

**Biogenic NO
emissions from soils
in a Sahelian
rangeland**

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Modelling the effect of soil moisture and organic matter degradation on biogenic NO emissions from soils in Sahel rangeland (Mali)

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Abstract

This work is an attempt to provide seasonal variation of biogenic NO emission fluxes in a sahelian rangeland in Mali (Agoufou, 15.34° N, 1.48° W) for years 2004–2008. Indeed, NO is one of the most important precursor for tropospheric ozone, and the contribution of the Sahel region in emitting NO is no more considered as negligible. The link between NO production in the soil and NO release to the atmosphere is investigated in this study, by taking into account vegetation litter production and degradation, microbial processes in the soil, emission fluxes, and environmental variables influencing these processes, using a coupled vegetation-litter decomposition-emission model. This model includes the Sahelian-Transpiration-Evaporation-Productivity (STEP) model for the simulation of herbaceous, tree leaf and fecal masses, the GENDEC model (GENERAL DEComposition) for the simulation of the buried litter decomposition and microbial dynamics, and the NO emission model (NOFlux) for the simulation of the NO release to the atmosphere. Physical parameters (soil moisture and temperature, wind speed, sand percentage) which affect substrate diffusion and oxygen supply in the soil and influence the microbial activity, and biogeochemical parameters (pH and fertilization rate related to N content) are necessary to simulate the NO flux. The reliability of the simulated parameters is checked, in order to assess the robustness of the simulated NO flux. Simulated yearly average of NO flux ranges from 0.66 to 0.96 kg(N) ha⁻¹ yr⁻¹, and wet season average ranges from 1.06 to 1.73 kg(N) ha⁻¹ yr⁻¹. These results are in the same order as previous measurements made in several sites where the vegetation and the soil are comparable to the ones in Agoufou. This coupled vegetation-litter decomposition-emission model could be generalized at the scale of the Sahel region, and provide information where little data is available.

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1 Introduction

In the continental biosphere, most of the N cycle is accomplished through internal processes such as mineralization/assimilation, because N is mostly assimilated in the biosphere from its mineral form (nitrates NO_3^- , ammonium NH_4^+). In natural soils, these compounds come from the mineralization of organic matter through the bacterial and fungal decomposition of dead matter. N cycle in the soil is dominated by microbial transformations. Bacterial processes involve important reactive gaseous components, e.g. NO formation through nitrification and denitrification (Delmas et al., 1995). A significant fraction of these compounds can be released to the atmosphere. NO is one of the most important precursor for tropospheric ozone, and participates to the formation of nitric oxide, participating in N deposition. NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) are also involved in the abundance of the hydroxyl radical (OH) which determines the lifetime of some pollutants and greenhouse gases (Fowler et al., 2009).

Atmospheric NO_x is coupled to the earth's nitrogen cycle through complex interactions involving soil microbial activity, soil N content and N inputs to the soil, either from anthropogenic or atmospheric origin (Hudman et al., 2012; Parton et al., 2001). The processes of NO production and consumption in the soil have been studied through modelling, laboratory or field studies by several authors (Butterbach-Bahl et al., 2004a; Schindblacher et al., 2004; Li et al., 2000) for different types of soils and climates (Butterbach-Bahl et al., 2009, and Kesik et al., 2005 for european soils, Feig et al., 2008 and Meixner et al., 1997 for tropical soils as examples). A difference has to be defined between NO production in the soil and NO emission (release) to the atmosphere. NO emission to the atmosphere might deviate significantly from the production of NO in soil. Several biotic and abiotic processes in soils and plants are responsible for the production and consumption of NO (Galbally and Johansson, 1989; Conrad, 1996). Microbial nitrification and denitrification constitute the principal processes (Ludwig et al., 2001). According to McCalley and Sparks (2008) and references therein, fluxes are regulated by factors that include the concentration of

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inorganic N (NO_3^- and NH_4^+), soil moisture, temperature, accessibility of labile C, and physical soil properties. Most of the trace gas production and consumption processes in soil are probably due to microorganisms. Oxidation of NO to nitrate has been found to be the dominant NO consumption mechanism in some soils (Conrad, 1996 and references therein). Release rates of NO can be much lower than the NO production rates, since NO consumption is of similar magnitude to NO production. NO shows both high and variable production and consumption rates in soil and consequently highly dynamic compensation points (Conrad, 1996). The concept of the compensation concentration is based on the observation that production and consumption of a trace gas occur simultaneously in a soil and that the consumption rate is a function of the trace gas concentration, whereas the production rate is not (Conrad, 1994). According to Ludwig et al. (2001), the net exchange of NO between ecosystems and the atmosphere is globally dominated by biogenic emissions of NO from soils. Only at exceptionally high ambient NO concentration, direct deposition to plants might constitute a significant removal mechanism for atmospheric NO (Ludwig et al., 2001).

NO release in arid and semi arid soils are mainly governed by pulse events, produced when first precipitations shower long-dried soils at the beginning of the rainy season. Several studies have shown that pulse emissions of NO contribute strongly to the total emission (Yan et al., 2005; Hudman et al., 2010; Jaeglé et al., 2004; Kim et al., 2012), specifically in semi arid regions. In those regions, mineral and organic substrates tend to accumulate at the soil surface and in the soil during the long dry season, when there is little nutrient demand, leading to an excess of mineralization during the early phases of the wet cycle (Schwinning et al., 2004).

At the global scale, NO emissions from soils have been estimated to be approximately 21 Tg(N) yr^{-1} (Davidson and Kinglerlee, 1997) at the ground level (below canopy), a portion of the NO_2 being deposited within the canopy. Above canopy emissions were estimated to be $5.45 \text{ Tg(N) yr}^{-1}$ by one of the first global modelling study on the subject (Yienger and Levy, 1995), and more recently up to $8.6 \text{ Tg(N) yr}^{-1}$ (Steinkamp and Lawrence, 2011) and $10.7 \text{ Tg(N) yr}^{-1}$ (Hudman et al., 2012). Above

al., 2009). The area is used as livestock grazing under communal access. Because of the proximity of the Agoufou permanent pond, the grazing pressure is high during the dry season. Agoufou can be considered as representative of sahelian dry savannas. A comprehensive description of the site can be found in Mougin et al. (2009).

2.1 Meteorological and vegetation data

At the Agoufou site, woody and herbaceous plant density and species composition are organised in facieses following finer topography and soils nuances or differences in land use practices and histories (Hiernaux and Le Houérou, 2006). The herbaceous layer has been monitored using a two-level stratified random sampling design, as described in Hiernaux et al. (2009). Total and green vegetation cover (visual and digital photograph estimates in %, Mougin et al., 2014), standing and litter mass (destructive measure, with harvest, air drying and weighing) and species composition (list with visual estimates of contribution to bulk) are assessed in 1 m × 1 m plots randomly sampled in each of the vegetated strata along the transect. Above ground green and dry masses and surface litter mass have been sampled during several years, but only the years 2004–2008 are used in this study to evaluate the performance of the model. Indeed, these years represent contrasted meteorological conditions, with low rainfall years (2004 and 2008) and years with normal rainfall for the region (2005–2007). Furthermore, vegetation data are more numerous during these years, when the AMMA experiment took place in West Africa.

