowest in the treatments with high WFPS and bulk density (Table ~~5; Fig. S.4~~2). N_2+N_2O fluxes decreased over time in treatments ~~I$_{20N_73\%_1.4}$; II$_{10N_80\%_1.4}$; IV$_{20N_80\%_1.46}$; VI$_{20N_80\%_1.4}$~~I, II, IV, VI whereas the opposite was the case in treatments ~~III$_{40N_80\%_1.4}$; V$_{20N_88\%_1.52}$~~III, V, and ~~VII$_{20N_90\%_1.4}$~~VII (Fig. S.~~1~~3a). Cumulative N_2+N_2O fluxes decreased in the order ~~V$_{20N_88\%_1.52}$ > III$_{40N_80\%_1.4}$ > IV$_{20N_80\%_1.46}$ > I$_{20N_73\%_1.4}$ > VII$_{20N_90\%_1.4}$ > VI$_{20N_80\%_1.4}$ > II$_{10N_80\%_1.4}$. The highest~~ $V \geq III \geq IV = VII > I = VI = II$

(p<0.05; Tukey HSD), showing treatments III to V, which were characterized by elevated bulk density or N level, exhibited higher fluxes than the other treatments. Highest cumulative N_2+N_2O fluxes were thus related to higher bulk density and WFPS (Table ~~5~~4). The treatment with lowest NO_3^- application (~~II~~~~10N_80%_1.4~~II) showed the lowest N_2+N_2O flux, while the highest bulk density resulted in higher N_2+N_2O flux compared to all other treatments (Table ~~5~~4). The N_2O/(N_2+N_2O) ratio was generally low (between 0.088 and 0.264, Table ~~5~~4).

~~Table 5: Measured~~Table 4: Averages and standard deviation (n=4) of measured cumulative fluxes (N_2, N_2O, N_2+N_2O: g N m^{-2} day^{-1}; CO_2: g C m^{-2} day^{-1}) and N_2O/(N_2+N_2O) ratio of cumulated fluxes (dimensionless) ~~– over 34 days – of 7 different treatments, during a~~from two laboratory ~~incubation of~~incuations: arable, silt-loam soil from Hattorf, Germany~~.~~ (34 days; 7 treatments) and arable, sandy soil from Fuhrberg, Germany (58 days; 2 treatments). Shown in the treatment ~~headings~~column are added ~~N~~NO_3^- (10/20/40 mg KNO_3-N / kg dry soil), water-filled pore space (WFPS; 73-90%) and bulk density~~. (~~ (BD; 1.4-1.52 g cm^{-3}~~).~~) for the silt-loam soil. Superscript letters indicate significant differences within sites, between treatments (p<0.05; Tukey HSD for silt-loam and Wilcoxen for sand).

	Treatment~~I~~ ~~20N_73%_1.4~~	~~II 10N_80%_1.4~~	~~III 40N_80%_1.4~~ N_2	~~IV 20N_80%_1.46~~ N_2O	~~V 20N_88%_1.52~~ N_2+N_2O	~~VI 20N_80%_1.4~~ N_2O/(N_2+N_2O)	~~VII 20N_90%_1.4~~ CO_2
~~N_2~~I	~~0.118~~N: 20 WFPS: 73 BD: 1.4		0.~~156~~118±0.133	0.~~114~~019±0.022	0.~~278~~137^c±0.140	0.~~049~~139	1.295^a ±0.~~064~~715
~~N_2O~~II	~~0.019~~N: 10 WFPS: 80 BD: 1.4	~~0.042~~Silt-loam soil	0.~~056~~042±0.026	0.~~026~~004±0.002	0.~~055~~046^c±0.025	0.~~009~~088	1.142^a±0.~~017~~273
~~N_2+N_2O~~III	~~0.137^c~~N: 40 WFPS: 80 BD: 1.4	~~0.004~~	0.~~212^{ab}~~156±0.116	0.~~140^{bc}~~056±0.025	0.~~334^a~~212^{ab}±0.137	0.~~058^c~~264	0.~~081^{bc}~~368^{bc}±0.515
~~N_2O/(N_2+N_2O)~~IV	~~0.139~~N: 40 WFPS: 80 BD: 1.46	~~0.046^c 0.088 1.142^a~~	0.~~264~~114±0.107	0.~~184~~026±0.025	0.~~166~~140^{bc}±0.131	0.~~148~~184	1.041^{ab}±0.~~207~~434
V	N: 20 WFPS: 88 BD: 1.52		0.278±0.124	0.055±0.016	0.333^a±0.138	0.166	0.158^c±0.212

~~CO_2~~ VI	N: 20 WFPS: 80 BD: 1.~~622^{a}~~4		0.~~368^{bc}~~049±0.049	~~1.041^{ab}~~0.009±0.011	0.~~158^{c}~~058^{c}±0.059	~~1.483^{a}~~0.148	1.251^{a}±0.~~190^{c}~~503
VII	N: 20 WFPS: 90 BD: 1.4		0.064±0.049	0.017±0.009	0.081^{bc}±0.051	0.207	0.190^{c}±0.316
C1-4	Added ryegrass	Sandy soil	0.490±0.075	4.82±0.632	5.31^{a}±0.677	0.908	52.7^{a}±9.74
C5-8	Control		0.053±0.005	0.638±0.097	0.691^{b}±0.100	0.924	15.2^{b}±2.06



~~Figure 1 a-d: Measured fluxes of N_2+N_2O (a), N_2 (b), N_2O (c) and CO_2 (d) of an arable, silt-loam soil from Hattorf, Germany (values shown are the mean of four replicates over a 34 days laboratory incubation). The background colors show the temperature during each time period (light grey: 10°C, middle grey: 6°C, dark grey: 2°C).~~

3.2 Sand soil

~~Fluxes are shown for individual replicates of both treatments (Fig. 2 and Fig. 3), as variable pressure (see section 2.1.4) resulted in differing water content within and between treatments (Table S.1; Fig. S.4). The initial water content of 80% WFPS was equivalent to a water potential of -3 kPa according to the water retention curve of this soil (Fig. S.2). Leaching dynamics were also highly variable between replicates (Table S.1).~~

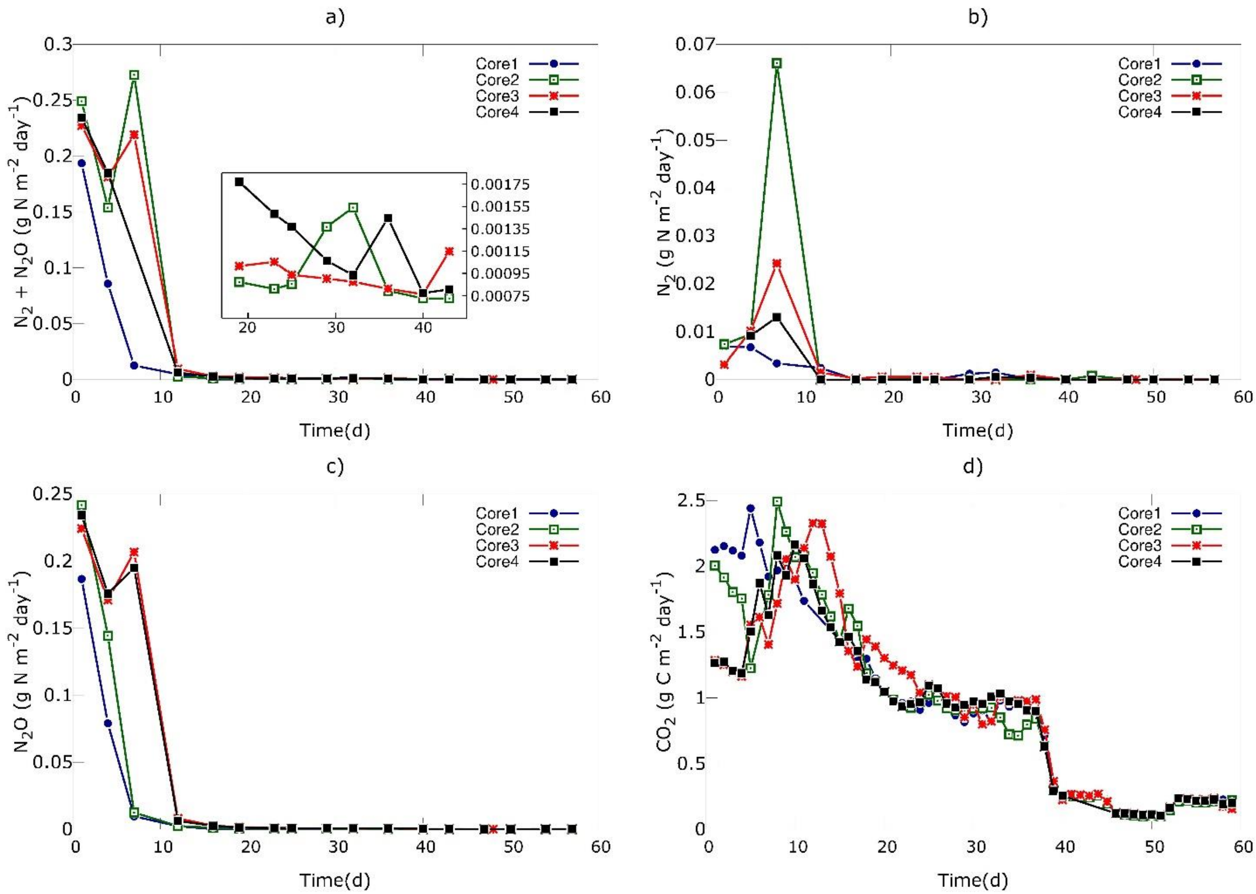
~~Table 6: Measured cumulative fluxes (N_2, N_2O, N_2+N_2O: g N m^{-2} day^{-1}; CO_2: g C m^{-2} day^{-1}) and product ratios over a 58 days laboratory incubation of sandy soil from Fuhrberg, Germany. Shown are averages and standard deviation of 4 replicate cores with (C1-4) and without (C5-8) added ryegrass.~~

	~~N_2~~	~~N_2O~~	~~N_2+N_2O~~	~~$N_2O/(N_2+N_2O)$~~	~~CO_2~~
~~C1-4~~	~~0.490±0.075~~	~~4.82±0.632~~	~~5.31±0.677~~	~~0.908~~	~~54.6±0.646~~
~~C5-8~~	~~0.053±0.005~~	~~0.638±0.097~~	~~0.691±0.100~~	~~0.924~~	~~15.1±0.136~~

