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Urea hydrolysis and lateral and vertical movement in the soil: effects of urease inhibitor and irrigation

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Abstract A glasshouse-based study was conducted to investigate the effect of urease inhibitor N-(n-butyl) thiophosphoric triamide ('Agrotain') and irrigation on urea hydrolysis and its movement in a Typic Haplustept silt loam soil (in 72 repacked soil cores). Half (36) of these cores were adjusted to soil moisture contents of 80% field capacity (FC) and the remaining 36 cores to 50% FC. Granular urea with or without Agrotain was applied at a rate equivalent to 100 kg N ha⁻¹. There were three replicates to these two sets of soil cores. After 1 day of treatment application, soil cores of the 50% FC were adjusted to 80% FC by applying surface irrigation. Twelve pots were destructively sampled at each day after 1, 2, 3, 4, 7 and 10 days of treatment application to determine urea

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J. Blennerhassett Summit-Quinphos (NZ) Ltd, Private Bag 12508, Tauranga Mail Centre, Tauranga 3143, New Zealand hydrolysis and its lateral and vertical movement in different soil layers. Agrotain-treated urea delayed urea hydrolysis during the first 7 days after its application. This delay in urea hydrolysis caused by Agrotain enabled added urea, which is uncharged, to move away from the surface soil layer to the sub-surface soil layer both vertically and laterally. In contrast, most urea hydrolysed to soil NH_4^+ within 2 days of its application. Irrigation after 1 day resulted in further urea movement both laterally and vertically from the surface soil layer (0-10 mm) to the sub-soil layer (30-50 mm) in Agrotain-treated urea. These results suggest that Agrotain delayed urea hydrolysis and allowed more time for rainfall or irrigation to move added urea from the surface layer to sub-soil layers where it is likely to make good contact with plant roots. This distribution of urea in the rooting zone has the potential to enhance N use efficiency and minimize N losses associated with ammonia volatilization from surfaceapplied urea.

Keywords Agrotain \cdot Hydrolysis \cdot Irrigation \cdot Movement \cdot N-(n-butyl) thiophosphoric triamide (NBPT) \cdot Urea \cdot Urea inhibition

Introduction

Urea is the predominant chemical fertilizer applied to grazed pastures in New Zealand and to arable crops worldwide. However, a major potential disadvantage associated with the use of urea is gaseous loss of N via ammonia (NH₃) emission, especially when applied under hot and dry soil conditions, high pH and high wind (Cabrera et al. 2001; Gioacchini et al. 2002; Khalil et al. 2002; Kissel et al. 2004; Ahmed et al. 2006; Pacholski et al.

2006; Zaman et al. 2008; Rochette et al. 2009). A number of options have been proposed to improve urea use efficiency. These include physical (altering the rate, timing and method of application and producing large-granule urea) and chemical (coating urea with different materials and with chemicals) approaches. The application of urease inhibitors has been considered a promising way to reduce N losses and enhance urea-N use efficiency. Several synthetic (Chen et al. 2008) and natural (Patra et al. 2009) urease inhibitors have been identified and tested, but Agrotain has been shown to retard urea hydrolysis at a very low concentration (Carmona et al. 1990; Gill et al. 1997; Rawluk et al. 2001; Watson et al. 2008).

In our previous studies, we found that treating urea with Agrotain has the potential to increase N use efficiency and herbage production in pasture grass (Dawar et al. 2010). Other researchers also reported increased herbage dry matter and N uptake after application of Agrotain-treated urea (Blennerhassett et al. 2006; Martin et al. 2008; Zaman et al. 2008). The mechanism underlying such responses has yet to be fully elucidated. The delay in urea hydrolysis by Agrotain has been suggested to provide an opportunity for direct plant uptake of an increased proportion of the applied urea-N than is the case for urea alone (Dawar et al. 2010). However, there is also a possibility that there is another benefit of retaining N in the urea form-that is, being an uncharged particle, urea is likely to diffuse easily into the rooting zone at moderate-high moisture content. Such diffusion of urea thus provides herbage an extended opportunity to take up added urea through a greater proportion of the root system (in addition to the previously established benefit of direct uptake via the leaves) (Matsumoto et al. 1966; Bollard et al. 1968; Harper 1984; Watson and Miller 1996).

