Economic and environmental impacts of increased nitrogen use in grazed pastures and role of inhibitors in mitigating nitrogen losses

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Addition of nitrogen (N) to soils not only increases plant productivity but also results in increased nitrate (NO_3^-) leaching and release of gaseous N such as ammonia (NH_3) and nitrous oxide (N_2O). Recent sharp increases in fertiliser N inputs to grazed pastures in New Zealand have rekindled the debate on its impact on atmospheric, terrestrial and aquatic environments. There has been increasing interest in the use of inhibitors to mitigate environmental impacts of N losses from animal excreta and effluent application through leaching and gaseous emissions. This article gives an overview of the environmental impacts of N losses, discusses the role of inhibitors in mitigating N losses, and identifies gaps and limitations from existing New Zealand information. It also suggests the main research needed for devising mitigation strategies with inhibitors.

The issue

New Zealand's managed grasslands are highly productive, with increased pasture production being the major goal for the pastoral farmers, for higher per hectare animal productivity. In grazed pastures, nitrogen (N) is derived from biological fixation of atmospheric N (N-fixation), through the addition of manures and fertilisers, and the uneven deposition of animal excreta. Although in legume-based pastures most of the N is derived from N-fixation, a small amount of fertiliser N is traditionally added during the early spring, mainly to overcome the deficiency caused by the slow rates of N-fixation and mineralisation of soil organic matter.

Nitrogen is extremely dynamic in grazed pastoral soils, always changing or moving (Figure 1). It is the major nutrient that most strongly regulates pasture production, but is also a contributor to environmental degradation. In intensively grazed pastures, urine is the major source contributing to N losses.

It is estimated that New Zealand agricultural systems receive an annual input of about 3 million tonnes of N, with 1.58 million tonnes from animal excreta, 0.9–1.1 million tonnes from N-fixation, 0.33 million tonnes from fertilisers and about 0.01–0.015 million tonnes from atmospheric deposition (Saggar 2004). The animals void almost 5 times more N than the N fertiliser input.

Recently, fertiliser N inputs to grazed pastures have increased sharply, and this increase is expected to continue in the foreseeable future. N fertiliser use in 1990 was 59 265 tonnes and the estimates for 2003/04 were 348 000 tonnes (Ministry for the Environment 2005). This increased use of reactive-N

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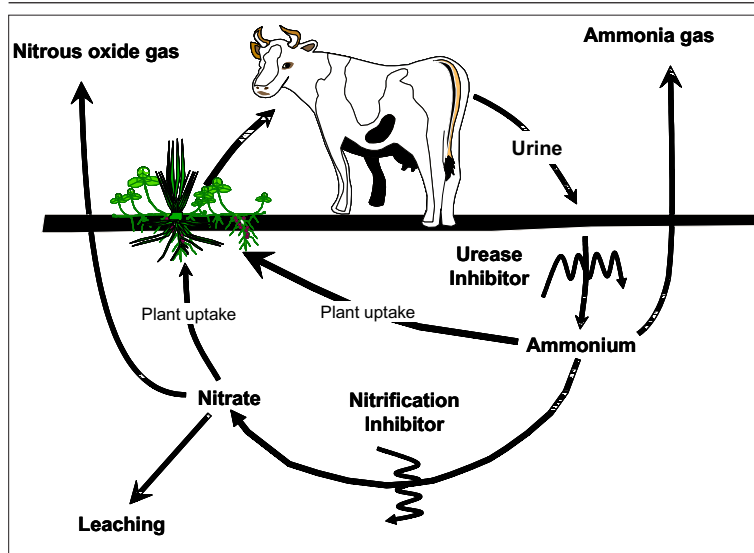
Figure 1. Dynamics of N transformations in legume-based pastures.

