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Simulating N_2O fluxes from a Brazilian cropped soil with contrasted tillage practices

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ABSTRACT

Assessing the N_2O fluxes balance is a key challenge to estimate the effect of agriculture practices on greenhouse gas production. N_2O fluxes remained difficult to measure on a field scale due to high spatial and temporal variability and usually low concentrations. Our work aimed at (i) characterizing by laboratory measurements soil potential N_2O emissions from nitrification and denitrification and (ii) testing a modelling approach of N_2O emissions that circumvents the problem of discrete measurements for two Brazilian rainfed rice cropping systems, no-tillage (NT) vs. disk tillage (DT). This latter approach consisted in the combination of 2 models: a mechanistic water transfer model and a N_2O emission model, namely PASTIS and NOE. Simulations with the PASTIS + NOE approach showed for both NT and DT treatments that: (i) the soil emitted low amounts of N_2O, (ii) emissions by denitrification corresponded to short periods of high N_2O emissions (15 times as high as emission by nitrification), (iii) nitrification contributed to ca 35% of the total N_2O emissions at the crop cycle scale, (iv) field N_2O emission measurements corresponded to the low bound of simulated emissions from nitrification.

1. Introduction

Although nitrous oxide (N_2O) is only present as a trace gas in the atmosphere, it has 298 times the global warming potential of carbon dioxide (CO_2) and a lifespan of ~120 years (Crutzen, 1981). The continued increase of N_2O in the atmosphere (+18% since 1750; IPCC, 2007) is a serious environmental concern. However, the N_2O budget is at present not well quantified, making it difficult to determine the sources and the cause of its increase precisely (IPCC, 2007). Agricultural soils contribute to about 60% of the global anthropogenic N_2O flux (IPCC, 2007). N_2O is produced during numerous nitrogen transformations in soils (Robertson and Tiedje, 1987), but on most occasions denitrification and nitrification are the main sources. The contribution of each process to N_2O flux depends on climate, soil conditions characteristics and cropping systems. The number of published measurements of N_2O fluxes from soils is increasing steadily at mid-latitudes (Europe and North America) but there are still few flux data from tropical and subtropical regions (Bouwman et al., 2002; Stehfest and Bouwman, 2006). The current IPCC methodology for producing national inventories of N_2O from agricultural land provides a default emission factor (EF) of 1% of all N added to the soil (IPCC, 2007) while applying this mean value may overestimate the N_2O flux for tropical agricultural soils (Chapuis-Lardy et al., 2009). In order to find the best constraints to the N_2O budget, the representation of tropical agricultural systems in datasets really needs to be improved to provide additional information about driving factors of emissions. This will also allow an improvement of global N-emission models and IPCC N_2O flux factors.

Our field measurements in Brazil (Metay et al., 2007b) show high variability in time and space of N_2O fluxes from soils as also reported by others in tropical (e.g. Chapuis-Lardy et al., 2009) and temperate (e.g. Yanai et al., 2003) systems. Ideally, the N_2O fluxes should be extensively and continuously recorded at a field scale. Unfortunately, for practical reasons, most of the N_2O studies are only based on a series of enclosed chamber measurements, and the uncertainty associated with up-scaling such discrete measurements to seasonal or annual budget estimates is often extremely large (Parkin, 2008). In the last fifteen years, the prediction of N_2O fluxes within process-based agro-ecosystem models has emerged as a promising route to deal with these issues and improve the emission estimates (Cannavo et al., 2008; Chen et al.,

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2008). They are based on the numerous soil and environmental factors controlling denitrification and nitrification such as soil moisture, soil temperature, and ammonium and/or nitrate contents. Amongst those models, Hénault et al. (2005) elaborate in successive steps NOE (nitrous oxide emission), a semi-empirical sub-model simulating the production and reduction of N_2O in agricultural soils through both the denitrification and nitrification pathways. The denitrification component is derived from the NEMIS model (Hénault and Germon, 2000). Although NOE was developed for temperate soil and climate and validated on temperate datasets, its use was promising for tropical conditions (Hénault et al., 2005; Hergoualc'h et al., 2009). NOE parameterization required laboratory determination of site-specific biological activities, characterizing the nitrification and denitrification processes.

These N_2O-emitting processes also depend on the water-filled pore space (WFPS) in soils which is an indirect measure for the degree of soil aeration (Freney et al., 1978; Davidson, 1991; Bandibas et al., 1994). Soil moisture dynamics were satisfactorily simulated in tropical soils by PASTIS (predicting agriculture solute transport in soils; Lafolie, 1991), a mechanistic water transfer model (Reyes, 2002; Hergoualc'h et al., 2009). Here, we also used PASTIS to rebuild a 1-h time step estimation of soil water content from discrete measurements, over the whole cropping cycle. This estimate was introduced in the NOE model as the input data in replacement of daily soil water content measurements.

Our approach described the combined use of PASTIS and NOE models to simulate N_2O fluxes from a tropical cropped soil. *In situ* N_2O fluxes and detailed data necessary for the parameterization of these models were collected from tilled and no-till soils in the Cerrado region (Central Brazil). The area under no-till (NT) in Brazil reached 18 million ha, with a large part in the Cerrado (Bernoux et al., 2006). The aim is to explore how this model approach can be applied to better predict N_2O fluxes from the no-till systems developed in Brazil.

2. Material and methods

2.1. Site description

The study area was located at the CNPAF (Centro Nacional de Pesquisa sobre Arroz e Feijão) research center near the city of Goiânia, Goiás state, Brazil (16° 37′ S, 49° 13′ W). Local natural vegetation is a tree savannah, the Cerrado, which gave its name to the region. The climate was tropical with a humid season from October to March and a dry season from April to September. The mean annual air temperature was 22.5 °C and the mean annual precipitation was 1500 mm. The soil was a clayey Oxisol (Soil Survey Staff, 1999) (latosolo vermelho escuro distrofico according to the Brazilian classification), with clay content around 40% in the upper layer. Topsoil organic carbon and total nitrogen contents were 16.4 mg C g^{-1} soil and 1.1 mg N g^{-1} soil respectively. Soil fractionation (Metay et al., 2007a) showed low amounts of aggregates with a size >2 mm. This soil had a low cation exchange capacity (3.3 cmol(+) kg^{-1}), dominated by exchangeable Ca, and a pH (in water) of 6.0.

