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Effect of nitrification and urease inhibitors on nitrous oxide and methane emissions from an oat crop in a volcanic ash soil

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ABSTRACT

Nitrous oxide (N_2O) emissions from the Chilean agricultural sector are primarily associated with the use of nitrogen (N) fertilizers, so that the use of nitrification and urease inhibitors may represent a potential mitigation option. However, their effectiveness in volcanic ash soils with high organic matter is still uncertain. In this study, the effect of Dicyandiamide (DCD) and *N*-(*n*-butyl) thiophosphoric triamide (NBPT) on soil N_2O and CH_4 emissions from an oat crop was determined using a fully automated greenhouse gas measuring system. Three urea treatments were evaluated: 120 kg N ha^{-1}, 120 kg N ha^{-1} + DCD and 120 kg N ha^{-1} + NBPT (n = 3). A zero treatment (-N) was also considered. Annual N_2O emissions ranged from 0.36 to 1.00 kg N_2O-N ha^{-1} ($P > 0.05$) whereas the net uptake of CH_4 ranged from 6.72 to 7.00 kg CH_4-C ha^{-1} ($P > 0.05$). Increases in N_2O emissions were associated with rainfall events, as characteristic of Mediterranean rain fed ecosystems. Soil CH_4 uptake did not vary among treatments but had a significant role offsetting N_2O emissions, resulting in total emissions ranging from −17.1 to 239.0 kg CO_{2eq} ha^{-1} ($P < 0.001$). There was no significant effect of DCD or NBPT on average soil mineral N concentration, and total N_2O and CH_4 emissions. NBPT significantly increased crop yield and crop N uptake by 27% and 33% respectively ($P < 0.05$), resulting in greater N use efficiency. The use of DCD did not increase productive parameters, but resulted in a 35% reduction of the N_2O-N emission intensity ($P < 0.05$). The study shows that volcanic ash soils have a relatively low N_2O emission potential due to physic-chemical characteristics and that NBPT could be used to increase N use efficiency in crops, while DCD has a potential to reduce N_2O losses per unit yield.

1. Introduction

Agriculture plays a major role in the global nitrous oxide (N_2O) fluxes, as this gas is produced mainly by soil microbial processes occurring in fertilized soils (Paustian et al., 1995). Main sources of N_2O are nitrogen (N) fertilizers, urine and dung deposition during grazing, and manure application onto grasslands (Snyder et al., 2009). Globally, 3.3 Tg N_2O-N yr^{-1} and 1.8 Tg N_2O-N yr^{-1} are emitted from fertilized croplands and grasslands, respectively. Moreover, according to US-EPA (2006), an increase of 50% on N_2O emissions is expected worldwide by 2020 due to the increasing use of N fertilizer and animal manure.

In the troposphere, N_2O is stable for about 120 years and contributes to the greenhouse effect, while in the stratosphere N_2O is reactive and participates in the destruction of the ozone layer (Crutzen, 1981). In soils, direct N_2O emissions result from two microbial processes: nitrification and denitrification. Nitrification is the conversion of ammonium (NH_4^+) to nitrite (NO_2^-) and then nitrate (NO_3^-); and denitrification is the conversion of NO_3^- to N_2O and then dinitrogen gas (N_2). The conversion of NH_4^+ to N_2 could be complete, but a small and variable portion of the N escapes to the environment, primarily as intermediaries, like N_2O (Robertson and Groffman, 2007; Snyder et al., 2009). Indirect N_2O emissions can also be produced by secondary deposition of ammonia volatilization (NH_3; Erisman et al., 2007).

During the last years several countries have evaluated options to mitigate N losses and increase N-use efficiency (NUE) in crops and pastoral lands using inhibitors of the N cycle, such as urease and nitrification inhibitors (Di and Cameron, 2006; Subbarao et al., 2006; Saggar et al., 2009; Zaman and Blennerhassett, 2010; Sanz-Cobena et al., 2012).