A meteorological station has been installed from 2002 to 2010, giving data on rainfall, wind speed, relative humidity, air temperature and global radiation. These data were quality checked and gap filled for the years 2004 to 2008 only. Data on soil moisture at different levels and different places (top, middle and bottom locations of dune slope), and soil temperatures at different levels are also available, except for year 2004. A detailed description of the soil moisture network and methodology and of the meteorological station is given in De Rosnay et al. (2009) and Mougin et al. (2009). Meteorological data and a part of vegetation data are available in the AMMA data

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base: <http://bd.amma-catch.org/amma-catch2/main.jsf>. Other data are progressively integrated in this data base.

2.2 Calculation of NO flux

NO flux were determined at Agoufou during summers 2004 and 2005, from closed dynamic chambers (flowed-through-non-steady-state) measurements. Stainless steel chambers of 800 cm² area (40 × 20) and 18 cm height were used. A stainless steel frame is inserted into the ground before the measurement which starts when adjusting the chamber on the frame, sealing being assured by a slot filled with water. The air inlet is on one side of the chamber, the air outlet on the other side is connected to the analyser with two meters of Teflon tubing, so that the chamber is swept with an air flow only due to the pump of the instrument. The residence time of the air inside the chamber is approximately 10 min. No significant change in air temperature in the chamber has to be noticed during this lapse time. Pressure is assumed to be constant throughout the flux measurement and equal to ambient pressure. Stainless steel is known to be quasi inert to NO, as well as Teflon for tubing, ensuring that NO does not react with the walls of the chamber (Laville et al., 2011). This method has been widely used in the field, as reported for example in Davidson (1991), Serça et al. (1994, 1998), Jambert et al. (1997), Scholes et al. (1997), Laville et al. (2011).

Several different places at the site of Agoufou have been sampled. In June–July 2004, 180 fluxes were sampled. The chambers were placed on the soil, 90 with short vegetation inside, 90 over bare soil. In August 2005, 70 fluxes were sampled, mostly over vegetation, the whole site being covered by vegetation in the core of the wet season. Fluxes were sampled every day between 30 June and 12 July 2004 and between 11 and 13 August 2005, in the morning and in the afternoon, and daily means were calculated and plotted in Fig. 6b. SDs are indicated on the plot, showing the spatial heterogeneity of fluxes at the same site.

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The net flux is calculated from the slope of the increase of concentration within the chamber.

$$F = \left(\frac{dC[\text{NO}]}{dt} \right) \left(\frac{VMN}{SRT} \right) \quad (1)$$

$\frac{dC[\text{NO}]}{dt}$ is the initial rate of increase in NO concentration calculated by linear regression (ppb s⁻¹), MN is the nitrogen molecular weight (g mol⁻¹), $S = 800 \text{ cm}^2$ is the surface of the chamber, $V = 18 \text{ L}$ is the volume of the chamber, $R = 0.082 \text{ cm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$ is the gas constant, $T(\text{K})$ is the air temperature in the chamber, F is the resulting flux in ng(N) m⁻² s⁻¹ (Serça et al., 1994).

NO concentration in the chamber was measured using a ThermoEnvironment 42 CTL analyser. This analyser detects NO by chemiluminescence with O₃. Detection limit and sensitivity is around 0.05 ppbv. Flow rate in the analyser and the chamber is about 0.8 L min⁻¹. Multipoint calibration was checked before and after each field experiment with a dynamical calibration system.

The NO flux rate was computed from the slope of the initial linear increase in NO concentration in the chamber, following Davidson (1991) and Serça et al. (1994).

The magnitude of zone concentrations is around 20 ppb in July, NO₂ concentrations around 2.5 ppb (Adon et al., 2010), and NO₂ deposition velocity was estimated to be 0.13 cm s⁻¹ (Adon et al., 2013; Delon et al., 2010) at the Agoufou site. NO ambient concentrations during the 2004 field campaign were 0.60 ± 0.57 ppb (information not available for the 2005 field campaign). The NO flux is underestimated if neither deposition nor conversion to NO₂ through reaction with O₃ is taken into account, but the underestimation should be limited considering the low ozone concentrations and low NO₂ deposition velocities. Laville et al. (2011) show that artefacts can be introduced when NO concentrations are high (up to 60 ppb). In our case, NO concentrations are much lower than the values indicated by these authors. Other studies such as Schindblacher et al. (2004) did not consider reactions with ozone either because ozone concentrations were low.

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Unfortunately, it is not possible to precisely recalculate the underestimation of NO flux in our study since NO₂ concentrations measured by the 42C are not available anymore. However, following Laville et al. (2011) and Pape et al. (2009), we have calculated the underestimation with the mean climatological ozone concentration found in Adon et al. (2010), which is 20 ppb in July, with $k = 5.32 \times 10^{-4} \text{ ppb}^{-1} \text{ s}^{-1}$ (reaction rate constant at 1013 hPa and 313 K, estimated pressure and temperature in the chamber), and with the mean NO concentration 0.6 ppb obtained with the field measurements in 2004. The mean underestimation ($k \cdot [\text{NO}] \cdot [\text{O}_3] = 5.32 \times 10^{-4} \cdot 20 \cdot 0.6 = 0.0064 \text{ ppbs}^{-1}$) is 7.6 % of the mean slope (0.0847 ppbs^{-1} , obtained from Eq. 1). The mean under estimation is therefore estimated at 7.6 %.

During summer 2004 (from 30 June to 12 July), NO daily fluxes ranged from 0.78 to 3.58 kg(N)ha⁻¹yr⁻¹ (mean = $2.11 \pm 0.77 \text{ kg(N)ha}^{-1} \text{ yr}^{-1}$, Delon et al., 2007). During summer 2005 (from 11 to 13 August), NO fluxes ranged from 0.57 to 1.01 kg(N)ha⁻¹yr⁻¹ (mean = $0.72 \pm 0.25 \text{ kg(N)ha}^{-1} \text{ yr}^{-1}$, unpublished data). In the following simulations, NO fluxes were not measured at Agoufou during years 2006 to 2008. However, since NO flux data are scarce, these field measurements from 2004 and 2005 will be helpful to give an order of magnitude of NO emission at the beginning and during the wet season.

