

Effects of Urea, Humic Acid and Phosphate Interactions in Fertilizer Microsites on Ammonia Volatilization and Soil Ammonium and Nitrate Contents

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Abstract: The objectives of this study were to compare the effect of four different types of urea-TSP-humic acid mixtures on NH₃ loss, soil NH₄ and NO₃ contents with surface-applied urea (urea alone). Surface soil samples from Typic Kandiuults (Bungor Series) were used. Four different types of urea-TSP-humic acid mixtures and surface-applied urea were compared. All the mixtures significantly reduced ammonia loss ranging between 35 and 50% compared with urea alone. The mixture with the highest amount (1 g) of humic acid showed a pronounced ammonia loss reduction. All the mixtures of acidic P fertilizer and humic acid with urea significantly increased soil NH₄ content but no such observation was made for NO₃. The nitrate contents for all of the five treatments were similar. The mixtures of acidic P fertilizer and humic acid with urea also significantly increased soil exchangeable Ca, K and Mg compared with urea alone. The effect of acidic phosphate and humic acid in the mixtures on NH₃ loss was related to their effect in benefiting formation of NH₄ over NH₃, increase in exchangeable cations and reduction in pH (that may have retarded urea hydrolysis in the fertilizer microsite). Surface-applied urea fertilizer efficiency could be increased if applied together with TSP and humic acid.

Key words: Ammonia volatilization, triple super phosphate, urea, humic acid, ammonium, nitrate, pH

Introduction

Ammonia volatilization is a major pathway for N loss from surface-applied urea (Cai *et al.*, 2002; Prasertsak *et al.*, 2001). Volatilization losses can occur in acid soils due to high pH and NH₄ in the microsite where urea granules dissolve and hydrolyze (Siva *et al.*, 1999; Fan and Machenzie, 1993). A promising approach to the problem involves control of the dissolution and hydrolysis rate of urea. Controlling availability of urea-N by reducing microsite pH with acid materials (Siva *et al.*, 1999; Fan and Machenzie 1993; Stumpe *et al.*, 1984) has received attention in recent years. Urea and TSP mixtures were found to decrease NH₃ and at the same time increased soil NO₃ and NH₄ contents (Fan and Machenzie, 1993). But high level of soil NH₄ without good retention does not guarantee plant N use efficiency. This is because plant N use efficiency can be decreased by the biological transformation of NH₄ to NO₃ (Brady and Well, 2002). Although both NH₄ and NO₃ are plant available forms, NO₃ is more mobile than NH₄ thus making it more susceptible to leaching losses. Also, under anaerobic conditions (Brady and Well, 2002) NO₃ may be biologically denitrified to gasses which

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results in additional N loss from soil (Brady and Well, 2002). One of the means of improving plant N use efficiency of urea and TSP mixtures is to mix urea and TSP with a material that has the ability to retain NH_4 as well as aiding in NH_3 ammonia volatilization reduction. Such a possible material is humic acid because humic acids are known to have chemical properties such as high total acidity (CEC) useful in retaining soil cations (Tan, 2003). Siva *et al.* (1999) has reported pronounced reduction in NH_3 volatilization upon addition of a tropical peat soil to an acid soil. The high reduction of the NH_3 volatilization was indirectly associated with the acidic nature and the high CEC of humic acids in the added peat. We hypothesized that urea combined with TSP and humic acid will not only reduce NH_3 loss but would also lead to effective accumulation of NH_4 in acid soils. The objectives of this study were to compare the effect of four different types of urea-TSP-humic acid mixtures on NH_3 loss and exchangeable NH_4 (formation and retention) and NO_3 contents with surface-applied urea alone.

Materials and Methods

This study was carried out between March and August 2005 in Soil Fertility Laboratory 2 of the Department of Land Management, Universiti Putra Malaysia. The soil type used in this study was a Typic Kandiuults (Bungor Series). Surface soil samples (0-15 cm) were collected from Puchong, Universiti Putra Malaysia Agricultural Farm. The samples were taken from a cultivated field that had received little fertilization. Soil samples were air dried and ground to pass 2 mm sieve. Humic acid and TSP used in this study were also ground to pass 250 μm .

The selected chemical properties of soil, humic acid and TSP were determined using standard procedures. Soil, humic acid and TSP pH [water and (CaCl_2)] were determined on a 1:2 (soil:distilled water/0.01 N CaCl_2) using glass electrode (Peech, 1965). Soil and humic acid organic carbon were determined using a Leco CR-412 total organic carbon analyzer (LECO Corporation, St. Joseph, MI). Soil CEC was determined by leaching with 1 M ammonium acetate buffer adjusted to pH 7.0 followed by the steam distillation techniques (Breemer, 1982), exchangeable K by flame photometry and exchangeable Ca and Mg by atomic absorption spectrophotometry. Carboxylic and phenolic groups and total acidity of the humic acid were determined by the method described by Inbar *et al.* (1990). Generally, N content in humic acids is low so it was not determined.

