

Mitigation of ammonia losses from urea applied to a pastoral system: The effect of nBTPT and timing and amount of irrigation

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Abstract

To investigate the effect of applying urea with or without the urease inhibitor (UI) N-(n-butyl) thiophosphoric triamide (nBTPT – trade name Agrotain®) and to assess impact of the amount and timing of irrigation on subsequent ammonia (NH_3) emission, a field trial was set up on a research farm at Massey University, Palmerston North, New Zealand in December 2012. Measurements of the daily NH_3 emission showed that majority of NH_3 losses occurred during the first 1–3 days following urea application. Delaying irrigation for 48 hr post urea application resulted in high average $\text{NH}_3\text{-N}$ losses, at 23% and 28.3% for urea applied at 30 and 60 kg N ha^{-1} , respectively. However, even when 5 or 10 mm of irrigation was applied 8 hours after urea application, average NH_3 losses were still 11.3% and 14.4% of the N applied at 30 and 60 kg N ha^{-1} , respectively. Our results suggest that 5 to 10 mm of irrigation/rainfall is needed very soon (<8 hr) after urea application to suppress NH_3 volatilisation depending on initial soil moisture contents. If this rainfall/irrigation is not guaranteed, then NH_3 losses associated with standard urea application can effectively be reduced by 47% using urea treated with nBTPT.

Keywords Agrotain, ammonia losses, irrigation, nBTPT, urea, volatilisation

Introduction

For managed grasslands in New Zealand, the supply of nitrogen (N) after every rotation of grazing is critical if enough pasture is to be grown to meet stock feed demand. In New Zealand's legume-based pastures, N application rates have traditionally been much lower because of N fixation by white clover (Ledgard *et al.* 1999). However, this state of affairs has changed dramatically in New Zealand with increasing intensification of grazing over the last 15 years (Statistics New Zealand 2012). In addition to maintenance phosphorus, sulphur and potassium, it is the supply of N that generally represents the greatest limitation to pasture growth because of (i) the non-uniform distribution of excreta-N in grazed pastures, and (ii) the fact that N released from mineralisation of

soil organic N or organic wastes (farm dairy effluent, dairy pond sludge) cannot meet the pasture N demand (Zaman *et al.* 1998). Thus, applying chemical N fertiliser, predominantly urea, is necessary to maintain current levels of productivity. However, urea has been reported to have lower fertiliser use efficiency (FUE) relative to ammonium- and nitrate-based fertilisers (Zaman *et al.* 2008). This lower FUE also occurs if urea is applied in conditions of sub-optimal soil moisture or at too low or high a temperature. The reduction in efficiency is related to N losses via ammonia (NH_3) volatilisation. In New Zealand, the twin effects of rising fertiliser N prices, both domestic and international, and increasing environmental restrictions on fertiliser N use by regulatory authorities have led research scientists and companies to develop a variety of management practices and technologies to improve the FUE of urea. One such approach is to treat granular urea with the urease inhibitor (UI) N-(n-butyl) thiophosphoric triamide (nBTPT – trade-name Agrotain®) which delays urea's hydrolysis by 7 to 10 days and thus significantly reduces NH_3 losses (Zaman *et al.* 2008, 2013; Saggar *et al.* 2013).

Ammonia loss, a chemical process catalysed by the ubiquitous urease enzyme, can have negative effects on our wider ecosystem, and has been linked to agronomic losses on farm, soil acidification, poor atmospheric quality, nutrient-N enrichment of sensitive habitats and the eutrophication of surface water bodies, and health issues (Barthelmie & Pryor 1998; Zaman *et al.* 2008; Sanz-Cobena *et al.* 2011).

