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Using Clinoptilolite Zeolite for Enhancing Potassium Retention in Tropical Peat Soil

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INTRODUCTION

Potassium (K) is an essential nutrient for plant growth because large amount of K is absorbed from the root zone during the growth of most agronomic crops (Rehm and Schmitt, 2002). After nitrogen (N) and phosphorus (P), K is most important nutrient element as it is taken up by crops in larger amounts than any other nutrients (Brady, 2002). Potassium is easily lost to the environment and hence it is not readily available for plant uptake and this leads to economic loss. Furthermore, excessive use of K fertilizers causes environmental pollution. Tropical peat soils are not suitable for crop production unless they are adequately ameliorated. Tropical peat soils tend to lose nutrients, especially K, through leaching due to low clay and absence of mineral matter (Ahmed *et al.,* 2005; Stevenson 1994; Shickluna *et al.*, 1972). One of the ways to improve nutrients (including K) retention in peat soils is through the use of zeolite. Adoption of new management techniques such as using clinoptilolite zeolite to control nutrient released from compound fertilizers has in recent times attracted attention in agriculture (Rabai *et al.,* 2012).

According to Payra and Dutta (2003), clinoptilolite zeolite is a hydrated aluminosilicate with three-dimensional rigid crystalline networks that are 10^{-9} m in size which contain internal exchange sites that have high affinity for ammonium ions. Clinoptilolite zeolite offers a better solution for K retention because it has special cation exchange, molecular sieving and absorption properties (Payra and Dutta 2003). Clinoptilolite zeolite can be used both as a carrier of nutrients as well as a medium to free nutrients (Glisic and Milosevic, 2008; Noori *et al.,* 2006). Pores and voids are the key characteristics of zeolites (Ramesh and Reddy, 2011). The size of clinoptilolite zeolite channels control the size of the molecules and ions that can pass through them and hence act as a chemical sieve which allows some ions to pass through while blocking others (Mumpton, 1999). Clinoptilolite zeolite can therefore control the release of K from fertilizers for optimum use by plants.

A brief overview on the roles and leaching problems associated with the use of potassium in agricultural soils and its management is presented in this article. The paper also provides evidence on the potential usefulness of zeolite to reduce the leaching of K in tropical peat soils.

POTASSIUM IN AGRICULTURE, SOILS AND THE ENVIRONMENT

Potassium is vital to many plant processes which include some basic biochemical and physiological systems of plants. However, it receives less attention than N and P in most crop production activities. Although potassium does not become part of the chemical structure of plants, it plays many important regulatory roles in plant development. Some specific roles of K in plants include osmoregulation, internal cation/ anion balance, enzyme activation, proper water relations, photosynthate translocation and protein synthesis. Tolerance of external stress, such as frost, drought, heat, and high light intensity is enhanced with good K nutrition (Mikkelsen, 2008).

Potassium deficiency in cereal crops results in reduced growth, delayed maturity, lodging caused by weaker straw and lower bushel weight. About 90% to 95% of the total soil K is contained in clay minerals, but it is locked within the structure of the layered clay sheets and is not readily available for plants. Further, about 5% to 10% of the total soil K slowly becomes available to plants because of weathering where 1% and 2% of the K pool is available K and exchangeable K, respectively (McKenzie and Pauly, 2013).

Less attention has been devoted to the release of nutrients from NPK compounds although the processes are expected to be more complex than with a single nutrient fertilizer (Rabai *et al.,* 2013). Potassium is not considered to be a nutrient of environmental (water quality) concern. However, high K forages are becoming increasingly of concern in intensively farmed areas. For instance, when K uptake in forages exceeds acceptable concentrations, there can be a significant impact on cattle health. The level of soil K increases when it is applied in the form of manure or fertilizer over a long period of time at rates well above crop requirements. The K balance on many farms is negative, where more K is removed by the harvested crops than is returned to the soil (Mikkelsen, 2008).

