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Evaluation of calcium ammonium nitrate and urea-based fertilisers applied to grassland in Ireland

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Abstract. *This study investigated the influence of N source and rate, and timing of N application on dry matter yield (DMY), N responses, N uptake and N use efficiency (NUE) in a grass crop. The experiment used three fertiliser treatments: CAN, urea and nBTPT-coated urea (nBTPT-U), three N rates (0 – control, 25, 50 and 75 kg ha⁻¹), and 18 fertiliser application timings. The agronomic performance of urea was lower than CAN in early spring. This included relatively lower N responses, lower relative DMY (90%) and N uptake (85%) which translated in lower NUE (0.45 vs. 0.70 kg kg⁻¹). For N applications later in the spring both urea and nBTPT-U showed relative DMY and NUE which were within ±5% compared with CAN (100%). nBTPT enhanced the overall performance of urea which was shown with increased temperature towards the summer or increased N rates. In the summer, the efficiency of urea was lower than CAN or nBTPT-U in all measured parameters. The variability of urea and nBTPT-U as N-sources for grass was comparable to CAN but DMY with urea was ≤95% that of CAN (100%) at 8 out of the 19 application timings. Increasing the application rate of urea-N to offset its relatively lower efficiency may not be recommended since DMY of urea-N relative to CAN decreased with increased N fertilisation levels. However, with the use of nBTPT this may be possible, but fertiliser choice needs to be based on the relative costs per unit N.*

Keywords. *Urea, calcium ammonium nitrate, nBTPT, fertiliser use efficiency, temperate grassland.*

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Introduction

Urea is the main source of N fertiliser used in agriculture worldwide. Its consumption is set to increase from currently 50% of the total N fertiliser usage to about 60% to 70% by 2020 (Dampney et al., 2003). In Ireland, urea and calcium ammonium nitrate (CAN) represent 17% and 40%, respectively, of the total N fertiliser applied on managed grassland and their use as straight N sources has increased in recent years (Lalor et al., 2010). The study of the agronomic efficiency of urea relative to CAN or ammonium nitrate (AN) applied as a top dressing in temperate grassland has received considerable attention. Scholefield (2003) indicated that the majority of the data produced were obtained from field-scale trials conducted in the UK (e.g. Devine and Holmes, 1963; Chaney and Paulson, 1988) and Ireland (e.g. Keane et al., 1974; Murphy, 1978, 1983) before the middle of 1980's with limited information produced thereafter (e.g. Lloyd, 1992; Chambers and Dampney, 2009).

The relatively lower price of urea-N compared to AN-N recorded before 1985 (Nix, 1980-85) brought about the need for further research into the subject but the data available are limited (Scholefield, 2003). The information available was largely compiled by Tomlinson (1970) and later by Watson et al. (1990). Subsequently, the report of the NT26 Project (DEFRA, 2003) presented and discussed existing knowledge on the effects of the use of alternative N-containing fertiliser materials to AN; in particular, urea, by focusing on aspects related to crop performance, fertiliser application, environmental impacts and possible mitigation options. Tomlinson (1970) highlighted that the inherent risk of variability in the effectiveness of urea arises in response to a number of interacting factors such as N rate and method of application, soil type, and temperature and rainfall patterns.

The initial attempts to increase its efficiency as fertiliser had been partially successful while the use of coatings had resulted in changes to the pattern of N availability (Tomlinson, 1970). The critical aspects concerning the use of urea on temperate grasslands are its efficiency relative to AN, the factors affecting it, and the opportunities for increasing fertiliser use efficiency (Watson et al., 1990; 2009). The efficiency of urea has been shown to be similar (e.g. Keane et al., 1974; Murphy, 1983; Stevens et al., 1989) or higher (e.g. Herlihy and Sheehan, 1977) compared with CAN when used in spring grass production. By contrast, other work (Chaney and Paulson, 1988; Swift et al., 1988) showed lower relative efficiencies. Scholefield (2003), based on Devine and Holmes (1963), indicated that the use of urea on grass crops can result in DMY reductions in the range of 10% to 15% compared with AN depending on the conditions in which the fertiliser was applied. Lloyd (1992) showed that the effectiveness of urea compared with CAN increased with the amount of rainfall that occurred within three days of fertiliser application. Watson et al. (1990) concluded that the effectiveness of urea is similar to CAN or AN for applications in the spring but it can be lower in the summer (relative yields $\leq 95\%$). Their study, however, indicated that there was not sufficient evidence to suggest that urea is a significantly more variable N source than CAN for spring grass production but maximum DMY is expected to be lower.

Urea has a suggested lower susceptibility for NO_3^- leaching and denitrification than CAN (Jordan, 1989) but relatively higher potential for NH_3 volatilisation which is the main reason for its inefficiency (Freney et al., 1983). These N losses represent an economic loss to farmers and have environmental implications for water quality and GHG emissions (Watson et al., 2009). The interaction between temperature and rainfall was shown to be one of the main factors influencing the relative effectiveness of the two N fertiliser sources (Bussink and Oenema, 1996; Scholefield, 2003). The risk of NH_3 emissions from applied urea is greater than that of nitrate-based fertilisers but this varies depending on the environmental and soil conditions following fertiliser application (McGarry et al., 1987; Bhogal et al., 2003).

In Ireland, the current limit for ammonia (NH₃) emissions under the EU National Emissions Ceilings Directive is 116 kt NH₃ per year and estimates (EPA, 2012) suggested that natural emissions are 106 kt. This implies that current NH₃ emission targets do not appear to be a restriction to adopting higher levels of usage of urea-based fertilisers in the short term but meeting this obligation may be cumbersome if a significant switch in fertiliser practices from CAN to urea was implemented at national level. Ammonia emissions from urea applied to grass may be reduced with the use of urease inhibitors which offers advantages compared with other alternatives (Bhogal et al., 2003). N-(*n*-butyl) thiophosphoric triamide (nBTPT) acts as a urease inhibitor following conversion to its oxygen analogue (Creason et al., 1990; Manunza et al., 1999). The use of nBTPT allows for the N saved in volatilisation to be taken up by the grass crop increasing N uptake and DMY compared with urea alone (Watson and Miller, 1996; Watson et al., 2008). Watson et al. (1994) showed that nBTPT-treated urea at 0.05% increased DMY by 9% and reduced NH₃ emissions from 13% to 2.2% on average compared with untreated-urea.

The data presented in this paper provide a dataset which is intended to address some of the questions formulated by Watson et al. (1990) concerning the use of urea on temperate grassland and, in particular, under Irish conditions. Therefore, the objectives of this work were to: **(1)** determine the fertilising efficiency of urea and nBTPT-coated urea (nBTPT-U) compared with CAN for a range of fertiliser application timings, and **(2)** develop a fertiliser-specific model that can be used to simulate DMY based on meteorological data for short-term temperature and rainfall before and after fertiliser application.

Materials and Methods

Site description

The study was conducted at Teagasc Johnstown Castle, Ireland (52°29' N, 6°5' W) on a moderately well drained (Schulte et al., 2005) clay loam soil (Gardiner and Ryan, 1964). The site was a permanent grassland sward (>5 years old) dominated by perennial ryegrass (*Lolium perenne* L). Soil P and K contents, and pH (Morgan, 1941; Byrne, 1979; MAFF, 1986) for the bulked 0-0.25 m layer determined prior to the experiment were: 4.8 mg L⁻¹ of P (soil P Index 2), 120 mg L⁻¹ of K (soil K Index 3) and soil pH of 5.3. Rainfall and temperature records are summarised in Figure 1.

Experimental design

The experiment was conducted in 1 m × 3 m plots subjected to the following treatments. Three types of fertiliser were used: urea (46% N), urea coated with N-(*n*-butyl) thiophosphoric triamide (nBTPT-U) at a rate of 0.48 g kg⁻¹, and calcium ammonium nitrate (CAN, 27% N). These were hand-applied at N rates equivalent to 0 (control), 25, 50 and 75 kg ha⁻¹ over 19 application timings (T1 to T19 – except for nBTPT-U, T3-T19) on a weekly basis (26 February to 22 April 2010) or a fortnightly basis (6 May to 9 September 2010) (Table 1). The experiment was laid out in a randomised block design with four replicated blocks. Each block consisted of 19 strips; one for each fertiliser application timing. The N application rate and fertiliser type treatments (three fertiliser types by three N application rates plus an unfertilised control plot) were randomised within each strip resulting in a total of 760 plots.

Table 1: Timing of fertiliser applications and corresponding dates of harvest (Year: 2010).