Urea, when used strategically and efficiently, can enhance farm productivity and profitability while causing minimal environmental impact on waterways and the atmosphere. Efficient use includes applying urea at the right time and weather conditions, treating urea with urease inhibitors (UIs), or incorporating urea into soil or applying irrigation water (UNECE 2001). On irrigated lands, e.g., some parts of Canterbury in New Zealand, farmers usually irrigate after applying urea; in non-irrigated areas, farmers usually apply urea based on their anticipation of rainfall. However, applying the correct amount of irrigation soon after

urea application is critical in minimising NH_3 losses. For example, Sanz-Cobena *et al.* (2011) reported that addition of 7 and 14 mm of water to the soil immediately after urea application, reduced NH_3 emission by 77 and 89%, respectively; however a simulated 3 mm rainfall, immediately after fertilising, significantly enhanced NH_3 volatilisation (with an 8% increase in emission compared to urea application without water addition). Washing urea from surface soil through irrigation water or rain water facilitates the transport of added urea to sub-surface soil layers, dilutes surface NH_4^+ concentration, and reduces NH_3 partial pressure and thereby minimise NH_3 losses; however NH_3 loss is exacerbated by a delay in water application by 8 to 24 hr (Black *et al.* 1987; Dawar *et al.* 2011; Sanz-Cobena *et al.* 2011). Therefore, the objectives of our study were to quantify NH_3 emissions from pastoral systems as influenced by urea treated with nBTPT, and the timing and amount of irrigation water after urea application.

Methods

Study site

Field experiments were set up on a permanent ryegrass-clover pasture managed for grazing dairy cows (3 cows ha^{-1}) at Massey University Research Dairy Farm 4, Palmerston North, Manawatu, New Zealand ($40^\circ 23' 40'' \text{S}$, $175^\circ 36' 28'' \text{E}$) in December 2012 and January 2013. The soil is a poorly drained Tokomaru silt loam and is classified as an Argillic-fragic Perch-gley Pallic Soil or Typic Fragiaqualf (Soil Survey Staff 1998) derived from deep deposits of loess-brown river sediments. The Tokomaru soil consists of a weakly to moderately developed brown silt loam A-horizon, a

weakly developed grey, strongly mottled, clay loam B-horizon, and a highly compacted, weakly developed, pale gray, silt loam fragipan C-horizon that acts as a natural barrier to drainage (Hewitt 1998). Soil pH is 5.8, soil bulk density ranges from 1.1 to 1.3 g cm^{-3} and soil C and N contents range from 3.2 to 3.6% and 0.26 to 0.27%, respectively.

Experimental design

The trial was laid out in a randomised block design with all treatments replicated four times (Table 1). The treatments of urea treated with 250 mg nBTPT per kg of urea, and urea alone, were applied by 9 am on day 1 of urea application. Spray irrigation equivalent of 5 and 10 mm was applied to appropriate plots after 8, 24 and 48 hr of urea applications with or without nBTPT. Daily ammonia losses were measured over the subsequent 14 days.

Gas sampling

The active flow method described by Kissel *et al.* (1977) was modified to measure NH_3 emission. Ammonia emission was measured by inserting a PVC chamber (0.0491 m^2 area and 0.03 m height above surface soil (or 1.47 L volume) with two holes in the middle and a tightly sealed transparent lid to allow photosynthesis) on the perimeter of each field plot. Air from each chamber was sucked through a manifold at a constant flow rate (6 to 7 L min^{-1}) using a pump, and passed through 250 ml 0.05N sulphuric acid as an ammonia trapping solution in a glass bottle. The acid solution in each bottle was replaced with fresh 0.05N H_2SO_4 solution every 24 hours and analysed for $\text{NH}_4^+ \text{-N}$ concentration by a

Table 1 Details of the fertiliser application rate, irrigation amount and timing.

Fertiliser	N rate (kg N/ha)	Irrigation amount and timings after fertilisation	
		(mm)	(hr after fertilisation)
Urea	30	5	8
			24
			48
Urea	30	10	8
			24
			48
Urea	60	5	8
			24
			48
Urea	60	10	8
			24
			48
Urea+nBTPT	60	5	8
			24
			48
Urea+nBTPT	60	10	8
			24
			48

flow injection analyser. The temperature inside each chamber was checked periodically with a thermometer. However no rise in temperature was observed during the measurement period because of continuous air suction from each chamber.

