Use of Clinoptilolite Zeolite on Selected Soil Chemical Properties, Dry Matter Production, Nutrients Uptake and Use Efficiency of Zea mays Cultivated on an Acid Soil

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ABSTRACT

In acid soils of the humid tropics, Phosphorus (P) deficiency due to its fixation by Al and Fe is common. It is therefore important to ensure adequate supply of P for optimum crop production. The use of zeolite on acid soils could fix Al and Fe and thus, rendering P readily available for crop use. The objective of the study was to determine the effects of including clinoptilolite zeolite in Zea mays cultivation on an acid soil on selected soil chemical properties, dry matter production, nutrient uptake and use efficiency of Zea mays. Triple Super Phosphate (TSP), urea and Muriate of Potash (MOP) were used in this study. Twenty five percent of the recommended N, P and K fertilizers for Zea mays were replaced with Clinoptilolite zeolite. Standard procedures were used to determine soil pH, exchangeable ammonium, available nitrate, available phosphorus, exchangeable aluminium, iron, cations and organic matter before and after planting. The plants were harvested at tasselling stage and measured for dry matter production, nutrients uptake and use efficiency. The effect of zeolite application with 75% of fertilization (T2) and 100% fertilization (T1) on soil chemical properties were statistically similar. Similar observation was made on dry matter production, nutrients concentration, nutrients uptake and nutrients use efficiency. The findings reported in this paper indicated that Clinoptilolite zeolite could be used to reduce the use of N, P and K fertilizers use of Zea mays on acid soils. At least three cropping cycles are recommended to confirm the findings of this study. It is also essential to estimate the economic benefits of including zeolite in Zea mays cultivation. These aspects are being investigated in on-going field trial.

Key words: Zeolites, acid soils, nutrient use efficiency, fertilizers

INTRODUCTION

Adequate supply of P from the very early growth stage is essential for optimum crop production. Poor availability of P does not only limit N availability but it also leads to poor yield of crops. In acid soils of the tropics, soluble P is fixed by Al and Fe hydrous oxide. This reaction renders P unavailable for plant uptake. Only P among the three macro-nutrients (N, P and K), is facing worldwide issue such quantity and quality of supply since world P resources is the lowest
Thus, efficient use of P is crucial especially for developing countries where the need for achieving sustainable food security to sustain their ever growing human population is urgent.

The fertilizers import bill of Malaysia from 2004 to 2006 averaged about USD$ 8 billion. In 2007 and 2008 the fertilizers import bills were USD$ 18.67 billion and USD$ 29.34 billion, respectively (Sabri, 2009). A forecast suggests that fertilizer prices will increase yearly. Long-term application of chemical fertilizers and their excessive use lead to soil health degradation and environmental pollution such as eutrophication. It is also economically unsustainable. For example, when accumulated P in the soils reaches soil maximum capacity and the soil can no longer retain additional supply, P movement to surface and ground water causes eutrophication which endangers aquatic quality (Grant et al., 2005; Schindler, 1977). Prolong application of inorganic fertilizers on intensely cultivated soils also jeopardizes soil resources sustainability due to increase in soil acidity (Okigbo, 1997). Therefore, an effective management of fertilizers is important to attain optimum crop yield, reduce costs of production, conserve finite resources and at the same time ensure that the environment is not degraded. The inclusion of soil amendments in fertilization programs is therefore essential. Clinoptilolite zeolite is a hydrated aluminosilicate of alkali and alkaline earth metals (Na⁺, K⁺, Ca²⁺, Mg²⁺ and Ba²⁺). It has an infinite three-dimensional crystal structure (Dakovic et al., 2007). These minerals are able to exchange ions, absorb gases and vapour. They are also known for their efficient molecular sieve (Ramesh and Reddy, 2011). Studies have shown that zeolite can be used to reduce ammonia loss by inhibiting microbial nitrification (Rabai et al., 2012; Lija et al., 2012), improve nutrients uptake and use efficiency of Zea mays cultivated on acid soils (Omar et al., 2011; Ahmed et al., 2010). The use of zeolite also improves rice grain yield, N recovery and use efficiency (Kavossi, 2007). They also effectively ameliorate salinity stress and improve nutrient balance in a sandy soil (Al-Busaidi et al., 2008). Mixing zeolite with urea and TSP also enhances phosphorus uptake in plants (Pickering et al., 2002).