3 Model description

3.1 Modelling approach

Biogeochemically based model of instantaneous trace gas production can be parameterized for individual sites, describing locally nitrification and denitrification processes responsible for emission, but more generalized models are needed for the calculation of temporally or regionally integrated models (Potter et al., 1996). In that purpose, a new approach for the calculation of biogenic NO emissions from soils has been developed by Delon et al. (2007), in order to use general environmental

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parameters easily available as inputs. This approach was used at the regional scale to simulate pulse events in the Sahel (Delon et al., 2008) and at the yearly scale at several Sahelian sites (Delon et al., 2010; Laouali et al., 2012). This approach has been partly inspired by the hole-in-the-pipe (HIP) concept, developed by Firestone and Davidson (1989), presenting the environmental parameters which control the variation of trace-N-gases by nitrification and denitrification with different levels of regulation, from proximal (e.g. mineralization, immobilization, respiration, plant uptake) to distal (e.g. pH, soil porosity, soil type). Using two functions based on soil N availability and soil water content, the HIP model characterizes a large fraction of the observed variation of NO emissions from soils (Davidson et al., 2000).

The NO emission model will be described in the following sections. In its previous version, (Delon et al., 2010), the N availability in the soil was driven by the N input at the surface (organic and livestock fertilisation) and considered constant in time (a similar amount of N was injected each month). In the new version, the N in the soil is calculated from buried litter (vegetation and feces) decomposition and varies in time, thanks to the coupling with the other models which provide vegetation and organic matter in a dynamic way. The N input used to calculate the NO flux is therefore more realistic than in the previous version where it was prescribed without any link with vegetation growth and decay. The link between vegetation, litter decomposition, microbial dynamics in the soil and NO emission is explained in the following sections.

The on line coupled models are presented here and used at the daily scale: the herbaceous and tree leaf masses are simulated using the Sahelian-Transpiration-Evaporation-Productivity (STEP) model (Mougin et al., 1995), the buried litter decomposition and microbial dynamics is simulated in GENDEC (Moorhead and Reynolds, 1991), and the NO release to the atmosphere is simulated with the NOFlux model (Delon et al., 2007).

A schematic view of the model imbrications is given in Fig. 1. Inputs for each model are detailed in Table 1.

3.2 STEP

STEP is an ecosystem process model for sahelian herbaceous vegetation. In its current version, tree phenology (leaf mass set-up and fall) is also described by considering six phenological types which proportions must be known. This model is defined to be used at local or regional scale in order to simulate the temporal variation of the main parameters and processes associated with vegetation functioning in sahelian savannas. In this study, the model will be used at the local scale. In previous studies, STEP has been coupled to radiative transfer models in the optical (Lo Seen et al., 1995) and active/passive microwave domain (Frison et al., 1998), allowing an indirect comparison of satellite observations and modeling results of the vegetation growth (e.g. Jarlan et al., 2002). The performance of the STEP process model in predicting herbage mass variation over time and herbage yield along a north-south bio-climatic gradient within the Sahel was tested along a 15 years period, and gave high correlation coefficients between model and measurements when the model is calibrated for each site (Tracol et al., 2006). Modifications brought to the first version of the model have been given in Jarlan et al. (2008). A recent regional scale use of the model is illustrated in Pierre et al. (2012).

STEP is driven by daily standard meteorological data obtained from site measurements in Agoufou (precipitations, global radiation, air temperature, relative humidity and wind speed), prepared for years 2004 to 2008. Site specific parameters like sand and clay percentage, pH, C3/C4 percentage, initial green biomass, initial dry biomass and initial litter, number of soil layers, initial water content in each layer, livestock composition (between 6 different categories, cattle, sheep, goats, donkeys, horses, camels) and livestock total load are given as input parameters (see Table 1). The seasonal dynamics of the herbaceous layer, major component of the Sahelian vegetation, is represented. The processes simulated are: water fluxes in the soil, evaporation from bare soil, transpiration of the vegetation, photosynthesis, respiration, senescence, litter production, and litter decomposition at the soil surface.

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input to the soil).

$$\text{NOfluxnorm} = w_{24} + w_{25} \tanh(S1) + w_{26} \tanh(S2) + w_{27} \tanh(S3)$$

Where NOfluxnorm is the normalized NO flux. The normalization is used for all inputs and output to give them the same order of magnitude and facilitate the calculation process (Delon et al., 2007).

$$S1 = w_0 + \sum_{i=1}^7 w_i X_{j,\text{norm}}$$

$$S2 = w_8 + \sum_{i=9}^{15} w_i X_{j,\text{norm}}$$

$$S3 = w_{16} + \sum_{i=17}^{23} w_i X_{j,\text{norm}}$$

j is 1 to 7, $X_{1,\text{norm}}$ to $X_{7,\text{norm}}$ correspond to the seven normalized inputs, as follows:

$$j = 1: X_{1,\text{norm}} = c_1 + c_2 \times (\text{surface soil temperature}),$$

$$j = 2: X_{2,\text{norm}} = c_3 + c_4 \times (\text{surface WFPS}),$$

$$j = 3: X_{3,\text{norm}} = c_5 + c_6 \times (\text{deep soil temperature}),$$

$$j = 4: X_{4,\text{norm}} = c_7 + c_8 \times (\text{fertilisation rate}),$$

$$j = 5: X_{5,\text{norm}} = c_9 + c_{10} \times (\text{sand percentage}),$$

$$j = 6: X_{6,\text{norm}} = c_{11} + c_{12} \times \text{pH},$$

$$j = 7: X_{7,\text{norm}} = c_{13} + c_{14} \times (\text{wind speed}).$$

Weights w and normalisation coefficients c are given in Table 2.

WFPS = Water Filled Pore Space.

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The resulting NO flux is obtained after de-normalization of NOfluxnorm ($\text{NOFlux} = x_{15} + x_{16} \times \text{NOfluxnorm}$).

A CRF is applied to the NO flux. The CRF ranges between 1 (no reduction because no vegetation, LAI = 0) and 0.83 (LAI = 1.8 at the most, Mougin et al., 2014).

Considering the CRF applied, the maximum quantity of N re-deposited above canopy during the wet months when LAI is at its maximum is negligible compared to the total N input from fecal, herbal and root masses. Indeed, the proportion of N re-deposition compared to total N input ranges between 0.24 and 1.5 %, depending on the year.

In this study, we use a new approach to calculate the fertilization rate (this input was given as constant in the previous versions of the algorithm). This approach is based on the one of Potter et al. (1996), who have developed an extended version of the CASA (Carnegie Ames Stanford) model, where potential emission of total nitrogen trace gases ($\text{N}_T = \text{NO} + \text{NO}_2 + \text{N}_2\text{O} + \text{N}_2$) at the soil surface is treated as a given percentage (2 %) of gross mineralized nitrogen at any given time step (this corresponds to the definition of the emission factor). This version of the simple conceptual model is not designed to distinguish between nitrification and denitrification as sources of N gases. In order to adapt this approach to our own study, we made the assumption that the sandy soil texture in Agoufou favours predominantly aerobic conditions and subsequently nitrification processes (Li et al., 2000; Blagodatsky et al., 2011). Furthermore, the WFPS remains below 20 % (volumetric soil moisture below 10 %), and according to Davidson (1991) the total oxidized N emitted would be composed of 95 to 100 % of NO.

