

## AN ASSESSMENT OF THE THRESHOLD CONCENTRATIONS OF NITRIFICATION INHIBITORS TO REDUCE URINE NITROGEN NITRIFICATION RATES ON PASTURE SOILS

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### Abstract

Information on the threshold concentrations of nitrification inhibitors (NIs) to reduce urine nitrogen (N) nitrification rates is required for the targeted treatment of urine patches to mitigate gaseous and leaching losses of N to the environment. This study measured the threshold concentrations of three NIs: dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP) and 2-chloro-6-(trichloromethyl) pyridine (nitrapyrin) to reduce urine N nitrification rates on two contrasting pasture soils. Four rates of each NI (3-27 mg DCD kg<sup>-1</sup> soil, 1-13 mg DMPP kg<sup>-1</sup> soil and 1-14 mg nitrapyrin kg<sup>-1</sup> soil) were added to urine-amended soils and incubated at laboratory room temperature. The amended soils were sampled periodically to monitor changes in mineral-N concentrations. Under the experimental conditions, the threshold concentrations of the NIs required to reduce urine N nitrification rates on the examined pasture soils are equivalent to 13 kg DMPP ha<sup>-1</sup> soil, 5-7 kg nitrapyrin ha<sup>-1</sup> soil and 3 kg DCD ha<sup>-1</sup> soil, assuming a soil bulk density of 1000 kg m<sup>-3</sup> in the top 0.1 m soil depth. Greater NI efficacy corresponded to greater NI persistence, with higher ( $p < 0.05$ ) half-life values observed for DCD ( $16 \pm 2$  days, mean  $\pm$  s.e.) compared with nitrapyrin ( $10 \pm 2$  days) and DMPP ( $9.2 \pm 0.3$  days). All three NIs persisted longer ( $p < 0.05$ ) with higher application rates.

### Introduction

A targeted management approach is required when using nitrification inhibitors (NIs) for the mitigation of nitrous oxide (N<sub>2</sub>O) emissions from livestock urine deposited on pasture soils. This approach involves applying the right amount of an ideal NI directly onto the urine patch at the right time to maximise NI effectiveness while limiting any unintended consequences on non-target organisms and the environment (Adhikari *et al.*, 2021). Thus, targeted urine patch treatment would limit the risk of NI transfer into the food chain as was reported for dicyandiamide (DCD), which is no longer commercially available in New Zealand.

In addition to DCD, other commonly used NIs include 3,4-dimethylpyrazole phosphate (DMPP) and 2-chloro-6-(trichloromethyl) pyridine (nitrapyrin), but there is very limited information on the use of these alternative NIs on livestock urine. Specifically, there is no information on the threshold concentrations of DMPP and nitrapyrin (relative to DCD) to reduce urine nitrogen (N) nitrification rates on pasture soils. Because this information is

required to achieve targeted urine patch treatment, the current research was designed to help fill this knowledge gap.

