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A field evaluation of coated urea with biodegradable materials and selected urease inhibitors

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Urease inhibitor and biodegradable polymer coatings are two most suitable startegies to increase urea fertilizer efficiency. Coating of urea with selected inhibitors can increase the crop production by slowing down the hydrolysis process of urea in the soil. For this purpose, a field experiment was conducted to evaluate the effects of newly coated urea with biodegradable materials, $CuSO_4$ and $ZnSO_4$. Guinea grass was used as a test crop. Six treatments (urea alone, palm stearin + Cu coated urea, agar + Cu coated urea, gelatin + Cu coated urea, Cu coated urea, and Zn + Cu coated urea) were applied to field plots as nitrogen sources at the recommended dose of urea (217 kg ha⁻¹), with triple super phosphate (100 kg ha⁻¹) and muriate of potash (217 kg ha⁻¹). The soil and plant analyses were conducted by standard method for mineral N, soil pH and nutrient content of plant. The outcomes of the study showed 50% increase in dry matter yield and N uptake of grass and 20% reduction in ammonium accumulation on the soil surface in the coated urea plots. A concomitant decrease in soil pH to 4.2 or 4.3 was measured after 15 days of fertilizer application, which was due to the acidic effects of CuSO₄ and ZnSO₄. All coated urea treatments facilitated significantly for better pasture production and nutrient uptake.

Key words: Coated urea, micronutrients, pasture, urease inhibitor.

INTRODUCTION

Nitrogen (N) is an important nutrient required for growth by grasses and other plant species. However, the efficient uptake and incorporation of N in established grass pastures is difficult due to N mobility (Lightner et al., 1990). Studies investigating N losses from grazed lands indicate that most of the N loss occurs by NO_3 leaching and NH_3 volatilization and only 20 to 40% of the applied N is taken up by plants (Vlek and Byrnes, 1986; Rao et al., 1993; Owens and Bonta, 2004).

Urea is used most often as the N source in agricultural fields and 51% is consumed by the agricultural world due to its low cost and high availability (IFA statistics, 2006).

However the low N efficiency of urea becomes a concern in the entire world. The minimal modification of urea using coating and urease inhibitors offers an attractive approach to reduce N losses from this most popular source of nitrogen (Buresh et al., 1988). Many improved management practices and modifications of urea have been investigated and introduced using polymer coatings and inhibitors. Some methods were successful but not applicable in large fields due to a lack of availability, high cost and other drawbacks of the products. The extensive and frequent applications of these modified forms of urea can cause seedling damage, phytotoxicity and environmental pollution. Hence, there is need to produce a fertilizer that is easily made, cost-effective, slows the hydrolysis process, slow down the ammonia formation in the soil solution and increases the nitrogen use efficiency of plants without any side effects (Watson, 2000).

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Table	1. Soil	properties.
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Parameter	Value	Remark
Soil	Typic paleudult	(Paramananthan, 2000)
рН	4.5	Strongly acid (Bruce and Rayment, 1982)
Texture	Sandy clay loam	
Sand (%)	50	Learne (Unified Opilites touch Obersification Operation 1000)
Silt (%)	17	Loam (Unified Soil textural Classification System, 1983)
Clay (%)	33	
Organic C (%)	1.5	Moderate (Charman and Roper, 2007)
Total N %	0.2	Medium (Bruce and Rayment, 1982)
Cu (mg kg ⁻¹)	0.01	Low (Metson, 1961)
Zn (mg kg⁻¹)	0.03	Low (Metson, 1961)
K (cmol⁺kg⁻¹)	0.24	Low (Metson, 1961)
Ca (cmol⁺kg⁻¹)	0.7	Very low (Metson, 1961)
Mg (cmol⁺kg ⁻¹)	5	High (Metson, 1961)

Chemicals that act simultaneously as fertilizers and urease inhibitors, such as Cu and Zn, may be useful for reducing ammonia loss and enhancing the amount of nitrogen from urea available to plants for extended periods of time by inhibition of urease activity (Tabatabai 1977; Reddy and Sharma, 2001; Purkayastha and Chhonkar, 2006). In addition, the use of natural materials instead of synthetic polymers provides a stable coating without any unintended effects on the ecosystem. Natural polymers and waxes had been used as adhesive agents and could effectively combine urea and Cu on the microsites of fertilizers. The study was conducted to evaluate the effects of coated urea added to fields in combination with biodegradable polymers (agar, gelatin), fatty acids (palm stearin) and micronutrient as urease inhibitors (Cu, Zn) under field conditions.