benefits society, but it also represents a significant cost to society through increased nitrate (NO_3^-) leaching and enhanced emissions of NO_x (pronounced 'knox', sum of NO and NO_2), ammonia (NH_3), nitrous oxide (N_2O) and deposition of NO_y (sum of knox plus all other oxidised forms of N such as nitric acid (HNO_3) and peroxyacetyl nitrate in the atmosphere) and NH_x (Mosier *et al*. 2001). The increasing fertiliser N input to grazed pastures has rekindled the debate on its impact on atmospheric, terrestrial and aquatic environments (Parliamentary Commissioner for the Environment 2004). Results of studies conducted by Landcare Research (Saggar *et al.* 2004, 2005a, b) show a 5- to 10-fold increase in nitrous oxide (N_2O) emissions in grazed pasture compared with ungrazed pasture, and also a much higher N_2O emission factor for dairy-grazed than sheep-grazed soils. Therefore, the increasing amounts of N going on hill country could increase both leaching and gaseous emissions of N and create further problems in the future.

Loss of N, occurring mainly through NH_3 volatilisation, biological denitrification and nitrate NO_3^- leaching, has both economic and environmental implications (Bolan *et al*. 2004a). Nitrogen is an important plant nutrient and its loss affects both the quality and quantity of feed and animal production. An increase in NO_3^- concentration in groundwater resulting from leaching has been linked to increasing incidences of NO_3^- toxicity in human and livestock (i.e. methaemoglobinaemia) (Gupta *et al*. 1999; Bolan *et al*. 2004b). Nitrate leaching is one of the biggest issues facing the New Zealand agriculture sector at present. Similarly, grazed pastures are identified as an important source of NH_3 and nitrous oxide (N_2O). While NH_3 is implicated in acid rain, N_2O is involved in ozone depletion and global warming (i.e. greenhouse gas).

Various approaches have been used to mitigate the economic and environmental impacts of N losses. One such approach is the use of nitrification and urease inhibitors (NIs and UIs). Recently in New Zealand there has been increasing interest in the use of commercially formulated NIs and UIs (e.g. Eco-N™, N-Care™, and SustaiN™)* to reduce the loss of N through leaching and gaseous emissions.

*Eco-N, Ravensdown Fertiliser Co-operative Ltd; N-Care, Balance AgriNutrients Ltd; SustaiN, Summit-Quinphos Ltd.

The purpose of this paper is to present: (i) a brief summary of environmental impacts of N losses; (ii) an overview of the role of inhibitors in mitigating N losses; (iii) a brief discussion on research on the use of inhibitors in New Zealand; and (iv) conclusions about the main future research needs.

Environmental impact of N losses

In the context of environmental pollution and global climate change, while NO_3^- leaching attracts attention because of its potential effects on human and animal health, and on water pollution, gaseous forms of N, such as NH_3, N_2O and NO, cause concern because of their radiative or chemical effects on the atmosphere. In New Zealand, both NO_3^- leaching and gaseous emissions are considered a more important issue for dairying than for sheep and beef farms. The environmental effects of NO_3^- leached to groundwater and other waterways and the potential damage to soils are a major concern to the farming industry, the scientific community, and society (Parliamentary Commissioner for the Environment 2004).

The accumulation of NO_3^- in the environment results mainly from non-point source leaching and runoff from over-application of N fertilisers, voided urine and dung, and poorly or untreated effluents and sewage. In addition, NO_3-containing wastes are produced by many industrial processes including paper manufacture. As agriculture is implicated in the NO_3^- pollution problem, farmers and rural communities are the most affected. Environment Waikato data suggest the quality of about 10% of the groundwater in the livestock farming area of the region is below World Health Organisation drinking water standards (Anon. 2005). The declining water quality of Lake Taupo and the Rotorua Lakes has been linked to land use practices within the catchment and the export of N from farming as well as other sources. Farming has been shown to be a major contributor to the algal blooms occurring in Lake Rotoiti (Ministry for the Environment 2003)

High concentrations of NO_3^- in lakes, rivers, and estuaries can result in eutrophication and algal blooms, and links have also been made between high NO_3^- and toxicity in fish eggs, amphibian eggs, and tadpoles (Agriculture and Agri-Food Canada 2003). Health impacts to humans and animal life occur from drinking water, and/or eating foods such as vegetables that are high in NO_3^-. Nitrate consumption at high concentrations has been linked to ailments such as gastric cancer, ulceration of the mouth and/or stomach lining and especially to infants, causing the condition known as methaemoglobinaemia, also called "blue baby syndrome". Nitrates have a direct, caustic effect on the lining of the gut if consumed in large quantities. Signs of poisoning include diarrhoea, salivation and abdominal pain. Nitrate is converted in the gut to NO_2^-, which then combines with haemoglobin to form methaemoglobin, thus decreasing the ability of the blood to carry oxygen. Infants are more susceptible to NO_3^- toxicity than older children or adults.