PEAT SOILS

Total world coverage of peat soils is approximately 30 million hectares with Canada and Russia having the largest distribution of peats (Zainorabiddin, 2010). More than 60% of the world's tropical peatlands are found in Southeast Asia (Lette, 2006). Most notable are the large peatland areas on the island of Borneo (Adon *et al.*, 2012). Approximately 440,000 km^2, or 11% of the global peatlands are located in the tropics (Page *et al.*, 2011).

Tropical peat soils are considered as soils with low economic benefit, apart from being use for agricultural purposes (Adon *et al.*, 2012) and they have very low bulk densities compared to mineral soils (Andriesse, 1974). In tropical peats consisting of pure organic materials, a presumed ash percentage of one percent seems reasonable. Therefore, mineral matter weight loss on heating due to loss of water and in some cases by volatilization of calcium carbonate is more difficult to assess.

Skaven-Haug (1972) indicated values of 0.4-1.3% for sand and silt and of 3.9-6.0% for very fine clay material in peaty materials. Thus, the nature of the mineral component in organic soils must be understood as it has a bearing on soil fertility and agricultural potential. Moreover, the exchange capacity of both mineral and organic soil materials depend on the number of negatively-charged exchange sites. These adsorbed cations such as Ca, Mg, K, and Na replace hydrogen ions at the sites. However, in general, the ion adsorption and exchange is associated with the hydrophilic colloids of the peat, namely humic acids and hemicelluloses (Volarovich and Churaev 1968). According Ahmed *et al.* (2005), K deficiency can be severe, particularly in pineapple cultivation on peat soils where K loss through leaching can be high due to low clay and the absence of mineral matter.

ZEOLITES AND AGRICULTURE

Zeolites are hydrated crystalline aluminosilicate minerals of alkaline and alkaline earth metals, structured in rigid three dimension nets, organized by AlO_4 and SiO_4 tetrahedral, which come together to compose a system of canals, cavities, and pores and are of natural occurrence (Ming and Mumpton, 1989). According to Ramesh and Reddy (2011), most of the initial research on the use of zeolite in agriculture had been carried out since 1960 in Japan. Review of the literature has revealed that farmers in Japan used zeolites rock to control moisture and to increase pH of acid soils in acidic volcanic soils. The worldwide number of identified natural zeolite (about forty) demonstrates both their great variety and the present-day interest in their potential applications in industry and agriculture (Ming and Dixon, 1987). Among these minerals, analcime (sometimes known as analcite), clinoptilolite, erionit, chabazite, mordenite and philipsite are the most well known (Doğan, 2003). Clinoptilolite zeolite has also been reported to have a relatively high cation adsorption capacity (Oste *et al.,* 2002; Li *et al.,* 2000; Mineyev *et al.,* 1990). The large internal porosity of clinoptilolite zeolite allows high cation exchange capacity for nutrient retention, especially selective retention of NH_4^+ and K^+. These minerals have three main properties, which are of great interest for agricultural purposes: high cation exchange capacity, high water holding capacity in the free channels and high adsorption capacity (Mumpton, 1999).

SOIL NUTRIENTS MANAGEMENT USING ZEOLITE

The use of minerals for agricultural purposes is becoming widespread (Van Straaten, 2006), and zeolitic concentrates have a special niche in this category. Zeolites can be utilized as slow release fertilizer and soil conditioner (Alberto *et al.,* 2010). They have been shown to improve phosphate rock availability, nitrogen utilization and minimizing K leaching (Barbarick *et al.* 1990; Pickering *et al.* 2002).

Potassium deficiencies are most common in well drained, coarse-textured soils and peat soils. These deficiencies can be corrected with application of K fertilizers such as muriate of potash (49.8% K) which is commonly used in crop cultivation. Based on a related study on nutrient retention, another alternative method is the use of zeolite, which add a sticky-like mineral to capsulate or trap the nutrients available or applied inside the soil and thus prevents it from being leached from the soil.

