

Controlling Ammonia Volatilization by Mixing Urea with Humic Acid, Fulvic Acid, Triple Superphosphate and Muriate of Potash

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Abstract: Problem statement: Inefficient use of inorganic fertilizer such as urea is caused by substantial losses of ammonia when urea is surface-applied. Ammonia losses can be controlled by adding acidic material such as TSP, HA or FA. In order to reduce ammonia loss and retain soil exchangeable ammonium and available nitrate as well as producing complete organic based fertilizer, this study was conducted to compare the effects of urea-TSP-MOP, urea-TSP-MOP-HA, urea-TSP-MOP-FA, urea-TSP-MOP-acidified (HA + FA) mixtures on ammonia loss, soil pH, soil exchangeable ammonium and available nitrate accumulation compared to urea alone. **Approach:** The effects of urea amended with or without TSP, MOP, HA and FA were evaluated in a laboratory condition using a closed-dynamic air flow system. Ammonia loss, soil pH, soil exchangeable ammonium and available nitrate were determined using standard procedures. **Results:** Urea-TSP-MOP-HA, Urea-TSP-MOP, Urea-TSP-MOP-FA and Urea-TSP-MOP-Acidified (HA + FA) mixtures significantly reduces ammonia loss by 12.92, 20.12, 29.54 up to 100 % compared to urea alone. The same observation was made for soil exchangeable ammonium. From all the treatments, only Urea-TSP-MOP-FA and Urea-TSP-MOP-Acidified (HA + FA) significantly retained soil available nitrate accumulation and the findings were consistent with pH found in the study. It must be stressed that results obtained in the incubation experiment using an acidic ($\text{pH}_{\text{water}} 6.32$) soil of Typic Paleudults (Bekenu series) might only be applicable to similar acid soils. **Conclusion:** Urea, TSP and MOP amended with HA or HA and FA significantly reduced ammonia loss. The outcome of this study may contribute to the improvement of urea N, P and K use efficiency as well as reducing environmental pollution.

Key words: Ammonia volatilization, urea, triple superphosphate, muriate of potash, humic acids, fulvic acids, pH, exchangeable ammonium, available nitrate

INTRODUCTION

Malaysia is the largest producer and exporter of palm oil in the world^[1] and this contributes about US\$ 7.3 billion in export earnings each year^[2]. With such large production of palm oil there is also abundant by-products such as Palm Oil Mill Effluent (POME). The POME contains high Bio-Chemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) which pose a great threat to water environment. Disposal of this highly polluting waste is an economic burden on communities and industries^[3] therefore adding value to this waste could be economically viable.

POME could be put into good use in view of its high content of organic matter^[1] potentially present in the form of Humic Acids (HA) and Fulvic Acids (FA).

In some studies, acidic material such as HA and TSP have been used to reduce ammonia loss from surface-applied urea^[4-8] but an information such as this is lacking for POME. These acidic materials lower the soil microsite pH immediately around the fertilizer, reduce the hydrolysis of urea thus reducing the ammonia loss. The use of MOP may help to prevent the deficiency of chlorine under field conditions since chlorine is only very weakly adsorbed to soil colloids^[9]. High total acidity (CEC) associated with HA aid to retain NH_4 and NO_3 ^[4-7] which are the plant usable form of nitrogen. The exchange capacity of FA is more than double that of HA due to the total number carboxyl (COOH) groups present and this is expected to retain more NH_4 and NO_3 . High contents of NH_4 and NO_3 in the soil without good retention may not guarantee plant

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N use efficiency because both NH_4 and NO_3 are prone to leaching^[9]. The additional loss of N from soil is caused by the biological transformation of NH_4 to NO_3 under anaerobic condition and denitrification process of converting NO_3 to N_2 ^[9]. Inefficient use of urea gives impact to economy, waste of money and reduces crop quality. The objective of the study was to compare the effects of urea-TSP-MOP, urea-TSP-MOP-HA, urea-TSP-MOP-FA, urea-TSP-MOP-acidified (HA + FA) on NH_3 loss, pH, exchangeable NH_4 and available NO_3 accumulation with urea alone. This study may improve urea N use efficiency as well as reducing environmental pollution.

