

# UREA VOLATILISATION: THE RISK MANAGEMENT AND MITIGATION STRATEGIES

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## **Abstract:**

A review of international ammonia volatilisation trials from surface applied urea, showed the potential risk from ammonia volatilisation to be in the range of 0 to 65% of applied N, dependent on soil properties (Martens and Bremner 1989; Watson 1990). Martens & Bremner (1998) and Watson (1990) showed that in 20 Iowa and 20 Irish soils respectively, the maximum volatilisation ( $V_{max}$ ) of urea was negatively affected by cation exchange capacities (CEC), exchangeable acidity and buffering capacity but increased with calcium carbonate equivalence and soil pH in 0.1 M KCl (pH-KCl).

In addition to soil properties the realisation of  $V_{max}$ , under field condition is dependent on climatic and management practices, which assist the migration of urea into the soil profile. The main climatic effect is rainfall greater than 16 mm (Black et al. 1987; Bowman et al. 1987; Freney et al. 1992), occurring shortly after surface application and in terms of crop management, the placement of urea below 30 mm at seeding (Connell et al. 1979; Palma et al. 1998; Prasertsak et al. 2002). The post planting surface urea applications poses a high risk in cropping systems, but can be reduced by timing application with rainfall and allowing the crop canopy to develop prior to application.

From the assessment of field trial data the losses of N from agricultural applications of urea is globally 10% in arable cropping (Turner et al. 2010) and 20% from pasture. These results are similar to the findings of New Zealand and Australian field trials dependent on the methodology used. Trials in which rainfall was allowed to influence the measurements (meteorological and rain compensated chamber methods) resulted in an observed mean that was significantly lower than (mean 10.4%, SD 4.6) the covered chamber methods (mean 27.1%, SD 6.9). The results show average ammonia volatilisation from urea application in New Zealand has little economic importance given the cost of mitigation, as long as urea is not surface applied to soils with high  $V_{max}$  potential without impending rainfall.

In terms of mitigation of urea volatilisation the use of management tools, mainly timing of broadcast applications and placement/incorporation of urea at planting are the most cost effective strategies. The use of urease inhibitors mainly NBPT has proven, in eight international field trials to reduce ammonia volatilisation by between 28 to 88%. However this may represent a mean saving of only 2.8% to 17.7% of applied N in medium risk soils ( $V_{max}$  10-20%) and 5.6 to 35.2% in high risk soils as illustrated by the GIS ammonia volatilisation risk map of New Zealand (Figure 1).

## **Introduction:**

The loss of applied fertiliser N from urea application via ammonia volatilisation has received significant attention over recent years in the Australian and New Zealand pastoral and arable sectors, with the active marketing of urease inhibitor (NBPT) as a N loss mitigation strategy. In this review the potential risks of urea N losses via volatilisation is considered in terms of laboratory assessments (maximum volatilisation,  $V_{max}$ ) and the observed losses under field conditions. The difference between the  $V_{max}$  and the field observation may vary greatly as the volatilisation of ammonia at the soil/air interface is governed by the mass transfer of ammonia gas by turbulence in with in the air close to the soil surface (wind speed) and thermal convection as the result of the surface heating and evaporation of water due to solar radiation. The loss of ammonia from the crop system is also affected by the crop canopy interaction with ammonia being absorbed by plants foliage (Denmead et al. 1976; Denmead et al. 2008) and respiration, which can increase the concentration of CO<sub>2</sub> in the soil pH during the night (Flechard et al. 2007) and dew formation on the crop canopy combine to reduce ammonia losses during the night. These effects result in a strong diurnal pattern of ammonia volatilisation with high losses during the day and low losses at night.

## **Risk of Volatilisation**

Based on the theory of volatilisation the risk potential is a function of:

- Soil properties - ammonium concentration, pH
- Climatic – temperature, evaporation and wind speed.