Results and Discussion

Effects of urea application rate and nBTPT on ammonia emissions

Daily NH_3 emissions and cumulative $\text{NH}_3\text{-N}$ losses (measured over a 2-week period) were significantly ($P<0.01$) influenced by the N application rates and urease inhibitor nBTPT (Figure 1, Table 2). The largest peak of the daily NH_3 emission from urea 60 and 30 kg N ha^{-1} treatments appeared on day 3 following urea application, reflecting fast urea hydrolysis (Zaman *et al.* 2008; Dawar *et al.* 2011). Daily NH_3 emission rates in urea treatments declined sharply after day 3, confirming that the majority of NH_3 losses occur during the first 1–3 days following urea application, depending on initial soil moisture content (Zaman *et al.* 2008; Dawar *et al.* 2011; Sanz-Cobena *et al.* 2011). The pattern of daily $\text{NH}_3\text{-N}$ losses from urea-nBTPT applied at 60 kg N ha^{-1} was different from that of the urea alone treatment. Ammonia losses from urea-nBTPT applied at 60 kg N ha^{-1} slowly increased after day 2, reached their maximum on day 5 and declined thereafter. This indicates that nBTPT partially inhibited soil urease activity, which reduced the NH_4^+ concentration in the soil solution and hence lowered the potential for NH_3 volatilisation (Zaman *et al.* 2008).

The cumulative NH_3 losses measured over a 2-week period showed that the higher urea rate (60 kg N ha^{-1}) resulted in 2.4 times more $\text{NH}_3\text{-N}$ loss (13.2 kg N ha^{-1}) compared to the lower rate (30 kg N ha^{-1}), which lost 5.6 kg N ha^{-1} (Table 2). The proportions of NH_3 loss from applied urea were 21.8% and 18.3% of the applied N for 60 and 30 kg N ha^{-1} rates respectively (Table 2). A wide range of NH_3 losses have been reported in the literature depending on soil physical, chemical and biological properties as well as the techniques used

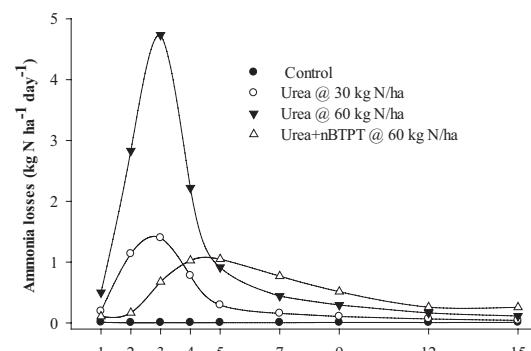


Figure 1 Daily ammonia emission as influenced by N rates and urea applied with urease inhibitor (nBTPT) to pasture soils. Values are means ($n=4$).

for NH_3 measurements. Black *et al.* (1989) compared the active method (the one used in this study) with the micrometeorological technique and reported similar NH_3 losses after 9 days of NH_3 measurements. The higher NH_3 losses from the 60 kg N ha^{-1} rate reflect the abundant availability of substrate (NH_4^+), which acts as a precursor for NH_3 emission, therefore frequent applications of lower N rates on farm could also offer potential benefit of reduced NH_3 emission, but frequent application incurs additional cost for spreading fertiliser. In contrast, at the 60 kg N ha^{-1} rate, urea + nBTPT lost only 7 kg N ha^{-1} (11.6% of the applied N); this is a 46% lower NH_3 loss than the equivalent urea alone treatment. A number of studies have reported that NH_3 losses can be reduced significantly by treating urea with the urease inhibitor nBTPT (Zaman *et al.* 2008; Dawar *et al.* 2011; Soares *et al.* 2012). Slowing urea hydrolysis with nBTPT allows more time for urea to diffuse away from the application site or for rain or irrigation to dilute the urea and NH_4^+ concentration at the soil surface and disperse it laterally and downward in the soil, which subsequently helps retain NH_3 in the soil (Dawar *et al.* 2011).

Table 2 Average $\text{NH}_3\text{-N}$ loss from urea and urea+nBTPT treatments, the proportion of applied N lost as $\text{NH}_3\text{-N}$ and percent changes during 15 days of the experiment.

