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Landcare Research Manaaki Whenua

Reductions in FracGASM and FracGASF in the GHG inventory when urease inhibitor has been applied to the soil and with N fertiliser

**Final Report** 

Contract: LC232, MAF Contract: MAF -12207 (IR-C 4)

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#### **Project Code**

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#### **Business/Institution**

Landcare Research

#### **Programme Leader**

• Surinder Saggar

#### **Programme Title**

• Urease Inhibitors

#### Goal

• To provide a framework to incorporate urease inhibitor into National agriculture inventory including activity data acquisition and use, and confirm the emission factor reduction. Urease inhibitor [N-(n-butyl) thiophosphoric triamide; nBTPT] sold under the trade name Agrotain® and applied at 0.025% w/w to soil and with fertiliser or urine reduces NH3 emission resulting in reductions in  $Frac_{GASF}$  (fraction of total nitrogen (N) fertiliser emitted as nitrogen oxides (NO<sub>x</sub>) and NH<sub>3</sub>) and for  $Frac_{GASM}$  (fraction of total N excretion emitted as NO<sub>x</sub> and NH<sub>3</sub>).

#### Approach

• Review of national and international Literature

#### Outcomes

• The recommended reduction in FracGASM and FracGASM and FracGASF will result in reducing nitrous oxide emissions in NZ greenhouse gas (GHG) inventory.

#### Recommendations

• See the report

#### Summary

• Included in the report

#### Publications

This report, MS to be submitted for publication in July 2011.

## 1 Executive Summary

Urease inhibitors (UIs) can be used as a mitigation technology to control nitrogen (N) losses from urea fertiliser and urine N. UIs act on the biological process of hydrolysis of urea ((CH<sub>2</sub>)<sub>2</sub>CO) to ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) by inhibiting the action of the urease enzyme thereby slowing urea hydrolysis and reducing NH<sub>3</sub> volatilisation. Many compounds could potentially be used as UIs. The compound N-(n-butyl) thiophosphoric triamide (nBTPT), commercially available under the trade name of Agrotain<sup>®</sup>, is the most widely tested UI for its efficacy, particularly in cropping systems. The compound is effective in reducing NH<sub>3</sub> volatilisation when applied at low concentrations (less than 0.1%, w/w) with urea fertiliser and animal urine.

This report, which was commissioned to meet the critically important international IPCC Good Practice Guidance standards, therefore seeks to determine the impact of UI on changes in both the emission factors  $Frac_{GASF}$  (fraction of total nitrogen (N) fertiliser emitted as nitrogen oxides (NO<sub>x</sub>) and NH<sub>3</sub>) and for  $Frac_{GASM}$  (fraction of total N excretion emitted as NO<sub>x</sub> and NH<sub>3</sub>) for urea fertiliser-N and urine-N deposition in grazed pasture soils.

This report also outlines other aspects of UIs that need to be further evaluated to determine the effect of UI on reductions in the  $NH_3$  lost from animal urine-N deposited during grazing, including their effectiveness (a) in different soil types, (b) at a range of soil temperatures and soil moistures. The mode of application of UI to urine patches and the frequency of its application to provide quantitative estimates of emission reductions from excretal N inputs during grazing also need to be assessed.

## 1.1 Outcomes

A report prepared by Saggar et al. (2009) for MAF was fully reviewed. As no significant new information has become available since its publication, the review does not require updating. The 40% mean reduction in the N lost as  $NH_3$  due to the use of UI (nBTPT) @ 0.025% w/w with urea fertiliser, in New Zealand national agricultural greenhouse (GHG) inventory calculation, remains valid. It is therefore recommedned that the  $Frac_{GASF}$  (fraction of total fertiliser emitted as  $NO_x$  and  $NH_3$ ) should be reduced from 0.1 to 0.06 for New Zealand where nBTPT is applied together with urea fertiliser.

Only a limited number of published data sets are available describing the effectiveness of UI for reducing NH<sub>3</sub> losses from urine in a grazed pasture system. The method of UI application is flawed as all experiments were conducted by mixing UI with urine before its application to soil. Therefore, based on the existing data, it is not possible to estimate accurately the effect of UI on reductions in the NH<sub>3</sub> lost from animal urine-N deposited during grazing, and no changes are recommended in FRAC<sub>GASM</sub>.

### 1.2 Frame work to incorporate UI into National agriculture inventory

Ammonia is not a GHG, but when it is re-deposited on land it acts as an indirect source of  $N_2O$ . New Zealand's  $N_2O$  inventory currently uses the NZIPCC specific emission values of 0.1 for both  $Frac_{GASM}$  (fraction of total nitrogen excretion emitted as  $NO_x$  and  $NH_3$ ) and  $Frac_{GASF}$  (fraction of total fertiliser nitrogen emitted as  $NO_x$  and  $NH_3$ ). Application of the UI nBTPT with urea or animal urine reduces the amount of  $NH_3$  emission, and a further reduction in the value of  $Frac_{GASF}$  and  $Frac_{GASM}$  could be justified. To our knowledge, no other country has revised its emission factors to account for the effect of nBTPT application on  $NH_3$  emissions from fertiliser N or animal-deposited excretal N in grazed pasture soils.

The average reduction rate in NH<sub>3</sub> emissions was  $42.8 \pm 5.1\%$  (mean ± standard error) (95% confidence of interval of mean 10.2) from UI-treated urea (Saggar et al. 2009). However, in the absence of adequate data the effect of UI on reductions in the NH<sub>3</sub> lost from animal urine-N deposited during grazing can not be estimated. Based on urea reduction rates, a New Zealand specific value of 0.06 for Frac<sub>GASF</sub> is recommended for adoption where the urease inhibitor, nBTPT, is applied with urea fertiliser.

Changing the  $Frac_{GASF}$  from 0.1 to 0.06 for the 2009 use of 18.4 Gg N of SustaiN (urea containing nBTPT) reduces indirect N<sub>2</sub>O emissions by 0.012 Gg, which equates to 3.6 Gg CO<sub>2-equiv</sub>. However, assuming all the urea is applied with NBPT in New Zealand, changing the  $Frac_{GASF}$  from 0.1 to 0.06 will reduce the indirect N<sub>2</sub>O emissions by 0.14 Gg, which equates to 43.4 Gg CO<sub>2-equiv</sub> (Saggar et al. 2009).

The requirements for the use of UI nBTPT are similar to those for the nitrification inhibitor DCD, i.e. a requirement for accurate and verifiable records of (a) the sale of total fertiliser N, urea-N and UI treated urea-N from the fertiliser industry, and (b) the amount of nBTPT imported from the Agrotain International. Long-term record, storage and availability for independent review are also required.

## 2 Introduction

New Zealand recently recommended a specific value of 0.1 both for  $Frac_{GASF}$  (fraction of total nitrogen (N) fertiliser emitted as nitrogen oxides (NO<sub>x</sub>) and NH<sub>3</sub>) and for  $Frac_{GASM}$  (fraction of total N excretion emitted as NO<sub>x</sub> and NH<sub>3</sub>). This value has been accepted for adoption in the national GHG inventory. The application of UI with urea fertiliser and animal urine can reduce NH<sub>3</sub> emissions and further reduces the values of  $Frac_{GASF}$  and  $Frac_{GASM}$ .