The application of urea to soil and its hydrolysis results in the formation of ammonium and bicarbonate ions, the fate of these ions are strongly dependent on the chemical properties of the soil. Ammonium ions (NH<sub>4</sub><sup>+</sup>) maybe exchangeably absorbed on to clay minerals or organic matter, releasing H<sup>+</sup> or cations into the soil solution. The bicarbonate ions maybe lost as CO<sub>2</sub> gas increasing the soil pH as an OH<sup>-</sup> ion is produced or in the presents of calcium ions in solution calcium bicarbonate may form and precipitate as calcium carbonate producing CO<sub>2</sub> and water, buffering the soil pH as no OH<sup>-</sup> is produced and the anion associated with the calcium is able to stabilise the NH<sub>4</sub><sup>+</sup> in solution (Fenn 1988). Thus, the higher a soils CEC and exchangeable H<sup>+</sup> and the lower the soil pH are, the lower the risk of volatilisation. This is supported by the laboratory results of Martens & Bremner (1989) and Watson (1990) who carried out evaluations of the maximum volatilisation ( $V_{max}$ ) on 20 Iowa and Irish soils, respectively.

Watson (1990), showed for an application of 100 kg N as urea at 10°C,  $V_{max}$  could be simply explained by using the following equation based on soil pH-KCl(0.1M KCl), CEC (meq 100g<sup>-1</sup>) and N (%) ( $R^2=0.86$ , Standard error = 3.4).

$$V_{max} = -10.52 + 5.932(pH - KCl) - 0.416 (CEC) + 7.93 (\%N) \quad \text{Eq.1}$$

The addition of the total soil %N is used to infer urease activity based on biological activity. Watson et al. (1994) in their laboratory assessment of NBPT in 16 Irish soils at 13°C found  $V_{max}$  to be a function of pH-KCl and total acidity (TA, meq kg<sup>-1</sup>)(  $R^2=0.95$ , Standard error 2.6).

$$V_{max} = -17.49 + 7.37(pH - KCl) - 0.11 TA \quad \text{Eq.2}$$

The application of this model equation to the previous work (Watson, 1990) however give a poor correlation for soils with TA >150 meq kg<sup>-1</sup>.

The work carried out by Martens & Bremner (1989) in the Iowa soils incubated at 30°C showed the loss of ammonia via volatilisation was significantly affected by the presence of calcium carbonate and the nitrification of ammonia during the 10 day incubations.

The trials of Watson (1990&1994) and Martens & Bremner (1989) show an increase in volatilisation with increasing soil pH in water and KCl solution and a decrease with increasing CEC and TA. A simple analysis of common soil properties reported in these three trials initial indicated that soil pH in water and CEC gives a poor correlation ( $R^2 = 0.45$ , Standard error = 9.6) after exclusion of results affected by calcium carbonate or nitrification.

$$V_{max} = -33.68 + 9.28pH - 0.238CEC \quad \text{Eq.3}$$

The application of the simplified model ( Equation 3) to Watson’s data showed a better correlation ( $R^2 = 0.75$ , Standard error = 4.9) allowing accurate estimations of the maximum volatilisation of ammonia from surface applied urea at 100 kgN ha<sup>-1</sup> at 10 to 13 °C.

This type of simplification of the emission model of ammonia from agricultural soils (Sheppard et al., 2009) in terms of soil pH and CEC along with application method and climate factors has been used in GIS modelling of regional and global scale emissions of ammonia from the agricultural sector (Bouwman et al. 2002). Bouwman et al. (2002) developed a formula to estimate ammonia emission factor (%) based on the summing of coefficients which describe the fertilizer type, placement, soil properties, farming practice and climate (Table 1).

**Table 1 : Emission factor (%) = 100 e<sup>(sum of relevant coefficients)</sup>**

<b>Condition where coefficient</b>	<b>Coefficients</b>
<b>Annual upland crops</b>	-0.045
<b>Perennial crops</b>	-0.158
<b>Urea</b>	0.66
<b>Broadcast</b>	-1.305
<b>Incorporated</b>	-1.895
<b>Soil pH &lt; 7.25</b>	-1
<b>Soil 8.5&gt;pH&gt;7.25</b>	-0.608
<b>Soil CEC &lt; 25(meq 100g<sup>-1</sup>)</b>	0.507
<b>Soil CEC&gt; 25 (meq 100g<sup>-1</sup>)</b>	0.0848
<b>Temperate climate (constant)</b>	-0.402

