



The effect of nitrification inhibitors on nitrous oxide emissions from cattle urine depositions to grassland under summer conditions in the UK



A.S. Barneze^{a,*}, E.P. Minet^b, C.C. Cerri^a, T. Misselbrook^c

^a Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Av. Centenário, 303, São Dimas, 13400-970 Piracicaba, SP, Brazil

^b Teagasc, Johnstown Castle, Wexford, Ireland

^c Rothamsted Research, North Wyke, Okehampton, Devon EX20 2SB, UK

HIGHLIGHTS

- We evaluated the effects of DCD and pyrazole derivatives on N₂O emission.
- Laboratory and field experiments were conducted under UK summer conditions.
- N₂O emissions showed similar temporal dynamics in both experiments.
- The nitrification inhibitors did not significantly reduce N₂O emissions.
- The lack of effectiveness was presumably due to the higher soil temperature.

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ABSTRACT

Nitrous oxide (N₂O) has become the prime ozone depleting atmospheric emission and the third most important anthropogenic greenhouse gas, with a global warming potential approximately 300 times higher than CO₂. Nitrification and denitrification are processes responsible for N₂O emission from the soil after nitrogen input. The application of a nitrification inhibitor can reduce N₂O emissions from these processes. The objective of this study was to assess the effect of two different nitrification inhibitors (dicyandiamide (DCD) and a commercial formulation containing two pyrazole derivatives (PD), 1H-1,2,4-triazole and 3-methylpyrazole) on N₂O emissions from cattle urine applications for summer grazing conditions in the UK. Experiments were conducted under controlled conditions in a laboratory incubator and under field conditions on a grassland soil. The N₂O emissions showed similar temporal dynamics in both experiments. DCD concentration in the soil showed an exponential degradation during the experiment, with a half-life of the order of only 10 d (air temperature c. 15 °C). DCD (10 kg ha⁻¹) and PD at the highest application rate (3.76 kg ha⁻¹) reduced N₂O emissions by 13% and 29% in the incubation experiment and by 33% and 6% in the field experiment, respectively, although these reductions were not statistically significant (*P* > 0.05). Under UK summer grazing conditions, these nitrification inhibitors appear to be less effective at reducing N₂O emissions than reported for other conditions elsewhere in the literature, presumably due to the higher soil temperature.

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1. Introduction

Nitrous oxide (N₂O) contributes about 6% to the anthropogenic greenhouse effect and it has approximately 300 times the global warming potential of carbon dioxide (CO₂) on a mass basis (IPCC, 2007). Agriculture is a major source of N₂O emission, accounting for 79% of the total anthropogenic emission for the UK

(MacCarthy et al., 2011). Nitrous oxide is mainly produced through the microbial processes of nitrification and denitrification.

The use of nitrification inhibitors (NI) has been shown to be a useful technique to reduce N₂O emissions and to promote better nitrogen utilization in the soil. The application of NI to the soil temporarily delays the bacterial oxidation of the NH₄⁺ to nitrite by inhibiting enzyme activity of Nitrosomonas spp. in the soil (Zerulla et al., 2001). A number of studies have been conducted, particularly in New Zealand, showing that NI can reduce N₂O emission by 30–80% (Di et al., 2007; Saggar et al., 2009; Zaman et al., 2009; Akiyama et al., 2010). Also, NI can increase the efficiency

* Corresponding author. Tel.: +55 19 981068959.

E-mail address: arletesb@gmail.com (A.S. Barneze).

of applied fertilizers by reducing nitrogen (N) losses due to denitrification (Bronson et al., 1992) and preventing leaching (Aulakh and Rennie, 1984).

Dicyandiamide (DCD), in particular, has been shown to be an effective NI (e.g. Di and Cameron, 2006; Di et al., 2007; de Klein and Eckard, 2008; Smith et al., 2008a). The efficacy of DCD depends on a number of factors including soil moisture, temperature and DCD application rate, among others (Guiraud and Marol, 1992; Kumar et al., 2000; Chaves et al., 2006). A large effect of DCD on N₂O emissions from soils treated with animal urine (60–85% reduction) has been reported, predominantly from studies in New Zealand (Di and Cameron, 2006; Di et al., 2007; de Klein and Eckard, 2008; Kelliher et al., 2008; Smith et al., 2008a,b).

Pyrazole derivatives (PD) have also been reported to act as effective NI (e.g. McCarty and Bremner, 1990; Aulakh and Kuldip-Singh Doran, 2001). Piadin® (SKW, Piesteritz, Germany) is a commercial formulation incorporating two active PD compounds: 1H-1,2,4-triazole and 3-methylpyrazole at inclusion rates of approximately 3.1% and 1.6%, respectively, which is marketed as a product to improve N use efficiency and improve crop yields when used with livestock slurry applications to soils.

Most of the previous studies relating to NI use with urine have been conducted under autumn, or spring conditions, which are considered as the key risk times for nitrate leaching in particular for New Zealand grazing management systems, with very few data relate to summer conditions. The objective of the present study, therefore, was to evaluate the effects of these two different NI (DCD and PD) on N₂O emissions from the soil after application of cattle urine under typical UK summer grazing conditions. Significant quantities of urine are returned to the soil by grazing cattle during the summer months (cattle are predominantly housed throughout the winter) when soil temperatures are higher than those under which many previously reported assessments of NI have been conducted. Our evaluation consisted of two experiments: (1) a controlled laboratory incubation experiment; and (2) a replicated small-plot field experiment.

