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Ammonia volatilization from urea at different levels of zeolite

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Ammonia (NH_3) loss due to hydrolysis of urea can be substantial. When applied to the soil, up to 50% NH_3 volatilizes. This decreases urea-N use efficiency. The objective of this study was to minimize ammonia loss from urea using different levels of clinoptilolite zeolite. Six treatments were evaluated; (1) soil alone, (2) 2.60 g granular urea, (3) 2.60 g liquid urea, (4) 2.60 g liquid urea + 4 g of zeolite, (5) 2.60 g liquid urea + 8 g of zeolite and (6) 2.60 g liquid urea + 12 g of zeolite. The incubation study was conducted using close-dynamic air flow system method to measure the amount of NH_3 released. At the end of this study, soils samples were analyzed for pH, exchangeable ammonium (NH_4^+) and available nitrate (NO_3^-) using standard procedures. When urea was applied in liquid form, NH_3 loss was reduced when compared with granular urea, but not significantly different among the treatments with and without zeolite inclusion. Increase in soil pH was observed upon addition of higher amount of zeolite when compared with urea alone. High NH_4^+ content and low NH_3 loss for T5 directly showed that high cation exchange capacity (CEC) of the amended soil due to inclusion of zeolite was responsible for retention of more NH_4^+ in the soil even though the soil pH was higher when compared with T1 and T2. Liquid urea mixed with zeolite reduced NH_3 loss and increased NH_4^+ retention in the soil.

Key words: Ammonia volatilization, granular urea, liquid urea, zeolite.

INTRODUCTION

When urea is applied to soil, urea hydrolysis occurs because urea's enzyme breaks down urea molecule into NH_4^+ (Mengel and Kirkby, 1987) resulting in up to 50% loss of urea in the form of NH_3 (Sommer et al., 2004). This loss is associated with application method, soil factors and environmental conditions (Sharpley et al., 1998). Many approaches and additives have been used by researchers to reduce NH_3 loss from urea (Voss, 1984; Gould et al., 1986).

Combination of acidic and high CEC materials showed reduction in NH_3 loss (Ahmed et al., 2006, 2008, 2010) because urea hydrolysis is reduced when pH of soil is less than 5.5 (Fan and Mackenzie, 1993) and retention of NH_4^+ by the cation- exchange sites. Application of clinoptilolite zeolite has been effective in reducing NH_3 volatilization in alkaline, coarse-textured soil (Lewis et al., 1984). This depends on the amounts of zeolite used (Ahmed et al., 2008). This is because of its high CEC and great affinity for NH_4^+. The small channels of zeolites have been reported to reduce nitrification by microbes and protect NH_4^+ physically (Ming and Dixon, 1986; Ferguson and Pepper, 1987).

When liquid urea is used, NH_3 loss may be reduced, because it penetrates into the soil layer. For instance, NH_3 loss decreased when urea was used in fertigation (Papadopoulos, 2000). Furthermore, NH_3 loss from broadcasting urea could be reduced if the amount of rainfall is sufficient to disperse urea and the reaction product indirectly reduce alkaline condition to soil (Harper et al., 1983). Therefore, this study was carried out to minimize ammonia loss from urea using different levels of clinoptilolite zeolite.

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MATERIALS AND METHODS

The soil used in this experiment was Tipik Tualemkuts (Bekenu, Series), collected from an undisturbed area at Universiti Putra Malaysia, Bintulu Sarawak Campus, Malaysia. Samples were collected at 0 to 20 cm soil depth, air dried, meshed and sieved to pass a 2 mm sieve. The zeolite used was in powder form.

The soil and zeolite pH were determined in a 1:2.5 soil:distilled water suspension and 1 M potassium chloride (KCl) using a glass electrode (Peech, 1965). Soil texture was determined using the hydrometer method (Tan, 2005). Soil CEC was determined by the leaching method with 1 N ammonium acetate followed with steam distillation technique (Bremner, 1965) and CEC of clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). Exchangeable K, Ca and Mg were extracted using the leaching method (Cottenie, 1980) and determined by atomic absorption spectrometry (AAS). Inorganic N (NH_4^+ and NO_3^-) was determined using the method of Keeney and Nelson (1982). Total N of the soil was determined by the method described by Bremner (1965).