The ammonia emission model (Bouwman et al. 2002) includes only two soil factors, pH and CEC which are divided into coarse criteria. The division of pH and CEC into low emission risks for pH <7.5 and CEC>25 is based on ammonium salt fertiliser which require high soil pH to produce ammonia. The model also includes a climate factor which significantly reduction emission factor for temperate climates were evaporation is dominated by solar radiation and rainfall is more frequent. Using this model the application of broadcast urea to pasture in New Zealand would result in an average loss of 18.4% of applied urea in typical soils (pH<7.5 and CEC<25) while cropping on soil with CEC > 25 reduced the loss of

ammonia to 7.5% when the urea was incorporated at planting ( Table 2). These values are consistent with the mean value of 19% (SD 9.5) obtained from 13 international field trials on ammonium volatilisation of urea at application rates of 30 to 536kg N ha<sup>-1</sup> to pasture (Table 3). The analysis of these trials however shows that the New Zealand mean volatilisation is considerably lower (mean 10.4%, SD 4.6) than the international mean. This is most likely due to the frequency of rainfall and lower mean temperatures.

**Table 2. Typical emission factors for urea applied to New Zealand pasture and cropping systems (calculated from Sheppard et al., 2010)**

<b>Farming system and application rate</b>	<b>Coefficient</b>	<b>Emission Factor</b>
<b>Pastoral application broadcast</b>		
<b>pH&lt;7.25 and CEC&lt;25</b>	-1.692	18.4%
<b>Cropping incorporated at planting</b>		
<b>pH&lt;7.25 and CEC&gt;25</b>	-2.591	7.5%
<b>Cropping broadcasts</b>		
<b>pH&lt;7.25 and CEC&gt;25</b>	-2.001	13.5%

**Table 3. International results of field trials of ammonia volatilisation from urea surface application to pasture.**

<b>Location</b>	<b>Rate of N applied kg N ha-1</b>	<b>Mean % N - volatilised</b>	<b>SD</b>	<b>N</b>	<b>Range</b>	<b>Reference</b>
<b>Argentina</b>	180	22.8	-	2	10.3-35.2	Barbieri & Echeverria, 2006
<b>Canterbury NZ</b>	15-200	17.6	8.4	10	7.4-33.3	Black et al. 1984; 1985a; 1985b
<b>USA</b>	50	36	-	1	-	Bowman 1987
<b>UK</b>	30-150	26.7	12.9	15	10-58	Chadwick et al., 2005
<b>Canterbury NZ</b>	25	7.5	-	1	-	Di & Cameron, 2004
<b>Waikato NZ</b>	23-536	11.6	2.4	14	7.5-15.0	Ledgard et al. 1999
<b>UK</b>	70-437	17.7	8.6	10	5.7-35.7	Ryden et al., 1987
<b>Denmark</b>	90	17.8	-	1	-	Sommer & Jensen, 1994
<b>UK</b>	70-280	28.1	10.5	8	12.1-46.0	Van der Weerden & Jarvis., 1997
<b>Netherlands</b>	80-120	19.3	12.5	3	-	Velthof et al.,1990
<b>Waikato NZ</b>	150	4.2	-	1	-	Zaman et al., 2008
	Mean	19.0	9.5			

In terms of arable cropping systems (Table 4), the mean data from 10 trials appears to overestimate the losses (20.0%) of ammonia compared to the model (7.5-13.5) this is due to the high number of calcareous soils (Rawluk et al., 2001; Sanz-Cobena et al., 2008; Grant et al.,1996) which show high volatilisation losses.