MATERIALS AND METHODS

The methods for preparing and coating of urea and its characterization were as previously described by Junejo et al. (2009, 2011).

Site preparation and fertilizer applications

A pasture site with an area of 100 m^2 was fenced and prepared for the experiment. The pasture (guinea grass, *Penicum maximum* Jacq.) was sampled and its soil properties were analyzed (Table 1). The site was divided into 24 plots and arranged in a completely randomised block design with four replicates. There were six treatments labelled as U (urea alone), UPSCu (palm stearin + Cu + urea), UAGCu (agar + Cu + urea), UGCu (gelatine + Cu coated urea), UCu (Cu coated urea) and UCuZn (Cu + Zn coated urea), which were surface applied once at the start of the experiment after clearing previously grown grass and irrigating the plot site. The plot was never fertilized for the last five years. The fertilizer treatments (Table 2) were applied according to recommendation given by Malaysian Agriculture Research Institute (MARDI). The rates of applied fertilizers were 217 kg ha⁻¹ for uncoated urea and 220 kg ha⁻¹ for coated urea, TSP (100 kg ha⁻¹) as phosphorus source, and 217 kg ha⁻¹ KCI, as potassium, respectively.

Plant and soil analysis

Soil samples were collected fortnightly from the depth of 0 to 15 cm to determine mineral N, while soil pH, Cu, and Zn were analysed every month after fertilizer applications. The soil mineral N (NH_4 and NO_3) analysis was determined by the steam distillation method (Keeney and Nelson, 1982; Siva et al., 1999). The micronutrients (Cu and Zn) concentration in soil was extracted by double acid method and analyzed by an atomic absorption spectrophotometer (Benton Jones, 2001). Grass was harvested two times at the flowering stage (the first and second cuttings described below), and dry matter yield was recorded two times. Plant samples were analysed for total N (Bremner and Mulvaney, 1982), Cu and Zn uptake on monthly basis by dry ash method (Benton Jones, 2001).

Statistical analysis

An analysis of variance (ANOVA) and Tukey's test were used to evaluate the treatment effects using the Statistical Analysis System, version 9.1 (SAS Institute Inc., 2001).

RESULTS AND DISCUSSION

Soil properties

The soil was sandy loam and acidic with a medium-low pH of 4.5. The soil pH immediately increased up to 5.5 in uncoated urea treated soil after fertilizer applications and remained unchanged throughout the experiment; however, the pH of soil treated with coated urea decreased from 4.4 to 4.2 (Figure 1). The acidifying chemicals (CuSO₄ and ZnSO₄) and urease inhibitor slowed down the process of hydrolysis which caused the stable and decreased pH at the urea microsite (Fernery and Black,

Table 2. Fertilizer treatments of coated and uncoated urea.

Treatment	Label	N (%)	pH (H₂O)
Urea	U	46	8.0
Palm stearin + Cu coated urea	UPSCu	44	5.0
Agar + Cu coated urea	UAGCu	44	4.5
Gelatine + Cu coated urea	UGCu	44	4.5
Cu coated urea	UCu	44	4.5
Cu + Zn coated urea	UCuZn	44	5.0

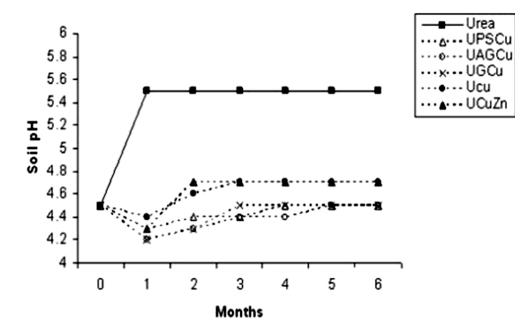


Figure 1. Effect of coated and uncoated urea on soil pH under field conditions.

1988). Reductions in N loss have been associated with the inhibition of urease activity by applied urea treatments (Ahmed et al., 2006).

N, Cu and Zn content of soil

Overall, the Cu and Zn content in soil declined gradually within six months due to the nutrient uptake of plants (Figure 2a and 2b). The maximum concentration of Zn in soil, 20 mg kg⁻¹ was analysed for UCuZn (micronutrientcoated urea) (Figure 2b). The Cu content in soil ranged from 2 to 10 g kg⁻¹ in coated and uncoated urea treated soil within six months (Figure 2a). An increase in Cu and Zn content in soil from the coated urea treated plot was observed in the second month after fertiliser application, while all other treatments showed a gradual decline in micronutrients due to deficiency of these nutrients in soil (Figure 2). The percentage of total N was more in plots treated by natural materials and micronutrient coated urea (UPSCu, UAGCu and UGCu), compared to the plots treated only with micronutrient coated urea (UCu and UCuZn). The observed values for total N were very similar among the U (0.25 to 0.2%), UCu (0.29 to 0.2%) and UCuZn (0.29 to 0.2%) treatments. In addition, the measured N in plots treated with urea that was coated by multiple chemicals (UPSCu, UAGCu and UGCu) was 0.3 to 0.35% throughout the study period (Figure 2c).

