AGRICULTURE AND FOOD DEVELOPMENT AUTHORITY

TITLE: Ammonia emissions from urea, stabilised urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland

AUTHORS: Patrick J. Forrestal, Mary Harty, Rachael Carolan, Gary J. Lanigan, Catherine J. Watson, Ronnie J. Laughlin, Gavin McNeill, Brian J. Chambers, Karl G. Richards

Title: Ammonia emissions from urea, stabilised urea and calcium ammonium nitrate: insights into loss abatement in temperate grassland

Authors and order: Patrick J. Forrestal[1], Mary Harty[1,2], Rachael Carolan[3], Gary J. Lanigan[1], Catherine J. Watson[2,3], Ronnie J. Laughlin[3], Gavin McNeill[3], Brian J. Chambers[4], Karl G. Richards[1]

[1] Crops Environment and Land Use Program, Teagasc, Johnstown Castle, Wexford, Ireland.

[2] Queen's University Belfast, University Road, Belfast BT7 1NN, Northern Ireland.

[3] Agri-Food and Biosciences Institute (AFBI), Newforge Lane, Belfast BT9 5PX, Northern Ireland.

[4] ADAS Gleadthorpe, Meden Vale, Mansfield, Nottinghamshire NG20 9PD, U.K.

Corresponding author: Patrick J. Forrestal[1] patrick.forrestal@teagasc.ie

Short running head title: Ammonia emissions from fertilisers

Abstract

Fertiliser nitrogen (N) contributes to ammonia (NH_3) emissions, which European Union member states have committed to reduce. This study evaluated NH_3-N loss from a suite of N fertilisers over multiple applications, and on gaining insights into the temporal and seasonal patterns of NH_3-N loss from urea in Irish temperate grassland using wind tunnels. The fertilisers evaluated were: calcium ammonium nitrate (CAN), urea, and urea with the N stabilisers **N-(n-butyl)** thiophosphoric triamide (NBPT), dicyandiamide (DCD), DCD+NBPT, and a maleic and itaconic acid polymer (MIP). 200 (and 400 for urea only) kg N/ha/yr was applied in five equal applications over the growing season at two grassland sites (one for MIP). Mean NH_3-N losses from CAN were 85% lower than urea which had highly variable loss (range 45% points). The effect of DCD on NH_3 emissions was variable. MIP did not decrease loss but NBPT caused a 78.5% reduction, and when combined with DCD, a 74% reduction compared with urea alone. Mean spring and summer losses from urea were similar, although spring losses were more variable with both the lowest and highest loss levels. Maximum NH_3-N loss usually occurred on the second day after application. These data highlight the potential of stabilised urea to alter urea NH_3-N loss outcomes in temperate grassland, the need for caution when using season as a loss risk guide and that urea hydrolysis and NH_3-N loss in temperate grassland is rapid. Micrometeorological measurements focused specifically on urea are needed to determine absolute NH_3-N loss levels in Irish temperate grassland.

Key words: ammonia, volatilisation, urea, ammonium nitrate, inhibitors, grassland, fertiliser

Introduction

Global ammonia (NH_3) emissions from fertiliser nitrogen (N) are estimated at 10 to 12 Tg N/yr (Beusen *et al*., 2008). These emissions are of concern from economic, environmental, and national policy perspectives. As addition of supplemental fertiliser N is a cornerstone of many agricultural systems N lost as NH_3-N must be replaced, typically at an economic and environmental cost, in order to sustain agro-ecosystem productivity. Ammonia lost from agricultural systems may be re-deposited contributing to eutrophication and acidification of terrestrial and aquatic ecosystems (Sutton *et al*. 1992) and indirect emissions of nitrous oxide (N_2O), a potent greenhouse gas. In terms of national policy, EU member states have committed to reducing NH_3-N emissions under the National Emissions Ceiling Directive (EU, 2001).

The use of urea in place of ammonium nitrate-based fertiliser has some potential for mitigating fertiliser N related N_2O emissions (Dobbie & Smith, 2003). However, urea is vulnerable to NH_3 volatilisation (Chambers & Dampney 2009). Promisingly N stabilised using N inhibitors can play a role in mitigating losses of NH_3-N (Watson *et al*., 2009), N_2O (Di *et al*., 2007) and nitrate leaching (Dennis *et al*. 2012). These inhibitors can be divided into two groups: i) urease inhibitors and ii) nitrification inhibitors. Urease inhibitors reduce NH_3 volatilisation from urea by inhibiting the enzyme urease which catalyses urea hydrolysis. The urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) has been shown to reduce NH_3 loss from urea (Watson *et al*., 1990, 1994; Goos *et al*., 2013). The maleic and itaconic acid polymer (MIP) has been marketed globally and claims to be a urease and a nitrification inhibitor. However, a number of studies (Franzen *et al*., 2011; Goos *et al*., 2013) have shown that urea treated with MIP did not reduce NH_3 loss from urea. Nitrification inhibitors, such as dicyandiamide (DCD), inhibit ammonia monooxygenase, which catalyses oxidation of ammonium (NH_4^+) to nitrite (Kim *et al*. 2012). Although effective for reducing N_2O

emissions and leaching, nitrification inhibitors may increase NH_3 emissions. In a meta-analysis, Kim *et al*. (2012) reported that the effect of DCD on NH_3 emissions was inconsistent, with increased NH_3 emissions in 26 studies, no change in 14 studies and decreased emissions in 6 studies. They linked nitrification inhibitor related increases in NH_3 loss to increasing soil pH and decreasing cation exchange capacity (CEC).