Although, zeolites have been used to improve crops production, plant nutrients uptake and use efficiency, there is dearth of information on the use of zeolites to reduce P fixation not to mention reduction of N, P and K fertilizers use in agriculture. Thus, this study was carried out to: (1) Determine dry matter production, nutrients concentration, uptake and use efficiency of Zea mays by including Clinoptilolite zeolite in the fertilization program of Zea mays planted on an acid soil and (2) Determine the effect of including Clinoptilolite zeolite in the fertilization program of Zea mays on selected chemical properties of an acid soil.

MATERIALS AND METHODS
The Clinoptilolite zeolite used in this study was imported from Indonesia. The mineral soil which is Typic Paleudults (Bokomo Series) used in this study was sampled in an undisturbed area of Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia using an auger. The soil sample taken at 0-15 cm depth was air dried and ground to pass 5.0 mm sieve for pot study and 2.0 mm for laboratory analysis. Soil texture was determined using hydrometer method (Bouyoucos, 1962) and its field capacity and bulk density were determined by the method described by Tan (2005). The pH of the soil and zeolite were determined in a 1:2 (soil: distilled water) using a digital pH meter (Peech, 1965). 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 color development (Murphy and Riley, 1962), after which it was determined using UV-spectrometer. Exchangeable cations were extracted using the leaching method (Cottenie, 1980)
and the concentrations were then determined using Atomic Absorption Spectrometry (AAS). Soil CEC was determined by the leaching method followed by steam distillation (Bremner, 1965). The CEC of the Clinoptilolite zeolite was determined using the CsCl method (Ming and Dixon, 1986). The CsCl method used avoids underestimation CEC of zeolites as the method does not lead to entrapment of ammonium ions in its channels. Soil exchangeable aluminium was extracted using 1 M KCl (1:10 soil/solution) and determined using colorimetric method (Rowell, 1994).

The pot experiment was conducted in a rain-shed at Universiti Putra Malaysia Bintulu Sarawak Campus using completely randomized design with four replicates. The size of each pot was 22×28 cm and 8 kg soil (based on soil bulk density) was used. Maize (Zea mays L) Hibrimas variety was used as test crop. The N, P and K fertilizers recommended were 60, 60 kg and 40 kg K ha⁻¹ (MARDI, 1990). It must be noted that the rates used in this study were a scaled down of the standard fertilizer recommendation (MARDI, 1990). The soil moisture was maintained at 60% of field capacity. Treatments evaluated were as follows:

T0: No fertilizer
T1: 4.85 g urea+2.47 g MOP+4.84 g TSP
T2: 3.64 g urea+1.85 g MOP+3.63 g TSP+10.14 g zeolite

The treatments consisted of without fertilizer (T0), application of 100% recommended fertilizers (T1) and 75% recommended fertilizers plus replacing 25% of the fertilizers with Clinoptilolite zeolite (T2). T2 was arrived at based on previous laboratory incubation study (unpublished).

The Clinoptilolite zeolite was mixed thoroughly with soil a day before planting. Five seeds were sown and thinned to one at the 7 days after sowing (DAS). The MOP (60% K₂O) and TSP (45% P₂O₅) were surface applied whereas urea (46% N) was buried in the soil to avoid loss of urea through ammonia volatilization. Split applications of fertilizers were carried out on 10th and 28th Days After Seeding (DAS) and plants were harvested at 50 DAS (tasseling stage). Tasselling stage is the maximum growth stage for the plants before they go to reproductive stage (Kasim et al., 2009). A day before harvesting, soil samples were sampled and analyzed for pH, total acidity, exchangeable cations and available P using standard procedures as described previously.

