

Full Length Research Paper

Reduced loss of NH₃ by coating urea with biodegradable polymers, palm stearin and selected micronutrients

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Accepted 27 May, 2011

In agricultural lands, the loss of NH₃ from surface-applied urea and micronutrient deficiencies are the two most common problems, which can be solved by using coated urea with micronutrients and biodegradable natural materials. These coatings can improve the nutrient status in the soil and simultaneously reduce nitrogen loss from urea. To control ammonia loss and urea's hydrolysis process, two laboratory studies were conducted to compare the effects of using coated urea with that of using only urea. Both studies consisted of consecutive incubation experiments that were conducted on the same Typic Paleudult soil (Serdang Series). Eight treatments (labeled as Urea, UPS1, UPS2, UPS3, UAG1%, UAG2%, UG1% and UG2%) in study 1 and six treatments (labeled U, UPSCu, UAGCu, UGCu, UCu, and UCuZn) in study 2 were prepared and used to determine the effects of various concentrations of natural materials and the inhibitory effects of micronutrients on both ammonia loss and the hydrolysis process. The NH₃ loss was measured by forced draft techniques; the soil's exchangeable ammonium, available nitrate and urea-N were determined by using standard procedures. The outcomes of the study did not show any significant difference among various concentrations of natural material. Coated urea treatments significantly reduced ammonia loss by 30 to 40% in study 1 and by 40 to 67% in study 2 in comparison to urea alone. The same observation was made with respect to urea hydrolysis. All of the coated urea treatments significantly slowed down the hydrolysis process in comparison to urea. The outcomes of the study may improve urea fertilizer by reducing the loss of NH₃ volatilization.

Key words: Biodegradable polymers, coated urea, CuSO₄, NH₃ volatilization loss, urease inhibitor, urea.

INTRODUCTION

Urea is the most popular nitrogen fertilizer due to its high N content, low cost and ease of handling (Mulvaney and Bremner, 1981; Vlek and Byrnes, 1986). However, the poor efficiency of urea as an N-fertilizer was reported widely due to a substantial loss of ammonia (Shamsuddin et al., 2009). Broadcasting urea onto the surface of moist soils results in alkaline microsites after its hydrolysis. An alkaline pH with a high concentration of ammonium ions (NH₄) is the stirring force for NH₃ volatilization. In the past, several strategies were adopted to fulfill the

requirements of plant nutrition and to reduce NH₃ loss from surface-applied urea, such as coating urea with polymers, urease inhibitors and acidifying materials (Fenn and Richards, 1986).

Most of the modified urea forms have limited use due to their high cost and lack of availability (Ahmed et al., 2006). In addition, some of the urease inhibitors are phytotoxic and are banned in most of the world (Watson, 2000).

The use of micronutrients, such as Cu and Zn as inhibitors, was found to effectively reduce ammonia loss from urea (Bremner and Douglas, 1971). Previous studies have shown that Cu and Zn in relatively small amounts are efficient in minimizing urea volatilization loss through urease inhibition. Furthermore, the addition of Cu

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Table 1. Soil properties.

Soil texture	Sandy clay loam
Sand %	50
Clay %	17
Silt %	33
pH in water	5.0
Total C %	2.0
Total N %	0.1
Cu mg kg ⁻¹	0.05
Exchangeable cations	
K (cmol _c kg ⁻¹)	0.2
Mg (cmol _c kg ⁻¹)	4.0
Ca (cmol _c kg ⁻¹)	0.9
Urease activity (µg/g)	15

to urea will give an added advantage because it is an essential micronutrient that has the potential to increase crop yields, especially in Cu deficient soils (Purakayastha and Katyal, 1998; Reddy and Sharma, 2000). Holding urea and a micronutrient together on a fertilizer microsite through the use of biodegradable materials and natural by-products, such as coating or adhesive agents, proves to be a good replacement for synthetic materials, and polymers may be used to reduce environmental hazards. The concept of releasing more than one nutrient through one source is useful for improving the efficiency of chemical fertilizers (Mikkelsen and Behal, 1988). When such alternatives are applied, the modified urea is economically and environmentally useful in large agricultural fields.