Previous studies have evaluated NH_3 loss from urea and urea with inhibitors, particularly in cropping systems; however field measurements in temperate grassland are more limited. To address this knowledge deficit, the current study assessed NH_3-N loss from fertiliser formulations with and without N stabilisers over multiple applications.

Materials and methods

Site description and experimental design

Experiments were conducted at grassland sites located at Hillsborough (HB), Co. Down, Northern Ireland (54°46′N; 6°08′W) and Johnstown Castle (JC), Co. Wexford, Ireland (52°17′N; 6°30′W). Hillsborough is a moderately drained loam classified as a Dystric Umbric Stagnosol (FAO, 2014) (45% sand, 33% silt, 22% clay, 11% organic matter, pH 5.6, CEC 24.43 $cmol^+$/kg). Johnstown Castle is a moderately drained loam classified as a Stagnic Cambisol (FAO, 2014) (52% sand, 34% silt, 14% clay, 7% organic matter, pH 5.8, CEC 15.46 $cmol^+$/kg). Swards were dominated by perennial ryegrass (*Lolium perenne* L.). Precipitation, ambient and soil temperature were measured by a meteorological station (ca. 500 m from the study site). A HH2 moisture meter (Delta Devices, Burwell, Cambridge, England) was used to measure soil volumetric moisture content on site.

Fertiliser treatments were applied in five equal split applications. Treatments were CAN, urea, urea+NBPT, urea+DCD, urea+NBPT+DCD and at JC only urea+MIP. All treatments were applied at 200 kg N/ha and both sites also included a urea 400 kg N/ha/yr treatment.

The source of the urease inhibitor NBPT was Agrotain® which was coated onto urea granules at 660 ppm NBPT (on a urea weight basis). Koch Agronomic Services supplied the urea+DCD granules, where DCD had been added to urea at the molten stage at the rate of 3.5% on a urea-N basis. Urea+DCD granules were coated with Agrotain® on site to make urea+NBPT+DCD. The source of MIP was commercially available urea treated with Nutrisphere®. A randomised block design with three replicates was used except for the urea 400 kg N/ha/yr and urea+MIP treatments at JC, each of which had two replicates. Fertiliser treatments were applied between March and September 2014 (Figures 1 and 2).

Ammonia measurements

Ammonia loss from the treatments was measured using a system of wind tunnels similar in design to Lockyer (1984) and Meisinger *et al*. (2001). In brief, each wind tunnel unit consisted of a 0.5 m x 2 m polycarbonate canopy with an integrated inlet air sampling line, an axial fan to draw air through the canopy, an anemometer to measure air speed, which was 0.9 to 1.0 m/s at the anemometer, and an outlet air sampling line. A control box housed a diaphragm pump for air sampling, a flow meter and a critical orifice for both air sampling lines. Inlet and outlet air NH_3-N was measured by passing through individual conical flasks containing 100 ml of 0.02 M orthophosphoric acid. If the difference in concentration between the inlet and outlet acid trap was negative the loss was set to zero. The NH_3-N flux rate was calculated by dividing the emission by the exposure time.

Measurements were conducted for between 14 and 19 days following each fertiliser application (Figure 1 and 2) and in all cases until NH_3-N emissions had returned to background levels. Each plot (2.5 m by 2.5 m) could accommodate wind tunnel moves sequentially through three positions on each acid trap change occasion to minimise interference of the wind tunnel canopy on precipitation reaching the plots. The fourth move returned the wind tunnel to its starting position. Acid solutions were changed at each wind

tunnel move and NH_4^+-N content was determined colormetrically using a QuAAtro 3 (Seal Analytical, Fareham, U.K.) at HB and an Aquakem 600A Analyser (Thermo Electron OY, Vantaa, Finland) at JC.

Data analysis and interpretation

The acid trap change period varied during the study, consequently the time-integrated hourly flux (g N/ha/hr) (Engel *et al.*, 2011) is presented with the flux indicated at the mid-point of the sampling period in Figures 1 and 2. A repeated measures analysis of variance was conducted for both i) the time-integrated flux of NH_3-N and ii) the percentage NH_3-N loss using the PROC MIXED procedure of SAS (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.). The sources of variation in the model were time (of sampling in the case of time-integrated NH_3-N flux or application date in the case of per application loss) and fertiliser N treatment. A generalised linear mixed modelling approach was used to test for a fertiliser N treatment effect on annual NH_3-N loss using the PROC GLIMMIX procedure of SAS 9.3. Differences between fertiliser treatments were determined using the F-protected least significant difference (LSD) test at the 95% confidence level.

Results and discussion

Ammonia loss from CAN and urea

The mean NH_3-N loss from CAN of 4.2% was higher than the mean emission of 0.8% reported by Black *et al*. (1985). Higher losses from CAN in the present study may be partially attributable to more rapid dissolution of the calcium carbonate ($CaCO_3$) in CAN, which causes a small initial rise in soil pH around the granule (Black *et al*., 1985). In contrast, the average loss from urea was much higher at 25.1% for HB and 30.6% for JC and spanned a wide range (7.5 to 52.8%) across the five 40 kg N/ha applications. While these average