Ammonium-N in soil

The rate of urea hydrolysis was slower in plots treated with coated urea than in plots treated with uncoated urea (Figure 3). Formation of ammonical N was higher in the first through the fifth sampling period (3 months) in plots containing uncoated urea, compared to soils treated with coated urea, which ranged from 10 to 32 μ g g⁻¹ After the first cutting of the pasture, ammonical N started to decline, due to a reduction in added N in soil; however,

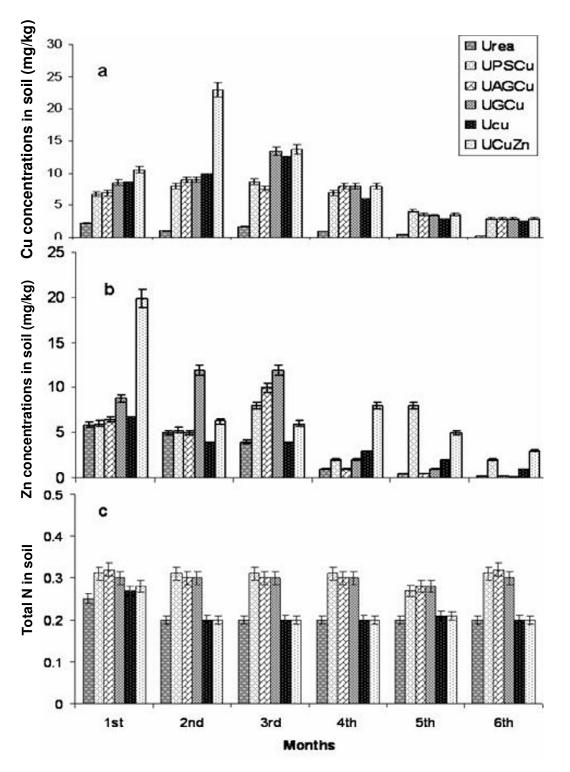


Figure 2. Effect of coated urea treatments on Cu, N and Zn content in soil during experiment, (a) Cu; (b) Zn; (c) total N contents in soil.

the amount of ammonium was estimated to be 5 to 20 μg g^-1 in the coated urea treated plots. The results reveal a

decreased rate of the hydrolysis caused by coating the urea (Figure 3b). The highest mean value of the NH_4 -N

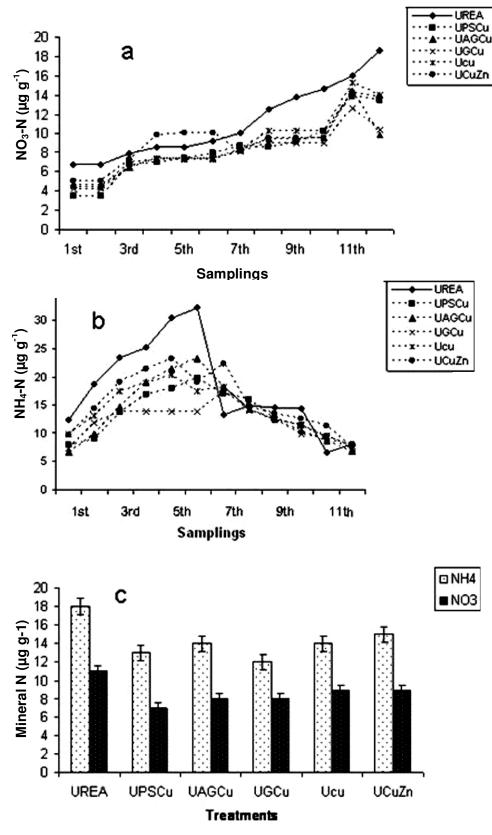


Figure 3. Mineralization of N in soil in six months. (a) NH₄-N; (b) NO₃-N; (c) average mineral N.

