# Reducing $N_2O$ emissions from nitrogen fertilisers with the nitrification inhibitor DMPP

**Helen Suter**<sup>A</sup>, Deli Chen<sup>A</sup>, Huilin Li<sup>AB</sup>, Robert Edis<sup>A</sup> and Charlie Walker<sup>C</sup>

#### **Abstract**

Emission of nitrous oxide (N<sub>2</sub>O) from fertilisers applied to soils comes from the process of nitrification, carried out by ammonia oxidizing bacteria (AOB) such as *Nitrosomonas*, and subsequent denitrification. Nitrous oxide emissions from agricultural soils are estimated at around 3% of the total greenhouse gas budget for Australia (Department of Climate Change 2009). A nitrification inhibitor, such as 3,4-dimethylpyrazole phosphate (DMPP) suppresses the activity of the AOB and thereby reduces nitrification and associated losses. This paper reports on a study of the impact of DMPP on N<sub>2</sub>O emissions from four soils fertilised with urea (100-160 kg N/ha) over a range of temperatures (5-35°C) in small scale (40-150g soil) incubation studies. DMPP was highly effective at reducing N<sub>2</sub>O emissions in one soil (Pin Gin, Qld Australia) by more than 93% at 25 and 35°C and temperature had no impact on the reductions. DMPP was less effective in reducing N<sub>2</sub>O emissions from the other soils examined (19-89% reductions) and temperature influenced the reductions. The ability of DMPP to reduce emissions was related to the pH, organic C and mineral N status of the soils examined. The results show that DMPP has the potential to be used as a tool for mitigation of N<sub>2</sub>O emissions from Australian agricultural systems.

## **Key Words**

3,4-dimethylpyrazole phosphate; nitrification rates; incubation studies.

## Introduction

Losses of applied fertiliser nitrogen (N) as leachable nitrate ( $NO_3$ ) and as emissions of nitrogenous gases ( $N_2$ ,  $N_2O$ ,  $NO_x$ ) can occur from both nitrification and subsequent denitrification. There is increasing concern about the contribution of greenhouse gas (GHG) emissions to climate change, from industry, transport and agriculture. Nitrous oxide ( $N_2O$ ) from agricultural soils accounts for 3% of the Australia's total GHG emissions.

One method of reducing N losses from nitrification is to reduce the rate of nitrification by inhibiting autotrophic ammonia oxidizing bacteria (AOB), increasing plant uptake of ammonium (NH<sub>4</sub><sup>+</sup>), and this can be achieved using nitrification inhibitors. Various nitrification inhibitors have been tested in cropping systems and have shown variable reductions in N<sub>2</sub>O emissions (Chen *et al.* 2008; Hatch *et al.* 2005; Li *et al.* 2008; McCarty 1999; Yu *et al.* 2007). This is partly because nitrification inhibitors are affected by soil properties and climatic variables such as temperature and moisture (Barth 2006; Kelliher *et al.* 2008). 3,4-dimethylpyrazole phosphate (DMPP) is one inhibitor which can be used at lower concentrations than other inhibitors with similar results (Zerulla *et al.* 2001).

DMPP has not been tested in Australian dryland agriculture and knowledge of its viability for high temperature situations is unknown, with studies covering temperatures to a maximum of 30°C (Irigoyena *et al.* 2003).

This paper reports on laboratory studies investigating the effect of temperature and DMPP application rate on N<sub>2</sub>O emissions from urea applications to Australian soils, in small-scale incubation experiments.

## Methods

Soils

Soils were collected from a number of locations, air dried and sieved to <2 mm. Table 1 provides details of the soils used.

<sup>&</sup>lt;sup>A</sup>Melbourne School of Land and Environment, The University of Melbourne, Victoria 3010, Australia. helencs@unimelb.edu.au <sup>B</sup>Institute of Soil Science (ISSAS), Chinese Academy of Sciences (CAS), Nanjing 210008.

