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Improving the management of mineral fertilizers for nitrous oxide mitigation: The effect of nitrogen fertilizer type, urease and nitrification inhibitors in two different textured soils

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ABSTRACT

The production of nitrous oxide (N_2O) in soil is mainly related to nitrification and denitrification processes, taking place under aerobic and anaerobic conditions, respectively. Oxygen, ammonium (NH_4^+) and nitrate (NO_3^-) concentrations in soil are the main factors controlling the N_2O production processes. Many studies confirm that N_2O emissions in agroecosystems are stimulated by increasing the N fertilizer rate. Beside the N rate, the fertilizer formulation may affect soil N_2O emissions, though the effects are still unclear and may be different according to soil type, soil water content and oxygen availability expressed as soil water filled pores space (WFPS). Enhanced efficiency fertilizers, such as fertilizers with nitrification and urease inhibitors (NIs, UIs) may slow down N_2O production processes, although different results were reported regarding their effectiveness.

This study contributed to the evaluation of the effect of mineral N fertilizer formulation on N_2O and CO_2 emissions, through two laboratory experiments carried out on soil cores distributing to two different textured soils: i) nitrate or ammonium-based fertilizer under increasing WFPS levels (Exp.1), and; ii) NIs and UI with various N fertilizers, including a new NI (DMPSA) (Exp.2).

The highest N_2O and CO_2 emissions were recorded after the application of an ammonium-based fertilizer in both soils, suggesting the preponderance of nitrifying organisms. The results confirmed that WFPS is a key driver for N_2O emissions, with highest N_2O emissions occurring at WFPS > 75%, while CO_2 emissions decreased linearly with increasing WFPS across all fertilizer treatments and in both soils. NIs were effective only in the soil with the highest nitrification activity and the lowest clay content, decreasing N_2O emissions by an average of 50%, while the UI did not reduce N_2O emissions in either soil. These results proved that soil characteristics significantly affect NIs capacity to mitigate N_2O emissions from soil.

1. Introduction

There is high interest within the scientific community in processes that regulate nitrous oxide (N_2O) emissions from agricultural soils, mainly because soil is a major source of this potent and ozone-depleting greenhouse gas (Bouwman et al., 2002; Ravishankara et al., 2009). N_2O emissions from agricultural soils account for about 70% of the total annual N_2O emissions at the European scale (European Environment Agency, 2015). The production of N_2O by soils is primarily attributed to the microbial processes of nitrification and denitrification. Through nitrification, in aerobic conditions, ammonium ion (NH_4^+) is oxidized to form nitrate ion (NO_3^-), and the availability of NH_4^+ and oxygen are the dominant factors controlling the process (Firestone and Davidson, 1989). During denitrification, in anaerobic conditions, NO_3^- is reduced to N_2 and N_2O can be emitted as an intermediate product. The availability of carbon (C), NO_3^- and oxygen are the major factors controlling microbial denitrification (Tiedje, 1988). However, a complex set of processes are involved in the production of N_2O in soil, as was clearly summarized by Butterbach-Bahl et al. (2013), and the relative proportion of the end products of these processes is influenced by different factors such as environmental conditions, and the biological and physico-chemical characteristics of the soil. Moreover, the processes contributing to the emission of N_2O from agricultural soils are often regulated by management practices, with nitrogen (N)

Abbreviations: CS, clay soil; CLS, clay loam soil; NI, nitrification inhibitor; UI, urease inhibitor; AN, ammonium nitrate; ANi, ammonium nitrate + 3.4-dimethylpyrazol succinate (EuroChem Agro, DMPSA); ASN, ammonium sulphate nitrate; ASNi, ammonium sulphate nitrate + 3.4-dimethylpyrazole phosphate (ENTEC®, DMPP); UREA, urea; UREAi, urea + N-(n-butyl) thiophosphoric triamide (NBPT); AS, ammonium sulphate; KN, potassium nitrate

