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Use of formulated nitrogen, phosphorus, and potassium compound fertilizer using clinoptilolite zeolite in maize (*Zea mays* L.) cultivation

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Abstract

Adoption of new management techniques, such as clinoptilolite zeolite (CZ) utilization has attracted much attention in the fertilizer industry. Accordingly, the aims of this study is to evaluate: if CZ, acting as an inert material, when applied to the soil, might improve the selected soil properties, height, dry matter, nutrient concentration, nutrient uptake, nutrient use efficiency on maize cultivation; the potential for (N:P:K) compound fertilizer when incorporated with CZ to serve same standard as the commercial fertilizer in fertilizer industry. The effect of T₁, T₃ and T₆ on soil total N was found to be significant, when compared with T₇. Treatments with CZ on soil total P, K and available P, K differed significantly relatively to T₁ and T₇. The treatments T₅ and T₆ had the highest accumulation of exchangeable NH₄⁺ and available NO₃⁻ relatively to T₁ and T₇. The significant effect of the treatments having CZ on N concentration, in uptake and use efficiency, suggests that CZ incorporated with fertilizer can reduce NH₃ loss, triggering the formation of NH₄⁺ and NO₃⁻ over ammonia and increase maize uptake. Relatively to P concentration, uptake and use efficiency, it was found that in most treatments having CZ, lower values were obtained, relatively to the commercial fertilizer, although T₃ clearly improved P uptake in roots. Most of the treatments with CZ remained statistically similar in K concentration, uptake and use efficiency compared to commercial fertilizer. It may be concluded that treatments with higher amounts clinoptilolite zeolite ensured good retention of soil exchangeable cations, available P, and NO₃⁻ within the soil. Treatments with CZ improved N uptake and use efficiency in the maize crop tested.

Key words: Clinoptilolite zeolite (CZ), N:P:K compound fertilizer, Nutrient uptake, Nutrient use efficiency, Selected soil properties.

Abbreviation lists: Atomic absorption spectrophotometry, AAS; Cation exchange capacity, CEC; Day after planting, DAP; Dry weight, DW; Muriate of potash, MOP; Triple Superphosphate, TSP

Introduction

Many studies have been conducted, mainly on nitrogenous fertilizers, to minimize any possible adverse environmental effects (Trenkel, 2010). However, less attention has been devoted to the release of nutrients from N:P:K compounds, in which case the processes are expected to be more complex than with a single nutrient fertilizer. Adoption of new management techniques, such as using clinoptilolite zeolite to control nutrient release from compound fertilizers had in recent times

attracted the attention in the fertilization systems. Clinoptilolite zeolite is a porous mineral with high CEC up to 3000 mol cm⁻³ and with great affinity for NH₄⁺ (Ming and Mumpton, 1989), yet it can physically protect NH₄⁺ against microbial nitrification (Ferguson and Pepper, 1987). Clinoptilolite zeolite, which maximizes N use efficiency and water use efficiency, may decrease environmental degradation through the use of balanced fertilizers in agriculture (Ramesh and Reddy, 2011). Slow release of N fertilizers can be produced by amending N fertilizers, such as urea with clinoptilolite zeolite (Omar et al., 2011; Ahmed et al., 2008). The mechanism for slow release of K may be similar to the reactions shown for PO₃⁻ and NH₄⁺. This is possible because of the sequestering effect of the exchanger of clinoptilolite zeolite (Payra and Dutta, 2003; Lai and Eberl, 1986). According to Gholizadeh (2008), clinoptilolite

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zeolite when saturated with monovalent nutrient cations, such as NH_4^+ and K^+ , increases the solubility of phosphate rock. Besides, clinoptilolite zeolite acts as carriers of nutrients for cations and as a medium with free exchangeable nutrient (Perez et al., 2008). Clinoptilolite zeolite has also been reported to have a relatively high cation adsorption capacity (Oste et al., 2001; Li et al., 2001; Mineyev et al., 1990). Accordingly, the aims of this study is to evaluate: if clinoptilolite zeolite, acting as an inert material, when applied to the soil, might improve the selected soil properties, height, dry matter, nutrient concentration, nutrient uptake, nutrient use efficiency on maize cultivation; the potential for (N:P:K) compound fertilizer when incorporated with clinoptilolite zeolite to serve same standard as the commercial fertilizer in fertilizer industry.

Materials and Methods

A pot trial study was conducted to test the selected N:P:K compound fertilizers in a completely randomized block design with 3 replications. The soil used in this study was a *Tipik Tualemkuts* (Bekenu Series). Soil samples were taken at 0-15 cm depth using an auger, air dried and ground to pass a 5 mm sieve. The treatments evaluated were:

- i. 14.88 g commercial compound fertilizer with ratio 15:15:15 (control) (T1)
- ii. Compound fertilizer with ratio 15:15:15 (4.85 g urea + 4.85 g TSP + 3.72 g MOP) mixed with 1.46 g clinoptilolite zeolite (T2)
- iii. Compound fertilizer with ratio 13:15:13 (4.85 g urea + 5.61 g TSP + 3.73 g MOP) mixed with 3.01 g clinoptilolite zeolite (T3)
- iv. Compound fertilizer with ratio 10:10:10 (4.85 g urea + 4.85 g TSP + 3.73 g MOP) mixed with 8.92 g clinoptilolite zeolite (T4)
- v. Compound fertilizer with ratio 8:8:8 (4.85 g urea + 4.85 g TSP + 3.71 g MOP) mixed with 14.46 g clinoptilolite zeolite (T5)
- vi. Compound fertilizer with ratio 5.5:5.5:5.5 (4.85 g urea + 4.85 g TSP + 3.72 g MOP) mixed with 27.04 g clinoptilolite zeolite (T6)
- vii. Soil alone (control) (T7)

The amounts of the compound fertilizers applied were based on N standard requirements for mature Masmadu Maize (Malaysian Agricultural Research and Development Institute, 1990). The fertilizers were surface applied at the 9th DAP and 27th DAP. Two out of eight seedlings were maintained for observation before first fertilization in pots (25 cm of top diameter x 21 cm of height).