## Materials and methods

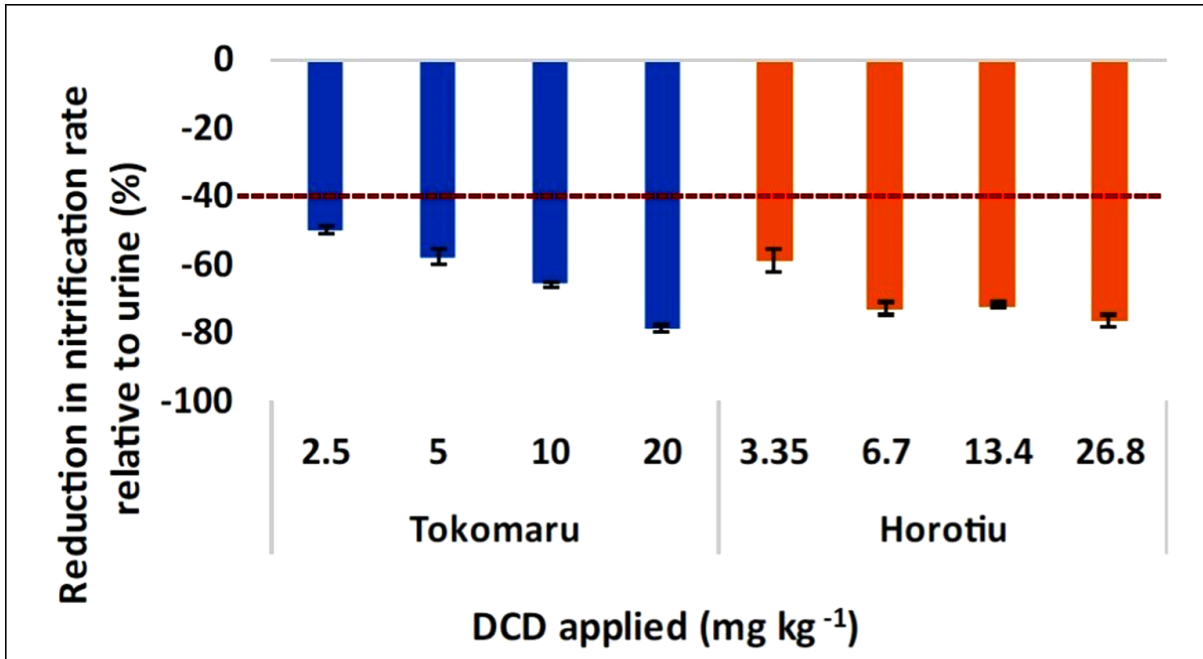
Two dairy pasture soils contrasting in organic carbon (C) and clay contents were used in this study. The soils – Tokomaru (total C: 33.8 g kg<sup>-1</sup>; clay: 24%) and Horotiu (total C: 119.2 g kg<sup>-1</sup>; clay: 12%) were sampled from the surface 10 cm soil depth, sieved (2 mm) and preincubated for 2 weeks to stabilise the microbial population. Thereafter, four rates of DMPP (1-13 mg DMPP kg<sup>-1</sup> soil) and nitrapyrin (1-14 mg nitrapyrin kg<sup>-1</sup> soil) were applied to the soils amended with fresh dairy cattle urine (approximately 1000 mg N kg<sup>-1</sup>, averaged across soils). DCD (3-27 mg DCD kg<sup>-1</sup> soil) was used as a reference NI. The treatments (4 replicates) were incubated at laboratory room temperature (20-21°C) and maintained at a constant soil moisture (70-80% field capacity). They were sampled periodically for mineral-N and NI concentrations which were used to calculate the nitrification rate and NI half-life, respectively. For more details on this experiment, the reader is referred to the published manuscript (Chibuike *et al.*, 2022).

To establish the ‘threshold concentration’, a literature review (Adhikari *et al.*, 2021) was conducted which identified field studies that used either DMPP (2 publications), nitrapyrin (4 publications) or DCD (41 publications) to manage N<sub>2</sub>O emissions from livestock urine. The review showed that the effectiveness of DMPP, nitrapyrin and DCD to reduce N<sub>2</sub>O emissions from urine was 28 ± 38% (mean ± s.e.), 28 ± 5% and 44 ± 2%, respectively. Given the larger number of publications on DCD relative to DMPP and nitrapyrin, the higher reduction achieved by DCD was chosen when defining the threshold concentration. Thus, in this study, threshold concentration is the minimum concentration of the NI that can achieve at least 40% reduction in nitrification rate (relative to the urine-only treatment) within the first 2-3 weeks of their application. The duration (2-3 weeks) was chosen based on the specific NI persistence in the soil.