Timing (T)	Date of application	Cut 1	Cut 2	Timing (T)	Date of application	Cut 1	Cut 2
1	26 Feb	31 Mar	29 Apr	11	20 May	17 Jun	15 Jul
2	4 Mar	1 Apr	29 Apr	12	3 Jun	1 Jul	28 Jul
3	11 Mar	8 Apr	6 May	13	17 Jun	15 Jul	11 Aug
4	18 Mar	15 Apr	12 May	14	1 Jul	28 Jul	24 Aug
5	26 Mar	22 Apr	20 May	15	15 Jul	11 Aug	9 Sept
6	1 Apr	29 Apr	26 May	16	28 Jul	24 Aug	21 Sept
7	8 Apr	6 May	3 Jun	17	12 Aug	9 Sept	4 Oct
8	15 Apr	12 May	10 Jun	18	26 Aug	-----	-----
9	22 Apr	20 May	16 Jun	19	9 Sept	4 Oct	4 Nov
10	6 May	2 Jun	1 Jul	-----	-----	-----	-----

Site maintenance

A blanket application of P (30 kg ha⁻¹) was applied to all plots in late March 2010 to ensure these nutrients would not limit crop growth. During the experiment, all plots that were not scheduled for N application in the subsequent four weeks received a maintenance application of N using CAN at a rate of 15 kg ha⁻¹ of N every five weeks. Maintenance N was applied on 10 February (T7-T15), 16 April (T11-T15), and 22 May (T14-T19). Plots that were not under treatment were cut every one to three weeks depending on crop growth, with the harvested herbage being mulched and returned to the plot.

Measurements and analyses

Grass yield was determined at four and eight weeks after fertiliser application (cuts 1 and 2 respectively). The entire plots were cut to a height of 40 mm using a push lawnmower to replicate the standard field practice before application of the fertiliser at the corresponding timing. Total fresh weight was determined and a subsample was taken for determination of dry matter content and total N content (MAFF, 1986). N use efficiency (NUE, kg kg⁻¹) of applied N fertiliser was estimated using the difference method (Equation [1]) (Cassman et al., 1998; Johnston and Poulton, 2009).

$$NUE = \frac{N_F - N_{F=0}}{N_{Rate}} \quad [1]$$

Where: $N_{F=0}$ and N_{Rate} are the N uptake of the control (zero-fertiliser) and the N application rate respectively.

Statistical analyses

Statistical analyses were undertaken with GenStat (14th Edition) and involved analysis of variance (ANOVA) and the least significant differences (LSD) to compare the means with a probability level of 5%. Grass responses to the application of N were investigated by means of simple (linear) regression analyses.

Non-linear (quadratic) responses were also tested and results are discussed. Since nBTPT-U was applied from T3 onwards, ANOVA was conducted separately for the fertiliser applications corresponding to T1 and T2, from those performed from T3 and after. Hence, comparisons between treatments for the first two fertiliser applications were only made between urea and CAN; subsequently, all three fertiliser types were included in the analyses. There were no data collected for the application of fertiliser corresponding to T18 at cut 2 due to weather difficulties restricting harvesting operations. Therefore, this was excluded from all analyses and the corresponding results are not reported. Repeated measurement analyses of variance were conducted to compare levels of DMY and NUE obtained at cuts 1 and 2 respectively.

A covariance analysis (ANCOVA) using a 5% probability level was conducted to investigate the effects of short-term temperature and rainfall on N responses (β) for the three N sources. From this, a model was developed which simulates β for cut 1 and 2 using the following variables: **a.** total rainfall and mean temperature for the 4 weeks period between N application and cut 1, and between cut 1 and cut 2; and **b.** total rainfall and mean temperature within five days prior to, and within three days after N application. These parameters were included because of reported evidence (Bouwmeester et al., 1985; Herlihy and O’Keeffe, 1987; Lloyd, 1992; Bussink and Oenema, 1996) which showed that the effectiveness of N fertilisers can be significantly influenced by temperature and rainfall before and after broadcast application. The model was validated with experimental data from a separate trial which was conducted in 2011 in a neighbouring field in the same farm but on a slightly heavier, poorly drained, clay loam soil (Gardiner and Ryan, 1964). The experiment used the same fertiliser types but only four N application timings (8 April, 1 May, 12 June and 11 July) and three rates of N fertilisation (0 – control, 25 and 50 kg ha⁻¹ of N). DMY was determined at four and eight weeks after fertiliser application as described earlier. A simple (linear) regression analysis was conducted to determine the relationship between observed and predicted data.

Results and Discussion

Rainfall and temperature

Meteorological records for Johnstown Castle are shown in Figure 1. Rainfall was measured at ground level using a tipping bucket rain gauge. Air temperature was measured at 1.52 m height with a dry platinum resistance thermometer. The mean total annual rainfall for the period 1981-2010 was 1059 mm compared with 913 mm for 2010 and 840 mm for 2011 (Met Eireann, 2012). Rainfall distribution for 2010 and 2011 differed markedly from the 30 years records. Total rainfall for the period January-June, and August 2010 were below their corresponding long-term records whereas July and September 2010 were well above average. The mean temperatures in 2010 were relatively lower compared with the same records.

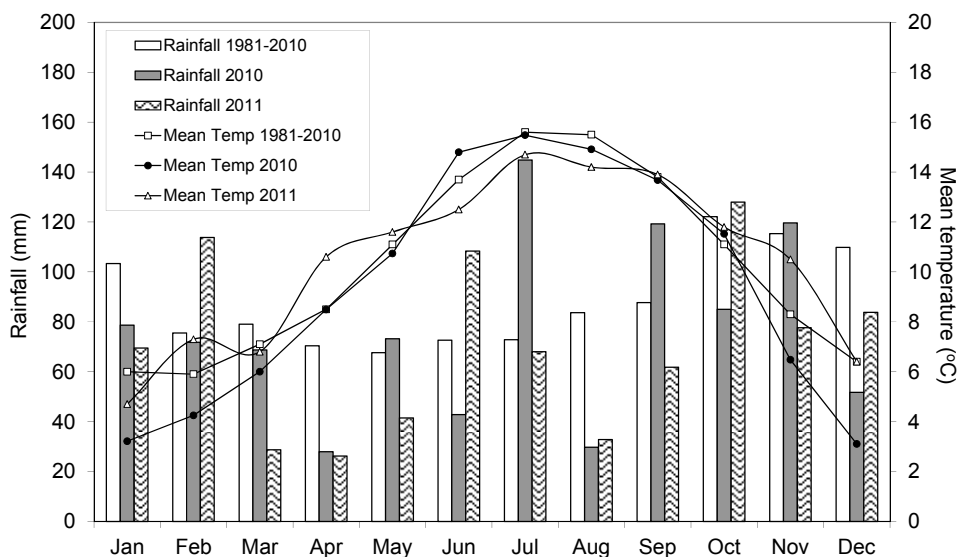


Figure 1: Rainfall and temperature records for Johnstown Castle, Wexford, Ireland (Met Eireann, 2012).

Dry matter yield (DMY)

At cut one, there was a significant effect of the timing of fertiliser application (P -values <0.05), the N application rate ($P < 0.001$); except when considering T1 and T2 ($P = 0.26$), and the fertiliser type (P -values < 0.05) on DMY levels. On average, across the entire experiment, DMY increased with the N application rate from approximately 1250 kg ha^{-1} (control) to 2235 kg ha^{-1} at 75 kg ha^{-1} of N. The overall effect of the fertiliser type observed at cut one was mainly due to differences in DMY between urea and CAN (Figure 2). For T1 and T2, the application of urea resulted, on average, in lower DMY relative to CAN. The values of DMY recorded at these timings were low (490 and 600 kg ha^{-1} for urea and CAN respectively) but differences were significant for an LSD value (5% level) of 92 . For T3 to T19, the overall differences between these two fertilisers were significant for an LSD (5% level) value of 62 but relatively small ($< 85 \text{ kg ha}^{-1}$). The differences in DMY recorded between nBTPT-U and CAN (T3-T19) were not significant. At cut one (T1-T19), DMY with urea and nBTPT-U relative to CAN (100%) were, on average, 95% and 98% respectively. For nBTPT-U, this value may be slightly overestimated since it is not computing the relative efficiencies for T1 and T2. For urea, the relative efficiencies at these two timings were low ($\leq 82\%$).