values are similar to the 30% reported by Chambers & Dampney (2009) in UK grassland, also using wind tunnels, they are much higher than those of Black *et al*. (1985) who reported average loss over four seasons of 11.9% for urea. Black *et al*. (1985) state that, due to the measurement method these losses were likely near the upper limit for grassland in Canterbury, New Zealand. Similarly, we suspect that the losses recorded by the wind tunnels in the current study are at the upper limit of losses for Irish temperate grassland. One reason is that in a parallel study (Harty *et al.*, 2015) there were similar apparent N fertiliser recoveries in herbage of 65% for CAN and 60% for urea. Also the average urea-N losses of 25.1 to 30.6% are similar to the 27% loss measured by Schwenke *et al*. (2014) from urea applied on neutral to alkaline grassland with limited or no precipitation for two weeks after application, conditions expected to promote NH_3-N loss. Our sites were acidic (pH 5.6 at JC and 5.8 at HB) and significant precipitation was a feature of many periods following fertiliser application. It is known that NH_3-N losses measured by wind tunnels can differ from integrated horizontal flux (IHF) because wind tunnels interfere with wind speed and precipitation in particular. Schwenke *et al*. (2014) used the IHF micrometeorological approach. Ryden & Lockyer (1985) demonstrated that where precipitation was not a factor, urea NH_3-N loss measured by wind tunnels differed from a micrometeorological approach when the wind speed difference between the wind tunnel canopy and external conditions varied by >20%. Additionally, Ryden & Lockyer (1985) found that wind tunnels can overestimate NH_3-N losses by a factor of 2.4 to 6 during periods of rainfall. In the current study, wind tunnels were moved daily to minimise effects on rainfall although such effects are potentially not completely excluded. Wind tunnels were chosen for the current study because they permitted inter-comparison of a large suite of fertilisers in replicate, which would not have been practical using IHF which requires homogeneous fetch and relatively large land areas.

Temporal pattern of ammonia loss from urea

The maximum rate of NH_3-N loss from urea typically occurred on the second day after urea application (8 out of 10 cases), but in all cases within < 3 days (Figure 1 and 2). This indicates rapid hydrolysis of urea in Irish temperate grassland, in agreement with Watson & Miller (1996) who reported that 1.3% of N remained in the urea form in the soil 1.75 days after application. Black *et al.* (1985) also reported a one to three day delay in maximum loss rate from urea in New Zealand pasture. Grass and thatch is a zone of very high urease activity, 18 to 30 times higher than the soil (Torello & Wehner, 1983), which promotes rapid hydrolysis of urea in the presence of adequate moisture. Moisture limitation can inhibit urea hydrolysis and NH_3-N loss (Ferguson & Kissel, 1986) however such limitation is rare in Irish grasslands even in the absence of significant precipitation e.g. JC on March 10 (Figure 1) and HB on September 8 (Figure 2). In these examples, appreciable NH_3-N loss occurred rapidly (within <2 days) although precipitation was limited or absent. Urea is a hygroscopic substance with a critical relative humidity of 80% at $20^{o}C$ (Adams and Merz, 1929), a humidity level frequently surpassed in Irish grassland. In the two examples above mean relative humidity on the days of application was c. 87%. Additionally, dew in the evening and/or mornings could have provided additional moisture.

Effect of precipitation

Urea granules absorb moisture, therefore hydrolysis and resultant NH_3-N loss proceeds quickly with maximum loss rates occurring within 3 days in this Irish temperate grassland study. Holcomb *et al.* (2011) reported that 14.6 mm irrigation immediately following application reduced urea NH_3-N losses by 90% however these levels were not reached in the present study. The highest precipitation level on the day post application was 5.8 mm on May 6 at HB and the resultant loss was 8% (Table 1), much lower than the

average loss of 25.1% at this site. This initial 5.8 mm was followed by daily precipitation of 1.8 to 3.6 mm/day for three days and 11.6 mm on the fifth day. A similar rainfall input of 5.4 mm on July 7 at JC followed by 0.6 mm on the day after produced a loss of 26% (Table 1). Temperatures were warmer in July than in May, however if NH_3-N loss reduction only is the goal, the importance of precipitation approaching 15 mm on the day of application or sustained lower levels of precipitation over several days is apparent. The trade-off between NH_3-N abatement and potential N leaching and/or runoff risk potential requires evaluation.

The highest losses occurred after the March 10 application at JC under cool air and soil temperatures (Figure 1), with peak loss from urea occurring on the third day. There was little precipitation in the week following March 10, thus loss was not suppressed (Figure 1) and losses continued at appreciable levels over at least seven days. Similarly, in an incubation study using Irish soils, McGarry et al. (1986) observed high losses at 8^oC with maximum loss > 3 days following application and loss rates remaining high for up to 9-16 days. Accordingly, large NH_3-N losses from urea can occur over time in temperate grasslands when precipitation does not arrest loss even under cooler conditions as was seen following the March 10 application at JC. This finding is in agreement with Engel et al. (2011) who showed that large NH_3-N losses can occur from urea applied to wheat stubble in Montana under cold or frozen conditions.

However, the effect of precipitation is not straightforward; McInnes et al. (1986) previously reported that small precipitation inputs enhance rather than suppress loss. Accordingly the minor precipitation levels observed at JC (<0.3 mm/day) in the week following March 10 (Figure 1) are likely to have promoted loss, thus at least partially explaining very high loss at this site. The implication is that the timing, volume, and duration of precipitation following urea application all affect the influence of precipitation on urea NH_3-N loss. While precipitation patterns make this difficult to achieve farmers can maximise

suppression of NH_3 loss from urea by applying shortly before the onset of appreciable and sustained precipitation. Development of more specific guidance based on a larger dataset is warranted.

Seasonality

Traditional advice in Ireland that urea is less vulnerable to loss of NH_3-N in spring due to cooler temperatures is supported by the HB data with average loss of 32.3% in summer and 14.5% in spring. Conversely, the average NH_3-N loss at the JC site was 25.3% in summer and 39% in spring. Temperatures (Figure 1 and 2) and soil moisture (Table 1) were broadly similar between sites in spring yet losses were very different. The notable difference was the occurrence of almost daily precipitation following urea application at HB in spring (Figure 2) and the near absence of precipitation in the first two days following application at JC. The high losses in spring are compatible with McGarry *et al*. (1987) whose laboratory study using Irish soils showed that appreciable NH_3-N loss can occur not only from warm/cool-dry [18/8°C, 35% field capacity (FC)] but even from cool-wet (8°C, 85% FC) soils. As discussed earlier, important differentiating factors in spring loss outcomes appear to be time until precipitation onset and precipitation persistence.

