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Landcare Research

A review of the potential of nitrification inhibitors DMPP and nitrapyrin to reduce N_2O emissions following urine deposition in grazed pastures

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A review of the potential of nitrification inhibitors DMPP and nitrapyrin to reduce N_2O emissions following urine deposition in grazed pastures

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Executive summary

Nitrification inhibitors (NIs) have been proposed as an option to reduce nitrous oxide (N_2O) emissions and nitrate (NO_3^-) leaching from livestock deposited urine in grazed pastures. The NIs are compounds that can slow nitrification as they temporarily delay the bacterial oxidation of ammonium (NH_4^+) to NO_3^- in the soil by depressing the activity of Nitroso-group. As a result, they can decrease NO_3^- leaching, increase nitrogen (N) assimilation and pasture yield, and mitigate N_2O emissions. The most frequently used commercial NIs in agriculture are dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP) and [2-chloro-6-(trichloromethyl) pyridine] (nitrapyrin). The efficacy of DCD as a N_2O mitigation option is well known, but this product is no longer available for commercial use in New Zealand (NZ).

We conducted a mini literature review to examine the effect of DMPP and nitrapyrin on N_2O emissions from urine patches in temperate grazed pastures, to supply information related to the regulatory rules and unintended consequences of their use. From this we provide recommendations on the viability of using these products as N_2O mitigation options in NZ grazed pastures. Both DMPP and nitrapyrin are listed as hazardous substances but are generally considered as having low toxicity. They specifically inhibit the activity of ammonia oxidisers and degrade in soil after certain time. Regarding their inhibitory effect, previous studies suggest an application rate of ≥ 1 kg NI ha^{-1} is necessary for an efficient reduction in N_2O emissions in various agriculture and grassland soils. The lower mobility and water solubility of DMPP and nitrapyrin compared with DCD may have an advantage when applied to reduce N_2O emissions from urine patches in grazed pastures. However, high volatility of nitrapyrin may affect its effectiveness following surface application to grazed pastures.

Our literature search found that the efficacy of these inhibitors for reducing N_2O emissions has been widely evaluated when they are applied with N-based fertilisers in cropping soils. However, there were only four field studies that examined their effect on N_2O emissions from animal urine patches in temperate pasture soils: two DMPP studies (NZ and United Kingdom (UK)) and two nitrapyrin studies (NZ and Australia). The NZ studies indicated that DMPP or nitrapyrin applied on top of urine patches reduced N_2O emissions by 66% (in winter) and 43–48% (in spring), respectively. In the UK study, where DMPP was added to urine before urine application in summer, there was no reduction in emissions. Finally, the Australian study showed that nitrapyrin application reduced N_2O emissions from urine patches by 0–29%, depending on the season.

The half-lives of DMPP and nitrapyrin in soil are 50–60 days and 43–77 days at 20°C, respectively. Hence, these inhibitors should not persist in the soil environment for extensive periods of time, thus limiting any negative impacts on non-targeted soil and aquatic organisms at the recommended rates of application. However, findings of laboratory studies indicate their potential to accumulate in above-ground parts of plants and enter the food chain via grazing animals.

The Codex Alimentarius, a food standards program for international food safety standards, has not established maximum residual levels (MRL) for either DMPP or nitrapyrin. The MRL for these NIs are also not available in NZ Food Notice released by Ministry for Primary

Industries. This notice has provided a default residue level of 0.1 mg kg^{-1} for all types of food in NZ where specific levels are not mentioned, and both NIs fall under this group.

Our review suggests that both DMPP and nitrapyrin show promise as potential options for reducing N_2O emissions from urine deposited by grazing animals in NZ pastures. Based on the toxicological information available, both DMPP and nitrapyrin when applied with in the recommended rates can be considered as relatively safe compounds for further research to reduce N_2O emissions from urine patches in NZ grazed pastures. However, given that neither compound is included in the Codex, their commercial use is likely to face the same issues as DCD and it is therefore recommended that in future research initially focuses on gathering the required evidence for inclusion of a MRL for these compounds in the Codex Alimentarius.