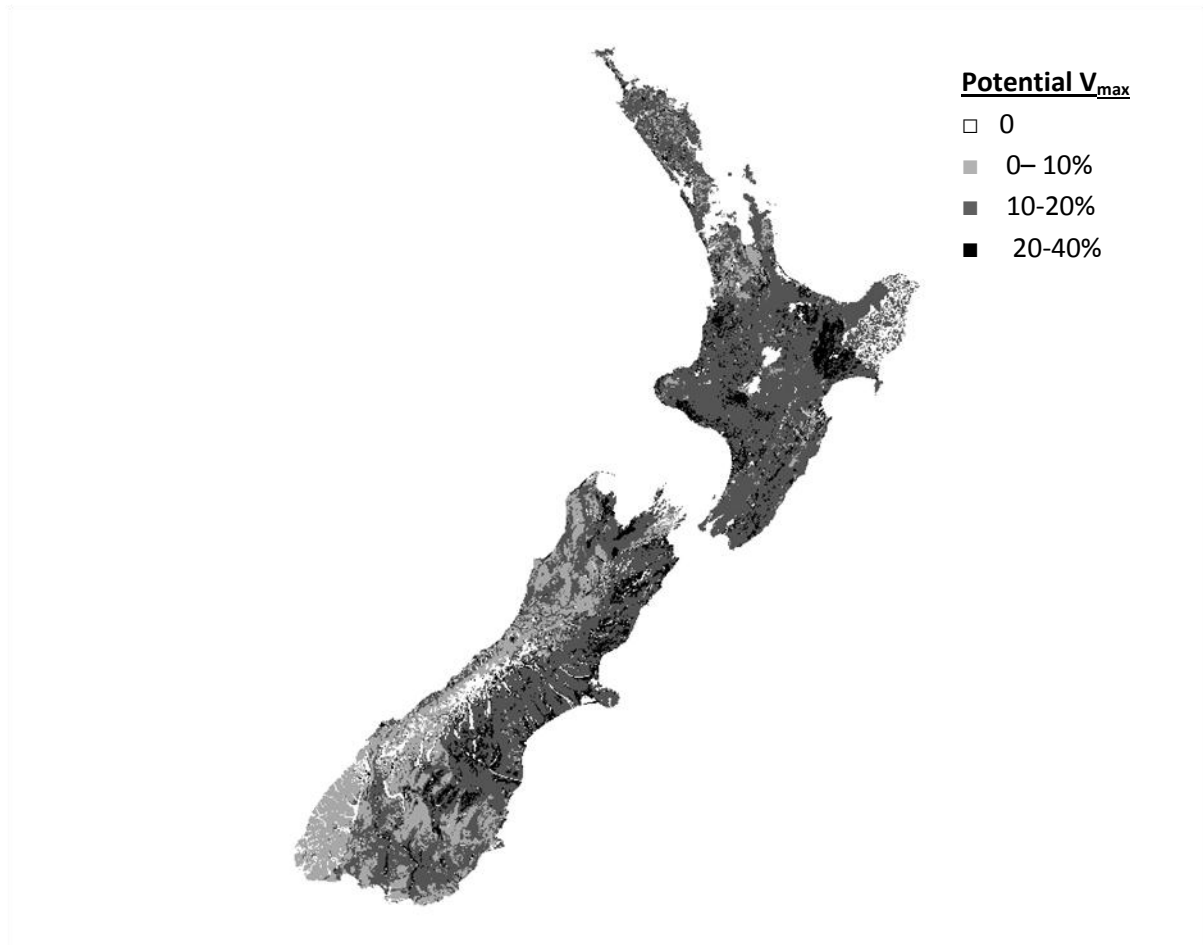
**Table 4. International results of field trials on ammonia volatilisation from urea application to arable cropping soils.**

<b>Location</b>	<b>Rate of N applied kg N ha<sup>-1</sup></b>	<b>Mean % N - volatilised</b>	<b>SD</b>	<b>N</b>	<b>Range</b>	<b>Reference</b>
<b>Denmark</b>	90	17.8	-	1	-	Sommer & Jensen, 1994
<b>Canada</b>	100	26.9	9.5	8	20-50	Rawluk et al.,2001
<b>Canada</b>	140	17.3	8.9	3	9.2 - 26.9	Rochette et al., 2009
<b>India</b>	200	30	-	1	-	Beyrouty et al., 1988
<b>NZ</b>	100	11.7	10.1	3	1-21.1	Black et al. 1989
<b>Spain</b>	170	17.3	-	1	-	Sanz-Cobena et al.,2008
<b>Australia</b>	80	9.5	-	1	-	Turner et al.2010
<b>Argentina</b>	60	7.9	2.7	4	-	Palma et al., 1998
<b>Canada</b>	100	33	35	2	33	Grant et al.,1996
<b>USA</b>	120	10	6.5	3	7-17	McInnes et al., 1986
	<b>Mean</b>	20.6	15.0			