Previous researchers have also noted that the seasonal effects are not pronounced. Black *et al*. (1985) noted no marked seasonal pattern of NH_3-N loss from urea in New Zealand grassland with 13.1, 15 and 11.2% from a summer, autumn and winter application, respectively, although there was a slight tendency for lower loss in spring at 10%. We also observed this slight tendency with average loss of 26.8% in spring and 28% in summer but spring NH_3-N losses were more variable (8 to 53%) than summer losses (20 to 33%). What is clear from this study is that NH_3-N loss from urea can be a significant issue in both spring and summer.

Influence of N stabilisers

Nitrification inhibitors can potentially reduce both N_2O emissions (Smith *et al*., 2012; Chen *et al*., 2010) and nitrate leaching (Di & Cameron, 2005; Díez-López *et al*., 2008) whilst increasing plant N use efficiency (Abalos *et al*., 2014). Nitrification inhibitors may also affect NH_3-N loss from urea, although Kim *et al*. (2012) reported that the effect was inconsistent. The current data show that this is also an issue in temperate grassland, with DCD significantly increasing NH_3-N loss at JC at three applications (by 15.8% to 23.9 percentage points, Table 1) and having no effect at two applications. The cumulative effect was a 36% increase in NH_3-N loss attributable to using DCD (Table 2). Aisling *et al*. (2008) reported that NH_4^+ remains in the soil longer when a nitrification inhibitor is used, with approximately 40% more NH_4^+-N in the soil one day after application when DCD was used with urea. Fox & Bandel (1989) suggested that a reduction in nitrification by DCD reduces soil acidification, thereby prolonging the pH spike caused by hydrolysis, thus increasing the period of NH_3-N emission. Gioacchini *et al*. (2002) suggested that maintaining NH_4^+-N in the soil causes a priming effect mineralising soil organic N. At JC, there is evidence of a more protracted period of NH_3-N loss from the DCD treated urea when losses increased significantly i.e. following the March 10, April 28 and August 18 applications (Figure 1). A longer duration of emission from DCD treated urea is compatible with the suggestions that NH_3-N remains in the soil for longer and that the soil pH peak is prolonged, although this could not be confirmed in the current study.

In contrast, a significant decrease in NH_3-N loss in four out of five applications was observed for urea+DCD at HB, with an annual mean loss reduction of 45% compared with urea only (Table 2). A meta-analysis by Kim *et al*. (2012) also reported a limited number of cases where DCD decreased NH_3-N emissions but the reduction was much lower than that observed at HB. One possible mechanism may be associated with non-target effects of DCD

on the soil nitrogen mineralisation-immobilisation turnover (MIT) at HB. In a field study on MIT at HB McGeough *et al*. (2014) observed significant but inconsistent effects of DCD on MIT including net immobilisation of N. Furthermore, Ernfors *et al*. (2014) in a laboratory study with slurry found that the effects of DCD on MIT varied between soils. Increased net NH_4^+-N immobilisation could, therefore be a possible mechanism for reduced NH_3 loss with urea+DCD. However, further detailed process studies would be needed to understand this mechanism. It is clear that use of DCD adds to the NH_3-N loss uncertainty associated with using urea as its effects on loss were so variable. With regard to the non-significant effect of DCD observed on June 3 and July 7 at JC and on May 6 at HB (Table 1) this was associated with lower initial peaks in NH_3-N loss from urea and the early onset of precipitation.

The urease inhibitor NBPT was effective in reducing NH_3-N emissions from urea in nine out of ten split applications (Table 1). For the single application where NBPT did not produce a significant reduction (May 6 2014 at HB) NH_3-N emissions from urea were not significantly different from CAN because of precipitation following application. Averaged across the two sites, NBPT reduced NH_3-N emissions from urea by 78.5% which is similar to Chambers & Dampney (2009) who reported an average 77% reduction in UK field studies and Watson *et al*. (2008) who found on average a 79% reduction in laboratory studies with granular formulations (at 500 mg/kg NBPT).

When the urease inhibitor NBPT was included with urea+DCD, NH_3-N losses were 74% lower than for urea (Table 1). This is similar to the 78.5% reduction when the urease inhibitor was used alone, thus NBPT inclusion with DCD may be a strategy for overcoming the variable NH_3-N loss responses associated with DCD.

MIP is a co-polymer of maleic and itaconic acid which is marketed as both a urease and nitrification inhibitor. It was evaluated at JC only and produced the same loss as urea in

four out of five applications and a significantly higher loss following the August 18 application. Averaged over the five applications there was no significant difference in cumulative NH_3-N loss between urea and urea+MIP. There is little information on the efficacy of MIP in temperate grassland However, Goos *et al.* (2013) did not find MIP to be an effective inhibitor of soil or jack bean urease and a meta-analysis by Chien *et al.* (2014) found that urea+MIP did not provide a significant average plant yield response above urea.