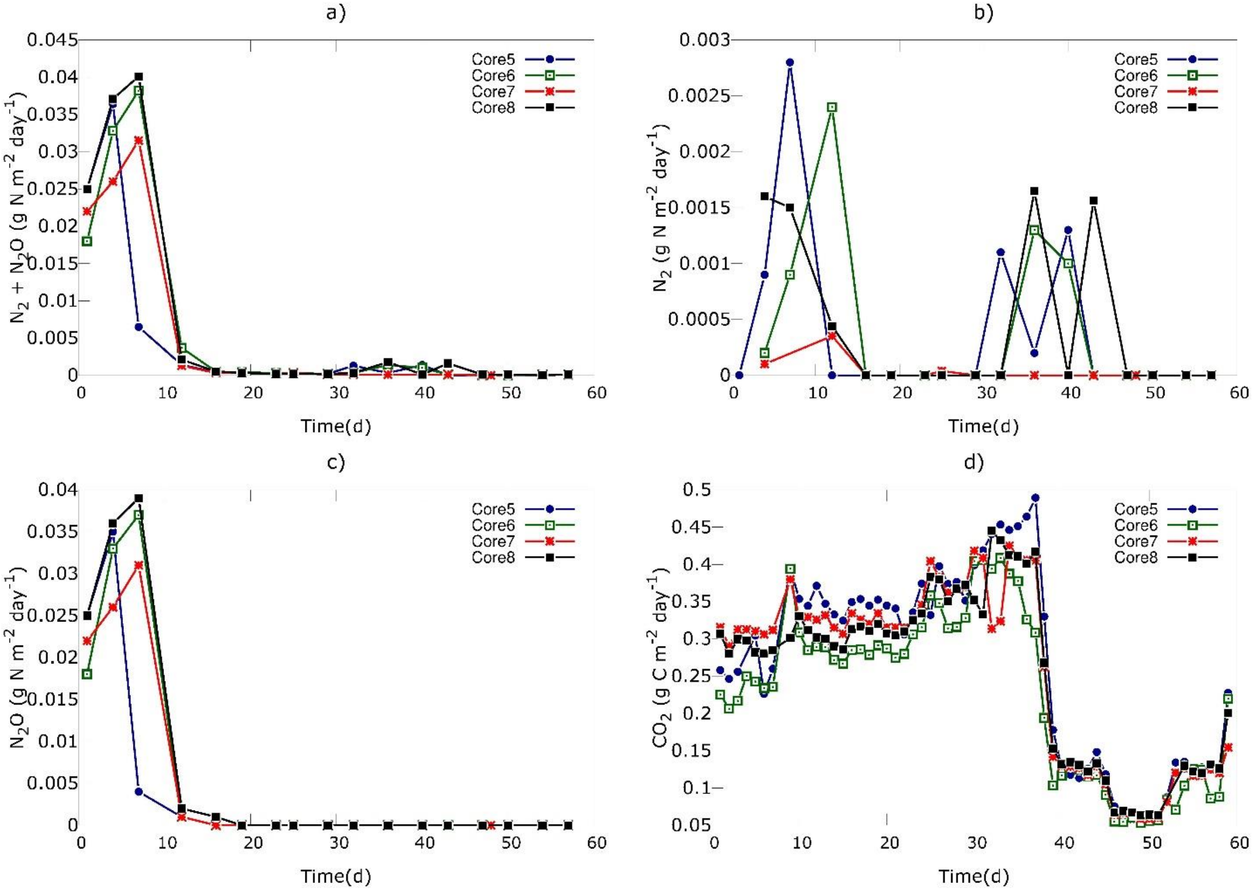
Comparing the cumulative CO_2 fluxes of the two treatments, ryegrass-amended columns were (2-4 times) higher than those without ryegrass (Table ~~6~~4). The CO_2 fluxes reached a maximum after 8-13 days and then slightly decreased until the Day 32 (Fig. S.2d), when both irrigation (Fig. S.~~3~~4) and temperature (~~Fig. S.2~~Table 3) manipulation events occurred. ~~There were several small fluctuations in the CO_2 fluxes within both treatments between the days 25 and 32.~~ In the control, CO_2 fluxes were at a lower level and slowly increased until temperature was changed. Lowering temperature from 20ºC to 10ºC (~~Fig. S.~~Table 3, Fuhrberg, day 38) drastically decreased CO_2 fluxes in both treatments, whereas further temperature changes had smaller effects.

The cumulative N_2+N_2O fluxes were almost 8 times higher in ryegrass compared to the control treatment. N_2+N_2O fluxes were initially high in both treatments (Figs. ~~2a~~S.1a and ~~3a~~S.2a) but decreased rapidly following the ~~initial~~ drainage period ~~(~~during the first 12 days of incubation (see Table S.~~2~~5 and Fig. S.4). During the remainder of the experiment, fluxes remained low and were only to a minor extent affected by the experimental manipulations. Initially, the ryegrass treated cores had high N_2+N_2O fluxes which rapidly decreased during the incubation. ~~Between the first and the second (09/02 and 14/02) water content manipulation events, cores 2 and 3 responded with smaller N_2 and N_2O (core 3 only) peaks.~~

The $N_2O/(N_2+N_2O)$ ratio of fluxes (Table ~~6~~4) shows that N_2O dominated the N fluxes. The $N_2O/(N_2+N_2O)$ ratio was similar for both treatments. During the irrigation-fertilization period at day 31, the N_2 production increased in both treatments (Fig. ~~2b~~S.1b and Fig. ~~3b~~S.2b) and the $N_2O/(N_2+N_2O)$ ratio decreased (Fig. S.5). This response occurred 1-2 days after the onset of irrigation.



~~Figure 2 a-d: Measured fluxes of (a) N_2+N_2O, (b) N_2, (c) N_2O and (d) CO_2 throughout a laboratory incubation of a sandy, arable soil from Fuhrberg, Germany. The four re-packed soil cores shown were amended with ryegrass prior to incubation. The nested figure in figure (a) shows the effect of the irrigation and fertilization event on Day 32.~~



~~Figure 3 a-d: Measured fluxes of (a) N_2+N_2O, (b) N_2, (c) N_2O and (d) CO_2 throughout a laboratory incubation of a sandy, arable soil from Fuhrberg, Germany. The four re-packed soil cores shown had no ryegrass amendment prior to incubation.~~

3.3 Modeled results of silt-loam soil

DeNi and Coup overestimated CO_2 production, with predicted CO_2 fluxes 3 to 10 times higher than the measured values, whereas DNDC mostly underestimated the measured fluxes (Table ~~8~~5). The variability of the model calculations is quite low, and the fluctuation of the values does not always follow the changes of the measured values. The time series of the CO_2 flux calculation of DeNi followed the fluctuation of the temperature settings whereas the other models mostly predicted only decreasing trends over time as shown for treatment ~~VI$_{20N_80\%_1.4}$~~VI (Fig. ~~4~~1a-c).

On average, DeNi calculated ~4 times higher N_2+N_2O fluxes than measured. In contrast to this, N_2+N_2O fluxes obtained from Coup were about ~~9~~4 times lower than the measured values, despite the fact that the N_2O estimation of Coup was quite close to the measured values~~.~~ (Table 5). In DNDC, it is notable that N_2 fluxes were always zero and it therefore underestimated N_2+N_2O fluxes even more (~30 times) than Coup~~.~~ (Table 5). Coup and DNDC results show little variation between treatments, both measurements and DeNi exhibit a large range between minimum and maximum N_2+N_2O fluxes (Table 5). The DeNi results follow the general trend of the changes of the measured values quite well, responding to increases of NO_3^- (II < VI < III) and WFPS (I < VI < V < VII) though not bulk density (IV = VI). In contrast, N_2+N_2O fluxes by Coup increased with decreasing NO_3^- (II with lowest fluxes). DNDC did not calculate any N_2 fluxes. The calculated N_2O fluxes did not respond to moisture or NO_3^-, calculating almost the same values for all 5 treatments of the same bulk density (Table 5., I, II, III, VI and VII). However, DNDC responded positively to bulk density (highest values for IV and V). The $N_2O/(N_2+N_2O)$ ratio of DeNi ~~(Fig. S.6)~~ fitted the ratio of the measured values quite well, whereas this was not the case for Coup and DNDC, which overestimated this ratio~~.~~ (Fig. S.6). The time courses of the N_2+N_2O fluxes of DNDC and DeNi mostly agreed with measurements but to a lesser extent for Coup (Figs. ~~4a-c~~1d and f). Coup predictions exhibited an inverse trend with measured values during the first 10 days.

~~Table 7: Normalized treatment effects on N_2+N_2O fluxes (silt-loam soil) of modelled relative to observed results.~~In addition to comparing average fluxes, we also assessed treatment response using normalized ratios (Table 6.; see calculation description in Section 2.3). ~~Treatments differ with respect to NO_3^- content (10-40 mg N kg^{-1} dry soil), WFPS (73-90%) and bulk density (1.4-1.52 g cm^{-3}). Values shown are the ratio of treatment differences between modeled and measured values, e.g. $((I_{Mod}-II_{Mod})/I_{Mod})/((I_{Meas}-II_{Meas})/I_{Meas})$.~~

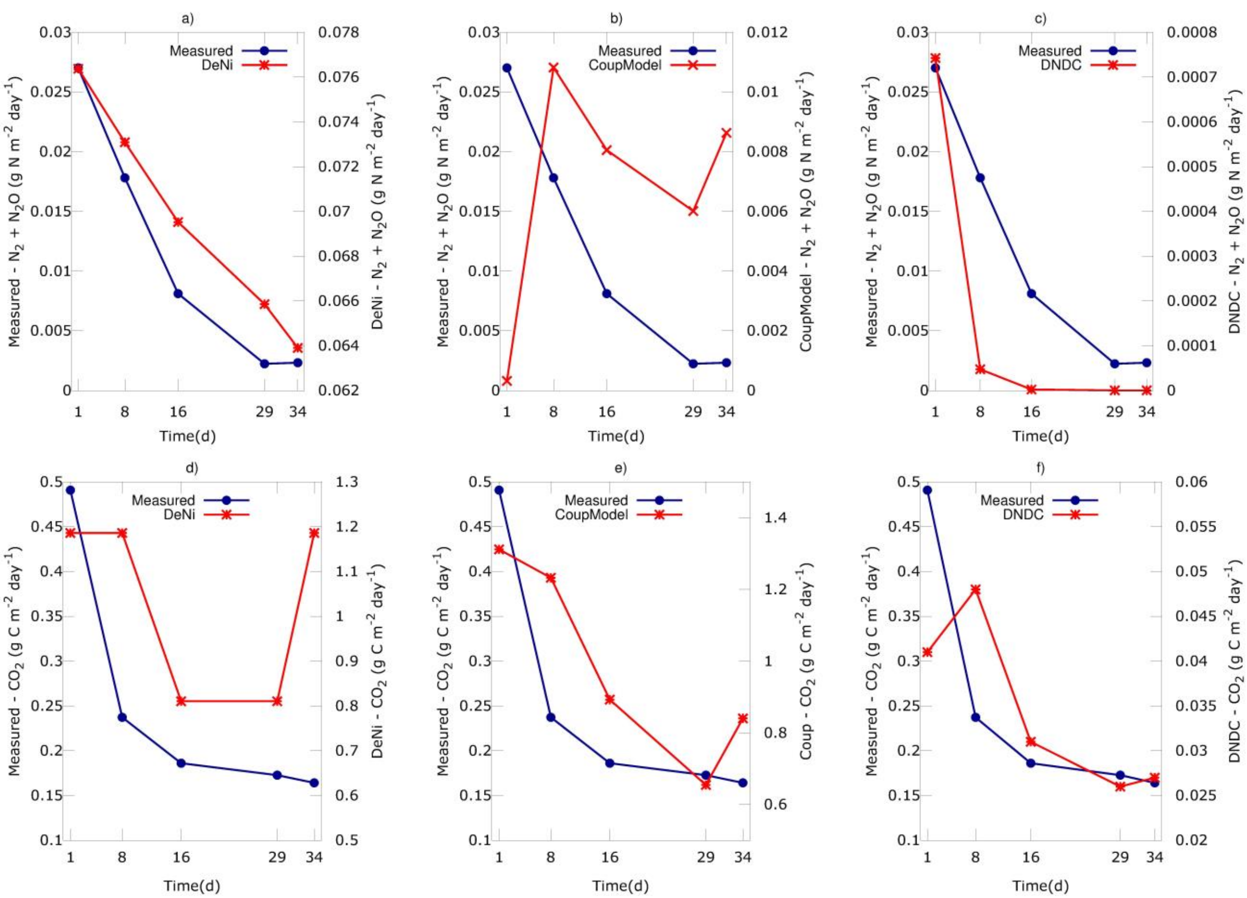
~~Coup/Measured~~	~~$II_{10N\_80\%\_1.4}$~~	~~$III_{40N\_80\%\_1.4}$~~	~~$IV_{20N\_80\%\_1.46}$~~	~~$V_{20N\_88\%\_1.52}$~~	~~$VI_{20N\_80\%\_1.4}$~~	~~$VII_{20N\_90\%\_1.4}$~~
~~$I_{20N\_73\%\_1.4}$~~	~~-0.21~~	~~0~~	~~0~~	~~0~~	~~0~~	~~0.70~~
~~$II_{10N\_80\%\_1.4}$~~	~~-~~	~~-0.03~~	~~-0.06~~	~~-0.02~~	~~-0.38~~	~~-0.48~~
~~$III_{40N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~0~~	~~0~~	~~0~~	~~0.46~~
~~$IV_{20N\_80\%\_1.46}$~~	~~-~~	~~-~~	~~-~~	~~0~~	~~0~~	~~0.67~~
~~$V_{20N\_88\%\_1.52}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~0~~	~~0.38~~
~~$VI_{20N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-0.86~~