Although not always toxic to animals, NO_3^- toxicity in grazing animals is likely to occur when they ingest water and forage containing high concentrations of NO_3^-. Ruminants are more susceptible to NO_3^- toxicity than simple-stomached animals because rumen microbes enhance the reduction of NO_3^- to NO_2^- in the digestive tract. Uncertainty exists about the level of NO_3^-

ingestion that is considered the minimum lethal dose. Studies have indicated that 7.6–9.0 g NO_3^- -N per 100 kg body weight is lethal to animals. Assuming that the average daily pasture intake by dairy cattle is 4% of the body weight, pasture with a NO_3^- -N content of more than 0.21% is likely to be toxic to animals with a live body weight of 300 kg (Bolan *et al.* 2004).

Ammonia affects atmospheric visibility, aerosol chemistry, health and climate, and leads to acidification and eutrophication when deposited in soils and waters. It also acts as a neutralising agent for acidic aerosols, besides affecting vegetation and forming NO_3^-. Ammonia has a short lifetime in the atmosphere, oxidising to form NO and N_2O, which play an important role in troposphere chemistry. They are directly or indirectly involved in global warming, the production and consumption of atmospheric oxidants (such as ozone), and the photochemical formation of nitric acid (acid rain).

Inhibitors in the nitrogen cycle
Types and mode of action
By controlling N dynamics, urease inhibitors (UIs) and nitrification inhibitors (NIs) can reduce the leaching of NO_3^-, and/or the emissions of NO_x, NH_3, N_2O and deposition of NO_y. Such environmental benefits may increase the importance and use of UIs and NIs in the future. The general theory of using these inhibitors is that they slow down N turnover by slowing the oxidation of N to NO_3^-, causing N to stay in the more immobile form of NH_4^+. NIs do not inhibit nitrification indefi-

nitely, but usually for 4 to 10 weeks depending upon soil temperature and pH.

The inhibitors include both specific and non-specific compounds. Specific inhibitors tend to control micro-organisms/enzymes involved in specific biochemical reactions during ammonification (UIs) and nitrification (NIs) processes, whereas the non-specific inhibitors tend to have a blanket effect on microbial community in soils. The mechanisms involved in the inhibitory actions of these compounds are outlined in Table 1.

UIs are used to control urea hydrolysis by blocking the activity of the urease enzyme which breaks down urea to form ammonium (Figure 2). This allows urea to remain in its unhydrolysed form longer. This results in less potential volatilisation loss of NH_3 from surface-applied urea. UIs have little or no effect on the nitrification process in soil. Therefore, UIs should not be expected to influence NO_3^--leaching. Given the ubiquitous and highly specific activity of soil urease, urease inhibition is generally difficult to achieve in soils.

NIs are used to control the oxidation of NH_4^+ to NO_2^- (Figure 2) and are intended to minimise the losses of NO_3^- from soil due to leaching and denitrification by slowing the activity of soil bacteria which convert NH_4^+ to the more easily lost NO_3^--N.