This study was conducted to evaluate both the influence of coated urea (with combined coatings of agar, gelatin, palm stearin and micronutrients) on the ammonia volatilization loss as well as urea's hydrolysis process from a sandy loam tropical soil.

MATERIALS AND METHODS

Soil sampling and analysis

A sandy clay loam soil (siliceous, isohyperthermic, Typic Paleudult) was collected from an undisturbed area of Serdang. The soil samples were taken at a 0 to 15 cm depth, air dried and ground to pass a 2 mm sieve. The samples were analyzed for physiochemical properties (Table 1), which included the pH in H₂O (McLean, 1982), organic C (g/kg) (Walkley and Black, 1934), cation exchange capacity (cmol_c /kg), and total N (Bremner and Mulvaney, 1982). A mechanical analysis of the soil was done by using a pipette method, and the texture class was determined by the United States Department of Agriculture (USDA) soil textural triangle.

Preparation of coated urea treatments

Granule urea (100 g) was coated and recoated with palm stearin,

agar, gelatin and different concentrations of CuSO₄ and ZnSO₄ solutions, as mentioned in Table 2. The urea was coated by using a fluidized bed coating machine and was then kept in desiccators for 48 h. The amount of Cu was estimated on the basis of various trials that were performed in the laboratory. For Experiment 1, eight treatments (labeled as T1 (urea alone), T2 (UPS1), T3 (UPS2), T4 (UPS 3), T5 (UAG1%), T6 (UAG 2%), T7 (UG1%) and T8 (UG2%)) were prepared and evaluated to analyze the ammonia volatilization loss as well as urea hydrolysis. Subsequently, on the basis of the outcomes of the first experiment, three selected treatments from Experiment 1 (named UPS1, UAG1%, and UG 1%) were recoated with CuSO₄ as well as with a mixture of CuSO₄ and ZnSO₄. In addition, one more treatment of only CuSO₄ was made to the urea to evaluate its inhibitory effects on the ammonia loss and urea hydrolysis. Six total coated and uncoated urea treatments were prepared and labeled as U (urea alone), UPSCu (palm stearin + Cu coated urea), UAGCu (agar + Cu coated urea), UGCu (gelatin + Cu coated urea), UCu (Cu coated urea), and UCuZn (Cu + Zn coated urea).

Measurement of the NH₃ volatilization

Eight treatments (Table 1) and six treatments (Table 2) were used to compare the percent of ammonia volatilization loss in the sandy clay loam soil. The experimental setup was based on a force draft technique (Siva et al., 1999). The closed dynamic (aerobic) air flow system contained both an air-exchange chamber (500 ml Erlenmeyer flask) and a trapping flask (250 ml Erlenmeyer flask); the stopper on each flask was fitted with an inlet and outlet facility. The inlet was linked to an air pump, while the outlet was connected by polyethylene tubing to the trapping flask. The trapping flask was fitted with a glass distribution rod, which was immersed in a trapping solution of 2% boric acid. The chamber was filled with 300 g of air-dried soil. The soil was wetted at field capacity, and the equivalent of 400 µg/g of urea fertilizer was added to each soil sample. The extracted solution was titrated with a solution of 0.1 N hydrochloric acid once each day until the loss declined by 1% of the N that had been added as coated and uncoated urea. Each fertilizer treatment was replicated three times and arranged in a completely randomized design. The data were analyzed by the analysis of variance and mean comparison procedures (SAS version 9.1; SAS Institute, Cary, North Carolina, USA).

Incubation study

An incubation study was conducted to compare the effect of coated and uncoated urea. The soil samples were treated with 400 µg/g of coated and uncoated urea in both experiments. Each treatment was applied on air-dried, finely ground samples of sandy loam acidic soil (20 g). The 96 soil samples in the first experiment and 72 in the second experiment were incubated in plastic vials of 20 cm³ at a constant moisture and temperature (25°C) for up to four weeks. The treated samples were analyzed weekly for NH₄-N and NO₃-N by using a steam distillation method (Keeney and Nelson, 1982). The experiments were set up in a completely randomized design with three replications, and an analysis of variance (ANOVA) was performed by using SAS version 9.1 (SAS Institute Inc., Cary, N. C.)

