Full Length Research Paper

# Enhancing nutrient use efficiency of maize (*Zea mays* L.) from mixing urea with zeolite and peat soil water

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Accepted 31 May, 2011

The use of urea as N fertilizer has increased globally but lack of efficiency due to loss through ammonia volatilization has become a subject of considerable recent attention. In line with this, a pot experiment was conducted to determine the effect of mixing urea with zeolite and peat soil water on: (1) uptake and use efficiency of N, P and K in maize cultivation, and (2) soil exchangeable ammonium, available nitrate, pH, exchangeable K, and available P contents. The treatments evaluated were: No fertilizer (T0), 2.02 g urea (T1), 2.02 g urea + 30 g zeolite + 7 L peat soil water (T2), 2.02 g urea + 40 g zeolite + 7 L peat soil water (T3), and 2.02 g urea + 7 L peat soil water (T4). The fertilizers of TSP and MOP were applied twice that is 10 and 28 days after planting for all the treatments except T0. The application of peat soil water, and zeolite with urea had significant effect on dry matter, N, P, K uptake and N, P, K use efficiency compared with urea without additives. The soil exchangeable ammonium, K, Ca, Mg, available P, and nitrate contents were significantly increased compared with urea without additives. Formation of ammonium and nitrate over ammonia were reflected by the mixtures of peat soil water, and zeolite, with urea. Amending urea with zeolite and peat soil water can reduce ammonia loss by encouraging formation of ammonium and nitrate over ammonia. In addition, the mixtures ensure N, P, K uptake and their use efficiency while at the same time rendering soil ammonium, K, Ca, Mg, P, and nitrate available for plant use.

Key words: Urea, peat soil water, exchangeable ammonium, available nitrate, maize, nutrient use efficiency.

## INTRODUCTION

Broadcasting urea at the soil surface is a common practice in agriculture because of the ease of application and the low cost of urea (Phillipe et al., 2009). When applied at the soil surface, up to the 60% of the urea N can be volatilized as  $NH_3$  (Gioacchini et al., 2002). Surface application of  $NH_4$ –N based fertilizer often results in considerable  $NH_3$  volatilization (Sommer et al., 2004). During the past 25 years, the use of urea as an N fertilizer has increased significantly and it is now the most important N fertilizer in world agriculture (Bremner, 1995). However, the loss of urea N through volatilization reduces its efficiency particularly if it is not promptly incorporated into the soil (Cai et al., 2002). Ammonia volatilization does not only result in increased production costs, but also raises concern regarding N contamination of surface water and groundwater (Gupta et al., 1997). The amount of  $NH_3$  volatilization from urea N fertilizers in laboratory studies has been related to soil properties such as pH and cation exchange capacity (Bremner, 1995). He et al. (1999) reported that 150 to 240 g kg<sup>-1</sup> of the applied N is lost by volatilization in a Riviera fine sand (pH 7.9), depending on fertilizer sources. Soil acidification and nutrient imbalances may occur due to the redeposition of  $NH_4^+$  (He et al., 1999).

For acidic soil which is low in cation exchange capacity,  $NH_3$  volatilization can be minimized by appropriate sinks in the soil for  $NH_4$ –N. Zeolites can be used because of their high specific surface areas and their rigid framework but the most commercially valuable and dynamic property

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of zeolite is the CEC (Ming and Mumpton, 1989). Clinoptilolite zeolites which are porous minerals with high CEC and great affinity for  $NH_4^+$  (Ming and Mumpton, 1989) have been used to reduce  $NH_3$  emission from farm manure (Amon et al., 1997). They have also been used to eliminate  $NH_3$  toxicity to plants (Bremner, 1995).

Peat soil water (pH 3 to 4) is abundant in Malaysia as for instance, the state of Sarawak alone has 1.5 million peatland (Andriesse, 1998). 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, this study seeks to put to good use of peat water which is drained from peatlands when they are opened for inevitable cultivation. The objectives of this pot experiment were to determine the effect of mixing urea with zeolite and peat soil water on:

(1) Uptake and use efficiency of N, P and K in maize cultivation

(2) Soil exchangeable  $NH_4^+$ , available  $NO_3^-$ , pH, exchangeable K, and available P contents.