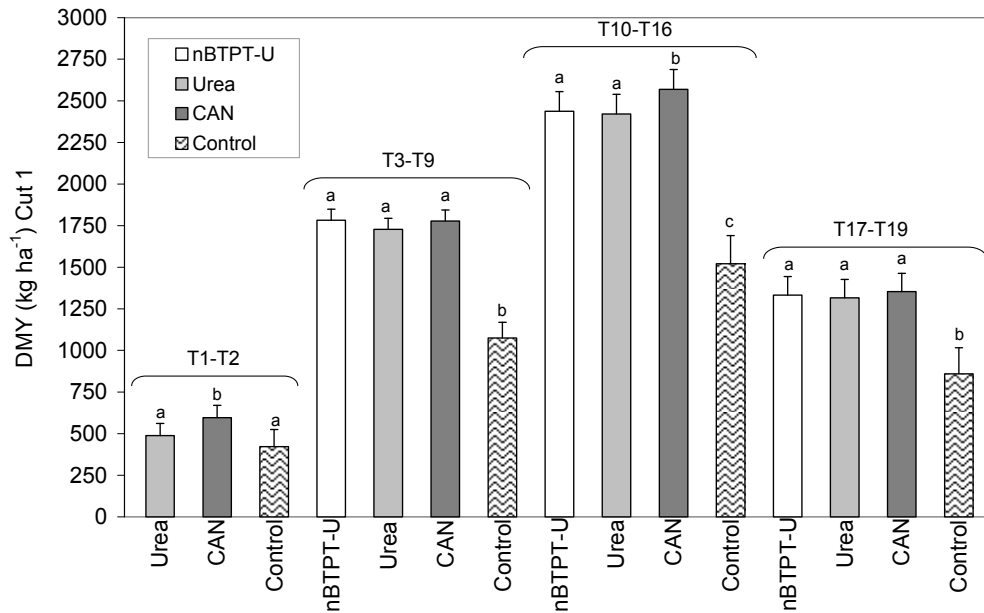


Figure 2: DMY recorded at cut one as affected by fertiliser type and timing of fertiliser application. The error bars show the LSD value (5% level). For T1-T2: $P=0.005$, $n=8$ (control) and $n=24$ (treatments). For T3-T9: $P>0.05$, $n=28$ (control) and $n=84$ (treatments). For T10-T16: $P=0.03$, $n=28$ (control) and $n=84$ (treatments). For T17-T19: $P>0.05$, $n=8$ (control) and $n=24$ (treatments).

At cut two, there was a significant effect of the timing of fertiliser application ($P<0.001$); except when considering T1 and T2 ($P>0.05$), the N application rate (P -values <0.001), and the fertiliser type ($P=0.01$); except when considering T3-T19 ($P>0.05$). On average, across the entire experiment, DMY increased with the N application rate from approximately 1100 kg ha^{-1} (control) to 2000 kg ha^{-1} at 75 kg ha^{-1} of N.

The overall effect of the fertiliser type on DMY at cut two is shown in Figure 3. For T1 and T2, the differences recorded between urea and CAN at cut two were greater compared with those encountered at cut one ($c.150$ vs. $110 \text{ kg DM ha}^{-1}$ respectively). This suggested that losses of applied N-fertiliser occurred to a larger extent in urea- compared with CAN-treated crop, and that there was a greater efficiency in the uptake of residual fertiliser N after the first harvest with the use of CAN. For T3 to T19, the overall differences between fertiliser types were marginal ($<25 \text{ kg DM ha}^{-1}$). At cut two (T1-T19), DMY with urea and nBTPT-U relative to CAN (100%) were, on average, 98% and 100% respectively. For urea, the relative efficiency at T1 and T2 was 92% which indicates a greater recovery of N compared with that obtained at cut one at the same timings but still lower than CAN. At both cuts, the interactions timing \times fertiliser type (Figures 4 and 5), and fertiliser type \times N rate were not significant, and the same effect was observed when the fertiliser application timing was factored in (P -values >0.05).

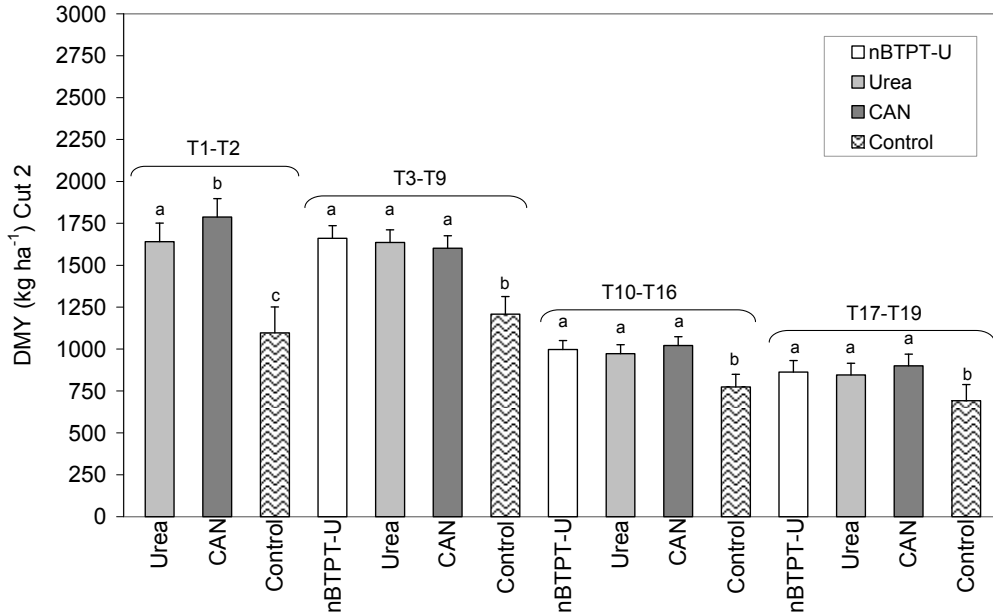


Figure 3: DMY recorded at cut two as affected by the fertiliser type and timing of fertiliser application. The error bars show the LSD value (5% level). For T1-T2: P=0.01, n=8 (control) and n=24 (treatments). For T3-T9 and T10-T16: P>0.05, n=28 (control) and n=84 (treatments). For T17-T19: P>0.05, n=8 (control) and n=24 (treatments).

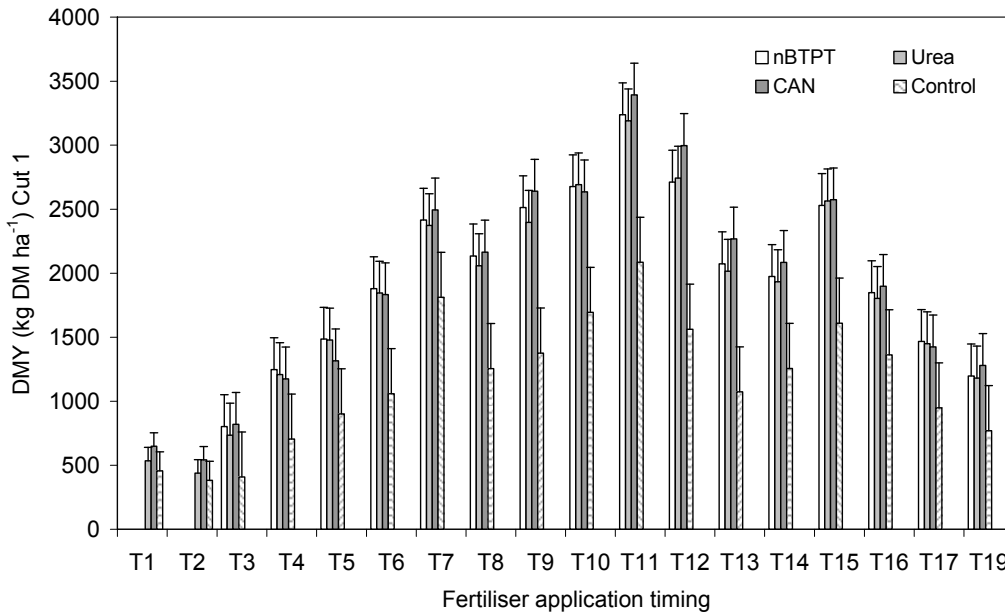


Figure 4: DMY recorded at cut one for each of the fertiliser application timings showing the control vs. the treatments (mean values across the three N application rates). The error bars show the LSD value (5% level); P-values >0.05; n=4 (control), n=12 (treatment).