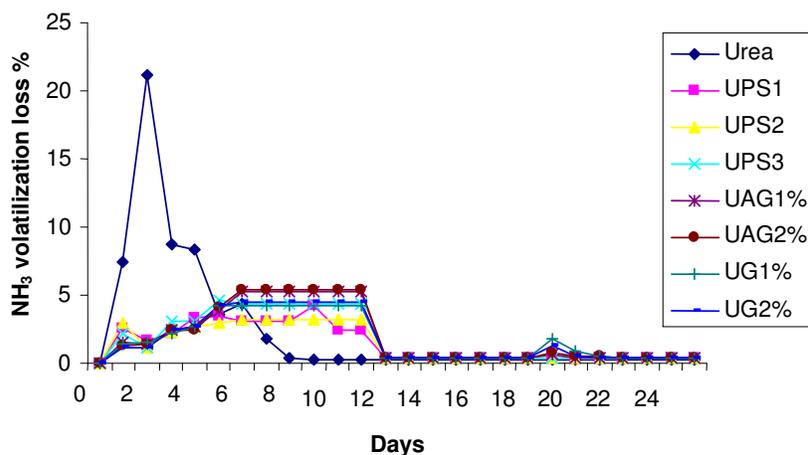
RESULTS AND DISCUSSION

Experiment 1

As shown in Table 1, the selected properties of the soil

Table 2. Fertilizer treatments and the rate of application in each experiment.

Treatment	Weight (g) of coating material per 100 g of urea	N applied in each study ($\mu\text{g g}^{-1}$)
Experiment 1		
Urea (U)	100	400
Palm stearin coated urea (UPS1)	7	400
Palm stearin coated urea (UPS2)	10	400
Palm stearin coated urea (UPS3)	12	400
Agar coated urea (UAG 1%)	1	400
Agar coated urea (UAG 2%)	2	400
Gelatin coated urea (UG1%)	1	400
Gelatin coated urea (UG2%)	2	400
Experiment 2		
Urea (U)	5	400
Palm stearin +Cu coated urea (UPSCu)	5	400
Agar + Cu coated urea (UAGCu)	5	400
Gelatin + Cu coated urea (UGCu)	5	400
Cu coated urea (UCu)	5: 5 (Cu: Zn)	400
Cu + Zn coated urea (UCuZn)	5	400

**Figure 1.** Daily ammonia volatilization loss from soil in Study 1.

were typical of the Serdang series and were consistent with those reported by Paramanathan (2000). In subsequent studies, mineralization and volatilization of coated and uncoated urea were measured and compared concurrently.

The daily ammonia volatilization losses are shown in Figure 1, while the cumulative percent of NH_3 losses are presented in Table 5. The NH_3 loss of U (urea alone) was consistently higher than that of UPS1, UPS2, UPS3, UAG1%, UAG2%, UG1% and UG2%. All of the coated urea treatments effectively reduced the ammonia loss in comparison to the uncoated urea; however, there was no significant difference found among the various concentrations of coatings. The maximum ammonia loss from

treatment U occurred on the 2nd day of the experiment; afterwards, there was a general decline until the 8th day when the ammonia loss was about 1% of the N added as urea. Other treatments that showed a gradual increase in ammonia loss started on the 2nd day of the experiment and continued until the 12th day, at which point it started to decrease in the same way (Figure 2).