Treatment	Dry matter yield	Nutrient concentration in plant			Nutrient uptake in plant (kg ha ⁻¹)		
Treatment	(t ha⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Total N (%)	Cu	Zn	Total N
Urea (U)	17.05 ^a	0.001	0.007	1.8	0.017 ^c	0.12 ^c	32.00 ^d
UPSCu	15.07 ^{bc}	0.01	0.01	2.6	0.015 ^c	0.15 ^b	39.18 ^c
UAGCu	16.67 ^b	0.02	0.01	3.1	0.33 ^b	0.16 ^b	51.67 ^b
UGCu	14.73 [°]	0.04	0.01	2.5	0.58 ^a	0.14 ^{cb}	36.82 ^c
UCu	16.10 ^{ab}	0.02	0.01	3.8	0.32 ^b	0.16 ^b	61.18 ^ª
UCuZn	18.77 ^a	0.03	0.01	3.2	0.53 ^a	0.18 ^a	60.06 ^a

Table 3. Effects of micronutrient coated urea on dry matter yield and nutrient up take (first harvest of grass).

Means with different letters are significantly different by Tukey's test (P< 0.05).

concentration was analysed as 18 μ g g⁻¹ for urea alone. Thus, the ammonium accumulation was lower in coated urea treated soils and was measured as 12 μ g g⁻¹ in the UGCu, 13 μ g g⁻¹ in UPSCu, 14 μ g g⁻¹ in UAGCu and UCu, and 15 μ g g⁻¹ in UCuZn plots (Figure 3c).

Nitrate-N in soil

Nitrification was lower in coated urea plots compared to plots treated with uncoated urea or control (Figure 3). The highest amount of NO₃-N was measured at 11 µg g in the plots treated by using uncoated urea, while the lowest value was recorded for UPSCu at 7 μg g $^{1},$ which was due to special characteristics of palm stearin as a fatty acid. Fatty acids can reduce nitrification due to the presence of lanolin and lanoline acid in their chemical structures (Subbarao et al., 2008). The mean values of NO₃-N for other coated urea treatments were not significantly different from each other and were recorded as follows: 8 μ g g⁻¹ for the UAGCu plots, 8 μ g g⁻¹ for UCu, 9 μ g g⁻¹ for UCu and 9 μ g g⁻¹ for UCuZn. In contrast, all coated urea treated plots were significantly different from the uncoated urea treatment, showing lower rates of nitrification. The reduction in nitrification is attributed to the effects of multiple coating (Figure 3c). A gradual increase was observed for nitrification from month to month in all treatments. Moreover, the amount of NO₃-N was higher (6 to 11 μ g g⁻¹) in soil treated with coated urea during the experiment compared to NO₃-N in soil treated with control. The values were recorded as follows: 3 to13 $\mu g g^{-1}$ for UPSCu, 4 to 9 $\mu g g^{-1}$ for UAGCu, 4 to 10 $\mu g g^{-1}$ for UGCu, 4 to 14 μ g g⁻¹ for UCu and 5 to 15 μ g g⁻¹ for UCuZn (Figure 3b).

Pasture production N, Cu and Zn uptake in the first harvest

Coated urea fertilizers had a significant effect on pasture dry matter production at both the first and second cuttings (Table 3). The pasture production was found in the UCuZn plots at first cutting, indicating that the pasture soil naturally harbour a micronutrient deficiency. However, the treatments of biodegradable material and selected micronutrient coated urea (UPSCu, UAGCu and UGCu) gave lower yield as compared to the control and UCuZn due to slow release of N, but this was not statistically significantly different from control (Table 3). The results of plant data showed that the highest N uptake that occurred in coated urea treated plots was attributed to the physiological effects of Cu and Zn, which affects N availability to plants and reduction of N loss in soil by ammonia volatilization and leaching. The maximum N uptake was recorded for UCu (61.8 kg ha⁻¹) and 32 kg ha⁻¹ for the control (U) (Table 3).

The soil was deficient in Cu and Zn, as shown in Table 1. Copper uptake by plants ranged from 0.017 to 0.58 mg kg⁻¹ for the various treatments and stayed below sufficient levels (5 mg kg⁻¹) (Benton Jones, 2001). More concentrations of Zn were found in Cu coated urea than in the control because the coating chemical CuSO₄ had some impurities with a little amount of Zn (0.1% wt/wt), which had effect on plant Zn content. The maximum Zn content and uptake were observed at 0.01% and 0.18 kg ha⁻¹, respectively for the UCuZn plots. The lowest Zn content was recorded for the U plots, while all other coated urea treatments showed no significant differences in Zn content (Table 3). The data revealed that at first cutting, the control plots produced similar yield as other coated urea treatments except Cu and Zn coated urea. The reason was the fast hydrolysis process of urea and fast availability for plants. However, N. Zn and Cu uptake remained low at U, which indicate high ammonia loss under field conditions (Purkayastha and Chhonkar, 2006).