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Urease inhibitors reduce NH_3 loses from surface applications of urea fertilizer, inhibiting urease activity and thereby retarding the urea hydrolysis when applied to soils with the fertilizer, increasing NUE. Ammonia itself is not a greenhouse gas; however, it acts as a secondary source of N_2O in the atmosphere and thus contributes to global warming (Martikainen, 1985). One of the most efficient urease inhibitors is the *N*-(*n*-butyl) thiophosphoric triamide (NBPT; Bremner and Chai 1986; Bronson et al., 1990; Gioacchini et al., 2002; Zaman et al., 2009). This inhibitor is transformed in the soil to its oxon analog *N*-(*n*-butyl) phosphoric triamide (NBPTO), which then forms a tridentate ligand with the urease enzyme, thus inactivating the enzyme (Manunza et al., 1999), slowing urea hydrolysis. Among the nitrification inhibitors, dicyandiamide (DCD) has also been successfully tested (Zaman et al., 2009; Di and Cameron, 2016). This odourless powder when applied to the soil inhibits ammonia oxidation, the first step of the nitrification process, slowing the activity of nitrifying bacteria responsible for the oxidation of NH_4^+ to NO_2^-, reducing NO_3^- concentration, and thus reducing N_2O emissions. The NH_4^+ can be adsorbed onto the soil cation exchange complex and then gradually utilized for plant growth, favoring an increase of NUE by plants (Abbasi and Adams, 2000; Cameron et al., 2005; Di and Cameron, 2016).

Agricultural soils can also produce or capture methane (CH_4), another greenhouse gas (GHG). Methane is emitted under anaerobic soil conditions, like in paddy rice soils, by methanogenic bacteria (Chan and Parkin, 2001), and it is consumed through the CH_4 oxidation of methanotrophic bacteria in well-drained aerobic soils (McLain and Martens, 2006).

Chilean agricultural sector is the second largest emitter, accounting for 15.1% of total GHG emissions in 2010 (13,825.6 $GgCO_2$ eq). Emissions from this sector increased by 29% since 1990, mainly caused by the steady increase in the use of synthetic N-based fertilizers (MMA, 2014). The methodology used to estimate GHG from agricultural soils for the national GHG Inventory in Chile includes the use of default Emission Factors (EF) given by the Intergovernmental Panel on Climate Change (IPCC). This approach has the risk of not properly reflecting national circumstances, and the development and improvement of country-specific emission factors for major categories, such as agricultural soils are urgently needed and prioritized by Chile (MMA, 2014).

Little information is available on the effect of inhibitors on N_2O emissions on cropping soils in Chile (Muñoz et al., 2010, 2011), and only one preliminary study reports CH_4 capture in a grassland soil (Vistoso et al., 2014). We hypothesize that the use of N cycle inhibitors, combined with the capacity of the volcanic soil to capture CH_4, will significantly reduce the overall GHG emissions of an oat cereal crop. Thus, the aim of this study was to quantify the effect of a urease and nitrification inhibitors on N_2O and CH_4 emissions, and its secondary effect on crop yield parameters.

2. Materials and methods

2.1. Study site

The field experiment was conducted during the 2012/13 cropping season at the Instituto de Investigaciones Agropecuarias (INIA), Centro Regional de Investigación Remehue (40° 31′ S, 73° 03′ W), in southern Chile. The soil at the experimental site was an Andisol from the Osorno soil series (Typic hapludans; CIREN, 2003), of adequate soil fertility conditions for oat production (Table 1). Prior to the establishment of the experiment, the site had been under permanent pasture (*Lolium perenne* L., *Holcus lanatus* L. *and Dactylis glomerata* L.) for a period of 25 years.

The mean annual rainfall at the experimental site is 1253.6 mm and the mean daily minimum and maximum temperatures are 4.3 and 13.1 °C in winter, and 7.3 and 20.4 °C in summer, respectively, as average of the last 39 years.

Table 1
Initial soil characteristics (2nd of March 2012, 0–20 cm, n = 3, ± standard error of the mean).