The subsurface horizon of these soils has a weak pulverized structure known as “coffee powder” (EMBRAPA, 1984) with a uniform macropore distribution (Van den Berg et al., 1997). Even if the structural stability is higher in the surface horizon, its porosity distribution remains uniform (Castro and Logan, 1991).

2.2. Experimental design

The experimental design was established in the station in 1998 on a 6 ha field and consisted in randomised blocks of rainfed rice–soyabean rotation conducted with or without tillage (Metay et al., 2007a,b). Our present study focused on four plots sown with rice (*Oryza sativa*) with previous crop (soyabean) residues left on the soil after harvest. In no-till (NT) treatment, the leguminous *Crotalaria spectabilis* was sown to cover the soil after rice harvest. NT plots were treated before planting with paraquat and glyphosate as needed for weed control (Metay et al., 2007a). Tillage (DT) was practised in other plots with an offset disc harrow at 15 cm depth. Mineral N fertilization, in both NT and DT treatments, consisted of ammonium sulphate (100 kg ha^{-1}) immediately after seeding and urea (100 kg ha^{-1}) 2 weeks and 6 weeks after seeding. The P and K fertilization (in supertriple phosphate and potassium chloride forms) corresponded to 52.8 kg P ha^{-1} and 49.8 kg K ha^{-1} respectively. Soil bulk densities were 1.26 and 1.24 g cm^{-3} in NT and DT treatments respectively.

2.3. In situ N_2O fluxes and ancillary soil properties

Soil N_2O fluxes from Metay et al. (2007b) were measured from static chambers at key periods as recommended in literature (Baggs et al., 2003; Davidson et al., 1996; Dick et al., 2001; Smith et al., 2003): (i) during the rainy season (November to March) that is the most relevant period to measure N_2O fluxes under tropical conditions, (ii) during the first days after N-fertilizer application (December and January), and (iii) during the first stages of cover residue decomposition (from grass or legumes) (November) that are both favourable to N_2O fluxes. Three times a week, during the morning, gas samples were taken using a gas-tight syringe in 6 chambers per plot at chamber closure and 10, 30, 60 and 120 min after closure. Gas samples were stored in 13 mL vacutainer® tubes which were previously purged and analyzed for N_2O by gas chromatography (Varian 3800, 3 m Porapak Q column, vector gas N_2) within one month after collection. Hourly fluxes were calculated from the linear increase in gas concentration in the chamber headspace with time according to Metay et al. (2007b) after being tested for nonlinearity.

Soil temperature was recorded with a digital thermometer at 5 cm depth and a topsoil (0–10 cm depth) composite sample was collected on each N_2O flux measurement date. Soil mineral ammonium (NH_4^+) and nitrate (NO_3^-) contents were determined after soil extraction in 1 M KCl on a continuous flow colorimeter (Alliance® Integral Futura equipment) using a cadmium reduction to nitrite and Griess reagent for NO_3^- and Berthelot reaction for NH_4^+, as described by Mulvaney (1996). Soil moisture was determined gravimetrically by drying intact soil core samples at 105 °C during 48 h in order to calculate water filled pore space (WFPS) (Linn and Doran, 1984).

2.4. Soil moisture simulation using the PASTIS model

Soil moisture has a large influence on N_2O fluxes through its impact on the volume of soil in which denitrification occurs and the duration of denitrifying conditions. The monodimensional mechanistic model PASTIS (Lafolie, 1991) was used to simulate the water transfer in the soil during plant growth in the presence of surface mulch when appropriate (Findeling, 2001) for both NT and DT treatments. The model provides for each time step the soil water content on a vertical profile of soil structured in homogeneous horizontal layers (0–10 cm and 10–30 cm). Boundary conditions for heat and water flows were taken from Reyes (2002) who worked in related systems in the study area. Initial conditions derived from a soil water content profile which was measured at the beginning of the rainy season. The calibration was carried out by slightly tuning soil hydraulic properties (Table 1). We finally checked parameter consistency by comparison with the range obtained by Reyes (2002).

Table 1
Soil hydraulic properties parameterizing the PASTIS (prediction of agricultural solute transfer in mulch soils) model in no-till (NT) and tillage (DT) treatments.

	NT		DT	
	0–10	10–30	0–10	10–30
Soil saturation volumetric water content, θ_s ($m^3\,m^{-3}$)	0.50	0.41	0.45	0.43
Soil residual volumetric water content, θ_r ($m^3\,m^{-3}$)	0.156	0.180	0.160	0.180
Saturated soil hydraulic conductivity, K_{sat} ($10^{-4}\,m\,s^{-1}$)	28.3	3.1	17.7	3.1

0–10 and 10–30 indicate soil depth (cm).

2.5. N_2O flux simulation using the NOE model

NOE (Hénault et al., 2005) is an algorithm to predict N_2O fluxes from soil (Table 2). NOE model was used to simulate N_2O flux on the whole cropping cycle in 2002–2003 which also corresponded to the rainy season (November 15th–March 5th), particularly favourable to N_2O fluxes. Total N_2O flux from the soil simulated by NOE was the sum of the N_2O fluxes produced by denitrification (N_2O denit) and by nitrification (N_2O nit).

