

Full Length Research Paper

Minimizing ammonia loss from urea through mixing with zeolite and acid sulphate soil

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Ammonia volatilization is a major cause of nitrogen loss from surface applied urea. While all top dressed ammonia and ammonium-based fertilizers can be volatilized, the potential is greatest with urea and fluid containing urea. This laboratory study compared the effect of four different urea-zeolite-acid sulphate soil mixtures on NH₃ volatilization and, soil exchangeable NH₄ and available NO₃ contents of an acid soil with surface-applied urea without additives. The soil used in the study was a sandy loam Typic Paleudults (Nyalau Series). The mixtures significantly minimized NH₃ loss by 6 to 15% compared to urea alone. These treatments also significantly increased soil exchangeable NH₄ and available NO₃ contents compared to urea without additives. The increase in the formation of NH₄⁺ over NH₃ and the temporary decrease in soil pH retarded urea hydrolysis at the microsite immediately around the fertilizer. Surface applied urea fertilizer efficiency could be increased by mixing it with zeolite and acid sulphate soil.

Key words: Ammonia loss, urea, zeolites, acid sulphate soils.

INTRODUCTION

Nitrogen has always been an essential nutrient element and plays an important role in crop production. Yet ammonia volatilization from nitrogenous fertilizers such as urea is very serious in almost all agricultural systems (Prasertsak et al., 2001; He et al., 2002). Ammonia volatilization after urea application is the most likely mechanism responsible for variation in urea performance even on acidic soils (Stevens et al., 1989). Ammonia volatilization after urea hydrolysis is the common mechanism for decreasing urea efficiency (Fenn and Hossner, 1985). Volatilization can occur in acidic soils due to alkaline conditions at the microsites where urea granules dissolve and hydrolyse (Fan and Mackenzie, 1993). It is also known that high ammonium ions without good retention upon application of urea to acidic soils leads to ammonia loss. As a result, the rate of ammonia

loss from urea during the first week after its application in the field is substantial (Cai et al., 2002).

Acid materials such as acidic phosphates and phosphoric acid have extensively been used to control the dissolution and hydrolysis of urea (Fan and Mackenzie, 1993; Ahmed et al., 2006, Ahmed et al., 2008). However, the cost involved to amend urea with these materials limits their use on large scale. Furthermore, urea phosphate (mixture of urea and phosphoric acid) is corrosive and requires extra ordinary precautionary measures in handling and storing a fertilizer of this kind. An alternative way of controlling the availability of urea-Nitrogen via reduction of the microsite pH is by amending urea with acid sulphate soils which are noted for their low pH, example, 3.5 or less (Shamshuddin et al., 1986). An approach of this kind also ensures provision of sulphur in the form of sulphate for use as the genesis of the acidity of acid sulphate soils is due to oxidation of sulphur in pyrite. In order to improve the retention and timely availability of ammonium ions upon urea hydrolysis, clinoptilolite zeolite could also be

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used to amend urea. This is because this type of zeolite is known for its rigid three-dimensional lattice with channels which are 10^{-9} m in size with internal exchange complexes that have high affinity for ammonium ions (Ferguson and Pepper, 1987). The high retention ability of ammonium ion by zeolite means that the ammonium ions are physically protected from excessive nitrification by microbes and hence the reduction of ammonia loss by this process. Besides the ability of zeolites to retain ammonium ions, sequestering crystallized urea in the zeolite pores is possible. To this end, the objective of this study was to compare the effect of four different urea-zeolite-acid sulphate soil mixtures on NH_3 volatilization and, soil exchangeable NH_4 and available NO_3 contents of an acid soil with surface-applied urea without additives.

MATERIALS AND METHODS

The soil used in the experiment was Typic Paleudults (Nyalau Series). Soil samples were taken at 0 to 15 cm using an auger after that the samples were air-dried and ground to pass through 2 mm sieve. The clinoptilolite zeolite used in this study was in powder form. The acid sulphate soil used was ground to pass a 250 μm sieve.