Effect of inhibitors on N losses
The effects of UIs and NIs on the transformations and losses of N are presented in Figure 2. Many research trials have con-

Table1. Selected examples of urease and nitrification inhibitors and their mode of inhibitory action

Process	Specific/ non-specific	Example	Mechanisms
Urease inhibitor			
$CO(NH_2)_2 \rightarrow 2NH_4^+$	Non-specific	Fungicides (e.g. Maneb, anilazine, benomyl, chloranil), pesticides (e.g. methanol, carbaryl, atrazine)	Inhibit the growth or activity of soil organisms that produce urease enzyme
	Specific	Reactive compounds (e.g. alk(en)yl thiosulfinate, hydroquinone, p-benzoquinone)	Bind irreversibly with the SH group (Cys592) found in the active site of urease
	Specific	Metal chelators (e.g. caprylohydroxamic acid, acetohydroxamic acid)	Bidentate co-ordination of hydroxamate to nickel
	Specific	Competitive inhibitors (e.g. phosphoroamides, PPDA, NBPT)	Possess tetrahedral geometry thus act as transition state analogue in enzymatic catalysis
Nitrification inhibitors			
$NH_4^+ \rightarrow NO_3^-$	Non-specific	chloroform, phenol, acetone, sulfones, azide, thiourea, pesticides	Inhibit the growth or activity of organisms by: (i) creating unfavourable microenvironments, (ii) stimulating the growth of competitive micro-organsims, (iii) disturbing membranes and changing cell structure, and (iv) interfering with the reductive assimilation of N
$NH_4 \rightarrow NH_2OH$	Specific	allylthiourea, salicylaldoxime, cyanide	Inhibition through metal chelation of copper enzymes involved in ammonia oxidation
	Specific	Short-chain primary alcohols (e.g. methanol)	By reacting with catalase-like enzymes or by trapping free radicals
	Specific	hydrazine, H_2O_2	Through their effects on cytochrome
$NH_2OH \rightarrow NO_2^-$	Specific	cyanate, DCD	Toxic to nitrite oxidase
		quinacrine	Inhibits flavoprotein
		citrate	Interferes with the flavoprotein-cytochrome and respiratory system

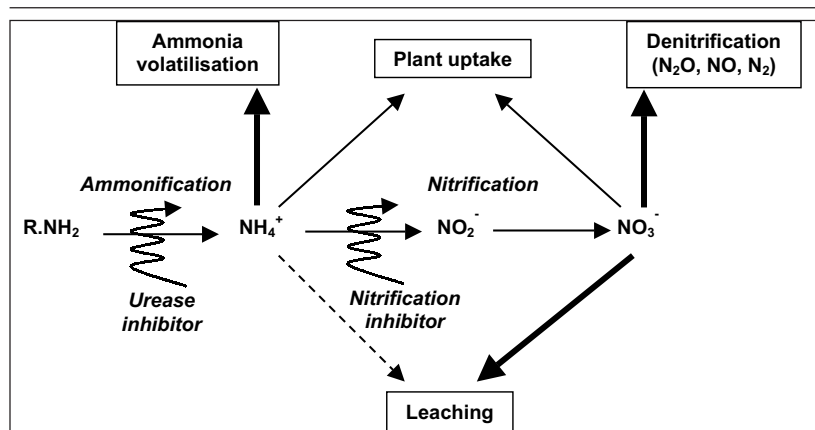PPDA, phenyl phosphorodiamidate; NBPT, N-(n-butyl)thiophosphoric triamide; DCD, dicyandiamide

Figure 2. Role of inhibitors in controlling N transformations and losses.

firmed that inhibitors are effective in delaying the conversion of either urea to NH_4^+ (UIs) or NH_4^+ to NO_3^- (NIs). Most of this research indicates that the application of UIs to soils with fertiliser urea or urine reduces NH_3 volatilisation while the application of NIs reduces NO_3^- leaching and N_2O emissions. Several studies also showed NIs increase NH_3 volatilisation (Davies & Williams 1995; Nastri *et al.* 2000). There is also evidence that both UIs and NIs may have a deterimental effects on plant leaves, e.g. transient leaf tip scorch with UIs and dicyandiamide (DCD) phytoxicity under certain weather condition (Bremner 1995; Prasad & Power 1995; Watson 2000; Belastegui-Macadam *et al.* 2003). However, the benefits of inhibitors in reducing N losses and increasing pasture production would appear to outweigh these short-term detrimental effects. These same trials show a wide range of economic returns, depending upon soil type, drainage, time of application, and environmental conditions. Some recent studies in the Netherlands (Peter Kuikman, pers. comm.) suggest that, although inhibitors are effective in reducing gaseous losses of N under glasshouse conditions, their efficiency varies widely under field application. The greatest likelihood of N losses is from coarse-textured or poorly drained soils; it is in these situations where the use of inhibitors might appear to be most economical. However, inhibitors do not work well in coarse-textured soils, as in these soils, urea and NH_4^+ ions have a tendency to move away from the inhibitor with rainfall or irrigation (University of Illinois [undated]).

