Emissions and spatial variability of N_2O, N_2 and nitrous oxide mole fraction at the field scale, revealed with ^{15}N isotopic techniques

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Abstract

The accurate measurement of nitrous oxide (N_2O) and dinitrogen (N_2) during the denitrification process in soils is a challenge which will help to estimate the contribution of soil N_2O emissions to global warming. Oxygen concentration, nitrate concentration and carbon availability are generally the main factors that control soil denitrification rate and the amount of N_2O or N_2 emitted. The aim of this paper is to present a database of the N_2O mole fraction measured at the field scale, and to test hypotheses concerning its regulation. A ^{15}N-nitrate tracer solution was added to 36 undisturbed soil cores on a 20 m $\times$ 20 m cultivated field plot. Fluxes of CO_2, N_2O and N_2 from the soil surface were monitored for 24 h. Soil moisture, bulk density, carbon, nitrogen and mineral nitrogen concentration were also measured to investigate possible spatial relationships between their variations and those of N_2O, N_2 and nitrous oxide mole fraction. Under high water content, nitrous oxide and N_2 emissions were highly variable with variation coefficients of 70–140%. N_2O emission rates were about twice as high as those of N_2, with a total denitrification rate ranging from 269 to 3843 g N ha^{-1} d^{-1}. After 24 h of incubation, the values of nitrous oxide mole fraction ranged from 0.15 to 0.94 and no significant decline during incubation time was observed. Spatial variability of N_2O, N_2 and nitrous oxide mole fraction was high and no spatial dependence was observed at the scale of the experimental plot. Only tenuous relationships between gaseous nitrogen emissions and soil properties (mainly nitrate concentration and moisture content) were found. Meanwhile, a positive correlation was observed between N_2 and CO_2 emissions. This result supports the hypothesis that an increase in soil available organic carbon leads to N_2 emissions as the end product of denitrification.
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1. Introduction

The greenhouse gas, nitrous oxide, is largely emitted in nitrogen fertilised agricultural soils during denitrification (IPCC, 2001). In this anaerobic respiration, nitrate (NO_3^-) is used as the terminal acceptor for electrons (Payne, 1973). The three main factors controlling soil denitrification rates are usually considered to be oxygen concentration, nitrate concentration and availability of easily metabolizable organic matter (Tiedje, 1988). It is generally admitted, firstly that denitrification occurs only in limited conditions of oxygen, and secondly that denitrification rates are controlled by the degree of anaerobiosis and by NO_3^- content (or other N oxides) as oxidant, and organic carbon content as reductant. Temperature also controls denitrification rates. These factors interact in

a complicated manner. N_2O is an obligatory free intermediate of this process. Emissions of N_2O can represent 0–100% of denitrification products (Aulakh et al., 1992). The ratio of N_2/N_2O evolution from soils during the denitrification process is also affected by environmental factors. Weier et al. (1993) observed that the largest ratios were found at the highest available C rate and generally at the highest soil water content.

Models of nitrogen cycling in soils have assessed N_2O as well as N_2 production through the denitrification process (Parton et al., 1996; Frolking et al., 1998). The latter authors observed sizeable discrepancies between models in the assessment of N_2 emissions and then concluded that accurate partitioning into N_2O and N_2 is a challenge for all models. Hence, more field and laboratory work is needed to understand the influence of soil environmental parameters on the variation of the N_2/N_2O ratio under a range of conditions.

Compared to the measurement of soil N_2O production, the measurement of soil N_2 emission requires the discrimination of a very small amount of emitted gas which is diluted in atmospheric N_2. Two general techniques exist to measure soil N_2 emission at the field scale. The acetylene technique, based

on N_2O reductase inhibition, has been largely used although it does not allow N_2O and N_2 fluxes to be measured at the same time. Moreover, complete inhibition of N_2O reductase cannot be guaranteed, particularly when this technique is used *in situ* and when soils are wet, clayey or compacted (Klemedtsson et al., 1988; Stevens et al., 1993; Malone et al., 1998). The ^{15}N labelling techniques (Parkin et al., 1985; Mosier et al., 1986; Tiedje et al., 1989) can solve both these problems. When ^{15}N-enriched amendment is coupled with mass spectrometry analysis, high precision for N_2 emissions is attained, with the limit of detection at less than 15 g N ha^{-1} d^{-1} (Siegel et al., 1982).

At the field scale, denitrification is characterised by an extreme spatial and temporal variability (Folorunso and Rolston, 1984, 1985; Parkin, 1987; Parkin et al., 1987; Tiedje et al., 1989; Van den Pol-van Dasselaar et al., 1998). Parkin and Robinson (1989) have suggested developing stochastic models as an alternative to deterministic models to improve prediction of positively skewed distributions for field denitrification resulting from the combined influence of variables known to affect denitrification.