In the present work, we have adapted the concept developed in CASA in a different way: the fertilization rate (i.e. N entering the soil and further available for NO emission) is 2 % (same percentage as in Potter et al., 1996) of the mineral N content in the soil (which depends both on N input and N content). The mineral N is obtained from STEP-GENDEC calculations. The main difference between Potter et al. (1996) approach and the one of this study is that the NO emission is now modulated by additional parameters such as pH and wind speed, as well as soil moisture and temperature which have an

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5 impact on both mineralization and emission. When soil moisture is too low, microbial
respiration is blocked in the model, microbial dynamics is frozen, and mineralization
is stopped. If the value of mineral N is 0, a minimum value of 0.01 g m^{-2} is applied as
a first guess in the NOFlux model to avoid null values of NO emission. Indeed, very little
15 is known about mineral N dynamics and subsequent NO emission at low soil moisture,
but experimental studies show low emission even during the dry season (Scholes et
al., 1997).

The principal advantage of this NO parameterization is to depend on different factors
at two levels. The first level concerns climatic impacts and environmental parameters,
10 such as precipitations, soil texture and pH, temperatures, wind speed, and the second
level concerns intrinsic processes of N turnover in the soil, through the organic matter
degradation from vegetation and livestock, and the microbial dynamics. The majority
of the first level variables are easily available on site or/and from atmospheric model
reanalysis and global databases, the second level is a sophistication of the model,
15 making it possible to add biotic processes in this parameterization of NO emission.

4 Results and discussion

Several parameters, included in the NO emission model, play an important role in
modulating emission. These parameters can be classified in two categories: physical
parameters (soil moisture and temperature, wind speed, sand percentage) which affect
20 substrate diffusion and oxygen supply in the soil and influence the microbial activity
(Skopp et al., 1990), and biogeochemical parameters (pH and fertilization rate related
to N content). In this paragraph, we will discuss the reliability of the simulated variables,
in order to assess the robustness of the simulated NO flux.

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4.1 Soil moisture

Soil moisture has a strong influence on NO emission from soils, particularly in hot and dry regions, as reported in the literature until today from studies at the global, regional, or local scale (Williams et al., 1992; Yienger and Levy, 1995; Meixner et al., 1997; Hartley and Schlesinger, 2000; Yan et al., 2005; Feig et al., 2008; Hudman et al., 2012). This variable needs to be well reproduced by the model in order to calculate reliable NO release. Volumetric soil moisture is calculated by STEP at different soil layers, using a tipping bucket approach. Figure 2 shows the volumetric soil moisture calculated by STEP between 0 and 2 cm from 2004 to 2008, compared to the volumetric soil moisture measured at Agoufou at 5 cm depth in 2005–2008. From 2006 to 2008, these measurements are actually an average of 3 datasets from soil moisture probes operating at the top, middle and bottom locations of dune slopes. In 2005, only bottom slope data were available.

The comparison between STEP and measurements in Fig. 2 is not direct, because depths are not exactly equivalent. Indeed, it is in general quite difficult to have in situ soil moisture measurements in the very first soil centimetres especially over sandy soils. Despite this, the comparison gives satisfying results from 2005 to 2008. In the surface layer, the measurements reach 10 to 12% during summers and show lower values during the dry season than those calculated by STEP. A threshold at 8% is observed on the STEP plot. This value corresponds to the field capacity calculated by STEP. In reality, this theoretical value may be overstepped, and water is not systematically transferred to the layer underneath. In the model, when the field capacity is reached, the excess water is transferred to the second layer, between 2 and 30 cm. The higher soil moisture peaks observed in the measurements as compared to STEP may be also due to the deeper soil depth at which the measurements are taken. For all years, the model is consistent and correctly reproduces the temporal dynamics, the increase and decrease of the soil moisture are well in phase, and the filling and emptying of the

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rainfall, and starts again later in the season. The maximum simulated green biomass value seems to be slightly late in 2006 and 2007, and early in 2008, compared to measurements, whereas the seedling emergence is correctly simulated for these three years. In 2008, the quantity of precipitation is lower, but the soil moisture is sufficient to trigger seedling emergence in the model. Overall, simulations and measurements are in good agreement with $R^2 = 0.72$ for green biomass for the five years.

The change over time of the herbaceous standing mass is driven by mechanical and biological degradation, influenced, among other causes, by livestock grazing. Forage consumption and trampling by livestock have major effects on herbage offtake, decay and decomposition including seed dispersal (Tracol et al., 2006). The STEP model allows the drying from green to dry standing biomass, and the degradation of the dry biomass by livestock. The minimum value for the initialization of dry standing biomass in 2004 is $10 \text{ g(d.m.) m}^{-2}$. The increase of the senescent aboveground biomass at the end of the wet season is well reproduced by the simulation (light blue in Fig. 4). R^2 between simulations and measurements is 0.56 for dry standing biomass for the five years of simulation. The maximum of dry standing biomass is underestimated in 2006 and 2008 and well reproduced in 2004 (despite a particular feature) and 2007. No measurements were available for year 2005.

The minimum value for the initialization of the surface litter in 2004 (red in Fig. 4) is $30 \text{ g(d.m.) m}^{-2}$. The maximum value is encountered in December–January (end of november in 2004). Litter decay is sharper in the measurements than in the simulation, with minimum occurring in the middle of the wet season. R^2 between simulations and measurements is 0.5 for litter for the five years of simulation.

The evolution of simulated buried litter (dark blue in Fig. 4) is closely linked to that of surface litter. The first days of rain induce a sharp decrease of buried litter, which is rapidly decomposed. The minimum is observed in september (August in 2004), when it begins to increase again with the surface litter accumulation. That accumulation feeds the C and N pools, and is the N resource for soil mineral N and N losses to the atmosphere.

a comparison, Butterbach-Bahl et al. (2004b) found average fluxes of $18 \text{ kg(N) ha}^{-1} \text{ yr}^{-1}$ in tropical forests soils at the transition between dry and wet season, where the quantity of decomposed litter is far greater than in dry savanna sites of the Sahel, and where the nutrient content of the soil is far larger, since semi arid soils are generally nutrient poor.

The ratios of fluxes from wet to dry seasons in this study are 2.3, 2.9, 3.0, 3.1 and 3.0 respectively for the years 2004–2008, in the (lower) range of what has been reported in the literature (Meixner and Yang, 2006), but showing undoubtedly the difference between the two periods in terms of emission.