The pH of the soil, clinoptilolite zeolite and acid sulphate soil were determined in a 1:2 soil:distilled water suspension and/or 1 M KCl solution using a glass electrode (Peech, 1965). Soil CEC was determined by leaching with 1 M ammonium acetate buffer adjusted to pH 7.0 and followed by steam distillation (Bremmer, 1965). The double acid method (Tan, 2005) was used to extract soil exchangeable K, Ca and Mg and their concentrations were determined by atomic absorption spectrophotometry (AAS). The CEC of the clinoptilolite zeolite was determined by using the CsCl method (Ming and Dixon, 1986). The exchangeable K, Ca and Mg of the zeolite were extracted using the method of Ming and Dixon (1986) and their concentrations determined as previously outlined. The soil texture was determined using the hydrometer method (Tan, 2005). The treatments per 200 g of soil evaluated were:

- 1). 2.02 g urea without additives (T1)
- 2). 2.02 g urea + 0.25 g zeolite + 0.25 g acid sulphate soil (T2)
- 3). 2.02 g urea + 0.5 g zeolite + 0.5 g acid sulphate soil (T3)
- 4). 2.02 g urea + 0.75 g zeolite + 0.75 g acid sulphate soil (T4)
- 5). 2.02 g urea + 1 g zeolite + 1 g acid sulphate soil (T5)

The urea, zeolite and acid sulphate were put into a plastic vial and shaken in a reciprocal shaker at 190 rpm for 30 min to ensure a uniform mix. The amount of urea used was calculated from the standard recommendation for mature oil palm in Malaysia. The zeolite and acid sulphate soil rates used in this study gave better results in our earlier laboratory trials. In addition, more of these materials were not used because of the cost that may be incurred in amending urea.

Ammonia volatilization from soil was measured by a closed dynamic airflow system (Siva et al., 1999) with modifications. The system consisted of an exchange chamber and a trap (500 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 connected by polyethylene tubing to the trap containing boric acid solution (250 ml conical flask). Soil (200 g) was placed in the exchange chamber. The soil was moistened to 60% of field capacity and maintained at this content. The treatments were applied to the soil surface and the air passed through the chambers was at a rate of $3.5 \text{ L}^{-1} \text{ min}^{-1}$ chamber⁻¹. This rate of airflow,

corresponding to 8.5 volume exchanges min^{-1} , was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, NY, USA) to measure and adjust the airflow. The released NH_3 was captured in the trapping solution containing 75 ml of boric acid with bromocresol green and methyl red indicator (colour indicator). The incubation chambers were maintained at room temperature. Boric acid-indicator traps were replaced every 24 h and back titrated with 0.01 M HCl, to estimate the NH_3 released. Measurement was continued until the loss declined to 1 % of the N added in the urea (Ahmed et al., 2008).

After the incubation period, the soil samples were taken and pH, exchangeable NH_4 and available NO_3 were determined. Exchangeable NH_4 and available NO_3 were extracted from the soil by the method of Keeney and Nelson (1982), and their amounts were determined using steam distillation method. The experimental design was fully randomized with three replicates. Analysis of variance (ANOVA) was used to test for treatment effects and means of treatments were compared using Tukey's test.

RESULTS AND DISCUSSION

The selected physical and chemical properties of Nyalau series are presented in Table 1. The pH in water and salt solution (1 M KCl) of the soil were comparable to those reported by others including Paramanathan (2000). However, Ca, Mg, Na and K values were found to be lower than those reported by Paramanathan (2000). Additionally, the CEC in this study was higher to that reported by Paramanathan (2000). These differences could be because the soil had been cropped for some time.

The selected chemical properties of clinoptilolite zeolite are given in Table 2. The pH of the zeolite was close to neutral, probably because of its relatively high exchangeable Ca, Mg and K (Table 2). The CEC of the zeolite was comparable with that reported by Prama (2004). The selected chemical properties of the acid sulphate soil are presented in Table 3. The pH and the exchangeable cations of the acid sulphate soil were low (Table 3) compared to those reported by Shamshuddin et al. (1986).

The daily loss of ammonia (NH_3) recorded during the experiment is shown in Figure 1. The NH_3 loss started on the first day of incubation for all of the treatments except for T4 and T5, where loss in NH_3 occurred on the second day of incubation. The former observation was similar to the work of Ahmed et al. (2008). Even though the maximum NH_3 loss of the treatments occurred on the second day of incubation, those of T2, T3, T4 and T5 were lower than that of T1. After this maximum loss of NH_3 , there was a general decline until day 10 when the NH_3 loss was about 1% of the Nitrogen added as urea (Figure 1). In a related work, maximum NH_3 loss occurred at 3 days after urea-zeolite-triple superphosphate mixture was applied to an acid soil (Ahmed et al., 2006). It was also observed that, 3 days after treatments application, the loss decreased until the end of the study. This observation may be due to the similarities in soil properties such as texture, total organic carbon and pH.