In the previous MAF-funded study, Saggar et al. (2009) conducted a literature review to examine the contribution of UI with urea fertiliser N to emissions reductions in New Zealand's national GHG inventory. This report suggested a 40% reduction in  $NH_3$  emissions from urea fertiliser N where UI is applied. A method to describe how  $NH_3$  emissions from urea fertiliser N in agriculture soils can be reduced using UI:

a) where UI is applied as recommended,  $Frac_{GASF}$  should be termed  $Frac_{GASF}$  $FN_{UI}$  and calculated as follows:

$$Frac_{GASF} FN_{UI} = [(FN_{UI}) \times 0.06]$$
(1)

 $Frac_{GASF}FN_{UI}$  is the fraction of UI treated urea fertiliser N emitted as NH<sub>3</sub>, FN<sub>UI</sub> is the amount of applied fertiliser N treated with UI.

b) where fertiliser N is applied without any amendment,  $Frac_{GASF}$  termed  $Frac_{GASF} FN_{U}$  and calculated as follows:

$$Frac_{GASF} FN_U = [(FN_U) \times 0.10]$$

 $Frac_{GASF} FN_U$  is the fraction of unamended fertiliser N emitted as  $NH_3$ ,  $FN_U$  is the amount of applied urea N.

Changing the  $Frac_{GASF}FN_{UI}$  from 0.10 to 0.06 for the 2009 use of 18.4 Gg N of SustaiN (urea coated with UI) reduces indirect N<sub>2</sub>O emissions by 0.012 Gg, which equates to 3.6 Gg CO<sub>2-equiv</sub>. However, assuming all the urea is applied with UI in New Zealand, changing the  $Frac_{GASF}$  from 0.1 to 0.06 will reduce the indirect N<sub>2</sub>O emissions by 0.14 Gg, which equates to 43.4 Gg CO<sub>2-equiv</sub>.

In the absence of New Zealand data on direct application of UI on deposited animal urine N in pasture soils, the earlier report (Saggar et al. 2009) did not include emission reductions from excretal N when UIs was applied directly to grazed pasture soil.

Therefore, this report, which is required to meet the critically important international IPCC Good Practice Guidance standards, seeks to determine the impact of UI on changes in both emission factors  $Frac_{GASF}$  and  $Frac_{GASM}$  for urea fertiliser-N and urine-N deposition in grazed pasture soils through:

- detailed examination of all the new and previously reviewed (Saggar et al. 2009) relevant overseas and New Zealand literature, both published and unpublished. This will be used to determine the contribution of UIs both directly applied to soil and in amended urea fertiliser to the reduction of NH<sub>3</sub> emissions for a range of pasture management systems
- devising an appropriate technique for integrating the activity data into the national agricultural inventory
- establishing a framework for incorporation of UIs by linking the activity data with reductions in Frac<sub>GASM</sub> and Frac<sub>GASF</sub>
- implementing proposed changes to the treatment of Frac<sub>GASF</sub> and Frac<sub>GASM</sub> in the Tier 1 Inventory model, including the development of a test (using the Tier1 model) to assess the impact of the changes on total emissions.

## 3 Objectives

- To determine the changes in Frac<sub>GASM</sub> and Frac<sub>GASF</sub> for grazed pasture soils following the application of UIs (Agrotain<sup>®</sup>) to soil and with urea fertiliser N.
- To determine the contribution of Agrotain<sup>®</sup> to emission reductions in New Zealand's national agriculture GHG inventory.
- To establish a framework to incorporate UI into national agriculture inventory.

## 4 Literature Review

### 4.1 Scope of this review

This review examines all the new and previously reviewed (Saggar et al. 2009) relevant New Zealand and overseas literature, both published and available unpublished, to determine the contribution of UIs, both directly applied to soil and with urea fertiliser, to reduction in N losses and GHG emissions from grazed pasture management systems.

Our approach was to update the MAF-funded review by Saggar et al. (2009) on the efficacy of the UIs in reducing  $NH_3$  losses when applied with urea fertiliser N, and review the national and international published data on the effectiveness of the UI on  $NH_3$  emission reduction from excretal N when UI is applied directly onto soil. Based on the information gleaned from the literature, we then sought to draw some general conclusions on the potential reduction that can be obtained from the use of UIs in grazed pasture systems. If the information was inconclusive then a framework would be proposed to capture information (data) that could help to further refine the Frac<sub>GASM</sub> from animal excretal inputs in grazed pastures.

## 4.2 Urease Inhibitors applied to urea fertiliser

Many synthetic UIs have been shown to delay the hydrolysis of urea applied to soil, either as fertiliser or in animal excreta. The modes of action of many of these UI compounds have been well described by Saggar et al. (2009). Briefly, based on their binding modes, these compounds can be broadly divided into two categories: (1) substrate-analogue inhibitors; and (2) non-substrate-like or mechanism-based inhibitors (Amtul et al. 2002). The UIs delay urea hydrolysis, which reduces the concentration of  $NH_4^+$  and prevents localised zones of high pH in soils. The volatilisation of  $NH_3$  generally occurs when soil pH is >7.5.

The most widely tested and promising UI is Agrotain<sup>®</sup> (trade name), a structural analogue of urea, which has been shown to be compatible with urea. Its urease inhibitory activity in soil is associated with the activity of its derivative, the oxygen analogue N-(*n*-butyl) thiophosphoric triamide (nBTPT). Slowing the hydrolysis of urea allows more time for the urea to disperse from the urine patches, or for rain or irrigation water to dilute the urea and NH<sub>4</sub><sup>+</sup> concentration at the soil surface and increase its dispersal in the soil. Therefore, the use of UIs can potentially increase the efficiency of use of animal urea and urine-N by plants. Commercially available in New Zealand, nBTPT is sold as SustaiN<sup>®</sup>, a urea-based fertiliser treated with Agrotain<sup>®</sup>. Studies conducted by Zaman et al. (2008) have shown nBTPT consistently inhibited the activity of the urease enzyme for up to two weeks. This field study with nBTPT also showed delayed urea hydrolysis and significant reduction in the subsequent leaching of NO<sub>3</sub><sup>-</sup> (Zaman et al. 2008).

Urease is a naturally occurring enzyme that catalyzes the hydrolysis of urea to unstable carbamic acid. Rapid decomposition of carbamic acid occurs without enzyme catalysis to form NH<sub>3</sub> and carbon dioxide. Volatilisation loss of N as NH<sub>3</sub> from urea fertiliser and urine is one of the major pathways of N loss in cropping and pasture soils. Results reported in the literature show considerable variability (5–50%) in total volatilisation losses of N as NH<sub>3</sub> from urea fertiliser, depending on the conditions of the experiments (Ledgard 2001; Watson et al. 2008; Saggar et al. 2009). The factors that influence NH<sub>3</sub> volatilisation from urine are soil pH, temperature, moisture, and rainfall (e.g., Nelson 1982; Francis et al. 2008). The volatilisation of NH<sub>3</sub> from urea fertiliser is greater when soil pH is high (>7.5), coupled with warm and moist soils under windy conditions (e.g., Nelson 1982; Francis et al. 2008).

## **4.2.1** Factors regulating the effectiveness of urease inhibitors in minimising volatilisation loss of NH<sub>3</sub> from fertiliser urea

The influence of the soil and climatic factors and the mode of action of UI (nBTPT) in reducing  $NH_3$  volatalisation have already been extensively covered in a recent review of the literature by Saggar et al. (2009), which was presented to the Ministry of Agriculture and Forestry (MAF). Since then no new knowledge has become available regarding UI's mode of action.

