Understanding the variability in performance of the nitrification inhibitor 3,4-Dimethylpyrazole phosphate in Australian agricultural soils

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Abstract

The nitrification inhibitor 3,4-Dimethylpyrazole phosphate (DMPP) is being widely used across Australian agricultural systems to reduce nitrogen loss from soils, particularly targeting the greenhouse gas nitrous oxide, and to improve nitrogen use efficiency. However, the effectiveness of DMPP is variable and the reason for this has been unclear. A laboratory investigation was undertaken using 30 soils collected from a range of agricultural land uses to identify the key drivers influencing the performance of DMPP. Average nitrification over 14 days across all treatments ranged from -4.61 to 26.89, with a median of 2.57 µg NO_3^-N produced/g soil/day. Cumulative N_2O emissions ranged from 0.01 to 7.74 µg N_2O-N/g soil. However only 3 soils contributed to high emissions and the remaining soils had < 0.63 µg N_2O-N/g soil. DMPP effectively reduced average nitrification by 9-100% (average of 42%) and N_2O emissions by 0-100% (average of 55%) Only manganese and the interaction between organic C and clay influenced DMPP's efficacy at reducing nitrification, having a negative impact. The efficacy of DMPP at inhibiting N_2O emissions was positively related to pH, Cu and Zn and negatively related to Fe. The results suggest that further investigation of the soil metal-inhibitor interaction, and the role of metals in soil microbial function (nitrifiers and denitrifiers) is required to understand when the DMPP will work best.

Key Words

3,4-Dimethylpyrazole phosphate, nitrification inhibitor, nitrification, soil properties

Introduction

Fertiliser nitrogen recovery in Australian agriculture is often low (<50% recovery) with loss occurring through multiple pathways, including nitrate leaching and denitrification, with the potent greenhouse gas, nitrous oxide (N_2O) produced from nitrification and denitrification. Australian agriculture accounts for 76% of the national total N_2O emissions, with around 50% of this from mineral fertiliser application (DCCEE 2011). Nitrification inhibitors have the potential to reduce nitrate leaching and N_2O losses from agriculture, however their effectiveness is not consistent across different soils, crops and climates (Chen et al. 2008). The nitrification inhibitor 3,4-Dimethylpyazole phosphate (DMPP) is a readily available nitrification inhibitor currently used in Australia with varying effect. Previous studies have found that particular soil properties influence the efficacy of DMPP, however the observed relationships do not appear to hold in Australian soils (Barth et al. 2001). The interactions of DMPP and other nitrification inhibitors with soil properties and how this influences their effectiveness is complex, and a more complete understanding is necessary before nitrification inhibitors can be established in mitigation methodologies in Australia.

A laboratory incubation experiment was conducted utilising 30 soils sourced from Australian agricultural systems to investigate the impact of the nitrification inhibitor DMPP on nitrification rates and N_2O emissions with the view to identifying key soil properties that influenced the efficacy of DMPP.

Methods

Thirty soil samples with variable properties were collected from different locations in Victoria, South Australia, NSW, Qld and Tasmania from different land uses (dairy pasture (6), cropping (15), vegetables (5), sugarcane (4)). The soils ranged in clay content from 1 to 83%, sand content from 7 to 91%, CEC from 2.6 to 60.4 meq/100g soil, pH (water) from 4.6 to 8.5, organic C (OC) from 0.6 to 5.6%, total N from 0.1 to 0.6%, sulfate S from 4.1 to 520 mg/kg, DTPA manganese (Mn) 0.9 to 140 mg/kg, DTPA Copper (C) 0.24 to 13 mg/kg, DTPA iron (Fe) 7.6 to 490 mg/kg and DTPA zinc (Zn) 0.4 to 19 mg/kg (Figure 1).

