# Mitigating gaseous losses of nitrogen from pasture soil with urease and nitrification inhibitors

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# Abstract

Addition of nitrogen (N) to soil from various sources (i.e., animal excreta, farm effluents, synthetic fertilizers, crop residues and biological fixation), results in release of gaseous N such as nitrous oxide  $(N_2O)$  and ammonia  $(NH_3)$ . In grazed pasture soils, mitigation options need to focus on limiting the loss of N directly from animal excreta, farm effluents and synthetic fertilizers, and the indirect loss caused by leaching and (NH<sub>3</sub>) volatilization. One such approach is the use of urease (UI) and nitrification inhibitors (NI). Urease inhibitors retard the hydrolysis of urea N in urea-based fertilizers and urine, thereby decreasing the concentration of ammonium  $(NH_4^+)$  in soil solution and the subsequent  $NH_3$  volatilization. Whereas NIs specifically retard the oxidation of  $NH_4^+$  to nitrite (NO<sub>2</sub>), thereby decreasing the concentration of nitrate ( $NO_3^-$ ) and the subsequent leaching and denitrification. However, strategies to reduce emission of one gas may affect the emission of the other. Therefore, abatement strategies require simultaneous measurements of NH3 and N2O emissions. In a joint project, Massey University and Landcare Research are attempting various approaches for the abatement of gaseous N emissions. This paper reports the impacts of UI (N-(n-butyl) thiophosphoric triamide; Agrotain) and NI (Dicyandiamide; DCD) on the emissions of NH<sub>3</sub> and N<sub>2</sub>O from urine and urea applied to intact pasture soil cores. Our results indicate that the addition of UI Agrotain delayed the onset and reduced NH<sub>3</sub> emissions by 27% and 23% from urea and urine, respectively. Urease inhibitor also reduced  $N_2O$  emissions significantly from urine. DCD applied at 25 kg/ha to urea in the presence and absence of UI Agrotain reduced the amount of N<sub>2</sub>O emissions by 68% and 74% respectively. However, DCD did not cause any significant change in NH<sub>3</sub> emissions. Our results suggest that there is a considerable scope for reduction of N<sub>2</sub>O emissions by applying (DCD) both in the presence and absence of Agrotain.

# Keywords

Agrotain – Dicyandiamide –grazed pastures – nitrification inhibitor – urease inhibitor.

# Introduction

The major land use in New Zealand is pastoral farming of sheep and cattle. In these legume based pastures, nitrogen (N) is derived from biological N fixation by clover, fertilizer and farm effluent application and the uneven deposition of animal excreta, especially urine. It is estimated that New Zealand agricultural systems receive an annual input of about 3 million tonnes of N, with 1.5 million tonnes through animal excreta, 1.1 million tonnes through biological nitrogen fixation, 0.30 million tonnes through fertilizers and about 0.01-0.015 million tonnes through atmospheric deposition (Bolan *et al.* 2004). Recently there has been a sharp increase in fertilizer N inputs to grazed pastures and this increase is expected to continue in the foreseeable future. The N fertilizer use in 2002 was 279 000 tonnes and the estimates for 2003 were 342 000 tonnes (National Inventory Report New Zealand 2004). The increasing N input to grazed pastures has rekindled the debate on its impact on atmospheric, terrestrial and aquatic environments.

Loss of N occurs mainly through NH<sub>3</sub> volatilization, biological denitrification and NO<sub>3</sub><sup>-</sup> leaching. This has both economical and environmental implications. An upsurge of interest in gaseous losses of N from the soil has occurred during the last decade because of the environmental impacts of these losses. Ammonia is major form of gaseous N loss. The efficient use of urea fertilizer in arable and pastoral agriculture is often prejudiced by the loss of a portion of the applied N by NH<sub>3</sub> volatilization (Freney *et al.* 1981; Vlek and Craswell 1981). Large losses up to 30% are associated with urea containing fertilizers (Fenn and Hossner 1985; Lightner *et al.* 1990 and Termen 1979) and with ammonium-based fertilizers applied to high pH soils (Hargrove *et al.* 1977; Whitehead and Raistrick 1990). Enclosure measurements indicate that 4-41% of the N from applied cattle urine may volatilize (Lockyer and Whitehead 1990; Whitehead and Raistrick 1993). Ammonia affects visibility, aerosol chemistry, health, and climate as it causes acidification and eutrophication when deposited to soils and waters. Ammonia has a short life time