The clinoptilolite zeolite was powder applied. The pH of the soil and clinoptilolite zeolite were

determined in a ratio of 1:2.5 soil:distilled water suspension and 1M KCl solution using a glass electrode (Tan, 2005). Soil organic carbon was determined using Loss on Ignition (Piccolo, 1996). Soil total N was determined by the Kjeldahl method (Tan, 2005). Soil total P and K were extract using aqua regia (Tan, 2005). Filtrates were analyzed for K by AAS and UV-spectrometer for P. Soil CEC was determined by leaching with ammonium acetate buffer adjusted to pH 7.0 followed by steam distillation (Bremmer, 1965) and exchangeable K using AAS. The CEC of clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). Exchangeable K of the clinoptilolite zeolite was extracted using the method of Ming and Dixon (1986) and the concentration determined as previously outlined. The soil texture followed the hydrometer method (Tan, 2005). The exchangeable NH_4^+ and available NO_3^- were extracted from the soil by the method of Keeney and Nelson (1982), being the amounts determined using the steam distillation method (Tan, 2005).

The plants were monitored for 65 days. At the 65th DAP, the plants were harvested and partitioned into leaves, roots and stems. These parts were oven-dried until a constant weight at 60°C and recorded for their mass of dry weight. At the 65th DAP, soil samples were taken and analyzed for total and exchangeable N, P and K, exchangeable NH_4^+ , available NO_3^- and pH as previously outlined. Nitrogen concentrations in the selected plant parts were determined by the Kjeldahl (Bremmer, 1965), while the single dry ashing method (Cottenie, 1980), for the extraction of P and K in the plant tissues. The filtrates were analyzed for K by AAS and UV-spectrometer for P. The concentrations of N, P and K in the plant parts were multiplied by their dry matter to obtain the amount of N, P and K taken up by the plant parts. Nitrogen, P, and K use efficiency were calculated using the subtraction method (Pomares-Gracia and Pratt, 1987). Analysis of variance (ANOVA) was used to test the treatment effects and means of treatments were compared using Tukey's test.

Results

Selected soil physico-chemical properties before planting

The selected physio-chemical properties of *Tipik Tualemkuts* (Bekenu Series) and clinoptilolite zeolite are presented in Table 1. The soil pH (water), exchangeable K and texture were consistent with the report of Paramanathan (2000). Total organic carbon and CEC contents were higher than the standard range probably due to previous cultivation.

Table 1. Selected chemical and physical properties of Bekenu Series and clinoptilolite zeolite.

Property	Soil (0-15cm)		Clinoptilolite zeolite
	Value obtained	Standard data range	
pH(water)	4.70	4.6-4.9	7.03
pH(0.01M KCl)	3.43	3.8-4.0	6.37
Total organic carbon (%)	3.6	0.57-2.51	Nd
CEC(cmol kg ⁻¹)	12.8	3.86-8.46	75.4
Exchangeable K (cmol kg ⁻¹)	0.174	0.05-0.19	22.29
Texture	SL	SL	Nd
Bulk density(gm ⁻³)	1.01	Nd	Nd

CEC, Cation exchange capacity; SL, Sandy Loam; nd, not determined; standard data range (Paramanathan, 2000).

Table 2. Effect of treatments on selected soil physico-chemical properties at 65 DAP.

Treatment	pH (water)	Total			Available	Exchangeable
		N (%)	P	K (mgkg ⁻¹)	P	K
T1	4.30 ^d	0.15 ^a	342.5 ^c	110.6 ^d	188.8 ^c	82.0 ^{cd}
T2	4.70 ^c	0.15 ^a	1412.5 ^{ab}	679.6 ^c	606.4 ^a	412.6 ^c
T3	4.69 ^c	0.11 ^{ab}	969.8 ^b	599.6 ^c	487.4 ^{ab}	346.5 ^{cd}
T4	4.92 ^{bc}	0.11 ^{ab}	1519.8 ^a	1132.1 ^b	423.0 ^b	835.7 ^b
T5	5.09 ^b	0.08 ^{ab}	1587.5 ^a	1407.5 ^b	495.0 ^{ab}	1144.7 ^{ab}
T6	5.50 ^a	0.13 ^a	1707.8 ^a	1886.9 ^a	463.3 ^b	1293.6 ^a
T7	4.65 ^{dc}	0.05 ^b	65.3 ^c	53.8 ^d	22.13 ^d	5.2 ^d

Different letters (with column) indicate significant different between means using Tukey's test at P ≤ 0.05. For key to treatments see Materials and methods.