<sup>&</sup>lt;sup>C</sup>Incitec Pivot Limited, Geelong, Victoria 3215, Australia

Table 1. Selected source and soil properties

	Pin Gin	Mackay	Dookie –topsoil	Dookie-subsoil
Source site	Far northern Queensland	Queensland	Northern Victoria	Northern Victoria
Agricultural activity colour	sugarcane Dark reddish brown	sugarcane Black	pasture Very dark grey	pasture Brown
Texture				
%clay	39	15	21	33
%silt	10	12	28	30
%sand	51	72	50	37
рН	4.5	4.0	5.4	5.5
Org C (%)	3.9	1.5	10.0	2.4
Total N (%)	0.2	0.1	1.0	0.2
Nitrifying potential (mg/kg/day)	1.8	1.2	18	4

## Incubation trials

Soil (40-200g) was pre-wetted 2 days prior to commencement of the experiment. Granular urea was applied at a rate of 100 (pasture soils) and 160 (sugarcane soils) kg N/ha (175 and 1325 ug N/g soil). DMPP was applied as the commercial product Urea with ENTEC<sup>TM</sup> (1.84 kg DMPP active ingredient/t urea (0.7  $\Box$ g DMPP/g soil (pasture) 5.3  $\Box$ g DMPP/g soil (sugarcane)). Urea (1325  $\Box$ g N/g soil) was also applied as a solution with DMPP (2.8  $\Box$ g/g soil) to the sugarcane growing soils for temperature comparison. A control treatment (no fertiliser) was included to measure background N transformations. Samples were incubated at 5, 15, 25 and 35°C and at 60 % water filled pore space (WFPS). Experiments ran for 70 days with sample aeration and water replenishment at regular intervals. Nitrous oxide (N<sub>2</sub>O) samples were collected in triplicate and analysed using a Hewlett Packard 6890 GC with 2 Porapak Q columns and a carbosorb column with an ECD detector. Emissions on a per hectare basis were calculated from the area of the vials (35 cm<sup>2</sup>).

#### Results

Nitrous oxide emissions from the control treatments were generally lower than fertilised soils ( $<2.6 \text{ kg N}_2\text{O}$  /ha) with the exception of the Dookie topsoil (Table 2). Nitrous oxide emissions from the unamended urea were greatest from the Dookie topsoil at 25°C (Table 2) (55 kg N<sub>2</sub>O/ha), followed by the Mackay (11.8 kg N<sub>2</sub>O/ha), Dookie subsoil (10.5 kg N<sub>2</sub>O/ha) and Pin Gin ( $8.0 \text{ N}_2\text{O}$ /ha) soils. The high level of emission from the Dookie topsoil reflects the high emissions from the control treatment for this soil. Emissions of N<sub>2</sub>O from all treatments increased with temperature in the Dookie soils to 25°C but were reduced in the Pin Gin and Mackay soils when the temperature was increased from 25 to 35°C.

Table 2. Cumulative N<sub>2</sub>O emissions after 70 days

Soil	Temperature (°C)	DMPP rate (μg/g soil)	N <sub>2</sub> O (kg/ha)			%
			Control	Urea	Urea + DMPP	reduction with DMPP
Pin Gin	25	2.81	0.0	8.0	0.1	94
	25	11.5	0.0	5.8	0.3	93
	35	2.81	0.0	5.3	0.3	99
Mackay	25	2.81	0.9	12.1	4.4	64
	25	11.5	0.9	11.8	1.3	89
	35	2.81	1.2	7.9	6.3	19
Dookie - topsoil	5	1.6	0.6	1.6	0.6	65
	15	1.6	1.7	4.9	1.9	61
	25	1.6	44	55	35	37
Dookie - subsoil	5	1.6	1.7	3.6	0.8	76
	15	1.6	1.3	7.4	1.9	74
	25	1.6	2.5	10.5	7.2	31

The reduction in  $N_2O$  emissions due to application of DMPP was greatest in the Pin Gin soil (>93%) regardless of application rate or temperature (Table 2). In the Mackay soil the rate of DMPP applied did influence the inhibition achieved, with greater inhibition with higher rates of DMPP (5.3  $\Box$ g/g soil) (89%). In all the other soils increased temperature decreased the degree of reduction in  $N_2O$  emissions as a result of using DMPP, as observed in other studies (Irigoyena *et al.* 2003). At 25°C DMPP reduced  $N_2O$  emissions in the order Pin Gin > Mackay > Dookie topsoil > Dookie subsoil.