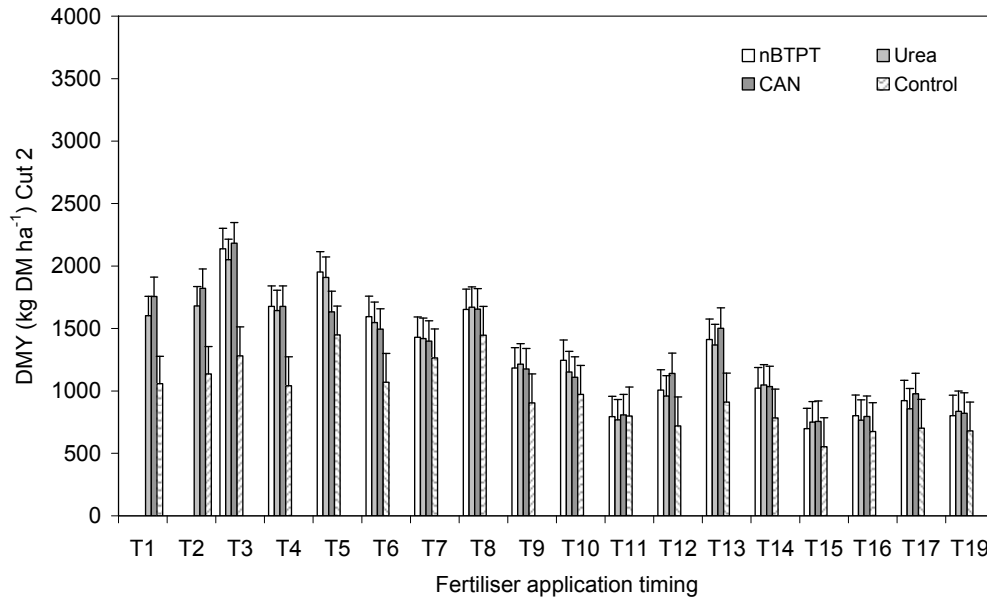


Figure 5: DMY recorded at cut two for each of the fertiliser application timings showing the control vs. the treatments (mean values across the three N application rates). The error bars show the LSD value (5% level); P-values >0.05; n=4 (control), n=12 (treatment).

It can be seen from Figures 4 and 5 that the fertiliser applications conducted between T1 and T5 resulted in relatively higher (P-values <0.001) DMY levels at cut two (range of 1590 to 2050 kg ha⁻¹) compared with cut one (range of 475 to 1375 kg ha⁻¹) which was observed for the three fertiliser types. However, over the range of fertiliser application timings (T1-T19), mean DMY was higher (P<0.001) at cut one (1940 kg ha⁻¹) than at cut two (1230 kg ha⁻¹). Using a ±5% range with respect to CAN (100%), it may be possible to generalise that the fertiliser choice is not significantly affected when the corresponding agronomic performance falls within that range. Watson et al. (1990) used a similar approach to clustering data from a wide range of studies so that urea was considered to be a less effective N source than CAN (100%) when its relative efficiency (URY) was below 95% and vice-versa when it was above 105%. Based on cumulative DMY, the use of CAN may be preferred to urea for applications conducted at T3 or earlier (before middle of March), and also between T11 and T13 (late May to middle of June). For applications conducted between T4 and T10 (middle of March to early May), and after T14 (beginning of July), either CAN or urea may be recommended. Similarly, CAN may be preferred to nBTPT-U between T12 and T13 (beginning to middle of June). Outside these dates, both fertilisers may be recommended. In general, nBTPT-U showed a marginally better agronomic performance than urea but differences in relative DMY (cumulative) between the two materials were within ±3% for all timings, except at T3 when relative DMY of nBTPT-U (nRY) was 5% higher than URY. Temperatures for February and March 2010 were low (mean T=5.7°C) which restricted growth, affected responses and consequently DMY in the early part of the spring. These conditions are likely to have affected urease activity; hence, reducing urea-N availability. The effectiveness of urea and nBTPT-U relative to CAN showed some variability which responded to the combined effect of the N application rate and the timing of fertiliser application. Since the coefficients of variation (c.v., %) for the data corresponding to cumulative DMY were of similar magnitude for all N sources (range of 13.4% to 13.7%), the variability in the effectiveness of urea and nBTPT-U was similar to that of CAN when compared to the controls.

Nitrogen uptake

There was an effect of the timing of fertiliser application (P -values <0.05) which was observed in both cuts (except for T1 and T2 at cut two, $P>0.05$). The overall effect of the fertiliser type was significant (P -values <0.05 – except at cut two for applications between T3 and T19). At cut one, for applications conducted at T1 and T2, CAN showed N uptakes which were 14% to 25% higher than urea. From T3 to T19, differences between fertiliser treatments were due to the use of CAN or nBTPT-U which increased N uptake by about 7% on average compared with urea. There was no effect of the interaction fertiliser type \times N application rate, and the same was observed when the timing of fertiliser application was factored in (P -values >0.05).

In Figure 6, cumulative N uptakes (cuts one + two) showed significant differences ($P<0.001$) with respect to the timing of fertiliser application; except for T1 and T2 ($P=0.2$). Relatively high N uptakes (range of 90 to 125 kg N ha⁻¹) were observed when N was applied at 50 and 75 kg ha⁻¹ at T7, and between T11 and T13; especially, in the grass treated with CAN and nBTPT-U. The cumulative N uptakes were influenced (P -values <0.05) by the fertiliser type but the effect was not observed when the timing of application was factored in (P -values >0.05). The effect of the fertiliser type was due to the use of CAN or nBTPT-U which increased N uptake by about 5% on average compared with urea between T3 and T19. For T1 and T2, mean N uptake in CAN-fertilised grass was about 12 kg ha⁻¹ of N higher than that of urea. There was no effect fertiliser type \times N rate on cumulative N uptake and the same holds true when factoring in timing of fertiliser application (P -values >0.05).

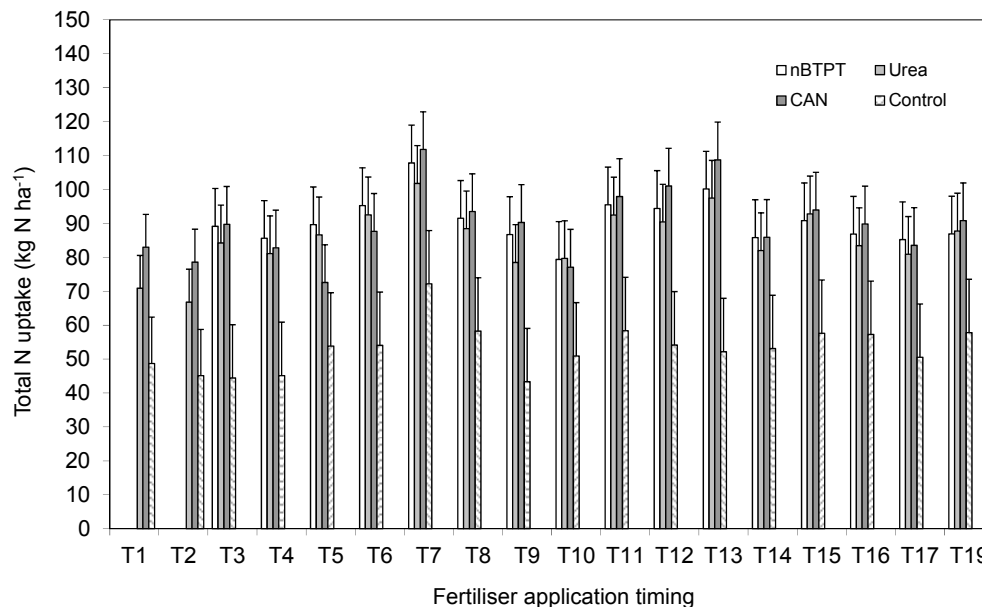


Figure 6: Cumulative N uptake for each of the fertiliser application timings showing the control vs. treatment (mean values across the three N application rates). The error bars show the LSD value (5% level); $P>0.05$, $n=4$ (control), $n=12$ (treatment).

The relative values of cumulative N uptake of urea and nBTPT-U compared with CAN (100%) were found to be 95% or lower in 11 out of 18, and in 2 out of 16 timings respectively (Figure 7). By contrast, these were $\geq 5\%$ that of CAN in only two occasions (T5 and T6) for both fertiliser materials. The overall mean N uptake of urea relative to CAN was 95% and it ranged from 85% (T1 and T2) to 119% (at T5) whereas for nBTPT-U the mean matched that of CAN (100%) but it ranged from 92% (T13) to 123% (T5).