The N_2O denit (kg $N\text{-}N_2O\,ha^{-1}\,d^{-1}$) is calculated according to Garrido et al. (2002):

$$N_2O\ \text{denit} = r_{max} D_A \tag{1}$$

where D_A (kg N $ha^{-1}\,d^{-1}$) is the actual denitrification rate, and r_{max} (dimensionless) is the maximum ratio of accumulated emitted N_2O and denitrified NO_3^- under anaerobic condition (Hénault et al., 2001). D_A is defined by a multiplicative function of potential denitrification rate and dimensionless functions of soil NO_3^- content, WFPS and temperature (Hénault and Germon, 2000):

$$D_A = D_P F_N F_T F_W \tag{2}$$

where D_P (kg N $ha^{-1}\,d^{-1}$) is the potential denitrification rate, F_N, F_T and F_W are the response factors to soil nitrate, soil temperature and water-filled pore space (WFPS), respectively. The process of denitrification is highly sensitive to WFPS and starts to occur above a site-specific threshold value $WFPS_{th}$ (Hénault et al., 2005) which determination was detailed at a later point in this methodology section.

The NOE model considers that in denitrifying conditions, N_2O produced by nitrification is denitrified at the same rate (r_{max}) that N_2O produced by denitrification. Nitrification is also known to be inhibited in aeration-limited conditions (Mosier et al., 1998). Nitrous oxide produced by nitrification (N_2O nit; kg $N\text{-}N_2O\,ha^{-1}\,d^{-1}$) is calculated as:

$$N_2O\ \text{nit} = zN_A \quad \text{when} \quad WFPS < WFPS_{th} \tag{3}$$

$$N_2O\ \text{nit} = r_{max} z N_A \quad \text{when} \quad WFPS = WFPS_{th} \tag{4}$$

where z (dimensionless) is the proportion of nitrified nitrogen emitted as N_2O (Garrido et al., 2002), and N_A (kg N $ha^{-1}\,d^{-1}$) is the actual nitrification rate (Hénault et al., 2005). The nitrification rate is calculated as follows:

$$N_A = N_W N_{NH_4} N_T \tag{5}$$

where N_W (kg N $ha^{-1}\,d^{-1}$), N_{NH_4}, N_T are the response functions to soil water content, soil ammonium content and soil temperature (Hénault et al., 2005). N_W is assumed to be a linear function of soil water content:

$$N_W = a\text{WC} + b \tag{6}$$

where WC ($kg\,kg^{-1}$) is soil gravimetric water content, a and b (kg N $ha^{-1}\,d^{-1}$) are soil-specific parameters (Garrido et al., 2002).

Table 2
List of parameters used in NOE model – definition and method for determination.

Parameter	Definition	Dimension	Determination (calculation or laboratory)	References
D_P	Potential denitrification rate	kg N $ha^{-1}\,d^{-1}$	Laboratory determination	Hénault and Germon, 2000
F_N	Denitrification response factor to soil NO_3^- content	Dimensionless	$F_N = \frac{[NO_3^-]}{Km1+[NO_3^-]}$ with $[NO_3^-]$ derived from field data collection and Km1 constant equal to 22 mg $N\text{-}NO_3^-\,kg^{-1}$ soil	Hénault and Germon, 2000
F_T	Denitrification response factor soil temperature (T)	Dimensionless	$F_T = \exp\left[\frac{(T-11)\ln(89)-9\ln(2.1)}{10}\right]$, if $T < 11\,^\circ C$ $F_T = \exp\left[\frac{(T-20)\ln(2.1)}{10}\right]$, if $T \geq 11\,^\circ C$, calculated from field data collection	Hénault and Germon, 2000
F_w	Denitrification response factor to water-filled pore space (WFPS)	Dimensionless	$F_w = \left[\frac{WFPS-0.7}{0.3}\right]^{BD}$ with BD: bulk density determined from field data and WFPS (water-filled pore space) calculated from field data or water content simulation using PASTIS model	Hénault and Germon, 2000
z	Proportion of nitrified nitrogen emitted as N_2O	Dimensionless	Laboratory determination	Garrido et al., 2002
N_w	Nitrification response function to gravimetric soil water content (WC)	kg N $ha^{-1}\,d^{-1}$	$N_w = a\text{WC} + b$ from laboratory determination	Garrido et al., 2002
$N_{NH_4^+}$	Nitrification response function to NH_4^+ content	Dimensionless	$N_{NH_4} = \frac{[NH_4^+]}{Km2+[NH_4^+]}$ with $[NH_4^+]$ determined from field data and Km2 constant equal to 2.6 mg $N\text{-}NH_4^+\,kg^{-1}$ soil	Hénault et al., 2005
N_T	Nitrification response function to temperature	Dimensionless	Equal to F_T	Hénault et al., 2005
r_{max}	Maximum ratio of accumulated N_2O to denitrified NO_3^- under anaerobic incubations	Dimensionless	Anaerobic incubation	Garrido et al., 2002

While F_N, N_{NH_4}, F_T and N_T were derived from data field collection (soil NO_3^-, NH_4^+ contents; soil temperature measured three times a week for all treatments), WFPS and F_W were obtained using on-field measurements (bulk density, soil gravimetric water content) and soil moisture as simulated by PASTIS. The biological parameters required by NOE (D_P, r_{max}, a, b, z) were obtained in laboratory incubations as described in Section 2.6. The NOE model was used to simulate the soil N_2O fluxes during a crop cycle in the rainy season, from November to March.