Treatments	$\text{NH}_3\text{-N}$ losses (kg ha^{-1})	%N lost as NH_3 of the applied N	% changes in NH_3 relative to urea alone
No N	0.09		
Urea @ 30 kg N ha^{-1}	5.58	18.29	
Urea @ 60 kg N ha^{-1}	13.17	21.80	
Urea + nBTPT @ 60 kg N ha^{-1}	7.07	11.62	- 46.7
standard error ('SE)	0.47		

– indicates a reduction. *SE of the urea treatments

Effects of irrigation timing and amount on ammonia emissions

Irrigation application time (hr) and amount (mm) had a significant effect on NH_3 losses from urea alone and urea+nBTPT (Figure 2.a,b,c). The three treatments (urea applied at 30 and 60 kg N ha⁻¹ and urea+nBTPT at 60 kg N ha⁻¹) showed similar NH_3 loss trends when the 5 and 10 mm of spray irrigation were applied 8, 24 or 48 hr after urea application. Our results showed that applying 10 or 5 mm irrigation 8 hr after urea application was

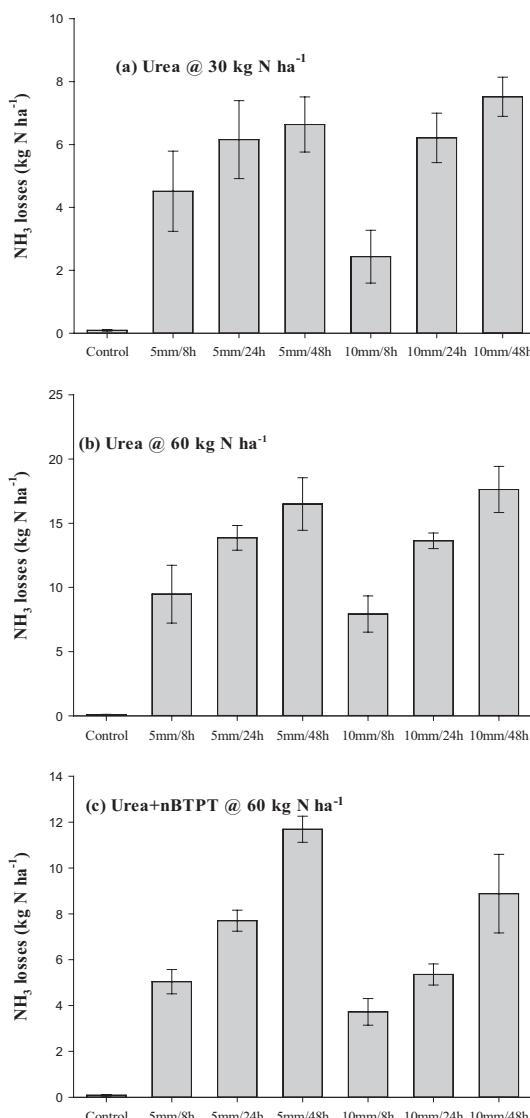


Figure 2 Ammonia emission as influenced by amount of irrigation water (5 mm and 10 mm) and timing (8, 24 and 48 hr) after urea applied at 30 and 60 kg N ha⁻¹ and urea+60 with nBTPT to pasture soils. Values are means ($n=4$). Vertical bars indicate standard error (SE). Note different scales on vertical axis.

more efficient at minimising NH_3 losses than applying the same amount of irrigation 24 hr after the urea was spread. Our results agree with those of Sanz-Cobena *et al.* (2011), who also reported that the addition of 7 and 14 mm of water to the soil at 61% water filled pore space (WFPS), immediately after urea spreading, reduced NH_3 emission by 77 and 89%, respectively. In contrast, they found that a simulated 3 mm rainfall to soil at 39% WFPS, immediately after urea fertilising, significantly enhanced NH_3 volatilisation (with an 8% increase in emission compared to urea application without water addition). Thus the amount of applied irrigation depends on initial soil moisture level. For example Black *et al.* (1987) showed that applying 4 mm of irrigation on to the soil at field capacity within 3 h of urea application resulted in significant reduction of NH_3 losses. Delaying irrigation for 48 hr further reduced its effects and resulted in even higher NH_3 -N losses (i.e., 25% and 29% of the applied urea-N at 30 and 60 kg N ha⁻¹, respectively). The minimal impact of 5 or 10 mm of irrigation applied at 24 hr and 48 hr highlights the fact that NH_3 loss is a very quick chemical process and therefore requires early intervention. A number of studies have confirmed that the majority of NH_3 loss occurs within the first 1 to 2 days after urea application (Black *et al.* 1985, 1987; Dawar *et al.* 2011; Soares *et al.* 2012). Therefore, the concentrations of NH_3 and NH_4^+ present in the soil solution near the surface need to be diluted by applying the right amount of irrigation water to reduce its potential for volatilisation losses (Grant *et al.* 1996).