From the models and field trial data the potential risk of ammonia volatilisation in acid soils is on average  $20 \pm 10\%$  for pasture application and  $14 \pm 7\%$  for arable systems.

The potential risk posed by ammonia volatilisation in New Zealand can be modelled using the Bouwman et al., (2002) formula at a country level, more detail is however required at a regional and farm level to enable risk management practices to be applied. For this level of detail the application of equation 3 to the New Zealand soils data base ([www.lris.scinfo.org.nz](http://www.lris.scinfo.org.nz)) allowed the estimation of the maximum potential for ammonia volatilisation in a GIS map (Figure 1).

The risk map of potential ammonia volatilisation shows that the majority of New Zealand soils used for agricultural production have a  $V_{max}$  in the range of 10-20% of applied urea. This estimate excludes climatic factors which may increase or lower risk such as high evaporation rates and rainfall, respectively. Figure 1 indicates a very low risk of volatilisation in the poverty bay due to very low soil pH and a number of high risk areas due to calcareous soils or low CEC.



**Figure 1. Potential maximum ammonia volatilisation ( $V_{max}$ ) risk map of New Zealand based on GIS soil pH and CEC (Mod data layers) from Landcare Research and modelled using equation 3 based on Irish soils at 10-13 °C (Watson 1990; 1994).**

### **Summary of Risk**

The potential and measured field emission factors for surface applied urea show highly variable results dependent on soil properties and climatic factors. For soils with low pH (<5.4) and high CEC (>25 meq 100g<sup>-1</sup>) the potential risk is less than 10% (Eq.3 ) and mitigation options may have little effect, however for soils with pH > 6 volatilisation has the potential to result in losses higher than 20% in which case mitigation options may be considered cost effective.

### **Mitigation of ammonia volatilisation from urea application**

A number of mitigation tools and strategies have been trialled including:

- Placement of urea below the soil surface
- Application of broadcast urea prior to rainfall
- Addition of acids and salts to buffer the soil pH
- Addition of urease inhibitors to slow hydrolysis of urea

### *Application of urea prior to rain*

The effect of rainfall or irrigation on the reduction in volatilisation is has been investigated by an number of researches (Black et al. 1987; Bowman et al. 1987) who found that the application of 10 -16 mm of water within 3 to 8 hrs following urea application was capable of reducing volatilisation 80-93%, while a delay of 24 hrs may reduce volatilisation by only 33%. These results are, however, dependent on the rate of urea hydrolysis in the soil which was high in both studies, under field conditions a very dry soil surface may prevent hydrolysis until sufficient rainfall (Rochette et al. 2009) while moist soils with high organic matter increase the hydrolysis rate reducing the effectiveness of rainfall to within the day of application (Ferguson and Kissel 1986; Reynolds and Wolf 1987).

### *Urea Placement*

The placement of urea 3-5 cm below the surface can effectively reduce ammonia volatilisation by 86-95% (Connell et al. 1979; Prasertsak et al. 2002) in moist soils. However in arid soils the incorporation of urea can result in increased volatilisation due to dissolution of the incorporated urea in the soil while the surface applied urea remains un-dissolved until sufficient rain occurs (Rochette et al. 2009).

### *Addition of Acid and Salts*

The addition of mineral salts to urea to increase the acidity and buffering around the granule site has shown mixed results dependent on the incorporation of the salts in the soil.

