

Reduction of Ammonia Loss from Urea through Mixing with Humic Acids Isolated from Peat Soil (Saprists)

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Abstract: Problem statement: Application of urea as a source of nitrogen fertilizer has an adverse effect on ammoniacal loss to the environment. This study was conducted to reduce ammonia loss from urea by mixing with Humic Acids (HA) isolated from Saprists peat. **Approach:** The effects of urea amended with four different amounts of humic acids, 0.25, 0.50, 0.75 and 1.00 g were evaluated in laboratory conditions using a closed dynamic air flow system. The mineral soil that was used as medium for the study was Bekenu series (typic paleudults). Ammonia loss, soil pH, exchangeable ammonium, available nitrate, exchangeable K, Ca, Mg and Na were determined using standard procedures. **Results:** All the treatments with HA significantly reduced ammonia loss compared to urea alone. Increasing the amount of HA also significantly retained soil exchangeable ammonium and available nitrate. Treatments with HA had no significant effect on the concentrations of Mg, K and Ca, except for Na. The effect of HA in the mixtures on ammonia loss was related to their effect on the formation of ammonium over ammonia. **Conclusion:** Surface-applied urea fertilizer efficiency could be increased when coated with 1.00 g of HA.

Key words: Ammonia loss, ammonia volatilization, humic acids, peat soil, Saprists, urea

INTRODUCTION

As Malaysia strives to become one of the leading agro based nations in South-East Asia, efficient use of fertilizers particularly nitrogenous fertilizers such as urea cannot be overemphasized as most of the agricultural land is poor in nitrogen, a nutrient vital for plant growth and development. Ammonia loss from fertilizers is a major problem confronting farmers. This problem arises especially using ammonia based Nitrogen (N) fertilizers such as anhydrous ammonia, ammonium nitrate and urea. Urea in particular has the potential of volatilizing into ammonia gas and escape into the atmosphere, hence reducing the N availability in the soils particularly when it is surface broadcast on soils^[1,2]. The factors which influence ammonia volatilization include levels of urease activity, availability of moisture, soil texture and nitrification rate. The main concern at present is the pH-buffer capacity and Cation Exchange Capacity (CEC) of the soil, as well as the presence of soil organic matter.

Ammonia volatilization is most likely to occur even in acidic soils due to relatively high pH and also high concentration of NH_4^+ ion around the microsite where the urea granules hydrolyses^[3-5]. The pH in particular affects the equilibrium between NH_4^+ ion and NH_3 (g) such that the relative concentration of NH_3 (g) increases from 0.1-1, 10 and 50% as the pH changes respectively from 6, 7, 8 and 9. It has been found that mixtures of urea and acidic materials can decrease ammonia loss while increasing the concentration of NO_3^- and NH_4^+ ions^[3,5-7]. According to Brady and Weil^[8], high concentration of NO_3^- and NH_4^+ ions in the soil may not guarantee plant N use due to lack of good retention and leaching. Mixing Humic Acids (HA) with urea can reduce the pH and ammonia volatilization because they are high in CEC and total acidity thus providing good NH_4^+ retention as well as preventing its loss through leaching^[9].

According to Siva *et al.*^[5], ammonia volatilization could be reduced by mixing urea with tropical peat soil but the cause of the reduction in ammonia loss due to

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humic substances such as humic and fulvic acids was not investigated. As it is well known, peat soils are high in organic matter which contributes to the availability of HA^[10]. Since peat soils contain a considerable amount of organic matter, HA can be isolated from them and used to reduce ammonia volatilization. This study was conducted on the basis of the above hypothesis.

MATERIALS AND METHODS

The peat samples were collected at 0-15 cm depth using a peat auger from Woodman Plantation, Kuala Tatau, Sarawak, Malaysia. The peat soil is classified as Haplosaprists under USDA classification system and locally known as Linggi or Telok Buloh series. The mineral soil used in this study was Bekenu series (typic paleudults) collected around University Putra Malaysia, Bintulu Campus. The soil samples were also collected at 0-15 cm depth using a mineral auger. The samples were air dried and ground to pass through a 2 mm sieve. The peat soil was used to isolate HA.