EXPERIMENTAL FINDINGS

The following sections are details of findings of our experiment to examine the effects of clinoptilolite zeolite on the retention and availability of K (using muriate of potash) in a tropical peat soil. For the sake of this paper, only T5 and T6 are discussed in details. The treatments evaluated in our study are shown in Table 1.

Table 1 Treatments used in the study

Treatment No	Treatment description
T1	390 g of peat soil alone
T2	78 g of zeolite alone
T3	1.88 g of muriate of potash alone
T4	390 g of peat soil mixed with 78 g of clinoptilolite zeolite
T5	390 g of peat soil mixed with 1.88 g of muriate of potash
T6	390 g of peat soil mixed with 1.88 g of muriate of potash and 78 g of clinoptilolite zeolite

Chemical Properties of the Peat Soil and Clinoptilolite Zeolite

Table 2 shows the results of selected chemical properties of the soil used in this study which are consistent with those reported by Paramananthan (2000).

Table 2 Chemical properties of peat soil and clinoptilolite zeolite

	Data obtained (0-25 cm)	Standard data range*
Soil		
Soil exchangeable K (ppm)	4998	nd
Soil total K (cmol(+) kg^{-1})	33.3	11.7-35.1
Ca (ppm)	9.49	<0.4-2.0
Mg (ppm)	2.33	<0.24
Na (ppm)	52.6	<0.24
pH (water)	3.63	4.6-4.9
CEC (cmol (+) kg^{-1})	8.5	3.86-8.46

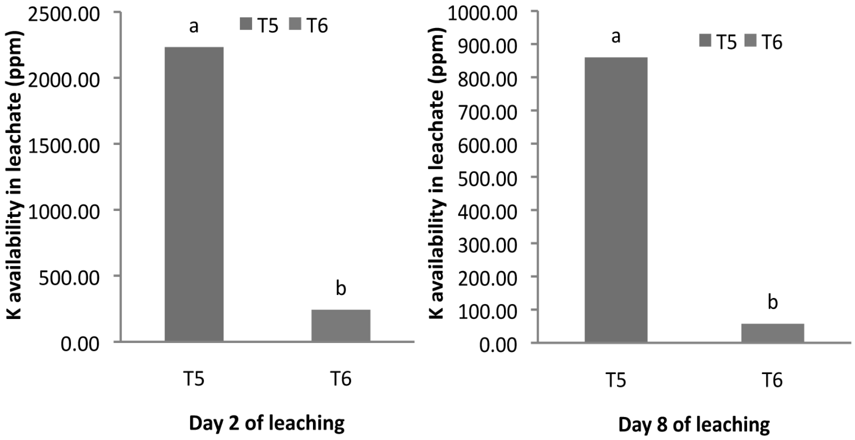
cont'd Table 2

Clinoptilolite Zeolite		
K (ppm)	2429	nd
Ca (ppm)	892	nd
Mg (ppm)	57.4	nd
Na (ppm)	435	nd
pH (water)	8.44	nd
pH (KCl)	7.27	nd
CEC (cmol (+) kg^{-1})	75.4	nd

nd= not determined. *Standard data range (Paramananthan, 2000)

Leachate Potassium

The effects of the treatments T5 and T6 on K were significantly different (Figure 1). Potassium loss from T5 from day 2 to day 30 of leaching was higher than in T6 (Figure 1). On day 2 of leaching, K loss from T5 was higher compared with that in the leachate of T6. Subsequently, there was a general decrease in K with increasing time of leaching, but that from T5 was generally higher than in the leachate of T6 (Figure 1).