2.6. *Laboratory determination of biological parameters required by NOE*

2.6.1. *Soil collection for laboratory determination*

For both denitrification and nitrification determinations, composite soil samples were formed by pooling sub-samples randomly collected near each chamber at the end of the cropping season in both treatments to ensure at least the representativeness of the spatial soil heterogeneity under a chamber (0.08 m^2). Based on the N_2O soil profiles reported by Metay et al. (2007b) for this experimental design, the soil was sampled in the surface layers. Composite soil samples were sieved through 2-mm mesh and stored at 4 °C before incubation

2.6.2. *Potential denitrification rate (D_P) and the proportion of denitrified N emitted as N_2O (r_{max})*

The capacities for production and reduction of N_2O during denitrification were investigated in the laboratory according to Hénault et al. (2001). Three replicates of soil sample equivalent to 10 g of dry soil were placed in 125-ml flasks and put under anaerobic conditions by five successive cycles of vacuum-filling by helium. Two sets of incubation were carried out with the addition of NO_3^- (38.25 μg N g^{-1} dry soil) as electron acceptor (1) in the presence of acetylene (C_2H_2; 10% of the gas atmosphere) in order to determine D_P, the potential denitrification rate, i.e. N_2O and N_2 normally produced by denitrification and (2) without the addition of acetylene in order to measure the potential production of N_2O during denitrification. The difference between these two treatments was used to calculate the soil potential for N_2O reduction. The flasks were maintained at 28 °C during 8 days in the dark. An aliquot of the atmosphere in the flask was sampled after 1, 2, 3, 6, 8 days of incubation (t_i) for N_2O analysis on a gas chromatographer equipped with an electron capture detector (Varian 3800).

The proportion of denitrified N emitted as N_2O is defined as:

$$r_{max} = \max\left(\frac{N_2O_{0\,C_2H_2}}{N_2O_{10\%\,C_2H_2}}\right)_{t_i} \qquad (7)$$

where $N_2O_{0\,C_2H_2}$ is the production of N_2O in absence of C_2H_2 and $N_2O_{10\%\,C_2H_2}$ is the N_2O production in the presence of C_2H_2, i.e. the total gaseous N production ($N_2O + N_2$) (Hénault et al., 2001). Since denitrification, as a heterotrophic process, is dependent on organic C supply, the CO_2 released during incubations was also monitored to assess concomitant respiration rates and control that organic carbon was not a limiting factor. Measurement of NH_4^+ and NO_3^- in soil samples was performed after KCl extraction at the end of the incubation.

2.6.3. *Determination of the WFPS threshold for N_2O production by denitrification*

As the water filled pore space increases, diffusion of oxygen into soil will decrease, and a rapidly increasing fraction of the soil volume will become anaerobic, causing increased N_2O production by denitrification (Dobbie and Smith, 2003). The NOE model uses a soil moisture threshold value ($WFPS_{th}$) to switch on/off denitrification. Soil samples were incubated in the laboratory at five WFPS levels (37, 50, 60, 70 and 80%) following WFPS adjustment procedure as described by Hergoualc'h et al. (2007). Eighty grams of dry soil were placed in plastic cylinders (8 cm in diameter), mixed with a solution of KNO_3 with 1.15 g N L^{-1}, and packed to simulate the bulk density observed on field for each treatment (NT and DT). Distilled water was added to reach the specific WFPS values. The cylinders were incubated in airtight glass flasks at 28 °C in the dark during four days. The atmosphere in the flasks was sampled daily and analyzed for N_2O by gas chromatography. Mineral N content (NH_4^+ and NO_3^-) were determined in KCl extracts of soil samples by methods previously described.

2.6.4. *N_2O production by nitrification as a function of WFPS*

The methodology used was to determine how soil moisture influenced the production of N_2O by nitrification adapted from Garrido et al. (2002). Soil sample equivalent to 10 g of dry soil were placed in 125-ml airtight glass flasks, packed to simulate the bulk density observed on field and incubated in the laboratory at five WFPS values (20, 26, 32, 37, 46%). Non-limiting NH_4^+ conditions were provided by addition of ammonium sulphate (0.4 mg N g^{-1} dry soil) at the same time as water to adjust soil moisture to the appropriate WFPS level. Flasks were incubated for 9 days at 28 °C in the dark. Soil moisture was regularly checked and adjusted during at the incubation period and no significant evolution was observed. Each treatment is repeated three times. N_2O concentrations were measured in the flask atmosphere while measurements of NH_4^+ and NO_3^- were performed in KCl extracts of soil, both with previously described methods and instrumentation. An additional series of 36 samples is placed in flask serums of 125 ml to determine potential nitrate losses at the end of the incubation. The nitrification rates were determined as the soil nitrate production. The z parameter in Eqs. (3) and (4) was the proportion of nitrified N emitted as N_2O, and a and b values in Eq. (6) were the slope and the Y-intercept, respectively, of the linear relationship between soil nitrification rate and soil moisture (Garrido et al., 2002).

2.7. *Statistics*

Data are presented as mean values with standard deviation. Data were analyzed using XLSTAT software (AddinSoft). Student's unpaired t-test was applied to identify significant differences between data set at a 0.05 probability level. The PASTIS and NOE simulations were compared with field observations using graphics to capture dynamic trends. We used an efficiency criterion (EFF) based on the comparison of simulated and measured soil water contents for the different studied layers (Nash and Sutcliffe, 1970) to estimate PASTIS model performance:

$$\mathrm{EFF} = 1 - \frac{\sum_i^n (x_{\mathrm{sim},\,i} - x_{\mathrm{mes},\,i})^2}{\sum_i^n (\bar{x}_{\mathrm{moy}} - x_{\mathrm{mes},\,i})^2} \qquad (8)$$

with $x_{\mathrm{sim},\,i}$, i simulation of soil water content; $x_{\mathrm{mes},\,i}$, i measurement of soil water content; $\bar{x}_{\mathrm{moy}}$, mean of the $x_{\mathrm{mes},\,i}$.

3. Results

3.1. *Parameters in NOE model*

3.1.1. *Potential denitrification rate (D_P) and the proportion of denitrified N emitted as N_2O (r_{max})*

The potential denitrification rate (D_P) was around 1 kg N-N_2O ha^{-1} d^{-1} with a slightly higher value for tilled (DT) than for no-tilled (NT) treatments (1.072 vs. 0.987 kg N-N_2O ha^{-1} d^{-1} respectively) (Table 3). The N_2O production in anaerobic conditions in the presence or absence of C_2H_2 was monitored over 10 days but the reduction of N_2O to N_2 was only observed after 6 days

Table 3
Soil microbial parameters integrated into NOE model: potential denitrification rate (D_P); proportion of denitrified N emitted as N_2O (r_{max}) (with standard deviation in parentheses); slope (a) and intercept (b) of nitrification response function to soil water content (Garrido et al., 2002; Hénault et al., 2005); and proportion of N nitrified emitted as N_2O (z).