Soil pH, total N, P and K and available P and K at 65 DAP

The soil pH (water), total N, P and K and available P and K after harvest under fertilized and unfertilized condition are summarized in Table 2. At harvest, the soil pH (water) for T1 (commercial fertilizer) and T7 (soil alone) were 4.30 and 4.65. The soil pH (water) was significantly affected in the treatments with higher amounts of clinoptilolite zeolite contents (T5 and T6). The effect of T1, T3 and T6 on the soil total N was significant (when compared with T7). The effects of the treatments with clinoptilolite zeolite on soil total P and available P differed significantly relatively to T1 and T7. Soil total K of all treatments with clinoptilolite zeolite significantly increased compared to T1 and T7. T6, showing the treatment with the highest content of clinoptilolite zeolite the highest soil K content (1886.9 mg kg⁻¹). T6, T5 and T4, treatments with higher clinoptilolite zeolite significantly

increased soil exchangeable K content, relatively to the other treatments.

Exchangeable NH₄⁺ and available NO₃⁻ accumulation at 65 DAP

There were significant differences in the accumulation of exchangeable NH₄⁺ and available NO₃⁻ for all treatments (Table 3). In the case of soil exchangeable NH₄⁺, T6 showed a significant effect (when compared to the other treatments, except for T5). T5 and T6 showed the highest accumulation of available NO₃⁻.

Plant height at 65 DAP

The height of maize at 65 DAP is presented in Figure 1. T6, treatment with the highest clinoptilolite zeolite significantly increased the height of maize plants compared to T2, T4 and T7, but its effect was statistically similar to those of T5, T3 and T1.

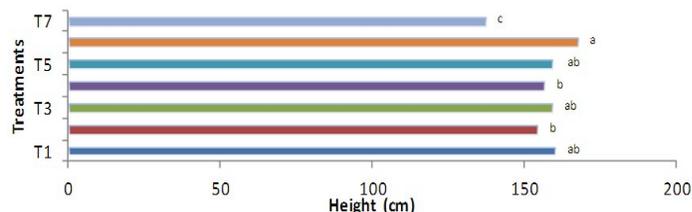


Figure 1. Height of maize plant at the 65th DAP. Different letters indicate significant different between means using Tukey's test at P ≤ 0.05. For key to treatments see Materials and methods.

Table 3. Effect of treatments on exchangeable NH₄⁺ and available NO₃⁻ accumulation at 65 DAP.

Treatment	T1	T2	T3	T4	T5	T6	T7
NH ₄ -N (%)	0.07 ^{cd}	0.07 ^{cd}	0.06 ^{cd}	0.12 ^{bc}	0.18 ^{ab}	0.21 ^a	0.04 ^d
NO ₃ -N (%)	0.007 ^c	0.007 ^c	0.007 ^c	0.014 ^b	0.021 ^a	0.021 ^a	0.007 ^c

Different letters (with row) indicate significant different between means using Tukey's test at P ≤ 0.05. For key to treatments see Materials and methods.

Table 4. DW of maize at the 65th DAP

Dry weight (g plant ⁻¹)	Stem	Leaf	Root	Total
T1	11.13 ^{ab}	18.60 ^a	13.22 ^a	42.95 ^a
T2	10.35 ^b	17.89 ^a	13.29 ^a	41.52 ^a
T3	14.03 ^a	17.76 ^a	16.10 ^a	47.89 ^a
T4	10.94 ^{ab}	19.15 ^a	14.53 ^a	44.61 ^a
T5	13.65 ^a	17.69 ^a	12.62 ^a	43.95 ^a
T6	12.47 ^{ab}	17.41 ^a	11.20 ^a	41.09 ^a
T7	6.22 ^c	10.00 ^b	10.74 ^a	28.91 ^b

Different letters (with column) indicate significant different between means using Tukey's test at P ≤ 0.05. For key to treatments see Materials and methods.

Dry weight at 65 DAP

The DW of maize stems, leaves and roots and total DW are presented in Table 4. In the case of dry matter production (stem, leaves and total DW), T1 to T6 caused significant effect compared to T7. Regardless all the treatment, roots dry matter production was not statistically different.

N, P, and K concentrations

Nitrogen, P, and K concentrations in stems, leaves and roots are presented in Table 5. Except for root, N concentration for all treatments differed statistically. In the case of stem, T1, T2 and T4 caused the highest concentrations of N (when compared to the T7). In the leaves, N concentrations for T1, T5 and T6 were statistically higher, relatively to that of T7. The differences in P and K concentrations in the stems, leaves and roots for all the treatments were significant. For P concentrations in the stems, T1, T2 and T3 caused significantly higher amounts compared to T7. Among these treatments, T1 caused the highest P accumulation (when compared to the other treatments). Except for T1, P concentration in roots, were statistically similar to that of T6. T1, T2, T3, T4, T5 and T6 improved K concentrations in all the parts of maize compared with T7. T1 and treatments with clinoptilolite zeolite did not statistically differ in K concentrations for all stems and leaves. T1 caused the highest K accumulation in the roots, when compared to the other treatments. Overall, all treatments with clinoptilolite zeolite significantly improved N and K concentrations in all plant parts relatively to T7. Only T1 clearly improved P concentrations in all plant parts.

Table 5. Effect of treatments on N, P, and K concentrations in maize plant parts at 65 DAP.