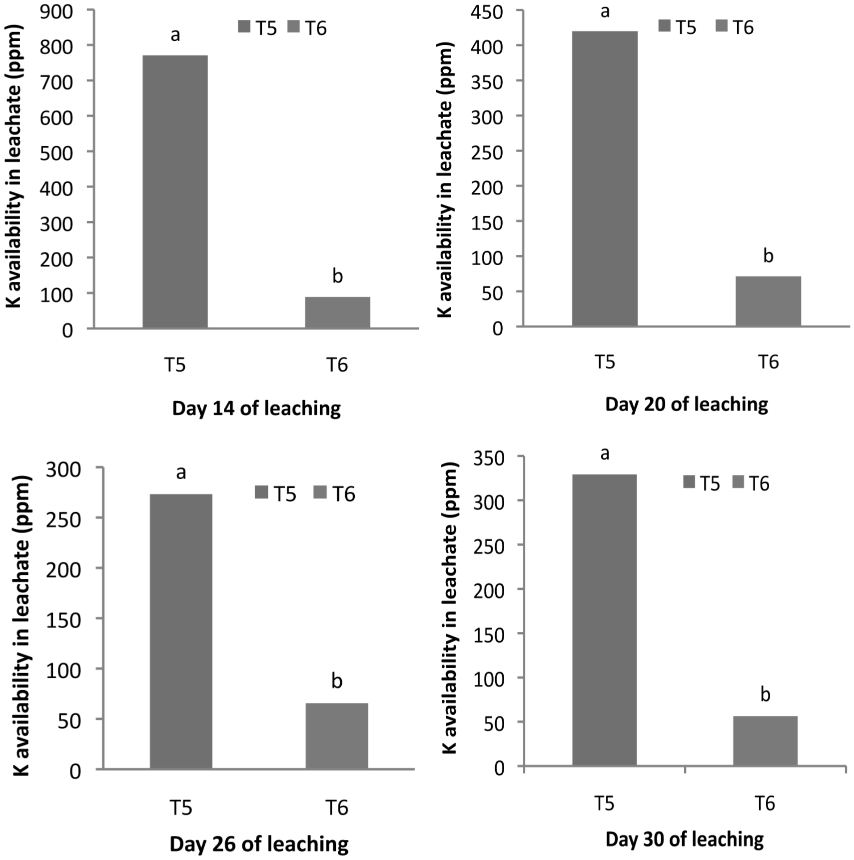


Figure 1 Effects of T5 (peat+muriate of potash) and T6 (peat+muriate of potash+zeolite) on K availability in leachate (ppm) at 2, 8, 14, 20, 26 and 30 days of leaching. Different letters on bars indicate significant difference between means using t test ($p \leq 0.05$).

Leachate K, Ca, Mg, Na, Fe, and Mn over Thirty Days of Leaching

The contents of K, Ca, Mg, Na, Fe and Mn in the leachates of T5 and T6 over the 30 days of leaching are presented in Figure 2. Unlike the contents of K and Fe which were higher in the leachate of T5 compared to that of T6, the opposite was true for Ca, Mg, Na and Mn. Potassium content in the leachate decreased from day 2 to day 30 of leaching whereas those of Ca, Mg, Na and Mn fluctuated, but eventually decreased over the 30 days of leaching (Figure 2).