in the atmosphere but it can act as secondary source of nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O). Nitrous oxide is a potent greenhouse gas contributing to global warming (Bouwman 1990). It accounts for about 2-4% of the total anticipated Global Warming Potential (Watson et al. 1992) and is also involved in catalytic destruction of stratospheric ozone. The major processes responsible for N<sub>2</sub>O emissions are nitrification and denitrification. The N excreted by sheep and cattle onto grazed pastures provides high localized concentrations of available N and C in the soils and is the main source of anthropogenic N2O emissions in New Zealand, contributing to about 85% of total N<sub>2</sub>O emissions (Cameron et al. 2000). Various approaches have been attempted to mitigate the economic and environmental impacts of N losses. One such approach is the use of urease and nitrification inhibitors. The UIs occupy the urease active site inactivating the urease enzyme and thus reducing the loss through NH<sub>3</sub> volatilization. Nitrification inhibitors offer potential for decreased losses of NO<sub>3</sub><sup>-</sup>N through denitrification and leaching by delaying the microbial transformation of  $NH_4^+$  to  $NO_3^-$  (Trenkel 1997). Although a number of research works have been undertaken to study the independent effect of these inhibitors on individual N gaseous emissions, little attention has been paid to study the impact of UIs and NIs in combination, on the simultaneous emissions of NH<sub>3</sub> and N<sub>2</sub>O. Developing mitigation strategies for loss of N through gaseous emissions require simultaneous quantification of NH<sub>3</sub> and N<sub>2</sub>O emissions. Therefore the objective of this joint project by Massey University and Landcare Research was to evaluate the impacts of UI (N-(n-butyl) thiophosphoric triamide; Agrotain) and NI (Dicyandiamide; DCD) on the emissions of NH<sub>3</sub> and N<sub>2</sub>O simultaneously from urine and urea applied to pasture soil.

# Materials and methods

Two experiments were conducted to assess the impact of a UI (N-(n-butyl) thiophosphoric triamide - NBPT known as Agrotain) and a NI (Dicyandiamide – DCD) on the emissions of  $NH_3$  and  $N_2O$  from urea and urine applied to intact pasture soil cores.

# Collection and preparation of intact soil cores

Intact soil cores (100 mm diameter, 100 mm depth) from three representative sites were collected from a sheep-grazed permanent legume-based pasture at Massey University Frewens Research Block, Turitea campus. The soil at this site was a Manawatu fine sandy loam, classified as weathered fluvial recent soil (a Fluvent). Some pertinent soil chemical and physical properties are given in Table 1. These cores were first saturated overnight with deionised water and then kept on pressure plates at -10 kPa pressure for 2 days to bring them to field capacity. Cores were weighed every day and the moisture content was adjusted to field capacity during the measurement of  $NH_3$  and  $N_2O$  emissions.

	Depth (cms)	Total-N (%)	Total C (%)	pH (soil : water 1: 2.5)	Bulk Density (mg/m <sup>3</sup> )	C.E.C. (coml. charge kg <sup>-1</sup> )
Manawatu	0-5	0.30	3.5	5.7	1.2	16
fine sandy loam	5-10	0.15	1.5	6.2	1.2	

## Table 1. Soil chemical and physical properties

## Experiment 1

This experiment was set up on  $16^{th}$  April 2003 by placing three cores in each chamber in a glass house maintained at a near constant temperature ranging from  $15-20^{\circ}$ C. All treatments with three replications were applied the following day. The experiment comprised of six treatments that included: T1- Control without UI; T2 – Control with UI; T3 – Urine without UI; T4 – Urine with UI; T5 – Urea without UI; T6 – Urea with UI (It is a commercial fertilizer product called 'SustaiN' in which sulfur-coated urea granules are mixed with Agrotain). Nitrogen in the form of urine and urea was added at the rate of 600 kg N/ ha. Urease inhibitor was added following urine application, and the fertilizer grade urea and SustaiN granules (2-4 mm) were applied onto the soil surface. The amount of UI Agrotain (liquid form) added to urine treatment was similar to that present in SustaiN (@1 litre/ton urea). In intensively grazed grassland ecosystems, the main source of N<sub>2</sub>O-N and NH<sub>3</sub>-N is derived from the N returned in the localized areas of pasture as urine. The N loading rate under a urine patch can be as high as 1000 kg N/ha for dairy cattle with 70-80% being urea N (Haynes and Williams 1993). The main objective of this experiment was to examine the effect of UI on simultaneous emissions of NH<sub>3</sub> and N<sub>2</sub>O from cattle urine or urea applied to pasture. The gaseous emissions were monitored for 10 weeks (6 weeks for NH<sub>3</sub>) using the method developed and described below and analysed for NH<sub>3</sub> and N<sub>2</sub>O emissions.