Treatments evaluated per 250 g of soil were:

(i) T0 = Soil alone
(ii) T1 = 2.60 g granular urea
(iii) T2 = 2.60 g liquid urea
(iv) T3 = 2.60 g liquid urea + 4 g of zeolite
(v) T4 = 2.60 g liquid urea + 8 g of zeolite
(vi) T5 = 2.60 g liquid urea + 12 g of zeolite

The amount of zeolite used was because previous study showed reduction of NH_4^+, leaching was 66% by adding 8 g of natural zeolite kg^{-1} of sandy soil (Zwingmann et al., 2009). The amounts of urea used were calculated from the N fertilizer recommendations for pepper (Sadanandan, 2000). Soil (250 g) was well mixed with different levels of zeolite and was wetted with distilled water for granular and for liquid fertilizer using mixture of urea and distilled water to get the 60% of soil field capacity. For granular urea treatment, urea was applied at the surface of the soil. Daily ammonia loss from the soil was measured using a close-dynamic air flow system method until the loss was reduced to 1% of urea added (Siva et al., 1999; Ahmed et al., 2006).

The incubation chamber was kept at room temperature and air passed through the chambers at a rate of 3.5 L/min. This rate of air flow, corresponding to 8.5 volume exchanges per minute and it was maintained throughout the incubation period using a Gilmont flow meter (Gilmont Instrument, Great Neck, New York) to measure and adjust the air flow.

At the end of this study, soils samples were analyzed for pH, NH_4^+ and NO_3^- contents. Treatments were arranged in complete randomized design (CRD) with three replications. Analysis of variance (ANOVA) was used to test for treatment effects while means were compared using Duncan's test using Statistical Analysis System (SAS Version 9.2).

RESULTS AND DISCUSSION

The selected physical and chemical characteristics of the soil used in this study are presented in Table 1. The soil texture was sandy clay loam. The soil was acidic and total N was consistent with that reported by Paramananthan (2000). The pH of zeolite was high as expected.

All the treatments with urea (Figure 1) showed NH_3 loss except for soil alone (T0). Volatilization loss rapidly

Table 1. Selected chemical and physical characteristics of soil and zeolite.

Property	Soil	Zeolite
pH $_{Water}$	4.11	7.90
PH $_{KCl}$	3.53	6.64
Exchangeable K^+ (cmoL kg^{-1})	8.20	21.53
Exchangeable Ca^{2+} (cmoL kg^{-1})	1.92	39.47
Exchangeable Mg^{2+} (cmoL kg^{-1})	2.33	26.30
Bulk density (g cm^{-3})	1.09	nd
CEC (cmoL kg^{-1})	7.13	100.20
Total nitrogen (%)	0.06	nd
Clay (%)	26.35	nd
Sand (%)	46.47	nd
Silt (%)	27.18	nd

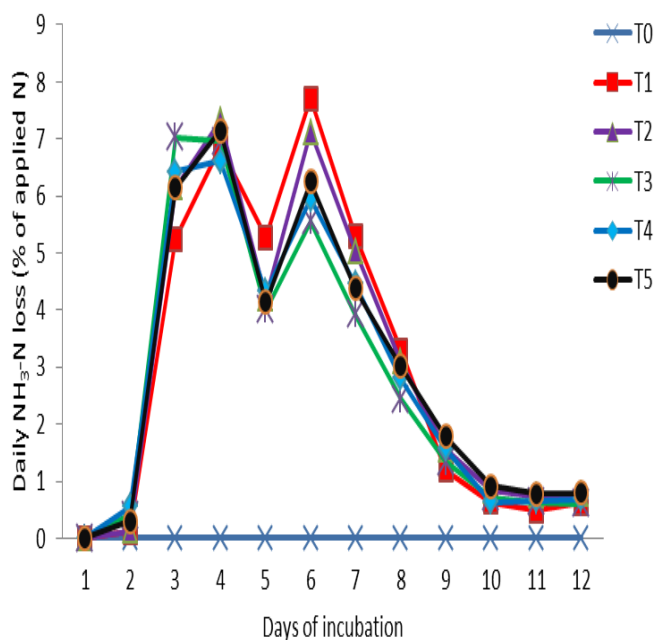CEC, cation exchange capacity; nd, not determined.