The co-application of potash (KCl) with urea at 0.76:1 to 1:1 mass ratio in non-calcic soils has shown in laboratory trials to reduce ammonia volatilisation by 30% (Christianson et al. 1995) to 50% (Gameh et al. 1990) applied in the solid form and 90% (Rappaport and Axley 1984) as solutions. This has, however, not been proven in field trials. Under field conditions the use of liquid urea ammonium nitrate (32N) which contains 35% urea has shown a 48% reduction in the volatilisation of it urea content (Grant et al. 1996).

The addition of acids such as phosphoric acid is capable of reducing volatilisation of ammonia by 30 to 70% depending on the soil (Stumpe et al. 1984), however the required level of phosphoric acid to achieve this results in a product with an analysis of 19N:22P very similar to MAP or DAP. The production of urea nitricphosphate (23N:12P) (Christianson 1989) also shows a reduction in volatilisation of 50% compared to urea. With the additional N from the nitric acid urea nitricphosphate is also able to deliver a more balanced supply of N to P than urea phosphoric acid fertiliser.

### *Urease Inhibitors*

The addition of urease inhibitors such as phenylphosphorodiamidate (PPD) or N- (n-butyl) thiophosphoric triamide (NBPT) result in similar reductions to the placement of urea below the soil surface as their use allows urea to remain on the soil surface without the formation of ammonia until rain is able to wash the urea into the soil. The two inhibitors vary in both efficacy and application rate, with PPD producing between 0 to 91% reductions in ammonia volatilisation at 0.5 to 1% addition to urea (Watson 1990) while NBPT at 0.28% added to urea produced 54 to 95% reductions (Watson et al. 1994), with both sets of results being dependent on soil types.

In the examination of NBPT field trial data (Table 5), shows a reduction in volatilisation from a average 11.8% to 7.2% due to the addition of > 0.15% NBPT (a 39% reduction), which

contrasts strongly with laboratory and covered field trials (not presented) 31.3 to 7.2 a 76% reduction in volatilisation.

**Table 5. Field trial data supporting the effect of NBPT in which rainfall was not excluded.**

Country	N rate kgN ha <sup>-1</sup>	% Volatilisation Urea	% Volatilisation Urea +NBPT	Reference
AU	80	9.5	1	Turner et al. 2010
NZ	150	4.2	1.9	Zaman et al.2008
NZ	600	5.9	2.95	Zaman et al. 2009
NZ	600	6	2.5	Zaman & Blennerhassett 2009
Brazil	90	11.2	7.2	Cantrarella et al.2008
Brazil	90	25.4	15.2	Cantrarella et al.2008
Brazil	90	25.1	21.3	Cantrarella et al.2008
Brazil	90	7.2	1.6	Cantrarella et al.2008
Brazil	90	16.4	13.4	Cantrarella et al.2008
Brazil	90	1.1	0.8	Cantrarella et al.2008
Brazil	90	15.2	11.2	Cantrarella et al.2008
Spain	170	17.3	10	Sanz Cobena et al 2008
Can	140	9.5	4.8	Rochette et al. 2009
	<b>Mean</b>	<b>11.8</b>	<b>7.2</b>	

#### *Coated Urea*

The coating of urea with a material to slow the initial dissolution of urea, prior to significant rainfall can reduce losses via volatilisation (Torello et al. 1983; Blaise and Prasad 1995; Knight et al. 2007; Rochette et al. 2009) reducing losses of ammonia from 9-40% for urea to 0.7-4% for polymer coated urea at urea application rates from 96 to 400 kgN ha<sup>-1</sup>. These results show that polymer coated urea is an effective method of reducing ammonia volatilisation. In addition the application of coated urea may allow the direct drilling with seed of the total crop requirement up to 120 kgN ha<sup>-1</sup> at seeding without affecting germination (McKenzie et al. 2007) with urea drilled with seed was limited to less than 30 kgNha<sup>-1</sup>. The ability of polymer coated urea to be placed with seed removes the requirement for side dressing of urea on the surface which increases volatilisation losses. The surface application of polymer coated urea to arable crops winter wheat can result in low grain yields and protein content (McKenzie et al. 2010), while surface application to pasture in winter with higher rainfall ( 72-138 mm compared to 372 mm) can result in incorporation of the polymer coated urea into the soil surface and release of urea over the growing season (Bishop et al. 2008).