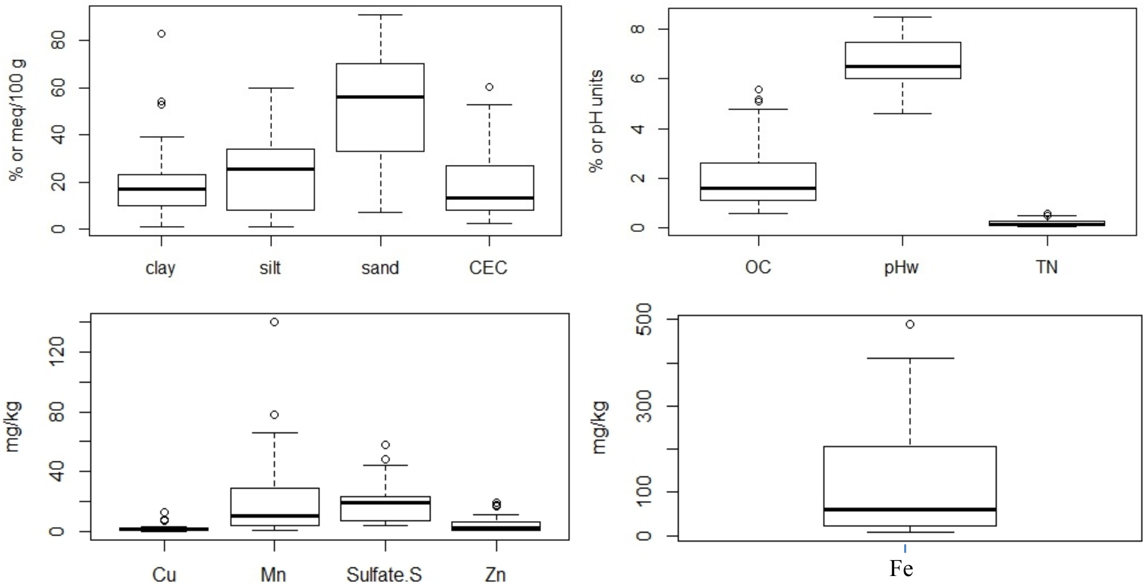

Figure 1. Boxplot of selected soil properties (note: outlier of Sulfate S of 520 for one soil removed).

Soil samples (air dried and sieved (<2mm), 60 g oven dried equivalent) were placed into 500 ml vials, pre-wetted to just below their final moisture content (60 % WFPS), and incubated at 25^{o}C for 3 weeks prior to commencement of the fertiliser treatment. After 3 weeks, on day 0 of the experiment, the treatments were applied in solution to achieve a final moisture of 60% WFPS. Treatments applied were 1) Control (no nitrogen), 2) 100 mg nitrogen (N) / kg soil in ammonium (NH_4^+) form (Fertiliser), and 3) 100 mg nitrogen (N) / kg soil in ammonium (NH_4^+) form plus DMPP (0.7% active per unit NH_4^+-N) (DMPP).

Samples were incubated for 28 days at 60% WFPS and 25^{o}C and replicated 4 times. Mineral N (2M KCl extract 1:5 soil:solution) and N_2O samples were collected at regular intervals. Average nitrification rates were determined over 14 days (except for 2 soils where nitrification was delayed and an average over 22 days was used) when the rate of NO_3^- production remained linear. Net nitrification of the fertiliser treatments (F and DMPP) was calculated to account for NO_3^- production from indigenous N. Cumulative N_2O emissions were calculated after the fertiliser induced N_2O flux was completed and net-N_2O emissions were calculated to determine the fertiliser induced emissions.

Statistical analysis was performed with one-way ANOVA using Minitab 17 after ensuring normality of the data using the Ryan-Joiner test. Cumulative N_2O data was not normally distributed and statistical analysis was performed using the $\log_{10}$ transformed data. The importance of soil properties and N processes on the reduction in nitrification rates or N_2O emissions was determined using multiple linear regression in R studio (Version 0.97.248).