MATERIALS AND METHODS

The soil used in this study was a sandy loam of typic paleudults (Bekenu series) taken from University Putra Malaysia, Bintulu Sarawak campus. The soil samples taken at 0-15 cm depth were air dried and ground to pass a 2 mm sieve. The selected chemical and physical properties of the soil were determined using standard procedures. The soil pH was determined in a 1:2.5 of soil: Distilled water suspension and 1 M KCl using a glass electrode. Soil organic carbon was determined by 58% of the total loss of weight on ignition^[10]. The hydrometer method was used to determine soil texture^[11]. The leaching method was used to determine cation exchange capacity. The exchangeable cations (K, Ca, Na and Mg) were determined by the double acid method. Total N was determined using Micro-kjedhal method.

HA and FA used in this study were isolated using the method described by Stevenson^[12] with some modifications^[13]. The extraction and fractionation periods used were 24 h. Humic acid and FA was isolated using 0.05 M KOH and 6 N H_2SO_4 , respectively. Total organic carbon was determined using loss on ignition method^[10]. The carboxylic-COOH, phenolic-OH functional groups and total acidity were determined by the method described by Inbar *et al.*^[14]. E_4/E_6 was determined using E_4/E_6 ratio^[13]. The solid HA and TSP were ground to pass 250 μm , the MOP was in powder form and the urea was in granules form. Fulvic acid and acidified HA + FA were in liquid form.

The treatments evaluated were:

- Soil alone (T0) (1)
- 2.02 g urea without additives (T1) (2)
- 2.02 g urea+1.52 g TSP+1.34 g MOP (T2) (3)

2.02 g urea+1.52 g TSP+1.34 g MOP+0.75 g HA (T3) (4)

2.02 g urea+1.52 g TSP+1.34 g MOP+60 mL FA (T4) (5)

2.02 g urea+1.52 g TSP+1.34 g MOP+60 mL Acidified (HA + FA) (T5) (6)

The quantity of urea, TSP and MOP used were based on the standard recommendation for mature oil palms grown on Bungor Series (Typic Kandiuudults) in Malaysia. The amounts of HA used were based on earlier unpublished laboratory trials that gave better mixtures. Treatment 2 was prepared by mixing 2.02 g urea with 1.52 g TSP and 1.34 g MOP. Treatment 3 was prepared by mixing 2.02 g urea with 1.52 g TSP, 1.34 g MOP and 0.75 g HA. Treatment 4 was prepared by mixing 2.02 g urea with 1.52 g TSP, 1.34 g MOP and 60 mL FA, while T5 was prepared by mixing 2.02 g urea with 1.52 g TSP, 1.34 g MOP and 60 mL acidified HA and FA. Afterwards, the treatments were transferred into a set of plastic vials, tightly closed and shaken on a reciprocal shaker at 150 rpm for 30 min to ensure they were uniformly mixed.

Daily ammonia loss was measured for 15 days by the closed-dynamic air flow system method^[4]. The system consisted of an exchange chamber (500 mL Erlenmeyer flask) and a trap (250 mL Erlenmeyer flask), both stoppered and fitted with an inlet/outlet. The inlet of the chamber was connected to an air pump and the outlet was connected by polyethylene tubing to the trap containing boric acid solution. The 250 g of soil that was placed in the exchange chamber was moistened to 60% field capacity.

The treatments were applied to the soil surface. Air was passed through the chambers at a rate of 2.75 $\text{L}^{-1} \text{min}^{-1} \text{chamber}^{-1}$ and released NH_3 captured in the trapping solution containing 75 mL boric acid bromocresol green and methyl red indicator. The incubation chambers were maintained at room temperature. Boric acid indicator traps were replaced every 24 h and back titrated with 0.01 N HCl, to estimate the NH_3 released. Measurement was continued until the loss declined to 1% of the N added in the urea^[5,7,8]. After 15 days of incubation, soil samples were evaluated for pH, exchangeable NH_4 and available NO_3 ^[15].

The experimental design was a randomized complete block design with 3 replications for each treatment. Analysis of variance (ANOVA) was conducted to test for treatment effect while means of treatments were compared using Tukey's test^[16].

RESULTS

The chemical and physical characteristics of soil, HA, FA and acidified (HA + FA) are shown in Table 1.