Objectives

- To examine the effect of DMPP and nitrapyrin on N_2O emissions from urine patches in temperate grazed pastures, and supply information related to the regulatory rules and unintended consequences of their use.
- To provide recommendations on the viability of using these products as N_2O mitigation options in NZ grazed pastures.

Approach

- A review of national and international peer-reviewed, and web-based literature was undertaken to address the objectives.

Conclusions and recommendations

- Both DMPP and nitrapyrin show promise as potential options for reducing N_2O emissions from urine deposited by grazing animals in NZ pastures.
- Both DMPP and nitrapyrin when applied with in the recommended rates can be considered as relatively safe compounds for further research to reduce N_2O emissions from urine patches in NZ grazed pastures.
- As both DMPP and nitrapyrin are not included in the Codex, their commercial use is likely to face the same issues as DCD. It is therefore recommended that future research initially focusses on gathering the required evidence for inclusion of an MRL for these compounds in the Codex Alimentarius.

1 Introduction

Globally, the livestock sector accounts for 14.5% of total anthropogenic greenhouse gas (GHG) emissions, 44% of which are due to enteric methane (CH_4), while 29% are attributed to nitrous oxide (N_2O) emissions from animal excreta (Gerber et al. 2016; Cardoso et al. 2018). Nitrous oxide is an important GHG and the agricultural sector represents its largest source, producing approximately 60% of annual global emissions (Reay et al. 2012). In New Zealand (NZ), the agricultural sector is responsible for 48% of national GHG emissions and N_2O emissions contributes to 22% of those emissions. The vast majority of the agricultural N_2O (99%) is emitted from agricultural soils, which primarily are grazed pastures (Ministry for the Environment 2019). Under the Paris Agreement, NZ is committed to reduce its national GHG emissions by 30% below 2005 levels, by 2030.

In soils, N_2O production occurs via the microbial processes of nitrification and denitrification that, respectively, convert soil ammonium (NH_4^+) into nitrate (NO_3^-) and NO_3^- into N_2O (and N_2) gas. The N_2O emissions rates vary depending on N availability, soil, climate and vegetative conditions (Selbie et al. 2015; Gerber et al. 2016). In grazed pasture systems, denitrification is considered as the main mechanism of N_2O production due to the addition of readily available nitrogen (N) and carbon (C) via animal excretion, with increases in soil water-filled pore space (WFPS) being a driver of emissions (van der Weerden et al. 2017). To mitigate these emissions, the use of nitrification inhibitors (NIs) has been widely investigated (e.g. de Klein & Ledgard 2005; Qiao et al. 2015). The NIs are a group of chemical compounds that suppress the NH_4^+ oxidation by inhibiting the activity of soil microorganisms that oxidize NH_4^+ to nitrite (NO_2^-), and therefore delay the nitrification process (Zerulla et al. 2001). These compounds reduce emissions from both a direct effect on nitrification, and an indirect effect on denitrification by lowering soil NO_3^- levels (Wolt 2004). The NIs performed best in soils where conditions favour slower biological degradation of the inhibitor. Thus, optimal performance is more common with late autumn, winter and early spring application when soil temperatures are low.

Some NIs such as, Dicyandiamide (DCD), 3,4-dimethylpyrazole phosphate (DMPP) and [2-chloro-6-(trichloromethyl) pyridine] (nitrapyrin) have shown extensive benefit at reducing N_2O emissions when used together with fertilizers (Ruser & Schulz 2015; Rose et al. 2018). A review of previous NZ studies reported an average reduction of 57% of N_2O emissions after applying cattle urine with DCD (Di & Cameron 2016). Similarly, another review on the efficacy of DCD applied to reduce N_2O emissions from animal urine under UK temperate climate presented an average reduction of 42% (Chadwick et al. 2018). However, limited studies have evaluated the effectiveness of DMPP and nitrapyrin to reduce N_2O emissions from urine and there is no review conducted regarding the use of DMPP and nitrapyrin to treat urine patches. Based on the limited field studies conducted, this review summarises the effectiveness of DMPP and nitrapyrin in mitigating N_2O emissions from urine patches in temperate pastures, supplies information related to the regulatory rules and unintended consequences of their use, and provides recommendations for a pathway forward to be used as mitigation options at reducing N_2O emissions from urine in NZ grazed pastures.

