Stabilized Nitrogen Fertilizers to Reduce Greenhouse Gas Emissions and Improve Nitrogen Use Efficiency in Australian Agriculture

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ABSTRACT

Loss of nitrogen (N) from applied fertilizer is a major cause of inefficiency in N fertilizer utilization. This loss of N can occur through many pathways including ammonia (NH_3) volatilization, nitrate (NO_3^-) leaching and emissions of gases such as nitrous oxide (N_2O). One way of addressing these losses is to amend N fertilizers with compounds that slow the production of the forms of N that can be lost. Two such compounds are urease inhibitors, designed to reduce NH_3 loss, and nitrification inhibitors, designed to reduce NO_3^- leaching and gaseous emissions. However, the impact of these compounds on N loss is variable across soil type, region, cropping system and temperature. An examination of where these compounds may be beneficial requires detailed laboratory investigation plus field validation. This paper reports on the results of experiments performed under both laboratory and field conditions and draws conclusions regarding the suitability of these compounds for improving N use efficiency in Australian agriculture.

INTRODUCTION

Nitrogen (N) use efficiency from applied fertilizer in a variety of Australian agricultural systems ranges from 8 to 88 percent with an average of around only 50 percent of the N recovered in the plant (Chen *et al.*, 2008). Losses from applied N fertilizers occur mostly as gaseous emissions (ammonia [NH_3], nitrous oxide [N_2O] and other gases [N_2, NO_x]) or nitrate (NO_3^-) leaching. Some fertilizer N is retained by the soil where it is either immobilised or remains available for later crop use. Losses of up to 30 percent of applied N as NH_3 have been reported from pasture systems in Australia (Eckard *et al.*, 2003; Prasertsak *et al.*, 2001). Denitrification, can also be a major pathway of N lost as N_2O, N_2 and NO_3^- during periods of irrigation or waterlogging, with losses of up to 80 percent of applied N recorded in irrigated cotton (Chen *et al.*, 1994). In Australia, N_2O emissions from agriculture account for 71 percent of the national total. Fertilizer usage is a major contributor, with current fertilizer emission factors for N_2O ranging from 0.05 to 2.8 percent (DCCEE, 2011).

Use of stablized N fertilizers, those treated with urease and/or nitrification inhibitors, is one approach to reduce N losses from fertilizers and to mitigate both direct (N_2O) and indirect (NH_3) nitrogenous greenhouse gas emissions from agriculture. The urease inhibitors work by slowing the pathway of N transformations through inhibition of the activity of the urease enzyme which is involved in hydrolyzing urea. The nitrification inhibitors suppress the activity of NH_3 oxidizing bacteria and hence slow the conversion of NH_3 to nitrite and subsequently NO_3^-. Research has found that the impact of these inhibitors in reducing N loss and improving crop yield is highly variable with temperature and soil type (Carmona *et al.*, 1990; Barth 2006).

Australia has a wide range of climatic conditions and soil types and hence the few studies examining the use of stabilized fertilizers are not sufficient to assess comprehensively their potential use across Australian agricultural systems.

This research presents findings from laboratory and field experiments investigating the impact of stabilized fertilizers on N transformations and losses on a range of soil types from different regions in Australia, covering pasture, cropping and sugarcane production systems. The stabilized fertilizers used were urea treated with the urease inhibitor *N*-(n-butyl) thiophosphoric triamide (NBPT), and the nitrification inhibitors dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP) and nitrapyrin (N-serve).

MATERIALS AND METHODS

Laboratory incubation experiments

Air-dried and sieved (< 2mm) top soil (0–20 cm depth from sugarcane sites and 0–10 cm from all others) was placed into an incubation vessel (250–500 mL capacity) and pre-wetted to 60 percent water filled pore space for all experiments.

Soils of varying physical and chemical properties were collected from both pasture (dairy) and cropping sites in Victoria, Australia (Table 1) for assessing the impact of the urease inhibitor NBPT on urea hydrolysis rates. The methodology followed that described in Suter *et al.* (2011) with slight modifications for soil mass (40 to 150 g of oven-dried equivalent used), N application rate, temperature of incubation (5, 15, 25 and 35 °C) and extraction soil:solution ratio (1:5 for all except those reported in Suter *et al.*, 2011). Urease activity was measured following the method of Douglas and Bremner (1971). The minor variations in methodology as described above were not considered to have a major influence on the results achieved because the trends observed for different soil types were consistent, and so it is possible to compare results from all experiments.