The Saggar et al. (2009) report on UI effects on fertiliser N is summarised below:

- i) nBTPT appears to has no effect on soil microbial biomass. It only affects the specific activity of urease, the enzyme that hydrolyses urea, and is only effective for 7–14 days.
- the optimum concentration of nBTPT for temperate grassland soils was reported to be 0.1% (w/w) but there was little commercial benefit in using nBTPT concentration above 0.025% (w/w) (Watson et al. 2008). Therefore, Most of New Zealand studies have used 0.025% (w/w).
- iii) different levels of nBTPT application (up to 0.1%) with urea reduce average NH<sub>3</sub> emission by 63% and an effective 0.025% (w/w) application in New Zealand resulted in an average 42.8% reduction in NH<sub>3</sub> emission and an overall 6.5% increase in pasture production comapred to urea alone. Chadwick et al. (2005) obtained an average 75% reduction in NH<sub>3</sub> emission where average emissions were 26%, but found no signifacnt difference (P>0.05) in reduction between 0.025, 0.05 and 0.1% nBTPT application. Thus the lower (average 42.8%) reduction obtained in New Zealand studies may be attributed partly to overall lower NH<sub>3</sub> emission (10%; Sherlock et al. 2009).
- iv) nBTPT is more effective in soil with light texture, low organic C, high pH and low buffering capacity. These soils also lead to high NH<sub>3</sub> losses. Thus the overall efficiency depends on a combination of soil physical and chemical properties rather than one single factor. A narrow acidic pH range and high organic C of New Zealand pastoral soils may result in low and less variable NH<sub>3</sub> losses and lower reductions.

v) it is generally considered that nBTPT effectiveness decreases with temperature as the urea hydrolysis rate may surpass the rate of nBTPT conversion to nBPTO, or the rate of inhibitor degradation. Tempeartue effects are less pronounced between 5 and 25°C (Watson et al. 2008) and appear to become more significant at soil tempratures above 25°C. A more recent Australian laboratory study (Suter et al. 2011) suggests that for pasture soils with high urease activity where temperatures are higher (25°C), a greater rate of nBTPT may be required to effectively reduce urea hydrolysis. However, reductions in NH<sub>3</sub> emissions were not measured in this study.

The results of a DEFRA funded UK field study examining the influence of various factors on NH<sub>3</sub> emissions and the effectiveness of nBTPT (0.05% w/w) to reduce these emissions on a number of soils (Chadwick et al. 2005) show that despite the variability among field-based studies the nBTPT effectiveness is constant across all soil temperatures from ~2 to ~15 degrees. We performed a linear regression analysis on NH<sub>3</sub> emission from urea and % reduction in emissions with nBTPT against temperature. Neither the emissions from urea or % reduction in emissions with nBTPT showed a significant trend with temperature (p-values = 0.32 and 0.40 respectively) (Figures 1 and 2) Another regression model showed 73% reduction in NH<sub>3</sub> emission with nBTPT (with a 95% confidence interval of 66% to 80%).



Figure 1: Ammonia emissions from urea only vs temperature.



Figure 2: % reduction in ammonia emission due to nBTPT vs temperature.

Therefore, the review does not require updating. Thus the 40% reduction [based on  $(42.8 \pm 5.1\% \text{ (mean} \pm \text{standard error)} (95\% \text{ confidence of interval of mean 10.2)] in the N lost as NH<sub>3</sub> due to the use of UI (nBTPT) @ 0.025% w/w, in New Zealand national agricultural greenhouse (GHG) inventory calculation, remains valid. It is recommended that Frac<sub>GASF</sub> be reduced from 0.1 to 0.06 for New Zealand where UI is applied with urea fertiliser.$ 

This adjustment in  $Frac_{GASF}$  could potentially reduce calculated indirect N<sub>2</sub>O emission by 0.14 Gg, equivalent to 43.4 Gg CO<sub>2</sub>. The review by Saggar et al. (2009) covered, more specifically, the effectiveness of the UI nBTPT when applied with urea-based fertilisers. Information was lacking on the effectiveness of nBTPT application in reducing NH<sub>3</sub> emission from grazed pasture systems where urine-N is the dominant N input and where potentially significant gains could be made through the use of this technology in reducing New Zealand's national GHG liability.

### 4.3 Urease inhibitors applied to grazed pastures

In New Zealand, pastoral agriculture is the dominant land use and animals are grazed all year round. Animal excreta (urine and dung) from grazing animals make up to 50% of the total N decoupled and recycled in grazed pastures (Saggar et al. 2004). About 60–70% of these animal excretal N inputs are from animal urine, which is one of the major sources of N loss from grazed pastures. Approximately 80% of urine N is in the form of urea (Bolan et al. 2004; Zaman et al. 2007). Utilization efficiency of urine-N by plants in pasture is estimated to be less than 30%. Loss of N as NH<sub>3</sub> gas from urine patches ranges between 7 and 10% of the total N applied as urea (Ledgard 2001; Zaman & Blennerhassett 2010). These figures provide a compelling argument to reduce N losses from animal excretal inputs. Any efficiency gain in utilisation of N from urine patches on grazed pastures through minimising gaseous losses (NH<sub>3</sub> and N<sub>2</sub>O) would have a significant impact on the New Zealand GHG inventory. Therefore, a desktop scoping study commissioned by MAF to evaluate the possible use of UIs on grazed pasture for reducing net N loss is a step in the right direction.

## 4.3.1 Effectiveness of urease inhibitors in minimising volatilisation loss of NH<sub>3</sub> from animal urine

Although there are no published overseas data on the effectiveness of UIs in reducing volatilisation losses of N as  $NH_3$  from urine on grazed pasture soils, a limited number of studies in New Zealand have evaluated the effect of application of UI alone, or in combination with nitrification inhibitors (NI), on gaseous losses ( $NH_3$  and  $N_2O$ ) of N from applied animal urine (Table 1).

Specific experimental details of the published papers are described below:

## 4.3.1.1 Singh et al. (2003) & (2008)

- A glasshouse study was carried out using in situ soil cores to determine the effects of Agrotain<sup>®</sup> on N losses (NH<sub>3</sub> volatilisation, N<sub>2</sub>O emission, and NO<sub>3</sub> leaching) from urine-treated soil. The soil used was Tokomaru silt loam, which is a poorly drained soil. The study was conducted between April and July 2003. The cattle urine application rate was 600 kg N ha<sup>-1</sup>. Agrotain<sup>®</sup> was applied at a rate of ~1 L / 460 kg N.
- There was an 11% reduction in volatilisation of NH<sub>3</sub> from urine treated with Agrotain<sup>®</sup> compared with non-treated urine. Some reduction in N<sub>2</sub>O emission was also achieved, especially during the early stages of the experiment.
- In another field-plot study conducted between May and June 2005 on the same soil, Singh et al. (2008) reported a 23% reduction in NH<sub>3</sub> volatilisation when Agrotain<sup>®</sup> was applied to urine patches compared with urine alone.

## 4.3.1.2 Menneer et al. (2008)

- This study was carried out to determine whether UI (Agrotain<sup>®</sup>) and nitrification inhibitors (dicyandiamide (DCD) or 4-methyl pyrozole (4MP)), either alone or in combination, could decrease losses of NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O, and NH<sub>3</sub> and improve the cycling efficiency of N in pastures. This study used <sup>15</sup>N-labelled cow urine containing different N inhibitors, applied to soil lysimeters under field conditions. The soil used was a free-draining soil (Podzolic Orthic Pumice soil). The study was conducted over about 200 days from May 2004 under a high rainfall regime. The urine application rate was 775 kg N ha<sup>-1</sup>. The Agrotain<sup>®</sup> was mixed with the urine @ 17 l/1000 kg N.
- Agrotain<sup>®</sup> reduced NH<sub>3</sub> volatilisation by 64% (equivalent to 70 kg N ha<sup>-1</sup>) over the first 25 days. The application rate of Agrotain<sup>®</sup> in this experiment was considerably higher than the recommended rate for field application.
- The Agrotain<sup>®</sup> significantly increased the amount of urea-N in the leachate (25 kg N ha<sup>-1</sup>) from the lysimeters compared with all other treatments. When DCD was used with Agrotain<sup>®</sup>, the amount of urea in the leachate increased to 45 kg N ha<sup>-1</sup>. The presence of urea in the leachate was probably due to the increased residence time of urea-N in the soil when Agrotain<sup>®</sup> was present, which would have increased its potential for movement down the soil profile.
- In all treatments the majority of the N measured in the leachate was in the form of  $NH_4^+$  (accounting for up to 75% of the total N leached), and differences in the total  $NH_4^+$ -N leached from the urine treated lysimeters, with or without N inhibitors, were not significant. At this study site, high rainfall and wet soils during the first 30 days following urine application provided optimal conditions for macro-pore flow during a critical period of elevated  $NH_4^+$ -N. This led to the large amount of  $NH_4^+$ -N leaching loss.