Urea use efficiency may be improved through reduced gaseous losses of NH₃, especially if it is moved into the soil with small amounts of irrigation. Zhengping et al. (1996) previously studied the effect of urease inhibitor on movement and transformation of urea and its hydrolysis products in the soil following sub-surface application. Similarly, other studies investigated urea hydrolysis and production of NH₄⁺ after surface application of urea with Agrotain (Watson and Miller 1996; Rawluk et al. 2001; Zaman et al. 2008), but none of those studies investigated urea movement both lateral as well as downward in the soil profile in the presence of urease inhibitor. The objective of the present study was to investigate urea movement (both lateral and downward) after surface application as influenced by Agrotain and a simulated light irrigation. We tested the hypothesis that applying urea with Agrotain in granular form to the soil surface will delay urea hydrolysis and thus allow far greater diffusion of the intact urea molecule into the dense pasture rooting system in the soil.

Materials and methods

A glasshouse experiment was conducted at the University of Canterbury using topsoil (0-75 mm) collected from a grazed pasture site near Lincoln, Canterbury New Zealand (43°64'32.00" S, 172°38'58.90" E). The soil used was Paparua silt loam, Typic Haplustept (Soil Survey Staff 1998). The soil was sieved (<2 mm) and then brought to the two moisture levels (80% field capacity (FC) or 50% FC) either by air drying or adding additional water. Sieved soil (1.6 kg bag^{-1}) was packed in 100-mm-long and 140-mm diameter plastic bags, which were then placed into standard planting pots. Four soil samples, each comprising ten randomly collected soil cores, were analysed for key soil properties. The soil is free draining and had a pH of 5.75, total N of 0.36%, organic matter of 6%, Olsen P of 20 μ g mL⁻¹ and cation exchange capacity of 15 cmol_{c} kg⁻¹. The bulk density of the packed soil core was 0.88 g cm^{-3} . The experiment consisted of five treatments (urea only, urea + Agrotain, urea + irrigation on day 1, urea + Agrotain + irrigation on day 1 and a control receiving no N). Urea granules, with or without Agrotain, were placed on the soil surface in the centre of each core (a diameter of 40 mm at a rate equivalent to 100 kg N ha⁻¹ or 240 mg N bag⁻¹. After 1 day of treatment application, soil cores of the 50% FC were brought to the 80% FC by applying surface irrigation equivalent to 8 mm with a hand mist sprayer. Afterward, the two sets of soil cores were maintained at 80% FC level by weighing them every day to account for any moisture losses during the experimental period. Soil cores were then incubated at 20°C under glasshouse conditions.

Three soil cores per treatment were destructively sampled at 1, 2, 3, 4, 7 and 10 days after treatment application. The soil in each core was divided into ten layers, each 10 mm thick, to measure vertical movement of N, and the soil mass recorded. In addition, the soil in each layer was divided into three concentric sub-samples using rings of radius 20, 40 and 60 mm from the centre of the core to the pot to the outer edge of the pot to monitor lateral movement of N. A sub-sample of each soil sample was used for moisture determination, and an additional subsample was extracted with 2 M KCl for 1 h and filtered through Whatman 42 filter paper. Soil extracts were immediately frozen and then used to determine the concentration of different N forms (i.e. urea-N, NH4⁺-N and NO₃⁻-N) in the soil. Urea-N was analysed using quantitative colorimetric urea determination (Quanti-ChormTM urea assay kit) by bioassay systems Hayward

(USA). Ammonium-N and NO₃⁻N concentrations were determined by flow injection analysis.

Statistical analysis

Analyses of variance (ANOVA) were performed using Minitab (Version 12, Minitab Inc., USA). Least significant differences (LSD) were calculated to compare treatment means at P<0.05. Repeated-measure ANOVA was used to determine if time had a significant effect on the concentration of the N species, and ANOVA was then used at individual time points when the treatment × time interaction was found to be significant.