As for DMY, the variability observed in relative N uptakes resulted from the combined effects of the N application rate, fertiliser type and timing of fertiliser application. The latter closely related to the effects of rainfall and temperature on DMY ($P < 0.05$) and responses pre- and post-fertiliser application as discussed later. The c.v. (%) for the data corresponding to cumulative N uptake were of similar order of magnitude for all three fertiliser materials (range of 15.5% to 17.2%) when compared to the unfertilised controls; hence, the variability in the effectiveness of N uptake from urea and nBTPT-U was comparable to CAN.

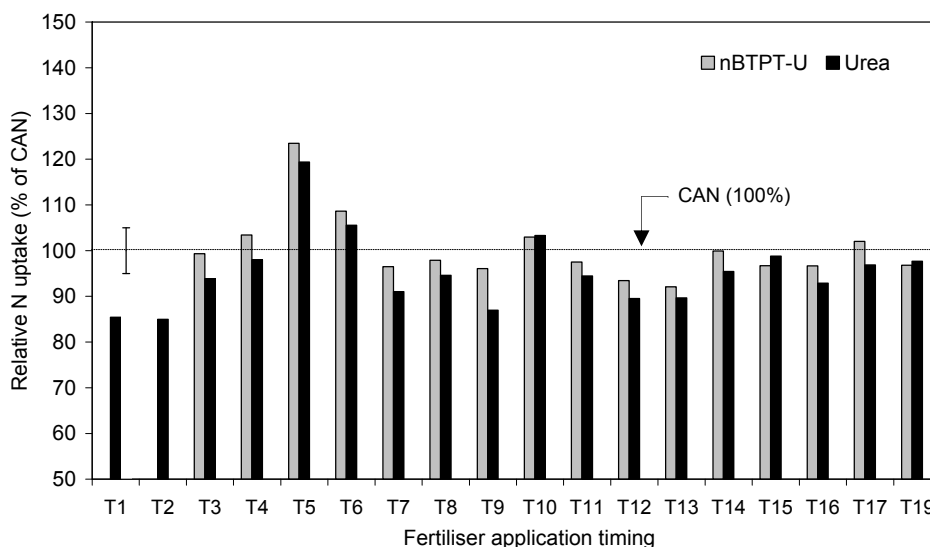


Figure 7: Percentage (cumulative) N uptake of urea and nBTPT-U relative to CAN for each of the fertiliser application timings. The error bar shows a $\pm 5\%$ range with respect to CAN (100%) denoted by the dotted line. Mean values across the three N application rates ($n=12$).

Nitrogen responses

The responses to the application of fertiliser N were linear for the range of N application rates investigated. Based on earlier studies (Reid, 1970, 1978; Sparrow, 1979; Morrison et al., 1980), non-linear responses were first fitted to the data which showed acceptable fits to the quadratic function. However, the estimates of parameters for the square term were not significant (p -values > 0.05) in most circumstances. Therefore, responses were better explained by linear functions which showed significance to the linear term. This was expected given the range of N application rates investigated but non-linear functions may be possible with a more complete dataset (Sparrow, 1979; Morrison et al., 1980). Linear regression analyses for each fertiliser type explained, individually, no more of the variation than it did a common slope ($P < 0.001$; $R^2 = 96\%$; s.e. = 115) since there was no systematic fertiliser \times N rate effect. However, the value encountered for urea applied at 75 kg ha^{-1} of N decreased its yield to N response curve slightly which resulted in a marginally lower response in the range of 50 to 75 kg ha^{-1} of N, as predicted by the linear model, compared with the other two fertiliser materials. Although the interaction fertiliser type \times N rate was not significant ($P = 0.10$), DMY obtained with CAN or nBTPT-U compared to urea at 75 kg ha^{-1} of N appeared to be significantly higher for the calculated LSD value. Overall, responses were greater in the first (Figure 8 top) compared with the second cut (Figure 8 bottom) except for applications conducted between T1 and T4 which were higher at cut two. Over the growing season, the responses recorded in the first cut, followed well the pattern of temperature.

The relatively higher responses encountered in the second cut for applications conducted between T1 and T4 were due to residual fertiliser N which resulted from the combined effect of low temperatures and reduced N uptake earlier in the spring, and the characteristic pattern of the seasonal rate of growth of grass (Anslow and Green, 1967). The opposite effect was observed for applications conducted after T5; especially, between T8 and T13 when responses were higher than about 15 kg DM kg⁻¹ N.

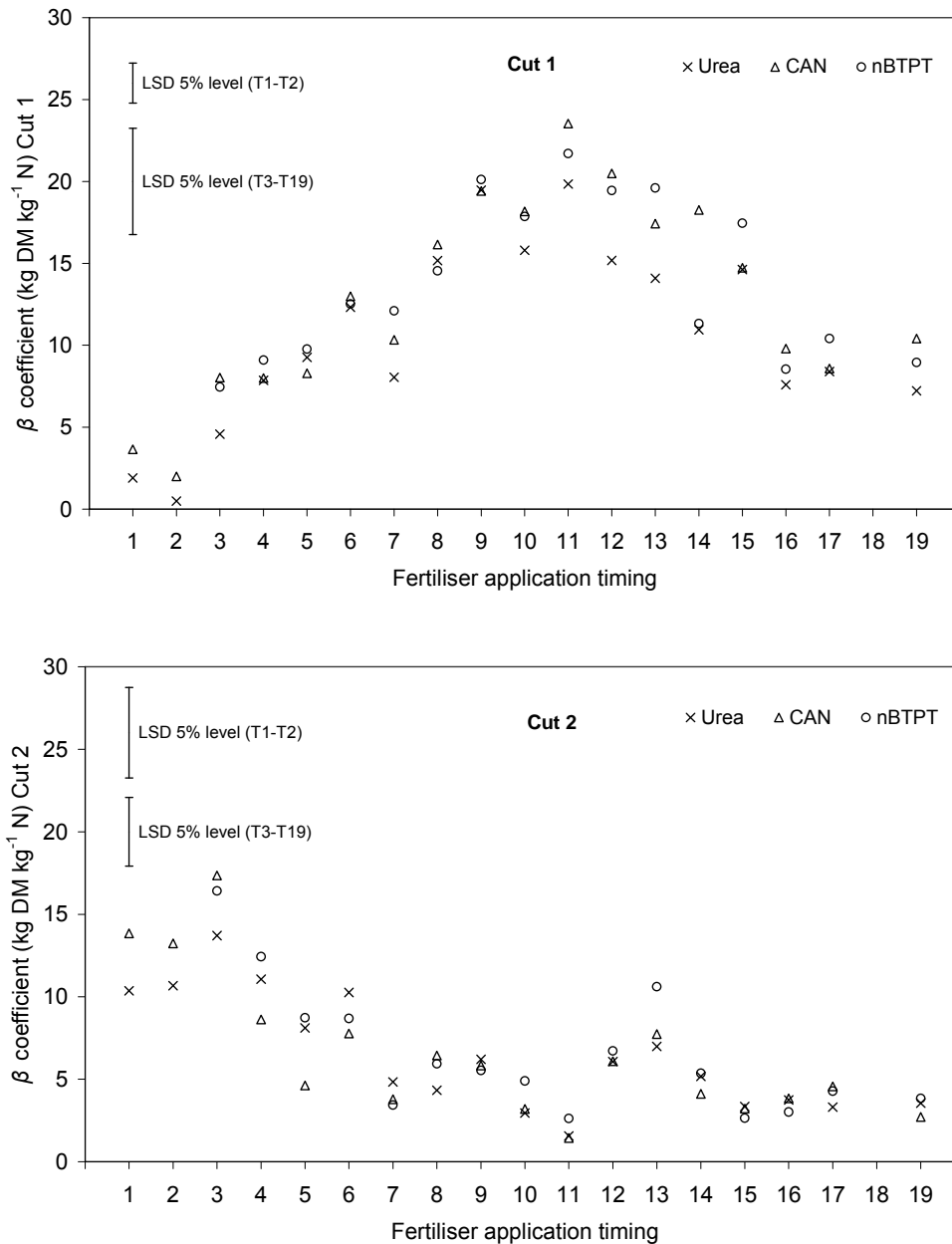


Figure 8: Responses of grass (β) to the application of fertiliser N recorded at cut one (*top*) and two (*bottom*) for each of the fertiliser application timings. The error bars show the LSD values (5% level).