The isolation of HA was carried out according to the method modified by Susilawati *et al.*^[11] Ten grams samples were placed into polyethelene centrifuge bottles and 100 mL of 0.5 N NaOH solution was added. The samples were equilibrated on a reciprocal mechanical shaker at 180 rpm for 24 h. The samples were centrifuged at 16,211 G for 15 min. The dark supernatant (mixture of HA and FA) was decanted. After the extraction process, the pH of the solution was adjusted to 1.0 with 6 N HCl in order to separate the HA and FA since FA dissolves in acid whereas HA does not. After the acidification, the samples were equilibrated for 24 h. After fractionation, the suspension containing the HA and FA were transferred to the polyethelene bottles and centrifuged at 16,211 G for 10 min and the supernatant was decanted. The remaining suspension which contains HA was purified by washing in 100 mL of distilled water through centrifugation at 16,211 G for 10 min. This purification method was repeated 3 times in order to reduce the mineral content. The washed HA was oven dried at 40°C until it reaches a constant weight. The isolated HA and the peat soil chemical properties were determined using standard procedures.

The selected physical and chemical properties of HA, peat, mineral soil and urea were determined using standard procedures. Soil pH was determined using a glass electrode on a sample soil and 2 N KCl in a ratio of 1:2. Organic carbon was determined by combustion method^[12]. Soil CEC was determined by leaching with 1 M ammonium acetate buffer adjusted to pH 7.0 followed by the steam distillation technique. The

exchangeable Na, K, Ca and Mg were derived using double-acid method and then measured using atomic absorption spectrophotometry^[13,14]. The humification level of HA was determined by analyzing E₄: E₆ (HA) based on Stevenson^[15]. Carboxylic and phenolic groups and total acidity of the HA were determined using the method described by Inbar *et al.*^[16].

There were six treatments namely; (i) soil only (T0), (ii) 2.02 g urea only (T1), (iii) 2.02 g + 0.25 g HA (T2), (iv) 2.02 g urea + 0.50 g HA (T3), (v) 2.02 g urea + 0.75 g HA (T4) and (vi) 2.02 g urea + 1.00 g HA (T5). The treatments were prepared by first weighing the 2 materials (for each treatment) separately into plastic vials. The materials were then transferred into a set of plastic vials, tightly closed and shaken with a reciprocal shaker at 150 rpm for 30 min to ensure that they were thoroughly and uniformly mixed.

The amount of ammonia loss was measured daily until the loss declined to 1% of the N added in the urea in a closed-dynamic air flow system method with modifications^[5-7]. The system consisted of an exchange chamber with 500 mL conical flask and a trap (250 mL conical flask), both stoppered and fitted with an inlet/outlet. The inlet of the chamber was connected to an air pump and the outlet was to the trap which contains boric acid. A 250 g soil sample was placed in the 500mL flask and was moistened to 60% field capacity and maintained at this moisture content. The treatments were applied on the surface and air passed through the chambers at the rate of 3.5 L⁻¹ min⁻¹ chamber⁻¹. The released NH₃ (g) was captured in a trapping solution which contains 75 mL of boric acid bromocresol green and methyl red indicator. This rate of air flow, corresponding to 8.5 volume exchange min⁻¹ was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, New York) to measure and adjust the air flow. The incubation chambers were kept at room temperature. Boric acid indicator traps NH₃ (g) and was replaced every 24 h and back titrated with 0.01 N HCl, to estimate the amount of NH₃ (g) released.

After the incubation period, soil samples were analyzed for pH, exchangeable Na, Mg, Ca and K were extracted with double acid method and analyzed as described previously^[13,14]. Exchangeable NH₄⁺ and available NO₃⁻ were determined using standard procedures. The experimental design used in this study was completely randomized design with three replicates for each treatment. Analysis of variance was used to test treatment effects while means of treatments were compared using Tukey's test.