For experiments on the impact of nitrification inhibitors (DCD, DMPP and N-serve) on nitrification rates and N_2O emissions, urea with or without the nitrification inhibitors was applied either as a buried granule or as a liquid. Five different soils, three from Victoria and two from Queensland were examined. The selected properties

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L.K. Heng, K. Sakadevan, G. Dercon and M.L. Nguyen (eds), Proceedings — International Symposium on Managing Soils for Food Security and Climate Change Adaptation and Mitigation. Food and Agriculture Organization of the United Nations, Rome, 2014: 33–36

TABLE 1. Selected properties of soils used for the urease inhibitor incubation experiments

Soil	Soil texture	Industry	pH_w	Clay (%)	Silt (%)	Sand (%)	Organic C (%)	Urease activity (mg urea-N/g soil/h)
1	Clay loam	Dairy	5.5	20	25	55	3.9	134
2	Fine sandy clay loam	Dairy	5.4	21	28	51	10*	186
3	Silty loam	Dairy	5.5	22	38	40	2.4	97
4	Clayey sand	Cropping	7.8	9	2	89	1.3	54
5	Medium clay	Cropping	8.1	37	24	39	1.0	78
6	Medium clay	Cropping	8.1	39	21	40	1.3	90

*Note: this soil included the pasture thatch layer and hence a large organic component

TABLE 2. Selected properties of the soils used for nitrification inhibitor incubation experiments

Soil no.	Soil texture	Region	Industry	pH_w	Clay (%)	Organic C (%)
7	Clay loam	Queensland	sugarcane	5.3	39	1.9
8	Loam	Queensland	sugarcane	4.8	13	1.5
9	Fine sandy loam	Victoria	dairy	5.4	21	10
10	Medium clay	Victoria	dairy	5.5	33	2.4
11	Clay loam	Victoria	grains cropping	7.8	30	1.3

*Note: this soil included the pasture thatch layer and hence a large organic component

of these soils are provided in Table 2. The methodology followed for the cropping soil from Victoria is provided in Chen *et al.* (2010) and the studies on the pasture and sugarcane soils followed a similar method with the modification of soil mass used (40 and 80 g of oven dried equivalent for the sugarcane and pasture soils, respectively) and soil:solution ratio of the extraction (1:5).

Field experiments

A field experiment was conducted on a ryegrass seed crop in Victoria, Australia where NH_3 loss, N_2O emissions, soil mineral N transformation and biomass production were measured regularly over an eight-month period where regular fertilization occurred. Details of the soil properties at the field site and the methodology used for the NH_3 volatilization study are reported in Suter *et al.* (2013). Another NH_3 volatilization field experiment was conducted on cropping soils from southern Australia and details of the methodology are reported in Turner *et al.* (2010).

The N_2O emissions from surface applied granular urea with and without the addition of the nitrification inhibitor DMPP were investigated using manual chambers (23 cm diameter, 25 cm height) in a small (2 x 1 m) plot trial in the ryegrass seed crop experiment. Fertilizer was applied every 1 to 2 months while the pasture was cut to five cm height above ground level to simulate grazing in the same period. A nitrogen-15 (^{15}N) micro-plot (25 cm internal diameter × 20 cm depth) study using ^{15}N granular urea to determine the fate of applied fertilizer N was also conducted at the ryegrass seed crop site and is described in Suter *et al.* (2013).

RESULTS AND DISCUSSION

Urease inhibitors

In the laboratory incubation experiments, use of NBPT reduced urea hydolysis across all soil types examined, with the level of reduction dependent upon soil properties including soil urease activity and temperature. Typical responses from pasture and cropping soils are shown in the data provided for two of the soils (Soils 1 and 4) in Figure 1. In the cropping soils (Soils 4, 5 and 6), NBPT was found to reduce urea hydrolysis rates markedly under cooler conditions, but increasing temperature reduced the level of inhibition. In the more organic pasture soils (Soils 1, 2 and 3), the trend was for rapid urea hydrolysis for both urea and urea with the added NBPT. The differences in urea hydrolysis and in the impact of NBPT between the soils are attributed mainly to the urease activity (54–90 mg urea-N g·soil/h measured in cropping soil compared with 134–186 mg urea-N g·soil/h in pasture soils).

In field experiments on cropping soils, NBPT reduced NH_3 loss from urea by 89 percent compared with no NBPT (from 10 to 1 percent of applied N lost) (Turner *et al.,* 2010), and on pasture soils by between 42 and 67 percent depending upon the season (reducing losses from 30 to 9 percent of applied N in autumn and from 2 to 1 percent of applied N in spring) (Suter *et al.*, 2013). These results show that the urease inhibitor NBPT can reduce N losses in high urease activity systems. Despite the large N saving with the use of the urease inhibitor, biomass production was not altered in the pasture site. This is likely due to the presence of sufficient N in the soil to support the pasture growth, as indic ated by the results obtained from the ^{15}N micro-plot study which showed that of the total N taken up by the plant (52 kg·N/ha in the biomass) the fertilizer supplied only around 30 percent (17.7 kg·N/ha) of the required N to the plant (Suter *et al.,* 2013). Of the applied ^{15}N, 27 percent was unaccounted for and considered to be lost as NH_3 based on measured loss of NH_3 on the site of 30 percent of applied N, 42 percent was taken up by the plant and the remainder (31 percent) was found in the soil.