Studies on the effect of inhibitors on N economy (Table 2) have shown that their inhibitory action depends on their persistence and bioactivity in soils, which in turn are affected by the intrinsic properties of the compound, soil properties, and

Table 2. Selected references on the effects of inhibitors in the nitrogen economy.

Inhibitor	Dose	N source	kg N/ha	Reduction in N losses	Crop	Effect on DM yield	Country	Reference
Urease inhibitor (NBPT)	0.05% (w/w)	Urea	100	82.8% decr. in NH_3 loss	Perennial ryegrass	9% increase	Ireland	Watson et al. 1994
Urease inhibitor (NBPT)	0.05%, 0.10%, 0.15%	Urea	100	SL* 75-81% CL* 75-85% decr. (w/w)	-	-	Canada	Rawluk et al. 2001
Urease inhibitor (NBPT)	0.25% (w/w)	Urea	120	SL* 89% CL* 47% decr. in NH_3 loss	Wheat	No change in yield	Italy	Gioacchini et al. 2002
Nitrification inhibitor (DCD)	25 kg/ha	Ca amm. nitrate Cattle slurry	80 85	42% 60% decr. in N_2O emissions	Perennial ryegrass pasture	-	Spain	Merino et al. 2002
Urease inhibitor (HQ) + Nitrification inhibitor (DCD)	0.3% (w/w) 5% (w/w)	Urea	130	62% decr. in N_2O emissions	Rice	35–37% increase	Belgium	Xu et al. 2002
Nitrification inhibitor (DCD)	12 kg /ha	Dairy farm effluent	1100	18% decr. in NO_3^--N leaching	Ryegrass pasture	19.2% incr.	New Zealand	Williamson et al. 1998
Nitrification inhibitor (Didin)	25 kg/ha	Cattle urine	450	35.6% decr. in NO_3^--N content (0–100 mm)	Ryegrass– clover pasture	No sign. effect	New Zealand	Cookson & Cornforth 2002
Nitrification inhibitor (DCD)	15 kg/ha 7.5 kg/ha	Cattle urine, urea	1000 25	76% (autumn) 42% (spring) reduction in NO_3^--N leaching	Ryegrass– clover pasture	30% incr.	New Zealand	Di & Cameron 2002a
Nitrification inhibitors (DCD)	6 kg/ha	Urea	60	-	Wheat	22–25% incr.	USA	Rao & Popham 1999
Urease inhibitor (Agrotain)	0.1% (w/w)	Urea Urine	600 600	27% 23% reduction in NH_3 losses	Ryegrass– clover pasture	-	New Zealand	Singh et al. 2003, 2004
Nitrification inhibitor (DCD)	25 kg /ha	Urine	100	74% reduction in N_2O emissions				

NBPT, N-(n-butyl)thiophosphoric triamide; DCD, dicyandiamide; HQ, hydroquinone; Didin, dicyandiamide

climatic conditions. The half-lives of inhibitors may vary from a few days to several weeks, depending on the nature of the compound, rate of application, soil type, pH and season (soil temperature). The ideal inhibitor for use in agriculture should:

- specifically block an enzymatic reaction (e.g. NIs should block ammonium oxidation to nitrite, but not nitrite oxidation to nitrate, during the nitrification process);

- remain in close contact with N compounds (e.g. UIs must move with urea molecules, which are not readily absorbed by soil, whereas NIs must be close to NH_4^+ ions, which are readily retained by soil);

- not adversely affect other beneficial soil organisms and higher plants;

- remain effective in soil for several weeks after N input through fertiliser addition and excretal deposition;

- not be toxic to animals and humans at the levels used to effectively inhibit nitrification;

- be cost-effective to use.