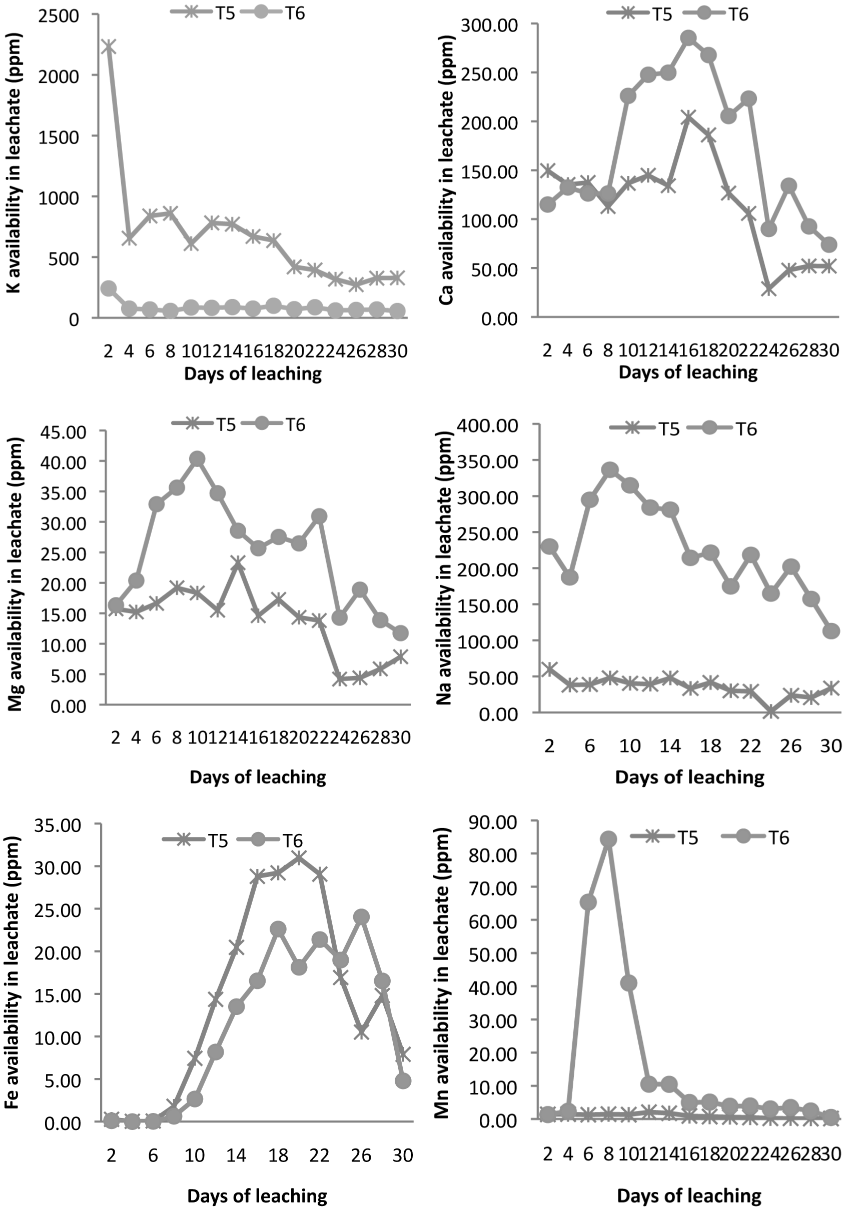


Figure 2 Effects of treatment T5 (peat+muriate of potash) and T6 (peat+muriate of potash+zeolite) on K , Ca, Mg, Na, Fe and Mn availability over 30 days of leaching (ppm).

Leachate pH over Thirty Days of Leaching

The pH of the leachates of treatments T5 and T6 over the 30 days of leaching are shown in Figure 3. The pH of the leachate from T6 was relatively higher than that of T5.