~~DeNi/Measured~~	~~$II_{10N\_80\%\_1.4}$~~	~~$III_{40N\_80\%\_1.4}$~~	~~$IV_{20N\_80\%\_1.46}$~~	~~$V_{20N\_88\%\_1.52}$~~	~~$VI_{20N\_80\%\_1.4}$~~	~~$VII_{20N\_90\%\_1.4}$~~
~~$I_{20N\_73\%\_1.4}$~~	~~-0.47~~	~~3.17~~	~~23.45~~	~~1.15~~	~~-1.52~~	~~-4.59~~
~~$II_{10N\_80\%\_1.4}$~~	~~-~~	~~0.30~~	~~0.20~~	~~0.16~~	~~1.20~~	~~1.52~~
~~$III_{40N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~0.97~~	~~-0.03~~	~~0.47~~	~~-0.06~~
~~$IV_{20N\_80\%\_1.46}$~~	~~-~~	~~-~~	~~-~~	~~0.32~~	~~0.02~~	~~-1.25~~
~~$V_{20N\_88\%\_1.52}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~0.39~~	~~-0.08~~
~~$VI_{20N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-~~	~~1.67~~

~~DNDC/Measured~~	~~$II_{10N\_80\%\_1.4}$~~	~~$III_{40N\_80\%\_1.4}$~~	~~$IV_{20N\_80\%\_1.46}$~~	~~$V_{20N\_88\%\_1.52}$~~	~~$VI_{20N\_80\%\_1.4}$~~	~~$VII_{20N\_90\%\_1.4}$~~
~~$I_{20N\_73\%\_1.4}$~~	~~-0.08~~	~~0.10~~	~~10.80~~	~~0.60~~	~~-0.10~~	~~-0.16~~

~~$II_{10N\_80\%\_1.4}$~~	~~-~~	~~0~~	~~0.16~~	~~0.12~~	~~0~~	~~0.02~~
~~$III_{40N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~-0.99~~	~~1.34~~	~~0~~	~~-0.02~~
~~$IV_{20N\_80\%\_1.46}$~~	~~-~~	~~-~~	~~-~~	~~0.25~~	~~0.43~~	~~0.56~~
~~$V_{20N\_88\%\_1.52}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~0.54~~	~~0.57~~
~~$VI_{20N\_80\%\_1.4}$~~	~~-~~	~~-~~	~~-~~	~~-~~	~~-~~	~~0.04~~

~~After the initial 10 days and until day 29, the pattern of Coup is more or less similar to the measured values, but the magnitude of the modeled values is approximately 2-3 times smaller (Fig. 4).~~



~~**Figure 4 a-f: An example (treatment $VI_{20N\_80\%\_1.4}$) for the measured and modeled (DeNi, Coup and DNDC) N_2+N_2O (a, b, c) and CO_2 (d,e,f) fluxes of a silt-loam arable soil from Hattorf, Germany**~~

~~There were a few similarities between measured and modeled fluxes when comparing the cumulative N_2+N_2O fluxes (Fig. 5) and the ratio of the N_2+N_2O fluxes (Table 7) of the seven silt-loam treatments. While Coup results show little variation, both measurements and DeNi exhibit a large range between minimum and maximum N_2+N_2O fluxes (Fig. 5). The DeNi results follow the changes of the measured values quite well, responding to increases of NO_3^- ($II_{10N\_80\%\_1.4}$ < $VI_{20N\_80\%\_1.4}$ < $III_{40N\_80\%\_1.4}$) and WFPS ($I_{20N\_73\%\_1.4}$ < $VI_{20N\_80\%\_1.4}$ < $V_{20N\_88\%\_1.52}$ < $VII_{20N\_90\%\_1.4}$) though not bulk density ($IV_{20N\_80\%\_1.46}$ =~~

~~$VI_{20N\_80\%\_1.4}$). In contrast, N_2+N_2O fluxes by Coup increased with decreasing NO_3^- ($II_{10N\_80\%\_1.4}$ with lowest fluxes). DNDC did not respond to moisture or NO_3^-, calculating almost the same values for all 5 treatments of the same bulk density (Table 8., $I_{20N\_73\%\_1.4}$, $II_{10N\_80\%\_1.4}$, $III_{40N\_80\%\_1.4}$, $VI_{20N\_80\%\_1.4}$ and $VII_{20N\_90\%\_1.4}$). However, DNDC responded positively to bulk density (highest values for $IV_{20N\_80\%\_1.46}$ and $V_{20N\_88\%\_1.52}$). For the change from the wettest treatment ($VII_{20N\_90\%\_1.4}$) to each of the other 6 treatments, the Coup-estimated fluxes decreased together with the measured fluxes in 4 of 6 cases, while the DeNi-estimated fluxes increased in 4 of 6 cases (Table 7).~~

~~Normalized treatment effects of model results and measurements are shown in Table 7. The ratio between relative treatment differences of measured and modeled values is 1, if the measured and the modeled values changed with the same magnitude in the same direction. If the ratio is bigger than 1, the direction of measured and modeled values is the same, but the magnitude of the response is bigger in the model than was seen in the measured values. If the value is between 0 and 1, the direction is the same, but the magnitude of the response is smaller in the model than was seen in the measured values. If the ratio is negative, the direction of the response is opposite in the model as compared to the measurements. For ratios of 0, there was no model response to differences between treatments.~~

For Coup, ratios showed that modeled treatment differences were either absent (10 of 21), lower than (4 of 21) or opposite (7 of 21) to measured differences. For DeNi, the model always responded to treatments (i.e. no 0 ratios), with most (14 of 21) cases showing a model response in the same direction as measured values, and two cases where the model had significantly higher ratios than the measured values. For DNDC, with two exceptions, ratios indicated either lower (11 of 21) or opposite (5 of 21) response of the model as compared to measured values, with 3 instances where the model did not respond (i.e. ratio of 0).

Table ~~8~~5: Average measured (average of the 5 measurement events for 34 days) and modeled (Coup, DeNi and DNDC models) N_2, N_2O (~~g~~mg N m^{-2} day^{-1}) and CO_2 (g C m^{-2} day^{-1}) fluxes of 7 incubation treatments for a silt-loam, arable soil from Hattorf, Germany. Treatments include different levels of NO_3^- addition (10, 20 and 40 mg N kg^{-1}), WFPS (73-90%) and soil bulk density (1.4-1.52 g cm^{-3}).

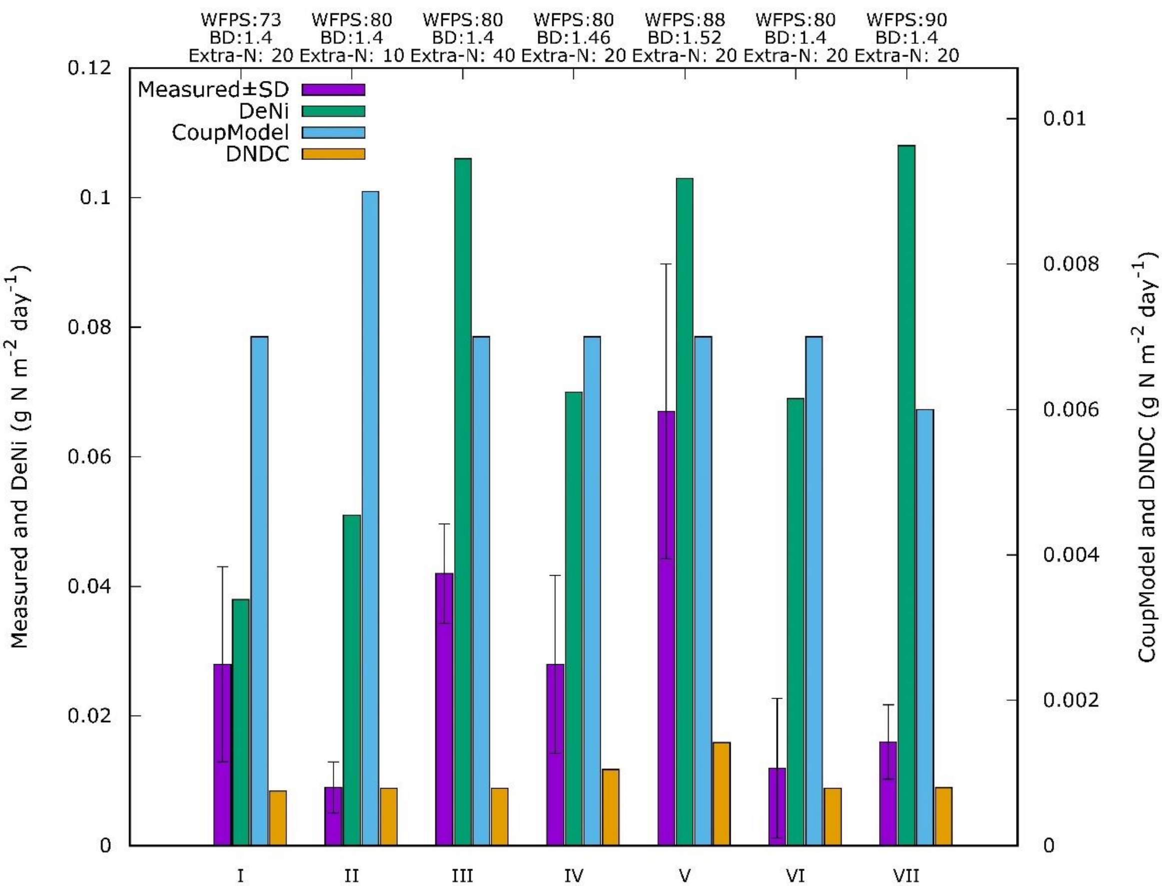
~~Treatments include different levels of NO_3^- addition (10, 20 and 40 mg N kg^{-1}), WFPS (73-90%) and soil bulk density (1.4-1.52 g cm^{-3}).~~