## **Experiment** 2

The soil cores from three representative sites were collected in the same way as described above. The experiment was set up on  $11^{\text{th}}$  August 2003 in a glass house maintained at a near constant temperature ranging from  $15-20^{\circ}$ C and background emissions for NH<sub>3</sub> and N<sub>2</sub>O were taken before applying treatments. Three replications were used for each treatment. The treatments included: T1- Control without NI; T2 – Control with NI; T3 – Urea without NI; T4 – Urea with NI; T5 – SustaiN without NI; T6 – SustaiN with NI. Nitrogen in the form of urea and SustaiN was applied @100kg/ha. Nitrification inhibitor DCD (liquid form) was added @ 25kg/ha after the surface application of urea and SustaiN. The gaseous emissions were monitored for six weeks (3 weeks for NH<sub>3</sub>). In this experiment the effect of NI DCD on gaseous emissions from urea was examined both in presence and absence of UI Agrotain.

## Description of the sampling system

A simplified schematic diagram of the basic components is shown in Fig 1. It consists of an air tight closed chamber with two ports, chemical trap and air supply measuring NH<sub>3</sub> gas. A new technique using active flux for NH<sub>3</sub> and passive flux for N<sub>2</sub>O measurements simultaneously was developed and tested. The system consisted of chambers (Saggar et al. 2002, 2004), a constant air supply and chemical traps to capture  $NH_3$ . The chambers were designed with removable lids having different fittings for sampling  $N_2O$ and NH<sub>3</sub> in the system. The lid with two ports, one input port connected to an air supply and other exhaust port connected to a chemical trap of 50 ml of  $0.05 \text{ M H}_2\text{SO}_4$  was used to measure NH<sub>3</sub> volatilization. A manifold with 12 air valves was used to connect the compressed air supply with the chambers. Air flow (a) 1 dm<sup>3</sup>/min was adjusted in each chamber using the valves in the manifold. The other lid with one port was used for measuring N<sub>2</sub>O emission. Ammonia was collected by flushing air @ 1 dm<sup>3</sup>/min continuously through each chamber for 12 hrs during night. This NH<sub>3</sub> charged air was then passed through 50 ml of 0.05M H<sub>2</sub>SO<sub>4</sub> (Wulf et al. 2001) to trap ammonia. After taking NH<sub>3</sub> measurements, lids from chambers were removed to achieve equilibrium with ambient conditions. Nitrous oxide samples were taken after sealing the chambers with another lid having one port, for a period of one hour, with 60 ml polypropylene syringes fitted with 3-way stopcocks. Three gas samples were taken from each chamber at times t<sub>0</sub>, t<sub>30</sub>, t<sub>60</sub> (Time 0 min, 30 min and 60 min after closing of the chamber respectively). Water was top up every day to bring the soil cores to field capacity after taking measurements for both NH<sub>3</sub> and N<sub>2</sub>O.



measurements

measurement



# Analysis

The sulphuric acid solution was then analysed for total  $NH_4^+$ -N using an auto analyser. The gas samples collected were analysed for N<sub>2</sub>O using a Shimadzu GC – 17A gas chromatograph with a <sup>63</sup>Ni-Electron capture detector and N<sub>2</sub>O (mg/m<sup>2</sup>/hr) flux was estimated from the measurements made at three time periods (t<sub>0</sub>, t<sub>30</sub> and t<sub>60</sub>). Daily emission rates were calculated from these fluxes. Although these gaseous

emissions were found to be affected by temperature, no allowance was made for the slight variation in temperature in the glasshouse.