Treatment	N	P (%)	K
Stems			
T1	1.16 ^a	0.130 ^a	1.65 ^{ab}
T2	1.04 ^a	0.110 ^{ab}	1.95 ^a
T3	0.62 ^c	0.100 ^{bc}	1.41 ^{ab}
T4	1.00 ^{ab}	0.080 ^{bcd}	1.51 ^{ab}
T5	0.65 ^{bc}	0.070 ^d	1.12 ^{bc}
T6	0.86 ^{abc}	0.077 ^{cd}	1.80 ^{ab}
T7	0.56 ^c	0.063 ^d	0.40 ^c
Leaves			
T1	1.42 ^{ab}	0.17 ^a	1.53 ^a
T2	1.66 ^a	0.11 ^b	1.47 ^a
T3	0.60 ^c	0.11 ^b	1.43 ^a
T4	1.49 ^{ab}	0.11 ^b	1.40 ^a
T5	1.66 ^a	0.09 ^b	1.30 ^a
T6	1.76 ^a	0.09 ^b	1.35 ^a
T7	0.73 ^{bc}	0.07 ^b	0.54 ^b
Roots			
T1	1.36 ^a	0.13 ^a	1.15 ^a
T2	1.20 ^a	0.09 ^{ab}	0.70 ^b
T3	1.28 ^a	0.10 ^{ab}	0.79 ^b
T4	1.45 ^a	0.08 ^{ab}	0.62 ^b
T5	1.30 ^a	0.09 ^{ab}	0.61 ^b
T6	1.32 ^a	0.07 ^b	0.64 ^b
T7	1.07 ^a	0.09 ^{ab}	0.19 ^c

Different letters indicate significant different between means using Tukey's test at P ≤ 0.05. For key to treatments see Materials and methods.

N, P, and K uptake

The influence of treatments on N, P and K uptake in plant stems, leaves and roots are summarized in Figure 2. In the case of N uptake in stem, all treatments showed no significant difference. However, treatments with clinoptilolite zeolite caused significantly higher effect compared to T7, but its effect was statistically similar to that T1 (in terms of N uptake in leaves). Only T3

statistically improved N uptake in roots (as compared to T7). All treatments enhanced P and K uptake in the stem, leaves and roots (Figures 3, 4). Treatments with clinoptilolite zeolite significantly increased P and K uptake, relatively to T7 in all plant parts. It was observed the effect of T1 was statistically similar with those of T2 and T3 for P uptake in stem. T1 significantly improved P uptake in leaves (when compared to T7). Only T3 statistically improved P uptake in roots, as compared with T7. Higher P uptake in roots was attained because T3 had higher rock phosphate content (13:15:13 ratio of N:P:K), when compared to the other treatments with clinoptilolite zeolite. The effect of T1 on K uptake in stem and leaves was statistically similar to those of T2, T3, T4, T5 and T6. However, only T1 significantly improved K uptake in the roots (as compared to T7). In Figure 5, T2, T3, T4, T5 and T6 significantly enhanced total N, P and K uptake (when compared to T7) in stem, leaves and roots (when compared with T7). However, total N and K uptake triggered by T2, T3, T4, T5 and T6 were not statistically different from T1. T1 caused the highest P uptake compared to other treatments. A similar trend was observed for N and K uptake whereby all treatments with clinoptilolite zeolite significantly differed in the effect on N and K uptake.

Table 6. Nitrogen, K and P use efficiency of maize plant parts after 65 DAP.

Treatments	N	P %	K
Stems			
T1	4.19 ^a	1.08 ^a	8.31 ^{ab}
T2	3.18 ^a	0.73 ^{ab}	9.19 ^{ab}
T3	2.29 ^a	0.90 ^{ab}	7.68 ^{ab}
T4	3.23 ^a	0.48 ^b	7.37 ^{ab}
T5	2.82 ^a	0.58 ^{ab}	7.21 ^b
T6	4.00 ^a	0.62 ^{ab}	11.74 ^a
Leaves			
T1	8.68 ^a	3.02 ^a	10.91 ^a
T2	6.08 ^{ab}	1.44 ^b	11.01 ^a
T3	1.54 ^b	1.45 ^b	8.71 ^b
T4	10.23 ^a	1.50 ^b	10.67 ^a
T5	9.99 ^a	1.05 ^b	7.44 ^b
T6	9.34 ^a	0.86 ^b	8.85 ^b
Roots			
T1	2.14 ^b	1.04 ^{ab}	7.50 ^a
T2	2.67 ^{ab}	0.53 ^b	3.93 ^b
T3	6.21 ^a	1.10 ^a	3.70 ^b
T4	5.63 ^{ab}	0.50 ^b	4.28 ^b
T5	3.87 ^{ab}	0.21 ^b	2.94 ^c
T6	1.95 ^b	0.27 ^b	2.33 ^c

Different letters indicate significant different between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods.