Implications for ammonia inventories

Firstly, this study has shown that CAN has low and consistent NH_3-N loss across a range of conditions in temperate grassland (Table 1). Thus dependable estimates of national loss can be made based on the quantities applied irrespective of season of application or weather patterns within a given year. Secondly, urea usage brings challenges because its use in place of CAN will increase national NH_3-N emissions. The calculation of this increase is not straightforward because urea emissions are strongly influenced by climatic conditions following application. In the present study, NH_3-N loss from urea varied by 45 percentage points; moreover weather patterns can affect the volume of urea applied in conditions favouring loss. Thirdly, an application rate effect on NH_3-N loss from urea may be expected; in the present study this rate effect was detectable at the 95% confidence level in four out of ten cases (Table 1). Averaged across application timings, doubling the urea N rate increased the annual NH_3-N loss rate by 31% and 27% at JC and HB, respectively. Applying a NH_3-N loss factor to the nationally utilised volume of urea, to the exclusion of the rate effect will introduce added uncertainty to loss estimates. Fourthly, the present study demonstrated that the NH_3-N abatement potential of NBPT was on average 78.5% when used with urea alone or 74% when used in combination with the nitrification inhibitor DCD and that MIP had no significant effect on NH_3-N loss. This is important information because the use of urea

with/without inhibitors is a potential strategy for reducing national N_2O emissions which needs to be implemented without causing large increases in NH_3-N emissions.

Whilst this study using wind tunnels has provided comparative data on ammonia emissions for a range of fertiliser strategies, there is a lack of quantitative data for urea applied to temperate Irish grasslands which could be obtained using micrometeorological techniques. In the context of a national ammonia emission ceiling there is a need to address this knowledge gap.

Conclusions

The use of urea poses challenges at both local management and national inventory scales and will increase ammonia loss compared with CAN. Maximum NH_3-N loss rates from urea occur quickly in Irish temperate grassland (within two to three days); consequently, to reduce loss appreciably, it is desirable to apply urea shortly before sustained precipitation is forecast where possible. One site had higher losses in spring and the other higher losses in summer owing to environmental conditions but average losses were similar between seasons, highlight the importance of having large multi-site databases for generation of general advice. The urease inhibitor NBPT effectively abates NH_3-N loss from urea when used with or without a nitrification inhibitor. This study has provided information on the abatement potential of a suite of N fertiliser options, however there is an important knowledge gap regarding absolute levels of NH_3-N loss from urea in Irish grassland which could be addressed by a campaign of micrometeorological measurements. Such knowledge is of critical importance in the context of national commitments to reduce NH_3-N loss whilst growing the agri-food sector.

References

Abalos, D., Jeffery, S., Sanz-Cobena, A., Guardia, G. & Vallejo, A., 2014. Meta-analysis of the effect of urease and nitrification inhibitors on crop productivity and nitrogen use efficiency. Agriculture Ecosystems and Environment, 189: 136-144.

Adams, J.R & Merz, A.R., 1929. Hygroscopicity of fertilizer materials and mixtures. Industrial and Engineering Chemistry. 21: 305-307.

Asing, J., Saggar, S., Singh. J. & Bolan, N.S., 2008. Assessment of nitrogen losses from urea and an organic manure with and without nitrification inhibitor, dycandiamide, applied to lettuce under glasshouse conditions. Australian Journal of Soil Research 46:535-541.

Beusen, A.H.W., Bouwman, A.F., Heuberger, P.S.C., Van Drecht, G. & Van Der Hoek, K.W., 2008. Bottom-up uncertainty estimates of global ammonia emissions from global agricultural production systems. Atmospheric Environment, 42(24): 6067-6077.

Black, A.S., Sherlock, R.R., Smith, N.P., Cameron, K.C. & Goh, K.M. 1985. Effects of form of nitrogen, season, and urea application rate on ammonia volatilisation from pastures. New Zealand Journal of Agricultural Research, 28:4, 469-474.

Chambers B. & Dampney P., 2009 Nitrogen efficiency and ammonia emissions from urea-based and ammonium nitrate fertilizers. Proc No. 657, Internat Fert Soc, York, UK.

Chen, D.L., Suter, H.C., Islam, A. & Edis, R., 2010. Influence of nitrification inhibitors on nitrification and nitrous oxide (N2O) emission from a clay loam soil fertilized with urea. Soil Biology & Biochemistry, 42(4): 660-664.

Chien, S.H., Edmeades, D., McBride, R. & Sahrawat, K.L., 2014. Review of Maleic-Itaconic Acid Copolymer Purported as Urease Inhibitor and Phosphorus Enhancer in Soils. Agronomy Journal, 106(2): 423-430.

Dennis S.J., Cameron K.C., Di H.J., Moir J.L., Staples V., Sills P. & Richards K.G. 2012. Reducing nitrate losses from grazed grassland in Ireland using a nitrification inhibitor (DCD). Biology and the Environment 112B issue 1, 79-89.

Di, H.J. & Cameron, K.C., 2005. Reducing environmental impacts of agriculture by using a fine particle suspension nitrification inhibitor to decrease nitrate leaching from grazed pastures. Agriculture Ecosystems & Environment, 109(3-4): 202-212.

Di, H.J., Cameron, K.C. & Sherlock, RR. 2007. Comparison of the effectiveness of a nitrification inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four different soils under different climatic and management conditions. Soil Use and Management, 23, 1–9

Díez-López, J.A., P. Hernaiz-Algarra, P., Arauzo-Sánchez, M., & Carrasco-Martín, I., 2008. Effect of a nitrification inhibitor (DMPP) on nitrate leaching and maize yield during two growing seasons. Spanish Journal of Agricultural Research 6(2): 294-303.

Dobbie, K.E. & Smith, K.A., 2003. Impact of different forms of N fertilizer on N2O emissions from intensive grassland. Nutrient Cycling in Agroecosystems, 67(1): 37-46.

Engel, R., Jones, C. & Wallander, R., 2011. Ammonia Volatilization from Urea and Mitigation by NBPT following Surface Application to Cold Soils. Soil Science Society of America Journal, 75(6): 2348-2357.