4.5.2 Sensitivity tests

Several sensitivity tests have been performed in the NOFlux model to highlight the effects of soil temperature, soil humidity, and mineral N content on the NO flux to the atmosphere. The sensitivity of NO emission to deep soil temperature and wind speed will not be shown here, because their influence on NO emission is less important. In the first example (Fig. 8), soil moisture is set successively to a low (2%) and a high (10%) value, associated respectively to a low (0.01 gm^{-2}) and a high (0.1 gm^{-2}) value of mineral N content in the soil. The associated high and low values of mineral N with soil moisture have been chosen according to realistic outputs given by the GENDEC model (see Fig. 7), and corresponding to dry and wet season quantities. The results are shown for year 2006 only, to lighten the figures, because 2006 is a standard year in terms of pluviometry, and the same conclusions would appear anyway for the other years. When soil moisture is low and constant (associated to low and constant mineral N content), NO fluxes are only driven by soil temperature at high (diurnal) frequency. Pulses usually linked to soil moisture variation do not occur and the mean value of the flux remains low. When soil moisture is high (associated to a high value of mineral N content), the mean value of the flux is larger, directly resulting from high mineral N content. The seasonal cycle of fluxes is not correlated to the seasonal cycle of soil

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temperature, as already found by Meixner and Yang (2006) (low frequency variation), whereas their diurnal cycle are correlated, in accordance with previous studies. As an example, Ludwig et al. (2001) have stated that soil temperature fluctuations can explain short term variations of NO fluxes.

In the second example (Fig. 9), soil moisture and mineral N content are not forced, soil surface and bottom temperatures are set successively to both a low (33 and 32 °C respectively) and a high (48 and 47 °C respectively) value, for the year 2006. These temperatures correspond to possible values encountered during the dry and wet seasons. At the beginning of the year, during the dry season, the soil moisture is low, and fluxes are constant if soil temperature is constant. During both seasons, the lowest NO fluxes are found for the highest values of soil temperature, even if differences are reduced between mean annual fluxes (1.08 vs. 0.69 kg(N) ha⁻¹ yr⁻¹ for $T = 33$ and $T = 48$ °C respectively) despite a large temperature difference (15 °C). Temperature effect on NO emissions has been studied in other circumstances, and is still under debate still no clear conclusion could be raised. Contrasted results have been found in tropical and temperate regions: most studies have shown that NO emissions increase with increasing temperature as reported for example in Martin et al. (1995), Meixner and Yang (2006), and Van Dijk and Meixner (2001), other studies do not find any clear tendency (Cardenas et al., 1994; Sullivan, 1996), while Butterbach-Bahl et al. (2004b) find a linear relationship during only certain periods of the year in a tropical rain forest. Temperature effect in our study is moderate in dry season, and almost not visible in wet season.

In addition, soil pH effects have also been tested (not shown here), within a reasonable range of pH from 6.1 to 8. Pulse effects and modulation by soil temperature present the same feature as in the reference case, with a slight decrease of the base level when pH increases. Serça et al. (1994) and Yan et al. (2005) have also found the same kind of variation, with decreasing emissions while increasing pH in tropical soils.

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Sensitivity tests of the NO emission model used in this study have already been explored in Delon et al. (2007) for the elaboration of the model. The most straightforward conclusion from these tests is that soil moisture is the main driver for NO fluxes in the particular conditions of semi arid soils (with immediate effect on soil N content), modulated by soil temperature effect (mostly visible during the dry season) and adjusted by soil pH and wind effects.

5 Limitations and uncertainties

Estimating NO fluxes in semi arid regions through modeling studies remains a difficult exercise, considering the scarcity of data. Uncertainties in the calculation of NO fluxes in the model are related to uncertainties on the main drivers of NO emission, i.e. soil moisture, and mineral N. Furthermore, the mineral N concentration in the soil is also driven by soil moisture. The uncertainty on the NO flux has been estimated around 20% when calculated with the present algorithm (Delon et al., 2010). Despite the scarcity of validation flux measurements, and of data on N cycle in the soil, this work gives results that can be added to the existing knowledge on emission processes. Simulated fluxes are in the order of magnitude of previous measurements performed in the same semi arid region. As mentioned in Davidson et al. (2000), a model based on regression parameters between NO emissions and nitrogen cycling in the ecosystem will have only order of magnitude prediction accuracy. The temporal variation of the quantity of live and dry biomass (straw and litter) have been accurately compared to measurements, but the case is different for the seasonal cycles of the N pools in the soil. Comparisons have been made with the available experimental data at a given time, but do not give access to the whole yearly cycle. The mineral N concentration in the soil used as input in the calculation of NO fluxes is set to zero by the model during the dry season because the respiration of microbes is blocked when soil moisture is too low. In this work it was set to a non zero value to avoid null NO fluxes. This value should

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be moderated and readjusted according to experimental results of available nitrogen in the soil during the dry season.

While the STEP model was initially designed for 1-D-simulations in well documented study sites, it has also been recently used at the regional scale in the Sahelian belt (12–20° N; 20° W–35° E) by Pierre et al. (2012) and Pierre et al. (2011), to estimate the amount of dust emissions in that region. The NO flux model has also been applied in the region of Niamey, Niger (Delon et al., 2008), to reproduce NO pulses at the beginning of the wet season, and their impact on ozone formation during the AMMA field campaign in 2006. Furthermore, it has been used at the regional scale in the Sahel (Delon et al., 2010) and in West Africa (Delon et al., 2012) to calculate NO release to the atmosphere. Concerning the GENDEC model, it has been successfully applied for situations very different from those upon which it was based (Moorhead and Reynolds, 1993; Moorhead et al., 1996). In other words, we can seriously consider using this coupled STEP-GENDEC-NOflux model in the Sahelian belt by making approximations, concerning for example biomass, livestock, N and C pools. Considering the need of information in this region of the world, it would be conceivable to simulate such processes of emissions at a larger scale. The challenge is worth to be done, knowing that NO emissions participate at a larger scale to the production of tropospheric ozone.

6 Conclusions

The present work is an attempt to estimate NO fluxes in the semi arid region of the Sahel. Simulations are performed at the site of Agoufou (Mali), with a coupled vegetation–litter decomposition–NO emission model, for years 2004–2008. The vegetation model STEP correctly reproduces the temporal dynamics of soil moisture in the first layer of the model (layer involved in the soil N cycle), as well as the increase and decrease, and the filling and emptying of the surface layer. The temperature in the first two layers of the model are also in accordance with measurements. The green and dry biomass calculated by STEP show a correct feature when compared to measurements

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in terms of vegetation growth, vegetation quantity, decay and production of litter, despite slight time lags in the peak of green biomass for the years 2006 and 2008. The quantity of N is calculated in GENDEC, and is directly derived from organic matter and C contents, both quantities calculated from litter degradation and microbial dynamics in the soil. Sahelian soils are usually considered as N poor, and the comparison of the N content in the soil calculated in GENDEC (around 0.2–0.3 %) is well in accordance with experimental values, and with the few references found in the literature. The coupling between the three models is successful, and well adapted to the specific functioning of semi arid ecosystems, where mechanistic models have usually not been tested. The biomass management in the Sahel is also driven by the presence of livestock, which provides fecal biomass and buries surface litter by trampling.