A 30 to 45% reduction in the ammonia loss occurred in all of the coated urea-treated soil samples. The cumulative percentage of ammonia loss showed significant differences for all of the treatments with coated urea in comparison to those with uncoated urea (Table 5). The total ammonia loss at the end of the incubation period as a percentage of lost ammonia was 61, 36, 37, 45, 47, 49,

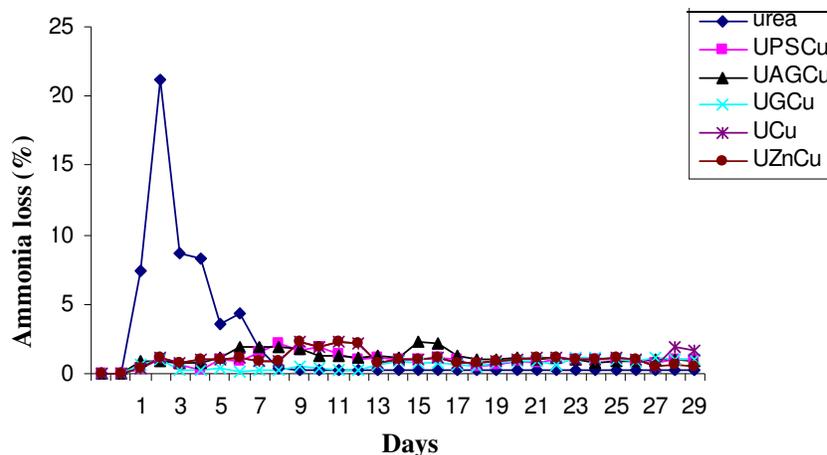


Figure 2. Daily ammonia volatilization loss from soil in study 2.

44 and 44 for Urea (U), UPS1, UPS2, UPS3, UAG1%, UAG2%, UG1% and UG2%, respectively. The addition of urea fertilizer to soils immediately increases the soil's pH and microbial activity, which ultimately increases its hydrolysis in the soil as well as its susceptibility to ammonia volatilization losses. When urea was encapsulated by coatings, it delayed its reaction in the soil, which positively affected its loss from the soil. The reduction in ammonia loss may be attributed to a slower urea hydrolysis and N release from the fertilizer due to the coating (Fan and Mackenzie, 1993).

The urea hydrolysis measurement indicated that the coating of urea significantly reduced the hydrolysis process by reducing the mineralization of N (Figure 3a).

The ammonical-N concentrations were found to be higher in the uncoated urea treated soils (U) after the 7th (92 $\mu\text{g/g}$) and 14th day (143 $\mu\text{g/g}$) of incubation; however, the concentration did not show any significant effects. At the 21st and 30th day, the ammonical-N concentrations decreased in the uncoated urea treatments in comparison to the coated urea treated samples due to slow hydrolysis of urea N with the coated urea treatments. In four weeks, the ammonical-N concentration reduced by 30, 35, 20, 21, 26, and 14% for the UPS1, UPS2, UPS3, UAG1%, UAG2%, UG1% and UG2% treated soils, respectively, in comparison to urea alone (U) (Table 4). Week by week, the ammonium concentration gradually increased due to coating effects, which reduced the release of N from the urea.

The recovery of urea was significantly higher in the Cu coated urea treatments during four weeks as compared to the uncoated urea soils (Figure 3c); therefore, the cumulative amount of available nitrate in the urea treatments was estimated to be 148, 120, 111, 106, 102, 102, 95, and 88 $\mu\text{g/g}$ for urea alone, UAG2%, UPS3, UPS1, UPS2, UG2%, UAG1% and UG1%, respectively, which was lower than that of urea alone (Table 4). A gradual increase in nitrification was observed at 7, 21,

and 30 days in all of the treatments (Figure 3b).

The urea N was found to be 5, 29, 29, 30, 34, 39, 44, and 47 $\mu\text{g/g}$ for urea, UPS2, UPS3, UPS1, UAG2%, UAG1%, UG2%, and UG1% in descending order, respectively (Figure 3c), which may be attributed to coating with layers of natural materials that slow down the release of nitrogen.

There was no significant difference found among the various concentrations that were applied as coatings on the urea; therefore, the urea coatings with minimum concentrations (UPS1, UAG1% and UG1%) were selected for the next experiment.