Ernfors, M., Brennan, F.P., Richards, K.G., McGeough, K.L., Griffiths, B.S., Laughlin, R.J., Watson, C.J., Philippot, L, Grant, J., Minet, E.P., Moynihan, E., & Muller, C., 2014. The nitrification inhibitor dicyandiamide increases mineralization-immobilization turnover in slurry-amended grassland soil. Journal of Agricultural Science, 152, S137-S149.

EC, 2001. Directive 2001/81/EC of the European Parliament and the Council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants. L 309/22. 27.11.2001 Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2001:309:0022:0030:EN:PDF

Ferguson, R.B. & Kissel, D.E. 1986. Effects of drying on ammonia volatilization from surface-applied urea. Soil Science Society of America Journal 50: 485-490.

Franzen, D., Goos, R.J., Norman, R.J., Walker, T.W., Roberts, T.L., Slaton, N.A., Endres, G., Ashley, R., Staricka, J. & Lukach, J., 2011. Field and Laboratory Studies Comparing Nutrisphere-Nitrogen Urea with Urea in North Dakota, Arkansas, and Mississippi. Journal of Plant Nutrition, 34(8): 1198-1222.

FAO, 2014. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome.

Goos, R.J., 2013. A Comparison of a Maleic-Itaconic Polymer and N-(n-butyl) Thiophosphoric Triamide as Urease Inhibitors. Soil Science Society of America Journal, 77(4): 1418-1423.

Harty, M., Richards, K.G., Lanigan, G.J., Krol, D., Carolan, R., McGeough, K., Watson, C.J., Hennessy, D. & Forrestal P.J. (2015) Comparing fertiliser nitrogen alternatives to calcium ammonium nitrate: the impact on nitrogen uptake and fertiliser recovery in grassland. Proceedings Agricultural Research Forum, Tullamore, Ireland.

Hinton, N.J., Cloy, J.M., Bell, M.J., Chadwick, D.R., Topp, C.F.E., & Rees R.M., 2015. Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland. Geoderma Regional 4: 55-65.

Holcomb, J.C., Sullivan, D.M., Horneck, D.A. & Clough, G.H., 2011. Effect of Irrigation Rate on Ammonia Volatilization. Soil Science Society of America Journal, 75(6): 2341-2347.

IPCC, 2006. Guidelines for National Greenhouse Gas Inventories. In: Eggleston, H.S, Buendia, L., Miwa, K. *et al*. (Eds.) Volume 4, Chapter 11, N_2O emissions from managed soils and CO_2 emissions from lime and urea application. IGES, Japan.

IPCC., 2013. Climate Change 2013 The Physical Science Basis Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. In: Stocker, T.F., Qin, D., Plattner, G.K., *et al*. (Eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Kim, D.G., Saggar, S. & Roudier, P., 2012. The effect of nitrification inhibitors on soil ammonia emissions in nitrogen managed soils: a meta-analysis. Nutrient Cycling in Agroecosystems, 93(1): 51-64.

Lockyer, D.R., 1984. A System for the Measurement in the Field of Losses of Ammonia through Volatilization. Journal of the Science of Food and Agriculture, 35(8): 837-848.

McGarry, S.J., O'Toole, P., & Morgan, M.A. 1987. Effects of soil temperature and moisture content on ammonia volatilization from urea-treated pasture and tillage soils. Irish Journal of Agricultural Research, 173–182.

McGeough, K.L., Muller, C., Laughlin, R.J., Watson, C.J., Ernfors, M., Cahalan, E., & Richards, K.G. 2014. The effect of dicyandiamide addition to cattle slurry on soil gross nitrogen transformations at a grassland site in Northern Ireland. Journal of Agricultural Science, 152, S125-S136.

McInnes, K.J., Ferguson, R.B., Kissel, D.E., & Kanemasu, E.T. 1986. Field measurements of ammonia loss from surface applications of urea solution to bare soil. Agronomy Journal 78:192-196.

Meisinger, J.J., Lefcourt, A.M., & Thompson, R.B. 2001. Construction and validation of small mobile wind tunnels for studying ammonia volatilization. Applied Engineering in Agriculture 17, 375–384.

Schwenke, G.D., Manning, W. & Haigh, B.M., 2014. Ammonia volatilisation from nitrogen fertilisers surface-applied to bare fallows, wheat crops and perennial-grass-based pastures on Vertosols. Soil Research, 52(8): 805-821.

Smith, K.A., Dobbie, K.E., Thorman, R., Watson, C.J., Chadwick, D.R., Yamulki, S. & Ball, B.C., 2012. The effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland. Nutrient Cycling in Agroecosystems, 93(2): 127-149.

Sutton, M.A., Moncrieff, J.B. & Fowler, D., 1992. Deposition of atmospheric ammonia to moorlands. Environ Pollut, 75(1): 15-24.

Torello, W.A. & Wehner, D.J., 1983. Urease activity in a Kentucky bluegrass turf. Agronomy Journal, 75: 654-656.

Watson, C.J., Akhonzada, N.A., Hamilton, J.T.G. & Matthews, D.I., 2008. Rate and mode of application of the urease inhibitor N-(n-butyl) thiophosphoric triamide on ammonia volatilization from surface-applied urea. Soil Use and Management, 24(3): 246-253.

Watson, C.J. & Miller, H., 1996. Short-term effects of urea amended with the urease inhibitor N-(n-butyl) thiophosphoric triamide on perennial ryegrass. Plant and Soil, 184(1): 33-45.

Watson, C.J., Stevens, R.J. & Laughlin, R.J. 1990. Effectiveness of the urease inhibitor NBPT (N-(n-butyl) thiophosphoric triamide) for improving the efficiency of urea for ryegrass production. Fertilizer Research 24; 11-15.