The ultimate goal of any inhibitor is to increase the efficiency of N use. For an economic benefit to occur, the N saved from leaching and gaseous losses by using the inhibitors would have to either result in an increase in pasture production, with a value greater than the cost of the inhibitors, or allow a reduction in fertiliser input. Over the long term, the economic benefits from reduced pollution and reduced future damage to the environment are of higher significance than productivity gains. The value of inhibitors in reducing N losses from N fertilisers and increasing crop yields is well established in arable soils. The inhibitors are also reported to increase pasture production, but the increase in stocking rates needed to utilise this extra pasture may enhance emissions of other greenhouse gases. De Klien & Monaghan (2005) have shown that the use of NIs had a limited effect in reducing total greenhouse gas emissions compared with N_2O emissions, because of an increase in both CH_4 and CO_2 emissions from the farm system.

Current research in New Zealand

In lysimeter studies at Lincoln University, Di & Cameron (2002a, b, 2003, 2004a, b) showed that DCD reduced NO_3^--leaching and N_2O emissions from urine and urea applications. They are continuing to measure the effects of DCD on NO_3^--leaching and gaseous emissions of N under field conditions in collaboration with Ravensdown Fertiliser Co-operative Ltd. Unpublished results of a current PhD study on impact of inhibitors on N dynamics (Jagrati Singh, pers. comm.) show that, although DCD application reduces soil N_2O emissions and NO_3^--leaching from cattle urine, it also increase NH_3 volatilisation and NH_4^+-N leaching losses. The addition of NIs and UIs directly into the urine stream from an animal mounted dispenser is being tested in a project aiming to develop technology to minimise N losses from grazed dairy pastures involving Summit-Quinphos and AgResearch, Landcare Research, HortResearch, and Crop & Food. Landcare Research and Massey University have recently initiated a project to understand the soil and plant processes controlling DCD decomposition, the variable response in different soils, and the impact DCD has in causing changes in the N cycle. This research is examining the effect of inhibitors on soil microbial processes,

N transformations and gaseous emissions of N in both laboratory and field studies, and the effect of inhibitors on the bioactivity of micro-organisms in a range of soils. This will allow simple assays to monitor the degradation of these inhibitors and regression models to predict degradation in various soil types to be developed.

Conclusions

Eventually, the value of these inhibitors in mitigating N losses in grazed pasture will depend on their rate of biodegradation and persistence in soils. Currently, there is a strong debate in New Zealand on the effectiveness of DCD in mitigating N loss. However, it is difficult to devise mitigation strategies from existing New Zealand information because the key soil and environmental factors influencing DCD efficiency are poorly understood. Furthermore, there is little information on the long-term impact these inhibitors will have on the N cycle of our grazed pasture systems, and on issues of toxicity.

A quantitative understanding of the interrelations between N_2O and NH_3 emissions, and NO_3^- and NH_4^+ leaching, is central to understanding how pasture systems behave and respond to inhibitors and to determining the effectiveness of land management strategies to reduce overall N losses. Mitigation strategies neglecting these interrelations may be sub-optimal. For example, there are claims that NIs lead to increased NH_3 volatilisation and enhance NH_4^+ leaching. However, limited quantitative New Zealand specific field data are available to accurately assess the NH_3 volatilisation and NH_4^+ leaching contribution of NIs.

Further research is required to identify the best inhibitors for efficient management of urine and fertiliser N inputs and to reduce economic and environmental impacts. In assessing the benefits from the use of inhibitors by way of extra N retention in pastoral systems, the medium- to long-term reductions in N-fixation by pasture legumes and other associated changes in management practices need to be considered. This research will not only provide an invaluable tool to assess the effectiveness and sustainability of land-management strategies to reduce N_2O and NH_3 emissions and N leaching losses but also contribute to refining strategies to further reduce N losses.

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