

Reduction of Ammonia Volatilization through Mixing Urea with Humic and Fulvic Acids isolated from Palm Oil Mill Effluent Sludge

¹Shamsuddin Rosliza, ¹Osumanu Haruna Ahmed,
²Nik Muhamad Ab. Majid and ³Mohamadu Boyie Jalloh
¹Department of Crop Science, Faculty of Agriculture and Food Sciences,
University Putra Malaysia Bintulu Campus, 97008 Bintulu, Sarawak, Malaysia
²Department of Forest Management, Faculty of Forestry,
University Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
³School of Sustainable Agriculture, University Malaysia Sabah,
Locked Bag 2073, 88999 Kota Kinabalu, Sabah, Malaysia

Abstract: Problem statement: Ammonia volatilization from surface-applied urea may be substantial but it is possible to control it by mixing urea with acidic substances such as Humic Acids (HA) and Fulvic Acids (FA). The objective of this study was to compare the effects of urea-HA, urea-FA, urea-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 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:** Humic acid alone was not effective in controlling ammonia volatilization even though ammonium retention was found to be significantly higher compared to urea alone. Fulvic acid significantly reduced ammonia volatilization by 50% compared to urea alone. It also caused the highest retention of soil exchangeable ammonium and available nitrate. However, there was no ammonia volatilization with acidified HA and FA. Ammonium and nitrate accumulation for FA was better than acidified HA and FA. Ammonia loss could be reduced by improving ammonium retention. 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) may only be applicable to similar acid soils. **Conclusion:** Urea amended with HA or HA and FA significantly reduced ammonia loss. The outcome of this study might be contributed to the improvement of urea N use efficiency as well as reducing environmental pollution.

Key words: Ammonia volatilization, urea, 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 evidence of this type is lacking for POME. These acidic materials lower the soil micro-site pH immediately around the fertilizer, hence, they reduce the hydrolysis of urea thus reducing the ammonia loss. High total acidity (CEC) associated with HA aids in retaining NH_4 and NO_3 ^[4-7] compounds which are the plant usable form of nitrogen. The exchange capacity of FA is double that of HA due to the

Corresponding Author: Osumanu Haruna Ahmed, Department of Crop Science, Faculty of Agriculture and Food Sciences, University Putra Malaysia Bintulu Campus, Sarawak, Malaysia Tel: +6086855406 Fax: +608685415

total number carboxyl (COOH) groups present and this also helps to retain more NH_4 and NO_3 . High contents of NH_4 and NO_3 in soils without good retention may not guarantee plant 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 may cause environmental pollution, monetary loss and poor crop quality. The objective of this study was to compare the effects of urea-HA, urea-FA, urea-acidified (HA+FA) on NH_3 loss, pH, exchangeable NH_4 and available NO_3 accumulation with urea alone. This study may contribute to improvement of 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 as 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^[12]. The exchangeable cations (K, Ca, Na and Mg) were determined by the double acid method^[13]. Total N was determined using Kjeldhal method.

HA and FA used in this study were isolated using the method described by Stevenson^[14] with some modifications^[15,16]. The extraction and fractionation periods used was 24 h. HA and FA were isolated using 0.05 M KOH and 6 N H_2SO_4 respectively. Total organic carbon was determined using the loss on ignition method^[10]. The carboxylic-COOH, phenolic-OH functional groups and total acidity were determined using the method described by Inbar *et al.*^[17]. The E_4/E_6 was determined using E_4/E_6 ratio^[14]. The solid HA was ground to pass 250 μm and the urea was in granular form. FA and acidified (HA+FA) were in liquid form.

The treatments were: (i) Soil alone (T0); (ii) 2.02 g urea without additives (T1); (iii) 2.02 g urea + 0.75 g HA (T2); (iv) 2.02 g urea + 60 mL FA (T3); (v) 2.02 g urea + 60 mL acidified (HA+FA) (T4). The quantity of

urea used was based on the standard recommendation for mature oil palms grown on Bungor Series (Typic Kandiuults) 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 0.75 g HA. Treatment 3 was prepared by mixing 2.02 g urea with 60 mL FA, while T4 was prepared by mixing 2.02 g urea with 60 mL acidified HA and FA. Afterwards, the treatments were transferred into a set of plastic vials, tightly closed and shaken using a reciprocal shaker at 150 rpm for 30 min to ensure they were uniformly mixed.

Daily ammonia loss was measured for 15 days using the closed-dynamic air flow system method^[5]. 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. Soil weighing 250 g was placed in the exchange chamber and 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 $\text{L}^{-1} \text{min}^{-1}$ 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 .

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^[18].

RESULTS

The selected chemical properties of soil (Table 1) were typical of the Bekenu Series and were consistent with those reported by Paramanathan^[19] except for the high values of pH, organic carbon, CEC and exchangeable calcium which may be due to soil liming. The pH of urea was high as expected. The carbon, carboxylic, phenolic, total acidity and E_4/E_6 values of the HA were within the range reported by^[14,20].