RESULTS

The pH (water and KCl) of the mineral soil were close to neutral probably because of the high exchange cations particularly for Ca. The pH of both Saprists peat and HA were acidic. As expected, the pH of the urea was basic (Table 1). The exchangeable ammonium, available nitrate and CEC of the soil were low while the organic matter was high for a sandy clay loam. The yield of the HA obtained was 34.20%. The carbon content, phenolic groups and E₄/E₆ ratio of the isolated HA were consistent with those reported by Tan^[9] and Stevenson^[15]. However, the total acidity and carboxylic groups were found to be higher than that reported in the literature.

The daily loss of NH₃ is shown in Fig. 1. The release of NH₃ started on the first day after application of treatments except for T0 and T5. Except for T0, the maximum NH₃ loss occurred on the second day of incubation. After the second day of incubation, there was a general decline in loss until day 16 when NH₃ loss was about 1% of the N added in the form of urea^[5-7].

All the treatments with HA significantly reduced ammonia volatilization compared to urea only (Table 2). This observation was consistent with that reported by Ahmed *et al.*^[6,7] Interestingly, NH₃ loss was not significantly reduced with increasing amount of HA. There was a significant accumulation of NH₄⁺ in 0-1.5 cm depth for the treatments with HA compared with urea alone (Table 3) except for T2. This finding is comparable with that of Fan and Mackenzie^[3]. Nitrate accumulation was statistically different for T4 and T5 only. This observation contradicts that reported by Fan and Mackenzie^[3].

Table 1: Selected physico-chemical properties of soil, HA, urea and saprists peat (S- Peat)

Properties	Soil	HA	Urea	S-Peat
pH (water)	6.90	1.55	8.59	3.20
pH (1 N KCl)	6.15	1.20	nd	2.23
Total Organic Matter (%)	17.54	96.18	nd	98.32
Total Organic Carbon (%)	10.17	55.79	nd	57.02
CEC ¹ (cmol kg ⁻¹)	11.41	nd ³	nd	nd
Soil Texture	SCL ²	nd	nd	nd
Exchangeable Na (ppm)	64.00	nd	nd	nd
Exchangeable K (ppm)	49.50	nd	nd	nd
Exchangeable Mg (ppm)	85.50	nd	nd	nd
Exchangeable Ca (ppm)	1840.00	nd	nd	nd
Available Ammonium (ppm)	24.52	nd	nd	nd
Available Nitrate (ppm)	16.81	nd	nd	nd
Phenolic group (cmol kg ⁻¹)	nd	366.70	nd	nd
Carboxylic group (cmol kg ⁻¹)	nd	683.33	nd	nd
Total acidity (cmol kg ⁻¹)	nd	1050.00	nd	nd
E ₄ /E ₆	nd	8.76	nd	nd

Note: ¹CEC: Cation Exchange Capacity; ²SCL: Sandy Clay Loam; ³nd: Not determined

The effect of treatments on the pH of the mineral soils after 16 days of incubation was generally neutral (Table 4). This observation was similar to those reported by Ahmed *et al.*^[7,8] At 0-1.5 cm, the soil pH for the treatment with HA was significantly low compared with urea alone. All the treatments had no significant effect on the contents of exchangeable Na,

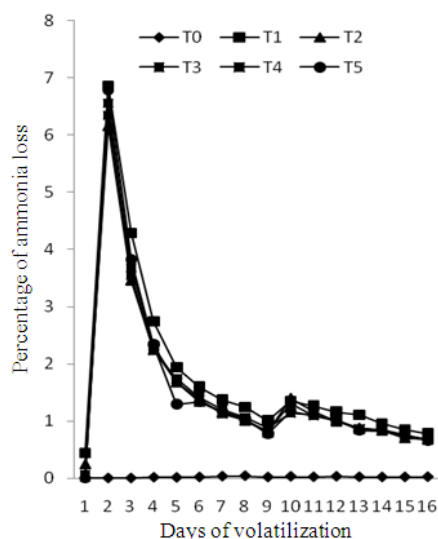


Fig. 1: Effect of treatments on Ammonia Volatilization for 16 days of incubation

Table 2: Total amount of ammonia released over 16 days of incubation

Treatment	Loss of NH ₃ (%)
T0	0.30 ^a
T1	28.90 ^b
T2	24.82 ^c
T3	24.89 ^c
T4	25.00 ^c
T5	24.87 ^c