The quantity of N in the soil is the consequence of the presence of vegetation and livestock at the surface, and mineral N constitutes the N pool available for N release to the atmosphere, in the form of NO (and other compounds). The NO flux calculated by the model is of course highly dependent on soil moisture, as well as on mineral nitrogen, and a 2 % fraction of this pool is used as input to calculate the NO release, modulated by the effect of environmental parameters such as wind speed, soil moisture and temperature, pH and sand percentage. Simulated NO emissions during the wet season are in the same order as previous measurements made in several sites where the vegetation and the soil are comparable to the ones in Agoufou. Very few measurements have been made during the dry season, which complicates the validation of the modelling results for that season. However, the annual budget of emissions is mostly dominated by emissions occurring during the wet season, as already highlighted in different studies in semi arid regions.

This modelling study has been strengthened at each step of the calculation process by comparison with experimental values. It would be necessary to obtain more measurements through field campaigns, especially for the N content in the soil, the grazing pressure, the soil N uptake by plants, and the concentrations and fluxes of N compounds in the atmosphere. Taking into account the difficulty of organizing field

campaigns in these remote regions, modelling is an essential tool to link N cycles both in the soil and in the atmosphere, and to understand specific processes involved in semi arid regions. This study is a step forward in the representation of biogenic NO release to the atmosphere in semi arid regions, where processes of emissions are usually adapted from temperate regions, and not specifically designed for semi arid ecosystems.

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Table 1. Inputs for the models used.

STEP	Inputs	Unit	Value
Initial parameters	Conversion efficiency	g(d.m.)MJ ⁻¹	4
	Initial green biomass	g(d.m.)m ⁻²	0.8
	% C3	%	29.3
	Initial Specific Leaf Area	cm ² g ⁻¹	180
Meteorology	Precipitations	mm	Daily variation
	Global radiation	MJm ⁻²	Daily variation
	Min and max air temperature	°C	Daily variation
	Pressure	hPa	Daily variation
	Wind speed	ms ⁻¹	Daily variation
Soil	Thicknesses (4 layers)	cm	2;28;70;200
	Initial water stock (4)	mm	0.1;1.5;7.3;38
	Clay content (4)		4.5;5.5;5.2;5.5
	Sand content (4)		91.2;91.3;91;92.3
	pH (4)		6.7;6.7;6.7;6.7
Annual vegetation	Initial dry biomass and litter	g(d.m.)m ⁻²	10;30
	Root fraction (3)		0.75;0.2;0.05
	% dycotiledone	%	29.5
	Max tree biomass (year before and current year)	kgha ⁻¹	600;400
Animals	Animal categories (bovine, caprine, ovine, asine, cameline, equine)	%	Monthly variation Ex for Jan: 0.826;0.091;0.055;0.024;0.001;0
	Animal stock (12 months)	Head number	2893;5288;15 626;22 537 13 874;7832;1191;408 3168;2835;2510;3348
	Grazing area	ha	5000
GENDEC	Inputs	Unit	Value
	Soil temperature	°C	From STEP
	Matrix potential	bars	From STEP
	Microbial assimilation efficiency		0.6
	Carbon pool	gC	From STEP
	Microbial death rate		0.2
	N/C (6: labile compounds, holocellulose, resistant compounds, dead and living microbial biomass, nitrogen pool)		10;1000;34;8;25;9
NOFlux	Inputs	Unit	Value
	surface WFPS	%	From STEP soil moisture
	surface soil temperature	°C	From STEP
	Deep soil temperature	°C	From STEP
	Wind speed	ms ⁻¹	From meteorological forcing
	pH		6.7
	Sand content		91.2
	Mineral nitrogen	g(N)m ⁻²	From GENDEC

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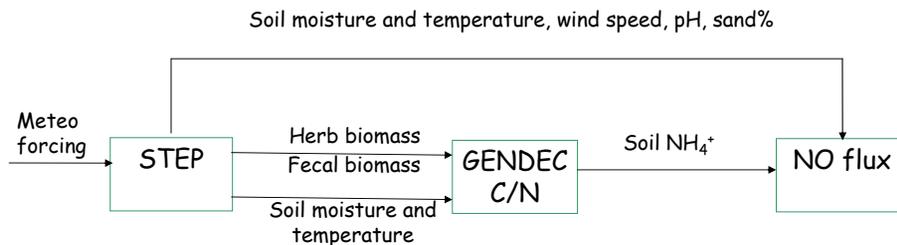
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Table 3. Comparison of experimental and simulated NO fluxes (daily scale) during various wet seasons in dry savanna sites. The model used are indicated in parenthesis. No model specified means experimental data.

Site name	NO flux (kg(N) ha ⁻¹ yr ⁻¹)	Period	Reference
Banizoumbou	1.92 ± 0.83	Wet season 1992	Le Roux et al. (1995)
Agoufou	2.11 ± 0.77	Wet season 2004	Delon et al. (2007)
Agoufou	0.72 ± 0.25	Wet season 2005	Unpublished
South Africa	1.7–2.5	Wet season 1993	Otter et al. (1999)
Chihuahuan desert	0.76	Watered soils 1993	Hartley and Schlesinger (2000)
Agoufou (STEP)	1.06 ± 1.00	Wet season 2004	This work
Agoufou (STEP)	1.54 ± 1.35	Wet season 2005	This work
Agoufou (STEP)	1.56 ± 1.52	Wet season 2006	This work
Agoufou (STEP)	1.55 ± 1.43	Wet season 2007	This work
Agoufou (STEP)	1.73 ± 1.65	Wet season 2008	This work
Agoufou (ISBA)	2.52 ± 1.14	Wet season 2006	Delon et al. (2010)
Agoufou (STEP)	0.66 ± 0.65	Year 2004	This work
Agoufou (STEP)	0.86 ± 0.92	Year 2005	This work
Agoufou (STEP)	0.86 ± 1.02	Year 2006	This work
Agoufou (STEP)	0.85 ± 0.97	Year 2007	This work
Agoufou (STEP)	0.96 ± 1.13	Year 2008	This work

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*Schematic representation of NO flux modeling
coupled to STEP-GENDEC*

Figure 1. Schematic view of links between the models STEP, GENDEC and NO emission model.