#### 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 (Bekenu series, Tipik Tualemkuts, Sandy clay loam) 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 a 2.0 mm sieve for pot experiment (greenhouse). Soil texture was determined using the hydrometer method (Bouyoucos, 1962) 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 KCI using a glass electrode (Peech, 1965). However, the pH of peat soil water was determined directly from filtered samples using a glass electrode. The soil total carbon, N and organic matter were determined using LECO CHNS Analyzer (Leco Truspec Micro Elemental Analyzer CHNS, New York). Soil available P was extracted using the double acid method (Tan, 2005) and the blue method (Murphy and Riley, 1962) was used to develop blue colour afterwhich P content was determined by spectroscopy. The Kjedhal 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 atomic absorption spectrometry (AAS). Soil CEC was determined by the leaching method followed by steam distillation (Tan, 2002). 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 zeolite channels (Ming and Dixon, 1986).

The pot experiment was conducted in a greenhouse at the University Putra Malaysia Bintulu Sarawak Campus using completely randomized design with three replicates. The pots used were in a size of  $22 \times 28$  cm and consisted of 10 kg soil (based on soil bulk density). Maize (*Zea mays* L.) hybrid No. 5 variety was used as test crop. The N, P, and K requirement of the test crop were 60 kg N, 60 kg P<sub>2</sub>O<sub>5</sub> and 40 kg K<sub>2</sub>O (130 kg ha<sup>-1</sup> urea: 130 kg ha<sup>-1</sup> TSP: 67 kg ha<sup>-1</sup> MOP) (Department of Agriculture, 2003). The

fertilizer requirement was scaled down to per pot basis equivalent to 2.02 g of urea, 5 g of TSP and 5 g of MOP. The volume of water used for each pot was based on field capacity (70%). The treatments evaluated were: no fertilizer (T0), 2.02 g urea (T1), 2.02 g urea + 30 g zeolite + 7 L peat soil water (T2), 2.02 g urea + 40 g zeolite + 7 L peat soil water (T3), and 2.02 g urea + 7 L peat soil water (T4).

Zeolites and first application of peat soil water of 3.5 L were applied a day before planting meanwhile another 3.5 L of peat soil water were applied at 28 days after planting for all treatments except for T0 and T1. For T0 and T1, soils were moistened with 3.5 L of tap water. Triple super phosphate (TSP) and muriate of potash (MOP) were used as sources of P and K for all the treatments except for T0. These fertilizers were applied twice that is 10 and 28th days after planting. Phosphorus and K requirements of the test crop were met by applying TSP and MOP (standard rate for the test crop) to plants of all the treatments except for T0.

At 56 days after planting (tasseling stage), the maize plants were harvested. Tassel stage is the maximum growth stage for the plant before it goes to reproductive stage (Susilawati et al., 2009). The whole plant was partitioned into roots, stem and leaves. The remaining roots in soil were removed carefully and cleaned using tap and distilled water. Leaves, stems, and roots were oven dried at 60 ℃ until constant weight was attained and their dry weights were determined. Each plant part was ground and analyzed for total N, P and K uptake and their use efficiency. Total N of plant tissues were determined by the Kjedhal method (Bremner, 1965). Exchangeable Ca. Mg. and K of plant tissues were extracted with the double acid method (Tan, 2005) and the extracts were analyzed using AAS. Total P of the plant tissues was extracted using dry ashing method (Tan, 2005) followed by blue method (Murphy and Riley, 1962) as described previously. After harvest, soil samples were analyzed for pH, accumulation of NH4<sup>+</sup>, and NO3<sup>-</sup>, exchangeable cations, and available P. Exchangeable Ca, Mg, and K were extracted with the double acid method (Tan, 2005) and the extracts was analyzed as described earlier. Exchangeable  $NH_4^+$  and  $NO_3^-$  were extracted from the soil using method of Keeney and Nelson (1982) and the amount was determined using steam distillation. Soil available P was extracted using the double acid method (Tan, 2005) followed by the blue method (1962) as described earlier.

Nitrogen, P and K use efficiency were determined by the formula (Pomares-Garcia and Pratt, 1987):

% Efficiency = 
$$(\underline{A - B}) \times 100$$
  
C

Where A = uptake with fertilizer, B = uptake without fertilizer, C = total amount of fertilizer that had been applied; uptake = concentration ×dry weight (g).

Nitrogen, P and K uptake in leaves, stem, and roots were determined by multiplying their concentrations with the dry weight of the plant parts. Analysis of variance (ANOVA) was used to test the effect of treatments while means of treatments were compared using Duncan's New Multiple Range Test (DNMRT). Statistical Analysis System (SAS version 9.2) was used for the statistical analysis.