Results

Recovery of urea-N in soil

Agrotain-treated urea exhibited delayed urea hydrolysis and significantly higher amounts of urea remained during the first 7 days of its application (Fig. 1a). Contrary to this, urea disappeared quickly within 2 days of its application in urea alone treatment. The applied irrigation facilitated urea



Fig. 1 Recovery of urea-N (a), NH₄⁺-N (b) and NO₃⁻-N (c) as a percentage of total applied N to the soil core. *Vertical bars* represent LSD values where treatment means are significantly different at P= 0.05

movement but had no significant effect on total urea-N retention in two urea treatments.

Soil NH₄⁺-N and NO₃⁻-N

Decreases in urea-N concentration were paralleled by concomitant increase in the NH_4^+ -N concentration in the soil core (Fig. 1b). Agrotain-treated urea (with or without irrigation) delayed urea hydrolysis and released NH₄⁺ into the soil at a slower rate (Fig. 1b) than with urea alone with or without irrigation. In contrast, urea applied alone, with or without irrigation, exhibited more rapid hydrolysis soon after its application, as evident by significantly higher concentrations of soil NH_4^+ -N on days 1 and 2. In the urea alone treatment, with or without irrigation, more NH₄⁺-N was recovered compared with Agrotain-treated urea, with or without irrigation, from the soil on day 1; this increased on day 2 when it reached its maximum and decreased thereafter. Soil NO₃-N concentrations were much lower than NH₄⁺-N and were not significantly influenced by urea addition, with or without Agrotain and irrigation (Fig. 1c).

Downward movement of urea-N and NH₄⁺-N in soil

The vertical distribution of urea-N in the soil layers after treatment application is shown in Fig. 2. After day 1, in all treatments, most of the urea-N remained in the surface soil layer and did not diffuse below the 10–30-mm soil layer. In contrast, the application of irrigation after day 1 produced a significantly greater urea-N concentration at 20–40 mm depth (with or without Agrotain). Regardless of irrigation, Agrotain treatment retained more N in the urea form and this moved down through the soil layer up to day 7.

Irrigation applied to 50% FC pots after 1 day of treatment application facilitated urea movement from the surface soil to the sub-surface soil layers (30–50 mm) in those treatments, particularly up to day 4 (Fig. 2). Such urea movements were more in Agrotain-treated urea than those of urea alone. After 4 days of treatment application, 48% of the added urea was found in 30–50 mm in Agrotain-treated urea with irrigation compared with 20% without irrigation.

Changes in the distribution and concentration of NH_4^+ -N in different soil layers after N application are presented in Fig. 3. After day 1, in all treatments, most of the NH_4^+ -N remained at the surface soil layer and did not diffuse below the 10–20-mm soil layer. However, the concentration of NH_4^+ -N following application of urea alone was significantly greater than that following application of urea with Agrotain. Importantly, the NH_4^+ -N in the absence of irrigation was primarily in the upper surface soil layer and was not more evenly distributed down the sub-surface soil layers (a result which is similar to that of Agrotain-treated urea without irrigation). When irrigation was applied after Fig. 2 Effect of urease inhibitor and irrigation on downward movement of urea-N in soil, expressed as a percentage of the total added urea-N. *Bars* are means \pm SEM, where n=3



day 1, a significantly greater proportion of NH_4^+ -N was found 30–50 mm below the soil surface up to day 7 (Fig. 3). At day 2, 28% of recovered N remained as NH_4^+ -N at 30– 50 mm in response to the urea with irrigation treatment, compared with 8% in the urea without irrigation treatment. After day 2, the concentration increased in the sub-surface soil layers, and 36% and 44% of recovered N remained as NH_4^+ -N at 30–50 mm in the urea with irrigation treatment compared with 20% and 24% in the urea without irrigation treatment at day 3 and day 4, respectively. A similar trend, but of lower magnitude, was observed for Agrotain-treated urea (with and without irrigation).