Experiment 2

The additional coating of CuSO_4 decreased the ammonia loss by more than 50% when it was combined with the urea that was coated with natural material, which proved to have a significant inhibitory effect on the Cu in the soil. This finding was in agreement with previous studies (Reddy and Sharma, 2000), in which a 30% reduction in the percentage of ammonia loss was reported if urea was amended with CuSO_4 . The inhibitory effect of Cu increased after combining it with palm stearin, agar and gelatin-coated urea. The $\text{NH}_3\text{-N}$ emissions from the soil were reduced by 50, 60 and 60% for UPSCu, UAGCu and UGCu, respectively (Table 3). In addition, the urea that was only coated with Cu (UCu) and CU + Zn (UCuZn) also showed a 50% reduction in ammonia loss.

The reduction in ammonia loss was observed more in Study 2 than in Study 1 (Figures 1 and 2) from multiple urea coatings; this may be attributed to multiple coatings of polymers and Cu, which slows down the release of N, inhibits urease activity and reduces the soil's pH by inducing the acidic effects of CuSO_4 fertilizer microsites (Fan and Mackenzie, 1993; Ouyang et al., 1998; Reddy and Sharma, 2000). When the soil's pH was less than

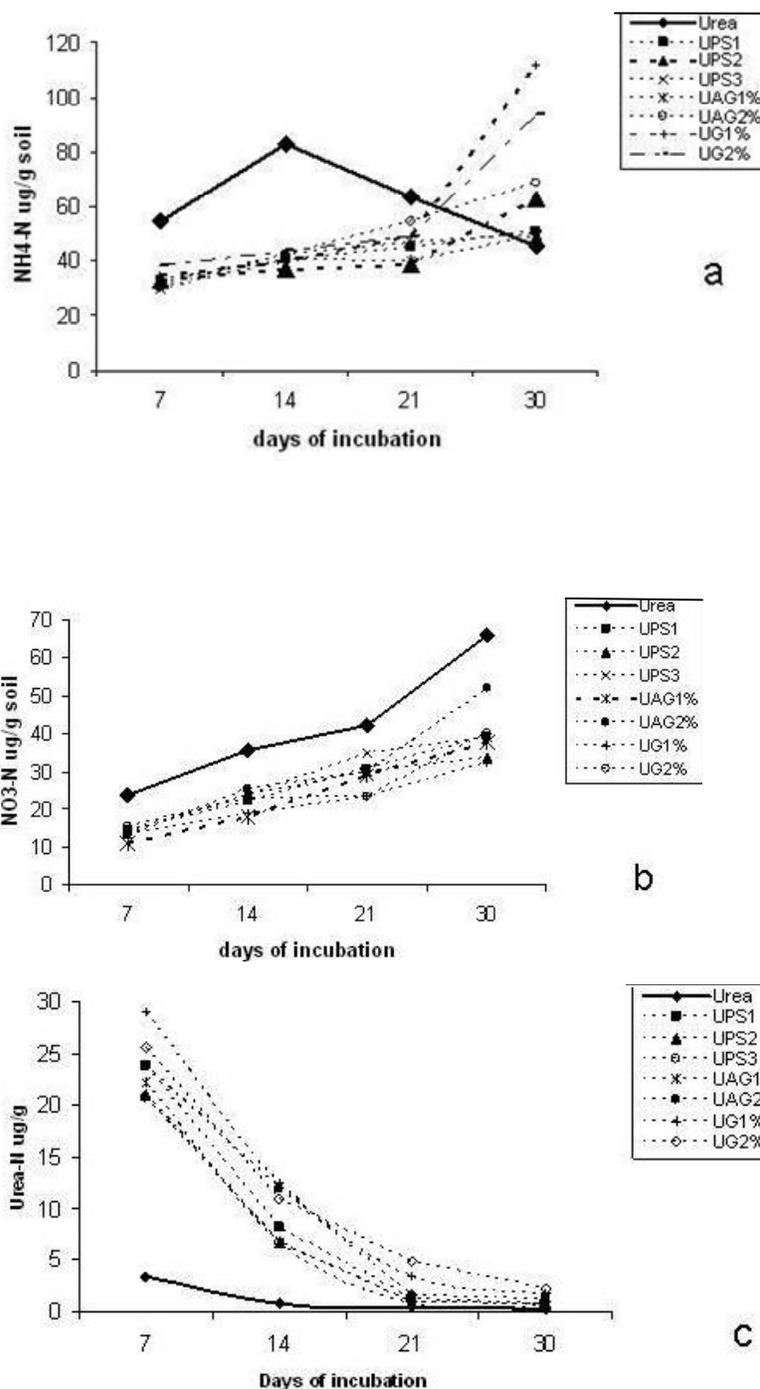


Figure 3. Influence of urea coated with natural biodegradable material on the NH₄-N (a); NO₃-N (b); and Urea - N content (c) in the soil under laboratory conditions (Experiment 1).

