

*Full Length Research Paper*

# Ammonia loss, ammonium and nitrate accumulation from mixing urea with zeolite and peat soil water under waterlogged condition

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**Ammonia loss from urea significantly hinders efficient use of urea in agriculture. In order to reduce ammonia loss and, at the same time, improve beneficial accumulation of soil exchangeable ammonium and nitrate for efficient utilization by plants, this laboratory study was conducted to determine the effect of mixing urea with zeolite and peat soil water on ammonia volatilization, soil exchangeable ammonium and available nitrate contents, compared with urea without additives under waterlogged condition. The soil used was Bekenu Series (Fine loamy, siliceous, isohyperthermic, red-yellow to yellow Tipik Tualemkuts). The mixtures significantly reduced ammonia loss by 25 to 38% compared with urea (straight urea, 46% N). All the mixtures of zeolite and peat soil water with urea significantly increased soil exchangeable ammonium (by 59 to 80 mg kg<sup>-1</sup>) and available nitrate (by 5 to 12 mg kg<sup>-1</sup>) contents. The temporary reduction of soil pH may have retarded urea hydrolysis. It could be possible to improve the efficiency of urea surface-applied to high value crops by addition of zeolite and peat soil water.**

**Key words:** Ammonia volatilization, peat soil water, exchangeable ammonium, available nitrate.

## INTRODUCTION

Ammonia volatilization (loss) from nitrogen based fertilizers such as urea occurs in acid, alkaline and waterlogged soils because during hydrolysis, urea N is converted into ammonia which subsequently reacts with a proton to produce ammonium ions. As a result, ammonia loss is more serious if urea is surface applied and not incorporated into soils. Therefore, ammonia loss reduces the effectiveness of urea for surface application (Howard and Tyler, 1989). This is because after surface application, urea quickly hydrolyzes within a day or two through an enzyme called urease to produce ammonium (NH<sub>4</sub><sup>+</sup>), hydroxyl (OH<sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. This process sharply increases soil pH and ammonium ions around

the urea granule. Under this alkaline condition, the equilibrium of NH<sub>3</sub> + H<sub>2</sub>O  $\leftrightarrow$  NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup> shifts more to NH<sub>3</sub> thus increasing volatilization losses which in turn causes lower fertilizer use efficiency (Fan and Mackenzie, 1993).

Acidic substances such as phosphoric acid and acidic phosphates have been used to control ammonia loss through reduction of microsite pH (Bremner and Douglas, 1971; Fenn and Ricahrds, 1989; Fenn et al., 1990). However, besides the high cost of amendment of these acidic materials which prohibits their use, the mixture of these acidic materials and urea as example, is corrosive and as such requires special precautions in handling and storage. Even if the use of these acidic materials favour formation of ammonium ions over ammonia gas, without good retention of the ammonium ions in the soil, efficient use of these ions by plants cannot be guaranteed. This is because both ammonium and nitrate ions are subject to leaching (Brady and Weil, 2002). Furthermore, while plant N can be decreased by the biological transformation of ammonium to nitrate, under anaerobic conditions, and

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**Abbreviations:** CEC, Cation exchange capacity; SCL, sandy clay loam.

nitrate can also be biologically denitrified to gases which lead to additional loss of N from soil (Brady and Weil, 2002). In order to reduce ammonia loss and at the same time addressing the aforementioned problems associated with the use of inorganic acids which lack the ability to efficiently retain ammonium ions in the soil, peat soil water (for reducing microsite pH because its organic acid nature) and zeolite (for retention of ammonium ions) could be used to amend urea.

Peat soil water (pH 3 to 4) is abundant in Malaysia as for instance, the State of Sarawak alone has 1.5 million peatland (Andriess, 1988). The peat water becomes waste water when peatland is farmed. Before and after a peatland is opened for cultivation peat water is drained out and usually the drained water becomes more of a liability than asset. It is in line with that in this study which seeks to put to good use peat water that is drained from peatlands when they are opened for inevitable cultivation. On the other hand, zeolites can be used to reduce ammonia loss because of their high cation exchange capacity (CEC) and great affinity for ammonium ions (Stumpe et al., 1984; Mackdown and Tucker, 1985; Ming and Dixon, 1986) thus the higher the CEC, the lower the ammonia volatilization losses. The importance of zeolite has been recognized by some studies because of their small internal channels which have been found to protect ammonium ions from excessive nitrification by microbes (Ferguson and Pepper, 1987).