Nitrogen use efficiency (NUE)

On average, across all timings (T1-T19), NUE was greater ($P < 0.001$) at cut one (0.57 kg kg^{-1}) compared with the recoveries obtained at cut two (0.17 kg kg^{-1}). NUE was influenced (P -values < 0.05) by the timing of fertiliser application, except at T1 and T2 (P -values > 0.05) and it showed a significant decrease with the N application rate (P -values < 0.05). Fertiliser applications conducted in early spring resulted in relatively lower NUE ($< 0.6 \text{ kg N kg}^{-1} \text{ N}$) compared with those conducted later in the season, except at T16 and T19 (Figure 9). There were no significant differences in NUE as a result of the fertiliser type for applications conducted between T3 and T19 (P -values > 0.05) but CAN showed relatively higher NUE than urea and nBTPT-U; except at T5 which appeared to be significantly lower for the calculated LSD value. For T1 and T2, the use of CAN resulted in higher NUE (P -values < 0.05) than urea (0.7 vs. $0.45 \text{ kg N kg}^{-1} \text{ N}$ respectively).

Based on cumulative N uptakes, the calculated NUE for urea and nBTPT-U relative to CAN (100%) were 91% and 97% respectively between T3 and T19 whereas for T1 and T2 this was 65% (urea only). The interaction timing \times fertiliser type was not significant and the same was observed when the N application rate was factored in (P -values > 0.05). N uptake showed a significant, positive, correlation with the response of the grass to the application of N (β) which was observed for all fertiliser types ($P < 0.001$; $R^2 = 41\%$; $s.e. = 6.9$). A similar relationship was obtained between β and NUE ($P < 0.001$; $R^2 = 46\%$; $s.e. = 0.12$) which indicated that the higher the response from the N fertiliser applied, the higher the N uptake and the N recovery. This has agronomic and as well as environmental implications since the N applied with the fertiliser is likely to be removed from the soil and incorporated into the crop biomass at a faster rate; hence, reducing the risk of N losses from the fertiliser applied.

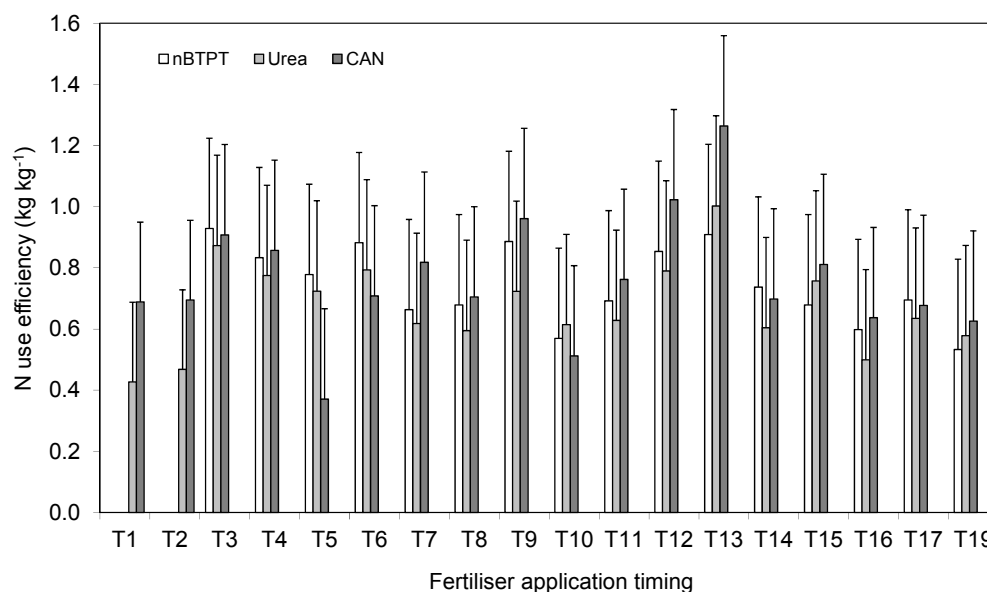


Figure 9: N use efficiency of urea, nBTPT-U and CAN calculated using the difference method and based on cumulative values of N uptake. The error bars show the LSD value (5% level); $P > 0.05$, $n = 12$.

Model predictions of dry matter yield

The general form of the model is shown in Equation [2] and the values of specific parameters are given in Table 2.

$$DMY = \mu + F_i + \delta_{Fi}r + \delta_1T_5 + \delta_2T_3 + \delta_3R_5 + \delta_4R_3 + \delta_5(R_3)^2 + \delta_6(T_5)^2 + \delta_{Fij}rT_5 + \delta_{Fik}rT_3 \quad [2]$$

Where: DMY is dry matter yield (kg ha⁻¹); μ : constant; F_i and δ_F are fertiliser-specific coefficients; r is the N application rate (kg ha⁻¹); δ_n depends on mean temperature (°C) and total rainfall (mm) recorded within 5 days prior to, and within 3 days after fertiliser application which are denoted as T_5 and R_5 , and T_3 and R_3 respectively.

Table 2: Values of coefficients corresponding to Equation [4]. SE is standard error of observations; DF is degrees of freedom.

Parameter	Fertiliser	Estimate	SE	DF	t-value	P > t
μ	-	176.6	340.9	3	0.52	0.64
F_i	nBTPT-U	-54.4	55.7	693	-0.98	0.33
F_i	CAN	5.5	55.7	693	0.10	0.92
F_i	Urea	0	-	-	-	-
δ_F	nBTPT-U	24.3	2.7	693	1.05	0.29
δ_F	CAN	16.7	2.7	693	-1.81	0.07
δ_F	Urea	21.5	-	-	-	-
δ_1	-	428.0	79.3	693	5.40	<0.001
δ_2	-	72.0	44.0	693	1.66	0.01
δ_3	-	-8.3	2.7	693	-3.02	0.003
δ_4	-	-41.3	12.5	693	-3.31	0.001
δ_5	-	0.9	0.27	693	3.32	0.001
δ_5	-	-23.5	3.0	693	-7.72	<0.001
δ_{Fij}	nBTPT-U	-1.7	0.5	693	-3.13	0.002
δ_{Fij}	CAN	-2.9	0.5	693	-5.42	<0.001
δ_{Fij}	Urea	-1.3	0.5	693	-2.42	0.016
δ_{Fik}	nBTPT-U	1.3	0.6	693	2.09	0.037
δ_{Fik}	CAN	3.0	0.6	693	5.05	<0.001
δ_{Fik}	Urea	0.9	0.6	693	1.51	0.13

The model indicated that, all other factors being constant, an increase in R_5 and/or R_3 in the range of 0 to 40 mm will result in reduced DMY but differences in predicted responses between fertiliser types will be small (<5%).

Cumulative rainfalls in excess of 40 mm do not yield satisfactory results since possible losses of N (e.g. by means of leaching or gaseous evolution) cannot be accounted for with use of this model. An increase in T_3 up to a maximum of 20°C is likely to result in increased DMY but to a greater extent (about 10% to 15%) with CAN compared with nBTPT and urea. Predictions made for higher temperatures appear to be unrealistic and to ignore the effect that warmer weather

has on increased volatilisation of ammonia with the use of urea. This upper limit suggested for temperature is, however, reasonable if compared with historical weather data over the main growing season (Figure 1). The interaction N rate \times temperature showed a significant effect (P -values <0.05); therefore, the response for a given N input can be significantly modified by temperature pre- or post-N application with all fertiliser materials. This interaction was not observed for rainfall ($P>0.05$) but the effect of rainfall on DMY before and after fertiliser application was significant (P -values <0.05). The overall effect of R_3 is that it will tend to decrease DMY because of the large negative coefficient associated with its linear term (δ_4); this, within the suggested range, will offset the effect of its square term which carries a smaller coefficient (δ_5). Predicted values of DMY for N application rates in excess of 75 kg ha^{-1} (upper limit in this study) should be treated with caution because of the effect of the interaction with temperature indicated earlier. Since δ_{fik} is positive, an increase in T_3 will have a beneficial effect on DMY which may not hold true for urea above the suggested upper limits of temperature and N application rate. It was shown that urea-N applied at 75 kg ha^{-1} resulted in relatively lower responses compared with the other two fertiliser materials (Figure 8). This was attributed to increased volatilisation of ammonia at higher fertilisation levels; effect that is not computed in this model. However, this may be offset by T_5 since the relatively large coefficient associated with its square term is negative but it is still an artefact of the model.

Predicted DMY from the model was validated with observed experimental data collected in 2011 (Figure 10). Individual regressions for each N source did not explain significantly more of the variation ($71\% > R^2 > 84\%$; P -values <0.001) than it did a common slope which showed a reasonably good agreement between observed and predicted data ($R^2 = 78\%$; $P < 0.001$). However, predictions of DMY for individual N sources may still be made to allow for comparisons of relative efficiencies between fertilisers given the N rate, and the short-term rainfall and temperature prior or post-fertiliser application.