The surface application of polymer coated urea turf or pasture (Torello et al. 1983; Knight et al. 2007) reduce ammonium volatilisation and increase N to drymatter conversion efficiency (Bishop et al. 2008), while in arable cropping polymer coated urea allows all the N requirement to be drilled at planting removing the risk of surface application later in the crop development.



### **Summary of field trial data and mitigation strategies**

The most effective mitigation optimums for the reduction of ammonia volatilisation from urea applications are presented in the following tables 6 and 7 for pasture and arable systems.

**Table 6. New Zealand Pastoral Field Trial Summary (with no separation of data based on methodology)**

	<b><u>Mitigation optimums</u></b>			
Volatilisation losses Mean% (SD) of 9 trials* 15-1000kgNha <sup>-1</sup>	16 mm Rainfall in day 1	Placement Below 3-5cm	NBPT	Polymer coated urea**
Annual 14.6 (8.3)	80 to 93% reduction	86 to 95% reduction	39% reduction	50 to 98% reduction
Summer 17.6(9.7)				
Autumn 19.2 (11.4)				
Winter 7.7 (3.9)				
Spring 18.3(12.2)				

(\*) (Black et al. 1984; Sherlock and Goh 1984; Black et al. 1985; Black et al. 1985; Black et al. 1987; Ledgard et al. 1999; Di and Cameron 2004; Zaman et al. 2008; Zaman et al. 2009; Zaman and Blennerhassett 2010)

(\*\*) international trial data (Torello et al. 1983; Blaise and Prasad 1995; Knight et al. 2007; Rochette et al. 2009)

### **Australian Arable Field Trial Summary**

	<b><u>Mitigation optimums</u></b>				
Volatilisation losses Mean% (SD) of 3 trials * 60-172kgNha <sup>-1</sup>	Rainfall in day 1 >6.8mm	Placement Below 5cm	NBPT	Polymer coated urea**	UAN
8.8(8.5)	50% reduction	75% reduction	89% reduction	50 to 98% reduction	30% reduction

(\*) (Bacon et al. 1986; Bacon et al. 1988; Turner et al. 2010)

(\*\*) international trial data (Torello et al. 1983; Blaise and Prasad 1995; Knight et al. 2007; Rochette et al. 2009)

### **Conclusion:**

The risk of ammonia volatilisation from surface applied urea application is highly variable, dependent on soil and climate factors. In the temperate New Zealand climate the mean losses from the pastoral sector has a potential emission factor of 18% (Sheppard et al. 2010) close to the mean of 20% based on 39 international field trials. In contrast to this New Zealand and Australian data shows an average of 11 and 12 %, respectively for field trials which incorporate rainfall. The lower results are partly due to the separation of field data into groups which included and excluded rainfall within their methodologies. The practice of rain

exclusion in field trials using the enclosure method (Black et al. 1985) results in significantly higher volatilisation compared to micro-metrological methods which allow rainfall to influence the outcome of the trial.

The mitigation of the potential loss of ammonia from surface application of urea to pasture can be achieved by timing urea application to coincide with rainfall, with a minimum of 16mm of rainfall within 24 hrs. As the process timing of urea application to pasture may not be possible due to equipment and labour availability the addition of urease inhibitor to the urea extends the optimal rainfall occurrence from within 1 to 14 days.

In the arable cropping sector, management practices which avoid surface application of urea such as incorporation of the full N fertiliser requirement at planting. As this may result in seed damage due to high ammonia concentration the co-application of a urease inhibitor or urea in a controlled release form may be required when drilling urea with seed. If additional N is required during the crop growth, topdressing/sidedressing of urea should be carried out when the crop canopy has established to take advantage of foliar absorption or the co-application of urease inhibited with the urea should be considered.

In high risk soils with low CEC and high pH the co-application of urease inhibitor should be considered, however this applies to a small area in New Zealand indicated by the GIS risk map (Figure 1). The application of urea during hot dry summer conditions should be avoided to prevent volatilisation due to high temperatures and low rainfall

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