Considering the acidic nature of peat water (pH 3 to 4), the water could be put to good use by using it to reduce  $\text{NH}_3$  loss from urea, as ammonia loss in flooded or waterlogged soils is largely controlled by pH and ammonium ions. Amending urea with peat water and zeolite may control soil pH through inhibition of ureolytic activity of microorganisms while the aforementioned properties of zeolite may contribute to reduction of ammonia loss by reducing nitrification. Hence, the objective of this study was to determine the effect of mixing urea with zeolite and peat water on ammonia volatilization, soil exchangeable ammonium and available nitrate contents, compared with applied urea without additives under waterlogged condition.

## MATERIALS AND METHODS

The clinoptilolite zeolite used in this study was imported from Indonesia. Peat soil water (waste water) was collected from natural flows of peat water at Suai Miri Sarawak, Malaysia. The mineral soil used in this study was sampled in an undisturbed area of University Putra Malaysia Bintulu Sarawak Campus, Malaysia using an auger. The soil taken at 0 to 15 cm depth was air dried and ground to pass 2.0 mm sieve for laboratory experiment. The soil texture was determined using the hydrometer method (Tan, 2005) and its field capacity and bulk density determined by the method described by Tan (2005). The pH of the soil and zeolite were determined in a 1:2 soil:distilled water suspension and KCl using a glass electrode (Peech, 1965). However, the pH of the peat soil water was determined directly from filtered samples using a glass electrode. The soil total carbon was determined using the loss-on-ignition

method (Piccolo, 1996). Soil available P was extracted using the double acid method (Tan, 2005) followed by blue method (Murphy and Riley, 1962). The Kjeldhal method was used to determine total N (Bremner, 1965). Exchangeable cations were extracted using the leaching method (Cottenie, 1980) and their concentrations were afterwards determined using followed Atomic Absorption Spectrometry (AAS). Soil cation exchange capacity (CEC) was determined by the leaching method followed by steam distillation (Bremner, 1965). The CEC of clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). It must be noted that the CsCl method used is the most suitable method because the leaching method tends to underestimate CEC of zeolites because of trapping of ammonium ions in the zeolites channels. The treatments evaluated per 250 g soil were:

- 1) Soil only (T0)
- 2) 2.02 g urea (T1)
- 3) 2.02 g urea + 0.75 g zeolite + 175 ml peat soil water (T2)
- 4) 2.02 g urea + 1.00 g zeolite + 175 ml peat soil water (T3)
- 5) 2.02 g urea + 175 ml peat soil water (T4).

These materials were mixed thoroughly to get homogenous mixture. The 250 g soil samples in 500 ml volumetric flask were moistened with distilled water at 70% field capacity. To achieve waterlogged condition, the treatments were used to saturate the soil samples in the 500 ml volumetric flasks after which they were sealed with parafilm and kept closed throughout entire experiment.

The daily loss of  $\text{NH}_3$  from urea was measured by using a closed-dynamic air flow system method (Siva et al., 1999; Ahmed et al., 2006a, 2006b). The system consisted of an exchange chamber of 500 ml conical flask containing 250 g soil sample and 250 ml conical flask containing 75 ml of boric acid which were both stop and fit with an inlet/outlet. The inlet of the chamber was connected to an air pump and the outlet was connected by polyethylene tubing which contains boric acid and indicator solution to trap ammonia gas (Ahmed et al., 2006a,b). Air was passed through the chamber at the rate of 3.5/L/min/chamber. This rate of air flow was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, New York) to measure and adjust the air flow when necessary.

The released  $\text{NH}_3$  (g) captured in a trapping solution which contains 75 ml of boric acid with bromocresol green and methyl red indicator was titrated with 0.1 M HCl to estimate the amount of  $\text{NH}_3$  (g) released. The entire incubation was conducted at room temperature. The boric acid indicator which was used to capture  $\text{NH}_3$  (g) was replaced every 24 h during incubation for 13 days, a period when ammonia loss was less than 1% (Ahmed et al., 2006a,b). After 13 days of incubation, soil samples were analysed for pH, exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$ . Soil pH was determined by the method previously stated. The method of Keeney and Nelson (1982) was used to extract soil exchangeable  $\text{NH}_4^+$  and available  $\text{NO}_3^-$  followed by steam distillation. The experimental design was a completely randomized design with three replicates for each treatment. Analysis of variance was used to test treatment effects and means of treatments were compared using Tukey's test (SAS version 9.2).