The decision regarding N fertiliser applications on farms is generally made on the availability of water from irrigation (under irrigation) or on the farmer's assessment of the likelihood of adequate rainfall arriving. Managed grassland is usually grazed every 3–4 weeks depending on the pasture growth rate, therefore urea fertiliser application is recommended at 1–5 days after rotational grazing. All paddocks are not grazed at once on farm, and urea is also not spread concurrently. Even under the most efficient irrigation system, it is practically impossible to apply irrigation water to all those paddocks soon after urea application. There will always be a lag time between urea application and the following irrigation or rainfall, suggesting that applying urea with nBTPT may have the most potential to allow more time for the urea to diffuse away from the application site after a rainfall or irrigation event (Dawar *et al.* 2011), and to enhance N use efficiency of the applied urea. Watson *et al.* (2008) observed that that nBTPT protects urea from degradation by the urease enzyme from 7 to 9 days. This has worldwide implications for urea use in pastoral and cropping systems, where there is a high risk of NH_3 losses due to low soil moisture and high temperatures.

Recommendations

These results have shown that there is considerable potential for improving urea fertiliser use efficiency by either treating it with nBTPT or applying 5–10 mm of irrigation soon after (less than 8 hr) urea application to suppress NH₃ volatilisation. If the 5–10 mm of irrigation/rainfall is not highly likely to occur, the use of urea treated with nBTPT is strongly advised as it will considerably reduce NH₃ losses. This represents a low-cost method to increase fertiliser N efficiency. However, the cost of the nBTPT by itself and the cost of coating it onto urea, means that urea treated with nBTPT will costs more than urea alone. In New Zealand grassland, nBTPT treated urea at typical application rate at 25 kg N/ha will cost \$3.2/ha more than applying commercial urea. However the additional cost of nBTPT-treated urea can be easily offset by taking into account the 47% reduction in NH₃ losses. Using the 20% NH₃ loss as shown in this study from a typical urea application rate of 25 kg N/ha on pastoral soil, farmers will lose about 5 kg N/ha. In contrast with this, urea + nBTPT (SustaiN) will conserve 2.5 kg N/ha. At a typical 10:1 N response, this means 25 kg more pasture DM/ha from SustaiN. Assuming a conversion efficiency of 12.5 kg DM/kg milk solid (MS), and a milk pay out of \$7 per kg MS, the value of the 2 kg extra milk solid will be \$14 as opposed to the cost of \$3.2/ha for SustaiN.

There are also associated environmental benefits, i.e., reduced NH₃ losses, of using nBTPT-treated urea compared to commercial urea. An extensive review collected by Saggar *et al.* (2013) reported that nBTPT-treated urea applied to temperate grasslands in New Zealand can reduce NH₃ emissions by 44.7%. Ammonia itself is not a greenhouse gas, but can indirectly contribute to the production of N₂O after land deposition. The above review suggests that the Ministry of Primary Industry (MPI) should include a specific value of 0.055 for FracGASF FNUI (fraction of urease inhibitor treated total fertiliser N emitted as NH₃) in New Zealand Greenhouse Inventory, meaning lower environmental foot prints of nBTPT treated urea.

Previous claims that volatilisation of ammonia from applied urea is “insignificant” and “in the range of 0–5% of the applied N” in New Zealand conditions (Edmeades & McBride 2012) have not been born out by this study. Combined analysis (meta-analysis) of many different trials can actually distort the facts if due attention is not paid to trial site conditions, and how well or otherwise they represent the typical range of actual farming conditions, and/or the situations in which a given product is recommended for use. Certainly, it is possible to identify conditions in advance that are less conducive to volatilisation (Stafford *et al.* 2008), but in the authors’ considered opinion, considerably higher

losses than 5% are typical of that reported by Edmeades & McBride (2012).

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