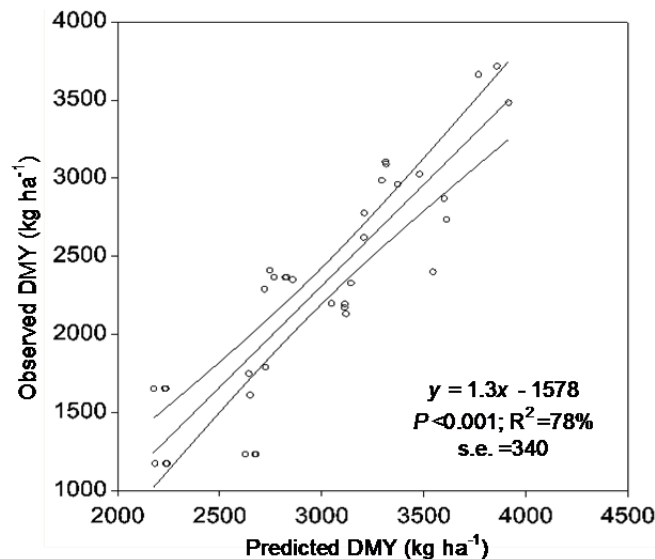


Figure 10: Predicted vs. observed DMY based on Equation [2] and experimental data for 2011 with a common slope for the three N sources used in this study. The two curves on both sides of the fitted line represent its 95% confidence interval.

Discussion

Efficiency of applied fertiliser N as affected by rainfall and temperature

The absence of significant R_3 and R_5 rainfall (<2 mm) between T1 and T3 appeared to have enhanced the efficiency of CAN (reduced N leaching) compared with urea which was reflected in their relative yields (URY: 89%-93%). Fertiliser applications conducted early in the season resulted in relatively lower responses at cut one compared with cut two which was attributed to the low temperatures recorded in February ($T_{\text{MEAN}} = 4.3^\circ\text{C}$) and March ($T_{\text{MEAN}} = 6.1^\circ\text{C}$). Since ryegrass requires a minimum temperature of 5°C to initiate growth (Lawrence et al., 1973) and urease activity is reduced at low temperatures (Moyo et al., 1989), these conditions restricted growth, N availability from applied urea and therefore N uptake up to the first cut. Therefore, the proportionally higher responses at cut two (T1-T4) were due to the combined effects of residual N from the fertiliser applied and climatic conditions on the rate of accumulation of DM.

The seasonal distribution of DM and N uptake is influenced by temperature and the timing of N application (Wolton et al., 1971). For perennial ryegrass, this is characterised by a peak in May followed by a decline in June, and a second but smaller peak in July (Anslow and Green, 1967). The applications conducted between early April and late May showed proportionally higher responses at cut one suggesting that fertiliser-N was primarily taken up within the first four weeks from application. From approximately early June responses started to decline in line with the overall decline in radiation. The peak in the responses observed at cut one for T15 matched well the expected rate of grass growth around this time described by Anslow and Green (1967); thus, the enhanced responses encountered. A similar effect was observed at cut two for the application conducted at T13 which responded to the proportionally higher rates of growth expected after the middle of July when the first harvest took place.

The relatively low responses obtained with urea at T1 and T2 also indicated low NUE from urea-N applied at these timings given that a significant ($P < 0.001$), positive, linear relationship was found between NUE and β . Therefore, under relatively cold conditions, urea was less effective compared with CAN for the same N input as responses (β), and consequently, NUE, were lower; especially, when comparing the two fertilisers at cut two. This suggested that some N was lost to the environment and to a greater extent in urea-fertilised grass. This observation, however, does not appear to support those of Clarkson et al. (1986) and Scholefield and Stone (1995) who suggested preferential uptake of NH_4^+ -N compared to NO_3^- -N by forage crops exposed to low temperatures. Fertiliser applications conducted in the summer (T10-T16) led to lower responses to urea-N which resulted in relatively lower NUE compared with the other two fertiliser materials (0.69, 0.73 and 0.81 kg N kg^{-1} N for urea, nBTPT-U and CAN respectively).

The model developed to simulate DMY from N input and source, and short-term rainfall and temperature showed that predictions can be satisfactorily made when the required variables are within the range of values reported in this study. This was confirmed when predicted DMY data was regressed against that obtained experimentally which showed an acceptable fit ($R^2 = 78\%$) to the linear model. This model constitutes a valuable tool which enables comparing the efficiency of different N sources as affected by changes in weather variables.

Comparison of the three N sources

Early applications of N in the spring allow for anticipation in the date of grazing (Blackman, 1936; McFeely and MacCarthy, 1981) which therefore requires the fertiliser choice to take account of the likely responses to N in this part of the season. The review conducted by Watson et al. (1990) summarised a series of contrasting results which indicated that urea can be equally effective as CAN for spring grass production (e.g. Murphy, 1983).

There is also evidence which showed relative efficiencies below and above compared with CAN (e.g. Herlihy and Sheehan, 1977; Chaney and Paulson, 1988) whereas for summer applications, efficiencies are usually lower.

The results obtained for T1 and T2 showed that cumulative responses (β) were lower with urea (c.12 kg DM kg⁻¹ N) compared with CAN (c.16 kg DM kg⁻¹ N). This was reflected in the calculated N use efficiency which was 55% higher with CAN compared with urea, the value of URY (c.90%) and relative N uptake (c.85%). The relatively lower agronomic performances encountered with urea agrees closely with the conclusions reached by Chaney and Paulson (1988) for (early) spring applications of N. Although the uptake of un-hydrolysed urea had been reported (Mengel and Kirkby, 1987), its rate of absorption is relatively lower compared with ammonium-N or nitrate-N (Bradley et al., 1989). Watson et al. (1990) suggested that the translation of N uptake into DMY may be less effective with urea than CAN. Given that grass crops provide a major sink for N (Whitehead et al., 1978; Whitehead, 1995), maximising responses from the N applied with the fertiliser immediately following application is an important agronomic and environmental consideration which allows for that mineral N to be rapidly removed from the soil-fertiliser and sequestered into the crop biomass.

The average rate of N uptake between fertiliser application and first harvest was slightly higher with CAN compared with urea. The differences were greater in early spring (1.1 vs. 0.8 kg N ha⁻¹ day⁻¹) and summer (2.4 vs. 2.2 kg N ha⁻¹ day⁻¹). For spring applications these were, approximately, within $\pm 5\%$ with all three fertiliser materials (range of 1.9 to 2.0 kg N ha⁻¹ day⁻¹). Montemurro et al. (1998) highlighted that reduced N uptake and NUE from urea will result in higher soil mineral N which in turn can increase the risk of N losses to the environment (Bhogal et al., 2003). For applications conducted in the spring (T3-T9), relative yields with urea and nBTPT-U were, on average, within a $\pm 5\%$ range compared with CAN (100%). The use of nBTPT improved the overall performance of urea which was more evident with increased N application rate in the range of 25 to 75 kg ha⁻¹ (Figure 11 *top*). Similarly, relative N uptakes with urea and nBTPT-U were, on average, within the suggested $\pm 5\%$ range of CAN (except for nBTPT-U at 50 kg ha⁻¹ of N) but these tended to be slightly lower than CAN towards the summer, especially with urea.

The use of nBTPT enhanced the uptake of urea-N when the N application rate was increased within the range used in this study (Figure 11 *bottom*). Ammonia volatilisation increases significantly with the application rate of urea (Overrein and Moe, 1967) which is one of the main reasons for urea to result in lower yields relative to CAN or AN (Lloyd, 1992; Chambers and Dampney, 2009). This effect had been shown in earlier studies (Chaney and Paulson, 1988; Murphy, 1983; Van Burg et al., 1982) and it can be the reason for the relatively lower response to urea-N in the range of 50 to 75 kg ha⁻¹. The differences in the response between fertilisers are expected to be greater at higher N application rates than those used in this study (Overrein and Moe, 1967). It is therefore implied that urea is a relatively less effective N source at high N application rates, in particular, for summer applications but with overall lower DMY and N uptake when used in the spring (Figures 11 *top* and *bottom* respectively).