Parameter	Results
Clasification[a]	Typic Hapludands
Series	Osorno
Soil texture	Loamy
pH H_2O (soil:water, 1:2.5)	5.61 ± 0.04
pH $CaCl_2$ (soil:$CaCl_2$, 1:2.5)	4.73 ± 0.03
Organic Matter, g kg^{-1}	168.8 ± 14.2
Available N, mg kg^{-1}	19.99 ± 0.65
Olsen P, mg kg^{-1}	16.39 ± 2.06
Available S, mg kg^{-1}	8.06 ± 1.43
Exchangeable Ca, cmol $_{(+)}$ kg^{-1}	3.07 ± 0.37
Exchangeable Mg, cmol $_{(+)}$ kg^{-1}	0.76 ± 0.10
Exchangeable K, cmol $_{(+)}$ kg^{-1}	0.73 ± 0.03
Exchangeable Na, cmol $_{(+)}$ kg^{-1}	0.10 ± 0.02
Al Saturation, %[b]	7.27 ± 0.29
Initial bulk density, g cm^{-3}	0.66 ± 0.02
Final[c] bulk density, g cm^{-3}	0.72 ± 0.01

[a] Acording to CIREN (2003).
[b] Al Saturation: Proportion of available Al in relation to total cation content (Ca + Mg + K + Na + Al).
[c] Bulk density determination carried out at the site, in the natural grassland established after harvest.

Three representative soil samples (0–20 cm) were collected prior to tillage, for chemical and physical characterization following the methods compiled by Sadzawka et al. (2006), and outlined by Rowell (1997), respectively. Briefly, soil pH was measured in water and $CaCl_2$ solution by potentiometry, organic matter concentration was estimated using a modified Walkley-Black method by wet digestion. Exchangeable cations (Ca, Mg, K, and Na) and exchangeable Al were extracted with a solution of ammonium acetate (NH_4Ac) 1 M at pH 7.0 and potassium chloride (KCl) 2 M, respectively, an analysed by atomic absorption spectrophotometry (AAS). Sulfate (SO_4^-) and phosphate (PO_4^-) anions were extracted in a solution of sodium bicarbonate ($NaHCO_3$) 0.5 M at pH 8.5 and calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$) 1 M and analysed by the Murphy and Riley method and turbidimetry, respectively (Tabatabai, 1982).

Conventional tillage was used (0–20 cm), and lime (1 t ha^{-1}, Soprocal) was applied 15 days before the experiment started, to increase the initial soil pH (Table 1).

2.2. Experimental design

An oat cereal crop (*Avena sativa* cv Nehuén) was seeded on 3 × 4 m plots on March 20th of 2012. Four treatments were considered: Zero N (0 N kg N ha^{-1}), Urea (120 kg N ha^{-1}), Urea + *N*-(*n*-butyl) thiophosphoric triamide (NBPT) as urease inhibitor (120 kg N ha^{-1} + 0.25 g NBPT kg N^{-1}), and Urea + Dicyandiamide (DCD) as nitrification inhibitor (120 kg N ha^{-1} + 10 kg DCD ha^{-1}), following a completely randomized block design (n = 3). The N rate used is representative of that used by farmers for an oat crop in southern Chile, while the inhibitors rates used were based on the respective commercial recommendations.

Each experimental plot received a basal fertilizer application at seeding, including 150 kg P_2O_5 ha^{-1} (Triple Superphosphate, 46% P_2O_5), 150 kg K_2O ha^{-1} (Potassium chloride, 62% K_2O), 40 kg S ha^{-1} (Gypsum, 18% $CaSO_4$) and 40 kg MgO ha^{-1} (Magnesium oxide, 85% MgO). Also at this time all +N treatments received an initial N dose of 30 kg N ha^{-1} (Urea, 46% N). The difference to complete the total N rate was top dressed onto the plots at tillers stage (11th May 2012). The inhibitors treatments were sprayed immediately after this second fertilizer application with the use of gardening water

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