## 4.3.1.3 Zaman et al. (2009)

- This study was carried out to identify the best N inhibitor, or combination of inhibitors, for minimising N losses from urine patches while improving pasture production. The experiment was carried out at Massey University dairy farm as a small-scale plot trial. The soil type was Tokomaru silt loam, which is a poorly draining soil. The study began in May 2005 and concluded in August 2006. The cow urine was applied at the rate of 600 kg N ha<sup>-1</sup>. Agrotain<sup>®</sup> was applied at 3 L ha<sup>-1</sup> and DCD at 7 kg ha<sup>-1</sup>.
- Inhibitors were mixed with urine and applied on the plots in three different seasons (autumn, spring, and summer). Regular measurements of  $NH_3$ ,  $N_2O$  and leached  $NO_3^-$  were carried out up to 88 days after the date of application.
- The total amount of NH<sub>3</sub> volatised was significantly reduced in treatments containing only Agrotain<sup>®</sup> as a UI. A maximum of 93% reduction in NH<sub>3</sub> volatilisation compared with urine only was achieved in spring. Summer and autumn reductions were about 30%.
- On average, Agrotain<sup>®</sup> had little effect on N<sub>2</sub>O emissions in autumn and summer, but a 16% reduction compared with urine only was measured in spring.

- Application of DCD was effective in reducing  $N_2O$  emission with 52%, 39%, and 17% less  $N_2O$  being emitted in plots that were treated with DCD in autumn, spring, and summer, respectively.
- The combination of UI and NI was consistently effective in reducing NH<sub>3</sub> and N<sub>2</sub>O losses when compared with urine only.

## 4.3.1.4 Zaman and Blennerhassett (2010)

- This study was a follow-up from their earlier study to identify the best rate of Agrotain<sup>®</sup> and DCD to minimise gaseous losses of N as well as to reduce NO<sub>3</sub><sup>-</sup> leaching from urine patches. The experiment was carried out at Lincoln using intact soil cores, to a depth of 40 cm. These were collected from an established pasture paddock. The soil type was Paparua silt loam, which is a moderately draining soil. The study started during February/March 2007 and concluded in July 2008.
- The cow urine was applied at a rate of 600 kg N ha<sup>-1</sup>. Three rates of DCD (5, 7 and 10 kg DCD ha<sup>-1</sup>) were used, either applied alone or in combination with 1 or 2 L ha<sup>-1</sup> Agrotain<sup>®</sup>. Both UI and NI were mixed with urine and then applied to the lysimeters. Two seasonal applications (autumn and spring) of these treatments were made and the concentrations of NH<sub>3</sub> and N<sub>2</sub>O in the gaseous emissions and of NO<sub>3</sub><sup>-</sup>-N in the leachate were regularly measured using standard techniques.
- The greatest reduction in NH<sub>3</sub> volatilisation was achieved with 2:7 Agrotain<sup>®</sup>: DCD, where reductions of 51% and 73% were achieved in autumn and spring respectively compared with the urine-only treatment. Application of 7 kg ha<sup>-1</sup> DCD, which would have increased NH<sub>4</sub><sup>+</sup> concentration in the soil, caused an increase of 41% and 18% volatilisation loss of NH<sub>3</sub> in autumn and spring respectively.
- The greatest reduction in N<sub>2</sub>O emission was obtained using 1:7 Agrotain<sup>®</sup>:DCD, where 55% and 63% less N<sub>2</sub>O was observed in autumn and spring compared with the urine-only treatment. DCD applied at 7 and 10 kg ha<sup>-1</sup> with urine was more effective than at 5 kg ha<sup>-1</sup> and reduced N<sub>2</sub>O emissions by 37–53% (autumn) and 47% (spring), and NO<sub>3</sub><sup>-</sup> leaching losses by 57–55% (autumn) and 26–10% (spring) compared with urine alone.

## 4.3.1.5 Zaman (unpublished)

• This study was carried out to identify the best application time for DCD, or a combination of inhibitors (DCD and UI Agrotain<sup>®</sup>), to minimise N losses from urine patches while improving pasture production. The experiment was carried out using undisturbed lysimeters/small field plots at Lincoln from May 2008 to July 2009. The soil type was Paparua silt loam soil, which is a moderately draining soil.

• The 4 treatments – cow urine only (600 kg N ha<sup>-1</sup>), urine with DCD (10 kg DCD ha<sup>-1</sup>), urine with 1:7 Agrotain<sup>®</sup>:DCD, and the control (no urine) – were used. The inhibitors were applied at 4 different times: (a) 10 days before urine applications, (b) 5 days before urine applications, (c) the same day as urine application, and (d) 5 days after urine application. Two seasonal applications (autumn and spring) of these treatments were made and the concentrations of NH<sub>3</sub> and N<sub>2</sub>O in the gaseous emissions and of NO<sub>3</sub><sup>-</sup> in the leachate were regularly measured using standard techniques.

The greatest reduction in NH<sub>3</sub> emissions was obtained using 1:7 Agrotain®:DCD. In this treatment, reductions of 38–66% and 25–28% were observed in autumn and spring compared to the urine only treatment. Overall, 1:7 Agrotain®:DCD applied 5 days before urine application offers the best overall option for both reducing the gas emissions of NH<sub>3</sub> and N<sub>2</sub>O, and NO<sub>3</sub><sup>-</sup> in the leachate losses and improving the bioavailability of urine-N.

## 4.4 Data analysis

As discussed above, only a comparatively small number of studies investigated the effect of UIs on NH<sub>3</sub> emissions from urine patches. The criteria used for this data analysis were:

- The study was performed under New Zealand field conditions, rather than laboratory conditions.
- The study included measurements of NH<sub>3</sub> emissions for urine only and 'urine + UI' treatments. Urine plus double (urease and nitrification) inhibitor treatments were included for those studies that did not look at UIs and urine only.
- The UI was applied at the same time as the urine.

This gave a total of 7 datasets from 4 studies covering 3 soils. These results were analysed using a random effects meta-analysis procedure. Such analyses are useful for comparing results across multiple studies where there may have been differences in procedures (e.g., different numbers of replicates). The "random" (as opposed to "fixed") effect in part accounts for the fact that the studies represent only a sample of the possible range of conditions (e.g., temperature) that could occur, and that these differences in conditions affect the actual value of the effect being measured.

A meta-analysis was performed using R version 2.12.1 with the "meta summaries" procedure from the add-on package rmeta (Lumley 2009) available from the R website http://cran.stat.auckland.ac.nz/ (accessed 25-03-2011). This method calculated the reduction in NH<sub>3</sub> emissions due to UIs as 53% with a 95% confidence interval of 33–73%. Figure 3 highlights the ranges and the level of uncertainty in reduction in NH<sub>3</sub> emissions from animal urine with the application of UI.



**Figure 3** Reduction in  $NH_3$  emissions from urine applied with UI (%). The centre point of each block is the point estimate of the mean for that study and the area is the weight given to the individual mean. The whiskers are the 95% confidence intervals of the individual studies. The centre of the diamond represents the pooled point estimate, and its horizontal tips represent the 95% confidence interval.