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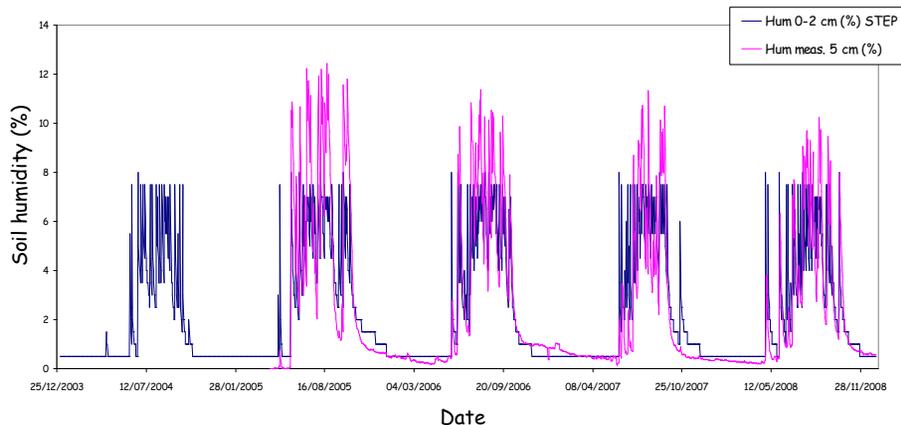


Figure 2. Soil moisture calculated by STEP at the surface layer (0–2 cm) in blue, mean soil moisture measured at 5 cm in pink, for years 2004 to 2008 at Agoufou.

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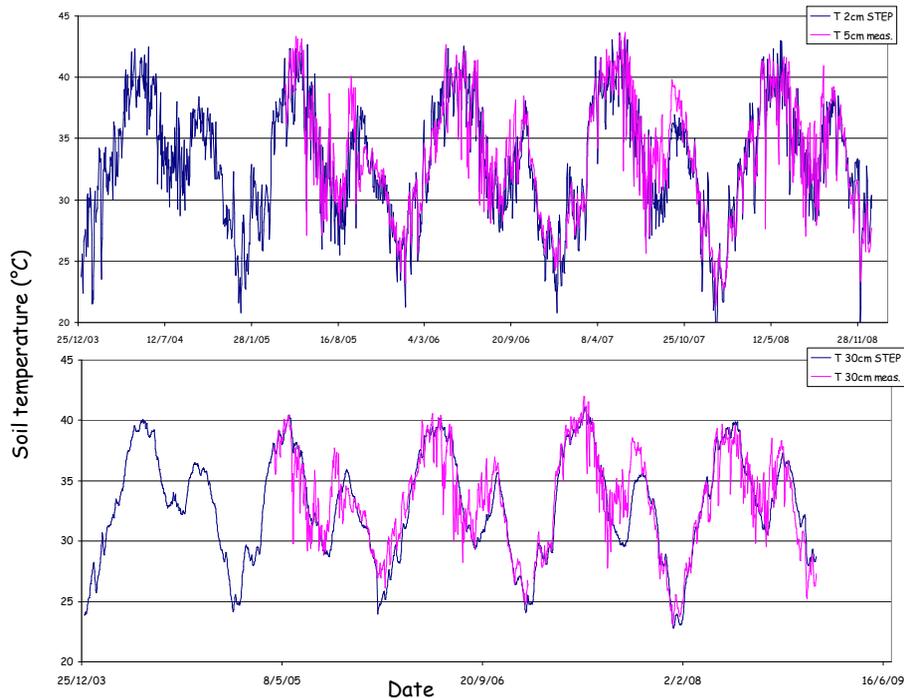


Figure 3. (a) Soil temperature measured at 5 cm at the low slope station (in pink), soil temperature simulated at the surface layer in blue; **(b)** soil temperature measured at 30 cm at the low slope station (in pink), soil temperature simulated at the second layer (2–30 cm) in blue, for years 2004 to 2008 at Agoufou.

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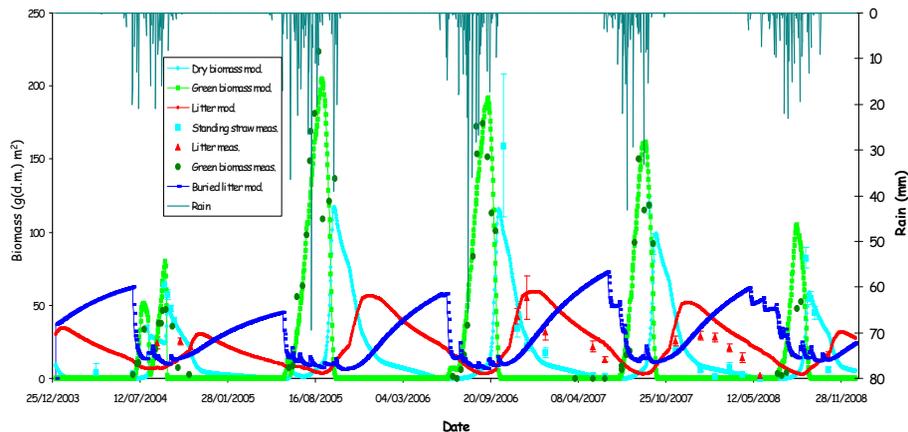


Figure 4. Green biomass in green, dry biomass in light blue, surface litter in red, buried litter in dark blue (line for the model, dots for measurements), in g(d.m.) m^{-2} . SDs are indicated for the measurements. Rain in blue-grey in mm, for years 2004 to 2008 at Agoufou.

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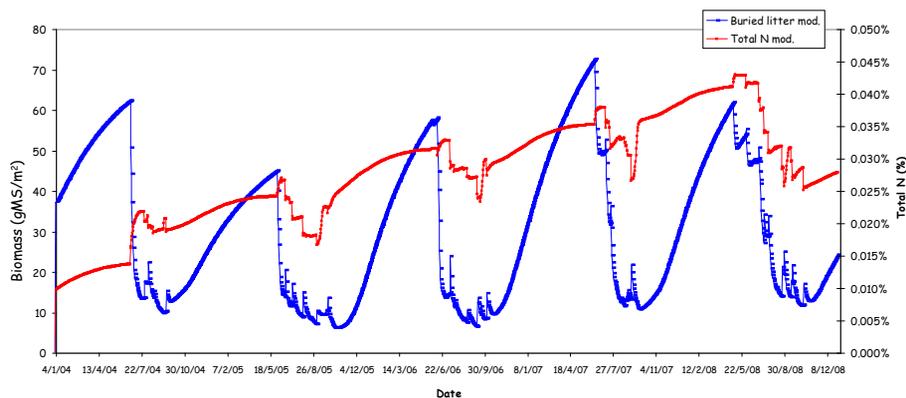


Figure 5. Simulated buried litter in g(d.m.)m^{-2} in dark blue and total N content in the soil in %, for years 2004 to 2008 at Agoufou.