2 General description of inhibitors

Both DMPP and nitrapyrin are listed as hazardous substances but are generally considered as low toxic (Weiske et al. 2001; USEPA 2005). The basic information of these NIs are presented in Table 1. Use of DMPP as NI is more common in China and Europe whereas nitrapyrin is widely used in United States in cropping systems. The safety data sheet of these NIs are provided as supplementary materials with this report for more detailed information.

Table 1. General characteristics of DMPP and nitrapyrin

Characteristic	DMPP	Nitrapyrin
common name	3,4-dimethylpyrazole phosphate	2-Chloro-6-(trichloromethyl)pyridine
CAS number	202842-98-6	1929-82-4
molecular formula	$C_5H_8N_2 \bullet H_3PO_4$	$C_6H_3Cl_4N$
solubility in water	low solubility	insoluble
vapour pressure	not available	0.4 Pa at 23 °C
available forms	solid and liquid	solid and liquid
inflammable	not available	explosive
most common uses	combined with mineral fertilisers and liquid manures	combined with mineral fertilisers and liquid manures
reactivity with other products	reacts with base	reacts with Al and Mg
chemical stability	unstable in contact with base	stable
decomposition products	dimethylpyrazole (DMP)	6-chloropicolinic acid (6-CPA)

3 Efficacy of inhibitors to mitigate N_2O emissions from animal urine

A global review of previous field studies by Akiyama et al. (2010) reported a higher effectiveness of DMPP and nitrapyrin (50%) compared with DCD (30%) at reducing N_2O emissions from conventional fertilisers (mineral fertiliser and liquid manure) under various land uses. However, in a recent review (Ruser & Schulz 2015), the observed reduction in emissions by all NIs are similar (approximately 35%). The optimum application rates of DMPP and nitrapyrin when applied with conventional fertilisers are ranged of 0.5–2 kg ha^{-1} (Dittert et al. 2001; Weiske et al. 2001; Merino et al. 2005) and 0.5–4 kg ha^{-1} (Dow Agrosciences 2013, 2018), respectively, depending on fertiliser type and N application rate. The lower mobility and water solubility of DMPP and nitrapyrin should give these inhibitors an advantage over DCD when applied to reduce N_2O emissions from urine patches in grazed pastures because these properties lower the spatial separation of DMPP and nitrapyrin with NH_4^+ (Subbarao et al. 2006). However, high volatility of nitrapyrin (Trenkel 1997) may affect its effectiveness following surface application to grazed pastures. Only a few field studies have evaluated the effectiveness of DMPP or nitrapyrin to reduce N_2O emissions from urine in temperate pasture soils. The summary of the effectiveness of DMPP and nitrapyrin at reducing N_2O emissions from urine applied to pasture soils are presented in Table 2. The emission reductions from DMPP and nitrapyrin ranged from 0 to 66% and 0 to 48%, respectively. The ineffectiveness of DMPP in Marsden et al. (2017) could be due to faster microbial degradation of inhibitor at higher summer temperatures as reported by Menéndez et al. (2012). However, the observed significant reduction in emissions in a NZ study (Di & Cameron 2012) could be attributed to double applications of 5-fold higher rate of DMPP (5 kg ha^{-1}) in wet winter period compared with single application of DMPP at a rate of 1 kg ha^{-1} in a study reported by Marsden et al. (2017).

The ineffectiveness of nitrapyrin in one of the summer-initiated experiments reported by Ward et al. (2016) could be due to faster degradation of inhibitor. Overall, it can be inferred that DMPP and nitrapyrin have potential to reduce N_2O emissions following animal urine deposition in grazed pastures.