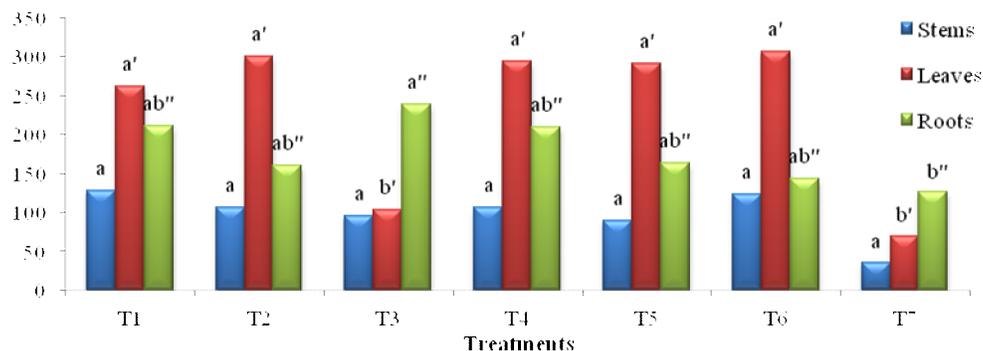


Figure 2. Effect of treatments on N uptake of maize (stems, leaves and roots) at 65 DAP. Different letters indicate significant difference between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods. Note: Letters without prime represent stems; single prime superscript is for leaves and double prime superscript is roots.

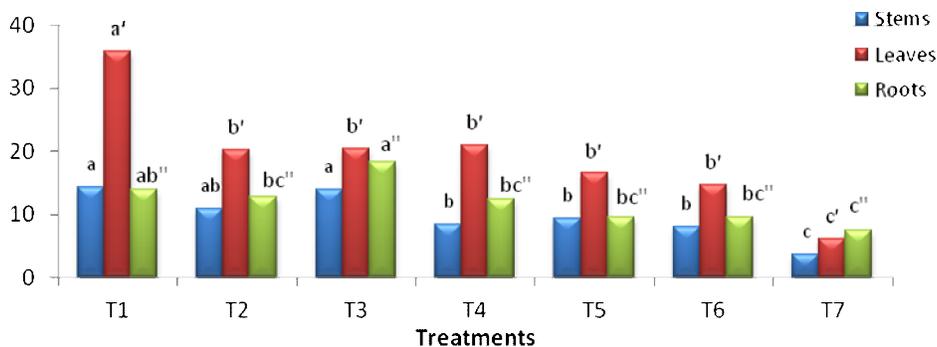


Figure 3. Effect of treatments on P uptake of maize (stems, leaves and roots) at 65 DAP. Different letters indicate significant difference between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods. Note: Letters without prime represent stems; single prime superscript is for leaves and double prime superscript is roots.

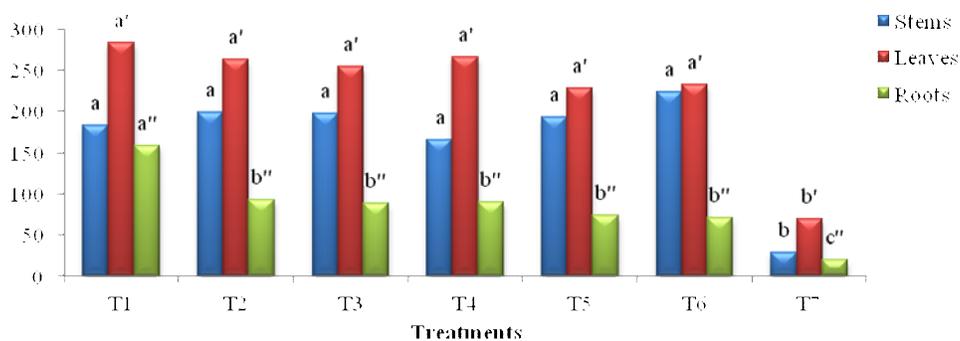


Figure 4. Effect of treatments on K uptake of maize (stems, leaves and roots) at 65 DAP. Different letters indicate significant difference between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods. Note: Letters without prime represent stems; single prime superscript is for leaves and double prime superscript is roots.

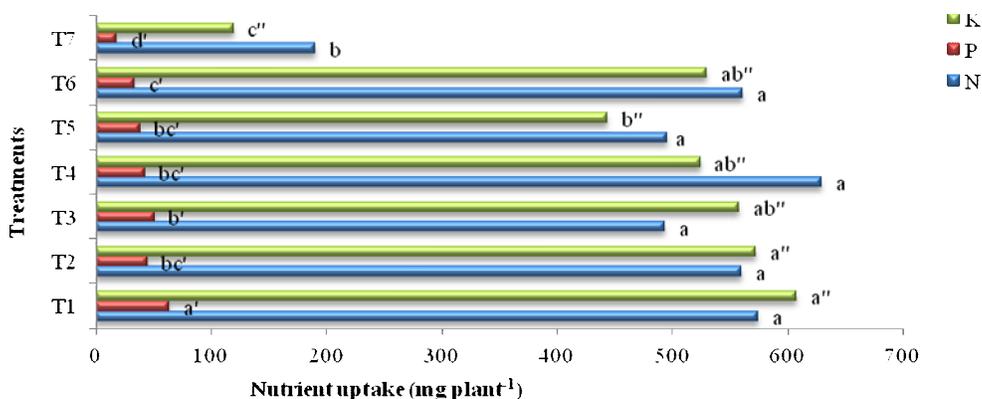


Figure 5. Effect of treatments on total N, P, and K uptake of maize at 65 DAP. Different letters indicate significant difference between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods. Note: Letters without prime represent Nitrogen; single prime superscript is for Phosphorus and double prime superscript is Potassium.