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fertilization playing a key role in stimulating N_2O emissions, especially when the N rate exceeds crop demand (Crutzen et al., 2008; Snyder et al., 2014; Sainju, 2016). The total worldwide consumption of N fertilizer is expected to increase in order to feed a growing population, meaning that greenhouse gas (GHG) emissions, especially N_2O, are also expected to rise (Food and Agriculture Organization of the United Nations (FAO), 2009; Tilman et al., 2011). Previous studies have indicated, as regards N fertilizer management, that the N rate, fertilizer formulation and fertilizer splitting are key aspects influencing N_2O emissions (Sainju, 2016; Burger and Venterea, 2011). Laboratory and field studies have studied whether the application of an NO_3-based or NH_4-based fertilizer can influence the intensity of N_2O emissions by affecting the NH_4^+ and NO_3^- soil concentrations. However, limited studies compare different N fertilizer types, often reporting contradictory results. The lack of clear results on the effect of N fertilizer formulation is probably due to the strong relation between N_2O emissions, fertilizer application technique and soil properties (Lebender et al., 2014; Stehfest and Bouwman, 2006; Tenuta and Beauchamp, 2003). Thus, further studies are necessary in order to draw solid conclusions for the individuation of N_2O emission mitigation strategies. Together with NH_4^+ and NO_3^- soil concentration, water filled pore space (WFPS), which depends on the combination of water availability and soil physical and chemical characteristics, is often indicated as the main soil parameter regulating N_2O emissions (Dobbie and Smith, 2003). In fact, WFPS regulates the microbial processes of nitrification and denitrification by affecting the oxygen availability in soil (Del Prado et al., 2006). In field trials, high peaks in N_2O emissions are frequently detected after rainfall events, caused both by a stimulation of mineralization and a change in gas diffusivity (Ball, 2013; Chen et al., 2013; Laville et al., 2011). In particular, it is commonly indicated that N_2O from nitrification occurs with WFPS of around 50–60%, while N_2O derived from denitrification peaks occur at a WFPS higher than 60%, though these figures may change in response to different soil properties (Davidson et al., 1991; Grundmann and Rolston, 1987). Previous studies have reported that when WFPS is above 80%, oxygen is limiting and N_2O may be reduced to N_2, though this threshold may vary depending on the soil texture, soil temperature, nitrogen content and pH level (Bouwman, 1998; Chapuis-Lardy et al., 2007).

Furthermore, in regards to N fertilizer formulation, enhanced efficiency N fertilizers, such as fertilizers with nitrification (NIs) or urease inhibitors (UIs), were developed to improve the efficiency of N use by crops and minimizing the N losses. The NIs act by delaying the bacterial oxidation of NH_4^+, halting the nitrifying activity in soil, while the UIs slow down the hydrolysis of urea. NIs and UIs can potentially mitigate N_2O soil emissions, given their effect on the presence of NO_3^- and NH_4^+ in soil (Akiyama et al., 2010; Khalil et al., 2009; Ruser and Schulz, 2015). However, it is difficult to draw any specific conclusions about the N_2O mitigation potential of NIs and UIs, because their efficiency depends on site-specific parameters such as climate conditions, soil properties and management practices. This uncertainty is especially relevant for N_2O mitigation by UIs (Barth et al., 2001; McGeough et al., 2016; Francisco et al., 2011). The main objective of this study was to analyze the N_2O emissions from two different textured soils in a laboratory experiment on soil cores as a response to: i) different N fertilizer formulations (nitrate vs ammonium-based fertilizers) at increasing WFPS levels (experiment 1), and; ii) the application of different N fertilizers with or without NI or UI (experiment 2). Finally, to expand our knowledge of the potential effect of the factors being analyzed on soil respiration, carbon dioxide (CO_2) emissions were also measured in both experiments.