The present experiment provides a database of the nitrous oxide mole fraction, defined as $N_2O/(N_2O+N_2)$, measured at the field scale. Gas chromatography and ^{15}N labelling techniques were used to measure N_2O, CO_2 and N_2 emissions during denitrification throughout the selected plot. The database included 36 replicates for both gaseous flux measurements and environmental parameters (moisture, carbon and nitrogen contents). We were thus able to investigate spatial variability and spatial dependence of N_2 and N_2O in relation to these soil parameters. The database was also used to test the hypothesis that the combination of high available carbon, and low oxygen diffusion promotes high N_2/N_2O ratios.

2. Materials and methods

2.1. Experimental site

The soil used for this experiment was a cultivated Gleyic luvisol located at Cîteaux (47°08′N, 5°06′E) in the Saône river plain, near Dijon (Eastern France). Cultivated Gleyic luvisols are widespread in Burgundy. The experimental plot exhibits no relief variation. In the surface (0–20 cm) soil, the pH_{water} was 7.1. The inorganic fraction of the soil contained 13.5% clay, 51.9% silt and 34.6% sand. Mean carbon and nitrogen contents were of 8.0 mg C g^{-1} soil and 0.8 mg N g^{-1} soil, respectively. The mean soil bulk density was 1.4 and, assuming a solid density of 2.6, the soil total porosity was 0.46. The volumic soil water content at the zero hydric potential was 0.38, in accordance with the maximum water-filled pore space of 0.82. At the time of sampling, the plot was cultivated with winter wheat and a fertilisation of 80 kg N ha^{-1} (ammonium nitrate) had been applied by the farmer 15 days before.

The experiment was conducted on undisturbed soil cores (10 cm diameter, 23 cm depth), enclosed in steel cylinders (25 cm depth). The cores were obtained by manually driving
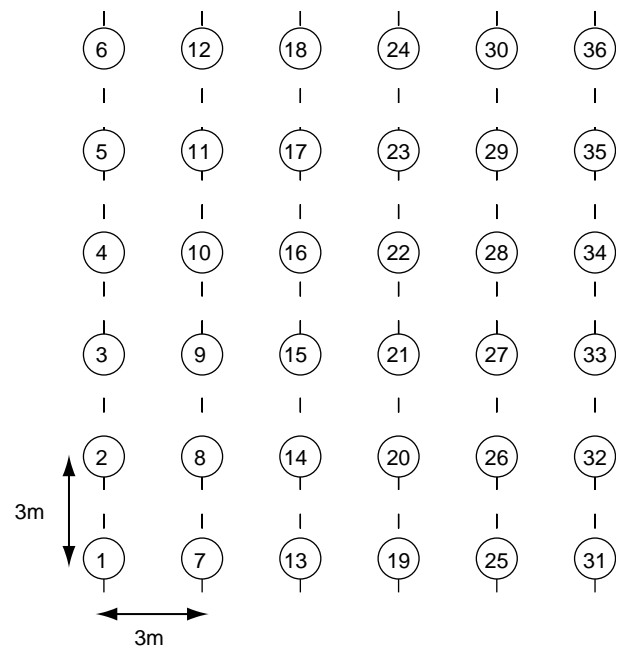

Fig. 1. Schematic representation of the sample map, with a constant distance of 3 m between each cylinder.

the steel cylinders into the soil and removing them (Hénault and Germon, 2000). Sampling of 36 cores was performed in April 2003 on a 20 m × 20 m plot with a constant distance of 3 m between cores (Fig. 1). At the date of sampling, soil moisture content was 17% (w/w). Cores were stored outside for 5 days before incubation. Soil moisture content fell to 15% (w/w).

2.2. Pre-treatment and ^{15}N labelling

Enriched nitrate was added to each soil core through 250 ml of equimolar ammonium:nitrate $((NH_4)_2SO_4:K^{15}NO_3)$ solution at 235 mg N l^{-1}, which represents a fertilisation of 75 kg N ha^{-1}. The solution was gently poured on to the soil surface. The volume added was calculated to fill 80% of the soil porosity. Slight leakage left a final water-filled pore space of around 74%. The nitrate was enriched in ^{15}N at 60 atom%. It was assumed that native and added nitrate formed a uniformly ^{15}N-labelled pool. After ^{15}N labelling, cylinders were stored outside for 24 h to avoid gas cross-contamination during preincubation (temperature decreased to 5 °C overnight). Then the cylinders were kept in an air-conditioned room at 18 °C, the average outside temperature during the day of measurement. In a control cylinder, soil temperature was periodically measured several times to evaluate the kinetics of the temperature increase. An average period of 8 h was required to achieve a constant temperature of 18 °C.

2.3. Kinetic gas emission

At the start of the incubation, the 36 steel cylinders were closed with an air-tight PVC system (Fig. 2). Five millilitres of krypton (Alphagaz, France) were injected into the cylinders to