		I	II	III	IV	V	VI	VII	SD
		~~20N_73%_1.4~~	~~10N_80%_1.4~~	~~40N_80%_1.4~~	~~20N_80%_1.46~~	~~20N_88%_1.52~~	~~20N_80%_1.4~~	~~20N_90%_1.4~~	
~~N_2~~	~~Meas.~~	~~0.024~~	~~0.01~~	~~0.03~~	~~0.02~~	~~0.06~~	~~0.01~~	~~0.01~~	~~0.02~~
	~~Coup~~	~~0.003~~	~~0.005~~	~~0.002~~	~~0.002~~	~~0.003~~	~~0.003~~	~~0.0022~~	~~0.001~~
	~~DeNi~~	~~0.033~~	~~0.044~~	~~0.092~~	~~0.061~~	~~0.085~~	~~0.06~~	~~0.088~~	~~0.023~~
		N: 20	N: 10	N: 40	N: 20	N: 20	N: 20	N: 20	
		WFPS: 73	WFPS: 80	WFPS: 80	WFPS: 80	WFPS: 88	WFPS: 80	WFPS: 90	

		BD: 1.4	BD: 1.4	BD: 1.4	BD: 1.46	BD: 1.52	BD: 1.4	BD: 1.4	
N_2	Meas.	23.6	8.38	31.2	22.8	55.5	9.80	12.8	16.4
	Coup	2.75	4.64	1.69	1.69	2.65	2.59	1.83	1.03
	DeNi	33.4	43.6	91.7	61.1	84.8	60.4	88.2	22.8
	DNDC	0	0	0	0	0	0	0	0
N_2O	Meas.	3.81	0.81	11.2	5.16	11.1	1.7	3.36	4.2
	Coup	4.29	3.53	4.86	4.86	4.41	4.17	3.52	0.55
	DeNi	4.64	6.76	13.7	9.48	17.7	9.35	20.5	5.8
	DNDC	0.75	0.79	0.79	1.05	1.42	0.79	0.8	0.25
N_2+N_2O	Meas.	27.4	9.19	42.3	28.0	66.6	11.5	16.2	20.2
	Coup	7.04	8.17	6.55	6.55	7.07	6.77	5.35	0.84
	DeNi	38.1	50.4	105.4	70.5	102.5	69.8	108.7	28.2
	DNDC	0.75	0.79	0.79	1.05	1.42	0.79	0.8	0.25
CO_2	Meas.	0.324	0.228	0.074	0.208	0.032	0.297	0.038	0.123
	Coup	1.033	0.986	0.986	0.986	1.033	0.986	0.795	0.081
	DeNi	1.239	1.036	1.036	1.032	0.758	1.036	0.677	0.191
	DNDC	0.173	0.173	0.173	0.188	0.2	0.173	0.173	0.011

~~N_2O~~	~~Meas.~~	~~0.004~~	~~0.001~~	~~0.011~~	~~0.005~~	~~0.011~~	~~0.001~~	~~0.003~~	~~0.004~~
	~~Coup~~	~~0.004~~	~~0.004~~	~~0.005~~	~~0.005~~	~~0.004~~	~~0.004~~	~~0.004~~	~~0.001~~
	~~DeNi~~	~~0.005~~	~~0.007~~	~~0.014~~	~~0.01~~	~~0.017~~	~~0.01~~	~~0.019~~	~~0.006~~
	~~DNDC~~	~~0.00075~~	~~0.00079~~	~~0.00079~~	~~0.00105~~	~~0.00142~~	~~0.00079~~	~~0.0008~~	~~0.00025~~
~~N_2+N_2O~~	~~Meas.~~	~~0.028~~	~~0.009~~	~~0.042~~	~~0.028~~	~~0.067~~	~~0.011~~	~~0.016~~	~~0.02~~
	~~Coup~~	~~0.007~~	~~0.009~~	~~0.007~~	~~0.007~~	~~0.007~~	~~0.007~~	~~0.0062~~	~~0.002~~
	~~DeNi~~	~~0.038~~	~~0.051~~	~~0.106~~	~~0.071~~	~~0.102~~	~~0.07~~	~~0.107~~	~~0.029~~
	~~DNDC~~	~~0.00075~~	~~0.00079~~	~~0.00079~~	~~0.00105~~	~~0.00142~~	~~0.00079~~	~~0.0008~~	~~0.00025~~

~~CO_2~~	~~Meas.~~	~~0.324~~	~~0.228~~	~~0.074~~	~~0.208~~	~~0.032~~	~~0.297~~	~~0.038~~	~~0.123~~
	~~Coup~~	~~1.033~~	~~0.986~~	~~0.986~~	~~0.986~~	~~1.033~~	~~0.986~~	~~0.795~~	~~0.081~~
	~~DeNi~~	~~1.239~~	~~1.036~~	~~1.036~~	~~1.032~~	~~0.758~~	~~1.036~~	~~0.677~~	~~0.191~~
	~~DNDC~~	~~0.173~~	~~0.173~~	~~0.173~~	~~0.188~~	~~0.2~~	~~0.173~~	~~0.173~~	~~0.011~~



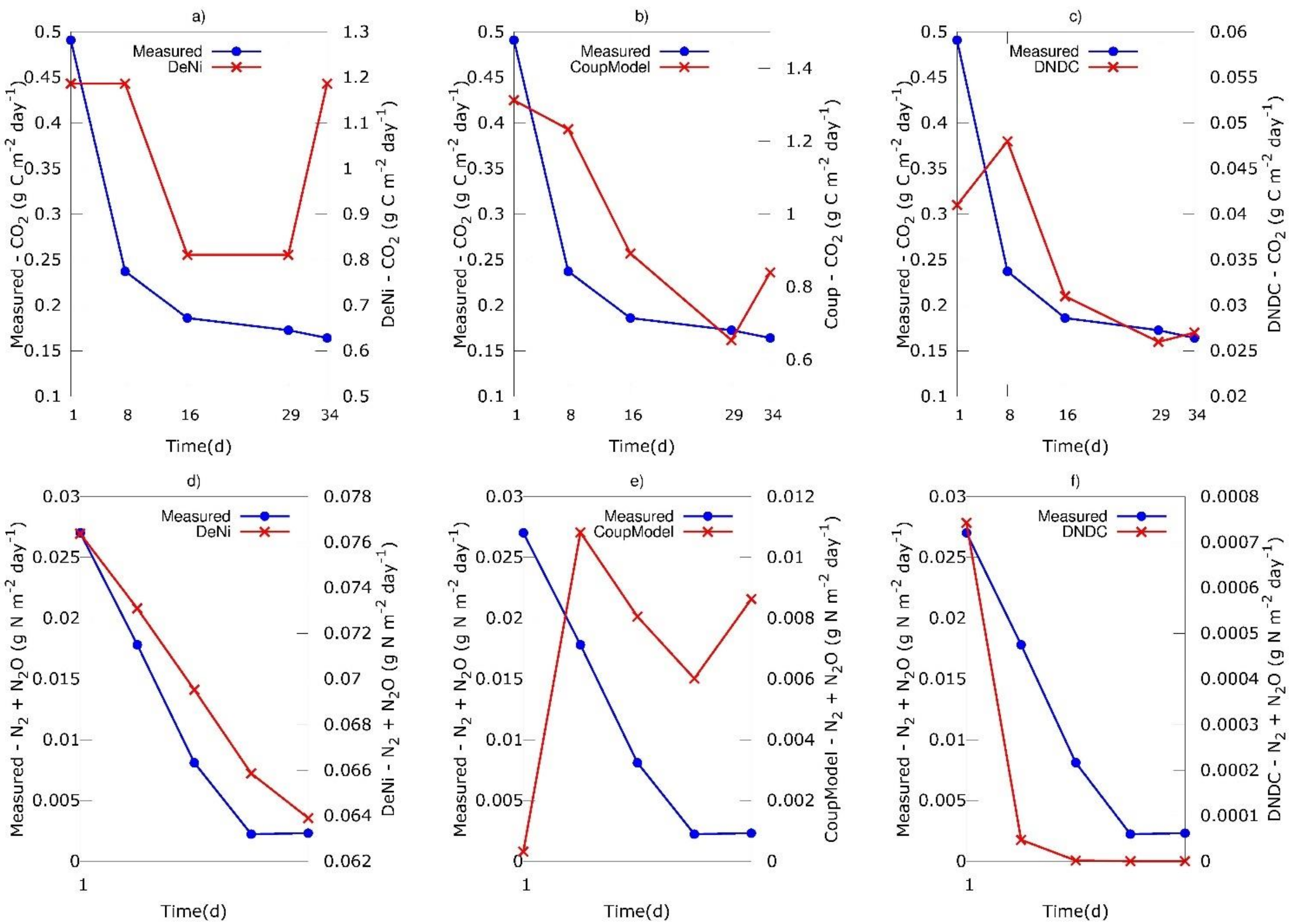


Figure ~~5: Measured~~1 a-f: An example (treatment VI) for the measured and modeled ~~cumulative~~(DeNi, Coup and DNDC) CO_2 (a, b, c) and N_2+N_2O (d,e,f) fluxes of a silt-loam arable soil from Hattorf, Germany~~.~~

Table 6: Normalized treatment effects on N_2+N_2O fluxes (silt-loam soil) of modeled relative to observed results. Treatments differ with respect to NO_3^- content (10-40 mg N kg^{-1} dry soil), WFPS (73-90%) and bulk density (1.4-1.52 g cm^{-3}). Values shown are the ratio of treatment differences between modeled and measured values, e.g. $((I_{Mod} - II_{Mod})/I_{Mod})/((I_{Meas} - II_{Meas})/I_{Meas})$.

Coup/Measured	II	III	IV	V	VI	VII
I	-0.21	0	0	0	0	0.70

II	-	-0.03	-0.06	-0.02	-0.38	-0.48
III	-	-	0	0	0	0.46
IV	-	-	-	0	0	0.67
V	-	-	-	-	0	0.38
VI	-	-	-	-	-	-0.86

DeNi/Measured	II	III	IV	V	VI	VII
I	-0.47	3.17	23.45	1.15	-1.52	-4.59
II	-	0.30	0.20	0.16	1.20	1.52
III	-	-	0.97	-0.03	0.47	-0.06
IV	-	-	-	0.32	0.02	-1.25
V	-	-	-	-	0.39	-0.08
VI	-	-	-	-	-	1.67

DNDC/Measured	II	III	IV	V	VI	VII
I	-0.08	0.10	10.80	0.60	-0.10	-0.16
II	-	0	0.16	0.12	0	0.02
III	-	-	-0.99	1.34	0	-0.02
IV	-	-	-	0.25	0.43	0.56
V	-	-	-	-	0.54	0.57
VI	-	-	-	-	-	0.04

3.4 Modeled results of sand soil

~~For the ryegrass-treated sand, the Coup-estimated CO_2 fluxes fitted the measured emission pattern quite well (Fig. 6e).~~