## RESULTS AND DISCUSSION

The selected physical and chemical properties of Bekenu series are summarized in Table 1. The chemical properties were consistent with those reported by Paramanathan (2000) except for exchangeable Ca, which was relatively high probably because of liming. The pH of the peat soil water and zeolite were acidic while the pH of urea was

**Table 1.** Selected physico-chemical properties of Bekenu series.

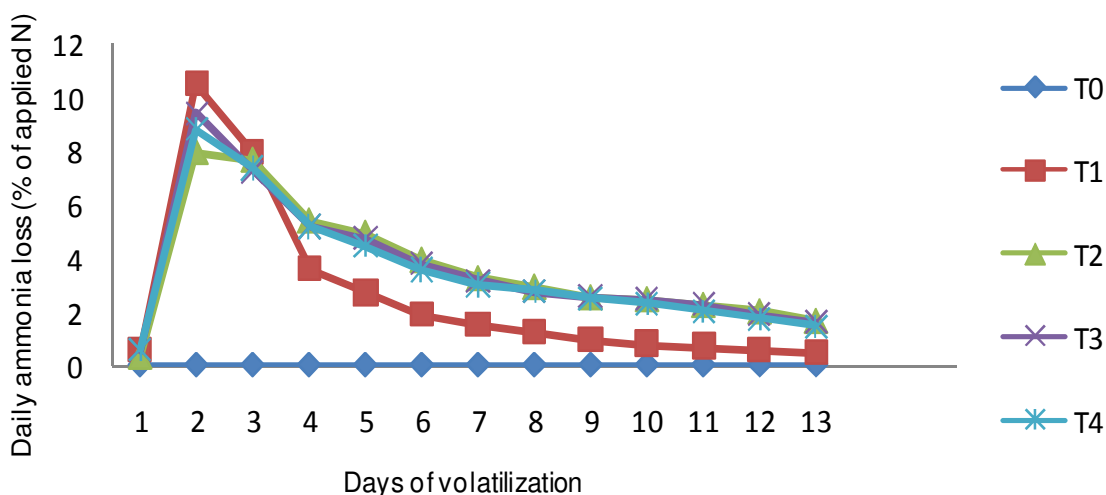
| Property                               | Value obtained | Standard data range* |
|--|----------------|----------------------|
| pH (water)                             | 4.11           | 4.6 – 4.9            |
| pH (KCl)                               | 3.86           | 3.8 – 4.0            |
| CEC (cmol kg <sup>-1</sup> )           | 7.33           | 3.86 – 8.46          |
| Texture                                | SCL            | SCL                  |
| Bulk density (g cm <sup>-3</sup> )     | 1.51           | nd                   |
| Organic matter (%)                     | 2.28           | nd                   |
| Available P (mg kg <sup>-1</sup> )     | 2.39           | nd                   |
| Total nitrogen (%)                     | 0.15           | 0.04 – 0.17          |
| Organic carbon (%)                     | 0.57           | 0.57 – 2.51          |
| Exchangeable Ca (mg kg <sup>-1</sup> ) | 2.05           | 0.05 – 0.19          |
| Exchangeable Mg (mg kg <sup>-1</sup> ) | 0.18           | 0.07 – 0.21          |
| Exchangeable K (mg kg <sup>-1</sup> )  | 0.16           | 0.05 – 0.19          |

CEC, Cation exchange capacity; SCL, sandy clay loam, nd, not determined.\*Standard data range (Paramanathan, 2000).

**Table 2.** Selected chemical properties of zeolite, peat soil water and urea.

| Property                               | Zeolite | Peat soil water | Urea |
|--|---------|-----------------|------|
| pHw                                    | 6.52    | 3.90            | 8.00 |
| pH (KCl)                               | 5.38    | nd              | nd   |
| CEC (cmol kg <sup>-1</sup> )           | 100.33  | nd              | nd   |
| Total nitrogen (%)                     | nd      | 0.16            | nd   |
| Exchangeable Ca (mg kg <sup>-1</sup> ) | 20.19   | 0.42            | nd   |
| Exchangeable Mg (mg kg <sup>-1</sup> ) | 31.50   | 0.12            | nd   |
| Exchangeable K (mg kg <sup>-1</sup> )  | 28.16   | 0.02            | nd   |

CEC, Cation exchange capacity; nd, not determined.