N, P, and K use efficiency

The effect of treatments on N, P and K use efficiency in stems, leaves and roots are shown in

Table 6. Except for stems, there were significant differences for leaves and roots in N use efficiency for all treatments. T1, T4, T5 and T6 caused higher

N use efficiency in the leaves (when compared to T3). However, T3 caused higher N use efficiency in roots, relatively to the T1 and T6. The effect of T1, T2, T3, T5 and T6 were statistically similar in P use efficiency for stems. T1 had the highest effect on P use efficiency in the leaves, relatively to the treatments with clinoptilolite zeolite. T3 caused higher P use efficiency (when compared to T2, T4, T5 and T6). However, its effect was similar to that of T1. In the case of K use efficiency, T6 caused higher effect in stems, when compared to T5. However, T6 was statistically similar to other treatments. T1, T2 and T4 significantly improved K use efficiency in the leaves compared to T3, T5 and T6. In the roots, K use efficiency significantly improved in T1 (relatively to the treatments with clinoptilolite zeolite). However, T2, T3 and T4 significantly affected total K use efficiency in roots

compared to T5 and T6. From Figure 6, T1, T2, T4 and T6 showed similar total N use efficiency. In the case of P use efficiency (Figure. 7), T1 showed the best total P use efficiency compared to treatments with clinoptilolite zeolite but that of T3 was higher compared to T6. The effect of T3 was similar to those of T2, T4 and T5. Total K use efficiency for T1, T2 and T3 were significantly higher compared with that of T6 (Figure. 8). Overall, with the exception of T1, treatments with higher clinoptilolite zeolite (T4, T5 and T6) significantly improved N use efficiency (when compared to the other treatments). In the case of the overall P use efficiency, treatments with lower clinoptilolite zeolite content (T2 and T3) significantly enhanced it compared to T4, T5 and T6 but lower than that of T1.

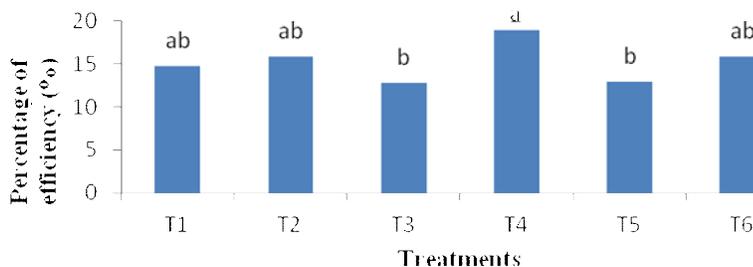


Figure 6. Effect of treatments on total N use efficiency at 65 DAP. Different letters indicate significant different between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods.

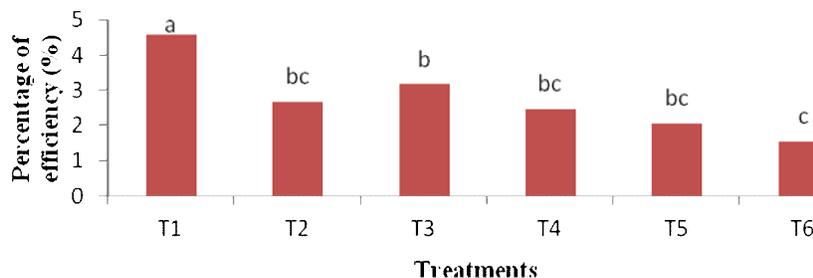


Figure 7. Effect of treatments on total P use efficiency at 65 DAP. Different letters indicate significant different between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods.

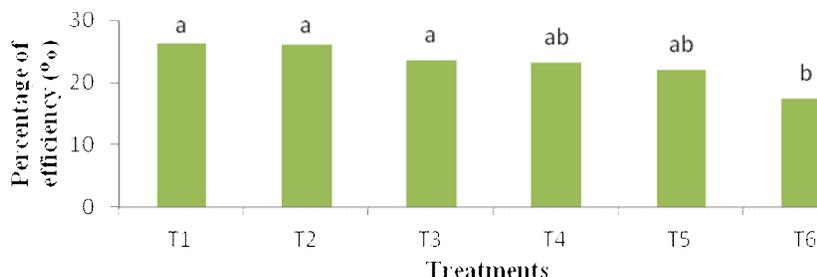


Figure 8. Effect of treatments on K use efficiency at 65 DAP. Different letters indicate significant different between means using Tukey's test at $P \leq 0.05$. For key to treatments see Materials and methods.

Discussion

Soil pH, total and available N, P, and K at 65 DAP

There were significant effects of the treatments with clinoptilolite zeolite on soil pH, total N, P and K and available P and K. This was because of the compatibility of the clinoptilolite zeolite with mineral fertilizers to attain soil buffering and indirectly regulate the soil pH (Polat et al., 2004; Mumpton, 1999). This observation agrees with the reports of Ahmed et al. (2009) and Junrungreang et al. (2002), who also reported significant improvement of in soil chemical properties upon the application of clinoptilolite zeolite. The large internal porosity of clinoptilolite zeolite allows high cation exchange capacity for nutrients retention especially selective retention of NH_4^+ and K^+ . Clinoptilolite zeolite also might favoured the release of soluble P when Ca^{2+} ions are exchanged with NH_4^+ or K^+ ions.

Exchangeable NH_4^+ and available NO_3^- accumulation at DAP

The significant effects of the treatments with clinoptilolite zeolite on exchangeable NH_4^+ and available NO_3^- accumulation suggest that clinoptilolite zeolite incorporated in fertilizer could be because of the high CEC of clinoptilolite zeolite ($75.4 \text{ cmol kg}^{-1}$). Clinoptilolite zeolite can store NH_4^+ and NO_3^- temporally in the internal before it is slowly released and becomes readily for plant uptake (Mumpton, 1999).