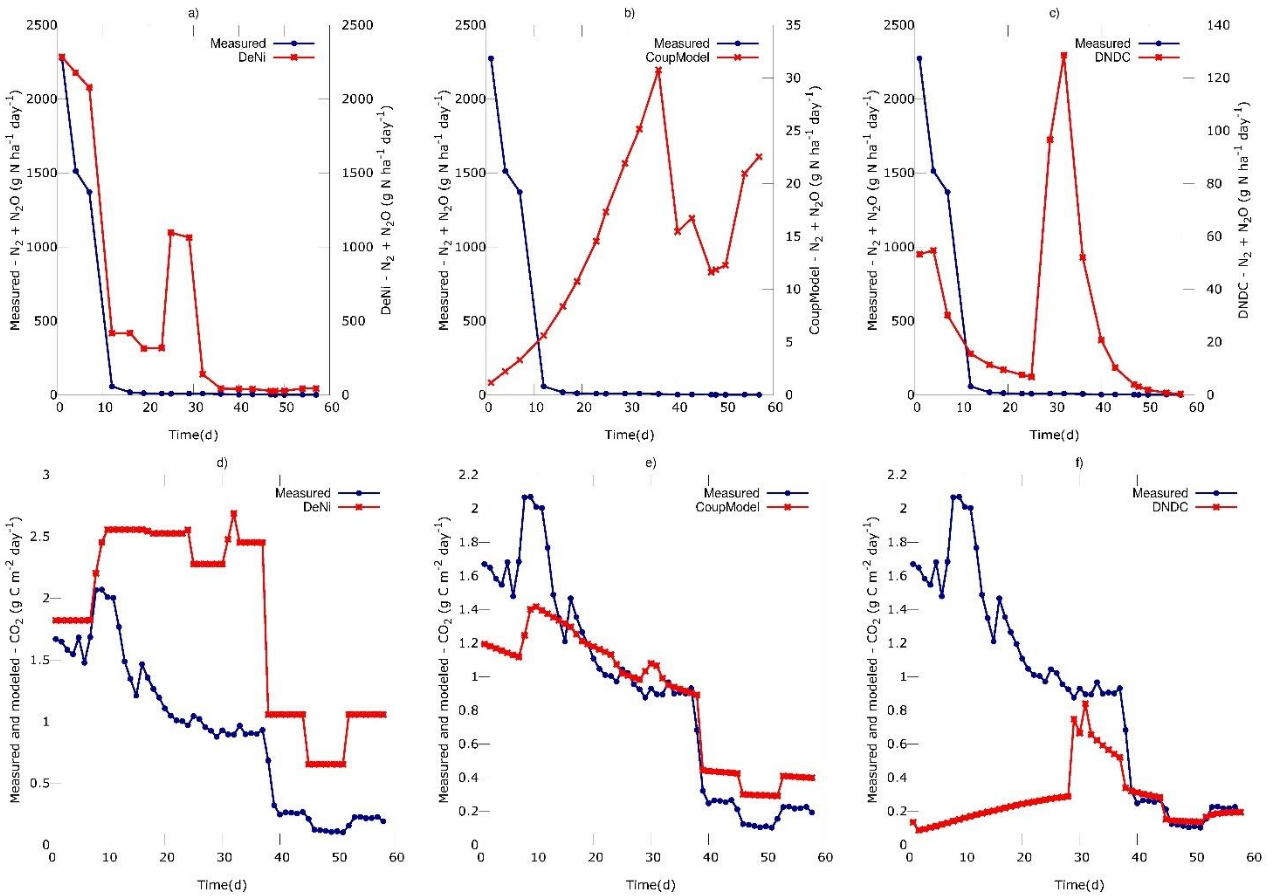
~~Except for an initial peak, the pattern and the magnitude of measured and modeled fluxes were almost identical.~~

Coup overestimated the soil respiration for the control treatment (Fig. ~~7e~~2b), but the temporal pattern of the modeling – especially for the temperature manipulation – fitted the measured values.
Similarly, in the ryegrass-treated sand, the pattern and the magnitude of measured and modeled fluxes were almost identical (Fig. 3), except for an initial peak. DeNi overestimated the CO_2 fluxes for both treatments and as shown by the identical CO_2 fluxes of both treatments, did not respond to the labile organic C of the ryegrass treatment~~, since modeled CO_2 fluxes of both treatments were almost identical (Fig. 6d and~~ (Fig. ~~7d). While the pattern of the modeled fluxes followed the changes of~~ 2a and Fig. 3a). DeNi did respond to temperature and soil water content, but the magnitude of the response to these changes was too large.
DNDC calculated the smallest CO_2 fluxes among the three models. ~~The modeled estimates~~The model provided a reasonable estimation for the magnitude of CO_2 fluxes of the control treatment (Fig. 2c) but did not reflect a litter effect and underestimated the measured values for the ryegrass-treated soil (Fig. ~~6f). The model provided much better estimation for the magnitude of CO_2 fluxes of the control treatment (Fig. 7f).~~3c). While there was not an ideal agreement in the temporal pattern, some of the changes of the environmental conditions ~~are~~were clearly reflected.

Similar to the silt-loam experiment (Fig. ~~4b~~1e), the pattern of the estimated N_2+N_2O fluxes by Coup was opposite to the trend of the measured fluxes, exhibiting a constant initial increase in both treatments (Fig. ~~6b, 7b~~2e, 3e). The subsequent rapid decrease of CO_2 and N_2+N_2O fluxes resulted from the temperature manipulation. The modeled patterns of DeNi and DNDC (Figs. ~~7a~~2d and ~~c~~f) are closer to the measured fluxes and both clearly reflect the wetting phase, which caused an increase in measured N_2+N_2O fluxes of the treatment without litter but only elevated N_2 fluxes in the ryegrass treatment.
The response of N_2+N_2O fluxes to soil moisture following irrigation differed among models, with DeNi and DNDC predicting immediate responses (Fig. 3d and f), while no response was observed from Coup during the initial growth of denitrifiers (Fig. 3e).

Comparing the order of magnitude of cumulative modeled and measured N_2+N_2O fluxes (Table ~~9~~7), DeNi showed agreement in the ryegrass treatment, but overestimated fluxes of the control treatment by one order. Conversely, DNDC and Coup showed close agreement in the treatment without ryegrass but underestimated fluxes with ryegrass by one to two orders.
The N_2O/(N_2+N_2O) ratio of cumulative fluxes modeled by DeNi and Coup was between 0.3 and 0.45 in both treatments (Table ~~9~~7) and thus much lower than the measured ratios (>0.9, ~~Fig. S.7,~~ Table ~~9). The modeled N_2O/(N_2+N_2O) ratio of~~7). DNDC was close to 1 because the N_2 flux estimation of DNDC was almost zero, i.e. five orders of magnitude lower than measured fluxes.

~~The response of modeled N_2+N_2O fluxes to increasing soil moisture following irrigation differed among models, with DeNi and DNDC predicting immediate responses (Fig. 6a and c). The response for the soil moisture manipulation of Coup was not observed during the initial growth of denitrification (Fig. 6b).~~



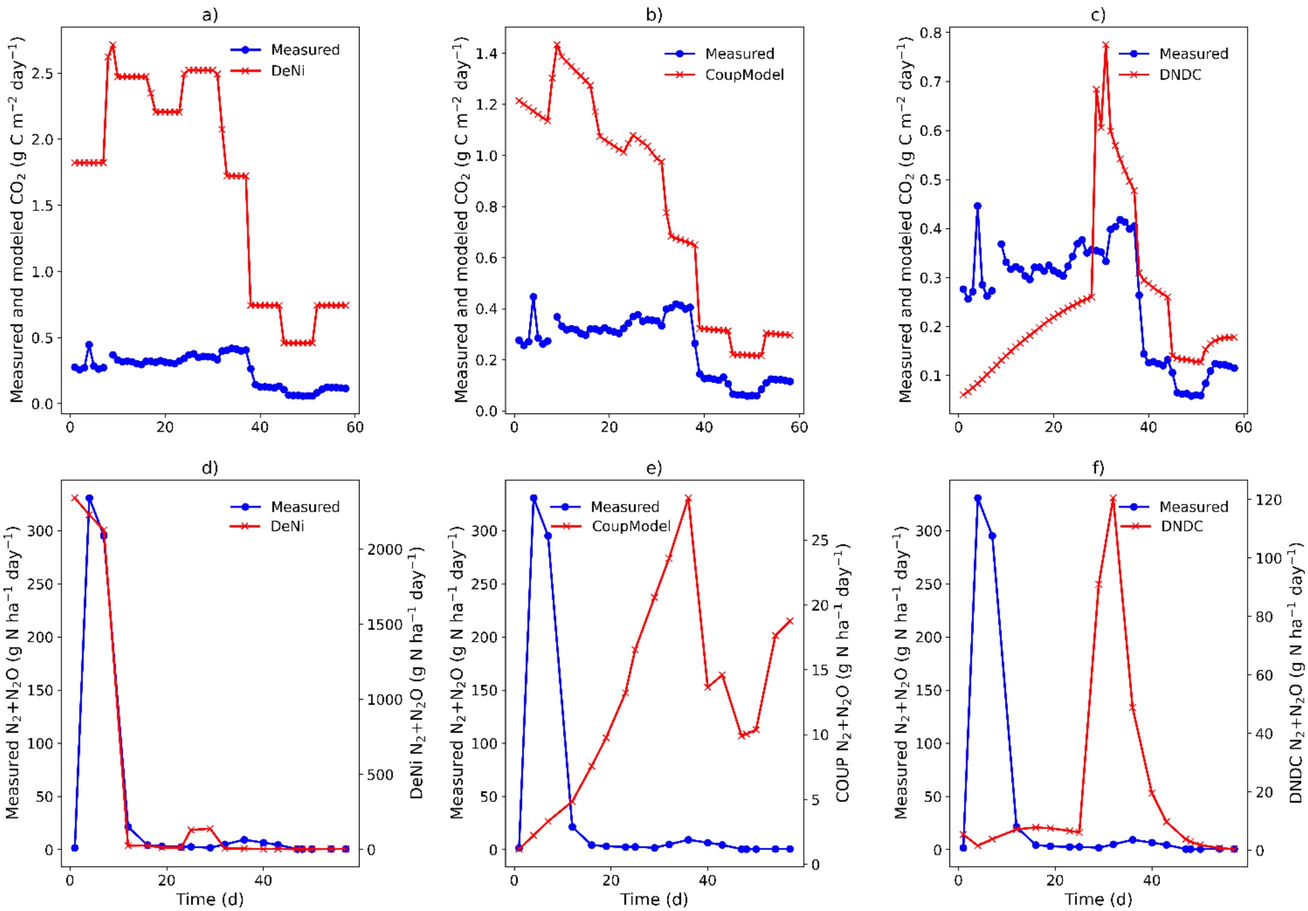
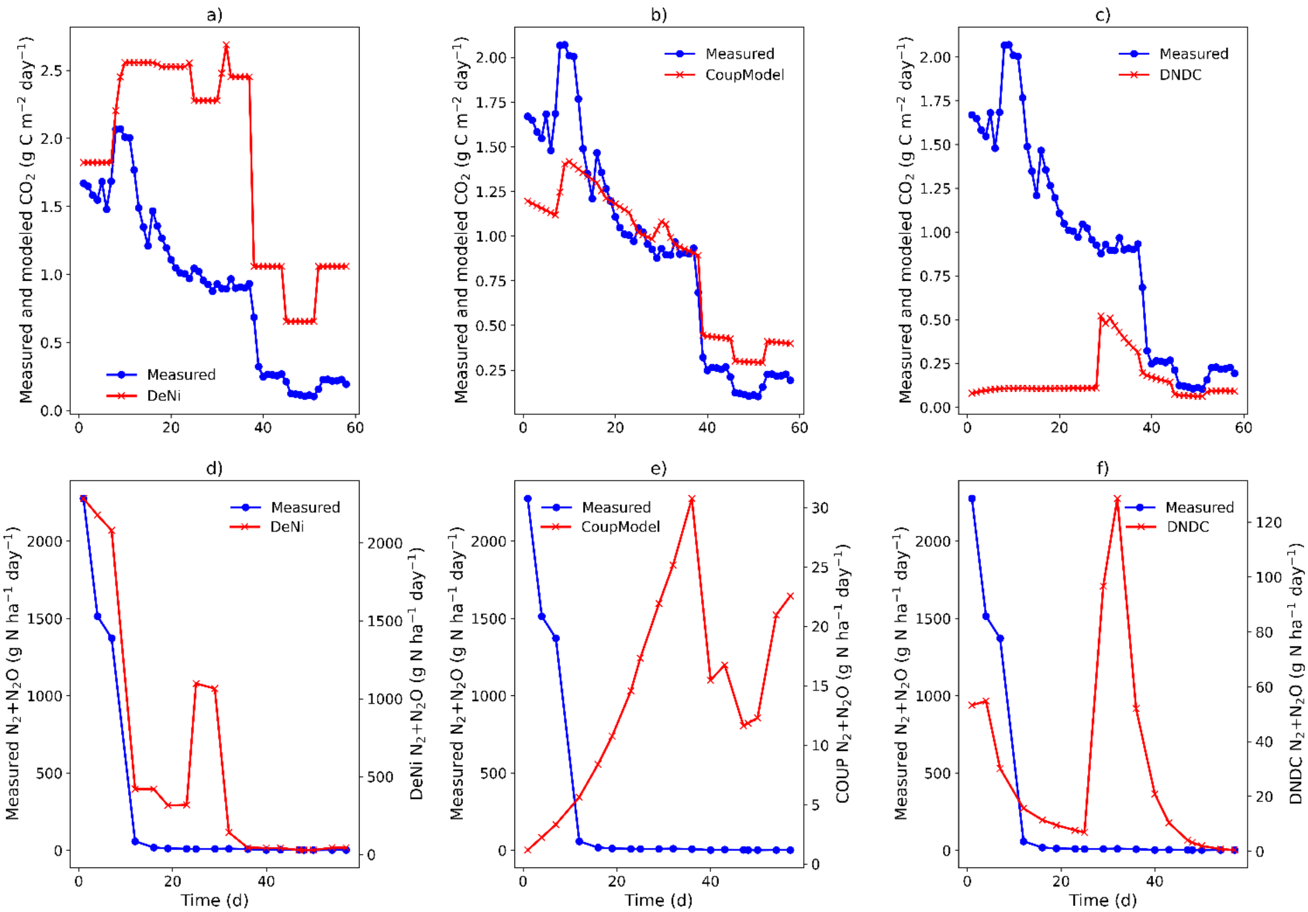