**Figure 1.** Ammonia volatilization over 13 days of incubation under waterlogged condition.

basic (Table 2). The cation exchange capacity (CEC) and the exchangeable Ca, Mg and K contents of the zeolite were high.

As presented in Figure 1, soil alone did not contribute to ammonia loss throughout the incubation period. The ammonia loss started a day after the treatments were

**Table 3.** Mean cumulative ammonia loss and soil pH after 13 days incubation under waterlogged conditions.

| Treatment | Ammonia loss (%)    | Soil pH (water)    |
|-----------|---------------------|--------------------|
| T0        | 0 <sup>d</sup>      | 5.40 <sup>c</sup>  |
| T1        | 42.87 <sup>a</sup>  | 7.21 <sup>a</sup>  |
| T2        | 28.20 <sup>bc</sup> | 7.27 <sup>a</sup>  |
| T3        | 26.65 <sup>c</sup>  | 7.08 <sup>b</sup>  |
| T4        | 32.29 <sup>b</sup>  | 7.16 <sup>ab</sup> |

Means with the same letter are not significantly different by Duncan's test at  $p \leq 0.05$ .

**Table 4.** Mean cumulative exchangeable ammonium and available nitrate during 13 days of incubation.

| Treatment | NH <sub>4</sub> <sup>+</sup> N (mg kg <sup>-1</sup> ) | NO <sub>3</sub> <sup>-</sup> N (mg kg <sup>-1</sup> ) |
|-----------|---|---|
| T0        | 12.07 <sup>c</sup>                                    | 1.55 <sup>c</sup>                                     |
| T1        | 78.09 <sup>b</sup>                                    | 22.80 <sup>b</sup>                                    |
| T2        | 148.72 <sup>a</sup>                                   | 34.93 <sup>a</sup>                                    |
| T3        | 158.09 <sup>a</sup>                                   | 31.42 <sup>a</sup>                                    |
| T4        | 137.44 <sup>a</sup>                                   | 27.5 <sup>ab</sup>                                    |

Means with the same letter are not significantly different by Duncan's test at  $p \leq 0.05$ .

applied but for the second and third days of incubation, the mixtures that is urea amended with zeolite and peat soil water (T2, T3, and T4) reduced ammonia loss (Figure 1). Afterwards, the loss significantly declined regardless of treatment.

The total amounts of ammonia lost over the 13 days of incubation are summarized in Table 3. All the treatments with zeolite and peat soil water (T2, T3, and T4) significantly reduced ammonia loss compared with urea without additives (T1). The mixtures significantly reduced ammonia loss partly because the peat soil water may have temporarily acidified the soil surrounding urea-zeolite-peat soil water mixture because when the soil pH is less than 5.5, urea hydrolyzes slowly (Fan and Mackenzie, 1993). This process may have effectively increased the volume soil with which urea mixes, and also increased the time required for complete hydrolysis (Fan and Mackenzie, 1993). During urea hydrolysis, lower soil pH favoured formation of ammonium ions over ammonia, therefore the significant reduction in ammonia loss observed.

The significant accumulation of soil exchangeable ammonium and available nitrate with all the mixtures compared with urea without additives (Table 4) was comparable with that of Fan and Mackenzie (1993). The high content of ammonium ions in this study indicates that the inclusion of zeolite has improved the soil ammonium retention. The inclusion of zeolite also minimized the conversion of ammonium to nitrate. At 13 days of

incubation, only the soil pH of T3 among the mixtures was significantly different compared with T1 (urea alone), and this was because the ammonia loss at this period did not vary significantly, that is about 1% of the N added as urea (Figure 1).

The high retention of ammonium observed could be attributed to the high CEC (100.33 cmol/kg) of the zeolite in the mixtures (T2, T3, and T4). This is because the channels in zeolites effectively absorb ammonium ions and release them slowly. In a related study, Lewis et al. (1984) reported that ammonium-exchanged clinoptilolite zeolite acted as a slow-release fertilizer in a medium textured, porous soil. They also observed that clinoptilolite zeolite reduced ammonia volatilization when urea and clinoptilolite were applied to a coarse-textured alkaline soil. In relation to this, the high loss of ammonia from urea without additives was possible because of the increased alkalinity from urea hydrolysis exceeding the localized buffer capacity of the soil or its ammonium retention ability.

## Conclusion

Mixing urea with zeolite and peat soil water controls ammonia loss better than urea without additives. Besides increasing the formation of ammonium and available nitrate ions over ammonia, the mixture ensures good retention of ammonium and nitrate within the soil.

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