### **RESULTS AND DISCUSSION**

The selected physical and chemical properties of Bekenu Series are summarized in Table 1. The aforementioned properties were comparable with those reported by Paramananthan (2000) except for exchangeable Ca, which was relatively high probably because of liming.

Property	Value obtained	Standard data range*
pH (water)	4.11	4.6 - 4.9
pH (KCI)	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)	2.39	nd
Total Nitrogen (%)	0.15	0.04 - 0.17
Organic carbon (%)	0.57	0.57 - 2.51
Exchangeable Ca (mgkg <sup>-1</sup> )	2.05	0.05 - 0.19
Exchangeable Mg (mgkg <sup>-1</sup> )	0.18	0.07 - 0.21
Exchangeable K (mgkg <sup>-1</sup> )	0.16	0.05 - 0.19

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

Cation exchange capacity (CEC); sandy clay loam (SCL); not determined (nd); \* means: Standard data range (Paramananthan, 2002).

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)	100.33	nd	nd
Total Nitrogen (%)	nd	0.16	nd
Exchangeable Ca (mgkg <sup>-1</sup> )	20.19	0.42	nd
Exchangeable Mg (mgkg <sup>-1</sup> )	31.50	0.12	nd
Exchangeable K (mgkg <sup>-1</sup> )	28.16	0.02	nd

Cation exchange capacity (CEC); not determined (nd).

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Treatment	NH₄-N (ppm)	NO₃-N (ppm)
T0	18.47 <sup>e</sup>	3.67 <sup>d</sup>
T1	23.40 <sup>d</sup>	5.34 <sup>c</sup>
T2	27.10 <sup>c</sup>	8.21 <sup>b</sup>
Т3	37.36 <sup>a</sup>	10.67 <sup>a</sup>
T4	31.13 <sup>b</sup>	5.43 <sup>c</sup>

**Table 3.** Effect of treatments on ammonium and nitrate at56 days after planting.

Means with same letter are not significantly different by DNMRT test at  $p \le 0.05.$ 

The pH of the peat soil water and zeolite were acidic while the pH of urea was basic (Table 2). The CEC of the zeolite was high as well as its exchangeable Ca, Mg and K contents.

The accumulation of exchangeable  $NH_4^+$  and available  $NO_3^-$  is presented in Table 3. The mixtures (T2, T3, and T4) significantly improved the retention of  $NH_4^+$  and available  $NO_3^-$  compared to urea alone (T1). A similar finding was reported by Ahmed et al. (2008) who

evaluated effect of zeolite and TSP on acid soils. The findings in this study suggest that retention of  $NH_4^+$  may be due to the effect of zeolite, which is noted for  $NH_4^+$  releasing slowly as well as protecting it from excessive nitrification in soil (Fan and MacKenzie, 1993). In another study, Huang and Petrovic (1993) found significant retention of  $NH_4^+$  and  $NO_3^-$  when a sandy soil was amended with zeolite. This was attributed to increased soil surface area and CEC (Huang and Petrovic, 1993).

Treatment	pH (water)	P (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)
TO	4.58 <sup>a</sup>	0.28 <sup>d</sup>	1.28 <sup>d</sup>	1.26 <sup>d</sup>	1.28 <sup>e</sup>
T1	3.94 <sup>a</sup>	0.46 <sup>c</sup>	2.32 <sup>c</sup>	2.36 <sup>c</sup>	2.63 <sup>d</sup>
T2	3.95 <sup>ª</sup>	1.04 <sup>b</sup>	2.87 <sup>ab</sup>	4.84 <sup>a</sup>	3.51 <sup>b</sup>
Т3	4.08 <sup>a</sup>	1.32 <sup>a</sup>	3.21 <sup>a</sup>	5.11 <sup>a</sup>	4.58 <sup>a</sup>
T4	3.89 <sup>a</sup>	1.32 <sup>a</sup>	2.62 <sup>c</sup>	3.34 <sup>b</sup>	3.09 <sup>c</sup>

**Table 4.** Effect of treatments on selected soil chemical properties at 56 days after planting.

Means with same letter are not significantly different by DNMRT test at  $p \le 0.05$ .

Table 5. Effect of treatments on dry weight of maize plant at 56 days after planting.