Nitrification inhibitors

Nitrification inhibitors (DCD, DMPP and N-serve) were found to reduce N_2O emissions across a range of soils, temperatures and moisture contents by between 15 and 98 percent in laboratory experiments, whilst their impact on NO_3^- production was variable (Table 3). The reason for the variability between soil types could not be clearly identified from the dataset developed to date. It is hypothesized that

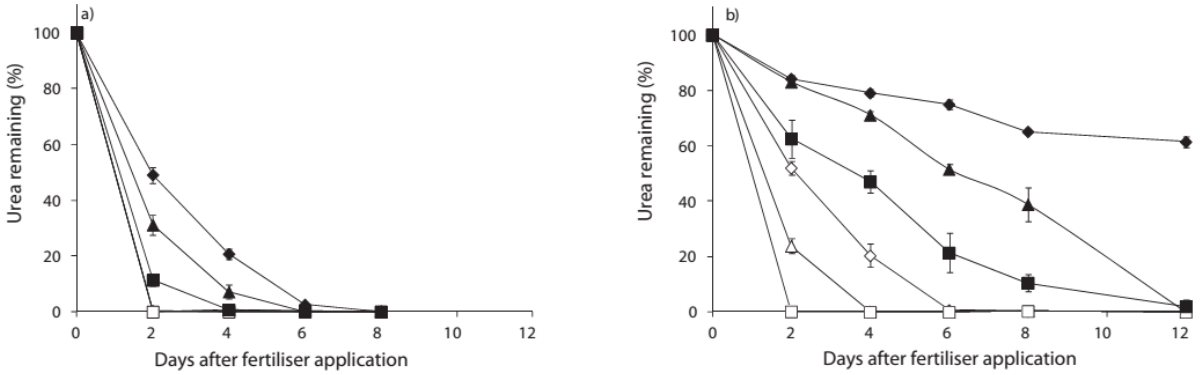

FIGURE 1. Urea remaining in soil during incubation for: (a) clay loam dairy pasture soil (Soil 1), and (b) clayey sand wheat cropping soil (Soil 4), with application of granular urea with and without NBPT. Urea at 15°C (◇), 25°C (Δ)and 35°C (□); Urea + NBPT at 15°C (◆), 25°C (▲) and 35°C (■)

TABLE 3. Summary of incubation experiments with Queensland and Victorian soils showing the effect of nitrification inhibitors on NO_3^- formation and cumulative N_2O emissions over the indicated range of temperatures. Note the values presented are percent reduction relative to the control.

Soil texture	Region	Temp. (°C)	NO_3^- reduction (%)			N_2O reduction (%)		
			DMPP	DCD	N-serve	DMPP	DCD	N-serve
Clay loam	Queensland	25–35	> 85	—	—	> 94	—	—
Loam	Queensland	25–35	0	—	—	19–64	—	—
Fine sandy loam	Victoria	5–25	0	0	—	36–68	15–83	—
Medium clay	Victoria	5–25	0–51	0–81	—	31–76	44–88	—
Clay loam	Victoria	5–25	4–70	—	83–98	> 95	—	> 95

the soil microbial community may have an important role in determining whether the inhibitors work as they are only considered to target the autotrophic NH_3 oxidizing bacteria whilst other microbes such as heterotrophic bacteria or archaea can perform the same function and are not affected by the inhibitors (Amberger 1993; Di *et al.,* 2010). Differences in soil properties such as texture, carbon, pH and nutrient status, will impact on the microbes found in the soils and consequently the response to the use of the inhibitors (Nicol *et al.,* 2008).

In the field experiment on the ryegrass seed crop, the use of the nitrification inhibitor DMPP reduced the fertilizer induced N_2O emissions over an eight-month period by 64 percent. The greatest impact was seen during spring when soils that were saturated over winter were drying and soil temperatures were warming. The saved N from reduced N_2O emissions did not translate into increased biomass as the amount lost was small relative to the amount applied. No other nutrient limitation to plant growth (such as phosphorus, sulphur and potassium deficiency) was observed on-site. At this site, NO_3^- leaching was considered to be minimal due to the nature of the soils (texture contrast) and the site topography (flat to slightly undulating). This helps to explain the lack of observed difference in biomass production with the use of the nitrification inhibitor.

CONCLUSIONS

Stabilized fertilizers, those amended with urease or nitrification inhibitors, show promise for reducing N losses from applied fertilizers and mitigating emissions of both N_2O and NH_3 gases in targeted Australian agricultural industries. Further research is required into the productivity effects of the use of urease inhibitors, the variable response seen with the nitrification inhibitors and the role of the soil microbial community in nitrification inhibition.

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