Watson, C.J., Poland P., Miller H., Allen M.B.D., Garrett M.K. & Christianson C.B 1994. Agronomic assessment of ^{15}N recovery of urea amended with the urease inhibitor nBTPT (N-(n-butyl) thiophosphoric triamide) for temperate grassland. Plant and Soil 161: 167-177.

Watson, C.J., Laughlin R.J. & McGeough K. 2009. Modification of nitrogen fertilisers using inhibitors: Opportunities and potentials for improving nitrogen use efficiency. Proceeding 658 International Fertiliser Society, York, UK 1-40.

Table captions

Table 1 Ammonia (NH_3) loss as affected by fertiliser N treatment for each application date at Johnstown Castle and Hillsborough sites.

Table 2 Annual ammonia (NH_3) loss as measured by wind tunnels and the change (Δ) in loss compared with the urea 200 kg N/ha rate for the other treatments. N applied to grassland N input in five equal split applications (40 or 80 kg N/ha).

Figure captions

Figure 1 Hourly ammonia (NH_3) emissions by fertiliser N treatment, daily precipitation and mean daily air temperature for each fertiliser N application date at the Johnstown Castle site.

March 10 application

April 28 application

June 3 application

July 7 application

August 18 application

CAN
Urea
Urea + NBPT
Urea + DCD
Urea + NBPT + DCD
Urea + MIA

Precipitation
Air temperature
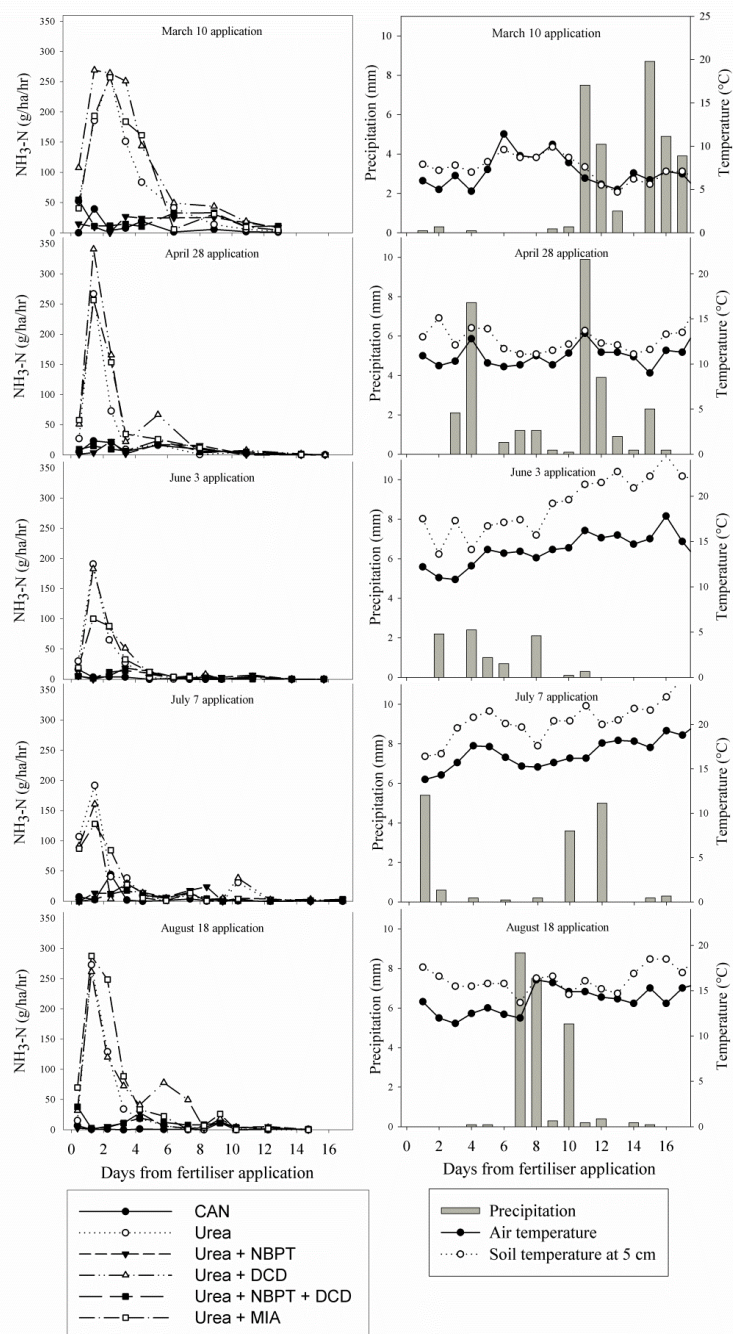Soil temperature at 5 cm

Figure 2 Hourly ammonia (NH$_3$) emissions by fertiliser N treatment, daily precipitation and mean daily air temperature for each fertiliser N application date at the Hillsborough site.