Five treatments were used. The treatments were as follows: (i) 2.02 g urea only (T_0), (ii) 2.02 g urea + 0.62 g TSP + 0.25 g humic acid (T_1), (iii) 2.02 g urea + 0.62 g TSP + 0.50 g humic acid (T_2), (iv) 2.02 g urea + 0.62 g TSP + 0.75 g humic acid (T_3) and (v) 2.02 g urea + 0.62 g TSP + 1 g humic acid (T_4). The amounts of urea and TSP used were calculated from the standard recommendation for matured oil palms grown on Bungor Series in Malaysia. The humic acid rates were adopted because they gave better mixtures (based on several trials). Additionally, studies have shown that less than 1 g humic acid per kg soil is sufficient to condition soils (Piccolo, 1996). Treatments 1 to 4 were prepared by first weighing the 3 materials (for each treatment) separately into plastic vials. The materials were then transferred into a set of plastic vials, tightly closed and shaken on a reciprocal shaker at 150 rpm for 30 min to ensure that they were thoroughly and uniformly mixed.

Ammonia volatilization was measured for 15 days by a closed-dynamic air flow system method described by Siva *et al.* (1999). At the final recording day (15 days incubation), soil samples were taken at 0-3 cm (microsite) and 3-7.5 cm analyzed for pH, exchangeable NH_4 , Ca, Mg and K. Nitrate was also determined. After 15 days, exchangeable NH_4 and NO_3 were extracted from the soil samples according to the method described by Keeney and Nelson (1982) and their contents determined using a LACHAT Autoanalyzer (LACHAT Instruments, Milwaukee, WI). The exchangeable Ca, Mg and K

were extracted by the double acid method outlined in Tan (1996) and the extractant analyzed as previously mentioned. The experimental design was a completely randomized design with 3 replications. Analysis of variance was conducted to test for treatment effect while means of treatments were compared using Tukey's test. These statistical analyses were conducted using the Statistical Analysis System (SAS Institute, 2001).

Results and Discussion

Some of the chemical characteristics of soil, humic acid, TSP and urea are presented in Table 1. The selected chemical properties of the soil were typical of Bungor Series and were consistent with those reported by Paramanathan (2000). The carbon, phenolic, carboxylic contents and total acidity of the humic acid were within the range reported by Schnitzer (1978). The high total acidity (summation of carboxylic and phenolic contents) indicates the high cation exchange capacity or cation retention ability of the humic acid (Tan, 2003). The reasonable amounts of K, Ca and Mg recorded were not abnormal and indicated that the humic acid was not 100% pure. A reflection of this was the relatively high pH recorded. The pH of the TSP was low but relatively higher than that reported by Sample and Soper (1980). This difference may also be due to the acceptable amounts of K, Mg and Ca in the TSP. The pH of urea was high as expected and very low in the cations analyzed.

The NH₃ loss started a day after incubation for all the treatments except for T₄ where the loss started after 2 days of incubation (probably due to delay in urea hydrolysis) (Fig. 1). The NH₃ loss for T₀, T₁, T₂ and T₃ for the first two days of incubation was similar, after which that of T₄ was consistently higher until the end of the incubation period. It can be noted that T₄ being the treatment with the highest amount of humic acid (1 g) was more pronounced in reducing NH₃ loss compared to the other treatments until the fourth day of incubation, after which NH₃ with time for T₁, T₂, T₃ and T₄ were relatively similar (Fig. 1). A similar observation has been made when an acid soil was acidified with a higher amount of peat (Siva *et al.*, 1999). The maximum loss of NH₃ for T₀ (urea alone) was between 8.5 and 8.57% and the time of peak NH₃ loss occurred between 4 and 5 days after application of urea. The maximum NH₃ loss for T₁, T₂, T₃ and T₄ were 5.93, 5.97, 5.58 and 5.09%, respectively (Fig. 1). The total amounts of NH₃ lost at the end of the study are shown in Table 2. All the treatments with TSP and humic acid (T₁, T₂, T₃ and T₄) significantly reduced NH₃ loss compared to urea alone (T₀). However, T₄ was more pronounced in reducing NH₃ loss than the treatments with lower quantities of