5.5, urea hydrolysis became slow (Ahmed et al., 2008).

During the four weeks, the rate of urea hydrolysis was significantly higher in the Cu coated urea treatments as compared to the uncoated urea soils (Figure 4); therefore, the total amount of exchangeable ammonium and available nitrate in treatments UPSCu, UAGCu,

UGCu, UCu and UCuZn were estimated to be lower than that of urea (Table 5). However, the unhydrolyzed urea N was found in higher amounts in the coated urea treatments in comparison to urea alone.

The urea transformation decreased by 50%. Statistically, the cumulative values showed a significant

Table 3. Cumulative percentage of NH₃ loss.

Treatment	NH ₃ loss (%)
Experiment 1	
Urea (U)	61 ^a
Palm stearin coated urea (UPS1)	36 ^c
Palm stearin coated urea (UPS2)	38 ^c
Palm stearin coated urea (UPS3)	45 ^b
Agar coated urea (UAG 1%)	47 ^b
Agar coated urea (UAG 2%)	49 ^b
Gelatin coated urea (UG1%)	44 ^b
Gelatin coated urea (UG2%)	44 ^b
Experiment 2	
Urea(U)	61 ^a
Palm stearin + Cu coated urea (UPSCu)	31 ^b
Agar + Cu coated urea (UAGCu)	20 ^c
Gelatin + Cu coated urea (UGCu)	24 ^{bc}
Cu coated urea (UCu)	35 ^b
Cu + Zn coated urea (UCuZn)	32 ^b

Means with different letters are significantly different at P = 0.05.

Table 4. Effect of various concentrations of biodegradable material as well as coated and uncoated urea on the hydrolysis process in the soil.

Treatment	NH ₄	NO ₃	Urea N
			µg/g
Urea (U)	242 ^a	140 ^a	5 ^d
Palm stearin coated urea (UPS1)	161 ^c	106 ^{bc}	34 ^b
Palm stearin coated urea (UPS2)	172 ^c	102 ^c	29 ^c
Palm stearin coated urea (UPS3)	171 ^c	111 ^{bc}	29 ^c
Agar coated urea (UAG 1%)	171 ^c	95 ^{cd}	39 ^b
Agar coated urea (UAG 2%)	195 ^b	120 ^b	35 ^b
Gelatin coated urea (UG1%)	198 ^b	88 ^d	47 ^a
Gelatin coated urea (UG2%)	207 ^b	102 ^c	44 ^a

Means with different letters are significantly different at P = 0.05.

Table 5. Effect of the urea's coating of micronutrients and biodegradable materials on its hydrolysis.

Treatment	NH ₄	NO ₃	Urea N
			µg/g
Urea (U)	245 ^a	148 ^a	2 ^c
Palm stearin + Cu coated urea (UPSCu)	124 ^b	115 ^c	50 ^b
Agar + Cu coated urea (UAGCu)	110 ^c	112 ^c	74 ^a
Gelatin + Cu coated urea (UGCu)	114 ^c	124 ^b	54 ^b
Cu coated urea (UCu)	134 ^b	121 ^b	47 ^b
Cu + Zn coated urea (UCuZn)	129 ^b	122 ^b	48 ^b

Means with different letters are significantly different at P = 0.05.