Plant height at 65 DAP

A similar finding was reported by Junrungreang et al. (2002), stating that the chemical fertilizer with the highest content of clinoptilolite zeolite improved the height, diameter, and yield of sugarcane. However, in another study, the highest increase of weight or length ratio of maize primary root was obtained for treatment with micronized clinoptilolite at the lower dose of 0.1% compared to higher dose of 3.0% (Trinchera et al., 2010).

Dry weight at 65 DAP

In several studies, the dry matter production of test crops, such as silage corn, strawberries, and swan significantly improved when fertilizers were enriched with clinoptilolite zeolite (Bernardi et al., 2010a; Ahmed et al., 2009; Rehakova et al., 2004). In the findings of Bernardi et al. (2010b), urea coated with inhibitor, produced a statistically similar rygrass yield (when compared to the urea coated with clinoptilolite zeolite). This observation is in agreement with the findings of this study,

where the effect of the commercial fertilizer (T1) was statistically similar compared to treatments with clinoptilolite zeolite (T2, T3, T4, T5 and T6). According to Mishra and Shrivastava (1985), availability of NH_4^+ and NO_3^- in soils leads to increase in dry matter production of maize primary leaves.

N, P, K concentrations, uptake, and use efficiency

The significant effects of the treatments with clinoptilolite zeolite on N concentration, uptake, and use efficiency suggest that clinoptilolite zeolite incorporated in fertilizer can reduce NH_3 loss by encouraging formation of NH_4^+ and NO_3^- over NH_3 (Ahmed et al., 2008). NH_3 loss reduces N losses and increases its uptake in maize. Higher amount of clinoptilolite zeolite may have retained higher exchangeable NH_4^+ and available NO_3^- hence the higher N concentration, uptake, and use efficiency in the maize dry matter production. In terms of P concentration, uptake, and use efficiency, most of the treatments with clinoptilolite zeolites showed lower P content than the commercial fertilizer but T3 clearly improved P uptake in roots. This may due to the higher TSP content in T3. This might have increased the solubility of the phosphate in the TSP. According to Mumpton (1999), the equilibrium of soil solution is disturb when small amount of Ca^{2+} in the soil solution with the apatite exchanges onto the zeolite forces more Ca^{2+} into solution. The apatite is ultimately destroyed, releasing P into the soil solution. The zeolite with rock phosphate combination possibly acted as an exchange fertilizer, with Ca^{2+} exchanging onto the zeolite in response to plant uptake of nutrient cations enhancing the dissolution of the rock phosphate (Ramesh and Reddy, 2011; Lai and Eberl, 1986). Most of the treatments with clinoptilolite zeolite had similar effect on K concentration, uptake, and use efficiency compared to T1. This suggests that clinoptilolite zeolite incorporated in the fertilizers enhanced maize growth. Most cations such as K^+ , Ca^{2+} and Mg^{2+} neutralize the negative charges in the zeolite tunnels. According to Gholizadeh (2008), some natural zeolites contain considerable amounts of exchangeable K^+ that can improve plant growth in potting media. This suggests that clinoptilolite zeolite does play an important role as nutrients carriers and ensuring good retention of soil exchangeable cations within the soil.

Conclusion

Treatments with higher amounts clinoptilolite zeolite showed the highest accumulation of exchangeable NH_4^+ and available NO_3^- compared to the commercial fertilizer used in this study. Most of the treatments with clinoptilolite zeolite had similar effect on plant height, dry weight, N, P, and K concentrations, uptake, and use efficiency compared to commercial fertilizer used. It may also be concluded that treatments with higher amounts clinoptilolite zeolite ensured good retention of soil exchangeable cations within the soil.