Table 1: Some chemical characteristics of soil, humic acid, TSP and urea

Property	Soil	Humic acid	TSP	Urea
pH (water)	4.54	3.51	2.53	8.07
pH (0.01 CaCl)	3.99	3.03	nd	nd
Phenolic group (cmol kg ⁻¹)	nd	300	nd	nd
Carboxylic group (cmol kg ⁻¹)	nd	433	nd	nd
Total acidity (cmol kg ⁻¹)	nd	733	nd	nd
Total organic carbon (%)	1.19	42.28	nd	nd
Cation exchange capacity (cmol kg ⁻¹)	6.60	733	nd	nd
Exchangeable Al (cmol kg ⁻¹)	1.80	nd	nd	nd
Exchangeable K (cmol kg ⁻¹)	0.01	0.11	nd	nd
Exchangeable Mg (cmol kg ⁻¹)	0.04	1.46	nd	nd
Exchangeable Ca (cmol kg ⁻¹)	0.20	5.40	nd	nd
Soluble K (cmol kg ⁻¹)	nd	nd	0.02	trace
Soluble Mg (cmol kg ⁻¹)	nd	nd	0.54	trace
Soluble Ca (cmol kg ⁻¹)	nd	nd	5.40	0.12

nd = not determined

Table 2: Total amounts of ammonia lost over 15 days of incubation

Treatment	NH ₃ loss (%)
T ₀	48.80 ^a
T ₁	31.51 ^b
T ₂	28.96 ^{bc}
T ₃	26.82 ^{cd}
T ₄	24.62 ^d

Note: Different alphabets indicate significant difference between means using Tukey's test at p = 0.05

Table 3: Effect of treatments on exchangeable ammonium and nitrate accumulation with soil depth

Treatment	Exchangeable ammonium (ppm)		Nitrate (ppm)	
	0-3 cm	3-7.5 cm	0-3 cm	3-7.5 cm
T ₀	838 ^a	520	4.40	2.27
T ₁	1076 ^b	518	5.67	2.13
T ₂	1115 ^{bc}	520	4.23	2.40
T ₃	1166 ^{bc}	520	4.30	2.07
T ₄	1199 ^c	519	5.27	3.07

Note: Different alphabets (within column) indicate significant difference between means using Tukey's test at p = 0.05. No alphabets (within column) indicate no significant difference between means using Tukey's test at p = 0.05

humic acid, particularly T₁ and T₂. The findings agree with the works of Siva *et al.* (1999) and Fan and Mackenzie (1993) who also found a reduction in NH₃ loss when urea was mixed with TSP or peat. The workers found that when urea was mixed with TSP or peat, the acidic products lowered microsite pH, reduced urea hydrolysis (microsite) and caused a large reduction in NH₃. In this study, the phosphoric acid produced from hydrolysis of TSP and humic acid in the soil (microsite) might have acidified the soil surrounding the urea-phosphate-humic acid mixture (microsite) to slow urea hydrolysis (microsite) and this might have caused urea to diffuse out the acidified soil and hydrolyzed (Fan and Mackenzie, 1993). This may have effectively increased the volume of soil with which urea mixed with and also increased the time required for complete hydrolysis (Fan and Mackenzie, 1993). After urea hydrolysis, the lower pH might have benefited the formation NH₄⁺ over NH₃ (Fan and Mackenzie, 1993).

There was significant accumulation of exchangeable NH₄ at 0-3 cm depth (microsite) for all the mixtures (T₁, T₂, T₃ and T₄) with TSP and humic acid compared to urea alone (T₀) but no such observation was made for NO₃ at the same depth (Table 3). The former finding was consistent with the works of Siva *et al.* (1999) and Fan and Mackenzie (1993) but the latter observation contradicted the finding of Fan and Mackenzie (1993) where they reported significant accumulation of NO₃ for urea-phosphate treatments. This difference can be explained based on the fact that in this present study, the addition of humic acid might have improved the soil NH₄ retention ability at 0-3 cm depth and hence favoring adsorption of NH₄ over rapid NH₄ nitrification to form NO₃. The fact that NH₄ at 0-3 cm depth was higher than at 3-7.5 cm depth as well as no significant difference between exchangeable NH₄ and NO₃ contents of T₁, T₂, T₃ and T₄ and urea alone at 3-7.5 cm depth also proves the effectiveness of the humic in improving NH₄ retention at 0-3 cm only. The improvement in the soil retention ability of NH₄ at 0-3 cm may also partly explain the high loss of NH₃ for urea alone in this study as it was possible that increased alkalinity from urea hydrolysis may have exceeded the buffer capacity or the retaining ability of soil near the microsite of urea alone compared to the treatments with humic acid which had higher exchangeable NH₄. Hence the significant loss of NH₃ from the microsite where urea alone was applied.