The plants harvested were partitioned into roots, stems, tassels and leaves. Afterwards, they were washed using tap water and distilled water before being oven dried at 60°C until constant weight was attained. The dry weight were recorded and separately, plant parts were ground and analyzed for total N, P and K uptake and their use efficiency. Total N of plant tissues was determined using the Kjedhal method followed by steam distillation (Bremner, 1965), available NO₃ and exchangeable NH₄ were also determined using Keeney and Nelson method (Keeney and Nelson, 1982). Total P, Ca, Mg and K in plant tissues were extracted using single dry ashing method (Tan, 2005). Total P was determined using UV-VIS spectrometer after blue color development (Murphy and Riley, 1962). Potassium and Ca values were determined using AAS as described previously. Nitrogen, P and K uptake in leaves, stems and roots were determined by multiplying their concentrations with the dry weight of the plant parts while N, P and K use efficiency (agronomic effectiveness) were determined by the formula shown below (Dobermann, 2005):
Nutrient use efficiency (%) = \( \frac{\text{Uptake with fertilizer-Uptake without fertilizer}}{\text{Total amount of fertilizer that had been applied}} \times 100 \)

Analysis of variance (ANOVA) was used to test significant effect of treatments while means of treatments were compared using Tukey test. Statistical Analysis System (SAS, 2008) was used for the statistical analysis.

RESULTS AND DISCUSSION

The selected physico-chemical properties of Bekenu Series, zeolite and TSP are presented in Table 1. The soil pH in water, CEC and total N were 4.32, 5.33 cmol kg\(^{-1}\) and 0.06%, respectively. These results were consisted with those reported by Paramanathan (2000). Total carbon, exchangeable K, Ca and Mg were slightly higher than the standard range and this could possibly be due to litter decomposition with time at the soil surface of undisturbed area.

Table 2 shows selected soil chemical properties at 50 DAS. The soil pH significantly reduced with application of T1 and T2 compared to that of soil alone (T0). This could be attributed to active protonation-deprotonation and dissolution-precipitation of acidulated TSP and urea hydrolysis upon application. According to Marschner (1995), pH change is mainly affected by cation/uptake ratios and nitrogen assimilation. The change of pH in rhizosphere is also related to soil buffering capacity, microbial activities and plant genotypes (Hinsinger et al., 2005; Vance et al., 2003; Raghothama, 1999). Percentage of organic matter and \(\text{NO}_3^-\) were not significantly affected by fertilization. Although more fertilizers were used in T1 compared to T2, exchangeable Ca and Mg contents were statistically similar suggesting better retention of Ca and Mg in T2. A Similar observation was reported in tomato cultivated with zeolite (Stylianou et al., 2004). However, this observation was not true for monovalent K. Zeolite addition was unable to significantly affect K concentration since its availability is mainly regulated by soil properties and plant requirements. However, stronger affinity of Clinoptilolite zeolite exchange sites for divalent cations may have suppressed monovalent ions thus, the low K availability in T2.

Table 1: Selected chemical properties of soil, Clinoptilolite zeolite and Triple superphosphate

<table>
<thead>
<tr>
<th>Property</th>
<th>Soil Value obtained</th>
<th>Standard data range*</th>
<th>Clinoptilolite zeolite</th>
<th>Triple superphosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (water)</td>
<td>4.32</td>
<td>4.90-4.90</td>
<td>8.54</td>
<td>2.80</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>1.01</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>CEC (cmol kg(^{-1}))</td>
<td>5.33</td>
<td>3.86-8.46</td>
<td>75.40</td>
<td>Nd</td>
</tr>
<tr>
<td>Total N (%)</td>
<td>0.06</td>
<td>0.04-0.17</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Total P (%)</td>
<td>0.005</td>
<td>Nd</td>
<td>Nd</td>
<td>21.70</td>
</tr>
<tr>
<td>Available P (mg kg(^{-1}))</td>
<td>2.48</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>5.60</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Total carbon (%)</td>
<td>3.25</td>
<td>0.57-2.51</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Exchangeable Al (cmol kg(^{-1}))</td>
<td>0.9</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Exchangeable H (cmol kg(^{-1}))</td>
<td>0.48</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Total acidity (cmol kg(^{-1}))</td>
<td>1.38</td>
<td>Nd</td>
<td>Nd</td>
<td>Nd</td>
</tr>
<tr>
<td>Exchangeable K (cmol kg(^{-1}))</td>
<td>0.24</td>
<td>0.05-0.19</td>
<td>6.16</td>
<td>10.37</td>
</tr>
<tr>
<td>Exchangeable Ca (cmol kg(^{-1}))</td>
<td>0.76</td>
<td>0.06-0.19</td>
<td>22.30</td>
<td>9.64</td>
</tr>
<tr>
<td>Exchangeable Mg (cmol kg(^{-1}))</td>
<td>0.45</td>
<td>0.07-0.21</td>
<td>2.36</td>
<td>26.10</td>
</tr>
<tr>
<td>Texture</td>
<td>Sandy loam</td>
<td>Sandy loam</td>
<td>Nd</td>
<td>Nd</td>
</tr>
</tbody>
</table>