Table 2. Effect of DMPP and nitrapyrin on reducing N_2O emissions from urine applied to pasture soils

Country	Inhibitor rate (kg ha^{-1})	Timing of inhibitor application	N rate (kg ha^{-1})	Season	Reduction in N_2O emissions relative to urine alone (%)	Reference
DMPP						
NZ	5	immediately and again 6 weeks after cattle urine	1000	winter	66	Di & Cameron (2012)
UK	1	immediately before sheep urine	725	summer	0	Marsden et al. (2017)
Nitrapyrin						
Australia	1	immediately after cattle urine	759–1000	spring, summer, autumn, winter	0–29	Ward et al. (2016)
NZ	1	4 hrs after cattle urine	211–530	spring	43–48	Hoogendoorn et al. (2018)

4 Toxicological concerns with the use of inhibitors

The United States Environmental Protection Agency (USEPA) has registered nitrapyrin as NI. However, DMPP is even not included on USEPA Toxic Substance Control Act (TSCA) inventory that regulates the introduction of new or already existing chemicals (USEPA 2005, 2012). According to USEPA (2005), there is reasonable certainty that there is no harm to any population subgroup from aggregate exposure to nitrapyrin when considering dietary (food and water) exposure. There could be risks of concern to small and medium birds and mammals when nitrapyrin is not incorporated into the soil immediately after application. From this it could be inferred that the application of nitrapyrin to the grazed pastures could result in ecological risks. However, no studies have assessed the impact of DMPP and nitrapyrin on soil microbes, plants, animals, humans and water bodies following urine application in pasture soils.

4.1 Effect on soil microbes

Both DMPP and nitrapyrin specifically inhibit the activity of ammonia oxidisers, (Li et al. 2008; Shen et al. 2013) and degrade in soil after certain time. The decomposition of DMPP occurs in the soil by micro-organisms through the breakup of the pyrazole ring, releasing carbon-dioxide (CO_2) (Di & Cameron 2016). Similarly, nitrapyrin hydrolyses and photodegrades rapidly to 6-Chlorpicolinic acid (6-CPA), which further degrades via hydroxylation (breaking the pyridine ring) and microbial mineralisation in soil (USEPA 2005). The DT50 values (time required for the concentration to decline to half of the initial value) for DMPP and nitrapyrin in soil are 50–60 days and 43–77 days at 20°C, respectively (Weiske et al. 2001; Tindaon et al. 2012). Hence, it is unlikely that these inhibitors will persist in soil environment for a long period.

Studies suggest that DMPP and nitrapyrin do not possess negative impact on the activity of non-target soil microorganisms at a recommended as wells as up to 10 times higher rates of application in various agricultural systems including grassland (Laskowski et al. 1975; Maienza et al. 2014; Kong et al. 2016). However, the application at very high rate has shown negative impact on non-target organisms, e.g. evidence of negative effect of DMPP on soil microbial activity at concentrations surpassing the recommended doses by 25–90 times was reported by Tindaon et al. (2012). Similarly, Redemann et al. (1964) reported that the growth of *Thiobacillus thioxydans* and *Bacillus subtilis* were retarded when nitrapyrin was applied at a rate of 1000 and 100–1000 mg kg^{-1} soil, respectively. To our best knowledge, only one publication, Dong et al. (2013), has reported the effects of long-term application of DMPP with urea on non-target organisms or microbial activity in a field study. They did not observe negative effect of application of DMPP (1.8 kg ha^{-1}) for 7 years on soil total bacterial population size. Based on the results reported, it is less likely that short-term application of DMPP and nitrapyrin at rates used in agricultural systems have negative impact on non-targeted soil organisms in grazed pastures. However, for NZ intensively grazed pasture systems further research will be required to assess the impact of short- and long-term applications of both DMPP and Nitrapyrin on soil microbial communities.

4.2 Effect on plants

The phytotoxicity of inhibitors depends on plants' capacity to take up inhibitors and its translocation to plant parts (Rodrigues et al. 2018). The increase in pasture dry matter production may achieved if the inhibitors do not possess phytotoxicity to pasture species. Only one study assessed the effect of DMPP on pasture biomass following urine application and its results showed that there was no effect of DMPP (Marsden et al. 2017). Similarly, field studies conducted with cattle slurry (Macadam et al. 2003; Merino et al. 2005) also reported no effect of DMPP on dry matter production of ryegrass and white clover. However, the evidence of positive effect of DMPP on dry matter yield of ryegrass (increased by 70%) was reported by Fangueiro et al. (2009) when applied at 2 kg ha^{-1} with cattle slurry. Wells (2016) reported the higher yield of ryegrass from the urea treated with nitrapyrin compared to urea alone.