Lateral movement of urea-N and NH4+-N in soil

In all treatments, soil urea-N concentrations at day 1 were very high in the inner ring (0-20 mm radius) close to the

granule placement position and decreased laterally (Fig. 4). Addition of Agrotain-treated urea resulted in a significantly greater proportion of urea being found in the outer rings of the soil up to day 4 compared with other treatments (Fig. 4). At day 2 (after irrigation at day 1), 28% of recovered N was found in urea form in the middle ring (20-40 mm radius) in Agrotain-treated urea compared with 23% without irrigation. In the outer ring (40-60 mm radius), 18% of recovered N was found as urea following application of Agrotain-treated urea with irrigation while urea did not move to the outer ring in the corresponding without irrigation treatment. After day 2, the concentration of urea increased in the outer ring, so that by day 3, 15% of recovered N was found in the outer ring (40-60 mm) following the addition of Agrotain-treated urea with irrigation compared with 8% without irrigation. In Agrotain-treated urea with irrigation, 27% of the recovered

Fig. 3 Effect of urease inhibitor and irrigation on downward movement of NH_4^+ -N in soil, expressed as a percentage of the total added urea-N. *Bars* are means \pm SEM, where n=3



N remained as urea in the outer ring (40–60 mm radius) even after day 4, compared with 5% in the same treatment without irrigation. During the experiment, urea-N moved through the soil away from the central placement zone (0–20 mm radius). In the outer ring (40–60 mm radius), urea-N concentration following the addition of Agrotain-treated urea without irrigation was 8% on day 3 and had decreased to 5% by day 4. Over the same time period, the proportion of applied N recovered as urea in soils following the addition of Agrotain-treated urea with irrigation increased from 15% to 27%.

The recovery of NH_4^+ -N tended to mirror that of urea-N (Fig. 5). After day 1 in all treatments, most of the NH_4^+ -N remained in the inner ring (0–20 mm radius) and did not diffuse to the outer ring. However, the concentration of NH_4^+ -N in the inner ring was significantly greater in the urea alone treatments than in those of urea with Agrotain treatments. The applied irrigation also facilitated NH_4^+ -N

production from the applied urea; therefore, more NH_4^+-N was found in the middle (20–40 mm radius) and outer rings (40–60 mm radius) than those urea without irrigation. For example, 52% of recovered N was found as NH_4^+-N in the middle ring (20–40 mm radius) of the urea alone with irrigation treatment compared with 29% without irrigation. At day 4, the NH_4^+-N concentration increased further in the outer ring, and 22% of recovered N was found as NH_4^+-N in the urea alone with irrigation treatment compared with 29% without as NH_4^+-N in the urea alone with irrigation treatment compared with 9% without irrigation.

Discussion

This experiment provides us with important insights into urea hydrolysis and its movement in soil as influenced by urease inhibitor (Agrotain) under optimum soil moisture and temperature. Urea hydrolysis was delayed Fig. 4 Effect of urease inhibitor and irrigation on lateral movement of urea-N in soil, expressed as a percentage of the total added urea-N. *Bars* are means \pm SEM, where n=3