Parameters	Symbol (unit)	NT	DT
Potential denitrification rate	D_P (kg N ha^{-1} d^{-1})	1.072 (0.004)	0.987 (0.035)
Proportion of denitrified N emitted as N_2O	r_{max}	0.48	0.59
Slope of nitrification response function to soil water content	a (kg N ha^{-1} d^{-1})	0.15	0.06
Intercept of nitrification response function to soil water content	b (kg N ha^{-1} d^{-1})	−1.66	−0.66
Proportion of N nitrified emitted as N_2O	z	0.0003	0.00044

(data not shown). The proportion of denitrified N emitted as N_2O (r_{max}) was slightly higher for DT than for NT treatments (0.59 vs. 0.48 respectively) (Table 3).

3.1.2. WFPS threshold for N_2O production by denitrification

Fig. 1 shows the shape of the response of denitrification to WFPS in non-limiting N conditions. N_2O was not substantially emitted (<0.04 g N-N_2O kg^{-1} soil) at soil WFPS below 70% while the N_2O production reached values up to 58 times higher at 80% WFPS (from 0.2 to 1.0 and from 0.4 to 2.1 g N-N_2O kg^{-1} soil in DT and NT, respectively). It is worth noting that at this WFPS level (80%), N_2O fluxes from NT were significantly higher than those from DT soils. The WFPS threshold beyond which denitrification may occur is 70% in the studied soil. The $WFPS_{th}$ parameter in NOE model might be raised from 0.62 (default value) to 0.70.

3.1.3. Nitrification kinetics

The rates of nitrification were calculated, for each WFPS level, from the nitrate accumulation during 9-d soil incubation. Soil nitrification rates increased along with soil moisture from 0.21 to 2.16 mg N-NO_3^- kg^{-1} soil d^{-1} in NT and 0.10 to 0.92 mg N-NO_3^- kg^{-1} soil d^{-1} in DT treatments, respectively (Table 4). The nitrification parameters entering NOE model, i.e. the slope (a) and the intercept (b) of the linear relationship between soil nitrification rate and soil moisture were presented in Table 3. The proportion of nitrified N emitted as N_2O (z) was lower in no-till (NT) compared to tillage (DT) treatment (0.00030 vs. 0.00044, respectively; Table 3).

Table 4
Nitrification rates (N_w) for NT (no-till) and DT (disc-tilled) soils.

WFPS (%)	N_w (mg N-NO_3^- kg^{-1} soil d^{-1})	
	NT	DT
20	0.21 (0.07) a	0.10 (0.04) b
26	0.70 (0.05) c	0.39 (0.02) d
32	1.22 (0.12) e	0.42 (0.04) d
37	1.68 (0.10) f	0.76 (0.05) c
46	2.16 (0.24) g	0.92 (0.03) h

Nitrification rates (N_w) of soils were determined after NH_4^+ addition and incubation for 9 days at five levels of WFPS. NT: no-till, DT: disc-tilled soils. Mean (standard deviation, $n = 3$). Different letters indicate statistical differences between data at a 0.05 probability level.

3.2. Simulation of soil water content using PASTIS

The PASTIS model simulated satisfactorily the soil water content for both treatments at 0–10 cm (Fig. 2) and 10–30 cm (data not shown) soil depth. However some discrepancies were observed for the NT treatment where the presence of mulch reduced the model efficiency when simulated the water content in the 0–10 soil layer (EFF = 0.67 vs. 0.74 for NT and DT, respectively). Simulations highlighted for both treatments that the soil reached quite high water contents (~0.4 m^3 m^{-3}), mainly after rainfall events, which were

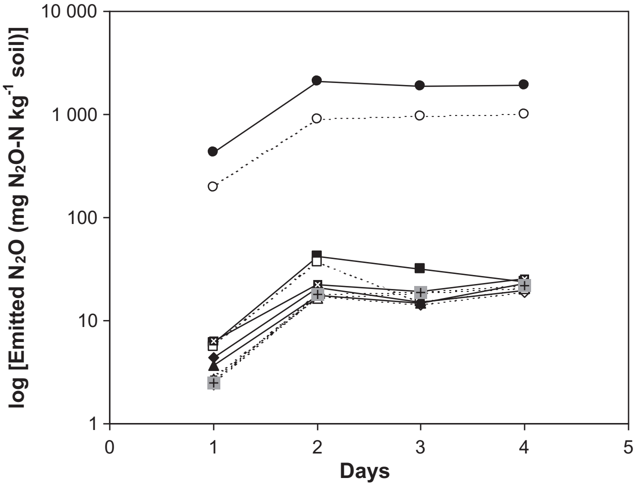

Fig. 1. N_2O production (mg N_2O-N kg^{-1} soil) from NT (black shapes; solid lines) and DT (white shapes; dashed lines) soils incubated in non-limiting N conditions at different WFPS levels (37%: square, 50%: diamond, 60%: triangle, 70%: shaped cross, 80%: circle). Note the log scale on the y axis.