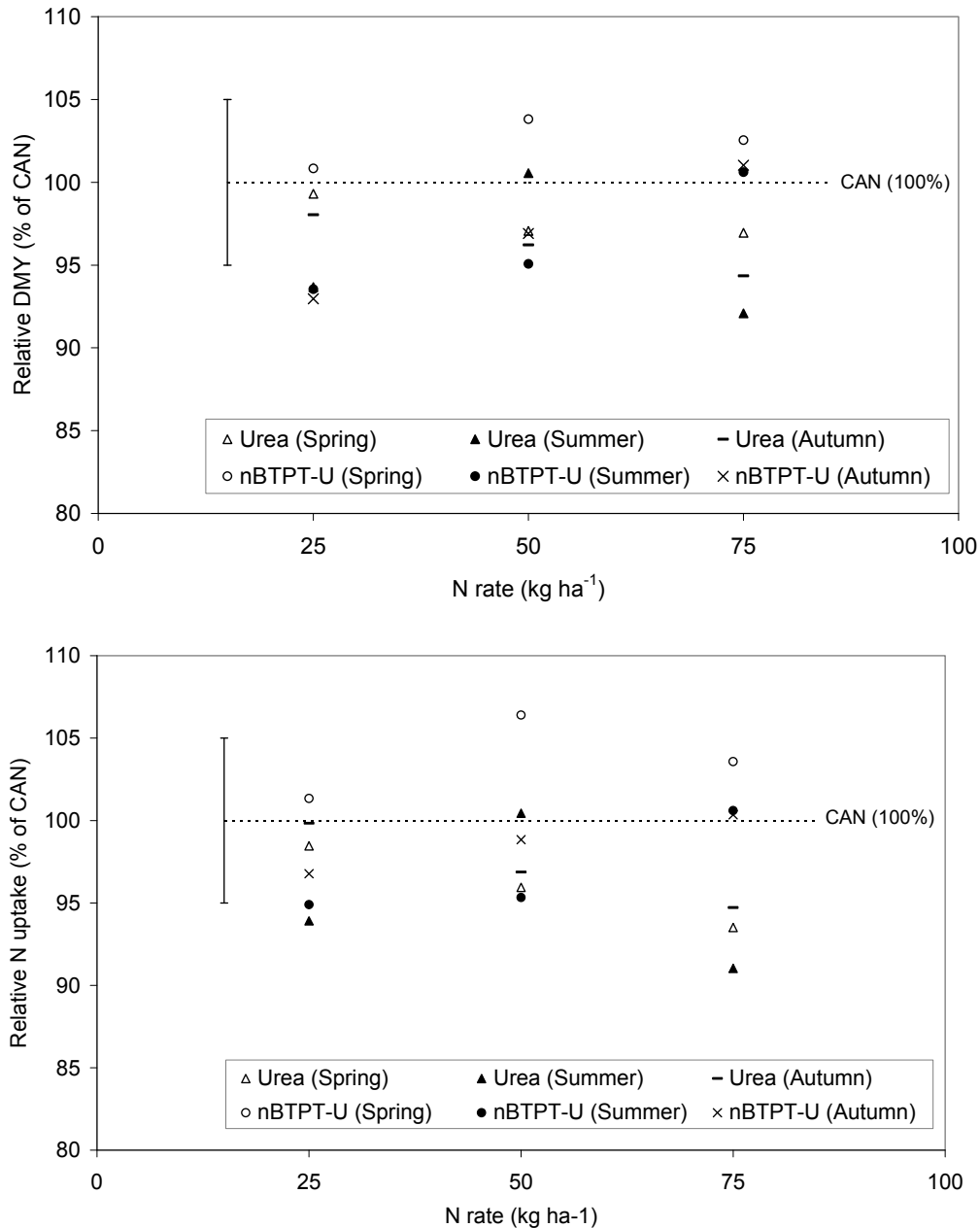


Figure 11: Cumulative DMY (*top*) and N uptake (*bottom*) of urea and nBTPT-U relative to CAN vs. the N application rate for fertiliser applications conducted in spring, summer and autumn. The error bars show a $\pm 5\%$ range with respect to CAN (100%) denoted by the dotted lines.

Increasing the rate of urea-N to counteract possible yield reductions (relative to AN) may not be reasonable (Lloyd, 1992) since gains in DMY above the optimum N rate will not be sufficiently high to match the yields that can be potentially achieved with AN (Sylvester-Bradley et al., 1982). This is supported by the fact that maximum yields with the use of urea are expected to be lower than with CAN (Van Burg et al., 1982). The relatively lower DMY levels encountered in the grass fertilised with urea did not lead to increased N content in harvested plant material (N_{PLANT}); conversely, CAN or nBTPT-U did not show a dilution effect (Marino et al., 2004).

The differences encountered in N_{PLANT} between-fertiliser treatments (range of 2.6 to 2.65%) were not significant ($P>0.05$), and they responded to the expected seasonal variation in N content in the herbage (Wilkins et al., 2000). Lloyd (1992) suggested that the reason for this is not differential DMY between urea and the other fertilisers but factors that reduce N availability following fertiliser application; namely, volatilisation of ammonia. This was better reflected in the calculated values of β and NUE corresponding to the summer fertiliser applications (T10-T16) which showed a decline with the N application rate that occurred to a greater extent in urea-fertilised grass. There appears to be a combined effect of the N application rate and increased temperature (towards the summer) which reduced the efficiency of urea; this can be demonstrated by simulating DMY with the model. In general, the range of responses (β) encountered in this study (range of 10 to 30 kg DM kg⁻¹ N) were within the range (from 14 to 29 kg DM kg⁻¹ N) reported in the literature (e.g. Morrison et al., 1980). Mean responses for the season were comparable between CAN and nBTPT (c.20 kg DM kg⁻¹ N) but higher than urea (17 kg DM kg⁻¹ N). These exceeded those reported by McFeely and MacCarthy (1981), and O'Donovan et al. (2004) (range of 5 to 17 kg DM kg⁻¹ N) but approximated the mean value for the season (23 kg DM kg⁻¹ N) obtained by Morrison et al. (1980).

The reasons for the relative enhanced performance observed in all measured parameters at T5 in the plots fertilised with urea and nBTPT-U compared with CAN are not clear. R_5 records showed 22 mm but there was no rainfall subsequent to fertiliser application that could have reduced N availability from CAN-treated grass; for example, by leaching. It is possible however that, given favourable soil moisture conditions and temperature, the rate of hydrolysis and therefore the rate of N uptake had occurred rapidly in urea- and nBTPT-fertilised grass. This combined with typically high rates of accumulation of DM in this part of the season (Anslow and Green, 1967) resulted in higher performances relative to CAN. Based on the c.v. (%) for the data corresponding to DMY and N uptake, it is not possible to indicate that urea or nBTPT are more variable N sources than CAN which agrees with Watson et al. (1990). Bussink and Oenema (1996) predicted that in order for urea to be as profitable as CAN, R_3 needed to be in excess of 6 mm (cut one) or 10 mm (cut two) and that its application would be unprofitable for later cuts. Chaney and Paulson (1988) concluded that DMY losses from urea are likely to occur in all cut silage and Watson et al. (1990) based on studies conducted in Scotland suggested that urea-N needs to be about 10% to 20% cheaper than AN-N to be equally cost effective.

Conclusions

1. A model was developed to simulate DMY based on the combined effects of N application rate and source, and short-term rainfall and temperature. This model is a simple, yet effective, tool for assessing the efficiency of different N sources as affected by weather variables. It aids the fertiliser choice and management in grass crops.
2. Urea was less effective than CAN for early spring applications as shown by the lower N responses obtained, relative yield and N uptake compared with CAN which translated into reduced agronomic and N use efficiencies. Reduced N uptake from the fertiliser-N can lead to increased soil mineral N which is likely to be lost to the environment by leaching or gaseous evolution.
3. For spring applications, relative yields and N uptakes with urea and nBTPT-U were, on average, within $\pm 5\%$ compared with CAN (100%); hence, the efficiencies of the three N sources were comparable. The use of nBTPT enhanced the overall performance of urea; especially, towards the summer and with increasing N application rate.

4. For summer applications, urea was less effective than CAN or nBTPT-U both of which showed comparable efficiencies after early May. There was no evidence to suggest that urea or nBTPT-U were more variable N sources than CAN but, overall, cumulative DMY were to be lower. Increasing the application rate of urea-N to compensate for its relatively lower efficiency is not recommended due to greater risk of ammonia volatilisation. This may be done with nBTPT depending on the relative costs of both fertiliser sources.
5. The average rate of N uptake between fertiliser application and first cut was about 30% higher with CAN compared with urea in early spring, and about 7% higher in the summer while differences between fertiliser types in the spring were within $\pm 5\%$. This rate determines the velocity at which N is removed from the soil-fertiliser following application thereby reducing the opportunities for N losses to the environment.

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