2. Material and methods

2.1. Soil samples collection and preparation

The two soils used in this study were collected during the field trials of the LIFE + "Improved flux Prototypes for N_2O emission reduction from Agriculture" (IPNOA) project, carried out at two different sites in the Tuscany region of Italy: the "Enrico Avanzi" Centre for Agro-Environmental Research of the University of Pisa, located in San Piero a Grado (Pisa, Italy) (43°40′48″N 10°20′55″E) and the "Terre Regionali Toscane" Center for Innovation Testing, located in Cesa (Arezzo, Italy) (40°57′55″ N 14°13′51″E). Soil samples were collected from the bare topsoil (0–20 cm layer) after wheat harvest in July 2015, and were subsequently analyzed for the main physical and chemical characteristics (Table 1). The two soils derive from alluvial sediments: the soil from San Piero a Grado is a clay loam soil (CLS) classified according to the United States Department of Agriculture (USDA) soil taxonomy as a Typic Haplustert, while the soil from Cesa is a clay soil (CS) classified as a Chromic Haplustert. The bulk density of the two soils was estimated from the soil texture, as proposed by Saxton et al. (1986), and was equal to 1.29 g cm^3 for both CLS and CS.

Table 1
Soil characteristics in the top layer (0–20 cm) of the two soils.

Parameter	Unit	CLS	CS
Sand (2 mm–0.05 mm)	g kg^{-1}	204	403
Silt (0.05–0.002 mm)	g kg^{-1}	461	156
Clay (< 0.002 mm)	g kg^{-1}	335	440
pH	1:1 w/v	7.9	7.3
Organic matter	g kg^{-1}	18.1	9.9
Total Kjeldhal N	g kg^{-1}	1.4	0.5
Available P	mg kg^{-1}	30.3	167.8
Exchangeable K	mg kg^{-1}	228.5	79.6
C/N		7.7	11.9

The soil was air dried and then sieved at 4 mm to improve the homogeneity of the samples, removing stones, and plant roots and residues. The soil was stored in a cold chamber at 4 °C until the beginning of the first experiment (for about 3 weeks in total).

In both experiments, the soil was packed to form soil cores in aluminum cylinders 4.9 cm high and with an inner diameter of 5.6 cm, with three replicates per treatment. A fresh weight of soil corresponding to 90 g of dry soil was placed in the cylinders for each soil. Being the weight of the soil in the cylinders defined, we obtained the pre-determined bulk density (1.29 g cm^{-3}) pressing the soil to regulate the height of the soil in the cylinders. The water content in each cylinder was kept constant, by monitoring the weight of the cylinders and adding water on the soil surface by infiltration when needed. Watering was carried out the evening before the gas sampling in order to avoid possible gas emission pulses caused by the watering. The cylinders were kept in a climatic chamber at 20 °C throughout the duration of the experiments.

2.2. Experiment 1: effect of the application of nitrate- or ammonium-based fertilizers at increasing WFPS levels

The experiment was carried out on both soils in order to study how soil type (CLS, CS) and nitrogen sources affect the emission of N_2O and CO_2 at different WFPS levels. The two fertilizers supplied were KNO_3 (KN) and $(NH_4)_2SO_4$ (AS), with an N rate of 200 mg N kg dry $soil^{-1}$.

Eight levels of WFPS (%) were tested for each soil: 45, 55, 60, 65, 70, 75, 80, 85.

WFPS was defined according to the following Eq. (1):

$$WFPS = \frac{W \times bd}{H_2O \times Tp} \times 100 \quad (1)$$

where W is the mass of water per mass unit of oven-dried soil g g^{-1}, bd denotes the soil bulk density (g cm^{-3}), H_2O is the water density (g cm^{-3}) and Tp is the total soil porosity calculated as $1 - \left(\frac{bd}{pd}\right)$, where pd is the particle density (2.65 g cm^{-3}). With the bulk density kept at a constant, the different WFPS levels were determined by varying the