Table 1: Some chemical and physical characteristics of soil, HA, FA and acidified (HA + FA)

| Property | Soil | HA | FA | Acidified (HA + FA) |
|---|------|--------|------|---------------------|
| pH (water) | 6.32 | nd | 1.13 | 1.00 |
| pH (1N MOP) | 5.52 | nd | nd | nd |
| Total organic carbon (%) | 4.72 | 54.95 | nd | nd |
| Nitrogen (%) | 0.17 | nd | nd | nd |
| CEC (cmol kg ⁻¹) | 13.3 | nd | nd | nd |
| Exchangeable K (cmol kg ⁻¹) | 0.18 | nd | nd | nd |
| Exchangeable Ca (cmol kg ⁻¹) | 1.21 | nd | 0.89 | nd |
| Exchangeable Na (cmol kg ⁻¹) | 0.01 | nd | 2.78 | nd |
| Exchangeable Mg (cmol kg ⁻¹) | 0.12 | nd | 0.29 | nd |
| Texture | LS | nd | nd | nd |
| Carboxylic group (cmol kg ⁻¹) | nd | 538.81 | nd | nd |
| Phenolic group (cmol kg ⁻¹) | nd | 293.89 | nd | nd |
| Total acidity (cmol kg ⁻¹) | nd | 832.70 | nd | nd |
| E ₄ /E ₆ | nd | 8.02 | nd | nd |

CEC: Cation Exchange Capacity; LS: Loamy Sand; nd: Not determined; *CEC of HA: Total acidity

Table 2: pH of urea, TSP and MOP

| Property | Urea | TSP | MOP |
|----------|------|------|------|
| pH | 8.06 | 2.89 | 7.52 |

The selected chemical properties of the soil were typical of the Typic Paleudults (Bekenu Series) and were consistent with those reported by Paramanathan^[17] except for the high values of pH, organic carbon, CEC and exchangeable calcium. The pH of HA and FA were low. The carbon, carboxylic, phenolic, total acidity and E₄/E₆ values of the HA were within the range reported by some authors^[12,18]. The pH of urea was high as expected (Table 2). The pH of TSP was low and the pH of MOP was neutral.

Daily loss of ammonia is shown in Fig. 1. Ammonia loss started a day after incubation for urea, three days of incubation for T2, T3 and T4 while no loss was found for T5. T2, T3, T4 and T5 reduced the maximum daily rate of loss of ammonia from 13-6.24, 9.18, 6.26 and 0% (of the N added as urea) respectively. The maximum ammonia loss for T1 occurred on the second day, T3 and T4 on the fourth day, T2 on the seventh day of incubation when the ammonia loss was about 1% of the N added as urea. The total amounts of ammonia lost at the end of the incubation period as a percentage of urea-N were 0, 48.21, 38.51, 41.98 and 0% for T0, T1, T2, T3, T4 and T5 respectively (Table 3).

All the treatments with TSP, MOP, FA, HA significantly reduced ammonia loss compared with urea without additives (T1) with T5 mixture of urea, HA, FA, TSP and MOP having the greatest effect on ammonia loss. Ammonia loss was found to be zero for T0 and T5. No loss for T0 shows the soil does not contribute to ammonia loss in this study. The reduction of ammonia loss was highly related to the significantly low soil pH obtained for T4 and T5 with significantly highest retention of soil nitrate compared to urea alone.

Table 3: Total amounts of ammonia loss, pH, exchangeable ammonium and available nitrate over 15 days of incubation

| Treatments | NH ₃ (%) | pH (H ₂ O) | NH ₄ (ppm) | NO ₃ (ppm) |
|------------|---------------------|-----------------------|-----------------------|-----------------------|
| T0 | 0.00 ^e | 6.7 ^d | 81.73 ^e | 11.68 ^c |
| T1 | 48.21 ^a | 7.9 ^{bc} | 378.27 ^d | 23.35 ^c |
| T2 | 38.51 ^c | 8.4 ^{ab} | 665.48 ^b | 30.36 ^c |
| T3 | 41.98 ^b | 7.7 ^c | 651.47 ^c | 28.02 ^c |
| T4 | 33.97 ^d | 6.2 ^e | 1169.84 ^a | 123.76 ^a |
| T5 | 0.00 ^e | 2.8 ^f | 546.39 ^c | 58.38 ^b |

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

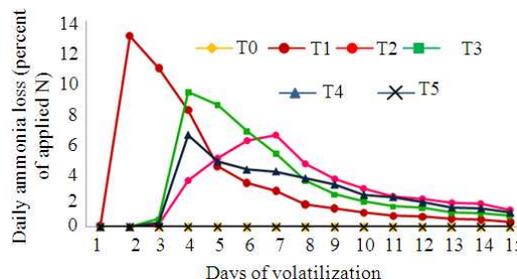


Fig. 1: Daily loss of ammonia from incubation

Soil pH and nitrate accumulation for T2 and T3 was found not significantly different from urea alone.