Table 1. Selected chemical and physical properties of Nyalau Series.

Property	Soil, present study	Soil, reference*
pH (water)	4.67	4.7
pH (KCl)	3.47	4.0
CEC (cmol kg ⁻¹)	9.30	5.89
Exchangeable Ca (cmol kg ⁻¹)	0.012	0.05
Exchangeable Mg (cmol kg ⁻¹)	0.006	<0.01
Exchangeable Na (cmol kg ⁻¹)	0.001	0.09
Exchangeable K (cmol kg ⁻¹)	0.001	<0.01
Texture	SL	SL

SL = Sandy Loam .Source: *Paramanathan (2000).

Table 2. Selected chemical properties of zeolite.

Property	Values
pH (water)	7.84
pH (1M KCl)	6.48
CEC (cmol kg ⁻¹)	106
Exchangeable Ca (cmol kg ⁻¹)	24
Exchangeable Mg (cmol kg ⁻¹)	32
Exchangeable K (cmol kg ⁻¹)	31

Table 3. Selected chemical properties of acid sulphate soil.

Property	Values
pH (water)	2.56
pH (1M KCl)	2.48
CEC (cmol kg ⁻¹)	23.87
Exchangeable Ca (cmol kg ⁻¹)	0.092
Exchangeable Mg (cmol kg ⁻¹)	0.082
Exchangeable Na (cmol kg ⁻¹)	0.259
Exchangeable K (cmol kg ⁻¹)	0.001

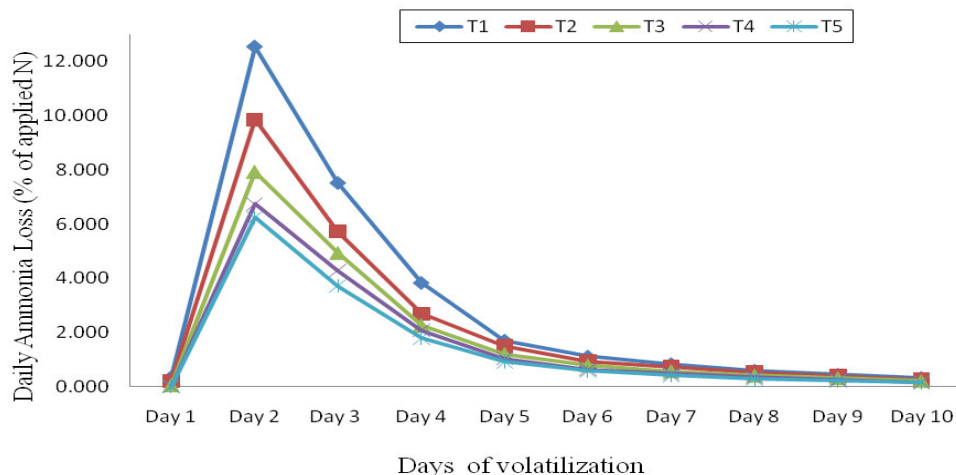
**Figure 1.** Daily NH₃ loss with time over 10 days of incubation.

Table 4. Total amount of NH₃ lost over 10 days of incubation and the decrease in NH₃ loss in comparison with the loss in T1 (urea without additives).

Treatments	Ammonia loss (% of urea-Nitrogen)	Decrease in total NH ₃ loss as compared to T1 (%)
T1	29.34 ^a ± 0.67	none
T2	22.81 ^b ± 0.31	6.53
T3	18.69 ^c ± 1.09	10.65
T4	16.04 ^{cd} ± 0.63	13.30
T5	14.35 ^d ± 0.11	14.99

Note: Mean values with different letters are significantly different between treatments at $p \leq 0.05$ using Tukey's test.

Table 5. Effects of 2.02 g urea without additives (T1), 2.02 g urea + 0.25 g zeolite + 0.25 g acid sulphate (T2), 2.03 g urea + 0.5 g zeolite + 0.5 g acid sulphate soil (T3), 2.03 g urea + 0.75 g zeolite + 0.75 g acid sulphate soil (T4), and 2.03 g urea + 1 g zeolite + 1 g acid sulphate soil (T5) on soil exchangeable ammonium and available nitrate nitrogen after 10 days of incubation.