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

Property	Soil	Urea	HA	FA	Acidified (HA + FA)
pH (water)	6.32	8.06	nd	1.13	1.00
pH (1N KCl)	5.52	nd	nd	nd	nd
Total organic carbon (%)	4.72	nd	54.95	nd	nd
Nitrogen (%)	0.17	nd	nd	nd	nd
CEC (cmol kg ⁻¹)	13.3	a	nd	nd	nd
Exchangeable K (cmol kg ⁻¹)	0.18	nd	nd	nd	nd
Exchangeable Ca (cmol kg ⁻¹)	1.21	nd	nd	0.89	nd
Exchangeable Na (cmol kg ⁻¹)	0.01	nd	nd	2.78	nd
Exchangeable Mg (cmol kg ⁻¹)	0.12	nd	nd	0.29	nd
Texture	LS	nd	nd	nd	nd
Carboxylic group (cmol kg ⁻¹)	nd	nd	538.81	nd	nd
Phenolic group (cmol kg ⁻¹)	nd	nd	293.89	nd	nd
Total acidity (cmol kg ⁻¹)	nd	nd	832.70	nd	nd
E _d /E ₆	nd	nd	8.02	nd	nd

CEC: Cation Exchange Capacity; LS: Loamy Sand; nd: Not Determined. ^aCEC of HA = Total acidity

Table 2: 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 ^c	6.7 ^b	81.73 ^c	11.68 ^c
T1	48.21 ^a	7.9 ^{ab}	378.27 ^d	23.35 ^c
T2	46.32 ^a	7.8 ^b	532.38 ^c	25.69 ^c
T3	37.05 ^b	6.1 ^c	1167.50 ^a	112.08 ^a
T4	0.00 ^c	2.9 ^d	672.48 ^b	53.71 ^b

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

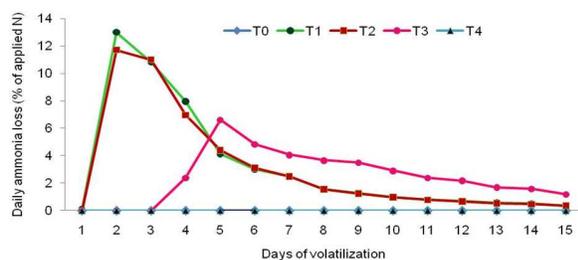


Fig. 1: Daily loss of ammonia from incubation

The NH₃ loss started a day after incubation for T1, second day for T2, fourth day for T3 and no NH₃ loss was found for T0 and T4 (Fig. 1). The maximum daily rate of NH₃ loss for T1 (13%) and T2 (11.69%) was similar on the second day while the maximum NH₃ loss for T3 was 6.61% and it occurred on day 5 of incubation. The decreasing trend after the maximum loss of ammonia for T1, T2 and T3 was similar until day 15 when the ammonia loss was about 1% of the N added in the form of urea.

The total amounts of NH₃ lost, pH, exchangeable ammonium and available nitrate at the end of the study are shown in Table 2. Urea with FA (T3) significantly reduced the total amount of NH₃ loss compared to urea without additives (T1) while urea with acidified HA

and FA (T4) had the greatest effect because there was no ammonia volatilization for 15 days of incubation. Urea with HA (T2) did not significantly reduce ammonia loss compared to the control (T1). The pH for T2 was not significantly different from T1 but significantly different from T3 and T4. This observation was consistent with those reported elsewhere^[4-7]. Urea with additives caused significant accumulation of exchangeable ammonium compared to urea alone (Table 2). T3 and T4 had pronounced effect on available nitrate accumulation compared to other treatments (Table 2).

DISCUSSION

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.

T3 and T4 significantly reduced ammonia volatilization because when urea is mixed with acidic material, the acidic product lowers the micro-site pH, reduces the hydrolysis of urea thus causing a significant reduction in NH₃. The low soil pH for T3 and T4 obtained in this study also confirms the study of Delaune and Patrick^[21] that urea hydrolyzes slowly when soil pH is less than 5.5 and lasted until it moves away from the acidified soil^[4,21]. In this study, fulvic acid (T3) and acidified humic and fulvic acids (T4) which are acidic materials, acidified the soil, thus slowing urea hydrolysis. This may have effectively increased the volume of soil with which mixing of urea occurred and also increased the time required for complete hydrolysis. There was significant accumulation of exchangeable NH₄ for T2, T3 and T4 compared to urea alone suggesting its retention in these 3 treatments. The amount of available nitrate was significantly different for T3 and T4 compared to urea without additives but no significant difference for T2 suggesting that the retention of exchangeable ammonium for urea treatments with additives (T3 and T4) had profound effect on NO₃ accumulation.

CONCLUSION

Humic acid alone was not effective in controlling ammonia volatilization even though ammonium retention was found to be significantly higher compared to urea alone. Fulvic acid significantly reduced ammonia volatilization by 23% compared to urea alone. It also caused the highest retention of ammonia and nitrate. However, there was no ammonia volatilization with acidified humic and fulvic acids (T4). Exchangeable ammonium and available nitrate

accumulation under T3 was better than for T4. Ammonia loss could be reduced by improving exchangeable ammonium retention. It must be stressed that results obtained in the incubation experiment using an acidic ($\text{pH}_{\text{water}} 6.32$) soil of Bekenu series may only be applicable to similar acid soils. This may improve urea N use efficiency as well as reducing environmental pollution.

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