There was a significant accumulation of soil exchangeable ammonium for all the treatments compare to urea without additives. Exchangeable ammonium retention was twice for T4 compared to T2, T3 and T5. Available nitrate accumulation was better for T4 and T5.

DISCUSSION

The values of pH, organic carbon, CEC and exchangeable calcium in selected chemical properties of the soil were higher compared to those reported by Paramanathan^[17] may be due to liming. The low pH of HA and FA suggests that they were fully saturated with hydrogen ions during their fractionation via acidification using 6 N H₂SO₄. The consistent values of carbon, carboxylic, phenolic, total acidity and E₄/E₆ of the HA indicates the purity of the acids.

A rapid loss of ammonia from urea alone was probably due to increased of pH at the soil microsite as urea hydrolysis leads to consumption of hydrogen ions (H⁺) from the soil solution. Removal of more H⁺ associated with low buffering capacity of soil used in the study, increased the soil pH and enhanced more formation of NH₄ over NH₃. The rate of urea hydrolysis for urea-TSP-MOP, urea-TSP-MOP-HA and urea-TSP-MOP-FA mixtures were slower by 2 days than volatilization of urea alone because more hydrogen ion contained in phosphoric acid or in the HA and FA's

functional groups effectively replaced the removed H^+ during urea hydrolysis thus aiding in buffering the soil pH from increasing sharply and slowing down the rate of ammonia volatilization. The greatest effect can be seen from the mixture of urea-TSP-MOP-acidified (HA + FA) whereby the combination of the two acids (HA and FA) together with TSP and MOP significantly slowed the rate of urea hydrolysis by hundred percent. The combination of the two gave such result due to increased number of functional groups embedded in them.

The significant reduction of ammonia volatilization and higher amount of soil exchangeable ammonium for urea-TSP-MOP mixtures was because of phosphoric acid produced by hydrolysis of acidic phosphate. The acid might have acidified the soil microsite and resulted in low pH that encouraged higher formation of ammonium over ammonia^[8].

Urea-TSP-MOP-HA mixtures effectively reduced ammonia loss and retained soil exchangeable ammonium compared to urea alone. The acidic nature and high CEC of HA aided in reduction of ammonia loss and retained soil exchangeable ammonium^[4]. However, the addition of HA in the urea-TSP-MOP mixtures was not beneficial since the mixtures alone without HA able to reduce NH_3 loss and improved NH_4 retention. This may be due to K^+ contained in the acid that reduce the quantity of H^+ in the mixtures thus increased soil pH.

The mixtures of urea-TSP-MOP-FA significantly reduced ammonia volatilization with the highest accumulation of soil exchangeable ammonium and available nitrate. The reduction was favored by the addition of both phosphoric acid and FA. The exchange capacity of FA is twice that of HA due to the total number carboxyl (COOH) groups present and this helped to hold more exchangeable ammonium from converting to ammonia. The significantly low pH retarded the urea hydrolysis in the soil microsite immediately around the fertilizer^[7].

The mixture of urea, HA, FA, TSP and MOP had a greatest effect reducing ammonia loss up to hundred percent and also retained exchangeable ammonium and available nitrate in the soil compared to urea without additives. Zero loss of ammonia related to the low pH found in the study that also confirms the work of Delaune and Patrick^[19,20] that urea hydrolyzes slowly when soil pH is less than 5.5 and lasted until it moves away from the acidified soil^[5,19]. The amendment effectively increased the volume of soil with which urea was mixed and increased the time required for complete hydrolysis^[5].

CONCLUSION

Urea-TSP-MOP-HA, Urea-TSP-MOP, Urea-TSP-MOP-FA and Urea-TSP-MOP-Acidified (HA + FA) mixtures significantly reduced ammonia loss by 12.92, 20.12, 29.54 up to 100% compared to urea alone. The similar observation was made for soil exchangeable ammonium. Urea-TSP-MOP-FA and Urea-TSP-MOP-Acidified (HA + FA) significantly increased soil available nitrate accumulation and the findings were consistent with pH found in the study. It must be stressed that results obtained in the incubation experiment using an acidic (pH_{water} 6.32) soil of Typic Paleudults (Bekenu Series) may only be applicable to similar acid soils. The outcome of this study may contribute to the improvement of urea N, P and K use efficiency as well as reducing environmental pollution.

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