#### 4.5 Conclusions

Only a limited number of published data sets are available describing the effectiveness of nBTPT for reducing NH<sub>3</sub> losses and subsequent N<sub>2</sub>O emission from urine patches in a grazed pasture system. Most of the New Zealand studies were conducted in the autumn or early spring seasons, and showed a significant reduction in the volatilisation loss of NH<sub>3</sub> when UI was mixed with urine compared with non-treated urine. There was a wide range of reductions (11–93%) reported in the these studies. The average reduction rate was about 53% with a 95% confidence interval of 33-73%.

These studies used three different rates of UI and two rates of urine-N loading and were carried out in field lysimeters or small plots. UI was mixed with animal urine before application, allowing maximum opportunity to inhibit urease activity, which is an unlikely scenario under field conditions, thus UI could be less effective. Furthermore, there is not enough New Zealand or overseas data to determine the effects of season, soil temperature, soil moisture, rainfall, and soil organic C on the effectiveness of UI on NH<sub>3</sub> volatalisation losses from animal urine under grazed pasture conditions. Therefore, it is not possible to estimate accurately the effect of UI on reductions in the NH<sub>3</sub> lost from animal urine-N deposited during grazing based on the existing data, and no change in  $Frac_{GASM}$  is recommended.

More data are required to understand the issues of effective rates of UI application on different soil types for a comprehensive analysis of the effect of UIs on urine-N deposited in grazed pastures. The efficacy of repeated application of UI also needs to be examined. However, the most critical aspects requiring research were timing of application (i.e. how many days before a grazing event), and the method of application (e.g., sprayed on the ground in liquid or powder form, or given to the animal to ingest, or inserted as a bolus) to obtain the maximum reduction in N loss through NH<sub>3</sub> volatilisation.

Inhibitor(s)	Rate of UI	Rate of urine N (kg N ha <sup>-1</sup> )	Reduction in N loss relative to urine alone application	Land use	Soil type	Country	Reference
Agrotain <sup>®</sup>	~1 L 460 kg N <sup>-1</sup> ha <sup>-1</sup>	600	–11% NH₃ –50% N₂O –23% NH₃	Pasture	Tokomaru silt loam (poorly drained)	New Zealand	Singh et al. (2003) Singh et al. (2008)
Agrotain <sup>®</sup>	17 L 1000 kg N <sup>-1</sup> ha <sup>-1</sup>	775	–63% NH₃ +3% leached NH₄ <sup>+</sup> –27% leached NO₃ <sup>−</sup> +217% leached urea	Pasture	Pumice (well drained)	New Zealand	Menneer et al. (2008)
Agrotain <sup>®</sup>	3 L ha <sup>-1</sup>	600	Autumn –29% NH <sub>3</sub> , + 9.5% N <sub>2</sub> O, Spring –93% NH <sub>3</sub> , –16% N <sub>2</sub> O Summer –31% NH <sub>3</sub> , –1.5 N <sub>2</sub> O	Pasture	Tokomaru silt loam (poorly drained)	New Zealand	Zaman et al. (2009)
Agrotain <sup>®</sup> & DCD	1:7::L:kg ha <sup>−1</sup>	600	Autumn -48% NH <sub>3</sub> -55% N <sub>2</sub> O -56% NO <sub>3</sub> Spring -51% NH <sub>3</sub> -63% N <sub>2</sub> O -42% NO <sub>3</sub>	Pasture	Paparua silt loam (moderately drained)	New Zealand	Zaman and Blennerhassett (2010)
Agrotain <sup>®</sup> & DCD	1:7::L:kg ha <sup>−1</sup>	600	Autumn -3866% NH <sub>3</sub> -4863% N <sub>2</sub> O -3156% NO <sub>3</sub> Spring -2528% NH <sub>3</sub> -1145% N <sub>2</sub> O -2241% NO <sub>3</sub>	Pasture	Paparua silt loam (moderately drained)	New Zealand	Zaman (2011,unpublished)

Table 1 Effects of application of urease inhibitors (UIs) on reducing volatilisation loss of N as NH<sub>3</sub> from animal urine

# 5 Method development for estimating the effect of urease inhibitors in reducing NH<sub>3</sub> loss from animal urine deposited in grazed pasture soils

As discussed in section 4 it is not possible, based on the existing data, to estimate accurately the effect of UI on reductions in the NH<sub>3</sub> lost from animal urine-N deposited during grazing. At this stage no change in  $Frac_{GASM}$  is recommended. Further research is suggested to determine the emission reductions. When the emission reductions and changes in  $Frac_{GASM}$  are quantified, the following method can be used to account for reductions in NH<sub>3</sub> loss due to the use of nBTPT in grazed pasture soils, in New Zealand national agricultural greenhouse gas (GHG) inventory calculation.

## **Estimation method of Frac**<sub>GASM</sub>

The method for determining the effect of UIs on  $Frac_{GASM}$  is similar to that recommended by Saggar et al. (2009) to calculate  $Frac_{GASF}$ . However, there are certain differences in the calculations that reflect the nature and timing of excretal N input, and the effectiveness of UI:

- In contrast to urea fertiliser N, where the UI is incorporated into the fertiliser product, the UI is applied directly to the soil immediately before or after the excretal deposition in the form of dung (mainly organic N) and urine (mainly urea). The UI will mostly affect the ammonium-N resulting from the hydrolysis of urine. Thus only urine-N should be considered in the calculation, although in the current inventory practice all excretal N is multiplied by Frac<sub>GASM</sub> to calculate NH<sub>3</sub> emissions.
- UI is only effective for Urinel-N deposited in one grazing event as the urease enzyme reactivates in 1–2 weeks following UI application. Moreover, the active ingredient nBTPT in Agrotain<sup>®</sup> also decomposes in soils in 1–2 weeks (Hendrickson & Douglas 1993).

Therefore even on farms that use UI, it is likely that only a fraction of annual urine-N deposited will be affected with UI. The total urine-N subjected to UI application is referred to as  $M_{NUI}$ .

 $M_{NUI}$  can be estimated from the total amount of nBTPT applied and its recommended rate of application. If the reduction in NH<sub>3</sub> emission from deposited urine-N patches is say R% the revised equations for Frac<sub>GASM</sub> will become:

c) For the urine-N subjected to UI applied according to best management practice  $(M_{NUI})$ , **Frac**<sub>GASM</sub> becomes **Frac**<sub>GASM</sub>**MN**<sub>UI</sub> defined as:

## $Frac_{GASM}MN_{UI} = [(100 - R)/100] \times M_{NUI}$

where  $M_{NUI}$  is the total urine N receiving UIs according to best management practice (that is applied within few days of grazing), and **R** is the fraction of reduction.

d) where no UI is applied to animal urine deposited on soil, **Frac**<sub>GASM</sub>, termed as **Frac**<sub>GASM</sub> **MN**<sub>U</sub>, becomes:

 $Frac_{GASM} MN_U = [(MN_U) \times 0.10]$ 

where  $MN_{\rm U}$  is the total urine N deposited on farms that is not subjected to UI applicaton.

The following section (section 6) provides some examples of potential reductions in  $NH_3$  loss using a hypothetical value of 40% reductions similar to the reductions obtained from UI treated urea fertiliser N.

# 6 Effect of urease inhibitors in reducing NH<sub>3</sub> loss from animal urine deposited in grazed pasture soils and on inventory estimates

Studies conducted by Hendrickson and Douglas (1993) and Zaman et al. (2008) have shown nBTPT inhibited the activity of the urease enzyme for up to two weeks. Therefore, in practice nBTPT should be applied to the soil immediately after or within a couple of days of animal grazing in order to reduce NH<sub>3</sub> volatilisation from newly deposited urine during grazing. To maximise the potential for reducing NH<sub>3</sub> volatilisation from grazed pastures, nBTPT should ideally be applied after every grazing event and with farm dairy effluent.