Figure ~~6~~2 a-f: Measured and modeled (DeNi, Coup and ~~Coup) N$_2$, N$_2$O and~~DNDC) CO_2 and N_2+N_2O fluxes from a 58-day laboratory incubation of soil cores from a sandy, arable site in Fuhrberg, Germany. Measured values shown are the average of the control cores (cores 5-8), which were given no additional substrate.~~Shown is the average of the treated cores (cores 1-4), which were amended with ryegrass prior to incubation.~~

Table ~~9~~7: The measured and modeled (Coup, DeNi, DNDC) average, cumulative N_2, N_2O and N_2+N_2O, CO_2 fluxes (g N ha^{-1} and kg C ha^{-1}) and product ratios (dimension less) for sand, arable soil from Fuhrberg, Germany. C1-4 means the first 4 parallel columns for the ryegrass treatment. The C5-8 means the 4 parallel columns of the control/non ryegrass treatment.

		Cores 1-4 (ryegrass)	Cores 5-8 (control)
N_2O	Measured	4818	638.5

	DeNi	4351	2460
	Coup	81.90	70.15
	DNDC	507.9	345.4
N_2	Measured	489.8	52.63
	DeNi	6264	4607
	Coup	170.7	155.8
	DNDC	0.022	0.019
N_2+N_2O	Measured	5308	691.1
	DeNi	10615	7067
	Coup	252.6	226.0
	DNDC	507.9	345.4
$N_2O/(N_2+N_2O)$	Measured	0.9077	0.924
	DeNi	0.410	0.348
	Coup	0.324	0.310
	DNDC	0.999	0.999
CO_2	Measured	525	152
	DeNi	1061	954
	Coup	508.5	463
	DNDC	~~157.1~~89.72	141.4


a)
b)
c)
d)
e)
f)
Measured and modeled CO2 (g C m-2 day-1)
Measured
DeNi
CoupModel
DNDC
Measured N2+N2O (g N ha-1 day-1)
DeNi N2+N2O (g N ha-1 day-1)
COUP N2+N2O (g N ha-1 day-1)
DNDC N2+N2O (g N ha-1 day-1)
Time (d)

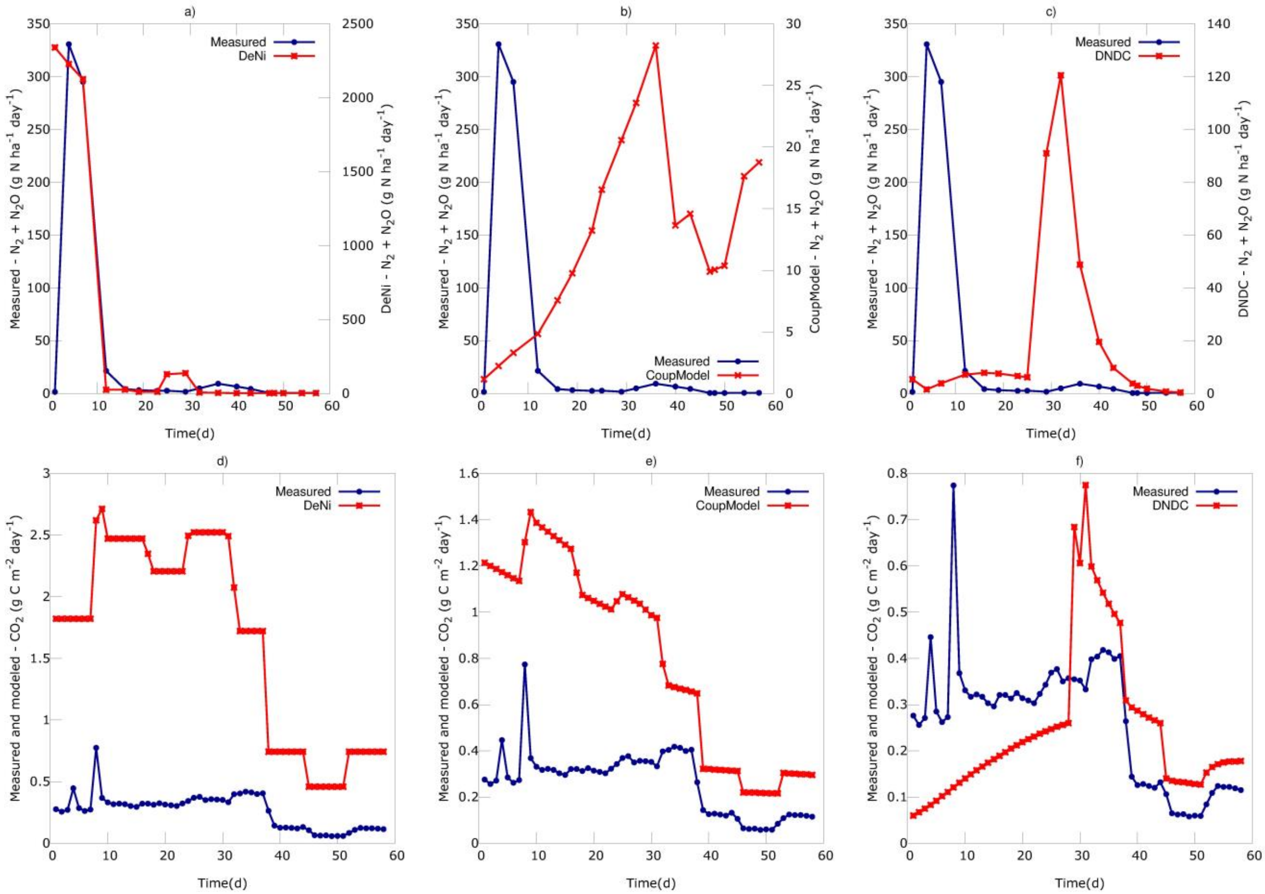


Figure ~~7~~3 a-f: Measured and modeled (~~DeNi, Coup~~DeNiCoup and DNDC) ~~N_2, N_2O~~CO_2 and ~~CO_2~~N_2+N_2O fluxes from a 58-day laboratory incubation of soil cores from a sandy, arable site in Fuhrberg, Germany. Shown is the average of the treated cores (cores 1-4), which were amended with ryegrass prior to incubation.~~Measured values shown are the average of the control cores (cores 5-8), which were given no additional substrate.~~

4 Discussion

4.1 Experimental results

4.1.1 Silt-loam soil

~~The~~The general trend shows that the highest cumulative CO_2 fluxes were measured at low WFPS/bulk density and the lowest fluxes at high WFPS/bulk density (Table ~~5~~4). Respiration thus reflected the ~~typical responses~~expected response to temperature and aeration (Davidson et al., 2000). Figure 1a shows that the total denitrification was controlled by several interacting factors, where decreasing nitrification can be explained by the combination of substrate exhaustion and temperature (Müller ~~&~~and Clough, 2014). The increasing denitrification in the wettest treatment (~~VII$_{20N_90\%_1.4}$)~~VII; treatments description: Table 2.) could be due to ongoing O_2 depletion resulting from respiration at low diffusivity during the early phase of the incubation (Well et al., 2019).

The low $N_2O/(N_2+N_2O)$ product ratio (between 0.088 and 0.264, Table ~~5~~4) indicated that N_2O was effectively reduced to N_2, so that total fluxes were dominated by N_2. Since high NO_3^- contents and low pH are known to inhibit N_2O reduction (Müller ~~&~~and Clough, 2014), the low $N_2O/(N_2+N_2O)$ ratios might explained by near-neutral pH values or low NO_3^- contents, below the reported threshold for N_2O reduction inhibition (45 mg N kg^{-1}; Senbayram et al., 2019). The relevance of NO_3^- content for controlling the product ratio is supported by the fact that the lowest $N_2O/(N_2+N_2O)$ ratio was observed in the treatment with lowest NO_3^--N concentration (~~II$_{10N_80\%_1.4}$~~II), whereas the highest values were obtained at the highest NO_3^- content (~~III$_{40N_80\%_1.4}$~~III). However, it is notable that the highest NO_3^- in this study (40 mg N kg^{-1}) was still below the 45 mg N kg^{-1} threshold.