Pasture production N, Cu and Zn uptake in the second harvest

The recorded yield of plots (t ha⁻¹) treated by coated urea for the second harvest was 17.67 for UPSCu plots, 21.75 for UAGCu, 18.87 for UGCu, 19.17 for UCu and 24.17 for UCuZn, all of which were greater than the U treatment.

Treatment	Dry matter yield	Nutrient concentration in plant			Nutrient uptake in plant (kg ha ⁻¹)		
meatment	(t ha⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg⁻¹)	Total N (%)	Cu	Zn	Total N
Urea (U)	10.75 ^e	0.01	0.01	1.1	0.10 ^d	0.10 ^d	12.00 ^d
UPSCu	17.67 ^d	0.03	0.02	2.6	0.53 ^b	0.35 ^b	46.00 ^b
UAGCu	21.75 ^a	0.03	0.02	2.9	0.65 ^a	0.43 ^b	63.07 ^a
UGCu	18.87 ^c	0.03	0.02	2.2	0.56 ^b	0.37 ^b	41.51 ^b
UCu	19.17 ^b	0.03	0.02	1.3	0.57 ^b	0.38 ^b	25.00 ^c
UCuZn	18.22 ^c	0.02	0.08	1.6	0.36 ^c	1.45 ^ª	29.15 [°]

Table 4. Dry matter yield and nutrient uptake at second cutting of grass.

Means with different letters are significantly different by Tukey's test t (P< 0.05).

Overall, the plots treated with coated urea yielded more than the control plots. Such a difference in pasture dry matter was attributed to the bioavailability of N and the use of micronutrient urease inhibitors in coating the fertilizers. The pasture yield in control plots was greater in the first harvest (17.75 t ha⁻¹) than in the second harvest (10 t ha⁻¹). However, in coated urea treated plots, the amount of grass production increased in the second harvest which showed the beneficial residual effects of coated urea treatments (Table 4). The high dry matter yield in coated urea plot was attributed to slow hydrolysis or mineralization and less ammonia volatilization loss. Soil nutrient levels were lower in the second harvest than for the first harvest in uncoated urea treated plots. The highest nutrient uptake levels were observed in coated urea plots, due to the slow release of nutrients caused by the fertilizer coating. The maximum N uptake (137.85 kg ha⁻¹) was observed in UCuZn plots, while the other treatments showed the following levels of N uptake: 96.73 kg ha⁻¹ for UCu, 94.33 kg ha⁻¹ for UGCu, 87.25 kg ha⁻¹ for UAGCu, and 24.67 kg ha⁻¹ for UPSCu and U (Table 4). The Cu concentrations were 0.05 kg ha⁻¹ for all coated urea treatments. The lowest amount of Cu was measured as 0.1 kg ha 1 in the control (U) plot, and the highest Cu uptake was 0.56 kg ha⁻¹ in the UCuZn plot (Table 4). The UCuZn plots showed the highest Zn content and uptake at 0.08 mgkg⁻¹ and 1.45 kg ha⁻¹ respectively. The minimum quantity of Zn was analysed for the control (U) plots, while all other coated urea treatments showed similar value for Zn content (Table 4).

This study indicates a 25 to 50% increase in pasture production and N uptake due to the application of micronutrients because the soil was deficient in Cu and Zn (Gupta et al., 2008). In addition, it has been reported that coated urea can produce a high yield due to the slow release of nitrogen. This is another potential explanation for the lower yield at the first harvest and the increase in nutrient uptake and pasture production at the second harvest for palm stearin, agar, gelatin and Cu coated urea treatments.

Conclusion

This study revealed that coating urea with natural materials and micronutrients is an effective method of not only increasing pasture production under field conditions. but also reducing urea hydrolysis. The mineralization data indicate a reduction of 30 to 35% in ammonium accumulation and nitrification in soils treated with urea that was coated by multiple chemicals, while a 25% reduction was observed in plots treated only with micronutrient-coated urea. Slow hydrolysis allows urea to remain in fertilized fields for long period of time due to the reduced loss of ammonia via volatilization and increased soil pH caused by high amounts of ammonium accumulation on fertilizer microsite. Urea with multiple coatings enhanced the N availability of urea fertilizer and reduced ammonia loss by reducing soil pH and ammonium accumulation on the soil surface. This study indicates that coating urea with natural materials (agar, gelatin, palm stearin and chemical additives such as Zn and Cu) modified the urea, reduced ammonia volatilization loss and enhanced grass production.

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