There has been no report on the application of UIs to actual urine patches in a grazed pasture to reduce  $NH_3$  losses. Therefore, here we consider only those potential reductions in  $NH_3$  losses from surface application of nBTPT that contribute to a reduction in  $Frac_{GASM}$ . There could be seasonal differences in  $NH_3$  losses from deposited urine due to soil and climatic conditions. The effect of nBTPT can also be different between different seasons of the year. However, given the lack of evidence from the limited research available the seasonal differences will not be considered in the following scenario analysis. Although no research has been carried out to determine the effect of nBTPT on  $NH_3$  losses from application of dairy farm effluent, in this report we consider the effect would be the same for farm dairy effluent as for deposited urine.

We conducted a scenario analysis based of potential reductions using a hypothetical value of 40% reductions in NH<sub>3</sub> similar to the reductions obtained from UI treated urea fertriliser N.

In the following scenario analysis, we incorporate the revised  $Frac_{GASM}$  into the standard Tier one approach to estimate N<sub>2</sub>O emissions from New Zealand's dairy farms. The amount of animal excreta deposited in dairy farms in 2009 was derived from dry matter intake data. We used the standard feeding Tier II model approach to determine animal dry matter intake. The dry matter intake data are then multiplied by dry matter N content data to get animal N intake. Considering N in product (milk and meat for dairy cows), excreta and urine N would be estimated on a monthly base (Table 2). We assume that there are a total of 11 grazing events on a dairy farm per year and grazing intensity is different between seasons (Luo et al. 2008).

Month	Excreta N (kg)	Urine N (kg)	
Jan	4,379,017	32,225,190	
Feb	41,591,054	30,606,857	
Mar	43,598,800	32,084,357	
Apr	29,704,324	21,859,412	
May	23,128,071	17,019,947	
Jun	25,867,433	19,035,844	
Jul	50,798,155	37,382,363	
Aug	47,053,765	34,626,865	
Sep	45,420,057	33,424,620	
Oct	44,102,497	32,455,028	
Nov	43,922,255	32,322,387	
Dec	50,197,584	36,940,402	
Total	489,174,170	359,983,271	

Table 2 Dairy urine N deposited (including from grazing and dairy sheds) in 2009

Scenario 1: Assuming nBTPT is applied after every grazing event and with all farm dairy effluent applications on all New Zealand's dairy farms, we used the revised  $Frac_{GASM}$  of 0.06 for the national N<sub>2</sub>O inventory calculation (Table 3). The NZIPCC default emission factor for indirect N<sub>2</sub>O emissions from volatilising N is 0.01 kg N<sub>2</sub>O-N/kg urine-N. To convert this to N<sub>2</sub>O we multiply by 44/28. Thus, the reduction in indirect N<sub>2</sub>O emissions due to the application of nBTPT in this scenario equates to 70.1 Gg CO<sub>2</sub>-equivalent. Using the total N<sub>2</sub>O emissions from the NZ agriculture of 9560 Gg CO<sub>2</sub>-equivalent, this is a reduction of 0.73%.

**Scenario 2:** Assuming nBTPT is applied to half of the total animal excreta and farm dairy effluent for all New Zealand's dairy farms, the weighted average  $Frac_{GASM}$  would then be 0.08 for the national N<sub>2</sub>O inventory calculation (Table 3). The reduction in indirect N<sub>2</sub>O emissions due to application of nBTPT in this scenario equates to 35.1 Gg CO<sub>2</sub>-equivalent. Using the total N<sub>2</sub>O emission from the NZ agriculture of 9560 Gg CO<sub>2</sub>-equivalent, this is a reduction of 0.37%.

**Scenario 3:** Assuming nBTPT is applied to 20% of total excreta and farm dairy effluent for all New Zealand's dairy farms, the weighted average  $Frac_{GASM}$  would be 0.092 for the national N<sub>2</sub>O inventory calculation (Table 3). The reduction in indirect N<sub>2</sub>O emissions due to application of nBTPT in this scenario equates to 14.0 Gg CO<sub>2</sub>-equivalent, a reduction of 0.15% from the total N<sub>2</sub>O emissions from the NZ agriculture.

**Scenario 4:** nBTPT was applied after every grazing event in December 2009 for all New Zealand's dairy farms. According to Luo et al. (2008), animals would graze about an average of two times in December. The monthly cow urine (including direct deposited onto pasture and that in farm dairy effluent) would be 36 940 tonnes (Table 2). Considering the total annual cow urine of 359 983 tonnes and assuming 0.1% was affected by nBTPT, the wieghted average  $Frac_{GASM}$  would be 0.096 for the national N<sub>2</sub>O inventory calculation (Table 3). The reduction in indirect N<sub>2</sub>O emissions due to the application of nBTPT in this scenario equates to 7.0 Gg CO<sub>2</sub>-equivalent (Table 3), a reduction of 0.07% from the total N<sub>2</sub>O emissions from the NZ agriculture.

**Scenario 5:** nBTPT was applied after one grazing event in September, one in November, one in January, and one in March 2009 for all New Zealand's dairy farms (this could be done with N fertiliser application after grazing on farms). According to average monthly grazing events (about an average of two times in September or November and once in January or March; Luo et al. 2008), we can estimate that 16 712 tonnes of cow urine (including direct deposited onto pasture and that in farm dairy effluent) would receive nBTPT in September, 16 161 tonnes of cow urine in November, 32 225 tonnes of cow urine in January, and 32 084 tonnes of cow urine in March. Then the urine affected by nBTPT would be 97 183 tonnes, or 27% of the total annual cow urine. Therefore, the weighted average  $Frac_{GASM}$  would be 0.089 for the national N<sub>2</sub>O inventory calculation in this scenario (Table 3). Thus, the reduction in indirect N<sub>2</sub>O emissions due to application of nBTPT in this scenario equates to 18.9 Gg CO<sub>2</sub>–equivalent (Table 3). Using the total N<sub>2</sub>O emissions from the NZ agriculture of 9560 Gg CO<sub>2</sub>–equivalent, this is a reduction of 0.20%.

analyses and comparison with the current national GHG inventory value (2009)								
Scenario <sup>1</sup>	Fraction of annual excretal- N affected by nBTPT	Revised Frac <sub>GASM</sub>	Annual NH <sub>3</sub> volatilisation (Gg NH <sub>3</sub> –N)	Annual indirect N <sub>2</sub> O emissions (Gg N <sub>2</sub> O)	GHG equivalent (Gg CO <sub>2</sub> equiv.)	Reduction of GHG (Gg $CO_2$ equiv.) <sup>2</sup>	% reduction of total N <sub>2</sub> O emission from NZ agriculture	
Current	0	0.1	36.00	0.57	175.36	0	0	
NZIPCC								
default								
1	1	0.06	21.60	0.34	105.22	70.1	0.73	
2	0.5	0.08	28.80	0.45	140.29	35.1	0.37	
3	0.2	0.092	33.12	0.52	161.33	14.0	0.15	
4	0.1	0.096	34.56	0.54	168.35	7.0	0.07	
5	0.27	0.089	32.11	0.50	156.42	18.9	0.20	

**Table 3** Potential for reducing NH<sub>3</sub> volatilisation from dairy grazing farms by using nBTPT – five scenario analyses and comparison with the current national GHG inventory value (2009)

1 See scenario descriptions in text. 2 Total GHG ( $CH_4$  and  $N_2O$ ) from NZ agriculture equates to 32,810.5 Gg  $CO_2$  equiv.