Figure 1. Daily losses of ammonia from urea fertilizer over 12 days of incubation.

occurred in liquid urea treatments (T2, T3, T4 and T5) and the maximum NH_3 loss occurred at 3 and 4 days after incubation while that of T1 occurred at day 6. This was because the dissolved urea reacted with soil water to form NH_4^+. As soil surface rapidly dried due to air velocity in the chamber, NH_3 from urea treatment decreased at day 5 of incubation. Ammonia loss decreased when soil water was insufficient for the necessary chemical reactions and it increased at day 6 after the second addition of water. Similar results have been reported by Raison et al. (1978) and Cabrera et al. (2005), where NH_3

Table 2. Total amounts of ammonia loss and soil pH after 12 days of incubation.

Treatment	NH₃ loss (% of urea-N)	pH
T0	0.00[c]	3.88[e]
T1	37.48[a]	7.18[cd]
T2	32.15[b]	7.12[d]
T3	33.65[b]	7.22[c]
T4	34.66[b]	7.30[b]
T5	33.20[b]	7.40[a]

Different alphabets indicate significant difference between means using Duncan' test at $p \leq 0.05$.

Table 3. Effect of treatments on soil exchangeable ammonium and nitrate accumulation after 12 days of incubation.

Treatment	Exchangeable NH_4^+-N (ppm)	Available NO_3^--N (ppm)
T0	67.72[d]	30.36[b]
T1	905.98[c]	42.03[a]
T2	997.05[b]	46.70[a]
T3	1032.07[b]	39.70[a]
T4	1048.42[b]	39.70[a]
T5	1144.15[a]	42.03[a]

Different alphabets indicate significant difference between means using Duncan' test at $p \leq 0.05$.

loss increased by rain or re-wetting of the soil after several days of application because of an increase in the rate of urea hydrolysis. After the maximum NH_3 loss as previously discussed, NH_3 loss declined until day 12 of incubation where the loss was 1% of nitrogen added as urea. Treatments T2, T3, T4 and T5 significantly reduced NH_3 loss when compared with T1 (Table 2). When applied with water, urea penetrates into the soil layer and held by the soil colloids consequently lowering the air velocity when compared with surface application. During urea infiltration, hydrolysis occurs and converts urea into NH_4^+ after application (Nkrumah et al., 1989). Hence, hydrolysis of urea not only occurs at the surface but in the soil profile and directly reduces NH_3 loss. This observation was consistent with the result reported by Sigunga et al. (2002) and Nyord et al. (2008) where reduction of NH_3 loss in the soil was affected by the depth of soil injected with fertilizer.

After 12 days of incubation, soil pH (Table 2) increased with increasing level of zeolite (T3 to T5) when compared with liquid urea alone (T2). Application of zeolite created more soil alkalinity and this was possible because of the high pH of the zeolite added. Increase in soil pH upon application of zeolite has been previously reported (Lin et al., 1998). Higher accumulation of NH_4^+ after 12 days of urea application was found for treatment T5, while the lowest was recorded for T1 (Table 3). There was no

significant difference in NH_4^+ content for liquid urea only (T2) and addition of zeolites (T3 and T4) except for T5 where 12 g of zeolite was added. Application of zeolites to the soil increased the amount of NH_4^+ and reduced NH_3 loss when compared with urea without additive due to the exchange sites of zeolite which can retain NH_4^+ produced from urea during hydrolysis (Ahmed et al., 2008; Latifah et al., 2010). High NH_4^+ and low NH_3 loss for T5 was because the CEC of the zeolite favoured formation of NH_4^+. In related studies, Ahmed et al. (2008) and Latifah et al. (2010) reported that mixing triple superphosphate (TSP) or Sago waste water with zeolite increased accumulation of NH_4^+ over NH_3 in the soil. The authors showed that application of liquid urea combined with zeolite had no significant effect on NO_3^- when compared with granular urea. This was because high NH_3 loss due to soil pH exceeding soil buffer capacity for T1 and zeolite has good selectivity for NH_4^+ (Pabalan and Bertetti, 2001) than formation of NO_3^- in the soil.

Conclusion

Ammonia volatilization from urea can be reduced by mixing urea with zeolite. The exchanger site from zeolite was able to retain ammonium ion from urea as compared to the formation of ammonia as well as increasing the accumulation of ammonium ion.

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