Results

Average nitrification rates over 14 days ranged from 0 to 27 µg NO_3^-N produced/ g soil/ day for all treatments (Table 1) and averaged 1.37 (Control), 6.47 (Fertiliser) and 4.00 (DMPP) µg NO_3^-N produced g $soil^{-1}$ day^{-1}. One soil had substantially higher average nitrification (Control; 26.89, Fertiliser; 25.45, DMPP; 22.02 µg NO_3^-N produced / g soil/ day) than the others (Figure 2). This soil was an acidic (pHw 4.9), organic (4.8% OC) sandy loam cropping soil with high background NH_4^+-N (31 µg/g soil) and nitrate (NO_3^-)-N (180 µg/g soil), high sulfate S (48 mg/kg), DTPA Mn (140 mg/kg) and Fe (290 mg/kg). Excluding this soil, the nitrification rate of the remaining 29 soils was in the range of 0-15 µg NO_3^-N produced / g soil/ day. The median average nitrification was 0.43, 5.54 and 3.09 µg NO_3^-N produced / g soil/ day for the Control, Fertiliser and DMPP treatments respectively (Figure 2a). The average nitrification rate was significantly ($P<0.05$) higher in the F treatment compared to the control.

DMPP reduced average nitrification over 14 days from 6.47 to 4.00 µg NO_3^-N produced / g soil/ day, an average reduction of 38 % compared to the Fertiliser treatment, with the range from 9 % reduction to complete inhibition. DMPP significantly ($P<0.05$) reduced net-nitrification (Table 1). There were slight differences in the inhibition achieved with DMPP across the different landuse soils, ranging from 0-95% (average of 46%) in the cropping soils, 14-94% (average of 43%) in the dairy pasture soils, 61-82% (average of 63%) in the sugarcane soils, and 0-92% (average of 35%) in the vegetable soils. Multiple linear regression found that the reduction in average nitrification with DMPP was significantly negatively related to the clay and OC interaction ($P<0.05$) and to a lesser extent Mn content ($P<0.1$). Both clay and organic matter have been reported to impact the efficacy of nitrification inhibitors by either binding the inhibitor and thereby making it less effective or protecting the inhibitor from degradation (Barth et al. 2001; Zhang et al. 2004; McGeough et al. 2016). Other soil properties have been identified as influencing the efficacy of DCD such as oxalate extractable iron (Fe) and aluminium (Al), and copper (Cu) (McGeough et al. 2016). Manganese at levels of around 120 ppm or above (DTPA soluble) has been found to inhibit nitrification and additions of 100 ppm of N stimulated mineralisation in a silt loam soil (Chang and Broadbent 1982). In our soils, the soil with highest Mn had significantly higher rates of nitrification than the other soils examined, including from the Control. In our study Mn was found to significantly decrease the inhibition of nitrification by DMPP even when the high Mn soil was excluded from the statistical analysis, which is expected based on the previous reported studies in the literature. If Mn inhibits nitrification, then when Mn is high, inhibition may occur even without the addition of DMPP, so DMPP may appear to be less effective. However this relationship between Mn and nitrification is still not clear, for example we observed high nitrification in the high Mn soil, and it is likely confounded by the influence of other soil properties which warrants further investigation. We also observed a weak positive correlation between the reduction in nitrification with DMPP and DTPA Cu ($R^2=0.236$).

Cumulative N_2O emissions from the soils ranged from 0.01 to 7.74 μg N_2O-N/g soil (equal to 0.83 to 1298 g N_2O-N/ha) across all treatments (Table 1). Three soils were responsible for the high emissions and the remaining soils (89% of the sample size) recorded emissions between 0.01 and 0.63 μg N_2O-N/g soil. These high emissions soils were all cropping soils and were an alkaline (pHw 7.5) low OC (1.1%) sand (89%) from central NSW (0.9 (Control), 7.74 (Fertiliser), 6.69 (DMPP) μg N_2O-N/g soil), an acidic (pHw 5.4), organic (3.1% OC) sandy loam from western Victoria that had recently been converted from pasture to cropping (1.11 (Control), 2.39 (Fertiliser), 2.52 (DMPP) μg N_2O-N/g soil), and an acidic (pHw 5.8), low OC (1.6%) sandy loam from southern NSW (0.86 (Control), 1.61 (Fertiliser), 0.87 (DMPP) μg N_2O-N/g soil). The range of N_2O emissions for the Control, Fertiliser and DMPP treatments, excluding the 3 soils mentioned, is shown in Figure 2b. DMPP reduced fertiliser induced N_2O emissions over 28 days by on average 55 % compared to the F treatment, with the range from zero to 100% reduction.