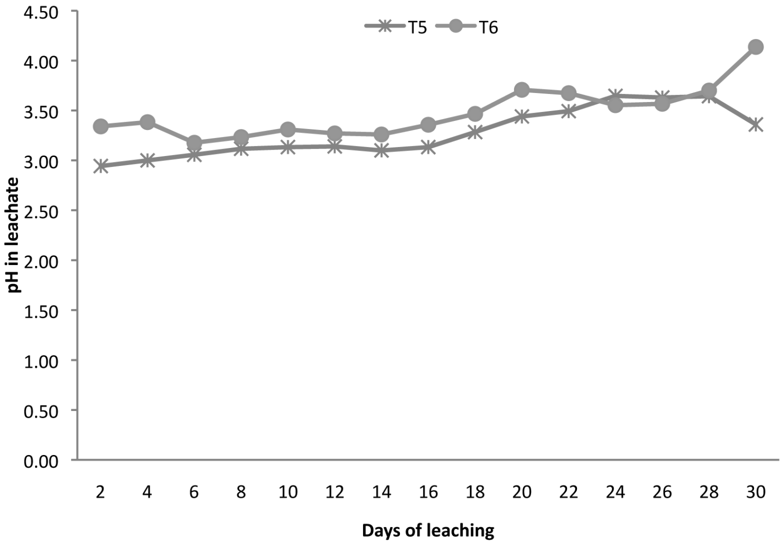


Figure 3 Effects of T5 (peat+muriate of potash) and T6 (peat+muriate of potash+zeolite) on pH over 30 days of leaching.

Soil exchangeable K and Total K after Thirty Days of Leaching

The soil exchangeable K and total K after leaching are summarized in Figures 4 and 5. The soil exchangeable K and total K were higher in the treatment with zeolite (T6) than in the treatment without zeolite (T5).

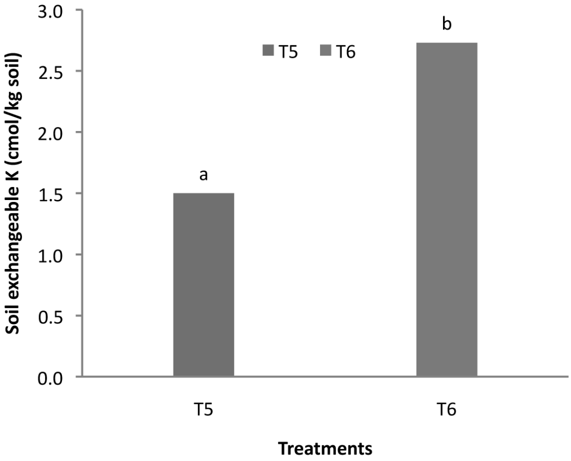


Figure 4 Effects of treatment T5 (peat+muriate of potash) and T6 (peat+muriate of potash+ zeolite) on soil exchangeable K at 30 days of leaching. Different letters on bars indicate significant difference between means using t test (p≤ 0.05).

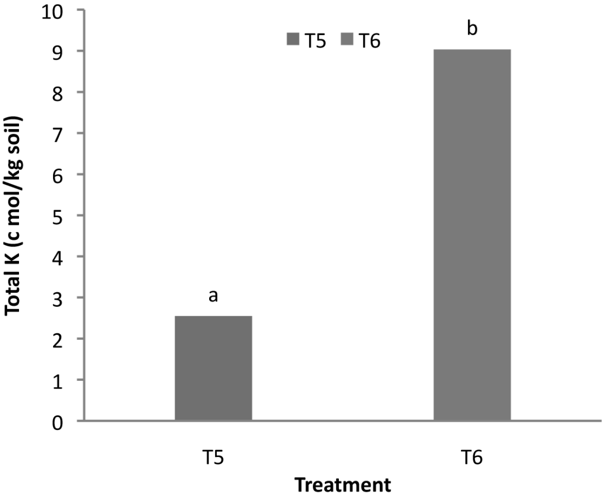


Figure 5 Effects of treatment T5 (peat+muriate of potash) and T6 (peat+muriate of potash+ zeolite) on soil total K at 30 days of leaching. Different letters on bars indicate significant difference between means using t test (p≤0.05).

Soil pH and Cation Exchange Capacity after Thirty Days of Leaching

The pH of the soil treated with zeolite (T6) was slightly acidic (pH 5.12) compared with the soil without zeolite (T5) which was pH 3.4. The cation exchange capacity of the soil with (T6) and without zeolite (T5) were 9.96 cmol (+) kg^{-1} soil and 11.64 cmol (+) kg^{-1} soil, respectively.

GENERAL DISCUSSION

Chemical Properties of the Peat Soil and Zeolite before the Leaching Experiment

Selected chemical properties of the peat soil are summarized in Table 2. The values obtained for soil total K were consistent with those reported by Paramananthan (2000), except for Ca^{2+}, Mg^{2+} and Na^{+}. Cation exchange capacity, exchangeable Ca and Mg contents of the soil were higher than the standard range probably due to cultivation (Rabai *et al.,* 2012).