Note: Different alphabets indicate that there are significant differences at p = 0.05 between mean values using Tukey's standardized range test

Table 3: Effects of treatment on available ammonium and nitrate accumulation with soil depth

Treatments	Available NH ₄ ⁺ (ppm)		Available NO ₃ ⁻ (ppm)	
	0-1.5 cm	1.5-3.0 cm	0-1.5 cm	1.5-3.0 cm
T0	39.72 ^a	40.86 ^a	23.35 ^{abc}	16.35 ^a
T1	402.79 ^b	380.61 ^c	16.34 ^a	23.69 ^{ab}
T2	429.62 ^{bc}	345.58 ^b	19.85 ^{ab}	23.35 ^{ab}
T3	532.38 ^{cd}	367.76 ^{bc}	35.03 ^{abc}	29.18 ^{ab}
T4	539.39 ^{cd}	367.76 ^{bc}	36.15 ^{bc}	23.69 ^{ab}
T5	559.21 ^d	384.11 ^c	38.53 ^c	31.52 ^b

Note: Different alphabets within the same column indicate that there are significant differences at p = 0.05 between mean values using Tukey's standardized range test

Table 4: Soil pH after 16 days of incubation

Treatments	pH (1 N KCl)		pH (water)	
	0-1.5 cm	1.5-3.0 cm	0-1.5 cm	1.5-3.0 cm
T0	6.22 ^a	6.26 ^a	7.10 ^a	7.09 ^a
T1	7.25 ^b	7.22 ^{bc}	7.98 ^b	7.96 ^b
T2	7.23 ^b	7.26 ^c	8.01 ^b	7.97 ^b
T3	7.06 ^c	7.10 ^b	7.77 ^c	7.74 ^c
T4	7.10 ^c	7.20 ^{bc}	7.77 ^c	7.84 ^{bc}
T5	7.11 ^c	7.27 ^c	7.75 ^c	7.90 ^b

Note: Different alphabets within the same column indicate that there are significant differences at $p = 0.05$ between mean values using Tukey's standardized range test

Table 5: Exchangeable Na, Mg, K and Ca in the soil after 16 days of incubation

Treatments	Exchangeable cations (ppm)			
	0-1.5 cm			
	Na	Mg	K	Ca
T0	61.33 ^a	77.50	43.33	1826.2
T1	60.17 ^a	76.67	52.83	1869.0
T2	88.00 ^b	81.00	58.75	1888.7
T3	110.67 ^c	78.00	52.17	1987.3
T4	140.67 ^d	80.50	53.17	1912.7
T5	159.67 ^e	82.83	57.00	1957.8
	1.5-3.0 cm			
T0	76.33 ^{ab}	95.00	55.88	2217.5
T1	63.67 ^a	77.33	65.50	1915.5
T2	81.17 ^{ab}	81.83	56.50	2103.2
T3	97.00 ^{ab}	78.67	50.83	1900.8
T4	120.83 ^{ab}	86.83	55.83	2272.7
T5	135.17 ^b	77.50	52.17	1820.3

Note: Different alphabets within the same column (respectively to depth) indicate that there are significant differences at $p = 0.05$ between mean values using Tukey's standardized range test

Mg, K and Ca, but for Na the concentration increased with increasing amount of HA for 0-1.5 cm (Table 5). Ahmed *et al.*^[7] reported a similar finding.

DISCUSSION

The selected physico-chemical properties of the soil were not typical of Bekenu series as reported by Paramanathan^[17]. The soil's pH, organic content, CEC and exchangeable cations (Na, Mg, K and Ca) were found to be higher than those reported, especially Ca (Table 3). These could be due to liming. The soil texture was consistent with that reported in the literature. Sandy Clay Loam soils are usually high in CEC due to their high clay content. However, Malaysian soils contain clays comprising kaolinite minerals which are notably low in exchange sites^[17].