up to 7 days by adding Agrotain as can be seen by the greater recovery of urea-N (Figs. 1a and 2) and low NH₄⁺ concentrations in different soil layers (Fig. 3) compared with urea alone. Other researchers found that Agrotain delayed urea hydrolysis up to 2 weeks (Zhengping et al. 1991; Hendrickson and Douglass 1993; Watson 2000; Rawluk et al. 2001; Zaman et al. 2008; Dawar et al. 2010). We do not have an explanation for the relatively lower N recovery as evident from the three forms of N (urea, NH_4^+ and NO_3^- ; Fig. 1a–c) because we did not use ¹⁵N in our study, which would have enabled us to measure those N pools with more confidence and greater accuracy. Such lower N recovery could not be related to high N losses especially to NH₃ volatilization in the presence Agrotain and relatively high moisture content (80% FC), but we presumed that some unknown N consumption processes including those of microbial and chemical could have contributed to such lower N recovery. The duration of NBPT activity is shorter at optimum soil moisture and high temperatures because of increased urease activity (Clay et al. 1990; Bremner et al. 1991). Such delay in urea hydrolysis by Agrotain has implications for N losses via NH₃ volatilization (Zaman et al. 2008). Delayed urea hydrolysis by Agrotain allows more time for rainfall or irrigation to wash the applied urea from the surface soil to the sub-surface soil layers as evident from the vertical and lateral movement of urea in our experiment under 80% FC as well as in 50% FC after 1 day of irrigation (Figs. 2 and 4). Such lateral and downward movements of urea could be due to the fact that urea is an uncharged particle and therefore unlikely to be adsorbed by soil organic matter or by exchange sites, therefore applying irrigation after 1 day of treatment application accelerated urea movement: 25-48% of the total recovered urea-N was below 20 mm depth and 18-27% to the outer rings, particularly from day 2 and day 4. Downward urea movement under field and controlled laboratory conditions after flood irrigation was also observed by other researchers (Stillwell and Woodmansee 1981; Bowman and Rice 1986). However, those studies were conducted under saturated soil condition. Similarly, neither of these studies looked at the lateral movement in the presence of urease inhibitor like Agrotain. Applying irrigation after 1 day of treatment application brought back the moisture content to 80% FC; therefore, the pattern of urea movement was similar in the two moisture treatments.

Fig. 5 Effect of urease inhibitor and irrigation on lateral movement of NH_4^+ -N in soil, expressed as a percentage of the total added urea-N. *Bars* are means \pm SEM, where n=3

The decrease in urea-N concentration in the urea alone treatment (with or without irrigation) was paralleled by a concomitant increase in the NH₄⁺-N concentration in the soil layers (Fig. 1b). The concentration of NH₄⁺-N formed from the hydrolysis of urea alone (without irrigation) treatment was significantly higher around the placement ring (0–20 mm diameter) in the surface layer of the soil. In the absence of Agrotain, the majority of urea hydrolysis occurred in the topsoil layer, which led to the production of high concentrations of NH₄⁺ in the surface soil layer (Fig. 3).

The increase in NH_4^+ -N in sub-surface soil layers could be due to its macro-pore leaching and movement of unhydrolysed urea. These results support the idea that urea use efficiency may be improved through reduced gaseous losses of NH_3 if urea is moved into the soil with small amounts of irrigation (Black et al. 1987). Irrigation facilitates the transport of added urea into the root-zone of sub-surface soil layers, dilutes surface NH_4^+ concentration, reduces NH_3 partial pressure and thereby minimizes NH_3 losses possibly due to low soil pH in sub-surface soil (Whitehead and Raistrick 1993). The distribution and movement of applied N during an irrigation event will depend on N form (urea versus NH_4^+). The source of NH_3 is mainly the exchangeable NH_4^+ present in the soil. We suggest that, although soil colloids adsorb NH_4^+ ions, applying irrigation of up to 10 mm could reduce the higher concentration of NH_4^+ -N in the surface soil layer, thereby resulting in its even distribution down the soil profile and laterally away from the application point.

Conclusions

This experiment has shown that Agrotain not only delays urea hydrolysis and increases urea-N recovery by inhibiting the urease enzyme in the soil, but it also results in greater movement of urea both vertically and laterally in the soil layers. This may partly explain our previous findings (Dawar et al. 2010) of an improved yield response in pasture herbage in response to fertilization with Agrotaintreated urea. In addition, irrigation allows for both greater movement of urea to the potential rooting zone of the pasture from the application point and also a reduction in the concentration of NH_4^+ present in the surface soil layer. In combination, these effects may have important implications for the effective management of N addition under field conditions. Acknowledgements The authors thank Summit Quinphos (NZ) Ltd. for providing funding to support this project and for preparing and coating the urea with Agrotain. A University of Canterbury Doctoral Scholarship to Khadim Dawar is also gratefully acknowledged.

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