Table 2: Selected chemical properties of soil without fertilization, recommended fertilization and 75% fertilization with 25% clinoptilolite zeolite at 50 days after seedling.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>pH</th>
<th>Organic matter (%)</th>
<th>Exchangeable cation (cmol kg⁻¹)</th>
<th>Exchangeable</th>
<th>Available</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>K</td>
<td>Ca</td>
<td>Mg</td>
</tr>
<tr>
<td>T0</td>
<td>5.31⁺</td>
<td>5.75⁺</td>
<td>0.10⁺</td>
<td>0.53⁺</td>
<td>0.41⁺</td>
</tr>
<tr>
<td>T1</td>
<td>5.11⁺</td>
<td>5.99⁺</td>
<td>0.43⁺</td>
<td>0.38⁺</td>
<td>0.44⁺</td>
</tr>
<tr>
<td>T2</td>
<td>4.98⁺</td>
<td>5.65⁺</td>
<td>0.26⁺</td>
<td>0.19⁺</td>
<td>0.47⁺</td>
</tr>
</tbody>
</table>

Means with different letter indicates significant differences using Tukey test at p<0.05, T0: Soil without fertilization, T1: Recommended fertilization, T2: 75% fertilization with 25% clinoptilolite zeolite.

Fig. 1: Available P of soils without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS. Means with different letter indicates significant differences using Tukey test at p<0.05.

Even though T1 had higher amount of urea compared to T2, NH₄⁺ contents were not significantly different. This was possible because Clinoptilolite zeolite in T2 had higher CEC and greater affinity for NH₄⁺ and this may have reduced nitrification and prevented NO₃⁻ ion from leaching (Robai et al., 2013; Li et al., 2012; Ahmed et al., 2010; Inglezakis et al., 2004; He et al., 2002). Besides, acidic materials such as phosphoric acid and ammonium at plant roots cause rhizosphere acidification (Shen et al., 2011; Rosliza et al., 2009). Figure 1 shows the status of available P in soil as affected by treatments. The higher available P in T1 was due to higher amount of P fertilizer applied. This was possible because exchangeable Al and Fe known to fix available P were not significantly different in T1 and T2 (Fig. 2 and 3).

Soil exchangeable H⁺ represents active acidity in soil solution. Statistically, there was no significant difference in H⁺ ions (Fig. 4) regardless of treatment. Higher H⁺ concentration in soil solution was in equilibrium with those held on the soil's cation exchange complex and thus reducing absorption of other cations (Alam et al., 1999). This explains the significant soil pH reduction in T1 and T2. Total soil acidity is the sum of H⁺ and Al³⁺. The significant reduction of total soil acidity in T1 and T2 was because of reduction of Al³⁺ (Fig. 5).

Plant dry matter production and nutrients concentration results are presented in Table 3. Regardless of plant part, dry matter production showed significant increase in T1 and T2 compared to soil alone (T0). Low dry matter for T0 was due to no fertilization to sustain plant growth and development. No significant difference in T1 and T2 in terms of dry matter production suggests that
Fig. 2: Exchangeable $\text{Fe}^{2+}$ of soils without fertilization (T0), 75% fertilization with 25% Clinoptilolite zeolite (T2) at 50 DAS. Means with different letter indicates significant differences using Tukey test at $p \leq 0.05$.