NH$_3$-N (g/ha/hr) — March 24 application, May 6 application, June 9 application, July 28 application, September 8 application

Precipitation (mm) / Temperature (°C) — March 24 application, May 6 application, June 9 application, July 28 application, Septemeber 8 application

Days from fertiliser application

CAN
Urea
Urea + NBPT
Urea + DCD
Urea + DCD + NBPT

Precipitation
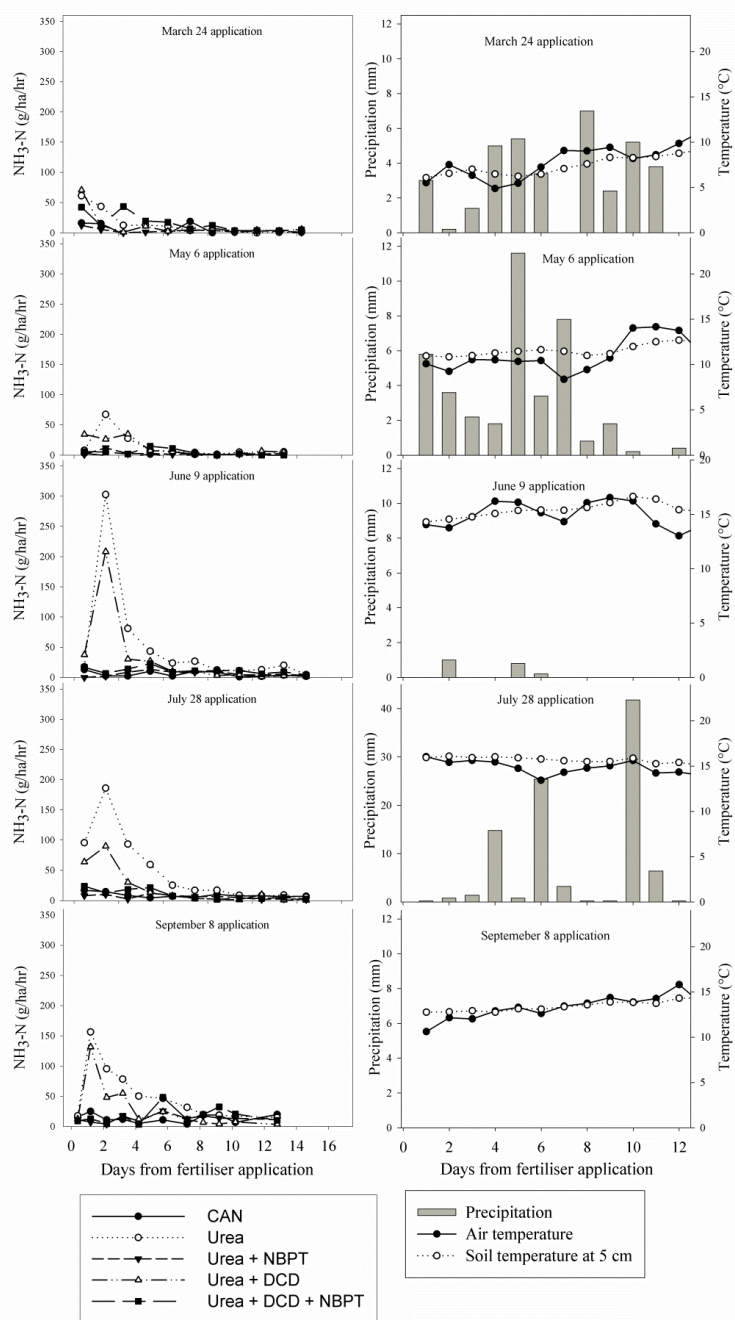Air temperature
Soil temperature at 5 cm

Table 1 Ammonia loss as affected by fertiliser N treatment for each application date at the Johnstown Castle and Hillsborough sites.

Site		Johnstown Castle					Hillsborough				
Season		Spring		Summer			Spring		Summer[b]		
Fertiliser application date		Mar 10	Apr 28	Jun 3	Jul 7	Aug 18	Mar 24	May 6	Jun 9	Jul 28	Sept 8
Volumetric moisture 0-5cm on day after application (%)		45.4	37.4	34.4	28.8	27.5	46	41.7	24.9	16.8	25.5
Treatment	N rate/ application (kg N/ha)	NH_3-N loss (% of applied N)									
CAN	40	5 e[a]	7 c	2 b	4 c	2 c	4 bc	2 b	3 d	4 b	8 b
Urea	40	53 c	25 b	20 a	26 a	30 b	21 a	8 b	33 b	31 a	33 a
Urea	80	68 ab	38 ab	24 a	24 a	43 a	14 ab	19 a	49 a	34 a	43 a
Urea+NBPT	40	15 de	6 c	5 b	9 bc	6 c	2 c	2 b	4 d	4 b	9 b
Urea + DCD	40	77 a	42 a	22 a	22 a	45 a	9 bc	7 b	20 c	13 b	19 b
Urea+NBPT+DCD	40	18 d	6 c	4 b	5 c	8 c	6 bc	2 b	7 d	6 b	11 b
Urea+MIP	40	55 bc	34 ab	16 ab	21 ab	47 a	-	-	-	-	-

[a] Treatments with different letters within columns are different according to F-protected LSD test ($P<0.05$).
[b] for the purposes of seasonal comparison the conditions following the Sept 8 application were considered close to those of summer and loss did not differ from summer at HB

Table 2 Annual ammonia loss as measured by wind tunnels and the change (Δ) in loss compared with the urea 200 kg N/ha rate for the other treatments. N applied to grassland N input in five equal split applications (40 or 80 kg N/ha).

Site Treatment	N rate (kg/ha/yr)	JC	HB	JC	HB
		Total NH$_3$-N loss (% of applied)		Δ NH$_3$-N loss (%Δ from urea 200 kg N/ha)	
CAN.	200	4.1 d[†]	4.2 bc	-87	-83
Urea	200	30.6 c	25.1 a		
Urea	400	40.0 ab	32.0 a	31	27
Urea + NBPT	200	8.2 d	4.0 c	-73	-84
Urea + DCD	200	41.6 a	13.7 b	36	-45
Urea + NBPT + DCD	200	8.1 d	6.5 bc	-74	-74
Urea + MIP	200	35.1 bc	-	15 n.s.	-

[†] Treatments with different letters within columns are different according to F-protected LSD test (*P*<0.05).
n.s. not significant

Deleted: .

Deleted: .