According to Stevenson^[15], the high total acidity could be due to contamination with inorganic acids. Based on the E_4/E_6 ratio, the HA were found to be of

low molecular weight HA^[9]. Low molecular weight HA possess large surface area with more exchange sites compared to higher molecular weight HA. Total acidity represents CEC for the HA^[14]. Hence, the high CEC of HA enables NH_4^+ retention.

The release of NH_3 gas started on the first day of incubation except for T0 and T5. However, the maximum loss occurred on the second day due to rapid hydrolysis of urea. The levels of urease activity were affected by high organic matter content in the soil. The higher the organic matter in soil, the higher is the amount of urease. Urease activity is similar to any other enzymatic reaction whereby the initial stage is slow. Once there is considerable amount of products formed, e.g. NH_4^+ , the enzymatic reaction will be more rapid and this explains the optimum release on the second day. The peak of NH_3 loss occurred on the second day of incubation where T1 and T5 showed the highest amount of release (Fig. 1). All of the treatments successfully reduce NH_3 loss compared to urea only (Table 2). However, there were no significant differences in the loss of NH_3 for all the treatments with HA. This suggests that increasing amount of HA does not lead to decreasing amount of ammonia loss. These observations contradict the findings of Ahmed *et al.*^[5]

The accumulation of NH_4^+ was found to be higher at 0-1.5 depth and this could be due to the application of HA and due to the high CEC, they were able to retain NH_4^+ . Since HA does not dissolve in water, there were no possibilities for it travel down below the surface^[9]. However, when the surface area is concentrated with NH_4^+ ions, they move down deeper into the soil through diffusion. Once NH_4^+ is deeper in the soil, they bind with clay colloids^[18]. Hence, the significant increase in NH_4^+ accumulation in the soil with increasing amount of HA. Throughout the experimental period, there were significant differences in the accumulation of NO_3^- in the soil only at 0-1.5 cm depth (Table 3). This observation contradicts that reported by Fan and Mackenzie^[3]. This could be due to lack of microbial activity to nitrify NH_4^+ into NO_3^- .

The pH of the soil for all of the treatments increased due to hydrolysis of urea. The pH values for T1 and T2 were not significantly different. However, the pH values for T3, T4 and T5 were significantly lower than T1 and T2 (Table 4). This contradicted those reported by Ahmed *et al.*^[6,7] This suggests that the application of HA above 0.25 g could affect the soil pH (Table 5). The increasing concentration of Na with increasing amount of HA was because the HA was not 100% pure even after purification by washing of HA thrice^[6,7]. The ash content of the HA should be $\pm 1\%$ in order to be pure but the ash content for the isolated HA

was higher than those reported^[9,15]. The exchangeable Ca was the limiting factor for H⁺ ions in the soil whereby Ca replaces H⁺ on the colloidal, hence, raising the soil pH near neutral^[4]. Since the exchange sites were taken up by Ca, the remaining ones were exchanged with NH₄⁺ when H⁺ attaches to NH₃.

CONCLUSION

Based on the results of this study, application of urea mixed with HA isolated from peat soil (saprist) could provide better urea use efficiency. When urea is mixed with an appropriate amount of HA, ammonia loss is reduced while ammonium and the available nitrate retention is enhanced but not soil exchangeable cations except for sodium. Based on this study, 1.00 g HA mixed with urea provides better results than 0.25 g, 0.50 g and 0.75 g HA. It must be stressed that this study was conducted using a sandy clay loam soil with a pH (KCl) of 6.15 and the results may be only applicable to similar soils.