Linear regression, excluding the data for the Dookie topsoil, showed that the level of  $N_2O$  emissions measured with DMPP influenced the percentage reduction in  $N_2O$  emissions as a result of using DMPP ( $R^2$ =0.80). However there was no relationship between the level of  $N_2O$  emissions measured for urea and the percentage reduction in emissions due to DMPP, and no relationship between emissions from urea treatments and emissions from DMPP treatments.

Soil pH appeared to influence the level of reduction in  $N_2O$  emissions with less emission in the highly acidic Mackay soil compared to the Pin Gin soil. Soil texture may also influence inhibition with less inhibition in the sandier soil from Queensland (Mackay) than in the clayey soil (Pin Gin). The level of organic C and mineral N also influenced the level of emissions and the reduction achieved, with a high level of organic matter, such as found in the Dookie topsoil, leading to high emissions of  $N_2O$  and a lower ability for the DMPP to reduce these emissions. Where a greater number of AOB exist, greater levels of DMPP may achieve similar levels of inhibition as seen in less organic soils such as the Pin Gin. The composition of the biological community in the soil is likely to influence the level of reduction achieved also both in terms of numbers of heterotrophic and autotrophic organisms and also in the composition of the autotrophic populations.

#### Conclusion

Reductions in N<sub>2</sub>O emissions with addition of DMPP to urea from four different soils at 60% WFPS and at temperatures of 5 to 35°C ranged from 19 to 99%. DMPP was very effective in reducing N<sub>2</sub>O emissions compared to urea, by more than 93% in a sugarcane growing soil from far northern Queensland (Pin Gin) under all conditions. DMPP was able to reduce N<sub>2</sub>O emissions in another sugarcane growing soil but to a lesser extent (19 to 89%) and in pasture soils from Victoria (31-76%), and the level of reduction in these instances was decreased with increasing temperature.

Soil pH, texture and organic C content are considered to be the factors influencing the level of N<sub>2</sub>O emissions seen and the degree of reduction shown with the addition of DMPP.

## References

- Barth G (2006) Influence of soil properties on the effect of 3,4 dimethylpyrazole phosphate as nitrification inhibitor. Technischen Universität München.
- Chen D, Suter HC, Islam A, Edis R, Freney JR (2008) Prospects of improving efficiency of fertilizer nitrogen in Australian agriculture; a review of enhanced efficiency fertilizers. *Australian Journal of Soil Research* **46**, 289-301.
- Department of Climate Change (2009) 'Australia's national greenhouse accounts: National Greenhouse Gas Inventory accounting for the KYOTO target May 2009.'
- Hatch D, Trindade H, Cardenas L, Carniero J, Hawkins J, Scholefield D, Chadwick D (2005) Laboratory study of the effects of two nitrification inhibitors on greenhouse gas emissions from slurry-treated arable soil: impact of diurnal temperature cycle. *Biology and Fertility of Soils* **41**, 225-232.
- Irigoyena I, Muro J, Azpilikueta M, Aparicio-Tejo P, Lamsfus C (2003) Ammonium oxidation kinetics in the presence of nitrification inhibitors DCD and DMPP at various soil temperatures. *Australian Journal of Soil Research* **41**, 1177-1183.
- Kelliher FM, Clough TJ, Clark H, Rys G, Sedcole JR (2008) The temperature dependence of dicyandiamide (DCD) degradation in soils: A data synthesis. *Soil Biology and Biochemistry* **40**, 1878-1882.
- Li H, Liang X, Chen Y, Lian Y, Tian G, Ni W (2008) Effect of nitrification inhibitor DMPP on nitrogen leaching, nitrifying organisms, and enzyme activities in a rice-oilseed rape cropping system. *Journal of Environmental Sciences* **20**, 149-155.
- McCarty GW (1999) Modes of action of nitrification inhibitors. Biology and Fertility of Soils 29, 1-9.
- Yu Q-G, Chen Y-X, Ye X-Z, Tian G-M, Zhang Z-J (2007) Influence of the DMPP (3,4-dimethyl pyrazole phosphate) on nitrogen transformation and leaching in multi-layer soil columns. *Chemosphere* **69**, 825-831.
- Zerulla W, Barth T, Dressel J, von Locquenghien KEKH, Pasda G, Rädle M, Wissemeier AH (2001) 3,4-Dimethylpyrazole phosphate (DMPP) a new nitrification inhibitor for agriculture and horticulture. *Biology and Fertility of Soils* **34**, 79-84.