Treatments	Exchangeable ammonium(mg L ⁻¹)	Available nitrate(mg L ⁻¹)
T1	26.340 ^a ± 3.92	6.730 ^a ± 0.00
T2	39.227 ^b ± 3.42	6.165 ^a ± 0.57
T3	45.950 ^b ± 1.12	10.650 ^b ± 2.80
T4	49.880 ^b ± 0.56	15.690 ^b ± 1.12
T5	37.545 ^b ± 2.81	16.350 ^b ± 0.75

Note: Mean values with different letters (within column) are significantly different between treatments at $p \leq 0.05$ using Tukey's test.

The total amount of NH₃ loss at the end of the study is shown in Table 4. All of the treatments with zeolite and acid sulphate soil (T2, T3, T4 and T5) significantly decreased NH₃ loss compared to urea alone (T1). However, there was no significant difference between those of T3 and T4. This suggests that although the maximum loss of NH₃ was reduced by half in T4, the loss throughout the subsequent days for T3 was higher than T4, hence resulted in similar amount of NH₃ loss between these treatments. Nonetheless, T5 was more pronounced in minimizing NH₃ loss compared to other treatments. As a result, the total NH₃ loss was effectively reduced to 14.99% compared to the total loss in T1 (Table 4).

The mixtures (T2, T3, T4 and T5) evaluated were able to significantly reduce NH₃ loss because the acid sulphate soil used may have temporarily acidified the soil surrounding the urea-zeolite-acid sulphate soil mixture as it has been reported that when soil pH is less than 5.5, urea hydrolyzes was slow (Delaune and Patrick, 1970) and the effect lasts until it moves away from the acidified soil (Delaune and Patrick, 1970; Fan and Mackenzie, 1993). In this regard, the amendment may have effectively increased the volume of soil with which urea is mixed, and also increased the time required for complete hydrolysis (Fan and Mackenzie, 1993). Additionally, after urea hydrolysis, the lower pH may have enhanced the formation of NH₄ over NH₃ (Table 5). An increase in the retention of NH₄ on the zeolite could be another reason for that (Table 5).

As shown in Table 5, there was a significant

accumulation of soil exchangeable NH₄ and available NO₃ for all the mixtures compared with urea without additives. This was possible because of retention of NH₄ on the cation-exchange sites of the zeolite whose CEC was high (106 cmol kg⁻¹). This observation also explains why the urea-zeolite-acid sulphate soil mixtures effectively decreased ammonia volatilization, as compared to urea without additives (Figure 1). A study has shown that ammonium-exchanged clinoptilolite does only served as a slow-release fertilizer in a medium textured soil, porous soil but it also reduces volatilization of NH₃ when urea and clinoptilolite were added to an alkaline, coarse-textured soil (Lewis et al., 1984). In the case of T1, the increased loss of NH₃ from urea without additives was possibly due to the increased alkalinity from urea hydrolysis exceeding the soil retention capacity for NH₄. Besides improving the retention of soil exchangeable NH₄, the inclusion of zeolite in this study may have reasonably reduced the conversion of NH₄ to NO₃.

Regardless of treatment, the soil pH in both water and salt solution (1 M KCl) were not significantly different on the 10th day of incubation (Table 6). This was possible because the NH₃ loss at this period varied little, about 1% of the N was added as urea (Figure 1).

Conclusion

The results from this study suggest that applying urea

Table 6. pH of soil after 10 days of incubation.

Treatments	pH (water)		pH (1 M KCl)	
	Before air dried	After air dried	Before air dried	After air dried
T1	7.3900 ^a ± 0.04	7.2200 ^a ± 0.03	6.2867 ^a ± 0.05	6.4200 ^a ± 0.05
T2	7.4533 ^a ± 0.05	7.2967 ^a ± 0.03	6.3733 ^a ± 0.04	6.4867 ^b ± 0.04
T3	7.4867 ^a ± 0.05	7.3633 ^a ± 0.12	6.4467 ^a ± 0.06	6.5733 ^b ± 0.03
T4	7.5433 ^a ± 0.06	7.4267 ^a ± 0.14	6.5133 ^a ± 0.13	6.6600 ^b ± 0.09
T5	7.5533 ^a ± 0.05	7.5667 ^a ± 0.06	6.5200 ^a ± 0.03	6.6867 ^b ± 0.02

Note: Mean values with different letters (within column) are significantly different between treatments at $p \leq 0.05$ using Tukey's test.

amended with zeolite and acid sulphate soil has a significant advantage over urea without additives by increasing the formation of soil exchangeable NH_4 over NH_3 , and as well as retaining more exchangeable NH_4 and available NO_3 in the soil. However, these results are only applicable to similar acid soils.

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