### **Results and discussion**

Effect of urease inhibitor

## Ammonia emissions

Addition of UI Agrotain resulted in significant reductions in NH<sub>3</sub> emissions from both urea and urine (Fig.1). Overall there was 27 % and 23 % decline in NH<sub>3</sub> loss from SustaiN and urine with Agrotain as compared to that in urea and urine respectively (Table 2). Initially (5-7 days after application of urea and SustaiN treatments to the soil cores) the amount of NH<sub>3</sub> emitted was markedly higher from unamended urea than from SustaiN. This may be due to the fact that in the absence of UI and elemental sulphur coating, most of the urea added to soil is hydrolysed to NH<sub>4</sub><sup>+</sup> ions, whereas substantial amounts of urea could remain in soil in the presence of UI Agrotain for approximately one week (Watson *et al.* 1994). The inhibitor occupies the urease active site, inactivating the enzyme (Mobley and Hausinger 1989) to delay the onset and reduce the rate of NH<sub>3</sub> emissions (Christianson *et al.* 1990). Our results suggest that the delay in the hydrolysis reduced the concentration of NH<sub>3</sub> present near the soil surface, which decreased the potential for emissions and improved the opportunity for urea molecules to move deeper to the soil with added water. However, at the end of the experiment, the rate of NH<sub>3</sub> emissions was similar in both the treatments, indicating that the effect of the inhibitor was beginning to diminish and also that the rate of NH<sub>3</sub> loss from untreated urea was decreasing.

Application of urine resulted in sudden increase in  $NH_3$  loss within 24 hours of application (Fig 2). As the urea  $(CO(NH_2)_2)$  in urine undergoes hydrolysis in the presence of urease enzyme within the first 24 hours of urine addition to soils (Eq.1) so this high loss of  $NH_3$  was expected. In this process, large amounts of  $NH_4^+$  ions accumulate in the soil. This process also releases alkali ions (OH<sup>-</sup>) and hence the pH in soil increases to a maximum of 8. The  $NH_4^+$  ions dissociate into  $NH_3$  in the presence of  $OH^-$  (Eq 2), resulting in the release of  $NH_3$  gas.

$$CO(NH_2)_2 \rightarrow 2NH_4^+ + 2OH^- + CO_2 \tag{1}$$
  

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \tag{2}$$

In contrast, the urine application with UI Agrotain did not result in high  $NH_3$  volatilization from urine application within 24 hrs (Fig 2). The cumulative  $NH_3$ -N (kg N/ ha) released from urine (44.0kg N/ ha) decreased to 33.9 kg N/ ha with the addition of UI resulting in 23% decline in  $NH_3$  emissions (Table 2). Surface application of urea resulted in higher  $NH_3$  emissions than the urine treatments as the  $NH_4^+$  ions from urine moved down the soil while urea remained at the soil surface.



Fig 2. Ammonia volatilization losses with and without UI from urine and urea applications. The inset gives the enlarged graph for NH<sub>3</sub> emissions from urine and urine+UI treatments.

## Nitrous oxide emissions

The emission of  $N_2O$  was also affected by the presence of UI Agrotain, especially in case of urine. Nitrous oxide emissions were higher from urine than from urine with UI soon after application (Fig 3).



Fig 3. Nitrous oxide losses with and without UI from urine and urea applications. The inset gives the enlarged graph for  $N_2O$  emissions from urea and SustaiN treatments.

The total N<sub>2</sub>O emissions (8.51 kg N<sub>2</sub>O-N/ha) from urine decreased to 3.14 with the addition of Agrotain (Table 2). However, there was no significant difference in N<sub>2</sub>O emissions from urea and SustaiN (Fig 3). Our results are similar to those reported by Xu *et al.* (2000) who found that application of urease inhibitor to urea didn't have any significant effect on N<sub>2</sub>O emissions.

	N added	NH <sub>3</sub> -N	N <sub>2</sub> O-N	% of added N emitted
Treatment	(kg N/ ha)	(kg N/ ha) emitted	(kg N/ha) emitted	$(NH_3 + N_2O)$
Control		1.34	0.13	
Control + UI		1.13	0.15	
Urine	487	44.0	8.51	10.5
Urine + UI	487	33.9	3.14	7.34
Urea	615	196	2.06	32.0
SustaiN	615	142	2.38	23.2
LSD (0.05%)		9.96	2.18	
LSD (0.01%)		15.1	3.31	
CV %		5.82	32.7	

Table 2. Total N applied and total N emitted  $(NH_3-N + N_2O-N)$  (kg N/ha) over the experimental period from various treatments with and without UI applied