4.1.2 Sand soil

The dramatic differences between measured fluxes of control and ryegrass soils (2-4 orders of magnitude for CO_2 and almost 8 for N_2+N_2O; Table ~~6~~4) can be explained by the effects of labile carbon from ryegrass on microbial respiration and enhancement of denitrification due to increased O_2 consumption and supply of reductants for denitrifiers (e.g. Senbayram et al., 2018). ~~In contrast, the control soils not only had no ryegrass amendment but were also pre-incubated (decreasing the what labile carbon was present) to avoid an initial peak in CO_2 fluxes after the re-wetting of the dry soil (see methods).~~ The CO_2 fluxes of the ryegrass treated cores (cores 1-4) between days 4 and 12 show a rapid increase (~~Figs.~~ Fig. S.2d~~, 3d).~~). The large response of respiration to the ryegrass treatment almost hides the smaller effects resulting from the changing water and NO_3^- content, while these effects were clearly visible in the control~~ treatment~~. However, small effects with a similar pattern to that seen in the control soils were also evident in the ryegrass treatments (Figs. ~~2d, 3d, S.4 day 25-35 increasing trend all cores expect core 2). Other notable responses in Figs. 2d, 3d are the higher peaks of CO_2 on day 7 and a big decrease in the CO_2 flux values for both treatments on day 38. On day 7, the water content of the soil cores was decreased (Fig. S.4) and it resulted the higher CO_2 emission. On day 38, a simultaneous increase in water content and decrease in temperature (Fig. S.3 and S.4), which presumably caused lower CO_2 flux.~~S.1d, S.2d, S.4 day 25-35 increasing trend all cores expect core 2). Although the control was almost one magnitude smaller than the ryegrass treated soil, the initial high water and nitrate content (80% WFPS, 66 mg N kg^{-1} dry soil, Table 2 and 3) resulted in measurable N_2+N_2O fluxes in the first 4 days of both treatments. The time course in N_2+N_2O fluxes (Figs. 2a and 3a) can be then explained by the combination of easily available carbon, the effect of soil water content and changes in the soil NO_3^- content. The ~~control treatment – without organic matter amendment – was almost one~~ magnitude ~~smaller than the ryegrass treated soil cores, but the initial high water~~ and ~~nitrate content (80% WFPS, 66 mg N kg~~$^{-1}$ ~~dry soil, Table 2 and 3) resulted~~ variability in ~~higher~~ ~~N_2+N_2O fluxes in the first 4 days of the experiment for both treatments. The water potential at the bottom of the cores was changed at day 4 and the~~ water and NO_3^- content ~~decreased in the soil cores (Table S.1 and S.2). The increase of the water (Fig. S.4) and~~ ~~NO_3^- content (Table S.1 at 08.03.2017) between the days 24 and 27 led to increasing~~ ~~N_2+N_2O~~ might explain some of the measured variability in gaseous N fluxes (initially high fluxes in both treatments but decreasing quickly (Figs. 2a and 3a)). While the organic matter amendment clearly enhanced denitrification in the initial phase with high water content, this was not the case during the later phases when fluxes of both treatments were similarly low, likely since anoxic micro-sites disappeared due to improved aeration (Schlüter et al., 2018). The product ratio of fluxes shows that mostly N_2O was emitted, which we attribute to the high NO_3^--N level and the low pH (Müller and Clough, 2014). The product ratio was similar with and without litter amendment. This might indicate that the combined inhibitory effect on N_2O reduction by low pH and high NO_3^- was more effective than the potential enhancement in N_2O reduction in presence of labile C in the ryegrass treatment (Müller ~~–~~and Clough, 2014).

The NO_3^- content and the seepage of leachate show some variability between replicates (Table S.~~1~~4 and S.~~2~~5) which we attribute to the fact that initial water content (80% WFPS) was located in the steep sloping section of the water retention curve (Fig. S.~~2~~7), where small changes in water potential would be related to large change in water content. The variable leaching is thus probably due to the limited precision of water potential control (Table S.~~1~~5). At 80% WFPS, our estimated uncertainty in pressure head control of 20 mbar would lead to an uncertainty in soil water contents equivalent to 0.023 g g^{-1} or 8.1% WFPS. ~~Presumably, the possible uncertainty of the manual compaction of the soil columns may also have resulted in minor variability in water retention properties among the soil columns.~~

~~Seepage of the cores not only lowered water contents but also caused loss of~~ ~~NO_3^- (Table S.1 and S.2). The high and variability in water and~~ ~~NO_3^- content might explain some of the measured variability in gaseous N fluxes (initially high fluxes in both treatments, but decreasing quickly (Figs. 2a and 3a)). While the organic matter amendment clearly enhanced denitrification in the initial phase with high water content, this was not the case during the later phases when fluxes of both treatments were similarly low, likely since anoxic micro-sites disappeared due to improved aeration.~~
~~The product ratio of fluxes (Table 6) shows that mostly~~ ~~N_2O was emitted, which we attribute to the high~~ ~~NO_3^--N level and the low pH (Table 1) (Müller & Clough, 2014).~~ ~~The product ratio was similar with and without litter amendment. This might indicate that the combined inhibitory effect on~~ ~~N_2O reduction by low pH and high~~ ~~NO_3^- was more effective than the potential enhancement in~~ ~~N_2O reduction in presence of labile C in the ryegrass treatment (Müller & Clough, 2014).~~

4.2 Possible explanations for the deviations between measurement and modeling

~~The goal of this work was to test and evaluate the denitrification sub-modules of the models and not to harmonize~~

Overall, there were large differences between the measured and modeled ~~values by calibration or to rate the performance of the different models.~~results. A clear possibility for some deviations between measurement and modeling is our choice not to calibrate the models. Clearly, after calibration, the models ~~can~~should better simulate ~~results of the same magnitude as the measured values~~our measurements. Our aim, however, was to find the missing processes and limitations of the sub-modules for further model development~~.~~, rather than to harmonize the measured and modeled values by calibration.

~~Overall, there were large differences between the measured and modeled results. Modeled N_2+N_2O fluxes were between 10 and 580% of measured fluxes in the silt-loam incubation and between 1 and 9060% in the sand incubation (Table 8 and 9).~~

~~DNDC, originally developed to accommodate field conditions, calculated almost zero N_2 emissions for both treatments. The structure of the model with a simple soil water management sub-module, rather than the option to manually set up the daily soil water content, may not be a good fit for laboratory experiments. The model provided a higher amount of leachate in the first days of the simulations. This could be the reason for the lower N_2O and the almost zero N_2 production.~~

~~In theory, there should be a certain lag time between rainfall or irrigation and the occurrence of denitrification in the soil (Tiedje 1978; Smith and Tiedje 1979). DNDC ignores this lag time (Fig. 6c and 7c, day 25), as shown by the modeled N_2 and N_2O fluxes, which occurred almost immediately after the rewetting of the soil. In contrast, because Coup assumes growth of denitrifiers as a prerequisite of denitrification, there are no abrupt changes in the modeled denitrification, as any possible response was masked by the ongoing growth of the denitrifier community (refer to 4.2.3).~~

~~There was also disagreement in the N_2O/(N_2+N_2O) ratio and the temporal dynamics of the modeled fluxes, which did not always fit well with the measurements (Fig. 4, 6, 7 (a, b, c), S.6 and S.7). Models were used with the default settings of coefficients because it was not the objective of this study to calibrate them using the measured~~

4.2.1 Control factors within the experiments

The availability of sufficient and suitable input data~~. It was therefore not expected that the modeled data would fit the magnitude of measured fluxes. However, the poor fit in temporal dynamics and the N_2O/(N_2+N_2O) ratio shows that some of the model routines were not adequate to obtain correct responses to the denitrification control parameters established in the experiments. It~~ is necessary for the proper model estimations and it is notable~~, though,~~ that some model parameters were not assessed in ~~the~~our experiments (e.g. labile C content, denitrifier biomass, anaerobicity of the soil) and also that the temporal and spatial resolution in the measurement of control factors such as mineral N and soil moisture was limited; including these may have improved model estimates

~~**4.2.1 Complexity of models**~~

~~The agreement of measured and modeled results depends not~~ . Within the sand incubation, another reason for the underestimations of denitrification products by Coup and DNDC could be properties of the soil itself. The soil had a low pH, which has a direct influence on denitrification processes (Leffelaar and Wessel, 1988). However, while the denitrification sub-module of DeNi is sensitive to changes in soil temperature, moisture, NO_3^- and SOC content, the pH of the soil only influences nitrification processes. Therefore, the low pH may have had less effect on the N_2O flux estimation of DeNi, as compared to Coup and DNDC. Another reason for the smaller denitrification fluxes of Coup and DNDC could be the soil texture. Texture influences the hydrology, the anaerobe soil volume fraction (ansvf) and the diffusion of the gases, which altogether control denitrification processes (Smith et al., 2003). According to the water retention curve, the range of water contents in the incubation were located in a section of the curve where small changes in water potential could lead to large changes in WFPS (Fig. S.4). In Coup and DNDC, WFPS has multiple effects on denitrification through respiration and diffusion processes. The challenge for these models is to describe these direct and indirect effects correctly to match the observed response of denitrification. Because DeNi does not use a fully process-based approach, the effects of environmental factors – like WFPS – are considered with various empirical functions. We suspect that the use of empirical functions (functions derived from~~on the~~ experimental ~~set-up, and~~lab data to ~~which extent model parameters are represented by measurements, but also on the model complexity.~~ ~~DNDC and Coup are complex, with more parameters and more elaborate descriptions of denitrification and decomposition than DeNi.~~ ~~However, using this detailed approach may allow some factors to dominate the denitrification calculations and give biased results (Metzger et al., 2016).~~describe WFPS) was more successful in modeling WFPS effects on denitrification than the fully process-based approaches.

4.2.2 Complexity of model structure

Model structure and the complexity with which models are developed, may have affected the accuracy of results. DNDC and Coup are complex, with more parameters and more elaborate descriptions of denitrification and decomposition than DeNi. However, using a detailed approach may allow some factors to dominate the denitrification calculations and give biased results (Metzger et al., 2016). For example, the almost-zero N_2 emissions that DNDC estimated for both experiments may be reflecting how soil water is managed in the model. There is no option to manually enter daily soil water content, and the soil water management sub-module has been shown to be problematic (Smith et al., 2008; Smith et al., 2019; He et al., 2019, 2018; Brilli et al., 2017; Congreves et al., 2016; Dutta et al., 2016a; Cui et al., 2014; Abdalla et al., 2011; Uzoma et al., 2015; Deng et al., 2011). The DNDC model estimates of water in this study resulted in too much leachate in the first days of the simulations (data not shown) and could be the reason for the lower N_2O and the almost zero N_2 production. Another issue with DNDC is response time. In theory, there should be a certain lag time between rainfall or irrigation and the occurrence of denitrification in the soil (Tiedje 1978; Smith and Tiedje 1979). DNDC ignores this lag time (Fig. ~~Laboratory mesocosm experiments simplify 'real' field conditions, and the~~2c and 3c, day 25), and modeled N_2 and N_2O fluxes instead occurred almost immediately after the rewetting of the soil.

The simplicity of DeNi could be one reason why it had reasonably good success modeling the ~~incubation experiment.~~measured fluxes and also the treatment effects. The pure nitrification and denitrification approach of DeNi minimizes the influence of the complex sub-modules that ~~represent more complex processes, which~~ are present in Coup and DNDC. ~~For example, rather than using a water management sub-model~~Moreover, for DeNi, we were able to input measured daily water and soil NO_3^- content ~~into DeNi, which may have contributed to the better predictions. In contrast, Coup and DNDC use sub-models to predict changes in soil water and NO_3^- content. Coup has~~, which allowed those values to be more accurate than model estimates. Coup does have an option to overwrite the calculated daily water ~~content data~~, which we used, but this option was not available for DNDC. ~~In fact, Coup provides numerous options~~ The option to turn ~~on or off different sub-modules and use constant values instead of dynamically changed parameters (Table S.6 and S.7). Simplifying by turning~~ off sub-modules decreases the complexity of ~~the model and, in 'simplified' experiments, such as ours, may actually improve the final results~~models in situations where that added complexity is not relevant or even problematic, as in the case of soil water mentioned above.