Treatment	Stems	Leaves	Roots(gplant <sup>-1</sup> )	Total
T0	5.37 <sup>d</sup>	4.23 <sup>d</sup>	3.14 <sup>c</sup>	12.74 <sup>d</sup>
T1	5.71 <sup>d</sup>	6.00 <sup>c</sup>	3.18 <sup>c</sup>	14.89 <sup>c</sup>
T2	7.70 <sup>b</sup>	6.95 <sup>bc</sup>	3.40 <sup>c</sup>	18.05 <sup>b</sup>
Т3	8.21 <sup>ª</sup>	7.43 <sup>a</sup>	6.24 <sup>a</sup>	21.88 <sup>a</sup>
T4	6.46 <sup>c</sup>	6.33 <sup>bc</sup>	4.62 <sup>b</sup>	17.41 <sup>b</sup>

Means with same letter are not significantly different by DNMRT test at  $p \le 0.05$ .

The ability of T2 and T3 to cause significant accumulation of exchangeable NH<sub>4</sub><sup>+</sup> and available NO<sub>3</sub><sup>-</sup> was partly due to the retention property of zeolite as explained by Ferguson and Pepper (1987). In their study, they reported that clinoptilolite zeolite is characterized by a rigid three-dimensional lattice with channels containing internal exchange sites which have affinity for NH4<sup>+</sup> (Ferguson and Pepper, 1987). Formation of soil exchangeable  $NH_4^+$  and available  $NO_3^-$  over  $NH_3$  is thought to be related to the small size of the channels which are reported to protect NH<sub>4</sub><sup>+</sup> physically from excessive nitrification (Fan and MacKenzie, 1993). Formation of NH<sub>4</sub><sup>+</sup> could also be partly attributed to the addition of peat soil water (T2, T3 and T4). The ability of peat soil water to reduce soil pH determines the equilibrium between  $NH_4^+$  and  $NH_3$  in the system. The relative concentration of NH<sub>3</sub> decreased with decreasing pH whiles the NH4<sup>+</sup> concentration increases (Fan and MacKenzie, 1993; Latifah et al., 2010) and this minimizes NH<sub>3</sub> loss.

Soil exchangeable Ca, Mg, K, and available P were significantly increased in all mixtures compared with urea alone (Table 4) except for soil pH. This result suggests that the high CEC (100.33 cmol kg<sup>-1</sup>) of zeolites in T2 and T3 had a significant effect on the accumulation of exchangeable cations such as Ca, Mg and K in this study. This is because when a molecule of NH<sub>3</sub> is hydrated, the reaction produces  $NH_4^+$ , which is readily exchanged for all or part of the Ca, K, and Mg cations adsorbed on to its stable aluminosilicate lattice (Ming and Mumpton, 1989). The exchangeable cations found in natural zeolite molecules such as Na, Ca, K, and Mg

(Ming and Mumpton, 1989) may also have affected the accumulation of cations in all mixtures (T2, T3, and T4).

Dry weight of stem, leaves and roots for T2, T3, and T4 were significantly higher than that of T1 (Table 5). This observation is contrary to the finding of a study (Ahmed et al., 2008) that all treatments with additives had effect on only dry weight of leaves and stem of maize compared with urea alone. Ahmed et al. (2008) found that only treatment with higher amounts of TSP and zeolite significantly increased the dry matter of stem and leaves production of Swan (test crop). This may be due to the maize variety used in their study as a test crop. The significant effect of T2, T3 and T4 on dry weight of maize compared to T1 could be associated with their ability to retain exchangeable  $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and available  $NO_3^-$ .

All the mixtures enhanced N uptake and use efficiency in all the parts of the test crop when compared with that of urea alone (Tables 6 and 7). This was because the mixtures may have encouraged formation of NH4<sup>+</sup> over NH<sub>3</sub>. A similar observation has been reported by Ahmed et al. (2008). The ability of the mixtures to improve N uptake and use efficiency can also be related to their ability to reduce NH<sub>3</sub> volatilization (Latifah et al., 2010). This was because the acidic nature of peat soil water may have 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). Consequently, this process increased the volume soil which mixes with urea and the time required for hydrolysis to complete also increased (Fan and MacKenzie, 1993). Upon urea hydrolysis, lower soil pH favoured the