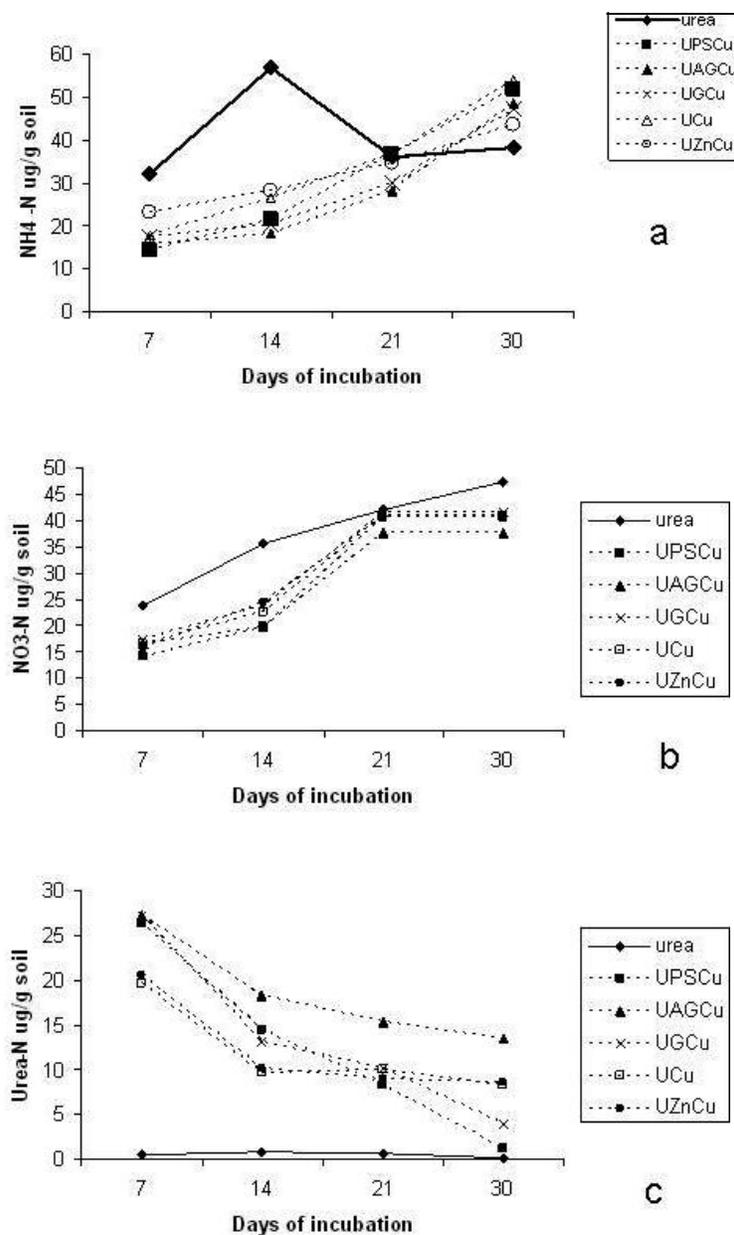


Figure 4. Influence of urea that is coated with natural biodegradable material, Cu and Zn on the NH₄-N (a); NO₃-N (b); and Urea-N content (c) in the soil under laboratory condition.

difference between the Cu-coated urea and the uncoated urea treatments (Table 5). Large amounts of added fertilizer in urea alone were transformed into ammonium ions; the amount transformed in nitrate was 30% of the mineralized N, while nitrification increased day by day (Figure 4b).

The amount of unhydrolyzed urea was lowest (as 2.1 µg/g) in comparison to the Cu-coated urea, which was 50, 74, 54, 47 and 48 µg/g for UPSCu, UAGCu, UGCu, UCu and UCuZn, respectively (Table 5).

The sources of Cu and Zn were CuSO₄ and ZnSO₄,

which are urease inhibitors as well as acidifying materials. In addition, the use of natural materials kept Cu and Zn at the fertilizer microsite with urea, which resulted in a decline in the rate of the hydrolysis process that reduced the ammonia volatilization losses.

Conclusion

These results prove the significance of multiple coatings of urea with biodegradable materials and micronutrients,

which have the ability to reduce ammonia volatilization loss effectively.

ACKNOWLEDGEMENTS

The authors would like to thank the Asian Development Bank for financially supporting the project and the University Putra Malaysia for providing the laboratory facility.

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