The $\log_{10}$ transformed N_2O data showed use of DMPP significantly ($P<0.05$) reduced fertiliser induced N_2O emissions to a similar level to that seen in the Control (Table 1). A multiple linear regression showed that pHw ($P<0.01$), DTPA Zn and Mn ($P<0.05$) positively affected the reduction in N_2O emissions achieved with the DMPP, whilst DTPA Fe ($P<0.01$) had the reverse effect. As expected DTPA Fe and pHw are inversely correlated ($R^2=0.58$). McGeough et al. (2016) reported a similar influence of primarily oxalate extractable Cu, but also Fe, on DCD efficacy. A recent review discussed the role of Fe in the reduction of nitrite (NO_2^-) and production of N_2O (Heil et al. 2016), however in our study we did not find any significant correlation between Fe and N_2O, but did for Zn ($P<0.1$).

Table 1. Average nitrification over 14 days (for all but 2 soils which was over 22 days), and cumulative N_2O emissions

Average nitrification (μg NO_3^-N produced/g soil/day)			N_2O emissions * (μg N_2O-N/g soil)		
Treatment	Range	Average ± standard error	range	Average ± standard error	Log_{10}
Control	-4.61-26.89	1.37 ± 0.99^{a}	0.01-1.1	0.06±0.30	-1.20 ± 0.64^{a}
Fertiliser	1.33-25.45	6.47 ± 0.93^{b}	0.07-7.74	0.62±0.28	-0.59 ± 0.45^{b}
DMPP	-0.43-22.02	4.00 ± 0.78^{ab}	0.01-6.96	0.49±0.26	-0.92 ± 0.64^{ab}
	Average net-nitrification			Net-N_2O emissions **	
Fertiliser	-1.44-12.63	4.82 ± 0.55^{b}	-0.10-9.54	0.71±0.39	-0.57 ± 0.48^{a}
DMPP	-4.86-8.02	2.39 ± 0.45^{a}	-0.01-10.75	0.52±0.35	-1.17 ± 0.78^{b}

*n=28,** n=27

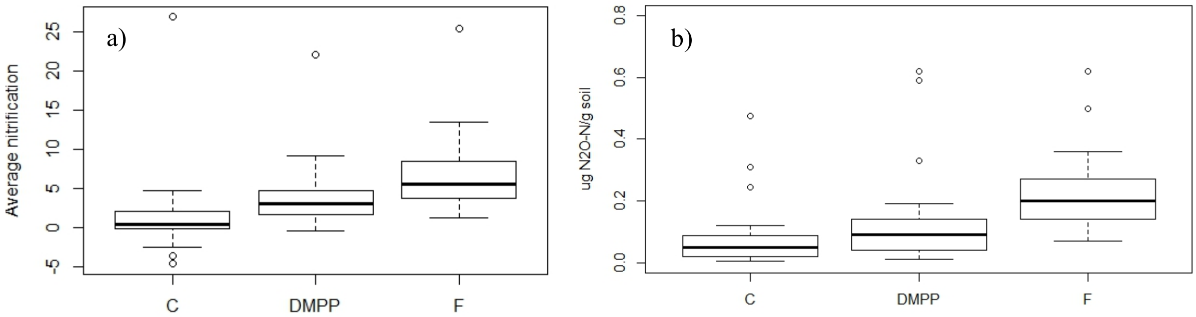

Figure 2. a) Average nitrification (µg NO_3^-N produced/g soil/day), and b) Cumulative N_2O emissions (excluding the three high N_2O emitting soils), for the Control (C), Fertiliser (F) and DMPP treatments across all soils.

Conclusion

The findings from this work show that DMPP is an effective tool for reducing nitrification and N_2O emissions across Australian agricultural soils with different land use and different soil properties. The influence of soil properties on the effectiveness of DMPP requires further consideration of the importance of properties other than organic matter and pH, and the role of soil trace elements and metals for their interactions with the inhibitor, and on soil microbial function.

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