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References

- Ahmed, O. H., H. Aminuddin and M. H. A. Husni. 2008. Ammonia volatilization and ammonium accumulation from urea mixed with zeolite and triple superphosphate. *Acta Agri. Scandinavica Sect. B Soil Plant Sci.* 58:182-186.
- Ahmed, O. H., A. Hussin, H. M. N. Ahmad, M. B. Jalloh, A. A. Rahim and N. M. A. Majid. 2009. Enhancing the urea-N use efficiency in maize (*Zea mays*) cultivation on acid soils using urea amended with zeolite and TSP. *Am. J. App. Sci.* 6(5):829-833.
- Bernardi, A. C. D. C., P. P. O. Oliveira, M. B. D. M. Monte, J. C. Polidaroand and F. Souza-Barros. 2010a. Brazilian sedimentary zeolite use in agriculture. In: *Proceedings of 19th W.C.S.S., Soil solutions for a changing world.* Publisher CABI, Australia, pp. 37-40.
- Bernardi, A. C. D. C., E. P. D. Mota, S. D. C. H. D. Souza, R. D. Cardodo and P. P. A. Oliveira. 2010b. Ammonia volatilization, dry matter yield and nitrogen levels of Italian ryegrass fertilized with urea and zeolite. In: *Proceedings of 19th W.C.S.S., Soil solutions for a changing world.* Publisher CABI, Australia, pp. 22-25.
- Cottenie, A. 1980. Soil testing and plant testing as a basis of fertilizer recommendation. *FAO Soils Bull.* 38:70-73.
- Ferguson, G. A. and I. L. Pepper. 1987. Ammonia retention in sand amended with clinophilolite. *Soil Sci. Soc. Am. J.* 51:231-234.
- Gholizadeh, A. 2008. Iran International Zeolite Conference. Zeolite slow release fertilizer: A brief review. April 29- May 1, 2008. Tehran-Iran.
- Junrungreang, S., P. Limtong, K. Wattanaprat and T. Patsarayeangyong. 2002. 17th W.C.S.S. Symposium 2002. Effect of zeolite and chemical fertilizer on the change of physical and chemical properties on Lat Ya soil series for sugar cane. August 14-21, 2002. Thailand.
- Keeney, D. R. and D. W. Nelson. 1982. Nitrogen-inorganic forms. In: A. L. Page, D. R. Keeney, D. E. Baker, R. H. Miller, R. Ellis and J. D. Rhoades (Eds.). *Method of Soil Analysis, Part 2 (2nd Ed), Agron. Monogr., 9.* ASA and SSSA, Madison, Wisconsin.
- Lai, T. M. and D. D. Eberlm. 1986. Controlled and renewable release of phosphorus in soils from mixtures of phosphate rock and NH_4 -exchanged clinophilolite: Zeolite 6(2): 129-132. U.S. Geological Survey, Water Resources Division, Colorado, USA.
- Li, Z., D. Alessi and L. Allen. 2000. Influence of quaternary ammonium on sorption of selected metal cations onto clinoptilolite zeolite. *J. Env. Qual.* 31:1106-1114.
- Malaysian Agricultural Research and Development Institute. 1990. *Jagung Manis Baru*, Masmadu, Serdang, Malaysia.
- Mineyev, V. G., A. V. Kochetavkin and N. V. Bo. 1990. Use of natural zeolites to prevent heavy metal pollution of soils and plants. *Sov. Soil Sci.* 22:72-79.
- Ming, D. W. and J. B. Dixon. 1986. Clinoptilolite in South Texas soils. *Soil Sci. Soc. Am. J.* 50:1618-1622.
- Ming, D. W. and F. A. Mumpton. 1989. Zeolite in soils. In: J. B. Dixon and S. B. Weed (Eds.). pp. 874-911. *Mineral in soil environment.* (2nd ed), SSSA Publisher Inc., Madison, WI.
- Mishra, P. K. and H. S. Shrivastava. 1985. Role of inorganic nitrogen in synthesis and degradation of protein in maize leaves. *Indian J. Plant Physiol.* 28(1):43-52.
- Mumpton, F. A. 1999. *La Roca Magica: Uses of natural zeolites in agriculture and industry.* *Proc. Natl. Acad. Sci., USA* 96(7):3463-3470.
- Omar, L., O. H. Ahmed and A. M. Nik Muhamad. 2011. Reducing ammonia loss from urea and

- improving soil exchangeable ammonium and available nitrate in non waterlogged soils through mixing zeolite and sago (*Metroxylon sago*) wastewater. *Internat. J. Phys. Sci.* 6(4):866-870.
- Oste, L. A., T. M. Lexmond and W. H. V. Riemsdij. 2002. Metal immobilization in soils using synthetic zeolites. *J. Env. Qual.* 31:813-821.
- Paramanathan, S. 2000. Soil of Malaysia: Their characteristics and identification. Academy of Science Malaysia, Kuala Lumpur, Malaysia, Vol. 1.
- Payra, P. and P. K. Dutta. 2003. Handbook of zeolite science and technology. Ohio, USA.
- Perez, R., J. Caballero, C. Gil, J. Benitez and L. Gonazalez. 2008. The effect of adding zeolite to soils in order to improve the N-K nutrition of olive trees: preliminary results. *Am. J. Agric. Biol. Sci.* 2(1):321-324.
- Piccolo, A. 1996. Humic and Soil Conservation. Humic Substances in Terrestrial Ecosystem. Amsterdam: Elsevier.
- Polat, E., M. Karaca, H. Demir and A. Naci-Onus. 2004. Use of natural zeolite (clinophilolite) in agriculture. *J. Fruit Ornamental Plant Res.* 12:183-189.
- Pomares-Gracia, F. and P. F. Pratt. 1987. Recovery of 15N-labelled fertilizer from manured and sludge-amended soils. *Soil Sci. Soc. Am. J.* 42:712-720.
- Ramesh, K. and D. D. Reddy. 2011. Zeolite and their potential uses in agriculture. In: D. L. Sparks (Eds.), *Advances in agronomy*, vol. 113, Indian Institute of soil Sci, India.
- Rehakova, M., S. Cuvanova, M. Dzivak, J. Rimarand Z. Gaval'ovac. 2004. Agricultural and agrochemical uses of natural zeolite of the clinoptilolite type. *Curr. Opin. Solid State Mat. Sci.* 8:397-404.
- Tan, K. H. 2005. Soil sampling, preparation, and analysis (2nd ed). Boca raton, Florida, USA.
- Trenkel, M. D. 2010. Slow and controlled-release and stabilized fertilizers: An option for enhancing nutrient efficiency in agriculture, (2nd ed). International Fertilizer Industry Association, France.
- Trinchera, A., C. Mario Rivera, S. Rinaldi, A. Salerno, E. Rea and P. Sequi. 2010. Granular Size Effect of Clinoptilolite on Maize Seedlings Growth. *Open Agric. J.* 4:23-30.