Some previous laboratory studies (Redemann et al. 1964; Rodrigues et al. 2018) have shown that DMPP and nitrapyrin do not possess phytotoxicity at a rate similar to field application as well as at concentration up to 10 times higher. However, at a very high dose, phytotoxic symptoms and reductions in plant biomass are reported. For example, DMPP at 100 mg L^{-1} showed phytotoxicity to red clover and reduced shoot biomass in hydroponic solution (Rodrigues et al. 2018). Similarly, nitrapyrin at 39 mg L^{-1} exhibited phytotoxicity to Lucerne grown in soil suspension (Naik et al. 1972). The uptake and translocation of inhibitor is expected to be lower in the agricultural systems (grazed pastures) in the presence of competing physical and biological processes in soil than in hydroponic solution or soil suspension. Therefore, phytotoxicity may not be a concern for DMPP and nitrapyrin at a rate used in grazed pastures. However, further research will be required to determine the absorption/retention of these inhibitors by standing pasture plants during application, and subsequent uptake and translocation during pasture growth (as described under 4.3).

4.3 Effect on grazing animals and their products

The potential entry of inhibitors into the food chain through grazing animals depends on the capacity of pastures to take up inhibitors either directly following its foliar spray application or by root uptake, and the root to shoot translocation and metabolization of the inhibitors within the plants. This could then lead to inhibitors exhibiting negative effect on grazing animals, their products and/or humans.

The Codex Alimentarius, a food standards program for international food safety standards, has not established maximum residual levels (MRL) for both DMPP and nitrapyrin. The MRL for these NIs are also not available in NZ Food Notice released by Ministry for Primary Industries. This notice has provided a default residue level of 0.1 mg kg^{-1} in all types of food where specific levels are not mentioned, and both NIs fall under this group (Ministry for Primary Industries 2019). There is evidence that the pasture species red clover has the capacity to take up DMP (the degradation product of DMPP) via its root system, which then translocates and accumulates in the above-ground parts even at the low application rate typically used in the field (1 mg L^{-1} in hydroponic solution) (Rodrigues et al. 2018). Similarly, the residues of nitrapyrin were noticed in extracts of oat seeds, and corn, lettuce and tomato leaves grown in soil treated with nitrapyrin at 10 mg kg^{-1} soil. However, the concentrations of 6-CPA (hydrolysis product of nitrapyrin) observed were < 1% of the chronic Population Adjusted Dose (cPAD), the maximum acceptable intake of chemicals for long run (Redemann et al. 1965). Other species, including other pasture species, may also have potential to take up DMPP and nitrapyrin from soil. The DMPP and nitrapyrin sprayed onto soil may also adhere to the pasture canopy and accumulate in above-ground parts as mobility and water solubility of these NIs are lower compared with DCD. To our best knowledge, there is no evidence that plants have the metabolism for degradation of these NIs. Therefore, there is a possibility that these NIs enter the food chain via animal ingestion, which could potentially pose risks to grazing animals and humans. The establishment of acceptable MRL of these NIs in grazed animals' products help to determine the risks associated with their entry in food chain and will be critical before widespread use can be considered.

4.4 Effect on water bodies

The inhibitors applied to pastures or their metabolites may leach into the surface and ground water under high rainfall conditions and thereby pose risks for humans and aquatic health. The potential leaching losses of inhibitors applied to pastures depends on its mobility in soil. The mobility of inhibitors is positively correlated with its water solubility and negatively correlated with its adsorption potential into the soil. As mentioned in Section 2, DMPP and nitrapyrin have low solubility and are insoluble in water, respectively. Additionally, both NIs bind strongly to organic matter and are moderately mobile in soil (The Dow Chemical Company 2012; Benckiser et al. 2013). Therefore, the risks of leaching losses of these NIs can be considered as low.