## 7 Discussions and conclusions

A large body of research reviewed in the previous report to MAF (Saggar et al. 2009), together with additional recent research included in section 4 (review) of this report, have confirmed that  $NH_3$  emission losses can be substantially reduced if a UI is used with the fertiliser. UIs slow the conversion of urea to  $NH_4^+$  by inhibiting the urease enzyme, which reduces  $NH_4^+$  concentration in the soil solution and hence lowers the potential for  $NH_3$  emission. This also allows more time for urea/urine to diffuse away from the application site or for rain or irrigation to dilute urea and  $NH_4^+$  concentrations at the soil surface and increase its dispersion in the soil, thereby retaining  $NH_3$  in the soil.

- UI, N-(n-butyl) thiophosphoric triamide (nBTPT), sold under the trade name Agrotain<sup>®</sup>, is currently the most promising and effective inhibitor for reducing NH<sub>3</sub> emission and thus reducing the value Frac<sub>GASF</sub>.
- Reductions in Frac<sub>GASF</sub> and Frac<sub>GASM</sub> from application of Urease inhibitor

New Zealand studies involving optimum nBTPT application (0.025% w/w) with urea show an overall reduction in  $NH_3$  emissions of 43% (Saggar et al. 2009).

Based on the peer-reviewed literature and our above estimates of reductions in  $NH_3$  emission, an average New Zealand specific value of 0.06 for  $Frac_{GASF}$  is recommended for adoption where urea fertilisers containing UI, nBTPT are applied.

Based on the existing data, it is not possible to accurately estimate the effect of UI on reductions in the  $NH_3$  lost from animal urine-N deposited during grazing. Therefore, at this stage no changes in  $FRAC_{GASM}$  are recommended.

As reported previously by Saggar et al. (2009), changing the  $Frac_{GASF}$  from 0.10 to 0.06 for the current use of 18.4 Gg N of SustaiN reduces indirect N<sub>2</sub>O emissions by 0.012 Gg, which equates to 3.6 Gg CO<sub>2-equiv</sub>. However, assuming all the urea is applied with nBTPT in New Zealand, changing the  $Frac_{GASF}$  from 0.1 to 0.06 will reduce the indirect N<sub>2</sub>O emissions by 0.14 Gg, which equates to 43.4 Gg CO<sub>2-equiv</sub>.

• Effect of urease inhibitor on ammonia losses

It is evident from research on the use of UI nBTPT in the peer-reviewed literature and unpublished reports detailed previously (Saggar et al. 2009) and in this report, that an nBTPT application rate of 0.025% w/w with urea most effectively reduces NH<sub>3</sub> emissions from temperate grasslands. New Zealand studies involving optimum nBTPT application (0.025% w/w) with urea show an average reduction in NH<sub>3</sub> emissions of  $42.8 \pm 5.1\%$  (mean  $\pm$  standard error) (95% confidence of interval of mean 10.2).

In all the experiments on animal urine reported in this review UI was mixed with urine before application, which gave a better chance for the active ingredient to interact with urine. However, in grazed pastures reduction of  $NH_3$  emissions from urine requires that the UI be applied to the soil either immediately before or immediately following a grazing event. Therefore, the method of UI application is flawed.

The effectiveness of UI in soil varies with the soil carbon content, texture, pH, soil N status, and microbial activities of the soils. Little New Zealand and overseas research has been conducted to evaluate the mode of application of nBTPT to urine patches and the frequency of application that would be required to determine the potential for direct use of nBTPT in pastures. Based on the New Zealand research reviewed earlier (Saggar et al. 2009) and in this report, it is not possible to assess the relative contribution of the key soil and environmental factors (e.g., soil organic C, temperature and moisture) influencing the response rate of nBTPT in reducing NH<sub>3</sub> emission from urine N deposited during grazing . It is also not possible from this existing New Zealand information to account for this quantitatively in the national inventory. For these reasons we recommend no change in  $Frac_{GASM}$  until further research has been conducted.

Quantitative data for the rate, time, and mode of application of UI in major soil types on reduction in  $NH_3$  emission are needed for a comprehensive analysis of the effect of UIs on urine-N deposited in grazed pastures. As more information on the effectiveness of nBTPT for soils across a range of soil temperature, moisture, and organic C contents become available, more accurate parameter estimates could be developed for modelling the effectiveness of nBTPT at regional and national scales.

• Application of UI on the NZ dairy-grazed farms

The UI (nBTPT) does not kill microbes, but inhibits the activity of the urease enzyme for a period of 1–2 weeks. As the effect of nBTPT diminishes, the amount of urease enzyme is built up quickly. Thus, the effect of nBTPT directly applied to pasture soils is only likely to last up to 2 weeks. This means that, unlike DCD, each UI application is only likely to reduce emissions from the excretal N deposition of a single grazing event. The application of UI after every grazing event is unlikely to be practically and economically feasible for farmers. The best strategy might be to target the grazing periods where the greatest emission reductions are possible.

Clough et al. (2008) assume that users of the NI DCD will apply it twice a year to maintain its effectiveness in reducing nitrification over the period May–September. Some cost savings might be possible by applying UIs and NIs together. However, NH<sub>3</sub> emissions are highest when temperatures are high, whereas NIs should be applied at times of low temperature to prolong the inhibitor's lifetime in the soil. Therefore, the optimal time for NI application will be sub-optimal for UI application and vice versa.

## 8 Recommendations

- 1. Based on the peer-reviewed literature and estimates of reductions in NH<sub>3</sub> emission from the previous study (Saggar et al. 2009), a New Zealand specific value of 0.06 for Frac<sub>GASF</sub> is recommended for adoption where urea fertilisers containing UI, nBTPT are applied. We recommend that Frac<sub>GASF</sub> should be calculated as follows:
  - a) where nBTPT is applied as recommended, **FracGASF** should be termed as **FracGASF FNUI** and calculated as follows:

$$Frac_{GASF} FN_{UI} = [(FN_{UI}) \times 0.06]$$
(1)

 $Frac_{GASF}FN_{UI}$  is the fraction of UI treated urea fertiliser N emitted as  $NH_3$ ,  $FN_{UI}$  is the amount of applied urea fertiliser N treated with UI, nBTPT.

b) where fertiliser N is applied without any amendment,  $Frac_{GASF}$  termed as  $Frac_{GASF}$  FN<sub>U</sub> and calculated as follows:

 $Frac_{GASF} FN_U = [(FN_U) \times 0.10]$ 

(2)

 $Frac_{GASF} FN_U$  is the fraction of unamended fertiliser N emitted as NH<sub>3</sub>, FN<sub>U</sub> is the amount of applied urea N.

- 2. Based on the peer-reviewed and existing data, it is not possible to estimate accurately the effect of UI on reductions in the  $NH_3$  lost from animal urine-N deposited during grazing. Therefore no changes in  $FRAC_{GASM}$  are recommended until further has been conducted.
  - Activity data

The requirements for the use of UI (nBTPT) are similar to those for the nitrification inhibitor DCD, i.e. a requirement for accurate and verifiable records of (a) the sale of total fertiliser N (b) sale of urea-N and (c) sale of UI treated urea-N (SustaiN<sup>®</sup>) from the fertiliser industry, and the amount of nBTPT imported from the Agrotain International. Long-term record, storage and availability for independent review are also required.

## 9 Future research needs

The UI (nBTPT) reduces the rate of urea hydrolysis to  $NH_4^+$  but urea hydrolysis cannot be inhibited indefinitely by nBTPT. The value of nBTPT for mitigating  $NH_3$  emission losses in grazed pastures will depend on its rate of biodegradation and persistence in soils. nBTPT is likely to last in soils up to 2 weeks, the period during which  $NH_3$  is emitted from urea-N.

Soil temperature, moisture, and soil organic C levels are key factors that affect the rate of  $NH_3$  emission and its % reduction with the UI inhibitor. However, it is difficult to assess the relative contribution of these factors from the existing New Zealand information. More information on the effectiveness of nBTPT across a range of soil temperature, moisture, and organic C concentrations are now needed to quantitatively estimate reductions in  $NH_3$  emission.