2. Material and methods

2.1. Laboratory experiment

Soil was collected from the 0–10 cm layer from the site at which the field experiment was conducted (see Section 2.2.1). The soil was air dried and manually sieved at 2 mm, mechanically homogenized and stored at 4 °C until required.

2.1.1. Experimental design

The experiment consisted of a soil-only control (C) plus five treatments: soil-urine (U), soil-urine-DCD (U+DCD) and soil-urine-PD with PD applied at three rates of Piadin® solution, 5, 20 and 80 L ha⁻¹ (giving active ingredient application rates of 0.24, 0.94 and 3.76 kg ha⁻¹ of the 1H-1,2,4-triazole and 3-methylpyrazole) for urine low PD (U+LPD), urine medium PD (U+MPD) and urine high PD (U+HPD) treatments, respectively. The DCD was applied at a rate of 10 kg ha⁻¹, in accordance with current commercial guidelines (Moir et al., 2007). The commercial recommended rate for Piadin® as used with livestock slurry is 5 L ha⁻¹ and DCD and Piadin® were incorporated into the urine immediately prior to application to the soil. The urine application was not adjusted to account for N content of the added NI (DCD is 67% N and Piadin is based on a solution of 14% urea-N, 7% ammonium-N and 7% nitrate-N). An equivalent of 6.7 kg N ha⁻¹ was applied as DCD and 1.4, 5.6 and 22.4 kg N ha⁻¹ as Piadin® solution for the LPD, MPD and HPD treatments, respectively.

The urine was obtained from a group of Holstein/Friesian dairy cows. Their diet is based on a grass and maize silage supplemented with concentrates. A composite sample of all urine was made and immediately frozen until required to avoid urea hydrolysis. Immediately prior to application, after the addition of any NI, a subsample of urine was taken from each treatment for analysis of total N content.

The experiment was carried out in a controlled temperature laboratory at a constant temperature of 15 °C. Soil was packed into 0.8 L Kilner jars (5 jars per treatment for N₂O sampling and 1 jar per treatment for soil sampling) with the equivalent of 0.27 kg dry soil per jar to achieve a bulk density of 0.9 g cm⁻³, leaving a headspace volume > 400 cm³. The soil moisture content at packing was such that the soil water-filled pore space (WFPS) after treatment addition would be 60%. The treatments were then applied at a rate of urine equivalent to 5 L m⁻²; the control treatment received an equivalent amount of deionised water instead of urine. The septa from the lids of the Kilner jars were removed between sampling dates to ensure aerobic conditions and development of a uniform headspace above the soil surfaces. During the incubation, the soils were maintained at 60% WFPS for 7 d following urine application, by spraying deionised water onto the soil surface as required (checked through daily weighing of the jars). After 7 d, the WFPS was increased to 80%, representing a significant rainfall event, and maintained at this WFPS until the end of the experiment at 43 d.

2.1.2. Nitrous oxide measurement

For each measurement, the Kilner jars were hermetically sealed by replacing the lids and septa. The initial headspace concentration (time-zero, t₀ sample) was assumed to be the same as the average ambient air value in the controlled temperature laboratory for which 6 samples were taken at Kilner jar height on each sampling occasion (3 at the beginning of sampling and 3 at the end) using a syringe and stored in 60 mL pre-evacuated gas vials. After 30 min the headspace of each jar was sampled again (t₃₀ sample). The jar lids were then removed and kept off until the next sampling day. Nitrous oxide concentrations in the sampled air were measured using a Perkin Elmer Clarus 580 Gas Chromatograph and TurboMatrix 110 auto headspace sampler with an electron capture detector (ECD). The separation column was a Perkin Elmer EliteQ PLOT megabore capillary (30 m × 0.53 mm i.d.), operated at 50 °C. The ECD detector was set at 300 °C and the carrier gas was N₂. Gas fluxes were calculated from the increase in headspace concentration between t₀ and t₃₀, assuming linear increase, and were corrected for temperature according to Eq. (1):

$$F = \rho \frac{V \Delta c}{A \Delta t} \frac{273}{(T + 273)} \quad (1)$$

where F = N₂O flux (mg m⁻² h⁻¹); ρ = density of N₂O (mg m⁻³); V = volume of Kilner jar (m³); A = base area of Kilner jar (m²); $\Delta c / \Delta t$ = average rate of change of concentration with time (ppmv h⁻¹) and T = temperature in the Kilner jar (°C). Gas measurements were carried out daily during the first week of the experiment, then three times per week for the next two weeks, then twice a week up to day 43, when the N₂O emissions had fallen to background levels. Cumulative gas losses between two successive measurement times were calculated as the product of the mean flux rate and the time interval between the measurements. These were then summed to derive total cumulative gas loss for the duration of the experiment.

2.1.3. Soil mineral N and DCD concentrations

To follow the soil mineral N dynamics, narrow core samples were taken from three random points inside the soil sampling jar for each treatment for analysis of NH₄⁺-N and NO₃⁻-N. Samples were

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