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Treatments	N (%)	P (%)	K (%)
		Stems	
TO	28.59 <sup>c</sup>	11.27 <sup>d</sup>	11.40 <sup>c</sup>
T1	32.84 <sup>bc</sup>	12.29 <sup>cd</sup>	22.24 <sup>b</sup>
T2	37.08 <sup>ab</sup>	13.23 <sup>bc</sup>	22.24 <sup>b</sup>
Т3	39.19 <sup>a</sup>	18.88 <sup>a</sup>	33.24 <sup>a</sup>
T4	32.88 <sup>bc</sup>	14.08 <sup>b</sup>	22.25 <sup>b</sup>
		Leaves	
TO	43.03 <sup>e</sup>	1.82 <sup>c</sup>	9.11 <sup>d</sup>
T1	60.92 <sup>d</sup>	4.31 <sup>b</sup>	11.75 <sup>c</sup>
T2	67.05 <sup>b</sup>	4.24 <sup>b</sup>	22.34 <sup>b</sup>
Т3	76.21 <sup>a</sup>	5.87 <sup>a</sup>	33.03 <sup>a</sup>
T4	62.71 <sup>°</sup>	4.24 <sup>b</sup>	22.48 <sup>b</sup>
		Roots	
T0	12.44 <sup>c</sup>	1.76 <sup>d</sup>	12.43 <sup>e</sup>
T1	22.94 <sup>b</sup>	4.93 <sup>c</sup>	17.79 <sup>d</sup>
T2	23.11 <sup>b</sup>	8.13 <sup>b</sup>	22.74 <sup>c</sup>
Т3	26.91 <sup>a</sup>	9.76 <sup>a</sup>	25.13 <sup>b</sup>
T4	22.79 <sup>b</sup>	4.89 <sup>c</sup>	36.96 <sup>a</sup>

Table 6. Effect of treatments on N, P, and K uptake of maize plant at 56 days after planting.

Means with same letter are not significantly different by DNMRT test at  $p \le 0.05$ .

Treatment	Stem	Leaves	Roots	Total	_
		N (%)			
Т0	nd	nd	nd	nd	
T1	0.24 <sup>d</sup>	1.26 <sup>d</sup>	0.37 <sup>c</sup>	1.87 <sup>d</sup>	
T2	1.17 <sup>c</sup>	2.36 <sup>c</sup>	2.51 <sup>b</sup>	6.04 <sup>c</sup>	
Т3	2.69 <sup>a</sup>	4.84 <sup>a</sup>	4.58 <sup>a</sup>	12.11 <sup>a</sup>	
T4	1.55 <sup>b</sup>	3.34 <sup>b</sup>	3.09 <sup>b</sup>	7.98 <sup>b</sup>	
		P (%)			
ТО	nd	nd	nd	nd	
T1	0.32 <sup>d</sup>	0.31 <sup>c</sup>	0.40 <sup>c</sup>	1.03 <sup>c</sup>	
T2	1.87 <sup>b</sup>	1.90 <sup>b</sup>	0.82 <sup>b</sup>	4.59 <sup>b</sup>	
Т3	2.21 <sup>ª</sup>	3.48 <sup>a</sup>	2.24 <sup>a</sup>	7.93 <sup>a</sup>	
T4	1.65 <sup>°</sup>	1.89 <sup>b</sup>	0.49 <sup>c</sup>	4.03 <sup>b</sup>	
		K (%)			
ТО	nd	nd	nd	nd	
T1	2.17 <sup>b</sup>	1.17 <sup>b</sup>	1.75 <sup>°</sup>	5.09 <sup>c</sup>	
T2	3.19 <sup>a</sup>	1.55 <sup>b</sup>	2.34 <sup>b</sup>	7.08 <sup>b</sup>	
Т3	3.31 <sup>a</sup>	2.69 <sup>a</sup>	3.03 <sup>a</sup>	9.03 <sup>a</sup>	
T4	2.40 <sup>ab</sup>	1.51 <sup>b</sup>	2.51 <sup>b</sup>	6.42 <sup>b</sup>	

 Table 7. Effect of treatments on N, P, and K use efficiency in stem, leaves, and roots of maize plant at 56 days after planting

Means with same letter within column are not significantly different by DNMRT test at  $p \le 0.05$ .

formation of  $NH_4^+$  over  $NH_3$ . The findings of this work is consistent with other studies which used acidic materials

such as humic and fulvic acids isolated from various sources such as coal, peat and palm oil mill effluent sludge

sludge to amend urea (Susilawati et al., 2009; Ameera et al., 2009; Regis et al., 2009; Rosliza et al., 2009a, 2009b).

#### Conclusion

Amending urea with zeolite and peat soil water can reduce ammonia loss by encouraging formation of ammonium and nitrate over ammonia. In addition, the mixtures ensure N, P, K uptake and their use efficiency while at the same time rendering soil ammonium, K, Ca, Mg, P, and nitrate available for plant use.

#### ACKNOWLEDGEMENT

The researchers acknowledge the financial support (Research University Grant Scheme) they received for the research from University Putra Malaysia, Malaysia.

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