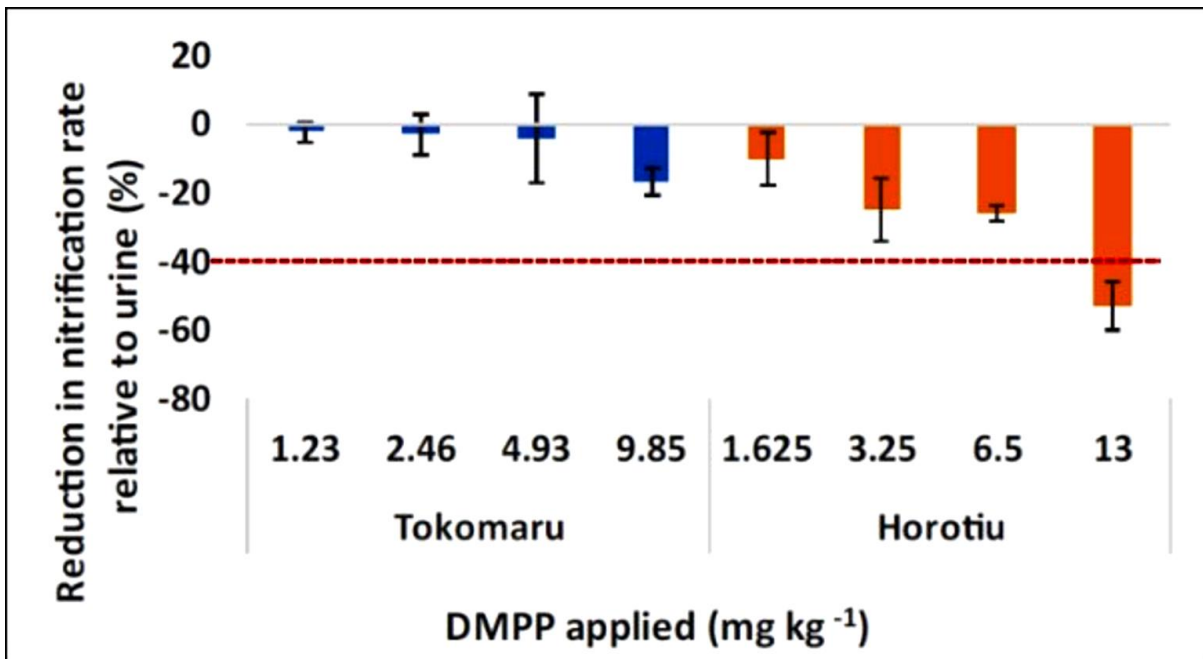
## Results and discussion

DCD efficacy was 50-79% on the Tokomaru soil and 59-77% on the Horotiu soil (Figure 1). Approximately 3 mg DCD kg<sup>-1</sup> soil (lowest concentration tested) was the threshold concentration required to reduce urine N nitrification rates on both soils. Higher DCD application rates achieved greater ( $p < 0.05$ ) nitrification inhibition on both soils.

DMPP was not as effective as DCD, with an efficacy of 2-17% and 10-53% on the Tokomaru and Horotiu soils, respectively (Figure 2). Given that the efficacy of DMPP was below 40% on the Tokomaru soil, there was no DMPP threshold concentration on this soil. However, a threshold concentration of 13 mg DMPP kg<sup>-1</sup> soil (highest concentration tested) was observed on the Horotiu soil. DMPP has been shown to be more effective on sandy soil than on clay soil (Barth *et al.*, 2019; Guo *et al.*, 2021). Thus, this likely contributed to lower DMPP efficacy on the Tokomaru soil which had twice the clay content of the Horotiu soil (24 vs 12%). However, the varying DMPP application rates on both soils could have also influenced the results.