Leaching of K and Other Cations

During leaching, the content of K in the leachate of T5 was high. This was because most of the K in T5 was leached as the soil had no zeolite to retain K. A similar observation has been reported in pineapple cultivation on peat soil by Ahmed *et al.,* 2005, wherein recovery of K in pineapple cultivation on tropical peat soil was low (28.22%) partly due to leaching of K. High rainfall also accelerates leaching of K in peats (Hashim, 2003). Although peat soils have high CEC, they do not readily adsorb exchangeable K. A large proportion of the total available K is present in the soil solution. This form of K is mobile and prone to leaching (Adriesse, 1988). Leachate K for T6 was significantly lower as compared to that for T5 which is attributed to the zeolite in T6. Zeolites have high affinity for K ions due to their high CEC and Thus, because of high CEC and high negative charge which causes it to effectively absorb the soil exchangeable K and release it slowly.

There were higher contents of Ca, Mg and Na in the leachate of T6 as compared with that of T5 because the zeolite used in this experiment had these ions. However, the preference of K^{+} and Al^{3+} ions at the zeolite exchange complex may have caused displacement of these cations in the soil solution which were leached over time (Saidah *et al.,* 2013).

Iron in the leachate of treatment T5 was significantly higher as compared with that of T6. The zeolite in treatment (T6) controlled the amount of Fe released into the leachate. This is because the high pH of zeolite neutralized the peat acidity to prevent the Fe from being transformed. On the whole, soils have sufficient quantity of Fe, but the Fe is in unavailable form. The acidic nature of the peat soil used in this study probably caused the concentration of Fe to increase. This finding is consistent with that by Pokrosvsky *et al.* (2004), who reported high release of Fe due to low soil pH.

Manganese concentration in the leachate of T6 was significantly higher as compared with the leachate of T5 due to the Mn content in the zeolite.

Soil Exchangeable K and Total K after Thirty Days of Leaching

The soil exchangeable K and total K were significantly higher in the treatments with zeolite (T6) as compared to without zeolite (T5). This was because the K^+ ions leached in treatment T6 were lower than in treatment T5. The zeolites in treatment T6 improved retention of K in the peat soil because the zeolite used has the ability to adsorb nutrients from K fertilizers as well as reduce leaching in the soil (Sumalatha *et al.,* 2010). This suggests that mixing zeolite with K fertilizers could improve K retention in tropical peat soils.

Soil pH

Soil pH in the treatments with zeolite (T6) was significantly higher than for the treatments without zeolite (T5). This finding is consistent with that of a study where pH was reported to increase with application of zeolite (Perez *et al.,* 2008). According to Mumpton (1999), zeolite is not acidic but marginally alkaline and its use with fertilizers can help buffer the soil pH, thus reducing the need for lime application. Thus, the increase in soil pH because of zeolites may contribute to nutrient availability in soils. The leaching of cations such as Na, Mg and Ca from T5 partly explains the lower pH of the soil without zeolite (T5).

Soil CEC

The treatment with zeolite (T6) resulted in significantly higher soil CEC compared with the treatment without zeolite (T5). According to Sumalatha *et al.* (2010), increase in soil CEC relates to the amount of channels in the zeolite as these channels are responsible for selective cation exchange in zeolites.

CONCLUSION

Application of clinoptilolite zeolite has the potential to improve the availability of K in tropical peat soil by controlling the leaching of K from fertilizers. Zeolite also improves other soil chemical properties such as pH, CEC, exchangeable K, Ca, Mg and Na, Fe and Mn. Mixing muriate of potash with clinoptilolite zeolite will be beneficial to the agricultural production as it can enhance and increase nutrient availability in tropical peat soils.

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