USEPA (2012) has indicated that the concentrations of DMPP above 19 μg L^{-1} in surface water may have negative effect on human and aquatic health. Similarly, the ecotoxicity test conducted for DMPP using the aquatic gram-negative bacterium *Vibrio fischeri* (commonly used bacterium for ecotoxicity tests) derived the EC50 value of 16.6 mg L^{-1} (Rodrigues et al. 2018). The concentration of nitrapyrin ≥300 μg L^{-1} in drinking water is considered as harmful (USEPA 2005). However, the Drinking-water Standards for New Zealand (DWSNZ) has not derived a Maximum Acceptable Value (MAV) for DMPP and nitrapyrin in drinking water. Additionally, the World Health Organization (WHO) guidelines for drinking water has not included MAV for DMPP and nitrapyrin (Ministry of Health 2019).

The evidence of leaching losses of DMPP following its application with N fertiliser was reported by Fettweis et al. (2001) in a 3 years field study. However, the concentration of DMPP in leachate samples was not above 0.1 μg L^{-1}. These concentrations were below the threshold of the toxicological level of DMPP in the leachate,10 mg L^{-1} as mentioned by European Commission (2013). In another study conducted to evaluate the off-field transport of nitrapyrin and 6-CPA across 11 streams (region with wide use of nitrapyrin), Woodward et al. (2016) reported the concentrations of nitrapyrin ranging from 12 to 240 ng L^{-1}; however, 6-CPA was not detected. The concentrations measured were below LC50 toxicity levels for freshwater vertebrates and invertebrates, 1.7 – 9.3 mg L^{-1} as reported by USEPA (2005). Although, higher contamination of DMPP and nitrapyrin in water bodies is considered as harmful chemical for human and aquatic organisms, it is unlikely that it could be leached from agricultural soil to a rate that provoke negative effect on human and aquatic health.

The summary of toxicological concerns with the use of DMPP and nitrapyrin as NIs are presented in Table 3.

Table 3. Toxicological concerns associated with the use of DMPP and nitrapyrin

Property	DMPP	Nitrapyrin
soil microbes	• no evidence of negative effect at field application as wells as up to 10 times higher rate • evidence of negative effect at high doses	• no evidence of negative effect at field application as wells as up to 10 times higher rate • evidence of negative effect at high doses
phytotoxicity	• no evidence at field application rate with sheep urine and cattle slurry (rye grass, white clover) • some evidence at high doses in hydroponic solution (red clover)	• no evidence at field application rate with urea (rye grass) • some evidence at high doses in soil suspension (Lucerne)
pasture yield	• nil to positive effect at field application rate with sheep urine and cattle slurry • evidence of negative effect at high doses in hydroponic solution (red clover)	• evidence of positive effect at field application rate with urea
grazing animals and their products	• evidence of accumulation in plant aerial parts at field application rate (red clover grown in hydroponic solution) • potential to enter the food chain via grazing animals	• evidence of accumulation in plant aerial parts at about 5–10 times higher than field application rate (oat seeds, and corn, lettuce and tomato leaves) • potential to enter the food chain via grazing animals
water bodies	• detected in leachate at field application rate but were below than the threshold of the toxicological level	• detected in water streams at field application rate but were below than the threshold of the toxicological level

5 Conclusions and recommendations

Our review suggests that both DMPP and nitrapyrin show promise as potential options for reducing N_2O emissions from urine deposited by grazing animals in NZ pastures. Based on the toxicological information available, both DMPP and nitrapyrin when applied within the recommended rates can be considered as relatively safe compounds for further research to reduce N_2O emissions from urine patches in NZ grazed pastures.

However, given that neither compound is included in the Codex, their commercial use is likely to face the same issues as DCD and it is therefore recommended that future research initially focusses on gathering the required evidence for inclusion of a MRL for these compounds in the Codex Alimentarius.

Additional research needs to include:

- quantifying the concentration of inhibitors in pasture and their effect on pasture production and grazing animals.
- evaluating the effect of DMPP and nitrapyrin at reducing N_2O emissions and NO_3^{-} leaching from urine across a wide range of soil and environmental conditions.
- quantifying inhibitor in leachate and water bodies.
- examining the short-term and long-term impacts of DMPP and nitrapyrin application to urine patches on soil microbes, pasture plants, grazing animals and animal products, and quantifying any ecological risk.
- establishing standard analytical technique with improved precision for accurately measuring the concentrations of DMPP and nitrapyrin to meet established MRL in soil and plant samples.

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