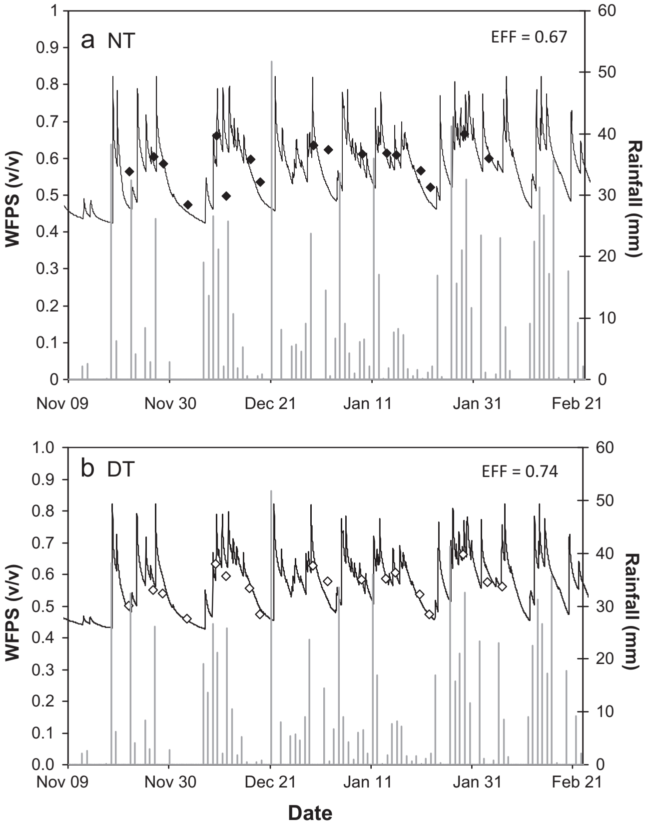

Fig. 2. Rainfall (mm) (grey vertical lines) and water-filled pore space (WFPS, v/v) of the 0–10 cm soil layer simulated (black line) and measured (diamonds) during the rainy season in the (a) no-till (NT) and (b) tillage (DT) treatments. EFF: model efficiency.

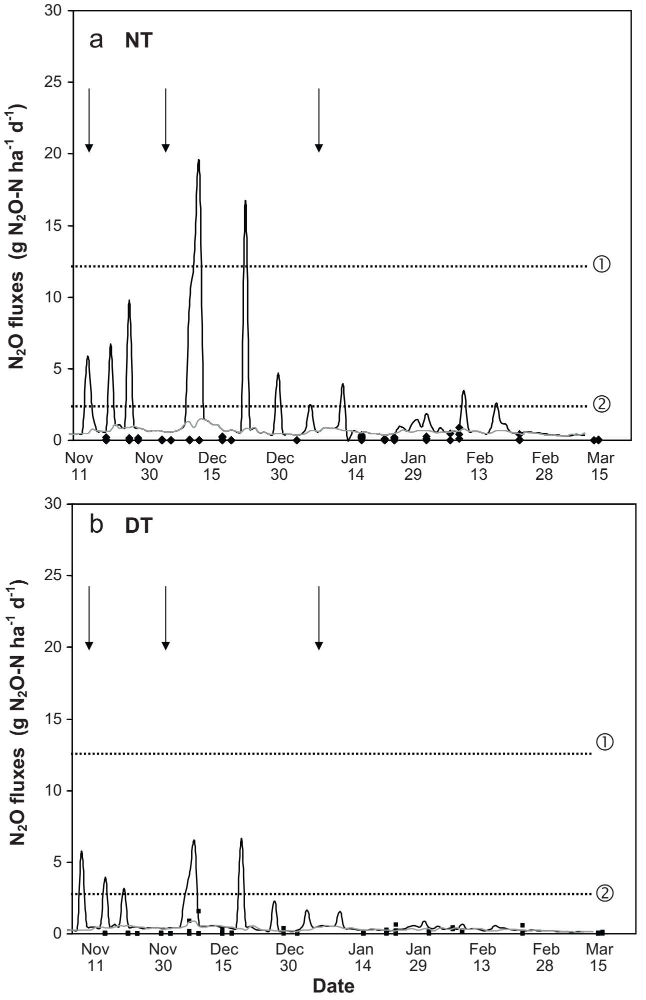

Fig. 3. Soil N_2O fluxes simulated with nitrification function only (grey line) and with both nitrification and denitrification (black line), and measured in no-till (black diamond) and tillage (black square) systems of Central Brazil. Each measurement represents the mean for 6 repetitions. The arrows indicate the fertilizer applications, and the horizontal dashed lines represent low (①) and very low (②) N_2O emissions levels according to Scheer et al. (2008).

not captured by discrete measurements (Fig. 2). The simulated soil water content was introduced in NOE to estimate the F_w and N_w functions at a 1-h time step. The WFPS threshold value ($WFPS_{th}$) was set at 0.7 to trigger denitrification in the NOE model. The PASTIS model revealed that, during the simulation period of 155 days, such moist conditions occurred only 4–6 h d^{-1} on 36 and 34 days for NT and DT systems respectively, and mainly at the end of the day after rainfalls or during the night while field measurements were scheduled in the morning.

3.3. N_2O fluxes simulated by NOE

The daily N_2O fluxes obtained from frequent and numerous field measurements (Metay et al., 2007b) ranged from 0 to 0.88 and 1.54 g N ha^{-1} d^{-1} in NT and DT systems respectively (Fig. 3). N_2O fluxes derived from nitrification in NOE model were in the same order of magnitude, ranging from 0 to 1.46 and to 0.9 g N ha^{-1} d^{-1} in NT and DT systems respectively (Fig. 3) while when denitrification was considered in the model the estimated total N_2O fluxes reached maximum values of 6.6 and 19.3 g N ha^{-1} d^{-1} in NT and DT systems respectively (Fig. 3) that largely exceeded the observed fluxes. Simulation by NOE suggested increases in N_2O fluxes after rainfall events and fertilizer applications that if occurred were not well captured by the discrete measurements (Fig. 3). Considering the whole cropping cycle (Table 5), nitrification calculated from NOE simulations accounted for 35% and 31% of the total N_2O fluxes in NT and DT systems respectively.

Table 5
Cumulative N_2O fluxes (g N ha^{-1}) from soil during the cropping season (155 days) estimated from field measurements and from NOE simulations in no-till (NT) and tillage (DT) systems.