Furthermore, New Zealand field studies involving nBTPT used a single application rate of 100 or 150 kg N ha<sup>-1</sup>. No research has yet been conducted using lower application rates of 25 and 50 kg N ha<sup>-1</sup> to allow conclusions to be made on the effectiveness of nBTPT. This aspect also needs to be considered in future studies.

Finally, field research is required to evaluate the mode of application of nBTPT to urine patches, and the frequency of its application, to determine the potential for direct use of nBTPT in New Zealand pastures.

Strategic use of UI could be a useful tool in minimising GHG liability from grazed pastures. However, data are limited and more focussed studies are recommended to address specific questions relevant to inventory reporting:

- What are the optimum level, effective duration, and seasonal variability of a single nBTPT application in grazed pasture soils?
- How does the UI effectiveness vary following repeated application on grazed pastures or on urine patches? What is the most effective method of application of UI to grazed pasture soils?
- How does the soil type influence the effectiveness of UI? For example, soil mineralogy and soil carbon levels?
- What are the optimum timing of soil application of UI (how many days before a grazing event), and the method of application (e.g., sprayed on the ground in liquid or powder form, or given to the animal to ingest, or inserted as a bolus) to obtain the maximum reduction in N loss through NH<sub>3</sub> volatilisation?
- Would polymer coating of UI (slow-release) enhance their lonevity in soil and improve their effectiveness?

## **10** References

- Amtul Z, Siddique AR, Choudhary MI 2002. Chemistry and mechanism of urease inhibition. Current Medical Chemistry, 9: 1323–1348.
- Bolan NS, Saggar S, Luo J, Bhandral R, Singh J 2004. Gaseous emissions of nitrogen from grazed pastures: processes, measurements and modelling, environmental implications and mitigation. Advances in Agronomy, 84: 37–120.
- Clough TJ, Di HJ, Cameron KC, Sherlock RR, Metherell AK, Clark H, Rys G 2007. Accounting for the utilization of a N2O mitigation tool in the IPCC inventory methodology for agricultural soils, Nutrient Cycling in Agroecosystems 78:.1–14.
- Francis DD, Vigil MF, Moiser AR 2008. Gaseous losses of nitrogen other than through denitrification. In: Schepers JS, Raun WR, eds Nitrogen in agricultural systems. Agronomy Monograph 49. Madison, WI, USA, American Society of Agronomy Pp. 255–279.
- Hendrickson LL, Douglas EA 1993. Metabolism of the urease inhibitor N-(nbutyl)thiophosphoric triamide (NBPT) in soils. Soil Biology and Biochemistry 25: 1613–1618.
- Kelliher FM, Clough TJ, Clark H 2007. Developing revised emission factors for nitrous oxide emissions from agricultural pasture treated with nitrification inhibitors. Landcare Research Contract Report LC0607/89. Prepared for the Ministry of Agriculture and Forestry, Wellington. 71 p.
- Ledgard SF 2001, Nitrogen cycling in low input legume-based agriculture, with emphasis on legume/grass pastures. Plant and Soil, 228: 43–59.
- Luo J, Ledgard SF, de Klein CAM, Lindsey SB, Kear M 2008, Effects of dairy farming intensification on nitrous oxide emissions. Plant and Soil 309: 227–237.
- Lumley T 2009. rmeta:Meta-analysis. R package version 2.16. http://CRAN.R-project.org/package=rmeta.
- MfE (Ministry for the Environment) 2010. New Zealand's Greenhouse Gas Inventory 1990– 2008. (Submitted to United Nations Framework Convention on Climate Change 15 April 2010). Ministry for the Environment, Wellington.
- Menneer JC, Ledgard SF, Sprosen M 2008. Soil N process inhibitors alter nitrogen leaching dynamics in a pumice soil. Australian Journal of Soil Research 46: 323–331.
- Nelson DW 1982. Gaseous losses of nitrogen other than through denitrification. In: Stevenson FJ ed. Nitrogen in agricultural soils. Madison, WI, USA, American Society of Agronomy. Pp. 327–363.
- Saggar S, Andrew RM, Tate KR, Hedley CB, Rodda NJ, Townsend JA 2004. Modelling nitrous oxide emission from New Zealand dairy grazed pastures. Nutrient Cycling in Agroecosystems 68: 243–255.

- Saggar S, Singh J, Catto W, Stafford A, Blennerhassett JD, Zaman M 2009. Desktop study of emission factors from urease inhibitors for nitrogen fertiliser. Landcare Research Contract Report: LC0809/141 presented to Ministry of Agriculture and Forestry, June 2009.
- Sherlock R, Jewell P, Clough T 2009. Review of New Zealand specofic Frac<sub>GASM</sub> and Frac<sub>GASF</sub> factors. Report for Ministry of Agriculture and Forestry, October 2008. 52 p.
- Singh J 2007. The role of inhibitors in mitigating nitrogen losses from cattle urine and nitrogen fertiliser inputs in pastures. PhD thesis, Massey University.
- Singh J, Bolan NS, Saggar S 2003. A method for simultaneous measurement of ammonia volatilization and nitrous oxide emissions from intact soil cores. In: Currie LD, Hanly JA eds Proceeding of workshop 'Tools for nutrient and pollutant management – applications to agriculture and environmental quality', Massey University, Palmerston North, New Zealand. Pp. 224–231.
- Singh J, Saggar S, Bolan NS and Zaman M 2008. The role of inhibitors in the bioavailability and mitigation of nitrogen losses in grassland ecosystems. In: Naidu R ed. Development in soil science, Volume 2. Netherlands, Elsevier. Pp. 327–360.
- Suter HC, Pengthamkeerati P, Walker C, Chen D 2011. Influence of temperature and soil type on inhibition of urea hydrolysis by N- (n-butyl) thiophosphoric triamide in wheat and pasture soils in south-eastern Australia. Soil Research 49: 315–319.
- Watson, CJ 2000. Urease activity and inhibition principles and practice. Paper presented to the International Fertiliser Society at a meeting in London, 28 November 2000. Proceedings of International Fertiliser Society No. 454.
- Watson CJ, Akhonzada NA, Hamilton JTG, Mathews DI 2008. Rate and mode of application of the urease inhibitor N-(n-butyl) thiophosphoric triamide on ammonia volatilisation from surface-applied urea. Soil Use and Management 24: 246–253.
- Zaman M, Nguyen ML, Matheson F, Blennerhassett JD, Quin BF 2007. Can soil amendments (zeolite and lime) shift the balance between nitrous oxide and dinitrogen emissions from pasture and wetland soils receiving urine or urea-N? Australian Journal of Soil Research 45: 543–553.
- Zaman M, Nguyen ML, Blennerhassett JD, Quin BF 2008. Reducing NH<sub>3</sub>, N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup>-N losses from a pasture soil with urease or nitrification inhibitors and elemental S-amended nitrogenous fertilizers. Biology and Fertility of Soils 44: 693–705.
- Zaman M, Saggar S, Blennerhassett JD, Singh J 2009. Effects of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide, pasture yield and N uptake in a grazed pasture system. Soil Biology and Biochemistry 41: 1270–1280.

- Zaman M, Blennerhassett JD 2010. Effects of different rates of urease and nitrification inhibitors on gaseous emissions of ammonia and nitrous oxide, nitrate leaching and pasture production from urine patches in an intensive grazed pasture system. Agriculture, Ecosystems and Environment 136: 236–246.
- Zaman M 2011. Influence of urease inhibitor N-(n-butyl) thiophosphoric triamide and nitrification inhibitor DCD and their application times on NH3, N2O and NO3– losses from pastures soil receiving cow urine (unpublished).