## Effect of Nitrification Inhibitor

## Ammonia emissions

Ammonia emissions peaked two days after the N fertilizer application in both urea and urea+DCD treatments (Fig 4). However, there was no significant difference in total NH<sub>3</sub> emissions between these two treatments (Table 3). As DCD inhibits the conversion of  $NH_4^+$  to  $NO_3^-$  thus it can maintain higher concentration of  $NH_4^+$  in the soil resulting in increased NH<sub>3</sub> volatilization (Davies and Williams 1995). However, since NH<sub>3</sub> volatilization loss is affected by a number of factors, including temperature, pH and the location of the N source, the use of DCD, therefore, may or may not result in increased NH<sub>3</sub> volatilization (Prakasa Rao and Puttanna 1987; Clay *et al.* 1990). Clay *et al.* (1990) did not find any increase in NH<sub>3</sub> volatilization by combining urea with DCD. Similar results were found in SustaiN with and without DCD (Table 3). However, we can see a marked decrease in NH<sub>3</sub> emissions from SustaiN as compared to that from urea alone which is in accordance with the results of experiment 1. The cumulative NH<sub>3</sub> emissions were much less from SustaiN (1.78 kg N/ha) than from urea (7.44 kg N/ ha) (Table 3).



Fig 4. Ammonia volatilization losses with and without NI and NI+UI from urea. The inset gives the enlarged graph for NH<sub>3</sub> emissions from SustaiN and SustaiN+NI treatments.

#### Nitrous oxide emissions

Both urea and SustaiN showed lower levels of N<sub>2</sub>O emissions in the presence than in the absence of DCD (Fig 5). Nitrous oxide emissions in urea without DCD application peaked to 2.94 mg N<sub>2</sub>O-N mg/m<sup>2</sup>/day before gradually declining to background levels. In contrast, where DCD was applied to urea, N<sub>2</sub>O flux was reduced to below 0.40 mg N<sub>2</sub>O-N/m<sup>2</sup>/day. Overall with DCD, the N<sub>2</sub>O flux was reduced by 74%. These findings corroborate the results of a number of previous international (McTaggart *et al.* 1997; Dobbie *et al.* 2003) and New Zealand (Di and Cameron 2003) studies. Nitrous oxide emissions were higher from SustaiN than those observed from urea. However, with the addition of DCD to SustaiN, similar reductions were observed as in urea. N<sub>2</sub>O emissions peaked two weeks after application of SustaiN alone whereas no such peak was observed in case of SustaiN with DCD (Fig 5). With the addition of DCD to SustaiN, cumulative N<sub>2</sub>O-N loss (kg N/ha) decreased from 0.56 kg N/ ha to 0.19 kg N/ha (Table 3) causing 68% reduction. Thus the use of DCD with and without UI to urea is an effective way of reducing N<sub>2</sub>O emissions (Xu *et al.* 2000 and 2002).



Fig 5: Nitrous oxide losses with and without NI and NI+UI from urea.

Treatment	N added (kg N/ ha)	NH3-N (kg N/ ha) emitted	N <sub>2</sub> O-N (kg N/ ha) emitted	% of added N emitted (NH <sub>3</sub> + N <sub>2</sub> O)
Control		0.05	0.03	
Control + NI		0.07	0.04	
Urea	103	7.44	0.43	7.55
Urea + NI	103	6.12	0.11	5.95
SustaiN	103	1.78	0.56	2.18
SustaiN + NI	103	1.68	0.19	1.72
LSD (0.05 %)		1.47	0.17	
LSD (0.01 %)		2.06	0.24	
CV %		28.9	43.5	

Table 3. Total N applied and total N emitted ( $NH_3$ -N +  $N_2O$ -N) (kg N/ha) over the experimental period from urea and SustaiN with and without NI

# Conclusions

Our study showed that UI (Agrotain containing NBPT) reduced the NH<sub>3</sub> loss from the surface applied urea and urine by 27% and 23% respectively and also delayed the time of maximum NH<sub>3</sub> loss. Addition of Agrotain to urine reduced N<sub>2</sub>O emissions but no reduction in emissions was observed from Agrotain added to urea fertilizer. Further studies should be done to see the effect of urease inhibitor on N<sub>2</sub>O emissions with various sources of N. The NI (DCD) significantly reduced the N<sub>2</sub>O emissions when added alone or along with UI Agrotain but there were no significant changes in NH<sub>3</sub> volatilization. These experiments were conducted under controlled glass house conditions which require further testing under field conditions.

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