4.2.~~2~~3 Labile organic carbon (litter)

~~While treatments without litter amendment were relatively low in labile C content, the~~The ryegrass treatment in the sandy soil was established to mimic incorporation of crop residues ~~and thus contained~~, a common field practice, and resulted in large amounts of labile organic C. Coup and DNDC provide options to modify the labile C and N pools, and in running these models, the C and N content of the ryegrass was added to the respective labile pools. ~~However, the results of Coup and DNDC didn't reflect the extremely fast decomposition that was observed in the experimental results (Fig. 6f). Although the measured results showed that soils with ryegrass amendment had 345% higher CO_2 than control soils (Table 9.), Coup calculated similar CO_2 fluxes for both treatments (Fig. 6e and 7e) as well as only a 10% difference in the modeled N_2 and the N_2O fluxes between the treatments (Fig. 6b and 7b). DNDC actually calculated 40% higher CO_2 fluxes for the control treatment as compared to the ryegrass-amended soils (Fig. 6f and 7f). The decomposition rate of the ryegrass in the models needed to be much higher than the decomposition rate that is currently provided for the labile pools. Because DeNi has a simple, one C pool approach for calculating soil respiration, it was also unable to handle the extra ryegrass as rapidly decomposable carbon. Similar to Coup, DeNi calculated similar soil respiration and N_2+N_2O fluxes for both treatments of the sand soil (Fig. 6a,d and 7a,d).~~DeNi has a simple soil respiration calculation, which is not dependent on a defined soil C pool, so the ryegrass treatment was added as a higher C/N ratio. However, none of the models was able to handle the extremely fast decomposition from rapidly decomposable carbon (Fig. 2 and 3). Similar to CO_2 fluxes, measured N fluxes in response to added ryegrass were significantly higher (668% higher) than the modeled estimates, again highlighting that all of the models were too conservative.

In these models, decomposition processes are assumed to be driven by soil water content and temperature (Table S.~~6), thus the~~3). The microbial response to treatments (e.g. NO_3^- addition, pH), although they are known to influence microbial carbon use (Manzoni et al., 2012), ~~cannot be~~are not explicitly simulated. It should also be noted that decomposition of the labile and recalcitrant pools in ~~these~~Coup and DNDC models are calculated independently. However, field and empirical data

(Kuzyakov, ~~2012~~2010) suggest adding labile C could also enhance the decomposition of resistant pool, e.g. priming effects, which none of these models account for. Our results ~~also suggest~~highlight the importance of better simulating microbial dynamics~~ of decomposition explicitly~~ to better account for the drivers of decomposition, because these ultimately influence the denitrification flux estimations~~. It means that the~~ (Philippot et al., 2007). The direct application of these models with first order kinetics for decomposition to simulate the effects of fertilization or changing N deposition on denitrification fluxes could be largely biased. ~~Future research should aim to quantify more appropriate decomposition rates for models to better take into account labile pools.~~

4.2.~~3~~4 Denitrifiers

In Coup, the biomass of denitrifiers directly limits the maximum denitrification rate. We assume that the slow increase of fluxes obtained from Coup (Fig. ~~6b, 7b~~2b, 3b) was due to the modeled growth of denitrifiers, since the default setting assumed a low abundance of denitrifiers, hence the denitrifiers had to first grow before reaching maximum denitrification rates (denitrifier growth was observed in the model output although this data was not shown). It can be concluded that when modeling denitrification ~~during incubation experiments~~in Coup, the model initialization must include inducement of denitrifier growth to match current soil conditions. Although our 3-day sampling interval was able to capture the rapid change in fluxes, to really fine-tune the initial activity after a disturbance (i.e. fertilizer addition), a higher frequency of measurements would be ideal.

~~Another reason for the slow increase of the denitrifier biomass at sandy soil modelling could be that the modeled anaerobic soil volume fraction (ansvf) is orders of magnitude smaller than the measured ansvf (Rohe et al., 2020) and the small ansvf was not ideal for the growth of denitrifiers. This may have led to a non-realistic, too small denitrifier community, and therefore low~~ ~~N_2O and N_2 fluxes.~~

The stepwise denitrification growth, death, and respiration for N_2O, NO, N_2 approach in Coup were similar to DNDC, thus they represent the high complex end of the denitrification process, but the coefficients for these denitrifiers are obtained from culture studies over 30 years old. These coefficients in the denitrification sub-modules (Li et al., 1992) are not universal for different soils, as here a silt-loam and sandy soil show contrasting results, which means the microbial community needs specific calibration for each application. Large uncertainties in microbial coefficients must be addresses, as shown in Coup, where the denitrifier biomass was able to override the other known environmental factors for denitrification, leading to biased simulations.

4.2.~~4~~5 Anaerobic soil volume fraction (ansvf)

DNDC and Coup use a similar calculation of the ~~ansvf~~ anaerobic soil volume fraction and both models use it for the calculation of ~~the~~ denitrification processes. While the ansvf estimations of DNDC were not available as an output, the Coup results were obtained ~~showing~~and showed that ansvf was almost constant~~.~~ (ansvf was observed in the model output although this data was not shown). This is not plausible since the parameters affecting ansvf~~, i.e.~~ (diffusivity and O_2 consumption~~, must have been highly variable since~~), reflected in this study by soil moisture and respiration ~~exhibited large differences~~, changed significantly between treatments and experimental phases. The underestimation of N_2+N_2O fluxes by Coup could therefore result from the inappropriate calculation of ansvf in the model (see in section 4.2.~~3).~~

~~One of the main goals of this study was to test the ability of the existing biogeochemical models to predict the temporal dynamics of N_2 and N_2O fluxes and identify where the models could be improved.~~4). The slow increase of the denitrifier biomass that Coup modeled in the silt-loam soil could be the reason that the modeled ansvf is orders of magnitude smaller than the ansvf measured in another silt-loam soil of similar WFPS (Rohe et al., 2021). This non-realistic, too small and slowly increased denitrifier community led therefore to low N_2O and N_2 fluxes. Ensuring correct ansvf calculations could significantly improve the efficiency of denitrification sub-modules, and thus further work on these algorithms within Coup is one area for future research that we would strongly recommend. Similarly, it would be beneficial to test the ansvf calculations of DNDC, which was not possible in our study, as the source code was not available and the ansvf is not included in output data.

5 Summary and suggestions for future improvements

~~4.2.5 Determination of control factors in the experiments~~

~~Within the sand incubation, another reason for the underestimations of denitrification products by Coup and DNDC could be properties of the soil itself. The soil had a low pH, which has a direct influence on denitrification processes (Leffelaar and Wessel, 1988). However, while the denitrification sub-module of DeNi is sensitive to changes in soil temperature, moisture, NO_3^- and SOC content, the pH of the soil only influences nitrification processes. Therefore, the low pH may have had less effect on the N_2O flux estimation of DeNi, as compared to Coup and DNDC. Another reason for the smaller denitrification fluxes of Coup and DNDC could be the soil texture. Texture influences the hydrology, the anaerobic soil volume fraction and the diffusion of the gasses, which altogether control denitrification processes. According to the water retention curve, the range of water contents in the incubation were located in a section of the curve where small changes in water potential could lead to large changes in WFPS (Fig. S.4). In Coup and DNDC, WFPS has multiple effects on denitrification through respiration and diffusion processes. The challenge for these models is to describe these direct and indirect effects correctly to match the observed response of denitrification. Because DeNi does not use a fully process-based approach, the effects of environmental factors – like WFPS – are considered with various empirical functions. We suspect that the use of empirical~~

~~functions (functions derived from experimental lab data to describe WFPS) was more successful in modeling WFPS effects on denitrification than the fully process-based approaches.~~

~~4.3 Suggestions for future model evaluation experiments and model improvement~~

~~This study has demonstrated advantages and shortcomings of modelling denitrification processes using current models. We suggest the following to improve model algorithms and parameters by targeted experimental studies: (1) design experiments to specifically evaluate sensitive input variables (e.g. decomposition of labile organic carbon), which can then be used to improve current model algorithms; (2) take more frequent measurements in future studies (ideally daily) to allow better descriptions and evaluations of temporal dynamics (3) use updated techniques to take measurements. To the best of our knowledge, all previous model evaluation studies (NGAS and DailyDayCent) using measured denitrification data were based on the outdated acetylene inhibition technique (Bollmann and Conrad, 1997; Nadeem et al., 2013; Sgouridis et al., 2016). Future studies should (as was done in this study) be based on He/O_2 or ^{15}N gas flux methods; (4) take measurements to evaluate unknown/hypothetical parameters in the model equations (e.g. static growth and death rate of the denitrifiers, rate coefficients for the different denitrification processes, etc.) (5) adapt models so that the parameters better represent measurements from real soils (e.g. measured SOC fractions v.s. SOC pools in the models); (6) continue to re-evaluate how processes are describe in models. These models were developed decades ago, and new technical solutions appear constantly. There are several missing or poorly described processes in the models. Strong simplification of some process descriptions (e.g. no or inadequate or poorly calibrated microbial dynamics (see section 4.2.2)) have to be overcome or their implications have to be estimated. Further experiments are thus necessary to describe more precisely the effect of temperature, moisture and substrate manipulations on the microbial/denitrifier community and therefore on N_2 and trace gas fluxes. These kinds of datasets will help to (i) identify inadequate process descriptions, (ii) calibrate the sub-modules separately from the other parts of the model and finally, (iii) develop new, better approaches for the description of the processes.~~

~~5 Conclusions~~

~~The goal of this study was to assess the ability of the denitrification sub-modules in three biogeochemical models to predict the N_2 and N_2O fluxes of incubated soils in response to different initial soil conditions and changing environmental factors. The results show that the models did not calculate fluxes of the same magnitude as the experimental results; measurements were overestimated by DeNi and underestimated by DNDC and Coup. However, with only a few exceptions, the temporal patterns of the measured and modeled emissions were quite similar for the sandy soil. For the silt-loam soil, Coup and DNDC showed no response in 47% and 14% of cases, respectively, and responded in the same direction in 19% and 52% of cases, respectively. For DeNi, the model responded in the same direction in 67% of cases, with 33% in the opposite direction.~~ In this study, we presented the N_2, N_2O and CO_2 fluxes from two laboratory incubations, which explored the response of these fluxes to different control factors. In the silt-loam soil, the general trend of CO_2 fluxes was a negative correlation with WFPS, while for N_2+N_2O fluxes, together with the effect of increased BD, the correlation was positive. The lowest NO_3^- application resulted in the lowest N_2+N_2O fluxes. In the sand soil, addition of ryegrass resulted in significantly higher CO_2 and N_2+N_2O fluxes as compared to control soils without ryegrass addition.

We suggest the following to improve targeted experimental studies for model developments: (1) design experiments to specifically evaluate sensitive input variables (e.g. decomposition of labile organic carbon); (2) take more frequent measurements during periods of suspected activity (ideally daily or more often) and (3) use updated techniques, such as He/O_2 or ^{15}N gas flux methods, to take measurements.

We suggest the following to improve models algorithms to reflect denitrification and decomposition: (1) address model complexity to facilitate modeling of all datasets (2) add missing priming effect of CO_2 fluxes for the models (3) calibrate denitrifer microbial dynamics (4) evaluate anaerobic soil volume concept, given the possibility of measured data.

We have shown that there are a number of possibitilies in how experiemnts are designed and how models could be altered in order to improve denitrification and decomposition modelling. Further development of the models to overcome the identified limitations can largely improve the predicting power of the models. Models should then often be re-evaluated to keep them up-to-date with current research developments.

~~Treatment responses of the models suggest that in addition to calibration, improvement of the model functions is needed to better predict N_2O and N_2 fluxes from denitrification. While none of the models was able to determine litter-induced decomposition dynamics correctly, the complex models Coup and DNDC were apparently further hampered by their limited ability to give realistic estimates of soil moisture, anaerobic soil volume and denitrifier biomass. The simple structure of the DeNi model, using more empirical functions, thus can be more accurate for some experiments. This suggests that the potential advantage of Coup and DNDC to include more control factors is only useful when the control factors have been more thoroughly researched and respective functions are more reliable. Developing reliable functions for complex control factors requires experimental data with more detail in temporal resolution and parameter determination. Further development of the models to overcome the identified limitations based on experiments with enhanced denitrification activity and control parameter determination can largely improve the predicting power of the models.~~

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