The above observation in NH₄ retention can be useful in improving urea efficiency because high level of soil NH₄ without effective retention does not guarantee plant N use efficiency. This is because plant N use efficiency can be decreased by the biological transformation of NH₄ to NO₃

Table 4: pH status of soil at the end of the experiment

Treatment	pH	
	0-3 cm	3-7.5 cm
T ₀	7.20	7.33
T ₁	7.14	7.26
T ₂	7.32	7.25
T ₃	7.29	7.00
T ₄	7.42	7.19

Note: No significant difference within column between means using Tukey's test at p = 0.05

Table 5: Exchangeable Ca at the end of the experiment

Treatment	Exchangeable Ca (cmol kg ⁻¹ soil)	
	0-3 cm	3-7.5 cm
T ₀	0.09 ^a	0.09 ^a
T ₁	2.55 ^b	0.34 ^b
T ₂	2.66 ^b	0.30 ^b
T ₃	2.92 ^b	0.31 ^b
T ₄	3.08 ^b	0.31 ^b

Note: Different alphabets within column indicate significant difference between means using Tukey's test at p = 0.05

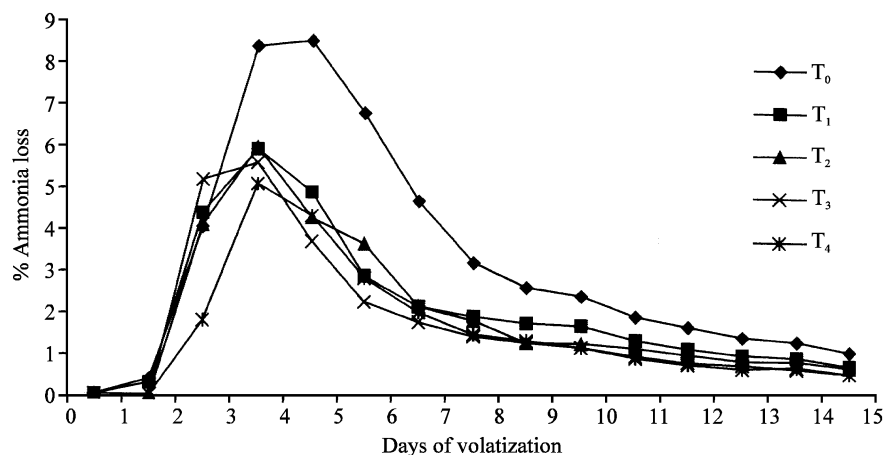


Fig. 1: Ammonia volatilization with time

(Brady and Well, 2002). Although both NH₄ and NO₃ are plant available forms, NO₃ is more mobile than NH₄ thus making it more susceptible to leaching losses particularly in areas of high rainfall. Also, under anaerobic conditions (Brady and Well, 2002) NO₃ may be biologically denitrified to gasses which results in additional N loss from soil (Brady and Well, 2002).

Regardless of treatment, the pH at 0-3 and 3-7.5 cm depths at the end of the study were not significantly different (Table 4). This could be due to the fact that on the fifteenth day of the experiment, the rates of NH₃ evolution from all the treatments were relatively not different (Fig. 1). The NH₃ loss during this period was around 1% for all the treatments. A study has shown that it took about 18 days for the pH of an acid soil with surface-applied urea-phosphate fertilizer to reach neutrality (Urban *et al.*, 1987).

Table 6: Exchangeable Mg at the end of the experiment

Treatment	Exchangeable Mg (cmol kg ⁻¹ soil)	
	0-3 cm	3-7.5 cm
T ₀	0.014 ^a	0.016 ^a
T ₁	0.087 ^b	0.027 ^b
T ₂	0.094 ^b	0.025 ^b
T ₃	0.121 ^b	0.027 ^b
T ₄	0.134 ^b	0.027 ^b

Note: Different alphabets within column indicate significant difference between means using Tukey's test at p = 0.05

Table 7: Exchangeable K at the end of the experiment

Treatment	Exchangeable K (cmol kg ⁻¹ soil)	
	0-3 cm	3-7.5 cm
T ₀	0.007 ^a	0.005
T ₁	0.014 ^b	0.006
T ₂	0.013 ^b	0.006
T ₃	0.016 ^b	0.006
T ₄	0.015 ^b	0.005

Note: Different alphabets (within column) indicate significant difference between means using Tukey's test at p = 0.05. No alphabets (within column) indicate no significant difference between means using Tukey's test at p = 0.05

The exchangeable Ca, Mg and K for the mixtures were significantly higher than that of urea alone at 0-3 and 3-7.5 cm depths except for exchangeable K at 3-7.5 cm depth where no significant difference was observed between all the treatments (Table 5-7). The general response might be through the addition of these cations from TSP and humic acid (Table 1). Formation of metastable reaction products such as Ca(NH₄)₂(HPO₄)₂ (Terman, 1979) may have also been responsible in part for the greater effect on reducing NH₃ volatilization by treatments with humic acid and TSP compared to urea alone.

Conclusions

The results indicate that applying urea with TSP and humic acid may offer a significant advantage over urea alone as applying urea with TSP and humic acid has the ability to benefit formation of NH₄ over NH₃ thus increasing surface-applied urea fertilizer efficiency as well as contributing to reduction of environmental pollution through excessive use of N fertilizers.

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