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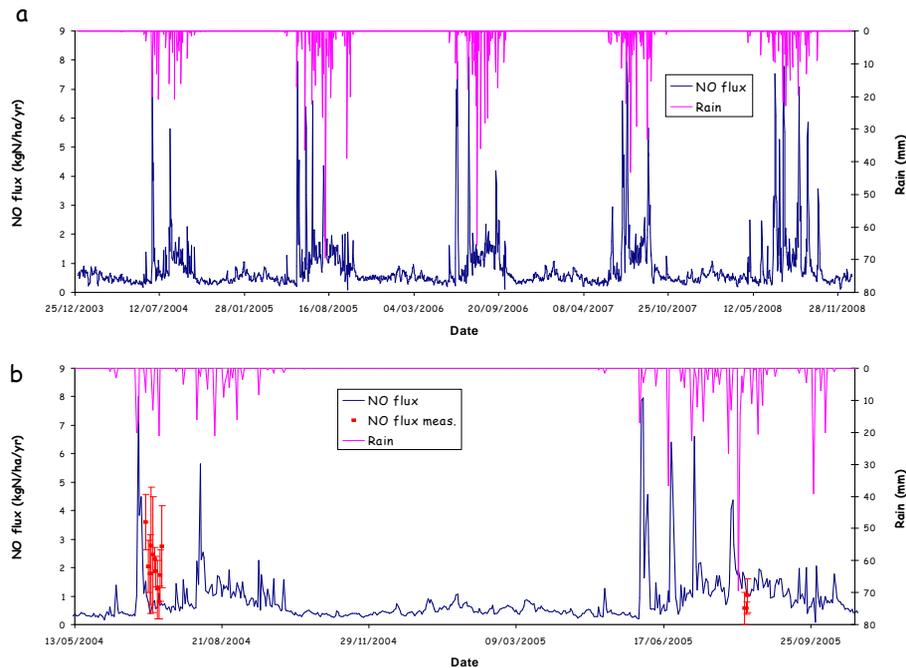


Figure 6. Simulated NO flux in $\text{kg(N)ha}^{-1}\text{yr}^{-1}$ and rain in mm, for years 2004 to 2008 at Agoufou.

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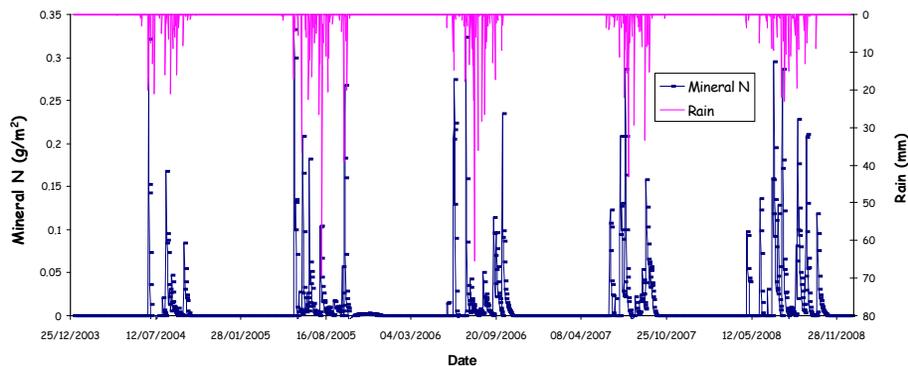


Figure 7. Simulated mineral N in g m^{-2} and rain in mm for years 2004 to 2008 at Agoufou.

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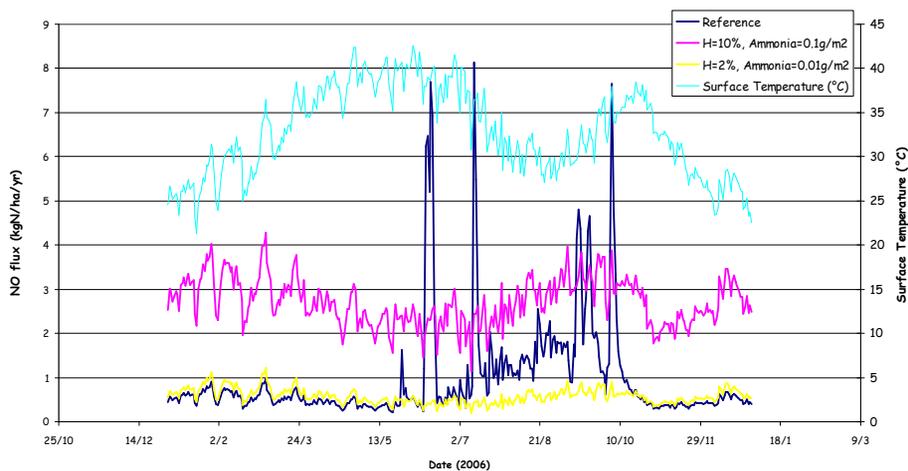


Figure 8. Sensitivity test. In dark blue: reference NO flux in $\text{kg(N) ha}^{-1} \text{yr}^{-1}$, in yellow: NO flux with $H = 2\%$ and mineral $N = 0.01 \text{ g m}^{-2}$, in pink: NO flux with $H = 10\%$ and mineral $N = 0.1 \text{ g m}^{-2}$, in light blue: surface temperature in $^{\circ}\text{C}$, for year 2006.

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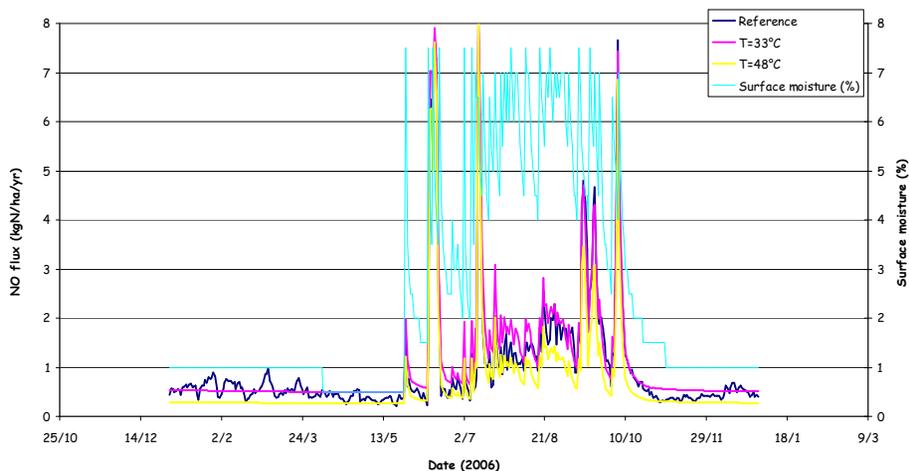


Figure 9. Sensitivity test. In dark blue: reference NO flux in $\text{kg(N) ha}^{-1} \text{ yr}^{-1}$, in yellow: NO flux with $T = 48^\circ\text{C}$, in pink: NO flux with $T = 33^\circ\text{C}$, in light blue: surface moisture in %, for year 2006.

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