	N_2O fluxes (g N ha^{-1})	
	NT	DT
Measured		
Total	9.3	13.9
Simulated		
Nit	88.9	47.2
Denit	123.1	84.7
Total (Nit + Denit)	212.0	131.9

4. Discussion

4.1. Soil sampling and limits of the approach

While intact soil cores were preferred in such determination, numerous studies on gas diffusivity and water transport have been based on repacked and structureless soil columns, which suffer from the flaw of not reflecting preferential transport/diffusion through macropores (Allaire et al., 2008). Sieving and breaking the physical mm-scale structure of the soil may effectively decrease the proportion of macropores and using repacked soil cores probably affects the proportion of the effective pore space for gas diffusion and water transport. However, the studied oxisols were well-drained, with a relatively uniform pore structure. These soils develop in subsurface layers a microstructure known as coffee powder (Empresa Brasileira de Pesquisa Agropecuaria, 1984). Although higher than in depth, the structural stability in the surface layer remains low enough to limit the biases due to sieving and repacking the soil cores. Moreover, aggregation larger than 2 mm in very limited in these soils. Therefore, we hypothesize that the repacking of the uniformly fine-structured soil in this study is not likely to deeply alter transport properties and the gas-exchange occurring within the intact soil cores. Keeping these limitations in mind, we consider that the bias was quite equivalent from a sample to another and that the use of repacked soil allows the comparison between treatments as long as the compaction was restored to the field-observed bulk density for each treatment.

4.2. Modelling or how to circumvent the limits of discrete measurements

Instantaneous N_2O fluxes measured in field using static chambers revealed very low N_2O fluxes when extrapolated on a daily basis (<1.6 g N ha^{-1} d^{-1}). Such low values were reported in other studies on tropical agricultural systems (e.g. Jantilia et al., 2008; Chapuis-Lardy et al., 2009) and are consistent with the conclusions of Yamulki et al. (2001) about the strong diurnal variations in N_2O fluxes with minimum fluxes generally occurring during the morning. At field scale, soil N_2O flux is characterized by an extreme spatial and temporal variability that would ideally require continuous monitoring during the year and spatially extensive measurement scheme (Folorunso and Rolston, 1984; Parkin, 1987; Mathieu et al., 2006). For practical and cost reasons, the experimental design is often limited to discrete measurements while resulting data are commonly used for calculating N_2O budget on larger temporal and spatial scales. Amongst the process-based models proposed to simulate fluctuations in N_2O fluxes and improve global estimates, NOE algorithm considered both nitrification and denitrification as N_2O-emitting pathways (Hénault and Germon, 2000). When nitrification was the only pathway considered in the model, the simulated N_2O data fitted quite well to the field measurements. When denitrification is triggered, the model suggested N_2O fluxes which, if really occurred, were poorly captured by discrete *in situ* measurements. The simulated N_2O fluxes by both nitrification and denitrification may be considered as low regarding thresholds reported in the literature (Bouwman et al., 2002; Scheer et al., 2008). Divergence in N_2O flux levels between measurements and simulations may be caused either by inadequate field measurements (sampling time in particular) or by uncertainties of the modelling approach.

4.3. WFPS: a key factor to simulate N_2O fluxes

The soil water content has a complex effect on N_2O-emitting pathways by controlling aeration, diffusion of substrate and microbial activity while WFPS is commonly considered as a determining factor in N_2O flux. Davidson (1991) suggests that N_2O fluxes by nitrification occur between 30 and 70% WFPS with a maximum at 50%, whereas N_2O fluxes by denitrification occur between 50 and 90% WFPS with a maximum at 70%. In addition, according to Davidson (1991) N_2 starts being emitted at 70% WFPS and is the main product of N gas emissions when soil moisture exceeds 75% WFPS. The main point of discussion concerning the validity of the water function F_W in various simulations in NOE model performed by Hénault et al. (2005) dealt with the WFPS threshold ($WFPS_{th}$) for an existing denitrification activity. These authors set 62% WFPS as the threshold default value in their model developed for medium-textured temperate soils. They also suggested that it could vary with soil texture and therefore be clearly site-specific. Heinen (2006) also showed that denitrification was highly sensitive to the WFPS threshold triggering denitrification, and that this parameter was dependent on soil type. The exponential form of the F_W induces a large variation of denitrification rate for a small variation in the soil water filled pore space. This implies that the $WFPS_{th}$ requires precise definition. Laboratory experiments showed that 70% WFPS was a clear trigger point for the production of N_2O by denitrification in our soils which was in good agreement with results from Hergoualc'h et al. (2007) for a tropical soil under coffee agroforestry plantation in Costa Rica. Such a value was also in the range extracted from a literature review by Lehuger et al. (2009). Thus, this value was used in place of the default model's threshold of 62% WFPS in our NOE simulation. We simulated soil water content at 1-h time step during the whole cropping period using PASTIS model parameterized with site-specific hydraulic properties. It provided a satisfactory estimation of water content dynamics in the soil profile. Simulated volumetric water content showed several peaks, some of which corresponded to WFPS up to 80% for NT and 83% for DT, respectively. While soil water contents were rarely high enough to favor N_2O production by denitrification (36 and 34 events for NT and DT respectively out of 155 days), these "denitrifying" conditions generally occurred at the end of the day or during the night. As field measurements were realized on each occasion during the morning, N_2O potentially emitted during these time-periods was systematically not captured by the discrete measurements and not taken into account in the calculation of N_2O fluxes on a daily basis by extrapolation of field measured data.