Fig. 3: Exchangeable $\text{Al}^{3+}$ of soils without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS. Means with different letter indicates significant differences using Tukey test at $p \leq 0.05$.

Fig. 4: Exchangeable $\text{H}^+$ of soils without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS. Means with different letter indicates significant differences using Tukey test at $p \leq 0.05$.
Fig. 5: Total acidity of soils without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS. Means with different letter indicates significant differences using Tukey test at p<0.05

Fig. 6: Nitrogen uptake of plant without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS. Means with different letters indicate significant difference using Tukey test at p<0.05

inclusion of zeolite contributed to nutrients retention and their timely release for plant growth and development. Lack of statistical differences in nutrients concentration in the plant parts could be attributed to dilution effect (Marschner, 1995). Similar observation has been reported by other authors (Ahmed et al., 2010; Mengel and Kirkby, 1996). Plant nutrients uptakes are shown in Fig. 6, 7 and 8. The use of zeolite with reduced amount of fertilizers (T2) showed significant reduction in N uptake in leaves and reduction of K and P uptake in roots compared those of T1 (standard fertilization). Total P uptake in T1 and T2 were similar suggesting the need to reduce use of fertilizers to avoid loss and environmental pollution. Despite low N and K uptake, N, P and K use efficiency in T2 was comparable to those of T1 (Fig. 9, 10 and 11). Successful retention of cations and their timely releases by Clinoptilolite zeolite according to plant needs may have led to significant use efficiency of these nutrients in T2 as compared to T1. Improvement in N, P and K uptake and use efficiency in Zea mays were noted in studies using inorganic fertilizers mixed with zeolite (Ahmed et al., 2010) and mixing zeolite with compound fertilizer (Rabai et al., 2013). However, such observation was not true in this study due to lower amount (economic reasons) of zeolite and fertilizer applied. Inclusion of zeolite in fertilization is reported to cause a phenomenal
Table 3: Dry matter production and nutrients concentration of plant without fertilization, recommended fertilization and 75% fertilization with 25% clinoptilolite zeolite at 50 days after seeding

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Leaf</th>
<th>Stem</th>
<th>Root</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry matter (g)</td>
<td>N (%)</td>
<td>P (%)</td>
<td>K (%)</td>
</tr>
<tr>
<td>T0</td>
<td>0.97&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.56&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.27&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.25&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>T1</td>
<td>16.46&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.66&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.20&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.29&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>T2</td>
<td>14.94&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.74&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.23&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.86&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Means within column with different letters indicate significant differences using Tukey test at p<0.05. T0: Soil without fertilization, T1: Recommended fertilization, T2: 75% fertilization with 25% clinoptilolite zeolite.
Fig. 7: Phosphorus uptake of plant without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS, Means with different letters indicate significant difference using Tukey test at p ≤ 0.05.

Fig. 8: Potassium uptake of plant without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS, Means with different letters indicate significant difference using Tukey test at p ≤ 0.05.

Fig. 9: Nitrogen use efficiency of plant without fertilization (T0), recommended fertilization (T1) and 75% fertilization with 25% clinoptilolite zeolite (T2) at 50 DAS, Means with different letters indicate significant difference using Tukey test at p ≤ 0.05.
growth of the microorganisms in the soil, increased nutrient intake of plants, reduced effects of soil acidity, prevented soil erosion and increased storage capacity of soil as well as contributing to building of precious humus complexes (Grant et al., 2005; Beqiraj et al., 2008). Although in this study the effect of zeolite on selected soil chemical properties was not glaring, perhaps long term application could cause significant effect.

CONCLUSION AND RECOMMENDATION

The effect of zeolite application with 75% of fertilization (T2) and 100% fertilization (T1) on soil chemical properties were statistically similar. Similar observation was made on dry matter production, nutrients concentration, nutrients uptake and nutrients use efficiency. The findings reported in this paper indicate that Clinoptilolite zeolite could be used to reduce the use of N, P and K fertilizers use of Zea mays on acid soils. At least three cropping cycles are recommended to confirm the findings of this study. It is also essential to estimate the economic benefits of including zeolite in Zea mays cultivation. These aspects are being investigated in on-going field trial.
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