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REFERENCES

1. Cai, G.X., D.L. Chen, H. Ding, A. Polcholski, X.L. Fan and Z.L. Zhu, 2002. Nitrogen losses from fertilizers applied to maize, wheat and rice in North China plain. *Nutr. Cycl. Agroecosyst.*, 63: 187-195. DOI: 10.1023/A:1021198724250
2. Prasertsak, P., J.R. Freney, P.G. Saffiga, O.T. Denmead and B.G. Prove, 2001. Fate of Urea nitrogen applied to a banana crop in the wet tropics of Queensland. *Nutr. Cycl. Agroecosyst.*, 59: 65-73. DOI: 10.1023/A:1021198724250
3. Fan, M.X. and A.F. Mackenzie, 1993. Urea and phosphate interactions in fertilizer microsites: Ammonia volatilization and pH changes. *Soil Sci. Soc. Am. J.*, 57: 839-845. <http://soil.scijournals.org/cgi/reprint/57/3/839>
4. Fenn, L.B. and J. Richards, 1986. Ammonia loss from surface applied urea-acid products. *Fertil. Res.*, 9: 265-275. DOI: 10.1007/BF01050352
5. Siva, K.B., H. Aminuddin, M.H.A. Husni and A.R. Manas, 1999. Ammonia volatilization from urea as affected by tropical-based palm oil mill effluent (pome) and peat. *Communications in Soil Sci. Plant Anal.*, 30: 785-804. DOI: 10.1080/00103629909370246
6. Ahmed, O.H., H. Aminuddin and M.H.A. Husni, 2006a. Effects of urea, humic acid and phosphate interactions in fertilizer microsites on ammonia volatilization and soil ammonium and nitrate contents. *Int. J. Agric. Res.*, 1: 25-31. DOI: 10.3923/ijar.2006.25.31
7. Ahmed, O.H., H. Aminuddin and M.H.A. Husni, 2006b. Reducing ammonia loss from urea and improving soil-exchangeable ammonium retention through mixing triple superphosphate, humic acid and zeolite. *Soil Use Manage.*, 22: 315-319. DOI: 10.1111/j.1475-2743.2006.00040.x
8. Brady, N.C. and R.R. Weil, 2001. *The Nature and Properties of Soils*. 13th Edn., Prentice Hall, ISBN: 0130167630.
9. Tan, K.H., 2003. *Humic Matter in Soil and the Environment: Principles and Controversies*. Marcel Dekker, Inc., Routledge, USA., New York, ISBN: 0824742729.
10. Andriesse, J.P., 1988. *Nature and Management of Tropical Peat Soils*. FAO Soils Bulletin 59. ISBN: 9251026572.
11. Susilawati Ahmed, O.H., A.M. Nik Muhamad and M.Y. Khanif, 2007. Simple method of Purifying humic acids isolated from tropical hemist (peat soil). *Am. J. Applied Sci.*, 5: 1812-1815.
12. Chefetz, B., P.G. Hatcher, Y. Hadar and Y. Chen, 1996. Chemical and biological characterization of organic matter during composting of municipal waste. *J. Environ. Qual.*, 25: 776-785. <http://jeq.scijournals.org/cgi/reprint/25/4/776>
13. Mehlich, A., 1976. New buffer method for rapid estimation of exchangeable acidity and lime requirement. *Commun. Soil Sci Plant Anal.*, 7: 637-52. DOI: 10.1080/00103627609366673
14. Tan, K.H., 1996. *Soil Sampling, Preparation and Analysis*. 1st Edn., Marcel Dekker, Inc., ISBN: 0824796756.
15. Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition and Reaction*. 2nd Edn., John Wiley and Sons, New York, ISBN: 0471594741.
16. Inbar, Y., Y. Chen and Y. Hadar, 1990. Humic Substances formed during composting of organic matter. *Soil Sci. Soc. Am. J.*, 54: 1316-1323. <http://soil.scijournals.org/cgi/reprint/54/5/1316>
17. Paramanathan, S., 2000. *Soils of Malaysia. Their characteristics and identification*. Academy of Science Malaysia. Kuala Lumpur. ISBN: 9839445065.
18. Juo, A.S.R. and K. Franzluebbers, 2003. *Tropical Soils: Properties and Management for Sustainable Agriculture*. Oxford University Press, USA., ISBN: 0195115988.