4.4. Laboratory determination of N_2O potential of emissions to calibrate the model

We also tried to minimise uncertainties due to the modelling approach by an efficient and site-specific parameterization which was determined in laboratory experiments. According to Garrido et al. (2002), nitrification rates estimations are based on the study of $NO_3{}^-$ production in non-limiting $NH_4{}^+$ conditions for various WFPS. In our study, maximum nitrification rate was obtained for a WFPS close to 45% while Linn and Doran (1984) found that nitrification occurred for WFPS ranging between 10 and 80% with a maximum at 60%. Potentials of nitrification were significantly higher for NT than for DT (2.16 vs. 0.92 mg N kg^{-1} d^{-1}). While mineral N was larger in NT than in DT soils microbial biomass was probably more active under systems NT than under DT (Rabary et al., 2008; Sparrow et al., 2006). De Boer and Kowalchuk (2001) proposed that autotrophic nitrification was possibly restricted to pH-neutral micro-sites in acid soils. While these values were lower than those reported by Hergoualc'h et al., 2009 for Costa-Rican soils or by Garrido et al. (2002) for temperate soils, it was in good agreement with the low N_2O fluxes simulated by nitrification or measured in the field. The proportion of nitrified N emitted as N_2O were lower than the range of 0.5–0.9‰ reported by Hénault et al. (2005) for temperate soils or by Hergoualc'h et al., 2009 for tropical soils in Costa-Rica. The potential denitrification rate (D_P) was similar in both treatments (NT vs. DT), circa 1 kg N ha^{-1} d^{-1}. Low values were also observed in soils from other tropical agricultural systems, such as in Puerto Rico (Hénault et al., 2005), Costa-Rica (Hergoualc'h et al., 2009) and Madagascar (Chapuis-Lardy et al., 2009) while temperate soils commonly exhibited potentials larger than 5 kg N ha^{-1} d^{-1} (Hénault and Germon, 2000). In a literature review, Barton et al. (1999) reported that in 85% of the cultivated soils they examined denitrification potentials were higher than 1 kg N ha^{-1} yr^{-1}, with an average value of 13 kg N ha^{-1} yr^{-1}. As availability of organic labile compounds is a key factor in denitrification (e.g. Williams et al., 1999; Granli and Bøckman, 1994), the low C contents in our soils may limit microbial activity and explain these low rates. Soil acidity and probable P deficiency as commonly observed in Brazilian Oxisols (Chapuis-Lardy et al., 2002) may also impact soil microbial processes. These physiochemical conditions were implicitly taken into account by the virtue of the site-specificity of the model parameterization. The proportion of denitrified N emitted as N_2O (r_{max}) showed that N_2O can be reduced to N_2 in the studied soils while elsewhere in more acidic soils this capacity was limited (Hénault et al., 2001; Hergoualc'h et al., 2009). Potential key controls such as structure and activity of denitrifying communities still require further investigations (Baudoin et al., 2009). This capacity along with limited denitrification potentials may explain the weakness of simulated N_2O fluxes which can be considered as low regarding literature reports (Bouwman et al., 2002; Scheer et al., 2008).

4.5. Specificity and heterogeneity of the soil to produce N_2O

The relationship between the nitrification and denitrification rates and the N_2O evolution in soil is not straightforward, and the contribution of both pathways to N_2O fluxes is highly dependent on soil conditions such as availability of a mineral N source (substrate for nitrification or denitrification), and on soil temperature, soil water content, and (for denitrification) the availability of labile organic compounds (e.g. Granli and Bøckman, 1994; Skiba and Smith, 2000). These observations underlined the importance of site-specificity in NOE model parameterization. Nitrification and denitrification processes may occur simultaneously in different microsites of the same soil (Stevens et al., 1997) but there is often uncertainty associated with which process is predominantly contributing to emissions from a particular soil. Nitrification is a relatively constant process in soils, whereas denitrification acts with high time and space fluctuations. Nitrification is the predominant process contributing to N_2O fluxes at WFPS from 35 to 60% (Bateman and Baggs, 2005; Gilliam et al., 2010). At higher water contents, N_2O fluxes are much greater in magnitude and are associated primarily with the denitrification process (Bateman and Baggs, 2005). As various studies underlined high denitrification activity in 'hot spots' created by decomposing organic matter which generated anaerobic microsites, our simulation revealed larger N_2O fluxes in no-till situations with mulch at the soil surface (NT) than under tillage treatment (DT). Considering the whole cropping season, the relative proportion of nitrification calculated from NOE simulations accounted for 35 and 31% for NT and DT, respectively (data not shown). These results confirmed those obtained by Hénault et al. (2005) from simulation in Puerto Rico soils and by Hergoualc'h et al. (2007) in Costa Rica soils. The use of urea as N-fertilizer in our soils may explain the contribution level of nitrification to N_2O flux (Bremmer, 1997).

5. Conclusions

The approach we proposed in this study, which consisted in continuous simulations of WFPS using the water transfer model PASTIS to implement the NOE model and simulate the N_2O fluxes derived from both denitrification and nitrification pathways brought complementary information to field approach and potentially improved assessment of N_2O budget. As the studied soil is well-aerated, this result is in agreement with the conclusions of Rochette (2008) who stated that N_2O fluxes only counterbalance no-till positive effects on carbon sequestration (Metay et al., 2007a) in case of poorly-fine-textured agricultural soils in regions with a humid climate. Further studies, especially in case of soils with a well-marked structural profile should address these specific methodological points by (i) using intact soil cores to prevent errors in estimating nitrification and denitrification potentials (Booth et al., 2006); (ii) testing the interest in having vertical soil sampling design to parameterize the model and better estimating the gas emissions occurring at soil surface and (iii) considering both the spatial heterogeneity of soil and the chambers position on the field prior to sampling soil cores for laboratory determination. It would also be interesting to look further into such approaches to improve data sets on N_2O fluxes under tropics with specific attention paid to soil water content estimation in these soils and its consequences on N_2O fluxes. In particular, the reasons for such low N_2O fluxes, the possible soil sink for N_2O (Chapuis-Lardy et al., 2007) and the consequences of straw mulch on a possible reduction of greenhouse gas emissions (Xu et al., 2003) are to be investigated. Further research efforts should also address validations of model and the potential development of a "tropical version" of NOE (Hénault et al., 2005; Hergoualc'h et al., 2009) that integrates the specificity of N cycle and soil organic matter decomposition under tropical climate (Abbadie and Lensi, 1990; Six et al., 2002).

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