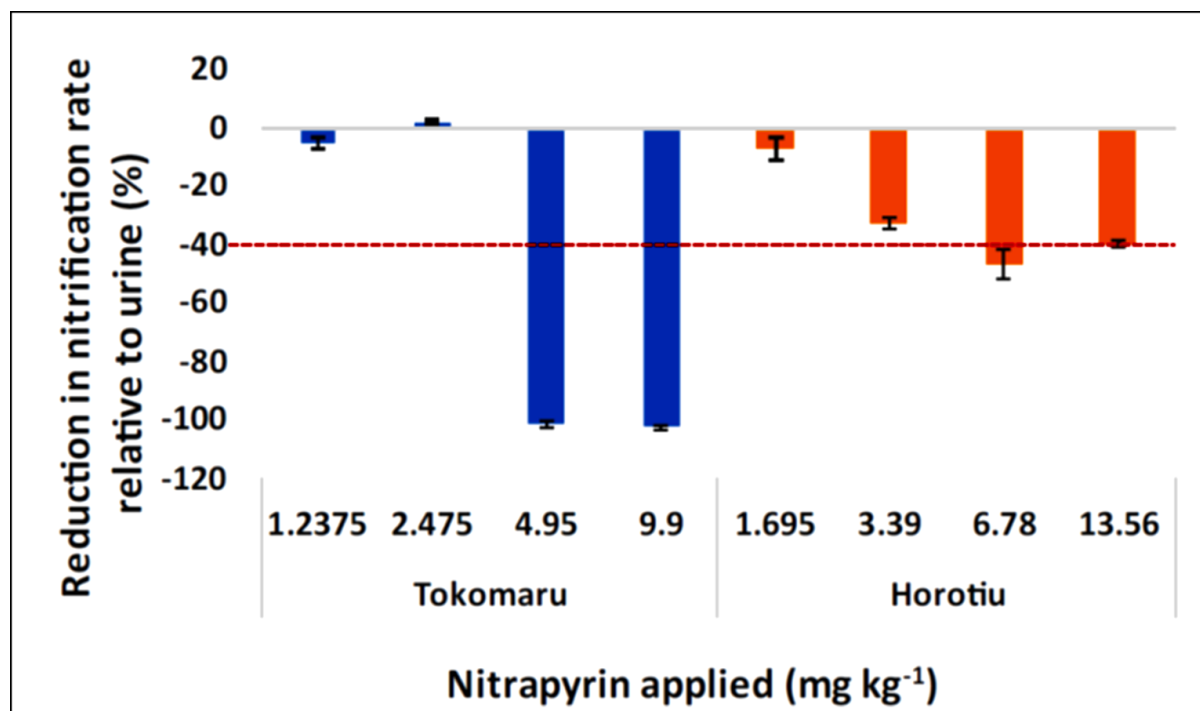


**Figure 1:** DCD efficacy at different application rates in the test soils. *The dotted red line goes across the application rates that attained  $\geq 40\%$  reduction in nitrification rate. Error bars are s.e. ( $n = 4$ ).*



**Figure 2:** DMPP efficacy at different application rates in the test soils. *The dotted red line goes across the application rates that attained  $\geq 40\%$  reduction in nitrification rate. Error bars are s.e. ( $n = 4$ ).*

The efficacy of nitrapyrin was highly variable on the Tokomaru soil (-2 -103%) compared with the Horotiu soil (7-47%) (Figure 3). Its threshold concentration on both soils was approximately 5-7 mg nitrapyrin kg<sup>-1</sup> soil (Figure 3). The volatile nature of nitrapyrin (0.43-0.64 Pa at 25°C; Adhikari *et al.*, 2021) likely reduced its efficacy at lower application rates in the Tokomaru soil which had lower number of organic C sorption sites.



**Figure 3:** Nitrapyrin efficacy at different application rates in the test soils. *The dotted red line goes across the application rates that attained  $\geq 40\%$  reduction in nitrification rate. Error bars are s.e. ( $n = 4$ ).*

DCD half-life was greater ( $p < 0.05$ ) than that of DMPP and nitrapyrin (Table 1). All NIs persisted longer in the test soils at higher application rates. A negative relationship was observed between NI half-life and nitrification rate (data not shown). This suggests that the NIs were more effective when they persisted longer in the soil.

**Table 1:** NI half-life values (days)

	NI half-life values (lowest – highest) across application rates		#Average half-life values $\pm$ s.e.
	<i>Tokomaru</i>	<i>Horotiu</i>	
DCD	9.8 – 27.2	11.0 – 19.2	16 $\pm$ 2 <sup>a</sup>
DMPP	7.4 – 9.3	9.3 – 10.1	9.2 $\pm$ 0.3 <sup>b</sup>
Nitrapyrin	5.4 – 17.3	4.8 – 22.7	10 $\pm$ 2 <sup>b</sup>

<sup>#</sup> Data from both soils were aggregated.

## Conclusion

Relative to DCD and nitrapyrin, a higher DMPP application rate was required to effectively inhibit urine N nitrification in the test soils. In practice, an NI efficacy would depend on all factors that contribute to its biophysical disappearance from the soil, e.g. microbial degradation and leaching losses, as well as NI capture by the pasture canopy.

## Acknowledgements

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## References

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